

Petroleum source rock assessment in non-marine sequences: pyrolysis and petrographic analysis of Australian coals and carbonaceous shales

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Abstract—A series of Australian coals and terrestrial sediments ranging in age from Permian through Tertiary have been analysed to assess their petroleum source character and the suitability of various techniques for assessment of source rock potential in non-marine sequences. The procedures used include organic petrography, Rock-Eval pyrolysis, elemental analysis and quantitative pyrolysis–gas chromatography. The latter procedure was used to assess the potential yield of paraffins which is critical to the assessment of most non-marine source rocks. Principal components analysis was used to assist in the analysis of the data. Although the petroleum potential of the samples follows the broad trends in petrographic composition established for Australian coals, i.e. relative proportions of vitrinite, inertinite and liptinite, there is much variation which cannot be explained petrographically at the maceral group level. Further, pyrolytic hydrocarbon yield is not related to overall elemental composition below an atomic H/C ratio of 1.0. The yield of phenols in flash pyrolysis is related to depositional setting as well as degree of maturation. The yield and carbon number distribution of normal hydrocarbons in flash pyrolysis varied widely depending on the age, nature and amount of liptinite macerals particularly in samples with Hydrogen Indices below 300. Liptinite-poor (< 10%) samples may yield significant amounts of hydrocarbons, but typically they have a low wax content. Sporinite-rich and liptodetrinite-rich samples give lower yields of normal hydrocarbons. These are predominantly of lower molecular weight. Suberinite and to a lesser extent cutinite are associated with high yields of waxy normal hydrocarbons, but some samples with high yields did not contain large amounts of these macerals. The correlation of T_{\max} to vitrinite reflectance varies with petrographic composition. The results have implications for the way source rock analyses are conducted and interpreted in non-marine sequences.

Key words—petroleum, non-marine, source, pyrolysis, petrography, Australia

INTRODUCTION

A small but significant proportion of global oil reserves is derived from organic matter of land plant origin (Hedberg, 1968; Tissot and Welte, 1984). In Australia, they represent the main source of petroleum (Brooks and Smith, 1967, 1969; Brooks *et al.*, 1971; Powell and McKirdy, 1972, 1975; Shibaoka *et al.*, 1978; Smyth, 1979, 1983; Thomas, 1982; Kantsler *et al.*, 1983; Smith and Cook, 1984; Stainforth, 1984; Shanumgan, 1985; Vincent *et al.*, 1985; Philp and Gilbert, 1986; Alexander *et al.*, 1987) and occur in reservoirs ranging in age from Permian to Tertiary (Fig. 1). However, the extent to which coals and carbonaceous shales, in general, can be a source for liquid hydrocarbons remains controversial (Saxby and Shibaoka, 1986). One view suggests that many humic coals and associated dispersed organic matter can be a source for oil (Durand and Paratte, 1983). An example is the association of oil and gas-condensate with coals and carbonaceous shales dominated by inertinitic macerals in the Cooper Basin, Australia

(Smyth, 1979, 1983). An alternative proposition is that only rocks which contain abundant hydrogen-rich macerals (liptinite) can yield sufficient hydrocarbons for them to be effective oil sources (Saxby, 1980; Snowdon and Powell, 1982; Powell and Snowdon, 1983; Powell, 1984; Thompson *et al.*, 1985).

Hydrogen is a limiting factor in the generation of hydrocarbons from sedimentary organic matter since hydrocarbons are enriched in hydrogen compared with the starting material. This has led to the classification of sedimentary organic matter based on elemental ratios (Tissot *et al.*, 1974). Hydrogen-rich organic matter yields greater amounts of hydrocarbons than the hydrogen-poor materials. The association of the microscopic components of coal with a particular hydrogen content (Van Krevelen, 1961; Tissot *et al.*, 1974; Saxby, 1980) forms the basis for the use of petrography in source rock assessment. The inertinite and vitrinite macerals are derived predominantly from the structural part of plants and are deficient in hydrogen (Van Krevelen, 1961); they correspond to Types III and IV (Tissot *et al.*, 1974;

Harwood, 1977) depending on preservational conditions. In contrast, spore and leaf cuticles form part of the liptinite group and can be classified as Type II whereas plant resin can be classified as Type I (Snowdon, 1980; Mukhopadhyay and Gormly, 1984). Sedimentary organic matter derived from land plants is generally composed of hydrogen-poor organic matter, but with various amounts of hydrogen-rich components. From first principles then, the source rock potential of terrestrial sediments is explicable in terms of the relative mix of hydrogen-rich and hydrogen-poor components (Saxby, 1980; Snowdon and Powell, 1982; Powell, 1984; Saxby and Shibaoka, 1986) that can be related to different plant parts and is potentially recognisable by petrographic means. However, there are several difficulties in using this concept in source rock assessment of carbonaceous sequences.

- (1) The link between petrographic and geochemical characteristics of coals often appears variable and not systematic (Durand and Paratte, 1983; Thompson *et al.*, 1985; Bertrand 1984; Bertrand *et al.*, 1986). This in part can be attributed to the heterogeneous nature of the vitrinite macerals (Stach *et al.*, 1982) and their variation both between coal provinces of the same age (Jones *et al.*, 1984) and between coal provinces of different ages (Cook, 1975; Bertrand *et al.*, 1986).
- (2) The recognition that humic macerals may contain microscopic and submicroscopic liptinite particles some of which may be of bacterial origin suggests a degree of heterogeneity may exist in coal macerals that may have relevance to oil source rock assessment (Taylor *et al.*, 1988). This is also suggested by the work of Evans *et al.* (1984) who showed that the yield of paraffins in mild hydrogenation of Australian coal derived inertinites and vitrinites was essentially the same and that the hydrogenation yield in coals was independent of liptinite content. The variable behaviour of Australian inertinites during carbonisation (Diessel, 1983) also points to the chemical heterogeneity of the inertinite group of macerals.
- (3) Hydrocarbon yields from liptinite concentrates, e.g. sporinite concentrates of Carboniferous coals from northern England (Allan and Douglas, 1977; Allan *et al.*, 1977) are not readily relateable to their expected hydrocarbon potential based on hydrogen content (cf. Saxby, 1980; Saxby and Shibaoka, 1986).
- (4) Studies of Carboniferous vitrinite and sporinite concentrates suggest some degree of homogeneity in the chemical composition of these macerals (Allan and Larter, 1983). Macerals are not distinct chemical entities, but rather they are relict structures partly reflecting the original plant tissues which become partly homogenised

with other seam constituents during both the biochemical and the physico-chemical stages of coalification and catagenesis (Allan and Larter, 1983).

- (5) Organic matter derived from different land plant communities, environments and stages of land plant evolution may have inherently different oil source potential (e.g. proportion of natural oils or thickness of wax coatings on leaves) despite similar petrographic compositions. This may be important in comparing the potential of Permian and Carboniferous sequences with much younger sequences (Thomas, 1982). In addition subtle variations in extent of oxidation during deposition may change source potential, but may not be reflected in morphological appearance without the most rigorous of comparative studies.

Geochemical techniques used in source rock evaluation also present some difficulties when applied to carbonaceous sequences. In contrast to petrographic methods, geochemical methods are dependent on bulk properties such as elemental analysis, pyrolysis and bulk extraction. Because coal is more heterogeneous than conventional marine source rock, the results obtained are only the average of the component chemical entities (Thomas, 1982; Powell, 1984; Saxby and Shibaoka, 1986). Since geochemical data (extractable hydrocarbons and pyrolysis yields) are normalised to organic carbon content it is not clear which values represent the boundaries between source and non-source rocks because of the dilution effects of possible non-source components. There is the additional uncertainty that there may be major differences between marine and non-marine source rocks in the mechanism of expulsion and migration. It is not at all clear what is the threshold of liquid hydrocarbon concentration at which migration from a coal or carbonaceous shale might occur. In the main phase of oil generation in terrestrial source rocks, considerable quantities of hydrocarbon gases (Monnier *et al.*, 1983; Saxby *et al.*, 1986) and carbon dioxide (Hunt, 1979; Saxby *et al.*, 1986; Strachan *et al.*, 1988) are formed which are not present in marine source rocks at comparable levels of maturation and which may allow migration at lower $C_{15} +$ saturation thresholds than is the case for marine source rocks (Snowdon, 1980; Snowdon and Powell, 1982).

The purpose of this paper is to present data on the pyrolytic behaviour and petrographic composition of a range of Australian coals and carbonaceous sediments with a view of refining our understanding of the oil potential of such material. Australia is an ideal location for such a study since commercial coal seams range from Permian to Tertiary in age and non-marine oils and gases are associated with each major group (Fig. 1; Powell and McKirdy, 1975; Thomas, 1982). The techniques selected consist of the well established procedures of elemental analysis,

Rock-Eval Pyrolysis and organic petrography in combination with the more recently developed procedures of quantitative pyrolysis–gas chromatography (Larter and Sentfle, 1985; Larter, 1985) to assess the yield of paraffins which is critical to the assessment of most non-marine source rocks. As has been pointed out by Smith *et al.* (1987) assessment of source rocks should be based on the components that contribute to migrateable oil during normal maturation. In the general case of non-marine oils, these are largely paraffinic hydrocarbons except in the case of some resin-rich sources (Snowdon and Powell, 1982).

SAMPLES AND METHODS

Samples were chosen to represent the principal coal-forming periods in Australia and in particular those areas associated with non-marine petroleum production (Fig. 1) (Tables 1–5). Samples with lower levels of maturation ($R_o < 0.9$) were selected, except in the case of the Permian, where a wider range of maturation was studied. Permian coals and carbonaceous shales were obtained from core in the Toolachee and Patchawarra and Murteree Formations in the Cooper Basin and from selected coal seams in the Sydney Basin (Fig. 1). Triassic samples

are from scattered locations in eastern and western Australian basins. Of particular interest are three sets of paired samples representing the dull and bright bands which are a characteristic feature of many commercially exploited Australian Permian and Triassic coals. Jurassic samples are from the Walloon Coal Measures and the immediately underlying strata in the Clarence–Moreton Basin (Fig. 1). These formations are the lateral equivalents to some of the petroleum producing intervals in the Eromanga Basin (Fig. 1). Cretaceous coals are largely from the Winton Formation in the Eromanga Basin and one sample is from the Otway Basin. Cretaceous lacustrine shales were sampled from the Murta Member of the Mooga Formation in the Eromanga Basin. Upper Cretaceous to Tertiary coals and carbonaceous shales are from the off-shore Gippsland Basin and the Latrobe Valley brown coal deposits (Fig. 1). Sample 1969 represented a pale lithotype and 1968 a dark lithotype. Three Tertiary samples from New Zealand were also included. The vitrinite reflectance and maceral analyses were carried out in accordance with the general procedures recommended by the International Committee for Coal Petrology (1963, and supplements 1971, 1975). The mean maximum reflectance in oil (R_o max %) was measured on the Permian



Fig. 1. Distribution of coal measures and associated oil and gas occurrences in Australia.

Table 1. Petrographic and geochemical data Permian samples

Sample No.	TOC (%)	VR ^a mean max R _o %	Petrographic composition (%)		Kerogen atomic ratios		Rock-Eval		Pyrolysis-GC			
			Overall (V/I/Lp)	Liptinite (S/C/R/Sb/Ld/A)	H/C	O/C	T _{max} (°C)	HI (mg/g)	Alk (mg/g)	Wax (%)	Alk arom	Ph (mg/g)
Selected Coals												
1978	73.7	0.68	71/16/13	7/3/1/0/2/0	0.94	0.12	435	235	22	48	4.8	8.3
1974	75.3	0.70	78/11/11	3/4/1/1/2/0	0.97	0.15	434	163	15	47	5.3	4.3
1980	71.2	0.75	74/17/9	5/1/1/0/2/0	1.07	0.12	436	170	18	56	4.0	7.9
1984)	63.4	0.80	58/36/6	3/tr/tr/0/2/0	0.89	0.11	440	135	6	35	1.7	4.6
1983)	74.0	0.83	90/5/5	3/tr/1/0/1/0	0.89	0.13	440	143	7	35	2.0	6.8
1970)	75.4	1.12	37/62/1	tr/0/0/0/tr/0	0.78	0.05	466	162	2	39	1.0	1.3
1971)	86.1	1.20	67/33/0		0.78	0.05	461	217	4	28	1.4	2.0
1981	72.7	1.30	55/45/0		0.81	0.04	472	155		40	1.4	1.6
1982	78.3	1.35	45/55/0		0.71	0.06	479	110	2	34	0.9	0.4
Cooper Basin-Toolachee and Patchawarra Formations												
3053	5.2	0.76			0.64	0.26	445	117	10	32	2.1	1.9
3054	13.1	0.80			0.67	0.20	442	131	11	20	2.3	2.0
3055	14.5	0.93	5/91/4	3/1/0/0/0/tr	0.60	0.12	447	111	7	33	1.5	2.4
3069	38.4	0.90	15/74/11	8/2/1/0/0/tr	0.67	0.10	444	195	12	31	2.6	2.0
3057	78.7	0.86	80/17/3	3/tr/tr/0/0/0	0.70	0.14	446	139	5	38	1.0	2.3
3059	6.8	0.81			0.69	0.19	442	184	12	28	3.2	1.9
3061	70.7	0.78	27/59/14	11/3/tr/0/0/0	0.88	0.20	444	229	15	30	2.8	3.1
3062	6.4				0.65	0.18	442	136	11	28	2.9	1.9
3068	77.1				0.80	0.15	449	224	13	45	0.9	6.1
3071	77.2	0.86	14/78/8	3/2/0/0/2/0	0.76	0.17	449	141	7	32	0.6	1.9
3073	80.4				0.73	0.12	448	235	11	42	0.9	4.5
3075	75.5	0.83	33/55/12	6/2/tr/tr/3/0	0.71	0.15	446	192	11	30	1.5	3.0
3077	77.8				0.77	0.12	448	116	5	35	1.2	1.1
3079	8.9				0.72	0.17	441	209	14	30	2.8	2.6
3080	2.5				0.60	0.27	454	56	4	22	1.5	0.6
3083	74.7	0.88	11/79/10	5/1/0/0/4/0	0.72	0.13	449	135	7	31	0.6	2.4
3085	2.0				0.76	0.03	445	94	9	18	2.3	1.5
3087	8.4	0.87	72/11/17	6/6/tr/tr/4/0	0.71	0.03	445	210	12	29	3.3	1.5
3088	1.9				0.60	0.02	463	63	3	25	1.4	0.9
Cooper Basin-Murteree Formation												
3115	14.4				0.78	0.02	439	232	15	32	3.4	3.6
3116	12.6				0.71	0.02	433	189	11	34	3.4	2.2

TOC = total organic carbon; VR = mean maximum vitrinite reflectance; petrographic composition is in volume percent on mineral matter free basis; V = vitrinite; I = inertinite; Lp = liptinite; S = sporinite; C = cutinite; R = resinite; Sb = suberinite; Ld = liptodetrinite; A = alginite; HI = Hydrogen Index; mg/g = milligrams per gram organic carbon; Alk = sum of C₇-C₂₇ normal hydrocarbons; Wax = C₁₇-C₂₇ normal hydrocarbons as percent of total normal hydrocarbons; Alk/arom = ratio of total normal hydrocarbons to total of C₇-C₉ aromatics; Ph = C₆-C₈ phenols;) = paired samples.

Table 2. Petrographic and geochemical data Triassic samples

Sample No.	TOC (%)	VR ^a mean max R _o %	Petrographic composition (%)		Kerogen atomic ratios		Rock-Eval		Pyrolysis-GC					
			Overall (V/I/Lp)	Liptinite (S/C/R/Sb/Ld/A)	H/C	O/C	T _{max} (°C)	HI (mg/g)	Alk (mg/g)	Wax (%)	Alk arom	Ph (mg/g)		
<i>Callide and Ipswich Coal Measures</i>														
1986)	57.3	0.51	17/74/9	3/4/tr/0/1/0	0.74	0.23	441	64	5	40	2.3	2.4		
1985)	62.2	0.52	65/26/9	4/5/tr/0/tr/0	0.90	0.25	440	134	10	37	2.8	4.5		
3675	7.4	0.85	45/41/14	1/8/1/0/4/0	1.02	0.01	446	158	14	24	2.7	5.3		
3676	6.0	0.86	30/33/37	10/4/2/0/21/0	0.98	0.01	443	198	20	34	4.6	4.3		
<i>Bowen Basin-Cabawin Formation</i>														
3670	45.3	0.37	69/2/29	3/3/1/20/2/0			430	485	34	57	7.2	9.5		
3671	26.4	0.81	67/24/9	1/1/0/3/4/0	0.64	0.20	445	151	10	28	3.6	0.9		
3674	30.5	0.82	41/55/4	3/0/0/0/1/0	0.98	0.02	442	173	11	25	4.2	0.5		
<i>Cooper Basin-Yongala Formation</i>														
3667	8.0	0.66	85/0/15	6/tr/0/0/8/1	1.26	0.53	446	506	52	48	8.0	8.0		
3669	28.3	0.66	69/18/13	5/1/1/1/5/0	0.75	0.09	444	373	23	36	4.7	4.3		
3668	54.3	0.74	88/2/10	1/1/5/0/3/0	0.84	0.08	444	400	20	36	2.9	7.9		
<i>Carnarvon Basin-Mungaroo Beds</i>														
3672	41.9	0.78	84/4/12	0/1/tr/0/10/1/0	0.67	0.19	446	116	7	30	1.6	5.7		
3673	29.4	0.80	94/3/3	0/0/0/2/1/0	0.62	0.20	458	137	10	30	2.3	4.9		
3677	44.9	0.85	83/1/16	0/1/3/10/2/0	0.69	0.20	445	139	7	33	1.9	3.8		
3678	39.4	0.86	93/0/7	1/0/0/3/3/0	0.79	0.03	433	111	6	26	1.6	4.2		

TOC = total organic carbon; VR = mean maximum vitrinite reflectance calculated from mean average reflectance; petrographic composition is in volume percent on mineral matter free basis; V = vitrinite; I = inertinite; Lp = liptinite; S = sporinite; C = cutinite; R = resinite; Sb = suberinite; Ld = liptodetrinite; A = alginite; HI = Hydrogen Index; mg/g = milligrams per gram organic carbon; Alk = sum of C₇-C₂₇ normal hydrocarbons; Wax = C₁₇-C₂₇ normal hydrocarbons as percent of total normal hydrocarbons; Alk/arom = ratio of total normal hydrocarbons to C₇-C₉ aromatics; Ph = C₆-C₈ phenols;) = paired samples.

Table 3. Petrographic and geochemical data Jurassic samples Clarence–Moreton Basin

Sample No.	TOC (%)	VR ^a mean max R _o %	Petrographic composition (%)		Kerogen		Rock-Eval		Pyrolysis-GC			
			Overall (V/I/Lp)	Liptinite (S/C/R/Sb/Ld/A)	Atomic ratios H/C O/C	T _{max} (°C)	HI (mg/g)	Alk (mg/g)	Wax (%)	Alk arom	Ph (mg/g)	
Samples < 10% Liptinite												
1907	19.0	0.53	91/1/8	4/1/0/2/1/0	0.93	0.15	425	247	13	30	3.0	7.7
1646	5.1	0.55	94/0/6	tr/tr/4/0/2/0	0.93	0.32	443	150	20	48	4.1	9.7
1917	5.9	0.58	98/2/0		0.84	0.12	441	187	13	46	4.4	2.8
1914	78.3	0.67	90/1/9	3:tr/tr/5/1/0	0.89	0.18	433	152	9	40	1.5	7.4
2335	5.5	0.75	82/12/6	6/0/0/0/0/	0.75	0.20	460	248	36	31	9.2	0.5
2313	14.9	0.91	100/0/0				453	283	29	36	8.3	1.9
Samples 10–30% Liptinite												
2987	59.7	0.59	81/2/17	3/3/6/2/3/0	0.90	0.20	430	239	36	48	4.1	6.7
2985	12.6	0.58	89/0/11	9/0/tr/0/1/1	0.84	0.16	433	212	11	38	5.0	6.5
1913	49.4	0.58	88/1/11	1/7/3/0/0/0	0.98	0.12	436	372	42	48	8.8	6.4
2316	34.3	0.60	76/1/23	16/2/2/0/3/0	0.79	0.06	449	396	60	36	12.4	4.8
1921	43.4	0.63	81/2/17	3/0/7/7/0/0	1.22	0.19	435	379	39	53	7.9	9.2
Sample 30–40% Liptinite												
2301	6.0	0.43	65/0/35	29/0/0/0/6/0	1.05	0.20	442	460				
2983	69.3	0.46	63/0/37	4/4/5/23/1/0	0.89	0.12	425	260	18	53	12.5	6.7
1926	56.6	0.49	40/30/40	8:tr/6/23/3/0	1.05	0.14	438	316	51	52	9.5	6.7
Samples 40–50% Liptinite												
2990	28.7	0.55	54/3/43	1/1/10/31/0/0	1.01	0.13	432	326	52	61	13.1	8.1
1929	68.0	0.62	52/2/46	1/1/14/30/0/0	1.05	0.16	437	263	30	52	5.1	11.5
2999	17.6	0.65	58/2/40	2:tr/6/31/1/0	0.89	0.15	445	598	137	46	17.0	6.4
Samples > 50% Liptinite												
1897	12.8	0.36	45/2/53	29/4/1/0/17/2	0.96	0.11	439	530	64	54	7.4	4.2
1900	1.0	0.43	40/0/60	50/0/0/0/10/0	0.96	0.27	438	454	47	39	3.6	6.1
1932	1.4	0.43	29/14/57	29/14/0/0/14/0	0.90	0.14	443		32	43	5.3	4.7
1931	1.7	0.45	8/4/88	72/12/0/0/4/0	1.20	0.35	444		65	38	7.2	3.7
1928	8.4	0.43	44/2/54	33/3/2/3/12/1	1.08	0.14	436	512	88	60	10.5	6.3
1909	63.7	0.36	tr/5/95	56/0/0/0/39/tr	0.89	0.19	425	211	16	43	1.4	9.1
1923	11.3	0.50	27/1/72	32/23/1/0/16/tr	1.05	0.12	438	484	61	52	11.1	6.4
1649	62.9	0.52	40/1/59	1/0/3/55/0/0	1.12	0.15	434	341	32	58	10.7	7.1
1645	14.2	0.30	28/0/72	37/4/4/1/21/5	1.54	0.02	440	709	150	42	24.2	6.2
1647	9.5	0.30	42/3/55	33/3/5/3/8/3	1.45	0.18	447	906	196	54	29.4	5.7

TOC = total organic carbon; VR = mean maximum vitrinite reflectance calculated from mean average reflectance; petrographic composition is in volume percent on mineral matter free basis; V = vitrinite; I = inertinite; Lp = liptinite; S = sporinite; C = cutinite; R = resinite; Sb = suberinite; Ld = liptodetrinite; A = alginite; HI = Hydrogen Index; mg/g = milligrams per gram organic carbon; Alk = sum of C₇–C₂₇ normal hydrocarbons; Wax = C₁₇–C₂₇ normal hydrocarbons as percent of total normal hydrocarbons; Alk/arom = ratio of normal hydrocarbons to C₇–C₉ aromatics; Ph = C₆–C₈ phenols.

Table 4. Petrographic and geochemical data Cretaceous samples

Table 4. Petrographic and geochemical data Cretaceous samples												
Sample No.	TOC (%)	VR ^a mean max R _o %	Petrographic composition (%)		Kerogen		Rock-Eval		Pyrolysis-GC			
			Overall (V/I/Lp)	Liptinite (S/C/R/Sb/Ld/A)	Atomic ratios H/C O/C	T _{max} (°C)	HI (mg/g)	Alk (mg/g)	Wax (%)	Alk arom	Ph (mg/g)	
<i>Eromanga Basin–Winton Formation</i>												
3659	42.3	0.42	50/0/50	12/4/4/11/19/0	0.77	0.71	423	49	0.7	20	0.4	9.0
3660	44.2	0.44	88/5/7	1/2/1/2/1/0	1.04	0.79	429	83	3.3	31	1.2	5.9
3661	54.5	0.42	8/76/16	5/1/0/0/10/0	0.73	0.42	430	66	6.6	40	2.3	3.0
3662	28.0	0.44	72/2/26	12/tr/2/6/6/0	0.91	0.58	431	154	7.4	37	2.2	8.1
3665	47.0	0.44	92/2/6	0/0/0/5/1/0	0.90	0.64	427	71	2.4	23	1.3	7.7
3663	13.5	0.45	77/4/19	7/2/1/6/3/0	0.90	0.38	436	189	12.2	43	2.8	7.2
3664	36.2	0.46	73/tr/27	6/1/5/8/7/0	0.89	0.54	426	134	7.9	41	2.6	7.0
<i>Eromanga Basin–Murta Member, Mooga Formation</i>												
3378	1.5				1.01	0.04	439	403	39.2	41	7.4	2.7
3381	1.1		3/13/83	37/0/0/0/43/3	0.94	0.02	439		35.9	33	6.0	3.1
3382	1.3		0/34/66	37/2/0/0/25/2	1.30	0.06	439	459	46.6	26	5.5	3.7
3402	1.3	0.50	42/5/53	20/0/0/0/33/tr	0.93	0.04	439	350	35.5	38	7.0	5.1
3376	1.1				1.08	0.03	440	361	45.3	30	5.2	2.6
3387	1.0		5/24/71	38/0/0/0/33/0			441	383	51.7	34	5.9	4.3
3392	1.0		3/27/70	46/0/0/0/24/tr	1.11	0.08	444	408	49.3	38	5.9	2.9
<i>Otway Basin–Sherbrook Group</i>												
3666	23.2	0.48	47/9/44	11/1/1/25/6/0	0.98	0.54	434	199	17.9	53	4.7	5.0

TOC = total organic carbon; VR = mean maximum vitrinite reflectance calculated from mean average reflectance; petrographic composition is in volume percent on mineral matter free basis; V = vitrinite; I = inertinite; Lp = liptinite; S = sporinite; C = cutinite; R = resinite; Sb = suberinite; Ld = liptodetrinite; A = alginite; HI = Hydrogen Index; mg/g = milligrams per gram organic carbon; Alk = sum of C₇–C₂₇ normal hydrocarbons; Wax = C₁₇–C₂₇ normal hydrocarbons as percent of total normal hydrocarbons; Alk/arom = ratio of normal hydrocarbons to C₇–C₉ aromatics; Ph = C₆–C₈ phenols.

Table 5. Petrographic and geochemical data Upper Cretaceous and Tertiary samples from Gippsland Basin and Tertiary samples from New Zealand

Sample No.	TOC (%)	VR ^a mean max R _o %	Petrographic composition (%)		Kerogen		Rock-Eval		Pyrolysis-GC			
			Overall (V/I/Lp)	Liptinite (S/C/R/Sb/Ld/A)	Atomic ratios H/C O/C	T _{max} (°C)	HI (mg/g)	Alk (mg/g)	Wax (%)	Alk arom	Ph mg/g	
Gippsland Basin (on shore)–Latrobe Valley Coal Measures												
1969	67.1	0.26	71/3/26	5/0/2/1/18/0	1.24	0.28	402	375	17	48	2.0	4.7
1968	58.2	0.31	96/1/3	1/0/0/0/2/0/0	0.92	0.44	406	62	4	24	1.4	8.6
1987	73.3	0.25	2/0/98	0/0/98/0/0/0	1.53	0.17	399	720				
Gippsland Basin (offshore)–Latrobe Group												
3555	46.9	0.44	79/9/11	3/3/1/1/3/0	1.00	0.15	412	278	17	54	4.6	7.0
3554	30.6	0.41	60/2/38	8/6/6/0/18/0	1.07	0.19	417	292	25	57	6.2	4.8
3544	21.7				0.98	0.28	419	228	19	50	4.4	2.8
3540	45.8				0.94	0.22	424	272	20	36	5.6	6.6
3542	45.7	0.54	78/9/13	2/2/2/3/4/0	0.73	0.16	426	213	13	52	3.4	4.3
3543	36.5	0.62	62/12/26	5/2/6/3/9/0	0.76	0.14	432	245	28	49	5.1	5.8
3538	27.2				0.87	0.20	434	269	24	52	4.3	5.1
3559	63.8				0.85	0.14	435	221	31	54	5.3	4.7
3541	26.1	0.57	58/21/21	4/6/2/2/6/0	0.75	0.19	436	205	20	49	3.1	5.1
3551	33.3				1.06	0.14	437	234	31	41	7.9	5.8
3558	23.0	0.65	71/11/18	3/6/1/2/6/0	1.04	0.13	437	319	45	54	10.3	4.2
3546	42.4	0.75	80/9/11	2/2/2/1/3/0	0.75	0.16	435	190	19	48	4.6	5.7
3552	43.2	0.87	80/11/9	2/2/1/1/3/0	0.90	0.13	443	173	18	49	4.4	4.1
3549	14.8	0.86	74/5/21	3/3/2/3/10/0	0.78	0.18	447	226	21	46	5.5	4.0
3553	26.3	0.89	90/6/4	tr/tr/1/1/2/0	0.91	0.12	449	225	23	46	6.1	3.1
3550	22.6	0.89	89/3/8	tr/1/1/2/3/0	0.74	0.13	451	214	17	41	3.3	3.1
New Zealand Coals												
1972	61.3	0.38	50/8/42	13/3/7/5/14/0	0.97	0.31	428	142	9	24	2.3	6.3
1973	70.0	0.59	52/6/42	7/3/13/5/14/0	1.05	0.17	438	261	35	35	10.4	2.6
1975	85.9	1.11	86/6/8	4/1/2/tr/tr/0	0.83	0.06	463	218	11	33	4.9	1.1

TOC = total organic carbon; VR = mean maximum vitrinite reflectance; petrographic composition is in volume percent on mineral matter free basis; V = vitrinite; I = inertinite; Lp = liptinite; S = sporinite; C = cutinite; R = resinite; Sb = suberinite; Ld = liptodetrinite; A = alginite; HI = Hydrogen Index; mg/g = milligrams per gram organic carbon; Alk = sum of C₇–C₂₇ normal hydrocarbons; Wax = C₁₇–C₂₇ normal hydrocarbons a percent of total normal hydrocarbons; Alk/arom = ratio of normal hydrocarbons to C₇–C₉ aromatics; Ph = C₆–C₈ phenols.

samples from the Cooper Basin and the Tertiary samples from the Gippsland Basin. The mean average reflectance in oil (R_{o,m} %) was recorded for the Jurassic, Triassic and Cretaceous samples. The latter values were converted to mean maximum reflectance values by multiplying by 1.066 (Ting, 1978) to facilitate comparisons.

All samples were screened by total organic carbon analysis and Rock-Eval pyrolysis. Most samples had very high TOC contents (>10%) and the mineral matrix effect in Rock-Eval analysis was not a concern. Where TOC values are less than 5% the quoted Hydrogen Indices were obtained from kerogen concentrates. All samples were extracted and subjected to standard kerogen isolation procedures (Durand and Niçaise, 1980). Elemental analyses were performed by AMDEL (Adelaide). Pyrolysis gas chromatograms of the kerogens were obtained using a Model 120 Pyroprobe connected to an HP5700 gas chromatograph equipped with a SGE inlet splitter and a 25 m × 0.25 mm fused silica capillary column (Ultra 1, Hewlett–Packard). Between 0.5 and 2 mg of kerogen were weighed accurately and pyrolysed using the coil probe at 700°C and the quantitative yield of C₇–C₂₇ *n*-alkanes and *n*-alkenes (normal hydrocarbons), low molecular weight aromatics (C₇–C₉) and phenols (C₆–C₈) was determined by copyrolysis with a known amount of poly- α -methylstyrene as in internal standard as described by Larter and Sentfle (1985). Peak identifications of alkanes/alkenes, low molecular weight aromatics and phenols were made

by coinjection of authentic standards and by GC–MS and analytical reproducibility was tested to the limits described by Larter and Sentfle (1985). The potential for molecular weight discrimination and reproducibility of the inlet splitter was tested by comparison of gas chromatograms of a high wax oil obtained on a GC equipped with an on-column injector with gas chromatograms obtained by injection of the oil through the pyrolysis system. Under the conditions of operation no discrimination was observed. Figure 2 illustrates pyrograms representing the compositional range observed. They ranged from humic coals with low yields of predominantly aromatic pyrolysate to samples with increasing proportions of predominantly lower molecular weight normal hydrocarbons to samples in which the normal hydrocarbons were predominantly higher molecular weight.

The accumulated data were subjected to "Principal Components Analysis" which looks for linear combinations of the variables in a data set that explain most of the variability. The STATSGRAPHICS™ (Statistical Graphics Corporation) computer program was used for the analysis.

RESULTS

Permian samples

The Permian samples fall into two groups. Those from the Cooper Basin contain mainly inertinite (Fig. 3). The kerogens are Type IV (Fig. 4). The

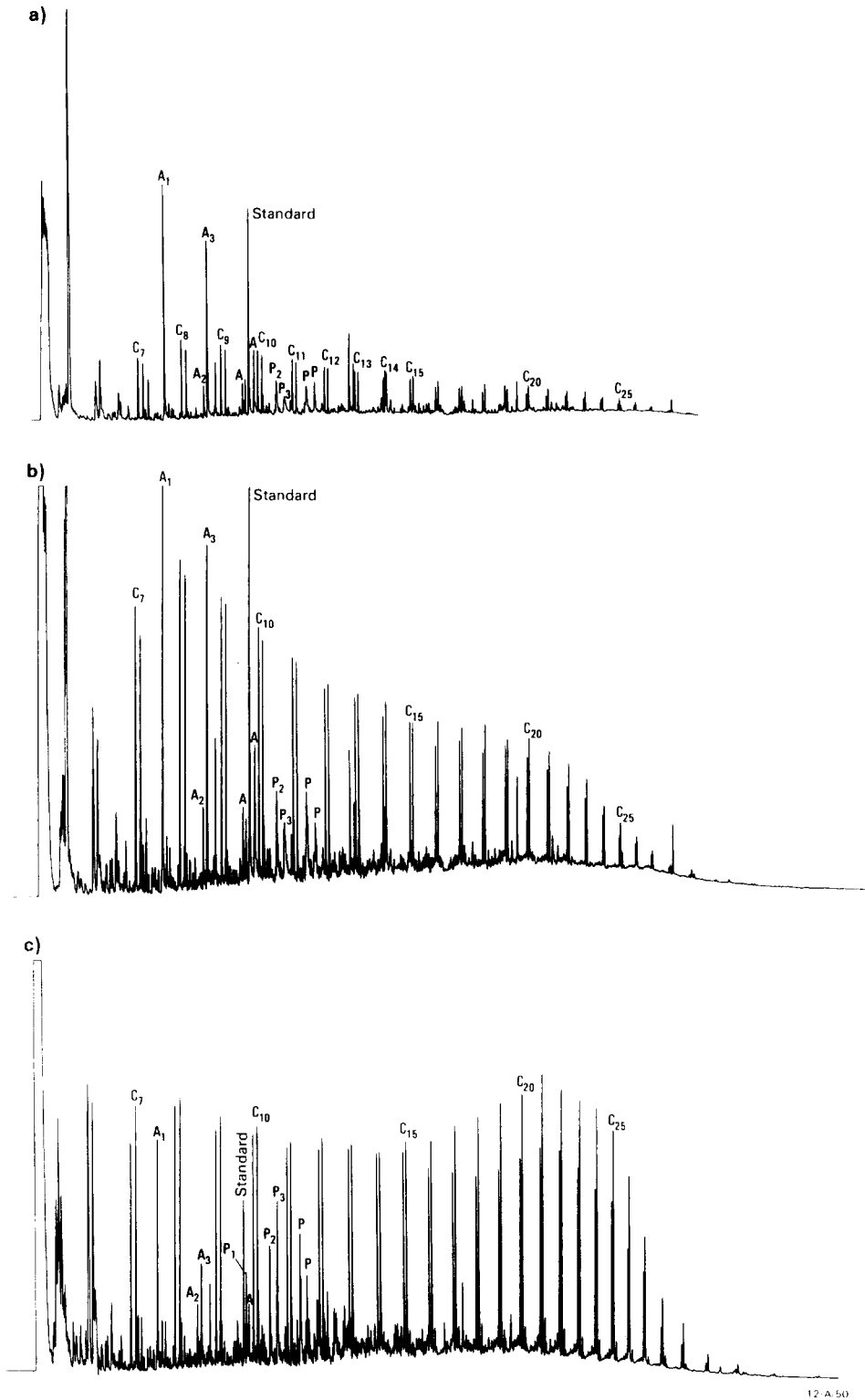


Fig. 2. Representative pyrolysis gas chromatograms: (a) Permian sample 3055 showing dominance of low molecular weight aromatics and phenols over normal hydrocarbons; (b) Permian sample 3069 showing high yield of predominantly low molecular weight normal hydrocarbons; (c) Tertiary sample 3558 showing high yield of predominantly high molecular weight normal hydrocarbons. Peaks used in quantification: C₇–C₂₇ alk-1-enes/alkanes; aromatics—A₁-toluene, A₂-ethylbenzene, A₃-*m* + *p*-xylene, A₄-*o*-xylene, A—a set of five C₃-benzenes; phenol—P₁-phenol, P₂-*o*-cresol, P₃-*m* + *p*-cresol, P—a set three C₂-phenols.

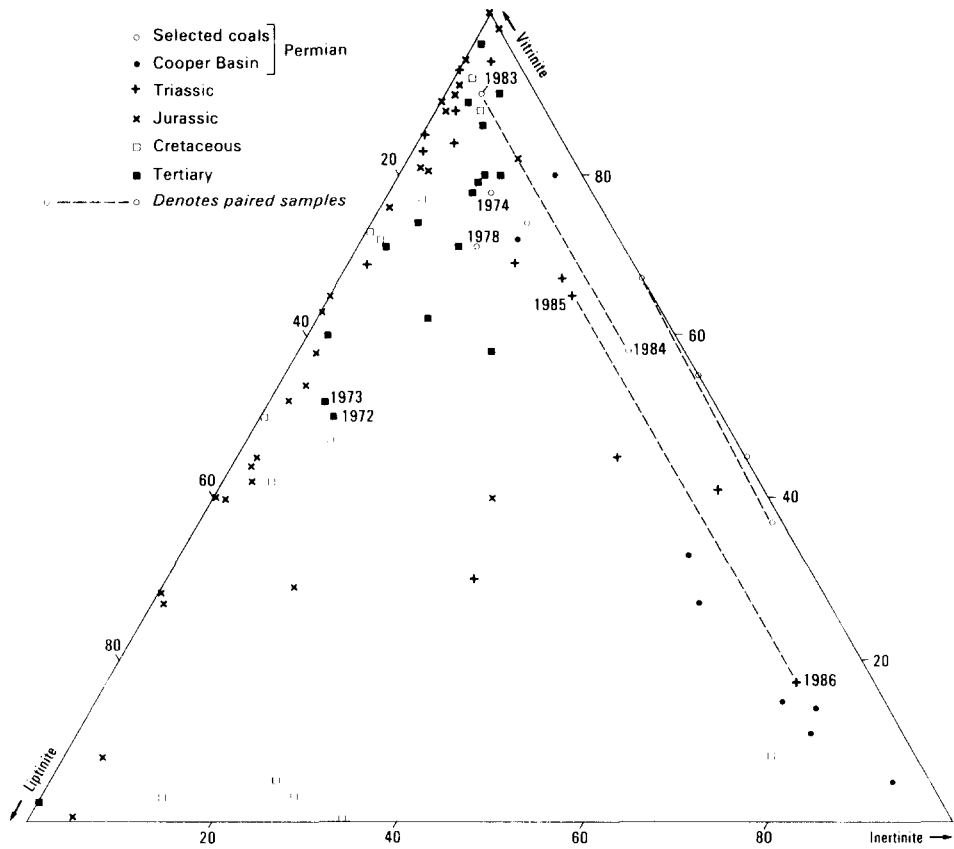


Fig. 3. Triangular diagram showing petrographic composition of samples. Numbered samples are those discussed in text.

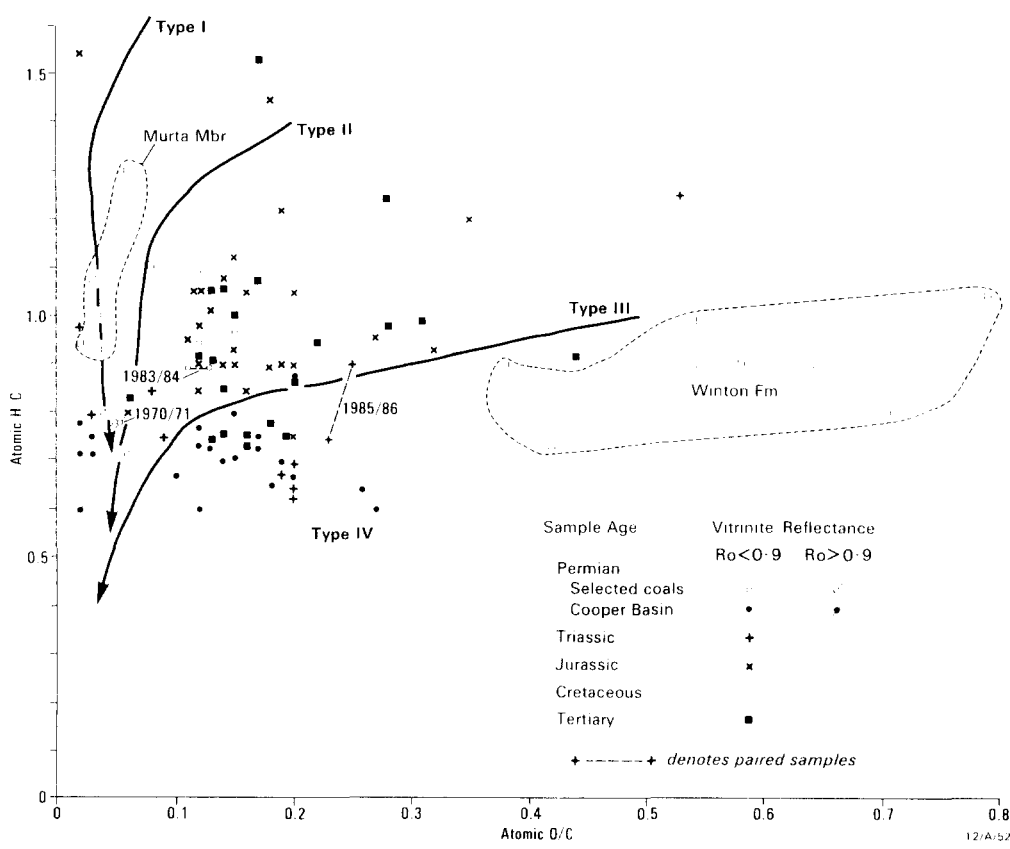


Fig. 4. Van Krevelen diagram showing variation in atomic H/C and O/C ratios and classification and evolution lines of various kerogen types. Numbered samples are those discussed in text.

remainder contain mainly vitrinite (Fig. 3) and the kerogens are Type III or Type II/III (Fig. 4). All but one sample have liptinite contents below 14%. There is no simple correlation between atomic H/C ratio and inertinite content in the low rank coals ($<0.9\%R_o$) [Fig. 5(a)]. The paired samples 1983/84 and 1971/72 have markedly different inertinite contents, but have virtually identical elemental ratios (Figs 4 and 5; Table 1).

The Hydrogen Indices range from 63 to 235 mg per gram organic carbon and are largely independent of atomic H/C ratios (Fig. 6). This lack of correlation has been observed previously in humic coals (Sentfle *et al.*, 1986). The amount of normal hydrocarbons obtained from flash pyrolysis also shows a wide variation at a given atomic H/C ratio (Fig. 6). The yield of light aromatic hydrocarbons is relatively constant and is reflected in the steadily increasing ratio of normal hydrocarbons to aromatics as the amount of normal hydrocarbons increases (Fig. 7).

The amount of phenols obtained in flash pyrolysis declines with increasing rank (Fig. 8) and has been observed previously (Schenk *et al.*, 1981b; Sentfle *et al.*, 1986). There is no significant difference in the yield of phenolic compounds between the dull and bright paired coals (Fig. 8). There is much variation in the amount of normal hydrocarbons pyrolysed from the low rank coals (Fig. 6), but in the more mature samples ($T_{max} > 450^\circ\text{C}$; $R_o > 0.9\%$) the yield is uniformly low (Table 1).

The low rank vitrinitic coals ($R_o < 0.9\%$) give slightly more normal hydrocarbons than the higher rank, inertinite-rich samples from the Cooper Basin (Fig. 6 and Table 1). There is very little difference in the chemical composition of the dull and bright parts of the Lambton Dudley seam (1983/1984, Table 1) despite widely differing proportions of vitrinite and inertinite (Fig. 2). This pair have relatively high atomic H/C ratios (0.89), but yield very little pyrolysate. Despite their lower atomic H/C ratios, some coals and kerogens from the Cooper Basin have surprisingly high yields of pyrolysable normal hydrocarbons (Fig. 6; Table 1). Their liptinite contents are comparable (c. 11–12%) to many of the vitrinite-rich coals. Other samples from the Cooper Basin have lower yields of normal hydrocarbons (Fig. 6; Table 1) and produce mainly aromatic and phenolic compounds [e.g. 3055, Fig. 2(a)].

The proportion of pyrolysable normal hydrocarbons in the wax range is also independent of liptinite content (Fig. 9). Samples 1974, 1978 and 1980 yield a high proportion of waxy normal hydrocarbons (Fig. 9; Table 1). Most of the pyrolysates are dominated by normal hydrocarbons below C_{17} irrespective of location and rank [e.g. Fig. 2(a) and (b), Table 1].

Triassic samples

In general, the Triassic coals have similar chemical characteristics to those from the Permian

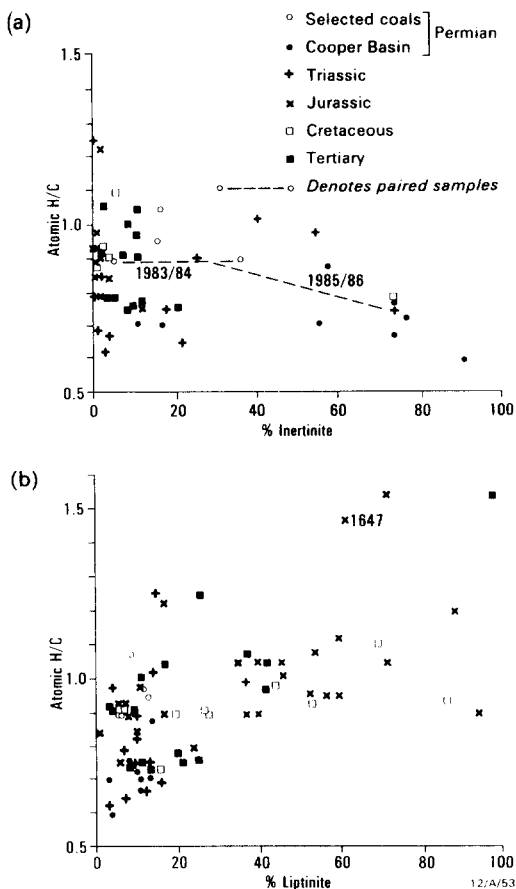


Fig. 5. Variation in atomic H/C ratio of kerogens with petrographic composition; (a) samples containing less than 20% liptinite and with vitrinite reflectance values $<0.9\%R_o$; (b) all samples. Numbered samples are those discussed in text.

(Figs 4, 7 and 8) despite being more diverse petrographically (Fig. 2). The bright and dull parts of the Callide seam (1985/86, Figs 4–8; Table 2) have similar liptinite contents (c. 8%), but their proportions of vitrinite and inertinite are markedly different. The atomic H/C ratios and pyrolysis yields reflect this variation. Despite the two-fold difference in normal hydrocarbon yield, the ratio of normal hydrocarbons to light aromatics is very similar (Table 2). The vitrinite-rich sample has a greater yield of phenolic compounds (Fig. 8).

Other vitrinite-rich samples from the Triassic have low atomic H/C ratios (Fig. 5). No simple relationship exists between liptinite content and pyrolysable hydrocarbon yield and composition. Samples 3670 and 3676 are liptinite-rich, but give smaller amounts of pyrolysable normal alkanes than those with low liptinite contents (Table 2). With two notable exceptions all Triassic coals and kerogens yield small amounts of waxy normal hydrocarbons. One of these exceptions (3670) contains substantial amounts of suberinite.

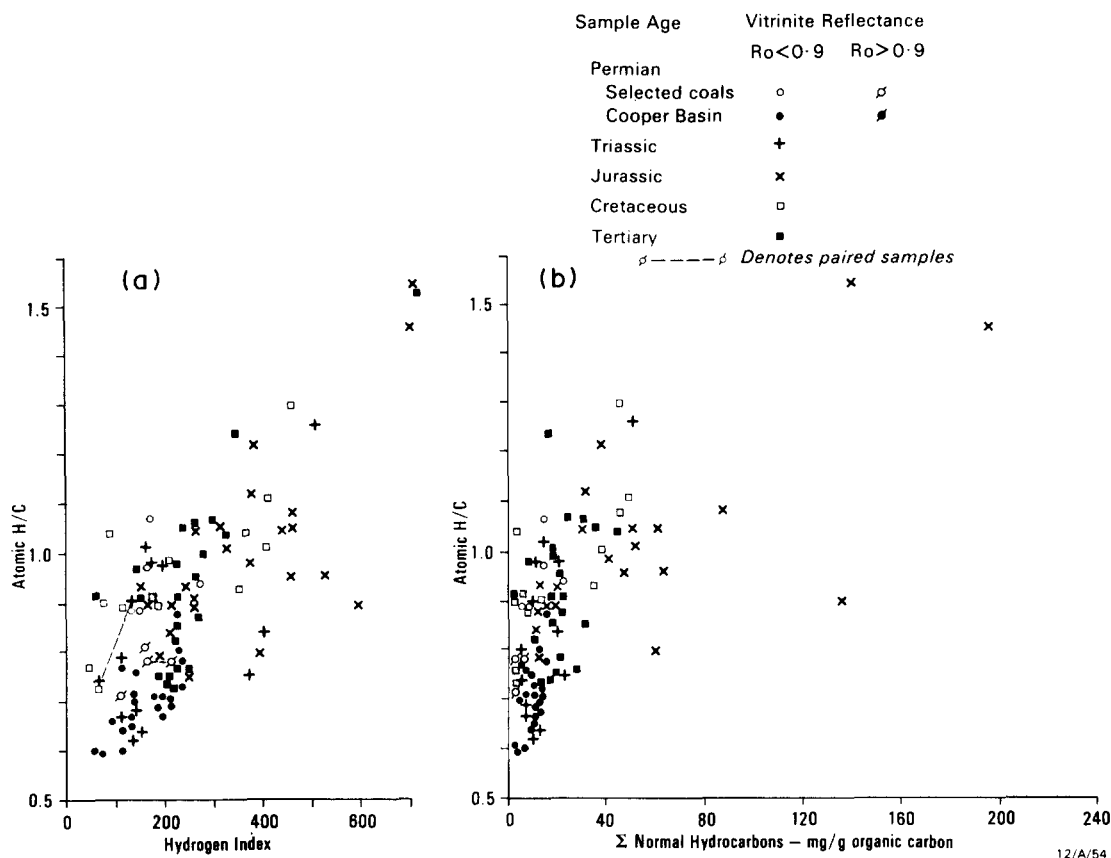


Fig. 6. Variation in pyrolysable hydrocarbon yield with atomic H/C ratio of kerogen: (a) from Rock-Eval analysis; (b) from flash pyrolysis. Numbered samples are those discussed in text.

Jurassic samples

The Jurassic coals and kerogens in this study comprise almost exclusively vitrinite and liptinite (Fig. 2). Their atomic H/C ratios and pyrolysis yields are generally higher than the Permian and Triassic samples (Figs 4 and 6). Most are classified as Type II/III kerogens (Fig. 4). Again the correlation between atomic H/C ratio and amount of pyrolysate (Fig. 6) is poor. The ratio of normal hydrocarbons to light aromatics increases systematically with rising hydrocarbon yield (Fig. 7). The yield of phenols decreases with increasing rank (Fig. 8).

In spite of the very low content of inertinite in the Jurassic samples, the relationship between atomic H/C ratio and liptinite content (Fig. 5) is not well defined. Those with the highest atomic H/C ratios have abundant liptinite, the highest Hydrogen Indices and the greatest yield of normal hydrocarbons from flash pyrolysis (e.g. 1647, Figs 5–7 and 9). At lower H/C ratios there is a broad range of pyrolysis yields and liptinite contents. This is illustrated in Table 3 where the samples are ordered according to increasing liptinite abundance. There is considerable overlap in geochemical properties between the different petrographic groups. Members of the group with less than 10% liptinite have atomic H/C ratios ranging from

0.83 to 0.93 whereas those of the group with greater than 50% liptinite have H/C ratios ranging from 0.90 to 1.54. Samples with intermediate liptinite contents overlap both ranges. In contrast, pyrolysis yields increase more systematically from one category to another although again there is some overlap. The yields of normal hydrocarbons and their ratio to the light aromatic hydrocarbons tend to be lower in samples with less than 10% liptinite. The proportion of waxy normal hydrocarbons varies in all categories, but is consistently below 50% in samples with less than 10% liptinite (Table 3).

Some of the variation in the composition and yield of pyrolysate appears to be related to the nature of the liptinite macerals. All samples in which suberinite is the dominant liptinite maceral give abundant waxy normal hydrocarbons [Table 3; e.g. 2990, Fig. 2(c)]. In contrast, where sporinite is the predominant fluorescent maceral, the yield of normal hydrocarbons, the proportion of waxy components and the normal hydrocarbon to aromatic ratios are all lower (Fig. 9, Table 3). This is particularly evident in the samples with in excess of 50% liptinite (1900, 1931, 1932 and 1909).

Cretaceous samples

The Cretaceous sample set is rather heterogeneous. The Winton coals (Table 4 and Fig. 4) have very high

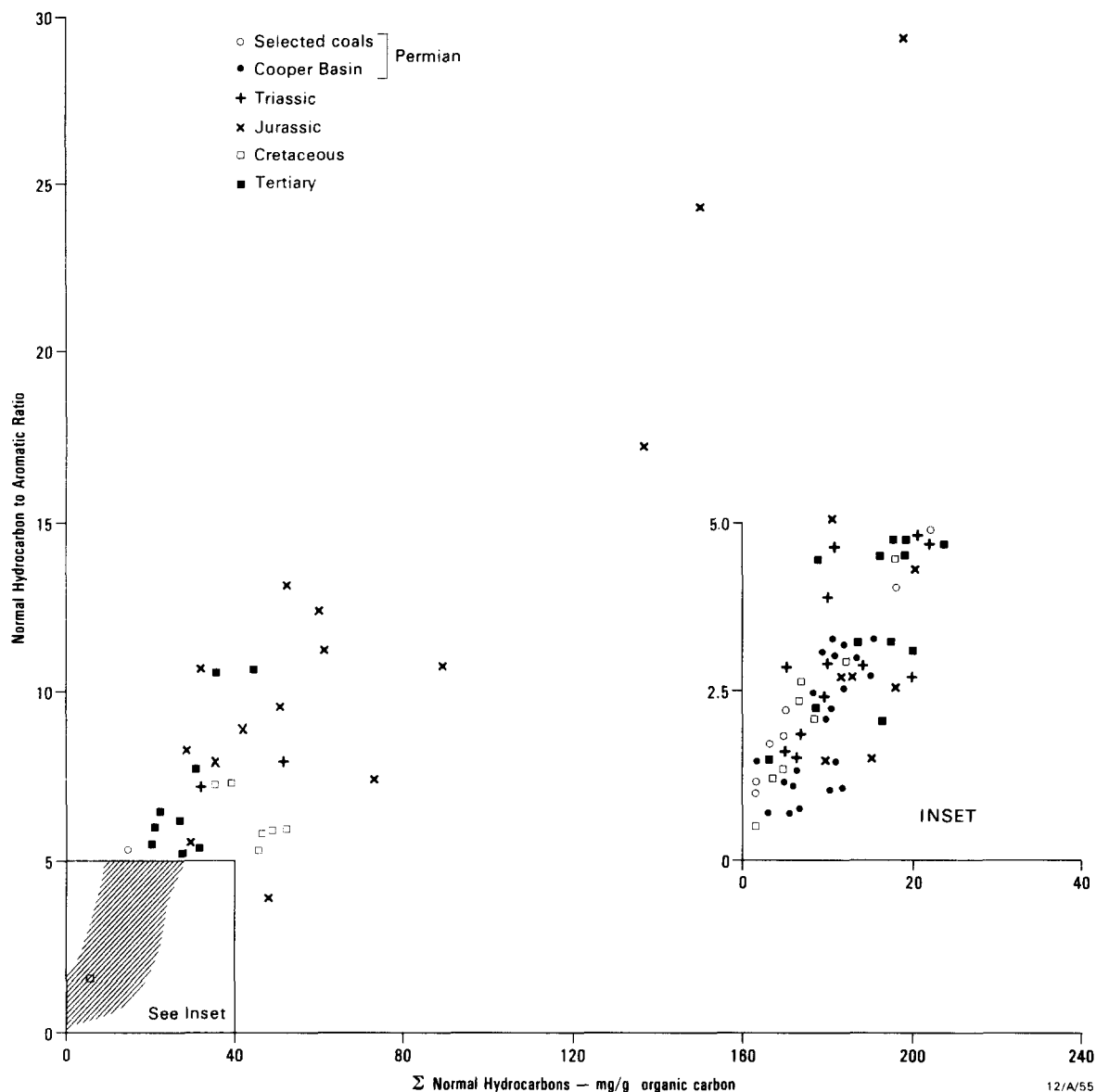


Fig. 7. Variation in yield of normal hydrocarbons with ratio of normal hydrocarbons to C_6-C_8 aromatics in flash pyrolysis. Numbered samples are those discussed in text.

atomic O/C ratios. This is partly due to their low rank, but several show petrographic evidence of oxidation due to weathering. These latter samples have low to very low pyrolysis yields of mainly aromatic and phenolic components in spite of high liptinite contents (e.g. 3659 Table 4). The Sherbrook coal (3666) and the least altered of the Winton coals (3663) give intermediate yields of pyrolysate (Table 4). The former has a relatively high content of waxy normal hydrocarbons.

The kerogens from the lacustrine Murta Member have atomic H/C ratios in the range 1.0–1.1 with very low atomic O/C ratios (c. 0.03) (Table 4). They are classed as Type II kerogens, although they are depleted in oxygen considering their relative immaturity. The dominant maceral is sporinite (Table 4); the

liptodeterinite generally has sporinite affinities and small amounts of alginite are typically present. Inter-tinite is less abundant than liptinite and vitrinite is typically a minor component. The organic content of the sediments is low (1–1.5% TOC). On pyrolysis, these kerogens yield moderate amounts of normal hydrocarbons, dominated by the lower molecular weight members (c. 70% < C_{17} , Table 4 and Fig. 9). The Cretaceous coals have similar levels of phenolic components to their Jurassic and Permian counterparts (Fig. 8).

Upper Cretaceous–Tertiary samples

The atomic H/C ratios of most Upper Cretaceous–Tertiary samples vary from 0.73 to 1.07 and Hydrogen Indices with one exception range from

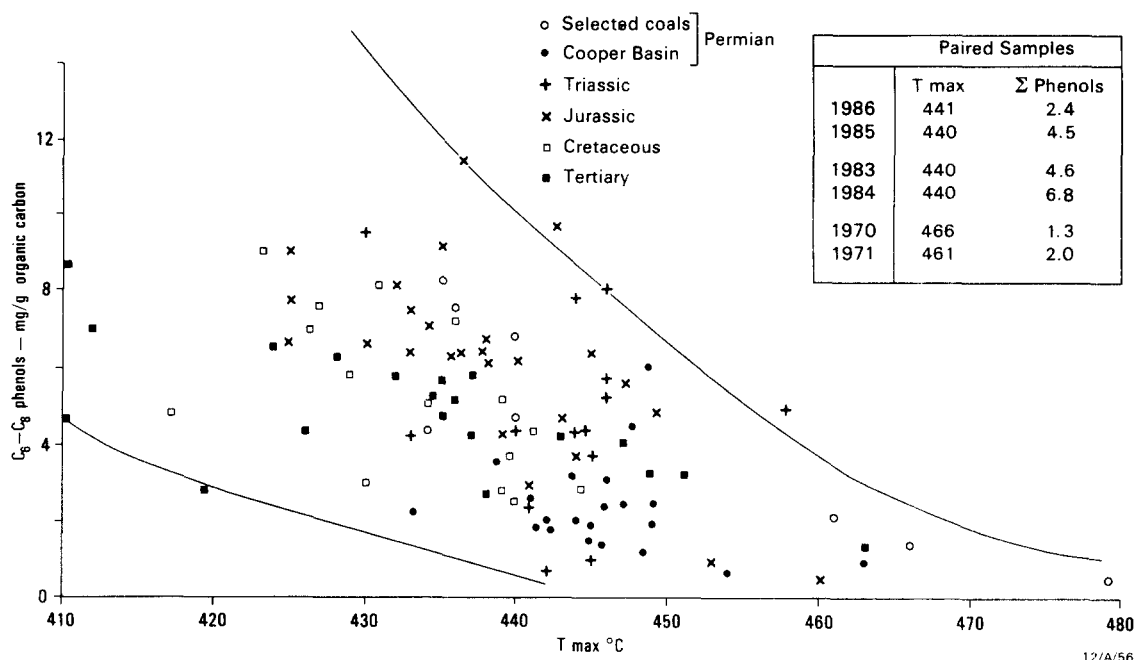


Fig. 8. Variation in yield of C_6 – C_8 phenols in flash pyrolysis with maturation as measured by T_{max} from Rock-Eval analysis.

< 100 to 300. Petrographically they are in some ways intermediate in composition between the Permian and Jurassic samples (Fig. 2). They are vitrinite dominated with more or less equal proportions of liptinite and inertinite.

Again the Hydrogen Indices and yield of normal hydrocarbons from pyrolysis-GC show no clear relationship with atomic H/C ratio (Fig. 8). All of the off-shore coals have high ratios of normal hydrocarbons to aromatics in pyrolysis-GC (Fig. 7). Most

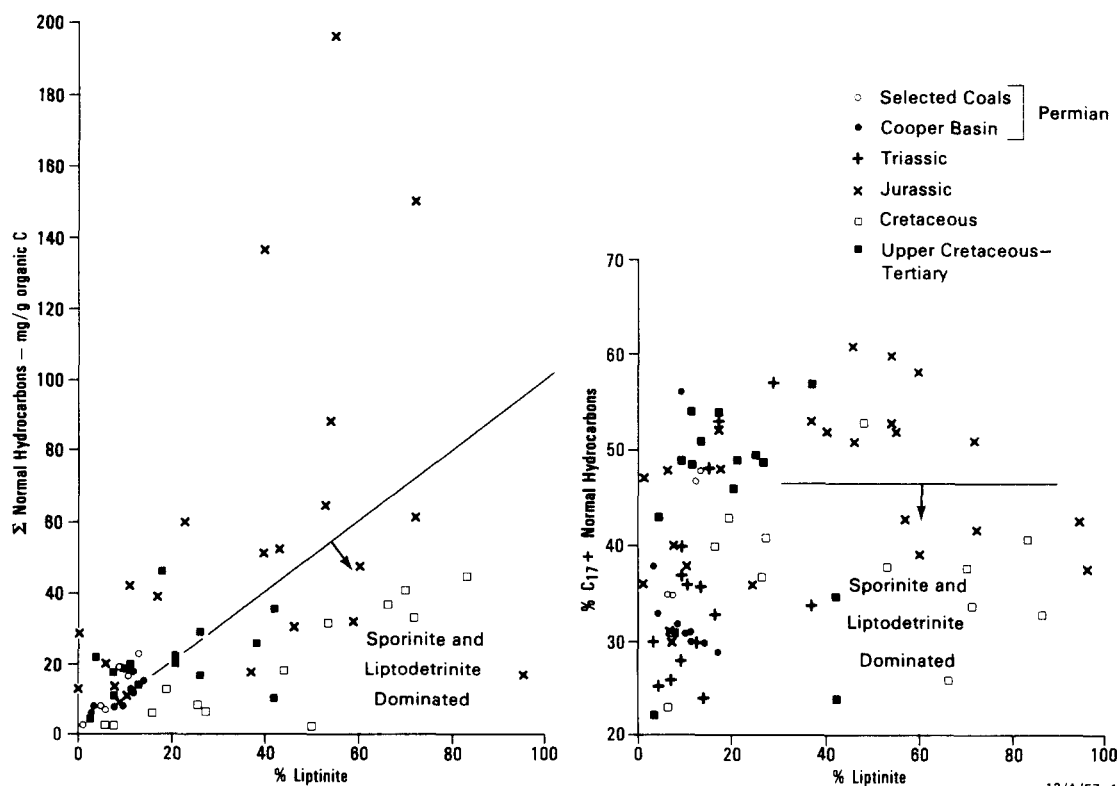


Fig. 9. Variation in yield and composition of normal hydrocarbons in flash pyrolysis with proportion of liptinite in kerogen. Numbered samples are those discussed in text.

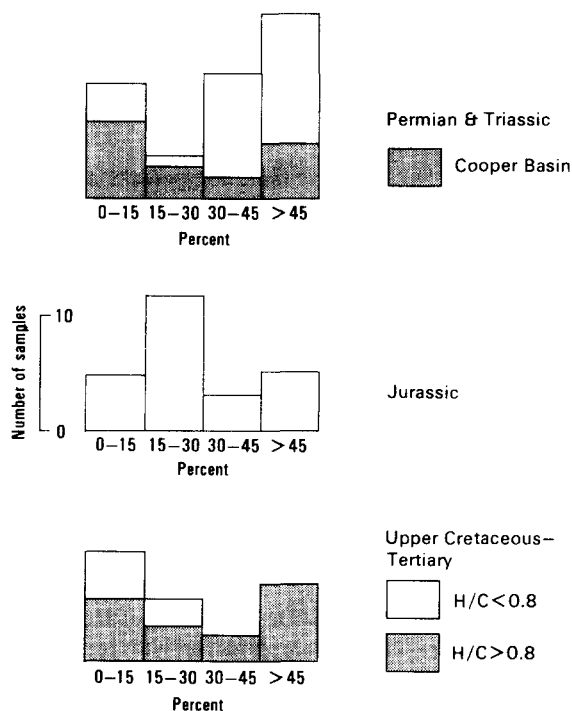


Fig. 10. Histograms showing deviations in measured Hydrogen Indices from Rock-Eval analysis from Hydrogen Indices calculated from elemental ratios using equation (1) (Orr, 1983).

samples give abundant waxy normal hydrocarbons (Table 5). Notable exceptions are two liptinite-rich coals from New Zealand (1972 and 1973). They give pyrolysates dominated by low molecular weight normal hydrocarbons. Their liptinites consist of predominantly liptodetrinite and sporinite with some resinite. A few samples with lower yields (e.g. 3540, Table 5) are dominated by normal hydrocarbons below C_{17} . The pale and dark lithotypes from the on-shore brown coals (1968 and 1969) yield little pyrolysate given their relatively high atomic H/C ratios. The Gippsland samples give significantly lower yields of phenols from immature samples than their Jurassic and Permian counterparts (Fig. 8).

DISCUSSION

Interrelationships of chemical parameters

For homogeneous hydrogen-rich kerogens and humates the Hydrogen Index (HI) derived from Rock-Eval Pyrolysis shows a predictable relationship with elemental composition according to the following formula (Orr, 1983).

$$HI = 694(H/C - 0.29) - 800 O/C \quad (11)$$

where H/C and O/C represent the atomic hydrogen to carbon and oxygen to carbon ratios respectively. Orr (1983) has observed that practically all Hydrogen Indices obtained from kerogens fall within 12% of the calculated value. This is clearly not the case for

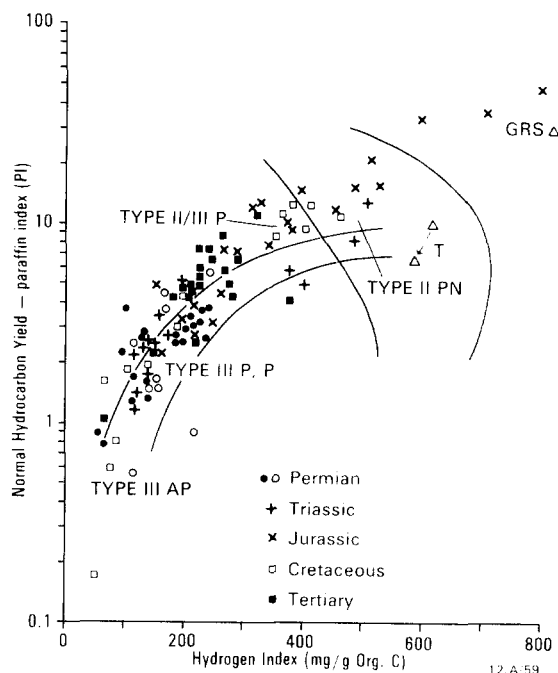


Fig. 11. Distribution of samples on Paraffin Index-Hydrogen Index crossplot of Larter and Sentele (1986). Paraffin Index is based on pyrolysis-GC unit = 0.25% by weight. Hydrogen Index is measured not calculated. Classification of fields is after Larter and Sentele (1986). Type Ip—torbanite kerogens rich in alginite; Type Ipn—tasminite (alginite) rich kerogens; Type In—resinite derived kerogens; Type IIPn—marine source rock kerogens; Type II/IIIp—exinite-rich kerogens; Type IIIpp—vitrinite-rich kerogens from deltaic shales; Type IV—inertinite-rich kerogens. Reference samples are GRS—Green River Shale and T—Toolebuc Formation. Dashed lines denote evolution path for typical Type II marine kerogen.

the samples examined here (Fig. 10) and is attributable to the heterogeneous nature of coals and terrestrial kerogens. The vitrinite-dominated Permian coals have substantially lower Hydrogen Indices than would be predicted from their atomic H/C ratios (0.78–1.07). In contrast, a greater proportion of the measured Hydrogen Indices on the Cooper Basin samples (atomic H/C = 0.6–0.8) fall within 15% of the calculated values. The Jurassic coals and kerogens are the most hydrogen-rich in this sample set and also show a significant deviation between measured and predicted Hydrogen Indices. Only the most hydrogen-rich kerogens (H/C = 1.1–1.5) have measured Hydrogen Indices similar to the predicted values. The relatively few Upper Cretaceous to Tertiary samples with atomic H/C ratios below 0.8 had pyrolysate yields close to the predicted values, whereas the more hydrogen-rich kerogens (H/C = 0.8–1.07) often showed significant variation from the predicted values. These data suggest that for terrigenous kerogens it is not possible to relate pyrolysate yields to atomic H/C ratio between 0.8 and 1.1.

Recently, Larter and Sentele (1985) have used the yield of C_9 – C_{30} normal hydrocarbons, the calculated

Hydrogen Index from elemental analysis and the qualitative appearance of the pyrolysis chromatogram to refine the classification of kerogen types. Figure 11 shows a plot of the normal hydrocarbon yield versus the measured Hydrogen Index for the samples in this study. For many of the samples, the yield of normal hydrocarbons is considerably higher than is encountered in marine kerogens and reflects the large proportion of the pyrolysate that is aliphatic. Remarkably some samples with low atomic H/C ratios (e.g. Gippsland Basin) yield more normal hydrocarbons than marine kerogens with higher H/C ratios. For instance, two samples from the Toolebuc Formation (a marine organic-rich shale, kerogen atomic H/C = 1.27—Boreham and Powell, 1988) have yields of normal hydrocarbons similar to many of the inertinite-rich coal samples from the Cooper Basin.

Chemical characteristics in relation to petrography, age and environment

Thomas (1982) has suggested that differences in hydrocarbon source potential between Palaeozoic and Mesozoic and Tertiary coals may be related to the evolution of successive floras and climatic controls. The results obtained in this study (Figs 3–11) show that samples from different ages and environments have overlapping compositions with samples of a particular age tending to one extreme or another. The samples can be ordered with decreasing hydrocarbon potential as follows Jurassic > Tertiary ≥ Cretaceous > Permian = Triassic. Whereas this sequence follows the broad trends in petrographic composition (i.e. relative proportions of vitrinite, liptinite, inertinite) of Australian coals (Cook, 1975; Thomas, 1982), there is a poor correlation between geochemical and petrographic compositions at the maceral group level on individual samples (Figs 5 and 9). This is not altogether unexpected since the geochemical properties measured are a combination of depositional and maturation controls whereas petrographic composition very largely reflects source and depositional controls and the extent of the chemical variations between individual macerals in each group.

In order to assist in understanding the nature and extent of the correlation between geochemical and petrographic composition, the data set was analysed by the multivariate technique of "Principal Components Analysis". This procedure is a means of organising a large number of variables which may or may not be acting independently and which may react to varying extents to different processes. It seeks for linear combinations of the variables in a data set that explain most of the variability. In this context the procedure is only valid if these combinations can be related to a geological association or process. The total data set and the Permian, Jurassic and Upper Cretaceous–Tertiary subsets were analysed separately to look for systematic effects related to age and/or

depositional conditions. The Triassic and Cretaceous data sets were too small and heterogeneous to yield significant results as separate entities. The parameters used and the results for the first three components are illustrated in Fig. 12.

In all analyses the first three components account for between 59 and 72% of the variance. The first component from the analysis of the total data set conforms to the expected relationships, namely there is an association of pyrolysis yields with liptinite macerals and in opposition to inertinite and maturity as measured by T_{\max} . However, this first component only accounts for 32% of the variance. The Permian sample set most clearly show the influence of inertinite and maturation on hydrocarbon potential reflecting its greater range in maturation and inertinite content.

The principal components analysis of the Permian samples shows that the atomic H/C ratios and pyrolysis yields are partly attributable to the degree of maturation and the relative proportion of inertinite compared to the vitrinite and liptinite macerals [component 1, Fig. 12(a)]. Component 2 indicates an association of atomic H/C ratio with vitrinite content, but this is not reflected in the two sets of paired samples (1984/83 and 1970/71, Table 1). In contrast the dull/bright pair of the Triassic Callide seam (1985 and 1986; Table 2) display a marked variation in atomic H/C ratio with proportion of inertinite and vitrinite.

The highest yields of normal alkanes in the Permian sample set were obtained from the lower rank, vitrinite dominated samples (Table 1); there are no large variations in liptinite content. There is also an association between vitrinite and the yield of waxy normal hydrocarbons (component 2, and Table 1). The inertinite dominated samples from the Cooper Basin gave lesser amounts of predominantly low molecular weight hydrocarbons ($<C_{17}$) irrespective of rank (e.g. 3115, 3116; Table 1). Similar results were obtained from the dull/bright pair of the Triassic Callide seam (1985 and 1986; Table 2) where there is significant variation in normal hydrocarbon yield between the two samples with relatively low and constant liptinite contents. These data suggest a substantial aliphatic component in the vitrinite. In contrast another dull/bright pair (1983/84) shows no difference in atomic H/C ratio, no difference in normal hydrocarbon yield and a small difference in Hydrogen Index (Table 1). The pyrolysates are essentially the same in composition and the differences in yield presumably relate to the degree of cross-linking of the hydroaromatic structures (Nip *et al.*, 1988).

The Jurassic and Upper Cretaceous–Tertiary sample sets show most clearly the influence of liptinite content on hydrocarbon potential [component 1, Fig. 12(a)], but the proportion of the variance explained by this association is relatively low (~33%). Detailed examination of the results suggest

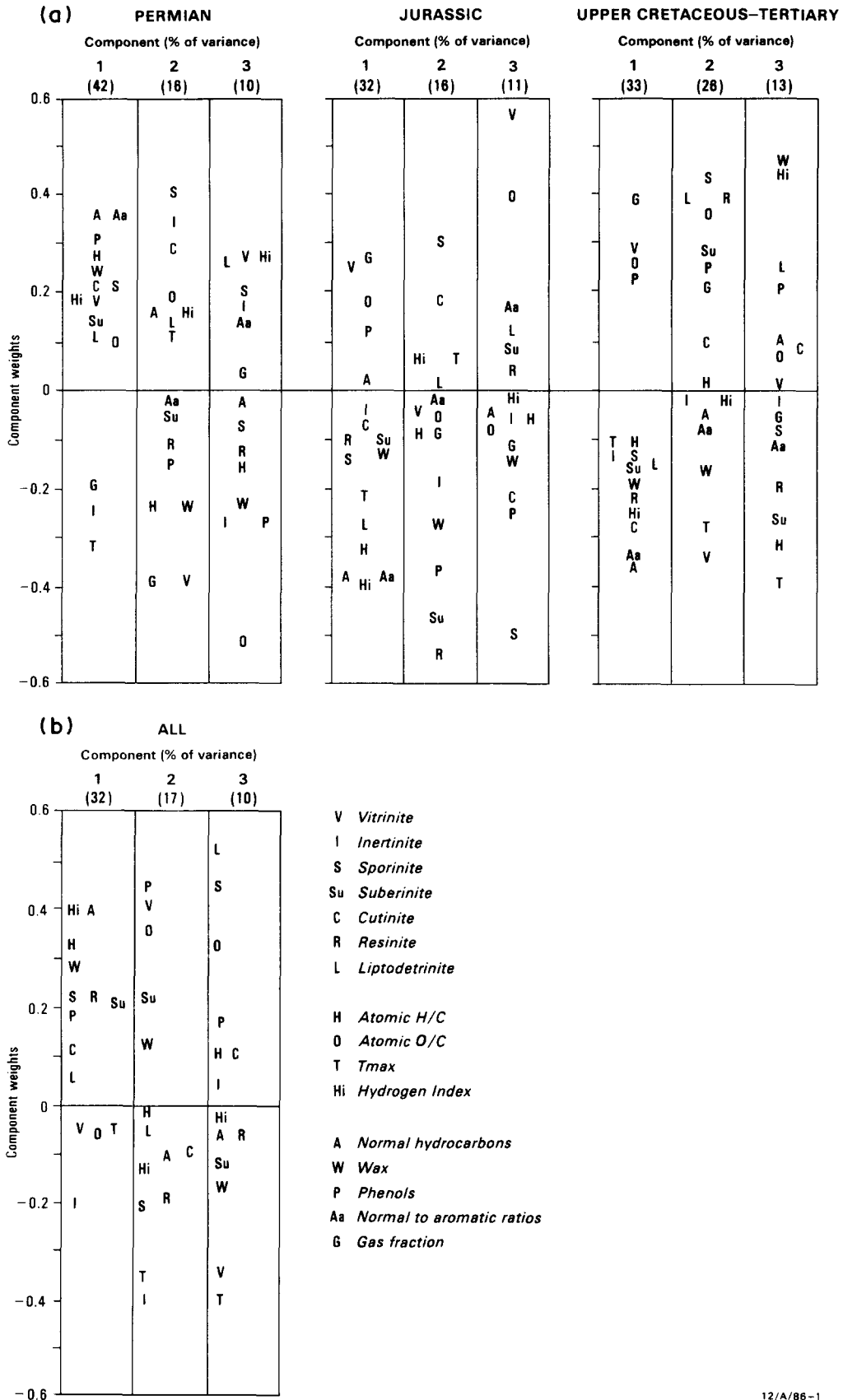


Fig. 12. Principal components analysis of listed variables: (a) Permian, Jurassic and Upper Cretaceous-Tertiary sample sets (phenol yield excluded); (b) all samples (phenol yield excluded). See Tables 1-5 for numerical values and explanation of variables.

the pyrolysis yield may reflect the floral origin and preservation of the liptinite. Irrespective of age, in samples where liptodetrinite and sporinite are the dominant fluorescent macerals, the yield of normal hydrocarbons is lower than in other samples with comparable liptinite contents and atomic H/C ratios (Fig. 9). Despite its relatively high atomic H/C ratio, sporinite is clearly not a major source of normal hydrocarbons since sporopollenin (the main polymeric material in spore walls) is an oxidative polymer of carotenoids (Brooks and Shaw, 1978) and would be expected to give predominantly branched and cyclic or aromatic hydrocarbons on thermal cracking (Schenck *et al.*, 1981a; Nip *et al.*, 1988; Larter and Sentfle, 1985). This is reflected in the relatively low normal to aromatic ratios in the Jurassic liptinite-rich samples (>50%) in which sporinite is by far the dominant maceral (Table 3). Further, the pyrograms of these samples, as well as the liptinite-poor kerogens, are dominated by normal hydrocarbons below C₁₇ (Fig. 9). The origin of these normal hydrocarbons is uncertain, but may reflect the product of pyrolysis of the recently identified "polyethylene-like" polymer found in plants (Nip *et al.*, 1986), but also may reflect contributions from micro-organisms during very early diagenesis: micro-organisms may contribute 10–15% of the biomass in peats (Stach *et al.*, 1982) and similar contributions could be expected in some lacustrine settings. This latter source may explain the association of degraded liptinite fragments (liptodetrinite) with this phenomenon (e.g. Murta Member). On the other hand, in the Jurassic examples there is a strong association between the occurrence of suberinite and the proportion of waxy normal hydrocarbons obtained in flash pyrolysis [Table 3 and Fig. 12(a)]. In the Jurassic and Upper Cretaceous–Tertiary sample sets, there is an association of suberinite with resinite which is independent of the other liptinite macerals [Fig. 12(a) and 12(b)]. The latter observation reflects the origin of resin and suberin within the wood of the parent plant in contrast to the other liptinite precursors which are associated with vegetative parts. Jurassic samples 1647 and 1645 plot as Type I kerogens and yield abundant normal hydrocarbons on pyrolysis (Table 3), but petrographically they are not markedly different from other liptinite-rich samples. Thus, only in some cases is there a clear association between the yield and composition of pyrolysates and petrographic composition.

In all ages there is a progressive decrease in yield of phenols with maturation (Schenck *et al.*, 1981b; Sentfle *et al.*, 1986). A striking variation in the low rank samples is the contrasting yields of phenolic compounds on pyrolysis–GC (Fig. 8). Low rank, Jurassic and Permian samples yield significantly higher amounts of phenols than some of their Cretaceous and Tertiary counterparts. These samples contain little or no inertinite in comparison to vitrinite which is the probable source of most of the

phenols (Nip *et al.*, 1988; Sentfle *et al.*, 1986). This association is demonstrated in the principal components analysis and is consistent with the results from the dull and bright portions of the Triassic Callide seam (1985 and 1986; Table 2). The vitrinite-rich portion yields nearly twice as much phenols as the inertinite-rich portion (Fig. 8); other bright dull pairs (Fig. 8) are of too high rank for original differences in phenol yield to be maintained. However, neither the Tertiary nor Cretaceous samples have high inertinite contents in general (Tables 4 and 5) and yet low rank samples have relatively low yields of phenols. A single Cretaceous coal has a high inertinite content (3661, Table 4) and has an even lower yield of phenols. These observations raise the question as to the extent to which chemical and petrographic composition should be expected to mirror each other in different settings and ages. Inertinite is considered to have a common precursor to vitrinite in the woody parts of plants but differs in having undergone mouldering or incipient carbonisation during initial decay (Stach *et al.*, 1982). Differences in yield of phenols between vitrinite-rich coals from different depositional systems may represent variations in source and depositional conditions. On the other hand, chemical data for one Permian dull/bright pair (1983 and 1984; Table 1) are very similar yet there is a marked difference in the relative proportions of vitrinite and inertinite. Obviously in this case depositional conditions were only subtly different and manifested themselves in petrographic appearance, but not in the chemical analyses conducted in this study.

There is clear evidence that vitrinites may contain significant aliphatic moieties that can yield small but significant amounts of normal hydrocarbons and this is consistent with the recently proposed structural models of Type III kerogen (Behar and Vandenbroucke, 1987). The relationship between wax yield and vitrinite content and the relatively low abundance of normal hydrocarbons in most vitrinite-rich samples, suggests that better correlations may be obtained if vitrinite is divided into telovitrinite and detrovitrinite (desmocollinite). Detrovitrinite is considered to have a higher hydrogen content than telovitrinite and should contain a higher proportion of bacterial lipids. The results presented here suggest that aliphatic moieties may also be present in inertinite macerals and reinforces the nature of the continuum between vitrinite and inertinite that is evident in petrographic observations (Stach *et al.*, 1982). It is one explanation for the ability of some inertinite-rich samples from the Cooper Basin to yield aliphatic hydrocarbons on pyrolysis and the reactive nature during carbonization of inertinites from some Permian coals (Diessel, 1983).

The present data indicate that while floral changes associated with evolution has imposed a time-trend on the chemical as well as the petrographic nature of

coals, local controls on organic facies associated with factors such as climate and sedimentary environment also exert a significant effect on chemical and petrographic characteristics.

Correlation of T_{\max} and vitrinite reflectance

The evolution of the T_{\max} obtained from Rock-Eval analysis varies with kerogen type since it is dependent on the distribution of bond energies in the kerogen. As a result the calibration of T_{\max} against vitrinite reflectance varies from one organic matter type to another (Espitalié, 1986; Espitalié *et al.*, 1985). Figure 13 shows the correlation trends found previously for coals and the results in this study. Permian and Tertiary samples generally conform to the correlation between T_{\max} and vitrinite reflectance published for Westphalian coals from the Paris Basin (Espitalié, 1986). In contrast liptinite-rich Jurassic and Cretaceous samples show consistently higher T_{\max} values for a given vitrinite reflectance indicative of the higher bond energies associated with the abundant aliphatic liptinites in these samples. They plot near the limits of the correlation trend obtained for a diverse group of samples by Teichmüller and Durand (1983). The abundance of detrovitrinite in the Jurassic samples (Smyth *et al.*, 1984) is also likely to be a contributory factor to the difference in T_{\max} vs R_o relationships for the Jurassic samples in comparison with the other coals. This is evident in R_o measurement obtained from different samples of a Jurassic coal seam at a single location (samples 1646–1649, Table 3), high liptinite contents typically being associated with a greater detrovitrinite to telovitrinite ratio. The samples richest in liptinite and with the highest yields of pyrolysable hydrocarbons have lower vitrinite reflectance values than samples with less abundant liptinite and/or lower pyrolysis yields. Clearly, because of the heterogeneous nature of coal it is to be expected that the correlation of T_{\max} with vitrinite reflectance will vary depending on petrographic composition.

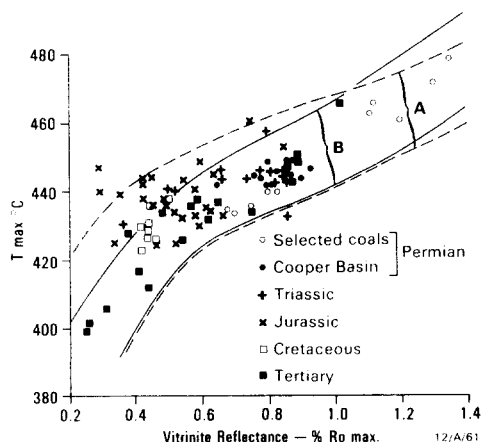


Fig. 13. Variation in T_{\max} with vitrinite reflectance. Correlation trends are those already published for coals. (A) Teichmüller and Durand (1983); (B) Espitalié *et al.* (1985).

IMPLICATIONS FOR SOURCE ROCK ASSESSMENT AND CONCLUSIONS

This study has confirmed that coals and terrestrial organic matter ranging in age from Permian to Tertiary can contain aliphatic structures capable of producing paraffinic oils. For most terrestrial kerogens this capability is not simply related to the gross elemental composition. Only above an atomic H/C ratio of 1.0 and below 0.8 is there a clear-cut relationship between pyrolysable hydrocarbon yield and elemental composition even in relatively immature samples. Between these values, atomic H/C ratios are controlled both by the degree of carbonisation and the content of aliphatic moieties. The formation of inertinite is related to depositional conditions. Nonetheless aliphatic moieties may occur in the kerogen even when the atomic H/C may be relatively low (0.7) and the organic matter can produce normal hydrocarbons on pyrolysis. Although vitrinite-rich samples yielded abundant phenols on pyrolysis, the amount of phenols produced is not simply related to vitrinite content. Below Hydrogen Indices of 300, Rock-Eval analysis is not a good indicator of the ability of coals and carbonaceous shales to yield aliphatic hydrocarbons. There is a broad range of aliphatic hydrocarbon yields from flash pyrolysis for a given Hydrogen Index below 300 and vice versa. As mentioned in the Introduction, the aliphatic hydrocarbon yield is an important factor in source rock assessment in non-marine sequences. In these circumstances, analysis of the pyrolysate is required to obtain an accurate picture of source rock quality.

In general the capability of Australian coals to generate normal hydrocarbons follows the established trends in petrographic composition, but can only be related to petrographic composition at the maceral group level in a broad sense. If the composition is examined at the maceral level better correlations hold. Liptinite-poor (<10%) samples may yield significant amounts of hydrocarbons, but typically these have a low wax yield. Liptinite-rich samples with abundant sporinite and liptodetrinite give lower yields of normal hydrocarbons. These are predominantly of lower molecular weight. They may derive from the hydrocarbon polymer recently found in plant materials or from bacterial lipids that may be incorporated in the plant material during accumulation and decay. Clearly sporinite is not a major source of normal hydrocarbons. Suberinite is associated with high yields of waxy hydrocarbons, but some samples with high yields did not contain large amounts of this maceral. There is no clear association with the intermediate to high yields of waxy normal hydrocarbons with particular macerals in Tertiary and some Permian samples, although no suberinite-rich Tertiary coals were included in this study. The relationship of suberinite and the various vitrinite categories to the occurrence of aliphatic moieties

requires further investigation. The varying petrographic and chemical composition is also reflected in the correlation between T_{\max} and vitrinite reflectance for coals of different ages and settings.

Coal samples that yield lower amounts of pyrolysate dominated by normal hydrocarbons below C_{17} are unlikely to generate enough hydrocarbons during normal maturation to allow migration as a discrete phase. However, such lower molecular weight hydrocarbons could migrate with co-generated gas (Snowdon and Powell, 1982) or carbon dioxide in a supercritical state (Strachan *et al.*, 1988) in the main or late phases of oil generation to produce paraffinic condensates and light oils such as are found in the Cooper Basin. However, the question of the lower limit of pyrolysable hydrocarbon yield at which coals and carbonaceous shales become effective source rocks for waxy oil is not easily answered, since it depends on the migration mechanism and its relation to the absorptive capacity and microporosity of coal. (Saxby and Shibaoka, 1986). Clearly however, a refined assessment of source rock potential in coals and carbonaceous sequences cannot be based on bulk geochemical techniques or petrographic techniques alone. Reconnaissance geochemical or petrographic techniques must be supported by a judicious application of pyrolysis gas chromatographic techniques for quantitative assessment of non-marine source rocks. For adequate petrographic assessment, the relative abundance of the different liptinite macerals is absolutely necessary and probably subdivision of the vitrinite group is desirable. Such analyses can only be made on "whole-rock" samples and cannot be made on demineralised samples due to loss of morphological features during processing.

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