



Experiment title: Interaction of radionuclides (U, Th, Ra) with natural and synthetic birnessite. Application to radionuclides mobility in natural systems.

Experiment number:
Me-310

Beamline:
BM 20

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Shifts: 15

Local contact(s): Tobias Reich

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

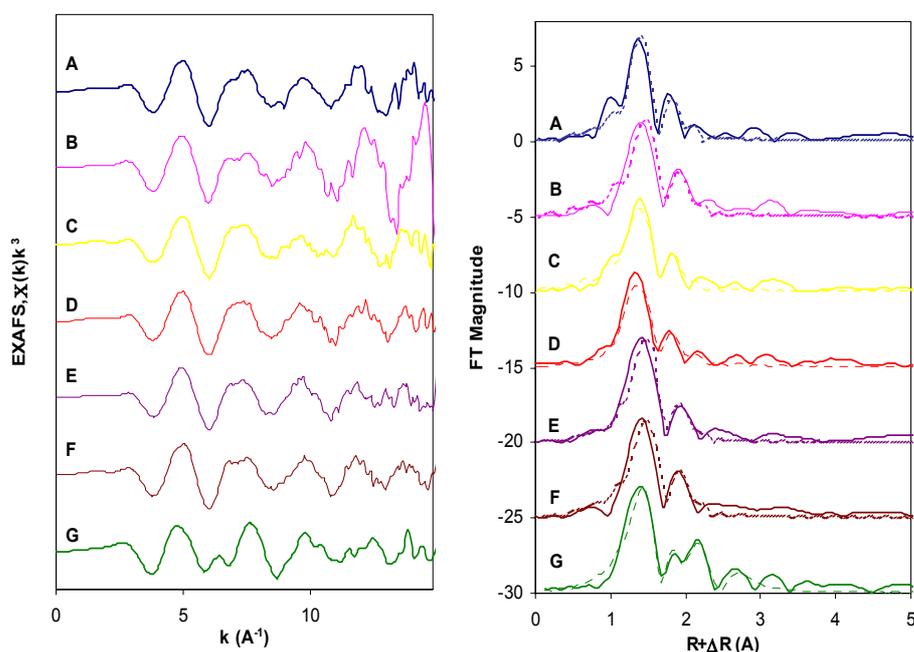
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Report: Our long-term objective is to study in detail the adsorption processes of several radionuclides (U, Th; Ra) on birnessite, the most common Mn-oxides in soils. Indeed, the affinity of these nuclides for Mn-oxides has been widely reported. Thus, neglecting their influence in natural systems would yield to significant errors in predicting radionuclides transport. Among these nuclides, focus has been placed first on U in 2001 and 2002.

EXAFS measurements on U^{VI} sorbed synthetic birnessites were performed at the ESRF beamline BM20. These birnessites were reacted with U^{VI} solutions for various experimental conditions (see the figure caption). Birnessite is a phyllosilicate characterized by edge-sharing Mn octahedra layers, separated by interlayer spaces filled with cations. A change in the interlayer spacing from 10\AA to 7\AA occurs when the solution pH decreases from basic to acidic [1]. For all except one experiments, U^{VI} was added to the solutions after the birnessite equilibration at pH 4 or 6, i.e. mineral interlayer = 7\AA . For one experiment (sample A), U^{VI} was added before this equilibration (i.e. mineral interlayer = 10\AA), then interlayer space decreased when decreasing the pH to a value of 4.



U-L_{III} EXAFS spectra and their Fourier Transforms for U^{VI} sorbed on birnessite. Aqueous initial $[U^{VI}]$ concentration = $1.2 \cdot 10^{-5}$ M. Unless notified, U^{VI} was added to the solutions after the birnessite equilibration to the aimed pH. Dashed lines are fits.

(A) pH = 4, 0.1M $NaClO_4$, U^{VI} added before birnessite equilibration, $[U]_{\text{sorbed}} = 867$ ppm; (B) pH = 4, 0.1M $NaClO_4$, $[U]_{\text{sorbed}} = 500$ ppm; (C) pH = 6, 0.1M $NaClO_4$, $[U]_{\text{sorbed}} = 980$ ppm; (D) pH = 6, 0.1M Na_2CO_3 , $[U]_{\text{sorbed}} = 830$ ppm; (E) pH = 6, 0.1M $NaNO_3$, $[U]_{\text{sorbed}} = 1230$ ppm; (F) pH = 4, 0.1M $NaNO_3$, $[U]_{\text{sorbed}} = 1200$ ppm; (G) $UO_2(NO_3)_2 \cdot 6H_2O$ model compound.

Fitting of the two first shells of U neighbors (axial and equatorial Oxygen atoms) of these spectra was performed. The theoretical modelling code FEFF8 was used to calculate the backscattering phases and amplitudes of the individual neighboring atoms. Results of these fits show a U-O_{eq} distance ranging from 2.31 to 2.35 Å, apart from the sorption experimental conditions. Analysis of the contribution from more distal neighbours has not been completed yet.

The distinct FTs shapes, and different sorbed [U^{VI}] concentrations shown by samples for which the same U^{VI} amount was added before or after birnessite equilibration (samples A and B), suggest that at least two different types of sorption sites are available on birnessite: within the cationic interlayer space and on edge sites. However, U^{VI} seems less able to enter the 7Å interlayer space sites (after low-pH mineral equilibration), and hence edge sites are probably the main sites during sorption at low pH. This is in agreement with complementary sorption experiments performed in our lab. The inability to fit our experimental sorption data with a Langmuir type isotherm (which assumes a single sorption site with a finite concentration) also suggests that the surface sites available for U^{VI} on birnessite are heterogeneous and/or not of finite concentration.

Another striking feature of our results is the influence of electrolyte background. Samples C and D show no difference in FTs distribution, despite completely different aqueous U^{VI} speciation ($\geq 96\%$ uranyl-hydroxyl complexes in sample C and 100% uranyl-carbonate complexes in sample D). In contrast, samples in NaNO₃ media (E and F) show a consistent difference (whatever the pH), with disappearance of the peak at R+ Δ R = 3.2 Å, although the main U^{VI} dissolved species are similar than in NaClO₄ samples (uranyl-nitrate complexes represent less than 7% in NaNO₃ media). Complete analysis of the more distal neighbours is needed to elucidate this feature, but possible minority uranyl-nitrate outer-sphere sorption will be tested. In contrast, the U-O_{eq} distance of 2.33 Å calculated for sample D (dissolved-carbonates media) suggests U^{VI} inner-sphere complexation for this sample. Indeed, based on the bond-valence theory, this distance corresponds to an equatorial coordination number of 5^[2], whereas aqueous uranyl-carbonates complexes display equatorial CN of 6. The implied change in the geometrical configuration of the equatorial O atoms during sorption suggests that dominant inner-sphere complexation occurs for U^{VI} sorption onto birnessite in carbonate media.

Finally, further analyses will carefully focus on the peak at R+ Δ R = 2.3 Å contains in FTs of all samples. Previous studies^[3-5] showed strong evidences for the presence of ternary uranyl-carbonates complexes sorbed on various mineral surfaces, and peaks at 2.3Å, which correspond to a shell of neighboring atoms at 2.9 Å, seem typical of an U-C interaction^[6]. Various experimental conditions were retained in the present study, in order to highlight this U-C interaction, but unexpected results appear. In experiments conducted at pH 4, a constant flux of Ar gas was held in the solutions, in order to definitively prevent some hypothetical carbonate-complexes formation (these complexes are in any way thermodynamically unexpected at this pH). In contrast, U^{VI} dissolved species were 100% uranyl-carbonate complexes in sample D. Despite these opposite conditions, all spectra show the same peak at 2.3Å in FTs, whatever the pH or the aqueous media. Moreover, no significative variation of this peak height occurs between samples with 0% and 100% of dissolved uranyl-carbonates species. Ternary uranyl complexes with nitrate ligands could produce a similar contribution at 2.3Å, however no such contribution can be involved in NaClO₄ media.

References:

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