Spatially resolved micro-X-ray fluorescence and micro-X-ray absorption fine structure study of a fractured granite bore core following a radiotracer experiment[☆]

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ABSTRACT

Spatially resolved X-ray absorption and fluorescence investigation with a micrometer-scale resolution on actinide-containing samples provide information necessary for safety assessment of nuclear waste disposal. In this paper one example of such an experiment is presented. This example entails neptunium speciation in a fractured granite bore core from the Swedish Äspö Hard Rock Laboratory following a radiotracer experiment using μ -XAFS and μ -XRF. In order to probe micro-volumes below the surface in the granite samples and thereby avoid potential changes in the Np speciation during cutting of the bore core, a confocal irradiation–detection geometry is employed. μ -XAFS results for a selected granite bore core cross section with ~ 3 nmol Np/g reveal that Np, originally introduced as Np(V) in the tracer cocktail, is present in the granite in its reduced Np(IV) form. The Np(IV) is often present as particles, tens of μ m in size. Elemental distribution maps show the tracer Np to be located in fissures and permeable channels not larger than 100 μ m. The Np distribution appears often correlated with Zn also present in some fissures. We observe small granite fissures containing Fe (presumably Fe(II)), where we do not detect any Np. It is feasible that inflowing Np(V) has a shorter residence time in large fractures, while in the smaller fissures migration is slower, leading to longer residence times, i.e., reaction times, where it is reduced to less soluble Np(IV) and becomes thereby immobilized.

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1. Introduction

We perform spatially resolved X-ray fluorescence and absorption investigations using a focused synchrotron beam with micrometer dimensions (μ -XRF and μ -XAFS) on granite bore core following a radiotracer experiment. Elemental distributions are obtained from μ -XRF measurements, correlations between elements are characterized by comparison of the elemental distribution maps, and the Np oxidation state in “hot spot” volumes in the sample, whose location is identified in the Np distribution maps, determined from μ -XAFS spectroscopy (both μ -XANES and μ -EXAFS). A confocal irradiation–detection geometry is employed, which, in addition to providing added depth information, allows us to minimize spectral interference from other elements by limiting the sample volume probed, as well as

to record spectra below the sample surface, thereby avoiding surface oxidation artifacts possibly caused by cutting and polishing the granite slice.

The granite stems from an underground laboratory (the Swedish Äspö Hard Rock Laboratory), where the migration of radionuclides under near-real in situ conditions can be investigated [1]. These investigations are relevant for safety of nuclear waste disposal. The overall aim of such investigations is to assess mechanisms leading to actinide immobilization in high level nuclear waste repository host rock formations. The goal of this specific study is to determine if Np introduced onto a granite column in a radiotracer study and immobilized in the granite is associated with any identifiable elements from the measured elemental distribution maps. In addition, we wish to determine the valence state of the immobilized Np from Np L3 μ -XAFS recorded at Np hot spots. This experiment is also designed to explore the applicability of the technique to a sample containing only a trace concentration level, in this case approximately 3 nmol Np/g granite.

2. Experimental section

A polished slice of a fractured granite bore core column (150 mm original column length, 52 mm in diameter) from the Swedish Äspö

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Fig. 1. Photograph of the granite bore core cross section studied and its autoradiographic image showing the distribution of radioactivity.

Hard Rock Laboratory used in a radiotracer experiment is studied in our μ -focus X-ray experiments. Details of the tracer experiment can be found in [2]. In this experiment, the bore core was subjected to 14 mL radioisotope containing tracer cocktail in Äspö groundwater. The cocktail included 10^{-5} mol/dm³ ²³⁷Np, added as Np(V). Elution was under pressure with 80 mL Äspö groundwater, whereby 26% of the Np introduced onto the column was finally recovered. At the end of the experiment, the column was cut perpendicular to the column axis into 4 mm thick sections. ICP-MS analysis of abraded material from cutting sections and g-counting (312 keV line of ²³³Pa daughter) of sections showed the highest Np concentration (~ 3 nmol Np/g granite material or < 1 ppm) remaining on the column to be located in the section originating 30 mm from the column top. A photograph of the section and an autoradiographic image showing the distribution of radioactivity in the granite core section are displayed in Fig. 1. Comparison of the autoradiographic and optical images of the sample shows the radioactivity to be localized in small granite fractures.

The μ -XRF measurements using a band pass of wavelengths are made at the Fluo-Topo Beamline (ANKA, Karlsruhe) and at beamline L (HASYLAB, Hamburg). Either a Si drift or a Si(Li) solid state fluorescence detector is used in all μ -XRF and μ -XAFS experiments. Fluorescence intensities of elements in the sample for generating distribution maps are isolated from the full fluorescence signal via least-square fits using the AXIL software package from the University of Antwerp [3]. In order to assure that the Np L α 1 signal (13.94 keV) is sufficiently well-resolved from the energetically similar Sr K α 1 line (14.17 keV), an excitation energy lying above the Np L2 absorption edge (21.6 keV) of ~ 23 keV is used to also observe the Np L β 1 line. The elemental distributions obtained using the L α 1 and L β 1 intensities are comparable, showing that spectral interference in the setup is not a problem.

Two half-lenses are used in the confocal setup; one is used to focus the incident primary beam and the other used as collimating half-lens in front of the detector [4]. Upon scanning sample areas at selected

Fig. 2. Elemental distributions for the elements indicated for a $300 \times 300 \mu\text{m}^2$ area of the granite section recorded $\sim 58 \mu\text{m}$ below the surface. Scanning stepsize = $10 \mu\text{m}$. Counting time = 5 s.

depths, tomographic cross sections visualizing the distribution of elements may be easily recorded. By varying the energy of the beam across the Np L3 absorption edge at a constant sample position, X-ray absorption fine structure (XAFS) spectra are recorded. The primary focusing optic 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 is fabricated at the Forschungszentrum Karlsruhe Institut für Mikrostrukturtechnik [5] and delivers a focused X-ray spot of $2 \times 5 \mu\text{m}^2$ ($V \times H$). The diameter of the focal spot delivered by the PC is measured to be $12 \mu\text{m}$ and the depth resolution $23 \mu\text{m}$.

Monochromatic X-rays from Si(111) crystals in the double-crystal monochromator are used for collecting μ -XAFS at beamline L. The energy of the monochromatic beam for recording Np L3 edge is calibrated against the first derivative XANES spectrum of a Zr foil, defined as 17.998 keV [6]. The Np L3 edge XANES and EXAFS are isolated from raw data using standard techniques and the Athena software [7].

3. Results and discussion

Fig. 2 shows the μ -XRF elemental distributions for the main elements having fluorescence lines above 3 keV observed in the sample, measured using the CRL confocal setup at ANKA, at a depth approximately $-58 \mu\text{m}$ below the sample surface. This image is recorded at a $300 \mu\text{m} \times 300 \mu\text{m}$ area of the granite section, where the autoradiographic image indicates major alpha activity and the optical image reveals a number of holes, which appear to be pore cross sections in the granite. The granite fracture fill material has a high Fe content [2] and we consider the Fe distribution to indicate locations of granite fractures. We observe areas of higher Np content to be located near, but necessarily on top of the pixels with high amounts of Fe. Visual comparison of the distributions shows the Zn and the Np distributions to be qualitatively similar.

One observation in Fig. 2 is clear: we are successful in dealing with potential spectral interference by using an excitation energy above the Np L2 edge. Fig. 3 depicts the XRF spectrum registered for a single pixel at the Np hot spot with high Np $L\alpha_1$ intensity observed in the Np distribution in Fig. 2. Numerous $K\alpha_1$ and $L\alpha_1$ lines (Rb, Th, U, Sr) lie energetically near the Np $L\alpha_1$ ($L3 \rightarrow M5$) line at 13.94 keV, whereas the Np $L\beta_1$ line ($L2 \rightarrow M4$) line at 17.75 keV is well-resolved (indicated with an arrow). This aids in fits to the XRF spectra using the AXIL program to extract intensities for constructing the Np distribution maps, as the theoretical intensity ratio for the $L\alpha_1$ and $L\beta_1$ helps

Fig. 3. The XRF spectrum registered for a pixel at the Np hot spot with high Np $L\alpha_1$ intensity observed in the Np distribution depicted in Fig. 2.

Fig. 4. μ -XRF distribution maps recorded in confocal geometry for Np, Fe, Zn, and Sr of a $300 \times 300 \mu\text{m}^2$ section ($20 \times 20 \mu\text{m}^2$ step size; 7 s counting time) of the granite core slice $\sim 40 \mu\text{m}$ below the surface.

constrain the fit. In addition, the confocal geometry is helpful by probing restricted volumes of the sample.

The good resolution is also demonstrated in the distributions in the granite measured using the PC as primary focus at a depth approximately $-40 \mu\text{m}$ below the surface (Fig. 4). That the measured Np and Sr distributions differ from one another is further indication that spectral interference is not a problem. We also observe in Fig. 4 that the Fe distribution follows a branched fissure in the granite with dimensions of $100 \mu\text{m}$ or less. The Np is located near the smaller branch in the upper part of the image, but is absent from the larger fissure portion at the lower part of the image. This particular μ -XRF map also displays our general qualitative observation that Np is often found associated with Zn. In addition, we find that the Np appears concentrated in small hot spots with tens of μm dimensions, which may indicate their being in a particulate form.

In order to determine the valence state of the immobilized Np in the granite, Np L3 μ -XANES and μ -EXAFS are recorded at pixels with high Np $L\alpha_1$ intensity. Note that these spectra are recorded for a specimen with a nominal Np concentration of 3 nmol/g or <1 ppm. The clear advantage of using a microfocus beam for X-ray spectroscopy on dilute, heterogeneous samples is obvious in this example. Comparison of the Np L3 XANES of Np in the granite with Np(IV) and Np(V) references (Fig. 5) reveals a similarity between the Np in granite and the Np(IV) XANES, indicating that the Np hot spot contains Np(IV). The symmetric form and high intensity of the main absorption feature, called the white line (WL), the energy position of this WL (17.621 keV for all sample volumes probed), and the lack of a multiple scattering feature at 10 to 15 eV above the WL, characteristic of the neptunyl (Np(V)) ion [8], are strong indicators that Np is in the tetravalent state in the granite.

We also register the Np L3 EXAFS spectrum, as systematic XANES/EXAFS investigations have shown that analysis of L3 edge EXAFS spectra is more sensitive than XANES for detecting Np(V) alongside Np(IV) cations in samples containing predominantly Np in the tetravalent oxidation state [8]. The EXAFS spectrum (Fig. 6) is noisy but the quality is sufficient to extract a meaningful Fourier transform

Fig. 5. Np L3 μ -XANES measured at the Np hot spot in Fig. 4 around $-50 \mu\text{m}$ below the sample surface. Inset: Np(IV) and Np(V) reference spectra.

Fig. 6. Np L3 edge EXAFS ($\chi(k)$; left) and its corresponding k^2 -weighted Fourier transform (FT) data (right).

(FT) spectrum. In the FT we observe no splitting of the first oxygen shell into two peaks expected for Np(V), representing the short Np–O_{ax} approximately 1.83 $\text{\AA}$ distance in Np(V) species (expected at $R - \Delta \sim 1.55 \text{ \AA}$ uncorrected for phase shifts) and an associated longer distance for atoms in the neptunyl equatorial plane coordination polyhedron [8]. The measured FT in the granite shows a single major first shell FT characteristic for Np(IV). Similar results are reported for U(IV) in a U-rich sediment [9].

In order to corroborate the qualitative observation that Np is associated with Zn, we plot the Zn K α 1 versus the Np L α 1 intensities, as well as the Fe K α 1 versus the Np L α 1 intensities, of individual pixels from the distribution images. The result is shown in Fig. 7. The lines in

the figure are a guide to the eye with slopes 1/2 and 2; most data points lie within the fan defined by these two slopes. This indicates a direct correlation between Np and Zn, as expected from our qualitative observations. In contrast, the Fe/Np correlation plots are more complicated. We observe a clustering of data points along the Fe K α 1 intensity baseline in these plots, indicative of there being no correlation between Fe and Np in the pixels associated with these data points. However, we also observe a few data points along a straight line in the plot at bottom right of Fig. 7 and a general linear trend in the Fe/Np correlation at bottom left. Obviously there are areas in the sample, where Np is associated with Fe.

4. Conclusions

Analysis of the μ -XAFS results allows us to conclude that Np, originally introduced as Np(V) into the column, is reduced to Np(IV) in the fractured granite following the radiotracer experiment. We note that without the spatial resolution of the experimental setup and the confocal geometry it would not have been possible to obtain this information on a dilute element (tracer concentration) in such a heterogeneous sample.

The distribution of Np(IV) is apparently associated with Zn. We assume that, under the anaerobic conditions prevalent at the depth this granite was obtained, this is likely ZnS. The observed correlation between Zn and Np may indicate that ZnS played a role in Np(V) reduction to Np(IV) and subsequent immobilization of this less soluble Np valence form. There are areas where a correlation between Np and Fe is observed, but other areas with none. The correlation between Np and Fe may indicate one or both of two things: Np(V) was immobilized by reduction to Np(IV) by Fe(II) and/or the Np is located in fissures, as Fe is an indicator element for granite fracture material. The sample regions, where no correlation between Fe and Np is found,

Fig. 7. Correlation plots created using normalized fluorescence intensities between Zn and Np (top left) and between Fe and Np using two different maps (bottom). The lines in the top figure are a guide to the eye with slopes 1/2 and 2.

may be associated with fissures not easily accessible by inflowing groundwater carrying the Np tracer.

The measured Np distributions reveal Np to form particulates of having dimensions on the order of tens of μm , which are themselves located in fissures and permeable channels in the granite not larger than 100 μm . It is feasible that during the tracer experiment inflowing Np has a shorter residence time in the large fractures, while in the smaller fissures migration is slower, leading to longer residence times, i.e., reaction times, resulting in Np(V) reduction and immobilization of less soluble Np(IV).

This study has implications for modeling scenarios of actinide release in a nuclear waste repository placed in a granite host rock formation. The redox conditions of the groundwater/granite obviously play a role, but so do the size and interconnectivity of the fractures and fissures in the granite.

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