Metals and Metal Complexes in Coal [and Discussion]

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Metals and metal complexes in coal

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Some of the metal compounds that occur in coal are soluble in organic solvents and are extracted in coal liquefaction processes. The material made by the extraction of coal with hydrogenated anthracene oil has been fractionated by sequential Soxhlet extraction with low-boiling solvents, and the distribution of the metallic elements in the various fractions has been determined.

Extraction of Daw Mill coal (92 kg) with acidic methanol furnishes 17.8 mg of a mixture of gallium complexes of homologous porphyrins (C_{27}–C_{32}). Similar metalloporphyrin concentrates are obtained from a variety of British bituminous coals, the amount detected being about 1 µg/g, but falling off as coal rank increases. Various lignites and a range of Polish coals have also been surveyed: here, iron porphyrins and (in one case) manganese porphyrins have been observed. The iron porphyrins tend to be confined to coals of lower rank: in the lignites, metal-free tetrapyrroles are also detected.

The metalloporphyrins are thought to be derived from the chlorophylls and haems of the biological precursors. Indeed, it is possible that the iron porphyrins are derived *directly* (i.e. without demetallation–metallation) from biological and microbiological haem compounds.

INTRODUCTION

The composition of coal with respect to the metallic elements is dominated by the almost inevitable association of the coal substance with inorganic mineral matter. Besides the common metals (e.g. iron from pyrites, aluminium from clays) that arise in this way, the coal substance is characterized by the presence of a remarkable range of metals, often present in little more than trace amounts (Goldschmidt 1937; Nicholls 1968). An example is given in table 1. It is the metal content associated with the organic structure of the coal that is of particular interest in the present work. This metal content is thought to arise partly from the metal compounds originally present in the biological precursors of the coal, and partly by enrichment at later stages. This enrichment could occur in various ways, but it seems likely that somewhere along the diagenetic pathway compounds are formed (humic acids, for example) that possess functional groups that can behave as powerful ligands. These compounds are expected to have a sequestering effect in removing metal ions from groundwater with some degree of selectivity.

A distinction between the metal content associated with organic material and that associated with inorganic material has sometimes been made on the basis of metal determinations carried out on the coal substance and on the coal ash derived from it (Nicholls 1968). We have adopted a different approach, which relies on extraction with organic solvents under various conditions.

This approach has an important bearing on coal liquefaction processes that are being developed in the search for alternative sources of the products that in the recent past have been generated from crude oil. One type of process involves extraction of coal with solvent at high temperatures: the solvents that have been used include hydrogenated anthracene oil (a neutral fraction of coal tar boiling above 200 °C, and consisting largely of phenanthrene and its derivatives) (Davies 1978), and lower-boiling solvents such as toluene (Bartle *et al.* 1975) under supercritical conditions. Such extracts contain metal compounds that because of their solubility in organic solvents are presumed to include either organometallic compounds (i.e. with metal–carbon bonds) or metal complexes of organic ligands. Metal compounds extracted in this way are known to have a deleterious effect on the activity of the catalyst in subsequent catalytic processes in which the coal extract is subjected to further chemical modifications (Kovach *et al.* 1978).

Table 1. Metal analysis of Daw Mill coal (N.C.B. coal rank code 902)

(Results are expressed as micrograms per gram or, where indicated, as percentages by mass.)

Li	Be											B	C	N
	0.6											240		
Na	Mg											Al	Si	P
900	0.18%											2%	2.6%	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
0.2%	0.7%		900	40	35	280	0.7%	9	30	24	26	4.5	< 2	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
30	60	5.5	50		3.5				< 0.7	< 0.5	< 0.6	< 0.4	< 2	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
< 7	280			< 12	< 7				< 15				18	3

Data provided by W. F. Wyss, National Coal Board. Analysis by direct arc emission spectrography at A.E.R.E., Harwell, Oxfordshire. The sign < means that the element was not detected, and refers to the detection limit under the conditions employed. The uncertainty associated with this type of analysis can be ± 30 % relative, except for B, Bi, Mo, Pb, Rb and Y where the uncertainty is greater in the present example.

Fractionation of coal extracts by sequential continuous extractions with low-boiling organic solvents

We have examined various extracts supplied by the Coal Research Establishment. For example, one extract (code D159/CHU (2) ER1) had been prepared by the extraction of coal (Annesley, South Nottinghamshire, N.C.B. coal rank code 702) with hydrogenated anthracene oil (400 °C, 400 kPa, 1 h, 85 % extraction yield). This extract was received as a black lustrous solid with an ash content of 0.17 %: it was freely soluble in tetrahydrofuran. To obtain some information about the extent to which inorganic particulate matter was present, the solution was filtered through Whatman GF/F glass fibre filters, which removes particles with a diameter greater than 0.7 μm. The ash content of the solid from the filtrate was 0.14 %, indicating that a large part of ash-generating material was present either as particles smaller than 0.7 μm or was in solution.

The coal extract was fractionated by continuous extraction at the Soxhlet apparatus by using the sequence of purified solvents: light petroleum (b.p. 40–60 °C), benzene, methanol, chloroform, tetrahydrofuran. This did not give complete dissolution in spite of the fact that the original material was soluble in the last solvent. This is possibly due to the leaching out, during the early stages of the extraction, of compounds that behaved as co-solvents with tetrahydrofuran, but it is also conceivable that some auto-oxidative polymerization had occurred during the lengthy extraction process. The progress of the extraction, the ash contents of the various fractions, and some metal analyses of the various ashes, are summarized in table 2.

In the sequential extractions only a small proportion of the metal content was dissolved in the low-boiling solvents employed, and the metals tended to be concentrated in the residual fraction. This is taken to mean that much of the metal content is associated with particulate or with components of high molecular mass. However, some metals did appear to suffer fractionation. Thus in the fractionation of the hydrogenated anthracene oil extract (table 2), both copper and manganese appear to be concentrated in the methanolic fraction, while nickel is marginally enriched in the benzene extract. This suggests the presence in such fractions of components that may well prove amenable to further chemical investigations.

TABLE 2. SEQUENTIAL SOLVENT EXTRACTION OF HYDROGENATED ANTHRACENE OIL EXTRACT CE-D159/CHU2 (2) ER1

solvent	duration h	percentage extracted	percentage ash†	metal content of extract or fraction/(μg/g)‡ Al	Cr	Cu	Fe	Ga	Mn	Ni	Ti	V
none	—	—	0.17	80	10	1.8	400	2.2	4	9	85	8
petroleum§	30	29.6	0.019	1.2	0.3	0.02	0.6	—	—	1.2	—	—
benzene	20	28.5	0.093	11	2	0.2	35	0.4	0.3	12	6	0.9
methanol	25	3.2	0.47	14	3	10	45	4	14	9	4	1.2
chloroform	27	4.9	0.077	15	3.5	1.4	120	0.9	0.9	5.5	18	3
tetrahydrofuran	39	5.8	0.20	80	11	1.6	500	3	3	6.5	90	10
residue	—	21.1	0.425	220	24	6.5	0.11%	5	9	14	220	20

† Determined throughout by slow pyrolysis in platinum, eventually at 825 °C for 1 h, except for the methanol fraction (4 h at 600 °C).

‡ Unless stated otherwise, these were determined throughout by direct current arc emission spectrography at A.E.R.E., Harwell, Oxfordshire.

§ Light petroleum, b.p. 40–60 °C.

THE DETECTION OF METALLOPORPHYRINS IN COALS

Extraction of coals and coal extracts with organic solvents gives very complex mixtures. Thus repeated thin-layer chromatography of the petroleum-soluble fraction and the benzene-soluble fraction from the hydrogenated anthracene oil extract (table 2) reveals many components. To simplify the problem we have chosen to use methanol, a rather poor solvent for the purely hydrocarbon components, but perhaps polar enough to coordinate to, and possibly to extract, certain metal complexes. We have employed acidic conditions (sulphuric acid) in the hope that, for stable metal complexes at least, the bonding of the metal complex to the residual coal structure would be weakened, thus liberating the metal complex. Provision has been made for any metal sulphates that are formed to be transferred into aqueous solution.

This approach has been employed initially in a search for metalloporphyrins, the presence of which might be detected at an early stage by the appearance of an absorption band at about 400 nm (the Soret band). In addition, those metalloporphyrins in which the metal ion had a complete d shell might be detected by their red fluorescence in ultraviolet light; any metal-free porphyrin, present as such or formed by demetallation under the acidic conditions, would be expected to show up in the same way.

Metalloporphyrins (particularly vanadyl and nickel derivatives) are minor constituents of crude oil and its close relatives (Baker & Palmer 1978), but the presence of such compounds in coal has not been clearly established. Although coal samples were among the earliest examined in this context (Weigelt & Noack 1932; Treibs 1935, 1936) the majority of subsequent workers have followed Treibs (1934) in focusing attention on crude oils, asphaltenes and shales. Weigelt & Noack (1932) provide evidence for chlorophyll derivatives in fossilized leaves found in brown coal, while Treibs (1935, 1936) found trace amounts of metal-free porphyrins in various coals (see also Hodgson *et al.* 1963). Uspenskii & Gorskaja (1938) confirmed the latter observation, finding a much higher content of porphyrins in sapropelic coals than in hard coals. Treibs (1935, 1936) had reported bands in the visible spectrum of some coal extracts which he interpreted in terms of vanadyl and (particularly) iron complexes. The situation was clouded, however, when Glebovskaia & Volkenshtein (1948), again using visible spectroscopy but working with material obtained from crude oil and bitumens, reassigned to nickel porphyrins the visible absorption which Treibs had regarded as being due to haems.

Our preliminary experiments were carried out in the following way. The powered dried coal was stirred with 7 vol. % sulphuric acid in methanol for 30 h at room temperature. The mixture was filtered; the filtrate was neutralized with aqueous sodium bicarbonate and extracted with chloroform. The extract was concentrated and submitted to thin-layer chromatography: porphyrins were detected by examining the chromatograms under ultraviolet light.

A peat sample showed three fluorescent bands, while samples of German and Polish (Konin) brown coals showed a fluorescent band with different properties. In a Turkish lignite and in four British bituminous coals another component was detected. It was decided to carry out a large-scale experiment to isolate this last substance, the electronic spectrum of which resembled that of a metalloporphyrin.

THE ISOLATION OF GALLIUM PORPHYRINS

The powdered coal employed for the large-scale work was from the Daw Mill Colliery (South Midlands, N.C.B. Code 902), the metal analysis of which was given in table 1. A sample (92 kg) was extracted in several batches according to the scheme shown in table 3 (Bonnett & Czechowski 1980). Although the progress of the fluorescent material through the various separations was of prime importance, the effect of the column chromatographic purification on metal distribution was also observed. Some metal analyses of ashed samples from fractions 1, 2 and 3 from the column chromatography on silica gel (table 3) are given in table 4. Again these results suggest that it would be worth while to search in these materials for other metal complexes, particularly of iron and titanium. Subsequently, as summarized in table 3, the fractions containing red fluorescent components were combined and submitted to repeated thin layer chromatography on silica gel to isolate the red fluorescent zones. Finally the material was subjected to precipitations from dichloromethane with petroleum ether. In this way a metalloporphyrin concentrate was obtained as a dark red solid weighing 17.8 mg, representing 0.19 µg/g of the original coal.

The electronic spectrum of this material (figure 1; λ_{max} 405, 532 and 570 nm)† could be immediately identified as that expected for a metalloporphyrin, and clearly, since the solution exhibited a strong orange–red fluorescence in ultraviolet light, the metal was unlikely to be a transition element. Metal analysis by thermal neutron activation (A.E.R.E., Harwell, Oxfordshire) showed, to our suprise, that gallium was the main metal present, although much smaller

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† This spectrum rather resembles that of a vanadyl polyalkyporphyrin (e.g. vanadyl octaethylporphyrin in chloroform has λ_{max} 407, 534 and 572 nm) (Bonnett *et al.* 1978). It is clear that identifications in this series cannot securely be based on electronic spectroscopy alone.

amounts of sodium, iron, potassium, magnesium and aluminium were also detected (table 5). These metals probably represent inorganic impurities, although iron and (particularly) aluminium may be present as metalloporphyrins.

Comparison of the coal metalloporphyrin with synthetic samples of hydroxogallium(III) etioporphyrin I and hydroxogallium(III) octaethylporphyrin showed considerable similarities

TABLE 3. SCHEME FOR THE ISOLATION OF A GALLIUM PORPHYRIN CONCENTRATE FROM A BITUMINOUS COAL (DAW MILL COLLIERY, SOUTH MIDLANDS, N.C.B. CODE 902).

(The analytical data for certain metals in the ashes from fractions 1, 2 and 3 from the column chromatography are given in table 4.)

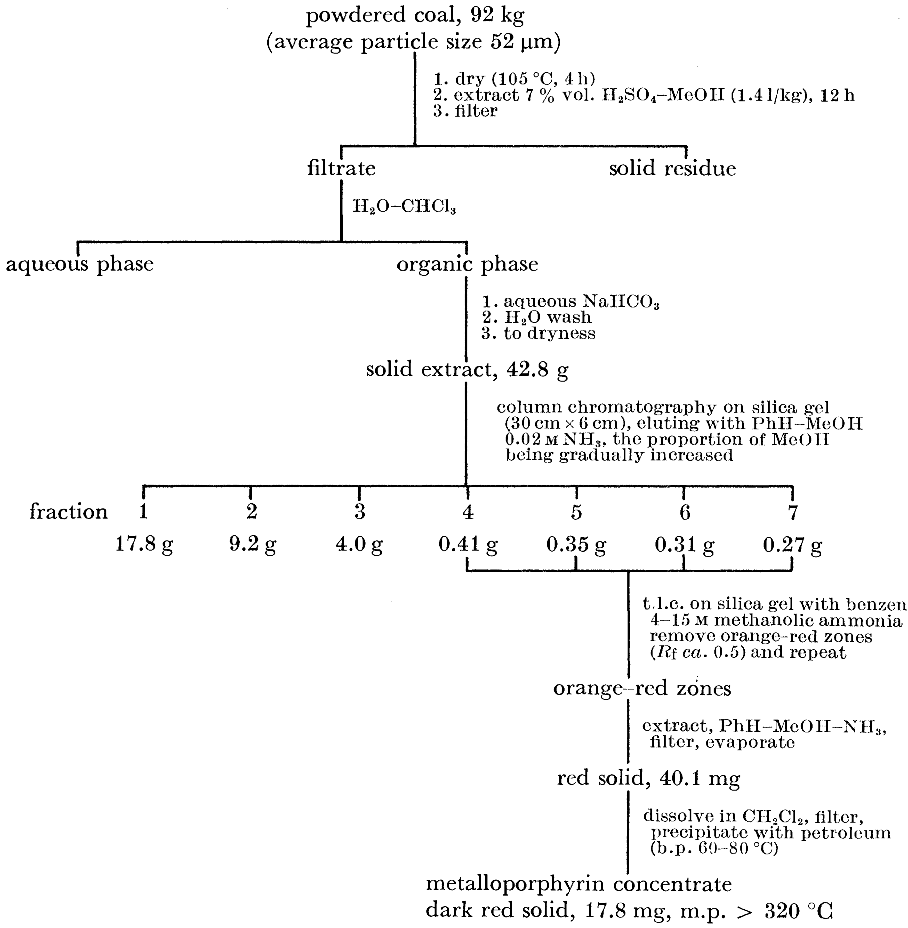


TABLE 4. METAL ANALYSES OF ASHED SAMPLES FROM FRACTIONS 1, 2 AND 3 (COLUMN CHROMATOGRAPHY) FROM ACIDIC METHANOL EXTRACT OF DAW MILL COAL

			metals in ash†								
	mass/g	percentage ash	Co	Cr	Cu	Fe	Ga	Ni	Sn	Ti	Zn
fraction 1	17.8	0.25	0.35 %	0.25 %	800	5.5 %	450	0.12 %	700	1.2 %	0.25 %
fraction 2	9.2	0.41	0.3 %	0.2 %	600	7 %	0.1 %	0.12 %	0.1 %	1.8 %	0.12 %
fraction 3	4.0	0.29	0.55 %	0.25 %	0.1 %	7 %	0.3 %	0.12 %	0.12 %	4 %	0.14 %

† Micrograms per gram unless shown as percentage.

(Bonnett & Czechowski 1980). A comparison of the nuclear magnetic resonance spectra is shown in figure 2.

The mass spectrum of the material (figure 3) clearly indicated a mixture of gallium complexes of porphyrin homologues, the most abundant being the gallium complexes of the porphyrins of molecular formulae $C_{30}H_{34}N_4$ and $C_{32}H_{38}N_4$. Ions that had lost the axial ligand, and ions with chlorine as the axial ligand, were identified on the basis of accurately measured m/z values (table 6). It is not clear whether the chlorine ligand is present as such in the coal or whether it is introduced during the extraction procedure. It is not the only ligand present in the metalloporphyrin concentrate since the chlorine content (1.89 %) amounts to only 44 % of the stoichiometric requirement based on the gallium content.

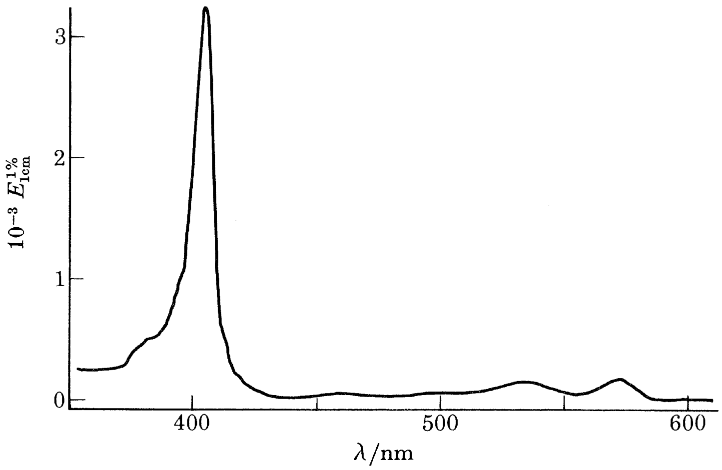


FIGURE 1. Electronic spectrum of a metalloporphyrin concentrate from Daw Mill coal. The solvent is chloroform.

TABLE 5. METAL ANALYSES (PERCENTAGES) OF A METALLOPORPHYRIN CONCENTRATE ISOLATED FROM DAW MILL COAL†

Ga	Na	Fe	K	Mg	Al
5.7	0.49	0.36	< 0.2	< 0.2	0.17

† By thermal neutron activation analysis (A.E.R.E., Harwell, Oxfordshire). A confirmatory analysis for gallium only by atomic absorption spectroscopy gave a value of 5.3 %.

The molecular formula $C_{32}H_{36}N_4GaCl$ corresponds to the chlorogallium(III) complex of etioporphyrin III (**1**) or an isomer of this. The C_{30} molecular formula corresponds to isomers (such as **2**) of the analogous complexes of didemethyletioporphyrin III. Although each ion is expected to represent an isomeric mixture, the formulations suggested (**1**, **2**) are favoured on geobiogenetic grounds (see below) and by the general analogy with the petroporphyrins (Baker & Palmer 1978). Chromatographic comparisons, particularly high-pressure liquid chromatography (Bonnett & Czechowski 1980) support, although they do not prove, these formulations.

The origins of the metal and of the ligand are of considerable interest. It is first necessary to recognize the danger of contamination, ever present in organic geochemistry. In various control experiments (e.g. item 8 in table 7) the introduction of contaminants during the extraction and work-up procedures has not been detected. Gallium is an unlikely contaminant, and we had not made gallium porphyrins in our laboratory before this discovery. Porphyrins are possible contaminants, but the commonest porphyrin in our laboratory is octaethylporphyrin, the gallium complex of which does not appear in the mass spectrum (figure 3). The possibility that gallium is incorporated into a metal-free porphyrin under the extraction conditions has been considered: it is discounted because control experiments, including some carried out in the presence of powdered coal, show that gallium is not incorporated into a polyalkylporphyrin (octaethylporphyrin) under the acidic conditions of the coal extraction.

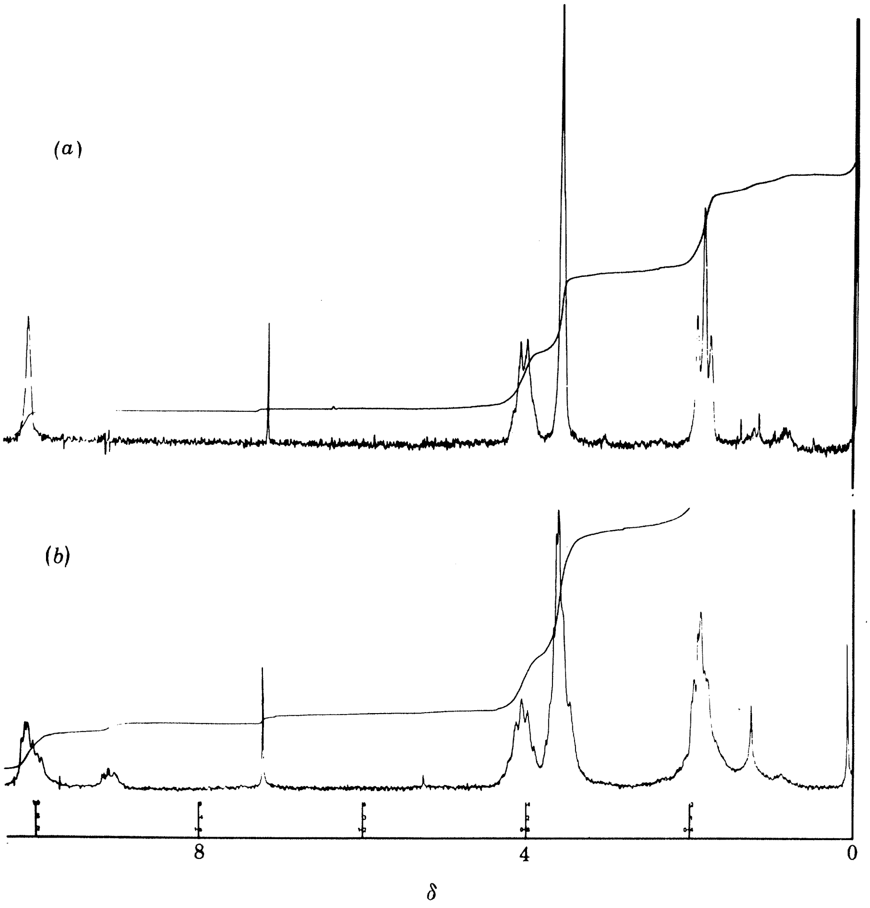


FIGURE 2. The nuclear magnetic resonance spectra of a metalloporphyrin concentrate extracted from Daw Mill coal (*b*) and of hydroxogallium(III) etioporphyrin I (*a*) measured in [^{2}H]chloroform at 90 MHz. In the metalloporphyrin sample from coal, the signal at *ca.* $\delta = 9$ is attributed to hydrogen at β-positions of the pyrrole rings. Such porphyrins would arise by a cleavage of type *c* shown in figure 5.

In one sense the presence of gallium is not unexpected: it has long been known to be one of the metals enriched in many coals, and, indeed, processes have been described for the isolation of gallium from this source (Ryczek 1971). Moreover, studies have been reported of the association of gallium with the inorganic constituents and with the organic constituents of bituminous coals (Ratynski & Zharov 1979). However, the occurrence of gallium as a porphyrin complex is unexpected. Gallium is widely distributed, but its abundance in the Earth's crust is only 15 μg/g (Weast 1977), which is an order of magnitude less than that of vanadium (porphyrin complexes of which occur in crude oil). It is apparently strongly selected for in the presence of

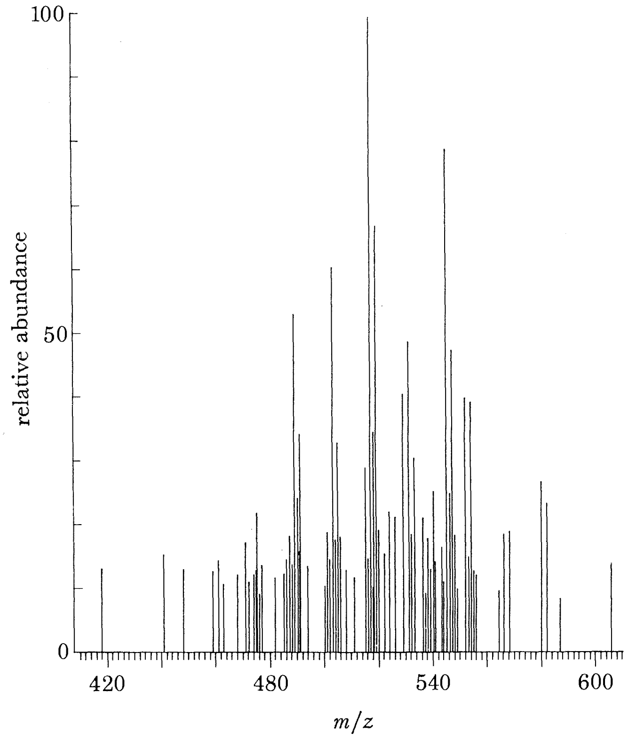


FIGURE 3. The mass spectrum of a metalloporphyrin concentrate isolated from Daw Mill coal (direct insertion 300 °C, measured at the Physico-Chemical Measurements Unit, Aldermaston).

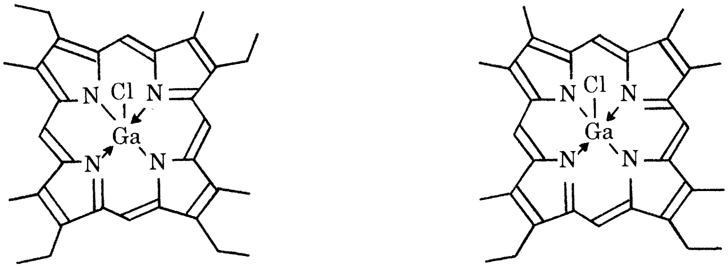
TABLE 6. SOME ACCURATELY MEASURED IONS IN THE MASS SPECTRUM OF A METALLOPORPHYRIN CONCENTRATE FROM DAW MILL COAL†

observed m/z	abundance	formula	calculated m/z
		(*a*) ions that have lost the axial ligand	
547.220	47.3	$C_{32}H_{36}N_4{}^{71}Ga$	547.219
545.218	78.7	$C_{32}H_{36}N_4{}^{69}Ga$	545.220
533.205	30.3	$C_{31}H_{34}N_4{}^{71}Ga$	533.203
531.200	48.5	$C_{31}H_{34}N_4{}^{69}Ga$	531.204
519.188	66.7	$C_{30}H_{32}N_4{}^{71}Ga$	519.188
517.185	100	$C_{30}H_{32}N_4{}^{69}Ga$	517.188
505.171	32.8	$C_{29}H_{30}N_4{}^{71}Ga$	505.172
503.169	60.2	$C_{29}H_{30}N_4{}^{69}Ga$	503.173
491.157	34.0	$C_{28}H_{28}N_4{}^{71}Ga$	491.156
489.155	53.0	$C_{28}H_{28}N_4{}^{69}Ga$	489.157
477.140	13.6	$C_{27}H_{26}N_4{}^{71}Ga$	477.140
475.137	21.7	$C_{27}H_{26}N_4{}^{69}Ga$	475.141
		(*b*) ions with halogen as axial ligand	
582.186	23.3	$C_{32}H_{36}N_4{}^{71}Ga^{35}Cl$	582.188
580.184	26.7	$C_{32}H_{36}N_4{}^{69}Ga^{35}Cl$	580.189
568.172	19.0	$C_{31}H_{34}N_4{}^{71}Ga^{35}Cl$	568.172
566.172	18.5	$C_{31}H_{34}N_4{}^{69}Ga^{35}Cl$	566.173
554.155‡	39.1	$C_{30}H_{32}N_4{}^{71}Ga^{35}Cl$	554.156
552.157	39.8	$C_{30}H_{32}N_4{}^{69}Ga^{35}Cl$	552.157

† Measured at P.C.M.U., Aldermaston, on a Kratos (A.E.I.) MS50 mass spectrometer with a DS-50SM data system. Direct insertion, 300 °C at 70 eV.

‡ As elsewhere, this could be assigned to the isotopomer ($C_{30}H_{32}N_4{}^{69}Ga^{37}Cl$, calc. $m/z = 554.154$), but the latter would be expected to have a lower abundance.

excess aluminium, which is 8.13% of the Earth's crust: the chemical basis of this selectivity deserves further study, but evidently the gallium complex has considerable thermodynamic and kinetic stability, and is able to build up and persist. Although gallium is reported to be accumulated by some biological systems (Hutchinson 1943), its metabolic function, if any, does not appear to be known. Gallium porphyrins are not known to occur naturally, and have been little studied.



1 chlorogallium(III) etioporphyrin III

2 chlorogallium(III) didemethyletioporphyrin III

FIGURE 4. Possible structures for the C_{32} (**1**) and C_{30} (**2**) components of the metalloporphyrin mixture isolated from Daw Mill coal. Structures that are isomeric with respect to alkyl substititution are also expected to be present. The complexes are drawn with chlorine as the axial ligand, but this is not the only ligand present in the isolated material.

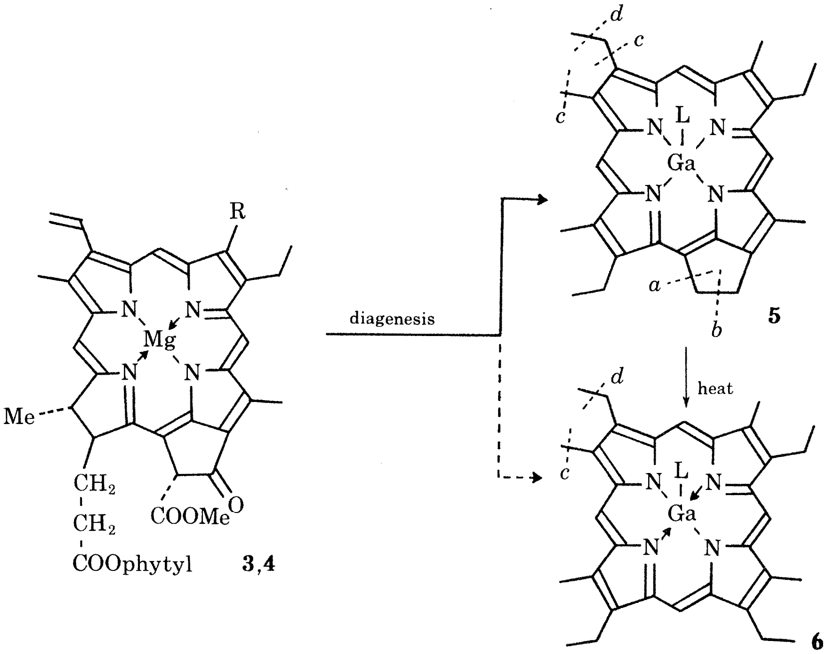


FIGURE 5. Proposed origin of gallium porphyrin homologues from chlorophyll (**3**, Chl *a*, R = Me; **4**, Chl *b*, R = CHO), based on Treibs's scheme (1936). See text. In **5** (13^2,15-cycloetioporphyrin III as a gallium complex), thermolysis/hydrogenolysis at *a* generates **6** (etioporphyrin III as a gallium complex). Cleavage at *b* might also occur but would generate an isomeric, *meso*-substituted system that would be sterically overcrowded (Woodward 1961). In **5** and **6**, dealkylation to give a series of lower homologues might occur by protodealkylation (ionic, pathway *c*) or, more likely, by thermal homolysis to generate a pseudo-benzylic radical (pathway *d*). Alternative and additional sites are evidently available for pathways *c* and *d* to generate a mixture of lower homologues.

The precursors of the ligands, that is the mixture of porphyrin homologues (*ca.* C_{27}–C_{32}), are believed, as with the petroporphyrins, to be the chlorophylls (and possibly the haems) of the biological (mainly plant) and microbiological material in the original deposit. Following a diversity of pathways involving reactions proposed by Treibs (1936), the chlorophylls *a* and *b* (**3**, **4**; figure 5) are believed to be transformed, during the deposition–coalification sequence, into homologues of 13^2,15-cycloetioporphyrin III (also called desoxophylloerythroetioporphyrin) (**5**) and etioporphyrin III (**6**), here present as their gallium complexes.

The distribution of porphyrins in the Daw Mill Coal fraction differs somewhat from that commonly found in crude oils (Baker & Palmer 1978). First, if it is assumed that the peaks in the mass spectrum at $m/z = 543 - 14n$ (figure 3) represent homologues of the complex of 13^2,15-cycloetioporphyrin III (**5**), then evidently the ratio of the two homologous series (**6**) : (**5**) is high. In contrast, for many crude oils the 13^2,15-cycloetioporphyrin III derivatives predominate. However, Didyk *et al.* (1975) have provided evidence for the conversion of vanadyl 13^2,15-cycloetioporphyrin III homologues to vanadyl etioporphyrin III homologues under thermal conditions. The predominance of the etio homologues is thus ascribed to the harsher thermal conditions required for coalification, which lead to thermolysis (hydrogenolysis) at *a* (structure **5**, figure 5).

The second difference concerns carbon number. In crude oils the porphyrin homologues are often distributed about the value (C_{32}) expected for etioporphyrin III: in the Daw Mill sample the distribution of homologues which can be seen clearly in the mass spectrum (figure 3), is almost entirely *below* C_{32}, and shows a double peak (C_{32}, C_{30}). The reason for this preponderance may reside in the largely aromatic nature of coal, it being postulated that after homolysis *d* in **6** (figure 5) the aromatics present compete effectively for the alkyl (methyl) radical generated.

A PRELIMINARY SURVEY: THE DETECTION OF OTHER METALLOPORPHYRINS IN COALS

Although a fluorescent metalloporphyrin had been isolated, the possibility remained that non-fluorescent compounds of this series remained undetected. Treatment of various fractions with concentrated sulphuric acid was expected to cause demetallation, and very recently in several instances porphyrins have indeed been found.

A preliminary survey of a variety of lignites, bituminous coals and anthracites has been carried out. In certain of the coals, especially those of lower rank, iron porphyrins have been detected and in one sample (a lignite from Canakkale-Can, Turkey) a manganese porphyrin has been tentatively identified. These identifications rest, for the manganese complex, on qualitative X-ray fluorescence observations and on the electronic spectrum. For the iron porphyrins the identification is more secure, resting on qualitative X-ray fluorescence observations, electronic spectra and mass spectra, including an accurately measured molecular ion for iron etioporphyrin (found $M^+ = 532.234$; $C_{32}H_{36}N_4Fe$ requires 532.229, the axial ligand having been lost). Nickel and vanadyl complexes have not as yet been identified.

For the purposes of the survey the extraction of the samples (*ca.* 1 kg) was carried out as before except that 5% sulphuric acid in methanol was used throughout, and the extraction was stopped when no obvious inflexion at 400 nm could be detected in the chloroform extract (corresponding to the 'organic phase' of stage 2 in table 3). Unless the amount of extract was large (more than 1 g) the column chromatography step was omitted, and the metalloporphyrins were purified by repeated thin-layer chromatography.

The results of the survey are presented in tables 6 and 7, and can be summarized in the following way.

(i) Metal-free porphyrins and chlorins are present in the less mature samples, particularly in the lignites.

(ii) Iron porphyrins are detected in the lignites and coals of lower rank: they seem not to be detected in coals of high rank, where gallium may appear instead.

(iii) Gallium porphyrins are detected in one lignite and in various coals: among the British bituminous coals there appears to be a rough inverse correlation between coal rank and the amount of (gallium) porphyrin that can be extracted.

TABLE 7. SURVEY OF PORPHYRIN DERIVATIVES (MICROGRAMS PER GRAM†) IN SOME FOREIGN COALS

sample	national code	chlorins	porphyrins	FeP‡	GaP	MnP
1. Maras Elbistan lignite (Turkey)		0.06	0.12	—	—	—
2. brown coal (Germany)		—	1.17	3.36	—	—
3. Canakkale-Can lignite (Turkey)		0.02	1.65	27.6	1.30	0.06
Polish coals						
4. Siemianowice	31	—	0.35	0.30	—	—
5. Mystowice	32	—	trace	0.79	0.19	—
6. Sosnica	33	—	trace	0.04	0.22	—
7. Jastrzebie	35.1	—	—	trace	0.021	—
8. Victoria	38	—	—	—	—	—

† Estimated from the electronic spectrum (Soret band) in chloroform assuming a molecular mass of 600 and the following molar extinctions: chlorin, 160000; porphyrin, 160000; FeP, 105000; GaP, 400000; MnP, 45000.

‡ FeP = iron porphyrin, etc.

TABLE 8. SURVEY OF PORPHYRIN DERIVATIVES IN SOME BRITISH COALS

sample	N.C.B. coal rank code†	ash (%)‡	C (%)§	volatile matter (%)‖	porphyrins¶ µg/g	FeP¶ µg/g	GaP¶ µg/g
9. Daw Mill (S.M.)††	902	12.6	81.5	40.6	trace	trace	0.90
10. Linby (S.N.)	802	6.0	82.4	39.1	—	—	1.56
11. Allerton (N.Y.)	802	6.0	81.8	38.2	—	—	0.58
12. Annesley (S.N.)	702	2.9	82.9	37.2	—	—	0.26
13. Hickelton (D.)	602	3.9	83.7	38.1	trace	—	0.46
14. Bersham (W.)	502	4.0	85.8	38.0	—	—	0.09
15. Cortonwood (S.Y.)	401/2	3.4	87.2	35.5	—	—	0.11
16. Beynon (S.W.)	301a	9.3	89.5	27.2	—	—	0.002
17. Tymawr (S.W.)	204	5.2	90.8	18.7	—	—	trace
18. Garw (S.W.)	204	9.0	91.5	17.9	—	—	trace
19. Bettws (S.W.)	100	5.1	93.8	6.2	—	—	trace

† Data on rank, ash, carbon and volatile matter analyses supplied by Mr W. F. Wyss (Coal Research Establishment, Stoke Orchard), whom we thank.

‡ As determined.

§ Dry, mineral-matter free.

‖ Dry, ash-free.

¶ See first footnote, table 7.

†† Location of collieries: S.M., South Midlands; S.N., South Nottinghamshire; N.Y., North Yorkshire; D, Doncaster; W., Western Region; S.Y., South Yorkshire; S.W., South Wales.

Work is proceeding to confirm and extend these results, which suggest that Treibs may, after all, have been right about the presence of haems in coals. Tables 7 and 8 also suggest the sequence – loss of magnesium, incorporation of iron, incorporation of gallium – for chlorophyll diagenesis, a sequence that is, to some degree, open to test by laboratory experiment. A major question that emerges, however, is whether the iron of the iron porphyrins found in coal (table 7) has been introduced during diagenesis or whether these coal haems are, in whole or in part, *directly* derived from the haem molecules of the original biological material.

It seems unlikely, perhaps, that the low levels of metalloporphyrins detected so far will have an appreciable effect on catalyst activity in the hydrocracking process: this remains to be explored. However, the approach described here does offer a useful way of tackling what is, after all, a rather difficult problem, and we propose to develop it further in the search for other metal-containing organic compounds in coals.

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Discussion

G. J. LAWSON (*Department of Minerals Engineering, University of Birmingham, U.K.*). Professor Bonnett has used methanol as the extracting solvent to recover metal complexes from coal; it is a ‘poor solvent’ and consequently selective. Is there any evidence that the insoluble residue still contains substantial amounts of metal–porphyrin complexes, possibly of greater molecular mass than those extracted by methanol, and is it possible to assess this by a gallium balance or similar means?

R. Bonnett. As far as solvent is concerned, although methanol is a poor solvent for many of the coal constituents, we considered that it might well coordinate with metal compounds and thus help to solubilize them in a selective way. Pyridine would have a similar effect and was used by Treibs (1935) in making coal extracts. Methanol by itself is not very effective, but methanolic sulphuric acid is so: we presume that the acid is needed to break bonds between the metal of the metalloporphyrin and axial nitrogenous ligands, which are part of the macromolecular coal structure.

We have not had metal analyses done on the coal residue after extraction, but analyses have been made on fractions from the column chromatography (table 4). Daw Mill coal contains gallium at 4.5 μg/g, of which we have accounted for only a small proportion in the extract (about 2.3% of the gallium occurs as extractable gallium porphyrins; fractions 1, 2 and 3 (table 4) account for 0.003, 0.008 and 0.008% respectively). Much of the remaining gallium is presumed to be retained in the coal: we agree with Dr Lawson that there it may be associated with high molecular mass porphyrin complexes. It is conceivable, for example, that during coalification some porphyrin structures become incorporated into polycyclic aromatic sheets: the porphyrin nucleus is essentially planar and models suggest that the porphyrin could be bonded to the edge of a graphitic sheet with little or no distortion. In such a situation the metal complex would be expected to be very difficult to extract.

It is also likely that other metalloporphyrins besides those described here will be found in coal: it might be useful to change the 'poor' solvent for a better one, such as pyridine, which, though it is unpleasant to use, would be expected to extract more material, including more metal complexes.

Addendum by R. Bonnett (26 *September* 1980). During the discussion period Dr A. J. G. Barwise (British Petroleum Company Ltd, Sunbury-on-Thames) expressed the view that the gallium porphyrins arose by contamination. I subsequently asked him if he would repeat the experiment in his laboratory, using a sample of coal collected directly from the National Coal Board (and so avoiding contact with my laboratory altogether). This he has since done, and he has written (3 September 1980) as follows.

> Our repetition of your extraction procedure for gallium porphyrins from Daw Mill coal worked well, and our experimental findings completely validate your published data in *Nature*. The initial extract from Daw Mill coal was analysed for metals by atomic absorption spectroscopy and then separated on sulphonic acid functionalized silica (developed by BP Sunbury) which removes polar background oil. An orange–red solid was obtained and this was then purified by silica t.l.c. The final extract showed a typical metalloporphyrin visible absorption spectrum and was analysed by mass spectrometry. The mass spectrum is very similar to that published by yourself in *Nature*.

I am grateful to Dr Barwise for undertaking this check on what must seem to many to be a most surprising result, and to the BP Research Centre for agreeing to fit this experiment into a busy laboratory schedule.