

Trace element geochemistry and surface water chemistry of the Bon Air coal, Franklin County, Cumberland Plateau, southeast Tennessee

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Abstract

Mean contents of trace elements and ash in channel, bench-column, and dump samples of the abandoned Bon Air coal (Lower Pennsylvanian) in Franklin County, Tennessee are similar to Appalachian COALQUAL mean values, but are slightly lower for As, Fe, Hg, Mn, Na, Th, and U, and slightly higher for ash, Be, Cd, Co, Cr, REEs, Sr, and V, at the 95% confidence level. Compared to channel samples, dump sample means are slightly lower in chalcophile elements (As, Cu, Fe, Ni, Pb, S, Sb, and V) and slightly higher in clay or heavy-mineral elements (Al, K, Mn, REEs, Th, Ti, U, and Y), but at the 95% confidence level, only As and Fe are different. Consistent abundances of clay or heavy-mineral elements in low-Br, high-S, high-ash benches that are relatively enriched in quartz and mire-to-levee species like *Paralycopodites* suggest trace elements are largely fluvial in origin.

Factor analysis loadings and correlation coefficients between elements suggest that clays host most Al, Cr, K, Ti, and Th, significant Mn and V, and some Sc, U, Ba, and Ni. Heavy accessory minerals likely house most REEs and Y, lesser Sc, U, and Th, and minor Cr, Ni, and Ti. Pyrite appears to host As, some V and Ni, and perhaps some Cu, but Cu probably exists largely as chalcopyrite. Data suggest that organic debris houses most Be and some Ni and U, and that Pb and Sb occur as Pb–Sb sulfosalt(s) within organic matrix. Most Hg, and some Mn and Y, appear to be hosted by calcite, suggesting potential Hg remobilization from original pyrite, and Hg sorption by calcite, which may be important processes in abandoned coals. Most Co, Zn, Mo, and Cd, significant V and Ni, and some Mn probably occur in non-pyritic sulfides; Ba, Sr, and P are largely in crandallite-group phosphates. Selenium does not show organic or “clausthalite” affinities, but Se occurrence is otherwise unclear. Barium, Mn, Ni, Sc, U, and V, with strongly divided statistical affinities, likely occur subequally in multiple modes.

For study area surface waters, highest levels of most trace elements occur in mine-adit or mine-dump drainage. Effluent flow rates strongly affect both acidity and trace element levels. Adit drainages where flow is only a trickle have the most acidic waters (pH 3.78–4.80) and highest trace element levels (up to two orders of magnitude higher than in non-mine site waters). Nonetheless, nearly all surface waters have low absolute concentrations of trace elements of environmental concern, and all waters sampled meet U.S. EPA primary drinking water standards and aquatic life criteria for all elements analyzed. Secondary drinking water standards are also met for all parameters except Al, pH, Fe, and Mn, but even in extreme cases (mine waters with pH as low as 3.78 and up to 1243 ppb Al, 6280 ppb Fe, and 721 ppb Mn, and non-mine dam-outflow waters with up to

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18,400 ppb Fe and 1540 ppb Mn) downslope attenuation is apparently rapid, as down-drainage plateau-base streams show background levels for all these parameters.

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1. Introduction

Trace elements in coal include both paleoecologically important elements (Al, B, Br, Cr, Fe, K, REEs, Rb, S, Sr, Th, U, V, Y, and/or Zr, used to assess paleomire influx) (e.g., Hickmott and Baldridge, 1995; Hower et al., 2005c), and those of environmental concern (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Th, V, U, and Zn) (Swaine, 1990; Finkelman, 1995; U.S. EPA, 2002a,b, c). Health and environmental impacts from coal are primarily associated with inhalation of airborne particulates generated by coal mining or combustion, or ingestion of ground- or surface waters that contact coal or its waste products (Wiese et al., 1987; Dreher and Finkelman, 1992; Finkelman, 1995; Finkelman et al., 2002). Thirteen trace elements (As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Se, Sb, Th, U) are identified as Hazardous Air Pollutants (HAPs) by the 1990 Amendments to the U.S. Clean Air Act (U.S. Statutes at Large, 1990; U.S. EPA, 1994, 2003). Mercury emissions from power plants are of particular concern and the subject of recent new regulations (U.S. EPA, 2005) that should lessen the currently wide variations in Hg capture achieved by pollution control equipment (Hower et al., 2005b). In addition, Al, Ag, Ba, Cu, Fe, Tl, Zn, and all HAPs except Ni are drinking water contaminants (U.S. EPA, 2002b,c), and Al, Ag, As, Cd, Cr, Cu, Hg, Mo, Ni, P, Pb, Se, Sn, V, and Zn impact aquatic or terrestrial flora and fauna (U.S. EPA, 2002a).

Studies of trace element contents of Cumberland Plateau (Tennessee) coal or the surface waters affected by it are few, and only two (Byerly, 1979; Hanchar, 1995) pertain to southeast Tennessee (the area of our study). No studies except Harris et al.'s (1981) study of the Peewee and Upper Grassy Spring seams report coal trace element data. Limited aqueous trace element data are given for Cumberland Plateau groundwaters (Hanchar, 1995) and spring waters (O'bara and Estes, 1985) affected by coal mining, but most plateau-area geochemical studies deal with coal mine impacts on water quality (pH, alkalinity, conductance, Ca, Mg, Fe, Mn, SO₄ and/or TDS) (Rose et al., 1979; Byerly, 1979; Gottfried et

al., 1984; Gottfried, 1985; Sasowsky and White, 1993; Loop et al., 2001) or trace elements in sediment of impacted streams (Upham and Rule, 1975; Schrader and Rule, 1975; Schrader and Furbish, 1977).

The Bon Air coal is a bituminous coal that was important in Tennessee from the 1800s to early 1900s. Small abandoned workings, most underground and now collapsed, occur across six Tennessee counties (Fig. 1). We focused on Bon Air coal near Sewanee, Franklin County, southeast Tennessee, where there are 59 adits (largely worked 1874–1922) and one strip mine (dating to the 1940s or 1950s), and where ochreous precipitates (“yellow-boy”) in adit effluent have generated local concern about impacts of the old mines on surface streams. No other studies to date address trace element contents of southeast Cumberland Plateau coals, their mine effluents, or their impact on surface waters. The purpose of our study is threefold: to characterize the trace element contents of the Bon Air coal, to discuss likely modes of elemental occurrence, and to show pH and trace element impacts of the coal on area surface waters. Our work complements a companion palynologic-petrologic-geochemical study of the Bon Air coal in this same area (Shaver et al., 2006—this volume), which interpreted the Bon Air paleomires as small, Early Pennsylvanian (Westphalian A, Langsettian), fluviodeltaic mires that evolved from planar to domed, and that were nutrient-fed by intermittent inputs almost exclusively fluvial in character.

2. Geologic setting

The Bon Air coal occurs as one to six seams (generally <20–48 in. thick, 0.5–1.2 m) that are discontinuously distributed within upper, middle, and/or lower parts of the Lower Pennsylvanian fluviodeltaic Raccoon Mountain Formation (RMF) (Knoll and Potter, 1998; Shaver et al., 2006—this volume) (Figs. 1 and 2). The study area is a 40 square miles (104 km²) part of the southwestern Cumberland Plateau near Sewanee, Tennessee, where mineable Bon Air coal (>10 in. thick, >25 cm) occurs largely in four multiple-adit mine sites (Armfield, Dotson,

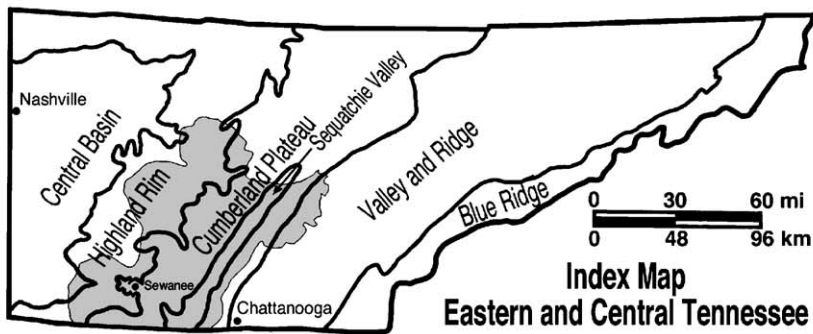
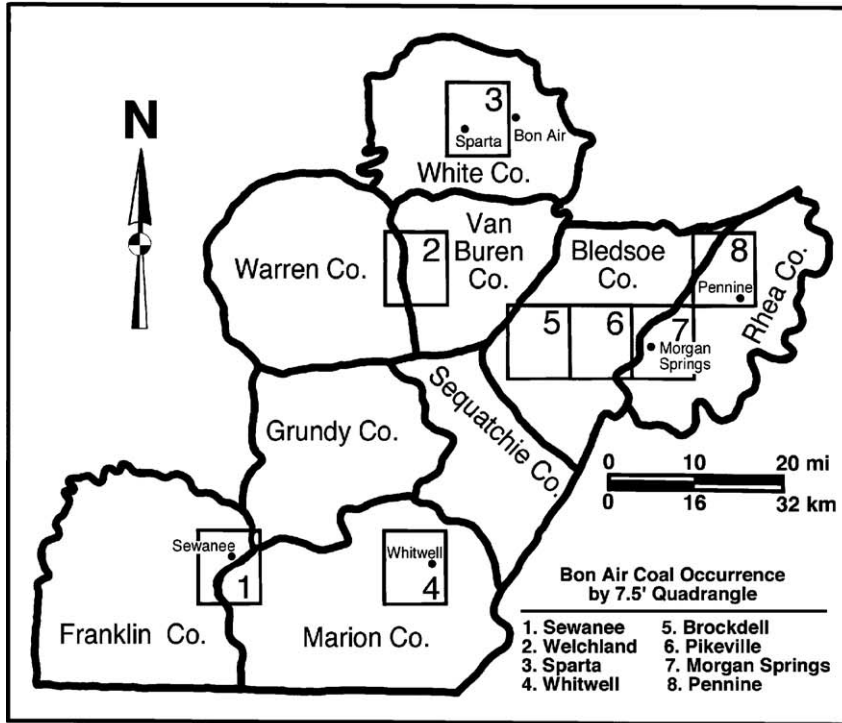


Fig. 1. Occurrence of the Bon Air coal, by Tennessee quadrangle and county.

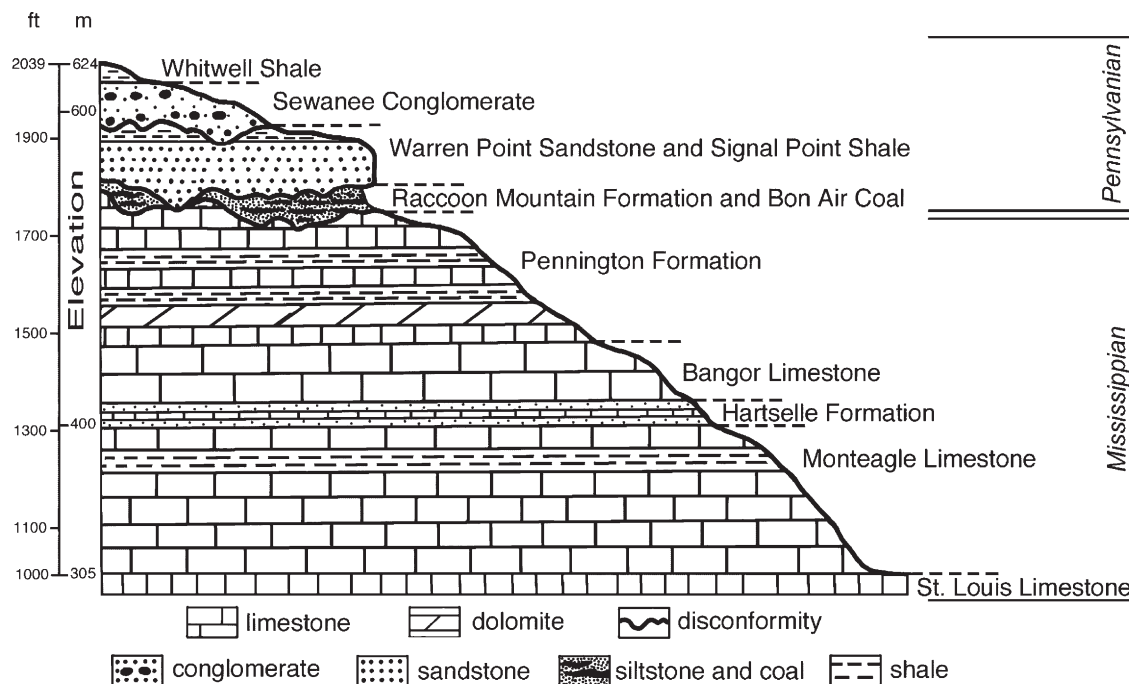


Fig. 2. Generalized Cumberland Plateau stratigraphy near Sewanee, Tennessee, modified after Knoll and Potter (1998).

Rutledge, and Shakerag) 1–1.5 miles (0.6–0.9 km) from one another (Fig. 3). The Armfield site has a single Bon Air seam (1.2 ft thick, 0.36 m) in the top one-third of well-exposed RMF otherwise comprised only of shale. The other mine sites have two to four seams in the top, middle, and/or bottom of RMF composed of complexly interbedded shales, sandstones, and flaser-bedded siltstones. In the few accessible Shakerag adits, the main seam is well-exposed, 1.5–2.0 ft thick (0.45–0.6 m), and abruptly overlain by intraclastic scour-and-fill channel sandstones. All adits at Dotson and Rutledge are collapsed, but data suggest that seams at Rutledge were the thickest in the area (avg. 2.5 ft, 0.76 m, locally to 3.5 ft, 1.1 m), while those at Dotson were thin (<1.5 ft, 0.45 m) (Shaver et al., 2006—this volume). Coal petrology, palynology, and clay mineralogy suggest the mires forming these seams were not identical, even though all domed (Shaver et al., 2006—this volume). The Armfield paleomire was likely low-lying and channel-distal, perhaps an oxbow lake or floodplain depression. Shakerag’s mire appears to have been channel-proximal and especially prone to intermittent clastic incursion and channel truncation. Mires at Dotson and Rutledge were probably topographically elevated or protractedly domed mires that were particularly vulnerable to drought or fire.

3. Previous studies of trace element modes of occurrence in coal

Because trace elements occur in both organic material and inorganic ash “impurities” in coal (especially clay, sulfide, carbonate, or heavy minerals), the likelihood of elemental release to the environment, and the effectiveness of coal washing as a means of mitigating this release, are controlled significantly by the mode of occurrence of an element (Finkelman, 1995) and the size and textural relationships of the three minerals (pyrite, kaolinite, and illite) that collectively contain most of the trace element mass balance in Euramerican bituminous coals (Palmer and Lyons, 1996). For example, elements housed in large mineral grains in cleats or fractures would be relatively easy to remove by coal washing (Diehl et al., 2004). Those in organometallic compounds, in clays in porous pyrite, or in micron-sized sulfides enmeshed in organic matrix would be difficult to remove by washing (Finkelman, 1995; Wiese et al., 1990). Washing may produce even higher element levels in the coal in some cases (e.g., Mastalerz et al., 2004).

A voluminous and ever-growing literature discusses trace element modes of occurrence in coals. Bulk-sample analytical techniques (atomic absorption, INAA, ICP-MS, XRD, or XRF), coupled with sink-float mineral/

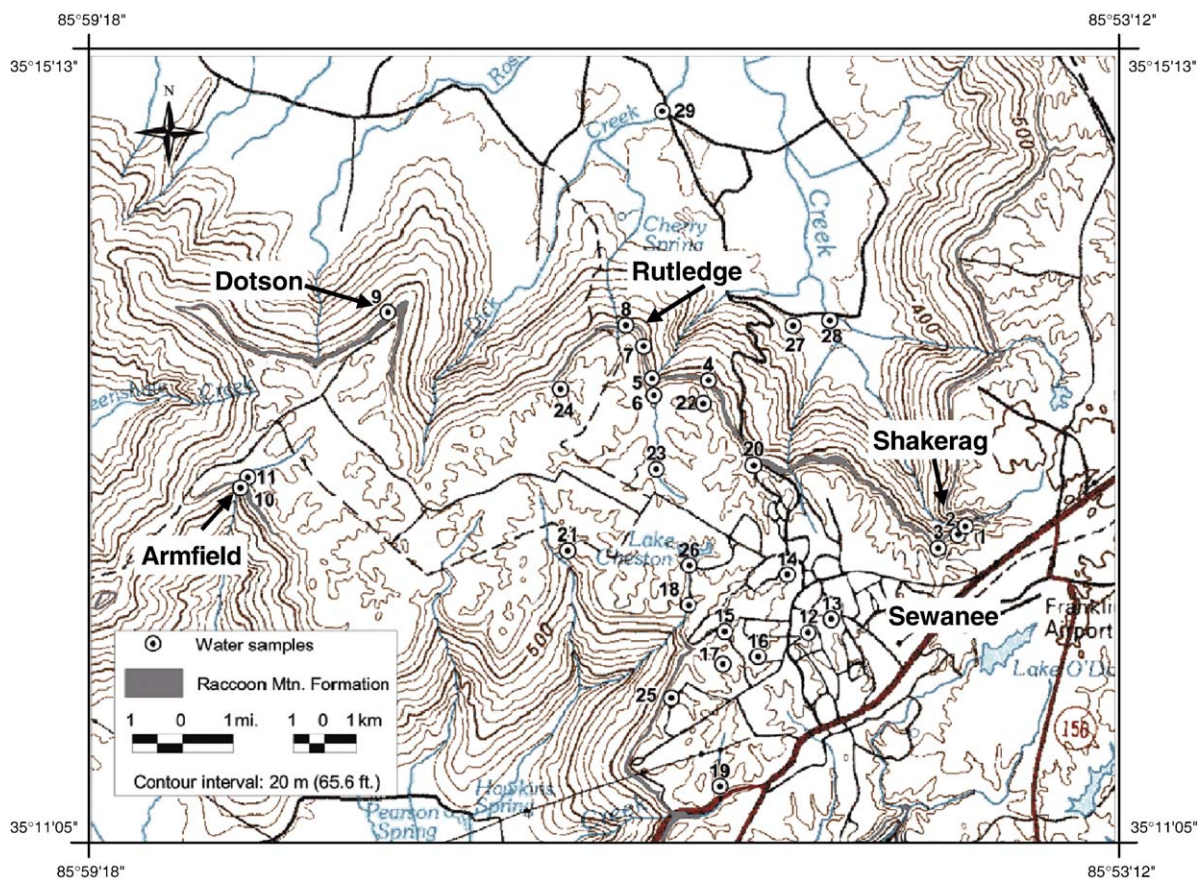


Fig. 3. A portion of the Sewanee 7.5' topographic quadrangle, showing Bon Air coal mine sites (Armfield, Dotson, Rutledge, and Shakerag) and host Raccoon Mountain Formation in relation to surface water samples (1–29) detailed in Table 7.

maceral separations, demineralization or leaching procedures, ion-exchange treatments, statistical correlations between elements, or ash to whole-coal comparisons (e.g., Gluskoter et al., 1977; Kuhn et al., 1980; Spears and Zheng, 1999; Alastuey et al., 2001; Zhuang et al., 2003), are among the indirect techniques that provide the bulk of elemental mode-of-occurrence data for coals. Direct, microanalytical techniques provide further insights. These include scanning electron microscopy/energy dispersive X-ray fluorescence analysis (SEM-EDX), electron microprobe analysis (EPMA), transmission electron microscopy (TEM), proton-induced X-ray emission (PIXE) microanalysis, secondary ion mass spectrometry (SIMS), laser-ablation inductively coupled plasma mass spectrometry (LA ICP-MS), and synchrotron-radiation induced X-ray fluorescence (SXRF) (e.g., Finkelman, 1981a; Hickmott and Baldrige, 1995; Vassilev and Vassileva, 1996; Huggins and Huffman, 1996, 2004). While more data are still needed for some elements (especially Be, Co, Hg, Mo, Ni, and Sb), studies collectively suggest the following associations

for elements of environmental concern in most coals of sub-bituminous or greater rank:

- As occurs largely in Fe-sulfides, and less often as discrete As-sulfides.
- Ag, Co, Cu, Hg, Mo, Ni, Pb, Sn, Tl, and Zn, all chalcophile elements, often occur as distinct metal sulfides or within Fe-sulfides. However, Co data are somewhat unclear; Hg can have many hosts, especially in Hg-rich coals; Mo and Zn can occur in organic debris or other sulfides; Ni can occur in heavy minerals (chromite or spinel), or in organics or clays; and Pb can occur in selenides.
- Ba occurs mostly in barite or secondary crandallite-group aluminum phosphates, but witherite (BaCO_3) and Ba-bearing feldspars are also known.
- Be and Se are often organically bound, but Be is known in clays and Se may occur in sulfides or complex Pb-bearing selenide(s) that may be clausthalite.
- Cd largely occurs in sphalerite, but it may also occur in pyrite.

- Cr and V are generally in clays (particularly illite); they are less common in heavy minerals like chromite, ilmenite, magnetite, or spinel, but also occur as amorphous(?) oxides and hydroxides (of unclear abundance) in organic debris.
- Mn commonly substitutes for Ca and Fe in calcite, ankerite, or siderite, but it can also be organically bound, or occur in clays or Fe-sulfides.
- P occurs in apatite, crandallite-group phosphates, or heavy minerals such as xenotime (YPO₄) and monazite ((REE, Sc,Th,Y)PO₄).
- Sb data are unclear, but suggest both organic and sulfide associations.
- Th and U, chiefly in heavy minerals like monazite, zircon, or xenotime, can also occur in uraninite, organic debris (especially at lower ranks), or clays.

4. Methods

Representative 4-kg Bon Air coal samples were collected at 26 mine sites (23 adits, two strip mine sites, and one cliff-face working) from the four mine areas. Sampling avoided clearly weathered coal, and samples were taken from the seam(s) best exposed or most intensely mined in the past at each site (the single Armfield seam, both Dotson seams, the thick “main” seam at Rutledge and Shakerag, and the Upper Shakerag cliff-face seam). At 20 of the adits, collapsed workings necessitated sampling the coal entirely from adit dumps. At sites where both seams and their dumps were exposed (Shakerag 1, 2, and 3; Armfield 3 and 4), both channel and dump samples were collected in order to assess trace element variations between these two sample types. Because many components in seams and benches can show abrupt lateral variations (Greb et al., 2002), multiple channel samples were also collected at two sites (Upper Shakerag 1 and Shakerag 1) to assess channel sample variability at a single location. In all, 35 dump and channel samples were collected. In addition, 13 samples from bench-columns of two seams and their caprocks and seatrocks (Armfield 4 and Shakerag 1) were collected to study bench-to-bench variations in trace elements.

Following standard procedures (Meier et al., 1996; Crock et al., 1999), all 48 coal samples were split and analyzed by Activation Laboratories in Ancaster, Ontario. Analytical methods used were instrumental neutron activation analysis (INAA) for Au, As, Ba, Br, Co, Cr, Cs, Fe, Hf, Mo, Na, Rb, Sb, Sc, Se, Ta, Th, U, W, and rare earths (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu); inductively coupled plasma emission spectrometry (ICP) for Ag, Al, Be, Ca, Cd, Cu, K, Mg, Mn, Ni, P,

Pb, Sn, Sr, Ti, V, Y, Zn, and Zr; inductively coupled plasma mass spectrometry (ICP-MS) for Cd; cold vapor atomic absorption spectroscopy (AAS) for Hg; and combustion infrared spectroscopy (IR) for S. Relative advantages and disadvantages of these techniques (see Tables 1 and 2 for detection limits) are discussed by Huggins (2002).

To determine pH and elemental impacts of the coal on study area surface waters, water samples were collected from 29 sites (11 mine-adit or mine-dump effluents, 15 plateau-top streams or lake-dam outflows far upslope of mine sites, and three plateau-base sites downstream of mine sites). Sample collection and handling methods are given by Ficklin and Mosier (1999). Water-sample trace element contents were determined by ICP-MS at Activation Laboratories in Ancaster, Ontario. Measurement of pH and TDS (total dissolved solids) was conducted in the field using an Orion Model 290A pH/ISE meter and a KCl-calibrated Orion Model 125 conductivity/salinity meter, respectively, following protocols of Crock et al. (1999) and Ficklin and Mosier (1999).

5. Results and discussion

5.1. Bon air coal compared to means for Appalachian Basin coals

Bon Air coal trace elements (Tables 1 and 2) have means that are broadly similar to means for Appalachian Basin coals (Table 3). For the 35 channel and dump samples, As, Fe, Hg, Mn, Na, Th, and U are somewhat lower at the 95% confidence level, and Be, Cd, Co, Cr, REEs, Sr, and V are somewhat higher, than means for Appalachian Basin coals (COALQUAL) (Table 3, Fig. 4) (Bragg et al., 1998; Kolker and Finkelman, 1998; R.B. Finkelman, personal communication, 2003). Bon Air channel sample means taken alone show fewer differences from the Appalachian data, with no elements higher and only five elements (Hg, Mn, Na, Th, and U) lower than Appalachian means at the 95% confidence level. Mean ash contents for Bon Air samples (15.1% for channel samples and 14.4% for dump samples; Shaver et al., 2006—this volume), however, are considerably higher than the Appalachian mean (9.6%) (Table 3, Fig. 4).

5.2. Statistical methods used to infer elemental modes of occurrence

Statistical analysis has been widely used to quantify affinities between trace elements in coals, with

Table 1

Trace elements in the Bon Air coal and under- or overlying beds, as determined by instrumental neutron activation analysis (INAA), except Hg (by cold vapor atomic absorption spectroscopy, AAS), S (by LECO combustion infrared spectrometry, IR), and Cd and Pb (by inductively coupled plasma emission spectroscopy (ICP/OES) after ashing the sample)

Sample	Type	As ppm	Au ppm	Ba ppm	Br ppm	Cd ppm	Co ppm	Cr ppm	Cs ppm	Fe wt.%	Hf ppm	Hg ppb	Mo ppm	Na wt.%	Pb ppm	Rb ppm	S wt.%	Sb ppm	Sc ppm	Se ppm	Ta ppm	Th ppm	U ppm	W ppm	La ppm	Ce ppm	Nd ppm	Sm ppm	Eu ppm	Tb ppm	Yb ppm	Lu ppm
Dotson 1	d	4.3	14	<50	36	0.34	8	16	<1	0.32	<1	13	2	0.02	2.8	<15	0.70	0.6	5.0	3.2	<0.5	1.1	1.2	<1	23.8	49	23	3.7	0.9	0.6	1.7	0.27
Dotson 2	d	3.4	<2	<50	36	0.28	8	14	<1	0.32	<1	5	2	0.01	3.5	<15	0.61	0.6	5.1	2.4	<0.5	1.0	1.1	<1	28.8	48	24	3.5	0.8	0.5	1.5	0.24
Upper Shakerag 1A	c	59.0	10	<50	21	<0.05	6	21	1	2.06	2	6	2	0.02	156.7	<15	1.14	11.0	6.1	<0.5	<0.5	1.7	1.3	<1	6.9	15	<5	1.2	0.4	<0.5	1.0	0.16
Upper Shakerag 1B	c	40.0	<2	<50	19	<0.05	4	12	1	1.36	<1	<5	2	0.01	35.4	<15	1.39	3.5	4.2	2.0	<0.5	1.3	0.5	<1	5.9	15	8	1.4	0.4	<0.5	1.0	0.17
Shakerag 1A	c	47.0	<2	<50	18	0.16	9	16	<1	1.18	2	<5	3	0.01	14.3	<15	1.63	0.5	3.3	3.3	<0.5	1.2	0.5	2	17.1	21	12	1.6	0.4	<0.5	0.9	0.14
Shakerag 1B	c	55.0	<2	92	19	0.31	10	21	<1	1.50	<1	<5	4	0.02	8.9	<15	1.38	0.6	3.7	3.4	<0.5	1.7	0.7	<1	15.8	23	7	1.5	0.3	<0.5	0.9	0.16
Shakerag 1C	c	48.0	<2	88	18	0.13	11	19	<1	1.92	<1	<5	3	0.01	10.5	<15	1.15	0.6	3.4	3.4	<0.5	1.6	<0.3	<1	16.3	24	13	1.7	0.4	<0.5	0.9	0.15
Shakerag 1 Dump 1	d*	14.0	<2	<50	18	0.24	12	19	<1	0.95	<1	138	3	<0.01	12.2	<15	1.34	0.4	3.3	3.9	<0.5	1.2	0.5	1	11.3	17	11	1.6	0.4	<0.5	0.9	0.17
Shakerag 1 Dump 2	d*	44.0	<2	63	15	<0.05	9	13	<1	1.76	<1	220	3	<0.01	29.2	<15	1.98	0.6	3.5	2.5	<0.5	0.9	0.6	2	13.2	19	10	1.5	0.5	<0.5	1.1	0.18
Shakerag 2	c	27.0	<2	110	19	0.29	11	23	1	1.44	<1	287	3	0.02	10.1	<15	1.34	0.6	4.1	3.1	<0.5	1.9	0.6	<1	16.8	24	13	1.8	0.5	<0.5	1.0	0.16
Shakerag 2 Dump	d*	5.6	<2	250	9	0.25	6	65	3	0.95	3	87	1	<0.01	11.0	23	0.51	0.3	9.5	2.7	<0.5	8.4	2.1	<1	65.3	101	60	8.9	1.8	1.0	2.3	0.36
Shakerag 3	c	35.0	<2	92	16	<0.05	8	20	<1	1.92	<1	26	2	0.01	6.1	<15	2.10	0.5	3.0	3.9	<0.5	1.2	0.5	<1	9.7	14	8	1.6	0.4	<0.5	1.0	0.17
Shakerag 3 Dump	d*	53.0	8	100	15	0.18	8	12	<1	1.66	<1	<5	2	0.01	3.8	<15	2.26	0.6	2.5	3.9	<0.5	0.9	<0.3	2	19.7	22	13	1.6	0.4	<0.5	0.9	0.16
Shakerag 4	d	25.0	<2	85	14	0.24	5	19	<1	1.82	2	39	1	<0.01	5.1	<15	2.72	0.3	2.7	2.6	<0.5	1.2	1.0	2	15.9	24	11	1.9	0.5	<0.5	1.0	0.14
Shakerag 5	d	49.0	3	100	15	<0.05	4	24	1	1.95	1	352	3	0.02	10.9	16	0.77	0.9	4.2	4.2	<0.5	1.8	<0.3	<1	22.6	28	12	2.4	0.6	<0.5	1.5	0.25
Shakerag 6	d	20.0	<2	120	21	0.28	22	30	2	1.00	1	185	6	0.03	8.1	24	0.98	0.6	4.8	2.5	<0.5	2.7	0.7	<1	16.7	26	13	2.0	0.5	<0.5	1.0	0.16
Shakerag 7	d	17.0	<2	<50	19	0.07	10	24	<1	1.48	2	314	3	0.02	4.4	<15	2.32	0.7	3.6	3.5	<0.5	1.6	0.5	2	11.9	18	9	1.9	0.5	<0.5	1.2	0.20
Rutledge CH-1	d	24.0	<2	60	15	0.20	6	19	<1	1.21	<1	159	2	<0.01	7.9	<15	1.75	0.8	5.0	3.7	<0.5	1.5	<0.3	<1	10.3	15	10	1.5	0.4	<0.5	1.2	0.20
Rutledge CH-2	d	6.9	<2	<50	20	0.38	12	36	2	0.70	1	19	4	0.02	8.7	<15	0.93	0.4	6.3	2.7	<0.5	3.3	<0.3	<1	15.0	28	15	2.1	0.5	<0.5	1.2	0.19
Rutledge CH-3	d	11.0	<2	75	24	0.39	8	21	<1	0.74	<1	39	2	0.01	6.9	<15	1.09	0.4	3.5	4.1	<0.5	1.9	0.6	<1	10.0	17	12	1.6	0.5	<0.5	0.9	0.15
Rutledge CH-4	d	9.0	12	<50	19	0.43	10	32	1	0.84	1	62	5	<0.01	12.9	16	0.93	0.6	5.4	4.1	<0.5	3.2	1.0	<1	18.9	30	17	2.7	0.6	<0.5	1.2	0.21
Rutledge CH-5	d	6.0	<2	84	15	0.53	21	43	3	0.65	2	25	7	0.03	12.8	22	0.53	0.5	8.2	3.2	<0.5	4.8	1.5	<1	18.9	37	15	2.8	0.7	<0.5	1.5	0.25
Rutledge AR-1	d	14.0	<2	<50	21	0.58	10	21	<1	1.25	<1	128	8	0.02	9.0	<15	1.25	0.7	6.0	3.2	<0.5	2.2	1.5	<1	30.0	59	30	4.5	1.0	0.7	1.9	0.29
Rutledge AR-2	d	14.0	<2	160	26	0.30	10	21	<1	1.23	<1	161	3	0.02	8.2	<15	0.82	0.4	6.0	5.2	<0.5	2.3	1.0	<1	33.9	68	29	5.3	1.2	0.7	1.8	0.28
Rutledge AR-3	d	8.7	5	<50	30	0.36	15	15	<1	0.79	<1	65	2	<0.01	2.8	<15	0.80	0.4	3.3	3.5	<0.5	1.2	1.0	<1	21.1	43	23	3.3	0.8	0.5	1.5	0.23
Rutledge AR-4	d	11.0	3	<50	31	0.25	15	15	<1	0.61	<1	90	5	<0.01	8.7	<15	0.75	1.1	3.8	4.2	<0.5	1.0	0.9	<1	23.3	49	24	3.8	0.9	0.7	2.4	0.39
Rutledge AR-5	d	5.1	<2	90	33	0.27	10	14	<1	0.70	<1	35	3	0.02	2.7	<15	0.83	0.5	5.1	4.5	<0.5	1.7	0.7	2	39.4	80	41	6.0	1.3	0.9	2.0	0.31
Rutledge AR-6	d	5.5	3	110	38	0.41	10	15	<1	0.42	<1	118	6	<0.01	4.0	<15	0.77	0.5	3.2	3.1	<0.5	1.0	<0.3	<1	21.8	42	20	3.3	0.8	<0.5	1.4	0.21
Rutledge AR-7	d	8.6	<2	76	39	0.20	8	14	<1	0.85	<1	207	9	0.01	5.8	<15	1.05	0.6	3.2	3.2	<0.5	1.1	0.7	<1	19.6	41	19	3.1	0.8	<0.5	1.2	0.20
Rutledge AR-8	d	11.0	<2	180	31	0.19	8	20	<1	0.76	<1	128	1	0.02	7.9	<15	1.03	0.6	6.4	3.3	<0.5	2.4	0.5	<1	51.8	86	38	5.0	1.0	0.6	1.5	0.24
Rutledge AR-9	d	5.8	<2	<50	37	0.17	9	27	<1	0.49	1	56	2	0.02	20.8	<15	0.45	0.6	9.6	3.3	<0.5	3.7	1.8	<1	42.0	74	43	6.6	1.5	0.9	2.5	0.40
Armfield 3	c	23.0	<2	88	16	0.25	16	20	<1	1.37	<1	7	4	0.02	4.0	<15	1.71	0.9	6.9	4.3	<0.5	2.0	<0.3	<1	25.1	42	25	3.8	0.9	0.6	1.8	0.28
Armfield 3 Dump	d*	5.7	<2	63	18	0.26	15	20	<1	0.63	<1	17	5	0.02	4.0	<15	0.97	0.4	5.2	<0.5	<0.5	1.8	0.5	<1	22.9	48	27	4.1	0.9	0.6	1.6	0.25
Armfield 4	c	37.0	<2	170	12	0.21	23	50	2	2.13	1	<5	4	<0.01	21.8	22	2.52	1.9	15.0	3.9	<0.5	3.8	1.8	<1	32.2	65	29	5.1	1.1	0.6	2.3	0.36
Armfield 4 Dump	d*	15.0	<2	130	22	0.10	14	15	<1	0.80	<1	87	4	0.02	5.1	<15	1.02	0.7	6.1	3.7	<0.5	1.6	0.6	<1	41.0	67	39	5.0	1.0	0.6	1.8	0.29
Armfield 4 Caprock	bc	16.4	<2	580	<0.5		21	124	11	6.39	4	17	<1	0.13	13.9	148	0.14	0.9	21.6	1.2	1.3	14.8	3.1	<1	53.9	104	39	8.7	1.8	1.0	3.8	0.56
Armfield 4 Overlay	bc	43.8	<2	570	<0.5		5	111	11	4.24	5	87	3	0.12	67.8	151	0.73	2.5	16.9	1.4	1.0	10.4	3.0	<1	52.7	90	39	6.6	1.2	0.8	3.2	0.48
Armfield 4 Upper Top	bc	70.5	<2	100	16.9		10	18	<1	2.28	<1	436	6	0.02	4.1	<15	2.16	1.0	5.3	2.3	<0.5	1.2	0.3	<1	19.0	24	11	2.6	0.6	<0.5	1.4	0.22
Armfield 4 Lower Top	bc	99.0	<2	370	11.5		6	33	<1	2.76	1	635	7	0.03	7.5	<15	2.92	0.6	6.7	3.9	<0.5	4.3	1.3	<1	100.0	105	50	8.7	1.8	0.9	2.2	0.31
Armfield 4 Upper Middle	bc	13.6	<2	<50	17.7		10	17	<1	1.14	<1	591	3	0.02	3.6	<15	1.17	0.3	3.6	1.7	<0.5	1.8	1.1	<1	28.4	36	20	3.5	0.7	<0.5	1.4	0.22
Armfield 4 Lower Middle	bc	18.2	<2	<50	17.8		21	23	<1	1.35	<1	141	5	0.02	6.7	<15	1.40	1.1	7.2	1.3	<0.5	2.1	0.6	<1	20.2	36	17	3.7	0.8	<0.5	1.5	0.24
Armfield 4 Basal	bc	44.5	<2	<50	8.3		22	80	5	1.95	2	119	6	0.05	37.0	42	1.19	4.1	21.6	2.3	0.6	7.1	3.0	<1	46.0	81	33	6.6	1.3	0.8	2.5	0.38
Armfield 4 Underclay	bc	33.9	<2	630	<0.5		7	126	8	1.34	10	181	3	0.14	27.7	102	0.16	1.0	17.3	1.8	1.6	18.3	4.5	<1	49.9	94	41	8.3	1.8	1.1	4.6	0.69
Shakerag 1 Top	bc	66.0	<2	<50	18.0		7	14	<1	2.29	<1	188	<1	0.02	8.1	<15	2.34															

Table 2

Trace elements in the Bon Air coal and under- or overlying beds, as determined by inductively coupled plasma emission spectroscopy (ICP/OES)

Sample	Type	Ag ppm	Al wt.%	Be ppm	Ca wt.%	Cu ppm	K wt.%	Mg wt.%	Mn ppm	Ni ppm	P wt.%	Sn ppm	Sr ppm	Ti wt.%	V ppm	Y ppm	Zn ppm	
Dotson 1	d	<0.4	0.96	4	0.14	12	0.05	0.03	22	10	0.008	<10	74	0.03	22	23	17	
Dotson 2	d	<0.4	0.86	4	0.12	12	0.03	0.02	10	10	0.022	<10	180	0.03	28	19	9	
Upper Shakerag 1A	c	0.9	1.08	11	0.08	19	0.21	0.04	4	45	0.010	<10	39	0.06	57	14	13	
Upper Shakerag 1B	c	<0.4	0.59	17	0.13	12	0.09	0.02	5	23	0.004	<10	47	0.03	29	18	18	
Shakerag 1A	c	<0.4	1.39	3	0.14	15	0.09	0.03	8	12	0.019	<10	156	0.04	44	15	8	
Shakerag 1B	c	<0.4	1.50	2	0.16	15	0.10	0.04	12	14	0.019	<10	181	0.05	46	15	10	
Shakerag 1C	c	<0.4	1.85	2	0.17	26	0.13	0.05	13	13	0.051	<10	336	0.05	67	17	9	
Shakerag 1 Dump 1	d*	<0.4	1.55	3	0.23	12	0.14	0.05	24	12	0.018	<10	182	0.05	35	17	12	
Shakerag 1 Dump 2	d*	<0.4	0.97	4	0.14	24	0.09	0.03	19	14	0.014	<10	116	0.04	30	17	8	
Shakerag 2	c	<0.4	1.96	3	0.23	23	0.14	0.06	14	17	0.056	<10	347	0.06	58	18	13	
Shakerag 2 Dump	d*	<0.4	8.54	5	0.16	18	0.65	0.26	33	19	0.049	<10	179	0.32	68	28	21	
Shakerag 3	c	<0.4	1.36	2	0.21	20	0.08	0.04	27	16	0.011	<10	156	0.04	59	20	9	
Shakerag 3 Dump	d*	<0.4	1.03	3	0.25	17	0.10	0.04	12	9	0.023	<10	302	0.03	42	16	7	
Shakerag 4	d	<0.4	2.09	3	0.16	26	0.18	0.06	21	10	0.022	<10	158	0.07	75	17	10	
Shakerag 5	d	<0.4	1.70	4	0.20	23	0.19	0.06	20	13	0.025	<10	222	0.07	59	25	9	
Shakerag 6	d	<0.4	2.92	3	0.16	20	0.30	0.10	20	31	0.010	<10	82	0.10	36	16	106	
Shakerag 7	d	<0.4	1.54	4	0.18	16	0.12	0.04	24	17	0.007	<10	113	0.05	49	20	7	
Rutledge CH-1	d	<0.4	1.93	3	0.15	11	0.25	0.06	18	11	0.011	<10	92	0.07	43	19	11	
Rutledge CH-2	d	<0.4	3.11	3	0.14	15	0.24	0.09	16	25	0.011	<10	83	0.12	58	15	14	
Rutledge CH-3	d	<0.4	1.90	2	0.13	13	0.17	0.05	19	16	0.009	<10	78	0.07	32	15	8	
Rutledge CH-4	d	<0.4	4.79	3	0.12	21	0.44	0.13	43	34	0.021	<10	77	0.19	82	17	23	
Rutledge CH-5	d	<0.4	5.17	3	0.13	19	0.46	0.14	31	33	0.016	<10	75	0.22	81	15	25	
Rutledge AR-1	d	<0.4	1.88	4	0.16	16	0.10	0.05	17	16	0.027	<10	241	0.05	43	25	12	
Rutledge AR-2	d	<0.4	2.46	5	0.18	23	0.09	0.05	34	13	0.037	<10	259	0.07	60	31	10	
Rutledge AR-3	d	<0.4	0.95	4	0.17	9	0.06	0.03	11	16	0.007	<10	131	0.02	14	19	7	
Rutledge AR-4	d	<0.4	1.47	6	0.15	20	0.09	0.03	15	15	0.024	<10	175	0.04	43	28	8	
Sample	Type	Ag ppm	Al wt.%	Be ppm	Ca wt.%	Cu ppm	K wt.%	Mg wt.%	Mn ppm	Ni ppm	P wt.%	Sn ppm	Sr ppm	Ti wt.%	V ppm	Y ppm	Zn ppm	Zr ppm
Rutledge AR-5	d	<0.4	0.77	3	0.15	14	0.04	0.02	6	11	0.008	<10	149	0.02	27	22	3	
Rutledge AR-6	d	<0.4	1.06	3	0.15	14	0.05	0.03	14	10	0.009	<10	134	0.03	29	20	13	
Rutledge AR-7	d	<0.4	1.26	4	0.16	20	0.07	0.02	10	10	0.064	<10	445	0.02	67	20	9	
Rutledge AR-8	d	<0.4	2.55	5	0.15	16	0.10	0.04	10	10	0.142	<10	947	0.08	40	25	5	
Rutledge AR-9	d	<0.4	2.96	5	0.10	9	0.14	0.06	23	16	0.029	<10	161	0.13	41	29	30	
Armfield 3	c	<0.4	1.63	4	0.11	19	0.10	0.04	11	29	0.010	<10	84	0.06	27	19	8	
Armfield 3 Dump	d*	<0.4	1.59	5	0.12	18	0.08	0.03	6	18	0.027	<10	190	0.05	37	18	7	
Armfield 4	c	<0.4	5.18	6	0.08	30	0.36	0.13	21	68	0.031	<10	196	0.17	94	21	50	
Armfield 4 Dump	d*	<0.4	1.43	4	0.16	14	0.12	0.03	15	15	0.038	<10	243	0.05	31	21	8	
Armfield 4 Caprock	bc	<0.2	1.34	1	0.26	28	0.26	0.61	1116	61	0.044	<10	24	<0.01	28	16	97	11.1
Armfield 4 Overlay	bc	<0.2	0.64	<1	<0.01	10	0.30	0.13	62	12	0.010	<10	19	<0.01	18	8	18	13.2
Armfield 4 Upper Top	bc	<0.2	0.13	<1	0.11	11	0.03	0.01	28	9	0.005	<10	78	<0.01	7	4	7	1.9
Armfield 4 Lower Top	bc	<0.2	0.33	3	0.07	22	0.04	0.01	20	10	0.059	<10	521	<0.01	18	9	4	4.5
Armfield 4 Upper Middle	bc	<0.2	0.14	1	0.11	26	0.01	0.01	9	8	0.020	<10	199	<0.01	11	5	3	1.6
Armfield 4 Lower Middle	bc	<0.2	0.16	1	0.09	22	0.02	0.02	8	19	0.003	<10	54	<0.01	14	5	7	2.1
Armfield 4 Basal	bc	<0.2	0.62	1	0.03	28	0.08	0.03	7	37	0.006	<10	29	<0.01	52	10	59	7.5
Armfield 4 Underclay	bc	<0.2	0.80	<1	<0.01	5	0.18	0.05	11	12	0.009	<10	18	<0.01	12	10	7	8.6
Shakerag 1 Top	bc	<0.2	0.10	<1	0.20	18	0.02	0.02	24	10	0.012	<10	231	<0.01	21	2	4	1.5
Shakerag 1 Upper Middle	bc	<0.2	0.20	<1	0.11	16	0.04	0.02	12	13	0.004	<10	68	<0.01	28	3	6	3.3
Shakerag 1 Lower Middle	bc	<0.2	0.17	<1	0.12	9	0.03	0.02	9	11	0.002	<10	66	<0.01	14	1	7	2.1
Shakerag 1 Basal	bc	<0.2	0.17	<1	0.10	11	0.03	0.02	7	11	0.003	<10	55	<0.01	19	2	9	2.6

Table 3

Mean values for trace elements and ash in Appalachian coals (Bragg et al., 1998; R.B. Finkelman, 2003, personal communication), as compared to those of Bon Air coal channel and dump samples (this study)

		Appalachian coal			Bon Air coal channel samples			Bon Air coal dump samples		
		Mean value	Std. dev.	No. of samples	Mean value	Std. dev.	No. of samples	Mean value	Std. dev.	No. of samples
Ag	ppm	0.07	0.19	4119	<0.5	n.d	9	<0.4	n.d	26
Al	wt.%	1.56	1.07	4636	1.84	1.32	9	2.21	1.71	26
As	ppm	35	74	4603	41	12	9	15	14	26
Au	ppb	13	130	434	<3	n.d	9	<3	n.d	26
Ba	ppm	91	93	4552	79	48	9	77	57	26
Be	ppm	2.5	1.8	4656	5.6	5.2	9	3.8	0.9	26
Bi	ppm	0.3	0.9	515	<5	n.d	9	<5	n.d	26
Br	ppm	20	19	4288	18	3	9	24	9	26
Ca	wt.%	0.19	1.1	4637	0.15	0.05	9	0.16	0.03	26
Cd	ppm	0.10	0.14	4464	0.15	0.13	9	0.27	0.14	26
Ce	ppm	20	17	4475	27	17	9	44	24	26
Co	ppm	7.2	7.5	4617	11	5.7	9	11	4.4	26
Cr	ppm	18	12	4611	22	11	9	22	12	26
Cs	ppm	1.2	1.1	4282	<1.1	n.d	9	<1.2	n.d	26
Cu	ppm	19	16	4657	20	5.7	9	17	4.6	26
Eu	ppm	0.42	0.26	4440	0.53	0.27	9	0.80	0.36	26
Fe	wt.%	1.47	1.43	4622	1.65	0.35	9	0.96	0.46	26
Hf	ppm	0.75	0.60	4379	<1.2	n.d	9	<1.2	n.d	26
Hg	ppb	210	200	4468	38	94	9	106	93	26
K	wt.%	0.22	0.23	4639		0.09	9	0.17	0.15	26
La	ppm	11	8.0	4553	16	8.5	9	25	14	26
Lu	ppm	0.16	0.10	4291	0.19	0.07	9	0.24	0.07	26
Mg	wt.%	0.06	0.07	4645	0.05	0.03	9	0.06	0.05	26
Mn	ppm	29	74	4656	13	7	9	19	9	26
Mo	ppm	3.7	4.8	4380	3.0	0.9	9	3.6	2.2	26
Na	wt.%	0.04	0.04	4589	0.01	0.01	9	0.01	0.01	26
Nd	ppm	12	8.7	3908	13	9.1	9	23	13	26
Ni	ppm	17	13	4654	26	19	9	16	7	26
P	ppm	330	1300	3172	230	190	9	260	270	26
Pb	ppm	8.4	12	4614	30	49	9	8.4	5.9	26
Rb	ppm	25	19	2135	<16	n.d	9	<16	n.d	26
S	wt.%	1.54	2.11	4299	1.60	0.46	9	1.12	0.60	26
Sb	ppm	1.4	1.7	4412	2.2	3.4	9	0.6	0.2	26
Sc	ppm	4.2	2.7	4620	5.5	3.8	9	5.0	1.9	26
Se	ppm	3.5	3.3	4511	3.0	1.3	9	3.3	1.0	26
Sm	ppm	1.9	1.4	4419	2.2	1.3	9	3.5	1.8	26
Sn	ppm	1.2	2.0	2341	<10	n.d	9	<10	n.d	26
Sr	ppm	110	99	4568	170	110	9	200	180	26
Ta	ppm	0.23	0.17	3901	<0.5	n.d	9	<0.5	n.d	26
Tb	ppm	0.33	0.22	4301	<0.5	n.d	9	<0.6	n.d	26
Th	ppm	3.0	2.3	4514	1.8	0.8	9	2.1	1.6	26
Ti	wt.%	0.09	0.07	4616	0.06	0.04	9	0.08	0.07	26
U	ppm	1.7	2.3	4316	0.7	0.6	9	0.8	0.6	26
V	ppm	23	16	4656	53	20	9	45	18	26
W	ppm	0.9	0.6	4003	<1.1	n.d	9	<1.2	n.d	26
Y	ppm	8.2	5	4652	17	2.4	9	21	4.7	26
Yb	ppm	1.04	0.67	4565	1.2	0.5	9	1.5	0.5	26
Zn	ppm	21	49	4658	15	13	9	15	20	26
Zr	ppm	23	22	4651	3	2	9*	–	–	–
Ash	wt.%	9.6	1.9	4299	15.1	2.3	4	14.4	3.1	7

n.d. = not determined.

* Data for Zr in the Bon Air are from nine bench-column samples.

correlation coefficients (r) perhaps the most common parameter used to date (e.g., Spears and Zheng, 1999; Pentari et al., 2004). Particularly when coupled with XRD identification of mineral phases present in a coal (e.g., Pollock et al., 2000; Alastuey et al., 2001; Zhuang et al., 2003), correlation coefficients have proven quite powerful in inferring trace element occurrence modes for coals. Factor analysis, a statistical technique well-suited to grouping elements of similar affinity has also been used to assess trace element associations, albeit less commonly in coal

(Metcalf et al., 1987; Martínez et al., 2001) than in other geological studies (e.g., Nayak et al., 1997; Hwang et al., 2001; Oprea and Mihul, 2003; Stüben et al., 2003). Some coal workers use both factor analysis and r -values for their trace element inferences (Christanis et al., 1998) and we follow this approach. Below, factor analysis loadings (Table 4) and correlation coefficients (Table 5) are coupled with limited petrographic and XRD data on Bon Air mineral phases (quartz, pyrite, gorceixite, calcite, illite, smectite, illite-smectite, chlorite, and kaolinite; Shaver

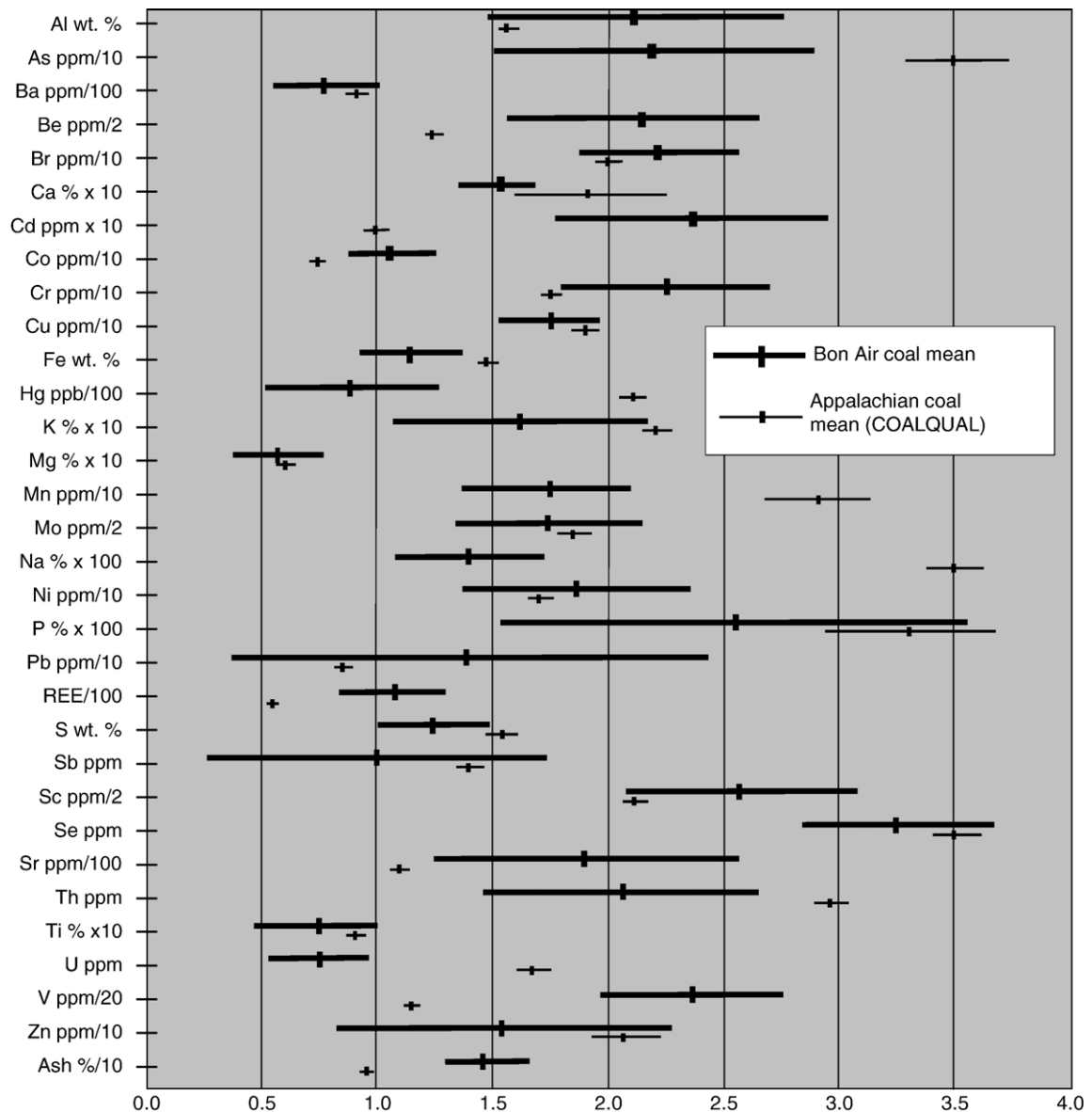


Fig. 4. Comparison of selected Bon Air coal trace element means and ash (at the 95% confidence level) to Appalachian Basin coal means (COALQUAL database: Bragg et al., 1998; R.B. Finkelman, 2003, personal communication). (REE = \sum La+Ce+Nd+Sm+Eu+Yb+Lu+Y).

Table 4

Varimax-rotated R-mode factor analysis matrix for Bon Air coal trace elements, showing factor loadings for all factors with Eigenvalues >1.00

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8
Al	0.29	0.94	-0.06	-0.01	0.09	0.11	-0.05	0.06
As	-0.41	-0.10	0.29	0.73	0.04	-0.08	0.00	-0.08
Ba	0.37	0.43	-0.18	0.30	0.53	0.12	0.10	-0.23
Be	0.14	-0.09	0.78	0.09	-0.10	-0.05	0.03	-0.12
Br	0.31	-0.54	0.06	-0.62	0.09	-0.02	0.06	0.15
Ca	-0.27	-0.10	-0.53	0.16	0.18	-0.24	0.48	-0.18
Cd	0.03	0.24	-0.37	-0.60	-0.06	0.21	-0.27	0.33
Co	0.11	0.13	-0.18	-0.01	-0.07	0.87	-0.19	0.11
Cr	0.25	0.92	0.02	0.06	0.01	0.19	-0.05	0.02
Cu	-0.05	0.27	-0.01	0.63	0.26	0.24	0.13	0.43
Fe	-0.27	0.08	0.18	0.89	0.04	-0.05	0.11	0.09
Hg	-0.03	-0.02	-0.13	0.03	0.13	0.03	0.89	0.07
K	0.04	0.97	0.07	0.02	-0.04	0.12	0.01	0.02
Mn	0.11	0.67	-0.36	0.00	-0.26	-0.10	0.29	0.28
Mo	-0.07	-0.04	-0.10	-0.31	0.05	0.57	0.12	0.53
Ni	0.06	0.43	0.44	0.31	-0.17	0.54	-0.24	0.24
P	0.25	0.06	-0.02	-0.01	0.91	-0.10	0.09	0.08
Pb	-0.15	0.06	0.90	0.15	-0.06	-0.08	-0.03	0.10
S	-0.31	-0.09	-0.14	0.76	-0.06	0.00	-0.14	0.02
Sb	-0.13	-0.03	0.91	0.17	-0.08	-0.05	-0.06	0.08
Sc	0.61	0.50	0.23	0.14	-0.01	0.34	-0.25	0.11
Se	0.27	-0.05	-0.68	0.19	-0.13	-0.09	0.17	0.21
Sr	0.19	-0.16	-0.12	0.04	0.91	-0.10	0.10	0.05
Th	0.38	0.88	0.05	-0.10	0.07	0.07	-0.05	-0.08
Ti	0.24	0.95	0.02	-0.05	0.01	0.07	-0.06	0.03
U	0.53	0.48	0.29	-0.15	-0.17	0.04	-0.09	0.20
V	-0.07	0.65	0.03	0.36	0.19	0.02	0.01	0.57
Y	0.85	-0.01	-0.08	-0.04	0.06	-0.19	0.38	0.10
Zn	-0.02	0.37	0.11	-0.02	-0.10	0.74	0.20	-0.17
REE	0.90	0.19	-0.10	-0.19	0.28	-0.02	-0.04	-0.09
La	0.83	0.26	-0.11	-0.13	0.38	-0.06	-0.04	-0.17
Ce	0.90	0.16	-0.05	-0.21	0.30	0.03	-0.09	-0.05
Nd	0.87	0.20	-0.19	-0.23	0.22	0.00	-0.09	-0.17
Sm	0.92	0.25	-0.05	-0.19	0.15	0.00	-0.05	-0.07
Eu	0.93	0.21	-0.02	-0.21	0.09	0.01	-0.02	-0.03
Yb	0.95	0.10	0.01	-0.09	-0.12	0.13	-0.03	0.12
Lu	0.93	0.11	0.00	-0.09	-0.13	0.12	0.00	0.13
Eigenvalue	12.6	6.9	4.1	3.5	2.0	1.8	1.4	1.1
% of variance	24.3	20.9	10.4	10.2	7.2	6.4	4.4	3.9
Cumulative %	24.3	45.2	55.5	65.8	73.0	79.4	83.8	87.7

Extraction method: Principal Component Analysis. Factor loadings >0.30 are shown in bold.

REE=[La+Ce+Nd+Sm+Yb+Lu+Y]; S=total sulfur.

et al., 2006—this volume) to infer likely modes of occurrence for most trace elements in the Bon Air coal (Table 6).

5.3. Bon Air coal factor analysis and correlation coefficients

Table 4 shows the eight factors (87.7% of total variance) and their factor loadings extracted by Varimax-rotated R-mode factor analysis from the Bon Air coal trace element data. Although some studies use

only factor loadings >0.50 to determine elements defining a given factor (Piper, 2001; Stüben et al., 2003), others have shown that loadings of 0.30–0.50 also help define factors, especially for elements with mixed affinities (Szefer et al., 1995; Nayak et al., 1997; Tao, 1998; Martínez et al., 2001; Oprea and Mihul, 2003). For the Bon Air coal, trace elements largely in one mode of occurrence appear to be defined by high factor loadings (generally >0.70) in a single factor, while “moderate” (0.50–0.70) to “low” (~0.30–0.49) loadings in two or more factors define elements likely

Table 5

Correlation coefficients (r) between Bon Air coal trace elements, from highest to lowest r for each element pair

	r		r		r		r		r
Al–Ti	0.98	Ca–Hg	0.44	Fe–Co	–0.13	Ni–Be	0.32	Se–As	–0.12
Al–Cr	0.96	Ca–Se	0.37	Fe–Mo	–0.21	Ni–As	0.18	Se–U	–0.15
Al–Th	0.95	Ca–Sr	0.27	Fe–Cd	–0.55	Ni–S	0.17	Se–Ni	–0.18
Al–K	0.93					Ni–Br	–0.36	Se–Be	–0.43
Al–Sc	0.68	Cd–Al	0.29	Hg–Ca	0.44			Se–Sb	–0.52
Al–Mn	0.64	Cd–Zn	0.12	Hg–Sr	0.22	P–Sr	0.95	Se–Pb	–0.54
Al–V	0.63	Cd–S	–0.35	Hg–Mn	0.21	P–Ba	0.52		
Al–U	0.56	Cd–Sb	–0.37	Hg–P	0.20	P–REE	0.47	Th–Al	0.95
Al–Ba	0.55	Cd–Be	–0.39	Hg–Se	0.19	P–Al	0.22	Th–Ti	0.95
Al–REE	0.46	Cd–Fe	–0.55	Hg–Cu	0.19	P–Ca	0.12	Th–REE	0.55
Al–Ni	0.46	Cd–As	–0.59	Hg–Mo	0.17	P–Be	–0.05	Th–U	0.59
Al–Zn	0.38			Hg–Fe	0.14	P–Sb	–0.14	Th–V	0.48
Al–Cd	0.29	Co–Ni	0.55	Hg–S	0.01			Th–Br	–0.32
Al–Cu	0.29	Co–Zn	0.55	Hg–As	–0.03	Pb–Sb	0.97		
Al–Co	0.27	Co–Mo	0.48	Hg–Al	–0.05	Pb–Be	0.57	Ti–Al	0.98
Al–P	0.22	Co–Sc	0.43	Hg–Co	–0.13	Pb–As	0.45	Ti–K	0.95
Al–Mo	0.04	Co–Cr	0.32	Hg–Pb	–0.14	Pb–Fe	0.37	Ti–Cr	0.94
Al–Sr	0.00	Co–Al	0.27	Hg–Be	–0.14	Pb–V	0.13	Ti–REE	0.40
Al–Fe	–0.04	Co–Cu	0.23	Hg–Sb	–0.18	Pb–Cu	0.10	Ti–Br	–0.41
Al–Hg	–0.05	Co–V	0.12	Hg–Ni	–0.23	Pb–S	0.01		
Al–Be	–0.09	Co–REE	0.10			Pb–Al	–0.06	U–Th	0.59
Al–Sb	–0.14	Co–Se	0.08	K–Ti	0.95			U–Al	0.56
Al–S	–0.16	Co–S	–0.04	K–Al	0.93	REE–Y	0.77	U–Ti	0.56
Al–As	–0.24	Co–Fe	–0.13	K–Cr	0.90	REE–Sc	0.57	U–REE	0.48
Al–Br	–0.40	Co–Sb	–0.17	K–Th	0.86	REE–Th	0.55	U–Ni	0.39
		Co–Pb	–0.18	K–REE	0.19	REE–Ba	0.54	U–Cr	0.36
As–Fe	0.84	Co–Be	–0.20	K–Br	–0.53	REE–U	0.48	U–V	0.31
As–S	0.52	Co–As	–0.22			REE–P	0.47	U–Be	0.20
As–Sb	0.44			Mn–Al	0.64	REE–Al	0.46	U–Sb	0.17
As–Hg	–0.03	Cr–Al	0.96	Mn–V	0.50	REE–Ti	0.40	U–Mo	0.02
As–Be	–0.08	Cr–Ti	0.94	Mn–Cu	0.24	REE–Cr	0.37		
		Cr–V	0.62	Mn–Ni	0.15	REE–Be	–0.01	V–Cu	0.71
Ba–Al	0.55	Cr–Ni	0.57	Mn–Ca	0.12	REE–V	–0.01	V–Al	0.63
Ba–REE	0.54	Cr–REE	0.37	Mn–Fe	–0.02	REE–Sb	–0.25	V–Cr	0.62
Ba–Th	0.53	Cr–Co	0.32	Mn–S	–0.05	Sb–Pb	0.97	V–Mn	0.50
Ba–P	0.52	Cr–Br	–0.44	Mn–As	–0.28	Sb–Be	0.65	V–Ni	0.49
Ba–Cr	0.50			Mn–Be	–0.31	Sb–Ni	0.48	V–S	0.22
Ba–Ti	0.47	Cu–V	0.71	Mn–Sb	–0.32	Sb–As	0.44	V–As	0.18
Ba–Sr	0.44	Cu–Fe	0.64			Sb–Fe	0.36	V–Mo	0.18
Ba–K	0.41	Cu–Ni	0.41	Mo–V	0.18	Sb–S	0.03	V–Sb	0.08
Ba–Ca	0.15	Cu–S	0.39	Mo–Cu	0.17	Sb–Cu	–0.11	V–REE	–0.01
Ba–S	0.02	Cu–As	0.38	Mo–Hg	0.17	Sb–Al	–0.14	V–Be	–0.08
		Cu–Cr	0.30	Mo–Sb	–0.14	Sb–Se	–0.52	V–Hg	–0.13
Be–Sb	0.65	Cu–Al	0.29	Mo–Be	–0.16			V–Br	–0.45
Be–Ni	0.32			Mo–S	–0.20	Se–Mn	0.41		
Be–As	0.20	Fe–As	0.84	Mo–Fe	–0.21	Se–Ca	0.37	Zn–Co	0.55
Be–U	0.20	Fe–S	0.70	Mo–As	–0.23	Se–Ba	0.20	Zn–Ni	0.51
Be–Fe	0.14	Fe–Cu	0.64			Se–Hg	0.19	Zn–Al	0.38
Be–S	–0.04	Fe–V	0.43	Ni–Co	0.55	Se–Cd	0.18	Zn–Mo	0.25
Be–Cu	–0.08	Fe–Sb	0.36	Ni–V	0.49	Se–V	0.06	Zn–Cu	0.19
Be–Al	–0.09	Fe–Ni	0.32	Ni–Sb	0.48	Se–Al	0.06	Zn–Cd	0.12
Be–Hg	–0.14	Fe–Hg	0.14	Ni–Ti	0.48	Se–S	0.05	Zn–Be	0.04
Be–Mo	–0.16	Fe–Be	0.14	Ni–Al	0.46	Se–Cu	0.05	Zn–Sb	0.02
Be–Mn	–0.31	Fe–Cr	0.05	Ni–Cu	0.41	Se–Mo	0.00	Zn–As	–0.04
Be–Se	–0.43	Fe–Al	–0.04	Ni–Fe	0.32	Se–Zn	–0.12	Zn–S	–0.05

REE=[La+Ce+Nd+Sm+Eu+Yb+Lu+Y]. S=total sulfur.

Table 6

Likely modes of occurrence of Bon Air coal trace elements having paleoecological or environmental significance

Element	Likely mode (s) of occurrence	Element	Likely mode (s) of occurrence
Ag	Below detection in nearly all samples	Ni	Strongly divided between clays, organic debris, pyrite, and other sulfides
Al	Clays; also in Ba–Al or Sr–Al phosphates (gorceixite and goyazite, respectively)	P	Crandallite-group secondary phosphates (goyazite and gorceixite) and REE phosphates
As	Pyrite, some of which is organically enmeshed	Pb	Organically enmeshed Pb–Sb sulfosalts
Ba	Crandallite-minerals such as gorceixite (BaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O); clays; trace barite?	REE's	Heavy accessory minerals such as xenotime (YPO ₄) and monazite ((REE, Sc,Th,Y)PO ₄)
Be	Organic matter; no inorganic affinities shown	Sn	Below detection in all samples
Cd	In non-pyritic sulfides (probably sphalerite)	Sb	Organically enmeshed Pb–Sb sulfosalts
Co	Mostly in non-pyritic sulfides; trace amounts in clays and heavy minerals	Se	Organic association appears unlikely, but other associations are unclear
Cr	Clays, with minor fraction in heavy accessory minerals such as magnetite	Sr	Crandallite-minerals such as goyazite (SrAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O)
Cu	Chalcopyrite and pyrite	Th	Mostly in clays, some in heavy minerals
Hg	Calcite - sorbed onto calcite surface during weathering from original pyrite mode?	Ti	Clays; minor fraction in heavy minerals such as ilmenite or rutile
K	Clays	U	Clays and heavy minerals; some in organics
Mn	Clays; some in calcite and non-pyritic sulfides	V	Clays and non-pyritic sulfides; some in pyrite
Mo	In non-pyritic sulfides (probably molybdenite)	Zn	In non-pyritic sulfides (probably sphalerite)

having multiple, subequal modes of occurrence (Ba, Mn, Ni, Sc, U, and V) (see below). For all Bon Air trace elements except Pb, Sb, and Se, factor loadings appear to be useful indicators of an element's affinity for a specific mode of occurrence.

5.3.1. Factor 1 (heavy mineral affinity)

Factor 1 reflects an association of REE and related elements (Y and Sc) with U, Th, and P. These elements typify heavy accessory minerals in coals (e.g., monazite and xenotime, which dominate REE fractions in higher-rank coals, and zircon (U and Th only)) (Zubovic, 1966; Filby et al., 1977; Finkelman, 1981a; Palmer and Filby, 1984; Palmer and Wandless, 1985; Palmer et al., 1990). Highest factor loadings are for total REEs (0.90), individual REEs (0.83–0.95), and Y (0.85). (For our calculations, total “REE” = \sum La+Ce+Nd+Sm+Eu+Yb+Lu+Y). Lower loadings for other elements that typify REE phosphates or zircon (0.61 for Sc, 0.53 for U, 0.38 for Th, and 0.25 for P) are consistent with correlations between these elements and total REE ($r=0.77$ for Y, and 0.57 – 0.47 for Sc, Th, U, and P; Table 5, Fig. 5a,c,d,f), and with the multiple affinities these elements have in the Bon Air (see Factor 2 below). Small Factor 1 loadings (0.24–0.25) are also expressed for Ti and Cr. These occur in heavy minerals in some coals (Ti in ilmenite or rutile, Cr in magnetite or, rarely, as chromite in Cr-rich coals, Ren et al., 2004; Kolker and Finkelman, 1998), but they are more common in clays in most coals (Finkelman, 1981a; Ward et al., 1999) including the Bon Air coal (see Factor 2, below).

Any REE-organic association in the Bon Air coal appears to be small. Such affinities occur in some coals (Eskenazy et al., 1986; Eskenazy, 1987a,b,c, 1995; Vassilev et al., 1995), but are more common in coals with lower ash yield (<8%) (Wood et al., 1983) than the Bon Air coal (14–15%). Moreover, Be, which has significant organic affinity in bituminous coals, has a very low loading in this heavy-mineral factor (0.14), and negative correlation with total REEs ($r=-0.01$).

The data suggest that for the Bon Air coal, heavy accessory minerals house most of the REE fraction, important fractions of U, Sc, Th, and P, and minor amounts of Ti and Cr. Heavy minerals can have detrital, volcanic, or authigenic origins in coals (Finkelman, 1981b; Lindahl and Finkelman, 1986; Hower et al., 1999), but fluvial inputs (not volcanic or marine) appear to have dominated the Bon Air mines (Shaver et al., 2006—this volume). Such inputs include both heavy minerals and clays, and Bon Air REEs show some correlation with clay elements ($r=0.46$, 0.40 , and 0.37 for Al, Ti, and Cr, respectively, Table 5; see also Factor 2 below). Whether Bon Air REEs were ever remobilized by groundwater (Schatzel and Stewart, 2003) into secondary REE phosphates (monazite or others) is unclear.

5.3.2. Factor 2 (clay affinity)

Factor 2 has highest loadings (0.88–0.97) for K, Ti, Al, Cr, and Th (which show striking sample-to-sample correlation, Fig. 5a), and smaller loadings for Mn (0.67), V (0.65), Sc (0.50), U (0.48), Ni (0.43), and Ba (0.43).

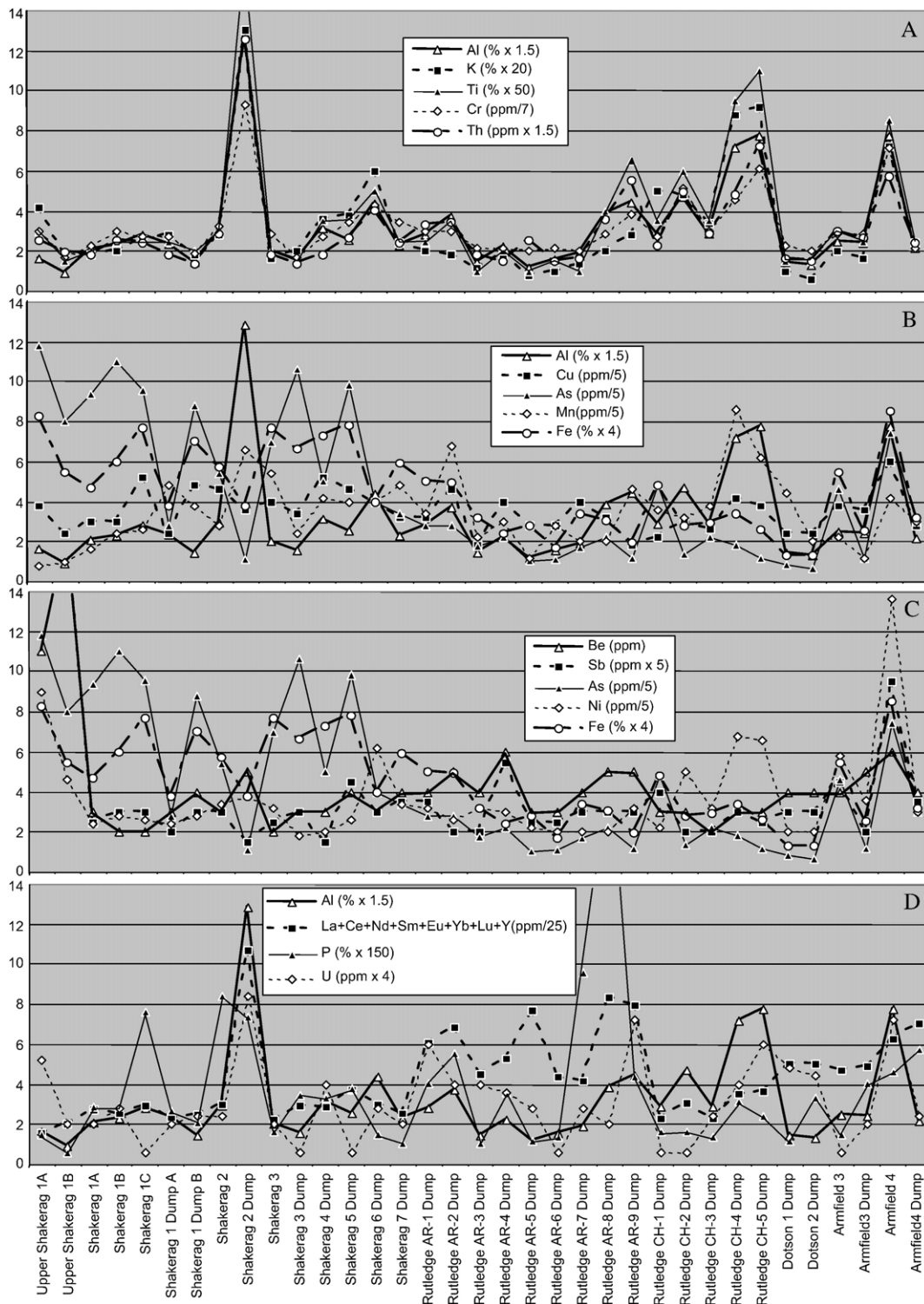


Fig. 5. Localized sample-to-sample correlations between selected trace elements in the Bon Air coal. Associations with Al relate to clay mineral affinities; those with Cu, As, Fe, and/or S, to pyritic affinities; those with Be, to organic affinities; and those with P, to heavy mineral or (where also with Al) to crandallite affinities.

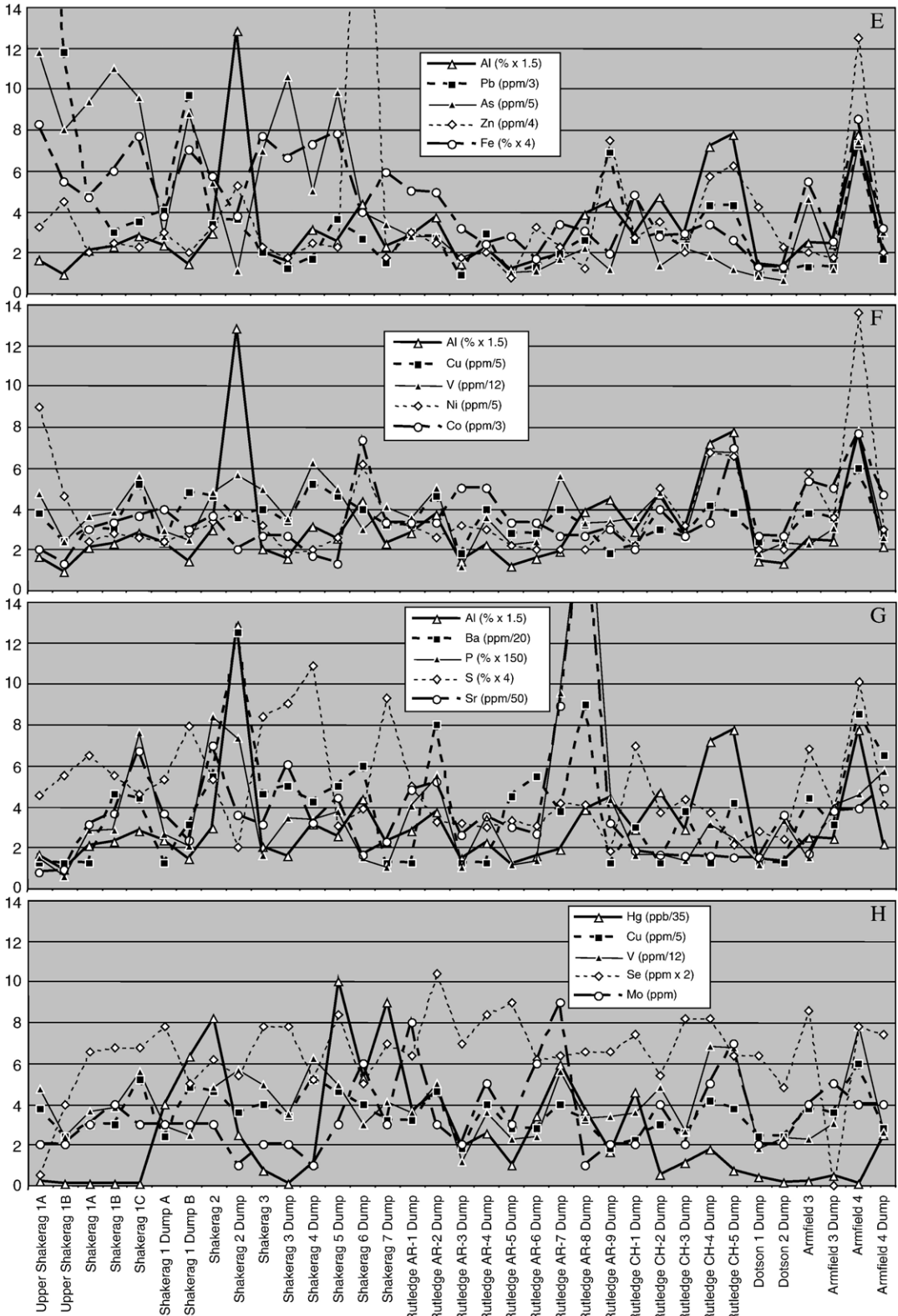


Fig. 5 (continued).

Except for U and Ba, these elements often have significant clay association in coals, with clay minerals serving either as the dominant mode of occurrence (K, Al, Ti, and Cr), or an important mode (Th, Mn, V, Sc, and Ni) (Finkelman, 1981a, 1993; Huggins and Huffman, 1996; Palmer and Lyons, 1996; Kolker and Finkelman, 1998; Ward et al., 1999). The strong negative loading of Br in this factor (-0.54) suggests non-marine input of these elements (Rimmer, 1991; Hickmott and Baldrige, 1995) and lends further support to fluvial influx as the dominant source of Bon Air inorganic elements (Shaver et al., 2006—this volume), including those now in detrital or authigenic clays. Factor 2 loadings are consistent with correlation coefficients between respective pairs of these elements (e.g., $r=0.86$ – 0.98 for K, Ti, Al, Cr, and Th pairs, $r=-0.53$ for K–Br, and $r_{Al}=0.46$ – 0.68 for Mn, V, Sc, U, Ni, and Ba, Table 5). Most clay-associated trace elements in coal occur in illite, smectite, and illite-smectite (Palmer and Lyons, 1996; Kolker and Finkelman, 1998), and this is likely also true for the Bon Air.

Affinities of many of these elements for clays are well known. Transition metals such as Cr, Mn, Ti, V, Sc, and Ni readily substitute into the illite structure (Huggins and Huffman, 1996; Kolker and Finkelman, 1998) and Th is readily adsorbed onto clays due to both its charge and its mobility in natural waters (Langmuir and Herman, 1980). Many of these elements, however, have both clay and non-clay affinities in coals. For example, while V and Ni have been detected by SIMS in coal clays (Wiese et al., 1990), they also occur in other modes (see Factors 3, 6 and 8, below), and Mn can have carbonate and sulfide affiliations (Finkelman, 1981a; Finkelman and Stanton, 1978; Lindahl and Finkelman, 1986). Likewise, Cr, Ti, V, (and Zr) can occur in organic association in coals as amorphous, nano-sized particles of oxide or oxyhydroxide that may be abundant in some coals (Huggins and Huffman, 1996; Huggins et al., 2000a).

The high Factor 2 loadings for K, Ti, Al, Cr, and Th (0.88 – 0.97) and high correlation coefficients between pairs of these elements ($r=0.86$ – 0.98) make a strong case that all five of these elements *primarily* occur in Bon Air clays. By contrast, Mn, V, Sc, U, Ni, and Ba, with smaller Factor 2 loadings (0.43 – 0.67), probably have important, but not dominant, affinities with clay minerals. These elements appear to divide their affinities between clays and other modes of occurrence, as evidenced by their more-subequal loadings across several factors. For example, Mn and V loadings in Factor 2 (0.67 – 0.65) are not hugely disparate to their other factor loadings (0.57 for V in

“sulfide” Factor 8, 0.36 for V in “organic” Factor 4, and 0.28 – 0.29 for Mn in “calcite” Factor 7 and “sulfide” Factor 8, see below). Similarly, loadings for Sc, U, Ni, and Ba in Factor 2 (0.43 – 0.50) largely mirror their important loadings in other factors discussed below (0.61 for Sc, 0.29 – 0.53 for U, 0.31 – 0.54 for Ni, and 0.37 – 0.53 for Ba).

Likewise, U has a mixed association in most higher-rank coals. It is often in both heavy minerals and organic debris, and infrequently also in uraninite (Finkelman, 1981a; Kolker and Finkelman, 1998). In the Bon Air, U affinities are also divided, but largely between clays and heavy minerals (with lesser organic affinity, Factor 3 below). The Factor 2 “clay” loading for U (0.48) is similar to its Factor 1 “heavy mineral” loading (0.53), and correlation coefficients between U and clay elements are nearly the same as those between U and heavy mineral elements (e.g., $r_U=0.56$ for Al, 0.59 for Th, 0.48 for REE) (Tables 4 and 5). In spite of the wide range of stable aqueous complexes that U forms at low temperature (Langmuir, 1978), and the ease with which clays adsorb aqueous U (Tsunashima et al., 1981), significant U in higher rank coals is not common as either uraninite (which is authigenic in coals), nor in clays. The Bon Air mires were thinner, and apparently less-compacted, than the thick peats responsible for most mineable Carboniferous coals (Shaver et al., 2006—this volume), but whether this significantly affects U remobilization and/or adsorption processes in paleomires is unclear.

5.3.3. Factor 3 (organic affinity)

Factor 3 has highest factor loadings for Sb (0.91), Pb (0.90), Be (0.78), Ni (0.44), U (0.29) and As (0.29). Except for Pb and As, these elements have been inferred to have important organic affinities in other coals, especially Be. For the Bon Air coal, we suggest below that these loadings associate most Be, some Ni, and minor U with organic matter, but that the Pb and Sb loadings reflect organic enmeshment of sulfosalts. It's noteworthy that the Factor 3 loading for Se, an element having organic affinity in many coals (Finkelman, 1995), is -0.68 , suggesting no Se-organic affinity in the Bon Air coal.

While Be has been found in coal clays (Eskenazy and Valceva, 2003), consistent Be enrichment in float fractions of sink-float experiments (Finkelman, 1981a) suggests that Be is dominantly housed in organic debris in most coals (Kolker and Finkelman, 1998). The larger factor loading for Be in “organic” Factor 3 (0.78) than in any other factors (0.14 to -0.12), and Be's small to negative correlation with elements indicative of other

modes of occurrence (e.g., $r=0.20$ to -0.08 for sulfidic elements (As, Fe, S, or Cu), -0.09 for clay element Al, -0.01 for REE, and -0.05 for crandallite element P, Table 5), are consistent with a dominant organic association of Be in the Bon Air coal.

By contrast, organic affinities for Ni and U in coal are often less dominant. Organic debris can host up to 10's of ppm Ni (Minkin et al., 1982, 1987), but Ni also has sulfide, clay, and heavy mineral affinities in coal (Kolker and Finkelman, 1998; Ward et al., 1999). For the Bon Air coal, Ni's small but subequal loadings across "clay" Factor 2 (0.43), "organic" Factor 3 (0.44), "pyrite" Factor 4 (0.31), and "other sulfide" Factor 6 (0.54) suggest it is strongly divided among these four occurrences. Its correlation coefficient with Be ($r=0.32$) suggests an organic association that is important, but not strong. For U, its weaker loading in "organic" Factor 3 (0.29) than in Factor 1 (0.53) or Factor 2 (0.48) suggests an organic affinity that is not as strong as its heavy mineral and clay affinities.

The prominence of Pb in "organic" Factor 3 appears odd for an element that is normally strongly chalcophile in coals. It most often occurs as galena, less often in pyrite (Swaine, 1990; Finkelman, 1995; Kolker and Finkelman, 1998), and locally as unusual Pb-bearing selenide grains long called clausthalite (PbSe), but now known to be of such small size and complex chemistry (Pb and Se, but also Co, Ni, Cu, Zn, and perhaps Fe) that their mineralogy is undefined (Hower and Robertson, 2003). The high Factor 3 loading for Pb (0.90), coupled with Pb's striking correlation with Sb ($r=0.97$, Table 5), suggest that most Pb and most Sb in the Bon Air probably occur as Pb–Sb sulfosalts finely enmeshed in organic matrix. Enmeshed Sb-sulfides have been suspected for some time (Finkelman, 1995) as the origin of the apparent strong organic affinity that Sb, another chalcophile element, displays in many coals. Enmeshed Fe-sulfides have also been suspected (Finkelman, 1995), and this may account for the small but conspicuous loading shown by As (0.29) in this "organic" factor of the Bon Air coal. Although few workers (e.g., Vassilev and Vassileva, 1996) have noted Pb–Sb sulfosalts in coals, Pb and Sb very readily form sulfosalts, and Pb–Sb-rich ore deposits may contain over a dozen complex Pb–Sb sulfosalts (e.g., sorbyite $Pb_{19}(Sb,As)_{20}S_{49}$, zinkenite $Pb_9Sb_{22}S_{42}$, and also Pb–Sb–Cu or Pb–Sb–Ag sulfosalts) (Chovan et al., 1998). It is reasonable to suspect that Pb and Sb in coals might show phase complexity more akin to that noted recently by Hower and Robertson (2003) for Pb and Se than the simple sulfide mineralogies (galena and stibnite) typically recognized. Correlations of Pb with As and Fe

in the Bon Air ($r=0.45$ and 0.37 , respectively) imply that some Pb–S phases may occur in pyrite grains, although the Pb–As correlation coefficient of 0.45 statistically relates at most only 20.25% (0.45^2) of the Pb to the pyritic element As.

5.3.4. Factor 4 (pyrite affinity)

Factor 4, with highest positive loadings for Fe (0.89), S (0.76), As (0.73), Cu (0.63), V (0.36) and Ni (0.31), reflects elements that likely occur dominantly (Fe, S, As) or significantly (Cu, V, Ni) in pyrite in the Bon Air coal. Factor 4 also has negative loadings for two other chalcophile elements, Cd (-0.60) and Mo (-0.31), suggesting these elements do not occur within pyrite, either as other sulfides (e.g., ZnS or MoS_2) or as disseminated ions. In higher rank coals As and Cu are so strongly associated with Fe-sulfides and chalcopyrite, respectively, that they are viewed as indirect markers of these minerals (Finkelman, 1985; Kolker and Finkelman, 1998; Kolker et al., 2000; Huggins et al., 2000b). It is true, however, that Fe-sulfide grains in a single coal can vary widely in As content (Ruppert et al., 2005), and even though Fe-sulfide association is dominant in most higher-rank coals, even these coals can contain important As fractions in organic debris (more in inertinite than in vitrinite) as well as in acid-leachable, sorbed arsenate forms (Yudovich and Ketris, 2005a). Pyritic association of As and Cu appears likely in the Bon Air, evidenced by these Factor 4 loadings and by paired element correlations (Table 5, Fig. 5b) (e.g., $r=0.84$, 0.64 , 0.52 and 0.39 , respectively, for As–Fe, Cu–Fe, As–S, and Cu–S). Some Cu in coals also occurs disseminated in pyrite (Wiese et al., 1990). The Factor 4 loading for Cu (0.63), coupled with some Cu correlation not only with Fe, S, and As, but also with other chalcophiles known in coal pyrite (e.g., $r=0.71$ for Cu–V and 0.41 for Cu–Ni) (Wiese et al., 1990; Kolker and Finkelman, 1998), suggests that while chalcopyrite likely houses a large proportion of Cu in the Bon Air, some Cu, and/or some of this chalcopyrite, is likely disseminated in pyrite.

5.3.5. Factor 5 (crandallite affinity)

Factor 5 has high loadings for Sr and P (each 0.91), and smaller loadings for Ba (0.53), La (0.38), Ce (0.30), and total REEs (0.28). These loadings suggest that crandallite-group secondary minerals like gorcexite ($BaAl_3(PO_4)_2(OH)_5 \cdot H_2O$) and goyazite ($SrAl_3(PO_4)_2(OH)_5 \cdot H_2O$) host large fractions of Sr, P, and Ba in the Bon Air coal. Gorcexite is one of the most common forms of Ba in coals, the other being barite (Finkelman, 1981a), and while REE phosphates and apatite

(generally diagenetic, rarely coprolitic or bone material) often house P in coals, goyazite is a major P and Sr source in coals and often forms with other crandallite minerals like gorceixite (Brown and Swaine, 1964; Swaine, 1977; Finkelman, 1981a, 1995; Ward, 2002; Zhang et al., 2004).

Correlation coefficients between individual pairs of these elements ($r=0.95$ for P–Sr, 0.55 for Ba–Al, 0.52 for Ba–P, and 0.44 for Ba–Sr), combined with Ba loadings in “clay” Factor 2 (0.43) and “heavy mineral” Factor 1 (0.37) are consistent with goyazite associations for Sr and P, and mixed Ba affinities that include gorceixite. Secondary crandallite-type aluminophosphates are the expected P minerals in coal horizons formed from oxidized peats with sufficiently low pH to mobilize Al at the site of phosphate deposition (Ward et al., 1996; Rao and Walsh, 1997). It’s not surprising, then, that highest concentrations of Ba, Sr, and P in the Bon Air tend to occur where inertinite is particularly abundant (Rutledge AR-8; Armfield and Shakerag upper benches) (Shaver et al., 2006—this volume). Although Bon Air REEs appear to be largely in heavy mineral phosphates like monazite and xenotime (Factor 1), the strength of REE loadings in this factor (up to 0.30) indicate a spatial relationship between these REE phosphates and the crandallite phosphates, suggesting the REE phosphates provided the P for the secondary crandallite growth. The data also suggest that neither barite (BaSO_4) nor apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$] are significant hosts of Ba or P. Calcium has a low Factor 5 loading (0.18) and little correlation with P ($r=0.12$, Table 5), and Ba has a low correlation coefficient with S ($r=0.02$, Table 5), only a 0.30 loading with S in Factor 4, and no local correlations with S (Fig. 5g).

5.3.6. Factors 6 and 8 (non-pyritic sulfide affinity)

These factors reflect elements known in coal to form discrete sulfides outside of pyrite. Factor 6 has highest loadings for Co (0.87), Zn (0.74), Mo (0.57), and Ni (0.54), while Factor 8 has highest loadings for V (0.57), Mo (0.53), Cu (0.43), Cd (0.33), and Mn (0.28).

Zinc in coals is often restricted to sphalerite, but it also occurs in small amounts in organic matter or other sulfides (Finkelman, 1995; Davidson, 2000). Cadmium typically occurs in sphalerite in coal (Kolker and Finkelman, 1998), but some Cd may occur in pyrite (Swaine, 1990; Cavender and Spears, 1995). Although Cd in the Bon Air has a small correlation coefficient with Zn ($r=0.12$, Table 5) and is loaded much less strongly in Factor 6 (0.21) than Zn (0.74), its strongly negative correlation with both Fe ($r=-0.55$) and As ($r=-0.59$) and its strong negative loading with “pyrite”

Factor 4 (-0.60) suggests that it is more likely in sphalerite than in pyrite. Some of the highest contents of Zn and Cd (as well as Pb and Cu) occur in Bon Air samples where Al contents are also high (Fig. 5b,e). Loadings for all these chalcophile elements (except Pb) in “clay” Factor 2 are small (0.24–0.37), but well above median Factor 2 loadings. Such localized clay-chalcophile associations in coal can form from weathering-induced leaching of chalcophiles from sulfides, followed by chalcophile element redeposition in clays marginal to original sulfide sites (Wiese et al., 1990). Simultaneous increases in Al and either S^{2-} or chalcophile concentrations in the mire may produce the same result. In the Upper Freeport coal (OH–WV–PA, USA), for example, correlations of Cu, Pb, and Zn with Si, Al, and ash were attributed to contemporaneous detrital introduction of aluminosilicates and aqueous chalcophile species, followed by sulfide and selenide precipitation in situ with the other detrital components (Cecil et al., 1979; Finkelman, 1993). In the Bon Air coal, precipitation of metal sulfides with small solubility product constants (e.g., Pb, Zn, and Cu) within accumulating Al-rich ash may have been forced by mire doming, which produced higher ash and, importantly, higher S^{2-} concentrations in the resultant peats (Shaver et al., 2006—this volume).

Finkelman (1995) and Kolker and Finkelman (1998) note considerable ambiguity in Co data, but both infer sulfide association to be important. For the Bon Air coal, negative Co correlations with pyritic elements ($r=-0.13$ for Fe and -0.22 for As), a strong Co loading in Factor 6 (0.87), and the Factor 6 loadings of Zn (0.74) and Mo (0.57), which have near-zero or negative loadings in “pyrite” Factor 4, collectively suggest that Co largely has non-pyritic sulfide affinity in the Bon Air. The data also imply that these Bon Air Co-sulfides often contain Ni (Factor 6 loading for Ni=0.54, and $r=0.55$ for Co–Ni). There does not appear to be any Co-organic association in the Bon Air coal, as has been questioned in some coals (Finkelman, 1995), in view of both Be’s negative loading in Factor 6 (-0.05) and Co’s negative loading in “organic” Factor 3 (-0.18).

Most Mo data for coals are ambiguous. It has been inferred to have organic and sulfide affiliations (Finkelman, 1993; 1995), even though Mo is strongly chalcophile and PIXE data show Mo concentrations an order of magnitude higher in Fe-sulfides than in vitrinites in some coals (Hickmott and Baldrige, 1995). For the Bon Air coal, Mo has a negative loading (-0.31) in “pyrite” Factor 3. But it also shows localized correlations with other chalcophiles (Fig. 5h), and has conspicuous loadings in Factors 6 and 8 (0.57 and 0.53),

factors that are defined by chalcophiles (Mo, Co, Ni, Zn in Factor 6; Mo, V, Cu, and Cd in Factor 8). Overall, the data suggest Mo is most likely hosted by discrete Mo sulfides outside of pyrite.

5.3.7. Factor 7 (calcite affinity)

Factor 7 has highest factor loadings for Hg (0.89) and Ca (0.48), and lower Y (0.38) and Mn (0.29) loadings. These loadings appear to reflect a strong Hg association, and weaker Y and Mn association, with calcite, whose ability to remove these and other heavy metals from aqueous media is the subject of considerable environmental research. Sorption processes, including adsorption, diffusion, or surface dissolution/precipitation (Stipp et al., 1992; Hay et al., 2003), readily produce metal carbonates ($MeCO_3$) or solid solutions (Me,Ca) CO_3 on the surface of calcite (Paquette and Reeder, 1995; Tesoriero and Pankow, 1996; Rimstidt et al., 1998; Godelitsas et al., 2003a). Sorption of Hg^{2+} by calcite has produced hydrated montroydite ($HgO \cdot nH_2O$), but $HgCO_3$ or $HgCO_3 \cdot 2HgO$ would also be expected to form (Godelitsas et al., 2003b). Calcite also sorbs REEs and Mn (Temmam et al., 2000; Stipp et al., 2003), and Mn occurrence in calcite is common in many coals (Kolker and Finkelman, 1998).

In most coals, however, Hg is a strongly chalcophile element. A continuing Hg correlation with As and pyritic sulfur suggest Hg is mainly hosted by Fe-sulfides, but some variability exists (Kolker and Finkelman, 1998; Sakulpitakphon et al., 2004; Mardon and Hower, 2004; Mastalerz et al., 2004). For example, direct measurements of Alabama's Black Warrior coal show its Hg dominantly in As-rich pyrite, but locally also in organic matrix (Diehl et al., 2004), and while some Indiana coals have pyrite as the dominant Hg host, others show significant Hg in organic association (Mastalerz and Drobnik, 2005). Other studies (Hower and Robertson, 2004) show that Hg is not evenly distributed among all Fe-sulfides in a given coal, and Zhang et al. (2002) noted Hg-bearing hydrothermal calcite and chlorite in Guizhou coal (China). Despite a varied occurrence that also includes cinnabar, meta-cinnabar, kleinite ($Hg_2N(Cl,SO_4) \cdot nH_2O$), native Hg, Hg-rich gold, and Hg-bearing clausthalite (Seredin, 2004; Yudovich and Ketris, 2005b; Brownfield et al., 2005), and although low-sulfur coals are more likely to contain significant Hg in organic matter than higher-sulfur coals (Yudovich and Ketris, 2005b), Fe-sulfides seem to be the primary Hg host in most coals (Hower et al., 2005a). In the Bon Air coal, however, Hg appears to be sorbed onto calcite, evidenced both by the factor loadings Hg and Ca show in Factor 7, as well

as the negative to near-zero loadings (−0.13 and 0.03) for Hg in “organic” Factor 3 and “pyrite” Factor 4, respectively. Some weathering typifies all exposed Bon Air coal at its long-abandoned mine sites. Mercury presence now in calcite may imply calcite sorption of Hg that was remobilized by weathering from original pyrite, and these processes may be particularly important in abandoned coals.

5.3.8. Selenium

The occurrence of Se in the Bon Air is not clear, but a pyritic affinity appears more likely than other potential associations. Most Se in coals has an organic affinity, but it also is known in pyrite, other sulfides, and as Pb-bearing selenide (Kolker and Finkelman, 1998; Hower and Robertson, 2003). Dreher and Finkelman's (1992) study of Se in Powder River Basin coal and overburden found 70–80% of the Se in organic debris, 5–10% in pyrite, 1–5% in other sulfides and selenides, and the remainder in secondary Se salts formed by oxidation of Se-bearing pyrite. In the Bon Air coal, Se is not strongly loaded in any factor. Its highest loadings are 0.27 in “heavy mineral” Factor 1, 0.21 in “other sulfide” Factor 8, and 0.19 in “pyrite” Factor 4. It also shows a strong negative loading with “organic” Factor 3 (−0.68), quite negative correlation with Be ($r = -0.43$), and strong negative correlation with Pb ($r = -0.54$), making both organic and selenide association less likely than pyritic association.

5.4. Trace element geochemistry of dump versus channel samples

For most trace elements we considered (Tables 1 and 2), it appears that mine dumps in the study area provide slightly imperfect samples of the coal that was mined there. For the 26 dump and nine channel samples collected, dump samples as a group have somewhat lower mean concentrations of many sulfide- or sulfosalt-associated elements (As, Cu, Fe, Ni, Pb, S, Sb, and V), and somewhat higher mean concentrations of elements in clay, heavy mineral, crandallite, or calcite associations (Al, Hg, K, Mn, REEs, Sr, Th, Ti, U, and Y), than the channel sample group (Table 3). However, only As and Fe are statistically different between dump and channel samples at the 95% confidence level, (15.3 ± 6.2 ppm vs. 41.2 ± 9.3 ppm for As, and 0.96 ± 0.21 wt. % vs. 1.65 ± 0.27 wt. % for Fe).

For mine adits where both a dump and a channel sample were collected (Shakerag 1, 2, and 3; Armfield 3 and 4), there are consistent trace element variations between dump and channel samples (Fig. 6). In general,

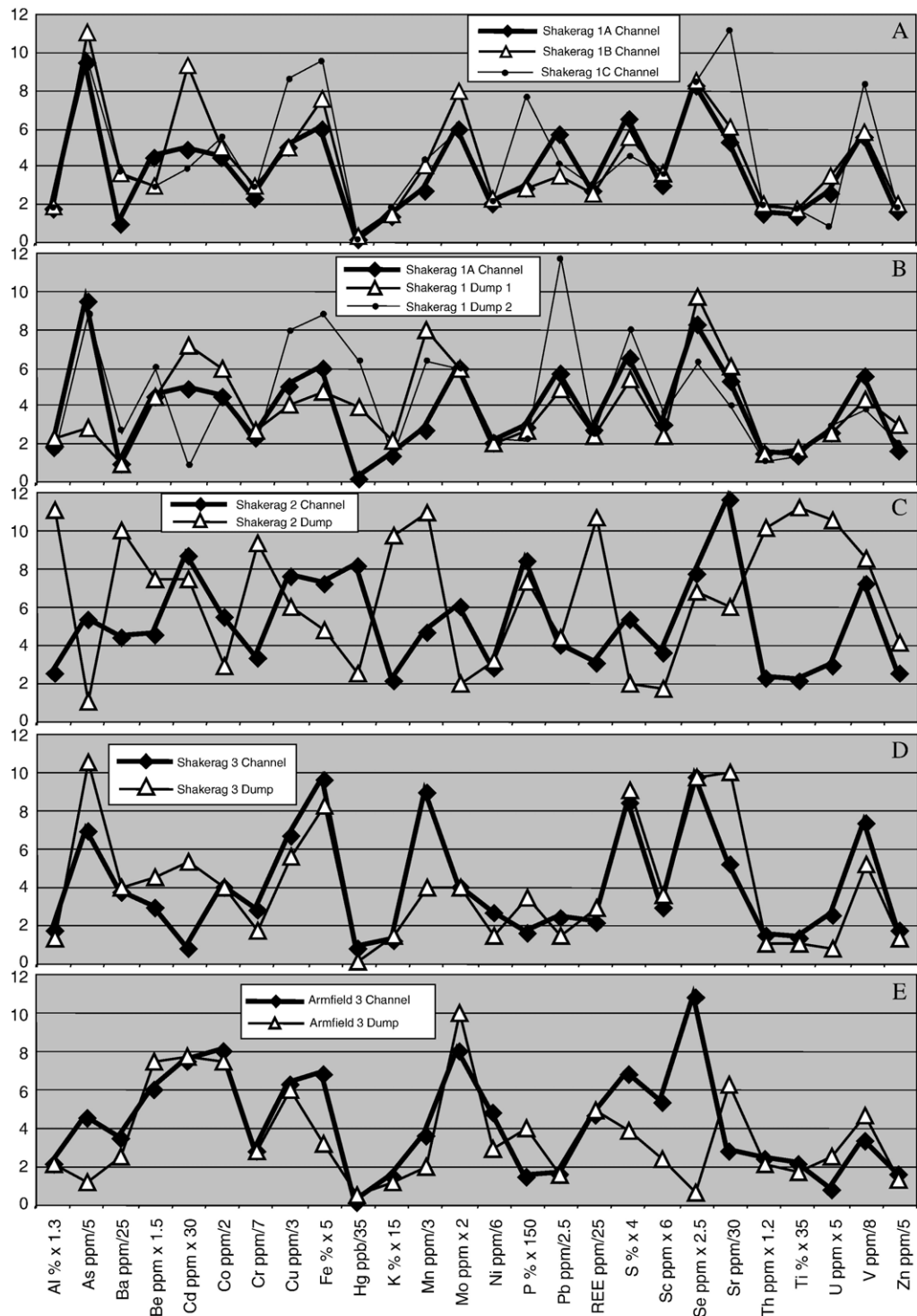


Fig. 6. Trace element variations in repeated Bon Air coal samples from a given sample site, showing (A) variations between repeated channel samples of a single site (Shakerag-1), and (B–E) variations between dump and channel samples at several sites (Shakerag-1, 2, and 3, and Armfield-3).

dump samples show lower concentrations of As, Cu, Fe, Ni, Pb, and S, but generally higher concentrations of Be, Sr, and REEs, relative to their respective channel

samples (Fig. 6b–e, Tables 1 and 2). Overall, however, although dramatic differences between dump and channel samples exist in a few cases (Shakerag 2, Fig.

6c and Armfield 4, Tables 1 and 2), most channel-vs.-dump variations are typically small (within 1–2 σ of their means) and on a scale similar to that shown by multiple channel samples of a given site (Shakerag 1, Fig. 6a and Tables 1 and 2; and Upper Shakerag 1, Tables 1 and 2).

5.5. Paleoenvironmental control on trace elements

Trace element contents and variations within the Bon Air coal and its seat- and caprocks appear to have been strongly controlled by extra-mire influxes into Bon Air paleomires, particularly fluvial ones. In moderate- to high-ash coals like the Bon Air, Finkelman (1981a) noted that ash consists largely of detrital quartz, clays, and heavy minerals (zircon, rutile, and REE phosphates). Consistent with other work indicating that the Bon Air paleoenvironment was almost exclusively fluvial and had little marine (Bergenback et al., 1992a,b; Bergenback, 1993; Knoll and Potter, 1998) or volcanic (Shaver et al., 2006—this volume) influence, seat- and caprocks of the Bon Air coal (Tables 1 and 2) are enriched in elements typical of clays and heavy-mineral detritus (Al, Ce, Cr, Hf, K, La, Mn, Nd, Rb, Sc, Th, U, Y, V, and Zr; Wedepohl, 1978; Harris et al., 1981; Palmer and Wandless, 1985; Hower et al., 2005c), yet are depleted in Br, which is generally associated with marine influx (Rimmer, 1991; Hickmott and Baldridge, 1995). Marine influence on the Bon Air coal is also contra-indicated by its moderately low sulfur content (1.24% avg.), in contrast to much higher sulfur contents (often ≥ 2 –4%, at times up to 5–10%) in strongly marine-influenced coals (Williams and Keith, 1963; Shao et al., 2003).

Within individual coal benches of the Bon Air, abundances of elements associated with these clay and heavy minerals consistently occur with high Fe and S in high-ash, high-inertinite benches where quartz rather than kaolinite or illite is the dominant ash phase and where mire-to-channel transition species like *Paralycopodites* are relatively abundant (Shaver et al., 2006—this volume). These high-ash, quartz-rich, and heavy-element rich benches are also enriched in Sr, which has been shown to be fluvially controlled in other coals (Rimmer, 1991). Volcanic or volcanoclastic inputs have been noted as unlikely to account for the trace element signatures of either Bon Air coal benches or its seat- or caprocks (Shaver et al., 2006—this volume). Ultimately, detritus is the primary inorganic source of all trace elements in coal, especially fluvial or marine detritus that may source the coal's own caprock, interbeds, or overburden (Spears, 1987; Schatzel and

Stewart, 2003), but also including aerosol and groundwater input (Lindahl and Finkelman, 1986; Finkelman, 1993). Our data suggest that for the Bon Air, the dissolved and clastic input was overwhelmingly fluvial in nature. In spite of possible post- or syn-coalification migration of elements that may alter original coal geochemistry (Yudovich, 2003; Hower et al., 2005c) and some post-mining remobilization, especially of chalcophile elements, fluvial influxes were likely the major control on many of the Bon Air's present trace element variations.

5.6. Surface water chemistry and precipitates

For the 29 surface water samples in our study (Table 7), highest levels of many trace metals (Al, Cd, Co, Cr, Cs, Cu, Fe, Li, Mg, Mn, Ni, Pb, REEs, Sc, Si, Sr, Th, Ti, Tl, Y, and Zn) occur in mine waters, with low-pH adits (pH 3.78–4.80) (Shakerag 1, Rutledge CH-2, Rutledge CH-4, and Rutledge AR-5) having levels up to two orders of magnitude higher than non-mine waters. Nonetheless, almost all of these high metal levels meet EPA drinking water standards, a phenomenon observed in other coal-impacted Cumberland Plateau streams (Gottfried et al., 1984). Of the 11 trace elements analyzed for which the U.S. Environmental Protection Agency (EPA) has set enforceable primary drinking water standards (As, Ba, Cd, Cr, Cu, Hg, Pb, Sb, Se, Tl, and U) (U.S. EPA, 2000b), none exceed the primary standards in any sample collected (although we did not analyze for Be or F, which are also regulated for primary standards). For the nine elements for which EPA has recommended aquatic life criteria (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn) (U.S. EPA, 2000a), all samples met these criteria as well.

Of those components analyzed for which EPA sets non-enforceable secondary drinking water standards (pH, TDS, Ag, Al, Cu, Fe, Mn, and Zn) (U.S. EPA, 2000c), the Al standard (50–200 ppb) was exceeded in four mine sites (228, 544, 752, and 1243 ppb, respectively, for Shakerag 7, Rutledge CH-4, Rutledge CH-2, and Shakerag 1) and one non-mine site (210 ppb). The Fe standard (300 ppb) was exceeded in three minesites (1100, 2370, and 6280 ppb, respectively, for Dotson 1, Rutledge CH-4, and Rutledge CH-2), and 13 non-mine sites (up to 4080–18,400 ppb in outflow seeping from lake dams). The Mn standard (50 ppb) was exceeded in six mine sites (66–721 ppb) and eight non-mine sites (up to 650–1540 ppb in the dam outflows), and the pH standard (6.5–8.5) was exceeded in seven minesites (pH 3.78–6.20) and four non-mine sites (pH 6.20–6.41).

Table 7

Trace element chemistry of surface waters in the vicinity of Bon Air coal mine sites, as determined by inductively coupled plasma mass spectrometry (ICP/MS) and compared to U.S. EPA primary and secondary drinking water standards and aquatic life criteria

Site	Sample	Site type	Flow (CFS)	pH	TDS (ppm)	Ag	Al	As	Au	Ba	Bi	Br	Ca (ppm)	Cd	Ce	Co	Cr	Cs	Cu	Dy
1	Shakerag 1	AD	<0.001	3.78	117	-0.2	1243	0.24	-0.002	22	0.005	9	9.7	0.14	2.79	12.750	1.9	0.024	3.2	0.395
2	Shakerag 2	MS	0.2	6.20	24	-0.2	12	0.09	-0.002	21	0.008	25	3.9	-0.01	0.03	0.073	1.1	0.004	-0.2	0.010
3	Shakerag 7	MS	0.5	7.87	95	-0.2	228	0.21	-0.002	38	-0.01	26	23.9	0.05	1.22	0.916	0.7	0.014	0.3	0.108
4	Rutledge AR-5	AD	<0.01	4.80	33	-0.2	103	0.06	-0.002	30	-0.01	10	4.5	0.06	0.47	3.034	0.8	0.012	1.8	0.049
5	Rutledge AR-8	MS	0.5	6.78	33	-0.2	68	0.31	-0.002	39	0.009	25	9.2	0.02	0.45	0.419	-0.5	0.015	0.3	0.038
6	Above RutAR-8	UA **	0.5	7.05	33	-0.2	60	0.41	-0.002	35	0.008	25	9.5	0.02	0.39	0.401	-0.5	0.008	-0.2	0.034
7	Rutledge CH-2	AD	<0.1	3.95	100	-0.2	752	0.16	-0.002	26	0.007	12	10.1	0.05	3.70	10.27	1.0	0.096	0.8	0.476
8	Rutledge CH-4	AD	<0.1	4.27	70	-0.2	544	0.16	-0.002	29	0.006	12	8.2	0.05	3.23	4.319	0.5	0.016	0.9	0.365
9	Dotson 1	AD	<0.1	6.02	63	-0.2	58	0.24	-0.002	27	-0.01	18	10.5	0.02	0.37	2.200	0.6	0.012	-0.2	0.044
10	Armfield 4	MS	0.2	6.20	33	-0.2	50	0.10	-0.002	22	0.005	38	1.6	0.02	0.24	0.166	-0.5	0.017	0.2	0.038
11	Above Arm-4	UA **	0.2	6.73	9	-0.2	21	0.09	-0.002	19	-0.01	42	2.1	-0.01	0.12	0.134	-0.5	0.003	-0.2	0.014
12	Jgarden-1	SS	<0.1	7.23	192	-0.2	16	0.55	-0.002	44	-0.01	59	69.0	0.06	0.07	1.078	0.7	0.018	5.6	0.009
13	Stirling-1	SS	<0.1	6.37	113	-0.2	53	0.75	-0.002	39	-0.01	44	47.1	0.04	0.22	0.455	0.5	0.012	0.5	0.016
14	Upperabbo-1	WSS	0.1	7.39	154	-0.2	18	0.48	-0.002	30	-0.01	52	59.0	0.03	0.09	0.222	-0.5	0.007	0.3	0.008
15	Mikell-1	WSS	0.3	7.68	106	-0.2	26	0.46	-0.002	30	-0.01	45	35.4	0.02	0.10	0.202	-0.5	0.009	-0.2	0.011
16	McDonald-1	WSS	<0.1	7.28	76	-0.2	86	0.47	-0.002	30	-0.01	21	22.0	0.03	0.33	0.241	-0.5	0.018	1.1	0.027
17	SasHouse-1	WSS	<0.1	6.32	24	-0.2	210	0.14	-0.002	31	0.005	14	4.7	0.04	0.58	0.256	-0.5	0.009	0.5	0.065
18	Clarapoint-1	WSS	0.3	7.22	37	-0.2	37	0.18	-0.002	30	-0.01	21	11.4	0.02	0.12	0.181	-0.5	0.006	-0.2	0.010
19	Hwy41a-1	UR	0.2	6.88	21	-0.2	63	0.20	-0.002	13	-0.01	25	5.4	-0.01	0.17	0.134	-0.5	0.007	-0.2	0.018
20	AltoRoad-1	UR	0.5	6.78	26	-0.2	52	0.10	-0.002	30	-0.01	27	6.3	0.02	0.31	0.306	-0.5	0.007	-0.2	0.033
21	TomPack-1	FS	0.2	6.25	8	-0.2	21	0.08	-0.002	24	-0.01	28	1.5	0.02	0.14	0.124	-0.5	0.003	-0.2	0.016
22	BridgeMove-1	FS	0.1	6.83	37	-0.2	45	0.90	-0.002	28	0.006	22	10.0	0.01	0.48	0.386	-0.5	0.013	-0.2	0.028
23	Eqcenter-1	FS	<0.1	6.88	47	-0.2	28	0.87	-0.002	28	-0.01	24	13.5	-0.01	0.21	0.873	-0.5	0.012	-0.2	0.015
24	Fcabin-dam-1	DO	0.1	6.41	45	-0.2	26	1.12	-0.002	23	-0.01	20	1.5	-0.01	0.91	2.404	-0.5	0.017	-0.2	0.031
25	Bratton-dam-1	DO	0.2	6.82	50	-0.2	10	0.71	-0.002	14	-0.01	18	12.5	0.02	0.46	1.456	-0.5	0.01	-0.2	0.012
26	Cheston-dam-1	DO	0.2	6.68	36	-0.2	17	0.49	-0.002	17	-0.01	35	7.0	0.01	0.32	1.343	-0.5	0.018	-0.2	0.014
27	WetCave-1	CSM	0.2	7.66	106	-0.2	60	0.16	-0.002	28	-0.01	15	31.2	0.02	0.37	0.152	-0.5	0.005	-0.2	0.033
28	MudCreek-1	SMFD	>0.5	7.59	101	-0.2	16	0.14	-0.002	30	-0.01	14	30.0	0.03	0.08	0.127	-0.5	0.002	-0.2	0.008
29	Dick Crk-1	OMFD	<0.1	6.59	92	-0.2	24	0.40	-0.002	29	-0.01	15	26.5	0.03	0.34	0.811	-0.5	0.008	-0.2	0.020

U.S. EPA Primary Drinking Water Standards, Secondary Drinking Water Standards, and Aquatic Life Criteria

MCLG														5			100			1300	
MCL or TT								10		200				5			100			1300 (TT)	
Secondary Standard			6.5–8.5	500		100	50–200													1000	
Aquatic Life CMC						3.2		340												570 (16)*	13
Aquatic Life CCC								150						0.25						74 (11)*	9

Site	Sample	Site type	Flow (CFS)	Er	Eu	Fe	Ga	Gd	Ge	Hf	Hg	Ho	I	In	K	La	Li	Lu	Mg	Mn
1	Shakerag 1	AD	<0.001	0.159	0.153	419	0.05	0.653	0.02	0.004	-0.2	0.061	2	-0.001	1720	1.035	19	0.018	7660	721
2	Shakerag 2	MS	0.2	0.004	0.006	28	-0.01	0.015	-0.01	-0.002	-0.2	0.002	2	-0.001	352	0.031	-1	-0.001	1020	9
3	Shakerag 7	MS	0.5	0.051	0.041	479	0.04	0.162	0.01	0.002	-0.2	0.017	12	-0.001	549	0.790	-1	0.007	1560	66
4	Rutledge AR-5	AD	<0.01	0.018	0.026	42	0.01	0.092	0.01	-0.002	-0.2	0.007	1	-0.001	1110	0.154	11	0.002	3470	113
5	Rutledge AR-8	MS	0.5	0.014	0.021	200	0.02	0.071	-0.01	-0.002	-0.2	0.006	22	-0.001	1790	0.275	-1	0.002	1620	29
6	Above AR-8	UA**	0.5	0.014	0.018	341	0.02	0.057	-0.01	-0.002	-0.2	0.006	24	-0.001	1870	0.297	-1	0.002	1310	33
7	Rutledge CH-2	AD	<0.1	0.178	0.200	6280	0.20	0.852	0.04	0.007	-0.2	0.069	5	-0.001	26800	1.285	18	0.019	6160	659
8	Rutledge CH-4	AD	<0.1	0.138	0.144	2370	0.07	0.658	0.02	0.004	-0.2	0.054	3	-0.001	1810	1.409	17	0.014	5700	330
9	Dotson 1	AD	<0.1	0.016	0.022	1100	0.03	0.083	0.01	-0.002	-0.2	0.006	5	-0.001	1650	0.190	9	0.002	5720	487
10	Armfield 4	MS	0.2	0.016	0.015	95	0.03	0.055	-0.01	-0.002	-0.2	0.006	13	-0.001	554	0.131	-1	0.002	738	25
11	Above Arm-4	UA**	0.2	0.007	0.008	81	0.01	0.022	-0.01	-0.002	-0.2	0.002	22	-0.001	455	0.093	-1	0.001	614	32
12	Jgarden-1	SS	<0.1	0.008	0.009	645	0.01	0.011	0.04	-0.002	-0.2	0.002	62	-0.001	2970	0.041	-1	0.003	2850	107
13	Stirling-1	SS	<0.1	0.011	0.010	701	0.02	0.025	0.04	-0.002	-0.2	0.003	30	-0.001	1680	0.109	-1	0.002	2080	57
14	Upperabbo-1	WSS	0.1	0.004	0.008	391	0.01	0.011	0.02	-0.002	-0.2	0.001	56	-0.001	1180	0.044	-1	-0.001	2420	23
15	Mikell-1	WSS	0.3	0.006	0.008	422	-0.01	0.015	0.02	-0.002	-0.2	0.002	40	-0.001	971	0.056	-1	0.001	1680	35
16	McDonald-1	WSS	<0.1	0.013	0.014	503	0.02	0.050	0.03	-0.002	-0.2	0.005	14	-0.001	1360	0.193	-1	0.002	1280	19
17	SasHouse-1	WSS	<0.1	0.03	0.026	72	0.03	0.100	0.01	0.002	-0.2	0.011	8	-0.001	705	0.479	-1	0.004	816	8
18	Clarapoint-1	WSS	0.3	0.006	0.007	132	-0.01	0.017	-0.01	-0.002	-0.2	0.002	10	-0.001	846	0.098	-1	-0.001	933	13
19	Hwy41a-1	UR	0.2	0.007	0.008	383	0.02	0.027	-0.01	-0.002	-0.2	0.003	23	-0.001	675	0.104	-1	0.001	730	28
20	AltoRoad-1	UR	0.5	0.014	0.015	139	0.02	0.051	0.01	-0.002	-0.2	0.005	10	-0.001	1190	0.255	-1	0.002	784	11
21	TomPack-1	FS	0.2	0.008	0.008	50	-0.01	0.021	-0.01	-0.002	-0.2	0.003	8	-0.001	380	0.086	-1	0.001	491	16
22	BridgeMove-1	FS	0.1	0.013	0.014	943	0.02	0.049	0.01	0.003	-0.2	0.004	34	-0.001	2110	0.264	-1	0.001	1170	66
23	Eqcenter-1	FS	<0.1	0.007	0.008	850	0.02	0.022	-0.01	-0.002	-0.2	0.002	33	-0.001	1490	0.092	-1	-0.001	1450	182
24	Fcabin-dam-1	DO	0.1	0.014	0.015	18400	0.14	0.060	0.04	0.003	-0.2	0.005	57	-0.001	637	0.266	-1	0.002	546	1540
25	Bratton-dam-1	DO	0.2	0.006	0.008	4080	0.03	0.027	0.01	-0.002	-0.2	0.002	52	-0.001	579	0.125	-1	0.001	1180	650
26	Cheston-dam-1	DO	0.2	0.006	0.007	5640	0.10	0.028	0.02	-0.002	-0.2	0.003	147	-0.001	668	0.102	-1	0.001	941	1270
27	WetCave-1	CSM	0.2	0.016	0.017	232	0.03	0.053	-0.01	-0.002	-0.2	0.006	28	-0.001	873	0.187	-1	0.002	5880	18
28	MudCreek-1	SMFD	>0.5	0.004	0.006	162	-0.01	0.010	-0.01	-0.002	-0.2	0.001	12	-0.001	822	0.044	-1	-0.001	4420	26
29	Dick Crk-1	OMFD	<0.1	0.008	0.009	306	0.02	0.031	-0.01	-0.002	-0.2	0.003	18	-0.001	965	0.111	-1	0.001	4070	416

U.S. EPA Primary Drinking Water Standards, Secondary Drinking Water Standards, and Aquatic Life Criteria

MCLG	2	
MCL or TT	2	
Secondary Standard		300
Aquatic Life CMC		
Aquatic Life CCC	1.4	50
	0.77	

All values in ppb except as noted. Samples below detection limit are denoted by negative numbers. Site numbers: 1–11 are plateau slope Bon Air mine sites; 12–26 are plateau top streams and dam outflow; and 27–29 are plateau base streams fed by and 0.8–1.6 miles (1.3–3.0 km) downstream of the other sites. Site types: AD=Adit drainage, MS=minesite stream, UA=upstream of adit, SS=suburban stream, WSS=wooded suburban stream, UR=upstream of roadway, FS=Forest Stream, DO=dam outflow, CSM=cave mouth stream, SMFD=Shakerag mines flow destination, OMFD=other mines flow destination.

MCLG, MCL, and TT=Maximum Contaminant Level Goal, Maximum Contaminant Level, and Treatment Technique Action Level, respectively, for National Primary Drinking Water Regulations (U.S. EPA, 2002b); Secondary Standards=National Secondary Drinking Water Regulations (U.S. EPA, 2002b). CMC and CCC=Criteria Maximum Concentration and Criterion Continuous Concentration, respectively, for Aquatic Life Criteria (U.S. EPA, 2002b).

* First value shown for Chromium CMC and CCC is for Cr III; second CMC and CCC number for Chromium, in parenthesis, is for Cr VI.

** Samples "Above AR-8" and "Above Arm-4" were taken 10 ft (3 m) upstream from Rutledge AR-8 and Armfield-4 coal mine sites, respectively.

Table 7 (continued)

Site	Sample	Site type	Flow (CFS)	Mo	Na	Nb	Nd	Ni	Os	Pb	Pd	Pr	Pt	Rb	Re	Ru	Sb	Sc	Se	Si
1	Shakerag 1	AD	<0.001	-0.1	2430	0.01	1.970	24.9	-0.002	0.5	-0.02	0.436	-0.02	2.511	-0.001	-0.02	0.01	2	0.4	5760
2	Shakerag 2	MS	0.2	-0.1	2500	-0.01	0.051	0.56	-0.002	0.3	-0.02	0.011	-0.02	0.763	0.001	-0.02	0.02	-1	-0.2	2240
3	Shakerag 7	MS	0.5	-0.1	19900	-0.01	0.697	0.86	-0.002	1.6	-0.02	0.179	-0.02	1.616	-0.001	-0.02	0.02	-1	-0.2	2100
4	Rutledge AR-5	AD	<0.01	-0.1	1050	-0.01	0.285	13.4	-0.002	0.2	-0.02	0.066	-0.02	1.495	-0.001	-0.02	-0.01	1	-0.2	3970
5	Rutledge AR-8	MS	0.5	-0.1	1140	-0.01	0.277	0.65	-0.002	0.2	-0.02	0.068	-0.02	3.406	-0.001	-0.02	0.03	-1	0.2	1850
6	Above RutAR-8	UA **	0.5	-0.1	1030	-0.01	0.244	0.51	-0.002	0.2	-0.02	0.068	-0.02	3.568	-0.001	-0.02	0.06	-1	-0.2	1730
7	Rutledge CH-2	AD	<0.1	-0.1	1880	0.07	2.612	29.0	-0.002	0.9	-0.02	0.570	-0.02	5.081	-0.001	-0.02	0.01	3	-0.2	7390
8	Rutledge CH-4	AD	<0.1	0.2	1310	-0.01	2.045	16.5	-0.002	0.5	-0.02	0.477	-0.02	3.201	-0.001	-0.02	0.01	2	-0.2	5450
9	Dotson 1	AD	<0.1	-0.1	2050	-0.01	0.275	12.2	-0.002	0.1	-0.02	0.063	-0.02	2.356	-0.001	-0.02	-0.01	1	-0.2	4090
10	Armfield 4	MS	0.2	-0.1	506	-0.01	0.186	1.12	-0.002	0.1	-0.02	0.043	-0.02	1.407	0.001	-0.02	0.02	-1	-0.2	2450
11	Above Arm-4	UA **	0.2	-0.1	512	-0.01	0.107	0.23	-0.002	-0.1	-0.02	0.025	-0.02	1.251	0.001	-0.02	-0.01	-1	-0.2	2420
12	Jgarden-1	SS	<0.1	0.3	8250	-0.01	0.032	0.27	-0.002	0.4	-0.02	0.009	-0.02	5.008	0.002	-0.02	0.20	1	1.9	2890
13	Stirling-1	SS	<0.1	0.2	2550	-0.01	0.099	0.41	-0.002	1.0	-0.02	0.024	-0.02	3.222	-0.001	-0.02	0.09	-1	0.2	2450
14	Upperabbo-1	WSS	0.1	0.2	1930	-0.01	0.047	0.13	-0.002	0.2	-0.02	0.011	-0.02	2.329	0.001	-0.02	0.17	-1	0.2	1940
15	Mikell-1	WSS	0.3	0.2	2930	-0.01	0.064	0.23	-0.002	0.1	-0.02	0.015	-0.02	2.079	0.001	-0.02	0.07	-1	0.3	1820
16	McDonald-1	WSS	<0.1	-0.1	2920	-0.01	0.164	0.27	-0.002	1.0	-0.02	0.046	-0.02	2.755	-0.001	-0.02	0.10	-1	0.6	1950
17	SasHouse-1	WSS	<0.1	-0.1	1260	-0.01	0.369	0.57	-0.002	1.1	-0.02	0.104	-0.02	1.260	-0.001	-0.02	0.03	-1	-0.2	1590
18	ClaraPoint-1	WSS	0.3	-0.1	838	-0.01	0.069	0.22	-0.002	0.1	-0.02	0.018	-0.02	1.867	-0.001	-0.02	0.02	-1	-0.2	1810
19	Hwy41a-1	UR	0.2	-0.1	830	-0.01	0.099	0.30	-0.002	0.1	-0.02	0.026	-0.02	1.378	-0.001	-0.02	0.02	-1	-0.2	2170
20	AltoRoad-1	UR	0.5	-0.1	717	-0.01	0.201	0.36	-0.002	0.4	-0.02	0.052	-0.02	2.067	-0.001	-0.02	0.03	-1	-0.2	2090
21	TomPack-1	FS	0.2	-0.1	431	-0.01	0.086	0.37	-0.002	-0.1	-0.02	0.021	-0.02	1.109	-0.001	-0.02	0.02	-1	-0.2	2390
22	BridgeMove-1	FS	0.1	-0.1	967	-0.01	0.22	0.37	-0.002	0.3	-0.02	0.057	-0.02	4.179	-0.001	-0.02	0.04	-1	-0.2	1490
23	Eqcenter-1	FS	<0.1	-0.1	1090	-0.01	0.092	0.23	-0.002	-0.1	-0.02	0.023	-0.02	3.117	-0.001	-0.02	0.02	-1	-0.2	1350
24	Feabin-dam-1	DO	0.1	-0.1	463	-0.01	0.266	0.21	-0.002	0.2	-0.02	0.066	-0.02	2.803	-0.001	-0.02	-0.01	-1	-0.2	1990
25	Bratton-dam-1	DO	0.2	-0.1	1360	-0.01	0.120	0.45	-0.002	-0.1	-0.02	0.030	-0.02	1.957	0.001	-0.02	0.04	-1	-0.2	1430
26	Cheston-dam-1	DO	0.2	-0.1	525	-0.01	0.117	0.13	-0.002	-0.1	-0.02	0.030	-0.02	2.959	-0.001	-0.02	0.01	-1	-0.2	1540
27	WetCave-1	CSM	0.2	0.1	1440	-0.01	0.208	0.25	-0.002	0.2	-0.02	0.051	-0.02	1.064	0.002	-0.02	0.02	1	-0.2	2460
28	MudCreek-1	SMFD	>0.5	0.1	2630	-0.01	0.043	0.21	-0.002	-0.1	-0.02	0.012	-0.02	1.060	0.001	-0.02	0.05	-1	-0.2	2300
29	Dick Crk-1	OMFD	<0.1	-0.1	868	-0.01	0.134	0.38	-0.002	-0.1	-0.02	0.031	-0.02	1.274	-0.001	-0.02	0.04	-1	-0.2	2570

U.S. EPA Primary Drinking Water Standards, Secondary Drinking Water Standards, and Aquatic Life Criteria

MCLG	0	6	50
MCL or TT	15 (TT)	6	50
Secondary Standard			
Aquatic Life CMC	470	65	
Aquatic Life CCC	52	2.5	5

Site	Sample	Site type	Flow (CFS)	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
1	Shakerag 1	AD	<0.001	0.572	-0.1	95	-0.01	0.081	-0.2	0.015	9.5	0.098	0.021	0.179	0.53	-0.02	1.655	0.125	54.0	0.031
2	Shakerag 2	MS	0.2	0.013	-0.1	32	-0.01	0.002	-0.2	-0.003	5.2	0.010	-0.001	0.015	0.35	-0.02	0.052	0.004	1.8	0.009
3	Shakerag 7	MS	0.5	0.152	-0.1	105	-0.01	0.021	-0.2	0.021	-0.1	0.011	0.006	0.090	0.48	-0.02	0.563	0.041	5.0	0.029
4	Rutledge AR-5	AD	<0.01	0.091	-0.1	61	-0.01	0.011	-0.2	-0.003	5.3	0.023	0.002	0.022	0.22	-0.02	0.213	0.015	16.0	-0.010
5	Rutledge AR-8	MS	0.5	0.068	-0.1	45	-0.01	0.008	-0.2	0.017	-0.1	0.009	0.002	0.014	0.27	-0.02	0.185	0.014	2.2	0.042
6	Above AR-8	UA **	0.5	0.056	-0.1	35	-0.01	0.006	-0.2	0.013	-0.1	0.011	0.002	0.014	0.28	-0.02	0.163	0.011	2.3	0.046
7	Rutledge CH-2	AD	<0.1	0.822	-0.1	66	-0.01	0.102	-0.2	0.075	11.7	0.083	0.020	0.073	0.82	-0.02	2.011	0.13	25.0	0.132
8	Rutledge CH-4	AD	<0.1	0.537	-0.1	102	-0.01	0.079	-0.2	0.028	0.5	0.077	0.016	0.042	0.21	-0.02	1.731	0.099	19.0	0.027
9	Dotson 1	AD	<0.1	0.080	-0.1	113	-0.01	0.008	-0.2	0.015	3.0	0.023	0.002	0.025	0.24	-0.02	0.192	0.013	8.0	0.016
10	Armfield 4	MS	0.2	0.055	-0.1	13	-0.01	0.007	-0.2	0.014	0.1	0.009	0.002	0.013	0.19	-0.02	0.163	0.015	4.0	0.039
11	Above Arm-4	UA **	0.2	0.024	-0.1	12	-0.01	0.003	-0.2	0.006	0.2	0.007	0.001	0.006	0.15	-0.02	0.077	0.006	2.6	0.014
12	Jgarden-1	SS	<0.1	0.012	-0.1	324	-0.01	0.001	-0.2	0.005	-0.1	0.018	0.002	0.276	0.36	-0.02	0.054	0.015	16.0	0.023
13	Stirling-1	SS	<0.1	0.023	-0.1	183	-0.01	0.003	-0.2	0.012	-0.1	0.019	0.001	0.161	0.50	-0.02	0.095	0.012	5.7	0.047
14	Upperabbo-1	WSS	0.1	0.010	-0.1	257	-0.01	0.001	-0.2	0.007	-0.1	0.008	-0.001	0.225	0.36	-0.02	0.040	0.006	6.6	0.038
15	Mikell-1	WSS	0.3	0.016	-0.1	131	-0.01	0.002	-0.2	0.006	-0.1	0.011	-0.001	0.125	0.31	-0.02	0.056	0.006	2.6	0.031
16	McDonald-1	WSS	<0.1	0.040	-0.1	115	-0.01	0.005	-0.2	0.021	-0.1	0.015	0.002	0.031	0.34	-0.02	0.128	0.013	5.0	0.041
17	SasHouse-1	WSS	<0.1	0.084	-0.1	29	-0.01	0.013	-0.2	0.005	-0.1	0.009	0.004	0.015	0.33	-0.02	0.347	0.028	5.9	0.042
18	Clarapoint-1	WSS	0.3	0.015	-0.1	33	-0.01	0.002	-0.2	0.006	-0.1	0.009	-0.001	0.010	0.30	-0.02	0.066	0.005	1.8	0.030
19	Hwy41a-1	UR	0.2	0.024	-0.1	26	-0.01	0.004	-0.2	0.021	-0.1	-0.010	0.001	0.012	0.19	-0.02	0.079	0.006	1.6	0.031
20	AltoRoad-1	UR	0.5	0.041	-0.1	30	-0.01	0.006	-0.2	0.005	-0.1	0.009	0.002	0.007	0.15	-0.02	0.178	0.014	2.7	0.020
21	TomPack-1	FS	0.2	0.021	-0.1	12	-0.01	0.003	-0.2	0.005	-0.1	0.008	-0.001	0.005	0.08	-0.02	0.076	0.008	2.3	0.011
22	BridgeMove-1	FS	0.1	0.045	-0.1	37	-0.01	0.005	-0.2	0.017	-0.1	0.013	0.002	0.016	0.34	-0.02	0.137	0.01	1.6	0.066
23	Eqcenter-1	FS	<0.1	0.016	-0.1	45	-0.01	0.003	-0.2	0.012	-0.1	0.011	0.001	0.014	0.18	-0.02	0.070	0.006	1.4	0.036
24	Fcabin-dam-1	DO	0.1	0.054	-0.1	13	-0.01	0.006	-0.2	0.024	-0.1	-0.010	0.002	0.011	0.11	-0.02	0.158	0.015	1.5	0.061
25	Bratton-dam-1	DO	0.2	0.024	-0.1	33	-0.01	0.003	-0.2	0.010	-0.1	0.009	-0.001	0.013	0.10	-0.02	0.064	0.006	2.1	0.022
26	Cheston-dam-1	DO	0.2	0.026	-0.1	24	-0.01	0.003	-0.2	0.010	-0.1	0.006	0.001	0.005	0.06	-0.02	0.067	0.007	1.4	0.014
27	WetCave-1	CSM	0.2	0.047	-0.1	210	-0.01	0.006	-0.2	0.004	-0.1	-0.010	0.002	0.297	0.28	-0.02	0.200	0.014	2.3	0.032
28	MudCreek-1	SMFD	>0.5	0.010	-0.1	162	-0.01	0.002	-0.2	-0.003	-0.1	-0.010	-0.001	0.186	0.15	-0.02	0.047	0.004	1.7	0.008
29	Dick Crk-1	OMFD	<0.1	0.030	-0.1	120	-0.01	0.004	-0.2	0.005	-0.1	0.011	0.001	0.046	0.22	-0.02	0.124	0.008	1.4	0.019

U.S. EPA Primary Drinking Water Standards, Secondary Drinking Water Standards, and Aquatic Life Criteria

MCLG	0.5	0	
MCL or TT	2	30	
Secondary Standard			5000
Aquatic Life CMC			120
Aquatic Life CCC			120

Aqueous Mn contents are used by many agencies as indicators of other trace elements in solution (Tennessee Division of Water Pollution Control, 2003, personal communication). In our water samples (Table 7), this does not generally hold true. While Mn correlation (Table 8) is high for Fe ($r=0.85$), it is weaker for Co, As, Th, Sb, Ni, Al, Zn, Tl, Cr, and Pb ($r=0.46$ – 0.14), near-zero for Cd and Cu ($r=0.05$ – 0.01) and negative for V, U, and Ba ($r=-0.11$ to -0.40). Of course, both Fe and Mn levels in study area mine waters are rather low overall, especially compared to particularly acidic coal mine effluents in Tennessee ($\text{pH}<3.0$), which show up to 259,000 ppb Fe and 9600 ppb Mn (O'bara and Estes, 1985).

Fe-sulfides are the primary acid-former in coal and the pH of coal mine drainage is largely controlled by their abundance relative to acid-neutralizing carbonate minerals (Brady et al., 1997; Mayo et al., 2000). Acid from pyrite hydrolysis in turn leaches trace elements from other coal phases, further increasing trace element contents of acidic mine effluent (Mayo et al., 2000). Even SiO_2 solubility, generally pH-independent below pH 9, increases at lower pH in Fe^{+3} -rich mine waters, as the $\text{FeH}_3\text{SiO}_4^{2+}$ complex forms (Reardon, 1979; Al et al., 1994). For study area waters, highest trace element concentrations occur in the four lowest-pH mine waters (pH 3.78–4.80) and a statistical correlation between pH and many elements exists at all pH levels. Low pH correlates most strongly (Table 7) with Li, Ni, Si, Tl, Co, Y, REEs, Ti, Al, Zn, and Sc ($r=-0.89$ to -0.69 , respectively, for pH versus metal), less strongly with Cr,

Cs, Mg, Cd, K, Th ($r=-0.66$ to -0.47 , respectively), and weakly with Mn, V, Cu, Zr, Rb, Fe, and Pb ($r=-0.34$ to -0.12 , respectively). A few elements (U, Ba, Sr, As, Na, I, and Ca) are more concentrated at higher pH ($r=0.12$ – 0.41 , respectively), in some cases (e.g., As) due to stable complexes favored at higher pH. The trace elements correlating most strongly with low pH include those with sulfide affinities (Zn, Cd, Co, Cu, Ni), and those with clay or heavy-mineral affinities (Al, Cr, Mn, Ni, REEs, Si, Ti, Th, V, Y, and Zr), and mobility of both chalcophile and non-chalcophile elements during coal weathering and pyrite hydrolysis is well documented (e.g., Wiese et al., 1990; Hower et al., 1999). For the Bon Air coal, however, greater chalcophile mobility appears to be the case, as channel samples and associated dump samples show greater differences for chalcophile elements than for clay or heavy-mineral elements (Fig. 6).

Pyrite hydrolysis in the Bon Air coal locally produces white to yellow coal-seam coatings of well-crystallized acid sulfates identified by XRD as dominantly halotrichite [$\text{Fe}^{+2}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$] and ferricopiapite [$\text{Fe}^{+3}_5(\text{SO}_4)_6\text{O}(\text{OH}) \cdot 20\text{H}_2\text{O}$], but neither of these form in study area mine effluents. Rather, both mine and non-mine waters are marked by poorly crystallized Fe^{3+} precipitates (“yellow-boy”) which are likely goethite (FeOOH) or ferrihydrite ($\text{Fe}(\text{OH})_3$) that typify “yellow-boy” in near-neutral to weakly acidic effluents (Williams et al., 2002).

Flow rates through mine adits and dumps appear to significantly affect trace element levels and acidity in the

Table 8
Correlation coefficients (r) for surface water components in the Bon Air coal study area

	r		r		r		r
Li-pH	-0.89	Yb-pH	-0.79	V-pH	-0.34	Fe-Mn	0.85
Ni-pH	-0.88	Pr-pH	-0.78	Cu-pH	-0.31	Co-Mn	0.46
Si-pH	-0.85	Ti-pH	-0.78	Zr-pH	-0.24	As-Mn	0.44
Tl-pH	-0.84	Al-pH	-0.76	Rb-pH	-0.23	Th-Mn	0.35
Co-pH	-0.82	Lu-pH	-0.76	Fe-pH	-0.17	Sb-Mn	0.31
Gd-pH	-0.81	Zn-pH	-0.76	Pb-pH	-0.12	Ni-Mn	0.30
Tb-pH	-0.81	Sc-pH	-0.73	Se-pH	0.12	Al-Mn	0.27
Dy-pH	-0.80	La-pH	-0.69	U-pH	0.17	Zn-Mn	0.24
Eu-pH	-0.80	Cr-pH	-0.66	Ba-pH	0.22	Tl-Mn	0.21
Ho-pH	-0.80	Cs-pH	-0.56	Sr-pH	0.23	Cr-Mn	0.14
Sm-pH	-0.80	Mg-pH	-0.54	As-pH	0.23	Pb-Mn	0.14
Er-pH	-0.79	Cd-pH	-0.53	Na-pH	0.27	Cd-Mn	0.05
Nd-pH	-0.79	K-pH	-0.47	I-pH	0.32	Cu-Mn	0.01
Tm-pH	-0.79	Th-pH	-0.47	Ca-pH	0.41	Se-Mn	-0.11
Y-pH	-0.79	Mn-pH	-0.34			V-Mn	-0.11
						U-Mn	-0.15
						Ba-Mn	-0.40

Columns 1–3 are correlations between pH and selected trace elements, arranged from lowest to highest r (most to least correlative with low pH). Column 4 shows the degree to which Mn concentrations track those of other elements, from highest to lowest r .

study area (Table 7). Low flow rates and incomplete mine adit inundation increase the time coal sulfides are exposed to atmospheric oxygen (Lopez et al., 1999; Cravotta and Bilger, 2001; Rees et al., 2002). This results in decreased water/rock ratios (Mayo et al., 2000), standing water pools enriched in accumulated cations from increased water-mineral contact time (Stoertz et al., 1997), and decreased dilutional flushing of mine adits by surface or subsurface recharge (Stoertz et al., 1998, 1999, 2001; Younger, 2000). The end result is weak discharge of lower pH and higher trace metal content. In our study, the lowest-pH mine sites are typified by very low adit flow rates ($<0.01 \text{ ft}^3/\text{s}$, $<0.0003 \text{ m}^3/\text{s}$). The lowest pH (3.78) and highest overall trace metal contents occur at the Shakerag 1 adit, where water pools behind an earthen berm in front of the adit and effluent is an almost imperceptible seep. In general for our study area, metal concentrations and acidity are inversely proportional to flow volume, a relationship common in acidic drainage (Rose et al., 1979; Aubele et al., 1998; Lopez et al., 1999; Mayo et al., 2000; Centeno, 2001; Cravotta and Bilger, 2001; Stoertz et al., 2001).

Bon Air coal mine sites appear to have produced little or no downstream geochemical impact. Even though Fe, Mn, and pH fall well outside drinking water or aquatic life standards in some mine waters (Table 7), the three down-drainage (plateau-base) streams we sampled have pH, Fe, Mn and all other elements at background levels typical of unmined areas of the Cumberland Plateau (Hanchar, 1995; Aycock and Haugh, 2001; Williams and Aycock, 2001). Slopes down-drainage from study area mine sites are dominated by leaf-litter rich soils and underlying Mississippian carbonate rocks able to neutralize Cumberland Plateau mine waters (Gottfried et al., 1984) through sequential buffering reactions which drive pH progressively higher: organic carbon and/or Fe-hydroxide equilibria to pHs of 3.5–5.0 (Blodau and Peiffer, 2003), Al-hydroxide equilibria to pHs of 5.5–6.0 (Driscoll and Bisogni, 1984; Barker and Donovan, 1998), and carbonate equilibria to pHs of 6.5–7.5 (Barker and Donovan, 1998; Cook and Fritz, 1999; Maree et al., 1999; Mayo et al., 2000). Although acidic waters in both natural and mine-remediation systems can travel long distances through carbonate rock without neutralization if Al- and/or Fe-hydroxide precipitation armors rock surfaces against continued aqueous contact (Sasowsky and White, 1993; Loop et al., 2001), Fe and Al precipitates in our study area are localized and volumetrically insignificant. The background levels of acidity and trace elements we observe downstream in plateau-base surface waters suggest strong downslope attenuation of aqueous species, likely due to both low

effluent volumes and rapid infiltration, dilution, and neutralization.

Outside of mine sites, surface water pH is apparently most strongly affected by both natural and other sources of carbonate rock. The three plateau-base streams are all buffered strongly by carbonate bedrock (limestones and dolomites), resulting in near-neutral to slightly alkaline pHs (6.59–7.66) and high Ca concentrations (26.5–31.2 ppm, Table 7) that are typical of surface and ground waters in nearby unmined areas of the Cumberland Plateau (Hanchar, 1995; Aycock and Haugh, 2001; Williams and Aycock, 2001). Many of the non-mine, plateau-top sites of our study area have a similarly high pH (6.25–7.68) and Ca concentration (up to 69.0 ppm), even though their non-calcareous, locally shaley, siliciclastic bedrock and soils would be expected to be buffered by aluminum hydrolysis and organic acids to pHs of 4.5–6.0 (Dickson, 1978; Johannessen, 1980; Driscoll and Bisogni, 1984; Cronan et al., 1990). Many plateau-top samples also have relatively high Na concentrations (often $>1000 \text{ ppb}$) and the correlation coefficient between Ca and Na for all 15 plateau-top sites is quite high ($r=0.81$). One streamside minesite (Shakerag 7), which lies downstream of limestone rip-rap of U.S. Highway 41-A, has the highest pH measured in our study (7.87), much higher Ca than other mine sites (23.9 ppm), and high Na levels (19,900 ppb) that are 3–10 times greater than typical Na levels observed in our study (400–2500 ppb) or in other Cumberland Plateau surface waters (5400 ppb) (Aycock and Haugh, 2001) or groundwaters (7000 ppb) (Hanchar, 1995). We suspect the high pHs and Ca and Na concentrations of our plateau-top samples are largely anthropogenic, sourced by abundant concrete culverts and winter-salted limestone-gravel roads crossing the area. Regardless of the origin of its alkalinity, this surface water ultimately joins, dilutes, and further neutralizes Bon Air mine waters throughout the study area.

6. Summary

For the Bon Air coal, statistical relationships suggest that clay minerals host most of its Al, K, Cr, Ti, and Th, significant Mn and V fractions, and lesser Sc, U, Ba, and Ni. Heavy accessory minerals likely host most REEs and Y, lesser Sc, U, and Th, and a small fraction of Ba, P, Cr, and Ti. Pyrite is the main host for As, and a minor host for V, Ni, and perhaps also Cu, which probably mostly occurs as chalcopyrite. Organic debris likely hosts most Be, and some Ni, U, and finely enmeshed arsenical pyrite, while Pb and Sb likely occur as organically enmeshed Pb–Sb sulfosalt(s). Crandallite-

group phosphates are likely the main hosts for Ba, Sr, and P. Most Hg, and some Y and Mn, appear to be hosted by calcite, but Hg may have been remobilized by weathering from original pyrite. Non-pyritic sulfides probably host most Co, Zn, Mo, and Cd, significant V and Ni, and minor Mn. Data contra-indicate Se-organic or Se–Pb associations, but a strong case for Se in Bon Air pyrite cannot be made. Elements whose affinities appear most strongly divided between two or more modes are Ba, Mn, Sc, U, Ni, and V.

All Bon Air coal trace elements appear to have originated largely as fluvial detritus (particulate or dissolved), and most elemental variations likely reflect original variations in fluvial influx. Elements associated with heavy minerals and clays are consistently abundant in high-ash, high-inertinite, low-Br, high-sulfur benches where quartz rather than kaolinite or illite is the main ash phase and where mire/levee transition species like *Paralycopodites* are relatively abundant.

Bon Air coal trace element means are similar to Appalachian Basin COALQUAL means, but are slightly lower for As, Fe, Hg, Mn, Na, Th, and U, and slightly higher for Be, Cd, Co, Cr, REEs, Sr, and V, at the 95% confidence level. Channel sample means are lower than dump sample means for many chalcophile elements (As, Cu, Fe, Ni, Pb, S, Sb, and V) and higher for elements of clay, heavy mineral, crandallite, or calcite affinity (Al, Hg, K, Mn, REEs, Sr, Th, Ti, U, and Y), but the elemental variance between channel and dump samples is small (in most cases within $1-2\sigma$), and only As and Fe are different at the 95% confidence level.

Surface waters document that some elemental leaching of the Bon Air coal occurs in most sites, as most trace elements have their highest concentrations in mine-adit or mine dump waters. Effluent flow rates control acidity and thereby also trace element levels. Mine drainages where flow is only a seep are the most acidic waters of the area (pH 3.78–4.80) and have trace element concentrations up to two orders of magnitude higher than nearby non-mine site waters.

Nonetheless, geochemical impacts of the Bon Air coal on area surface waters appear quite small. All waters sampled meet U.S. EPA primary drinking water standards and aquatic life criteria for all elements analyzed. Secondary standards are also met for all parameters except Al, pH, Fe, and Mn, but even in extreme cases (mine waters with pH as low as 3.78 and up to 1243 ppb Al, 6280 ppb Fe, and 721 ppb Mn, and non-mine dam-outflow waters with up to 18,400 ppb Fe and 1540 ppb Mn) downslope attenuation apparently occurs rapidly, as plateau-base streams show background levels for all these parameters.

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