CONCENTRATION OF ARSENIC, SELENIUM, AND OTHER TRACE ELEMENTS IN PYRITE IN APPALACHIAN COALS OF ALABAMA AND KENTUCKY[1]

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Abstract. Coals in the Appalachian basin host pyrite that is locally enriched in trace elements, including As, Mo, Hg, and Se. Trace element enrichment in the coals is the result of migrating hydrothermal fluids generated during the late Paleozoic Allegheny orogeny. A comparison study of coal between the Black Warrior Basin in northwestern Alabama and coal in eastern Kentucky reveals differences in concentrations and mode of occurrence of these elements in host pyrite. Although pyrite occurs in similar morphologic forms in the two coal basins and in similar structures (e.g., pyrite-filled cellular structures and veins), trace element content differs as does their sequence of emplacement. The highest arsenic content in pyrite in eastern Kentucky coal occurs in cellular-filled structures (up to 1.1 wt. %), whereas the highest arsenic content in pyrite in Alabama coal occurs in pyrite-filled veins (up to 2.6 wt. %). Selenium content is highest in pyrite-filled cells (up to 670 ppm Se) in eastern Kentucky, whereas selenium content in Alabama is highest in pyrite-filled veins associated with a major fault zone (up to 590 ppm Se). Coal samples from eastern Kentucky commonly contain marcasite-filled veins, whereas marcasite is not recognized in pyrite-filled veins in Warrior Basin samples. Differences in sulfide mineralogy may reflect different fluid composition in the two regions or different timing of deformation and migration of metal-bearing fluids.

Samples from both localities show deformation structures at thin section scale; however, the coal samples from Alabama exhibit greater late-stage microfaulting and microveining. The pyrite-filled microstructures that cross-cut earlier pyrite-filled woody cell structures and clay-filled desiccation cracks are host to elevated levels of arsenic, selenium, thallium, and the potentially toxic trace metals lead and mercury. The formation of fractures and faults requires that coalification proceeded to a point where brittle failure occurred after considerable burial. Therefore, trace element enrichment is post depositional.

Characterizing the morphological occurrence of pyrite and its trace element content can contribute to a better understanding of the progression of weathering of pyrite in coals, and release of the trace elements into the environment. Dendritic pyrite, for example, has many branched projections, which offers a large surface area for reaction with fluids and oxygen, which increases its susceptibility to weathering and dissolution. Dendritic pyrite in Alabama coal contains up to 1.2 wt. % arsenic.

Additional Key Words: Black Warrior Basin; mine waste, metals; laser ablation

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Introduction

Arsenic and selenium contamination of soils, vegetation, and aquatic environments is a concern in coal mining areas (Lemly and Smith, 1991; Lemly, 2002). A potential source for this contamination is arsenic and selenium that is enriched in pyrite in eastern and western U.S. coals. These metals may be released to the environment during coal mining, processing, or combustion (Cecil et al., 1981; Minkin et al., 1984). Trace elements that are considered hazardous air pollutants (e.g., arsenic, selenium, mercury, lead, antimony) are commonly hosted in coal by inorganic clays and sulfide minerals (Eble et al., 1999; Kolker and Finkelman, 2001; Palmer et al., 2002). To minimize potential environmental impacts, it is important to identify the mineralogic source and mode of occurrence of potentially toxic elements in coal and adjacent rock. This identification aids in (1) predicting the mobility of these hazardous elements and (2) developing methods of removal of trace element-rich minerals hosted in coal. The goal of this study is to document the mineralogic and microstructural occurrence of arsenic, selenium, and other potentially toxic trace elements in coals of the Warrior Basin, Alabama, and the eastern coalfield of Kentucky (Fig. 1). Trace element content is highly variable in pyrite at microscopic- to mine-scale, and at local- to regional-scale in the coalfields because of the inhomogeneous distribution of trace elements in different morphological forms and multiple generations of sulfide minerals. This study provides insight into the distribution of arsenic and selenium in pyrite phases and quantifies trace-element content.

This project is in the data gathering and analysis phase, but differences in the two coal regions are already apparent. Based on a USGS database of coal chemical analyses, coalfields in the Appalachian region have locally elevated arsenic (Fig. 2) and selenium levels (Goldhaber et al., 2000; Bragg et al., 2001). However, Kentucky has a greater proportion of samples with a low concentration of arsenic (< 50 ppm), whereas Alabama has a wide spread of samples with higher concentrations of arsenic, up to 2.7 wt. % in pyrite-filled veins (Figs. 2A, 2B; Diehl et al., 2004).

The residence sites of arsenic, selenium, molybdenum, antimony, thallium, copper, and mercury in Alabama coal samples was determined in previous studies to be concentrated in the mineral pyrite (Kolker et al., 2001; Diehl et al., 2002; Goldhaber et al., 2002a, 2002b; Tuttle et al., 2002). These studies suggest that the metal-bearing solutions were introduced into the coal beds along faults and fractures by a fluid migration event during the Alleghanian Orogeny (Goldhaber et al., 1997; Goldhaber et. al., 2002b; Tuttle et al., 2002). Introduction of trace elements in eastern Kentucky coal may also be structurally controlled. Kentucky coals enriched in arsenic and other metals tend to align along cross-strike discontinuities thought to represent basement faults (Coleman et al., 1988; Fig. 1B). A structural geologic map of northwest Alabama shows a strong northwest-southeast system of normal faults that were generated during the Alleghanian Orogeny (Pashin, 1991; Fig. 1C). The northwest-southeast trending structures, perpendicular to the Appalachian thrust front, may have focused fluid flow westward during tectonic events in the Appalachian Basin.

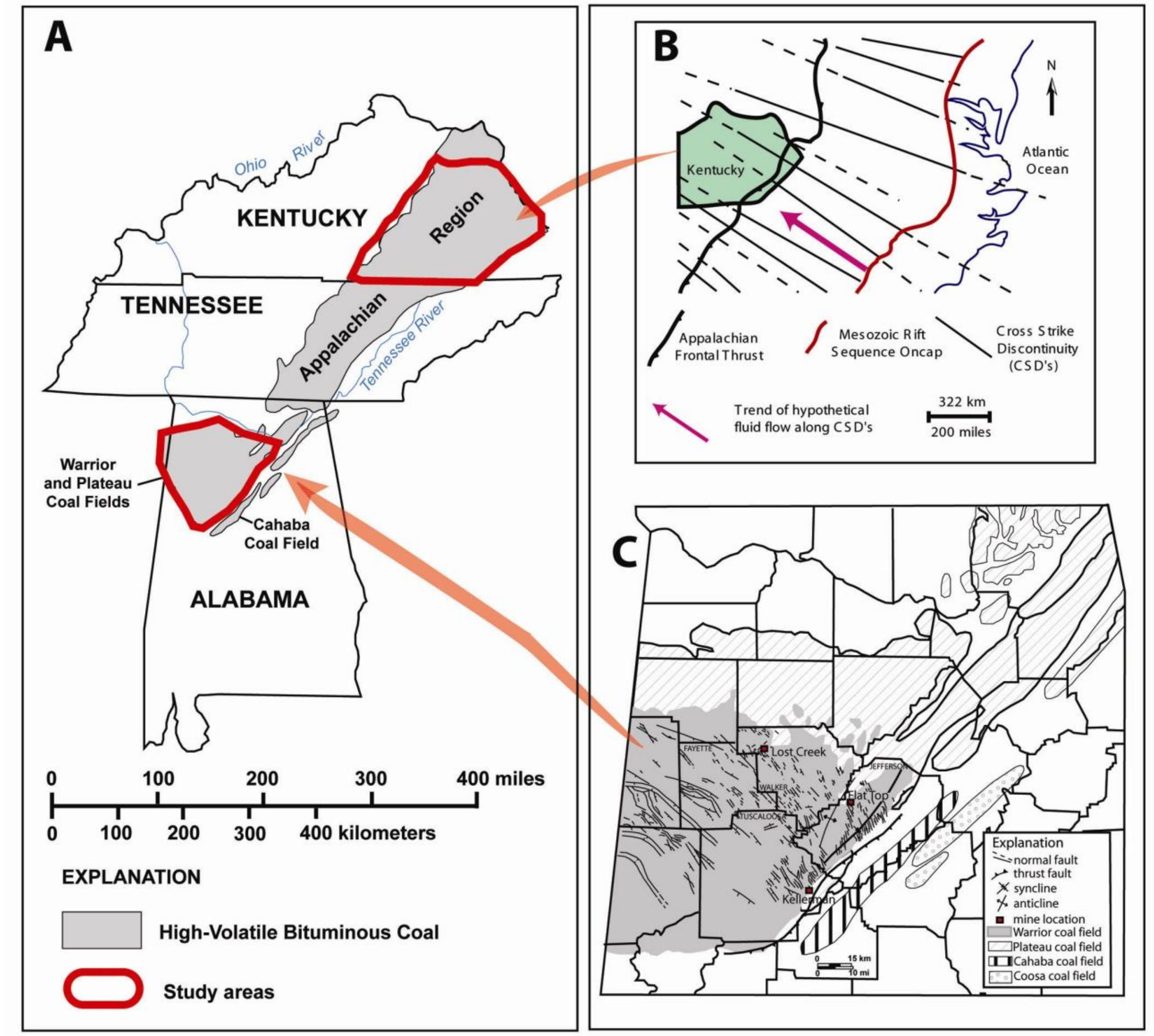

Figure 1. Location map of Alabama and Kentucky coalfields. **A**. Outline of study areas, the Warrior Basin, Alabama, and the eastern Kentucky coalfields. **B**. Structural map showing Appalachian Frontal Thrust and Cross Strike Discontinuities (assumed to be faults, Coleman and others, 1988). **C**. Structural map of the Warrior coalfield, Alabama, showing swarm of normal faults perpendicular to the Appalachian Frontal Thrust (Pashin, 1991).

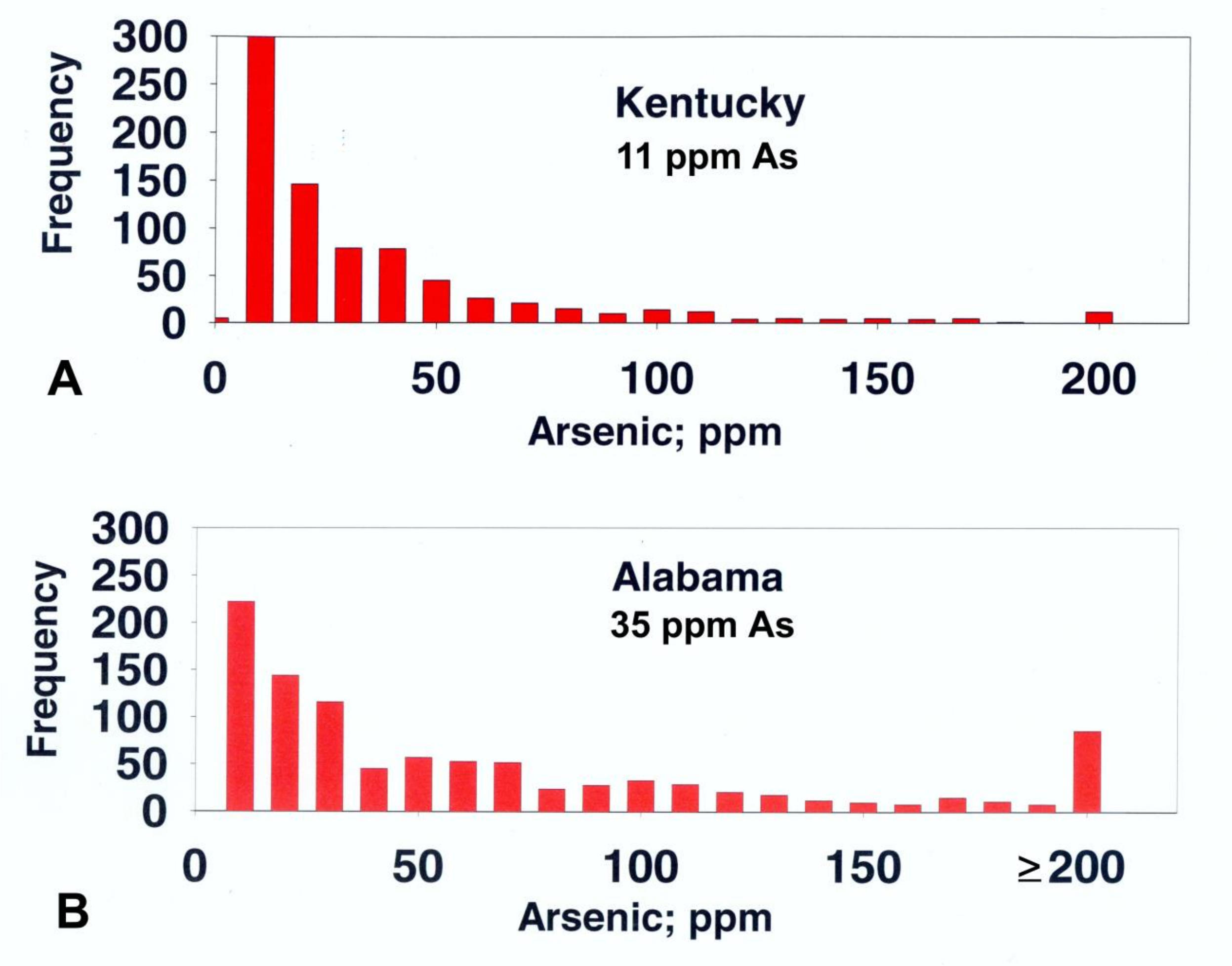

Figure 2. Geometric mean values of arsenic in eastern Kentucky (11 ppm As) and Alabama (35 ppm As) coals. **A**. A high number of Kentucky samples show low concentrations of arsenic. **B**. Alabama coals are more enriched in arsenic, up to 12,000 ppm (Goldhaber et al., 2002b).

Climate plays an important role in determining how much arsenic or selenium is released and concentrated in the environment. The U.S. Fish and Wildlife Service is concerned with increasing concentrations of selenium in streams and the detrimental effect of the element on fish populations, especially in the humid Appalachian coal-mining regions (Lemly, 2004). In the western U.S., where there is less rainfall, selenium content in streams is not the main problem. The problem is elevated levels of selenium in soil, where selenium is transferred to vegetation, such as grasses, and consumed by herbivores. Selenium then accumulates in higher animals along the food chain (Erdman et al., 1991).

Methods

We collected pyrite-bearing coal samples from coal mines in the Warrior coalfield, Alabama, and the eastern Kentucky coalfield (Table 1; Fig. 1). We selected elements for analysis based on those listed as hazardous air pollutants in the Title III 1990 Clean air Act Amendments (e.g., As, Se, Sb, Co, Pb, Hg, and Ni). Polished samples of these pyrite-rich coals were analyzed using a scanning electron microscope with energy dispersive x-ray spectrometer (SEM/EDS), an electron microprobe (EPMA), and laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS, Ridley and Lichte, 1998; Ridley, 2000). LA-ICP-MS analyses were performed on a Perkin-Elmer Sciex Elan 6000 quadrupole mass spectrometer attached to a CETAC LSX500 laser system. Trace element concentrations are typically much lower in coal than pyrite, requiring a larger beam to obtain usable data; therefore, we used a 25- to 50-micron beam size to analyze for trace elements in pyrite and a 100- to 200-μm micron-beam size for coal (Table 2). U.S.G.S. sulfide standard MASS-1 (formerly PS-1; Wilson et al., 2002.) was used as a calibration standard for pyrite, and NIST 1632B and NIST 1632C were used as standards for coal analysis. Digital element maps were obtained on a JEOL JXA-8900 electron probe microanalyzer (EPMA) to determine the spatial distribution of S, As, and Se.

For a more complete listing of mine samples and data tables of the geochemistry of trace element concentrations in pyrite in individual coal mines of northeastern Alabama and eastern Kentucky coalfields see Diehl et al. (2002) and Tuttle et al. (2002).

Results

Pyrite-filled Structures in Coal

Pyrite mineralization in the Kentucky and Alabama samples is multigenerational. Pyrite occurs as framboids and as coarse-grained massive pyrite that fills cellular structures and micro-deformation structures (Fig. 3). Microcrystalline aggregates of framboidal pyrite are the first generation of sulfide mineralization in both Kentucky and Alabama samples. In both regions, cell lumens are filled with second generation arsenic-rich and arsenic-poor sulfide phases. Pyrite-filled veins are contemporaneous with, or are later and cross cut the pyrite phases that fill cells.

Framboidal pyrite, the early diagenetic sulfide phase, is composed of aggregates of microcrystalline cubes of pyrite, clustered in lenses or spherical framboidal form (Figs. 3C, 3D). Framboids in Alabama coal are ≤ 10 μm in diameter, whereas framboids in eastern Kentucky samples range up to 30 μm in diameter. Framboidal pyrite is more common in coals in Alabama than eastern Kentucky samples (Fig. 3C, 3D). Framboidal pyrite may be overgrown by later generations of pyrite that precipitated in veins or cellular structures. Framboidal pyrite in the Kentucky coal samples analyzed to date are confined to cracks and veins, and have been recrystallized by late-stage coarse-grained pyrite (Fig. 3D).

Table 1. List and description of pyrite-rich coal samples used in the reconnaissance study.

Sample Number	Stratigraphic Setting	Sample Characteristics
Alabama, Lost Creek NC-3	Newcastle Coal; folded and sheared coal layer	Pyrite-filled cellular structures (lumens) with cross-cutting microfaults and microveins
Alabama, Flat Top AM-2	American Coal; 6-8’ from fault	Pyrite-filled cellular structures (lumens) with cross-cutting microfaults and microveins
Alabama, Kellerman 2-7	Milldale Coal; Major normal fault zone	Cross-cutting pyrite-filled vein network
Kentucky, 01KY33	Pyrite-rich at base of coal	Pyrite-filled veins perpendicular to pyrite-filled cellular structures
Kentucky, 01KY36	Pyrite in cleat	Pyrite-filled veins
Kentucky, 01KY37	Pyrite in cleat	Pyrite-filled veins in cleat/fracture
Kentucky, 01KY42.6	Pyrite on coal	Pyrite-filled veins; pyrite nodules
Kentucky, 01KY42.7	Taylor Coal?, Pyrite on coal	Pyrite-filled veins, pyrite nodules (<2 mm)
Kentucky, 01KY44	Taylor Coal? Pyrite in cleat	Pyrite-filled veins, nodules

Table 2. Comparison in selected samples of arsenic and selenium content in whole coal, ash, and ICP-LA-MS coal and pyrite analyses (bdl = below detection limit; n = number of spot analyses; na = not available).

Sample Number	**As Ash Basis ppm**	**Se Whole Coal ppm**	**As in Coal LA-ICP-MS Average (Range) ppm**	**Se in Coal LA-ICP-MS Average (Range) ppm**	**As in Massive Pyrite LA-ICP-MS Avg (Range)**	**Se in Massive Pyrite LA-ICP-MS Avg ppm (Range)**
01KY33	7510	247	13 (2-32) n = 6	2 (1-3.4) n = 6	4224 (800-12525) n = 18	196 (34-537) n = 18
01KY36	912	25	0.25 (0.2-0.3) n = 2	0.8 (0.73-0.87) n = 2	1629 (387-4299) n = 21	108 (13-348) n = 21
01KY42.6	na	na	0.22 (bdl-.45) n = 2	0.71 (0.58-0.84 n = 2)	944 (28-2137) n = 11	31 (bdl -106) n = 11
01KY42.7	1420	26	na	na	1560 510-1978 n = 15	222 (11-469) n = 15
01KY44	2100	62	bdl n = 2	0.6 (bdl - 1.11) n = 2	1113 (188-2074) n = 28	51 (6-270) n = 28
Kellerman 2-7, Alabama	na	na	0.3 (bdl - 0.57) n = 2	0.7 (0.6-0.8) n = 2	2700 (25-7500) n = 34	80 (4-590) n = 34
Lost Creek NC3, Alabama	na	na	2 (0.4-3) n = 2	bdl n = 2	6470 (80-27400) =	bdl
Flat Top AM-2 Alabama	na	na	.63 (bdl - 1.26) n = 2	0.3 (bdl - 0.53) n = 2	1595 (101-2490) n = 52	180 (7-510) n = 52

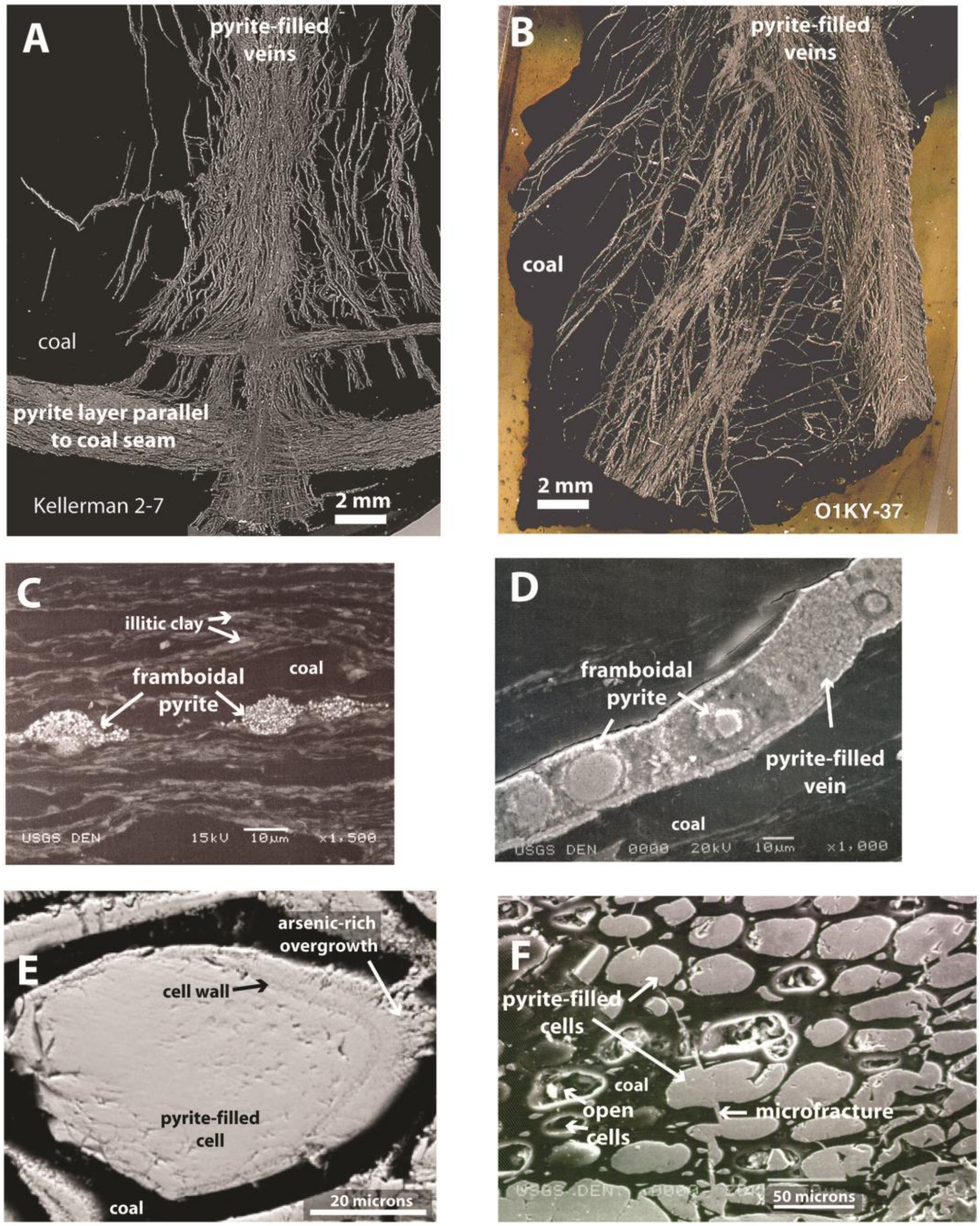

Figure 3. Pyrite-filled structures and morphological forms of pyrite in coal. **A**. Pyrite fills orthogonal sets of veins, Kellerman 2-7, Alabama, normal fault zone. **B**. Feathery textured pyrite-filled veins associated with cleats (fractures) in coal, Kentucky. **C**. Early diagenetic framboidal pyrite, Lost Creek, Alabama. **D**. Recrystallized (?) framboidal pyrite in Kentucky 01KY33 coal. **E**. Pyrite-filled cellular structure, Lost Creek, Alabama. Arsenic-rich pyrite commonly has a pitted appearance such as in the outermost overgrowth on the cell. **F**. Pyrite-filled cell structures, 01KY33, Kentucky. Pyrite-filled microfractures cross-cut cellular structures. Some cells are non-mineralized with open void space.

In both the Kentucky and Alabama samples, pyrite-filled remnant woody cell structures occur in lenses and discontinuous layers parallel to coal-seam beds (Figs. 3E, 3F, 4). Woody cell structures in Alabama coal samples commonly show several generations of pyrite overgrowths outside the cell boundary wall with varying arsenic content (Fig. 3E). The youngest overgrowth generation is the most arsenic-rich (Fig. 4). To date, such overgrowth structures have not been observed in the pyrite-filled cells of the Kentucky samples.

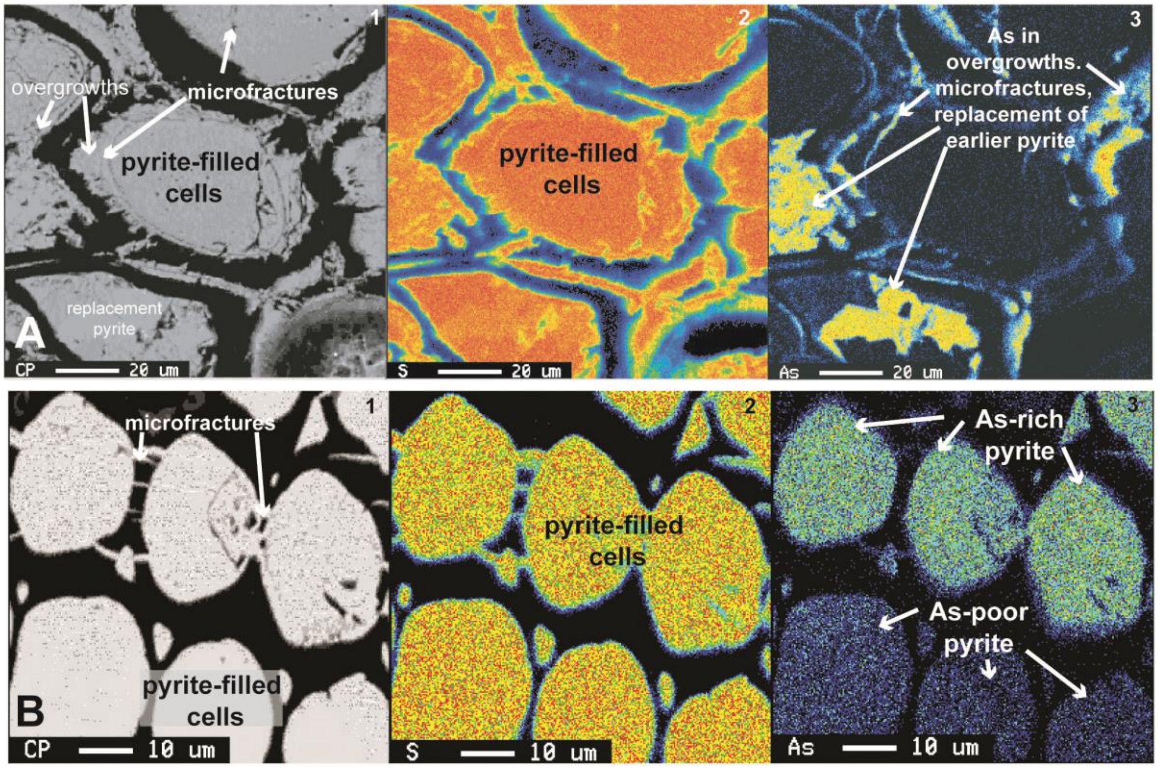

Figure 4. Element distribution maps illustrate that several generations of chemically distinct pyrite precipitated in cells and microstructures and the inhomogeneous distribution of arsenic in pyrite. Bright warm colors, yellow-green to yellow-orange, indicate high metal content and darker cooler colors, blues, indicate low metal content. **A**. Early stage pyrite-filled cells in the Lost Creek sample are depleted in arsenic, whereas late-stage pyrite in microfractures, overgrowths, and replacement in cells is arsenic rich (Lost Creek NC-3 sample, Alabama. **B**. Pyrite-filled cells in the 01KY33 Kentucky sample show two generations of pyrite. The three cells in the lower part of Figure $4B_3$ are arsenic-poor. The three cells in the upper part of the photomicrograph, which are connected by microfractures, are arsenic-rich.

Pyrite is the most common sulfide mineral that fills veins in the Alabama and eastern Kentucky coal (Fig. 3), although marcasite occurs in horizontal veins in some Kentucky samples. Kaolinite- and calcite-filled veins in Alabama samples are early diagenetic cements in shrinkage cracks and cleat (fracture) structures; these are cross cut and partially replaced by later pyrite-filled veins. Clay-filled veins in Kentucky samples are also an early diagenetic phase, predating pyrite.

Veins commonly form perpendicular to coal layers and to layers of pyrite-filled remnant woody cellular structures (Fig. 3A, 3B). Veins in both Kentucky and Alabama samples are complex because they formed during cracking and sealing of coal by multiple generations of fluid influx and mineral precipitation. Pyrite generations are identified by textural boundaries (Fig. 3D, 3E) and abrupt changes in chemistry (Fig. 4). Veining commonly occurs in orthogonal sets, especially in highly deformed samples in or adjacent to fault zones (Fig. 3A). Veins typically range from 10- to 100-μm in thickness. Pyrite in veins associated with early formed cleats is commonly feathery in outline, thicker along the vertical central core of the vein, thinning as the veins fan outward (Fig. 3B). Dendritic pyrite is also a branching sulfide morphology that fills veins. Pyrite in cleats commonly has lower arsenic content than fault-related veins.

The first generation of pyrite in cleats is commonly an early arsenic-poor pyrite. Coal bands from both the Alabama (e.g., Flat Top) and Kentucky (e.g., 01KY33) samples bend around the edges of the cleat-related feathery veinlets, indicating that compaction of the coal was not complete during formation of these veinlets (Cobb, 1985). Arsenic-rich pyrite-filled veins in the Alabama samples, however, formed during a late-stage mineralizing event, evidenced by arsenic-rich veins cross cutting arsenic-poor pyrite-filled cell lumens (Fig. 4A).

Arsenic and Selenium in Pyrite

Data in Table 2 illustrate that arsenic and selenium contents are elevated in coarse-grained massive pyrite in both veins and cellular structures. These values are higher than or overlap the whole coal values, which suggest that arsenic and selenium are mainly hosted in the pyrite. Direct LA-ICP-MS spot analyses of coal are substantially lower than are values in pyrite.

Arsenic distribution in pyrite-filled structures in Lost Creek NC-3, Alabama, and 01KY33, Kentucky, coal samples show that the relative timing of arsenic-rich sulfide mineralization differs between the two regions (Fig. 4). Element distribution maps of pyrite-filled cells cross cut by microveins and microfaults show that arsenic is hosted in pyrite associated with a late-stage sulfide mineralization event in the Lost Creek mine sample (Fig. 4A). Late-stage is defined by the latest observed pyrite generation based on cross cutting structural relations. This late-stage mineralization event also introduced elevated concentrations of thallium and mercury (Diehl et al., 2004). In pyrite-filled structures in the Kentucky 01KY33 sample, late-stage sulfide mineralization in cross cutting veins is arsenic-poor (Fig. 5). Cellular structures in the Alabama samples typically have arsenic-poor pyrite, whereas pyrite-filled cell lumens in the Kentucky samples are arsenic-rich (Figs. 4A, 4B).

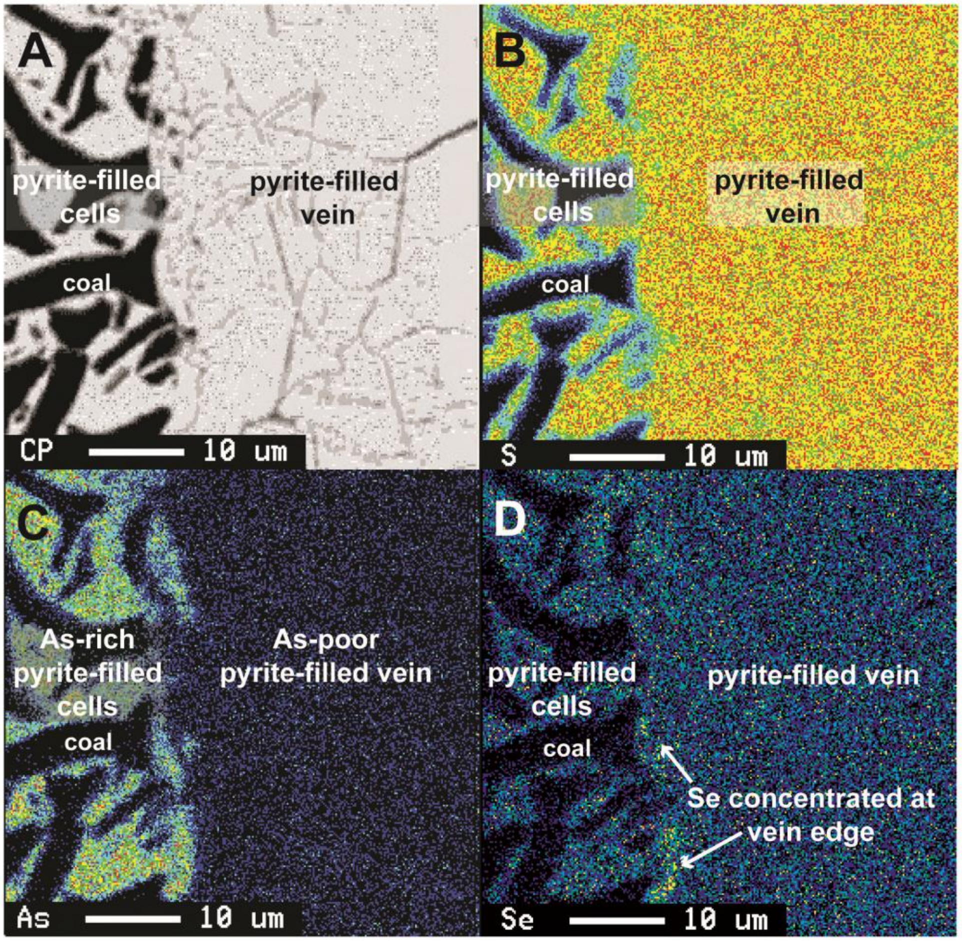

Figure 5. Element distribution maps of arsenic and selenium in Kentucky coal sample 01KY33. **A**. Backscatter image of deformed pyrite-filled cells crosscut by a later pyrite-filled vein. **B**. Sulfur distribution map delineating the pyrite-filled cells and vein. **C**. Arsenic distribution map, showing that arsenic is concentrated in the early pyrite-filled deformed cells. **D**. Selenium distribution map, showing that a selenium-rich sulfide phase at the edge of the vein.

Bivariate plots of arsenic versus selenium suggest element associations occur during the mineralization process (data determined by LA-ICP-MS; Fig. 6). Framboidal, coarse-grained cell- and vein-filling pyrite has high metal contents in Kentucky and Alabama samples. Arsenic and selenium exhibit a positive correlation in the Kentucky samples, suggesting that these elements precipitated together during the same mineralizing event(s) (Fig. 6A). Arsenic and selenium show positive correlative trends in the Alabama coals (Fig. 6B). Arsenic and selenium exhibit differing enrichment trends at the Flat Top and Kellerman mines in Alabama. Arsenic is more enriched in fault-related sulfide mineralization from the Kellerman mine located near the thrust front (Fig. 1C). Selenium is generally more enriched in pyrite-filled veins from the Flat Top mine (Fig.6B). An important comparison between the two plots is the difference in arsenic content in the cell-filling pyrite (red circles). Cell-filling pyrite in the eastern Kentucky coal sample has markedly higher arsenic content than cell-filling pyrite in the Alabama site. Framboidal pyrite is enriched in arsenic and selenium in the Kentucky 01KY33 sample (green inverted triangles) and overlaps the data field of the coarse-grained pyrite-filled veins (black circles). Pyrite in the fault-related veins (inverted yellow triangles) at the Kellerman site, Alabama, is depleted in selenium, except for a few outliers.

Trace element concentrations differ in the varying morphological forms of pyrite (Fig. 7). Framboids in both Kentucky and Alabama are relatively enriched in cobalt, nickel, copper, zinc, and lead compared to coarse-grained forms. The greatest discrepancy is the lack of selenium in Lost Creek mine pyrite, either in framboids or coarse-grained pyrite. Zinc is lacking in coarse-grained pyrite in both Kentucky and Alabama. Nickel is absent in the coarse-grained Lost Creek, Alabama sample.

Preliminary observations suggest that the trace-element rich pyrite is more susceptible to dissolution (Savage et al., 2000; Diehl et al., 2002). Arsenic-rich pyrite-filled veins from the Kellerman 2-7 sample show dissolution etching at the edges of the vein. The remnant needle-like pyrite and etch pits show depleted arsenic content (0.36 % As) in contrast to the less weathered portion of the vein (1.20 wt, % As), suggesting that arsenic has been released into solution (Fig. 8).

Discussion and Summary

Trace elements that are positively correlated are evidence for simultaneous precipitation and enrichment in a fluid migration and precipitation event. Preliminary results suggest that pyrite-bearing coal in eastern Kentucky and northwest Alabama differ in timing of trace element enrichment in sulfide minerals. Alabama samples reflect a late-stage arsenic-enriched pyrite phase in veins, whereas the late-stage vein-filling pyrite in Kentucky samples is arsenic-poor.

Selenium is variable in pyrite-rich Alabama coal samples–framboid and vein-filling pyrite in Lost Creek samples are devoid of selenium, but pyrite at the Flat Top and Kellerman sites exhibit several hundred ppm selenium. Framboidal pyrite at the Kentucky 01KY33 site is enriched in selenium; the framboids are commonly coated by marcasite and later generations of pyrite, which may have enriched the framboids in trace elements. Selenium is introduced late in the Alabama pyrite-rich coals, where it is associated with elevated arsenic content in late-stage veins (Diehl et al., 2002). LA-ICP-MS analyses demonstrate that arsenic and selenium are mainly hosted in the pyrite rather than coal.

Samples from all sites exhibit deformation structures that were evidently fluid pathways for metal-bearing solutions. Within the Warrior Basin, there are different element correlations between sample sites. Pyrite-filled veins generally show a correspondence between arsenic and selenium (e.g. Flat Top mine, Alabama), except for fault-related veins, which are rich in arsenic, but depleted in selenium (e.g. Kellerman mine, Fig. 4). This suggests that mineralizing fluids migrated along faults in the basin during different fluid pulses. The same would hold true for fluid flow along structures in the eastern Kentucky coalfield. The coals were probably influenced by metal-bearing fluids at different times during thrust faults and subsequent development of folds and normal faults perpendicular to the folds.

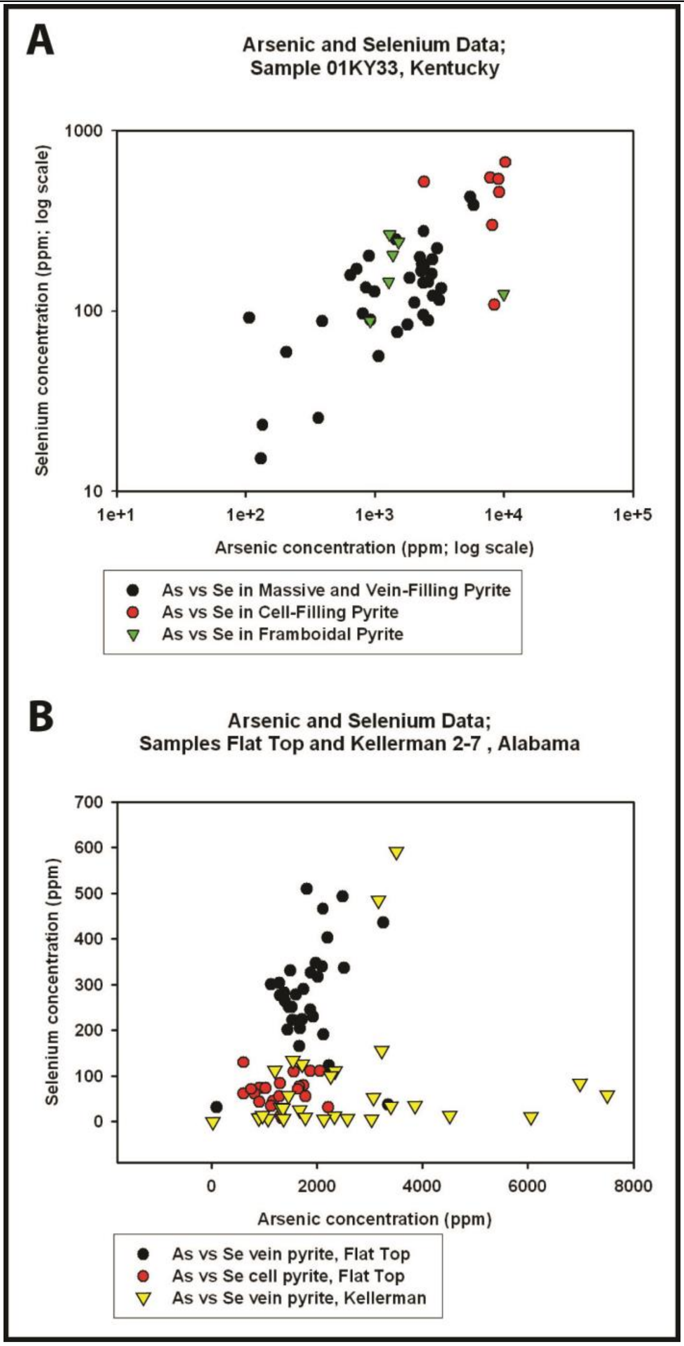

Figure 6. Plots of arsenic and selenium in framboid and massive coarse-grained cell- and vein-filling pyrite, eastern Kentucky coal samples 01KY33, and Alabama coal samples Flat Top AM-2 and Kellerman 2-7. **A**. Arsenic and selenium demonstrate a positive correlation in Kentucky pyrite-rich coal samples. **B**. Arsenic and selenium do not demonstrate a positive correlation in the Alabama coals. However, Flat Top samples are more enriched in selenium, and the Kellerman samples are generally more enriched in arsenic. Selenium was not detected in the Lost Creek sample.

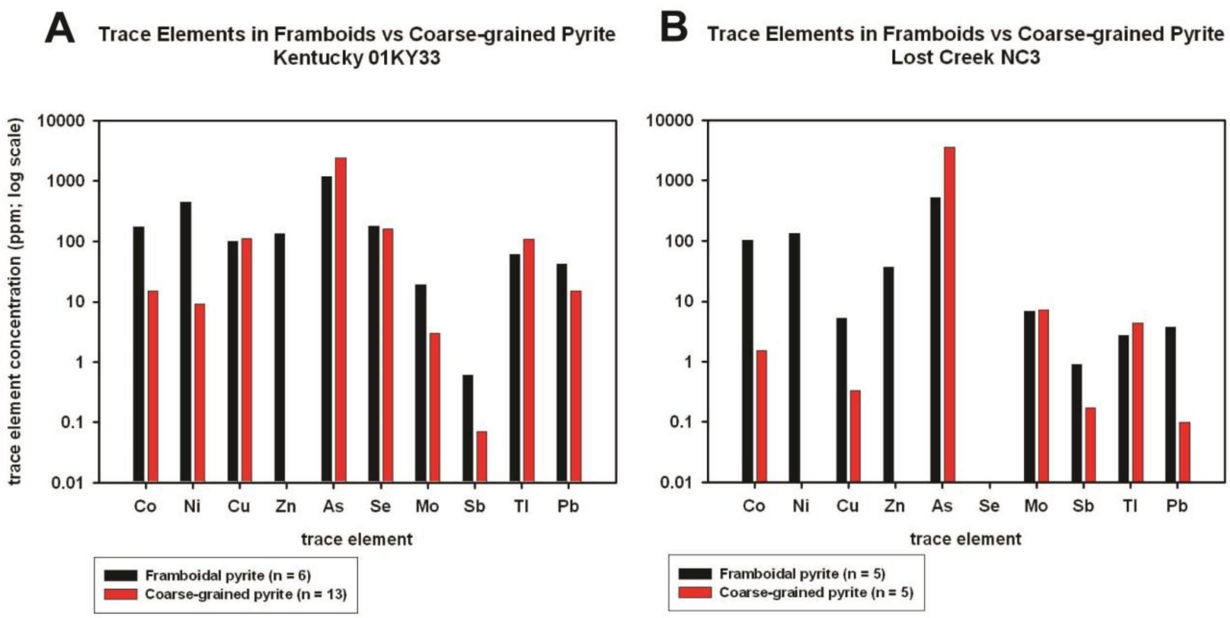

Figure 7. Plot of selected trace elements, showing mean-value content of metals in framboidal pyrite versus adjacent massive coarse-grained pyrite in: **A.** Kentucky coal sample 01KY33 and **B.** Alabama sample Lost Creek NC3. Selenium was not detected in the Lost Creek sample.

Figures 4 and 5 document that pyrite precipitated in multiple generations of fluid influx in both Alabama and Kentucky coal samples. This is evidenced by arsenic-rich pyrite along microscale structures that acted as fluid pathways (Fig. 4A), pyrite-filled cells of different chemistry (Fig. 4B), and crosscutting veins (Fig. 4A; Fig. 5).

Arsenic, selenium, copper, zinc and other metals may be leached from sulfides in coalmine waste at harmful levels to aquatic and land-based wildlife. The impact of dissolution of the trace-metal rich pyrites in coal and elevated arsenic concentrations in solution is documented in stream sediments (Fig. 9). Elevated arsenic concentrations exist in stream sediments in the study areas (Goldhaber et al., 2000; Morrison et al., 2003; Tuttle et al., 2002; Fig. 9B). Stream sediments with high arsenic concentration occur in the eastern Kentucky coal region where Pennsylvanian shale interbedded with coal is the dominant lithology. Stream sediments with high arsenic content occur throughout the Warrior Basin drainages (Fig. 9B). Arsenic is released to the environment either through natural weathering processes or human activity such as coal mining. Trace metals may be more easily removed during coal processing if arsenic and selenium are hosted in coarse-grained pyrite rather than finely crystalline framboidal pyrite.

Characterizing the emplacement processes that enriched coal in trace elements can contribute to a better understanding of the progression of weathering of pyrite in coals, and release of the trace elements into the environment. For example, dendritic pyrite in both the Kentucky and Alabama samples is commonly arsenic-rich, up to 1.2 wt. % As in Alabama pyrite dendrites.

Dendritic pyrite has many branched projections, which offers a large surface area for reaction with fluids and oxygen. This great surface area increases the susceptibility of dendritic pyrite to weathering and dissolution.

The release of trace elements, especially arsenic and selenium, from pyrite-rich coals can impact aquatic systems; and therefore, human health. Aquifers that functioned as transport paths for metal-bearing fluids in the geologic past can serve as drinking-water aquifers in the modern environment. Therefore, it is important to understand the mineralogic and structural controls on the abundance and form of arsenic and other trace elements in rocks in order to predict where health problems may arise.

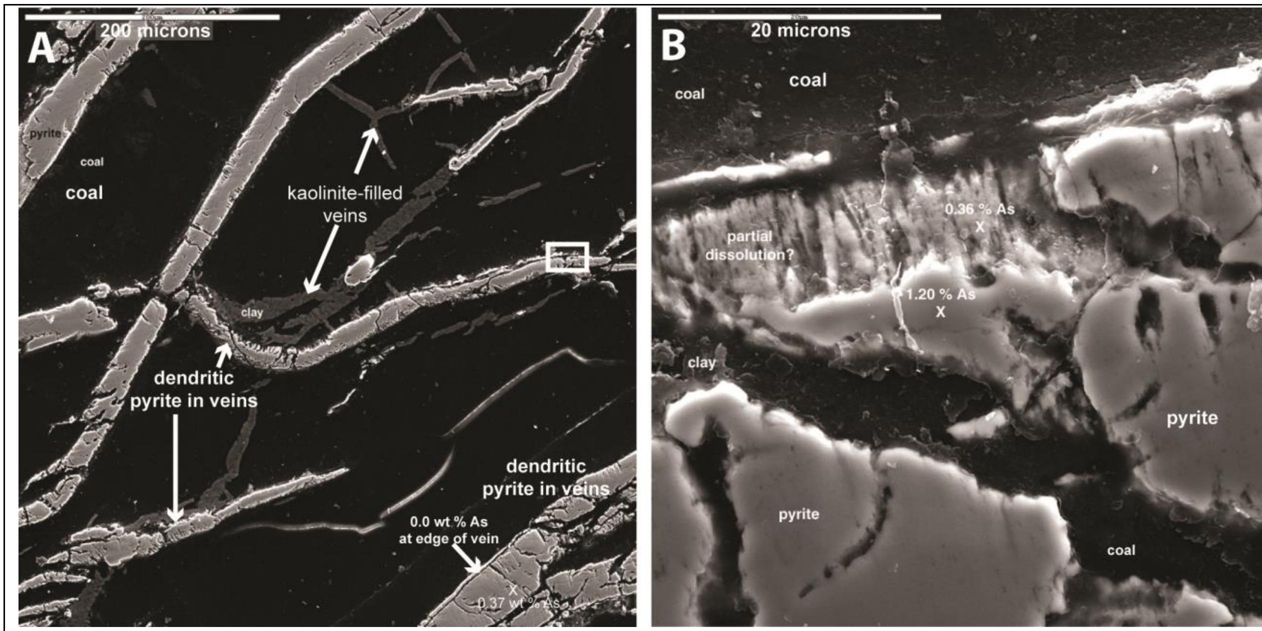

Figure 8. Scanning electron photomicrographs of clay and arsenic-rich pyrite-filled veins, Kellerman site, Alabama (scale bar approx. 200 microns). **A**. Arsenic content varies in pyrite-filled veins. At lower right, the first generation of pyrite along the edge of the vein is devoid of arsenic. The second generation of vein-filling pyrite is weathered and etched and has 0.37 wt. % As. White rectangle depicts enlargement of vein in B. **B**. Photo shows etched pitted dissolution textures in the arsenic-rich pyrite-filled veins. SEM/EDX data shows that the pyrite-filled vein has a content of 1.20 wt. % arsenic, whereas the weathered, partially dissolved part of the vein has 0.36 wt. % arsenic.

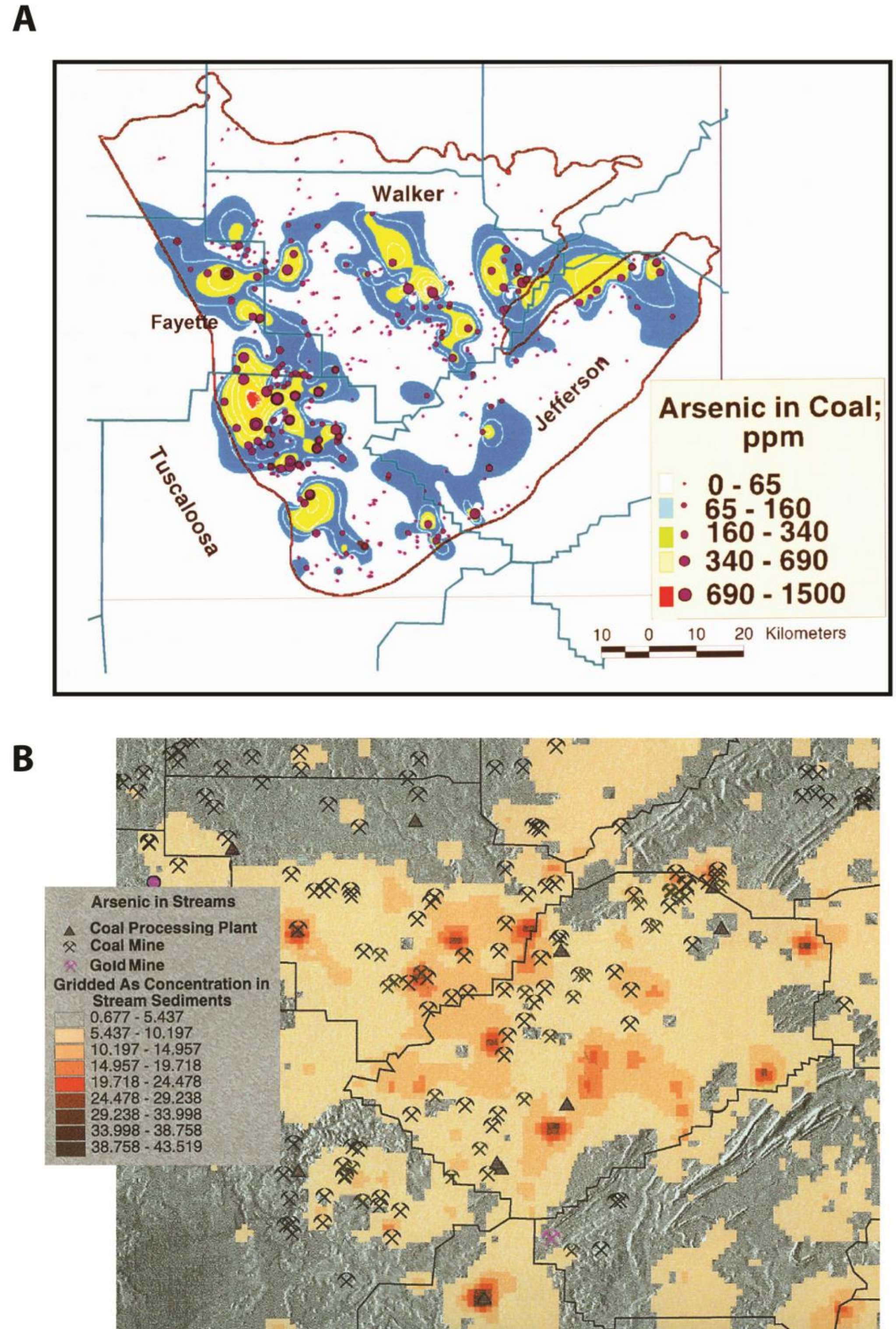

Figure 9. Arsenic concentration in: **A**. coals, and **B**. stream sediments in the Warrior coalfield, Alabama (Goldhaber et al., 2002).

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