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# Coffinite, $USiO_4$, Is Abundant in Nature: So Why Is It So Difficult To Synthesize?

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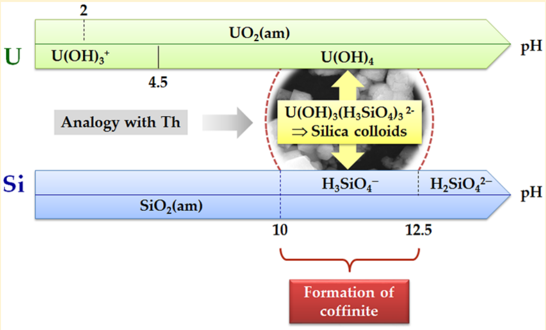
*Supporting Information*

**ABSTRACT:** Coffinite, $USiO_4$, is the second most abundant $U^{4+}$ mineral on Earth, and its formation by the alteration of the $UO_2$ in spent nuclear fuel in a geologic repository may control the release of radionuclides to the environment. Despite its abundance in nature, the synthesis and characterization of coffinite have eluded researchers for decades. On the basis of the recent synthesis of $USiO_4$, we can now define the experimental conditions under which coffinite is most efficiently formed. Optimal formation conditions are defined for four parameters: pH, $T$, heating time, and U/Si molar ratio. The adjustment of pH between 10 and 12 leads probably to the formation of a uranium(IV) hydroxo-silicate complex that acts as a precursor of uranium(IV) silicate colloids and then of coffinite. Moreover, in this pH range, the largest yield of coffinite formation (as compared with those of the two competing byproduct phases, nanometer-scale $UO_2$ and amorphous $SiO_2$) is obtained for 250 °C, 7 days, and 100% excess silica.



## 1. INTRODUCTION

In contrast to the hundreds of naturally occurring, very different, and complex compositions of $U^{6+}$ minerals, there are very few $U^{4+}$ minerals, mainly uraninite, $UO_{2+x}$, and coffinite, $USiO_4$.[1,2] For decades, it was believed that the principal ore mineral of uranium was the oxide, uraninite; however, it has been realized that a large proportion of the fine-grained, uranium-rich phase, particularly in sandstone roll-front deposits, is actually coffinite, the uranium silicate.

Goldschmidt[3] first suggested the possibility of the presence of uranium in thorite, $ThSiO_4$, but it was not until 1955 that coffinite was identified as a new uranium mineral in the La Sal uranium mine in Colorado.[4] A subsequent survey of other uranium deposits of the Colorado Plateau demonstrated the pervasive abundance of coffinite in uranium sandstone deposits.[5] Very detailed studies have demonstrated that coffinite formation is associated with the presence of organic matter[6] and apatite[7] at the micro- to nanoscale.[8] Coffinite has now been identified in a wide variety of localities in different geochemical and hydrological environments, such as in the natural nuclear reactors of Oklo, Gabon,[9−11] and the hydrothermal deposits of Cigar Lake, Canada.[1,12] Coffinite is the primary ore mineral in the sandstone deposits of Australia, a major source of the world's uranium.[13−15]

The conditions of coffinite formation have also been important in discussions of the long-term stability of the $UO_2$ in spent nuclear fuel in a geologic repository. A major question has been whether coffinitization of the $UO_2$ in the fuel will occur under reducing conditions in the presence of silica-rich groundwater, which is present in granite and clay formations.[16] An understanding of the mechanism and energetics of the formation of coffinite is essential to understanding the release of radionuclides from altered or corroded nuclear fuels. Specifically, it is important to know whether coffinite will control the U concentration in solution. This requires thermodynamic data on coffinite, which until now remain poorly constrained. Langmuir[16] has discussed the contradictions between the field evidence, e.g., the occurrence of uraninite with quartz, and the concentration of silica in the associated groundwater. Naturally occurring coffinite is generally so fine-grained that identification, characterization, and measurement of its physical and chemical properties have not been possible.[6]

From a structural point of view, tetragonal coffinite ($I4_1/amd$) is isostructural with zircon ($ZrSiO_4$),[17] hafnon

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($HfSiO_4$),[18] and thorite ($ThSiO_4$)[19] and forms as end-member compositions of the transuranium elements, such as Pu,[19−21] in the zircon structure type ($ASiO_4$, where A = Zr, Hf, Th, Pa, U, Np, Pu, and Am). A projection of the coffinite structure ($USiO_4$) is viewed approximately down the *c* axis in Figure 1.

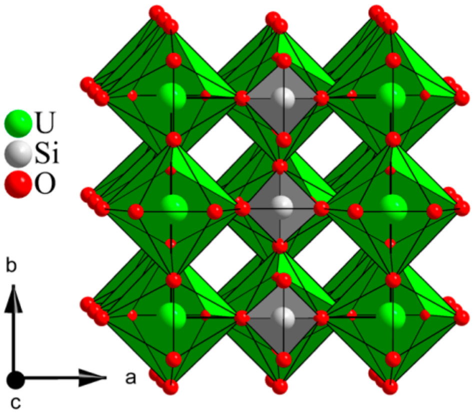

**Figure 1.** Projection of the coffinite ($USiO_4$) structure down the *c*-axis.

The A-site cations are surrounded by eight oxygen atoms, and the $AO_8$ polyhedra form edge-sharing chains parallel to the *a*-axis. The $SiO_4$ monomers join the $AO_8$ polyhedra in an alternating, edge-sharing arrangement parallel to the *c*-axis. The structure has a large tunnel parallel to the *c*-axis that can accommodate molecular water.[22] Hydroxyl may also substitute for oxygen, such that the formula is $U(SiO_4)_{1-x}(OH)_{4x}$.[5] Coffinite may incorporate substantial amounts of rare earth elements and phosphorus by coupled substitution mechanisms.[1]

Despite more than a half-century of research on the structure and properties of coffinite, important questions remain unanswered. First, the initial proposal by Stieff, i.e., $U(SiO_4)_{1-x}(OH)_{4x}$ by analogy to $Th(SiO_4)_{1-x}(OH)_{4x}$ thorogummite,[5] now seems to be unlikely on the basis of spectroscopic studies.[11,23,24] Indeed, Deditius et al.[6] and Clavier et al.[24] infer a general formula of $USiO_4 \cdot nH_2O$ for both natural and synthetic samples. Second, there is the challenge of understanding why it is so difficult to synthesize coffinite. Because of the pressing need for accurate thermodynamic data, such as $K_S$ and associated thermodynamic data ($\Delta_rH$, $\Delta_rG$, and $\Delta_rS$), a number of investigators have sought to obtain pure synthetic coffinite and associated $Th_{1-x}U_xSiO_4$ uranothorite solid solutions.[25,26]

Despite the fact that the synthesis of isostructural zircon,[27−29] hafnon,[30,31] or thorite[32−35] has been reported without any difficulty through various experimental protocols, only a few researchers have succeeded in the preparation of coffinite.[19,33,36−38] Fuchs et al. were the first to report the synthesis of $USiO_4$, using a precipitation route under hydrothermal conditions ($T$ = 250 °C, and $t$ = 1 day),[36] starting from a mixture of uranium tetrachloride and $Na_2SiO_3$ as a silicon source. Apart from the initial mixture of reactants, this seminal publication already showed the need for several steps of pH regulation and buffering before the performance of the heat treatment, and the inherent difficulties illustrated by a very narrow pH range of formation. Moreover, the experiments described were systematically conducted under an inert atmosphere to avoid the oxidation of tetravalent uranium into uranyl. Comparable hydrothermal methods were further developed by other authors with minor modifications of the initial protocol, such as the uranium source.[25] In 2009, Pointeau et al. reported the synthesis of coffinite; however, the yield was very low, and the crystals were extremely small, 50 nm.[38] More recently, Labs et al. have reported a synthesis of coffinite with excess of silica.[37] The samples obtained by hydrothermal method were frequently mixtures of phases, mainly composed of $UO_2$ and $SiO_2$, with small amounts of $USiO_4$.

On the other hand, several attempts were also made through dry chemistry methods or sol−gel chemistry. In the first case, a mixture of $UO_2$ and $SiO_2$ was encapsulated in a platinum container and then heated between 250 and 300 °C under a pressure of 50−100 MPa and using a Si/SiO redox buffer.[39] The second method was based on the preparation of gelatinous mixtures of $UO_2(NO_3)_2 \cdot 6H_2O$, TEOS, and $NH_4OH$,[40] heated under hydrothermal conditions ($T$ = 395 °C, and $P$ = 500 bars) in platinum capsules. For both methods, the temperature range was limited by the expected decomposition of coffinite into $UO_2$ and $SiO_2$ above 500−600 °C,[41] and no reliable proof arguing for the formation of coffinite was provided.

From these results, the precipitation of coffinite from a mixture of a $U^{4+}$-containing acidic solution and sodium metasilicate thus appeared as the most promising method for providing $USiO_4$ samples. In this context, several recent papers proposed a reinvestigation of the hydrothermal methods, for the preparation of either coffinite or $Th_{1-x}U_xSiO_4$ solid solutions,[37,38,42] all aiming to prepare pure and single-phase samples. Although the conditions of preparation and precipitation were in some ways slightly different, particularly in terms of U/Si ratio and temperature, they systematically ended up with mixtures composed of $USiO_4$, $UO_2$, and $SiO_2$ oxides. Once again, these results illustrate the “coffinite problem”, already evocated in the 1950s to point out the lack of pure samples required to obtain a precise formulation.[43]

However, despite these persistent difficulties, no real systematic study has been undertaken to delineate the precise role of the experimental parameters (heating time and temperature, molar ratio between the reactant, chemical form of the reagents, and pH) that could drive the formation of coffinite in aqueous media. Moreover, no tentative mechanism was proposed to explain the formation of $USiO_4$ in the pH range usually described in the literature. On this basis, this Article reports a thorough multiparametric study of coffinite synthesis. The aim of this investigation is to determine the effect of experimental parameters, such as pH, heating time, U/Si mole ratio, and temperature, to establish the optimal synthesis conditions for the preparation of coffinite. In parallel, the speciation of uranium and silicon in the reacting media was also examined to explain the formation of $USiO_4$ over a restricted pH range. These conditions are discussed in the context of the formation of coffinite under natural conditions, such as those that may be encountered by spent nuclear fuel in a geologic repository.

## 2. MATERIALS AND METHODS

**Caution!** *Depleted U is an α-emitting element and as such is considered a health risk. Experiments involving actinides require appropriate installation and persons trained in handling of radioactive materials.*

**2.1. Synthesis.** All starting reagents were obtained from Sigma-Aldrich and were of analytical grade, except the $UCl_4$ stock solution, which was made in the laboratory. The uranium(IV) chloride solution was prepared by dissolving depleted U metal chips in hydrochloric acid (6 mol $L^{-1}$), following the method of Dacheux et al.[44,45] The final concentration of this stock solution was measured by ICP-AES, and the UV−visible spectra collected (Figure S1b of the Supporting Information) clearly confirm the absence of uranyl (five characteristic bands between 350 and 450 nm). Moreover, according to the literature, the absorption bands located at 429, 495, 549, 648−671, and 886 nm were assigned to the $^3P_2$, $^1I_6$, $^3P_1$, $^1G_4$−$^1D_2$−$^3P_0$, and $^3H_6$ U(IV) levels, respectively.[46,47]

With regard to the difficulties of establishing a reliable protocol for the synthesis of the coffinite ($USiO_4$), even via application of the protocols published previously,[36,48] different parameters (i.e., pH, heating time, temperature, and U/Si ratio) were considered in evaluating their impact on the type and yield of the reaction products. Thus, we performed different syntheses derived from that reported initially by Fuchs and Hoekstra,[36,48] and applied later by Pointeau et al.[49] The experimental protocol consists of mixing a solution of dissolved $Na_2SiO_3$ in water and the solution of uranium(IV) chloride (prepared in 6 mol $L^{-1}$ HCl). The pH of the greenish solution was increased by adding NaOH (8 mol $L^{-1}$) in steps to the desired pH value, and then the solution was buffered to 8.7 ± 0.1 by adding $NaHCO_3$. The final green gelatinous mixture was poured into a Teflon-walled acid digestion bomb and placed in an oven. All these reactions were performed in a glovebox filled with Ar and free of oxygen (<2 ppm). The deionized water used in the syntheses was also boiled for 1 h and cooled under a $N_2$ steam. At the end of each experiment, the final product was separated by centrifugation twice with water then with ethanol and dried overnight at room temperature. As mentioned previously by Dreissig et al.,[50] uranium is expected to remain in the tetravalent oxidation state throughout the different steps leading to the formation of coffinite. To check this point, UV−visible spectra were recorded not only on the starting uranium solution but also on the greenish coffinite gelatinous precursor obtained at pH ∼11 and on the resulting supernatant after centrifugation (Figure S1 of the Supporting Information). Despite the difficulties in collecting the absorption spectrum of the gelatinous precursor due to light scattering, no uranium(VI) was detected. Furthermore, because all uranyl-based species should be soluble under our conditions, the separated supernatant was also analyzed. No uranyl was evidenced in the UV−visible absorption spectrum, as a confirmation of the stabilization of at least 99% of the initial uranium(IV) during the whole coffinite synthesis process.

The experiments related to the pH and U/Si molar ratio effects were completed in small volumes. For those considering the influence of pH, 5 mL of outgassed distilled water was first added to hydrochloric acid containing 1.2 mmol of uranium(IV) and then mixed with 5 mL of a $Na_2SiO_3$ solution (1.2 mmol + 10% excess). Then the pH was increased to the target value (i.e., 8.7−12) and finally buffered to 8.7, and the sample was poured into a 23 mL Teflon container (taking into account a dead volume equal to one-third of the total volume). Afterward, the mixture was enclosed in the acid digestion bomb, placed in an oven, and heated at 250 °C for 15 days. For the reactions considering the effect of excess $Na_2SiO_3$, the same protocol was repeated with U/Si molar ratios of 1/1.03, 1.1, 1.5, and 1.2 (i.e., 3, 10, 50, and 100% of the molar excess of silicate, respectively).

For the studies investigating the effects of temperature and heating time, the same protocol was repeated twice, but in a larger amount with a targeted final quantity of 2 g of coffinite. The final buffered mixtures were divided equally into five small solutions transferred into separated PTFE acid digestion bombs. The first series of reaction mixtures were heated at 250 °C for 5, 22, 122, 384, and 792 h, while the second series were placed at room temperature, 150 °C, and 250 °C for 122 h.

### 2.2. Characterization of the Coffinite Samples.

*2.2.1. Powder X-ray Diffraction (PXRD).* PXRD data were collected on the produced powders using the Bruker D8 advance diffractometer equipped with lynxeye detector and using Cu K$\alpha$ radiation ($\lambda$ = 1.54184 Å) in a reflection geometry (parallel beam). Data were acquired using adapted sample holders to avoid any contamination. PXRD powder patterns were recorded between 5° and 100° (2$\theta$) with steps of 0.019° and a total counting time of approximately 3 h per sample. Pure silicon was used as a standard to extract the instrumental function.

*2.2.2. $\mu$-Raman Spectroscopy.* Raman spectra have been collected with the use of the Horiba-Jobin Yvon Aramis device equipped with an edge filter and a Nd:YAG laser (532 nm) that delivers 60 mW at the sample surface. Two samples were selected and characterized (as synthesized "raw" and purified coffinite). With the concern of preventing the degradation of the samples because of the laser induced on the surface, the power was turned down to ∼15 mW by the means of optical filters. The laser beam was then focused on a sample using an Olympus BX 41 microscope, resulting in a spot area of ∼1 $\mu m^2$. For each spectrum, a dwell time of 30−60 s was used with an average of four scans. Data were collected on different areas of the powder for each sample.

*2.2.3. Extended X-ray Absorption Fine Structure (EXAFS).* EXAFS measurements were taken at the Rossendorf beamline[51] at the European Synchrotron Radiation Facility. The Si(111) double-crystal monochromator was used in the channel cut mode. The spectra were collected in fluorescence mode using a 13-element high-purity Ge detector (Canberra) with a digital signal analyzer (XIA-XMAP). Energy calibration of the EXAFS spectra was performed by simultaneous measurement of a Y metal foil (first inflection point at 17.038 keV). The coffinite samples were mixed with saccharide by vibrating at 60 Hz over 15 min in a jar mill, pressed under 250 MPa in a 1 cm diameter tungsten carbide die, and then the pellet was enclosed in polyethylene sample holders. For EXAFS measurements, the samples were placed in a closed-cycle He cryostat at 15 K to improve signal quality by eliminating thermal contributions to the Debye−Waller factor. The EXAFS oscillations were extracted from the raw data with Athena code and adjusted with Artemis code. Self-absorption correction was performed. Adjustment was based on the structure of the coffinite with a parametrized set of parameters as described below. Phases and amplitudes were calculated on the basis of this model with Feff9 code. One single energy shift parameter and global amplitude factor were used for all paths.

## 3. RESULTS AND DISCUSSION

### 3.1. Verification of the Uranium Oxidation State in the Coffinite Samples.

Considering the controversy about the uranium oxidation state in the solid, PXRD, EXAFS, and Raman spectra were collected on several selected samples (raw and purified).[52] All the obtained results proved the formation of strictly U(IV)-based compounds, in agreement with those recently reported on coffinite,[24,50] and with the greenish color of all the powders.

*3.1.1. PXRD Analyses.* During the refinements of all the PXRD patterns, only two U(IV)-based phases were detected, namely, $USiO_4$ that crystallizes in the zircon structure type ($ZrSiO_4$) in the tetragonal $I4_1/amd$ space group with $a$ = 6.9879(1) Å, $c$ = 6.2614(1) Å, and $V$ = 305.75(1) Å$^3$ and uranium dioxide $UO_2$ that crystallizes in the fluorite structure type (cubic, $Fm\bar{3}m$) with $a$ = 5.4317(1) Å and $V$ = 160.26(1) Å$^3$ (sample heated at 250 °C for 122 h). All the PXRD patterns were refined by the Rietveld method with the use of the Fullprof_suite package.[53] The results of the Rietveld refinement of the powder pattern corresponding to the synthesis conducted at 250 °C over 122 h (16 days) are shown in Figure 2. The refined molar amounts of both phases in each experiment are listed in Table 1. Also, the refined unit cell parameters are compiled in Table S1 of the Supporting Information.

*3.1.2. EXAFS.* EXAFS data were recorded at the U $L_{III}$ edge at 15 K to assess the local order around the uranium atoms. Comparison between the EXAFS spectra of pure coffinite and as-prepared samples is shown in Figure 3. Similar oscillations are clearly visible in both spectra up to 14 Å, showing thereby that the same order is present in both samples. Qualitatively, the only significant difference between the two experimental

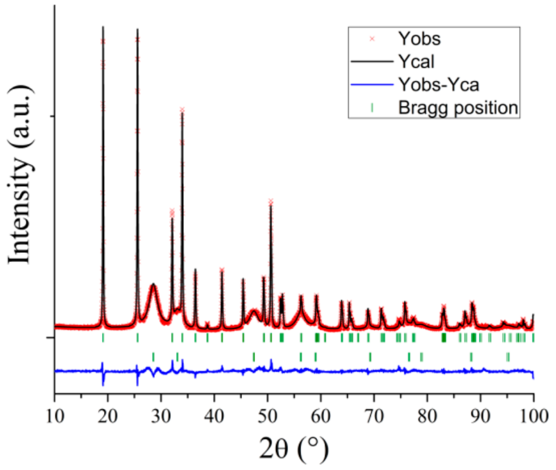

**Figure 2.** Phase quantification of the $USiO_4/UO_2$ mixture obtained after it had been heated at 250 °C for 384 h.

spectra is an inversion of intensity of the beating located between 7.8 and 8.9 $Å^{-1}$. EXAFS data fitting has been performed with a parametrized set of variables (see Materials and Methods for details). The best fit metrical parameters are given in Table S3 of the Supporting Information and are very similar in both cases, suggesting that very few structural differences exist between the two samples.

Comparison between the XANES spectra of both samples (not shown) does not exhibit any visible signature of the uranyl unit: the transdioxo unit of hexavalent U is responsible of a multiple-scattering feature well-known to be located ~15 eV after the edge.[54] In addition, the Fourier transformation of both EXAFS spectra (not shown) does not exhibit a short-range contribution that would indicate uranyl content significantly lower than 10% in the raw or purified samples.

*3.1.3. Raman Spectroscopy.* The Raman spectra collected on a selected $USiO_4$ powder (Figure 3) exhibit the expected internal vibrations mode of $SiO_4$ entities at 424, 591, 961, and 919 $cm^{-1}$, in agreement with those published recently by Clavier et al.[24] No active vibration was detected in the 800−880 $cm^{-1}$ range, which usually corresponds to the symmetric stretching vibration mode of the $UO_2^{2+}$ ($\nu_1$), strongly active in Raman spectroscopy.[55]

The presence of only uranium(IV) in the samples is not surprising. Indeed, on the basis of the dead volume of the closed digestion bomb just before the hydrothermal treatment (33% of the total volume, i.e., ~7.7 mL) and according to the partial pressure of dioxygen in the glovebox surrounding the sample when the autoclave is closed (<0.2 Pa of $O_2$), <6.2 × $10^{-10}$ mol of $O_2$ was trapped in the autoclave. From this calculation, only 1.24 × $10^{-4}$ mol % of the initial quantity of the uranium(IV) could have been oxidized. The colorlessness of the final supernatant clearly supports the absence of uranium(VI). Furthemore, when the synthesis did not succeed, the uranium was finally precipitated as $U(OH)_4$ that rapidly turned into hydrated $UO_2$. The presence of $U_3O_8$ or even partly oxidized uranium oxide was not evidenced during the characterization of all the polyphase samples prepared (PXRD, Raman, and EXAFS). This clearly confirms that the experimental conditions of this protocol were sufficient to ensure that a large proportion of the uranium remained in the tetravalent oxidation state.

### 3.2. Optimization of Coffinite Formation.

The qualitative analysis of the PXRD patterns shows that the reaction product depends strongly on several experimental parameters. In fact, pH, *T*, and heating time influence markedly the yield of

**Table 1. Results of $USiO_4$ and $UO_2$ Quantification Obtained from Rietveld Refinement as a Function of the Conditions of Preparation**

| reaction | temperature (°C) | pH (±0.1) before buffering | heating time (h) | buffer ($NaHCO_3$) | U/Si molar ratio | $USiO_4$ (mol %) | $UO_2$ (mol %) |
|---|---|---|---|---|---|---|---|
| | | | Heating Time | | | | |
| 1 | 250 | 11.4 | **5** | yes | 1/1.1 | 4.6(2) | 95.4(6) |
| 2 | 250 | 11.4 | **22** | yes | 1/1.1 | 29.9(2) | 70.1(5) |
| 3 | 250 | 11.4 | **122** | yes | 1/1.1 | 61.4(3) | 38.6(3) |
| 4 | 250 | 11.4 | **384** | yes | 1/1.1 | 61.0(3) | 39.0(3) |
| 5 | 250 | 11.4 | **792** | yes | 1/1.1 | 68.5(3) | 31.5(2) |
| | | | Temperature of Synthesis | | | | |
| 4 | **250** | 11.4 | 384 | yes | 1/1.1 | 61.0(3) | 39.0(3) |
| 6 | **150** | 11.2 | 384 | yes | 1/1.1 | 7.8(4) | 92.2(9) |
| 7 | **25** | 11.2 | 384 | yes | 1/1.1 | – | – |
| | | | pH Effect | | | | |
| 8 | 250 | **8.8** | 384 | yes | 1/1.1 | 16.3(2) | 80.7(5) |
| 9 | 250 | **9** | 384 | yes | 1/1.1 | 45.2(2) | 54.8(4) |
| 10 | 250 | **10** | 384 | yes | 1/1.1 | 74.1(3) | 25.9(3) |
| 4 | 250 | **11.4** | 384 | yes | 1/1.1 | 61.0(3) | 39.0(3) |
| 11 | 250 | **12.** | 384 | yes | 1/1.1 | 70.5(3) | 29.5(2) |
| | | | Buffer | | | | |
| 12 | 250 | 11.3 | 384 | **no** | 1/1.1 | 0 | 100 |
| 13 | 250 | 11.7 | 384 | **no** | 1/1.1 | 0 | 100 |
| | | | U/Si Molar Ratio | | | | |
| 14 | 250 | 11.2 | 480 | yes | **1/1.03** | 46.3(4) | 53.7(3) |
| 4 | 250 | 11.4 | 384 | yes | **1/1.1** | 56.2(3) | 43.8(5) |
| 15 | 250 | 11.4 | 384 | yes | **1/1.5** | 86.3(8) | 13.7(6) |
| 16 | 250 | 11.3 | 384 | yes | **1/2** | 93.1(6) | 6.9(4) |

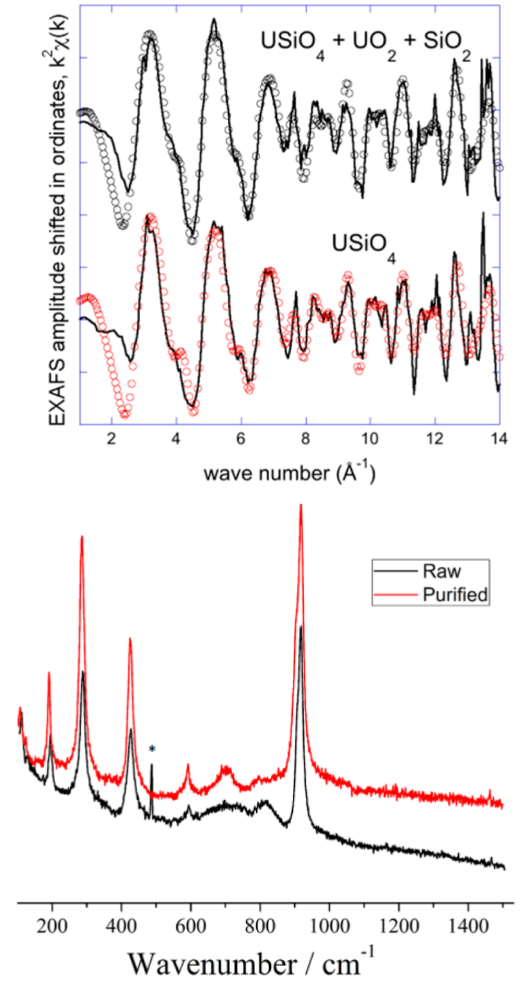

**Figure 3.** Experimental (straight line) and adjusted (dots) EXAFS spectra of the raw sample (black) and single-phase coffinite sample (red). Spectra are represented in $k2\chi(k)$ and shifted on the ordinate for the sake of clarity (top). Raman spectra of the raw (black) and purified (red) $USiO_4$ powder. The line denoted with a star corresponds to $UO_2$ (bottom).

coffinite formation. Moreover, the uranium/silicate mole ratio plays an important role during the preparation of the uranium silicate samples. The role of each parameter is discussed in detail in the following sections.

*3.2.1. Influence of the pH of the Starting Mixture.* During the synthesis of coffinite, the pH plays an important role. In fact, after both solutions have been mixed and before the buffering step, the pH was increased to different values ranging between 8.7 and 12. Each reaction product was analyzed by PXRD and refined by the Rietveld method. The amounts of $USiO_4$ and $UO_2$ phases in each sample are presented in Figure 4. When the initial pH of the synthesis prior the buffering step was between 9 and 12, $USiO_4$ formed but was always associated with nanometric $UO_2$. Moreover, all attempts to prepare pure coffinite at pH <8.7 or >12 led to irreproducible results (with rather high $UO_2$ contents).

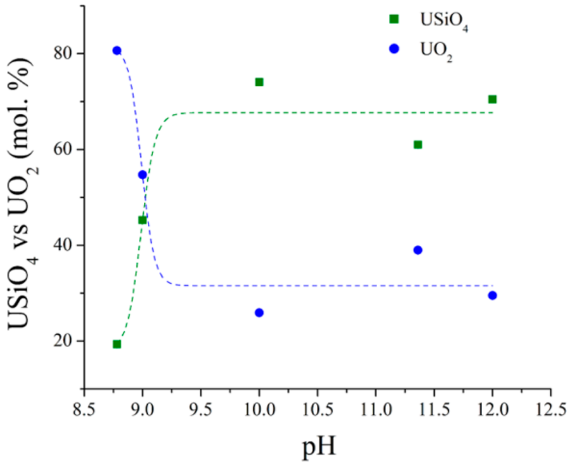

**Figure 4.** Variation of the refined molar percentages of $USiO_4$ vs $UO_2$ in the prepared mixtures vs the pH value of the reaction before the buffering step.

Consequently, the optimal conditions for preparing pure coffinite in terms of the pH of the starting mixture before making the buffering step ranged from 10 to 12. To understand this observation, tetravalent U and Si speciation was examined under the conditions of the synthesis using the Phreeqc 2 software.[56−58] Considering the data reported in the literature (Table S2 of the Supporting Information of the supporting data), the following $U^{4+}$ mononuclear and polynuclear hydroxides species were considered: $U(OH)_3^+$, $U(OH)_2^{2+}$, $U(OH)^{3+}$, and $U(OH)_4$. The hydrolysis constants of $U(OH)^{3+}$ and $U(OH)_4$ were those selected by the NEA TDB project,[59] while the hydrolysis constants considered for $U(OH)_3^+$ and $U(OH)_2^{2+}$ were taken from ref 60. Because of their high ionic potential (i.e., charge/size), tetravalent actinide ions have a strong tendency toward hydrolysis in aqueous solution and undergo polynucleation or further colloid formation.[60−62] Generally, high concentrations of dissolved uranium in neutral or alkaline media are ascribed to the presence of hexavalent U.[63] To prevent uranium(VI) formation, the synthesis of the coffinite was initially achieved under an Ar atmosphere in a glovebox maintaining <0.2 Pa $pO_2$. Under these conditions, the volume of the gas trapped inside the Teflon container (dead volume of 7.7 mL) contains a very limited amount of oxygen that may oxidize $<1.24 \times 10^{-4}\%$ of the starting uranium(IV) content.[64] The simulation performed with Phreeqc 2 software considered this low mole content of available $O_2$ surrounding the solution.

From the speciation of tetravalent uranium reported in Figure 5a, it clearly appears that the mixture became oversaturated with respect to $UO_2$(am) for pH values of >2. In the optimized pH range for coffinite formation (i.e., between 8.7 and 12), $U(OH)_4$ is thus the predominant U(IV) aqueous species. Indeed, considering the solubility of $UO_2$(am) under alkaline conditions, only 0.4% mol of the tetravalent uranium is dissolved as $U(OH)_4$ aqueous species. This ratio does not evolve significantly in the pH interval that led to the largest yields of coffinite formation. However, the complexation of uranium(IV) by silicate species could modify this ratio. Under these conditions, the silicon speciation (Figure 5b) was also clearly helpful in understanding the role of several silicate species during coffinite formation. Indeed, silicon appeared to be fully solubilized under alkaline conditions [the saturation index of $SiO_2$(am) becomes negative for pH >11.3]. Under these conditions, the predominant species in solution is the anionic monocharged $H_3SiO_4^-$. From all of these calculations, it was clear that the optimal pH range associated with the synthesis of coffinite corresponds to the full availability of silicon as $H_3SiO_4^-$. No thermodynamic data for U(IV) complexes with aqueous Si are available in the literature.

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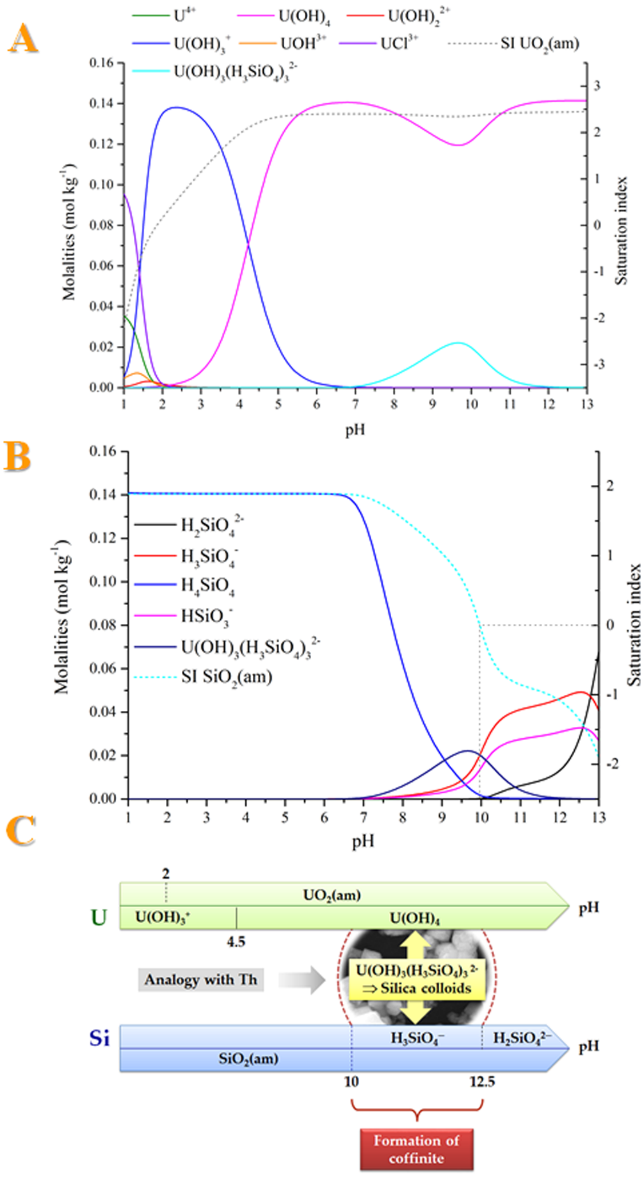

**Figure 5.** Distribution of the main (A) U and (B) Si species in the typical mixture of $Na_2SiO_3$ (10% excess) and a U(IV) chloride solution vs pH under an Ar atmosphere. (C) Description of the conditions of synthesis favorable to coffinite formation.

However, Peketroukhine et al.[65] 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) at pH 8 and 10, respectively, 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 $ThO_2 \cdot nH_2O$. Rai et al.[66] reported similar results. The interpretation of their data required the existence of a mixed thorium hydroxo-silicate complex whose structure was determined by density functional theory calculations. The fitted value of the equilibrium constant [$\log K^\circ$ (298 K) = $-18.5 \pm 0.7$] for the reaction

$$\begin{aligned} &ThO_2(am) + 3H_4SiO_4 + H_2O \\ &\quad \leftrightarrows Th(OH)_3(H_3SiO_4)_3^{2-} + 2H^+ \end{aligned}$$

showed that under alkaline solutions, dissolved silicon species make very strong complexes with thorium. Because of the similar charge and ionic radius, the analogy between U(IV) and Th was made to estimate the equilibrium constant for the complexation reaction:

$$U^{4+} + 3H_2O + 3H_4SiO_4 \leftrightarrows U(OH)_3(H_3SiO_4)_3^{2-} + 6H^+$$

by taking into account the solubility of $UO_2$(am) instead of $ThO_2$ (am) (Table S2 of the Supporting Information). However, this chemical analogy probably minimizes the strength of the interaction of U(IV) with silicates. Indeed, the reported apparent stability constants of U(IV) with a large variety of ligands, including citrate[67] and nitrilotriacteic acid,[68] were systematically found to be higher than that involving thorium. The similarity between Th and U(IV) behavior in silicate-rich solution was also underlined by Dreissig et al.[50] They showed that silicate stabilizes tetravalent uranium at a concentration of $10^{-3}$ mol $L^{-1}$ in a colloid-borne form. These stable colloids were obtained by dilution of the $U^{4+}$ stock solution with a 0.24−2.7 × $10^{-3}$ mol $L^{-1}$ silicate solution. The resulting pH of the solution reached 9.5. The prevailing particle size was <20 nm with a minor fraction of submicrometer particles. Their results indicated that the higher the silicate concentration and pH, the smaller and more stable the colloids. The structure of the $U^{4+}$-silica colloids was reported to be highly disordered, but from EXAFS measurements, Dreissig et al.[50] stated that a structure such as $U(SiO_4)_{1-x}(OH)_{4x}$ was possible. Under the conditions of the synthesis, the simulation performed with Phreeqc 2 software and presented Figure 5a indicated that $U(OH)_3(H_3SiO_4)_3^{2-}$ species could be formed in the pH interval of 8−11, which is the optimized pH range for coffinite formation.

Obviously, as reported for thorium, the conditions leading to increased amounts of coffinite were also favorable to the formation of stable uranium(IV) hydroxo-silicate colloids that could be considered as a coffinite precursor. The pH plays a key role in stabilizing the appropriate U(IV)-silicate species necessary to form coffinite (Figure 5c). However, more details are still lacking, in particular those related to the possible existence of intermediary U(IV)−Si(IV) oligomer complexes leading to the formation of these colloids. A complete study to identify such a possible U(IV)−Si(IV) oligomer complex by combining several techniques such as $^{29}$Si NMR, EXAFS, and SAXS is underway.

*3.2.2. Influence of the Heating Time.* Because a suitable pH range was identified, 10−12, for the stabilization of the $USiO_4$ and in continuation of our previous works,[42,69] the evolution of the system of coffinite versus uraninite was studied as a function of the heating time. The PXRD powder patterns recorded for each synthesis with different heating times (5, 22, 122, 384, and 792 h) are presented in Figure 6. On the basis of the PXRD patterns, the coffinite phase appears in the system after thermal treatment at 250 °C for 5 h. The qualitative analysis of the data demonstrates that the yield of coffinite formation increased when the heating time was extended. Thereafter, the coffinite/uraninite ratio stabilizes after 5 days. The results of Rietveld refinement and phase quantification are summarized in Table 1 and plotted in Figure 7. After 5 h, the yield of coffinite formation remained very low [~4.6(2) mol %] compared with that of uranium dioxide. This yield increased to ~68.5(3) mol % when the heating time was extended and reached a plateau after only 5 days. With regard to the experimental results, it appears that the formation of the

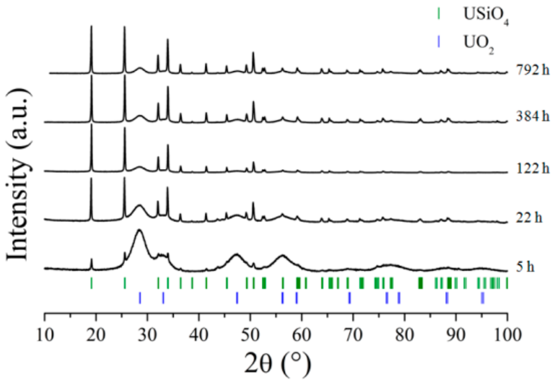

**Figure 6.** PXRD patterns showing the evolution of coffinite and side products when the heating time is extended.

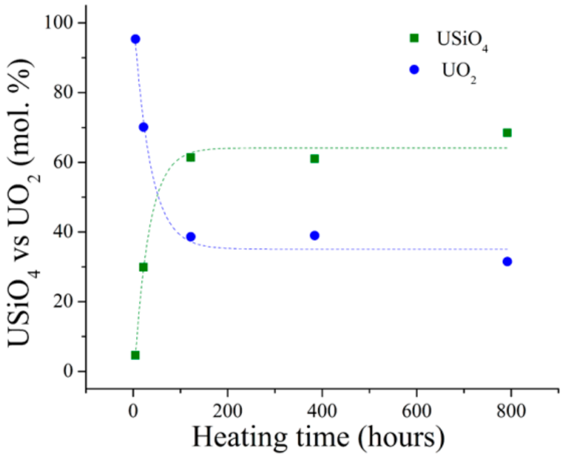

**Figure 7.** Evolution of the sample composition ($USiO_4$ vs $UO_2$) vs heating time at 250 °C (pH of the starting mixture of 11.4).

coffinite is driven at an early stage by a kinetic part that could be associated with the initial reaction between $U(OH)_4$ and $H_3SiO_4^-$. Moreover, the small amount of coffinite observed at an early stage by PXRD can be connected to the very small size of the coffinite crystallites compared to the size of those of $UO_2$ (3 nm). Therefore, when the heating time is extended, an apparent steady state between $USiO_4$ and $UO_2$ is reached, which corresponds certainly to the growth of the coffinite crystallites.

*3.2.3. Influence of the U/Si Molar Ratio.* In previous studies, attempts to prepare pure coffinite by considering a molar excess of 10% in $Na_2SiO_3$ failed and always led to a mixture composed of $USiO_4$, $UO_2$, and amorphous $SiO_2$, even with an extended heating time (33 days). Moreover, Labs et al.[37] recently synthesized coffinite, without forming uranium dioxide, according to the protocol previously reported by Fuchs and Hoekstra.[36] However, amorphous silica was always produced as a byproduct with a high yield taking into account the initial excess of $Na_2SiO_3$ used for the synthesis (up to 500%, i.e., 1/6 U/Si molar ratio). In both cases, the prepared samples always consist of multiple phases with an additional amorphous component with the coffinite. Because there is an obvious need to prepare pure coffinite to complete reliable solubility measurements, the experimental protocol was optimized in the framework of the increase in coffinite content and the decrease in that of uranium dioxide and amorphous silica. Therefore, the influence of excess silica was investigated by varying the U/Si molar ratio (1/1.03, 1/1.1, 1/1.5, and 1/2); all these experiments included heating over 15 days. The PXRD data corresponding to the reaction products are presented in Figure 8, while the results of $USiO_4$ and $UO_2$ quantification obtained from Rietveld refinements are shown in Figure 9. Given these results, the quantity of coffinite that forms increases with the amount of excess $Na_2SiO_3$. On the basis of these results and those recently reported by Labs et al.,[37] we can infer from the data presented in Figure 9 that coffinite free of coexisting $UO_2$ with a smaller quantity of amorphous silica can be obtained, using a U/Si molar ratio of 1/2. To understand this result, tetravalent uranium and silicon speciation were examined for all the synthesis conditions using the Phreeqc 2 software[56] and the thermodynamic data reported in Table S2 of the Supporting Information.[57,58] Considering the results reported in the previous section, the mole ratio of the uranium(IV) hydroxo-silicate complex that is expected to finally form the coffinite precursor was calculated in terms of the U/Si mole ratio considered in the starting mixture. This ratio was found to increase from ~15 mol % (1/1 = U/Si) to 25 mol % (1/2 = U/Si). This variation could be responsible for the observed increase of the coffinite content coming from Rietveld refinement.

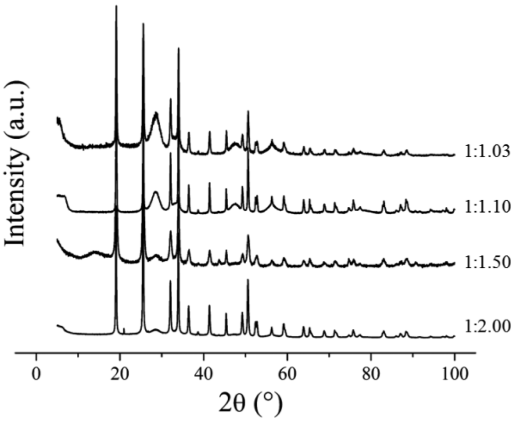

**Figure 8.** PXRD patterns obtained as a function of the initial U/Si molar ratio ($T$ = 250 °C).

On the basis of all these results, the purification procedure already proposed for uranothorite solid solutions is still necessary for the preparation of a single-phase coffinite sample regardless of the chemical conditions considered. However, when the U/Si ratio was adjusted to 1/1.5, the yield of $UO_2$ formation was considerably decreased and the amorphous silica content remained low. The decrease in $UO_2$ and amorphous $SiO_2$ contents makes the purification step of coffinite easier.[70]

*3.2.4. Influence of Temperature.* All the attempts to synthesize the coffinite phase were completed at 250 °C by following the procedure reported in the literature.[19,33,36] Also in this work, our experiments were completed at 250 °C. However, there are ongoing discussions about the appropriate conditions of the formation of coffinite.[71,72] In fact, it has been stated that the natural coffinite should form at lower temperatures, between 80 and 130 °C, or even lower for some uranium deposits, particularly sandstone deposits. Now, on the basis of an improved understanding of the experimental conditions required to synthesize the coffinite, two supplementary synthesis protocols have been developed: (i) one at room temperature and (ii) one at 150 °C for 15 days. The

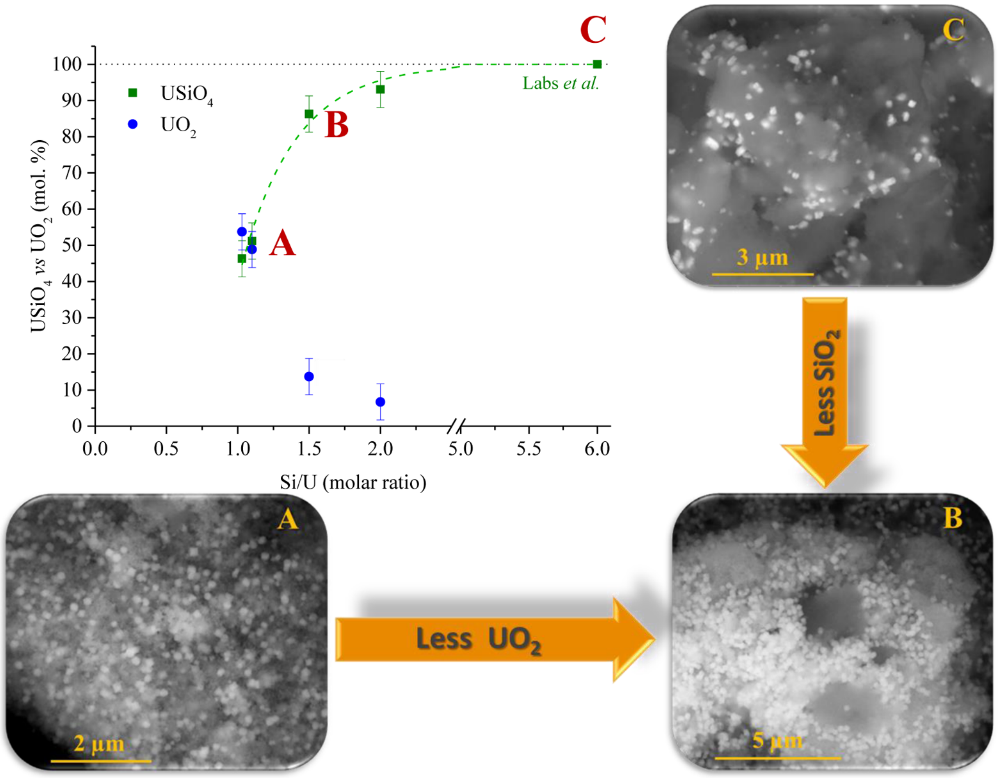

**Figure 9.** Molar ratio of $USiO_4$ and $UO_2$ (%) as a function of Si/U molar ratio (for Labs et al., see ref 37).

PXRD pattern corresponding to each reaction is presented in Figure 10. At the end of the experiments, greenish powders were obtained. The reaction at 150 °C gives a small yield of coffinite mixed with $UO_2$ [7.8(4) mol % instead of 61.0(3) mol % at 250 °C], while the experiment completed at room temperature did not show any XRD peaks characteristic of coffinite. With regard to these results, it is demonstrated that under favorable pH conditions, coffinite can be synthesized at temperatures below 250 °C. However, the low yield of coffinite formation could result from a slow kinetic rate probably due to the $U(OH)_4/H_3SiO_4^-$ starting reaction and also could explain the absence of crystallized phases at room temperature despite the greenish color of the powder. Complementary experiments are now required to show whether a uranium-silicate-based colloid could be stabilized (or not) at room temperature.

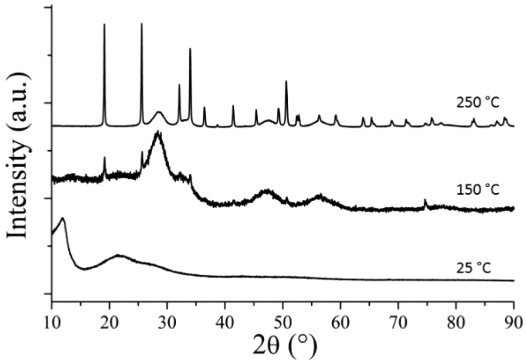

**Figure 10.** XRD patterns of the systems obtained as a function of heating temperature.

## 4. CONCLUSION

The synthesis of coffinite has eluded researchers for decades.[19,33,36] To solve this problem, i.e., "why coffinie, $USiO_4$, is abundant in nature and so difficult to synthesize", we have established the conditions under which coffinite can be reproducibly synthesized. In fact, the formation of coffinite results from a complex interplay among pH, $T$, Si/U ratio, and heating time. The pH is definitively the dominant parameter that is responsible for the stabilization of the coffinite. In fact, it seems necessary to adjust the pH to a range of 10−12.5 to stabilize appropriate uranium silicate complex $U(OH)_3(H_3SiO_4)_3^{2-}$. Additionally, the other parameters may be adjusted, temperature (250 °C), heating time (1 week), and silica excess (100%), to substantially increase the coffinite yield. However, this always leads to an equilibrium between $USiO_4$, $UO_2$, and $SiO_2$ (as always observed in natural samples). Most importantly, for uranium deposits in sandstone, we have demonstrated that coffinite forms at low temperatures (150 °C) in the absence of hydrothermal solutions. Our results are consistent with the observation of coffinite in the uranium deposits, where Si is found in excess and the equilibrated solution is weakly alkaline, as reported by Evins and Jansen.[73]

This article provides new insights into understanding the difficulties encountered during the synthesis of the coffinite and its relation to the presence of uraninite. However, important questions remain unanswered. Specifically, additional investigation is needed to confirm the existence of the proposed U(IV) hydroxo-silicate complex and to determine the associated formation constant. It is also necessary to investigate the possible formation of a U(IV)−Si(IV) oligomer complex leading to the subsequent formation of stable U(IV) hydroxo-silicates colloids and then, finally, coffinite. Second, a challenge needs to be overcome to directly synthesize pure coffinite (without any need of additional purification process) and/or to grow single crystals. Many routes could be explored such as redox-based hydrothermal methods as reported by Nocera et al. in the case of Jarosites.[74,75]

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

UV spectra of a $UCl_4$ stock solution, coffinite gel, its suspension, and that of a $UO_2(NO_3)_2$ stock solution (Figure S1), refined unit cell parameters for $USiO_4$ and $UO_2$ (Table S1), thermodynamic data for the main reactions involving U and Si in the considered system (Table S2), and best fit metrical parameters obtained from the EXAFS data of $USiO_4$ and $UO_2/SiO_2$ samples (Table S3). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/ic502808n.

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### Notes

The authors declare no competing financial interest.

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