

Chapter 31

Distribution of Organic Sulfur Compounds in Mesozoic and Cenozoic Sediments from the Atlantic and Pacific Oceans and the Gulf of California

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Gas chromatography - mass spectrometry data of the "aromatic hydrocarbon" fractions of nearly 100 Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) sediment samples have been re-examined for the occurrence of organic sulfur compounds (OSC). Approximately 70% of the samples contain OSC with varying distribution patterns, although C₂₀ isoprenoid thiophenes are invariably present.

Cenozoic samples, mostly from high productivity areas, often contain a large variety of OSC with the C₂₅ and/or C₂₇ 2-alkylthiophenes sometimes being particularly abundant. In others, two stereoisomeric C₂₅ highly-branched isoprenoid thiophenes are the dominant compounds, although the saturated counterparts were tentatively identified only in a few cases. In samples from the Peruvian upwelling area a C₂₀ isoprenoidal cyclic trisulfide is often the most significant organic sulfur component.

In Mesozoic samples, mostly Cretaceous and Jurassic black shales, the abundance and variance of OSC is generally low. A few samples of Jurassic age show a distribution pattern of C₂₀ isoprenoid thiophenes which may indicate increased salinity during deposition. A C₂₀ isoprenoid thiolane is the most abundant compound in black shales from the Falkland Plateau, whereas at other locations the C₃₅ thienylhopane dominates. In one case two C₃₃ mid-chain 2,5-dialkylthiophenes were identified.

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Treib's discovery of porphyrins in geological samples (1) is considered to be the beginning of molecular organic geochemistry, relating organic compounds occurring in the geosphere to natural precursors in the biosphere; this is known as the biological marker concept. The identification of a thiophene-containing hopanoid (2) marks the start of a new epoch, featuring studies related to the organic geochemistry of sulfur compounds. Several papers, dealing with the occurrence, distribution, and structural identification of organic sulfur compounds (OSC) have been published recently (e.g., 3-8). Some of the most common OSC have previously been tentatively identified as alkylated thiophenes in sediments recovered by the Deep Sea Drilling Project (DSDP) (9-12). Here we extend the report on the occurrence and distribution of OSC in deep-sea sediments by a re-examination of gas chromatography - mass spectrometry (GC-MS) data of the "aromatic hydrocarbon" fractions of almost 100 samples from various parts of the world's oceans (Figure 1), collected and analyzed during 12 years participation of the Institute of Petroleum and Organic Geochemistry (KFA Jülich, F.R.G.) in the Deep Sea Drilling Project and its successor project, the Ocean Drilling Program (ODP).

Samples and Experimental Methods

The samples re-investigated are listed in Table I, together with information on their sub-bottom depth, age, lithology, and organic-carbon content. The locations of the drilling sites are shown in Figure 1. Offshore California, in the Gulf of California and on the Falkland Plateau the present geothermal gradients are particularly high (ca. 70-150°C/km), whereas in the other holes moderate geothermal conditions were encountered (ca. 20-40°C/km) (13).

The procedures for sample preparation and the operating conditions of the GC-MS system have been described elsewhere (9-12, 14-16; ten Haven *et al.*, Proc. ODP, Sci. Results, 112, in press). All GC-MS data had been stored on magnetic tapes, but in some cases could not be retrieved. In these cases, indicated by an asterisk in Table I, old hardcopy files were checked for the occurrence of OSC. Mass chromatograms of characteristic ions (m/z 87, 97, 98, 101, 111, 115, 125, 129, 139, 195, 265, 331, 341), in combination with published information on relative retention times (3-5, 8), were used to identify the various compounds.

To confirm the identification of 2-tricosylthiophene, this compound was synthesized following standard procedures (17) with thiophene and tricosanoic acid as starting products.

The polar fraction of one sample from the Peru continental margin (679, E24359) was subjected to Raney Nickel desulfurization (5). The hydrocarbon fraction isolated from the desulfurized mixture was analyzed by GC-MS.

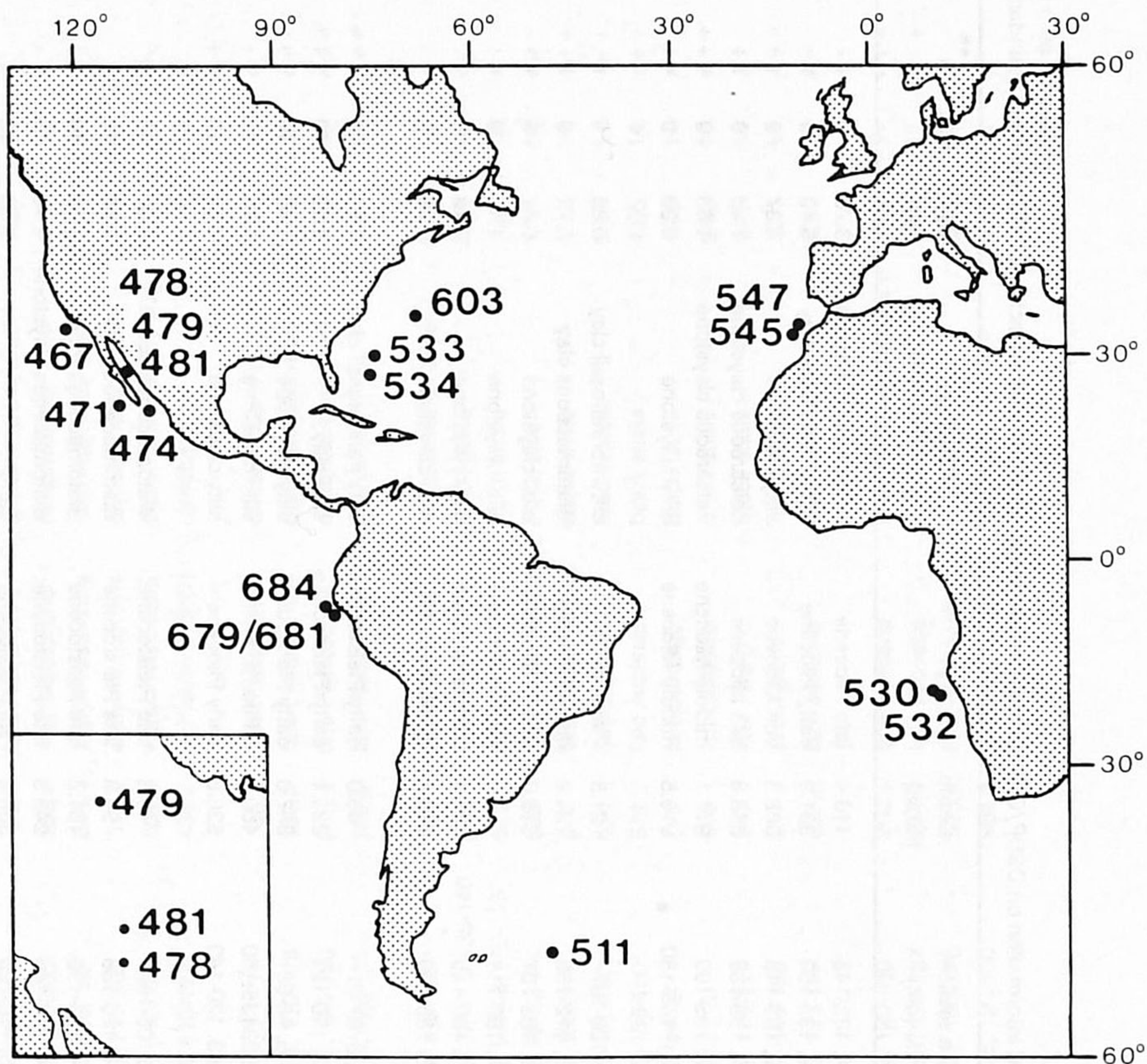


Figure 1. Map showing locations of DSDP/ODP drilling sites in the Atlantic and Pacific Oceans and in the Gulf of California (inset).

Table I. Background information on DSDP/ODP samples investigated, abundance of extractable OSC and most abundant OSC

Lab. code	Hole, core, section, interval (cm)	Depth (mbsf)	Age	Lithology	C _{org} (%)	Ref.	A ^{**}	B ^{***}
E8444 [*]	467-13-4, 132-148	116.4	late Pliocene	calcareous claystone	3.70	9	++	7
E8445 [*]	467-36-2, 133-150	331.9	early Pliocene	silty nannofossil clay	5.40	9	+	7
E8446	467-54-2, 100-115	502.6	late Miocene	silty claystone	4.37	9	+++	8
E8447	467-63-2, 130-133	588.3	late Miocene	calcareous claystone	1.46	9	++	2
E8448	467-97-2, 105-109	911.1	middle Miocene	calcareous claystone	1.63	9	+++	8
E8449 [*]	467-104-1, 145-150	976.5	middle Miocene	silty claystone	2.30	9	++	8
E8450	471-3-2, 120-137	21.8	Pleistocene	silty nannofossil clay	0.86	9	0	
E8451	471-13-7, 112-130	124.2	late Miocene	diatomaceous clay	0.72	9	+	7
E8452 [*]	471-34-2, 103-107	316.0	late(?) Miocene	silty claystone	0.81	9	++	8
E8453 [*]	471-44-1, 100-118	409.6	middle Miocene	silty claystone	1.12	9	++	8
E8454 [*]	471-57-3, 100-126	536.1	middle Miocene	silty claystone	0.78	9	+	8
E8455 [*]	471-69-3, 135-150	650.4	m. Miocene (?)	silty claystone	0.70	9	+	8
E8456 [*]	474-6-5, 0-15	46.0	early Pleistocene	silty nannofossil clay	1.24	10	+++	7
E8457	474A-7-2, 110-125	223.1	early Pleistocene	silty clay	1.16	10	+++	7
E8458	474A-21-6, 48-63	352.0	early Pleistocene	silty claystone	1.49	10	++	7
E8459	474A-32-2, 135-150	450.7	I. Plio./e. Pleist.	silty claystone	1.78	10	++	7
E8460	474A-40-3, 120-140	528.8	early Pliocene	silty claystone	0.52	10	++	8
E8461	478-6-3, 120-137	45.8	late Pleistocene	diatomaceous ooze	1.37	10	0	
E8462	478-11-4, 120-136	94.8	late Pleistocene	diatomaceous mud	1.59	10	+	2
E8463 [*]	478-17-4, 120-139	151.8	late Pleistocene	diatomaceous mud	1.12	10	0	
E8464 [*]	478-28-4, 120-140	248.3	late Pleistocene	diatomaceous claystone	2.19	10	++	8
E8465	478-35-5, 110-125	305.2	late Pleistocene	sand	0.50	10	+	8

E8466	479-9-2, 110-125	72.2	late Pleistocene	diatomaceous mud	2.36	10	+	2
E8467	479-17-5, 120-135	152.8	late Pleistocene	diatomaceous mud	2.19	10	o	
E8468	479-27-4, 135-150	246.4	early Pleistocene	diatomaceous mud	2.78	10	+	8
E8469	479-34-5, 110-125	314.2	early Pleistocene	diatomaceous mud	3.13	10	+	8
E8470	479-39-4, 110-125	359.2	early Pleistocene	diatomaceous silty clay	3.80	10	++	8
E8471	479-47-4, 110-122	436.2	e. Pleistocene (?)	claystone	1.15	10	+	8
E8472	481-8-2, 130-140	36.1	late Pleistocene	diatomaceous mud	1.54	10	o	
E8473	481A-10-2, 110-125	130.2	late Pleistocene	diatomaceous mud	5.76	10	+++	2
E8474	481A-22-4, 126-150	246.4	late Pleistocene	diatomaceous mud	1.92	10	+++	8
E8475	481A-26-5, 120-135	286.8	late Pleistocene	claystone	1.31	10	+++	8
E11369	511-16-1, 135-150	139	early Oligocene	diatomaceous ooze	0.60	14	o	
E11373	511-57-2, 37-41 & 135-140	504	Albian	black shale	0.69	14	o	
E11374	511-58-1, 9-14 & 120-125	513	Aptian	black shale	1.88	14	+	4
E11376	511-60-2, 78-82	533	Barremian/Aptian	black shale	3.84	14	+++	4
E11377	511-61-1, 139-143	542	Barremian/Aptian	black shale	5.17	14	+++	4
E11378	511-62-5, 135-150	554	late Jurassic	black shale	5.07	14	+++	4
E11379	511-64-4, 135-150	571	late Jurassic	black shale	4.66	14	+++	4
E11380	511-65-1, 41-46	577	late Jurassic	black shale	4.46	14	+	4
E11381	511-66-1, 23-28	586	late Jurassic	black shale	5.02	14	+	4
E11382*	511-67-1, 114-118	597	late Jurassic	black shale	5.43	14	++	4
E11384*	511-69-2, 145-150	617	late Jurassic	black shale	4.11	14	++	4
E11385	511-70-3, 135-150	627	late Jurassic	black shale	4.31	14	++	4
E13096*	530A-9-2, 120-130	203.8	late Miocene	mud-clast conglomerate	1.04	11	+++	7
E13097*	530A-13-5, 120-137	246.3	late Miocene	nannofossil ooze	0.44	11	+++	7
E13101*	530A-43-1, 130-140	525.4	late Paleocene	mudstone	0.10	11	+	10
E13104	530A-89-5, 120-130	965.3	Coniacian	claystone	0.05	11	o	

Continued on next page.

Table 1, continued

Lab. code	Hole, core, section, interval (cm)	Depth (mbsf)	Age	Lithology	C _{org} (%)	Ref.	A ^{**}	B ^{***}
E13105	530A-93-5, 135-145	997.4	Coniacian	claystone/black shale	2.30	11	o	
E13106	530A-97-3, 105-110	1030.1	Cenomanian	black shale	10.60	11	o	
E13107	530A-99-5, 0-10	1050.1	Cenomanian	mudstone/black shale	0.73	11	o	
E13109	530A-103-3, 110-120	1084.3	Alb./Cenoman.	mudstone	2.79	11	o	
E13110	530A-105-1, 90-100	1095.0	Alb./Cenoman.	mudstone	0.82	11	o	
E13111	532-1-2, 110-120	2.7	late Pleistocene	nannofossil/foram. ooze	2.76	11	o	
E13115	532-29-2, 90-100	123.3	late Pliocene	nannofossil marl	3.92	11	+++	6
E13116	532-37-2, 110-120	153.3	early Pliocene	nannofossil/foram. ooze	1.92	11	+++	6
E13435	533A-11-5, 117-136	225.9	late Pliocene	silty nannofossil mud	2.24	15	++	7
E13440	534A-34-1, 141-150	832.5	Albian	claystone	1.70	15	o	
E13442	534A-44-2, 130-140	925.9	Aptian	claystone	1.82	15	o	
E13443	534A-50-2, 132-142	975.4	Barremian	claystone	1.71	15	o	
E13445	534A-77-2, 120-130	1213.8	Valangian	claystone/limestone	0.71	15	o	
E13450	534A-125-5, 127-131	1619.8	Callovia	nannofossil claystone	2.81	15	o	
E12730	545-31-1, 49-65	284.6	Cenomanian	nannofossil clay	1.01	12	+	1
E12731	545-34-1, 70-81	313.3	Cenomanian	claystone clast	1.90	12	++	1
E12733	545-38-1, 65-80	351.2	Albian	nannofossil claystone	1.30	12	+	1
E12735	545-43-2, 130-140	400.9	Albian	nannofossil claystone	2.29	12	+	1
E12740	547A-16-3, 90-105	216.5	Cretac. slump (?)	clayey nannofos. chalk	0.30	12	o	
E12743	547A-20-3, 60-75	254.2	Cretac. slump (?)	clayey nannofos. chalk	3.96	12	++	11
E12747	547A-35-2, 15-30	394.7	Campanian	clayey nannofos. chalk	0.06	12	o	
E12748	547A-41-1, 30-48	440.9	Cenomanian	claystone	0.67	12	+	1
E12750	547A-56-1, 23-28	583.3	Cenomanian	nannofossil claystone	0.74	12	+	1
E12751	547A-66-2, 115-130	680.7	Albian	nannofossil mudstone	0.69	12	+	1

E12753	547B-5-6, 83-101	770.9	Albian	nannofossil claystone	1.29	12	+++	5
E12755	547B-6-1, 77-84	772.8	Albian	nannofossil claystone	1.87	12	++	10
E12756	547B-15-2, 8-12	847.6	Jurassic	black shale	4.75	12	+	10
E12757	547B-15-2, 14-17	847.7	Jurassic	black shale	1.13	12	o	
E12759	547B-18-1, 100-117	874.1	Jurassic	black shale	0.70	12	+	2
E12760	547B-20-2, 92-104	893.5	Jurassic	black shale	1.63	12	++	3
E12761	547B-22-1, 13-18	905.2	Jurassic	black shale	1.03	12	+	3
E12764	547B-30-3, 59-75	981.2	Triassic (?)	sandy mudstone	0.28	12	o	
E18099	603B-32-1, 30-32	1109.8	Coniac./Turon.	clayey sandstone	0.14	16	o	
E18100	603B-34-1, 77-99	1128.2	Cenomanian	black claystone	9.32	16	+	1
E18101	603B-34-3, 68-70	1132.6	Cenomanian	black claystone	14.50	16	++	10
E24353	679C-2-4, 30-37	13.9	Quaternary	diatom./foram. mud	3.72	17	+	2
E24355	679C-4-4, 30-37	32.9	Quaternary	diatom./foram. mud	3.21	17	+	2
E24357	679C-6-4, 30-37	51.9	Quaternary	diatomaceous mud	2.57	17	+	2
E24359	679C-8-2, 30-37	67.9	late Pliocene	diatomaceous mud	7.52	17	+	12
E24361	681C-1-1, 30-37	0.4	Quaternary	diatomaceous mud	4.65	17	+	2
E24363	681C-2-6, 5-12	13.5	Quaternary	diatomaceous mud	1.32	17	+	12
E24365	681C-4-4, 30-36	29.8	Quaternary	diatomaceous mud	6.51	17	+	2
E24369	681C-9-4, 30-37	77.3	Quaternary	mud, silt, silty sand	0.53	17	+	2
E24371	684C-1-1, 30-37	0.4	Quaternary	diatomaceous mud	3.56	17	o	
E24375	684C-3-6, 30-37	25.2	Pliocene	diatomaceous mud	5.89	17	o	
E24376	684C-4-3, 30-37	30.2	Pliocene	silty diatomaceous mud	7.46	17	+++	12
E24377	684C-4-7, 30-37	36.2	Pliocene	diatomaceous mud	4.09	17	+++	12

* Only old output data available. ** Occurrence: o = absent, + = present, ++ = minor, +++ = abundant, ++++ = very abundant.
 *** Most important organic sulfur compound (numbers refer to Figure 3).

Results and Discussion

Approximately 70% of the samples re-investigated contain OSC (Table I). In Cenozoic samples they are more common and more diverse than in Mesozoic sediments (Table II). Most of the Cenozoic samples were collected from areas of present-day high surface-water bioproductivity, which presumably prevailed already when these sediments were deposited (18). The samples of Mesozoic age are predominantly so-called black shales, for which the exact paleodepositional environment (oxygen depletion due to restricted water circulation or due to high productivity) is still a matter of debate (19).

The maturity of the organic matter in all samples is low, although differences were noted based on the extent of isomerization at chiral centers of certain unsaturated steroids: diasterenes and spirosterenes at C-20, and monoaromatic anthrasteroids at C-14 (13, 20). In areas with a high geothermal gradient these isomerization reactions have gone to completion at a shallower sub-bottom depth whereas in areas with a low geothermal gradient they are sometimes not even completed at much greater depth (13).

There is no correlation between the presence or abundance of extractable OSC in the "aromatic hydrocarbon" fraction and the organic-carbon content of a sediment, e.g., in a Miocene nannofossil ooze from the Angola Basin (530, E13097) with a C_{org} content of 0.44% the "aromatic hydrocarbon" fraction consists almost entirely of OSC, whereas no OSC occur in the "aromatic hydrocarbon" fraction of a Cretaceous black shale (530, E13106) from the same hole with a C_{org} content of 10.60%. Clearly, the competition between hydrogen sulfide and/or polysulfides on one hand and available reactive iron on the other determines whether sulfur is incorporated in sedimentary organic matter. The absence of extractable OSC in the "aromatic hydrocarbon" fraction, however, does not imply that sulfur has not been incorporated at all, because sulfur-containing moieties may, of course, occur in the kerogens, asphaltenes and polar fractions of the samples. The investigation of these fractions is beyond the scope of this paper.

Partial reconstructed ion chromatograms (RIC) of three samples show how variable the distributions of OSC are (Figure 2; due to different capillary columns and different GC-MS operating conditions the elution times of identical compounds differ). In almost all samples the aromatic hydrocarbon, perylene, is dominantly present, but in the upper trace 2-tricosylthiophene (7; confirmed by coinjection of an authentic standard) is by far the most abundant OSC, while in the other two examples this compound does not occur at all. Two stereoisomeric C_{25} highly-branched isoprenoid thiophenes (8) dominate in a late Pleistocene claystone from the Gulf of California (481, E8474), while 3-methyl-2-(3,7,11-trimethyldodecyl)thiolane (4) is abundant in a late Jurassic black shale from the Falkland Plateau (511, E11381). The most abundant OSC of each sample is given in Table I and their structures are shown in Figure 3. Reference to these structures in the text is made by bold numbers. The abundances of these OSC

Table II. Relative abundance of the major OSC in the "aromatic hydrocarbon" fraction of DSDP/ODP sediment extracts *

Site	Sample	Compounds **										others ***		
		1	2	3	4	5	6	7	8	9				
467	E8444	+	++	-	-	-	+	++	+	+	-			
	E8445	+	+	-	-	-	+	+	+	+	+			
	E8446	+++	+++	+	+	+++	+	+	+	+	+	+	9	
	E8447	+	+++	+	+	+	0	+	+	+	+	+		
	E8448	+	++++	0	+	+	0	+	+	+	+	+	9	
	E8449	+	+	+	-	+	+	+	+	+	+	+	+	
471	E8451	0	0	0	0	0	0	0	0	0	0	+	0	
	E8452	+	+	0	-	+	0	0	0	0	0	0	+	9
	E8453	+	+	+	+	+	+	+	+	+	+	+	+	9
	E8454	+	+	-	-	-	-	-	-	-	-	-	+	
	E8455	-	-	-	-	-	-	-	-	-	-	-	+	
	E8456	+	+	-	-	-	+	+	+	+	+	+	+	
474	E8457	+	+	+	0	+	+	+	+	+	+	+	+	
	E8458	0	+	0	0	0	0	0	0	0	0	+	+	
	E8459	+	+	0	+	+	+	+	+	+	+	+	+	
	E8460	+	+	0	+	0	0	0	0	0	0	+	+	
	E8462	+	+	0	0	0	0	0	0	0	0	0	0	
478	E8464	+	++	-	-	-	-	-	-	-	-	-	+	
	E8465	+	+	0	0	0	0	0	0	0	0	0	+	

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Table II, continued

Site	Sample	Compounds ^{**}										others ^{***}		
		1	2	3	4	5	6	7	8	others				
603	E18100	++	++	+	0	+	0	0	0	0	0	0	0	
	E18101	++	++	+	+	+	0	0	0	0	0	0	0	10
679	E24353	+	++	0	0	0	0	0	0	0	0	0	0	12
	E24355	+	++	0	0	0	0	0	0	0	0	0	0	12
	E24357	+	+	0	0	+	0	0	0	0	0	0	0	12
	E24359	+	+	0	0	+	0	0	0	0	0	0	0	12
681	E24361	+	++	0	0	0	0	0	0	0	0	0	0	
	E24363	0	+	0	0	0	0	0	0	0	0	0	0	12
	E24365	+	+	0	0	0	0	0	0	0	0	0	0	12
	E24369	+	+	0	0	0	0	0	0	0	0	0	0	12
684	E24376	+	++	0	0	0	0	0	0	0	0	0	0	12
	E24377	+	++	0	0	+	0	0	0	0	0	0	0	12

* expressed as percentages of the relative intensity in the total ion current: - = not determined (only old output data

available, 0 = < 1%, + = 1 - 10%, ++ = 10 - 30%, +++ = 30 - 60%, + + + + = 60 - 100%.

** Numbers refer to Figure 3

*** abundance higher than 10%.

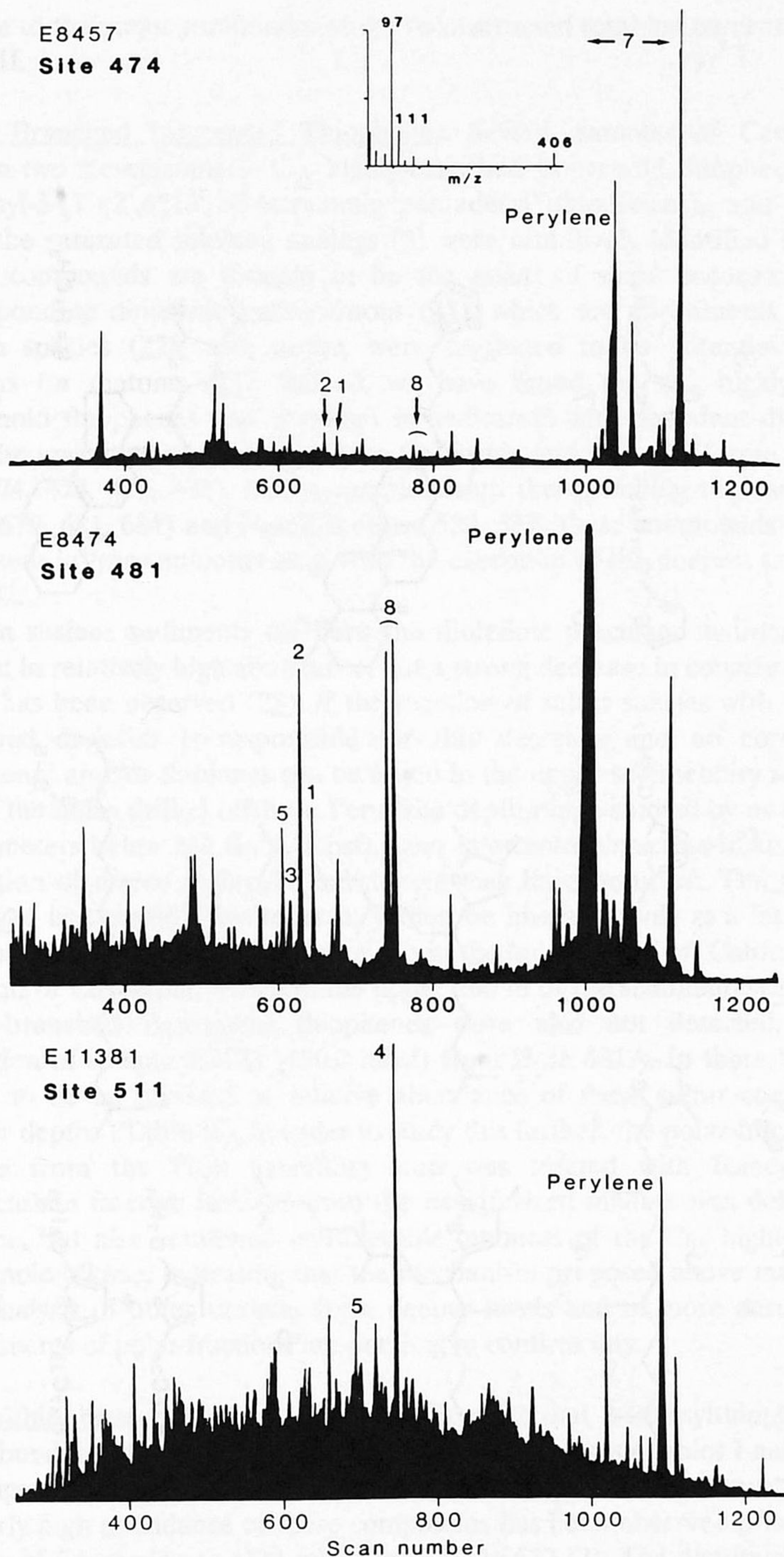


Figure 2. Partial reconstructed ion chromatograms of the "aromatic hydrocarbon" fraction of three samples. Numbers refer to Figure 3.

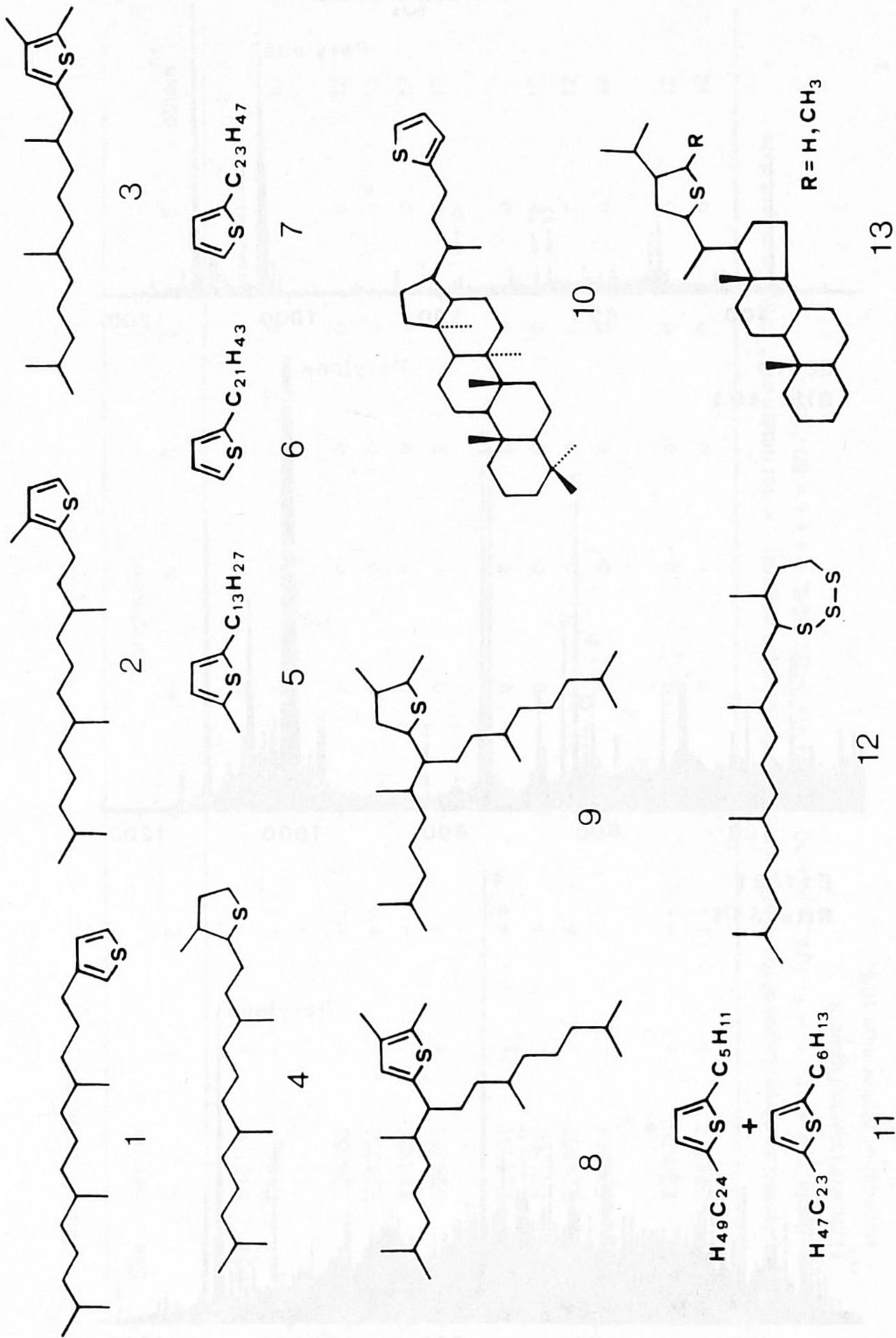


Figure 3. Selected structures of OSC discussed in text.

relative to the major component of the reconstructed total ion current is given in Table II.

Highly-Branched Isoprenoid Thiophenes. Several samples of Cenozoic age contain two stereoisomeric C₂₅ highly-branched isoprenoid thiophenes (**8**; 2,3-dimethyl-5-(7'-(2',6',10',14'-tetramethylpentadecyl))thiophenes), and in a few cases the saturated thiolane analogs (**9**) were tentatively identified (Table II). These compounds are thought to be the result of sulfur incorporation into corresponding diolefinic hydrocarbons (**21**), which are constituents of certain diatom species (**22**), and, hence, were suggested to be potential biological markers for diatoms (**21**). Indeed, we have found the C₂₅ highly-branched isoprenoid thiophenes and thiolanes in sediments with abundant diatom tests from the upwelling areas off southern California and Baja California (Sites 467, 471, 474, 478, 479, 481), but in samples from the upwelling regimes off Peru (Sites 679, 681, 684) and Namibia (Sites 530, 532) these compounds are absent or present in trace amounts only, with the exception of the deepest sample from Site 532.

In surface sediments off Peru the diolefinic precursor hydrocarbons are present in relatively high abundance, but a strong decrease in concentration with depth has been observed (**23**). If the reaction of sulfur species with the highly-branched diolefins is responsible for this decrease and no corresponding thiophenes and/or thiolanes can be found in the upper sedimentary sequence of any of the holes drilled offshore Peru (the depth range studied by us was from 0 to 80 meters below sea floor, mbsf), then intermolecular cross-linking with the formation of macro molecular substances may have occurred. The C₂₅ highly-branched isoprenoid thiophenes may then be liberated only at a later stage of diagenesis. There are indications for this in the holes drilled off California and in the Gulf of California, where in the upper 200 m of the sedimentary column the highly-branched isoprenoid thiophenes were also not detected, with the exception of sample E8473 (130.2 mbsf) from Hole 481A. In these holes there seems to be an increase in relative abundance of these sulfur compounds at greater depths (Table II). In order to study this further, the polar fraction of one sample from the Peru upwelling area was treated with Raney Ni. The hydrocarbon fraction isolated from the desulfurized mixture was dominated by phytane, but also contained considerable amounts of the C₂₅ highly-branched isoprenoid alkane, indicating that the mechanism proposed above may be valid. The analysis of other samples from deeper levels and of more desulfurization experiments of polar fractions are pending to confirm this.

2-Alkylthiophenes. We have shown in Figure 2 that 2-tricosylthiophene (**7**) is very abundant in several samples studied. In a few cases (Tables I and II) this is accompanied by 2-henicosylthiophene (**6**) in high relative concentration. A similarly high abundance of these compounds has been observed previously in a sample of Cenozoic age (173 mbsf) from Hole 532 (**3**). The distribution pattern

of 2-alkylthiophenes in nine samples is given in Figure 4, which is based on peak height measurements in mass chromatograms of m/z 97+98. It includes the relative abundance of 3-(4,8,12-trimethyltridecyl)thiophene (1), which has a base peak at m/z 98 (8). Prominent C_{25} and C_{27} thiophenes occur in many of the Cenozoic but not in Mesozoic sediments studied (e.g., samples E12731, E12743 of Cretaceous age from the Mazagan Escarpment, Sites 545 and 547; Figure 4). Instead, the older samples often contain a homologous series of 2-alkylthiophenes over a wider carbon number range (Figure 4). It is noteworthy that the distribution of 2-methyl-5-alkylthiophenes, according to mass chromatograms of m/z 111, does not reveal any predominance of C_{25} and/or C_{27} compounds. Hence, the precursors of the C_{25} and C_{27} 2-alkylthiophenes and the diagenetic reaction leading to their formation must be highly specific. Suitable precursors of these two 2-alkylthiophenes can be proposed based on the model of quenching of labile functionalised lipids by inorganic sulfur species (24), but such precursors have not yet been reported to occur in the biosphere.

Isoprenoid Thiophenes and Thiolanes. The two C_{20} isoprenoid thiophenes, 3-(4,8,12-trimethyltridecyl)thiophene (1) and 3-methyl-2-(3,7,11-trimethyldodecyl)thiophene (2), are the only OSC which occur in almost all the sediments included in this study. In several samples another C_{20} isoprenoid thiophene isomer, 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiophene (3), is also present, but usually only in trace amounts. Only in the Jurassic black shales from Hole 547B at the Mazagan Escarpment on the Moroccan margin (Figure 1) the concentration of compound 3 exceeds those of the other two C_{20} isoprenoid thiophenes. This is shown in Figure 5 by a mass chromatogram of m/z 308, the parent ion of C_{20} thiophenes. A distribution pattern like the one shown for the Jurassic sample has been interpreted to indicate increased salinity in the water column during deposition (25). For the Moroccan continental margin this interpretation is supported to some extent by local geological features (26). After rifting started in the Triassic, a series of small basins were created, separated by faulted and rotated basement blocks. In some of these basins halite with minor potash salts was deposited in shallow marine salt ponds, although not in the basin drilled at Site 547. Possibly in this basin the salinity never reached the level of oversaturation with respect to gypsum and/or halite, but nevertheless the salinity may have been enhanced.

The occurrence of a C_{20} isoprenoid thiolane, 3-methyl-2-(3,7,11-trimethyldodecyl)thiolane (4), is more restricted (Table II), but it is the most important compound of the "aromatic hydrocarbon" fraction of several Mesozoic black shales from the Falkland Plateau (e.g., late Jurassic sample E11381 from Site 511; Figure 2). In these samples, additional isoprenoid thiolanes with a base peak at m/z 115 occur in great abundance. Thiolanes have tentatively been suggested as intermediates in the formation of the corresponding thiophenes (24). This is in contradiction to the observation of abundant isoprenoid thiolanes in samples which have experienced more thermal stress and thus are

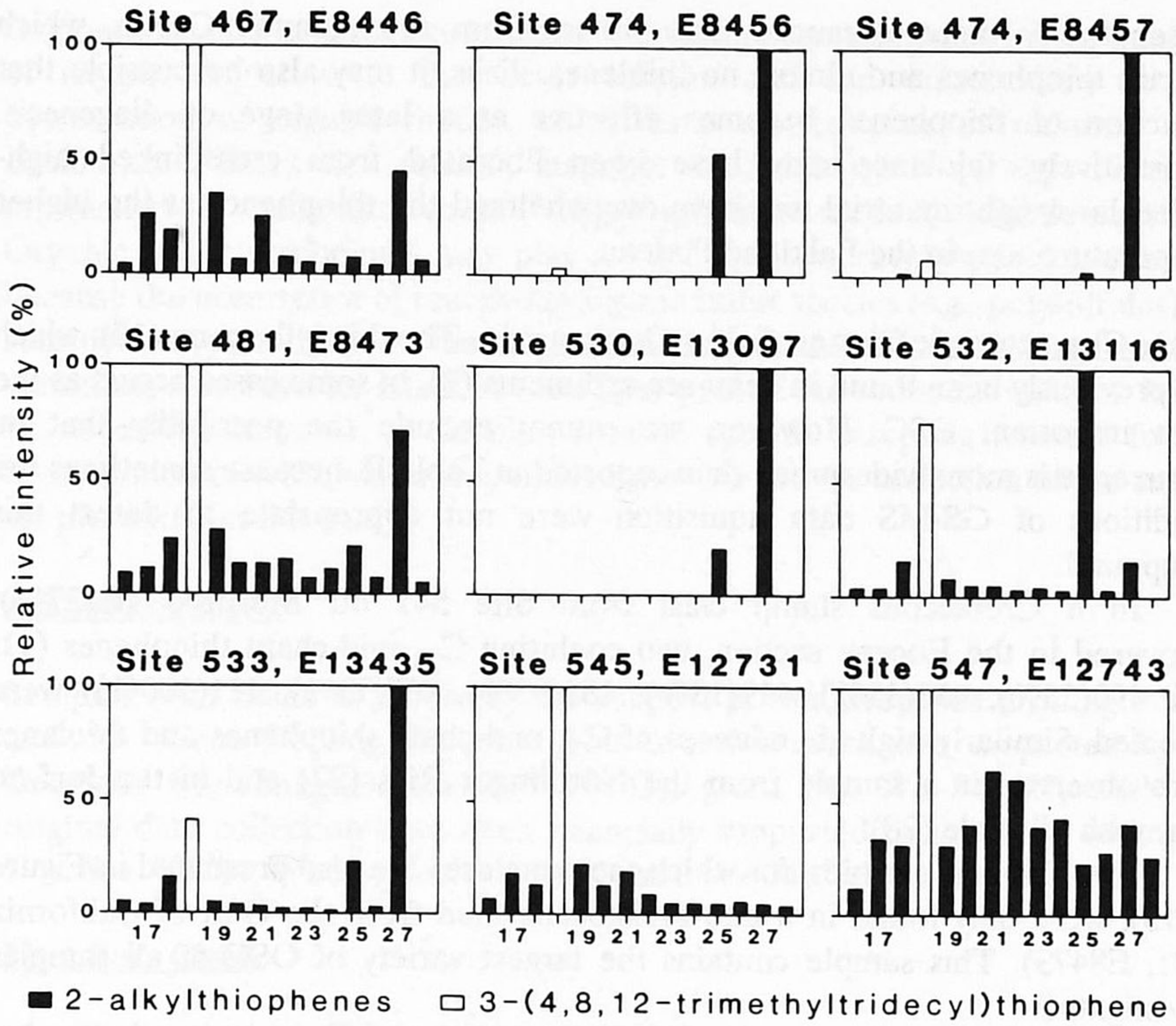


Figure 4. Histograms, based on mass chromatograms of m/z 97+98, showing distribution of 2-alkylthiophenes and 3-(4,8,12-trimethyltridecyl)thiophene.

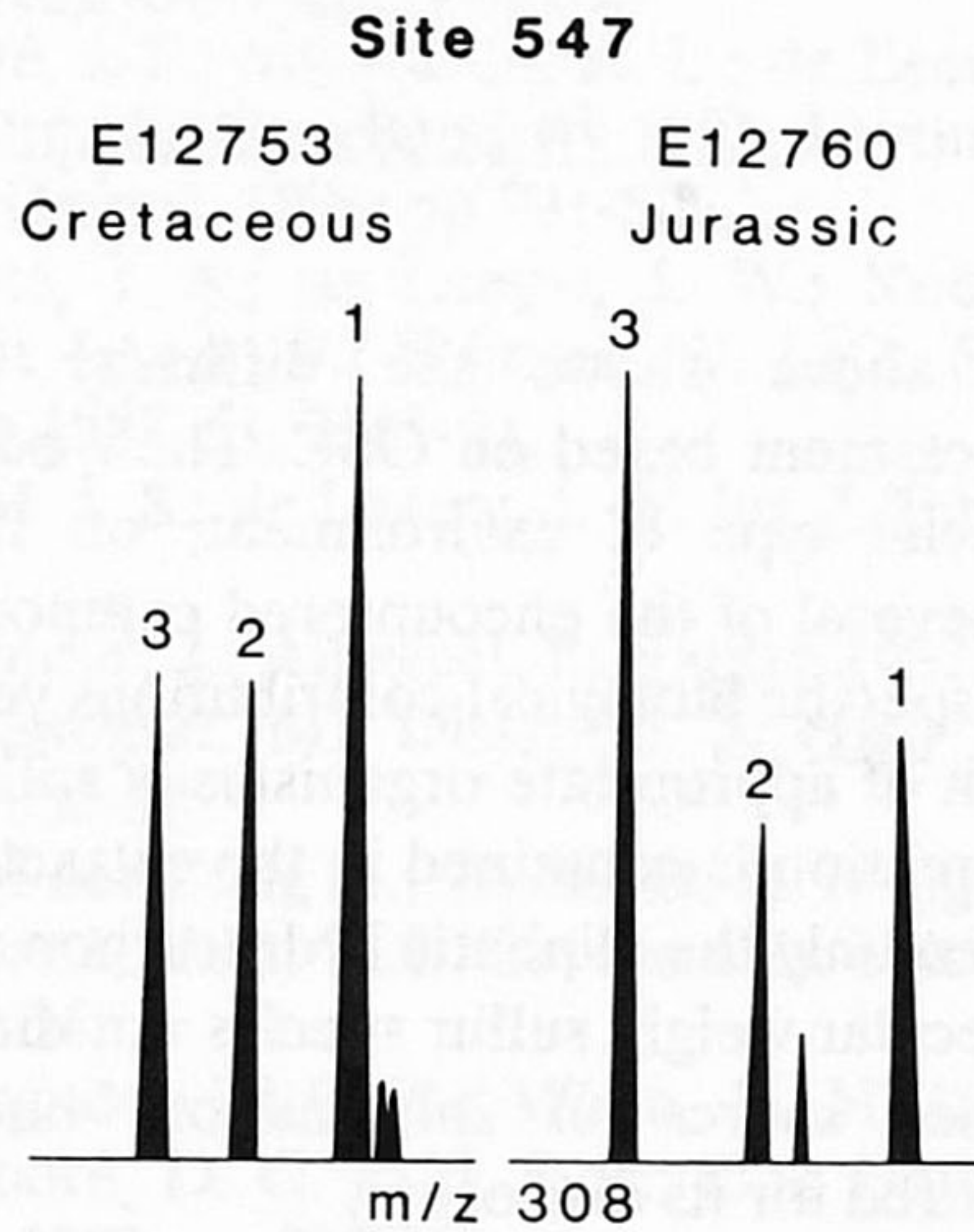


Figure 5. Partial mass chromatograms of m/z 308, showing the distribution of C_{20} isoprenoid thiophenes. Numbers refer to Figure 3.

diagenetically more advanced than others from the Atlantic Ocean, which contain thiophenes and almost no thiolanes. Thus, it may also be possible that reduction of thiophenes becomes effective at a later stage of diagenesis. Alternatively, thiolanes may have been liberated from cross-linked high-molecular-weight material and have overwhelmed the thiophenes at the higher temperature, *e.g.*, in the Falkland Plateau.

Other Characteristic Organic Sulfur Compounds. The thienylhopane (10), which has previously been found in deep-sea sediments (2), in some cases occurs as the most important OSC. However, we cannot exclude the possibility that its occurrence is more widespread than reported in Table II, because sometimes the conditions of GS-MS data acquisition were not appropriate to detect this compound.

In a Cretaceous slump clast from Site 547 off Morocco (E12743), recovered in the Eocene section, two coeluting C_{33} mid-chain thiophenes (11; m/z 490(55%), 433(15%), 419(18%), 181(92%), 167(73%), 111(100%)) were detected. Similarly high abundances of C_{33} mid-chain thiophenes and thiolanes were observed in a sample from the Nördlinger Ries (27) and in the Jurfed Darawish oil shale (28).

Two thiolane steroids, for which the structures are also presented in Figure 3 (13), were only found in a late Pleistocene mud from the Gulf of California (481, E8473). This sample contains the largest variety of OSC of all samples investigated.

Most sediments from the Peruvian upwelling area contain a C_{20} isoprenoid trisulfide (12), as well as the corresponding isoprenoid disulfides. These compounds have been found to date only in one sediment from the northern Apennines and an incorporation of polysulfides has been invoked to explain their occurrence (29).

Conclusions

The brief discussion above shows the difficulty of a straightforward paleoenvironmental assessment based on OSC. Their occurrence seems not to be related to any special type of environment; on the contrary, they are widespread. However, several of the encountered compounds cannot be related chemotaxonomically to specific biological contributions yet, because information on the lipid composition of appropriate organisms is still scant. Nevertheless, it is clear that much information is contained in the extractable OSC, information which is not evident when only the aliphatic hydrocarbon fraction is investigated. Furthermore, high-molecular-weight sulfur species not directly amenable to GC-MS analysis is another source of information, but chemical treatment (desulfurization) is required for its disclosure.

For the paleoenvironmental assessment of deep-sea sediments the study of the concentrations and distribution patterns of various OSC is just another

fragment needed to reconstruct a larger mosaic centering around the question of oxygen depletion in the water column and the subsequently favored preservation of organic matter, either as a consequence of reduced water circulation ("Black Sea model", stagnant conditions), or by high biological productivity in the surface water ("oxygen minimum model", dynamic situation). Organic sulfur compounds may play a key role in unraveling this controversy because the occurrence of reactive inorganic sulfur species (e.g., polysulfides) are sensitive to variations in the degree of oxygen depletion as long as these variations also have an effect in the upper part of the sediment column. It may be necessary, however, to develop a more specific sampling strategy for the investigation of OSC, which may differ from that for the collection of the sample set presented in this study.

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