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# First experimental determination of the solubility constant of coffinite.

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ABSTRACT.

Dissolution experiments have been performed in order to determine the solubility constant of coffinite,  $\text{USiO}_4$ . Several assemblages of phases were used in under-saturated experiments performed in  $0.1 \text{ mol L}^{-1}$  HCl under Ar atmosphere, as well as in air. These samples were fully-characterized and were composed of either  $\text{USiO}_4$ , solely, or  $\text{USiO}_4$  and additional oxide byproducts that resulted from the synthesis procedure. The solubility constant of coffinite was determined at  $25^\circ\text{C}$  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  $25^\circ\text{C}$  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  $\Delta_f G^\circ$

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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  $\text{UO}_2$  matrix will be more slowly released by dissolution of the  $\text{UO}_2$  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 ( $7.2 \pm 0.2$ ), low redox potential ( $E_{\text{hSHE}} = -199$  mV) and Si concentration ( $1.4 \cdot 10^{-4}$  mol  $\text{L}^{-1}$ ), 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  $1.8 \cdot 10^{-4}$  mol  $\text{L}^{-1}$  and  $1.5 \cdot 10^{-4}$  mol  $\text{L}^{-1}$ , 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  $\text{UO}_2$  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 ( $\text{ThSiO}_4$ ) (Brookins, 1975) or from available geologic information. In 1978, Langmuir first postulated that the average silica concentration (about  $10^{-3}$  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

29 associated groundwaters. Thus, Langmuir estimated the standard free energy of formation of coffinite ( $\Delta_f G^\circ(\text{USiO}_4$ ,  
30 cr) = -1891.17 kJ mol<sup>-1</sup>) and of the enthalpy of formation ( $\Delta_f H^\circ(\text{USiO}_4$ , cr) = -2001.21 kJ mol<sup>-1</sup>). However, these  
31 values were corrected later by Langmuir and Chatham (1980). The corresponding corrected free energy and enthalpy  
32 values were -1882.38 kJ mol<sup>-1</sup> and -1990.33 kJ mol<sup>-1</sup>, respectively (Langmuir, 1978). They also calculated the  
33 standard molar entropy of coffinite ( $S_m^\circ = 117.15$  J mol<sup>-1</sup> K<sup>-1</sup>) as the sum of the molar entropies of quartz (41.46 J mol<sup>-1</sup>  
34 K<sup>-1</sup>) and uraninite (77.03 J mol<sup>-1</sup> K<sup>-1</sup>). These values are CODATA values (Cox et al., 1989), which were also used  
35 later by Grenthe (1992). In 1982, Hemingway performed thermodynamic calculations, also based on an estimate of  
36 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  
37 standard free energy of formation of coffinite ( $\Delta_f G^\circ(\text{USiO}_4$ , cr) = -1886 ± 20 kJ mol<sup>-1</sup>). Hemingway indicated that the  
38  $\Delta_f G^\circ(\text{USiO}_4$ , cr) value given by Langmuir (1978) was not consistent with his estimate for the equilibrium silicate  
39 activity for reaction (1). The NEA Thermodynamic Data Base (TDB) (Grenthe et al., 1992) accepted Langmuir's  
40 assumption for the average silica concentration (10<sup>-3</sup> mol L<sup>-1</sup>) at equilibrium for reaction (1) but recalculated the  
41  $\Delta_f G^\circ(\text{USiO}_4$ , cr) value and associated error using auxiliary data selected by the NEA-TDB. The obtained value,  
42  $\Delta_f G^\circ(\text{USiO}_4$ , cr) = -1883.6 ± 4.0 kJ mol<sup>-1</sup> was consistent with that of Hemingway. Considering that  $S_m^\circ = 118 \pm 12$  J  
43 mol<sup>-1</sup> K<sup>-1</sup>, the enthalpy of formation was calculated internally with the Gibbs-Helmholtz equation, leading to  
44  $\Delta_f H^\circ(\text{USiO}_4$ , cr) = -1991.326 ± 5.367 kJ mol<sup>-1</sup>. In 1997, Langmuir determined a value for the standard free energy of  
45 formation of amorphous coffinite based on chemical analyses of low Eh groundwater from coffinite-bearing ore zones  
46 (Cigar Lake, Canada and Palmottu, Finland). These waters were found to be at saturation with respect to UO<sub>2</sub>(am),  
47 suggesting that the associated coffinite phase may be amorphous. This calculation is the basis for the determination of  
48  $\Delta_f G^\circ(\text{USiO}_4$ , am) = -1835.23 kJ mol<sup>-1</sup>. Naturally occurring coffinite is generally so fine-grained that identification and  
49 characterization, as well as the determination of physical and chemical properties, is not possible (Deditius et al.,  
50 2012; Deditius et al., 2008). Based on Langmuir's interpretation of the geologic conditions of formation, the  
51 equilibrium constant of reaction (2) increases by almost 8 orders of magnitude if the coffinite is considered to be  
52 amorphous rather than crystalline:



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

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

58 Fleche, (2002) derived thermodynamical functions for coffinite using *ab initio* calculations. The  $\Delta_f H^\circ(\text{USiO}_4,$   
59 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  
60 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  
61 determination of  $\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1915.9 \pm 32.4 \text{ kJ mol}^{-1}$ .

62 By extrapolation from the uranothorite solid-solution binary, Szenknect et al. (2013) determined a value for the  
63 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  
64 Langmuir's assumptions of geologic conditions. Thermodynamic calculations based on this extrapolation and  
65 auxiliary data from the NEA TDB II (Guillaumont et al., 2003) resulted in a standard free energy of formation for  
66 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  
67 enthalpy of formation of coffinite by high temperature oxide melt solution calorimetry. They found that coffinite is  
68 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  
69 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  
70  $S_m^\circ = 118 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$  (selected by the NEA), the free energy of formation was calculated internally using the  
71 Gibbs-Helmholtz equation:  $\Delta_f G^\circ(\text{USiO}_4, \text{cr}) = -1862.3 \pm 7.8 \text{ kJ mol}^{-1}$ .

72 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  
73 of investigators have sought to obtain pure synthetic coffinite, but only few have succeeded (Costin et al., 2011;  
74 Fuchs and Gebert, 1958; Fuchs and Hoekstra, 1959; Hoekstra and Fuchs, 1956; Labs et al., 2014; Pointeau et al.,  
75 2009). The synthetic coffinite was always obtained by minor modifications of the initial protocol proposed by Fuchs  
76 and Hoekstra (1959). This seminal publication already showed the need for several steps to buffer the pH prior to heat  
77 treatment and the difficulty of maintaining a very narrow pH range for formation. Nevertheless, the samples obtained  
78 were mixtures of phases, mainly composed of  $\text{USiO}_4$ ,  $\text{UO}_2$  and  $\text{SiO}_2$ . An optimized protocol was used to obtain pure  
79 coffinite that was fully characterized before and after under-saturated experiments. The purpose of this study is to  
80 determine the solubility of coffinite and to use these results to calculate the standard free energy of formation of  
81 coffinite, which enables one to infer the relative stability of coffinite and uraninite as a function of groundwater

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

84

## 85 2. EXPERIMENTAL METHODS

### 86 2.1. Synthesis of solid phases

87 A solution of uranium tetrachloride was prepared by dissolving uranium metal fragments provided by CETAMA  
88 (Analytical Methods Committee, CEA, France) in cooled 6 mol L<sup>-1</sup> HCl according to the method of Dacheux et al.  
89 (1995). The hot solution was then centrifuged at 12000 rpm during 15 min while slow H<sub>2</sub> degassing from black  
90 residues was observed. The centrifuged solution was stored under Ar atmosphere, then the final concentration was  
91 determined by ICP-AES. The other reactants (Na<sub>2</sub>SiO<sub>3</sub>, NaHCO<sub>3</sub> and NaOH) were used as supplied by Sigma-Aldrich  
92 and were of analytical grade.

93 Coffinite (USiO<sub>4</sub>) powder was synthesized under hydrothermal conditions by a modification of previous procedure  
94 (Fuchs and Gebert, 1958; Fuchs and Hoekstra, 1959; Hoekstra and Fuchs, 1956). 20 mL of out-gassed water (boiled  
95 for 1 hour and cooled under nitrogen stream) containing 6 mmol of UCl<sub>4</sub> was mixed to 20 mL of a solution of  
96 Na<sub>2</sub>SiO<sub>3</sub> (6 mmol + 10% excess) resulting in a greenish solution. Afterward, the pH was raised to 11.4 ± 0.1 by  
97 adding 8 mol L<sup>-1</sup> NaOH, buffered to 8.7 by adding NaHCO<sub>3</sub>, poured in a 50-mL Teflon container that was placed in  
98 acid digestion bomb. All these reactions were performed in a glove box filled with Ar and free from oxygen (less than  
99 2 ppm). The digestion bomb was then heated at 250 °C for 16 days. At the end of the reaction, the final product was  
100 separated by centrifugation twice with water then with ethanol and dried overnight in the glove box at room  
101 temperature.

102 In order to evaluate whether the byproducts (oxide and amorphous silica) control the concentrations in solution,  
103 another reaction was performed in order to synthesize only these side products. Basically, the same procedure was  
104 followed; however, the pH was raised to 12.5 before buffering the pH to 8.7. Mesbah et al. (2015) determined the  
105 optimal conditions in terms of pH, T, heating time and molar ratio of U:Si for the hydrothermal synthesis of coffinite.  
106 The yield of coffinite was found to decrease drastically when the pH of the initial mixture of reactants was lower than  
107 10 or higher than 12. This result was attributed to the formation of colloidal coffinite precursors in a narrow range of  
108 pH. Without these colloidal precursors, acting as nuclei for the crystallization of coffinite, the kinetics of coffinite  
109 precipitation was too slow to allow the precipitation of a sufficient amount of coffinite.

110

## 111 2.2. Coffinite purification

112 The powders were purified prior to dissolution experiments in order to eliminate  $\text{UO}_2$  and  $\text{SiO}_2$  that have been  
113 retained in the synthesized powders. The protocol for purification developed for uranothorite solid solutions (Clavier  
114 et al., 2013) yielded very high losses for coffinite; thus, the protocol was modified. One purification cycle consisted  
115 of several steps: *i.*) 100 mg of solid were placed into contact with 50 mL of  $10^{-2}$  mol  $\text{L}^{-1}$   $\text{HNO}_3$  for 3 to 5 days; *ii.*) the  
116 solid was centrifuged and washed three times with deionized water; *iii.*) the remaining solid was dispersed in 50 mL  
117 of  $10^{-2}$  mol  $\text{L}^{-1}$   $\text{KOH}$  for 3 to 5 days, and then washed three times with deionized water. Two or three purification  
118 cycles were performed, and the resulting samples were dried overnight in an oven at  $60^\circ\text{C}$ .

119

## 120 2.3. Characterization of the solids

121 All samples were analyzed by powder X-rays diffraction (PXRD) using the Bruker D8 advance diffractometer  
122 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  
123 in the angular range from  $5^\circ$  to  $100^\circ$  for a total counting time of about 3 hours per sample. Mainly, two phases were  
124 detected, tetragonal coffinite ( $\text{USiO}_4$ ;  $I4_1/amd$ ) and cubic urania ( $\text{UO}_2$ ;  $\text{Fm}\bar{3}m$ ). The data were refined using  
125 Fullprof\_suite (Frontera and Rodriguez-Carvajal, 2003) by applying the Rietveld method and using the Thomson Cox  
126 profile function (Thompson et al., 1987). Pure silicon was used as a standard to determine instrumental parameters.  
127 Zero shift, unit cell parameters, overall displacement, preferred orientation and an anisotropic size model for the  
128 microstructural characteristics were considered for all refinements. The obtained unit cell parameters and estimated  
129 amounts of each phase are reported in Table 2, while an example of the refinement results for pure coffinite is given  
130 in Figure S1 of the supplementary data showing the observed, calculated and difference patterns.

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

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

138 spectroscopy (EDS) analyses were performed using a Bruker AXS X-Flash 5010 detector coupled to the SEM device.  
139 In order to quantify the elemental percentages, the powders were first embedded in epoxy resin. The surface of the  
140 samples was then polished to optical grade and then carbon coated. Experimental data were finally collected from 100  
141 different locations using  $\text{UO}_2$  and albite ( $\text{NaAlSi}_3\text{O}_8$ ) as standards.

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

144

#### 145 2.4. Solubility experiments

146 The dissolution experiments were performed in air or under anoxic conditions by flushing the chamber with argon.  
147 As-prepared, purified samples were used for the dissolution experiments. Respectively, 100 mg or 30 mg of as-  
148 prepared or purified samples were introduced in sealed polytetrafluoroethylene (PTFE) jars (Savillex) and placed in  
149 contact with 30 mL of  $0.10 \text{ mol}\cdot\text{L}^{-1}$  HCl solution prepared by volumetric dilution of concentrated HCl (37 %) from  
150 Sigma-Aldrich with deionized water. The solution was then out-gassed for anoxic experiments by boiling it for  
151 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  
152 before being used in the dissolution experiments in order to reach equilibrium with the  $\text{O}_2(\text{g})$  partial pressure. Using  
153 the Henry's law constant provided in the ANDRA thermodynamic database `thermochimie-PHREEQC_SIT_v9`  
154 (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  
155  $\text{O}_2(\text{aq})$  concentration in the HCl solution did not exceed  $2.5 \cdot 10^{-9} \text{ mol L}^{-1}$ . The dissolution reactors were then filled  
156 with HCl solution and closed in the glove box. All the experiments were performed in duplicate at  $298 \pm 2 \text{ K}$ . The  
157 dissolution continued for up to several months. During this time, the reactors were stirred at least twice a week and  
158 opened only to sample the solution. The dissolution of the solid was then monitored through regular pH  
159 measurements using a Metrohm combination-glass electrode calibrated against pH buffers (Inlab® Solutions, Mettler  
160 Toledo, pH = 2.00; 4.01 and 7.00 at  $25^\circ\text{C}$ ), whereas uranium and silicon concentrations in the leachate were measured  
161 by inductively coupled plasma atomic emission spectroscopy (ICP-AES). For each sample, 2 mL of the leaching  
162 solution was withdrawn and centrifuged at 12,000 rpm for 2 min. These conditions ensured the removal of colloids  
163 larger than 10 nm. Then 1.8 mL of the solution was diluted in 4.2 mL of  $0.2 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution for further ICP-  
164 AES analyses using a Spectro Arcos EOP device. For this purpose, the spectrometer was calibrated with SPEX  
165 standard solutions. Finally, fresh HCl solution was introduced into the reactors in order to maintain a constant volume

166 of solution in contact with the solid. The volume of the gas phase in the dissolution reactor corresponded to the  
167 internal volume of the Teflon screw cap that did not exceed 3 cm<sup>3</sup>. Thus, each time the reactor was opened in the  
168 glove box, the renewed volume of gas contained about 2.5 10<sup>-10</sup> moles of O<sub>2</sub>(g). The maximum number of samples  
169 reached 30, the maximum amount of O<sub>2</sub>(g) introduced into the system by solution sampling thus did not exceed 7.5  
170 10<sup>-9</sup> moles. The elementary uranium concentration in solution at steady state was in the range between 6.4 10<sup>-5</sup> and  
171 2.6 10<sup>-3</sup> mol L<sup>-1</sup>. Assuming that the oxidation of aqueous U(IV) by O<sub>2</sub> in the system was complete and that the 7.5 10<sup>-9</sup>  
172 moles of oxygen entering the system were consumed by U<sup>4+</sup> oxidation in solution, 5 10<sup>-7</sup> mol L<sup>-1</sup> of UO<sub>2</sub><sup>2+</sup> must have  
173 formed. This concentration represents a maximum of 0.8 % of the elemental concentration of U. A calculation was  
174 performed using the PHREEQC 2 software and the thermochimie\_PHREEQC\_SIT\_v9 database (selected reaction  
175 constants are indicated in Table 1) in order to estimate the oxygen fugacity of the gas phase in equilibrium with a HCl  
176 0.1 mol L<sup>-1</sup> solution containing 10<sup>-4</sup> mol L<sup>-1</sup> of uranium. Based on this calculation the U(VI) over U(IV) ratio did not  
177 exceed 1 mol. %. The calculations (see Figure S2 of the supporting data) indicated that the f(O<sub>2</sub>) did not exceed 10<sup>-69</sup>  
178 atm. As stated by Rai et al. (1990), such a low value for the O<sub>2</sub>(g) fugacity ensures that the uranium remains  
179 tetravalent. This fugacity was then used in the calculation of the speciation of the dissolved uranium. For all  
180 subsequent calculations, the ratio  $[UO_2^{2+}]/[U] \approx 1\%$  was used.

181

### 182 3. RESULTS

#### 183 3.1. Characteristics of the solids

184 PXRD patterns of synthesized and pure coffinite samples are shown in Figure 1. All of the samples were prepared  
185 for 16 days at pH = 11.2 before the buffering step at T = 250°C. Three phases were identified: coffinite, nanoscale  
186 crystals of UO<sub>2</sub> and amorphous SiO<sub>2</sub> (the latter being identified by SEM and X-EDS measurements). The specific  
187 surface areas of the as-prepared sample and the pure coffinite were not significantly different and reached 38 ± 2 m<sup>2</sup>  
188 g<sup>-1</sup>. Additionally, the PXRD pattern of the sample obtained at pH = 12.5, before the buffering step, clearly shows the  
189 presence of UO<sub>2</sub> nanoparticles as the only crystalline phase. For the refinement of the X-ray data, two phases were  
190 considered: tetragonal USiO<sub>4</sub> (*I4<sub>1</sub>/amd*): **a** = 6.9920(1) Å, **c** = 6.2633(1) Å and V = 306.20(1) Å<sup>3</sup> and isometric UO<sub>2</sub>  
191 (*Fm $\bar{3}$ m*): **a** = 5.4329(1) Å and V = 160.36(1) Å<sup>3</sup>. The amount of USiO<sub>4</sub> vs. UO<sub>2</sub> was quantified based on PXRD data  
192 from the Rietveld refinement (Table 2). The complete characterization of the synthesized solids has been reported by

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

196 TEM images and associated electron diffraction patterns of a coffinite grain isolated in the pure coffinite sample  
197 obtained after three purification cycles and one coffinite grain surrounded by uranium oxide nanoparticles in the as-  
198 prepared sample are shown, in Figure 2 (a) and (b), respectively. These images show well crystallized coffinite grains,  
199 200 to 400 nm. The crystallites (*i.e.*, the length of coherent domains determined by Rietveld refinement), which  
200 formed the grains, were ~80 nm, confirming the polycrystalline nature of the coffinite grains. Grain size can affect the  
201 thermodynamic properties of crystalline materials (Castro, 2013), the particle size of this synthetic sample is similar  
202 to that of natural coffinite and that produced by the corrosion of spent nuclear fuel (Bros et al., 2003; Deditius et al.,  
203 2012; Deditius et al., 2008; Janeczek, 1999; Janeczek and Ewing, 1992b; Jensen and Ewing, 2001; Pownceby and  
204 Johnson, 2014); thus, the data obtained here are representative of the occurrence of coffinite in nature and as an  
205 alteration product of UO<sub>2</sub> in spent nuclear fuel. The TEM images of the as-prepared samples also revealed the  
206 presence of uranium oxide nanoparticles, 3 to 5 nm in diameter. The length of coherent domains determined by  
207 Rietveld refinement for the UO<sub>2</sub> phase reached 4 nm. This analysis indicated that diffraction occurs from essentially  
208 the entire particle. These structural observations are consistent with the structural model proposed by Schofield et al.  
209 (2008) for biogenic uraninite nanoparticles of ~2 nm. They showed through synchrotron powder diffraction and  
210 EXAFS, that UO<sub>2</sub> sublattice is preserved in the biogenic sample (as in our nanoparticles), and they assumed that  
211 structural distortion is local, mostly occurring in the periphery of the particles. Another important result is that such  
212 biogenic nanoparticles are structurally homologous to stoichiometric UO<sub>2.00</sub>. One proposed explanation is that  
213 hyperstoichiometric UO<sub>2+x</sub> is stabilized by the presence of U(VI) impurities that are exsolved from the bulk UO<sub>2</sub> as a  
214 nanoscale phase. Such phase segregation may not be possible in nanoparticles because they are too small. However,  
215 we cannot exclude this possibility because the size of the nanoparticles in the as-prepared sample is slightly greater  
216 than that of biogenic nanoparticles, and the mechanism of formation is not promoted by biogenic processes that could  
217 prevent the incorporation of U(VI).

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

221 be rather wide (with values ranging from 0.13 to 1.68), which reflects the presence of  $\text{UO}_2$  and amorphous  $\text{SiO}_2$ . The  
222 composition of the mixture of three components was estimated by both XRD and EDS analysis. The molar ratios are:  
223 59 mol. % of  $\text{USiO}_4$ , 24 mol. % of  $\text{UO}_2$  and 16 mol. % of amorphous  $\text{SiO}_2$ . After three purification cycles (each  
224 purification cycle consisted of the following steps: *i.*) the solid was placed in contact with  $\text{HNO}_3$  then washed  
225 with deionized water; *ii.*), the remaining solid was placed in contact with  $\text{KOH}$  and washed three times with deionized  
226 water) the distribution of U/Si mole ratios was narrowed. After this treatment, the average U/Si mole ratio was  $1.01 \pm$   
227  $0.08$ , which is that of the pure coffinite. An SEM micrograph of the pure coffinite is shown in Figure 3 (c). For the  
228 sample that underwent only two purification cycles, the distribution of the U/Si mole ratio, as determined by X-EDS,  
229 shifted towards values lower than 1, indicating the presence of amorphous  $\text{SiO}_2$ , also confirmed by SEM (Figure 3  
230 (b)). Throughout the paper, the  $\text{USiO}_4 + \text{SiO}_2$  assemblage obtained after two purification cycles is identified as a  
231 “purified sample”. These observations clearly show that three purification cycles are required in order to remove the  
232 entire amount of oxide by-products through dissolution and that the resulting sample was finally single-phase  
233 coffinite.

234

### 235 3.2. Dissolution experiments

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

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

249 conditions considered (0.1 mol·L<sup>-1</sup> HCl, Ar atmosphere), the dissolution of UO<sub>2</sub> nanoparticles was rapid and led to U  
 250 concentration higher than 10<sup>-3</sup> mol L<sup>-1</sup> in solution after only one day. However, after 60 days of leaching, the  
 251 dissolution of the as-prepared sample became virtually stoichiometric (U/Si = 1.4). Then, the U and Si concentrations  
 252 reached a constant value after almost 70 days. Importantly, the elemental concentrations obtained at steady-state for  
 253 the as-prepared sample (UO<sub>2</sub> + SiO<sub>2</sub> + USiO<sub>4</sub>) and the pure coffinite are very close. Consequently, we assume that the  
 254 coffinite phase controlled this equilibrium. Thus, the solubility of the coffinite was reached from over-saturated  
 255 conditions, whereas it was reached from under-saturated conditions for the pure coffinite solubility experiment  
 256 (Figure 4 (b)). The purified sample (USiO<sub>4</sub> + SiO<sub>2</sub>) exhibited a different trend than the as-prepared sample due to the  
 257 absence of UO<sub>2</sub> nanoparticles (Figure 4 (c)). The U/Si molar ratio was lower than 1 for the entire duration of the  
 258 experiment. The Si concentration increased during the first 30 days of dissolution, then reached a constant value.  
 259 Simultaneously, the uranium concentration decreased and stabilized. Assuming that the coffinite phase controlled the  
 260 equilibrium, the rapid dissolution of amorphous silica led to over-saturated conditions for USiO<sub>4</sub>. In the case of the as-  
 261 prepared sample, these oversaturation conditions were imposed by the faster dissolution of UO<sub>2</sub> nanoparticles.  
 262 Oversaturation conditions were created by the faster dissolution of amorphous SiO<sub>2</sub> in the case of the purified sample.  
 263 In both cases, the resulting uranium concentration decreased. A dissolution test of the UO<sub>2</sub>+SiO<sub>2</sub> assemblage (Figure  
 264 4 (d)) indicated an initial rapid dissolution of UO<sub>2</sub> nanoparticles and amorphous SiO<sub>2</sub> followed by a steady-state  
 265 concentration. The solubility of amorphous SiO<sub>2</sub> was reached after 50 days based on the value provided by the  
 266 thermochemie\_PHREEQC\_SIT\_v9 database: (log \*K<sub>S</sub><sup>o</sup>(SiO<sub>2</sub>,am) = -2.710). This could be the explanation for the  
 267 constant silica concentration. The uranium concentration also stabilized at a value of 2.6 10<sup>-3</sup> mol L<sup>-1</sup> after 50 days of  
 268 dissolution, which was more than one order of magnitude higher than for the phases assemblages containing coffinite.  
 269 This value corresponds to a solution oversaturated with respect to UO<sub>2</sub>(cr), with a saturation index,  
 270 
$$SI = \log \left( \frac{\text{Ion activity product}}{K_S^o} \right)$$
, of about 4 (based on the NEA-TDB value for the solubility product), but  
 271 undersaturated with respect to UO<sub>2</sub>(am), with a saturation index of -2.4 (based on the NEA-TDB value for the  
 272 solubility product). As previously stated in the review of Neck and Kim (2001), values reported in the literature for  
 273 solubilities of UO<sub>2</sub>·xH<sub>2</sub>O(s) are extremely scattered. These discrepancies are ascribed either to different redox  
 274 conditions or to different degrees of crystallinity (Casas et al., 1998; Rai et al., 1990). The uranium oxide phase in our  
 275 samples cannot be described as amorphous, as the PXRD patterns showed broad diffraction maxima characteristic of

276 nanometric crystals. A possible effect of grain size on solubility was proposed by Casas et al. (1998) based on the  
277 relation established by Stumm et al., (1992). Small crystals are thermodynamically less stable and have a greater  
278 solubility than larger ones. This could possibly explain the high uranium concentration observed for the  $\text{UO}_2+\text{SiO}_2$   
279 mixture. More importantly, the role of silicates in this experiment is not taken into account in the evaluation of  
280 tetravalent uranium speciation. The existence of U(IV)-Si(IV) complexes is undocumented, but they could play an  
281 important role in coffinite formation (Mesbah et al., 2015). Due to similar charge and ionic radius, the analogy  
282 between U(IV) and Th can be made. Peketroukhine et al. (2002) showed that the solubility of amorphous thorium  
283 hydroxide was increased in the presence of soluble silicates in 0.1 M  $\text{NaClO}_4$  and at pH 6-12. They reported a  
284 solubility of  $10^{-6}$  to  $10^{-5}$  mol  $\text{L}^{-1}$  Th(IV) respectively at pH = 8 and 10 in the presence of 0.14 mol  $\text{L}^{-1}$   $\text{Na}_2\text{SiO}_3$ . This  
285 increase was attributed to the formation of colloids of thorium hydroxo-silicate whose solubility was higher than that  
286 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  
287 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.  
288 If the existence of such mono- or polynuclear complexes could be demonstrated for uranium, this would be a serious  
289 limitation on the interpretation of uranium oxide solubility experiments performed without dissolved silicates.

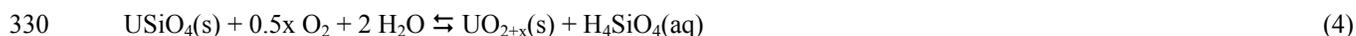
290 The dissolution experiments were also completed under air. Under these conditions, tetravalent uranium is usually  
291 found to be unstable. Thus, the impact of oxygen partial pressure on the dissolution of coffinite was evaluated only  
292 from a kinetic point of view by the comparison of the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

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

$$305 \quad N_L(i) = \frac{\Delta m_i}{f_i S} = \frac{C_i V}{f_i S} \quad \text{and} \quad R_{L,0}(i) = \frac{dN_L(i)}{dt}, \quad (3)$$

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

309 Thereafter, the dissolution reaction is considered to be congruent when all of the normalized dissolution rates are  
310 identical (*i.e.* when all the elements were released with the same ratios as the stoichiometry of the initial material).  
311 The initial normalized dissolution rates determined for the pure  $\text{USiO}_4$  sample and the  $\text{UO}_2 + \text{SiO}_2$  assemblage in out-  
312 gassed  $0.1 \text{ mol L}^{-1}$  HCl solution, either under Ar atmosphere or in air, are summarized in Table 3. The dissolution of  
313  $\text{USiO}_4$  was found to be congruent regardless of the dissolution conditions. The normalized dissolution rates of both U  
314 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  
315 compared with the experiments performed under an argon atmosphere, while the normalized dissolution rates for  $\text{UO}_2$   
316 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  
317  $\text{SiO}_2$  dissolution was not significantly affected by the increase of  $p\text{O}_2$  and  $p\text{CO}_2$ . To our knowledge, there is no  
318 previous study of the kinetics of dissolution of synthetic coffinite. The dissolution rate of  $\text{UO}_2$  nanoparticles in the  
319  $\text{UO}_2 + \text{SiO}_2$  sample under reducing conditions can be compared with values obtained by Bruno et al. (1991) for  $50 \mu\text{m}$   
320 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  
321 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  
322  $\text{UO}_2$  at pH 1 under reducing conditions, calculated by using the rate laws provided either by Bruno et al. (1991) or  
323 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  
324 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  
325 under reducing and acidic conditions, the amorphous  $\text{SiO}_2$  in which  $\text{UO}_2$  nanoparticles are embedded could act as a  
326 passive layer, preventing protons access to the reactive surface sites. As noted by Amme et al. (2005), coffinite is  
327 susceptible to release of uranium in oxygenated water in a manner similar to that of  $\text{UO}_2$ . However, the normalized  
328 dissolution rate of coffinite was at least one order of magnitude lower than that for  $\text{UO}_2$ . As proposed by Janeczek and  
329 Ewing (1992b), the replacement of coffinite by uraninite may be written as:



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

335 The PXRD patterns of  $\text{USiO}_4$  sample measured after dissolution either under Ar atmosphere or in air are shown in  
 336 Figure 5. In both cases, the PXRD patterns exhibit the characteristic XRD diffraction maxima of coffinite with no  
 337 evidence of additional secondary phases. Under these conditions, the solubility constant of  $\text{USiO}_4$  was determined  
 338 from the elemental concentrations measured in solution under Ar atmosphere and the pH at equilibrium that was  
 339 found to range from 1.09 to 1.33 (Table 4).

340

#### 341 4. DISCUSSION

##### 342 4.1. Thermodynamic analysis

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

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

355 
$$*K_s^\circ(\text{USiO}_4) = (\text{U}^{4+})(\text{H}_4\text{SiO}_4)(\text{H}^+)^{-4} \quad (5)$$

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

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

$$359 \quad {}^*K_S^\circ(\text{USiO}_4) = (\gamma_{\text{U}^{4+}} m_{\text{U}^{4+}}) (\gamma_{\text{H}_4\text{SiO}_4} m_{\text{H}_4\text{SiO}_4}) (\gamma_{\text{H}^+} m_{\text{H}^+})^{-4} = \prod_i (\gamma_i^{\nu_i}) {}^*K_S(\text{USiO}_4) \quad (6)$$

360 where  $\gamma_i$  denotes the activity coefficient for ion  $i$ ,  $\nu_i$  is the stoichiometric coefficient, and  $m_i$  ( $\text{mol kg}^{-1}$ ) is the molality  
 361 of  $i$ .

362 From the average elemental concentrations, pH value and the calculated oxygen fugacity  $f(\text{O}_2)$  ( $10^{-69} \text{ atm}$ ), in the  
 363 system at equilibrium, the molalities were calculated with the geochemical speciation model PHREEQC-2 (Parkhurst  
 364 and Appelo, 1999). The solubility product calculations accounted for the aqueous complexation reactions listed in the  
 365 Table 1. The ANDRA Thermochemie thermodynamic database, recently available for the PHREEQC software, was  
 366 used. In the ANDRA Thermochemie database, the existence of  $\text{U}(\text{OH})_2^{2+}$  and  $\text{U}(\text{OH})_3^+$  and the associated equilibrium  
 367 constants from Neck and Kim (2001) are taken into account. The values selected by the NEA-TDB (Grenthe et al.  
 368 1992; Guillaumont et al., 2003) are systematically included in this database and recalculated for internal consistency.  
 369 The values of the equilibrium constants and solubility products of the ANDRA Thermochemie database can be  
 370 compared to other sources in Table 1. The speciation calculations indicate that the  $\text{U}^{4+}$  species represented 29 to 34  
 371 mol. % of the tetravalent uranium under the experimental conditions, whereas  $\text{U}(\text{OH})_2^{2+}$ ,  $\text{U}(\text{OH})_3^+$ , and  $\text{UCl}^{3+}$  species  
 372 were in the same range, between 20 and 25 mol. %.  $\text{UO}_2^{2+}$  molality depended on the  $f(\text{O}_2)$  selected and reached  
 373 almost 1 mol. %. As the estimate of  $m_{\text{U}^{4+}}$  was affected by the experimental uncertainty of pH, the speciation  
 374 calculations were made at a maximum and a minimum pH value, defined as the average pH value  $\pm 2$  standard  
 375 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  
 376 uncertainty of the pH values, as  $\text{H}_4\text{SiO}_4$  is the predominant species in this range of pH. The uncertainty in the  
 377 evaluation of  $m_{\text{H}_4\text{SiO}_4}$  thus depends only on the variability observed experimentally for the Si concentration at  
 378 equilibrium between successive measurements. Finally, the uncertainty in the determination of  ${}^*K_S$  was estimated by  
 379 propagating the uncertainties on  $m_{\text{U}^{4+}}$ ,  $m_{\text{H}_4\text{SiO}_4}$ , and  $m_{\text{H}^+}$ .

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

$$381 \quad \log(\gamma_i) = -\frac{A z_i^2 \sqrt{I_m}}{1 + B a_i \sqrt{I_m}} + \sum_j \varepsilon(i, j, I_m) m_j \quad (7)$$

382 where  $A$  and  $Ba_i$  are constants that depend on the temperature and are defined in the database (at 25°C and 1 bar,  $A =$   
383  $0.509 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ ,  $Ba_i = 1.5 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ ),  $z_i$  corresponds to the charge of the ion,  $I_m$  ( $\text{mol kg}^{-1}$ ) is the ionic strength of  
384 the solution. The calculated activities of  $\text{U}^{4+}$  and  $\text{H}_4\text{SiO}_4$  at equilibrium, as well as the solubility constant extrapolated  
385 to standard conditions,  $*K_S^\circ$ , are listed in Table 4.

386 The log  $*K_S^\circ$  values obtained from the three phase assemblages that contained  $\text{USiO}_4$  range from -4.63 to -5.34.  
387 The only value that was found to be significantly different from others was obtained for the phase assemblage  $\text{USiO}_4$   
388 +  $\text{SiO}_2$  #2 in Table 4. This difference resulted from a significantly higher pH value at equilibrium. As the presence of  
389 coffinite was not detected in the PXRD pattern of the  $\text{UO}_2 + \text{SiO}_2$  assemblage at the end of the dissolution  
390 experiment, the value of  $*K_S$  was not calculated. However, considering the values of the activities of  $\text{U}^{4+}$  and  $\text{H}_4\text{SiO}_4$   
391 at steady state, supersaturated conditions should have been reached relative to coffinite. The value determined for the  
392 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  
393 the pure coffinite sample, the solubility product can thus be attributed unambiguously to crystalline coffinite. This log  
394  $*K_S^\circ(\text{USiO}_4, \text{cr})$  value is higher than that estimated from solubility studies developed from uranotorite solid  
395 solutions: ( $\log *K_S^\circ(\text{USiO}_4, \text{cr}) = -6.1 \pm 0.2$ ) (Szenknect et al., 2013). However, the thermodynamic calculations of  
396 that study were performed using the Lawrence Livermore National Laboratory (LLNL) database, whereas ANDRA  
397 Thermochemie database has been used in the present work. The main difference between the databases is the value of  
398 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  
399 46.0 in the ANDRA Thermochemie-TDB. This difference has a strong impact on the uranium speciation that led to a  
400 discrepancy of almost 1 log unit in the solubility product. Thus, it should be stressed here, that the choice of the  
401 thermodynamic database is a key step in the evaluation of standard equilibrium constant and that the estimate of error  
402 does not take into account the uncertainties on the thermodynamic constants implemented in the database. Thus, using  
403 the solubility product reported here for coffinite with a different set of thermodynamic data will lead to inconsistent  
404 and erroneous results.

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

$$406 \quad \Delta_r G^\circ(T) = -RT \ln *K_S^\circ(T) \quad (8)$$

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

408 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  
409 from the NEA TDB II (Table S1 of the supporting information) were used in the Hess's law (Eq. 9) to determine the  
410 standard molar Gibbs energy of formation of coffinite:

$$411 \quad \Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ \quad (9)$$

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

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



419 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  
420 quartz (Table S1 of the supporting information). The obtained positive value reached  $20.6 \pm 5.2\text{ kJ mol}^{-1}$ , which  
421 indicates unambiguously that coffinite is less stable than a quartz + uraninite mixture at 298 K. This is in agreement  
422 with Hemingway (1982), who pointed out that coffinite must be less stable than the mixture of binary oxides in light  
423 of the natural occurrence of coffinite and the paragenetic sequence described by Cuney in 1978 (Cuney, 1978). The  
424 thermal stability of coffinite is not well known. Fuchs and Hoekstra (1959) placed the upper limit of coffinite stability  
425 as compared with uraninite and amorphous silica at 1273 K. On the basis of this observation, Hemingway (1982)  
426 estimated the Gibbs free energy related to the formation of coffinite from oxides at 298.15 K, assuming that the  
427  $\Delta_{r,ox} G^\circ$  value of reaction (10) is equal to zero at 1273 K and using the heat capacities of quartz and uraninite to  
428 approximate the heat capacity of coffinite between 298 and 1273 K, as well as auxiliary thermochemical data from  
429 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  
430 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  
431 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  
432 coffinitization reaction indicates that, depending on the sign of the  $\Delta_{r,ox} H^\circ$ , this equilibrium might be easily reversed  
433 to favor the formation of coffinite at higher temperatures and pressures. Recent results obtained by Guo et al. (2015)  
434 from calorimetry in sodium molybdate and lead borate and using the same pure coffinite sample as in the present

435 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  
436 formed directly from the mixture of the binary oxides and decomposes upon heating to a moderate temperature as  
437 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  
438 same coffinite sample and the  $\Delta_{r,ox}G^\circ$  (298 K) determined by the solubility measurements in the present study, we  
439 derived the standard molar entropy of formation of coffinite from the mixture of the binary oxides. The  $\Delta_{r,ox}S^\circ$  term at  
440 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  
441 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  
442 Table S1,  $S_m^\circ = 136 \pm 25 \text{ J mol}^{-1} \text{ K}^{-1}$ .

443 This analysis shows that coffinite is thermodynamically metastable relative to quartz and uraninite at 25°C. It is  
444 noteworthy that isostructural ThSiO<sub>4</sub>, thorite behaves differently. Mazeina et al. (2005) determined a  $\Delta_{r,ox}H^\circ$  value for  
445 the formation of thorite from thorianite and quartz that is slightly lower than for coffinite:  $\Delta_{r,ox}H^\circ(\text{ThSiO}_4, \text{thorite}) =$   
446  $19.4 \pm 2.1 \text{ kJ mol}^{-1}$ . On the other hand, thorite was found to be more stable in Gibbs energy at 25°C than the mixture  
447 of quartz and thorianite by Szenknect et al. (2013) and Schuiling et al. (1976). They obtained  $\Delta_{r,ox}G^\circ(\text{ThSiO}_4, \text{thorite})$   
448  $= -19.0 \pm 5.5$  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  
449  $\Delta_{r,ox}G^\circ$ , the entropy term must be large enough to offset the enthalpy. Thus, coffinite cannot be formed from the  
450 mixture of uraninite and quartz; whereas, thorite, which is entropy stabilized, can be formed from thorianite and  
451 quartz.

452

#### 453 4.2. Environmental implications

454 In uranium ores, coffinite is commonly coexists with uraninite. Thus, the geologic evidence seems to contradict  
455 these experimental results that confirm that coffinite is metastable relative to uraninite plus quartz. The calculation  
456 based on the Gibbs free energy of formation of coffinite determined by the solubility measurements and auxiliary data  
457 (Table S1) gives the Gibbs free energy of the coffinitization reaction (1) to be:  $-2.3 \pm 5.6$ , which is essentially zero  
458 within error. Even though coffinite is metastable at room temperature with respect to crystalline UO<sub>2</sub> and SiO<sub>2</sub>,  
459 coffinite can form from aqueous U(IV) in contact with silica-rich solutions. From the recent review by Evins and  
460 Jensen (2012), it appears that it is not possible to constrain the conditions that favor the formation of coffinite based  
461 on geological occurrences because temperature, pressure, pH and silica activity of the fluids are not known.  
462 Mercadier et al. (2011) estimate that the temperature of the mineralizing fluids in the Athabasca basin deposits

463 (Canada), where uraninite and coffinite precipitated in the uranium front, were not higher than 50°C. Mesbah et al.  
464 (2015) showed that, under appropriate conditions, small amounts of coffinite in a UO<sub>2</sub> plus SiO<sub>2</sub> (amorphous) mixture  
465 can be obtained by hydrothermal treatment at 150°C. The low yield of coffinite at low temperatures may result from  
466 slow kinetics of nucleation, but hydrothermal conditions would not be required to precipitate coffinite. Finally, the  
467 values of the silica and tetravalent uranium activity seem to be the key parameters that facilitate the precipitation of  
468 coffinite.

469 The solubility product of coffinite determined experimentally in this study was used in the  
470 Thermochimie\_PHREEQC\_SIT\_v9 database for geochemical simulations using PHREEQC-2 software. This allows  
471 one to delineate the stability fields of UO<sub>2</sub> and USiO<sub>4</sub> at low temperature in terms of silica activity and pH. The  
472 conditions that favor the formation of coffinite as compared with uraninite at pH = 6 under anoxic condition are  
473 shown in Figure 6. Using the solubility constant of uraninite selected by the NEA TDB project ( $\log K_{s,0}^{\circ}(\text{UO}_2,$   
474 crystalline, 298.15 K) = -60.86 ± 0.36), it appears that a solution in equilibrium with uraninite becomes supersaturated  
475 with respect to coffinite if the silica concentration exceeds 0.41 mol L<sup>-1</sup>. Such high silica concentrations are unlikely  
476 in natural systems. This limit is obviously determined by the choice of the solubility constant for UO<sub>2</sub> that controls the  
477 U(OH)<sub>4</sub> concentration in solution. However, this has been intensely debated (Langmuir, 1997; Neck and Kim, 2001;  
478 Rai et al., 1990, 2003). Based on the assumption that amorphous UO<sub>2</sub> ( $K_{s,0}^{\circ}(\text{UO}_2, \text{am}, 298.15 \text{ K}) = -54.5 \pm 1.0$ )  
479 controls the U(OH)<sub>4</sub> concentration, the lower limit of the silica concentration necessary to precipitate coffinite is 1.8  
480 10<sup>-7</sup> mol L<sup>-1</sup>. The value measured by Parks and Pohl (1988), which is generally accepted for the solubility of  
481 crystalline uraninite, corresponds to a silica concentration in solution of 1.8 10<sup>-6</sup> mol L<sup>-1</sup>, which is in equilibrium with  
482 coffinite.

483 White (1995) reported the aqueous concentration of H<sub>4</sub>SiO<sub>4</sub> in soil solutions and observed that the upper limit  
484 corresponds to the solubility of amorphous SiO<sub>2</sub> (5 10<sup>-3</sup> mol L<sup>-1</sup>), whereas the lowest values were below the solubility  
485 of quartz (less than 10<sup>-4</sup> mol L<sup>-1</sup>). Most of the soil solution data fall within the kaolinite stability field (silica  
486 concentrations between 6.6 10<sup>-5</sup> and 5 10<sup>-3</sup> mol L<sup>-1</sup>). Kaolinite is the most commonly reported weathering product of  
487 silicate rocks in soils. Silica concentrations in soil solutions are thus strongly affected by the precipitation of  
488 secondary clay minerals, even though, in some cases, the soil solution approaches saturation with primary silicate  
489 minerals such as K-feldspar. Appelo and Postma (1996) reported the normal ranges of dissolved silica concentrations  
490 in uncontaminated fresh water to be between 7 10<sup>-5</sup> and 10<sup>-3</sup> mol L<sup>-1</sup> (gray area in Figure 6). Thus, the values

491 commonly encountered for the dissolved silica concentrations in soil solutions and groundwaters are much higher  
492 than the calculated limit of coffinite formation, considering the Parks and Pohl values for the solubility of uraninite.  
493 Thus coffinitization of tetravalent uranium oxide whose solubility is intermediate between uraninite ( $\log K_{s,0}^{\circ}(\text{UO}_2,$   
494  $\text{cr}) = -60.86$ ) 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  
495 in natural groundwaters. Figure 7 shows the variation of the tetravalent uranium concentration in solution with an  
496 aqueous Si concentration of  $7 \cdot 10^{-5} \text{ mol.L}^{-1}$  in equilibrium with coffinite at 298 K, under anoxic conditions as a  
497 function of pH. Based on these calculations, it appears that a solution that contains more than  $10^{-11} \text{ mol L}^{-1}$  of  $\text{U}(\text{OH})_4$   
498 is oversaturated with respect to coffinite in a pH range from 4 to 10. As this pH interval encompasses the typical  
499 values for groundwater, the presence of coffinite in ores cannot be related to a precise range of pH that allows its  
500 formation. However, it is important to stress that this solution remains oversaturated relative to uraninite. Elevated  
501 silica and uranium concentrations are common in uranium ores, especially in sandstone deposits or highly  
502 fractionated Si-rich igneous rocks (Amme et al., 2005; [Deditius et al., 2008](#); [Pownceby and Johnson, 2014](#); [Stieff et](#)  
503 [al., 1955, 1956](#)). Different mechanism can lead to conditions oversaturated with respect to  $\text{UO}_2(\text{s})$ . For example, high  
504 temperature brines can cause the dissolution of  $\text{UO}_2(\text{crystalline})$  under reducing conditions, or U(IV) concentration  
505 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  
506 resulting U(IV) concentration may be orders of magnitude higher than the solubility of  $\text{UO}_2(\text{cr})$ . The degree of  
507 crystallinity of uranium dioxide is another parameters that can affect its solubility. For natural  $\text{UO}_2$ , it is strongly  
508 affected by radiation damage. Small, metamict crystals are thermodynamically less stable; their dissolution in  
509 appropriate conditions can lead to uranium concentration sufficiently high to form coffinite (Matzke, 1992). Most  
510 importantly, the impact of silica in solution is not taken into account in the evaluation of tetravalent uranium  
511 speciation; as a result, the evaluation of  $\text{UO}_2$  solubility in silica-rich groundwater based on the currently available  
512 thermodynamic data may not be correct. The existence of U(IV)-Si(IV) complexes is speculative, but Mesbah et al.  
513 (2015) suggested that these complexes could play an important role in coffinite formation. The existence of mono- or  
514 poly-nuclear complexes of U(IV) with silicates and hydroxydes, as it was evidenced for Th by Peketroukhine et al.  
515 (2002) and Rai et al. (2008), would significantly increase the solubility of  $\text{UO}_2$  under alkaline conditions and favor  
516 coffinite precipitation. Such mechanism could explain the fact that uraninite and coffinite are often found in intimate  
517 intergrowths in many natural samples (Deditius et al., 2008).

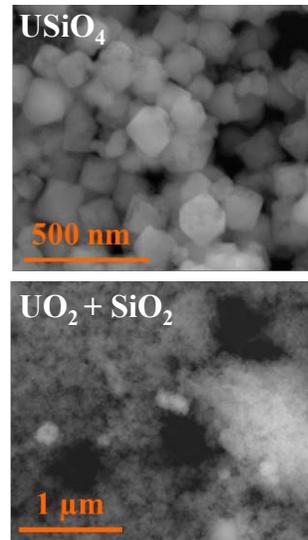
518 These results allow the assessment of the risk of coffinitization of  $\text{UO}_2$  in the spent nuclear fuel in a geological  
519 repository. Based on the values of the Si concentration ( $1.4 \cdot 10^{-4} \text{ mol L}^{-1}$ ) measured by Gaucher et al. (2009) in the  
520 French site porewater (Callovo-Oxfordian argillite), or in the granitic groundwater of Forsmark and Äspö in Sweden  
521 ( $1.8 \cdot 10^{-4} \text{ mol L}^{-1}$  and  $1.5 \cdot 10^{-4} \text{ mol L}^{-1}$ , respectively), it appears that coffinitization of the  $\text{UO}_2$  matrix may occur only if  
522 the dissolution of  $\text{UO}_2$  matrix leads to tetravalent uranium concentrations in solution of at least  $8 \cdot 10^{-12} \text{ mol L}^{-1}$ .  
523 Obviously, the concentration levels of U (IV) in the vicinity of the geological repository are hardly predictable.  
524 Indeed, they are controlled by the dissolution rate of the  $\text{UO}_2$  matrix in spent nuclear fuel, and this depends on the  
525 groundwater velocity, composition (modified locally by radiolysis), pH, Eh and temperature, as well as the complex  
526 microstructure and composition of the SNF (Burns et al., 2012). These parameters, which are spatially and temporally  
527 variable (Ewing, 2015), in turn depend on the emplacement strategy and the types of near-field engineered barriers.

528

## 529 5. CONCLUSION

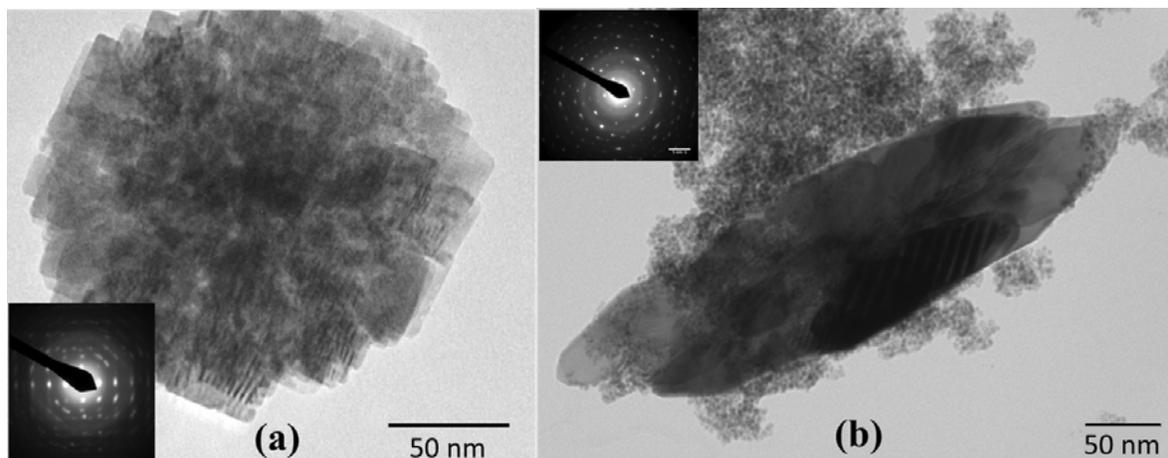
530 In response to the pressing need for more accurate thermodynamic data required for the evaluation of the formation  
531 of coffinite, as well as the coffinitization of uraninite, the solubility constant of coffinite has been determined at  $25^\circ\text{C}$   
532 and 1 bar:  $\log *K_S^\circ(\text{USiO}_4, \text{cr}) = -5.25 \pm 0.05$ . This value, the first to be experimentally determined, allows for an  
533 evaluation of the conditions under which the coffinitization of  $\text{UO}_2$  may occur as a function of the pH and Si  
534 concentration of the groundwater. Thermodynamically, the coffinitization reaction occurs at 298 K, under reducing  
535 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  
536 concentrations are common in uranium ores, especially in sandstone deposits or highly fractionated Si-rich igneous  
537 rocks. This is consistent with the natural occurrence of coffinite. The positive value obtained for the  $\Delta_{r,ox}G^\circ(298\text{K}) =$   
538  $20.6 \pm 5.2 \text{ kJ mol}^{-1}$  associated with the formation of coffinite from a mixture of the binary oxides indicates that  
539 coffinite is energetically metastable at low temperature with respect to uraninite plus quartz. Coffinite is thus formed  
540 through a precipitation mechanism following the dissolution of uraninite in silica-rich solutions. Chemical  
541 simulations indicate that coffinite is stable with respect to aqueous species over a wide range of concentrations, which  
542 explains the occurrence of coffinite in uranium ore deposits. Although metastable with respect to uraninite and quartz,  
543 coffinite persists in uranium ore deposits owing to its slow kinetics of dissolution.

544

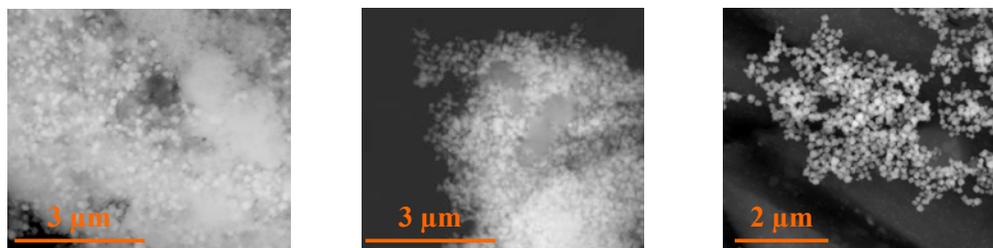


545  
 546 Figure 1. PXRD patterns of an as-prepared sample obtained from the synthesis at pH =12.5 (black line), as-prepared  
 547 sample obtained from the synthesis at pH = 11.4 (red line) and of the pure coffinite obtained after three purification  
 548 cycles with  $\text{HNO}_3$   $10^{-2}$  mol  $\text{L}^{-1}$  and  $\text{KOH}$   $10^{-2}$  mol  $\text{L}^{-1}$  (blue line). SEM micrographs of the  $\text{UO}_2 + \text{SiO}_2$  assemblage  
 549 and of the pure coffinite sample.

550



551  
 552 Figure 2. TEM images of (a) one grain of pure coffinite isolated in the sample obtained after three purification cycles  
 553 and (b) one grain of coffinite surrounded by nanoparticles of uranium oxide by-product in the as-prepared sample.



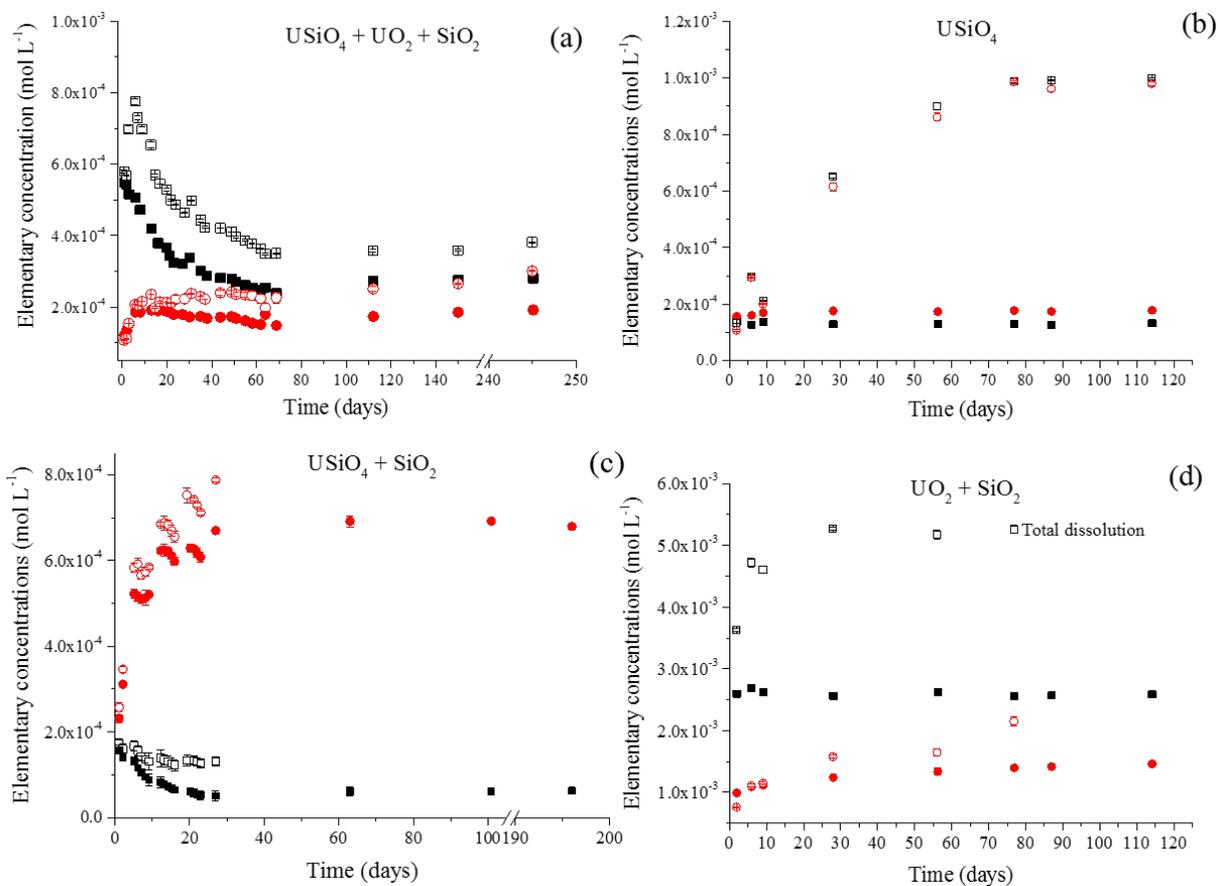
(a)

(b)

(c)

554  
555  
556 Figure 3. SEM micrographs and X-EDS analyses of (a) as-prepared sample, (b) sample after two purification cycles  
557 with  $\text{HNO}_3$   $10^{-2}$  and  $\text{KOH}$   $10^{-2}$  mol  $\text{L}^{-1}$  and (c) pure coffinite sample obtained after three purification cycles.  
558 Histograms represent the distribution of U/Si mole ratio determined by X-EDS (expressed in %).

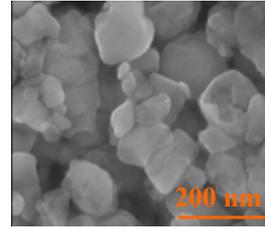
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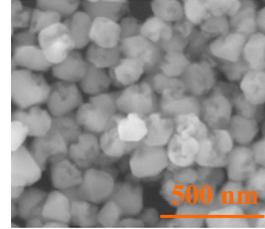
560  
 561 Figure 4. Evolution of the elemental concentrations (U: black symbols, Si: red symbols) during the dissolution of (a)  
 562 as-prepared sample containing USiO<sub>4</sub>, UO<sub>2</sub> and SiO<sub>2</sub>(am), (b) pure USiO<sub>4</sub>, (c) purified sample containing USiO<sub>4</sub> and  
 563 SiO<sub>2</sub>(am) and (d) as-prepared containing UO<sub>2</sub> and SiO<sub>2</sub>(am) only. Closed and open symbols are for experiments under  
 564 an Ar atmosphere and air, respectively.

565

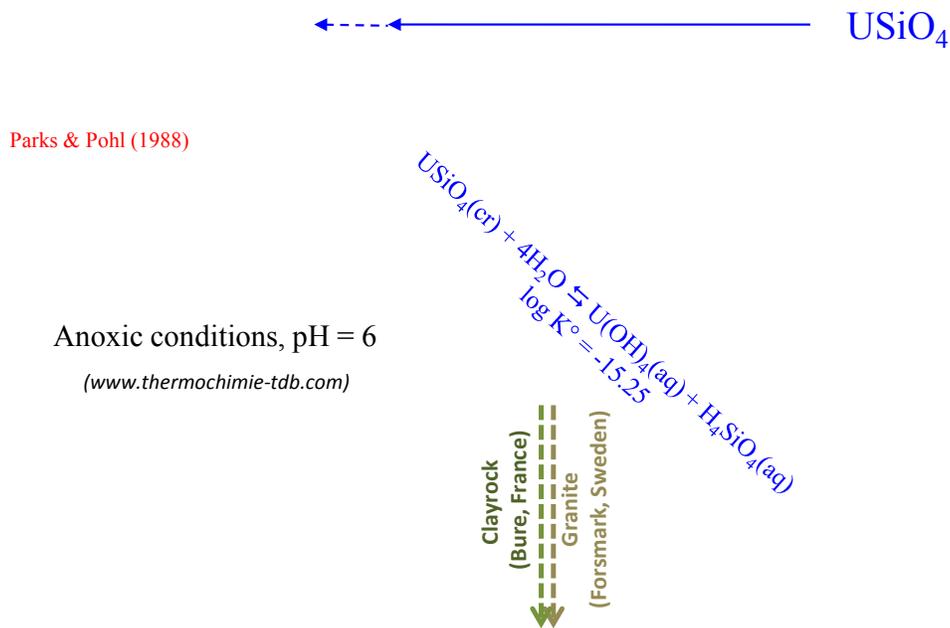
**USiO<sub>4</sub> / Air**



**USiO<sub>4</sub> / Ar**



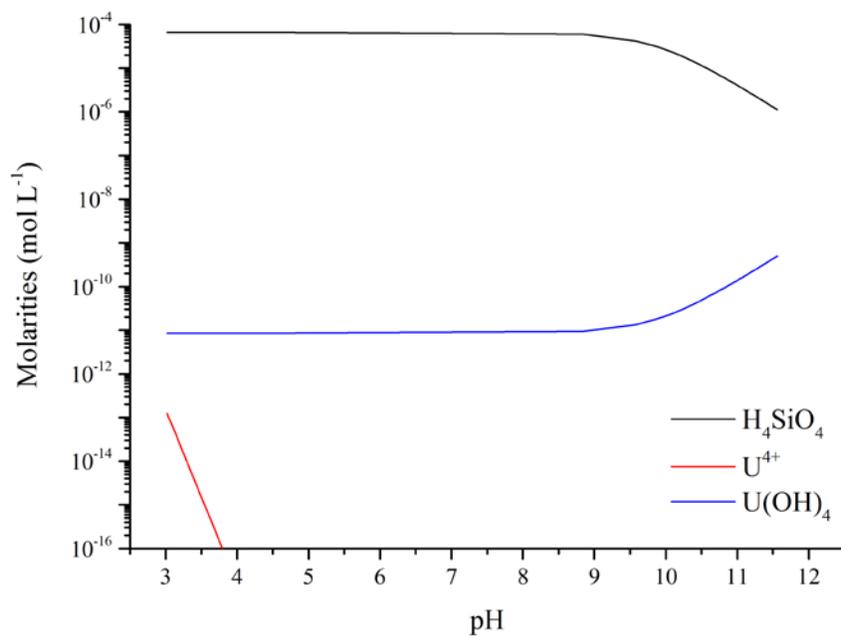
566  
567 Figure 5. SEM images and PXRD patterns of USiO<sub>4</sub> sample at the end of under-saturated experiments performed in  
568 0.1 M HCl solution under Ar atmosphere (black line) and under air (red line). Blue lines represent Bragg peak  
569 positions for coffinite from JCPDS file #11-0420.



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  $pH = 6$ ,  $f(O_2) = 10^{-69}$  atm and  $Cl^-$  molarity of  $0.01 \text{ mol L}^{-1}$ , with  $\log$   
 573  $*K_s^\circ(USiO_4, cr) = -5.25 \pm 0.05$ . 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  $U(OH)_4(aq)$  concentration is controlled by the solubility of  
 575  $UO_2(am)$  (dashed green line). Solid green line represents the lowest limit of the stability domain of coffinite for a  
 576 silica concentration of  $0.41 \text{ mol L}^{-1}$  assuming that  $U(OH)_4(aq)$  concentration is controlled by the solubility of  $UO_2(cr)$   
 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  $U(OH)_4(aq)$  concentration is controlled by the solubility of  
 579  $UO_2(cr)$  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  $U(OH)_4(aq)$  and silica  
 581 concentrations in the experiments performed by Amme et al. (2005).

582



583  
 584 Figure 7. Variation of the  $U(OH)_4$  concentration in equilibrium with coffinite (blue line) with the pH of the solution.  
 585 Simulation was performed at 298 K for a total concentration of Si =  $7 \cdot 10^{-5}$  mol L<sup>-1</sup> (corresponding to the left-hand  
 586 limit of the gray area in figure 6),  $f(O_2) = 10^{-69}$  atm, and ionic strength < 0.01 mol L<sup>-1</sup>.

587  
 588

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

597

598 Table 2. Estimated quantities of USiO<sub>4</sub> and UO<sub>2</sub> based on Rietveld refinements of the PXRD patterns of the samples  
 599 used for dissolution experiments and the corresponding cell parameters. Average U/Si molar ratio and two standard  
 600 deviations determined from X-EDS analyses.

Sample ID	U/Si		USiO <sub>4</sub>				UO <sub>2</sub>			
	Mole ratio	a (Å)	c (Å)	Volume <sup>a</sup> (Å <sup>3</sup> )	USiO <sub>4</sub> (mol.%)	Crystal size (nm)	a (Å)	Volume (Å <sup>3</sup> )	UO <sub>2</sub> (mol.%)	Crystal size(nm)
USiO <sub>4</sub> +UO <sub>2</sub> +SiO <sub>2</sub>	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 <sub>2</sub> + SiO <sub>2</sub>	-	-	-	-	-	-	5.4180(4)	159.05(2)	100	4(1)
USiO <sub>4</sub> +SiO <sub>2</sub>	0.65 ± 0.08	6.9833(2)	6.2575(2)	305.16(2)	100	79(7)	-	-	-	-
USiO <sub>4</sub>	1.01 ± 0.08	6.9856(2)	6.2582(2)	305.39(2)	100	79(7)	-	-	-	-

601 <sup>a</sup> the molar volume of USiO<sub>4</sub> reached V<sup>o</sup>(298.15K) = 45.98 ± 0.04 cm<sup>3</sup> mol<sup>-1</sup>

602

603

604 Table 3. Initial normalized dissolution rates of USiO<sub>4</sub> and UO<sub>2</sub>+SiO<sub>2</sub> samples determined in 0.1 mol L<sup>-1</sup> HCl at room  
 605 temperature under Ar atmosphere and air, respectively.

Sample ID	Ar		Air	
	R <sub>L,0</sub> (U) (g m <sup>-2</sup> d <sup>-1</sup> )	R <sub>L,0</sub> (Si) (g m <sup>-2</sup> d <sup>-1</sup> )	R <sub>L,0</sub> (U) (g m <sup>-2</sup> d <sup>-1</sup> )	R <sub>L,0</sub> (Si) (g m <sup>-2</sup> d <sup>-1</sup> )
USiO <sub>4</sub>	(3 ± 2) 10 <sup>-5</sup>	(6.0 ± 0.9) 10 <sup>-5</sup>	(4.0 ± 0.2) 10 <sup>-4</sup>	(3.8 ± 0.1) 10 <sup>-4</sup>
UO <sub>2</sub> + SiO <sub>2</sub>	(6.0 ± 0.8) 10 <sup>-4</sup>	(2.1 ± 0.1) 10 <sup>-4</sup>	(1.1 ± 0.2) 10 <sup>-2</sup>	(1.5 ± 0.4) 10 <sup>-4</sup>

606

607

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

Sample ID:	USiO <sub>4</sub>	UO <sub>2</sub> + SiO <sub>2</sub> +USiO <sub>4</sub>		SiO <sub>2</sub> +USiO <sub>4</sub>		UO <sub>2</sub> + SiO <sub>2</sub>	
		1	2	1	2	1	2
[U]	(1.30 ± 0.04) 10 <sup>-4</sup>	(2.63 ± 0.08) 10 <sup>-4</sup>	(1.4 ± 0.2) 10 <sup>-4</sup>	(5.7 ± 0.4) 10 <sup>-5</sup>	(6.4 ± 0.3) 10 <sup>-5</sup>	(2.58 ± 0.05) 10 <sup>-3</sup>	(2.61 ± 0.05) 10 <sup>-3</sup>
[Si]	(1.76 ± 0.07) 10 <sup>-4</sup>	(1.7 ± 0.1) 10 <sup>-4</sup>	(1.12 ± 0.07) 10 <sup>-4</sup>	(6.3 ± 0.2) 10 <sup>-4</sup>	(3.7 ± 0.1) 10 <sup>-4</sup>	(1.63 ± 0.08) 10 <sup>-3</sup>	(1.4 ± 0.1) 10 <sup>-3</sup>
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
$m_{\text{H}^+}$	(8.8 ± 0.2) 10 <sup>-2</sup>	(1.02 ± 0.02) 10 <sup>-1</sup>	(8.4 ± 0.2) 10 <sup>-2</sup>	(9.7 ± 0.2) 10 <sup>-2</sup>	(5.7 ± 0.1) 10 <sup>-2</sup>	(6.2 ± 0.1) 10 <sup>-2</sup>	(6.2 ± 0.1) 10 <sup>-2</sup>
$m_{\text{U}^{4+}}$	(3.8 ± 0.1) 10 <sup>-5</sup>	(8.8 ± 0.5) 10 <sup>-5</sup>	(3.9 ± 0.5) 10 <sup>-5</sup>	(1.8 ± 0.1) 10 <sup>-5</sup>	(1.15 ± 0.08) 10 <sup>-5</sup>	(5.5 ± 0.4) 10 <sup>-4</sup>	(5.6 ± 0.4) 10 <sup>-4</sup>
$m_{\text{UOH}^{3+}}$	(2.85 ± 0.09) 10 <sup>-5</sup>	(5.5 ± 0.4) 10 <sup>-5</sup>	(3.1 ± 0.4) 10 <sup>-5</sup>	(1.2 ± 0.1) 10 <sup>-5</sup>	(1.44 ± 0.07) 10 <sup>-5</sup>	(5.9 ± 0.4) 10 <sup>-4</sup>	(5.9 ± 0.4) 10 <sup>-4</sup>
$m_{\text{U(OH)}_2^{2+}}$	(3.3 ± 0.2) 10 <sup>-5</sup>	(5.3 ± 0.5) 10 <sup>-5</sup>	(3.8 ± 0.5) 10 <sup>-5</sup>	(1.3 ± 0.1) 10 <sup>-5</sup>	(2.7 ± 0.1) 10 <sup>-5</sup>	(9.7 ± 0.4) 10 <sup>-4</sup>	(9.8 ± 0.4) 10 <sup>-4</sup>
$m_{\text{U(OH)}_3^+}$	(5.6 ± 0.7) 10 <sup>-8</sup>	(7.7 ± 0.9) 10 <sup>-8</sup>	(6.8 ± 0.9) 10 <sup>-8</sup>	(1.9 ± 0.2) 10 <sup>-8</sup>	(7.3 ± 0.6) 10 <sup>-8</sup>	(2.4 ± 0.2) 10 <sup>-6</sup>	(2.4 ± 0.2) 10 <sup>-6</sup>
$m_{\text{UCl}^{3+}}$	(3.0 ± 0.1) 10 <sup>-5</sup>	(6.6 ± 0.4) 10 <sup>-5</sup>	(3.1 ± 0.4) 10 <sup>-5</sup>	(1.4 ± 0.1) 10 <sup>-5</sup>	(1.02 ± 0.06) 10 <sup>-5</sup>	(4.4 ± 0.2) 10 <sup>-4</sup>	(1.02 ± 0.06) 10 <sup>-5</sup>
$m_{\text{U(OH)}_4}$	(3.1 ± 0.5) 10 <sup>-12</sup>	(3.7 ± 0.6) 10 <sup>-12</sup>	(4.0 ± 0.5) 10 <sup>-12</sup>	(1.0 ± 0.1) 10 <sup>-12</sup>	(6.3 ± 0.9) 10 <sup>-12</sup>	(1.9 ± 0.3) 10 <sup>-10</sup>	(1.9 ± 0.3) 10 <sup>-10</sup>
$m_{\text{UO}_2^{2+}}$	(1.21 ± 0.08) 10 <sup>-6</sup>	(1.9 ± 0.9) 10 <sup>-6</sup>	(1.4 ± 0.2) 10 <sup>-6</sup>	(0.5 ± 0.2) 10 <sup>-6</sup>	(1.0 ± 0.5) 10 <sup>-6</sup>	(3.6 ± 1.9) 10 <sup>-5</sup>	(3.6 ± 1.9) 10 <sup>-5</sup>
$m_{\text{H}_4(\text{SiO})_4}$	(1.78 ± 0.07) 10 <sup>-4</sup>	(1.7 ± 0.1) 10 <sup>-4</sup>	(1.13 ± 0.07) 10 <sup>-4</sup>	(6.4 ± 0.2) 10 <sup>-4</sup>	(3.7 ± 0.1) 10 <sup>-4</sup>	(1.64 ± 0.08) 10 <sup>-3</sup>	(1.4 ± 0.1) 10 <sup>-3</sup>
$*K_S(\text{USiO}_4)$	(1.1 ± 0.1) 10 <sup>-4</sup>	(1.4 ± 0.1) 10 <sup>-4</sup>	(0.9 ± 0.3) 10 <sup>-4</sup>	(1.3 ± 0.2) 10 <sup>-4</sup>	(4.0 ± 0.6) 10 <sup>-5</sup>		
$\log *K_S(\text{USiO}_4)$	<b>-3.95 ± 0.05</b>	<b>-3.86 ± 0.08</b>	<b>-4.05 ± 0.13</b>	<b>-3.88 ± 0.07</b>	<b>-3.40 ± 0.07</b>		
(U <sup>4+</sup> )	(7.9 ± 0.7) 10 <sup>-7</sup>	(1.6 ± 0.7) 10 <sup>-6</sup>	(8.4 ± 1.2) 10 <sup>-7</sup>	(3.6 ± 0.3) 10 <sup>-7</sup>	(3.0 ± 0.2) 10 <sup>-7</sup>	(1.19 ± 0.08) 10 <sup>-5</sup>	(1.20 ± 0.08) 10 <sup>-5</sup>
(H <sub>4</sub> SiO <sub>4</sub> )	(1.78 ± 0.07) 10 <sup>-4</sup>	(1.7 ± 0.1) 10 <sup>-4</sup>	(1.13 ± 0.07) 10 <sup>-4</sup>	(6.4 ± 0.2) 10 <sup>-4</sup>	(3.7 ± 0.1) 10 <sup>-4</sup>	(1.64 ± 0.08) 10 <sup>-3</sup>	(1.4 ± 0.1) 10 <sup>-3</sup>
$*K_S^\circ(\text{USiO}_4)$	(5.6 ± 0.7) 10 <sup>-6</sup>	(6.4 ± 1.1) 10 <sup>-6</sup>	(4.5 ± 1.4) 10 <sup>-6</sup>	(6.3 ± 1.0) 10 <sup>-6</sup>	(2.4 ± 0.4) 10 <sup>-5</sup>		
$\log *K_S^\circ(\text{USiO}_4)$	<b>-5.25 ± 0.05*</b>	<b>-5.19 ± 0.08</b>	<b>-5.34 ± 0.13</b>	<b>-5.20 ± 0.07</b>	<b>-4.63 ± 0.07</b>		
$\Delta_r G^\circ$	<b>30.0 ± 0.3</b>	<b>29.6 ± 0.4</b>	<b>30.5 ± 0.8</b>	<b>29.7 ± 0.4</b>	<b>26.4 ± 0.4</b>		
$\Delta_f G^\circ$	<b>-1867.6 ± 3.2</b>	<b>-1867.2 ± 3.4</b>	<b>-1868.1 ± 3.7</b>	<b>-1867.3 ± 3.3</b>	<b>-1864.0 ± 3.3</b>		
$\Delta_{r,ox} G^\circ$	<b>20.6 ± 5.2</b>	<b>20.9 ± 5.4</b>	<b>20.0 ± 5.7</b>	<b>20.8 ± 5.3</b>	<b>24.1 ± 5.3</b>		

613 \*Value selected in the present study

614

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

	$\Delta_f G^\circ$	$\Delta_f H^\circ$	$S_m^\circ$	$\Delta_f S^\circ$	$\Delta_{r,av} G^\circ$	$\Delta_{r,av} H^\circ$	$\Delta_{r,av} S^\circ$	$\Delta_r G^\circ$	$\log {}^*K_S^\circ$
	<b>kJ mol<sup>-1</sup></b>	<b>kJ mol<sup>-1</sup></b>	<b>J mol<sup>-1</sup> K<sup>-1</sup></b>	<b>J mol<sup>-1</sup> K<sup>-1</sup></b>	<b>kJ mol<sup>-1</sup></b>	<b>kJ mol<sup>-1</sup></b>	<b>J mol<sup>-1</sup> K<sup>-1</sup></b>	<b>kJ mol<sup>-1</sup></b>	
Langmuir (1978)	<b>-1891.17</b>	<b>-2001.21</b>	<b>117.15</b>	-369.26 <sup>1</sup>	-3.10 <sup>a</sup>	-4.4 <sup>a</sup>	-1.3 <sup>1</sup>	52.38 <sup>a</sup>	-9.18
Langmuir & Chatham (1980)	<b>-1882.38</b>	<b>-1990.33</b>	117.15	-362.24 <sup>1</sup>	5.69 <sup>a</sup>	5.3 <sup>a</sup>	-1.4 <sup>1</sup>	43.60 <sup>b</sup>	-7.64
Hemingway (1982)	<b>-1886 ± 20</b>				2 ± 22 <sup>b</sup>			47 ± 23 <sup>b</sup>	-8 ± 4
Fleche (2002)	-1915.9 ± 32.4 <sup>1</sup>	<b>-2021.7 ± 30.3</b>	<b>124.3 ± 6.6</b>	-355.0 ± 7.0 <sup>c</sup>	-27.8 ± 34.4 <sup>c</sup>	-26.0 ± 32.3 <sup>c</sup>	6.0 ± 7.0 <sup>1</sup>	78.3 ± 35.3 <sup>c</sup>	-13.73 ± 6.19
Grenthe et al. (1992) Guillaumont et al. (2003)	<b>-1883.6 ± 4.0</b>	<b>-1991.326 ± 5.367<sup>1</sup></b>	<b>118 ± 12</b>	-361 ± 12 <sup>c</sup>	4.52 ± 6.06 <sup>c</sup>	4.374 ± 7.367 <sup>c</sup>	-0.49 ± 12.40 <sup>1</sup>	46.005 ± 6.921 <sup>c</sup>	-8.06 ± 1.21
Szenknect et al. (2013)	<b>-1872.6 ± 3.8<sup>c</sup></b>	-1980.3 ± 7.4 <sup>1</sup>	118 ± 12	-361 ± 12 <sup>c</sup>	<b>15.5 ± 5.8<sup>c</sup></b>	15.4 ± 9.4 <sup>c</sup>	-0.31 ± 12.40 <sup>1</sup>	<b>35.0 ± 0.9</b>	<b>-6.1 ± 0.2</b>
Guo et al. (2015)	-1862.3 ± 7.8 <sup>1</sup>	<b>-1970.0 ± 4.2<sup>c</sup></b>	118 ± 12	-361 ± 12 <sup>c</sup>	25.8 ± 9.8 <sup>c</sup>	<b>25.6 ± 3.9</b>	-0.64 ± 12.40 <sup>1</sup>	24.73 ± 10.72 <sup>c</sup>	-4.34 ± 1.88
This work	<b>-1867.6 ± 3.2<sup>c</sup></b>	-1970.0 ± 4.2 <sup>c</sup>	136 ± 25 <sup>c</sup>	-344 ± 25 <sup>1</sup>	<b>20.6 ± 5.2<sup>c</sup></b>	25.6 ± 3.9	17 ± 31 <sup>1</sup>	<b>30.0 ± 0.3</b>	<b>-5.25 ± 0.05</b>

619 <sup>a</sup> calculated with auxiliary data given by Langmuir (1978)

620 <sup>b</sup> calculated with auxiliary data given by Hemingway (1982)

621 <sup>c</sup> calculated with auxiliary data given by Grenthe et al. (1992)

622 <sup>1</sup> calculated internally with the Gibbs-Helmholtz equation

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