



## The occurrence and distribution of low-molecular-weight sulfoxides in polar fractions of sediment extracts and petroleum\*

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**Abstract**—Polar fractions of sediment extracts and a crude oil were isolated and analyzed for low-molecular-weight (LMW) sulfoxides. Sediment extracts were found to contain relatively high amounts of sulfoxides as demonstrated by X-ray absorption analyses and chemical reduction of sulfoxides followed by the isolation of the formed LMW sulphides. The amounts of cyclic sulfoxides are comparable to the amounts of cyclic sulphides present as such. The distribution of sulphides and sulfoxides were slightly different indicating preferential oxidation of specific sulphides. The sulfoxides may be formed during long-time storage of samples or during weathering of sediment outcrop samples. The results further indicate that carbon skeletons released by desulphurization of polar fractions are partially (up to 60%) derived from LMW sulfoxides.

**Key words**—organic sulphur compounds, polar fraction, sulfoxides, XANES, desulphurization, reduction of sulfoxides

### INTRODUCTION

Recent findings in the field of organic sulphur compounds (OSC) present in sediments and oils has greatly increased the knowledge on their geochemical significance (for a review see Sinninghe Damsté and de Leeuw, 1990). It has become clear that they originate from abiotic reactions of inorganic sulphur species with functionalized lipids during early diagenesis (Kohnen *et al.*, 1990a; de Graaf *et al.*, 1992; Schouten *et al.*, 1993a). Low-molecular-weight (LMW) OSC were the subject of the first investigations since they are readily isolated and are amenable to gas chromatography and gas chromatography-mass spectrometry (e.g. Payzant *et al.*, 1983; Valisolalao *et al.*, 1984; Schmid, 1986; Brassell *et al.*, 1986; Sinninghe Damsté *et al.*, 1986). Compound classes which were identified are thiophenes, thiolanes, thianes and benzothiophenes. These compounds are usually present in so-called "apolar" fractions isolated using standard column or thin layer chromatography methods and apolar solvents as eluents (e.g. Schmid, 1986; Sinninghe Damsté *et al.*, 1986). Later work focused on high-molecular-weight (HMW) OSC which do not elute as discrete peaks in gas chromatograms due to their high boiling points. Because of their high-molecular-weight nature these OSC are predominantly present in so-called "polar" and/or asphaltene fractions which are isolated using more polar solvents (Kohnen *et al.*, 1991; Trifilieff,

1987). Besides OSC these fractions also contain (LMW) functionalized compounds like ketones, alcohols and acids which elute in these fractions because of their polarity. Using several chemical degradation methods (notably methods cleaving C-S bonds) these HMW OSC can be reduced to apolar LMW compounds and subsequently isolated from the remaining functionalized compounds and analyzed by GC-MS (e.g. Schmid, 1986; Sinninghe Damsté *et al.*, 1988, 1990; Kohnen *et al.*, 1991; Adam *et al.*, 1992; Hoffman *et al.*, 1992; Richnow *et al.*, 1992).

The presence of sulfoxides in sediments and oils has been reported by only a few authors. Payzant *et al.* (1983, 1986) found evidence for their presence in Athabasca asphalts using infrared-spectroscopy and by the detection of cyclic sulphides after reduction of the asphalts with  $\text{LiAlH}_4$ . Kohnen *et al.* (1990a) found small amounts of highly branched isoprenoid sulfoxides in a Black Sea sediment extract. The compound distribution was found to be similar to that of the corresponding cyclic sulphides. The reason for the incidental reports of their presence is given by Trifilieff (1987). The sulfoxides elute in the polar fraction which is not routinely analyzed by GC-MS due to its polar nature. Indirect analysis is possible by reducing the sulfoxides to sulphides with  $\text{LiAlH}_4$  and subsequent separation by column chromatography (Payzant *et al.*, 1983).

Recently a novel technique for the analyses of sulphur speciation in complex organic matter has become available. Least squares analysis of the X-ray absorption near edge structure (XANES)

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region of sulphur K-edge X-ray absorption fine structure (XAFS) spectra (in short XANES-analysis) allows the quantification of both the organic and inorganic functional forms of sulphur in complex organic matter such as petroleum (Gorbaty *et al.*, 1990), coals (Gorbaty *et al.*, 1990), asphalts (George and Gorbaty, 1989) and bitumens (Eglinton *et al.*, 1994). The distribution of thiophenic, sulphide and sulphoxide forms of sulphur present can thus be determined. This technique is non-destructive and allows direct analyses.

In this paper the presence of sulphoxides in two selected polar fractions is determined by XANES-analyses. Molecular analyses were performed by chemical reduction of a number of polar fractions, thus converting sulphoxides into sulphides, and subsequent isolation and analyses of formed LMW sulphides. The data show that LMW sulphoxides sometimes represent substantial proportions of the OSC present in polar fractions.

## EXPERIMENTAL

### *Samples*

The NAM-sample was taken from a fresh outcrop of a marl layer from the Perticara Basin (Italy). The compositions and distributions of the hydrocarbons and OSC from the sediment extract have been described by ten Haven *et al.* (1985) and Sinninghe Damsté *et al.* (1986).

The JED-156 sample was taken from a core of a drill hole at a depth of 156 m from the Jurf ed Darawish oil shale (Jordan). Hydrocarbon and OSC-compositions have been described by Kohnen *et al.* (1990b).

The KG-1 sample was taken from a fresh outcrop of the carbonaceous-marl member of the Monterey Formation at Naples Beach, U.S.A. (Isaacs *et al.*, 1992). Sample KG-3 comes from the underlying Rincon Shale. The hydrocarbons and OSC present in the extracts have been reported by Schouten *et al.* (1995a). These samples have been studied in the framework of the Cooperative Monterey Organic Geochemistry Study (Isaacs *et al.*, 1992).

The West Rozel Point Oil (RPO) is from a shallow reservoir in the north-western part of Utah (U.S.A.). The hydrocarbons and LMW OSC have been described by ten Haven *et al.* (1988), Sinninghe Damsté *et al.* (1987) and Schmid (1986).

### *Isolation and analysis of alkylsulphide and polar fractions*

The sediments were extracted with a dichloromethane/methanol (7:1 v/v) mixture. The polar and alkylsulphide fractions were isolated from the extracts or oil by column chromatography and preparative argentation thin layer chromatography as described previously (Kohnen *et al.*, 1991). The polar fractions and alkylsulphide fractions were

desulphurized using either Raney nickel (Kohnen *et al.*, 1991) or Nickel boride (Schouten *et al.*, 1993b). The released hydrocarbons were isolated by column chromatography (CC) using Al<sub>2</sub>O<sub>3</sub> and a hexane/dichloromethane (9:1 v/v) mixture as eluent. The hydrocarbon fractions were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Selected polar fractions were reduced with LiAlH<sub>4</sub> (see below) and a sulphide fraction was isolated using column chromatography and analyzed by GC and GC-MS. The sulphide fraction was desulphurized by Raney nickel or nickel boride.

### *Oxidation of model compounds*

Two model compounds [2,3-dimethyl-5-(1',1'-d<sub>2</sub>-hexadecyl)thiolane and didodecylsulphide] were dissolved in ethyl acetate and the solution was stirred at room temperature. Air was bubbled through the solution for three months. The mixtures were analyzed by GC and GC-MS.

### *Lithium aluminum hydride reduction (Fig. 1)*

Typically 20 mg of a polar fraction was dissolved in 1,4-dioxane and refluxed for 2 h with an excess amount (*ca* 100 mg) of LiAlH<sub>4</sub> (Payzant *et al.*, 1986). After cooling and centrifugation, the supernatant was collected and the residue washed with dichloromethane (3 ×). The collected reaction mixture was subsequently washed with slightly acidified doubly distilled water and subsequently dried using MgSO<sub>4</sub>. LMW OSC were isolated from the reaction mixture using column chromatography (stationary phase: Al<sub>2</sub>O<sub>3</sub>; eluent hexane/dichloromethane 9:1 v/v) and analyzed by GC and GC-MS. The residual polar fractions of two selected samples were analyzed by XANES.

### *Gas chromatography*

GC was performed using a Carlo Erba 5300 instrument, equipped with an on-column injector. A fused silica capillary column (25 m × 0.32 mm) coated with CP Sil-5 (film thickness 0.12 μm) was used with helium as carrier gas. For detection both a flame ionization detector (FID) and a sulphur-selective flame photometric detector (FPD) was used, using a stream-splitter at the end of the column (split ratio FID:FPD = 1:2). The samples (dissolved in ethyl acetate) were injected at 75°C and subsequently the oven was programmed to 130°C at 20°C/min and then at 4°C/min to 320°C at which it was held for 20 min.

### *Gas chromatography-mass spectrometry*

GC-MS was performed on a Hewlett-Packard 5480 gas chromatograph interfaced to a VG-70S mass spectrometer operated at 70 eV with a mass range *m/z* 40–800 and a cycle time 1.8 s (resolution 1000). The gas chromatograph was equipped with a fused silica capillary column (25 m × 0.32 mm)

Table 1. Results of the XANES-analyses of selected polar fractions before LiAlH<sub>4</sub>-treatment and the residual fraction after LiAlH<sub>4</sub>-treatment

	Sulphide (%)	Sulphoxide (%)	Thiophene (%)	Others*
JED-156 polar fraction	26	27	45	2
JED-156 residue	56	1	43	1
KG-1 polar fraction	33	28	36	3
KG-1 residue	51	9	35	5

\*Mainly sulphonic acid and sulphate.

coated with CP Sil-5 (film thickness = 0.2 μm). The carrier gas was helium. The samples were on-column injected at 50°C and subsequently the oven was programmed to 130°C at 20°C/min and then at 4°C/min to 300°C at which it was held for 10 min.

#### XANES-analyses

XANES-analyses were performed as described by Eglinton *et al.* (1994). In short, X-ray absorption spectroscopy was performed on Beamline X-19A at the National Synchrotron Light Source at Brookhaven National Laboratory. Samples (in CHCl<sub>3</sub>) were heat-sealed in Mylar (2.5 μm film thickness) bags or adsorbed on to pre-ashed glass fiber filters. The samples were mounted in a He-purged sample chamber for analysis. XANES spectra were acquired from 2440 eV to 2700 eV using a Lytle fluorescence detector. The reference standards used included FeS<sub>2</sub>, elemental sulphur, cysteic acid, sodium sulphate, dibenzylsulphide, dibenzothiophene and dibenzylsulphoxide. Values are reported as a fraction of the total sulphur in the sample.

### RESULTS AND DISCUSSION

XANES-analyses of two selected samples, KG-1 and JED-156, revealed that a substantial part of the sulphur in the polar fraction is present as sulphoxide (Table 1). Sulphoxides are thus, at least in these two samples, a major part of the OSC present in the polar fractions. Results of XANES-analyses on recent sediments (Vairavamurthy *et al.*, 1993) also revealed that a significant part of the organic sulphur may be present as sulphoxide.

The polar fractions were subsequently reduced with LiAlH<sub>4</sub> (Payzant *et al.*, 1983) and subjected to column chromatography to isolate formed LMW sulphides. In this way the amount of sulphoxide-moieties present as LMW compounds can, indirectly, be determined (Fig. 1). XANES-analyses performed on the residues of the polar fractions, present after isolation of the sulphides formed, of samples KG-1 and JED-156 revealed that the relative amount of sulphoxide was indeed substantially lower after reduction (Table 1). The relative amount of thiophenes appears to be unchanged yet the relative amount of sulphides has increased substantially. This latter result seems to be somewhat puzzling since substantial amounts of LMW sulphides have been removed (Fig. 1; Table 3) while the relative amount

of sulphide increases. This may be explained by the reduction of intermolecular sulphoxide-bridges which are reduced to sulphides but remain in the polar fraction due to their HMW nature. Furthermore LMW sulphoxides with additional functional groups (alcohol, acid) may be present in the polar fraction which despite reduction with LiAlH<sub>4</sub> remain in there due to these functional groups. Alternatively it can be suggested that part of the thiophenes present in these polar fractions was hydrogenated by treatment with LiAlH<sub>4</sub>. To this end, a model thiophene[2,3-dimethyl-5-(1',1'-d<sub>2</sub>-hexadecyl)thiophene] was subjected to LiAlH<sub>4</sub> reduction and the reaction mixture was analyzed by GC and GC-MS. No thiolanes could be detected in the product mixture indicating that thiophenes are unaffected by the chemical reduction. It is therefore unlikely that thiophenes present in the polar fraction became hydrogenated to thiolanes.

#### LMW sulphoxides vs LMW sulphides

When the proportions of the free sulphide fraction and the "sulphoxide" fraction (i.e. the sulphides isolated after reduction of the polar fraction) are compared, it becomes clear that the amount of sulphoxides is in the same order of magnitude as the amount of free sulphides (Table 2). The only exception is the West Rozel Point oil which contains relatively low amounts of sulphoxides. These data indicate that oxidation of sulphides may introduce a severe bias in the sedimentary record of LMW alkyl-sulphides since a significant part is sequestered in a fraction which is not routinely analyzed by GC and GC-MS.

GC-MS analyses of the sulphide fraction isolated from the reduced polar fraction of the JED-156 extract show that it consists mainly of thiolanes (Fig. 2 upper panel). The distribution of these compounds is similar to that of the LMW sulphides present as such in this sample (Fig. 2 lower panel)

Table 2. Weight percentage (of total bitumen) of LMW sulphide fraction and LMW sulphide fraction obtained by LiAlH<sub>4</sub>-treatment of polar fraction

	Sulphide fraction (wt%)	Sulphides from reduced polar fraction (wt%)
JED-156	4.9	3.6
KG-3	0.5	1.2
KG-1	0.6	1.6
NAM	6.9	3.7
RPO	11.7	0.5

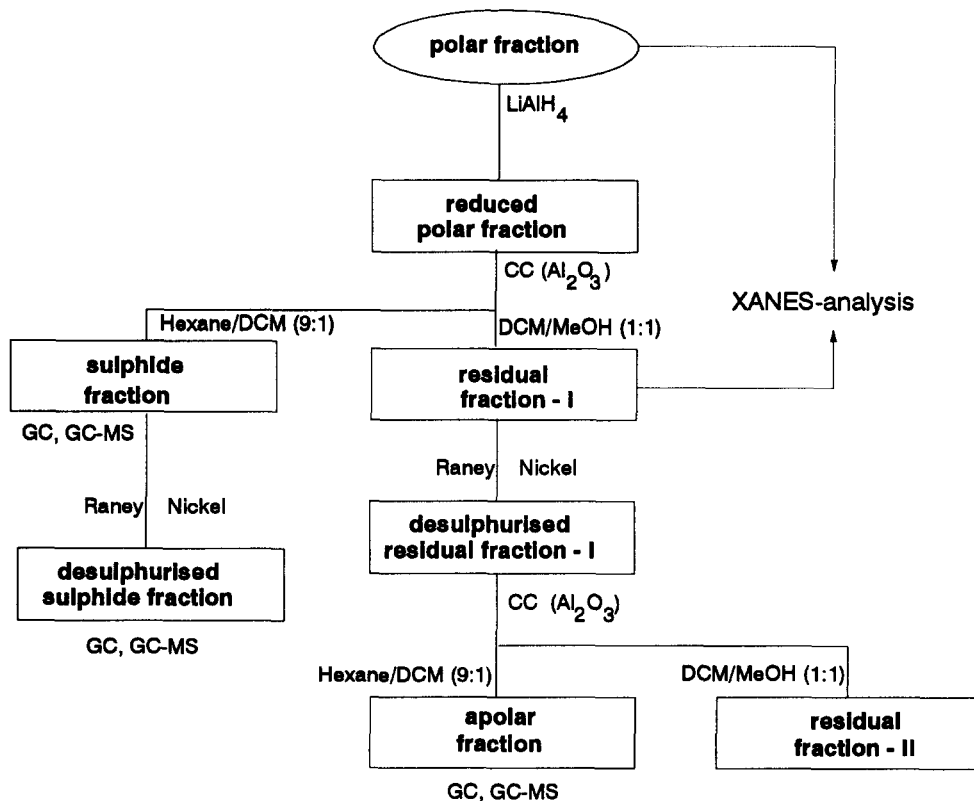


Fig. 1. Analytical scheme used for the study of sediment extracts and oil.

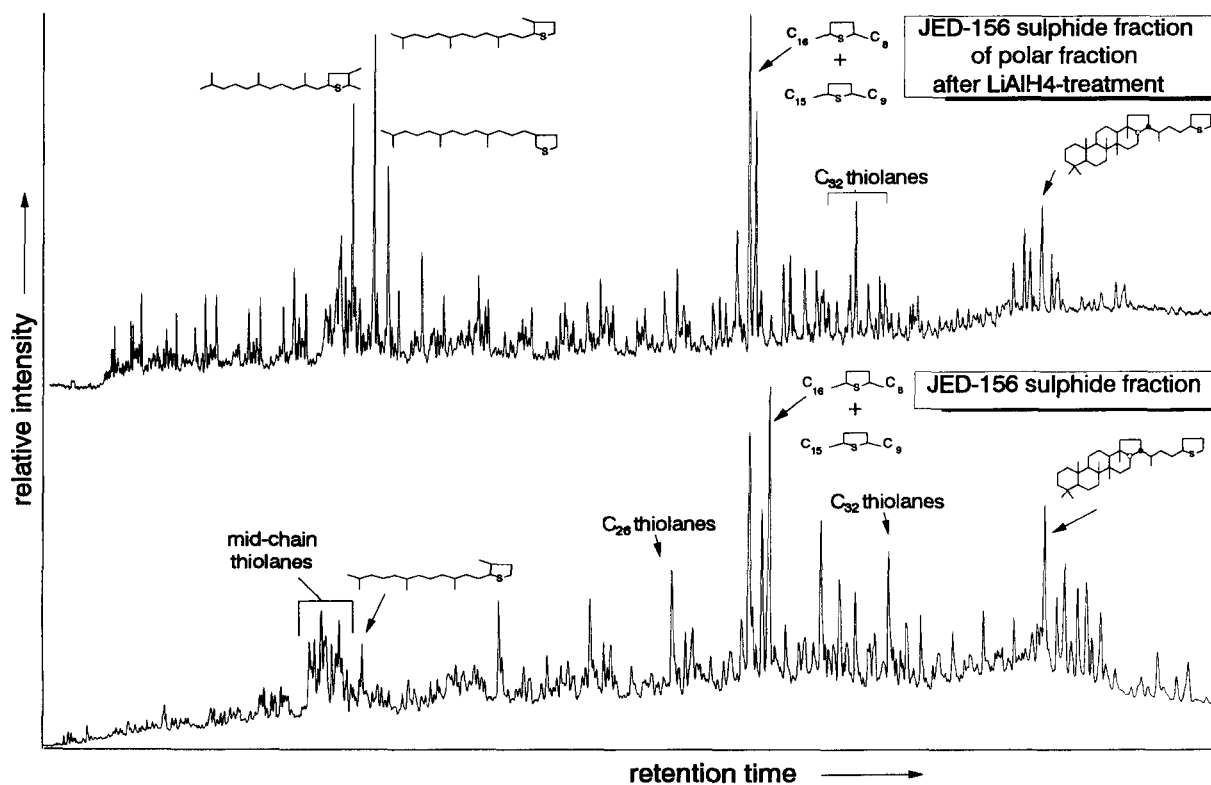


Fig. 2. Gas chromatogram of generated LMW sulphides after reduction of the polar fraction with  $\text{LiAlH}_4$  (upper panel) and of LMW sulphides present as such in the JED-156 sediment extract (lower panel).

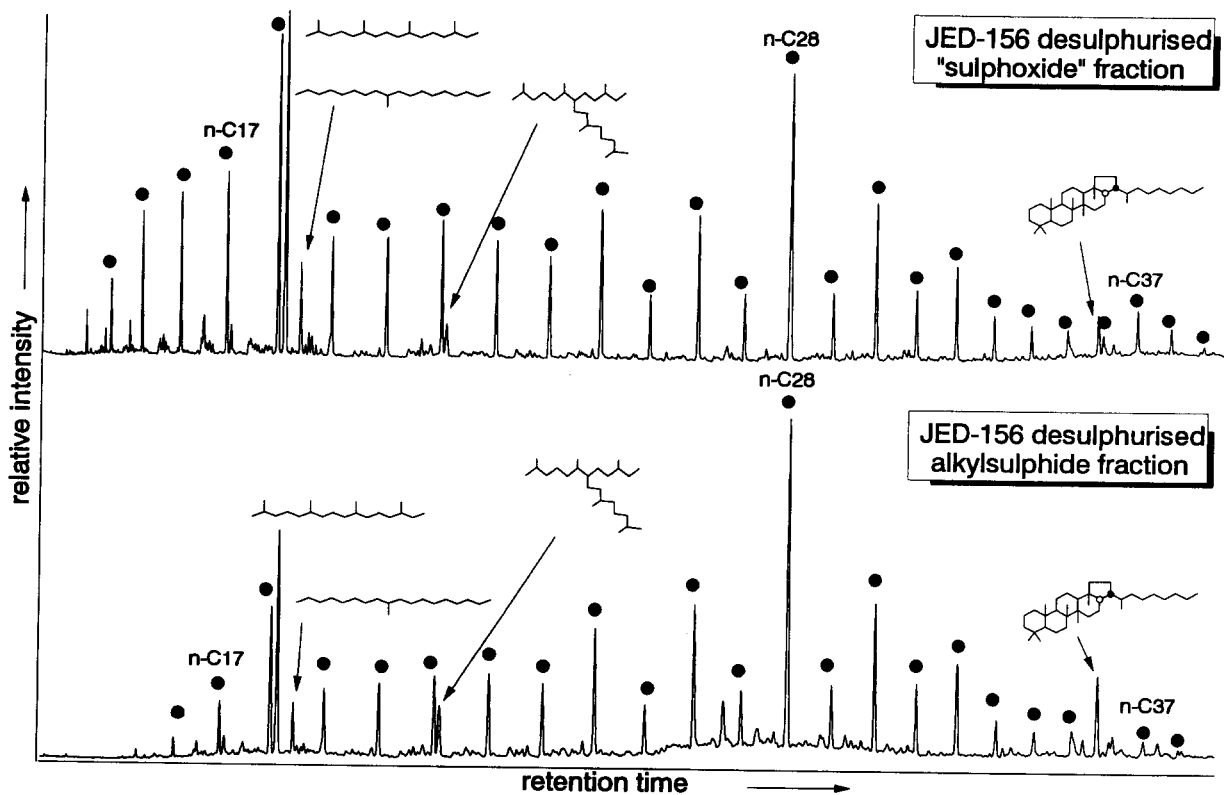


Fig. 3. Gas chromatogram of released hydrocarbon fractions from desulphurized LMW sulphides generated after reduction of the polar fraction (upper panel) and of desulphurized LMW sulphides present as such in the JED-156 sediment extract (lower panel). (●) = *n*-alkanes.

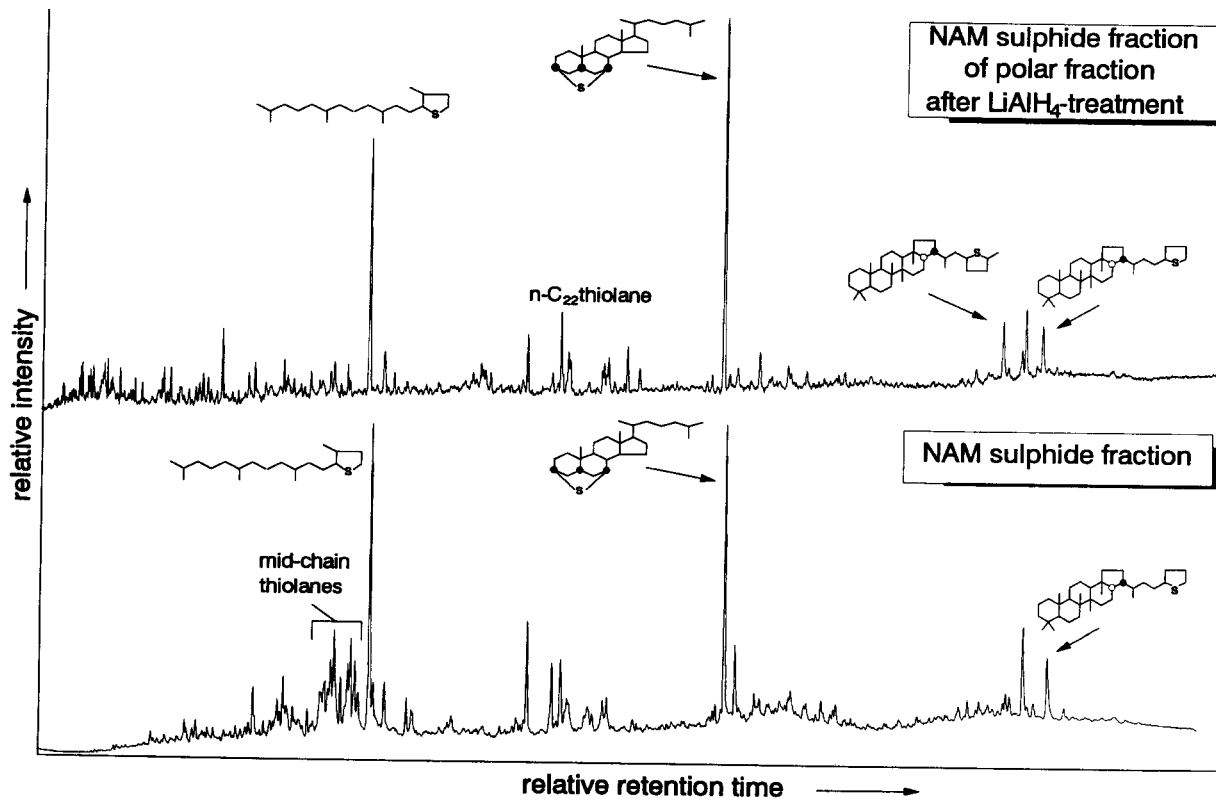


Fig. 4. Gas chromatogram of generated LMW sulphides after reduction of the polar fraction (upper panel) and of LMW sulphides present as such in the NAM sediment extract (lower panel).

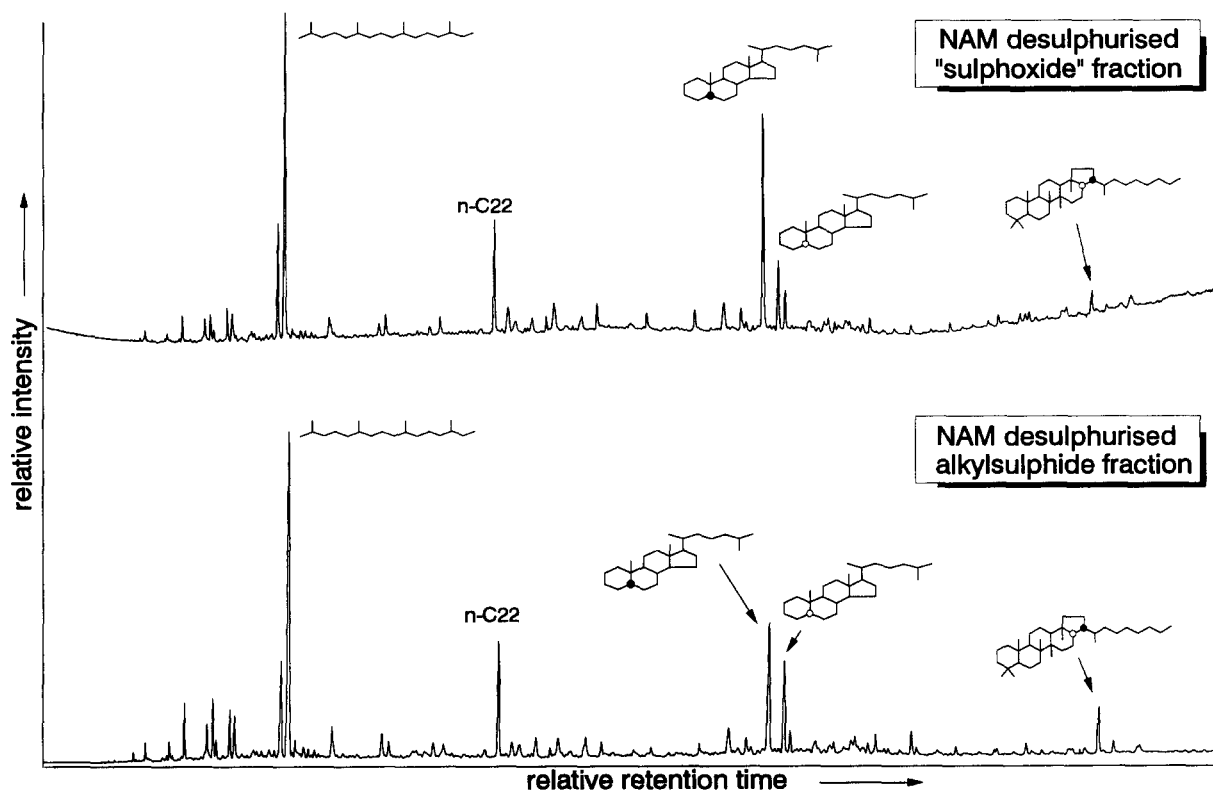


Fig. 5. Gas chromatogram of released hydrocarbons from desulphurized LMW sulphides generated after reduction of the polar fraction (upper panel) and of desulphurized LMW sulphides present as such in the NAM sediment extract (lower panel).

though several differences can be noted. In the sulphide fraction isolated from the reduced polar fraction the relative amount of 3-methyl-2-(3,7,11-trimethyldodecyl)thiolane seems to be higher. Furthermore, the ratio of *cis* and *trans*  $C_{28}$  mid-chain thiolanes is reversed when the alkylsulphide fraction is compared to the reduced polar fraction. This may indicate that these compounds [i.e. *trans*  $C_{28}$  mid-chain thiolanes and 3-methyl-2-(3,7,11-trimethyldodecyl)thiolane] are relatively easier to oxidize to sulphoxides compared to other sulphides. Desulphurization of both the "sulphoxide" fraction and the alkylsulphide fraction yielded a similar composition of the released hydrocarbon fractions (Fig. 3). Minor differences in relative abundances can be observed for  $17\alpha,21\beta(H)$ -pentakishomohopane carbon skeleton which seems present in relatively higher amounts in the alkylsulphide fraction. The same

holds for the  $C_{25}$  highly branched isoprenoid carbon skeleton.

The NAM polar fraction was also reduced and the gas chromatogram of the resulting sulphide fraction is shown in Fig. 4 (upper panel) together with the alkylsulphide fraction present as such (lower panel). The distribution of sulphides is generally similar but a difference in the distribution of thiolanes possessing a phytane carbon skeleton can be noted. In the alkylsulphide fraction mid-chain thiolanes are relatively more dominant than in the reduced polar fraction. Desulphurization of both fractions yielded hydrocarbon fractions with a similar distribution (Fig. 5). As in the JED-156 sample the  $C_{35}$  hopane seems relatively more abundant in the alkylsulphide fraction than in the "sulphoxide" fraction. Intriguingly,  $5\alpha$ -cholestane is in much higher abundance compared to the  $5\beta$ -cholestane in the alkylsulphide fraction than in the "sulphoxide" fraction.  $5\beta$ -Cholestane is derived from  $3\alpha,7\alpha$ -epithio- $5\beta$ -cholestane (Schouten *et al.*, unpublished results) present in both the alkylsulphide and in the "sulphoxide" fraction. There are, however, no LMW sulphur compounds which possess a  $5\alpha$ -cholestane carbon skeleton. This indicates that the alkylsulphide fraction contains  $5\alpha$ -cholestane in some sulphur-bound form which is not reflected as a discrete chromatographic peak in the gas chromatogram. It is suggested

Table 3. Yields (weight %) of apolar fractions released by  $LiAlH_4$  and Raney Nickel treatment versus amount of polar fractions

	Yield $LiAlH_4$ (%)	Yield Ra Ni (%)
JED-156	10	17
KG-3	5	9
KG-1	6	10
NAM	6	20
RPO	1	14

that it is present as sulphur-bound di- or trimers which do not elute as a discrete peak but as a broad "hump" due to the thermally induced disintegration on the GC-column (Schouten *et al.*, 1993a). This observation has been reported previously by Kohnen *et al.* (1991) who showed that a sulphur-rich "hump" in the gas chromatogram of the alkylsulphide fraction of the Vena del Gesso sediment consisted predominantly of oligomers with sterane carbon skeletons.

Sulphide and "sulphoxide" compound distributions of samples from the Monterey Formation are similar as is also the case for the Rozel Point oil. These results indicate that the alkylsulphides and sulphoxides have a more or less similar origin and that, therefore, the sulphoxides are likely derived by oxidation of the sulphides. Certain compounds, however, do seem to be relatively enhanced in the reduced "sulphoxide" fraction indicating that particular thiolanes are more prone to oxidation than others.

The question remains at what stage sulphides are oxidized to sulphoxides. It has been suggested that oxygen present in the depositional environment or in the sediment can be the cause (Payzant *et al.*, 1983). Since OSC are formed in anoxic environments this must have been post-depositional, i.e. the water column may have turned more oxic after deposition of the OSC. Oxidation of cyclic sulphides during long-time storage of samples or isolated alkylsulphide fractions has been noted by Kohnen *et al.* (1990a).

Another cause could be the sample preparation during which sulphides are isolated from the sediment. This latter hypothesis seems, however, unlikely since fractions from the RPO oil were isolated in a similar manner to the other samples but still did not contain high amounts of sulphoxides. It is also possible that the sulphides were oxidized by weathering of the sediment sample, as was also observed for sulphur-rich oils (Burwood and Speers, 1973). The Monterey sample which contains high amounts of sulphoxides was taken from an outcrop at Naples Beach and contains oxidized pyrite. The NAM sample is also an outcrop sample. The JED sample was taken from a core, but was stored for a long time after crushing at room temperature probably causing the high degree of oxidation of sulphides.

To investigate the effect of oxidation on sulphides a thiolane model compound [*cis* and *trans* 2,3-dimethyl-5-(1',1'-d<sub>2</sub>-hexadecyl)thiolane] was dissolved in ethyl acetate and air was bubbled through for 1200 h. GC analyses revealed that *ca* 90% of the thiolane was oxidized to the corresponding sulphoxides. When, however, a dialkylsulphide model compound [didodecylsulphide] was submitted to the same experimental conditions no formation of sulphoxides could be observed after 1200 h. This indicates, as does literature data (e.g. Drushel and Sommers, 1967), that thiolanes are more easily oxidized and may be converted to sulphoxides upon long-time storage.

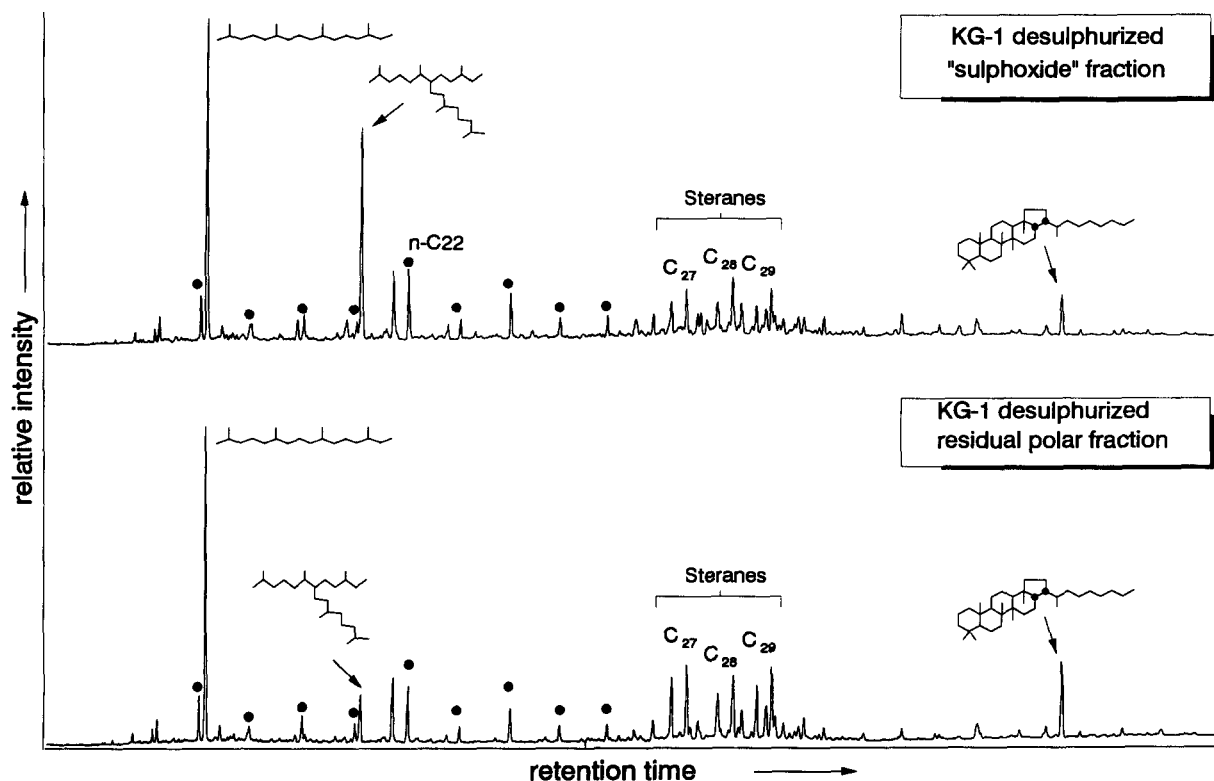


Fig. 6. Gas chromatogram of hydrocarbons obtained by desulphurization of generated LMW sulphides obtained after reduction of the polar fraction (upper panel) and of LMW sulphides present as such in the KG-1 sediment extract (lower panel). (●) = *n*-alkanes.

Furthermore the speed of oxidation of sulphides depends on the structure of the compound (e.g. Drushel and Sommers, 1967), which confirms the results previously mentioned for compounds in the polar fractions.

#### LMW sulphoxides vs HMW OSC

A comparison can be made between the amounts of compounds obtained by  $\text{LiAlH}_4$ -treatment of the

polar fraction and the amounts of compounds obtained by desulphurization of the polar fraction. The former will reflect the amount of LMW sulphoxides in the polar fraction while the latter will reflect the sum of LMW sulphoxides and HMW OSC in the polar fraction. Table 3 shows the yields of compounds released by  $\text{LiAlH}_4$  and Raney Nickel. In case of the sediment extracts the carbon skeletons released by Raney Nickel or nickel boride are up to ca 60 wt%

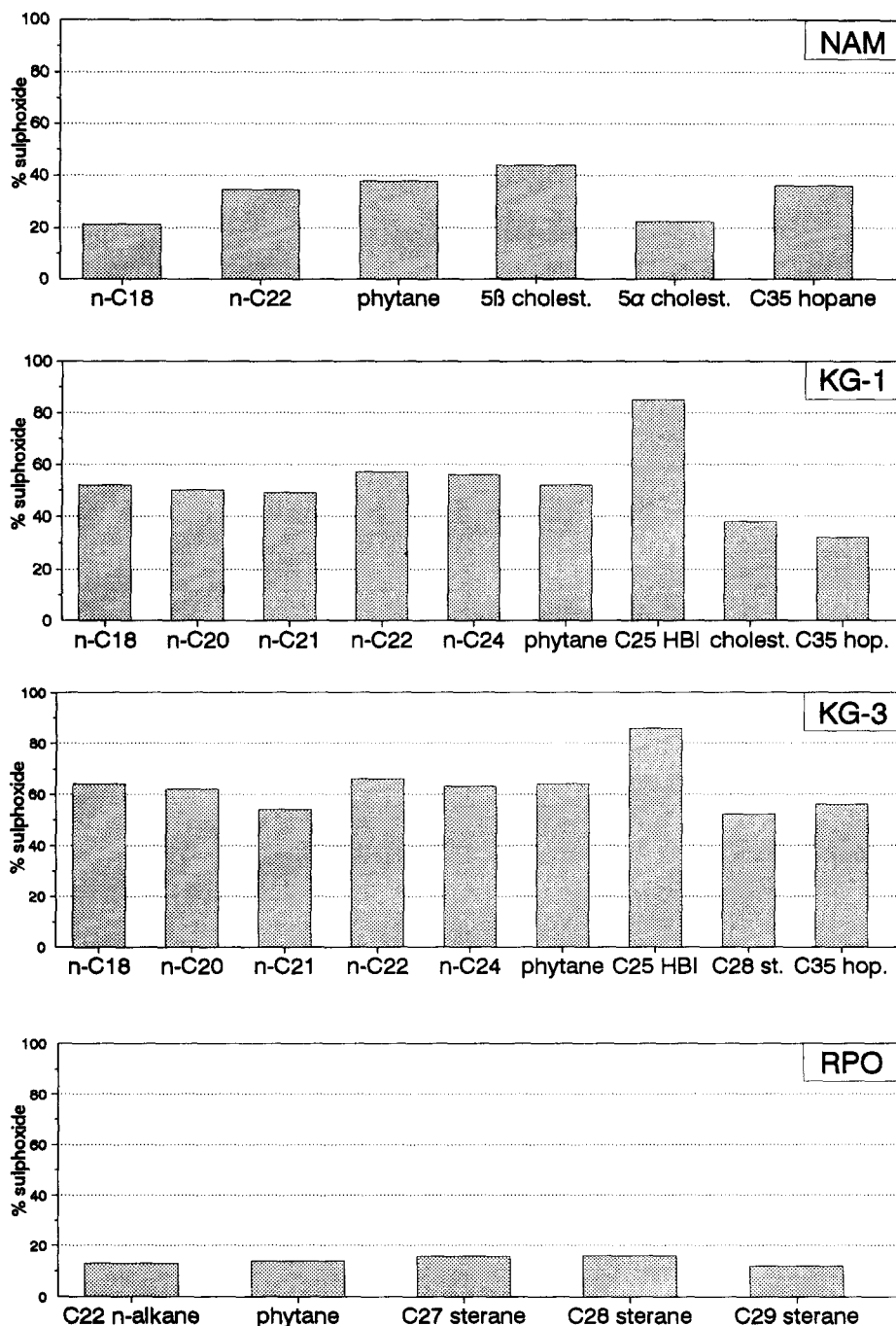


Fig. 7. Bar graphs showing the fraction of carbon skeletons obtained after desulphurizing the sulphide fraction from the polar fraction vs the amount released by desulphurization of the residual polar fraction.



derived from LMW sulphoxides. In the case of the Rozel Point oil this amount is much lower (ca 10%). This implies in general that carbon skeletons released by desulphurization of polar fractions may contain varying amounts of products derived from LMW sulphoxides. Kohnen *et al.* (1992a, b) have shown that LMW OSC and HMW OSC may have different precursor lipids even though they possess identical carbon skeletons. For instance, the carbon isotopic composition of the C<sub>35</sub> hopanoid thiolane differed by more than 3‰ from the δ<sup>13</sup>C value of the C<sub>35</sub> hopane released by desulphurization of the polar fraction of a marl from the Vena del Gesso basin. On the other hand Schouten *et al.* (1995b) determined the carbon isotopic compositions of carbon skeletons derived from LiAlH<sub>4</sub>-treatment and those released from subsequent Raney Nickel desulphurization of polar fractions of two Monterey samples. In this case no differences were noted in the isotopic compositions of carbon skeletons released from the "sulphoxides" fraction and carbon skeletons from the residual fraction (i.e. derived from HMW OSC). This indicates that, in this instance, the precursor lipids were identical in these Monterey samples. Still, care must be taken in interpreting results obtained from desulphurization of polar fractions.

A comparison can be made between the carbon skeletons present as LMW sulphoxides and those present as HMW OSC in polar fractions. The analytical scheme presented in Fig. 1 was followed for samples KG-1 (Fig. 6), KG-3, NAM and RPO. The different carbon skeletons were quantified using internal standards and the results are presented in Fig. 7. As was already clear from the bulk yield data a significant fraction of the sulphurized carbon skeletons in polar fractions is present as LMW sulphoxides. Some differences can be noted for the different carbon skeletons of LMW sulphoxide and HMW OSC origin. For instance, steranes in the polar fractions of the Monterey samples seem to be mainly macromolecularly bound while the C<sub>25</sub> highly branched isoprenoid is mainly present as LMW sulphoxide. In this case the reason is the difference in precursor lipids; the C<sub>25</sub> HBI lipids possessed closely spaced multiple double bonds suitable for both inter and intramolecular sulphur incorporation (Kohnen *et al.*, 1991; Schouten *et al.*, 1994). The precursors for sulphur-bound steranes do not have closely spaced multiple double bonds thus prohibiting the formation of significant amounts of steroid thiolanes (and therefore sulphoxides; Kohnen *et al.*, 1991; Schouten *et al.*, 1994). This is not the case for the NAM sample since it contains high amounts of 3α,7α-epithio-5β-sterane and its sulphoxide counterpart.

#### CONCLUSION

Polar fractions of sediment extracts may contain high amounts of oxidized cyclic sulphides. They are

sometimes as abundant as their reduced counterparts present in alkylsulphide fractions and may make up to 60% of the OSC present in polar fractions. Specific OSC can be more easily oxidized than others, thus introducing a bias in the thiolane distributions. Hydrocarbons released by desulphurization of polar fractions are in part (up to 60%) derived from LMW sulphoxides.

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