



Submicron-scale mineralogy of lithotypes and the implications for trace element associations: Blue Gem coal, Knox County, Kentucky

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ABSTRACT

Transmission electron microscopy accompanied by energy-dispersive spectroscopy and selected area electron diffraction of density-gradient separates from two lithotypes of the low-ash, low-sulfur Blue Gem coal, eastern Kentucky, revealed an array of previously unrecognized (in this coal, and arguable in most others) sub-micron minerals, some < 10 nm in size. The sample representing the 1.22–1.24 specific gravity fraction of the middle bench contains a mineral identified as a La-, Ce-, Nd-bearing monazite; other minerals with Cr–Fe, Cu–Fe–S, Fe–Zn–S, and Pb; and areas, probably comprising agglomerates of several grains, if not several minerals, with concentrations of Mg, Ca, Ti, Fe, Zn, Zr, and Mo. The sample representing the 1.30–1.31 specific gravity fraction of the basal lithotype has aggregates of particles enriched in Mg, Ca, Ti, and Fe. Individual grains not specifically quantified include Cr–Ni–Mn–Cu–Fe–S, Ag–S, and Cu–S. Detailed investigation of one area (most of the variation within a < 4 μm² region) demonstrates the presence of greenockite (CdS); minute phases containing Ni–Co–Ge and Ag–Cd–Bi, the latter with a more evident S association than the former; metallic Bi; nisnite (Ni₃Sn); silver cadmium; manganosite (MnO); and siderite. Some minerals, such as the monazite, are most likely of detrital or tuffaceous origin. Many of the other assemblages could be of hydrothermal origin, a hypothesis supported by known regional geochemical and coal rank trends, but not previously demonstrated in mineral assemblages at the 10's of nm scale in this region.

1. Introduction

1.1. Trace element associations in coal

Trace element associations in coals have long been of interest with respect to both the utilization of coal and a better understanding of depositional environments, spawning numerous studies (Eskenazy, 1967, 1970, 1972, 1974, 1977, 1979, 1999, 2015; Finkelman, 1981, 1994, 1995; Bouska, 1981; Valković, 1983; Miller and Given, 1986, 1987; Given and Miller, 1987; Filby and Van Berkel, 1987; Swaine, 1990; Rimmer, 1991; Davidson, 1993; Davidson and Clarke, 1996; Seredin, 1996; Yudovich and Ketris, 2001, 2002, 2004a,b, 2005a,b,c, 2006a,b; Ward, 2002, 2016; Huggins, 2002; Seredin and Finkelman, 2008; Seredin and Dai, 2012; Dai et al., 2018; Hower et al., 2016a,b; among others). Among the elements of recent interest are the rare earth elements (REE), a suite which reflects the complexity of associations,

ranging from known terrigenous (detrital), tuffaceous (Seredin and Dai, 2012; Dai et al., 2008, 2016; Hower et al., 2016a,b; Wei et al., 2017), and hydrothermal (Dai and Finkelman, 2018) mineral associations, to organic (chelation) associations (Eskenazy, 1999, 2015; Wei and Rimmer, 2017).

The simplest way to infer the presence of organically associated trace elements in coal is to evaluate their correlation with the coal's ash yield. Traditional density-separation methods, such as the float/sink methods applied in planning coal processing operations, however, may not account for fine-grained minerals, and therefore trace elements associated with those minerals may erroneously be assigned an organic association. Organic associations of trace elements in coal have been evaluated by a number of methods and have been described by Finkelman (1981), Yudovich and Ketris (2002, 2006b), Huggins (2002), Finkelman et al. (2018), and Liu et al. (2018) among many others. Aside from organic sulfur, ubiquitous in coal and occurring in a wide

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E-mail address: james.hower@uky.edu (J.C. Hower).

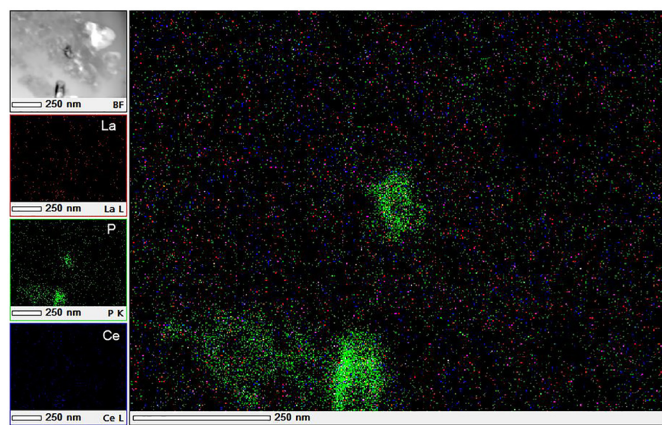


Fig. 1. La, Ce, and P element maps overlay from sample 5445/ DGC, split 4-4-5. Phosphorous dominates the two high-relief grains (note BF image at top left), but there is some indication of La in the center of both grains.

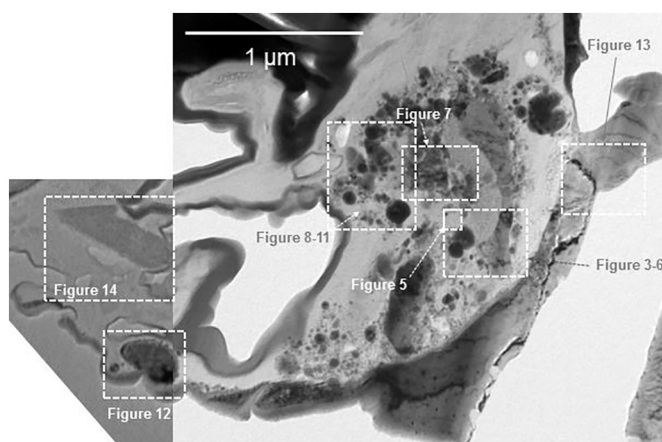


Fig. 2. Image of grain extracted by FIB (focused ion beam) with locations of Figs. 3–14 indicated. Sample 5447/ DGC, split 44-1-12.

range of concentrations from < 0.5% up to 8–12% in the Mequinenza coal (Spain) (Querol et al., 1996), Raša coal (Croatia) (Ignasiak et al., 1978; White et al., 1990; Medunić et al., 2016), and some late Permian coals from southern China (e.g., Yanshan, Yunnan Province, Dai et al., 2008), determination of organic associations of trace elements have been elusive and the descriptions of the associations have not necessarily been straightforward. Experiments investigating the possible mechanisms for binding of elements to the organic matter of coals have been carried out for many years and reported in eastern European geological journals. Research by Eskenazy (1967, 1970, 1972, 1974, 1977, 1979, 1999, 2015) includes experiments on the sorption of Ga (on peat and humic acids (HA)); Be (on peat and some lithotypes); Ti (on peat, HA, xylain, telinite, semifusain); and W (on peat and telinite); Ag and In (on peat, xylain and vitrain); REE (on xylain and HA); Mn, Cu, Zn, Co, Ni, and Sr (on xylain); and Ge (on peat and xylain) (unpublished data for Ge; Eskenazy, 2015, personal communication to Hower).

The transition from a chelated organic association in peat and low-rank coals to inorganic associations in high volatile bituminous Illinois Basin coals was discussed by Huggins and Huffman (2004). While they demonstrated that some of the Cr, Ti, V, and Zr in those coals could be present in an organic component, there is an overall trend towards decreasing organic association with increasing coal rank. Decarboxylation and the loss of other oxygen-bearing functional groups with

rank increase implies a loss of the –COOM binding of metals. The metals released can be incorporated into clays and other minerals. In addition, with the loss of moisture accompanying rank increase, cation-bearing solutions become saturated; consequently, the cations can form oxyhydroxide or oxide species if they are isolated from clays.

Another avenue of more recent investigations include several studies on the occurrence of sub-micron minerals, including nanoscale minerals and amorphous associations. Cutruneo et al. (2014), in an investigation of Permian-age Santa Catarina, Brazil, coal-cleaning rejects, found Cr-enriched hematite closely associated with quartz, jarosite, goethite, ferrihydrite, rutile, and amorphous phases; Cr-spinel associated with clays; spherical nanoquartz; ankerite; and galena. Fdez-Ortiz de Vallejuelo et al. (2017), in a study of coal-cleaning rejects from Santa Catarina preparation plants, found spherical hematite, goethite, jarosite, gibbsite, clays, ferrihydrite, and schwertmannite. In an investigation of medium-sulfur Oligocene coals from northeast India, Saikia et al. (2014) found pyrite, including As-, Pb-, Se-bearing pyrite; jarosite; pyrrhotite; marcasite; chalcophyrite; sphalerite; and As, Cd, Cr, Hg, Pb, and V associated with hematite, magnetite, and goethite. Oliveira et al. (2014), in a study of the feed coal to a power plant in northeast India, found jarosite; pyrite; ferricopiapite; and a Al–Si–O–Fe–K–Ca nanosphere with included Cu, Cr, and anatase. There was no mention of the form of the Cu and Cr. Saikia et al. (2015) examined coals, mine overburden, and fly ashes from Assam, northeast India. They noted goethite with As and Se in the overburden. In the coals (their table 7, with supplemental information from the text), they found anatase, calcite, galena, goethite, gypsum, hematite (including Cu-bearing hematite), illite, jarosite, kaolinite, melanterite (including a Cu-bearing variety), pyrite, pyrrhotite, quartz, schwertmannite, siderite, and sphalerite. They also noted nanoparticles associated with amorphous compounds; hematite; elemental sulfur; and metallic Fe, Cu, and Hg. Zhao et al. (2017) found < 10-nm Ti oxides to be associated with Cr and V in Permian high-organic-sulfur coals from Yunnan, China.

1.2. Previous studies of the Blue Gem coal

The Blue Gem coal has been extensively mined in southwestern Kentucky, particularly in portions of Knox and Whitley counties to the northwest of the Pine Mountain thrust fault (Hower et al., 1991b). The coal is notable in having low S, low mineral yield (in places, < 1% ash), and an ash chemistry dominated by Fe₂O₃ as siderite.

Density gradient centrifugation (DGC) samples of a middle (sample no. 5445) and basal bench (sample no. 5447) of the Blue Gem coal were originally studied by Hower et al. (1994a,b). In the latter study, DGC concentrates were generated in small, generally 0.01 specific gravity increments, and analyzed by proton-induced X-ray emission (PIXE).

As was known from other previous investigations of the coal (Hower et al., 1991b), the basal bench has a slightly higher ash yield (with the caveat that the whole-coal ash yield is < 1% at many locations) with a higher concentration of Ti, Zr, and other elements associated with detrital, heavy-mineral suites. For the basal bench, Ti concentrations peak in the high-vitrinite fractions. Zirconium follows the same trend with over 6.5% Zr in the 1.29–1.30 g/mL density fraction (the sample selected for this study); V (14%) and Cr (1.77%) are also unusually high in this density fraction. Aside from the Ti–Zr (heavy mineral) and V–Cr (clays) associations, the authors noted Cr–Ni–Cu–Mn–Zr–Pb associations in the lighter, liptinite-rich density fractions.

The middle benches of the Blue Gem coal can be very low in ash (as low as ca. 0.4% in the Hower et al. (1994a,b) study) (Rimmer et al., 2000), with an ash chemistry dominated by siderite and other carbonates (Fe–Ca associations through the lighter and medium densities; Mg–Ca and Mn–Ca in the higher densities). The lighter fractions have a relative enrichment in Cr, Ni, Cu, Mn, and Zn. Lead reaches its highest

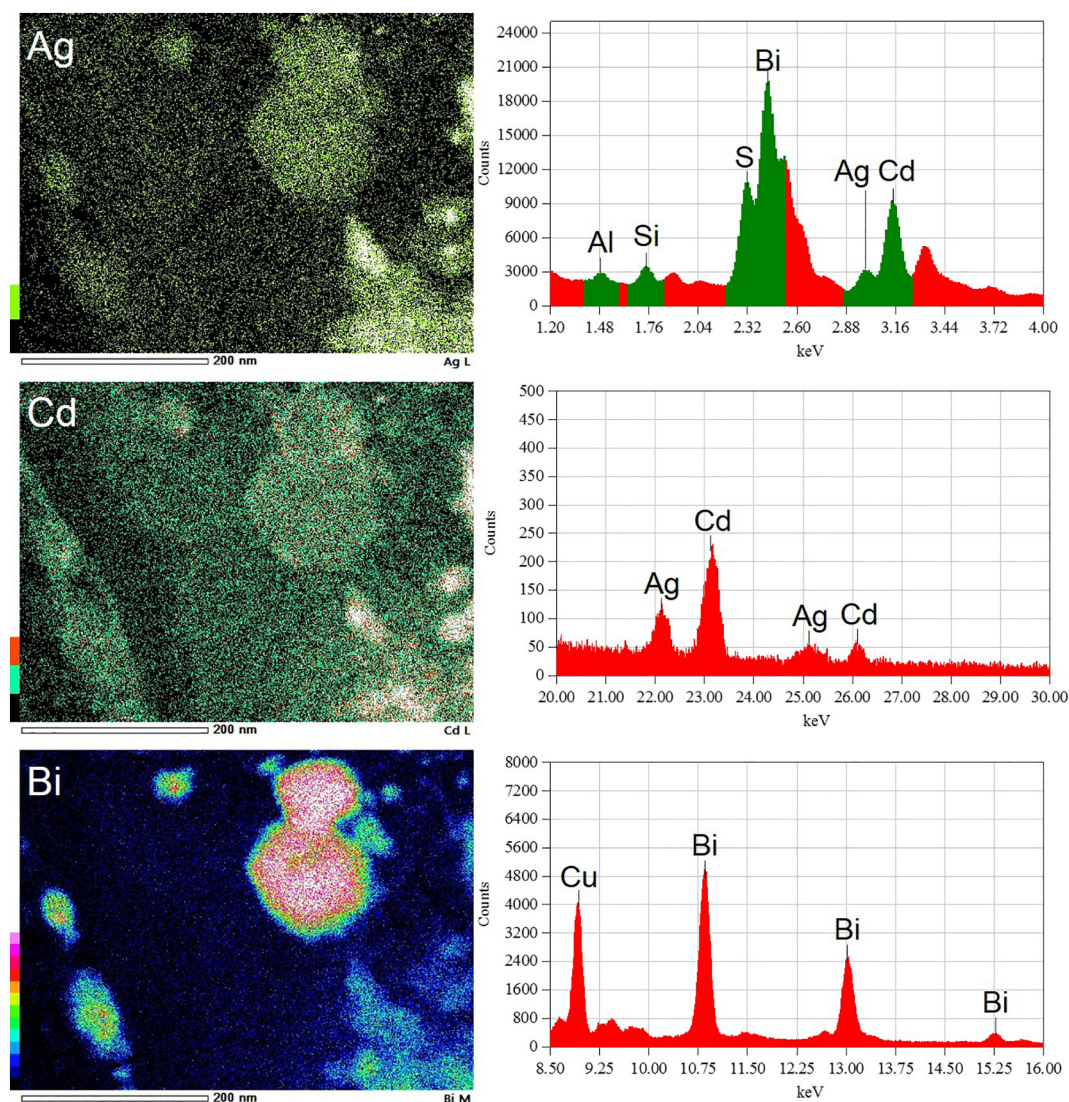


Fig. 3. Elemental maps of Ag, Cd, and Bi from EDS map 1 along left column. Right column shows the portion of the EDS spectrum showing the presence of S, Ag, Cd, and Sn (top); the region used for the positive identification of Ag and Cd (middle); and the region used for the positive identification of Bi (bottom). The latter region also shows lines for Cu, associated with the Cu grid used in the TEM, and Ge. Sample 5447/ DGC split 44-1-12.

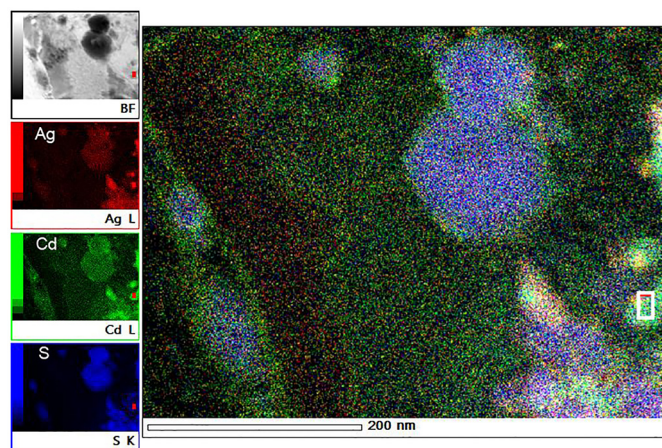


Fig. 4. Silver, Cd, and S overlay of EDS map 1. Sample 5447/ DGC split 44-1-12.

concentration (0.67%) in the 1.12–1.15 g/mL fraction. To a lesser extent, As and Se are also enriched in the low-density fractions. As with the basal lithotype, a Ti–Zr association was noted. The low-density fractions have a Cr–Ni–Cu–Mn–Zn–Pb association and Co–Ni, Cu–Zn, Ga–Ge–Y, and As–Se elemental associations noted throughout the density spectrum. Needless to say, the ash-basis geochemistry of very low-ash coals can appear to be unusual. But, considering that such low-ash, low-S lithotypes have rarely been studied in such detail, perhaps the Blue Gem coal is not as unusual as first appearances would suggest.

1.3. Scope of current study

The emphasis of the current study is to re-examine some of the trace element assemblages noted in the Hower et al. (1994a,b) study. Transmission electron microscopy permits the examination of nanometer-scale minerals in close association with the macerals. Certain of

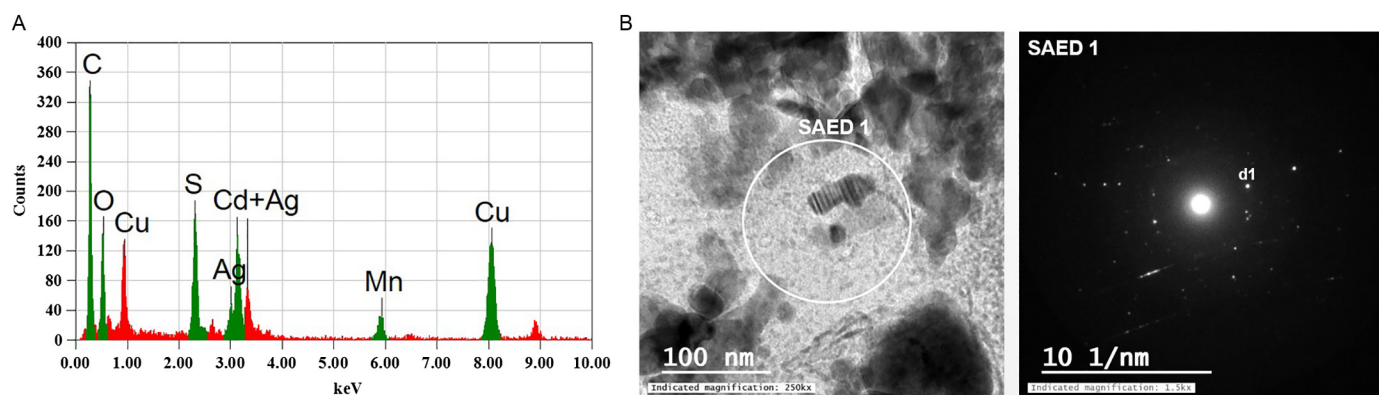


Fig. 5. (A) EDS spectrum of rectangular area in lower right quadrant in Fig. 4. (B) A 13- to 25-nm $\times$ 58-nm grain with $d_1 = 0.34$ nm and alternating dark and light bands. Sample 5447/ DGC split 44-1-12.

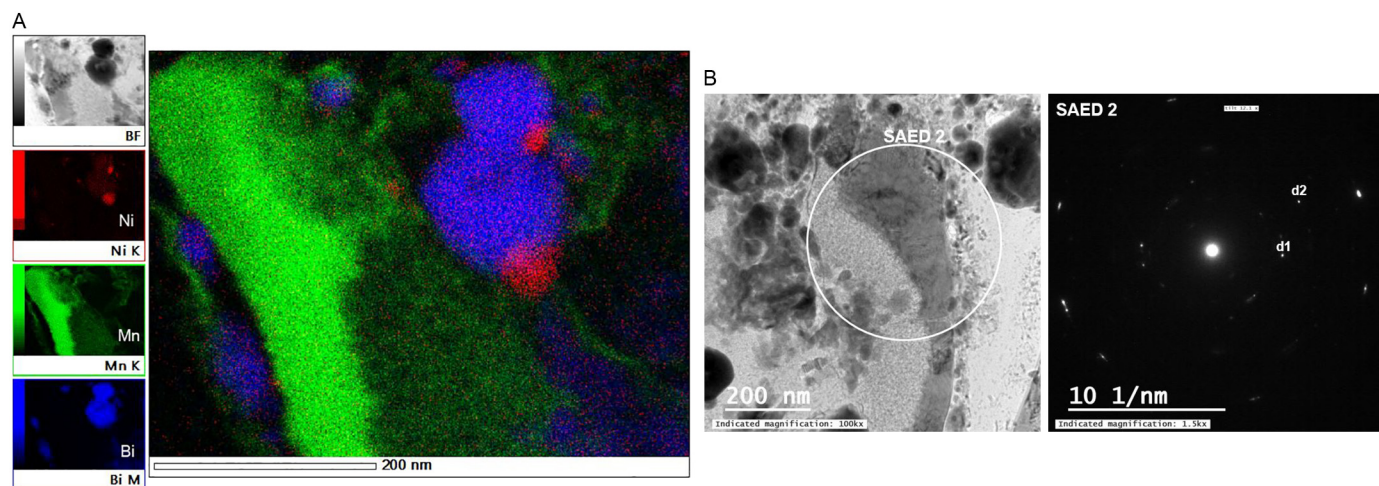


Fig. 6. (A) Ni, Mn, and Bi overlay map. (B) Manganosite (MnO). Sample 5447/ DGC split 44-1-12.

these minerals are not seen or even hinted at upon larger-scale investigation. While the very-low-ash levels of the investigated coals may suggest that many elements could be in an organic association, the TEM-based examination of minerals allows us to see that the elements are associated, at least in part, with very fine-grained minerals dispersed in the macerals.

In addition to investigating the associations of the elements noted in the latter work, this study is driven by the need (based on the interest in extracting REE from coal) to determine the mode and scale of the rare earth element + yttrium (REY) associations in coal. As such, we chose to investigate in more detail two samples from the Hower et al. (1994a,b) study: (1) coal sample 5445/ DGC separate 44-4-5 with 35% P (ash basis), and (2) coal sample 5447/DGC separate 44-1-12 with 5.86% Ti, 14.03% V, 6.54% Zr, and 0.24% Y (all on ash basis).

2. Procedure

The DGC samples were originally prepared, in part, as 2.54-cm-diameter epoxy-bound pellets prepared to a final 0.05- μ m-alumina polish for petrographic examination. For this study, thin slices of coal sample 5445/ DGC separate 44-4-5 and coal sample 5447/DGC separate 44-1-12 were cut from the polished surface and sent to the Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure (NanoEarth), Blacksburg, Virginia.

For Scanning Electron Microscopy (SEM) (FEI Quanta 600), samples

were coated with carbon to prevent charging and then observed in the backscatter (BSE) mode to find particles with high average atomic numbers. Energy-dispersive Spectroscopy (EDS) analyses were made on particles with high BSE contrast.

Based on the SEM-EDS analyses, two areas were selected for more thorough analysis. A FEI Helios 600 NanoLab Focused Ion Beam (FIB) was used to extract and lift out thin slices of the latter minerals. The slices were ion milled to approximately 100-nm thickness. Transmission electron microscopy was conducted on a lanthanum hexaboride JEOL JEM-2100 analytical electron microscope operated at 200 keV and equipped with a JEOL 60-mm²-window silicon drift detector (SDD)-based EDS system for chemical mapping. Selected area electron diffraction (SAED) was employed for mineralogical identification of grains.

3. Results and discussion

3.1. SEM-EDS

The polished slices of the epoxy-bound particulate pellets were examined by SEM-EDS in order to find areas of interest that warranted further study. In many cases, it was apparent that the spatial resolution of SEM-EDS analyses was not sufficient to effectively determine the phases present due to their sub-micron size, along with the close proximity and/or aggregation of many minute grains in the coal matrix.

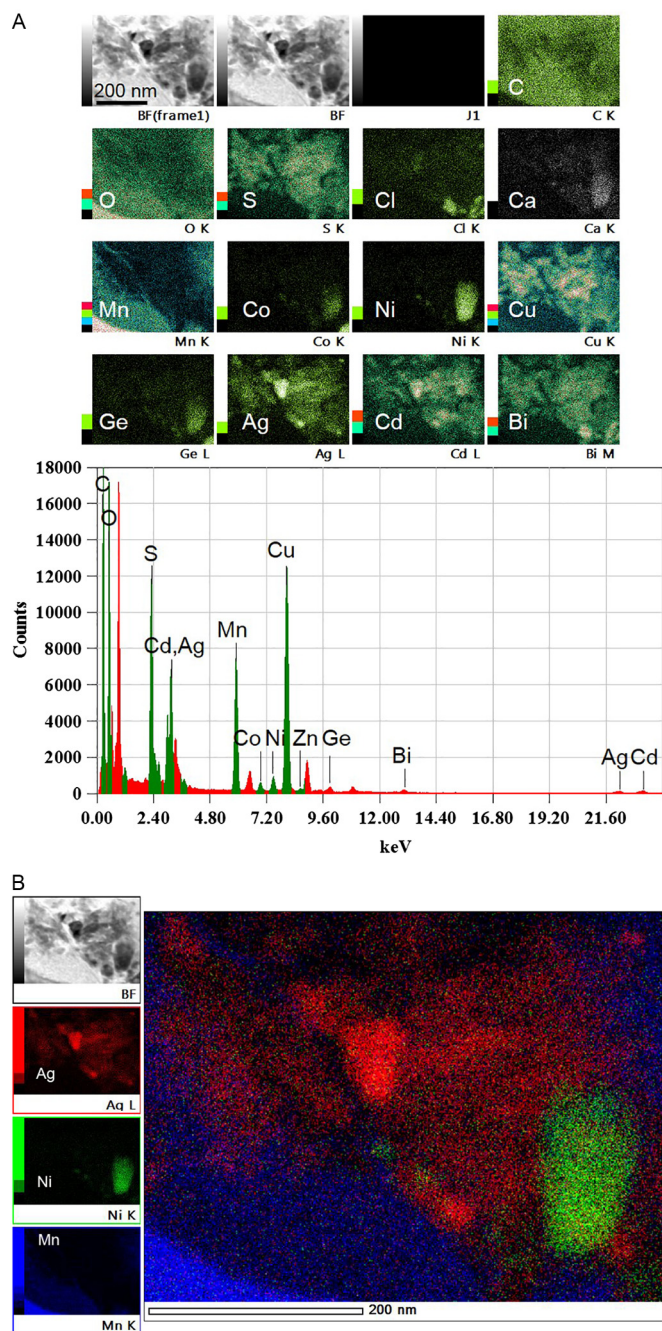


Fig. 7. (A) EDS map 2 all analyzed elements. (B) Ag, Ni, and Mn overlay map. Sample 5447/ DGC split 44-1-12.

3.1.1. 5445/ DGC separate 44-4-5

Keeping in mind that many of the scanned areas include coal and are carbon coated, carbon and coal-associated oxygen contributions to EDS spectra are unavoidable. In addition, mineral associations with carbon include carbonates, with siderite known to be among the more common minerals in portions of the Blue Gem coal (Hower et al., 1991b; Hower et al., 1994a,b). Among the areas scanned in the SEM-EDS assessment were individual particles (or aggregates of particles) with up to 19.83% Mg, 26.41% Ca, 88% Ti, 65% Fe, 11.4% Zn, 13.13% Zr, and 8.25% Mo (the latter particle having 8.51% Fe). Individual grains not specifically quantified include a Cr–Fe particle, possibly chromite; Cu–Fe–S, possibly chalcopyrite or bornite; Fe–Zn–S, sphalerite; and galena. An area containing a La–Ce–Nd-rich particle with

lesser amounts of Fe was selected for FIB lift out and therefore analyzed further using TEM analysis.

3.1.2. 5447/DGC separate 44-1-12

Among the areas scanned in the SEM-EDS assessments were individual particles (or aggregates of particles) with up to 5.31% Mg, 49% Ca, 43.34% Ti, 64.57% Fe, and 82% Cu (with 12.48% Zn).¹ Individual grains not specifically quantified include Cr–Ni–Mn–Cu–Fe–S, Ag–S, and Cu–S. An area with Ag–Bi–Cd ($\pm$ Sn)-, Mn-, and S-bearing particles was selected for FIB lift out and analyzed further using TEM analysis.

3.2. TEM analysis

3.2.1. 5445/ DGC separate 44-4-5

TEM analysis showed that the FIB-extracted area had some grains with high P but with lesser La, Ce, and Nd concentrations than anticipated from the SEM-EDS scan (Fig. 1). Lanthanum does appear to have a slight concentration in the core of the two high-relief mineral grains, suggesting that part of the grain may be monazite, but mineralogical analysis was not definitive.

3.2.2. 5447/ DGC separate 44-1-12

Examination of the FIB-extracted slice showed the area consists of a diverse assemblage of mineral and (possibly) non-mineral grains (Fig. 2). Areas examined in Figs. 3–14 are outlined on Fig. 2.

The elemental maps and the accompanying EDS spectra for Fig. 3 clearly show the presence of S, Ag, and Sn (Ag map on top left of Fig. 3; supporting spectrum on top right); Cd and Ag (middle map and spectrum); and Bi with minor Ge (bottom map and spectrum). The overlay map of Ag, Cd, and S (Fig. 4) emphasizes that the distribution of these elements is far from uniform. For example, the Ag–Cd association is more apparent in the bright particles in the lower right quadrant than in the large, rounded particles in the upper right quadrant. Looking closely at the area in the white rectangle in Fig. 4, it is seen that Ag and Cd dominate the EDS spectrum (Fig. 5a). The EDS and SAED analysis of the crystal within this region (Fig. 5b) indicates that it is greenockite, a cadmium sulfide isostructural with wurtzite. The Ni, Bi, and Mn overlay map (Fig. 6a) shows that Ni occurs in association with Co and Ge (not shown on Fig. 6a) in discrete areas. Comparing Fig. 6a with Fig. 4 suggests that S is not as concentrated in the Ni–Co–Ge spots as in the adjacent Ag–Cd–Bi regions. The Bi map suggests that at least some of the Bi is not chemically associated with other elements. The element map also shows a broad area dominated by Mn–O; the lattice spacings, $d_1 = 0.22$ nm and $d_2 = 0.157$ nm determined from the SAED analysis, indicates that the mineral is manganosite (MnO), as per American Mineralogist Crystal Structural Database (AMCSD) 0008240 (Zhang, 1999) (Fig. 6b). As seen on Fig. 2, the manganosite area is much larger than the region covered by Fig. 6a.

The EDS map 2 spectrum and the array of all of the elements analyzed (Fig. 7a) shows distinct areas for Ag and Cd; Mn; Ni, Co, Ge, and possibly Ca; and Bi. This is supported by the element overlay map for Ag, Ni, and Mn (Fig. 7b), where each appears in isolated areas with minimal overlap.

The EDS map 3 spectrums and element-specific maps for Ag, Cd, Bi, and Ge (Fig. 8) and the Cd–Ag–Bi overlay map (Fig. 9) show a large degree of overlap between Ag and Cd, with an additional alignment of Bi and S (S not shown). An EDS spectrum from within the HRTEM 1 area (Fig. 10) shows strong Ag, Cd, and S peaks with lesser Sn and Bi peaks. The SAED diffraction pattern indicates multiple crystals among an amorphous material (Fig. 11). The two most intense spots have d spacings of $d_1 = 0.234$ nm and $d_2 = 0.325$ nm which match metallic bismuth (reference AMCSD 0011254; Wyckoff, 1963).

¹ This particle could represent contamination from the miner's pick used for sampling the coal.

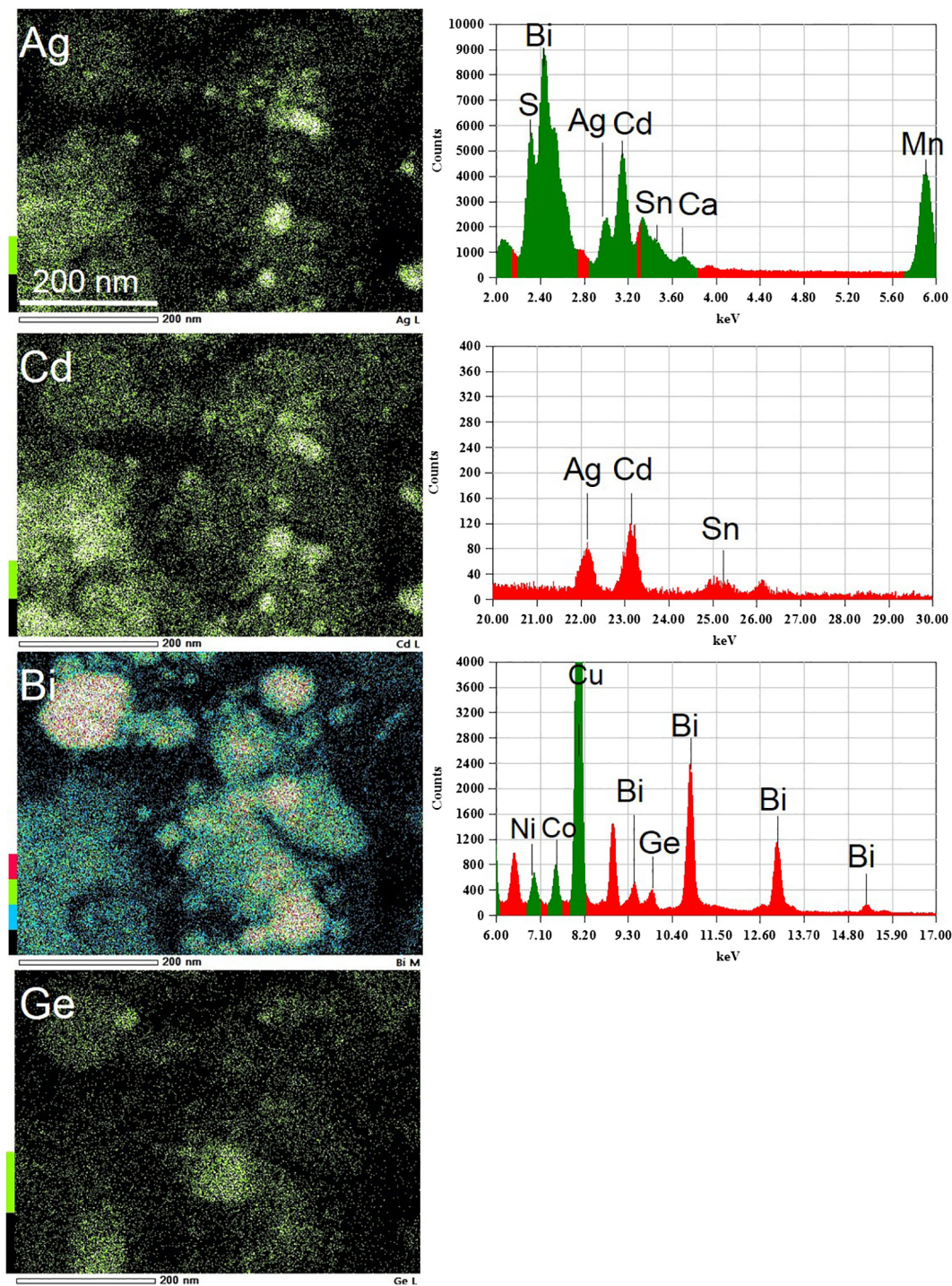


Fig. 8. Elemental maps of Ag, Cd, Bi, and Ge along left column. Right column shows the portion of the EDS spectrum used for the identification of S, Ag, Cd, and Sn (top); the region used for positive identification of Ag and Cd (middle); and the region used for the identification of Ge and Bi. Sample 5447/ DGC split 44-1-12.

The SAED diffraction pattern in Fig. 12 ($d_1 = 0.2$ nm, $d_2 = 0.206$ nm, $d_3 = 0.203$ nm, $d_4 = 0.128$ nm, and $d_5 = 0.115$ nm) is consistent with nisnite (Ni_3Sn) (AMCSD 0018385; Rowe et al., 2011). The SAED pattern ($d_1 = d_2 = 0.235$ nm, indicating the presence of two crystals in different orientations) on Fig. 13 suggests metallic silver cadmium (1,1) (database reference: AMCSD 0011474, Wyckoff, 1963) although several Cd–Ag solid solutions are possible and more extensive analysis is needed for positive identification. The EDS spectrum for the mineral shown on Fig. 14 is consistent with siderite. Siderite, at least, is a well-known mineral in the Blue Gem coal; in some seam sections and

lithotypes, it is the dominant mineral, accounting for Fe_2O_3 percentages of over 50% (ash basis) (Hower et al., 1991a, 1991b).

3.3. Discussion

Some complexity in the geochemistry, perhaps on the order seen in the area examined in sample 5447, is evident in sample 5445. Recall that SEM-EDS suggested a wide array of Mg-, Ca-, Ti-, Fe-, Zn, Zr-, and Mo-rich phases along with Cu–Fe (possibly chromite), Cu–Fe–S (possibly chalcocopyrite or bornite), Fe–Zn–S, ZnS (possibly sphalerite), and

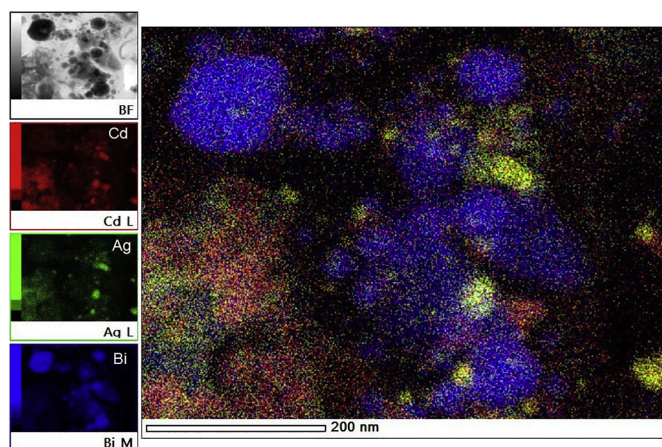


Fig. 9. Cd, Ag, and Bi overlay map. Note the association of Ag and Cd that causes the red (Cd) and green (Ag) to combine as a yellow area on the elemental map. Sample 5447/DGC, split 44-1-12. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

PbS (possibly galena) associations. While SAED analysis of the REE-bearing grains in sample 5445 was not performed, the elemental map (Fig. 1) shows that La and Ce are found in P-rich areas, suggesting that the REE are associated with a phosphate mineral such as monazite. Monazite can enter a peat by way of water-borne detrital sediments and as components of volcanic ash, both known mechanisms in certain eastern Kentucky coals (Hower et al., 2016a,b). There is no known volcanic influx into the Blue Gem coal but, considering the proximity of the Alleghenian Orogen at the time of the deposition of the peat, we cannot rule out a volcanic influence.

The sample 5447 region with Ag–Bi–Cd $\pm$ Sn, Mn, and S particles selected for FIB liftout and TEM and SAED analysis has a great diversity of minerals and, thus, a greater range of geochemical and mineralogical

influences are possible. It is distinctly possible that there are multiple and diverse origins for the minerals just within the FIB-liftout area. Siderite, a common mineral in the Blue Gem coal, indeed, the primary Fe-bearing mineral in many samples of the coal (Hower et al., 1991b), could have formed contemporaneously or nearly so with the deposition of the Blue Gem peat. Nothing observed in the Hower et al. (1991b) study suggested that siderite has a detrital origin. However, the origin of the Ag–Cd solid solution, along with Ag–Cd–Bi–S, Bi–S, Ni–Co–Ge, and other associations, is less clear. Many of the minerals in sample 5447, in addition to the Zn–S, Pb–S, and Cu–S associations in sample 5445, could have had hydrothermal origins (Hatch et al., 1976; Herzig and Hannington, 1995; Hagni, 2009; Maral et al., 2009a,b; Teja-Ruiz et al., 2017; among others). Hower et al. (1991a), Collins (1993), and Sakulpitakphon et al. (2004) discussed the possibility of hydrothermal influences within the coals to the northwest of the Pine Mountain thrust fault. Certainly, the slightly higher coal rank and the Cl and trace metal enrichments in the coals to the NW of the fault compared to the coals on the thrust sheet provide some evidence in support of this hypothesis (Hower et al., 1991a; Sakulpitakphon et al., 2004). While individual lithotypes may experience considerably different influxes of clastic minerals, such as monazite and other heavy minerals commonly concentrated in the basal lithotypes of many eastern Kentucky coals (Hower and Bland, 1989; Hower and Pollock, 1989; Hower et al., 1991b, 1994a,b, 1996; Hatton et al., 1992; Andrews Jr. et al., 1994; Mardon and Hower, 2004), the effects of hydrothermal fluids may be more distributed throughout the coal. The wurtzite and sulfide minerals identified in sample 5447 and inferred from SEM-EDS in sample 5445 are more likely to have been epigenetic as opposed to surviving erosion and transport from another source. The work of Schindler and Hochella Jr. (2017) regarding the sequestration of metal-rich nanoparticles in mineralized organic matter in soils may imply that multiple complex modes of incorporation of inorganics within coal are conceivable.

Certainly, time lines between syngenetic deposition of sediments and epigenetic influences can become blurred as the time of deposition of peat can be a complex continuum, with any given layer representing

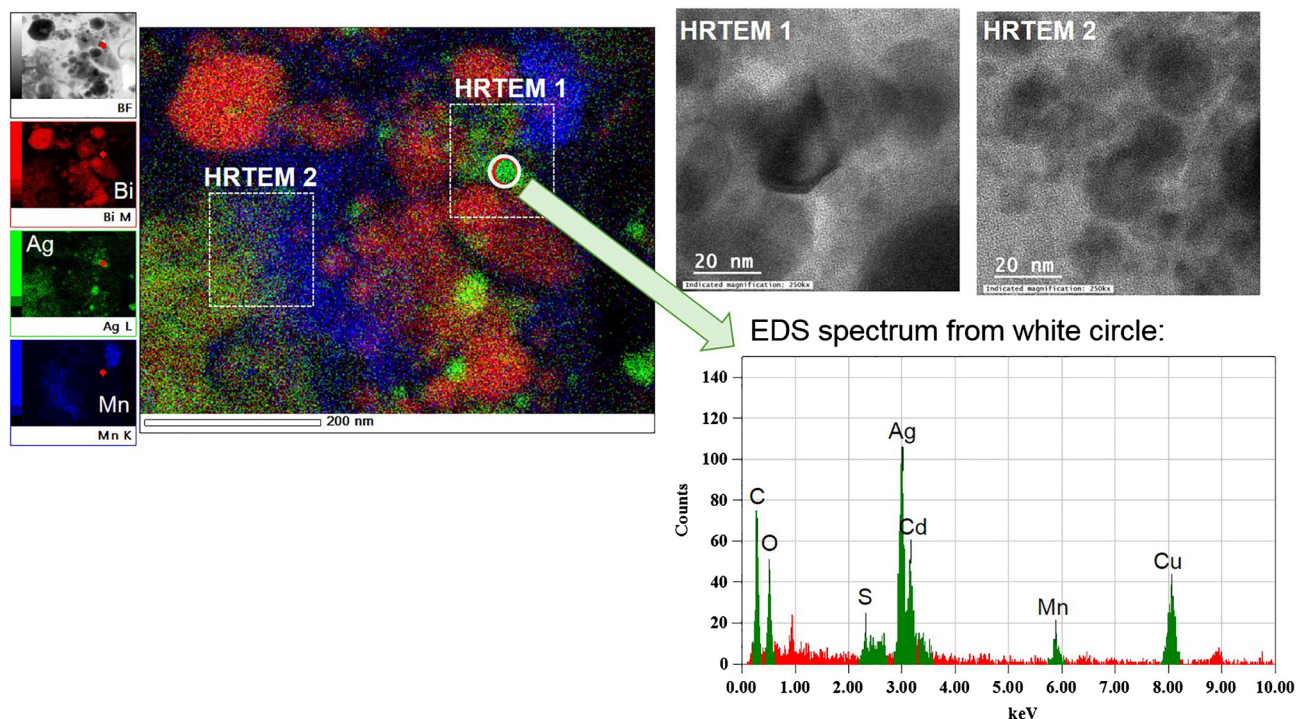


Fig. 10. Bi, Ag, and Mn overlay map with EDS spectrum from circle in HRTM 1 area showing Ag, Cd, and S signals. Sample 5447/ DGC, split 44-1-12.

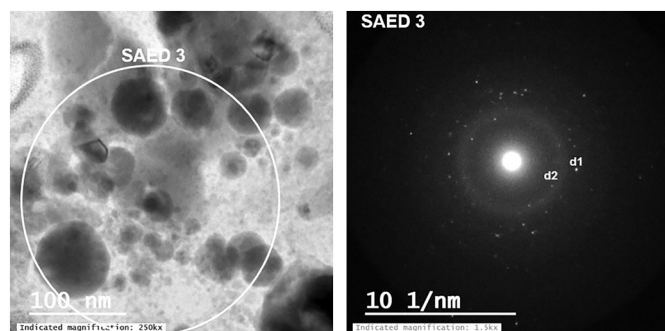


Fig. 11. The diffraction pattern indicates the presence of multiple crystals and some amorphous material (diffuse ring). The d spacings of the spots measured are consistent with metallic bismuth. Sample 5447/ DGC, split 44-1-12.

an age range given the influences of primary deposition of woody (and other) material, the degradation of the plant parts, and the rooting through older peat by later plants (O'Keefe et al., 2013). While hydrothermal influences may be less dependent upon the position within the coal bed, they are not independent of coal lithology as certain peat/coal lithotypes may be more permeable or may contain minerals more prone to alteration.

The few areas thoroughly investigated here are but a small window into the total diagenetic story of the Blue Gem coal bed and may not be indicative of what happened elsewhere in the Blue Gem or in other coals in the region, much less the full story of what happened at this location. Coal geochemistry is complex and finer scales of investigation emphasize that it can be more complex than we imagined before nano-scale techniques were readily available.

4. Conclusions

The TEM investigation of selected density-gradient separates of low-ash Blue Gem coal revealed that elements can have mineral

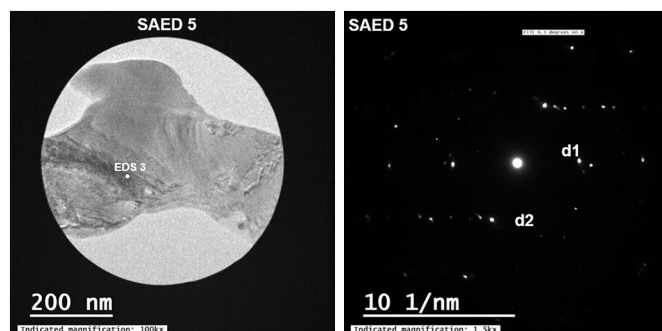


Fig. 13. Crystal of metallic silver cadmium (AgCd). Sample 5447/ DGC, split 44-1-12.

associations. In bulk studies, such elements could have been noted, in general, as having an “organic association” simply because it was not routine, at least at the time of our 1989–1990 investigation (Hower et al., 1994a,b), to examine submicron to nanometer-scale particles. There is a fundamental difference between “organic association”, implying chemically associated (chelated) elements with organics, and an “association with organics”, implying elements incorporated in minerals that, basically, cannot be removed by float-sink or chemical methods.

The density-gradient separate from the basal bench, sample 5445, contains both detrital minerals, as indicated by the monazite studied by TEM, and sulfides, as suggested by the SEM-EDS examination. Sample 5447 from the vitrinite-rich portion of the middle bench contains a suite of possible hydrothermal Ag-, Cd-, Bi-, and other metal-bearing minerals but also (probable) low-temperature diagenetic minerals such as siderite. The overall picture emerging from this investigation shows that the incorporation of minerals within a low-ash coal such as the Blue Gem, or any coal for that matter, is complex and any attempt at a complete understanding of the story requires a wide range of tools. Every coal could be a unique setting based on the original depositional

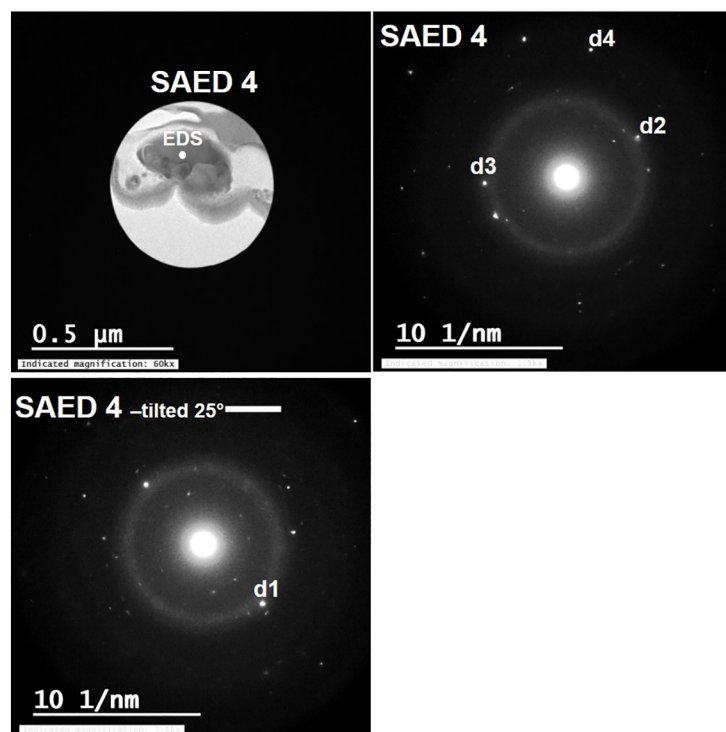
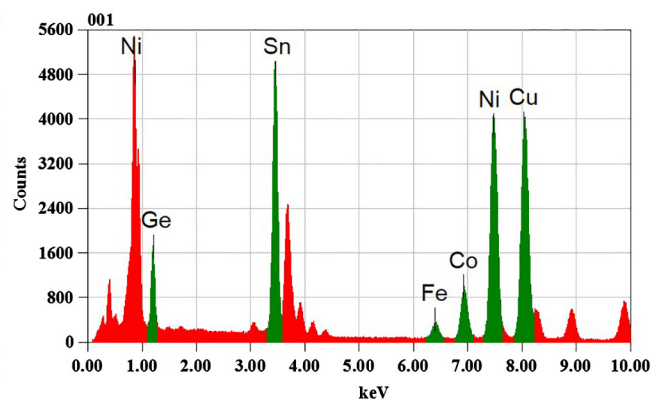


Fig. 12. Diffraction patterns show a diffuse ring from amorphous material and spots that indicate the presence of crystalline material as well. Sample 5447/ DGC, split 44-1-12.



Standardless Quantitative Analysis

Element	(keV)	Mass%	Counts	Sigma	Atom%
Fe K*	6.398	1.48	4205.88	0.03	2.23
Co K	6.924	5.12	13416.88	0.06	7.33
Ni K	7.471	25.34	64187.55	0.14	36.45
Ge L	1.188	12.37	12385.03	0.15	14.38
Sn L (Ref.)	3.443	55.70	67693.72	0.25	39.62
Total		100.00			100.00

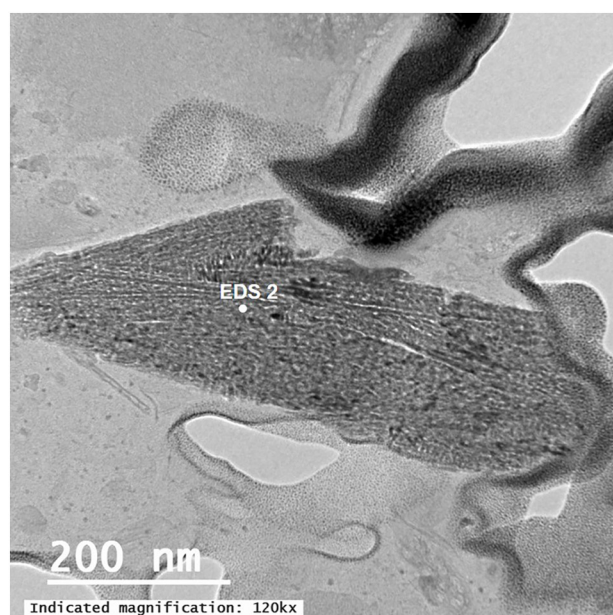


Fig. 14. Siderite. Sample 5447/ DGC split, 44-1-12.

setting, including both the maceral and mineral and non-mineral inorganic inputs and the diagenetic and metamorphic overprints. Broad, chemical-based and bulk-mineralogy-based inferences such as by those of Collins (1993) and Sakulpitakphon et al. (2004) cannot begin to unravel the nature and origin of the fine element associations present in coals.

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References

- Andrews Jr., W.M., Hower, J.C., Hiatt, J.K., 1994. Investigations of the Fire Clay coal bed, southeastern Kentucky, in the vicinity of sandstone washouts. *Int. J. Coal Geol.* 26, 95–115.
- Bouska, V., 1981. *Geochemistry of Coal*. Elsevier, Amsterdam (284 pp).
- Collins, S.L., 1993. Statistical Analysis of Coal Quality Parameters for the Pennsylvania System Bituminous Coals in Eastern Kentucky, USA. Unpublished PhD thesis. The University of North Carolina, Chapel Hill, pp. 401.
- Cutruone, C.M.N.L., Oliveira, M.L.S., Ward, C.R., Hower, J.C., de Brum, I.A.S., Sampaio, C.H., Kautzmann, R.M., Taffarel, S.R., Teixeira, E.C., Silva, L.F.O., 2014. A mineralogical and geochemical study of three Brazilian coal cleaning rejects: demonstration of electron beam applications. *Int. J. Coal Geol.* 130, 33–52.
- Dai, S., Finkelman, R.B., 2018. Coal as a promising source of critical elements: progress and future prospects. *Int. J. Coal Geol.* 186, 155–164.
- Dai, S., Li, D., Chou, C.-L., Zhao, L., Zhang, Y., Ren, D., Ma, Y., Sun, Y., 2008. Mineralogy and geochemistry of boehmite-rich coals: new insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. *Int. J. Coal Geol.* 74, 185–202.
- Dai, S., Graham, I.T., Ward, C.R., 2016. A review of anomalous rare earth elements and yttrium in coal. *Int. J. Coal Geol.* 159, 82–95.
- Dai, S., Yan, X., Ward, C.R., Hower, J.C., Zhao, L., Wang, X., Zhao, L., Ren, D., Finkelman, R.B., 2018. Valuable elements in Chinese coals: a review. *Int. Geol. Rev.* 60, 590–620.
- Davidson, R.M., 1993. Organic Sulphur in coal. IEACR/60. IEA Coal Research, London, U.K.
- Davidson, R.M., Clarke, L.B., 1996. Trace Elements in Coal. IEA Coal Research, London (IEAPER/21, 60 p).
- Eskenazy, G., 1967. Adsorption of gallium on peat and humic acids. *Fuel* 46 (3), 187–191.
- Eskenazy, G., 1970. Adsorption of beryllium on peat and coals. *Fuel* 49 (1), 61–67.
- Eskenazy, G., 1972. Adsorption of titanium on peat and coals. *Fuel* 51 (3), 187–191.
- Eskenazy, G., 1974. Studies on the binding form of silver. *Ann. de L'Univ. de Sofia, Livre 1, Andean Geol.* 279–284 (in Russian).
- Eskenazy, G., 1977. On the binding form of tungsten in coals. *Chem. Geol.* 19, 153–159.
- Eskenazy, G., 1979. Model experiments on the binding form of indium in coals. *Ann. de L'Univ. de Sofia, Livre 1, Geol.* 235–240 (in Russian).
- Eskenazy, G.M., 1999. Aspects of the geochemistry of rare earth elements: an experimental approach. *Int. J. Coal Geol.* 38, 285–295.
- Eskenazy, G., 2015. Sorption of trace elements on xylain: an experimental study. *Int. J. Coal Geol.* 150–151, 166–169.
- Fdez-Ortiz de Vallejuelo, S., Gredilla, A., da Boit, K., Teixeira, E.C., Sampaio, C.H., Madariaga, J.M., Silva, L.F.O., 2017. Nanominerals and potentially hazardous elements from coal cleaning rejects of abandoned mines: environmental impact and risk assessment. *Chemosphere* 169, 725–733.
- Filby, R.H., Van Berkel, G.J., 1987. Geochemistry of metal complexes in petroleum, source rocks, and coals: an overview. In: Filby, R.H., Branthaver, J.F. (Eds.), *Metal complexes in fossil fuels*. Am. Chem. Soc., Symp. Ser. 344, pp. 2–39.
- Finkelman, R.B., 1981. Modes of occurrence of trace elements in coal. U. S. Geol. Sur. Open-File Rep. 81-99, 312.
- Finkelman, R.B., 1994. Modes of occurrence of potentially hazardous trace elements in coal: levels of confidence. *Fuel Process. Technol.* 39, 21–34.
- Finkelman, R.B., 1995. Modes of occurrence of environmentally-sensitive trace elements in coal. In: Swaine, D.J., Goodarzi, F. (Eds.), *Environmental Aspects of Trace Elements in Coal*. Kluwer Academic Publishers, Dordrecht, pp. 24–50.
- Finkelman, R.B., Palmer, C.A., Wang, P., 2018. Quantification of the modes of occurrence of 42 elements in coal. *Int. J. Coal Geol.* 185, 138–160.
- Given, P.H., Miller, R.N., 1987. The association of major, minor and trace inorganic elements with lignites. III. Trace elements in four lignites and general discussion of all data from this study. *Geochim. Cosmochim. Acta* 51, 1843–1853.
- Hagni, R.D., 2009. The ore deposits of the South-East Missouri cobalt-copper-lead-zinc district - mineralogy, ore textures, applied mineralogy and ore controls. In: Australasian Institute of Mining and Metallurgy Publication Series 2008, Brisbane, QLD, Australia, pp. 29–38.
- Hatch, J.R., Gluskoter, H.J., Lindahl, P.C., 1976. Sphalerite in coals from the Illinois Basin. *Econ. Geol.* 71, 613–624.
- Hatton, A.R., Hower, J.C., Helfrich, C.T., Pollock, J.D., Wild, G.D., 1992. Lithologic succession in the Path Fork coal bed (Breathitt Formation, Middle Pennsylvanian), southeastern Kentucky. *Org. Geochem.* 18, 301–311.
- Herzig, P.M., Hannington, M.D., 1995. Polymetallic massive sulfides at the modern seafloor: a review. *Ore Geol. Rev.* 10, 95–115.
- Hower, J.C., Bland, A.E., 1989. Geochemistry of the Pond Creek Coal Bed, Eastern Kentucky Coalfield. *Int. J. Coal Geol.* 11, 205–226.
- Hower, J.C., Pollock, J.D., 1989. Petrology of the River Gem Coal Bed, Whitley County, Kentucky. *Int. J. Coal Geol.* 11, 227–245.
- Hower, J.C., Riley, J.T., Thomas, G.A., Griswold, T.B., 1991a. Chlorine in Kentucky coals. *J. Coal Qual.* 10, 152–158.
- Hower, J.C., Rimmer, S.M., Bland, A.E., 1991b. Geochemistry of the Blue Gem coal bed, Knox County, Kentucky. *Int. J. Coal Geol.* 18, 211–231.
- Hower, J.C., Andrews Jr., W.M., Wild, G.D., Eble, C.F., Dulong, F.T., Salter, T.L., 1994a. Coal quality trends for the Fire Clay coal bed, southeastern Kentucky. *J. Coal Qual.* 13, 13–26.
- Hower, J.C., Taulbee, D.N., Rimmer, S.M., Morrell, L.G., 1994b. Petrographic and geochemical anatomy of lithotypes from the Blue Gem coal bed, southeastern Kentucky. *Energy Fuel* 8, 719–728.
- Hower, J.C., Ruppert, L.F., Eble, C.F., Graham, U.M., 1996. Geochemical and palynological indicators of the paleoecology of the River Gem coal bed, Whitley County, Kentucky. *Int. J. Coal Geol.* 31, 135–149.

- Hower, J.C., Eble, C.F., Dai, S., Belkin, H.E., 2016a. Distribution of rare earth elements in eastern Kentucky coals: indicators of multiple modes of enrichment? *Int. J. Coal Geol.* 160–161, 73–81.
- Hower, J.C., Granite, E.J., Mayfield, D., Lewis, A., Finkelman, R.B., 2016b. Notes on contributions to the science of rare earth element enrichment. *Fortschr. Mineral.* 6. <http://dx.doi.org/10.3390/min6020032>.
- Huggins, F.E., 2002. Overview of analytical methods for inorganic constituents in coal. *Int. J. Coal Geol.* 50, 169–214.
- Huggins, F.E., Huffman, G.P., 2004. How do lithophile elements occur in organic association in bituminous coals? *Int. J. Coal Geol.* 58, 193–204.
- Ignasiak, B.S., Fryer, J.F., Jadernik, P., 1978. Polymeric structure of coal. 2. Structure and thermoplasticity of Sulphur-rich Raša lignites. *Fuel* 57, 578–584.
- Liu, J., Ward, C.R., Graham, I.T., French, D., Dai, S., Song, X., 2018. Modes of occurrence of non-mineral inorganic elements in lignites from the Mile Basin, Yunnan Province, China. *Fuel* 222, 146–155.
- Maral, D., Gedikoğlu, A., Maral, M., Kumral, M., Budakoğlu, M., 2009a. Investigation of precious metals related to Sulphur mineralizations in the Korudere (Umurbey-Çanakkale), Turkey. In: 9th International Multidisciplinary Scientific Geoconference and EXPO - Modern Management of Mine Producing. Geology and Environmental Protection, SGEM 2009, vol. 1. pp. 47–52.
- Maral, D., Gedikoğlu, A., Maral, M., Kumral, M., Budakoğlu, M., 2009b. Investigation of precious trace metals related to sulphur mineralizations in the Arapujandere (Yenice-Çanakkale)), Turkey. In: 9th International Multidisciplinary Scientific Geoconference and EXPO - Modern Management of Mine Producing, Geology and Environmental Protection, SGEM 2009. vol. 1. pp. 53–58.
- Mardon, S.M., Hower, J.C., 2004. Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant. *Int. J. Coal Geol.* 59, 153–169.
- Medunić, G., Radenović, A., Bajramović, M., Švec, M., Tomac, M., 2016. Once grand, now forgotten: what do we know about the superhigh-organic-sulphur Raša coal? [Nekada velik, danas zaboravljen: Što znamo o raškome ugljenu, iznimno bogatome organskim sumporom?]. *Rudarsko Geolosko Naftni Zbornik* 31, 27–45.
- Miller, R.N., Given, P.H., 1986. The association of major, minor and trace inorganic elements with lignites. I. Experimental approach and study of a North Dakota lignite. *Geochim. Cosmochim. Acta* 50, 2033–2043.
- Miller, R.N., Given, P.H., 1987. The association of major, minor and trace inorganic elements with lignites. II. Minerals, and major and minor element profiles, in four seams. *Geochim. Cosmochim. Acta* 51, 1311–1322.
- O'Keefe, J.M.K., Bechtel, A., Christanis, K., Dai, S., DiMichele, W.A., Eble, C.F., Esterle, J.S., Mastalerz, M., Raymond, A.L., Valentim, B.V., Wagner, N.J., Ward, C.R., Hower, J.C., 2013. On the fundamental difference between coal rank and coal type. *Int. J. Coal Geol.* 118, 58–87.
- Oliveira, M.L.S., Marostega, F., Taffarel, S.R., Saikia, B.K., Waanders, F.B., DaBoit, K., Baruah, B.P., Silva, L.F.O., 2014. Nano-mineralogical investigation of coal and fly ashes from coal-based captive power plant (India): an introduction of occupational health hazards. *Sci. Total Environ.* 468–469, 1128–1137.
- Querol, X., Cabrera, L.L., Pickel, W., López-Soler, A., Hagemann, H.W., Fernández-Turiel, J.L., 1996. Geological controls on the quality of the Mequinenza subbituminous coal deposit, Northeast Spain. *Int. J. Coal Geol.* 29, 67–91.
- Rimmer, S.M., 1991. Distributions and associations of selected trace elements in the Lower Kittanning seam, western Pennsylvania, U.S.A. *Int. J. Coal Geol.* 17, 189–212.
- Rimmer, S.M., Hower, J.C., Moore, T.A., Esterle, J.S., Walton, R.L., Helfrich, C.T., 2000. Petrography and palynology of the Blue Gem coal bed (Middle Pennsylvanian), southeastern Kentucky, USA. *Int. J. Coal Geol.* 42, 159–184.
- Rowe, R., Grice, J.D., Poirier, G., Stanley, C.J., Horvath, L., 2011. Nisnite, Ni₃Sn, a new nickel mineral species from the Jeffrey mine, asbestos, Quebec. *Can. Mineral.* 49, 651–656.
- Saikia, B.K., Ward, C.R., Oliveira, M.L.S., Hower, J.C., Baruah, B.P., Braga, M., Silva, L.F., 2014. Geochemistry and nano-mineralogy of two medium-sulfur northeast Indian coals. *Int. J. Coal Geol.* 121, 26–34.
- Saikia, B.K., Ward, C.R., Oliveira, M.L.S., Hower, J.C., Leao, F.D., Johnston, M.N., O'Bryan, A., Sharma, A., Baruah, B.P., Silva, L.F., 2015. Geochemistry and nano-mineralogy of feed coals, mine overburden, and coal-derived fly ashes from Assam (North-east India): a multi-faceted analytical approach. *Int. J. Coal Geol.* 137, 19–37.
- Sakulpitakphon, T., Hower, J.C., Schram, W.H., Ward, C.R., 2004. Tracking mercury from the mine to the power plant: geochemistry of the Manchester coal bed, Clay County, Kentucky. *Int. J. Coal Geol.* 57, 127–141.
- Schindler, M., Hochella Jr., M.F., 2017. Sequestration of Pb-Zn-Sb- and As-bearing incidental nanoparticles by mineral surface coatings and mineralized organic matter in coals. *Environ. Sci.: Processes Impacts* 19, 1016–1027.
- Seredin, V.V., 1996. Rare earth element-bearing coals from the Russian far east deposits. *Int. J. Coal Geol.* 30, 101–129.
- Seredin, V.V., Dai, S., 2012. Coal deposits as a potential alternative source for lanthanides and yttrium. *Int. J. Coal Geol.* 94, 67–93.
- Seredin, V.V., Finkelman, R.B., 2008. Metalliferous coals: a review of the main genetic and geochemical types. *Int. J. Coal Geol.* 76, 253–289.
- Swaine, D.J., 1990. Trace elements in coal. (London, Butterworths, 278 p).
- Teja-Ruiz, A.M., Juárez-Tapia, J.C., Hernández-Cruz, L.E., Reyes-Pérez, M., Patiño-Cardona, F., Reyes-Domínguez, I.A., Flores-Guerrero, M.U., Palacios-Beas, E.G., 2017. Influence of temperature on the formation of Ag complexed in a S₂O₃²⁻-O₂ system. *Fortschr. Mineral.* 7 (2). <http://dx.doi.org/10.3390/min7020016>.
- Valković, V., 1983. Trace Elements in Coal, Volume 1. FL, CRC Press, Boca Raton (210 p).
- Ward, C.R., 2002. Analysis and significance of mineral matter in coal seams. *Int. J. Coal Geol.* 50, 135–168.
- Ward, C.R., 2016. Analysis, origin and significance of mineral matter in coal: an updated review. *Int. J. Coal Geol.* 165, 1–27.
- Wei, Q., Rimmer, S.M., 2017. Acid solubility and affinities of trace elements in the high-Ge coals from Wulantuga (Inner Mongolia) and Lincang (Yunnan Province), China. *Int. J. Coal Geol.* 178, 39–55.
- Wei, Q., Rimmer, S.M., Dai, S., 2017. Distribution of trace elements in fractions after micronization and density-gradient centrifugation of high-Ge coals from the Wulantuga and Lincang Ge ore deposits, China. *Energy Fuel* 31, 11818–11837.
- White, C.M., Douglas, L.J., Anderson, R.R., Schmidt, C.E., Gray, R.J., 1990. Organosulfur compounds in Rasa coal. In: Orr, W.L., White, C.M. (Eds.), *Geochemistry of Sulfur in Coal*. American Chemical Society Symposium Series Vol. 429. pp. 261–286.
- Wyckoff, R.W.G., 1963. *Crystal Structures*, 2nd edition. John Wiley, New York.
- Yudovich, Ya.E., Ketris, M.P., 2001. Uranium in Coals. *Komi Sci. Center Ural Division RAN, Syktyvkar* (84 pp).
- Yudovich, Ya.E., Ketris, M.P., 2002. Inorganic Matter of Coal. Russian Academy of Sciences, Ural Division, Ekaterinburg, pp. 422.
- Yudovich, Ya.E., Ketris, M.P., 2004a. Vanadium in Coals. *Komi Sci. Center Ural Division RAN, Syktyvkar* (96 pp).
- Yudovich, Ya.E., Ketris, M.P., 2004b. Germanium in Coals. *Komi Sci. Center Ural Division RAN, Syktyvkar* (204 pp).
- Yudovich, Ya.E., Ketris, M.P., 2005a. Toxic Trace Elements in Coal. Russian Academy of Sciences, Ural Division, Ekaterinburg (655 p., in Russian).
- Yudovich, Ya.E., Ketris, M.P., 2005b. Mercury in coal: a review. Part 1. *Geochem. Int. J. Coal Geol.* 62, 107–134.
- Yudovich, Ya E., Ketris, M.P., 2005c. Arsenic in coal: a review. *Int. J. Coal Geol.* 61, 141–196.
- Yudovich, Ya.E., Ketris, M.P., 2006a. Valuable Trace Elements in Coal. Russian Academy of Sciences, Ural Division, Ekaterinburg (538 p., in Russian).
- Yudovich, Ya.E., Ketris, M.P., 2006b. Selenium in coal: a review. *Int. J. Coal Geol.* 67, 112–126.
- Zhang, J., 1999. Room temperature compressibilities of MnO and CdO: further examination of the role of cation type in bulk modulus systematics. *Phys. Chem. Miner.* 26, 644–648.
- Zhao, Y., Zeng, F., Liang, H., Tang, Y., Li, M., Xiang, J., Wen, X., 2017. Chromium and vanadium bearing nanominerals and ultra-fine particles in a super-high-organic-sulfur coal from Ganhe coalmine, Yanshan coalfield, Yunnan, China. *Fuel* 203, 832–842.