 ROBL-CRG	<b>Experiment title:</b> Reduction of uranium(VI) by adsorbed Fe(II) on clays and by structural Fe(II) in smectites in O <sub>2</sub> , CO <sub>2</sub> free atmosphere	<b>Experiment number:</b> 20-01-676
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 12.06.09 to: 14.06.09	<b>Date of report:</b> 15.2.11
<b>Shifts:</b> 6	<b>Local contact(s):</b> Dipanjan Banerjee	<i>Received at ROBL:</i> 15.2. 11
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## Report:

### Introduction

Uranium is an important element because of its presence in soils and sediments as a result of mining activities and for predicting the fate of spent fuel in nuclear waste repositories. The reduction of U(VI) to U(IV) greatly decreases uranium mobility through precipitation of sparingly soluble U(IV) minerals and therefore has been extensively studied using biotic and abiotic processes. Montmorillonite is a constituent clay mineral of various soils, sediments in reducing environments, and the major component of bentonite, which is a candidate material for the backfill of radioactive waste repositories. However, almost no studies have evaluated the reactivity of Fe(II) in heterogeneous sorption-reduction of U(VI) mediated by a montmorillonite surface. The aim of this study is to (1) investigate the influence of pH on the reduction capacity of surface-bound Fe(II) in U(VI) reduction and (2) identify reduced uranium product using wet chemistry, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

### Experimental

X-ray absorption near-edge structure (XANES) and extended X-ray absorption finestructure (EXAFS) spectra were collected at the Rossendorf Beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The energy of the X-ray beam was tuned by a doubled crystal monochromator operating in pseudo channel-cut mode using a Si(111) crystal pair. Two platinum-coated Si mirrors before and after the monochromator were used to collimate the beam into the monochromator and to reject higher harmonics. Uranium LIII-edge spectra were collected in fluorescence mode using a 13-element high purity germanium detector (Canberra) together with a digital signal processing unit (XIA). Spectra were collected at 15 K using a closed cycle He cryostat with a large fluorescence exit window and a low vibration level (CryoVac). The energy was calibrated using the maximum of the first derivative of the yttrium K-edge (17038 eV).

### Results

The normalized XANES spectrum of the Fe-free reference sample (MONT + U(VI) at pH 5.9) in Figure 1A shows the characteristic features of the uranyl ( $\text{U}^{\text{VI}}\text{O}_2^{2+}$ ) structure, including a white line peak centered at 17179 eV and a shoulder centered at approximately 17190 eV. The feature at 17190 eV has previously been shown to result from multiple scattering resonances of the linear uranyl ion structure, specifically due to the short U-O<sub>ax</sub> bonds (1). The XANES spectrum of U1 at pH 6.1 is very similar to the U(VI) reference, implying that the dominating phase of uranium in these samples is in +VI oxidation state. With increasing pH, the shoulder at 17190 eV starts to diminish (U2 at pH 7.5)

and disappears completely in U3 (pH 8.5). The latter spectrum is similar to the reference U(IV) ( $\text{UO}_2$ ) spectrum but different from the spectrum of  $\text{U}_3\text{O}_8$ , suggesting a reduction of uranium from +VI to the +IV state. On the basis of visual observation, one can conclude that the reduction increases with pH. This observation is consistent with the XANES quantitative estimation obtained from linear combination fit (LCF) with U(VI) and U(IV) references. However, none of the spectra of partially reduced samples (U1-U3) are similar to that of the reference mixed valence spectra of  $\text{U}_3\text{O}_8(\text{s})$ .

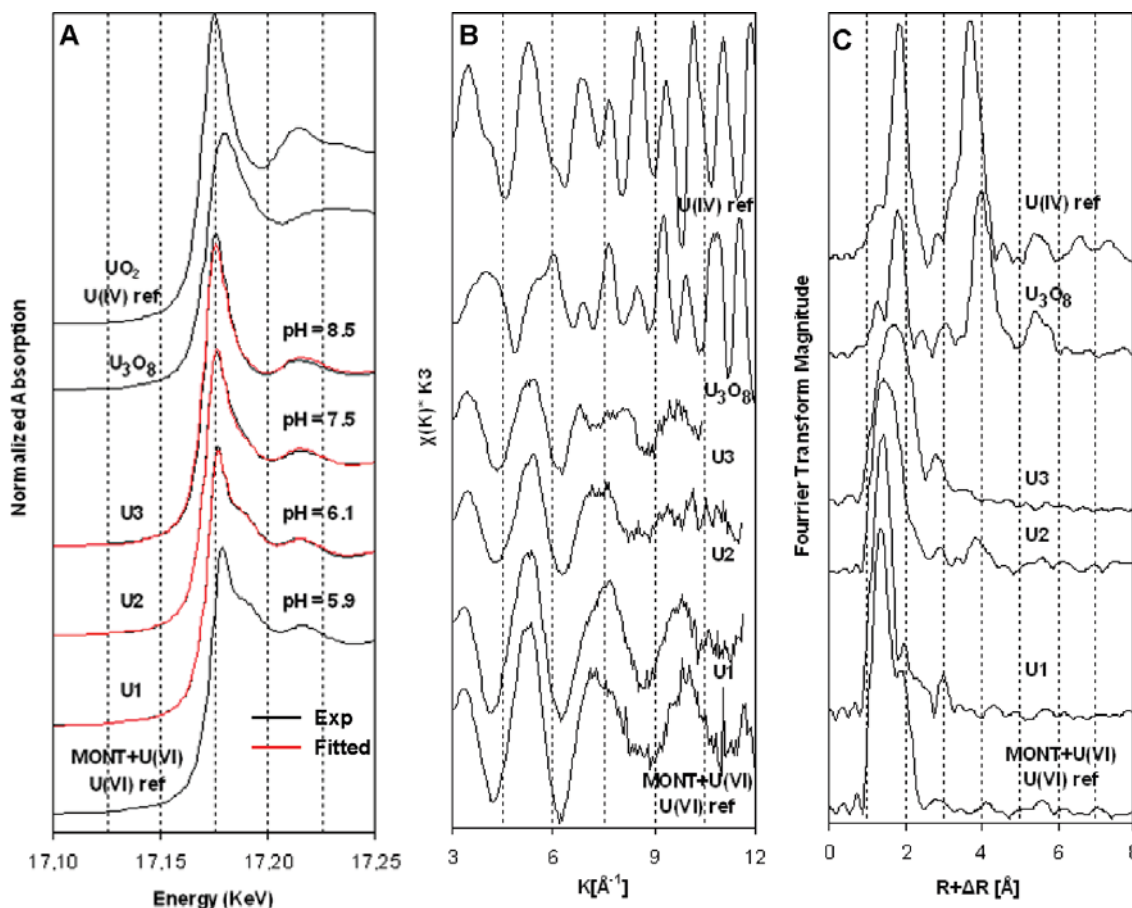


Fig 1. U  $L_{III}$ -edge XAS spectra of U(VI) sorbed on MONT in the presence of Fe(II) compared to the U(VI) and U(IV) references. (A) fitted XANES; (B) EXAFS, and (C) Fourier transform of EXAFS.

The corresponding U  $L_{III}$ -edge background-subtracted,  $k^3$ -weighted EXAFS spectra are shown in Figure 1B. A qualitative comparison of the Fourier-transformed EXAFS data of the samples with U(VI) and U(IV) references (Figure 1C) indicates that the average local chemical environments of uranium in U1-U3 are not similar to that of  $\text{UO}_2$  or  $\text{U}_3\text{O}_8$ . Most notably, the strong FT peaks between 3.5 and 4.0 Å (uncorrected for phase shift), which are due to U-U interactions are completely absent in the samples, suggesting that the uranium phase formed after reduction is not a solid. Fitting of the EXAFS part of the spectra (results not presented) was only successful in obtaining U-O distances of 1.78, 2.26, and 2.47 Å. The distance of 1.78 Å is in line with the axial oxygen of U(VI). The other two distances are the equatorial shell of U(VI) and the first coordination sphere of U(IV). However, the possibility of a split equatorial shell of U(VI) due to inner sphere sorption cannot be ruled out (2). In addition, multiple scattering (MS) from the axial oxygens in the first shell overshadowed any weak backscattering signal from the clay surface (Si or Al).

#### Reference

Allen, P. G.; Shuh, D. K.; Bucher, J. J.; Edelstein, N. M.; Palmer, C. E. A.; Silva, R. J.; Nguyen, S. N.; Marquez, L. N.; Hudson, E. A. *Radiochim. Acta* **1996**, 75, 47–53.  
Catalano, J. G.; Brown, G. E. *Geochim. Cosmochim. Acta* **2005**, 69, 2995–3005.