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AN INVESTIGATION OF COAL USING SECONDARY ION MASS SPECTROMETRY (SIMS)

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AN INVESTIGATION OF COAL USING SECONDARY ION MASS SPECTROMETRY (SIMS)

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ABSTRACT

Secondary Ion Mass Spectrometry (SIMS) has been used to examine the organic and inorganic content of a variety of coal macerals of differing rank. Oxidation studies using an ^{18}O enriched atmosphere have been used to identify the areas of primary oxygen uptake during oxidation. Ion imaging clearly reveals elemental associations in the mineral matter in coal as in the various coal macerals.

INTRODUCTION

Secondary Ion Mass Spectrometry (SIMS) has been described in detail elsewhere[1]. It is essentially a mass spectrometric technique in which ionization of the sample is achieved by bombardment with a primary ion beam. SIMS was chosen as the analytical tool in this study because it is better adapted to surface analysis than complementary techniques such as Scanning Electron Microscopy and is capable of detecting virtually all elements into the ppm range. It also exhibits better spacial resolution than the related methods such as Fast Atom Bombardment[2], Plasma Desorption[3], and Laser Microprobe[4].

This study has sought to examine the geochemistry, organic content and low temperature oxidation of coal and an attempt has been made to correlate these with the coal rank and maceral type. Five SIMS techniques were used: The acquisition of bar graphs in conjunction with mass resolution of peaks to approximately one part in 2000, depth profiling and step scanning in which ion intensities are monitored while the primary beam penetrates the sample or as the sample is moved past the primary beam; finally the instrument used functions as an ion microscope, providing surface resolution as low as 1 μm.

EXPERIMENTAL

The instrument used was a Cameca IMS-3F ion microscope which has been described previously[5]. A wide variety of primary ion beams were used (Ar^+, O_2^+, O^- and Cs^+) and the primary ion current and kinetic energy were varied over a wide range.

The coals used were cut with a diamond saw perpendicular to the bedding plane and polished on a silk wheel using diamond grit with water as the only lubricant. Petrographic analysis was carried out before and after each SIMS analysis. When charging problems were encountered a 100 A gold layer was sputtered onto the surface prior to analysis.

It was found that high rank (80% carbon) coals could often be used in the SIMS instrument after air drying. Lower rank coals were often dried at 110°C while lignites sometimes required vacuum drying.

Oxidation of the coal was carried out using an atmosphere of 90% ^{18}O at temperatures from 90°C to 190°C and pressures from 0.2 to 0.5 atmospheres, though most oxidations were carried out at 100°C and 0.2 atmospheres.

RESULTS AND DISCUSSION

Bar graphs and mass resolution: The bar graph results are summarized in Figures 1-4. Figures 1 and 2 compare the positive and negative secondary ion spectra obtained for a vitrinite band with that of graphite. A series of carbyne peaks is visible in both the graphite spectra and is reflected in the coal results. The positive secondary ions are, as expected, richer in metal ions. For this reason the negative secondary ions are used primarily as a probe for organic fragments.

Fig. 3 shows the mass resolve peak at 72^-. The peak is found to consist of masses corresponding to C_6^-, TiC_2^- and FeO^-. This result raises the interesting prospect of identifying organometallic species in coal while illustrating the difficulties presented by the presence of molecular ions in the spectrum. This difficulty has been partially resolved by the use of a molecular ion suppression technique developed in this laboratory[6]. If a poorly conductive sample is allowed to change and only secondary ions of high kinetic energy are accepted at the analyzer then molecular ions are effectively eliminated from the spectrum, Fig. 4a. This result contrasts with those obtained in the normal mode (Fig. 1). This method has proved particularly valuable in oxidation studies using ^{18}O as a tracer (Fig. 4b,c).

Ion Microscopy/Line scans

Ion microscopy and line scans have been used to determine the distribution of elements between macerals and to probe the detailed geochemistry of the coal. In each of the following examples ion images were obtained from an area 150 µm in diameter and the conditions (primary beam current and film exposure time) were selected to obtain sharp, intense images so that ion concentrations and image intensity are not related in any simple way.

Fig. 5 shows the ion images obtained from a well defined fusinite fragment embedded in a surrounding vitrinite matrix. Fig. 5a is the image of carbon and clearly shows the outline of the maceral while Fig. 5b shows the relative hydrogen depletion of the fusinite. Fig. 5c shows how aluminum has been excluded from the maceral. The partitioning of elements between macerals has been observed previously[7]; Fig. 5d shows a sheath of calcium surrounding the fusinite. It is tempting to speculate that this feature is epigenetic calcium carbonate. A clear image Fig. 5e was also obtained showing the fusinite to be rich in fluorine. Fig. 6 is a step scan across the maceral indicating that it is enriched in fluorine (and to a lesser extent in oxygen). Subsequent XPS analysis confirms the presence of the fluorine-graphite compound graphite monofluoride in this region[8].

A final set of images was obtained from an exceptionally large piece of fusinite, revealing an unusually rich elemental distribution. Fig. 7, a,b and c are those of C^-, C_2^- and Mg^+ respectively. C^- and C_2^- serve to outline the organic-rich coalified material while Mg^+ serves both to emphasize the use of positive secondary ions to identify metals and negative secondaries for organics and to outline the purely inorganic material in the coal. Fig. 7d defines the areas associated with Na (and K). Fig. 7e shows that the highest oxygen yield is from the inorganic region. Fig. 7f confirms the presence of fluorine in the organic phase while Fig. 7g shows a surprising and unique distribution for calcium, which appears to be associated primarily with the organic matter. Note that calcium and fluorine are also associated to some extent with the inorganic material.

These results give direct evidence of the association of elements with mineral and/or organic phases. This area has been subject to considerable study but results remain inconclusive and the evidence that elements are held inorganically is usually circumstantial[9,10,11].

Oxidation Studies

The coal oxidation studies are summarized in Tables 1 and 2.

Table 1 presents the $^{18}O/C$ and $^{16}O/C$ ratios as functions of carbon content and, in one case, maceral type. The results for ^{18}O uptake and ^{16}O present as a function of carbon content are not surprising. They are both negatively correlated with carbon content. In fact, reasonably good linear plots can be obtained for ^{18}O uptake in vitrinite when plotted against carbon content.

Fig. 8 is the depth profile of a coal sample treated with ^{18}O and shows a gradual decline in ^{18}O with depth. Sample penetration was to a maximum depth of 10µm.

This result is atypical in that it was chosen to illustrate the role of depth profiling with SIMS. Other results have shown a much less marked decline in ^{18}O with depth.

The data for the ^{18}O uptake as a function of maceral type reported in Table 1 for coal sample 8 are surprising because the uptake is much higher in fusinite than in vitrinite whereas the fusinite would be expected to be the less reactive maceral. The simplest implication of these results is to suggest that the ^{18}O is adsorbed on the coal surface and that the effect observed is a measure of the surface area rather than the reactivity of the maceral. This hypothesis was investigated by treating coal with ^{18}O then placing it in vacuum for various periods. These results are shown in Table 2 and suggest that 90% of the ^{18}O is removed during 12 hours in vacuum. The ^{18}O would seem to have been reversibly adsorbed on the surface as part of the first step in the oxidation process.

Conclusions:

1. That SIMS is an appropriate tool for the study of coal.
2. That the elemental distribution varies significantly between macerals (though the distribution may not be unique to specific macerals).
3. That ion imaging reveals the elemental associations in the mineral matter in coal as well as inorganic/organic phases.
4. Oxygen adsorption on the coal as a function of maceral type and coal rank reveals that fusinite adsorbs oxygen more readily than vitrinite.

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TABLE 1

Coal Sample	%C	$^{18}O/C\times10^3$	$^{16}O/C\times10^2$
1 Lignite	47.86	3.0	10.0
2 Sub-bit. (vitrinite)	67.93	2.1	5.6
3 Med. Vol. Bit.	73.43	2.5	32.0
4 High Vol. Bit.	73.70	8.0×10^{-2}	1.0
5 Med. Vol. Bit.	80.84	3.5×10^{-1}	3.5
6 High Vol. Bit.	84.28	4.4×10^{-2}	6.9×10^{-1}
7 Fusinite (from 6)		5.4×10^{-1}	
8 High Vol. Bit. (Vitrinite)	84.0	6.9×10^{-2}	1.2

Various coals heated at 100°C in ^{18}O for 24 hrs. $P\,^{18}O = 0.2$ atm.

TABLE 2

a) Coal held for 60 hrs at 100°C then in vacuum at 100° for 12 hrs. High volatile bituminous coal. Sample 8.

Maceral	$^{18}O/C$ Before	$^{18}O/C$ After
Fusinite	3.36×10^{-3}	3.2×10^{-4}
Vitrinite	0.82×10^{-4}	3.4×10^{-4}
Micrinite	0.64×10^{-3}	0

b) Coal held at 100°C for 24 hrs $P\,^{18}O = 0.2$ atm then in vacuum for 6 hrs. at 23°C. Sample 6.

Maceral-	$^{18}O/C$ Before	$^{18}O/C$ After
Fusinite	5.4×10^{-4}	2.5×10^{-4}
Vitrinite	4.4×10^{-5}	3.0×10^{-5}

Figure 1

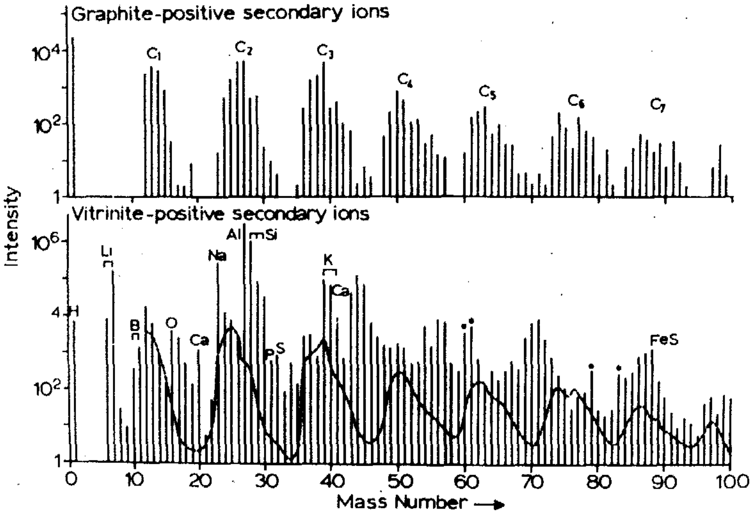

Figure 2

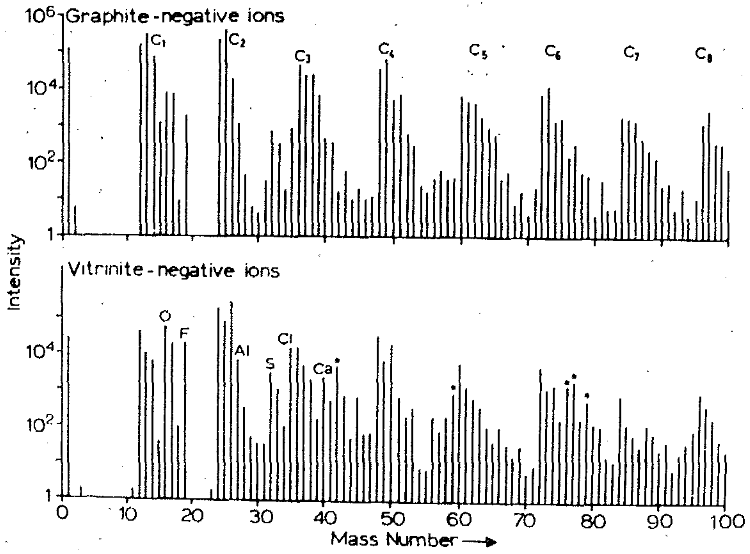

Figure 5

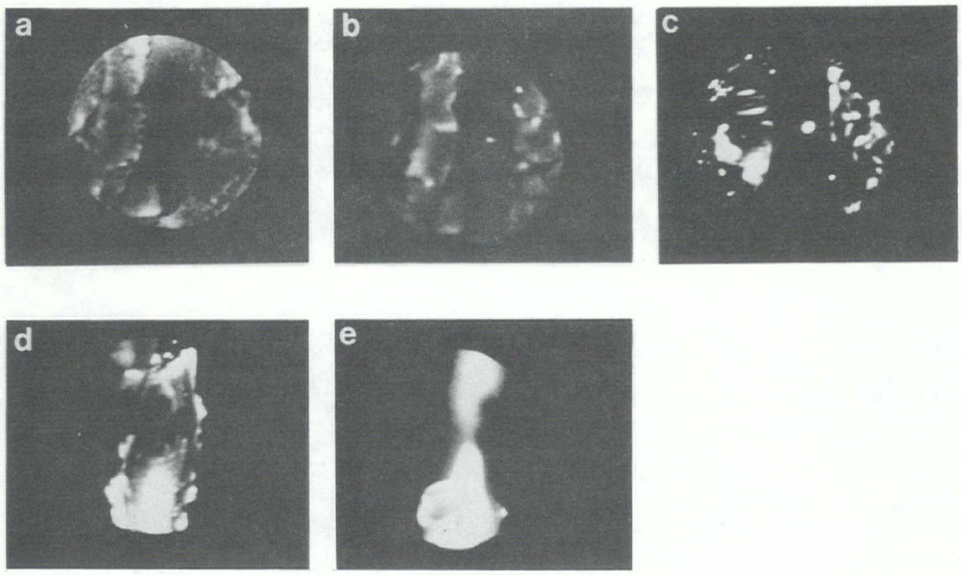

FIGURE 6

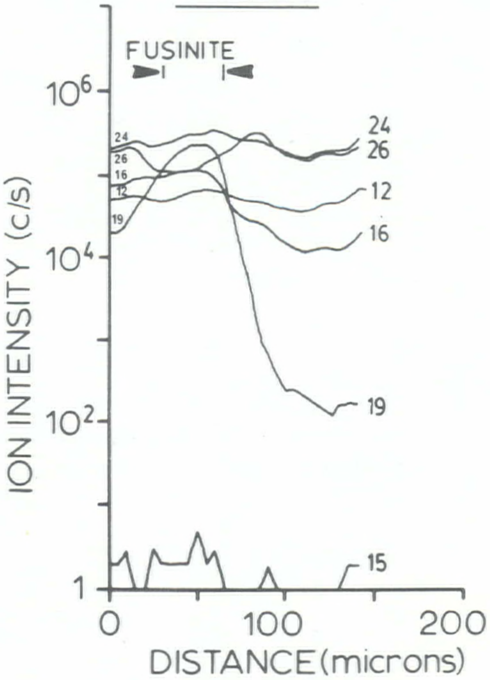

Figure 3

MASS RESOLVED PEAK AT 72 DALTONS

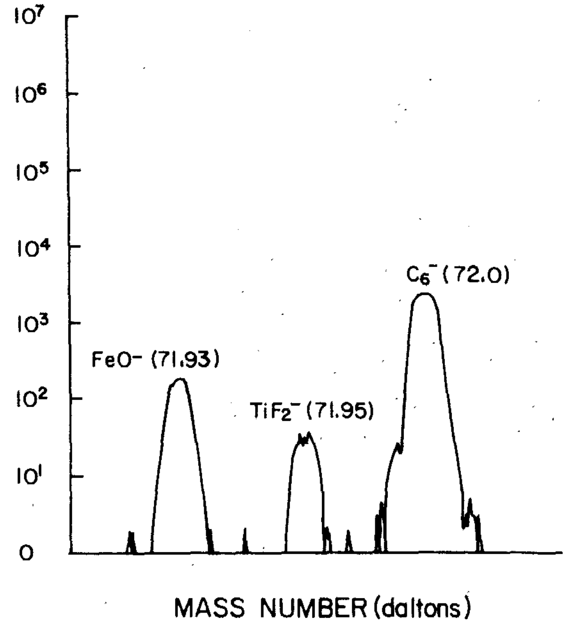

Figure 4

MASS SPECTRUM USING MOLECULAR ION SUPPRESSION

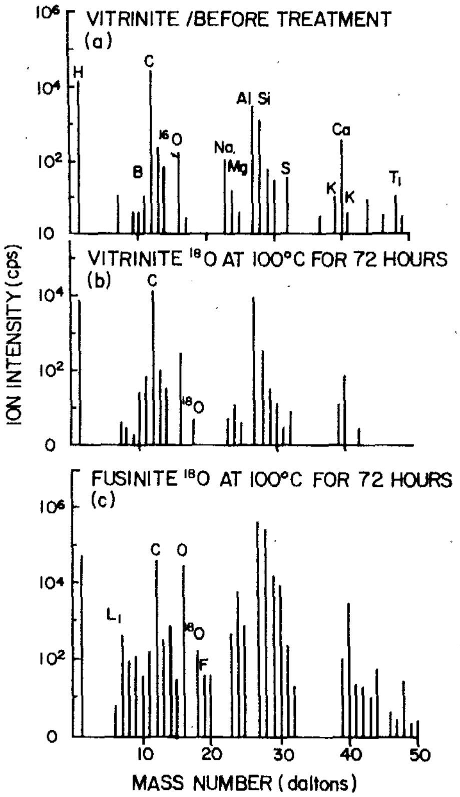

Figure 7

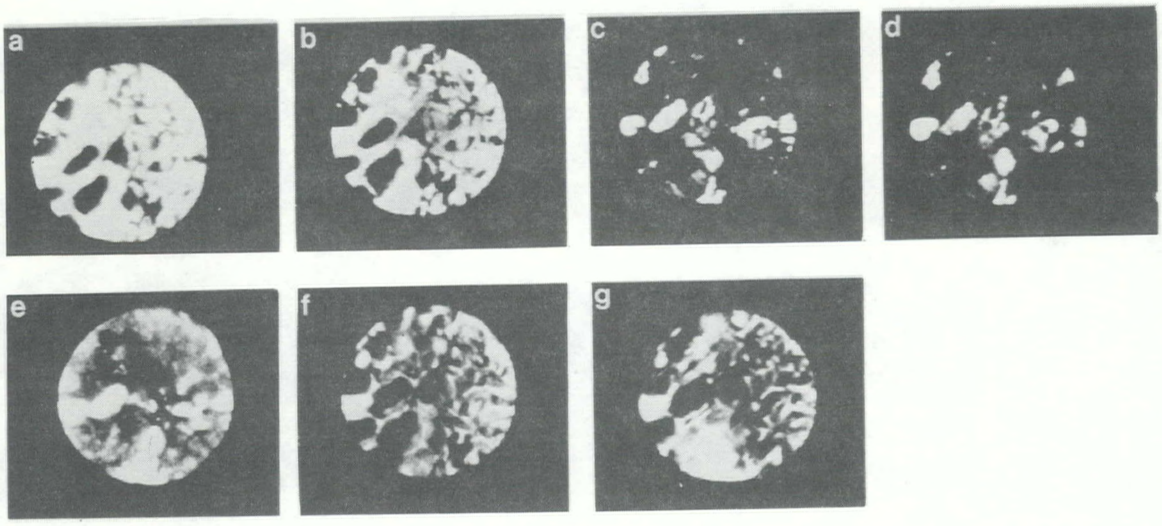

Figure 8

DEPTH PROFILE