



Experiment title: Resonant inelastic X-ray scattering of mixed actinide oxides

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HE-3500

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Report:

The original title of the proposal HE-3500 was “Resonant inelastic X-ray scattering of mixed actinide oxides”. Due to complications during the sample preparation the mixed actinide oxides were not made before the beginning of the experiment. We use the granted beamtime to study the electronic structure of uranium compounds using X-ray absorption near-edge spectroscopy (XANES) and resonant inelastic X-ray scattering (RIXS) across M_4 U edge.

XANES and RIXS experiments were performed for two sets of uranium systems with different oxidation states. First set of the samples were homogeneous Ca-Mg-Al-Si±Fe oxide glasses containing 0.5 wt% of U. The motivation for this research was to understand the rate at which basaltic magma, which cools to form the oceanic plates, moves from the source of melting in the mantle to the surface [1]. This is a controversial topic with different models predicting rates that differ by three orders of magnitude. Integral to one of these models is the abundance of U (which may occur as U^{4+} , U^{5+} , and U^{6+}) relative to Th (only Th^{4+}). The oxidation state of an element exerts a first order control on the way it partitions between a melt and crystalline residue during the partial melting process that produces these magmas. Previously recorded U L_3 edge XANES spectra (at the Photon Factory and Diamond) of glasses prepared over a range of oxygen fugacities and for which the oxidation state varies systematically from entirely U^{4+} to entirely U^{6+} (Fig. a). The oxygen fugacity range over which the spectra change indicate that U^{4+} does not convert directly to U^{6+} but via U^{5+} . Due to the big life time broadening of features in the XANES spectra at the U L_3 edge (a simple white line that varies in energy and intensity) it is impossible to quantify the proportions of U^{4+} , U^{5+} , and U^{6+} . We have recorded preliminary U M_4 edge spectra for three samples with 51 wt% SiO_2 , 15 wt% Al_2O_3 , 10 wt% MgO , 24 wt% CaO and 0.5 wt% U_3O_8 . All glasses only vary in the relative proportions of the major component oxides and few of them contained Pt wire, which were used to suspend the molten samples in a furnace.

High energy resolution fluorescence detected (HERFD) X-ray absorption spectra were recorded using X-ray emission spectrometer based on a vertical Rowland circle geometry, exploiting the (2 2 0) reflection of four spherically bent 1m radius Si crystal analyzers. Fig.b shows that these spectra exhibit more complexity and each U oxidation state appears to be associated with a distinct spectral feature (Fig. b). Those results indicate that HERFD at the U M_4 edge is a very powerful tool in detection of the

oxidation state of such materials. This research will be continued and more glass samples will be studied in nearest future in order to quantify the oxidation state ratio of U (proportions of U^{4+} , U^{5+} , and U^{6+}) in each silicate glass to better than 5% absolute. By studying a series of compositionally different glasses we aim to identify those parameters that stabilise each oxidation state, allowing the oxidation state ratio to be predicted for other melt compositions. The results will be used to understand how U partitions during partial melting and will almost certainly necessitate a reassessment of melt transport rates based on models of U series disequilibrium.

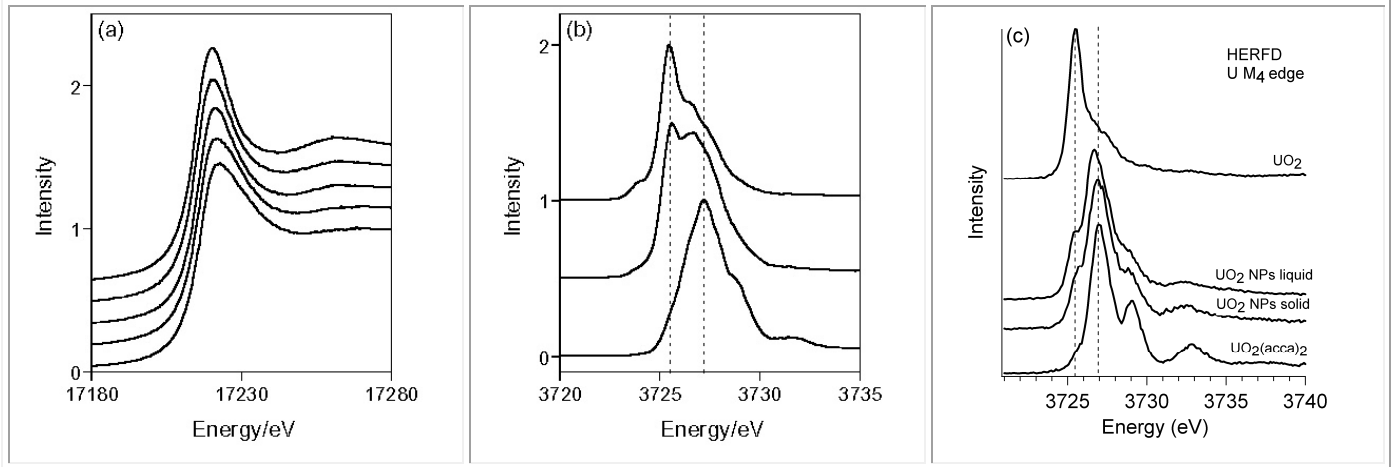


Figure: (a) U L_3 edge and (b) U M_4 edge spectra of selected glasses. In each case the top and bottom spectra correspond to samples containing only U^{6+} and U^{4+} respectively. c) U M_4 edge spectra of UO_2 NPs compared to hexavalent $UO_2(acca)_2$ and tetravalent UO_2 model systems. The dotted lines indicate U^{4+} and U^{6+} peaks.

Another set of samples was UO_2 nanoparticles (NPs) in 10-15nm size isolated in a mesoporous silica matrix. Figure (c) shows HERFD spectra at the U M_4 edge of the UO_2 NPs in solid and liquid forms compared to tetravalent UO_2 and hexavalent U acetylacetonate $UO_2(acca)_2$ model systems. The main spectral features represent the distribution of the U 5f states due to the dipole transitions from $3d_{3/2}$ to unoccupied 5f states at the U M_4 edge. The shape of the absorption features in HERFD spectrum of the UO_2 show the asymmetry, which has been already observed during the standard XANES experiment [2]. The HERFD spectrum of $UO_2(acca)_2$ show an evidence of two features at ~ 3727 eV and ~ 3729 eV. The presence of the shoulder on the high energy site (~ 3729 eV) of the hexavalent compound $UO_2(acca)_2$ is attributed to the characteristic feature of the uranyl ion [2]. The position of the main features in HERFD spectra of model U systems clearly shows the energy shift (~ 2.5 eV) of the white line towards higher energy from the U^{4+} to U^{6+} compounds. Unfortunately the HERFD spectra UO_2 NPs samples in the liquid and solid forms show a main contribution from U^{6+} with small admixture of U^{4+} signal. The UO_2 NPs were synthesised by infiltrating the silica matrix with $UO_2(acca)_2$ solution under sonification. The shape of the spectral features in HERFD spectra of UO_2 NPs indicate the presence of uranyl group in the material which might be due to the presence of $UO_2(acca)_2$. For the moment we try to adjust the synthesis procedure of UO_2 NPs and characterise the produced UO_2 NPs using HR-TEM technique.

References

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