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Paul Estevenon, Éléonore Welcomme, Christelle Tamain, Gauthier Jouan, Stephanie Szenknect, et al.. The formation of PuSiO<sub>4</sub> under hydrothermal conditions. Dalton Transactions, 2020, 49 (19), pp.6434-6445. <10.1039/D0DT01183E>. <hal-03013951>

**HAL Id: hal-03013951**

**<https://hal.science/hal-03013951v1>**

Submitted on 19 Nov 2020

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# Formation of PuSiO<sub>4</sub> under hydrothermal conditions

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Attempts to synthesize plutonium (IV) silicate, PuSiO<sub>4</sub>, have been performed on the basis of the results recently reported in the literature for CeSiO<sub>4</sub>, ThSiO<sub>4</sub> and USiO<sub>4</sub> under hydrothermal conditions. Although it was not possible to prepare PuSiO<sub>4</sub> by applying the conditions reported for thorium and uranium, an efficient way of PuSiO<sub>4</sub> synthesis was established following those optimized for CeSiO<sub>4</sub> system. This method was based on the slow oxidation of plutonium (III) silicate reactants under hydrothermal conditions at 150°C in hydrochloric acid (pH = 3–4). This result shed a new light on the potential behavior of plutonium in reductive environment, highlighted the representativeness of cerium surrogates to study plutonium in such conditions and brought some important pieces of information on plutonium chemistry in silicate solutions.

## Introduction

Silica and silicate phases are by far among the main components of the earth crust and are omnipresent in most natural environments.<sup>2</sup> Among them, one can note natural actinide silicates ThSiO<sub>4</sub> (thorite), USiO<sub>4</sub> (coffinite) and associated uranothorite solid solutions.<sup>4</sup> The potential impact of actinide silicate species onto the actinide mobility<sup>5-13</sup> imply to take into account the chemical interactions between actinide elements and silica. Understanding their behavior appears as a crucial issue especially in the case of direct disposal of spent nuclear fuel (SNF) in deep geological repository conditions.

The synthesis of plutonium silicate, PuSiO<sub>4</sub>, was reported once by Keller<sup>3, 14</sup> in 1963. This silicate was obtained by performing hydrothermal treatments (7 days at 230°C, argon atmosphere) starting from mixtures of PuO<sub>2</sub> and SiO<sub>2</sub> co-precipitated in carbonate ions rich reactive media (C<sub>NaHCO<sub>3</sub></sub> = 1M). PXRD measurements performed on this sample allowed to identify that PuSiO<sub>4</sub> crystallized in a zircon type structure (tetragonal, space group I4<sub>1</sub>/amd), which is shared by M<sup>IV</sup>SiO<sub>4</sub> silicates (with M<sup>IV</sup> = Zr, Hf, Ce, Th, Pa, U, Np and Am).<sup>15</sup> This study also established that dry chemistry routes performed at high temperatures were inadequate to obtain this plutonium bearing silicate phase. However, to our knowledge, PuSiO<sub>4</sub> has never been obtained again since. The yields of the actinide silicate syntheses under hydrothermal conditions were unclear and previous transpositions of this protocol to the USiO<sub>4</sub> system showed a poor repeatability. More recently, *ab initio* calculations determined that PuSiO<sub>4</sub> could be metastable<sup>16-22</sup> compared to the mixture of crystalline PuO<sub>2</sub> and SiO<sub>2</sub>. However, it was also suggested that this phase may be stable at low temperature compared to amorphous plutonium oxide and silica.<sup>17</sup> According to the literature, Pu(III) and Pu(VI) silicate species have been reported.<sup>23-28</sup> It is also the case for plutonium(IV) silicate aqueous species<sup>29-31</sup>, especially for Pu(OSi(OH)<sub>3</sub>)<sup>3+</sup>.

Since zircon type silicate, ZrSiO<sub>4</sub> and HfSiO<sub>4</sub>, have been identified for long as potential specific waste forms for high-level radioactive waste,<sup>32</sup> the synthesis of (Zr,Pu)SiO<sub>4</sub> and (Hf,Pu)SiO<sub>4</sub> solid solution<sup>33-50</sup> became a key issue to prepare materials which could incorporate large amounts of plutonium. However, these two solid solutions are not ideal

and the solubility limit of plutonium in such materials was limited to only 7 – 10 mol.%.<sup>45, 49</sup>

Th(IV), U(IV) and Ce(IV) are often used as Pu(IV) surrogates due to their ionic radii and chemical behavior (such as hydrolysis properties) close to those observed for plutonium. These elements are also known to form silicate-based phases, which crystallize in the zircon-type structure. Moreover, all these silicate-based phases could be obtained by hydrothermal methods.<sup>3, 51</sup> Therefore, ThSiO<sub>4</sub>, USiO<sub>4</sub> and CeSiO<sub>4</sub> may be considered as potential analogues in order to study the hydrothermal synthesis of PuSiO<sub>4</sub>.

Since the first synthesis proposed by Frondel and Collette in 1957,<sup>52</sup> the hydrothermal synthesis of ThSiO<sub>4</sub> has been widely studied.<sup>3, 14, 53-61</sup> Two ways of synthesis were identified, from these results. The first was performed in carbonate ions rich reactive media (carbonate ions playing the role of ligand with regard to thorium) and the second, which was developed in ligand free reactive media. We recently studied both of these ways in order to identify the key parameters which may impact the synthesis of ThSiO<sub>4</sub>, particularly the concentrations of the reactants, the pH of the reactive media or the temperature and duration of the hydrothermal treatment.<sup>62, 63</sup>

Hydrothermal synthesis of USiO<sub>4</sub> was also extensively studied.<sup>3, 14, 53, 61, 64-73</sup> However, from a general point of view, this synthesis remained poorly reproducible. Recently, Mesbah et al.<sup>74</sup> identified an efficient way to prepare coffinite, allowing its formation with a good repeatability. This protocol consisted in preparing a mixture of uranium (IV) and sodium metasilicate under inert atmosphere, in alkaline media (10 ≤ pH ≤ 12). Finally, NaHCO<sub>3</sub> was added in order to set the pH at 8.7. This mixture was then treated through hydrothermal conditions (150°C ≤ T ≤ 250°C) under inert atmosphere and then purified by specific dissolution of UO<sub>2</sub> and SiO<sub>2</sub>.

The synthesis of CeSiO<sub>4</sub> was based on the hydrothermal oxidation of Ce(III) species. This silicate was obtained from Ce(III) aqueous species in weakly basic reactive media.<sup>51, 75, 76</sup>

However, the synthesis of CeSiO<sub>4</sub> was strongly limited by the very restrictive conditions in terms of reactants, pH and working atmosphere.<sup>76</sup> Recently, we developed a very efficient way of synthesis based on the hydrothermal oxidation of Ce(III) silicate solid compounds.<sup>77</sup> In these conditions, CeSiO<sub>4</sub> was obtained in a wide pH range under aerated atmosphere. Among the solid Ce(III) silicates precursors considered,

$Ce_{4.67}(SiO_4)_3O$  and  $G-Ce_2Si_2O_7$  have known plutonium analogs.<sup>23-25</sup>

Thus, this work was dedicated to the hydrothermal synthesis of  $PuSiO_4$  considering the transposition of the conditions optimized for  $ThSiO_4$ ,  $USiO_4$  and  $CeSiO_4$  or starting from Pu(III) silicate precursors.

## Materials and methods

### Reagents

**Caution!**  $^{238}Pu$ ,  $^{239}Pu$ ,  $^{240}Pu$  and  $^{242}Pu$  are  $\alpha$  emitter whereas  $^{241}Pu$  is  $\beta^-$  emitter, which are considered as a health risk. Experiments involving actinides require appropriate facilities and trained persons in handling of radioactive materials.

Experiments were performed in the ATALANTE facility of Marcoule Research Center, France. The plutonium solution (isotopic composition of  $^{238}Pu$  (0.2%),  $^{239}Pu$  (76.6%),  $^{240}Pu$  (21.3%),  $^{241}Pu$  (1.2%) and  $^{242}Pu$  (0.7%)) was purified by a standard anion-exchange method, in order to avoid the presence of  $^{241}Am$ , produced by  $\beta$  decay of  $^{241}Pu$ . Plutonium was stabilized in the +IV oxidation state, in  $1.5 \text{ mol}\cdot\text{L}^{-1}$   $HNO_3$  solution. Plutonium stock solution was then titrated by UV-visible spectrophotometric method, using standard deconvolution from reference measurements, leading to  $C_{Pu} = 0.30 \pm 0.03 \text{ mol}\cdot\text{L}^{-1}$ .

$HNO_3$  and  $HCl$  solutions were prepared by dilution of Sigma Aldrich ACS grade solutions:  $HNO_3$  (70%) and  $HCl$  (37%). All the other reagents used for the syntheses were of analytical grade and supplied by Sigma-Aldrich.  $Na_2SiO_3\cdot 9H_2O$  (98%) and  $SiO_2$  5-20 nm (99.5%) powders were used as silicate precursors. The pH adjustments were performed thanks to  $8 \text{ mol}\cdot\text{L}^{-1}$  and  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $NaOH$  solutions freshly prepared from  $NaOH$  (98 %) pellets.  $NaHCO_3$  (99.7%) was used as the carbonate source.

### Samples preparation

**Transposition of the Keller's protocol.** Experiments were first adapted from the protocol described by Keller for the preparation of  $AnSiO_4$  ( $An^{IV} = Th, Pa, U, Np, Pu$  and  $Am$ ).<sup>3, 14</sup> Nanometric  $PuO_2$  was prepared by precipitation with the help of ammonia according to the protocol developed for U(IV)<sup>78</sup> and mixed together with commercial nanometric  $SiO_2$  powder. This mixture was then put in a  $1 \text{ mol}\cdot\text{L}^{-1}$   $NaHCO_3$  aqueous solution in order to obtain a final solution of  $C_{Pu} = 0.21 \text{ mol}\cdot\text{L}^{-1}$  and a silicate excess of 3 mol.% in the reacting mixture

(synthesis pathway B1 in **Table 1**). The mixture was transferred into 23 mL Teflon lined reactors in air atmosphere and then heated in Parr autoclaves under hydrothermal conditions for 7 days at  $237^\circ\text{C}$  or for 15 days at  $150^\circ\text{C}$  under autogenous pressure. Thus, the obtained precipitates were separated from the supernatant by centrifugation for 1 min at 14 000 rpm, washed twice with deionized water and once with ethanol, and then finally dried overnight under the glovebox atmosphere (air).

This transposition did not produce any trace of  $PuSiO_4$  while the formation of  $PuO_2$  was always observed. More generally, as described below, all the attempts to prepare  $PuSiO_4$  from Pu(IV) reactant under hydrothermal conditions based on the optimized protocols reported for U<sup>74</sup> and Th,<sup>62, 63</sup> as Pu analogs failed (synthesis pathways A, B2, B3 and B4 in Table 1). The detailed protocols for these experiments are available in supporting information.

### Hydrothermal synthesis of $PuSiO_4$ from Pu(III) silicate precursors solid compounds.

In order to develop hydrothermal synthesis from Pu(III), several solid Pu(III) based silicate precursors ( $Pu_{4.67}(SiO_4)_3O$  and  $Pu_2Si_2O_7$ ) were prepared from mixtures of nanometric hydrated  $PuO_2$  and  $SiO_2$  taking into account the protocols described by De Alleluia et al.<sup>23, 24</sup> and Uchida et al.<sup>25</sup>, respectively. This route of synthesis has been recently described for the preparation of Ce(III) silicate precursors.<sup>77</sup>

Nanometric hydrated  $PuO_2$  was prepared by ammonia precipitation according to the protocol developed for U(IV).<sup>78</sup> The as-precipitated hydrated oxo/hydroxo was mixed with nanometric silica powder then the powders were milled together in ethanol in an agate mortar in order to improve the mixture homogeneity). As previously described, the sample was dried at room temperature under the glovebox atmosphere (air). The resulting mixture was pelletized and heated during 1 hour at  $800^\circ\text{C}$  in Ar – 4%  $H_2$  atmosphere in order to prepare dense pellets of  $PuO_2$  and  $SiO_2$  mixture. The resulting pellets were finally heated for 9 hours at  $1350^\circ\text{C}$  in Ar – 4%  $H_2$  atmosphere in a 90% Pt-10% Ir crucible, allowing the formation of both  $Pu_{4.67}(SiO_4)_3O$  and  $Pu_2Si_2O_7$  which are identifiable by PXRD. Both  $Pu_2Si_2O_7$  and  $Pu_{4.67}(SiO_4)_3O$  were blue colored compounds. They were stable during more than a week under aerated atmosphere without exhibiting any traces of  $PuO_2$ , which could result from the oxidation of plutonium (III).

**Table 1.** Synthesis parameters for the reported  $PuSiO_4$  hydrothermal syntheses.

Synthesis pathway	Label	Plutonium precursor	Reactive media	pH <sub>initial</sub>	T (°C)	Δt (days)	Final phase
A1	(12)	$Pu^{IV}aq$	$HNO_3$	8.8	150	7	$PuO_2$
	(13)			6.2		7	
	(14)			2.6		12	
	(15)			1.9		15	

	(16)			[H <sub>3</sub> O <sup>+</sup> ] = 2.2 M		7				
	—	Pu <sup>IV</sup> aq	HNO <sub>3</sub>	0.8	237	10	PuO <sub>2</sub>			
<b>B1</b>	(17)	Pu <sup>IV</sup> O <sub>2</sub>	<b>Carbonate</b> Starting C <sub>NaHCO<sub>3</sub></sub> = 1.0 M	9.7	150	15	PuO <sub>2</sub>			
	(18)			9.3	237	10	PuO <sub>2</sub>			
<b>B2</b>	(19)	Pu <sup>IV</sup> aq	<b>Carbonate</b> Starting C <sub>NaHCO<sub>3</sub></sub> = 1.0 M	8.7	237	15	PuO <sub>2</sub>			
<b>B3</b>	(20)	Pu <sup>IV</sup> aq	<b>Carbonate</b> Starting C <sub>NaHCO<sub>3</sub></sub> = 1.0 M	8.6	150	15	PuO <sub>2</sub>			
	(21)			8.7	237	10				
<b>B4</b>	(22)	Pu <sup>IV</sup> (CO <sub>3</sub> ) <sub>5</sub> <sup>6-</sup>	<b>Carbonate</b> Starting C <sub>NaHCO<sub>3</sub></sub> = 2.1 M	8.6	150	15	PuO <sub>2</sub> + Na <sub>3</sub> (PuO <sub>2</sub> )(CO <sub>3</sub> ) <sub>2</sub> ·xH <sub>2</sub> O			
	(23)			8.8	237	11	PuO <sub>2</sub>			
<b>C1</b>	(3)	Pu <sup>III</sup> <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O	HNO <sub>3</sub>	7.2	150	7	Pu <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O			
	(4)			3.9		7	Pu <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O			
	(5)			3.7		15	Pu <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O			
	(6)			1.8		7	PuO <sub>2</sub> + Pu <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O			
	(6)			1.1		7	PuO <sub>2</sub>			
	(24)			8.0		7	Pu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>			
	(25)			Pu <sup>III</sup> <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		HNO <sub>3</sub>	3.9	150	7	PuO <sub>2</sub> + Pu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
	(26)						3.7		20	PuO <sub>2</sub>
	(26)						0.9		7	PuO <sub>2</sub>
	(27)			Pu <sup>III</sup> <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O		HNO <sub>3</sub>	1.9	60	21	PuO <sub>2</sub> + Pu <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O
(28)	Pu <sup>III</sup> <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	1.7	21	Pu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>						
<b>C2</b>	(7)	Pu <sup>III</sup> <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	HCl	7.6	150	20	Pu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>			
	(8)			3.6		20	PuSiO <sub>4</sub> + PuO <sub>2</sub>			
	(9)			2.0		20	PuO <sub>2</sub>			
	(10)			Pu <sup>III</sup> <sub>4.67</sub> (SiO <sub>4</sub> ) <sub>3</sub> O		4.0	150	20	PuSiO <sub>4</sub> + PuO <sub>2</sub>	
	(11)*			Pu <sup>III</sup> <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>		3.4	150	14	PuSiO <sub>4</sub> + PuO <sub>2</sub> + Pu <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	

\*: C<sub>Pu</sub> = 0.21 M for all of the syntheses except for (11), C<sub>Pu</sub> = 0.42 M.

Synthesis pathways: - A1: based on ThSiO<sub>4</sub> synthesis in carbonate ions free reactive media.<sup>62</sup>

- B1, B2, B3: based on PuSiO<sub>4</sub>,<sup>3,14</sup> ThSiO<sub>4</sub><sup>63</sup> and USiO<sub>4</sub><sup>74</sup> syntheses in carbonate ions rich reactive media, respectively.

- C1 and C2: based on CeSiO<sub>4</sub> syntheses from Ce(III) silicate precursors.<sup>77</sup>

The nature of the final phase obtained was strongly dependent on the molar ratio between PuO<sub>2</sub> and SiO<sub>2</sub> in the starting mixtures. The synthesis of Pu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> was performed with a molar ratio PuO<sub>2</sub>:SiO<sub>2</sub> = 1:1 (sample 1) whereas Pu<sub>4.67</sub>(SiO<sub>4</sub>)<sub>3</sub>O (sample 2) was prepared starting with a molar ratio PuO<sub>2</sub>:SiO<sub>2</sub> equal to 8:6 (corresponding to the stoichiometry of Pu<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub> described by De Alleluia et al.<sup>23, 24</sup>). However, the experimental systems led to polyphase samples containing both plutonium (III) silicates, free of PuO<sub>2</sub> and crystalline SiO<sub>2</sub>. A 1:1

molar ratio led to mixtures richer in Pu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (**Figure S2**) while the samples prepared with a 8:6 molar ratio led to mixtures richer in Pu<sub>4.67</sub>(SiO<sub>4</sub>)<sub>3</sub>O (**Figure S3**). These mixtures were used to evaluate the behavior of both Pu(III) silicates during dissolution tests and will be subsequently identified as Pu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and Pu<sub>4.67</sub>(SiO<sub>4</sub>)<sub>3</sub>O precursors to facilitate the discussion.

The formation of Pu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> at 1350°C could be considered as quite surprising considering the results reported by de Alleluia

et al.<sup>23, 24</sup>, who did not obtain Pu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> after a heat treatment up to 1500°C under reducing atmosphere (H<sub>2</sub>). However, this might easily be explained by the high specific surface of the nanometric compounds used during our experiments (nanometric Pu(IV) oxo/hydroxo obtained by rapid precipitation and 5-20 nm commercial SiO<sub>2</sub>), which enabled a high chemical reactivity.

In order to prepare PuSiO<sub>4</sub>, some amounts of solid Pu(III) silicate precursors, i.e. Pu<sub>4.67</sub>(SiO<sub>4</sub>)<sub>3</sub>O or Pu<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (synthesis presented thereafter), were dispersed in a 1 mol·L<sup>-1</sup> acid solution (HNO<sub>3</sub> and HCl for synthesis pathway C1 and C2, respectively, see **Table 1**). The pH of this suspension was then adjusted to the expected value, ranging between pH = 1 and pH = 8 by the means of 8 mol·L<sup>-1</sup> and 0.1 mol·L<sup>-1</sup> NaOH solutions. All of the mixtures were put into Teflon lined reactors in Parr autoclaves and then treated thermally between 60°C and 150°C under autogenous pressure for 7 to 21 days. The precipitates were separated from the supernatant by centrifugation for 1 min at 14 000 rpm, washed twice with deionized water and once with ethanol, and then finally dried overnight under the glovebox atmosphere.

## Characterization

All the spectrophotometric measurements were performed on a Varian Cary 6000i spectrometer. The spectrophotometer was installed outside the glovebox and the signal was collected via optical fiber. Measurements were performed in PMMA cuvettes between  $\lambda = 350$  nm and 900 nm. The plutonium concentrations were determined by deconvolution of the UV-Visible spectra, using a set of reference spectra containing actinide solutions with known concentrations previously recorded in the same conditions.

PXRD data were recorded on the resulting powders using the Bruker D8 advance diffractometer equipped with a lynxeye detector and using the Cu K<sub>α</sub> radiation ( $\lambda = 1.54184$  Å) in a Bragg Brentano geometry. The data were acquired using adapted sample holders to avoid any potential radioactive contamination. Gold (99.96% pure grade, Alpha Aesar) was added to the sample as an internal standard in order to calibrate the angular positions of the observed XRD lines (PDF 00-004-0784<sup>79</sup>). The XRD lines of this internal standard and those of sample holders have been putted in grey in the following XRD patterns. PXRD patterns were recorded between 5° and 100° (2 $\theta$ ) with steps of 0.02° and counting times of 2 s·step<sup>-1</sup>. All the collected data were then refined by the Rietveld method using the Fullprof suite package.<sup>80</sup> During the refinements, different profile and structure parameters were allowed to vary such as the zero shift, unit-cell parameters, scale factor, and overall displacement factor. However, the occupancy of each site was fixed to the calculated values.

$\mu$ -Raman spectra were recorded with a Horiba-Jobin Yvon LabRam device used in conjunction with a nuclearized optical microscope (Optique Peter, Lyon, France) with a  $\times 20$  objective. A Nd:YAG LASER (532 nm) with a output power

adjustable from 20 to 120 mW was used with a variable filter to provide low-excitation-beam power levels, to avoid the LASER beam damage. The microscope was mounted in a glovebox, while the Raman spectrometer and the laser were installed outside the gloves box with a fiber-optic signal transmission line. For each spectrum, a measurement time of 100 to 3600 s was chosen.

FTIR spectra were recorded in the 600 – 4000 cm<sup>-1</sup> range using a dual channel Vertex 70 FTIR spectrophotometer from Bruker Optics equipped with an ATR module which enabled solid samples to be examined directly inside the glovebox without any prior preparation. The spectra collected in such operating conditions exhibited a resolution of 1 cm<sup>-1</sup>. Sixty scans were performed for each sample in order to average the measurement error.

SEM observations were conducted on powder samples deposited on carbon adhesive sticks and metallized with gold, using a Zeiss SUPRA-55 electronic microscope, equipped either with an Everhart-Thornley Detector (ETD) or a Back-Scattered Electron Detector (BSED) under high vacuum conditions with accelerating voltage between 5 and 30 kV. These conditions were chosen in order to obtain high resolution images.

## Results

### Syntheses based on the actinide protocols for An<sup>IV</sup>SiO<sub>4</sub> (An = Th, U and Pu)

Several attempts to prepare PuSiO<sub>4</sub> were made using the protocols reported in the literature for ThSiO<sub>4</sub> in ligand free reactive media and for ThSiO<sub>4</sub>, USiO<sub>4</sub> and PuSiO<sub>4</sub> in carbonate ions rich reactive media.

### Syntheses in ligand free reactive media (synthesis pathway A1).

According to the results obtained for the synthesis of ThSiO<sub>4</sub>,<sup>62</sup> experiments have been performed in nitric reactive media with initial acidity ranging from [H<sub>3</sub>O<sup>+</sup>] = 2.2 mol·L<sup>-1</sup> to pH = 8.8 for a hydrothermal treatment performed at 150°C for 7 to 15 days. From the PXRD characterization (**Figure S5**), it is clear that PuSiO<sub>4</sub> was not formed on this acidity range at this temperature. Only PuO<sub>2</sub> was obtained as a crystallized final phase. Moreover, the increase of FWHM of the XRD lines associated to PuO<sub>2</sub> was observed when increasing the pH of the starting mixture, as the consequence of the decrease of the crystallite size.

In highly acidic media, e.g. [H<sub>3</sub>O<sup>+</sup>]<sub>initial</sub> = 2.2 mol·L<sup>-1</sup>, it was observed that the hydrothermal treatment only led to the partial precipitation of Pu(IV) with a remaining plutonium(IV) concentration of 10<sup>-2</sup> mol·L<sup>-1</sup> (determined from visible spectrum) in the final supernatant solution. At higher pH (pH  $\geq$  1.9), the plutonium precipitation was quantitative. Whatever the pH considered, the synthesis of PuSiO<sub>4</sub> was strongly limited by the plutonium(IV) hydrolysis which results in the quick formation of plutonium hydroxide and its evolution to PuO<sub>2</sub>.

According to the conditions identified for the synthesis of thorium silicate<sup>62</sup> an additional hydrothermal synthesis was performed at a higher temperature (237°C, pH<sub>initial</sub> = 0.8). However, the results of this synthesis were similar to those obtained at 150°C, with the precipitation of PuO<sub>2</sub> (**Table 1**).

**Syntheses in carbonate ions rich reactive media (synthesis pathways B).** As previously stated, attempts to prepare PuSiO<sub>4</sub> based on the protocol reported by Keller<sup>3, 14</sup> were performed at 150°C and 237°C for 10 to 15 days in 1 mol·L<sup>-1</sup> NaHCO<sub>3</sub> reactive media under air atmosphere (synthesis pathway B1). None of these syntheses led to the formation of PuSiO<sub>4</sub>. Only crystallized PuO<sub>2</sub> was obtained in the final mixtures according to PXRD analyses (**Figure S6**). These contrasting results may be explained by the difference of reactant concentrations between our study ( $C_{Si} \approx C_{Pu} = 0.21 \text{ mol}\cdot\text{L}^{-1}$ ) and the ones used by Keller (not described in his study).<sup>3, 14</sup> Nevertheless, the conditions selected for this study were based on the concentrations allowing the formation of CeSiO<sub>4</sub>, USiO<sub>4</sub> and ThSiO<sub>4</sub>.<sup>62, 63, 74, 76, 77</sup> Another explanation could come from the working atmosphere considered : aerated atmosphere for this study compared to argon atmosphere for Keller's protocol.<sup>3, 14</sup> However, no proof of plutonium oxidation was evidenced in the solution or the solid phase, therefore redox reactions involving plutonium were not sufficient to explain these differences.

Very similar statements have been made for experiments conducted in the conditions which allowed to form ThSiO<sub>4</sub> in carbonate ions rich media, starting from Pu(IV) in aqueous solution, at 237°C for 15 days in aerated atmosphere (synthesis pathway B2).<sup>63</sup> The PXRD diagram corresponds to the precipitation of nanometric or poorly crystallized PuO<sub>2</sub> (**Figure S7**).

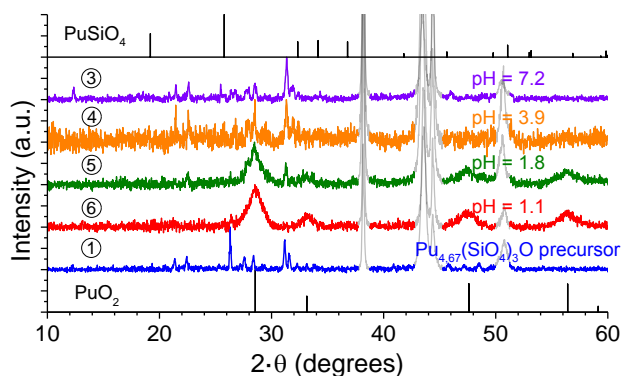
Experiments based on the protocol developed by Mesbah et al.<sup>74</sup> for coffinite, starting from Pu(IV) in aqueous solution, were performed at 150°C and 237°C for 10 to 15 days in air (synthesis pathway B3). This protocol did not allow to prepare PuSiO<sub>4</sub> either. The results were similar to those obtained for the two protocols mentioned above, leading to the formation of PuO<sub>2</sub> as the sole crystalline phase identified by PXRD (**Figure S8**).

It might be inferred that the precipitation of PuO<sub>2</sub> (due to its use as a reactant or to the pH adjustment by NaOH which would quickly lead to the formation of Pu(OH)<sub>4</sub> and then to PuO<sub>2</sub>) and the fact that the pH of the reactive media strongly disfavors PuO<sub>2</sub> dissolution, are very limitative to form PuSiO<sub>4</sub>. Therefore, in order to avoid the formation of PuO<sub>2</sub>, complementary experiments were performed with a Pu(IV) solution stabilized in carbonate ions rich media (2.1 mol·L<sup>-1</sup> instead of 1.0 mol·L<sup>-1</sup>, synthesis pathway B4). Spectrophotometric analyses of the reactive media before the hydrothermal treatment did not exhibit any evidence of the Pu(IV) complexation by silicate ligands but suggested that plutonium speciation was dominated by a limiting plutonium(IV) carbonate complex, Pu(CO<sub>3</sub>)<sub>5</sub><sup>6-</sup> (**Figure S9**).

Hydrothermal treatments were performed at 150°C and 237°C for 11 to 15 days. On the one hand, the hydrothermal treatment at 237°C led to the formation of nanometric or poorly crystallized PuO<sub>2</sub> identified by PXRD (**Figure S10**). On the other hand, the synthesis performed at 150°C led to the formation of a mixture of crystallized Pu(V) sodium carbonate, Na<sub>3</sub>(PuO<sub>2</sub>)(CO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O, and nanometric or poorly crystallized PuO<sub>2</sub> which were both identified by PXRD (by analogy with Na<sub>3</sub>(NpO<sub>2</sub>)(CO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O,<sup>81</sup> **Figure S10**) and Raman spectroscopy (from Na<sub>3</sub>(PuO<sub>2</sub>)(CO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O reference spectrum,<sup>82</sup> **Figure S11**). These species result from the hydrothermal oxidation of stabilized plutonium carbonate species and their precipitation. Moreover, spectrophotometric characterizations performed on the supernatant after hydrothermal treatment exhibited the quantitative precipitation of plutonium as PuO<sub>2</sub>. Nevertheless, no precipitation of PuSiO<sub>4</sub> was observed in these conditions.

#### **Syntheses by hydrothermal oxidation of Pu(III) silicate precursors**

Since the attempts to prepare PuSiO<sub>4</sub> using the protocols reported for ThSiO<sub>4</sub> and USiO<sub>4</sub> failed, complementary experiments were performed using the method optimized for CeSiO<sub>4</sub>, i.e. starting from cerium (III) silicate reactants.<sup>77</sup> Indeed, as reported for cerium, the use of Pu(III) precursors could prevent the hydrolysis of Pu(IV) and then lead to the formation of plutonium silicate.<sup>76</sup>

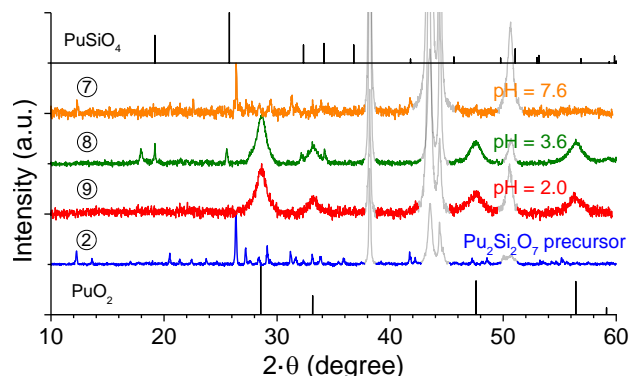


**Fig 1.** PXRD patterns obtained after hydrothermal treatment ( $T = 150^{\circ}\text{C}$ ,  $t = 7$  days, air atmosphere) of  $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$  (1) starting with 0.84 mmol of Pu in nitric media (4mL) for starting pH values of 7.2 (3), 3.9 (4), 1.8 (5) and 1.1 (6). Characteristic XRD lines of  $\text{PuO}_2$  and  $\text{PuSiO}_4$  were extracted from references <sup>1</sup> and <sup>3</sup>, respectively.

### Syntheses in nitric acid reactive media (synthesis pathway C1).

Based on the protocols developed for the preparation of  $\text{CeSiO}_4$  from  $\text{Ce(III)}$  silicate precursors,<sup>77</sup> hydrothermal treatments were developed in air at  $150^{\circ}\text{C}$  for 7 to 20 days on  $\text{Pu}_2\text{Si}_2\text{O}_7$  and  $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$  precursors for various initial pH values ranging from 1 to 7. None of these experiments succeeded in forming  $\text{PuSiO}_4$ . Only mixtures containing the remaining precursor and/or  $\text{PuO}_2$  crystalline phases were evidenced by PXRD. However, a clear difference was observed between the hydrothermal treatment performed in acidic media, which led to  $\text{PuO}_2$  and  $\text{SiO}_2$  mixtures for  $\text{pH} \leq 2$  and those developed in much more alkaline reactive media for which the starting  $\text{Pu(III)}$  silicate was poorly altered (**Figure 1** and **Figure S12**, for  $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$  and  $\text{Pu}_2\text{Si}_2\text{O}_7$  respectively). The fact that these residues obtained after using alkaline conditions had the same chemical form (according to PXRD) as the starting precursor, however, to be taken with caution. Indeed, the color of these samples changed from blue to greenish-brown. This change in color might be explained by the oxidation of the plutonium (III) silicate at the solid/solution interface or by the formation of an amorphous  $\text{Pu(IV)}$  phase. However, this oxidation seems to be limited due to the very slow dissolution process of the precursor in these experimental conditions and was not clearly evidenced by PXRD, Raman or infrared characterization (amorphous secondary phase).

It may be inferred that the absence of  $\text{Pu(III)}$  silicate dissolution for  $2 < \text{pH} < 8$  may be associated to the low dissolution rate of these silicate based species in these conditions compared to more acidic media. Another explanation of this phenomenon might result from the formation of a silica based passive layer onto the surface of the plutonium (III) silicate precursor, due to the very low solubility of  $\text{SiO}_2$  in this pH range.<sup>2</sup> However, even if these two mechanisms could be complementary, the apparent absence of  $\text{Ce(III)}$  silicate dissolution was also observed in alkaline conditions ( $\text{pH} > 8$ ) which would promote the solubility of silica.<sup>77</sup> Therefore, it might be supposed that the same behavior occurred for the  $\text{Pu(III)}$  silicate analogs.



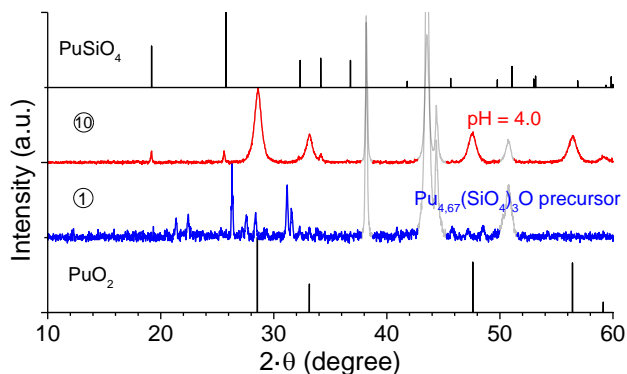
**Fig 2.** PXRD patterns obtained after hydrothermal treatment ( $T = 150^{\circ}\text{C}$ ,  $t = 20$  days, air atmosphere) of  $\text{Pu}_2\text{Si}_2\text{O}_7$  reactant (2) starting with 0.84 mmol of Pu in nitric media (4mL) for starting pH values of 7.6 (7), 3.6 (8) and 2.0 (9). Characteristic XRD lines of  $\text{PuO}_2$  and  $\text{PuSiO}_4$  were extracted from references <sup>1</sup> and <sup>3</sup>, respectively.

The oxidation of plutonium (III) may be caused by both the oxygen of the working atmosphere and the considered nitric media which could facilitate the oxidation of  $\text{Pu(III)}$  bearing species. It has to be noticed that extending the duration of the hydrothermal treatment from 7 to 20 days in weakly acid media (i.e.  $\text{pH} = 4$ ) led to similar results. Moreover, additional experiments performed at lower temperature ( $60^{\circ}\text{C}$ ) and for  $\text{pH} = 2$ , starting from  $\text{Pu}_2\text{Si}_2\text{O}_7$  and  $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$ , did not allow to form  $\text{PuSiO}_4$  (**Figure S13**) but only led to the formation of a  $\text{PuO}_2$  and  $\text{Pu(III)}$  silicate mixture, probably due to the slow dissolution kinetic of  $\text{Pu(III)}$  silicate at low temperature. Therefore, decreasing the temperature did not seem to prevent the oxidation reaction leading to the formation  $\text{PuO}_2$ .

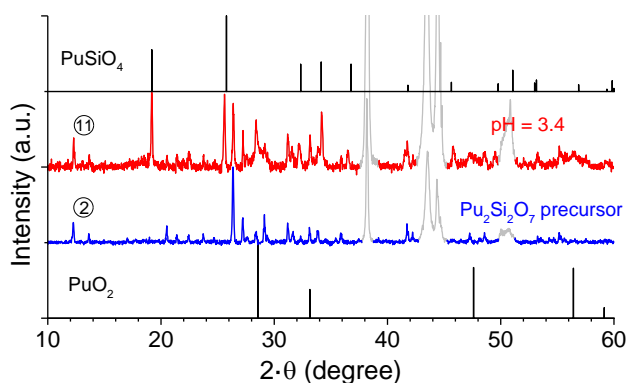
### Syntheses in hydrochloric acid reactive media (synthesis pathway C2).

In order to determine if less oxidative reactive media could be suitable to form  $\text{PuSiO}_4$ , hydrothermal treatments of  $\text{Pu}_2\text{Si}_2\text{O}_7$  and  $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$  precursors were performed at  $150^{\circ}\text{C}$  in air, for various initial pH values ranging from 2 to 8. These conditions corresponded to maximal concentrations of Pu of  $0.21 \text{ mol}\cdot\text{L}^{-1}$  and  $0.42 \text{ mol}\cdot\text{L}^{-1}$  in solution (i.e. 0.84 mmol and 1.7 mmol of Pu, respectively in 4mL), when considering the full dissolution of plutonium precursors.

For the lowest plutonium content (i.e. 0.84 mmol of Pu) using  $\text{Pu}_2\text{Si}_2\text{O}_7$  as precursor and for hydrothermal treatment performed with an initial pH of 3.6, the formation of  $\text{PuSiO}_4$  as a minor phase was observed (mixed with  $\text{PuO}_2$  as the major phase) (**Figure 2**). The synthesis performed at lower pH values (i.e.  $\text{pH} = 2$ ) led to the formation of mixtures of  $\text{PuO}_2$  (observed by PXRD and Raman spectroscopy) and  $\text{SiO}_2$  (identified by IR spectroscopy). As previously stated in nitric reactive media, no apparent degradation of the  $\text{Pu(III)}$  silicate precursor was observed when working with higher pH values (i.e.  $\text{pH} = 7.6$ ). In order to compare the two  $\text{Pu(III)}$  silicate precursors, an additional experiment was conducted at  $\text{pH} = 4.0$ , with 0.84 mmol of Pu,  $T = 150^{\circ}\text{C}$  and in air atmosphere, starting with  $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$ . These conditions allowed the formation of  $\text{PuSiO}_4$  as minor phase of a two-phased system also composed by  $\text{PuO}_2$  (**Figure 3**).



**Fig 3.** PXRD patterns obtained after hydrothermal treatment ( $T = 150^\circ\text{C}$ ,  $t = 20$  days, air atmosphere) of  $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$  (1) starting with 0.84 mmol of Pu in hydrochloric medium (4mL) and with pH = 4.0 (10). Characteristic XRD lines of  $\text{PuO}_2$  and  $\text{PuSiO}_4$  were extracted from references <sup>1</sup> and <sup>3</sup>, respectively.



**Fig 4.** PXRD patterns obtained after hydrothermal treatment ( $T = 150^\circ\text{C}$ ,  $t = 14$  days, air atmosphere) of  $\text{Pu}_2\text{Si}_2\text{O}_7$  reactant (2) starting with 1.7 mmol of Pu in hydrochloric medium (4mL) and with pH = 3.4 (11). Characteristic XRD lines of  $\text{PuO}_2$  and  $\text{PuSiO}_4$  were extracted from references <sup>1</sup> and <sup>3</sup>, respectively.

In order to evidence the impact of the Pu(III) silicate relative concentration on the formation of  $\text{PuSiO}_4$ , an additional experiment was performed starting with higher content of  $\text{Pu}_2\text{Si}_2\text{O}_7$  (i.e. 1.7 mmol of Pu) at pH = 3.4. The hydrothermal treatment performed for 14 days at  $150^\circ\text{C}$  in air led to the formation of mixture composed by  $\text{PuSiO}_4$ ,  $\text{PuO}_2$  and  $\text{Pu}_2\text{Si}_2\text{O}_7$ . The results obtained by PXRD analyses highlighted that the increase of the reactants amounts in the starting media increased the yield of formation of  $\text{PuSiO}_4$  (Figure 4). Indeed, the fraction of  $\text{PuSiO}_4$  was estimated by Rietveld refinement to 30 wt.% in the later conditions while it was found to be under 5 wt.% for the experiments performed with 0.84 mmol of Pu. Moreover, the presence of remaining Pu(III) silicate in the final mixture (over 60 wt.%) suggested that the formation of  $\text{PuSiO}_4$  was kinetically-limited by the dissolution of the starting Pu(III) silicate.

Rietveld refinement performed on the samples containing  $\text{PuSiO}_4$  as a minor phase enabled the determination of the following set of lattice parameters:  $a = 6.9676(9)$  Å,  $c = 6.2007(9)$  Å and  $V = 301.05(7)$  Å<sup>3</sup> (Figure S14). As it might be expected based on the closeness between  $\text{Ce}^{4+}$  and  $\text{Pu}^{4+}$  ionic radii for octacoordinated cation (0.97 Å against 0.96 Å),<sup>83</sup> these values are close to what was obtained for pure  $\text{CeSiO}_4$ :  $a = 6.9523(2)$  Å,  $c = 6.2036(2)$  Å and  $V = 300.06(2)$  Å<sup>3</sup>,<sup>77</sup> but

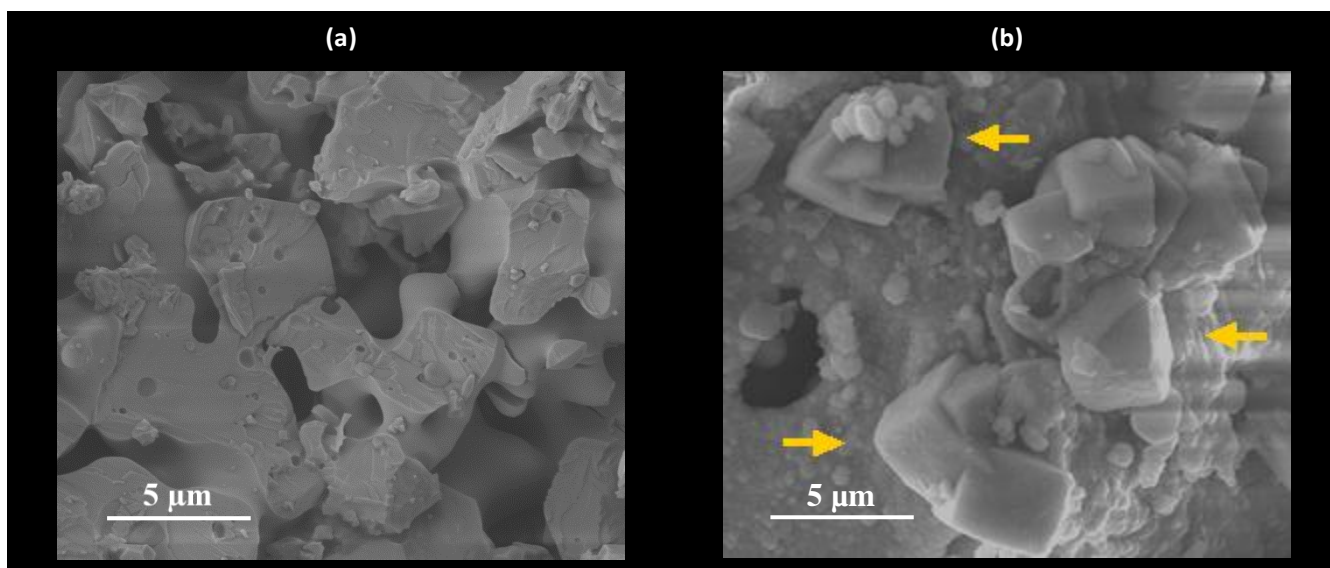
differed significantly from those reported by Keller:  $a = 6.906(6)$  Å,  $c = 6.221(6)$  Å and  $V = 296.6(5)$  Å<sup>3</sup>.<sup>3, 14</sup> This difference could be explained by the synthesis route used to prepare  $\text{PuSiO}_4$ , i.e. by the potential incorporation of hydroxide species in the  $\text{PuSiO}_4$  structure, as already suggested for  $\text{ThSiO}_4$ <sup>62</sup> and by Frondel and Collette<sup>52</sup>. It could also result from the misestimation of the reference parameters. Indeed, the lattice parameters reported by Keller were obtained on diffuse PXRD peaks and no yield of synthesis was reported.<sup>3, 14</sup> Additionally, one cannot completely exclude the occurrence of  $\text{PuSiO}_4$  metamictization (i.e. amorphization under radiation), which might lead to the increase of the  $a$  parameter and to the decrease of the  $c$  parameter.

The characterization of the samples by Raman spectroscopy (Figure S15) allowed to identify some of the characteristic bands of  $\text{PuSiO}_4$ . Indeed, the symmetric and antisymmetric stretching modes of  $\text{SiO}_4$  were observed at  $910\text{ cm}^{-1}$  and  $929\text{ cm}^{-1}$ , respectively, whereas the symmetric bending mode was located  $432\text{ cm}^{-1}$ . The bands associated to the antisymmetric bending mode of  $\text{SiO}_4$  were not evidenced because of their low intensity. These results are in good agreement with the data reported for isostructural silicate-based phases (Table 2).

**Table 2.** Assignment of the bands associated to the silicate groups observed by Raman spectroscopy for  $\text{PuSiO}_4$  and comparison with other isostructural silicate based phases.

$\text{MSiO}_4$	Ionic radius of $\text{M}^{4+}$ (Å) <sup>83</sup>	$\nu_2$	$\nu_4$	$\nu_1$	$\nu_3$
$\text{HfSiO}_4$ <sup>84-86</sup>	0.83	$448\text{ cm}^{-1}$	$620\text{ cm}^{-1}$	$984\text{ cm}^{-1}$	$1018\text{ cm}^{-1}$
$\text{ZrSiO}_4$ <sup>87,88</sup>	0.84	$439\text{ cm}^{-1}$	$608\text{ cm}^{-1}$	$974\text{ cm}^{-1}$	$1008\text{ cm}^{-1}$
<b><math>\text{PuSiO}_4</math></b>					
(this study)	<b>0.96</b>	<b><math>432\text{ cm}^{-1}</math></b>	—	<b><math>910\text{ cm}^{-1}</math></b>	<b><math>929\text{ cm}^{-1}</math></b>
$\text{CeSiO}_4$ <sup>76</sup>	0.97	$416\text{ cm}^{-1}$	$592\text{ cm}^{-1}$	$903\text{ cm}^{-1}$	$919\text{ cm}^{-1}$
$\text{USiO}_4$ <sup>55</sup>	1.00	$424\text{ cm}^{-1}$	$591\text{ cm}^{-1}$	$906\text{ cm}^{-1}$	$919\text{ cm}^{-1}$
$\text{ThSiO}_4$ <sup>55</sup>	1.05	$438\text{ cm}^{-1}$	$592\text{ cm}^{-1}$	$887\text{ cm}^{-1}$	$914\text{ cm}^{-1}$

SEM observations performed on both Pu(III) bearing silicate precursors and  $\text{PuSiO}_4$ -containing samples allowed to clearly observe a change in the material morphology consequently to the hydrothermal treatment (Figure 5). Indeed, from the typical morphology of the high-temperature sintered  $\text{Pu}_2\text{Si}_2\text{O}_7$ , the sample was covered by square-based bipyramid grains, which is characteristic of silicate phases of the zircon group resulting from hydrothermal treatment. This change in morphology was quite similar to what was observed during the progressive conversion of Ce(III) silicates into  $\text{CeSiO}_4$ .<sup>77</sup> Moreover,  $\text{PuSiO}_4$  crystals were precipitated onto the surface of a dense substrate which might correspond to the remaining  $\text{Pu}_2\text{Si}_2\text{O}_7$  precursor or to a  $\text{PuO}_2$  and  $\text{SiO}_2$  mixture. Such kind of precipitation on a solid substrate might be compared to the results obtained for the coffinitisation process for  $\text{USiO}_4$  formation from  $\text{UO}_2$  and  $\text{SiO}_2$ . All of these observations underline the kinetic limitation of the precursor chemical reactivity and suggest that the  $\text{PuSiO}_4$  formation occurs by a



**Fig 5.** SEM micrographs obtained for sintered  $\text{Pu}_2\text{Si}_2\text{O}_7$  precursor (9 hours,  $T = 1350^\circ\text{C}$ ,  $\text{Ar} - 4\% \text{H}_2$ ) (a) and for  $\text{PuSiO}_4$ -containing sample ( $\text{PuSiO}_4$  on the bottom, right and top left) obtained after hydrothermal treatment of  $\text{Pu}_2\text{Si}_2\text{O}_7$  for 14 days at  $150^\circ\text{C}$  in air (hydrochloric acid and  $\text{pH} = 3.4$ ) (b).

slow dissolution, oxidation and precipitation process at the solid-liquid interface.

## Discussion

### Statements on the attempts to synthesize $\text{PuSiO}_4$ from Pu(IV) reactants

The impossibility to prepare  $\text{PuSiO}_4$  in acidic, carbonate ions free, reactive media could be explained by the weak interactions between plutonium and silicate ions in acidic solution. Indeed, the coexistence of free plutonium (IV) ions and silicate ions is very limited in terms of pH range because of the low solubilities of plutonium(IV) hydroxide over  $\text{pH} = 1$ <sup>89</sup> and of silica below  $\text{pH} = 8$ .<sup>2</sup> Moreover, due to the very refractory character of plutonium dioxide, the remobilization of plutonium to enable the formation of  $\text{PuSiO}_4$  is strongly disadvantaged from kinetic and thermodynamic points of view according to the ab-initio calculations which showed that  $\text{PuSiO}_4$  could be metastable<sup>16-22</sup> compared to the mixture of crystalline  $\text{PuO}_2$  and  $\text{SiO}_2$ .

Considering the results reported for actinide analogs,<sup>3, 63, 74</sup> it might be inferred that performing hydrothermal synthesis in carbonate rich media would favor the formation of plutonium silicate due to the pH conditions which could promote the simultaneous presence in solution of silicate and tetravalent plutonium (through carbonate ions assisted dissolution of  $\text{PuO}_2$ ). However, none of the synthesis conditions explored enabled the formation of  $\text{PuSiO}_4$ , probably because of the strong competition between hydroxide, silicate and carbonate complexations with tetravalent plutonium. Thermodynamic data allowing the evaluation of these competitive effects under hydrothermal conditions are lacking. Nevertheless, since plutonium oxide was formed, the use of silicate and carbonate ligands were insufficient to counterbalance its precipitation or to enhance its dissolution. When plutonium carbonate

complexes are formed, the competitive effects between carbonate and silicate ligands did not seem to promote the formation of silicate-based species. At low temperatures (i.e.  $150^\circ\text{C}$ ), hydrothermal treatments led to the formation of plutonium carbonate solid phases, while at higher temperatures (i.e.  $237^\circ\text{C}$ ) carbonate ions complexation was probably disfavored and plutonium reactivity with hydroxide species led to the formation of  $\text{PuO}_2$ . We considered, therefore, the formation of  $\text{PuSiO}_4$  in these conditions to be quite uncertain even if its formation has been reported in the literature by this path of synthesis.<sup>3</sup> These results suggest that at least one unidentified key parameter was involved in the synthesis reported by Keller.

### Statements on the synthesis of $\text{PuSiO}_4$ from Pu(III) silicate reactants

The development of syntheses starting from Pu(III) silicate precursors proved that the formation of  $\text{PuSiO}_4$  was possible using such reactants. The pH of the reactive media was found to play a key role for the formation of the Pu(IV) silicate. Indeed, the dissolution of Pu(III) silicate was promoted in acidic media ( $\text{pH} < 3$ ), leading to the precipitation of  $\text{PuO}_2$ , whereas the low dissolution rate of the starting precursors in alkaline media only led to the oxidation of plutonium at the solid/solution interface. However, the formation of  $\text{PuSiO}_4$  was observed in an intermediate pH window (typically between pH 3 and 4) which was sufficient to provide the dissolution of the Pu(III) based precursor, slow oxidation of Pu(III) into Pu(IV) (or its oxidative dissolution) followed by the precipitation of  $\text{PuSiO}_4$ .

The nature of the reactive media used also impacted the formation of  $\text{PuSiO}_4$ . Indeed, working in nitric media did not enable the formation of  $\text{PuSiO}_4$ , probably due to the too rapid oxidation of the Pu(III) by nitrous acid (from nitric acid) and/or dioxygen present in the system. Therefore, it may be inferred that the formation of  $\text{PuSiO}_4$  could be favored by the slow

oxidation of Pu(III) silicate species (at the solid-liquid interface or in solution), keeping low Pu(IV) concentrations in the solution and thus preventing the formation of Pu(IV) bearing hydroxide precipitates which could evolve rapidly into PuO<sub>2</sub>. Consequently, less oxidative media, such as a hydrochloric media, should be privileged to form PuSiO<sub>4</sub>.

It was also observed that the yield of formation of PuSiO<sub>4</sub> was improved by increasing the amount of the Pu(III) reactant in

the reactive media. Such higher yields could be explained either by the increase of the concentration of the intermediate species which are involved in the formation of PuSiO<sub>4</sub> or by the decrease of the oxidative species (such as O<sub>2</sub>) / Pu(III) precursor ratio in the reactive media (avoiding the quick oxidation of Pu(III) silicate precursors leading to PuO<sub>2</sub>).

**Table 3.** Constants of complexation of Ce(IV) and An(IV) with carbonate associated to the limit complexes at I = 0 (25°C).

Ln(IV)/An(IV)	Ionic radii VIII M <sup>4+</sup> (Å) <sup>83</sup>	Hydrolysis thermodynamic constants M(OH) <sub>n</sub> <sup>(4-n)+</sup> (logβ <sup>n</sup> ) <sup>89,90</sup>				logK <sub>sp</sub> <sup>o</sup> (MO <sub>2</sub> ·xH <sub>2</sub> O) <sup>89,91</sup>
		logβ <sup>1</sup>	logβ <sup>2</sup>	logβ <sup>3</sup>	logβ <sup>4</sup>	
Pu	0.96	14.6 ± 0.2	28.6 ± 0.3	39.7 ± 0.4	48.1 ± 0.9	- 58.5 ± 0.7
Ce	0.97	14.8	28.0	40.5	51.9	- 59.3 ± 0.3
U	1.00	13.6 ± 0.2	26.9 ± 1.0	37.3 ± 1.0	46.0 ± 1.4	- 54.5 ± 1.0
Th	1.05	11.8 ± 0.2	22.0 ± 0.6	31.0 ± 1.0	38.5 ± 1.0	- 47.0 ± 0.8

\* β<sup>n</sup> is associated to the reaction An<sup>4+</sup> + n HO<sup>-</sup> = An(OH)<sub>n</sub><sup>(4-n)+</sup>.

\*\* K<sub>sp</sub><sup>o</sup> is associated to the reaction AnO<sub>2</sub>·xH<sub>2</sub>O + (2-x) H<sub>2</sub>O = An<sup>4+</sup> + 4 HO<sup>-</sup>

### Comparison with the different zircon-type silicate systems

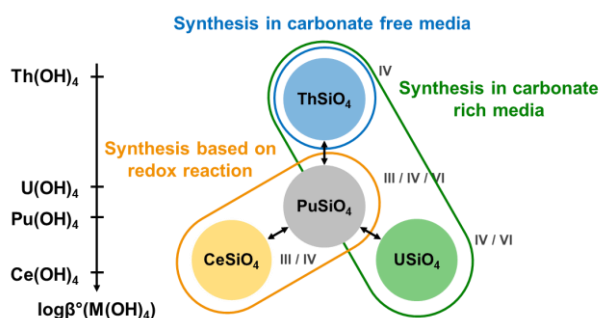
Among all the attempts to prepare PuSiO<sub>4</sub> adapted from the optimized conditions for the potential surrogates (Ce, Th and U), the chemical route leading to the formation of CeSiO<sub>4</sub> from Ce(III) silicate solid precursors in hydrochloric reactive media<sup>77</sup> has been identified as the only suitable way to prepare plutonium silicate. Similar experiments performed in nitric conditions did not lead to the formation of PuSiO<sub>4</sub>. This difference compared to CeSiO<sub>4</sub> was explained by the stronger oxidative character of nitrous acid from nitric media (establishing a redox potential around 1.0 V/ENH) for Pu(III) compared to Ce(III).<sup>77</sup>



Moreover, it might also be inferred that the complexation of tetravalent elements by silicates ligands could decrease the +IV/+III redox potential according to the Nernst law. This phenomenon could explain the easy oxidation to +IV oxidation state, and the formation of both PuSiO<sub>4</sub> and CeSiO<sub>4</sub>. However, to the best of our knowledge, no quantification of this modification has been reported yet.

All the experiments performed from a Pu(IV) reactant did not

allow to form Pu(IV) silicate and only led to the precipitation of plutonium oxide or plutonium carbonate. The different behaviors observed between plutonium (IV) and the surrogate elements studied could be explained by the competition between hydrolysis and silicate complexation. Indeed, the protocol of synthesis adapted from the ThSiO<sub>4</sub> synthesis in carbonate ions free acidic reactive media<sup>62</sup> was not efficient to form USiO<sub>4</sub>, CeSiO<sub>4</sub><sup>76</sup> or PuSiO<sub>4</sub>, and only led to mixtures of corresponding metal dioxide and silica. This difference was explained by the stronger trend in hydrolysis, and to precipitate as oxide phases, of U<sup>4+</sup>, Ce<sup>4+</sup> and Pu<sup>4+</sup> compared to Th<sup>4+</sup> (**Figure 6** and **Table 3**). The transposition of the protocols of synthesis reported in carbonate ions rich reactive media, which allowed the formation of pure ThSiO<sub>4</sub><sup>63</sup> and USiO<sub>4</sub> (in mixture with UO<sub>2</sub>),<sup>74</sup> didn't allow the formation of CeSiO<sub>4</sub><sup>76</sup> and PuSiO<sub>4</sub> but only gave a metal dioxide and silica mixture. These results might also be explained by the higher trend in hydrolysis and precipitation as oxide phases of Ce<sup>4+</sup> and Pu<sup>4+</sup> compared to Th<sup>4+</sup> and U<sup>4+</sup> (**Figure 6** and **Table 3**). Moreover, complexation of Ce<sup>4+</sup> or Pu<sup>4+</sup> by carbonate ions are stronger than that obtained for Th<sup>4+</sup> or U<sup>4+</sup> (**Table S2**). Both aspects would affect the availability of Pu<sup>4+</sup> to interact with other ligands. The feasibility of PuSiO<sub>4</sub> synthesis in the conditions reported in this article from plutonium (III) silicate precursors, could result from the formation of intermediate plutonium silicate species (**Figure S17**). According to the dissolution and precipitation process hypothesized, it seems likely that at least one of the intermediate species involved in the PuSiO<sub>4</sub> formation could be a plutonium silicate aqueous species. As we previously stated during the synthesis of CeSiO<sub>4</sub> from Ce(III) silicate precursors,<sup>77</sup> the formation of PuSiO<sub>4</sub> could be associated to a multistep mechanism. The dissolution of the silicate based precursors could occur through the hydrolysis of Si-O-Si bounds at the surface of the plutonium (III) silicate, leading to the release of Pu(III) bearing silicate complexes in solution. These complexes might be slowly oxidized (probably by O<sub>2</sub>), without breaking the plutonium-silicate bounds, to



**Fig 6.** Comparison of PuSiO<sub>4</sub> and its surrogates according to their ways of synthesis.

form Pu(IV) bearing silicate species, which could precipitate as PuSiO<sub>4</sub>. The presence of strong oxidants in the solution, such as nitrous acid, might be limitative because they would trigger a rapid surface oxidation of the Pu(III) silicate precursors, leading to the formation of PuO<sub>2</sub> or a Pu(IV) silicate passivating layer.

Due to the similar limitation encountered for Ce(IV) and Pu(IV) and the closeness between Ce(III) silicate and Pu(III) silicate reactivity when forming CeSiO<sub>4</sub> and PuSiO<sub>4</sub>, it is worth noting that cerium (IV) can be considered as the best surrogate element among those considered to mimic the behavior of plutonium (IV) in reductive and silicate rich media. Since CeSiO<sub>4</sub> was prepared from Ce(III) species at temperatures as low as 40°C,<sup>76</sup> it also raises crucial questions on the potential behavior of plutonium in the environment<sup>5-13</sup> in the presence of silicates. A particular impact could be found when storing Pu(III) based radioactive waste forms in reductive and silicate rich environments. Moreover, the in-situ formation of plutonium (III) by chemical reduction or by radiolysis might also lead to the formation of PuSiO<sub>4</sub>.

## Conclusions

Studying the hydrothermal synthesis of PuSiO<sub>4</sub>, by application of the ways of synthesis optimized for MSiO<sub>4</sub> analogs (Th, U, Ce) allowed to determine a method to form this silicate-based phase. It consisted in the preparation of Pu(III) silicate phases and their slow hydrothermal oxidation in hydrochloric reactive media at pH = 3–4. From a general point of view, our experiments suggested that the properties of plutonium (IV) in the presence of silicate ions were closer to those of cerium (IV) than those of uranium (IV) and thorium. Therefore, cerium (IV) may be considered as the best surrogate to mimic the behavior of plutonium (IV) in silicate rich media.

Our experiments did not confirm the results reported by Keller<sup>3, 14</sup> and, more generally, did not allow to form PuSiO<sub>4</sub> from Pu(IV) containing mixtures.

However, the identification of the intermediate species and the understanding of the formation of PuSiO<sub>4</sub> mechanism still remain very important issues. Determining the role of the Pu(III) bearing silicate species in solution during the synthesis of PuSiO<sub>4</sub> and their electrochemical behavior may be really challenging. Additionally, the identification of the oxidant species involved in the Pu(III) silicate oxidation is also a crucial point to be clarified in order to understand the relevance of these species under environmental conditions.

The formation of PuSiO<sub>4</sub> starting from Pu(III) silicate phases also shew a new light on the potential reactivity of americium and curium bearing silicate complexes<sup>96, 97</sup> and its consequences on the speciation of these actinides in the environment.

Even if this study did not allow the formation of pure PuSiO<sub>4</sub>, it shows that the formation of the plutonium (IV) silicate is possible in very specific conditions. Based on the results already obtained on the cerium-silicate system, it might be supposed that the reaction yield could be improved by working under inert atmosphere, increasing the amount of

reactant, the holding time under hydrothermal conditions or by modifying the working temperature. More specifically, the experiments performed on the CeSiO<sub>4</sub> surrogate have evidenced that the formation of cerium (IV) silicate was very limited at temperatures higher than 150°C but was possible at temperatures as low as 60°C starting with solid Ce(III) silicates.<sup>77</sup> Some other ways of synthesis involving complexing species such as carbonate ions (in order to determine the unidentified parameter in Keller's protocol) or fluoride ions (which were successfully employed to prepare ZrSiO<sub>4</sub>, HfSiO<sub>4</sub> and ThSiO<sub>4</sub> syntheses<sup>52, 98-100</sup>) might also allow the remobilization of the plutonium which would precipitate as PuO<sub>2</sub> and improve the synthesis yield of PuSiO<sub>4</sub>. However, the plutonium complexation by strong ligands such as fluoride might also disadvantage the formation of the silicate phase compared to more stable phases. Nevertheless, this study constitutes a first step in the formation of pure PuSiO<sub>4</sub> which is a crucial point in order to get solubility data on this phase and more importantly, to evaluate its importance in the study of plutonium environmental chemistry.

## Acknowledgements

The authors would like to thank V. Brethenoux and J. Hennuyer (from CEA) for supporting the syntheses experiments, J. R. Sevilla (from CEA) for supporting SEM experiments and P. Coste (from CEA) for supporting Pu(III) silicate syntheses experiments.

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## FOR TABLE OF CONTENTS ONLY

The study of  $\text{PuSiO}_4$  constitutes a crucial issue to get a better representation of the behavior of plutonium in silicate ions rich environments. This study reports an innovative way of synthesis of  $\text{PuSiO}_4$  by hydrothermal in situ oxidation of solid  $\text{Pu(III)}$  silicate precursors. It also identifies how representative thorium, uranium and cerium are of plutonium chemistry in silicate ions rich reactive media.

