

Formation of plutonium (IV) silicate species in very alkaline reactive media

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SUPPORTING INFORMATION

Table S1 Results of the pH and UV-visible monitoring on a Na_2SiO_3 $2 \text{ mol}\cdot\text{L}^{-1}$ aqueous solution depending on the addition of Pu(IV) nitric solution ($C_{\text{HNO}_3} = 1.5 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{Pu}} = 0.3 \text{ mol}\cdot\text{L}^{-1}$).

V(Na_2SiO_3 2M)	V(Pu 0.3M in HNO_3 1.5M)	pH	UV-visible spectroscopy observations
	0 mL	13.3	-
	0.100 mL	13.3	Pu(IV)-silicate species
	0.100 mL	13.2	Pu(IV)-silicate species
	0.100 mL	13.1	Pu(IV)-silicate species
	0.400 mL	13.0	Pu(IV)-silicate species
0.800 mL	0.500 mL	12.5	Pu(IV)-silicate species (weak intensity)
	0.600 mL	12.0	No Pu species observed
	0.700 mL	11.4	No Pu species observed
	0.900 mL	9.6	No Pu species observed
	1.000 mL	2.5	No Pu species observed

Table S2 Interatomic distances for ThSiO_4 , USiO_4 , CeSiO_4 and PuSiO_4 (zircon type silicates, space group $I4_1/amd$ ¹).

	Interatomic distances (ASiO_4)				Abundance
	ThSiO_4 ²	USiO_4 ³	CeSiO_4 ⁴	PuSiO_4 ⁵	
A-O ₁	2.46 Å	2.32 Å	2.27 Å	-	4
A-O ₂	2.56 Å	2.51 Å	2.37 Å	-	4
A-Si ₁ (bidentate)	3.16 Å	3.13 Å	3.10 Å	3.11 Å	2
A-Si ₂ (monodentate)	3.91 Å	3.83 Å	3.81 Å	3.79 Å	4
A-A	3.91 Å	3.83 Å	3.81 Å	3.79 Å	4

Table S3 Structural parameters for the Pu(IV)-silicate species determined in this study and reported in the literature for Th(IV)-, U(IV)- and Np(IV)-silicates colloids. The values fixed for the simulations have been marked by an asterisk.

Plutonium (IV)-silicate species (this study)					
Reference	R (Å)	N	σ^2 (Å ²)	$\Delta E_{k=0}$	F
Pu-O ₁	2.23 (2) Å	4 *	0.007 (3)	− 1.2 eV	0.02
Pu-O ₂	2.34 (3) Å	4 *	0.007 (3)		
Pu-Si ₁	3.21 (6) Å	1.1 (9)	0.009*		
Pu-Si ₂	3.46 (3) Å	5.4 (22)	0.012*		
Pu-Pu	3.77 (3) Å	6.0 (21)	0.020 (26)		
Filtered 0.45 μm					
Pu-O ₁	2.20 (1) Å	4 *	0.005 (2)	− 2.8 eV	0.03
Pu-O ₂	2.33 (2) Å	4 *	0.005 (2)		
Pu-Si ₁	3.04 (7) Å	2.1 (6)	0.009*		
Pu-Si ₂	3.49 (3) Å	5.3 (19)	0.012*		
Pu-Pu	3.73 (3) Å	5.1 (39)	0.017 (8)		
Filtered 100 kDa					
Pu-O ₁	2.24 (37) Å	4 *	0.007 (3)	− 2.7 eV	0.02
Pu-O ₂	2.30 (38) Å	4 *	0.007 (3)		
Pu-Si ₁	3.26 (14) Å	0.7 (18)	0.009*		
Pu-Si ₂	3.47 (5) Å	6.1 (39)	0.012*		
Pu-Pu	3.73 (4) Å	6.4 (32)	0.020 (1)		
1 year-old					
Pu-O ₁	2.23 (17) Å	4 *	0.007 (3)	− 2.3 eV	0.04
Pu-O ₂	2.29 (18) Å	4 *	0.007 (3)		
Pu-Si ₁	3.26 (8) Å	1.1 (6)	0.009*		
Pu-Si ₂	3.46 (3) Å	8.8 (19)	0.012*		
Pu-Pu	3.75 (3) Å	3.9 (39)	0.013 (7)		
Thorium (IV)-silicate colloids ⁶					
Th/Si = 1.4	R (Å)	N	σ^2 (Å ²)	$\Delta E_{k=0}$	F
Th-O	2.39 Å	8.9	0.016	− 0.9 eV	0.10
Th-Si	3.26 Å	1.3	0.011		
Th/Si = 1.7					
Th-O	2.38 Å	8.6	0.016	− 1.6 eV	0.07
Th-Si	3.25 Å	1.6	0.013		
Th/Si = 5.8					
Th-O	2.36 Å	8.3	0.018	− 2.1 eV	0.09
Th-Si	3.23 Å	2.5	0.011		
Uranium (IV)-silicate colloids ⁷					
Si/U = 0.83	R (Å)	N	σ^2 (Å ²)	$\Delta E_{k=0}$	F
U-O ₁	2.25 Å	4.1	0.0082	− 19 eV	0.19
U-O ₂ /Si	2.81 Å	2.7	0.0082		
U-U	3.85 Å	2.6	0.0067	− 6 eV	
Si/U = 1.68					
U-O ₁	2.23 Å	2.7	0.0081	− 16 eV	0.16
U-O ₂ /Si	2.83 Å	3.5	0.0081		

Uranium (IV)-silicate colloids ⁸					
4 mM _{Si} pH = 9	R (Å)	N	σ^2 (Å ²)	$\Delta E_{k=0}$	F
U-O ₁	2.26 (1) Å	4.3	0.009 (1)	4.1 (10) eV	0.0124
U-O ₂	2.44 (1) Å	3.8	0.009 (1)		
U-Si ₁	3.17 (2) Å	1.1	0.010 (3)		
U-Si ₂	3.70 (3) Å	2.5	0.013 (4)		
U-U	3.78(5) Å	1	0.013(7)		
4 mM _{Si} pH = 10.5					
U-O ₁	2.28 (1) Å	4.5	0.006 (1)	5.5 (9) eV	0.0076
U-O ₂	2.46 (1) Å	3.5	0.006 (1)		
U-Si ₁	3.18 (2) Å	1.6	0.011 (3)		
U-Si ₂	3.73 (4) Å	2	0.014 (5)		
U-U	3.79 (4) Å	1.8	0.014 (5)		
4 mM _{Si} pH = 12					
U-O ₁	2.29 (1) Å	4.4	0.007 (1)	6.1 (6) eV	0.0042
U-O ₂	2.46 (1) Å	3.0	0.007 (1)		
U-Si ₁	3.19 (2) Å	1.6	0.013 (3)		
U-Si ₂	3.71 (5) Å	0.8	0.012 (7)		
U-U	3.84 (2) Å	2.8	0.013 (2)		
2 mM _{Si} pH = 9					
U-O ₁	2.28 (1) Å	3.7	0.008 (1)	6.5 (5) eV	0.0024
U-O ₂	2.47 (1) Å	3.9	0.008 (1)		
U-Si ₁	3.19 (1) Å	1	0.009 (2)		
U-Si ₂	3.76 (3) Å	1	0.013 (2)		
U-U	3.85 (1) Å	2.5	0.013 (4)		
2 mM _{Si} pH = 10.5					
U-O ₁	2.28 (1) Å	4.4	0.007 (1)	4.5 (8) eV	0.0124
U-O ₂	2.45 (1) Å	3.5	0.007 (1)		
U-Si ₁	3.17 (2) Å	0.9	0.007 (3)		
U-Si ₂	3.74 (4) Å	1.5	0.011 (5)		
U-U	3.80 (3) Å	2.6	0.013 (3)		
2 mM _{Si} pH = 12					
U-O ₁	2.30 (1) Å	4.7	0.005 (1)	6.2 (8) eV	0.0121
U-O ₂	2.46 (1) Å	3.3	0.005 (1)		
U-Si ₁	3.18 (3) Å	1	0.009 (5)		
U-Si ₂	3.75 (5) Å	1.8	0.014 (7)		
U-U	3.86 (2) Å	5	0.015 (2)		
Neptunium (IV)-silicate colloids ⁹					
	R (Å)	N	σ^2 (Å ²)	$\Delta E_{k=0}$	F
Np-O	2.28(1) Å	7.1(2)	0.017(4)	- 9.3 eV	0.07
Np-Si	3.11(1) Å	1.3(1)	0.0091(2)		
Np-Np	3.75(2) Å	1.1(1)	0.0098(1)		

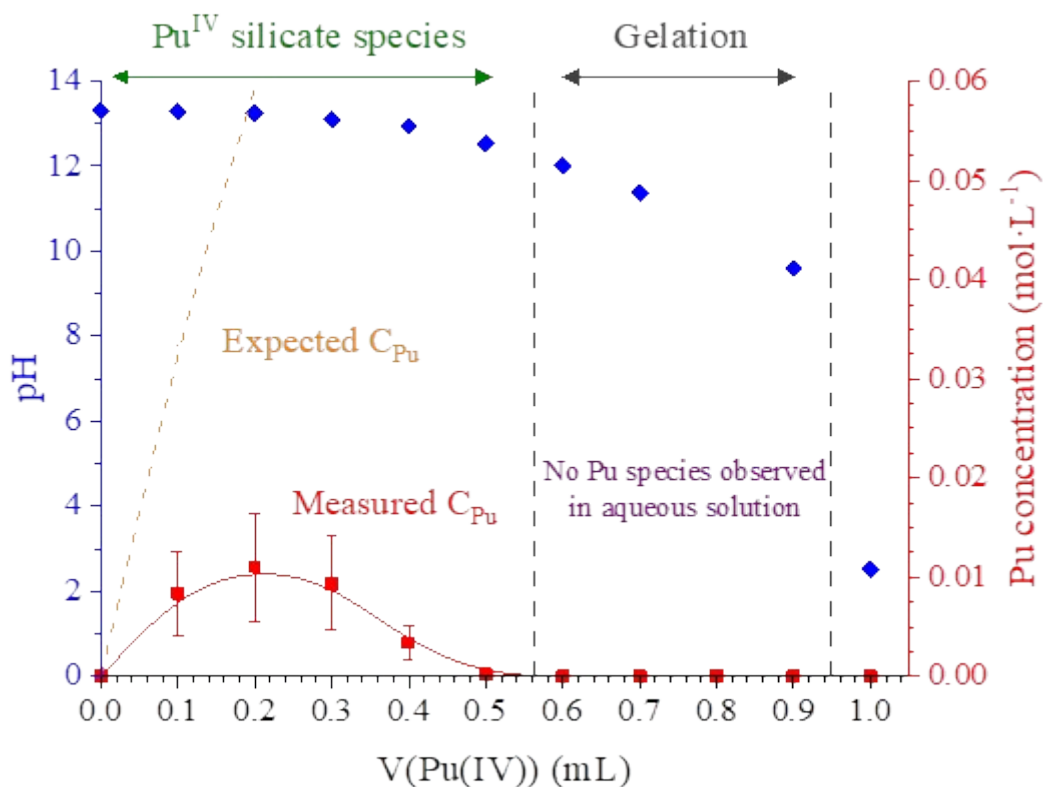


Figure S1 pH monitoring of a 2 mol·L⁻¹ aqueous Na₂SiO₃ solution depending on the addition of Pu(IV) mother solution in nitric acid media ($C_{\text{HNO}_3} = 1.5 \text{ mol}\cdot\text{L}^{-1}$; $C_{\text{Pu}} = 0.3 \text{ mol}\cdot\text{L}^{-1}$), according to [Table S1](#). The measured plutonium concentration was determined from the UV-visible spectra by Beer-Lambert law and the expected concentration is corresponding to the plutonium amount added to the system. The expected plutonium concentration is corresponding to the concentration expected by dilution of the mother solution (without precipitation).

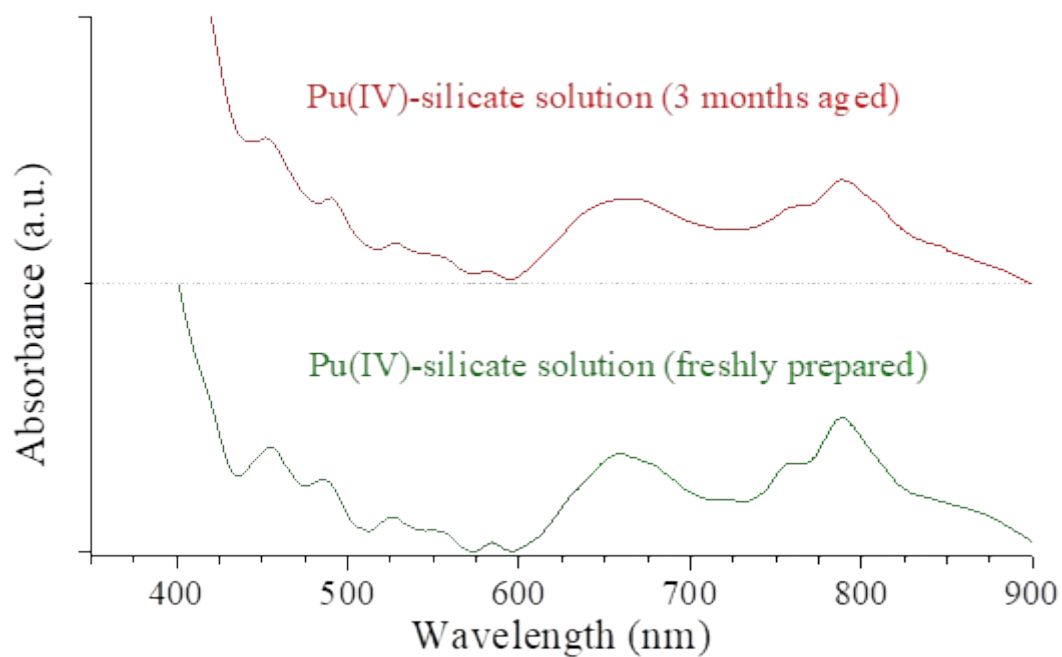


Figure S2 UV-visible spectra of a Pu(IV)-silicate solution ($\text{pH} = 13.2$, $C_{\text{Na}_2\text{SiO}_3} \approx 2 \text{ mol}\cdot\text{L}^{-1}$, $C_{\text{Pu}} = 3 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$) freshly prepared and after a 3 months ageing.

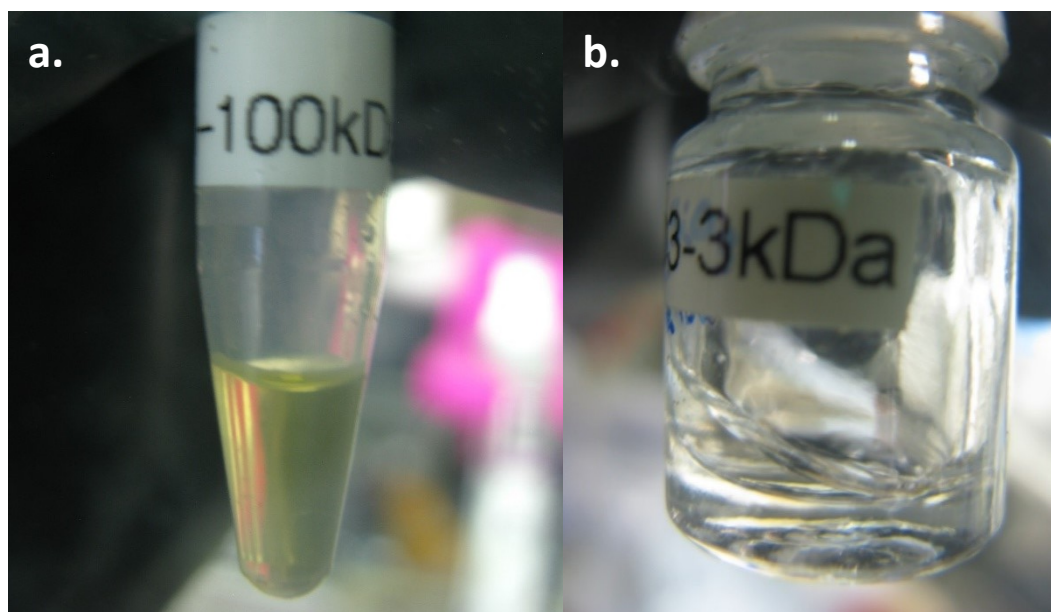


Figure S3 Pu(IV)-silicate solution ($\text{pH} = 13.2$, $C_{\text{Na}_2\text{SiO}_3} \approx 2 \text{ mol}\cdot\text{L}^{-1}$) filtrated at $0.1 \mu\text{m}$ (a.) and 3 kDa (b.).

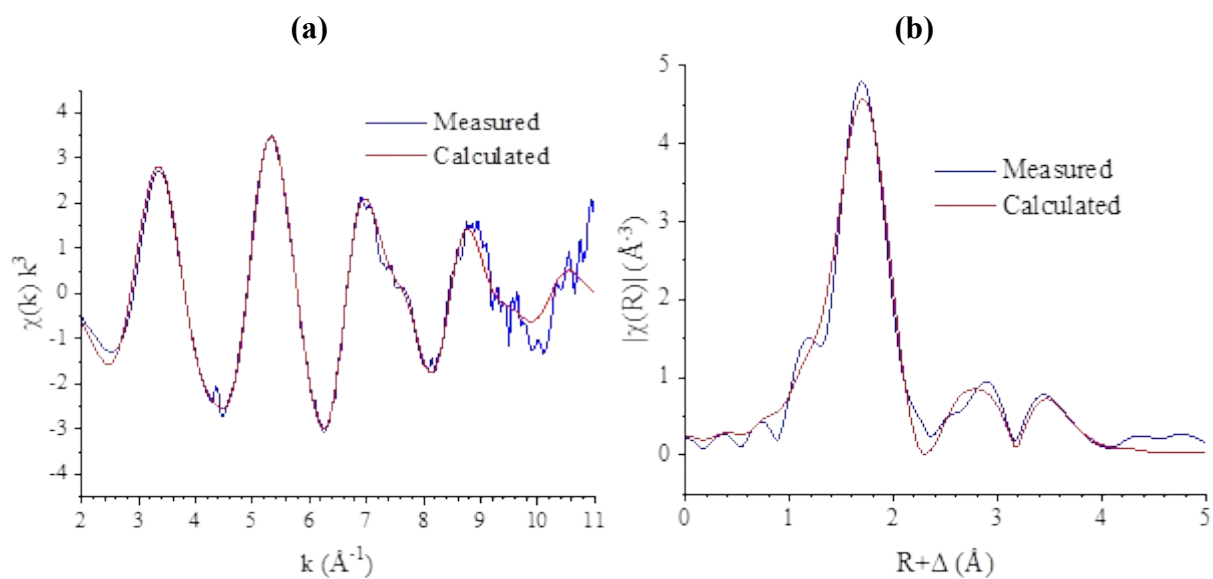


Figure S4 EXAFS spectra $2 \text{ \AA} < k < 11 \text{ \AA}$ (a) and respective Fourier Transform (b) at plutonium L_{III} edge for a Pu(IV)-silicate solution filtered at 0.45 \mu m .

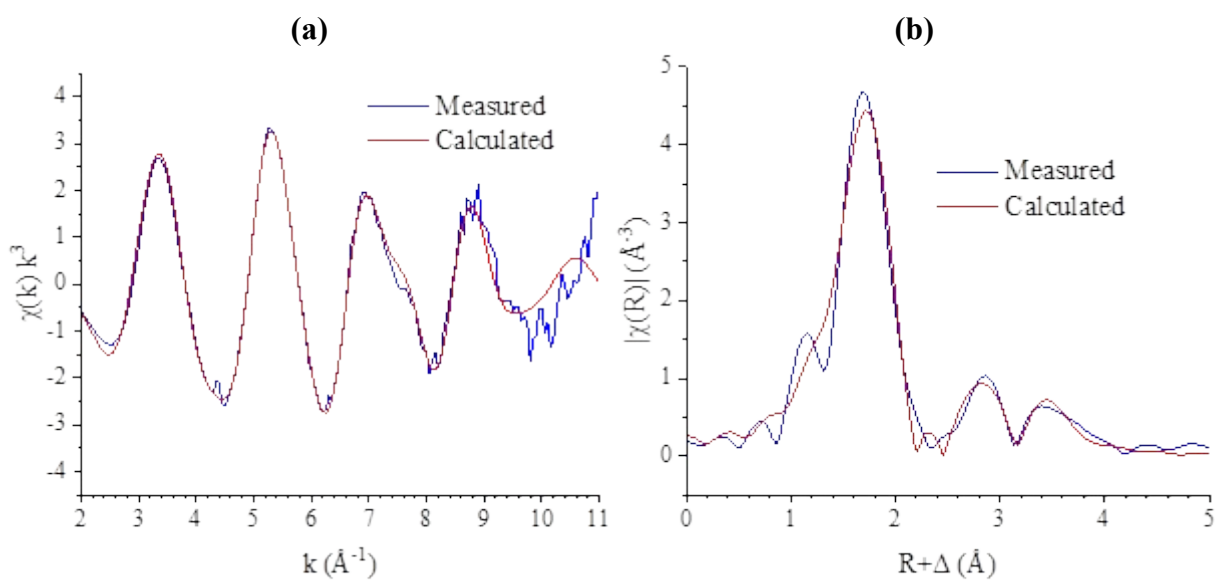


Figure S5 EXAFS spectra $2 \text{ \AA} < k < 11 \text{ \AA}$ (a) and respective Fourier Transform (b) at plutonium L_{III} edge for a Pu(IV)-silicate solution filtered at 100 kDa .

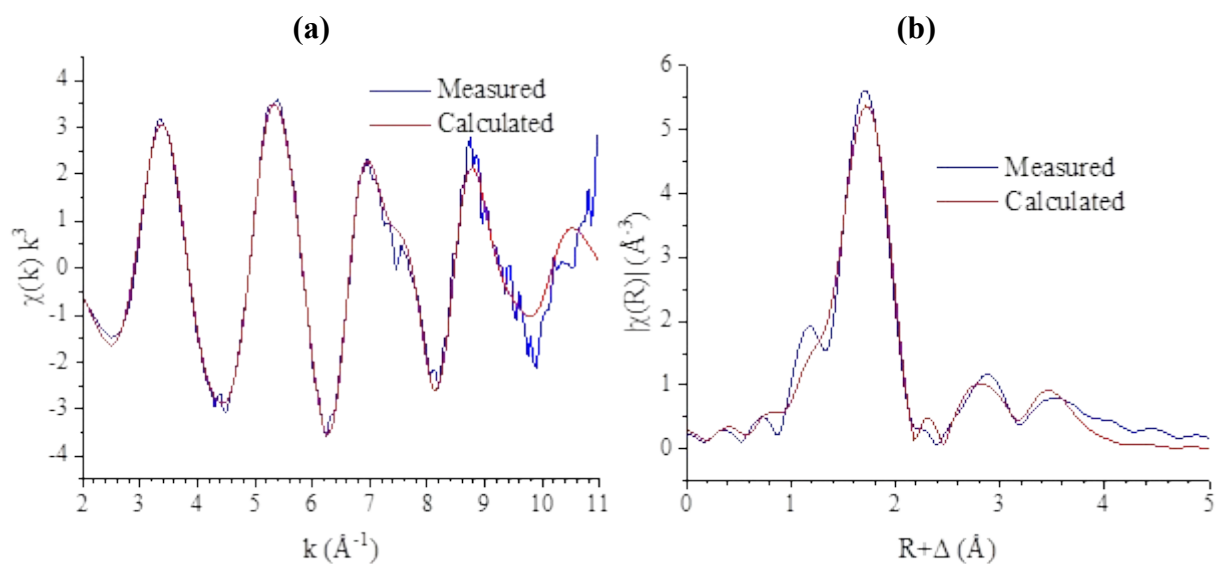


Figure S6 EXAFS spectra $2 \text{ \AA} < k < 11 \text{ \AA}$ (a) and respective Fourier Transform (b) at plutonium L_{III} edge for a Pu(IV)-silicate solution filtered at 100 kDa and 1 year old aged.

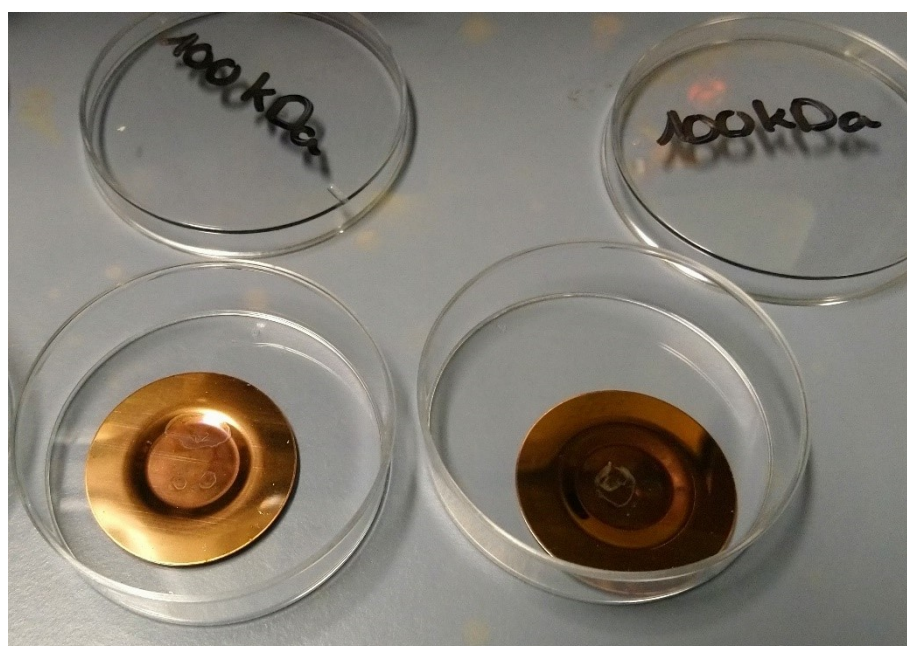
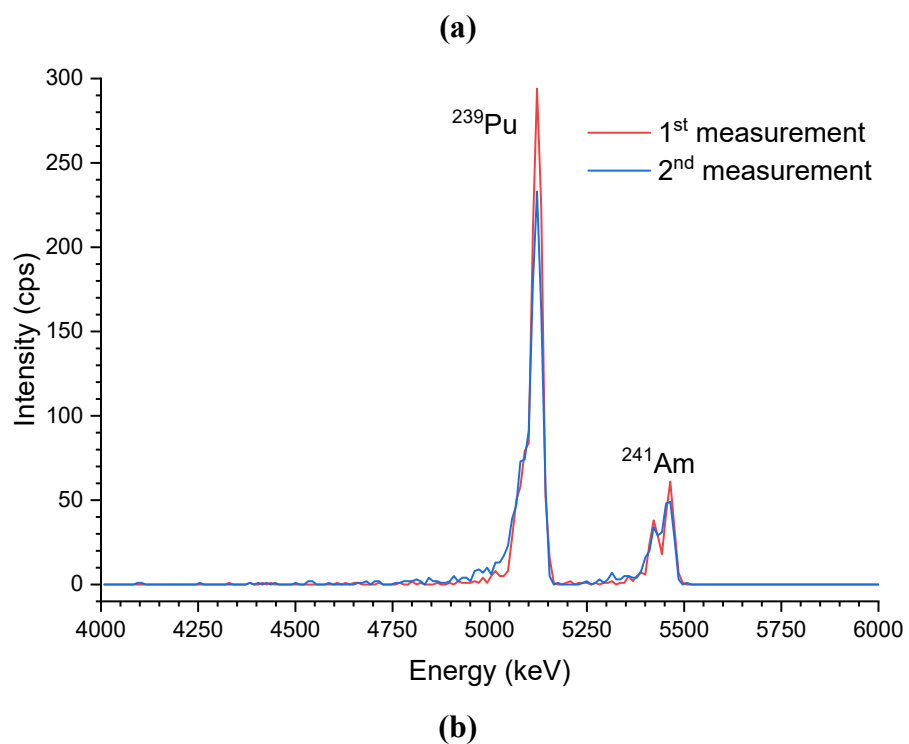


Figure S7 Alpha spectrometer measurements for the 100 kDa filtered Pu-silicate colloids samples (10 μL of sample after its dilution by a factor of 3200) (a) and corresponding platelets with the deposited sample (b).

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