# 36. PRELIMINARY LIPID ANALYSIS OF SECTION 481-2-21

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

#### ABSTRACT

We investigated the solvent-extractable lipids of a Quaternary diatomaceous ooze (Section 481-2-2) from the Guaymas Basin. The section contained high concentrations of lipids, principally derived from algae. We also recognized components derived from bacterial and terrestrial sources. Major dinoflagellate blooms were indicated by the presence of dinosterol as the major component. The lipid composition was typical of that of Recent marine sediments and reflected a very early stage of lipid diagenesis.

# INTRODUCTION

We investigated several classes of solvent-extractable lipids (hydrocarbons, alcohols, and acids) of a late Pleistocene diatomaceous ooze from the Guaymas Basin, Gulf of California (Section 481-2-2; 7.5 m subbottom; TOC = 1.4%). We evaluated the lipid distributions to determine their source, conditions of sediment deposition, and diagenetic alteration.

# METHODOLOGY

The experimental procedure used to extract "free" lipids has been reported in our previous DSDP investigation (Brassell et al., 1980a). We performed gas chromatography (GC) on a Carlo Erba 2150 gas chromatograph equipped with a 17-meter OV-1 glass capillary column (0.25-mm i.d.); the carrier gas was helium. Mass spectra were recorded with a Finnigan 4000 gas chromatograph-mass spectrometer (GC= MS), equipped with a 20-meter OV-1 glass capillary column. Data acquisition and processing were controlled by an INCOS 2300 data system. We made compound assignments from individual mass spectra and GC retention times-with reference to literature spectra and authentic standards-where possible. Mass fragmentography (MF) was used to characterize homologous and pseudohomologous series (Wardroper et al., 1977; Brassell et al., 1980b) and to aid compound identification. Where possible, we quantitated individual compounds from their GC response or by MF. The problems associated with quantitation are discussed elsewhere (Brassell et al., 1980a).

# RESULTS

The detailed compound distributions of aliphatic hydrocarbons, alcohols, and acids are reported herein. A brief description of the ketone fraction is given in Table 5. Aromatic components, although present, are not reported.

# **Aliphatic Hydrocarbons**

### **Acyclic Components**

The *n*-alkanes of Section 481-2-2 ranged from  $nC_{17}$  to  $nC_{35}$  with an odd/even carbon preference index (CPI) of 7.2. The absolute concentration of individual homologues (quoted in ng/g dry-sediment weight) are shown in Figure 1A. In the  $C_{23}$  to  $C_{35}$  range, the overall distribution is dominated by odd-numbered homologues in



Figure 1. Lipid concentrations in Section 481-2-2. A. Principal acyclic alkanes (solid lines = n-alkanes; dashed lines = acyclic isoprenoids in GC-elution positions. Bar numbers correspond as follows:
1. pristane, 2. phytane; 3. 2,6,10,15,19-pentamethyleicosane, 4. squalane, 5. lycopane). B. Acyclic alcohols (solid lines = n-alkanols; dashed lines = 1. phytol, 2. C<sub>24:1</sub> n-alken-1-ol, 3. C<sub>26:1</sub> n-alken-1-ol. C. n-alkanoic acids.

the  $C_{23}$  to  $C_{35}$  range and maximizes at  $nC_{29}$ . No *n*-alkenes or branched alkanes or alkenes were detected. The concentrations of acyclic isoprenoid alkanes, pristane, phytane, 2,6,10,15,19-pentamethyleicosane (I), squalane (II), and lycopane (III) are given in Figure 1. No unsaturated isoprenoid hydrocarbons were detected.

<sup>&</sup>lt;sup>1</sup> Curray, J. R., Moore, D. G., et al., Init. Repts. DSDP, 64: Washington (U.S. Govt. Printing Office).

# **Cyclic Components**

No diterpenoid alkanes, alkenes, tetracyclic alkanes, or alkenes derived from 3-oxytriterpenoids (Corbet et al., 1980) were detected.

Steranes were recognized as trace components, but the low intensity of diagnostic ions in MF and individual mass spectra precluded compound assignment. No 4methylsteranes, diasteranes, or 4-methyldiasteranes were detected by MF. A complex mixture of mono-, di-, tri-, and tetra-unsaturated sterenes (C27-C29) occurs in Section 481-2-2; Table 1 shows the concentrations of the major components. We recognized C27 to C29 ster-2-enes and stera-3,5-dienes from their characteristic mass spectra and GC-retention times (Wardroper, 1979); the C<sub>27</sub> compounds predominate. Lack of standard spectra prevented the assignment of nuclear double-bond positions in steradienes (except stera-3,5-dienes), steratrienes, and steratetrenes, but several components have been tentatively assigned as monoaromatic steroids by comparison with literature spectra (Spyckerelle, 1975; Schaeffle et al., 1978). In general, the C27 sterenes are the most abundant ( $C_{27} > C_{28} > C_{29}$ ), and the  $C_{28}$  sterenes show the greatest diversity of individual components. No 4-methylsterenes, diacholestenes, or 4-methyldiacholestenes were detected.

The major triterpanes and triterpenes of Section 481-2-2 are listed in Table 2 and are shown in a partial MF of m/z 191 (Fig. 2). Their distribution is limited to C<sub>27</sub>, C<sub>30</sub>, and C<sub>31</sub> carbon numbers, and hop-22(29)-ene is the most abundant. We recognized several triterpenes (Components D, E, I, J, L and M) and a triterpadiene

Table 1. Concentrations of sterenes in Section 481-2-2.

Assignment <sup>a</sup>	Formula	Structure <sup>b</sup>	Concentration <sup>C</sup> (ng/g)
$C_{28}$ $3\Delta^n$ (aromatic), $\Delta^{scd}$	C28H42	IV	< 1.0
C28 34n (aromatic), Ascd	C28H42	IV	< 1.0
$C_{28}$ $3\Delta^n$ (aromatic) <sup>d</sup>	C28H44	IV	<1.0
$C_{27} \Delta^n, \Delta^{22}$	C27H44	IV	16.6
$C_{27} \Delta^n, \Delta^{24}$	C27H44	IV	11.5
$C_{27} \Delta^2$	C27H46	$IV R_1 = R_2 = H$	60.5
$C_{27} 2\Delta^n, \Delta^{sc}$	C27H42	IV Ž	12.8
$C_{28} \Delta^n, \Delta^{22}$	C28H46	IV	9.4
C27 43,5	C27H44	$IV R_1 = R_2 = H$	74.6
$C_{28}^{\circ} 2\Delta^n, \Delta^{24}$	C28H44	IV 2	16.6
$C_{28} \Delta^n, \Delta^{24}$	C28H46	IV	18.1
$C_{28} \Delta^n, \Delta^{24}$	C28H46	IV	1.8
$C_{28} \Delta^2$	C28H48	$IV R_1 = H.R_2 = CH_3$	15.3
$C_{28} \Delta^n, \Delta^{24}$	C28H46	IV	13.4
$C_{29} \Delta^n, \Delta^{22}$	C29H48	IV	3.2
$C_{28} 2\Delta^n, \Delta^{24}$	C28H44	IV	20.4
C28 43,5	C28H46	$IV R_1 = H_1R_2 = CH_3$	10.4
$C_{28} 2\Delta^n, \Delta^{24}$	C28H44	IV	11.2
$C_{29} \Delta^2$	C29H50	IV $R_1 = R_2 = CH_3$	7.3
C29 34	C29H46	IV	14.3
$C_{29} \Delta^2$	C29H50	$IV R_1 = H_1R_2 = C_2H_5$	28.2
$C_{27} 3\Delta^n$ (aromatic) <sup>e</sup>	C27H42	. <sub>IV</sub> 2 5	16.1
C <sub>27</sub> 3∆ <sup>n</sup> (aromatic) <sup>e</sup>	C27H42	IV	3.2
$C_{29} \Delta^n, \Delta^{24}$	C29H48	IV	5.4
C29 43,5	C29H48	$IV R_1 = H_1R_2 = C_2H_5$	21.0
$C_{28} 3\Delta^n$ (aromatic), $\Delta^{sce}$	C28H42	IV	2.8
$C_{28} 2\Delta^n, \Delta^{24}$	C28H44	IV	2.3
C <sub>27</sub> 4∆ (aromatic) <sup>e</sup>	C27H40	IV	<1.0
C29 4Δ	C29H44	IV	<1.0
C29 3∆n (aromatic) <sup>e</sup>	C29H46	IV	1.7

<sup>a</sup> Nomenclature: double bond positions assigned where possible; otherwise,  $\Delta^n$  and Δ<sup>SC</sup> indicate double bonds in nucleus or side chain, respectively. b See Appendix for general structure not showing double-bond positions.

<sup>c</sup> Dry-weight sediment (quantitated from GC response and MF of diagnostic ions). d C-ring aromatic.

e A- or B-ring aromatic.

Component <sup>a</sup>	Assignment <sup>b</sup>	Structure <sup>C</sup>	Concentration (ng/g) <sup>d</sup>
Α	22 29 30-trisnorneohop-13(18)-ene	v	4.9
B	22.29.30-trisnorhop-17(21)-ene	VI	13.0
Č	178-22 29 30-trisporhopane	VII	8.8
Ď	Cao-triterpene		42.8
F	Cao-triterpene		17.6
E	hon-17(21)-ene	VIII	31.0
G	Coo-triteradiene		38.9
-	fern-8-ene	1X	1.4
н	neohon-13(18)-ene	x	30.7
÷	Coostriterpene	-	14.8
	fern-9(11)-ene	IX	1.2
1	Capatriterpene		47.4
v	peopon 12 ene	XI	13.8
ĸ	forp 7 one	IX	9.9
7	Can triterpane	173	6.7
L.	C30-triterpene		15.2
M	C30-triterpene	VII	100.0
N	nop-22(29)-ene	VIII	20.3
0	pp-homonopane	ЛШ	29.5

See Figure 2; fernenes do not exhibit intense m/z 191 in their mass spectra. Assignments made by mass spectral interpretation, mass fragmentography, and

GC-retention times. See Appendix.

d Dry-weight sediment.

(Component G) of unknown structure but with spectra similar to those of hop-22(29)-ene and hop-21-ene. No  $\alpha\beta$ - or  $\beta\alpha$ -hopanes were detected, and three fernenes  $(\Delta^7, \Delta^8, \text{ and } \Delta^{9(11)})$  occur in the section.

### Alcohols

### **Acvelic Components**

The relative abundance of individual n-alkanols and their absolute concentrations are shown in Figure 1B. The n-alkanols range from C<sub>14</sub> to C<sub>30</sub> with the evennumbered members predominant and maximizing at nC20. No simple-branched alcohols were detected. Two unsaturated n-alkenols (C24:1 and C26:1) and a single isoprenoid (phytol) were recognized. Their concentrations are shown in Figure 1B.

#### **Cyclic Components**

The concentrations of the major stenols and stanols in Section 481-2-2 are given in Table 3. They are the most abundant extractable lipids in the section. Series of  $\Delta^5$  and  $\Delta^{5,22}$  stenols and their corresponding 5 $\alpha$ -stanols were detected. Dinosterol (4,23,24-trimethyl-5 $\alpha$ -cholest-22-en-3 $\beta$ -ol, XVIf) is the major component and occurs in approximately four times the concentration of any other sterol. No C<sub>26</sub> sterols or short side-chain sterols (C19-C25) were detected. Two extended hopanoid alcohols,  $\beta\beta$ -homohopan-31-ol (XVIIIa) and  $\beta\beta$ -bishomohopan-32-ol (XVIIIb), occur in concentrations of 94 and 180 ng/g dry-sediment weight, respectively.

Three components recently recognized in Black Sea sediment and assigned as a series of straight-chain C<sub>30</sub>, C31, and C32 hydroxyalkanones ("keto-ols"; de Leeuw et al., personal communication), were identified (Table 4).

#### **Carboxylic Acids**

The carboxylic acids of Section 481-2-2 (Fig. 1C) are predominantly straight-chain components, ranging from  $nC_{14}$  to  $nC_{30}$ . The distribution is bimodal, max-



Figure 2. Total alkanes of Section 481-2-2. Gas chromatographic-mass spectrometric analysis: partial mass fragmentogram for m/z 191 diagnostic for triterpenoid hydrocarbons (Table 2).

Table 3. Concentrations of sterols in Section 481-2-2.ª

Assignment <sup>b</sup>	Structure <sup>c</sup>	Concentration (ng/g) <sup>d</sup>
cholesta-5,22-dien-3ß-ol	XIVa	84
$5\alpha$ -cholest-22-en-3 $\beta$ -ol	XVa	47
cholest-5-en-3β-ol	XIVb	201
$5\alpha$ -cholestan- $3\beta$ -ol	XVb	104
24-methylcholesta-5,22-dien-38-ol	XIVc	275
24-methyl-5α-cholest-22-en-3β-ol	XVc	78
C28 stanol		42
24-methylenecholest-5-en-38-ol	XIVd	97
C28 stanol	-	18
24-methylene- $5\alpha$ -cholestan- $3\beta$ -ol	XVd }	115
24-methylcholest-5-en-5p-of	XIVE	42
24-methyl-5 $\alpha$ -cholestan-5 $\beta$ -01	Ave	42
23,24-dimethylcholesta-5,22-dien-3p-ol	AIVI	09
23,24-dimethyl-5 $\alpha$ -cholest-22-en-3p-of	AVI	135
24-ethylcholesta-5,22-dien-3p-ol	XIVg	224
24-ethyl-5 $\alpha$ -cholest-22-eh-3 $\beta$ -ol	XVg	95
23,24-dimethylcholest-5-en-3p-ol	XIVN	127
23,24-dimethyl-5 $\alpha$ -cholestan-3 $\beta$ -ol	XVn	83
24-ethylcholest-5-en-3 $\beta$ -ol	XIVi	331
24-ethyl-5 $\alpha$ -cholestan-3 $\beta$ -ol <sup>2</sup>	XVi	633
4,23,24-trimethyl-5 $\alpha$ -cholest-22-en-3 $\beta$ -ol	XVIf	1933
C <sub>30</sub> 4-methylsterol	-	81
C <sub>30</sub> 4-methylsterol		54
C <sub>30</sub> 4-methylstanol		95
4,23,24-trimethyl-5 $\alpha$ -cholestan-3 $\beta$ -ol	XVIh	309

<sup>a</sup> Sterols analyzed as TMS ethers.

<sup>b</sup> Based on mass spectral interpretation, comparison with literature spectra, and GC-retention times.

<sup>c</sup> See Appendix.

d Dry-weight of sediment.

e Concentration of this component greatly enhanced by coelution with an unknown C29 4-methylsterol.

Table 4. Concentrations of long-chain hydroxy ketones ("15-keto-1ols") in Section 481-2-2.

Assignment <sup>a</sup>	Formula	Structureb	Concentration (ng/g) <sup>c</sup>
-hydroxytriacontan-15-one	C30H60O2	XVII. $n = 14$	1070
-hydroxyhentriacontan-15-one	C31H62O2	XVII, $n = 15$	30
-hydroxydotriacontan-15-one	C32H64O2	XVII, $n = 16$	520

<sup>a</sup> Based on comparison with compounds assigned by de Leeuw et al. (personal communication) from comparison with synthetic homologues. <sup>b</sup> See Appendix.

<sup>c</sup> Dry-weight sediment.

imizing at  $nC_{16}$  and  $nC_{24}$ , with an even over odd preference of 4.3. Minor amounts of unsaturated ( $C_{16:1}$  and  $C_{18:1}$ ) and branched (*iso-* and *anteiso-* $C_{15}$  and  $C_{17}$ ) components were also detected.  $\beta\beta$ -bishomohopanoic acid (XVIIIc) also occurs as a minor component.

# DISCUSSION

The high amount of extractable lipids in Section 481-2-2 is similar to that obtained from anoxic bottom sediments in areas of high productivity, such as Walvis Bay (Wardroper, 1979).

# Paleoenvironment

# **Acyclic Components**

The distributions of straight-chain components (nalkanes, n-alkanols, and n-alkanoic acids) suggest allochthonous and autochthonous contributions to the sediment. The *n*-alkane maximum at  $nC_{29}$  and the prominent odd/even preference in the  $C_{22}$  to  $C_{35}$  range suggest that the origins of the *n*-alkanes are predominantly terrestrial (Simoneit, 1975). The absence of major concentrations of short-chain components—particularly  $nC_{17}$ , a major alkane of phytoplankton (Oro et al., 1967; Gelpi et al., 1970; Blumer et al., 1971; Brassell et al., 1978)—may reflect preferential degradation of these components in the water column or sediment rather than low productivity (Johnson and Calder, 1973).

The origin of *n*-alkanols in marine sediments is not well understood. Their distribution in the Guavmas Basin (Fig. 1B) differs from that of the Japan Trenchwhere the predominant source of n-alkanols (maximizing at  $nC_{24}$ ) has been assigned as terrestrial (Brassell et al., 1980a; Brassell, 1980)-and Walvis Bay, where phytoplankton have been suggested as the source of the n-alkanols (maximizing at nC16) (Wardroper, 1979). Zooplankton wax esters may be the source of the n-alkanols of the Guaymas Basin, as indicated by the predominance of  $nC_{20}$  and  $nC_{22}$ , which are major fatty-alcohol moieties of wax esters (Sargent et al., 1976; Boon and de Leeuw, 1979). But the minor concentrations of  $nC_{16}$  and  $nC_{18}$  in the sediment argue against a wax-ester origin for the n-alkanols, as they are major alcohol components of these compounds (Boon and de Leeuw, 1979).

The bimodal distribution of the *n*-alkanoic acids (Fig. 1C) provides evidence of a mixed contribution from terrestrial and bacterial/algal sources (Simoneit, 1978; Brassell et al., 1980a, 1980b). It is also possible that the shorter-chain compounds may originate from saponified wax esters. We found trace amounts of *iso*-and *anteiso*- $C_{15}$  and  $C_{17}$  acids, whose origins are probably bacterial (Simoneit, 1975, 1978; Brassell et al., 1980a, 1980b).

Two major sources for the production of the isoprenoids pristane and phytane have been suggested: They may result from the degradation of plant phytol (also recognized in this sample) or they may be direct contributions from methanogenic bacteria (Holzer et al., 1979). But the recognition of 2,6,10,15,19-pentamethyleicosane (I) and squalane (II) in Section 481-2-2 (which are constituents of archaebacteria [Holzer et al., 1979]) and other evidence for methanogenic bacterial activity in this hole (Oremland et al., this volume) suggest that methanogens are a source of these lipids. The origin of lycopane (III) in sediments is unclear, but a direct bacterial origin from methanogens (Brassell et al., 1981) seems more likely than diagenetic hydrogenation of lycopene, a constituent of marine algae.

The source of the 1-hydroxyalkan-15-ones is unknown. They are probably of direct biological origin but have not yet been recognized as constituents of organisms. A marine source of these components in Section 481-2-2 seems likely because of their occurrence in other Quaternary and Neogene marine sediments from the Black Sea (de Leeuw et al., personal communication), the Cariaco and Japan trenches, and the Californian continental borderland (University of Bristol [England], Organic Geochemistry Unit, unpublished).

# **Cyclic Components**

The wide range of sterols and stanols in Section 481-2-2 is typical of areas of high productivity such as Walvis Bay and the Japan Trench (Wardroper et al., 1977; Brassell et al., 1980a).

Although  $C_{27}$  to  $C_{29}$ ,  $\Delta^5$ ,  $\Delta^{5,22}$ , and  $\Delta^{22}$  sterols are widespread in organisms, their source probably is phytoplankton (Boutry and Jacques, 1970; Boutry and Barbier, 1974; Orcutt and Patterson, 1975; Ballantine et al., 1979; Volkman et al., 1980). Certainly 23,24-dimethyl sterols have been recognized only in marine sediments (Wardroper, 1979; Brassell et al., 1980b). Dinosterol (XVIf) is the predominant sterol in this section. It is the principal sterol of dinoflagellates (Shimizu et al., 1976) and a marker for major dinoflagellate blooms (Boon et al., 1979). Other 4-methylsterols may also derive from dinoflagellates (Withers et al., 1978) or, perhaps, from methanotrophic bacteria (Bird et al., 1971).

The hopanoids are probably an original bacterial contribution to the sediment (De Rosa et al., 1971; Rohmer, 1975). Hop-17(21)-ene (VIII) and neohop-13(18)ene (X) are probably isomerization products of hop-22 (29)-ene (Ensminger, 1977). But the absence in Section 481-2-2 of hop-21-ene, the proposed intermediate of this isomerization, suggests that these hopanoids also may have a primary origin from bacteria. The recent report of the presence of several hopenes and fernenes in a photosynthetic anaerobic bacterium (Howard, 1980) supports this view and suggests that, in the marine environment, fernenes, as well as hopenes, may originate from bacteria as well as from terrigenous sources (e.g., from ferns; Berti and Bottari, 1968). Since no isomerization of hopenes has occurred, the unknown triterpenoid hydrocarbons in Section 481-2-2 are probably derived directly from bacteria, rather than from the diagenetic alteration of other triterpenes.

# Diagenesis

The study of a single section precludes the evaluation of major diagenetic trends in Hole 481. But the lipid data for Section 481-2-2 can be related to proposed diagenetic pathways, which enables us to assess the maturity of the sediment. The odd/even preference of the n-alkanes, although an insensitive indicator, and the presence of n-alkanols and n-alkanoic acids as major components are characteristic of immature Deep Sea Drilling Project (DSDP) sediments (Simoneit, 1978; Brassell et al., 1980a, 1980b). The predominance of sterols over their defunctionalized counterparts also attests to the immaturity of the section. The wide range of sterenes, including  $\Delta^2$ -sterenes,  $\Delta^{3,5}$ -steradienes, and partially characterized  $\Delta^{22}$ - and  $\Delta^{24}$ -steradienes and  $\Delta^{24}$ steratrienes, is similar to that of other Quaternary DSDP sediments from the Japan Trench (Brassell, 1980; Brassell et al., 1980a) and the California continental borderland (McEvoy et al., in press). The absence of  $\Delta^4$ -and  $\Delta^5$ -sterenes, thought to be acid-clay catalyzed diagenetic products of  $\Delta^2$ -sterenes (Rubinstein et al., 1975) is characteristic of immature sterene distributions, although they do occur in immature Quaternary sediment elsewhere (Simoneit, 1975; Brassell, 1980; Dastillung and Albrecht, 1977). This observation may reflect the high alkalinity in Hole 481 (see site chapter, this volume) when compared with other environments. Or these other sediments may receive rederived material.

The absence of 4-methylsterenes is surprising in view of the presence of 4-methylsterols, particularly of 4,23, 24-trimethyl-5 $\alpha$ -cholest-22-en-3 $\beta$ -ol (dinosterol; XVIf). This concurs with data from other marine sediments and suggests steric hindrance by 4-methyl substitution in the defunctionalization of 4-methylsterols and 4-methylstanols. Thus, it appears that microorganisms effect sterol-to-sterene conversion, since a geochemical pathway would not be expected to exhibit such selectivity between 4-methyl- and 4-desmethyl-sterols.

In Section 481-2-2, the presence (in minor concentrations) of steranes, which are of anomalous maturity for Recent sediments, suggests a contribution of rederived material or, perhaps, minor core contamination from "pipe-dope" (drilling lubricant) (Brassell and Eglinton, 1981; Thomson et al., in press).

The distribution of hopanoids is characteristic of Recent aquatic sediment. The hopanoid alcohols,  $\beta\beta$ homohopan-31-ol (XVIIIa),  $\beta\beta$ -bishomohopan-32-ol (XVIIIb), and  $\beta\beta$ -bishomohopanoic acid (XVIIIC), are probably early-stage diagenetic products of polyhydroxybacteriohopanes (Rohmer, 1975) and are widespread in immature marine sediments. Hop-22(29)-ene (XII) is often the major triterpene of contemporary sediments (Brooks, 1974). In Section 481-2-2, its isomerization has not yet occurred to any significant extent. The absence of  $\beta\alpha$ - and  $\alpha\beta$ -hopanes is consistent with the section's immaturity and precludes major pipe-dope contamination of cores and contributions from thermally mature reworked material.

# CONCLUSIONS

Table 5 summarizes the results and discussion of the lipid classes and gives the concentration of the major component of each class. We draw the following conclusions:

1) 4,23,24-trimethylcholest-22-en- $3\beta$ -ol (XVIIf) is the single most-abundant lipid, and its concentration is approximately four times that of any other sterol. Hence, dinoflagellate blooms may have been important contributors to the sedimentary biomass.

2) The activity of methanogenic bacteria is indicated by the presence of particular acyclic isoprenoid hydrocarbons.

3) Hydroxyalkanones are major components, which, although as yet unrecognized in organisms, are probably of marine origin.

4) Contributions from terrestrial, algal, and bacterial sources are indicated by marker lipids; the algal contribution predominates.

5) The lipid data are typical of those sediments underlying highly productive water columns.

6) Lipid distributions are characteristic of Recent marine sediments, and typify a very early diagenesis stage.

Thus, the lipid composition of older sediment in Hole 481 will determine the constancy of paleoenvironmental conditions of deposition in the Guaymas Basin. It will especially enable us to evaluate the sources of the sedimentary organic matter, the activity of methanogenic bacteria, and the history of water column productivity, especially dinoflagellate blooms. The changes in the lipid distributions with depth will also enable us to assess diagenetic trends and processes in an environment of rapid sedimentation.

### ACKNOWLEDGMENTS

We thank the Natural Environment Research Council (GR3/2951 and supplement GR3/3758) for support. I. D. Thompson acknowledges a research studentship from the Science Research Council. We are grateful to A. P. Gowar for help with C-GC-MS analyses and to P. A. Comet, J. McEvoy and B. R. T. Simoneit for useful discussions and manuscript review.

#### REFERENCES

- Ballantine, J. A., Lavis, A., and Morris, R. J., 1979. Sterols of the phytoplankton—effects of illumination and growth stage. *Phyto*chemistry, 18:1459-1466.
- Berti, G., and Bottari, F., 1968. Constituents of ferns. In Reinhold, L., and Liwschitz, Y. (Eds.), Progress in Phytochemistry (Vol. 1): New York (John Wiley), 589-685.
- Bird, C. W., Lynch, J. M., Pirt, S. J., et al., 1971. Steroids and squalene in *Methylococcus capsulatus* grown on methane. *Nature*, 230: 473-475.
- Blumer, M., Guillard, R. R. L., and Chase, T., 1971. Hydrocarbons of marine phytoplankton. *Mar. Biol.* (Berlin), 8:183-189.
- Boon, J. J., and de Leeuw, J. W., 1979. The analysis of wax esters, very long mid-chain ketones and sterol ethers isolated from Walvis Bay diatomaceous ooze. *Mar. Chem.*, 7:117-132.
- Boon, J. J., Rijpstra, W.I.C., De Lange, F., et al., 1979. The Black Sea sterol—a molecular fossil for dinoflagellate blooms. *Nature*, 277:125-127.
- Boutry, J., and Barbier, M., 1974. La diatomiíe marine Chaetoceros simplex calcitrans Paulsen et son environement. I. Relations avec le milieu de culture; étude de la fraction insaponifiable des stérols libres et des acides gras. Mar. Chem., 2:217-227.
- Boutry, J., and Jaques, G., 1970. Étude biochimique des planctons. III. Insaponifiables et stérols de plancton marine végétal. Bull. Soc. Chim. Biol., 52:349-352.
- Brassell, S. C., 1980. The lipids of deep sea sediments; their origin and fate in the Japan Trench [Ph.D. dissert.]. University of Bristol, England.
- Brassell, S. C., Comet, P. A., Eglinton, G., et al., 1980a. Preliminary lipid analyses of Sections 440A-7-6, 440B-3-5, 440B-8-4, 440B-68-2, and 436-11-4 from DSDP Legs 56 and 57. In Scientific Party, Init. Repts. DSDP, 56, 57, Pt. 2: Washington (U.S. Govt. Printing Office), 1367-1390.
- \_\_\_\_\_, 1980b. The origin and fate of lipids in the Japan Trench. In Douglas, A. G., and Maxwell, J. R. (Eds.), Advances in Organic Geochemistry, 1979: Oxford (Pergamon), pp. 375-392.
- Brassell, S. C., and Eglinton, G., 1981. Organic geochemical studies of Sections 447A-10-2 and 448-1-1 from DSDP Leg 59. In Kroenke, L., Scott, R. B., et al., Init. Repts. DSDP, 59: Washington (U.S. Govt. Printing Office), 647-648.
- Brassell, S. C., Eglinton, G., Maxwell, J. R., et al., 1978. Natural background of alkanes in the aquatic environment. *In* Hutzinger, O., van Lelyveld, L. H., and Zoeteman, B. C. J. (Eds.), *Aquatic Pollutants, Transformations and Biological Effects:* Oxford (Pergamon), pp. 69-86.
- Brassell, S. C., Wardropes, A. M. K., Thomsen, I. D., et al., 1981. Specific acyclic isoprenoids as biological markers of methanogenic bacteria in marine sediments. *Nature*, 290:693-696.
- Brooks, P. W., 1974. Isoprenoids and other lipids in Recent sediments. [Ph.D. dissert.]. University of Bristol, England.
- Corbet, B., Albrecht, P., and Ourisson, G., 1980. Photochemical or photomimetic fossil triterpenoids in sediments and petroleum. J. Am. Chem. Soc., 102:1171-1173.
- Dastillung, M., and Albrecht, P., 1977. Δ<sup>2</sup>-sterenes as diagenetic intermediates in sediments. *Nature*, 269:678-679.

- De Rosa, M., Gambacorta, A., Minale, L., et al., 1973. Isoprenoids of *Bacillus acidocaldarius*. *Phytochemistry*, 12:1117–1123.
- Ensminger, A., 1977. Évolution de composés polycycliques sédimentaires [Ph.D. dissert.]. Université Louis Pasteur, Strasbourg.
- Gelpi, E., Schneider, H., Mann, J., et al., 1970. Hydrocarbons of geochemical significance in microscopic algae. *Phytochemistry*, 8: 603-612.
- Holzer, G., Oro, J., and Tornabene, T. G., 1979. Gas chromatographic-mass spectrometric analysis of neutral lipids from methanogenic and thermoacidophilic bacteria. J. Chromatog., 186: 795-809.
- Howard, D. L., 1980. Polycyclic triterpenes of the anaerobic photosynthetic bacterium *Rhodomicrobium vannielli* [Ph.D. dissert.]. University of California—Los Angeles.
- Johnson, R. W., and Calder, J. A., 1973. Early diagenesis of fatty acids and hydrocarbons in a salt marsh environment. Geochim. Cosmochim. Acta, 37:1943-1955.
- McEvoy, J., Eglinton, G., and Maxwell, J. R., in press. Preliminary lipid analyses of sediments from Sections 467-3-3 and 467-97-2. In Haq, B. U., Yeats, R. S., et al., Init. Repts. DSDP, 63: Washington (U.S. Govt. Printing Office).
- Orcutt, D. M., and Patterson, G. W., 1975. Sterol, fatty acid and elemental composition of diatoms grown on chemically defined media. *Comp. Biochem. Physiol.*, 50B:579-583.
- Oro, J., Tornabene, T. G., Nooner, D. W., et al., 1967. Aliphatic hydrocarbons and fatty acids of some marine and freshwater microorganisms. J. Bacteriol., 93:1811-1818.
- Rohmer, M., 1975. Triterpenoids de prokaryotes [Ph.D. dissert.]. Université Louis Pasteur. Strasbourg.
- Rubinstein, I., Sieskind, O., and Albrecht, P., 1975. Rearranged sterenes in a shale: Occurrence and simulated formation. J. Chem. Soc. Perkin Trans. 1:1833-1835.
- Sargent, J. R., Lee, R. F., and Nevenzel, J. C., 1976. Marine waxes. In Kolattukudy, P. E. (Ed.), Chemistry and Biochemistry of Natural Waxes: New York (Elsevier), pp. 50-91.

- Schaeffle, J., Ludwig, B., Albrecht, P., et al., 1978. Aromatic hydrocarbons from geological sources VI: New aromatic steroid derivatives in sediments and crude oils. *Tetrahedron Lett.*, 4163-4166.
- Shimizu, Y., Alam, M., and Kobayashi, A., 1976. Dinosterol, the major sterol with a unique side chain in the toxic dinoflagellate, Gonyaulax tamarensis. J. Am. Chem. Soc., 98:1059-1060.
- Simoneit, B. R. T., 1978. The organic chemistry of marine sediments. In Riley, J. P., and Chester, R. (Eds.), Chemical Oceanography (Vol. 7): New York (Academic), 233-311.

\_\_\_\_\_, 1975. Sources of organic matter in oceanic sediments [Ph. D. dissert.]. University of Bristol, England.

- Spyckerelle, C., 1975. Constituants aromatiques de sédiments [Ph.D. dissert.]. Université Louis Pasteur, Strasbourg.
- Thomson, I. D., Brassell, S. C., Comet, P. A., et al., in press. Preliminary lipid analyses of cores 49, 54, and 59 from Hole 462. In Schlanger, S. O., Larson, R. L., et al., Init. Repts. DSDP, 61: Washington (U.S. Govt. Printing Office).
- Volkman, J. K., Corner, E. D. S., and Eglinton, G., 1981. Transformations of biolipids in the marine food web and in underlying bottom sediments. Paris. In Daumas, R. (Ed.), Biogeochimie de la matiere organique à l'interface eau-sediment marin: Paris (Editions du CNRS), pp. 185-197.
- Wardroper, A. M. K., 1979. Aspects of the geochemistry of polycyclic isoprenoids [Ph.D. dissert.]. University of Bristol.
- Wardroper, A. M. K., Brooks, P. W., Humberston, M. J., et al., 1977. Analysis of steranes and triterpanes in geological extracts by automatic classification of mass spectra. *Geochim. Cosmochim. Acta*, 41:499-510.
- Withers, N. W., Tuttle, R. C., Holz, G. G., et al., 1978. Dehydrodinosterol, dinosterone and related sterols in a non-photosynthetic dinoflagellate, *Crypthecodinium cohnii*. *Phytochemistry*, 17:1987-1989.

Table 5. Summary of lipids from Section 481-2-2 (7.5 m sub-bottom; late Pleistocene diatomaceous ooze).

Lipid Class	Results	Comments
n-alkanes	Long-chain components predominant; Coo major (189 ng/g); high CPI	Terrestrial origin; immature
n-alkanols	C <sub>20</sub> -C <sub>24</sub> predominant; C <sub>20</sub> major (728 ng/g); high CPI	Marine(?) origin; immature
n-acids	Bimodal distribution; $C_{16}$ and $C_{24}$ major (317 and 155 ng/g); high CPI	Terrestrial and marine origin; immature
hydroxyalkanones	Major components; C <sub>30</sub> predominant (1030 ng/g)	Unknown origin but probably marine
acyclic isoprenoid hydrocarbons	Lycopane major (68 ng/g)	Methanogenic bacterial origin
steranes	Very minor components (compound <1.0 ng/g)	Rederived material or minor pipe-dope contamination
steroidal alkenes	Minor components: wide range; $C_{27} \Delta^{3,5}$ predominant (74.6 ng/g); sterenes all $\Delta^2$	Typical of Recent sediment; immature; no monosterene isomerization
sterols	Major components; wide range; 4,23,24- trimethyl-5 $\alpha$ -cholest-22-en-3 $\beta$ -ol predominant (1933 ng/g)	Typical of highly productive marine environments and dinoflagellate blooms
triterpanes	Minor components; only $\beta\beta$ -homohopane (29 ng/g) and $\beta$ -trisnorhopane detected; no $\alpha\beta$ -hopanes	Bacterial origin; immature; argues against pipe-dope contamination
triterpenes	Minor components; hop-22(29)-ene major (100 ng/g); several unidentified components	Bacterial origin; no apparent hopene isomerization; immature
hopanols	Minor components; $\beta\beta$ -bishomohopanol major (180 ng/g)	Characteristic of Recent sediments; bacterial contribution; immature
hopanoic acid	Minor component; 88-homohopanoic acid	
ketones	Complex mixture of steroidal and triterpenoidal ketones; no major amounts of long-chain unsaturated ketones; minor components dino- sterone and C18 isoprenoid ketone	Fraction not examined in detail

APPENDIX

