



## Experiment Report Form

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- fill in a separate form for each project or series of measurements.
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- include the reference number of the proposal to which the report refers.
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- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Surface complexes of uranium onto magnetite and olivine	<b>Experiment number:</b> 20-01-49
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 7/09/01 to: 11/09/01	<b>Date of report:</b> March , 2002
<b>Shifts:</b> 12	<b>Local contact(s):</b> Tobias Reich Andreas Bauer	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Joan de Pablo Lara Duro Mireia Grivé* Jordi Bruno		

## Report:

### INTRODUCTION

The aim of this experiment is to examine the structure and the oxidation state of uranium sorbed onto the surface of magnetite ( $\text{Fe}_3\text{O}_4$ ) and FeO-rich olivine. The Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) provides explicit information about the structure and coordination of the metal on mineral surfaces, which may prove helpful in characterizing the uranyl sorption complexes. Our main aim in using EXAFS is to elucidate the type and structure of the surface complexes formed as well as to identify, if possible, different structural arrangements depending on whether U(IV) or U(VI) is present on the mineral surface. The U L3-edge XANES spectra can be useful to derive information about the oxidation state of actinides on the solid surface (Morris et al., 1996; Conradson et al., 1998). Magnetite was chosen for this study as it has been identified as one of the potential corrosion product of the carbon steel canisters intended to be used as containers in deep high level nuclear waste (HLNW) repositories (Blackwood et al., 1995). Olivine has been proposed as a redox-active backfill-additive in deep HNLW repositories (Hellmuth et al., 1992). The capacity of a FeO-high olivine-rock to retain U(VI) on its surface has been already assessed (El Aamrani et al., 2002). The ability of the solid to immobilize U(VI) via its reduction to U(IV) is being investigated by means of solution and solid techniques and some preliminary results have been published elsewhere (Rodrigues et al., 1998; Hellmuth et al., 1994).

### EXPERIMENTAL

Four different uranium standards were prepared:

- Standard of U(VI) (XRD-characterised as meta-schoepite  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ) was prepared by precipitation of an homogeneous U(VI) solution by means of carbonate-free NaOH.

- Standard of U(IV) (XRD-characterised as  $\text{UO}_2(\text{s})$ )
- Standard with a known proportion of U(VI) and U(IV) (XRD-characterised as  $\text{U}_3\text{O}_8(\text{s})$ ) was prepared by roasting  $\text{UO}_2(\text{NO}_3)_2$  at  $900^\circ\text{C}$  during 12 hours.
- Equimolar mixture of 50% schoepite and 50% of  $\text{UO}_2(\text{s})$ .

Uranium-coated magnetite samples were prepared with commercial Aldrich magnetite with a purity of 98%, a particle size lower than  $5\ \mu\text{m}$  and a  $\text{N}_2$ -BET surface area of  $1.58 \pm 0.01\ \text{m}^2\text{g}^{-1}$ . The sorption of U(VI) onto the magnetite samples was conducted at  $25^\circ\text{C}$  from a homogeneous solution containing  $10^{-5}\ \text{mole}/\text{dm}^3$  of U(VI) at pH ranging from 6 to 7 and by continuous  $\text{N}_2$  or  $\text{H}_2$  (g) bubbling.

Uranium-coated olivine samples were prepared in analogy to the magnetite samples. The  $\text{N}_2$ -BET surface area of the rich-olivine solid was of  $0.17 \pm 0.01\ \text{m}^2\text{g}^{-1}$ .

## RESULTS

XAS spectra of the samples were recorded by fluorescence detection, due to the low uranium content. Furthermore, given that the substrates were in all cases iron-containing solids and that Fe represents an important interference to the detection of uranium by fluorescence, we used a filter of Chromium.

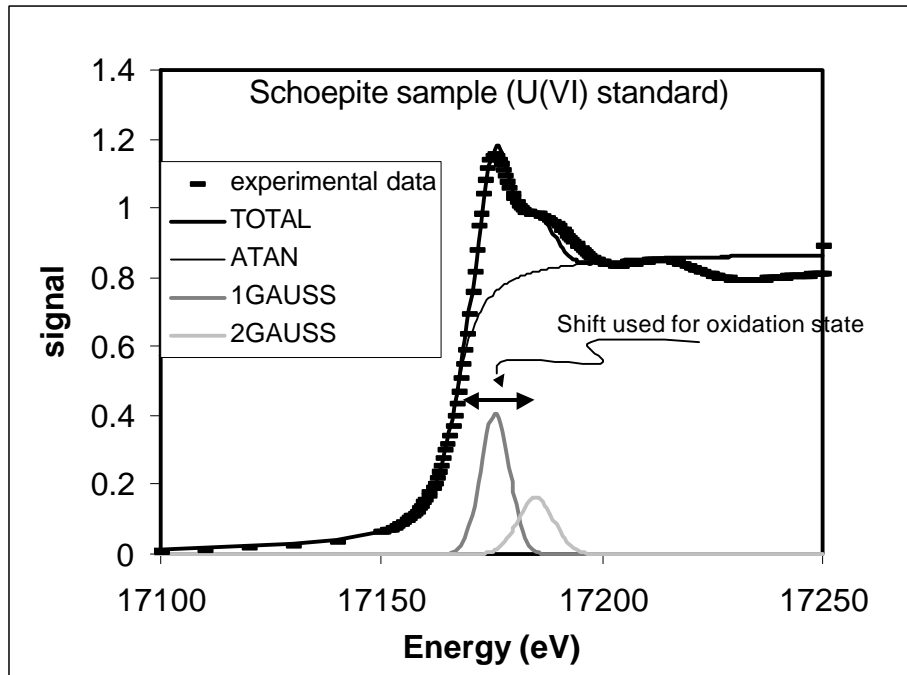
XANES signal was sufficiently good in all cases as to conduct a proper interpretation of the results.

Due to the low U content of the samples, the EXAFS signal obtained for most of our samples was very weak. Besides the standards, only two of the samples rendered a sufficiently good EXAFS signal as to permit their interpretation. One of these samples corresponded to the one labelled “cop”, which was prepared by co-precipitation of iron (III) with U(VI) by means of carbonate-free NaOH under atmospheric conditions. The other sample for which a relatively good EXAFS signal was obtained corresponded to a U(VI)-coated magnetite prepared by 30 days continuous re-circulation of a solution containing  $10^{-5}\ \text{mole}/\text{dm}^3$  of U(VI) through the solid magnetite sample under continuous  $\text{N}_2$  bubbling (labelled “MN30CR”).

We present a preliminary analyses of the results in the following sub-sections.

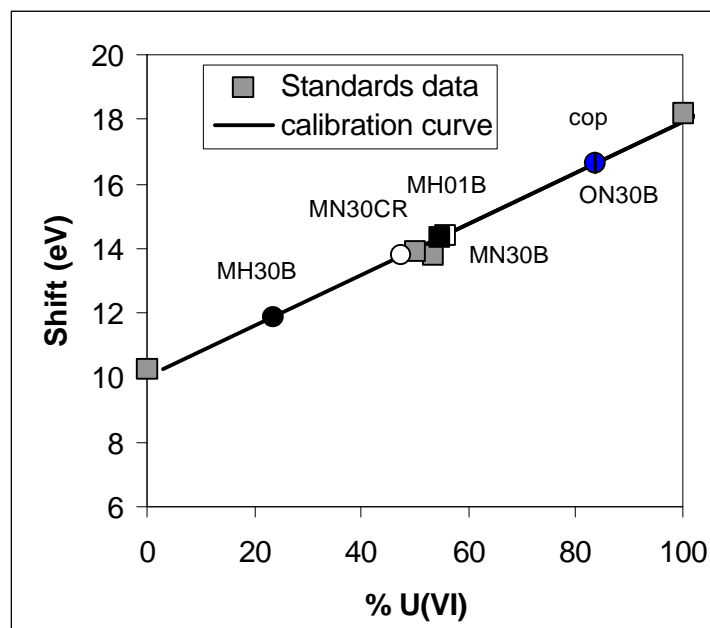
### XANES analyses

There are some publications dealing with the use of XANES results to ascertain the oxidation state of the metals coating the surface of different solids (see for example Conradson et al., 1998 and Morris et al., 1996). These authors used a de-convolution methodology for obtaining three different contributions to the XANES signal: A first contribution reproduces the edge of the XANES signal in terms of an arctan function. The second and the third contribution are Gaussian-like curves. In the publication dealing with uranium, Morris et al. obtained a good correlation between the ratio U(VI) to U(IV) of the sample and the shift between the inflection point of the arctan function and the maximum of the second Gaussian signal. We have proceeded in a similar manner to de-convolute all the signals obtained for our samples and we have obtained a “calibration curve” (see Figure 1) of the oxidation state of uranium by using the data from our standards. This has allowed us the obtention of the theoretical ratio U(VI) to U(IV) in the uranium-coated olivine and magnetite samples. In Figure 1 we show a typical XANES spectrum obtained from our samples were we also shown the de-convolution of the signal in the different components previously mentioned.



*Figure 1.* XANES spectrum of the U(VI) standard and de-convolution of the peak into an ATAN and two Gaussian functions. The arrow indicates the shift used for the determination of the U(VI) to U(IV) ratio in the sample.

The resulting shifts of the standards and the samples analysed are presented in Figure 2, from where we can see that a good correlation is obtained and, therefore, that the methodology used can be useful for the determination of the oxidation state of uranium in the samples.



*Figure 2.* Calibration curve of the shift over the percentage of U(VI) in the samples obtained by using data on the standards and data of the standards superimposed. Sample labels: M indicates magnetite; O indicates olivine; H and N indicate whether the sample has been prepared under hydrogen (reducing) or under nitrogen (anoxic) conditions; 01 and 30 indicate the days during which the solid sample have being in contact with the uranium(VI) solution. The sample labelled “cop” is the one prepared by coprecipitation of U(VI) with Fe(III), for which no U(VI) reduction to U(IV) is possible.

The parameters of the calibration curve are the following:

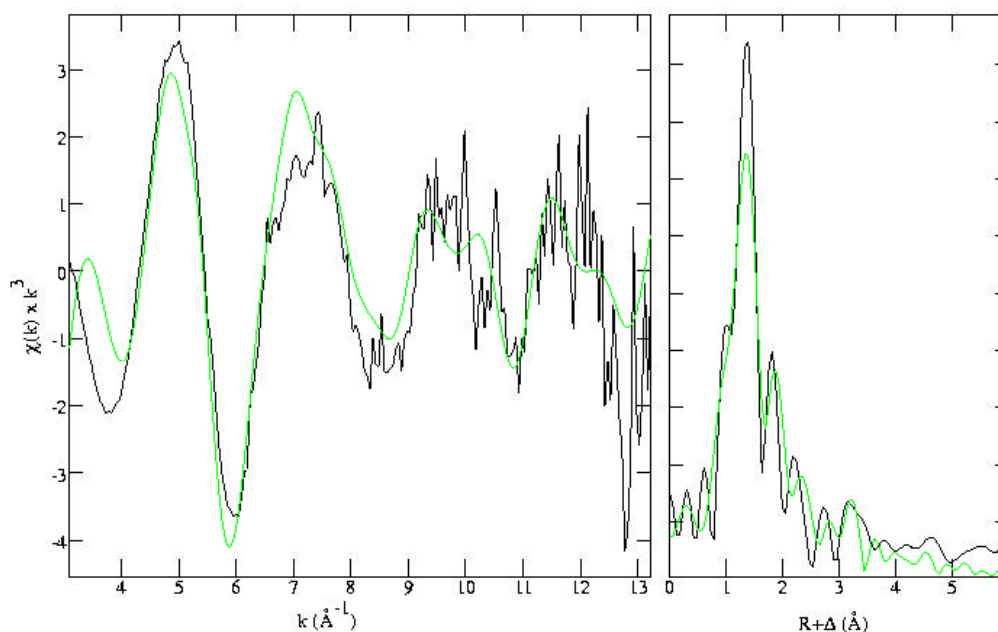
$$\% \text{U(VI)} = (12.459 \pm 0.869) \cdot (\text{SHIFT}) - (124.37 \pm 12.465)$$

$$r^2 = 0.9808$$

From the previous results we can see that the sample MH30B, that was prepared under more reducing conditions and for which the interaction magnetite-Uranium was allowed to proceed for the longest time (30 days), is the one plotting at lower %U(VI), indicating that reduction of uranium has proceeded. On the other hand, the sample prepared with U(VI) and Fe(III) for which no reduction is feasible, plots in the highest range of the graph, indicating the highest U(VI) percentage. We can see that there is some error in this analyses, given that this sample should plot on the right axis (U(VI) = 100%) and it behaves as if it had only a 83.5% of U(VI). This deviation can be also due to the different coordination environment of the samples, that is, the fact that the substrate in this case was ferrihydrite while in the other cases were either olivine, magnetite or uranium pure phases for the standards. However, we can say that, in general, this analyses permits a rather good estimation of the percentage of reduction of U(VI) to U(IV). Data is being analysed in order to see which is the rate at which the reduction process is occurring.

### EXAFS analyses

Besides the standard, good EXAFS data were only obtained for two of the samples. Here we will present a preliminary interpretation of one of them (“cop”) that has been conducted with the EXAFSPAK program. Apart from the interactions U-O we have also included U-Fe and U-U interactions in our interpretation. The right hand side of the spectrum cannot be interpreted without introducing U-Fe interactions. The U-U interactions improve slightly the interpretation of the spectrum, as it can be seen in Figure 3.



**Figure 3**  $k^3$ -weighted uranium  $L_{III}$ -edge EXAFS spectrum (left) and its Fourier transform (right) assuming U-O, U-Fe and U-U interactions. Solid black line: data. Solid green line: fit.

Although the signal is noisy, fairly well defined EXAFS oscillations continue out to  $13 \text{ \AA}^{-1}$ . Fourier transforms of the EXAFS sample is shown in the right side of Figure 3. The first four-peak region of the FT contains information on the various U-O bonds. The peak near  $3 \text{ \AA}$  contains information about the U-Fe contribution and the peak above  $3 \text{ \AA}$  seems to give some information about the U-U interactions.

As a preliminary treatment of the data, we did not filter the separate EXAFS contributions in the EXAFS structure function for fitting. The values obtained in our fitting process are listed in table 1.

	Coordination number (N)	Distance (R) in $\text{\AA}$
Oax	2.00	1.80

Oeq	3.98	2.14
Oeq	2.00	2.32
Fe	3.69	2.96
U	0.33	3.15

From the parameters fitted in Figure 3, there are 3 different oxygen atoms: two Oax at 1.8 Å and six Oeq; four of them at a distance of 2.14 Å and the other two at 2.32 Å. In addition, we have obtained 3.69 neighbouring iron atoms at a distance of 2.96 Å. However, it was difficult to fit the peak at  $R+\Delta \approx 3.1$  Å unless we consider a contribution of the uranium atom (with  $N=0.33$ ).

At this moment we are trying to improve the fitting by filtering the different EXAFS contributions in order to obtain a better fit to have more accurate parameters to elucidate the possible structure of this “cop” sample. The fact of obtaining such a high coordination number for Fe in the sample might be a direct consequence of the sample preparation procedure given that it had been prepared by simultaneous precipitation from a homogeneous solution containing uranium and iron, which may result in a coprecipitate presenting different structural arrangements to the solid obtained by a sorption experiment. This difference will be investigated in more detail in further experiments after a better analyses of the EXAFS data have been conducted.

## References

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