

STRUCTURAL FEATURES OF A CRETACEOUS COAL OF ALGAL AFFINITIES

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This coal from the King Cannel seam in southwest Utah attracted attention some years ago because of its high hydrogen content (>7%), high volatile matter yield (65%) and excellent performance in liquefaction (1). The principal macerals in it have been provisionally identified as bituminite (55%), vitrinite (20%), alginite and liptodetrinite (2). Bituminite has been thought to be derived from disrupted algal or bacterial cells (3). Infrared spectra (2) and ^{13}C CP-MAS nmr (4) show that the samples are highly aliphatic ($f_a=0.38$), but less so than such purely algal coals as torbanite ($f_a=0.19$) (5). Very little is known of the chemistry of bituminite or liptodetrinite, and so the coal has been extensively studied by various methods. We wish to report here some of the results, as they bear on the structures present in a particularly interesting, if somewhat unusual, coal.

The original sample collected (in 1967) was designated PSOC 155 and represented, it was discovered later, only part of one lithotype in a seam in which four can be readily distinguished. In 1978 fresh samples, including all four lithotypes, were collected. Of these the middle two (PSOC 1109 and 1110) are the ones of interest here, having cannelloid-boghead character, and 1109 is the lithotype corresponding closely to PSOC 155. The lines of investigation pursued were: GC/MS analysis of solvent extracts and the hexane-soluble part of liquefaction products; oxidation of coals and asphaltenes from liquefaction with trifluoroperoxyacetic acid and dilute nitric acid; FTIR and ^1H nmr spectra of asphaltenes. Only a selection of the results will be presented here.

EXPERIMENTAL

A selection of analytical data for the coals is shown in Table 1. FTIR spectra indicate that the samples had been slightly weathered in the seam, PSOC 1110 somewhat more than the others (2).

Liquefaction was performed in tubing bomb reactors with tetralin and hydrogen as previously described (6,7) (10 MPa pressure at 400°C for 1 h). After removal of the ethyl acetate extraction solvent, the liquefaction products were mixed with a large excess of hexane and left to stand for 24 h before being filtered. Hexane, naphthalene and excess tetralin were removed as completely as possible by distillation, the latter two substances *in vacuo*. The hexane-solubles were separated into five fractions by column chromatography on alumina (hexane, toluene, chloroform and methanol used as eluants).

Oxidation with trifluoroperoxyacetic acid was carried out by the procedure described by Deno et al. (8), and also by a modified procedure. The principal feature of the latter is that the reaction is carried out in the presence of chloroform. The boiling of this serves as a heat sink and to regulate the temperature at 62°. Also, products extracted by it from the acidic aqueous phase are to some extent protected from further oxidation.

Product analyses were performed in a Finnigan Model 4000 GC/MS/data system, using a Microflexil DB-5 capillary column, with 95% methyl-5% phenyl silicone bonded to the wall. An ionization potential of 70 e.v. was used, and a range of 50 to 700 a.m.u. was scanned every two seconds during a chromatogram.

RESULTS AND DISCUSSION

Of particular interest in the results is the diverse evidence, from several sources, of the importance of long aliphatic chains both in the extractable mobile phase and in the macromolecular network. Also of interest is the evidence of the presence of some aromatic structures.

The FTIR spectra of the coals show intense well-resolved bands near 2920 and 2850 cm^{-1} , characteristic of methylene chains (2). The hexane-soluble part of both the pyridine and benzene/ethanol extracts represents 5-6% of the coal. Regenerated single ion chromatograms ($m/z = 74, 98, 60$ and 58) showed that the extracts consisted chiefly of a mixture of the methyl esters of series of long-chain mono- and dicarboxylic acids, with some free alkanolic acids and long-chain methyl alkyl ketones (see examples of chromatograms in Figure 1). These oxygenated compounds were not found in the liquefaction products, but a nearly equivalent quantity of alkanes was found. The alkanes consisted chiefly of straight chain hydrocarbons, but pristane, phytane and minor amounts of cyclic hydrocarbons were present as well. There is a difficulty in assuming that the alkanes were generated from the oxygenates during liquefaction: the homologous series of the latter extended up to about C_{23} , whereas alkanes up to C_{32} were found. However, the oxygenates are considerably less volatile than the hydrocarbons, and it is quite likely that the higher homologs simply failed to get through the capillary column with the elution times used.

Extensive use was made of regenerated single ion chromatograms in the analysis of the fractions of hexane-soluble oil from liquefaction of the samples. These are specially useful when homologous series are present, as they proved to be here. Thus all alkyl benzenes give the tropylium ion ($C_7H_7^+$) as a major mass spectral peak, and alkylnaphthalenes give a corresponding peak of m/z 141 and/or 142 (9). Thus homologous series of alkylnaphthalenes (m/z 142), alkylfurans (m/z 82) and alkylphenols (m/z 108) were major constituents of fractions 2,3 and 5 from the column chromatography. An example of a single ion chromatogram is shown in Figure 2. It was generally true that the peaks are so uniformly spaced in the single ion chromatograms that we infer that mono-substituted long-chain alkyl derivatives are present rather than poly-substituted short chain. In confirmation of this, there were in the alkylnaphthalene and alkylfuran chromatograms closely spaced doublets for each carbon number, corresponding to the 1- and 2-isomers. We have inferred that these homologous series were physically trapped in the coal as part of the mobile phase (they were not found in the solvent extracts), rather than being part of the macromolecular network.

Estimating as well as possible from integrations of peak areas in total ion current chromatograms it was concluded that the alkanes and the linear alkyl chains (with the aromatic nuclei subtracted) together account for 15-16% of dmf coal in each of the 3 samples studied. Not included in these estimates are the alkyl chains in the substituted cyclohexenones and hydroxy-pyridines and quinolines present, since the evidence is not clear that the alkyl groups are long, linear, chains.

The ratio of hexane-soluble oils to asphaltenes for these coals was 2.0-2.4, whereas the mean ratio for 6 other coals of more normal vitrinite content was 0.94. The mean hydrogen content of the asphaltenes from the same 6 coals was 6.3%, while it was 7.5% for the 3 canneloid-boghead samples. ^1H nmr showed that only about 20% of the hydrogen atoms are attached to aromatic nuclei, and about the same fraction of aliphatic H is on carbon atoms in the benzylic position. That is, about 60% of

the H atoms are in aliphatic carbon atoms not adjacent to an aromatic ring. The aromaticity calculated by assuming the average composition of the aliphatic structures to be CH_2 is about 0.55. The aliphatic C-H stretching bands at 2920 and 2850 in the FTIR spectra of the asphaltenes are particularly intense and sharp (Figure 2). The frequencies are characteristic of long hydrocarbon chains, and this is confirmed by the presence of a weak skeletal vibration at 720 cm^{-1} . There is a small but distinct aromatic C-H vibration at 3030 cm^{-1} , and a distinct 1600 cm^{-1} band. There is also a small carbonyl band at 1705 cm^{-1} .

In what follows all of the information about the oxidation of the coal samples is provided by A. Daniel Jones (10), to whom we are indebted. Data on asphaltenes were generated in this laboratory, using the same techniques.

The principal products from the oxidation of the coals with dilute nitric acid were a mixture of long-chain fatty acids (C_9 - C_{23} , maximum at C_{13} - C_{18}) and long-chain dicarboxylic acids (C_4 - C_{20} , maximum at C_7) the latter being much more abundant than the former (see Table 2). Products from oxidation of the asphaltenes showed similar distributions (see Figure 3) but the mono-carboxylic acids were relatively more important.

The yields of acids from oxidation of the coals are equivalent to the presence of 20% by weight of long alkyl chains (determined with the aid of m. xylene as internal standard). It was noted above that the alkanes and the alkyl chains attached to aromatic nuclei in the hexane-soluble liquefaction products account for 15-16% of the coal. The oxidation products indicate that 17.7% of the asphaltenes consists of long alkyl chains, which corresponds to 3.7% of the coal. Thus the liquefaction products *in toto* contain alkyl chains equivalent to 19-20% of the coal, in remarkably good agreement with the estimate for the coal itself. However, the oxidation yields predominantly di-carboxylic acids, which presumably are derived from α,ω -diarylalkanes; but no evidence of these has been sought yet in the hexane-soluble liquefaction products or the asphaltenes.

When the procedure described by Deno et al. (8) was used for oxidation of the coals with trifluoroperoxyacetic acid, the major products were aliphatic dicarboxylic acids in the range C_3 to C_8 , malonic dominating. The second most abundant class of product was alkyl butyrolactones, in which the alkyl group has 0-6 carbon atoms. The asphaltenes gave similar distributions, but the relative abundance of the lactones was somewhat less, and succinic acid predominated over malonic acid, as it does with the asphaltenes from other coals (11). Also, acids derived from aromatic and hydroaromatic structures (benzene and oxirane polycarboxylic acids) are somewhat more abundant in the asphaltene oxidation products.

Use of the modified procedure for trifluoroperoxyacetic acid oxidation gave results very appreciably different from those provided by the original procedure. Butyrolactones became much less important. The lower dicarboxylic acids (C_3 - C_8) became less abundant relative to the higher dicarboxylics (C_9 - C_{22} ; see Table 3), and the highest concentration was now found for succinic rather than malonic acid. The distribution of longer chain dicarboxylic acids is rather flat compared with that of the monocarboxylics (see Figure 4). The asphaltenes gave similar distributions (see Figure 4), but the ratios of the total concentrations of mono- and di-acids were quite different (see Table 2).

The benzene-insoluble residue from the liquefaction of PSOC 1109 also gave abundant long-chain acids on oxidation; the distribution of mono-acids was quite similar to that in the coal and its asphaltene, but the distribution of di-acids was different.

Estimation of the fraction of the coal corresponding to the long-chain material

in the TFPA oxidation products gave a value of only 6%. The work-up procedure for isolation of products from the two oxidation reactions is identical, so evidently in the Deno oxidation secondary reactions shorten the chain and/or destroy some of the primary products to a greater extent than in the nitric acid oxidation. The butyrolactones presumably result from the oxidation of long chains. Their abundance is less with the modified procedure but is not zero.

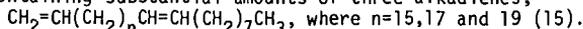
The hydrogen contents of alginite macerals is 10-11%; and the aromaticity of a sample was found to be 0.18 (5). Other alginites show little evidence of aromatic character in their IR spectra; pyrolysis at 375° for 24 h yields much straight chain aliphatic material but also some aromatic hydrocarbons, thought to be generated during the pyrolysis (12). Curie-point pyrolysis of some alginite-rich coals (at 610° for 12.5 sec.) gave a series of n. alkanes and alk-1-enes in the range C₈ to C₃₅, but significant amounts of polycyclic aromatic hydrocarbons were generated during the pyrolysis (13,14). The aromaticity of the coals studied here is higher (0.38), but additional aromatic structures could be generated during liquefaction. Polycyclic aromatic hydrocarbons (biphenyls, 3-, 4- and 5-fused ring compounds) were detected in the hexane-soluble part of the liquefaction products, as well as the long-chain alkyl aromatics discussed above (yet the hexane-soluble part of the solvent extracts was almost totally aliphatic).

The 25-30% vitrinite in these samples might have an aromaticity around 0.65-0.7. The value for the liptodetrinite, if, as is likely, this is related to sporinite, would be a little lower. Presumably the alginite and bituminite are largely aliphatic, though probably we need to assume some aromaticity to achieve a mean value of 0.38 for the whole coal.

The asphaltene from PSOC 1110 showed somewhat fewer benzylic protons in the ¹H nmr, and oxidation afforded less malonic and succinic acids, suggesting that dihydroaromatic structures are less abundant, perhaps because of weathering of the coal. Also, the (H/C)_{ar} ratio inferred from the nmr data was somewhat less than for the other lithotypes, indicating a higher degree of condensation to fused ring systems.

The analysis of the products from the modified trifluoroperoxyacetic acid oxidation of PSOC 1109 is shown in Table 3, classified by structural type. Acids having linear aliphatic structures account for 44% of the total products. Compounds deriving from aromatic or aromatic/hydroaromatic structures account for some 37% of the products. This is not a fair comparison, since some of the aliphatic diacids derive from hydroaromatic structures, and the other acids with aromatic associations will include in the structures what were aliphatic carbon atoms. Nevertheless, comparisons of the data with results for other coals are consistent with the suggestion of low aromaticity and the structural importance of long aliphatic chains in the Utah coal. Indeed, as we have seen, long aliphatic chains are prominent in the solvent extracts, hexane-soluble liquefaction oils, asphaltenes and insoluble residues from the liquefaction of this coal. Such chains are clearly important in the macromolecular network as well as in the mobile phase of relatively small molecules.

The alginite in these samples, as in most other coals that contain the maceral, is derived from the colonial green alga, *Botryococcus braunii* (2,3). This alga is peculiar in containing substantial amounts of three alkadienes,



The organism has many habitats. It is commonly found in coastal lagoons along the south coast of Australia. When these dry out, as they sometimes do, the lagoon bed is left covered with a sheet of rubber-like substance, thought to have been formed by the oxygen-catalyzed polymerization of the alkadienes (16). This polymer, not necessarily formed only in dried-out lagoons, is considered to be the precursor of alginite macerals, though this view does not explain how the colonial morphology is preserved, or why visible fluorescence should be excited by illumination with the 365 nm line of the mercury arc.

If bituminite is indeed derived from disrupted algal cells, then the colonial morphology is not preserved, but it still seems a reasonable possibility that a major part of the Utah cannelloid-boghead coal is derived from metamorphism of the rubber-like polymer associated with *B. brownii*. An open water pond is envisaged as a probable environment of deposition, rather small amounts of woody material being washed in from wooded areas around the margin (2).

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Table 1. Some Analytical Data for One of the Coals Used, PSOC 155
[abstracted from full data in Given et al. (2)]

% by vol., vitrinite	24	%dmmf C	74.5
alginate	7	H	7.4
liptodetrinite	12	S (org)	1.0
bituminite	52	O (diff)	15.0
inertinites	2	VM	~70

MM, 25.3% of dry coal

Table 2. Yields of Long-Chain Acids from Oxidation of PSOC-1109

	<u>Coal</u>	<u>Asphaltene</u>
HNO ₃ Oxidation:		
diacids, C ₄ -C ₂₀	66.0	48.5
monoacids, C ₉ -C ₂₃	<u>11.1</u>	<u>26.5</u>
Total	77.1	75.0
Deno Oxidation:		
diacids, C ₇ -C ₂₅	26.7	10.3
monoacids, C ₉ -C ₂₅	<u>16.7</u>	<u>12.4</u>
Total	43.4	22.7

Table 3. Yields of Product Classes from TFPA Oxidation of Asphaltene (PSOC 1109)
(Modified procedure)

<u>Class of Acids</u>	<u>% of GC area</u>	<u>Breakdown of alkane dioic acids</u>	<u>% of G-C area</u>
alkane dioics, C ₃ -C ₇	14.5		
alkane dioics, C ₈ -C ₂₂	12.0	malonic	1.7
alkane monoic, C ₉ -C ₂₆	10.5	succinic	3.6
alkyl lactones, C ₄ -C ₁₀	3.0	glutaric	4.7
alkane trioic	4.0	adipic	2.3
cyclohexene dioic	0.2	pimelic	<u>2.2</u>
aryl alkanolic	3.2		14.5%
alkene dioic	1.9		
oxirane polycarboxylic	7.7		
benzene polycarboxylic	23.1		
phenol polycarboxylic	<u>3.2</u>		
Total	84.3%		

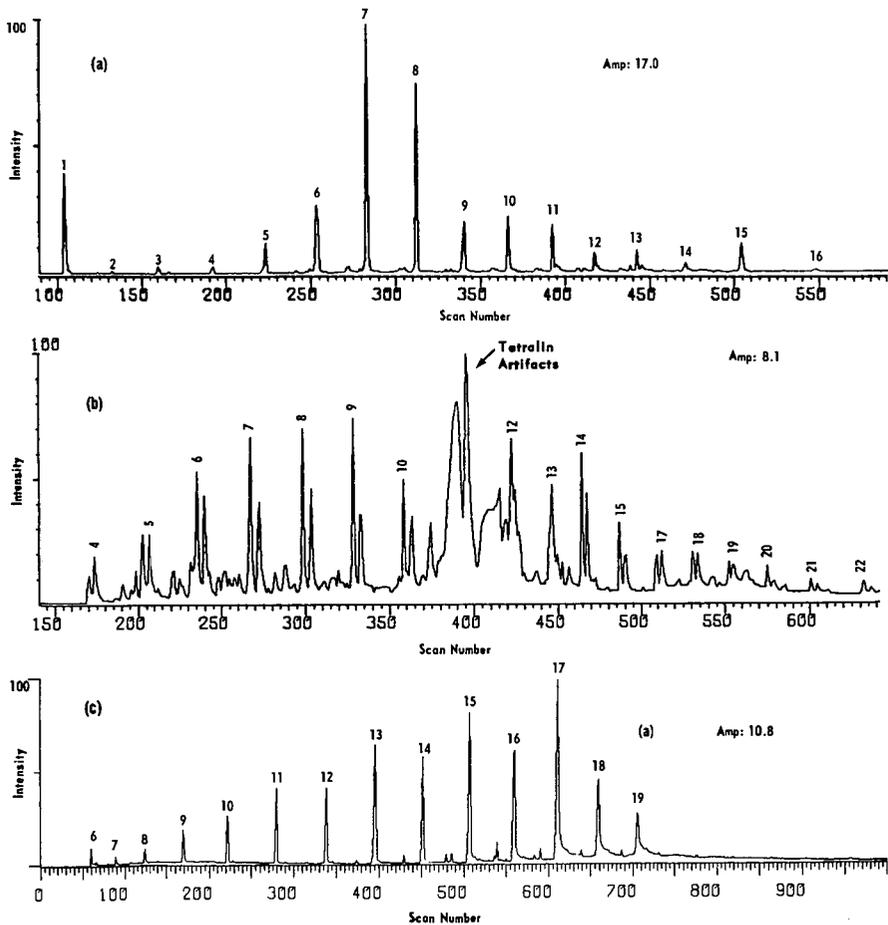


Figure 1. SINGLE ION CHROMATOGRAMS FOR HEXANE-SOLUBLE FRACTIONS FROM KING CANNEL COAL
 (a) pyridine extract, $m/z = 60$ (fatty acids), (b) liquefaction product fraction 2, $m/z = 142$ (alkyl naphthalenes), (c). liquefaction product fraction 5, $m/z = 108$ (alkyl phenols)

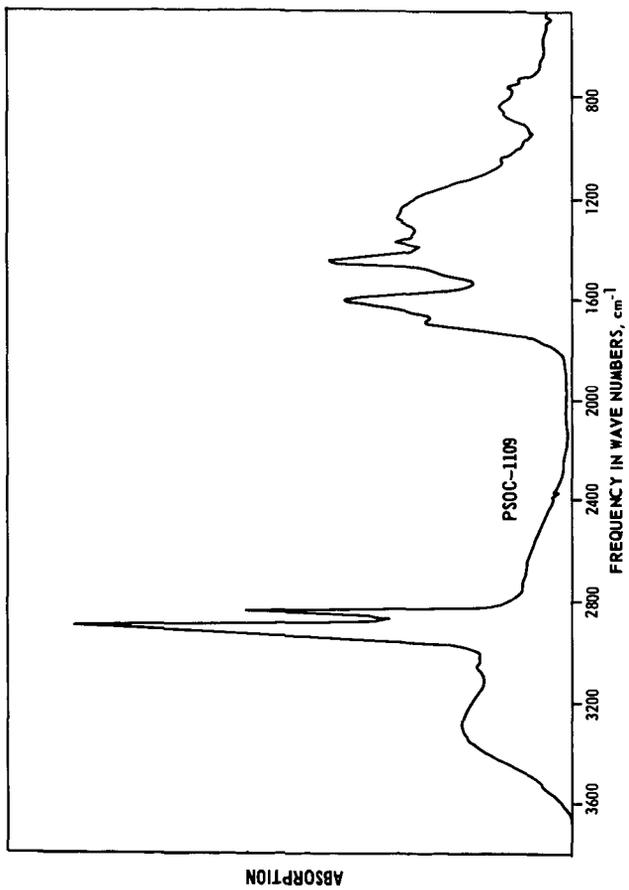


Figure 2. FTIR SPECTRUM OF ASPHALTENE FROM KING CANNEL COAL

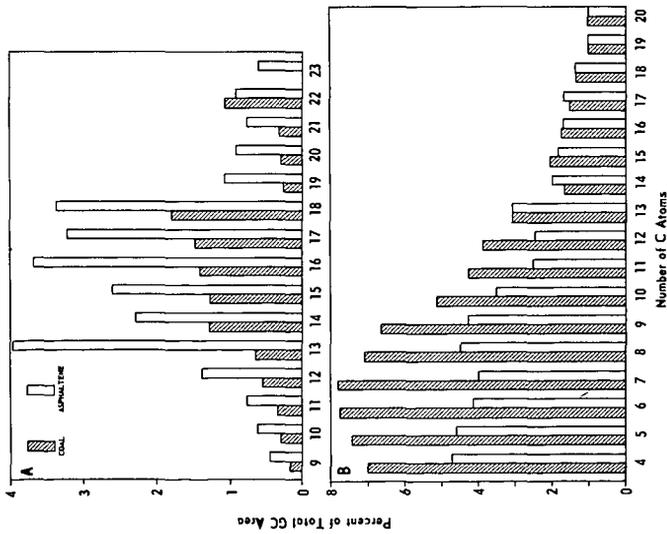


Figure 3. LONG-CHAIN ACIDIC PRODUCTS FROM NITRIC ACID OXIDATION OF PSOC-1109 A. Monocarboxylic Acids B. Dicarboxylic Acids

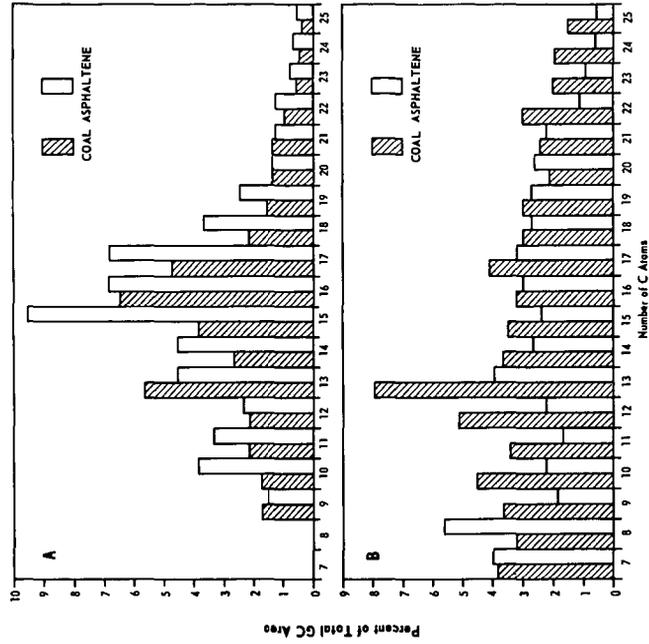


Figure 4. DENO OXIDATION PRODUCTS OF PSOC-1109 USING PROCEDURE II A. Monocarboxylic Acids B. Dicarboxylic Acids