

Characterization of Peats by X-ray and NMR Methods

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X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) spectroscopy and solid state CP MAS ^{13}C NMR spectroscopy have proven to be viable non-destructive techniques for quantifying heteroatom functionalities in complex carbonaceous systems. Coals and kerogens have been examined extensively by these techniques. However, much less attention has been given to diagenetic stage precursors of these fossil materials. In this work, a set of eight well-defined peat samples has been examined by X-ray and NMR methods. Oxygen is by far the most abundant heteroatom species in peat derived from lignin and cellulose materials. A combination of XPS and NMR methods has been examined for quantifying organic oxygen species in peat. Total organic oxygen determined by XPS was significantly less than the amount obtained from oxygen determined by difference. XPS and NMR results confirm that carbon bonded to a single oxygen species are the predominant form in all peat samples studied and that multiply bonded carbon oxygen species make up only 25% of the oxygen population in these peat samples. The advantages of a multiple technique approach for quantifying organic oxygen forms in carbonaceous solids is discussed.

I. Introduction

X-ray and NMR are viable non-destructive techniques for quantification of organic nitrogen, sulfur and oxygen species in complex carbonaceous systems. For coal and kerogen, chemistry of heteroatom transformations is important for understanding both geological and utilization processes. Next to carbon and hydrogen, oxygen is usually the most abundant atom in organic sedimentary material. Nevertheless, determining the amount and kinds of organic oxygen species remains a formidable analytical challenge for these materials. Total organic oxygen is usually determined by difference [1]. Other methods involve fast neutron activation analysis for oxygen corrected for inorganic forms or pyrolysis followed by coulometry [1]. Infrared spectroscopy [2-4], solid-state (SS) ^{13}C NMR analysis [5] and X-ray Photoelectron Spectroscopy (XPS) [6-8] have been used to directly gain information about the kinds of organic oxygen species in coal.

Peat is a sedimentary deposit composed primarily of plant derived material and is a precursor of coal. The organic oxygen content exceeds that of coal. The physical and chemical make-up of peat varies widely and differences in organic oxygen functional group distributions are expected [9]. The present work uses a combination of XPS and SS ^{13}C NMR to quantify oxygen species in a set of eight well-defined peat samples.

II. Experimental

A) Samples

The peat samples were obtained from the peat sample bank of the University of South Carolina [9]. The elemental data for the peat samples are shown in Table 1. These peats differ significantly in composition due to the variety of source plants and depositional settings. The fresh starting coal samples were obtained in sealed ampoules from the Argonne Premium Coal Sample Program [10]. Other coal samples were obtained from the Penn State coal sample bank [11]. The elemental data for these coals are included in Table 1.

B) X-ray Photoelectron Spectroscopy

The XPS spectra were obtained with a Vacuum Generators (VG) ESCA Lab system using Al K alpha non-monochromatic radiation and a five channel detection arrangement. The samples were evacuated to remove moisture and ground into fine powders. The powders were mounted on a metallic nub via non-conducting double-sided tape. An energy correction was made to account for sample charging based on the carbon (1s) peak at 284.8 eV. The elemental concentrations are reported relative to carbon on an atomic basis, calculated from XPS spectra based on the area of the characteristic

photoelectron peaks after correcting for atomic sensitivity. The amount of organic oxygen was derived from the total oxygen (1s) signal by taking into account inorganic contributions [8]. The main inorganic elements observed via XPS are found in Table 2. For coal, the amount of each inorganic element determined by XPS may differ from the bulk inorganic elemental composition due to particle size effects and organic encapsulation [8].

The nature of the organic oxygen species present in lignite and lignin were determined by analyzing oxygen's effect on the XPS carbon (1s) signal of adjacent carbon atoms [8]. The level of carboxyl and carbonyl is derived from the curve resolved carbon (1s) spectrum. The amount of oxygen associated with carbon-oxygen single bond species is determined by subtracting the carboxyl and carbonyl oxygen levels from the total amount of organic oxygen. The relative amount of aromatic carbon was determined by the method of Π to Π^* signal intensity [12]. A complete list of XPS data for samples contained in this report is found in Table 2.

Five peaks were used to curve resolve the XPS carbon (1s) signal for peat. These occur at 284.8, 285.3, 286.3, 287.5, and 289.0 (± 0.1) eV. The 284.8 eV peak represents contributions from both aromatic and aliphatic carbon. The 286.3 eV peak (Type I) represents carbon bound to one oxygen by a single bond (e.g., C-O, C-OH etc.). The 287.5 eV peak (Type II) corresponds to carbon bound to oxygen by two oxygen bonds (C=O, O-C-O). The 289.0 eV peak (Type III) corresponds mainly to carbon bound to oxygen by three bonds (O=C-O). The 285.3 peak will have contributions mainly from carbon adjacent to carboxyl carbon (beta peak) and carbon bound to nitrogen (i.e. pyrrole, pyridinic). The 285.3 eV peak is therefore fixed to the sum of the intensity of the 289.0 eV peak and the intensity of carbon adjacent to nitrogen (i.e. twice the nitrogen level). The results shown in Table 3 assume 1) that two oxygens are associated with the Type III carbon (1s) signal and 2) that one oxygen is associated with the Type II carbon (1s) signal. The amount of oxygen associated with the Type I carbon (1s) signal is obtained by subtracting the oxygen associated with the Type II and the III carbon (1s) signal from the amount of total organic oxygen.

C) Solid State ^{13}C NMR Spectroscopy

High-resolution solid-state ^{13}C NMR measurements of peat samples were performed using a Chemagnetics CMX-200 spectrometer operating at a static magnetic field of 4.7 T (50.2 MHz ^{13}C). Peat samples were packed into a 5-mm diameter zirconia rotor and spun at 8-kHz using dry nitrogen gas. Cross-polarization magic-angle spinning (CPMAS) NMR was used to characterize the peat samples. The CPMAS experiments were performed at a ^1H - ^{13}C CP contact time of 3 ms and a pulse repetition delay of 2 seconds. The ^1H and ^{13}C radio-frequency fields for cross-polarization and the proton high power decoupling during data acquisition were at 62.5 kHz. The definition of ^{13}C NMR structural parameters and chemical shift ranges are shown in Table 4. A complete list of structural parameters obtained by solid-state ^{13}C NMR for samples contained in this report is found in Table 5.

III. Results and Discussion

The atomic H/C and O/C ratios are plotted for peat, lignite and coal in Figure 1 (called a Van Krevelan Diagram [13]). The O/C values were obtained from XPS data. All peat samples have higher H/C and O/C values than coal and lignite. These results are in good general agreement with established ordering for these materials [13]. The range of organic oxygen determined by XPS for peat is roughly between 20 and 30 oxygen per 100 carbons, (Table 3). These results are significantly lower than the amount of oxygen determined by difference, (Table 1).

A combination of XPS and SS ^{13}C NMR was used to characterize the peat samples. Figure 2 shows excellent agreement between the percent aromatic carbon determined by XPS and NMR methods. Previously published results for coal and lignite are included for comparison [12]. Not surprisingly, peat has significantly lower levels of aromatic carbon. The close correspondence between the XPS and NMR values for peat indicate that the aromatic carbon level at the surface of finely ground peat is comparable to the bulk.

XPS was used to distinguish the kinds of organic oxygen species present in peat. Table 3 shows the results based on the methodology described in the experimental section. Carboxyl oxygen accounts for roughly 1/3 of the oxygen present in peat. Carbon oxygen single bond species account for roughly half of the oxygen species. For coal, carbonyl is the predominant Type II oxygen form. This situation may be different for peat. Species such as O-C-O (present in cellulose) would contribute to the Type II carbon (1s) signal. The presence of a significant amount of O-C-O species in peat would complicate the interpretation for the amount of oxygen associated with Type II carbon (1s) signal. The C=O values listed in Table 3 therefore represent upper limits.

Table 4 provides the definition of ^{13}C NMR structural parameters based on the carbon species and chemical shift ranges. Table 5 shows results obtained for the different structural parameters as a fraction of the total ^{13}C signal. SS ^{13}C NMR parameters fa^{C} , (carboxyl, carbonyl, amide), fa^{P} (phenolic, phenoxy) and fa^{O} (alcohol, ether) have oxygen associated with them. The range for the percentage of carbon associated with oxygen ($\text{fa}^{\text{C}} + \text{fa}^{\text{P}} + \text{fa}^{\text{O}}$) in peat is 32 to 49. It is not possible to determine the total amount of oxygen relative to carbon from the sum of oxygen related ^{13}C NMR signals (fa^{C} , fa^{P} , fa^{O}) because it is uncertain what oxygen stoichiometry to assign to each oxygen related ^{13}C NMR signal. Nevertheless, a conservative estimate of the amount of oxygen associated with fa^{C} is 1.0 (i.e. carbonyl, amide etc.) and 0.5 for fa^{P} and fa^{O} (i.e., aliphatic ether, methoxy etc.). Undoubtedly other species will have a combined impact on fa^{C} , fa^{P} and fa^{O} . A comparison of the XPS derived total organic oxygen signal and the NMR estimate based on $\text{fa}^{\text{C}} + 0.5(\text{fa}^{\text{P}} + \text{fa}^{\text{O}})$ is shown in Figure 3. The NMR parameter fa^{C} is expected to be related to the amount of oxygen with O-C=O (Type III) determined by XPS. Figure 3 shows a close correspondence for these XPS and NMR parameters with all peat samples. Figure 3 also shows that the amount of oxygen found with Type I plus Type II XPS species is closely related to $0.5(\text{fa}^{\text{P}} + \text{fa}^{\text{O}})$. We would expect this correspondence if most of the oxygen species associated with the XPS Type II carbon (1s) signal are O-C-O species and if ether species predominate in fa^{P} and fa^{O} .

IV. Summary

A self-consistent interpretation of oxygen derived XPS and ^{13}C NMR signals provides insight into the kinds of oxygen species present in peat. Multiply bonded carbon oxygen species make up only 25% of the oxygen population in these peat samples. XPS and NMR results indicate that carbon oxygen single bonded species are the predominant form in all peat samples studied. It is likely O-C-O species and, in general, ether species make up a large part of the carbon oxygen single bond population.

V. References

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Table 1

Peat Sample	(per 100 C) Hydrogen	(per 100 C) Nitrogen	(per 100 C) Sulfur	(per 100 C) Oxygen*
Mian. Hem.	117	4.5	0.2	42.1
Me. Sph.	131	0.8	0.1	58.9
Lox. Nym.	130	6.3	0.5	39.1
Lox. Saw.	111	4.8	0.7	40.1
Sh. Rv. Rhiz.	118	3.9	2.8	50.4
Oke. Tax.	121	4.0	0.2	41.0
Oke. Nym.	122	5.3	0.3	39.4
N.C. 1 st Col.	107	1.3	0.1	35.0
Coal/Lignite				
DECS-11 Beulah	73	1.2	0.4	31.0
DECS-25 Post	82	1.2	0.2	17.6
PSOC-1468 Buck Mountain	16	0.8	0.2	0.9

(*) determined by difference

Table 2

Sample	Aromatic Carbon	Nitrogen	Sulfur	Si	Al	Ca
<u>Peat</u>						
Minn. Hem. (Peat) SCSB	26	2.8	0.2	0.5	0.3	--
Me. Sph. (Peat) SCSB	24	1.0	0.1	--	--	--
Lox. Nym. (Peat) SCSB	23	3.9	0.2	--	--	0.7
Lox. Saw. (Peat) SCSB	28	3.2	0.3	--	--	0.7
Sh. Rv. Rhiz. (Peat) SCSB	35	2.3	1.9	3.8	2.9	--
Oke. Tax. (Peat) SCSB	25	2.7	0.1	2.4	--	--
Oke. Nym. (Peat) SCSB	23	4.4	0.1	1.5	--	--
N.C. 1 st Col. (Peat) SCSB	29	1.1	<0.1	--	--	--
<u>Coal/Lignite</u>						
DECS-11 Beulah	55	1.3	0.3	2.4	2.5	1.1
DECS-25 Pust	52	1.3	0.3	3.2	4.1	1.3

Table 3

Sample	Total Organic Oxygen	-O	C=O	O-C=O
Minn. Hem. (Peat) SCSB	24.2	11.3	6.7	6.2
Me. Sph. (Peat) SCSB	22.4	10.7	6.1	5.6
Lox. Nym. (Peat) SCSB	22.2	8.6	6.6	7.0
Lox. Saw. (Peat) SCSB	27.0	9.3	8.3	9.4
Sh. Rv. Rhiz. (Peat) SCSB	24.3	7.3	8.8	8.2
Oke. Tax. (Peat) SCSB	25.6	9.3	6.9	9.4
Oke. Nym. (Peat) SCSB	30.2	14.5	7.9	7.8
N.C. 1 st Col. (Peat) SCSB	21.2	11.1	3.7	6.4

Table 4 - Definition of ¹³C NMR Structural Parameters

Parameter	Chemical Shift		Carbon Type
	Range (ppm)		
fa	90-240		Aromatic/Carboxyl/Carbonyl/Amide
fa'	90-165		Aromatic
faC	165-240		Carboxyl/Carbonyl/Amide
fa ^P	150-165		Phenoxy/Phenolic
fa ^S	135-150		Alkyl-Substituted Aromatic
fa ^B	90-135		Bridgehead Aromatic
fal	0-90		Aliphatic
fa ^H	22-50		Methylene/Methine
fa [*]	0-22 & 50-60		Methyl/Methoxy
fa ^O	50-90		Alcohol/Ether

Table 5

	fa	fa'	faC	fa ^P	fa ^S	fa ^B	fal	fa ^H	fa [*]	fa ^O
Minn. Hem.	0.41	0.35	0.07	0.04	0.06	0.24	0.59	0.19	0.11	0.37
Me. Sph.	0.40	0.33	0.06	0.04	0.04	0.24	0.60	0.18	0.07	0.39
Lox. Nym.	0.35	0.24	0.11	0.03	0.04	0.16	0.65	0.30	0.12	0.30
Lox. Saw.	0.43	0.33	0.10	0.05	0.06	0.22	0.57	0.20	0.11	0.33
Sh. Rv. Rhiz.	0.40	0.33	0.06	0.04	0.06	0.23	0.60	0.18	0.13	0.38
Oke. Tax.	0.38	0.29	0.09	0.04	0.05	0.19	0.62	0.30	0.10	0.28
Oke. Nym.	0.40	0.30	0.10	0.04	0.05	0.21	0.60	0.18	0.11	0.38
N.C. 1 st Col.	0.45	0.36	0.09	0.05	0.07	0.23	0.56	0.33	0.09	0.18

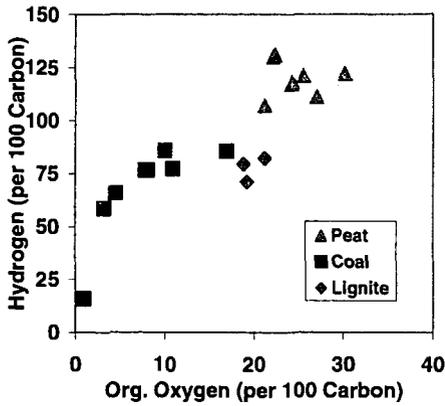


Figure 1 - H/C vs. O/C diagram for peat, and lignite. The O/C values were obtained from XPS data. H/C values are from elemental data. Previously reported results from Argonne Premium Coal are included for reference.

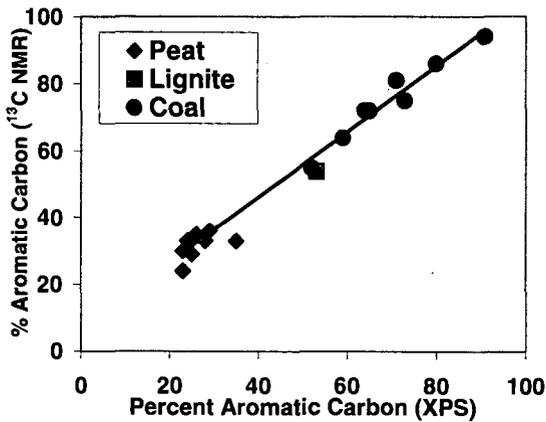


Figure 2 - Comparison of XPS and ¹³C NMR results for aromatic carbon from peat, coal and lignite. Previously reported results for Argonne Premium Coal [12] are included for reference.

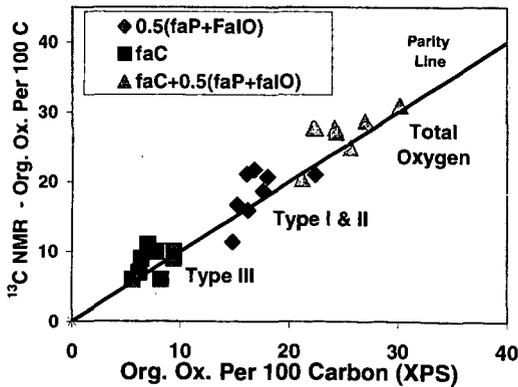


Figure 3 - Comparison of XPS and ¹³C NMR derived parameters for organic oxygen species in peat.