

Sulphur-containing Compounds in Sulphur-rich Crude Oils from Hypersaline Lake Sediments and Their Geochemical Implications

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Abstract

Three sulphur-rich commercial crude oils have been studied, which contain sulphur as high as up to 4–12%. These samples were collected from Tertiary hypersaline lake sediments of the Jiangnan Basin, Hubei Province at different depths, but above the oil generation threshold (2200m). FPD-GC and GC-MS data show that aromatic fractions of the crude oils are composed of different homologues of sulphur-containing compounds, including long-chain normal alkyl-thiophenes and -thiolanes, long-chain isoprenoid-thiophenes and -thiolanes, and benzothiophenes. It is worth noting that the distribution patterns of long-chain alkyl-thiophenes and -thiolanes from two shallow-seated crude oils are quite similar to those of normal alkanes showing marked even-odd predominance. It seems that the even-odd predominance of sulphur-containing compounds decreases with increasing burial depth of the crude oils. The major component of aliphatic fraction is phytane, and similarly the major peaks of aromatic fractions also represent C₂₀ isoprenoid thiophenes.

Some preliminary conclusions have been drawn from the above discussion: (1) Abundant sulphur-containing compounds may be used as an indicator of low mature or immature crude oils produced from hypersaline lake sediments; (2) Sulphur-containing compounds are considered to be early diagenetic products of reactions between elemental sulphur or sulfides and alkanes or their precursors (phytols, fatty acids, alcohols, etc.), or of bacterial activities, but not direct inputs of organisms.

The sulphur contents of crude oils are generally less than 4%, mostly ranging from 0.1% to 3%^[1]. As most organic sulphur compounds are low molecular weight compounds and present in polar fractions of crude oils, very little work has so far been done on them. Hence the nature and structure of the sulphur compounds remain unclear. Recently, a seepage of unknown age collected from Utah, America has been studied, and many high molecular weight sulphur compounds have been identified by Sinnighe, et al. (1985)^[2] and Ocampo et al. (1985)^[3].

Sulphur-rich crude oils generated from hypersaline lake sediments of the Jiangnan Basin, China have been studied, and the results show that the main compounds of their aromatic fractions are made up of various homologues of alkyl-thiophenes and alkyl-thiolanes. It is interesting that

the carbon number ranges and distribution patterns of the long-chain alkyl-thiophenes and long-chain alkyl-thiolanes are quite similar to those of alkanes from the same crude oils, showing a marked even-odd predominance. Reported here are sulphur compounds detected in sulphur-rich commercial crude oils and their geochemical implications.

Experimental

Samples Samples of three sulphur-rich crude oils have been studied, which were collected from Paleogene hypersaline lake sediments of the Jiangnan Basin, China (Fig.1). Crude oil J_{18} was recovered from an oölitic limestone layer at a depth of 610—658 m, while crude oils J_3 and J_1 were collected from siltstone-fine-grained sandstone at a depth of 1254—1293 m and clayey oölitic limestone at a depth of 1829.3—1829.6 m, respectively. All the samples are dark brown in colour and high in density. Crude oils J_{18} and J_3 also have a strong smell of organic sulphur compounds.

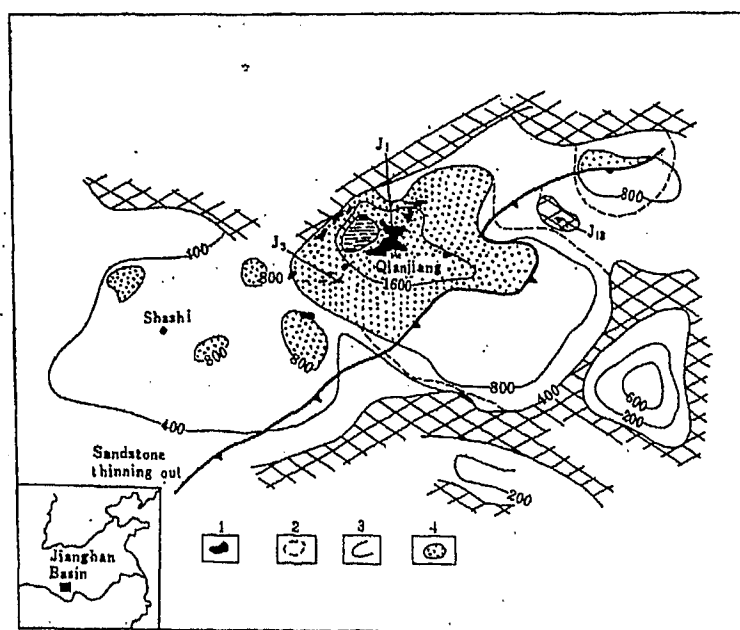


Fig. 1. Map of the Jiangnan Basin showing sample localities.

1. Oil field; 2. saline lake; 3. isopach; 4. source and reservoir rock zones.

Extraction and separation Crude oils were fractionated into aliphatic fractions, using silica-gel TLC. Sulphur compounds were detected in the aromatic fractions.

Gas chromatography Gas chromatography of the aromatic fractions extracted was carried out on two instruments: one is equipped with a flame photometric detector (FPD) giving a selective response for organic sulphur compounds, and the other—Shimadzu GC-9A gas chromatograph is equipped with an FPD and a flame ionization detector (FID). A fused silica capillary column ($L = 50$ m, I.D. = 0.31 mm) coated with SE 54 ($d_f = 0.17 \mu\text{m}$) was used with nitrogen as carrier gas. Samples were injected at 80°C and the oven temperature was programmed

to 300°C at 4°C/min. The Carlo Erba 4610 instrument was equipped with an FID and an on-column injector. The fused silica capillary column (L = 50 m, I.D. = 0.31 mm) coated with OV-1 ($d_f = 0.1 \mu\text{m}$) was used with helium as carrier gas. The temperature was programmed from 80 to 300°C at 4°C/min.

Gas chromatography-mass spectrometry GC-MS was carried out on a Carlo Erba 4610 gas chromatograph combined with a Finnigan-Mat MS 4000 quadrupole mass spectrometer with an INCOS computer system. The gas chromatography is equipped with an on-column injection system. Separation was effected by fused silica capillary column (L = 25 m, I.D. = 0.25 mm) coated with SE 54 ($d_f = 0.52 \mu\text{m}$). The temperature was programmed from 80 to 100°C at 10°C/min, and from 100 to 280°C at 4°C/min. The mass spectrometer was operated at 40 eV, 350 μA (ionization current) and 250°C (ion source temperature).

Assignment of compounds Sulphur-containing compounds were identified by FPD and FID of a gas chromatograph in Organic Geochemistry Unit, Delft University of Technology and the Institute of Geochemistry, Academia Sinica. Several compounds have been attested by comparing their mass spectra with those of the standards synthesized at Delft University of Technology. The carbon numbers of any homologue were determined in terms of their retention time, with special reference to the related standards.

Results and Discussion

Elemental composition of sulphur-rich crude oils The elemental compositions of the three crude oil samples are shown in Table 1. The sulphur contents of crude oils J₁₈ and J₃ are unusually high, up to 12.9% and 10.41% respectively, which is the second major elemental constituent of the oils. The elemental composition of crude oil J₁₈ is quite similar to that of Rozel point seepage from Utah, America (Table 1). It must be pointed out that both J₁₈ and J₃ are commercial oils. The sulphur content of oil sample J₃ is so low as to be 3.59%, but it still belongs to sulphur-rich oils. The oil samples collected at different depths but above the oil generation threshold (OGT: 2200 m) show a decrease in sulphur content with increasing burial depth. The sulphur contents of crude oils above OGT vary greatly, decreasing from 12.9% to 3.59% at a depth interval of only 1200 m between J₁₈ and J₁. Such a variation is quite unusual with respect to other elements. So sulphur

Table 1. Elemental compositions of sulphur-rich crude oils (%)

Sample No.	Stratigraphic unit	Depth	C	H	N	S
J ₁₈	E ₃	610.23—658.50	74.48	10.39	0.69	12.91
J ₃	E ₁	1254 —1293	74.19	10.20	1.05	10.41
J ₁	E ₁	1829.3 —1829.6	74.50	11.26	0.59	3.59
Rozel point			75.23	10.04	0.69	12.90

seems to be an important component of crude oils in a certain environment, and the study of its migration and environment during diagenesis is vital to the understanding of the genesis and evolution of petroleum. On the basis of elemental sulphur contents of crude oils from the Jiangnan Basin, a diagram is plotted to show the relationship between sulphur content and burial depth (Fig. 2). As shown in Fig. 1, sulphur-rich crude oils only occur above OGT, and the content of sulphur decreases considerably with burial depth. The sulphur contents of crude oils below OGT vary over a narrow range (1.05—0.1%). So elemental sulphur is considered to be an important component of crude oils from a typical environment, especially during early diagenesis.

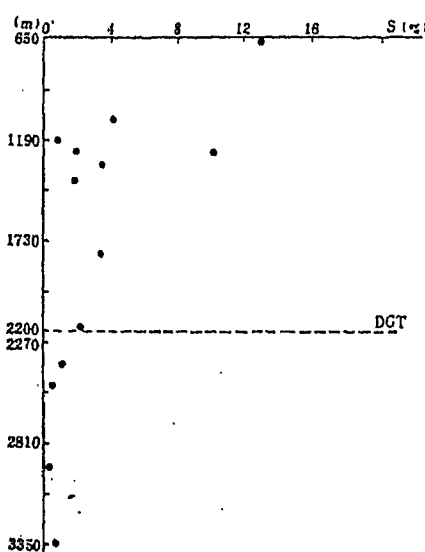


Fig. 2. Sulphur content of crude oils and its relationship to the burial depth.
OGT = oil generation threshold.

Characteristics of aromatic fractions of crude oils FPD-GC analyses of the aromatic fractions of crude oils J_{18} and J_3 indicate that the main components of the aromatic fractions are sulphur compounds. Shown in Fig. 3a-b are their RIC traces. RIC traces of both J_{18} and J_3 are different from those of normal oils, though they are similar to each other, exhibiting a series of unseparated group peaks with two major peaks.

The distribution of aromatics in the deepest sample (crude oil J_1) is quite different from that of the above two samples (Fig. 3c). As determined by FPD-GC and GC-MS, J_1 gives group peaks with sulphur compounds, but the major peaks in its RIC trace represent dehydroxytocopherols^[4]. Small amounts of benzene, naphthene and their alkyl derivatives, except for mono- and tri-aromatic steranes, were identified in the three oil samples.

The sulphur compounds so far detected include:

(1) *Alkyl-thiophenes* Normal alkane- and isoprenoid-thiophenes include seven homologues with m/z 111, 125, 139, 153, 167, 181 and 195. Various compounds were assigned either by standard compounds or by reference to the data on mass spectra and retention time as reported in the literature. These compounds include:

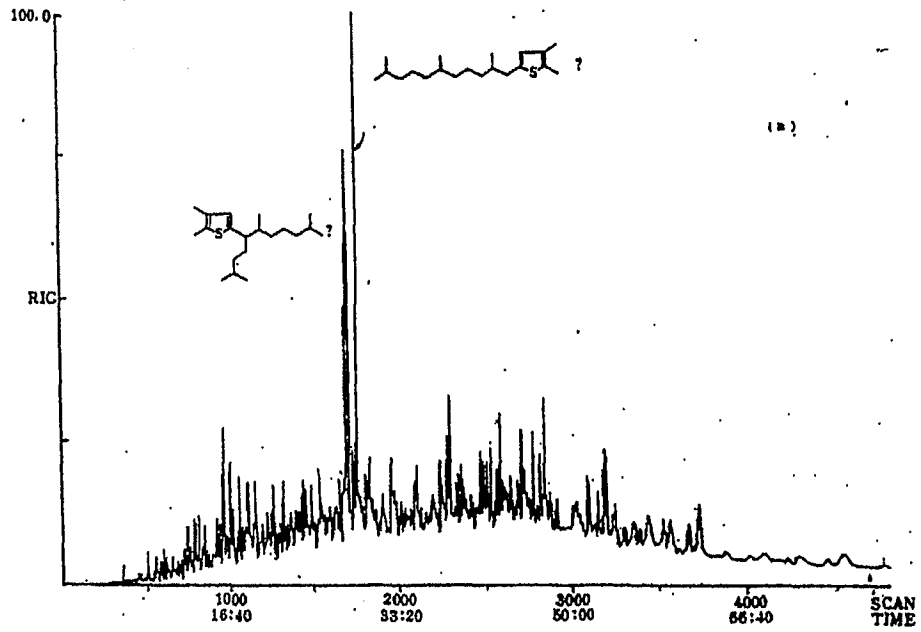


Fig. 3.

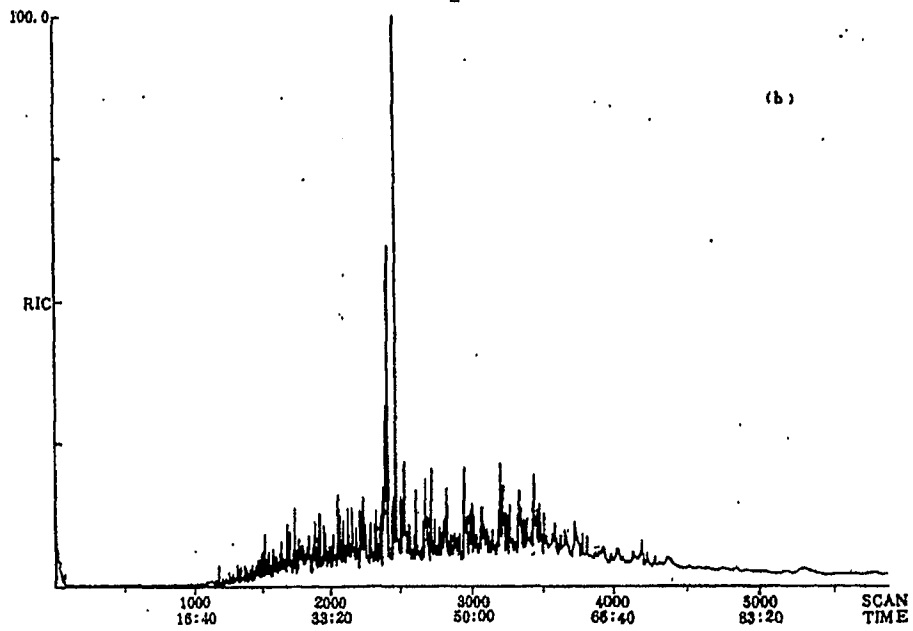


Fig. 3.

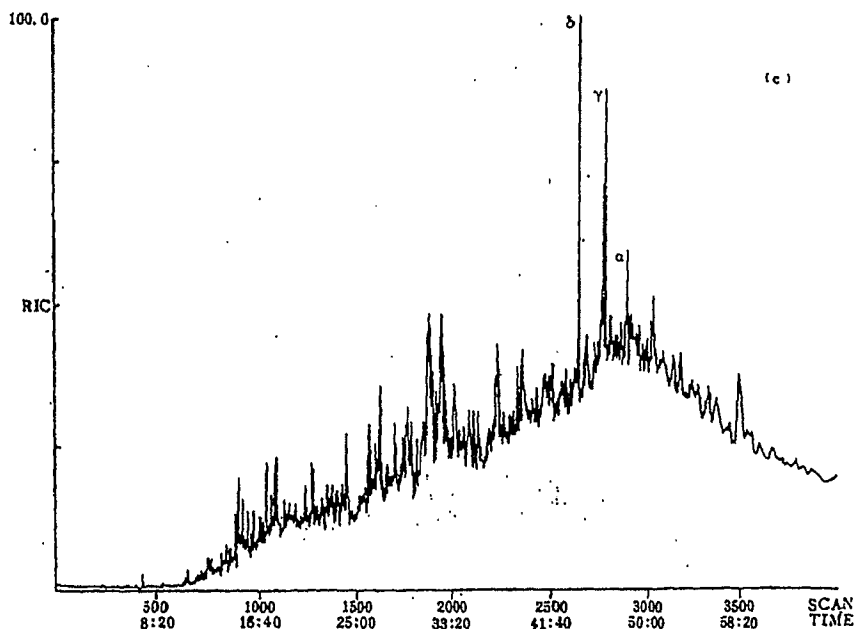


Fig. 3. Total ion current traces of the aromatic fractions.

(a) = J_{18} ; (b) = J_3 ; (c) = J_1 .

a. Normal alkyl-thiophenes such as 2-methyl-5-tridecyl thiophene $C_{18}H_{32}S$ (m/z 111, M^+ 280, Fig. 4a);

b. Isoprenoid alkyl-thiophenes, as represented by the two major peaks in aromatics of crude oils J_{18} and J_3 , which are compared with those of Rozel point Seepage^[2] and identified possibly as 2,3-dimethyl-5-(2,6,10-trimethylundecyl) thiophene (m/z 125, M^+ 308, Fig. 4b) and 2,3-dimethyl-5-[2,6-dimethyl-1-(3'-methylbutyl)]-heptyl-thiophene (m/z 195, M^+ 308, Fig. 4c).

c. Benzothiophenes such as 2-(3,7-dimethyloctyl)-3,6-dimethylbenzothiophene (m/z 175, M^+ 302, Fig. 4d).

(2) *Alkyl-thiolanes* There are five homologues of alkyl-thiolanes detected, with the base ions of m/z 101, 115, 129, 143 and 157. Both the homologues with m/z 101 and 115 are more complete with respect to their component series:

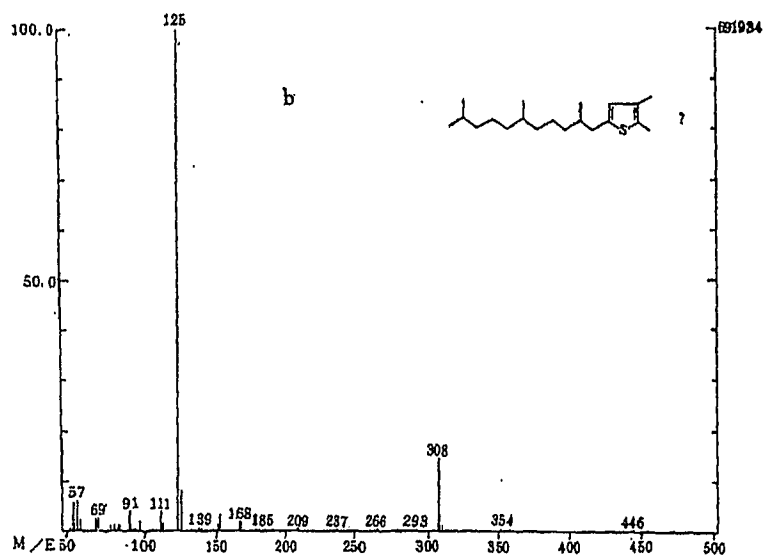
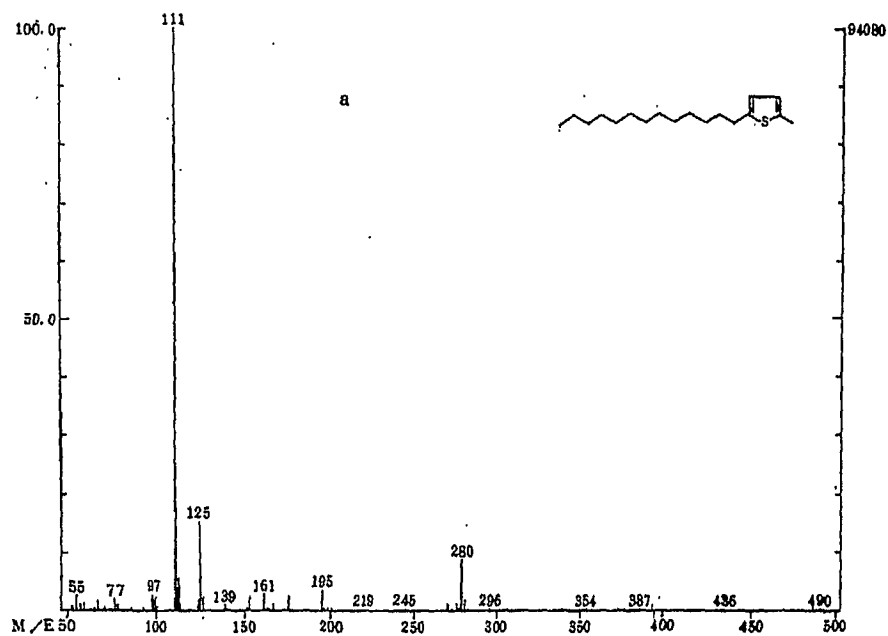
a. Normal alkyl-thiolanes such as 2-methyl-5-dodecylthiolane (m/z 101, M^+ 284), 2-ethyl-5-tetradecylthiolane (m/z 115, M^+ 312);

b. Isoprenoid thiolanes: 2-(3',7',11-trimethyldodecyl)-3-methylthiolane (m/z 101, M^+ 312).

(3) *Sulphur steranes* In addition to C_{28} and C_{29} compounds having the base ion of m/z 341, compounds with the base peaks of m/z 355 and 369 were also detected, which are considered to be possible 4-methyl and 4,4-dimethyl-sulphur steranes.

Distribution characteristics of long-chain alkyl-thiophenes and long-chain alkyl-thiolanes

(1) *Even-odd predominance shown within the higher carbon number range* Alkyl-thiophenes from crude oils J_{18} and J_3 exhibit normal distribution characteristics and marked



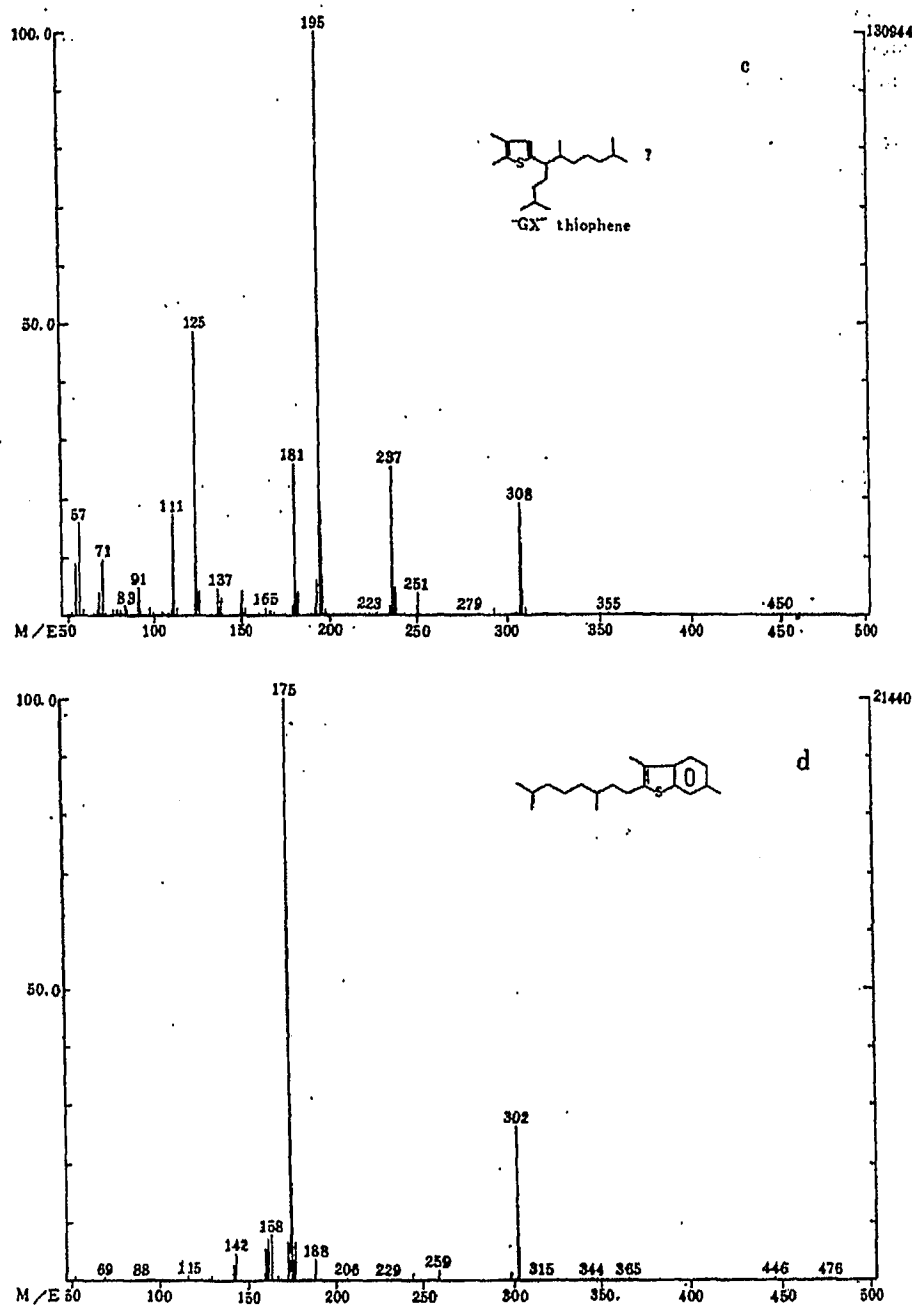


Fig. 4. Mass spectra of sulphur compounds.

- (a) = 4-methyl-5-(3,7,11-trimethyltridecyl)-thiophene;
- (b) = 5-(2,6,10-trimethylundecyl)-thiophene;
- (c) = 2,3-dimethyl-5-[2,6-dimethyl-1-(3'-methylbutyl)] heptyl-thiophene;
- (d) = 2-(3,7-dimethyloctyl)-3,6-dimethylbenzothiophene.

even-odd predominance for each homologue (C_{16} - C_{30} , Table 2), as expected in normal alkanes of the same oil samples. This is particularly true for alkyl-thiophene homologues with m/z 111 and 125, and alkyl-thiolane homologues with m/z 111 and 115. It is interesting to note that each of the

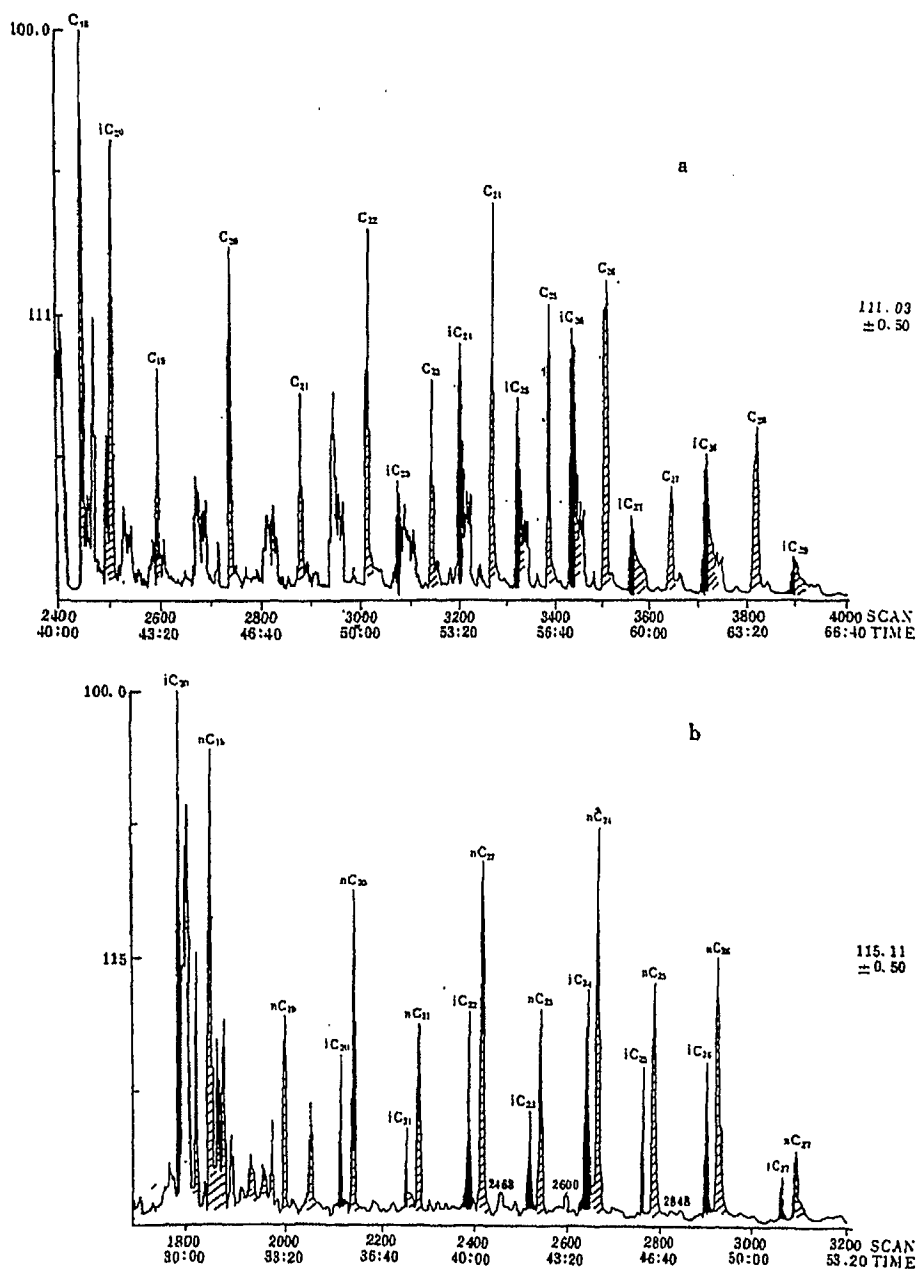


Fig. 5. Even-odd predominance of thiophene and thiolane.

(a) = alkyl-thiophene series (m/z 111);

(b) = alkyl-thiolane series (m/z 115).

compounds has two isomers, which have similar even-odd predominance (Fig. 5a—b). With the method used to calculate CPI_S values for normal alkanes, we obtained the CPI_S (S stands for sulphur compounds) values for alkyl-thiophenes and alkyl-thiolanes. As can be seen from Table 2, CPI_S values for various homologues (C_{24} — C_{30} compounds) are quite close to one another. For example, CPI_S values for four alkyl-thiophene homologues in oil sample J_3 vary from 0.61 to 0.67, and those for four alkyl-thiolane homologues vary from 0.51 to 0.63. CPI_S values for two isomer series with m/z 115 are 0.58 and 0.54, respectively. By interpreting their mass spectra, the second series of isomers showing m/z 115 may be determined as alkylthiocyclohexane and also have marked even-odd predominance.

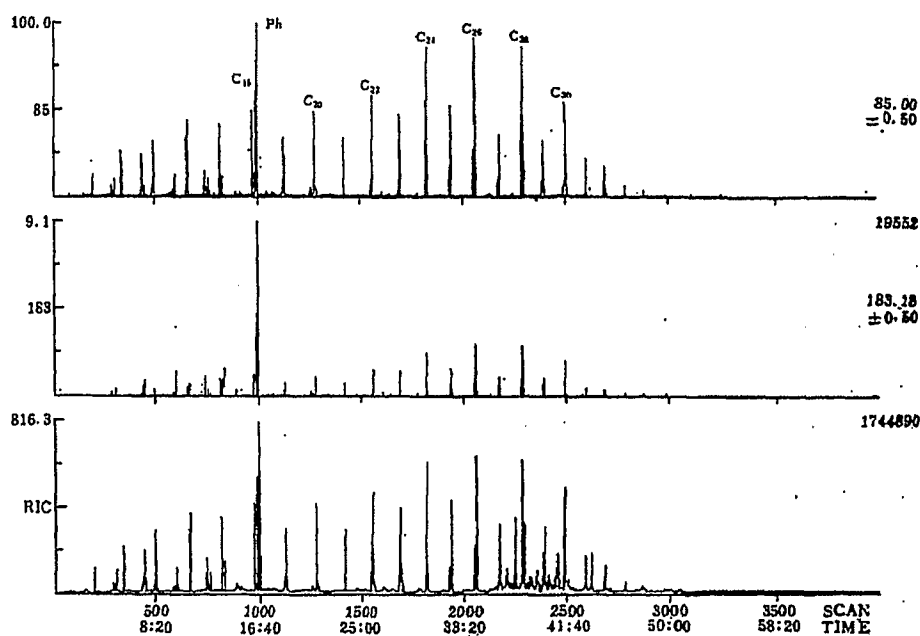


Fig. 6. Mass chromatograms of the aliphatic fraction (Mass chromatograms of n-alkanes (m/z 85) and isoprenoids (m/z 183)).

By comparing the GC traces of n-alkane (m/z 85) (Fig.6) and compound homologues with the base ions of m/z 101 and 115, it can be seen clearly that their distribution patterns are quite similar in oil sample J_{18} . Their CPI_S values are 0.54, 0.51 and 0.58, respectively.

(2) *Abundant C_{20} isoprenoid thiophenes and alkyl-thiolanes* All alkyl-thiophene homologues, except for a few homologues, show abundant iC_{20} in their mass spectra. For example, homologues with m/z 125, 167, 195, etc. from oil sample J_{18} all give very high iC_{20} peaks. Alkyl-thiolane homologues also are high in abundance of iC_{20} compounds, such as homologues with the base ion of m/z 115. The major peaks in RIC traces of the aromatic and aliphatic fractions extracted from oil sample J_{18} represent alkyl-thiophenes and phytane.

Because of the similar distribution patterns in both aromatic and aliphatic fractions from the oil sample, it is reasonably considered that the distribution patterns of sulphur compounds and CPI_S might be used as an organic geochemical indicator as the CPI indicator of normal alkanes.

For attesting this, we compared oil samples J_{18} and J_3 which were collected from different levels with a depth difference of more than 600 m between them. Because of a variety of alkyl-thiophene isomers which would lead to coeluting phenomenon, CPI_S values are only compared for alkyl-thiolanes (Table 3). As shown in Table 2, CPI_S values for various homologues of the shallow sample (oil J_{18}) are less than those for the deep sample (oil J_3). As discussed previously, the deepest sample (oil J_1) only shows the major peaks of dehydroxytocopherol and has a small amount of sulphur compounds in the aromatic fraction^[4]. More work is needed to find out whether the distribution patterns and CPI_S values for the sulphur compounds are good maturity, especially low-maturity, indicators of evaporite sediments.

Geochemical implications

(1) Organic sulphur compounds of various types might be important constituents of sulphur-rich oils. Various sulphur compounds of high molecular weight are mostly found in carbonate-evaporite sediments. The compounds mentioned here have been reported from commercial crude oils occurring above OGT. Geological and molecular parameter data provide evidence suggesting that these oils are immature oils^[6]. So the abundant sulphur compounds discussed in this paper may be used as organic geochemical indicators of hypersaline environments and low mature-immature crude oils.

(2) Similar distribution patterns of sulphur compounds and n-alkanes as discussed previously in conjunction with other facts indicate that these sulphur compounds in hypersaline lake sediments may not come from organism inputs directly. It is reasonably considered that these compounds might be early diagenetic products of reactions between elemental sulphur or/and sulphides and precursors including phytol, fatty acids, alcohols and other organic constituents, or products of bacterial activities during diagenesis.

(3) The discovery of low mature or even immature oils and their association with abundant sulphur compounds raise a problem concerning the genesis of petroleum. At least, part of oils may be considered to be derived from biopolymers rather than from kerogens in certain environments. This problem is worth further studying, both in theory and in practice, in consideration of its great significance in organic geochemistry.

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