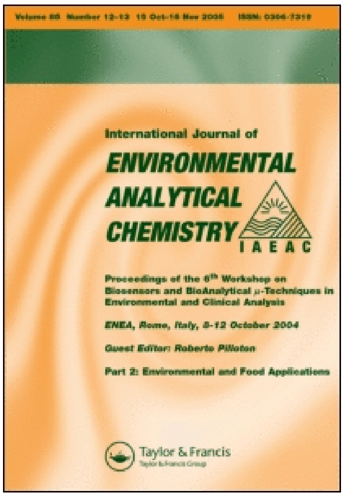

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# The Origin and Fate of Isoprenoid $C_{20}$ and $C_{15}$ Sulphur Compounds in Sediments and Oils†

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(*Received March 20, 1986*)

The identification of isoprenoid $C_{20}$ and $C_{15}$ sulphur compounds in Rozel Point Oil is described. The occurrence of isoprenoid-thiophenes, -thiolanes, -benzothiophenes, -bithiophenes, -(thienyl)alkylthiophenes and -thienylthiolanes in this oil and in other oils and sediments is reported. These compounds are thought to originate from sulphur incorporation into unsaturated phytanols and farnesol at the early stages of diagenesis. Compounds, that contain two sulphur atoms, are thought to originate from polyunsaturated phytanols, compounds especially abundant in hypersaline environments due to the presence of archaebacteria and green and purple sulphur bacteria. A diagenetical scheme, indicating relationships between precursors and products is presented.

KEY WORDS: Organic sulphur compounds, isoprenoid $C_{20}$ sulphur compounds, hypersaline environment, Rozel Point Oil, mass spectrometry.

## INTRODUCTION

The occurrence of organic sulphur compounds (OSC) in oils and extracts of ancient and recent sediments is well known. Neither the

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origin nor the diagenetical fate of OSC is however understood. This lack of knowledge is partly due to the fact that the structures of OSC presently known are not very characteristic; the carbon skeletons do not seem to carry information about appropriate biosynthetic precursors. Only recently some OSC which seem to be related with such biosynthetic precursors were reported by several investigators.[1–5]

We have encountered isoprenoid and straight chain alkylthiophenes, -thiolanes, -thiacyclohexanes and -benzothiophenes with chain lengths of $C_{12}$–$C_{28}$ in several sediment extracts and oils.[4–8] Especially the $C_{20}$ isoprenoid thiophenes occurring in several sediment extracts and oils give clues to their biosynthetic origin. In this paper we concentrate on data obtained for these isoprenoid OSC.

Over the years Berner has pointed out very elegantly that bacterial sulphate reduction is the mechanism for formation of anorganic sulphur compounds in sediments.[9] In normal marine sediments the rate of sulphate reduction is determined by the reactivity of the organic matter substrate. Hence, the presence of high quality organic matter causes a high production of $H_2S$ and its fixation products ($FeS, FeS_2$). From the organic chemical point of view one can expect the interaction of $H_2S$ or other sulphur reagents like polysulfides with suitable functional groups present in the organic compounds present. Especially when no "suitable" Fe ions are available—e.g. in hypersaline evaporitic environments—one can expect relatively high abundancies of OSC since no competition for $H_2S$ between the organic compounds and Fe ions exists. Therefore we have investigated sediment extracts and crude oils which were known to originate from anaerobic environments of sedimentation and from evaporitic environments of sedimentation. Especially a seep oil—Rozel Point Oil—the organic matter of which is thought to originate from an evaporitic playa lake environment[7,10] was investigated because of its high abundance of OSC.

## EXPERIMENTAL

Rozel Point Oil was obtained from the Geological Survey of Utah (USA). This seep oil came from a site in the North Western part of Utah.

Details on the fractionation of the oil and subfractionation of the aromatic fraction of the oil have been described elsewhere.[8] The aromatic fraction was also fractionated into a so called total low molecular weight aromatic and a total high molecular weight aromatic fraction by column chromatography ($Al_2O_3$, 25 cm × 1 cm) using hexane/toluene (9:1) and toluene as eluents respectively. The total low molecular weight aromatic fraction contains most of the GC amenable compounds of the aromatic fraction.[8] Gas chromatography of the obtained fractions was carried out on a Varian 3700 gas chromatograph equipped with a flame ionization (FID) and a flame photometric detector (FPD). A fused silica capillary column ($l = 25$ m, i.d. $= 0.32$ mm) coated with CP-Sil 5 (film thickness $= 0.12\,\mu$m) was split at the end of the column with a splitter device. The conditions used were described previously.[5]

GC–MS analysis was carried out on a Varian 3700 gas chromatograph connected to a MAT-44 quadrupole mass spectrometer as described previously.[5]

Exact mass measurements were performed on a Varian MAT 311 double focussing mass spectrometer by peak matching using selected masses from perfluorkerosine as the reference at a resolution of 5000.

## RESULTS

The Rozel Point Oil was separated by conventional techniques into the so called aliphatic, aromatic and hetero fractions. Because of the very complex nature of the aromatic fraction a further fractionation was performed by column chromatography over alumina using several eluents sequentially. The resulting fractions (in case of the Rozel Point Oil called RPO-1, -2, etc.) were investigated by capillary gas chromatography with dual FID and FPD detection and by capillary gas chromatography–mass spectrometry. Since—in this paper—we will concentrate on the most abundant isoprenoid $C_{20}$ components present Figure 1 shows the appropriate parts of the total ion current (TIC) traces of the total low molecular weight aromatic fraction and the fractions RPO-1, -2, -5 and -6. The symbols used in these traces indicate compounds with structures shown in Schemes 2 and 3 and in the Appendix.

Fraction RPO-1 almost entirely consisted of $C_{20}$ isoprenoid thiophenes and thiolanes. The major isoprenoid thiophenes were

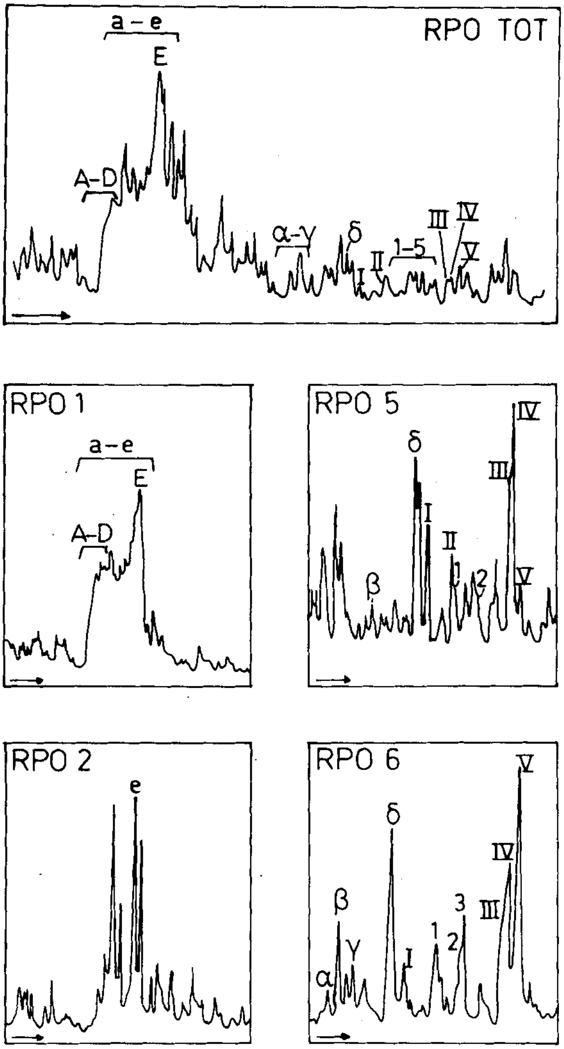


FIGURE 1 Partial total ion current traces of appropriate fractions of the aromatic fraction and of the total low molecular weight aromatic fraction of the Rozel Point Oil showing the distributions of the isoprenoid $C_{20}$ sulphur compounds. Symbols refer to compounds assigned in Table I.

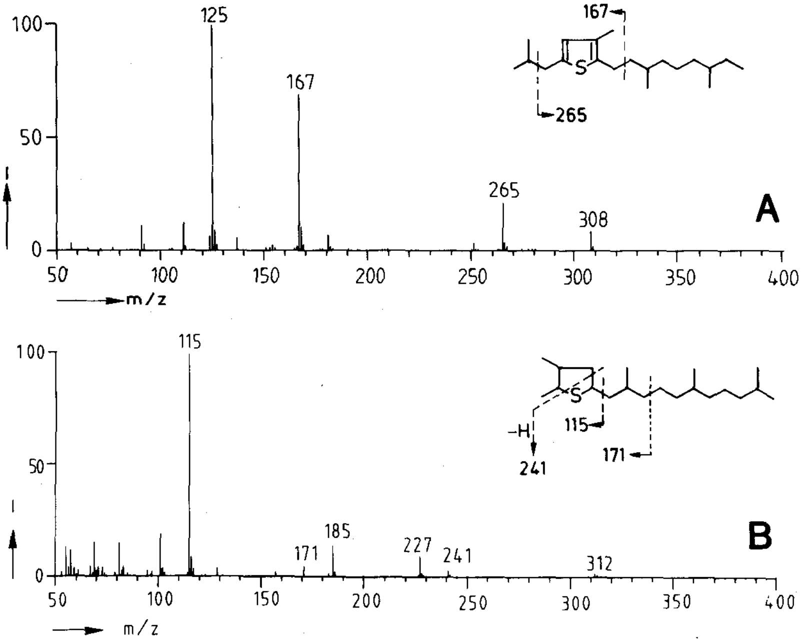


FIGURE 2 Mass spectra of (A): 2-(3,7-dimethylnonyl)-5-(2-methylpropyl)-3-methylthiophene (D), (B): a mixture of 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiolane (5) and an unknown compound (with major fragment ions at m/z 185 and 227 in its mass spectrum).

identified based on their relative GC retention times and on comparison of their mass spectra with mass spectra of synthesized isoprenoid thiophenes.[4,11] A typical mass spectrum of 2-(3,7-dimethylnonyl)-5-(2-methylpropyl)-3-methylthiophene (D) is shown in Figure 2a. This mass spectrum is characterized by two fragments (m/z 167 and 265) originating from $\beta$-cleavages of both side chains. The base peak m/z 125 is thought to be a secondary fragment ion originating from both primary fragments (m/z 167 and 265) by a rearrangement in which the other alkyl side chain is removed as an alkene. This mass spectrum is in agreement with those of a series of 2*n*-alkyl-3-methyl-5-(2-methyl-*n*-alkyl)thiophenes,[12] in which the base peak also appeared at m/z 125.

Appropriate mass chromatography using the m/z values of ions generated by characteristic $\beta$-cleavages clearly indicated the presence of the major isoprenoid thiophenes present (Figure 3). They are listed in Table I and the structures tentatively identified are given in both Schemes 2 and 3.

The isoprenoid thiolanes were present in RPO-1 through RPO-4. The identifications of these thiolanes are based on comparison of

TABLE I

Isoprenoid $C_{20}$ sulphur compounds identified in the Rozel Point Oil

| | |
|---|---|
| *isoprenoid thiophenes* | |
| A | 5-(2,6-dimethylheptyl)-2-(3-methylpentyl)-3-methylthiophene |
| B | 2-(3,7-dimethyloctyl)-5-(2-methylbutyl)-3-methylthiophene |
| C | 5-(2,6-dimethyloctyl)-2-(3-methylbutyl)-3-methylthiophene |
| D | 2-(3,7-dimethylnonyl)-5-(2-methylpropyl)-3-methylthiophene |
| E | 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiophene |
| *isoprenoid thiolanes* | |
| a | 5-(2,6-dimethylheptyl)-2-(3-methylpentyl)-3-methylthiolane |
| b | 2-(3,7-dimethyloctyl)-5-(2-methylbutyl)-3-methylthiolane |
| c | 5-(2,6-dimethyloctyl)-2-(3-methylbutyl)-3-methylthiolane |
| d | 2-(3,7-dimethylnonyl)-5-(2-methylpropyl)-3-methylthiolane |
| e | 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiolane |
| *isoprenoid bithiophenes and (thienyl)alkylthiophenes* | |
| I | 2-(4-(2′,3′-dimethyl-5′-thienyl)-3-methylbutyl)-5-(2-methylpropyl)-3-methylthiophene |
| II | 5-(3-(2′,3′-dimethyl-5′-thienyl)-2-methylpropyl)-2-(3-methylbutyl)-3-methylthiophene |
| III | 5′-(3-methylpentyl)-5-(2-methylpropyl)-3,4′-dimethyl-2,2′-bithiophene |
| IV | 5-(2-methylbutyl)-5′-(3-methylbutyl)-3,4′-dimethyl-2,2′-bithiophene |
| V | 5-(2,6-dimethylheptyl)-3,4′,5′-trimethyl-2,2′-bithiophene |
| *isoprenoid thienylthiolanes* | |
| 1 | 5-(5′-(2-methylbutyl)-3′-methyl-2′-thienyl)-2-(3-methylbutyl)-3-methylthiolane |
| 2 | 2-(2′-(3-methylbutyl)-3′-methyl-5′-thienyl)-5-(2-methylbutyl)-3-methylthiolane |
| 3 | 2-(2′-(3-methylpentyl)-3′-methyl-5′-thienyl)-5-(2-methylpropyl)-3-methylthiolane |
| 4 | 5-(2,6-dimethylheptyl)-2-(2′,3′-dimethyl-5′-thienyl)-3-methylthiolane |
| 5 | isomer of 4 |
| *isoprenoid benzothiophenes* | |
| α | 4-(2,6-dimethylheptyl)-2,3,6-trimethylbenzo(b)thiophene |
| β | 4-(2-methylbutyl)-2-(3-methylbutyl)-3,6-dimethylbenzo(b)thiophene |
| γ | 2-(3-methylpentyl)-4-(2-methylpropyl)-3,6-dimethylbenzo(b)thiophene |
| δ | 2-(3,7-dimethyloctyl)-3,6-dimethylbenzo(b)thiophene |

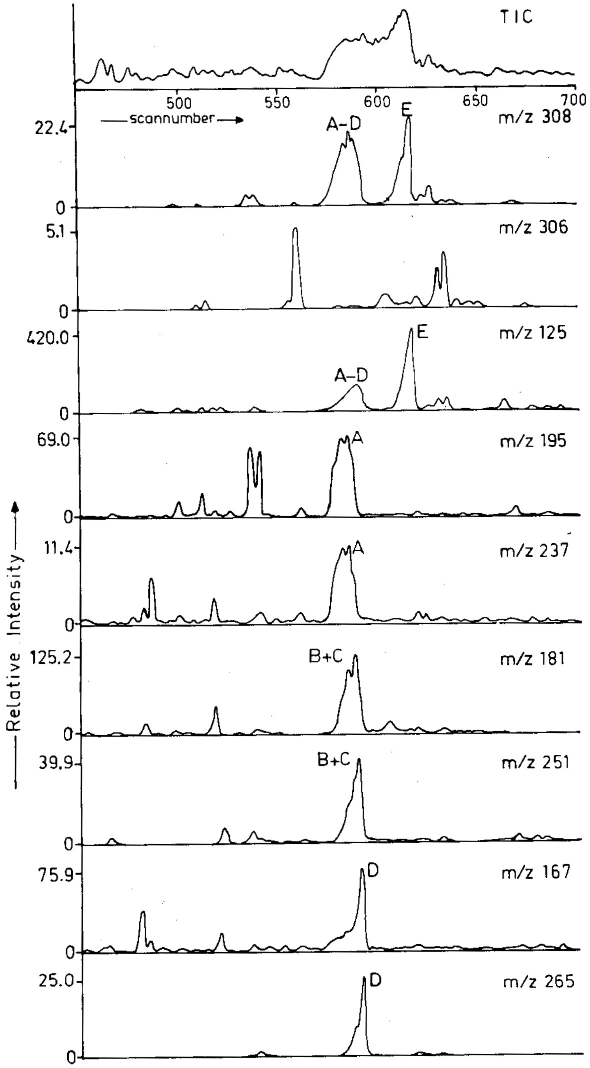


FIGURE 3 Partial mass chromatograms of m/z 308, 306, 125, 195, 237, 181, 251, 167 and 265 and the partial total ion current trace (TIC) of fraction 1 of the aromatic fraction of the Rozel Point Oil (RPO-1). Symbols refer to compounds assigned in Table I. The mass chromatogram of m/z 306 reveals the presence of several isoprenoid $C_{20}$ alkenylthiophenes.

mass spectra with those of synthesized standards[5,8] and relative retention times with respect to the *n*-alkylthiolane series. It is notable that the retention behaviour on the alumina column is dependent on the position of the thiolane ring in the molecule; isoprenoid thiolanes with the thiolane ring at the end of the chain elute later than those possessing the ring in the centre of the molecule. A typical mass spectrum of 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiolane (5), is shown in Figure 2b. The mass spectrum of this compound, exhibiting fragment ions at m/z 115, 171, 237 and 308, is completely analogous with that of 3-methyl-2-(3,7,11-trimethyldodecyl)thiolane as reported by Sinninghe Damsté *et al.*[5]

In the fractions RPO-5 and RPO-6 four new series of isoprenoid sulphur compounds were encountered; bithiophenes (III–V), (thienyl)alkylthiophenes (I–II), benzothiophenes ($\alpha$–$\delta$) and thienylthiolanes (1–5). The assignment of the structures of these compounds is based on mass spectral data, GC-retention times and on the differences in response of flame ionization and flame photometric detection. Figure 4, for example, shows the partial GC-FID and GC-FPD traces of fraction RPO-6. It is clearly seen that some compounds (i.e. 1, 2, III, IV and V) have a much higher response with FPD detection than is expected from the FID-trace if only one sulphur atom is present. Such an enhanced response on the FPD therefore indicates the presence of more than one sulphur atom. From a comparison of the ratio $\beta/1$ and $\gamma/2$ in the FID and FPD chromatogram, bearing in mind the quadratic response of the FPD, it was estimated that the compounds 1 and 2 contain two sulphur atoms per molecule. The relative intensity of the M+2 isotope peak in the mass spectra of the bithiophenes, (thienyl)alkylthiophenes and thienylthiolanes (see Figure 5a–c) of about 10% of the intensity of the molecular ion, indicative for the presence of two sulphur atoms, also supports these identifications. Exact mass measurements of the molecular ion (m/z 334) of the bithiophenes and a fragment ion of the bithiophenes III and IV (m/z 220) with high resolution mass spectrometry (exact mass: found 334.173, calculated for $C_{20}H_{30}S_2$ 334.179; exact mass: found 220.037, calculated for $C_{12}H_{12}S_2$ 220.038) established the presence of two sulphur atoms per molecule in these bithiophenes.

Typical mass spectra representing these four new series of isoprenoid sulphur compounds are shown in Figures 5a–d.

Figure 5a shows the mass spectrum of a bithiophene, 5′-(3-

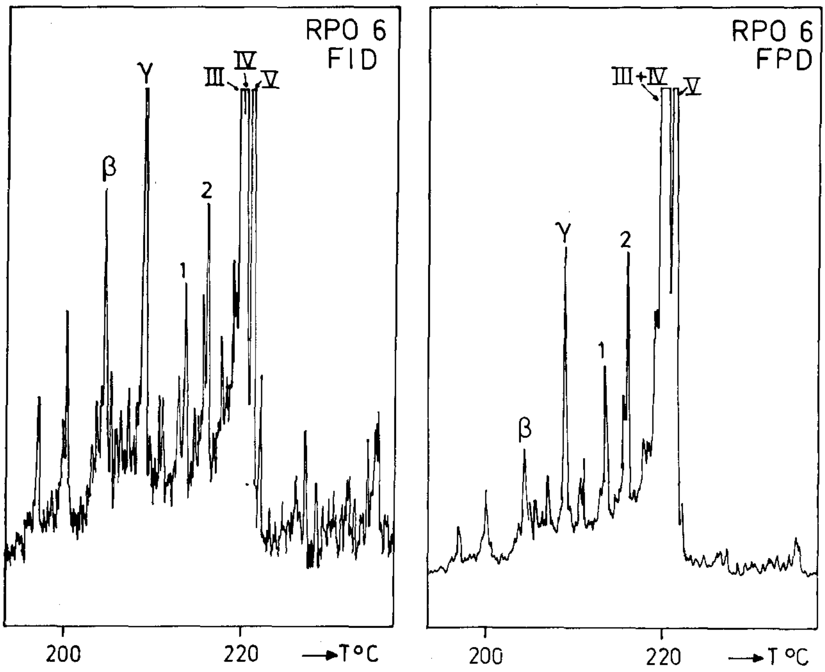
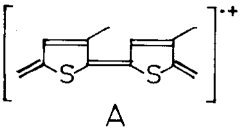
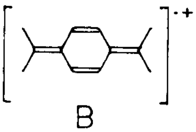


FIGURE 4 Partial GC-FID (left) and GC-FPD (right) traces of fraction 6 of the aromatic fraction of the Rozel Point Oil (RPO-6). Symbols refer to compounds assigned in Table 1. Note the differences in the β/1 and γ/2 ratio between the two traces. These differences in response on the FID and FPD strongly support the identification of the bithiophenes, (thienyl)alkylthiophenes and thienylthiolanes.

methylpentyl)-5-(2-methylpropyl)-3,4′-dimethyl-2,2′-bithiophene (III). This mass spectrum is characterized by a molecular ion (m/z 334), two primary fragments (m/z 291 and 263) originating from β-cleavages of both side chains and a fragment ion at m/z 220. This last fragment ion cannot be formed directly from the molecular ion because that should imply loss of the saturated $C_8H_{18}$ since the exact mass measurements of m/z 220 showed that this fragment ion still contains two sulphur atoms. Therefore it is assumed that this highly aromatic ion ($C_{12}H_{12}S_2$; note also the double charged ion at m/z 110 in the mass spectrum) originates from the two primary fragments (m/z 291 and 263) due to loss of the other alkyl side chain as an alkyl radical. Although this is an unusual fragmentation, its formation is explained by the stability of the structure of the fully conjugated ion A. A similar process is observed in the mass spectral fragmentation pattern of 1,4-di-*t*-butylbenzene[13] where a loss of two $CH_3$-radicals leads to the fully conjugated ion B.



A



B

Figure 5b shows the mass spectrum of a (thienyl)alkylthiophene, 5-(3-(2′,3′-dimethyl-5′-thienyl)-2-methylpropyl)-2-(3-methylpropyl)-3-methylthiophene (II). The mass spectral fragmentation pattern of this compound is outlined in Scheme 1.

Figure 5c shows the mass spectrum of a thienylthiolane. Apart from the molecular ion at m/z 338, two fragment ions at m/z 267 and 281, which originate from cleavages of the alkyl side chains at the thiophene and the thiolane moieties in the molecule, give clues to the identity of these compounds. The spectrum, however, is not assigned to a particular compound because three of the five thienylthiolanes present (1, 2 and 3) explain the fragment ions at m/z 267 and 281. Four rearrangement ions (m/z 144, 156, 200 and 214) are also observed in this mass spectrum.

Figure 5d shows the mass spectrum of a typical isoprenoid benzothiophene, 2-(3, 7-dimethyloctyl)-3, 6-dimethylbenzo(b)thiophene (*δ*). $\beta$-cleavage leads to the base peak in the mass spectrum at m/z 175. The alkyl side chain of this compound is thought to be branched because of its relative GC retention time with respect to the 4-*n*-alkyl-2-ethylbenzothiophene series.[8]

Several isoprenoid $C_{15}$ sulphur compounds were also encountered in the Rozel Point Oil. They are listed in Table II.

Although the results reported here focus on the isoprenoid $C_{20}$ and $C_{15}$ sulphur compounds occuring in Rozel Point Oil, most of the identified compounds were also present in other oils from China and from Sicily (Italy) and in extracts from recent and ancient sediments. In Table III an overview of the samples investigated and the presence of isoprenoid $C_{20}$ sulphur compounds in these samples is given. The first four samples or their source rocks (in case of oils) originate from hypersaline environments.

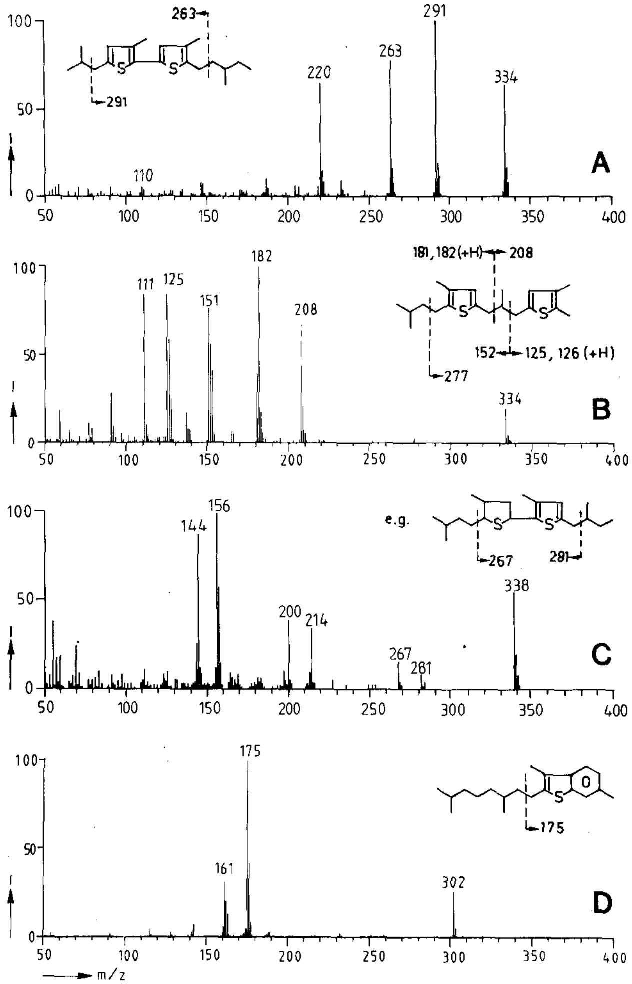
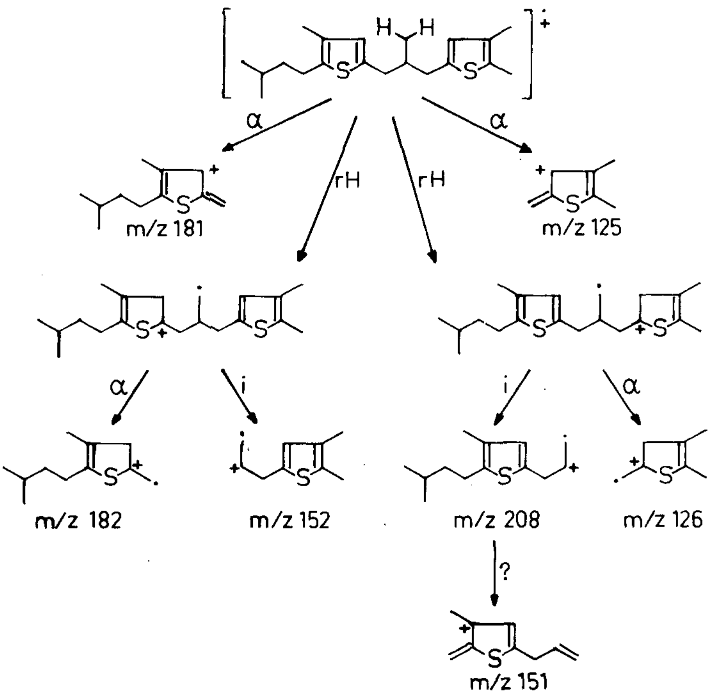


FIGURE 5 Mass spectra corrected for background of (A): 5′-(3-methypentyl)-5-(2-methylpropyl)-3,4′-dimethyl-2,2′-bithiophene (III), (B): 5-(3-(2′,3′-dimethyl-5′-thienyl)-2-methylpropyl)-2-(3-methylbutyl)-3-methylthiophene (II), (C): a thienyl thiolane (3) and (D): 2-(3,7-dimethyloctyl)-3,6-dimethylbenzo(b)thiophene ($\delta$).



SCHEME 1 Some fragmentation pathways of the (thienyl)alkylthiophene, 5-(3-(2′,3′-dimethyl-5′-thienyl)-2-methylpropyl)-2-(3-methylbutyl)-3-methylthiophene (II). The symbols that refer to the fragmentation reactions are adopted from McLafferty.[26]

TABLE II

Isoprenoid $C_{15}$ sulphur compounds identified in the Rozel Point Oil

| | |
|---|---|
| *isoprenoid thiophenes* | |
| F | 2-(3-methylpentyl)-5-(2-methylpropyl)-3-methylthiophene |
| G | 5-(2-methylbutyl)-2-(3-methylbutyl)-3-methylthiophene |
| H | 5-(2,6-dimethylheptyl)-2,3-dimethylthiophene |
| *isoprenoid thiolanes* | |
| g | 5-(2-methylbutyl)-2-(3-methylbutyl)-3-methylthiolane |
| h | 5-(2,6-dimethylheptyl)-2,3-dimethylthiolane |
| *isoprenoid bithiophenes* | |
| VI | 5-(2-methylpropyl)-2,4′,5′-trimethyl-2,2′-bithiophene |

TABLE III

Occurrence of isoprenoid $C_{20}$ sulphur compounds in several oils and sediment samples

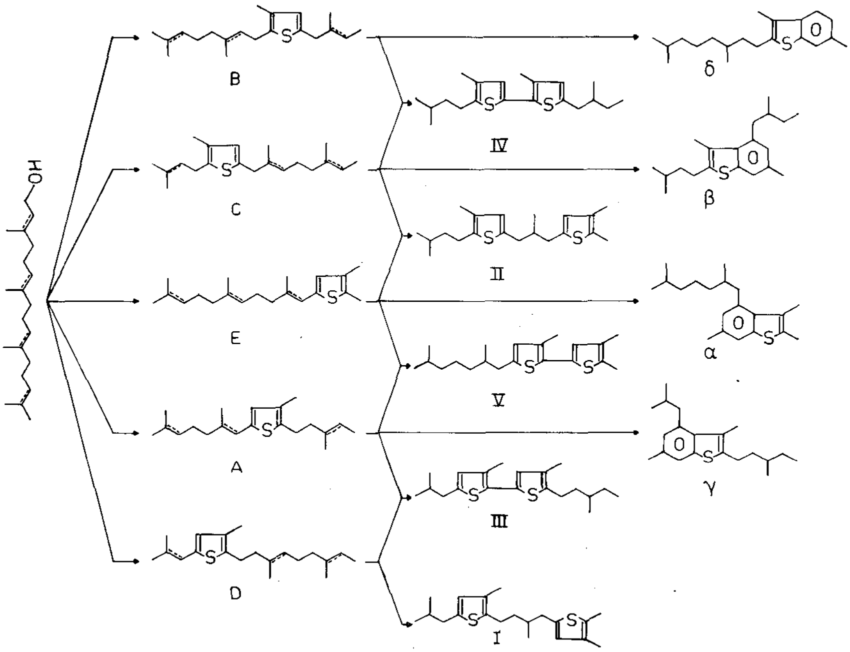
| Sample | Description | thiophenes | thiolanes | bithiophenes | thienylthiolanes | benzothiophenes |
|---|---|---|---|---|---|---|
| Rozel Point Oil | Seep oil from Utah (USA) (Miocene) | + | + | + | + | + |
| Three Sicily seep oils | Seep oils from Sicily (Italy) (Miocene)[27] | + | + | + | + | + |
| Two Chinese oils | Crude oils from the Jianghan basin (Paleogene)[28] | + | + | + | + | + |
| Northern Apennines Marl | Marlstone (Miocene)[29] | + | + | – | – | – |
| Phosphoria Retort shale | Phosphatic mudstone and dolomitic marlstone (Permian)[30, 31] | + | + | – | – | + |
| Cariaco Trench | DSDP 15-147 (Quaternary)[4] | + | n.d.[a] | n.d. | n.d. | n.d. |
| Middle America Trench | DSDP 67-496 (Quaternary)[4] | + | n.d. | n.d. | n.d. | n.d. |
| Namibian Shelf | Diatomaceous ooze (Quaternary)[32] | + | n.d. | n.d. | n.d. | n.d. |
| Walvis Ridge | DSDP 75-532 (Quaternary/Pliocene)[4] | + | n.d. | n.d. | n.d. | n.d. |
| Japan Trench | DSDP 56-436 (Pliocene)[4] | + | n.d. | n.d. | n.d. | n.d. |
| Gulf of California | DSDP 64-479 (Pleistocene)[4] | + | n.d. | n.d. | n.d. | n.d. |
| Japan Trench | DSDP 57-440 (Pleistocene/Miocene)[4] | + | n.d. | n.d. | n.d. | n.d. |
| Livello Bonarelli | Black shale (Cenomian/Turonian)[33] | + | n.d. | n.d. | n.d. | n.d. |

[a] Not determined.

## DISCUSSION

At this stage it is thought that the $C_{20}$ isoprenoid sulphur compounds originate from $C_{20}$ isprenoid alcohols with different degrees of unsaturation. Phytol, the alcohol moiety of (bacterio)chlorophylls *a* and *b*,[14] is very abundantly present in recent sediments which receive an input from algae.

Especially photosynthetic green and purple sulphur bacteria—omnipresent and sometimes abundantly present in evaporitic environments—are known to biosynthesize di- and poly-unsaturated isoprenoid alcohols such as geranylgeraniol, $\Delta^{2,10}$- and $\Delta^{2,6}$-phytadienol as alcohol moieties of bacteriochlorophylls.[15–18] Geranylgeraniol has also been reported to occur as such in archaebacteria.[19]

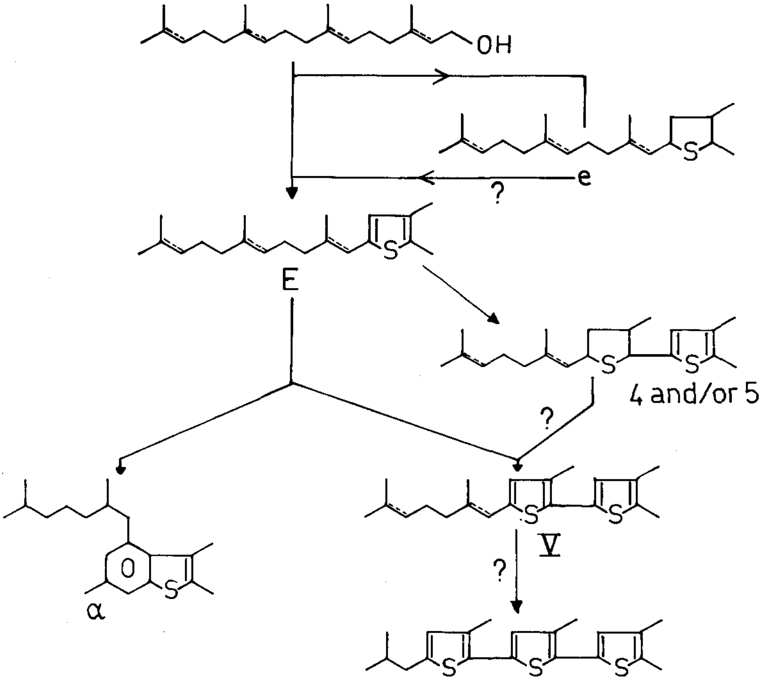


SCHEME 2 Diagenetical scheme showing the possible origin and presumed pathways of several organic sulphur compounds encountered in several oils and sediment extracts starting from unsaturated phytanols. The symbols refer to the compounds assigned in Table I. Dotted lines in the structures indicate the possible presence of double bonds. Symbols A–E refer to the structures with saturated alkyl side chain(s).

These isoprenoid $C_{20}$ alcohols have been encountered in relatively high concentrations in very recent hypersaline environments like Solar Lake,[20] the Gavish Sabkha[21] and Roquetas de Mar.[22] Therefore an origin from these precursors is suggested. The reaction of these precursor molecules or their diagenetical products such as unsaturated phytenes might result in the formation of a number of isoprenoid thiophenes (A–E) as indicated in Scheme 2. These kinds of sulphur incorporation reactions are postulated to occur in recent sediments to explain the presence of several isoprenoid thiophenes[4] and of a thiophene containing hopane.[2] Whether or not the corresponding isoprenoid thiolanes (a–e) are intermediate structures in the thiophene formation remains to be seen (Scheme 3). A further incorporation of sulphur triggered by the presence of additional double bonds might result in the formation of bithiophenes (III–V) and (thienyl)alkylthiophenes (I and II). Supporting evidence for this diagenetical pathway is the presence of several alkenylthiophenes in RPO-1 as revealed by the m/z 306 mass chromatogram in Figure 3. Here too, it remains to be seen whether the corresponding thienylthiolanes are intermediates. Another possibility for subsequent reactions of the unsaturated isoprenoid thiophenes is the formation of the corresponding isoprenoid $C_{20}$ benzothiophenes ($\alpha$–$\delta$) (Scheme 2).

Further circumstantial evidence for this diagenetical scheme is obtained from data concerning isoprenoid $C_{15}$ sulphur compounds. Farnesol (2,6,10-trimethyldodecatrienol) has been reported as the alcohol moiety of bacteriochlorophylls *c*, *d* and *e*[14] and those of green photosynthetic bacteria[15,18,23] and has been identified, although in much lesser abundance as the $C_{20}$ isoprenoid alcohols, in the microbial mat of the Gavish Sabkha.[21] In the playa lake environment in which the source rock of the Rozel Point Oil is thought to be deposited,[7,10] an input of farnesol seems highly probable. Therefore, analogous to the diagenetical pathways of the isoprenoid $C_{20}$ alcohols, isoprenoid $C_{15}$ sulphur compounds were expected from sulphur incorporation into farnesol. Indeed, although much less abundant, some isoprenoid $C_{15}$ sulphur compounds were identified (Table II) in Rozel Point Oil. In addition, an isoprenoid $C_{15}$ alkenylthiophene was encountered.

It can be speculated that an additional thiophene ring is formed upon further sulphur incorporation into bithiophene V (Scheme 3).



SCHEME 3 Part of the diagenetical scheme proposed for OSC, showing the presumed role of thiolanes and thienylthiolanes as intermediates. The symbols refer to the compounds assigned in Table I. Symbols refer to the structures with a saturated alkyl side chain.

The benzothiophenes and bi- and trithiophenes might upon further cyclization give rise to the highly aromatic, one to three sulphur atoms containing compounds reported to occur in several crude oils.[24,25]

To summarize we can conclude that $C_{20}$ isoprenoid sulphur compounds of types described here do occur in both recent and ancient sediments and in crude oils. Hence, in sediments anaerobically laid down or of evaporitic nature these compounds are naturally formed. These types of depositional environments show their signature in the composition of the OSC. In hypersaline environments relatively high concentrations of polyunsaturated phytanols show up, which lead to the formation of "midchain"-thiophenes (A–D), -thiolanes (a–d) and two sulphur atoms containing OSC (1–5, I–V). In anaerobically deposited sediments (not hypersaline) no polyunsaturated phytanols occur and only the formation of OSC that originate from sulphur incorporation into phytol (E, e) is expected.

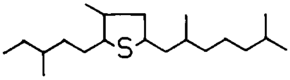
Erosion of more ancient sediments in the hinterland or human caused oil spills are other pathways by which the isoprenoid $C_{20}$ and $C_{15}$ sulphur compounds can contribute to recent sediments.

## References

1. J. D. Payzant, D. S. Montgomery and O. P. Strausz, *Tetrahedron Lett.* **24,** 651 (1983).
2. J. Valisolalao, N. Perakis, B. Chappe and P. Albrecht, *Tetrahedron Lett.* **25,** 1183 (1984).
3. J. D. Payzant, T. D. Cyr, D. S. Montgomery and O. P. Strausz, *Tetrahedron Lett.* **26,** 4175 (1985).
4. S. C. Brassell, C. A. Lewis, J. W. de Leeuw, F. de Lange and J. S. Sinninghe Damsté, *Nature* **320,** 160 (1986).
5. J. S. Sinninghe Damsté, H. L. ten Haven, J. W. de Leeuw and P. A. Schenck, *Advances in Organic Geochemistry 1985* (D. Leythaeuser and J. Rullkötter, eds.) (Pergamon, New York, 1986), in press.
6. J. W. de Leeuw, *ACS Symposium Series No. 305: Organic Marine Geochemistry* (M. Sohn, ed.) (American Chemical Society, Washington D.C., 1986), pp. 33–61.
7. H. L. ten Haven, J. W. de Leeuw, J. S. Sinninghe Damsté, P. A. Schenck, S. E. Palmer and J. E. Zumberge, *Lacustrine Petroleum Source Rocks* (K. Kelts, A. J. Fleet and M. Talbot, eds.) (Blackwell, London, 1986), in press.
8. J. S. Sinninghe Damsté, J. W. de Leeuw, A. C. Kock, M. A. de Zeeuw, F. de Lange, W. I. C. Rijpstra and P. A. Schenck, *Geochim. Cosmochim. Acta*, submitted (1986).
10. F. F. Meissner, J. Woodward and J. L. Clayton, *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region* (J. Woodward, F. F. Meissner and J. L. Clayton, eds.) (Rocky Mountain Association of Geologists, Denver, 1984), pp. 1–34.
11. J. S. Sinninghe Damsté, A. C. Kock, J. W. de Leeuw and P. A. Schenck, *Tetrahedron Lett.*, submitted (1986).
12. J. G. Pomonis, C. L. Fatland and R. G. Zaylskie, *J. Chem. Eng. Data* **21,** 380 (1976).
13. B. van de Graaf, *Applications of Mass Spectrometry in Organic Chemistry, Biochemistry and Medicine* (E. Baranowska and B. Zielinska, eds.) (Polish Academy of Sciences, 1979), pp. 53–71.
14. A. Gloe, N. Pfennig, H. Brockmann, Jr. and W. Trowitch, *Arch. Microbiol.* **102,** 103 (1975).
15. J. J. Katz, H. H. Strain, A. L. Harkness, M. H. Studier, W. A. Svec, T. R. Janson and B. T. Cope, *J. Amer. Chem. Soc.* **94,** 7938 (1972).
16. A. Gloe and N. Pfennig, *Arch. Microbiol.* **96,** 93–101 (1974)

17. R. Steiner, W. Schäfer, I. Blos, H. Wieschoff and H. Scheer, *Z. Naturforsch.* **36C,** 417 (1981).
18. M. B. Caple, Hsi-chao Chow and C. E. Strouse, *J. Biol. Chem.* **253,** 6730 (1978).
19. S. C. Kushwaha and M. Kates, *Phytochem.* **17,** 2029 (1978).
20. J. J. Boon and J. W. de Leeuw, *Cyanobacteria: Current Research* (P. Fay and C. van Baalen, eds.) (Elsevier, Amsterdam, 1986), in press.
21. J. W. de Leeuw, J. S. Sinninghe Damsté, J. Klok, P. A. Schenck and J. J. Boon, *Ecological studies* 53, *Hypersaline ecosystems* (G. M. Friedman and W. E. Krumbein, eds.) (Springer Verlag, Berlin, 1985), pp. 350–367.
22. H. Goossens, W. I. C. Rijpstra, J. W. de Leeuw and P. A. Schenck, in preparation.
23. H. Rapoport and H. P. Hamlow, *Biochem. Biophys. Res. Commun.* **6,** 134 (1961).
24. H. J. Coleman, J. E. Dooley, D. E. Hirsch and C. J. Thompson, *Anal. Chem.* **45,** 1724 (1973).
25. J. E. Dooley, D. E. Hirsch, C. J. Thompson and C. C. Ward, *Hydrocarbon Processing* **53**(11), 187 (1974).
26. F. W. McLafferty, *Interpretation of Mass Spectra* (W. A. Benjamin Inc., Reading, 1973), 2nd ed.
27. S. E. Palmer and J. E. Zumberge, *Organic Maturation Studies and Fossil Fuel Exploration* (J. Brooks, ed.) (Academic Press, London, 1981), pp. 393–426.
28. Fu Jiamo, Sheng Guoying, Peng Pingan, S. C. Brassell, G. Eglinton and Jiang Jigang, *Lacustrine Petroleum Source Rocks* (K. Kelts, A. J. Fleet and M. Talbot, eds.) (Blackwell, London, 1986), in press.
29. H. L. ten Haven, J. W. de Leeuw and P. A. Schenck, *Geochim. Cosmochim. Acta* **49,** 2181 (1985).
30. J. C. Winters, J. A. Williams and M. D. Lewan, *Advances in Organic Geochemistry 1981*, (M. Bjorøy *et al.*, eds.) (John Wiley & Sons, Chicester, 1982), pp. 524–533.
31. M. D. Lewan, personal communication.
32. J. Klok, *Composition and Origin of Complex Organic Matter in Recent Sediments*, Ph.D. Thesis (Delft University of Technology, the Netherlands, 1984), 111 pp.
33. G. van Graas, *Organic Geochemistry of Cretaceous Black Shale Deposits from Italy and France*, Ph.D. Thesis (Delft University of Technology, the Netherlands, 1982), 94 pp.

# Appendix



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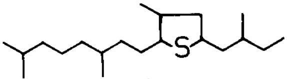

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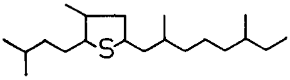

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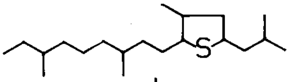

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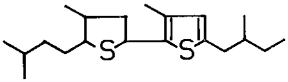

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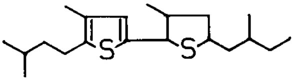

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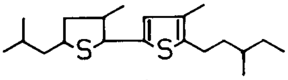

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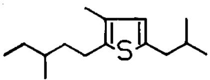

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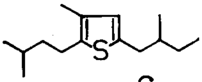

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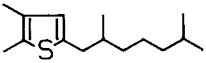

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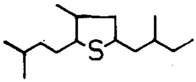

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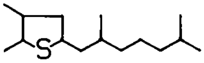

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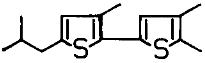

VI