

PYROLYSIS—HYDROGENATION—GAS CHROMATOGRAPHY OF CARBONACEOUS MATERIAL FROM AUSTRALIAN SEDIMENTS, PART II: KEROGENS FROM SOME AUSTRALIAN COALS

D.J. McHUGH¹, J.D. SAXBY² and J.W. TARDIF¹

¹ *Department of Chemistry, Faculty of Military Studies, University of New South Wales, Duntroon, A.C.T. (Australia)*

² *CSIRO Minerals Research Laboratories, North Ryde, N.S.W. (Australia)*

(Received July 7, 1976; accepted for publication December 7, 1976)

ABSTRACT

McHugh, D.J., Saxby, J.D. and Tardif, J.W., 1978. Pyrolysis—hydrogenation—gas chromatography of carbonaceous material from Australian sediments, Part II: Kerogens from some Australian coals. *Chem. Geol.*, 21: 1-14.

Pyrolysis—hydrogenation—gas chromatography (PHGC) has been used to compare the carbon-skeleton structures of kerogens before and after demineralisation. Coals were demineralised by either of two processes involving successive extractions with organic solvents, hydrochloric acid, hydrofluoric acid and then either nitric acid or lithium aluminium hydride. The last two reagents are necessary to remove minerals such as pyrite, by either oxidation or reduction respectively.

Both processes cause some change in the kerogen. HNO₃ treatment leads to a general loss of organic material, especially high in lower-rank coal, and infrared spectroscopy gives evidence of some nitration; the products of PHGC indicate considerable change to the carbon-skeleton structure of the kerogen. LiAlH₄ treatment results in much smaller losses of organic material, particularly in lower-rank coal and PHGC shows that only minor changes in kerogen structure occur. Neither demineralisation process is perfect but that involving LiAlH₄ is preferable.

Some general features of the chemical structure of the kerogen in the original coal are proposed. These proposals are based on comparisons of the quantities of individual PHGC products from each coal and its HNO₃-treated kerogen. The kerogen structures have in turn been related to the rank of the coals, which ranged from peat to anthracite.

INTRODUCTION

Investigation of the chemical structure of kerogen, the insoluble organic matter in sedimentary rock, involves the separation of the kerogen from soluble organic matter and the inorganic components of the rock. Although physical methods of separation have been used with some success, the usual procedure is firstly to extract soluble organic matter with solvents, then to dissolve the inorganic matter by successive treatments with hydrochloric and hydrofluoric acids, followed by an oxidising or reducing agent to remove iron sulphides. The methods used and their effects on the chemical composition of the kerogen have been reviewed by Forsman (1963), Robinson (1969)

and Saxby (1970a). Two techniques for the isolation of kerogen from sulphide ores have since been described by Saxby (1970b), in which either nitric acid or lithium aluminium hydride was used in the demineralisation.

The degree of alteration of the kerogen in the demineralisation process can be measured by applying analytical procedures before and after demineralisation. These procedures include elemental analysis, IR spectroscopy and X-ray analysis, but none of these can give reliable results on the original kerogen before demineralisation. If the kerogen content of a rock is low, such methods are useful only to compare kerogens after demineralisation.

The technique of pyrolysis—hydrogenation—gas chromatography (PHGC) described previously (McHugh et al., 1976) offers a convenient method of determining whether any change has occurred in the carbon skeleton of kerogen during demineralisation. The procedure uses small samples and can be used on isolated kerogen or on rock samples with a low kerogen content. Results are not affected by the mineral or water content of the sample. It is thus possible to compare the carbon skeleton of the kerogen before and after demineralisation.

In the present work, seven Australian coals and a sample of anthracite were demineralised by treatment with HCl and HF, followed by either HNO₃ or LiAlH₄. The resulting kerogens and the original coals were subjected to PHGC, IR spectroscopy and elemental analysis. These results have been used to assess the effect of each demineralisation treatment on the chemical structure of the kerogen.

EXPERIMENTAL

Samples

The seven Australian coals and the anthracite were those used in the previous study (McHugh et al., 1976). The coals and their commercial rank classification are shown in Table I.

Chemical isolation of kerogen

Details of the methods of demineralisation are given by Saxby (1970b). Each coal was extracted with benzene—methanol (3:1), then treated with HCl (5 M, 2 h at 60–70°C) followed by HF (mixture of 22 M HF and 10 M HCl, 2 h at 60–70°C). The sample was then divided into two parts. One part was treated with HNO₃ (2 M, 1 h at 60–70°C) and then sequentially with HCl, HF and HNO₃ until no loss in sample weight was observed as a result of any of the three reagents; this part was finally extracted twice with benzene to remove any elemental S formed during the oxidation. The second part was treated with LiAlH₄ [in tetrahydrofuran (THF), 1 h at room temperature, 5 min, at 66°C] and then sequentially with HCl, HF and LiAlH₄ until no loss in sample weight was observed.

TABLE I

Coal and kerogen samples

Coal origin*1	Coal rank	Sample	Moisture*1 (%)	Ash*2 (%)	Elemental analysis (% d.a.f. basis)*3				Original C remaining**4
					C	H	O	N S	
Botany Basin	peat	untreated peat	~75	6.4	59.7	5.1	30.0	3.1	2.1
		HNO ₃ kerogen	0	0.5	57.7	3.9	33.8	3.5	1.1
		LiAlH ₄ kerogen	0	0.5	63.0	4.4	29.4	1.0	2.2
Yallourn	lignite	untreated coal	10.8	2.0	64.7	4.4	30.2	0.2	0.5
		HNO ₃ kerogen	0	0.9	57.5	3.6	36.2	2.6	0.1
		LiAlH ₄ kerogen	0	0.0	64.6	4.1	31.1	0.1	0.1
Leigh Creek	sub-bituminous	untreated coal	15.0	7.1	66.8	3.8	27.2	1.3	0.9
		HNO ₃ kerogen	0	0.1	62.1	2.6	31.0	4.2	0.1
		LiAlH ₄ kerogen	0	0.1	69.7	3.7	24.7	1.4	0.5
Collie	sub-bituminous	untreated coal	7.2	2.5	70.0	3.9	24.6	1.4	0.1
		HNO ₃ kerogen	0	0.0	62.0	2.6	31.4	3.9	0.1
		LiAlH ₄ kerogen	0	0.7	73.5	3.9	21.2	1.3	0.1
Greta	high-volatile bituminous	untreated coal	2.6	4.4	81.6	6.1	9.5	1.8	1.0
		HNO ₃ kerogen	0	0.1	68.3	4.2	23.1	3.6	0.8
		LiAlH ₄ kerogen	0	0.2	79.8	5.6	11.8	2.0	0.8
Bulli	medium-volatile bituminous	untreated coal	3.1	11.8	82.4	4.8	10.2	1.8	0.8
		HNO ₃ kerogen	0	0.0	69.0	3.0	23.0	4.4	0.6
		LiAlH ₄ kerogen	0	0.0	81.1	4.4	11.9	1.9	0.7
Bluff	low-volatile bituminous	untreated coal	0.8	14.1	86.9	4.3	5.8	1.7	1.3
		HNO ₃ kerogen	0	0.0	77.0	3.3	15.4	3.8	0.5
		LiAlH ₄ kerogen	0	1.7	85.9	4.3	7.5	1.6	0.7
Bluff	anthracite	untreated coal	1.8	3.0	89.0	2.8	6.0	1.0	1.2
		HNO ₃ kerogen	0	0.0	82.8	2.5	11.8	1.9	1.0
		LiAlH ₄ kerogen	0	0.1	89.7	3.0	5.4	0.9	1.0

*1 District or Seam. Further descriptions of these deposits are given by Brown and Waters (1962).

*2 Untreated coals were air-dried; kerogens were dried under vacuum, 105°C.

*3 On dry, ash, F-, Cl-free basis.

*4 Original C is the mass of organic C in the coal sample taken for demineralisation; the percentage of this remaining after demineralisation is given in this column.

Pyrolysis—hydrogenation—gas chromatography

The equipment and techniques used were those described previously (McHugh et al., 1976). Pyrolyses were run under the conditions shown in Table II. The normal sample size (2.0 mg) had to be increased for anthracite

TABLE II

Experimental conditions for PHGC

Temperatures (°C):		GC temperature programme:		Gas flow:	
furnace	700	initial temperature	50° C	carrier (H ₂)	30 ml min ⁻¹
valve and piping	240	initial time	10 min	make-up (N ₂)	50 ml min ⁻¹
hydrogenator	300	rate of increase	6° C min ⁻¹	Sample size:	0.4–8 mg
FID	250	final temperature	250° C	Pyrolysis time:	30 sec
		final time	20 min	GC columns:	
				size:	2.25 m × 3 mm i.d.
				packing:	10% Apiezon L on Chromosorb P

and its kerogens (8.0 mg) to obtain an adequate detector response. Exploratory pyrolysis showed that some kerogen samples were contaminated with organic solvents from the demineralising process. Therefore all kerogen samples were dried under vacuum at 150°C until either all the solvent was removed or no further reduction of solvent could be achieved. All coals and kerogens listed in Table I were pyrolysed. One coal and the two kerogens derived from it were pyrolysed on the same day; a standard sample (Bulli coal) and a blank were also run daily.

The PHGC peaks were identified by coinjection of standard compounds during pyrolysis, by copyrolysis with polyethylene, which in PHGC produces mainly *n*-alkanes, and by comparison with published retention data (Preston, 1969). The identification has more recently been confirmed by combined gas chromatography—mass spectrometry, a technique which was not available to us at the time this work was carried out.

A full list of identified compounds is given in Table III. The numbering of peaks in Figs 1–3 corresponds to this list.

Analyses and spectra

Elemental analyses were carried out by the Australian Microanalytical Service, Melbourne. IR spectra were recorded on a Unicam SP200 spectrophotometer. All samples were prepared in KCl discs, but difficulty was experienced in grinding samples to a suitable particle size. The following procedure gave useful spectra. The coal/kerogen sample (1 mg) was ground for 20 min with KCl (250 mg, added gradually) using a mortar and pestle.

TABLE III

Compounds identified in PHGC of coal and kerogens

1 = alkane gases	9 = <i>n</i> -heptane	17 = <i>o</i> -xylene
2 = 2-methyl butane	10 = methylcyclohexane	18 = <i>n</i> -decane
3 = <i>n</i> -pentane	11 = ethylcyclopentane	19 = <i>n</i> -undecane
4 = cyclopentane	12 = toluene	20 = <i>n</i> -dodecane
5 = <i>n</i> -hexane	13 = <i>n</i> -octane	21 = <i>n</i> -tridecane
6 = methylcyclopentane	14 = ethyl benzene	22 = <i>n</i> -tetradecane
7 = benzene	15 = <i>m</i> -xylene and <i>p</i> -xylene	23 = <i>n</i> -pentadecane
8 = cyclohexane	16 = <i>n</i> -nonane	

During grinding the mixture was continually wetted with CCl_4 and this was removed under an IR lamp before pressing the disc.

RESULTS

Elemental analyses

The elemental composition of each coal and the two kerogens prepared from it are listed in Table I. By calculating the total organic C in both the original coal sample and the isolated kerogen it was possible to obtain a carbon balance for each sequence of chemical treatments. This was expressed as the percentage of the original C remaining in the kerogen and the results are listed in Table I.

Infrared spectra

Spectra were obtained from the following coal and kerogen samples: Botany Basin, Yallourn, Bulli and anthracite. As expected, the anthracite spectra exhibited the continuous absorption characteristic of partially graphitized structures with broad functional-group peaks. The principal peaks in each spectrum are shown in Table IV.

Pyrolysis—hydrogenation—gas chromatography (PHGC)

Comparisons were made between the PHGC trace obtained from each kerogen and that from its parent coal. The comparisons were based: (a) on the overall pattern of peaks (fingerprint comparison); and (b) on the heights of peaks common to both samples. The pyrograms in Figs. 1–3 illustrate fingerprint comparisons for a low-, a medium- and a high-rank coal. For each kerogen, the peak heights of the *n*-alkanes and selected aromatics were measured, corrected for moisture and ash in the kerogen, and divided by the corresponding figures for the parent coal. The resulting ratios are shown in Table V. A ratio of 1.0 shows equal quantities of that component are produced by both the coal and its kerogen during pyrolysis.

TABLE IV

Infrared spectra of some coals and their kerogens

Sample origin	Sample	Main IR peaks (cm ⁻¹)*							
		O-H	C-H	C=O	(1)		-NO ₂	C-H	-NO ₂
					(1)	(2)			
Botany Basin	peat	3400 P	2900 M	1700 S	1620 P		1450 S		
	HNO ₃ -kerogen	3400 P	2900 M	1710 P	1640 P	1550 S	1450 S		
	LiAlH ₄ -kerogen	3400 P	2900 S		1620 P				
Yallourn	coal	3400 P	2900 M	1700 S	1620 P		1410 S		
	HNO ₃ -kerogen	3400 P	2900 M	1710 P	1620 P	1540 S	1450 S		
	LiAlH ₄ -kerogen	3400 P	2900 M	1700 S	1620 P				
Bulli	coal	3400 P	2900 M		1650 P		1450 M		
	HNO ₃ -kerogen	3400 P	2900 S	1710 M	1610 P	1540 M	1450 S	1350 S	
	LiAlH ₄ -kerogen	3400 P	2900 S		1600 P		1450 M		
Anthracite	coal	3400 P	2900 S		1620 PB				
	HNO ₃ -kerogen	3400 P	2900 S		1620 PB				
	LiAlH ₄ -kerogen	3400 P	2900 S		1640 PB				

*P = prominent peak; M = moderate peak; S = small peak; PB = prominent, broad peak.
OH absorption possibly due to moisture.

TABLE V

Ratio of kerogen peak height to coal peak height for selected PHGC products*

Coal	Kerogen	n-C ₇	n-C ₈	n-C ₉	n-C ₁₀	n-C ₁₁	n-C ₁₂	n-C ₁₃	n-C ₁₄	n-C ₁₅	Toluene	Ethyl benzene	p-Xylene	m-Xylene
Botany Basin	HNO ₃	0.66	0.75	0.68	0.67	0.65	0.63	0.55	0.52	0.50	0.93	0.98	0.74	0.96
	LiAlH ₄	1.33	0.90	0.72	0.93	0.78	0.88	0.88	0.85	0.81	1.19	1.04	1.39	1.08
Yallourn	HNO ₃	0.73	0.74	0.67	0.70	0.62	0.57	0.46	0.44	0.51	1.13	0.78	0.76	0.93
	LiAlH ₄	0.81	0.81	0.77	0.74	0.73	0.77	0.78	0.91	0.76	0.98	0.92	0.81	0.85
Leigh Creek	HNO ₃	0.36	0.38	0.38	0.38	0.37	0.30	0.28	0.30	0.33	0.39	0.38	0.28	0.34
	LiAlH ₄	0.79	0.77	0.77	0.78	0.83	0.83	0.81	0.98	1.00	0.98	0.96	0.86	0.91
Collie	HNO ₃	0.38	0.37	0.37	0.36	0.32	0.27	0.23	0.24	0.22	0.50	0.38	0.34	0.39
	LiAlH ₄	0.78	0.79	0.79	0.77	0.78	0.77	0.76	0.78	0.78	0.91	0.85	0.86	0.84
Greta	HNO ₃	0.33	0.29	0.42	0.30	0.23	0.21	0.16	0.16	0.10	1.29	0.79	0.71	0.95
	LiAlH ₄	0.93	0.78	1.24	0.84	0.79	0.81	0.78	0.76	0.74	1.14	0.84	0.92	1.03
Bulli	HNO ₃	0.18	0.15	0.09	0.13	0.13	0.09	0.07	0.10	—	0.37	0.24	0.14	0.15
	LiAlH ₄	0.85	0.80	0.81	0.74	0.73	0.72	0.61	0.73	0.85	0.70	0.74	0.55	0.69
Bluff	HNO ₃	0.16	0.19	0.19	0.15	0.45	0.29	0.42	0.36	—	0.29	0.17	0.10	0.20
	LiAlH ₄	0.74	0.56	0.55	0.54	0.76	0.81	0.83	0.71	0.85	0.76	0.69	0.63	0.68

* All figures relate to the same weight (2.0mg on a dry, ash-free basis) of each coal and its kerogens.

DISCUSSION

Relative merits of kerogen-extraction methods

The elemental analyses of the kerogens show that the HNO_3 treatment causes major changes while the products of LiAlH_4 treatment are more like the original coal. Thus for HNO_3 -treated kerogen (HNO_3 -kerogen) the results in Table I indicate: (a) for low-rank material, a considerable loss of original C during isolation (40–80%) and some oxidation of the isolated kerogen (elemental O, compared with parent coal, increased by 10–20%); and (b) for bituminous and higher-rank materials, much smaller loss of original C during isolation (5–15%) but a marked increase in the degree of oxidation of the isolated kerogen (elemental O increased by 95–165%). In every case the N content of the HNO_3 -kerogen is greater than that of the original coal. The LiAlH_4 -treated kerogens (LiAlH_4 -kerogen) appear to undergo much less change during demineralisation. Only the peat and the lignite samples suffer appreciable loss of original C and this loss is far lower than that for the HNO_3 treatment; for sub-bituminous and higher rank the loss is only 2.5–5%. The O content of the LiAlH_4 -kerogens fluctuates either side of the parent-coal values (–14 to +29%). Comparison of the overall elemental analysis of each coal–kerogen pair indicated that changes in composition of the LiAlH_4 -kerogens are minimal.

Comparison of the principal absorption peaks in the IR spectra of four of the samples (Table IV) also provides evidence of changes due to the HNO_3 isolation procedure. One HNO_3 -kerogen (Bulli) developed a carbonyl peak ($1,700\text{ cm}^{-1}$), while two others (Botany Basin, Yallourn) had more intense carbonyl peaks than found in the original coal. All three samples showed absorption peaks typical of nitro groups ($1,540\text{ cm}^{-1}$, $1,350\text{ cm}^{-1}$). The spectrum of the HNO_3 -kerogen from anthracite did not differ to any significant extent from that of the parent coal.

The pyrograms resulting from PHGC reflect the carbon-skeleton structures in the material pyrolysed. Comparisons based on the overall pattern of peaks (fingerprint comparison) are therefore a useful indication of the degree of similarity of the carbon skeletons in the original coal and the extracted kerogen. The peak patterns of each coal and its HNO_3 -kerogen differed for every sample except that from Leigh Creek but the LiAlH_4 -kerogens were similar to the untreated coals in all cases. A true indication of these similarities and differences can only be obtained by examination of the pyrograms themselves and examples from a low-, a medium- and a high-rank coal are reproduced in Figs. 1–3.

The Yallourn coal (lignite) and its LiAlH_4 -kerogen show virtually identical pyrograms (Fig. 1); the HNO_3 -kerogens show minor differences between *n*-hexane and *n*-octane but major differences are evident above *n*-undecane. Greta coal (high-volatile bituminous) is known to have a high exinite content

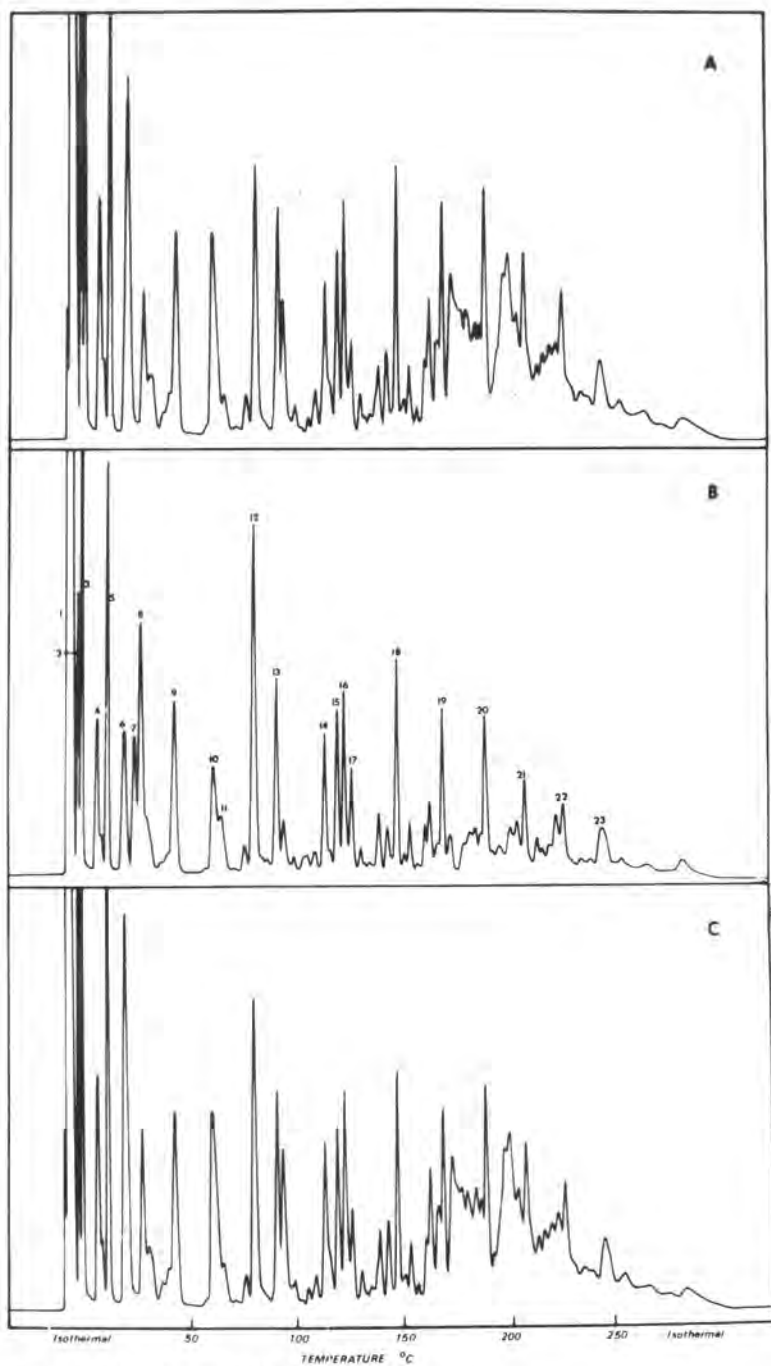


Fig.1. PHGC traces of Yallourn samples.
 A. untreated coal. B. LiAlH₄-kerogen. C. HNO₃-kerogen.
 For identification of peaks see Table III.

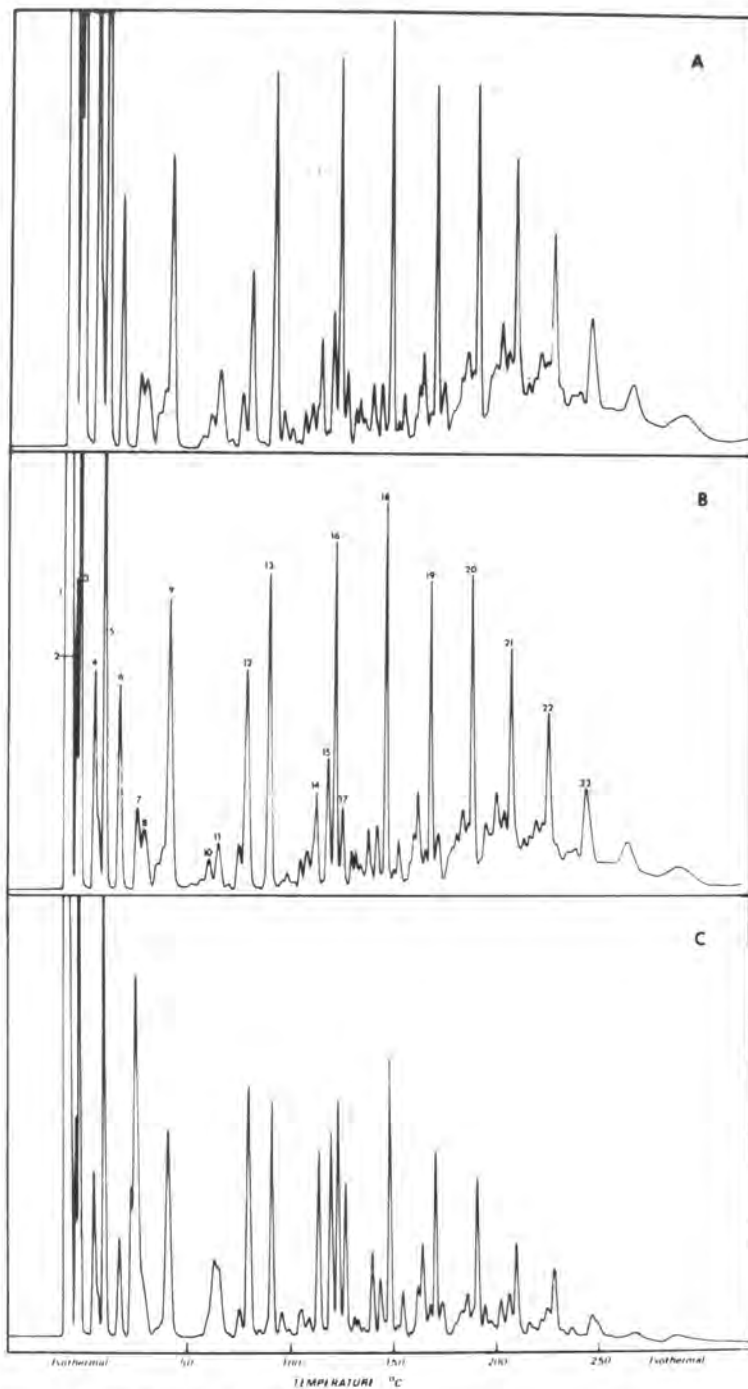


Fig. 2. PHGC traces of Greta samples.
 A. untreated coal. B. LiAlH₄-kerogen. C. HNO₃-kerogen.
 For identification of peaks see Table III.

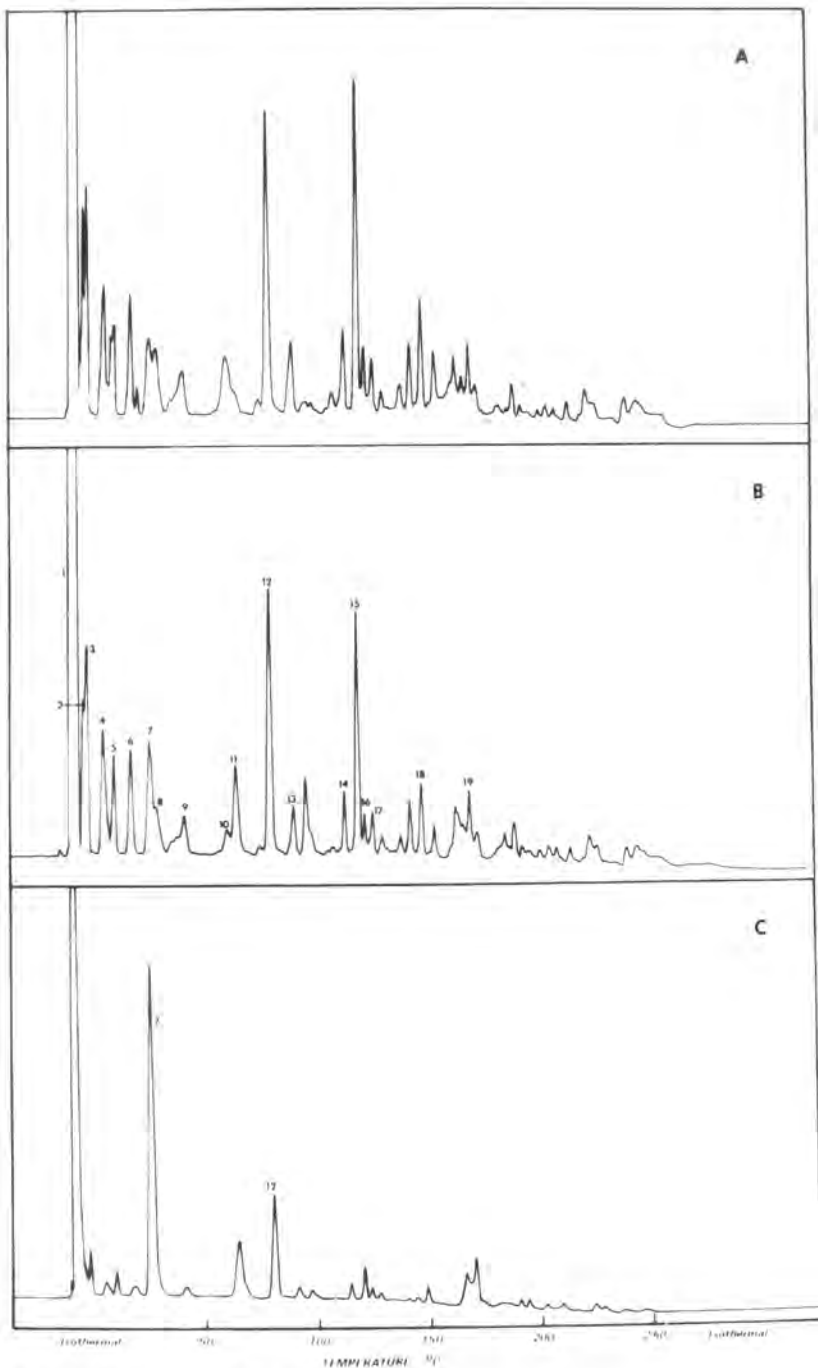


Fig. 3. PHGC traces of Bluff samples.

A. untreated coal. B. LiAlH₄-kerogen. C. HNO₃-kerogen.

For identification of peaks see Table III.

and this is reflected in the large proportion of *n*-alkanes in its pyrogram (Fig.2A). The LiAlH_4 -kerogen again gives a pyrogram very similar to the original coal (Fig.2B) but the HNO_3 -kerogen shows marked differences. These differences are particularly evident in the relative proportions of *n*-alkanes and aromatics, the latter being more abundant in the HNO_3 -treated sample. The pyrograms for Bluff coal (low-volatile bituminous) and its LiAlH_4 -kerogen (Fig.3) compare well, although the degree of similarity is not as striking as for the two previous samples. However, the HNO_3 -kerogen gives a quite different pyrogram and the total amount of pyrolysate is considerably reduced. This pyrogram has an unusually high benzene peak and illustrates a problem arising from the demineralisation process. Organic solvents, such as benzene and THF, used in the process can apparently be adsorbed by the kerogen; these solvents can usually be removed by drying but are more tenacious in high-rank material. The HNO_3 -kerogen in Fig.3C was dried for 24 h under vacuum at 150°C ; this treatment considerably reduced the benzene peak but it is still anomalously high. The benzene and THF in kerogen from anthracite were not completely removed after 60 h drying. When pyrograms were run on several samples before and after drying, the only differences found were in the heights of the benzene and THF peaks.

A more quantitative estimate of the effect of isolation procedure on kerogen composition can be made by comparing peak heights (Table V). In the Botany Basin and Yallourn series, the *n*-alkanes were depleted in the HNO_3 -kerogens but only marginally more than the LiAlH_4 -kerogens; the aromatics were largely unaffected by either treatment. However for the remaining five series there was a significant reduction in *n*-alkanes for all the HNO_3 -kerogens and in aromatics for all but the Greta sample; the losses for the LiAlH_4 -kerogens were much smaller in comparison. In summary, all peak heights were reduced by HNO_3 treatment to a marked degree in samples of sub-bituminous and higher rank but none of the peak heights were significantly affected by LiAlH_4 treatment.

This consideration of elemental analyses, IR spectra and pyrograms from PHGC shows that the kerogen isolation procedure using HNO_3 leads to significant changes in chemical structure while the LiAlH_4 procedure is milder and causes much less change. Thus, whenever it is desired to isolate unchanged kerogen from a shale, the procedure involving HCl , HF and LiAlH_4 treatments is likely to be the more satisfactory.

Chemical structure of kerogen

The results of PHGC give some useful insights into the chemical structure of the kerogens. In the earlier discussion we compared ratios of pyrolysis products within each coal/kerogen group and obtained a measure of the effect of isolation method on kerogen composition in that group. Comparison of ratios between one group and another gives information on changes in kerogen structure with increasing rank. The HNO_3 -kerogens give the most useful information.

For example, the HNO_3 -kerogens of the higher-rank samples, Bulli and Bluff, showed small losses of organic C during isolation (Table I) yet the quantity of pyrolysis products is very significantly reduced when compared to the original coal (Table V). This behaviour can be explained by proposing that these kerogens, in the untreated coals, consist of large aromatic polycyclic structures with aliphatic and mono- or dicyclic components (containing oxidizable functional groups) projecting around the edges. HNO_3 treatment would lead to oxidation and chain breaking in these projecting fragments and the resulting small molecules would be lost as soluble material. These side-chains would represent only a small proportion of the total polymer mass, so that the loss of organic C during isolation could be low. Pyrolysis of polycyclic structures with these side-chains should give products originating exclusively from the side-chains since the polycyclic nucleus has a high thermal stability. Removal of a sizeable proportion of these side-chains by HNO_3 would result in a structure consisting almost entirely of the polycyclic nucleus, so that pyrolysis products would be drastically reduced. On the other hand, reduction of the original coal kerogen with LiAlH_4 is unlikely to break off projecting side-chains from the polycyclic nucleus so that the LiAlH_4 -kerogen behaves like the original kerogen when pyrolysed.

At the other end of the rank scale, we found that the peat and the lignite suffer large losses of organic C during HNO_3 treatment (Table I) yet the residual kerogens give pyrolysis products much more comparable with their original coals (Table V) than was found for the high-rank coal/kerogens. To account for this we propose that the kerogen in the original peat and lignite has a polymeric structure with some large polycycles but mainly small-ring structures joined by aliphatic chains containing oxidizable functional groups. PHGC of such a material should give a high yield of alkanes and simple aromatics. HNO_3 treatment of this kerogen should lead to oxidation and chain breaking, the extent being dependent on the proportion of functional groups still in the kerogen and the physical accessibility of such groups to the acid. Smaller molecules resulting from oxidation would be lost as soluble material in the isolation procedure. The insoluble kerogen that remained would contain: (a) material with less reactive or fewer functional groups and so be less susceptible to oxidation; and (b) material with a higher proportion of large polycycles. This HNO_3 -kerogen could be expected to give similar PHGC products to the original kerogen but in somewhat lower proportion because of the higher concentration of polycyclic structures.

The sub-bituminous coals are intermediate between the two extremes we have discussed. Polycyclic structures have developed further than in low-rank materials but there are still many oxidizable functional groups left in the aliphatic—mono/dicyclic systems. Many of these are removed during HNO_3 treatment and the resulting kerogen, richer in polycycles, gives a lower yield when pyrolysed.

Greta coal has an unusually high H content for a medium-rank coal, and this is associated with the known high exinite content. Pyrolysis of the un-

treated coal gives large quantities of straight-chain alkanes, a fact which also correlated with its high exinite content. In comparison with the untreated coal, the HNO_3 -kerogen gives smaller quantities of straight-chain aliphatics but similar quantities of simple aromatics. We suggest that the kerogen of this coal consists of a mixed aromatic—aliphatic polymer together with another polymer, formed chiefly from the exinite, composed of mainly aliphatic structures with some oxidizable functional groups. If this latter polymer were much more susceptible to oxidation than the former, its destruction during HNO_3 treatment would account for the significant reduction of *n*-alkanes in the pyrolysis of the HNO_3 -kerogen. The former polymer, derived from non-exinite macerals, would be more difficult to oxidize so that the aromatic ring structures remain and contribute to the pyrogram.

REFERENCES

- Brown, H.R. and Waters, P.L., 1962. Characteristics of Australian coals and their influence on the pattern of coal utilisation. *Trans. 6th World Power Conf.*, 7: 2631—2655.
- Forsman, J.P., 1963. Geochemistry of kerogen. In: L.A. Breger (Editor), *Organic Geochemistry*, Pergamon, London, pp. 148—182.
- McHugh, D.J., Saxby, J.D. and Tardif, J.W., 1976. Pyrolysis—hydrogenation—gas chromatography of carbonaceous material from Australian sediments, Part I: Some Australian coals. *Chem. Geol.*, 17: 243—259.
- Preston, S.T., 1969. A guide to the analysis of hydrocarbons by gas chromatography. Polyscience Corporation, Evanston, Ill., 2nd ed., 577 pp.
- Robinson, W.E., 1969. Isolation procedures for kerogens and associated soluble organic materials. In: G. Eglinton and M.T.J. Murphy (Editors), *Organic Geochemistry*, Springer, Berlin, pp. 181—195.
- Saxby, J.D., 1970a. Isolation of kerogen in sediments by chemical methods. *Chem. Geol.*, 6: 173—184.
- Saxby, J.D., 1970b. Technique for the isolation of kerogen from sulphide ores. *Geochim. Cosmochim. Acta*, 34: 1317—1326.