

MODES OF OCCURRENCE OF TRACE ELEMENTS IN COAL FROM XAFS SPECTROSCOPY

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INTRODUCTION

It is well known that elements exist in coal in a variety of different modes of occurrence [1,2]. Such modes can vary from the element being totally dispersed in the macerals (e.g. organic sulfur, carboxyl-bound Ca in lignite) to discrete mineral occurrences (e.g. pyrite, FeS₂, quartz, SiO₂, etc.). Recently, we showed that X-ray absorption fine structure (XAFS) spectroscopy is capable of recording spectra from elements present in coal at concentration levels as low as 5 ppm [3]. Such information, obtained directly with a minimum of sample preparation, is proving to be invaluable for the elucidation of a trace element's mode of occurrence. In the previous work, we used XAFS spectroscopy to identify the principal modes of occurrence of arsenic and chromium in various coals. Here, we present more recent XAFS spectroscopic observations on these and other trace elements in coal and take the opportunity to discuss the ramifications of such XAFS studies for geochemical investigation of trace elements in coal.

EXPERIMENTAL

XAFS spectra of trace elements in coal were obtained at one or other of the two major U.S. synchrotron sources: the Stanford Synchrotron Research Laboratory (SSRL), at Stanford University, CA, and the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory, NY. Procedures for obtaining XAFS spectra of trace elements are described in detail elsewhere [3]. Spectra were recorded, usually in multiple scans, by means of a 13-element germanium detector specifically designed for trace element studies [4]. Coal samples were suspended in the X-ray beam in thin (6 μm) polypropylene bags. Analysis of the XAFS spectra was performed at the University of Kentucky on a MicroVAX II computer. As is usually done, the XAFS spectrum was subdivided into the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions. All XANES spectra shown here are calibrated with respect to a reference material containing the element of interest. The zero energy points in the Cr, Mn, As, and Br XANES spectra are defined as the first maximum in the derivative of the spectrum of Cr in stainless steel (5.989 keV), the spectrum of metallic Mn (6.539 keV), the spectrum of As₂O₃ (11.867 keV), and the spectrum of KBr (13.474 keV), respectively.

XAFS RESULTS

(a) Chromium:

The XANES spectra of chromium in most U.S. bituminous coals vary little from coal to coal, indicating that there is probably just one major chromium mode of occurrence [3]. Furthermore, the XANES spectra clearly demonstrate that chromium is present in coal exclusively in the trivalent state, Cr³⁺. Previously, chromium has been postulated to occur in coals in association with clay minerals, or as chromite (FeCr₂O₄) [1,2], and possibly as an organic complex in low-rank coals [5,6]. However, comparison of the XANES spectra of a wide variety of Cr³⁺ compounds and minerals with the common XANES spectrum of Cr in coal eliminated all of the previously postulated chromium-bearing mineral forms as the Cr XANES spectra of coals showed little resemblance to either Cr³⁺-bearing silicates or to chromium oxide minerals, including chromite. Finally, based on some published spectra of other Cr³⁺ phases [7], it was decided to investigate the chromium hydroxides and oxyhydroxides, although based on the rarity of such phases in nature [8,9], it appeared to be unlikely. Cr(OH)₃ was prepared by precipitation from a solution of chromium nitrate at 25°C using ammonium hydroxide. The blue-green precipitate was filtered, washed, and then dried in air. The XANES spectrum of Cr hydroxide closely resembled that published elsewhere [7], but, although there were superficial similarities to the Cr XANES of coal, it was not a compelling match. The chromium hydroxide was then heated overnight (18 hours) at 140°C. A weight loss of about 19% was recorded that corresponded well to the elimination of one water molecule from the unit formula of chromium hydroxide and the formation of CrOOH:



X-ray diffraction of the CrOOH phase formed this way showed that it was an amorphous phase, closely related to ferrihydrite [10], rather than one of the very rare crystalline chromium oxyhydroxide minerals that have been found only in unique localities in Guyana and Finland [8]. More importantly, the Cr XANES of this material did closely resemble (Figure 1) the Cr XANES of coal and it now appears that the Cr XANES of coal arises from Cr in an oxyhydroxide form. However, it still remains to be demonstrated whether Cr exists as CrOOH in one of its own mineral forms, or whether it is in a complex oxyhydroxide solid solution with other trivalent ions. As has been demonstrated synthetically [10], substitution of Cr in goethite, FeOOH, can occur up to at least 10% of the Fe, and hence, Cr-substituted goethite might be considered a possible mode of occurrence for Cr. However, such an occurrence would only be possible if goethite were a primary occurrence of iron in coal. There is little or no evidence for such a supposition, and much against.

Once the primary occurrence of Cr in coal was established, some Cr XANES spectra that were not fully compatible with just CrOOH as the only Cr-bearing phase were re-examined. To assess the presence of a second Cr phase in addition to CrOOH in these spectra, spectral addition and subtraction procedures were attempted. Figure 2 shows the simulation of the Cr XANES spectrum of a lignite from Indonesia, in which personnel at the U.S. Geological Survey had observed chromite microscopically (R. B. Finkelman and L. F. Ruppert, pers. comm. 1992). A reasonably good simulation of this spectrum can be made from the weighted addition of the spectra of CrOOH (60%) and FeCr_2O_4 (40%). The sensitivity of this spectral simulation method of XANES analysis is about $\pm 10\%$.

(b) Arsenic:

As demonstrated elsewhere [3], it is possible to use As XANES spectroscopy to discriminate between arsenical pyrite, in which arsenic substitutes for sulfur in the pyrite structure, and arsenopyrite (FeAsS), in which it is an essential element. Of the coals examined to date, only one, a Pittsburgh seam coal, has been found to contain significant arsenopyrite. More recently, we have examined coals of relatively low As content (<5 ppm) from low-rank coals from western U.S. coal-fields. Despite the poor signal-noise ratio of these spectra (Figure 3), it is possible to conclude that the As XANES spectra of such coals are similar to each other and different from those of the bituminous coals of higher arsenic content (>10 ppm) reported earlier. From the position of the main peak, it would appear that the oxidation state of the arsenic is As^{3+} ; however, better quality data are needed to identify whether arsenic is enclosed in a sulfur or oxygen nearest neighbor environment.

(c) Manganese

As reviewed by Swaine [1], manganese has been postulated to occur in a variety of geochemical environments in coal, including carbonates, clays, pyrite, porphyrins, and, in lower-rank coals, in organic association. Owing to a similar ionic size and electronic structure, the geochemistry of Mn^{2+} tends to be similar to that of calcium, except that Mn has much a higher chalcophilic nature and can form sulfide minerals more readily.

Some preliminary XAFS data have been obtained on manganese in U.S. coals. A progression of Mn XANES spectra with rank are shown in Figure 4. The lowest rank coal (Beulah) exhibits a Mn XANES spectrum that is closely similar to that exhibited by calcium in carboxyl form in low-rank coals, whereas the Mn XANES spectrum of the Pocahontas #3 coal of highest rank, exhibits an asymmetric split main peak similar to that found for Mn in carbonates. The intermediate spectra, with the exception of the Wyodak coal, can not be simulated by additions of the two extreme spectra. Hence, there is at least one more Mn form of occurrence that contributes significantly to the Mn XANES spectra of the Pittsburgh and Upper Freeport coals. This form has yet to be identified.

(d) Bromine

XAFS spectroscopy has proven very useful for investigating the mode of occurrence of chlorine in coal [11]. XAFS spectroscopy clearly shows that chlorine is neither present as an organochlorine functionality nor as an inorganic chloride; rather, chlorine exists in coal as chloride anions in the moisture associated with the macerals, most probably held at the maceral surface by ionic attraction to polar organic functional groups. On geochemical grounds, it would be expected that the trace halogens (bromine and iodine) should have a similar mode of occurrence to that of chlorine. Some preliminary XAFS experiments on bromine in coal confirm this expectation. Bromine K-edge XANES spectra of KBr, KBr in aqueous solution, and of two coals are shown in Figure 5. The profiles of all four of these spectra are very

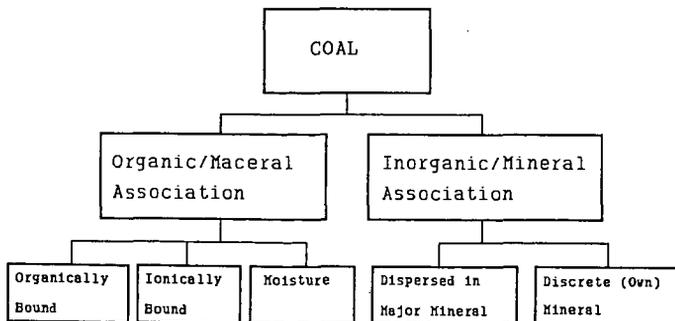
similar to the corresponding chlorine K-edge XANES spectra [11], indicating that the bromine mode of occurrence in coal is similar to that of chlorine.

DISCUSSION:

The unanticipated observation of Cr in oxyhydroxide form in coal by XAFS spectroscopy begs the question of whether other elements might also be present in coal in similar oxyhydroxide form or even hydroxide form. Presumably, such species would have to be sufficiently lithophilic not to react with sulfur, but incompatible with aluminosilicate (clay) structures. A number of elements that are typically trivalent in geochemical behavior would appear to fit such requirements; these include Sc, V, Y, and the rare-earth elements. All of these species have been reported to form an oxyhydroxide or hydroxide phase with stability fields compatible with geological conditions of coal formation [12]. Hence, it is possible, by analogy to chromium, that these elements may be found in coal as oxyhydroxide or hydroxide minerals. However, the larger trivalent cations (Y, REE) are also candidates for reaction with phosphate anions that may also be present during coal formation.

For two of the elements discussed here, arsenic and manganese, the mode of occurrence has been demonstrated to be quite different between low-rank coals (lignites and subbituminous coals) from the western U.S. and higher-rank coals (bituminous) from the eastern U.S. In previous work [13], the occurrence of calcium has also been shown to be distinctly different between such groups of coals. Many more elements are postulated [1,5] to be in organic association in low-rank coals than in higher-rank coals because of carboxyl groups present in the former. Clearly, this "decarboxylation" transition from low-rank coal to high rank coal is a key factor in the mobilization and mineralization of many elements during coalification and needs to be investigated in detail.

The terminology applied to elemental modes of occurrence is currently relatively imprecise because previous methods used to infer such information have not been sufficiently discriminating. For example, float/sink testing can be used to categorize elements by their "organic affinity", but such a concept does not impart any information as to how the element is actually bound to the coal macerals. Similarly, X-ray mapping in the electron microscope or microprobe can demonstrate that certain elements are associated with the organic matter, but do not provide information as to how the element is bound. However, in principle, such information can now be obtained from XAFS spectroscopy and a more expanded classification for elemental forms-of-occurrence is required. Such a proposed classification scheme with precise definitions for modes of occurrence is shown below. This scheme would appear to be sufficient for all the methods, both direct and indirect, that are currently used to infer elemental modes of occurrence in coal.



Organic/Maceral Association:

Organically bound: Involves direct covalent -M-C- or similar bond

Ionically bound: Involves an ionic bond with polar organic group

Moisture: Soluble anionic or cationic species in maceral pore moisture

Inorganic/Mineral Association:

Dispersed mineral: substitution of minor element for major element

Discrete mineral: element is essential to mineral's existence.

CONCLUSIONS:

The potpourri of data on trace element modes of occurrence in coal presented in this paper demonstrate the value of XAFS spectroscopy in trace element geochemistry. All measurements are made directly on the coal with a minimum of preparation and,

hence, with minimal chance of alteration or contamination of the mode of occurrence. Furthermore, XAFS is equally capable of determining dispersed elements (e.g. carboxyl bound Mn in Beulah lignite; Br in moisture), as well as the discrete mineralogical occurrences (Mn in carbonates, CrOOH, etc.). Such direct measurements afford the opportunity to provide much new information about trace elements in coal and put to rest various misconceptions about trace element occurrences in coal that have accumulated over the years.

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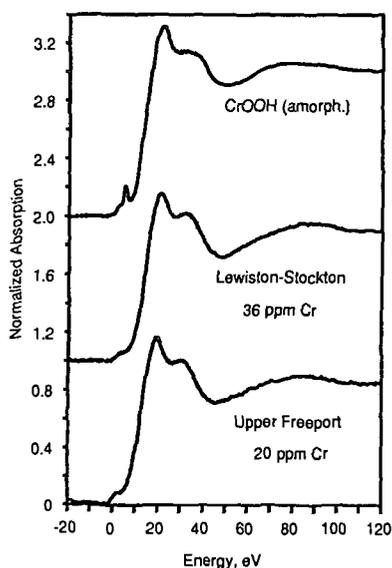


Figure 1: Comparison of Cr XANES spectrum of CrOOH with those for two bituminous coals.

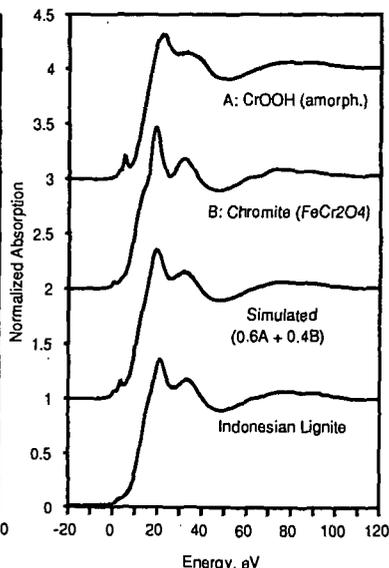


Figure 2: Simulation of Cr XANES for a coal by addition of Cr standard spectra.

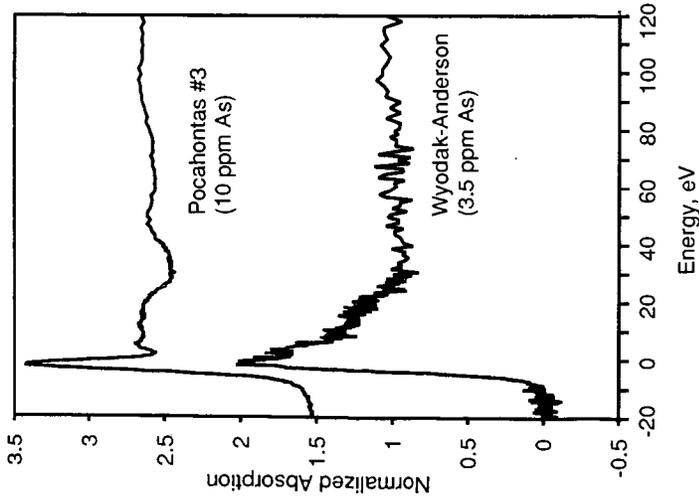


Figure 3: Comparison of As XANES spectra of bituminous and subbituminous coals.

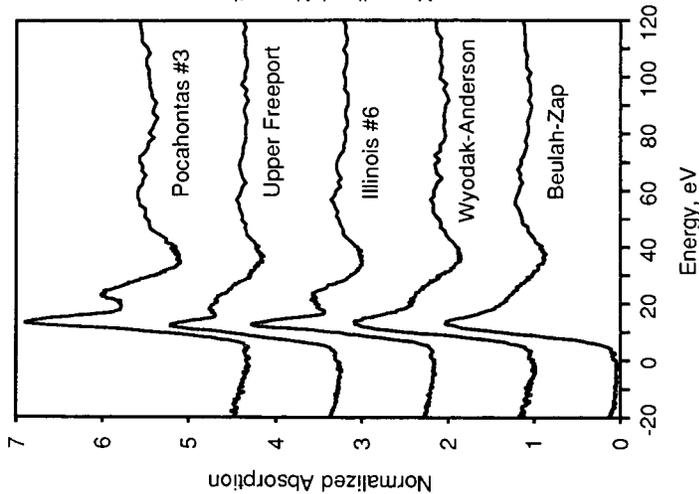


Figure 4: Mn XANES spectra of five Argonne premium sample coals

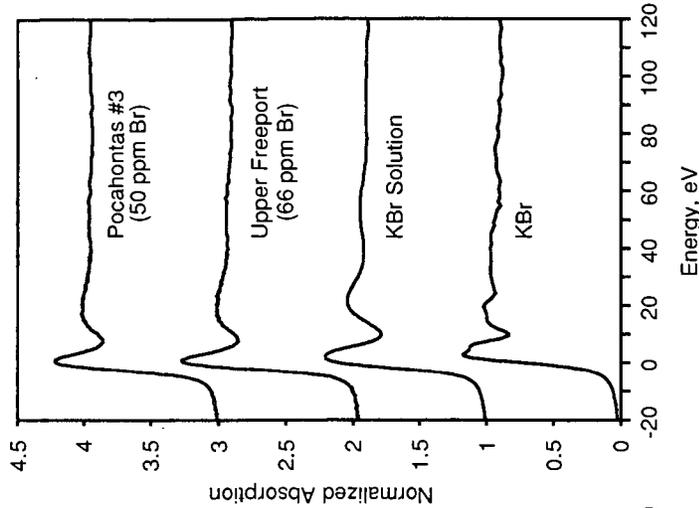


Figure 5: Br XANES spectra of two coals, KBr, and KBr in aqueous solution.