

## Chemical structures in coal: NMR studies and a geochemical approach

Patrick G. Hatcher and Irving A. Breger

U.S. Geological Survey  
Reston, VA 22092

Larry W. Dennis and Gary E. Maciel

Colorado State University  
Fort Collins, CO 80523

### INTRODUCTION

Coal is composed of a complex, heterogeneous mixture of plant residues whose chemical composition has been the subject of research for the past 70 years (1). The work of van Krevelen and Schuyer (2) has in recent years been the pinnacle of our understanding of its chemical structure. Recent renewed interest in conversion processes for coal along with the availability of new analytical techniques have stimulated intensified research (1).

Most structural models for coal are based on vitrinite and ignore the fact that any whole coal is composed of macerals of widely differing compositions and chemical structures. Thus, although representations of an average model for coal (3) in terms of the types of constituent molecules may be useful from a broad statistical view, such structural models cannot be considered representative for a whole coal or even a particular maceral other than vitrinite. It has been particularly misleading, therefore, to depict coal as a hydroaromatic structure in which aliphatic groups are connected to aromatic groups on the basis of relatively meager direct evidence.

Hatcher (4) suggested, on the basis of NMR studies, that the aliphatic structures in coal may actually be molecularly distinct constituents derived from sources other than vascular plants and not chemically bound to the aromatic structure of which coal is mainly composed. Hayatsu *et al.* (5) reached the same conclusions. On the basis of different NMR relaxation data for nuclei of aromatic and aliphatic structures, Sullivan and Maciel (6) suggested that coal may contain aromatic-rich and aliphatic-rich domains that are spatially distinct. Hatcher and his co-workers (7) further suggested that the aliphatic structures in coal and its precursor, peat, originated as residues from algal and microbial sources.

Van Krevelen (8) and Breger (9) recognized that coal as well as kerogen in shales is a mixture of vascular plant and algal remains that had undergone coalification. Inasmuch as the two source components vary widely in chemical composition and structure, the terrestrial component being highly aromatic and low in hydrogen and the aquatic component being highly aliphatic and high in hydrogen, it seemed logical to conclude that coal formed from the mixture of these components would have a chemical composition dependent on the relative contributions from each of the two sources. Coal derived predominantly from the remains of vascular plants is termed "humic coal", and that derived predominantly from algal remains is termed "sapropelic coal". Although many coals are either exclusively humic or sapropelic, mixed varieties are also abundant. Unfortunately, van Krevelen (8) and Breger (9) did not have the currently available sophisticated tools for structural analysis for defining and quantifying the two individual components. As a result, a general lack of information has existed concerning the chemical structures of coal and kerogen.

In this study, we have used the principles advocated by van Krevelen (8) and Breger (9) and have examined the chemical structure and composition of the humic and sapropelic contributors to coal and kerogen by solid-state  $^{13}\text{C}$  NMR using the technique of cross polarization and magic-angle spinning (CPMAS). This has been accomplished by examination of modern (Holocene) precursors of both humic and sapropelic coal (peat and sapropel), and by study of coal and kerogen.

## METHODS

### Sample preparation

Samples of peat, sapropel, and coal were air-dried or freeze-dried and then ground, using a mortar and pestle or a disc grinder, to pass a 100-mesh screen. The peats and sapropels were treated sequentially with a 1:1(V/v) benzene/methanol mixture, a 0.1 N aqueous HCl solution, and a 0.5 N aqueous NaOH solution to isolate, as residues, the insoluble fractions from each. These residues (humins) were then freeze-dried and stored. The insoluble residues isolated in this way from the sapropels were additionally treated with a 1:1(V/v) concentrated HCl/HF mixture to remove the mineral matter and hydrolyzable substances. These residues were then also freeze-dried and stored.

### Nuclear magnetic resonance

$^{13}\text{C}$  NMR spectra were obtained at a field strength of 1.4 T. Details of the method have been published (10).

## RESULTS AND DISCUSSION

### Holocene precursors of coal

The Everglades of Florida and the Okefenokee Swamp of Georgia are Holocene precursors of ancient peat-forming swamps. Although vascular (terrestrial) plants contribute greatly to such peat, aquatic plants make substantial contributions. Because the mixture of terrestrial and aquatic organic debris tends to obscure determinations of the true chemical structure of coal, we decided to examine the changes that wood undergoes when it is buried under anaerobic conditions and coalified. Fig. 1 shows the CPMAS  $^{13}\text{C}$  NMR spectra of samples of modern spruce wood and the same type of wood buried anaerobically for various lengths of time. These spectra, in part published earlier (11), demonstrate that carbohydrates (peaks at 65, 72-85, 106 ppm) decompose and are removed from wood during diagenesis and that lignin (peaks at 55, 120, 130, 150 ppm) is concentrated by difference in the residue. The signal at 55 ppm in lignin is caused by methoxyl carbons and the signals at 120, 130 and 150 ppm are due to aromatic carbons (the peak at 150 ppm is that of oxygen-substituted aromatic carbons). The spectrum of a Miocene brown coal (Fig. 1) is nearly identical to that of periodate lignin. Our conclusion is that lignin is relatively unaffected and remains relatively well preserved under anaerobic conditions, whereas cellulose and other carbohydrates are degraded and removed from the wood. Lignin and cellulose are the major components of vascular plants. In a peat swamp, the cellulose predictably would be decomposed when wood is buried anaerobically; in contrast, lignin would be concentrated differentially. Because it is insoluble, the lignin would be characterized as humin.

To determine whether the same coalification processes are effective in a peat swamp dominated by non-woody vascular plant remains, two cores of peat were collected where sawgrass is the dominant vegetation. The first, the basal 2.2 m of a 16-m core, was collected near the contact of a peat underlying a sapropel in Mangrove

Lake, Bermuda. This sawgrass peat was formed at the time of a lower stand of water in the lake approximately 10,000 years ago (12). The sawgrass peat was sectioned and treated to isolate humin, the major component of the peat. The CPMAS  $^{13}\text{C}$  NMR spectra of humins in four stratigraphic layers are shown in Fig. 2.

Spectra for the humin isolates from the Mangrove Lake peat clearly demonstrate that highly aromatic vascular plant residues are predominant, as large peak intensities are observed in the aromatic region (110-160 ppm). The presence of strong signals for oxygen-substituted aromatic carbons (150 ppm) and for methoxyl carbons (55 ppm) in all the spectra indicate that lignin-derived structures abound. An additional peak is observed in the paraffinic carbon region (0-50 ppm) of some spectra of the humins. Though it is inconspicuous in the more deeply buried or older cored peat units, this aliphatic peak is more pronounced in the shallower or younger cored peat units, where conditions at the time of deposition were probably beginning to be more conducive to the sedimentation of the aquatic sapropel observed immediately above it in the core. The spectra, appear to indicate a decreasing trend in the concentrations of carbohydrates (peak at 72 ppm) as a function of depth. The carbohydrates do not appear to be major components which is in agreement with the results of chemical analyses published by Hatcher (12).

The second core was collected by Z.S. Altschuler in Conservation District 1A of The Everglades, Florida. The vegetation in this area of The Everglades is also dominated by sawgrass, but periphyton algae and other species of algae that form mats are also very common. The peat at this site is, therefore, receiving contributions of organic matter from multiple sources. A 95-cm core of the peat, studied by Breger *et al.* (13), was sectioned, and samples from six stratigraphic units were treated to recover the humin isolates and to obtain the CPMAS  $^{13}\text{C}$  NMR spectra shown in Fig. 2.

Referring to the humin isolates from the peat from The Everglades (Fig. 2), carbohydrate signals (72 and 106 ppm) and signals representative of lignin (55, 130, and 150 ppm) are major contributors to the total intensity. Other signals, however, such as those for paraffinic carbons (30 ppm) and for carboxyl carbons (175 ppm), also make major contributions to the total intensity. The signals assigned to carbohydrate carbons diminish in relative intensity with increasing depth in the core as observed for peat from Mangrove Lake, Bermuda; the intensities of the noncarbohydrate peaks increase as those for the carbohydrates decrease. This observation probably reflects the loss of carbohydrates with increasing depth and age in the peat. Given and co-workers (14) reported a similar observation throughout The Everglades. Breger *et al.* (13) studied the same samples as used in this study and reported that the concentrations of holocellulose and cellulose follow the same trend as that established from the NMR spectra.

It is important to note that the intensity of paraffinic carbons (0-50 ppm) is particularly significant with respect to peaks related to lignin (55, 130, and 150 ppm). This paraffinic component of humin, along with the carboxyl group (peak at 175 ppm), most likely originates from a source other than lignin.

Though the origin of lignin-like structures and carbohydrates is known to be mostly from vascular plants, paraffinic structures such as those detected by CPMAS  $^{13}\text{C}$  NMR have only recently been determined from peat (15). These structures may be related to the nonhydrolyzable, lignin-free residues that have been reported in peat (16). We have previously suggested that they are derived from sapropelic algal or microbial residues (7).

Humic substances derived from aquatic vegetation have been shown to be more aliphatic in structure than their terrestrial counterparts (17). NMR spectra (both  $^1\text{H}$  and  $^{13}\text{C}$  NMR) confirm these findings and further demonstrate that these are highly branched paraffinic structures (18). To investigate the formation of

these paraffinic macromolecules, we examined a Holocene algal sapropel deposited in Mangrove Lake, Bermuda. Approximately 14 m of gelatinous algal sapropel overlies the 2.2-m section of peat examined earlier. The sapropel is currently being deposited in marine waters approximately 2 m deep at a rate of accumulation of 0.3 cm/yr under strict anaerobic conditions (12).

CPMAS  $^{13}\text{C}$  NMR spectra of the whole sapropel and humin from a marine unit in the core (5 m below the marine water-sediment interface) are shown in Fig. 3. The spectra clearly demonstrate that paraffinic carbons (0-50 ppm) are the dominant signals in both the sapropel and the humin. The peak in this region is centered at 30 ppm. The spectrum of the whole sapropel shows additional peaks at 72 and 106 ppm that are characteristic of polysaccharide carbons. The loss of a major fraction of the intensity of these peaks in the humin is indicative that these polysaccharides have been hydrolyzed and extracted by the HF/HCl treatment used to remove mineral matter. Aromatic carbons (peak at 130 ppm) and carboxyl or amide carbons (peak at 175 ppm) are also present in these algal or microbially derived substances (Fig. 3). Thus, it appears that humins from Holocene algal sapropels are composed of complex paraffinic substances containing amide and carboxyl groups but few aromatic structures.

These paraffinic compounds are very likely similar to those observed in the humin isolates of peat. It can be concluded, then, that the aquatic microflora of peat swamps contribute these paraffinic structures to the humin. The ramifications of such a conclusion are extremely important when we consider that these structures constitute a significant fraction of the humin of peat as determined from the NMR spectra. In all likelihood, these paraffinic components of algal or microbial origin exist as separate components of peat. The relative proportions of paraffinic and lignin-derived aromatic components in the humin of a modern peat should provide a quantitative estimate of the contributions from algal or microbial residues and from vascular plants, respectively.

A method, demonstrated in Fig. 4, was attempted for such quantitative measurements. The spectrum of humin from the marine sapropel of Mangrove Lake is assumed to be representative of complex macromolecular paraffinic structures derived from algal or microbial sources; the spectrum of lignin is presumed to be representative of vascular plant contributions. The digital data from each spectrum are summed in varying proportions to yield for each summation a spectrum that represents the sum of the two source contributions. Fig. 4 shows the results of summing the indicated amounts of lignin and humin and comparing the resultant spectra with that of humin from one of the Everglades peat samples (30-35 cm stratigraphic unit). The simulated spectrum, representing 60% aquatic humin mixed with 40% lignin, is nearly identical to that of humin from the Everglades peat. This humin, therefore, is probably composed of a physical mixture of 60% humin from aquatic sources and 40% from vascular plant sources. Clearly, these two major components could exist as a mixture. If this peat were eventually to form coal, it is likely that these two phases would undergo differential and separate coalification.

#### Transformations of Holocene humins to coal or kerogen

Vascular plant remains have been shown, in this study, to yield humins whose chemical compositions are vastly different from those of aquatic plant remains. Therefore, these two different materials, when buried anaerobically for varying amounts of geologic time, probably will yield coal or kerogen also having vastly different structural compositions. The chemical compositions of humic coal and coaly kerogen are very different from those of aquatic kerogen and sapropelic coal (9). Presumably, the primary difference lies in the relative aromaticity of humic coals inherited from the lignin of contributing plant matter at the earliest stages of deposition. We have shown that at the early stage of sedimentation of swamp vegetable material, when plant remains are buried, insoluble macromolecular humins

are most likely formed as mixed components from both vascular and aquatic plants. These components can be expected to persist as mixtures and to undergo separate diagenetic processes at individual rates (19).

Coalification of vascular plant remains - Because, as shown, peat is most likely composed of at least two major mixed components in variable proportions, it is not entirely representative of pure vascular plant debris. Coalification of vascular plant debris can best be studied by the examination of coalified logs buried in shale or sandstone where contribution from the remains of aquatic plants has been minimal. Hatcher *et al.* (20) have reported, based on their study of coalified logs by CPMAS  $^{13}\text{C}$  NMR, that coalification of wood to the rank of bituminous coal proceeds in three stages. The first stage involves hydrolysis and removal of cellulose and concomitant concentration of the lignin. The second stage involves chemical alteration of lignin, whereby methoxyl groups and  $\text{C}_3$  side chains are lost and the lignin becomes depleted in hydrogen. Coalified wood of lignite rank, a product of such diagenetic changes, is formed directly from the lignin. The third stage involves conversion of the lignite to coalified wood of subbituminous and high-volatile bituminous rank via the loss of oxygen-bearing functional groups. Soluble, oxygen-rich humic acids, are probably formed as products of these chemical changes and are mobilized and transported from the coal, thereby providing an effective mechanism for the removal of oxygen during this stage of coalification. The amount of paraffinic structures in coalified logs is small. In all likelihood, some paraffinic components can be derived from resinous substances that are known to occur in wood and from residual aliphatic side chains of lignin.

Coalification of aquatic plant remains - Earlier, we demonstrated that humins isolated from algal sapropel are composed of macromolecular paraffinic structures that contain carboxyl and amide functional groups. To examine the transformation of this aquatic humin to aquatic kerogen or algal coal, CPMAS  $^{13}\text{C}$  NMR spectra were obtained of samples of kerogen and coal known to have been derived from aquatic sources. These samples range in age from Upper Paleozoic to Miocene; their spectra are shown in Fig. 5. The samples include a Miocene sapropelic coal from Turow, Poland, kerogen from the Eocene Green River Formation (Mahogany zone), an Upper Paleozoic Tasmanian tasmanite consisting mainly of spores of the alga Tasmanites, and an Australian torbanite (Upper Paleozoic boghead coal).

It is strikingly apparent that all spectra of aquatic kerogen are predominantly aliphatic with a major peak centered at 30 ppm. This peak is also the most intense peak in the spectrum of humin from Mangrove Lake also shown in Fig. 5. Paraffinic structures of the type determined to be in humin of Holocene sediments are apparently preserved through time. Elemental data suggest a highly aliphatic structure; atomic H/C ratios of approximately 1.5 for nearly all samples suggest that these paraffinic structures are highly cross-linked and similar to those of the humin from Mangrove Lake. Published reports dealing with kerogen from the Green River Formation have indicated that the structure is that of a highly cross-linked paraffinic macromolecule (21). Young and Yen (21) proposed that the kerogen is composed of fused alicyclic rings grouped in clusters that are joined by long-chain polymethylene bridges. Such a structure would have an H/C ratio of approximately 1.5, consistent with the observations made in this present study.

The similarity between the various spectra in Fig. 5 should be emphasized because such spectral similarities reinforce arguments concerning the origin and formation of aquatic kerogen or algal coal. In many respects the spectrum of the Miocene sapropelic coal from Poland is nearly identical to that of humin from Mangrove Lake, Bermuda. The only differences appear to be in the relative amounts of carbohydrate/ether carbons having a peak at 72 ppm and of carboxyl or amide carbons at 175 ppm. Both of these functional groups are thought to

diminish in concentration during coalification (2). Continued loss of such peaks leads to spectra similar to those of kerogen from the Green River Formation, Tasmanian tasmanite, and the Australian torbanite. These determinations are consistent with those derived from elemental data that indicate a significant reduction in the amount of oxygen associated with these functional groups.

The NMR data consistently show that diagenetic changes in the samples of aquatic kerogen and boghead coal primarily involve loss of carbons associated with oxygenated functional groups such that, only paraffinic structures, with a small percentage of aromatic structures, are left as residues, with increasing rank of the coal. Because elemental data demonstrate that H/C ratios are reasonably constant throughout this process, the highly cross-linked paraffinic structures that are formed at the earliest stages of deposition in sapropel remain virtually unchanged during this stage of diagenesis.

### Coalification of peat

Earlier, we demonstrated that modern peat is mostly likely composed of the remains of both aquatic and vascular plants and that these two kinds of vegetation produced humic substances whose chemical structures were vastly different. Peat, of mixed plant sources, eventually forms bedded coal and we can, therefore, expect the individual plant remains to contribute their characteristic chemical components to the coal. These components (macerals) could exist as mixtures in much the same way as they exist in peat. The relative amounts of each component will depend on the relative contributions of aquatic or vascular plants. Thus, where coal is predominantly composed of vascular plant remains, the coal will be a humic coal composed predominantly of lignin-derived aromatic structures and resinous paraffinic structures. Where the coal is predominantly composed of aquatic plant debris, the coal will be composed of predominantly paraffinic structures and will be called a sapropelic or algal coal. Consequently, coal derived from mixtures of aquatic and vascular plant residues will be composed of a mixture of aromatic and paraffinic structures.

CPMAS  $^{13}\text{C}$  NMR spectra of samples of bedded coal up to the rank of bituminous coal have been published elsewhere (22). Some of the published spectra are shown in Fig. 6 along with similar spectra of The Everglades peat and the Brandon lignite (sample obtained from Rutland County, Vermont, near Brandon). Both aromatic and paraffinic carbons are the dominant components of all spectra. Oxygenated carbons associated with functional groups such as methoxyl, carbohydrate, alcoholic, carboxylic, and phenolic groups decrease in relative abundance with increasing rank as expected. However, aromaticity does not appear to follow any pattern as rank increases. Aromaticities calculated from integration of the aromatic region (100-160 ppm) of these spectra (Table 1) are plotted against the carbon content as the rank parameter in Fig. 7. Data obtained by Miknis *et al.* (22) for 9 samples of coal are plotted in Fig. 7, which shows that, in coal having a rank equal to or lower than that of high-volatile bituminous coal, a poor correlation exists between aromaticity and rank. In plotting Fig. 7, the peak for paraffinic carbons was taken at 30 ppm for all the samples; as shown in Fig. 5, the major paraffinic peak occurred at this value (30 ppm) in spectra for the sapropels and aquatically derived kerogens. The incorporation of variable percentages of such sapropelic substances in the peat precursors of coal would explain why aromaticities do not correlate well with rank, as would be expected if it is assumed that increasing coalification leads to aromatic-ring condensation (2). The relationship between rank and aromaticity up to the rank of high-volatile bituminous coal, therefore, depends on two basic factors: 1) the percentage of paraffinic component in the peat, and 2) the relative rates of aromatization.

Table 1. Source, carbon content, and carbon aromaticities of coal samples examined by CPMAS  $^{13}\text{C}$  NMR

No.	Sample	Origin	C(%maf)	fa*
1	Brandon lignite	Brandon, Vt.	63.5	0.52
2	North Dakota lignite <sup>†</sup>	Fort Union Fm., N. Dak.	70.2	0.66
3	Wyoming subbituminous C <sup>†</sup>	Powder River Basin, Wyo.	73.7	0.61
4	Wyoming subbituminous B <sup>†</sup>	Powder River Basin, Wyo.	74.6	0.68
5	Wyoming subbituminous A <sup>†</sup>	Hanna Basin, Wyo.	72.7	0.66
6	Herrin high-volatile C Bituminous <sup>†</sup>	Herrin (No. 6) coal member, Carbondale Formation, Ill.	71.9	0.72
7	Herrin high-volatile C Bituminous <sup>†</sup>	Herrin (No. 6) coal member, Carbondale Formation, Ill.	77.2	0.66
8	High-volatile B Bituminous <sup>†</sup>	Harrisburg (No. 5) Coal member, Carbondale Formation, Ill.	81.0	0.70
9	High-volatile A Bituminous <sup>†</sup>	Sumnum (No. 4) coal member, Ill.	79.6	0.73

<sup>†</sup> Data of Miknis *et al.* (22)

\* Carbon aromaticity =  $^{13}\text{C}$  NMR intensity of the aromatic region/total NMR intensity

A third potential contribution to peat that can later be identified in bedded coal is resin derived from contributing trees. We have previously noted that some coalified logs have rather high paraffinic contents even though they have never been subjected to swamplike conditions (20). Petrographic observations have indicated these logs to contain unusually high concentrations of wood resins. As further examples of resinous coal,  $^{13}\text{C}$  CPMAS spectra have been obtained for a lignite collected from the Wilcox Group of Arkansas, for coal resin isolated from the Brunner coal of New Zealand (collected by the late J.M. Schopf and taken from his collection), and for fossil amber. The spectrum for the lignite (Fig. 8) illustrates nearly equal proportions of paraffinic and aromatic carbons. Moreover, the peaks for the aromatic carbons are similar to corresponding peaks for other lignites (Fig. 6). The peaks for the paraffinic carbons of the Wilcox lignite are almost identical to those for the resin and amber (22 and 37 ppm). Fig. 8 clearly shows that the paraffinic carbons of the Wilcox lignite are associated with its resin content.

Paraffinic components of coals can thus have multiple origins. In the Wilcox lignite, resins predominate; however, in other coals, such as the Brandon lignite, algal or microbial sapropels have probably contributed to the chemical structure of the coal. These substances should not be confused as being part of a hydroaromatic structural complex. Rather, these aliphatic substances, sapropelic or resinous in origin, represent a component or components of a coal which, if the means were available, could be separated from the aromatic components.

#### CONCLUSIONS

The following conclusions have been reached on the basis of our studies:

- 1) Logs that have been coalified on burial in sandstone or other sedimentary environments in the absence of swamplike conditions normally have a small amount of paraffinic carbons. Only those logs carrying inherent resinous material may have a significant percentage of paraffinic carbons.
- 2) The paraffinic carbons of bedded coals generally originate from the algal, microbial, and planktonic organisms of the peat-forming swamp water. Residues of this biota are intimately mixed with residues of the decomposing vascular plants.
- 3) The aromatic components of coal, at least up to the rank of high-volatile bituminous coal, are derived from the lignin of vascular plants. These components are separate and distinct from resins and aquatic plant-derived components and, if means were available, might be separated.

4) Previous chemical structures proposed for coal that are based on oxidative, reductive, or other degradative techniques are invalid if the techniques are based on the assumption that the aromatic and aliphatic products recovered in the analytical procedures represent fragments derived from "a coal structure."

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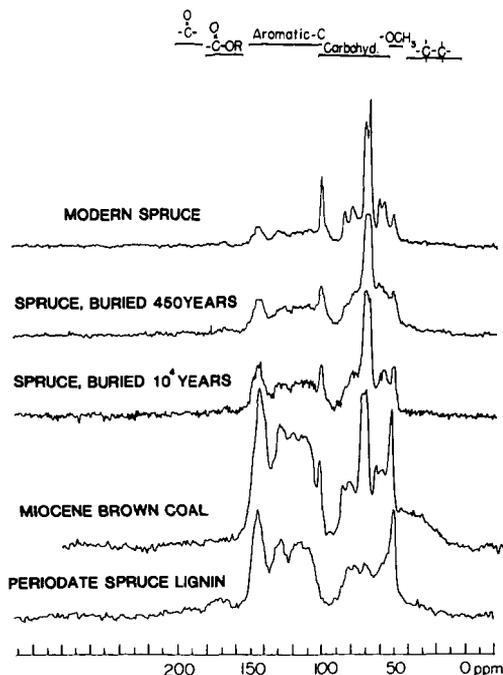


Fig. 1. CPMAS <sup>13</sup>C NMR spectra of modern spruce, a lignin isolate from modern spruce, and coniferous woods buried for various lengths of time in sediments. All spectra, except that of modern spruce, are reproduced from Hatcher *et al.* (11).

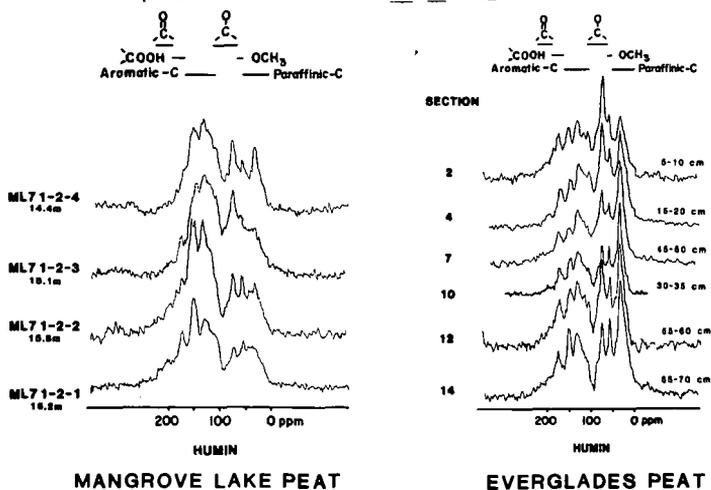


Fig. 2. CPMAS <sup>13</sup>C NMR spectra of humin isolates from various sample depths in peat from Mangrove Lake, Bermuda, and The Everglades, Florida.



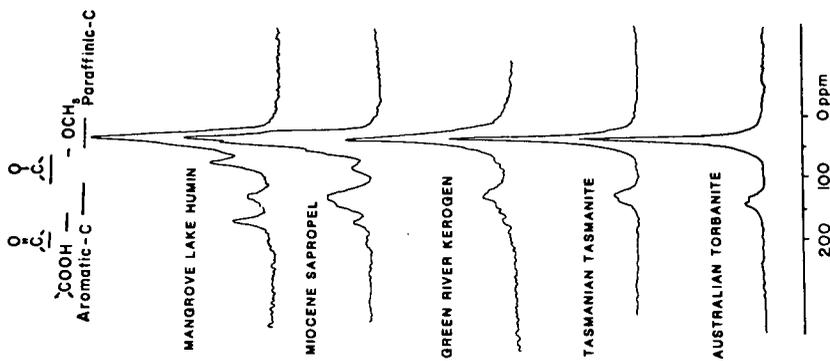


Fig. 5. CPMAS  $^{13}\text{C}$  NMR spectra of humin, kerogen, and boghead coal derived from aquatic sources.

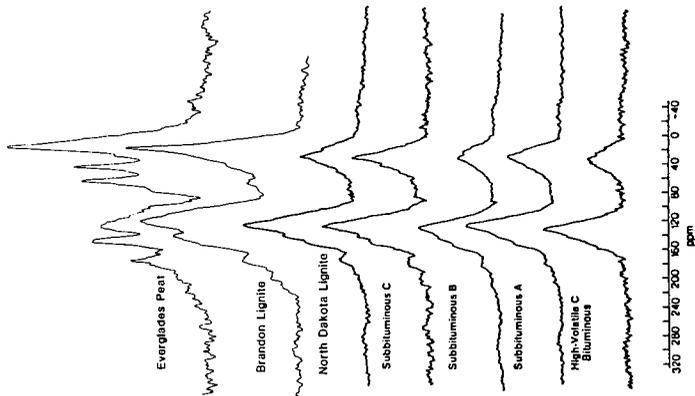


Fig. 6. CPMAS  $^{13}\text{C}$  NMR spectra of peat and bedded coal samples of various ranks. The spectra of peat and Brandon lignite are from this present study and the others were obtained from Miknis et al. (22). Origin of the coal samples are listed in Table 1.

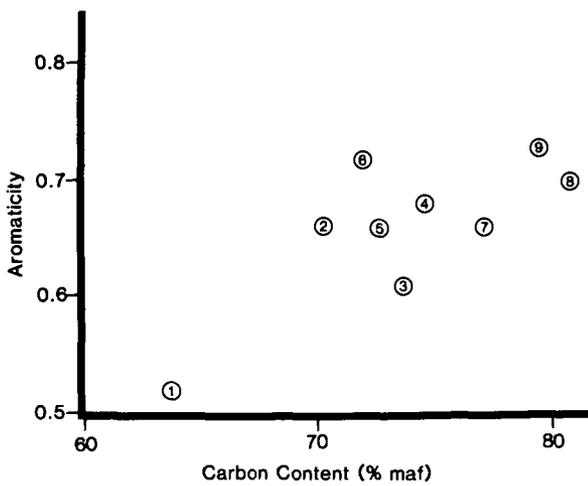


Fig. 7. Carbon aromaticities plotted against carbon contents (% moisture and ash-free basis) for samples of lignite, subbituminous coal, and bituminous coal listed in Table 1.

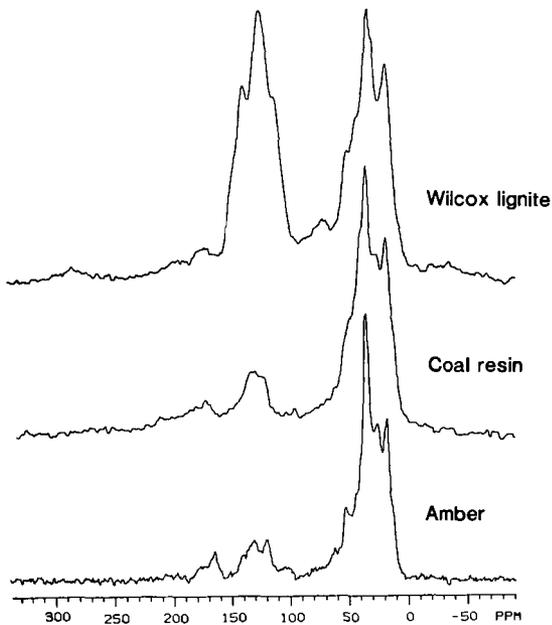


Fig. 8. CPMAS <sup>13</sup>C NMR spectra of a coalified log from the Wilcox Group in the Reynolds bauxite pit near Malvern, Arkansas, resin from coal of the Brunner mine near Buller Gorge, New Zealand, and amber.