Chapter 27

Analysis of Maturity-Related Changes in the Organic Sulfur Composition of Kerogens by Flash Pyrolysis—Gas Chromatography

Timothy I. Eglinton^{1,2,4}, Jaap S. Sinninghe Damsté¹, Mathieu E. L. Kohnen¹, Jan W. de Leeuw¹, Steve R. Larter², and Richard L. Patience³

¹Faculty of Chemical Engineering and Materials Science, Organic Geochemistry Unit, Delft University of Technology, De Vries van Heystplantsoen 2, 2628 RZ Delft, Netherlands

²Department of Geology, University of Oslo, P.O. Box 1047, Blindern, N-0316, Oslo 3, Norway

³BP Research Centre, Sunbury-on-Thames, TW16 7LN, United Kingdom

Analysis of several sedimentary rock sequences by Pyrolysis-Gas Chromatography (Py-GC) has revealed that thiophene precursors are preferentially removed from kerogen during maturation. This was illustrated by a decrease with increasing maturity in the TR ratio: [2,3-dimethylthiophene]/[*n*-non-1-ene+1,2-dimethylbenzene]. Quantitative Py-GC data for a series of Monterey Fm. kerogens were used to determine *pseudo*-activation energies for the loss of precursors for these species during maturation. Preliminary kinetic calculations gave mean activation energies for the loss of precursors for 2,3-dimethylthiophene, *n*-non-1-ene and 1,2-dimethylbenzene to be 181, 193 and 203 kJ/mol respectively. The low value for the loss of the thiophene precursors supports the argument that S_{org} is, at least partly, responsible for the early petroleum generation from S-rich kerogens. Specific changes observed in the distributions of organic sulfur pyrolysis products with increasing maturity include: an increase of alkylbenzothiophenes relative to alkylthiophenes; a shift in the carbon number distributions within these compound classes; and preferential removal of alkylthiophenes with linear carbon skeletons. It is postulated that cyclisation and subsequent aromatisation of kerogen-bound alkylthiophene precursors possessing linear carbon skeletons could account for these maturity-related changes in pyrolysis product distributions. Both the quantitative and qualitative changes in S_{org} composition were supported by results from the analysis of a suite of artificially matured kerogens.

NOTE: Organic Sulfur in Macromolecular Sedimentary Organic Matter, Part IV

⁴Current address: Fye Laboratory, Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

One of the main reasons for the recent interest in organic sulfur in sedimentary organic matter is the growing evidence that it plays a role in the petroleum generation process. Organically-bound sulfur has been implicated in the formation of low API gravity, asphaltene-rich petroleums at a low level of thermal exposure (1). Recent studies indicate that organically-bound sulfur in kerogen is formed very early during diagenesis mainly *via* incorporation of inorganic sulfur into functionalised lipids which become part of the kerogen (2). Indeed, sulfur may facilitate cross-linking of low molecular weight structural units to form insoluble, high molecular weight substances including sulfur-rich kerogen (*i.e.* "natural vulcanisation") (2,3).

It has been recently shown that the most abundant sulfur-containing pyrolysis products of kerogens isolated from immature organic-rich sedimentary rocks are low molecular-weight alkylthiophenes (*i.e.* typically containing 1 to 6 carbon atoms attached to the thiophene ring) (3,4). The abundance of thiophenes relative to aromatic and aliphatic hydrocarbons in flash pyrolysates of kerogens and asphaltenes has been shown to be strongly correlated with organic sulfur content (5). This suggests that thiophene moieties are a major form of kerogen-bound organic sulfur. We have therefore proposed a ratio (termed "TR") based on the relative abundance of alkylthiophenes in pyrolysates as a rapid means of estimating organic sulfur content in kerogens (5). Figure 1 shows a ternary plot of the relative abundance of a thiophene (2,3-dimethylthiophene) in relation to two hydrocarbon products (1,2-dimethylbenzene and *n*-non-1-ene) from pyrolysis-gas chromatography of a wide variety of immature (vitrinite reflectance, $R_o < 0.5\%$) kerogens and coals. The figure shows that those samples designated "Type II-S" (*i.e.* $S_{org}/C > 0.04$; (1)) are easily distinguished from other kerogens. Moreover, the other types of kerogens are also discriminated in such a diagram as expected from previous studies (6,7). However, maturity also effects sample position in the diagram (5).

The aim of the present investigation was to study the variation in organic sulfur composition of kerogens with maturity. Samples from four well-known sedimentary sequences (Upper Jurassic shales of the North Sea, Toarcian shales of the Paris Basin, Tertiary coals of the Mahakam Delta and Miocene Monterey shales of offshore California) were analysed by flash pyrolysis-gas chromatography (Py-GC) using both flame ionisation (FID) and sulfur-specific flame photometric detection (FPD) to yield both qualitative and quantitative information on the amounts and types of sulfur-containing pyrolysis products. In addition, a suite of residues from artificial maturation (hydrous pyrolysis) of Kimmeridge kerogen (8) was analysed for comparison. For one sequence (Monterey Fm.) quantitative pyrolysis data were used together with information on the geothermal history of the basin to determine values for *pseudo*-kinetic parameters relating to the loss of thiophene precursors from the kerogen. These

Figure 1. Ternary plot showing the relative abundances of 2,3-dimethylthiophene, *n*-non-1-ene and 1,2-dimethylbenzene (determined from FID chromatograms after flash pyrolysis, 610°C, 10s) of immature kerogens and coals (modified after Eglinton *et al.* (5)).

Table I. Sample details

Name and Location	Depth (m)	TOC (%)	R _o (%)	T _{max} (°C)	HI	TR ^a
Mahakam Delta, Indonesia	993	53.20	0.35	408	116	0.33
	1390	66.20	0.38	420	275	0.14
	1920	69.00	0.43	424	278	0.15
	2020	71.10	0.47	420	291	0.13
	2480	74.30	0.52	435	274	0.07
	2600	73.60	0.58	435	277	0.11
	2950	77.50	0.59	442	264	0.12
	3100	77.60	0.65	445	261	0.09
	3140	75.20	0.89	456	116	0.01
Paris Basin, France [*]	500	6.50	0.32	427	672	0.23
	600	8.00	0.33	424	523	0.29
	600	8.10	0.37	424	736	0.26
	700	5.80	0.41	426	601	0.19
	1016	7.10	0.36	427	692	0.25
	1280	6.50	0.38	430	787	0.24
	1320	7.20	0.36	425	662	0.28
	2065	2.90	0.43	436	536	0.27
	2207	n.d.	n.d.	n.d.	n.d.	0.05
	2130	1.30	0.40	435	128	0.04
	2430	7.80	0.42	440	598	0.24
	2633	1.80	0.52	448	80	0.16
Draupne Fm. North Sea	1326	2.70	0.51	424	210	0.61
	1550	4.90	0.45	425	319	0.33
	2065	5.10	0.40	424	422	0.44
	2132	6.70	0.50	426	427	0.37
	2322	7.00	0.47	421	303	0.31
	2911	7.20	0.50	427	344	0.20
	3902	3.20	0.77	429	53	0.11
	4130	4.30	0.76	452	301	0.09
Monterey Fm. CA, U.S.A.	1326	3.80	n.d.	393	458	1.58
	2362	6.40	n.d.	389	553	1.37
	3651	3.60	n.d.	418	503	0.64
	4063	3.50	n.d.	421	411	0.54
	5002	4.10	n.d.	426	335	0.16
	5242	1.70	n.d.	424	238	0.07

^aTR = [2,3-dimethylthiophene]/[1,2-dimethylbenzene + *n*-non-1-ene].

n.d. = not determined. ^{*}Maximum depths are indicated.

values are discussed in terms of the role of organic sulfur in the decomposition of kerogens and the generation of petroleum.

The results are described in several sections. The first section deals with gross variations in organic sulfur with maturity as determined by Py-GC. The relationship between organic sulfur and Rock-Eval $T_{\max}$ is discussed in the second section. In the third section, yields from flash pyrolysis are used to determine kinetic parameters for the loss of precursors for organic sulfur and other compounds from the kerogen during maturation. The last section describes the maturity-related variations in organic sulfur pyrolysis products.

Materials and Methods

Sample description and preparation. The samples analysed in this study are listed in Table I together with available geochemical data. Table II provides general burial history information for the four sedimentary sequences.

Table II. Burial history information for the four sedimentary sequences studied

Sequence	Age (Ma)	Temp. Gradient (°C/Km)	Max. Temp. (°C)
Mahakam	< 25	34	132
Kimmeridge	150	33-35	155
Paris Basin	180-190	34	100
Monterey	< 25	28-35	150

Nine coals from the Mahakam Delta, Kalimantan, Indonesia which were supplied by Institute Francais du Petrole (IFP) formed one sample set. The samples were taken from two wells penetrating this Miocene deltaic sequence, seven samples came from one borehole (Handil 627). The Mahakam Delta has been extensively studied (9-12). It is believed that the coals represent a relatively uniform sequence containing organic matter varying in properties due only to maturity. The kerogen in these samples is considered to be Type III, derived primarily from terrestrial (equatorial forest) material deposited in the delta. The organic sulfur content of the coals is low ($S_{\text{org.}}/C < 0.01$). The vitrinite reflectance values for the sequence range from immature to mature ($R_0 = 0.35\% - 0.89\%$). The temperature history of the basin is relatively simple with the threshold of oil generation placed at *ca.* 3000 meters. Maturity-related geochemical transformations have been described for related samples from the

Mahakam Delta (12-17). The coal samples were solvent-extracted prior to analysis.

The second suite also supplied by IFP comprised twelve Toarcian shale samples from the Paris Basin, France. These consisted of both outcrop and core samples from the same stratigraphic zone across the basin. These sediments have also been the subject of numerous geochemical investigations (18-20) and are believed to have been deposited under shallow, normal salinity marine conditions, giving rise to a predominantly carbonate lithology and oil-prone Type II/I-II kerogen. Although not measured for the samples used in the present study, the organic sulfur content of the Paris basin kerogens is generally quite low, with atomic S/C ratios ranging from 0.025 (immature) to less than 0.01 (mature). The thermal history of the Paris Basin is more complex than that of the Mahakam Delta due to substantial uplift in the eastern part of the basin. Oil generation is believed to occur below *ca.* 1500 meters. The samples used in the present study were analysed as extracted rocks without prior kerogen isolation. Maturity-related geochemical transformations have been described for related samples from the Paris Basin (21-25).

A set of eight core samples of Upper Jurassic shales from the Norwegian continental shelf of the North Sea were analysed. The samples covered a depth range of *ca.* 1000 - 4000 meters. The North Sea basins have been the subject of numerous geochemical studies (26-32) and sophisticated models describing their thermal history have been constructed. These shales typically contain Type II kerogen of marine origin, however, significant facies variations are observed across the basin. In particular, samples from the basin flanks (*i.e.* the shallowest samples) received a significant input of land-derived organic matter as evidenced by relatively low Rock-Eval hydrogen indices (Table I). Although variable, the upper limit of oil generation is typically estimated to be at *ca.* 3000 meters. The core samples were analysed as extracted rocks.

Six samples (provided by BP) from four separate wells penetrating the Miocene Monterey Fm., Santa Barbara Channel Basin were studied. The drill cuttings were obtained from depths varying between *ca.* 1000 and 5300 meters. Previous geochemical investigations of the Monterey Fm. sediments (33-35) indicate that they have been deposited in an upwelling environment and are comprised mainly of biogenic silica, carbonate and phosphate with very little clastic material. The total organic carbon (TOC) contents of these particular sediments varies from *ca.* 2-5%, the most immature samples containing Type II-S kerogen (*e.g.* sample from 1326 m, $S_{org}/C = 0.07$). Because of the very low terrestrial input, reliable determination of vitrinite reflectance was not possible. Independent measurements of maturity (R. Patience, unpublished results) show that these samples range from immature through peak oil generation, the present-day temperature of the deepest sample being approximately 150°C and the

upper limit of petroleum generation inferred at *ca.* 3500 meters. The samples were analysed as isolated kerogens.

The starting material for the artificial maturation experiments was kerogen isolated from an outcrop sample of Upper Jurassic Kimmeridgian shales from Dorset, U.K. The particular horizon sampled (Blackstone band) is a highly bituminous (TOC = *ca.* 45%) calcareous shale containing immature ($R_o = 0.35\%$, $T_{max} = 421^\circ\text{C}$), sulfur-rich kerogen ($S_{org.}/C = 0.047$). Several organic geochemical studies on this and related samples from this area have been conducted previously (36-41). The Dorset Kimmeridge shales are geochemically different from their stratigraphic equivalents in the North Sea, so direct comparisons between the two are not valid. This is exemplified by the much higher abundance of organic sulfur in the Dorset compared to North Sea Kimmeridge equivalents. Detailed information concerning the conditions employed for the artificial maturation experiments are described elsewhere (8,41). Briefly, aliquots (*ca.* 250mg) of isolated kerogen were heated in sealed stainless steel vessels in the presence of excess water (*i.e.* "hydrous pyrolysis", 42,43). In each case the duration of heating at the allotted temperature was 72 hours. It is suggested that these conditions closely mimic natural petroleum generation (42,43). Selected geochemical information for the solvent-extracted residues are shown in Table III.

Table III Artificial Maturation (Hydrous Pyrolysis) of
Kimmeridge Kerogen (Dorset, U.K.)

Name/Location	Temp. ($^\circ\text{C}$)	% R_o	H/C	TR
Kimmeridge	Unheated	0.35	1.24	0.86
Blackstone,	200	0.18	1.20	0.88
Dorset, U.K.	250	0.20	1.12	0.70
	280	0.28	1.14	0.61
	310	0.58	1.02	0.40
	330	0.95	1.00	0.28
	340	1.13	0.67	0.29
	350	1.24	0.67	0.27
	360	1.86	0.63	0.34

Kerogens were isolated from the Monterey and Dorset Kimmeridge rock samples according to standard procedures involving successive HCl/HF treatments (41). Elemental analysis of the Monterey Fm. kerogens was performed by the Analytical Division at BP Research Centre (Sunbury, U.K.). Elemental compositions of the Mahakam coals were provided by IFP. No differentiation was made in these analyses between total S and organic S, however correction for inorganic S was made for the Mahakam

coal samples on the assumption that all Fe was in the form of FeS_2 (pyrite). Rock-Eval pyrolysis was performed either at the University of Oslo, at BP Research Centre or at IFP. Vitrinite reflectance determinations (*ca.* 20 measurements/sample) were made at the Organic Geochemistry Unit, University of Newcastle upon Tyne.

Pyrolysis-Gas Chromatography. Flash pyrolysis analyses were performed according to previously described methods (3). In brief, samples were pyrolysed (10 s) on a wire with a Curie temperature of 610°C. The products were separated on a fused silica column (25 m x 0.32 mm i.d.) coated with a methyl silicone phase (CP Sil-5, Chrompack, film thickness 0.45 μm) using a temperature programme from 0°C (5 min.) to 300°C (15 min.) at 3°C/min. The separated products were detected simultaneously by both a flame ionisation detector (FID) and a sulfur-selective flame photometric detector (FPD) using a stream splitter at the end of the chromatographic column. Peak data (sampling rate 6 points/sec.) were acquired and processed using Maxima Chromatography software (Waters Assoc.). Peak assignments were made on the basis of GC retention data and were confirmed using pyrolysis-gas chromatography-mass spectrometry (4). Any partial co-elution of components was compensated for during peak integration.

Absolute quantitation of individual components in the FID chromatograms was achieved using the method described by Larter and Senftle (44) in which a known amount of polymer standard (poly-*p-t*-butylstyrene, Polysciences Inc.) dissolved in dichloromethane was mixed with the sample prior to pyrolysis. This polymer degrades quantitatively and reproducibly to its monomer, *p-t*-butylstyrene (85% conversion under the pyrolysis conditions employed). The calibration of the polymer standard on the Curie-point pyrolysis system will be described separately (45). Yields were determined from triplicate Py-GC analyses. The analyses were performed under only one set of pyrolysis conditions since the relative and absolute amounts of individual pyrolysis products are known to vary with heating conditions. These relationships are currently being investigated.

Variation in Abundance of Pyrolysis Products with Organic Sulfur Content and Maturity

Partial pyrolysis-gas chromatograms of representative immature kerogens or coals from the four sequences studied are shown in Figure 2. The abundance of thiophenes relative to aliphatic and aromatic hydrocarbons in the partial FID chromatograms differs markedly for the four samples shown. This is reflected by the ratio of the peak area of 2,3-dimethylthiophene relative to those due to 1,2-dimethylbenzene and *n*-non-1-ene (*i.e.* $\text{TR} = [\text{2,3-dimethylthiophene}] / [\text{1,2-dimethylbenzene} + \textit{n}\text{-non-1-ene}]$).

Figure 2. Partial chromatograms (n -C₈ to n -C₉ region) from flash pyrolysis of immature kerogen/coal samples. Open and closed circles in FID chromatograms (left) indicate n -alk-1-enes and n -alkanes respectively. See Materials and Methods for pyrolysis and chromatographic conditions.

1-ene], Table I). This ratio, which is measured from the FID chromatograms after flash pyrolysis, broadly reflects organic sulfur content (5) and therefore indicates large variations in %S_{org.} for these four sample sets. A detailed description of the relationship between S_{org.} and TR is presented elsewhere (5).

Natural Maturity Sequences. Figure 3 shows partial FID chromatograms from flash pyrolysis of a suite of Monterey Formation kerogens taken from different depths in the Santa Barbara Basin, offshore California. With increasing depth, there is a preferential loss of the C₂-thiophenes relative to the *n*-C₈ and *n*-C₉ alkene/alkane doublets and, most noticeably, the C₂-benzenes in the pyrolysates. This trend is clearly reflected by a decrease in the TR ratio from almost 1.6 in the shallowest sample to less than 0.1 in the deepest (Figure 4). Figure 5 shows the variation in absolute yields of 2,3-dimethylthiophene and the two hydrocarbons from flash pyrolysis of kerogens from the Monterey depth sequence. There is a sharp decrease in the absolute amounts of the thiophene with depth. The decrease is more dramatic than that of the hydrocarbons (as would have been predicted from the decreasing thiophene ratio) and therefore provides additional evidence for the early generation of sulfur compounds from sulfur-rich kerogens (1,46). While the yield of 2,3-dimethylthiophene drops to very low values in the deeper samples, hydrogen indices remain high (e.g. 335mg HC/g TOC at 5002m, Table I), indicating that some hydrocarbon potential remains in the kerogen.

The variation in the TR with depth for three other natural maturity sequences (Mahakam Delta, Paris Basin, North Sea) is plotted with that for the Monterey Fm. in Figure 4. While the geothermal histories of these sequences are different, there is in each case a strong relationship between maximum temperature experienced by the sample and depth. Depth is therefore used here as a common maturity axis for comparative purposes. Each of these sequences show a slight but significant decrease in this ratio with increasing depth. The extent of the decrease is, however, less dramatic than that for the Monterey sequence due mainly to their lower initial organic sulfur contents.

Figure 6 shows the evolution of samples from the four sequences within a ternary diagram. With the exception of the North Sea samples, a general trend towards the lower left of the diagrams with increasing maturity is evident for each sequence, indicating a relative enrichment in 1,2-dimethylbenzene compared to the alkene and thiophene. There are some reversals within the overall trend, most noticeably for samples lean in organic sulfur (Mahakam, Paris Basin) and these probably reflect combinations of small-scale facies variations and analytical errors. For the Mahakam coals the main process appears to be depletion of *n*-non-1-ene. Loss of thiophene (in addition to loss of the alkene) is slightly more predominant in the Paris Basin suite. Thiophene loss appears to precede

Figure 3. Partial FID chromatograms (n -C₈ to n -C₉ region) from flash pyrolysis of Monterey Fm. kerogens, Santa Barbara basin. Open and closed circles indicate n -alk-1-enes and n -alkanes respectively. Depth of burial, Rock-Eval pyrolysis T_{max} , Hydrogen Index (HI), and the thiophene ratio (TR) are shown.

Figure 4. Continued.

Figure 5. Variation in absolute yields of 2,3-dimethylthiophene, *n*-non-1-ene and 1,2-dimethylbenzene ($\mu\text{g/mg}$ kerogen) with depth for the Monterey Fm. kerogens. Yields determined from FID chromatograms after co-pyrolysis of the kerogens with known amounts of poly-*p-t*-butylstyrene (Larter and Senftle, 44).

the loss of the alkene in the North Sea sequence, initially resulting in a relative enrichment of the latter. This trend, *i.e.* an early increase in "aliphaticity" with maturity supports previous observations from Py-GC of kerogens from natural maturity sequences (24,47) and is consistent with the evolution tracks of the principal kerogen types (48).

The trend with depth for the Monterey samples is dominantly due to the loss of thiophene but the maturity trend within the ternary plot (Figure 6) suggests that a significant depletion of the alkene occurs in association with thiophene loss.

Artificial Maturation. Laboratory maturation studies provide a means to determine the influence of temperature on kerogen composition, since other variables (*e.g.* source input) can be eliminated. In order to study the behaviour of organically bound sulfur under these controlled conditions, Py-GC-FID/FPD was performed on a suite of solvent-extracted residues from sealed vessel (hydrous pyrolysis) experiments aimed at simulating maturation over the range involved in petroleum generation.

The unheated Kimmeridge kerogen sample used for the artificial maturation experiments (chromatogram not shown) gave rise, on flash pyrolysis, to abundant thiophenes both in relative and in absolute terms (5). A clear trend has already been observed in flash pyrolysates of these samples in which the ratio, 2-methylthiophene/toluene decreases with increasing artificial maturation temperature or time (8). Figure 7 shows the variation in the TR ratio for extracted residues from artificial maturation at each of a variety of temperatures ranging from 200°C to 360°C (duration of heating, 72 hours). The ratio steadily decreases with increasing maturation temperature up to 330°C. The ratio for residues heated above this temperature remains approximately constant. These results support the findings of Eglinton *et al.* (8). From a ternary plot (Figure 7), it is evident that up to temperatures of 330°C, the main process operative is loss of the thiophene. In the residues from artificial maturation at temperatures above 330°C substantial loss of the alkene also appears to take place, thus giving the appearance of no further depletion of the thiophene and a relatively constant value for TR. The residues from artificial maturation at temperatures between 310°C and 340°C are therefore somewhat analogous to the changes observed in the natural North Sea maturity sequence. The temperatures involved in these experiments are, however, by no means equivalent (being necessarily much higher in the laboratory experiments in order to promote kerogen degradation in a reasonable period of time).

Relationship between Maturity, Rock-Eval $T_{\max}$ and Organic Sulfur content

The relationship between Rock-Eval $T_{\max}$ and depth for the different sedimentary sequences is depicted in Figure 8. For a given sequence

Figure 6. Ternary plots showing the variation in relative abundances of 2,3-dimethylthiophene, *n*-non-1-ene and 1,2-dimethylbenzene with depth (meters) for samples from the four sedimentary sequences. Maximum depths of burial are given for samples from the Paris Basin.

Figure 6. Continued.

Figure 7. Variation in the thiophene ratio (TR; upper diagram) and Ternary plot showing the variation in the relative abundances of 2,3-dimethylthiophene, *n*-non-1-ene and 1,2-dimethylbenzene (lower diagram) with artificial maturation temperature for a suite of kerogen residues obtained from hydrous pyrolysis (72 hrs) of Kimmeridge kerogen (Dorset, U.K.). NB. Integrated peak areas for 2,3-dimethylthiophene also include 2-vinylthiophene.

Figure 8. Relationship between Rock-Eval pyrolysis $T_{\max}$ and depth for samples from the four sedimentary sequences (modified after Eglinton et al., 5). *Continued on next page.*

Figure 8. Continued.

$T_{\max}$ increases with increasing depth. However, examination of a large number of samples differing widely in organic sulfur content (as measured by the thiophene ratio), but all of low maturity gives the relationship in Figure 9. Samples with the highest thiophene ratio (organic sulfur content) give rise to the lowest $T_{\max}$ values. Rock-Eval analyses of solvent-extracted, isolated kerogens as well as whole rock samples demonstrate that the low $T_{\max}$ values from thiophene-rich samples are not due to bitumen adsorption effects (*i.e.* tightly held bitumen contributing to the "S₂" peak). The samples shown in Figure 9 are all at the pre-oil generation stage and fall within a relatively narrow reflectance range ($R_o = 0.3-0.5\%$). The figure shows that organic sulfur content influences the thermal lability of the kerogen (as measured by $T_{\max}$). These results indicate that $T_{\max}$ should be used cautiously as a source of maturity information for rock sequences with marked facies variations.

Kinetic Analysis of Quantitative Pyrolysis Data

In order to better understand the factors controlling the loss of thiophenic and other moieties from the kerogens during maturation *pseudo*-kinetic parameters for loss of the different precursor species from the kerogens were determined. It is now generally agreed that kinetic analysis of geochemical processes involved in kerogen maturation requires a distributed activation energy solution (49-51). Attempts to simulate complex reaction systems using single reactions invariably lead to absurd, heating rate dependent parameters of no chemical significance (49). It is preferable to monitor rates of reactant (kerogen-bound species) loss, rather than product (bitumen species) generation. This is because primary migration from mature, organic-rich rocks is pervasive and efficient (52,53). Thus, bitumen species concentrations are not a reliable indicator of production rates, and it follows that kinetic parameters derived from bitumen analyses will reflect these errors.

In the present study the approach of Larter (51) was used. The initial concentrations of kerogen-bound species (precursors for 2,3-dimethylthiophene, 1,2-dimethylbenzene and *n*-non-1-ene) were determined based on analysis of immature Monterey Fm. kerogens using quantitative Py-GC methods. Concentrations of these species in the kerogen were calculated assuming that Py-GC yields are directly proportional to the actual precursor species concentrations in the kerogens (54) and that this proportionality is invariant with maturity. Concentrations of precursor species for mature kerogens were determined in the same manner but were normalised to initial kerogen concentration by allowing for loss of material during maturation. This correction was performed on the assumption that the amount of inert material in the immature and mature kerogens was constant (52,53). Estimates of inert organic matter were based on "Rock-Eval" hydrogen index determinations.

Figure 9. Relationship between the thiophene ratio, TR, and Rock-Eval T_{max} for samples of varying kerogen type. NB. All samples are immature with respect to oil generation (i.e. vitrinite reflectance, $R_o < 0.5\%$).

It was assumed that kerogen decomposition was governed kinetically by first order reactions proceeding with, initially, a Gaussian distribution of activation energies with a mean activation energy E_m and a standard deviation σ . Using the method of Larter (51) the kinetic parameters are derived using regression methods by comparing the quadratic errors between the measured concentrations of components (corrected to initial kerogen concentration) with a computed concentration based on geologically determined subsurface heating rates and maximum burial temperatures. When this was performed it was found that the six data points available from the Monterey Fm. were insufficient to adequately constrain all three parameters (*i.e.* too few data points, too much data scatter). Therefore a single, mean pre-exponential frequency factor of $1 \times 10^{13}/\text{sec.}$ was assumed for all three reactions and the best fit E_m and σ values were re-computed. These values are shown in Table IV.

Table IV. Kinetic Parameters for the Loss of Thiophene and Hydrocarbon Precursors from Monterey Fm. Kerogens

Compound	E_m (kJ/mol)	σ (% E_m)
2,3-Dimethylthiophene	181	8
1,2-Dimethylbenzene	203	8
<i>n</i> -Non-1-ene	193	12
Pre-exponential factor, $A = 1 \times 10^{13}/\text{sec.}$ (assumed)		

These preliminary calculations confirm the conclusion obtained by inspection, *i.e.* that the loss of thiophenic species from kerogens requires a lower average activation than does hydrocarbon generation. However, all reactions show significant distributions about the mean with σ ranging from 8 to 12% E_m (Table IV). With these limited data it is probable that this standard deviation represents an error assessment rather than a true estimate of the actual activation energy distribution. With the data available it is unwise to pursue these results too far and more rigorous analysis will await additional data to better confine the kinetic solutions. Nevertheless, several independent observations appear to support the kinetic results from the present study. Gransch and Posthuma (46) noted that the early generation products from artificial maturation of a sulfur-rich kerogen (La Luna, Venezuela) contained much more sulfur than did the later products. This trend was also observed by Eglinton *et al.* (41) for the organic-soluble products from artificial maturation of Kimmeridge kerogen.

As the thiophene ring is rather stable, the early release of these species suggests that the weak linkages are in the alkyl chains bonding the

thiophenes to the kerogen. As there is evidence for the presence of aliphatic carbon-sulfur bonds in condensed organic matter (55) it is quite possible that these weak linkages may be related to such.

Comparison of these kinetic parameters with those for bulk "hydrocarbon" generation from source rocks containing Type II kerogen, using similar distributed activation energy kinetic models (49,50) is risky because our data are insufficient to adequately confine the frequency factors. Assuming, however, that the frequency factor estimate is approximately correct, the value for loss of the thiophene is significantly lower than that of the average activation energy of petroleum generation, even from Type II-S kerogens (56). This might be expected, since thiophene loss is probably partly responsible for a shift of the activation energy distribution to lower values. However, the activation energy for loss of *n*-non-1-ene (Table IV) is also substantially lower than that compared to E_a values for generation from highly aliphatic (Type I) kerogens, which are typically in the order of 250 kJ/mol (56,57). This may reflect the limited data set used for the present study. Nevertheless, a concomitant loss of the alkene in association with the thiophene was also apparent in Figure 6. This suggests that in the Monterey kerogens the nature of the alkene/alkane precursors (as exemplified by *n*-non-1-ene) is different from those in the other kerogens studied. It has been postulated that one precursor of alkenes/alkanes in sulfur-rich kerogens may result from natural vulcanisation of *n*-alkyl-containing substrates (58,59). Due to the relative weakness of the carbon-sulfur bond it is likely that alkenes/alkanes would be generated at a lower thermal stress from these precursors than from kerogens containing alkylchains linked by predominantly carbon-carbon bonds. While Type II-S kerogens differ structurally from Type II kerogens, the general similarity between overall yields of *n*-hydrocarbon moieties on pyrolysis (60) suggests that we do not yet fully understand the influence of organic sulfur on alkyl group incorporation into kerogens. We are currently extending these kinetic studies to a larger sample set and to different sedimentary sequences to determine the importance of these different influences.

Variation in distributions of organic sulfur pyrolysis products with maturity

Natural Maturity sequences. Figure 10 shows FPD chromatograms of the pyrolysates of seven Mahakam coal samples studied by flash pyrolysis. Peak identifications are listed in Table V.

Even in these relatively sulfur-lean samples, organic sulfur pyrolysis products are detected throughout the maturity range studied. The FPD chromatogram of the most immature sample is dominated by C_1 - C_4 alkylthiophenes. Compared to a wide variety of kerogens, pyrolysates of the Mahakam coals tend to contain relatively high amounts of thiophenes substituted at positions 3 and 4 (61).

Figure 10. FPD chromatograms from flash pyrolysis of Mahakam coals. Sample depth, vitrinite reflectance, Rock-Eval T_{max}, hydrogen index (HI) and the thiophene ratio (TR) are shown. Peak identifications are given in Table V.

Table V. Peak identifications for FPD chromatograms.

Peak	Compound	Peak	Compound
1	Thiophene	10	2-Ethyl-5-methylthiophene
2	2-Methylthiophene	11	2-Ethyl-4-methylthiophene
3	3-Methylthiophene	12	2,3,5-Trimethylthiophene
4	2-Ethylthiophene	13	2-Methyl-5-vinylthiophene
5	2,5-Dimethylthiophene	14	2,3,4-Trimethylthiophene
6	2,4-Dimethylthiophene	15	Benzo[<i>b</i>]thiophene
7	2,3-Dimethylthiophene (+ 2-Vinylthiophene)	16	Methylbenzo[<i>b</i>]thiophenes
8	3,4-Dimethylthiophene	17	C ₂ -Benzo[<i>b</i>]thiophenes
9	2-Propylthiophene	18	C ₃ -Benzo[<i>b</i>]thiophenes

Several distinct maturity-related trends emerge through detailed examination of the traces (Figure 10). There are variations in both the relative abundance of different compound classes and within individual compound classes. The most marked trend is an increase in abundance of alkylbenzothiophenes relative to alkylthiophenes. This is clearly seen in Figure 11 where the ratio of these two compound classes is plotted with respect to depth. There is also an apparent shift in the internal carbon number distributions of both the alkylbenzothiophenes and alkylthiophenes. Specifically, there appears to be a preferential loss of short-chain alkylthiophenes and alkylbenzothiophenes (e.g. methylthiophenes decrease relative to dimethylthiophenes). The exception to this depth trend is the sample from 2480m which appears less mature (on the basis of sulfur compound distribution) than the adjacent sample of shallower depth (2020m).

A number of trends in isomer distributions for a given compound class are also evident with maturity. On the basis of previous observations (3) it appears that alkylthiophenes derived from precursors with a linear carbon skeleton are preferentially depleted relative to those derived from branched thiophenic precursors in the coal. For example, there is a decrease in the amount of 2-ethyl-5-methylthiophene relative to 2-ethyl-4-methylthiophene (Peaks 10 and 11 respectively, Figure 10) with increasing depth. The trend with maturity is illustrated in Figure 12 where the ratio of short-chain thiophenes of "branched" origin (*i.e.* at least one substitution at position 3 or 4 on the thiophene ring) relative to those of "linear" origin (*i.e.* substituted at positions 2 and/or 5 only) is plotted *versus* depth. Isomer trends within the alkylated benzothiophenes were generally more difficult to see because of their lower relative abundance.

With regard to the Monterey kerogens there are some similar trends to those observed for the Mahakam coals although the transformations are

Figure 11. Variation in the ratio of ΣC_1-C_3 alkylbenzo[*b*]thiophenes (Peaks 16-18, Figs. 10 and 13) relative to ΣC_1-C_3 alkylthiophenes (Peaks 2-14, Figs. 10 and 13) with respect to depth or temperature of artificial maturation. Maximum depths of burial are used for samples from the Paris Basin. Values determined from peak height data, corrected for quadratic response of FPD. *Continued on next page.*

Figure 11. Continued.

Figure 12. Variation in the ratio of C_1 - C_3 alkylthiophenes derived from precursors with branched carbon skeletons (Peaks 3,6,7,8,11,12,14, Figs. 10 and 13) relative to those with linear carbon skeletons (Peaks 2,4,5,9,10,13, Figure 10 and 13) with respect to depth or temperature of artificial maturation. Note: For samples from the Paris Basin maximum depths of burial were used. Values determined from peak height data, corrected for quadratic response of FPD. *Continued on next page.*

Figure 12. Continued.

generally smaller and less consistent. Examples include a carbon number shift in the alkylthiophenes, an increase in alkylbenzothiophenes relative to alkylthiophenes (Figure 11) and an increase in the ratio of "branched" versus "linear" thiophenes (Figure 12).

The trends described above can, to a certain extent, also be discerned in the Paris Basin maturity sequence (see Figures 11 and 12) but facies variations, which have been previously noted for these samples (62), also appear to significantly influence the distributions.

The samples from the North Sea were analysed as extracted whole rocks. The low TOC content of these samples prevented analysis by dual FID/FPD. Descriptions of maturity-related changes in kerogens isolated from these shales will be given elsewhere.

Artificial Maturation. Figure 13 shows FPD chromatograms from flash pyrolysis of the series of artificially matured kerogens. Analyses of these samples revealed several trends consistent with those observed in the natural maturity sequences. The dominance of 2-methyl-5-alkylthiophenes in the pyrolysate of the unheated sample appears to be characteristic of immature kerogens of marine origin (3,61). With increasing artificial maturation temperature there is an increase in the amounts of alkylbenzothiophenes relative to alkylthiophenes (Figure 11) and a depletion of the C_1 -substituted homologues of both compound classes. Similar observations were reported previously for a number of these samples (8). There is also a change in the isomer distribution in favour of those derived from moieties with "branched" relative to "linear" carbon skeletons as noted for the natural maturity sequences (Figure 12).

The fact that the above transformations are evident both in the artificial as well as the natural maturation series strongly suggests that they are temperature dependent and are not simply facies-related. One process which could explain the three maturity-related trends (*i.e.* increase in alkylbenzothiophene/thiophene ratio; preferential loss of C_1 -substituted homologues; depletion of thiophenes with a "linear" as opposed to a "branched" origin) is cyclisation and subsequent aromatisation of alkylthiophene precursors in the kerogen with linear carbon skeletons. This would explain the increased importance of alkylbenzothiophenes in the pyrolysates of mature kerogens and, since alkylthiophenes with linear carbon skeletons are commonly the dominant isomers, their conversion to alkylbenzothiophenes would cause the observed carbon number shift. The preferential aromatisation of linear thiophene precursors could arise partly because 2,3-disubstituted thiophene units cannot aromatised. Other branched precursors, such as 2,4-disubstituted thiophene units, may aromatised but would give rise, on pyrolysis, to alkylbenzothiophenes with substitution patterns which differ from those commonly observed in kerogen pyrolysates (3,4). In contrast, alkylbenzothiophenes with substitution patterns consistent with aromatisation of linear alkylthiophenes are usually the dominant

Figure 13. FPD chromatograms from flash pyrolysis of Kimmeridge kerogen residues from artificial maturation (72 hr) at different temperatures. For peak identifications see Table V.

isomers present in kerogen pyrolysates and immature oils (4,63-65), thus lending support to this hypothesis. The reasons why 2,4-disubstituted thiophene units do not appear to aromatise is not completely understood. It may be that either the substitution pattern on the thiophene ring affects the aromatisation reaction (*cf.* differences in mass spectral behaviour of various thiophene isomers) or that these units originate partly from steroidal side-chains (3) and thus cannot aromatise.

While the absolute amounts of alkylthiophenes decreased dramatically with increasing maturity in the Monterey sequence there was only a slight increase in the ratio of alkylbenzothiophenes *versus* alkylthiophenes. This suggests that while cyclisation/aromatisation may occur with maturation, the dominant process is loss of labile, organically-bound sulfur.

Conclusions and Geochemical Implications

Pyrolysis-gas chromatography shows that precursors for thiophenes are preferentially eliminated from kerogen during burial maturation. Results from the preliminary kinetic study implicate thiophenic sulfur in the early thermal degradation of sulfur-rich kerogen. Whilst this analysis is far from conclusive, further kinetic studies of this type, with larger and better calibrated data sets may enable us to make a more objective assessment of the chemical characteristics of bonds being cleaved during maturation processes. Monitoring the disappearance of thiophenes and other specific compounds (*e.g.* phenols) from pyrolysates of samples over a maturity range may provide important information regarding the kinetics of kerogen degradation, particularly for Type II-S kerogens. The systematic variations with depth in the distributions of thiophenes released on pyrolysis do not hold much promise as maturity indicators because of their strong source dependence. Nevertheless, they may provide useful information on changes in kerogen structure with maturity as well as allowing further classification of kerogens according to organic sulfur composition.

Acknowledgments

The following organisations are thanked for their kind donation of samples: Institute Francais du Petrole, British Petroleum, Norsk Hydro. We are grateful to the analytical departments at Bristol University and at BP Research Centre for the elemental analyses. Dr. A. Pepper (BP) is acknowledged for provision of burial history information for the Monterey Fm. kerogens. L. Buxton (Geolab Nor) is thanked for selected TOC determinations. Dr. J.M. Jones (University of Newcastle) is thanked for vitrinite reflectance analyses. We thank Dr. A.K. Burnham for supplementary kinetic analyses. W. Pool is thanked for technical assistance. Drs. K. Peters, W.L. Orr and C.M. White are thanked for critical reviews.

Literature cited

1. Orr, W.L. *Org. Geochem.* 1986, 10, 499-516.
2. Sinninghe Damsté, J.S.; Rijpstra, W.I.C.; de Leeuw, J.W.; Schenck, P.A. *Geochim. Cosmochim. Acta* 1989, 53, 1343-1355.
3. Sinninghe Damsté, J.S.; Eglinton, T.I.; de Leeuw, J.W.; Schenck, P.A. *Geochim. Cosmochim. Acta* 1989, 53, 873-889.
4. Sinninghe Damsté, J.S.; Kock-van Dalen, A.C.; de Leeuw, J.W.; Schenck P.A. *J. Chromatogr.* 1988, 435, 435-452.
5. Eglinton, T.I.; Sinninghe Damsté, J.S.; Kohnen M.E.L.; de Leeuw J.W. *Fuel* 1989 (submitted).
6. Larter, S.R.; Douglas, A.G. In *Advances in Organic Geochemistry*, 1979; Douglas, A.G.; Maxwell J.R., Eds.; Pergamon Press: Oxford, 1980, pp. 579-584.
7. Larter, S.R. In *Analytical Pyrolysis - Methods and Applications*; Voorhees, K. Ed.; Butterworths: London, 1984, pp. 212-275.
8. Eglinton, T.I.; Philp, R.P.; Rowland, S.J. *Org. Geochem.* 1988, 12, 33-41.
9. Magnier, P.L.; Oki, T.; Kartaaipoetra, L. *Proc. 9th World Pet. Congr.* 1975, 2, 239-250.
10. Vandenbroucke, M.; Durand, B. In *Advances in Organic Geochemistry*, 1981. Bjorøy, M. *et al.* Eds. 1983, pp. 147-155. Wiley and Sons Ltd.
11. Schoell, M.; Teschner, M.; Wehner, H.; Durand, B.; Oudin, J.C.; In *Advances in Organic Geochemistry*, 1981. Bjorøy, M. *et al.* Eds.; Wiley and Sons, 1983, pp. 156-163.
12. Mackenzie, A.S.; Mackenzie, D. *Geol. Mag.* 1983, 120, 417-528.
13. Combaz, A.; Matharel, M. *Bull. Amer. Assoc. Petrol. Geol.* 1978, 62, 1684-1695.
14. Boudou, J.P. *Org. Geochem.* 1984, 6, 431-437.
15. Boudou, J.P.; Durand, B.; Oudin, J.L. *Geochim. Cosmochim. Acta* 1984, 48, 2005-2010.
16. Hoffman, C.F.; Mackenzie, A.S.; Lewis, C.A.; Maxwell, J.R.; Oudin, J.L.; Durand, B.; Vandenbroucke M. *Chem. Geol.* 1984, 42, 1-23.
17. Monthioux, M.; Landais, P.; Monin, J-C. *Org. Geochem.* 1985, 8, 275-292.
18. Durand, B.; Espitalie, J.; Nicaise, G.; Combaz, A. *Rev. Inst. Francais du Petr.* 1972, 865-884.
19. Alpern, B.; Cheymol, D. *Rev. Inst. Francais du Petr.* 1978, 515-535.
20. Mackenzie, A.S.; Hoffman, C.F.; Maxwell, J.R. *Geochim. Cosmochim. Acta* 1981, 45, 1345-1355.
21. Louis, M.C. In *Advances in Organic Geochemistry*, 1964 Hobson, G.D.; Louis, M.C. Eds.; Pergamon Press: Oxford, 1966, pp. 85-94.
22. Tissot, B.; Califert-Debyser, Y.; Deroo, G.; Oudin, J.L. *Bull. Amer. Assoc. Petrol. Geol.* 1971, 58, 499-506.

23. Mackenzie, A.S.; Patience, R.L.; Maxwell, J.R.; Vandenbroucke, M.; Durand, B. Geochim. Cosmochim. Acta 1980, 44, 1709-1721.
24. van Graas, G.; de Leeuw, J.W.; Schenck, P.A.; Haverkamp, J. Geochim. Cosmochim. Acta 1981, 45, 2465-2474.
25. Espitalie, J. In Petroleum Geology of North West Europe; Brooks, J.; Glennie, K.W. Eds.; Graham and Trotman: London, 1987, pp. 71-86.
26. Thomas, B.M.; Moller-Pedersen, P.; Whiticar, M.F.; Shaw, N.D.; In Petroleum Geochemistry in Exploration of the Norwegian Shelf. Thomas, B.M. *et al.* Eds.; Graham and Trotman: London, 1985, 3-26.
27. Pearson, M.J.; Watkins, D.; Small, J.S.; In Developments in Sedimentology 35 van Olphen, H.; Veriale, F. Eds.; Elsevier: Amsterdam, 1982, pp. 665-675.
28. Dypvik, H.; Rueslatten, H.G.; Throndsen, T. Bull. Amer. Assoc. Petrol. Geol. 1979, 63, 2222-2226.
29. Barnard, P.C.; Cooper, B.S. In Petroleum Geology of the Continental Shelf of N.W. Europe; Illing, L.V.; Hobson, G.D. Eds.; Institute of Petroleum: London, 1981, pp. 169-175.
30. Illing, L.V.; Hobson, G.D. Eds. Petroleum Geology of the Continental shelf of N.W. Europe; Institute of Petroleum, London 1981,
31. Goff, J.C. J. Geol. Soc. Lond. 1983, 140, 445-474.
32. Mackenzie, A.S.; Maxwell, J.R.; Coleman, M.L.; Deegan C.E. Proc. 11th World Petrol. Cong. 1983, 2, 45-56.
33. Isaacs, C.M. Oil and Gas J. 1984, 82, 75-81.
34. Curiale, J.A.; Cameron, D.; Davis, D.V. Geochim. Cosmochim. Acta 1985, 49, 271-288.
35. Kruege, M.A. Org. Geochem. 1986, 10, 517-530.
36. Farrimond, P.; Comet, P.; Eglinton, G.; Evershed, R.P.; Hall, M.A.; Park, D.W.; Wardroper, A.M.K.; Mar. Petrol. Geol. 1984, 1, 340-354.
37. Williams, P.F.V.; Douglas, A.G.; Fuel 1986, 65, 1728-1734.
38. Williams, P.F.V.; Mar. Petrol. Geol. 1986, 3, 258-281.
39. Gallois, R.W. Rep. Inst. Geol. Sci. 1978, 78, 13.
40. Douglas, A.G.; Williams, P.F.V. In Organic maturation studies and fossil fuel exploration. Brooks, J. Ed.; Academic Press, 1981, 255-269.
41. Eglinton, T.I.; Douglas, A.G.; Rowland, S.J. Org. Geochem. 1988, 13, 655-663.
42. Lewan, M.D.; Winters, J.C.; McDonald J.H. Science 1979, 203, 897-899.
43. Lewan, M. Phil. Trans. R. Soc., Lond. 1985, A315, 123-134.
44. Larter, S.R.; Senftle, J.T. Nature (London) 1985, 318, 277-280.
45. Kohnen, M.E.L.; Eglinton, T.I.; Sinninghe Damsté, J.S.; de Leeuw, J.W. 1989 In Prep.

46. Gransch, J.A.; Posthuma, J. In Advances in Organic Geochemistry, 1973; Tissot, B.; Biennier, F. Eds.; Editions Technip: Paris, 1974, pp. 727-739.
47. Solli, H.; van Graas, G.; Leplat, P.; Krane, J. Org. Geochem. 1984, 6, 351-358.
48. Tissot, B.P.; Welte, D.H. Petroleum Formation and Occurrence (Second Edition). Springer-Verlag: Berlin, 1984, 699pp.
49. Braun, R.L.; Burnham, A.K. Energy and Fuels, 1987, 1, 153-161.
50. Quigley, T.M.; Mackenzie, A.S.; Gray, J.R. In Migration of hydrocarbons in sedimentary basins Doligez, B. Ed.; Editions Technip: Paris, 1987, pp. 649-655.
51. Larter, S.R. Geol. Rund. 1989, 78, 1-11.
52. Cooles, G.P.; Mackenzie, A.S.; Quigley, T.M. Org. Geochem. 1986, 10, 235-246.
53. Larter, S.R. Marine and Petrol. Geol. 1988, 5, 193-204.
54. Larter, S.R.; Horsfield, B. In Organic Geochemistry; Engel, M.; Macko, S. Eds. 1990, In Press
55. Boudou, J.P.; Boulegue, J.; Malechaux, L.; Nip, M.; de Leeuw, J.W.; Boon, J.J. Fuel 1987, 66, 1558-1569.
56. Tissot, B.P.; Pelet, R.; Ungerer, P. Bull. Amer. Assoc. Petrol. Geol. 1987, 71, 1445-1466.
57. Burnham, A.K.; Braun, R.L.; Gregg, H.R.; Samoun, A.M. Energy and Fuels 1987, 1, 452-458.
58. de Leeuw, J.W.; Sinninghe Damsté, J.S. In Geochemistry of Sulfur in Fossil Fuels; Orr, W.L.; White, C.M., Eds. ACS Symposium Series; American Chemical Society: Washington, DC, 1989; this volume.
59. Sinninghe Damsté, J.S.; Eglinton, T.I.; Rijpstra, W.I.C.; de Leeuw, J.W. In Geochemistry of Sulfur in Fossil Fuels; Orr, W.L.; White, C.M., Eds. ACS Symposium Series; American Chemical Society: Washington, DC, 1989; this volume.
60. Larter, S.R. In Petroleum Geochemistry in Exploration of the Norwegian Shelf; Thomas, B.M. *et al.* Eds. Graham and Trotman: London, 1985, pp. 269-286.
61. Eglinton, T.I.; Sinninghe Damsté, J.S.; de Leeuw, J.W.; Boon, J.J. 1989 Abstract, 14th International Meeting on Organic Geochemistry, Paris Sept. 1989.
62. Goossens, H.; Due, A.; de Leeuw, J.W.; van de Graaf, B.; Schenck P.A. Geochim. Cosmochim. Acta 1988, 52, 1189-1193.
63. Sinninghe Damsté, J.S.; de Leeuw, J.W.; Kock-van Dalen, A.C.; de Zeeuw, A.; de Lange, F.; Rijpstra, W.I.C.; Schenck P.A. Geochim. Cosmochim. Acta 1987, 51, 2369-2391
64. Sinninghe Damsté, J.S.; Rijpstra, W.I.C.; de Leeuw, J.W.; Schenck, P.A. Geochim. Cosmochim. Acta 1989, 53, 1323-1341.
65. Perakis, N. Ph.D. Thesis, University of Strasbourg, Strasbourg, 1986.