Chapter 26

Characterization of Organically Bound Sulfur in High-Molecular-Weight, Sedimentary Organic Matter Using Flash Pyrolysis and Raney Ni Desulfurization

Jaap S. Sinninghe Damsté, Timothy I. Eglinton¹, W. Irene C. Rijpstra,
and Jan W. de Leeuw

Faculty of Chemical Engineering and Materials Science, Organic
Geochemistry Unit, Delft University of Technology, De Vries
van Heystplantsoen 2, 2628 RZ Delft, Netherlands

Organically-bound sulfur in three types of high-molecular-weight organic matter (kerogen, asphaltenes and resins) obtained from three organic S-rich sedimentary rock samples has been studied. Kerogen, asphaltene and resin fractions were isolated and analysed by flash pyrolysis-gas chromatography-mass spectrometry. The resin fractions were desulfurised with Raney Ni and the products obtained were characterised by gas chromatography-mass spectrometry. These experiments revealed that S_{org} in high-molecular-weight sedimentary organic matter at least partially occurs in moieties with linear, isoprenoid, branched, steroid, hopanoid and carotenoid carbon skeletons. In kerogen and asphaltenes evidence was obtained for the presence of these types of moieties as thiophenes, which are thought to be mainly bound to the macromolecular matrix by multiple C-S bonds. In resins S-containing moieties are thought to be primarily bound by only one C-S bond though they may contain additional intramolecular S-linkages. The different properties of S-rich kerogens and asphaltenes on the one hand and S-rich resins on the other hand may be explained by differences in the degree of (sulfur) cross-linking and thus by differences in molecular size and in degree of condensation. These S-rich geopolymers are formed by incorporation of inorganic sulfur species into functionalised lipids in an intermolecular fashion during early diagenesis. In depositional environments with high amounts of available S-donors these reactions may be regarded as an important pathway for the generation of high-molecular-weight material ("natural vulcanisation").

¹Current address: Fye Laboratory, Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

Organically-bound sulfur in fossil fuels and related sedimentary organic matter is present in both low-molecular-weight ($MW < 800$) organic sulfur compounds (OSC) and in complex macromolecules (*i.e.*, kerogen, coal, asphaltenes and resins). Major advances in the characterisation of low-molecular-weight OSC in bitumens and crude oils have been reported during the last decade with more than a thousand novel OSC identified during this period (1-17). Many of these represent new classes of sulfur-containing biological markers because their carbon skeletons are identical to the well-known hydrocarbons (*e.g.*, *n*-alkanes, isoprenoid alkanes, steranes, hopanes) occurring in the geosphere and their inferred biochemical precursors. Evidence has been presented that these OSC are formed by incorporation of inorganic sulfur species (hydrogen sulfide, polysulfides) into functionalised lipids during the early stages of diagenesis (2,8,9,11-18).

So far, less attention has been given to the characterisation at a molecular level of organically-bound sulfur in high-molecular-weight substances in sediments and crude oils, although the major part of the organic sulfur is bound in these fractions. Kerogen, which normally represents at least 90% of the organic matter in immature sediments, may contain more than 14% (by weight) organic sulfur (19). Organic sulfur in kerogen and other sedimentary macromolecules is thought to be present in sulfide, di- and/or polysulfide moieties and as a constituent of aromatic heterocycles (20), but reliable data on this subject is scant.

It is generally accepted (19,21-23) that the early generation of petroleum from sulfur-rich kerogens is due to the abundant presence of weak sulfur-sulfur (average bond energy *ca.* 250 kJ/mol) and carbon-sulfur bonds (*ca.* 275 kJ/mol) relative to carbon-carbon bonds (*ca.* 350 kJ/mol). The presence of these weak bonds lowers the maximum of the activation energy distribution for the thermal degradation of the kerogen. Indeed, sulfur-rich kerogens exhibit a much lower Rock-Eval T_{max} than sulfur-lean kerogens of the same maturity (24,25). However, the form in which organic sulfur is present in kerogen is of major importance in this respect since mono-, di- and polysulfide moieties contribute significantly to the relative thermal instability whilst the presence of thiophene and condensed thiophene units has little or no effect. Therefore, determination of the kinds of sulfur-bonding in sedimentary high-molecular-weight substances, *i.e.* relative abundances of different sulfur functional groups/bond types, is of great interest for petroleum geochemistry. This kind of information is, however, difficult to obtain. Recently, George and Gorbaty (26) reported an X-ray absorption spectroscopic method for the determination of the forms and the amounts of

organically-bound sulfur in asphaltenes. Although this method will be of great use for the assessment of the abundance of thermally labile *versus* thermally stable forms of organic sulfur in macromolecules, it does not provide information on moieties bound by sulfur in the macromolecules. In this paper two techniques are described which can give such information, although these methods both suffer from other disadvantages.

The first method is flash pyrolysis-gas chromatography-massspectrometry, which has been shown to be a powerful technique for the characterisation of bio- and geopolymers, such as lignins (27,28), humic substances (29,30), coal and its maceral fractions (31-33), asphaltenes (34-36) and kerogen (31,35-43). This method induces thermal dissociation of macromolecules with a minimum of secondary reactions. At lower Curie point temperatures ($< 610^{\circ}\text{C}$) the products formed are mainly generated by cleavage of one chemical bond (per product). Some subsequent internal rearrangement reactions associated with these bond cleavages (*e.g.*, elimination of H_2O , H_2S) do occur. Only recently, it has been realised that the sulfur compounds produced on flash pyrolysis of macromolecular substances may provide insight into the form and molecular arrangement in which organic sulfur is bound into these macromolecules. This has led to a number of studies (24,44-49) in which flash pyrolysates were analysed by gas chromatography in combination with sulfur-selective flame photometric detection. Sinninghe Damste *et al.* (48,49) and Eglinton *et al.* (24) have shown that flash pyrolysis of kerogens, coals and asphaltenes may yield abundant OSC, many of which provide useful information with respect to the characterisation of sulfur-containing moieties present in these substances. Payzant *et al.* (50) have similarly shown that the oil obtained from off-line pyrolysis of the Athabasca asphaltene contains abundant series of OSC.

The second method is sulfur-selective chemical degradation (*i.e.*, Raney Ni desulfurisation) of high-molecular-weight substances. It achieves a reductive cleavage of carbon-sulfur bonds, whereby units, bound in macromolecules by sulfur-carbon bond(s) only, are released and can be characterised by gas chromatography-mass spectrometry (7,18). This method can only be applied to high-molecular-weight substances which are soluble in organic solvents (*i.e.*, resins). Asphaltenes tend to form aggregates in certain organic solvents, which causes problems with desulfurisation.

In this paper organically-bound sulfur in three types of high-molecular-weight organic matter (kerogen, asphaltenes and resins) obtained from three organic sulfur-rich sedimentary rock samples has been studied. Kerogen, asphaltene and resin fractions were isolated and characterised by the two described techniques.

Materials and Methods

Samples. Three immature sulfur-rich sedimentary rock samples were selected for study of both the kerogens and extractable bitumens. Selected properties of the specific samples together with references to previous descriptions and investigations of these deposits are as follows:

Jurf ed Darawish-156: This is a bituminous calcareous marlstone from the Jurf ed Darawish Oil Shale (Upper Cretaceous) located 130 km south of Amman (Jordan) (51), which was deposited in an anoxic, marine environment. This sample is a composite sample from a core at 156-157 m with 17.3% TOC and $R_o = ca. 0.30\%$. The organic sulfur content of the isolated kerogen was not measured but the atomic $S/C = 0.084$ and the pyrite-S/organic-S ratio is presumably low since microscopical examination indicated a low pyrite content. Detailed information on the hydrocarbon biological markers (51), the OSC (15,16,52) and kerogen pyrolysate (48,49) have been published elsewhere.

Monterey-25: This sample is from the Upper Miocene Monterey Formation (California, U.S.A.), a phosphatic-siliceous-carbonate rock sequence, and was collected from an outcrop near Vandenberg Air Force Base (Santa Barbara County). This Formation and similar samples have been described by Isaacs (53) and Orr (19). This sample (TOC = 17.3%) also contains immature ($R_o = ca. 0.30\%$), sulfur-rich (atomic $S_{org}/C = 0.054$) kerogen.

Northern Apennines Marl: This sample is from Miocene strata in the Perticara basin (Italy) which consists of gypsum deposits interbedded with bituminous marl layers deposited during the Mediterranean salinity crisis (54). Detailed information on the hydrocarbons and OSC in the bitumen of this sample have been reported elsewhere (9,16,54).

Separation methods. Extraction and fractionation (Figure 1) methods have been described elsewhere (16). The kerogen from Jurf ed Darawish-156 was concentrated by decarbonating the extracted whole rock followed by re-extraction. The kerogen from the Monterey-25 was fully isolated using standard HCl/HF techniques. Asphaltene fractions were obtained and purified from bitumens by repeated precipitations with *n*-heptane.

Desulfurisation. Aliquots of polar and High-Molecular-Weight Aromatic (HMWA; Figure 1) fractions were desulfurised using Raney Ni as described elsewhere (18). The mixture after desulfurisation was separated over a small (5 x 0.5 cm) alumina column using hexane/ CH_2Cl_2 (9:1) to elute the saturated and aromatic hydrocarbons and CH_2Cl_2 to elute more polar

Figure 1. Analytical flow diagram.

compounds. The first fraction was analysed by GC-MS under conditions described previously (16).

Flash pyrolysis-gas chromatography-massspectrometry. Flash pyrolysis-GC-MS analyses were performed as described in detail previously (48), although another mass spectrometer (VG-70S) was used. Electron impact mass spectra were obtained at 70 eV with a cycle time of 1.7 s and a mass range m/z 50-800 at a resolution of 1000. Data acquisition was started 1 min. after pyrolysis.

Organically-Bound Sulfur in Kerogen

Structure of Sulfur-Containing Moieties. In one of our recent studies it was shown that H_2S , thiophene and C_1 - C_6 alkylated thiophenes are the major sulfur-containing products in flash pyrolysates of immature kerogens (48,49). H_2S is formed by thermal degradation of cyclic and acyclic sulfide and polysulfide moieties in the kerogen (49). Thermal degradation of these moieties already starts when using ferromagnetic wires with a Curie temperature of 358°C ("358°C pyrolysate"). This thermal instability is probably due to the lower amount of energy required to cleave S-S and S-C bonds in comparison with C-C bonds (49). Unless these cleavages result in the release of GC-amenable molecules from the macromolecular substances (as in the case of polar fractions; see below) little information on the moieties bound by sulfur is obtained. This is the case for kerogens. Cleavage of the C-S bond in aromatic sulfur-containing moieties (thiophene and benzo-thiophene units) in macromolecules requires much more energy and thermal degradation results mainly in saturated alkylated thiophenes and benzo-thiophenes predominantly by cleavage of the relatively weak C-C bond at the β position to the aromatic ring (49). This thermal degradation reaction starts only using ferromagnetic wires with higher Curie temperatures (from 510°C). H_2S in flash pyrolysates thus reflects the amount of thermally less stable forms of organic sulfur, whereas the alkylthiophenes represent the thermally more stable form of organic sulfur. However, the amounts of H_2S generated upon pyrolysis cannot be used as a measure of the total amount of thermally less stable forms of organic sulfur since H_2S can also be formed from pyrite present in the kerogen. Currently we are undertaking studies to determine whether the H_2S evolved during flash pyrolysis of asphaltenes correlates to their (poly)sulfide sulfur content.

Figure 2a shows the total ion chromatogram (TIC) of the flash pyrolysate of a sulfur-rich (Type II-S) kerogen from the Jurf ed Darawish Oil Shale. The major peaks are alkylated thiophenes, shown more clearly in

Figure 2. Total ion currents (TIC) of flash pyrolysates of several high-molecular-weight fractions of the Jurf ed Darawish-156.

Figure 3a and b. Other immature ($R_0 < 0.5\%$), sulfur-rich kerogens also show an abundance of thiophene and C_1 - C_6 alkylated thiophenes in their flash pyrolysates (e.g., Figure 4a and b). Pyrolysates of kerogens with lower organic sulfur contents (e.g., Type II kerogens) contain smaller amounts of these thiophenes in both relative and absolute terms. However, even in sulfur-poor, hydrogen-rich Type I kerogens the C_1 - C_6 alkylated thiophenes are present (49). Eglinton *et al.* (24) have recently shown that the amount of one of these thiophenes (i.e. 2,3-dimethylthiophene) relative to an aromatic hydrocarbon (1,2-dimethylbenzene) and an aliphatic hydrocarbon (non-1-ene) as measured by flash pyrolysis-GC shows a distinct correlation with organic sulfur content of the macromolecular substances. The C_1 - C_6 alkylated thiophenes in the pyrolysates typically represent, however, only a small portion of the total organic sulfur of the macromolecules ($< 10\%$; 24). George and Gorbaty (26) have reported that in asphaltenes more than 50% of the total organic sulfur is present as thiophenes. It appears therefore that upon flash pyrolysis only a part of the thiophenic sulfur is transformed into GC-amenable alkylthiophenes. The distinct correlation mentioned above indicates that this is a representative portion of the total organic sulfur content of the kerogen. Low yields have been observed for other compound classes (e.g., hydrocarbons, phenols) generated on flash pyrolysis of kerogens as well. In these cases good agreement has also been obtained in comparison with bulk geochemical data (e.g., elemental analysis, ^{13}C nmr) (55).

Detailed mass spectroscopic studies combined with the synthesis of a number of authentic standards has led to the identification of the major C_1 - C_6 alkylated thiophenes present in flash pyrolysates of kerogens (48). A study (49) of approximately 50 different immature kerogens (including 13 coals) showed that the alkylated thiophenes in the flash pyrolysates are dominated by a limited number of the theoretically possible isomers, although the isomer distributions vary. This is exemplified by the Py-GC-MS analyses of the Jurf ed Darawish-156 kerogen and an immature, sulfur-rich kerogen of the Monterey Shale as shown in Figures 3 and 4. Peak identifications (numbers) refer to compounds listed in Table I. The distributions of the alkylated thiophenes are in both cases dominated by only a limited number of isomers; e.g., (i) in the C_1 -cluster 2-methylthiophene is much more abundant than 3-methylthiophene, (ii) of the six C_2 -thiophenes 3-ethylthiophene and 3,4-dimethylthiophene are very minor and (iii) the C_3 -thiophenes are dominated by 2-ethyl-5-methylthiophene and 2,3,5-trimethylthiophene. However, significant variations in isomer distributions are observed between samples. For example, despite their similar inferred palaeoenvironment of deposition the Jurf ed Darawish-156 kerogen pyrolysate contains relatively larger amounts of 2,3,4,5-tetramethylthiophene (compound 19, Figure 3b) and 2-ethyl-3,4,5-methyl-

thiophene (compound 23) and lesser amounts of 2-methyl-3-isopropylthiophene (compound 13) compared with the Monterey kerogen pyrolysate.

Closer examination of the alkyl substitution patterns of the dominant alkylated thiophene isomers (48) showed that they bear a strong similarity to those of OSC recently identified in immature bitumens and crude oils (7-17). A considerable portion of the alkylated thiophenes has a 2-alkyl or 2,5-dialkyl substitution pattern indicating that these thiophenes possess a linear carbon skeleton. OSC with this type of carbon skeleton (*i.e.*, 2,5-dialkylthiophenes, 2,5-dialkylthiolanes, 2,6-dialkylthianes) are often major compounds in sulfur-rich, immature bitumens and crude oils (7,9,10,12,15-17). Three other groups of OSC have been assigned in pyrolysates of kerogens, *i.e.* those with isoprenoid, branched (*iso* and *anteiso*) and steroidal side-chain carbon skeletons (49). The four groups of alkylated thiophenes account for approximately 90% (by weight) of the total amount of alkylated thiophenes formed upon pyrolysis in all samples studied. Since C_1 - C_6 alkylated thiophenes are primarily formed by β -cleavage, they can be ascribed to specific thiophene moieties within the kerogen. Based on the structures of the alkylated thiophenes it is considered that these moieties have mainly linear, branched, isoprenoid and steroidal side-chain carbon skeletons (Figure 5). The observed differences in abundances and isomer distributions of the C_1 - C_6 alkylated thiophenes in different kerogen pyrolysates presumably reflect differences in both relative and absolute abundances of these specific thiophene moieties within the kerogens.

Origin of Sulfur-Containing Moieties. The only difference between thiophene moieties in kerogen and the alkylthiophenes present in immature crude oils and bitumens is that in kerogen they are attached *via* one or more bonds between the alkyl side chain(s) of the thiophene moieties and the kerogen matrix. It is therefore likely that the thiophene moieties present in immature kerogens are formed in an identical way to alkylated thiophenes and other OSC in immature bitumens and crude oils; namely by incorporation of inorganic sulfur species into functionalised lipids (2,8,9,11-18). By reaction with sulfur these lipids may become part of the kerogen structure or may remain as extractable bitumen. The former process may (partially) lead to formation of kerogen.

Less explicit statements can be made concerning the origin of other sulfur-containing moieties (*e.g.*, cyclic and acyclic (poly)sulfide moieties), since the Py-GC-MS method fails to properly characterise these functional groups. However, it is noteworthy that small amounts of alkylthiolanes and -thianes with linear carbon skeletons have been identified in kerogen pyrolysates (48). This suggests the presence of thiolane and thiane moieties in the kerogen

Figure 3. Partial TIC (black dots indicate alkylbenzenes) and accurate (window 0.04 dalton), summed mass chromatograms of m/z 97.03 + 98.03 + 111.04 + 112.04 + 125.06 + 126.06 + 139.08 + 140.08 + 153.10 + 154.10 + 167.11 + 168.11 of flash pyrolysates of several high-molecular-weight fractions of Jurf ed Darawish-156. Peak numbers refer to Table I. Black and stippled peaks indicate alkylthiophenes with linear and isoprenoid carbon skeletons, respectively.

Figure 4. Partial TIC (black dots indicate alkylbenzenes, black squares indicate alkylpyrroles) and accurate (window 0.04 dalton) summed mass chromatograms of m/z 97.03 + 98.03 + 111.04 + 112.04 + 125.06 + 126.06 + 139.08 + 140.08 + 153.10 + 154.10 + 167.11 + 168.11 of flash pyrolysates of several high-molecular-weight fractions of Monterey-25. Peak numbers refer to Table I. Black and stippled peaks indicate alkylthiophenes with linear and isoprenoid carbon skeletons, respectively.

Table I. Major alkylthiophenes identified in pyrolysates of the Jurfed Darawish Oil Shale and Monterey kerogens and asphaltenes^a

compound		possible origin (precursor moieties) ^b
1	2-methylthiophene	L
2	3-methylthiophene	I
3	2-ethylthiophene	L
4	2,5-dimethylthiophene	L
5	2,4-dimethylthiophene	B,S
6	2,3-dimethylthiophene	I,B
7	3,4-dimethylthiophene	S
8	2-propylthiophene	L
9	2-ethyl-5-methylthiophene	L
10	2-ethyl-4-methylthiophene	B
11	2,3,5-trimethylthiophene	I,B
12	2,3,4-trimethylthiophene	S
13	3-isopropyl-2-methylthiophene	S
14	2-methyl-5-propylthiophene and 2,5-diethylthiophene	L L
15	2-butylthiophene	L
16	2-ethyl-3,5-dimethylthiophene and 3-ethyl-2,5-dimethylthiophene	I
17	5-ethyl-2,3-dimethylthiophene and an ethyldimethylthiophene	B
18	an ethyldimethylthiophene	
19	2,3,4,5-tetramethylthiophene	
20	2-ethyl-5-propylthiophene	L
21	2-butyl-5-methylthiophene	L
22	2-pentylthiophene and 2,3-dimethyl-5-propylthiophene	L I,B
23	2-ethyl-3,4,5-trimethylthiophene	
24	2,3-dimethyl-5-isobutylthiophene	I
25	2-methyl-5-pentylthiophene	L
26	2-hexylthiophene	L

^a numbers refer to Figures 3 and 4.

^b L = derived from alkylthiophene moieties with linear alkyl carbon skeletons; B = derived from alkylthiophene moieties with *iso* and *anteiso* alkyl carbon skeletons; I = derived from alkylthiophene moieties with isoprenoid alkyl carbon skeletons; S = derived from alkylthiophene moieties with steroidal side chain carbon skeletons.

matrix. These compounds, however, are believed to mainly yield H_2S upon thermal degradation through cleavage of the carbon-sulfur bond in the ring. A similar origin as proposed for the thiophene moieties in kerogen for these putative thiolane and thiane moieties seems probable. The, not unlikely, formation of acyclic (poly)sulfide moieties in a similar fashion would be an important pathway for the generation of high-molecular-weight material (e.g., kerogen) from low-molecular-weight precursors.

Bonding of Alkylthiophene Units. The presence of acyclic (poly)sulfide moieties in kerogen is further supported by the preferential elimination of alkylthiophene and alkane units from sulfur-rich kerogen (Monterey) upon maturation reported elsewhere in this volume (25). From the structures of the alkylthiophene units in kerogen (Figure 5) it is not easy to understand why these units are preferentially eliminated (as compared with alkylbenzene units) upon maturation since the energy required for cleavage of the C-C bond β to the thiophene and benzene system is approximately the same. Therefore, the attachment of these alkylthiophene units to the kerogen has to be different as compared to that of the alkylbenzene units. Three model structures may be envisaged in an attempt to explain the above observations (Figure 6). Alkylthiophene units linked by a single C-C bond to the macromolecular matrix (model 1, Figure 6a) would generate low-molecular-weight alkylthiophenes upon both flash pyrolysis and maturation, but does not explain the preferential elimination of alkylthiophene units. Alkylthiophene units linked by a single C-S bond to the macromolecular matrix (model 2, Figure 6b) may explain the preferential elimination of alkylthiophene units over alkylbenzene units from sulfur-rich kerogens upon maturation by cleavage of the relatively weak C-S bond. However, this bond is also the most susceptible to cleavage upon flash pyrolysis and low-molecular-weight alkylthiophenes would, therefore, not be major pyrolysis products. This model may explain, however, the occurrence of series of longer-chain alkylthiophenes in pyrolysates of sulfur-rich kerogens (48,49). Alkylthiophene units linked by multiple acyclic C-S bonds to the macromolecular matrix (model 3, Figure 6c) explain both observations; upon flash pyrolysis (high temperature, short reaction time) it is unlikely that multiple, relatively weak, C-S bonds are broken, resulting in the release of higher-molecular-weight alkylthiophenes. Instead, cleavage of the somewhat stronger, but single, C-C bond β to the thiophene unit is more likely and would therefore give rise to low-molecular-weight alkylthiophenes. Upon maturation under natural conditions (relatively low temperature, very long reaction time) the cleavage of the multiple C-S bonds is more likely than cleavage of the C-C bond β to the thiophene unit and this may explain the preferential elimination of thiophene units from

sulfur-rich kerogen upon maturation. It is therefore likely that in sulfur-rich kerogens, such as the Monterey kerogen, alkylthiophene units are mainly bonded by several acyclic sulfur linkages to the kerogen matrix. This model is also consistent with the observation that the abundance of C₁-C₆ alkylated thiophenes in pyrolysates shows a distinct correlation with the total organic sulfur content of kerogens and other geopolymers despite the fact that they represent only a small portion of the total organic sulfur content of the kerogen (24). It is also the most satisfactory way of explaining the extremely high organic sulfur contents of Type II-S kerogens (up to 14%, 19).

Organically-Bound Sulfur in Asphaltenes

Asphaltenes isolated from immature sediments and crude oils yield the same types of sulfur compounds as immature kerogens on flash pyrolysis do; *i.e.* H₂S, thiophene and C₁-C₆ alkylated thiophenes and small amounts of benzothiophene and C₁-C₄ alkylated benzothiophenes. Furthermore, the distributions of the C₁-C₆ alkylated thiophenes are dominated by the same isomers as in the kerogen pyrolysates as illustrated by these distributions in flash pyrolysates of the asphaltene fractions isolated from the bitumens of the Jurf ed Darawish Oil Shale and Monterey Shale described above (Figures 3c and 4c). Moreover, a comparison of the mass chromatograms of the asphaltene pyrolysates with those of the corresponding kerogen pyrolysates (*cf.* Figures 3b and 3c and 4b and 4c, respectively) indicates that similar fingerprints are obtained. For example, compounds 18, 19 and 23 are relatively abundant in both the kerogen as well as the asphaltene pyrolysate of the Jurf ed Darawish Oil Shale. These compounds are much less abundant in the pyrolysates of the corresponding fractions from the Monterey Shale, where compound 13 is more abundant. Minor differences in the distributions of the C₁-C₆ alkylated thiophenes of the corresponding kerogen and asphaltene pyrolysates also occur. In both cases compounds 6 and 11, both derived from thiophene moieties with isoprenoid carbon skeletons, are relatively more abundant in the asphaltene pyrolysates. It is noteworthy within this context that Solli *et al.* (36) noted a general feature of asphaltenes; their pyrolysates contain higher abundances of isoprenoids than their corresponding kerogen pyrolysates.

The structure and origin of the thiophene moieties in asphaltenes is believed to be identical to those in kerogens. Furthermore, the similar C₁-C₆ alkylated thiophene fingerprints of pyrolysates of asphaltenes and kerogen from the same sediments testifies to the concept of asphaltenes as being small "soluble" fragments of kerogen having comparable structures (19,20,34,35,56). Asphaltenes isolated from crude oils do exhibit a small

difference compared to those isolated from bitumens; their pyrolysates contain somewhat more abundant alkylthiophenes with extended alkyl side-chains (*i.e.* $>C_6$). This probably indicates that asphaltenes from crude oils contain relatively higher amounts of "Model 2" (Figure 6) alkylthiophene units.

Organically-Bound Sulfur in Resins

The resin fraction of a crude oil or bitumen is defined as the high-molecular-weight ($MW > ca. 800$) fraction soluble in light hydrocarbons (20). With conventional separation methods for bitumens and crude oils the resins mainly elute in the so-called polar (or NSO or hetero compound) fraction (Figure 1). However, the "aromatic hydrocarbon" fraction of immature bitumens and crude oils may also contain substantial amounts of high-molecular-weight, low volatile (non-GC amenable) substances, especially in sulfur-rich samples. These substances can be separated from lower-molecular-weight aromatic (LMWA) hydrocarbons and OSC by a simple column chromatographic step (Figure 1) since they are somewhat more polar. This yields the so-called "high-molecular-weight aromatic" (HMWA) fraction (12,16). From an analytical point of view resins are easier to characterise than kerogens and asphaltenes since they are completely soluble in the appropriate organic solvents required for chemical degradation.

Jurf ed Darawish-156. Flash pyrolysis of polar fractions of immature bitumens and crude oils generates pyrolysates which differ markedly from those of kerogens and asphaltenes. Whilst pyrolysates of asphaltenes and kerogens are dominated by volatile compounds ($< C_{12}$), pyrolysates of polar fractions comprise a complex, partially unresolved mixture of mainly $C_{15}+$ components. This is illustrated in Figure 2b which shows the TIC from flash pyrolysis ($610^{\circ}C$) of the polar fraction from the extracted bitumen of the Jurf ed Darawish-156 sample. This pyrolysate is not dominated by C_1 - C_6 alkylated thiophenes as are the kerogen (Figure 2a) and asphaltene (not shown) pyrolysates. Another major difference from flash pyrolysates of kerogens and asphaltenes is that similar results are obtained for the polar fraction when wires with a Curie temperature of $358^{\circ}C$ are used (Figure 2c). This indicates that either (i) the polar fraction is comprised of mainly low-molecular-weight compounds ($MW < 800$) which simply evaporate or (ii) that the polar fraction contains mainly high-molecular-weight substances which are thermally much more labile than the kerogens and asphaltenes or (iii) that both phenomena occur.

Some of the major compounds in the $358^{\circ}C$ pyrolysate were identified as series of 2-alkylthiolanes, -thianes, 2,5-dialkylthiolanes and 2,6-dialkylthianes,

all OSC with linear carbon skeletons. Figure 7 shows partial mass chromatograms of m/z 87 and 101 visualizing the distributions of some of these series. All these series are characterised by a strong even-over-odd carbon number predominance with (sub)maxima at C_{18} , C_{28} and/or C_{30} . The m/z 101 mass chromatogram also reveals the presence of saturated and monounsaturated C_{20} isoprenoid thiolanes. Since these compounds have a polarity which results in their presence exclusively in the LMWA fraction upon fractionation of the bitumen with column chromatography (Figure 1), these compounds have to be formed by thermal degradation of resin-like material. Further support for this theory came from the identification of monounsaturated thiolanes and thianes; the presence of a double bond strongly suggesting a pyrolytic origin (*cf.* n -alk-1-enes). On the basis of mass spectra of these compounds it is thought that their double bond positions are not located at the end of the long alkyl side-chain (*cf.* n -alk-1-enes) but in the alkyl side-chain near the ring system. These results indicate that alkylthiolane and -thiane units with linear carbon skeletons are bonded by one (poly)sulfide moiety to the macromolecular matrix of resins. It is unlikely that these units are bound by more than one acyclic (poly)sulfide linkage to the macromolecular matrix since their release would then require the cleavage of more than one bond.

Raney Ni desulfurisation of this polar fraction yields 28 wt.% hydrocarbons dominated by n -alkanes, also with a strong even-over-odd carbon number predominance and with (sub)maxima at C_{18} , C_{28} and C_{30} (Figure 8a, 18). Since Raney Ni reductively cleaves carbon-sulfur bonds selectively, this experiment provides further support for the proposed structure of the resin fraction as mainly consisting of a network of predominantly straight-chain hydrocarbons with relatively high abundances of octadecane, octacosane and triacontane. These units are connected to each other by one or more (poly)sulfide linkages. It is, as yet unknown, whether these linkages in this geopolymer are mainly mono-, di- and/or polysulfide moieties. Kohnen *et al.* (17) have recently shown that OSC with di- and trisulfide groups occur in immature sediments. It is therefore not unlikely that these groups also occur in macromolecules. In addition to the (poly)sulfide linkages connecting the several units to each other, the flash pyrolysis results show that these units themselves consist mainly of linear thiolanes and thianes, which may be considered as intramolecular sulfide linkages. These units are also desulfurised which explains the high amounts of n -alkanes obtained. Desulfurisation of the polar fraction also yields phytane (and very small amounts of pristane) and 22R pentakishomohopane, indicating the presence of these units in these sulfur-rich macromolecules. Raney Ni desulfurisation of the HMWA fraction of the same sample also yields hydrocarbons (43 wt.%) dominated by n -

Figure 7. Partial mass chromatograms of the flash pyrolysate of the polar fraction of the Jurf ed Darawish-156 bitumen. Numbers indicate total number of carbon atoms.

Figure 8. Gas chromatograms of the hydrocarbons obtained by desulfurisation of the polar and HMWA fractions of the Jurf ed Darawish-156 bitumen. Numbers indicate total number of carbon atoms of *n*-alkanes.

alkanes with (sub)maxima at C_{18} , C_{21} and C_{37} (Figure 8b, 18). However, the distribution pattern of the *n*-alkanes obtained by desulfurisation of the polar fraction is completely different, indicating that the resins in the HMWA fraction are structurally different from those present in the polar fraction.

Northern Apennines Marl. Figure 9 shows the partial TIC of the pyrolysates of the polar fraction of the Northern Apennines Marl bitumen by using ferromagnetic wires of both 358 and 610°C. The composition of both pyrolysates is similar but differs markedly from those of the polar fraction of the Jurf ed Darawish-156 bitumen, although the pyrolysates of both samples are dominated by $C_{15}+$ components. The major products identified in both pyrolysates are phytenes and phytane, saturated and monounsaturated C_{20} isoprenoid thiolanes and thiophenes, saturated and monounsaturated, linear C_{22} thiolanes and thianes, Δ^2 - and Δ^3 -cholestenes and cholestane and an, as yet unknown, C_{27} sulfur-containing steroid, tentatively identified as cholestane-3,19-episulfide (7). The generation of these relatively apolar compounds at 358°C again indicates that structurally related units are bonded to the macromolecular matrix of the resin fraction by probably one (poly)sulfide linkage. The pyrolytic origin of these compounds is also further supported by the generation of their unsaturated counterparts.

The selective generation of (poly)sulfide-linked molecules from the resin macromolecules at lower pyrolysis temperatures is exemplified by Figure 10, which shows mass chromatograms of m/z 57 of the 358 and 610°C pyrolysates. At 358°C, phytenes and phytane dominate this mass chromatogram, whilst at 610°C in addition to the phytenes and phytane a series of *n*-alkanes and isoprenoid alkanes (C_{12} - C_{18}) and prist-1-ene are observed. These latter compounds are probably formed mainly by other cleavages than those of carbon-sulfur bonds. The higher amounts of phytane relative to the phytenes in the 610°C pyrolysate is also notable. The ratio cholestane/cholestenes also increased in the 610°C pyrolysate; this probably indicates that a change in the composition of the products from carbon-sulfur bond cleavage occurs with increasing pyrolysis temperature.

Apart from phytanyl moieties bound by a (poly)sulfide linkage to the macromolecular matrix such phytanyl moieties also occur with an additional intramolecular sulfide linkage. A mass chromatogram of m/z 101 of the 358°C pyrolysate (Figure 11b) shows the presence of a C_{20} isoprenoid thiolane and its monounsaturated counterparts which are major pyrolysis products. C_{20} isoprenoid thiophenes also occur in the pyrolysates but are less abundant.

Units consisting of linear carbon skeletons occur less abundantly in the resins of the Northern Apennines Marl bitumen than in those of the Jurf ed Darawish-156 bitumen. Mass chromatograms of m/z 87 and 101 (Figure 11)

Figure 9. Partial total ion chromatograms of the flash pyrolysates (358 and 610°C) of the polar fraction of the Northern Apennines Marl bitumen.

Figure 10. Mass chromatograms of m/z 57 of the flash pyrolysates (358 and 610°C) of the polar fraction of the Northern Apennines Marl bitumen.

Figure 11. Partial mass chromatograms of the flash pyrolysate of the polar fraction of the Northern Apennines Marl bitumen. Numbers indicate total number of carbon atoms.

reveal the presence of a series of 2-alkylthiolanes and -thianes and 2-alkyl-5-methylthiolanes and unsaturated counterparts highly dominated by C₂₂ members.

The dominance of Δ^2 - and, tentatively identified, Δ^3 -cholestenes and 5 α (H),14 α (H),17 α (H),20R-cholestane in the 358°C pyrolysate (Figure 9a) indicates that relatively high amounts of cholestanyl units bound by a (poly)sulfide linkage to the macromolecular matrix occur in the Northern Apennines Marl resins. These (poly)sulfide linkages are probably connected to position 3 of the cholestane units since high amounts of Δ^2 - and, less stable (57), Δ^3 -cholestenes are formed upon pyrolysis. This is consistent with the work of Schmid (7) who reported that steroid units in a high-molecular-weight fraction of the Rozel Point seep oil were bonded *via* sulfur bridges at position 3 of the steroid units because of the formation of 3-thiosteroids upon heating (200°C, 48h) of this fraction and by treating it with LiAlH₄. Furthermore, desulfurisation of this fraction with deuterated Raney Ni yielded steranes which had incorporated one deuterium atom in the A-ring (58).

The flash pyrolysis results are in full agreement with those obtained by sulfur-selective chemical degradation of this resin fraction. Raney Ni desulfurisation of this fraction yielded saturated and aromatic hydrocarbons (11 wt.%) dominated by phytane, docosane, 5 β (H),14 α (H),17 α (H),20R-cholestane, 17 α (H),21 β (H),22R-pentakishomohopane and β -carotane (Figure 12a). A mass chromatogram of *m/z* 57 (Figure 11b) shows the distribution of the *n*-alkanes with a strong even-over-odd carbon number predominance and with (sub)-maxima at C₁₈, C₂₂, C₂₈ and C₃₇ and the strong dominance of phytane over pristane. A partial mass chromatogram of *m/z* 113 (inset in Figure 12b) reveals the presence of a number of C₂₅-C₂₇ isoprenoid hydrocarbons with the indicated carbon skeletons. Alkylthiophenes with these carbon skeletons occur in the LMWA fraction of the Northern Apennines Marl bitumen (59), but the ratio of the various isomers is different. A mass chromatogram of *m/z* 217 (Figure 13a) shows the distribution of the steranes formed by desulfurisation, which are dominated by 5 β (H),14 α (H),17 α (H),20R-steranes. The reason for this is not completely understood since flash pyrolysis yielded predominantly 5 α (H),14 α (H),17 α (H),20R-cholestane. Desulfurisation of polar fractions of other samples yielded steranes which were not dominated by 5 β (H),14 α (H),17 α (H),20R-stereoisomers(60,61). The *m/z* 191 mass chromatogram (Figure 13b) reveals the exclusive presence of C₃₅ extended hopanes. Besides β -carotane several other, tentatively identified, mono- and diaromatic carotenoids are also present in the desulfurised polar fraction as revealed by the partial mass chromatogram of *m/z* 134 (Figure 13c). The diaromatic carotenoids have been reported to occur as such in bitumens of Toarcian shales (62) and are thought to be derived from the highly unsaturated

Figure 12. Total ion chromatogram (a) and m/z 57 mass chromatogram (b) of the hydrocarbons obtained upon desulfurisation of the polar fraction of the Northern Apennines Marl bitumen. Numbers indicate total number of carbon atoms of n -alkanes. The inset in Figure 12b shows a partial mass chromatogram of m/z 113.

Figure 13. Partial mass chromatograms of (a) m/z 217, (b) m/z 191 and (c) m/z 134 of the desulfurised polar fraction of the Northern Apennines Marl bitumen.

carotenoids renieratene, isorenieratene and renierapurpurin, which occur in photosynthetic bacteria and marine sponges (63,64) or their symbiotic bacteria (65,66).

In summary, Raney Ni desulfurisation of the polar fraction of the Northern Apennines Marl further supports the presence of (poly)sulfide-linked phytanyl, docosanyl and cholestanyl moieties (some of them with additional intramolecular sulfur linkages) in the resin fraction as proposed from the pyrolysis experiments. In addition, a number of other structural units are revealed; *e.g.* pentakishomohopane, carotenoids, *n*-alkanes and isoprenoid alkanes. The reason why these structural units are not revealed by the pyrolysis experiments may be: (i) their much lower relative abundance (*e.g.*, other *n*-alkanes and isoprenoid alkanes), (ii) their attachment in the macromolecules by more than one (poly)sulfide linkage, which make their release from the macromolecule by flash pyrolysis unlikely (*e.g.*, pentakishomohopane, carotenoids). The latter explanation is strongly supported by Mycke *et al.* (58). These authors reported that upon desulfurisation with deuterated Raney Ni of a high-molecular-weight fraction of the Rozel Point seep oil C₃₅ hopanes were formed with up to four deuterium atoms in the side-chain. This indicates that C₃₅ hopane units (probably originating from bacteriohopanetetrol) are bonded in sulfur-rich macromolecules *via* up to four sulfur bridges.

Origin of Sulfur-Rich Resins. The resin fractions of the examined bitumens comprise macromolecules which contain specific units linked by (poly)sulfide bridges to the macromolecular matrix. These units possess carbon skeletons identical to the well-known geologically occurring hydrocarbons (*i.e.*, *n*-alkanes, isoprenoid alkanes, steranes, hopanes). These units also contain intramolecular sulfur linkages and may therefore be considered as macromolecularly-bound OSC. The structures of these OSC (alkylthiolanes, thianes and -thiophenes) are identical to those occurring in GC-amenable fractions of immature bitumens and crude oils (2-16). Since low-molecular-weight OSC are formed by incorporation of inorganic sulfur species into specific functionalised lipids during early diagenesis (2,8,9,11-18) a similar origin is likely for the sulfur cross-linked geopolymer. Instead of incorporation of inorganic sulfur species into functionalised lipids in an intramolecular fashion, leading to the formation of low-molecular-weight OSC (15), these reactions also occur on an intermolecular basis giving rise to the sulfur cross-linked geopolymer. The formation of these sulfur-rich high-molecular-weight substances during early diagenesis by inter- and intramolecular sulfur cross-linking of functionalised lipids is supported by several observations from the present study.

Firstly, the composition of both the flash pyrolysates and the desulfurisation mixtures obtained from the resin fractions described here and elsewhere (60,61) indicate that specific functionalised lipids react with H_2S and/or polysulfides, yielding sulfur-rich high-molecular-weight substances. All three mixtures of hydrocarbons obtained after desulfurisation of resin fractions show a strong even-over-odd carbon number predominance for the *n*-alkanes, a very low pristane/phytane ratio and a hopane distribution dominated by the C_{35} homologue. This is interpreted as reflecting the reaction of *n*-alcohols, chlorophyll-derived phytenes and bacteriohopanetetrol, respectively, with inorganic sulfur species during the early stages of diagenesis. These compounds would otherwise be mainly mineralised or diagenetically transformed to other compounds (e.g., hydrocarbons). The relative abundance of bound C_{22} linear alkylthiolanes and -thianes in the resin fraction of the Northern Apennines Marl bitumen may be ascribed to a high abundance of docosaheanoic acid and/or docosaheanol during deposition of this sediment. The presence of sulfur-bound carotenoids in the resin fraction also has to be explained by incorporation of labile carotenoids such as β -carotene and the aromatic carotenoids renieratene, isorenieratene and/or renierapurpurin into high-molecular-weight material by reactions with inorganic sulfur species during early diagenesis. It is not known at present whether these bound aromatic carotenoids also contain intramolecular sulfur linkages. Thermal maturation of such thiophene-containing units in sulfur-rich macromolecules may explain the distribution patterns of the C_{13} - C_{31} aryl isoprenoids identified in bitumen and oils (67,68). The relative abundance of the C_{37} and, to a lesser extent, C_{38} *n*-alkanes in the desulfurisation products of the Northern Apennines Marl and Jurf ed Darawish-156 polar fractions and, especially, of the HMWA fraction of the Jurf ed Darawish-156 is probably due to reaction with inorganic sulfur species of C_{37} and C_{38} unsaturated ketones or their corresponding alkadienes and alkatrienes present in sediments (69-77).

Secondly, in the case of the bound steroids it was possible to locate the position of the (poly)sulfide linkages in these structural units; *i.e.* mainly at position 3 of the steroid units. This strongly supports the argument that functionalised lipids are incorporated into these macromolecules by reaction of H_2S and/or polysulfides with functionalities, since sterols or corresponding sterenes are the only likely precursors for the steroid units in these macromolecules.

Other sulfur-selective chemical degradation techniques (work in progress) will probably yield additional information to further resolve remaining questions with respect to structure, origin and thermal behaviour of these sulfur-rich geopolymers.

Relationship between Molecular Weight and Organic Sulfur in Sulfur-Rich Sedimentary Organic Matter

Based on both our analyses of the different sulfur-rich high-molecular-weight fractions and on previous observations from studies on low-molecular-weight OSC (1-17) we propose that there is a direct relationship between the type (and degree) of sulfur cross-linking and molecular weight for sulfur-rich sedimentary organic matter (Figure 14). The zonations in this simplified diagram are somewhat arbitrary, however, the chemical and physical properties of the various organic matter fractions and their interrelationships may, at least partially, be explained in this general framework.

Sulfur is incorporated into sedimentary organic matter during early diagenesis through reaction of functionalised lipids with inorganic sulfur species. The extent to which intra- *versus* intermolecular sulfur cross-linking occurs determines the molecular weight of the formed products and, thus, the relative proportions of low-molecular-weight OSC ($MW < 800$), sulfur-rich resins, asphaltenes and kerogen. To give an indication of the type of cross-linking involved the positions of the three models proposed for the bonding of alkylthiophene units (Figure 6) are plotted along the X-axis. In kerogen relatively abundant intermolecular sulfur cross-links are thought to be present (*cf.* Model 3) and kerogen, therefore, plots in the upper-right corner of the diagram. Low-molecular-weight OSC (*cf.* Model 1) contain only intramolecular sulfur linkages and plot, consequently, in the lower-left corner of the diagram. Asphaltenes and resins may be seen as intermediates in this respect. In this context the differences in solubility between the different fractions may be explained by the extent of sulfur cross-linking.

Maturation will give rise to cleavage of relatively weak C-S and S-S bonds and to aromatisation of thiolane moieties (which contain cyclic, intramolecular sulfide linkages). The latter reaction achieves conversion of a thermally labile to a more stable form of organic sulfur. This conversion can only happen with intramolecular sulfur linkages. The result of both aforementioned reactions is a shift of the composition of the sulfur-containing substances from the upper-right corner to the lower-left corner of the diagram. A concomitant loss of organic sulfur will occur also during maturation.

Conclusions

- (1) Immature kerogens and asphaltenes contain thiophene units in their macromolecular structure, which have mainly linear, isoprenoid, branched and steroidal side-chain skeletons. These units and possibly other sulfur-

Figure 14. Relationship between the degree of intermolecular *versus* intramolecular sulfur cross-linking and molecular weight for sulfur-rich sedimentary organic matter.

containing moieties, such as cyclic and acyclic (poly)sulfide moieties, are formed by incorporation of inorganic sulfur species into functionalised lipids during early diagenesis. In depositional environments with high amounts of available sulfur donors these reactions may be regarded as an important pathway for the generation of high-molecular-weight material ("natural vulcanisation"). The fact that sulfur-containing moieties in asphaltenes are similar to those in kerogen supports the concept of asphaltenes as being small "soluble" fragments of kerogen having comparable structures.

- (2) The resin fractions of organic sulfur-rich bitumens are for a substantial part composed of monomers with linear, isoprenoid, steroid, hopanoid and carotenoid carbon skeletons connected to each other by (poly)sulfide linkages. These structural units may contain additional intramolecular sulfur linkages. This sulfur-rich geopolymer is also formed by sulfur incorporation into functionalised lipids in an intermolecular fashion during early diagenesis.
- (3) The formation of sulfur-rich macromolecules is, therefore, analogous to the formation of low-molecular-weight OSC in immature sediments, which are formed by similar reactions but in an intramolecular fashion.
- (4) The different properties of sulfur-rich kerogen and asphaltenes, on the one hand, and sulfur-rich resins on the other hand (*e.g.*, differences in solubility and flash pyrolysis behaviour) may be explained only by differences in degree of (sulfur) cross-linking and thus by differences in molecular size and in degree of condensation.
- (5) Raney Ni desulfurisation of resins may be used in fingerprinting oils and bitumens since certain so-called biomarkers may be selectively incorporated (and preserved) in the resins (*e.g.*, carotenoids, unsaturated C₃₇ and C₃₈ ketones or alkenes). This may provide additional information on the palaeoenvironment of deposition as well as on the structure of these complex materials.

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