32. ORGANIC GEOCHEMISTRY OF SEDIMENTS FROM THE MOUTH OF THE GULF OF CALIFORNIA, LEG 64, SITES 474 AND 476

Bernd R. T. Simoneit, Institute of Geophysics and Planetary Physics, University of California—Los Angeles, Los Angeles, California

ABSTRACT

Diatomaceous mud and an organically-rich claystone from holes at Sites 474 and 476 at the mouth of the Gulf of California were analyzed by organic geochemical methods to characterize their organic matter. The lipids of all three samples are primarily marine autochthonous, with the exception of Sample 474-5-3, 105-107 cm, which also contains some vascular plant wax. Based on the lipid composition, the sediment was deposited mainly under oxic environmental conditions. The kerogens were aliphatic and autochthonous marine. Two lignite fragments were also analyzed, and the data indicate that they are driftwood that absorbed marine bitumen from the surrounding sediment during coalification.

INTRODUCTION

Sedimentation during the Pleistocene epoch off Cabo San Lucas reflects the influence of open ocean communication with the Pacific; it consists of diatomaceous mud (Curry et al., 1979). Samples from holes at Site 474 were chosen to compare similar diatomites from the central Gulf of California.

The deepest sediment in Hole 476 is an organic claystone just above the conglomerates of metamorphic cobble. This represents some of the earliest sediment (Pliocene) accumulated on the subsiding continental fault blocks of the proto-Gulf. The lithology is banded to thinly laminated, containing 7.5% organic carbon with quartz silt, sparse glauconite, and many blue-green algal threads. Pollen and fungal spores are rare. The depositional environment for this sequence is equivocal but must represent moderately shallow water (initially in the photic zone) in a semirestrictive setting, such as an offshore bank. Thus, it was of interest to determine if the data from the organic geochemical analyses of this sample supported this environmental interpretation.

The bulk parameters of two wood fragments were also analyzed to assess their origin.

METHODS

The small core samples were dried in an oven at 105°C and extracted after C, H, N analysis (onboard) with toluene and methanol (4:1). The larger sample was freeze dried and then extracted with methylene chloride and methanol (4:1) using ultrasonication. The extracts were concentrated on a rotary evaporator and treated with BF3 in methanol to derivatize free fatty acids. The extracts were then subjected to thin-layer chromatography (TLC) on silica gel, using methylene chloride as eluent. The bands (after development with iodine vapor) corresponding to hydrocarbons, esters, and ketones were scraped off the TLC plates and eluted with methylene chloride. The hydrocarbon and combined ester and ketone fractions were analyzed by gas chromatography (GC) and GC mass spectrometry (MS).

The GC analyses were carried out on a Hewlett-Packard 5830 gas chromatograph, using a 16 m x 0.25 mm glass capillary column coated with SE-54. The mass spectrometric data was acquired and processed with a Finnigan-Ionics 2300 data system. The carrier gas was He at a flow rate of 3 ml/min. A Finnigan 4000 quadrupole mass spectrometer interfaced directly to a Finnigan 9610 gas chromatograph and equipped with a 30 m x 0.25 mm glass capillary column coated with SE-54 was used for the GC/MS analyses. The GC conditions for the GC/MS analyses were the same as those used for the analytical GC system. The mass spectrometric data was acquired and processed with a Finnigan-Ionics 2300 data system.

The residual organic matter (i.e., kerogen) was separated by demineralization, using 40 to 60% hydrofluoric acid according to the method described by Stuermer et al. (1978). The University of California (Berkeley) Department of Chemistry Microanalytical Laboratory performed the elemental analyses. The methods described by Kaplan et al. (1970) and the Chicago PDB as a reference standard were used for the stable carbon isotope analyses.

RESULTS AND DISCUSSION

Table 1 presents the results of the carbon, lipid, and kerogen analyses. The lipid content is high and consists of predominantly polar material. Figure 1 indicates the distribution of various homologous compound series in the lipids.

Samples from Site 474

The n-alkanes of Samples 474-5-3, 105-107 cm and 474-6-5, 32-34 cm exhibit bimodal distributions, with maxima at C16 and C18 in the lower carbon number range and at C25 and C27 in the higher range (overall CPI = 1.12 and 1.11, respectively; Fig. 1A,B). The source of the n-alkanes > C25 with an odd carbon number predominance is vascular plant wax (Simoneit, 1975; in press a, b), especially for Sample 474-5-3, 105-107 cm. The distributions < C25, when coupled with the unresolved complex mixture (hump) of branched and cyclic hydrocarbons maximizing at the GC retention of n-C19, indicate a degraded microbial origin (Simoneit, in press a, b). The predominance of n-hexadecane and n-octadecane (also n-eicosane) may reflect a microreducing environment, as, for example, anaerobic microbial degradation in individual diatoms deposited in the sediment (Simoneit, 1975, 1977). The pristane-to-phytane ratio is 1.6 for both samples; perylene, other pigments

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and sulfur could not be detected. This indicates that the overall environmental conditions of sedimentation were oxic and open marine (Didyk et al., 1979), which agrees with the lithologic description (Curray et al., 1979). The distribution of the \( n \)-fatty acids is unimodal (Fig. 1D and E), ranging from \( \text{C}_{10} \) to \( \text{C}_{18} \), with a strong even-to-odd carbon number predominance (CPI = 4.7 and 5.0, respectively) and a maximum at \( \text{C}_{16} \) (and a slight dominance of \( \text{C}_{22} \)). These distributions indicate an autochthonous origin for this lipid fraction, again from microbial residues (Simoneit, 1975). No unsaturated fatty acids were detected. Dehydroabietic acid, the dominant molecular marker of resinous higher plants, was not detected (Simoneit, 1977). The ketones consist primarily of \( \text{C}_{10} \), \( \text{C}_{18} \), \( \text{C}_{20} \) and \( \text{C}_{22} \) n-alkan-2-ones [dotted line indicates isoprenoids], which reflects an origin from phytol by microbial degradation. Ster-4-
Pigment, or sulfur were detected. This indicates that the bial detritus, possibly blue-green algae and bacteria, range of marine organic matter (Kaplan, 1975). The N/C ratios are about 0.05. These atomic ratios indicate an origin from microbial (mostly algal and bacterial) residues (Stuermer et al., 1978; Simoneit, in press a). No unsaturated fatty acids are detectable. Further possible microbial indicators are the alkylcyclcopentanes (Fig. 1G), with which may be reduction products from the corresponding fatty acids (even carbon-number predominance). The ketone fraction (Fig. 1H) consists of n-alkan-2-ones—ranging from C₁₂ to C₂₉, with maxima at C₁₂ and C₁₇ and essentially no carbon number predominance—and the isoprenoidal ketones 6,10-dimylundecan-2-one and 6,10,14-trimylpentadecan-2-one. These compounds are probably microbial degradation products from lipids and phytol (Simoneit, 1973; in press b).

No dehydroabietic acid was detected, and its absence indicates that no influx of resinous plant detritus occurred (Simoneit, 1977). There are traces of sesquiterpenoid residues, consisting of cadalene (IV) and probably cadinane (V). These compounds have an autochthonous algal origin (Simoneit, in press b). Ster-4-enes (I) and ster-3-ones (VI) occur in significant amounts (Fig. 1K and L, respectively). The range of ster-4-enes, from C₂₇ to C₂₉ and a maximum at C₂₉, indicates a non-marine distribution (Huang and Meinschein, 1979). The ster-3-ones range from C₂₇ to C₂₉ with a maximum at C₂₇ (a marine distribution), and the 4-methylster-3-ones range from C₂₇ to C₃₁ with a maximum at C₂₉. The 4-methylster-3-ones also indicate a source from microbacteria (Bird et al., 1971), and thus the source of most of the steroidal markers is autochthonous marine. The triterpenoids (Fig. 1) predominantly consist of 17β(H)-hopanes, moretanes, and hopanes. Hopane is the major homolog, and the series ranges to C₃₄ with only the 22S stereomer present >C₃₁. The moretanes consist of the C₂₇, C₂₉-C₃₁ homologs and hop-17(21)-ene (III) in the major olefin. The predominance of the 17β(H) stereochemistry with the presence of the moretanes indicates a very immature lipid mixture (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980; Simoneit et al., 1979). These triterpenoids are autochthonous and derived from the diagenesis of bacteriohopane polypeptides and diplopentane (Rohmer, 1975). Triterpenoidal acids are present and consist of the extended hopanoic acids (VII), ranging from C₃₁ to C₃₃ with the 17α(H) stereomers predominant over the 17β(H). The major homolog is 17α(H)-bishomohopanoic acid. A minor amount of bishomohop-17(21)-enoic acid (VIII) is also present. The source of these compounds is bacteriohopane polypeptides (Rohmer, 1975).

The kerogen isolated from this sample is aliphatic, with an H/C ratio of 1.48, N/C ratio of 0.061, and a δ¹³C value of -20.6‰. The H/C and N/C indicate an origin from microbial residues (Stuermer et al., 1978; Simoneit, in press a, b), and the stable carbon isotope composition falls within the range of organic matter from marine sources (Kaplan, 1975).

Sample 476-2-2, 22-23 cm consists of a wood (lignite) fragment with H/C = 1.17, N/C = 0.013, and δ¹³C = -23.6‰. On comparison with the data typical for peat and vascular plant detritus (H/C = 1.0, N/C = 0.03-0.06, and δ¹³C = -27 to -28%) [Stuermer et al., 1978]), these values indicate a minor dilution of the ter-
CONCLUSION

The lipids of all three samples are of a primarily autochthonous marine origin from algae and bacteria. The only exception, Sample 474-5-3, 105-107 cm, also contains a significant higher plant wax component. None of the samples exhibit any influx of diterpenoids from resinous higher plants. Bulk geochemical data (e.g., Pr/Ph) indicate that the environmental conditions of sedimentation were oxic. Low-molecular weight even n-alkanes (C₁₆ and C₁₈) indicate that some of the lipids were preserved in reducing microenvironments.

The kerogens of all three samples are primarily marine autochthonous. This is indicated by the aliphatic nature of their composition (H/C ~ 1.5) and the stable carbon isotope data.

The data for the two lignite fragments indicate that they were driftwood that absorbed some of the surrounding sedimentary organic matter (e.g., bitumen) during in situ coalification.

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REFERENCES


APPENDIX

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<th>I. Ster-4-enes</th>
<th>II. Hopanes</th>
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<th>III. Hop-17(21)-ene</th>
<th>IV. Cadalene</th>
<th>V. Cadinane</th>
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<tr>
<td>R = H, C₂H₅C₇H₁₅</td>
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<th>VI. Ster-3-ones</th>
<th>VII. Extended hopanoic acids</th>
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<td>R = COOH, CH₂COOH, CH₂CH₂DOOH</td>
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| VIII. Bishomohop-17(21)-enoic acid | |
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