47. LIPIDS OF AN UPPER ALBIAN LIMESTONE, DEEP SEA DRILLING PROJECT SITE 465, SECTION 465A-38-3[1]

P. A. Comet, J. McEvoy, S. C. Brassell, G. Eglinton, J. R. Maxwell, and I. D. Thomson,
Organic Geochemistry Unit, University of Bristol, School of Chemistry, Cantock's Close, Bristol BS8 1TS, England

ABSTRACT

The lipids of an Albian carbonaceous limestone show evidence of high algal productivity. They contain a preponderance of chlorophyll derivatives, algal markers, and marine sterol distributions. The low percentages of lipids derived from terrestrial plant waxes and resins suggest that no major vegetated continental landmasses were present nearby. This agrees with the plate-tectonic reconstructions for the Albian of the northwest Pacific. However, as an exposed feature the Hess Rise may well have contributed the small amounts of terrestrial material found. The predominance of hopanoids over other polycyclic isoprenoids may indicate extensive bacterial activity at the time of sedimentation. Nevertheless, these bacteria have not extensively altered the algal lipid distribution. The association between high productivity, good lipid preservation, and bacterial activity is rationalized here in terms of an oxygen-minimum zone, overlain by productive water masses.

Diagenesis has progressed to the medium stage, on the basis of lipid defunctionalization, the polycyclic isoprenoids being essentially present as hydrocarbons. However, late-stage diagenetic hydrogenation of sterenes and triterpenes has occurred only slightly, indicating that diagenesis is not as advanced as in the top zone of the Paris Basin. Backbone rearrangements of the steroidal alkenes have occurred to only a minimum extent.

INTRODUCTION

The free lipids (hydrocarbons, ketones, alcohols, acids, and porphyrins) of an upper Albian carbonaceous limestone from the Hess Rise (DSDP Section 465A-38-3) were investigated to evaluate (1) organic inputs, in an attempt to understand the conditions of deposition of the Lower Cretaceous Pacific "black shale" facies, and (2) the maturity of the sample.

The distribution of each functional group of compounds is described. The lipid components are also grouped into structural classes, whose proportions are held herein to be of paleoenvironmental importance and relatively free from diagenetic–maturational bias. Finally, some of the functional and(or) structural groups of compounds are markers for particular types of organisms, and these further clarify input problems.

In the preliminary survey, six samples (465-3-4, upper Paleocene; 465-10-3 and 465A-3-5, upper Maastrichtian; 465A-11-3, lower Maastrichtian; 465A-15-3, Upper Campanian—all nannofossil/foraminifer oozes—465A-38-3, upper Albian limestone) were examined for visual kerogen by the use of acid dissolution. All but one sample were entirely acid-soluble; consequently, only this remaining sample (465A-38-3) was examined in detail.

EXPERIMENTAL

The experimental scheme used was similar to that of our previous DSDP investigations (Barnes et al., 1979; Brassell, Comet, Eglinton, McEvoy, et al., 1980) but differs in the following respects: (1) acid dissolution was used for a preliminary evaluative step in the analyses of these carbonate-rich samples, (2) Section 465A-38-3 was pulverized in a Tema disc mill because of its high degree of lithification, prior to

sonication, and (3) for gas chromatography–mass spectrometry (GC–MS) analyses, an INCOS 2300 data system was employed (Brassell, Gower, et al., 1980). In addition, the metalloporphyrin fractions were re-chromatographed on silica-gel H plates, using dichloromethane/toluene (1:8) as developer. Electronic spectra (UV/visible) were obtained on a Perkin-Elmer 552 spectrophotometer, in dichloromethane, using 1 cm (3 ml capacity) quartz cells. Mass spectra for the metalloporphyrin fractions were obtained on a Finnigan 4000 spectrometer, using an INCOS 2300 data system, by direct-insertion probe. The scan cycle was 4 seconds, and the mass range was m/z 50–650. Operating conditions were: source temperature 250°C, electron energy 35 eV, emission current 350 µA, acceleration voltage 1.8 kV. Compound assignments were made from their individual mass spectra and GC retention data, with reference to authentic standards where possible. Mass fragmentography was used extensively to characterize homologous and pseudohomologous series (Wardroper et al., 1977; Brassell, Gower, et al., 1980), and to aid compound identifications. Each component was quantitated from its gas chromatographic response.

RESULTS

Lithology and Palynology

Section 465A-38-3 is an upper Albian, olive-gray, well-lithified, finely laminated limestone. A sub-sample (~5 g), analyzed by the British Petroleum Co. Ltd., was 92.2% acid-soluble (carbonate), with an organic carbon content of 2.1%. Visual examination of kerogen showed that the bulk of the organic matter is amorphous material of marine–algal origin. Numerous foraminifer linings were seen, but no dinoflagellate cysts were observed. Miospores are rare, suggesting only minor terrestrial input. The sample is immature; its autochthonous vitrinite reflectance ($\bar{R}_o$) is 0.33.

Aliphatic Hydrocarbons

Acyclic Components

The n-alkanes in Section 465A-38-3 range from C_{15} to C_{34}, with a CPI (odd/even carbon preference index)

of 1.08. The absolute concentrations of the individual homologs (quoted in ng/g dry weight of sediment) are shown in Figure 1. The C_{17}–C_{21} homologs predominate. In general, *n*-alkane concentrations decrease with increasing carbon number, with the exception of nonacosane, which is more abundant than octacosane. No *n*-alkenes were detected. No monomethyl or other simple branched alkanes were detected in Section 465A-38-3. In contrast, 2,6,10,14,19,23,27,31-octamethyldotriacontane (lycopane, III) is the major alkane in the sample, whereas the other acyclic isoprenoids, 2,6,10-trimethylpentadecane, pristane, phytane, 2,6,10,15,19-pentamethyleicosane (I), and 2,6,10,15,19,23-hexamethyltetracosane (squalane, II) are all present as minor components (Fig. 1). The pristane-to-phytane ratio is 0.56. Isoprenoid alkenes are present as trace components, but their low relative abundance precluded their identification.

Cyclic Components

Neither diterpenoid alkanes nor alkenes were detected in Section 465A-38-3. A wide range of 5α- and 5β-steranes were recognized (Table 1; Fig. 2), with 5α-isomers predominating. The higher series homologs (i.e., C_{27}–C_{30}) were the major components. Individual 4-methylsteranes and $\beta\alpha$-diasteranes were identified, rather than compound series.

Hopanes ranging from C_{27} to C_{35} were recognized (Table 2). $\beta\beta$-hopanes are the dominant series, with $\beta\beta$-homohopane (XIId) the major component. $\alpha\beta$-hopanes are more abundant than $\beta\alpha$-hopanes, and, for the extended members (C_{31}–C_{33}), their 22R diastereoisomers greatly dominate the 22S epimers.

The principal sterenes (Table 3) present were C_{27}–C_{29} series of Δ^4 and Δ^5 isomers, the former isomers more abundant. The lack of reference spectra for Δ^{22}-steradienes prevented the assignment of positions of unsaturation in their nuclei. A single 4-methyldiasterene (XIIIc) was recognized.

A series of $\Delta^{17(21)}$-hopenes ranging from C_{27} to C_{35} (excluding C_{28} and C_{34}), and dominated by hop-17(21)-ene (XIXc) was found (Table 4). 22R and 22S epimers of the extended ($>C_{31}$) components were identified, with the 22R diastereoisomers more abundant. Four bisnorhopenes were tentatively identified from their mass

Table 1. Concentration of steranes in Section 465A-38-3.

Component[a]	Assignment[b]	Structure[c]	Concentration (ng/g)[d]
A	5β-Androstane	IVa	0.10
B	5α-Androstane	Va	0.30
C	5β-Pregnane	IVb	0.05
D	5α-Pregnane	Vb	0.26
E	4-Methyl-5α-pregnane	VIb	0.11
F	20-Methyl-5α-pregnane	Vc	0.09
G	20-Ethyl-5α-pregnane	Vd	0.03
H	5β-Cholane	IVe	0.07
I	5α-Cholane	Ve	0.26
J	20S $\beta\alpha$-Diacholestane	VIIh	0.13
K	24-Methyl-5α-cholane	Vf	0.06
L	4-Methyl-5α-24-norcholane	VIg	0.18
M	20R $\beta\alpha$-Diacholestane	VIIi	0.12
N	5β-Cholestane	IVi	0.93
O	5α-Cholestane	Vi	2.01
P	24-Methyl-5β-cholestane	IVj	0.54
Q	24-Methyl-5α-cholestane	Vj	1.10
R	24-Ethyl-5β-cholestane	IVk	1.34
S	23,24-Dimethyl-5α-cholestane	VI	0.71
T	24-Ethyl-5α-cholestane	Vk	3.76
U	24-Propyl-5β-cholestane[e]	IVm	0.20
V	24-Propyl-5α-cholestane[e]	Vm	1.15

[a] See Figure 2.
[b] Based on mass spectral interpretation, comparison with authentic standards, and GC retention values.
[c] See Appendix.
[d] Dry weight of sediment.
[e] May be 24-isopropyl isomers.

spectra. In addition, neohop-13(18)-ene (XX); 22,29,30-trisnorneohop-13(18)-ene, (XVIII); Δ^7-, Δ^8-, and $\Delta^{9(11)}$-fernenes (XXI); and very tentatively, arbor-9(11)-ene (XXII) were recognized.

Aromatic Hydrocarbons

Among the aromatic hydrocarbons, the non-hopanoid polynuclear aromatic hydrocarbons were present in relatively minor amounts, except for perylene (XXIX) and methylperylene (XXX) (Table 5). Three diterpenoidal trienes of unknown structure (probably bisnorabietatrienes) were the dominant diterpenoids in the sample. The aromatic hopanoids (XXXI–XXXVII) were the major aromatic components. They occur as the full series of partially to fully aromatic compounds (Spyckerelle et al., 1977a, b). No aromatic components related to amyrin-type triterpenoids were detected.

Ketones

Acyclic Components

A series of *n*-alkan-2-ones, ranging from C_{14} to C_{29}, maximizing at C_{18}, were found as minor components (Fig. 3); no odd-over-even preference was apparent (CPI value 0.64). 6,10,14-trimethylpentadecan-2-one (XXVIII), dominating the series of *n*-alkan-2-ones, was the only acyclic isoprenoid ketone detected.

Cyclic Components

Cyclic ketones were more abundant than acyclic components. Both steroidal and triterpenoidal ketones were detected, but several of these compounds could not be identified, because of the lack of reference mass spectra. Series (C_{27}–C_{29}) of 5α- and 5β-stan-3-ones (Table 6), and ster-4-en-3-ones (Table 7), were present in similar con-
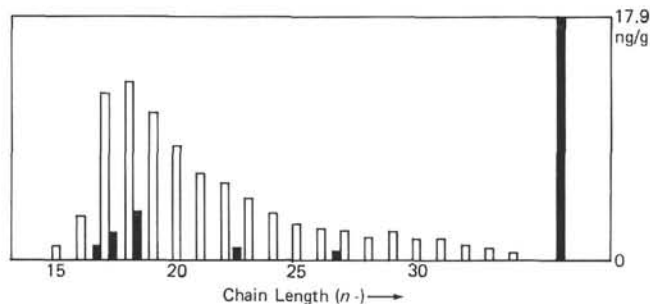

Figure 1. Distribution of acyclic alkanes in Section 465A-38-3. Hollow bars = *n*-alkanes. Solid bars = acyclic isoprenoid alkanes (from left to right: C_{18}, C_{19} [pristane], C_{20} [phytane], C_{25} [2,6,10,15,19-pentamethyleicosane], C_{30} [squalane], and C_{40} [lycopane]).
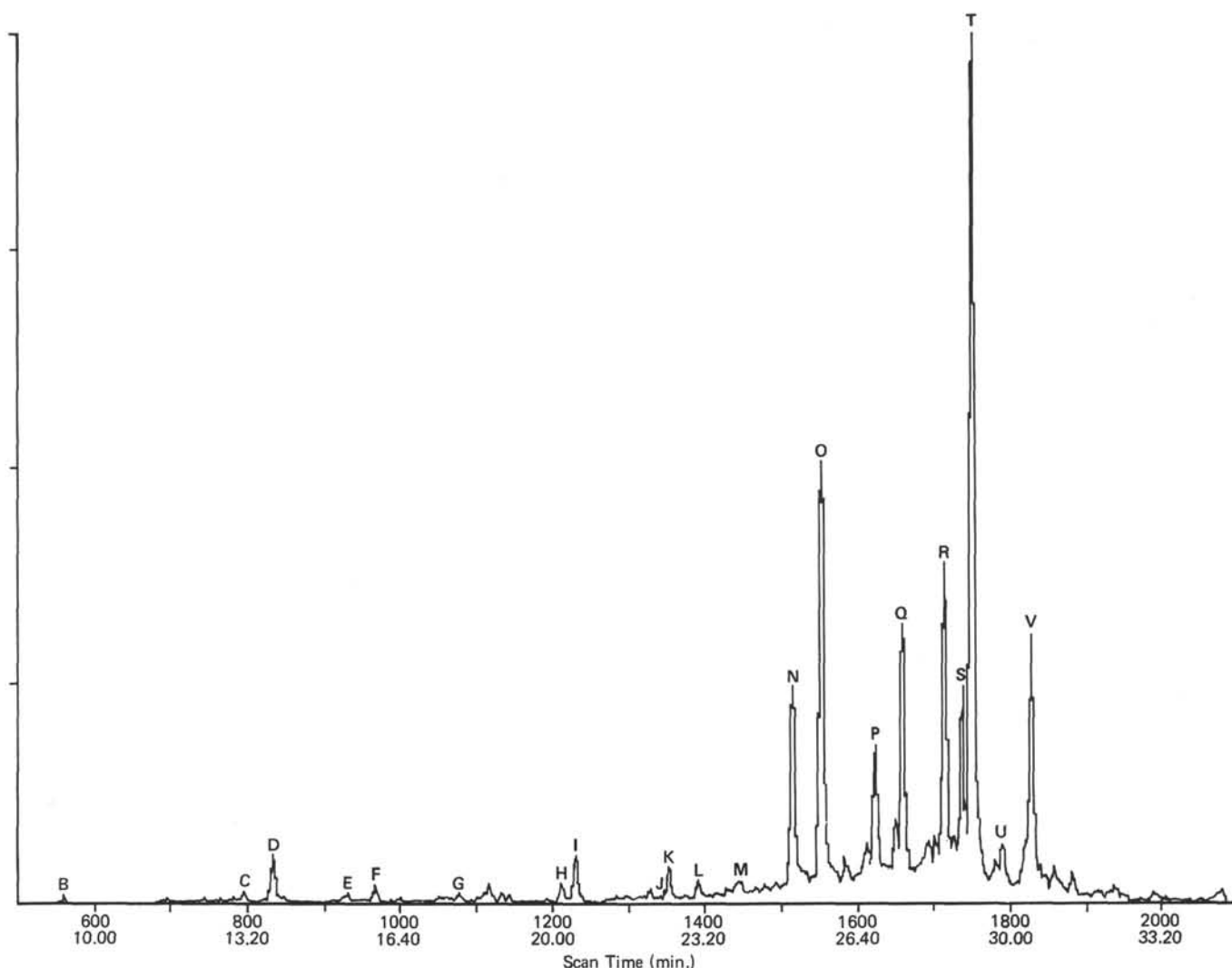
Figure 2. Mass fragmentogram of m/z 217, showing the distribution of steranes in Section 465A-38-3. (Lettered peaks refer to Table 1.)

centrations. In addition, 4,24-dimethylcholest-4-en-3-one (Table 7) was speculatively identified. A complex series of components, tentatively assigned as 4-methylstenones, was detected (Table 8). The two C_{30} components possess almost identical mass spectra, consistent with that of 4,23,24-trimethylcholest-22-en-3-one (dinosterone; XLII). Trace amounts of 4-methylstanones were found, but the low concentrations prevented compound identification. In addition, among the numerous minor components, nuclear diunsaturated steroidal ketones were tentatively identified.

A series of hopanones (C_{27}–C_{34}, excluding C_{28} and C_{30}) was detected, with one of the two 22,29,30-trisnorhopan-21-one (XLIII) isomers greatly dominant (Table 9).

Alcohols

Acyclic Components

Only C_{12}, C_{13}, and C_{16} n-alkanols were recognized. No unsaturated, branched or acyclic isoprenoid alcohols (e.g., phytol) were detected.

Cyclic Components

Series (C_{27}–C_{29}) of Δ^5-stenols and their corresponding 5α-stanols were identified (Table 10), with the former series dominant. In addition, 4,23,24-trimethylcholest-22-en-3β-ol (dinosterol, LId) was recognized as a significant component of the relatively minor sterol fraction. No other Δ^{22}-sterols and no 4,23,24-trimethylcholestan-3β-ol or sterols less than C_{27} were detected.

Carboxylic Acids

Acyclic Components

The carboxylic acids in Section 465A-38-3 are dominated by straight-chain components ranging from $nC_{10:0}$ to $nC_{27:0}$, maximizing at $nC_{16:0}$ (Fig. 4). The higher carbon number acids (nC_{21}–nC_{27}) were present in relatively minor amounts. A marked even-over-odd preference was apparent (CPI 8.1). Significant amounts of unsaturated carboxylic acids were found, especially $nC_{16:1}$ and $nC_{18:1}$, (cis Δ^9) as well as small relative amounts of $nC_{15:1}$ and $nC_{17:1}$. Branched components were also de-

Table 2. Concentration of hopanes in Section 465A-38-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
18αH-22,29,30-Trisnorneohopane	VIII	0.23
17αH-22,29,30-Trisnorhopane	IXa	2.73
17βH-22,29,30-Trisnorhopane	Xa	5.40
17α,18αH,21βH-18,30-Bisnorhopane	XI	0.89
Bisnorhopane[d]	—	0.76
αβ-30-Norhopane	IXb	2.15
βα-30-Norhopane	Xb	0.71
αβ-Hopane	IXc	3.59
ββ-30-Norhopane	XIIb	3.26
βα-Hopane	Xc	1.32
22S αβ-Homohopane	IXd	0.24
22R αβ-Homohopane	IXd	3.14
ββ-Hopane	XIIc	4.56
βα-Homohopane	Xd	1.23
22S αβ-Bishomohopane	IXe	0.08
22R αβ-Bishomohopane	IXe	0.80
βα-Bishomohopane	Xe	0.26
ββ-Homohopane	XIId	13.26
22R αβ-Trishomohopane	IXf	0.47
ββ-Bishomohopane	XIIe	3.26
ββ-Trishomohopane	XIIf	2.03
ββ-Tetrakishomohopane	XIIg	0.83
ββ-Pentakishomohopane	XIIh	1.23

[a] Based upon mass spectral interpretation, comparison with authentic standards, and GC retention values.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Tentative assignment based on mass spectral interpretation; stereochemistry unknown.

Table 3. Concentration of sterenes in Section 465A-38-3.

Assignment	Structure[a]	Concentration (ng/g)[b]
4,23,24-Trimethyldiacholest-13(17)-ene[d,e]	XIIIc	2.04
Cholest-4-ene[c]	XIVa	11.05
Cholest-5-ene[c]	XVa	2.42
24-Methylcholest-4-ene[c]	XIVb	4.86
24-Methylcholest-5-ene[c]	XVb	0.69
23,24-Dimethylcholestadiene[d,f]	—	2.36
23,24-Dimethylcholest-22-ene[d]	XVId	2.64
24-Ethylcholest-4-ene[c]	XIVc	10.35
24-Ethylcholest-5-ene[c]	XVc	2.32
4,23,24-Trimethylcholestadiene[d,f]	XVIId	6.84

[a] See Appendix.
[b] Dry weight of sediment.
[c] Based on comparison with authentic spectra and GC retention data.
[d] Based on spectral interpretation and GC retention data.
[e] May be 24-ethyl, rather than 23,24-dimethyl.
[f] Position of the double bonds: one in Δ^{22} position; the other unknown, but nuclear.

tected as minor components, in particular iso- and ante-iso-C_{15} and C_{17} acids. No unsaturated branched carboxylic acids were detected, but small amounts of acyclic isoprenoid acids were found.

Cyclic Components

Dehydroabietic acid (LII) and a series of hopanoid acids were detected as trace constituents. The hopanoids could not be characterized from their weak mass spectra.

Table 4. Concentration of hopenes in Section 465A-38-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
22,29,30-Trisnorneohop-13(18)-ene	XVIII	13.05
Bisnorhopene[d]	—	1.37
22,29,30-Trisnorhop-17(21)-ene	XIXa	5.30
Bisnorhopene[d]	—	8.74
Bisnorhopene[d]	—	4.18
30-Norhop-17(21)-ene	XIXb	13.76
Bisnorhopene[d]	—	1.62
Hop-17(21)-ene	XIXc	18.83
Fern-8-ene	XXI	2.03
Neohop-13(18)-ene	XX	12.42
Fern-9(11)-ene	XXI	0.51
22S Homohop-17(21)-ene	XIXd	2.42
Fern-7-ene	XXI	0.09
22R Homohop-17(21)-ene	XIXd	3.56
Arbor-9(11)-ene	XXII	0.17
22S Bishomohop-17(21)-ene	XIXe	1.47
22R Bishomohop-17(21)-ene	XIXe	1.64
22S Trishomohop-17(21)-ene	XIXf	1.12
22R Trishomohop-17(21)-ene	XIXf	1.68
22S Pentakishomohop-17(21)-ene	XIXg	0.45
22R Pentakishomohop-17(21)-ene	XIXg	0.73

[a] Based on mass spectral interpretation, comparison with authentic standards, and GC retention data.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Stereochemistry and structures unknown.

Metalloporphyrins

Nickel and vanadyl porphyrin fractions were separated by TLC and characterized by, and quantitated from their respective UV/visible absorption values (Table 11), and by mass spectrometry. The relative concentrations of metalloporphyrins with respect to the dominant component in each fraction is given in Table 12. All the vanadyl porphyrins belong to the DPEP series (LIVa), ranging from C_{27} to C_{32}, with C_{31} dominant; they account for approximately 95% of the total metalloporphyrins. The nickel porphyrins include both DPEP (LIVb) and etio (LIII) types, with a DPEP/etio ratio of approximately unity. The nickel DPEP series ranges from C_{27} to C_{32}, with C_{30} dominant.

Additional metalloporphyrin series were detected, but were not characterized. The major uncharacterized series eluted with the vanadyl porphyrins and ranges from m/z 455 to m/z 553 in a continuous homologous series ($455 + 14n$, $n = 0$–7), with m/z 553 and m/z 539 dominating (Table 12). Metal-free porphyrins were not detected. However, a range of C_{30}–C_{32} zinc DPEP porphyrins were detected as minor constituents, and the possibility that these compounds are artifacts generated from metal-free porphyrins is under investigation.

DISCUSSION

Paleoenvironment: Lipid Indicators

Acyclic Components

The distributions of straight-chain components, n-alkanes, n-alkan-2-ones, n-alkanoic and alkenoic acids,

Table 5. Concentration of aromatic hydrocarbons in Section 465A-38-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
Phenanthrene	XXIII	0.38
Methylphenanthrene[d]	XXIV	0.19
Methylphenanthrene[e]	XXIV	0.18
Bisnorabieta-8,11,13-triene[f]	—	2.19
Bisnorabieta-8,11,13-triene[f]	—	0.55
Bisnorabieta-8,11,13-triene[f]	—	1.30
Fluoranthene	XXV	0.22
Pyrene	XXVI	0.19
Chrysene	XXVII	0.08
Methylchrysene	XXVIII	0.13
Perylene	XXIX	3.10
Methylperylene	XXX	1.50
(3'-Ethylcyclopenteno-7,8)-1,1,4a,10b-tetramethyldodecahydro(1,2,3,4,4a,4b,5,6,10b,11,12,12a)chrysene	XXXI	6.05
(3'-Ethylcyclopenteno-7,8)-1,1,4a-trimethyloctahydro(1,2,3,4,4a,11,12,12a)chrysene	XXXII	2.49
7-Methyl-1,2-cyclopentenochrysene	XXXIII	5.26
(3'-Ethylcyclopenteno-7,8)-1,1-dimethyltetrahydro(1,2,3,4)-chrysene	XXXIV	4.63
7-Methyl-3'-ethyl-1,2-cyclopentenochrysene	XXXV	6.32
(3'-Isopropylcyclopenteno-7,8)-1,1-dimethyltetrahydro(1,2,3,4)chrysene	XXXVI	0.34
7-Methyl-3'-isopropyl-1,2-cyclopentenochrysene	XXXVII	1.32

[a] Based on mass spectral interpretation, comparison with authentic spectra, and GC retention data, except where otherwise stated.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Mixture of 2- and 3-methylphenanthrenes from GC co-injection.
[e] Probably a mixture of 1- and 9-methylphenanthrenes from GC retention data.
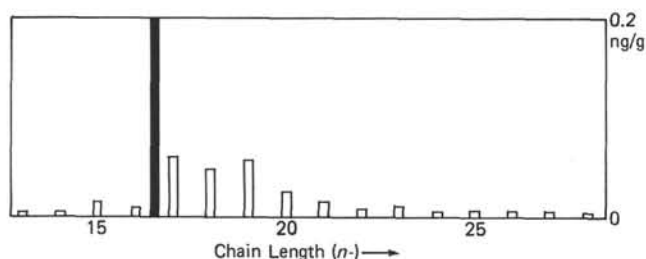[f] Based on mass-spectra interpretation, GC retention data, and TLC characteristics.

Figure 3. Distribution of acyclic ketones in Section 465A-38-3. Hollow bars = n-alkan-2-ones. Solid bars = 6,10,14-trimethylpentadecan-2-one.

Table 6. Concentrations of stanones in Section 465A-38-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
5β-Cholestan-3-one	XXXIXa	1.06
5α-Cholestan-3-one	XLa	0.70
24-Methyl-5β-cholestan-3-one	XXXIXb	0.30
24-Methyl-5α-cholestan-3-one	XLb	0.36
24-Ethyl-5β-cholestan-3-one	XXXIXc	1.03
24-Ethyl-5α-cholestan-3-one	XLc	1.25

[a] Assignment based on mass spectral interpretation, comparison with literature spectra, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.

Table 7. Concentrations of ster-4-en-3-ones in Section 465A-38-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
Cholest-4-en-3-one	XLIa	1.5
24-Methylcholest-4-en-3-one	XLIb	0.3
4,24-Dimethylcholest-4-en-3-one[d]	—	0.3
24-Ethylcholest-4-en-3-one	XLIc	1.1

[a] Assignment based on mass spectral interpretation, comparison with literature spectra, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Speculative assignment based on mass spectral interpretation alone.

Table 8. Concentrations of 4-methylstenones in Section 465A-38-3.

Assignment	Structure[a]	Concentration (ng/g)[b]
4-Methylcholesten-3-one[c]	—	1.0
4-Methylcholesten-3-one[c]	—	2.0
4,24-Dimethylcholesten-3-one[c]	—	0.3
4,24-Dimethylcholesten-3-one[c]	—	0.3
4,24-Dimethylcholesten-3-one[c]	—	0.6
4,23,24-Trimethylcholest-22-en-3-one[d]	XLII	0.6
4,23,24-Trimethylcholest-22-en-3-one[d]	XLII	1.3

[a] See Appendix.
[b] Dry weight of sediment.
[c] Speculative assignment based on mass spectral interpretation; double-bond position uncertain.
[d] Assignment based on mass spectral interpretation and comparison with literature spectra (Gagosian and Smith, 1979); these two isomers cannot be differentiated from their mass spectral characteristics.

and n-alkanols are consistent with inputs from marine algae (cf. Simoneit, 1978). The absence of series of long-chain (i.e., $>C_{21}$) compounds, especially n-alkanes with pronounced CPI values, argues against a major lipid contribution from higher-plant waxes (e.g., Eglinton and Hamilton, 1967). The monomethyl branched compounds appear as carboxylic acids; their presence is an indication of bacterial input (e.g., Cranwell, 1973).

Two major sources of the C_{18}–C_{20} acyclic isoprenoids are possible; plant phytol and(or), for the alkanes, methanogen lipids (Holzer et al., 1979). At present, isoprenoids from these two origins cannot be distinguished, but it seems probable in view of the data given

below that both may be contributors in this instance. 2,6,10,15,19-pentamethyleicosane (I) and squalane (II) occur in methanogens (Holzer et al., 1979) and are probably biological markers of sediment lipid contributions from these organisms. The source of lycopane (III) is unclear; it could be formed by diagenetic hydrogenation of lycopene from algae, but a direct bacterial origin

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Table 9. Concentrations of hopanones in Section 465A-38-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
22,29,30-Trisnorhopan-21-one[d]	XLIII	5.0
22,29,30-Trisnorhopan-21-one[d]	XLIII	0.4
30-Norhopan-22-one[d]	XLIV	0.1
30-Norhopan-22-one[d]	XLIV	0.1
Homohopan-29-one[d]	XLV	0.2
Homohopan-29-one[d]	XLV	0.1
Bishomohopan-31-one	XLVI	0.2
Trishomohopan-32-one	XLVII	0.25
Tetrakishomohopan-33-one	XLVIII	0.2

[a] Based on mass spectral interpretation, comparison with literature spectra, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Stereochemistry at C-17 or C-17 and C-21 undefined.

Table 10. Concentrations of sterols[a] in Section 465A-38-3.

Assignment[b]	Structure[c]	Concentration (ng/g)[d]
Cholest-5-en-3β-ol	XLIXa	4.0
5α-Cholestan-3β-ol	La	0.4
24-Methylcholest-5-en-3β-ol	XLIXb	0.6
24-Methyl-5α-cholestan-3β-ol	Lb	0.4
24-Ethylcholest-5-en-3β-ol	XLIXc	1.0
24-Ethyl-5α-cholestan-3β-ol	Lc	0.4
4,23,24-Trimethyl-5α-cholest-22-en-3β-ol	LId	1.2

[a] Analyzed as TMS ethers.
[b] Based on mass spectral interpretation, comparison with literature spectra, and GC retention times.
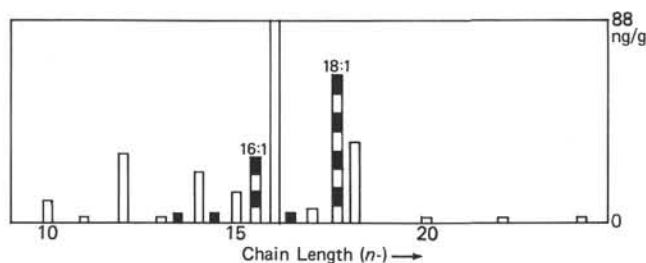[c] See Appendix.
[d] Dry weight of sediment.

Figure 4. Distribution of acyclic carboxylic acids in Section 465A-38-3. Hollow bars = n-alkanoic acids. Striped bars = alkenoic acids (from left to right: $C_{16:1}$ and $C_{18:1}$). Solid bars = branched alkanoic acids (from left to right: C_{14}, C_{15}, and C_{17}).

Table 11. Metalloporphyrins in Section 465A-38-3: UV/visible data (in CH_2Cl_2) and concentrations.

Species	Bands (nm ± 1) Soret	β	α	Concentration (μg/g)[a]
Nickel	391	513	549	0.02
Vanadyl	409	532	571	0.62

[a] Pigment yield calculated using the following molar extinction coefficients (ϵ): nickel porphyrins, $\epsilon = 34820$ at 549 nm; vanadyl porphyrins, $\epsilon = 26140$ at 571 nm.

Table 12. Relative abundances of metalloporphyrins in Section 465A-38-3.

Series (structure)		C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}
Vanadyl porphyrins										
DPEP series	M.W.[a]	429	443	457	471	485	499	513	527	541
(LIV)	R.A.[b]	—	—	—	2	9	23	60	100	44
Nickel porphyrins										
DPEP series	M.W.[a]	420	434	448	462	476	490	504	518	532
(LIV)	R.A.[c]	—	—	—	13	50	75	100	38	40
Etio series	M.W.[a]	422	436	450	464	478	492	506	520	534
(LIII)	R.A.[c]	10	25	65	55	80	35	40	10	15
Unidentified series[d]										
	M.W.[a]	455	469	483	497	511	525	539	553	
	R.A.[b]	1	3	4	2	8	19	53	60	

[a] Molecular weight.
[b] Relative abundance with respect to C_{31} DPEP vanadyl porphyrin.
[c] Relative abundance with respect to C_{30} DPEP nickel porphyrin.
[d] The molecular weights of this series are not assigned to any particular carbon number; however, 553 is possibly a C_{33} homolog.

(e.g., from methanogens) is also conceivable (Brassell, Wardroper, et al., 1981).

Cyclic Components

The minor amounts of dehydroabietic acid (LII) and the aromatic diterpenoids provide evidence of a small terrigenous input from higher plants (Simoneit, 1977).

Among the steroidal components of Section 465A-38-3, there are several compounds that can be attributed to marine origins, such as the dinoflagellate marker 4,23,24-trimethylcholest-22-en-3β-ol (LId) (Boon et al., 1979). C_{29} sterols have been used as indicators of terrestrial inputs (Huang and Meinschein, 1976), but without knowledge of their stereochemistry at C_{24} it is uncertain whether the 24-ethylcholesteroids in Section 465A-38-3 are principally derived from higher plant or algal sources. Indeed, the sterol and sterone distributions differ from that of the steranes, where 24-ethylcholestanes dominate, suggesting that there may have been contributions of C_{29} steroids from various sources. Certainly 23,24-dimethylcholesteroids are known only in marine organisms. The steroidal ketones also may reflect direct inputs from marine organisms; for example, sponges and dinoflagellates contain cholest-4-en-3-one (XLIa) (Delseth et al., 1979) and 4,23,24-trimethylcholest-22-en-3-one (XLII) (Withers et al., 1978), respectively. Alternatively, these compounds may be diagenetic derivatives of sterols (Gaskell and Eglinton, 1975; Gagosian and Smith, 1979). The origin of the C_{19} to C_{25} steranes is uncertain. They may be related to the 5α-stanols with degraded side chains previously recognized in sponges (Ballantine et al., 1977) and Neogene sediments (Brassell, Comet, Eglinton, Isaacson, et al., 1980). In addition, sponges are known to contain 24-isopropylcholesteroids (Hofheinz and Oesterhelt, 1979), which may be precursors of some C_{30} steranes. Two principal sources of 4-methylsteroids are possible: dinoflagellates (e.g., Withers et al., 1978, 1979) and methanotrophic bacteria (Bird et al., 1971). Although these organisms contain only 4-methylsterols and 4-methylsterones, such compounds are the probable precursors of the steroidal hydrocarbons with 4-methyl substitution. The overall distribution of 4-methylsteroids in Section 465A-38-3 is

more suggestive of inputs from dinoflagellates than from methanotrophic bacteria. In general, the variety of the steroid side chains in Section 465A-38-3 suggests that the steroids are predominantly of marine origin (Patterson, 1971; Wardroper, 1979).

Although hopanoids occur in both eucaryotes and procaryotes, bacteria are now generally regarded as the major source of most hopanoids in the marine system (Ourisson et al., 1979). However, neohop-13(18)-ene (XX) and hop-17(21)-ene (XIXc) both may be direct lipid contributions from ferns, rather than diagenetic products of hop-22(29)-ene (Brassell, Comet, et al., 1980). The recognition of an extended series of $\Delta^{17(21)}$-hopenes, however, suggests that bacteria are important contributors of hopanoids to Section 465A-38-3, because procaryotes are the only type of organisms known to biosynthesize such extended compounds. Aromatic hopanoids are generally interpreted as diagenetic products of hopanoids (e.g., Ourisson et al., 1979), and therefore may also be regarded as indicators of bacterial inputs to sediments.

Until recently, ferns were the only category of biota in which fernenes (XXI) and arbor-9(11)-ene (XXII) had been recognized and these compounds were therefore regarded as biological markers of terrestrial inputs. The discovery of fernenes in a bacterium (Howard, 1980) weakens the status of these compounds as terrestrial markers. The absence of cyclic triterpenoids other than fernenes and hopanoids and of their diagenetic derivatives argues against major angiosperm inputs.

Other Components

Various origins can be proposed for the non-hopanoid aromatic hydrocarbons. It has been suggested (Wakeham et al., 1980) that phenanthrene (XXIII) and methylphenanthrenes (XXIV) may be diagenetically formed by steroid degradation. By analogy, chrysene (XXVII) and methylchrysene (XXVIII) could conceivably be derived from pentacyclic triterpenoids, although direct inputs from terrestrial sources are also possible, especially as fluoranthene (XXV) and pyrene (XXVI) cannot easily be rationalized as diagenetic products of biolipids. The origin of perylene (XXIX) and methylperylene (XXX) is uncertain (Wakeham et al., 1979, 1980).

Porphyrins are the dominant lipid components of Section 465A-38-3. They are geochemically derived from chlorophylls, and therefore represent molecular evidence of productivity.

In summary, the lipid composition provides qualitative evidence of contributions to the sediment from marine, terrestrial, and bacterial sources. Additionally, by grouping the lipids according to their structural affinities (Table 13), a semi-quantitative indication of these inputs, which may serve as a paleoenvironmental signature (Fig. 5), emerges. The immediate problem arising from this approach is that numerous unrecognized or unknown compounds cannot be included in such a classification. However, the majority of such lipids are only minor components of the sample, so their absence should

not significantly affect the outcome. A further problem is that the lipid composition has not remained static since deposition, but has changed in response to diagenesis. The extent of the influence of diagenetic processes on the distribution of lipid structural types is uncertain. In general, however, the products of known diagenetic transformations can be related to their precursors, and therefore may be accounted for. It seems improbable that a significant proportion of lipids will lose their structural identity until the advent of catagenesis.

The dominance of lipids of marine algal origin in Section 465A-38-3 is clearly illustrated in the distribution of lipid structural types (Fig. 5; Table 13). Bacterial inputs, especially hopanoids, are also prominent, but lipids of terrestrial origin are only minor constituents. Such lipid data are consistent with those from visual examination of the kerogen; both show that the organic matter in the sample is principally derived from marine sources, possibly reflecting high algal productivity.

In addition to the overall structural grouping of lipids, the steroids can be subdivided according to their side chains and C-4 substitution (Table 14; Fig. 6). As a result of the taxonomic specificity of sterol biosynthesis, the occurrence of particular side chains appears restricted to specific classes of organisms (Patterson, 1971). Hence, several of the steroidal subdivisions of Table 14 reflect inputs from marine biota. Indeed, this classification represents a marked improvement on the simplistic approach of Huang and Meinschein (1979), although further improvements, especially the inclusion of data for steroidal C_{24} stereochemistry, are envisaged.

Paleoenvironment: Comparison of Section 465A-38-3 with Other Cretaceous DSDP Samples

The results from the Leg 62 Albian sample (when expressed as structural ratios) show major differences and some similarities with three other previously described Cretaceous samples of deep-sea origin (Table 15).

It must be stressed that each of these Cretaceous samples is of a different degree of maturity. Hence, the detailed composition in terms of individual compounds and of functionalized lipids as chemical classes (alcohols, carboxylic acids, ketones, etc.) varies greatly with maturity from sample to sample. However, by using structural summation, the effects of diagenesis are minimized, although not eliminated, and intersample lipid comparison becomes more acceptable; nevertheless, this approach will require further extensive study to evaluate the effect of increasing diagenesis (maturation) on the structural ratios. For example, the Leg 61 samples which are of high maturity showed relative enhancement of the n-alkanes, presumably as a consequence of their preferential catagenetic release from the kerogen with proximity to the oil-generation zone.

The most significant difference between Leg 62 and the lipids from previously described DSDP Legs is that the relative and absolute porphyrin content of the Leg 62 sample is much higher than in any Cretaceous sample previously described by us; this is rationalized in terms of a higher productivity environment for the vicinity of

Table 13. Quantitative distribution (ng/g) of gross structural types according to functionality, Section 465A-38-3.

No. in Figure 5	Structural Type	Functional Group						Total	Comment
		Acids[a]	Alcohols[b]	Ketones[c]	Alkanes	Alkenes[d,e]	Aromatics[e]		
1	Short chain ($nC_{10}-C_{20}$)	263	1.2	0.8	48.9	—	—	313.9	Algal
2	Long chain ($nC_{21}-C_{35}$)	6.8	—	0.2	36.5	—	—	43.5	Terrestrial/bacterial
3	Monomethyl branched straight chain ($nC_{10}-C_{20}$)	10.0	—	—	—	—	—	10.0	Bacterial
4	Acyclic diterpenoid (pristane, phytane, etc.)	0.5	—	0.2	6.2	—	—	6.9	Algal or bacterial
5	Acyclic sesterterpenoid (C_{25} irregular isoprenoid)	—	—	—	0.35	—	—	0.4	Bacterial
6	Acyclic triterpenoid (squalane)	—	—	—	1.0	—	—	1.0	Bacterial
7	Acyclic tetraterpenoid (lycopane)	—	—	—	17.9	—	—	17.9	?Marine algal or bacterial
8	Cyclic diterpenoid	1.0	—	—	—	—	4.0	5.0	Terrestrial
9	Hopanoid	1.0	—	6.2	52.4	92.3	26.4	178.4	Bacterial
10	Non-hopanoid triterpenoid	—	—	—	—	2.8	—	2.8	Mixed marine
11	Steroid	—	5.9	13.4	13.5	45.6	—	78.4	Marine
12	Non-biogenic PNA	—	—	—	—	—	1.4	1.4	Terrestrial?
13	Perylene + methylperylenes	—	—	—	—	—	4.6	4.6	Unknown
14	Porphyrin[e]	—	—	—	—	—	—	600	Marine

Note: — = not detected.
[a] Includes alkanoic and alkenoic acids; concentrations are quoted as mole fractions of the appropriate saturated hydrocarbon.
[b] Includes alkanols and alkenols (e.g., Δ^5-stenols and Δ^{22}-stanols); concentrations are quoted as mole fractions of the appropriate saturated hydrocarbon.
[c] Includes alkanones (e.g., stanones) and alkenones (e.g., ster-4-en-3-ones); concentrations are quoted as mole fractions of the appropriate saturated hydrocarbon.
[d] All compounds are monounsaturated.
[e] Concentrations of compounds quoted directly, not as mole fractions of saturated hydrocarbon, because of limits of experimental error.

the Hess Rise during the Albian. Similarly, the considerable abundance of short straight-chain material and minor amounts of long straight-chain material show that algal components appear to be greatly dominant over terrestrial. This is interpreted as indicating that the Hess Rise area during the Albian was under facies control different from that at the other described Cretaceous sites.

From the comparison of the relative abundances of lipid structural types (Table 15), Section 465A-38-3 most closely resembles the Leg 48 Albian limestone. Hence, the lipids appear to reflect the similarity of age and lithology of these samples, although this similarity is not always apparent from the individual lipid distributions; for example, sterenes dominate Section 465A-38-3, whereas diasterenes are the major steroids of Section 402A-18-1.

Visual kerogen results corroborate the lipid data. The organic matter consists mainly of sapropelic structureless "kerogen" of presumed marine algal origin; this predominantly autochthonous material contains a few vitrinite particles and some spores as a minor terrestrial contribution.

Diagenesis

General Appraisal

The detailed study of a single sample from a DSDP hole inevitably does not permit an evaluation of the major diagenetic trends at that site. However, the lipids of Section 465A-38-3 can be related to stages of known diagenetic pathways, thereby enabling an assessment of the maturity status of this sample.

Sample immaturity is shown by the presence of functional lipids, namely alkenes, ketones, alcohols, and carboxylic acids that do not survive extensive diagenesis. In particular, such a well-preserved Cretaceous assemblage of labile lipids suggests that post-depositional microbial activity has not drastically affected the lipid distribution. Furthermore, the sample has not experienced much thermal stress.

Acyclic Components

In general, acyclic lipids are less valuable indicators of sediment maturity than cyclic components, and the composition of Section 465A-38-3 reflects this fact. Low CPI values for n-alkanes typify both mature sediments and immature samples where these compounds are principally derived from algal and bacterial sources (e.g., Simoneit, 1978). The high CPI value for the n-alkanoic acids and the presence of alkenoic acids strongly suggest sediment immaturity. A similarity between n-alkan-2-one and n-alkane distributions may reflect their common biological origin, or indicate that alkane oxidation has occurred prior to deposition (Brassell, Comet, et al., 1980). For Section 465A-38-3, these two possibilities cannot be distinguished.

Most of the acyclic isoprenoid alkanes found in Section 465A-38-3 occur over a wide range of maturity, from recently deposited sediments to crude oils. The exceptions, lycopane (III) and 2,6,10,15,19-pentamethyleicosane (I), are less well-documented bio- and geolipids, although their presence is probably not significant as a diagenetic indicator. The stereochemistry of these acyclic isoprenoid alkanes, however, would denote their thermal maturity (cf., Patience et al., 1978). Since 6,10,
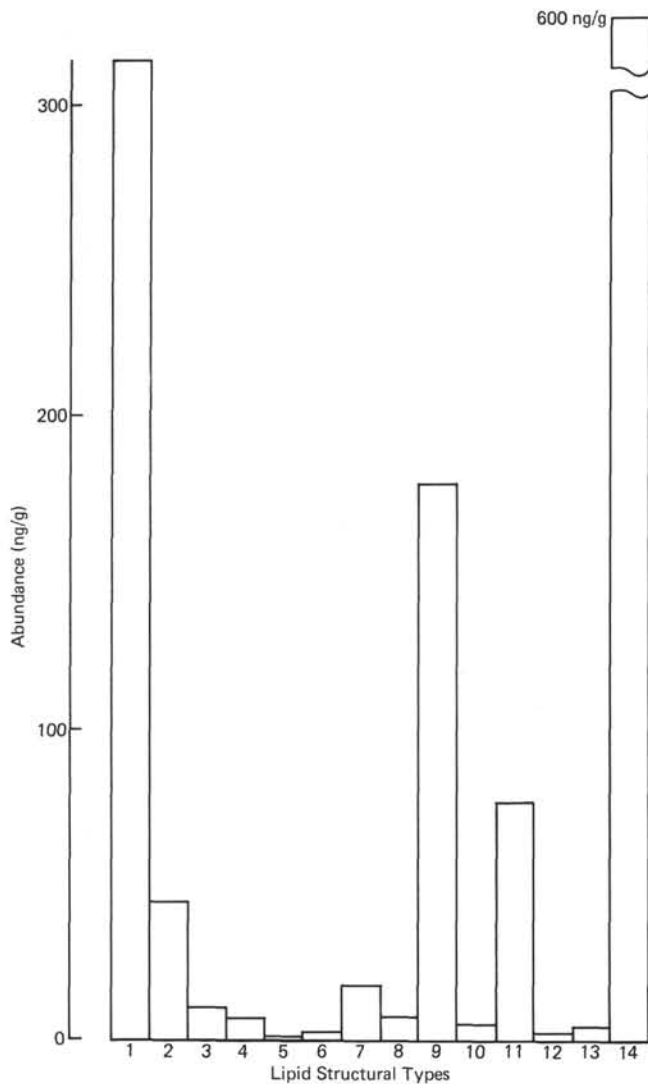
Figure 5. Distribution of lipid structural types in Section 465A-38-3 (cf., Table 13).

14-trimethylpentadecan-2-one (XXXVIII) is not known in mature sediments, its presence in Section 465A-38-3 indicates sample immaturity.

Cyclic Components

The minor amounts of diterpenoids in Section 465A-38-3 provide little evidence of diagenetic trends or sample maturity. In contrast, the steroidal constituents reflect various diagenetic processes. First, the stenones and stanones may be intermediates in the diagenetic conversion of stenols to stanols (Gaskell and Eglinton, 1975; Gagosian and Smith, 1979), although, as stated above, a direct input of steroidal ketones from organisms is possible. Indeed, steroidal ketones have not been widely reported as constituents of ancient sediments, and their role in steroidal diagenetic transformations is unclear. It may be significant, however, that the distributions of C_{27} to C_{29} Δ^5-stenols, 5α-stanols, 5α- and 5β-stan-3-ones and ster-4-en-ones are generally similar, suggesting a diagenetic or source related relationship between them. The distributions of sterenes and steranes also resemble that of the oxygenated steroids, except that carbon number ranges of the sterenes and steranes are greater. The absence of sterols or sterones with degraded side chains (i.e., C_{19}–C_{26} components) makes it uncertain whether their sterane counterparts are formed by steroidal degradation, or are diagenetically derived from precursors with similar carbon skeletons.

Δ^4-sterenes are the dominant steroidal alkenes, and Δ^5-sterenes are also abundant. Δ^2-sterenes are important intermediates in the formation of Δ^4- and Δ^5-sterenes, diasterenes, steranes, and diasteranes from stanols (e.g., Dastillung and Albrecht, 1977). The absence of Δ^2-sterenes here and the abundance of Δ^4- and Δ^5-sterenes provides an estimate of the maturity of the sediment. Δ^2-sterenes usually dominate the sterenes of young sediments, whereas older sediments tend to have Δ^4- and Δ^5-sterenes in greater abundance than Δ^2-sterenes (Wardroper, 1979). In Section 465A-38-3, Δ^2-sterenes were not detected, yet their presumed precursors

Table 14. Quantitative distribution (ng/g) of steroidal structures according to functionality, Section 465A-38-3.

No. in Figure 6	Hydrocarbon Skeleton	Alcohols[a]	Ketones[b]	Alkanes	Alkenes[c,d]	Total	Comment
1	Androstane	—	—	0.4	—	0.4	Marine
	Pregnane	—	—	0.3	—	0.3	Marine
	20-Methylpregnane	—	—	0.1	—	0.1	Marine
	20-Ethylpregnane	—	—	0.03	—	0.1	Marine
	Cholane	—	—	0.3	—	0.3	Marine
	24-Methylcholane	—	—	0.06	—	0.1	Marine
2	Cholestane	3.3	3.2	3.2	13.5	23.1	Mixed
3	24-Methylcholestane	0.8	1.0	1.6	5.6	8.9	Mixed
4	23,24-Dimethylcholestane	—	—	0.7	5.0	5.7	Marine
5	24-Ethylcholestane	1.1	3.3	5.1	12.7	22.1	Terrestrial?
6	24-Propylcholestane	—	—	1.4	—	1.4	Marine
7	4-Methylpregnane	—	—	0.1	—	0.1	Marine algal
8	4-Methyl-24-norcholestane	—	—	0.2	—	0.2	Marine algal
9	4-Methylcholestane	—	3.2	—	—	3.2	Marine algal
10	4,24-Dimethylcholestane	—	1.1	—	—	1.1	Marine algal
11	4,23,24-Trimethylcholestane	0.8	1.8	—	8.8	11.4	Marine algal

Note: — = not detected.
[a] Includes alkanols (e.g., stanols) and alkenols (e.g., Δ^5-stenols and Δ^{22}-stanols); concentrations are quoted as mole fractions of the appropriate saturated hydrocarbon skeleton.
[b] Includes alkenones (e.g., ster-4-en-3-ones) and alkanones (e.g., stanones); concentrations are quoted as mole fractions of the appropriate saturated hydrocarbon skeleton.
[c] Concentrations of compounds are not recalculated as mole fractions of saturated hydrocarbon, because of the limits of experimental error.
[d] Steratrienes and aromatic steroids present only in trace amounts are not included, because of incomplete characterization.
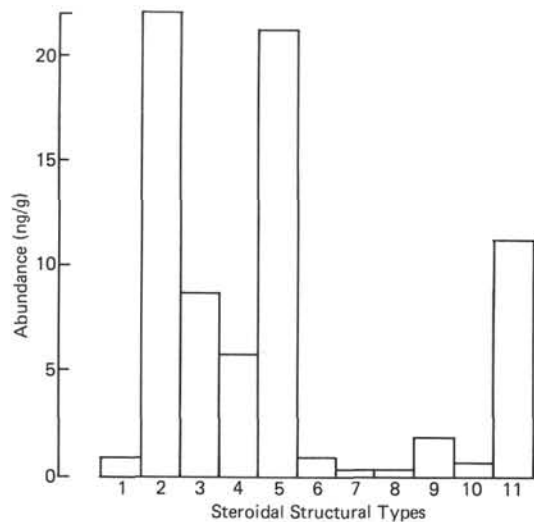
Figure 6. Distribution of steroidal structural types in Section 465A-38-3 (cf., Table 14).

(stanols) and various diagenetic products were found. A similar distribution of steroidal components were found in sediments from the deeper parts of Site 440 (Brassell, 1980). It appears either that the transformation of stanol to Δ^2-sterene occurs only within a particular early stage of diagenesis, or that at later stages any Δ^2-sterenes formed from stanols are rapidly converted into their Δ^4- and Δ^5-analogs. These data show that the published diagenetic processes of steroidal diagenesis (e.g., Dastillung and Albrecht, 1977) are simplistic approximations. The high carbonate and low clay content of the sediment and the alkaline conditions (site reports, this volume) may have affected the steroidal distributions. Perhaps the non-acidity of the sediment results in a low rate of hydrogenation; this may explain the presence of stenones.

The presence of a single diasterene (XIIIc), rather than a series of diasterenes, is curious. The distributions of diasterenes and diasteranes in Section 465A-38-3 dif-

fer markedly from those of the stanols or sterenes, apparently precluding a direct diagenetic relationship between them. The generally minor amounts of diasteroids recognized possibly reflect the low clay content of Section 465A-38-3, since the diasterene formation is catalyzed by acidic clay (Rubinstein et al., 1975). It may also be significant that this diasterene (XIIIc) possesses 4-methyl substitution; perhaps such substitution aids or stabilizes the backbone rearrangement process. Indeed, the 4,23,24-trimethylcholestadiene and 4-methyldiasterene found may be products of direct dehydration and rearrangement of dinosterol [4,23,24-trimethyl-5α-cholest-22-en-3β-ol (LId)], respectively. If so, it would appear that the proclivity of steroidal diagenetic processes may be dependent on the precursor sterol (i.e., whether it possesses 4-methyl substitution, Δ^7 unsaturation, etc.).

In general, the distribution of steroidal components of Section 465A-38-3 attests the immaturity of the sediment, as is also shown by the sterane stereochemistry (only 5α- and 5β-isomers of 20R-8α,14α,17α-steranes are present; cf. Mackenzie et al., 1980). In an attempt to describe the steroid maturity of Section 465A-38-3 in semi-quantitative terms, the relative concentrations of the cholesteroids can be plotted (Fig. 7).

Similar treatment of other DSDP samples may help establish a reference framework for accurate assessment of the diagenetic state of immature sediments. For Section 465A-38-3, cholesterenes dominate, with C_{27} sterols, sterones, and steranes all present in significant amounts. In less mature samples, the sterols and sterones can be expected to dominate; in more mature sediments, the steranes will predominate. The sensitivity and utility of this approach to diagenetic assessment needs investigation.

The distribution of hopanoids is consistent with sample immaturity; ββ-hopanes dominate their αβ and βα isomers, and hopanoid alkenes, alkanones, and alkanoic acids are all present (Table 13). Few of the hopanoids recognized represent direct biological inputs; in the main, they are believed to be diagenetic products, many of which are formed from polyhydroxybacterio-

Table 15. Comparison of relative abundances of lipid structural types in DSDP Cretaceous sediments.

Molecular Structural Types	465A-38-3; Hess Rise, N.W. Pacific; Organic-Rich Limestone; U. Albian	462-54-2; Nauru Basin, N.W. Pacific; Organic-Poor Limestone; Campanian	416A-14-4; Moroccan Basin, N.E. Atlantic; Argillaceous Turbidite; Valanginian	402A-18-1; Bay of Biscay, N.E. Atlantic; Laminated Organic-Rich Limestone: Albian
Short chain (nC_{10-20})	+ + +	tr	+ + +	+ +
Long chain (nC_{21-35})	+ +	+ + + + +	+ + + +	+ +
Mono-methyl branched (straight-chain)	+	—	tr	tr
Acyclic diterpenoid	+ +	—	+ +	+ +
Acyclic sesterterpenoid	+	—	+	N.E.
Acyclic triterpenoid	+	—	+	N.E.
Acyclic tetraterpenoid	+ +	—	—	—
Cyclic diterpenoid	+	—	tr	tr
Hopanoid	+ + +	+ + + +	+ + +	+ + + +
Non-hopanoid triterpenoid	+	—	—	—
Steroid	+ +	+ + +	+ +	+ +
4-Me steroid	+ +	—	+ +	+
PNA (non-biogenic)	+	—	+	+
Porphyrin	+ + + +	—	+ +	+ +

Notes: Symbols employed for expressing semi-quantitative abundances (as % of the total) for the lipid fraction: + + + + + = 50-100%; + + + + = 25-50%; + + + = 10-25%; + + = 1-10%; + = 0.1-1%; tr = <0.1%; — = not detected; N.E. = not examined. Sources for data reported: Barnes et al., 1979; Wardroper, 1979 (Leg 48); Brassell, Comet, Eglinton, McEvoy, et al., 1980; Brassell, Wardroper, et al., 1981 (Leg 50); Thomson et al., in press (Leg 61); this paper (Leg 62). Data for the early legs, particularly Leg 48, are more qualitative than quantitative, owing to the procedures employed.
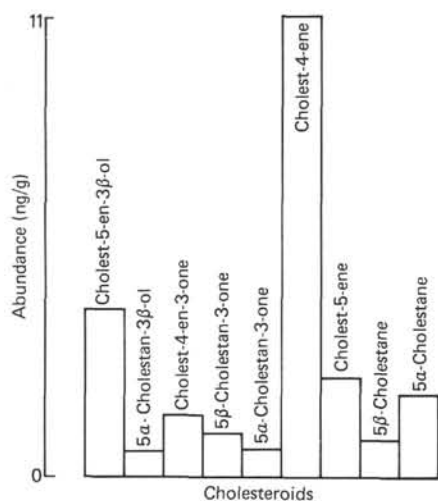
Figure 7. Distribution of cholesteroids in Section 465A-38-3.

hopanes. For examples, hopanoid acids and hopanones, other than $\beta\beta$-29-norhopan-22-one (e.g., Berti et al., 1963), have not been found in organisms, but both series of components probably arise from the poly-hydroxybacteriohopanes (e.g., Wardroper, 1979). Certainly, the lack of similarity in the distributions of hopanones and hopanes shows that the former are not oxidation products from the latter. As discussed above, hop-17(21)-ene (XIX) and neohop-13(18)-ene (XX) may both originate from the direct input of ferns (Berti and Bottari, 1968), or from diagenetic isomerization of hop-22(29)-ene via hop-21-ene (Ensminger, 1977).

For Section 465A-38-3, these two origins cannot be distinguished. The presence of an extended series of $\Delta^{17(21)}$-hopenes, however, supports the argument for diagenetic formation of the C_{30} hopenes; also, no traces of their precursors were detected. This situation parallels that found towards the bottom of Site 440 (Brassell, Comet, et al., 1980), and also at Sites 416 (Moroccan Basin; Brassell, Comet, Eglinton, McEvoy, et al., 1980) and 402 (Bay of Biscay; Barnes et al., 1979), suggesting that it may be typical of immature deep-sea sediments. In addition, $\beta\beta$-hopanes dominate their $\beta\alpha$- and $\alpha\beta$-isomers, as they do in other immature Cretaceous deep-sea sediments. A further measure of sediment maturity is provided by the ratio of 22S and 22R diastereoisomers of $\alpha\beta$-hopanes, which increases with increasing maturity (e.g., Ensminger, 1977; Mackenzie et al., 1980). In Section 465A-38-3, as in other Cretaceous samples (e.g., Barnes et al., 1979), the 22R isomers are greatly dominant (22R/22S = 13.8), indicating the immaturity of the sample, in contrast to Leg 61 samples (Thomson et al., in press), where only $\alpha\beta$-hopanes with 22S isomers dominant were detected. For the extended series of $\Delta^{17(21)}$-hopenes, the ratio of 22R to 22S isomers is markedly closer to unity (R/S = 1.4) than for the $\alpha\beta$-hopanes. This suggests that C_{22} epimerization occurs faster in hopenes than in hopanes.

The presence of partially to fully aromatized hopanoids in Section 465A-38-3 is consistent with the postulated diagenetic sequence of successive aromatization from ring D through rings C, B, and A (Greiner et al.,

1976, 1977; Spyckerelle et al., 1977a, b). These compounds are early-stage diagenetic products occurring in immature sediments of Recent (Tissier and Spyckerelle, 1977; Tissier and Dastillung, 1978) through Cretaceous age (Barnes et al., 1979; Brassell, Comet, Eglinton, McEvoy, et al., 1980). The significance of the aromatic hopanoids without side chains and with ethyl and isopropyl side chains is unclear.

The diagenetic transformations of fernenes are poorly understood. It has been postulated from data for Site 440 in the Japan Trench (Brassell, 1980) that fern-7-ene and fern-9(11)-ene may isomerize to fern-8-ene (XXI). In Section 465A-38-3, the dominance of fern-8-ene over its Δ^7 and $\Delta^{9(11)}$ isomers is greater than that towards the bottom of Site 440, probably reflecting the greater maturity of the Leg 62 sample.

Metalloporphyrins

Metalloporphyrins are the major class of lipid detected. Nickel porphyrins of both DPEP (deoxophyllo-erythroetioporphyrin) and etio types were present in approximately equal amounts. In contrast, vanadyl porphyrins comprise 95% of the total metalloporphyrins, yet they consist entirely of DPEP components. The absence of free base porphyrins indicates that chlorin diagenesis is complete. The defunctionalization of chlorophyll a would formally produce a C_{32} porphyrin (Treibs, 1936; Maxwell et al., in press), whereas in Section 465A-38-3 vanadyl C_{31} DPEP is predominant and the nickel porphyrins are dominated by C_{30} DPEP and C_{28} etioporphyrins. Such dealkylation is thought to be caused by high thermal stress, or possibly by an oxidative degradation of chlorophyll (Baker, Palmer, Huang, et al., 1978). In the present instance, we favor the latter possibility, as the alkaline nature of the sedimentary interstitial water (site report, this volume) suggests that conditions for oxidative degradation may have existed. In addition, the absence of vanadyl etioporphyrins and of extended porphyrins (i.e., $>C_{32}$) indicates a mild thermal history (Baker et al., 1978; Maxwell et al., in press). The dominance of vanadyl complexes over nickel complexes may be accounted for, in part, by their greater thermodynamic stability (Palmer et al., 1979). However, comparison with metalloporphyrin data for Cretaceous sediments from the Moroccan Basin (Leg 50; Brassell, Comet, Eglinton, McEvoy, et al., 1980; Palmer and Baker, 1980) reveals an anomaly. The total lipid distributions for Leg 50 were diagenetically more mature than Section 465A-38-3, yet only nickel porphyrins, comprising both DPEP and etioporphyrin series, were detected in Leg 50 material. These differences may reflect different source materials and(or) different inorganic sedimentary conditions, i.e., low clay and high carbonate contents and alkaline interstitial water for Leg 62, compared with the high clay content and acidic sedimentary environment for the Leg 50 turbidites.

CONCLUSIONS

General

The lipid composition of Section 465A-38-3 is dominated by components derived from marine algae, sug-

gesting a high productivity environment. The relative and absolute abundances of porphyrins and short straight-chain components attest this suggestion, which is also supported by the presence of specific marine markers such as dinosterol. Lipids that can be assigned to terrestrial origins are present in low amounts. They include diterpenoids and triterpenoids derived from conifer resins and ferns. No biological markers or lipid distributions characteristic of angiosperms were observed. In addition, the aromatic hydrocarbons not directly related to biogenic precursors (principally derived from terrestrial sources) were present in low amounts. Evidence of major bacterial contributions to the sediment is provided by abundant hopanoids. The branched components and acyclic isoprenoid alkanes, which are probably derived from various sulphate reducers and methanogens, are present in minor concentration.

The maturity of Section 465A-38-3 is comparable to that of other Cretaceous DSDP samples—greater than that of Neogene sediments from the Japan Trench, and less than that of Cretaceous Nauru Basin sediments. Its overall immaturity, as shown by the lipid data, is consistent with the low vitrinite reflectance of the sample.

Paleoenvironmental Interpretation

A predominantly algal assemblage in a Lower Cretaceous "black shale" is unusual; most "black shales" appear to be of terrestrial, bacterial, or mixed origins (Barnes et al., 1979; Tissot et al., 1980). The finding of a well preserved assemblage of highly biodegradable lipids such as alkenoic and alkanoic acids and low molecular weight alkanes, all of algal origin, implies that the post-depositional microbial activity may not have drastically altered the original lipid distribution pattern. However, the high relative hopane concentration implies that microbial activity was nevertheless considerable.

An extensive microbial population may have utilized the small amounts of oxygen in the water column and the more easily degradable organic material in the sediment, such as carbohydrates and amino acids, which were consumed preferentially, leaving a relatively undegraded lipid "resistate" fraction. The lipids were not degraded extensively, because of (1) the low levels of available oxygen and (2) their rapid burial in the sediment.

Three environmental situations may be proposed to explain this non-degraded assemblage of algal lipids in which hopane producers (probably mainly bacteria) still played a significant role:

1) The bottom waters were stagnant and overlain by a highly productive water mass. In stagnant basins, hydrogen sulfide is often present in the water column (e.g., Cariaco Trench).

2) The environment was oxygen-depleted, but not poisoned with H_2S. Residual oxygen was present in the lower levels of the water column. This environment can occur in some contemporary upwellings as oxygen minima. Bacterial activity is often very extensive in such environments (e.g., Walvis Bay).

3) The environment was characterized by high sediment-accumulation rates associated with high productivity. Lipid preservation resulted from rapid burial.

It is not easy to choose between these three models. From the available data (site reports, this volume), the upper Albian of Site 465 was deposited during a period of high sedimentation, thus favoring the third model. Further evidence for this model is implied by the plate-tectonic reconstructions of Lancelot and Larson (1975). Their reconstruction places the Hess Rise during the Early Cretaceous within the equatorial high productivity area. The work of Shackleton and Boersma (site reports, this volume) shows that warm water and high fertility accompanied deposition in the South Atlantic, and that this may have affected the Pacific as well during the Albian. The present lipid data strongly support the idea of a major autochthonous contribution, with a minor allochthonous component, high productivity being chiefly responsible for the lipid distributions. In support of this idea, the results at Sites 463 and 464 show that lower sedimentation rates occurred during the late Albian, and the organic carbon contents here are notably lower. It would therefore appear that a relationship exists between high productivity, sedimentation rate, and type and amount of organic matter. However, at Site 463 the high productivity during the Late Cretaceous has not resulted in enhanced organic carbon values, although it did produce a greater thickness of biogenic pelagic deposit, which tends to negate the idea of a direct relationship between sedimentation rate and organic carbon. An additional phenomenon must therefore be invoked to account for the enhanced organic carbon values in the Lower Cretaceous of the Hess Rise. We believe that this is some regional effect in which the levels of oxygen within the water column were sufficient to ensure oxidation of a low flux of slowly deposited organic matter, i.e., an oxygen minimum, but insufficient to oxidize the enhanced organic carbon input of a highly productive water column. The final product was the deposition of organic-rich oozes of algal derivation with a strong bacteria "overprint." Other evidence of oxygen deficiency during sedimentation in the Albian is provided by the extensive sequences with fine-scale sedimentary lamination (site reports, this volume).

Further confirmation of inimical benthic conditions comes from micropaleontological analysis (site reports, this volume). The presence of a restricted benthic microfauna, i.e., two species of Buliminacea in vertically adjacent core sections, and high-diversity, abundant tropical planktonic assemblages (both foraminifers and radiolaria) tend to corroborate the idea of an organic-rich, reducing bottom environment (at slope depths of a few hundreds of meters), in which some oxygen was present, overlain by productive tropical water masses, thereby favoring the second model rather than the third.

The "Hess Archipelago" also may have played some role in providing the nutrients that initiated the plankton blooms. Terrestrial run-off from the islands is indicated by lipids of fern and conifer origin. Certainly, the low amounts of terrestrial plant lipid do not require the

proximity of major continental areas. Some of the silica, calcium, phosphorous, etc. necessary for plankton nutrition may have been derived from the weathering of vegetated volcanic islands. The association between volcanism, high radiolarian input, and black shale may not be fortuitous, as has been noted (site reports, this volume).

Finally it is necessary to emphasize the restriction of the carbonaceous facies to the Aptian–Albian in this area of the Pacific (as in many other parts of the world ocean). The reasons for the restriction of this event to the Lower Cretaceous and the frequency of algal carbonaceous limestones and "black shales" within the carbonaceous facies will be the subject of subsequent work.

ACKNOWLEDGMENTS

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APPENDIX