Local-scale Variability of Arsenic in the Fire Clay coal zone, Middle Pennsylvanian Breathitt Formation, eastern Kentucky

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The arsenic content of coal beds varies at many scales. Examination of arsenic distributions at differing scales allows for the interpretation of geologic and geochemical processes ranging from large, regional-scale (Goldhaber and others, 2001), to bed-scale (Bragg and others, 2001), to mine-scale. A broad examination of all scales is critical to understanding the variability of arsenic within, and among, coal beds and coal zones.

In the 1990's, the Kentucky Geological Survey (KGS) and the Center for Applied Energy Research (CAER) studied local-scale variability in coal composition and coal quality (Eble and others, 1999; Hower and others, 1994). They collected representative coal samples from the Middle Pennsylvanian (Beathitt Formation of Kentucky) Fire Clay coal zone from 20 sites in an eight 7 ½-minute quadrangle area in Kentucky. The Fire Clay coal was analyzed because it is one of the top-producing coals in the central Appalachian Basin coal region. The Fire Clay coal zone (Fig. 1) is extensive, covering over 5,500 mi^2 throughout eastern Kentucky, southern West Virginia, southwestern Virginia, and northern Tennessee.

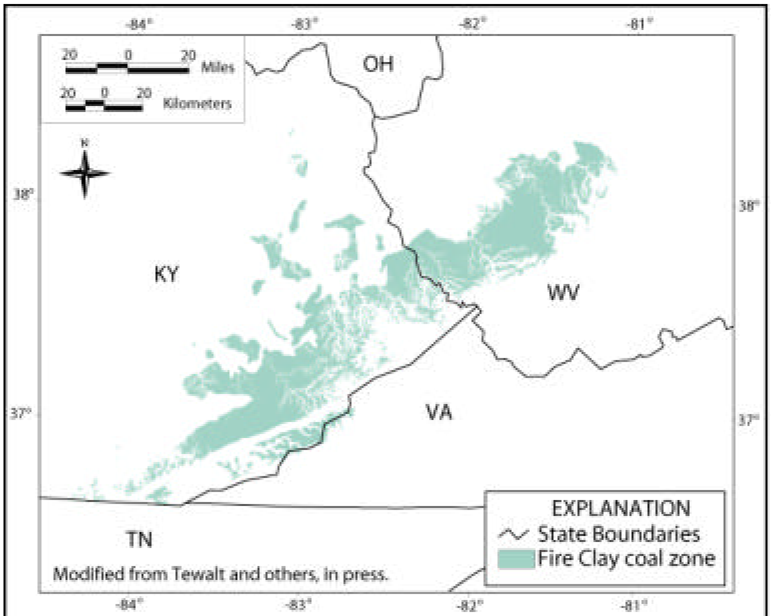

Figure 1- Extent of the Fire Clay coal zone assessed by the USGS.

The Fire Clay coal zone is a primary target for coal producers because it is typically thick (>7 ft), high in calorific value (12,910 ±780 Btu/lb weight percent (wt.%), as-received (ar), relatively low in ash yield (10.62 ±4.53 wt.%, ar), and low in sulfur (0.99 ±0.46, wt.%, ar) (Tewalt and others, in press). In addition, trace-element concentrations in the Fire Clay coals, including arsenic [mean of 11 ±13 ppm (parts per million), ar (Tewalt and others, in press)], are relatively low in comparison to the arithmetic mean of the nine top-producing coal beds in the central Appalachian Basin coal region [arsenic = 14 ppm, ar (Bragg and others, 2001)]. Sources of coal with low arsenic concentrations are especially important to power plants that use selective catalytic reduction (SCR) for nitrogen oxides control. Excessive arsenic in the flue gas stream can have deleterious effects on SCR catalysts.

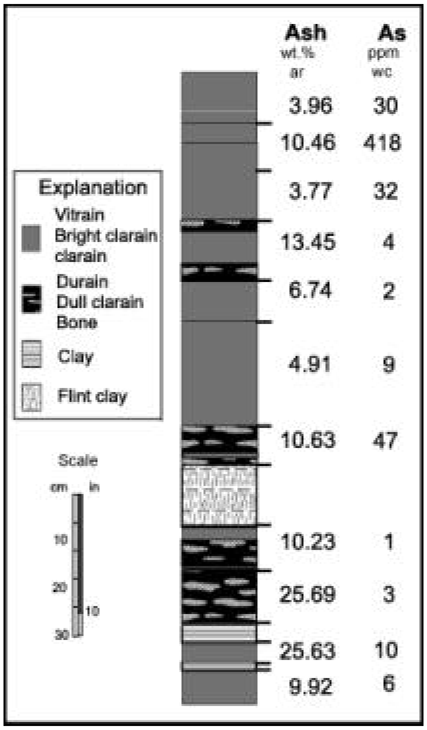

Figure 2. Stratigraphic column of the Fire Clay coal sample.

The USGS analyzed Fire Clay coal samples from four of the KGS/CAER sites by inductively coupled plasma-mass spectroscopy. One of the Fire Clay coal samples, a continuous 4.55 ft channel sample consisting of 11 vertically continuous bench sets from a working mine in the Hyden East 7½-minute quadrangle, Kentucky (Hower and others, 1997), contained high arsenic concentrations. Arsenic contents for individual benches range from 0.6 to 418 ppm, whole coal basis (wc) (fig. 2). The Fire Clay bench that contains 418 ppm arsenic (wc) is located near the top of the coal bed and is composed of bright clarain with fusain bands that grade laterally into iron-sulfide bands. To determine the mode of occurrence of arsenic in this lithotype, we examined the coal with scanning electron microscopy and analyzed its element content by energy-dispersive X-ray fluorescence.

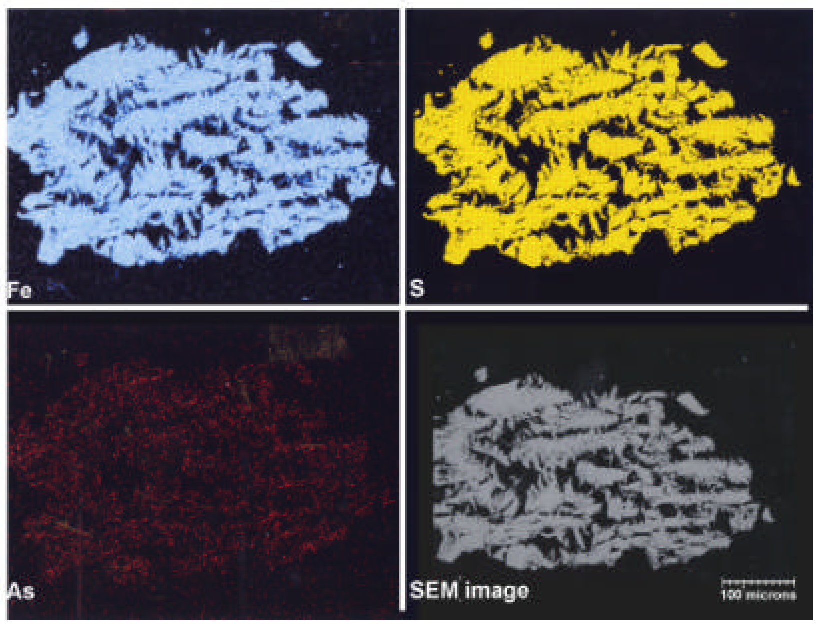

Figure 3. Elemental map of pyrite. Fe=iron, S=sulfur, As= arsenic. SEM= scanning electron microscopy. Scale bar=100

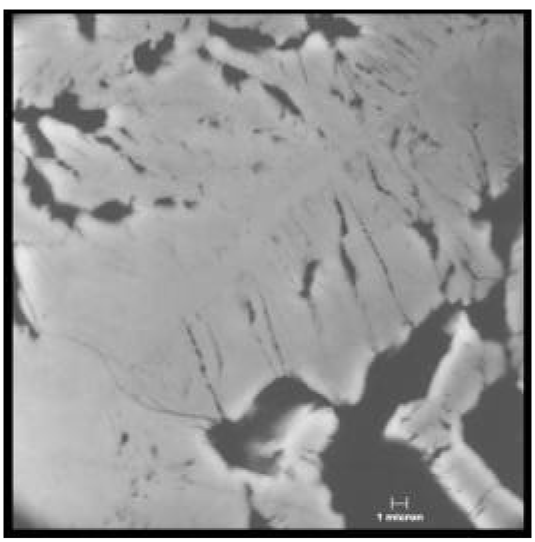

Figure 4. Scanning electron microscopy image of a radiating As-bearing pyrite grain. Scale bar=1 micron.

Massive, framboidal, cell-filling, cell-wall, and radiating morphologies of iron-sulfide (fig. 3) were observed. Arsenic was detected in all five morphologies, but it was extremely rare in all but the radiating Fe-sulfide forms. Examination of the radiating forms with optical light microscopy show that the majority are pyrite and the remainder are marcasite. Selected Fe-sulfide grains were also analyzed by electron microprobe microscopy: arsenic concentrations within individual grains range from 0-3.5 wt

Because arsenic in the Fire Clay coal bed at this locality is associated with Fe-sulfides that are, in general, larger than 150 μm, much of the arsenic should be removed from the coal during beneficiation. However, some of the delicate radiating pyrite forms may be susceptible to breakage along inter-grain boundaries. If this occurs, some of the arsenic will be incorporated in the clean coal product. In addition, disposal of the coal or wash waste could present some concern because most of the arsenic-bearing Fe-sulfides are porous, have a high surface area, and as solid solutions, have higher aqueous solubility than pure Fe- sulfides making them susceptible to oxidation and leaching.

Based on our observations, the occurrence of arsenic in the Fire Clay coal bed is highly variable. Only one bench sample from a much larger suite of Fire Clay coal zone samples was highly enriched in arsenic. At present, the control(s) on arsenic abundance in coal is not known. However, sporadic high (>75ppm, wcb) arsenic values are present in a variety of geographic and stratigraphic positions in the eastern Kentucky coal field (Bragg and others, 1998), suggesting that the process(es) that introduced arsenic into the coal beds was operative at larger than mine-scale.

In order to address the issue of geologic and geochemical controls on arsenic in coal, the USGS Energy Resource Team is currently studying mine-scale coal quality variability with the KGS, CAER, and the Minerals Resource Team. The study is designed to identify local-scale (mine) effects to characterize coal bed and regional scales for basin-scale modeling. In addition, geochemical data, especially arsenic data, will provide base-line information needed to evaluate the extent to which late Paleozoic Alleghanian orogenic fluid-flow may be responsible for increased arsenic-contents in coals of the Black Warrior Basin, Alabama. (Goldhaber and others 2001).

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