UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

HYDROCARBON GEOCHEMISTRY OF PETROLEUM ASSOCIATED WITH SEDIMENT-HOSTED SULFIDES FROM ESCANABA TROUGH, SOUTHERN GORDA RIDGE

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Open-File Report 87-375-C

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ABSTRACT

In 1986, three samples of sulfide-rich sediment, impregnated with hydrothermally-derived, asphaltic petroleum, were recovered in a dredge and by submersible in Escanaba Trough, the sediment-covered, southern end of the Gorda Ridge spreading axis, offshore northern California. The molecular distributions of hydrocarbons in the two pyrrhotite-rich samples recovered by submersible are similar and compare well with the hydrocarbon composition of the first pyrrhotite-rich sample containing petroleum discovered at a 1985 dredge site about 30 km to the south of the site of the submersible dive. In contrast, the 1986 dredged sample, composed of a polymetallic assemblage of sulfides, contains petroleum in which the distribution of hydrocarbons indicates a slightly higher level of maturity relative to the other samples. The observation that petroleum, associated with sulfides, occurs at two and probably more distinct sites and has a variable composition attests to the ubiquity of petroleum generation in the hydrothermally active Escanaba Trough.

INTRODUCTION

Escanaba Trough is the southern-most segment of the Gorda Ridge, an active oceanic spreading axis located in the northeast Pacific Ocean 200 to 300 km west of northern California and southern Oregon (Fig. 1). This location is within the Exclusive Economic Zone (EEZ) of the United States. Up to 500 m of Quaternary turbiditic sediment, derived mainly from drainages of the Klamath and Columbia Rivers, fill the trough (McManus and others, 1970; Moore, 1970; Vallier and others, 1973). Dredging at Gorda Ridge in 1983 recovered the first evidence for active hydrothermal processes there in the forms of altered basaltic lava, manganese oxide crusts, nontronite and sulfide (Clague and others, 1984). Further dredging in 1985 at Site 32 (Morton and others, 1987a) obtained 4.4 kg of pyrrhotite-rich massive sulfide, one piece of which, weighing 185 g, consisted of sediment impregnated with asphaltic petroleum and massive sulfide (Kvenvolden and others, 1986). Further studies of Escanaba Trough were conducted in 1986 (Zierenberg and others, 1986; Morton and others, 1987b; Benninger and Koski, 1987). Two sampling cruises (L1-86-NC and L2-86-NC), utilizing dredges and gravity corers, and sampling dives (T1-86-NC) by the U.S. Navy submersible, Sea Cliff, obtained additional evidence for hydrothermal activity. This report describes the hydrocarbons that are present in petroleum impregnated, sulfide containing sediment collected by dredge and submersible. A future paper will deal with the hydrocarbons extracted from sediment cores.

Geologic Setting

For the purpose of geological and geophysical investigations, three areas have been designated in Escanaba Trough (Fig. 1): the southern area (SESCA), the northern area (NESCA), and a region in between (MESCA). The areas have been described by Morton and others (1987b) and by Benninger and Koski (1987). At SESCA, sulfide deposits are spatially related to three flat-topped hills, formed by uplifted, steepsided, sediment-capped blocks that rise above the axial valley floor. Massive sulfide deposits occur as mounds at the base of the hills, and eroded chimneys populate the sulfide mounds as well as the sediment surface between the hills.

The NESCA area is dominated by two hills, one steepsided and sediment-capped, and the other, broader with exposed lava flows. Massive sulfides deposits occur at the base of the steepsided hill and in faulted sediment on the north flank of the volcanic hill. MESCA is a sediment-covered volcanic edifice located about halfway between SESCA and NESCA.

Methods

Samples for organic geochemical studies were collected from chain-bag dredges and by the mechanical arm of the submersible Sea Cliff. The procedure for analysis of hydrocarbons was adapted from Kvenvolden and others (1985) and involved extraction with dichloromethane, separation of the extract by silica gel/alumina chromatography into three fractions--aliphatic hydrocarbons, aromatic hydrocarbons, and non-hydrocarbons. The hydrocarbon fractions were further analyzed by high resolution gas chromatography and gas chromatography/mass spectrometry. Single ion monitoring (SIM) of m/z 191 and 217 produced mass chromatograms from which terpanes and steranes, respectively, were identified and compared. The procedures follow those previously used on the original sample of hydrothermally-derived petroleum recovered from Escanaba Trough (Kvenvolden and others, 1986).

Samples

Samples for this study came from two of the three designated areas--SESCA and NESCA (Fig. 1), and these samples are described in Table 1. A dredge sample (32D-2) of fine-grained sandstone intermixed with sulfide and petroleum was analyzed from SESCA An analysis of this sample has been reported previously (Kvenvolden and others, 1986). A dredge sample and two samples recovered by submersible were analyzed from the NESCA area. These samples are all characterized as partly indurated mudstone/siltstone with sulfide and a petroliferous odor. The odor was caused by petroleum which is characterized in this report. The dredge and submersible samples were obtained from approximately the same location. Submersible sample 659-R1 was broken off from the base of a sulfide chimney (dormant hydrothermal vent). This petroleum-bearing sample is the only one for which the in situ location is accurately known.

RESULTS

Geochemical results obtained on the four samples used in this study are summarized in Table 2. These results include measurements of organic carbon (OC), extractable organic material (EOM), and the weights of aliphatic (F-1) and aromatic (F-2) hydrocarbons in the extract. Distributions of several molecular marker compounds in the aliphatic hydrocarbon fraction are summarized through various ratios:

CPI (Carbon Preference Index). A measure of the dominance of odd-carbon-number n-alkanes, calculated over the range n-C_{24} to n-C_{34}, following the method of Cooper and Bray (1963).

Pr/Ph (Pristane/Phytane). The ratio of two major isoprenoid hydrocarbons that are used to interpret paleoenvironmental conditions (Didyk and others, 1978) with many restrictions (ten Haven and others, 1987).

C_{29} sterane (S/(S+R)). The ratio of the 20S and 20R epimers of 24-ethyl-5α(H),14α(H),17α(H)-cholestane. The biologically derived 20R epimer is converted through increasing temperatures and time to nearly equal mixtures of 20R and 20S (Mackenzie and others, 1980).

C_{29} α(R)/C_{27} α(R) sterane. The ratio of the 20R epimers of 24-ethyl-5α(H),14α(H),17α(H)-cholestane (20R) to 5α(H),14α(H),17α(H)-cholestane

(20R). This ratio has been used as a source indicator (Huang and Meinschein, 1979) with C_{29} steranes indicating terrigenous sources and C_{27} steranes indicating marine sources; however, Volkman (1986), has shown limitations to the application of this ratio as a source indicator.

C_{31} homohopane (S/(S+R)). The ratio of the 22S and 22R epimers of the triterpane 17α(H),21β(H)-30-homohopane. Only the 22R epimer occurs in natural products. With increasing maturity the preference for 22R is lost in favor of about a 60:40 mixture of 22S and 22R epimers (Ensminger and others, 1974).

C_{30} hopane (αβ/ββ). The ratio of 17α(H),21β(H)-hopane, the most stable C_{30} hopane, to 17β(H),21β(H)-hopane, the least stable C_{30} hopane and the one found in natural products (Ourisson and others, 1984).

C_{30} hopane (βα/αβ). The ratio of the 17β(H),21α(H)-hopane (moretane) to 17α(H),21β(H)-hopane. Moretanes are intermediates in the maturity scheme between the unstable, natural product precursor ββ hopanes and the stable αβ hopanes (Philp, 1985).

αβ hopane (C_{30}/C_{29}). The ratio of 17α(H),21β(H)-hopane to 17α(H),21β(H)-30-norhopane. These compounds are usually the most abundant of the stable triterpanes, and the ratio has been used for source-rock correlations (Palacas and others, 1984).

C_{27} (Tm/Ts). The ratio of 17α(H)-22,29,30-trisnorhopane to 18α(H)-22,29,30-trisnorhopane, described originally by Seifert and Moldowan (1978). The Tm/Ts ratio can be used as a maturity parameter if the hydrocarbons are from a similar source, or, if the hydrocarbons have similar maturities, the ratio can be used as a source parameter.

The four sediment-hosted sulfide samples contain significant amounts of extractable organic material (EOM) ranging from 14,000 to 55,000 μg/g of sediment (Table 2). From 1,000 to 1,500 μg/g of the EOM is composed of aliphatic hydrocarbons and from 7,500 to 24,000 μg/g of aromatic hydrocarbons. The composition of this EOM is typical of asphaltic petroleum.

The distributions of n-alkanes and of the isoprenoid hydrocarbons are illustrated in the gas chromatograms shown in Fig. 2. The detected n-alkanes range from about n-C_{14} to n-C_{40} in samples 32D-2, 14D-6, and 659-R1 with maxima at n-C_{27}, n-C_{27}, and n-C_{23}, respectively. In sample 659-R3 the range of n-alkanes is shifted slightly to about n-C_{10} to n-C_{39} with a maximum at n-C_{20}. All samples show a dominance of odd-carbon-number n-alkanes above n-C_{24} as indicated by CPI values ranging from 1.1 to 1.3 (Table 2). Pristane/phytane (Pr/Ph) ratios range from 0.9 to 1.7 (Table 2). Sample 14D-6 has both a low CPI value and a low Pr/Ph ratio.

The distributions of terpanes (including tricyclic and tetracyclic (?) terpanes and pentacyclic triterpanes) and of steranes are shown in Figs. 3 and 4 and identified in Table 3. All samples lack unstable ββ hopanes and have large amounts of Tm relative to Ts. With the exception of sample 14D-6, the terpane and sterane compositions and distributions of the other samples are similar. This observation is also reflected in the sterane and terpane ratios shown on Table 2. Sample 14D-6 has larger epimer ratios of the C_{29} α-sterane and C_{31} αβ-homohopane, a smaller ratio of C_{30} hopane to C_{30} moretane, and a larger ratio of C_{30} hopane to C_{29} norhopane than do the other samples. The mass chromatogram of the steranes in sample 14D-6 shows a more complex distribution than the mass chromatograms of the other samples.

The polycyclic aromatic hydrocarbons are present in all four samples as complicated mixtures dominated by non-alkylated species, in which phenanthrene and/or pyrene, of the identified compounds, are the most prominant. Sample 659-R1 is unusual in having a complex mixture of aromatic hydrocarbons manifest on the chromatogram (Fig. 5) as a chromatographic hump in the higher temperature range. The chromatograms of the polycyclic aromatic hydrocarbons of the other samples have a generally flat baseline.

DISCUSSION

The hydrocarbon geochemistry of petroleum-impregnated, sediment-hosted sulfide samples provides a basis for the interpretation of possible sources and processes in this hydrothermally active region of Escanaba Trough. The petroleum extracted from the four sediment-hosted sulfide samples has many geochemical features that support hydrothermal activity as an important element in the petroleum formation. Although the distributions of n-alkanes in SESCA dredge sample 32D-2 and NESCA submersible sample 659-R3 are slightly different (Fig. 2), the patterns of distributions of terpanes and steranes (Figs. 3 and 4) are remarkably similar, as are the ratios of molecular markers listed in Table 2. Distributions of polycyclic aromatic hydrocarbons are also similar (Fig. 5) and suggest high temperature processes. These two samples came from locations 30 km apart, and their discovery demonstrates that the petroleum-forming process is not a single-site event in Escanaba Trough.

The molecular characteristics of aliphatic hydrocarbons in submersible sample 659-R1 are also quite similar to those in the two samples just discussed, but the distribution of polycyclic aromatic hydrocarbons is different in that it has a more complex mixture of compounds (Fig. 5). Sample 659-R1 was broken off from the base of a massive sulfide chimney. Several samples of the chimney were recovered, but petroleum was found only at the base of the chimney. This sample, therefore, provides evidence that final steps of petroleum formation took place very near to the sediment-water interface (base of chimney) by processes strongly mediated by hydrothermal activity that resulted primarily in the construction of the sulfide chimney.

The petroleum in NESCA dredge sample 14D-6 has molecular characteristics that are slightly different from those of the other three samples. Of particular interest are the maturity-related parameters such as CPI and the S and R epimer ratios of the C_{29} α-sterane and C_{31} $\alpha\beta$-homohopane. The values of these parameters (Table 2) suggest that this petroleum is slightly more mature than the petroleum found in the other three samples. The polycyclic aromatic hydrocarbons are almost exclusively the non-alkylated species (Fig. 5). These observations imply a slightly different time-temperature history for sample 14D-6. We have argued previously (Kvenvolden and others, in press) that the petroleum in sample 32D-2 formed by intense heating (300 to 350°C) if the time of heating was as short as 100 years. This same time-temperature regime would apply to sample 659-R3 because its maturity parameters match those of sample 32D-2. If these arguments are correct, then sample 14D-6 must have formed at slightly higher temperatures for the short time period of 100 years or formed at slightly lower temperatures for longer periods of time. Present data are insufficient to determine the exact time-temperature history of the samples. There is a difference in mineralogy, however, which may be influenced by the temperature histories of these samples. Sample 14D-6 is classified with massive sulfide samples of the polymetallic type whereas the other three samples are classified with the pyrrhotite-rich type according to Benninger and Koski (1987).

The ultimate source of the hydrothermally-derived petroleum is most likely the organic matter of the sediment. The organic carbon content ranges from 0.1 to 0.5% (Vallier, 1970) in sediment from Deep Sea Drilling Project site 35 south of SESCA (Fig. 1), and from 0.13 to 0.72% in sediment samples collected for our studies. Microscopic examination of four sediment samples provides descriptions (Table 4) of the types of organic matter that we believe serve as the source of hydrothermal petroleum. These samples all have a significant terrigenous component. This observation agrees with those made previously by McManus and others (1970), Moore (1970), and Vallier and others (1973) who suggest that the sediment of Escanaba Trough contains terrigenous organic debris which comes mainly from the Klamath and Columbia Rivers. That the source organic matter is dominantly terrigenous is also supported by the fact that all four of the hydrothermal petroleum samples shows a dominance of odd-carbon-numbered n-alkanes, a distribution typical of immature petroleum from terrigenous source materials.

The maximum time available for the formation of petroleum is limited by the less than 0.7 m.y. age of the sediment in Escanaba Trough (McManus and others, 1970). The actual time of petroleum generation may be very short, measured perhaps in hundreds of years, because of the intense heating effects of volcanic and hydrothermal activity which mobilizes sediment organic matter. The process ends when petroleum condenses at vents on the cold sea floor. The postulated processes are similar to those proposed earlier for hydrothermally-derived petroleum in sediment of Guaymas Basin (Currey and others, 1982; Simoneit and Lonsdale, 1982; Simoneit and others, 1984). These processes can be expected to occur wherever the active rift zone of oceanic spreading axes has been blanketed with sediment (Simoneit. in press). Because Escanaba Trough is reasonably accessible, being within the EEZ of the United States, it provides a natural laboratory in which the processes of hydrothermal petroleum generation can be studied in detail.

SUMMARY

The finding of hydrothermally-derived petroleum in four different samples, one in the SESCA area and three in the NESCA area, at localities about 30 km apart, indicates that petroleum formation is a common byproduct of the hydrothermal process in Escanaba Trough. One petroleum-impregnated sample came from the base of a sulfide chimney, and this sample provides evidence that the final steps of petroleum generation and emplacement take place at or near the ocean bottom. Slight compositional differences in hydrocarbons between petroleum samples is believed to be related to slightly different time-temperature histories. Petroleum associated with pyrrhotite-rich massive sulfide is slightly less mature than is petroleum associated with polymetallic massive sulfide.

The main source of petroleum in the sediment-hosted sulfides is terrigenous organic matter derived mainly from the drainages of the Klamath and Columbia Rivers. The amount of organic carbon in the sediments is less than 1%, thus limiting the amount of petroleum that can ultimately be formed. The process of petroleum formation involves the intense heating effects of volcanic and hydrothermal activity on sediment organic matter which is mobilized by the volcanic intrusions and hydrothermal fluids. The process not only involves intense heating, but the duration of heating is probably short, measured in terms of hundreds of years. The newly formed petroleum condenses at vents on the sea floor. The process of hydrothermal petroleum generation takes place not only in sediment of Escanaba Trough, which is part of the Gorda Ridge oceanic spreading axis, but also at other active oceanic spreading axes where sediment covers the rifting valleys.

ACKNOWLEDGMENTS

We wish to thank Jan Morton, Randy Koski, and Rob Zierenberg for beneficial discussion and for sharing ideas. Dredge samples were provided by Jan Morton and Bill Normark, and submersible samples by Rob Zierenberg, to whom we are very grateful.

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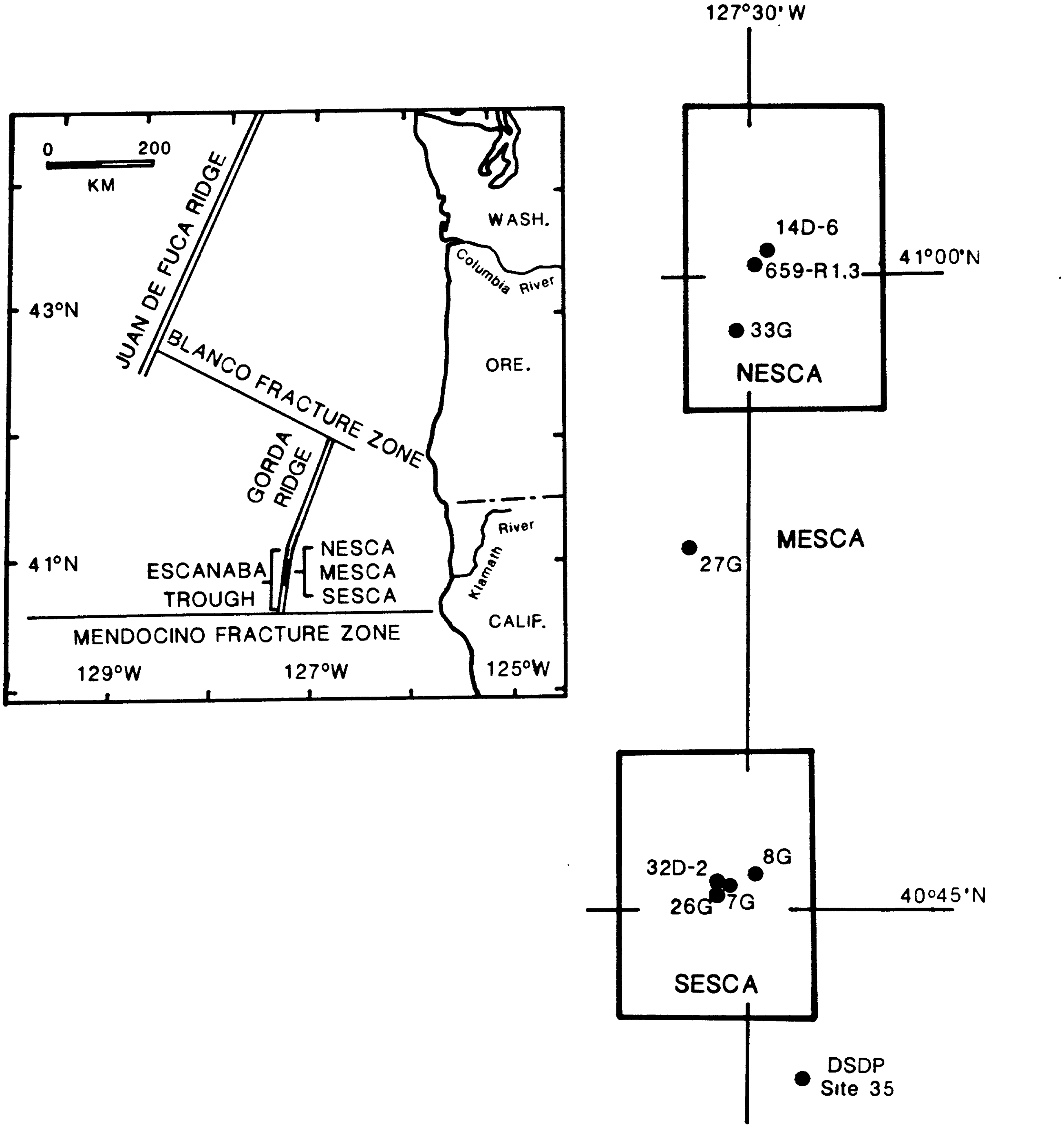

Figure 1. Map showing locations of samples recovered by dredge, submersible, and gravity coring in the SESCA, MESCA, and NESCA survey areas of Escanaba Trough at the southern end of the Gorda Ridge spreading axis offshore northern California and southern Oregon.

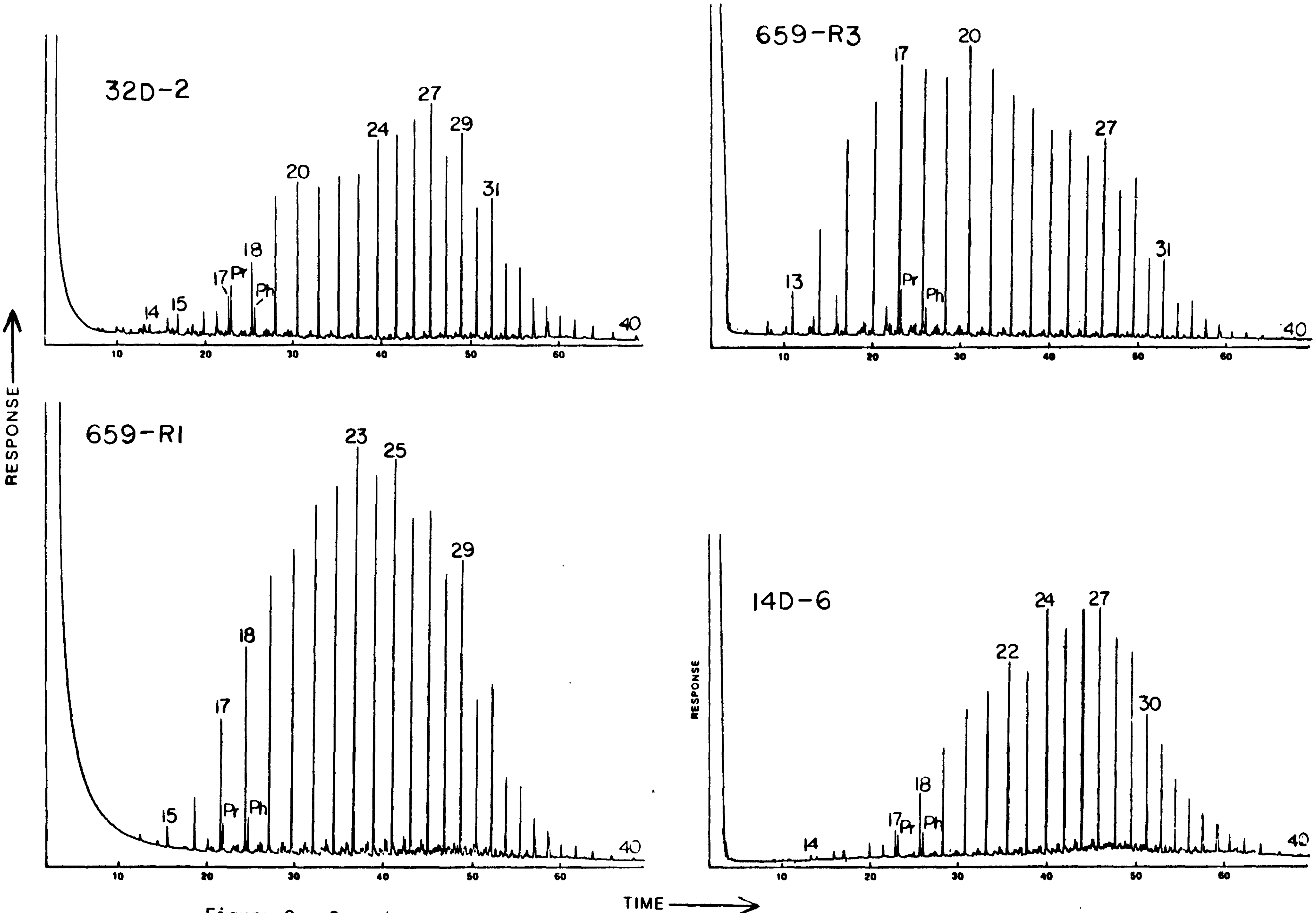

Figure 2. Gas chromatograms showing distributions of n-alkanes, pristane and phytane in petroleum extracted from four sediment-hosted, massive sulfide samples. Numbers specify carbon numbers of n-alkanes. Pr = pristane; Ph = phytane.

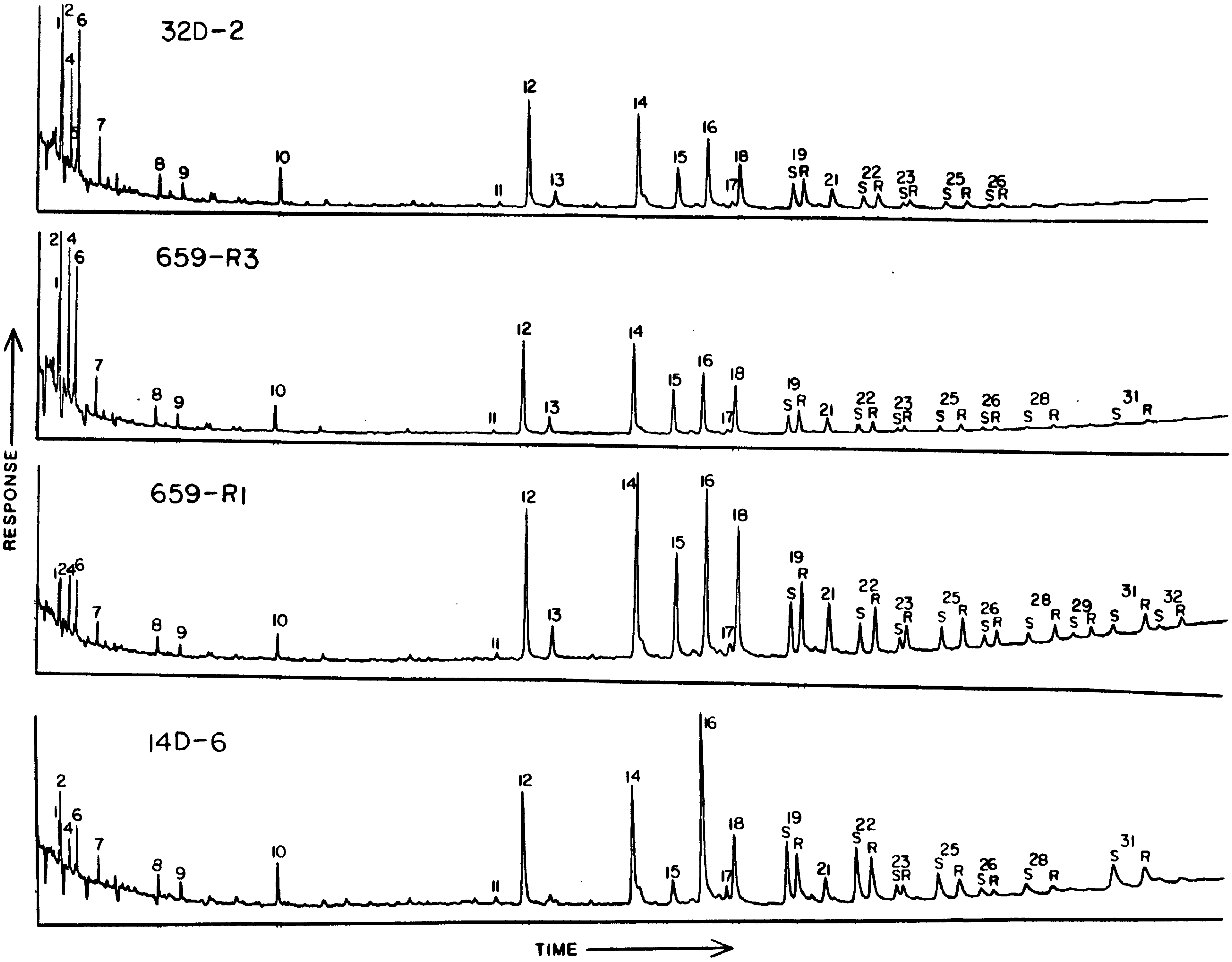

Figure 3. Mass chromatograms ($m/z = 191$) showing the distribution of terpanes in petroleum extracted from four sediment-hosted, massive sulfide samples. Identifications are listed in Table 3.

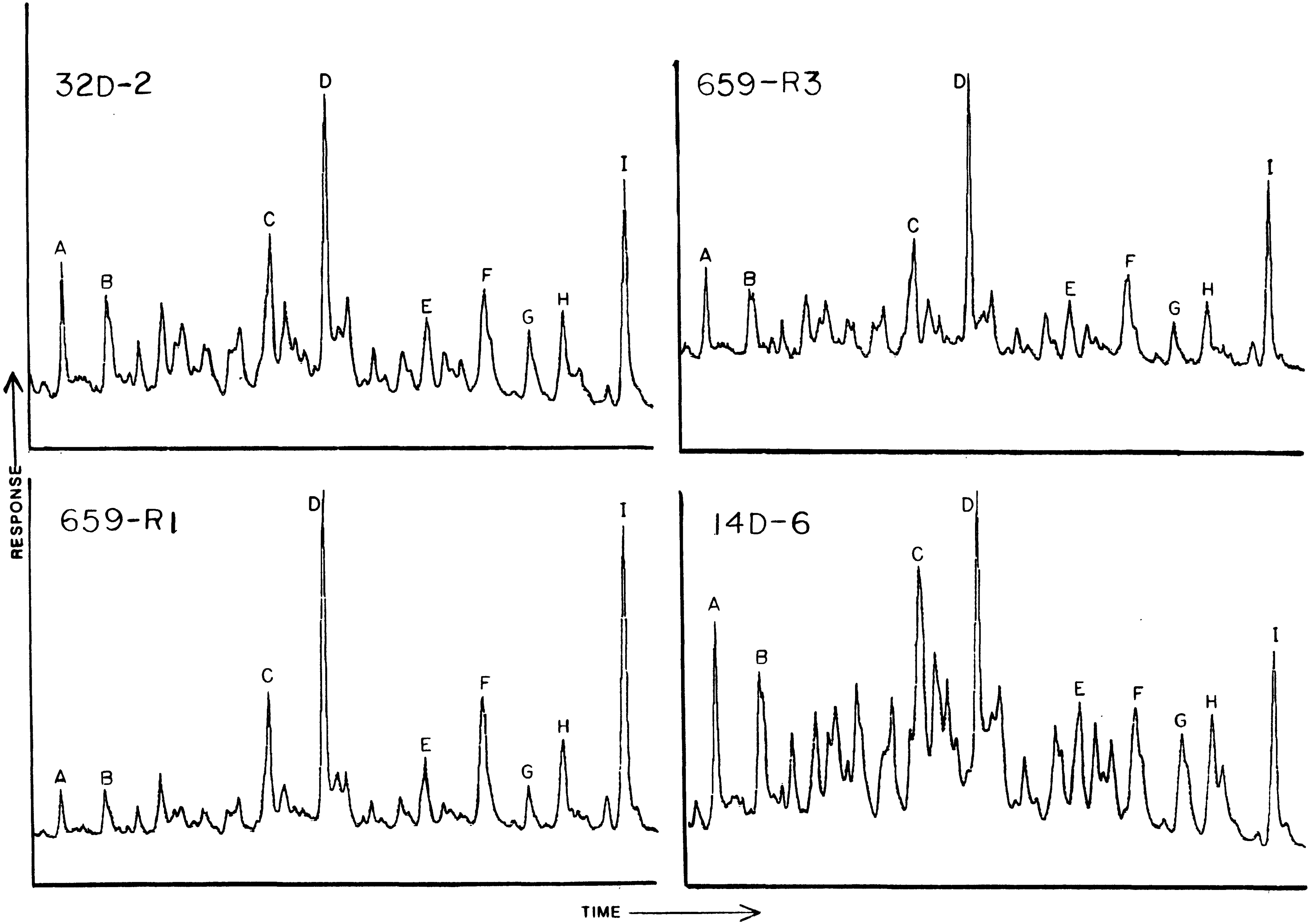

Figure 4. Mass chromatograms (m/z = 217) showing the distributions of steranes in petroleum extracted from four sediment-hosted, massive sulfide samples. Identifications are listed in Table 3.

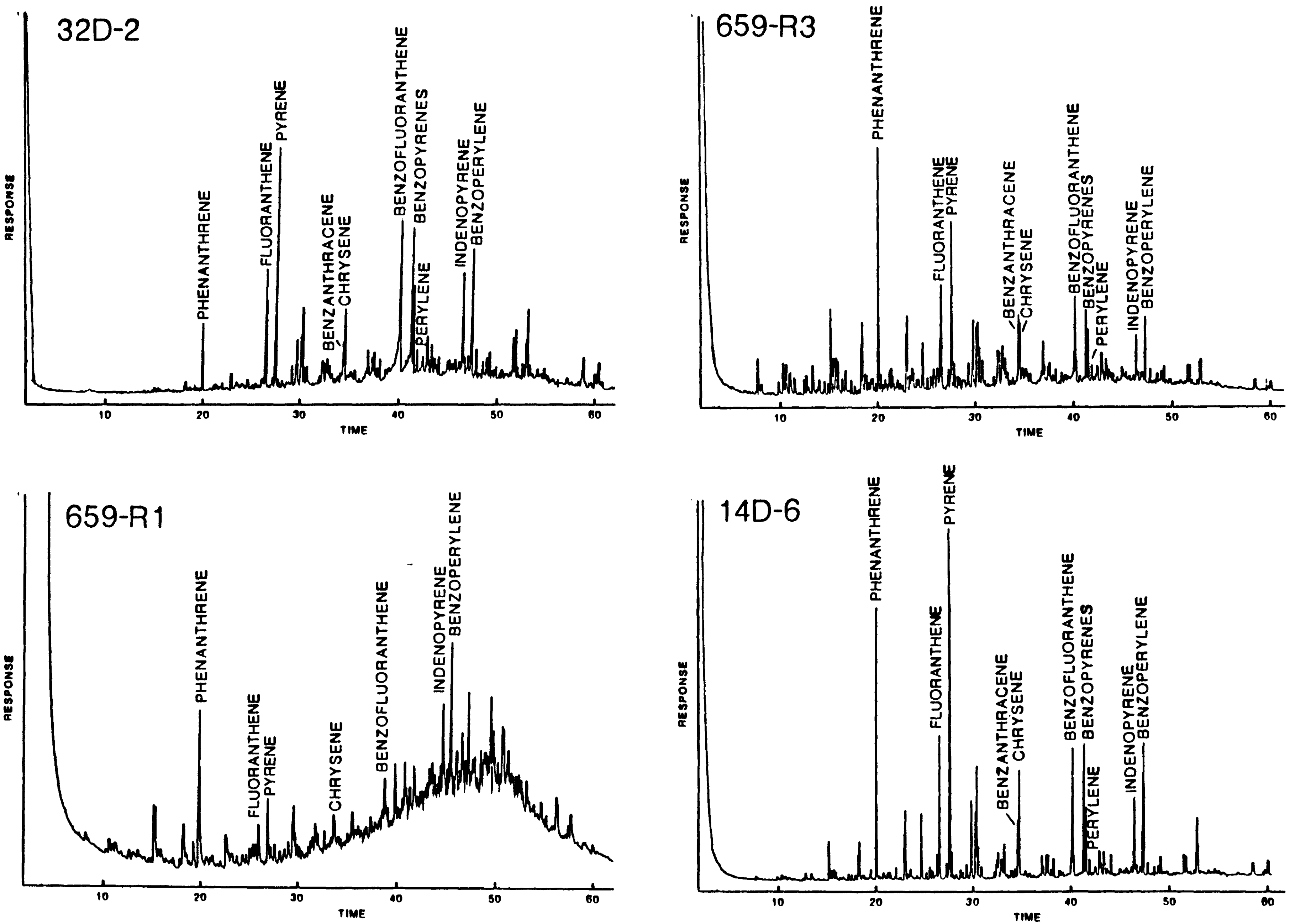

Figure 5. Gas chromatograms showing the distributions of polycyclic aromatic hydrocarbons in petroleum extracted from four sediment-hosted, massive sulfide samples.

Table 1. Sample Descriptions

Cruise	Station No.	Location N Latitude	Location W Longitude	Dredge Specimen	Description of Samples Used for Geochemical Analysis (Morton and others, 1987b; Zierenberg, written communication 1987)
SESCA L6-85-NC	32D-2	40°45'*	127°31'*	~185g of 4.5 kg	Clayey, silty, fine-grained sandstone interbanded with coarse- and fine-grained pyrrhotite and minor amounts of other sulfides. Asphaltic petroleum occurs throughout the sample.
L2-86-NC	14D-6	41°00.68' 41°01.08'	127°29.76' start 127°29.62' end	~40g of 5.6 kg	Partly indurated mudstone/siltstone with disseminated polymetallic sulfide. Strong petroliferous odor.
TI-86-NC	659-R1	41°01.11	127°29.63'	~10g of 3.5 kg	Partly indurated layered mudstone/siltstone with discrete grains of pyrrhotite-rich massive sulfide. Minor petroliferous odor. Collected at base of sulfide chimney approximately 25 cm high and 10 cm in diameter.
TI-86-NC	659-R3	41°01.11'	127°29.63'	~70g of 1.0 kg	Partly indurated mudstone/siltstone with disseminated pyrrhotite-rich sulfide. Strong petroliferous odor.

*Location approximate

Table 2. Organic Geochemical Data.

Station No.	Core Interval (cm)	Area	Weight Sample (g)	OC (%)	EOM (µg/g)	F-1 (µg/g)	F-2 (µg/g)	Alkanes CPI	Isoprenoids Pr/Ph	Steranes $C_{29}\ \frac{S}{S+R}$	Steranes $\frac{C_{29}\alpha R}{C_{27}\alpha R}$	$C_{31}\ \frac{S}{S+R}$	Terpane $C_{30}\ \frac{\beta\alpha}{\alpha\beta}$	$\alpha\beta\ \frac{C_{30}}{C_{29}}$	$C_{27}\ \frac{Tm}{Ts}$
Petroluem-impregnated samples															
32D-2		SESCA	1.1	5.6	55,000	1,000	24,000	1.2	1.7	0.24	0.82	0.47	0.66	0.73	21
14D-6		NESCA	1.0	5.3	19,000	1,200	9,300	1.1	0.9	0.40	0.60	0.57	0.33	1.60	15
659-R1		NESCA	1.0	5.1	16,000	1,400	9,900	1.3	0.9	0.10	0.90	0.42	0.74	0.73	20
659-R3		NESCA	1.0	4.4	14,000	1,500	7,300	1.3	1.6	0.21	0.59	0.47	0.72	0.66	28

Table 3. Identification of Terpanes and Steranes

Peak	Compound	
TERPANES and TRITERPANES (m/z 191)		
1	C_{19}-Tricyclic terpane	C_{19}
2	C_{19}-Tricyclic terpane	C_{19}
3	Fichtelite	C_{19}
4	? Sandaracopimarane	C_{20}
5	C_{20}-Tricyclic terpane	C_{20}
6	C_{20}-Tetracyclic terpane	C_{20}
7	C_{21}-Tricyclic terpane	C_{21}
8	C_{23}-Tricyclic terpane	C_{23}
9	C_{24}-Tricyclic terpane	C_{24}
10	C_{24}-Tetracyclic terpane	C_{24}
11	18α(H)-22,29,30-Trisnorhopane (Ts)	C_{27}
12	17α(H)-22,29,30-Trisnorhopane (Tm)	C_{27}
13	17β(H)-22,29,30-Trisnorhopane	C_{27}
14	17α(H),21β(H)-30-Norhopane	C_{29}
15	17β(H),21α(H)-30-Normoretane	C_{29}
16	17α(H),21β(H)-Hopane	C_{30}
17	17β(H),21β(H)-Norhopane, possible hopene overlap	C_{29}
18	17β(H),21α(H)-Moretane	C_{30}
19	17α(H),21β(H)-30-Homohopane(22S) and (22R)	C_{31}
20	17β(H),21β(H)-Hopane	C_{30}
21	17β(H),21α(H)-30-Homomoretane	C_{31}
22	17α(H),21β(H)-30,31-Bishomohopane(22S) and (22R)	C_{32}
23	17β(H),21α(H)-30,31-Bishomomoretane(22S) and (22R)	C_{32}
24	17β(H),21β(H)-30-Homohopane	C_{31}
25	17α(H),21β(H)-30,31,32-Trishomohopane(22S) and (22R)	C_{33}
26	17β(H),21α(H)-30,31,32-Trishomomoretane(22S) and (22R)	C_{33}
27	17β(H),21β(H)-30,31-Bishomohopane	C_{32}
28	17α(H),21β(H)-30,31,32,33-Tetrahomohopane(22S) and (22R)	C_{34}
29	17β(H),21α(H)-30,31,32,33-Tetrahomomoretane(22S) and (22R)	C_{34}
30	17β(H),21β(H)-30,31,32-Trishomohopane	C_{33}
31	17α(H),21β(H)-30,31,32,33,34-Pentahomohopane(22S) and (22R)	C_{35}
32	17β(H),21α(H)-30,31,32,33,34-Pentahomomoretane(22S) and (22R)	C_{35}
33	17β(H),21β(H)-30,31,32,33-Tetrahomohopane	C_{34}
34	17β(H),21β(H)-30,31,32,33,34-Pentahomohopane	C_{35}
STERANES and DIASTERANES (m/z 217)		
A	13β(H),17α(H)-diacholestane(20S)	C_{27}
B	13β(H),17α(H)-diacholestane(20R)	C_{27}
C	5α(H),14α(H),17α(H)-cholestane(20S)	C_{27}
D	5α(H),14α(H),17α(H)-cholestane(20R)	C_{27}
E	24-methyl-5α(H),14α(H),17α(H)-cholestane(20S) plus ?	C_{28}
F	24-methyl-5α(H),14α(H),17α(H)-cholestane(20R)	C_{28}
G	24-ethyl-5α(H),14α(H),17α(H)-cholestane(20S)	C_{29}
H	24-ethyl-5α(H),14β(H),17β(H)-cholestane(20R)	C_{29}
I	24-ethyl-5α(H),14α(H),17α(H)-cholestane(20R)	C_{29}

Table 4. Description of Sediment Organic Matter[1]

Designation	Area	OC (%)	
L1-86-NC-7G (82-90 cm)	SESCA	0.52	Abundant woody and coaly fragments. Common fine amorphous kerogen, aggregated amorphous kerogen and cuticles. Traces of pollen, spores, and fungal parts. Fragments of diatoms and radiolarians present. 1.5 TAI on bisaccate and other pollen; 2.6 TAI on resedimented spores.
L1-86-NC-8G (82-90 cm)	SESCA	0.31	Predominantly coaly fragments. Very common aggregated amorphous kerogen. Common fine amorphous kerogen and woody fragments. Traces of cuticles, pollen, spores, dinoflagellates, and fungal parts. 1.5 TAI on bisaccate pollen and spores; 2.4 TAI on resedimented bisaccate pollen.
L1-86-NC-26G (82-90 cm)	SESCA	0.72	Predominantly aggregated amorphous kerogen. Very common very fine grained coaly fragments. Traces of pollen, spores, and woody fragments. Abundant diatom and radiolarian fragments present. 1.5 TAI on bisaccate pollen and spores.
L1-86-NC-27G (87-95)	MESCA	0.13	Predominantly coaly fragments. Very common woody fragments. Common fine amorphous kerogen. Traces of aggregated amorphous kerogen, pollen, and spores. 1.5 TAI on bisaccate pollen.

[1] Clark Geological Services
Fremont, California