

## 48. ORGANIC GEOCHEMISTRY OF ALBIAN SEDIMENT FROM HESS RISE, DEEP SEA DRILLING PROJECT HOLE 466<sup>1,2</sup>

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### ABSTRACT

The lipids of Deep Sea Drilling Project Sample 466-29-2, 40–42 cm were analyzed. Based on the distributions of the *n*-alkanes, *n*-alkylcyclohexanes, *n*-fatty acids, hump and molecular markers, they are of an autochthonous marine source, deposited in anoxic paleoenvironmental conditions of sedimentation. The kerogen appears to be terrigenous, or possibly from a light biogenic carbon pool.

### INTRODUCTION

It has been proposed that vast oceanic areas during the late Mesozoic were anaerobic. It was therefore of interest to determine, by using organic geochemical parameters, the paleoenvironmental conditions of sedimentation for an organic-matter-rich claystone from the Cretaceous at DSDP Site 466, on Hess Rise.

Sample 466-29-2, 40–42 cm consists of pyritic claystone of upper Albian age, from 256 meters sub-bottom depth. The site is in 2665 meters of water, on Southern Hess Rise (34°11.46'N, 179°15.34'E; Vallier, Thiede, et al., 1979).

### METHODS

The core sample was freeze-dried, then extracted with methylene chloride and methanol (4:1) using ultrasonication. The extract was concentrated on a rotary evaporator and treated with BF<sub>3</sub> and methanol prior to silica-gel thin-layer chromatography (TLC), using hexane and ether (9:1) as eluent. The bands corresponding to hydrocarbons, esters, and ketones were scraped off the TLC plate after development with iodine vapor, and eluted with methylene chloride. The hydrocarbon and combined ester and ketone fractions were subjected to GC and GC/MS analyses.

The GC analyses were carried out on a Hewlett-Packard Model 5830 gas chromatograph, using a 16 m × 0.25 mm glass capillary column coated with OV-101, programmed from 110 to 280°C at 4°C/min, using He carrier gas at a flow rate of 3 ml/min.

The GC/MS analyses were carried out on a Finnigan Model 4000 quadrupole mass spectrometer interfaced directly to a Finnigan Model 9610 gas chromatograph equipped with a 30 m × 0.25 mm glass capillary column coated with SE-54. The GC conditions for the GC/MS analyses were as those for the analytical GC system. The mass spectrometric data were acquired and processed using a Finnigan-Incos Model 2300 data system.

The stable-carbon-isotope analyses were carried out by the methods described by Kaplan et al. (1970), using the Chicago PDB as reference standard.

### RESULTS AND DISCUSSION

The results of the carbon analyses carried out by DSDP are as follows: total carbon 16.48%, organic carbon 11.3%, CaCO<sub>3</sub> 43.0%. This organic-matter-rich

claystone also has a high lipid content (3400 µg/g dry weight of sediment, of which 84 µg/g is total hydrocarbons and 5 µg/g is total fatty acids).

The distribution of various homologous compound series in the lipid fractions is shown in Figure 1. The *n*-alkanes exhibit an essentially unimodal distribution, ranging from C<sub>11</sub> to C<sub>29</sub>, with maxima at C<sub>17</sub> and C<sub>19</sub> and a minor odd-carbon-number predominance (CPI = 1.3, summed from C<sub>11</sub> to C<sub>29</sub>) (Fig. 1A). Homologs >C<sub>25</sub> with an odd-carbon-number predominance are essentially absent, indicating no contribution from vascular plant waxes (Simoneit, 1975; in press a, b). The distribution <C<sub>25</sub>, when coupled with the presence of an unresolved complex mixture (hump) of branched and cyclic hydrocarbons maximizing at the GC retention of *n*-C<sub>19</sub>, indicates a degraded microbial origin (Simoneit, in press a, b). The presence of significant amounts of alkylcyclohexanes, C<sub>n</sub>H<sub>2n</sub>, *n* ranging from 16 to 24, with a maximum at C<sub>19</sub> (Fig. 1B) is further evidence for bacterial lipid residues. The pristane/phytane ratio is 0.6, and the presence of some elemental sulfur in the lipids indicate euxinic paleoenvironmental conditions of sedimentation (Didyk et al., 1978). This is in agreement with the preliminary findings of DSDP Leg 62 (Vallier, Thiede, et al., 1979). The *n*-fatty acids exhibit a bimodal distribution, ranging from *n*-C<sub>8</sub> to *n*-C<sub>30</sub>, with an even carbon-number predominance (CPI = 3.1, summed from C<sub>10</sub> to C<sub>30</sub>) and maxima at C<sub>16</sub>, C<sub>23</sub>, and C<sub>26</sub> (Fig. 1C).

The homologs >C<sub>24</sub> with the strong even-carbon-number predominance may be derived from higher plant wax, whereas the homologs <C<sub>20</sub> and possibly C<sub>23</sub> are of an autochthonous marine origin (Simoneit, 1975, in press a, b). Unsaturated fatty acids were not detectable. The ketones consist primarily of 6,10,14-trimethylpentadecan-2-one and 6,10-dimethylundecan-2-one, with traces of *n*-alkan-2-ones ranging from C<sub>12</sub> to C<sub>19</sub>. These compounds are probably microbial degradation products from phytol and other microbial lipids (Simoneit, 1973, in press b).

Dehydroabiatic acid, the dominant molecular marker of resinous higher plants, was not detectable (Simoneit, 1977a). Perylene, a possible terrigenous marker pre-

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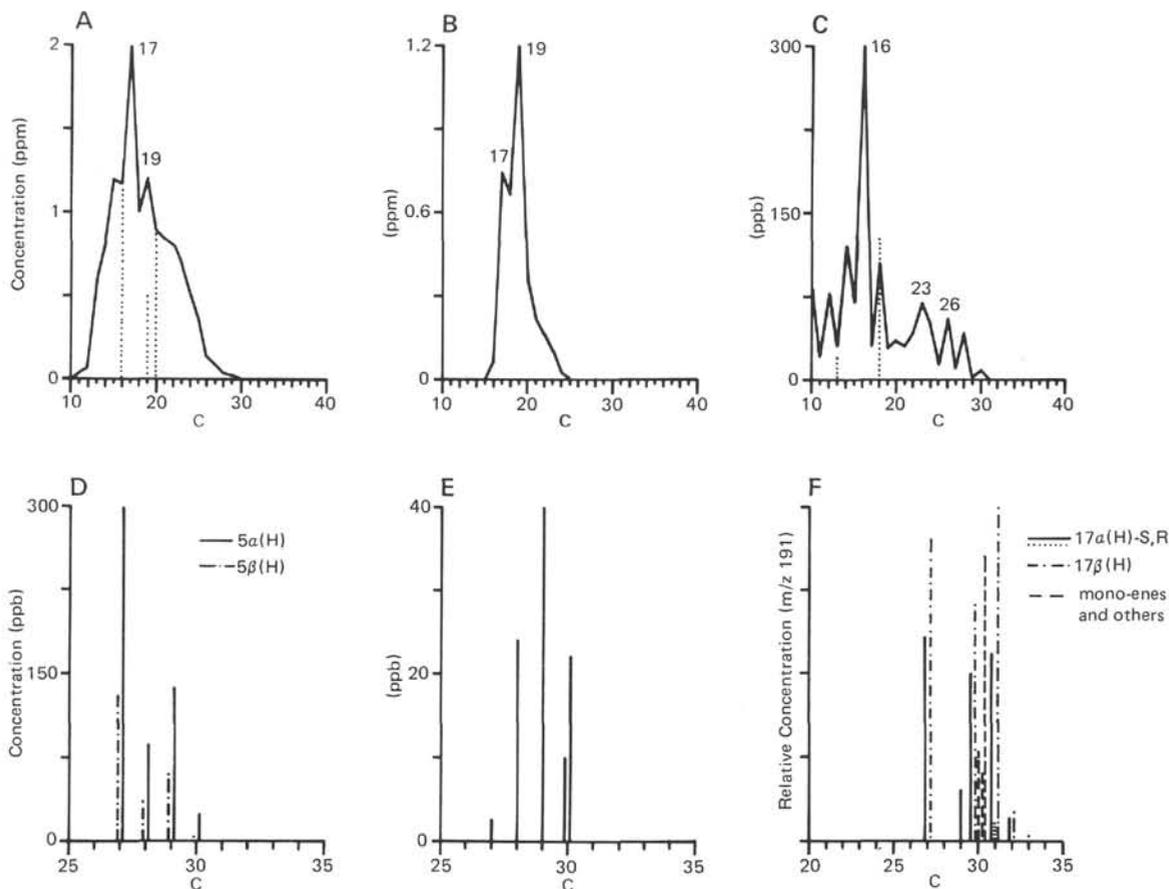


Figure 1. Concentrations of various lipid components of sample 466-29-2, 40-42 cm. A. *n*-alkanes (dotted line indicates isoprenoids). B. *n*-alkylcyclohexanes. C. *n*-fatty acids (dotted line indicates isoprenoid ketones). D. Steranes. E. 4-methylstan-3-ones. F. Relative concentration of triterpenoids.

served under anoxic sedimentary conditions (Aizenshtat, 1973; Didyk et al., 1978), was present as the major polynuclear aromatic hydrocarbon. Sesquiterpenoids and other diterpenoids were not present above background. The steroidal markers consist of steranes ( $5\alpha > 5\beta$ (H), I) (Fig. 1D) and 4-methylstan-3-ones (probably  $5\alpha$ (H), II) (Fig. 1E), both ranging from  $C_{27}$  to  $C_{30}$ . Cited chemical structures are shown in Figure 2; roman numerals in the text correspond to these structures. The ratios of the cis ( $5\beta$ ) to trans ( $5\alpha$ ) stereomers of the steranes are given in Table 1 and all are 0.4 or less. Ratios for mature source rocks and petroleum have been observed in the range 0.6 to 0.8 (e.g., Seifert and Moldowan, 1978). Cholestane (I,  $R=H$ ,  $5\alpha$ ) is the dominant sterane, and 4,24-dimethylcholestan-3-one (II,  $R=H$ ) is the dominant stanone. The presence of 4-methylstanones may indicate a source from various micro-organisms (e.g., Bird et al., 1971).

Triterpenoids are present primarily as the hopane series, with lesser amounts of the moretanes. The  $17\beta$ (H),  $21\beta$ (H) stereomers are predominant over the  $17\alpha$ (H),  $21\beta$ (H) isomers, and  $17\beta$ (H),  $21\beta$ (H)-homohopane (III,  $R=CH_3$ ) is the major analog. Their relative concentrations (based on the  $m/z$  191 peak intensity in the GC/MS data) are plotted in Figure 1F.

The hopane series consists of the trisnorhopanes (IV,  $R=H$ ),  $17\alpha$ (H)-norhopane (IV,  $R=C_2H_5$ ,  $17\alpha$ ),

hopanes (IV,  $R=C_3H_7$ ), homohopanes (III,  $R=H$ ), bishomohopanes (III,  $R=CH_3$ ) and  $17\beta$ (H)-trishomohopane. The moretane series consists of the  $17\beta$ (H),  $21\alpha$ (H) stereomers and ranges from  $C_{31}$  to  $C_{32}$ . Triterpenes were present as dominant components and were identified as hop-17(21)-ene (V), with lesser amounts of  $17\beta$ (H)-hop-21(22)-ene (VI) and trisnorhop-17(21)-ene (VII). These triterpenoids are probably autochthonous, derived from the diagenetic products of bacteriohopanepolyols and diploptene (Rohmer, 1975).

The dominance of the  $17\beta$ (H) stereochemistry (cf. ratios  $< 1.0$  in Table 1) indicates the geologic immaturity of these compounds (Dastillung and Albrecht, 1976; Simoneit and Kaplan, 1980). Similar triterpane distributions were found for Cretaceous shales from the Atlantic Ocean (Simoneit, in press a, b). Triterpenoidal acids were identified and consist of the extended hopanoic acids ranging from  $C_{31}$  to  $C_{33}$ , with the  $17\beta$ (H) stereomers predominant over the  $17\alpha$ (H) stereomers and bishomohopanoic acid (VIII) as the major homolog. These compounds are also derived from bacteriohopanepolyols (Rohmer, 1975) and are geologically immature.

Aromatic triterpenoid residues were also found as predominant lipid components. The following analogs were identified: 14,18-Bisnormethyladianta-13,15,17-triene (IX), with a minor amount of its next higher

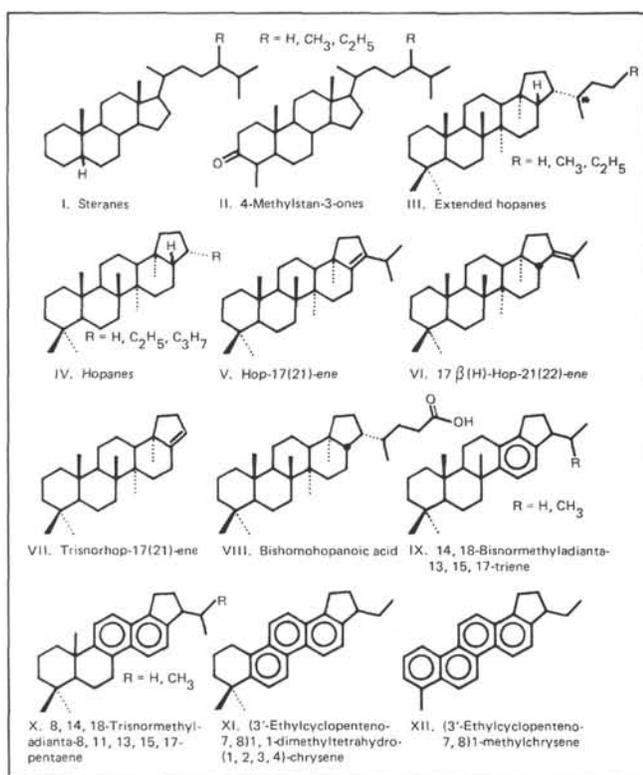


Figure 2. Chemical structures cited in the text.

Table 1. Stereometric ratios for the major triterpanes and steranes in Sample 466-29-2, 40-42 cm.<sup>a</sup>

Species	C27	C28	C29	C30	C31	C32
Hopanes:						
17 $\alpha$ (H)/17 $\beta$ (H)	0.67	—	—	0.71	0.56	0.88
Steranes:						
5 $\beta$ (H)/5 $\alpha$ (H)	0.43	0.43	0.44	0.13	—	—

<sup>a</sup> Determined by integration of peaks in the respective  $m/z$  191 and  $m/z$  217 mass chromatograms.

homolog; 8,14,18-trisnormethyladianta-8,11,13,15,17-pentaene (X), also with a minor amount of its next higher homolog; (3'-ethylcyclopenteno-7,8)1,1-dimethyltetrahydro-(1,2,3,4)-chrysene (XI); and (3'-ethylcyclopenteno-7,8)-1-methylchrysene (XII). These compounds appear to be diagenetic products derived from triterpanes (Greiner et al., 1976), and they have been identified in other Cretaceous shales from the Atlantic Ocean (Simoneit, 1977b, 1979a,b).

Kerogen was isolated from the sediment using the procedure of Stuermer et al. (1978) and the yield was 11.02% (as carbon, ash free). The H/C is 1.35, rather aliphatic and typical of microbial detritus (Stuermer et al., 1978). N/C is 0.031 and S/C is 0.061, which also correlate with typical values of microbial detritus (Simoneit, in press a; Stuermer et al., 1978). The  $\delta^{13}\text{C}$  value of the kerogen carbon is  $-27.9\%$ , which is within the range for organic matter of terrestrial origin. This incongruity with the lipid origin may be better explained

by possible autochthonous biosynthesis of a portion of the organic matter from a light carbon source (e.g., biogenic methane).

## CONCLUSION

The lipids of Sample 466-29-2, 40-42 cm are of a primarily autochthonous marine origin. This is indicated by the distributions of the  $n$ -alkanes,  $n$ -alkylcyclohexanes,  $n$ -fatty acids, hump and the molecular markers. The kerogen appears to be composed of terrigenous organic matter or autochthonous material biosynthesized from a light carbon source. The paleoenvironmental conditions of sedimentation were anoxic, with a high autochthonous productivity.

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