Proposal title: Study of speciation of uranyl in chloride solution by X-ray Absorption Fine Structure Spectroscopy		Proposal number: 30-02-1050
Beamline: BM30B	**Date(s) of experiment:** from: 25 June 2013 to: 02 Jully 2013	**Date of report:** 08 September 2017
Shifts: 18	**Local contact(s):** **Dr. Jean-Louis Hazemann (hazemann@grenoble.cnrs.fr)**	*Date of submission:* 08 Septembre 2017

Objective & expected results :

The goal of this study was to obtain direct data on the uranyl speciation in aqueous Cl-bearing solutions at high T-P and thus to quantify the possible role of hydrothermal NaCl-rich fluids in U transportation and concentration during ore deposition. The new expected results were to determine for the first time the stoichiometry and structure of aqueous U species at high T-P and different Cl concentrations and to identify and characterize new type of UO_2-Cl species detected previously by Raman spectroscopy (Dargent et al., 2013, *Eur. J. Miner.* **25**, 765)**.**

Results and discussion of this study :

The local atomic structure around U in aqueous solutions was studied by XAFS spectroscopy at the U L_{III}-edge (17.166 keV) at 30 – 350°C and 600 bar using specially designed high T-P X-ray optical cell developed at the Néel institute (Testemale D. et al., 2005, *Rev. Sci. Instrum.* **76**, 43905). All measurements were performed in initially uranyl(U^{VI}or UO_2^{2+})-bearing solutions as a function of Cl concentration (0-12M, where M denotes the number of moles of each solute per liter of solution) and temperature (30, 100, 200,250, 300, 350°C). Spectra were collected in both transmission and fluorescence mode at BM30B beamline (FAME).

Results from the uranyl-bearing Cl-free solutions. Two Cl-free solutions were examined: 0.01M $UO_2(NO_3)_2$ – 0.1M HNO_3 and 0.01M $UO_2(FMS)_2$ – 0.1M HFMS at T = 30-350°C and P = 600 bar. XANES and EXAFS spectra for both solutions at 30-250°C are very close. EXAFS spectra show that in both solutions U is coordinated by 2 oxygen atoms at 1.77±0.01Å and 5 oxygen atoms in at 2.40±0.01 Å. These structural data are consistent with the planar square $UO_2(H_2O)_5^{2+}$ cation in which U is doublebonded by 2 axial oxygen (O_{ax}) atoms in a rigid, nearly collinear arrangement (O_{ax}=U=O_{ax}) at 1.77 Å and hydrated by 5 water molecules in equatorial plan with U-O_{eq} distance 2.40±0.01 Å. Our data at 30°C are in excellent agreement with previous XAS studies (e.g., Kelly and Ravel, 2007, doi: 10.1063/1.2644452). With increasing T up to 250°C, the Debye-Waller factor increases by ~30% and by ~50% for O_{ax} and O_{eq}., respectively. At T > 250°C the uranyl ion becomes unstable resulting in U precipitation. Similar behavior at high T was also observed for cations of Cd (Bazarkina et al., 2010, *Chem.Geol*. **276**, 1), Pd (Bazarkina et al., 2014, *GCA* **146**, 107), Zn (Bazarkina et al., 2017, EXSF exp. report ES 253).

Results from the uranyl-bearing Cl-rich solutions. Four chloride concentrations (0.01, 0.1, 3.0, 12.0M) were studied at 30-350°C in the system UO_2Cl_2-HCl-LiCl-H_2O. At 30°C the evolution of XANES spectra with increasing Cl concentration is shown in Fig. 1 in comparison with Cl-free solutions. With Cl increasing from 0 to 12M Cl, the amplitude of the white line slightly decreases. The spectra of 0-3M Cl solutions are rather close indicating the predominance of $UO_2(H_2O)_5^{2+}$ cation, the spectrum of 12M Cl has the same XANES shape with the lowest white line amplitude indicating the speciation change. This is in line with EXAFS modeling results. In all solutions we found 2 O_{ax} atoms at 1.77 ±0.01 Å similarly with Cl-free solutions and typical for uranyl. However, significant changes appear in equatorial plane due to water molecules replacement by Cl atoms (see figure 2) accompanied by a decrease of equatorial coordination number (from 5 to 4 with Cl increasing from 0 to 12M). While Cl atoms incorporate, the interatomic distance U-O_{eq} increases up to 2.54±0.04Å in 12M Cl solution. The distance U-Cl in all solutions at 30°C is 2.72±0.03Å. Our data at 30°C agree with previous XAS studies (Allen et al., 1997, *Inorg. Chem.* **36**, 4676; Hennig et al., 2005, *Inorg. Chem.* **44**, 6655; Soderholm et al., 2011, J. *Phys. Chem. A* **115**, 4959).

Our XAS data on uranyl in Cl solutions at high *T* are pioneer. With increasing temperature up to 250°C, the the white line amplitude of all Cl-bearing solutions decreases (see 25 and 250°C in Fig. 1). This is accompanied by the decrease of the coordination number in equatorial plane. At 250°C both XANES and EXAFS spectra of 3 and 12M Cl solutions becomes almost the same indicating the predominance of the same U species with 2 O_{ax} atoms at 1.77±0.01Å and 3 Cl atoms at 2.68±0.02 Å in equatorial plane, whereas O_{eq} is under detection limit. This agrees with our previous Raman data indicating the predominance of new species at such conditions (Dargent et al., 2013, *Eur. J. Miner*. **25**, 765). However, no previously presumed polyuranyl complexes were detected by XAS. In contrast, we have found that this new species occuring at high T has trigonal bipiramidal structure. This structure is very unusual for uranyl. Possible reduction of U(VI) to U(V) cannot be excluded. This reduction is expected to be accompanied by very slight energy shift of XANES spectra. However, the energy resolution of conventional fluorescence measurements is not sufficient to measure it and thus, (VI) and U(V) species cannot be distingwished. However, such technique as HERFD-XAS is more powerfull (Proux et al., 2017, *J. Environ. Qual.*, doi: 10.2134/jeq2017.01.0023). Further measurements by HERFD are needed to better quantify this type of U species.

At 300-350°C, the XANES spectrum of 12M Cl solution is shifted by ~4eV to lower energy. This energy shift corresponds to the reduction of U(VI) to U(IV). It is generally considered that U(IV) has very low mobility in aqueous solutions. Our results show for the first time that U(IV) can be transported in high concentration (0.01mole U per kg of fluid) by highly

saline hydrothermal brines (12M Cl) as octahedral-like UCl_6^{2-} complex with average U-Cl distance 2.65±0.01 Å. No previous data on such complexes have been described. The chemistry of U in such reduced Cl-rich hydrothermal conditions requires further studies.

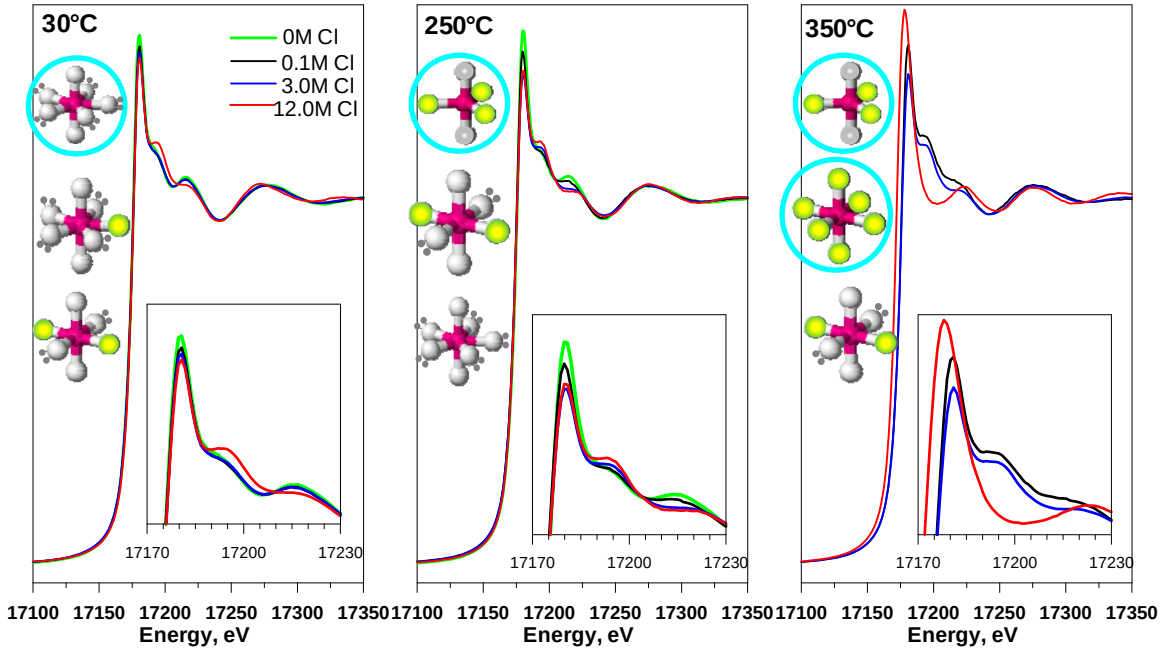

Fig 1. Evolution of XANES spectra and the major U aquoeus species at 25, 250 and 350°C. At 350°C, the XANES spectra of 12M Cl solution is shifted to lower energy by 4eV than corresponds to the reduction of U(VI) to U(IV).

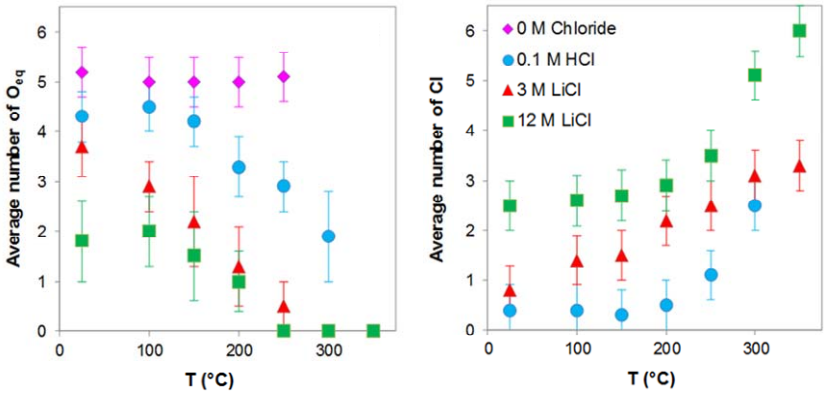

Fig 2. The number of O_{eq} and Cl atoms around U in aquoeus solutions as a function of temperature and Cl concentrations. The number of O_{ax} is 2 in all solutions except 12M Cl at 300-350°C, where uranyle is reduced to U(IV) and no O_{ax} is detected.

Conclusions and perspectives. Several important results were obtained in this study: 1) the structure of UO_2-Cl-H_2O complexes was characterized by in-situ spectroscopy for the first time; 2) the polyuranyl complexes questioned in Dargent et al., 2013(*Eur. J. Miner.* **25**, 765) were shown to be negligible in Cl solutions (up to 12M Cl) at 30-350°C; 3) the new type of U species observed by Dargent et al. by Raman spectroscopy is shown to have the unusial for uranyl trigonal dipiramidal structure; 4) existence of stable U(IV) chloride complexes at 300-350°C in Cl brines is shown by our in-situ experiments for the first time. These pioneer data demonstrate the strong complexing of U with Cl at high T-P and thus provide new insights into U geochemistry in Cl solutions at high T-P. To identify the valence of U in trigonal dipiramidal complex and to better quantify the stability of U(IV) chloride complexes at high T-P supplementary XAS data are needed. The best technique for these supplementary measurements is HERFD-XAS. To finalize our study these supplementary measurements are indispensable.

Justification and comments about the use of beam time :

All 18 shifts of allocated beamtime were fully used. About 2 shifts were necessary to align the X-ray cell, optimize the beam before starting the measurements, and test the HP-HT cell; the other 16 shifts were used to examine six different UO_2-bearing solutions at the *T* range from 20 to 350°C at 600 bar and to obtain spectra of UO_2Cl_2 solid (standard).

Publication(s):

The article with the results obtained during this project is in preparation for publication in *Geochimica et Cosmochimica Acta* journal. However, to finalize our study and to remove any ambiguity, HERFD-XAS experimented are required (proposal submitted in September 2017).