BIOGEOCHEMISTRY OF SELENIUM ON REMEDIATED PHOSPHATE-MINE TAILINGS IN SOUTHEASTERN IDAHO[1]

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Abstract. Selenium (Se) occurs in a wide variety of oxidation states and is a common element present in sedimentary geologic materials such as shale. Phosphate mining activities in southeastern Idaho have left shale materials near the surface, thus releasing the natural Se into a new weathering environment. In this study we are investigating the biogeochemistry of Se at remediated phosphate mining sites. Soil samples were collected from the rhizosphere of remediated sites and analyzed using microscopically focused X-ray absorption fine structure (XAFS) spectroscopy. A greenhouse study to measure the impacts of sulfate and manure amendments on plant bioavailability is also discussed in this paper. XAFS spectroscopy results provide knowledge of mineralogy and Se-oxidation state in the soils. XAFS spectroscopy revealed that Se exists in several different reduced forms in the parent shale materials, including elemental Se and ferroselite-type minerals. In weathered soils, Se was present as Se(IV) and reduced Se minerals. All of the Se(IV) species were associated with iron, likely goethite. Soil pore water analysis revealed that the soil solution contained both Se(IV) and Se(VI), the most soluble and plant-available forms. We hypothesize that the reduced Se in the shale-parent materials is weathering to Se(IV)-goethite type minerals, which further oxidize to Se(VI) in the rhizosphere and is taken up into the plant foliage. The mechanism that rhizosphere oxidation occurs is unknown, and may be biotic or abiotic. Results from this study provide insight into the weathering mechanism by which Se is made plant available, and will help in developing improved management strategies that will reduce Se exposure to animals.

Additional Keywords: Selenium, Speciation, Bioavailability, XAFS

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[1] Paper was presented at the 2004 National Meeting of the American Society of Mining and Reclamation and The 25th West Virginia Surface Mine Drainage Task Force , April 18-24, 2004. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Proceedings America Society of Mining and Reclamation, 2004 pp 1854-1861
DOI: 10.21000/JASMR04011854
https://doi.org/10.21000/JASMR04011854

Introduction

Selenium (Se), a sulfur analogue and a required trace element, has been shown to have the potential for chronic and acute toxicosis in environmental exposures (Frankenberger and Benson, 1994). Selenite (SeO_3^{2-}, (Se(IV)) and selenate (SeO_4^{2-}, Se(VI)) are the main selenium species in aqueous systems (Jacobs, 1989), while in soils both these forms and reduced, Se(0) and Se(II) species are observed. Although there is vigorous debate on the relative risks of different species (Chapman, 1999), there is general agreement that excess selenium in the environment requires careful study and management.

In the research presented in this presentation we examine selenium biogeochemical cycling in the Western Phosphate Resource Area (WPRA) with attention to the sources, pathways, receptors, and controls of this element. Located in and adjoining the Caribou National Forest (Fig. 1) in southeastern Idaho, the WPRA is a US strategic mineral resource, supplying about 15% of the nation's phosphate and generating nearly $750M for the regional economy. The middle waste shales associated with phosphoria mining in the WPRA are the source of widespread selenium mobilization in the local environment (Munkers, 2000). The management and control of selenium in mining-affected environments presents significant challenges due to its complex chemistry (Manceau and Gallup, 1997; Etzel and Kurek, 1997). To overcome these challenges requires information on chemical speciation and reaction processes. For instance, if we can discover the form of the Se in the soils we can develop models that predict Se availability for plant uptake or leaching, devise remediation strategies that reduce plant uptake, or plant species that do not absorb soil Se. We are testing one such hypothesis in a greenhouse study: high sulfate concentrations in the soils will inhibit selenate uptake. In general this hypothesis has already been verified, however, without information on the Se speciation in the soils it is difficult to know if this strategy will be successful in the P-mine waste remediated soils, and how best to optimize remediation (application time, application rate, fate of selenate that is not absorbed, etc.). We are also investigating if Se uptake from remediated soils varies between Alfalfa and Brome grass (two common plants that were used in revegetation that are also attractive forages for grazing animals). The data presented in this paper reports on the Se speciation in the soils that will be used to help understand the remediation trial results.

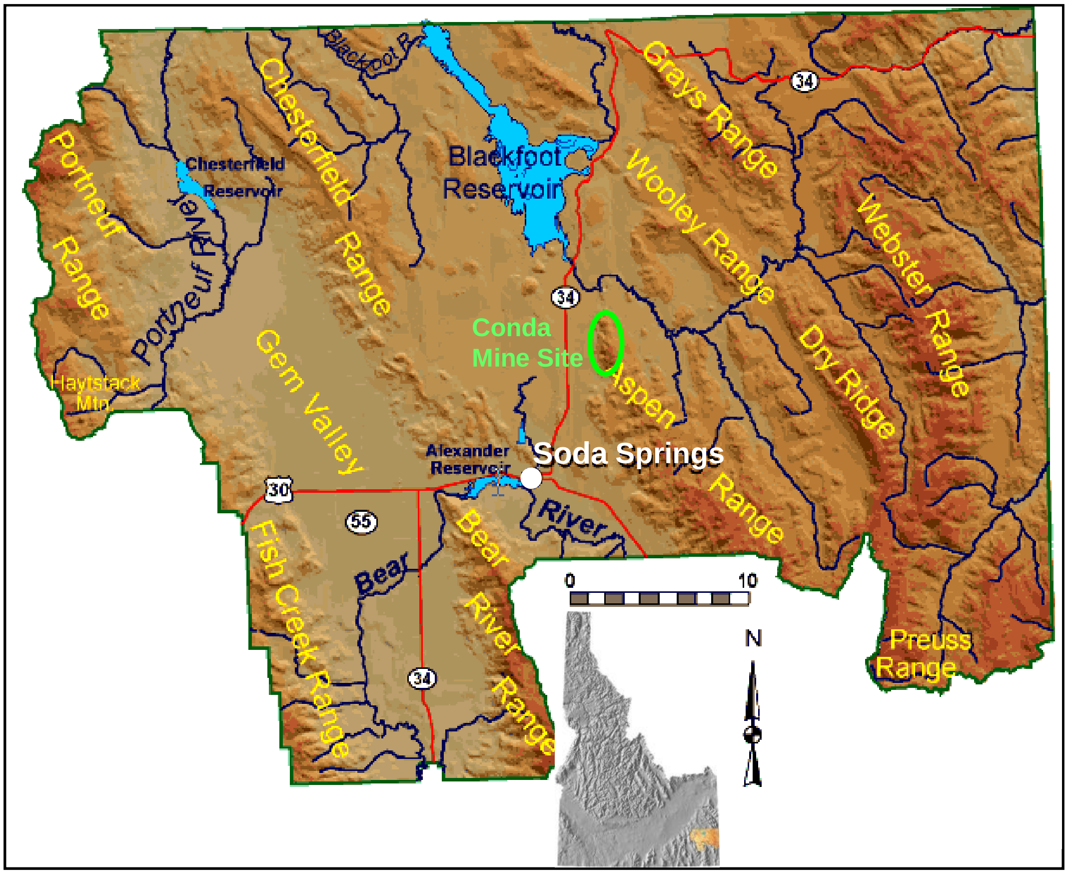

Figure 1. Map of Caribou County showing location of Conda Mine Site.

Materials and Methods

A test site was established at a reclaimed mine-site near Soda Springs Idaho. This site was reclaimed using the phosphoria-formation overburden materials nearly 25 years ago. The test site was divided into treatment plots and each was amended with calcium sulfate, cow manure, or no treatment, and allowed to incubate for a year in the field. Following field incubation samples from each plot were transferred into replicate pots in the greenhouse where they were planted with Alfalfa, Brome Grass, or no plant. When the plants reached maturity, plant tissues were harvested and soil samples were taken and analyzed for total Se. Plant-available Se in the soils was determined by extracting the soils with a DTPA extract.

Micro-XAFS spectroscopy was conducted at the Advanced Light Source in Berkeley, CA on beamline 10.3.2. Fine soil particles (<500 microns) were either mounted between trace element free Kapton tape or mylar film. A shale rock, representative of the parent material deposited on the surface of the remediated mine site, was cleaved along the depositional planes to expose a fresh face for analysis. Because our intent was to collect data on an unweathered shale rock we collected a sample from an active mine near Afton, WY. The samples were scanned taking ~10 micron steps in the x and y direction using a 5 x 10 micron beam with energy of 12,758 eV. After the xy scan was done several hot-spots were identified for further analysis using XAFS spectroscopy. XAFS spectra were recorded by scanning the pre-edge and near-edge regions of the hot-spots which comprise the X-ray absorption near edge spectra (XANES). From the XANES region the oxidation state can be determined and molecular identity may be inferred. All spectra were calibrated to the Se(0) edge position (12,658 eV) using gray Se(0) as a reference.

Results and Discussion

It has been established that DTPA-extractable Se is positively correlated with Se plant uptake (Soltanpour and Workman. 1980). The DTPA-extractable Se was higher in the sulfate treated soils prior to plant growth. If the inhibitory mechanism for uptake of selenate is only a result of higher concentrations of sulfate, then DTPA extract should not exhibit this selectivity. Further data analysis and plant tissue Se concentrations are pending and will allow us to evaluate if sulfate inhibition is occurring, or if manure amendment impacts Se bioavailability. We are also measuring DTPA-extractable Se after plant growth. The results from this study will help determine if manure or sulfate amendments are a possible remediation strategy.

In the shale-rock sample Se was positively correlated to Fe (Fig. 2). XANES spectra from seven different spots revealed that Se existed in primarily two different forms, zero or minus two oxidation states (Fig. 3). This is consistent with Se being present as both elemental Se or Se-Fe minerals such as ferroselite ($FeSe_2$).

Similar to the shale sample, the soil revealed that hot-spots of Se were present with and without iron (Fig. 4). However, unlike the shale, the XANES from the soil showed that Se four (selenite) was present (Fig. 5), as well as the more reduced forms. Analysis of the plant materials grown in the soils indicated that the Se was present as a reduced organic phase with oxidation state negative two, and oxidized Se with oxidation state six (selenate). Despite the presence of selenate in the plant, we have found no evidence of selenate in the soils. Strawn et al. (2001) using micro-XAFS found that the Se in shale derived soils from the California Coast Range existed as selenite and selenate. However, the California soils were more acidic than the soils used for this study (pH=4.0 vs. pH=7.5), and the iron oxide phases in the California soil were dominated by ferrihydrite, as opposed to primarily goethite in the remediated soil used in this study

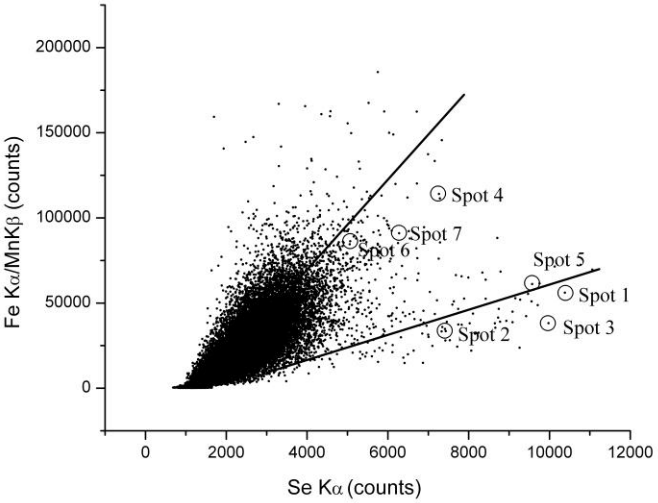

Figure 2. Relative concentration (counts) of Fe vs Se for shale sample. Lines indicate two populations with varying Fe/Se composition; circles indicate spots that XANES data were collected.

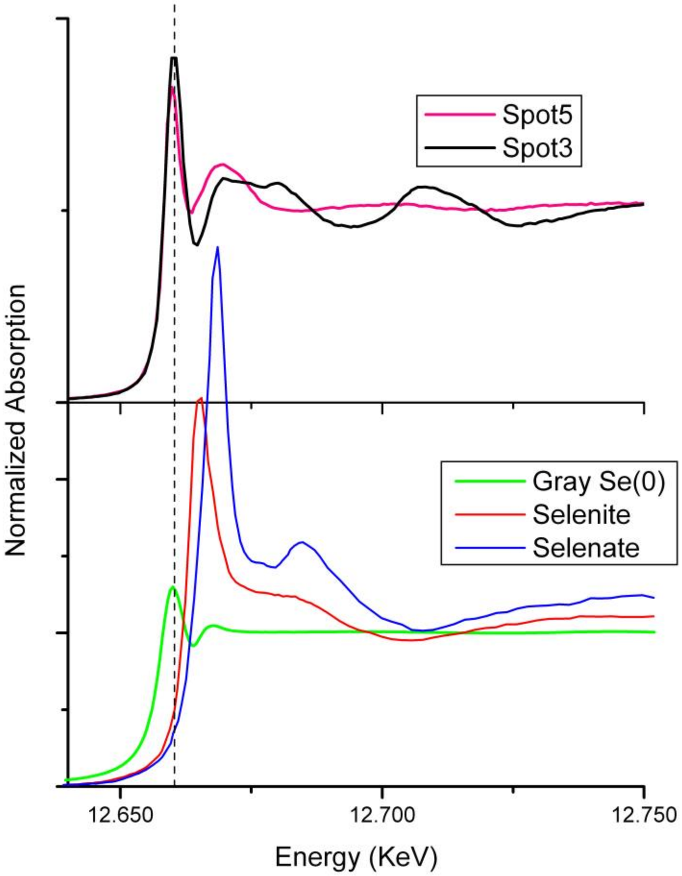

Figure 3. XANES from the shale sample and standards. Shown are the data from two spots, the other five spots probed were similar and were left out to simplify graphic.

We hypothesize that the Se and iron in the parent shale material is oxidizing to form goethite in which the oxidized selenite adsorbs by inner-sphere bonds, which stabilizes the Se from further oxidation. Furthermore, since pH is above 7 and the charge on the goethite is primarily negative, the oxidation of the Se to selenate, which is primarily an outer-sphere adsorbed cation as opposed to inner-sphere sorbed selenite, would make it available to leach out of the soils or be taken up by plants; thus accounting for the lack of Se(VI) observed in the soils.

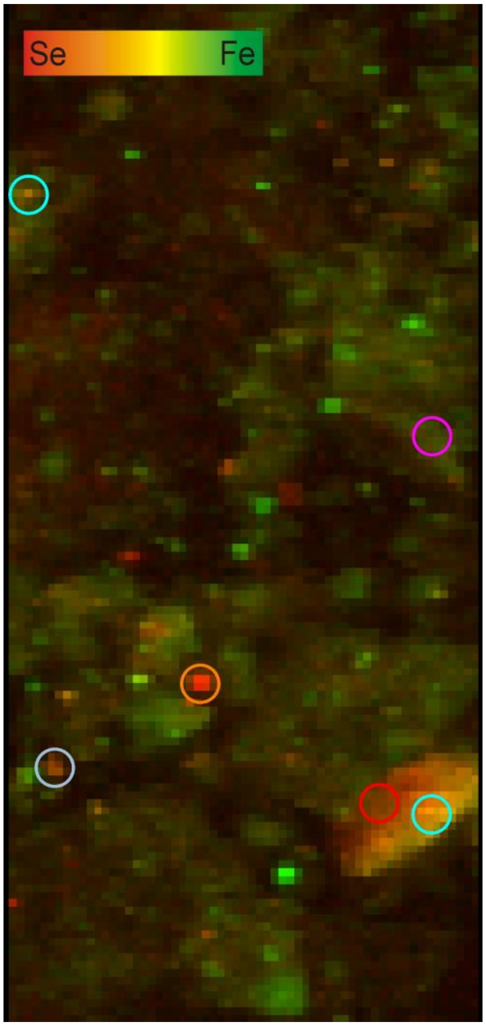

Figure 4. Iron and selenium elemental map of soil particles. Colored circles correspond to spots scanned and presented in Fig. 5. Color bar is 460 microns long.

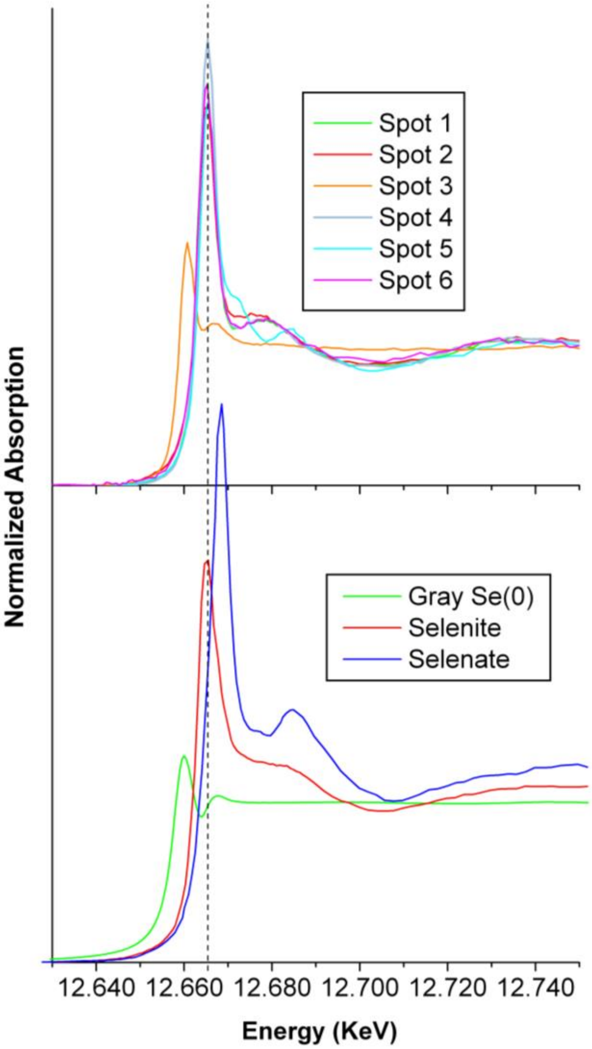

Figure 5. XANES data from soil particles shown in Fig. 4 and standards. Colors of soil XANES spectra correspond to the colors of circles in Fig. 4.

Results from this study provide insight into the Se-geochemical cycle occurring on the remediated mine sites. Results from the greenhouse study will provide insights on possible remediation strategies. Together the geochemical speciation information and remediation trials will allow for important insights on how best to remediate and manage sites contaminated with Se.

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