Matrix and Beam Effects on U Absorption Edge Measurements by X-ray Absorption Near Edge Structure (XANES) Spectroscopy

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Introduction

An important limitation of many analytical chemical speciation techniques is the introduction of artifacts during measurement. X-ray microprobe based techniques, noted for minimal sample preparation and non-invasiveness, are no exception. Perturbation of analyte oxidation state is particularly problematic since this information is often the object of measurements via X-ray absorption near-edge structure (XANES) spectroscopy. The linear relationship between the U L_{III} absorption edge position and proportion of U(VI) to U(IV) and the 4 eV difference between U(VI) and U(IV) edge positions provide a useful and sensitive approach for quantitatively determining uranium redox status via XANES measurements [1,2].

In this work, we report observations from X-ray absorption spectroscopy analyses on U in sediment thin-sections collected from the U.S. Department of Energy's (DOE) Savannah River Site. An estimated 43,500 kg of U, along with large quantities of Ni and other heavy metals, was discharged to a riparian-wetland system and accumulated in Steed Pond sediments, a farm pond pre-dating the SRS [3-5]. Long-term aging of U, Ni, and the other metals in organic- and Fe-rich sediments has resulted in significant redistribution into less labile forms [6].

Two-dimensional synchrotron X-ray fluorescence (SXRF) mapping performed on these sediment thin-sections at National Synchrotron Light Source (NSLS) beamline X26A suggests important and distinct roles for heterogeneous distributions (on 10's μm scale) of sediment organic matter and Fe-mixed oxide coatings in U and Ni sequestration. Results to date indicate preferential (and often mutually exclusive) partitioning of U into organic detritus and Ni association with Fe oxide coatings [7]. Previous XANES spectroscopy has indicated that U(VI) is the dominant oxidation state of U in SRS sediments from the same site, in spite of conditions favorable for U reduction [1,2,7].

Methods and Materials

Intact sediment core samples were thin-sectioned by Spectrum Petrographics (Winston, OR) according to a protocol developed for trace element analysis: resin embedding using a low metals epoxy (SCOTCHCAST Electrical Resin 3, 3M Corp., St. Paul, MN), thin-sectioning and polishing to 30 μm thickness with Al_2O_3, and mounting onto quartz petrographic slides using a low metals adhesive. XANES and EXAFS measurements were performed on the 13-ID-C Beamline at the Advanced Photon Source (APS), Argonne National Laboratory. The incident X-ray beam was tuned to 17.2 keV using a liquid nitrogen cooled Si(111) monochromator crystal and focused to a nominally 10 x 10 μm spot size using rhodium-coated Kirkpatrick-Baez mirrors [8]. The sample stage was placed at a 45° angle relative to the incident beam. A Canberra 13-element intrinsic Ge detector was used to collect energy dispersive fluorescence measurements at 90° relative to the incident beam. Measurements were conducted at two beam intensities: 5×10^{10} photons s^{-1} and 5×10^{9} photons s^{-1} at sample to detector distances of 24 cm and 12.5 cm, respectively.

Rapid XANES spectra were collected over an energy range 40 eV below and 150 eV above the U L_{III} absorption edge (17166 eV). Pre-edge data (60 to 20 eV below) were collected in 10 eV steps, data in the edge region (from 20 eV below to 20 eV above) were collected in 0.5 eV steps, and post-edge data (20 to 150 eV above) were collected in 2 eV steps. Dwell times of 1 and 3 s were employed for standards and samples, respectively. EXAFS scans were extended to 550 eV beyond the absorption edge with 2 eV steps.

An extensively characterized synthetic metaautunite $Ca[(UO_2)(PO_4)]_2 \cdot xH_2O$ [9] was used as a stable U(VI)-uranyl standard. A powder sample dried at 40 °C was finely ground in an agate mortar and pestle, dispersed in 1 μm boron nitride powder (Aldrich, Milwaukee, WI) to a nominal concentration of 1000 mg kg^{-1}, vacuum pressed into pellets, encapsulated in Kapton film, and mounted in cardboard 35 mm slide holders. Monochromator calibration at 20 keV was verified using a Mo foil standard. Monochromator stability was monitored throughout using the metaautunite U(VI) standard yielding a standard deviation (SD) of 0.5 eV and a standard error (SE) of 0.2 eV for measurements (n = 7) conducted over the 2-day period.

XANES data were normalized relative to incident beam intensity and post-processed using baseline subtraction and normalization to post-edge step height of unity ('XANES dactyloscope' for Windows, K. V. Klementiev, freeware: www.desy.de/~klmn/xanda.html, 16 January 2005). The absorption edge energy E_0 was determined at the edge-step half-height. Data fitting and statistical analyses, including ANOVA and Bonferroni/Scheffe means testing, were performed using ORIGIN v.7.0 analysis software (OriginLab Corp., Northhampton, MA).

Results

At a beam intensity of 5×10^{10} photons s^{-1} for a 10 x 10 μm beam, a consistent drift toward increasing energies for sample U absorption edge was observed for replicate measurements at the same locations on organic-rich features. Fig. 1 illustrates the effect observed for a series of 10 repeated rapid XANES scans for organic vs. mineral matrices high in U. Measurements performed on organic features suggested a partially reduced population of U ($\Delta E_{initial}$t of 2.4 eV below that of the U(VI) standard edge position at 17166.3 eV) that undergoes notable oxidation over the course of subsequent measurements (ΔE_{final} = 0.9 eV). Regression analysis revealed a significant linear correlation between edge position and beam exposure, i.e., sequential measurement no. ($R^2 = 0.89$; $p < 0.001$). For U-rich mineral matrices, repeated measurements reveal a much more modest shift in absorption edge position measurements with increasing beam exposure, as illustrated in Fig. 1, and a relatively weak linear correlation ($R^2 = 0.33$; $p = 0.08$).

No evidence for second shell structure was observed in EXAFS spectra. As concerns arose that sample-beam interactions may confound XANES and EXAFS measurements, the beam intensity was reduced an order of magnitude to approximately 5 x 10^9 photons s^{-1} for the 10 x 10 μm beam, and subsequent measurements focused exclusively on XANES measurements. Under this new measurement condition, very different behavior was observed for replicate XANES measurements on U in organic matrices. At the lower beam intensity, a consistent U absorption edge drift toward lower energies was observed for U associated with organic matrices. Fig. 2 illustrates the effect of repeated measurements on a previously unirradiated organic region. The initial edge position of 17164.9 eV ($\Delta E_{\mathrm{initial}}$ = 1.4 eV relative to 17166.3 eV) decreased to 17163.5 eV ($\Delta E_{\mathrm{final}}$ = 2.8) by the end of the measurement cycle. Linear regression indicates a correlation between edge position and measurement sequence ($R^2 = 0.61$, $p = 0.008$); fitting to a first order exponential decay equation yields a stronger correlation ($R^2 = 0.98$). Ten replicate measurements on a U-rich mineral matrix location revealed no such drift or correlation ($R^2 = 0.002$, $p = 0.9$).

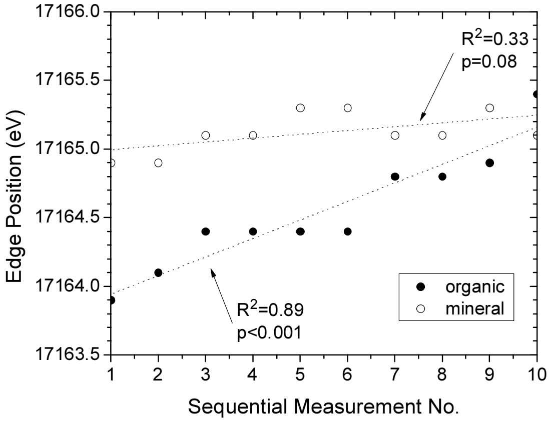

Fig. 1. Sequential measurements of U L_{III} absorption edge for organic and mineral matrices at high beam intensity.

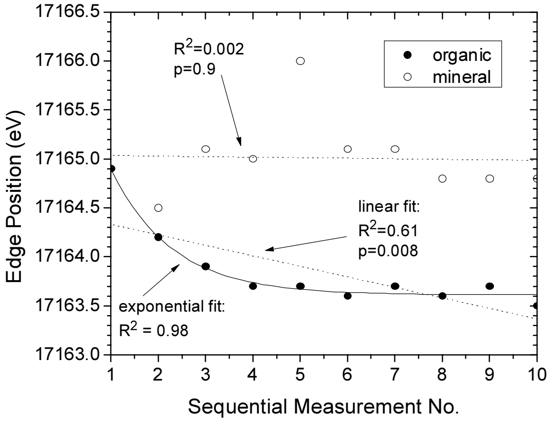

Fig. 2. Sequential measurements of U L_{III} absorption edge for organic and mineral matrices at low beam intensity.

Systematic monochromator drift was ruled out based on repeated measurements of the metaautunite U(VI) standard throughout the experimental period. Measured absorption edge positions for the metaautunite standard resulted in standard errors of 0.2 eV (n = 7) for high beam intensity measurements and 0.1 eV (n = 5) for low intensity measurements. Mean edge positions for the metaautunite standard were not significantly different (α = 0.05) for the two different beam intensities.

Individual U absorption edge measurements at other unirradiated sample locations (at low beam intensity) revealed no significant difference (α = 0.05) between U-rich organic features, E_0 = 17165.3 ± 0.1 eV (n = 7), and U-rich mineral matrices, E_0 = 17165.2 ± 0.2 eV (n = 12), as shown in Fig. 3. However, these mean sample edge positions were found to be significantly lower, by approximately 1 eV, than the mean U edge position for the U(VI) metaautunite standard.

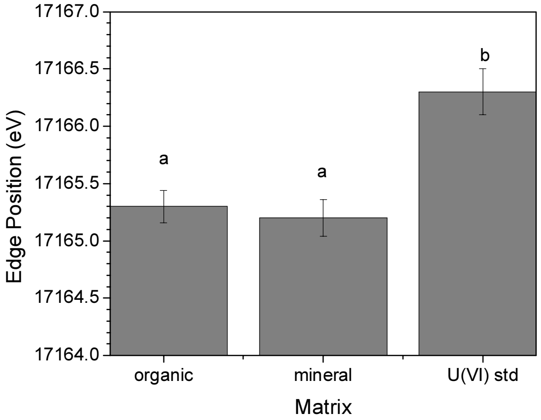

Fig. 3. Summary of U absorption edge position data for organic and mineral matrices relative to the U(VI) standard collected at low beam intensity. Error bars are for ± 1 standard error. Significantly different means (α = 0.05) are indicated by different lowercase letters.

Discussion

Oxidation state is a key factor determining the mobility and bioavailability of uranium in the environment. One objective of our continuing work with aged U contaminated sediments from the SRS is to obtain spacially resolved oxidation state information (from XANES) as well as local structure information (from EXAFS) to better define U speciation at the microscopic scale in heterogenous, organic- and Fe-rich sediments. Attempts to perform micro-scale XANES and EXAFS measurements on sediment thin-sections were complicated by apparent sample-beam interactions. At the initial beam intensity (approx. 5 x 10^{10} photons s^{-1}), the U L_{III} absorption edge position consistently drifted from lower to higher energies with subsequent measurements at, and hence more beam exposure of, a fixed sample position. This shift was far more pronounced for organic versus mineral matrices.

Dropping the incident beam intensity by an order of magnitude resulted in a dramatic change in this behavior. At the lower beam intensity (approx. 5 x 10^9 photons s^{-1}), the drift in edge position was reversed for U-rich organic regions, as the U L_{III} absorption edge position drifted from higher to lower energies with each subsequent measurement. No significant drift was observed for sequential measurements on predominately mineral matrices.

We believe that the changes observed at higher beam intensity are due to rapid reduction of U in the beam path, not resolvable under the measurement timeframe, followed by partial re-oxidation. At reduced beam intensity, we believe that the kinetics of photo-reduction are slowed to a rate at which repeated XANES measurements are able to capture the beam induced reduction in progress. The different behavior between

U populations in organic versus mineral matrices suggests that the presence of organic matter may facilitate or enhance photoreduction of U during irradiation by a sufficiently intense X-ray beam.

Acknowledgements

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