

# Surface Bond Structure of Uranium Adsorbed onto Mine Water Colloids

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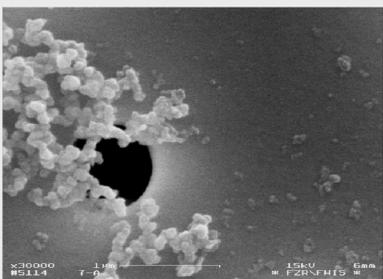
## 1 Objectives

Remediation and surveillance of abandoned uranium mines with  $>10^8$  m<sup>3</sup> total void volume which has to be flooded in East Germany [1]

Migration of contaminants from abandoned mines: Stimulated or attenuated by colloids?

Investigation of colloid composition and uranium bond structure

## 2 Typical Mine Water Colloids



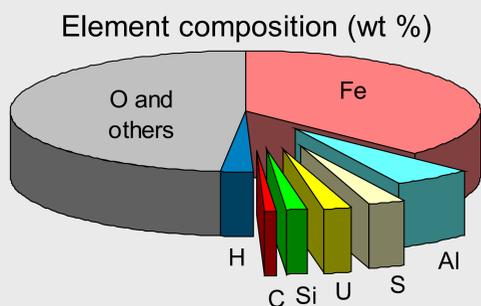
Element	mmol/g
[Fe]	6.68
[Al]	2.06
[S]	0.75
[Si]	0.50
[C]	0.54
[U]	0.09

SEM image (x 30,000): Colloidal particles on filter membrane, 1  $\mu$ m pore size.

Particle size (SEM, PCS): 50 - 150 nm

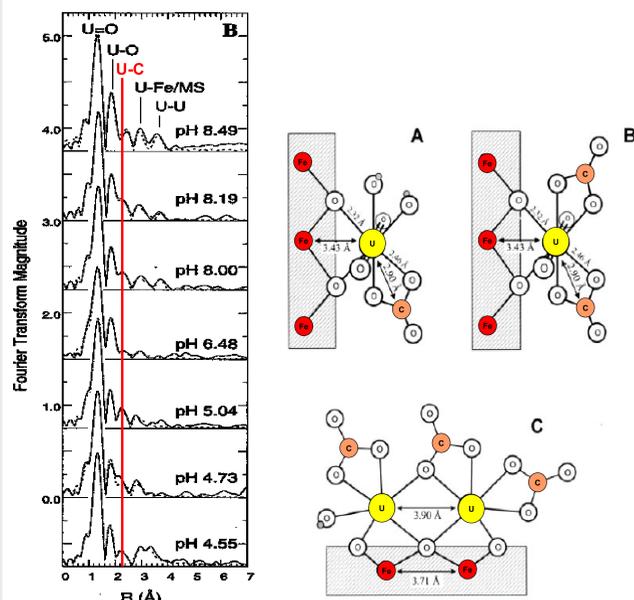
IEP: pH 6.1, Zeta Potential below IEP: +6 mV  $\rightarrow$  high tendency of agglomeration!

Mineralogy (XRD): 2L-Ferrihydrite (Fh)



## 3 State of the Art

Bargar et al. [2] favor sorption of ternary U(VI) carbonate complexes on hematite over wide pH range (based on electrophoretic mobility + FT-IR + EXAFS):



## 4 U-L<sub>III</sub> EXAFS Spectroscopy at BM20 (ROBL-CRG)

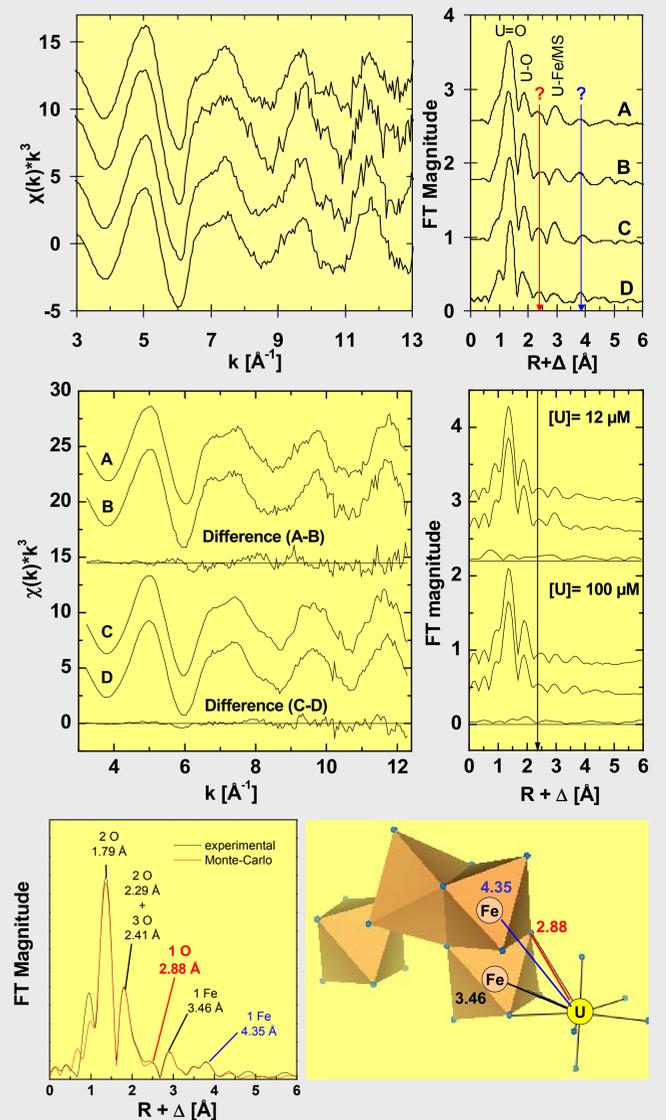
Fourier-transformed EXAFS spectra of colloid samples from mine water and of ferrihydrite (Fh) on which 12  $\mu$ M  $\text{UO}_2^{2+}$  was adsorbed at pH 5.5 (air atmosphere) in absence (D) or in presence of sulfate and silicate (1.2 mM each; A), of only sulfate (4.8 mM; B) or silicate (0.3 mM; C), all show the same peak at  $R+\Delta = 2.4$  Å. Hence these ions do not act as ligands in the near vicinity of  $\text{UO}_2^{2+}$ , and the peak remains unexplained.

### Does carbonate participate in U sorption on ferrihydrite?

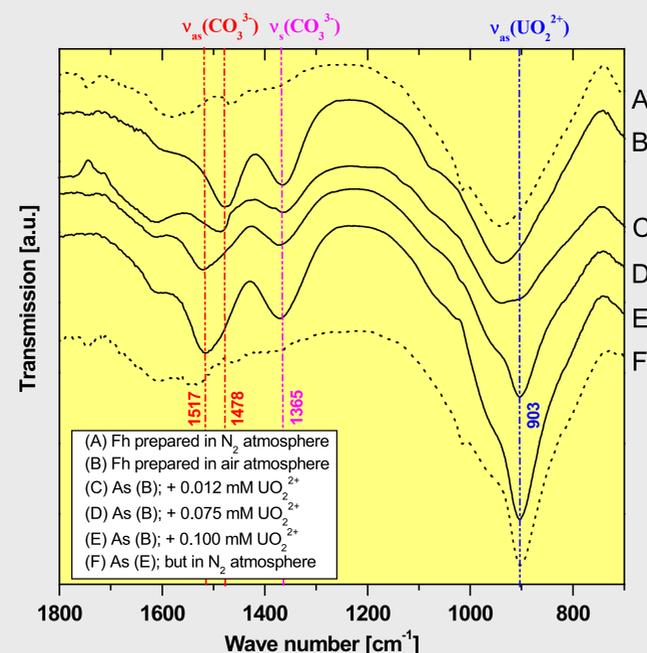
Sorption of 12  $\mu$ M  $\text{UO}_2^{2+}$  (A+B) and 100  $\mu$ M  $\text{UO}_2^{2+}$  (C+D) on Fh colloids in ambient (A+C) and  $\text{N}_2$  atmosphere (B+D). Calculated differences yield no backscattering contribution to the FT peak  $R+\Delta = 2.4$  Å. Thus the peak cannot result from ternary carbonate ligands bidentately bound on  $\text{UO}_2^{2+}$ .

### New solution of surface bond structure

EXAFS refinement by Monte-Carlo Target Transform Factor Analysis [3] suggests a new sorption structure: a binary complex without carbonate or other type of ligand as presented in the right figure. This model predicts a second Fe shell at  $\sim 4.35$  Å which tightly fits the experimental data.



## 5 ATR FT-IR Spectroscopy



$\delta(\text{OH})$  bending vibration of Fh at  $\sim 935$   $\text{cm}^{-1}$  (A-C). Antisymmetric ( $\nu_{as}$ ) stretching vibration of  $\text{UO}_2^{2+}$  adsorbed onto Fh at 903  $\text{cm}^{-1}$  (C-F). Symmetric ( $\nu_s$ ) and  $\nu_{as}$  stretching vibration of  $\text{CO}_3^{2-}$  sorbed onto Fh at  $\sim 1365$  and  $\sim 1500$   $\text{cm}^{-1}$  (B-E). Unaltered  $\nu_{as}(\text{UO}_2^{2+})$ , but shift of  $\nu_{as}(\text{CO}_3^{2-})$  to higher wavenumbers indicate ternary complexes of  $\text{CO}_3^{2-}$  equatorially bound onto the adsorbed  $\text{UO}_2^{2+}$ .

## 6 Conclusion

EXAFS suggests surface sorption of  $\text{UO}_2^{2+}$  on mine water colloids composed of ferrihydrite in a bidentate fashion to one  $\text{FeO}_6$  octahedron in a way that yields a distance of  $\sim 2.88$  Å to an edge-shared O atom of an adjacent  $\text{FeO}_6$  octahedron. Sulfate and silicate do not contribute as ligands. Ternary complexes of bidentately bound carbonate ligands not detected at pH 5.5,  $c(\text{U})=100$   $\mu\text{M}$ . Since ATR-IR suggests ternary uranyl carbonate complexes under these conditions open to the atmosphere, the linkage must be monodentate.

## References

- [1] Ulrich KU, Zänker H, Jenk U, In: Qaim SM, Coenen HH (Eds), Advances in Nuclear and Radiochemistry. Extended Abstracts of NRC 6. Schriften FZ Jülich, General and Interdisciplinary, Vol. 3, 645-647 (2004).
- [2] Bargar JR, Reitmeyer R, Lenhart JJ, Davis JA. Characterization of U(VI)-carbonato ternary complexes on hematite: EXAFS and electrophoretic mobility measurements. Geochim. Cosmochim. Acta 64, 2737-2749 (2000).
- [3] Rossberg A, Scheinost AC. Linking Monte-Carlo simulation and Target Transformation Factor Analysis: A novel tool for the EXAFS analysis of mixtures. Physica Scripta (2005), in press.

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