

## Selenium Concentrations and Solid-State Chemical Speciation in Black Shale Associated with a West Virginia Coal Seam

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### ABSTRACT

We determined concentrations of Se in strata from a West Virginia coal mine using inductively coupled plasma mass spectrometry (ICP-MS). Select samples with elevated Se concentrations were then analyzed using synchrotron-based scanning X-ray fluorescence spectroscopy (SXRF) and micro X-ray absorption near edge spectroscopy ( $\mu$ XANES). Our results indicate that elevated Se concentrations are contained within narrow bands of strata being found mostly in grey or black shale, fireclay and coal. Selenium was found either in elemental form or as PbSe in all of the samples that were analyzed. This suggests that waste handling techniques that slow the oxidation of these Se-containing minerals should reduce Se concentrations in mine effluents.

### INTRODUCTION

Selenium has emerged as a contaminant of concern within the Appalachian region of the United States due to its potential for release from coal mining sites as well as its potential to elicit adverse population level effects in oviparous vertebrates including birds, fish and amphibians.<sup>1</sup> Weathering of organic matter-rich shales has been identified as a potential source of Se in coal mine effluents. These shales comprise a major component of coal mining waste. Relatively few studies have investigated the chemical speciation of Se in coal mining waste, particularly within

the Appalachian region. A previous study utilized synchrotron X-ray techniques to investigate Se speciation in hard rock mine waste and found that Se was primarily associated with pyritic minerals.<sup>2</sup> In order to better understand the factors that influence weathering and release of Se from coal mine waste, we conducted an investigation to identify the Se-bearing strata in a core from a West Virginia coal mine and determine the chemical speciation of Se in those strata using X-ray absorption spectroscopy (XAS).

### METHODS AND MATERIALS

#### Sample Collection and Processing

A 93 m core sample was obtained from a West Virginia coal mine. The core was divided into 93, 1 m sections and each section was crushed and sieved using a 200  $\mu$ m mesh nylon sieve for ICP-MS analysis. We also sectioned 1–2 cm diameter pieces of the core that were retained after sieving using a diamond wafering blade to 1 mm for SXRF and  $\mu$ XANES analysis.

#### ICP-MS Analysis

We digested samples weighing approximately 0.1 g in sealed 55 mL Teflon bombs containing 10 mL of trace-metal grade nitric acid. The samples were heated using a microwave digestion system to 180 °C and held at that temperature for 10 min.<sup>3</sup> The samples were then diluted appropriately with ultra-pure (18.2 M $\Omega$ ) water prior

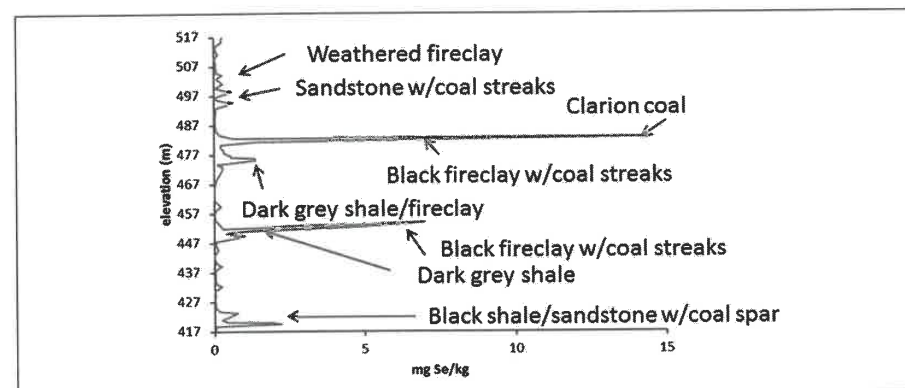


Figure 1. Se concentrations in a core from a West Virginia coal mine

to analysis. The samples were analyzed using an ICP-MS equipped with an octopole reaction cell pressurized with H<sub>2</sub> to remove Ar based interferences. We mixed the samples online with 5% octanol at a ratio of 1:1 to normalize the carbon content of the samples and standards. We used a standard reference shale provided by the U.S. Geologic survey (Green River shale, SGR-1b) as a control sample. This material has a reference Se concentration of 3.5 mg/kg. Our method resulted in a measured value of 3.54  $\pm$  0.09 (mean  $\pm$  SD, n = 4). Method detection limits were extremely low and averaged 40  $\mu$ g Se kg<sup>-1</sup> for a 100 mg sample.

#### Synchrotron Analyses

We selected four samples with the highest Se concentrations to analyze using a synchrotron based X-ray microprobe at beam line X26A, National Synchrotron Light Source, Brookhaven National Laboratory. The thin sections were mounted in the X-ray beam, which was focused to a spot size of about 5  $\times$  7  $\mu$ m<sup>2</sup>. A 4-element silicon drift detector was used to measure X-ray fluorescence of Se and other elements contained within the sample. The samples stage was rastered in the beam to produce 2 dimensional elemental images of the samples. Foci of elevated Se concentrations were then further analyzed using  $\mu$ XANES. To determine the Se speciation, the  $\mu$ XANES

spectra were compared to a standard Se (0) foil as well as selenomethionine (Se -II), lead selenide (Se -II), sodium selenate (Se +VI) and sodium selenite (Se +IV). Spectra for standards were collected in transmission mode using a pin diode detector while spectra for samples were collected in fluorescence mode using the silicon drift detector. The spectra were normalized and processed using Athena.<sup>4</sup>

### RESULTS AND DISCUSSION

The core sample contained a variety of rock types including sandstone, shale, coal and fireclay. Of these rock types, the highest Se concentrations were found within the coal, dark grey/black shale, and fireclay containing strata (Figure 1). Se concentrations in all rock types ranged from below the detection limit in a few sandstone strata to 14.2 mg/kg in clarion coal. Sandstone typically had the lowest Se concentrations but slightly elevated concentrations were observed in sandstone when coal streaks or spar were present.

In the SXRF images we observed localized areas of elevated Se concentrations that were several tens of  $\mu$ m in diameter, indicating that the Se was concentrated into relatively few mineral grains (Figure 2). Because the Se concentrations within these grains were at percent concentrations (data not shown), we were able to use the micro-focused X-ray beam to obtain spectral data.

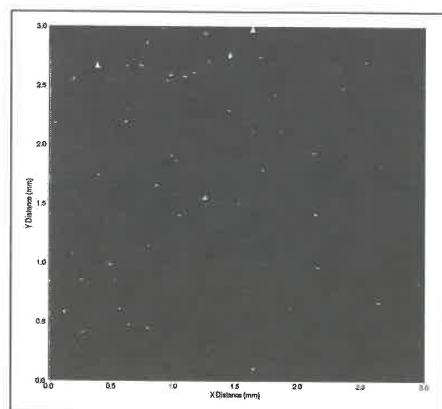


Figure 2. X-ray fluorescence micrograph showing the distribution of selenium in dark gray shale; each pixel is approx.  $10 \times 10 \mu\text{m}^2$  brighter colors indicate higher concentrations of Se

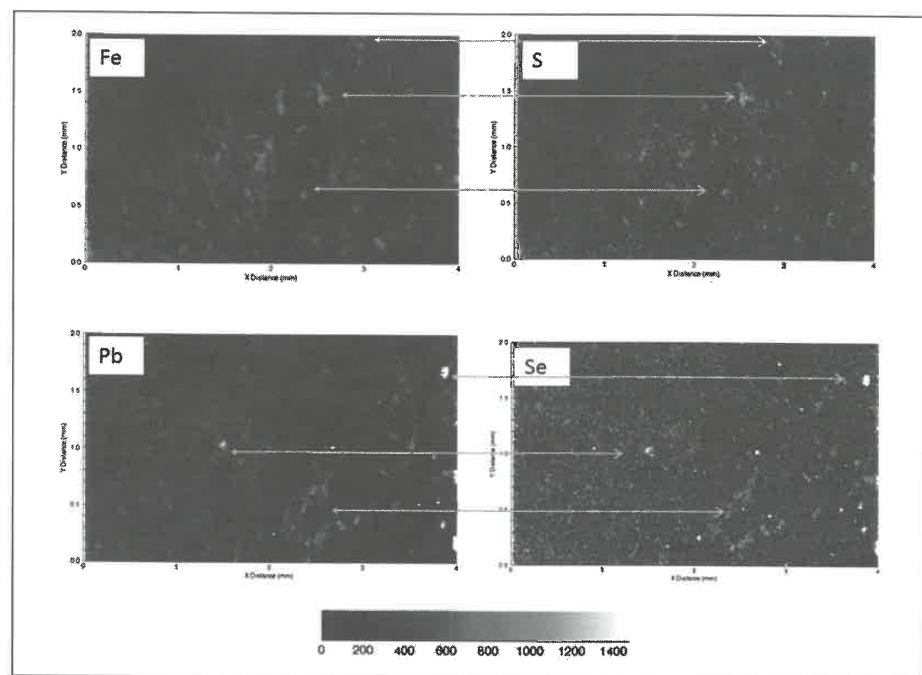


Figure 3. Distribution of Fe, S, Se and Pb in a section of dark gray shale; brighter colors indicate higher concentrations of the indicated element. Green arrows show examples of structures containing both Pb and Se or both Fe and S.

Good correspondence between Fe and S suggested the presence of pyrite in the sample; however, Se containing structures did not show good correspondence with Fe or S, suggesting that Se was not substituted for S in pyrite (Figure 2). On the other hand, Pb and Se showed a nearly identical spatial distribution in many of the samples (Figure 3). Based on this correspondence between Pb and Se, we hypothesized that PbSe was present within the samples and included PbSe as a standard in the  $\mu\text{XANES}$  analysis. We analyzed multiple foci of elevated Se concentrations from four different shale samples and one coal sample. In all cases we found excellent agreement between the spectra and spectra from either elemental Se or PbSe standards (Figure 4).

Taken together, our results indicate that the majority of Se within this core was found within

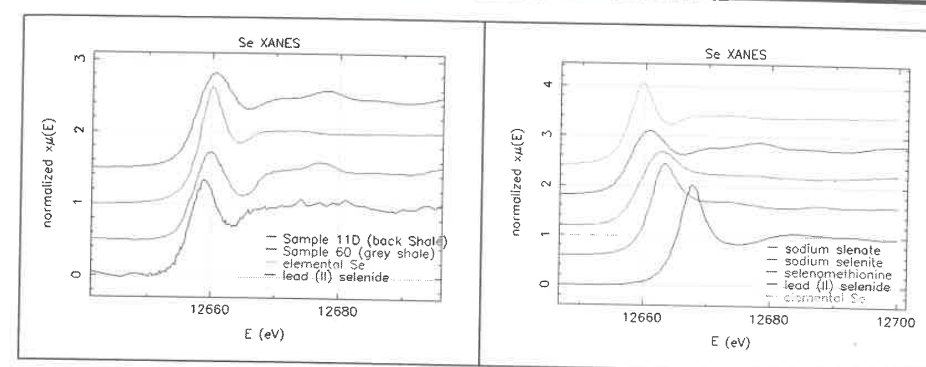


Figure 4. Se K-edge X-ray absorption near-edge spectroscopy (XANES) example spectra (left) and model compounds (right)

relatively narrow bands of strata. Strata containing dark, presumably organic-rich, shales as well as coal and fireclay contained the highest concentrations of Se. Selenium was present primarily as elemental Se or PbSe in these strata and was present in micron or sub-micron sized grains. These phases could have been formed in aquatic sediments (shale) or soils (fireclay) during the time of deposition or perhaps as a result of diagenesis. It is well known that elemental Se particle can be formed in sediments as a result of microbial activity<sup>5</sup> and may have been preserved in the shale. Lead selenide (clausthalite) has been previously thought to occur in coal.<sup>6</sup> Our results confirm this finding and also extend its occurrence to fireclay and organic-rich shale. This is in contrast to a previous synchrotron experiment that found Se substituted into sulfide minerals.<sup>2</sup> Selenium in coal mine effluents is primarily found in the +IV or +VI oxidation states.<sup>7</sup> Based on the present study, we hypothesize that oxidation is the rate limiting reaction for Se release from mine waste. Identification of procedures that limit the oxidative dissolution of Se in mine waste may provide a cost-effective means of Se source reduction. Future studies should focus on factors that influence weathering of elemental selenium and metal selenides under conditions relevant to different mine waste handling procedures.

## ACKNOWLEDGMENT

This study was sponsored by the Appalachian Research Initiative for Environmental Science (ARIES). The views, opinions and recommendations expressed herein are solely those of the authors and do not imply any endorsement by ARIES employees, other ARIES-affiliated researchers or industrial members. Information about ARIES can be found at <http://www.energy.vt.edu/ARIES>.

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