



Artificial maturation of an immature sulfur- and organic matter-rich limestone from the Ghareb Formation, Jordan

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Abstract—An immature ($R_o=0.39\%$), S-rich ($S_{org}/C = 0.07$), organic matter-rich (19.6 wt.% TOC) limestone from the Ghareb Formation (Upper Cretaceous) in Jordan was artificially matured by hydrous pyrolysis (200, 220, ..., 300°C; 72 h) to study the effect of progressive diagenesis and early catagenesis on the amounts and distributions of hydrocarbons, organic sulfur compounds and S-rich geomacromolecules. The use of internal standards allowed the determination of absolute amounts. With increasing thermal maturation, large amounts of alkanes and alkylthiophenes with predominantly linear carbon skeletons are generated from the kerogen. The alkylthiophene isomer distributions do not change significantly with increasing thermal maturation, indicating the applicability of alkylthiophenes as biomarkers at relatively high levels of thermal maturity. For a given carbon skeleton, the saturated hydrocarbon, alkylthiophenes and alkylbenzo[b]thiophenes are stable forms at relatively high temperatures, whereas the alkylsulfides are not stable. The large amount of alkylthiophenes produced relative to the alkanes may be explained by the large number of monosulfide links per carbon skeleton. These results are in good agreement with those obtained previously for an artificial maturation series of an immature S-rich sample from the Gessoso-solfifera Formation. © 1998 Elsevier Science Ltd. All rights reserved

Key words—Ghareb formation, hydrous pyrolysis, biomarkers, organic sulfur compounds, alkylthiophenes, alkylbenzo[b]thiophenes

INTRODUCTION

Geochemical research on organic sulfur compounds (OSC) has evolved from the identification of numerous series of new compounds (for a review see Sinninghe Damsté and de Leeuw, 1990) to the application of OSC as indicators of biological, chemical and physical conditions of past depositional environments (e.g. Sinninghe Damsté *et al.*, 1989d, 1990b; Kohnen *et al.*, 1990b; Kenig *et al.*, 1995). This biomarker concept is based on the observation that sulfurization of lipids occurs at functionalized sites (e.g. Valisolalao *et al.*, 1984; Brassell *et al.*, 1986), as confirmed by laboratory sulfurization experiments (e.g. Fukushima *et al.*, 1992; de Graaf *et al.*, 1992, 1995; Rowland *et al.*, 1993; Schouten *et al.*, 1993, 1994; Krein and Aizenshtat, 1994). Thus, the position of the S atom in an OSC reveals information about the position of the functional group of the precursor molecule.

Most of the OSC work has focused on thermally immature sedimentary rocks ($R_o \leq 0.3\%$) and “early

mature” crude oils. There are three reasons to expand the study of OSC and S-rich geomacromolecules to thermally more mature samples. First, alkylthiophenes with known biochemical precursors can be followed in a maturation series to see if they retain their palaeoenvironmental information. Second, the importance of S-bound carbon skeletons in the early generation of crude oil can be evaluated. Third, the generation of alkylbenzo[b]thiophenes and alkyldibenzothiophenes, important components of natural crude oils whose formation pathways are poorly understood (Sinninghe Damsté *et al.*, 1989a; Aizenshtat *et al.*, 1995), can be monitored.

Recently, this approach was followed in an artificial maturation study of an immature S-rich marl from the Gessoso-solfifera Formation (Messinian) in the Vena del Gesso Basin, Italy. Throughout a maturity interval representing the diagenetic stage, the isomer distribution of the alkylthiophenes remained essentially constant so that important palaeoenvironmental information could still be extracted (Koopmans *et al.*, 1995). S-bound phytane and steranes were thermally released as free hydrocarbons before significant C–C bond cleavage

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occurred, indicating the importance of S-bound carbon skeletons in the early generation of specific carbon skeletons (Koopmans *et al.*, 1996).

The aim of this work was to study the amounts and distributions of hydrocarbons, OSC and S-rich geomacromolecules in an artificial maturation series of a sample from the Ghareb Formation (Upper Cretaceous) at El Lajjun, Jordan. This sample contains more complex distributions of OSC than the sample from the Gessoso-solfifera Formation studied previously, and may therefore provide additional insights in the fate of organically-bound sulfur during diagenesis and catagenesis. The Ghareb Formation at El Lajjun is stratigraphically equivalent to the Lower Member of the Jurf ed Darawish oil shale. A sample from the latter (JED-156) has been the subject of many detailed molecular organic geochemical investigations (Sinninghe Damsté *et al.*, 1988b, 1989b,c,d, 1990a, 1995a; Kohnen *et al.*, 1990b; Hofmann *et al.*, 1992; Schouten *et al.*, 1995).

EXPERIMENTAL

Sample description

The sample used in this study is a limestone from the Ghareb Formation (Upper Cretaceous) at El Lajjun, Jordan. The sample has a TOC content of 19.6 wt.% with immature organic matter ($R_o = 0.39\%$). Elemental analysis of the isolated kerogen indicates it is an immature Type II-S kerogen with an atomic H/C ratio of 1.38, an atomic O/C ratio of 0.07, and an atomic S_{org}/C ratio of 0.07.

Hydrous pyrolysis

A detailed description of the experimental procedures of a typical hydrous pyrolysis experiment has been given by Lewan (1993). A one-liter Hastelloy-C276 reactor was filled with 300 g of rock chips and 350 g of distilled water. The remaining volume was purged and filled with helium at a pressure of 2.4 bar. In six different experiments, rock chips were heated isothermally for 72 h at 200, 220, 240, 260, 280 and 300°C, respectively. The temperatures were continuously monitored during the experiments at 30 s intervals. Standard deviations were between ± 0.1 and $\pm 0.4^\circ\text{C}$ for all experiments. Experiments at 280 and 300°C generated an expelled oil that was recovered from the water surface with a pipette. The reactor walls and the rock chips were rinsed with benzene to recover any sorbed oil films, which occurred in experiments at 260, 280 and 300°C. The residual rock chips were dried in a vacuum oven ($T \leq 50^\circ\text{C}$).

Extraction, fractionation and kerogen preparation

An aliquot (*ca.* 10 g) of the residual rock chips was freeze-dried, ground in a rotary disc mill and Soxhlet extracted with dichloromethane/methanol

(7.5:1 v/v). If a sorbed or expelled oil had been present, proportional amounts were combined with the extract. Details of the fractionation procedure have been given elsewhere (Koopmans *et al.*, 1996). The amounts of asphaltenes and of the apolar and polar fractions were determined gravimetrically. Separation of the apolar fraction by argentatious thin-layer chromatography yielded the A1 fraction (saturated hydrocarbons; $R_f = 0.9-1.0$), the A2 fraction (alkylthiophenes; $R_f = 0.4-0.9$), the A3 fraction (bi-, di-, benzo[*b*]- and dibenzothiophenes; $R_f = 0.05-0.4$), and the A4 fraction (alkylsulfides; $R_f = 0.0-0.05$). The extracted rock residue of the unheated sample was demineralized using standard procedures (Lewan *et al.*, 1986) to yield the isolated kerogen for elemental analysis.

LiAlH_4 reduction of alkylsulfoxides

A known amount (20–40 mg) of the polar fraction, to which a known amount of an internal standard [2,3-dimethyl-5-(1',1'-d₂-hexadecyl)thiophene] was added, was treated with LiAlH_4 to reduce alkylsulfoxides to alkylsulfides (Payzant *et al.*, 1983; Schouten *et al.*, 1995). The reaction mixture was chromatographed on Al_2O_3 into an alkylsulfide fraction and a residual polar fraction by consecutive elution with hexane/dichloromethane (9:1 v/v) and dichloromethane/methanol (1:1 v/v).

Raney Ni degradation

The A2, A3, A4 fractions, and the alkylsulfide and residual polar fractions, obtained after reduction of the polar fraction, were desulfurized with Raney Ni as described by Koopmans *et al.* (1996).

Ni_2B degradation

Asphaltene fractions were desulfurized with Ni_2B , which is more efficient in desulfurising geomacromolecules than Raney Ni (Schouten *et al.*, 1993; Hefter *et al.*, 1995). Before desulfurization, a known amount of an internal standard [2,3-dimethyl-5-(1',1'-d₂-hexadecyl)thiophene] was added to a known amount (*ca.* 40 mg) of asphaltene fraction. After the addition of 3 ml of a tetrahydrofuran/methanol (1:1 v/v) mixture, desulfurization was accomplished by adding 50 mg of NiCl_2 and 50 mg of NaBH_4 . The mixture was allowed to reflux for 1.5 h. A sodium chloride solution was added, and the reaction mixture was extensively extracted with dichloromethane. Column chromatography using Al_2O_3 yielded the released hydrocarbons (hexane/dichloromethane 9:1 v/v).

Hi/ LiAlH_4 degradation

The unheated sample and the sample heated at 260°C were analyzed for ether-bound carbon skeletons as described previously (Koopmans *et al.*, 1996).

MeLi/MeI degradation

The unheated sample was analyzed for polysulfide-bound carbon skeletons as described previously (Koopmans *et al.*, 1996).

Gas chromatography

Gas chromatography (GC) was performed using a Hewlett–Packard 5890 instrument equipped with an on-column injector. GC conditions were as described before (Koopmans *et al.*, 1996).

Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry (GC-MS) was carried out on a Hewlett–Packard 5890 gas chromatograph interfaced to a VG Autospec Ultima mass spectrometer. GC-MS conditions were as described before (Koopmans *et al.*, 1996).

Quantitation

Compounds in the A1 fraction and the desulfurized A2, A4, reduced alkylsulfoxide, residual polar, and asphaltene fractions were quantified by integration of mass chromatograms of their main fragment ion and the main fragment ion of the standard, 6,6-d₂-3-methylhenicosane. Compounds in the desulfurized A3 fraction were quantified by integration of mass chromatograms of their main fragment ion and the main fragment ion of the

standard, 2-methyl-2-(4,8,12-trimethyltridecyl)chroman. A correction was made to account for the intensity of the fragment ions relative to the total ion current. Because mass spectrometric detection of compounds gives a molar response, a factor was introduced taking into account the molecular weights of the compounds quantified and the standard to obtain absolute amounts ($\mu\text{g/g}$ TOC of unheated rock).

RESULTS

The amounts of asphaltene, polar and apolar fractions as a function of hydrous pyrolysis temperature are shown in Fig. 1. With increasing maturation temperature, the amount of extractable organic matter increases significantly to 82% of total organic matter at 300°C, implying that a large part of the insoluble organic matter (kerogen) in the unheated sample has been transformed into soluble compounds. The relative amounts of the polar and apolar fractions increase at high temperature, whereas the relative amount of asphaltenes stabilizes. This suggests that the asphaltenes are thermally degraded.

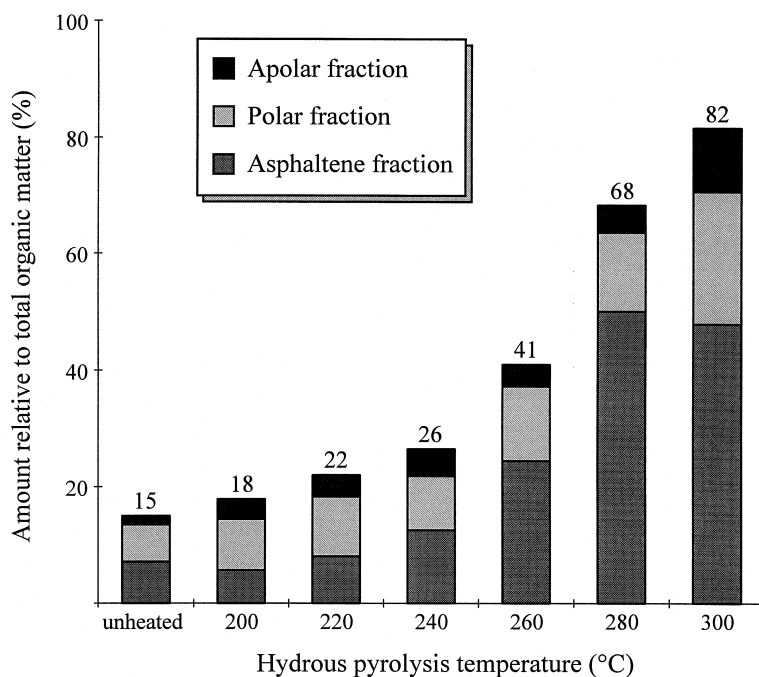


Fig. 1. Bar diagram showing the relative amounts of asphaltene, polar and apolar fractions (expressed as a percentage of total organic matter of the unheated sample) as a function of hydrous pyrolysis temperature. Numbers indicate the summed relative amount of the three fractions, and equal the percentage of extractable organic matter

Table 1. Absolute amounts ($\mu\text{g/g}$ TOC of unheated rock) of selected compounds in the A1 fraction of the unheated sample and the artificially matured samples. Also indicated are the Pr/Ph ratio, the CPI and the $S/(S + R)$ - $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane ratio. Roman numbers refer to structures in Appendix A

	unheated	200°C	220°C	240°C	260°C	280°C	300°C
<i>n</i> - C_{18}	29	33	44	39	110	220	420
<i>n</i> - C_{28}	49	46	48	67	110	180	330
<i>n</i> - C_{38}	3	2	2	3	5	9	14
9-methyloctadecane	0	0	1	1	3	8	15
Pr	19	16	18	13	84	250	590
Ph	66	61	59	43	130	240	400
HBI C_{25}	2	2	2	2	5	12	19
(20 <i>R</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane	20	44	51	86	240	340	160
(20 <i>S</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane	1	4	4	7	43	150	160
$5\alpha,14\beta$ C_{21} sterane (I)	0	2	2	4	19	46	100
$17\alpha,21\beta(\text{H})$ C_{35} hopanes	4	6	7	12	28	56	61
$13\alpha(\text{H}),14\beta(\text{H})$ C_{20} tricyclic terpane (III)	0	2	2	3	14	41	63
Gammacerane (II)	3	17	24	36	110	200	180
Pr/Ph	0.3	0.3	0.3	0.3	0.6	1.0	1.5
CPI	1.7	1.7	1.6	1.4	1.2	1.1	1.0
$S/(S + R)$ - $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane	0.03	0.08	0.07	0.08	0.15	0.31	0.50

Apolar fraction

A1 fraction. Absolute amounts of selected saturated hydrocarbons in the A1 fraction of the unheated sample and the artificially matured samples are given in Table 1.

In the unheated sample, the *n*-alkane distribution maximizes at C_{29} (Fig. 2(a)). The long-chain *n*-alkanes have a moderate odd-over-even carbon number predominance ($\text{CPI}_{24-34} = 1.7$; Bray and Evans, 1961). With increasing thermal maturation the CPI decreases until it is 1.0 at 300°C, due to the production of *n*-alkanes (Table 1). Short-chain *n*-alkanes are produced in larger amounts than long-chain *n*-alkanes, and at 300°C the *n*-alkanes maximize at C_{16} (Fig. 3(a)).

Isoprenoids are the most abundant branched alkanes in the unheated sample (Fig. 2(a)). In addition, small amounts of 2,6,10,14-tetramethyl-7-(3-methylpentyl)pentadecane (HBI C_{25}) and lycopane are present. With increasing thermal maturation, large amounts of these isoprenoids are generated (Table 1). The Pr/Ph ratio, which is 0.3 in the unheated sample, increases to 1.5 at 300°C (Fig. 3(a)).

The sterane distribution in the unheated sample consists mainly of (20*R*)- $5\alpha,14\alpha,17\alpha(\text{H})$ and (20*R*)- and (20*S*)- $5\alpha,14\beta,17\beta(\text{H})$ C_{27} - C_{29} steranes, with small amounts of (20*R*)- $5\beta,14\alpha,17\alpha(\text{H})$ C_{27} - C_{29} steranes and short-chain (C_{21} - C_{23}) steranes (Fig. 4(a)). The (20*R*)- $5\alpha,14\alpha,17\alpha(\text{H})$ steranes are dominated by the C_{27} and C_{29} members (Table 2). The (20*R*)- and (20*S*)- $5\alpha,14\beta,17\beta(\text{H})$ steranes, however, are dominated by the C_{28} member, suggesting an input into the sediment of Δ^7 C_{28} sterols, since Δ^7 sterols are known to be transformed into (20*R*)- and (20*S*)- $5\alpha,14\beta,17\beta(\text{H})$ steranes during relatively early stages of diagenesis (ten Haven *et al.*, 1986; Peakman *et al.*, 1989). With increasing thermal maturation the sterane distribution remains largely unchanged, but at 300°C it has become much more complex with

higher relative amounts of (20*S*)- $5\alpha,14\alpha,17\alpha(\text{H})$ steranes, (20*R*)- and (20*S*)- $5\alpha,14\beta,17\beta(\text{H})$ steranes, and short-chain steranes (Fig. 4). The increased absolute amount of the $5\alpha,14\beta$ C_{21} sterane (I) at 300°C (Table 1) is interesting in the light of the decreased amount of (20*R*)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane. Sterane generation profiles similar to that found in this study have been reported for other artificial maturation series (Eglinton and Douglas, 1988; Koopmans *et al.*, 1996).

The $20S/(20S + 20R)$ - $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane ratio increases from 0.03 in the unheated sample to 0.50 at 300°C (Table 1); this increase has been ascribed to isomerization of the chiral center at C-20 (e.g. Mackenzie *et al.*, 1980). We have determined absolute amounts of the individual isomers (Table 1), so that the presumed isomerization at C-20 can be tested. In the unheated sample, the biological (20*R*)-isomer is much more abundant than the (20*S*)-isomer, hence the low $20S/(20S + 20R)$ -ratio. Up to 280°C, both isomers are generated from the kerogen in comparable amounts, so that the $20S/(20S + 20R)$ -ratio increases. At 300°C the absolute amount of the (20*R*)-isomer decreases dramatically whereas the (20*S*)-isomer increases slightly, so that the $20S/(20S + 20R)$ -ratio increases further and approaches its equilibrium value. Thus, these generation profiles do not show any indication for direct conversion of free (20*R*)- into (20*S*)-isomers. Similar results have been reported for natural (Bishop and Abbott, 1993) and artificial (Abbott *et al.*, 1990) maturation series.

The carbon number distribution and speciation of the homohopanooids has been discussed in detail elsewhere (Köster *et al.*, 1997). Briefly, in the unheated sample the C_{27} to C_{35} hopanes are dominated by $17\alpha,21\beta(\text{H})$ isomers, with small amounts of $17\beta,21\alpha(\text{H})$ isomers (Fig. 5(a)). The C_{30} and C_{31} members are the most abundant. With increasing

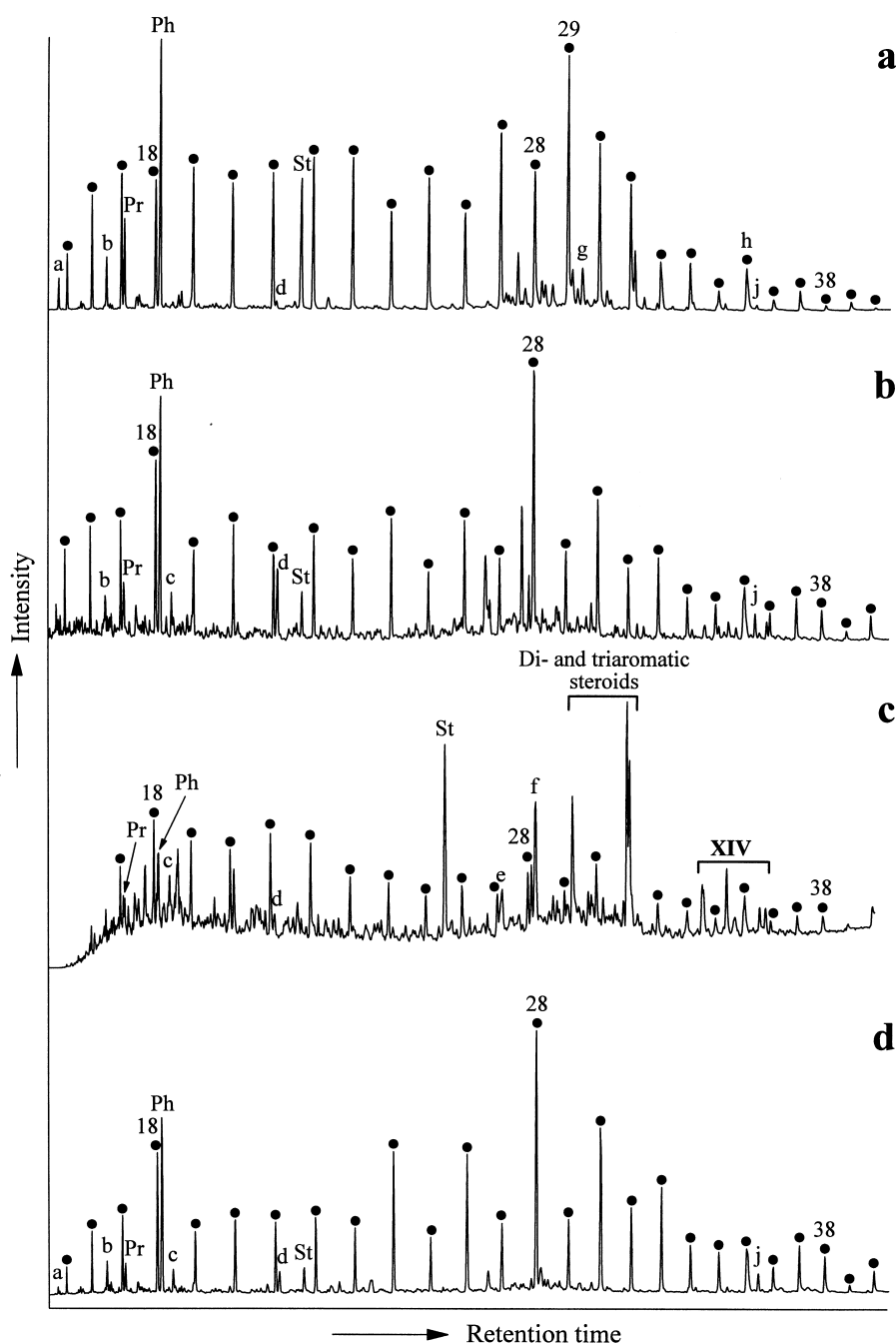


Fig. 2. Total ion current (TIC) of (a) the A1 fraction and the desulfurized (b) A2, (c) A3 and (d) A4 fractions of the unheated sample. Key: dots = *n*-alkanes (numbers indicate number of carbon atoms), Pr = pristane, Ph = phytane, St = standard, a = 2,6,10-trimethyltridecane, b = nor-pristane, c = 9-methyloctadecane, d = HBI C₂₅, e = 2,5,8-trimethyl-2-(4,8,12-trimethyltridecyl)chroman (**XIIIb**), f = 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman (**XIIIc**), g = (20*R*)-5 α ,14 α ,17 α (H) C₂₉ sterane, h = lycopane, j = (22*R*)-17 α ,21 β (H) C₃₅ hopane. Roman numbers refer to structures in Appendix A.

thermal maturation, the C₂₉ member becomes more abundant, and the 22*S*/(22*S* + 22*R*)-17 α ,21 β (H) ratios of the extended hopanes approach their equilibrium values (approximately 0.6; Mackenzie *et al.*,

1980; Mackenzie, 1984) (Fig. 5). At 300°C the summed amount of the (22*S*)- and (22*R*)-17 α ,21 β (H) C₃₅ hopanes still increases, suggesting that hopanes are more resistant to thermal

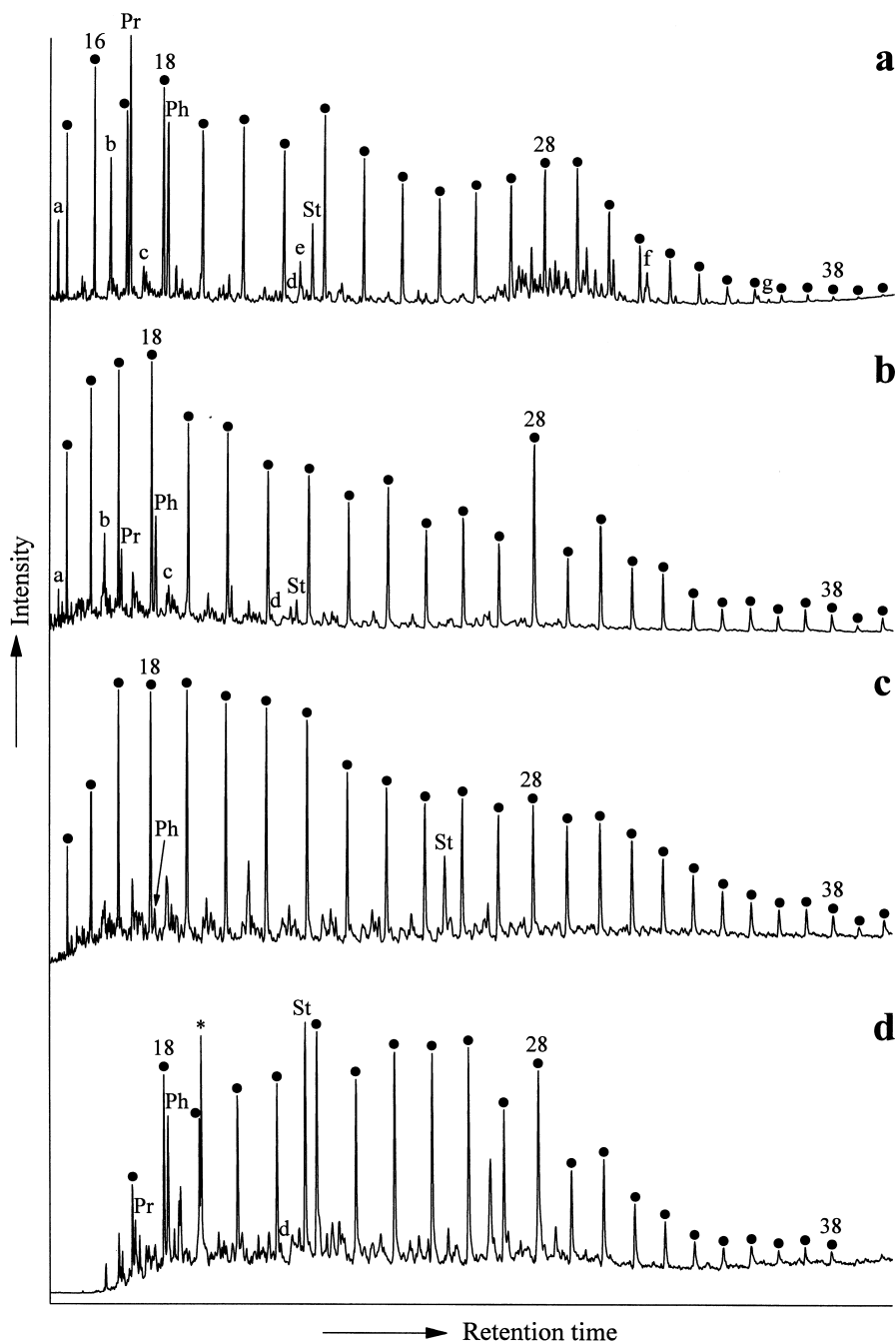


Fig. 3. TIC of (a) the A1 fraction and the desulfurized (b) A2, (c) A3 and (d) A4 fractions of the sample heated at 300°C. Key: dots = *n*-alkanes (numbers indicate number of carbon atoms), Pr = pristane, Ph = phytane, St = standard, a = 2,6,10-trimethyltridecane, b = nor-pristane, c = 9-methyloctadecane, d = HBI C₂₅, e = pregnane (I), f = gammacerane (II), g = (22*R*)-17 α ,21 β (H) C₃₅ hopane, * = contaminant

degradation than steranes (Table 1), in accordance with other studies (Eglinton and Douglas, 1988; Koopmans *et al.*, 1996).

Gammacerane (II), which is present in low abundance in the unheated sample, is formed in large

amounts on increased heating (Table 1). At 260°C it is the most abundant triterpane in the *m/z* 191 mass chromatogram (Fig. 5(c)). The formation of free gammacerane in this maturation series is probably governed by an early diagenetic sulfuri-

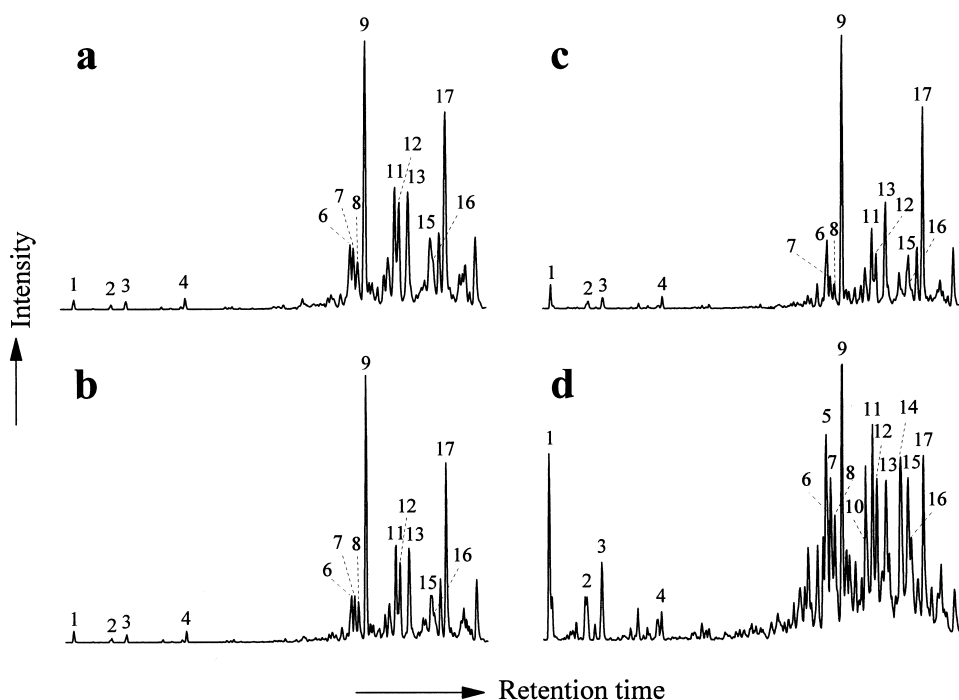


Fig. 4. Partial summed m/z 217 + 218 + 231 + 232 mass chromatogram of the A1 fraction of (a) the unheated sample, and the samples artificially matured at (b) 200°C, (c) 260°C and (d) 300°C. Identification of numbered compounds is given in Table 2

zation/desulfurization pathway of tetrahymanol, as described by Sinninghe Damsté *et al.* (1995b).

A suite of tri- and tetracyclic terpanes is formed during hydrous pyrolysis (Fig. 5). The $13\alpha(\text{H}),14\beta(\text{H})$ C_{20} component (**III**), identified by comparison of its mass spectrum and relative retention time with literature data (Chicarelli *et al.*, 1988), is the most abundant. Its amount increases more sharply than that of the $17\alpha,21\beta(\text{H})$ C_{35} hopanes (Table 1). A relative increase of tricyclic

terpanes compared to hopanes with increasing thermal maturation has been observed in heating experiments with immature sedimentary rocks and crude oils (Peters *et al.*, 1990; Aquino Neto *et al.*, 1983).

A2 fraction. The A2 fractions are dominated by several series of *n*-alkylthiophenes, as determined from summed m/z 97 + 111 + 125 mass chromatograms (cf. Sinninghe Damsté *et al.*, 1986). Absolute amounts of selected compounds in the desulfurized A2 fraction of the unheated sample and the artificially matured samples are given in Table 3. The A2 fractions were also analyzed before desulfurization to determine the alkylthiophene isomer distributions, and to study the amounts and distributions of alkylbenzenes and alkylbenzo[*b*]thiophenes, since alkylbenzo[*b*]thiophenes are converted to alkylbenzenes upon desulfurization.

The desulfurized A2 fraction of the unheated sample contains mainly *n*-alkanes and Ph, with smaller amounts of Pr, 9-methyloctadecane, HBI C_{25} , and $17\alpha,21\beta(\text{H})$ hopanes dominated by the C_{35} pseudohomologues (Fig. 2(b)). The *n*-alkanes show an even-over-odd carbon number predominance ($\text{CPI}_{24-34} = 0.5$) in which *n*- C_{28} is most pronounced. The A2 fraction contains three alkylthiophenes with a Pr carbon skeleton (**V–VII**). The 2–3‰ difference in $\delta^{13}\text{C}$ value between Pr in the desulfurized A2 fraction and free Pr in the A1 fraction (Koopmans

Table 2. Steranes identified by GC-MS in the A1 fraction of the unheated sample and the artificially matured samples (Fig. 4)

Peak number	Compound
1	$5\alpha,14\beta$ C_{21} sterane (<i>I</i>)
2	4-methyl- $5\alpha,14\beta$ C_{21} sterane
3	$5\alpha,14\beta$ C_{22} sterane
4	$5\alpha,14\beta$ C_{23} sterane
5	(20 <i>S</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{27} sterane
6	(20 <i>R</i>)- $5\beta,14\alpha,17\alpha(\text{H})$ C_{27} sterane
7	(20 <i>R</i>)- $5\alpha,14\beta,17\beta(\text{H})$ C_{27} sterane
8	(20 <i>S</i>)- $5\alpha,14\beta,17\beta(\text{H})$ C_{27} sterane
9	(20 <i>R</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{27} sterane
10	(20 <i>S</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{28} sterane
11	(20 <i>R</i>)- $5\alpha,14\beta,17\beta(\text{H})$ C_{28} sterane
12	(20 <i>S</i>)- $5\alpha,14\beta,17\beta(\text{H})$ C_{28} sterane
13	(20 <i>R</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{28} sterane
14	(20 <i>S</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane
15	(20 <i>R</i>)- $5\alpha,14\beta,17\beta(\text{H})$ C_{29} sterane
16	(20 <i>S</i>)- $5\alpha,14\beta,17\beta(\text{H})$ C_{29} sterane
17	(20 <i>R</i>)- $5\alpha,14\alpha,17\alpha(\text{H})$ C_{29} sterane

Table 3. Absolute amounts ($\mu\text{g/g}$ TOC of unheated rock) of selected carbon skeletons in the A2 fraction of the unheated sample and the artificially matured samples. Also indicated are the Pr/Ph ratio and the CPI. Roman numbers refer to structures in Appendix A

	unheated	200°C	220°C	240°C	260°C	280°C	300°C
<i>n</i> -C ₁₈	110	150	200	220	530	720	1100
<i>n</i> -C ₂₈	260	430	580	600	1500	1500	1500
<i>n</i> -C ₃₈	38	64	100	68	170	150	240
9-methyloctadecane	10	12	15	15	28	33	39
Pr	35	49	63	49	150	210	300
Ph	180	210	250	240	370	410	530
HBI C ₂₅	65	55	64	75	77	110	70
(20 <i>R</i>)-5 α ,14 α ,17 α (H) C ₂₉ sterane	6	19	40	54	53	16	0
17 α ,21 β (H) C ₃₅ hopanes	83	86	120	91	110	100	37
Gammacerane (II)	2	10	22	32	69	46	24
C ₃ alkylbenzo [<i>b</i>]thiophenes ^a	6	32	26	74	150	300	960
C ₁₀ alkylbenzo [<i>b</i>]thiophenes	15	30	33	42	80	89	270
Pr/Ph	0.2	0.2	0.3	0.2	0.4	0.5	0.6
CPI	0.5	0.5	0.5	0.5	0.8	0.6	0.7

^aSummed amount of C₃ alkylbenzo[*b*]thiophenes in the A2 and A3 fractions.

et al., unpublished results) suggests different precursors, e.g. pristenes, pristadienes and pristatrienes known to occur in zooplankton (Blumer and Thomas, 1965; Blumer *et al.*, 1969) for the alkylthiophenes, and bound tocopherols for free Pr (Goossens *et al.*, 1984). The high relative abundance of 9-methyloctadecane and HBI C₂₅ in the desulfurized A2 fraction compared to the A1 fraction (cf.

Figure 2(a–b)) is due to specific alkylthiophenes with 9-methyloctadecane (VIII–X) and HBI C₂₅ (XI and XII) skeletons identified by Sinninghe Damsté *et al.* (1989b,c)). Alkylbenzenes are minor compounds in the unheated sample, with the most prominent components, icosylbenzene and 1,2-dimethyl-4-phytanylbenzene (IV), amounting to *ca.* 10 $\mu\text{g/g}$ TOC. The latter component was identified

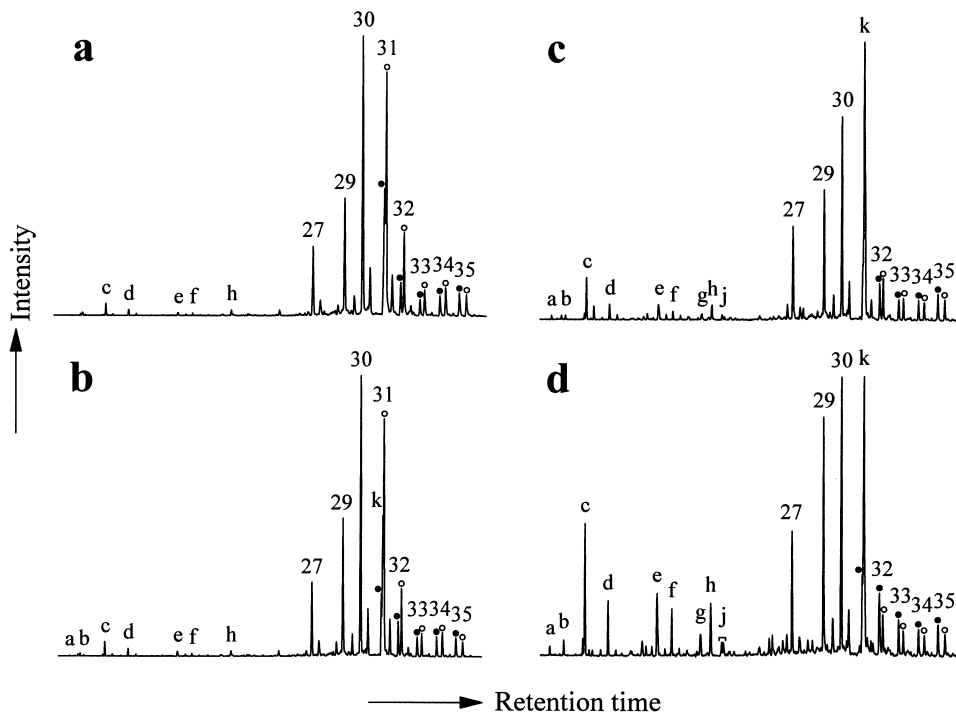


Fig. 5. Partial *m/z* 191 mass chromatogram of the A1 fraction of (a) the unheated sample, and the samples artificially matured at (b) 200°C, (c) 260°C and (d) 300°C. Key: numbers indicate carbon number of hopanes, solid dots indicate (22*S*)-17 α ,21 β (H) isomers, open dots indicate (22*R*)-17 α ,21 β (H) isomers, a = 13 β (H) C₁₉ tricyclic terpane, b = 14 α (H) C₁₉ tricyclic terpane, c = 13 α (H),14 β (H) C₂₀ tricyclic terpane (III), d = 13 α (H),14 β (H) C₂₁ tricyclic terpane, e = C₂₃ tricyclic terpane, f = C₂₄ tricyclic terpane, g = (22*S* + *R*) C₂₅ tricyclic terpanes, h = C₂₄ tetracyclic terpane, j = (22*S* + *R*) C₂₆ tricyclic terpanes, k = gammacerane

by comparison of its mass spectrum and relative retention time with literature data (Sinninghe Damsté *et al.*, 1988a). In addition, several series of C₂ to C₁₇ alkylbenzo[*b*]thiophenes are present in similar amounts as the alkylbenzenes (Table 3). Some monoaromatic steroids are also present.

Artificial maturation, especially at 260–300°C (Table 3), results in increasing amounts of alkylthiophenes with linear and isoprenoid carbon skeletons. Similar results have been reported for artificial maturation studies of a sample from the Gessoso-solfifera Formation (Koopmans *et al.*, 1995, 1996), in which it was concluded that alkylthiophenes are stable thermal degradation products of S-bound carbon skeletons in high-molecular-weight fractions, an interpretation shared by Aizenshtat *et al.* (1995). Alkylbenzenes are produced in small amounts (factor 2–3), so that at 300°C they are negligible compared to the alkylthiophenes. Alkylbenzo[*b*]thiophenes are produced in very large amounts; at 300°C the amounts of C₃ alkylbenzo[*b*]thiophenes are two orders of magnitude higher than in the unheated sample. The carbon number distributions of the alkylbenzenes and alkylbenzo[*b*]thiophenes shift to lower carbon numbers with increasing maturation, as follows from the generation profiles of the C₃ and C₁₀ alkylbenzo[*b*]thiophenes (Table 3). Inspection of the A2 fractions of the artificially matured samples reveals that the sterane and gammacerane carbon skeletons are represented mainly by Δ² sterenes and gammacer-2-ene, respectively, and not by alkylthiophenes.

Now that the generation profiles of the alkylthiophenes have been determined, their isomer distribution should be studied, because specific distributions can reveal information about the input of palaeobiochemicals into the sediment (e.g. Sinninghe Damsté *et al.*, 1989d, 1990b; Kohnen *et al.*, 1990b). With increasing thermal maturation, the relative amounts of the 2-*n*-alkylthiophenes increase slightly while the relative amounts of the mid-chain 2,5-di-*n*-alkylthiophenes decrease slightly (Fig. 6). Similar results have been reported for a sample from the Gessoso-solfifera Formation (Koopmans *et al.*, 1995). In that study, the isomer distribution of the C₃₁ alkylthiophenes at 330°C was dominated by isomers that were already the major isomers at low maturation temperatures, indicating that information about the original positions of functional groups of precursor molecules was retained at the highest temperature. Here, the isomer distribution of the C₂₈ alkylthiophenes may provide a valuable test case. Studies of the related Jurf ed Darawish oil shale showed that the C₂₈ alkylthiophenes are dominated by two isomers, i.e. 2-hexadecyl-5-octylthiophene and 2-nonyl-5-pentadecylthiophene, supposedly formed by sulfur incorporation into an octacos-9,12-diene precursor (Sinninghe Damsté *et*

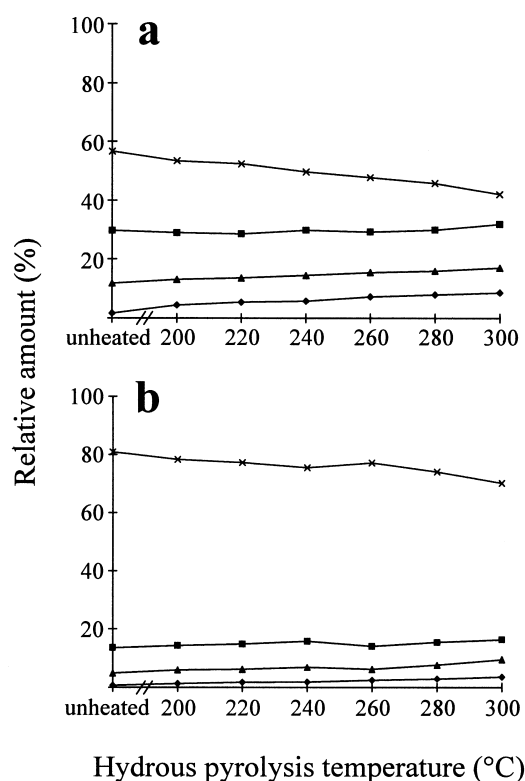


Fig. 6. Relative amounts of the alkylthiophene isomers with an (a) *n*-C₁₈ and (b) *n*-C₂₈ skeleton as a function of maturation temperature. Diamonds represent 2-alkylthiophenes, squares represent 2-alkyl-5-methylthiophenes, triangles represent 2-alkyl-5-ethylthiophenes, and crosses represent mid-chain 2,5-dialkylthiophenes

al., 1989c; Kohnen *et al.*, 1990b). In the unheated sample, 2-hexadecyl-5-octylthiophene and 2-nonyl-5-pentadecylthiophene make up 25 and 18% of the C₂₈ mid-chain 2,5-di-*n*-alkylthiophenes, respectively, whereas the other isomers represent 11% or less. With increasing thermal maturation, their relative abundance decreases to 20 and 16%, respectively, compared to 12% or less for the other isomers. Thus, although the predominance of 2-hexadecyl-5-octylthiophene and 2-nonyl-5-pentadecylthiophene becomes less marked with increasing thermal maturation, they are still the major mid-chain isomers. Their presence in the sample heated at 300°C suggests an octacos-9,12-diene precursor that was originally incorporated into the kerogen by reaction with reduced inorganic sulfur species, and that has been thermally released as alkylthiophene.

A3 fraction. The A3 fractions were analyzed both before and after desulfurization. Absolute amounts of selected compounds in the A3 fraction of the unheated sample and the artificially matured samples are given in Table 4.

The A3 fraction of the unheated sample contains methylated 2-methyl-2-(4,8,12-trimethyltridecyl)-chromans (**XIIIa-c**; Sinninghe Damsté *et al.*,

Table 4. Absolute amounts ($\mu\text{g/g}$ TOC of unheated rock) of selected carbon skeletons in the A3 fraction of the unheated sample and the artificially matured samples. Also indicated are the Pr/Ph and chroman ratio and the CPI. Roman numbers refer to structures in Appendix A

	unheated	200°C	220°C	240°C	260°C	280°C	300°C
<i>n</i> -C ₁₈	7	16	12	78	28	100	200
<i>n</i> -C ₂₈	8	59	30	140	37	130	240
<i>n</i> -C ₃₈	4	15	10	46	6	50	54
9-methyloctadecane	2	1	1	5	1	2	0
Pr	1	4	2	18	3	15	23
Ph	7	12	4	72	5	23	38
HBI C ₂₅	3	5	3	19	1	9	10
(20 <i>R</i>)-5 α ,14 α ,17 α (H) C ₂₉ sterane	0	4	5	0	0	0	0
C ₃₂ benzohopane (XIV)	9	22	28	12	25	32	18
C ₁ alkylbenzo[<i>b</i>]thiophenes	0	7	6	9	11	6	58
Monomethyl MTTC (XIIIa)	1	2	2	2	2	2	0
Dimethyl MTTC (XIIIb)	11	10	9	10	11	11	9
Trimethyl MTTC (XIIIc)	22	27	24	30	30	30	16
Pr/Ph	0.2	0.4	0.5	0.2	0.7	0.6	0.6
Chroman ratio	0.7	0.7	0.7	0.7	0.7	0.7	0.6
CPI	0.9	0.9	0.7	0.9	0.8	0.9	1.0

1987a), a series of C₃₂–C₃₅ benzohopanes (XIV) first identified by Hussler *et al.* (1984), and di- and triaromatic steroids. C₃–C₅ alkylbenzo[*b*]thiophenes are present in small amounts. Apparently, the benzo[*b*]thiophenes are present in both the A2 and A3 fractions, although the longer chain, slightly less polar components are only detected in the A2 fraction. Compounds with acyclic carbon skeletons are also present, as revealed by desulfurization of the A3 fraction (Fig. 2(c)). These are probably alkylbithiophenes (with two conjugated thiophene moieties) and/or alkyldithiophenes (with two non-conjugated thiophene moieties). Indeed, three bithiophenes with a Ph carbon skeleton (XV–XVII) were identified by comparison of their mass spectra with those reported earlier (Sinninghe Damsté and de Leeuw, 1987; Sinninghe Damsté *et al.*, 1987b).

With increasing thermal maturation, the absolute amounts of acyclic carbon skeletons generally increase (Table 4). Dibenzothiophene and C₁–C₃ alkyldibenzothiophenes are produced during heating, especially at 300°C. The generation profiles of the methylated 2-methyl-2-(4,8,12-trimethyltridecyl)-chromans are rather flat, so that it is not clear if

these compounds are thermally generated from high-molecular-weight precursors as observed previously for a sample from the Gessoso-solfifera Formation (Koopmans *et al.*, 1996). The chroman ratio, which has been used as an indicator for palaeosalinity (Sinninghe Damsté *et al.*, 1993), does not change with increasing thermal maturation (Table 4), as observed previously (Koopmans *et al.*, 1996).

A4 fraction. The A4 fractions contain mainly alkylsulfides with linear carbon skeletons, as determined from summed *m/z* 87 + 101 + 115 mass chromatograms (cf. Sinninghe Damsté *et al.*, 1986). The A4 fractions were desulfurized to enable quantitation of carbon skeletons. However, several alkylsulfides with cyclic carbon skeletons were identified before desulfurization of A4 fraction. Absolute amounts of selected carbon skeletons in the A4 fraction of the unheated and artificially matured samples are given in Table 5. Absolute amounts of alkylsulfoxides, which are thought to be formed from alkylsulfides by post-depositional oxidation or by oxidation during sample storage (Payzant *et al.*, 1983; Kohnen *et al.*, 1990a; Schouten *et al.*, 1995), are included in the amounts listed in Table 5. The

Table 5. Absolute amounts ($\mu\text{g/g}$ TOC of unheated rock) of selected carbon skeletons in the A4 fraction and the reduced alkylsulfoxide fraction as a function of maturation temperature. Also indicated is the Pr/Ph ratio. Roman numbers refer to structures in Appendix A

	unheated	200°C	220°C	240°C	260°C	280°C	300°C
<i>n</i> -C ₁₈	340	360	510	290	270	180	150
<i>n</i> -C ₂₈	910	1300	1700	970	940	410	260
<i>n</i> -C ₃₈	160	250	240	110	160	49	34
9-methyloctadecane	17	12	16	13	13	4	2
Pr	45	35	54	29	37	32	31
Ph	340	290	370	190	220	130	93
HBI C ₂₅	40	31	43	16	15	25	14
(20 <i>R</i>)-5 α ,14 α ,17 α (H) C ₂₉ sterane	8	25	23	9	18	17	5
5 α ,14 β C ₂₁ sterane (I)	0	0	0	0	1	1	0
17 α ,21 β (H) C ₃₅ hopanes	180	120	130	71	120	26	11
C ₂₃ tricyclic terpane	9	13	17	3	16	25	8
Gammacerane (II)	2	7	3	1	4	1	0
Pr/Ph	0.1	0.1	0.1	0.2	0.2	0.3	0.3

analysis of alkylsulfoxides is briefly discussed below.

The desulfurized A4 fraction of the unheated sample consists mainly of Ph and *n*-alkanes with a strong even-over-odd carbon number predominance ($CPI_{24-34}=0.4$; Fig. 2(d)), and, in fact, strongly resembles the desulfurized A2 fraction (Fig. 2(b)). Small amounts of nor-pristane, Pr, 9-methyloctadecane, HBI C_{25} and hopanes dominated by the $17\alpha,21\beta(H) C_{35}$ pseudohomologues are also present. Steranes are present in low amounts, and their distribution differs from that in the A1 fraction in that (20*R*)- and (20*S*)- $5\alpha,14\beta,17\beta(H)$ steranes have a higher relative abundance (cf. Fig. 4(a)). The C_{23} tetracyclic terpenoid sulfide XVIII, first identified by Payzant *et al.* (1988), is present in small amounts in the A4 fraction. Four compounds with unidentified C_{15} , C_{20} , C_{25} and C_{30} skeletons were recognized by mass spectrometry as polycyclic alkylsulphides. Their mass spectra show a major fragment ion at m/z 169, and each compound occurs as a 1:1 doublet in the m/z 169 mass chromatogram (not shown). These compounds are probably the same as those recently identified by Poinot *et al.* (1997).

Upon heating, the amounts of alkylsulfides with linear carbon skeletons increase significantly up to 220°C, after which they decrease (Table 5). This is

in sharp contrast with the results obtained for the A1 and desulfurized A2 fractions, where the amounts of compounds with linear carbon skeletons continuously increase, especially at 260–300°C. This indicates that alkylsulfides are not stable under the conditions used, and may suggest the transformation of alkylsulfides to alkylthiophenes. Interestingly, quite different results were obtained for artificially matured samples from the Gessosolfifera Formation (Koopmans *et al.*, 1996), where the alkylsulfide and alkylthiophene generation profiles were largely covariant and no indications were found for conversion of alkylsulfides to alkylthiophenes.

Polar fraction

The polar fraction contains S-rich macromolecules and low molecular weight (LMW) alkylsulfoxides, and to make a distinction between them, the polar fractions were reduced with $LiAlH_4$. Two fractions (reduced sulfoxide and residual polar fraction) were obtained by column chromatography, which were both desulfurized. In addition, HI/ $LiAlH_4$ degradation (cleavage of C–O bonds) and MeLi/MeI degradation (cleavage of S–S bonds) experiments were carried out on the polar fraction of the unheated sample and the sample heated at

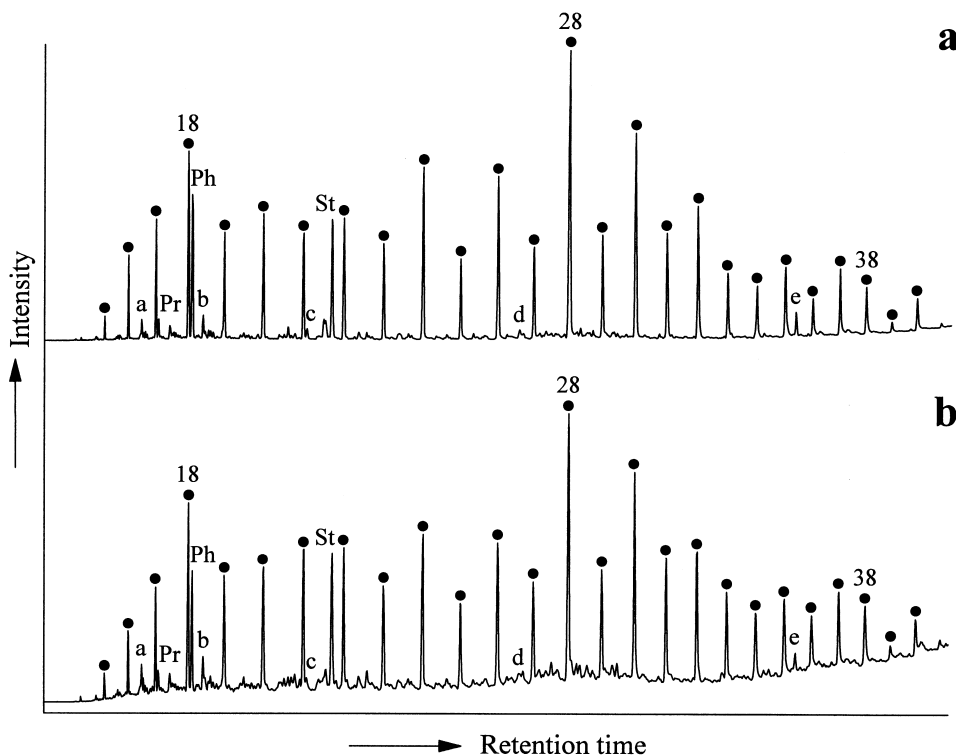


Fig. 7. TIC of (a) the desulfurized reduced sulfoxide fraction and (b) the desulfurized residual polar fraction of the unheated sample. Key: dots = *n*-alkanes (numbers indicate number of carbon atoms), Pr = pristane, Ph = phytane, St = standard, a = nor-pristane, b = 9-methyloctadecane, c = HBI C_{25} , d = squalane, e = (22*R*)- $17\alpha,21\beta(H) C_{35}$ hopane

260°C (only HI/LiAlH₄), because previous studies indicated that relatively large amounts of carbon skeletons can be released in this way (Koopmans *et al.*, 1996). However, the amounts released were low, thus it is concluded that only low amounts of carbon skeletons are sequestered via C–O or S–S bonds.

Reduced alkylsulfoxide fraction. The desulfurized reduced alkylsulfoxide fraction of the unheated sample (Fig. 7(a)) is similar in composition to the desulfurized A4 fraction (Fig. 2(d)), which confirms their common origin. Absolute amounts of selected carbon skeletons in the desulfurized reduced alkylsulfoxide fraction of the unheated sample and the artificially matured samples, together with the absolute amounts of these carbon skeletons in the A4 fractions, are listed in Table 5.

Residual polar fraction. Absolute amounts of selected carbon skeletons in the desulfurized residual polar fraction are listed in Table 6.

The unheated sample is dominated by Ph and *n*-alkanes with an even-over-odd carbon number predominance (CPI_{24–34}=0.6; Fig. 7(b)). In addition, smaller amounts of nor-pristane, Pr, 9-methyloctadecane, HBI C₂₅, squalane, (20*R*)-5 α ,14 α ,17 α (H) and (20*R*)- and (20*S*)-5 α ,14 β ,17 β (H) C₂₇–C₂₉ steranes, hopanes dominated by the 17 α ,21 β (H) C₃₅ pseudohomologues, tricyclic terpanes dominated by the C₂₃ pseudohomologues, and gammacerane are present.

With increasing thermal maturation, the amounts of these carbon skeletons first decrease, but at 260°C they increase again to a maximum at 280°C (Table 6). This is puzzling in the light of the relative weakness of the C–S bond (Claxton *et al.*, 1993), which is expected to lead to more or less continuously decreasing amounts of S-bound carbon skeletons in the polar fraction. In a study of a sample from the Gessoso-solfifera Formation, the amounts of most S-bound carbon skeletons in the polar fraction were relatively constant with increasing thermal maturation (Koopmans *et al.*, 1996). This was ascribed to the “intermediate” character of the

polar fraction abundant in S-rich macromolecules from thermal breakdown of the kerogen, thus releasing free hydrocarbons due to thermal cleavage of C–S bonds.

Asphaltene fraction

Desulfurization of the asphaltene fraction of the unheated sample yielded predominantly *n*-alkanes in low amounts. For example, *n*-C₂₈ amounts to 11 μ g/g TOC, which is <1% of the total amount of *n*-C₂₈ skeletons in the unheated sample. Desulfurization of the asphaltene fraction of the sample heated at 260°C also yields predominantly *n*-alkanes, in similarly low amounts. Because desulfurization of the asphaltene fraction of these two samples suggests flat generation profiles, asphaltene fractions of the other samples were not analyzed.

DISCUSSION

Carbon skeleton speciation as a function of maturation temperature

Now that the absolute amounts of selected carbon skeletons in all fractions as a function of maturation temperature are known, their relative amounts can be calculated in order to determine which compound classes are thermally stable and which are not. Linear, branched and cyclic carbon skeletons are discussed below. Alkylsulfides will be presented as a combined fraction (i.e. alkylsulfides present as such and as alkylsulfoxides; cf. Table 5).

Linear carbon skeletons. The summed amount of *n*-C₁₈ skeletons is relatively constant at low maturation temperatures and increases significantly only at 260°C. At 300°C it amounts to 2.3 mg/g TOC of unheated rock (Table 7). The relative amount of the *n*-C₁₈ skeleton in all fractions is shown in Fig. 8(a). In the unheated sample, it is mainly present in the form of alkylsulfides (crosses). With increasing thermal maturation, the relative amount of alkyl-

Table 6. Absolute amounts (μ g/g TOC of unheated rock) of selected carbon skeletons in the desulfurized residual polar fraction of the unheated sample and the artificially matured samples. Also indicated are the Pr/Ph ratio and the CPI. Roman numbers refer to structures in Appendix A

	unheated	200°C	220°C	240°C	260°C	280°C	300°C
<i>n</i> -C ₁₈	97	100	51	41	76	240	160
<i>n</i> -C ₂₈	270	180	88	84	170	650	230
<i>n</i> -C ₃₈	65	56	30	30	63	140	120
9-methyloctadecane	8	4	2	1	4	4	0
Pr	11	12	5	4	9	35	29
Ph	66	45	20	15	33	120	64
HBI C ₂₅	4	0	0	0	3	0	0
(20 <i>R</i>)-5 α ,14 α ,17 α (H) C ₂₉ sterane	12	19	10	6	6	5	0
5 α ,14 β C ₂₁ sterane (I)	1	0	0	0	1	0	0
17 α ,21 β (H) C ₃₅ hopanes	46	17	6	3	25	34	0
C ₂₃ tricyclic terpane	5	0	0	0	2	3	0
Gammacerane (II)	7	0	0	0	4	0	0
Pr/Ph	0.2	0.3	0.3	0.3	0.3	0.3	0.5
CPI	0.6	0.7	0.8	0.8	0.6	0.6	0.7

Table 7. Summed absolute amounts ($\mu\text{g/g}$ TOC of unheated rock) of selected carbon skeletons in all fractions as a function of maturation temperature. Roman numbers refer to structures in Appendix A

	unheated	200°C	220°C	240°C	260°C	280°C	300°C
$n\text{-C}_{18}^a$	600	700	850	710	1100	1500	2300
$n\text{-C}_{28}$	1500	2100	2400	1900	2800	2800	2600
$n\text{-C}_{38}$	270	380	380	250	400	400	470
Pr	110	120	140	110	290	540	970
Ph	660	610	700	560	760	920	1100
HBI C_{25}	110	93	110	110	100	150	110
(20 <i>R</i>)-5 α ,14 α ,17 α (H) C_{29} sterane	46	110	130	160	320	380	160
17 α ,21 β (H) C_{35} hopanes	310	230	260	180	270	220	110
Gammacerane (II)	14	33	49	70	190	240	200

^aIncludes C_{10} alkylbenzo[*b*]thiophenes (see Table 3).

sulfides decreases, suggesting that this form of the $n\text{-C}_{18}$ skeleton is thermally unstable. On the other hand, the relative amounts of the free hydrocarbon (diamonds), alkylthiophenes (squares) and alkylbenzo[*b*]thiophenes (solid circles) increase,

suggesting that these forms are thermally stable. Saturated hydrocarbons and alkylthiophenes have been noted before as being thermally stable compound classes under hydrous pyrolysis conditions (Koopmans *et al.*, 1995, 1996, 1997).

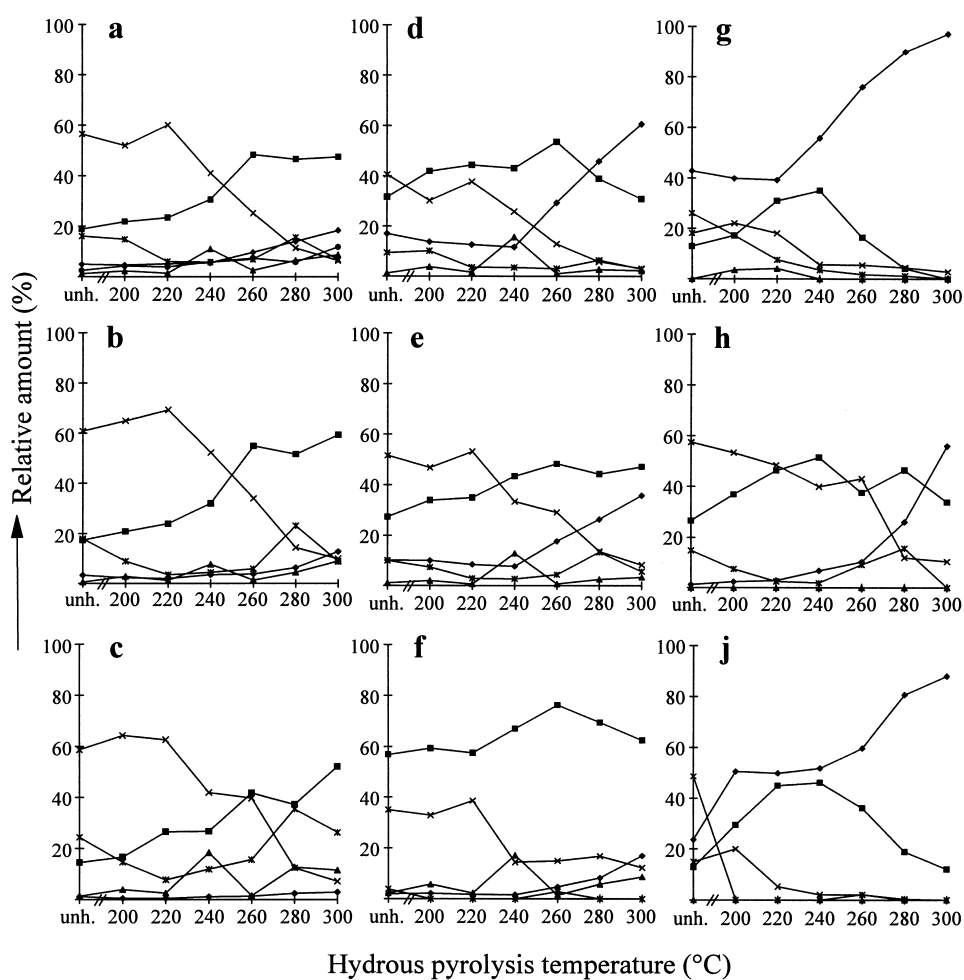


Fig. 8. Relative amounts of the carbon skeletons of (a) $n\text{-C}_{18}$, (b) $n\text{-C}_{28}$, (c) $n\text{-C}_{38}$, (d) Pr, (e) Ph, (f) HBI C_{25} , (g) (20*R*)-5 α ,14 α ,17 α (H) C_{29} sterane, (h) (22*R*)-17 α ,21 β (H) C_{35} hopane, and (j) gammacerane in the A1 fraction (diamonds), A2 fraction (squares), A3 fraction (triangles), A4 plus reduced alkylsulfide fraction (cf. Table 5; crosses), and desulfurized residual polar fraction (double crosses). Alkylbenzo[*b*]thiophenes in (a) are represented by dots

The n -C₂₈ skeleton is by far the most abundant carbon skeleton in the extract of the unheated sample (1.5 mg/g TOC; Table 7). Its summed amount increases already at low temperatures, and at 280°C it is 2.8 mg/g TOC of unheated rock. The relative amounts of the n -C₂₈ skeleton in the alkylsulfide, saturated hydrocarbon and alkylthiophene fractions show similar changes with maturation temperature as the n -C₁₈ skeleton (cf. Fig. 8(a–b)).

The distributions of the n -alkanes in all fractions of the unheated sample show slightly increased amounts of the C₃₇ and C₃₈ components compared to the other long-chain n -alkanes in the C₃₅–C₄₀ region (Figs 2 and 7). This distribution suggests an origin for these skeletons from n -C₃₇ and n -C₃₈ di- and tri-unsaturated ketones (alkenones) biosynthesized by several Prymnesiophyte algae, as concluded previously for a sample from the related Jurf ed Darawish oil shale (Sinninghe Damsté *et al.*, 1988b, 1989c; Kohlen *et al.*, 1990b). Recently, the speciation of the n -C₃₇ and n -C₃₈ skeletons in an artificial maturation series of a sample from the Gessoso-solfifera Formation was discussed in detail (Koopmans *et al.*, 1997). It was shown that, due to the reaction of reduced inorganic sulfur species with the functional groups of the alkenones, these compounds became sequestered in the kerogen so that n -C₃₇ and n -C₃₈ skeletons could not be detected in the extract of the unheated sample. After mild thermal treatment, the amounts of these skeletons in the polar fraction increased, due to thermal breakdown of S-linked moieties in the kerogen. After heating at higher temperatures, the n -C₃₇ and n -C₃₈ skeletons were released as free hydrocarbons, alkylthiophenes and saturated ketones, which were shown to be stable thermal degradation products (Koopmans *et al.*, 1997). In the sample under study, these effects are not observed. First, in the extract of the unheated sample n -C₃₈ skeletons are already present (Table 7), which may be due to the higher level of thermal maturity of the sample from the Ghareb Formation ($R_o = 0.39\%$) compared to that from the Gessoso-solfifera Formation ($R_o = 0.25\%$). Second, the production of the free hydrocarbon (diamonds) is marginal (3% at 300°C; Fig. 8(c)), whereas in the case of the Gessoso-solfifera Formation the free hydrocarbon represented 36% at 300 and 52% at 330°C (Koopmans *et al.*, 1997). Third, the production of the alkylthiophenes (squares) is significant (53% at 300°C; Fig. 8(c)), whereas it was marginal in the sample from the Gessoso-solfifera Formation. Thus, while artificial maturation of S-rich organic matter in the sample from the Gessoso-solfifera Formation produces mainly C₃₈ n -alkanes, in the sample from the Ghareb Formation it produces mainly C₃₈ n -alkylthiophenes. The relative amount of the n -C₃₈ skeleton in all fractions

changes with maturation temperature in a similar fashion to that of the n -C₁₈ and n -C₂₈ skeletons.

Branched carbon skeletons. The generation profile of the summed amount of the Pr carbon skeleton is comparable to that of the n -C₁₈ skeleton (Table 7). However, at 260–300°C the summed amount of the Pr carbon skeleton increases at a higher rate. The relative amount of the Pr carbon skeleton in all fractions changes similarly with maturation temperature as the linear carbon skeletons: at high temperatures, the free hydrocarbon (diamonds) and, to a lesser extent, the alkylthiophenes (squares) are thermally stable (Fig. 8(d)). These results are in sharp contrast with those previously reported for an artificial maturation series of a sample from the Gessoso-solfifera Formation (Koopmans *et al.*, 1996), where the Pr carbon skeleton was almost exclusively found as free hydrocarbon. This was taken as an indication that bound tocopherols and archaeobacterial ether lipids were the major precursors of Pr. Clearly, in the Ghareb Formation S-bound Pr, possibly originating from pristenes, pristadienes and pristatrienes known to occur in zooplankton (Blumer and Thomas, 1965; Blumer *et al.*, 1969), plays an important role as well.

The generation profile of the Ph carbon skeleton covaries with that of the Pr carbon skeleton (Table 7). However, at 260–300°C Ph is generated at a lower rate, hence the increasing Pr/Ph ratios in all fractions. The relative amount of the Ph carbon skeleton as a function of maturation temperature indicates that the free hydrocarbon (diamonds) and the alkylthiophenes (squares) are thermally stable (Fig. 8(e)).

The HBI C₂₅ skeleton differs from the other acyclic carbon skeletons in that its summed amount remains relatively constant throughout the maturation series (Table 7). This may be an indication that the HBI C₂₅ skeleton is not sequestered in the kerogen. The alkylthiophenes (squares) are much more abundant at high temperatures than the other forms (Fig. 8(f)).

Cyclic carbon skeletons. The summed amount of the (20*R*)-5 α ,14 α ,17 α (H) C₂₉ sterane skeleton increases to 0.38 mg/g TOC of unheated rock at 280°C, then decreases to 0.16 mg/g TOC of unheated rock at 300°C (Table 7). This may reflect the intrinsic lability of the sterane carbon skeleton, with its quaternary and tertiary carbon atoms, making the bonds with the secondary carbon atoms relatively weak. The question remains what are the sterane degradation products. The absolute amount of the 5 α ,14 β C₂₁ sterane in the A1 fraction is doubled between 280 and 300°C (Table 1), which argues against degradation of the sterane ring system. However, short-chain steranes may be thermal degradation products of C₂₇–C₂₉ steranes by cleavage of C–C bonds in the side chain. Such cleavage may be enhanced by cross-linking via the side

chain, which would weaken the C–C bonds in the side chain. Chemical degradation of the kerogen of the related Jurf ed Darawish oil shale indicated that the steranes were S-linked via the A-ring and the side chain (Hofmann *et al.*, 1992). However, thermal degradation of steranes that are S-linked in the side chain is also expected to yield steroid thiophenes, which are not observed. Moreover, decreasing summed amounts of C₂₇–C₂₉ steranes in an artificial maturation series of a sample from the Gessoso-solfifera Formation were not accompanied by increasing amounts of short-chain steranes (Koopmans *et al.*, 1996). Therefore, it seems unlikely that short-chain steranes are thermal degradation products of (bound) C₂₇–C₂₉ steranes. An alternative “degradation” pathway of the sterane carbon skeleton may be aromatization of the ring system.

Figure 8(g) shows the relative amount of the (20*R*)-5 α ,14 α ,17 α (H) C₂₉ sterane skeleton as a function of maturation temperature. The free hydrocarbon (diamonds) is the only stable form at high temperatures, approaching 100%. At $T \leq 240^\circ\text{C}$, both steranes (diamonds) and Δ^2 sterenes (squares) are formed. This may indicate that the formation of Δ^2 sterenes, supposedly from thermal degradation of sterane skeletons S-bound in the kerogen via C-3 (cf. Adam *et al.*, 1991; Kohnen *et al.*, 1991, 1993), is only favorable at relatively low temperatures. Apparently, quenching of radical sites (formed by thermal cleavage of C–S bonds) by water-derived hydrogen (Lewan, 1997) is more efficient at higher temperatures.

The carbon skeleton speciation of the extended hopanes as a function of maturation temperature has recently been discussed in detail by Köster *et al.* (1997). Here, we focus on the fate of the (22*S*)- and (22*R*)-17 α ,21 β (H) C₃₅ isomers. The summed amount of the 17 α ,21 β (H) C₃₅ hopanes in all fractions decreases with increasing maturation temperature (Table 7). In the unheated sample, they are almost exclusively present in an S-bound form (Fig. 8(h)). With increasing thermal maturation, the alkylsulfides (crosses) are not stable, whereas the free hydrocarbons (diamonds) and alkylthiophenes (squares) are. These generation profiles are similar to those of the *n*-alkanes, but quite different from those of the steranes. This is probably because hopanes, like *n*-alkanes, easily form LMW OSC with sulphide and thiophene moieties in the side chain, whereas steranes do not.

Gammacerane (II) is present in low amounts in the extract of the unheated sample (Table 7). Upon heating, large amounts of gammacerane are formed from thermal degradation of the kerogen. Desulfurization of the kerogen from the related Jurf ed Darawish oil shale released relatively large amounts of gammacerane (Hofmann *et al.*, 1992), suggesting that gammacerane in the kerogen may

be S-bound. The relative amount of the gammacerane carbon skeleton in different fractions (Fig. 8(j)) changes similarly with maturation temperature as that of the (20*R*)-5 α ,14 α ,17 α (H) C₂₉ sterane skeleton (Fig. 8(g)). These similar generation profiles are probably due to the identical mode of bonding (S-bound at C-3; cf. Adam *et al.*, 1993) of these carbon skeletons in the kerogen.

Role of S-rich kerogen during hydrous pyrolysis

The unheated sample contains immature ($R_o = 0.39\%$) Type II-S kerogen with an S_{org}/C ratio of 0.07. This amount of organic sulfur is comparable to that of a sample from the Gessoso-solfifera Formation ($S_{org}/C = 0.08$) studied previously (Koopmans *et al.*, 1995, 1996, 1997). However, the latter is less mature ($R_o = 0.25\%$) and contains abundant S–S linked carbon skeletons. Artificial maturation at relatively low temperatures ($T < 300^\circ\text{C}$) resulted in cleavage of these weak S–S bonds (Koopmans *et al.*, 1996). The sample from the Ghareb Formation contains only small amounts of S–S linked carbon skeletons, probably due to its higher level of thermal maturity. Consequently, the similar S_{org}/C ratios of both samples suggest that the sample from the Ghareb Formation contains a larger amount of C–S links per carbon skeleton. This may explain the increasing amount of extractable organic matter with increasing thermal maturation (Fig. 1). A kerogen consisting of highly sulfur cross-linked LMW carbon skeletons will thermally degrade at relatively low temperature to LMW (=soluble) organic matter through cleavage of relatively weak C–S bonds.

The different nature and amount of sulfide links in both samples may explain their different thermal behavior. In the Ghareb Formation acyclic carbon skeletons are mainly released as alkylthiophenes (Fig. 8), whereas in the Gessoso-solfifera Formation they are mainly released as alkanes (Koopmans *et al.*, 1996). Evidence is accumulating that alkylthiophenes are formed as thermally stable compounds from thermal degradation of (poly)sulfide-linked carbon skeletons (Krein and Aizenshtat, 1994, 1995; Schouten *et al.*, 1994; Aizenshtat *et al.*, 1995; Koopmans *et al.*, 1995, 1996). Thus, it seems likely that a carbon skeleton linked by a larger number of C–S bonds has a greater chance to be thermally transformed into an alkylthiophene. This is in agreement with the observations for the samples from the Ghareb and Gessoso-solfifera Formations.

Formation of alkylbenzo[b]thiophenes

Artificial maturation of the sample from the Ghareb Formation results in the formation of abundant alkylbenzo[b]thiophenes and, to a lesser extent, alkylidibenzothiophenes (Tables 3 and 4), compounds not detected in the artificially matured samples from the Gessoso-solfifera Formation

(Koopmans *et al.*, 1996) samples. This may be explained by the abundant formation of alkylthiophenes in the sample from the Ghareb Formation, because alkylthiophenes are the presumed precursors of alkylbenzo[*b*]thiophenes and alkyldibenzothiophenes (Sinninghe Damsté *et al.*, 1989a). Benzo[*b*]thiophenes and dibenzothiophenes are major compounds in crude oils (Ho *et al.*, 1974), so it seems that hydrous pyrolysis is indeed simulating the formation of crude oil from immature organic-rich sedimentary rocks (cf. Lewan *et al.*, 1979). This is supported by the "oil-like" distributions of the *n*-alkanes (i.e. a shift to lower carbon numbers and a decreasing CPI) in the A1 and desulfurized A2 and A3 fractions which develop with increasing thermal maturation (cf. Figures 2 and 3).

The discrepancy between the OSC present in immature sedimentary rocks and crude oils (alkylsulfides and alkylthiophenes) on one hand and more mature oils (e.g. benzo[*b*]thiophenes and dibenzothiophenes) on the other is still a matter of concern (Sinninghe Damsté *et al.*, 1989a; Sinninghe Damsté and de Leeuw, 1990). This discrepancy has been explained by the formation of benzo[*b*]thiophenes and dibenzothiophenes via cyclization and aromatization of the alkyl side chains of free or kerogen-bound alkylthiophenes (Sinninghe Damsté *et al.*, 1989a), although the exact mechanism of this reaction is still unknown (Aizenshtat *et al.*, 1995). The maturity set under study enables the quantitative analysis of both precursors (alkylthiophenes) and products (benzo[*b*]thiophenes and dibenzothiophenes) of this reaction. However, the relative amounts of the alkylthiophenes and alkylbenzo[*b*]thiophenes with e.g. the *n*-C₁₈ skeleton both increase with increasing maturation temperature (Fig. 8(a)), suggesting that both are thermally stable under the conditions used, and showing no indication that one is converted into the other. It seems that higher experimental temperatures are required to study this reaction. Preliminary results indicate that, at $T > 300^\circ\text{C}$, the absolute amount of C₁₈ alkylthiophenes decreases whereas the absolute amount of C₁₈ alkylbenzo[*b*]thiophenes increases. Experiments are planned to resolve the origin of these alkylbenzo[*b*]thiophenes from either free or kerogen-bound alkylthiophenes.

SUMMARY

(1) With increasing thermal maturation, alkanes and alkylthiophenes are generally stable forms of any given carbon skeleton, whereas alkylsulfides are not stable.

(2) The specific isomer distribution of the alkylthiophenes does not change significantly with increasing thermal maturation, even though these compounds are generated in large amounts. This indicates that the original position of the functional

groups of the precursor molecules can still be recognized, and thus that alkylthiophenes can be used as biomarkers throughout diagenesis.

(3) The high abundance of alkylthiophenes upon heating in the sample from the Ghareb Formation, as opposed to the sample from the Gessoso-solfifera Formation studied previously, is probably due to the relatively high number of monosulfide links per carbon skeleton.

(4) The formation pathways of alkylbenzo[*b*]thiophenes have not yet been resolved, although preliminary results at $T > 300^\circ\text{C}$ indicate that alkylbenzo[*b*]thiophenes are more stable than alkylthiophenes.

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APPENDIX A

