


**Experiment title:**

EXAFS study of uranium(VI) uptake by kaolinite

**Experiment**
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ME-817

**Beamline:**

BM 20

**Date of experiment:**

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**Shifts:**

12

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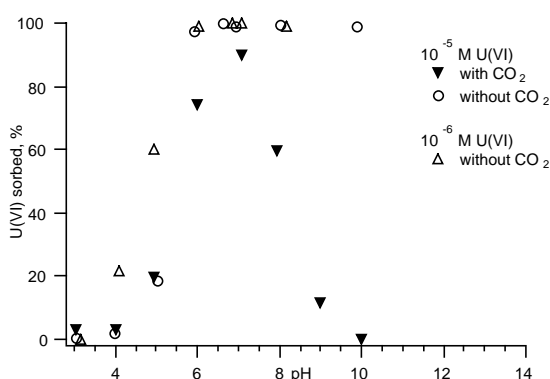
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**Report:**

We studied the uptake of uranium(VI) by kaolinite in batch experiments and by EXAFS spectroscopy. These experiments were performed as a function of pH, uranium concentration in solution, and partial CO<sub>2</sub> pressure. Experimental For batch experiments, kaolinite KGa-1b (Source Clays Repository) was contacted with 10<sup>-6</sup> and 10<sup>-5</sup> M U(VI) solutions, respectively, for 60 h following a 72 h pre-equilibration. The ratio kaolinite to solution was 4 g/L. The ionic strength was 0.1 M NaClO<sub>4</sub>. The pH was varied between 3.0 and 10.0. The sorption was studied under inert gas conditions in a glove box and at p(CO<sub>2</sub>) = 10<sup>-3.5</sup> atm. To study the influence of the chemical parameters mentioned above on the structure of the surface complexes, we prepared the following samples for EXAFS measurements. 1) Influence of pH: [U(VI)] = 1•10<sup>-5</sup> M, pH = 5, 6, 7, 8.5. 2) Influence of uranium concentration: pH = 7, [U(VI)] = 5•10<sup>-6</sup>, 1•10<sup>-5</sup>, 2•10<sup>-5</sup> M. 3) Influence of CO<sub>2</sub>: pH = 8.5, [U(VI)] = 1•10<sup>-5</sup> M, with and without ambient CO<sub>2</sub>. The solid and liquid phases were separated by centrifugation at 10000 rpm. The amount of uranium taken up by the kaolinite was measured by ICP-MS and INAA.

Results Figure 1 shows the results of the batch experiments. The uptake of uranium(VI) from 10<sup>-6</sup> M solution increases with pH up to pH 6.0. In the presence of CO<sub>2</sub>, the uptake decreases above pH 8 [1]. No decrease in uptake was observed in the absence of CO<sub>2</sub> (Fig. 1). When the total uranium concentration is increased from


**Fig. 1** U(VI) uptake by kaolinite

10<sup>-6</sup> M to 10<sup>-5</sup> M, the sorption pH edge shifts by one pH unit to higher pH. In addition, the decrease of uranium uptake at p(CO<sub>2</sub>) = 10<sup>-3.5</sup> atm due to competition between the formation of surface complexes and uranium(VI) carbonato complexes in solution occurs already below pH 8 (Fig. 1). Table 1 summarizes the analytical results for samples 1 – 8 that were studied as wet pastes by uranium L<sub>3</sub>-edge EXAFS spectroscopy in fluorescence mode at room temperature. The influence of pH and initial uranium concentration in solution in the presence of CO<sub>2</sub> was studied using samples 1 – 4 and 5 – 7, respectively. The effect of CO<sub>2</sub> was investigated by comparing samples 4 and 8. Table 2 shows the results of

**Table 1** Analytical results for EXAFS samples

Sample	[U(VI)]	pH <sub>final</sub>	% sorbed
1	1•10 <sup>-5</sup>	5.0	17
2	1•10 <sup>-5</sup>	5.9	79
3	1•10 <sup>-5</sup>	6.9	91
4	1•10 <sup>-5</sup>	8.4	12
5	5•10 <sup>-6</sup>	6.7	98
6	1•10 <sup>-5</sup>	6.7	98
7	2•10 <sup>-5</sup>	6.8	98
8	1•10 <sup>-5</sup>	8.5	99

Samples 1 – 7 were prepared at atmospheric levels of CO<sub>2</sub>. Sample 8 was prepared CO<sub>2</sub> free.

the EXAFS analysis. As expected for the UO<sub>2</sub><sup>2+</sup> moiety, two axial oxygen atoms at a distance of  $1.79 \pm 0.02$  Å surround uranium in all samples. In the equatorial plane of UO<sub>2</sub><sup>2+</sup>, an average of five oxygen atoms were found. The U-O<sub>eq</sub> bond distance varies as a function of pH (see samples 1 – 4 in Table 2). At pH 5.0 the average U-O<sub>eq</sub> bond distance equals  $2.32 \pm 0.02$  Å. With increasing pH and presence of CO<sub>2</sub>, this bond gets longer, i.e.,  $2.38 \pm 0.02$  Å at pH 8.4. When CO<sub>2</sub> is excluded from the system at pH 8.5 (sample 8), the U-O<sub>eq</sub> bond distance is  $2.32 \pm 0.02$  Å, i.e., identical to the value measured at pH 5. These results show that the presence or absence of CO<sub>2</sub> in the system has not only a strong influence on the amount

of uranium(VI) sorbed onto kaolinite (Fig. 1), but also on the structure of the surface complexes. The U-O<sub>eq</sub> bond distance in all samples is significantly shorter than 2.41 Å of the uranium(VI) aquo ion. This shortening of the U-O<sub>eq</sub> bond indicates the formation of inner-sphere surface complexes. This conclusion is supported by the detection of an additional Al/Si backscattering atom at an average distance of 2.7 Å. Following the discussion of a recent EXAFS study on uranium(VI) sorption on montmorillonite [2], this relatively short U-Al/Si distance can be rationalized by coordination of the uranium atom to the [SiO<sub>4</sub>] tetrahedrons of the kaolinite. In addition, we did not observe any evidence of U-U interaction up to initial concentrations of  $2 \cdot 10^{-5}$  M U(VI).

In summary, uranium(VI) forms mononuclear, inner-sphere complexes with [SiO<sub>4</sub>] tetrahedrons of kaolinite in the pH range of 5.0 – 8.5. At pH 8.5, the presence of carbonate leads to a longer U-O<sub>eq</sub> bond distance of 2.38 Å compared to the corresponding distance of 2.32 Å in the absence of CO<sub>2</sub>. This is the first spectroscopic indication of the possible formation of ternary surface complexes in the system uranium(VI)/kaolinite/carbonate.

**Table 2** Results of the analysis of the U L<sub>3</sub>-edge  $k^3$ -weighted EXAFS spectra in the  $k$  range of 3.1 – 12.4 Å<sup>-1</sup>

Sample	2 x O <sub>ax</sub>		5 x O <sub>eq</sub>		1 x Si	
	$R(\text{Å})$	$\sigma^2(\text{Å}^2)$	$R(\text{Å})$	$\sigma^2(\text{Å}^2)$	$R(\text{Å})$	$\sigma^2(\text{Å}^2)$
1	1.78	0.002	2.32	0.012	2.71	0.008
2	1.78	0.001	2.33	0.011	2.69	0.008
3	1.78	0.001	2.35	0.011	2.72	0.006
4	1.80	0.001	2.38	0.010	2.71	0.004
5	1.79	0.002	2.35	0.011	2.74	0.006
6	1.79	0.001	2.35	0.011	2.74	0.008
7	1.79	0.001	2.35	0.014	2.88	0.004
8	1.79	0.001	2.32	0.013	2.71	0.008

## References

- [1] K. Sekine, T.E. Payne, T.D. Waite, J.A. Davis; International Alligator Rivers analogue project (18): Experimental study of the uranium adsorption on kaolinite – pH dependence in air-equilibrated system; JAERI-memo 03-036 (1991) 1-14.
- [2] C. Hennig, T. Reich, R. Dähn, A.M. Scheidegger; Structures of uranium sorption complexes at montmorillonite edge sites; Radiochim. Acta 90 (2002) 653-657.