PROGRESS REPORT

MASTER

NMR ANALYSIS OF COAL MACERALS

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A second set of six vitrinite samples were hand picked from the Lower Kittanning Seam and obtained from Penn State University. The rank of the samples ranged from low volatile to high volatile B bituminous. The ultimate and proximate analyses are given in Table I. This set of samples was selected in order to assess the nature of structural changes observed when carefully selected coal samples from a given seam are examined using CP/MAS techniques. In each case, the samples contained greater than 95% vitrinite.

For purposes of clarity, the CP/MAS spectrum of PSMC-67 is given in Figure 1 as a composite of ^{13}C chemical shifts of structural units containing H, C, and O. The vitrinite spectra thus displays the range of chemical structural types that give rise to resonance lines in different spectral regions. No effort was made to eliminate from the presentation chemical species (e.g., acetylenes, allenes, etc.) which are not expected to be present to any significant extent in the coal. Nitrogen and sulfur were not included in the display for simplicity of presentation and also due to the low concentration of these elements relative to oxygen. The banded structure observed in Figure 1, however, does provide enough detail to discuss major structural types present. A casual observation demonstrates that a significant amount of aliphatic oxygen is present (50-95 ppm region). Assuming allene and acetylene groups are not present, the 75-95 ppm region suggests the presence of oxygen containing structural types such as glucoside or pyranoside moieties which would be associated with cellulose, lignin, etc. containing materials. The 50-75 ppm range would contain aliphatic carbons

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associated with ether (either aliphatic or aromatic) and ester structural units.

Figure 2 displays the spectral changes that occur with rank progression. The spectra of PSMC-67, -53, and -43 represent the extremes and mid-point, respectively, of the rank of the samples. It is clear from an examination of the spectra that significant structural changes are occurring in the aromatic region. These observations are as follows: 1) significant decrease in the intensity in the region beyond 150 ppm; 2) significant decrease in the 135-145 ppm region; 3) a decrease in the line intensity in the 110-120 ppm region. Observations 1 and 2 are most likely due to loss of aromatic oxygen (phenols, aryl-aryl and aryl-aliphatic ethers) and aromatic cyclic ethers (e.g. furans) and/or ring dealkylation. The 110-120 ppm region would represent alkene structures, β -carbons in aromatic cyclic ethers (furans), and α -carbons in phenols and phenolic ethers. Hence, decreasing relative intensity in these spectral regions suggests loss of aromatic oxygen structural units and possible ring dealkylation.

The six sample series studied exhibited progression from a highly functional aromatic structure to one that displays little functionality. The aromatic band in PSMC-53 spans a chemical shift range characterized primarily by simple aromatic and condensed aromatic ring systems with significantly less functionality than observed in lower rank samples in this series.

In the aliphatic region, subtle differences are observed in the 15-40 ppm range. However, the aliphatic oxygen region of the spectrum (50-95 ppm) exhibits little perceptible difference, being characterized by a broad featureless band in each case. A careful examination of the spectra of all six samples gives no indication of loss in oxygen functionality that is observed in the aromatic region. The rationale is not clear for the loss

of aromatic oxygen with rank progression with no concomitant loss in aliphatic oxygen in this sample set. Similar data from sample sets from additional coals of different rank, geological age and coal province, are needed to help interpret these observations.

Another interesting observation was made in this sample set. The f_a values (percent of observed aromatic carbon to total observed carbon) did not cover the range expected. In fact, little variation in f_a values was observed (0.67 - 0.72). While most workers in the field agree that paramagnetic centers (stable free radicals and paramagnetic materials in the mineral matter) will cause sufficient line broadening to prevent observation of carbons in the vicinity of such centers, it is generally assumed that such centers are randomly distributed through the coal structure and, hence, a representative structural framework is observed. Another possible source of error is lack of linear response by all carbons present due to complex and not well understood relaxation processes in solids when compared to liquids. In the case of bridgehead carbons that are far removed from protons, variations in T_1 and $T_{1\rho}$ processes probably produce spectral distortions which would lead to low values of f_a . If one were to progress from a highly protonated aromatic ring structure to a highly condensed ring structure, a bias in the line intensities in the aromatic region may occur. If such were the case, the measured f_a values may not increase as rapidly as one might expect. This matter is the subject of investigation in our laboratory.

A second set of macerals was obtained from a single coal source and were supplied to us by personnel (Horwitz and Dyrkacz) at Argonne National Laboratory. Using zonal gradient centrifugation techniques seven maceral samples (1 alginite, 1 sporinite, 2 vitrinite, and 3 inertinite) were separated from PSOC-297. This coal, obtained from the Pennsylvania State

University coal data base, is classified as a cannel-like coal of HVA rank. The analytical data and petrographic analysis of this coal is contained in Tables II and III. The data in Table IV provides information on the maceral type, purity, density and H/C for each of the seven samples examined. Figures 3 and 4 provide convenient comparisons of the liptonite, vitrinite, and inertinite materials. The alginite and sporinite spectra generally resemble those observed previously (see Appendix).

The f_a value for alginite (0.15) is within experimental error of that noted previously. The sporinite spectra, however, displays more structural information in the downfield aromatic region than was previously observed (Figure 2 in maceral preprint in Appendix) and is indicative of more aromatic functional groups. In the case of the vitrinite samples (Figures 3 C, D) the aliphatic region is quite different from that noted previously (Figure 3, maceral preprint).

An interesting observation is made regarding inertinite samples. First, the fusinite in the maceral preprint (Appendix) contains markedly different structural features in the aliphatic region than those observed in Figure 4. PSOC-297 contains essentially no fusinite which may partially explain the differences. Furthermore, one observes subtle differences between Figure 4 A and 4 B, C. The former is thought to be composed principally of inertodetrinite while the latter two samples are thought to be micrinite although the particle sizes are so small that it is difficult to determine if petrographic differences do actually exist. Since little is known chemically about inertinites, the observed differences, in the aliphatic regions, of fusinite, inertodetrinite (Figure 4 A), and micrinite (Figures 4 B and 4 C) is worthy of note and suggests that inertinites are composed of a broader range of structural features than polyaromatic hydrocarbons. This matter is

presently under study as we consider macerals or sources of macerals that may contain large amounts of a given inertinite. Such samples will be supplied by ANL as PSOC-104 and PSOC-124 (Table I) and other coals that have not yet been selected.

TABLE I

Ultimate and Proximate Analysis of Maceral Concentrates

	C	H	S	O	N	H/C	Volatile Matter	Fixed Carbon
<u>PSMC-</u>	(% daf)						(% daf)	
67	79.9	5.3	1.6	9.2	1.4	0.80	41.6	58.4
19	77.1	5.5	2.5	6.2	1.4	0.86	41.0	59.0
34	82.0	5.1	0.9	8.3	1.6	0.75	35.2	64.8
43	81.9	5.3	1.7	4.6	1.5	0.78	34.4	65.6
47	84.4	5.1	0.8	4.4	1.5	0.73	25.5	73.5
53	84.2	4.4	1.3	3.7	1.4	0.63	18.6	81.4

Table II. Analytical Data

			C	H	N	S	O	Ash
PSOC-297	A ^a	daf	77.36	5.62	1.72	2.28	13.3	20.4
		dmmf	79.79	4.32	1.78	--	12.6	--
	B ^b	daf	79.61	5.30	1.73	1.71	11.65	1.77
		dmmf	80.49	5.36	1.78	--	14.13	--

^aas received.

^bafter chemical demineralization.

Table III. Petrographic Analysis of Coal Samples^a

Maceral	PSOC-106	PSOC-124	PSOC-297
alginite	0.0	1.6	2.0
resinite	2.4	1.5	0.4
cutinite	0.3	1.7	0.4
sporinite	17.4	51.7	16.5
total exinite	20.1	56.5	19.2
vitrinite	35.2	14.6	63.0
micrinite	3.2	20.2	7.7
inertodetrinite	15.7	7.2	9.3
semi-fusinite	20.7	1.0	0.8
fusinite	5.7	0.4	0.4
total inertinite	45.3	28.8	18.2

^aAnalyses were performed with incident white light and incident blue light.
All values are % volume.

Table IV. Samples Separated from PSOC-297

Sample No.	Maceral Type	Purity	Density 2/cc	H/C
1	Alginite	>93%	1.0-1.144	1.3
2	Sporinite	>95%	1.169-1.180	1.17
3	Vitrinite	89% ^a	1.276-1.286	0-83
4	Vitrinite	82.5% ^a	1.295-1.305	0.79
5	Inertinite (mostly inerto- detrinite)	93% ^b	1.356-1.373	0.6
6	Inertinite	>95%	1.390-1.420	0.6
7	Inertinite	>95%	1.425-1.5	0.6

a. Contaminated with micrinite

b. Contaminated with vitrinite

After E. W. Wehrli and T. Wehrli (1976)

Figure 1. Composite of carbon-13 NMR correlation chart and PSMC-67

Figure 2. CP/MAS spectra of vitrinites. The spectra represent the changes that occur with rank progression.

PSOC-297

Alginite, Sporinite, and Vitrinites.

Figure 3. CP/MAS spectra of alginite, (A) sporinite (B), and vitrinite macerals (C, D)

Figure 4. CP/MAS spectra of inertinite samples.