

1 **Supplementary Information for the Manuscript:**

2  
3 **Time-resolved laser-induced fluorescence spectroscopy and chemometrics for**  
4 **fast identification of U(VI)-bearing minerals in a mining context**

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18  
19 This Supplementary Information describes the preparation and characterization of the  
20 synthetic samples, and gives the prediction results of models 1 and 2 for the training set.

21 Please note that the TRLF spectra of all samples are available upon request.

22 **Content**

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## 34 **S.1. Preparation of synthetic uranyl phases**

35 The uranyl nitrate hexahydrate salt used in these syntheses was purchased from Sigma-Aldrich, and  
36 the uranyl acetate dehydrate and uranyl sulfate from Prolabo. The solutions were prepared with  
37 deionised water (18.2 MΩ cm, MilliQ gradient system, Millipore) and analytical grade reagents were  
38 purchased from Sigma Aldrich, Fisher Scientific, Fluka and VWR.

### 39 **S.1.1. Uranium oxides and oxide-hydroxy-hydrates**

40 The  $\text{UO}_3$  powder (sample ICSM21-04) was obtained by the thermal conversion of a sample of studtite,  
41  $\text{UO}_2(\text{O}_2)\cdot 4\text{H}_2\text{O}$  at  $450^\circ\text{C}$  in air [S1]. Synthetic metaschoepite,  $\text{UO}_3\cdot 2\text{H}_2\text{O}$  (sample EA21-008) was obtained  
42 by the hydration of amorphous  $\text{UO}_3$  powder in steam for 1 h. 0.5 g of  $\text{UO}_3$  powder was spread in an  
43 alumina crucible above a vessel containing 1 L of boiling deionised water. The complete apparatus was  
44 covered with aluminium foil and the sample was exposed to steam for 1 hour. The colour of the sample  
45 turned progressively to yellow. The same protocol was used to prepare the  $\text{UO}_3\cdot 0.8\text{H}_2\text{O}$  (sample EA21-  
46 016) except that the steam exposure lasted 3 h. Then the samples were stored at room temperature  
47 in air. The hydration rate of the samples was determined by thermogravimetric analysis (TGA, Setaram  
48 Setsys Evolution). About 30 mg of powder was heated in air at a rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  from room  
49 temperature to  $800^\circ\text{C}$ , in order to follow the dehydration step and then the transition from  $\text{UO}_3$  to  
50  $\text{U}_3\text{O}_8$ .

51 Synthetic billetite,  $\text{Ba}(\text{UO}_2)_6\text{O}_4(\text{OH})_6\cdot n\text{H}_2\text{O}$  (sample EA21-049); becquerelite,  $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6\cdot n\text{H}_2\text{O}$   
52 (samples EA21-048 and EA21-055) and compreignacite,  $\text{K}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6\cdot n\text{H}_2\text{O}$  (sample EA21-050)  
53 were prepared following the protocol proposed by Vochten and Van Haverbeke [S2]. 0.1 g of  
54 metaschoepite was placed in a PFA reactor (Saville<sup>®</sup>) with respectively 200 mL of  $5\cdot 10^{-3}$  mol/L  $\text{BaCl}_2$ ,  
55  $5\cdot 10^{-3}$  mol/L  $\text{CaCl}_2$  or  $10^{-2}$  mol/L  $\text{KCl}$  aqueous solution. The reactors were closed and placed in an oven  
56 at  $60^\circ\text{C}$  for 7 days. Then, the remaining solid was filtered, and washed three times with deionised water  
57 and once with ethanol by centrifugation in 40 mL of solvent. The samples were then dried for 24 h at  
58  $60^\circ\text{C}$ .

### 59 **S.1.2. Uranium vanadate**

60 Carnotite,  $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2\cdot 3\text{H}_2\text{O}$  (sample ICSM15-03) was prepared using a dry chemistry process  
61 [S3][S4].  $\text{K}_2\text{CO}_3$ ,  $\text{UO}_3$  and  $\text{V}_2\text{O}_5$  precursors were first dried for 24 h at  $90^\circ\text{C}$ . Then, the reactants were  
62 mixed in stoichiometric proportion and three successive cycles of ball milling (30 min at 30 Hz) and  
63 calcination at  $600^\circ\text{C}$  for 24 h in air of the mixture were made to obtain the final sample.

### 64 **S.1.3. Uranium phosphates**

65 Synthetic chernikovite,  $(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2\cdot 6\text{H}_2\text{O}$  (sample ICSM15-04) was prepared by direct  
66 precipitation following the protocol initially proposed by Vochten and Deliens [S4][S5][S6]. For the  
67 synthesis of about 1 g of chernikovite, a 2 mol/L phosphoric acid solution was added to a 1.46 mol/L  
68 uranyl nitrate solution (in  $5\cdot 10^{-3}$   $\text{HNO}_3$ ) in order to obtain an excess of 10 mol. % of phosphates in the  
69 mixture. The resulting solution was stirred at room temperature for 1 h then aged for 3 days, following  
70 which the precipitate was recovered by filtration, washed three times with deionised water and once  
71 with ethanol by centrifugation in 40 mL of solvent. The samples were then dried for 24 h at  $40^\circ\text{C}$ .

72 Synthetic autunite,  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 10\text{-}12\text{H}_2\text{O}$  (sample ICSM15-02) was obtained from the chernikovite  
73 sample by cationic exchange, whereby 0.5 g of chernikovite was treated at  $40^\circ\text{C}$  with a 2 mol/L  $\text{CaCl}_2$   
74 solution for 30 days at a stoichiometric ratio  $\text{Ca}/\text{U} = 80$ . The complete exchange of the protons for  $\text{Ca}^{2+}$   
75 ions was controlled by X-ray diffraction. Similarly, ankoleite,  $\text{K}(\text{UO}_2)\text{PO}_4\cdot 6\text{H}_2\text{O}$  (sample ICSM15-01) was

76 obtained by immersing the chernikovite precursor in 1 mol/L KNO<sub>3</sub> solution for 7 days at a  
77 stoichiometric ratio K/U = 2 [S6].

78 Synthetic (meta-)torbernite, (H<sub>3</sub>O)<sub>0.4</sub>Cu<sub>0.8</sub>(UO<sub>2</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>·7.6H<sub>2</sub>O (sample ICSM15-05) was obtained by  
79 direct precipitation in one step. 85 mL of 0.2 mol/L uranyl nitrate solution (pH = 1.1) containing 1.46 g  
80 of CuCl<sub>2</sub>·2H<sub>2</sub>O was mixed with 8.5 mL of 2 mol/L H<sub>3</sub>PO<sub>4</sub> solution [S7]. After 3 days of maturation at  
81 60°C, the precipitate was recovered by centrifugation, then washed three times with deionised water  
82 and once with ethanol. The samples were then dried for 24 h at 40°C.

#### 83 **S.1.4. Uranium sulfates**

84 Synthetic zippeite, K<sub>3</sub>(UO<sub>2</sub>)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>O<sub>3</sub>(OH)·3H<sub>2</sub>O (sample SBb-005) and synthetic Na-zippeite  
85 Na<sub>5</sub>(UO<sub>2</sub>)<sub>8</sub>(SO<sub>4</sub>)<sub>4</sub>O<sub>5</sub>(OH)<sub>3</sub>·12H<sub>2</sub>O (sample SBb-015) were obtained using hydrothermal conditions  
86 following a protocol inspired from Sharifironizi et al. [S8], whereby 0.248 g of uranyl acetate and 0.056  
87 g of potassium sulfate or sodium sulfate were dissolved in 4 mL of deionised water. The resulting  
88 solution was placed in a 23 mL Teflon-lined Parr reaction vessel. The pH of the solution was adjusted  
89 to 4.35 using 1 mol/L KOH or NaOH solution. Then, the reaction vessels were closed and heated at  
90 150°C for 3 days in an oven. After cooling, the solid was washed three times with deionised water and  
91 once with ethanol by centrifugation in 40 mL of solvent. The samples were then dried for 24 h at 60°C.

#### 92 **S.1.5. Uranium silicates**

93 Synthetic soddyite, (UO<sub>2</sub>)<sub>2</sub>(SiO<sub>4</sub>)·2H<sub>2</sub>O (sample SBb-004) was prepared following the protocol described  
94 by Casas et al. [S9]. 20 mL of a solution of uranyl nitrate at 0.148 mol/L was added to 5 mL of sodium  
95 metasilicate solution at 0.074 mol/L. The pH of the resulting solution was adjusted to 4.4 by addition  
96 of a 4 mol/L HCl solution. The mixture was stirred at room temperature for 100 hours, then was heated  
97 under reflux at 80°C for 6 h. The precipitate was separated from the solution by filtration and washed  
98 with a large quantity of boiling deionised water. The precipitate was dried in an oven at 90°C for 24 h,  
99 then placed in a 23 mL Teflon-lined Parr reaction vessel with 15 mL of deionised water. The reaction  
100 vessel was closed and placed in an oven at 130°C for 2 weeks. After cooling, the solid phase was washed  
101 three times with deionised water and once with ethanol by centrifugation in 40 mL of solvent. The  
102 sample was then dried for 24 h at 60°C.

103 Synthetic weeksite, K<sub>2</sub>(UO<sub>2</sub>)<sub>2</sub>(Si<sub>5</sub>O<sub>13</sub>)·4H<sub>2</sub>O (sample SBb-019) was obtained using a protocol adapted  
104 from Vochten et al. [S10], initially designed for the synthesis of boltwoodite. Thus, 25 mL of a solution  
105 containing 0.133 mol/L uranyl nitrate, 0.269 mol/L of KCl and 0.287 mol/L of silica (Ludox AM silica  
106 colloidal, 30 wt.%, Sigma Aldrich) was prepared. The pH of the reactive medium was 11.4. This solution  
107 was then placed in a 45 mL Teflon-lined Parr autoclave and heated at 185°C for 21 days. After cooling,  
108 the precipitate was washed three times with deionised water and once with ethanol by centrifugation  
109 in 40 mL of solvent. The sample was then dried for 24 h at 60°C.

110 Synthetic boltwoodite, K(UO<sub>2</sub>)(SiO<sub>3</sub>OH)·1.5H<sub>2</sub>O (sample SBb-006) was prepared following a protocol  
111 adapted from Vochten et al. [S10]. 25 mL of a solution containing 0.136 mol/L of uranyl nitrate, 0.275  
112 mol/L of KCl and 2 mol/L of silica (quartz fine granular, Supelco) was prepared. The pH of the reactive  
113 medium was 12. This solution was then placed in a 45 mL Teflon-lined Parr autoclave and heated at  
114 185°C for 21 days. After cooling, the precipitate was washed three times with deionised water and  
115 once with ethanol by centrifugation in 40 mL of solvent. The sample was then dried for 24 h at 60°C.

116 Synthetic calcium uranyl silicate hydrate, Ca<sub>2</sub>(UO<sub>2</sub>)<sub>2</sub>(Si<sub>2</sub>O<sub>5</sub>)<sub>3</sub>·10 H<sub>2</sub>O (sample SBb-020) was obtained by  
117 mixing 25 mL of a solution of a 0.188 mol/L uranyl nitrate with 5 mL of 0.456 mol/L calcium nitrate  
118 solution and 15 mL of 0.3 mol/L sodium metasilicate solution. The pH of the resulting mixture was 10.4.  
119 The mixture was stirred at room temperature for 30 days. Then, it was heated under reflux at 90°C for

120 24 h. The precipitate was separated from the solution by filtration and washed with a large quantity of  
121 boiling deionised water. The precipitate was dried in a vacuum at room temperature, then placed in a  
122 45 mL Teflon-lined Parr reaction vessel with 30 mL of deionised water. The reaction vessel was closed  
123 and placed in an oven at 120°C for 2 weeks. After cooling, the solid phase was washed three times with  
124 deionised water and once with ethanol by centrifugation in 40 mL of solvent. The sample was then  
125 dried for 24 h at 60°C.

126 Synthetic sodium uranyl silicate hydrate,  $\text{Na}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 10\text{H}_2\text{O}$  (sample SBb-014) was obtained  
127 following a protocol initially proposed by Wall et al. [S11] for synthesizing Na-boltwoodite. 3 mL of a  
128 0.1 mol/L sodium acetate solution was mixed with 30 mL of a 0.01 mol/L uranyl acetate solution. 3 mL  
129 of a 0.1 mol/L solution of sodium metasilicate at pH 10 was added to this mixture. The pH of the  
130 reacting medium was adjusted to 10 by adding 1 mol/L NaOH solution. The reacting medium was  
131 placed in a PFA reactor (Savillex®), hermetically sealed and then heated at 90°C in an oven for 2 days.  
132 The precipitate formed was separated from the supernatant by centrifugation, then immersed in 30  
133 mL of deionised water in a 45 mL Teflon-lined reaction vessel. The autoclave was closed and heated at  
134 135°C during 7 days in an oven. After cooling, the solid phase was washed three times with deionised  
135 water and once with ethanol by centrifugation in 40 mL of solvent. The sample was then dried for 24  
136 h at 60°C.

137 Synthetic Uranophane- $\alpha$ ,  $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$  (sample EA21-064) was obtained by mixing 15 mL  
138 of 0.307 mol/L sodium metasilicate solution with 5 mL of 0.461 mol/L calcium chloride solution. Then,  
139 this mixture was added to 20 mL of 0.228 mol/L uranyl nitrate solution. The pH of the reacting mixture  
140 was adjusted to 8.5 by adding ammonia. The reacting mixture was stirred for 4 hours at room  
141 temperature. These steps were made in an inert-gas (Ar) glove box. Then, the reacting mixture was  
142 transferred from the glove box into a sealed flask and refluxed in an Ar atmosphere at 80°C for 24 h.  
143 The precipitate was separated from the supernatant and washed with deionised water by  
144 centrifugation before being placed in a 23 mL Teflon-lined Parr vessel with 11 mL of deionised and  
145 decarbonated water. The autoclave was also closed in the Ar glove box. The autoclave was then heated  
146 at 120°C for 21 days in an oven. After cooling, the solid phase was washed three times with deionised  
147 water and once with ethanol by centrifugation in 40 mL of solvent. The sample was then dried for 24  
148 h at 60°C.

### 149 **S.1.6. Uranium carbonates**

150 The synthesis of carbonate phases was done following the synthesis of liebigite ( $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}$ )  
151 described by Meyrowitz [S12]. A solution of 5.02 g of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 10 mL water was slowly added  
152 to a solution of 3.18 g of anhydrous  $\text{Na}_2\text{CO}_3$  in 100 mL water under constant agitation. A solution of  
153 4.72 g of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in 10 mL water was then slowly added to the uranyl carbonate solution under  
154 agitation. After pH adjustment to 8-8.2 with an  $\text{Na}_2\text{CO}_3$  solution, a solid was precipitated (fine powder)  
155 after 24 hours. The solid was separated from solution using a Buchner filter. The equilibrium solution  
156 was left to rest in a closed vessel. After two weeks a second solid (well-formed crystals) was  
157 precipitated. The XRD analyses showed mainly liebigite with andersonite ( $\text{Na}_2\text{CaUO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) in the  
158 first solid with remaining  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and calcite ( $\text{CaCO}_3$ ); the second solid was mainly composed of  
159 andersonite with liebigite.

160 This was supported by SEM analyses (see ) that showed crystals of liebigite and andersonite similar to  
161 Vochten et al. [S13], but also of a third phase recalling the identification of a  
162  $\text{Ca}_{1.54}\text{Na}_{0.63}[\text{UO}_2(\text{CO}_3)_3] \cdot x\text{H}_2\text{O}$  lath phase by Vochten et al. [S14].

163

### 164 **S.1.7. Adsorption of uranyl on clays**

165 Raw bentonite MX80 and purified clay materials used in previous works were conditioned following a  
166 protocol already described for bentonite MX80 [S15], Na-kaolinite [S16], Na-smectite [S17] and Na-  
167 illite du Puy [S18]. For sorption experiments, about 100 mg of clay material was first dispersed in 20  
168 mL of  $5 \cdot 10^{-2}$  mol/L  $\text{NaClO}_4$  solution in a 50 mL centrifuge tube (Corning®, polypropylene). The tubes  
169 were placed at room temperature on a roller shaker for 16 h to equilibrate the clay with the solution.  
170 After phase separation by centrifugation at 20 000 rpm for 20 min, the pH of the solution was  
171 measured. The pH at equilibrium was found to vary between 7.15 and 7.91 for Na-kaolinite and Na-  
172 illite, between 7.95 and 9.1 for Na-smectite and between 8.83 and 9.37 for MX80. Then, the solid phase  
173 was dispersed and the solutions were spiked with various amounts of a certified uranium standard  
174 solution in 1 %  $\text{HNO}_3$  (1 g/L or 10 g/L PlasmaCAL single element calibration standard, SCP Science) to  
175 reach initial uranium concentrations in the range between  $10^{-4}$  and  $2 \times 10^{-7}$  mol/L. The pH of the  
176 suspensions was measured after addition of the uranium solutions and adjusted if necessary to the  
177 previous equilibrium value with 1 mol/L NaOH. Then, the suspensions were equilibrated for 24 h on a  
178 roller shaker. After separation of the solid and liquid phases by centrifugation at 20000 rpm for 20 min,  
179 10 mL of solution was sampled to measure the remaining U elemental concentration. After  
180 acidification with concentrated  $\text{HNO}_3$  solution (65 %  $\text{HNO}_3$  Suprapur, for trace analysis, Merck), the U  
181 elemental concentration was analysed in the collected samples by an inductively coupled plasma mass  
182 spectrometry (ICP-MS) (iCAP RQ, Thermo Fisher). The ICP-MS was calibrated for U using several  
183 standard solutions prepared by dilution of a single element standard solution at 1 g/L (PlasmaCAL, SCP  
184 Science) in 1 %  $\text{HNO}_3$  solution (Suprapur, for trace analysis, Merck). The elemental concentration of  
185 uranium was calculated as the average of three replicates at mass 238. Under these analytical  
186 conditions, the detection limit for uranium reached  $1 \times 10^{-10}$  mol/L. The relative experimental error was  
187 calculated as twice the relative standard deviation of the three replicates and was less than 3 %.

188 The concentration of U adsorbed on the clay material surface,  $C_s^U$  in ppm was then calculated as  
189 follows:

$$190 \quad C_s^U = \frac{(C_0^U - C_{eq}^U)}{m_{\text{clay}}} \times V \quad (1)$$

191 With  $C_0^U$ , U initial concentration in mg/L,  $C_{eq}^U$ , U concentration at equilibrium in mg/L, V, volume of  
192 solution in L,  $m_{\text{clay}}$  mass of the sample in kg.

193 Table S.1 gives the calculated adsorbed U concentration of the clay samples used in the training,  
194 validation and test sets.

195

196 *Table S.1 List of clay samples used in this study, concentration of the uranium contact solution  $C_0^U$ , mass of clay*  
 197 *material ( $\pm 0.1$  mg), pH after addition of U solution ( $\pm 0.1$ ), U elemental concentration in solution after 24 h of*  
 198 *contact with clay material  $C_{eq}^U$  ( $\pm 5$  %), and calculated U concentration sorbed on the clay surface  $C_s^U$  ( $\pm 10$  %).*  
 199 *The sample set in which each sample is used for chemometric treatment is indicated in the last column.*

Clay material	Reference	$C_0^U$ (mol/L)	pH	$m_{clay}$ (mg)	V (mL)	$C_{eq}^U$ (mol/L)	$C_s^U$ (ppm)	Sample set
MX80	EA21-01	$1.12 \times 10^{-6}$	9.6	101.9	20	$2.14 \times 10^{-7}$	42	Validation set
	EA21-02	$7.32 \times 10^{-6}$	9.8	97.8	20	$1.41 \times 10^{-6}$	288	Validation set
	EA21-03	$9.89 \times 10^{-5}$	9.2	99.2	20	$1.90 \times 10^{-5}$	3834	Test set
	EA-21-018	$9.17 \times 10^{-6}$	8.9	100.7	20	$6.84 \times 10^{-6}$	110	Validation set
Na-illite	EA21-04	$1.72 \times 10^{-6}$	7.1	102.3	20	$3.31 \times 10^{-7}$	65	Validation set
	EA21-05	$1.23 \times 10^{-5}$	7.6	101.8	20	$2.36 \times 10^{-6}$	463	Training set
	EA-21-021	$3.1 \times 10^{-7}$	7.2	101.7	20	$7 \times 10^{-10}$	15	Validation set
	EA-21-025	$1.25 \times 10^{-6}$	7.5	101.4	20	$5.62 \times 10^{-8}$	56	Validation set
Na-kaolinite	EA21-07	$1.57 \times 10^{-6}$	8.7	99.5	20	$3.01 \times 10^{-7}$	61	Validation set
	EA21-08	$8.99 \times 10^{-6}$	8.7	102.7	20	$1.73 \times 10^{-6}$	336	Training set
	EA-21-027	$3.1 \times 10^{-7}$	7.1	101.7	20	$2.8 \times 10^{-9}$	15	Validation set
	EA-21-029	$1.94 \times 10^{-5}$	7.8	100.6	20	$9.44 \times 10^{-6}$	471	Training set
	EA-21-030	$9.17 \times 10^{-6}$	7.7	101.4	20	$1.27 \times 10^{-6}$	371	Validation set
	EA-21-032	$2.5 \times 10^{-7}$	7.1	102.1	20	$4.2 \times 10^{-9}$	11	Validation set
Na-smectite	EA21-10	$1.80 \times 10^{-6}$	9.4	98.8	20	$3.46 \times 10^{-7}$	70	Validation set
	EA21-11	$1.21 \times 10^{-5}$	9.4	99.5	20	$2.32 \times 10^{-6}$	466	Validation set
	EA-21-035	$1.94 \times 10^{-5}$	8.6	99.7	20	$6.17 \times 10^{-7}$	897	Training set
	EA-21-036	$9.17 \times 10^{-6}$	8.9	98	20	$2.42 \times 10^{-8}$	444	Training set
	EA-21-038	$2.5 \times 10^{-7}$	9.1	98.2	20	$7.7 \times 10^{-9}$	12	Validation set

200

## 201 **S.2. Characterisations of the synthetic samples**

202 The synthetic samples were systematically characterised by Powder X-ray diffraction (PXRD) and  
 203 Scanning Electron Microscopy (SEM). PXRD patterns were recorded using a Bruker D8 Advance  
 204 diffractometer with copper radiation ( $\lambda_{Cu} K\alpha_{1,2} = 1.54184 \text{ \AA}$ ) in a parallel mode and using the reflection  
 205 geometry. The patterns were recorded between  $5^\circ$  and  $100^\circ$  ( $2\theta$ ) with a step of  $0.02^\circ$  and a counting  
 206 time of 3 h. The PDF-2 release 2015 database (ICDD) was used to identify the prepared phase. Figure  
 207 S.1 shows PXRD patterns of most synthetic samples used in the training dataset and of two samples of  
 208 the validation dataset.

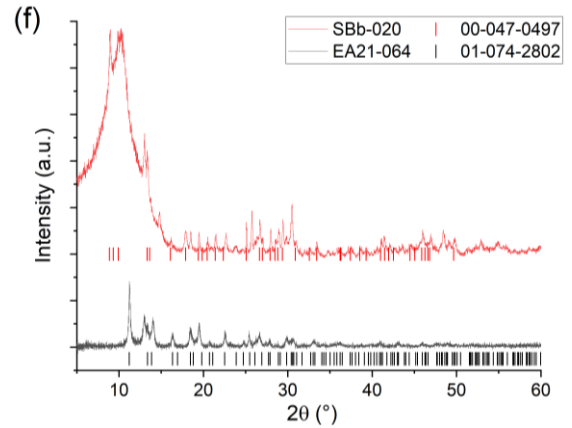
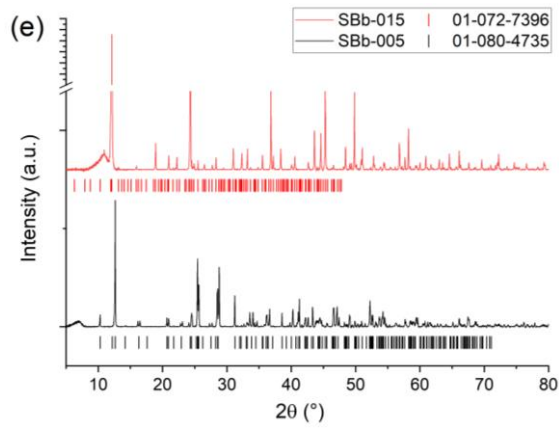
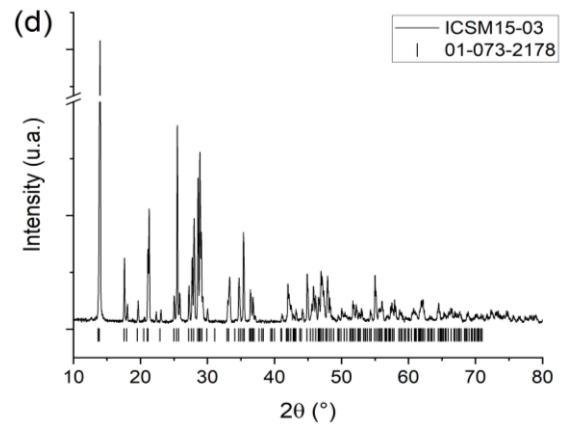
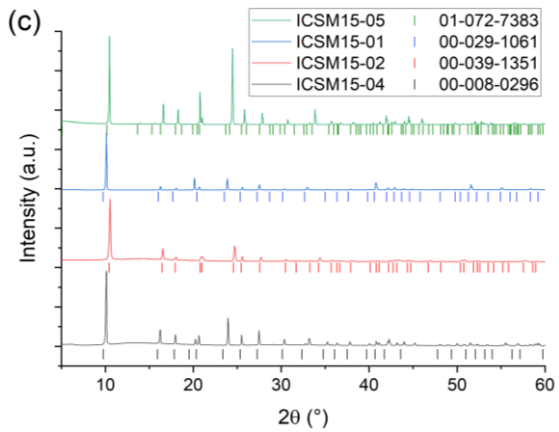
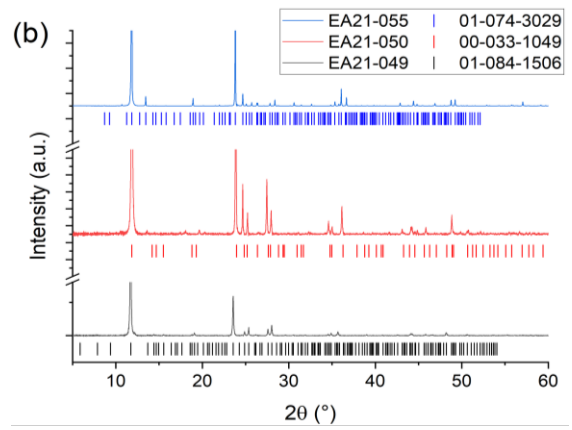
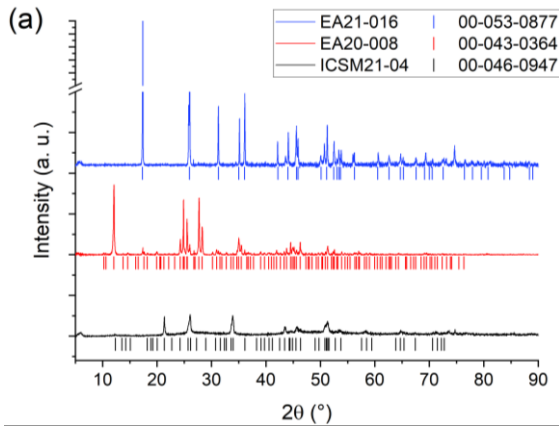
209 The Raman spectra were recorded with a Horiba-Jobin Yvon Aramis apparatus using a Nd:YAG laser  
 210 (532 nm) delivering 60 mW power at the sample surface and associated edge filter. The laser beam  
 211 was focused on the sample by an Olympus BX 41 microscope, with a spot size of about  $1 \mu\text{m}^2$ . For each  
 212 spectrum, a dwell time of 10 s and an average of four scans was used. FTIR spectra in the ATR mode  
 213 were recorded in the  $500\text{--}4000 \text{ cm}^{-1}$  range thanks to a Perkin-Elmer FTIR Spectrum 100 device.  
 214 Powdered samples were deposited on the surface of an ATR crystal without any prior preparation. The  
 215 spectra collected in such operating conditions exhibited a resolution lower than  $4 \text{ cm}^{-1}$ . The Raman  
 216 and IR spectra of the synthetic samples can be made available on request.

217 The scanning electron microscopy (SEM) analyses were conducted using a Quanta 200 ESEM FEG (FEI  
218 Company) electron microscope equipped either with a backscattered electron detector (BSED) in high  
219 vacuum conditions or with a secondary electron detector (SED) with a 25 kV accelerating voltage.

220 Figure S.2 shows one SEM/BSE micrograph for most synthetic samples used in the training and  
221 validation sets. The powders were directly analyzed without any preparation. X-ray energy dispersive  
222 spectroscopy (X-EDS) analyses were performed under the same conditions using the Bruker AXS X-  
223 Flash 5010 detector coupled to the SEM device. X-EDS spectra were obtained using the same detector  
224 and operating conditions. For that purpose, an aliquot of each sample was embedded in an epoxy  
225 resin, polished to optical grade and metalized by carbon deposition. 20 to 40 X-EDS measurements  
226 were performed for each sample. The average elemental concentration as well as twice the standard  
227 deviation are compiled in Table S.2 for most synthetic samples.

228 The composition of andersonite and liebigite (samples LANIE15-01 and LANIE 15-02) was determined  
229 by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses after complete  
230 dissolution of an aliquot of the sample in a 2 % HNO<sub>3</sub> solution. The ICP-AES device (Horiba Jobin Yvon)  
231 was calibrated for U, Ca and Na using several standard solutions prepared by dilution of single element  
232 standard solutions at 1 g/L in a 2 % HNO<sub>3</sub> solution. The recommended emission wavelengths of the  
233 elements were all considered in the analytical procedure. From the elemental concentrations in  
234 solution, the U, Ca and Na mass fractions of the samples were calculated. The obtained results as well  
235 as twice the standard deviation are given in Table S.3.

236





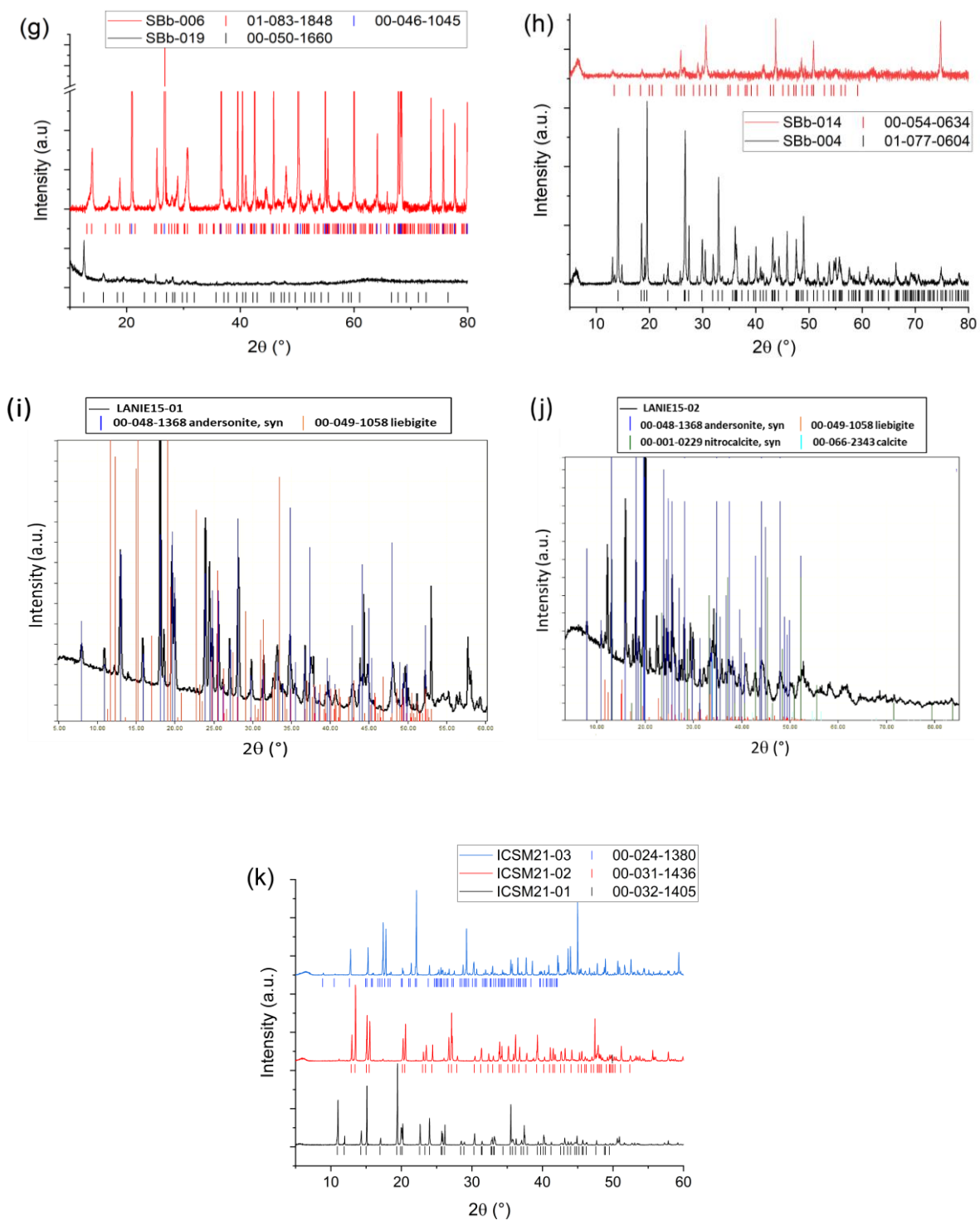
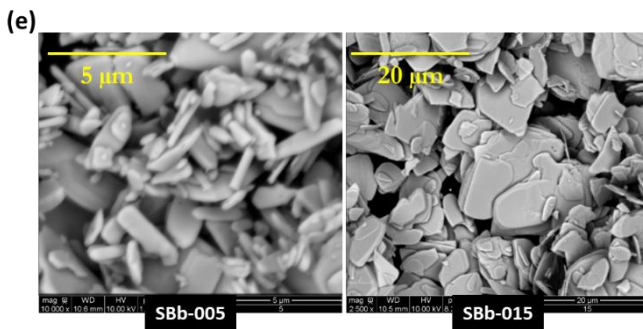
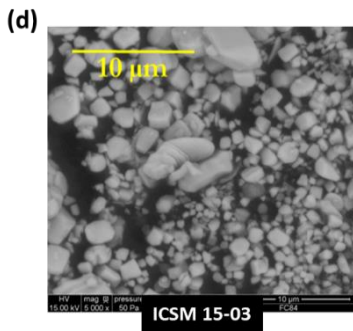
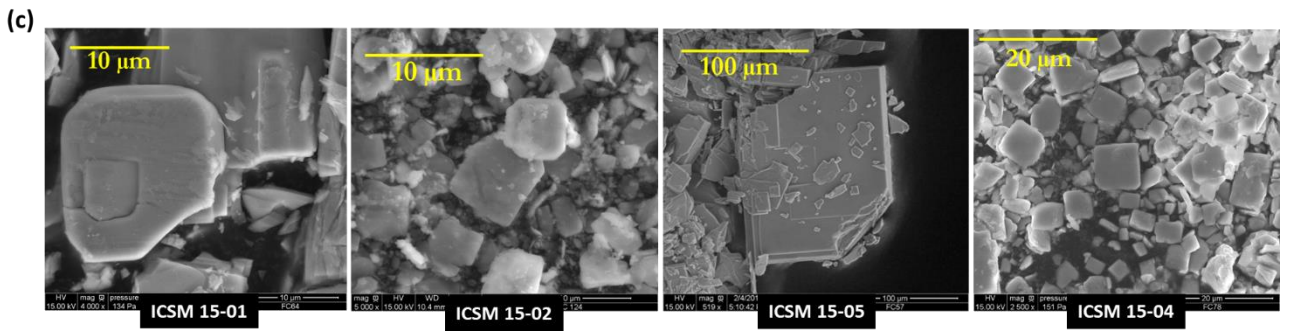
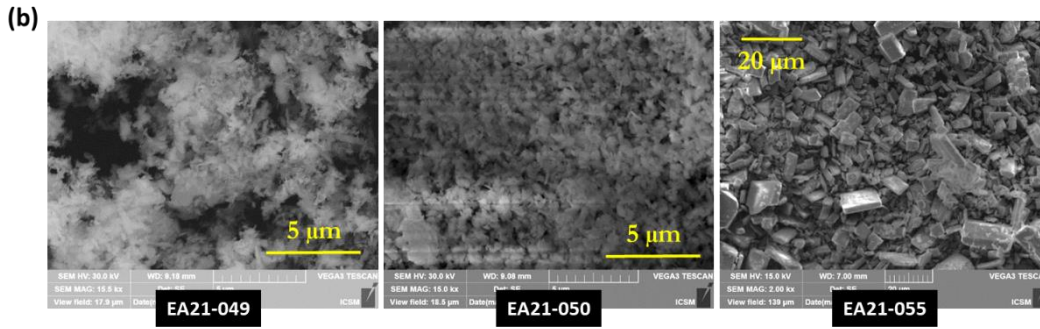
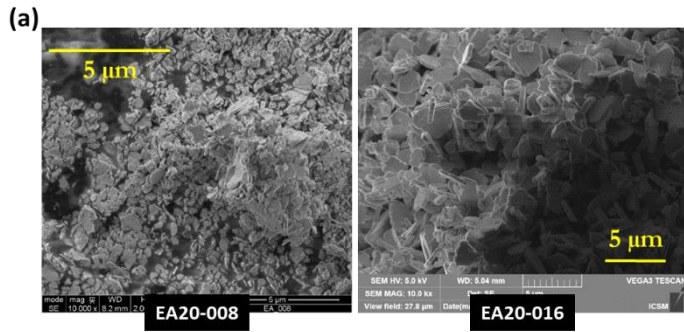
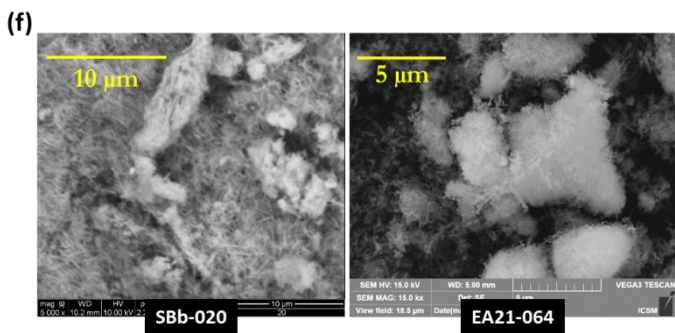


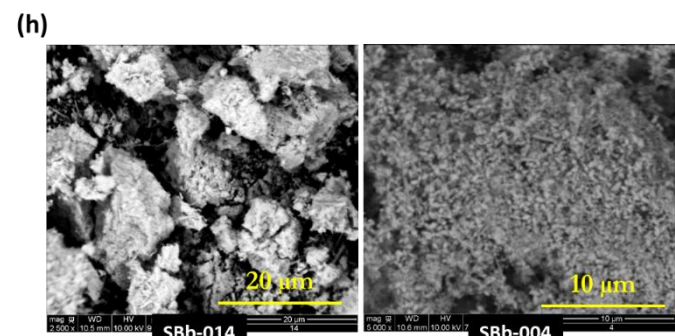
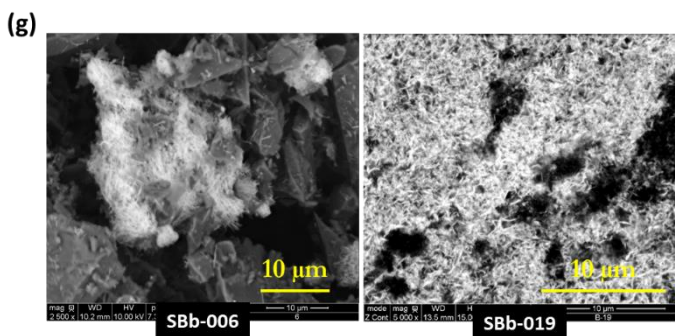
Figure S.1 Powder XRD patterns of some synthetic samples used in the training and validation sets compared to references from the PDF-2 release 2015 ICDD database. (a) Samples from the oxides and hydrated oxides family ( $\text{UO}_3 \cdot n\text{H}_2\text{O}$  with  $n = 0, 0.8, 2$ ); (b) samples from the oxide-hydroxy-hydrates family (billietite, compreignacite and becquerelite); (c) samples from the phosphates family (chernikovite, ankoleite, meta-autunite and meta-torbernite); (d) sample from the vanadates family (carnotite); (e) samples from the sulfates family (zippeite and Na-zippeite); (f) samples from the silicates family (uranophane- $\alpha$  and calcium uranyl silicate); (g) samples from the silicates family (boltwoodite and weeksite); (h) samples from the silicates family (soddyite and sodium uranyl silicate); (i, j) samples from the carbonates family (andersonite, liebigite); (k) commercial uranyl salts (acetate, nitrate and sulfate).



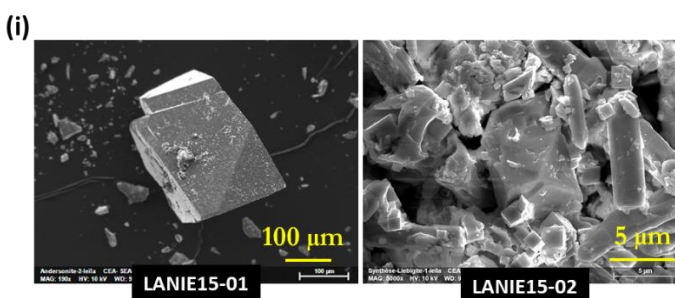
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254

246 *Figure S.2 SEM micrographs (BSE mode) of some synthetic samples used in the training and validation sets. (a)*  
 247 *Samples from the hydrated oxides family ( $UO_3 \cdot nH_2O$  with  $n = 0.8, 2$ ); (b) samples from the oxide-hydroxy-*  
 248 *hydrates family (billietite, compreignacite and becquerelite); (c) samples from the phosphates family*  
 249 *(chernikovite, ankoleite, meta-autunite and meta-torbernite); (d) sample from the vanadates family (carnotite);*  
 250 *samples from the sulfates family (zippeite and Na-zippeite); (f) samples from the silicates family*  
 251 *(uranophane- $\alpha$  and calcium uranyl silicate); (g) samples from the silicates family (boltwoodite and weeksite); (h)*  
 252 *samples from the silicates family (soddyite and sodium uranyl silicate) ; (i) samples from the carbonates family*  
 253 *(andersonite and liebigite).*

255 *Table S.2 X-EDS analyses of some synthetic samples used in the training and validation sets. The indicated atomic percentages were calculated as the average of at least 20 X-*  
 256 *EDS measurements. 2σ stands for twice the standard deviation and is related to the spatial heterogeneity of the composition.*

Sample reference	Sample name	Elemental composition (at.% ± 2σ)									
		U	Ba	Ca	Cu	K	Na	S	Si	P	V
ICSM15-01	ankoleite	33 ± 1				32 ± 3				35 ± 1	
ICSM15-02	autunite	42 ± 1		22 ± 2						36 ± 1	
ICSM15-05	torbernite	42 ± 1			14 ± 3					44 ± 2	
ICSM15-03	carnotite	36 ± 2				29 ± 3					35 ± 3
EA21-055	becquerelite	85 ± 6		15.0 ± 0.2							
EA21-048	becquerelite	91 ± 2		8.9 ± 1.7							
EA21-049	billietite	86.6 ± 0.7	13.7 ± 0.7								
EA21-050	compreignacite	83.5 ± 0.9				16.5 ± 0.9					
SBb-015	Na-zippeite	58 ± 1					24 ± 1	17.1 ± 0.3			
SBb-005	zippeite	61 ± 1				21 ± 2		17.7 ± 0.6			
SBb-020	Ca and U silicate	39 ± 2		12 ± 2					49 ± 2		
SBb-004	soddyite	49 ± 2							51 ± 17		
EA21-064	uranophane	51 ± 5		11.7 ± 0.2					38 ± 1		
SBb-019	weeksite	22 ± 3				14 ± 5			64 ± 7		
SBb-006	boltwoodite	30 ± 15				25 ± 10			45 ± 20		
SBb-014	Na and U silicate	41 ± 11					19 ± 7		37 ± 11		

257

258 *Table S.3 Elemental composition of synthetic samples of the carbonates family determined by ICP-AES analyses after total dissolution of the samples.*

Sample reference	Sample name	Elemental composition (wt.% ± 2σ)		
		U	Ca	Na
LANIE15-01	andersonite	36 ± 1	25 ± 1	9 ± 1
LANIE15-02	liebigite	37 ± 1	35 ± 1	6 ± 1

259

260 **S.3. Prediction results on the training set**

261 *Table S.4 Mineralogical family predicted by model 1 on the training dataset, expressed as a rate over the total number of spectra for each sample.*

SAMPLE :	Metazenerite							Andersonite		Liebigite	Illite 005	Kaolinite 008	Kaolinite 029	Smectite 035	Smectite 036	Acetate		Nitrate	Metaschoepite	Paraschoepite	UO3	Bequerelite 055	Billietite 049	Compreignacite 050	Ankoleite	Autunite	Autunite (synthetic)	Chernikovite	Torbernite (BN42)	Torbernite (synthetic)	Ca and U silicate		Soddyite	Uranophane 064	Weeksite	Na Zippeite	Sulfate	Zippeite	Carnotite	Francevillite
	MINERALOGICAL FAMILY :	Metazenerite							Andersonite		Liebigite	Illite 005	Kaolinite 008	Kaolinite 029	Smectite 035	Smectite 036	Acetate		Nitrate	Metaschoepite	Paraschoepite	UO3	Bequerelite 055	Billietite 049	Compreignacite 050	Ankoleite	Autunite	Autunite (synthetic)	Chernikovite	Torbernite (BN42)	Torbernite (synthetic)	Ca and U silicate		Soddyite	Uranophane 064	Weeksite	Na Zippeite	Sulfate	Zippeite	Carnotite
Reference :	Arsenates							Carbonates		Clays	Other		Oxides			Oxy-hydroxides			Phosphates						Silicates				Sulfates			Vanadates								
Predicted :	Arsenates							Carbonates		Clays	Other		Oxides			Oxy-hydroxides			Phosphates						Silicates				Sulfates			Vanadates								
Arsenates	0.96							0.04																																
Carbonates								1 1																																
Clays								0.92 1 1 1 0.96																																
Other								1 1																																
Oxides										1 1 1																														
Oxy-hydroxides													1 1 1																											
Phosphates	0.04																		1 1 1 1 1 1																					
Silicates																									1 1 1 1															
Sulfates								0.04		0.04																			1 1 1											
Vanadates																																1 1								

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Table S.5 Sample predicted by model 2 on the training dataset, expressed as a rate over the total number of spectra for each sample.

Reference : Predicted :	Acetate	Andersonite	Ankoleite	Autunite	Autunite (synthetic)	Becquerelite 055	Billietite 049	Ca and U silicate	Carnotite	Chernikovite	Compreignacite 050	Francevillite	Illite 005	Kaolinite 008	Kaolinite 029	Liebigite	Metaschoepite	Metazeunerite	Na Zippeite	Nitrate	Paraschoepite	Smectite 035	Smectite 036	Soddyite	Sulfate	Torbernite (BN42)	Torbernite (synthetic)	UO3	Uranophane 064	Weeksite	Zippeite	
Acetate	1																															
Andersonite		1																														
Ankoleite			1																													
Autunite				1														0.04														
Autunite (synthetic)					1																											
Becquerelite 055						0.88					0.04																					
Billietite 049							0.96																									
Ca and U silicate								1																								
Carnotite									1																							
Chernikovite										1																						
Compreignacite 050						0.12	0.04				0.96																					
Francevillite												1																				
Illite 005													0.92																			
Kaolinite 008														0.96	0.08																	
Kaolinite 029														0.04	0.92																	
Liebigite																1																
Metaschoepite																	1															
Metazeunerite													0.04					0.96														
Na Zippeite																			1					0.04								
Nitrate																					1											
Paraschoepite																						1										
Smectite 035																							1									
Smectite 036																								0.96								
Soddyite																									1							
Sulfate																										1						
Torbernite (BN42)																											1					
Torbernite (synthetic)																												1				
UO3																													1			
Uranophane 064																														1		
Weeksite																														1		
Zippeite												0.04																				1

## 265 S.4. References

266

- 267 [S1] Cordfunke, E.H.P. and P. Aling, Thermal Decomposition Of Hydrated Uranium Peroxides. Recueil  
268 Des Travaux Chimiques Des Pays-Bas-Journal of the Royal Netherlands Chemical Society, 1963.  
269 82(3): p. 257.
- 270 [S2] Vochten, R. and L. Vanhaverbeke, Transformation of schoepite into the uranyl oxide hydrates -  
271 becquerelite, billietite and wolsendorfite. Mineralogy and Petrology, 1990. 43(1): p. 65-72.
- 272 [S3] Abraham, F., C. Dion, and M. Saadi, Carnotite analogues: synthesis, structure and properties of  
273 the  $\text{Na}_{1-x}\text{K}_x\text{UO}_2\text{VO}_4$  solid solution ( $0 < x < 1$ ). Journal of Materials Chemistry, 1993. 3(5): p. 459-463.
- 274 [S4] Crétaz, F., Etude de la solubilité et des cinétiques de dissolution des phosphates et vanadates  
275 d'uranium : Implications pour l'amont du cycle électronucléaire. 2013, Université Montpellier II.  
276 p. 243.
- 277 [S5] Vochten, R. and M. Deliens, Transformation of curite into metaautunite paragenesis and  
278 electrokinetic properties. Physics and Chemistry of Minerals, 1980. 6(2): p. 129-143.
- 279 [S6] Clavier, N., et al., Vibrational spectroscopy of synthetic analogues of ankoleite, chernikovite and  
280 intermediate solid solution. Spectrochimica acta. Part A, Molecular and biomolecular  
281 spectroscopy, 2016. 156: p. 143-50.
- 282 [S7] Cretaz, F., et al., Solubility properties of synthetic and natural meta-torbernite. Journal of  
283 Nuclear Materials, 2013. 442(1-3): p. 195-207.
- 284 [S8] Sharifironizi, M., et al., Thermodynamic studies of zippeite, a uranyl sulfate common in mine  
285 wastes. Chemical Geology, 2016. 447: p. 54-58.
- 286 [S9] Casas, I., et al., Dissolution studies of synthetic soddyite and uranophane. SKB Technical Report,  
287 1997. 97-15: p. 36.
- 288 [S10] Vochten, R., et al., A new method of synthesis of boltwoodite and of formation of sodium  
289 boltwoodite, uranophane, sklodowskite and kasolite from boltwoodite. Canadian Mineralogist,  
290 1997. 35: p. 735-741.
- 291 [S11] Wall, N.A., S.B. Clark, and J.L. McHale, Synthesis and characterization of 1:1 layered uranyl  
292 silicate mineral phases. Chemical Geology, 2010. 274(3-4): p. 149-157.
- 293 [S12] Meyrowitz, R., Liebigite, in Systematic Mineralogy of Uranium and Thorium. U.S. Geological  
294 Survey Bulletin 1064 (1958), C. Frondel, Editor. 1954: Washington. p. 109-112.
- 295 [S13] Vochten, R., L. Van Haverbeke, and K. Van Springel, Synthesis of liebigite and andersonite, and  
296 study of their thermal behavior and luminescence. The Canadian Mineralogist, 1993. 31(1): p.  
297 167-171.
- 298 [S14] Vochten, R., et al., The structure and physicochemical characteristics of a synthetic phase  
299 compositionally intermediate between liebigite and andersonite. The Canadian Mineralogist,  
300 1994. 32: p. 553-561.
- 301 [S15] Bernachy-Barbe, F., Homogenization of bentonite upon saturation: Density and pressure fields.  
302 Applied Clay Science, 2021. 209: p. 106122
- 303 [S16] Reinoso-Maset, E. and J. Ly, Study of uranium(VI) and radium(II) sorption at trace level on  
304 kaolinite using a multisite ion exchange model. Journal of Environmental Radioactivity, 2016.  
305 157: p. 136-148.
- 306 [S17] Orucoglu, E., et al., From experimental variability to the sorption related retention parameters  
307 necessary for performance assessment models for nuclear waste disposal systems: The example  
308 of Pb adsorption on clay minerals. Applied Clay Science, 2018. 163: p. 20-32.
- 309 [S18] Asaad, A., et al., A baseline study of mineralogical and morphological properties of different size  
310 fractions of illite du Puy. Applied Clay Science, 2022. 224: p. 106517.

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