Spatially resolved XRF, XAFS, XRD, STXM and IR investigation of a natural U-rich clay

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Abstract. Combined spatially resolved hard X-ray µ-XRF and µ-XAFS studies using an X-ray beam with micrometer dimensions at the INE-Beamline for actinide research at ANKA and Beamline L at HASYLAB with those from scanning transmission soft X-ray microscopy (STXM) and synchrotron-based Fourier transform infrared microspectroscopy (µ-FTIR) recorded with beam spots in the nanometer range are used to study a U-rich clay originating from Autunian shales in the Permian Lodève Basin (France). This argillaceous formation is a natural U deposit associated with organic matter (bitumen). Results allow us to differentiate between possible mechanisms leading to U enrichment: likely U immobilization via reaction with organic material associated with clay mineral. Such investigations support development of reliable assessment of the long term radiological safety for proposed nuclear waste disposal sites.

1 Introduction
Investigations of actinide geological transport in the context of nuclear waste disposal are especially challenging; an accurate prognosis demands process understanding over a geological time domain over a wide range of spatial dimensions. One strategy for meeting this challenge is through investigations of natural analogues, or geological formations with characteristics considered similar to those for proposed nuclear waste disposal repositories. The sedimentary sequence found in the uranium ore-deposit (Lodève Basin, Massif Central, southern France) investigated in this study is similar to that for proposed spent fuel repositories in claystone formations, making it potentially suitable as a natural analogue. Samples originating from this formation are subject of this investigation. The goal of these studies is to identify and characterize determinant processes leading to uranium immobilization at this site.

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The sample studied originates from the Mas d´Alary faulted zone of the Lodève Basin, exhibiting elevated uranium content. More information on the geology of the area can be found in [1-4]. The uranium is closely associated with organic matter (mostly marine type III), mainly present in the form of bitumen occurring in the reservoir facies [5-8]. In the particular case of Lodève basin the conceptual model is that oxidized U(VI)-bearing fluids reacted within fault zones with the strongly reducing environment of the oil reservoir rocks to form/precipitate bitumen-type material and uranium ore [5]. Oils acting as reductants to precipitate U(IV)-phases from U-bearing hydrothermal fluids circulating in oil reservoirs has also been proposed, based on the organic chemistry as well as mineralogy, e.g., for the Oklo natural reactors [8].

The goal of this study is to characterize the oxidation state and speciation of uranium found in U-enriched regions of a sediment sample from the Lodève Basin and to elucidate if organic matter was directly responsible for uranium reduction or if mineral phases formed by anaerobic degradation of the organic matter may have been responsible for uranium immobilization and accumulation. For this purpose, investigations with micro- to nanoscale-resolution are applied; these are X-ray fluorescence and X-ray absorption fine structure with micro-focused hard X-ray beams (µ-XRF and µ-XAFS), scanning transmission X-ray microscopy (STXM) in the soft X-ray regime and synchrotron-based Fourier transform infrared microspectroscopy (µ-FTIR).

2. Experimental
The uranium ore sample is provided by CREGU (Nancy, France) and originates from the contact zone adjacent to the fault zone of the Autunian shales, collected in the breccia facies at the Mas d´Alary uranium mine located near Lodève. The clay fraction (<2µm) is shown by X-ray diffraction to be composed mainly of illite and chlorite minerals. A photograph and autoradiographic image of the sample is shown in figure 1. The autoradiograph is recorded with a Cyclone Phosphor Scanner (Packard BioScience, Dreieich, Germany). Quantification of U-rich hot spots, visible as dark grey areas in the autoradiograph, shows they contain ~25 mg 238-U/g material.

µ-XRF and micro-X-ray absorption near edge spectroscopy (µ-XANES) measurements are recorded at Beamline L at the Hamburger Synchrotronstrahlungslabor (HASYLAB). A confocal irradiation-detection geometry is used, providing added depth information and allowing probing sample volumes below the surface, thereby avoiding any surface oxidation artifacts caused by cutting and polishing of the clay sample. The principle of this technique is described elsewhere [9,10]. Poly-capillary half lenses are used for both focusing and collimating optics. The focal spot diameter is approximately 16 µm. µ-XRF measurements are recorded using a band pass of wavelengths with an average weighted energy of 17.6 keV using a Mo/Si multilayer pair (AXO Dresden GmbH, Germany) and a Si drift detector (Vortex, SII NanoTechnology USA Inc., Northridge, CA). U L3 µ-XANES are recorded using monochromatic X-rays at selected sample volumes of high U concentration identified in the µ-XRF maps at Beamline L. Both µ-XANES and extended XAFS (EXAFS) spectra are registered with a high purity Ge detector (Canberra) at the INE-Beamline at the Ångströmquelle Karlsruhe, ANKA [11]. U L3-edge EXAFS are measured at positions of high U concentration identified by line scans of windowed U Lα counts using the primary beam coming from the focusing mirror. The measured primary beamspot diameter for EXAFS is 300 µm. A focused secondary beam of around 30 µm is obtained using a poly-capillary lens for the µ-XANES measurements. Si(111) and Ge(422) crystals are used in the double crystal monochromator (DCM) at HASYLAB and ANKA, respectively. The DCM energy is calibrated relative to the first inflection point in the K XANES of a Y foil (defined as 17.038 keV) at both beamlines.

µ-XRD data at the Beamline L is collected from a thin section of a separate sample, using beam from a Mo/Si multilayer pair with a small band pass of wavelengths centered at 17.4 keV, focused to 15 µm by means of an elliptical single-bounce monocapillary, a high resolution CCD camera (MAR CCD, MARUSA Co.) positioned 278 mm behind the sample, and an exposure time of 10 s. The
incident beam energy, experimental geometry and detector parameters are calibrated against the pattern measured for LaB$_6$ (lattice parameter = 0.415690 nm, ICSD data sheet 340427). Experimental details and analysis are found in [12].

Scanning transmission X-ray microscopy investigations are conducted on the X1A1 undulator beamline at the National Light Source Synchrotron (NSLS), operated by the State University of New York at Stony Brook. The principle of this technique is described in detail elsewhere [13]. For STXM and µ-FTIR measurements, transmission mode ~100 nm thick sulfur embedded ultra-microtomes mounted on copper TEM grids are prepared (MVA, Inc., Norcross, GA, USA). Carbon K and potassium L-edge spectra are recorded at an undulator gap of 36.8 mm. The Fresnel zone plate used at X1A1 has a diameter of 160 µm and an outermost zone width of 45 nm. The spherical grating monochromator energy is calibrated using the CO$_2$ gas absorption band at 290.74 eV [14].

µ-FTIR measurements are performed at beamline U10B (NSLS) using a Nicolet Magna 860 Step-Scan FTIR instrument coupled to a Spectra-Tech Continuum IR microscope, which is equipped with a 32x Schwarzschild objective and a dual remote masking aperture [15]. Data acquisition is controlled with the Atlµs software (Thermo Nicolet Instruments), using a 8 µm x 8 µm aperture and 1024 scans per point in the mid-IR range (600 to 4000 cm$^{-1}$), under transmission mode with 4 cm$^{-1}$ spectral resolution. The background signal is measured in sample-free regions of the TEM grid.

$$\text{K} K_{\alpha}, \text{Ca} K_{\alpha}, \text{Ti} K_{\alpha}, \text{Fe} K_{\alpha}, \text{Zr} K_{\alpha}, \text{U} L_{\alpha}$$

Figure 2. Distribution maps for the elements indicated in two separate areas of the sample. Top row: 800 x 760 µm$^2$ recorded near the surface, Step size = 20 µm x 20 µm; bottom row 375 x 750 µm$^2$ area recorded -50 µm below the surface. Step size = 5 µm x 5 µm.

3. Results and discussion

3.1. µ-XRF, µ-XAFS and µ-XRD results

The elemental distributions extracted from measured Kα intensities for K, Ca, Ti, Fe and Zr and Lα signals of U in the µ-XRF data recorded in areas with the high radioactivity (dark regions in the autoradiogram, figure 1) are displayed in figure 2. Inspection of these images reveals two general observations: 1) the U distribution is often correlated with lighter weight element distributions, especially notable in the round features in the upper right corner of the maps and 2) the U distribution seems to be inversely correlated to areas rich in Fe. These observations are corroborated in the correlation maps displayed in figure 3; there is no correlation between Fe and U, but a large number of pixels exhibit a linear correlation between K and U.

In order to determine the U valence state, U L3 µ-XANES (figure 4) and µ-EXAFS (figure 5) are recorded at volumes and areas with high U Lα intensity. The energy position of the most prominent absorption peak in the XANES (the white line, WL) measured for different sample regions at two
different beamlines all lie below that of the U(VI) reference. Furthermore, no multiple scattering feature around 10 eV above the WL indicative of U(VI) \cite{16} is found. We conclude that U is likely present in the sample in the tetravalent state. The U L3 EXAFS for the sample also indicate U(IV) present (figure 5), as no short U-O distance expected for the U(VI) uranyl moiety is observed \cite{16}. The EXAFS data is well fit with an structural model similar to uraninite, UO$_2$ \cite{17}. Best fit results are obtained with 4-5 O atoms at 2.29 Å with $\sigma^2 = 0.013$ Å$^2$ and 2-3 U atoms at 3.78 Å with $\sigma^2 = 0.008$ Å$^2$. The distances are 2-3% smaller than expected for UO$_2$ and the intensities lead to a much smaller coordination number than expected (N(O) = 8; N(U) = 12). This may indicate that the UO$_2$-like phase is present as a nanoparticulate material with large surface area having relaxed distances at the surface.

The decrease in interatomic distances is also reflected in the $\mu$-XRD patterns measured for a thin section sample area, where $\mu$-XRF spectra indicate high U concentration. The 1D diffractogram extracted from a powder ring pattern from such a U-rich area is shown in figure 6. The expected 2$\Theta$ positions for uraninite are also indicated. The (111), (002) and (022) peaks for the UO$_2$ in the clay sample are shifted to higher 2$\Theta$ values, indicating approximately a 2% shortening of the lattice parameter and associated shortening of interatomic distances to values similar to those determined in the EXAFS analysis.

3.2. STXM results

The results of principle component analysis (PCA) and cluster analysis of STXM data (figure 7) reveal two areas marked yellow and red differing in their optical density (OD) and K content. The red areas exhibit a significantly higher OD below the carbon K-edge and absorption bands at K L$_{2,3}$-edge energies. This indicates that this organic material is associated with clay minerals possibly of illite-type. These areas also show a relatively large edge indicating that the clay is associated with rather large amount of organic material. The yellow areas are additional organic material not directly associated to these mineral phases. They have low OD below the carbon edge, which might indicate that they are of almost pure organic nature. The average cluster C(1s)-edge spectra extracted from both regions are generally similar, with yellow areas appearing to have a higher aromatic content (absorption at 285 eV) and the illite-clay associated organics in the red areas a higher aliphatic character or metal complexation (absorption in the 287 eV region \cite{18}).

3.3. $\mu$-FTIR results

Spectral maps imaging the spatial distribution of functional groups in the sample including aliphatics ($\nu_{\text{CHali}}$; 3000-2800 cm$^{-1}$), aromatics ($\nu_{\text{C=C}}$; 1750-1500 cm$^{-1}$), alcohols ($\nu_{\text{OH}}$; 3600-3100 cm$^{-1}$) or OH
vibrations of clay minerals (‘OH’; 3720-3680 cm\(^{-1}\)) are extracted from scanning µ-FTIR data (figure 8). A correlation between the clay mineral vibration bands (‘OH’) and the organic matter functionalities (\(\nu_{\text{CH}}\), \(\nu_{\text{C=C}}\), \(\nu_{\text{OH}}\)) is observed in these distribution maps, confirming the K (i.e., illite-type clay mineral) – organic matter correlation observed in the STXM investigations.

4. Conclusions
In summary, correlations between elements obtained using different techniques (µ-XRF, STXM and µ-FTIR) reveal that the U distribution in our sample is positively correlated to the distribution of lighter weight elements, notably K. We deduce a correlation between clay minerals of illite-type and organic matter in the sample based on both the STXM observation that K (as indicator element) is found associated with organic carbon and the observed spatial coincidence between µ-FTIR clay ‘OH’ vibrations and vibrations of organic functional groups. From the µ-XAFS analysis, we find that the U is present in its tetravalent form, likely as a nano-particulate oxide.

![Figure 5. U L3 \(k^2\)-weighted EXAFS (\(\chi(k)\); left bottom), Fourier-filtered data and best fit results (left top) and corresponding \(k^2\)-weighted Fourier transform (FT) data (right) plotted with best fit results. Experimental data = lines, Fit curves = symbols.](image)

From these observations we put forward a tentative hypothesis for the mechanism of uranium immobilization. Due to the lack of the correlation between uranium and Fe, we exclude Fe-minerals as the dominant reductant during immobilization of groundwater dissolved U(VI) to less soluble U(IV). Combining the knowledge that uranium is found associated with potassium and that clay minerals of illite-type are associated with organic matter we conclude that organic material associated with clay minerals might have been the reducing agent. This hypothesis remains to be scrutinized and a number of open questions remain. For example, what role did the clay play? Did it act as a catalyst [19] or was it merely an anchor for the organic material? To help refine our understanding of the redox partner involved in the reduction of U(VI) in this sediments further combined µ-XRD/µ-XRF studies are planned.

![Figure 6. One dimensional µ-XRD obtained from a U-rich area. The dotted lines show the expected values for uraninite [17].](image)
the macro-scale system of interest. In this study the area probed with μ-XRF is on the order of mm²; the STXM measurements are three orders of magnitude smaller. With this in mind, the correlations made in this study are surprisingly consistent with one another.

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Figure 7. (top) STXM PCA and cluster analysis results showing two distinguishable clusters in the distribution of organic functionality. No C absorption is in the grey area. The scale bar is 10 µm. (right). Average C(1s) XANES of the yellow and red areas.

Figure 8. (upper left) Visible light microscope image of the microtome studied and (lower left) μ-FTIR spectrum of the spot marked by the cross line in the image. (right) Maps of organic functional group distributions extracted from μ-FTIR data: alcohols (νOH; 3600-3100 cm⁻¹), aliphatics (νC-H; 3000-2800 cm⁻¹) and aromatics (νC=C; 1750-1500 cm⁻¹), as well as OH vibrations of clay minerals (‘OH’ 3720-3680 cm⁻¹).
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