Iron Porphyrins in Coal

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Evidence is presented for the occurrence in certain lignites of iron porphyrins, including the iron complex of mesoporphyrin or its isomers.

We recently reported the isolation of gallium complexes of homologous polyalkylporphyrins (C_{27}—C_{32}) from certain coals and lignites.[1,2] Iron complexes were also detected.[2] We initially viewed the latter result with some circumspection, since Treibs had much earlier reported bands in the visible spectra of fractions from fossil fuels which he interpreted in terms of iron porphyrin complexes.[3] Later Glebovskaia and Volkenshtein[4] reassigned to nickel porphyrins the visible absorption which Treibs had attributed to haems, and the reassignment has been generally accepted. We now report the isolation from certain lignites of fractions rich in iron porphyrins, including mesohaem, and comment on the origin of these substances.

Three lignites have been examined using the methanol–sulphuric acid extraction procedure.[2] No iron porphyrins could be detected in the sample of a Western Canadian lignite at our disposal. For a Turkish lignite (Canakkale-Can) we were able to confirm the earlier report[2] of porphyrins and metalloporphyrins (Fe, Ga, Mn). The iron porphyrin concentrate† was subjected to basic hydrolysis and then to further fractionation by repeated t.l.c. (4 stages). The resulting fractions, which were still mixtures, were examined by

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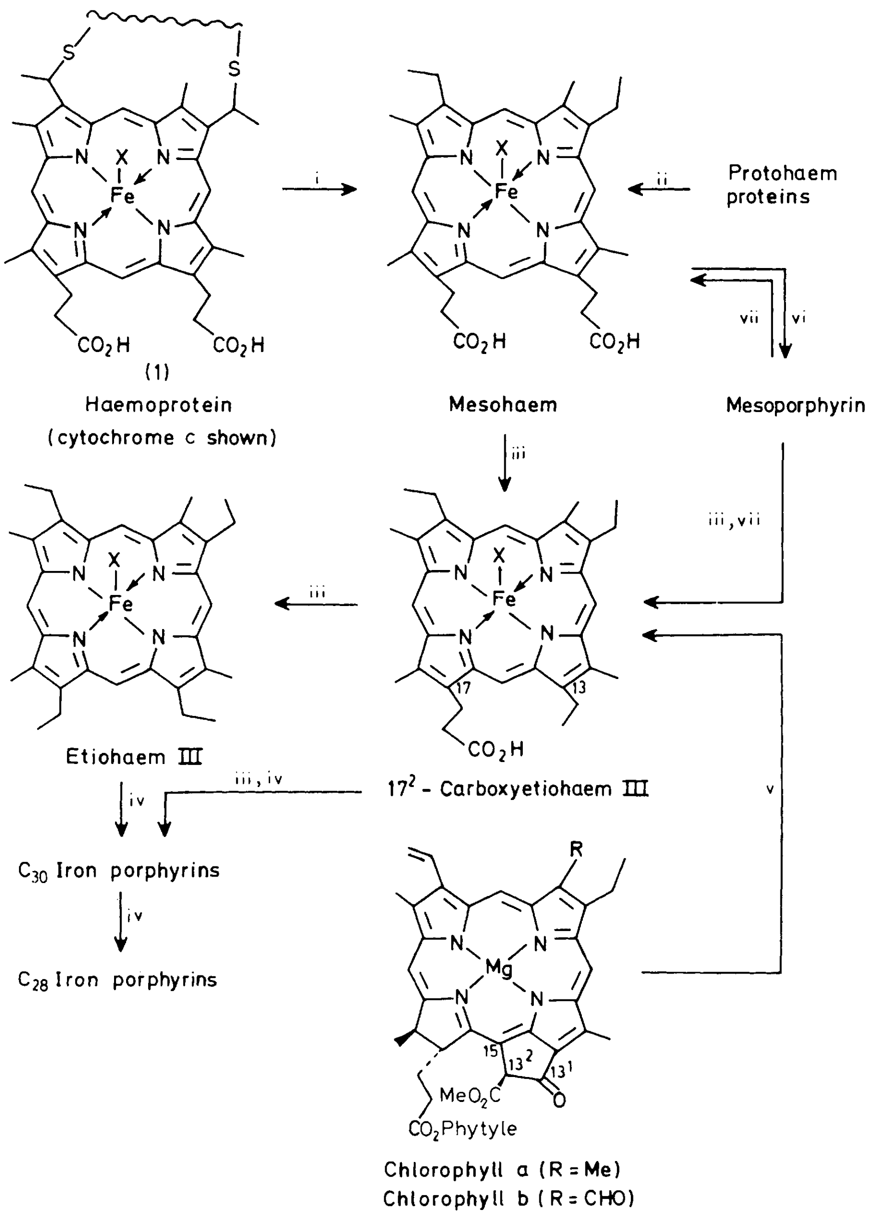
† Metals analysis (D.C. arc emission, A.E.R.E., Harwell): Fe, 2%; Na, 0.08%; Ca, 0.07%; B, 0.06%; Sn, 0.03%; Mg, 0.02%; Al, 0.02%. Only trace amounts of V and Ni were detected.

Table 1. Iron porphyrin fractions from the MeOH–H_2SO_4 extract of Canakkale-Can lignite.

Fraction	R_f[a]	$\lambda_{max}(CHCl_3)$[b]	µg/g[c]	Principal ions[d] (% relative abundance)	Accurate M^+ for major metalloporphyrin component[d]	Structure inferred for macrocyclic ligand[e]
1	0.38	391	1.54	530 (13), 532 (100), 567 (0.8)	532.228 ($C_{32}H_{36}N_4{}^{56}Fe$ requires 532.229)	Etioporphyrin
2	0.34	387	0.62	490 (22), 504 (100), 518 (5), 532 (10)	504.1975 ($C_{30}H_{32}N_4{}^{56}Fe$ requires 504.198)	C_{30} porphyrin
3	0.33	389	0.30	476 (100), 504 (19), 518 (5), 532 (5)	476.166 ($C_{28}H_{28}N_4{}^{56}Fe$ requires 476.166)	C_{28} porphyrin
4	0.27, 0.07	383	0.98	590 (6)	590.234 ($C_{34}H_{38}N_4O_2{}^{56}Fe$ requires 590.234)	Carboxyetioporphyrin
5	0.25, 0.00	376	0.05	648 (73)	648.239 ($C_{36}H_{40}N_4O_4{}^{56}Fe$ requires 648.240)	Mesoporphyrin

[a] Solvent system; 15% 1 M NH_3–MeOH in toluene, silica gel plates. For fractions 4 and 5 the first values are for the methyl esters and the second for the free acids obtained after hydrolysis. [b] Soret band only. [c] Micrograms of haemin per gram of dried lignite (100 °C, 4 h). Calculated using mol. wt. = 568 and ϵ = 105 000 throughout. [d] Measured at P.C.M.U., Harwell, the acids as methyl esters. [e] Isomeric structures (with respect to substituents) are not excluded.



Scheme 1. Proposed geobiogenesis of iron porphyrins (drawn as ferrihaems) detected in coals, emphasising the possibility of a microbial haem source in addition to the chlorophyll source. We suppose that under reducing conditions the co-ordinated iron might well be lost, so demetallation–metallation is regarded as feasible at one or more of the stages (shown only for mesohaem). i, Hydrogenolysis; ii, hydrogenation; iii, $-CO_2$; iv, $-2CH_2$; v, multiple chemical changes; vi, −Fe; vii, +Fe.

electronic spectroscopy and by mass spectrometry. As shown in Table 1 there is clear evidence for the presence of iron complexes of C_{28} porphyrin, C_{30} porphyrin, etioporphyrin (C_{32}), carboxyetioporphyrin, and dicarboxyetioporphyrin. For chemical and geobiogenetic reasons we suppose that the principal isomers present in the C_{32} and dicarboxylic acid fractions are etioporphyrin III and mesoporphyrin, respectively (see below).

In the Turkish lignite sample the mesohaem accounted for only a small proportion of the total haems extracted; a lignite from Victoria, Australia, showed a quite different composition in this respect. To aid identification in a large scale extraction of the Australian lignite (32 kg, dried), the iron porphyrin concentrate (estimated 0.27 μg/g dried weight) was demetallated, and the metal-free porphyrins were separated. A component which appeared to correspond to mesoporphyrin (converted by the extraction solvent into the dimethyl ester, M^+ 594.323, $C_{36}H_{42}N_4O_4$ requires 594.321) made up 70% of the total (iron) porphyrin content. The following properties of the porphyrin diester were indistinguishable from those of a sample of mesoporphyrin dimethyl ester prepared from protohaemin: R_f, λ_{max} in $CHCl_3$, and the ^1H n.m.r. spectrum (400 MHz, $CDCl_3$) of the zinc(II) complex in the presence of excess of nitrogenous base.[5] It is concluded that a porphyrin dicarboxylic acid exists as an iron complex in certain lignites, and is isomeric with, and probably identical to, mesoporphyrin.

The origin of these haems is of considerable interest. The possibility of contamination at the laboratory stage is a real one, but appears to be discounted by the reproducibility of the experiments (including negative ones). The possibility of metal incorporation during the extraction procedure exists, although treatment of octaethylporphyrin in the medium used for extraction (7% H_2SO_4 in MeOH, 36 h) with iron(III) salts does not give detectable amounts of iron porphyrin in the presence or absence of lignite, nor does appreciable demetallation of iron porphyrins appear to occur under these conditions. This is not to argue against demetallation–metallation processes occurring during coalification, but strongly suggests that the iron porphyrins, including mesohaem, exist as such in the native lignite.

Where does the mesohaem come from? Current views favour chlorophyll over protohaem as a precursor for geoporphyrins, because plant life is so abundant in the biosphere.[6] However, this is to neglect two factors: (i) the robustness of the iron porphyrin system compared with the magnesium chlorins, and (ii) the cytochromes as possible precursors. Most living things, including many micro-organisms,[7,8] possess cytochromes containing substituted mesohaem prosthetic groups [*e.g.* (**1**) in cytochrome c]. It may be here that some of the precursor molecules are to be found; indeed, the iron atom may in some circumstances be the original one incorporated during biosynthesis. The results suggest to us a mixed origin for geoporphyrins, and that the series of changes shown in Scheme 1 may have occurred in the early stages[10]‡ of coalification represented by the lignites studied here.

We are grateful to Dr. K. N. Bayraktar (M.T.A., Turkey), Dr. G. J. Lawson, Dr. D. F. Williams, and Mr. W. F. Wyss for advice and for the provision of samples, and to the N.C.B., S.E.R.C., and N.E.R.C. for support. Spectra at 400 MHz were run on the ULIRS facility at Queen Mary College (Dr. G. E. Hawkes).

Received, 7th June 1983; Com. 745

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7 Micro-organisms are emphasised here because they have a rapid turnover, and because microbiological action is generally and plausibly regarded as an important part of the early stages (deposition, peat formation) in the elaboration of coal *cf.* P. H. Given in 'Advances in Organic Geochemistry,' eds. H. R. von Gaertner and H. Wehner, Pergamon Press, Oxford, 1972, p. 69.
8 For cytochromes in bacteria and fungi see R. Lemburg and J. Barrett, 'Cytochromes,' Academic Press, London and New York, 1973, pp. 122 and 127.

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‡ It might also be supposed that mesohaem would be detected in peat samples. So far (three samples) our results have been negative in this respect.