24. LIPID/BITUMEN MATURATION BY HYDROTHERMAL ACTIVITY IN SEDIMENTS OF MIDDLE VALLEY, LEG 139[1]

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ABSTRACT

The accelerated diagenesis, maturation, and catagenesis of organic matter to hydrothermal petroleum was studied in sediments from Ocean Drilling Program Leg 139 in Middle Valley, northern Juan de Fuca Ridge. Sediments at Sites 855 and 856 have experienced high heat flow resulting in accelerated diagenesis of the immature organic matter without product migration. Fluid migration through these sediments has resulted in an influx of mature organic components, yielding diverse bitumen mixtures. At Site 857 the alteration has occurred in situ to the catagenetic stage and at Site 858, the hottest holes, the hydrothermal petroleums have migrated after generation. Maturation for the *n*-alkanes proceeds from high CPI values to <1.0 (i.e., strong even-carbon-number preference), and due to the low TOC these sediments do not generate high amounts of hydrocarbons from kerogen, thus revealing this unique carbon number preference. The biomarkers are converted from the biological precursors to the geological equivalents with various maturities. The organic matter is principally marine in origin and contains a significant terrigenous component, as confirmed by the alkane and biomarker distributions. High-temperature alteration yields polynuclear aromatic hydrocarbons, which in these sediments are concentrated in the high molecular weight range (>250 dalton).

INTRODUCTION

Hydrothermal systems associated with oceanic spreading centers are now recognized as a common phenomenon, and the morphology, mineralogy, sedimentology, and fluid chemistry of the active systems in spreading centers has been reviewed (e.g., Barrett and Jambor, 1988; Rona, 1988; Rona et al., 1983; Simoneit, 1990a; Von Damm, 1990). The geochemistry of the alteration of sedimentary organic matter and associated fluid interactions have also been studied extensively (e.g., Bazylinski et al., 1988; Gieskes et al., 1988; Simoneit, 1985, 1990b; Simoneit et al., 1984, 1992; Welhan and Lupton, 1987; Whelan et al., 1988). Only one sedimented hydrothermal system, the Guaymas Basin, had been drilled before 1991 (Curray, Moore, et al., 1982). The purpose of this chapter is to provide an insight into the fate and chemical alterations of the organic matter, especially the biomarkers, under hydrothermal conditions in Middle Valley. The sedimentary organic matter in this system is influenced more by terrestrial influx than is the sedimentary organic matter in the Guaymas Basin (cf. Kvenvolden and Simoneit, 1990), and thus this study will be of interest in comparing the results with data from the other areas.

Geological Setting

Middle Valley is a northern segment of the Juan de Fuca Ridge, just south of the Sovanco fracture zone (Fig. 1A), and was the drilling area for the Ocean Drilling Program (ODP) Leg 139 (Shipboard Scientific Party, 1992; Davis, Mottl, Fisher, et al., 1992). It is a sedimented spreading center over zero-aged crust with limited discharge of hydrothermal fluids. Four sites were drilled in four distinct hydrologic environments (Fig. 1B) (Davis, Mottl, Fisher, et al., 1992) and are detailed below.

Middle Valley is a fault-bounded, "failed" spreading center with large-scale hydrothermal deposits. Abundant turbidite and hemipelagic sedimentation has filled the graben to depths of up to 1.5 km in the center, with as little as 100 m of sediments at the eastern edge, and hydrothermal mounds rise as topographic features above the valley floor (Davis et al., 1987; Davis, Mottl, Fisher, et al., 1992). Efficient hydrothermal circulation maintains relatively uniform elevated temperatures in the upper igneous crust beneath a seal of low-permeability sediments (Davis and Villinger, 1992). The sediments at Sites 856, 857, and 858 were influenced by hydrothermal activity.

Site 855

Site 855 is located across the hanging-wall block of the normal fault bounding the rift valley in the east (Fig. 1B). This is part of the recharge area for the valley. The sediment interstitial water has a composition similar to seawater, which supports fluid drawdown (Shipboard Scientific Party, 1992; Davis, Mottl, Fisher, et al., 1992). Heat flow is low, and therefore this site is chosen as the thermally least affected reference location (Davis, Mottl, Fisher, et al., 1992). The oldest sediment recovered in the four holes drilled is of Pleistocene age and the sediments consist of silty clay.

Site 856

Site 856 is situated in the eastern part of the valley on Bent Hill (diameter about 500 m, elevation 60 m), about 3 km west from the normal fault scarp with Site 855 (Fig. 1B). There is no present heat-flow anomaly associated with Bent Hill (Davis and Villinger, 1992), but massive sulfide deposits just to the south were drilled. This site is interpreted to be a relict hydrothermal field that created the ore body (Shipboard Scientific Party, 1992; Davis, Mottl, Fisher, et al., 1992). The oldest sediment cored in the eight holes drilled is of Pleistocene age, and the Site 856 sequence consists of silty clay, silt, siltstone, and sulfidic breccia.

Site 857

Site 857 is located 5.2 km west from the normal fault scarp at Site 855 and 1.6 km south of the active hydrothermal system cored at Site 858 (Fig. 1B). A major thermal anomaly reaching 260°C was extrapolated at 476 m below seafloor (mbsf) and, because there is no active discharge, this site is considered to be the regional hydrothermal fluid reservoir (Davis and Wang, this volume; Shipboard Scientific Party, 1992; Davis, Mottl, Fisher, et al., 1992). Four holes were drilled and the oldest sediment is of Pleistocene age. The sedimentary sequence consists of silty clay, siltstone, claystone, and sulfidized matrix.
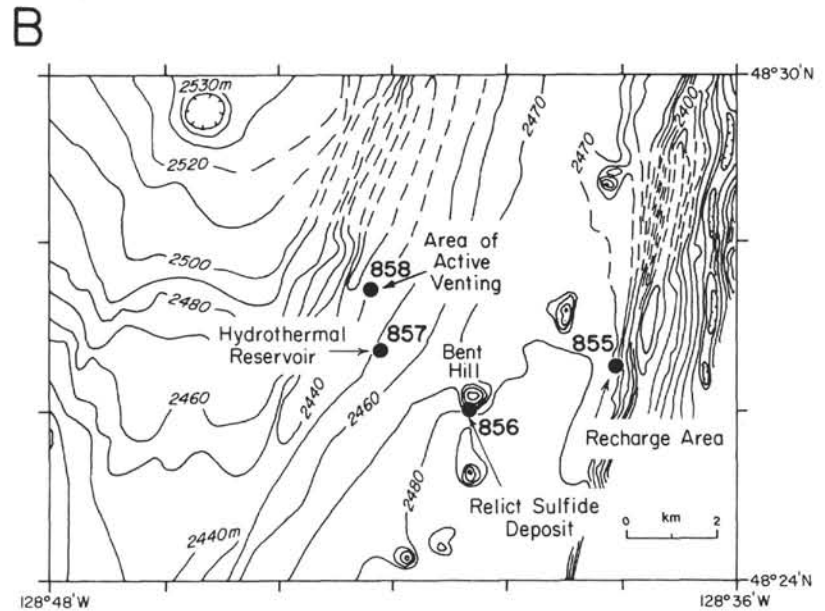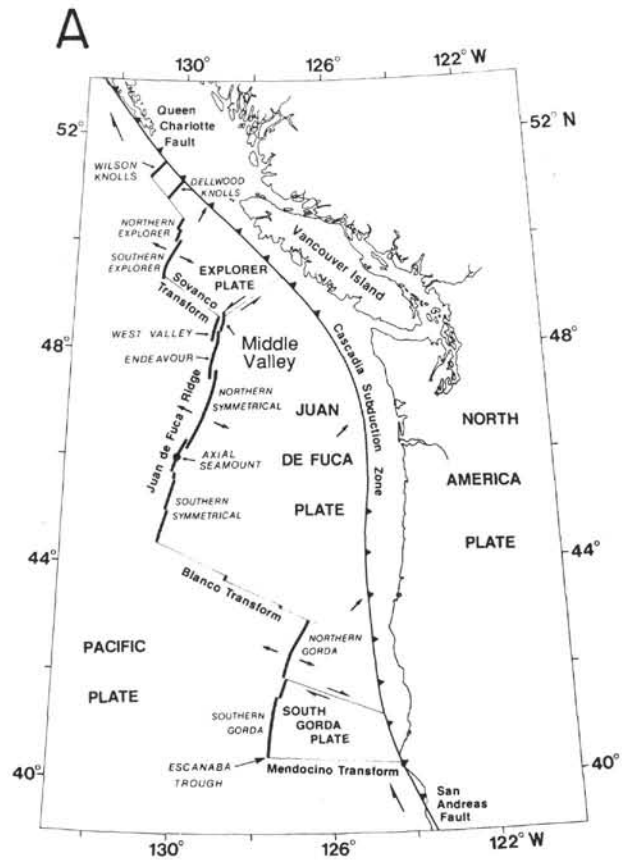
A

B

Figure 1. Location maps for the Middle Valley drilling area:
(A) the northeastern Pacific rift systems and (B) ODP Leg 139
drill sites in Middle Valley.

Site 858

Site 858 is located 1.6 km north of Site 857 in the same high thermal anomaly and in an active hydrothermal discharge area (800 × 400 m) (Fig. 1B). The vent field is located over a local basement high with a sediment thickness ranging from 400 to 700 m (Shipboard Scientific Party, 1992; Davis, Mottl, Fisher, et al., 1992). Fluids discharge at temperatures of 255°–265°C in most vents, and the conductive heat flow decreases systematically with distance from the field, falling to background levels within a few 100 m (Davis and Villinger, 1992). The results of previous piston coring and submersible sampling in this area have reported on the nature of the organic matter in those samples (Simoneit et al., 1992). The oldest sediment cored in the seven holes drilled is of Pleistocene age. Sediments from all holes are hydrothermally altered based on the occurrence of mineral assemblages, organic matter maturation (both diagenetic and thermal), bulk chemical

composition, and physical properties (Davis, Mottl, Fisher, et al., 1992). The sedimentary sequence consists of claystone and siltstone, and their hydrothermally altered counterparts.

EXPERIMENTAL METHODS

Wet sediments (3 cm³ each) taken by minicore were extracted both aboard ship and in the laboratory with methanol and *n*-hexane (1:2, 3 mL each) by shaking, subsequent centrifugation (2000 rpm), and removal of the hexane supernatant. The clear supernatant hexane extracts were pipetted into a second vial and evaporated under nitrogen blow-down at about 30°C to volumes ranging from 10 to 40 μL. Initial screening of sediment extracts was carried out aboard ship using the hexane supernatants from the extractions for fluorescence analyses (3 cm³ wet sediment each), which were removed and concentrated for analysis by the same method described (Davis, Mottl, Fisher, et al., 1992). Freeze-dried sediment samples (3 cm³ wet volume) were gently ground in an agate mortar and transferred into 1-dram screw-capped vials for similar extraction. Hexane (2 mL) and methanol (0.5 mL) were added, the suspension was heated at 60°C in a water bath and shaken occasionally for about 2 hr. After centrifugation a known volume of extract (usually 1 mL) was transferred into a second vial and reduced in volume under nitrogen blow-down at about 30°C to volumes ranging from 10 to 40 μL. The extraction efficiency for all samples was corrected based on the volume transferred. The freeze-dried samples are marked in the data set (Table 1) to distinguish them from the wet-extracted sediments. Three samples were extracted both wet and dry and the extract yields were comparable (marked in Table 1).

A 1- to 3-μL aliquot from a measured total volume was then injected onto the gas chromatograph (GC) or GC–mass spectrometer (MS) using normal protocol as detailed below. Compounds were identified by comparison of the retention times with those of authentic standards and confirmation by GC-MS. Response factors were determined for the various compound classes by GC and GC-MS analysis of representative standards, however, only hydrocarbons were quantitated in this study. (Note: The bitumen yield is based on the total GC signal due to resolved peaks and the unresolved complex mixture, or UCM, of branched cyclic hydrocarbons.) The final quantification of the results is based on the volume of wet sediment and the aliquot used in the injection. This type of quantitation allows the correlation of bitumen amount residing in a unit volume of sediment as it occurs in situ.

The shipboard GC is a Hewlett-Packard Model 5890A, fitted with a 30 m × 0.25 mm capillary column coated with DB-1 (0.33 μm film thickness). The temperature was programmed as isothermal for 3 min at 30°C, 10°C/min to 220°C, 4°C/min to 300°C, and isothermal for 15 min, with the injector at 250°C, flame ionization detector (FID) at 300°C, and helium as the carrier gas. The shore-based GC is also a Hewlett-Packard Model 5890A equipped with a 30 m × 0.25 mm capillary column coated either with DB-5 (0.25 μm film thickness) or with DB-1 (0.30 μm film thickness). The GC oven temperature was programmed from 65°C (hold for 2 min), to 310°C at 4°C/min, then isothermal for 30 min, with the injector at 290°C, FID at 325°C, and He as the carrier gas.

Analyses by GC-MS were carried out with a Finnigan Model 9610 gas chromatograph coupled to a Finnigan Model 4021 quadrupole mass spectrometer operated at 70 eV over the mass range 50–650. The GC was fitted with an identical column to that described previously for the analytical GC, and the same temperature program and operating conditions were used. The GC-MS data were acquired and processed with an on-line Finnigan-Incos Model 2300 computer data system.

RESULTS AND DISCUSSION

The data are discussed in two parts. First, the general trends of the lipid/bitumen parameters are summarized for each site, and second, the precursor-product relationships and interconversions of the bio-

marker compounds are presented. It should be emphasized that the lipid and biomarker data are presented as trends based on the alterations observed in conventional basin maturation (Hunt, 1979; Tissot and Welte, 1984) and *not* vs. sub-bottom depth for each hole. This is due to extensive lateral fluid invasion causing local organic matter alteration, thus resulting in complex sub-bottom trends. Some of the terms used in this text are defined in the Glossary at the end of this chapter.

Lipid/Bitumen Data

The discussion of the lipid results presents the initial data (Davis, Mottl, Fisher, et al., 1992) as updated by the additional shore-based analyses and recalculations. The revised data are listed in Table 1.

Site 855

The total organic carbon content ranges from 0% to 1.1%, with a mean of 0.5% (Davis, Mottl, Fisher, et al., 1992), which is low compared to the 2% mean in the Guaymas Basin hydrothermal system (Curray, Moore, et al., 1982). The bitumen yields range from 0.6 to 23.4 μg/cm³ (Table 1), with an average of 7.1 μg/cm³, which can be taken as a reference value for relatively unaltered precursor (source) sediment. The dominant compound series in the total extracts are *n*-alkanes ranging from C_{15} to C_{35} with pristane ($C_{19}H_{40}$, Pr) as the major isoprenoid alkane (Table 1). A typical GC trace for an immature sample is shown in Figure 2A and others can be found in the organic geochemistry chapters of the shipboard report (Davis, Mottl, Fisher, et al., 1992). The *n*-alkanes >C_{26} have a significant predominance of odd carbon numbers (e.g., Fig. 3A, carbon preference index, CPI, >1.0), typical for immature hydrocarbons that originate from terrestrial higher plants (Simoneit, 1977, 1978). The CPI for the range C_{26}–C_{35} decreases vs. sub-bottom depth and increasing thermal alteration from 3.9 to 1.3 for Site 855, where the latter value is for the strongly fluorescing bitumen in Core 139-855C-10R (Davis, Mottl, Fisher, et al., 1992). Maturation is also evident in the variable decreases of the isoprenoid to normal hydrocarbon ratios (Pr/*n*-C_{17} = 4.2 to 0.2, Ph/*n*-C_{18} = 1.3 to 0.4). The pristane to phytane ($C_{20}H_{42}$) ratios (Pr/Ph) range from 5.0 to 0.8, over depth intervals cored, possibly reflecting varying thermal stress. The *n*-alkane patterns <C_{24} with the unresolved complex mixture (UCM) of branched and cyclic compounds (e.g., Fig. 2A) are interpreted as typical for autochthonous marine bitumen derived from alteration of microbial detritus (Simoneit, 1977, 1978).

The hydrocarbon signature of these sediments represents an admixture of marine with lesser terrigenous components and is similar to those reported for shallow gravity cores taken near Site 858 at the Middle Valley hydrothermal vents (Simoneit et al., 1992). These hydrocarbon mixtures have matured significantly because of the high regional heat flow, which has accelerated diagenesis. At Site 855, the present bottom-water temperature is about 2°C and the sedimentary geothermal gradient is near 0.33°C/m, suggesting a maximum contemporary temperature of about 33°C in the deepest interval penetrated at about 100 mbsf. This temperature is too low to have produced any change in Pr/*n*-C_{17} ratios with depth at Site 855 and suggests that the geothermal gradient was higher in the past. The strongly fluorescing bitumen in Core 139-855C-10R is also consistent with previous exposure of the deepest sediments at this site to temperatures high enough to take them into the beginning of the oil window (>50°C) (Tissot and Welte, 1984; Hunt, 1979).

Site 856

The total organic carbon content varies from 0.1% to 0.9% with a mean of 0.34% (Davis, Mottl, Fisher, et al., 1992). The bitumen yields range from 0.4 to 5.6 μg/cm³ (Table 1), with an average of 1.9 μg/cm³ and significantly lower than the yields for Site 855. No migrated bitumen is evident based on these yields. The dominant compound series in the total extracts is *n*-alkanes ranging from C_{15} to C_{35}, with Pr and
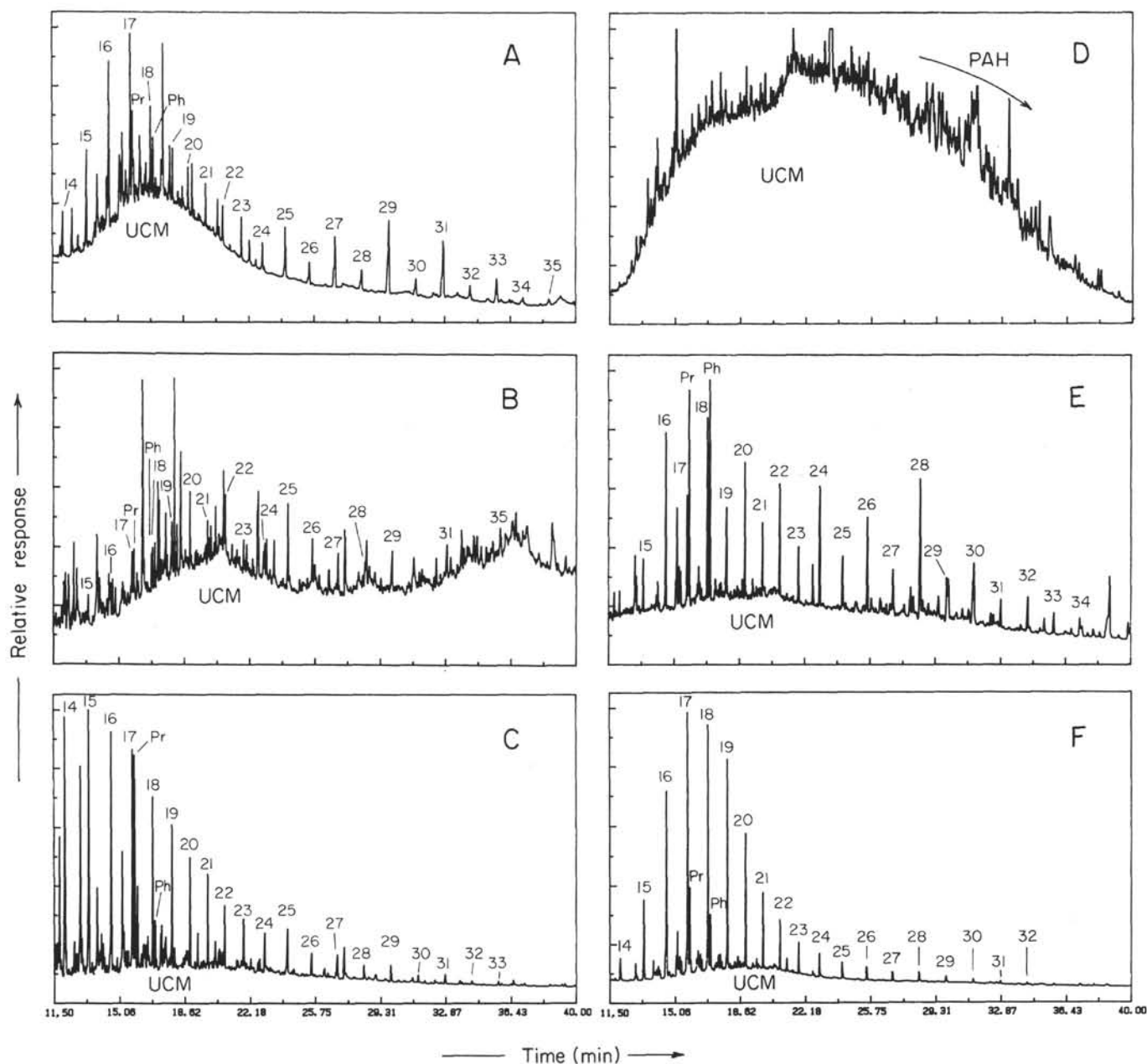
Figure 2. Gas chromatograms of total extracts of representative samples with immature lipids and hydrothermal petroleum or bitumen. **A.** Sample 139-855B-4R-3, 99–102 cm (immature). **B.** Sample 139-856A-1H-1, 0–1 cm (immature). **C.** Sample 139-858A-4H-4, 52–56 cm (mature). **D.** Sample 139-858A-6H-3, 137 cm (overmature). **E.** Sample 139-858C-2H-CC (mature). **F.** Sample 139-858D-4H-2, 133–135 cm (mature).

Ph as the major isoprenoid alkanes (Table 1). The n-alkanes $>C_{26}$ have, for the most part, a significant predominance of odd carbon numbers (CPI >1.0) and carbon number maximum (C_{max}) at C_{27}, C_{29}, or C_{31}, typical for immature hydrocarbons with an origin from terrestrial higher plants (e.g., Figs. 2A, 2B, and 3B; Simoneit, 1977, 1978). The n-alkane patterns $<C_{24}$ with the UCM of branched and cyclic compounds and the C_{max} at C_{17} (e.g., Fig. 2A) are interpreted as typical for autochthonous marine bitumen derived from alteration of microbial detritus (Simoneit, 1977, 1978).

The CPI for Hole 856A decreases to less than 1 below 20 mbsf (Davis, Mottl, Fisher, et al., 1992), indicative of an unusual hydrocarbon source with an even alkane predominance. Thermal maturation generally does not produce CPI values of less than 1 (Hunt, 1979; Tissot and Welte, 1984), so the decrease in CPI with depth in this hole must be at least partially source related.

Immature sediments usually exhibit n-alkane distributions with a strong odd-to-even carbon number predominance (CPI >1.0) over the range from C_{15} to C_{35} and especially $>C_{23}$ (Simoneit, 1978). This is also observed for many shallow sediment samples from Leg 139 (e.g., Fig. 3). However, there are numerous reports of even-to-odd carbon number predominances (CPI <1.0) for n-alkanes over various ranges ($<C_{20}$ common, $>C_{20}$ some, and full range rare) in a variety of sedimentary environments and some fossil-fuel samples (Welte and Ebhardt, 1968; Sever and Haug, 1971; Palacas et al., 1972; Welte and Waples, 1973; Albaiges and Torradas, 1974; Dastillung, 1976; Dembicki et al., 1976; Simoneit, 1975, 1977; Pelet and Debyser, 1977; Saliot and Tissier, 1978; Goutx and Saliot, 1980; Simoneit et al. 1980; Nishimura and Baker, 1986; Grimalt et al., 1986; Grimalt and Albaiges, 1987; Kennicutt and Brooks, 1990). In the case of the Leg 139 samples the n-alkane maturation proceeds from high CPI values to 1.0 and then for many

Table 1. Various parameters for the solvent-soluble organic matter in sediments from Leg 139.

Core, section, interval (cm)	Depth (mbsf)	Yield[a] (μg/cm³)	C_{max}[b]	$CPI_{(26-35)}$[c]	Pr/Ph	$Pr/n\text{-}C_{17}$	$Ph/n\text{-}C_{18}$
139-855A-							
1R-1, 77–79	0.78	11.60	17, 29	3.0	1.1	0.4	0.7
1R-3, 114–116	4.15	5.61	7, 31	3.0	1.8	0.7	0.7
2R-2, 106–108	10.17	4.20	17, 29	2.4	2.3	0.4	0.5
3R-3, 78–80	20.39	3.00	17, 27	1.9	2.5	0.5	0.4
4R-3, 31–33	29.32	7.00	17, 29	2.9	1.7	0.5	0.7
5R-1, 100–103	36.52	8.01	7, 29	1.7	1.2	0.4	0.4
6R-CC	55.10	5.20	Pr, 27	3.2	5.0	4.2	1.3
7R-3, 43–46	58.55	6.00	17, 27	2.8	1.7	0.6	0.9
139-855B-							
4R-3, 99–102	28.51	3.40	17, 29	2.6	1.6	0.5	0.6
6R-1, 25–29	44.17	9.80	17, 27	2.1	1.4	0.5	0.9
139-855C-							
1R-1, 66–69	0.68	23.40	17, 27	2.0	1.3	0.2	0.7
1R-5, 65–67	6.66	8.80	17, 31	2.1	1.1	0.2	0.8
2R-4, 67–71	13.80	98.00	17, 29	2.2	0.8	0.4	0.5
3R-4, 73–75	22.90	47.00	17, 29	2.4	1.4	0.6	0.5
6R-CC	56.10	0.60	29, 17	2.6	1.7	0.9	0.6
7R-4, 69–73	61.31	7.00	17, 29	3.9	1.5	0.4	0.6
10R-3, 0–5	87.93	7.20	Pr, 29	1.6	3.4	3.3	1.1
10R-4, 78–82	90.20	6.20	Pr, 29	2.2	2.0	3.3	1.2
10R-CC	94.60	2.40	Pr, 31	1.8	4.0	4.0	1.2
11R-1, 145–150	96.08	1.20	17, 29	1.6	1.8	0.9	1.2
139-855D-							
4R-1, 0–5	104.33	11.60	Pr, 29	1.3	4.5	4.0	1.1
4R-CC	108.50	8.03	1, Pr	2.6	2.5	1.8	0.7
139-856A-							
1H-1, 0–1	0.00	4.42	0, 29	1.2	1.3	1.0	1.0
1H-1, 69–72	0.70	3.60	17, 29	3.1	1.1	0.5	0.8
1H-2, 35–37	1.86	2.01	7, 29	2.1	1.1	0.3	1.0
1H-CC	2.70	1.42	7, 20	1.8	1.1	0.6	0.5
2H-1, 61–64	3.32	1.82	7, 17	2.2	1.6	0.6	0.9
2H-2, 62–64	4.83	2.61	7, 29	0.9	1.2	0.1	1.2
2H-3, 83–85	6.34	1.20	27, 17	2.8	1.8	0.6	1.0
2H-6, 109–111	11.30	0.61	7, 27	1.1	1.3	0.8	1.6
2H-7, 48–50	12.19	1.00	17, 29	3.4	1.7	0.8	1.1
2H-CC	12.20	1.20	29, 17	1.1	1.5	0.6	0.5
3H-1, 94–98	13.16	0.60	17, 27	3.1	1.2	0.9	0.3
3H-2, 67–71	14.39	1.40	17, 27	1.5	1.3	0.4	1.4
3H-CC	21.70	0.42	7, 17	1.0	0.8	0.2	0.5
4H-5, 78–82	28.50	4.61	7, 28	0.7	1.1	0.3	1.0
5H-2, 63–67	33.35	3.40	17, 28	0.8	1.2	0.1	1.2
5H-CC	40.70	2.40	29, 20	3.6	1.5	0.5	0.4
6H-4, 49–53	45.71	1.20	17, 28	0.7	1.1	0.1	0.8
7H-4, 57–61	55.29	0.60	17, 28	0.7	1.3	0.4	1.3
139-856B-							
1H-CC	1.80	n.a.	29, Pr	3.2	2.1	1.2	1.1
2H-6, 123–127	10.55	5.40	17, 27	0.9	0.8	0.2	0.7
2H-CC	11.30	0.40	29, 17	1.3	0.6	0.2	1.1
3H-6, 88–92	19.70	0.60	17, 18, 25	1.7	2.6	0.4	0.2
4H-5, 102–104	27.83	1.00	17, 28	0.7	0.8	0.1	0.9
5H-4, 34–39	35.16	1.20	17, 27	0.8	1.1	0.2	0.7
7H-2, 119–121	52.00	5.60	17, 27	1.1	1.2	0.4	0.9
139-856C-							
1H-CC	2.00	0.60	29, 21	1.2	0.9	1.6	1.6
139-856D-							
1H-CC	5.00	0.80	17, 27	1.0	0.4	0.4	2.2
139-856E-							
1H-CC	2.40	1.40	20, 27	1.1	0.5	0.4	0.6
139-857A-							
1H-1, 0–1	1.90	4.40	27, 21	2.6	0.5	0.9	0.7
2H-2, 73–75	13.64	8.00	17, 27	2.0	1.3	0.4	0.8
2H-CC	20.90	5.60	27, 17	2.8	0.8	0.4	1.0
3H-CC	21.90	5.80	17, 25	2.0	1.3	0.4	0.4
4H-2, 86–90	24.28	11.60	17, 27	4.1	1.5	0.4	0.9
4H-CC	31.40	4.80	27, 17	3.5	1.3	0.5	0.7
5H-CC	40.90	9.40	29, 17	3.6	1.6	1.1	0.8
6H-1, 67–71	41.60	3.80	17, 29	2.7	1.7	0.6	1.0
6H-4, 54–58	45.96	8.80	17, 29	3.2	1.4	0.4	1.2
7H-3, 81–85	54.23	6.20	17, 27	2.6	1.8	0.4	0.5
8H-2, 95–99	62.37	5.00	17, 29	2.4	1.9	0.9	1.0
9H-3, 86–90	73.28	9.00	17, 27	2.2	1.2	0.3	0.7
10H-2, 79–81	81.20	16.40	17, 27	2.2	1.2	0.8	0.8
10H-6, 26–28	86.67	4.40	17, 27	2.2	0.7	0.2	0.5
10H-6, 28–30	86.67	2.60	17, 27	2.4	1.1	0.3	0.6
13X-CC	111.20	14.60	18, 27	1.1	1.3	1.2	0.5
139-857C-							
2R-1, 63–67	57.16	7.40	17, 18	2.2	1.3	0.5	0.8
3R-1, 90–92	67.41	4.20	17, 29	3.0	1.3	0.3	0.7
3R-3, 38–40	69.89	3.40	17, 27	2.0	1.0	0.4	0.8
5R-1, 4–8	82.16	23.20	17, 27	2.1	1.3	0.4	1.2
6R-1, 66–68	86.87	5.40	17, 29	2.2	1.6	0.4	0.9
6R-CC	95.20	2.00	29, 21	2.0	2.0	1.5	0.9
8R-CC	114.50	4.00	20, 25	1.5	1.0	0.6	0.4
9R-CC	124.10	6.20	29, Pr	3.3	1.5	2.2	2.2
10R-CC	133.80	3.60	20, 29	2.4	1.2	0.8	0.7
11R-CC	143.50	0.80	25, 17	2.0	1.4	0.9	1.0
12R-CC	153.10	2.00	Pr, 29	2.0	2.2	3.3	1.3
14R-3, 0–3	165.83	1.00	Pr, 27	2.4	2.5	2.5	1.3
21R-2, 37–38	232.48	2.80	16, 28	0.9	1.7	0.8	0.7
22R-1, 124–127	241.55	2.40	14, 27	1.2	3.1	1.1	0.4
28R-3, 0–15	296.87	0.80	17, 18	1.5	1.5	0.2	0.3
31R-2, 102–105	325.24	1.80	18, 28	0.9	2.4	0.9	0.3
40R-2, 48–51	367.40	0.60	17, 28	0.9	0.6	0.2	0.6
43R-1, 66–70	385.38	0.80	Pr, 28	0.8	2.5	1.4	0.6
48R-1, 73–75	409.44	1.20	17, 30	0.8	1.2	0.5	0.6
51R-1, 28–30	423.69	0.80	17, 27	1.1	0.6	0.2	0.8
53R-1, 24–26	433.05	0.60	27, 17	1.0	1.6	0.6	0.7
139-858A-							
1H-1, 3–4	0.04	8.00	19, 29	1.5	1.0	1.1	1.5
1H-1, 5–7	0.06	118.00	17	n.d.	1.2	0.6	0.7
1H-1, 52–53	0.53	20.80	19, 27	1.7	1.7	1.2	0.5
1H-1, 57–58	0.58	5.00	29, Pr	2.8	1.8	1.2	0.6
1H-1, 75–76	0.76	6.80	Pr, 29	1.5	3.2	2.0	0.6
1H-1, 81–83	0.82	5.80	29, Pr	2.4	2.2	1.8	0.7
1H-1, 130–131	1.31	6.00	29, Pr	2.4	2.0	1.4	0.7
1H-1, 149–150	1.50	100.80	25	0.7	0.7	0.3	0.3
1H-2, 12–14	1.63	6.00	29, Pr	2.0	3.4	2.0	0.7
2H-1, 34–36	2.75	1.80	29, 20	2.1	1.4	0.6	0.5
2H-2, 85–87	4.76	13.00	17, 29	3.6	0.9	0.4	0.8
2H-3, 45–49	5.87	2.40	29, 20	1.8	1.7	0.8	0.6
2H-5, 28–32	8.70	0.60	29, Pr	2.3	2.9	1.0	0.4
2H-7, 40–42	11.80	n.a.	27	3.7	0.9	0.8	1.1
2H-CC	11.90	2.20	29, 20	1.7	0.7	0.5	0.5
3H-3, 81–85	15.73	1.60	29, 17	1.5	0.9	0.4	0.8
3H-6, 0–1	19.41	2.00	29, Pr	3.0	1.1	2.9	4.0
4H-2, 0–1	22.91	6.80	17, 27	1.0	4.2	0.6	0.2
4H-4, 52–56	26.44	1.60	15, 27	1.1	4.1	0.9	0.2
5H-5, 0–3	36.92	0.60	17, 27	1.0	1.0	0.3	0.5
6H-3, 55–56	43.96	1.80	17, 27	1.0	0.6	0.1	0.2
6H-3, 137	44.77	76.00	PAH	n.d.	n.d.	n.d.	n.d.
6H-CC	49.90	124.40	PAH	n.d.	n.d.	n.d.	n.d.
7H-CC	58.90	0.40	17, 27	1.5	0.2	0.1	0.8
11X-CC	81.60	1.80	27, 22	1.0	1.5	0.3	0.3
139-858B-							
1H-1, 17–18	0.18	2.20	Pr, 27	1.2	2.5	2.0	0.6
1H-1, 48–52	0.50	148.20	17, 27	1.2	1.6	0.4	0.8
1H-1, 54–55	0.55	29.20	Pr, 33	1.5	1.6	1.4	0.8
1H-1, 84–85	0.85	4.60	Pr, 27	1.0	1.7	1.1	0.7
1H-1, 124–125	1.25	4.00	20, 31	1.1	1.1	0.9	0.8
1H-2, 21–22	1.72	4.20	17, 27	1.1	1.2	0.5	0.7
1H-2, 31–32	1.82	1.20	27, Pr	0.9	1.4	1.1	1.4
1H-2, 41–42	1.92	16.00	17, 33	1.2	1.1	0.5	0.6
1H-2, 42–44	1.93	21.00	17, 20, 27	1.1	1.2	0.4	1.0
1H-2, 130–131	2.81	11.20	Pr, 31	1.4	2.5	1.9	0.8
1H-3, 23–27	3.25	5.20	17, 29	2.4	1.3	0.4	0.9
1H-3, 34–35	3.35	40.60	20, PAH	n.d.	0.7	0.6	0.8
1H-3, 100–101	4.01	17.20	20, PAH	n.d.	1.4	1.4	0.8
1H-4, 19–23	4.71	4.80	Pr, 29	4.2	1.2	0.6	0.9
1H-4, 38–39	4.89	2.00	29, 21	1.6	1.5	1.3	0.6
1H-4, 42–43	4.93	4.00	Pr, 29	1.6	2.0	2.5	1.1
1H-4, 102–103	5.53	2.80	29, 18	1.4	1.6	1.7	0.5
1H-5, 60–61	6.61	3.60	22, 27	0.9	1.1	0.4	0.3
1H-CC, 0–1	7.19	9.20	Pr, 26	0.8	1.7	3.0	2.1
1H-CC, 14–15	7.20	4.20	Pr, 27	0.9	2.0	3.7	1.6
2H-CC	16.70	7.40	17, 20, 27	0.8	0.4	0.2	1.3
5H-2, 112–113	26.53	1.00	20, 29	0.9	0.3	0.2	0.6
139-858C-							
1H-1, 22–26	0.24	5.20	Pr, 29	2.5	1.8	1.4	0.8
1H-2, 0–5	1.53	9.40	Pr, 29	2.4	2.2	1.4	0.8
1H-2, 42–46	1.94	4.00	17, 29	3.1	1.9	0.2	0.7
1H-3, 21–25	3.23	7.60	17, 29	4.0	1.0	0.2	1.2
2H-1, 42–44	3.93	21.40	17, 29	3.0	1.1	0.3	0.6
2H-2, 77–79	5.78	5.00	17, 29	2.9	0.9	0.3	0.7
2H-3, 98–100	7.49	58.60	17, 29	2.7	1.4	0.5	0.8
2H-4, 97–99	8.96	5.60	17, 29	3.1	1.1	0.8	1.1
2H-5, 71–73[d]	10.22	12.60	17, 27	1.7	1.1	0.3	0.9

Table 1 (continued).

Core, section, interval (cm)	Depth (mbsf)	Yield[a] (μg/cm³)	C_{max}[b]	CPI$_{(26-35)}$[c]	Pr/Ph	Pr/n-C$_{17}$	Ph/n-C$_{18}$
2H-6, 12–14	11.13	18.80	17, 29	2.0	1.1	0.3	0.6
2H-CC	13.00	114.40	Ph, 28	0.5	1.0	1.9	1.2
3H-1, 44–45	13.45	528.80	17, 28	0.7	0.2	0.2	2.2
3H-1, 90–91	13.91	170.80	17, 28	0.5	0.8	0.3	1.4
3H-2, 8–10	14.59	118.60	Ph, 26	0.5	0.6	0.6	1.2
3H-2, 18–19	14.69	145.40	Ph, 28	0.6	0.3	0.8	1.2
3H-2, 20–21	14.71	98.80	Ph, 28	0.6	0.4	0.6	1.5
3H-2, 53–54	15.04	169.60	Ph, 28	0.7	0.5	0.8	1.1
3H-2, 68–69	15.19	70.60	17, 28	0.7	0.5	0.4	1.4
3H-2, 108–109	15.59	42.20	17, 28	0.6	0.8	0.2	1.1
3H-2, 110–115[d]	15.50	26.60	28	0.6	0.3	2.0	2.5
3H-2, 121–122	15.72	30.40	17, 28	0.7	0.9	0.4	1.3
3H-3, 33–34	16.34	41.40	17, 30	0.9	1.0	0.6	1.0
3H-4, 120–121	17.21	21.60	17, 26	0.7	0.9	0.5	1.0
3H-CC	22.50	3.00	Ph, 27	0.9	0.2	0.3	2.0
5H-4, 19–20	28.20	24.00	17	1.1	1.3	0.4	0.8
5H-5, 63–64	30.14	35.80	17	1.2	1.3	0.5	0.8
5H-CC	33.00	1.40	26	0.9	n.d.	n.d.	n.d.
7H-CC	46.50	4.20	20, 26	0.9	0.7	0.4	0.4
10X-CC, 0–2	54.50	8.60	20, 26	1.0	0.8	0.5	0.4
12X-1, 80–82	64.81	1.80	17, 28	0.6	0.8	0.5	0.9
139-858D-							
1H-1, 0–1	0.00	1.40	29, 17	1.6	2.6	1.0	0.4
1H-1, 67–70[e]	0.70	5.80	29, Pr	1.7	1.4	1.4	0.8
1H-1, 145–150	1.48	3.00	29, Pr	2.5	2.9	1.7	0.6
1H-2, 19–21[e]	1.70	4.60	29, Pr	2.0	1.1	1.0	0.7
1H-3, 145–150	4.48	5.60	29, Pr	2.5	1.6	1.7	1.1
1H-4, 146–150	5.98	3.40	29, 17	1.8	2.0	1.0	0.8
1H-5, 145–150	7.48	3.80	29, 17	2.1	2.0	0.7	0.7
2H-3, 145–150	13.78	20.20	Pr, 28	0.7	1.9	2.4	1.1
2H-5, 144–150	16.78	8.80	Pr, 28	0.8	2.2	2.1	0.7
2H-CC, 37–40	18.80	45.80	17	0.7	1.2	0.2	0.3
3P-1, 54–56	19.35	166.40	18	0.9	1.9	0.3	0.2
4H-2, 133–135	22.64	30.40	17	0.5	1.6	0.3	0.2
4H-4, 144–148[e]	22.76	1.40	20, 26	0.7	0.6	0.2	0.4
4H-5, 144–150	27.28	5.60	24, Ph	0.9	0.3	0.4	1.4
4H-6, 100–103	28.32	0.40	26 (tr)	0.7	n.d.	n.d.	n.d.
6X-1, 96–105	29.81	3.60	26, 17	0.8	0.4	0.2	0.7

Notes: n.d. = not detected, n.a. = not analyzed, tr = trace, Pr = pristane, Ph = phytane, PAH = polynuclear aromatic hydrocarbons.

[a] Based on total GC signal integration of both resolved components and UCM, corrected for hydrocarbon response and aliquot fraction to the original wet sediment volume (using GC column with 0.33 μm film thickness).

[b] Major homologs are listed in decreasing order of intensity.

[c] Carbon preference index calculated as simple ratio of $\frac{(C_{27}+C_{29}+C_{31}+C_{33}+C_{35})}{(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})}$.

[d] Sample was freeze-dried prior to extraction.

[e] Duplicate extraction (i.e., one wet and one freeze-dried).

Figure 3. Mass fragmentograms of m/z 99 (a key ion for n-alkanes) for selected Leg 139 samples. **A.** Sample 139-855D-4R-CC. **B.** Sample 139-856A-2H-CC. **C.** Sample 139-857A-8H-2, 95–99 cm. **D.** Sample 139-857C-48R-1, 73–75 cm. Numbers refer to the carbon chain length of the n-alkanes. Ph = phytane.

hydrothermal petroleums (~30%) to <1.0 (as low as 0.46 for a sample from Hole 858C). This strong even-to-odd predominance was also observed over the full range from n-C$_{14}$ to n-C$_{34}$ for many samples (e.g., 858C-2H-CC and 858C-3H-2, 68–69 cm, Fig. 2E).

The origins of the even n-alkanes have been discussed in the literature as (1) microbial alteration of algal detritus, (2) reductive processes acting on acids or other lipid compounds, and (3) direct microbial lipid input (e.g., Dembicki et al., 1976; Welte and Waples, 1973; Simoneit, 1977; Welte and Ebhardt, 1968; Grimalt et al., 1986; Nishimura and Baker, 1986). I propose that process number 2 occurs for these Leg 139 samples. Because maturation in these sediments begins with immature organic matter (i.e., biogenic detritus) that has not completed early diagenetic alteration, the n-alkanols from marine microbial sources and from terrestrial plant waxes (Simoneit, 1977, 1978) may be the source of the even-chain alkanes. This would require low-temperature alteration by dehydration and double-bond reduction of the n-alkanols (possibly <100°C) analogous to that described for the alteration of sedimentary organic matter in the Bransfield Strait by the intrusion of a volcanic plug (Brault and Simoneit, 1988). Further evidence in support of this proposal is as follows: (1) presence of C$_{12}$–C$_{20}$ alk-1-enes with a strong even-to-odd carbon number predominance near sills of Deep Sea Drilling Project (DSDP) Leg 64 Holes 478 and 481 (Simoneit et al., 1984), (2) unsaturated isoprenoid and steroid hydrocarbons in Bransfield Strait sediments

derived from thermally driven dehydration of the precursor alcohols (Brault and Simoneit, 1988), (3) rapid reduction (i.e., hydrogenation) of olefins and alcohols (probably via olefins) in hydrothermal laboratory simulations (Leif et al., 1991, 1992; Leif, 1993), and (4) high concentrations of n-alkanols and n-alkanals (both with strong even predominance) from plant wax in continental shelf sediments of this region (Prahl and Pinto, 1987). One anomalous higher CPI value of 3.6 occurs in Sample 139-856A-5H-CC at 40.7 mbsf within this even CPI trend (Davis, Mottl, Fisher, et al., 1992), which is possibly diagnostic of turbidites or different organic matter sources in some sections of this hole below 20 mbsf. This CPI value is the highest observed in this hole, equivalent to those observed at shallower depth. The slightly elevated Pr/n-C$_{17}$ and Pr/Ph values and a somewhat lower Ph/n-C$_{18}$ values are also comparable between the shallow interval and the 40.7 mbsf sample.

CPI profiles for Holes 856B, 856C, 856D, and 856E have been reported (Davis, Mottl, Fisher, et al., 1992). The surficial CPI value of 3.2 in Hole 856B at 1.8 mbsf is in the same range as the highest values in the top 20 mbsf of Hole 856A. The CPI then decreases abruptly to values close to 1 in deeper sections of Hole 856B, suggestive of maturation. The samples with a CPI of <1.0 are diagnostic of a significant contribution from the even CPI source described previously for Hole 856A. CPI values for surficial samples from Holes 856C, 856D, and 856E are all near 1.0, consistent with those sediments experiencing higher thermal stress closer to the currently active hydrothermal vent area (Davis, Mottl, Fisher, et al., 1992).

Maturation is also evident by the decreases of the isoprenoid to normal hydrocarbon ratios (Pr/n-C$_{17}$) from a maximum ranging from 0.75 to 1.5 in the shallow sections of Holes 856A, 856B, and 856C to a minimum of 0.4 to 0.1 in deeper sections of Holes 856A and 856B, as well as within the surficial sediments of Holes 856D and 856E (Davis, Mottl, Fisher, et al., 1992). These low Pr/n-C$_{17}$ values (<0.5)

are characteristic of sediments that, at some time in their history, were heated to temperatures greater than 50°C, at the beginning of the oil thermal window (Farrington et al., 1988; Simoneit et al., 1981). The Ph/n-C$_{18}$ ratios do not show any systematic changes with depth or increasing geothermal gradients in these holes. These results are consistent with those observed elsewhere (Farrington et al., 1988; Simoneit et al., 1981).

Pr/Ph, which has been reported to be influenced both by source (e.g., Didyk et al., 1978) and by maturation (e.g., Simoneit et al., 1981), generally shows low and fluctuating values in the range of 0.8 to 1.5 in the 10 to 60 mbsf section of Hole 856A, as well as in most sections of Holes 856B, 856C, 856D, and 856E (overall range 0.4 to 2.6; Davis, Mottl, Fisher, et al., 1992). Pr/Ph values in some of the samples from less than 20 mbsf in Hole 856A are >1.5. It is possible that the variation and decrease in general with increasing depth and thermal stress are indicative of maturation effects.

The overall hydrocarbon signatures of the surficial intervals of the Site 856 sediments are also similar to those reported for shallow gravity cores taken near Site 858 at the Middle Valley hydrothermal vents (Simoneit et al., 1992). In the deeper intervals, however, the bitumens do not resemble other mature hydrothermal petroleums found in Escanaba Trough (Kvenvolden et al., 1986) or Guaymas Basin (Simoneit, 1985; Kawka and Simoneit, 1987).

Site 857

The total organic carbon (TOC) content varies from 0% to 0.8%, with a mean of 0.36% (Fig. 4A; Davis, Mottl, Fisher, et al., 1992), which is low compared to the Guaymas Basin hydrothermal system (Curray, Moore, et al., 1982). The bitumen yields for Site 857 range from 0.6 to 23.2 µg/cm^3 (Table 1), with an average of 5.3 µg/cm^3. These yields are similar to those for Sites 855 and 856 and are low compared to Site 858. Hole 857C shows a trend of gradually decreasing bitumen amounts vs. sub-bottom depth (Table 1). The low yields together with low TOC values (Davis, Mottl, Fisher, et al., 1992) indicate that migrated bitumens are probably not important and that the hydrocarbon signatures can be utilized as indicators for in-situ alteration conditions. The gradual concentration decrease vs. depth may indicate thermal alteration (oxidation) of the organic matter, possibly to CO_2.

The dominant compound series in the total extracts is hydrocarbons ranging from n-C$_{14}$ to n-C$_{35}$, with pristane and phytane as the major isoprenoid alkanes (Fig. 3C). The n-alkanes >C$_{26}$ have a significant predominance of odd carbon numbers (CPI >1.0) and C$_{max}$ at C$_{27}$ or C$_{29}$ in the upper sections of Holes 857A and 857C, which is typical for immature hydrocarbons with an origin from terrestrial higher plants (Simoneit, 1977, 1978). The n-alkane patterns <C$_{24}$ with the UCM of branched and cyclic compounds and the C$_{max}$ at C$_{17}$ are interpreted as typical for autochthonous marine bitumen derived from alteration of microbial lipids (Davis, Mottl, Fisher, et al., 1992).

The CPI for Hole 857A decreases gradually from 4 to 2 and then drops to 1 below 100 mbsf (Davis, Mottl, Fisher, et al., 1992), indicative of enhanced diagenesis/maturation resulting from high regional heat flow. The CPI profile for Hole 857C also decreases to values of 1 and <1 below 200 mbsf, consistent with increasing thermal stress vs. depth together with a source of the even-predominance alkanes. The variability of the surficial CPI values in both holes reflects different source inputs of marine and terrestrial organic matter. The CPI <1, that is, even-carbon-number predominance of n-alkanes, in the lower sections of Hole 857C (e.g., Fig. 3D) is comparable to distributions described for Site 856, DSDP sediments from Legs 5 and 18 in the northeastern Pacific to the south of this region (Simoneit, 1977), and other geographic areas (e.g., Grimalt and Albaiges, 1987). As discussed earlier, this decrease in CPI with depth in this hole may be partially source related and is a consequence of maturation.

Maturation was not evident in Pr/n-C$_{17}$ and Ph/n-C$_{18}$ ratios for Hole 857A and only a slight trend was observed below 170 mbsf for Hole 857C (Davis, Mottl, Fisher, et al., 1992). Low Pr/n-C$_{17}$ and
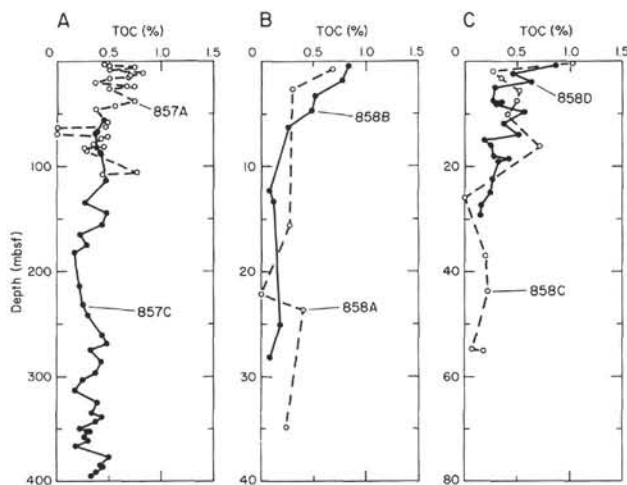
Figure 4. Plots of total organic carbon (%) vs. sub-bottom depth for Holes 857A and 857C (**A**), Holes 858A and 858B (**B**), and Holes 858C and 858D (**C**) (replotted from data by Davis, Mottl, Fisher, et al., 1992).

Ph/n-C$_{18}$ values (<0.5) are characteristic of sediments in conventional basins that have been heated to the beginning of the oil thermal window (Hunt, 1979). Pr/Ph, which has been reported to be influenced both by source and by maturation, generally shows fluctuating values in the range of 0.5 to 3.1 for both holes, which may reflect the organic matter sources rather than maturation (Davis, Mottl, Fisher, et al., 1992).

Site 858

The TOC values vary from 0% to 1.0%, with a mean of 0.32% and generally elevated values in the upper 5–10 mbsf (Figs. 4B and 4C; Davis, Mottl, Fisher, et al., 1992). The bitumen yields for Site 858 range from 0.4 to 528.8 µg/cm^3 (Table 1), with an average of 32.3 µg/cm^3. The yields are high within discrete intervals in the upper sections of Holes 858A, 858B, 858C, and 858D when compared to the other sites and approach similar levels at the other depths as observed for the previous sites (Table 1 and Fig. 5). These high yields, together with the elevated TOC values at shallow depths (Fig. 4; Davis, Mottl, Fisher, et al., 1992), indicate that migrated bitumens are important and the hydrocarbon signatures can in this case be utilized as indicators for hydrothermal petroleums. Thus, samples with high bitumen yields (yield >10 µg/cm^3, shown as solid points on Fig. 5) and/or mature n-alkane signatures are defined here as hydrothermal petroleum intervals.

The dominant compound series in the total extracts is n-alkanes ranging from C$_{14}$ to C$_{35}$ (some of the hydrothermal bitumens have ranges from n-C$_{10}$ to >n-C$_{36}$), with pristane and phytane as the major isoprenoid alkanes (e.g., Figs. 2C, 2E, 2F, and 3C). In the relatively unaltered sediments, the n-alkanes >C$_{26}$ have a significant predominance of odd carbon numbers (CPI >1.0) and C$_{max}$ at C$_{27}$ or C$_{29}$, which is typical for immature hydrocarbons with an origin from terrestrial higher plants (Simoneit, 1977, 1978). The n-alkane patterns <C$_{24}$ with the UCM of branched and cyclic compounds and the C$_{max}$ at C$_{17}$ are interpreted as typical for autochthonous marine bitumen derived from alteration of microbial detritus (Davis, Mottl, Fisher, et al., 1992).

Hydrothermal petroleums (bitumens) are products of rapid diagenesis/catagenesis and have alkane distributions analogous to those of conventional crude oils (Simoneit and Lonsdale, 1982; Simoneit, 1985, 1990a, 1992a, 1992b, 1993). The carbon number distributions and other geochemical parameters for hydrothermal petroleums generally reflect the source organic matter and the degree of thermal alteration or maturity (Kawka and Simoneit, 1987; Kvenvolden et al., 1986; Simoneit and Lonsdale, 1982; Simoneit, 1985, 1990a). The
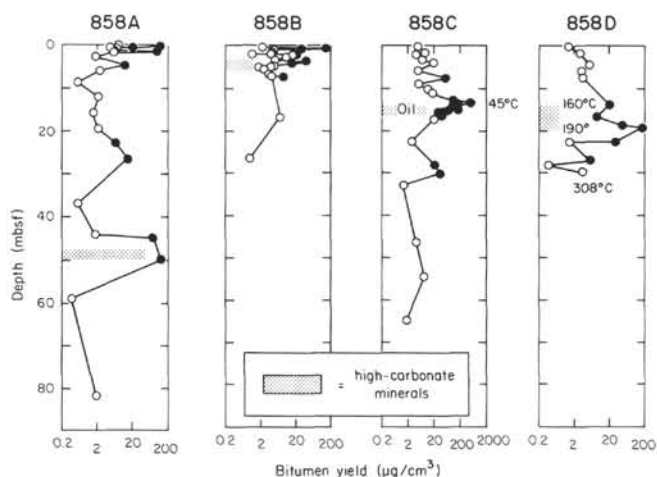
Figure 5. Yields of bitumen extracts for sediments from Site 858. Solid data points are for hydrothermal petroleum and some contemporary in-situ temperatures are given. Intervals with high amounts of carbonate minerals (5%–25%, Davis, Mottl, Fisher, et al., 1992) are also indicated.

hydrothermal bitumen horizons in the cores drilled at Site 858 have diverse n-alkane distributions (e.g., Fig. 6; also Davis, Mottl, Fisher, et al., 1992) and variable yields (cf. solid data points in the yield plots of Fig. 5).

Examples (Fig. 6) of immature hydrothermal bitumen are Samples 139-858B-1H-2, 31–32 cm, and 139-858D-1H-1, 67–71 cm, where the odd carbon n-alkanes are predominant; intermediate maturity is evident for Sample 139-858C-3H-2, 68–69 cm; full maturity is found for Samples 139-858A-1H-1, 149–150 cm, 139-858C-2H-CC (strong even-to-odd carbon number preference), 139-858D-2H-CC, 37–40 cm, and 139-858D-3P-1, 54–56 cm, where 139-858A-1H-1, 149–150 cm, is partially biodegraded as inferred from the low amounts of hydrocarbons $<n$-C_{22} (Simoneit, 1990b); and overmaturity is indicated for Sample 139-858A-6H-CC, consisting primarily of UCM and aromatic hydrocarbons typically generated at high temperatures ($>200°C$ or more, see also Fig. 2D). The hydrocarbon pattern of the latter sample is similar to that of the petroleum present in a barite chimney recovered with the deep-submersible *Alvin* from this vent/mound system (Simoneit et al., 1992).

The CPI is near or less than 1 in the hydrothermal bitumen intervals of Holes 858A, 858B, 858C, and 858D (Fig. 7), which is indicative of full petroleum maturity caused by the high thermal stress. The CPI profiles for all holes remain at values near 1 below the hydrothermal bitumen intervals, consistent with full maturity vs. depth together with a source input of the even-predominance alkanes. The same pattern is observed at Site 857. The CPI <1 in various intervals of Holes 858A, 858B, and 858C, especially for the hydrothermal petroleum of Sample 139-858C-2H-CC, which has a strong even-carbon-number predominance over the full range from n-C_{16} to n-C_{34} (Figs. 2E and 6D), should be emphasized. This low CPI seems to be a characteristic of these bitumens, as discussed earlier. The variability of surficial CPI values in these holes (Fig. 7) probably reflects different source inputs of marine and terrestrial organic matter, which are then overprinted by the degree of thermal stress or hydrothermal petroleum migration. The square data points in Figure 7 are examples of mixtures of lipids with hydrothermal bitumen, having both a high yield and high CPI.

With the additional samples analyzed, full maturation is still not always evident in the isoprenoid to normal hydrocarbon ratios (Pr/ n-C_{17} and Ph/n-C_{18}, Table 1) for the hydrothermal bitumen zones, but in general these ratios are low below those intervals (cf. Davis, Mottl, Fisher, et al., 1992). Low Pr/n-C_{17} and Ph/n-C_{18} values (<0.5) are characteristic of basin sediments that are mature (Hunt, 1979). The

Pr/Ph ratio fluctuates from 0.2 to 4.6 for these holes, showing no trends with the hydrothermal bitumen intervals. This may reflect the organic matter sources rather than lower temperature maturation.

The overall hydrocarbon signatures of the shallow intervals of the Site 858 sediments with low thermal alteration are similar to those of Sites 856 and 857, and of shallow gravity cores taken around Site 858 (Simoneit et al., 1992). The hydrocarbons in the near seafloor intervals with high extract yields probably reflect high temperature fluid invasion of the deeper intervals rapidly matured by hydrothermal processes, and petroleum migration both lateral and upward. The hydrothermal petroleum occurs at shallow depths in all holes (above 60 mbsf in Hole 858A, and above 30 mbsf in Holes 858B, 858C, and 858D, Fig. 5). Commonly, there appears to be an accumulation of hydrocarbons, as indicated by an increase in relative yield, in association with zones of high carbonate concentration (e.g., at 50 mbsf in Hole 858A; at 5 mbsf in Hole 858B; at 14 mbsf in Hole 858C; and the 13 to 19 mbsf interval of Hole 858D, Fig. 5; and Davis, Mottl, Fisher, et al., 1992). These carbonates probably act as a cap and are secondary hydrothermal precipitates (e.g., Früh-Green et al., this volume; Boni et al., this volume). Changes in CPI, Pr/n-C_{17}, Pr/n-C_{18}, and Pr/Ph also occur within the same intervals.

Temperature Regime and Petroleum Formation Processes

The changes in extractable hydrocarbons at Sites 855 and 856 have been discussed in terms of source and maturation changes. The lipid/ bitumen parameters described for these sites can be used to constrain sources and degrees of maturation in these sediments because the potential influences of other processes, including migration and biodegradation, can be ruled out. Specifically, it is not indicated that hydrocarbon compositions are influenced to any significant extent at Sites 855 and 856 by primary or secondary migration processes or by biodegradation (Davis, Mottl, Fisher, et al., 1992). The general processes that affect sedimentary organic matter are source, maturation, expulsion or primary migration, secondary and tertiary migration, and biodegradation. Primary oil migration in conventional basins, which is the rate-limiting step in the petroleum generation process (Lewan, 1987), is the initial expulsion of oil from the fine-grained source rock, where it is first formed, into a more permeable carrier or reservoir bed, such as a silt or sand or porous limestone. Secondary and tertiary migration processes occur as the petroleum moves and fractionates further within the carrier or reservoir beds (Hunt, 1979). In hydrothermal systems these consecutive processes are compressed into a single continuum due to rapid fluid passage (Simoneit, 1992a, 1992b; Didyk and Simoneit, 1989, 1990). The hydrothermal process also differs based on the extraction efficiency of the products by the fluid passing through the sediment (Simoneit, 1992a, 1992b, 1993; Didyk and Simoneit, 1989, 1990). These data (Davis, Mottl, Fisher, et al., 1992) indicate that hydrothermal bitumen migration, including both primary expulsion and migration of generated hydrocarbons from fine-grained intervals and secondary migration of hydrocarbons within more permeable sand and silt layers, has not occurred in the sediments at either Site 855 or 856. Thus, these hydrocarbon mixtures indicate rapid maturation by accelerated diagenesis resulting from high regional heat flow, and not from hydrothermal alteration by fluid transgression.

The overall hydrocarbon signatures of the upper intervals of the Site 857 sediments are similar to those of Site 856 and of shallow gravity cores taken near the Middle Valley hydrothermal vents (Simoneit et al., 1992). The hydrocarbons in the deeper intervals indicate rapid maturation by accelerated diagenesis, probably resulting from high regional heat flow rather than from hydrothermal alteration. The approximate present-day temperatures of the sediments can be estimated by extrapolating current subsurface temperatures from the surface heat-flow curves (Davis, Mottl, Fisher, et al., 1992). This indicates that the higher molecular weight compounds ($>C_{14}$) are surviving in these sediments to temperatures above those typical of the oil generation window (Hunt, 1979; Tissot and Welte, 1984). For example, long-
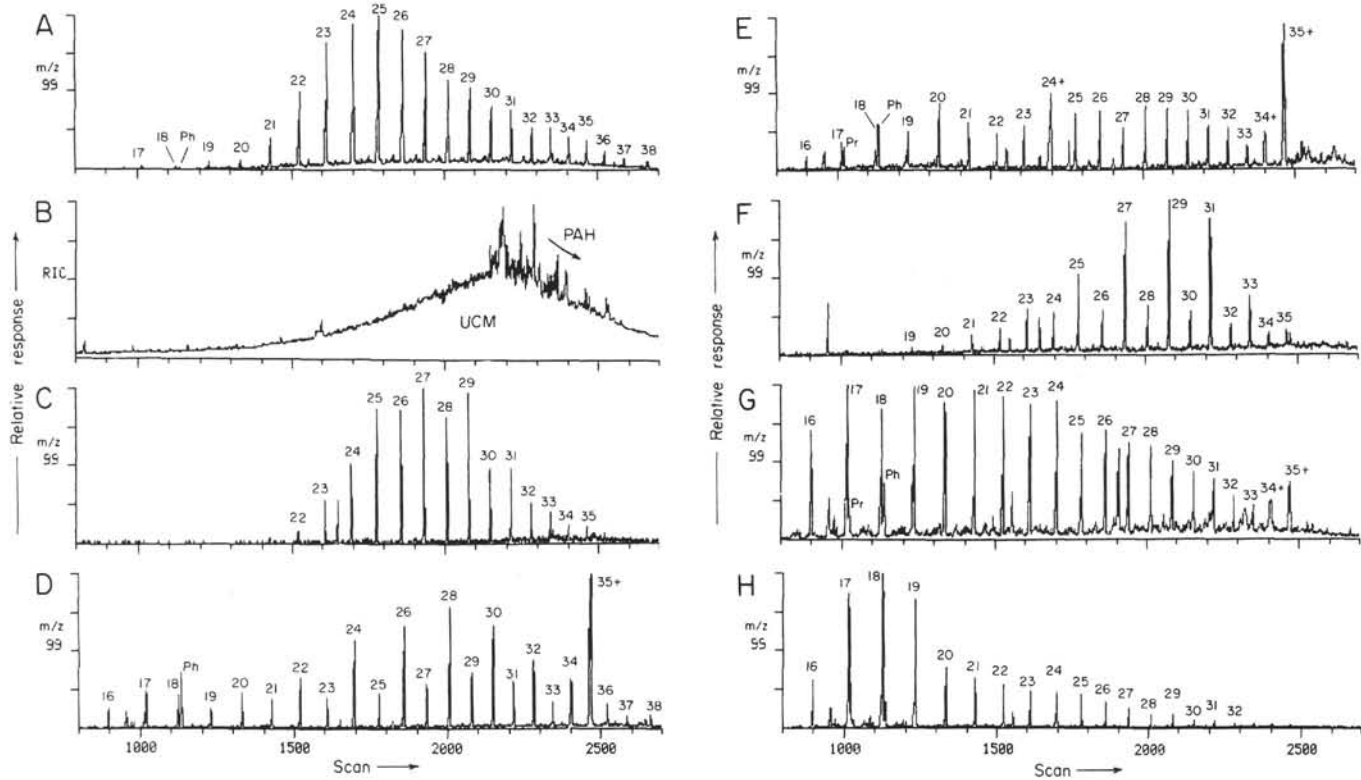
Figure 6. Mass fragmentograms of m/z 99 for selected samples from Site 858. **A.** Sample 139-858A-1H-1, 149–150 cm. **B.** Sample 139-858A-6H-CC (RIC, m/z 99 has no peaks attributable to *n*-alkanes). **C.** Sample 139-858B-1H-2, 31–32 cm. **D.** Sample 139-858C-2H-CC. **E.** Sample 139-858C-3H-2, 68–69 cm. **F.** Sample 139-858D-1H-1, 67–71 cm. **G.** Sample 139-858D-2H-CC. **H.** Sample 139-858D-3P-1, 54–56 cm. Numbers refer to the carbon chain length of the *n*-alkanes. Pr = pristane, Ph = phytane, + = coeluting isoprenoid hydrocarbon, UCM = unresolved complex mixture, PAH = polynuclear aromatic hydrocarbons.

chain alkanes ($>C_{23}$) are still measurable at 433 mbsf in Hole 857C, corresponding to a current temperature of ~270°C, considerably beyond the maximum range of 135° to 150°C normally claimed as the end of the oil window in conventional basins (Hunt, 1979). In addition, the CPI does not decrease to 1.0, diagnostic of maturation, until these sediments reach temperatures above 150°C at depths below 230 mbsf. Thus, the thermal alteration/destruction of these aliphatic hydrocarbons typical of petroleum is not complete up to temperatures of 270°C at 433 mbsf in Hole 857C (Davis, Mottl, Fisher, et al., 1992). Their survival is probably the result of the young age of the sediments (<250,000 yr; Davis, Mottl, Fisher, et al., 1992); that is, short residence time at high temperatures, as both time and temperature must be considered in maturation processes, which respond exponentially to temperature and linearly to time (Hunt, 1979; Tissot and Welte, 1984).

The approximate contemporary temperatures of the hydrothermal petroleum zones observed for Holes 858A, 858B, and 858C can be estimated to range from 3° to 70°C by extrapolating current subsurface temperatures from the heat-flow and temperature data (Davis, Mottl, Fisher, et al., 1992). The lowest temperature commonly cited for the beginning of the conventional oil generation window is 50°C, with peak generation occurring at about 80° to 100°C (Hunt, 1979; Tissot and Welte, 1984). Thus, these temperatures appear to be too low to have generated the observed amounts of hydrothermal petroleum in situ. Migration and deposition of bitumen into those intervals is more likely particularly into zones where hydrothermal flow may also have caused capping by carbonate precipitation (Davis, Mottl, Fisher, et al., 1992). Bitumen concentrations in the intervals below the hydrothermal petroleum zones are low, indicating that the bitumen which had formed there migrated either upward and laterally or laterally with hydrothermal fluids (Fig. 5).

The measured temperature at 20.9 mbsf in Hole 858D was >208°C, which indicates a gradient of about 10°C/m. The present zones of hydrothermal petroleum (14 to 28 mbsf) have experienced high tem-
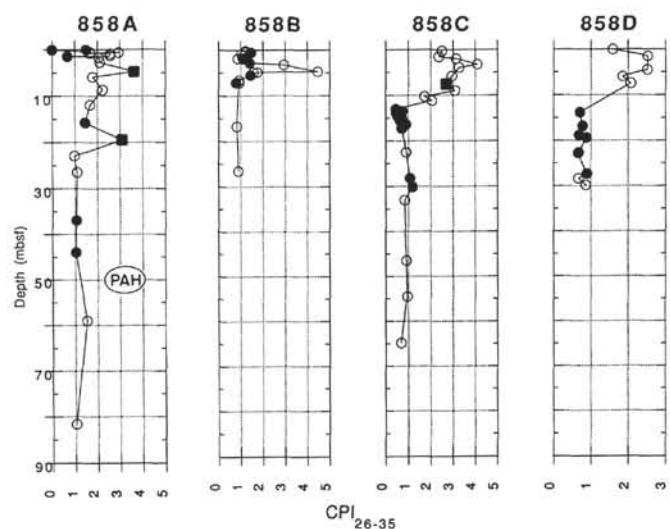
Figure 7. Carbon preference index (C_{26} to C_{35}) for the *n*-alkanes in the bitumen extracts of sediments from Site 858. Solid data points are for hydrothermal bitumen (solid squares are mixtures of bitumen and lipids).

peratures, possibly as high as 280°C, based on nearby vent fluid and downhole temperature measurements (Davis, Mottl, Fisher, et al., 1992). With such high temperatures, bitumen is unlikely to survive for any length of time. Therefore, it is postulated that (1) these hydrocarbons have only recently migrated with hydrothermal fluids into this interval, (2) they are currently being generated and/or migrating, or (3) they were generated recently as the surrounding sediments were exposed to a pulse of hot fluid. It should be noted that these hydrother-
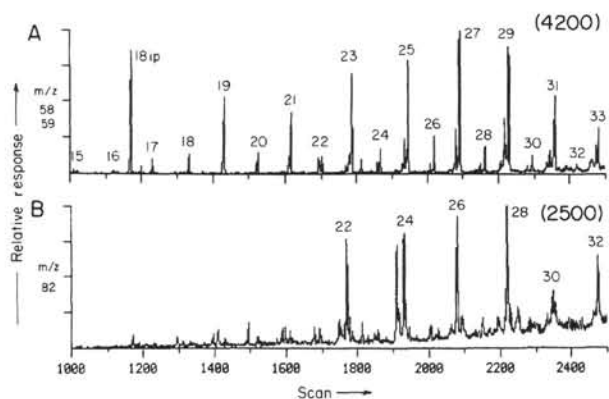
Figure 8. Representative mass fragmentograms for the carbonyl compounds in the bitumen extract of an immature sediment, Sample 139-855D-4R-CC: (**A**) m/z 58 + 59, *n*-alkan-2-ones, and (**B**) m/z 82, *n*-alkanals. Numbers refer to carbon chain length, 18ip = 6,10,14-trimethylpentadecan-2-one.

mal petroleum zones of Site 858 with variable compound compositions are considerably different from those of Hole 857C, where only trace amounts of bitumen were found at depth which were generated in situ reflecting both the organic matter sources and the highest formation temperatures (Davis, Mottl, Fisher, et al., 1992).

Biomarker Data

These samples contain a full spectrum of biomarkers from the biogenic precursors to the fully mature geological products (e.g., sterols to steranes). This is characteristic of hydrothermal organic matter alteration and is analogous to that observed elsewhere (e.g., Brault and Simoneit, 1988; Brault et al., 1989; Kawka and Simoneit, 1987; Simoneit, 1985, 1990a, 1992b; Simoneit et al., 1984). These samples exhibit the effects of thermal alteration on endogenous sedimentary organic matter, as well as the migrational mixing of hydrothermal petroleum with residual sedimentary lipids.

Immature Precursors

The biomarkers are immature in the upper sections of all holes and maturation is observed vs. sub-bottom depth, except in samples where mature or overmature hydrothermal bitumen or hot fluid invaded the section. The occurrences of the various biomarker classes and key maturity parameters are summarized for selected samples in Table 2. The bitumen extracts of the upper sediment sections of all sites contain C_{37} to C_{39} alkenones that are altered to unknown products at elevated in-situ temperatures. These compounds are generally used as indicators of past sea-surface temperatures and are discussed in a separate paper (Simoneit et al., this volume).

A preliminary search was made for potential precursors responsible for the enhancement of the even-carbon-chain length *n*-alkanes in the mature oils. As discussed earlier, the *n*-alkanols and/or *n*-alkanoic acids in the extractable lipids or bound in the organic detritus (e.g., as parts of membrane residues) could be these precursors. The *n*-alkanoic acids are not amenable for analysis in these total extracts because they are not esterified. The *n*-alkanols were also not detectable in these total extracts because their mass spectra as the un-derivatized compounds are not characteristic or easily resolved by a key ion search. Normal alkan-2-ones, generally ranging from C_{15} to C_{33} with a strong odd carbon number predominance, are present in many of the immature sediment extracts (e.g., Fig. 8A). These compounds decrease in concentration in the more mature samples but retain the odd carbon number predominance. Thus, the *n*-alkan-2-ones with the odd carbon predominance are not the precursors of the even-chain *n*-alkanes. Phytone (6,10,14-trimethylpentadecan-2-one) is usually the dominant ketone (e.g., Fig. 8A). It is an oxidation product of phytol from chlorophyll. A trace series of *n*-alkanals, ranging from C_{18} to C_{32} with a strong even-carbon-number predominance is found in some of the extracts (e.g., Fig. 8B). These aldehydes may be primary components derived from terrestrial higher plant wax or secondary oxidative derivatives from various lipid sources. Whether they are reduced to even-chain *n*-alkanes would need to be determined by further work.

Sterols (I, all structures cited are given in the Appendix) are major components in the upper sections of all holes and range from C_{27} to C_{29} (e.g., Figs. 9A and 9D). The general distribution for the samples
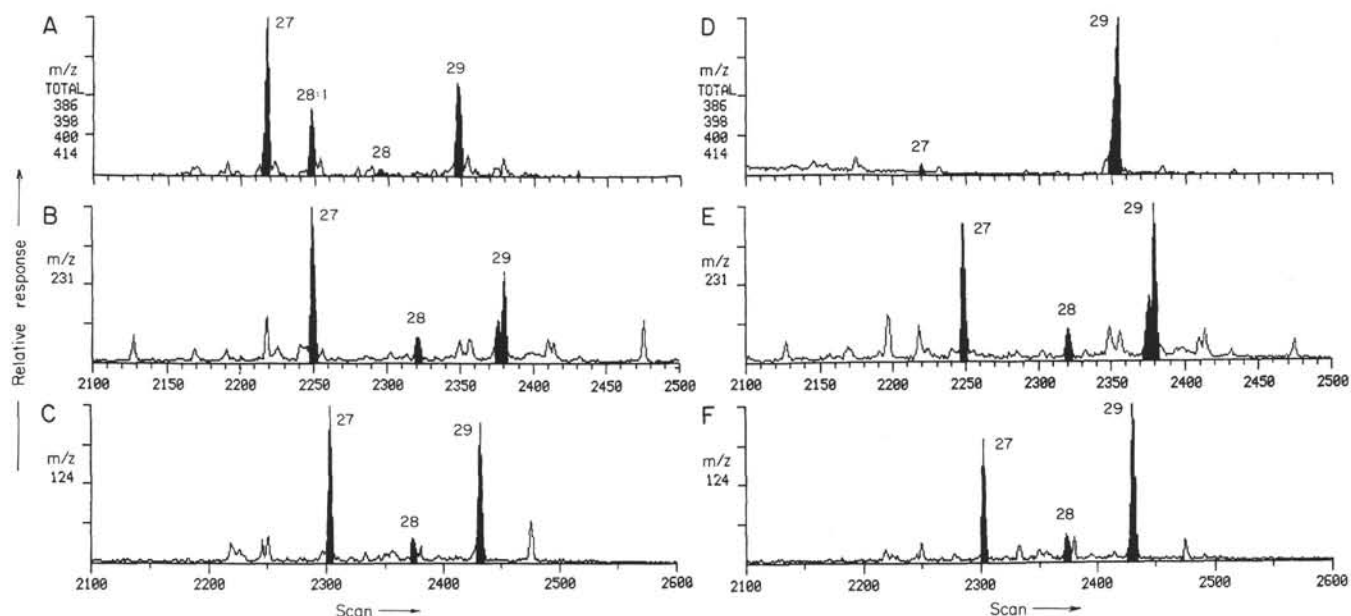
Figure 9. Representative mass fragmentograms for the steroid precursors of steranes in the bitumen extracts of sediments from Leg 139. Sterols (molecular ions 386, 398, 400 and 414 summed). **A.** Sample 139-855D-4R-CC. **B.** Sample 139-857A-8H-2, 95–99 cm. **C.** Sample 139-857A-8H-2, 95–99 cm. **D.** Sample 139-858A-1H-1, 149–150 cm, stanones (m/z 231, key ion). **E.** Sample 139-857C-6R-CC, stenones (m/z 124, key ion). **F.** Sample 139-857C-6R-CC. Numbers refer to carbon skeleton, and 28:1 = 24-methylcholesta-5,22-dien-3β-ol.)

Table 2. Presence and maturity parameters of biomarkers.

Core, section, interval (cm)	Depth (mbsf)	Immature biomarkers				Mature biomarkers				
		Sterols	Stenones	Stanones	Amyrins	C_{31} homohopane: $\dfrac{22S}{(22S + 22R)}$	$\dfrac{C_{27} \text{ sterane, 20R}}{C_{29} \text{ sterane, 20R}}$	C_{29} sterane: $\dfrac{20S}{(20S + 20R)}$	C_{27} diasterane: $\dfrac{20S}{(20S + 20R)}$	3,3,7-trimethyl-1, 2, 3, 4-tetrahydrochrysene
139-855D-										
4R-CC	108.5	+++	+	+	+++	0.48	0.58	0.38	0.50	++
139-856A-										
2H-CC	12.0	+	+	+	+	0.35	0.29	0.22		—
139-857A-										
1H-1, 0–1	1.9	—	—	—	—		0.33	0.27		++
8H-2, 95–99	62.0	+	+++	+++	+	0.38	—			
139-857C-										
6R-CC	95.0	+	+	+++	+	0.31	0.23	0.23	0.49	++
9R-CC	124.0	—	+	+++	—	0.29	0.82	0.15	0.50	+
48R-1, 73–75	409.0	—	—	—	—	0.58	—			
139-858A-										
1H-1, 149–150	1.5	+++	—	+	—	0.63	1.40	0.45	0.61	—
4H-4, 52–56	26.5	—	—	—	—	0.60				—
6H-CC	50.0	—	—	—	—					—
139-858B-										
1H-1, 48–52	0.5	+	+++	+++	—	0.44	1.30	0.41	0.56	—
1H-2, 31–32	1.8	+	+	+	—	0.30				—
1H-2, 42–44	1.9	+	+	+	—	0.40	0.50	0.38	0.50	—
139-858C-										
2H-5, 71–73	10.2	—	—	—	—	0.23	0.22	0.11		+
2H-CC	13.0	—	—	—	—	0.29	1.60	0.07	0.38	—
3H-1, 44–45	13.5	—	—	—	—	0.55	3.20	0.41	0.55	—
3H-2, 68–69	15.0	—	—	—	—	0.55	1.10	0.45	0.65	—
3H-2, 110–115	15.5	—	—	—	—	0.55	1.90	0.39	0.58	—
139-858D-										
1H-1, 0–1	0.0	+	+++	+	+	0.23				+
1H-1, 67–70	0.7	+	+	+	+	0.35	0.38	0.27		—
1H-4, 146–150	6.0	+	+	+	+	0.33	0.73	0.30	0.57	—
2H-CC, 37–40	18.8	—	—	—	—	0.53				—
3P-1, 54–56	19.3	—	—	—	—	0.50				—

Note: Presence indicated as: +++ = major components, ++ = intermediate, + = minor to trace, — = not detectable or sample too small.

analyzed is cholesterol (I, R = H) dominant or equal to β-sitosterol (I, R = C_2H_5), and one case with β-sitosterol predominant. Also, 24-methylcholesta-5,22-dien-3-ol (II) is present in these sterol suites, although it generally occurs as an ester or ether in sediments (Brassell et al., 1983). This compound, cholesterol, and possibly part of the β-sitosterol are interpreted to be derived from marine organic detritus. The sole dominance of β-sitosterol (Fig. 9D) or a portion of this compound in the other samples is interpreted to originate from terrigenous higher plant sources.

Alteration of sterols by accelerated diagenesis due to thermal stress is observed to yield stenones (III) and stanones (IV) with the same range from C_{27} to C_{29} (C_{26} is not detectable and C_{30} is present as a minor component) (e.g., Figs. 9B, 9C, 9E, and 9F). 24-Methyl-cholesta-4,22-dien-3-one or 24-methylcholest-22-en-3-one are not detectable, indicating that the precursor sterol (II) is altered to other products. Stanols, sterenes (e.g., Δ^2, Δ^3, or Δ^4) and steradienes (e.g., $\Delta^{2,4}$) are not detectable in any sample. This suggests that products from dehydration reactions of sterols, as were described for sediments from Bransfield Strait (Brault and Simoneit, 1988), are not preserved in this sample set.

Terrestrial triterpenoid markers are present in the shallow sections of all holes, but their mature derivatives are present as traces owing to the high concentrations of hopanes that are generated during thermal maturation. The dominant biological precursors identified are α-amyrin (V, R = OH) and β-amyrin (VI, R = OH) (Fig. 10A) from higher plants (Brassell et al., 1983; Simoneit, 1986). These compounds are altered primarily to α-amyrone (urs-12-en-3-one, V, R = O) and β-amyrone (olean-12-en-3-one, VI, R = O) and lesser amounts of olean-12-ene (VII) and urs-12-ene (Figs. 10B and 10C).

Various triterpenoid precursors for the hopanes are found in the shallow sections of all holes. Diploptene (VIII) occurs in the upper sections and is altered to 17β(H)-hop-21-ene (IX) and then to hop-17(21)-ene (X) (Figs. 11A and 11B). This is the same trend of thermally accelerated diagenesis as was described for Guaymas Basin surficial sediments and immature bitumens (Simoneit et al., 1979, 1984; Simoneit and Philp, 1982), and for Bransfield Strait sediments (Brault and Simoneit, 1988). Major amounts of oxygenated species, comprised mainly of 17β(H),21β(H)-bishomohopan-32- ol (XI) and 17β(H)-22,29,30-trisnorhopan-21-one (XII), are present in the shallow samples (Figs. 11A and 11B).

Fernene (XIII, $\Delta^{9(11)}$) is found in some samples (e.g., Fig. 11E) and is interpreted to be an indicator for bacterial detritus (Simoneit, 1986). An unknown triterpene is also present in some shallow sediment samples (e.g., Fig. 11G, peak 8, the mass spectrum has the following fragmentation pattern: m/z 69 (70), 81 (25), 151 (100), 189 (20), 191 (22), 206 (10), 410 (30)).

Sterane Maturation

Sterane hydrocarbons, useful for oil-source rock and maturity comparisons (Mackenzie et al., 1982; Seifert, 1978; Seifert and Moldowan, 1978, 1979), also exhibit differences among these samples. Examples of the sterane maturation in this sample suite are given in Figure 12 and the parameter data are listed in Table 2. The steranes have distributions with C_{27} dominant or with C_{29} dominant, and in all cases C_{28} is intermediate with C_{30} as a minor component. The $C_{27}(20R)/C_{29}(20R)$ ratios range from 0.22 to 3.2 for the samples analyzed (Table 2), in which values <1 indicate a stronger influx of C_{29} terrestrial marker steroids. This assumes a constant influx of marine derived C_{29} steroid residues (Volkman, 1986).

Sample 139-858C-2H-CC (13 mbsf) contains significant concentrations of C_{27} to C_{30} steranes (XX) primarily with the 5α(H), 14α(H), 17α(H)-20R and smaller amounts of the thermally less stable 5β(H), 14α(H),17α(H)-20R configurations (Kawka and Simoneit, 1987). Sam-
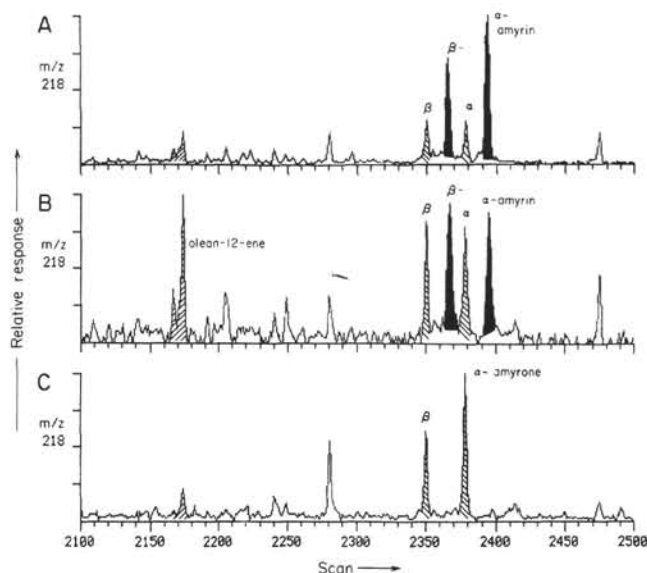
Figure 10. Representative mass fragmentograms of m/z 218 for the terrestrial triterpenoid biomarkers in the bitumen extracts of Leg 139 sediments. **A.** Sample 139-855D-4R-CC. **B.** Sample 139-857C-6R-CC. **C.** Sample 139-858D-1H-4, 146–150 cm. The transformation proceeds from amyrins to amyrones to oleanenes to oleananes.

ple 139-858C-3H-1, 44–45 cm, which is 50 cm deeper, exhibits the onset of epimerization at C-20, which occurs during thermal maturation (Seifert and Moldowan, 1978; Mackenzie et al., 1980). The epimerization ratio at C-20,

$$\left(\frac{20S}{20S + 20R}\right)$$

of C_{29}, increases from 0.07 to 0.41 for these two samples. Full maturity with a C_{29} epimerization ratio of 0.45 is found for the next deepest sample at 15.2 mbsf (139- 858C-3H-2, 68–69 cm) and also for the example in Figures 12D–12F (Sample 139-858A-1H-1, 149–150 cm). As the maturity increases, additional isomerization is evident as the 5a(H),14b(H), 17b(H)-20R and 20S-steranes (XXI, e.g., Figs. 12C and 12E), and the diasteranes (XXII, 13b(H),17a(H)-20S/R) increase in relative concentration to the regular steranes. The diasterane epimerization parameter,

$$\left(\frac{20S}{20S + 20R}\right)$$

for C_{27}, varies from 0.38 to 0.65 for these samples (Table 2).

These sterane compositions are analogous to those reported earlier for shallow samples from the hydrothermal vent area near Site 858 (Simoneit et al., 1992). The maturation also parallels the data for hydrothermal petroleums from Guaymas Basin and Escanaba Trough (Kawka and Simoneit, 1987; Simoneit, 1985; Kvenvolden and Simoneit, 1990).

Triterpane Maturation

The hopanes undergo maturation from immature precursors, including the 17β(H),21β(H)-hopanes (XIV) and moretanes (17β(H), 21α(H)-hopanes, XV), to the 17α(H),21β(H)-hopanes (XVI). The configuration of the biological precursors is 17β(H),21β(H) for this series as the R epimer at C-22 for the extended homologs >C_{31} (Ensminger et al., 1974, 1977). Maturation converts the precursors to the thermodynamically most stable configuration of 17α(H),21β(H), with the S and R epimers at C-22 for the extended homologs >C_{31} at an equilibrium ratio

$$\left(\frac{S}{S + R}\right)$$

of about 0.6 (Ensminger et al., 1974, 1977; Seifert and Moldowan, 1978). Typical examples for this series are shown in Figure 11 and the maturity parameters are given in Table 2.

Low levels of 17α(H),21β(H)-hopanes are detectable in the immature sections of all sites along with oxygenated and unsaturated precursors (e.g., Figs. 11A, 11B, and 11E). The homohopane epimer ratios in such sections vary from 0.23 to 0.40, are still immature, and yet no significant amounts of the 17β(H),21β(H)- and 17β(H), 21α(H)-hopanes are present. This is in contrast to the shallow sediments described earlier from the area of Site 858, where the hopanes contain the 17β(H),21β(H) series (Simoneit et al., 1992). Significant 17α(H),21β(H)-hopanes are found in deeper sections; for example, at about 13 mbsf in Hole 858C (Figs. 11C and 11D). The homohopane maturity parameter increases from 0.29 to 0.55 over a 50-cm increase in depth. The hopanes range from C_{27} to C_{35} and the dominant homologs are C_{35}, C_{30}, and C_{32}, for which the C_{32} to possibly the C_{35} homologs are derived from the respective hopanols found in the immature sections. The mature 17α(H),21β(H)-hopanes are predominant over the moretanes (XV) and only minor amounts of the 17β(H), 21β(H)-hopanes were detectable (Fig. 11D).

Traces of mature 17α(H),21β(H)-hopanes are found in the reference hole (e.g., Sample 139-855D-4R-CC, Fig. 11F), indicating accelerated diagenesis in situ or influx of mature bitumen with fluids at some time in the past. An example of a fully mature hopane signature is shown in Figure 11G, where the homohopane epimer ratio is 0.63 and the C_{35} and C_{32} extended hopanes have been cracked to the lower homologs which possibly enhances the 17α(H),21β(H)-29-norhopane concentration. This distribution is analogous to that described earlier for a seabed petroleum from the Site 858 area, except that sample also had a major amount of gammacerane (Simoneit et al., 1992). These hopane maturation trends are analogous to those described for sediments and hydrothermal petroleums from Guaymas Basin and Escanaba Trough (Kawka and Simoneit, 1987; Kvenvolden and Simoneit, 1990; Simoneit et al., 1984).

The amyrins, amyrones, and olean-12-ene characterized in the immature sections are in part altered to oleananes. The 18α(H)- and 18β(H)-oleananes (XVII) elute just prior to 17α(H),21β(H)-hopane by GC or GC-MS (Ekweozor and Udo, 1988) and have been utilized as maturity parameters for terrestrial organic matter. These two isomers elute as a minor, unresolved peak in most of these samples (Fig. 11, peak 0). This peak is also present in the data for the shallow cores reported earlier (Simoneit et al., 1992). A degraded triterpane residue, namely 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene (XVIII), is found as a major compound in the immature sections of most holes. This aromatic, degraded triterpenoid is interpreted to be derived from higher plants probably by microbial, photochemical, or photomimetic processes during sedimentation (e.g., Hauke et al., 1992; Corbet et al., 1980). Gammacerane (XIX), which was a dominant triterpane present in the seabed hydrothermal bitumen from the vent area of Site 858 (Simoneit et al., 1992), was not detectable except as a trace component in Sample 139-855D-4R-CC (Fig. 11F). A significant amount of an unknown pentacyclic triterpane (major MS fragments: 191 (100), 369 (7), 397 (10), 412 (5)) is also present in Sample 139-858D-1H-4, 146–150 cm (Fig. 11E).

Polynuclear Aromatic Hydrocarbons

The relative concentrations of selected polynuclear aromatic hydrocarbons (PAHs) and various ratios in these samples are given in Table 3. The low-molecular-weight aromatic and alkyl aromatic hydrocarbons are strongly depleted in the hydrothermal petroleums of Middle Valley (Table 3; Simoneit et al., 1992). Thus, alkyl naphthalenes and phenanthrene/alkyl phenanthrenes are present at significant concentrations only in Sample 139-858D-1H-4, 146–150 cm, although all samples contain trace amounts of the phenanthrene series, fluoranthene, pyrene, and chrysene. This indicates that these aromatics were removed and/or introduced into these shallow sub-bottom
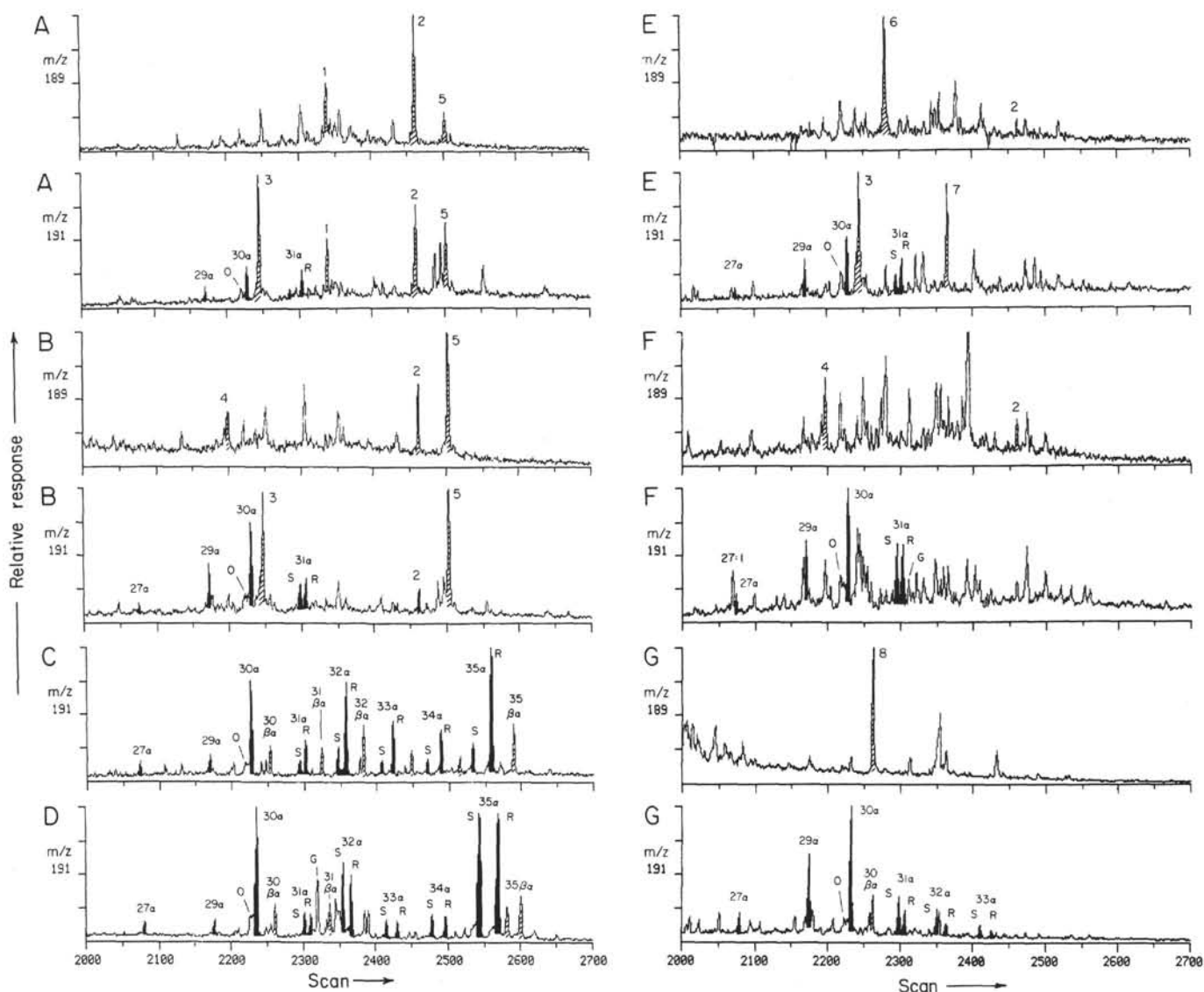
Figure 11. Representative mass fragmentograms of m/z 189 and 191 for the triterpenoid hydrocarbons in the bitumen of Leg 139 sediments. **A.** Sample 139-858D-1H-1, 0 cm. **B.** Sample 139-858B-1H-1, 48–52 cm. **C.** Sample 139-858C-2H-CC. **D.** Sample 139-858C-3H-1, 44–45 cm. **E.** Sample 139-858D-1H-4, 146–150 cm. **F.** Sample 139-858D-4R-CC. **G.** Sample 139-858A-1H-1, 149–150 cm. (1 = 17β(H)-hop-21-ene; 2 = diploptene; 3 = 17β(H)-22,29,30-trisnorhopan-21-one; 4 = hop-17(21)-ene; 5 = 17β(H),21β(H)-homohopan-31-ol; 6 = fernene; 7 = unknown C_{30} triterpane; 8 = unknown C_{30} triterpene; O = oleananes; G = gammacerane; iα = 17α(H),21β(H)-hopane series, with S and R entantiomers at C-22; iβα = 17β(H),21α(H)-hopane series, i.e., moretanes.)

sediments by aqueous fluids and that the lower molecular weight aromatics are depleted because of their greater water solubility (Kawka and Simoneit, 1990).

The phenanthrene to methylphenanthrenes (P/MP) ratio and the methylphenanthene indices, MPI 1 and MPI 2, were calculated according to Radke and Welte (1983). The ranges for all samples are P/MP = 0.14 to 1.35, MPI 1 = 0.24 to 1.66, and MPI 2 = 0.34 to 1.91 (Table 3). The higher alkyl homologs are present at typically decreasing concentrations, as observed for other hydrothermal petroleums, and the indices are also similar (Kawka and Simoneit, 1990; Kvenvolden and Simoneit, 1990). A dominant peak in the m/z 234 fragmentograms has a mass spectrum (m/z 101 (10), 189 (20), 190 (10), 191 (10), 202 (25), 203 (28), 204 (30), 217 (10), 219 (100), 220 (18), 234 (60), 235 (11)) that fits for retene or 1,7-dimethyl-8-ethylphenanthrene (XXIII). Retene has a terrestrial source and the latter compound could derive from marine algae (e.g., tasmanites; Simoneit et al., 1990). Coinjection of authentic standards is needed to confirm the compound identity.

The higher molecular weight PAHs are comprised mainly of benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, indenopyrene, benzo(ghi)perylene, coronene, and unknowns of molecular weight 326 (Fig. 13). There are seven compounds of molecular weight 326 that have been assigned structures based on emission and excitation spectra in an extract from carbon black (Peadon et al., 1980). Possible structural suggestions for these unknown compounds in the Leg 139 samples are tribenzo[a,cd,jk]pyrene (XXIV), dibenzo[b,pqr]perylene (XXV), naphtho[1,2,3,4-ghi]perylene (XXVI), dibenzo[cd,lm]perylene (XXVII), and naphtho[8,1,2-bcd]perylene (XXVIII), but confirmation would be necessary with authentic standards.

The presence of the analogs with a five-membered alicyclic ring (e.g., benzofluoranthenes, indenopyrene), as well as the other pericondensed aromatic hydrocarbons, confirms the high-temperature origin of these PAHs (Simoneit and Lonsdale, 1982; Blumer, 1975; Scott, 1982; Simoneit, 1984). The only trend observed in the PAH distributions from immature to mature samples (cf. Figs. 13A vs. 13B or 13C) is the relative decrease of perylene vs. benzofluoranthenes and
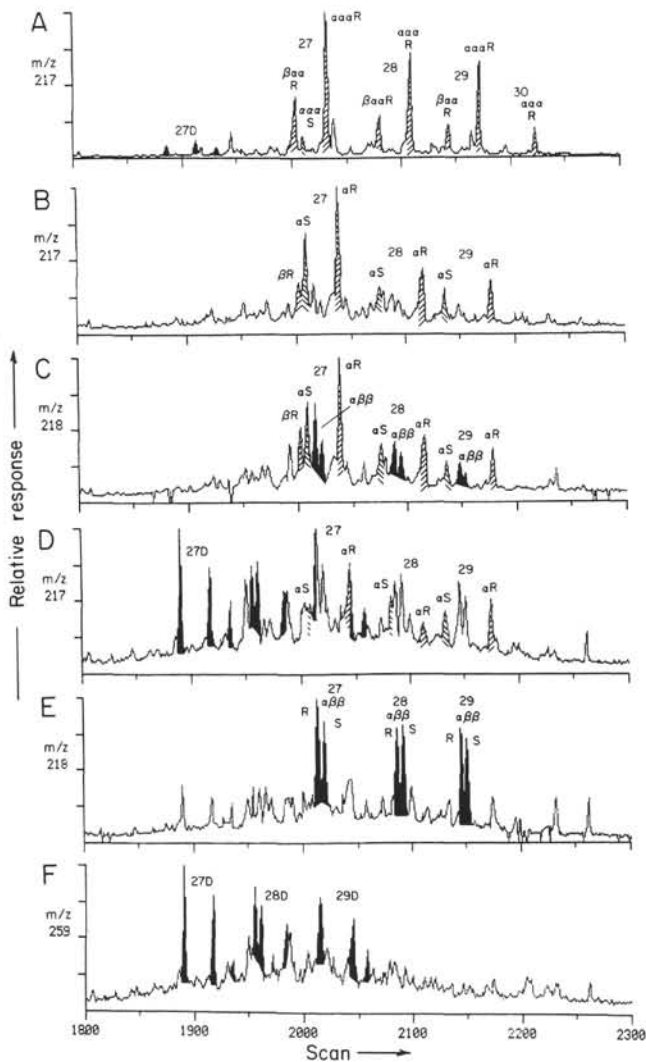
Figure 12. Representative mass fragmentograms (m/z 217, 218, and 259) for the steranes in the bitumen extracts of Leg 139 sediments. **A.** Sample 139-858C-2H-CC (**B**, m/z 217; and **C**, m/z 218). Sample 139-858C-3H-1, 44–45 cm (**D**, m/z 217; **E**, m/z 218; **F**, m/z 259). Sample 139-858A-1H-1, 149–150 cm ($\alpha\alpha\alpha$ or $\alpha = 5\alpha(H),14\alpha(H),17\alpha(H)$-steranes, $\beta\alpha\alpha$ or $\beta = 5\beta(H),14\alpha(H),$ $17\alpha(H)$ configuration, $\alpha\beta\beta = 5\alpha(H),14\beta(H),17\beta(H)$ configuration. S and R are diastereomers at C-20. D = diasteranes. Numbers refer to the carbon skeleton.

Figure 13. Salient features of the PAH distributions in samples from Leg 139. **A.** Sample 139-855D-4R-CC. **B.** Sample 139-858B-1H-2, 31–32 cm. **C.** Sample 139-858B-1H-2, 42–44 cm. (Peak numbers are: 1 = perylene, 2 = benzofluoranthene, 3 = benzo(e)pyrene, 4 = benzo(a)pyrene, 5 = indenopyrene, 6 = benzo (ghi)perylene, 7 = coronene, 8 and 9 = unknowns m.w. 326.)

reflects the content of PAHs with higher molecular weight and ranges from 0.02 to 6.7.

Implications

Although the organic matter content (TOC ranges from 0.0% to 1.2%; mean values: Site 855, 0.47%; Site 856, 0.34%; Site 857, 0.36%; Site 858, 0.32%; overall mean = 0.37%; Davis, Mottl, Fisher, et al. [1992]) is low for all sites, maturation and catagenesis occurred because of the hydrothermal activity. Maturation occurs in situ as accelerated diagenesis of the immature organic matter with the bio-marker precursors to catagenesis, yielding hydrothermal petroleum at Sites 856 and 857. Only accelerated diagenesis due to enhanced heat flow is observed in the sediments of Site 855. At Site 858 both hydrothermal petroleum generation and migration are observed, and based on the diverse hydrocarbon signatures, migration occurs more laterally rather than vertically, which results in discrete bitumen intervals.

The source organic matter in Middle Valley sediments is enriched in terrestrial detritus and thus the kerogen is inferred to be depleted in aliphatic moieties, in contrast to the aliphatic-rich marine organic matter in Guaymas Basin. Hydrothermal alteration of this Middle Valley organic matter yields high concentrations of hydrocarbons $>n$-C_{15}, and because of the low TOC content the maturation proceeds to a CPI of <1.0 for the n-alkanes (i.e., a strong even-carbon-number predominance). The origin of the excess of the even-carbon-numbered n-alkanes from fatty alcohols was inferred but could not be proven with these data. Maturation resulting from elevated temperatures is also evident in the ratios of Pr/Ph, Pr/n-C_{17}, and Ph/n-C_{18}. The isoprenoid hydrocarbons are lost from the system more rapidly than the n-alkanes and/or are overwhelmed by newly generated n-alkanes as the temperature rises.

The alteration of biomarkers from the natural product precursors to the geological products occurs according to the respective temperature regimes at all sites. The major precursor compound classes that were used as markers are sterols, terrigenous triterpenoids, and microbial hopanoids. Their major alteration products are saturated hydrocarbons (steranes and triterpanes) derived from reductive processes via various

benzopyrenes (from a ratio of 62 to 0.01, Table 3). This is the same trend as described for the Guaymas Basin sediments and hydrothermal petroleums (Baker and Louda, 1982; Simoneit and Philp, 1982; Simoneit et al., 1984; Kawka and Simoneit, 1990). Perylene is generated by diagenetic processes at depth but is not stable at catagenetic temperatures (Louda and Baker, 1984; Kawka and Simoneit, 1990). Minor amounts of fluoranthene and pyrene are present in highly variable ratios (fluoranthene/pyrene range 0.003 to 0.56, Table 3). Significant concentrations of the benzopyrenes are present in most samples. The ratio of benzo(a)pyrene to benzo(e)pyrene (BaP/BeP, Table 3) has been used to gauge the extent of atmospheric secondary oxidation of the PAH once formed, because BaP is less stable than BeP (Lane, 1989; Nielsen et al., 1984). At the seafloor these compounds may be reactive to other oxidizing agents, but with similar reactivities. The BaP/BeP range for these samples is from <0.02 to 1.0, where a typical precursor value is >0.4 and those samples with a ratio <0.4 have had an oxidative or thermal loss of BaP. The ratio of coronene to the total benzofluoranthenes plus BeP plus BaP (Table 3)

Table 3. Presence and maturity parameters of aromatic hydrocarbons in Leg 139 samples.

Core, section, interval (cm)	Depth (mbsf)	Presence of PAH[a]			Phenanthrene series[b]			Fluoranthene/ pyrene	Perylene/ benzofluoranthene + BaP + BeP	BaP/BeP	Coronene/BaP + BeP + benzofluoranthene
		Low molecular weight (<228)	Intermediate molecular weight (<300)	High molecular weight (>300)	P/MP	MPI 1	MPI 2				
139-855D-											
4R-CC	108.5	+	+	—	0.26	1.00	1.20	0.500	62.00		1.90
139-856A-											
2H-CC	12.0	+	+	—	0.83	0.24		0.560	50.00		0.03
139-857A-											
1H-1, 0–1	1.9	—	+	—							
8H-2, 95–99	62.0	+	+	—	0.55	0.78	0.82	0.310		<0.02	0.57
139-857C-											
6R-CC	95.0	+	+	—	0.26	0.94	0.91	0.300	11.00		0.60
9R-CC	124.0	+	+	—						<0.02	4.90
48R-1, 73–75	409.0	+	+	—					0.10	0.03	0.02
139-858A-											
1H-1, 149–150	1.5	+	+	—	0.47	0.67	0.74	0.140	1.80		0.33
4H-4, 52–56	26.5	+	+	—	0.40	1.46	1.63	0.500	0.16	0.20	0.05
6H-CC	50.0	—	+	+					0.15	1.0	6.70
139-858B-											
1H-1, 48–52	0.5	+	+	+	0.14	1.66	1.57	0.400	0.06	0.18	1.30
1H-2, 31–32	1.8	+	+	+					0.11	0.28	0.82
1H-2, 42–44	1.9	+	+	+	0.47	1.03	0.91	0.250	0.10	0.77	3.30
139-858C-											
2H-5, 71–73	10.2	+	+	—				0.170		<0.02	0.60
2H-CC	13.0	+	+	+	1.35	0.79	0.91	0.003	0.01	0.13	4.80
3H-1, 44–45	13.5	+	+	+						0.06	1.60
3H-2, 68–69	15.0	—	+	+						0.03	4.20
3H-2, 110–115	15.5	—	+	+					0.03	0.12	1.90
139-858D-											
1H-1, 0–1	0.0	+	+	+	0.49	0.89	0.99	0.20	0.31	0.10	2.20
1H-1, 67–70	0.7	+	+	—	0.71	0.68	0.91	0.36	4.00	0.50	1.30
1H-4, 146–150	6.0	+	+	—	0.86	0.41	0.34	0.48	5.60	0.12	0.46
2H-CC, 37–40	18.8	+	+	+	0.53	1.45	1.91	0.06		0.20	4.80
3P-1, 54–56	19.3	+	+	+	1.17	0.77	1.00	0.08		0.23	4.50

[a] Presence indicated as +, not detectable as —.

[b] P/MP = phenanthrene/methylphenanthrenes, $MPI\ 1 = \dfrac{1.5(3MP + 2MP)}{P + 9MP + 1MP}$ (Radke and Welte, 1983), $MPI\ 2 = \dfrac{3(2MP)}{P + 9MP + 1MP}$ (Radke and Welte, 1983).

oxygenated intermediates (e.g., ketones). The biomarkers consist of a major terrestrial component as reflected by the enrichment of the C_{29} steroidal compounds and the terrigenous triterpenoids. As the thermal stress increases the biomarkers are cracked to smaller moieties; for example, the C_{32} and C_{35} hopanes are converted to C_{27} and C_{29} norhopanes. At temperatures in excess of ~280°–300°C the biomarkers are destroyed.

All samples contain PAHs as is typical for hydrothermal petroleum (Simoneit, 1984; Kawka and Simoneit, 1990; Simoneit et al., 1992). The low molecular weight PAHs and alkyl-PAHs (e.g., alkylnaphthalenes, phenanthrene) are depleted in the deeper sediment sections where the temperature is higher and are found enhanced in shallow immature sediments of all Leg 139 sites. This indicates extensive water/hydrothermal fluid washing of these sections, which removed the lower molecular weight PAHs because of their greater solubility and redistributed them upward, although there is no enriched interval at any depth. The major PAHs are higher molecular weight (>250 dalton) components and in contrast to other hydrothermal petroleums (e.g., Escanaba Trough, Kvenvolden and Simoneit, 1990; Guaymas Basin, Simoneit, 1984), there are significant concentrations of unknown PAHs with molecular weights >300. These PAHs represent products from the high-temperature alteration of organic matter. The PAH mixture in the Middle Valley sediments is interpreted to derive from fluid contact in excess of 350°C and selective concentration by removal of the lower molecular weight constituents.

CONCLUSIONS

Organic compound maturation is observed at all Leg 139 sites. At locales with high heat flow resulting from hydrothermal activity,

the immature organic matter is efficiently converted to hydrothermal petroleum.

The compound signatures in sediments from Sites 855 and 856 reflect in situ accelerated diagenesis of the biological precursors without product migration. The biomarker tracers indicate an enrichment of terrestrial components, with a significant amount of biomarkers derived from marine autochthonous sources. Fluid migrations through these sediments have added minor amounts of dissolved organic compounds derived from higher temperature alteration (e.g., low-molecular-weight aromatic hydrocarbons) to the in-situ components, resulting in mixtures of bitumen with various maturities.

The organic matter in sediments at Site 857 has also experienced in-situ accelerated diagenesis and catagenesis, yielding fully mature bitumen at depth. One interval appears to contain a minor amount of migrated bitumen, based on elevated yield (Hole 857C, 82 mbsf). The biomarkers indicate a significant input of terrestrial components with the predominant material derived from marine autochthonous sources. Maturation has proceeded to yield n-alkanes with a strong even-carbon-number predominance, where the CPI varies from >1.0 in immature sections, to one, and then <1.0 in the fully mature sections. Due to the low TOC these sediments do not generate high amounts of hydrocarbons from kerogen, as is the case in Guaymas Basin, thus revealing the unique even-to-odd preference of the n-alkanes in the mature samples.

The sedimentary organic matter at Site 858 has been converted to hydrothermal petroleum. Relatively immature bitumen is encountered only in the upper few meters of the holes. The biomarkers in the upper sections show a moderate input of terrestrial components, with products derived predominantly from autochthonous marine sources. Maturation has progressed to form n-alkanes with a strong even-

carbon-number predominance (CPI <1.0) at depth in Holes 858A, 858B, 858C, and 858D. There is an overmature bitumen interval in Hole 858A at about 50 mbsf. The different hydrothermal petroleum intervals (zones with high bitumen concentrations) have many compositions (condensates to asphalts) and maturities, reflecting formation in various temperature windows followed by lateral migration into the sediment sections sampled.

The biomarkers are present as precursors, intermediates, and fully mature products. The sterols are altered to stenones, stanones, and then steranes; the terrigenous triterpenols proceed to triterpenones, triterpenes, and then triterpanes; and the bacterial hopenes and hopanols are converted to hopanes. Maturation of the biomarkers begins here with the biogenic precursors and results in their interconversion to the thermodynamically most stable configurations as known in conventional sedimentary basins with mature organic matter. Cracking reactions degrade higher molecular weight compounds to smaller molecules (e.g., waxy oil to condensate, C_{35} hopanes to the C_{29} and C_{27} nor compounds).

The high-temperature components in these bitumens are PAHs, as is the case for most hydrothermal petroleums studied to date. These samples contain only traces of low molecular weight PAHs and alkyl PAHs (e.g., phenanthrene/alkylphenanthrenes) and high concentrations of heavy PAHs. This is interpreted to result from the high solubility of the smaller PAHs in warm water and consequent removal from the sediments by pore-fluid flow. Such a process would then concentrate the high molecular weight PAHs in these sediment associated bitumens.

ACKNOWLEDGMENTS

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GLOSSARY

Bitumen. In the widest sense, any natural hydrocarbon ranging in state from rigid or highly viscous (asphalt), through the less viscous (tarry) to liquid (petroleum) varieties.

Catagenesis. Thermal alteration of organic material in sediments by increasing temperature. Catagenesis in conventional basins covers the temperature range between diagenesis and rock metamorphism, approximately 50°–200°C. Catagenesis occurs in hydrothermal systems in a higher temperature window (100°–400°C) over brief geological times and overlaps with diagenesis.

Diagenesis. Biological, physical, and chemical alteration of the organic debris in sediments without a pronounced effect from rising temperature. Diagenesis is accelerated due to the higher than normal heat flow in hydrothermal regions and the surrounding sediments, altering lipids and other immature organic detritus to geologically more mature products. The process can in such cases overlap with catagenesis.

Hydrothermal petroleum (bitumen). Product from organic matter alteration by contact with hydrothermal fluids. It consists of compounds generated over a greater temperature window (100°–400°C) than observed for conventional petroleums and can proceed from the biological precursors that have not undergone diagenesis. Fluid extraction and migration of hydrothermal petroleum from the source sediment is highly efficient.

Kerogen. Disseminated organic matter in sedimentary rocks which is insoluble in nonoxidizing acids, bases, and organic solvents. The organic matter initially deposited with unconsolidated sediments is not kerogen but a precursor that is converted to kerogen during diagenesis.

Lipids. A broad term that includes all oil-soluble, water-insoluble organic substances such as fats, waxes, fatty acids, sterols, pigments, and terpenoids.

APPENDIX

Chemical Structures Cited

I. Sterols
R = H,CH₃,C₂H₅

II. 24-Methylcholesta-5,22-dien-3β-ol

XI. 17β(H),21β(H)-Bishomohopan-32-ol

XII. 17β(H)-22,29,30-Trisnor-hopan-21-one

III. 4-Sten-3-ones
R = H,CH₃,C₂H₅

IV. Stan-3-ones
R = H,CH₃,C₂H₅

XIII. Fern-9(11)-ene

XIV. 17β(H),21β(H)-Hopanes
R = H, CH₃ - C₆H₁₃

XV. 17β(H),21α(H)-Hopanes
R = H, CH₃ - C₆H₁₃

V. Ursenoids
R = OH α-amyrin
  = O α-amyrone

VI. Oleanoids
R = OH β-amyrin
  = O β-amyrone

VII. Olean-12-ene

XVI. 17α(H),21β(H)-Hopanes
R = H, CH₃ - C₆H₁₃

XVII. 18α/β(H)-Oleanane

XVIII. 3,3,7-Trimethyl-1,2,3,4-tetrahydrochrysene

VIII. Diploptene

IX. 17β(H)-Hop-21-ene

X. Hop-17(21)-ene

XIX. Gammacerane

XX. 5α(H),14α(H),17α(H)-Steranes
R = H,CH₃,C₂H₅

XXI. 5α(H),14β(H),17β(H)-Steranes
R = H,CH₃,C₂H₅

XXII. 10α(H),13β(H),17α(H)-Diasteranes
R = H,CH₃,C₂H₅

XXIII. 1,7-Dimethyl-8-ethyl-phenanthrene

XXIV. Tribenzo[a,cd,jk]pyrene

XXV. Dibenzo[b,pqr]perylene

XXVI. Naphtho[1,2,3,4-ghi]-perylene

XXVII. Dibenzo[cd,lm]-perylene

XXVIII. Naphtho[8,1,2-bcd]-perylene