

## Application of XAFS spectroscopy to coal geochemistry

FRANK E. HUGGINS and GERALD P. HUFFMAN

Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506, U.S.A.

**Abstract**—Elements in coal can be found in various geochemical forms (modes of occurrence) that vary from elements covalently bound to the organic matrix to elements that form discrete minerals. Such wide variation in the modes of occurrence presents a significant challenge to a full understanding of the geochemistry and utilization behavior of elements in coal. The application of X-ray absorption fine structure (XAFS) spectroscopy for determining elemental modes of occurrence in U.S. coals is reviewed. The elements discussed are from the first transition-series row of the periodic table (K–Br) and vary in concentration from major elements such as calcium to trace elements such as selenium, as well as varying from alkali metals to halogens in their geochemical behavior. Although more data are needed, this work establishes that many elements occur in coal in two or more distinct forms: one is basically mineralogic; the other is an organic association that involves direct bonding with the macerals, most commonly via oxygen functional groups. This latter mode of occurrence is more prevalent in low-rank coals, but persists for many elements in coals of rank at least as high as high-volatile B bituminous. Formation of discrete minerals appears to be relatively uncommon for first transition-series row elements of trace abundance; they are more likely to be incorporated in illite or pyrite, depending on whether they are lithophilic or chalcophilic.

### INTRODUCTION

ROGER BURNS was largely responsible for demonstrating to the geoscience community the potential of spectroscopic techniques for resolving significant problems in mineralogy and geochemistry and for bringing such methods into the main-stream of research in Earth Sciences. The techniques he pioneered in the 1960s, electronic absorption spectroscopy (BURNS, 1965, 1970) and Mössbauer spectroscopy (in conjunction with G. M. Bancroft), provided mineralogists with the capability to focus on the behavior and properties of specific elements in minerals, a capability lacking in the traditional petrographic and crystallographic methods that had dominated mineralogy up to that time. In addition, this ability to focus on individual elements also forged a link to traditional geochemistry, and ever since the distinctions between the disciplines of crystallography, mineralogy, geochemistry, and petrography have been less apparent. In particular, Roger Burns was able to provide much valuable crystallochemical insight into the behavior of the specific elements in the first series of transition elements (Ti–Cu) in not only specific silicate and sulfide structures, but also in broader petrological and geochemical systems (BURNS, 1970).

Now, some twenty-five years later, spectroscopy-based papers make up significant, sometimes major portions of geoscience journals. Although the spectroscopic techniques and problems have changed to some extent, the goal of such investigations remains the same as that in much of Roger Burns' work: to understand better the behavior of

specific elements in earth science materials. With this goal in mind, we present a review of results relevant to the geochemistry of first transition-series row (K–Br) elements in coal obtained principally from X-ray absorption fine structure (XAFS) spectroscopy. Application of this method for element speciation in coal was pioneered in the early 1980s (MAYLOTTE *et al.*, 1981a, 1981b; SANDSTROM *et al.*, 1982; WONG *et al.*, 1983; HUGGINS *et al.*, 1983b). More recently, the impetus for such investigations has come from research related to potential environmental issues arising from the behavior of minor and trace elements in coal combustion (SWAINE, 1990; CLARKE and SLOSS, 1992) that may be subject to regulation under Title III of the 1990 Clean Air Act Amendments (CAAA, 1990) in the U.S. and similar legislation in other countries.

Coal is a difficult material with which to investigate the occurrence of minor and trace elements because it is composed of two dissimilar major components: the organic fraction and the mineral fraction. Consequently, there is a variety of possible occurrences for how a given element may be found in coal. Furthermore, elements tend to be dispersed at relatively low concentrations in the organic fraction, but to be much more localized and concentrated in mineralogical occurrences. Hence, determining the mode of occurrence of a specific minor element in coal can be a challenging problem just because of the diversity of the possible modes of occurrence.

As discussed in detail elsewhere (HUGGINS *et al.*, 1994a; HUGGINS and HUFFMAN, 1996), there are a

number of methods for determining the mode of occurrence of an element in coal. These vary from indirect methods based on how the element partitions in a particular test on the coal, such as float/sink testing, successive leaching by different solutions, or ashing at different temperatures, to direct microscopic or spectroscopic methods. The electron microscope and various microprobe methods are well suited for mineralogical occurrences in which the element is significantly enriched above its overall concentration in the coal, but are not so good for occurrences in which the trace element is widely distributed at relatively low concentrations throughout the organic matrix. Element-specific spectroscopic techniques, such as the synchrotron-based technique of XAFS spectroscopy, are not limited in this regard.

XAFS spectroscopy can provide information on specific elements in coal regardless of the mode of occurrence because it is more or less equally sensitive to both highly dispersed and discrete mineralogical occurrences of an element. Furthermore, it has excellent sensitivity, and is capable of providing useful information relevant to the mode of occurrence of elements in the middle of the periodic table (K–Mo) at concentrations as low as 5 ppm (HUGGINS *et al.*, 1993a). The main drawbacks of the technique are that (i) only a single spectrum is obtained that represents the weighted sum of all the element occurrences, and (ii) the need for a synchrotron as a high intensity source of X rays. In this review, we will summarize the geochemical implications of results obtained from XAFS spectroscopy applied to the determination of the mode of occurrence of specific elements in coal.

#### BACKGROUND ON MODES OF OCCURRENCE OF ELEMENTS IN COAL

As mentioned above, coal consists of two distinct components: the combustible organic matter and the noncombustible mineral matter. The organic fraction of coal is derived from plant residues accumulated in peat swamps that have undergone low-grade metamorphism (coalification). During this process, the plant-derived organic material is converted into carbon-rich entities that are known collectively as macerals (STACH *et al.*, 1975). Based on their optical properties, the macerals can be subdivided further into individual types, such as vitrinite, liptinite, fusinite, *etc.*; these components in coal are approximately analogous to the individual minerals in a rock. Elements can be covalently bound in the organic carbon matrix, in heterocyclic or other organic functional groups, or even as porphyrin structures (BONNETT *et al.*, 1987), or they may be present as ions associated with polar organic functional groups. In addition, coal usually contains a significant fraction of minerals, the so-called mineral matter or "ash" fraction, which generally consists of some combination of quartz, clays, carbonates, and sulfides (STACH

*et al.*, 1975). A minor or trace element in coal may be associated with one or more of these major minerals or it may form a discrete accessory mineral (defined as a minor mineral which would not exist except for the essential presence of the minor or trace element). Finally, there may also be a significant aqueous phase in coal that is largely associated with the pores and capillaries in the macerals. Depending on rank, the moisture content of coal can vary from as much as 65% in brown coal to less than 1% in anthracites (STACH *et al.*, 1975). Often, such moisture will contain significant amounts of soluble elements. Hence, as summarized in Fig. 1, the forms or modes of occurrence of elements in coal can run the gamut from highly dispersed, covalently-bound elements in the macerals to substitutional replacement in minerals, or to hydrated cations dissolved in the coal moisture.

Not only is coal heterogeneous with respect to the types of elemental occurrences present in coal, it is also heterogeneous with respect to distribution of these entities in the seam in both a vertical and horizontal sense. A coal seam is basically a sedimentary formation, and in a vertical (time) direction, there are clearly distinguishable layers on a variety of scales, both macroscopic and microscopic, reflecting different ratios of the macerals relative to the minerals, variation in sulfur content, and so on (STACH *et al.*, 1975). The chemistry of the individual layers will change in a horizontal direction, reflecting changes in the environment of deposition (*e.g.*, whether freshwater or brackish) and changes in distances to the sources of the different components in the original peat. In addition, these layers may also thin out or thicken as the distances to these sources change. Furthermore, there can be differences across the seam in terms of rank, reflecting regional or sometimes local variation in the geological conditions. The net result of these trends is that coal can be a highly variable material and that each sample of coal tends to be unique. Hence, extrapolation from results on a given sample to broader local or even regional conclusions for the coal seam must be approached conservatively.

The modes of occurrence of an element in different coals can be expected to reflect differences in both the rank and chemistry of the coals. Although probably of lesser significance, factors prevalent at the time of formation of the original peat swamp, such as the type of peat deposit, climate, *etc.*, may also be reflected in the mode of occurrence. Another factor that can be important in determining the mode of occurrence of an element in coal is weathering of the coal as a result of its exposure to air at an outcrop. The weathering zone associated with an outcrop can extend many meters back into the seam and the mineral and maceral constitution of the coal in this zone may become highly altered. Such alteration may promote the formation of unusual elemental forms (HUGGINS and HUFFMAN, 1989). Finally, one further factor that can also influence the mode of occurrence of an element is alteration of the coal sample after collection. Exposure of a pulverized sample to air promotes both drying of the coal and oxidation of principally mineral forms, especially sulfide minerals. Both of these phenomena have been demonstrated to alter the modes of occurrence of certain elements such as arsenic (HUGGINS *et al.*, 1993a) and chlorine (HUGGINS and HUFFMAN, 1995).

#### EXPERIMENTAL OVERVIEW

##### *XAFS spectroscopy*

XAFS spectroscopy is basically a measurement of the variation (or fine structure) of the X-ray absorption coef-

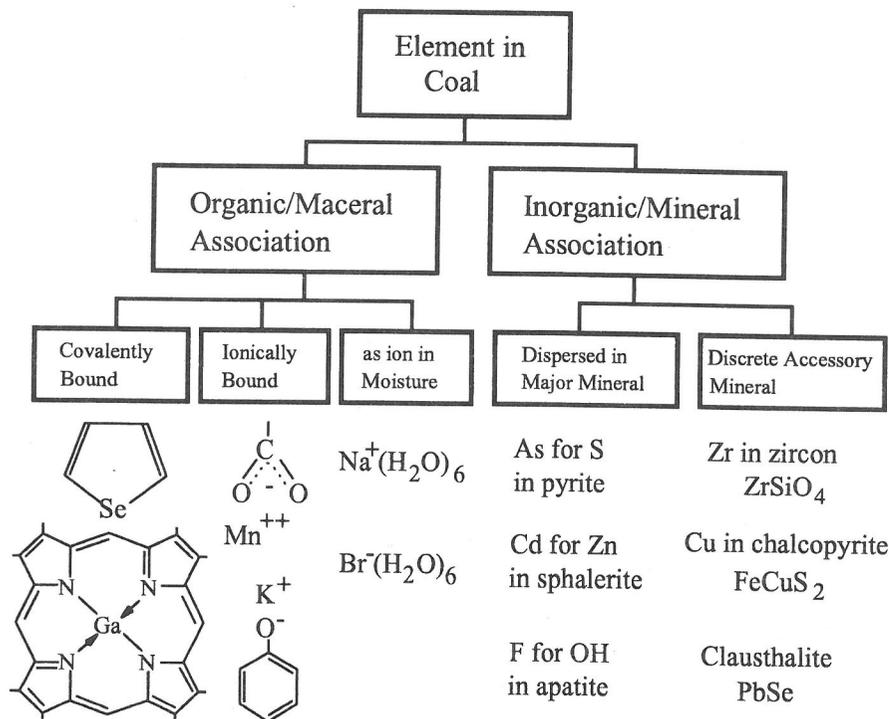


FIG. 1. Classification scheme for modes of occurrence of elements in coal.

ficient with energy associated with one of the characteristic absorption edges of the absorbing element. The XAFS spectrum is normally divided into two distinct regions for analysis: the X-ray absorption near-edge structure (XANES) region and the extended X-ray absorption fine structure (EXAFS) region. As these names imply, these regions incorporate the fine structure in the vicinity of the edge itself and further away from the edge, respectively (Fig. 2). Quite different analysis is done for each

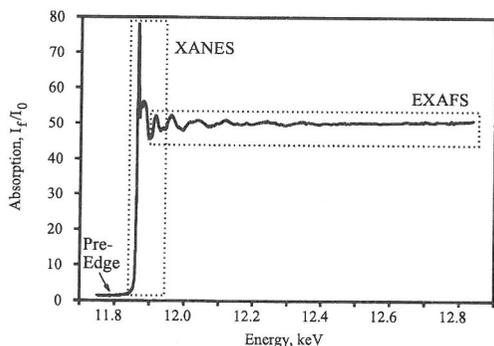


FIG. 2. Arsenic XAFS spectrum of arsenical pyrite, showing arbitrary division of spectrum into separate near-edge (XANES) and extended fine-structure (EXAFS) regions.

region of the spectrum. The XANES spectrum is used, without significant modification, as a "fingerprint" for the element in the material under investigation, whereas the EXAFS region can be extensively mathematically manipulated to obtain information on the short-range local structure around the absorbing atom or ion.

Owing to the low abundance of trace and minor elements, XAFS investigations of such elements in coal must be undertaken at a synchrotron radiation facility, where the X-ray flux is some 6 to 9 orders of magnitude greater than that available with a conventional laboratory X-ray tube. In the U.S., the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY, and the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University, CA are the best facilities currently available for XAFS spectroscopy of dilute species. All of the data discussed in this review were obtained at these two facilities.

Synchrotron radiation is produced by electron (or positron) storage rings in which highly energetic particle beams are "stored" in a stable orbit in an ultrahigh vacuum ( $10^{-9}$  torr). The particle beam in the storage ring emits synchrotron radiation as a consequence of the principle of conservation of momentum when the charged particles, moving at velocities very near to that of light, are forced to change direction through the application of a magnetic field normal to the path of the particle beam. This synchrotron radiation is a broad "white" radiation that is emitted tangentially to the orbit of the charged particles. It is then collimated by a series of slits and/or mirrors and delivered to an experimental beam-line sta-

tion. For XAFS experiments, a monochromatic beam is required rather than white radiation, so a monochromator or grating is inserted into the white beam to select a specific energy that is determined by the spacing of the reflection planes of the monochromator crystal or grating, the angle of the monochromator with respect to the beam, and application of Bragg's law. There are usually additional slits and focussing mirrors between the monochromator and the exit of the beam in the experimental hutch.

To generate an XAFS spectrum, the absorption by the sample is measured as a function of the monochromator angle or, equivalently, the energy of the incident X-ray beam. Although there exists a quick scanning XAFS method (QEXAFS) that records the spectrum continuously as the monochromator rotates (FRAHM, 1992), most XAFS spectra are still recorded in a discrete manner by stepping across an energy interval that includes an X-ray absorption edge of the element of interest. Typically, the energy interval may start as much as 100–200 eV below the edge and extend as much as 1000–1500 eV above the edge. However, the stepping will not be uniform across the energy interval but will be subdivided into at least three regions (the pre-edge, XANES, and EXAFS regions; *q.v.* Fig. 2) so as to maximize the information quality and thereby facilitate the data analysis. For the pre-edge region (from –200 eV to around –20 eV below the edge), which contains no spectral information but has to be measured in order to determine the pre-edge slope, the stepping is generally coarse with a short time/step. The edge or XANES region, which for trace elements often contains much, if not all, of the useful information, is then measured very carefully and slowly (0.1–0.25 eV/step with a longer time/step) from about –20 eV below the edge to as much as +50 eV above the edge. The EXAFS region is then measured out to at least +250 eV up to as much as +1500 eV above the edge, depending on the strength of the EXAFS oscillations or chi signal. The stepping across the EXAFS region is usually now done in terms of reciprocal-space inverse distance (*e.g.*, 0.05 Å<sup>-1</sup>/step) with the time per step determined by the actual interval in real space. This procedure gives a more uniform appearance to the chi vs. k spectrum, which, after application of a Fourier transform, results in a better quality radial structure function (RSF) spectrum.

The XAFS spectrum can be acquired by one of three different methods, depending on the concentration of the element under investigation. For standard samples or for samples in which the element of interest comprises more than about 5 wt% of a reasonably X-ray transparent material such as coal, the XAFS spectrum is best measured in absorption geometry (Fig. 3) by measurement of the X-ray intensity before and after absorption by the sample. Such measurements are made with simple ion chambers. The relationship between the X-ray intensity and the absorption coefficient ( $\mu(E)$ ) is as follows:

$$I_t = I_0 \exp(-\mu t) \quad (1)$$

where  $I_0$  is the intensity of the X-ray beam incident on the sample,  $I_t$  is the intensity of the X-ray beam after transmittance through the sample, and  $t$  is the thickness of the sample. The thickness of the sample is invariant; hence, any variation in  $\ln(I_0/I_t)$  with energy is directly equivalent to variation in the absorption coefficient. For samples with elements of interest with concentrations ranging from 0.1 to 5 wt%, it is better practice to measure the spectrum in fluorescence geometry. In this experiment, the intensity of the X rays fluoresced by the sample

in response to the absorption process is measured. Typically, a large solid angle ion chamber fluorescence detector (STERN and HEALD, 1979; LYTLE *et al.*, 1984) is located at 90° to the incident X-ray beam with the sample turned to 45° with respect to both the detector and the incident beam (Fig. 3). In this case, the relationship between the fluorescent X-ray intensity ( $I_f$ ) and the absorption coefficient is as follows:

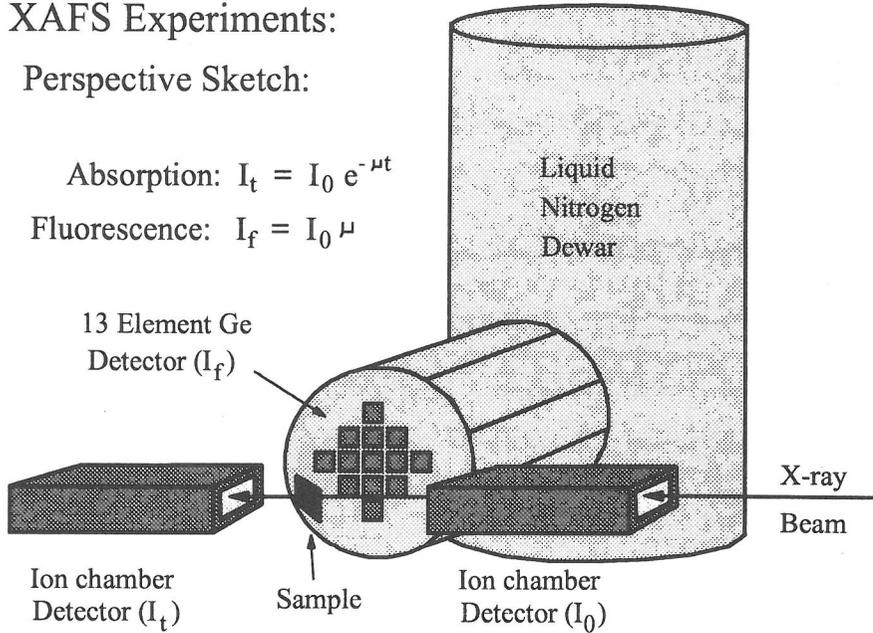
$$I_f = I_0 \mu(E) \quad (2)$$

It should be noted that this equation is only exact in the limit that the sample is thin and/or the element of interest is sufficiently dilute not to give rise to self-absorption phenomena. However, if the element of interest is of trace abundance only (5–500 ppm), the background fluorescent X-ray intensity from other elements will overwhelm the fluorescence signal from the desired element. At this point, the ion chamber should be replaced by a thirteen-element, solid-state germanium detector that has been optimized for the measurement of the XAFS spectra of dilute elements in materials (CRAMER *et al.*, 1988). This type of detector counts X rays only in a narrow energy window set specifically for the X rays fluoresced by the element of interest and thereby rejects most of the X rays fluoresced by other elements. This signal selection process can greatly enhance the signal/noise ratio. However, care must be taken to avoid count-rate saturation effects with this type of detector when the signal is reasonably strong. This can be achieved by simply moving the detector away from the sample or by increasing the filter thickness. Use of the appropriate filters and Soller slits (STERN and HEALD, 1979) will also enhance the signal/noise ratio with either fluorescent detection method (Fig. 3). Finally, for exceedingly dilute concentrations (<100 ppm), the spectra can be repetitively scanned and added together to obtain a composite spectrum of better quality.

Analysis of experimental XAFS data consists of the following steps: (i) isolation of the EXAFS from the edge step, (ii) conversion of the energy scale to reciprocal space (k-space) inverse dimensions, generating the "chi vs. k" spectrum, and (iii) application of a Fourier transform to the chi spectrum to create a radial structure function (RSF) that describes the position and coordination number of atomic shells that surround the absorbing atom or ion. These techniques and procedures are well described in reviews and textbooks on XAFS spectroscopy (EISENBERGER and KINCAID, 1978; LEE *et al.*, 1981; KONINGSBERGER and PRINS, 1988; BROWN *et al.*, 1988). Unfortunately, analysis of the EXAFS region for trace elements in coal generally becomes uninformative as the element's concentration decreases below about 50 ppm because the relatively weak EXAFS oscillations get lost in the background noise. Hence, much reliance is placed on interpretation of the XANES region for elements in coal that are in the concentration range 5 to 50 ppm. Generally, the interpretation of elemental modes of occurrence from just the XANES spectrum relies primarily upon comparison with standards. However, more creative measures are often needed if the element occurs in two or more distinct forms. Such measures may also have to be applied because of natural-world phenomena such as diadochy (solid solution), polymorphism in mineral systems, small-particle phenomena, *etc.*, that can cause the appearance of the XANES spectrum to vary from that of a particular bulk standard. Specific measures may include (i) comparison of derivative XANES spectra; (ii) comparison with XANES spectra from different but chemically similar elements; (iii) subdivision

## XAFS Experiments:

## Perspective Sketch:



## Top View:

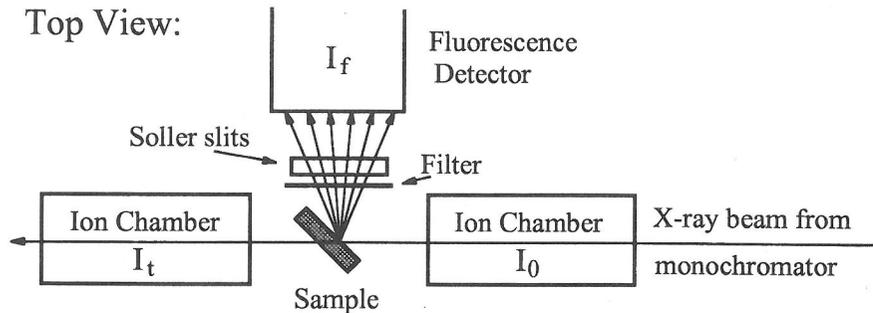


FIG. 3. Simplified schematic of experimental arrangement for X-ray absorption spectroscopy. Both absorption and fluorescent experimental geometries are indicated.

of the coal into different fractions to separate or concentrate different forms of occurrence; (iv) simulation of spectra from weighted additions of XANES spectra of standards and/or coals or coal fractions. Examples of these procedures applied to the interpretation of XANES spectra of minor and trace elements in coal are described elsewhere (HUGGINS and HUFFMAN, 1996).

#### Coal samples

Preparation of coal samples for XAFS analysis is not complicated except, as in any coal analysis, to ensure that the analyzed sample is representative of the bulk sample by following standard procedures for subdividing and pulverizing the collected sample (ASTM, 1976). At the synchrotron, the volume of coal sampled by the X-ray beam is estimated to be between about 0.01 and 0.1 cm<sup>3</sup>, depending on the X-ray energy. To sample at least 10,000 particles in the minimum volume requires that the mean

particle size of the coal be reduced to about 100  $\mu\text{m}$ . Hence, size reduction of the divided sample to pass at least a -150 mesh sieve (100  $\mu\text{m}$  top-size) should satisfy this requirement.

To measure the XAFS spectrum of a pulverized coal sample, the coal is generally suspended in the X-ray beam in a plastic bag made of ultrathin ( $\approx 6 \mu\text{m}$ ) polypropylene or in the form of a pellet made by pressing the coal into the surface of a boric acid ( $\text{HBO}_3$ ) pellet of 2.5 cm diameter. Generally all XAFS spectra of elements in coal are measured in fluorescence geometry.

XAFS data for a wide variety of coal samples are to be discussed in this review and space only permits the briefest description of the coals to be made. Most of the coals originate from deposits in various U.S. states. Their rank varies from lignite (lig), through subbituminous (sbb), and the various subdivisions of bituminous coal: high volatile C, B, and A (hvCb, hvBb, hvAb), medium volatile (mvb), and low volatile (lvb), to anthracite

(anthr). In this paper, only the seam name, state of origin, rank, and appropriate elemental concentration will be supplied. Further details can be found in the original publications. Table 1 lists the elements across the first transition-metal row of the periodic table and data on the range and average concentration of each element extracted from the compilation of over 12,000 U.S. coal analyses (COALQUAL database) recently published by the U.S. Geological Survey (BRAGG *et al.*, 1994).

### MODES OF OCCURRENCE OF ELEMENTS IN COAL

#### Potassium

The concentration of potassium in U.S. coals is generally in the range 120 to 5,000 ppm (Table 1), with a tendency to be higher in high-rank (bituminous, anthracite) coals than in low-rank (lignite, subbituminous) coals. XAFS studies of potassium in bituminous coals (SPIRO *et al.*, 1986, HUFFMAN *et al.*, 1986) indicate that much, if not all, of the potassium in such coals is associated with the clay mineral, illite. Illite and the closely related mica minerals, muscovite and biotite, exhibit similar yet distinctive potassium XAFS spectra that are mirrored by potassium XAFS spectra of bituminous coals (Fig. 4). The spectrum of a Pennsylvania anthracite reported by SPIRO *et al.* (1986) is closely similar to the muscovite spectrum shown in Fig. 4.

The small but prominent peak at about 12–15 eV above the potassium K-edge appears to reflect the crystallinity of the layer-silicate mineral and SPIRO *et al.* (1986) suggested that the rank of the coal might be estimated from this particular spectral feature.

The potassium XANES spectra of two low-rank coals from the western U.S. were found (SPIRO *et al.*, 1986) to be quite different from those of the bituminous coals. The reported spectra were very similar to that shown for the K-ion-exchanged lignite in Fig. 4. This particular spectrum was obtained from a lignite after exposure of it to a 0.2M solution of K<sup>+</sup> ions, which promotes exchange of the K<sup>+</sup> ions for carboxyl-bound Ca<sup>2+</sup> and Na<sup>+</sup> cations originally present in the lignite. Hence, it is clear that potassium in certain low-rank coals can have a quite different mode of occurrence to that in bituminous coals. However, further work needs to be done to document the significance of this form of potassium in low-rank coals as illite and other K-bearing silicate minerals have been routinely noted as being present in coals of all ranks.

#### Calcium

Calcium is generally the most abundant non-acidic element in low-rank coals and may contrib-

Table 1. Average Concentration, 90% Range, and Maximum Concentration in ppm for First Transition Row Elements in U.S. Coals Extracted from Analyses Compiled in the NCRDS COALQUAL Database.\*

Element	5% percentile	Mean (90% range)	95% percentile	Maximum
K	120	1450	5000	14000
Ca	420	3550	15000	71000
Sc	0.9	3.4	8	37
Ti	160	710	1800	9400
V	4.3	20	52	330
Cr	2.0	13	33	200
Mn	3.5	30	150	2500
Fe	1400	12000	40000	140000
Co	0.8	5.2	15	180
Ni	1.7	13	40	280
Cu	3.7	15	39	280
Zn	2.5	17	75	51000
Ga	1.25	5.2	12.5	41
Ge	0.22	4.3	20	220
As	0.7	16	100	2200
Se	0.4	2.6	7.5	150
Br	1.0	16	58	160

\*Source of data: BRAGG *et al.* (1994).

Number of coal analyses included in range and average calculations varies from a minimum of 4,855 for bromine to over 7,400.

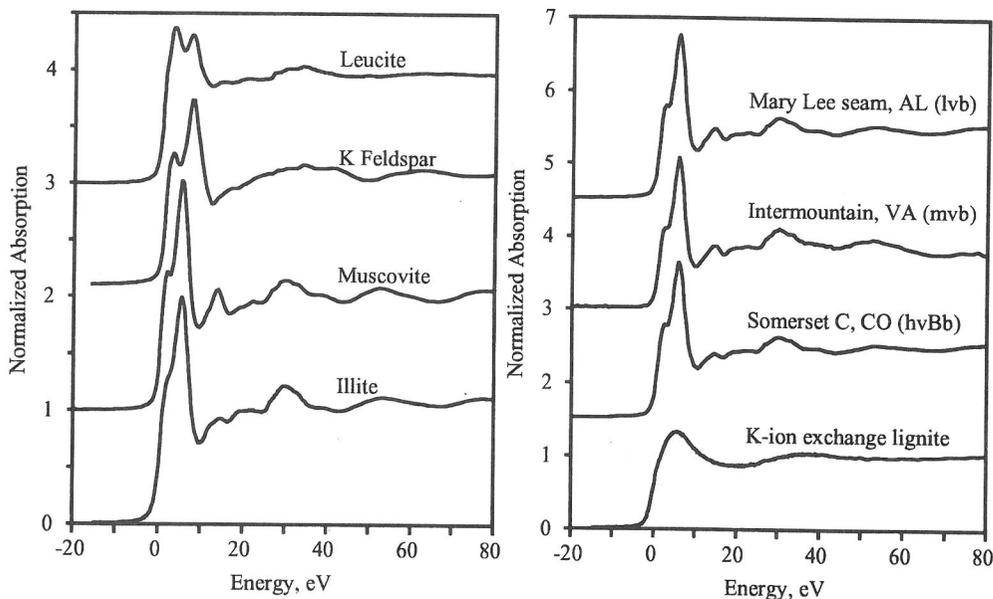


FIG. 4. Potassium XANES spectra of various mineral standards and of coals of different rank. Zero point of energy for potassium K absorption edge is 3,608.4 eV.

ute as much as 40% by weight (as oxide) to the ash of a lignite or a subbituminous coal. In high-rank coals, calcium is often much less significant. Hence, the concentration range for calcium in U.S. coals is broad, varying from as little as 400 ppm to as much as 15,000 ppm. The XAFS spectra of calcium in coal show significant variation with rank. As shown in Fig. 5, low-rank coals exhibit calcium XAFS spectra that are distinctive from those of bituminous coals. Such spectra are similar to the spectra of calcium salts of carboxylic acids, (*q.v.* the spectrum for Ca oxalate in Fig. 5) whereas spectra of high-rank bituminous coals show evidence for calcium as carbonate (HUGGINS *et al.*, 1983b; HUFFMAN and HUGGINS, 1984). Coals of intermediate rank (*e.g.* Illinois #6 in Fig. 5) can often be simulated as the sum of a carbonate component and a carboxyl component (HUFFMAN and HUGGINS, 1984). From analysis of the EXAFS region, the Ca-O bond distance and coordination number for the carboxyl-bound calcium were established as  $2.40 \pm 0.02 \text{ \AA}$  and 6, respectively, and it was speculated that at least some of the molecules around carboxyl-bound calcium were water molecules (HUGGINS *et al.*, 1983b).

It has also been demonstrated (HUGGINS *et al.*, 1983a) that extremely weathered bituminous coals can become significantly enriched in calcium, much of which appears to be present as carboxyl-

bound calcium, based on the similarity of the Ca XANES spectrum of the outcrop sample from the Lower Kittanning seam, PA, shown in Fig. 6, in comparison to those shown in Fig. 5 for low-rank coals and Ca carboxylate standards (*e.g.*, the spectrum for Ca oxalate). This carboxyl-bound calcium form in weathered bituminous coal may be derived partly from dissolution of calcite in the original coal, but it is also likely that  $\text{Ca}^{2+}$  ions in ground-water are captured by ion-exchange processes once carboxyl sites are formed in the weathered coal macerals.

#### Titanium

As a result of concerns expressed in the late 1970s regarding the possible poisoning of catalysts by titanium during coal liquefaction, XAFS investigations at the titanium K-edge (SANDSTROM *et al.* 1982; and WONG *et al.* 1983) were among the first to be carried out on coal. These early studies indicated the presence of two different major titanium forms in coal, one mineralogical, the other associated with the organic fraction of the coal. The more recent work to be discussed here is largely in agreement with such findings and has resolved the mineralogical forms better.

Titanium is a significant minor element in coal and is usually present in the range 150 to 2,000

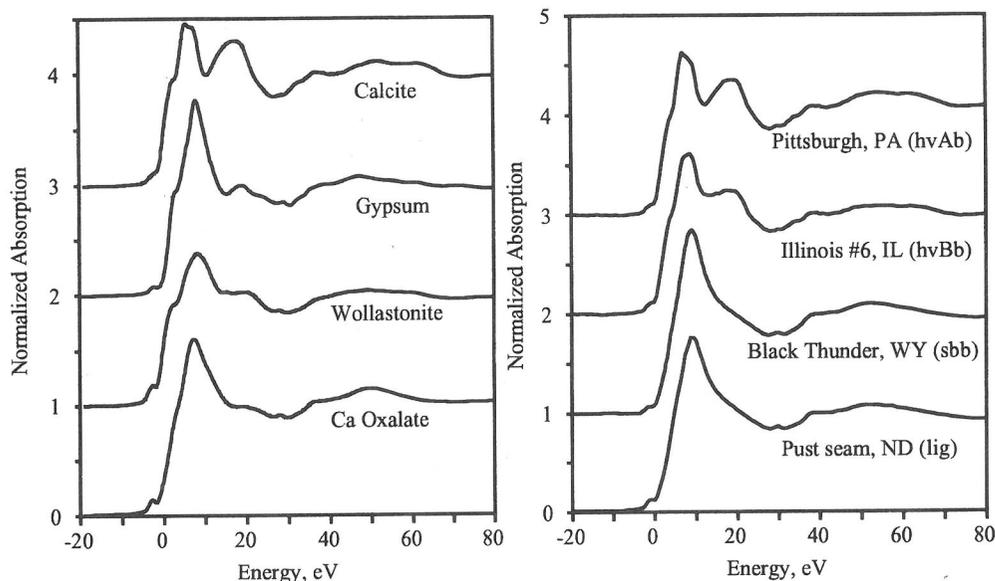


FIG. 5. Calcium XANES spectra of various standards and of four coals of different rank. Zero point of energy for calcium K absorption edge is 4,038.5 eV.

ppm in U.S. coals (SWAINE, 1990; BRAGG *et al.*, 1994). The XANES spectra of titanium in various coals are shown in Fig. 7. As can be seen by comparing these spectra with the spectra of titanium

minerals and compounds shown in the same figure and elsewhere (WAYCHUNAS, 1987), there is no convincing match between any one coal and any single standard. However, as shown elsewhere (HUGGINS and HUFFMAN, 1996), it is possible to simulate the spectra of the two highest-rank coals (Lewiston-Stockton, WV, and Pocahontas No. 3, VA) as the weighted sum of Ti in the form of illite, rutile, and/or anatase. Further, the Ti XANES spectra of the lower rank coals are all somewhat similar to each other, and to the spectra of the float (reduced mineral content) fractions from cleaning tests on the Kentucky #9 coal shown in Fig. 8. The spectra of the corresponding tailings (mostly mineral matter) fractions appear to derive principally from titanium in illite. Hence, it can be concluded that there is a significant non-mineralogical mode of occurrence for titanium in many coals in addition to various mineral forms such as Ti in illite and the Ti oxides, rutile and anatase. Such conclusions are consistent with findings from electron microscopy investigations (FINKELMAN and STANTON, 1978; FINKELMAN, 1988), which showed that the occurrence of mineralogical Ti forms could not account for all of the titanium present in coal.

Some information on the nature of the organically associated titanium in coal can be deduced both from the appearance of the XANES spectra and from analysis of the EXAFS regions. SANDSTROM *et al.* (1982) and WONG *et al.* (1983) noted

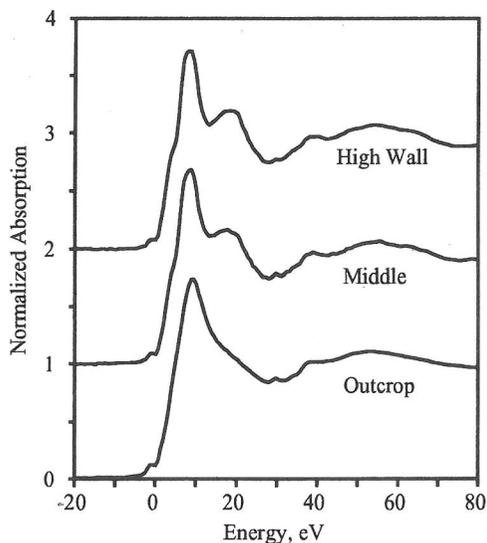


FIG. 6. Calcium XANES spectra of weathered coal samples from an outcrop on the Lower Kittanning seam in western Pennsylvania. Degree of weathering increases from the high wall to the outcrop.

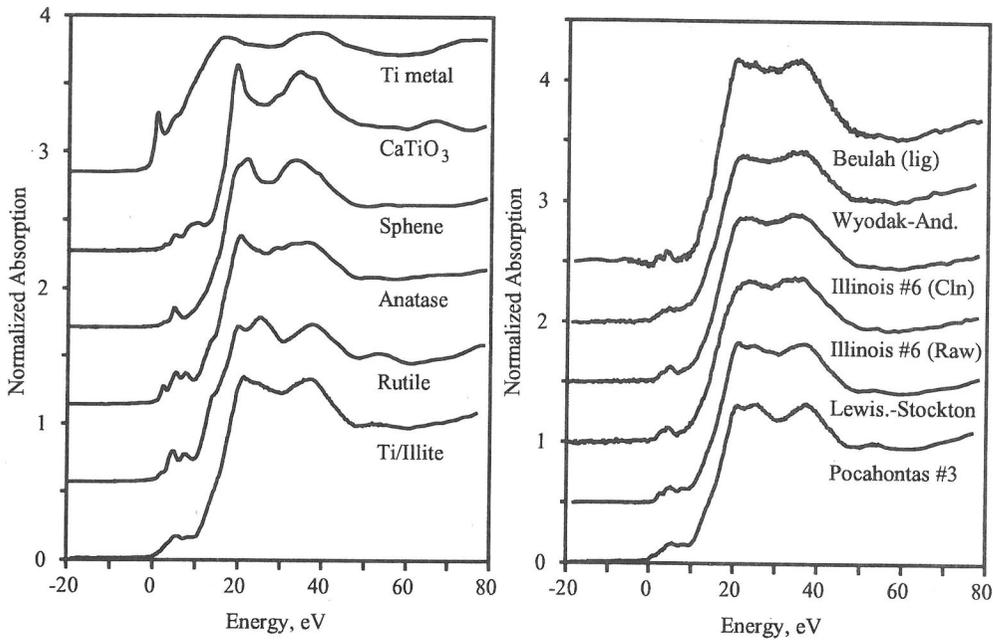


FIG. 7. Titanium XANES spectra of various standards and of five coals of different rank. Rank increases from top to bottom. Zero point of energy for titanium K absorption edge is 4,966 eV.

the close correspondence of the titanium XANES spectrum of the organically associated titanium with that of titanium alkoxides and closely related

organo-Ti ("Tyzor") compounds, respectively. In such compounds, the nearest neighbor shell to the titanium consists of six oxygen atoms. Further-

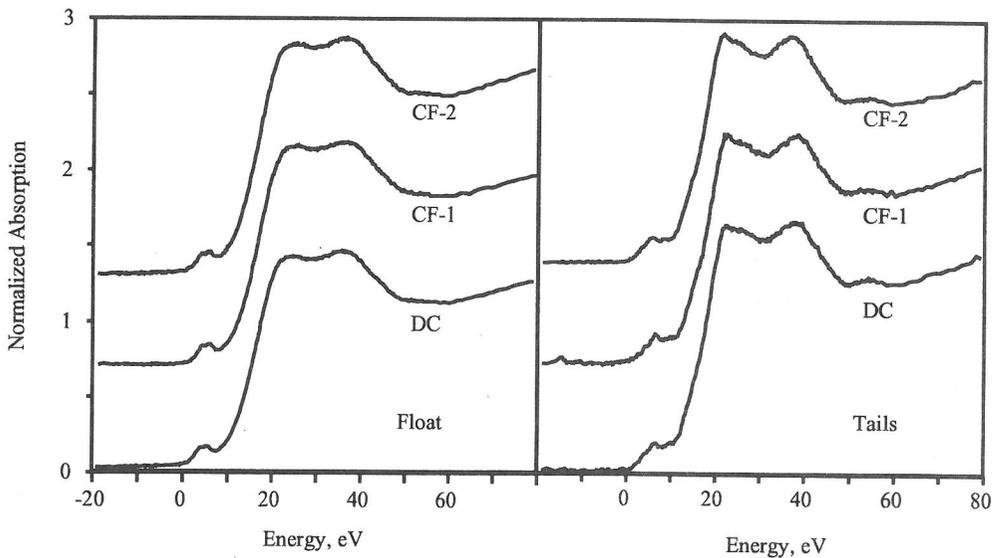


FIG. 8. Titanium XANES spectra of float and tailings fractions from a sample of Kentucky #9 coal subject to cleaning by Denver cell flotation (DC) and by column flotation (CF).

more, the lack of any significant enhancement of the pre-edge peak (*e.g.* spectra of float fractions in Fig. 8) indicates that the titanium site in coal is reasonably symmetric (WAYCHUNAS, 1987). Hence, it appears likely that the organically associated Ti in coal is found in octahedral coordination by oxygen. Analysis (HUGGINS *et al.*, unpublished work) of the EXAFS region of Ti in the Kentucky #9 float fractions is also compatible with such findings.

### Vanadium

Vanadium rarely exceeds 50 ppm in U.S. coal samples (Table 1), although local concentrations within seams at specific bedding horizons have been reported to be as high as 2,000 ppm. XAFS investigations of vanadium in one high vanadium bedding horizon in the Kentucky #9 coal (MAYLOTTE *et al.*, 1981a, 1981b; WONG *et al.*, 1983) and more recently from a whole seam sample of the same coal (HUGGINS *et al.*, 1995) indicate that there are two major vanadium forms present in this coal. As was observed for titanium, the vanadium XAFS spectra of float fractions are quite different from those of the tailings fractions (Fig. 9) and indicate the presence of both mineralogical and organically associated vanadium in this coal. Detailed analysis (MAYLOTTE *et al.*, 1981b; WONG *et*

*al.*, 1983) of the EXAFS region of the vanadium XAFS spectrum from a bedding horizon at the top of the Kentucky #9 seam that was highly enriched in vanadium ( $\approx 1800$  ppm) indicated that the organically associated vanadium was present as  $V^{4+}$  in a pyramidal or highly distorted octahedral structure with one short V—O bond at about 1.6 Å and 4 or 5 longer V—O bonds at about 2.0 Å. The XAFS spectrum for the mineralogical form was shown to be similar to that of the vanadium-rich muscovite, roscoelite (MAYLOTTE *et al.*, 1981b; WONG *et al.*, 1983). In this mineral form, the vanadium oxidation state is  $V^{3+}$ . However, it is more likely that the actual mineral in coal is illite, as this mineral appears to accumulate minor lithophile elements in Kentucky #9 coal (HUGGINS *et al.*, 1995).

### Chromium

The average concentration of chromium in U.S. coals is less than 15 ppm, with low-rank coals tending to have lower concentrations than higher-rank coals (BRAGG *et al.*, 1994). Compared to many other elements, there appears to be relatively little tendency for chromium to be found in anomalously high concentrations. Hence, as indicated in Table 1, its concentration range in U.S. coals is relatively small: 2 to 33 ppm. Despite this low abundance, chromium is an element of significant interest and concern during coal utilization because it is listed as one of the eleven "air-toxic" elements in the 1990 Clean Air Act Amendments (CAAA, 1990). The reason it appears on this list is because of the toxic and carcinogenic properties of the Cr(VI) oxidation state; the Cr(III) oxidation state poses no threat to human health at such low concentrations.

The pre-edge peak in chromium XAFS spectra is highly diagnostic for distinguishing between the  $Cr^{3+}$  and  $Cr(VI)$  oxidation states, because we need only consider Cr coordinated by oxygen in naturally occurring minerals (BURNS and BURNS, 1975). Owing to the variation of the crystal-field stabilization energy of  $Cr^{3+}$  in different coordination symmetries (BURNS, 1970, 1975),  $Cr^{3+}$  is found exclusively in octahedral coordination, whereas  $Cr(VI)$  is found exclusively in tetrahedral coordination in chromate,  $CrO_4^{2-}$ , or dichromate,  $Cr_2O_7^{2-}$ , oxoanions in terrestrial minerals (BURNS and BURNS, 1975). As shown in Fig. 10, the height of the chromium pre-edge peak amounts to no more than 5% of the edge-step for  $Cr^{3+}$ , but as much as 95% for  $Cr(VI)$ . Hence, often merely by inspection of the Cr XANES spectra, it can be concluded whether or not a significant fraction of  $Cr(VI)$  is present. None of the coals examined has shown evidence of  $Cr(VI)$ .

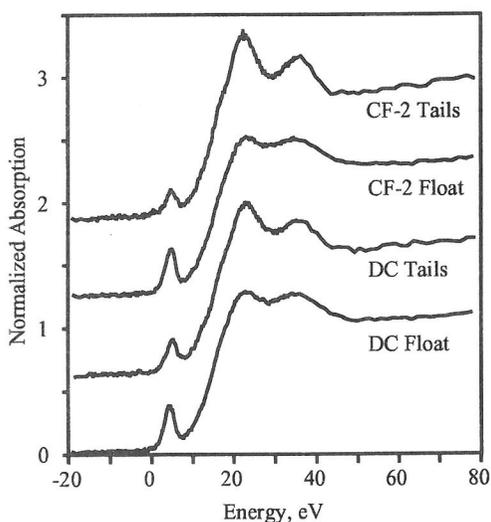


FIG. 9. Vanadium XANES spectra of float and tailings fractions (see Fig. 8 caption for identification) from a sample of Kentucky #9 coal subjected to cleaning by flotation methods. Zero point of energy for vanadium K absorption edge is 5,465 eV.

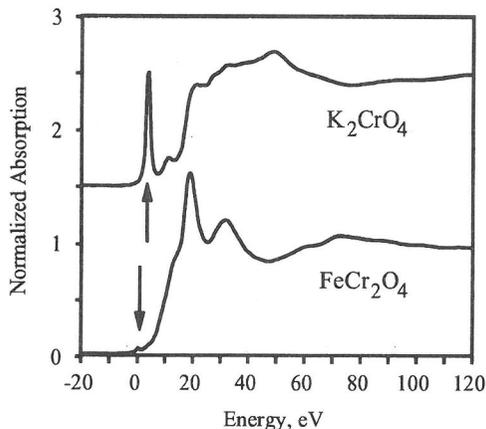


FIG. 10. Chromium XANES spectra of  $\text{Cr}^{3+}$  in chromite and of  $\text{Cr(VI)}$  in  $\text{K}_2\text{CrO}_4$ . The arrows indicate the contrast in intensity of the 1s-3d pre-edge feature at about 2–5 eV for the two oxidation states. Zero point of energy for chromium K absorption edge is 5,989 eV.

The chromium XANES spectra of coals tend to show relatively minor variations that are difficult to quantify. However, as discussed elsewhere (HUGGINS and HUFFMAN, 1996), it is easier to draw distinctions from derivative XANES spectra than from the spectra themselves. As was found for titanium and vanadium, there appear to be two major forms of chromium present in coal: one mineral, the other organic in association. The mineral form most often recognized from the XANES spectrum of a coal, especially tailings fractions, is a Cr-bearing illite. The spectra of the organically associated form most closely resemble that of an amorphous or small-particle chromium oxyhydroxide (HUGGINS *et al.*, 1993a), but the match is not exact. Well crystallized oxyhydroxide (*e.g.*, grimaldiite) and oxide (*e.g.*, chromite, eskolaite) minerals and other  $\text{Cr}^{3+}$  standards, however, do not match at all well. Hence, it is likely that the organically associated chromium consists of small clusters of  $\text{Cr(O,OH)}_6$  units that also involve bonding to the maceral surface by oxygen functional groups.

The lack of observation of chromite by XAFS spectroscopy deserves comment in view of the fact that this mineral is the only chromium mineral that has been positively identified in some coals (SWAINE, 1990; FINKELMAN, 1994; BROWNFIELD *et al.*, 1995). However, well characterized chromite occurrences have been reported only for coals with anomalously high chromium contents ( $\geq 100$  ppm), whereas the XAFS measurements have been made largely on coals with typical chromium contents that fall within the 90% range shown in Table 1.

Furthermore, as has been well documented by BROWNFIELD *et al.* (1995), the chromite in highly enriched chromium coals appears to be detrital and its origin can be traced to nearby weathered ultramafic (ophiolite) deposits. Hence, for the typical coal, uninfluenced by ultramafics, it would appear that detrital chromite is normally insignificant, based on its lack of observation in XAFS spectra, and that the chromium is introduced by different processes, such as ion-exchange or by incorporation in clay minerals.

### Manganese

The concentration of manganese in U.S. coals is generally in the range 5–150 ppm (Table 1). As established by XAFS studies (HUGGINS *et al.*, 1993b; HUGGINS and HUFFMAN, 1996), the geochemical behavior of manganese in coal is similar to that of calcium: it is principally present in low-rank coals as carboxyl-bound  $\text{Mn}^{2+}$  and in high-rank coals as  $\text{Mn}^{2+}$  in carbonate minerals. However, the manganese XANES spectra of some bituminous coals (Kentucky #9, Upper Freeport) can not be explained just by these two manganese forms. At least one other major manganese form, (for which there is no corresponding calcium form), must be present in these two coals. From the XANES systematics, this form is not a sulfide form, since oxygen is indicated as the next nearest neighbor to manganese, and our most recent work (HUGGINS *et al.*, unpublished data) suggests that this form arises from Mn in illite.

### Iron

Despite the importance of iron minerals in many utilization problems arising from coal, such as acid-mine drainage, slagging and fouling in coal combustion, acid rain, *etc.*, there have been very few investigations of coal using Fe K-edge XAFS spectroscopy. The main reason for this is that  $^{57}\text{Fe}$  Mössbauer spectroscopy is able to provide much the same information, but with considerably better precision and certainty of identification in most instances. Mössbauer investigations of coal have shown that iron is present in coal most commonly as pyrite, but if the sulfur content is low, then other minerals, such as iron-bearing clays (illite or chlorite) and siderite ( $\text{FeCO}_3$ ) are also present. Furthermore, a wide variety of iron oxyhydroxide and sulfate minerals derived from pyrite can be present in oxidized or weathered coal (HUGGINS and HUFFMAN, 1989). Often these minerals can be

identified and determined with a reasonable precision ( $\pm 3\%$  of the iron) from the parameters and relative areas of quadrupole or magnetic components in Mössbauer spectra, especially if spectra are also collected at cryogenic temperatures to supplement the room-temperature spectrum.

Experience with attempting to extract quantitative information about the relative contributions of individual forms to XANES spectra of coal, however, suggests that two distinct forms can be determined with a precision of typically no better than  $\pm 5$  to 10%. For three contributions, the precision may degrade to perhaps as much as  $\pm 20\%$ , and any attempt to extract more than three contributions is generally an exercise in futility. The reason for this difference in deconvolution of XAFS spectra compared to Mössbauer spectra is that the fitting of Mössbauer spectra is based on a well defined generic peak-shape (*viz.*, lorentzian), whereas the fitting of XANES spectra is based on combining unique standard spectra to match a unique unknown spectrum. The XANES spectrum of a material may show significant variation, due to compositional effects, particle-size effects, sample thickness effects, *etc.*, which contributes to uncertainty in fitting standard spectra to XANES spectra. Furthermore, whereas the Mössbauer spectrum itself will generally indicate the number of discrete contributions to the spectrum by the number of discernable peaks and shoulders, there is generally no way of knowing, *a priori*, how many forms of an element contribute to an XAFS spectrum.

For these reasons, Mössbauer spectroscopy is a much better technique for extracting information about iron minerals from spectra of coal. The only exception might be if iron in a particular coal sample was of very low concentration ( $<1,000$  ppm). In such a situation, the much better sensitivity of XAFS for trace quantities of an element in coal would compensate for the poorer precision of the data reduction.

### Nickel

Nickel is one of the more difficult elements in coal to examine by XAFS spectroscopy. The combination of relatively low concentrations (typically less than 40 ppm) and a strong background in the nickel XAFS spectrum because of fluorescence from the abundant iron in coal makes for relatively noisy spectra and ambiguous interpretation. The XANES spectra for nickel standards shown in Fig. 11 indicate that it is possible to discriminate between nickel in an oxygen nearest-neighbor environment and nickel in sulfide environment merely

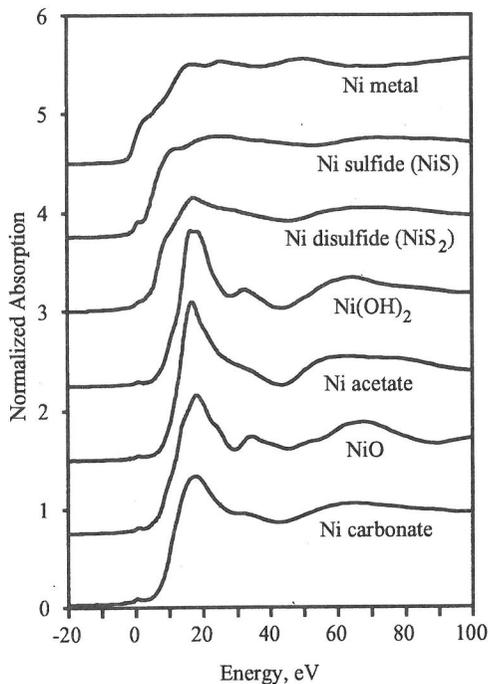


FIG. 11. Nickel XANES spectra of various nickel standard reference materials. Zero point of energy for nickel K absorption edge is 8,333 eV.

by inspection. Examination of nickel XAFS spectra of bituminous coals suggests that nickel may be found in coal in both oxidic and sulfidic environments. The Ni XANES spectrum for the Illinois #6 coal shown in Fig. 12 appears to be more like that expected from a sulfide, whereas the spectrum for the Kentucky #9 tailings, with its much more prominent white line, is more consistent with oxygen as the nearest neighbor. The float fraction from the Kentucky #9 appears to be intermediate. It should be noted that a number of other elements (iron, zinc, *etc.*) have been found in both sulfidic and oxidic environments in the same coal.

The nickel XANES spectrum of the Illinois #6 coal does not match either of the specific nickel sulfide phases shown in Fig. 11, and it has been tentatively proposed that the spectrum arises from nickel substituting for iron in pyrite (HUGGINS *et al.*, 1993b, 1994b). Such an occurrence would be similar to that proposed for nickel in U.K. bituminous coals based on synchrotron microprobe findings (WHITE *et al.*, 1989; SPEARS, 1991). Additional and better data are needed before the specific nickel form or forms present in the Kentucky #9 coal can be identified.

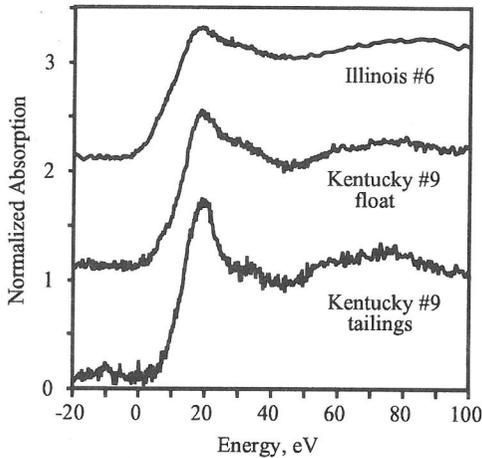


FIG. 12. Nickel XANES spectra for Illinois #6 coal and for Kentucky #9 coal fractions from Denver cell flotation tests.

### Zinc

An XAFS spectroscopy survey of zinc occurrences in various U.S. coals (HUGGINS and HUFFMAN, 1996) indicates that Illinois coals that are significantly enriched in zinc (>100 ppm) appear to contain predominantly, if not exclusively, zinc sulfide. This is true even for Illinois basin coals that are relatively low in sulfur (<2.0 wt% total sulfur). Such findings are consistent with previous mineralogical investigations (*e.g.*, HATCH *et al.*, 1976), which have reported significant concentrations of zinc (as much as 5,000 ppm or more on a whole coal basis) occurring as epigenetic sphalerite in Illinois basin coals. However, other bituminous coals from different coal regions in the U.S. with much lower and perhaps more typical zinc abundances (6–20 ppm) appear to exhibit a mixture of both sulfidic and oxidic forms, whereas a subbituminous coal (Wyodak, WY) appears devoid of zinc sulfide and may have most of its zinc present as carboxyl-bound cations, based on the similarity of the spectral profile to that for carboxyl-bound calcium or manganese.

### Arsenic

Investigations into the mode of occurrence of arsenic in bituminous coals have generally reported finding this element to be associated with sulfide minerals, especially pyrite (SWAINE, 1990; FINKELMAN, 1994), as might be expected given its chalcophilic nature. XAFS data for arsenic in unoxidized coals (HUGGINS *et al.*, 1993a; HUFFMAN *et*

*al.*, 1994) are generally in agreement with such findings. However, the same XAFS investigations have also shown that significant fractions of arsenic may be present in arsenate mineral form, if the coal has not been protected from oxidation, or if the XAFS examination is not carried out within a few days of sample pulverization. In fact, as much as 50% of the arsenic associated with pyrite in a coal may be oxidized to arsenate within six months.

One of the best demonstrations of the power of XAFS spectroscopy for mode of occurrence determinations is the fact that it has proved possible to discriminate between arsenic in the pyrite structure and arsenic in the mineral arsenopyrite (FeAsS), despite the close relationship that exists between the two structures (WYCKOFF, 1965). However, the EXAFS region shows (Fig. 13) clear distinctions between the two structures and reveals the presence of a peak in the XANES region that can also be used to discriminate between the different arsenic forms by inspection (Fig. 14). Virtually all bituminous coals examined by arsenic XAFS appear to contain mostly arsenical pyrite, rather than arsenopyrite.

In North American coals, however, arsenic is generally much less abundant in low rank than in bituminous coals (BRAGG *et al.*, 1994). Furthermore, the XANES spectra of arsenic in low-rank coals are quite different from those of arsenic in unoxidized bituminous coals (Fig. 14). Based on the close similarity with the spectrum of arsenic in a lignite in which arsenic had been greatly enriched by ion-exchange procedures, it would appear that the arsenic in low-rank coals may be present principally as  $As^{3+}$  at maceral carboxyl sites (HUGGINS *et al.*, 1996).

### Selenium

Selenium in U.S. coals rarely exceeds 5 ppm (BRAGG *et al.*, 1994). As a result, relatively little XAFS characterization of this element in coal has been attempted. XAFS spectra at the selenium K-edge have been recorded only from fresh and oxidized samples of two bituminous coals (HUGGINS and HUFFMAN, 1996), both of which contain above average concentrations of selenium. Based on the white-line positions in the selenium XANES spectra of the coals (Fig. 15), which are slightly positive (<1 eV) with respect to elemental selenium, it would appear that the selenium may well be present largely in an organoselenium form. This is consistent with previous deliberations on the mode of occurrence of selenium in coal (GOODARZI, 1988; SWAINE, 1990; FINKELMAN, 1994). There is some

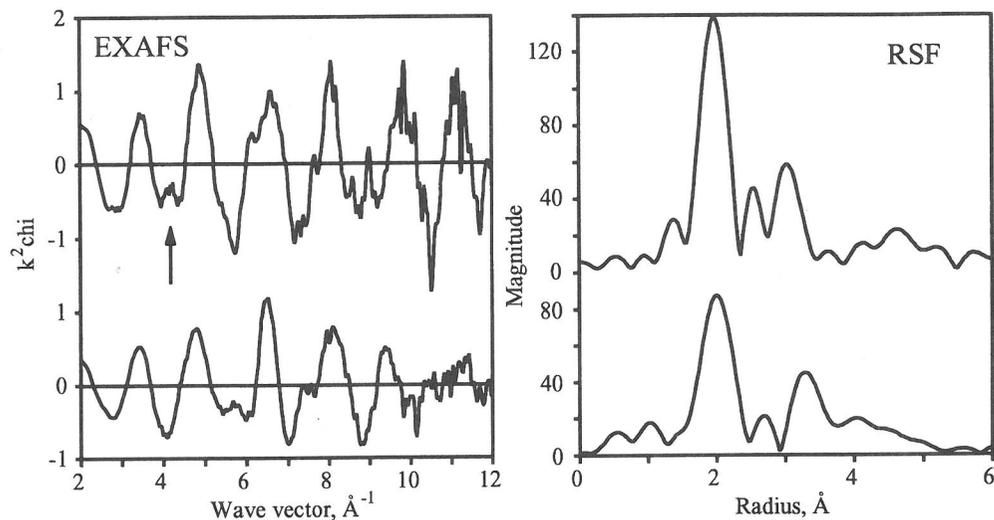


FIG. 13. Comparison of the isolated arsenic EXAFS regions and Fourier transforms (RSF) for arsenical pyrite (top) and arsenopyrite (bottom). The arrow indicates a small peak in the XANES that can be used to discriminate between arsenical pyrite and arsenopyrite by inspection.

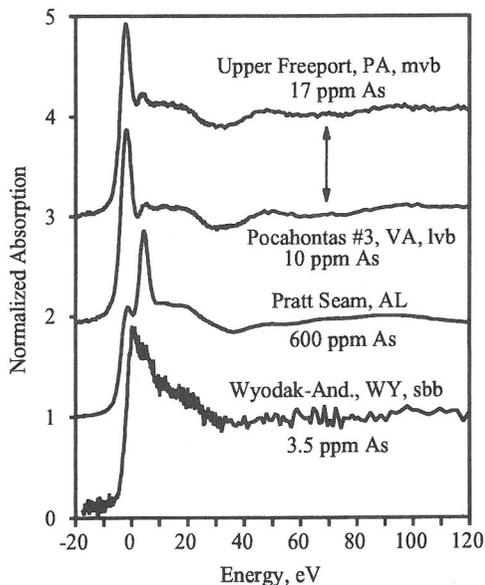


FIG. 14. Arsenic XANES spectra for two unoxidized bituminous coals, an highly oxidized bituminous coal from Alabama, and a subbituminous coal. The arrow denotes the same small peak as indicated in Fig. 13 that discriminates between arsenical pyrite and arsenopyrite. Zero point of energy for arsenic K absorption edge is 11,867 eV.

variation in the spectra between the fresh and oxidized samples, indicating that selenium is relatively susceptible to oxidation, even during storage. In one of the oxidized coal samples (Illinois #6), a second prominent peak was observed at a position characteristic of the selenate ( $\text{SeO}_4^{2-}$ ) oxidation state. A detailed study by DREHER and FINKELMAN (1992) of selenium in a Powder River Basin coal indicates just how complex the geochemical behavior of this element can be.

#### Bromine

As shown in Fig. 16, the XANES spectra of the two halogen elements, chlorine and bromine, appear very similar for the Upper Freeport coal, implying that the occurrence of bromine in coal is essentially identical to that of chlorine (HUGGINS and HUFFMAN, 1995). Also, such halogen XANES spectra from coals were found to be similar to spectra of the halide anions in aqueous solution and quite different from that of any organohalogen compound or inorganic halide. Hence, it was deduced, in part by elimination of all other postulated possibilities, that the halogen elements in coal exist largely as halide anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) associated with the moisture found in the pores and capillaries of the coal macerals. However, the XANES spectra are not exact duplicates of the XANES spectra of halide anions in aqueous solution because the EXAFS oscillations of the halide anions in coal are

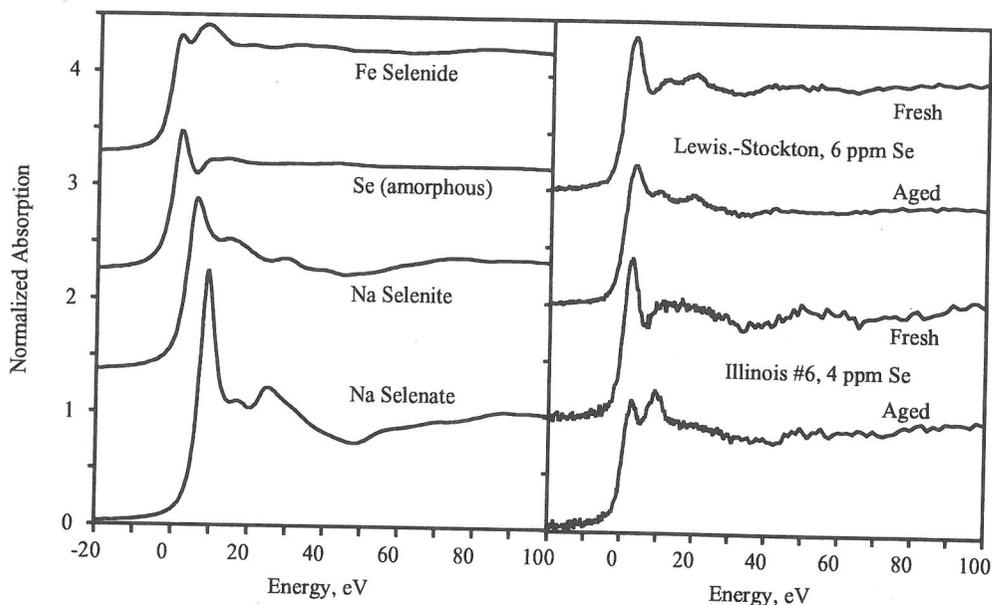


FIG. 15. Comparison of selenium XANES spectra of coals and standards. Note variation of coal spectra between fresh and aged samples. Zero point of energy for selenium K absorption edge is 12,658 eV.

broadened and flattened compared to those for the anions in solution. Furthermore, the halogen XANES profiles from coal persist to temperatures at which most of the free water is driven out from coal. Hence, it was inferred (HUGGINS and HUFFMAN, 1995) that there existed a positive interaction between the halide anions and polar organic functional groups that causes the halide anions to be anchored to the maceral surface and prevents them from behaving as if they were in a true solution. Essentially similar conclusions were reached by CHOU (1991) using less direct evidence.

The chlorine XANES spectrum of the Pocahontas #3 coal appears different from that of bromine in Fig. 16. In particular, there is a prominent small peak at about 12.5 eV in the chlorine spectrum that derives from crystalline sodium chloride. The observation of solid NaCl is relatively uncommon in chlorine XAFS spectra of coals (most spectra are closely similar to that of the Upper Freeport coal), and is thought to be an artefact brought about by crystallization of NaCl from a saturated solution of chloride anions in the moisture of coal as the sample of coal dries during storage after size reduction (HUGGINS and HUFFMAN, 1995). From the chlorine and moisture contents, it was calculated that the moisture in Pocahontas #3 coal is close to a saturated solution of NaCl. However, the much

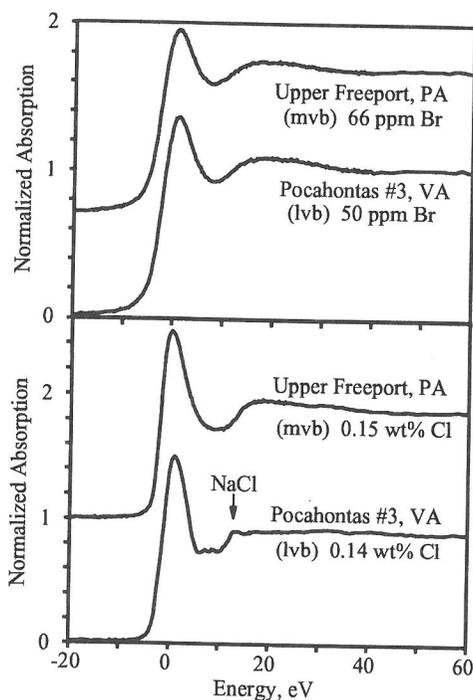


FIG. 16. Comparison of chlorine and bromine XANES spectra of Upper Freeport and Pocahontas #3 coals. Zero points of energy for chlorine and bromine K absorption edges occur at 2,825 and 13,474 eV, respectively.

lower concentration of bromine ensures that it would be entirely in solution as the solubility of NaBr is greater than that of NaCl.

## DISCUSSION

As has been demonstrated in this review, XAFS spectroscopy has an unparalleled ability to focus directly on a specific element in a coal sample and extract details about its local structure and chemical bonding, from which the modes of occurrence of the element in the coal may be deduced. Also, the application of this technique is essentially non-destructive and requires a minimum of sample preparation. Furthermore, because of the high X-ray flux of the synchrotron source coupled with the sensitivity of the 13 element Ge detector, measurements can be conducted at concentration levels as low as 5 ppm. In addition, because XAFS spectroscopy is sensitive to dispersed maceral occurrences as well as to discrete mineral occurrences of an element, it complements microscope or microprobe investigations, which provide information primarily on the more concentrated mineral occurrences of an element.

XAFS spectroscopy clearly demonstrates that for many elements there are often two distinct forms present in coal: one associated with minerals, the other associated with the organic matrix. For coals of intermediate rank (subbituminous-high volatile B bituminous), both of these major elemental forms have been observed in the same coal. Hence, the frequently raised question of whether there are distinct forms of an element in float and tailings fractions or whether there is merely an incomplete separation of one elemental form between float and tailings fractions appears to be resolved in favor of multiple forms for coals of this rank.

Hence, of the five different generalized modes of occurrence shown in Fig. 1, it would appear, from the data presented in this review for elements of the first transition row, that the most common modes are ionically-bound forms in organic association and substitutional mineralogical occurrences involving illite or pyrite for the lithophile and chalcophile elements, respectively. Except for abundant elements such as potassium, calcium and iron, which are necessary for forming some of the common major minerals in coal, the only first transition-row elements conclusively identified as forming their own specific minerals are titanium and zinc. The other exceptions include selenium, which appears to be present in organoselenium forms, and bromine, which like chlorine is principally present in anionic form in the moisture associated with the

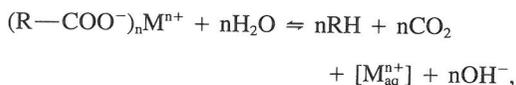
macerals. However, it should be remembered that the data obtained to date for these two elements are quite limited.

Also it should be recalled that this discussion has centered exclusively on the first transition-row elements, which are more compatible with incorporation into illite or pyrite than elements further down the periodic table. From evidence summarized by FINKELMAN (1988) and SWAINE (1990), it would appear that discrete accessory mineral formation involving heavier trace elements is much more common.

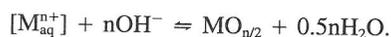
Those elements that are found in both an organic as well as a mineralogical association in coal tend to exhibit the organic association more completely in low-rank coals and the mineralogical occurrence more so in higher-rank coals. This observation implies that metamorphic grade plays a role in determining modes of occurrence. Possible evidence for regional variations in the mode of occurrence was demonstrated by zinc in coals of the Illinois basin, which was predominantly, if not exclusively in the form of sphalerite, whereas zinc in other coals was present in an oxidic environment as well. Variation of the mode of occurrence due to oxidation during storage has been noted for arsenic, selenium, and iron (from Mössbauer studies). Most other elements appear to be relatively insensitive to oxidation; however, for many elements, this aspect has not yet been adequately examined. Other factors that might influence the mode of occurrence, such as sulfur content, may also be important, but the XAFS database is not yet sufficient to test this possibility.

As many researchers have speculated in the past, one of the more important processes in coal geochemistry is the decarboxylation step that occurs near the rank boundary between bituminous and subbituminous coals. The loss of carboxyl functionality due to increasing coalification results in many elements undergoing mineralization as coals of bituminous rank start to form. The moisture in coal can be expected to play a major role in helping to transfer elements between the increasingly tenuous carboxyl sites and the more stable mineral forms. As rank increases, the concentration of oxygen functional groups at the coal surface decreases and ions are forced into solution, and thence into mineral formation. Furthermore, the moisture content also decreases and becomes increasingly saturated with respect to dissolved species as coalification increases, which further impels the ionic species to enter into mineralization. The valence state of the cation or, perhaps more appropriately, the ionic potential ( $Z/r$ , where  $Z$  is the formal va-

lence charge and  $r$  is the ionic radius, *q.v.* CARLEDGE, 1928) is likely to be largely responsible for the order in which cations are released by carboxyl groups, their solubility in aqueous fluids, and their rate of mineralization, either capture by a host mineral or precipitation of a new mineral. These factors basically act together to keep the lowest charge cations ( $M^+$ ) in solution in the highest concentrations and the highest charge cations the least. In the general case, decarboxylation may be written as:



where the coal is represented as R, and mineralization may be written as:



If  $K_1$  is the equilibrium constant for the decarboxylation reaction and  $K_2$  is the equilibrium constant for the mineralization reaction, represented by precipitation of the oxide, then, based on valence or ionic potential considerations, it follows that  $K_1$  decreases in the order  $M^+ > \dots > M^{4+}$  and  $K_2$  increases in the order  $M^+ < \dots < M^{4+}$ . Consequently,  $[M_{aq}^{n+}]$ , the concentration of the cation in moisture, can be expected to decrease in the order  $n = 1 \gg \dots \gg n = 4$ .

The observation of many elements with a distinct organic association in coals must also reflect the importance of geochemical processes occurring during peat formation. Hence, it would appear that one of the most important of these processes is the introduction of elements by ion-exchange between cations in the water flowing through the peat and acidic sites in the peat itself. Similar ideas have been expressed by MILLER and GIVEN (1986, 1987) and GIVEN and MILLER (1987).

### CONCLUSION

XAFS spectroscopy is capable of revealing information directly and nondestructively about the geochemical properties and behavior of elements in coal. With current synchrotron radiation facilities in the U.S., useful information can be obtained from as little as 5 ppm of an element in coal. With the much brighter Advanced Photon Source to be commissioned at Argonne National Laboratory within the next two years, it should be possible to extend such studies to many of the remaining elements in the periodic table, including most of the elements that are potentially of environmental concern (SWAINE, 1990).

The most important result presented in this review is the demonstration that many elements in coal, even of as high rank as high-volatile B bituminous, appear to have a significant organic association that is distinct from their mineralogical occurrences. This result has important ramifications not only with respect to the geochemistry of coal, but also to various options for the removal or control of trace elements in coal cleaning and utilization.

*Acknowledgements*—We are grateful to the following personnel from the University of Kentucky who have assisted us with the collection of XAFS spectra at NSLS or SSRL from 1989 to present: Bhaswati Ganguly, Fulong Lu, Sudipa Mitra, Mohammad Najih, Anup Shah, Naresh Shah, Mehdi Taghiei, Shreeniwas Vaidya, and Jianmin Zhao. In addition, we would like to acknowledge Drs. Farel Lytle and Robert Gregor who introduced us to XAFS spectroscopy in the early 1980s and who have shared with us many insights and data over the years. This work has been supported by contracts with the U.S. Department of Energy and the Electric Power Research Institute. We also acknowledge the U.S. Department of Energy for its support of synchrotron radiation facilities at both NSLS and SSRL.

### REFERENCES

- ASTM (1976) Coal and coke. In *1976 Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis*, pp. 179–426. American Society for Testing and Materials.
- BONNETT R., BURKE P. J. and CZECHOWSKI F. (1987) Metalloporphyrins in lignite, coal, and calcite. In *Metal Complexes in Fossil Fuels* (eds. R. H. FILBY and J. F. BRANTHAVER); *ACS Symposium Series 344*, Chapter 11, pp. 173–185. American Chemical Society.
- BRAGG L. J., OMAN J. K., TEWALT, S. J., OMAN, C. L., REGA, N. H., WASHINGTON, P. M. and FINKELMAN, R. B. (1994) Coal quality (COALQUAL) database: Version 1.3. *Open-File Report 94–205*, 35Mb CD-ROM. U.S. Geological Survey.
- BROWN G. E., JR., CALAS G., WAYCHUNAS G. A. and PETIAU J. (1988) X-ray absorption spectroscopy and its application in mineralogy and geochemistry. In *Spectroscopic Methods in Mineralogy and Geology* (ed. F. C. HAWTHORNE); *Rev. in Mineral. 18*, Chapter 11, pp. 431–512. Mineralogical Society of America.
- BROWNFIELD M. E., AFFOLTER R. H., STRICKER G. D. and HILDEBRAND, R. T. (1995) High chromium coals in Tertiary coal deposits of northwestern Washington—a key to their depositional history. *Int. J. Coal Geol.* **27**, 153–169.
- BURNS R. G. (1965) Electronic spectra of silicate minerals: applications of crystal field theory to aspects of geochemistry. Ph.D. Thesis, University of California, Berkeley, CA.
- BURNS R. G. (1970) *Mineralogical Applications of Crystal Field Theory*. Cambridge University Press.
- BURNS R. G. (1975) Crystal field effects in chromium and its partitioning in the mantle. *Geochim. Cosmochim. Acta* **39**, 857–864.
- BURNS V. M. and BURNS R. G. (1975) Mineralogy of chromium. *Geochim. Cosmochim. Acta* **39**, 903–910.

- CAAA (1990) Amendments to the Clean Air Act. *U.S. Public Law 101-549, Nov. 15, 1990*. 314 pp. U.S. Government Printing Office.
- CARTLEDGE G. H. (1928) Studies on the periodic system. I. The ionic potential as a periodic function. *J. Am. Chem. Soc.* **50**, 2855-2863; II. The ionic potential and related properties. *J. Am. Chem. Soc.* **50**, 2863-2872.
- CHOU, C.-L. (1991) Distribution and forms of chlorine in Illinois Basin coals. In *Chlorine in Coal* (eds. J. STRINGER and D. D. BANERJEE), pp. 11-29. Elsevier Science Publishers.
- CLARKE L. B. and SLOSS L. L. (1992) Trace Elements. *IEA Coal Research Report 49*, 111 pp. International Energy Agency.
- CRAMER S. P., TENCH O., YOCUM N. and GEORGE G. N. (1988) A 13-element Ge detector for fluorescence EXAFS. *Nucl. Instrum. Meth.* **A266**, 586-591.
- DREHER G. B. and FINKELMAN R. B. (1992) Selenium mobilization in a surface coal mine, Powder River, Wyoming. *Environ. Geol. Water Sci.* **19**, 155-167.
- EISENBERGER P. and KINCAID B. M. (1978) EXAFS: New horizons in structure determination. *Science* **200**, 1441-1447.
- FINKELMAN R. B. (1988) The inorganic geochemistry of coal: a scanning electron microscopy view. *Scanning Microscopy* **2**, 97-105.
- FINKELMAN R. B. (1994) Modes of occurrence of potentially hazardous elements in coal: levels of confidence. *Fuel Proc. Technol.* **39**, 21-34.
- FINKELMAN R. B. and STANTON R. W. (1978) Identification and significance of accessory minerals from a bituminous coal. *Fuel* **57**, 763-768.
- FRAHM R. (1992) Quick XAFS: potentials and practical applications in materials science. In *X-ray Absorption Fine Structure* (ed. S. S. HASNAIN), Chapter 191, pp. 731-737. Ellis Horwood.
- GIVEN P. H. and MILLER R. N. (1987) The association of major, minor, and trace inorganic elements with lignites. III. Trace elements in four lignites and general discussion of all data from this study. *Geochim. Cosmochim. Acta* **51**, 1843-1853.
- GOODARZI F. (1988) Elemental distribution in coal seams at the Fording coal mine, British Columbia, Canada. *Chem. Geol.* **68**, 129-154.
- HATCH J. R., GLUSKOTER H. J. and LINDAHL P. C. (1976) Sphalerite in coals from the Illinois basin. *Econ. Geol.* **71**, 613-624.
- HUFFMAN G. P. and HUGGINS F. E. (1984) Analysis of the inorganic constituents in low-rank coals. In *Chemistry of Low-Rank Coals* (ed. H. H. SCHOBERT); *ACS Symposium Series 264*, Chapter 10, pp. 159-174. American Chemical Society.
- HUFFMAN G. P., HUGGINS F. E., SHOENBERGER R. W., WALKER J. S., GREGOR R. B. and LYTLE F. W. (1986) Investigation of the structural forms of potassium in coke by electron microscopy and X-ray absorption spectroscopy. *Fuel* **65**, 621-632.
- HUFFMAN G. P., HUGGINS F. E., SHAH N. and ZHAO J. (1994) Speciation of arsenic and chromium in coal and combustion ash by XAFS spectroscopy. *Fuel Proc. Technol.* **39**, 47-62.
- HUGGINS F. E. and HUFFMAN G. P. (1989) Coal weathering and oxidation: the early stages. In *Chemistry of Coal Weathering* (ed. C. R. NELSON); *Coal Science and Technology 14*, Chapter 2, pp. 33-60. Elsevier.
- HUGGINS F. E. and HUFFMAN G. P. (1995) Chlorine in coal: an XAFS spectroscopic investigation. *Fuel* **74**, 556-569.
- HUGGINS F. E. and HUFFMAN G. P. (1996) Modes of occurrence of trace elements in coal from XAFS spectroscopy. To be published in *Proceedings, 1995 International Chemical Congress of Pacific Basin Societies* (eds. P. C. LYONS, C. A. PALMER and R. M. BUSTIN); *Internat. J. Coal Geol.*
- HUGGINS F. E., HUFFMAN G. P. and LIN M. C. (1983a) Observations on low-temperature oxidation of minerals in bituminous coals. *Int. J. Coal Geol.* **3**, 157-182.
- HUGGINS F. E., HUFFMAN G. P., LYTLE F. W. and GREGOR R. B. (1983b) An EXAFS investigation of calcium in coal. In *Proceedings, 1983 International Conference on Coal Science (Pittsburgh, PA)*, pp. 679-682. International Energy Agency.
- HUGGINS F. E., SHAH N., ZHAO J., LU F. and HUFFMAN G. P. (1993a) Nondestructive determination of trace element speciation in coal and ash by XAFS spectroscopy. *Energy & Fuels* **7**, 482-489.
- HUGGINS F. E., ZHAO J., SHAH N. and HUFFMAN G. P. (1993b) Speciation of trace elements in coal from XAFS spectroscopy. *Proceedings, 7th International Conference on Coal Science (Banff, Canada)*, (ed. K. H. MICHAELIAN), Vol. 1, pp. 660-663.
- HUGGINS F. E., HUFFMAN G. P. and HELBLE J. J. (1994a) Determination of the form of occurrence of hazardous trace elements in coal and ash. In *Proceedings: Second International Conference on Managing Hazardous Air Pollutants, 1993* (eds. W. CHOW and L. LEVIN); *EPRI Report TR-104295*, pp. II-113 to II-133. Electric Power Research Institute.
- HUGGINS F. E., ZHAO J., SHAH N. and HUFFMAN G. P. (1994b) Modes of occurrence of trace elements in coal from XAFS spectroscopy. *Preprints, ACS Div. Fuel Chem.* **39(2)**, 504-510. American Chemical Society.
- HUGGINS F. E., PAREKH B. K., ROBERTSON J. D. and HUFFMAN G. P. (1995) Modes of occurrence of trace elements in coal: geochemical constraints from XAFS and PIXE spectroscopic analysis of advanced coal cleaning tests. In *Proceedings, 8th International Conference on Coal Science (Oviedo, Spain)* (eds. J. A. PAJARES and J. M. D. TASCÓN), Vol. 1, 679-682. Elsevier.
- HUGGINS F. E., GOODARZI F. and LAFFERTY C. J. (1996) Nature of arsenic in subbituminous coals. *Energy & Fuels* **10**, in press.
- KONINGSBERGER D. C. and PRINS R. (1988) *X-ray Absorption. Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*. J. Wiley & Sons.
- LEE P. A., CITRIN P. H., EISENBERGER P. A. and KINCAID B. M. (1981) Extended X-ray absorption fine structure—its strengths and limitations as a structural tool. *Rev. Mod. Phys.* **53**, 769-808.
- LYTLE F. W., GREGOR R. B., SANDSTROM D. R., MARQUES E. C., WONG J., SPIRO C. L., HUFFMAN G. P. and HUGGINS F. E. (1984) Measurement of soft X-ray absorption spectra with a fluorescent ion chamber detector. *Nucl. Instrum. Meth.* **226**, 542-548.
- MAYLOTTE D. H., WONG J., ST. PETERS R. L., LYTLE F. W. and GREGOR R. B. (1981a) Trace vanadium in coal: An EXAFS study. In *Proceedings, International Conference on Coal Science (Düsseldorf, Germany)* (eds. International Energy Agency), pp. 756-761, Verlag Glückauf GmbH.
- MAYLOTTE D. H., WONG J., ST. PETERS R. L., LYTLE F. W. and GREGOR R. B. (1981b) X-ray absorption

- spectroscopic investigation of trace vanadium sites in coal. *Science* **214**, 554–556.
- MILLER R. N. and GIVEN P. H. (1986) The association of major, minor, and trace inorganic elements with lignites. I. Experimental approach and study of a North Dakota lignite. *Geochim. Cosmochim. Acta* **50**, 2033–2043.
- MILLER R. N. and GIVEN P. H. (1987) The association of major, minor, and trace inorganic elements with lignites. II. Minerals, and major and minor element profiles, in four seams. *Geochim. Cosmochim. Acta* **51**, 1311–1322.
- SANDSTROM D. R., FILBY R. H., LYTLE F. W. and GREGOR R. B. (1982) Study of Ti in solvent-refined coal by X-ray absorption spectroscopy. *Fuel* **61**, 195–197.
- SPEARS D. A. (1991) Pyrite in some U.K. coals. In *Processing and Utilization of High Sulfur Coals IV* (eds. P. R. DUGAN, D. R. QUIGLEY and Y. A. ATTIA); *Coal Science and Technology* **18**, pp. 85–93. Elsevier.
- SPIRO C., WONG J., MAYLOTTE D. H., LAMSON S., GLOVER B., LYTLE F. W. and GREGOR R. B. (1986) Nature of potassium impurities in coal. *Fuel* **65**, 327–336.
- STACH E., MACKOWSKY M.-TH., TEICHMÜLLER M., TAYLOR G. H., CHANDRA D. and TEICHMÜLLER R. (1975) *Coal Petrology*. Gebrüder Borntraeger.
- STERN E. A. and HEALD S. M. (1979) X-ray filter assembly for fluorescence measurements of X-ray absorption fine structure. *Rev. Sci. Instrum.* **50**, 1579–1582.
- SWAINE D. J. (1990) *Trace Elements in Coal*. Butterworths.
- WAYCHUNAS G. A. (1987) Synchrotron radiation XANES spectroscopy of Ti in minerals: Effects of Ti bonding distances, Ti valence, and site geometry on absorption edge structure. *Amer. Mineral.* **72**, 89–101.
- WHITE R. N., SMITH J. V., SPEARS D. A., RIVERS M. L. and SUTTON S. R. (1989) Analysis of iron sulphides from U.K. coal by synchrotron radiation X-ray fluorescence. *Fuel* **68**, 1480–1486.
- WONG J., MAYLOTTE D. H., LYTLE F. W., GREGOR R. B. and ST. PETERS R. L. (1983) EXAFS and XANES investigations of trace V and Ti in coal. In *EXAFS and Near Edge Structure* (eds. A. BIANCONI, L. INCOCIA and S. STIPCICH); *Springer Series in Chemical Physics* **27**, pp. 206–209. Springer-Verlag.
- WYCKOFF R. W. G. (1965) *Crystal Structures* (2nd. edition), Vol. 1. Interscience Publishers.

