First experimental determination of the solubility constant of coffinite.

Stephanie Szenknect^{†*}, Adel Mesbah[†], Théo Cordara[†], Nicolas Clavier[†], Henri-Pierre Brau[†], Xavier Le Goff[†],

Christophe Poinssot[§], Rodney C. Ewing[‡] and Nicolas Dacheux[†].

[†] ICSM, UMR 5257 CEA/CNRS/UM2/ENSCM, Site de Marcoule – Bât. 426, BP 17171, 30207 Bagnols-sur-Cèze cedex, France

[‡] Department of Geological Sciences, Stanford University, Stanford, CA 94305-2115 USA

[§] CEA, Nuclear Energy Division, RadioChemistry & Processes Department, CEA Marcoule, Bât. 400, BP 17171, 30207 Bagnols-sur-Cèze cedex, France

KEYWORDS. coffinite, uranium silicate, solubility constant, uraninite, silica, coffinitization.

ABSTRACT.

Dissolution experiments have been performed in order to determine the solubility constant of coffinite, USiO_4 . Several assemblages of phases were used in under-saturated experiments performed in 0.1 mol L^{-1} HCl under Ar atmosphere, as well as in air. These samples were fully-characterized and were composed of either USiO_4 , solely, or USiO_4 and additional oxide byproducts that resulted from the synthesis procedure. The solubility constant of coffinite was determined at 25°C and 1 bar ($\log {}^*K_S^\circ(\text{USiO}_4, \text{cr}) = -5.25 \pm 0.05$), as well as the standard free energy of formation of coffinite ($\Delta_f G^\circ(298 \text{ K}) = -1867.6 \pm 3.2 \text{ kJ mol}^{-1}$), which enables one to infer the relative stability of coffinite and uraninite as a function of groundwater composition. Geochemical simulations using PHREEQC 2 software and the Thermochimie data base indicate that coffinite precipitates at 25°C under reducing conditions, at $\text{pH} = 6$, for $\text{H}_4\text{SiO}_4(\text{aq})$ concentration of $7 \cdot 10^{-5} \text{ mol L}^{-1}$ and $\text{U}(\text{OH})_4(\text{aq})$ concentration of $10^{-11} \text{ mol L}^{-1}$. The $\Delta_f G^\circ$

*Author to whom correspondence should be addressed: stephanie.szenknect@cea.fr

value determined was used to calculate the standard free energy associated with the formation of coffinite from a mixture of uraninite and quartz. The value obtained ($\Delta_{r,ox}G^\circ = 20.6 \pm 5.2 \text{ kJ mol}^{-1}$) indicates unambiguously that coffinite is less stable than the quartz + uraninite mixture at 25°C. Geochemical simulations using PHREEQC 2 software indicate that coffinite precipitates in solutions supersaturated with respect to $\text{UO}_2(\text{cr})$, but undersaturated with respect to $\text{UO}_2(\text{am})$ in aqueous solutions with silica concentrations typical of groundwater. These favorable conditions during the formation of sedimentary uranium ore deposits, as well as slow dissolution kinetics, explain the common occurrence of coffinite.

1. INTRODUCTION

The direct disposal of spent nuclear fuel (SNF) in underground geological repositories is one of the main options pursued in a number of countries, such as Sweden, Finland, Switzerland and USA (Hogselius, 2009). Over time in a geologic repository, and after the early, rapid release of radionuclides that are at grain boundaries, the Instant Release Fraction (IRF), fission products and actinides dissolved in the UO_2 matrix will be more slowly released by dissolution of the UO_2 grains in the spent fuel after degradation of engineered barriers, such as the backfill and waste package (Poinssot et al., 2005). Secondary phases that form during SNF dissolution could become important sinks for uranium and other radionuclides and could control the subsequent mobility and the ultimate distribution of radiotoxic elements in the environment (Baker, 2014; Gorman-Lewis et al., 2008; Maher et al., 2012). Except for the Yucca Mountain site in the USA, most of the geologic sites under investigation for an underground repository are located in undisturbed clay-rich rock or granite, with silica-rich groundwaters, deep enough to have reducing conditions. For instance, pore-water samples collected at a depth of 490 m in Callovo-Oxfordian clayrock, in the Bure (France) underground research laboratory exhibited near neutral pH (7.2 ± 0.2), low redox potential ($E_{\text{H}_{\text{SHE}}} = -199 \text{ mV}$) and Si concentration ($1.4 \cdot 10^{-4} \text{ mol L}^{-1}$), high enough to allow silica precipitation (Gaucher et al., 2009). Granitic groundwater collected at a depth of 510 m in Forsmark and Äspö crystalline bedrock (Sweden) exhibited Si concentration of $1.8 \cdot 10^{-4} \text{ mol L}^{-1}$ and $1.5 \cdot 10^{-4} \text{ mol L}^{-1}$, respectively (Carbol et al., 2012). If coffinite is a less soluble phase than $\text{UO}_2(\text{s})$ under these conditions, it may precipitate and trap the tetravalent uranium released from the SNF (Amme et al., 2005; Hemingway, 1982; Janeczek and Ewing, 1992a, b; Langmuir, 1997). Such a process was already proposed based on observations of the natural nuclear reactors at Oklo and Oklobondo (Gabon), where uraninite, $\text{UO}_2(\text{cr})$ was observed to be altered to coffinite (Janeczek, 1999). In order to evaluate the likelihood of coffinitization of the UO_2 matrix, the thermodynamic data associated with the following reaction must be known:

However, the thermodynamic data for reaction (1) remain poorly constrained. The few data reported in the literature were estimated by analogy with thorite (ThSiO_4) (Brookins, 1975) or from available geologic information. In 1978, Langmuir first postulated that the average silica concentration (about $10^{-3} \text{ mol} \cdot \text{L}^{-1}$) found in groundwater draining the Grants Mineral Belt in New Mexico (USA), where both uraninite and coffinite occur in the ore deposits, represents a good estimate of the equilibrium silica activity for reaction (1). This inference was based on field evidence that is the common occurrence of uraninite with quartz in ore deposits, and the concentration of silica in

associated groundwaters. Thus, Langmuir estimated the standard free energy of formation of coffinite ($\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1891.17 \text{ kJ mol}^{-1}$) and of the enthalpy of formation ($\Delta_f H^\circ(\text{USiO}_4, \text{cr}) = -2001.21 \text{ kJ mol}^{-1}$). However, these values were corrected later by Langmuir and Chatham (1980). The corresponding corrected free energy and enthalpy values were $-1882.38 \text{ kJ mol}^{-1}$ and $-1990.33 \text{ kJ mol}^{-1}$, respectively (Langmuir, 1978). They also calculated the standard molar entropy of coffinite ($S_m^\circ = 117.15 \text{ J mol}^{-1} \text{ K}^{-1}$) as the sum of the molar entropies of quartz ($41.46 \text{ J mol}^{-1} \text{ K}^{-1}$) and uraninite ($77.03 \text{ J mol}^{-1} \text{ K}^{-1}$). These values are CODATA values (Cox et al., 1989), which were also used later by Grenthe (1992). In 1982, Hemingway performed thermodynamic calculations, also based on an estimate of the silica activity at equilibrium, for the coffinitization reaction ($(\text{H}_4\text{SiO}_4) = 2.6 \cdot 10^{-4}$), and derived a value for the standard free energy of formation of coffinite ($\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1886 \pm 20 \text{ kJ mol}^{-1}$). Hemingway indicated that the $\Delta_f G^\circ(\text{USiO}_4, \text{cr})$ value given by Langmuir (1978) was not consistent with his estimate for the equilibrium silicate activity for reaction (1). The NEA Thermodynamic Data Base (TDB) (Grenthe et al., 1992) accepted Langmuir's assumption for the average silica concentration ($10^{-3} \text{ mol L}^{-1}$) at equilibrium for reaction (1) but recalculated the $\Delta_f G^\circ(\text{USiO}_4, \text{cr})$ value and associated error using auxiliary data selected by the NEA-TDB. The obtained value, $\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1883.6 \pm 4.0 \text{ kJ mol}^{-1}$ was consistent with that of Hemingway. Considering that $S_m^\circ = 118 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$, the enthalpy of formation was calculated internally with the Gibbs-Helmholtz equation, leading to $\Delta_f H^\circ(\text{USiO}_4, \text{cr}) = -1991.326 \pm 5.367 \text{ kJ mol}^{-1}$. In 1997, Langmuir determined a value for the standard free energy of formation of amorphous coffinite based on chemical analyses of low Eh groundwater from coffinite-bearing ore zones (Cigar Lake, Canada and Palmottu, Finland). These waters were found to be at saturation with respect to $\text{UO}_2(\text{am})$, suggesting that the associated coffinite phase may be amorphous. This calculation is the basis for the determination of $\Delta_f G^\circ(\text{USiO}_4, \text{am}) = -1835.23 \text{ kJ mol}^{-1}$. Naturally occurring coffinite is generally so fine-grained that identification and characterization, as well as the determination of physical and chemical properties, is not possible (Deditius et al., 2012; Deditius et al., 2008). Based on Langmuir's interpretation of the geologic conditions of formation, the equilibrium constant of reaction (2) increases by almost 8 orders of magnitude if the coffinite is considered to be amorphous rather than crystalline:

Nevertheless, this $\Delta_f G^\circ(\text{USiO}_4, \text{am})$ value was mentioned, but not selected for the NEA Thermodynamic Data Base II (Guillaumont et al., 2003) because the solid phase was not identified; thus, there was no established

composition; specifically, the presence of molecular water in the structure was not determined. Hence, it is not possible to report a $\Delta_f G^\circ$ value for this amorphous coffinite.

Fleche, (2002) derived thermodynamical functions for coffinite using *ab initio* calculations. The $\Delta_f H^\circ(\text{USiO}_4, \text{cr})$ value obtained reaches $-2021.7 \pm 30.3 \text{ kJ mol}^{-1}$, using $S_m^\circ = 124.3 \pm 6.6 \text{ J mol}^{-1} \text{ K}^{-1}$ also given in Fleche (2002), it was possible to deduce $\Delta_f S^\circ(\text{USiO}_4, \text{cr}) = -355 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$, then the Gibbs-Helmholtz equation led to the determination of $\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1915.9 \pm 32.4 \text{ kJ mol}^{-1}$.

By extrapolation from the uranothorite solid-solution binary, Szenknect et al. (2013) determined a value for the equilibrium constant of reaction (2): $\log *K_S^\circ(\text{USiO}_4, \text{cr}) = -6.1 \pm 0.2$, which was higher than the estimate based on Langmuir's assumptions of geologic conditions. Thermodynamic calculations based on this extrapolation and auxiliary data from the NEA TDB II (Guillaumont et al., 2003) resulted in a standard free energy of formation for coffinite ($\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1872.6 \pm 3.8 \text{ kJ mol}^{-1}$). Recently, Guo et al. (2015) determined experimentally the enthalpy of formation of coffinite by high temperature oxide melt solution calorimetry. They found that coffinite is metastable with respect to a mixture of uraninite and quartz by $25.6 \pm 3.9 \text{ kJ mol}^{-1}$. From this $\Delta_{r,ox} H^\circ$ value, they calculated the standard enthalpy of formation of coffinite $\Delta_f H^\circ(\text{USiO}_4, \text{cr}) = -1970.0 \pm 4.2 \text{ kJ mol}^{-1}$. Considering that $S_m^\circ = 118 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$ (selected by the NEA), the free energy of formation was calculated internally using the Gibbs-Helmholtz equation: $\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1862.3 \pm 7.8 \text{ kJ mol}^{-1}$.

Because of the pressing need for more accurate thermodynamic data, such as $*K_S^\circ$, $\Delta_f G^\circ$, $\Delta_f H^\circ$, $\Delta_f S^\circ$, a number of investigators have sought to obtain pure synthetic coffinite, but only few have succeeded (Costin et al., 2011; Fuchs and Gebert, 1958; Fuchs and Hoekstra, 1959; Hoekstra and Fuchs, 1956; Labs et al., 2014; Pointeau et al., 2009). The synthetic coffinite was always obtained by minor modifications of the initial protocol proposed by Fuchs and Hoekstra (1959). This seminal publication already showed the need for several steps to buffer the pH prior to heat treatment and the difficulty of maintaining a very narrow pH range for formation. Nevertheless, the samples obtained were mixtures of phases, mainly composed of USiO_4 , UO_2 and SiO_2 . An optimized protocol was used to obtain pure coffinite that was fully characterized before and after under-saturated experiments. The purpose of this study is to determine the solubility of coffinite and to use these results to calculate the standard free energy of formation of coffinite, which enables one to infer the relative stability of coffinite and uraninite as a function of groundwater

composition. The results are interpreted in terms of likelihood of the coffinitization process of SNF and compared to field evidence, such as the occurrence of associated uraninite and coffinite in uranium sandstone deposits.

2. EXPERIMENTAL METHODS

2.1. Synthesis of solid phases

A solution of uranium tetrachloride was prepared by dissolving uranium metal fragments provided by CETAMA (Analytical Methods Committee, CEA, France) in cooled 6 mol L⁻¹ HCl according to the method of Dacheux et al. (1995). The hot solution was then centrifuged at 12000 rpm during 15 min while slow H₂ degassing from black residues was observed. The centrifuged solution was stored under Ar atmosphere, then the final concentration was determined by ICP-AES. The other reactants (Na₂SiO₃, NaHCO₃ and NaOH) were used as supplied by Sigma-Aldrich and were of analytical grade.

Coffinite (USiO₄) powder was synthesized under hydrothermal conditions by a modification of previous procedure (Fuchs and Gebert, 1958; Fuchs and Hoekstra, 1959; Hoekstra and Fuchs, 1956). 20 mL of out-gassed water (boiled for 1 hour and cooled under nitrogen stream) containing 6 mmol of UCl₄ was mixed to 20 mL of a solution of Na₂SiO₃ (6 mmol + 10% excess) resulting in a greenish solution. Afterward, the pH was raised to 11.4 ± 0.1 by adding 8 mol L⁻¹ NaOH, buffered to 8.7 by adding NaHCO₃, poured in a 50-mL Teflon container that was placed in acid digestion bomb. All these reactions were performed in a glove box filled with Ar and free from oxygen (less than 2 ppm). The digestion bomb was then heated at 250 °C for 16 days. At the end of the reaction, the final product was separated by centrifugation twice with water then with ethanol and dried overnight in the glove box at room temperature.

In order to evaluate whether the byproducts (oxide and amorphous silica) control the concentrations in solution, another reaction was performed in order to synthesize only these side products. Basically, the same procedure was followed; however, the pH was raised to 12.5 before buffering the pH to 8.7. Mesbah et al. (2015) determined the optimal conditions in terms of pH, T, heating time and molar ratio of U:Si for the hydrothermal synthesis of coffinite. The yield of coffinite was found to decrease drastically when the pH of the initial mixture of reactants was lower than 10 or higher than 12. This result was attributed to the formation of colloidal coffinite precursors in a narrow range of pH. Without these colloidal precursors, acting as nuclei for the crystallization of coffinite, the kinetics of coffinite precipitation was too slow to allow the precipitation of a sufficient amount of coffinite.

2.2. Coffinite purification

The powders were purified prior to dissolution experiments in order to eliminate UO_2 and SiO_2 that have been retained in the synthesized powders. The protocol for purification developed for uranothorite solid solutions (Clavier et al., 2013) yielded very high losses for coffinite; thus, the protocol was modified. One purification cycle consisted of several steps: *i.*) 100 mg of solid were placed into contact with 50 mL of 10^{-2} mol L^{-1} HNO_3 for 3 to 5 days; *ii.*) the solid was centrifuged and washed three times with deionized water; *iii.*) the remaining solid was dispersed in 50 mL of 10^{-2} mol L^{-1} KOH for 3 to 5 days, and then washed three times with deionized water. Two or three purification cycles were performed, and the resulting samples were dried overnight in an oven at 60°C .

2.3. Characterization of the solids

All samples were analyzed by powder X-rays diffraction (PXRD) using the Bruker D8 advance diffractometer equipped with a lynx eye detector and $\text{K}_\alpha(\text{Cu})$, $\lambda = 1.54118 \text{ \AA}$. All the data were collected in the reflection geometry in the angular range from 5° to 100° for a total counting time of about 3 hours per sample. Mainly, two phases were detected, tetragonal coffinite (USiO_4 ; I_4/amd) and cubic urania (UO_2 ; $\text{Fm}\bar{3}\text{m}$). The data were refined using Fullprof_suite (Frontera and Rodriguez-Carvajal, 2003) by applying the Rietveld method and using the Thomson Cox profile function (Thompson et al., 1987). Pure silicon was used as a standard to determine instrumental parameters. Zero shift, unit cell parameters, overall displacement, preferred orientation and an anisotropic size model for the microstructural characteristics were considered for all refinements. The obtained unit cell parameters and estimated amounts of each phase are reported in Table 2, while an example of the refinement results for pure coffinite is given in Figure S1 of the supplementary data showing the observed, calculated and difference patterns.

Low magnification transmission electron microscopy (TEM) analyses were conducted at 200 kV on a Jeol 200CX TEM equipped with a Photonic-Science camera. Samples were first dispersed in absolute ethanol then one drop was deposited on carbon coated grid prior to analysis.

Scanning electron microscopy (SEM) analyses were conducted using an FEI Quanta 200 electron microscope equipped either with an Everhart-Thornley detector (ETD) or a backscattered electron detector (BSED) in high vacuum conditions with a low accelerating voltage (2.0 - 3.1 kV). These conditions produced high-resolution images. Small powder samples were then directly analyzed without any additional preparation. X-ray energy dispersive

spectroscopy (EDS) analyses were performed using a Bruker AXS X-Flash 5010 detector coupled to the SEM device. In order to quantify the elemental percentages, the powders were first embedded in epoxy resin. The surface of the samples was then polished to optical grade and then carbon coated. Experimental data were finally collected from 100 different locations using UO_2 and albite ($\text{NaAlSi}_3\text{O}_8$) as standards.

The specific surface area of the solids was measured by nitrogen absorption at 77K using the Brunauer–Emmett–Teller (B.E.T.) method with a TRISTAR 3020 (Micromeritics) apparatus.

2.4. Solubility experiments

The dissolution experiments were performed in air or under anoxic conditions by flushing the chamber with argon. As-prepared, purified samples were used for the dissolution experiments. Respectively, 100 mg or 30 mg of as-prepared or purified samples were introduced in sealed polytetrafluoroethylene (PTFE) jars (Savillex) and placed in contact with 30 mL of $0.10 \text{ mol} \cdot \text{L}^{-1}$ HCl solution prepared by volumetric dilution of concentrated HCl (37 %) from Sigma-Aldrich with deionized water. The solution was then out-gassed for anoxic experiments by boiling it for 2 hours and cooling under bubbling with Ar 6.0. The 0.1 M HCl was then stored for several days in the glove box before being used in the dissolution experiments in order to reach equilibrium with the $\text{O}_2(\text{g})$ partial pressure. Using the Henry's law constant provided in the ANDRA thermodynamic database *thermochimie-PHREEQC_SIT_v9* (Giffaut et al., 2014): $\log K_H = 10^{-2.900}$ and the $\text{O}_2(\text{g})$ partial pressure measured in the glove box ($2 \cdot 10^{-6}$ bar), the initial $\text{O}_2(\text{aq})$ concentration in the HCl solution did not exceed $2.5 \cdot 10^{-9} \text{ mol L}^{-1}$. The dissolution reactors were then filled with HCl solution and closed in the glove box. All the experiments were performed in duplicate at $298 \pm 2 \text{ K}$. The dissolution continued for up to several months. During this time, the reactors were stirred at least twice a week and opened only to sample the solution. The dissolution of the solid was then monitored through regular pH measurements using a Metrohm combination-glass electrode calibrated against pH buffers (Inlab® Solutions, Mettler Toledo, pH = 2.00; 4.01 and 7.00 at 25°C), whereas uranium and silicon concentrations in the leachate were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). For each sample, 2 mL of the leaching solution was withdrawn and centrifuged at 12,000 rpm for 2 min. These conditions ensured the removal of colloids larger than 10 nm. Then 1.8 mL of the solution was diluted in 4.2 mL of 0.2 mol L^{-1} HNO_3 solution for further ICP-AES analyses using a Spectro Arcos EOP device. For this purpose, the spectrometer was calibrated with SPEX standard solutions. Finally, fresh HCl solution was introduced into the reactors in order to maintain a constant volume

of solution in contact with the solid. The volume of the gas phase in the dissolution reactor corresponded to the internal volume of the Teflon screw cap that did not exceed 3 cm³. Thus, each time the reactor was opened in the glove box, the renewed volume of gas contained about 2.5 10⁻¹⁰ moles of O₂(g). The maximum number of samples reached 30, the maximum amount of O₂(g) introduced into the system by solution sampling thus did not exceed 7.5 10⁻⁹ moles. The elementary uranium concentration in solution at steady state was in the range between 6.4 10⁻⁵ and 2.6 10⁻³ mol L⁻¹. Assuming that the oxidation of aqueous U(IV) by O₂ in the system was complete and that the 7.5 10⁻⁹ moles of oxygen entering the system were consumed by U⁴⁺ oxidation in solution, 5 10⁻⁷ mol L⁻¹ of UO₂²⁺ must have formed. This concentration represents a maximum of 0.8 % of the elemental concentration of U. A calculation was performed using the PHREEQC 2 software and the thermochimie_PHREEQC_SIT_v9 database (selected reaction constants are indicated in Table 1) in order to estimate the oxygen fugacity of the gas phase in equilibrium with a HCl 0.1 mol L⁻¹ solution containing 10⁻⁴ mol L⁻¹ of uranium. Based on this calculation the U(V) over U(IV) ratio did not exceed 1 mol. %. The calculations (see Figure S2 of the supporting data) indicated that the f(O₂) did not exceed 10⁻⁶⁹ atm. As stated by Rai et al. (1990), such a low value for the O₂(g) fugacity ensures that the uranium remains tetravalent. This fugacity was then used in the calculation of the speciation of the dissolved uranium. For all subsequent calculations, the ratio [UO₂²⁺]/[U] ≈ 1% was used.

3. RESULTS

3.1. Characteristics of the solids

PXRD patterns of synthesized and pure coffinite samples are shown in Figure 1. All of the samples were prepared for 16 days at pH = 11.2 before the buffering step at T = 250°C. Three phases were identified: coffinite, nanoscale crystals of UO₂ and amorphous SiO₂ (the latter being identified by SEM and X-EDS measurements). The specific surface areas of the as-prepared sample and the pure coffinite were not significantly different and reached 38 ± 2 m² g⁻¹. Additionally, the PXRD pattern of the sample obtained at pH = 12.5, before the buffering step, clearly shows the presence of UO₂ nanoparticles as the only crystalline phase. For the refinement of the X-ray data, two phases were considered: tetragonal USiO₄ (*I4₁/amd*): **a** = 6.9920(1) Å, **c** = 6.2633(1) Å and V = 306.20(1) Å³ and isometric UO₂ (*Fm $\bar{3}$ m*): **a** = 5.4329(1) Å and V = 160.36(1) Å³. The amount of USiO₄ vs. UO₂ was quantified based on PXRD data from the Rietveld refinement (Table 2). The complete characterization of the synthesized solids has been reported by

Mesbah et al., (2015) in order to confirm that only U(IV) was present in the solids. In addition, EXAFS and Raman spectroscopies were used to confirm that only U(IV)-based compounds were obtained from the synthesized and purified powders, consistent with previous reports on coffinite (Clavier et al., 2014; Dreissig et al., 2011).

TEM images and associated electron diffraction patterns of a coffinite grain isolated in the pure coffinite sample obtained after three purification cycles and one coffinite grain surrounded by uranium oxide nanoparticles in the as-prepared sample are shown, in Figure 2 (a) and (b), respectively. These images show well crystallized coffinite grains, 200 to 400 nm. The crystallites (*i.e.*, the length of coherent domains determined by Rietveld refinement), which formed the grains, were ~80 nm, confirming the polycrystalline nature of the coffinite grains. Grain size can affect the thermodynamic properties of crystalline materials (Castro, 2013), the particle size of this synthetic sample is similar to that of natural coffinite and that produced by the corrosion of spent nuclear fuel (Bros et al., 2003; Deditius et al., 2012; Deditius et al., 2008; Janeczek, 1999; Janeczek and Ewing, 1992b; Jensen and Ewing, 2001; Pownceby and Johnson, 2014); thus, the data obtained here are representative of the occurrence of coffinite in nature and as an alteration product of UO₂ in spent nuclear fuel. The TEM images of the as-prepared samples also revealed the presence of uranium oxide nanoparticles, 3 to 5 nm in diameter. The length of coherent domains determined by Rietveld refinement for the UO₂ phase reached 4 nm. This analysis indicated that diffraction occurs from essentially the entire particle. These structural observations are consistent with the structural model proposed by Schofield et al. (2008) for biogenic uraninite nanoparticles of ~2 nm. They showed through synchrotron powder diffraction and EXAFS, that UO₂ sublattice is preserved in the biogenic sample (as in our nanoparticles), and they assumed that structural distortion is local, mostly occurring in the periphery of the particles. Another important result is that such biogenic nanoparticles are structurally homologous to stoichiometric UO_{2.00}. One proposed explanation is that hyperstoichiometric UO_{2+x} is stabilized by the presence of U(VI) impurities that are exsolved from the bulk UO₂ as a nanoscale phase. Such phase segregation may not be possible in nanoparticles because they are too small. However, we cannot exclude this possibility because the size of the nanoparticles in the as-prepared sample is slightly greater than that of biogenic nanoparticles, and the mechanism of formation is not promoted by biogenic processes that could prevent the incorporation of U(VI).

The average U/Si mole ratio determined by X-EDS corresponding to each sample is reported in Table 2. The distributions of U/Si mole ratios for the as-prepared, purified and pure coffinite samples are shown in Figure 3 (a), (b) and (c), respectively. The distribution of the U/Si mole ratios corresponding to the as-prepared sample was found to

be rather wide (with values ranging from 0.13 to 1.68), which reflects the presence of UO_2 and amorphous SiO_2 . The composition of the mixture of three components was estimated by both XRD and EDS analysis. The molar ratios are: 59 mol. % of USiO_4 , 24 mol. % of UO_2 and 16 mol. % of amorphous SiO_2 . After three purification cycles (each purification cycle consisted of the following steps: *i.*) the solid was placed in contact with HNO_3 then washed with deionized water; *ii.*), the remaining solid was placed in contact with KOH and washed three times with deionized water) the distribution of U/Si mole ratios was narrowed. After this treatment, the average U/Si mole ratio was 1.01 ± 0.08 , which is that of the pure coffinite. An SEM micrograph of the pure coffinite is shown in Figure 3 (c). For the sample that underwent only two purification cycles, the distribution of the U/Si mole ratio, as determined by X-EDS, shifted towards values lower than 1, indicating the presence of amorphous SiO_2 , also confirmed by SEM (Figure 3 (b)). Throughout the paper, the $\text{USiO}_4 + \text{SiO}_2$ assemblage obtained after two purification cycles is identified as a “purified sample”. These observations clearly show that three purification cycles are required in order to remove the entire amount of oxide by-products through dissolution and that the resulting sample was finally single-phase coffinite.

3.2. Dissolution experiments

The evolution of elemental concentrations obtained during dissolution experiments at 298 K are presented in Figure 4. For the experiments completed under an Ar atmosphere, a plateau was reached within 30 to 50 days of leaching time. Under these conditions, the system was considered to be at thermodynamic equilibrium when at least three consecutive analyses were in the range of two standard deviations. The composition of the solution at saturation with respect to the solid phase was then calculated as the average of consecutive analyses that were not significantly different from each other. Finally, the average concentrations of the solutions at thermodynamic equilibrium with the solids, as well as the average pH of each experiment, are given in Table 4. The error associated with elemental concentrations and pH indicated in Table 4 represents the experimental error, as it resulted from the variability observed between at least three consecutive analyses of the solution at steady-state.

All samples, except the pure coffinite exhibited nonstoichiometric dissolution. For example, dissolution tests of the as-prepared sample showed a U/Si mole ratio of 5 during the first days of dissolution (Figure 4 (a)) that clearly indicates the preferential dissolution of the UO_2 nanoparticles as compared with SiO_2 , and this was confirmed by the evolution of U and Si concentrations for the $\text{UO}_2 + \text{SiO}_2$ assemblage (Figure 4 (d)). Under the experimental

conditions considered (0.1 mol·L⁻¹ HCl, Ar atmosphere), the dissolution of UO₂ nanoparticles was rapid and led to U concentration higher than 10⁻³ mol L⁻¹ in solution after only one day. However, after 60 days of leaching, the dissolution of the as-prepared sample became virtually stoichiometric (U/Si = 1.4). Then, the U and Si concentrations reached a constant value after almost 70 days. Importantly, the elemental concentrations obtained at steady-state for the as-prepared sample (UO₂ + SiO₂ + USiO₄) and the pure coffinite are very close. Consequently, we assume that the coffinite phase controlled this equilibrium. Thus, the solubility of the coffinite was reached from over-saturated conditions, whereas it was reached from under-saturated conditions for the pure coffinite solubility experiment (Figure 4 (b)). The purified sample (USiO₄ + SiO₂) exhibited a different trend than the as-prepared sample due to the absence of UO₂ nanoparticles (Figure 4 (c)). The U/Si molar ratio was lower than 1 for the entire duration of the experiment. The Si concentration increased during the first 30 days of dissolution, then reached a constant value. Simultaneously, the uranium concentration decreased and stabilized. Assuming that the coffinite phase controlled the equilibrium, the rapid dissolution of amorphous silica led to over-saturated conditions for USiO₄. In the case of the as-prepared sample, these oversaturation conditions were imposed by the faster dissolution of UO₂ nanoparticles. Oversaturation conditions were created by the faster dissolution of amorphous SiO₂ in the case of the purified sample. In both cases, the resulting uranium concentration decreased. A dissolution test of the UO₂+SiO₂ assemblage (Figure 4 (d)) indicated an initial rapid dissolution of UO₂ nanoparticles and amorphous SiO₂ followed by a steady-state concentration. The solubility of amorphous SiO₂ was reached after 50 days based on the value provided by the thermochimie_PHREEQC_SIT_v9 database: (log *K_S[°](SiO₂,am) = -2.710). This could be the explanation for the constant silica concentration. The uranium concentration also stabilized at a value of 2.6 10⁻³ mol L⁻¹ after 50 days of dissolution, which was more than one order of magnitude higher than for the phases assemblages containing coffinite. This value corresponds to a solution oversaturated with respect to UO₂(cr), with a saturation index,

$$\text{SI} = \log \left(\frac{\text{Ion activity product}}{K_S^\circ} \right), \text{ of about 4 (based on the NEA-TDB value for the solubility product), but}$$

undersaturated with respect to UO₂(am), with a saturation index of -2.4 (based on the NEA-TDB value for the solubility product). As previously stated in the review of Neck and Kim (2001), values reported in the literature for solubilities of UO₂·xH₂O(s) are extremely scattered. These discrepancies are ascribed either to different redox conditions or to different degrees of crystallinity (Casas et al., 1998; Rai et al., 1990). The uranium oxide phase in our samples cannot be described as amorphous, as the PXRD patterns showed broad diffraction maxima characteristic of

nanometric crystals. A possible effect of grain size on solubility was proposed by Casas et al. (1998) based on the relation established by Stumm et al., (1992). Small crystals are thermodynamically less stable and have a greater solubility than larger ones. This could possibly explain the high uranium concentration observed for the UO_2+SiO_2 mixture. More importantly, the role of silicates in this experiment is not taken into account in the evaluation of tetravalent uranium speciation. The existence of U(IV)-Si(IV) complexes is undocumented, but they could play an important role in coffinite formation (Mesbah et al., 2015). Due to similar charge and ionic radius, the analogy between U(IV) and Th can be made. Peketroukhine et al. (2002) showed that the solubility of amorphous thorium hydroxide was increased in the presence of soluble silicates in 0.1 M NaClO_4 and at pH 6-12. They reported a solubility of 10^{-6} to 10^{-5} mol L^{-1} Th(IV) respectively at pH = 8 and 10 in the presence of 0.14 mol L^{-1} Na_2SiO_3 . This increase was attributed to the formation of colloids of thorium hydroxo-silicate whose solubility was higher than that of $\text{ThO}_2 \cdot n\text{H}_2\text{O}$. Rai et al. (2008), reported similar results. The interpretation of their data required the existence of a mixed thorium hydroxo-silicate complex, $\text{Th}(\text{OH})_3(\text{H}_3\text{SiO}_4)_3^{2-}$ whose structure was determined by DFT calculations. If the existence of such mono- or polynuclear complexes could be demonstrated for uranium, this would be a serious limitation on the interpretation of uranium oxide solubility experiments performed without dissolved silicates.

The dissolution experiments were also completed under air. Under these conditions, tetravalent uranium is usually found to be unstable. Thus, the impact of oxygen partial pressure on the dissolution of coffinite was evaluated only from a kinetic point of view by the comparison of the normalized dissolution rates obtained under the anoxic condition with those obtained under air. The influence of oxygen partial pressure on the uranium chemistry at the solid/liquid interface or in solution has extensively demonstrated during the dissolution or leaching of UO_2 . The corrosion process of UO_2 in an oxic environment involves the complete conversion of tetravalent uranium into hexavalent UO_2^{2+} and the formation of secondary phases (Baker, 2014; Maher et al., 2012). The rate of this alteration process strongly depends on the activity of dissolved O_2 (Amme et al., 2005; Shilov et al., 2007); thus, on the partial pressure of $\text{O}_2(\text{g})$. Jerden and Sinha (2003), studied the alteration of primary ore samples from Coles Hill deposit (Virginia, USA) by oxygenated recharge water (from 4 to 8 mg L^{-1} dissolved O_2). The process by which uranium is released from coffinite (most abundant U^{4+} mineral in the Coles Hill deposit) to groundwater through the oxidation and dissolution of the primary minerals occurred within 4 to 5 weeks in highly fractured zones. However, the kinetics of this process had never been studied using synthetic, pure coffinite.

The release of an element i from the material is usually described by its normalized mass loss, $N_L(i)$ (g m^{-2}) and by the initial normalized dissolution rate $R_{L,0}(i)$ ($\text{g m}^{-2} \text{d}^{-1}$), calculated as follows:

$$N_L(i) = \frac{\Delta m_i}{f_i S} = \frac{C_i V}{f_i S} \quad \text{and} \quad R_{L,0}(i) = \frac{dN_L(i)}{dt}, \quad (3)$$

where Δm_i (g) is the mass of element i released in solution; C_i (g L^{-1}) is the elementary concentration; V (L) is the volume of the dissolution medium; S (m^2) is the surface area of the solid determined by the B.E.T. method and f_i (dimensionless) is the mass fraction of i in the solid.

Thereafter, the dissolution reaction is considered to be congruent when all of the normalized dissolution rates are identical (*i.e.* when all the elements were released with the same ratios as the stoichiometry of the initial material). The initial normalized dissolution rates determined for the pure USiO_4 sample and the $\text{UO}_2 + \text{SiO}_2$ assemblage in out-gassed 0.1 mol L^{-1} HCl solution, either under Ar atmosphere or in air, are summarized in Table 3. The dissolution of USiO_4 was found to be congruent regardless of the dissolution conditions. The normalized dissolution rates of both U and Si increased by one order of magnitude in HCl solution equilibrated with air (from $3 \cdot 10^{-5}$ to $3.8 \cdot 10^{-4} \text{ g m}^{-2} \text{d}^{-1}$) as compared with the experiments performed under an argon atmosphere, while the normalized dissolution rates for UO_2 increased by a factor of almost 20 (from $6 \cdot 10^{-4}$ to $1.1 \cdot 10^{-2} \text{ g m}^{-2} \text{d}^{-1}$). On the contrary, and as expected, the kinetics of SiO_2 dissolution was not significantly affected by the increase of $p\text{O}_2$ and $p\text{CO}_2$. To our knowledge, there is no previous study of the kinetics of dissolution of synthetic coffinite. The dissolution rate of UO_2 nanoparticles in the $\text{UO}_2 + \text{SiO}_2$ sample under reducing conditions can be compared with values obtained by Bruno et al. (1991) for $50 \text{ }\mu\text{m}$ grains size $\text{UO}_{2.001}$ (exhibiting low specific surface area of $0.201 \text{ m}^2 \text{g}^{-1}$) and by Ulrich et al. (2008) for biogenic nanoparticles of $\text{UO}_{2.00}$ (exhibiting a high specific surface area, $50.14 \text{ m}^2 \text{g}^{-1}$). Interestingly, the dissolution rates of UO_2 at pH 1 under reducing conditions, calculated by using the rate laws provided either by Bruno et al. (1991) or Ulrich et al. (2008) are close (0.08 and $0.4 \text{ g m}^{-2} \text{d}^{-1}$, respectively) and several orders of magnitude higher than the value determined in our study ($6.0 \pm 0.8 \cdot 10^{-4} \text{ g m}^{-2} \text{d}^{-1}$). This decrease in the normalized dissolution rate indicates that under reducing and acidic conditions, the amorphous SiO_2 in which UO_2 nanoparticles are embedded could act as a passive layer, preventing protons access to the reactive surface sites. As noted by Amme et al. (2005), coffinite is susceptible to release of uranium in oxygenated water in a manner similar to that of UO_2 . However, the normalized dissolution rate of coffinite was at least one order of magnitude lower than that for UO_2 . As proposed by Janeczek and Ewing (1992b), the replacement of coffinite by uraninite may be written as:

Following reaction (4), higher values of oxygen fugacity might favor the formation of non-stoichiometric uranium dioxide as an intermediate solid phase, which would be then dissolved after complete oxidation of U(IV) to U(VI). Thus, the steady-state concentration of uranium depends on the rate of formation of a partially oxidized UO_{2+x} from coffinite (following reaction 4) and the rate of dissolution of the intermediate UO_{2+x} .

The PXRD patterns of USiO_4 sample measured after dissolution either under Ar atmosphere or in air are shown in Figure 5. In both cases, the PXRD patterns exhibit the characteristic XRD diffraction maxima of coffinite with no evidence of additional secondary phases. Under these conditions, the solubility constant of USiO_4 was determined from the elemental concentrations measured in solution under Ar atmosphere and the pH at equilibrium that was found to range from 1.09 to 1.33 (Table 4).

4. DISCUSSION

4.1. Thermodynamic analysis

The determination of the solubility product is based on the data obtained for each system under steady-state conditions. Due to the oxidation of tetravalent uranium to hexavalent uranyl species during the dissolution, the results obtained in air were not considered in the thermodynamic analysis. For the oxygen-free experiments, the system was considered to be at thermodynamic equilibrium when at least three consecutive analyses were in the range of two standard deviations. The composition of the solution at saturation with respect to the solid phase was then calculated as the average of consecutive analyses that were not significantly different from one another. Finally, the average concentrations of the solutions at thermodynamic equilibrium with the solids, as well as the average pH values used in these calculations are compiled in Table 4. The errors associated with elemental concentrations and pH indicated in Table 4 represent the experimental error as calculated from the measured values among at least three consecutive analyses of the system at steady-state.

The thermodynamic equilibrium between coffinite and the solution is written following reaction (2). Thus, the solubility product of coffinite was calculated using the general equation:

$$^*K_s^\circ(\text{USiO}_4) = (\text{U}^{4+})(\text{H}_4\text{SiO}_4)(\text{H}^+)^{-4} \quad (5)$$

where () denotes the activity of ions in solution at equilibrium.

The solubility product calculated at $I = 0$ can be deduced from the solubility product determined at $I = 0.1 \text{ mol L}^{-1}$ following:

$$^*K_S^{\circ}(\text{USiO}_4) = (\gamma_{\text{U}^{4+}} m_{\text{U}^{4+}}) (\gamma_{\text{H}_4\text{SiO}_4} m_{\text{H}_4\text{SiO}_4}) (\gamma_{\text{H}^+} m_{\text{H}^+})^{-4} = \prod_i (\gamma_i^{\nu_i})^{\nu_i} K_S(\text{USiO}_4) \quad (6)$$

where γ_i denotes the activity coefficient for ion i , ν_i is the stoichiometric coefficient, and m_i (mol kg^{-1}) is the molality of i .

From the average elemental concentrations, pH value and the calculated oxygen fugacity $f(\text{O}_2)$ (10^{-69} atm), in the system at equilibrium, the molalities were calculated with the geochemical speciation model PHREEQC-2 (Parkhurst and Appelo, 1999). The solubility product calculations accounted for the aqueous complexation reactions listed in the Table 1. The ANDRA Thermochimie thermodynamic database, recently available for the PHREEQC software, was used. In the ANDRA Thermochimie database, the existence of $\text{U}(\text{OH})_2^{2+}$ and $\text{U}(\text{OH})_3^{3+}$ and the associated equilibrium constants from Neck and Kim (2001) are taken into account. The values selected by the NEA-TDB (Grenthe et al. 1992; Guillaumont et al., 2003) are systematically included in this database and recalculated for internal consistency. The values of the equilibrium constants and solubility products of the ANDRA Thermochimie database can be compared to other sources in Table 1. The speciation calculations indicate that the U^{4+} species represented 29 to 34 mol. % of the tetravalent uranium under the experimental conditions, whereas $\text{U}(\text{OH})_2^{2+}$, $\text{U}(\text{OH})_3^{3+}$, and UCl^{3+} species were in the same range, between 20 and 25 mol. %. UO_2^{2+} molality depended on the $f(\text{O}_2)$ selected and reached almost 1 mol. %. As the estimate of $m_{\text{U}^{4+}}$ was affected by the experimental uncertainty of pH, the speciation calculations were made at a maximum and a minimum pH value, defined as the average pH value ± 2 standard deviations in order to estimate a confidence interval for $m_{\text{U}^{4+}}$. The estimate of $m_{\text{H}_4\text{SiO}_4}$ was not affected by the uncertainty of the pH values, as H_4SiO_4 is the predominant species in this range of pH. The uncertainty in the evaluation of $m_{\text{H}_4\text{SiO}_4}$ thus depends only on the variability observed experimentally for the Si concentration at equilibrium between successive measurements. Finally, the uncertainty in the determination of *K_S was estimated by propagating the uncertainties on $m_{\text{U}^{4+}}$, $m_{\text{H}_4\text{SiO}_4}$, and m_{H^+} .

The activity corrections were performed using the specific ion interaction equation implemented in PHREEQC-2:

$$\log(\gamma_i) = -\frac{A z_i^2 \sqrt{I_m}}{1 + B a_i \sqrt{I_m}} + \sum_j \varepsilon(i, j, I_m) m_j \quad (7)$$

where A and Ba_i are constants that depend on the temperature and are defined in the database (at 25°C and 1 bar, $A = 0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $Ba_i = 1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$), z_i corresponds to the charge of the ion, $I_m (\text{mol kg}^{-1})$ is the ionic strength of the solution. The calculated activities of U^{4+} and H_4SiO_4 at equilibrium, as well as the solubility constant extrapolated to standard conditions, $*K_S^\circ$, are listed in Table 4.

The $\log *K_S^\circ$ values obtained from the three phase assemblages that contained USiO_4 range from -4.63 to -5.34. The only value that was found to be significantly different from others was obtained for the phase assemblage $\text{USiO}_4 + \text{SiO}_2 \#2$ in Table 4. This difference resulted from a significantly higher pH value at equilibrium. As the presence of coffinite was not detected in the PXRD pattern of the $\text{UO}_2 + \text{SiO}_2$ assemblage at the end of the dissolution experiment, the value of $*K_S$ was not calculated. However, considering the values of the activities of U^{4+} and H_4SiO_4 at steady state, supersaturated conditions should have been reached relative to coffinite. The value determined for the pure coffinite sample is: $\log *K_S^\circ(\text{USiO}_4, \text{cr}) = -5.25 \pm 0.05$. This value was selected afterwards as it corresponds to the pure coffinite sample, the solubility product can thus be attributed unambiguously to crystalline coffinite. This $\log *K_S^\circ(\text{USiO}_4, \text{cr})$ value is higher than that estimated from solubility studies developed from uranorthorite solid solutions: $(\log *K_S^\circ(\text{USiO}_4, \text{cr}) = -6.1 \pm 0.2)$ (Szenknect et al., 2013). However, the thermodynamic calculations of that study were performed using the Lawrence Livermore National Laboratory (LLNL) database, whereas ANDRA Thermochimie database has been used in the present work. The main difference between the databases is the value of the equilibrium constant for the reaction: $\text{U}^{4+} + 4 \text{OH}^- \rightleftharpoons \text{U}(\text{OH})_4 (\text{aq})$, $\log K^\circ = 51.43$ for LLNL-TDB; whereas, it is 46.0 in the ANDRA Thermochimie-TDB. This difference has a strong impact on the uranium speciation that led to a discrepancy of almost 1 log unit in the solubility product. Thus, it should be stressed here, that the choice of the thermodynamic database is a key step in the evaluation of standard equilibrium constant and that the estimate of error does not take into account the uncertainties on the thermodynamic constants implemented in the database. Thus, using the solubility product reported here for coffinite with a different set of thermodynamic data will lead to inconsistent and erroneous results.

The variation of the standard Gibbs energy associated with reaction (2) was then determined as:

$$\Delta_r G^\circ(T) = -RT \ln *K_S^\circ(T) \quad (8)$$

where R is the universal gas constant and T is the absolute temperature.

The $\Delta_r G^\circ(298\text{ K})$ for reaction (2) determined in this study and the $\Delta_f G^\circ$ of the species involved in reaction (2) taken from the NEA TDB II (Table S1 of the supporting information) were used in the Hess's law (Eq. 9) to determine the standard molar Gibbs energy of formation of coffinite:

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ \quad (9)$$

The standard Gibbs energy of formation of coffinite from the elemental concentrations in solution was found to be: $\Delta_f G^\circ(298\text{ K}) = -1867.6 \pm 3.2\text{ kJ mol}^{-1}$. As already mentioned, very few reliable thermodynamic data related to coffinite formation or solubility are reported in the literature. Table 5 provides a comparison of the thermodynamic data reported in this work to previously published data.

The relative stability of coffinite as compared with the binary mixture of the oxides can be derived from the $\Delta_{r,ox} G^\circ(T)$ value associated with reaction (10)

The value of $\Delta_{r,ox} G^\circ(298\text{ K})$ was calculated using $\Delta_f G^\circ$ of coffinite determined in this study and those of uraninite and quartz (Table S1 of the supporting information). The obtained positive value reached $20.6 \pm 5.2\text{ kJ mol}^{-1}$, which indicates unambiguously that coffinite is less stable than a quartz + uraninite mixture at 298 K. This is in agreement with Hemingway (1982), who pointed out that coffinite must be less stable than the mixture of binary oxides in light of the natural occurrence of coffinite and the paragenetic sequence described by Cuney in 1978 (Cuney, 1978). The thermal stability of coffinite is not well known. Fuchs and Hoekstra (1959) placed the upper limit of coffinite stability as compared with uraninite and amorphous silica at 1273 K. On the basis of this observation, Hemingway (1982) estimated the Gibbs free energy related to the formation of coffinite from oxides at 298.15 K, assuming that the $\Delta_{r,ox} G^\circ$ value of reaction (10) is equal to zero at 1273 K and using the heat capacities of quartz and uraninite to approximate the heat capacity of coffinite between 298 and 1273 K, as well as auxiliary thermochemical data from Robie et al. (1979). However, neither the $\Delta_{r,ox} G^\circ(298\text{ K})$ value of Hemingway ($2.12 \pm 8.01\text{ kJ}\cdot\text{mol}^{-1}$) nor the value selected in the NEA TDB ($4.52 \pm 6.01\text{ kJ}\cdot\text{mol}^{-1}$) were accurate enough to reach a conclusion regarding the relative stability of coffinite as compared with the mixture of binary oxides. The low value of the $\Delta_{r,ox} G^\circ(298\text{ K})$ of the coffinitization reaction indicates that, depending on the sign of the $\Delta_{r,ox} H^\circ$, this equilibrium might be easily reversed to favor the formation of coffinite at higher temperatures and pressures. Recent results obtained by Guo et al. (2015) from calorimetry in sodium molybdate and lead borate and using the same pure coffinite sample as in the present

study, report $\Delta_{r,ox}H^\circ$ of $25.6 \pm 3.9 \text{ kJ mol}^{-1}$. The substantially positive $\Delta_{r,ox}H^\circ$ also explains why coffinite cannot be formed directly from the mixture of the binary oxides and decomposes upon heating to a moderate temperature as observed by Guo et al. (2015). Using the Gibbs-Helmholtz equation, the $\Delta_{r,ox}H^\circ$ measured by Guo et al. (2015) for the same coffinite sample and the $\Delta_{r,ox}G^\circ$ (298 K) determined by the solubility measurements in the present study, we derived the standard molar entropy of formation of coffinite from the mixture of the binary oxides. The $\Delta_{r,ox}S^\circ$ term at room temperature is: $17 \pm 31 \text{ J mol}^{-1} \text{ K}^{-1}$. The same method was used to determine the standard entropy of formation of coffinite: $\Delta_f S^\circ = -344 \pm 25 \text{ J mol}^{-1} \text{ K}^{-1}$. The standard molar entropy can be calculated using auxiliary data from Table S1, $S_m^\circ = 136 \pm 25 \text{ J mol}^{-1} \text{ K}^{-1}$.

This analysis shows that coffinite is thermodynamically metastable relative to quartz and uraninite at 25°C. It is noteworthy that isostructural ThSiO_4 , thorite behaves differently. Mazeina et al. (2005) determined a $\Delta_{r,ox}H^\circ$ value for the formation of thorite from thorianite and quartz that is slightly lower than for coffinite: $\Delta_{r,ox}H^\circ(\text{ThSiO}_4, \text{thorite}) = 19.4 \pm 2.1 \text{ kJ mol}^{-1}$. On the other hand, thorite was found to be more stable in Gibbs energy at 25°C than the mixture of quartz and thorianite by Szenknect et al. (2013) and Schuiling et al. (1976). They obtained $\Delta_{r,ox}G^\circ(\text{ThSiO}_4, \text{thorite}) = -19.0 \pm 5.5$ and $-25.0 \pm 5.0 \text{ kJ mol}^{-1}$, respectively. In order for compounds with a positive $\Delta_{r,ox}H^\circ$ to have negative $\Delta_{r,ox}G^\circ$, the entropy term must be large enough to offset the enthalpy. Thus, coffinite cannot be formed from the mixture of uraninite and quartz; whereas, thorite, which is entropy stabilized, can be formed from thorianite and quartz.

4.2. Environmental implications

In uranium ores, coffinite commonly coexists with uraninite. Thus, the geologic evidence seems to contradict these experimental results that confirm that coffinite is metastable relative to uraninite plus quartz. The calculation based on the Gibbs free energy of formation of coffinite determined by the solubility measurements and auxiliary data (Table S1) gives the Gibbs free energy of the coffinitization reaction (1) to be: -2.3 ± 5.6 , which is essentially zero within error. Even though coffinite is metastable at room temperature with respect to crystalline UO_2 and SiO_2 , coffinite can form from aqueous U(IV) in contact with silica-rich solutions. From the recent review by Evins and Jensen (2012), it appears that it is not possible to constrain the conditions that favor the formation of coffinite based on geological occurrences because temperature, pressure, pH and silica activity of the fluids are not known. Mercadier et al. (2011) estimate that the temperature of the mineralizing fluids in the Athabasca basin deposits

(Canada), where uraninite and coffinite precipitated in the uranium front, were not higher than 50°C. Mesbah et al. (2015) showed that, under appropriate conditions, small amounts of coffinite in a UO_2 plus SiO_2 (amorphous) mixture can be obtained by hydrothermal treatment at 150°C. The low yield of coffinite at low temperatures may result from slow kinetics of nucleation, but hydrothermal conditions would not be required to precipitate coffinite. Finally, the values of the silica and tetravalent uranium activity seem to be the key parameters that facilitate the precipitation of coffinite.

The solubility product of coffinite determined experimentally in this study was used in the Thermochimie_PHREEQC_SIT_v9 database for geochemical simulations using PHREEQC-2 software. This allows one to delineate the stability fields of UO_2 and USiO_4 at low temperature in terms of silica activity and pH. The conditions that favor the formation of coffinite as compared with uraninite at pH = 6 under anoxic condition are shown in Figure 6. Using the solubility constant of uraninite selected by the NEA TDB project ($\log K_{s,0}^\circ(\text{UO}_2, \text{crystalline}, 298.15 \text{ K}) = -60.86 \pm 0.36$), it appears that a solution in equilibrium with uraninite becomes supersaturated with respect to coffinite if the silica concentration exceeds 0.41 mol L^{-1} . Such high silica concentrations are unlikely in natural systems. This limit is obviously determined by the choice of the solubility constant for UO_2 that controls the $\text{U}(\text{OH})_4$ concentration in solution. However, this has been intensely debated (Langmuir, 1997; Neck and Kim, 2001; Rai et al., 1990, 2003). Based on the assumption that amorphous UO_2 ($K_{s,0}^\circ(\text{UO}_2, \text{am}, 298.15 \text{ K}) = -54.5 \pm 1.0$) controls the $\text{U}(\text{OH})_4$ concentration, the lower limit of the silica concentration necessary to precipitate coffinite is $1.8 \cdot 10^{-7} \text{ mol L}^{-1}$. The value measured by Parks and Pohl (1988), which is generally accepted for the solubility of crystalline uraninite, corresponds to a silica concentration in solution of $1.8 \cdot 10^{-6} \text{ mol L}^{-1}$, which is in equilibrium with coffinite.

White (1995) reported the aqueous concentration of H_4SiO_4 in soil solutions and observed that the upper limit corresponds to the solubility of amorphous SiO_2 ($5 \cdot 10^{-3} \text{ mol L}^{-1}$), whereas the lowest values were below the solubility of quartz (less than $10^{-4} \text{ mol L}^{-1}$). Most of the soil solution data fall within the kaolinite stability field (silica concentrations between $6.6 \cdot 10^{-5}$ and $5 \cdot 10^{-3} \text{ mol L}^{-1}$). Kaolinite is the most commonly reported weathering product of silicate rocks in soils. Silica concentrations in soil solutions are thus strongly affected by the precipitation of secondary clay minerals, even though, in some cases, the soil solution approaches saturation with primary silicate minerals such as K-feldspar. Appelo and Postma (1996) reported the normal ranges of dissolved silica concentrations in uncontaminated fresh water to be between $7 \cdot 10^{-5}$ and $10^{-3} \text{ mol L}^{-1}$ (gray area in Figure 6). Thus, the values

commonly encountered for the dissolved silica concentrations in soil solutions and groundwaters are much higher than the calculated limit of coffinite formation, considering the Parks and Pohl values for the solubility of uraninite. Thus coffinitization of tetravalent uranium oxide whose solubility is intermediate between uraninite ($\log K_{s,0}^{\circ}(\text{UO}_2, \text{cr}) = -60.86$) and $\text{UO}_2(\text{am})$ ($\log K_{s,0}^{\circ}(\text{UO}_2, \text{am}) = -54.5$) is possible at 298 K for silica concentrations that are common in natural groundwaters. Figure 7 shows the variation of the tetravalent uranium concentration in solution with an aqueous Si concentration of $7 \cdot 10^{-5} \text{ mol.L}^{-1}$ in equilibrium with coffinite at 298 K, under anoxic conditions as a function of pH. Based on these calculations, it appears that a solution that contains more than $10^{-11} \text{ mol L}^{-1}$ of $\text{U}(\text{OH})_4$ is oversaturated with respect to coffinite in a pH range from 4 to 10. As this pH interval encompasses the typical values for groundwater, the presence of coffinite in ores cannot be related to a precise range of pH that allows its formation. However, it is important to stress that this solution remains oversaturated relative to uraninite. Elevated silica and uranium concentrations are common in uranium ores, especially in sandstone deposits or highly fractionated Si-rich igneous rocks (Amme et al., 2005; Deditius et al., 2008; Pownceby and Johnson, 2014; Stieff et al., 1955, 1956). Different mechanism can lead to conditions oversaturated with respect to $\text{UO}_2(\text{s})$. For example, high temperature brines can cause the dissolution of $\text{UO}_2(\text{crystalline})$ under reducing conditions, or U(IV) concentration can increase in a redox front by reduction of U(VI). A high oversaturation is necessary to form $\text{UO}_2(\text{s})$ nuclei, and the resulting U(IV) concentration may be orders of magnitude higher than the solubility of $\text{UO}_2(\text{cr})$. The degree of crystallinity of uranium dioxide is another parameters that can affect its solubility. For natural UO_2 , it is strongly affected by radiation damage. Small, metamict crystals are thermodynamically less stable; their dissolution in appropriate conditions can lead to uranium concentration sufficiently high to form coffinite (Matzke, 1992). Most importantly, the impact of silica in solution is not taken into account in the evaluation of tetravalent uranium speciation; as a result, the evaluation of UO_2 solubility in silica-rich groundwater based on the currently available thermodynamic data may not be correct. The existence of U(IV)-Si(IV) complexes is speculative, but Mesbah et al. (2015) suggested that these complexes could play an important role in coffinite formation. The existence of mono- or poly-nuclear complexes of U(IV) with silicates and hydroxydes, as it was evidenced for Th by Peketrroukhine et al. (2002) and Rai et al. (2008), would significantly increase the solubility of UO_2 under alkaline conditions and favor coffinite precipitation. Such mechanism could explain the fact that uraninite and coffinite are often found in intimate intergrowths in many natural samples (Deditius et al., 2008).

These results allow the assessment of the risk of coffinitization of UO_2 in the spent nuclear fuel in a geological repository. Based on the values of the Si concentration ($1.4 \cdot 10^{-4} \text{ mol L}^{-1}$) measured by Gaucher et al. (2009) in the French site porewater (Callovo-Oxfordian argillite), or in the granitic groundwater of Forsmark and Äspö in Sweden ($1.8 \cdot 10^{-4} \text{ mol L}^{-1}$ and $1.5 \cdot 10^{-4} \text{ mol L}^{-1}$, respectively), it appears that coffinitization of the UO_2 matrix may occur only if the dissolution of UO_2 matrix leads to tetravalent uranium concentrations in solution of at least $8 \cdot 10^{-12} \text{ mol L}^{-1}$. Obviously, the concentration levels of U (IV) in the vicinity of the geological repository are hardly predictable. Indeed, they are controlled by the dissolution rate of the UO_2 matrix in spent nuclear fuel, and this depends on the groundwater velocity, composition (modified locally by radiolysis), pH, Eh and temperature, as well as the complex microstructure and composition of the SNF (Burns et al., 2012). These parameters, which are spatially and temporally variable (Ewing, 2015), in turn depend on the emplacement strategy and the types of near-field engineered barriers.

5. CONCLUSION

In response to the pressing need for more accurate thermodynamic data required for the evaluation of the formation of coffinite, as well as the coffinitization of uraninite, the solubility constant of coffinite has been determined at 25°C and 1 bar: $\log *K_S^\circ(\text{USiO}_4, \text{cr}) = -5.25 \pm 0.05$. This value, the first to be experimentally determined, allows for an evaluation of the conditions under which the coffinitization of UO_2 may occur as a function of the pH and Si concentration of the groundwater. Thermodynamically, the coffinitization reaction occurs at 298 K, under reducing conditions, at near-neutral pH, for $[\text{U}(\text{OH})_4] \sim 10^{-11} \text{ mol L}^{-1}$ and $[\text{H}_4\text{SiO}_4] \sim 10^{-4} \text{ mol L}^{-1}$. Such silica and uranium concentrations are common in uranium ores, especially in sandstone deposits or highly fractionated Si-rich igneous rocks. This is consistent with the natural occurrence of coffinite. The positive value obtained for the $\Delta_{r,\text{ox}}G^\circ(298\text{K}) = 20.6 \pm 5.2 \text{ kJ mol}^{-1}$ associated with the formation of coffinite from a mixture of the binary oxides indicates that coffinite is energetically metastable at low temperature with respect to uraninite plus quartz. Coffinite is thus formed through a precipitation mechanism following the dissolution of uraninite in silica-rich solutions. Chemical simulations indicate that coffinite is stable with respect to aqueous species over a wide range of concentrations, which explains the occurrence of coffinite in uranium ore deposits. Although metastable with respect to uraninite and quartz, coffinite persists in uranium ore deposits owing to its slow kinetics of dissolution.

Figure 1. PXRD patterns of an as-prepared sample obtained from the synthesis at pH =12.5 (black line), as-prepared sample obtained from the synthesis at pH = 11.4 (red line) and of the pure coffinite obtained after three purification cycles with HNO_3 10^{-2} mol L^{-1} and KOH 10^{-2} mol L^{-1} (blue line). SEM micrographs of the $\text{UO}_2 + \text{SiO}_2$ assemblage and of the pure coffinite sample.

Figure 2. TEM images of (a) one grain of pure coffinite isolated in the sample obtained after three purification cycles and (b) one grain of coffinite surrounded by nanoparticles of uranium oxide by-product in the as-prepared sample.

(a)

(b)

(c)

Figure 3. SEM micrographs and X-EDS analyses of (a) as-prepared sample, (b) sample after two purification cycles with HNO_3 10^{-2} and KOH 10^{-2} mol L^{-1} and (c) pure coffinite sample obtained after three purification cycles. Histograms represent the distribution of U/Si mole ratio determined by X-EDS (expressed in %).

Figure 4. Evolution of the elemental concentrations (U: black symbols, Si: red symbols) during the dissolution of (a) as-prepared sample containing USiO_4 , UO_2 and $\text{SiO}_2(\text{am})$, (b) pure USiO_4 , (c) purified sample containing USiO_4 and $\text{SiO}_2(\text{am})$ and (d) as-prepared containing UO_2 and $\text{SiO}_2(\text{am})$ only. Closed and open symbols are for experiments under an Ar atmosphere and air, respectively.

USiO₄ / Air

USiO₄ / Ar

566
567 Figure 5. SEM images and PXRD patterns of USiO₄ sample at the end of under-saturated experiments performed in
568 0.1 M HCl solution under Ar atmosphere (black line) and under air (red line). Blue lines represent Bragg peak
569 positions for coffinite from JCPDS file #11-0420.

570

571 Figure 6. Plot of the tetravalent U concentration as a function of H_4SiO_4 concentration with the stability fields of
 572 coffinite. The diagram is constructed for $\text{pH} = 6$, $f(\text{O}_2) = 10^{-69}$ atm and Cl^- molarity of 0.01 mol L^{-1} , with $\log$
 573 $*K_s^\circ(\text{USiO}_4, \text{cr}) = -5.25 \pm 0.05$. Dashed green line represents the lowest limit of the stability domain of coffinite for
 574 a silica concentration of $1.8 \cdot 10^{-7} \text{ mol L}^{-1}$ assuming that the $\text{U}(\text{OH})_4(\text{aq})$ concentration is controlled by the solubility of
 575 $\text{UO}_2(\text{am})$ (dashed green line). Solid green line represents the lowest limit of the stability domain of coffinite for a
 576 silica concentration of 0.41 mol L^{-1} assuming that $\text{U}(\text{OH})_4(\text{aq})$ concentration is controlled by the solubility of $\text{UO}_2(\text{cr})$
 577 taken from NEA TDB (solid red line); dash-dot green line represents the lowest limit of the stability field for a silica
 578 concentration of $1.8 \cdot 10^{-6} \text{ mol L}^{-1}$ assuming that the $\text{U}(\text{OH})_4(\text{aq})$ concentration is controlled by the solubility of
 579 $\text{UO}_2(\text{cr})$ taken from Parks and Pohl (1988) (dash-dot red line). The gray area outlines the range of silica concentration
 580 encountered in soil solutions as reported by White (1995). The black square corresponds to the $\text{U}(\text{OH})_4(\text{aq})$ and silica
 581 concentrations in the experiments performed by Amme et al. (2005).

582

Figure 7. Variation of the U(OH)_4 concentration in equilibrium with coffinite (blue line) with the pH of the solution. Simulation was performed at 298 K for a total concentration of $\text{Si} = 7 \cdot 10^{-5} \text{ mol L}^{-1}$ (corresponding to the left-hand limit of the gray area in figure 6), $f(\text{O}_2) = 10^{-69} \text{ atm}$, and ionic strength $< 0.01 \text{ mol L}^{-1}$.

589 Table 1. Thermodynamic data for the main reactions involving U and Si in the considered system extracted from the
590 Thermochimie_PHREEQC_SIT_v9 database (Giffaut et al., 2014) used in the thermodynamic calculations performed
591 to derive the solubility product of coffinite. The thermodynamic constants for the reactions involving U^{4+} included in
592 the Thermochimie-TDB were taken either from NEA thermodynamic database (Guillaumont et al., 2003) or from
593 Neck and Kim (2001) and recalculated for the internal consistency of the Thermochimie-TDB. The constant for the
594 formation of $Si_4O_6(OH)_6^{2-}$ was taken from Felmy et al. (2001), the solubility constant for $SiO_2(am)$ was taken from
595 Gunnarsson and Arnorsson (2000). The uncertainties associated with the selected values are reported only in the
596 original data sources.

Reaction	$\log K^\circ$ Thermochimie-TDB	$\log K^\circ$ NEA-TDB	$\log K^\circ$ Neck and Kim, (2001)
$4 H^+ + 2 e^- + UO_2^{2+} = U^{4+} + 2 H_2O(l)$	9.04	9.038 ± 0.041	
$Cl^- + U^{4+} = UCl^{3+}$	1.72	1.72 ± 0.13	
$H_2O(l) + U^{4+} = H^+ + UOH^{3+}$	-0.54	-0.54 ± 0.06	-0.4 ± 0.2
$4 OH^- + U^{4+} = U(OH)_4(aq)$	46.0	46.0 ± 1.4	46.0 ± 1.4
$U^{4+} + 2 H_2O(l) = U(OH)_2^{2+} + 2 H^+$	-1.1		-1.1 ± 1.0
$U^{4+} + 3 H_2O(l) = U(OH)_3^+ + 3 H^+$	-4.7		-4.7 ± 1.0
$U^{4+} + 4OH^- = 2H_2O(l) + UO_2(am, hyd)$	54.5	54.5 ± 1.0	54.5 ± 1.0
$U^{4+} + 4OH^- = 2H_2O(l) + UO_2(cr)$	60.85	60.86 ± 0.36	60.86 ± 0.36
$Si(OH)_4(aq) = 2 H^+ + SiO_2(OH)_2^{2-}$	-23.14	-23.14 ± 0.09	
$Si(OH)_4(aq) = H^+ + SiO_2(OH)_3^-$	-9.84	-9.81 ± 0.02	
$4 Si(OH)_4(aq) = 4 H^+ + Si_4O_8(OH)_4^{4-} + 4 H_2O(l)$	-35.94	-36.3 ± 0.5	
$4 Si(OH)_4(aq) = 3 H^+ + Si_4O_7(OH)_5^{3-} + 4 H_2O(l)$	-25.10	-25.5 ± 0.3	
$4 Si(OH)_4(aq) = 2 H^+ + Si_4O_6(OH)_6^{2-} + 4 H_2O(l)$	-15.60		
$2 Si(OH)_4(aq) = 2 H^+ + Si_2O_3(OH)_4^{2-} + H_2O(l)$	-19.40	-19.0 ± 0.3	
$2 Si(OH)_4(aq) = H^+ + Si_2O_2(OH)_5^- + H_2O(l)$	-8.50	-8.1 ± 0.3	
$3 Si(OH)_4(aq) = 3 H^+ + Si_3O_6(OH)_3^{3-} + 3 H_2O(l)$	-29.30	-28.6 ± 0.3	
$3 Si(OH)_4(aq) = 3 H^+ + Si_3O_5(OH)_5^{3-} + 2 H_2O(l)$	-29.40	-27.5 ± 0.3	
$2 H_2O(l) + SiO_2(quar) = Si(OH)_4(aq)$	-3.74	-4.0 ± 0.1	
$2 H_2O(l) + SiO_2(am) = Si(OH)_4(aq)$	-2.71		

597

Table 2. Estimated quantities of USiO₄ and UO₂ based on Rietveld refinements of the PXRD patterns of the samples used for dissolution experiments and the corresponding cell parameters. Average U/Si molar ratio and two standard deviations determined from X-EDS analyses.

Sample ID	U/Si	a (Å)	c (Å)	USiO ₄			a (Å)	UO ₂		
	Mole ratio			Volume ^a (Å ³)	USiO ₄ (mol. %)	Crystal size (nm)		Volume (Å ³)	UO ₂ (mol. %)	Crystal size(nm)
USiO ₄ +UO ₂ +SiO ₂	1.14 ± 0.40	6.9879(1)	6.2614(1)	305.75(1)	61.0(3)	79(7)	5.4317(2)	160.26(1)	39.0(3)	4(1)
UO ₂ + SiO ₂	-	-	-	-	-	-	5.4180(4)	159.05(2)	100	4(1)
USiO ₄ +SiO ₂	0.65 ± 0.08	6.9833(2)	6.2575(2)	305.16(2)	100	79(7)	-	-	-	-
USiO ₄	1.01 ± 0.08	6.9856(2)	6.2582(2)	305.39(2)	100	79(7)	-	-	-	-

^a the molar volume of USiO₄ reached V°(298.15K) = 45.98 ± 0.04 cm³ mol⁻¹

Table 3. Initial normalized dissolution rates of USiO₄ and UO₂+SiO₂ samples determined in 0.1 mol L⁻¹ HCl at room temperature under Ar atmosphere and air, respectively.

Sample ID	Ar		Air	
	R _{L,0} (U) (g m ⁻² d ⁻¹)	R _{L,0} (Si) (g m ⁻² d ⁻¹)	R _{L,0} (U) (g m ⁻² d ⁻¹)	R _{L,0} (Si) (g m ⁻² d ⁻¹)
USiO ₄	(3 ± 2) 10 ⁻⁵	(6.0 ± 0.9) 10 ⁻⁵	(4.0 ± 0.2) 10 ⁻⁴	(3.8 ± 0.1) 10 ⁻⁴
UO ₂ + SiO ₂	(6.0 ± 0.8) 10 ⁻⁴	(2.1 ± 0.1) 10 ⁻⁴	(1.1 ± 0.2) 10 ⁻²	(1.5 ± 0.4) 10 ⁻⁴

Table 4. Composition of the equilibrated solutions from the dissolution experiments completed under Ar atmosphere (calculated $f(\text{O}_2) = 10^{-69}$ atm) at 298 K in 0.1 mol L⁻¹ HCl. Elemental concentrations, [U] and [Si], are expressed in mol L⁻¹. The calculated molalities of species are expressed in mol kg⁻¹. $*K_S(\text{USiO}_4)$ is the solubility product of USiO_4 for $I = 0.1$ mol L⁻¹. Activities of species in solution are calculated with the SIT equation. $*K_S^\circ(\text{USiO}_4)$ is the solubility product of USiO_4 extrapolated to $I = 0$. $\Delta_r G^\circ$, $\Delta_f G^\circ$ and $\Delta_{r,ox} G^\circ$ are expressed in kJ mol⁻¹.

Sample ID:	USiO ₄	UO ₂ + SiO ₂ +USiO ₄		SiO ₂ +USiO ₄		UO ₂ + SiO ₂	
		1	2	1	2	1	2
[U]	(1.30 ± 0.04) 10 ⁻⁴	(2.63 ± 0.08) 10 ⁻⁴	(1.4 ± 0.2) 10 ⁻⁴	(5.7 ± 0.4) 10 ⁻⁵	(6.4 ± 0.3) 10 ⁻⁵	(2.58 ± 0.05) 10 ⁻³	(2.61 ± 0.05) 10 ⁻³
[Si]	(1.76 ± 0.07) 10 ⁻⁴	(1.7 ± 0.1) 10 ⁻⁴	(1.12 ± 0.07) 10 ⁻⁴	(6.3 ± 0.2) 10 ⁻⁴	(3.7 ± 0.1) 10 ⁻⁴	(1.63 ± 0.08) 10 ⁻³	(1.4 ± 0.1) 10 ⁻³
U:Si	0.74 ± 0.07	1.5 ± 0.1	1.3 ± 0.2	0.09 ± 0.01	0.17 ± 0.01	1.58 ± 0.11	1.9 ± 0.1
pH	1.15 ± 0.02	1.09 ± 0.02	1.17 ± 0.02	1.11 ± 0.02	1.33 ± 0.02	1.30 ± 0.02	1.30 ± 0.02
m _{H⁺}	(8.8 ± 0.2) 10 ⁻²	(1.02 ± 0.02) 10 ⁻¹	(8.4 ± 0.2) 10 ⁻²	(9.7 ± 0.2) 10 ⁻²	(5.7 ± 0.1) 10 ⁻²	(6.2 ± 0.1) 10 ⁻²	(6.2 ± 0.1) 10 ⁻²
m _{U⁴⁺}	(3.8 ± 0.1) 10 ⁻⁵	(8.8 ± 0.5) 10 ⁻⁵	(3.9 ± 0.5) 10 ⁻⁵	(1.8 ± 0.1) 10 ⁻⁵	(1.15 ± 0.08) 10 ⁻⁵	(5.5 ± 0.4) 10 ⁻⁴	(5.6 ± 0.4) 10 ⁻⁴
m _{UOH³⁺}	(2.85 ± 0.09) 10 ⁻⁵	(5.5 ± 0.4) 10 ⁻⁵	(3.1 ± 0.4) 10 ⁻⁵	(1.2 ± 0.1) 10 ⁻⁵	(1.44 ± 0.07) 10 ⁻⁵	(5.9 ± 0.4) 10 ⁻⁴	(5.9 ± 0.4) 10 ⁻⁴
m _{U(OH)₂²⁺}	(3.3 ± 0.2) 10 ⁻⁵	(5.3 ± 0.5) 10 ⁻⁵	(3.8 ± 0.5) 10 ⁻⁵	(1.3 ± 0.1) 10 ⁻⁵	(2.7 ± 0.1) 10 ⁻⁵	(9.7 ± 0.4) 10 ⁻⁴	(9.8 ± 0.4) 10 ⁻⁴
m _{U(OH)₃⁺}	(5.6 ± 0.7) 10 ⁻⁸	(7.7 ± 0.9) 10 ⁻⁸	(6.8 ± 0.9) 10 ⁻⁸	(1.9 ± 0.2) 10 ⁻⁸	(7.3 ± 0.6) 10 ⁻⁸	(2.4 ± 0.2) 10 ⁻⁶	(2.4 ± 0.2) 10 ⁻⁶
m _{UCl³⁺}	(3.0 ± 0.1) 10 ⁻⁵	(6.6 ± 0.4) 10 ⁻⁵	(3.1 ± 0.4) 10 ⁻⁵	(1.4 ± 0.1) 10 ⁻⁵	(1.02 ± 0.06) 10 ⁻⁵	(4.4 ± 0.2) 10 ⁻⁴	(1.02 ± 0.06) 10 ⁻⁵
m _{U(OH)₄}	(3.1 ± 0.5) 10 ⁻¹²	(3.7 ± 0.6) 10 ⁻¹²	(4.0 ± 0.5) 10 ⁻¹²	(1.0 ± 0.1) 10 ⁻¹²	(6.3 ± 0.9) 10 ⁻¹²	(1.9 ± 0.3) 10 ⁻¹⁰	(1.9 ± 0.3) 10 ⁻¹⁰
m _{UO₂²⁺}	(1.21 ± 0.08) 10 ⁻⁶	(1.9 ± 0.9) 10 ⁻⁶	(1.4 ± 0.2) 10 ⁻⁶	(0.5 ± 0.2) 10 ⁻⁶	(1.0 ± 0.5) 10 ⁻⁶	(3.6 ± 1.9) 10 ⁻⁵	(3.6 ± 1.9) 10 ⁻⁵
m _{H₄(SiO)₄}	(1.78 ± 0.07) 10 ⁻⁴	(1.7 ± 0.1) 10 ⁻⁴	(1.13 ± 0.07) 10 ⁻⁴	(6.4 ± 0.2) 10 ⁻⁴	(3.7 ± 0.1) 10 ⁻⁴	(1.64 ± 0.08) 10 ⁻³	(1.4 ± 0.1) 10 ⁻³
$*K_S(\text{USiO}_4)$	(1.1 ± 0.1) 10 ⁻⁴	(1.4 ± 0.1) 10 ⁻⁴	(0.9 ± 0.3) 10 ⁻⁴	(1.3 ± 0.2) 10 ⁻⁴	(4.0 ± 0.6) 10 ⁻⁵		
log $*K_S(\text{USiO}_4)$	-3.95 ± 0.05	-3.86 ± 0.08	-4.05 ± 0.13	-3.88 ± 0.07	-3.40 ± 0.07		
(U ⁴⁺)	(7.9 ± 0.7) 10 ⁻⁷	(1.6 ± 0.7) 10 ⁻⁶	(8.4 ± 1.2) 10 ⁻⁷	(3.6 ± 0.3) 10 ⁻⁷	(3.0 ± 0.2) 10 ⁻⁷	(1.19 ± 0.08) 10 ⁻⁵	(1.20 ± 0.08) 10 ⁻⁵
(H ₄ SiO ₄)	(1.78 ± 0.07) 10 ⁻⁴	(1.7 ± 0.1) 10 ⁻⁴	(1.13 ± 0.07) 10 ⁻⁴	(6.4 ± 0.2) 10 ⁻⁴	(3.7 ± 0.1) 10 ⁻⁴	(1.64 ± 0.08) 10 ⁻³	(1.4 ± 0.1) 10 ⁻³
$*K_S^\circ(\text{USiO}_4)$	(5.6 ± 0.7) 10 ⁻⁶	(6.4 ± 1.1) 10 ⁻⁶	(4.5 ± 1.4) 10 ⁻⁶	(6.3 ± 1.0) 10 ⁻⁶	(2.4 ± 0.4) 10 ⁻⁵		
log $*K_S^\circ(\text{USiO}_4)$	-5.25 ± 0.05*	-5.19 ± 0.08	-5.34 ± 0.13	-5.20 ± 0.07	-4.63 ± 0.07		
$\Delta_r G^\circ$	30.0 ± 0.3	29.6 ± 0.4	30.5 ± 0.8	29.7 ± 0.4	26.4 ± 0.4		
$\Delta_f G^\circ$	-1867.6 ± 3.2	-1867.2 ± 3.4	-1868.1 ± 3.7	-1867.3 ± 3.3	-1864.0 ± 3.3		
$\Delta_{r,ox} G^\circ$	20.6 ± 5.2	20.9 ± 5.4	20.0 ± 5.7	20.8 ± 5.3	24.1 ± 5.3		

*Value selected in the present study

Table 5. Review of the previous determinations of thermodynamic data for coffinite. Bold characters indicate the values reported in publications (either estimated or measured). The other values were calculated in this study using the reported ones (bold characters) associated with auxiliary data (see the footnotes for the source of auxiliary data), or calculated using the Gibbs-Helmholtz equation.

	$\Delta_f G^\circ$	$\Delta_f H^\circ$	S_m°	$\Delta_f S^\circ$	$\Delta_{r,ox} G^\circ$	$\Delta_{r,ox} H^\circ$	$\Delta_{r,ox} S^\circ$	$\Delta_r G^\circ$	$\log {}^*K_S^\circ$
	kJ mol ⁻¹	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	J mol ⁻¹ K ⁻¹	kJ mol ⁻¹	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹	kJ mol ⁻¹	
Langmuir (1978)	-1891.17	-2001.21	117.15	-369.26 ¹	-3.10 ^a	-4.4 ^a	-1.3 ¹	52.38 ^a	-9.18
Langmuir & Chatham (1980)	-1882.38	-1990.33	117.15	-362.24 ¹	5.69 ^a	5.3 ^a	-1.4 ¹	43.60 ^a	-7.64
Hemingway (1982)	-1886 ± 20				2 ± 22 ^b			47 ± 23 ^b	-8 ± 4
Fleche (2002)	-1915.9 ± 32.4 ¹	-2021.7 ± 30.3	124.3 ± 6.6	-355.0 ± 7.0 ^c	-27.8 ± 34.4 ^c	-26.0 ± 32.3 ^c	6.0 ± 7.0 ¹	78.3 ± 35.3 ^c	-13.73 ± 6.19
Grenthe et al. (1992) Guillaumont et al. (2003)	-1883.6 ± 4.0	-1991.326 ± 5.367¹	118 ± 12	-361 ± 12 ^c	4.52 ± 6.06 ^c	4.374 ± 7.367 ^c	-0.49 ± 12.40 ¹	46.005 ± 6.921 ^c	-8.06 ± 1.21
Szenknect et al. (2013)	-1872.6 ± 3.8^c	-1980.3 ± 7.4 ¹	118 ± 12	-361 ± 12 ^c	15.5 ± 5.8^c	15.4 ± 9.4 ^c	-0.31 ± 12.40 ¹	35.0 ± 0.9	-6.1 ± 0.2
Guo et al. (2015)	-1862.3 ± 7.8 ¹	-1970.0 ± 4.2^c	118 ± 12	-361 ± 12 ^c	25.8 ± 9.8 ^c	25.6 ± 3.9	-0.64 ± 12.40 ¹	24.73 ± 10.72 ^c	-4.34 ± 1.88
This work	-1867.6 ± 3.2^c	-1970.0 ± 4.2 ^c	136 ± 25 ^c	-344 ± 25 ¹	20.6 ± 5.2^c	25.6 ± 3.9	17 ± 31 ¹	30.0 ± 0.3	-5.25 ± 0.05

^a calculated with auxiliary data given by Langmuir (1978)

^b calculated with auxiliary data given by Hemingway (1982)

^c calculated with auxiliary data given by Grenthe et al. (1992)

¹ calculated internally with the Gibbs-Helmholtz equation

REFERENCES

- Amme, M., Wiss, T., Thiele, H., Boulet, P. and Lang, H. (2005) Uranium secondary phase formation during anoxic hydrothermal leaching processes of UO_2 nuclear fuel. *J. Nucl. Mater.* **341**, 209-223.
- Appelo, C.A.J. and Postma, D. (1996) *Geochemistry, Groundwater and Pollution*. A.A. Balkema, Rotterdam, the Netherlands.
- Baker, R.J. (2014) Uranium minerals and their relevance to long term storage of nuclear fuels. *Coordin. Chem. Rev.* **266-267**, 123-136.
- Brookins, D.G. (1975) Coffinite-Uraninite Stability relations in Grants Mineral Belt, New-Mexico. *B.-Am. Assoc. Petrol. Geol.* **59**, 905-905.
- Bros, R., Hidaka, H., Kamei, G. and Ohnuki, T. (2003) Mobilization and mechanisms of retardation in the Oklo natural reactor zone 2 (Gabon) - inferences from U, REE, Zr, Mo and Se isotopes. *Applied Geochem.* **18**, 1807-1824.
- Bruno, J., Casas, I. and Puigdomènech, I. (1991) The kinetics of dissolution of UO_2 under reducing conditions and the influence of an oxidized surface layer (UO_{2+x}): Application of a continuous flow-through reactor. *Geochim. Cosmochim. Acta* **55**, 647-658.
- Burns, P.C., Ewing, R.C. and Navrotsky, A. (2012) Nuclear Fuel in a Reactor Accident. *Science* **335**, 1184-1188.
- Carbol, P., Wegen, D.H., Wiss, T. and Fors, P. (2012) 5.16 - Spent Fuel as Waste Material, in: Konings, R.J.M. (Ed.), *Comprehensive Nuclear Materials*. Elsevier, Oxford, pp. 389-420.
- Casas, I., de Pablo, J., Gimenez, J., Torrero, M.E., Bruno, J., Cera, E., Finch, R.J. and Ewing, R.C. (1998) The role of pe, pH, and carbonate on the solubility of UO_2 and uraninite under nominally reducing conditions. *Geochim. Cosmochim. Acta* **62**, 2223-2231.
- Castro, R.H.R. (2013) On the thermodynamic stability of nanocrystalline ceramics. *Mater. Lett.* **96**, 45-56.
- Clavier, N., Szenknect, S., Costin, D.T., Mesbah, A., Poinssot, C. and Dacheux, N. (2014) From thorite to coffinite: A spectroscopic study of $\text{Th}_{1-x}\text{U}_x\text{SiO}_4$ solid solutions. *Spectrochim. Acta A* **118**, 302-307.
- Clavier, N., Szenknect, S., Costin, D.T., Mesbah, A., Ravau, J., Poinssot, C. and Dacheux, N. (2013) Purification of uranothorite solid solutions from polyphase systems. *J. Nucl. Mater.* **441**, 73-83.
- Costin, D.T., Mesbah, A., Clavier, N., Dacheux, N., Poinssot, C., Szenknect, S. and Ravau, J. (2011) How To Explain the Difficulties in the Coffinite Synthesis from the Study of Uranothorite? *Inorg. Chem.* **50**, 11117-11126.
- Cox, J.D., Wagman, D.D. and Medvedev, V.A. (1989) *CODATA Key Values for Thermodynamics*. Hemisphere Publ. Corp., New York.
- Cuney, M. (1978) Geologic environment, Mineralogy, and fluid Inclusions of the Bois-Noirs-Limouzat Uranium Vein, Forez, France. *Econ. Geol.* **73**, 1567-1610.
- Dacheux, N., Brandel, V. and Genet, M. (1995) Synthèse et caractérisation de l'orthophosphate d'uranium a valence mixte: $\text{U}(\text{UO}_2)(\text{PO}_4)_2$. *New J. Chem.* **19**, 15-26.
- Deditius, A.P., Pointeau, V., Zhang, J.M.M. and Ewing, R.C. (2012) Formation of nanoscale Th-coffinite. *Am. Mineral.* **97**, 681-693.

- Deditius, A.P., Utsunomiya, S. and Ewing, R.C. (2008) The chemical stability of coffinite, $\text{USiO}_4 \cdot n\text{H}_2\text{O}$; $0 < n < 2$, associated with organic matter: A case study from Grants uranium region, New Mexico, USA. *Chem. Geol.* **251**, 33-49.
- Dreissig, I., Weiss, S., Hennig, C., Bernhard, G. and Zanker, H. (2011) Formation of uranium(IV)-silica colloids at near-neutral pH. *Geochim. Cosmochim. Acta* **75**, 352-367.
- Evins, L.Z. and Jensen, K.A. (2012) Review of spatial relations between uraninite and coffinite - implications for alteration mechanisms. *MRS Online Proc. Library* **1475**, 89-96.
- Ewing, R.C. (2015) Long-term storage of spent nuclear fuel. *Nature Mater.* **14**, 252-257.
- Felmy, A.R., Cho, H., Rustad, J.R. and Mason, M.J. (2001) An aqueous thermodynamic model for polymerized silica species to high ionic strength. *J. Sol. Chem.* **30**, 509-525.
- Fleche, J.L. (2002) Thermodynamical functions for crystals with large unit cells such as zircon, coffinite, fluorapatite, and iodoapatite from ab initio calculations. *Phys. Rev. B* **65**.
- Frontera, C. and Rodriguez-Carvajal, J. (2003) FullProf as a new tool for flipping ratio analysis. *Physica B* **335**, 219-222.
- Fuchs, L.H. and Gebert, E. (1958) X-Ray Studies of Synthetic Coffinite, Thorite and Uranothorites. *Am. Mineral.* **43**, 243-248.
- Fuchs, L.H. and Hoekstra, H.R. (1959) The Preparation and Properties of Uranium(IV) Silicate. *Am. Mineral.* **44**, 1057-1063.
- Gaucher, E.C., Tournassat, C., Pearson, F.J., Blanc, P., Crouzet, C., Lerouge, C. and Altmann, S. (2009) A robust model for pore-water chemistry of clayrock. *Geochim. Cosmochim. Acta* **73**, 6470-6487.
- Giffaut, E., Grivé, M., Blanc, P., Vieillard, P., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N., Madé, B. and Duro, L. (2014) Andra thermodynamic database for performance assessment: ThermoChimie. *Applied Geochemistry* **49**, 225-236.
- Gorman-Lewis, D., Burns, P.C. and Fein, J.B. (2008) Review of uranyl mineral solubility measurements. *J. Chem. Thermodyn.* **40**, 335-352.
- Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C. and Wanner, H. (1992) Chemical Thermodynamics of Uranium. *Chemical Thermodynamics, 1, OECD-NEA Eds* **1**, 715.
- Guillaumont, R., Fanghänel, T., Neck, V., Fuger, J., Palmer, D.A., Grenthe, I. and Rand, M.H. (2003) Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. *Chemical Thermodynamics, 5, OECD-NEA Eds*.
- Gunnarsson, I. and Arnorsson, S. (2000) Amorphous silica solubility and the thermodynamic properties of H_4SiO_4 degrees in the range of 0 degrees to 350 degrees C at P-sat. *Geochim. Cosmochim. Acta* **64**, 2295-2307.
- Guo, X., Szenknect, S., Mesbah, A., Labs, S., Clavier, N., Poinssot, C., Ushakov, S.V., Curtius, H., Bosbach, D., Ewing, R.C., Burns, P.C., Dacheux, N. and Navrotsky, A. (2015) Thermodynamics of formation of coffinite, USiO_4 . *Proceedings of the National Academy of Sciences* **112**, 6551-6555.
- Hemingway, B.S. (1982) Thermodynamic properties of selected uranium compounds and aqueous species at 298.15K and 1 bar and at higher temperatures. Preliminary models for the origin of coffinite deposits. *US. Geol. Survey Open-File Rep.* **82-619**, pp. 90.
- Hoekstra, H.R. and Fuchs, L.H. (1956) Synthesis of Coffinite- USiO_4 . *Science* **123**, 105-105.
- Hogselius, P. (2009) Spent nuclear fuel policies in historical perspective: An international comparison. *Energ. Policy* **37**, 254-263.

- Janeczek, J. (1999) Mineralogy and Geochemistry of Natural Fission Reactors in Gabon. *Rev. Mineral.* **38**, 321-392.
- Janeczek, J. and Ewing, R.C. (1992a) Coffinitization - A Mechanism for the Alteration of UO_2 under Reducing Conditions. *MRS Sympos. Proc.* **257**, 497-504.
- Janeczek, J. and Ewing, R.C. (1992b) Dissolution and alteration of uraninite under reducing conditions. *J. Nucl. Mater.* **190**, 157-173.
- Jensen, K.A. and Ewing, R.C. (2001) The Okelobondo natural fission reactor, southeast Gabon: Geology, mineralogy, and retardation of nuclear-reaction products. *Geol. Soc. Am. Bull.* **113**, 32-62.
- Jerden Jr, J.L. and Sinha, A.K. (2003) Phosphate based immobilization of uranium in an oxidizing bedrock aquifer. *Applied Geochem.* **18**, 823-843.
- Johnson, J.W., Oelkers, E.H. and Helgeson, H.C. (1992) SUPCRT92 - A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1 Bar to 5000 Bars and 0°C to 1000°C . *Comput. Geosci.* **18**, 899-947.
- Labs, S., Hennig, C., Weiss, S., Curtius, H., Zanker, H. and Bosbach, D. (2014) Synthesis of Coffinite, USiO_4 , and Structural Investigations of $\text{U}_x\text{Th}_{(1-x)}\text{SiO}_4$ Solid Solutions. *Environ. Sci. Technol.* **48**, 854-860.
- Langmuir, D. (1978) Uranium Solution-Mineral Equilibria at Low-Temperatures with Applications to Sedimentary Ore-Deposits. *Geochim. Cosmochim. Acta* **42**, 547-569.
- Langmuir, D. and Chatham, J.R. (1980) Groundwater prospecting for sandstone-type uranium deposits: a preliminary comparison of the merits of mineral-solution equilibria, and single-element tracer methods. *J. Geochem. Exploration* **13**, 201-219.
- Langmuir, D. (1997) Aqueous Environmental Geochemistry. Printice Hall Inc., New Jersey.
- Maher, K., Bargar, J.R. and Brown, G.E. (2012) Environmental Speciation of Actinides. *Inorg. Chem.* **52**, 3510-3532.
- Mazeina, L., Ushakov, S.V., Navrotsky, A. and Boatner, L.A. (2005) Formation enthalpy of ThSiO_4 and enthalpy of the thorite $\rightarrow$ huttonite phase transition. *Geochim. Cosmochim. Acta* **69**, 4675-4683.
- Matzke, H. (1992) Radiation damage-enhanced dissolution of UO_2 in water. *J. Nucl. Mater.* **190**, 101-106.
- Mercadier, J., Cuney, M., Cathelineau, M. and Lacorde, M. (2011) U redox fronts and kaolinisation in basement-hosted unconformity-related U ores of the Athabasca Basin (Canada): late U remobilisation by meteoric fluids. *Miner. Deposita* **46**, 105-135.
- Mesbah, A., Szenknect, S., Clavier, N., Poinssot, C., Ewing, R.C. and Dacheux, N. (2015) Coffinite, USiO_4 , is abundant in nature: So why is it so difficult to synthesize? *Inorg. Chem.* **54**, 6687-6696.
- Min, M.Z., Fang, C.Q. and Fayek, M. (2005) Petrography and genetic history of coffinite and uraninite from the Liueyiqi granite-hosted uranium deposit, SE China. *Ore Geol. Rev.* **26**, 187-197.
- Neck, V. and Kim, J.I. (2001) Solubility and hydrolysis of tetravalent actinides. *Radiochim. Acta* **89**, 1-16.
- Oelkers, E.H., Benezeth, P. and Pokrovski, G.S. (2009) Thermodynamic Databases for Water-Rock Interaction, in: Oelkers, E.H., Schott, J. (Eds.), *Thermodynamics and Kinetics of Water-Rock Interaction*, pp. 1-46.

- Parkhurst, D.L. and Appelo, C.A.J. (1999) User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. *U.S.G.S Water-Resources Investigations Report* **99-4259**.
- Parks, G.A. and Pohl, D.C. (1988) Hydrothermal solubility of uraninite. *Geochim. Cosmochim. Acta* **52**, 863-875.
- Peketrakhine, V., Riglet-Martial, C., Capdevila, H., Calmon, V., Bienvenu, P. and Laszak, I. (2002) Effect of Soluble Silicates on the Solubility of Thorium(IV) Hydrous Oxide. *J. Nucl. Sci. Technol.* **39**, 516-519.
- Poinssot, C., Ferry, C., Lovera, P., Jegou, C. and Gras, J.-M. (2005) Spent fuel radionuclide source term model for assessing spent fuel performance in geological disposal. Part II: Matrix alteration model and global performance. *J. Nucl. Mater.* **346**, 66-77.
- Pointeau, V., Deditius, A., Miserque, F., Renock, D., Becker, U., Zhang, J., Clavier, N., Dacheux, N., Poinssot, C. and Ewing, R. (2009) Synthesis and characterization of coffinite. *J. Nucl. Mater.* **393**, 449-458.
- Pownceby, M.I. and Johnson, C. (2014) Geometallurgy of Australian uranium deposits. *Ore Geol. Rev.* **56**, 25-44.
- Rai, D., Felmy, A.R. and Ryan, J.L. (1990) Uranium(IV) Hydrolysis Constants and Solubility Product of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$. *Inorg. Chem.* **29**, 260-264.
- Rai, D., Yui, M. and Moore, D.A. (2003) Solubility and solubility product at 22 °C of $\text{UO}_2(\text{c})$ precipitated from aqueous U(IV) solutions. *J. Solution Chem.* **32**, 1-17.
- Rai, D., Yui, M., Moore, D.A., Lumetta, G.J., Rosso, K.M., Xia, Y.X., Felmy, A.R. and Skomurski, F.N. (2008) Thermodynamic model for $\text{ThO}_2(\text{am})$ solubility in alkaline silica solutions. *J. Solution Chem.* **37**, 1725-1746.
- Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1979) Thermodynamic properties of minerals and related substances at 298.15K and 1 bar pressure and at higher temperatures (revised edition). *U.S. Geol. Survey Bull.* **1452**, 456 pp.
- Schofield, E.J., Veeramani, H., Sharp, J.O., Suvorova, E., Bernier-Latmani, R., Mehta, A., Stahlman, J., Webb, S.M., Clark, D.L., Conradson, S.D., Ilton, E.S. and Bargar, J.R. (2008) Structure of Biogenic Uraninite Produced by *Shewanella oneidensis* Strain MR-1. *Environ. Sci. Technol.* **42**, 7898-7904.
- Schuiling, R. D., Vergouwen, L., Vanderrijst, H. (1976) Gibbs energies of formation of zircon (ZrSiO_4), thorite (ThSiO_4) and phenacite (Be_2SiO_4). *Am. Miner.*, **61**, 166-168.
- Shilov, V.P., Yusov, A.B., Peretrukhin, V.F., Delegard, C.H., Gogolev, A.V., Fedosseev, A.M. and Kazansky, L.P. (2007) Oxidation of U(IV) by atmospheric oxygen in pH 1.5–7.4 aqueous solutions. *J. Alloy. Compd.* **444–445**, 333-338.
- Stieff, L.R., Stern, T.W. and Sherwood, A.M. (1955) Preliminary Description of Coffinite - New uranium Mineral. *Science* **121**, 608-609.
- Stieff, L.R., Stern, T.W. and Sherwood, A.M. (1956) Coffinite, a Uranous Silicate with Hydroxyl Substitution - A New Mineral. *Am. Mineral.* **41**, 675-688.
- Stumm, W., Sigg, L. and Sulzberger, B. (1992) Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems. John Wiley & Sons, Inc. pp. 428.
- Szenknect, S., Costin, D.T., Clavier, N., Mesbah, A., Poinssot, C., Vitorge, P. and Dacheux, N. (2013) From Uranothorites to Coffinite: A Solid Solution Route to the Thermodynamic Properties of USiO_4 . *Inorg. Chem.* **52**, 6957-6968.

Thompson, P., Cox, D.E. and Hastings, J.B. (1987) Rietveld Refinement of Debye-Scherrer
Synchrotron X-Ray Data from Al_2O_3 . *J. Appl. Crystallogr.* **20**, 79-83.
Ulrich, K.U., Singh, A., Schofield, E.J., Bargar, J.R., Veeramani, H., Sharp, J.O., Bernier-
Latmani, R. and Giammar, D.E. (2008) Dissolution of biogenic and synthetic UO_2 under
varied reducing conditions. *Environ. Sci. Technol.* **42**, 5600-5606.
White, A.F. (1995) Chemical Weathering Rates of Silicate Minerals in soils, in: White, A.F.,
Brantley, S.L. (Eds.), *Chemical Weathering Rates of Silicate Minerals*, Mineralogical Society
of America, Washington D.C., pp. 407-462.

ACKNOWLEDGMENT

Funding for this research was supported by the NEEDS Ressources program of the CNRS. EXAFS experiments were
performed with the financial support of the TALISMAN project. The authors are grateful to J. Ravaux and R. Podor
for ESEM and X-EDS analyses. The authors acknowledge Kastriot Spahiu (SKB) for his involvement in the
redaction, the helpful discussions and corrections made to the article. Support for RCE was provided by the U.S.
Department of Energy, Office of Science, Office of Basic Energy Sciences Energy Frontier Research Centers
program under Award Number DE-SC0001089.