31. PRELIMINARY LIPID ANALYSES OF SEDIMENTS FROM SECTIONS 467-3-3 AND 467-97-2[1]

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ABSTRACT

The free lipids of two samples from the Californian Continental Borderland, DSDP Site 467, have been investigated. The study of these two samples (one a Recent, shallow sample, situated near the sediment surface and the other a middle Miocene, much deeper sample, situated near the bottom of the hole) revealed differences in their lipid assemblages, thus providing some evaluation of the maturity and diagenetic trends operating at this site. The organic matter represents both a marine and a terrestrial input. Oxygenated components, such as sterols, *n*-alkanols, and very long chain ketones, were abundant, along with chlorins in the Recent sample. Hydrocarbons and nickel (II) porphyrins were abundant in the Miocene sample. A minor epigenetic contribution to the Recent sample was apparent.

INTRODUCTION

The free lipids (hydrocarbons, ketones, alcohols, and tetrapyrroles) of two samples from the eastern North Pacific Ocean, Californian Continental Borderland, DSDP Site 467, were investigated. The samples were chosen to evaluate the organic inputs and conditions of deposition and also their maturity and diagenetic status. Thus a shallow and a deep sediment were compared:

1) Section 467-3-3, Quaternary, diatomaceous silty clay; sub-bottom depth 21 meters.

2) Section 467-97-2, middle Miocene, calcareous claystone; sub-bottom depth 912 meters.

The distribution of each functional class of compounds is described (Figs. 1 to 5 and Tables 1 to 8). Table 9 gives an overview of the results. All tables and figures reflect the gas chromatography (GC) retention order of the components described. The diverse distributions of the steroidal hydrocarbons prevented us from constructing tables consisting of data from both Sections 467-3-3 and 467-97-2 for these components.

EXPERIMENTAL TECHNIQUES

The experimental procedures used as similar to those employed in previous DSDP investigations (Brassell, Comet, Eglinton, Issacson et al., 1980). Section 467-97-2 was crushed in a Tema mill prior to extraction. The analysis of metalloporphyrins has been previously described (Comet et al., in press). In addition, chlorins from Section 467-3-3 were detected and quantitated before saponification by their electronic spectra (uv/vis) (obtained on a Perkin-Elmer 552 spectophotometer) in acetone using 1-cm (3-ml capacity) quartz cells.

Each component was quantitated from its gas chromatographic response where possible, or by mass fragmentography. Mass spectra were recorded using a Finnigan 4000 gas chromatography mass spectrometer (GC-MS) system equipped with a 20-meter OV-1 glass capillary column, and an INCOS 2300 system was used for data acquisition and processing. Compounds assignments were made from their individual mass spectra and GC retention times, with reference to authentic standards where possible. Mass fragmentography was used to authentic standards where possible. Mass fragmentography was used to characterize homologous and pseudohomologous series (Wardroper et al., 1977; Brassell, Comet, Eglinton, McEvoy et al., 1980) and to aid compound identification as well.

RESULTS

A wide range of free lipids was detected and is reported herein. However, there are some compound classes that have not been included in this paper, although they were detected. Such components include carboxylic acids, steroidal and hopanoidal ketones, and aromatic hydrocarbons.

Hydrocarbons

Acyclic

The *n*-alkanes ranged from C_{15} to C_{35} (but see the material that follows), with CPIs (odd/even Carbon Preference Index) of 3.6 and 1.1 for Core 3, Section 3, and Core 97, Section 2, respectively. However, the CPIs for the C_{15} to C_{26} range were 1.1 and 0.7, respectively. Thus the odd homologues of the C_{27} to C_{35} carbon range dominate the even *n*-alkanes. The absolute concentrations of the individual homologues are shown in Fig. 1, A and C. In addition, three very long chain *n*-alkanes, C_{37}, C_{38}, and C_{39}, were detected in Section 467-97-2 (Fig. 1, C); C_{37} was the dominant *n*-alkane detected. 3-Methylheptadecane and 4-methyloctadecane were tentatively identified in Section 467-3-3 and an unusual branched C_{25} alkane, eluting just after *n*-C_{21} alkane, was detected in Section 467-97-2 (Fig. 1, D). 2,6,10-Trimethylpentadecane, 2,6,10,14-tetramethylpentadecane (pristane), 2,6,10,14-tetramethylhexadecane (phytane) and 2,6,10,15,19-pentamethyleicosane were present in both samples (Fig. 1, B and D). Section 467-97-2 contained an additional, very long chain, isoprenoid alkane, 2,6,10,14,19,23,27,31-octamethyldotriacontane (lycopane, I).

n-Alkenes were not present in sufficient concentrations to be quantitated, with the exception of two triunsaturated very long chain components, $C_{37:3}$ (II) and $C_{38:3}$ (III) present in Section 467-3-3. These components were recognized from their mass spectra and GLC retention times by comparison with the same components isolated from the marine coccolithophorid. *Emiliania huxleyi* (Volkman et al., 1980). The double-bond posi-

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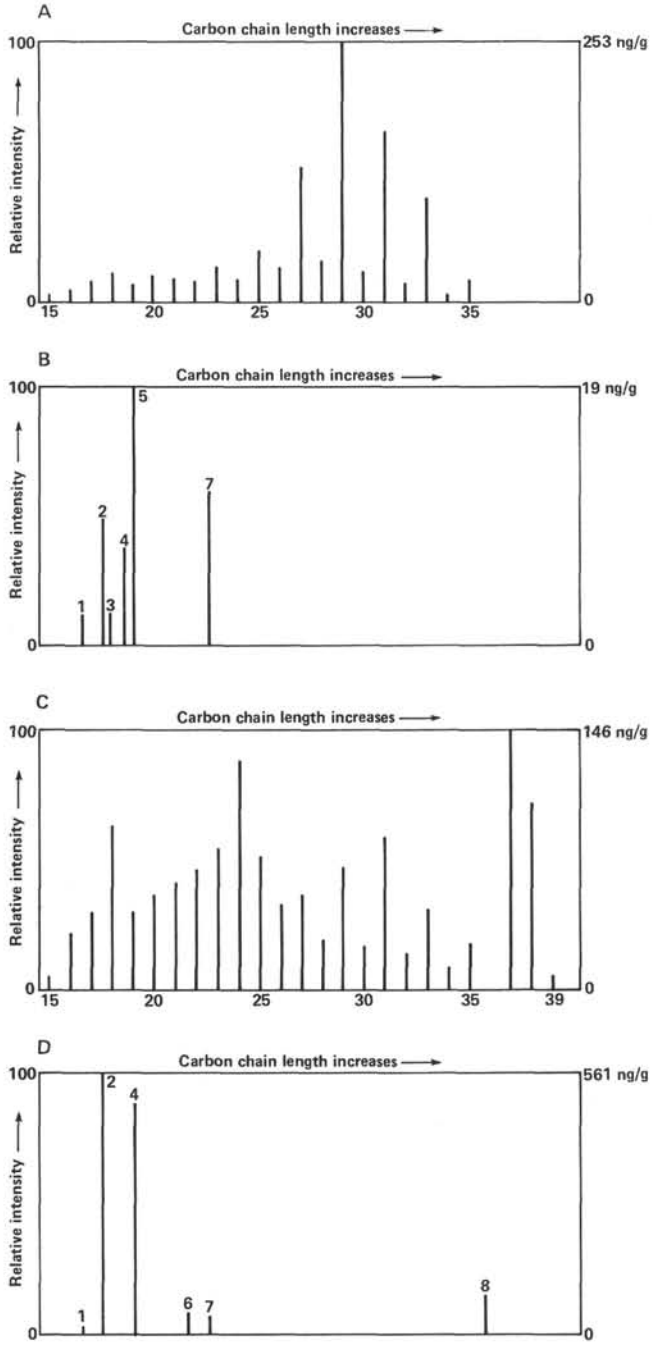

Figure 1. Distributions of acyclic alkanes at Site 467. A. Section 467-3-3: *n*-alkanes (C_{15}–C_{35}). B. Section 467-3-3: acyclic branched and isoprenoidal alkanes. (1 = 2,6,10-trimethylpentadecane; 2 = 2,6,10,14-tetramethylpentadecane [pristane]; 3 = 3-methylheptadecane [tentative assignment was made on the basis of the mass spectrum]; 4 = 2,6,10,14-tetramethylhexadecane [phytane]; 5 = 4-methylheptadecane [tentative assignment made on the basis of the mass spectrum]; 7 = 2,6,10,15,19-pentamethyleicosane.) C. Section 467-97-2: *n*-alkanes (C_{15}–C_{39}, C_{36} not detected). D. Section 467-97-2: acyclic isoprenoid alkanes (1, 2, 4, and 7, see Fig. 1, B for structures; 6 = unusual branched C_{25} saturated hydrocarbon; 8 = 2,6,10,14,19,23,27,31-octamethyldotriacontane [lycopane, 1]).

tions of these components are assumed to be analogous to those in the related long-chain ketones (De Leeuw et al., 1980); the compounds are therefore tentatively assigned as heptatriaconta-8-15,22-triene (II) and octatriaconta-9-16,23-triene (III). The stereochemistry of the double bonds is unknown. The $C_{37:3}$ to $C_{38:3}$ ratio is approximately 7 (Fig. 3).

Cyclic

A wide range of steranes and diasteranes was recognized in Section 467-3-3, with both 20R and 20S isomers (Table 1). They are present in relatively minor amounts and are similar in distribution to some Californian crude oils (Seifert and Moldowan, 1978; 1979). The deeper sample, Section 467-97-2, contains a wide range of 5α- and 5β-steranes with a less mature distribution than that observed in Section 467-3-3 (Mackenzie, Patience et al., 1980). Steranes are the major cyclic hydrocarbon components detected in Section 467-97-2, but diasteranes were not detected in this sample. A series of 19-norsteranes (XV), ranging from C_{26} to C_{28} was tentatively identified by mass spectral interpretation in Section 467-97-2 (Table 2).

Sterenes were present in minor quantities in Section 467-3-3. They range from C_{27} to C_{29} and consist of Δ^2-sterenes, $\Delta^{3,5}$-steradienes, $\Delta^{?,24}$-steradienes and steratrienes (Table 3). No diasterenes were detected in this sample, but they are the major sterene component of the deeper sample, Section 467-97-2, and range from C_{26} to C_{30} (Table 4). Nonrearranged sterenes present in this sample consist mainly of Δ^4- and Δ^5-sterenes and stera-

Table 1. Concentration of steranes and diasteranes in Section 467-3-3.

	Assignment[a]	Structure[b]	Concentration (ng/g)[c]
20S	13β,17α-Diacholestane	IVi	2.1
20R	13β,17α-Diacholestane	IVj	2.2
20S	24-Methyl-13β,17α-diacholestane	IVk	2.4
20R	24-Methyl-13β,17α-diacholestane	IVℓ	2.5
20S	5α,14α,17α-Cholestane	VIIi	3.7
20S	24-Ethyl-13β,17α-diacholestane	IVm	2.1
20R	5α,14α,17α-Cholestane	VIIj	4.1
20R	24-Ethyl-13β,17α-diacholestane	IVn	2.6
20S	4-Methyl,24-ethyl-13β,17α-diacholestane	VIm	1.6
20S	24-Methyl-5α,14α,17α-cholestane	VIIk	3.0
20R	24-Methyl-5β,14α,17α-cholestane	VIIℓ	5.3
20R	24-Methyl-5α,14β,17β-cholestane[d]	IXℓ	3.4
20S	24-Methyl-5α,14β,17β-cholestane[d]	IXk	
20R	4-Methyl,24-ethyl-13β,17α-diacholestane	VIn	1.1
20R	24-Methyl-5α,14α,17α-cholestane	VIIℓ	5.0
20S	24-Ethyl-5α14α,17α-cholestane	VIIm	3.2
20R	24-Ethyl-5β,14α,17α-cholestane[e]	VIIn	4.1
20R	24-Ethyl-5α,14β,17β-cholestane[e]	IXn	3.5
20S	24-Ethyl-5α,14β,17β-cholestane[e]	IXm	
20R	24-Ethyl-5α,14α,17α-cholestane	VIIn	6.0
20S	4-Methyl,24-ethyl-5α,14α,17α-cholestane	VIIIm	1.5
20R	4-Methyl,24-ethyl-5β,14α,17α-cholestane[f]	VIIIn	3.2
20R	4-Methyl,24-ethyl-5α,14β,17β-cholestane[f]	Xn	
20S	4-Methyl,24-ethyl-5α,14β,17β-cholestane[f]	Xm	
20R	4-Methyl,24-ethyl-5α,14α,17α-cholestane	VIIIn	1.9
Total			64.5

[a] Assigned on the basis of mass spectral interpretation, comparison with authentic standards, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Co-elute.
[e] Co-elute β,α,α and α,β,β isomers quantitated by mass fragmentography.
[f] Co-elute.

Table 2. Concentration of steranes in Section 467-97-2.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
5α-Androstane	VIIa	12.22
5α-Pregnane	VIIb	22
20-Methyl-5α-pregnane	VIIc	9
20-Ethyl-5α-pregnane	VIId	10
5α-Cholane	VIIe	9
24-Methyl-5α-cholane	VIIf	12
19-Nor-5α-cholestane[d]	XVj	41
24-Nor-5β-cholestane	VIIh	34
24-Nor-5α-cholestane	VIIh	66
19-Nor-24-methyl-5α-cholestane[d]	XVℓ	54
5β-Cholestane	VIIj	202
5α-Cholestane	VIIj	352
19-Nor-24-ethyl-5α-cholestane[d]	XVn	51
24-Methyl-5β-cholestane	VIIℓ	298
24-Methyl-5α-cholestane	VIIℓ	785
24-Ethyl-5β-cholestane	VIIn	106
4,24-Dimethyl-5β-cholestane	VIIIℓ	121
24-Ethyl-5α-cholestane	VIIn	407
4,24-Dimethyl-5α-cholestane	VIIIℓ	151
24-Propyl-5α-cholestane[e]	VIIr	24
4,23,24-Trimethyl-5β-cholestane[f]	VIIIp	76
4,23,24-Trimethyl-5α-cholestane[f]	VIIIp	131
4-Methyl-24-ethyl-5β-cholestane[f]	VIIIn	41
4-Methyl-24-ethyl-5α-cholestane[f]	VIIIn	67
Total		3.08 μg/g

[a] Assigned on the basis of mass spectral interpretation, comparison with authentic standards, and GC retention times. Configuration at C-14 and C-17 are 14α H, 17α H in all cases; where appropriate, the configuration at C-20 is R.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Tentative assignment based on mass spectral interpretation.
[e] May be isopropyl.
[f] Tentative assignment based on mass spectral interpretation and GC retention times.

Table 3. Concentration of sterenes in Section 467-3-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
$\Delta^{?,24}$-C_{27} steradiene	—[e]	0.9
Cholest-2-ene	XIj	2.9
Cholesta-3,5-diene	XIVj	2.7
$\Delta^{?,24}$-C_{28} steradiene	—	1.7
24-Methylcholest-2-ene	XIℓ	1.8
$\Delta^{?,24}$-C_{28} steradiene	—	6.8
24-Methylcholesta-3,5-diene	XIVℓ	0.2
C_{27} steratriene[d]	—	0.8
24-Ethylcholest-2-ene	XIn	5.0
C_{27} steratriene[d]	—	0.7
$\Delta^{?,24}$-C_{29} steradiene	—	3.8
24-Ethylcholesta-3,5-diene	XIVn	2.4
C_{28} steratriene[d]	—	0.4
C_{29} steratriene[d]	—	0.3
Total		30.4

[a] Based on mass spectral interpretation, comparison with authentic standards, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.
[d] May be A or B ring monoaromatic.
[e] — indicates structure is unknown.

trienes, ranging from C_{26} to C_{29}; two C_{30} sterenes were tentatively identified (Table 5). Several short-chain sterenes were also detected in this sample, ranging from C_{21} to C_{22}. They are mono-unsaturated but their structure is unclear; they may be rearranged, but authentic standards necessary for elucidation are unavailable at present. Also, the steratrienes present in both samples may be in fact monoaromatic in the A or B rings (Spyckerelle, 1975).

A wide range of hopanoid hydrocarbons has been recognized in both samples (Table 6). Section 467-3-3 contains relatively minor amounts of hopanes, exceptions being 17α,18α,21β-28,30-bisnorhopane (XXIV) (Seifert et al., 1978), 17α,21β,30-norhopane (XXIIb), 17α21β-hopane (XXIIc), 22S and 22R 17α,21β-homohopanes (XXIId), and 17β,21β-homohopane (XXVd). This sample also contains 17α21β and 17β,21α extended hopanes in both 22R and 22S isomeric forms. The 22S αβ isomer tends to be more abundant than the 22R αβ isomer, whereas the βα components are not as abundant as the αβ extended hopanes; ββ-hopanes were not detected in this upper sample for the C_{33} to C_{35} members and ββ-bishomohopane was only present in trace amounts.

The hopanes of Section 467-97-2 are not as varied as those of the more recent sample but are more abundant; 22S isomers were not detected. The C_{30}, C_{31}, C_{34}, and C_{35} αβ-hopanes are more abundant than their βα coun-

Table 4. Concentration of diasterenes in Section 467-97-2.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
20*S* 24-Nordiacholestene	Vg	22
20*R* 24-Nordiacholestene	Vh	54
20*S* Diacholestene	Vi	95
Methyldiacholestene	—	26
Diacholestene	—	84
Methyldiacholestene	—	24
20*R* Diacholestene	Vj	326
20*S* 24-Methyldiacholestene	Vk	217
Diacholestene[d]	—	5
Ethyldiacholestene[d]	—	
Methyldiacholestene	—	136
Diacholestene[e]	—	20
Methyldiacholestene[e]	—	32
20*S* 24-Ethyldiacholestene	Vm	81
20*R* 24-Methyldiacholestene	Vℓ	393
Methyldiacholestene	—	57
20*R* 23,24-Dimethyldiacholestene	Vp	63
20*R* 24-Ethyldiacholestene	Vn	427
4-Methyl-24-ethyldiacholestene	Vn[f]	186
Total		2.25 μg/g

Note: — indicates stereochemistry unknown.
[a] Based on mass spectral interpretation, comparison with authentic standards, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Co-elute.
[e] Co-elute, quantitated separately by mass fragmentography.
[f] Structure V (see Appendix) has methyl substitution at position 4.

Table 5. Concentration of sterenes in Section 467-97-2.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
C_{21} sterene[d]	—	38
C_{21} sterene[d]	—	14
C_{22} sterene[d]	—	28
Cholest-4-ene	XIIj	66
Cholest-5-ene	XIIIj	26
C_{27} steratriene[e]	—	29
24-Methylcholest-4-ene	XIIℓ	91
24-Methylcholest-5-ene	XIIIℓ	38
C_{27} steratriene[e]	—	31
24-Ethylcholest-4-ene	XII	83
24-Ethylcholest-5-ene	XIII	16
C_{28} steratriene[e]	—	82
4,23,24-Trimethylcholest-22-ene[f]	VIIIq	103
4-Methyl-24-ethylcholestene[f]	VIIIn[g]	171
C_{29} steratriene[e]	—	37
Total		853

[a] Based on mass spectral interpretation, comparison with authentic standards, and GC retention times.
[b] See Appendix; — indicates structure is unknown.
[c] Dry weight of sediment.
[d] Mono-enes, stereochemistry unknown, they may be rearranged.
[e] Structure unknown: may be A or B ring monoaromatic (Spyckerelle, 1975).
[f] Based on mass spectral interpretation and GC retention times.
[g] Structure VIII (see Appendix) has nuclear mono-unsaturation, position unclear.

terparts, but $\beta\alpha$-bishomohopane is more abundant than its $\alpha\beta$-isomer, $\alpha\beta$- and $\beta\alpha$-trishomohopanes are present in equal amounts. The $\beta\beta$-homologues are the most abundant isomers for each of the extended hopanes. 17α-22,29,30-Trisnorhopane (XXIIa), 17α, 18α,21β-28, 30-bisnorhopane (XXIV), 17α-30-norhopane (XXIIb), and 17β-30-norhopane (XXIIIb) are present in large amounts. 18α-22,29,30-Trisnorneohopane (XXI) and 17β-22,29,30-trisnorhopane (XXIIIa) were not detected. Gammacerane (XXXII) was also tentatively recognized in this deeper sample.

Hopenes were present in both samples. Section 467-3-3 contained neohop-12-ene (XXVIII), hop-21-ene (XXIX), and hop-22(29)-ene (XXX), which are normally associated with Recent, immature sediments (e.g., Wardroper, 1979; Brassell, 1980). These components are absent in Section 467-97-2; however, hop-17(21)-ene (XXVI) was significant in both samples and neohop-13(18)-ene (XXVII) was the major hopanoid hydrocarbon detected in both samples. A novel C_{37} hopene (M^+ 508) was tentatively identified in Section 467-97-2 and an unknown triterpene (M^+ 410) was present in significant amounts in Section 467-3-3. Several fernene isomers (XXXI) were present in both samples, fern-7-ene being the dominant isomer in 3-3 with smaller quantities of fern-9(11)-ene and fern-8-ene also present. Fern-8-ene was the dominant isomer in the deeper sample, Section 467-97-2, fern-9(11)-ene was present in a significant quantity, and fern-7-ene was absent.

Acyclic Ketones

Ketones were not detected in Section 467-97-2. A series of alkan-2-ones, ranging from C_{20} to C_{35} (C_{34} absent) was detected in Section 467-3-3 (Fig. 2). The odd-numbered homologues dominate with nonacosan-2-one as the major component. However, the even homologues are dominate over the C_{19} to C_{24} range. Their concentrations are shown in Figure 2, together with that of 6,10,14-trimethylpentadecan-2-one. This was the only isoprenoid ketone detected and was the predominant ketone.

A series of very long, straight-chain, C_{37}, C_{38}, and C_{39} di- and triunsaturated ketones was detected. These components were characterized by their GC retention times and by mass spectral comparison with the same

Table 6. Concentration of triterpenoid hydrocarbons in Hole 467, Sections 467-3-3 and 467-97-2.

Assignment[a]	Structure[b]	Concentration (ng/g)[c] 3-3	97-2
18αH-22,29,30-Trisnorneohopane	XXI	1	n.d.
17αH-22,29,30-Trisnorhopane	XXIIa	0.5	29
17βH-22,29,30-Trisnorhopane	XXIIIa	0.5	n.d.
17αH,18αH,21βH-28,30-Bisnorhopane	XXIV	17	30
17αH,21βH-30-Norhopane	XXIIb	15	16
Hop-17(21)-ene	XXVI	8	70
17βH,21αH-30-Norhopane	XXIIIb	6	32
17αH,21βH-Hopane	XXIIc	25	41
Fern-8-ene	XXXI	2	9
Neohop-13(18)-ene	XXVII	35	94
17βH,21βH-30-Norhopane	XXVb	8	9
Fern-9(11)-ene	XXXI	4	3
17βH,21αH-Hopane	XXIIIc	2	20
C_{30}-Triterpene	—	4	n.d.
Neohop-12-ene	XXVIII	17	n.d.
Fern-7-ene	XXXI	16	n.d.
22*S* 17αH,21βH-Homohopane	XXIId	12	n.d.
22*R* 17αH,21βH-Homohopane	XXIId	12	13
17βH,21βH-Hopane	XXVc	5	27
22*R* 17βH,21αH-Homohopane	XXIIId	2	9
Hop-22(29)-ene	XXX	3	n.d.
Hop-21-ene	XXIX	2	n.d.
22*S* 17αH,21βH-Bishomohopane	XXIIe	8	n.d.
22*R* 17αH,21βH-Bishomohopane	XXIIe	7	2
22*S* 17βH,21αH-Bishomohopane	XXIIIe	1	n.d.
22*R* 17βH,21αH-Bishomohopane	XXIIIe	1	8
17βH,21βH-Homohopane	XXVd	17	51
22*S* 17αH,21βH-Trishomohopane	XXIIf	6	n.d.
22*R* 17αH,21βH-Trishomohopane	XXIIf	5	3
22*S* 17βH,21αH-Trishomohopane	XXIIIf	tr.	n.d.
22*R* 17βH,21αH-Trishomohopane	XXIIIf	0.5	3
17βH,21βH-Bishomohopane	XXVe	tr.	19
22*S* 17αH,21βH-Tetrakishomohopane	XXIIg	3	n.d.
22*R* 17αH,21βH-Tetrakishomohopane	XXIIg	3	1
22*S* 17βH,21αH-Tetrakishomohopane	XXIIIg	tr.	n.d.
22*R* 17βH,21αH-Tetrakishomohopane	XXIIIg	tr.	tr.
17βH,21βH-Trishomohopane	XXVf	n.d.	33
22*S* 17αH,21βH-Pentakishomohopane	XXIIh	4	n.d.
22*R* 17αH,21βH-Pentakishomohopane	XXIIh	3	2
22*S* 17βH,21αH-Pentakishomohopane	XXIIIh	tr.	n.d.
22*R* 17βH,21αH-Pentakishomohopane	XXIIIh	tr.	tr.
17βH,21βH-Tetrakishomohopane	XXVg	n.d.	15
17βH,21βH-Pentakishomohopane	XXVh	n.d.	46
C_{37}-Hopene[d]	—	n.d.	2
Totals		256	596

Note: n.d. = not detected;— = structure unknown; tr. = trace.
[a] Based on mass spectral interpretation, comparison with authentic standards, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Based on mass spectral interpretation.

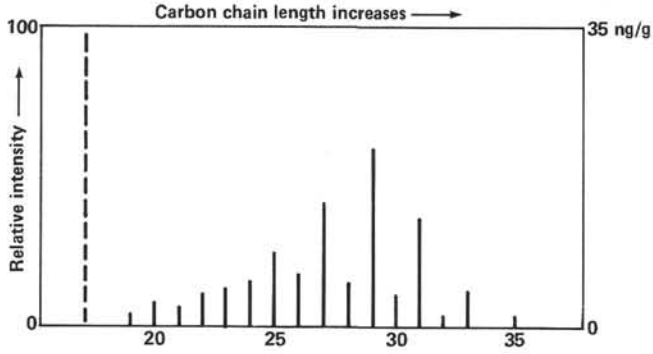

Figure 2. Distribution of alkan-2-ones (C_{20}–C_{35}) and 6,10,14-trimethylpentadecan-2-one (dashed line) in Section 467-3-3.

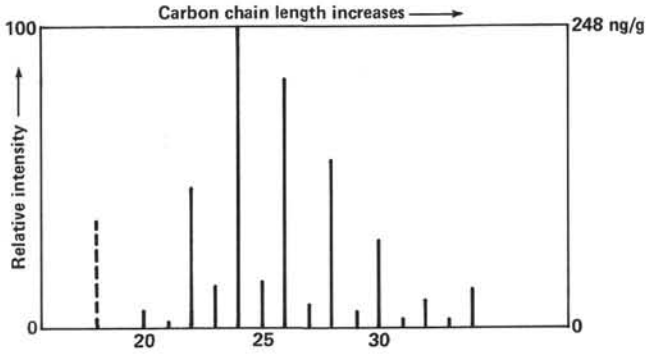

Figure 4. Distribution of alkanols (C_{20}–C_{34}) and 3,7,11,15-tetramethylhexadec-2-enol (phytol, dashed line) in Section 467-3-3.

compounds isolated from the marine coccolithophorid, *Emiliania huxleyi* (Volkman et al., 1980). The double-bond positions of the trienones are assumed to be analogous to those of the very long chain trienes (see earlier) and also to those of long-chain ketones recently identified in marine sediments (De Leeuw et al., 1980). Heptatriaconta-8,15,22-trien-2-one (XXXVa) and heptatriaconta-15,22-dien-2-one (XXXVIa) are the major triunsaturated and diunsaturated ketones detected, respectively. The concentrations are given in Figure 3, together with those of the long-chain alkenes.

Alcohols

Acyclic

Only traces of *n*-alcohols were detected in Section 467-97-2, but they were abundant in Section 467-3-3 where a range of C_{20} to C_{34} was detected, with tetracosanol predominant. There is a striking abundance of the even homologues as compared with the odd homologues (Fig. 4). A series of *n*-alkenols of even carbon number only was detected for the range C_{22} to C_{32}, each carbon number having two isomers (Fig. 5); the position of the double bond is unknown. This series is dominated by the C_{24} and C_{30} members. *n*-Alkenols were not detected in Section 467-97-2. A single isoprenoid, 3,7,11,15-tetramethylhexadec-2-en-ol (phytol) was recognized and is represented in Figure 4.

Cyclic

Cyclic components were not detected in Section 467-97-2. A wide range of sterols and stanols was detected in Section 467-3-3 (Table 7). They are the most abundant cyclic lipids present in this sample, with the exception of chlorins. Series of Δ^5-, Δ^7-, Δ^{22}-, and $\Delta^{5,22}$-stenols and the corresponding 5α-stanols were identified. In addition, 4α, 23,24-trimethylcholest-22E-en-3β-ol (dinosterol, XXq) was the most abundant sterol component; 4α,23,24-trimethyl-5α-cholestan-3β-ol (XXp) and 4α, 23,24-trimethyl-5α-cholestan-3β-ol (XXp) and 4α,24-dimethylcholestan-3β-ol (XXp) and 4α,24-dimethylcholestan-3β-ol were present in significant amounts. The ratio of 4-desmethylstanols to 4-desmethylstenols is approximately 0.5.

Tetrapyrroles

The total chlorin concentration in Section 467-3-3, quantitated by uv/vis using the extinction coefficient of

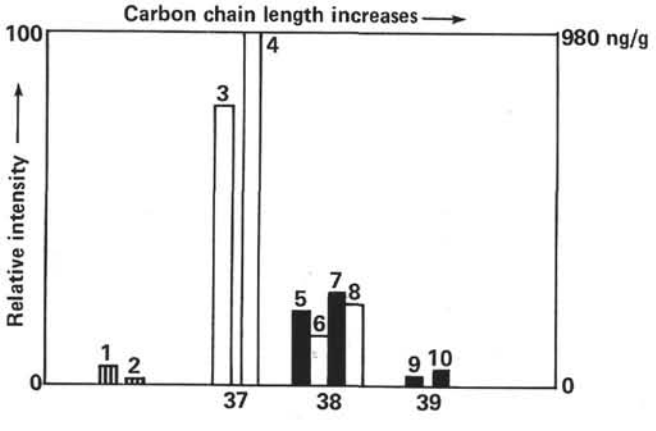

Figure 3. Distribution of very long straight-chain unsaturated ketones (C_{37}–C_{39}) and hydrocarbons (C_{37} and C_{38}) in Section 467-3-3. 1 = $C_{37}H_{70}$ (II) and 2 = $C_{38}H_{72}$ (III) (the positions of unsaturation are assumed to be analogous to the related long-chain ketones [De Leeuw et al., 1980]).3 = $C_{37}H_{68}O$ (XXXVa); 4 = $C_{37}H_{70}O$ (XXXVIa); 5 = $C_{38}H_{70}O$ (XXXVb); 6 = $C_{38}H_{70}O$ (XXXVIIa); 7 = $C_{38}H_{72}O$ (XXXVIb); 8 = $C_{38}H_{72}O$ (XXXVIIIa); 9 = $C_{39}H_{82}O$ (XXXVIIb); and 10 = $C_{39}H_{84}O$ (XXXVIIIb). (▥ = hydrocarbons, □ = methyl ketones, and ■ = ethyl ketones.

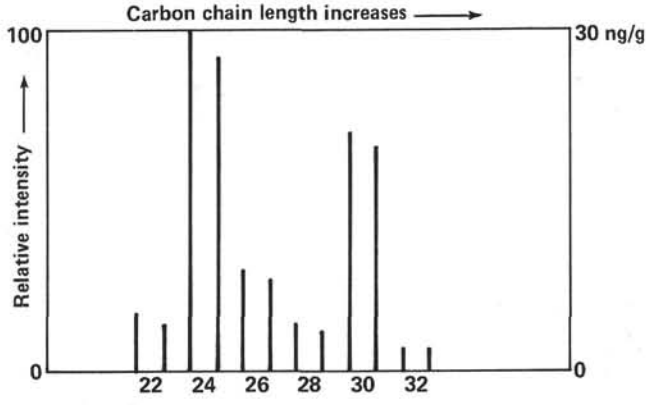

Figure 5. Distribution of *n*-alkenols (C_{22}–C_{32}, doublets of even homologues only) in Section 467-3-3.

Table 7. Concentration of sterols in Section 467-3-3.

Assignment[a]	Structure[b]	Concentration (ng/g)[c]
24-Norcholesta-5,22E-dien-3β-ol	XVIs	21
24-Nor-5α-cholest-22E-en-3β-ol	XVIIIs	5
24-Nor-5α-cholestan-3β-ol	XVIIIh	2
5β-Cholestan-3β-ol	XVIIIj	3
5β-Cholestan-3α-ol	XIXj	2
27-Nor-24-methylcholesta-5,22E-dien-3β-ol	XVIu	10
27-Nor-24-methyl-5α-cholest-22E-en-3β-ol	XVIIIu	2
Cholesta-5,22E-dien-3β-ol	XVIv	24
5α-Cholest-22E-en-3β-ol	XVIIIv	9
C_{27} stanol	—	5
Cholest-5-en-3β-ol	XVIj	54
5α-Cholestan-3β-ol	XVIIIj	28
27-Nor-24-methyl-5α-cholestan-3β-ol	XVIIIt	23
24-Methylcholesta-5,22E-dien-3β-ol	XVIw	84
{24-Methyl-5α-cholest-22E-en-3β-ol	XVIIIw	16
{5α-Cholest-7-en-3β-ol	XVIIj	6
{C_{28} stanol	—	13
{24-Methylenecholest-5-en-3β-ol	XVIx	17
{24-Methylene-5α-cholestan-3β-ol	XVIIIx	2
{24-Methylcholest-5-en-3β-ol	XVIℓ	5
24-Methyl-5α-cholestan-3β-ol	XVIIIℓ	27
23,24-Dimethylcholesta-5,22E-dien-3β-ol	XVIq	24
{23,24-Dimethyl-5α-cholest-22E-en-3β-ol	XVIIIq	60
{24-Ethylcholesta-5,22E-dien-3β-ol	XVIy	10
{24-Ethyl-5α-cholest-22E-en-3β-ol	XVIIIy	5
{C_{29} 4-Methylsterol	—	3
24-Methyl-5α-cholest-7-en-3β-ol	XVIIℓ	2
{23,24-Dimethyl-5α-cholestan-3β-ol	XVIIIp	31
{24-Ethylcholest-5-en-3β-ol	XVIn	41
{C_{29} 4-Methylstenol	—	9
{24-Ethyl-5α-cholestan-3β-ol	XVIIIn	38
{4α,24-Dimethyl-5α-cholestan-3β-ol	XXℓ	8
4α,23,24-Trimethylcholest-22E-en-3β-ol	XXq	95
24-Propyl-5α-cholest-22-ene[d]	XVIIIx	20
24-Ethyl-5α-cholest-7-en-3β-ol	XVIIn	18
{24Z-Propylidenecholest-5-en-3β-ol	XVIz	3
{C_{30} 4-methylstenol	—	2
{C_{30} 4-methylstanol[e]	—	3
{C_{30} 4-methylstenol	—	1
4α,23,24-Trimethyl-5α-cholestan-3β-ol	XXp	6
Total		737

Note: — = structure unknown. { signifies coelution. Compounds were quantitated by mass fragmentography.
[a] Based on mass spectral interpretation, comparison with authentic standards, and GC retention times.
[b] See Appendix.
[c] Dry weight of sediment.
[d] Tentative assignment based on mass spectral interpretation; may be isopropyl.
[e] Mass spectrum similar to XXp.

phaeophytin *a*, was approximately 0.8 μg/g (sediment dry weight). No porphyrins were detected in this Recent sediment. The deeper sample, Section 467-97-2, contained no chlorins, but abundant nickel (II) porphyrins of both the DPEP (deoxophylloerythroetioporphyrin, XXXIII) and the etio (etioporphyrin, XXXIV) series were detected in a ratio of 1:1. The DPEP series ranges from C_{25} to C_{33} with C_{30} predominant. The etio series ranges from C_{23} to C_{32} with C_{27} dominant. The total concentration of nickel porphyrins is 0.4 μg/g (dry weight of sediment, using extinction coefficient ϵ = 34820 at 549 nm). The relative concentrations of the metalloporphyrins with respect to the C_{30} DPEP nickel porphyrin are given in Table 8. Other metalloporphyrins and free-base porphyrins were not detected.

Table 8. Relative abundances of nickel porphyrins in Section 467-97-2.

Series		Carbon No. C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}
DPEP series (XXXIII)	M.W.[a]	420	434	448	462	476	490	504	518	532	546
	R.A.[b]	n.d.	30	36	44	65	93	100	80	52	16
Etio series (XXXIV)	M.W.[a]	422	436	450	464	478	492	506	520	534	548
	R.A.[b]	44	60	75	79	76	67	51	34	22	n.d.
Total											0.8 μg/g

Note: n.d. indicates not detected.
[a] Molecular weight.
[b] Relative abundance with respect to C_{30} DPEP.

DISCUSSION

Paleoenvironment: Lipid Indicators

Section 467-3-3

The prominent odd/even CPI for the C_{22} to C_{35} range of *n*-alkanes (Fig. 1) suggests a predominantly terrigenous origin. There is no evidence for a major marine autochthonous input from the *n*-alkanes, as their concentration below *n*-C_{25} is very low. The *n*-alkan-2-ones also show an odd/even dominance (Fig. 2), which is expected from a higher plant source (Morrison and Bick, 1966). Similarly, this is reflected in the *n*-alkanol data (Fig. 4) where the even homologues dominate over the odd, with tetracosanol predominant (Morrison and Bick, 1967). Other components, however, suggest a large marine input. These include the very long, straight-chain unsaturated ketones that have been identified in a marine coccolithophorid, *Emiliania huxleyi* (Volkman et al., 1980). Chlorins are also present in abundance and phytol, which is believed to originate from chlorophylls *a* and *b*, is the major unsaturated acyclic alcohol in this sample, and 6,10,14-trimethylpentadecan-2-one is the major acyclic saturated ketone. In addition, the abundance of sterols and the wide variety of side chains suggests a predominantly marine origin (Patterson, 1971; Wardroper, 1979). Dinoflagellates may be a major source of the 4-methyl steroids (Withers et al., 1978) and 4α,23,24-trimethyl-22E-en-3β-ol (XXq) (Shimizu et al., 1976) has been proposed as a dinoflagellate marker (Boon et al., 1979). Also, 23,24-dimethylcholesteroids have not been observed in terrestrial organisms. Sponge spicules are present in these sediments (see the Site 467 report, this volume) and sponges are known to contain 24-isopropylcholesteroids (e.g., Hofheinz and Oesterhelt, 1979; Kokke et al., 1979). Unfortunately, the structures of the C-24 propyl substituents in sterols could not be assigned (Table 7). Major inputs of sterols appear to come from diatoms, as shown by the high abundance of 24-methylcholesta-5,22E-dien-3β-ol (XVIw) relative to the C_{27} and C_{29} analogues (Ballantine et al., 1979). This compound, however, is also present in coccolithophorids as is the 24-ethyl homologue (XVIy) (Volkman et al., in press). The C_{26} sterols indicate a marine input (Schmitz, 1978).

A minor epigenetic background is apparent in this sample, as revealed by the presence of small quantities of relatively mature steranes (Table 1). There is some similarity in distribution to some Californian crude oils (Seifert and Moldowan, 1978; 1979). An analogous

Table 9. Summary of content and significance of lipid classes extracted from Sections 467-3-3 and 467-97-2.

	467-3-3	467-97-2
Lithologic description Depth (sub-bottom)	Quaternary; diatomaceous, silty clay. 21 m	Middle Miocene; calcareous claystone. 912 m
Lipid Class		
n-Alkanes	C_{29} dominant; significant higher plant input (Fig. 1A)	A more even distribution, perhaps a reduction in mean carbon-carbon chain length with maturation C_{37} dominant; a diagenetic product? (Fig. 1C)
Branched hydrocarbons	Low amounts of pristane and phytane (Fig. 1B)	Pristane and phytane in major amounts (Fig. 1D); released due to thermal maturation?
n-Alkan-2-ones	A significant input, denoting sample immaturity (Fig. 2)	Not detected
Very long chain unsaturated ketones	C_{37}–C_{39} present, suggesting a major marine source, i.e., coccolithophorids (Fig. 3)	Not detected, but may be the diagenetic precursors of C_{37}–C_{39} range of *n*-alkanes detected (Fig. 1C)
Acyclic alcohols	A major terrestrial input (Fig. 4).	Not detected, presumably as a consequence of defunctionalization
Sterols	A major marine input (Table 6)	Not detected, defunctionalized
Sterenes	Minor amounts, e.g., Δ^2-sterenes suggest sample immaturity (Table 3)	Significant amounts of Δ^4-, Δ^5-, and Δ^{22}-sterenes of diagenetic (Table 5)
Diasterenes	Not detected; sample immature (Table 3)	High abundance of diasterenes; acid-clay catalysis during diagenesis (Table 4)
Steranes	Very minor amount of mature steranes suggests an epigenetic source, probably natural seepage (Table 1)	High abundance of steranes, 5α-steranes dominate the 5β-steranes; a maturation indicator (Table 2)
Diasteranes	Small amounts detected from an epigenetic source (Table 1)	Not detected; sufficiently immature for diasterane formation
Hopenes	Immature, e.g., presence of hop-22(29)-ene (Table 6) Hop-17(21)-ene and neohop-13(18)-enes dominate	Hop-17(21)-ene and neohop-13(18)-ene are still present in large amounts (Table 6)
Hopanes	An epigenetic source indicated by major amounts of 17α-hopanes and presence of extended hopanes with 22S and 22R components (Table 6)	Only 22R components detected and $\beta\beta$-dominance in extended hopanes (Table 6); insufficiently mature for 22S formation
Fernenes	Fern-7-ene dominant (Table 6), reflecting immaturity	Fern-8-ene dominant (in accord with double bond migration [Table 6], during diagenesis)
Tetrapyrroles	Chlorins abundant; high productivity at this Site	Nickel (II) porphyrins abundant; diagenetic and maturity indication (Table 8)

ation is seen in the distribution of the hopanoid rocarbons, where a minor epigenetic mature input can be discerned, superimposed on the syngenetic components. This mature component is comprised of the 22S and 22R isomers of the extended $\beta\alpha$-and $\alpha\beta$-components (Table 6), with the latter being predominant. Of particular interest is the presence of a significant proportion of 17α,18α,21β-28,30-bisnorhopane (XXIV) (Seifert et al., 1978), a degraded hopane that has been detected in minor amounts in particulates collected by sediment traps situated off the Californian coast (Crisp et al., 1979). It is abundant in sediments from cores taken in the southern Californian Bight (Simoneit and Kaplan, 1980) and is present in some Californian crude petroleums (Seifert and Moldowan, 1978; 1979) and in the Monterey Shale.

The syngenetic component comprises significant amounts of hop-17(21)-ene (XXVI), neohop-13(18)-ene (XXVII), neohop-12-ene (XXVIII), hop-21-ene (XXIX), and hop-22(29)-ene (XXX), which may represent both direct biogenic input with or without diagenetic alteration. However, the probable origin of these hopenes is bacterial synthesis (c.f., Comet et al., in press).

Neohop-13(18)-ene (XXVII) and hop-17(21)-ene (XXVI) have been identified in ferns (Barton et al., 1971; Berti and Bottari, 1968) and may also represent a direct input from such a source in view of the presence of fernenes (particularly fern-7-ene [XXXI]) (Bottari et al., 1972). However, it has recently been shown that both hopenes and fernenes can be synthesized by the anaerobic photosynthetic bacterium *Rhodomicrobium vannielii* (Howard, 1980). If these components are shown to occur widely in bacteria, then such an origin may be the more likely one for the fernenes.

Thus the lipid components indicate significant biogenic inputs, both marine and terrestrial, as well as the presence of reworked older material (possibly from the Monterey Shale) and/or natural seepage from nearby oils. It should be emphasized, however, that such epigenetic material is present only in minor amounts when compared to the abundance of immature lipids in this sample.

Section 467-97-2

The *n*-alkane distribution (Fig. 1, C) differs from that in Section 467-3-3 in that there is an even/odd predominance for the C_{15} to C_{26} range and an odd/even predominance for the C_{27} to C_{35} alkane range, the latter ratio reflects a higher plant input. The shift in the mean carbon chain length from Section 467-3-3 to 97-2 may result from thermal maturation, but the significant amount of *n*-C_{18} and the dominance of *n*-C_{24} may reflect a large input from zooplankton (Giger and Schaffner, 1977). The three very long chain *n*-alkanes detected, C_{37}, C_{38}, and C_{39}, may derive from the long-chain *n*-alkenes and ketones found in a coccolithophorid and in Section 467-3-3 (see Results). The large amounts of pristane and phytane have probably been released from kerogen by thermal maturation and presumably derive initially from phytol; hence, high productivity is indicated. Lycopane (I) may be the diagenetic product of lycopene found in a wide variety of organisms. It seems more likely, however, that it repre-

sents an original input from methanogenic bacteria (cf., Brassell, Comet, Eglinton, Issacson et al., 1980).

The steranes, sterenes, and diasterenes detected cannot provide as detailed input information as their functionalized precursor steroids, but the high relative abundance of the C_{28} skeleton indicates that the precursor sterols probably derive mainly from marine sources. To confirm this derivation, however, the configuration at C_{24} remains to be determined. The origin of the C_{19} to C_{25} 5α-steranes (Table 2) and the C_{21} and C_{22} sterenes (Table 5) is uncertain, but they may be related to the 5α-stanols with degraded side chains previously detected in sponges (Ballatine et al., 1977; Delseth et al., 1978) and in Neogene sediments (Brassell, Comet, Eglinton, Issacson et al., 1980). C_{26} steroidal hydrocarbons may reflect a diagenetically altered autochthonous sterol input, and 4-methyl steroidal hydrocarbons may reflect altered dinoflagellate input. The C_{26} to C_{28} range of 19-normethylsteranes may have been derived from an initial input of 19-norsterols that have been found in sponges (e.g., Minale and Sodano, 1974). Sponge fragments detected in this core sample (see Site 467 Report, this volume) suggest that bottom waters were oxic at the time of deposition, whereas the good lipid preservation implies rapid burial in anoxic sediments.

Steranes from reworked mature material were not detected, but such an input could have been masked by the abundance of relatively immature steranes. However, if the epigenetic material noted in Section 467-3-3 resulted from natural seepage, then such a source may not have existed when these Miocene sediments were deposited. A significant input of reworked hopanes is also not apparent, as only 22R hopanes were recognized in this sample.

The hopanoids contain significant amounts of hop-17(21)-ene (XXVI) and neohop-13(18)-ene (XXVII), which may reflect an original bacterial source, as may the fernenes, particularly fern-8-ene (XXXI), which were also detected. Bacterial activity is further implied by the presence of extended (C_{31} to C_{35}) hopanes, which are considered to be the diagenetic products of the polyhydroxybacteriohopanes found in prokaryotes (e.g., Rohmer and Ourisson, 1976). The abundance of nickel porphyrins may reflect a significant autochthonous input at a site of high productivity.

Lipid Diagenesis

General Appraisal

The study of the two sections from greatly differing depths at Site 467 permits a preliminary evaluation of some of the major diagenetic trends operating at this site. The immaturity of the Recent sample is shown by the presence of major quantities of functionalized lipids such as chlorins, alcohols, and ketones that do not survive extensive diagenesis. The increased maturity of the deeper sample, Section 467-97-2, is indicated by the abundance of defunctionalized components, particularly steroidal hydrocarbons, and also by the presence of nickel porphyrins.

Section 467-3-3

The high CPI of the *n*-alkane fraction, particularly in the C_{25} to C_{35} range of homologues (Fig. 1, A), probably reflects a terrigenous input rather than the preferential biodegradation of short-chain *n*-alkanes (Johnson and Calder, 1973). The results do not suggest extensive oxidation of *n*-alkanes to alkan-2-ones (Fig. 2). 6,10,14-Trimethylpentadecan-2-one and its presumed diagenetic precursor, phytol, are the dominant isoprenoids detected in this sample and are present in great abundance compared to pristane and phytane.

Sterols and stanols constitute a major fraction of the extractable lipids detected in this sample. 5α-Stanols, Δ^5-, Δ^{22}-, and $\Delta^{5,22}$-sterols are in abundance, as is 4α,23, 24-trimethylcholest-22E-en-3β-ol (XXq). Sterenes are present in minor amounts in comparison to sterols, as extensive defunctionalization has not yet occurred. The sterenes are dominated by $\Delta^{7,24}$-steradienes, $\Delta^{3,5}$-steradienes, and Δ^2-sterenes and are similar in distribution to sediments of the Japan Trench (Brassell, 1980). 4-Methylsterenes and diasterenes were not detected. The steranes reflect a mature epigenetic input (see the preceding material). Overall, the steroidal distribution indicates that the sediment is at an immature stage of diagenesis. The distribution of hopanoidal hydrocarbons can be interpreted as both syngenetic and epigenetic inputs. The hopenes reflect the immaturity of the sediment, as hop-22(29)-ene (XXX) is often the major hopene in contemporary sediments (e.g., Brooks, 1974) but quickly isomerizes to hop-17(21)-ene (XXVI) *via* hop-21-ene (XXIX) (Ensminger, 1977). An extended series of $\Delta^{17(21)}$-hopenes was not detected and the C_{32} to C_{35} ββ-hopenes were present either in trace amounts or were not detected. This implies that the C_{30} hopenes may have been contributed as such to a significant extent. 22R ββ-Hopanes are found exclusively in Recent, unpolluted sediments but diagenetic isomerization occurs to give their αβ and βα isomers. In this sample, the αβ > βα > ββ isomers for extended hopanes. The epigenetic source is also shown by the ratio of 22S to 22R hopanes, which tends to increase with maturity (Ensminger, 1977). The ratio for Section 467-3-3 is >1. The dominance of Δ^7 over Δ^8 represents an immature stage of diagenesis (Brassell, 1980).

Section 467-97-2

This section contains only defunctionalized acyclics except for traces of *n*-alkan-2-ones. The mean carbon chain length for the *n*-alkanes (Fig. 1, C) is lower than that of Section 467-3-3. This shift to a lower value is possibly due to thermal maturation with increasing depth (Tissot et al., 1971). This is also reflected by CPI (1.1), which approaches unity as the maturity of the sample increases (Bray and Evans, 1961). Pristane and phytane are the most abundant aliphatic alkanes detected.

5α-Steranes are the most abundant lipids in this sample (Table 2). Defunctionalization of the original input on this major scale is in accord with the observed high

geothermal gradient. The steranes, however are relatively immature in that neither 5α,14β,17β-homologues nor diasteranes were detected. The sterenes were dominated by the backbone rearranged diasterenes (Table 4). This suggests that the sediment is sufficently rich in clay and acidic enough catalyze the rearrangement (Rubinstein et al., 1975). The nonrearranged sterenes consisted mainly of Δ^4- and Δ^5-4 desmethylsterenes and two C_{30} 4-methylsterenes (Table 5). 4,23, 24-Trimethylcholest-22-ene (VIIIq) is postulated as a biological fossil hydrocarbon of dinosterol (XXq), found in abundance in Section 467-3-3.

The abundance of Δ^2-sterenes and Δ^4- and Δ^5-sterenes provide an estimate of the maturity of the sediment, as Δ^2-sterenes tend to dominate the sterenes of Recent sediments and older sediments tend to have Δ^4- and Δ^5-sterenes present in greater abundance (e.g., Wardroper, 1979). The Δ^4- and Δ^5-sterenes are believed to be intermediates in the diagenetic formation of diasterenes and steranes from Δ^2-sterenes (Dastillung and Albrecht, 1977). The overall distributions of steroidal hydrocarbons suggest that this sediment is at a fairly mature stage of diagenesis as far as defunctionalization is concerned, but the steranes are still relatively immature when compared with those of very mature shales and sediments (e.g., Thomson et al., in press; Mackenzie, Patience et al., 1980). No 22S triterpane homologues were detected; the extended hopanes show a distribution similar to other DSDP Miocene samples (Brassell, Comet, Eglinton, Issacson et al., 1980) in that the ββ-hopanes dominate their βα- and αβ-isomers. But the αβ to βα ratio for their respective homologues is inconsistent; the αβ-isomers are more abundant than their βα counterparts for C_{31}, C_{34}, and C_{35} hopanes, but the isomers are equally abundant for trishomohopane whereas the βα-bishomohopane dominates the αβ-isomer. The extended hopanes and the steroidal hydrocarbons (no diasteranes and αββ-steranes were detected) are of similar maturity. Thus hop-17(21)-ene (XXVI) and neohop-13(18)-ene (XXVII) are present in abundance so reduction to hopanes is minor.

Fern-8-ene is the dominant isomer with a smaller amount of fern-9(11)-ene (XXXI) present. The absence of fern-7-ene indicates a migration of the double bond from position 7 to position 8. This diagenetic trend was noticed in the Japan Trench (Brassell, 1980).

The presence of nickel porphyrins of both DPEP and etio types is an indication of the maturity of the sample in that it is too mature for the survival of free-base porphyins but not mature enough for the appearance of vanadyl porphyrins (Mackenzie, Quirke et al., 1980).

CONCLUSIONS

1. The lipid compositions of both samples are made up of components from both marine and terrestrial sources. Comparison of the lipids from the samples, however, reveals differences in their composition. The lipids of Section 467-3-3 are mainly functionalized, e.g., ketones, alkanols, and sterols, whereas those of Section 467-97-2 are defunctionalized. These marked differences are ascribed to the high geothermal heat flux at this location (see Site 467 report, this volume).

2. Several diagenetic trends are apparent: (1) double-bond migration, as seen by the presence of Δ^2-sterenes in the Recent sample and Δ^4- and Δ^5-sterenes in the deeper sample, and the dominance of fern-7-ene in Section 467-3-3 and fern-8-ene in Section 467-97-2; (2) the formation of diasterenes; (3) the abundance of chlorins in Section 467-3-3 but nickel porphyrins in Section 467-97-2; and (4) the very long chain ketones in Section 467-3-3 and C_{37}, C_{38}, and C_{39} *n*-alkanes in the bottom sample.

3. New possible biological markers have been recognized, e.g., 4,23,24-trimethylcholest-22-ene (VIIIq), a probable diagenetic product of 4α,23,24-trimethylcholest-22E-en-3β-ol (dinosterol, XXq), a dinoflagellate marker; and the 19-normethylsteranes (C_{26} to C_{28}) possibly formed from 19-normethylsterols similar to those that have been reported in marine sponges (Minale and Sodano, 1974).

4. The environment of deposition was similar for both samples, characterized by a high rate of sediment accumulation and high productivity. Lipid preservation was due to rapid burial in anoxic sediments, although the presence of sponge fragments suggests the bottom waters may still have been oxic.

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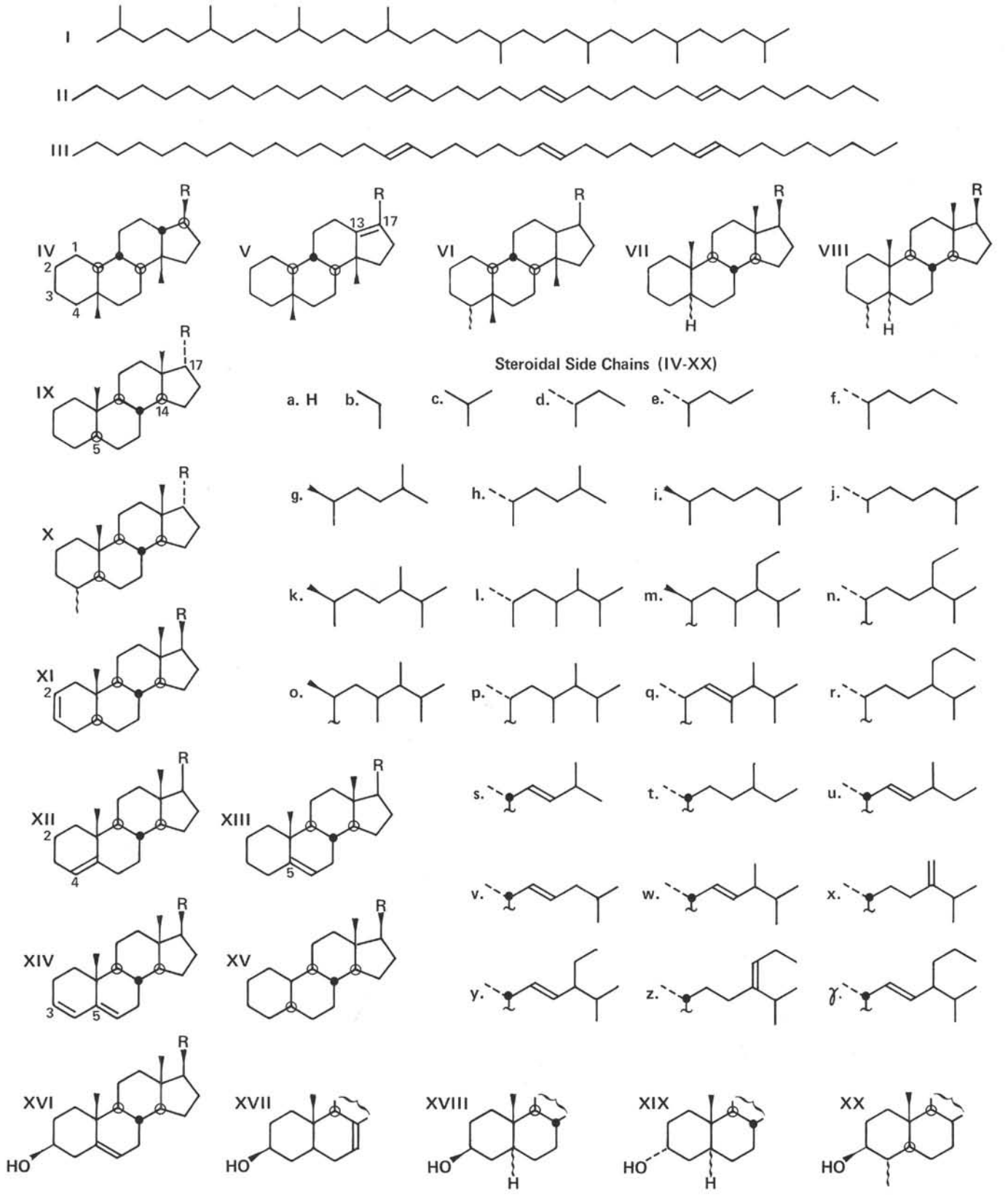
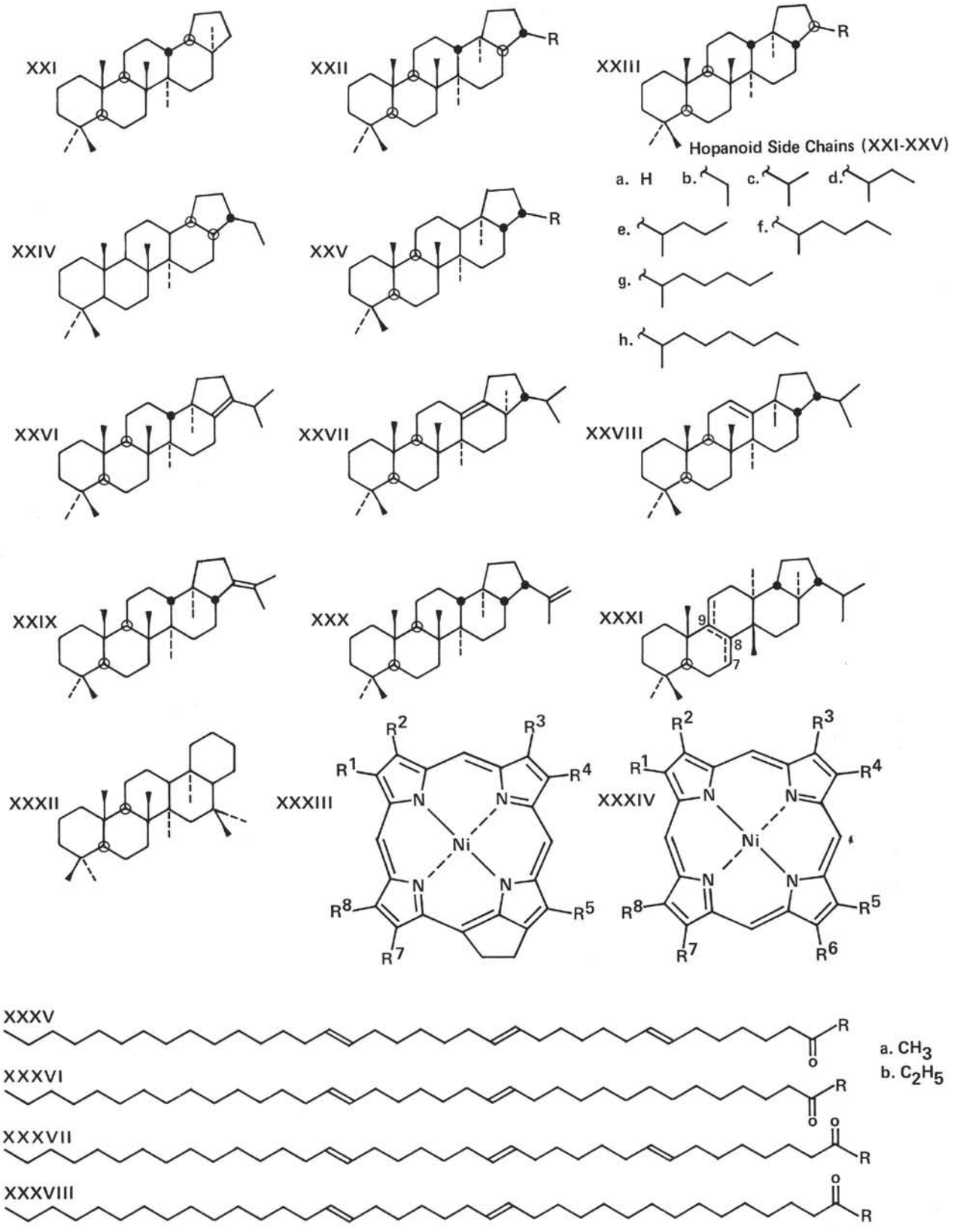
APPENDIX
Structures




XXI
XXII
R
XXIII
R
Hopanoid Side Chains (XXI-XXV)
a. H
b.
c.
d.
e.
f.
g.
h.
XXIV
XXV
R
XXVI
XXVII
XXVIII
XXIX
XXX
XXXI
9
8
7
XXXII
XXXIII
XXXIV
R1
R2
R3
R4
R5
R6
R7
R8
N
Ni
XXXV
XXXVI
XXXVII
XXXVIII
R
O
a. CH3
b. C2H5