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14. PRELIMINARY ASSESSMENT OF ORGANIC GEOCHEMICAL SIGNALS IN SEDIMENTS FROM HOLE 893A, SANTA BARBARA BASIN, OFFSHORE CALIFORNIA[1]

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ABSTRACT

Preliminary results of molecular organic geochemical analyses of 26 samples from Hole 893A are reported in this paper. Detailed lipid analyses of 10 selected samples show a complex molecular composition of marine, terrestrial, and bacterial origin. Numerous steroidal alcohols of predominantly autochthonous origin form the major compound class in the bitumen. Higher plant-derived long-chain *n*-fatty acids, *n*-alcohols, and *n*-alkanes are also present in significant concentrations. The hydrocarbon fractions of all investigated samples contain a series of 17α(H)-hopanes that show a signature typical of biodegraded petroleum. These compounds are derived from eroded Monterey Formation petroleum source rocks or related oil seeps, or—considered less likely—from local migration of oil from greater depths. Several molecular parameters appear to distinguish laminated from nonlaminated sediments.

INTRODUCTION

The assemblage of organic matter components in marine sediments is controlled by a number of factors, including the primary autochthonous productivity, the supply of allochthonous organic matter from the continent (terrestrial plant material or eroded rock), preservation during and after deposition, redeposition of material on subaquatic slopes, diagenetic alteration within the sediment, and migration of mobile components from deeper sediment layers. Most of the predepositional factors will be influenced by climatic and related oceanographic changes (sea level, currents) and these may eventually be reflected in the fossil organic matter composition. Drilling of recent and subrecent sediments in the Santa Barbara Basin by the Ocean Drilling Program (ODP) provided the opportunity to address this subject.

Site 893 is located at 34°17.25′N, 120°02.2′W, in the center of the Santa Barbara Basin on the southern Californian continental margin (Fig. 1). Drilling during Leg 146 recovered 196.5 m of sediment with a relatively uniform lithology, with the main variation being the extent of lamination. The sequence represents a sedimentary record of the last 160,000 yr (Fig. 2; Kennett, Baldauf, et al., 1994). The basin is semi-enclosed and has a maximum water depth of about 600 m. The sill to the open Pacific Ocean is at a water depth of 475 m and at present lies within the East Pacific Oxygen Minimum Zone. This results in suboxic bottom-water masses in the central basin below that depth (Sholkovitz and Gieskes, 1971; Kennett, Baldauf, et al., 1994). The high biological productivity in the surface water of the California Borderland is responsible for the accumulation of organic carbon-rich anoxic muds in the Santa Barbara Basin at high sedimentation rates. In the Holocene central basin, annual pairs of light and dark layers are induced by seasonal variation of marine and terrigenous sediment supply, growth of bacterial mats, and bottom-water redox conditions (e.g., Soutar and Crill, 1977; Pisias, 1978; Reimers et al., 1990; Schimmelmann and Tegner, 1990; Schimmelmann and Kastner, 1992).

The knowledge of the sedimentary history of the Santa Barbara Basin until now is restricted to the Holocene section. The results of high-resolution studies of varve chronology, sedimentology, stable oxygen isotopes, microfossil assemblages, and organic matter composition were interpreted in terms of changes in precipitation, terrigenous sediment supply, surface-water temperatures, primary productivity, intensity of the California Current, and oxygen level of the water masses by (e.g., Fleischer, 1972; Soutar and Crill, 1977; Heusser, 1978; Pisias, 1978; Dunbar, 1983; Lange et al., 1990; Bernhard and Reimers, 1991; Kennedy and Brassell, 1992a, 1992b).

The analysis of lipids at the molecular level so far is essentially restricted to the studies of Kennedy and Brassell (1992a, 1992b). They concentrated on the analysis of long-chain alkenones in order to establish a sea-surface temperature record with an approximately annual resolution. In addition, they investigated concentration profiles of biomarkers of marine origin (dinosterol, brassicasterol, and cholesterol) down a shallow hole, which were interpreted to reflect productivity trends. They related their results to historical climatic records such as sea-surface temperature measurements and reported El Niño events and found a good correlation between geochemical and historical records.

Heath et al. (1977) performed a high-resolution study of total organic carbon (TOC) contents of Santa Barbara Basin sediments from the last 10 ka in order to compare the diagenetic degradation rates of terrestrial and marine organic material. They found that the degradation of marine organic material occurs 3.5 times faster than that of terrigenous material.

Schimmelmann and Tegner (1990) and Schimmelmann and Kastner (1992) investigated the history of laminated sediments of the last 1000 yr on the basis of organic carbon contents, composition of reduced sulfur compounds, and stable carbon isotopes of bulk organic material. The diagenesis of sulfur compounds occurs mainly during the first 500 yr after deposition. Significant peaks in isotopic records correspond to historical El Niño events and strong storms.

Site 893 provides the opportunity to study the influences of longer-term climatic changes (glacial-interglacial cycles) on the sedimentary record of the Santa Barbara Basin. Sea-level changes control the transport mechanisms of terrestrial mineral and organic matter to the

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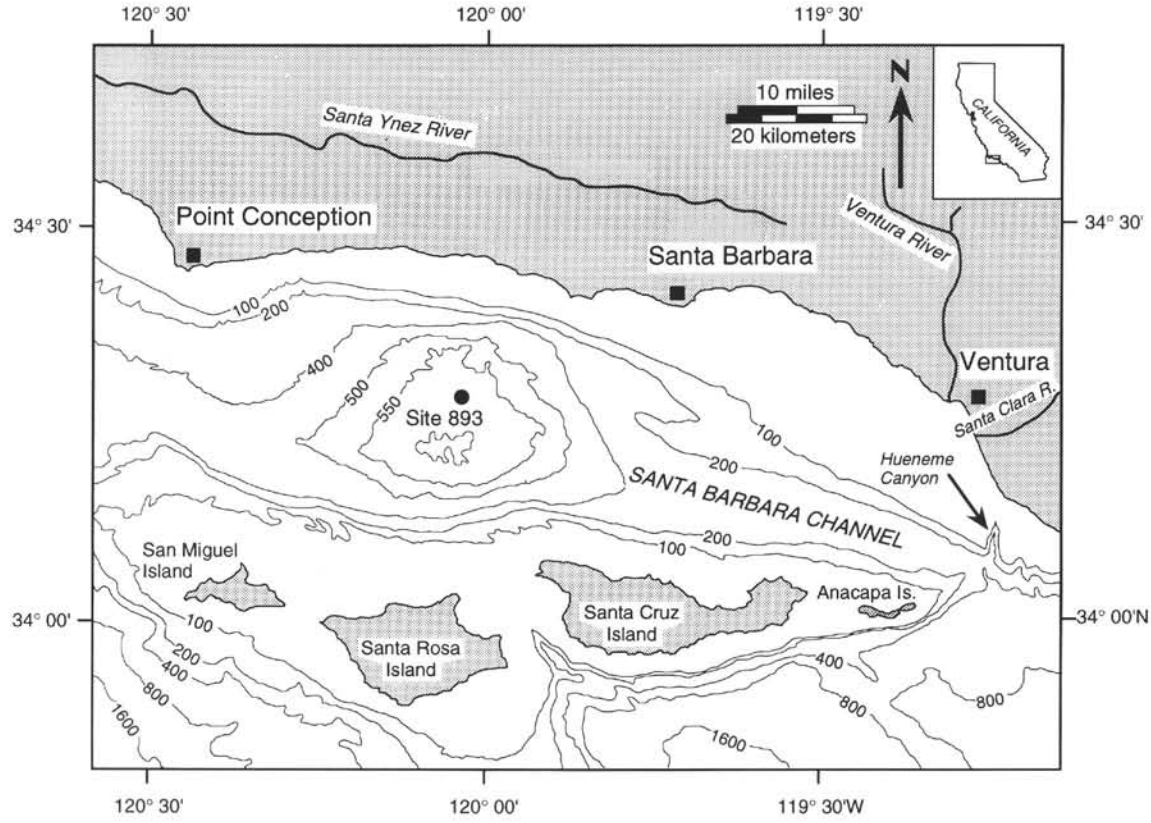

Figure 1. Map of the Santa Barbara Basin and location of Site 893 (from Kennett, Baldauf, et al., 1994).

central basin, and they may alter the marine primary productivity in the water column. Sea-level variations may also change the redox conditions at the sediment/water interface in the central Santa Barbara Basin, which greatly influence the rate of preservation of organic material and the development of benthic activities including the growth of bacterial mat communities.

This paper reports the preliminary results of a molecular study of lipid composition on a selected set of samples, using gas chromatographic (GC) and gas chromatographic/mass spectrometric (GC/MS) methods.

We focused our investigations on the following questions:

- What are the differences in molecular composition between laminated and homogeneous sediments in terms of provenance and preservation of organic matter, particularly with respect to the importance of bacterial organic matter?
- Are there similarities or differences in the lipid composition of sediments deposited under similar sea-level conditions (e.g., Holocene vs. isotopic Stage 5e)?
- Are there any biomarkers that are specific for particular paleoenvironmental (climatic) conditions in the Santa Barbara Basin?

The results are related to a high-resolution study of bulk organic matter characteristics that was performed by Stein and Rack (this volume).

EXPERIMENTAL METHODS

We investigated 26 core samples from Hole 893A (Fig. 2) of which 10 were selected for detailed studies of the molecular organic matter composition. After freeze-drying and grinding, the sediments were analyzed for their TOC, carbonate, and sulfur contents by combustion in a LECO CS-444 instrument. The release of hydrocarbons during temperature-programmed pyrolysis (Espitalié et al., 1977) was determined on a Rock-Eval II instrument (Geocom); results are presented as hydrogen indices (HI: mg hydrocarbons per g TOC). Solvent extractions were performed in a Soxhlet apparatus with dichloromethane plus 1% methanol over 48 hr.

Separation into fractions of different polarities was carried out on 80% of the total extract of each sample after addition of internal standards (squalane, erucic acid [n-$C_{22:1}$], 5α-androstan-17-one). The yield of each fraction was determined gravimetrically. Prior to separation, the hexane-insoluble fraction (asphaltenes) was precipitated.

The hexane-soluble portion was separated by medium-pressure liquid chromatography (MPLC; Radke et al., 1980) into fractions of aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds (NSO fraction). Subsequently, carboxylic acids were separated from the NSO fraction by using a column filled with KOH-impregnated silica gel (63–200 µm; a solution of 0.5 g KOH in 10 mL *iso*-propanol was added to 4 g silica gel). The nonacidic compounds were eluted from the column with 120 mL of dichloromethane. Following this, 120 mL of a solution of formic acid (2% in dichloromethane) transformed the potassium salts of the acids back to the original acids. The acid-free NSO fraction then was separated into ketones and alcohols by flash chromatography (Still et al., 1978) under a moderate overpressure of nitrogen. A 10-mm × 200-mm column was filled with 5 g silica gel 60 (40–63 µm, deactivated with 5% by weight of water) and washed with 50 mL of dichloromethane. Another 60 mL of dichloromethane was used to elute the fraction of ketones at a rate of two drops per second. The alcohols were removed from the column with 50 mL of a mixture of dichloromethane and methanol (10% by volume). For molecular studies, the acid fraction was methylated with diazomethane, and ketone and alcohol fractions

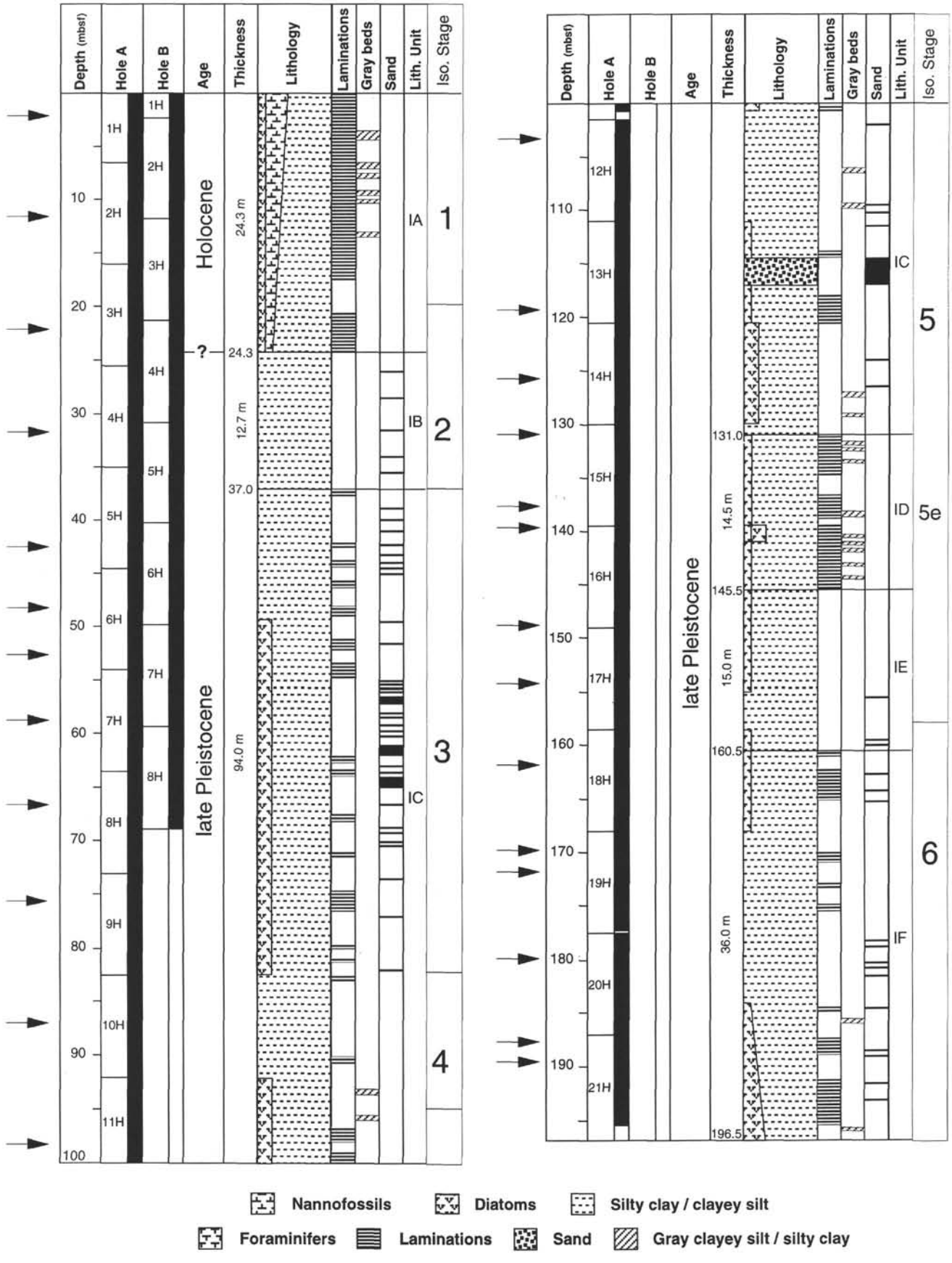

Figure 2. Lithostratigraphy of Holes 893A and 893B (from Kennett, Baldauf, et al., 1994). Arrows indicate origin of samples used for molecular organic geochemical bitumen analysis in this study.

Table 1. Bulk organic carbon data, carbonate contents, extract yields, U^k_{37} values, and void-corrected depths for Hole 893A sediments.

Core, section, interval (cm)	Depth* (mbsf)	Age (ka)	TOC (%)	$CaCO_3$ (%)	Total sulfur (%)	Hydrogen index (mg HC/g TOC)	Extract yield (mg/g TOC)	U^k_{37}/SST (°C)
146-893A-								
1H-1, 114–118	1.14	0.606	1.82	5.9	0.64		72	
2H-3, 109–113	10.51	6.371	1.82	9.3	1.45	123	49	
3H-4, 125–130	21.66	13.703	1.70	7.0	1.05		102	
4H-4, 142–146	30.74	19.854	1.75	10.4	0.33		84	
5H-5, 113–118	41.52	27.298	1.66	7.9	0.91	158	75	0.43/11.7
6H-3, 32–36	47.22	31.810	1.59	6.1	0.41		75	
6H-6, 43–48	51.56	34.933	1.38	13.2	0.73		79	
7H-5, 22–27	57.78	39.408	1.41	7.3	0.36	121	116	
8H-3, 75–80	65.64	45.064	1.41	6.7	0.10		161	
9H-2, 47–52	74.69	51.675	1.80	9.8	0.74		69	
10H-3, 65–70	86.00	61.213	1.12	6.1	0.10		114	
11H-4, 96–101	97.26	72.234	2.18	6.8	1.87	166	88	0.39/10.5
12H-2, 29–34	103.12	78.495	1.98	8.1	0.45		96	
13H-7, 131–135	119.36	93.223	1.93	3.6	1.11		81	
14H-4, 64–69	125.69	99.976	2.57	6.1	1.06	160	59	
15H-2, 77–82	131.96	106.675	2.03	5.7	0.93		69	
15H-6, 27–32	137.75	112.862	2.19	4.8	0.72	162	82	
16H-1, 55–59	139.91	115.170	3.18	8.2	0.81		66	
16H-7, 50–55	148.83	123.206	2.25	6.7	0.59		56	
17H-4, 70–75	154.24	125.759	1.73	13.2	1.32	192	69	
18H-3, 40–44	161.80	131.440	1.55	7.5	0.44		70	
19H-2, 45–50	169.86	138.699	1.69	8.5	0.80		70	
19H-3, 94–99	171.80	140.446	1.32	9.1	1.03	120	77	
20H-2, 108–112	179.92	147.759	1.38	9.7	0.23		81	
21H-1, 84–88	187.69	154.757	1.79	6.9	1.89	142	84	
21H-3, 7–12	189.62	156.495	1.47	8.3	1.22	157	78	0.41/11.1

Note: *Void-corrected depth from Merrill and Rack (this volume).

were silylated with trimethylsilyltrifluoroacetamide (MSTFA). Elemental sulfur, which elutes in the aliphatic hydrocarbon fraction, was removed by treatment with copper filings.

Gas chromatography was performed on a Hewlett Packard 5890 series II instrument equipped with a Gerstel temperature-programmed cold injection system and a fused silica capillary column (Column A, aliphatic hydrocarbons: length = 30 m, inner diameter = 0.25 mm, coated with SE-54, film thickness = 0.25 µm; Column B, polar fractions: length = 25 m, inner diameter = 0.22 mm, coated with siloxane-carborane copolymer, film thickness = 0.1 µm). Helium was used as the carrier gas, and the temperature was programmed from 60°C (2 min) to 300°C (50 min) at a rate of 3°C/min. For the determination of the U^k_{37}-alkenone index the temperature was programmed from 60°C (2 min) to 270°C at a rate of 10°C/min and then to 300°C at a rate of 1°C/min (final hold time). GC/MS studies were performed with the same type of gas chromatograph equipped with capillary Column A under the temperature conditions given above and coupled to a Finnigan SSQ 710 B mass spectrometer operated at 70 eV.

Compound identifications are based on comparisons of relative gas chromatographic retention times and mass spectra with those reported in the literature. Quantifications were performed relative to the amount of internal standards. Concentrations of alcohols (detected as TMS ethers) were calculated from their ratios to the injection standard behenic acid methyl ester (BAME).

RESULTS AND DISCUSSION

Bulk Characteristics

The bulk data of elemental analysis, Rock-Eval pyrolysis, and extract yields are summarized in Table 1. The table also includes the void-corrected depth for the samples studied (Merrill and Rack, this volume) and the interpolated absolute ages based on AMS ^{14}C chronology and stable-oxygen-isotope stratigraphy (Ingram and Kennett, this volume).

In general, TOC values vary between 1.3% and 3.2% (percent by weight of dry sediment) with the highest concentration in a laminated sample at 139.91 meters below seafloor (mbsf) (Sample 146-893A-16H-1, 55–59 cm), near the boundary of isotopic Stages 5e and 5d. In view of the elevated organic carbon contents, the hydrogen indices are conspicuously low, with values varying between 120 and 192 mg HC/g TOC. However, the TOC concentrations and hydrogen indices determined in this study fit well into the high-resolution concentration profiles reported and discussed in detail by Stein and Rack (this volume).

Total sulfur (TS) contents range from 0.1% to 1.9%, and there is no evidence for a trend in concentration profile that corresponds to other bulk organic geochemical or lithologic characteristics. At this stage, TS data are difficult to interpret without any knowledge about the chemical state of the sulfur, which may occur as sulfide, sulfate, elemental sulfur, and bound into organic matter. The carbonate contents (reported as percentage of calcium carbonate) generally range from 5% to 10% in most of the samples.

Most of the extract yields range between 60 and 100 mg/g TOC. Some higher values (116, 161, and 114 mg/g TOC, respectively) were observed for three samples between 57.78 and 86.00 mbsf (Samples 146-893A-7H-5, 22–27 cm; 146-893A-8H-3, 75–80 cm; and 146-893A-10H-3, 65–70 cm). All reported extract yields include average amounts of about 2.5 mg (≈6 mg/g TOC) of elemental sulfur, which is soluble in the organic solvent used. For a recent or subrecent sediment, typical values of the extract yields are about 15 mg/g TOC or less (e.g., data obtained for deep-sea sediments from the California Borderland, recovered during Deep Sea Drilling Project (DSDP) Leg 63; Rullkötter et al., 1981). High bacterial activity may result in elevated extract yields, as is known from lacustrine systems like the Messel oil shale (Rullkötter et al., 1988). Otherwise, elevated extract yields may indicate the presence of migrated oil.

The relative distributions of the gross chromatographic fractions, obtained by separation of the total extracts, are presented in Figure 3. This figure shows the extract composition as percentages of each fraction normalized to the total extract. Each of the extracts is dominated by the NSO fraction, which ranges from 30% to 63%. The portion of asphaltenes varies between 13% and 38% of the total extract. Laminated sediments tend to contain slightly more asphaltenes than nonlaminated sediments. The aliphatic hydrocarbons represent 5% to 10% of the total extracts, whereas the amount of aromatic hydrocarbons varies from 1% to 4% with a trend of slight increase with depth.

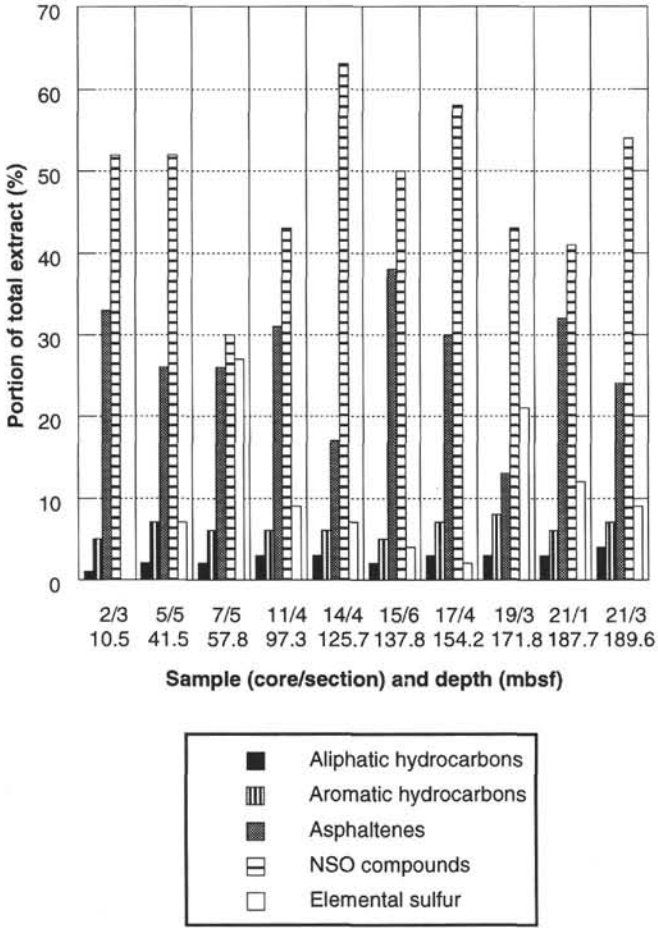

Figure 3. Yields of gross fractionation of total extracts of selected samples.

Elemental sulfur was present in all samples studied so far. The content varied between 2% and 27% with the highest percentage observed in Sample 146-893A-7H-5, 22–27 cm. In Sample 146-893A-2H-3, 109–113 cm, the amount of elemental sulfur was below the gravimetric detection limit. With the exception mentioned for the asphaltenes, there is no evidence for a significant relationship between bulk extract composition and lithology.

Molecular Investigations

Aliphatic Hydrocarbons

Figure 4 shows the gas chromatogram of the aliphatic hydrocarbon fraction of Sample 146-893A-5H-5, 113–118 cm, which is representative of the gas chromatograms of all investigated aliphatic hydrocarbon fractions. A major unresolved complex mixture (UCM) is common to all gas chromatograms, indicating bacterial degradation of hydrocarbons (Milner et al., 1977). The *n*-alkane distribution patterns are very similar for all samples studied and are typical for a supply from cuticular waxes of higher land plants (Eglinton and Hamilton, 1967). The *n*-alkanes maximize at n-$C_{29}H_{60}$ in nine of the samples and at n-$C_{31}H_{64}$ in Sample 146-893A-17H-4, 70–75 cm. Carbon preference index (CPI) values (Bray and Evans, 1961; Hunt, 1979) of *n*-alkanes in the carbon atom number range from 25 to 33 vary between 2.9 and 5.8.

Two phytene double bond isomers, phyt-1-ene and phyt-2-ene, were observed in all investigated hydrocarbon fractions. The summarized phytene concentration ranges from 2.5 to 15 µg/g TOC, with

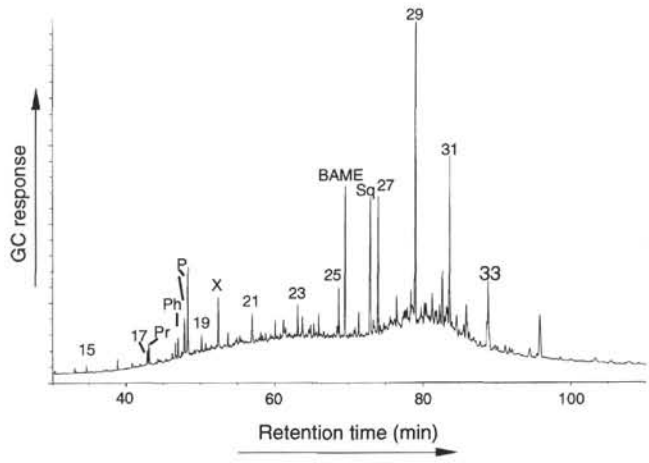

Figure 4. Gas chromatogram of the aliphatic hydrocarbon fraction of Sample 146-893A-11H-4, 96–101 cm. Odd-numbered *n*-alkanes are marked with their carbon numbers. Also marked are the standards used for quantification (BAME = behenic acid methyl ester; Sq = squalane). Pr = pristane, Ph = phytane, P = phyt-1-ene and phyt-2-ene, X = contaminant.

slightly higher concentrations of phyt-1-ene in each sample. They were identified by comparison of their mass spectra with literature data (Urbach and Stark, 1975) and relative retention times (Ikan et al., 1975). Most likely, these phytenes are diagenetic conversion products of phytol (Volkman and Maxwell, 1986; Didyk et al., 1978), which is derived from planktonic chlorophyll *a* by ester cleavage; methanogenic bacteria may be an additional source of phytenes (Brassell et al., 1981).

Except for the phytenes, compounds of autochthonous origin are present only in trace amounts in the aliphatic hydrocarbon fraction. Examples are series of sterenes and steradienes, which are derived from steroid alcohols by diagenetic transformations (de Leeuw et al., 1989; see also "Steroidal Alcohols" section in this paper for sources of steroid compounds) and from pentacyclic triterpenes like bacterial fernenes and diploptene derived from bacteria, respectively (Ourisson et al., 1979; Howard, 1980; Brassell et al., 1981; Brassell and Eglinton, 1983). However, the fact that sterenes and steradienes are present only in trace amounts emphasizes the very early diagenetic stage of the organic material. Therefore, the analysis of polar compounds such as fatty acids, alcohols, and ketones is appropriate for a more detailed assessment of origin and paleoenvironmental conditions of deposition of that part of the organic matter that is represented by the extractable fraction.

Migrated Hydrocarbons

An additional organic matter source of Santa Barbara Basin sediments is documented especially in the aliphatic hydrocarbon fraction by the presence of petroleum hydrocarbons as has been observed earlier for a wide range of shallow sediments in the California Bight by Simoneit and Kaplan (1980). All investigated aliphatic hydrocarbon fractions of sediments from Site 893 contain compound series that typically occur in sediments with mature organic matter or crude oil. The petroleum-type compound series comprise steranes and diasteranes as mixtures of stereoisomers characteristic of thermally matured organic matter, of tricyclic terpanes, and of hopanes with the thermally most stable 17α(H),21ß(H) configuration (Seifert and Moldowan, 1980; Simoneit and Kaplan, 1980). Compound identification is based on relative retention times and comparison of mass spectra with those reported in the literature (e.g., Peters and Moldowan, 1993; Rullkötter et al., 1984, 1987).

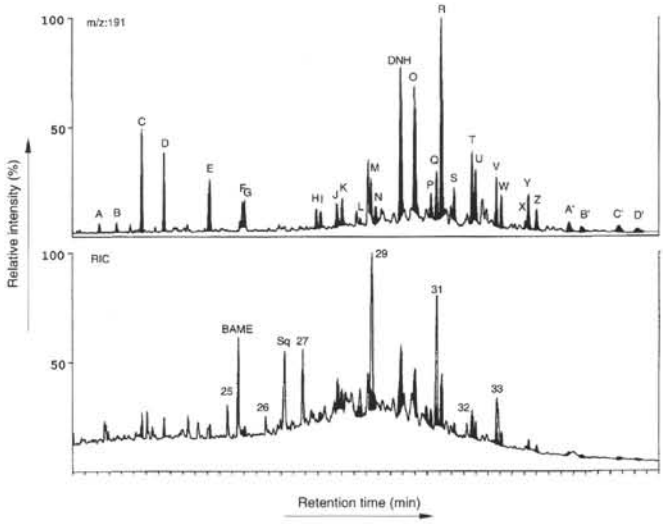

Figure 5. Reconstructed ion chromatogram and mass chromatogram of fragment m/z 191 from GC/MS analysis of Sample 146-893A-21H-3, 7–12 cm. The petroleum-type terpanes are shown in black. Compounds identified are listed in Table 2. The *n*-alkanes (numbers) and the internal standard (SQ = squalane) are marked in the RIC trace.

As an example, Figure 5 shows the reconstructed ion chromatogram (RIC) together with the mass chromatogram of fragment m/z 191 for the aliphatic hydrocarbon fraction of Sample 146-893A-21H-3, 7–12 cm. This mass spectrometric fragment is characteristic of tri- and pentacyclic terpanes. Figure 5 illustrates the dominance of petroleum-derived hopanes and tricyclic terpanes among the polycyclic saturated hydrocarbons (marked components are listed in Table 2). All investigated hydrocarbon fractions contain 28,30-*dinor*-hopane, which is a characteristic component in oils from the Californian

Table 2. Terpenoid compounds from migrated oil detected in the aliphatic hydrocarbon fractions of Santa Barbara Basin sediments.*

Symbol (Fig. 5)	Compound
A	C_{22}-tricyclic terpane
B	C_{23}-tricyclic terpane
C	C_{23}-tricyclic terpane
D	C_{24}-tricyclic terpane
E	C_{25}-tricyclic terpane
F	C_{26}-tricyclic terpane
G	C_{26}-tricyclic terpane
H	C_{28}-tricyclic terpane
I	C_{28}-tricyclic terpane
J	C_{29}-tricyclic terpane
K	C_{29}-tricyclic terpane
L	25, 28, 30-*trinor*-17α(H)-hopane
M	22, 29, 30-*trinor*-17α(H)-hopane
N	C_{30}-tricyclic terpane
DNH	28, 30-*dinor*-17α(H)-hopane
O	30-*nor*-17α(H), 21ß(H)-hopane
P	30-*nor*-moretane
Q	18α(H)-oleanane
R	17α(H), 21ß(H)-hopane
S	Moretane
T	17α(H), 21ß(H)-(22S)-*homo*-hopane
U	17α(H), 21ß(H)-(22R)-*homo*-hopane
V	17α(H), 21ß(H)-(22S)-*dihomo*-hopane
W	17α(H), 21ß(H)-(22R)-*dihomo*-hopane
X	17ß(H), 21ß(H)-*homo*-hopane
Y	17α(H), 21ß(H)-(22S)-*trihomo*-hopane
Z	17α(H), 21ß(H)-(22R)-*trihomo*-hopane
A′	17α(H), 21ß(H)-(22S)-*tetrakishomo*-hopane
B′	17α(H), 21ß(H)-(22R)-*tetrakishomo*-hopane
C′	17α(H), 21ß(H)-(22S)-*pentakishomo*-hopane
D′	17α(H), 21ß(H)-(22R)-*pentakishomo*-hopane

Note: *cf. Figure 5.

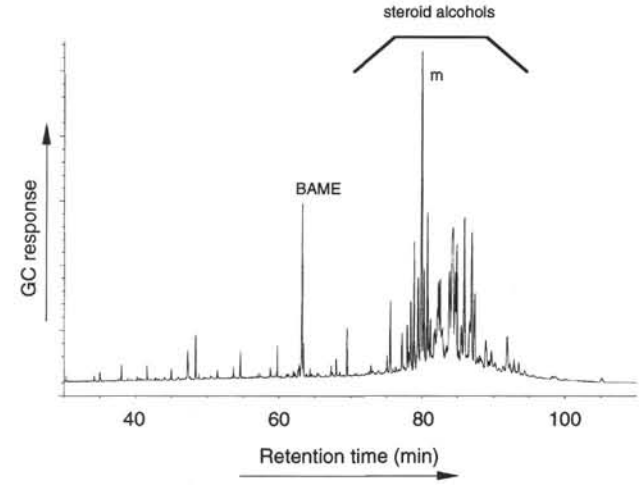

Figure 6. Gas chromatogram of the alcohol fraction of the nonlaminated Sample 146-893A-21H-3, 7–12 cm. The most abundant compound, 5α(H)-cholestan-3ß-ol (m) and the injection standard (BAME), are labeled.

Monterey Formation (Curiale et al., 1985) and is common in surface sediments of the California Bight as an indicator of weathered petroleum-type material (Simoneit and Kaplan, 1980; McEvoy et al., 1981; Rullkötter et al., 1981; Simoneit and Mazurek, 1981). Its concentration in the Santa Barbara Basin sediments from Hole 893A ranges from 10 to 42 µg/g TOC. Considering that the offshore California area is a major petroleum generation and production area with Monterey Formation source rocks outcropping on the coast and in the California mainland and with numerous petroleum seeps onshore and offshore, it is reasonable to assume that the observed petroleum hydrocarbons were supplied to the Santa Barbara Basin as part of eroded material. It is also possible—but considered less likely—that petroleum has locally migrated upward from fractured Monterey rocks to the subsurface and have impregnated the shallower Santa Barbara Basin sediments. The *n*-alkanes apparently were microbially degraded, so the unresolved complex mixtures and the petroleum-type polycyclic hydrocarbons are the only evidence for the supply of mature organic matter in the aliphatic hydrocarbon fractions.

n-*Alcohols*

A typical gas chromatogram of the alcohol fraction of a nonlaminated sediment sample (146-893A-21H-3, 7–12 cm), which demonstrates the predominance of a complex mixture of steroidal alcohols in this fraction, is presented in Figure 6. All alcohols were analyzed as their TMS ethers. Long-chain *n*-alcohols are not present in this fraction. In the liquid chromatographic separation procedure used, long-chain *n*-alcohols (with more than 20 carbon atoms) eluted in the ketone fraction whereas the more polar *n*-alcohols with less than 20 carbon atoms eluted in the alcohol fraction. However, in all investigated alcohol fractions, *n*-alcohols with less than 20 carbon atoms are only present in minor amounts with concentrations less than 1 µg/g TOC. The long-chain *n*-alcohols show a marked preference of even carbon atom number homologs. All odd-numbered *n*-alcohol concentrations are near the detection limit. Figure 7 compares the long-chain *n*-alcohol concentrations of Samples 146-893A-5H-5, 113–118 cm (nonlaminated), 146-893A-11H-4, 96–101 cm (laminated), and 146-893A-21H-3, 7–12 cm (nonlaminated). The most abundant *n*-alcohol in the nonlaminated samples is *n*-tetracosanol, followed by *n*-octacosanol, whereas the situation in the laminated sample is reversed. The *n*-alcohol concentrations of the two nonlaminated samples are

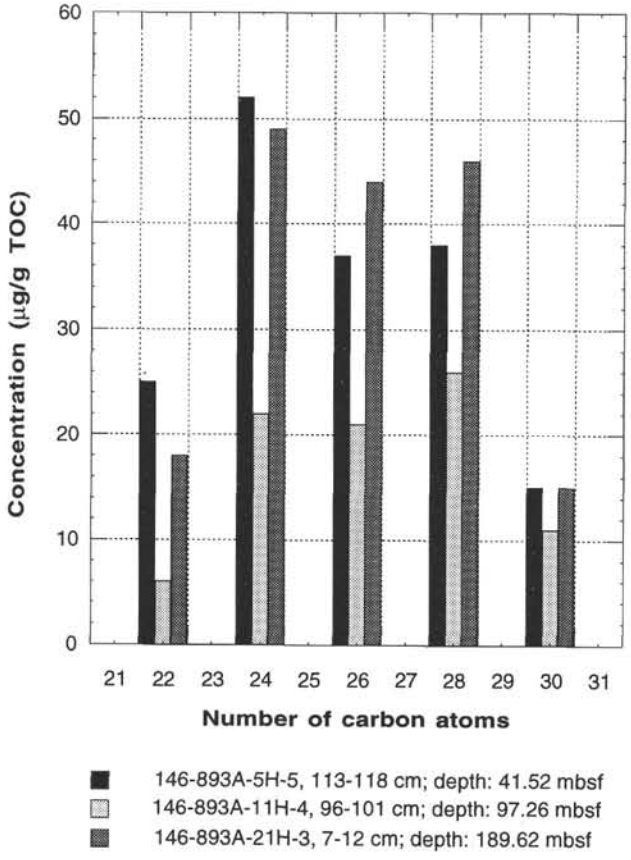

Figure 7. Distribution and concentrations of long-chain *n*-alcohols (C_{22} to C_{30}) in Samples 146-893A-5H-5, 113–118 cm (nonlaminated); 146-893A-11H-4, 96–101 cm (laminated); and 146-893A-21H-3, 7–12 cm (nonlaminated).

about twice as high as those in the laminated sample, probably indicating a reduced terrigenous organic matter supply during sea-level highstands.

Steroidal Alcohols

In Figure 8, the reconstructed ion chromatograms show the elution range of steroid alcohols for three selected Samples 146-893A-5H-5, 113–118 cm (nonlaminated); 146-893A-11H-4, 96–101 cm (laminated); and 146-893A-21H-3, 7–12 cm (nonlaminated). Compound identification, as compiled in Table 3, is based on relative retention times and comparison with mass spectra from the literature (Budzikiewicz, 1972; Brassell, 1980; McEvoy, 1983; Wardroper, 1979; Wyllie and Djerassi, 1968). Quantification of major components is based on FID response in the gas chromatograms. We identified about 40 different steroid alcohols with carbon numbers ranging from 26 to 30 and different numbers and positions of double bonds as well as different side-chain substituents at C-24. This complexity is characteristic for a steroid origin from a variety of marine organisms (Wardroper et al., 1978; Brassell, 1980). Except for dinosterol, 4-methylsterols are present only in minor amounts. The sterol distributions in the Santa Barbara Basin samples are largely similar to the distribution reported for a Quaternary sample from the nearby DSDP Site 467, San Miguel Gap (McEvoy et al., 1981).

With a few exceptions, the identified compounds are present in each investigated sample. Nevertheless, the samples show considerable differences in steroid distribution patterns. The concentrations of

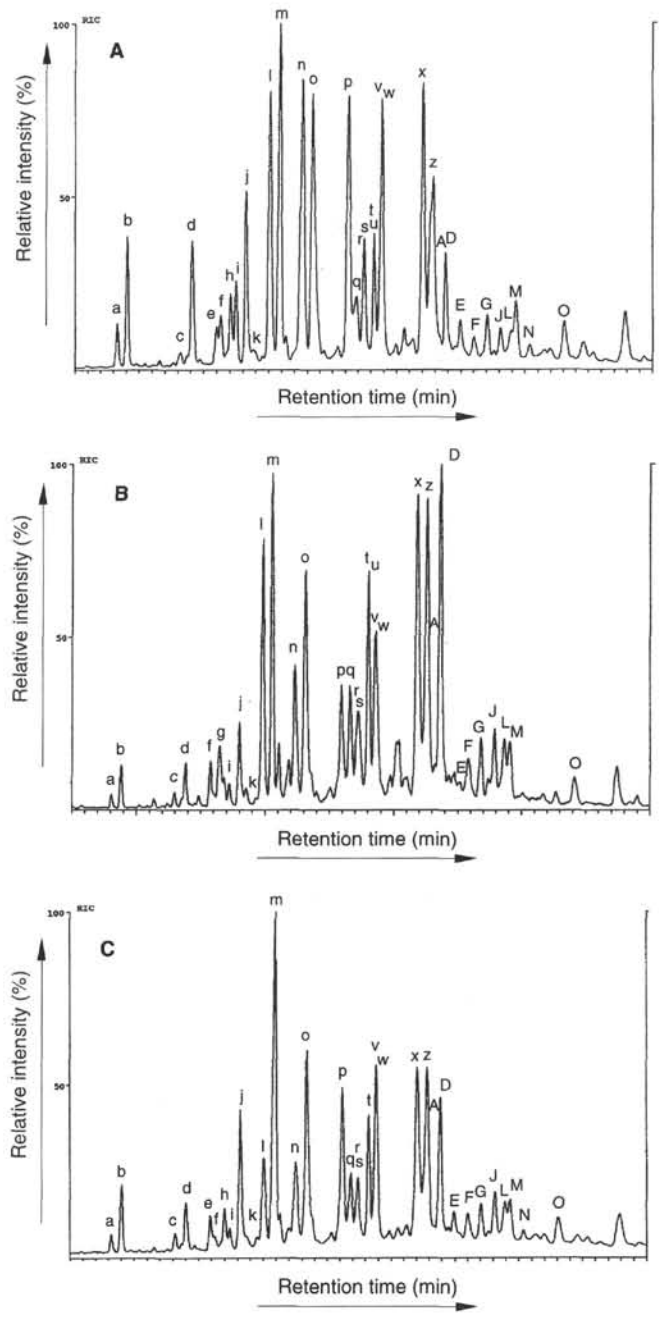

Figure 8. Partial reconstructed ion chromatograms of the alcohol fractions of three selected samples showing the elution range of steroid alcohols. The labeled identified compounds are listed in Table 3. **A.** Sample 146-893A-5H-5, 113–118 cm (nonlaminated). **B.** Sample 146-893A-11H-4, 96–101 cm (laminated). **C.** Sample 146-893A-21H-3, 7–12 cm (nonlaminated).

individual components in the laminated Sample 146-893A-11H-4, 96–101 cm, are noticeably lower than those in the two nonlaminated samples. In the laminated sample, dinosterol is the major steroidal alcohol, corresponding to the present-day situation in surface-near sediments in the center of the basin as reported by Kennedy and Brassell (1992b). Dinosterol is well known as a biosynthetic product of dinoflagellates (Boon et al., 1979), although in more recent studies other marine sources have been identified (Volkman et al., 1993).

Table 3. Steroid alcohols identified in selected samples, Hole 893A.*

Symbol (Fig. 8)	Compound	Concentration (µg/g TOC) 5H-5	11H-4	21H-3
a	24-*nor*-cholesta-5, 22(E)-dien-3ß-ol	5.3	1.1	4.9
b	24-*nor*-5α(H)-cholesten-22(E)-3ß-ol	22.2	6.8	20.4
c	24-*nor*-5α(H)-cholestan-3ß-ol	3.2	1.7	8.2
d	5ß(H)-cholestan-3ß-ol + 24-*nor*-cholesta-4, 22-dien-3-one ?			
e	5ß(H)-cholestan-3-ol	8.9	4.6	16.5
f	27-*nor*-24-methylcholesta-5, 22(E)-dien-3ß-ol** ?	11.4	1.0	5.9
g	Unknown compound (only present in Sample 146-893A-11H-4, 96–101 cm)			
h	27-*nor*-24-methyl-5a(H)-cholest-22(E)-en-3ß-ol** ?	15.9	3.8	15.6
i	Cholesta-5, 22(E)-dien-3ß-ol	34.9	11.7	23.6
j	5α(H)-cholest-22(E)-en-3ß-ol	38.0	9.5	48.8
k	Unknown C_{27}-stanol			
l	Cholest-5-en-3ß-ol	63.6	29.5	43.5
m	5α(H)-cholestan-3ß-ol	74.7	33.5	138.9
n	24-methylcholesta-5, 22-dien-3ß-ol	68.2	39.9	36.7
o	24-methyl-5α(H)-cholest-22(E)-en-3ß-ol	48.9	26.6	62.7
p	Unknown C_{27}-cholestenol			
q	24-methyl-5α(H)-cholest-24(28)-en-3ß-ol possibly coelutes with 24-methylcholest-5-en-3ß-ol			
r	24-methyl-5α(H)-cholestan-3ß-ol	27.2	9.1	26.6
s	23, 24-dimethylcholesta-5, 22-dien-3ß-ol			
t	23, 24-dimethyl-5α(H)-cholest-22(E)-en-3ß-ol			
u	+ 24-ethylcholesta-5, 22(E)-dien-3ß-ol			
v	24-methylcholesta-4, 22-dien-3-one			
w	+ 24-ethyl-5α(H)-cholest-22(E)-en-3ß-ol			
x	24-ethylcholest-5-en-3ß-ol	62.7	31.5	73.0
y	+ 23, 24-dimethyl-5α(H)-cholestan-3ß-ol (in trace amounts)			
z	Unknown C_{30}-steratrienol			
A	24-ethyl-5α(H)-cholestan-3ß-ol			
B	+ 24-ethylcholesta-5, 24(28)-dien-3ß-ol			
C	+ 4, 24-dimethyl-5α(H)-cholestan-3ß-ol			
D	4, 23, 24-trimethylcholest-22-en-3ß-ol (dinosterol)	19.3	42.4	50.8
E	24-propylcholest-5, 24-dien-3ß-ol			
F	24-ethyl-5α(H)-cholest-7-en-3ß-ol	3.8	7.9	10.0
G	24-propylcholest-5, 24(28)-dien-3ß-ol			
H	+ C_{30}-4-methylstenol			
I	+ 4, 23, 24-trimethyl-5α(H)-cholest-7-en-3ß-ol			
J	Unknown C_{30}-steradienol			
K	+ 4, 23, 24-trimethyl-5α(H)-cholestan-3ß-ol			
L	4, 23, 24-trimethyl-5α(H)-cholestan-3ß-ol, C-23 or C-24-epimer of K ?			
M	Unknown C_{29}-sterenone			
N	Unknown C_{30}-steradienol			
O	Unknown compound			

Notes: *cf. Figure 8. **27-*nor*-24-methyl-sterol isomers were reported by McEvoy (1983). Question marks indicate tentative assignments. Absolute concentrations are included where quantification was possible.

In contrast to this, the two nonlaminated samples contain 5α(H)-cholestan-3ß-ol (**m**) as the most abundant compound. This compound is presumably derived, at least in part, from diagenetic reduction of cholesterol (e.g., Mackenzie et al., 1982), but direct formation by marine organisms has also been described in the literature (red algae: Chardon-Loriaux et al., 1976; sponges: Erdman and Thomson, 1972; benthic organisms: Ballantine et al., 1981). In the two shallower samples, cholesterol (**l**) is present in a concentration similar to that of the saturated analog, 5α(H)-cholestan-3ß-ol (**m**), whereas in the deepest sample the concentration of compound **m** is 3 times higher than that of compound **l**. This probably indicates the progress of diagenetic transformation of cholesterol by microbial reduction. Other typical diagenetic reactions of steroid alcohols (e.g., the formation of hydrocarbons by loss of the hydroxyl group at C-3) are of minor importance in the investigated samples as it is indicated by the very low concentrations of sterenes in the aliphatic hydrocarbon fractions.

A more general way of comparing the steroid composition of different samples is to investigate their carbon number distribution. This approach has been introduced by Huang and Meinschein (1976, 1979), who used this method to determine the source of organic matter in near-surface sediments. It is based on the idea that C_{29} steroid alcohols are derived mainly from terrestrial higher plants. In fact, this is valid for 24-ethylcholest-5-en-3ß-ol, which is the main sterol in higher plants, but exceptions have been noted (e.g., for cyanobacteria; Volkman, 1986). In the case of the very complex steroid patterns of the Santa Barbara Basin sediments, we extended this approach to include mainly marine-derived C_{26} and C_{30} steroid alcohols in addition to the C_{27}–C_{29} components. The results for three samples are reported in Figure 9. For this purpose, semiquantitative calculations, based on the RIC signal intensity relative to a known steroid concentration (5α(H)-cholestan-3ß-ol (**m**), from GC-FID measurements), were performed to obtain the summed concentrations for each carbon atom number. Both nonlaminated samples are characterized by similar carbon number distributions with a maximum at C_{27}, whereas the

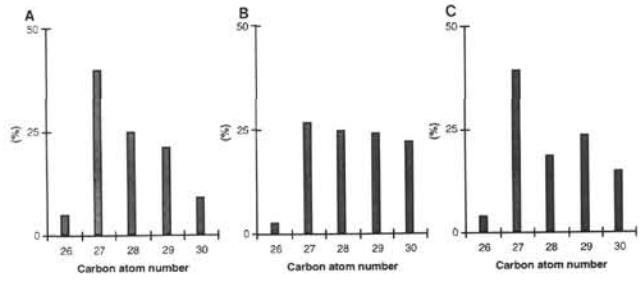

Figure 9. Carbon number distribution of steroid alcohols of three selected samples. The percentages are normalized to the total amount of steroid alcohols. Quantitative data were obtained by comparison of peak intensity relative to a known steroid concentration in the RIC. **A.** Sample 146-893A-5H-5, 113–118 cm (nonlaminated). **B.** Sample 146-893A-11H-4, 96–101 cm (laminated). **C.** Sample 146-893A-21H-3, 7–12 cm (nonlaminated).

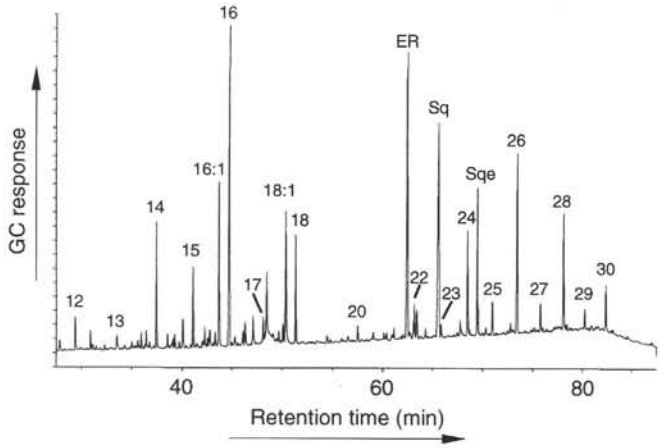

Figure 10. Gas chromatogram of the fatty acid fraction of Sample 146-893A-21H-3, 7–12 cm. The *n*-fatty acids are labeled with their carbon atom number. In addition, the internal standard (ER = erucic acid), the injection standard (Sq = squalane), and squalene (Sqe) are marked. The occurrence of squalene in this fraction is thought to result from chemical transformation of a more polar precursor during separation.

distribution of the laminated sample is characterized by a relatively uniform carbon number distribution from C_{27} to C_{30} with a weak maximum at C_{27}. An evaluation of steroid alcohol sources in terms of marine vs. terrestrial origin, based on the carbon number distributions, does not show significant differences among the samples, because the relative abundance of the predominantly terrigenous C_{29} sterols shows little variation. Thus, the different distributions most likely represent different assemblages of marine source organisms in the Santa Barbara Basin.

The summarized sterol concentration in the laminated Sample 146-893A-11H-4, 96–101 cm, is noticeably lower (360 µg/g TOC) than that of the two nonlaminated Samples 146-893A-5H-5, 113–118 cm (640 µg/g TOC) and 146-893A-21H-03, 7–12 cm (850 µg/g TOC). The C_{30} steroids, which are of a marine origin, have a significantly higher concentration in the laminated sample.

n-*Fatty Acids*

A gas chromatogram of a representative fatty acid fraction (Sample 146-893A-21H-3, 7–12 cm) is shown in Figure 10. In all investigated samples, we observed a bimodal distribution of *n*-fatty acids with a strong predominance of even carbon number homologs, maximized at C_{16} and C_{26}. Similar fatty acid distributions were observed in a study of lipid composition (Simoneit and Mazurek, 1981) in two Quaternary samples from the nearby Site 467. Monounsaturated acids occur in the carbon number range from 14 to 18, with a maximum at $C_{16:1}$. The long-chain fatty acids ($\geq C_{22}$) reflect a contribution of terrigenous higher plants (Kolattukudy, 1976) whereas the saturated and unsaturated fatty acids in the lower carbon number range are presumably derived mainly from algae (Cranwell, 1974). Figure 11 displays the fatty acid distribution and the concentrations of individual compounds, normalized to TOC, for three selected samples (146-893A-5H-5, 113–118 cm, nonlaminated; 146-893A-11H-4, 96–101 cm, laminated; and 146-893A-21H-3, 7–12 cm, nonlaminated). In these samples, n-$C_{16:0}$ is the major compound in the acid fraction with concentrations ranging from 61 to 81 µg/g TOC, followed by n-$C_{26:0}$ in the nonlaminated Samples 146-893A-5H-5, 113–118 cm, and 146-893A-21H-3, 7–12 cm, and n-$C_{16:1}$ in the laminated Sample 146-893A-11H-4, 96–101 cm. In contrast to the nonlaminated samples, the latter sample contains higher plant-derived long-chain fatty acids in lower concentrations (concentration of n-$C_{26:0}$: 21 µg/g TOC vs. 59 and 32 µg/g TOC in the nonlaminated samples). This is similar to the situation observed for the concentrations of higher plant-derived *n*-alcohols and of sterols.

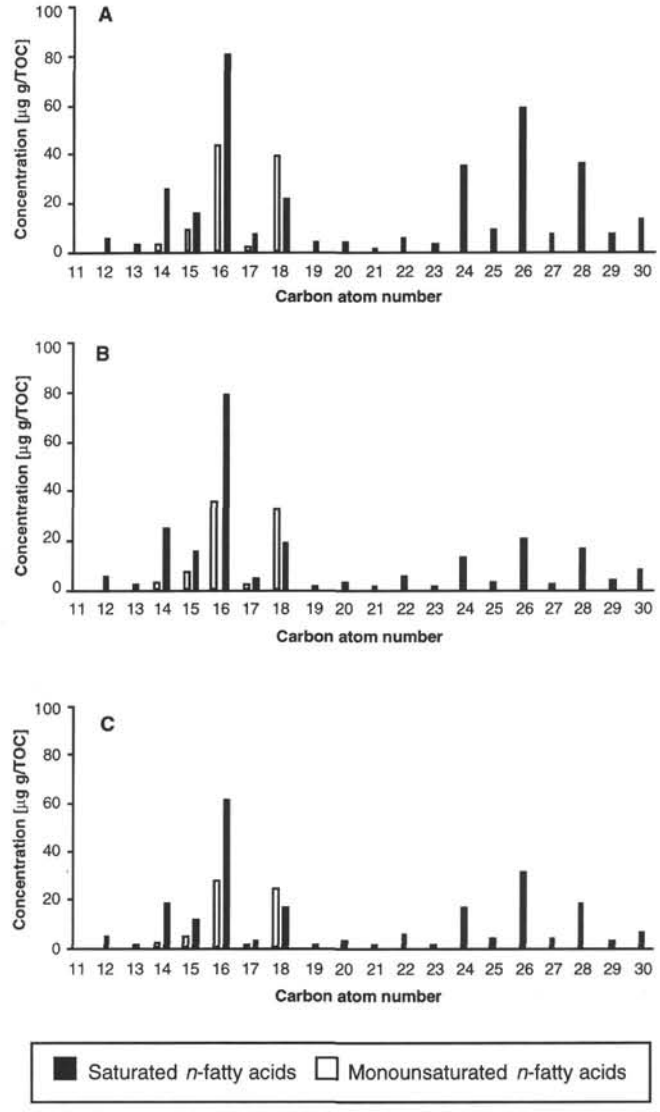

Figure 11. Distribution of saturated and monounsaturated *n*-fatty acids in three selected samples. **A.** Sample 146-893A-5H-5, 113–118 cm (nonlaminated). **B.** Sample 146-893A-11H-4, 96–101 cm (laminated). **C.** Sample 146-893A-21H-3, 7–12 cm (nonlaminated).

Ketones

We restricted our preliminary investigation of selected ketone fractions to the determination of the alkenone unsaturation index (U^{k}_{37}), which allows the calculation of proximate paleo-sea-surface temperatures (SST, Brassell et al., 1986; Prahl and Wakeham, 1987; Prahl et al., 1988). The values are reported in Table 1. In the sediments from Hole 893A, $C_{37:3}$ and $C_{37:2}$ alkenones were detected in low concentrations in the range of 2 to 5 µg/g TOC for the sum of both compounds. This is in contrast to results of Kennedy and Brassell (1992b), who investigated near-surface sediments of the 20th century from the central Santa Barbara Basin. In their study, the C_{37} alkenone concentrations are between one and two orders of magnitude higher

than ours although the concentrations of selected steroid alcohols were at similar levels. This may indicate a selective degradation of the unsaturated long-chain alkenones or a significant increase of the biomass of main producers, especially the coccolithophorid *Emiliania huxleyi* (Marlowe et al., 1984).

Using the equation of Prahl and Wakeham (1987), the U^{k}_{37} data in Table 1 result in estimated SST values of 10.5 to 11.7°C, with the lowest temperature in the laminated Sample 146-893A-11H-4, 96–101 cm. Averaged alkenone SST values for the Santa Barbara Basin based on sediments of this century as determined by Kennedy and Brassell (1992b) were just below 14°C.

CONCLUSIONS

Sediments in the Santa Barbara Basin, spanning the age range of the last 150,000 yr, are enriched in organic carbon. This reflects an intense primary marine bioproductivity as well as the supply of higher land-plant debris from the neighboring continent and of mature organic matter from the erosion of Monterey Formation petroleum source rocks or oil seeps. Local oil migration from greater depths cannot be excluded but is considered less likely. Relatively low hydrogen indices are consistent with a major fraction of refractory organic matter in the sediments, which may be due to oxidation of the terrigenous organic matter during transport and/or to extensive microbial reworking after deposition of marine and terrigenous organic matter. Elevated total sulfur contents and free elemental sulfur in the extracts indicate that the sediments were reducing with intense microbial sulfate reduction ongoing. Abundant methane in the cores shows that the microbial system extended into the methanogenesis zone. Thus, although the depositional conditions obviously were favorable for organic matter preservation throughout the time span covered, postdepositional microbial activity is likely to have converted a major portion of the labile (marine) organic matter into more refractory material.

The aliphatic hydrocarbon fractions of all sediments studied on the molecular organic matter level show clear indications of the presence of mature hydrocarbons that were bacterially altered either before or after impregnation of the shallow sediments. The distribution pattern of the pentacyclic triterpanes indicates that the migrated hydrocarbons were thermally generated in the Miocene Monterey Formation, which is an active petroleum source rock in this area. The aliphatic hydrocarbon fractions represent only a small amount of the extractable organic matter, but as common for biodegraded oils there will also be a significant amount of this type of allochthonous organic matter in the more polar extract fractions (NSO fraction, asphaltenes). Because these compounds are difficult to identify on a molecular level, it is difficult to estimate the total amount of biodegraded petroleum-type material in the Santa Barbara Basin sediments at Site 893. The high total extract yields may result both from this petroleum fraction and the intense activity of bacteria probably also thriving on the autochthonous primary marine organic matter.

Molecular indicators for the presence of terrigenous organic matter were found in all extract fractions. They range from long-chain *n*-alkanes to fatty acids and alcohols with similarly long straight chains. The C_{29} steroids may at least in part also be derived from terrestrial sources.

The alcohol fractions are dominated by sterols and stanols, most of which likely originated from the remnants of marine organisms. Dinosterol, probably from dinoflagellates as the major source, is the most abundant sterol in the laminated sample studied but occurs together with a series of steroids of similarly high concentrations. In the two nonlaminated samples studied so far, cholestan-3ß-ol is the most abundant single component, and dinosterol has a low relative concentration. This may indicate a change of primary productivity pattern with time, but this will have to be substantiated in the subsequent analysis of a greater number of samples.

Concentrations of long-chain alkenones in the Hole 893A sediments are much lower than those in surface sediments covering the 20th century. This again may reflect a change in primary productivity pattern (i.e., prymnesiophytes are more abundant in the most recent times), or a diagenetic destruction of these compounds. Because the double-bond homology is known not to change by this process, the determination of paleo-sea-surface temperatures should still be valid. The values determined for three samples show little variation with time, but temperatures calculated this way are 2°–3°C lower than those determined for surface sediments. The significance of this difference is not clear at this moment.

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REFERENCES

Ballantine, J.A., Lavis, A., and Morris, R.J., 1981. Marine sterols, XV. Sterols of some oceanic holothurians. *J. Exp. Mar. Biol. Ecol.*, 53:89–103.

Bernhard, J.M., and Reimers, C.E., 1991. Benthic foraminiferal population fluctuations related to anoxia: Santa Barbara basin. *Biogeochemistry*, 15:127–149.

Boon, J.J., Rijpstra, W.I.C., de Lange, F., de Leeuw, J.W., Yoshioka, M., and Shimizu, Y., 1979. Black sea sterol—a molecular fossil for dinoflagellate blooms. *Nature*, 277:125–127.

Brassell, S.C., 1980. The lipids of deep sea sediments: their origin and fate in the Japan Trench [Ph.D. dissert.]. Univ. Bristol.

Brassell, S.C., and Eglinton, G., 1983. Steroids and triterpenoids in deep-sea sediments as environmental and diagenetic indicators. *In* Bjorøy, M., et al. (Eds.), *Advances in Organic Geochemistry 1981:* Chichester (Wiley), 684–697.

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., and Sarnthein, M., 1986. Molecular stratigraphy: a new tool for climatic assessment. *Nature*, 320:129–133.

Brassell, S.C., Wardroper, A.M.K., Thomson, I.D., Maxwell, J.R., and Eglinton, G., 1981. Specific acyclic isoprenoids as biological markers of methanogenic bacteria in marine sediments. *Nature*, 290:693–696.

Bray, E.E., and Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta*, 22:2–15.

Budzikiewicz, H., 1972. Steroids. *In* Waller, G.R. (Ed.), *Biochemical Applications of Mass Spectrometry:* New York (Wiley), 251–289.

Chardon-Loriaux, I., Morisaki, M., and Ikewawa, N., 1976. Sterol profiles of red algae. *Phytochemistry*, 15:723–725.

Cranwell, P.A., 1974. Monocarboxylic acids in lake sediments, indicators, derived from terrestrial and aquatic biota, of paleoenvironmental trophic levels. *Chem. Geol.*, 14:1–14.

Curiale, J.A., Cameron, D., and Davis, V.D., 1985. Biological marker distribution and significance in oils and rocks of the Monterey Formation, California. *Geochim. Cosmochim. Acta*, 49:271–288.

de Leeuw, J.W., Cox, H.C., van Graas, G., van de Meer, F.W., Peakman, T.M., Baas, J.M.A., and van de Graaf, B., 1989. Limited double bond isomerisation and selective hydrogenation of sterenes during early diagenesis. *Geochim. Cosmochim. Acta*, 53:903–909.

Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., and Eglinton, G., 1978. Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature*, 272:216–222.

Dunbar, R.B., 1983. Stable isotope record of upwelling and climate from Santa Barbara Basin, California. *In* Thiede, J., and Suess, E. (Eds.), *Coastal Upwelling, Its Sediment Record, Part B. Sedimentary Records of Ancient Coastal Upwelling:* New York (Plenum), 217–246.

Eglinton, G., and Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science,* 156:1322–1335.

Erdman, T.R., and Thomson, R.H., 1972. Sterols from the sponges *Cliona celata* Grant and *Hymeniacidon perleve* Montagu. *Tetrahedron,* 28:5163–5173.

Espitalié, J., Laporte, J.L., Leplat, P., Madec, M., Marquis, F., Paulet, J., and Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pet.,* 32:23–42.

Fleischer, P., 1972. Mineralogy and sedimentation history, Santa Barbara Basin, California. *J. Sediment. Petrol.,* 42:49–58.

Heath, G.R., Moore, T.C., Jr., and Dauphin, J.P., 1977. Organic carbon in deep-sea sediments. *In* Andersen, N.R., and Malahoff, A. (Eds.), *The Fate of Fossil Fuel CO_2 in the Oceans:* New York (Plenum), 605–625.

Heusser, L., 1978. Pollen in Santa Barbara Basin, California: a 12,000 year record. *Geol. Soc. Am. Bull.,* 89:673–678.

Howard, D.L., 1980. Polycyclic triterpenes of the anaerobic photosynthetic bacterium *Rhodomicrobium vannielli* [Ph.D. dissert.]. Univ. Calif., Los Angeles.

Huang, W.Y., and Meinschein, W.G., 1976. Sterols as source indicators of organic materials in sediments. *Geochim. Cosmochim. Acta,* 40:323–330.

————, 1979. Sterols as ecological indicators. *Geochim. Cosmochim. Acta,* 43:739–745.

Hunt, J.M., 1979. *Petroleum Geochemistry and Geology:* San Francisco (W.H. Freeman).

Ikan, R., Baedecker, M.J., and Kaplan, I.R., 1975. Thermal alteration experiments on organic matter in recent marine sediment, II. Isoprenoids. *Geochim. Cosmochim. Acta,* 39:187–194.

Kennedy, J.A., and Brassell, S.C., 1992a. Molecular records of twentieth century El-Niño events in laminated sediments from the Santa Barbara basin. *Nature,* 357:62–64.

————, 1992b. Molecular stratigraphy of the Santa Barbara basin: comparison with historical records of annual climate change. *Org. Geochem.,* 19:235–244.

Kennett, J.P., Baldauf, J.G., et al., 1994. *Proc. ODP, Init. Repts.,* 146 (Pt. 2): College Station, TX (Ocean Drilling Program).

Kolattukudy, P.E., 1976. *Chemistry and Biochemistry of Natural Waxes:* New York (Elsevier).

Lange, C.B., Burke, S.K., and Berger, W.H., 1990. Biological production off southern California is linked to climatic change. *Clim. Change,* 16:319–329.

Mackenzie, A.S., Brassell, S.C., Eglinton, G., and Maxwell, J.R., 1982. Chemical fossils: the geological fate of steroids. *Science,* 217:491–504.

Marlowe, I.T., Brassell, S.C., Eglinton, G., and Green, J.C., 1984. Long-chain unsaturated ketones and esters in living algae and marine sediments. *Org. Geochem.,* 6:135–141.

McEvoy, J., 1983. The origin and diagenesis of organic lipids in sediments from the San Miguel Gap [Ph.D. dissert.]. Univ. Bristol.

McEvoy, J., Eglinton, G., and Maxwell, J.R., 1981. Preliminary lipid analyses of sediments from Sections 467-3-3 and 467-97-2. *In* Yeats, R.S., Haq, B.U., et al., *Init. Repts. DSDP,* 63: Washington (U.S. Govt. Printing Office), 763–774.

Milner, C.W.D., Rogers, M.A., and Evans, C.R., 1977. Petroleum transformation in reservoirs. *J. Geochem. Expl.,* 7:101–153.

Ourisson, G., Albrecht, P., and Rohmer, M., 1979. The hopanoids: paleochemistry and biochemistry of a group of natural products. *Pure Appl. Chem.,* 51:709–729.

Peters, K.E., and Moldowan, J.M., 1993. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments:* Englewood Cliffs, NJ (Prentice Hall).

Pisias, N.G., 1978. Paleoceanography of the Santa Barbara Basin during the last 8000 years. *Quat. Res.,* 10:366–384.

Prahl, F.G., Muehlhausen, L.A., and Zahnle, D.L., 1988. Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions. *Geochim. Cosmochim. Acta,* 52:2303–2310.

Prahl, F.G., and Wakeham, S.G., 1987. Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessment. *Nature,* 330:367–369.

Radke, M., Willsch, H., and Welte, D.H., 1980. Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography. *Anal. Chem.,* 52:406–411.

Reimers, C.E., Lange, C.B., Tabak, M., and Bernhard, J.M., 1990. Seasonal spillover and varve formation in the Santa Barbara Basin, California. *Limnol. Oceanogr.,* 35:1577–1585.

Rullkötter, J., Littke, R., Hagedorn-Götz, I., and Jankowski, B., 1988. Vorläufige Ergebnisse der organisch-geochemischen und organisch-petrographischen Untersuchungen an Kernproben des Messeler Ölschiefers. *CFS,* 107:37–51.

Rullkötter, J., Mukhopadhyay, P.K., Schaefer, R.G., and Welte, D.H., 1984. Geochemistry and petrography of organic matter in sediments from Deep Sea Drilling Project Sites 545 and 547, Mazagan Escarpment. *In* Hinz, K., Winterer, E.L., et al., *Init. Repts. DSDP,* 79: Washington (U.S. Govt. Printing Office), 775–806.

Rullkötter, J., Mukhopadhyay, P.K., and Welte, D.H., 1987. Geochemistry and petrography of organic matter from Deep Sea Drilling Project Site 603, lower continental rise off Cape Hatteras. *In* van Hinte, J.E., Wise, S.W., Jr., et al., *Init. Repts. DSDP,* 93 (Pt. 2): Washington (U.S. Govt. Printing Office), 1163–1176.

Rullkötter, J., von der Dick, H., and Welte, D.H., 1981. Organic petrography and extractable hydrocarbons of sediments from the eastern North Pacific Ocean, Deep Sea Drilling Project Leg 63. *In* Yeats, R.S., Haq, B.U., et al., *Init. Repts. DSDP,* 63: Washington (U.S. Govt. Printing Office), 819–836.

Schimmelmann, A., and Kastner, M., 1993. Evolutionary changes over the last 1000 years of reduced sulfur phases and organic carbon in varved sediments of the Santa Barbara Basin, California. *Geochim. Cosmochim. Acta,* 57:67–78.

Schimmelmann, A., and Tegner, M.J., 1991. Historical oceanographic events reflected in $^{13}C/^{12}C$ ratio of total organic carbon in Santa Barbara basin sediment. *Global Biogeochem. Cycles,* 5:173–188.

Seifert, W.K., and Moldowan, J.M., 1980. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. *In* Douglas, A.G., and Maxwell, J.R. (Eds.), *Advances in Organic Geochemistry, 1979:* Oxford (Pergamon Press), 229–237.

Sholkovitz, E.R., and Gieskes, J.M., 1971. A physical-chemical study of the flushing of the Santa Barbara Basin. *Limnol. Oceanogr.,* 16:479–489.

Simoneit, B.R.T., and Kaplan, I.R., 1980. Triterpenoids as molecular indicators of paleoseepage in Recent sediments of the Southern California Bight. *Mar. Environ. Res.,* 3:113–128.

Simoneit, B.R.T., and Mazurek, M.A., 1981. Organic geochemistry of sediments from the southern California Borderland, Deep Sea Drilling Project Leg 63. *In* Yeats, R.S., Haq, B.U., et al., *Init. Repts. DSDP,* 63: Washington (U.S. Govt. Printing Office), 837–853.

Soutar, A., and Crill, P.A., 1977. Sedimentation and climatic patterns in the Santa Barbara Basin during the 19th and 20th centuries. *Geol. Soc. Am. Bull.,* 88:1161–1172.

Still, W.C., Kahn, M., and Mitra, A., 1978. Rapid chromatographic technique for preparative separations with moderate resolutions. *J. Org. Chem.,* 43:2923–2926.

Urbach, G., and Stark, W., 1975. The C-20 hydrocarbons of butterfat. *J. Agr. Food Chem.,* 23:20–24.

Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. *Org. Geochem.,* 9:83–99.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., and Jeffrey, S.W., 1993. Geochemical significance of the occurrence of dinosterol and other 4-methyl sterols in a marine diatom. *Org. Geochem.,* 20:7–15.

Volkman, J.K., and Maxwell, J.R., 1986. Acyclic isoprenoids as biological markers. *In* Johns, R.B. (Ed.), *Biological Markers in the Sedimentary Record:* New York (Elsevier), 1–42.

Wardroper, A.M.K., 1979. Aspects of the geochemistry of polycyclic isoprenoids [Ph.D. dissert.]. Univ. Bristol.

Wardroper, A.M.K., Maxwell, J.R., and Morris, J.R., 1978. Sterols of a diatomaceous ooze from Walvis Bay. *J. Steroids,* 32:203–221.

Wyllie, S.G., and Djerassi, C., 1968. Mass spectrometry in structural and stereochemical problems, CXLVI. Mass spectrometric fragmentations typical of sterols with unsaturated side chains. *Org. Chem.,* 33:305–313.

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