Available online at www.sciencedirect.com
SCIENCE DIRECT®
Organic Geochemistry 37 (2006) 369–383
Organic Geochemistry
www.elsevier.com/locate/orggeochem

Compositional differences in biomarker constituents of the hydrocarbon, resin, asphaltene and kerogen fractions: An example from the Jet Rock (Yorkshire, UK)

Stephen A. Bowden [a,b,*], Paul Farrimond [a,c], Colin E. Snape [d], Gordon D. Love [e]

[a] School of Civil Engineering and Geosciences, Drummond Building, University of Newcastle Upon Tyne, NE1 7RU, UK
[b] Department of Geology and Petroleum Geology, Meston Building, University of Aberdeen, Aberdeen AB24 3UE, UK
[c] Integrated Geochemical Interpretation Ltd, Hallsannery, Bideford, Devon EX39 5HE, UK
[d] School of Chemical, Environmental and Mining Engineering (SChEME), University of Nottingham, Nottingham NG7 2RD, UK
[e] Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Received 21 January 2005; accepted 7 August 2005
(returned to author for revision 2 June 2005)
Available online 19 January 2006

Abstract

Soluble and insoluble fractions of the Jet Rock sedimentary organic matter have been subjected to hydropyrolysis to evaluate their biomarker content. Hydropyrolysis is the temperature-programmed pyrolysis of organic matter in an open system fixed bed reactor under high hydrogen pressure in the presence of a sulfided molybdenum catalyst. The hydrocarbon products contain fossil lipids and biomarkers including high carbon number homologues and compounds with stereochemical configurations that are sensitive to exposure to high temperatures. Distinct differences exist between the concentrations and composition of biomarkers present in the different organic matter fractions. The sterane carbon number distribution, the dominant hopane carbon number and the proportions of tricyclic terpanes and extended tricyclic terpanes are different in each fraction, so biomarker parameters measured for different fractions are not directly comparable. The samples are of early oil window maturity and yet the quantities of biomarkers covalently bound into the kerogen fraction are of equal magnitude to the quantities that are present in the extractable aliphatic hydrocarbon fraction. However, the quantities of biomarkers in the polar resin and asphaltene fractions are two orders of magnitude lower and these two organic matter fractions contain biomarkers that are compositionally very different from the bulk of the biomarkers present in the total sedimentary organic matter. Isorenieratene derivatives were found in all fractions, indicating that green sulfur bacteria were present during sedimentation and that water column anoxia extended into the photic zone periodically if not continuously during the deposition of the Jet Rock.

1. Introduction

Bound biomarkers in sediments (biomarkers which are covalently bound into macromolecular organic matter) have been studied for the last two

* Corresponding author. Tel.: +44 1224 273467.
E-mail address: s.a.bowden@abdn.ac.uk (S.A. Bowden).

0146-6380/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.orggeochem.2005.08.024

decades as a source of molecular information. However, few studies have investigated the biomarkers present in more than one bound fraction of the total sedimentary organic matter OM. Of the studies that have considered more than one bound fraction, only a few have considered all the fractions and most have been non-quantitative. By comparing the yields of free hydrocarbon biomarkers obtained by solvent extraction to the yields of biomarkers obtained from the pyrolysis or chemical degradation of other fractions, it has become apparent that considerable quantities of biomarkers can be present in the bound phases (e.g. Eglinton and Douglas, 1988).

1.1. Previous studies of macromolecularly-bound biomarkers

Pyrolysis-gas chromatography (Mukhopadhyay et al., 1995), hydrous pyrolysis (Eglinton and Douglas, 1988) and chemical degradation (Schaeffer et al., 1995) studies have used whole rock or whole bitumen samples as substrates. The products, while accounting for all of the biomarkers of a given type that are present in the total sedimentary organic matter, do not distinguish which of the fractions (e.g. resin, asphaltene and kerogen) contain the bound biomarkers. Additionally, unless a labelling technique is used, it is not possible to distinguish free phase biomarkers from their covalently bound counterparts.

Pyrolysis has been previously applied to asphaltene and kerogen fractions to release bound biomarkers for oil–oil and oil–source rock correlation purposes (Behar et al., 1984; Garg and Philp, 1984; Behar and Pelet, 1985; Philp and Gilbert, 1985; Pelet et al., 1986; Del Rio et al., 1996; Mukhopadhyay et al., 1995). In most instances this has involved comparing the hydrocarbon composition of asphaltene or kerogen pyrolysates with the hydrocarbon fraction of free bitumen extracts or asphaltene pyrolysates. Frequently in pyrolysis investigations biomarkers present in the resin fraction (i.e. covalently held in compounds that elute in the most polar part of a maltene fraction) are overlooked. This may be because asphaltenes are thought to have a greater homogeneity in terms of molecular weight and composition than resins (Pelet et al., 1986) and, when the need to streamline analytical methods arises, asphaltenes are perceived to be a more reliable organic substrate than the resin fraction. As well as typically addressing only part of the total sedimentary organic matter, most pyrolysis studies of bound biomarkers, particularly those using flash pyrolysis, have been non-quantitative.

Chemical degradation studies are time intensive and produce their highest yields of analysable products from low molecular weight polar molecules. Thus, chemolysis studies have tended to focus on soluble resin fractions, as degradation reactions are unlikely to go to completion in kerogen fractions due to steric hindrance of potentially reactive binding sites (Rullkötter and Michaelis, 1990). The practical consequence of this has been that asphaltene-bound biomarkers (Richnow et al., 1991; Koopmans et al., 1996c, 1997, 1999), kerogen-bound biomarkers (Kohnen et al., 1991), or both (Köster et al., 1997), have often been left unstudied in otherwise comprehensive investigations detailing biomarker compositions and binding mechanisms.

Of the studies that have examined biomarkers bound into all organic matter fractions, total or individual triterpanes and steranes were not quantified (Jenisch et al., 1990) or used less mild pyrolysis techniques in comparison to open-system hydropyrolysis (Michels et al., 2000). Additionally, many studies have used multiple degradation methods, typically combining a chemical degradation scheme with a pyrolysis technique for analysing kerogen (van Kaam-Peters and Sinninghe Damsté, 1997; Höld et al., 1999; Koopmans et al., 1999). While this latter approach greatly broadens the bound biomarker analytical window it complicates the comparison of products, as different methods selectively release biomarkers with different compositions. At the time of writing, only one paper has documented the complete bound biomarker content of individual organic matter fractions (kerogen, asphaltenes, resin and free hydrocarbons) using a consistent method, for just three samples from the Huqf formation in Oman (Höld et al., 1999). Clearly the bound biomarker content of the various fractions of sedimentary organic matter is still relatively poorly represented in the literature.

1.2. This study

In this study bound biomarkers have been released by hydropyrolysis, a degradation method with a unique ability to generate reproducibly high yields of structurally-unaltered bound biomarkers from all types of macromolecular organic fractions (Love et al., 1995, 1996, 1998; Bishop et al., 1998; Murray et al., 1998). Three of the most widely studied groups of polycyclic aliphatic hydrocarbon bio-

markers (tricyclic terpanes, hopanes and steranes) have been quantified within the four constituent organic fractions (free hydrocarbons, resins, asphaltenes, kerogens) in sediments from the Jet Rock Formation (Jurassic; Yorkshire, UK), to compile a complete biomarker inventory. By comparing the compositions of the four fractions, and the way in which different biomarker pools relate to each other, the inherent biomarker bias between different fractions is highlighted.

2. Experimental

2.1. Sample suite, organic matter type and thermal maturity

The Jet Rock is the most organic-rich part of the Whitby Mudstone Formation (Pye and Krinnsley, 1986), an early Jurassic (lower Toarcian) deposit laid down in the distal part of an epicontinental sea that covered much of NW Europe. From its coastal outcrop at Port Mulgrave (Yorkshire, UK), a series of 14 mudstone samples that covered an 8 m vertical section including beds 41, 38, 37 and 35 (for bed numbering details, see Howarth, 1962) was collected. Whether sampling foreshore or cliff, care was taken to obtain samples not visibly affected by surface weathering or oxidation (i.e. all were sampled from greater than 5 cm depth). All the samples are part of Morris's (1979) restricted bituminous facies, interpreted to have been deposited during periods of seabed anoxia. Despite its name, and the presence of small carbonaceous flakes and jet, Jet Rock organic matter has been previously shown to be derived chiefly from marine algae and comprises mostly amorphous organic matter with relatively minor terrestrial contributions (Farrimond et al., 1989; Ibrahim, 1995; Sælen et al., 2000). This is borne out by the average Hydrogen Index [HI; determined according to Langford and Blanc-Valleron (1990) to avoid matrix effects] of 554 mg HC/g TOC, and generally high TOC values (Table 1), typical of an organic matter-rich Type II marine source rock (Peters, 1986). Rock-Eval maturity parameters suggest that the samples are at the threshold of oil generation (Peters, 1986; Production Index (PI) > 0.1 but relatively low T_{max} of ~430 °C; see Table 1). This agrees with previously measured vitrinite reflectance values of % $R_0 = 0.55$–0.69 (Ibrahim, 1995).

2.2. Sample handling, preparation and analysis

The 14 samples were rinsed in distilled water and large fragments were quartered twice. Segments were taken from each quarter set and powdered in brief bursts to a fine powder in a Tema mill.

Rock-Eval pyrolysis data (S1 and S2 peaks only), collected with a Rock-Eval II instrument and reported according to Peters (1986), were measured in duplicate and, due to their acceptable precision,

Table 1
Bulk chemical and Rock-Eval data

Sample[a]	Bed[b]	depth, m[c]	TOC**, %	Sulphur[d], %	HI[d], mg/g	EOM mg/g	PI[d]	T_{max}[d], °C
1	41	3	3.6	3.3	459	6.1	0.12	433
2	41	2	3.5	3.5	468	5.5	0.15	431
3	41	1.3	3.8	4.3	514	5.8	0.14	433
4	41	0.8	4.2	3.9	523	8.0	0.16	431
5	41	0.2	6.8	5.8	564	13.1	0.17	430
6	38	−0.2	3.9	4.5	585	5.7	0.15	431
7	38	−0.8	4.9	4.7	556	9.6	0.16	430
8	38	−1.4	5.6	4.4	546	13.1	0.18	430
9	38	−1.7	5.1	5.1	543	11.7	0.18	431
10	37	−1.9	5.9	6.6	524	14.6	0.20	428
11	35	−3.4	11.2	4.7	549	20.7	0.16	431
12	35	−3.6	12.4	5.1	523	17.7	0.15	430
13	35	−3.8	8.9	4.0	545	18.7	0.16	429
14	35	−4.2	8.9	5.9	519	18.1	0.15	427
Mean			6.34	4.7	530	12.0	0.16	430
SD			2.92	0.9	34.3	5.4	0.02	1.6

[a] Samples in bold were subjected to hydropyrolysis.
[b] According to Howarth (1962).
[c] Distance from base of bed 41.
[d] Duplicate average.

were averaged. TOC and whole rock sulfur data were determined with a Leco CS-244, with total organic carbon values measured on $HCl_{(aq)}$ decarbonated samples.

Eight samples with a range of Rock-Eval parameters and TOC values (e.g. not only the highest values) were selected for detailed biomarker investigation. Aliquots of powdered rock (50 g) were exhaustively soxhlet extracted for >48 h with 93:7 dichloromethane/methanol (DCM/MeOH) in the presence of activated copper. Yields of extractable organic matter (EOM) were obtained by accurately weighing one tenth (1/10 by volume) of the extract and multiplying the result.

The extracted bitumen component was then deasphaltened by a four stage 40-fold excess *n*-heptane asphaltene precipitation. In this procedure the bitumen was dissolved in DCM to which was added a 40-fold excess of *n*-heptane. The mixture was stirred for 30 min before being centrifuged until the solution was clear. The soluble maltene fraction was decanted off and the *n*-heptane removed using a rotor-vap; the asphaltene precipitate was redissolved in DCM and the mixing and centrifuging process repeated a further three times. The maltene fractions from the four precipitations were combined and further separated on a packed silica column into aliphatic hydrocarbon, aromatic hydrocarbon and resin fractions by elution with petroleum ether, DCM/petroleum ether (3:1 v/v) and DCM/MeOH (2:1 v/v), respectively.

To provide a stable substrate for hydropyrolysis, resin and asphaltene fractions were adsorbed from solution on to coarse–grained (30–70 mesh) silica gel. These silica-adsorbed fractions and the solvent-extracted sediment (containing the kerogen fraction) were then impregnated with an aqueous/methanol solution of the ammonium dioxy dithiomolybdate catalyst. Samples were then freeze-dried under vacuum to remove any water. Analytical hydropyrolysis was undertaken after Love et al. (1995). The process comprised fixed bed pyrolysis carried out at high hydrogen pressures (15 MPa), with a stepped temperature programme (50–260 °C at 300 °C min^{-1} holding for 1 min before heating from 260 to 500 °C at 8 °C min^{-1}) and in a fast sweeping (~6 dm^3 min^{-1}) hydrogen stream. This is a method proven to efficiently fragment geological macromolecules to generate principally a dichloromethane-soluble tar product, with high overall conversions of typically 85 wt% being achieved for pre-oil-window kerogen (Love et al., 1995, 1998; Murray et al., 1998). Products were recovered from a dry ice cooled trap, separated into fractions as described for the maltene fraction and analysed using gas chromatography–mass spectrometry (GC–MS).

In total, excluding duplicates and blanks, 30 samples were analysed using GC–MS: the aliphatic hydrocarbons of 8 free fractions, and those generated by hydropyrolysis of 6 resin fractions, 8 asphaltene fractions and 8 kerogens. An HP 5890 series 2 gas chromatograph fitted with an HP-1 column (fused silica; 0.25 μm film thickness; 30 m × 0.25 mm ID) and connected to an HP 5972 mass detector (ionization energy 70 eV; SIM mode) was used. The oven heating programme was 50–175 °C at 6 °C min^{-1} and then from 175 to 300 °C min^{-1}, finally holding at 300 °C for 4 min. Quantification was performed relative to an internal d_4-cholestane standard.

3. Results and discussion

3.1. Bitumen bulk composition and hydropyrolysis yields

The yields of products obtained by solvent extraction and by hydropyrolysis of the resin, asphaltene and kerogen fractions are shown in Table 2. The bitumen comprises only a minor part (<20%) of the Jet Rock OM, whilst the kerogen constitutes between 80 and 90 wt.% (based on Rock-Eval and HyPy recovery data). Of the bitumen, typically around 40 wt.% or less is in the polar fractions (resin and asphaltene). The greatest amount of aliphatic hydrocarbons has been generated by hydropyrolyis of the kerogen fraction (~140 mg/g TOC) and in all cases this is greater than the free aliphatic hydrocarbons recovered by solvent extraction (~75 mg/g TOC). The aliphatic hydrocarbon fractions generated from the resin and asphaltene hydropyrolysates constitute a small part of the total OM, being markedly less abundant than the free aliphatic hydrocarbon fraction.

3.2. Biomarker abundance

Biomarker concentrations (μg/g TOC) are reported for total steranes, hopanes and tricyclic terpanes, as well as for the individual compounds [C_{29} 5α,14α,17α(H) (20R) sterane, C_{30} 17α,21β(H) hopane and C_{23} 13β,14α(H) tricyclic terpane (Table 3; the individual compounds are shown in italics)].

Table 2
Yield of products (mg/g TOC initial SED) obtained by solvent extraction and hydropyrolysis of kerogen, asphaltene and resin fractions

Sample	Solvent extract			Kerogen				Asphaltene					Resin				
	EOM	Ali	Aro	Tot	Ali	Aro	Pol	Init	Tot	Ali	Aro	Pol	Init	Tot	Ali	Aro	Pol
1	169	25	46	424	147	107	78	15	10	5.8	1.2	1.9	14	4.8	1.0	0.1	0.7
3	152	37	10	383	146	132	34	10	5.2	1.3	0.6	0.6	23	nd	nd	nd	nd
5	193	61	30	545	128	181	172	8	0.7	0.2	0.3	0.6	53	9.3	5.1	1.3	2.6
6	145	61	42	451	157	200	90	10	2.6	0.1	0.4	0.3	58	18	7.2	1.5	4.2
7	199	30	16	463	132	124	112	18	8.7	2.9	1.8	2.0	23	4.4	0.3	0.2	0.5
9	223	80	37	445	131	127	146	29	12	12	1.2	2.2	55	18	14	2.0	7.5
11	185	72	42	465	166	171	191	15	8.7	0.7	0.7	7.4	31	12	3.1	2.3	5.5
13	211	65	54	449	82	137	187	22	3.5	0.8	1.0	0.7	50	nd	nd	nd	nd
Dup 11	nd	nd	nd	640	192	127	132	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd = not determined; Init = initial amount recovered from solvent extract; Tot = total products recovered after HyPy; Ali = aliphatic hydrocarbons; Aro = aromatic hydrocarbons; Pol = polar.

Table 3
Biomarker yields (μg/g TOC initial sample) obtained by solvent extraction (free) and from hydropyrolysis (resin, asphaltene and kerogen)

	Steranes ppm TOC								Tricyclic terpanes ppm TOC								Hopanes ppm TOC							
	Free		Res		Asph		Ker		Free		Res		Asph		Ker		Free		Res		Asph		Ker	
1	140	*8.4*	0.5	*0.1*	0.2	*0.05*	35	*12*	17	*2.6*	0.4	*0.1*	0.9	*0.2*	15	*4.2*	85	*25*	0.8	*0.1*	0.5	*0.1*	88	*11*
3	220	*15*	nd	nd	0.3	*0.1*	22	*6.4*	30	*4.2*	nd	nd	nd	nd	nd	nd	150	*41*	nd	nd	0.7	*0.1*	50	*5.8*
5	220	*16*	1.1	*0.4*	0.2	*0.1*	27	*9.6*	83	*11*	2.4	*0.5*	0.1	*0.02*	36	*5.9*	210	*57*	1.6	*0.2*	0.3	*0.04*	90	*11*
6	150	*8.9*	1.3	*0.4*	0.5	*0.1*	25	*6.6*	17	*2.5*	1	*0.2*	0.8	*0.1*	18	*2.8*	93	*26*	1.1	*0.1*	1.3	*0.2*	65	*8.1*
7	130	*9.1*	0.8	*0.3*	0.4	*0.1*	31	*8.9*	30	*3.9*	0.3	*0.1*	1.6	*0.3*	16	*3*	99	*27*	1.1	*0.1*	0.9	*0.1*	65	*7.7*
9	270	*18*	3	*0.7*	0.3	*0.1*	30	*9.1*	66	*8.5*	2.8	*0.4*	0.4	*0.1*	15	*2.6*	240	*66*	6	*1*	1	*0.2*	88	*11*
11	260	*16*	0.8	*0.2*	0.2	*0.1*	32	*8.6*	42	*6.2*	0.8	*0.1*	0.02	*<0.01*	16	*2.8*	260	*75*	1.4	*0.1*	0.5	*0.1*	100	*12*
13	180	*11*	nd	nd	0.2	*0.1*	26	*7.1*	30	*4*	nd	nd	0.2	*0.04*	12	*1.7*	180	*52*	nd	nd	0.7	*0.04*	50	*8.5*

Free = hydrocarbon fraction of solvent extract; Res = resin; Asph = asphaltene; Ker = kerogen hydropyrolysate.
Number in italics corresponds to: Sterane = 5α,14α,17α(H) (20R) C_{29} sterane; Hopane = 17α,21β (H) C_{30} hopane; Tricyclic = 13β,14α (H) C_{23} tricyclic terpane.

These specific biomarkers have been reported so as to allow a comparison between this study and the work of Höld et al. (1999) who quantified these specific biomarkers for four geochemical fractions from the Huqf formation Oman, and Murray et al. (1998) who performed a hydropyrolysis study of hopanes and steranes for the free hydrocarbon and kerogen fractions of the Kimmeridge Clay across the oil window. It is important to note that different standards were used for biomarker quantification and the methods used to prepare and isolate the fractions of sedimentary OM differ between these studies.

The Jet Rock samples show a relative enrichment in biomarkers, most notably the steranes, in the free hydrocarbon fraction compared with the macromolecular fractions (Table 3; note that sterane concentrations include diasteranes). The kerogen fraction is by far the dominant bound biomarker pool. It contains a lower proportion of total biomarkers than the free aliphatic hydrocarbon fraction, but these still account for approximately 30–50% of the total biomarkers, for the tricyclic terpanes and hopanes. The resin and asphaltene fractions do not appear to be quantitatively significant biomarker pools, containing less than 4% of the tricyclic terpanes and hopanes and less than 1% of the steranes, in accord with the data of Höld et al. (1999). However, in cases where these polar bitumen fractions constitute a much greater proportion of the OM, their quantitative significance as biomarker pools will be accordingly larger (Schaeffer et al., 1995).

The kerogen fraction has been previously shown to contain a high proportion of the total biomarkers; in fact, Murray et al. (1998) used the same hydropyrolysis procedure to demonstrate a greater abundance of kerogen-bound biomarkers than free extractable hydrocarbon biomarkers both at the beginning and the end of the oil window. Hopanes are more abundant than both tricyclic terpanes and steranes in the kerogen of the Jet Rock samples studied here (Table 3) and a similar pattern was also generally observed in the data of Höld et al. (1999), resulting in the hopanes/sterane ratio (Table 4)

Table 4
Biomarker parameters measured for free hydrocarbon fraction and hydrocarbon fractions of resin, asphaltene and kerogen hydropyrolysis products for Jet Rock sediments

	Free	Resin	Asphaltene	Kerogen	Free	Resin	Asphaltene	Kerogen
	Sterane ααα C_{29} S/S + R[a]				Hopane αβ C_{31} S/S + R[b]			
1	0.43	0.40	0.24	0.30	0.57	0.61	0.56	0.50
3	0.43	nd	0.23	0.33	0.56	nd	0.59	0.51
5	0.46	0.24	0.27	0.32	0.58	0.67	0.60	0.53
6	0.46	0.25	0.28	0.34	0.58	0.67	0.64	0.51
7	0.45	0.28	0.31	0.34	0.57	0.64	0.59	0.51
9	0.47	0.36	0.30	0.36	0.59	0.60	0.59	0.49
11	0.44	0.30	0.34	0.36	0.58	0.56	0.56	0.50
13	0.44	nd	0.24	0.37	0.59	nd	0.60	0.50
	Sterane C_{27} αααR/C_{29} αααR[c]				Hopane C_{30} βα/αβ + βα[d]			
1	0.54	1.11	0.41	1.17	0.15	0.18	0.28	0.36
3	0.69	nd	0.70	1.06	0.15	nd	0.27	0.40
5	0.86	1.16	1.03	1.24	0.14	0.20	0.27	0.37
6	0.68	0.99	1.00	0.90	0.16	0.22	0.28	0.37
7	0.81	2.40	1.19	1.05	0.14	0.20	0.27	0.37
9	0.83	1.08	1.23	1.17	0.14	0.17	0.25	0.39
11	0.70	1.12	1.24	0.88	0.15	0.24	0.26	0.38
13	0.72	nd	0.78	0.89	0.14	nd	0.27	0.38
	C_{27-29} αααR steranes/C_{30} αβ + βα hopane[e]				C_{30} αβ hopane/C_{23} αβ tricyclic terpane[f]			
1	1.1	1.9	2.2	1.6	11.0	1.8	0.6	4.1
3	1.1	nd	2.0	1.8	11.3	nd	nd	nd
5	0.7	3.6	2.7	1.2	5.9	0.5	2.0	3.0
6	1.0	6.1	1.3	1.4	12.3	0.9	2.3	4.7
7	0.9	3.5	2.1	1.9	8.2	2.2	0.6	4.0
9	0.7	1.5	0.9	1.2	9.0	2.7	3.3	6.7
11	1.1	3.3	1.1	1.2	11.0	1.3	nd	7.1
13	0.6	nd	3.3	1.4	14.9	nd	1.4	8.1

[a] Sterane ααα C_{29} S/S + R = C_{29} ααα sterane (20S)/C_{29} ααα sterane (20S) + C_{29} ααα sterane (20R).
[b] Hopane αβ C_{31} S/S + R = C_{31} αβ hopane (22S)/C_{31} αβ hopane (22S) + C_{31} αβ hopane (22R).
[c] Sterane C_{27} αααR/C_{29} αααR = C_{27} ααα sterane (20R)/C_{29} ααα sterane (20R).
[d] Hopane C_{30} βα/αβ + βα = hopane C_{30} 17β,21α (H)/hopane C_{30} 17β, 21α (H) + hopane C_{30} 17α,21β (H).
[e] C_{27-29} αααR steranes/C_{30} αβ + βα hopane = C_{27} ααα sterane (20R) + C_{28} ααα sterane (20R) + C_{29} ααα sterane (20R)/hopane C_{30} 17β,21α (H) + hopane C_{30} 17α,21β (H).
[f] C_{30} αβ hopane/C_{23} βα tricyclic terpane = hopane C_{30} 17α,21β (H)/C_{23} 13β,14α (H) tricyclic terpane.

being consistently higher for kerogen-bound biomarkers than for free hydrocarbons. This could be due, at least in part, to the fact that hopanes are generally bound into macromolecules via a larger number of binding sites than both steranes (Hofmann et al., 1991; Rohmer, 1993) and tricyclic terpanes (Richnow et al., 1991); this may lead to their preferential incorporation into macromolecules, particularly kerogen, during early diagenesis, and their retention in bound fractions further into the oil window (Hofmann et al., 1991). Steroidal hydrocarbons are probably particularly abundant in the free aliphatic hydrocarbon fraction due to the early diagenetic formation of diasteranes (subsequently reduced to diasteranes; De Leeuw et al., 1989; van Kaam-Peters et al., 1998), which are not amenable to incorporation due to the hindered position of their only potential binding site, the double bond. In addition, steranes are generally bound by just a single linkage in the A-ring, sometimes supplemented by a binding site at the former position of a double bond in the side chain of the precursor sterol, leading to their preferential release from macromolecules (Eglinton and Douglas, 1988; Kohnen et al., 1991) and higher abundance in the free hydrocarbon fraction.

3.3. Biomarker composition

3.3.1. n-Alkanes

Fig. 1 shows the total ion chromatogram (TIC) of the free aliphatic hydrocarbon fraction and the

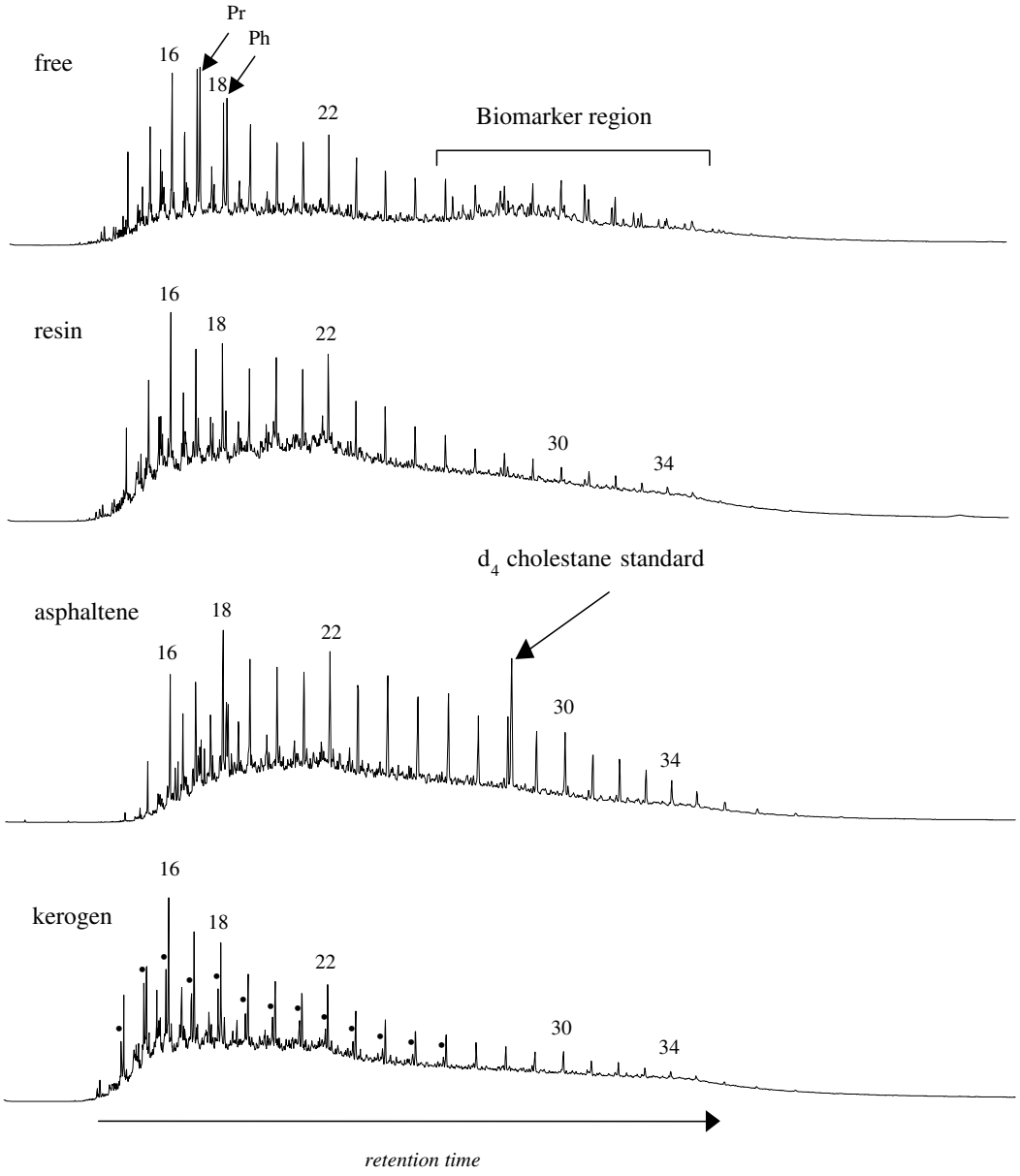

Fig. 1. TIC chromatogram of aliphatic hydrocarbons released from each of the organic matter fractions in a Jet Rock sediment (sample 5). There is only a very slight stratigraphic variation in the *n*-alkane traces.

aliphatic hydrocarbon fractions of the resin, asphaltene and kerogen hydropyrolysates of sample 5. The *n*-alkanes range up to C_{38} and beyond in all fractions, but the polycyclic biomarker peaks (hopanes and steranes) are only prominent in the TIC trace of the free aliphatic hydrocarbon fraction; *n*-Alkanes are only observed in significant amounts in the kerogen hydropyrolysates, as previously observed (Love et al., 1995, 1998; Murray et al., 1998). Of particular note are the pronounced C_{16} and C_{18} *n*-alkanes in the hydropyrolysis products (Fig. 1), a feature which has also been observed in chemical degradation products of resins and asphaltenes (Richnow et al., 1991). This suggests that even carbon number *n*-alkanes predominate as geomacromolecule sub-units, and that hydropyrolysis is a relatively mild degradation technique capable of liberating and preserving carbon number distributions in a similar manner to chemical degradation techniques. Indeed, hydropyrolysis experiments with

carboxylic acid model compounds (Love et al., 2005) show that complete reduction of the carboxyl group is favoured over decarboxylation (which typically occurs when performing pyrolysis in an inert gas atmosphere; e.g. He or N_2). Thus, the prominence of C_{16} and C_{18} *n*-alkanes represents a fossil lipid signature originating in the dominant carbon numbers of organic acids present in eukaryote and prokaryote cell membranes.

3.3.2. Steranes

All fractions contain C_{27} to C_{30} steranes dominated by the 5α,14α,17α(H) configuration (Fig. 2); in the bound fractions the 20R isomers are significantly more abundant than the 20S isomers (Table 4), whilst in the free hydrocarbon fraction the 20S and 20R isomers are in comparable abundance; 5β,14α,17α(H) steranes are clearly distinguished in the hydropyrolysates of the kerogen, resin and

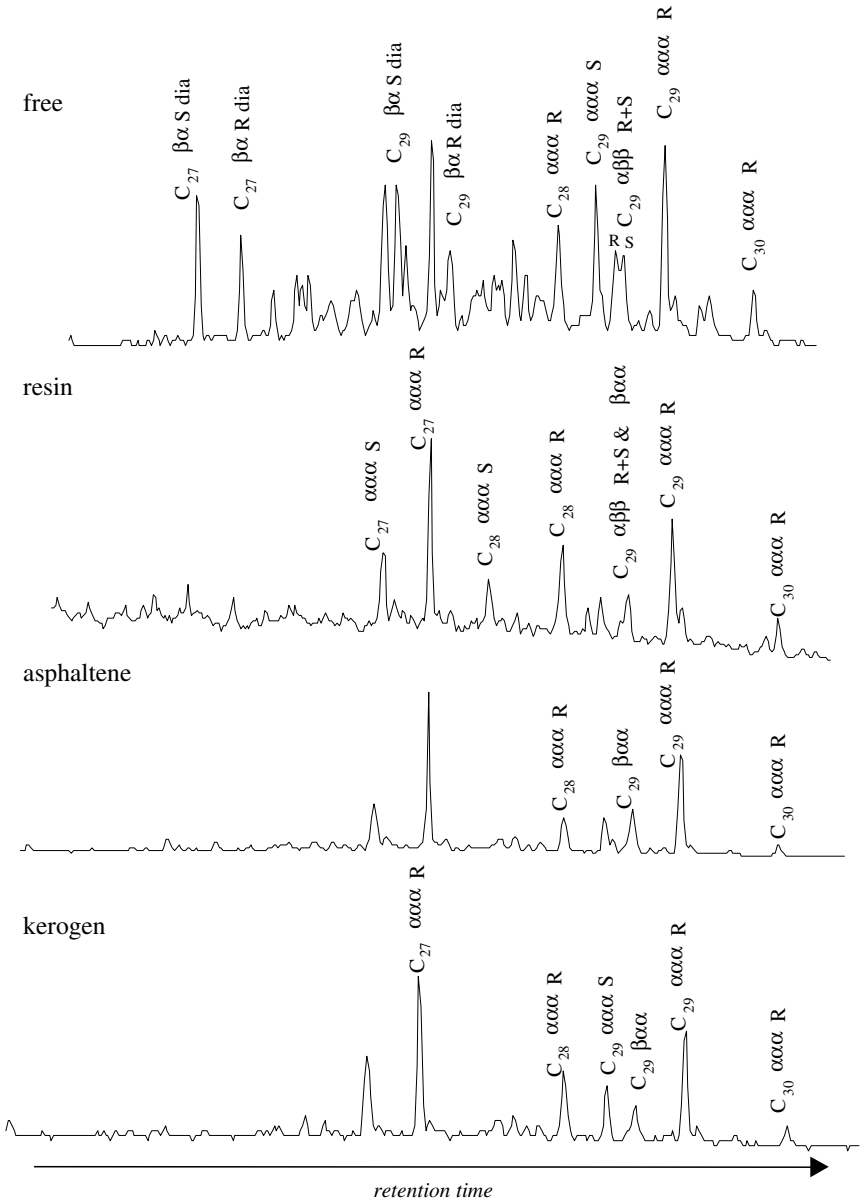

Fig. 2. Ion chromatograms (*m/z* 2217) for sample 5. C_{27} βαS dia = C_{27} 13β,17α(H) (20S) diasterane; C_{27} βαR dia = C_{27} 13β,17α(H) (20R) diasterane; C_{29} βαS dia = C_{29} 13β,17α(H) (20S) diasterane; C_{29} βαR dia = C_{29} 13β,17α(H) (20R) diasterane; C_{27} αααS = C_{27} 5α,14α,17α(H) (20S) sterane; C_{27} αααR = C_{27} 5α,14α,17α(H) (20R) sterane; C_{27} αββR + S = C_{27} 5α,14β,17β(H) (20S) + (20R) steranes; C_{27} βαα = C_{27} 5β,4α,17α(H) sterane.

asphaltene fractions but not in the free aliphatic hydrocarbon fraction, which contains the greatest proportion of 5α,14β,17β(H) steranes (Fig. 2). The αββ sterane isomers are also present to lesser degrees in the resin, asphaltene and kerogen fractions (seen in *m*/*z* 218 mass chromatograms; not shown) but they co-elute with βαα isomers and are less clearly resolved. As reported previously (Peters et al., 1990; Love et al., 1995; Murray et al., 1998), sterane isomerisation is more advanced in the free aliphatic hydrocarbon fractions compared with the bound fractions (Table 4). This is interpreted to be a consequence of the steric protection afforded to the bound biomarkers by their covalent binding within bulky macromolecular host networks.

Diasteranes are present in the free aliphatic hydrocarbon fractions (Fig. 2), but only trace amounts are found in some (and not all) of the bound biomarker fractions. The very low concentrations of diasteranes in the resin and asphaltene hydropyrolysates probably represent free compounds that are chelated by asphaltene and resin aggregates (Gurgey, 1998) as the compounds are not visible in kerogen hydropyrolysates. An instance of apparently-bound diasteranes in the maltene fraction of a source rock extract was reported by Peng et al. (1999), but most previous work suggests that diasteranes are not bound into asphaltene or kerogen fractions (Seifert, 1978; Philp and Gilbert, 1985; Murray et al., 1998; Strausz et al., 1999). Rather, they are formed from exclusively free phase rearrangement reactions of sterenes, involving clay mineral catalysis (De Leeuw et al., 1989), and the intermediate diasterenes are unlikely to become bound into macromolecules due to the hindered site of their double bond (De Leeuw et al., 1989; van Kaam-Peters et al., 1998).

Ternary plots of sterane carbon number are often used to facilitate oil–oil and oil–source rock correlation and to provide a general comparison of depositional environments (Peters and Moldowan, 1993). Significantly however, the steranes of the different organic fractions within a particular sample have different carbon number distributions (Fig. 3). In general, bound steranes appear to be slightly enriched in the C_{27} homologues compared with the free aliphatic hydrocarbon fraction. This has been previously observed in both hydrous pyrolysis products (Fowler and Brooks, 1987) and chemical degradation products (Richnow et al., 1991). This difference is significant at the 95% confidence interval (based on ANOVA results; i.e. ANalysis Of VAriance), but would probably not impact on the distinguishing of source rocks from significantly different depositional environments by using biomarkers from different organic fractions. Additionally, other key compounds indicative of specific depositional environments, such as the C_{30} sterane (present in all fractions) could be used to supplement parameters based on the regular steranes.

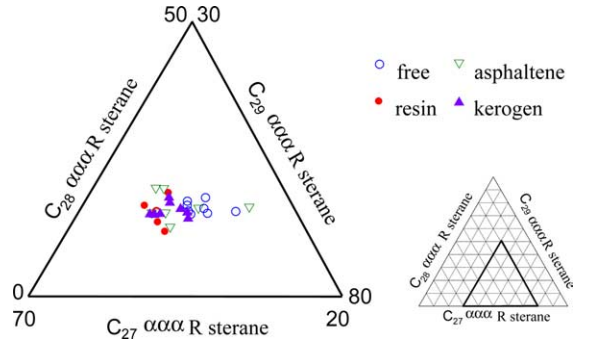

Fig. 3. Ternary plot showing sterane 5α,14α,17α (H) (20R) composition of the various organic fractions, and that the bound fractions are generally enriched in C_{27} steranes compared to the free steranes.

3.3.3. Hopanes

All fractions contain C_{27} to C_{35} (except C_{28}) hopanes, with 17α,21β(H) and 17β,21α(H) isomers being the dominant stereochemistry. However, the relative proportions differ in each fraction (Fig. 4). The free hydrocarbon fraction hopane profile is always dominated by C_{30} αβ hopane. Hopanes in the resin and asphaltene hydropyrolysis products (Fig. 4) show more varied carbon number distributions in which C_{32} (resin) or C_{31} αβ homohopanes, and C_{27} Tm hopanes (asphaltene) can also predominate, although this varies between samples. As noted in a previous study (Bishop et al., 1998), hopanes released from the kerogen phase of ancient sediments by hydropyrolysis are often dominated by the C_{29} hopane homologue. In contrast to the resin and asphaltene fractions the kerogen fraction displays a degree of uniformity in hopane composition similar to that of the free hydrocarbons.

The rearranged C_{27} and C_{29} 18α-neohopanes (Ts and C_{29}Ts) are significant only in the free hydrocarbon fractions and in the resin and asphaltene hydropyrolysis products of some of the samples. In the Jet Rock, their partitioning between fractions is broadly similar to that of the diasteranes, i.e. present in only small amounts in the hydropyrolysates due to the partial trapping of free hydrocarbons

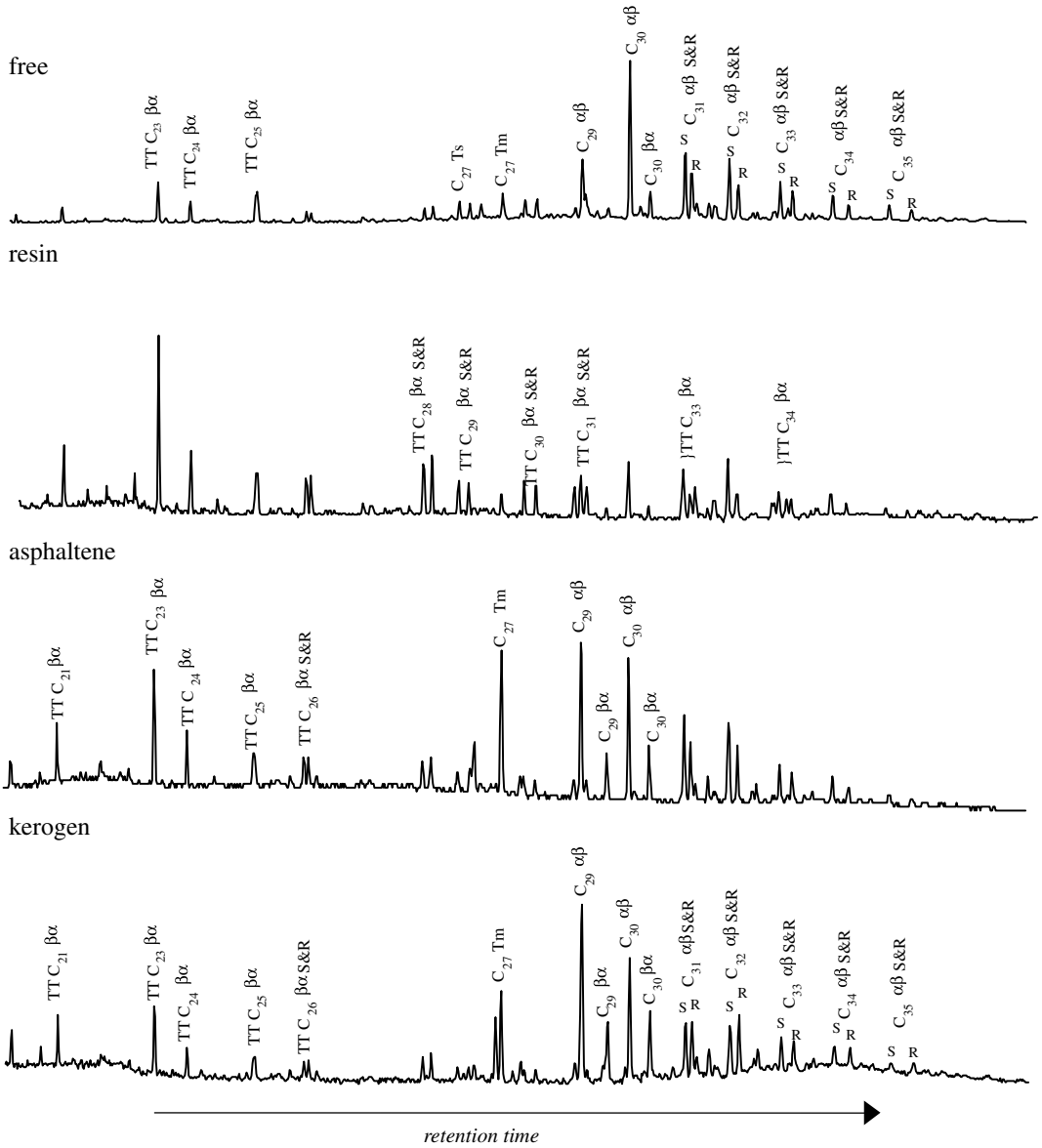

Fig. 4. Ion chromatograms (*m*/*z* 191). TT C_{23} $\beta\alpha = C_{23}13\beta(H),14\alpha(H)$ tricyclic terpane (note various tricyclic terpane isomers are not individually labelled); $C_{27}Ts = C_{27}$ 18α (H)-22,29,30 trisnorneohopanes; $C_{27}Tm = 17\alpha(H)$-22,29,30 trisnorhopane; C_{29} $\alpha\beta = C_{29}17\alpha(H),21\beta(H)$ hopane; C_{29} $\beta\alpha = C_{29}17\beta(H),21\alpha(H)$ hopane; C_{31} αβ S = C_{31} 17α(H),21β(H) (22S) hopane; C_{31} αβ R = $C_{31}17\alpha(H),21\beta(H)$ (22R) hopane. Tricyclic terpanes are more prominent in the resin and asphaltene fractions than in the free and kerogen fractions.

within the resin fraction during preparative column chromatography. It is likely that only negligible quantities of 18α-neohopanes are actually bound into the resin, asphaltene and kerogen fractions of the Jet Rock sedimentary organic matter.

Hopanes of βα configuration are more abundant, relative to their αβ hopane counterparts, in the bound fractions than in the free aliphatic hydrocarbon fraction and their relative abundance decreases progressively in the order: kerogen > asphaltene > resin > free hydrocarbon fractions (Table 4). Furthermore, the (22S)/(22S + 22R) parameter for C_{31} hopanes is lower for the kerogen-bound hopanes than those of the other fractions (Table 4), and suggests that the hopanes bound into kerogen are more protected than those of the other fractions. The higher values of this parameter in some of the resin fractions may be caused by co-eluting C_{33} extended tricyclic terpanes, or the defunctionalisation during hydropyrolysis of free hopanoic acids

that co-eluted with the macromolecular component of the resin fraction during preparative column chromatography.

3.3.4. Tricyclic terpanes

C_{20} to C_{30} 13β(H),14α (H) tricyclic terpanes are found in all fractions of all the samples. They are less abundant than the hopanes in *m/z* 191 mass chromatograms of the free aliphatic hydrocarbon and kerogen fractions (Fig. 4 and Table 3), but are of comparable abundance relative to the hopanes in the resin and asphaltene fractions. Due to the small proportion of the total OM comprised by the resin and asphaltene fractions (Table 2), the total tricyclic terpane content (adding contributions from all OM fractions in the sediment) is less than the hopane content (Table 3). Extended ($>C_{30}$) tricyclic terpanes are most visible in the chromatograms of the asphaltene and resin fractions where they range up to at least C_{34}, although they can also be seen to be very minor constituents of the free hydrocarbon fraction. Extended tricyclic terpanes have previously been found to be relatively enriched in chemical degradation products of resins in early oil window maturity (0.83% R°) coals (Jenisch et al., 1990), as well as in the resin chemical degradation products of a Tasmanites oil shale (McCaffrey et al., 1994). Tricyclic terpanes have been shown to be generated from kerogens at a relatively higher thermal maturity than homohopanes (Aquino Neto et al., 1983; Peters et al., 1990) and this suggests that tricyclic terpanes are bound into macromolecular organic matter by strong, and possibly multiple, covalent linkages. Deuterium incorporation during chemical degradation suggests that tricyclic terpanes, like hopanes, are bound into macromolecules via two or more sites on their side chain (Richnow et al., 1991; McCaffrey et al., 1994; Peng et al., 1997) that probably correspond to sites of conjugation in the biological precursors. Tricyclic terpanes are also reported to be bound into macromolecules via the terminal position on their side chain (Peng et al., 1999). Tricyclic terpanes are expected then to be enriched relative to hopanes and steranes in late oil window and overmature source rocks. From the Jet Rock biomarker profiles and abundances, it is apparent that tricyclic terpanes are enriched relative to hopanes and steranes in resin and asphaltene fractions in comparison with kerogen and free hydrocarbon products. This probably reflects the higher degree of covalent cross linking in kerogens compared with resins and/or a greater proportion of weak C–S (to C–O or C–C) relative bonds connecting biomarker structures into resins than other macromolecular fractions.

3.3.5. Aryl Isoprenoids

This study, in contradiction to previous work (Sælen et al., 2000), has found aryl isoprenoids in the free and kerogen fractions of every sample of the Jet Rock that was examined with GC–MS, and diaryl isoprenoids (derivatives of isorenieratene) in all of the free aromatic hydrocarbon fractions. The C_{13} to C_{16} homologues of 1-isoalkyl-2,3,6-trimethylbenzene were identified in the free and kerogen fractions from diagnostic spectra and comparison to relative retention times presented in other published work (Summons and Powell, 1987; Requejo et al., 1992). The diaryl isoprenoids (Fig. 5) were identified from their mass spectra and have previously been reported by Koopmans et al. (1996a). The aryl isoprenoids are most prominent in the free hydrocarbon fraction, where a clear series ranging up to C_{23} can be seen.

No spectra with a strong base peak at *m/z* 133 and clear molecular ion at *m/z* 546, that are diagnostic of isorenieratane, could be obtained. However, diagnostic spectra for C_{32} and C_{33} diaryl isoprenoids that are derived from isorenieratene via the formation of an eight membered ring transition state during diagenesis (Koopmans et al., 1996a; Clifford et al., 1998) were obtained, and these are shown in Fig. 5.

These diaryl isoprenoids are derived from isorenieratene, which is an undisputed biomarker for Chlorobiaceae (green sulfur bacteria) and can also be a potential source of aryl isoprenoids (Summons and Powell, 1986). However, aryl isoprenoids can also be derived from other sources, such as a β-carotene from algae and other organisms (Koopmans et al., 1996b), and those from Chlorobiaceae can only be distinguished using stable carbon isotopic data to show that the compounds are enriched in ^{13}C and were formed via the reversed TCA cycle. The presence of diaryl isoprenoids in all the sections of the Jet Rock sequence suggests that euxinic conditions prevailed throughout the Toarcian water column in the area of deposition.

4. Implications for biomarker studies

The differences in biomarker abundance and composition between the different organic matter fractions of a particular sediment sample will impact

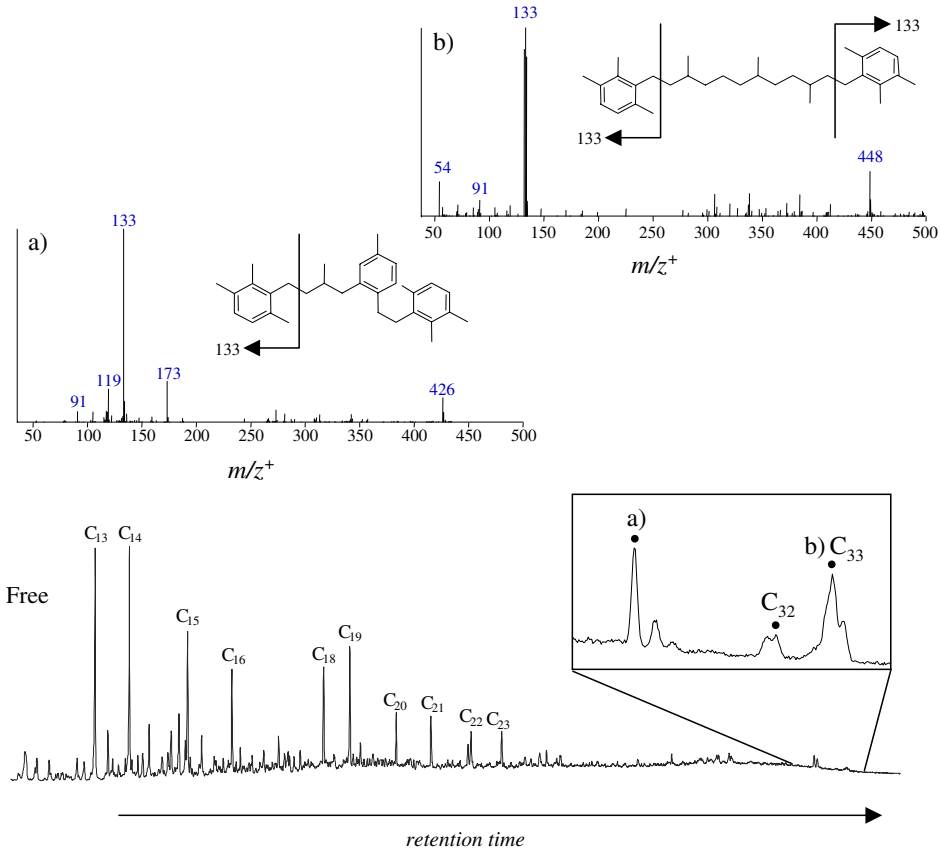

Fig. 5. Ion chromatograms (m/z 133) for free aromatic fraction showing presence of 1-isoalkyl-2,3,6-trimethylbenzenes and C_{32} and C_{33} diaryl isoprenoids (labelled C_{32} and C_{33} (b) and a diagenetic product of isorenieretane (a)) first identified by Koopmans et al. (1996).

upon biomarker interpretation in a number of ways. We have shown that the different organic matter pools (free hydrocarbon, resin, asphaltene and kerogen) have different biomarker compositions. For example, the m/z 191 chromatograms of the different fractions (Fig. 4) show major differences in the proportions of tricyclics to hopanes and in the hopane carbon number distributions: the resin and asphaltene fingerprints show very prominent extended tricyclic terpanes, and more prominent C_{32} hopanes. The sterane profiles of the different fractions are also different (see below). These observations suggest that care will be needed when correlating oils using biomarkers from different fractions of sedimentary organic matter. However, the fact that the C_{30} ααα regular sterane, an indicator of marine environmental conditions, was found in all organic matter fractions could prove useful in distinguishing oils from marine and non-marine sources using biomarker fingerprints obtained from the different fractions of sedimentary OM.

The difference in sterane composition between the fractions (Fig. 3) may represent a true compositional difference, or sterane cracking during the hydropyrolysis. The proportion of C_{27} steranes is known to increase in oils with maturity (Peters and Moldowan, 1993) and this could be envisaged to arise from the cracking of the alkyl side chain of higher number steranes (C_{28}–C_{30}). Similarly, laboratory pyrolysis techniques might induce some side chain cracking, and thus the hydropyrolysis products of this study and the hydrous-pyrolysis products of Fowler and Brooks (1987) might have become enriched in C_{27} steranes by this route. However, a recent study has shown that the amount of steroid sidechain cleavage occurring during hydropyrolysis is low (Love et al., 2005), and therefore can not account for the differences in sterane carbon number distribution that are observed for the Jet Rock.

Another explanation for the apparent enrichment of kerogen pyrolysis and degradation products in

C_{27} steranes exists as the kerogen phase has previously been reported as being enriched in algal-derived biomarkers (e.g. C_{27} steranes), whilst the extractable phase has been noted to be enriched in higher plant biomarkers (e.g. C_{29} steranes; Love et al., 1998). The quantities of kerogen-bound steranes are significant enough that their release during oil generation would enrich the free aliphatic hydrocarbon fraction in C_{27} steranes, consistent with the known increase in the proportion of C_{27} steranes with thermal maturity mentioned previously (Peters and Moldowan, 1993). Thus, it is possible that the kerogen-bound biomarker signal is naturally enriched in C_{27} steranes from the early incorporation of biomarkers into the kerogen phase during kerogen formation, and that it simply overwrites or alters the free fraction biomarker signal during catagenesis as biomarker hydrocarbons are released into the free phase.

The samples of this study are of marginal oil window maturity and, despite the expectation that many biomarkers would have been released into the free fraction by this stage of maturation, significant quantities of biomarkers are still present in the kerogen fraction. The obvious implication of this finding is that the kerogen fraction merits attention in geochemical studies as it represents a major biomarker pool even at the onset of oil generation, an observation that accords with a previous hydropyrolysis study of bound biomarkers across the oil window (Murray et al., 1998). Only in very immature and high organic sulfur sediments and rocks, where resin and asphaltene molecules comprise a greater proportion of sedimentary organic matter (e.g. the Green River Formation, see Eglinton and Douglas, 1988; Bishop et al., 1998), would it appear that resins and asphaltenes can be present in great enough quantities for biomarkers bound into these fractions to be a significant biomarker pool. In general, it would seem that only the kerogen fraction contains sufficient quantities (Table 3) of bound biomarkers at this stage of the oil window (the onset of oil generation) to alter the composition of the free aliphatic hydrocarbon fraction biomarkers in source rocks.

5. Conclusions

Analysis of the hydropyrolysis products of the Jet Rock sedimentary organic matter suggests that a large part of the organic matter comprises aliphatic hydrocarbons that are covalently bound into the kerogen fraction. Even though the Jet Rock is of near oil window thermal maturity the kerogen contains orders of magnitude more biomarkers than the resin and asphaltene fractions.

There is not only a difference in the quantity of biomarkers present in the different fractions, but also a distinct difference in the relative proportions of different biomarker types. The resin and asphaltene fractions are the most compositionally distinct and contain different proportions of tricyclic terpanes to extended tricyclic terpanes, and hopane and sterane homologues to the free and kerogen fractions. For some biomarker parameters these differences are significant to the extent that in certain instances they might prevent the direct comparison of biomarker parameters measured for different fractions. However, if these differences are taken into consideration, given the quantities of biomarkers and fossil lipids that are present in the kerogen fraction even at near oil window thermal maturity, the kerogen fraction represents a potential source of important molecular geochemical information.

Acknowledgements

Paul Donohoe and Kim Noke are thanked for GC-MS analyses, as is NERC for PhD award GT. 04/99//188/ES. Miguel Castro-Diaz is also thanked for assistance with hydropyrolysis. The manuscript was greatly improved by the comments of Martin Koopmans and Brian Cooper. Richard Pancost is also thanked for his comments on an earlier version of the manuscript.

Associate Editor—**Martin Fowler**

References

Aquino Neto, F.R., Trendel, J.M., Restle, A., Connan, J., Albrecht, P.A., 1983. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleum. In: Bjorøy, M. et al. (Eds.), Advances in Organic Geochemistry 1981. J. Wiley and Sons, New York, pp. 659–676.

Behar, F., Pelet, R., Roucache, J., 1984. Geochemistry of asphaltenes. Organic Geochemistry 6, 587–595.

Behar, F., Pelet, R., 1985. Pyrolysis-gas chromatography applied to organic geochemistry. Structural similarities between kerogens and asphaltenes from related rock extracts and oils. Journal of Analytical and Applied Pyrolysis 8, 173–187.

Bishop, A.N., Love, G.D., McAulay, A.D., Snape, C.E., Farrimond, P., 1998. Release of kerogen-bound hopanoids by hydropyrolysis. Organic Geochemistry 29, 989–1001.

Clifford, D.J., Clayton, J.L., Sinninghe Damsté, J.S., 1998. 2,3,6-/3,4,5-Trimethyl substituted diaryl carotenoid derivatives (Chlorobiaceae) in petroleums of the Belarussian Pripyat River Basin. Organic Geochemistry 29, 1253–1267.

De Leeuw, J.W., Cox, H.C., van Graas, F.W., van de Meer, F.W., Peakman, T.M., Baas, J.M.A., van de Graaf, B., 1989. Limited double bond isomerisation and selective hydrogenation of steranes during early diagenesis. Geochimica et Cosmochimica Acta 53, 903–909.

Del Rio, J.C., Martin, F., Gonzalez-Vila, F.J., Verdejo, T., 1996. Chemical structural investigation of asphaltenes and kerogens by pyrolysis-methylation. Organic Geochemistry 23, 1009–1022.

Eglinton, T.I., Douglas, A.G., 1988. Quantitative study of biomarker hydrocarbons released from kerogens during hydrous pyrolysis. Energy and Fuels 2, 81–89.

Farrimond, P., Eglinton, G., Brassel, S.C., Jenkyns, C., 1989. Toarcian anoxic events in Europe: an organic geochemical study. Marine and Petroleum Geology 6, 136–147.

Fowler, M.G., Brooks, P.W., 1987. Organic Geochemistry of Western Canada Basin Tar Sands and Heavy Oils. 2. Correlation of Tar Sands Using Hydrous Pyrolysis of Asphaltenes. Energy and Fuels 1, 459–467.

Garg, A.K., Philp, R.P., 1984. Pyrolysis-gas chromatography of asphaltenes/kerogens from source rocks of the Gandhar Field, Cambay Basin, India. Organic Geochemistry 21, 383–392.

Gurgey, K., 1998. Geochemical effects of asphaltene separation procedures: changes in sterane, terpane and methylalkane distributions in maltenes and asphaltene co-precipitates. Organic Geochemistry 29, 1139–1147.

Hofmann, I.C., Hutchinson, J., Robson, J.N., Chicarelli, M.I., Maxwell, J.R., 1991. Evidence for sulphide links in a crude oil asphaltene and kerogens from reductive cleavage by lithium in ethylamine. Organic Geochemistry 19, 371–387.

Höld, I.M., Schouten, S., Jellema, J., Sinninghe Damsté, J.S., 1999. Origin of the free bound midchain methyl alkanes in oils, bitumens and kerogens of the marine Infracambrian Huqf Formation, Oman. Organic Geochemistry 30, 1411–1428.

Howarth, M.K., 1962. The Jet Rock Series and the Alum Shale Series of the Yorkshire Coast. Proceedings of the Yorkshire Geological Society 303, 381–422.

Ibrahim, B.A., 1995. A geochemical study of the Jet Rock, the Kimmeridge Clay and the associated concretions. M. Phil. Thesis, University of Newcastle Upon Tyne.

Jenisch, A., Richnow, H.H., Michaelis, W., 1990. Chemical structural units of macromolecular coal components. Organic Geochemistry 16, 917–929.

Kohnen, M.E., Sinninghe Damsté, J.S., Kock-van Dalen, A.C., De Leeuw, J.W., 1991. Di- or polysulphide-bound biomarkers in sulphur rich geomacromolecules as revealed by selective chemolysis. Geochimica et Cosmochimica Acta 55, 1375–1394.

Koopmans, M.P., Köster, J., van Kaam-Peters, H.M.E., Kenig, F., Shouten, S., Hartgers, W.A., De Leeuw, J.W., Sinninghe Damsté, J.S., 1996a. Diagenetic and catagenetic products of isorenieratene: Molecular indicators for photic zone anoxia. Geochimica et Cosmochimica Acta 60, 4467–4496.

Koopmans, M.P., Schouten, S., Kohnen, M.E.L., Sinninghe Damsté, J.S., 1996b. Restricted utility of aryl isoprenoids as indicators for photic zone anoxia. Geochimica et Cosmochimica Acta 60, 4873–4876.

Koopmans, M.P., de Leeuw, J.W., Lewan, M.D., Sinninghe Damsté, J.S., 1996c. Impact of dia- and catagenesis on sulphur and oxygen sequestration of biomarkers as revealed by artificial maturation of an immature sedimentary rock. Organic Geochemistry 25, 391–426.

Koopmans, M.P., Schaeffer-Reiss, C., De Leeuw, J.W., Lewan, M.D., Maxwell, J.R., Schaeffer, P., Sinninghe Damsté, J.S., 1997. Sulphur and oxygen sequestration of n-C_{37} and n-C_{38} unsaturated ketones in an immature kerogen and the release of their carbon skeletons during early stages of thermal maturation. Geochimica et Cosmochimica Acta 61, 2397–2408.

Koopmans, M.P., Rijpstra, W.I.C., Klapwijk, M.M., De Leeuw, J.W., Lewan, M.D., Sinninghe Damsté, J.S., 1999. A thermal and chemical degradation approach to decipher pristane and phytane precursors in sedimentary organic matter. Organic Geochemistry 30, 1089–1104.

Köster, J., van Kaam-Peters, H.M.E., Koopmans, M.P., De Leeuw, J.W., Sinninghe Damsté, J.S., 1997. Sulphurisation of homohopanoids: Effects on carbon number distribution, speciation, and 22S/22R epimer ratios. Geochimica et Cosmochimica Acta 61, 2431–2452.

Langford, F.F., Blanc-Valleron, M.M., 1990. Interperating Rock-Eval pyrolysis data using graphs of pyrolizable hydrocarbons vs. total organic carbon. American Association of Petroleum Geologists 74, 799–804.

Love, G.D., Snape, C.E., Carr, A.D., Houghton, R.C., 1995. Release of covalently-bound biomarkers in high yields from kerogen via catalytic hydropyrolysis. Organic Geochemistry 23, 981–986.

Love, G.D., Snape, C.E., Carr, A.D., Houghton, R.C., 1996. Changes in molecular biomarker and bulk carbon skeletal parameters of vitrinite concentrates as a function of rank. Energy and Fuels 10, 149–157.

Love, G.D., Snape, C.E., Fallick, A.E., 1998. Differences in the mode of incorporation and biogenicity of the principal aliphatic constituents of a Type I oil shale. Organic Geochemistry 28, 797–811.

Love, G.D., Bowden, S.A., Jahnke, L.L., Snape, C.E., Campbell, C.N., Day, J.G., Summons, R.E., 2005. An optimized catalytic hydropyrolysis method for the rapid screening of microbial cultures for lipid biomarkers. Organic Geochemistry 36, 63–82.

McCaffrey, M.A., Simoneit, B.R.T., Aquino Neto, F.R., Moldowan, J.M., 1994. Functionalised biological precursors of tricyclic terpanes: information from sulfur-bound biomarkers in Permian Shale. Organic Geochemistry 21, 481–487.

Michels, R., Burkle, V., Mansuy, L., Langlois, E., Ruau, O., Landais, P., 2000. Role of polar compounds as source of hydrocarbons and reactive medium during the artificial maturation of Mahakam Coal. Energy and Fuels 14, 1059–1071.

Morris, K.A., 1979. A classification of Jurassic marine shale sequences: an example from the Toarcian (Lower Jurassic) of Great Britain. Palaeogeography, Paleoclimatology and Palaeoecology 137, 157–175.

Mukhopadhyay, P.K., Wade, J.A., Kruge, M.A., 1995. Organic facies and maturation of Jurassic/Cretaceous rocks, and possible oil-source rock correlation based on pyrolysis of asphaltenes, Scotian Basin, Canada. Organic Geochemistry 22, 85–104.

Murray, I.P., Love, G.D., Snape, C.E., Bailey, N.J.L., 1998. Comparison of covalently-bound aliphatic biomarkers released via hydropyrolysis with their solvent-extractable counterparts for a suite of Kimmeridge clays. Organic Geochemistry 29, 1487–1505.

Peng, P., Morales-Izquierdo, A., Hogg, A., Strausz, O.P., 1997. Molecular Structure of Athabasca Asphaltene: Sulfide, Ether, and Ester Linkages. Energy & Fuels 11, 1171–1187.

Peng, P., Fu, J., Sheng, G., Morales-Izquiredo, A., Lown, E.M., Strausz, O.P., 1999. Ruthenium-ion-catalyzed oxidation of an immature asphaltene: structural features and biomarker distribution. Energy & Fuels 13, 266–277.

Pelet, R., Behar, F., Monin, J.C., 1986. Resins and asphaltenes in the generation and migration of petroleum. Organic Geochemistry 10, 481–498.

Peters, K.E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. American Association of Petroleum Geologists 70, 318–329.

Peters, K.E., Moldowan, J.M., Sundararaman, P., 1990. Effects of hydrous pyrolysis on biomarker thermal maturity parameters: Monterey Phosphatic and Siliceous Members. Organic Geochemistry 15, 249–265.

Peters, K.E., Moldowan, J.M., 1993. The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, Englewood Cliffs, NJ.

Philp, R.P., Gilbert, T.D., 1985. Source rock and asphaltene characterization by pyrolysis gas chromatography-mass spectrometry-multiple ion detection. Geochimica et Cosmochimica Acta 49, 1421–1432.

Pye, K., Krinnsley, D.H., 1986. Microfabric, mineralogy and early diagenetic history of the Whitby Mudstone formation (Toarcian), Cleveland Basin, UK. Geological Magazine 123, 191–203.

Requejo, A.G., Allan, J., Creaney, S., Gray, N.R., Cole, K.S., 1992. Aryl isoprenoids and diaromatic carotenoids in Paleozoic source rocks and oils from the Western Canada and Williston Basins. Organic Geochemistry 19, 245–264.

Rohmer, M., 1993. The biosynthesis of triterpenoids of the hopane series in the Eubacteria: A mine of new enzyme reactions. Pure and Applied Chemistry 65, 1293–1298.

Richnow, H.H., Jenisch, A., Michaelis, W., 1991. Structural investigations of sulphur-rich macromolecular oil fractions and a kerogen by sequential chemical degradation. Organic Geochemistry 19, 351–370.

Rullkötter, J., Michaelis, W., 1990. The structure of kerogen and related materials. A review of recent progress and future trends. Organic Geochemistry 16, 829–852.

Sælen, G., Tyson, R.V., Telnæs, N., Talbot, M.R., 2000. Constraining watermass conditions during deposition of the Whitby Mudstone (Lower Jurassic) and Kimmeridge Clay (Upper Jurassic) formations, UK. Palaeogeography, Paleoclimatology and Palaeoecology 163, 163–196.

Schaeffer, P., Reiss, C., Albrecht, P., 1995. Geochemical study of macromolecular organic matter from sulfur-rich sediments of evaporitic origin (Messinian of Sicily) by chemical degradations. Organic Geochemistry 23, 567–581.

Seifert, W.K., 1978. Steranes and terpanes in kerogen pyrolysis for correlation of oils and source rocks. Geochimica et Cosmochimica Acta 42, 473–484.

Strausz, O.P., Mojelsky, T.W., Faraji, F., Lown, E.M., Peng, P., 1999. Additional structural details on Athabasca asphaltene and their ramifications. Energy and Fuels 13, 207–227.

Summons, R.E., Powell, T.G., 1986. *Chlorobiaceae* in Paleozoic seas revealed by biological markers, isotopes and geology. Nature 319, 763–765.

Summons, R.E., Powell, T.G., 1987. Identification of aryl isoprenoids in source rocks and crude oils: Biological markers for green sulphur bacteria. Geochimica et Cosmochimica Acta 51, 557–566.

van Kaam-Peters, H.M., Sinninghe Damsté, J.S., 1997. Characterisation of an extremely organic sulphur-rich, 150 Ma old carbonaceous rock: paleoenvironmental implications. Organic Geochemistry 27, 371–397.

van Kaam-Peters, H.M.E., Koster, J., van der Gaast, S.J., Dekker, M., De Leeuw, J.W., Sinninghe Damsté, J.S., 1998. The effect of clay minerals on diasterane/sterane ratios. Geochimica et Cosmochimica Acta 62, 2923–2929.