# Oxidation State of Selenium on Submillimeter-Sized Aggregates in Soils

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In this study we used the x-ray microprobe on beamline 13-ID-C to collect Se XANES spectra from small mineral aggregates in a soil thin section. Soils are heterogeneous materials with respect to mineral distribution. Due to this heterogeneity, XANES spectra collected using traditional bulk x-ray spectroscopy techniques yields an average spectra, making interpretation of element speciation difficult. The x-ray microprobe at the GeoSoilEnviroCARS beamline has a small and intense beam, making it ideal for investigating heterogeneous materials, such as soils.

The soils were collected from the hills on the east side of the California Coast Range. These soils are the parent materials for the agricultural soils located on the west side of the San Joaquin Valley. Intensive irrigation and evapotranspiration in these soils creates Se-laden salt buildup that must be leached in order for productivity to be sustainable. The leaching of the salts creates Se-contaminated water that must be properly disposed of to prevent Se toxicity to animals. Thus, in order to make accurate risk assessments and improve management strategies, it is important that the natural geochemical cycle of Se in soils be understood.

For this study we prepared thin sections of the soil by impregnating them with a hardening resin and cutting and polishing them to ~500 microns thick using thin sectioning equipment. The dominant mineral aggregates were identified as iron oxide, iron sulfate, and the shale parent materials. Previous synchrotron-based x-ray fluorescence microscopy indicated that the Se was concentrated in the iron oxide aggregates relative to the rest of the soil minerals. The bulk Se concentration in the soil is ~5 ppm. The XANES were collected on beamline 13-ID-C using a multi-element germanium detector with a 100 micrometer Al foil filter to prevent oversaturation of the detector from the intense Fe K fluorescence. The beam spot was focused to ~3 microns. XANES scans were taken using a 0.5 eV step size from 50 eV before to 200 eV after the Se K edge. The total time for one scan was ~20 minutes. The spectra from multiple channels were summed and then normalized to the step height. A separate experiment in which the successive spectra were collected on a single spot 5 minutes apart from each other did not reveal any x-ray induced oxidation or reduction in the soil samples.

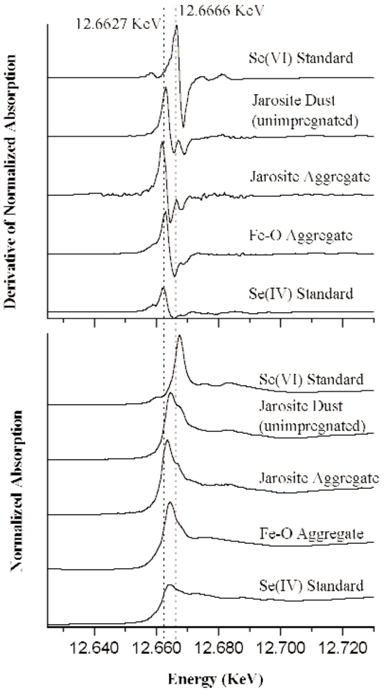

*FIG. 1. Se XANES from iron oxide and jarosite aggregates from soil thin section.*

The Se K XANES spectra are shown in Fig. 1. To test for the effects of resin impregnation and thin sectioning on the Se oxidation state, unimpregnated jarosite aggregates were collected using a dissecting microscope and tweezers. Jarosite was selected because the aggregates could be isolated from the rest of the soil in significant quantities to run as a unique unaltered phase. The XANES spectra from the unimpregnated jarosite dust and the impregnated jarosite aggregate show that the Se oxidation states are the same, indicating that the resin impregnation process did not change the oxidation state of Se in the soil. The inflection points in the first derivative of the XANES spectra are at 12.6627 keV and 12.6666 keV, indicating that both Se(IV) and Se(VI) are present in the iron oxide and the jarosite aggregates. In the iron oxide aggregate, the Se(VI) peak is smaller than in the jarosite aggregate suggesting that the ratio of Se(IV) to Se(VI) is highest in the iron oxide aggregate. Selenite (Se (IV)) is known to form strong bonds and/or coprecipitates with iron oxides in soils, particularly in acid soils. In alkali and/or oxidizing soils, selenate (Se (VI)) may also exist. Since selenate is less strongly adsorbed to oxides than selenite, it is considered to be more mobile. The soil used in this study has a low pH and is oxidizing. The selenate may be coprecipitating with the jarosite minerals since it has an analogous behavior as sulfate, accounting for the slightly higher concentration in the jarosite mineral aggregate.

In summary, these data show that μ-XANES is a valuable technique for interpreting chemical speciation information in heterogeneous materials, such as soils. This information will allow for new understanding on weathering processes and element availability for transport and bio-uptake; and can be used to design better management strategies and reduce contamination of ground and surface waters.

## Acknowledgments

We appreciate the help of Steve Sutton and Matt Newville for assisting us in collecting data. This research was supported by the Kearney Foundation of Soil Science. GeoSoilEnviroCARS is supported by NSF EAR-9906456 (M. Rivers, PI) and DOE DE-FG02-92ER14244 and DE-FG02-94ER14466 (S. Sutton, PI). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.