



# How do lithophile elements occur in organic association in bituminous coals?

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## Abstract

In some bituminous coals, typically of high-volatile bituminous rank, certain lithophile trace elements (e.g. Ti, V, Cr, Zr, etc.) often have surprisingly high organic affinities, defined as the fraction of the element reporting to the predominantly organic product (float fraction) in coal-cleaning tests. Examination of these elements in float fractions using XAFS spectroscopy reveals a spectral signature that is incompatible with the mineralogical occurrences of the element that are typically observed for the element in tailings fractions. The spectral signatures for Cr and Zr in float fractions appear similar to those obtained from precipitates from aqueous solution that have been heated at relatively low-temperatures. Such precipitates tend to be poorly crystallized oxides or hydroxides and to have small particle sizes, typically in the 2–10 nm range. However, the corresponding XANES signature for Ti appears more like that from organo-Ti<sup>4+</sup> complexes. Further, it has been observed that the XANES spectra for Cr in a float fraction and in the corresponding low-temperature ash (LTA) are not significantly different, whereas the XANES spectra for Ti in the float fraction and the LTA are different as a result of ashing. We interpret these observations as indicating that these lithophile elements are at different stages in the transition from carboxyl-bound ions to small particle oxide or hydroxide minerals, as a consequence of maceral ion-exchange sites that have undergone decarboxylation during coalification. Closed or isolated porosity of the macerals then prevents significant migration of the liberated inorganic species and their incorporation into larger mineral grains, leaving them as basically poorly crystalline nano-sized oxides or hydroxides. © 2003 Elsevier B.V. All rights reserved.

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## 1. Introduction

A number of lithophile inorganic elements, notably Ti, V, Cr, Zr, etc., can be found predominantly in organic association in certain high-volatile bituminous

coals, particularly some of the Illinois basin coals. Evidence for this comes from the high values of organic affinity (Zubovic, 1966) determined for such elements. For instance, as reported by Gluskoter et al. (1977) for eight U.S. bituminous coals, the organic affinity of Cr varied from a high of 0.80 (Illinois #6 coal) to a low of 0.08 (Illinois #2 coal), implying that the association of Cr can vary from quite highly organic to almost entirely inorganic, depending on the coal. Similar wide ranges

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in organic affinity were also reported for other elements, including Ti, V, and Zr. In the same manner, the observation of a much smaller difference in concentration of an element between float and sink fractions, relative to the difference in ash content, can also be taken to indicate a significant organic association. For example, Huggins et al. (1997) noted that the concentrations of Ti, Cr, V and Ni showed proportionately much less change than wt.% ash between float and tailings fractions of the Kentucky #9 coal, from which it was inferred that these elements had a significant organic association. Similar findings were also presented for an Illinois #6 coal in a recent IEA Round Robin on element speciation in coal (Huggins, 2000). In the same Round Robin study (Davidson, 2000), the fraction of the total Cr reported by different researchers as “organic” varied from an average value of ~ 70% for the Illinois #6 coal to ~ 23% for an English coal (Gascoigne Wood No. 2). These observations raise the question of how these lithophile elements exist in organic association in bituminous coals. Further, the behavior of such organically associated occurrences during coal combustion and other coal utilization processes is likely to be quite different from that of common mineralogical occurrences of the same element. For example, chromium and vanadium are typically listed as transitional from Group I to Group II in classification schemes of trace element volatility during combustion and gasification (Meij, 1989; Clarke and Sloss, 1992). This is somewhat surprising, given their well-recognized refractory behavior in other high-temperature systems, such as igneous petrology, and may indicate a significant occurrence of these elements in coals in “easily volatilizable” organic occurrences.

Indirect speciation methods, such as float/sink tests and leaching tests, however, do not generally provide specific information on how elements might occur in organic association. Direct methods, such as electron and ion-beam methods, performed on macerals, can provide useful information about the chemical associations of an element. However, information pertaining to the atomic scale, such as information on elemental oxidation state and the local structure around the element of interest, is generally difficult to obtain from such methods, especially for trace elements. XAFS spectroscopy, on the other hand, is capable of providing this information regarding the bonding and local structure around an element. In the case of Cr, Zr, and Ti,

XAFS spectral signatures for these elements in maceral-rich fractions of Illinois basin and other coals have been demonstrated to be quite different from those obtained from common mineral forms of these elements. For V, similar XAFS observations have been made, but less is documented about the mineral occurrences of this element in coal rendering such inferences less certain.

In this paper, we summarize observations relating to the occurrence of lithophile elements in organic association in high-volatile bituminous coals and present a hypothesis for how these elements might occur in organic association that we think is consistent with the observations.

## 2. Experimental

The data discussed in this paper are a synthesis of results from X-ray absorption fine structure (XAFS) spectroscopic observations made over a number of years. Such measurements provide a direct, non-destructive means of obtaining information on the local bonding and structure around the element of interest, from which the mode of occurrence of the element can be deduced. The measurements were made at beamline IV-3 at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University, CA, or at beamlines X-18B and X-19A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY. Details of the XAFS experiments have been discussed fully in a number of previous publications (Huggins and Huffman, 1996a; Huggins et al., 1993, 1997, 2000). Normally, the XAFS spectrum is divided into separate X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectral regions (Koningsberger and Prins, 1988). In this paper, only the XANES data are considered, since the data from V, Cr, and Zr in coal are of such limited range or insufficient quality that the EXAFS region cannot be reliably interpreted.

For the most part, the XAFS data to be discussed in this paper derive from samples of the two major coal seams in the Illinois Basin: a Kentucky #9 coal sample and an Illinois #6 coal sample. XAFS data for a number of elements in these two samples have been presented and discussed elsewhere (Huggins et al., 1997; Huggins, 2000), but not in the context

of the present study. Here, we show how the XAFS observations can be used to provide insight as to how Cr, V, Ti and Zr exist in organic association in these coals.

The arguments presented here are based in large part on comparisons of XANES spectra from coals, float and tailings fractions, low-temperature ash (LTA), and relevant standard compounds of the elements of interest. To augment qualitative comparisons of XANES spectra, which are almost entirely based on the shapes of the spectra, we have developed a statistical parameter for comparison of the spectra. This parameter, referred to here as the sum-of-squares comparison parameter or SCP, provides a quantitative measure of the similarity of two spectra. The parameter is calculated as follows: if  $S_a$  and  $S_b$  are arrays of  $(x, y)$  values representing the normalized XANES spectra of compounds A and B, respectively, then a convenient numerical value for the difference,  $D_{a,b}$ , between the spectra is defined as the sum of the squares of the differences,  $[y_a(i) - y_b(i)]$ , at each point,  $x(i)$ , in the spectral range of interest:

$$D_{a,b} = \sum_{x(i)} [Y_a(i) - Y_b(i)]^2. \quad (1)$$

In the standard data reduction of XANES spectra (e.g. Koningsberger and Prins, 1988), the absolute

height of the spectrum is always normalized by an arbitrary factor so that the step-height at the absorption edge is unity. Such normalization affords the best comparison of suites of XANES spectra. We have taken advantage of the arbitrariness of this normalization procedure to determine the value of  $D_{a,b}$  as a function of a multiplicative height factor,  $H$ , applied to one of the two normalized spectra. Hence,  $D_{a,b}$ , is calculated for each value of  $H$  over the range from 0.85 to 1.15 by 0.01 increments and the minimum value of  $D_{a,b}$  as a function of  $H$  is then defined as the sum of squares comparison parameter,  $SCP_{a,b}$ , for compounds A and B:

$$SCP_{a,b} = \min(D_{a,b}), \text{ at the point where } d(D_{a,b})/dH \text{ is } 0. \quad (2)$$

This calculation was carried out by means of a spreadsheet program for pairs of spectra interpolated to an identical energy scale in terms of the number of points and the energy-scale value for each  $x(i)$  point. The summations for  $D_{a,b}$  and  $SCP_{a,b}$  are extended over the edge region; that is, from about  $-40$  to  $+50$  eV. The more similar are the two spectra, the smaller is the  $SCP_{a,b}$  value. An example is shown in Fig. 1, where we consider how similar are the Zr XANES spectra of zircon and of Zr associated with an illite. Tables 1, 2 and 3 for Cr, Ti and Zr, respectively, list

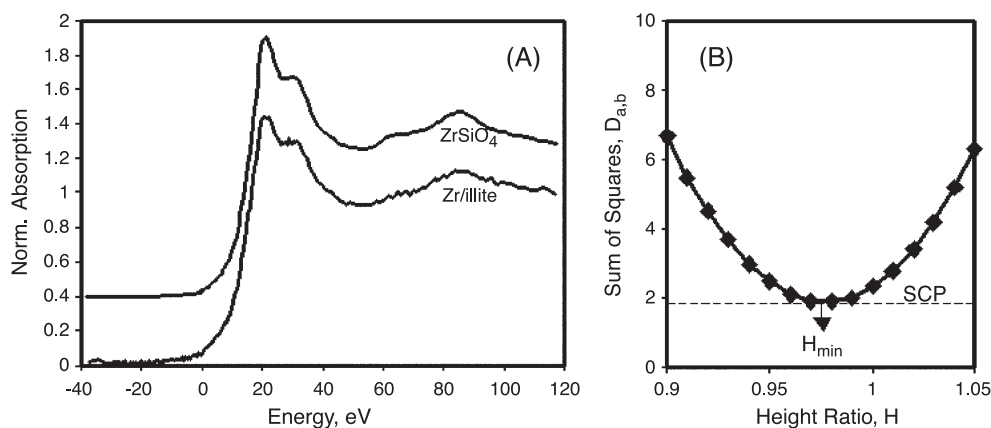


Fig. 1. (A) Comparison of Zr XANES spectra for synthetic zircon ( $ZrSiO_4$ ) and Zr contained in illite. Spectra are normalized to unit edge-step ( $H = 1.0$ ) and offset by 0.4 units in absorption. (B) Variation of the sum of squares,  $D_{a,b}$ , with  $H$ , a multiplicative factor applied to the absorption intensity of Zr/illite, for the spectral comparison. The SCP value is 1.90 for this spectral comparison; it is defined as the minimum value of  $D_{a,b}$ , which occurs at a value of  $H_{min} = 0.975$ . Such an SCP value is high relative to a value of  $\sim 0.2$  for an “ideal” fit and indicates that zircon is not the only Zr form contributing to the Zr XANES of this particular illite. The zero-point of energy for Zr XANES spectra occurs at 17,998 eV.

Table 1

SCP values for comparison of Cr XANES spectra for Illinois #6 coal and fractions and various Cr oxide minerals and Cr-bearing silicates

	Ill#6 Float	Ill#6 Raw	Ill#6 Tails	Cr(OH) <sub>3</sub>	CrOOH-a	CrOOH-g	Cr/illite
Ill#6 Float	0	<b>1.34</b>	7.6	<b>1.32</b>	4.6	7.3	12
Ill#6 Raw		0	6.1	<b>1.51</b>	4.6	6.7	11
Ill#6 Tails			0	5.1	7.5	5.5	<b>3.4</b>
Cr(OH) <sub>3</sub>				0	<b>2.7</b>	5.2	13
CrOOH-a					0	3.8	21
CrOOH-g						0	16
Cr/illite							0
Cr/musc							<b>1.49</b>

Low SCP values in *italics and bold* indicate closely similar spectra.

CrOOH-a, small-particle amorphous CrOOH—contains about 15% of total Cr as Cr(VI).

CrOOH-g, crystallized CrOOH (grimaldiite).

comparative SCP values for many of the spectra discussed in this paper.

### 3. Summary of observations

#### 3.1. Chromium

Based on a number of recent XAFS investigations into the mode of occurrence of chromium in various bituminous coals, chromium appears to occur in most bituminous coals in only two major forms: as Cr<sup>3+</sup> in organic association and as Cr<sup>3+</sup> in illite (Huggins et al., 1993, 1997, 2000). Other chromium occurrences, e.g. Cr<sup>3+</sup> in chlorite (Huggins, 2000), Cr<sup>3+</sup> in chromite/magnetite spinel (Brownfield et al., 1995; Ruppert et al., 1996; Pollock et al., 1989; Huggins et al., 2000), and crocoite (PbCrO<sub>4</sub>) (Li et al., 2001), which have all been recently identified, appear to be of quite restricted origin. For example, occurrences of Cr in chromite/magnetite spinel are found to be significant only in coals with unusually high Cr contents that are located close to ultramafic deposits (Foscolos et al., 1989; Brownfield et al., 1995; Ruppert et al., 1996). Such deposits weather easily and release Cr-bearing spinels that can then accumulate as detrital minerals in coal-forming peats.

The chromium XAFS spectra of float and tailings fractions of bituminous coals with more typical Cr contents (between 5 and 40 ppm Cr; Swaine, 1990; Bragg et al., 1998) consistently show a division into two characteristic spectral types (Fig. 2): the sink fraction generally yields a spectrum that is closely similar to that from Cr<sup>3+</sup> in illite (Fig. 3A), whereas

the float or organically associated fraction yields a spectrum that does not resemble any of the common mineralogical occurrences of chromium (Huggins et al., 1993, 1997, 2000). Note that the Cr XANES spectrum of the raw Illinois #6 coal shown in Fig. 2 more closely resembles that of the float fraction (SCP=1.34, Table 1) than it does the spectrum of the tailings fraction (SCP=6.1, Table 1). This observation indicates that most of the chromium in this coal is in the form associated with the organic fraction.

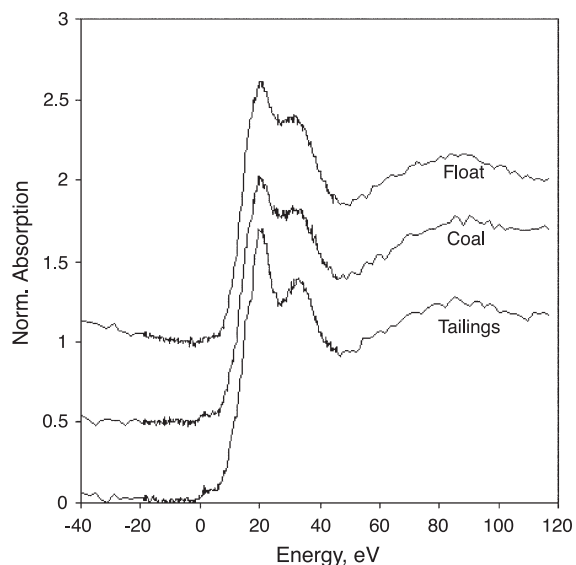


Fig. 2. Chromium XANES spectra of an Illinois #6 coal and the float and tailings fractions separated from the coal in a Denver flotation cell. The zero-point of energy for Cr XANES spectra occurs at 5989 eV.

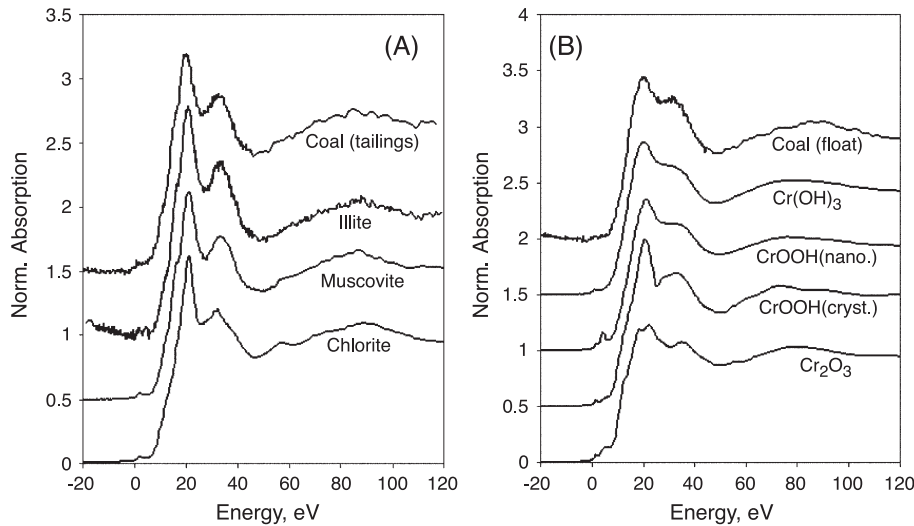


Fig. 3. Comparison of Cr XANES spectra for tailings and float fractions of Illinois #6 coal with Cr XANES spectra of (A) Cr-bearing clay minerals and (B) various Cr oxide minerals, respectively.

More refined separation schemes involving separation of a fraction that sinks in bromoform occasionally reveal additional Cr mineral forms such as chlorite (Huggins, 2000) or chromite-bearing spinel (Huggins et al., 2000); however, such occurrences are typically minor contributions (<5%) to the total chromium in coals of typical Cr contents.

Fig. 3b compares the XANES spectrum of the float fraction of the Illinois #6 coal with those of various chromium hydroxide and oxyhydroxide compounds. The closest match to the spectrum of the float fraction is exhibited by that of Cr(OH)<sub>3</sub> (SCP = 1.32, Table 1), although the small-particle CrOOH spectrum is also quite similar (SCP = 4.3, Table 1) and would be even more similar, if it did not contain 15% of its Cr as Cr(VI) (Huggins et al., 1999). The XANES spectrum of the crystalline CrOOH phase is not nearly so good a match as it has a much higher SCP value (SCP = 7.3, Table 1) in comparison to the Illinois #6 float fraction than either of the two hydroxide phases. These three chromium compounds were synthesized by first precipitation of Cr(OH)<sub>3</sub> from a Cr<sup>3+</sup> nitrate solution at room temperature, followed by heating to 140 °C for 18 hours that resulted in a 17% weight loss and the formation of small-particle CrOOH. A further 9% reduction in weight was achieved by heating the latter phase to 500 °C, consistent with the formation of Cr<sub>2</sub>O<sub>3</sub>. The small-particle CrOOH was also hydro-

thermally treated at 180 °C and ~ 500 psi for 1000 h, resulting in the formation of a crystalline phase. X-ray diffraction showed that the crystalline phase formed was the hexagonal isomorph of CrOOH, viz. grimaldite. X-ray diffraction of the small-particle CrOOH and the Cr(OH)<sub>3</sub> precipitate showed many fewer and much broader diffraction lines than were observed for the crystalline phase. However, the few lines observed for the small-particle CrOOH were at similar positions to major lines in the XRD pattern for crystalline CrOOH.

It has been noted (Huggins et al., 2000) that small particle CrOOH should be soluble at either the HCl or HNO<sub>3</sub> stage in sequential leaching protocols designed to speciate elements in coal, whereas the organically associated chromium phase identified by leaching protocols is insoluble in all acids (Davidson, 2000; Huggins et al., 2000). This apparent divergence between the XAFS and sequential leaching results can be resolved. For example, it could imply that the CrOOH is associated with the organic fraction in such a way that it is inaccessible to attack by acidic solutions. Finally, we note that the Cr XANES spectra of the low-temperature ash (LTA) of float and sink fractions of a Kentucky #9 coal are essentially identical to those of the corresponding coal fractions. This observation implies that the chromium associated with the organics in the float fraction is not intimately bonded to the carbonaceous material, but likely exists

in separate coherent entities that are minimally affected by the oxidation of the surrounding macerals during the low-temperature ashing.

Recent work by Wang et al. (2003) has shown that the leachability of Cr from coal can be quite different compared to that from the corresponding LTA with identical reagents. In all four coals that they investigated, only 10–20% of the chromium could be removed by 6% HCl and HNO<sub>3</sub> acid treatments, whereas as much as 60–80% of the Cr was removed from the corresponding LTA by the identical treatment. Such observations do appear to demonstrate that organically associated Cr in coal can be largely shielded from attack by acidic reagents. Wang et al. (2003) also presented similar findings for vanadium.

### 3.2. Titanium

Investigations into the mode of occurrence of titanium in coal have indicated that titanium occurs in a number of forms. As summarized by Swaine (1990), such forms include two varieties of TiO<sub>2</sub>, viz. rutile and anatase, Ti associated with clays, Ti associated with quartz, and Ti associated with macerals. Except for Ti associated with quartz, all of these forms have been recognized in Ti XANES spectra of various coals and fractions (Huggins and Huffman, 1996a). In addition, based on its XAFS spectral signature, significant Ti has been identified as occurring in illite in bituminous coals and, more clearly, in corresponding tailings fractions (Huggins and Huffman, 1996a; Huggins, 2000). Often, Ti/illite occurs in conjunction with one or other forms of TiO<sub>2</sub> in these coals and fractions (Huggins and Huffman, 1996a). XAFS examination of Ti in float/sink fractions of Illinois basin coals (Wong et al., 1983; Huggins and Huffman, 1996b; Huggins et al., 1997; Huggins, 2000) reveals a unique spectral signature in float fractions of certain coals that is quite clearly different from any of the common mineralogical occurrences of Ti listed above, as well as less common ones listed by Waychunas (1987). As shown previously (Huggins and Huffman, 1996b), similar spectral signatures have been noted for unfractionated subbituminous coals. The occurrences that give the most similar XANES spectra to that observed for organically associated Ti in coal arise from Ti in organo-titanium complexes of the type: (NH<sub>4</sub>)<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>).H<sub>2</sub>O (Fig. 4) or organo-Ti

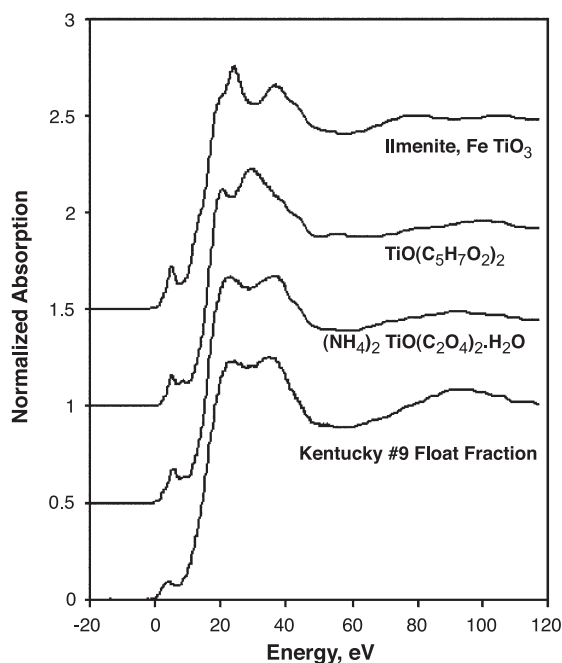


Fig. 4. Ti XANES spectra of Illinois #6 float fraction and of ilmenite (FeTiO<sub>3</sub>) and two organo-Ti compounds. The zero-point of energy for Ti XANES spectra occurs at 4966 eV.

(“Tyzor”) (Wong et al., 1983) compounds or alkoxide compounds (Sandstrom et al., 1982). In all three types of organic complexes, the titanium is present as Ti<sup>4+</sup> in distorted octahedral coordination by oxygen anions. However, there remain still minor differences between the spectra from Ti in coal float fractions and those from Ti in these compounds, particularly with respect to the small pre-edge peaks at about 2–5 eV.

Furthermore, unlike Cr for which no significant change was seen upon low-temperature ashing, the Ti XANES of the LTA of the float fraction of the Kentucky #9 coal (Fig. 5) is altered from that of the original float fraction (Fig. 4). A SCP value of 6.3 was found for the comparison of the Ti XANES spectrum of the Kentucky #9 float fraction with that of the corresponding LTA (Table 2). In contrast, the same comparison for the tailings fraction, which contains mostly Ti/illite, yielded a value of just 3.1. These observations suggest that significant interaction between Ti and the organic matrix must exist in the coal macerals, consistent with the occurrence of isolated Ti ions in organic combination. The closest match to the

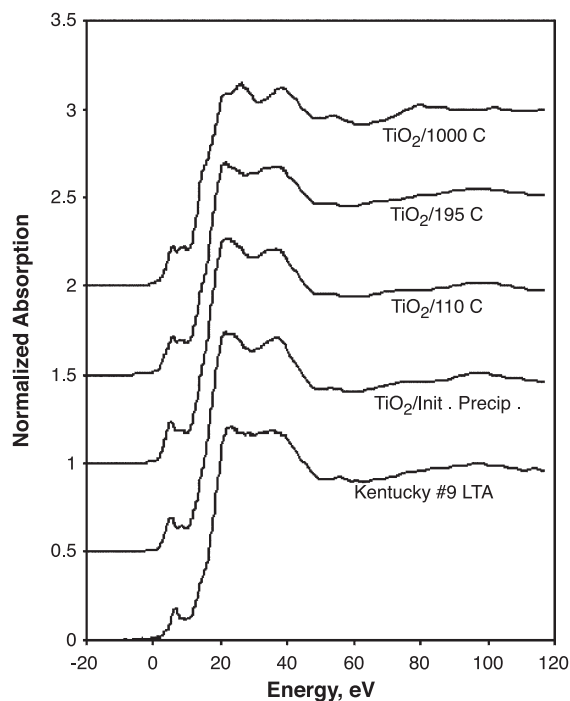


Fig. 5. Ti XANES spectra of the LTA of the Kentucky #9 float fraction and of a  $\text{TiO}_2$  precipitate heated to various temperatures. Note the difference in spectral appearance between the spectrum of the LTA and the corresponding float fraction shown in Fig. 4 (see also Table 2).

spectrum of Ti in the LTA of the float fraction is exhibited by small particle  $\text{TiO}_2$  heated to  $\sim 195^\circ\text{C}$  (SCP=4.4, Table 2). Again, the match is not exact as

there are minor differences in the pre-edge regions of the spectra.

### 3.3. Vanadium

Less is known about the occurrences of V in coal and coal fractions than of those of either Cr or Ti. As summarized by Swaine (1990), most authors indicate that a major association of V appears to be with clay minerals. XAFS investigations (Maylotte et al., 1981; Huggins et al., 1997) of inorganic-rich sink fractions derived from the Kentucky #9 coal are also consistent with such an occurrence, and suggest more specifically that illite is the likely host for vanadium. Again, as was observed for both Cr and Ti, the vanadium XANES spectra of the corresponding float fractions exhibit a quite different spectral signature; moreover, the XAFS data (Maylotte et al., 1981; Huggins et al., 1997) indicate that the oxidation state of V in organic association is mostly  $\text{V}^{4+}$  rather than  $\text{V}^{3+}$  that dominates the association with the clays. Also, as mentioned above for Cr, Wang et al. (2003) demonstrated significantly different leachability behavior for V in coal compared to the corresponding LTA under identical reagent treatments, indicating that organically associated forms of V are largely shielded by the macerals from attack by acid reagents. By analogy with other elements, we suspect that the vanadium occurrence in the float fraction consists of poorly crystalline oxide ( $\text{V}_2\text{O}_4$ ) or oxyhydroxide ( $\text{VO}(\text{OH})_2$ ) species that are intimately associated with coal macerals. However, further work is still needed to establish the exact identity of this occurrence.

Table 2

SCP values for comparison of Ti XANES spectra for Kentucky #9 coal, fractions, and LTA, and for various  $\text{TiO}_2$  compounds

	$\text{TiO}_2$ init. precipitate	$\text{TiO}_2$ 110	$\text{TiO}_2$ 195	$\text{TiO}_2$ 1000	KY9 Float	KY9 Tails	KY9 LTA Float	KY9 LTA Tails
$\text{TiO}_2$ init.	0	4.1	5.0	17	5.3	<b>2.9</b>	16	24
$\text{TiO}_2$ 110 °C		0	<b>1.1</b>	6.5	7.7	9.1	27	35
$\text{TiO}_2$ 195 °C			0	6.0	6.2	7.1	4.4	8.4
$\text{TiO}_2$ 1000 °C				0	16	20	37	41
KY9 Float					0	<b>3.2</b>	6.3	23
KY9 Tails						0	19	<b>3.1</b>
KY9 LTA Flt							0	<b>2.9</b>
KY9 LTA Tls								0

Low SCP values in *italics and bold* indicate closely similar spectra. LTA-low temperature ash.

The  $\text{TiO}_2$  samples were initially prepared by precipitation of  $\text{TiCl}_4$  in an aqueous solution and were then heated in air for 6 h at the indicated temperatures to promote small-particle crystal formation. The sample heated to 1000 °C has the rutile structure.

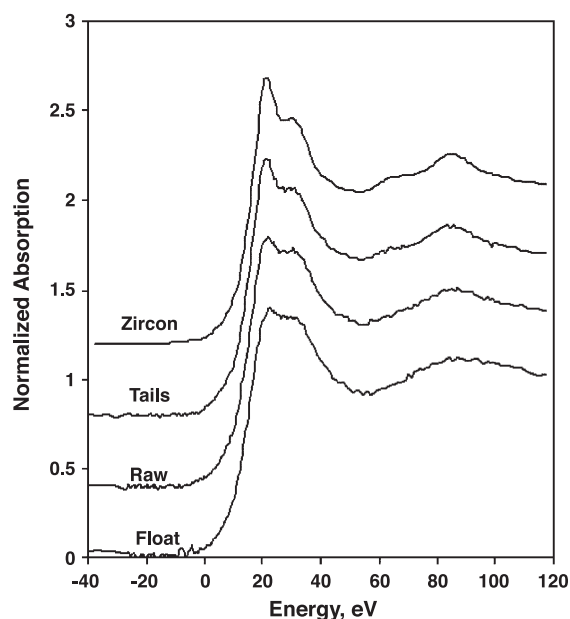


Fig. 6. Zr XANES of Wyee (Raw) coal, Australia, and of float and tailings fractions prepared from it by Denver cell flotation. Also shown is the Zr XANES spectrum for zircon ( $\text{ZrSiO}_4$ ).

### 3.4. Zirconium

Even less is established regarding the mode of occurrence of Zr in coal. Both mineralogical and organic associations have been postulated for this element in coal (Swaine, 1990). XAFS data for Zr in float and sink fractions from three coals, the Wyee coal (Australia), the Gascoigne Wood No. 2 coal (England), and the Illinois #6 coal, have been presented elsewhere (Huggins, 2000). All three coals exhibited spectra

similar to those shown in Fig. 6 for the Wyee coal and derived fractions. As documented in Table 3, such spectra do indicate that the dominant Zr occurrences in the float and tails fractions are different. The Zr XANES spectrum for the tails fraction is most similar to that of Zr/illite (SCP=0.36, Table 3). The spectrum of zircon ( $\text{ZrSiO}_4$ ) (SCP=0.88, Table 3), which is the zirconium mineral thought most likely to exist in coal (Swaine, 1990), does not provide quite as good a match. However, as indicated in Fig. 1, the illite standard may in fact contain a significant fraction of its Zr also in the form of zircon. The Zr XANES spectrum of the float fraction differs more substantially from either that of Zr/illite or zircon (SCP=1.8 and 4.4, respectively, Table 3); and, except possibly for the spectrum of  $\text{ZrO}_2$  (SCP=1.5, Table 3), it is different from those of all other standard Zr compounds included in Table 2, as well as those in published compilations of XANES spectra of Zr in other common minerals (Farges et al., 1994; Mountjoy et al., 2000a,b; Gregor et al., 2001). Recent studies of nano-sized zirconium hydroxides and oxides (Mountjoy et al., 2000b; Chadwick et al., 2001) provide examples of the Zr XANES spectra of small-particle  $\text{Zr}(\text{OH})_4$  and  $\text{ZrO}_2$ . These spectra appear to most closely resemble those observed for zirconium in float fractions of the Wyee coal (Fig. 6) and other coals (Huggins, 2000).

### 4. Proposed occurrence for Ti, V, Cr and Zr in organic association in bituminous coals

The following scenario is proposed to account for the above observations on the four lithophile elements

Table 3

SCP values for comparison of Zr XANES spectra for Wyee coal and fractions and various Zr standard compounds

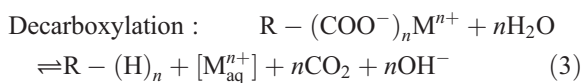
	Raw Coal	Coal Float	Coal Tails	ZrC	ZrFoil	Zr/illite	$\text{ZrO}_2$	$\text{ZrS}_2$	$\text{ZrSiO}_4$	$\text{ZrSO}_4$
Raw Coal	0	<i>0.45</i>	<i>1.1</i>	31	68	<i>0.74</i>	<i>1.4</i>	26	3.3	7.7
Coal Float		0	2.1	33	70	1.8	<i>1.5</i>	27	4.4	6.8
Coal Tails			0	36	76	<i>0.36</i>	3.1	32	<i>0.88</i>	7.8
ZrC				0	16	27	26	2.2	39	50
ZrFoil					0	75	72	15	92	106
Zr illite						0	9	28	1.9	9
$\text{ZrO}_2$							0	23	5.3	5.6
$\text{ZrS}_2$								0	45	52
$\text{ZrSiO}_4$									0	7.2
$\text{ZrSO}_4$										0

Low SCP values in *italics and bold* indicate closely similar spectra.



emphasized in this paper. In order for these elements to have a significant organic association that persists at least to the high volatile bituminous stage of coalification, it is probable that they were adsorbed by the organic matter in the peat stage and were well distributed throughout the organic matter. Various authors have argued that significant fractions of metals can be attached to organic matter in peat and low-rank coals via ion-exchange processes (Eskenazy, 1972; Kiss and King, 1977; Karner et al., 1984, 1986; Miller and Given, 1986, 1987; Given and Miller, 1987; Aida et al., 1997, 2001). Eskenazy (1972) has demonstrated specifically that titanium is attached to the organic matter in peat predominantly by an ion-exchange mechanism. Miller and Given (1986) found that “Sc, Cr, Y, Yb, V and Ni [in lignite] show a much greater degree of association with organic matter than has been reported for a number of bituminous coals”. They also reported that Zr is strongly enriched in the organic-rich fractions of one lignite they investigated, but also indicated that such an occurrence is not universal (Given and Miller, 1987).

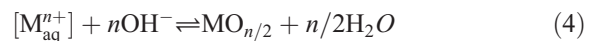
One of the more important processes that is thought to influence the behavior of elements during coalification is the decarboxylation process that occurs when low-rank coals are converted into higher (bituminous) rank coals. Aida et al. (1997, 2001) have determined separately the contents of carboxyl (–COOH) sites and those carboxyl sites bound to metals (–COOM) in many coals and have shown an approximate inverse relationship between the total carboxyl functionality (–COOH + –COOM) and increasing rank of coal. The loss of carboxyl and other oxygen functionality as coals of increasing rank evolve results in the mineralization of many elements. The moisture in coal is likely to play a major role in helping to transfer elements between the increasingly tenuous carboxyl sites and the increasingly stable mineral forms. In the general case, decarboxylation may be written as:



where R represents the maceral, –COO<sup>–</sup> represents a carboxyl group, and M<sup>n+</sup> represents a metal cation of oxidation state n+. Since carboxyl–cation bonds are

ionic, the strongest bonds and most stable carboxyl complexes will be formed by elements of the highest valence state and it is likely that such complexes containing higher valence cations will therefore also persist to more extreme conditions of coalification. Eventually, however, such complexes will undergo decomposition and the metal ions will be liberated for incorporation into minerals, especially clays. However, in the absence of clay minerals, an alternative mineralization would involve formation of an oxide or hydroxide species, by precipitation reactions similar to the following:

Oxide formation :



As rank increases further, the moisture content in the coal also decreases and becomes increasingly saturated with respect to dissolved species, which further impels ionic species to enter into mineralization. In addition, the aqueous solubilities of oxide and hydroxide compounds tend to decrease with increasing valency. Hence, compared to lower valence species, higher valent cations, such as Cr<sup>3+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, etc., should have a much more limited existence as aqueous ions in coal and more readily form oxide and hydroxide minerals than lower valent cations. In order for such microcrystalline oxyhydroxide and oxide species to avoid reaction and incorporation into clays, they must be precipitated into closed or highly restricted pores in the coal that do not allow significant interaction with clay minerals. In agreement with the recent findings of Wang et al. (2003), such occurrences in closed porosity would also prevent them from being attacked by reagents during leaching tests. Recent studies of porosity in coal (Larsen et al., 1995; Hall et al., 1998, 2000; Alexeev et al., 1999) argue strongly for the existence of closed pores in coal and the data do indicate that closed porosity becomes increasingly prevalent as rank increases (Alexeev et al., 1999; Hall et al., 2000). Such formation of microcrystalline oxides and oxyhydroxides in closed pores in coal macerals may be a natural analogue of the synthetic preparation of nanoparticles of materials inside a mesoporous host or template (Lakshmi et al., 1997; Moller and Bein, 1998; Chen et al., 1999; Zhang et al., 2000). In such syntheses, the host or template material restricts the growth of the guest phase to no more than the size of its pores.

It should be noted that whereas the organic association of Cr in coals of high-volatile bituminous rank seems to be quite well established as microcrystals of CrOOH, the evidence for Ti is more equivocal. Indeed, the evidence is perhaps better interpreted as indicating that Ti exists as both an organic complex and as microcrystalline TiO<sub>2</sub> and that the transition between the two may not be complete. Such differences between Ti and Cr would be consistent with the proposed scheme since the higher valent Ti organo-complex would be expected to resist decarboxylation to higher conditions of coalification than similar Cr species. Recent work by Aida et al. (1997, 2001) indicates that coals of high volatile bituminous rank and even higher may contain significant quantities of carboxyl sites bound to metals.

## 5. Conclusions

Data from XAFS spectroscopy on the occurrence of four lithophile elements, Ti, V, Cr and Zr, in coals, sink/float fractions, and low-temperature ash from high-volatile bituminous Illinois basin coals have been summarized and interpreted as indicating that these and similar elements may exist in organic association as nano-sized particles of oxides and oxyhydroxides or were arrested in the process of forming such entities. Such particles have formed as a result of their release by carboxyl and other oxygen functional groups that undergo decomposition with increasing coalification. They exist today because of the contemporaneous formation of closed porosity within the macerals that prevents the elements from being incorporated into clays or other minerals. Such an imbedded occurrence within macerals would also explain why these elements are immune to attack by reagents in sequential leaching protocols. Such occurrence as small particles within macerals would also explain the higher than anticipated volatility of these elements during combustion.

The emphasis in this study has been on high-volatile bituminous coals from the Illinois basin. However, similar but limited observations have been made in XAFS studies of coals from other coal regions and suggest that the findings presented here are more broadly applicable.

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