Confocal $\mu$-XRF, $\mu$-XAFS, and $\mu$-XRD Studies of Sediment from a Nuclear Waste Disposal Natural Analogue Site and Fractured Granite Following a Radiotracer Migration Experiment

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Abstract. Combined $\mu$-XRF, $\mu$-XAFS, and $\mu$-XRD investigations of a uranium-rich tertiary sediment, from a nuclear repository natural analogue site, and a fractured granite bore core section after a column tracer experiment using a Np(V) containing cocktail have been performed. Most $\mu$-XRF/$\mu$-XAFS measurements are recorded in a confocal geometry to provide added depth information. The U-rich sediment results show uranium to be present as a tetravalent phosphate and that U(IV) is associated with As(V). Arsenic present is either As(V) or As(0). The As(0) forms thin coatings on the surface of pyrite nodules. A hypothesis for the mechanism of uranium immobilization is proposed, where arsenopyrite acted as reductant of ground water dissolved U(VI) leading to precipitation of less soluble U(IV) and thereby forming As(V). Results for the granite sample show the immobilized Np to be tetravalent and associated with fracture material.

Keywords: microfocus, $\mu$-XRF, $\mu$-XAFS, $\mu$-XANES, $\mu$-EXAFS, $\mu$-XRD, natural analogue
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INTRODUCTION

We report results of spatially resolved investigations with a micrometer-scale resolution ($\mu$-focus XRF, XAFS, and XRD) of U speciation in a U-rich tertiary sediment. The sediment is collected from Ruprechtov, Czech Republic, a natural analogue to deep geological nuclear waste repository scenarios. We also report results of Np speciation in a fractured granite bore section from the Swedish Åspö Hard Rock Laboratory following a radiotracer experiment. Different, complementary methods are applied. Elemental and element chemical state distributions are obtained from $\mu$-XRF measurements, oxidation states determined from $\mu$-XANES, U speciation from $\mu$-EXAFS, and the crystalline structure of selected regions are studied by means of $\mu$-XRD.

MATERIALS AND METHODS

Both bulk samples and sediment thin sections collected from the Ruprechtov site [1] are investigated. Autoradiographic measurements of the samples allow identification and quantification of U hot spots (Noseck et al., 2004). Areas around spots in two different samples containing ~150 and up to 350 $\mu$g $^{238}$U/g material are investigated.

A polished slice of a fractured granite bore core column (52 mm in diameter) from the Swedish Åspö Hard Rock Laboratory used in a radiotracer experiment [2] is studied. The actinide tracer cocktail contained long-lived radioisotopes, including $10^{-5}$ mol/dm$^3$ $^{237}$Np (added as Np(V)). The slice studied is where most of the tracer activity was recovered and contains ~ 3 nmol Np/g.
**RESULTS**

**U-rich Sediment**

-U L$_3$ µ-XANES spectra recorded in confocal geometry at U-rich spots at different depths below the sample surface (not shown) all exhibit spectral features for U(IV). A U L$_3$ µ-EXAFS spectrum (Fig. 1) collected at a U-rich spot ~100 μm below the surface shows no evidence of any short “yl” O distance for U(VI). The µ-EXAFS is well modeled with an O shell and a P shell (Table 1). The coordination numbers and distances for both shells are comparable to those for the mineral ningyoite [4], a U(IV) phosphate mineral. Because S and P are Z+1 atoms, the U(IV) species may also be a sulfate.

Element distributions for a 150×150 μm$^2$ area are shown in Fig. 2. An inverse relationship between the Fe and U fluorescence signals is observed. As(0) and As(V) are identified from As K XANES (not shown) recorded at various sample positions. The distributions of these two oxidation states are recorded by varying the excitation energies (E$_{\text{excite}}$). The As(0) distribution is obtained using E$_{\text{excite}}$ 11.861 keV (large enough to excite As(0) but not As(V)). The As(V) distribution is obtained as a difference image (map at 11.87 keV minus the As(0) map; 11.87 keV is the As(V) XANES WL maximum). As(0) appears as As-rich layers on Fe nodules, where the total As signal is high. As(V) is concentrated in areas void of Fe and As(0). Normalized correlation plots (not shown) reveal a linear As(0)-Fe correlation, indicative of both elements being associated with the same phase. The As(V)-U correlation shows all U(IV) to be associated with As(V). The Sr distribution demonstrates the good energy resolution between its K$\alpha_1$ signal and the U L$_{\alpha_1}$ fluorescence.

![Figure 1](image1.png)  
*FIGURE 1* U L$_3$ µ-EXAFS and best fit result (left) and corresponding Fourier transformed data (right; magnitude in solid lines and imaginary part as symbols).

µ-XRF measurements using a band pass of wavelengths are made at the Flu-to-Topo Beamline (ANKA) and at beamline L (HASYLAB), while monochromatic X-rays are used at ID22 (ESRF). Monochromatic X-rays are used for collecting µ-XAFS and µ-XRD data at ID22 and beamline L. The primary focusing optic in the confocal set-up [3] is a planar compound refractive lens (CRL) at ANKA and a polycapillary (PC) at HASYLAB. A second PC between sample and detector is used as collimating optic at both stations. The CRL delivered a focal spot of 2 μm × 5 μm (V×H). Depending on the PC used, the focal spot diameter varied between 16 and 11 μm. The depth resolution is determined by scanning depth profiles of a thin glass standard to be ~16 μm. A Kirkpatrick-Baez mirror system is used at ID22, delivering a beam spot of 1.5 μm × 4 μm.

**TABLE 1.** Fit results for the µ-EXAFS in Fig. 1.

<table>
<thead>
<tr>
<th>shell</th>
<th>N</th>
<th>R [Å]</th>
<th>σ$^2$[Å$^2$]</th>
<th>$\Delta$E$_{\text{ex}}$[eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>8.1</td>
<td>2.33</td>
<td>0.01</td>
<td>2.46</td>
</tr>
<tr>
<td>P</td>
<td>6.2</td>
<td>3.65</td>
<td>0.003$^b$</td>
<td></td>
</tr>
</tbody>
</table>

The energy of the monochromatic beam for As K edge is calibrated against the XANES white line (WL) of As$_2$O$_3$, defined as 11.867 keV; the U L$_3$ edge measurements are calibrated relative to the XANES WL of schoepite, defined as 17.175 keV. The incident beam energy for the µ-XRD experiments is 27.4 keV(λ=0.453 Å). Either a Si drift or a Si(Li) solid state fluorescence detector is used in all µ-XRF and µ-XANES experiments. The µ-XRD transmission images are registered by means of a high resolution CCD camera (Bruker SMART 1000).

![Figure 2](image2.png)  
*FIGURE 2* µ-XRF distribution maps for the total As, Fe, Sr, and U measured with E$_{\text{excite}}$ = 18 keV and As chemical state distribution (As(V) and As(0)) of a 150 x 150 μm$^2$ section (2 ×4 μm$^2$ step size) of a thin section sample.

Both µ-XRD and µ-XRF data are collected at each pixel in scans of numerous areas of a ~45 μm thin section. The two-dimensional (2D) diffraction pattern extracted from two different pixels is shown in Fig. 3 and compared to calculated diffraction peaks for FeS$_2$ and for FeCO$_3$; their agreement is clear.

Figure 3 also depicts the intensity of measured diffraction reflexes corresponding to d=1.728 and 2.129 Å in FeCO$_3$ and d= 1.631 and 1.908 Å in FeS$_2$ in each pixel of a 240×240 μm$^2$ thin section area. The approximate area sampled is indicated in the micrograph. These phase distribution images show that FeCO$_3$ is located in the right side of the area and FeS$_2$ at left.
The μ-XRF distribution of Np in the fractured granite measured in confocal geometry is compared to distributions for Fe, Zn and Sr in Fig. 4. Autoradiographic images of the sample show the activity to be localized in small fractures. This is reflected in Fig. 4. The Fe distribution follows minute, branched fissures in the granite. The Np is near the smaller branch in the upper part of the image. This particular μ-XRF map also displays our observation that Np is often found associated with Zn. The Sr distribution again demonstrates the good resolution. This is particularly important here as the granite contains Rb, Th, U, Sr and Np, which have energetically close lying Kα1 and Lα1 fluorescence lines. The confocal geometry is helpful where spectral interference is a problem by probing restricted volumes.

A Np L3 μ-XANES is recorded at the darkest pixel in the Np distribution in Fig. 4 (Fig. 5). The spectrum features indicate that the Np hot spot contains Np(IV).

**CONCLUSIONS**

Results for the U-rich sediment corroborate our hypothesis for the mechanism of U immobilization in the sediment [5], where arsenopyrite (As(0)) reduced ground water dissolved U(VI) leading to precipitation of less soluble U(IV) and thereby forming As(V).

Studying the fractured granite following the radiotracer column experiment reveal that Np, originally as Np(V), is reduced to Np(IV). Further work is needed to support the conclusion that the distribution of Np results from local slice Np hot spot in Fig. 4.

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**REFERENCES**