Coal inclusions of the Athabasca tar sands: characterization and direct determination of vanadyl porphyrin content by electron spin resonance

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Abstract—Electron spin resonance provides a sensitive and specific technique for the detection and approximate quantification of low concentrations of vanadyl porphyrins in Athabasca tar sands without recourse to extraction. The technique was successfully extended to coal inclusions of the tar sands and to extracts of these, which also clearly demonstrated the presence of lower concentrations of vanadyl porphyrins. These results were confirmed quantitatively, and the fraction of complexed vanadyl was related to total vanadium present in all three sample types using neutron activation analysis. The fossiliferous inclusions are morphologically very similar to present day western hemlock, using scanning electron microscopy.

INTRODUCTION

The presence of porphyrins in petroleum and other fossil fuels was discovered over 40 yr ago by Treibs (1934, 1935a, 1935b, 1936), who identified the basic porphyrin fraction as spectroscopically identical with desoxophylloerythroetioporphyrin (DPEP). However, much later it was shown that the petroporphyrins were not a single species and that the homologs present range in carbon number from C_{28} to C_{38} in both the desoxophyllo- and etio- series, and evidence was also obtained for the presence of a rhodoporphyrin series (Baker et al., 1967a, b). All these petroporphyrins are encountered principally as their vanadyl and nickel complexes (Moore and Dunning, 1957; Constantinides and Arich, 1963; Dunning and Rabon, 1956; Millson et al., 1966; Beach and Shewmaker, 1957) and are quite stable. Carboxylated porphyrins have been reported (Baker, 1969; Dunning et al., 1969) but the metalloporphyrins of the desoxophylloery throetio- series are frequently the principal petroporphyrins, whose concentration in petroleum may range from 1 to 1000 ppm. Treibs explained that vanadyl DPEP resulted from a sequence of degradative steps making an explicit assumption that plant chlorophyll a must be the major source of the nucleus of the petroporphyrins.

The origin and other aspects of the role of porphyrins in the geochemistry of petroleum have been reviewed (Hodgson et al., 1963) where the possibility that the vanadyl porphyrins of petroleum arose from compounds in plants other than the chlorophylls was mentioned. The role of such compounds in plants was said to be obscure but that it was possible that they may be components of plant enzyme systems.

The origins of petroporphyrins and related compounds are closely related to the origins of crude oil itself since porphyrins arise in the same environment as the organic substrates which ultimately become crude oil. Thus, the study of petroporphyrins may help to define more clearly the role of the geologic environment in the origin of petroleum. According to studies carried out by several authors (Dunning et al., 1969; Hodgson and Baker, 1957; Champlin and Dunning, 1958), the Athabasca tar sands contain a crude oil which is similar in metalloporphyrin content to other high-sulfur oils (Scott et al., 1954), possibly because the metalloporphyrins facilitate reactions between organic petroleum precursors and hydrogen sulfide. The vanadyl porphyrin pigments present have been shown to predominate (338–500 ppm) over nickel pigments (31–100 ppm) in the tar sands (Hodgson et al., 1963). The bulk of the porphyrin material present is decarboxylated ($\sim 98\%$ desoxophylloerythroetio-) though a small quantity exists as free acids ($< 2\%$) together with traces of organic esters ($< 0.1\%$). However, as was pointed out by Champlin and Dunning (1958), frequently only one-tenth enough porphyrin is present to complex all of the vanadium and nickel present.

RESULTS AND DISCUSSION

The purpose of the present report was to carry out a qualitative electron spin resonance (ESR) study of the vanadyl porphyrins present in the Athabasca tar sands and newly-discovered coal inclusions, which it was expected might yield additional information of interest as a contribution to the general understanding of the origins of petroporphyrins and related compounds. The ESR spectra of the differentiated tar sands components were recorded on a Varian E-6S X band spectrometer operating at 100 kHz modulation.

Shales and traces of coals have been found to be associated with the Athabasca tar sands. By hand picking, small pieces of two types of coal were found, a fossiliferous younger one with a distinct grainy

Table 1. Elemental analysis of fossiliferous and amorphous tar sands inclusion samples related to that of typical lignite coal

Sample	% Carbon	% Hydrogen	% Nitrogen
Fossiliferous	42.59	4.66	0.69
	37.87	4.71	0.66
means:	40.23	4.69	0.68
Amorphous	39.97	5.87	0.54
	46.04	6.06	0.63
means:	43.00	5.97	0.59
Lignite coal*	42.4	6.7	1.7

*Data from *Chemical Engineer's Handbook* (1969).

appearance, and an amorphous older one (Fig. 1), in total comprising less than 1% by weight of the samples examined. Duplicated elemental analyses of both sample types after a benzene rinse and drying, established compositions which, except for nitrogen, approximated that of a typical lignite coal (Table 1).

Spectra on polycrystalline (randomly oriented) samples of tar sands and both types of coal inclusions, the latter previously rinsed with benzene and dried, were obtained at 77°K and 298°K. These were identical at the two temperatures for all samples examined,

apart from a greater intensity at 77°K, and gave a 16-line anisotropic pattern corresponding to the $g_{\parallel}$ and $g_{\perp}$ tensors. The experimental values of $g_{\parallel} = 1.95$, $g_{\perp} = 1.99$, $|A_{\parallel}(^{51}V)| = 159 \times 10^{-4}\,cm^{-1}$, $|A_{\perp}(^{51}V)| = 53 \times 10^{-4}\,cm^{-1}$ are in very close agreement with the experimental values for authentic vanadyl porphyrins measured by the ESR technique in a wide variety of glasses of liquids at 77°K (ERDMAN et al., 1956; O'REILLY, 1958, 1959; KIVELSON and LEE, 1964), and differ significantly from the experimental ESR parameters reported for petroleum asphaltenes (YEN et al., 1962). No ligand superhyperfine interactions were observed in the above spectra. Vanadyl porphyrins could not be detected in any of a number of bitumen samples which had been commercially extracted, presumably because they failed to survive the extraction variables: exposure to water under conditions of high heat and high pH in the presence of air.

Several additional coal samples of both types were then given a quick rinse with benzene following which they were finely powdered and exhaustively extracted in a Soxhlet apparatus with mixed benzene:methanol (90:10 v/v.). The filtered and evaporated extracts were
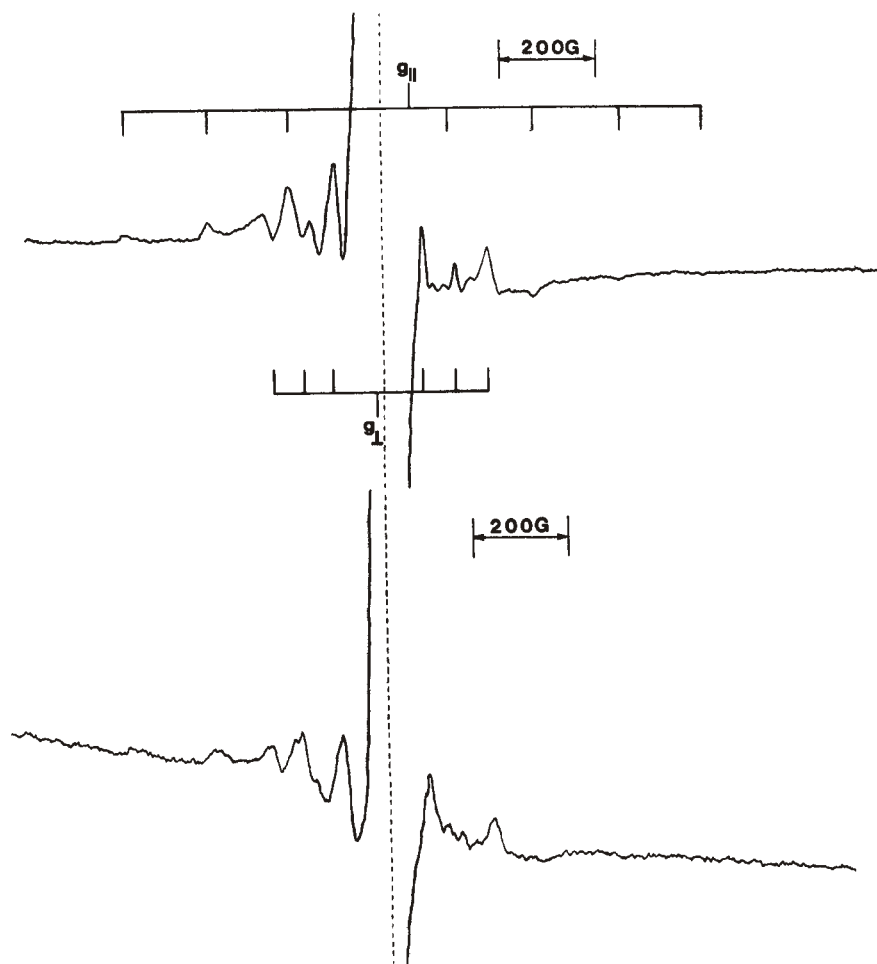

Fig. 2. Electron spin resonance spectra of fossiliferous (above) and amorphous (below) coal inclusions in Athabasca oil sands deposits obtained at 77°K.
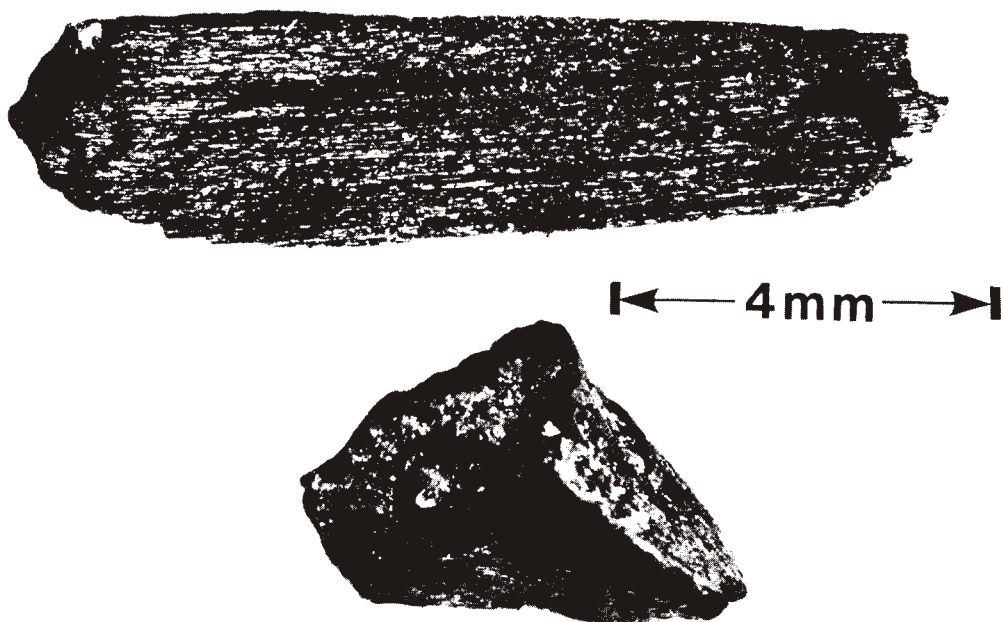
Fig. 1. Photographs of typical samples of fossiliferous, grainy (above) and amorphous (below) coal inclusions found in Athabasca oil sands deposits.
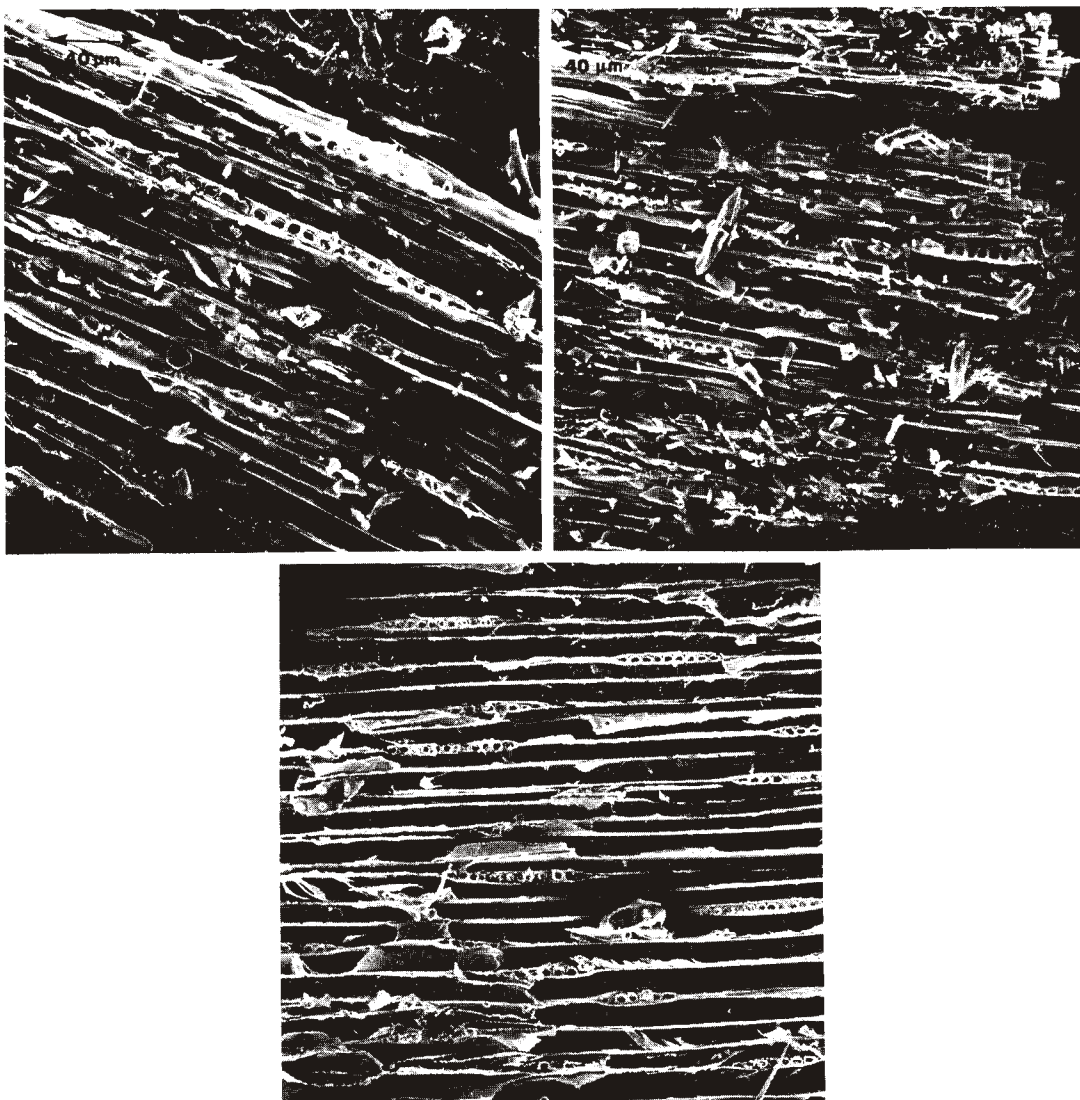
Fig. 3. Scanning electron microscope photographs of a fossiliferous coal inclusion (above), of a western hemlock chip (below). Magnification about 200 ×.

Table 2. Vanadium and manganese content of the coal inclusions obtained from
Athabasca tar sands

Sample	Vanadyl porphyrins by ESR		Total V concentrations by neutron activation, µg/g	Fraction of total V as porphyrin complex	Total Mn concentrations by neutron activation, µg/g
	Complex concentration, µg/g	Complexed V present, * µg/g			
Fossiliferous	170	16.5	94	0.175	16
Amorphous	40	3.9	590	0.0066	78

* Calculated from the fraction of vanadium in the measured vanadyl porphyrin complex concentrations.

examined by the ESR technique and at 77°K and 298°K the spectra of the extracted vanadyl porphyrins were identical with those obtained above on *in situ* material, apart from a greater intensity observed at liquid nitrogen temperature (Fig. 2). Moreover, the ESR parameters of both spectra were identical with the spectra of the Athabasca tar sands and inclusions obtained earlier directly from the solid material. However, from line broadening in spectra from the extracts of the amorphous samples there was a strong indication of the presence of another vanadyl compound with slightly different ESR features but of much lower concentration than the main component. Our estimation of the relative concentrations of the paramagnetic vanadyl porphyrins in the Athabasca tar sands, and in the fossiliferous and amorphous coal inclusions based on the integrated intensity of corresponding lines, was *ca.* 1:1/2:1/9 respectively.

All three sample types exhibited a strong "carbon free radical" resonance spectrum centred at $g = 2.003$, which is characteristic for fossil fuels of plant origin (YEN *et al.*, 1962). This signal was found to be especially intense for both types of coal inclusions (INGRAM, 1969).

If 350 ppm is accepted as the approximate mean concentration of vanadyl porphyrins present in the Athabasca tar sands from the analyses reported for three widely-separated samples (HODGSON *et al.*, 1963), then the concentrations of the paramagnetic vanadyl porphyrins found in the inclusions would be 170 ppm for the fossiliferous samples, and 40 ppm for the amorphous samples, calculated using the relative ratio of the concentrations of the paramagnetic vanadyl porphyrins in the three types of tar sands components investigated.

Quantitative confirmation of the presence of vanadium in the coal inclusion samples was obtained by neutron activation (30 sec, 5×10^{11} n/cm^2) in a SLOWPOKE-2 reactor, followed by counting using a Ge(Li) detector and Tracor Northern TN-11 γ-ray spectrometer. The 1434 keV γ-ray emission of ^{52}V qualitatively confirmed the presence of vanadium and the concentrations were determined by comparison of 100 second counts relative to those for a co-irradiated vanadium standard. The fossiliferous and amorphous samples contained 94 ppm and 590 ppm vanadium respectively. If 526 is taken as the mean molecular weight of the VO^{2+} complexed porphyrins

present (BAKER, 1969), then the paramagnetic complexed vanadium present is about 1/10 (0.097) of the vanadyl porphyrin concentrations found by ESR, or 16.5 ppm for the fossiliferous sample and 3.9 ppm for the amorphous sample. Thus, the ratio of paramagnetic complexed vanadium to total vanadium present in the fossiliferous samples is about 1/6; near the 1/4–2/5 range reported for the bitumen fraction itself (HODGSON *et al.*, 1963) and far higher than the 1/150 ratio found for the amorphous samples (Table 2).

Vanadium analysis by neutron activation also, incidentally, permitted facile simultaneous determination of manganese. The values obtained, 16 μg/g for the fossiliferous samples and 78 μg/g for the amorphous bracket the value of 50 μg/g reported for the inorganic matrix of Athabasca tar sands (Table 2; and BOWMAN, 1967).

Direct solid probe electron impact (EI; 70 eV) and chemical ionization (CI; isobutane) mass spectrometric examination of small powdered samples of either of the types of inclusions or of the tar sand itself failed to yield an ion recognizable (BAKER, 1966; BONNET *et al.*, 1972) as that of a porphyrin on repeated attempts in either ionization mode, probably because of the low concentrations present. However, a clear difference with respect to the other volatile components emerged from the CI spectra, with the fossiliferous sample showing the presence of components at only a relatively few discrete mass numbers, in particular at 113, 115, 117, 127, 133, 145, 163, 201 (m + 1) and 257 (m + 57). The amorphous sample, on the other hand, showed the presence of ions for every mass number to m/e 450, with higher intensities apparent for odd mass numbers and up to about m/e 300, and smaller for even mass numbers and for masses above 300, observations typical of that expected from a hydrocarbon mixture (BURLINGAME and SCHNOES, 1969).

Despite analyses for the inclusions demonstrating a composition approximately that of a typical lignite coal (Table 1), it was not possible to obtain a detectable signal for vanadyl phorpyrins (i.e. ≪10 ppm was present) on direct ESR examination of a number of coal samples of differing origins and ages. Nor could vanadyl porphyrins be detected by direct ESR examination of samples of the kerogen-rich Colorado River shales, though traces of paramagnetic manganese compounds were observed.

Visually, sufficient structural details of the fossiliferous coal samples were observed such that low power scanning electron microscopic examination of gold-coated material permitted a number of significant morphological details to be noted (Fig. 3). In combination, these observations clearly established that the original fossil tree species possessed a uniseriate arrangement of ray cells, each of which contained up to 16 rows of cells. These, and other details relating to the arrangement of border pits and the structural features of the cell lumens themselves obtained from the several sections examined, suggested that the original wood might be western hemlock (section for comparison, Fig. 3), *Tsuga heterophylla* (Raf.) Sarg., or a closely-related fossil species (WILLIAMS, 1977, personal communication).

CONCLUSIONS

It has been discovered that electron spin resonance is a sufficiently sensitive technique in this application that it enables detection and, with the use of standards, quantification of the vanadyl porphyrins present in the coal inclusions of the Athabasca tar sands, without prior extraction. This procedure provides a useful geochemical tool for examination of metalloporphyrins *in situ*, with about 1 ppm lower detection limit for vanadyl porphyrins using the instrumentation described. It is a method which is thus capable of yielding information not as readily or surely available via conventional extractive techniques followed by characterization of the extracts.

Two possibilities have been advanced to explain variations of vanadium background concentration in metamorphosed biological materials. The earlier theory, accorded to Treibs, attributes the concentration enhancement to an anaerobic degradation of chlorophyll *a* to porphyrins, with chelation-induced enhancement of vanadium content in the developing peat by selective extraction from formation waters. Vanadium, since it forms more stable porphyrin complexes than most other metals, tends to displace them, hence providing chemical support for this view. Alternatively, many living plants themselves enhance soil vanadium concentrations several times to the region of 20–1000 ppm (MITCHELL, 1944), providing the possibility of the vanadyl porphyrins arising via a more direct biogenetic pathway (HODGSON *et al.*, 1963). The data presented here are not sufficient in themselves to provide a clear cut decision between the possible diagenetic or biogenetic origins of the vanadyl porphyrins of the tar sands or coal inclusions.

Detailed morphological examination of the fossiliferous coal samples showed that the species from which these were derived was probably western hemlock or a closely related fossil species.

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