

Hydrothermally Derived Petroleum: Examples from Guaymas Basin, Gulf of California, and Escanaba Trough, Northeast Pacific Ocean¹

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ABSTRACT

Petroleum is associated with sulfide-rich sediment at two active oceanic spreading axes in the northeast Pacific Ocean. In the Guaymas Basin, a spreading axis in the Gulf of California, petroleum having a wide range of compositions forms by hydrothermal alteration of organic matter in Quaternary sediment composed mainly of marine diatomaceous ooze and muddy turbidites. In Escanaba Trough, at the southern end of the Gorda Ridge spreading axis offshore northern California, petroleum is formed by hydrothermal processes acting on mainly terrigenous organic material in Quaternary turbiditic river-derived sediment. Comparisons of the distributions of hydrocarbons—n-alkanes, isoprenoids, terpanes, steranes, and aromatics—show that chemical differences among four petroleum samples are such that two samples from Guaymas Basin can be distinguished from two samples from Escanaba Trough. Distinguishing characteristics resulting from differences in sources include n-alkane distributions and certain sterane ratios; distinguishing characteristics resulting from differences in thermal histories of the organic matter include hopane and sterane epimer ratios and various distributions of polycyclic aromatic hydrocarbons. These oils differ from conventionally derived petroleum in that they are admixtures of products generated over a wide range of thermal regimes, and their generation, expulsion, and migration occurred simultaneously over an “instantaneous” geological time period. The potential economic significance of hydrothermally derived

petroleum is uncertain, but the fact that petroleum can form at active oceanic spreading axes adds a new facet to understanding the processes of petroleum generation, expulsion, and migration.

INTRODUCTION

Both conventionally derived and hydrothermally derived petroleum results mainly from the thermal alteration of sedimentary organic materials. For conventionally derived petroleum, however, this process takes place over long periods of geologic time, exceeding at least 1 m.y. at geothermal temperatures between about 50 and 175°C (Hunt, 1979). In contrast, the formation of hydrothermally derived petroleum takes place at time and temperature scales quite different from conventional petroleum generation. Hydrothermally derived petroleum found at active oceanic spreading axes is believed to form “instantaneously” with respect to geologic time at temperatures reaching at least 315°C (Simoneit, 1985; 1990; Didyk and Simoneit, 1989). The exact time-temperature history of hydrothermal petroleum formation has not been defined, but intense heating at a temperature of about 300 to 350°C for periods as short as about 100 yr has been suggested as one possible scenario (Kvenvolden et al., 1988).

In the northeastern part of the Pacific Ocean is a system of spreading axes and transform faults that extends along the western coast of North America from the East Pacific Rise off Mexico to the Explorer Ridge off Canada, and includes the San Andreas Fault in California (Figure 1). Hydrothermal processes are active at these spreading axes as evidenced by the presence of numerous sulfide deposits (Koski et al., 1987). Thick sequences of sediment are present in troughs of ridge axes in the Guaymas Basin (Southern and Northern Troughs), Gorda Ridge (Escanaba Trough), and Juan de Fuca Ridge (Middle Valley), whereas elsewhere in these systems of spreading axes, the associated troughs generally are sediment starved. Hydrothermally derived petroleum has been discovered in the Southern and Northern Troughs of Guaymas Basin (Simoneit and Lonsdale, 1982) and in the Escanaba Trough portion of Gorda Ridge (Kvenvolden et al., 1986), where thick sedimentary deposits provide a source of organic matter from which the petroleum was generated. In this paper, we compare petroleum geochemical aspects of oil from these two

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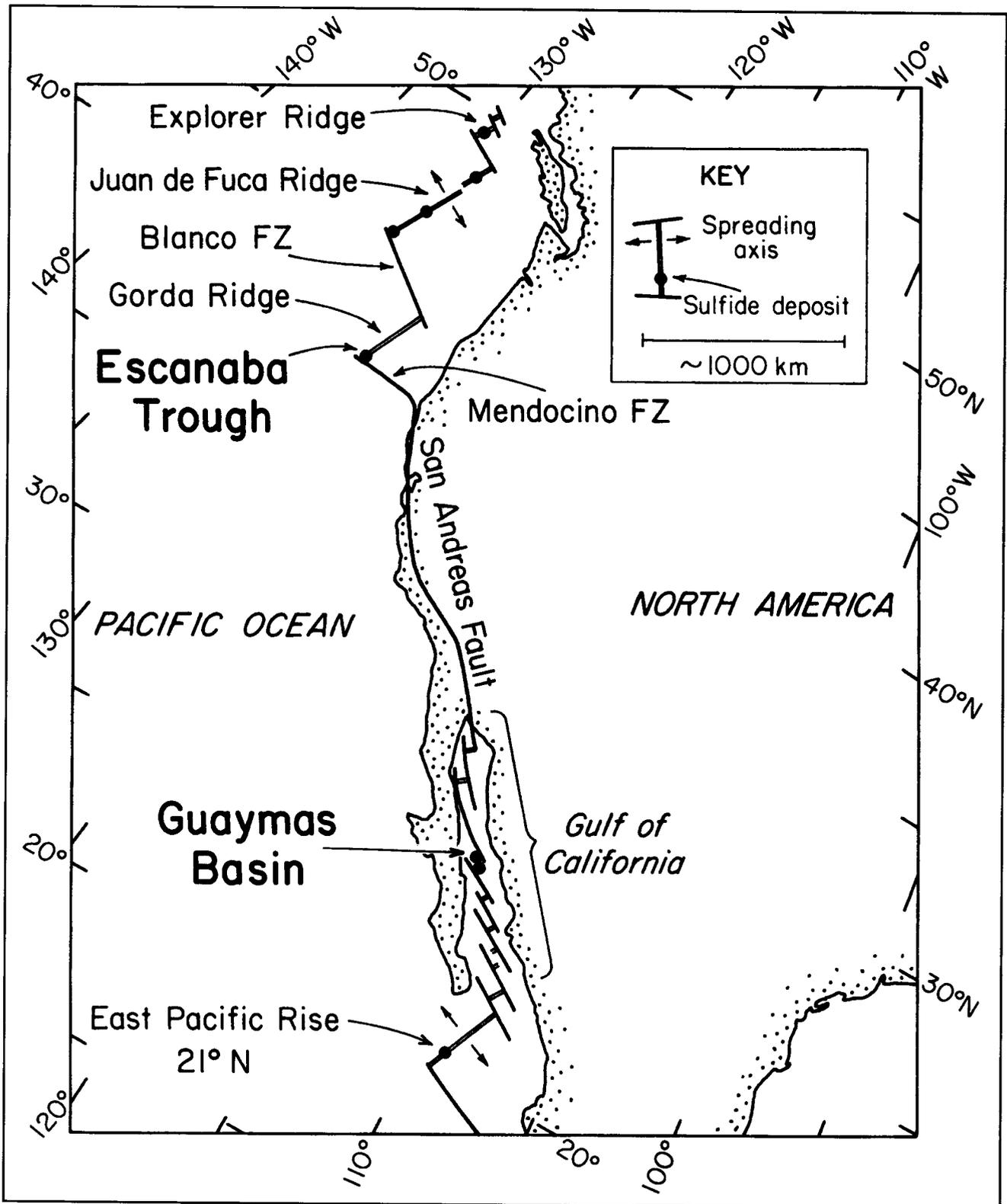


Figure 1—Location map showing Escanaba Trough and Guaymas Basin in the system of spreading axes and transform faults that extends along the western coast of North America. FZ = fracture zone. Modified from Koski et al. (1987).

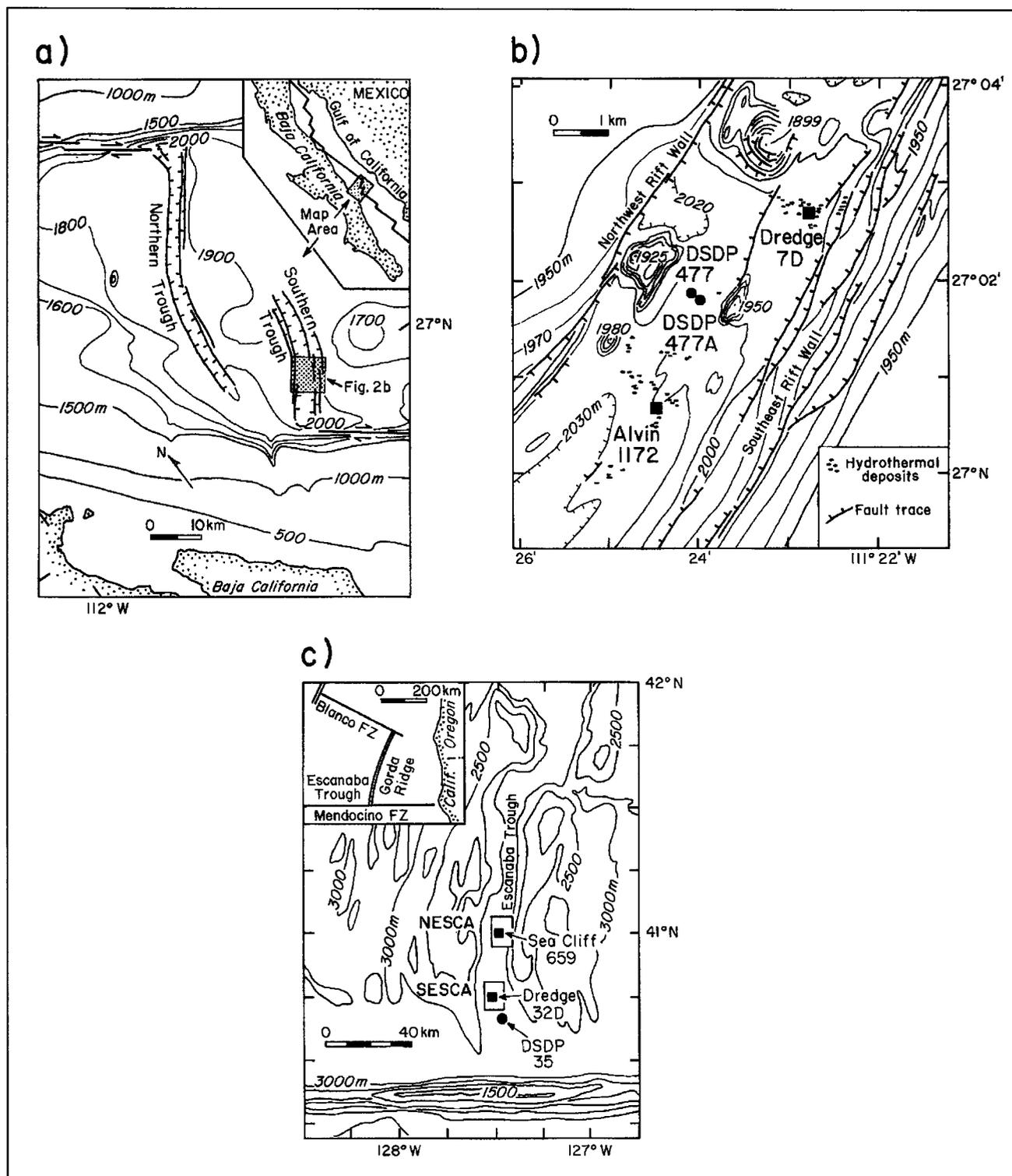


Figure 2—Location maps showing sample sites in the Guaymas Basin and Escanaba Trough. (a) Map of the Guaymas Basin locating northeast-trending Northern and Southern Troughs and area of sample sites. Modified from Lonsdale and Becker (1985). (b) Bathymetric and structural map of the Southern Trough showing distribution of hydrothermal deposits and location of sample sites (Dredge 7D and Alvin 1172). DSDP drill sites are shown for reference. Modified from Simoneit and Lonsdale (1982). (c) Bathymetric map of the Escanaba Trough showing sample sites, Sea Cliff 659 in NESCA survey area, and dredge 32D in SESCA survey area, and DSDP site is shown for reference. Modified from Koski et al. (1988).

regions, show some of the chemical differences between hydrothermally derived and conventionally derived petroleum (i.e., petroleum normally found in a reservoir), and suggest that former oceanic rifts may be sites of petroleum formation and occurrence. The economic significance of such sites and the process are not yet defined.

GEOLOGIC SETTING

The boundary between the Pacific and North American plates is characterized by a connected series of oceanic spreading axes and transform faults that link these plates, by means of the San Andreas transform fault and the Mendocino fracture zone, to the Pacific and Juan de Fuca plate boundary which is also characterized by a series of spreading axes and transform faults. Guaymas Basin, in the Gulf of California, occupies part of this tectonic system where Baja California is separating from mainland Mexico (Moore and Curray, 1982). This basin contains two overlapping en echelon troughs (Figure 2a) floored with as much as 500 m of semi-consolidated organic-rich diatomaceous ooze and turbiditic terrigenous silt of Quaternary, possibly to late Tertiary, age (Curray et al., 1982; Koski et al., 1985). In the Northern and Southern Troughs, the sediment pile has been intruded by a series of basaltic sills and plugs (Lonsdale and Lawver, 1980; Lonsdale et al., 1980; Einsele et al., 1980; Lonsdale, 1985). Hydrothermal vents; complex deposits of sulfide, sulfate, silicate, and carbonate minerals; colonies of tube worms; and bacterial mats are present at water depths of about 2000 m (Lonsdale and Becker, 1985; Koski et al., 1987; Peter and Scott, 1988). About 40 sediment samples containing hydrothermally derived petroleum have been recovered from the Southern Trough by means of dredge and submersible; analyses of these samples show that the petroleum has a wide variety of compositions (Simoneit, 1985; Kawka and Simoneit, 1987). From this collection of samples, two Southern Trough samples have been used to provide the chemical detail for comparison (Figure 2b).

North of the Mendocino fracture zone, the system of spreading axes and transform faults is composed of the Gorda, Juan de Fuca, and Explorer ridges. Gorda Ridge is located 200 to 300 km west of southern Oregon and northern California, entirely within the exclusive economic zone of the United States. The southernmost 90-km segment of the Gorda Ridge, called Escanaba Trough, is filled with as much as 500 m of Quaternary turbidite and hemipelagic sediment derived mainly from the drainage of the Klamath and Columbia rivers (McManus et al., 1970; Moore, 1970; Vallier et al., 1973).

Igneous rocks intrude the sediment fill, producing discrete edifices with both intrusive and extrusive components (Morton et al., 1987). Dredging and submersible dives recovered basaltic lava, manganese oxide and barite crusts, talc, and massive sulfides, both pyrrhotite rich and polymetallic (Clague and Holmes, 1987; Benninger and Koski, 1987), thus providing evidence for hydrothermal activity at this site. In addition, four sediment samples intermixed with petroleum and sulfide mineralization were recovered from the two areas at water depths of about 3200 m (Figure 2c) within Escanaba Trough (Kvenvolden et al., 1987). We consider two of these Escanaba Trough samples in detail.

EXPERIMENTAL PROCEDURE

The two samples from the Southern Trough of Guaymas Basin used for our study came from a 1980 dredge haul and from a 1982 submersible dive by DSV *Alvin*. Sample 7D-2B (Dredge 7D, Figure 2b) is massive sulfide collected in a dredge that also contained fragments of claystone, barite, talc, other hydrothermal minerals, and worm tubes. Many of the fragments were oil stained and had a petroleum odor (Simoneit and Lonsdale, 1982). Sample 1172-4 (Alvin 1172, Figure 2b) came from a submersible-dive collection of rock fragments from unspecified sources; however, in the same collection were mound fragments, mound crusts, fragments of a chimney, and red wax (Kawka and Simoneit, 1987). Samples 7D-2B and 1172-4 were obtained at locations about 5 km apart (Figure 2b).

The two samples from Escanaba Trough came from locations about 30 km apart (Figure 2c). Sample 32D-2 (Dredge 32D, Figure 2c) was dredged in 1985 from the flank of a volcanic edifice and is composed of fine-grained sandstone intermixed with massive polymetallic sulfide and petroleum (Kvenvolden et al., 1986). In 1986, the U.S. Navy submersible DSV *Sea Cliff* collected in one basket, fragments of a dormant chimney made of pyrrhotite-rich massive sulfide. Fragments from the sediment-water interface contained intercalated pellets of sediment. Sample 659-R1 (Sea Cliff 659, Figure 2c) came from the base of this chimney and contained partly indurated mudstone and siltstone with disseminated pyrrhotite-rich sulfides and had a strong petroleum odor.

These samples were extracted with dichloromethane, and the extracts were subjected to standard organic geochemical procedures including liquid chromatography, gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS). Details of the procedures used for the Guaymas Basin samples are in Simoneit and Lonsdale (1982) and

Table 1. Composition of Extracts of Hydrothermal Petroleum*

	Sample No.	Type of Sample	Aliphatic Hydrocarbons (%)	Aromatic Hydrocarbons (%)	Nonhydrocarbons (%)
Guaymas Basin	7D-2B	Dredge	5	42	53
	1172-4	Dive	71	12	17
Escanaba Trough	32D-2	Dredge	2	44	54
	659-R1	Dive	9	62	29

*Fractions determined gravimetrically.

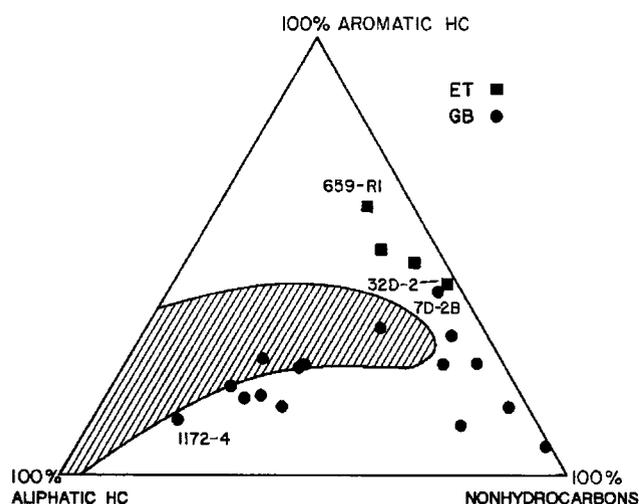


Figure 3—Ternary diagram representing gross (C_{15+}) compositions of hydrothermal petroleum as percentages of each of three major compound classes determined gravimetrically (Table 1). Guaymas Basin samples indicated by dots; Escanaba Trough samples indicated by squares. Samples used in this study are designated by number. Typical conventional petroleum falls within hachured area (Tissot and Welte, 1984). Modified from Kawka and Simoneit (1987).

Kawka and Simoneit (1987). For the Escanaba samples, the procedures were adapted from Kvenvolden et al. (1985, 1986). Extracts were separated into three fractions—aliphatic hydrocarbons, aromatic hydrocarbons, and nonhydrocarbons. After analysis by GC, the aliphatic and aromatic hydrocarbon fractions were further analyzed by high-resolution GC/MS. Single ion monitoring of mass-to-charge ratio (m/z) 191 and 217 produced mass fragmentograms from which terpanes and steranes, respectively, were identified and compared. (For a summary of background geochemical information on terpanes and steranes, see, for example, Johns, 1986.) Aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAH), were identified by comparison with authentic standards.

COMPARISON OF RESULTS

The normalized percentage compositions of the fractions from liquid chromatography of each sample are shown in Table 1 and plotted on a ternary diagram (Figure 3), where the gross (C_{15+}) composition of all analyzed petroleum-bearing samples from Guaymas Basin (GB) and Escanaba Trough (ET) are also shown. Selection of the four samples for this comparison study was based on type of sample and gross compositional considerations. Because the sample set from GB was ten times larger than from ET, we chose only two samples from each set to reduce the bias of the former. These samples were considered to be representative of the two areas and were examined in detail to determine if, at a molecular level, the petroleum from the two areas could be distinguished. Samples GB-7D-2B and ET-32D-2 are both dredge hauls; the gross

composition of each is very similar (Figure 3). GB-1172-4 and ET-659-R1 were both collected by means of submersibles. The former is an aliphatic-rich specimen (Figure 3), and the latter is the only sample from Escanaba Trough for which its in situ location is accurately known, i.e., the base of a dormant hydrothermal chimney.

Normal Alkanes and Isoprenoids

The distributions of *n*-alkanes and isoprenoid hydrocarbons are illustrated in the gas chromatograms shown in Figure 4, and ratios related to these distributions are listed in Table 2. The abundances of compounds smaller than approximately n - C_{15} have been progressively decreased by the procedural effects of evaporation. These effects may have altered the calculated ratios of compounds in the low-molecular-weight range, but it is assumed that the ratios are valid for comparison purposes among the four oil samples because they were subjected to similar procedures. All samples contain a homologous series of *n*-alkanes beginning with about n - C_{13} ; the series extends to about n - C_{32} in the GB samples and to about n - C_{40} in the ET samples. The distributions of *n*-alkanes from n - C_{18} to n - C_{22} in all samples show a slight odd-carbon-number predominance to a slight even-carbon-number predominance ($OEP_{20} = 1.05$ to 0.95). [OEP is a measure of the odd-even predominance of homologous series of *n*-alkanes, as defined by Scalan and Smith (1970). The OEP subscript defines the center of the range of carbon numbers used in the calculation (Table 2).] At higher molecular weights, for example in the region of n - C_{27} , the GB samples show a slight odd/even predominance ($OEP_{27} = 1.01$ and 1.06), whereas the ET samples have a distinctive dominance of odd-carbon-numbered *n*-alkanes ($OEP_{27} = 1.13$ and 1.12).

Isoprenoid hydrocarbons, phytane (Ph) and pristane (Pr), and lower molecular weight members of this series (indicated by an asterisk in figures) are present in all samples. In these four samples, Pr/Ph ratios range from 0.9 to 1.8 (Table 2). The amount of n - C_{18} greatly exceeds the amount of phytane in all samples; the amount of n - C_{17} exceeds the amount of pristane in three of the four samples, the exception being ET-32D-2 (Table 2).

The samples from GB show the presence of a significant amount of chromatographically unresolved aliphatic hydrocarbons manifested as a chromatographic hump. The chromatograms from ET have a flat baseline, which indicates that most of the aliphatic hydrocarbons in these samples are not complex and are resolved by high-resolution GC into mainly *n*-alkanes and isoprenoid hydrocarbons. Branched alkanes and cycloalkanes are present in minor amounts.

Terpanes and Steranes

The dominant terpanes in both GB and ET samples are hopanes [17 α (H),21 β (H)-hopane series] and moretanes [17 β (H),21 α (H)-hopane series] (Figure 5). The $\alpha\beta$ -hopanes range from C_{27} to C_{35} (C_{28} absent) with the high-molecular-weight members of this series apparently more abundant in the ET samples. The $\beta\alpha$ -moretanes are also present as a homologous series beginning at C_{29} and extending to C_{35} . In

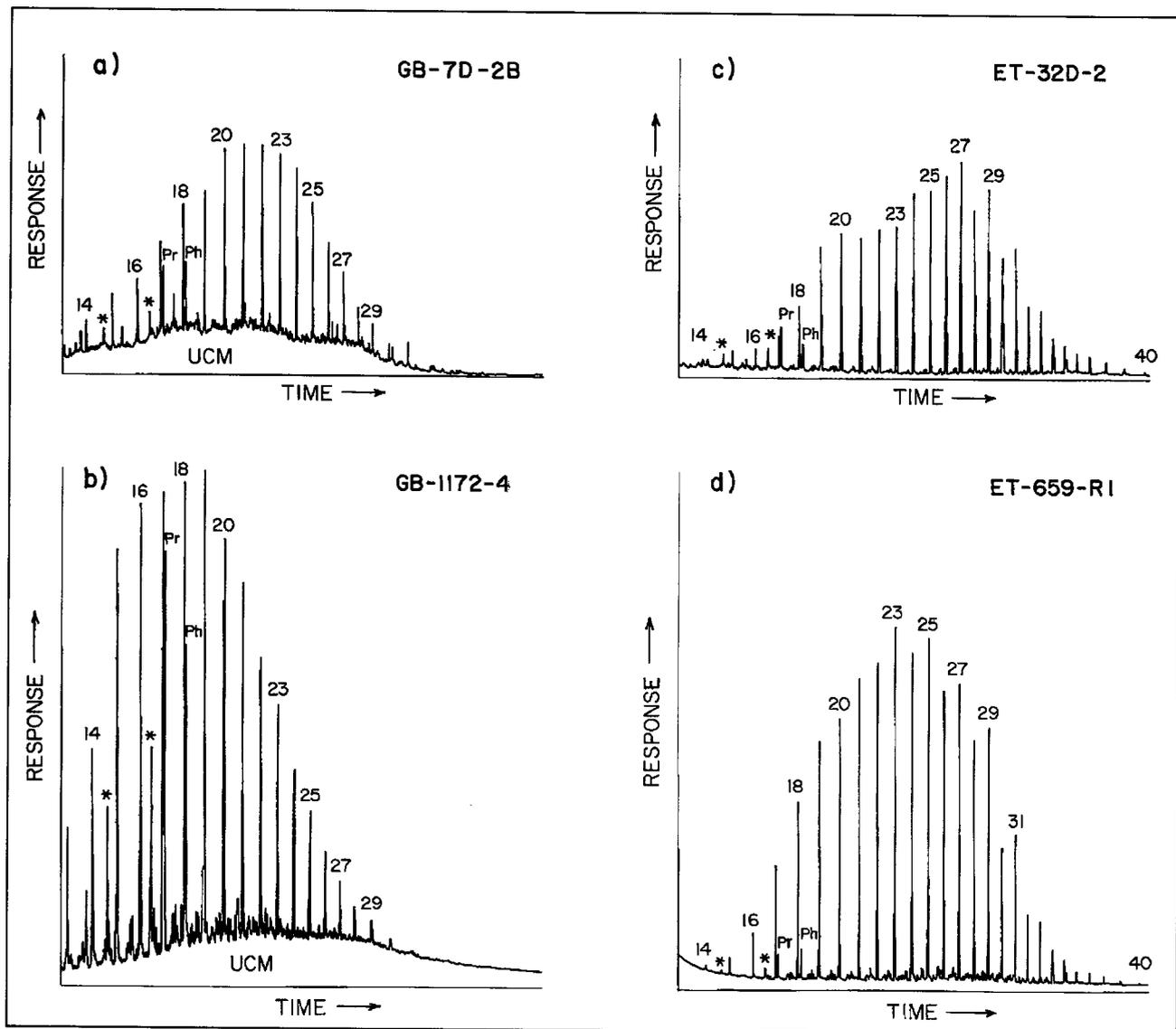


Figure 4—Gas chromatograms showing the distributions of n-alkanes (numbers specify the carbon number of molecules) and isoprenoid hydrocarbons in the Guaymas Basin (GB) and Escanaba Trough (ET) oils. Ph = phytane, Pr = pristane, asterisk = other isoprenoids. UCM = unresolved complex mixture.

addition to these compounds, the GB oils contain very minor amounts of $\beta\beta$ -hopanes and possibly hopenes. The ratios of various $\alpha\beta$ -hopanes and $\beta\alpha$ -moretanes are shown in Table 2. A pattern emerges in that, generally, for any given ratio, the values obtained from the two GB oils are similar as are the values obtained from the two ET oils, yet the values of the ratios for each area are different. For example, the T_m/T_s [$17\alpha(\text{H})$ -22,29,30-trisnorhopane/ $18\alpha(\text{H})$ -22,29,30-trisnorhopane] ratios for GB samples are 11 and 6.4, whereas for ET samples, they are 22 and 27. Likewise, the ratios of the sum of the C_{29} -, C_{30} -, and C_{31} -hopanes to the sum of the corresponding moretanes are 3.6 and 3.4 for GB samples and 2.0 and 1.6 for ET samples. The other ratios show similar groupings in which the GB ratios differ from the ET ratios.

The epimer ratios [$22\text{S}/(22\text{S}+22\text{R})$] of the C_{31}

[$17\alpha(\text{H}),21\beta(\text{H})$ -homohopane], C_{32} [$17\alpha(\text{H}),21\beta(\text{H})$ -bishomohopane], and C_{33} [$17\alpha(\text{H}),21\beta(\text{H})$ -trishomohopane] hopanes also provide consistent measures (Table 2), with the GB samples having an average value of 0.55 and ET samples a lower average value of 0.46.

Steranes are present as complex mixtures (Figure 6) with significant peak overlap making identifications of individual compounds difficult. However, it is evident from Figure 6 that the dominant sterane in all samples is $5\alpha(\text{H}),14\alpha(\text{H}),17\alpha(\text{H})$ -cholestane (20R). Values of ratios of 27R/29R [$\alpha\alpha\alpha$ -cholestane (20R)/24-ethyl- $\alpha\alpha\alpha$ -cholestane (20R)] are 1.4 and 2.2 for GB samples, whereas values of these ratios are 1.3 and 1.0 for ET samples (Table 2).

The ratios [$20\text{S}/(20\text{S}+20\text{R})$] of the C_{29} steranes are the only epimer ratios that could be measured with some confidence

Table 2. Molecular Ratios of Hydrocarbons*

	Guaymas Basin		Escanaba Trough	
	7D-2B	1172-4	32D-2	659-R1
OEP ₂₀	0.95	1.00	1.00	1.05
OEP ₂₇	1.06	1.01	1.13	1.12
Pr/Ph	1.0	1.4	1.8	0.90
Ph/n-C ₁₈	0.54	0.53	0.38	0.17
Pr/n-C ₁₇	0.73	0.69	1.20	0.22
$\frac{\Sigma 29,30,31H}{\Sigma 29,30,31M}$	3.6	3.4	1.8	1.6
30H/29H	1.6	2.2	0.71	0.98
30M/29M	1.7	2.9	1.2	1.4
T _m /T _s	11	6.4	22	27
S/(S+R) for 31H	0.56	0.53	0.48	0.46
S/(S+R) for 32H	0.57	0.57	0.48	0.42
S/(S+R) for 33H	0.54	0.54	0.49	0.42
27R/29R	1.4	2.2	1.3	1.0
27R/28R	1.7	2.1	2.5	2.1
28R/29R	0.86	1.0	0.52	0.48
S/(S+R) for 29Sterane	0.12	0.28	0.20	0.13
S/(S+R) for 27Diasterane	0.57	0.62	0.52	0.53

$$*OEP_{20} = \left[\frac{n-C_{18} + 6 \cdot n-C_{20} + n-C_{22}}{4 \cdot n-C_{19} + 4 \cdot n-C_{21}} \right] (-1) ;$$

$$OEP_{27} = \left[\frac{n-C_{25} + 6 \cdot n-C_{27} + n-C_{29}}{4 \cdot n-C_{26} + 4 \cdot n-C_{28}} \right] (+1) ;$$

Pr/Ph = Pristane/Phytane ;

$$\frac{\Sigma 29,30,31H}{\Sigma 29,30,31M} = \frac{C_{29} + C_{30} + C_{31}}{C_{29} + C_{30} + C_{31}} \frac{\text{Hopanes}}{\text{Moretanes}} ; \quad \frac{30H}{29H} = \frac{C_{30} \text{ Hopane}}{C_{29} \text{ Hopane}} ;$$

$$\frac{30M}{29M} = \frac{C_{30} \text{ Moretane}}{C_{29} \text{ Moretane}} ; \quad \frac{T_m}{T_s} = \text{defined in text} ;$$

S/(S+R) for 31H, 32H, and 33H, respectively = Hopane epimer ratios defined in text ;

$$\frac{27R}{29R} = \frac{C_{27} (20R) \text{ Sterane}}{C_{29} (20R) \text{ Sterane}} ; \quad \frac{27R}{28R} = \frac{C_{27} (20R) \text{ Sterane}}{C_{28} (20R) \text{ Sterane}} ; \quad \frac{28R}{29R} = \frac{C_{28} (20R) \text{ Sterane}}{C_{29} (20R) \text{ Sterane}} ;$$

S/(S+R) for 29 Sterane and 27 Diasterane, respectively = sterane and diasterane epimer ratios defined in text.

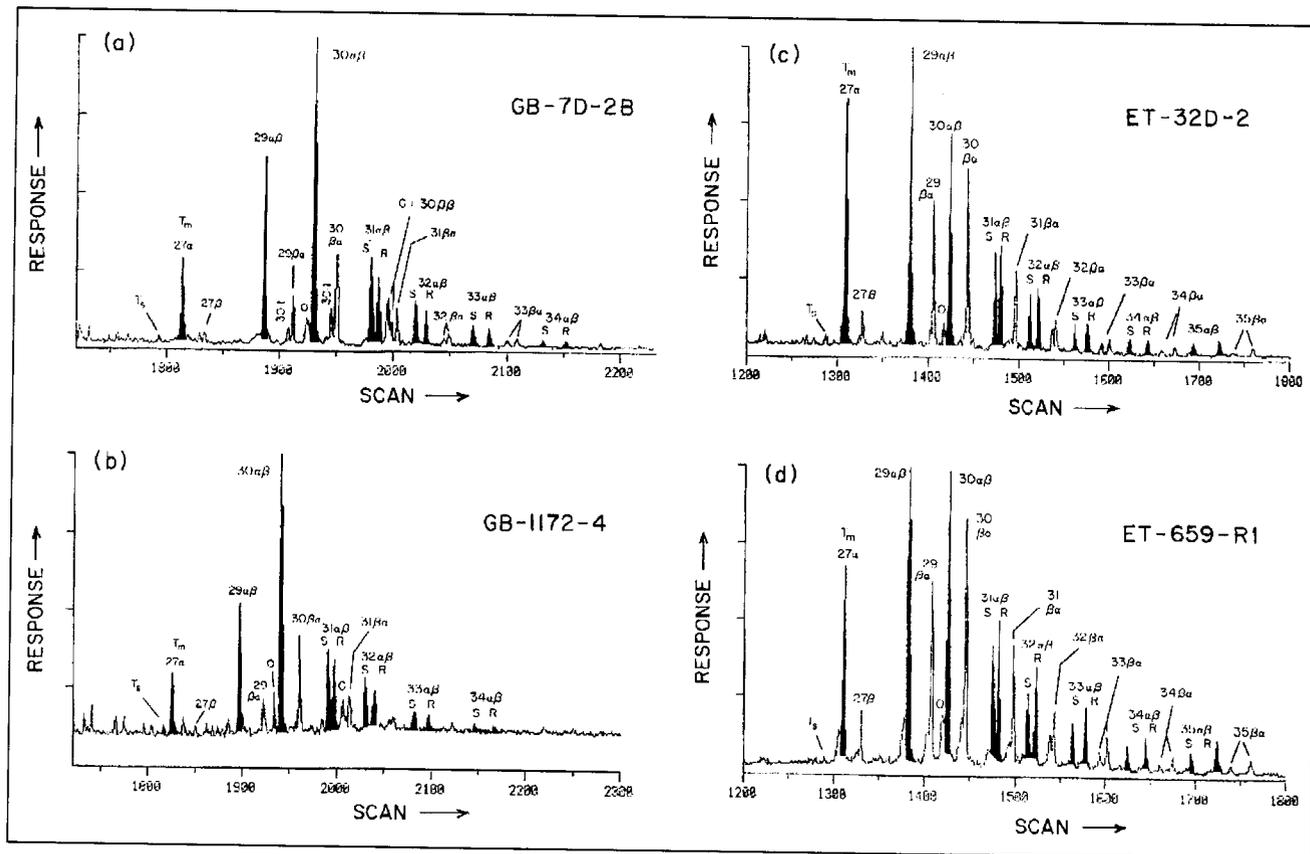


Figure 5—Mass fragmentograms (m/z 191) showing distributions of triterpanes in oil samples from GB and ET. Numbers indicate the carbon number of molecules; suffixes designate configuration: $\alpha\beta = 17\alpha(H), 21\beta(H)$ - (shaded); $\beta\alpha = 17\beta(H), 21\alpha(H)$ -; $\beta\beta = 17\beta(H), 21\beta(H)$ -; (:1) = hopene; Ts = $18\alpha(H)-22, 29, 30$ -trisorneohopane; Tm = $17\alpha(H)-22, 29, 30$ -trisorhopane; O = oleanane; G = gammacerane. In pairs of shaded compounds, 22S epimer is followed by 22R epimer.

(Table 2). They are variable in the four samples ranging from 0.12 to 0.28. Other sterane epimer ratios could not be determined because of peak overlap on the mass fragmentograms (Figure 6). Diasteranes are also present with the $13\beta(H)$, $17\alpha(H)$ -diacholestane 20S and 20R compounds most obvious (Figure 6). The epimer ratios of these isomers (Table 2) are 0.57 and 0.61 in the GB samples and 0.52 and 0.53 in the ET samples.

Aromatic Hydrocarbons

The aromatic hydrocarbons are present as complex mixtures (Figure 7). Unsubstituted polycyclic aromatic hydrocarbons (PAH) dominate over their alkyl-substituted analogs (Table 3). In the GB samples, most of the aromatic hydrocarbons are unresolved by high-resolution GC as evidenced by the rising baseline of the GC reflecting a complex mixture (i.e., unresolved complex mixture or UCM). The aromatic hydrocarbons of the ET samples also produce chromatographic humps, but the PAH are present in sufficient concentrations to be resolved as distinct chromatographic peaks. Common to all samples are phenanthrene, fluoranthene, pyrene, chrysene, benzopyrenes, benzofluoranthene, benzoperylene, and coronene (Table 3). Anthracene and Diels hydrocarbon (3'-

methyl-1,2-cyclopentenophenanthrene) are present mainly in the GB samples. Minor compounds listed in Table 3 (e.g., anthracene, dibenzothiophene) were detected by GC-MS analyses.

INTERPRETATION

The gross chemical composition (C_{15+}) of petroleum samples from GB and ET are quite variable as illustrated in Figure 3. This variability is particularly evident for GB, which has been sampled more extensively than has ET. However, future sampling probably will reveal a greater variability in compositions than is presently known and will provide a larger database for ET. Petroleum from GB ranges from aliphatic rich to nonhydrocarbon rich, whereas petroleum from ET is aromatic rich. The wide variation in gross chemical compositions is believed to result mainly from the great variability inherent in the hydrothermal processes and postgeneration effects. Hydrothermally active regions, where hot fluids reach the cold sea floor, must be characterized by extreme chemical and thermal gradients that affect sediment organic matter in different ways depending on the intensity of the hydrothermal process at any given site. Once petroleum is formed as a

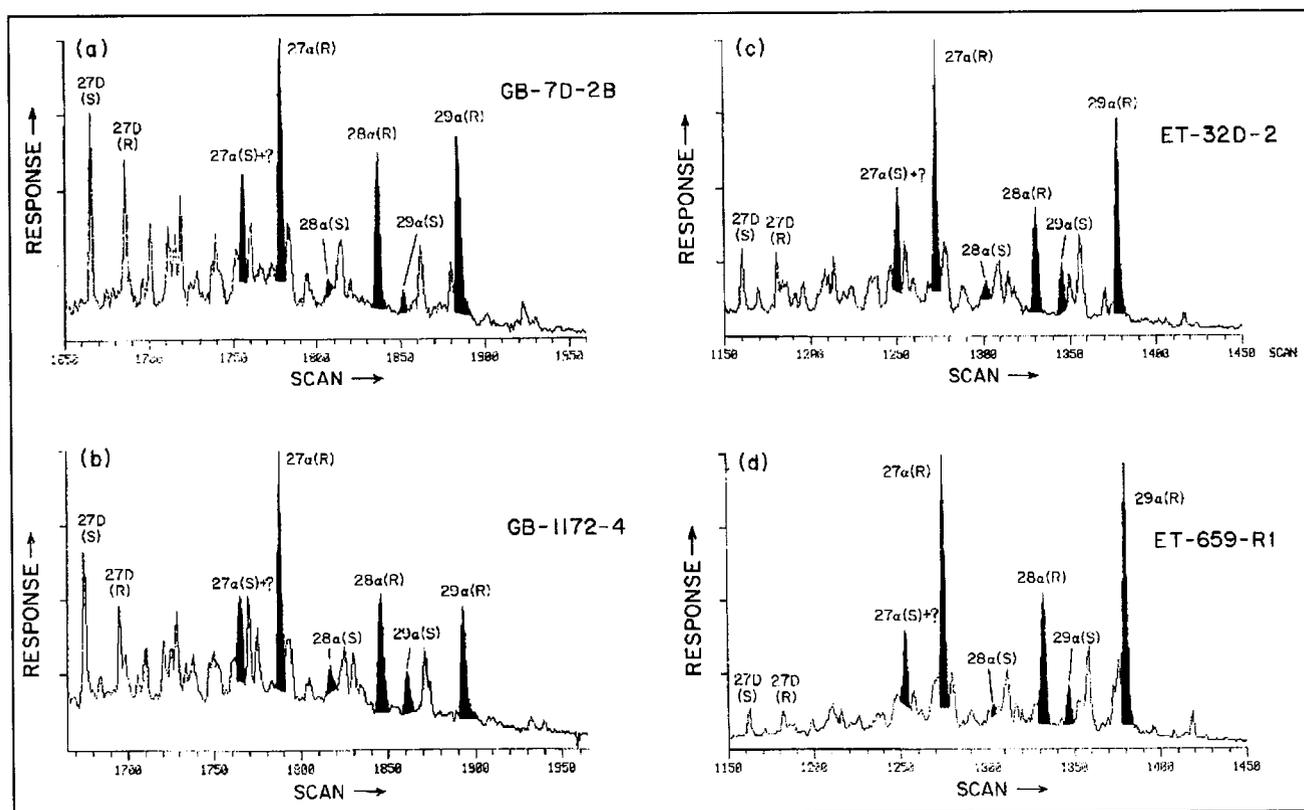


Figure 6—Mass fragmentograms (m/z 217) showing distributions of steranes and diasteranes in oil samples from GB and ET. Numbers indicate the carbon number of molecules; suffixes designate configuration: $\alpha = 5\alpha(H), 14\alpha(H), 17\alpha(H)$; D = diasterane [13 β (H), 17 α (H)-diacholestane]; R and S are epimer configurations at C-20.

result of this process, it is subject to postgeneration alterations, such as biodegradation. These alterations diminish the content of aliphatic hydrocarbons and increase amounts of nonhydrocarbons, depending on the petroleum's accessibility to seawater. Thus, the complexity and variability in this overall sequence of events would be expected to lead to a nonuniform product, in this case, hydrothermal petroleum of highly variable composition.

Normal and Isoprenoid Alkanes

The molecular distributions of various classes of hydrocarbons provide clues to possible sources of organic matter and to the maturity level of the products. Distributions of *n*-alkanes and isoprenoid hydrocarbons (Figure 4) can be interpreted in terms of both source and maturity. For example, the overall distribution of *n*-alkanes in GB-1172-4 is most oil-like, suggesting that this sample is more mature than the others where the *n*-alkane distributions suggest intermediate maturity; generally, oils with greater aliphatic quality tend to be more mature (Tissot and Welte, 1984).

Although maturation can obscure the original *n*-alkane signature of the source material, some hints concerning sources remain. A close examination of the *n*-alkane distributions reveals that ET samples have a significantly higher odd-even

predominance than do GB samples for the higher molecular-weight homologs (Table 2, OEP₂₇). The larger OEP₂₇ values for ET reflect input from terrigenous sources because land-plant waxes, the likely precursors for such *n*-alkanes, are characterized by high OEP values (Eglinton et al., 1962). This observation fits the sedimentological history of the two areas in that the ET sediments are primarily derived from continental rivers, whereas GB sediment is primarily marine diatomaceous ooze. In the intermediate molecular-weight range around C₂₀, the distributions of *n*-alkanes in all samples are such that any odd-even or even-odd predominance is slight (Table 2, OEP₂₀). These hydrocarbons are believed to reflect contributions from various marine sources (Simoneit, 1978).

The distribution of isoprenoid hydrocarbons, particularly Pr and Ph, commonly have been used as paleoenvironmental indicators (Didyk et al., 1978). In the case of our samples, however, the Pr/Ph ratios, and the relations between these compounds and the *n*-alkanes, are more likely the result of process rather than source. Maturation apparently increases Pr/Ph ratios, whereas, for example, Ph/*n*-C₁₈ ratios will decrease (ten Haven et al., 1987). The Pr/Ph ratios in our samples range from 0.9 to 1.8, and the Ph/*n*-C₁₈ and Pr/*n*-C₁₇ ratios are less than 1.0, with one exception. These results are consistent with what is expected in relatively mature petroleum.

The UCM of aliphatic compounds exhibited as a chromatographic hump for the samples from GB (Figure 4) is a feature

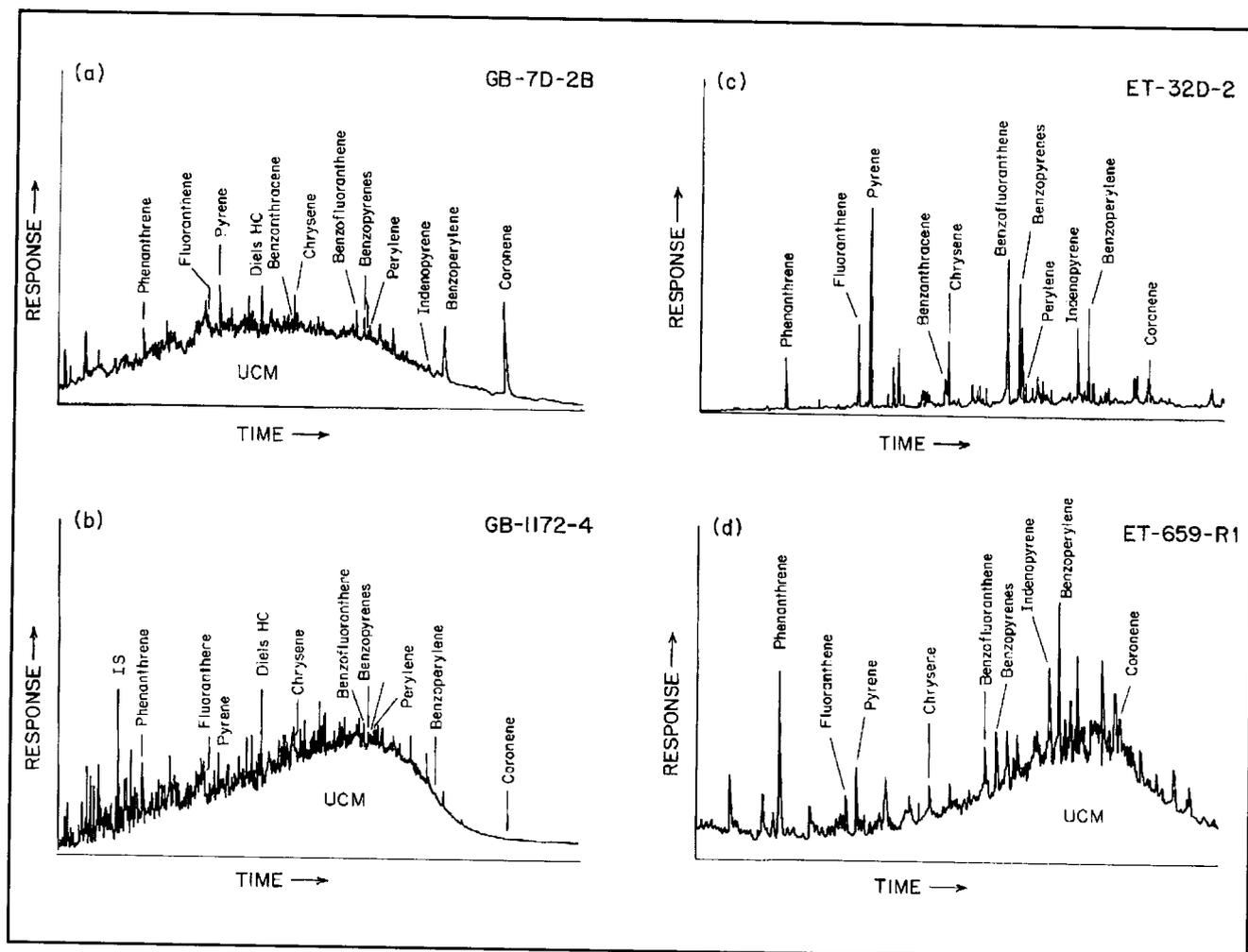


Figure 7—Gas chromatograms showing the distributions of aromatic hydrocarbons in oil samples from GB and ET. UCM = unresolved complex mixture, IS = internal standard.

commonly observed in many oils (for example see Rohrback, 1983). In samples from ET, the UCM is minor.

Cyclo-Biomarkers

The relative distributions of terpanes are useful in comparison of our samples from GB and ET (Figure 5). The most stable hopane configuration is that of the $17\alpha(H),21\beta(H)$ -hopanes (Ensminger et al., 1974, 1977; Seifert and Moldowan, 1978). This hopane series is the most abundant of the pentacyclic triterpanes in the four samples. In contrast, the natural product precursors of the $17\alpha(H),21\beta(H)$ -hopanes are the $17\beta(H),21\beta(H)$ -hopanes, which are least stable (Ourisson et al., 1984), and these $\beta\beta$ -hopanes are only minor compounds in the GB and ET samples. Of intermediate stability are the $17\beta(H),21\alpha(H)$ -hopanes, which are commonly called moretanes (Philp, 1985; Johns, 1986). Moretanes are second in abundance only to $\alpha\beta$ -hopanes. The ratios of $\alpha\beta$ -hopanes (C_{29} - C_{31}) to moretanes (C_{29} - C_{31}) indicate that moretanes are more abundant relative to $\alpha\beta$ -hopanes in ET samples compared with GB samples (Table 1). This relationship is clearly evident in Figure 5. The relative

amounts of moretanes are an indicator of maturity, but the evidence from this measurement alone does not permit an assessment of the relative maturity of oil from ET vs. oil from GB.

Ratios of the C_{30} -hopane to the C_{29} -hopane have been used for source rock correlations (Palacas et al., 1984). In our study, this ratio (Table 2) serves to distinguish GB samples from ET samples; that is, the GB ratios of 1.6 and 2.2 are different from the ET ratios of 0.71 and 0.98. Ratios of the C_{30} -moretane to the C_{29} -moretane show similar correlations (Table 2). The ratios of $17\alpha(H)$ -22,29,30-trisnorhopane (T_m) to $18\alpha(H)$ -22,29,30-trisnorhopane (T_s) have been used as a maturity parameter for hydrocarbons from a similar source and as a source parameter if they had similar maturities (Seifert and Moldowan, 1978). In the case of our study, maturities apparently are only slightly different between GB and ET samples; thus the T_m/T_s ratios, whose values are significantly different in the two areas (Table 2), likely indicate the signature of different sources. However, the specific nature of the contributing sources of these compounds is unknown.

The presence of an extended $\alpha\beta$ -hopane ($\geq C_{31}$) series that occurs as a mixture of two epimers, 22S and 22R (Figure 5),

Table 3. Relative Concentrations of Polycyclic Aromatic Hydrocarbons in Hydrothermal Petroleum from Guaymas Basin and Escanaba Trough

Compound	Mol. Weight	Guaymas Basin		Escanaba Trough	
		7D-2B	1172-4	32D-2	659-R1
Phenanthrene	178	5	80	43	100
Anthracene	178	0.9	15	n.d.**	n.d.
Dibenzothiophene	184	2	47	0.8	0.02
Methylenephenanthrene	190	0.02	1.6	1.1	1.9
Methylphenanthrenes*	192	14	140	16	30
Fluoranthene	202	10	13	65	16
Pyrene	202	50	56	100	26
Methylpyrenes and methylfluoranthenes	216	48	64	78	21
1,2-Cyclopentenophenanthrene	218	10	30	5.4	6.6
Chrysene	228	10	21	39	7
Diels Hydrocarbon	232	35	100	1.1	0.7
Naphthobenzothiophenes*	234	24	21	15	1.9
Benzofluoranthene	252	13	7	64	21
Benzo(a)pyrene	252	7	10	39	2.8
Benzo(e)pyrene	252	29	14	58	16
Perylene	252	6	2.3	12	0.9
Binaphthyls*	254	9	4.2	45	3.8
Indenopyrene	276	16	1.5	29	26
Benzoperylene	276	100	11.4	32	36
Dinaphthothiophenes*	284	9	n.d.	5.4	n.d.
Coronene	300	94	2	4	9.4
Dibenzo(a,e)pyrene	302	14	0.2	17	47

*Several isomers present (numbers reflect all isomer total).

**n.d. = not detectable.

provides one means of interpreting relative maturity of the hydrothermal oils. In this series of compounds, the biological precursor configuration is 22R. With increasing maturity the 22R configuration is converted to a mixture of 22S and 22R epimers, eventually reaching an equilibrium mixture [22S/(22S+22R)] of about 0.6 (Ensminger et al., 1974). The average epimer ratio of 0.55 for samples from GB is closer to the equilibrium ratio than is the average epimer ratio of samples from ET of 0.46. These results suggest that the GB oils are more mature than the ET oils. This statement assumes that the maturity of the whole oils can be directly related to the maturity assessment provided by these epimer ratios.

The distributions of steranes provide possible clues to source as well as maturity. The ratio of the C₂₉ to C₂₇ steranes has often been used as a source indicator (Huang and Meinschein, 1979), with C₂₉ steranes reflecting mainly terrigenous sources and C₂₇ steranes reflecting mainly marine sources. However, Volkman (1986) has shown limitations to the application of this ratio as a source indicator. Nevertheless, a comparison of 20R epimer ratios of C₂₇ and C₂₉ steranes (27R/29R) shows that C₂₉ is relatively more abundant compared to C₂₇ in oils from ET (Table 2, Figure 6). Such a relationship is consistent with the source predictions of Huang and Meinschein (1979) in that the ET sediment is known to be dominated by material from terrigenous sources. Another sterane ratio (28R/29R) distinguishes the oils from the two areas, but the 27R/28R ratio does not (Table 2).

The epimer ratios [20S/(20S+20R)] of the C₂₉ sterane (Table 2) have values (0.12 to 0.28) significantly less than the equilibrium ratio of about 0.5 (Mackenzie et al., 1980). The extent of sterane isomerization is less than the extent of hopane isomerization as expected from kinetic considerations (Mackenzie and McKenzie, 1983). In contrast to the hopane

epimer ratios, which are distinctly different in the GB and ET samples, the sterane epimer ratios are not. Also, the C₂₇ diasterane epimer ratios are not significantly different in the two areas. Thus, the sterane isomerization ratios do not contradict the hopane isomerization ratios, but they do not show the consistent difference between the two areas as do the hopane ratios. Because greater uncertainties are involved in the measurement of sterane epimer ratios due to potential peak overlap, more credence is given to the hopane epimer ratios.

Aromatic Hydrocarbons

Aromatic hydrocarbons are the most abundant hydrocarbons in three of the four samples being discussed (Table 1). Only in GB-1172-4 are the aliphatic hydrocarbons quantitatively more important. Most of the aromatic hydrocarbons, except perhaps in ET-32D-2, are present as a complex mixture as indicated by gas chromatography (significant UCM, Figure 7), with only minor amounts of resolved individual components. The major suite of aromatic compounds identified in both sample sets are nonalkylated, pericondensed (i.e., all fused six-membered ring aromatic structures) PAH with phenanthrene and pyrene as important components in ET samples, and benzoperylene, coronene, and Diels hydrocarbon as major compounds in the GB samples (Figure 7, Table 3). The overall PAH compositions are quite variable for both areas, probably due to the differential solubilities of these compounds in hot fluids and the range of formation temperatures (Simoneit, 1984). The presence of the PAH indicates that a part of the organic matter was subjected to high temperature pyrosynthesis, but the different organic matter sources for the two areas are not reflected in the PAH compositions. The pres-

Table 4. Ratios and Indices of Polycyclic Aromatic Hydrocarbons in Hydrothermal Petroleum and Reservoir Crudes

Ratio	Guaymas Basin		Escanaba Trough		Crude Oils*
	7D-2B	1172-4	32D-2	659-R1	
Phenanthrene/Methylphenanthrenes	0.36	0.57	2.69	3.33	0.1
Methylphenanthrene Index**					
MPI 1	0.76	1.00	0.42	0.39	
MPI 2	0.81	1.25	0.52	0.41	
Diels HC/Phenanthrene	7.0	0.64	0.03	0.01	
Diels HC/Cyclopentenophenanthrene	3.5	2.0	0.20	0.10	
Fluoranthene/Pyrene	0.20	0.23	0.65	0.61	0.6-1.4
Pyrene + Fluoranthene/					
Methylpyrenes + Methylfluoranthenes	1.20	1.06	2.13	2.04	
Benzo(e)pyrene/Benzo(a)pyrene	4.17	1.28	1.49	5.56	0.2-3.3

*Data tabulated in Neff (1979) and Gschwend and Hites (1981).

**Radke and Welte (1983).

ence of PAH with five-membered alicyclic rings (e.g., methylenephenanthrene, fluorene, fluoranthene, benzofluoranthene, 1,2-cyclopentenophenanthrene, etc.) is also evidence for elevated thermal stress. These compounds generally are found in pyrolysates from organic matter, and once formed, they do not easily convert to pericondensed polycyclic aromatic hydrocarbons (Blumer, 1975, 1976; Scott, 1982).

Various ratios of aromatic hydrocarbons are given in Table 4. The phenanthrene to methylphenanthrene index is lower for the GB samples than for the ET samples. All these ratios are higher than the one reported for crude oil (Table 4), and they indicate elevated thermal stress. These ratios can be compared with data from laboratory maturation studies of immature Tanner Basin (California Bight) kerogen (Ishiwatari and Fukushima, 1979), a process analogous to organic-matter alteration in Guaymas Basin. The phenanthrene to methylphenanthrene ratios ranged from 0.59 to 0.83 at 310°C for 18–100 hr, and 0.9 to 5.0 at 410°C for 5–32 hr. Based on this ratio, the GB oils fit with a temperature window of 310–350°C and the ET oils with temperatures exceeding 410°C. The methylphenanthrene indices (MPI, Radke and Welte, 1983), both MPI 1 and MPI 2, range from 0.39 to 0.52 for the ET samples and from 0.76 to 1.25 for the GB oils. In contrast to the previous evaluation, these results could be interpreted to indicate that the ET oils are immature at the onset of the oil window and the GB oils are more mature. However, this interpretation must be qualified as being not necessarily comparable with normal geological conditions due to the unknown effects of water solubilization processes and alteration reactions of organic compounds at high temperature.

Diels hydrocarbon and to a lesser degree 1, 2-cyclopentenophenanthrene are enriched relative to phenanthrene in the GB oils, and they are trace components in the ET oils (Table 3). The ratios of Diels hydrocarbon to phenanthrene and of Diels hydrocarbon to 1,2-cyclopentenophenanthrene again show a difference between the GB and ET oils (Table 4). Because C₂₇ steroids are enriched in the marine organic detritus of Guaymas Basin, these aromatic compounds may reflect rapid thermal alteration by aromatization reactions from steroid precursors (Simoneit, in press). Thio-PAH (e.g., dibenzothiophene, naphthobenzothiophenes, dinaphthothiophenes) are present in both sets of oils, but they are enriched in the GB

samples (Table 3). Although sulfur is present in organic compounds of these oils, its role in the formation of hydrothermal petroleum is not yet understood.

Pyrene is more concentrated than fluoranthene, especially in the GB oils, and methylpyrenes and methylfluoranthenes are also present at significant levels (up to 90% of the parent PAH) (Table 3). The fluoranthene to pyrene ratios are lower than or equal to the lower limit reported for conventionally derived crude oils (Table 4) (Neff, 1979), and the ratios for the GB samples are less than those for the ET samples. The ratios of benzo(e)pyrene to benzo(a)pyrene range from 1.28 to 5.56 for these samples (Table 4), and the variability may indicate secondary reactions of the less stable (a) isomer (e.g., oxidation, Neff, 1979; Roberts et al., 1984). Some of these values fall into the range reported for crude oils (Table 4). Nevertheless, the presence of this suite of PAH in the oils is additional evidence for a high-temperature component (Simoneit, 1984).

IMPLICATIONS

Our considerations of sample maturity, based on quantities of certain aliphatic compounds and distributions of the extended 17 α (H)-hopanes, led to the indication that oils from GB may be more mature than the oils from ET. However, the steranes indicate various maturities for both sets of oils. The aromatic hydrocarbon data, especially the PAH, provide additional, yet conflicting maturity interpretations. Various molecular indicators reflect compositional differences between these two sample sets, and these differences appear to be due to differences in the organic matter source, i.e., predominantly marine for GB and terrigenous for ET. Additional complicating and contributing factors that influence these oil compositions at the sea floor are solubility of components in water vs. cosolubility in oil, and biodegradation. However, the most important aspect that differentiates these oils from normal conventionally derived petroleum is the admixture of products generated over a range of thermal regimes. Table 5 summarizes some of the molecular characteristics that differentiate hydrothermally derived petroleum from conventionally derived petroleum.

Table 5. Summary of Comparison of Molecular Characteristics of Hydrothermal Petroleum and Normally Reservoired Petroleum

Gross Composition (Main Classes)	Hydrothermal Oils		Normal Oils
	Aliphatic Hydrocarbons Aromatic Hydrocarbons (PAH enriched) and Nonhydrocarbons (NSO)		Aliphatic Hydrocarbons Aromatic Hydrocarbons and Nonhydrocarbons (NSO)
	Guaymas Basin	Escanaba Trough	
Normal Alkanes (OEP ₂₇)	1.06 and 1.01	1.13 and 1.12	~1.0
Hopanes S/(S+R) for 31H	0.56 and 0.53	0.48 and 0.46	~0.6
Steranes S/(S+R) for 29S	0.12 and 0.28	0.20 and 0.13	~0.5
Polycyclic Aromatic Hydrocarbons (Ratios)			
<u>Phenanthrene</u> Methylphenanthrenes	0.36 and 0.57	2.69 and 3.33	0.1
<u>Fluoranthene</u> Pyrene	0.20 and 0.23	0.65 and 0.61	0.6-1.4
<u>Benzo(e)pyrene</u> Benzo(a)pyrene	4.17 and 1.28	1.49 and 5.56	0.2-3.3

The aliphatic material, including, for example, the 17 α (H)-hopane series, formed generally under lower temperatures than the PAH, which represent the high-temperature extreme. All of these products migrate to the sea floor, where the higher molecular-weight material solidifies (ambient temperatures ~3°C) and the volatiles (C₁-C₁₀) rise as plumes (Simoneit, 1984, 1985; Kawka and Simoneit, 1987). Thus, the petroleum in the hydrothermal mounds at the sea floor represents variable admixtures of low- to high-temperature-generation products.

Occurrences of hydrothermally derived petroleum at GB and ET clearly demonstrate that the processes of petroleum generation currently are active (Didyk and Simoneit, 1989; Simoneit, 1990). These same processes must have taken place throughout geologic time at oceanic spreading centers that received sediment during rifting. Thus, the sedimentary rocks of former spreading centers preserved in the geologic record can be potential sites for petroleum occurrence. The amount of petroleum one can expect to find at modern and ancient spreading centers is still uncertain, although sediments of the surrounding margin may also be involved (Lonsdale, 1985). The general geologic setting of modern spreading centers, such as GB and ET, is not particularly favorable for the preservation of an economically significant petroleum resource. At active spreading centers, the dynamic geologic processes that take place do not favor the formation of long-term traps for petroleum accumulation. Although the evidence is clear for the migration of petroleum-rich fluids at active spreading centers, the evidence for traps is lacking (Didyk and Simoneit, 1989; Lonsdale, 1985). Some petroleum is precipitated at or near the sea floor, but much is lost to the overlying water column and to biodegradation. Even if significant amounts of petroleum have somehow accumulated in sediment of the modern active spreading centers at GB and ET, the water depth

at these areas, 2000 m at GB and 3200 m at ET, is too great for present petroleum production technology. Although former spreading centers now preserved in the geologic record may be accessible to exploration and production drilling, we know of no ancient spreading center that has been drilled and shown to have significant amounts of petroleum associated with it. Nevertheless, the petroleum explorationist should be aware that in provinces with hydrothermally altered sediment, there is a possibility, albeit small, of finding petroleum that has formed as a result of the interaction of hydrothermal fluids with sedimentary organic matter.

SUMMARY

Guaymas Basin and Escanaba Trough are regions where petroleum is being formed as a result of the conversion of sedimentary organic matter by hydrothermal processes. From each of these regions, two samples were selected to compare various geochemical characteristics. Ratios of certain hydrocarbon molecules provide (1) a basis for distinguishing the oils, (2) a guide for interpreting possible sources for the hydrocarbons, and (3) a measure of the relative maturities of the oils.

In this study, the molecular ratios used include those that describe distributions of n-alkanes, isoprenoids, hopanes and moretanes, steranes and diasteranes, and aromatics. A consistent pattern emerged in that for many ratios, the values obtained for the two Guaymas Basin oils are generally similar as are the values obtained for the two Escanaba Trough oils, yet the ratios for each region generally are different. That is, these molecular parameters can be used to distinguish the oils from the two regions.

Distributions of n-alkanes are consistent with the dominant

sources of sediment for the two regions. For example, n-alkanes have a terrigenous signature in oils from Escanaba Trough, which contains mainly terrestrially derived sediment. In contrast, n-alkanes mainly have a marine signature in oils from Guaymas Basin, where the sediment is composed primarily of marine diatomaceous ooze.

Most of the molecular ratios reflect some influence of the maturity that results from the extent of the processes involved in the formation and alteration of these compounds. Epimer ratios of extended hopanes, for example, suggest that the two Guaymas Basin oils are slightly more mature than are the two oils from Escanaba Trough, but this suggestion is not fully supported by interpretations based on the steranes. The aromatic hydrocarbons, especially the PAH, provide various maturity interpretations, but more importantly, they represent a high-temperature component of these oils. Temperatures of reactions probably reached at least 315°C.

The conclusion that emerges is that it is difficult to generalize the time-temperature histories of petroleum formation in sediments of Guaymas Basin and Escanaba Trough because these oils are admixtures of fractions generated in various temperature windows. Although each area is unique in terms of the main sources of organic matter in the sediment, the hydrothermal processes in each area are complex and varied in thermal intensity. As a result, values of molecular maturity parameters can also be expected to vary. Additional field data, coupled with laboratory simulations, will provide the elucidation of the molecular processes involved in this novel petroleum generation process occurring within "instantaneous" geologic time.

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