
Uranium Distribution in Geochemically Diverse Sediments

Tyler Womble^{*a}, Dr. Wenyi Zhu^a, and Dr. Kaye Savage^a

^aWofford College, Spartanburg SC 29303

^{*}corresponding author: womblect@gmail.com; 904-415-3660

Received October 2011

Nuclear waste policy has been a long-running problem for the US government. Early policies involved dumping millions of liters of acidic waste into dump sites, such as the S-3 Waste Disposal Pond at the Oak Ridge National Laboratory (ORNL). A long-term effect of these policies is that radioactive contaminants are being detected in down-gradient groundwater plumes, soils, and sediments. The goal of this research is to determine mechanism(s) of uranium mobility and to characterize the geochemical environments of uranium in contaminated samples obtained from the ORNL site. Soil samples from ORNL were analyzed at the Stanford Synchrotron Radiation Lightsource (SSRL) by X-ray fluorescence (XRF) microprobe mapping at the uranium L(III) absorption edge and microbeam X-ray Absorption Near Edge Spectroscopy (XANES). XRF analysis showed that in some samples uranium had positive correlations with a variety of other elements, such as potassium, copper, manganese, and iron while in other samples, uranium exhibited a negative correlation with some of those elements. Uranium was also found in high abundance in some samples but was low in others. This information is valuable for recognizing the heterogeneity within the sediments. XANES analysis indicated that in all of the samples uranium occurred as U(VI). No U(IV) states were found. Spectral characteristics from XANES work suggested that uranium occurs as both adsorbed complexes and as solid precipitate phases.

Introduction

Waste of any sort has been a constant economic and environmental problem for the U.S. government. This also holds true for the government's policies surrounding the disposal of radioactive by-products from nuclear power plants and nuclear weapons production facilities. In the early stages of nuclear science, the primary method for disposal was dumping of millions of liters of contaminated radioactive waste into sites scattered across the U.S. One such site, at Oak Ridge National Labs, had about 320 million liters of uranium-contaminated waste dumped into the nearby S-3 Waste Disposal Pond over the course of thirty years (1951-1983) [1]. The pond was then "neutralized" and "denitrified" and a large parking lot now resides over three decades worth of nuclear waste. Now, uranium contamination is being detected in soil, sediments, and in a groundwater flow pathway.

The S-3 pond site lies above two rock units, the Nolichucky Shale and the Maynardville Limestone. The groundwater flow is parallel to the strike of the bedding planes and axis of the valley in a southeast direction [1]. The groundwater plume flows through two major regions: Area 2 being the shale/saprolite pathway and Area 3 being the carbonate pathway [1]. Uranium contamination has also been detected down several hundred feet deep into the bedrock and extends approximately 4 kilometers away from the former pond towards Bear Creek [1]. Other contaminants found in addition to uranium include nitrate, thorium, technetium-99, and dissolved organic compounds (>200ppm) [2].

The U.S. Department of Energy is now faced with remediation efforts pertaining to this site, as well as others

[3]. This comes with the challenge of preventing or slowing uranium mobility. Tracers have been applied to quantify the groundwater flow rate. However, the need for data characterizing uranium on the molecular and pore scale has become increasingly recognized as essential for understanding uranium transport. [4]. Several factors, such as limited thermodynamic data for uranium species, multitudes of minerals that contain uranium as a stoichiometric constituent, and a myriad of possible cationic aqueous uranyl species provide many difficulties in predicting uranium speciation [5-8]. Uranium transport is also dependent on local geochemical conditions such as the redox environment, pH, minerals present, and dissolved organic matter. Generally, U(VI) species tend to be more soluble and therefore mobile in underground water plumes.

The objectives of this research are to characterize uranium speciation on the molecular and pore scale, pose mechanism(s) of uranium transport away from the former S-3 pond area, and to verify geochemical models by simulating geochemical gradients in laboratory experiments (in progress). Soil samples collected from the S-3 site, primarily from areas 2 and 3, were analyzed using X-ray fluorescence mapping (XRF) and X-ray Absorption Near Edge Spectroscopy (XANES). The XRF mapping shows the distribution of uranium and other selected elements on the micro-scale, their relative concentrations within the samples, and used to determine the extent to which uranium is correlated with other elements. XANES work provided information on the oxidation state and chemical environment of uranium by determining the energy of X-ray absorption.

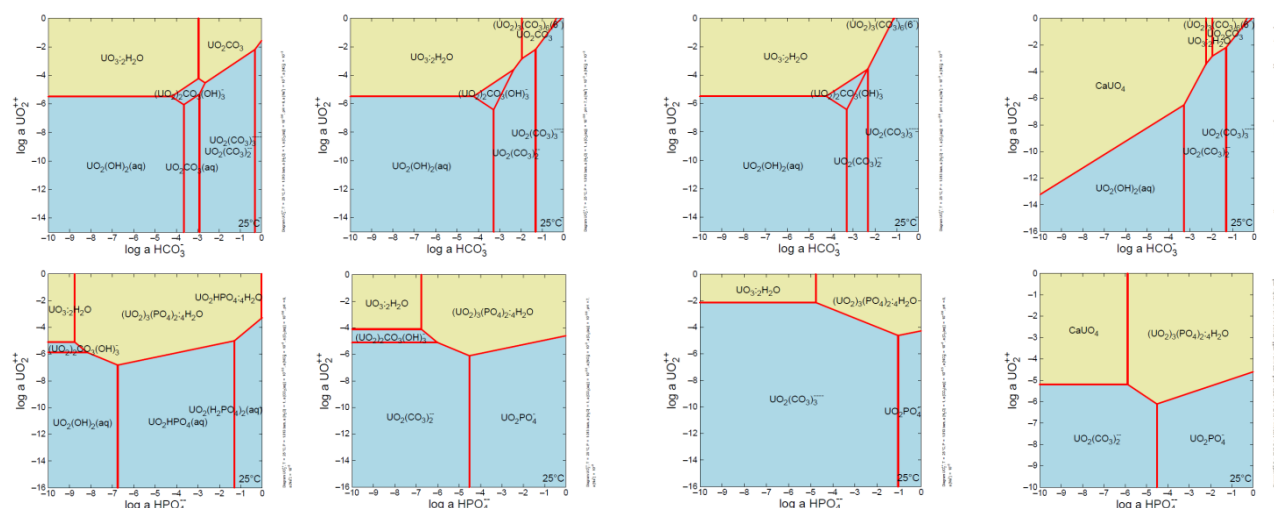


Figure 1. The top row shows uranium speciation plotted as a function of carbonate ligand concentration and the bottom row shows uranium speciation plotted as a function of phosphate ligand concentration. Going from left to the 3rd diagram in the row, the pH is fixed at 6, 7, and 8 respectively. The right most figures show uranium speciation plotted as a function of the respective ligand concentration at a pH of 7 and in the presence of calcite. The yellow areas represent solid phase uranium species and the blue areas represent aqueous species.

Data on the chemical properties of uranium, such as oxidation state and surrounding molecular-scale chemical environment, will further aid isolation and *in situ* remediation efforts conducted on site by the U.S. Department of Energy.

Experimental Methods

Several core samples were obtained from an archive of sediment cores collected near the former S-3 Waste Disposal Pond site at ORNL. Cores were chosen from areas surrounding the Nolichucky Shale and relative to the groundwater flow path, which extends from the former S-3 pond site towards Bear Creek. The samples were picked based on factors such as uranium concentration, distance away from the former pond site, sediment type, and pH. The texture of the sediment, depth taken, and color of the core was also noted. Small amounts of each core (<1g) were scraped off and mounted in Plexiglas slides that were wrapped with polyurethane Helicopter tape and heat sealed in a plastic LDPE bag for containment. The samples were then sent to the Stanford Synchrotron Radiation Lightsource (SSRL) where we performed XANES and XRF analysis.

Geochemical Modeling

Geochemical modeling software, Geochemist's Workbench (Bethke, University of Illinois), was used to predict uranium species likely to be present in subsurface media downgradient of the former S-3 pond based on site data from ORNL and thermodynamic reference databases. The Act2 module was used to graph uranium speciation as a function of several conditions, such as varying uranium concentrations, ligand concentrations, and pH. The temperature was designated as constant at 25°C. Carbonate, phosphate, and acetate ligands were chosen because they were the ligands expected to show

different behavior in binding with uranium [8,9]. Diagrams depict uranium species as both solid precipitates and as aqueous species. Dissolved oxygen concentration corresponding to typical on-site conditions was designated as approximately 8ppm for all simulations. Different minerals, such as quartz, calcite, and dolomite were included in some of the graphs to mimic the mineralogical setting of the S-3 site. A complementary module to Act2, called SpecE8, was used to create "snapshots" of uranium speciation based on specific points on the Act2 plots. Uranium concentration, pH, ligand concentration, mineralogical composition, and environmental factors, such as amounts of dissolved oxygen, CO₂, and organic compounds were input into the SpecE8 program to calculate concentrations of aqueous uranium species and saturation indices of solid uranium phases at chemical equilibrium. The program also predicted other chemical forms of the ligands or minerals present. The Act2 and SpecE8 calculations assisted in formulating the conditions for laboratory experiments designed to assess the effects of gradients of pH and varying ligands across cells, which contain minerals that are representative of the soils and sediments found at Oak Ridge. The experiments will seek to provide a comparison between on site samples, geochemical models, and samples generated in the lab. Geochemical models were used in conjunction with data collected at SSRL to determine possible uranium species found at ORNL.

XRF and XANES

X-ray fluorescence (XRF) microprobe mapping was conducted at beam-line 2-3 at SSRL. The monochromator controlling the incident X-ray energy was calibrated using a Yttrium foil. Data for uranium was collected at 17100, 17170, 17175, 17178, and 17190 eV. These energy values correspond to the maximum difference between the Rb-K edge and the upper limit of the U L(III) edge, the maximum difference

between the absorption edge energies of U(IV) and U(VI), the U(IV) white line peak, the U(VI) white line peak, and a spectral feature associated with the UO_2^{2+} complex respectively. Germanium crystal detector channels were configured to detect energies emitted by other elements such as manganese, iron, arsenic, lead, magnesium, phosphorous, chromium, copper, potassium, and zinc. Elements with lower excitation energies ($Z < 14$) could not be detected. The resulting fluorescence images show a field of view of a few millimeters wide and were matched up with a digital photo of the area scanned. The XRF data were analyzed using the software package SMAK (Webb, SSRL). The corresponding images were used to assess elemental correlations with uranium. A tri-plotter function was used to overlay three corresponding images and a correlation plotter was used to determine if there was any correlation, positive or negative, between a particular element and uranium.

X-ray Absorption Near Edge Spectroscopy (XANES) was used to determine the oxidation states of uranium and interpret its chemical environment. Locations of XANES scans were selected from the XRF images based on relative uranium concentration and correlations with other elements. Each scan was collected using a $2\mu\text{m}$ beam size.

The energy levels of the white line peak and adsorption edge for each scan were noted and compared to elemental uranium and with uranium standards of known oxidation state. XANES scans were analyzed and normalized through the iXAFS package, using an implementation of the code Athena (Ravel, Argonne National Laboratories). Data collected from the XANES scans were used with images produced by XRF mapping and with simulations produced by the Geochemist's Workbench software to interpret the species of uranium found in each location.

Results and Discussion

Uranium speciation was predicted using computational modeling and compared with data collected via XRF microprobe mapping and microbeam XANES analysis. Models generated from the Geochemist's Workbench program provided diagrams depicting the speciation of uranium. The diagrams, including those that incorporated different minerals and ligands, showed that solid uranium precipitates are thermodynamically stable and would be the predominant species at equilibrium when the uranium concentration is high ($\log[\text{U}] > -6$). At lower concentrations of uranium ($\log[\text{U}] < -6$), aqueous species would predominate at equilibrium regardless of the ligand represented. Uranium precipitate phases were primarily dependent on which ligand was included in the model [Fig. 1]. If the phosphate ligand was incorporated into the simulation, at high concentrations uranium would be expected to occur as a uranyl phosphate precipitate. Without these ligands, uranium would be expected to occur as a solid phase uranyl oxide compounds or would be hydrolyzed as an aqueous species depending on concentration and pH. Diagrams with uranium species plotted as a function of pH showed that at lower pH ranges, uranium should occur as an aqueous UO_2^{+2} species and would be further hydrolyzed as pH increased.

XRF mapping produced images that show the distribution and relative amount of uranium, as well as other elements, within the samples [Fig. 2]. Higher amounts of a particular element are indicated by yellow/orange/red areas on the images and lower amounts are indicated by bluer areas [Fig. 2b-d]. Elements that were found proximal to uranium were plotted using the tri-color function of the SMAK software [Fig 2e]. A correlation module plotted graphs of each element with uranium to determine if uranium exhibited any correlation with that element. Uranium was found to have positive correlations with manganese, silicon, iron, chromium, and copper in some samples or sample regions [Fig 3(a-e)]. However, in other instances, uranium exhibited negative correlations with some of the same elements, such as iron and manganese. In some cases, uranium showed no correlation with any other element in the scan [Fig. 3(a,b)]. Uranium in these locations was interpreted to be solid phase uranyl oxide compounds. Locations of uranium in low abundance but correlated with another element (typically Fe or Mn) were interpreted to be adsorbed complexes onto a mineral grain or coating. Several maps also showed no indication of uranium at all despite the presence of elements/minerals found in other scans. The multiplicity of uranium characteristics is important in recognizing the heterogeneity within the sediments.

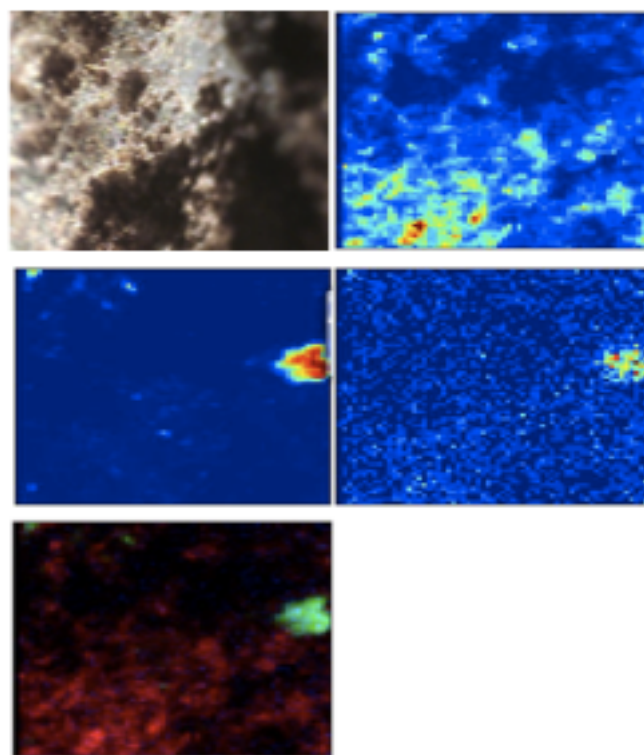


Figure 2(a-e). a) shows the magnified image of the soil sample from core #12418CT from Area 2. b), c), and d) show the XRF images for iron, uranium, and phosphorous respectively. The blue areas represent low concentrations and the red, orange, and yellow areas represent high concentrations of the respective element; with red being the greatest. e) shows the tri-color overlay of b), c), and d) with iron in red, uranium in green, and phosphorous in blue. The tri-color plot shows uranium having a correlation with phosphorous, but not with iron in the sample.

Individual locations on each XRF image that showed high uranium concentration and had significant correlations with a particular element(s) were selected for XANES analysis. XANES analysis determined the oxidation state and suggested the surrounding chemical environment of uranium by measuring the shifts of the white line peaks and absorption edge compared to elemental uranium. The L(III) absorption edge for elemental uranium is located at 17166 eV. XANES scans showed that uranium found in the samples had adsorption edges of approximately 17172 eV and white line peaks at 17176 eV, consistent with a U(VI) oxidation state [Fig 4]. XANES analysis also suggest that uranium occurs as both adsorbed complexes and precipitate forms. Spectra that had a high signal to noise ratio were interpreted to represent uranyl precipitate phases, for example uranyl oxide or uranyl phosphate phase, depending on the correlation, such as $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ [Fig 1,2,4 12418CT_night2_reg2_003]. Spectra that had a low signal to noise ratio were interpreted to represent U(VI) adsorbed complexes associated with a mineral surface, such as UO_2^{2+} on iron oxide [Fig 3(a,d,e)]. This was the predominant condition for uranium species in correlation with areas of high iron and/or manganese. All spectra were consistent with U(VI); no evidence for U(IV) was found in any of the scans.

XRF and XANES data, combined with predictive models generated using the Geochemist's Workbench software, show that uranium found in the soil, sediments, and groundwater near the former S-3 pond site exhibits a great variety of chemical environments. While some of the XRF images showed uranium in great abundance, many of the XRF images showed no indication of uranium at all despite being selected from radioactive cores. These images also showed many differences in the way uranium occurs in these samples, such as a uranyl oxide precipitate or as an adsorbed complex with iron. One commonality found between the uranium species was that XANES analysis showed that all instances of uranium existed as U(VI). These findings imply that (1) uranium may be easily mobilized in these sediments and (2) using reducing agents may help to limit its mobility.

Acknowledgements

A special thanks to Scott Brooks and Sally Mueller (ORNL) for their assistance in obtaining soil samples and Sam Webb (SSRL) for his technical assistance and help with the SMAK software. This research was funded by the U.S. Department of Energy Environmental Remediation Sciences Program under grant DE-FG02-09ER63802 to K. Savage. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. The SSRL Structural Molecular Biology Program is supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program (P41RR001209).

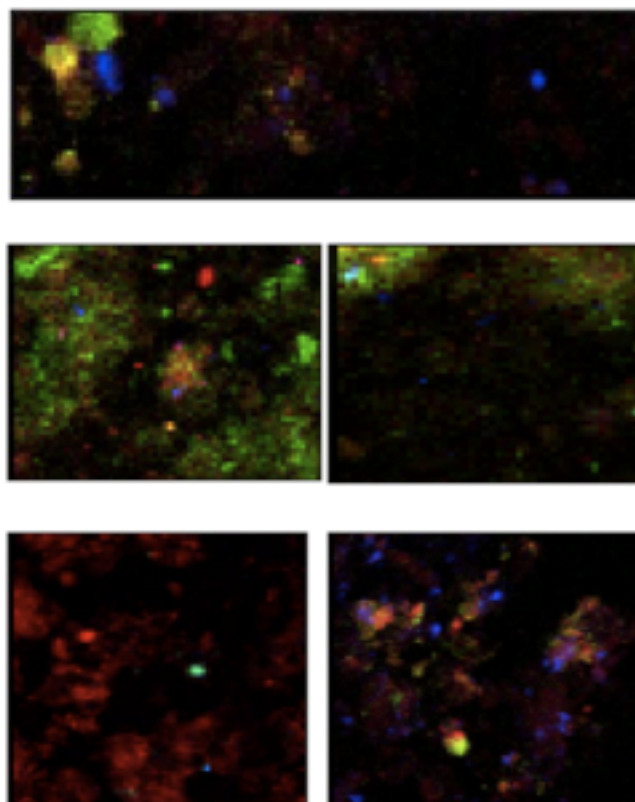


Figure 3(a-e). XRF images shows the heterogeneity found in the samples. Uranium shows correlations with iron (a), copper (d), and by itself (a-c). (d) and (e) shows uranium existing as a single spot on an iron or copper mineral. (a): Iron (red), Uranium (green), Manganese (blue). Core #1080100 Region 2 Area 3. b): Iron (red), Uranium (green), Manganese (blue). Core #1230200 Region 1 Area 3. (c): Iron (red), Uranium (green), Titanium (blue). Core #1230200 Region 3 Area. (d): Iron (red), Uranium (green), Copper (blue). Core #12418CT Region 1 Area 3. (e): Iron (red), Uranium (green), Manganese (blue). Core #1080100 Region 1 Area 3

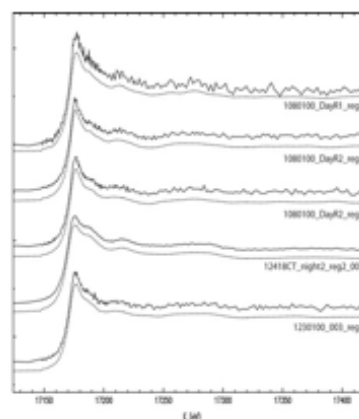


Figure 5. XANES spectra for several regions taken from XRF scans. Most of the lines exhibit a low signal to noise ratio, with the exception of 12418CT. These spectra are interpreted to be adsorbed uranium complexes associated with mineral surfaces. The smoother line of 12418CT is indicative of a solid mineral precipitate. All of the lines show absorption edges at 17172 eV and white line peaks at 17176 eV. The small "hump" just to the right of the white line peak is another characteristic of a U(VI) species specifically, the UO_2^{2+} group.

References

1. U.S. Department of Energy Office of Science. "Subsurface Biogeochemical Research." *ORNL*. <http://public.ornl.gov/orific/orfr3_site.cfm>
2. Brooks, S.C., *Waste Characteristics of the former S-3 ponds and outline of uranium chemistry relevant to NABIR field research studies*, ORNL/TM-2001/27. 2001, Oak Ridge National Laboratory: Oak Ridge, Tennessee. p. 28pp.
3. National Research Council, *Ground Water and Soil Cleanup: Improving Management of Persistent Contaminants*. 1999: National Academic Press. 304.
4. Philips, D.H., D.B. Watson, Y. Roh, T.L. Melhorn, et al. *Distribution of uranium contamination in weathered fractured saprolite/shale and ground water*. *Journal of Environmental Equality*, 2006. 35(5): p. 1715-1730.
5. Steefel, C.I., D.J. DePaolo, and P.C. Lichtner, *Reactive Transport Modeling: An essential tool and a new research approach for Earth sciences*. *Earth and Planetary Science Letters*. 2005. 240(3-4): p. 539-558
6. Hala, J. and H. Miyamoto, *IUPAC-NIST solubility data series. 84. Solubility of inorganic actinide compounds*. *Journal of Physical and Chemical Reference Data*, 2007. 36(4): p. 1417-1736.
7. Bostick, B.C., S. Fendorf, M.O. Barnett, P.M. Jardine, et al., *Uranyl surface complexes formed on subsurface media from DOE facilities*. *Soil Science Society of America Journal*, 2002. 66(1): p. 99-108.
8. Kelly, S.D., K.M. Kemner, and S.C. Brooks, *X-ray absorption spectroscopy identifies calcium-uranyl-carbonate complexes at environmental concentrations*. *Geochimica Et Cosmochimica Acta*, 2007. 71(4): p. 821-834.
9. Bailey, E.H., J.F.W. Mosselmans, and P.F. Schofield, *Uranyl acetate speciation in aqueous solutions - An XAS study between 25 degrees C and 250 degrees C*. *Geochimica Et Cosmochimica Acta*, 2004. 68(8): p. 1711-1722.