

SECONDARY ION MASS SPECTROMETRY AND X-RAY
PHOTOELECTRON SPECTROSCOPY OF DERIVATIZED COAL SURFACES.

R.R. Martin, N.S. McIntyre, J.A. MacPhee, K.T. Aye.

Department of Chemistry, University of Western Ontario
London, Ontario, Canada. N6A 5B7

ABSTRACT

Secondary Ion Mass Spectrometry (SIMS) and X-ray Photoelectron Spectroscopy (XPS) have been used to study the low temperature oxidation of coal. ^{18}O has been used to trace the oxygen distribution on the coal surface. Several chemical derivatizations have been observed on the oxidized coal surface and the reactivity of specific regions have been monitored.

INTRODUCTION

The low temperature oxidation of coal leads both to loss of coking ability⁽¹⁾ and autoignition⁽²⁾ of coal stock piles. In this study we report the use of secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) in conjunction with $^{18}\text{O}_2$ oxidation to examine the oxygen distribution on a coal surface in relation to specific other elements. The use of both XPS and SIMS in coal studies have been described elsewhere.⁽³⁾

EXPERIMENTAL

The coal used in this study was a pyrite-rich fusinite supplied by the Canadian Center for Mineral and Energy Technology (CANMET). The coal was cut with a diamond saw, and polished on a silk wheel using diamond grit as abrasive and water as lubricant. The resulting coal surfaces were exposed to 0.1 atm of $^{18}\text{O}_2$ for 10 days at room temperature.

The SIMS measurements were made on a Cameca IMS 3 f using a Cs^+ primary beam rastered over a $(400\ \mu\text{m})^2$ area. Ion images were collected from a central area $170\ \mu\text{m}$ in diameter, these images were obtained at a mass resolution as high as one part in 3500, though for certain ions the secondary ion yield was insufficient to permit imaging. In most cases where SIMS images were taken mass spectral scans were also obtained.

XPS studies were also carried out on regions adjacent to those studied by SIMS using a Surface Science Laboratory Model SSX-100 spectrometer with monochromatized $\text{AlK}\alpha$ radiation with a spot size of approximately $150\ \mu\text{m}$. The ^{18}O was used as an isotopic trace to distinguish between oxygen added to the coal as a result of this procedure and that already present.⁽⁴⁾ The pyrite-rich coal was selected because it provides remarkably well defined secondary ion images and pyrite is reported to play an important role in the self-heating of coal.⁽⁵⁾

RESULTS AND DISCUSSION

The assignment of ionic species to the secondary ion images obtained during high mass resolution imaging was achieved using two criteria. First the accompanying mass spectrum at a given nominal mass was analyzed to achieve a fit between the mass separation observed and that expected from the species assigned to the spectrum. Thus at mass 28 two peaks were observed separated by $.019 \pm .003$ daltons, only $^{28}\text{Si}^-$ and CO^- are likely to produce this pattern. In addition successive ion images may be used to eliminate some assignments, for example silicon molecular ions would not be expected in regions where silicon could not be detected. Finally, in one case at mass 30 high mass resolution was not used to distinguish between $^{30}\text{Si}^-$ and C^{18}O^- since the yield of C^{18}O^- was too low for effective imaging.

The ion images displayed in figure 1 are assigned to ions C_2^- , C_4^- , CO^- , S^- and CS^- . The images for C_2^- and C_4^- define the organic region of the coal surface while that of S^- outlines the pyrite region. The image for CO^- is confined entirely to the organic region and originates from a set of sources having a very small area. These represent oxidized areas on the coal surface and although the oxygen functional groups cannot be identified with certainty they may well be aldehydes or phenols.

The CS^- image is of particular interest since it is confined to the organic region of the coal. The XPS spectra from this area, figure 2, confirm the presence of organic sulfur. The suite of peaks associated with binding energies between 157 and 160 eV are assigned to iron sulfides while those between 163 and 165 eV are assigned to organic compounds probably dominated by sulfates. Thus the coal adjacent to the pyrite appears to have undergone a reaction which has tended to enrich the area in sulfur. It has been proposed elsewhere that pyrite oxidizes readily to form a series of hydrated ion sulfates and sulfuric acid.⁽⁶⁾ Since these reactions are exothermic⁽⁷⁾ the surrounding organic material would be exposed to sulfuric acid and simultaneously heated. Under these conditions sulfonation reactions would be expected. Accordingly we suggest that oxidation of pyrite is accompanied by sulfonation of the surrounding coal.

Figure 3 displays a series of oxygen-related images. The $^{16}\text{O}^-$ image which is coincident with OH^- is seen to be widely distributed in the coal, however there is oxygen enrichment in the organic region and in silicate regions identified in figure 4. A recurrent feature associated with silicate materials is identified by an arrow in figures 3 and 4. The persistence of oxygen-related species in this area (particularly $^{18}\text{O}^-$ and $^{18}\text{OH}^-$) provides evidence that the silicate serves as a catalyst during oxidation. The presence of $^{16}\text{O}^-$, $^{18}\text{O}^-$ and the molecular ions OH^- and $^{18}\text{OH}^-$ indicate that oxidation of the coal has taken place and that ^{18}O reacted with the coal surface under very mild conditions. The F^- image is diffuse within the organic region suggesting the presence of carbon monofluoride⁽⁴⁾ while other sources are clearly associated with the silicate material. The latter source represents fluoride replacement of OH^- in the mineral matter. The image obtained for H_2O indicates that traces of water are present in the sample.

Figure 4 serves to outline the silicate enriched regions as defined by the image at mass 28, which is a mixture of $^{28}\text{Si}^-$ and AlH^- since the mass resolution used cannot distinguish between these

species, by comparison with that obtained at mass 30⁻ (³⁰Si⁻ with traces of C¹⁸O⁻). A representative silicate mineral region is identified with an arrow in Figure 4(a). The images assigned to O₂⁻ and O₃⁻ also show some enhancement in the silicate region. The O₂⁻ originates from adsorbed oxygen while O₃⁻ may represent ozone on the coal surface.

It has been repeatedly suggested that the low temperature oxidation of coal proceeds by a free radical chain reaction(8). Minerals would be expected to act as catalysts in such reactions(5). Figure 3 shows the presence of ¹⁸O in molecular ions after mild oxidation while Figure 4 shows reactive oxygen species on the coal surface associated with mineral matter. These results would be expected if a free radical mechanism is involved in low temperature oxidation.

CONCLUSIONS

Detailed SIMS images can be obtained for ions differing in mass by as little as 1:3500.

The uptake of ¹⁸O and molecular ions containing ¹⁸O can be successfully studied using SIMS after exposure of coal surfaces to an ¹⁸O₂ atmosphere at room temperature.

The presence of organic sulfur in regions adjacent to pyrite probably result from sulfonation of the coal by the products of pyrite oxidation.

Molecular ions originating from oxidized regions of the coal surface are readily identified and reactive oxygen species have been imaged associated with mineral matter. These results support the suggestion that the low temperature oxidation of coal proceeds by a free radical chain mechanism.

REFERENCES

1. J. W. Larsen, D. Lee, T. Schmidt and A. Grint, *Fuel* (1986), 65, 595-6.
2. R.E. Jones and D.T.A. Townsend, *Nature* (1945), 155, 424-425.
3. N.S. McIntyre, R.R. Martin, W.J. Chauvin, C.G. Winder, J.R. Brown and J.A. MacPhee, *FUEL* (1985), 64, 1705-1712.
4. R.R. Martin, N.S. McIntyre and J.A. MacPhee, *Proceedings 1985 International Conference on Coal Science, Sydney, Australia*, 796-799.
5. R.G. Herman, G.W. Simmons, D.A. Cole, V. Kubicz and K. Klier, *FUEL* (1984), 63, 673-678.
6. F.E. Huggins, G.P. Huffman and M.C. Lin, *Int. Jour. Coal Geol.* (1983), 3, 157-182.
7. R.A. Robie, B.S. Hemingway and J.R. Fisher, *U.S. Geol. Survey Bull.* 1452, p. 456 (1978).
8. D.A. Cole, R.G. Herman, G.W. Simmons and K. Klier, *FUEL* (1985), 64, 303-6.



A

C_2^-

1/2 sec



B

C_4^-

1 sec



C

CO^-

120 sec



D

S^-

1/2 sec



E

CS^-

30 sec

Fig. 1

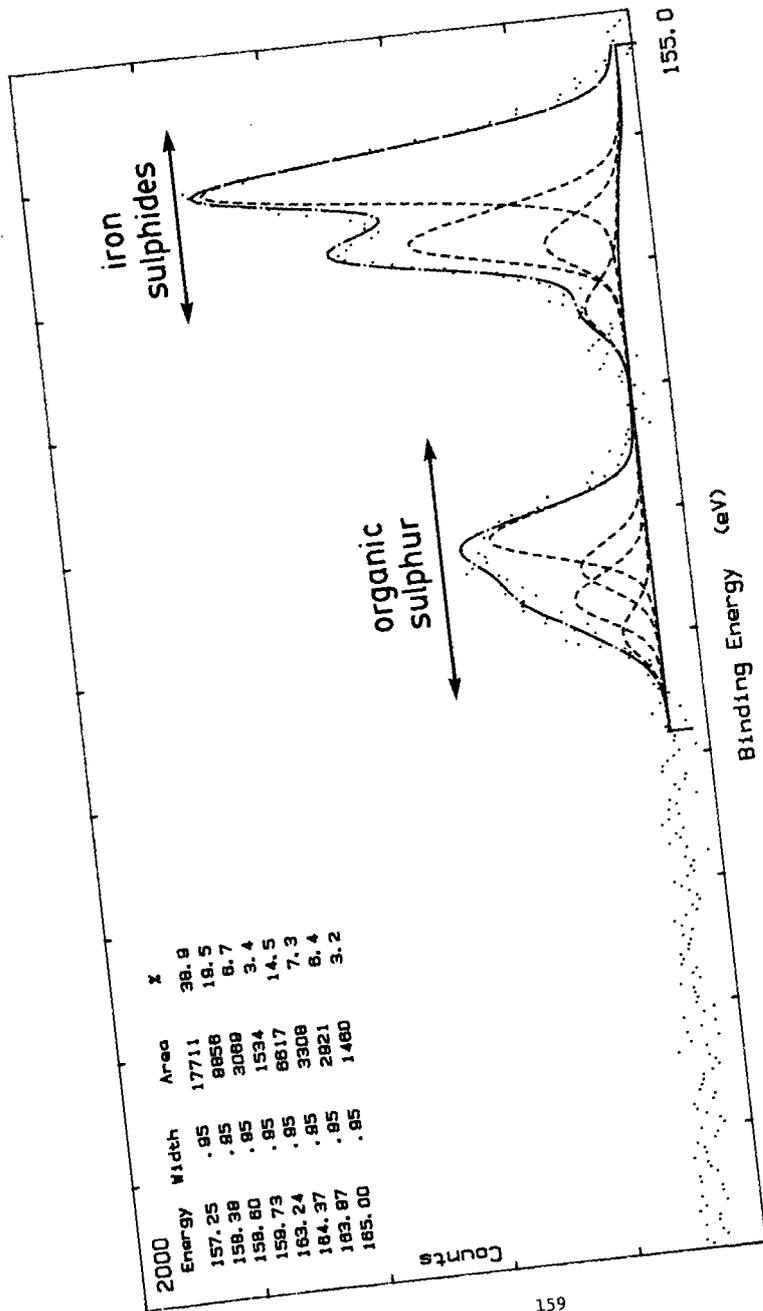
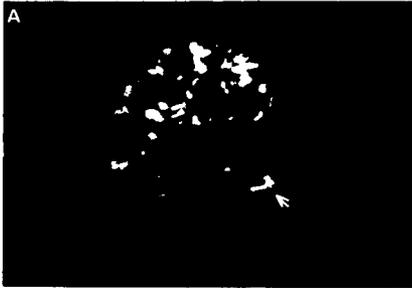


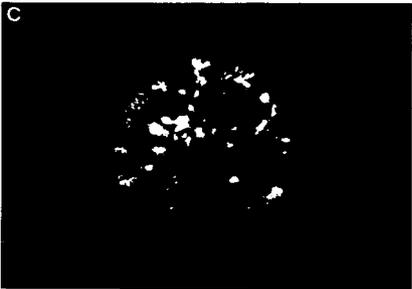
Figure 2
XPS SPECTRUM OF S_{2p} REGION



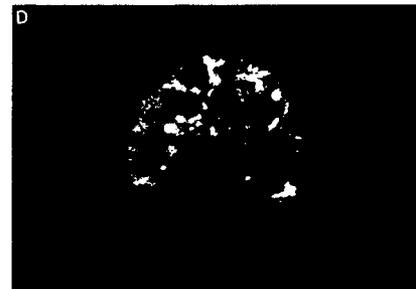
$^{16}\text{O}^-$ 1/2 sec



OH^- 2 sec



H_2O 60 sec



$^{18}\text{O}^-$ 30 sec



$^{18}\text{OH}^-$ 60 sec



F^- 60 sec

Fig. 3

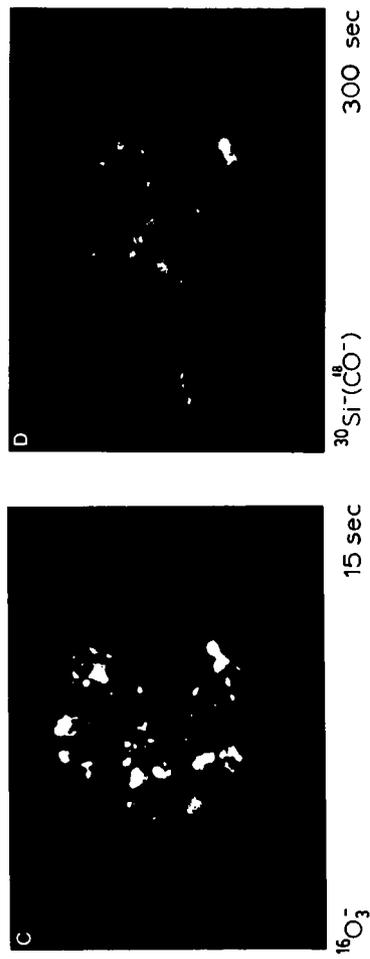
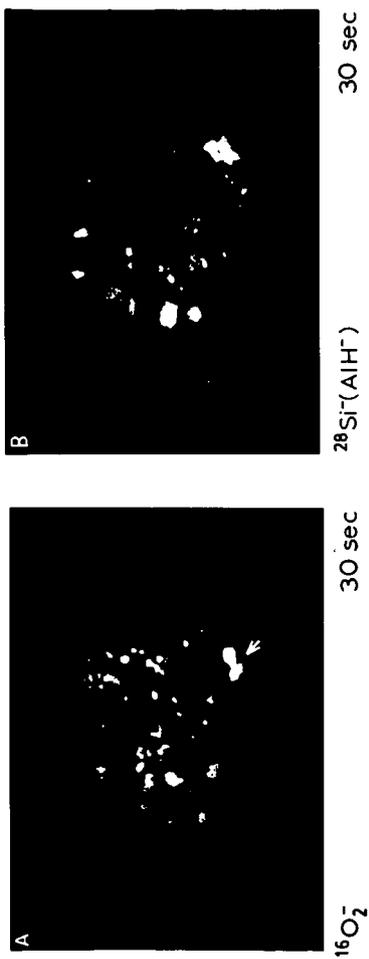


Fig. 4