

Scanning Transmission X-ray Microscopy: A New "Looking Glass" into Coal Chemical Structure

Robert E. Botto and George D. Cody

Chemistry Division, Argonne National Laboratory, 9700 So. Cass Ave.
Argonne, IL 60439

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Introduction

Since the early observations by Thiessen¹ and later by Stach,² who first recognized coal to be an extremely heterogeneous substance having distinguishable components that could be readily observed only with a microscope, the discipline of coal petrography has had enormous impact on the entire field of coal science. Following the realization that coal is composed of widely diverse, yet totally recognizable fossilized plant materials that have been converted into one or more macerals during coalification, coal chemists began to study the isolated maceral constituents individually. Characterization of their properties revealed that these individual constituents had chemistries as rich and diverse as the mosaic textures that had been seen for macerals microscopically, and as a result, a new level of understanding of the chemistry of coal has been attained.

Notwithstanding the enormous strides that have been made in the chemical characterization of macerals, facilitated primarily by the aid of elegant separation methods,³ there has been no direct correlation of the optical textures observed under a microscope with maceral chemistry. Moreover, an important issue still to be resolved is whether the macerals themselves are chemically homogeneous or whether there is heterogeneity on a still smaller scale.

In this paper we report, for the first time, the use of scanning transmission x-ray microscopy (STXM) to spatially map the chemistry of aromatic and aliphatic carbon functionalities in coal to a resolution of less than 0.1 μm . In addition, localized x-ray absorption spectroscopy recorded at the carbon K absorption edge have facilitated analysis of the variations in fundamental chemistry at maceral interfaces and within maceral boundaries.

Results and Discussion

Measurements were performed at the National Synchrotron Light Source at Brookhaven National Laboratory using the soft x-ray microscope facility (line X1A).^{4,5} The wavelength of the x-ray beam was selected by a spherical-grating monochromator having a bandwidth of 6 pm for a 180- μm exit slit; this corresponds to an energy band width of 0.7 eV at a photon energy of about 290 eV. The specimens were mechanically scanned under computer control, and transmitted x-rays were detected by a gas flow counter. The microscope was enclosed in a helium atmosphere and was separated from the beamline vacuum by a 120-nm silicon nitride membrane. Coal specimens were ultramicrotomed to a thickness of approximately 200 nm for analysis.

Images of three distinct regions within a microtomed thin section of hvA Pittsburgh bituminous coal (APCS No. 4) recorded at photon energies of 285.5 eV (left column) and 288.1 eV (right column) are shown in Figure 1. Chemical contrast can clearly be discerned between image pairs taken at the two energies, and this chemical specificity can be related to differences in x-ray absorption near-edge structure (XANES) cross sections of sp^2 - and sp^3 -carbon functional groups. Other features seen in the images may be due to variations in sample thickness or to regions of matter with different densities; however, these can easily be distinguished from chemical variations by the lack of contrast reversal between image pairs.

Two fundamental types of features can be readily distinguished within the top pair of micrographs shown in Figure 1. The narrow feature running from the top left to lower right portion of the image exhibits high absorptivity at 288.1 eV (sp^3 -absorption band) and correspondingly little absorptivity at 285.5 eV (sp^2 -absorption band). This response is typical of highly aliphatic material, and taken together with the morphology of this feature, suggests that it may be the maceral cutinite embedded within a more highly aromatic, or vitrinite, matrix. The diagonal stripes that traverse the image in the opposite direction show no contrast reversal, hence are likely to be scoring marks made by the microtome blade.

The middle two micrographs contain structures that exhibit somewhat different behavior. Two large elliptical bodies are evident which show lower absorptivity in the 285.5 eV image than the surrounding material; however, very little image contrast is observed at an energy of 288.1 eV. The contrast seen in the image recorded at the sp^2 absorption energy suggests that the elliptical bodies contain more highly aliphatic material than the surrounding regions, and given this difference in chemistry, lack of contrast in the sp^3 image implies that these domains contain less dense material as well. The morphology and chemistry suggests that these elliptical regions are microspores. Within the upper microspore, a small x-ray

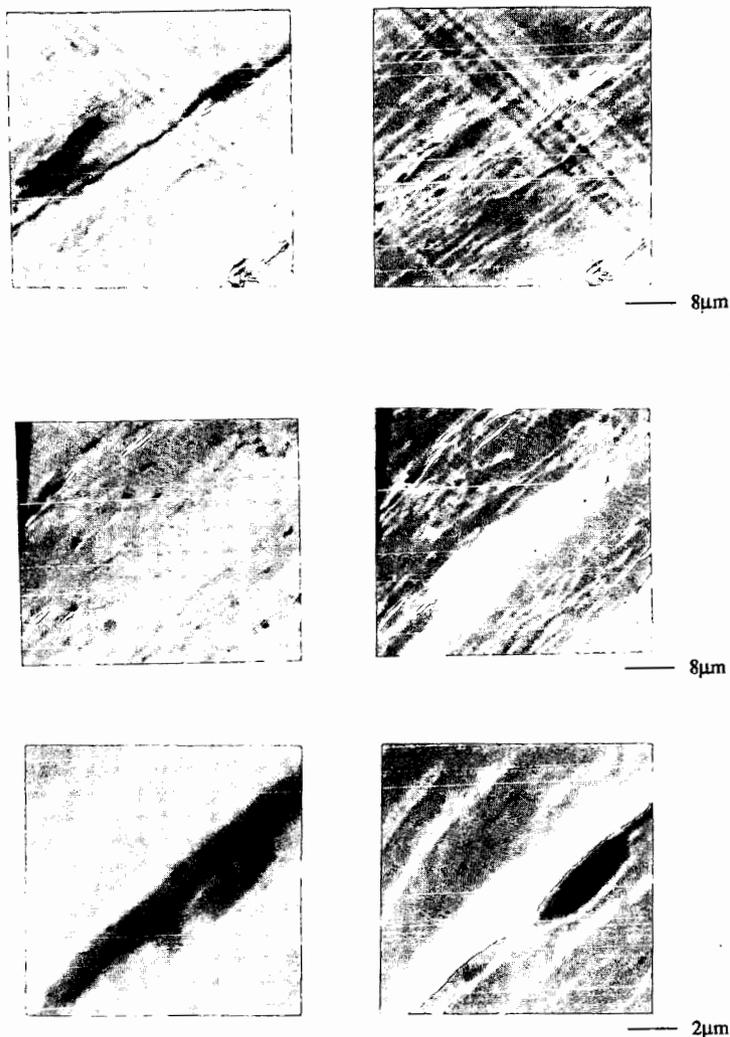


Figure 1. Scanning transmission x-ray micrographs of three regions within a 200-nm microtomed section of hvA Pittsburgh bituminous coal (APCS No. 4) recorded at photon energies of 285.5 eV (sp^2 absorption) and 288.1 eV (sp^3 absorption) at the carbon K-edge.

transparent region is observed whose sp^3 -absorption image contrast is reversed, clearly demonstrating intramaceral heterogeneity. Other aliphatic structures are also observed in the lower portion of the micrograph. The morphology of the thin sinuous feature at the lower right is suggestive of the maceral, cutinite. Bright features clearly visible at both energies are cracks which formed as a result of microtoming the sample.

The lower two micrographs represent an expanded view of a cutinite band similar to that represented in the first images above. The cusp found near the center provides additional support for the assignment that this maceral is cutinite. The dark pod that appears at the right of the cutinite band exhibits high absorptivity at both energies; upon careful inspection, several similar structures may be identified in the top pair of micrographs as well.

In order to elucidate the chemistry of the features seen in the lower micrographs, microfocus XANES spectra were taken at various points within individual structures. Figure 2 shows XANES spectra that were taken within regions of the cutinite band, the dark pod and surrounding vitrinite. It should be noted that the spectra are not totally quantitative, especially at the higher energies, due to high absorptivity of the specimens. These effects

also limit chemical contrast in images taken at the higher energy. The cutinite spectrum exhibits a strong absorption at 288.1 eV and a relatively weak absorption centered at 285.5 eV, which is consistent with its aliphatic nature. On the other hand, XANES spectra of the dark pod and surrounding vitrinite show intense sp^2 absorptions. The relative intensity ratios between sp^2 - and sp^3 - absorption bands in both spectra are also remarkably similar. This implies that the unknown pod structure must be composed of a denser material but is similar in chemical composition to the surrounding vitrinite.

Reflected light microscopic (ROM) analysis of the same sample using standard immersion oil techniques lends support to the assignment of vitrinite, cutinite, and microspores by STXM. Vitrinite and cutinite macerals are abundant in this coal; however, the assignment of microspores is somewhat more tenuous. ROM reveals some microspore structures having elliptical cross-sections with dimensions in the micron range. Moreover, no other potential candidates in this size range and with these morphologies were observed. Consequently, the assignment of microspores to the aliphatic entities shown in the middle micrographs is certainly reasonable.

The ability of STXM to map the chemical composition to this resolution has provided rich detail into the chemical and physical heterogeneity of a coal (APCS No. 4) regarded as being reasonably homogeneous, i.e., containing about 85% vitrinite. However, the variety of textures seen are not limited to those presented in this preliminary report. Vitrinite regions having subtle chemical differences, morphologically different exinite bodies, and microfine mineral particles and veins have also been observed and will be discussed. Recent studies toward the characterization of other Argonne Premium coals and results extending present capabilities to include STXM at the oxygen and calcium K-absorption edges will also be discussed.

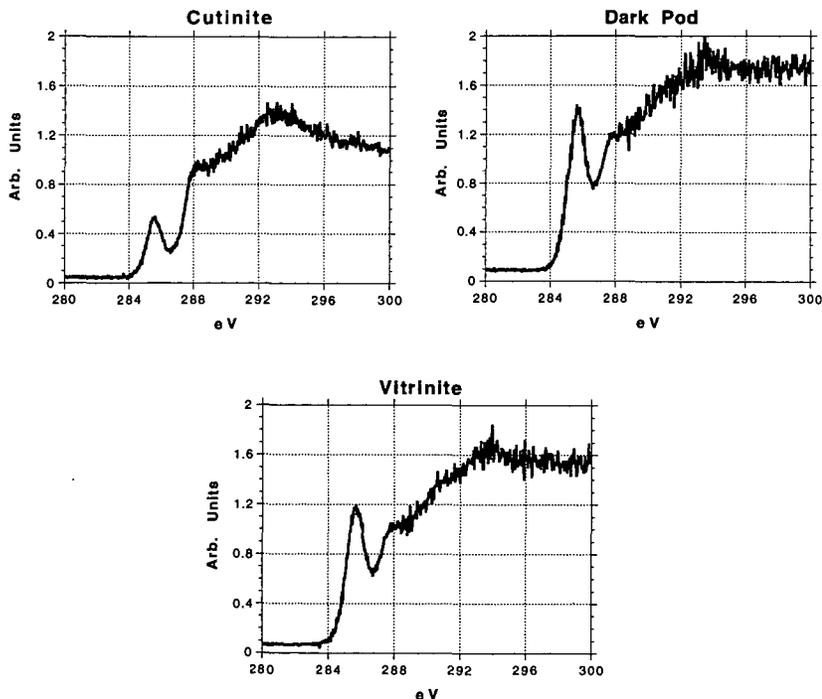


Figure 2. Carbon K-edge XANES spectra of selected regions within (A) the cutinite band, (B) the dark pod and (C) surrounding vitrinite that are identified (see text) in the lower micrographs of Figure 1.

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