



Characterization of uranothorite solid solution ($\text{Th}_{1-x}\text{U}_x\text{SiO}_4$) by EXAFS; from syntheses and purification to dissolution

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Report:

1 Summary

Physical-chemical and thermodynamic properties of the USiO_4 mineral, namely coffinite have been subject to many studies during the past decades¹ after uraninite/pitchblende. The coffinite mineral is called to play a huge role either in front-end and the back-end of the nuclear fuel cycle. Coffinite represents the second most abundant source of uranium (IV) on earth, often associated to pitchblende in ore deposits which are economically exploitable. In addition, the direct disposal of spent nuclear fuel (SNF) in deep geologic formations is considered as waste management option in several countries². Conservative safety assessments consider that the SNF could come into contact with groundwater after the long-term degradation of confinement barriers. Therefore coffinite could be formed by the interaction between the dissolved U(IV) and the host rocks which may exhibit reducing conditions associated with the silica enriched environment. In this purpose, multiparametric study dedicated to the stability and the thermodynamic properties of uranothorite solid solution, with a particular focus on the synthetic uranium(IV) silicate. In consequence, the recent research projects developed at the ICSM (Institut de Chimie Separative de Marcoule) in collaboration with CEA Marcoule (*Commissariat à l'énergie atomique et aux énergies alternatives*) have led to the synthesis of solid

solutions of $\text{Th}_{1-x}\text{U}_x\text{SiO}_4$ by the use of the hydrothermal techniques. These powders have been thoroughly analyzed by PXRD and SEM showing the presence of impurities of uranium dioxides (UO_2) and amorphous silica (SiO_2) especially for samples with uranium content ($x \geq 0.5$). With the failure of the synthesis of pure silicate samples, an original purification process was developed and optimized leading to pure silicate phases. Those pure samples have been used in the dissolution experiments aiming the determination of the thermodynamical properties such as solubility constants and associated thermodynamic data (standard variations of enthalpy, entropy and free energy associated to the formation of uranothorite solid solutions). In this project, EXAFS appeared to us as a valuable technique which can allow the detection of amorphous neoformed phases at traces level. A complete characterization of the uranothorite solid solution was carried out, not only, on the raw and purified samples in order to quantify the presence of side products, but also on leached uranothorite solid solutions (including both end members : coffinite and thorite). In this short report we will show the results obtained on the synthetic coffinite (raw and purified) which have been submitted for publication.

2 Highlights and Lowlights of the project

The EXAFS measurements were carried out at Rossendorf beamline at the European Synchrotron Radiation Facility. The Si (111) double crystal monochromator was used in the channel cut mode. The spectra were collected in the fluorescence mode using a 13 element high-purity Ge-detector (Canberra) with digital signal analyzer (XIA-XMAP). Energy calibration of the EXAFS spectra was performed by simultaneous measurement of a Y metal foil (first inflection point at 17.038 keV). Both coffinite samples were mixed with saccharide by vibrating at 60 Hz during 15 min in a jar mill, pressed under 250 MPa in a 1 cm diameter tungsten carbide die, then the pellet was enclosed in polyethylene sample holders. During the EXAFS experiments, both samples were placed in a closed-cycle He-cryostat at 15 K to improve signal quality by reducing the thermal contributions (Debye–Waller factor). The EXAFS oscillations were extracted from the raw data with Athena code and adjusted with Artemis code. Self-absorption correction was performed. Adjustment was based on the structure of the coffinite with a parameterized set of parameters as described below. Phases and amplitudes were calculated based on this model with Feff9 code. One single energy shift parameter and global amplitude factor were used for all paths.

The data collection was performed at the U LIII edge in order to assess the local order around the uranium atoms. Comparison between the EXAFS spectra of pure coffinite and as-prepared samples is shown in Figure 1. Similar oscillations are clearly visible in both spectra up to 14 Å showing thereby that the same order is present in both samples. Qualitatively, the only significant difference between the two experimental spectra is an inversion of intensity of the beating located between 7.8 and 8.9 Å⁻¹. EXAFS data fitting has been performed with a parameterized set of parameters. Metrical parameters are given in Table 1 and figure 1 are very similar in both cases, suggesting that very little structural differences occur between the two samples.

Table 1. Best fit metrical parameters obtained from the EXAFS data of USiO_4 and UO_2+SiO_2 samples. S_0^2 is the global amplitude factor, Δe_0 is the energy threshold factor and r is the agreement factor of the fit in %.

USiO₄			
$S_0^2 = 1.0$	4 O at 2.25 Å	2 Si at 3.11 Å	4 U at 3.83 Å
$\Delta e_0 = -1.23$ eV	$\sigma^2 = 0.0035$ Å ²	$\sigma^2 = 0.0053$ Å ²	$\sigma^2 = 0.0027$
r = 4.1 %	4 O at 2.41 Å		Å ²
	$\sigma^2 = 0.0030$ Å ²		
USiO₄ + UO₂ + SiO₂			
$S_0^2 = 1.0$	4 O at 2.24 Å	2 Si at 3.12 Å	4 U at 3.83 Å
$\Delta e_0 = -2.56$ eV	$\sigma^2 = 0.0016$ Å ²	$\sigma^2 = 0.0052$ Å ²	$\sigma^2 = 0.0024$
r = 3.6 %	4 O at 2.39 Å		Å ²
	$\sigma^2 = 0.0019$ Å ²		
Crystallographic model			
	4 O at 2.319 Å	2 Si at 3.131 Å	4 U at
	4 O at 2.511 Å		3.8324 Å

Comparison between the XANES spectra of both samples (not shown) does not exhibit any visible signature of the uranyl unit: the transdioxo unit of hexavalent U is responsible of a multiple scattering feature well known to be located ca. 15 eV after the edge. In addition, the Fourier transformation of both EXAFS spectra neither does exhibit a short

range contribution that would indicate a significant amount of uranyl in the structure. Thus, we can conclude that the purification protocol did not alter the structure of the coffinite phase.

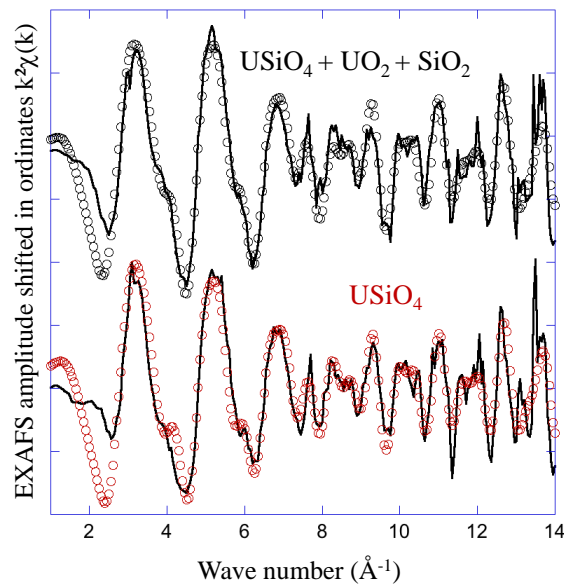


Figure 1. Experimental (straight line) and adjusted (dots) EXAFS spectra of the raw sample and single-phase coffinite sample. Spectra are represented in $k^2\chi(k)$ and shifted in ordinates for clarity.

In summary the present study gave some answers regarding the coffinite stability. Only U(IV) is involved in the coffinite compounds, XANES results did not show the presence of the uranyl species in our powder. The other conclusion, EXAFS data did not allow the clear verification of the coffinite purity. Indeed both spectra before and after purification are basically the same without any effect of UO₂ on the spectra collected on the RAW powder. The study of the uranothorite solid solutions are under progress and will be published soon.

3 Connections to other organizations and projects

This project was achieved in collaboration between ICSM (A. Mesbah-CNRS, S. Szenknect-CEA, N. Clavier-CNRS, T. Cordara-CEA (Undergraduate student), N. Dacheux-Univ Montpellier), CEA-DRCP Marcoule (C. Poinssot) and Univ. Nice Sophia-Antipolis (C. Den Auwer)

4 Use of pooled facilities

The experiment was performed in excellent conditions, the local staff was extremely professional. In fact, at the beginning of the run intended to perform our experiments in transmission mode but quickly, we noticed that the signal of the element (Th or U) with a low amount did not lead to the collection exploitable data. Therefore, the ROBL staff reacted very quickly and advised us to switch to the fluorescence mode.

5 Involved young researchers

The results obtained in this project were part of the research activities of new hired CNRS scientist (A. Mesbah) and the internship of an undergraduate student (Theo Cordara)

6 Use and dissemination

6.1 Foreseen publications

Stephanie Szenknect, Adel Mesbah, Théo Cordara, Nicolas Clavier, C. Den Auwer, Christophe Poinssot, Rodney C. Ewing and Nicolas Dacheux. *First experimental determination of the solubility constant of coffinite, submitted for publication in Geochimica et Cosmochimica Acta.*

6.2 Foreseen presentations at conferences

S. SZENKNECT, D.T. COSTIN, N. CLAVIER, A. MESBAH, C. POINSSOT, P. VITORGE, N. DACHEUX : "From uranothorite to coffinite : a solid solution route to the thermodynamic properties of $USiO_4$ ", MIGRATION 2013, Brighton, 8-13 septembre 2013.

S. SZENKNECT, D.T. COSTIN, N. CLAVIER, A. MESBAH, C. POINSSOT, P. VITORGE, N. DACHEUX : "From uranothorites to coffinite : a solid solution route to the thermodynamic properties of $USiO_4$ ", MRS Fall Meeting 2013 – Scientific Basis for Nuclear Waste Management XXXVII, Barcelone, 29 septembre - 03 octobre 2013.

S. SZENKNECT, N. CLAVIER, A. MESBAH, D.T. COSTIN, P. VITORGE, C. POINSSOT, N. DACHEUX: "From uranothorite to coffinite : a solid solution route to the thermodynamic properties of $USiO_4$ ", International REDUPP Workshop on "Surface reactivity and dissolution of spent nuclear fuel materials, Stockholm, 18-21 février 2014.

S. SZENKNECT, N. CLAVIER, A. MESBAH, D.T. COSTIN, P. VITORGE, C. POINSSOT, N. DACHEUX: "From uranothorite to coffinite : a solid solution route to the thermodynamic properties of $USiO_4$ ", IUMRS-ICA 2014, Fukuoka, 24-30 Août 2014.

N. DACHEUX, S. SZENKNECT, A. MESBAH, N. CLAVIER, C. POINSSOT, R.C. EWING: "Synthesis and solubility of purified coffinite.", 2014 Materials Science & Technology conference, Pittsburgh, 12-16 octobre 2014.

S. SZENKNECT, A. MESBAH, T. CORDARA, N. CLAVIER, C. POINSSOT, R. EWING, N. DACHEUX : "From the preparation of pure coffinite sample to the experimental determination of the solubility product", MRS Fall Meeting 2014 – Scientific Basis for Nuclear Waste Management XXXVIII, Boston, 30 novembre – 05 décembre 2014.

NATIONALE (France)

S. SZENKNECT, A. MESBAH, N. CLAVIER, C. POINSSOT, R.C. EWING, N. DACHEUX : "Utilisation de composés synthétiques pour la détermination de constantes de solubilité de phases minérales uranifères", Journées d'échanges du Défi NEEDS, Nantes, 21-22 Octobre 2014.

S. SZENKNECT, A. MESBAH, N. CLAVIER, C. POINSSOT, R. EWING, N. DACHEUX : "Utilisation de composés synthétiques pour la détermination des propriétés thermodynamiques de phases uranifères : l'exemple de la coffinite", Réunion de la Société Géologique de France « Journées Uranium », Orsay, 24-25 novembre 2014.

7 References

1. Deditius, A. P.; Utsunomiya, S.; Ewing, R. C., *Chemical Geology* **2008**, *251*, 33-49.
2. Hogselius, P., *Energy Policy* **2009**, *37*, 254-263.