

# Speciation of Colloid-borne Uranium by EXAFS and ATR-FTIR spectroscopy

Kai-Uwe Ulrich<sup>1</sup>, André Rossberg<sup>1,2</sup>, Andreas C. Scheinost<sup>1,2</sup>, Harald Foersterndorf<sup>1</sup>, Harald Zänker<sup>1</sup>, Ulf Jenk<sup>3</sup>

<sup>1</sup>Institute of Radiochemistry, FZ Rossendorf e.V., PF 510119, D-01314 Dresden, E-mail: k.ulrich@fz-rossendorf.de

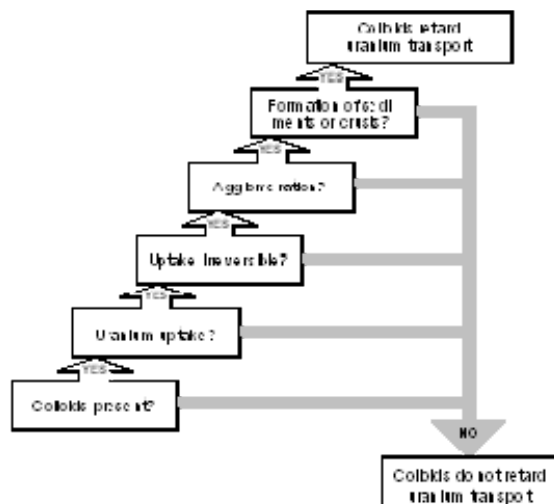
<sup>2</sup>Rossendorf Beamline at ESRF, B.P. 220, F-38043 Grenoble

<sup>3</sup>Wismut GmbH, Jagdschänkenstrasse 29, D-09117 Chemnitz

**Abstract.** De-acidification of acid mine waters transfers dissolved uranium into a colloidal form. Spectroscopic studies on colloid-borne uranium obtained by simulation of mine flooding in the laboratory showed that matrix ions such as sulfate and silicate are not involved in inner-sphere surface sorption complexes of  $\text{UO}_2^{2+}$  on ferrihydrite. At ambient air atmosphere, the data suggest the formation of ternary U(VI) carbonato surface complexes with either monodentate or bidentate coordination of carbonate and uranyl even at moderately acidic conditions. A revised model is proposed for  $\text{UO}_2^{2+}$  sorption on ferrihydrite in the absence of carbonate.

## Introduction

Flooding of abandoned uranium mines entails the risk of distributing contaminated water into adjacent groundwater aquifers and surface waters. Uranium in its oxidized state is highly soluble at both acidic and alkaline conditions, the latter being due to the formation of U(VI) carbonato complexes. However, moderately acidic conditions favor the sorption of uranyl onto colloids and mineral surfaces (e.g., Hsi and Langmuir 1985, Waite et al. 1994), and this process may retard the transport of the highly mobile uranium(VI) and even immobilize it (Fig. 1). Sulfide oxidation and hydrolysis reactions result in strongly acidic and highly mineralized pore waters in many mines. Similar waters result from in situ leaching of uranium with sulfuric acid as was applied in the Königstein mine (Saxony, Germany) from 1984-1991. Flooding this type of mines by near-neutral water will elevate the acidic pH up to the range where changing speciation of uranium may affect its migration *via* the water path.



**Fig. 1.** Flow diagram that indicates when colloids become significant for the retardation of uranium(VI) transport in flooded mines.

This study aims at (i) simulating mine flooding in a mesocosm experiment, (ii) characterizing the freshly formed colloids, their stability and U uptake, and (iii) investigating the structure and stability of sorbent and sorbate binding on the molecular level by Extended X-ray Absorption Fine Structure (EXAFS) and Attenuated Total Reflection Fourier-Transform Infrared (ATR-FTIR) spectroscopy.

## Mine flooding simulation experiment

Floodwater from the Königstein mine (pH 2.85, elevated concentrations of sulfate, iron, aluminum and uranium) and near-neutral, suboxic groundwater from an aquifer above the mine, served as the reaction partners (Table 1). A defined volume of floodwater (5–6 L) was mixed with up to 100 L of groundwater by stepwise addition of 10–20 L aliquots within five days. Bubbling of oxygen provided turbulence, accelerated the process of iron(II) oxidation, and removed most of the  $\text{CO}_2$ .

The pH increased as a function of the mixing ratio, i.e. the volume of the mixture divided by the initial floodwater volume (Fig. 2). The proportion of colloidal Fe rose with progressive iron oxidation (shown by falling  $[\text{Fe(II)}]/[\text{Fe}_{\text{tot}}]$  ratio) and pH increase and was thus a function of both mixing ratio and time. At  $\text{pH} > 4.5$  colloidal Al and U emerged, reaching a proportion of ~60% at pH 5 and of 95–99% at pH 6 (Fig. 2). The colloid concentration raised up to 40 mg/L. After filtration, scanning electron microscopy on the Nucleopore membrane visualized particles of 70–100 nm in both isolated and aggregated forms. The tendency of aggregation was caused by a low electrostatic stability. Below the point of zero charge at  $\text{pH} \sim 6$ , a low Zeta potential of 5–10 mV was measured. X-ray diffraction of the dried and pulverized colloid samples showed two weak, broad peaks which are

typical of two-line ferrihydrite (Fh) (Schwertmann et al. 1999). ICP-MS analysis of the digested sample MW2 verified the dominance of Fe (373 mg/g), besides Al (56 mg/g), S (24 mg/g), U (21 mg/g), Si (14 mg/g), and C (6.5 mg/g).

The U-L<sub>III</sub> EXAFS spectrum of the colloid sample MW2, concentrated to a wet paste, closely resembled spectra published before, but the interpretations given in the literature are inconsistent. For instance, Waite et al. (1994) described the uranyl sorption onto Fh by an inner-sphere surface complex. Whereas Allard et al. (1999) failed to identify this complex in case of a natural Fe-rich gel which had trapped uranium, Bargar et al. (1999) explained their spectra by ternary U(VI) carbonato complexes adsorbed onto hematite over a wide pH range. Owing to the sample composition, ternary complexes with sulfate and silicate came into consideration as well. In order to elucidate the molecular uranium binding structure in the colloid sample in detail, a set of simplified sorption experiments has been carried out to synthesize samples for comparative EXAFS and ATR-FTIR studies.

## Uranium sorption experiment

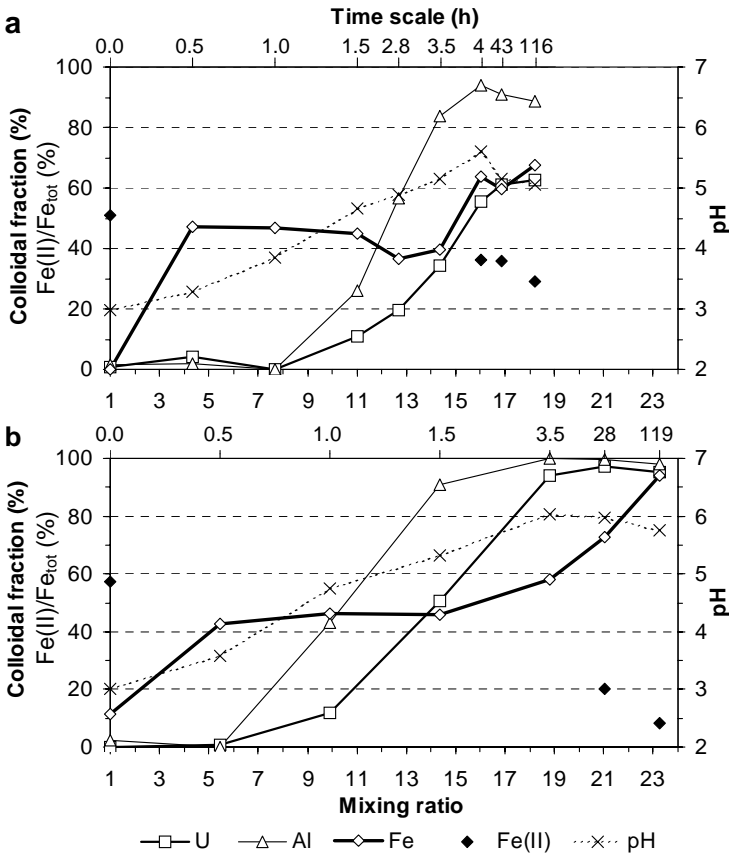
The first series of experiments checked the influence of sulfate and silicate on

**Table 1.** Analysis of floodwater (Königstein mine, Nov. 2003) and groundwater from an adjacent aquifer ( $E_H$  in mV, electrical conductivity in  $\text{mS cm}^{-1}$ , concentrations in  $\text{mg L}^{-1}$ ).

Parameter	Floodwater	Groundwater	Parameter	Floodwater	Groundwater
pH	2.85	6.50	[Fe(II)]	192	2.4
$E_H$	480	290	[Fe(III)]	84.0	0.8
EC	2.09	0.255	[K]	3.8	1.6
[O <sub>2</sub> ]	0.4	6.6	[Mg]	17.2	3.1
[TIC]	10.5	15.1	[Mn]	12.4	0.012
[TOC]	1.3	0.33	[Na]	25.2	4.9
[SO <sub>4</sub> <sup>2-</sup> ]	1260	64.8	[Si]	5.4	1.7
[Al]	41.8	0.50	[U]	16.3	0.005
[Ca]	122	35.5	[Zn]	13.0	0.116

U(VI) sorption. Precipitates of colloidal ferrihydrite (Fh) were prepared from solutions of 1 mM Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 10 mM NaNO<sub>3</sub> (background electrolyte), and 12  $\mu\text{M}$  UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in the presence of either sulfate or silicate or both anions at ambient air atmosphere ( $p\text{CO}_2=10^{-3.8}$  atm). Table 2 gives the initial concentrations and the ion uptake by the colloids.

A second series of experiments checked the contribution of carbonate to U(VI) sorption. Fh was prepared from solutions of 1 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 15 mM NaCl as background electrolyte, and varied concentrations of  $\text{UO}_2\text{Cl}_2$  added both at ambient air atmosphere ( $[\text{U}] = 0, 6, 12, 30, 50, 75, 100 \mu\text{M}$ ) and in a  $\text{N}_2$ -purged glove box ( $[\text{U}] = 0, 12, 100 \mu\text{M}$ ) with  $[\text{CO}_2] < 2 \text{ ppm}$ . To initiate the formation and aggregation of Fh colloids, 1 M or 0.1 M NaOH solution was added under vigorous stirring until pH 5.5 or pH 8.0 was reached. Control and re-adjustment of the pH were done after 6, 12, and 24 hours. After having reached equilibrium within 24 h, the aggregated colloids were allowed to settle for 65–70 h and then concentrated to a wet paste by ultra-centrifugation (285,000 g; 30 min). This paste was transferred into a polyethylene vial designed for use on a cryostat sample holder and stored in liquid  $\text{N}_2$  until the measurement to avoid sample alteration.



**Fig. 2.** Percentage of colloidal U, Al, Fe (based on 3 kD ultrafiltration),  $\text{Fe(II)/Fe}_{\text{tot}}$  fraction (left ordinate) and pH (right ordinate) as functions of mixing ratio (lower abscissa) and time (upper nonlinear abscissa) in two flooding simulation experiments MW1 (a) and MW2 (b).

**Table 2.** Initial concentration and uptake (based on 3 kD ultrafiltration) of sulfate, silicate, and uranyl by colloidal ferrihydrite in the sorption experiments at final pH 5.5.

Sample	Initial concentration (mM)			Uptake (%)		
	[SO <sub>4</sub> <sup>2-</sup> ]	[Si(OH) <sub>4</sub> ]	[UO <sub>2</sub> <sup>2+</sup> ]	SO <sub>4</sub> <sup>2-</sup>	Si(OH) <sub>4</sub>	UO <sub>2</sub> <sup>2+</sup>
A	1.2	-	-	7.6	-	98.2
B	4.8	-	0.012	3.5	-	95.6
C	-	0.075	0.012	-	66.5	99.4
D	-	0.3	0.012	-	63.2	98.9
E	-	1.2	0.012	-	32.4	98.3
F	1.2	1.2	0.012	5.2	34.2	99.2
G	4.8	0.3	0.012	4.8	31.8	96.3

## EXAFS study

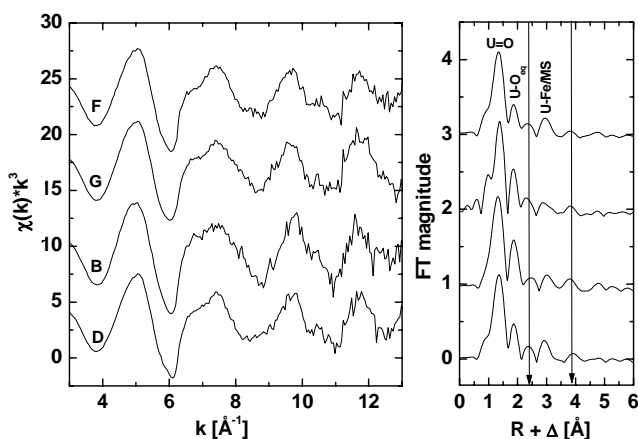
EXAFS spectroscopy at the U-L<sub>III</sub> absorption edge ( $E_0=17185$  eV) enables an element-specific detection of the type, number, and distance of atoms surrounding the U atom up to a radius of  $\sim 6$  Å (Teo 1986). The measurements were carried out at the Rossendorf Beamline (BM20) located at the European Synchrotron Radiation Facility in Grenoble using a He cryostat ( $\sim 30$  K). Since the relaxation of an excited core electron produces X-ray fluorescence which can be detected more sensitively at low U concentrations, a solid-state 13-element germanium fluorescence detector was used. Energy calibration was based on the X-ray absorption of an yttrium foil. For statistical reasons 6-8 spectra of each sample were averaged. The codes EXAFSPAK, WINXAS 3.0, and FEFF 7.02 were applied for data processing including dead-time correction of the fluorescence signal, shell fitting, and *ab initio* calculation of backscattering phase and amplitude functions. Further data refinement was achieved by a Monte-Carlo approach (Rossberg and Scheinost 2005).

The first approach of shell fitting explained the two highest peaks of the Fourier transforms (FTs) in Figs. 3 and 4 (right) and Fig. 5 (left) by two axial O atoms (U=O) of the UO<sub>2</sub><sup>2+</sup> cation as nearest neighbors of the U atom, and by  $5\pm 1$  O atoms of the -OH/H<sub>2</sub>O hydrate shell in the equatorial plane (U-O<sub>eq</sub>). Another prominent peak at  $R+\Delta\sim 2.9$  Å is mainly explained by the backscattering contribution of one Fe atom, including also a small contribution of the U=O multiple scattering (MS) amplitude. This result strongly suggests the binding of the UO<sub>2</sub><sup>2+</sup> cation to the Fe hydroxide surface by a bidentate inner-sphere complex. Two minor peaks at  $R+\Delta\sim 2.4$  Å and  $\sim 3.8$  Å (indicated by arrows in Fig. 3, right) remained unexplained. Since these FT peaks were visible in all spectra of the first series of sorption experiments, and also appeared in the absence of sulfate and silicate (Fig. 4A), S and Si could be excluded as backscattering atoms. Hence sulfate and silicate are not involved in the inner-sphere surface sorption complex of uranyl.

In the second series of sorption experiments the contribution of carbonate to the U sorption on Fh at pH 5.5 and 8.0 was examined. The EXAFS spectra of the

samples prepared in presence and in absence of  $\text{CO}_2$  were fairly alike (Fig. 4). However, in the case of pH 8.0, the FT of the calculated difference spectrum showed a noticeable backscattering contribution to the peaks at  $R+\Delta\sim 2.4\text{ \AA}$  and  $\sim 3.8\text{ \AA}$ . The first peak is explained by a carbon shell and the second by the backscattering of a distal carbonate O atom, supporting bidentate coordination of carbonate in the equatorial plane of  $\text{UO}_2^{2+}$ . This result at pH 8.0 suggests sorption of a ternary U(VI) carbonato complex on Fh. At pH 5.5 the backscattering contributions of bidentately coordinated carbonate are not visible in the difference spectrum, possibly because the concentration of these ternary complexes is below the limit of detection. It cannot be ruled out that substantial portions of monodentately bound carbonate are present at the lower pH, because the detection limit of such backscattering contributions is higher than for bidentately coordinated carbonate.

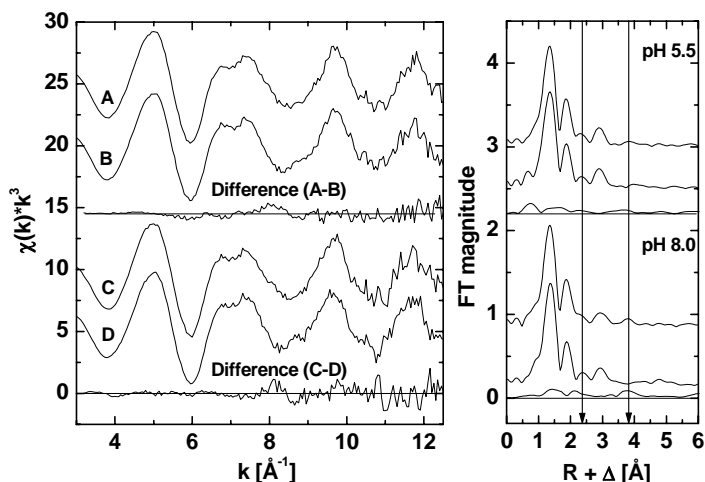
Since the FT peak at  $R+\Delta\sim 2.4\text{ \AA}$  was also observed for samples where great care had been taken to keep the system carbonate-free, the Monte-Carlo approach (Rossberg and Scheinost 2005) was used to test whether the experimental EXAFS spectra could be explained by uranyl adsorption on crystallites of hematite. The local hematite structure was chosen because EXAFS data from the Fe-K absorption edge supported the existence of face-sharing linkages between Fe octahedra which are characteristic of hematite and also occur in 2-line ferrihydrite (Janney et al. 2000). The resulting structural model (Fig. 5 right) indicates  $\text{UO}_2^{2+}$  bidentately bound to a  $\text{FeO}_6$  octahedron with atomic distances of  $R_{(\text{U-O})}\sim 2.30\text{ \AA}$  and  $R_{(\text{Fe-O})}\sim 2.21\text{ \AA}$ , yielding a distance of  $2.88\text{ \AA}$  to an edge-shared O atom of an adjacent  $\text{FeO}_6$  octahedron. This model includes the first Fe shell at a distance of  $3.46\text{ \AA}$  and predicts a second Fe shell at a distance of  $4.35\text{ \AA}$  which tightly fits the experimental data and is represented by the small FT peak at  $R+\Delta\sim 3.8\text{ \AA}$  (Fig. 5 left).



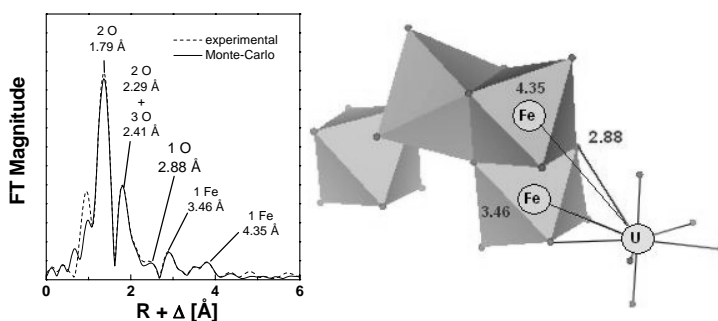
**Fig. 3.** U-L<sub>III</sub> EXAFS spectra and FTs of four selected colloid samples (pH 5.5; cf. Table 2).

## ATR-FTIR spectroscopy

The ATR technique provides direct acquisition of FTIR spectra of freshly ultra-centrifuged colloid pastes without further treatment. The respective supernatants of the concentrated colloid samples were used to record spectra for background correction. For each spectrum shown in Fig. 6, 128 scans were accumulated at a spectral resolution of  $4\text{ cm}^{-1}$ .



**Fig. 4.** U-L<sub>III</sub> EXAFS spectra and FTs of precipitated Fh colloids on which  $12\text{ }\mu\text{M}$   $\text{UO}_2^{2+}$  adsorbed at pH 5.5 (A+B) and pH 8.0 (C+D) at ambient air (A+C) and  $\text{N}_2$  atmosphere (B+D). Calculated difference spectra (A-B) and (C-D) and their FT magnitudes also shown.



**Fig. 5.** U-L<sub>III</sub> EXAFS-FT of a colloid sample from the mesocosm experiment (Fig. 2b) where carbonate was not detectable in solution at pH 5.5. The values in Angstrom above the peaks indicate the interatomic distances after phase shift correction, fitted by the Monte-Carlo approach (Rossberg and Scheinost 2005). A tentative structural model is shown on the right.

The spectrum of pure Fh prepared at pH 5.5 in NaCl matrix and N<sub>2</sub> atmosphere shows a broad absorption band around 937 cm<sup>-1</sup> representing the  $\delta(\text{OH})$  bending vibration of the Fh phase (Fig. 6A middle). The spectra of samples containing uranyl ions exhibit an additional band around 903 cm<sup>-1</sup>, the intensity of which correlates with increasing UO<sub>2</sub><sup>2+</sup> concentration (Fig. 6C-E middle). This band represents the antisymmetric ( $\nu_{as}$ ) stretching vibration of UO<sub>2</sub><sup>2+</sup> adsorbed to the Fe hydroxide phase. The assignment to dissolved UO<sub>2</sub><sup>2+</sup>-carbonato or -hydroxo complexes can be ruled out since these compounds are known to excite bands at substantially higher wavenumbers (> 920 cm<sup>-1</sup>).

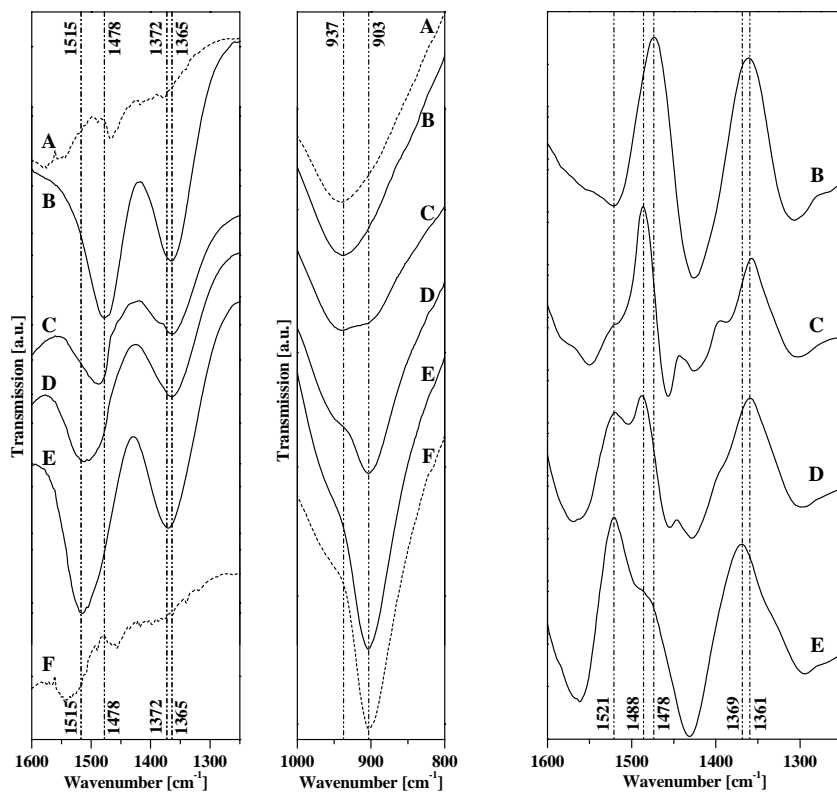
The spectra of the samples prepared at ambient air atmosphere show additional bands around 1365 and 1500 cm<sup>-1</sup> (Fig. 6B–D left) which are due to the symmetric ( $\nu_s$ ) and antisymmetric ( $\nu_{as}$ ) stretching vibration of carbonate (CO<sub>3</sub><sup>2-</sup>) anions bound to the colloidal phase, respectively. These bands show a continuous shift to higher wavenumbers with increasing UO<sub>2</sub><sup>2+</sup> concentration. In particular the frequency of the  $\nu_{as}(\text{CO}_3^{2-})$  vibration shifts from 1478 to 1515 cm<sup>-1</sup>, the latter being reached by the sample with initially 100  $\mu\text{M}$  UO<sub>2</sub><sup>2+</sup>. A similar, but smaller effect is observed for the  $\nu_s(\text{CO}_3^{2-})$  vibration ( $\Delta\nu \sim 7$  cm<sup>-1</sup>; Fig. 6E left).

To elucidate the peak positions of overlapping carbonate bands, the second derivatives (SD) of the transmission spectra were calculated in the spectral region of 1600–1250 cm<sup>-1</sup> (Fig. 6 right). SD maxima indicate the peak positions of components underlying the transmission bands. A comparison of the SD spectra of pure Fh (Fig. 6B right) and of Fh prepared in presence of 100  $\mu\text{M}$  UO<sub>2</sub><sup>2+</sup> (Fig. 6E right) again shows a clear difference in the spectral position of the  $\nu_{as}(\text{CO}_3^{2-})$  mode. Another maximum appears at 1488 cm<sup>-1</sup> in the SD spectrum of Fh prepared in presence of 50  $\mu\text{M}$  UO<sub>2</sub><sup>2+</sup> (Fig. 6D right), and forms the dominant maximum in the SD spectrum of the sample prepared in presence of 12  $\mu\text{M}$  UO<sub>2</sub><sup>2+</sup> (Fig. 6C right).

The FTIR results show that the axial O atoms of the UO<sub>2</sub><sup>2+</sup> sorption complex on Fh are not affected by the presence of CO<sub>2</sub> or HCO<sub>3</sub><sup>-</sup> in the system, since the frequency of the  $\nu_{as}(\text{UO}_2^{2+})$  mode is unaltered compared to the spectra recorded in absence of CO<sub>2</sub>. A coupling of carbonate *via* the axial O atoms is expected to induce a shifting of the  $\nu_{as}(\text{UO}_2^{2+})$  band (Čejka 1999).

In contrast, the Fh-carbonate interactions were strongly influenced by the presence of UO<sub>2</sub><sup>2+</sup>. Mono- or bidentate binding of carbonates to metal complexes can be distinguished by the degree of splitting of the  $\nu_{as}$  and  $\nu_s(\text{CO}_3^{2-})$  modes (Lefèvre 2004). The spectra of pure Fh show a splitting of  $\sim 115$  cm<sup>-1</sup> (Fig. 6B left) which can be interpreted as monodentate binding of the CO<sub>3</sub><sup>2-</sup> anions to the mineral phase (Lefèvre 2004, Bargar et al. 2005). In the presence of uranium this splitting expanded to 150 cm<sup>-1</sup> at pH 5.5 (Fig. 6D, E) and 160 cm<sup>-1</sup> at pH 8.0 (data not shown). For instance, a band splitting of  $\sim 190$  cm<sup>-1</sup> was found for the bidentate binding of CO<sub>3</sub><sup>2-</sup> to the equatorial hydrate shell of UO<sub>2</sub><sup>2+</sup> in the mineral Andersonite, Na<sub>2</sub>Ca[UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]·6H<sub>2</sub>O (Amayri et al. 2004). Since solutions in equilibrium with air exhibit substantially higher HCO<sub>3</sub><sup>-</sup> concentrations at pH 8.0 than at pH 5.5, and since the EXAFS data support bidentate sorption of carbonate to uranyl at pH 8.0, the band splitting of  $\sim 160$  cm<sup>-1</sup> may reflect a dominance of surface complexes with bidentate coordination of carbonate and uranyl. In contrast, the band splitting of  $\sim 125$  cm<sup>-1</sup> (Fig. 6C right) suggests another surface complex,

most likely with monodentate coordination of carbonate and uranyl. Nevertheless, the shifting of the carbonate band positions already at low  $\text{UO}_2^{2+}$  concentrations shows that ternary carbonato complexes contribute to the sorption of uranium on Fh at pH 5.5.



**Fig. 6.** ATR-FTIR spectra of the Fh- $\text{UO}_2^{2+}$  samples prepared at pH 5.5. The samples were prepared in  $\text{N}_2$  atmosphere (A, F) and in air atmosphere (B–E). Left panel: region of the carbonate stretching vibrations. Middle panel: region of the uranyl stretching vibration. Right panel: second derivative spectra of the carbonate stretching region. The initial  $\text{UO}_2^{2+}$  concentrations were as follows: 0  $\mu\text{M}$  (A,B); 12  $\mu\text{M}$  (C); 50  $\mu\text{M}$  (D); 100  $\mu\text{M}$  (E, F).

## Conclusion

Two spectroscopic approaches (EXAFS and ATR-FTIR) were applied on samples to identify the binding of uranyl on colloids formed during the experiment of simulated mine flooding. The experiments yielded the following results:

- Even though matrix anions such as sulfate or silicate were present in significant concentrations, these ions were not involved in the  $\text{UO}_2^{2+}$  adsorption on colloidal ferrihydrite at moderately acidic conditions.
- In absence of carbonate, the EXAFS data require a modification of the common structure of the binary, edge-shared inner-sphere surface complex of  $\text{UO}_2^{2+}$  and ferrihydrite in that the U atom has a neighbored oxygen atom at a distance of  $\sim 2.9$  Å, provided by two edge-shared  $\text{FeO}_6$  octahedra.
- At pH 5.5, low uranyl and air-equilibrated carbonate concentrations favor the sorption of ternary mononuclear complexes on Fh, most likely with monodentate coordination of carbonate and uranyl, as shown by the ATR-FTIR results.
- At pH 8.0, the same experimental conditions suggest a contribution of ternary mononuclear sorption species with bidentate coordination of carbonate and uranyl as derived from EXAFS measurements.
- At both pHs, FTIR spectra of samples with initially higher U concentrations (0.1 mM) and air-equilibrated carbonate concentration suggest a dominance of ternary sorption species with bidentate coordination of carbonate and uranyl.

Our next research step will focus on the stability of uranium binding during the transformation of colloids into sediments and crusts and during the aging of the metastable ferrihydrite into more crystalline iron minerals. The question of binding stability (reversibility vs irreversibility) is crucial for the role of colloids in uranium(VI) transport (cf. Fig. 1).

## Acknowledgements

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