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Uranium removal from mining water using Cu substituted hydroxyapatite

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ABSTRACT

In this study, synthetic copper substituted hydroxyapatite (Cu-Hap), $\text{Cu}_x\text{Ca}_{10-x}(\text{PO}_4)_6(\text{OH})_2$ were prepared by co-precipitation method and were used as reactive materials in batch experiments to immobilize uranyl. The limit of incorporation of Cu into a single-phased Cu-Hap reached $x_{\text{Cu}} \leq 1.59$. The synthetic Cu-Hap samples obtained with various Cu contents were contacted with

18 synthetic uranyl doped solutions and with real mining waters showing various pH and chemical
19 compositions. A fast and strong decrease of the uranium concentration was observed, followed
20 by the establishment of an equilibrium after 1 to 4 days of contact with the solutions.
21 Examination of the solid phase after uranium uptake was performed using a combination of
22 techniques. Depending on the composition of the solution and the copper content of the Cu-Hap,
23 various mechanisms of uranium removal were observed. Based on the experimental results and
24 geochemical simulations, it appeared that the main interest for using Cu-Hap is to enlarge the
25 domain of water compositions for which the precipitation of meta-torbernite,
26 $(\text{H}_3\text{O})_{0.4}\text{Cu}_{0.8}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 7.6 \text{H}_2\text{O}$ is the predominant mechanism associated to the uranium
27 removal, especially for $\text{pH} > 6.7$ where carbonate uranium species are predominant.

28

29 1. INTRODUCTION

30 Uranium ore mining, processing and manufacturing can contribute to groundwater
31 contamination. Uranium is transported in groundwater mainly as dissolved U(VI) species, which
32 can threaten ecosystems in the vicinity of contaminated sites. High costs associated with pump-
33 and-treat remediation strategies and toughening of regulatory requirements regarding sewage
34 discharge have prompted research into more effective methods^{1, 2}. In this field, new methods
35 involving hydroxyapatite (Hap) amendments to immobilize U(VI) as a nonlabile uranyl
36 phosphate phase have been extensively studied³⁻¹⁷. The rationale for using these methods is the
37 remarkable stability of uranyl phases of the autunite group ($M^{II}(UO_2)_2(PO_4)_2 \cdot xH_2O$ or
38 $M^I_2(UO_2)_2(PO_4)_2 \cdot xH_2O$) under environmental conditions¹⁸. The study of natural deposits in
39 oxidizing bedrock aquifers demonstrated that phases of the autunite group are stable for tens to
40 hundreds thousand years¹⁹. Examination of the reported standard solubility products of the
41 phases of the autunite group²⁰⁻²⁶ shows that meta-torbernite, $(H_3O)_{0.4}Cu_{0.8}(UO_2)_2(PO_4)_2 \cdot 7.6 H_2O$
42 is the less soluble one (Erreur ! Source du renvoi introuvable. of the supporting information).
43 The ubiquity of meta-torbernite in oxidized secondary U ore deposits, contaminated sediments or
44 mine tailings strengthen this conclusion²⁷.

45 However, the precipitation of U-phosphate phases of the autunite group is not the only
46 mechanism of immobilization observed when using Hap as reactive material to remove uranium
47 from contaminated solutions. Surface complexation, ion exchange^{5-8, 12} and surface
48 mineralization²⁸ can occur depending on the composition of the solution and the total uranium
49 concentration,. The fluor-apatite structure can also accommodate hexavalent uranium by
50 substitution in the Ca1 site²⁹. The precipitation of chernikovite or meta-autunite is the
51 mechanism responsible for the immobilization of uranyl either by surface precipitation following

52 sorption or by precipitation in the bulk solution. However, the stability of the precipitated phases
53 could be strongly impacted by the formation of uranyl carbonates species predominant in near
54 neutral pH and aerated groundwater, as observed by Simon et al.¹².

55 On the other hand, Cu-substituted hydroxyapatite (Cu-Hap) has been successfully prepared
56 for its antimicrobial activity and biocompatibility in bioceramics used as bone implants, or for its
57 catalytic properties in the removal of NO_x issued from diesel and lean burn gasoline³⁰⁻³⁴. Cu-Hap
58 was also prepared to improve the sorption capacity of the hydroxyapatite in groundwaters
59 contaminated with arsenate³⁵. Mainly two ways of synthesis were reported in the literature. The
60 first one consisted in the synthesis of an hydroxyapatite by the classical neutralization method
61 initially developed by Wallayes³⁶ followed by cation exchange step. This protocol led to the
62 preparation of Cu-Hap samples with low Cu incorporation contents. Samples prepared with Cu
63 molar contents higher than $x_{Cu} = 0.02$ were mixtures of phases^{31, 32}. The second way of synthesis
64 was based on the co-precipitation method^{30, 34}. Shanmugam et al.³⁰ and Stanic et al.³⁴ obtained
65 single phase Cu-Hap for $x_{Cu} < 0.53$ and for $x_{Cu} < 0.04$, respectively.

66 In this study, we assessed the feasibility of using synthetic Cu-Hap prepared by co-
67 precipitation method to immobilize uranyl as stable meta-torbernite phase. The limit of
68 incorporation of Cu into a single-phased Cu-Hap was determined, then the prepared samples
69 were used as reactive materials in batch experiments. The synthetic Cu-Hap samples obtained
70 with various Cu contents were contacted with synthetic uranyl doped solutions and with real
71 mining waters showing various pH and chemical compositions, thus different uranium speciation
72 in solution. The performance of the Cu-Hap was analyzed and compared to Hap based on the
73 rate and extent of uranium sequestration. The mechanism of immobilization was investigated

74 with respect to various conditions tested through geochemical calculations and solid phase
75 characterizations.

76 **2. MATERIALS AND METHODS**

77 **2.1. Synthesis of Cu substituted Hap**

78 Copper substituted hydroxyapatite, $\text{Cu}_x\text{Ca}_{10-x}(\text{PO}_4)_6(\text{OH})_2$ was precipitated by
79 neutralization of 200 mL of a solution prepared by dissolving $\text{Cu}(\text{OH})_2$ in 0.12 M H_3PO_4
80 (Solution A) Sigma-Aldrich, analytical grade, Carlo Erba, ACS reagent) with 0.4 M $\text{Ca}(\text{OH})_2$
81 (solution B) (Sigma Aldrich, ACS reagent). The weighted amount of $\text{Cu}(\text{OH})_2$ was adjusted to
82 reach the desired concentration of copper in the solution A: $C_{\text{Cu}} = 0.02 \times x_{\text{Cu}}$ M. A defined volume
83 of solution B was added considering the final stoichiometry of Cu-Hap. Solution A was heated at
84 70°C and solution B was rapidly added under vigorous stirring until a precipitate was formed at
85 $\text{pH} = 4$. Then, solution B was added slowly to avoid pH value of the mixture higher than 8. The
86 mixture was heated during 2 h under stirring, then ripened at ambient temperature during 16 h.
87 The precipitate was then filtered, washed with 1 L of deionized water then with ethanol (96 %
88 vol.) and finally dried at 60°C in an oven during 24 h. The yield of synthesis was determined
89 from the analysis of Cu, Ca and P elemental concentrations remaining in the initial supernatant
90 and in the washing solutions. This protocol allowed the synthesis of 4 mmol of Cu-Hap. No
91 particular caution was paid to the carbonate content of $\text{Ca}(\text{OH})_2$ solution.

92 **2.2. Batch experiments**

93 Batch experiments were performed at room temperature by contacting various Cu-Hap
94 samples with several solutions contaminated with uranium in a Teflon container (Savillex).
95 Synthetic solutions of 0.02 M NaNO_3 (Sigma Aldrich ReagentPlus) and Na_2SO_4 (Sigma Aldrich,
96 ACS reagent) spiked with 1.0 mM of uranium nitrate homemade solution or real mining waters

97 were used. The pH of the synthetic spiked solution was adjusted using 8 M NaOH solution. The
 98 uranium concentration in the synthetic solution prepared was analyzed by Inductively Coupled
 99 Plasma – Atomic Emission Spectroscopy (ICP-AES) following the procedure described below.
 100 **Table 1** summarized the experimental conditions used in the various batch experiments.

101 **Table 1.** Experimental conditions for the batch experiments.

Cu content, x_{Cu}	Cu-Hap (mg)	Solution	Volume (mL)	C_U (initial) (mol/L)	pH (initial)
0.44/ 1.15/ 1.59	100	0.02 M Na_2SO_4	100	$(0.91 \pm 0.01) \times 10^{-3}$	7.1 ± 0.1
0.44/ 1.15/ 1.59	100	0.02 M $NaNO_3$	100	$(1.02 \pm 0.01) \times 10^{-3}$	7.2 ± 0.1
0.44/ 1.15/ 1.45/ 1.59	60	V105	200	$(0.97 \pm 0.04) \times 10^{-6}$	4.5 ± 0.1
0.44/ 1.15/ 1.45/ 1.59	60	BD200	200	$(1.64 \pm 0.02) \times 10^{-6}$	7.1 ± 0.1

102
 103 The containers were placed in an orbital stirrer in order to ensure the homogeneity of the
 104 system. Regularly, pH were measured using a Metrohm combination-glass electrode calibrated
 105 against pH buffers (Inlab® Solutions, Mettler Toledo, pH =2.00; 4.01, 7.00 and 9.21 at 25°C)
 106 and 10 mL of solution were sampled to determine the elemental concentrations in U, Cu, Ca and
 107 P. The samples were first centrifuged at 4500 rpm during 10 min, then 9 mL of solution were
 108 taken off and acidified to pH ~ 2 with 0.5 mL of 0.2 M HNO_3 solution. The samples were
 109 analyzed either by ICP-AES (Spectro Arcos EOP device) or by ICP-MS (Thermo Scientific
 110 iCAP RQ). The calibration was performed using PlasmaCAL (SCP Science) single element
 111 calibration standards (C_U , C_{Ca} , C_{Cu} and C_P = 1000 ppm) diluted in HNO_3 solution.
 112 Concentrations and associated uncertainties were respectively the mean and twice the standard
 113 deviation of three replicates. This protocol allowed the detection as low as 50 ppb for Cu and 100

114 ppb for U, Ca and P. ICP-MS was used to measure lower concentrations using EN ISO 7980 and
 115 EN ISO 11885 standards for Ca, Cu and P analyses, respectively. NF M 60 805 4 standard was
 116 used to determine U elemental concentration.

117 The two mining waters (named V105 and BD200) were sampled at the former uranium mining
 118 site of Bellezane (Limousin, France). The composition of the two types of water was determined
 119 by ICP-AES calibrated against single element calibration standards (1000 ppm). The total
 120 inorganic carbon content was measured using a TOC analyzer (Shimadzu, Japan) after dilution
 121 of the mining water with 10 mL of deionized water. Total inorganic carbon concentration was
 122 measured using an external calibration curve prepared by dilution of a 500 ppm NaHCO₃
 123 standard solution with deionized water. The detection limit reached 0.5 ppm of total carbon. The
 124 main characteristics of the two mining waters are reported in **Table 2**. The two samples differed
 125 mainly in terms of pH, sulfate, carbonate and elemental concentrations resulting from their
 126 different hydrogeological origin. Uranium concentrations $C_U = (1.60 \pm 0.02) \times 10^{-6}$ and $(0.97 \pm$
 127 $0.04) \times 10^{-6}$ mol/L for BD200 and V105, respectively.

128 **Table 2.** pH, concentrations of main ions and inorganic carbon content determined by ICP-
 129 AES for the two mining waters collected in the Bellezane site. Simulations of
 130 uranium speciation in the two mining waters by Phreeqc Interactive³⁷ using
 131 Thermochemie^{38,39} and PRODATA⁴⁰ thermodynamic databases.

	BD 200	V 105
pH	7.1 ± 0.1	4.5 ± 0.1
Ca (mg/L)	71.7 ± 0.2	149.1 ± 0.6
K (mg/L)	8.0 ± 0.1	10.24 ± 0.1
Mg (mg/L)	22.0 ± 0.2	64 ± 3
Na (mg/L)	9.7 ± 0.4	12 ± 1
Al (mg/L)	0.33 ± 0.01	30.1 ± 0.1
Cu (mg/L)	< DL	< DL
U* (mg/L)	0.38 ± 0.01	0.23 ± 0.01
S (mg/L)	70 ± 2	225 ± 5
Si (mg/L)	6.8 ± 0.2	20.2 ± 0.6
C* (mg/L)	88.1 ± 0.2	4.36 ± 0.04

Main U(VI) species (%): Thermochimie TDB	
Ca ₂ UO ₂ (CO ₃) ₃ : 67.7 %	UO ₂ (SO ₄): 62.6 %
CaUO ₂ (CO ₃) ₃ ²⁻ : 30.5 %	UO ₂ ²⁺ : 24.1 %
UO ₂ (CO ₃) ₂ ²⁻ : 1.2 %	UO ₂ SiO(OH) ₃ ⁺ : 6.1 %
	UO ₂ (SO ₄) ₂ ²⁻ : 3.8 %
	UO ₂ (OH) ⁺ : 3.4 %
Main U(VI) species (%): PRODATA TDB[#]	
Ca ₂ UO ₂ (CO ₃) ₃ : 67 %	UO ₂ (SO ₄): 60 %
CaUO ₂ (CO ₃) ₃ ²⁻ : 32 %	UO ₂ ²⁺ : 27 %
	UO ₂ SiO(OH) ₃ ⁺ : 6 %
	UO ₂ (SO ₄) ₂ ²⁻ : 3 %
	UO ₂ CO ₃ : 2 %
	UO ₂ OH ⁺ : 2 %

132 *total inorganic carbon concentration analyzed by TOC meter. U analyzed by ICP-MS.
 133 [#]data extracted from Reiller and Descostes⁴⁰. PRODATA is a new thermodynamic database
 134 dedicated to mining and environmental monitoring activities.

135

136 **2.3. Characterization of the solid phases**

137 The stoichiometry of the prepared Cu-Hap was determined by complete dissolution of 30
 138 mg of the solid in 30 mL of 0.2 M HNO₃. Four dilutions of the resulting solution with 0.2 M
 139 HNO₃ were performed then measured by ICP-AES analyses. Cu-Hap samples were characterized
 140 before and after being contacted with uranium solutions by Powder X-ray diffraction (PXRD),
 141 Raman spectroscopy, Time-Resolved Laser-induced Fluorescence Spectroscopy (TRLFS) and
 142 Scanning Electron Microscopy (SEM). PXRD patterns were recorded using a Bruker D8
 143 advance diffractometer with copper radiation ($\lambda_{\text{Cu}} K\alpha_{1,2} = 1.54184 \text{ \AA}$) in a parallel mode and
 144 using the reflection geometry. The patterns were recorded between 5° and 100° (2 θ) with a step
 145 of 0.02 ° and a counting time of 3 h. The resulting data were refined using the Fullprof_suite⁴¹
 146 by applying the Rietveld method and using the Thomson Cox profile function⁴². Pure silicon
 147 was used as a standard to determine instrumental parameters. Zero shift, unit cell parameters,

148 overall displacement, preferred orientation and anisotropic size model for the microstructural
149 characteristics were considered for all the refinements.

150 Raman spectra were recorded by the means of a Horiba - Jobin Yvon Aramis apparatus
151 equipped with an edge filter and using a Nd:YAG laser (532 nm). In order to avoid any laser-
152 induced degradation of the compound, the power was turned down by the means of optical filters
153 to about 1–4 mW depending on the sample analyzed. The laser beam was then focused on a
154 small fraction of powder deposited on a glass lamella using an Olympus BX 41 microscope. A
155 $\times 100$ objective with a numerical aperture of 0.9 was used, resulting in a spot size of about $1 \mu\text{m}^2$.
156 The scattered Raman light was collected in a 180° backscattering geometry and dispersed by a
157 grating of 1800 grooves/mm after having passed a $150 \mu\text{m}$ entrance slit, resulting in a spectral
158 resolution lower than 1cm^{-1} . For each spectrum, a dwell time of 90 to 180 s was considered with
159 an average of 3 scans. Before analysis, the apparatus was calibrated with a silicon wafer, using
160 the first-order Si line at 520.7cm^{-1} .

161 TRLFS was performed with the experimental setup described in literature⁴³. A Nd:YAG
162 laser (266 nm, pulse duration 5 ns at 10 Hz) was used. In order to avoid laser ablation, the laser
163 beam was driven through an optical system and a $50\text{-}\mu\text{m}$ diaphragm to reduce the beam diameter
164 and the delivered energy. The beam was then focused close to the surface of the sample through
165 a microscope lens (model BX-51). The surface of the sample was positioned near the focal plane
166 of the laser to obtain a probed area of about 1 mm in diameter. TRLFS was performed on powder
167 samples deposited on double-sided tapes. The fluorescence emission was collected by an optical
168 fiber placed at 45° with respect to the axis of the laser and transmitted to a monochromator
169 Andor Shamrock SR-303i (grating of 300 grooves/mm, entrance slit of $150 \mu\text{m}$, spectral

170 resolution of about 15 nm). Each sample spectrum resulted from 300 accumulated spectra
171 recorded with a temporal gate of 200 μs delayed by 1 μs after the laser pulse.

172 Scanning electron microscopy (SEM) analyses were conducted using a Quanta 200 ESEM
173 FEG (FEI Company) electron microscope equipped either with a backscattered electron detector
174 (BSED) in high vacuum conditions with a 25 kV accelerating voltage. Powder samples were
175 directly analyzed without any preparation. Qualitative X-ray energy dispersive spectroscopy (X-
176 EDS) analyses were performed under the same conditions using the Bruker AXS X-Flash 5010
177 detector coupled to the SEM device. X-EDS maps were obtained using the same detector and
178 operating conditions. For that purpose, an aliquot of each sample was embedded in an epoxy
179 resin, polished to optical grade and metalized by carbon deposition.

180 The specific surface area of the synthesized Cu-Hap powder were determined using 10
181 point adsorption isotherm of $\text{N}_2(\text{g})$ at 77 K and the B.E.T. method (Tristar, Micromeritics).

182

183 **2.4. Speciation calculations**

184 From the composition of the synthetic solutions or mining waters (**Table 2**), the average
185 elemental concentrations and pH values of the systems at equilibrium, the saturation index of the
186 solutions with respect to the solid phases of interest were calculated with the geochemical
187 speciation model Phreeqc Interactive (Version 3.3.3)³⁷. The solutions were considered at
188 equilibrium with air ($p\text{O}_2 = 0.2 \text{ atm}$ and $p\text{CO}_2 = 10^{-3.5} \text{ atm}$). The calculations of the solubility
189 product accounted for the aqueous complexation reactions incorporated in the Thermochemie
190 database^{38, 39}. The thermodynamic database was completed for Cu speciation using the data
191 reported in the Minteq.V4 database⁴⁴ and for the standard solubility product of meta-autunite
192 ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$), uranyl hydrogen phosphate ($\text{UO}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$) and meta-torbernite

193 determined by Gorman-Lewis et al.²¹ and by Cretaz et al.²², respectively. The activity
194 coefficients were calculated using the Davies equation implemented in the Phreeqc software.

195

196 3. RESULTS AND DISCUSSION

197 3.1.Characterizations of prepared Cu-Hap

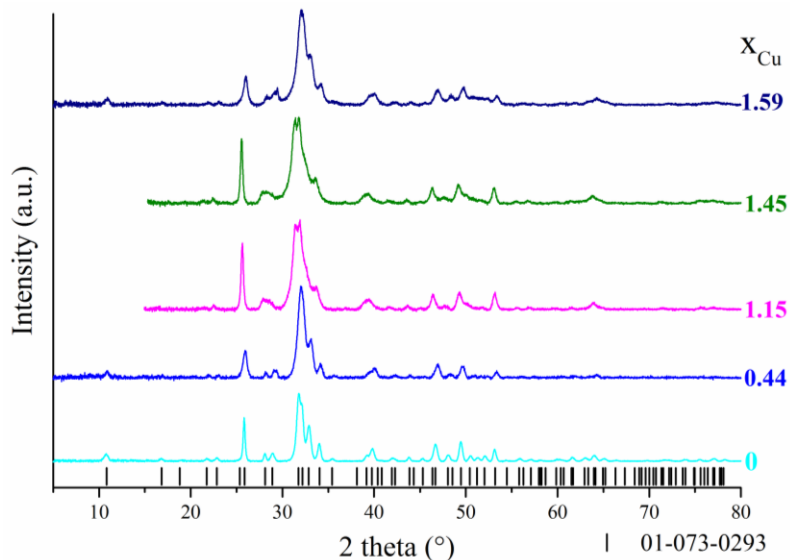
198 The composition of the prepared Cu-Hap is indicated in **Table 3**. The Cu mole fraction
199 determined by total dissolution of the sample differed slightly from the expected value and
200 showed a decrease of the Ca incorporation yield when increasing the Cu content in the starting
201 mixture. This decrease led to the formation of non-stoichiometric Cu-Hap (with $\frac{x_{Cu}+x_{Ca}}{x_p} \neq 1.67$).
202 The PXRD patterns of the synthesized Cu-Hap is presented in **Figure 1**. All patterns showed the
203 XRD lines related to the hexagonal structure of hydroxyapatite (space group P6₃/m), excluding
204 the presence of secondary phase. The prepared samples were thus single phase for $x_{Cu} \leq 1.59$.
205 The Rietveld refinement of the patterns indicated the contraction of the unit cell volume versus
206 the incorporation rate of copper (**Table 3**), as the result of the replacement of calcium by the
207 smaller copper in the structure. The unit-cell volume of the prepared Cu-Hap were also
208 compared to several values reported in the literature (**Figure S2** included in the supporting
209 information). The results agreed well with the data reported by Shanmugam et al.³⁰ and Li et al.³²
210 for Cu substituted Hap. The unit cell volume presented a minimum for $x_{Cu} = 0.44$ (i.e. $V =$
211 $524.86(8) \text{ \AA}^3$), then was found to be almost constant for $x_{Cu} = 1.15; 1.45$ and 1.59 . Shanmugam
212 et al.³⁰ obtained smaller unit cell volumes for $0.05 \leq x_{Cu} \leq 0.25$ then observed an increase for x_{Cu}
213 $= 0.5$ (i.e. $V = 525.6 \text{ \AA}^3$), which is in agreement with the data determined for $x_{Cu} = 0.44$. Such a
214 variation of the unit cell volume when substituting Ca by Cu could indicate different
215 incorporation modes in the solid solution, i.e. substitution in Ca1 or Ca2 sites and/or insertion in

216 the structure. Similar behavior was observed by Gomes et al.⁴⁵ for Zn-Hap in which Zn atoms
 217 occupy interstitial sites in Hap (Wyckoff site 2b), leading to solid solution with general
 218 composition $\text{Ca}_{10}\text{Zn}_x(\text{PO}_4)_6\text{O}_{2x}(\text{OH})_{2-2x}$. Even if different substitution/incorporation mechanisms
 219 could have led to the precipitation of these Cu-Hap samples, the variation of the unit cell volume
 220 versus the copper content indicates that copper was not only adsorbed at the surface of Hap, but
 221 incorporated in the lattice. This result suggests that the rate of Cu release in solution may be
 222 controlled by the dissolution of the Cu-Hap sample.

223 **Table 3.** Reaction yield of precipitation determined from the analysis of the supernatant by
 224 ICP-AES. Copper mole fraction x_{Cu} and $(x_{\text{Cu}}+x_{\text{Ca}})/x_{\text{P}}$ ratio determined by total
 225 dissolution of the precipitate, unit cell parameters determined by Rietveld refinement
 226 from PXRD patterns and specific surface area of the synthesized Cu-Hap. The
 227 copper contents in the Cu-Hap taken from the literature corresponds to the
 228 stoichiometry of the mixture of reactants during the synthesis (except for Stanić et
 229 al.³⁴).

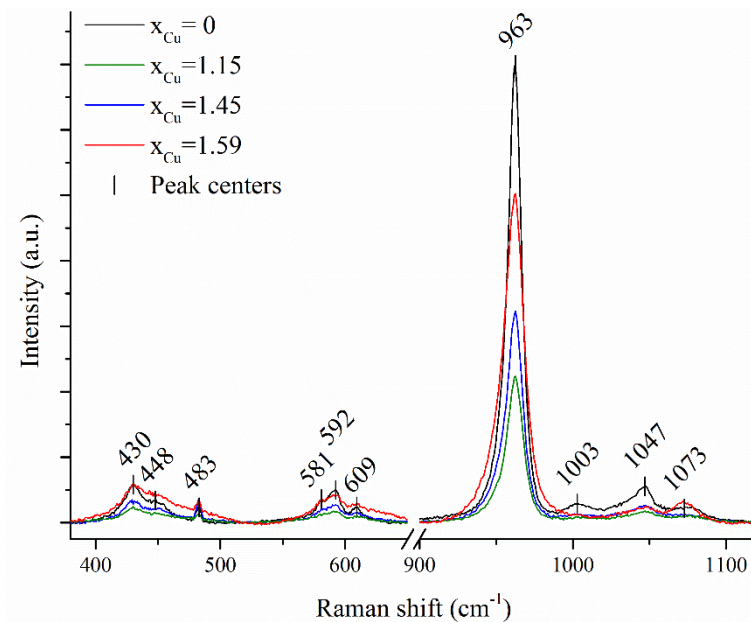
Ca yield (mol. %)	Cu yield (mol. %)	P yield (mol. %)	x_{Cu}	$\frac{x_{\text{Cu}} + x_{\text{Ca}}}{x_{\text{P}}}$	a (Å)	c (Å)	Cell volume (Å ³)	S_{BET} (m ² /g)
99.9 ± 0.1	N.D.	99.9 ± 0.1	0	1.7 ± 0.1	9.4213(3)	6.8908(2)	529.69(2)	80
97.6 ± 0.1	99.9 ± 0.1	99.8 ± 0.1	0.44 ± 0.01	1.9 ± 0.2	9.3859(8)	6.8794(6)	524.86(8)	85
88.5 ± 0.3	98.9 ± 0.1	95.6 ± 0.1	1.15 ± 0.01	1.4 ± 0.2	9.4240(5)	6.8500(4)	526.87(5)	147
82.9 ± 0.2	99.2 ± 0.1	96.0 ± 0.3	1.45 ± 0.01	1.5 ± 0.2	9.4282(6)	6.8493(4)	527.28(5)	76
N.D.	N.D.	N.D.	1.59 ± 0.01	1.6 ± 0.2	9.404(1)	6.8728(8)	526.4(1)	65
Shanmugam et al. ³⁰			0		9.42	6.88	528.8	
			0.05		9.328(4)	6.844(3)	515.6	
			0.1		9.358(9)	6.837(9)	518.7	
			0.15		9.333(0)	6.843(3)	516.2	
			0.2		9.353(2)	6.842(7)	518.4	
			0.25		9.337(8)	6.842(7)	516.7	
			0.5		9.397(0)	6.872(7)	525.6	
Karpov et al. ⁴⁶			0.54		9.4303(1)	6.9069(1)	531.95(1)	
Stanić et al. ³⁴			0	1.65	9.4261	6.8971	530.71	
			0.0042	1.65	9.4249	6.8957	530.40	
			0.041	1.63	9.4218	6.8954	530.10	

230 N.D.: not determined



231
 232 **Figure 1.** PXRD patterns of the synthesized Cu-Hap. Black bars are the Bragg positions for
 233 stoichiometric Hap (PDF 01-073-0293).

234 The Raman spectra recorded for all the synthesized Cu-Hap are showed in **Figure 2** as well
 235 as the position of the bands obtained for $x_{Cu} = 0$. The strongest Raman active mode ν_1 ^{45, 47, 48}
 236 associated to symmetric stretching of the P-O bond was observed at 963 cm^{-1} and did not shift
 237 when increasing the Cu content. As an example, O'Donnell et al.⁴⁸ showed that the position of
 238 the ν_1 band decreased linearly from 963 cm^{-1} (Hap) to 949 cm^{-1} for full substitution of Ca by
 239 heavier Sr. For Zn-substituted Hap, Gomes et al.⁴⁵ observed that the intense single band at 963
 240 cm^{-1} was split in three resolved contributions indicating a local structure ordering. The absence
 241 of shift in energy of this mode for the Cu-substituted hydroxyapatite indicates a negligible
 242 compositional effect. The variation of the peak intensity was not correlated to the Cu content, but
 243 rather revealed different degrees of crystallinity of the samples.

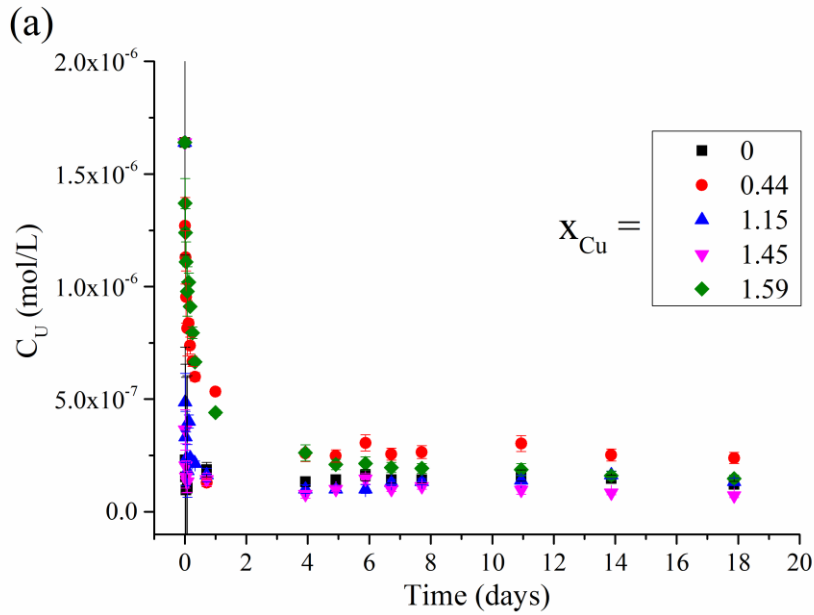


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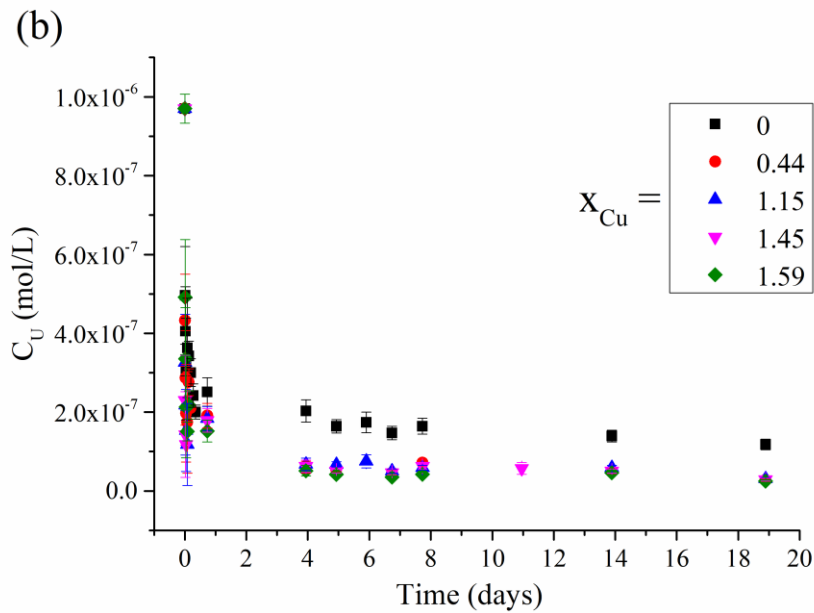
245 **Figure 2.** Raman spectra of the synthesized Cu-Hap.

246 **3.2. Batch experiments**

247 The prepared Cu-Hap were put in contact with solutions spiked with uranium. The
 248 composition of the solutions at equilibrium with the Cu-Hap is listed in **Table 4**. The evolution
 249 of the uranium concentration in the two mining waters contacted with the different Cu-Hap
 250 samples is reported in **Figure 3**. The evolution of phosphorus and copper concentrations in
 251 BD200 and V105 mining waters are showed in **Figure S3** and **Figure S4** of supporting
 252 information, respectively.



253



254

255 **Figure 3.** Evolution of the U elemental concentrations in BD200 (a) and V105 (b) mining
 256 waters when contacting with the different prepared Cu-Hap samples.

257 From these results, a fast decrease of the uranium concentration was observed, followed by
 258 the establishment of an equilibrium after 4 days of contact with the mining waters. For
 259 experiments involving BD200 mining water, uranium concentrations obtained at equilibrium

260 with the Cu-Hap were found to vary between 0.7×10^{-7} to 2.4×10^{-7} mol/L without any
261 correlation with the amount of Cu incorporated in the Cu-Hap. For V105 mining water, it ranged
262 between 0.2×10^{-7} to 1.2×10^{-7} mol/L and slightly decreased with increase of the Cu mole
263 fraction in Cu-Hap. The benefit linked to the increase of the Cu content in the hydroxyapatite
264 structure was only significant for V105 mining water. V105 is more acidic than BD200 and the
265 synthetic solutions and contains less carbonate ions and more sulfate ions, affecting the
266 speciation of uranium in the mine waters (**Table 2**). $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3$ and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ were
267 found to be the predominant species in BD200 (68 and 31%, respectively) whereas $\text{UO}_2(\text{SO}_4)$
268 and free UO_2^{2+} were predominant in V105 (63 and 24%, respectively).

269 The results obtained for the 0.02 mol/L NaNO_3 and Na_2SO_4 synthetic solutions spiked with
270 10^{-3} mol/L of uranium are given in supporting information (**Figure S5 and Figure S6,**
271 **respectively**). Once again, a strong and fast decrease of the uranium elemental concentration was
272 observed. Uranium concentration obtained at equilibrium with Cu-Hap varied from 0.5×10^{-6} to 2
273 $\times 10^{-6}$ mol/L whatever the Cu content in the Hap sample and the composition of the solution. This
274 decrease reached 3 orders of magnitude after only 1 day, showing that the presence of sulfate or
275 nitrate ions did not affect significantly the apparent solubility of the neoformed phase. This result
276 was supported by speciation calculations, which showed similar distribution of uranium in all the
277 synthetic solutions. Indeed, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ was the predominant species in both 0.02 M
278 NaNO_3 and Na_2SO_4 solutions (87.5 and 93.4%, respectively).

279

280 **Table 4.** Composition of the synthetic solutions at equilibrium with the Hap-Cu with various
 281 Cu contents. Calculated saturation index of the solutions relative to meta-torbernite
 282 (S.I. MT) and autunite (S.I. AU) using Phreeqc associated to selected thermodynamic
 283 data^{21, 22, 38, 39, 44}.

x_{Cu}	C_U (initial) (mol/L)	pH eq	C_U eq (mol/L)	C_{Cu} eq (mol/L)	C_P eq (mol/L)	C_{Ca} eq (mol/L)	S.I. (MT)	S.I. (AU)
0.02 M Na₂SO₄								
0	$(0.91 \pm 0.01) \times 10^{-3}$	7.1 ± 0.1	$(0.7 \pm 0.2) \times 10^{-6}$	< D.L.	$(6.9 \pm 0.8) \times 10^{-6}$	$(1.10 \pm 0.02) \times 10^{-3}$	N.D.	3.21
0.44	$(0.91 \pm 0.01) \times 10^{-3}$	7.1 ± 0.1	$(2.1 \pm 0.8) \times 10^{-6}$	$(1.3 \pm 0.2) \times 10^{-6}$	$(7.3 \pm 0.5) \times 10^{-6}$	$(1.13 \pm 0.02) \times 10^{-3}$	3.31	3.39
1.15	$(0.91 \pm 0.01) \times 10^{-3}$	7.1 ± 0.1	$(0.9 \pm 0.2) \times 10^{-6}$	$(1.7 \pm 0.5) \times 10^{-6}$	$(13.9 \pm 0.3) \times 10^{-6}$	$(1.16 \pm 0.02) \times 10^{-3}$	3.79	3.75
1.59	$(0.91 \pm 0.01) \times 10^{-3}$	7.1 ± 0.1	$(0.5 \pm 0.3) \times 10^{-6}$	$(1.5 \pm 0.5) \times 10^{-6}$	$(12.3 \pm 0.7) \times 10^{-6}$	$(1.14 \pm 0.01) \times 10^{-3}$	3.04	3.11
0.02 M NaNO₃								
0	$(1.02 \pm 0.01) \times 10^{-3}$	7.2 ± 0.1	$(1.6 \pm 0.9) \times 10^{-6}$	< D.L.	$(9 \pm 1) \times 10^{-6}$	$(1.26 \pm 0.04) \times 10^{-3}$	N.D.	5.04
0.44	$(1.02 \pm 0.01) \times 10^{-3}$	7.2 ± 0.1	$(1.8 \pm 0.4) \times 10^{-6}$	$(1.5 \pm 0.2) \times 10^{-6}$	$(6.5 \pm 0.2) \times 10^{-6}$	$(1.19 \pm 0.02) \times 10^{-3}$	4.20	4.21
1.15	$(1.02 \pm 0.01) \times 10^{-3}$	7.2 ± 0.1	$(1.5 \pm 0.8) \times 10^{-6}$	$(1.5 \pm 0.4) \times 10^{-6}$	$(15 \pm 1) \times 10^{-6}$	$(1.23 \pm 0.01) \times 10^{-3}$	5.20	5.12
1.59	$(1.02 \pm 0.01) \times 10^{-3}$	7.2 ± 0.1	$(1.0 \pm 0.6) \times 10^{-6}$	$(1.0 \pm 0.3) \times 10^{-6}$	$(10 \pm 1) \times 10^{-6}$	$(1.23 \pm 0.01) \times 10^{-3}$	4.72	4.74
V105								
0	$(0.97 \pm 0.04) \times 10^{-6}$	4.2 ± 0.1	$(1.2 \pm 0.1) \times 10^{-7}$	< D.L.	$(4.7 \pm 0.4) \times 10^{-5}$	$(3.8 \pm 0.6) \times 10^{-3}$	N.D.	-1.30
0.44	$(0.97 \pm 0.04) \times 10^{-6}$	5.1 ± 0.1	$(0.28 \pm 0.03) \times 10^{-7}$	$(1.87 \pm 0.04) \times 10^{-4}$	$(1.1 \pm 0.1) \times 10^{-5}$	$(4.0 \pm 0.6) \times 10^{-3}$	1.49	-0.50
1.15	$(0.97 \pm 0.04) \times 10^{-6}$	4.5 ± 0.1	$(0.31 \pm 0.03) \times 10^{-7}$	$(1.70 \pm 0.04) \times 10^{-4}$	$(4.0 \pm 0.3) \times 10^{-5}$	$(3.9 \pm 0.6) \times 10^{-3}$	0.74	-1.47
1.45	$(0.97 \pm 0.04) \times 10^{-6}$	4.6 ± 0.1	$(0.29 \pm 0.04) \times 10^{-7}$	$(2.20 \pm 0.03) \times 10^{-4}$	$(4.0 \pm 0.3) \times 10^{-5}$	$(3.9 \pm 0.6) \times 10^{-3}$	1.03	-1.23
1.59	$(0.97 \pm 0.04) \times 10^{-6}$	4.8 ± 0.1	$(0.25 \pm 0.03) \times 10^{-7}$	$(1.69 \pm 0.08) \times 10^{-4}$	$(5.8 \pm 0.4) \times 10^{-5}$	$(4.1 \pm 0.6) \times 10^{-3}$	1.65	-0.42
BD200								
0	$(1.64 \pm 0.02) \times 10^{-6}$	7.6 ± 0.1	$(1.2 \pm 0.1) \times 10^{-7}$	< D.L.	$(4 \pm 1) \times 10^{-6}$	$(1.49 \pm 0.02) \times 10^{-3}$	N.D.	-0.98
0.44	$(1.64 \pm 0.02) \times 10^{-6}$	7.7 ± 0.1	$(2.4 \pm 0.2) \times 10^{-7}$	$(1.1 \pm 0.1) \times 10^{-6}$	$(2.6 \pm 0.8) \times 10^{-6}$	$(1.63 \pm 0.02) \times 10^{-3}$	-2.07	-1.16
1.15	$(1.64 \pm 0.02) \times 10^{-6}$	7.7 ± 0.1	$(1.3 \pm 0.2) \times 10^{-7}$	$(1.3 \pm 0.2) \times 10^{-6}$	$(5 \pm 1) \times 10^{-6}$	$(1.55 \pm 0.03) \times 10^{-3}$	-1.61	-0.81
1.45	$(1.64 \pm 0.02) \times 10^{-6}$	7.7 ± 0.1	$(0.7 \pm 0.1) \times 10^{-7}$	$(1.4 \pm 0.1) \times 10^{-6}$	$(11 \pm 1) \times 10^{-6}$	$(1.58 \pm 0.02) \times 10^{-3}$	-1.50	-0.70
1.59	$(1.64 \pm 0.02) \times 10^{-6}$	7.7 ± 0.1	$(1.5 \pm 0.2) \times 10^{-7}$	$(0.69 \pm 0.06) \times 10^{-6}$	$(5 \pm 1) \times 10^{-6}$	$(1.59 \pm 0.03) \times 10^{-3}$	-2.00	-1.03

284 U concentrations at equilibrium with BD200 and V105 measured by ICP-MS for BD200 and
 285 V105 and by ICP-AES for the other solutions. The uncertainties associated to the concentrations
 286 at equilibrium were estimated as the standard deviation between consecutive concentrations
 287 values that were not significantly different considering the experimental errors. < D.L.: below
 288 detection limit. N.D.: not determined.

289 In order to gain insights in the mechanism associated to the uranium uptake by Cu-Hap, the
 290 saturation indices (S.I.) with respect to uranium containing phases were calculated using the final
 291 concentrations and pH for the various experiments (pH eq and C_i eq, **Table 4**) and the Phreeqc
 292 software associated to selected thermodynamic data^{21, 22, 38, 39, 44}. Positive S.I. values indicate that

293 the bulk solution is oversaturated with respect to the phase of interest, thus that precipitation of
294 the phase may occur.

295 For near neutral pH values, the synthetic solutions were found to be highly oversaturated
296 with respect to meta-autunite and meta-torbernite. The calculated S.I. of these two phases were
297 very close and did not allow to conclude which precipitation is privileged in the bulk solution. At
298 the end of these experiments, it is worth noting that the synthetic solutions were close to
299 equilibrium or slightly oversaturated with respect to hydroxyapatite⁴⁹ (S.I. (Hap) varying from -
300 0.35 to 2.17).

301 For BD200 mining water (pH eq = 7.7), the S.I. with respect to meta-torbernite and
302 autunite were negative, which indicated that precipitation in the bulk solution was not the driving
303 mechanism for uranium removal from solution. At the end of the experiments performed in
304 BD200, the solutions remained highly oversaturated with respect to hydroxyapatite, with S.I.
305 ranging from 4.7 to 6.5. The fact that the Cu-Hap was not dissolved in BD200 also argued in
306 favor of adsorption or surface precipitation caused by local saturation as the most likely
307 mechanisms.

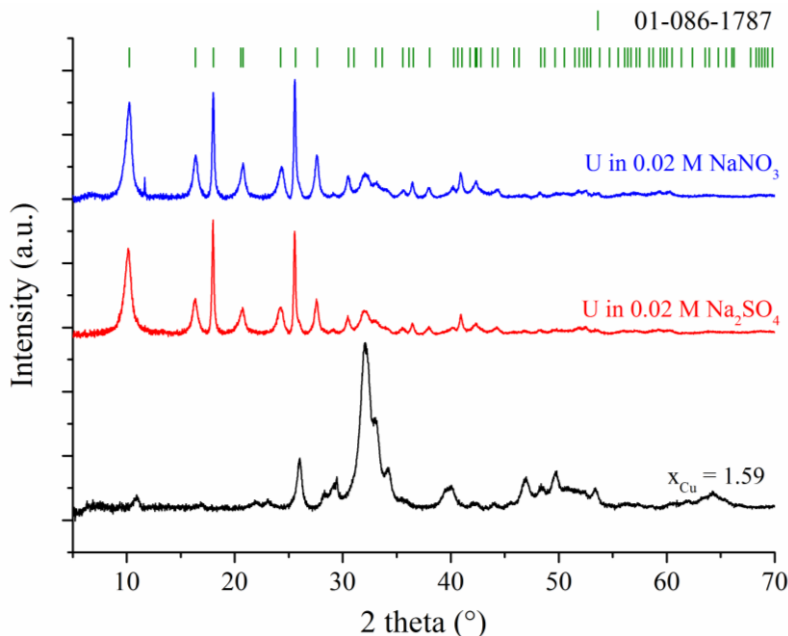
308 For V105 mining water (pH eq < 5), meta-torbernite was the only uranium bearing phase
309 with positive S.I. at the end of experiments. Also, the solutions remained highly undersaturated
310 with respect to hydroxyapatite with S.I. ranging from -12.4 to -7.9. In such acidic solution, Cu-
311 Hap was dissolved whereas meta-torbernite was precipitated in the bulk solution, leading to the
312 immobilization of uranium.

313 **3.3. Characterization of neoformed phases**

314 At the end of the batch experiments, solid and liquid phases were separated by
315 centrifugation and the solid phase was characterized systematically by PXRD. As an example,

316 the patterns recorded for the Cu-Hap with $x_{\text{Cu}} = 1.59$ contacted with the sodium nitrate and
317 sodium sulfate solutions spiked with uranyl are presented in **Figure 4**. The PXRD patterns
318 recorded for the Cu-Hap sample contacted with the synthetic solutions presented characteristic
319 peaks of a mixture of Hap and chernikovite (for $x_{\text{Cu}} = 0$) or meta-torbernite (for $x_{\text{Cu}} > 0$). These
320 patterns were refined by the Rietveld method to quantify the weight fraction of uranium bearing
321 phase in the mixture of crystalline phases (**Table 5**). All the samples exposed to the synthetic
322 solutions spiked with uranium at 10^{-3} mol/L presented high weight fraction of uranium (from 24
323 to 29 wt. %). The uranium loading calculated from the refinement of the PXRD patterns of the
324 remaining solid phase was found to be lower or close to the uranium weight fraction calculated
325 from the decrease of the uranium concentration in solution. This result indicated that a major part
326 of uranium (from 55 to 100 %) was uptaken from the solution by precipitation in a crystalline
327 phase. For Cu-undoped Hap structure, the neoformed phase was chernikovite (also called H-
328 autunite). It was also observed in the uranium phase precipitates by Fanizza et al.³, Lammers et
329 al.¹⁴, and Fuller et al.⁵. Simon et al.¹² reported the formation of chernikovite in mixtures with
330 autunite and meta-autunite. Mehta et al.⁶ also reported its formation in the absence of Ca or Na
331 co-solutes. Lingjun Kong et al.¹⁶, as well as Minhua Su et al.¹⁷ observed the incorporation of
332 U(VI) ions into autunite after removal from mining water by biochar Hap and porous Hap,
333 respectively. It is noteworthy that meta-autunite is the thermodynamically stable phase in our
334 conditions, but the formation of chernikovite is reported to be kinetically favored^{6, 12, 50}. Fuller et
335 al.⁵ determined a threshold for the onset of chernikovite formation. Below 0.58 ± 0.08 wt. % of
336 uranium loading (i.e. $0.44 \mu\text{mol}/\text{m}^2$ of uranium at the surface of Hap), the mechanism of sorption
337 is dominated by surface complexation. Above this limit, nucleation of chernikovite occurs either
338 at the Hap surface or in the bulk solution. Finally, depending on the composition of solution and

339 time, chernikovite can be transformed to meta-autunite by cationic exchange. For the synthetic
340 spiked solutions, U loadings of the Hap were much higher than the threshold authorizing
341 precipitation of chernikovite. Immobilization of uranium contacted with the Cu-Hap could have
342 followed a similar sorption mechanism. However, due to the presence of copper, meta-torbernite
343 was the uranium solubility controlling phase.



344
345 **Figure 4.** PXRd patterns of Cu-Hap sample ($x_{Cu} = 1.59$) before (black line) and after contact
346 with 0.02 M Na_2SO_4 (red line) and $NaNO_3$ (blue line) solutions doped with uranium
347 ($\sim 10^{-3}$ mol/L). The green bars correspond the Bragg positions obtained for meta-
348 torbernite (PDF 01-086-1787).

349 The PXRd patterns recorded for Cu-Hap samples contacted with V105 and BD200 mining
350 waters are gathered in the supporting information (**Figure S4**). The PXRd patterns recorded at
351 the end of the batch experiments were similar to the XRD diagram of the starting Cu-Hap.
352 Considering the low amount of U immobilized in the solid phase (**Table 5**), the weight fraction
353 of any precipitated crystalline phase would be too low to be identified by PXRd, except for the
354 sample corresponding to $x_{Cu} = 1.45$ and contacted with V105. Raman spectroscopy was used to

355 characterize the solid phase at the end of the batch experiments. In order to illustrate the results,
356 Raman spectra obtained for Cu-Hap samples ($x_{\text{Cu}} = 1.45$) contacted with V105 and BD200
357 mining waters are compared to the Raman spectrum of the synthetic meta-torbernite (**Figure S5**).
358 This comparison did not show the presence of the characteristic bands of meta-torbernite.
359 Especially, the very intense band ascribed to the symmetric stretching vibration of UO_2^{2+} at 826
360 cm^{-1} ⁵¹ was not observed in the Raman spectra of Cu-Hap samples contacted with mining waters.
361 These techniques are not sensitive enough to give insights into the mechanism of uranium
362 removal from the mining waters.
363

364 **Table 5.** Uranium loading of the solid phase calculated from C_U decrease in solution at
 365 equilibrium (by m^2 , mol or mass of Cu-Hap introduced in the batch experiment) and
 366 calculated from Rietveld refinement of the PXRD patterns of the solid phase after
 367 exposure to spiked synthetic solutions ($C_U \sim 10^{-3}$ mol/L) and mining waters ($C_U \sim 10^{-6}$
 368 mol/L). Summary of SEM observations of the samples.

x_{Cu}	From U analysis in solution			From solid phase characterizations			
	U loading $\mu\text{moles}/m^2$	U loading mol. %	U loading wt. %	U-phase wt. % XRD	Phase identified by XRD	U loading wt. % XRD	SEM
0.02 M Na₂SO₄							
0	12.8 ± 0.1	103 ± 1	24 ± 1	32 ± 1	H ₃ O(UO ₂)(PO ₄) ₂ ·3H ₂ O	20 ± 1	TP
0.44	12.1 ± 0.1	105 ± 1	25 ± 1	24 ± 2	Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	14 ± 1	TP
1.15	7.2 ± 0.1	108 ± 1	25 ± 1	30 ± 1	Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	18 ± 1	TP
1.59	16.3 ± 0.1	110 ± 1	25 ± 1	54 ± 1	Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	32 ± 1	TP+s
0.02 M NaNO₃							
0	14.6 ± 0.1	117 ± 1	28 ± 1	29 ± 1	H ₃ O(UO ₂)(PO ₄) ₂ ·3H ₂ O	18 ± 1	TP
0.44	13.7 ± 0.1	118 ± 1	28 ± 1	22 ± 1	Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	13 ± 1	TP
1.15	8.1 ± 0.1	123 ± 1	28 ± 1	40 ± 1	Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	24 ± 1	TP
1.59	18.5 ± 0.1	125 ± 1	29 ± 1	45 ± 1	Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	27 ± 1	TP
BD200*							
0	0.07 ± 0.01	0.6	0.13	< D.L.			TP
0.44	0.06 ± 0.01	0.5	0.12	< D.L.			TP
1.15	0.04 ± 0.01	0.6	0.13	< D.L.			TP
1.45	0.08 ± 0.01	0.6	0.14	< D.L.			TP+s
1.59	0.08 ± 0.01	0.6	0.13	< D.L.			TP
V105*							
0	0.04 ± 0.01	0.3	0.07	< D.L.			s
0.44	0.04 ± 0.01	0.3	0.07	< D.L.			S
1.15	0.02 ± 0.01	0.3	0.07	< D.L.			S
1.45	0.04 ± 0.01	0.3	0.07	2 ± 1	Cu(UO ₂) ₂ (PO ₄) ₂ ·8H ₂ O	1.2 ± 1	S
1.59	0.05 ± 0.01	0.3	0.07	< D.L.			S

369 < D.L.: below detection limit. H₃O(UO₂)(PO₄)₂·3H₂O: chernikovite (PDF 01-075-1106);
 370 Cu(UO₂)₂(PO₄)₂·8H₂O: meta-torbernite (PDF 01-086-1787).

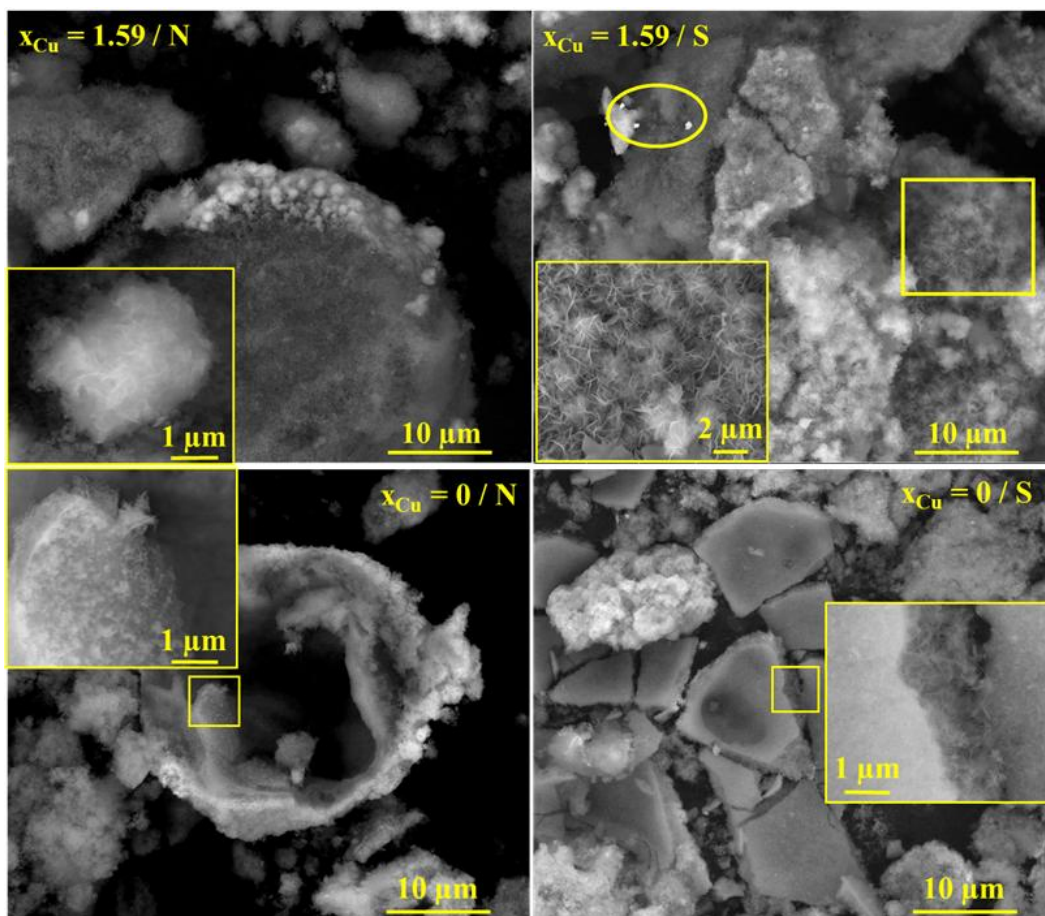
371 *Analyses of uranium concentrations at equilibrium performed by ICP-MS. TP: thin platelets
 372 covering Cu-Hap observed by SEM, s: presence of small square-shaped crystals (less than 1×1
 373 μm^2) observed by SEM, S: presence of large square-shaped crystals (more than 3×3 μm^2)
 374 observed by SEM.

375 In order to confirm the precipitation of uranium from the synthetic doped solutions either
376 as chernikovite (for $x_{Cu} = 0$), or as meta-torbernite (for $x_{Cu} > 0$), SEM micrographs were recorded
377 in the backscattered electron mode. The micrographs presented in **Figure 5** showed the presence
378 of Cu-Hap agglomerates covered by thin platelets showing a strong backscattered emission
379 indicative of uranium. X-EDS maps (supporting information, **Figure S6**) evidenced the
380 precipitation of uranium as secondary phase at the surface of Cu-Hap, which confirms the
381 uranium uptake from the synthetic solutions spiked with $C_U \sim 10^{-3}$ mol/L. Additionally, the
382 presence of bright platy squared-shape crystals of $0.5 \times 0.5 \mu m^2$ in size was identified for Cu-Hap
383 contacted with synthetic sulfate solution ($x_{Cu} = 1.59$, see $x_{Cu} = 1.59 / S$ in **Figure 5**). This
384 morphology was characteristic of crystals of the autunite family^{5, 16, 19, 22, 52}.

385 For Cu-Hap samples contacted with the BD200 mining water, U was not detected by X-
386 EDS. However, backscattered images showed the presence of thin platelets covering the surface
387 of agglomerates of Cu-Hap particles (**Figure 6**). In the samples contacted with V105, the
388 presence of bright and platy squared-shape crystals was systematically observed (**Figure 6**). The
389 crystals reached 2 to 4 μm in size for Cu-Hap compared to 0.5 μm for non-substituted Hap ($x_{Cu} =$
390 0). U, P, Ca, Cu and Al were detected by X-EDS in the squared-shape grains. Although the
391 quantification of the mass content of each element in the square-shaped crystals was difficult due
392 to the vicinity of Cu-Hap particles, U elemental content was found to vary between 40 wt.% (for
393 $x_{Cu} = 0$) and 62 wt. % for ($x_{Cu} = 1.59$), which was consistent with the precipitation of either
394 chernikovite, autunite or meta-torbernite phases.

395 The different morphologies of uranium bearing phase observed for the samples contacted
396 with V105 and BD200 mining waters could indicate the existence of different immobilization
397 mechanisms for uranium. This assumption was strengthened by the values of saturation index

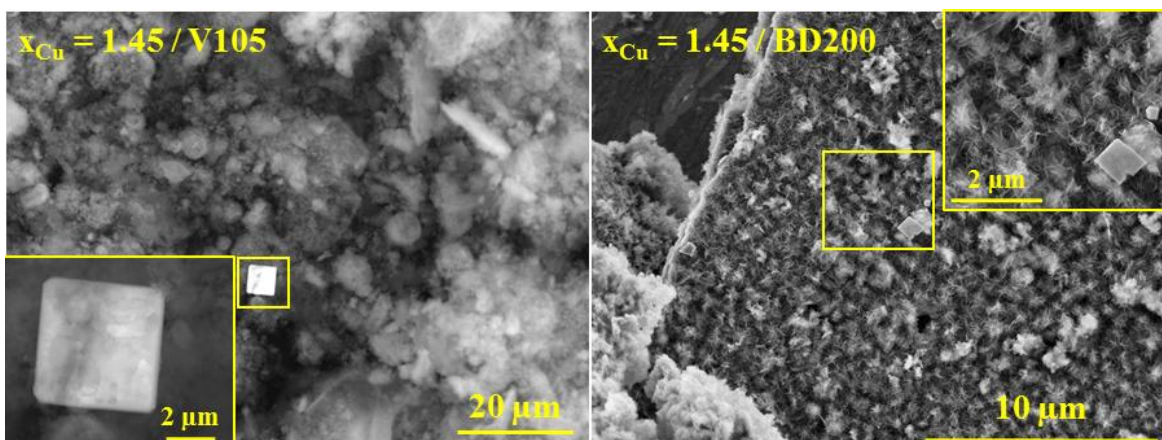
398 calculated for the bulk solution (**Table 4**). Indeed, positive saturation indexes was found for
399 meta-torbernite at the end of experiments for Cu-Hap contacted with V105, whereas negative
400 saturation indexes were determined for meta-torbenite and autunite for Cu-Hap contacted with
401 BD200. The main reason for this discrepancy was due to differences of the pH value, which was
402 much lower for V105 than for BD200. During the experiments with V105, such pH favored the
403 dissolution of the Cu-Hap and finally led to the strong increase of the Ca, Cu and P
404 concentrations in the solution. This allowed the establishment of oversaturated conditions in the
405 bulk solution with respect to meta-torbernite even for low uranium concentration in solution. On
406 the contrary, for experiments with BD200, the formation of thin platelet crystals could result
407 from local oversaturation when U, P, Ca and/or Cu concentrations were higher at the Cu-Hap
408 surface than in the bulk. A similar mechanism was evidenced by Ohnuki et al.²⁸. It was called
409 surface mineralization. Nevertheless, the presence of brighter thin platelets could also result from
410 uranium sorption phenomena onto the surface of Cu-Hap, as already evidenced by Fuller et al.⁵
411 for Hap using low uranium loadings.



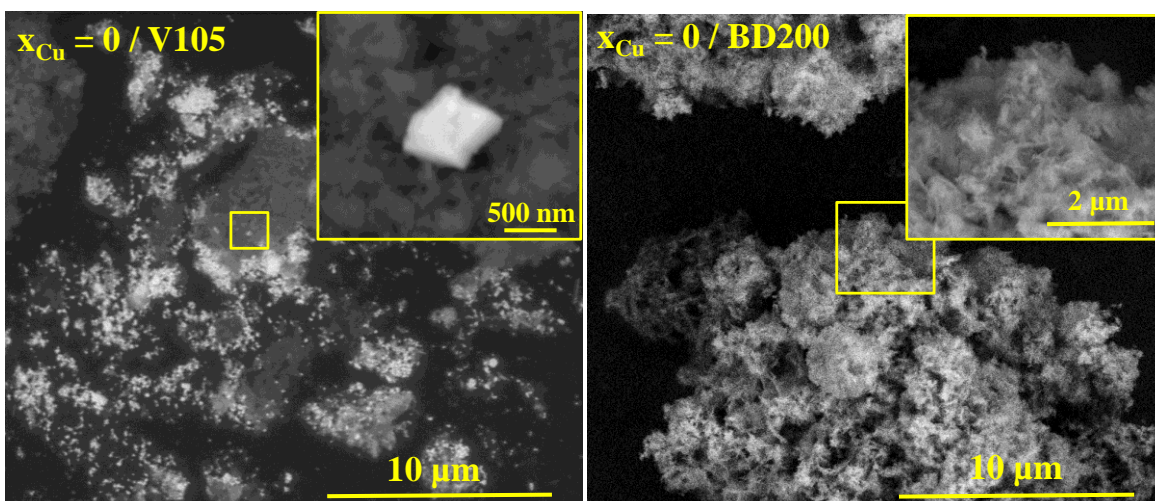
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413 **Figure 5.** SEM micrographs (backscattered electron mode) of Cu-Hap resulting from the
 414 contact with synthetic solutions doped with uranyl ($C_U \sim 10^{-3}$ mol/L), showing the
 415 presence of very thin platelets covering the Cu-Hap surfaces (bright areas). The
 416 yellow-circled zone highlights the presence of square-shaped uranium bearing
 417 crystals.

418



419



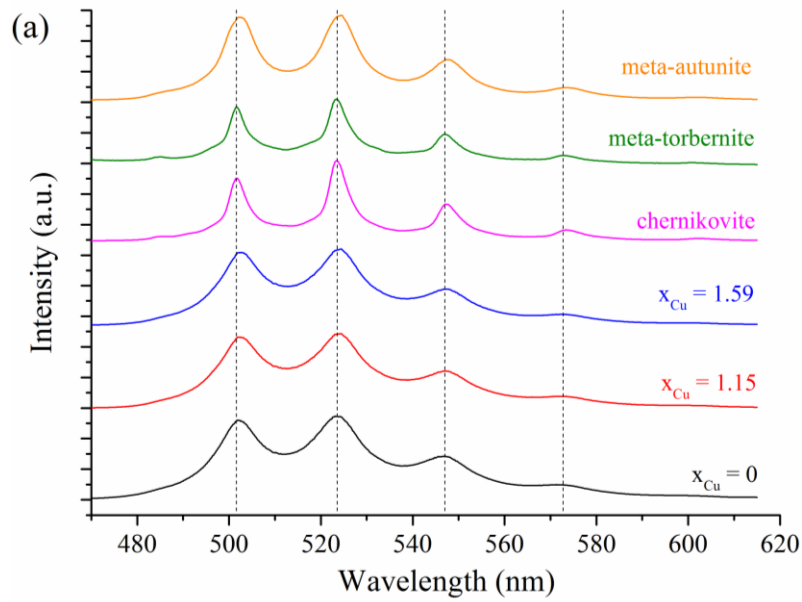
420
 421 **Figure 6.** SEM micrographs of Cu-Hap ($x_{\text{Cu}} = 1.45$) resulting from contact with mining waters
 422 V105 and BD200 (backscattered electron mode, except for $x = 1.45$ / BD200)
 423 containing uranyl ($C_{\text{U}} \sim 10^{-6}$ mol/L). The images at high magnifications highlights
 424 the presence of square-shaped uranium bearing crystals of various sizes.
 425

426 The TRLFS spectra of Cu-Hap samples at the end of the batch experiments are reported in
 427 **Figure 7.** All the spectra were characteristic of the luminescence of U(VI) compounds, with the
 428 observation of the five main peaks in the 480-600 nm range. The fluorescence spectra of the
 429 samples contacted with the synthetic solutions of uranyl in Na_2SO_4 (**Figure 7 a**) or NaNO_3
 430 (**Figure 7 b**) synthetic solutions were all similar whatever the Cu content. These spectra were
 431 also comparable, in terms of peak locations, to the spectra recorded for synthesized meta-
 432 autunite, meta-torbernite and chernikovite (peaks positions and FWHM are gathered in **Table S1**
 433 of the supporting information). The larger peak widths in the sample spectra probably suggested
 434 a lower degree of crystallinity or different crystal shapes. TRLFS hardly distinguished meta-
 435 torbernite from chernikovite, which appears in agreement with previous recordings on
 436 chernikovite⁵³ and meta-torbernite minerals⁵⁴. It can be inferred that the luminescence of U(VI)
 437 in both minerals is similar due to the very similar local environment of uranyl in both

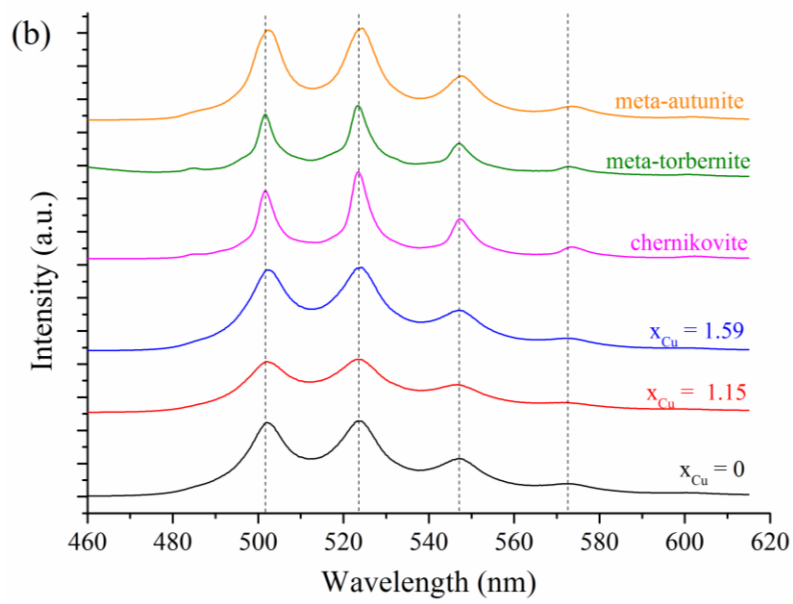
438 structures⁵⁵⁻⁵⁷. As a matter of fact, regardless of the Cu content in the Cu-Hap, the fluorescence
439 spectra suggest the precipitation of an uranium-bearing phase from the autunite family.

440 The spectra of Cu-Hap samples contacted with the mining waters differed from the
441 previous ones (**Figure 7 c**). It is noteworthy that the intensity of the TRFLS signal was much
442 lower than for the samples contacted with synthetic solutions due to lower uranyl loading (**Table**
443 **5**). The positions of the maximum of the peaks were shifted towards the lower wavelengths by
444 about 5 and 2 nm for the samples contacted with V105 and BD200, respectively. For
445 experiments developed with V105, no significant change in the peak position was observed with
446 increasing x_{Cu} . This suggests that the local structure around U(VI) was not significantly different.
447 For BD200, the fluorescence signal was only detected for $x_{\text{Cu}} = 0$. Because U loading is similar
448 in all the samples contacted with BD200, the absence of signal for $x_{\text{Cu}} > 0$ could be due to the
449 existence of fluorescence quenching effects. Cu^{2+} , among other metal cations, is well known to
450 be a quencher of the U(VI) luminescence in solution⁵⁸. The precise assignment of the spectra
451 recorded for Cu-Hap samples contacted with V105 and BD200 is difficult. It confirms that the
452 mechanism of interaction may be different to that observed when Cu-Hap was contacted with
453 synthetic uranyl solutions.

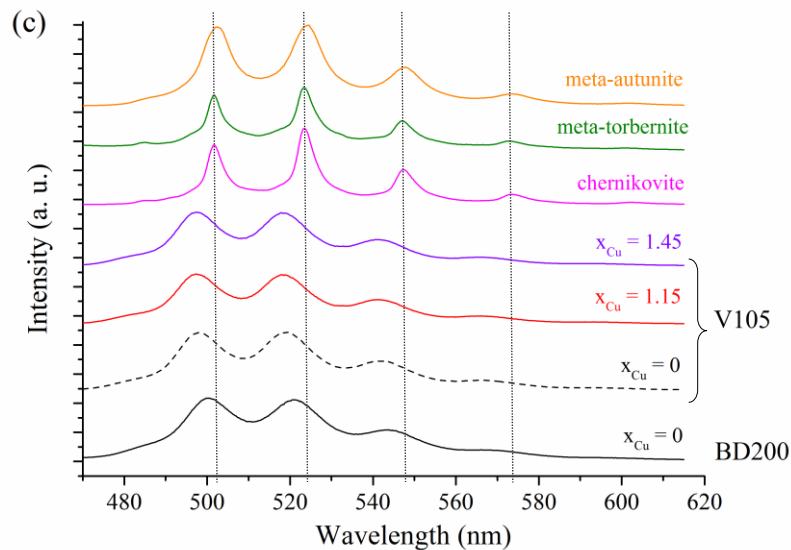
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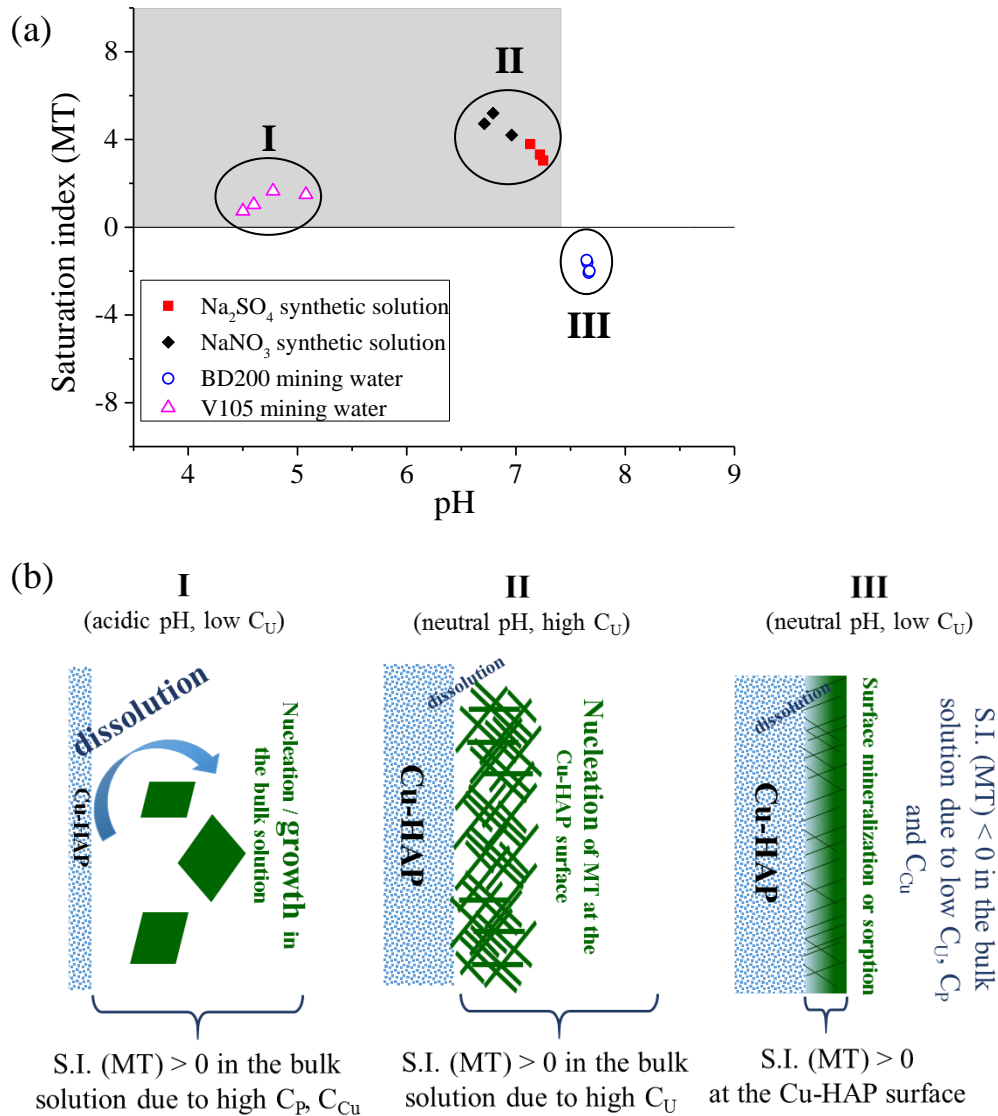
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458 **Figure 7.** TRLFS spectra of Cu-Hap samples resulting from contact with 0.02 M Na₂SO₄ (a);
 459 and 0.02 M NaNO₃ (b) synthetic solutions; with BD200 and V105 mining waters (c).
 460 The spectra are compared with reference spectra obtained for synthetic meta-
 461 torbernite, meta-autunite and chernikovite⁵⁹. Dotted lines indicate the position of the
 462 maximum of the peaks for the meta-torbernite reference.
 463

464 3.4.ENVIRONMENTAL IMPLICATIONS

465 This study demonstrated that Cu-Hap was effective in lowering U concentration when
 466 contacting with synthetic solutions or real mining waters. These results showed the high
 467 reactivity of the prepared Cu- Hap, which was associated to its poor crystallinity and high
 468 specific surface area. Furthermore, the potential carbonate substitution for OH⁻ and PO₄³⁻ in the
 469 Hap lattice is known to increase its solubility and thus its global reactivity^{60, 61}. Thus, this
 470 material appears as promising in the field of passive treatment devices such as permeable
 471 reactive barriers for mining water remediation. Depending on the initial pH and C_U of the mining
 472 or doped solutions, several processes were evidenced to support the uranium uptake (**Figure 8**).
 473 First, the precipitation of meta-torbernite actually occurred when the bulk solution was
 474 oversaturated (case I and II). For V105 (case I), the low pH of the mining water led to the

475 increase of the Cu-Hap solubility. As the S.I. of the bulk solution remained close to equilibrium,
476 the growth of MT crystals was favored. In the second case (synthetic solutions at near neutral
477 pH, case II), oversaturated conditions were reached due to the high uranium concentrations
478 whereas the low solubility of Cu-Hap led to low Cu and P concentrations in solution. As the S.I.
479 of the solutions were highly positive, the nucleation rate was high especially close to the
480 solid/solution interface, leading to the formation of clusters of small crystals covering the surface
481 of the Cu-Hap. These experimental results indicated that precipitation of meta-torbernite can be
482 considered as a potential effective strategy to remove uranium from contaminated water
483 contacted with Cu-Hap. For BD200 mining water (case III), the mechanism for U removal was
484 only speculative. As the bulk solution remained undersaturated, adsorption^{4, 5, 12, 15}, incorporation
485 in the Cu-Hap structure²⁸ or combination of both processes⁷ were likely to occur.



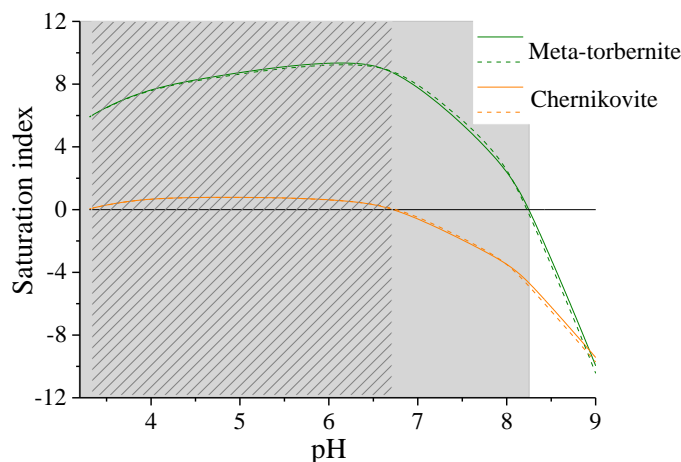
486

487 **Figure 8.** Saturation index of the synthetic solutions and mine waters with respect to meta-
 488 torbernite obtained at the end of the batch experiments after contact with Cu-Hap (a).
 489 Schematic representation of the three potential processes associated to the uranium
 490 uptake (b).

491

492 In the absence of Cu and as evidenced by several authors, chernikovite is the precipitating
 493 uranium-bearing phase. In order to illustrate the interest of incorporating copper in the Hap,
 494 simulations were performed with synthetic 0.02 M NaNO₃ and 0.02 M Na₂SO₄ solutions doped
 495 with 7.6 μM of uranium, which corresponds to the current French regulatory limit for water

496 discharges in the environment. Ca, Cu and P concentrations were calculated by dissolving Cu-
497 Hap with $x_{\text{Cu}} = 1.45$ until the solubility of Hap⁴⁹ was reached. Using the same selected
498 thermodynamic data^{21, 22, 38, 39, 44}, the S.I. were calculated in the solutions with respect to meta-
499 torbernite and chernikovite, for pH range representative of most of the mining waters. From
500 these calculations, it is clear that the pH range associated to the precipitation of meta-torbernite is
501 larger than for chernikovite (**Figure 9**). Especially, for $6.7 \leq \text{pH} \leq 8.2$, the solution remained
502 oversaturated regarding to meta-torbernite whereas it was undersaturated regarding to
503 chernikovite. Moreover, meta-torbernite was the most stable phase in the whole pH range. For all
504 the conditions examined, the simulations demonstrated that the precipitation of meta-torbernite
505 could occur in solutions contacted with Cu-Hap, leaving uranium concentration below the
506 regulatory limit in a wide pH range.



507
508 **Figure 9.** Variation of the saturation index relative to meta-torbernite (MT) and chernikovite
509 (CH) versus pH obtained for a synthetic solution doped with 7.6 μM of uranium.
510 Continuous and dashed lines correspond to 0.02 M NaNO_3 and 0.02 M Na_2SO_4
511 solution, respectively. Gray and hatched areas show the pH range for precipitation of
512 MT and CH, respectively.

513 To conclude, the main interest for using Cu-Hap is to enlarge the domain of water
514 compositions for which the precipitation of uranyl phosphate is the predominant mechanism

515 associated to the uranium removal, especially for $\text{pH} > 6.7$ where carbonate uranium species are
516 predominant in the speciation diagrams and $\text{pH} < 3.3$. Fast kinetics of precipitation associated
517 with large field of stability of the meta-torbernite made the formation of meta-torbernite crystals
518 less sensitive to the uranium speciation than for chernikovite or meta-autunite. This mechanism
519 of uranium immobilization led to the formation of crystals, highly enriched in uranium, which
520 could be separated afterwards from the Cu-Hap matrix (e.g. through differential sedimentation).
521 Using this kind of separation process could strongly reduce the amount of contaminated waste to
522 be treated or stored.

523

524 **Supporting Information.** Figure S1 to S6 and Table S1 are available in the supporting
525 information file.

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532

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