

Spatially Resolved XANES Analysis on U and Ni in Aged-Contaminated Savannah River Site Sediments

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Beamline(s): X26A

Introduction: In previous elemental mapping of 30 μm thin-sections from contaminated sediments on the Savannah River Site (SRS), localized concentrations of U and Ni were frequently observed [1]. Spatially resolved X-ray absorption near-edge structure (XANES) spectroscopy was applied to these heterogeneous regions to determine the oxidation state of U and Ni to corroborate results from earlier studies [2,3] for U and to complement scanning electron microscopy observations of discrete, potentially metallic Ni phases [4]. This information is valuable for understanding biogeochemical cycling of heavy metals and radionuclides that have undergone decades of aging in riparian and wetland sediments.

Methods and Materials: Spatially resolved XANES analyses were conducted at the dedicated hard X-ray microprobe on NSLS beamline X26A. Mono-energy scans were performed using a Si(111) monochromator with a 0.5 eV step size over absorption edge regions (17166 eV for the U L_{III} -edge; 8333 eV for the Ni K-edge). The spot size for the beam was approximately 15 x 20 μm . Absorption edge positions were evaluated with respect to U and Ni reference compounds.

Results: In spite of sediment conditions favorable for U reduction, i.e., seasonal flooding, fluctuating Eh, high organic carbon concentrations, and intimate contact of U with sediment organic matter, no evidence for U(IV) was observed (Fig. 1a). Instead, U appeared to be present exclusively as U(VI) in the uranyl form, UO_2^{2+} . This result is consistent with earlier studies on sediments from the same SRS riparian system and suggests that U reduction may be inhibited by geochemical or microbiological factors. Ni was found exclusively in the divalent state, Ni^{2+} , for the regions examined (Fig. 1b).

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References:

- [1]. Abstract No. Sowd0311, this report: A. Sowder and P. Bertsch, "Elemental Distribution of U and Ni in Contaminated Riparian Sediments", National Synchrotron Light Source Activity Report for Period Covering October 1, 2001 – September 30, 2002. Brookhaven National Laboratory, Upton, NY, (2002).
- [2]. P.M. Bertsch, D.B. Hunter, S.R. Sutton, S. Bajt, and M.L. Rivers, "In Situ Chemical Speciation of Uranium in Soils and Sediments by Micro X-ray Absorption Spectroscopy", *Environmental Science and Technology*, **28**, 980-984 (1994).
- [3]. D.B. Hunter and P.M. Bertsch, "In Situ Examination of Uranium Contaminated Soil Particles by Micro-X-ray Absorption and Micro-Fluorescence Spectroscopies", *Journal of Radioanalytical and Nuclear Chemistry*, **234**, 237-242 (1998).
- [4]. A.G. Sowder, P.M. Bertsch, and P.J. Morris. "Partitioning and Availability of Uranium and Nickel in Aged-Contaminated Riparian Sediments", *Journal of Environmental Quality*, *in press* (2002).

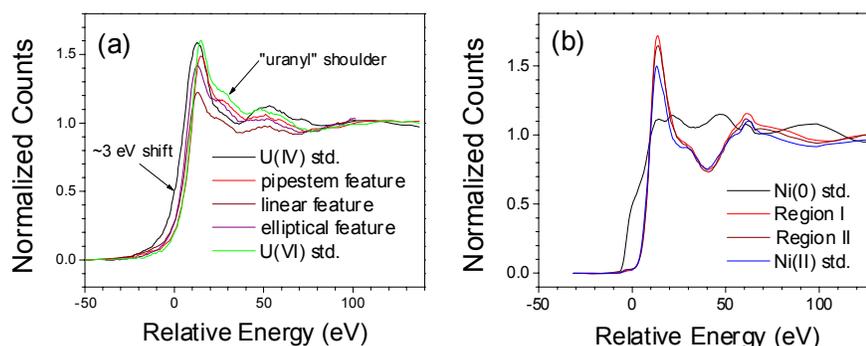


Figure 1. Representative XANES spectra for (a) U L_{III} -edge data collected from multiple U-rich organic features and (b) Ni K-edge data collected from a Ni-rich feature. Relative edge positions for all U-rich zones match those for U(VI) reference materials and post-edge shoulder indicates presence of uranyl structure. Ni edge positions reflect those for Ni(II) standard.