Uranium removal from mining water using Cu substituted hydroxyapatite: Supporting information.

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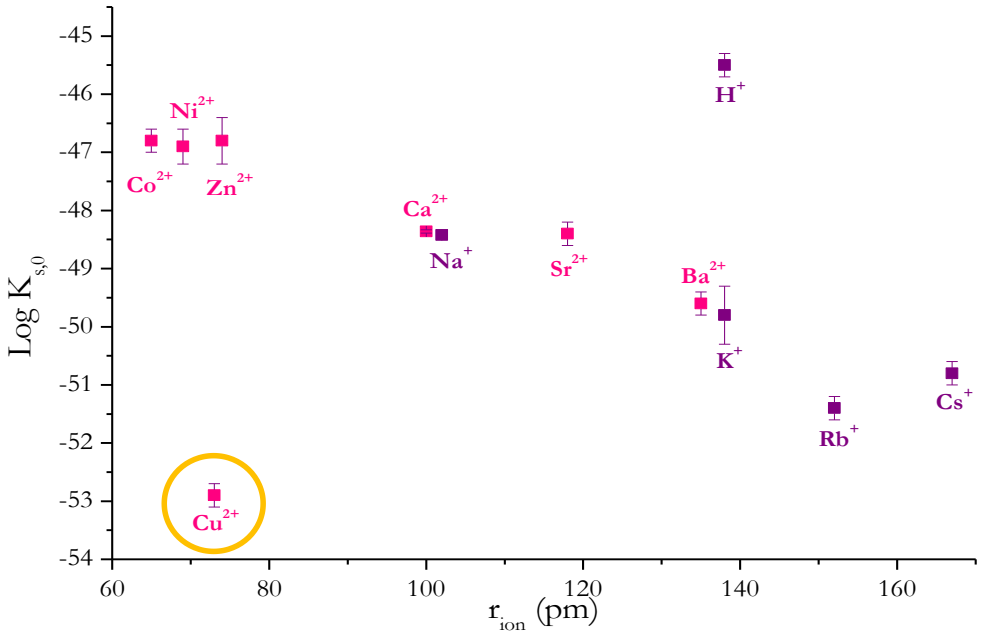


Figure S1. Variation of the standard solubility product $K_{s,0}$ (298.15 K) of phases from the autunite family, $M^{II}(UO_2)_2(PO_4)_2 \cdot xH_2O$ or $M^{I}_2(UO_2)_2(PO_4)_2 \cdot xH_2O$ versus the ionic radius of the incorporated cation.

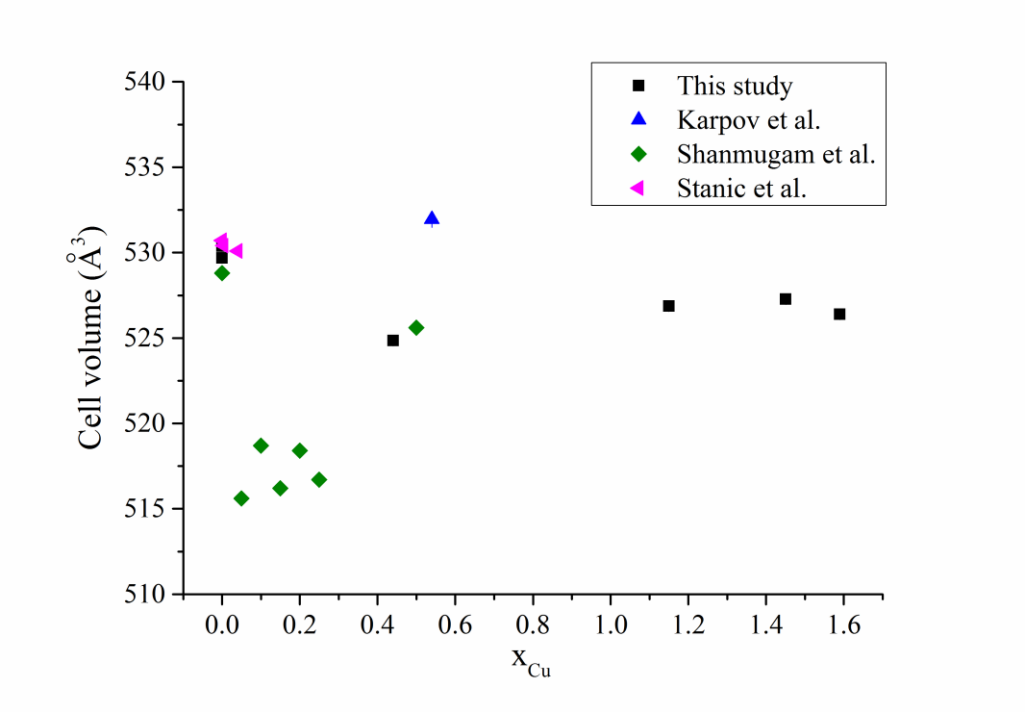
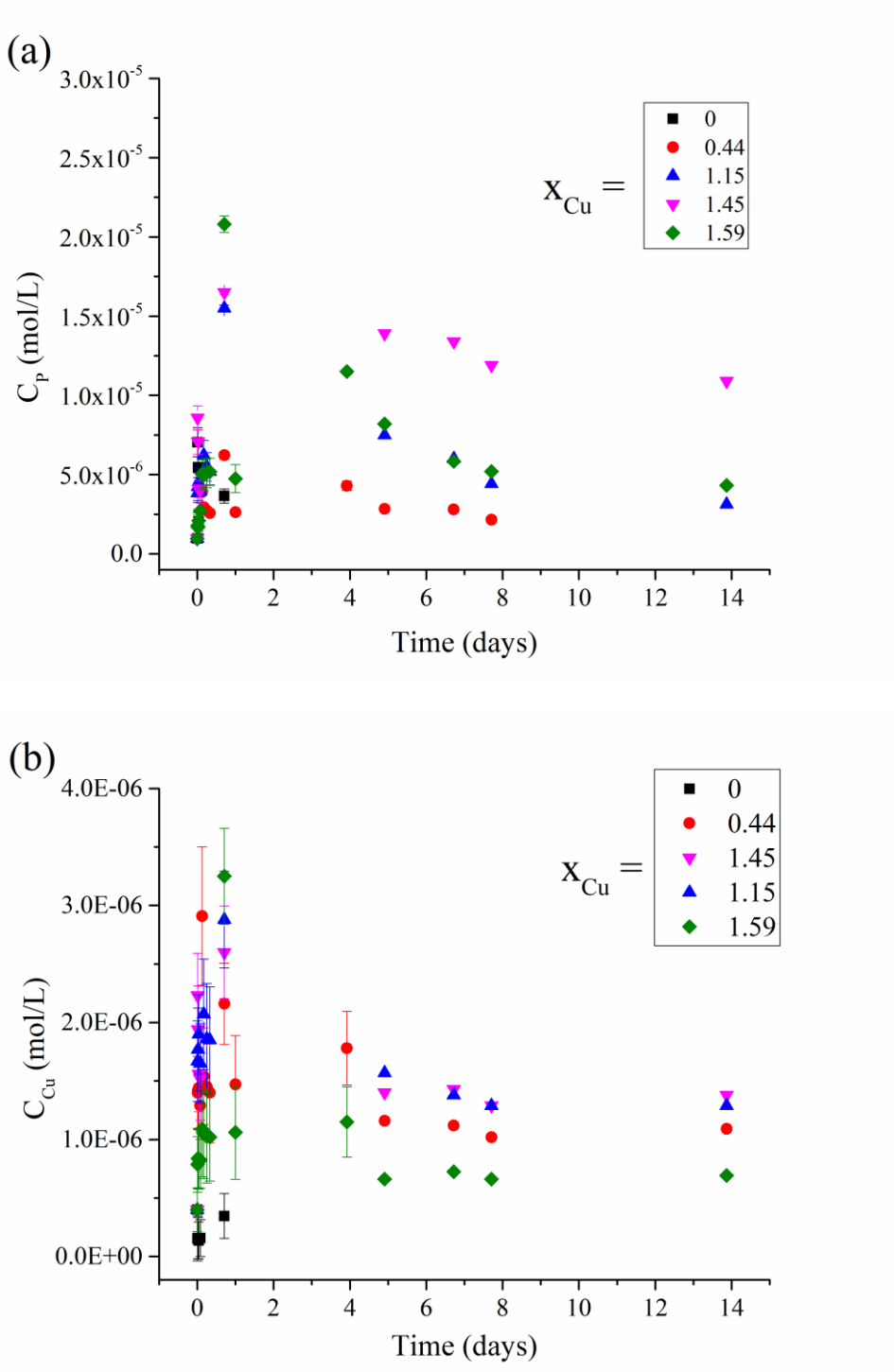


Figure S2. Variation of the cell volume of the Cu-HAP determined by Rietveld refinement of the PXRD patterns. Comparison of the results obtained in this study with [1-4].


(a)
3.0x10-5
2.5x10-5
2.0x10-5
1.5x10-5
1.0x10-5
5.0x10-6
0.0
Cp (mol/L)
0
2
4
6
8
10
12
14
Time (days)
xCu =
0
0.44
1.15
1.45
1.59
(b)
4.0E-06
3.0E-06
2.0E-06
1.0E-06
0.0E+00
CCu (mol/L)
0
2
4
6
8
10
12
14
Time (days)
xCu =
0
0.44
1.45
1.15
1.59

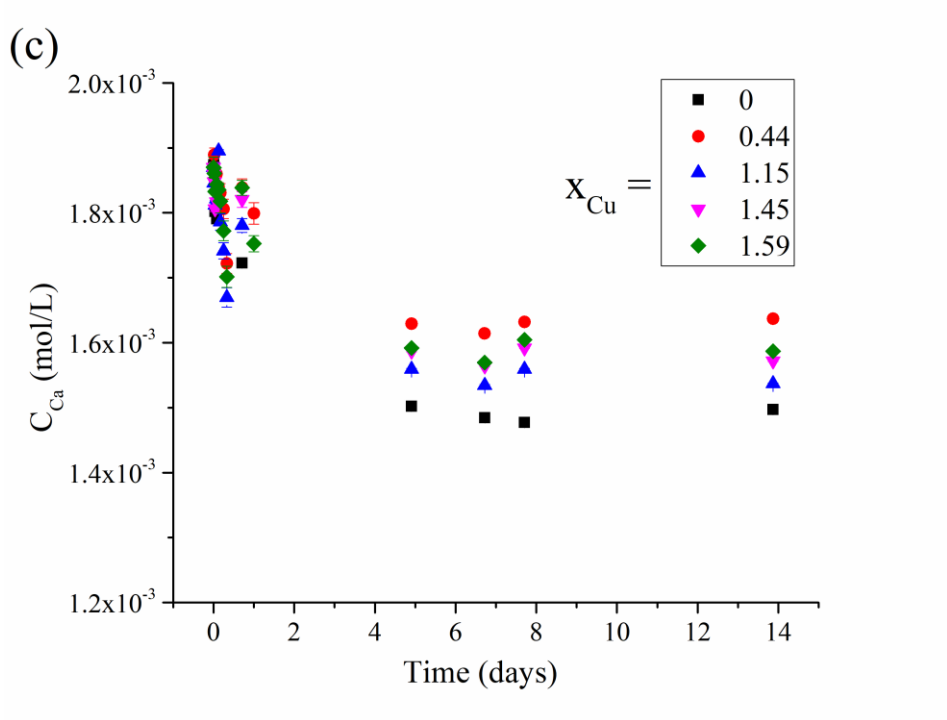
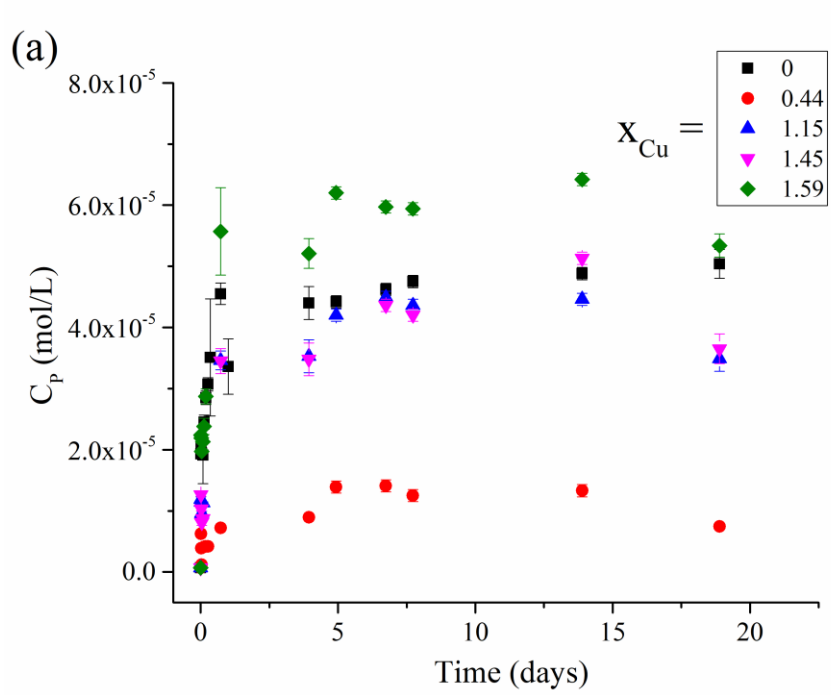
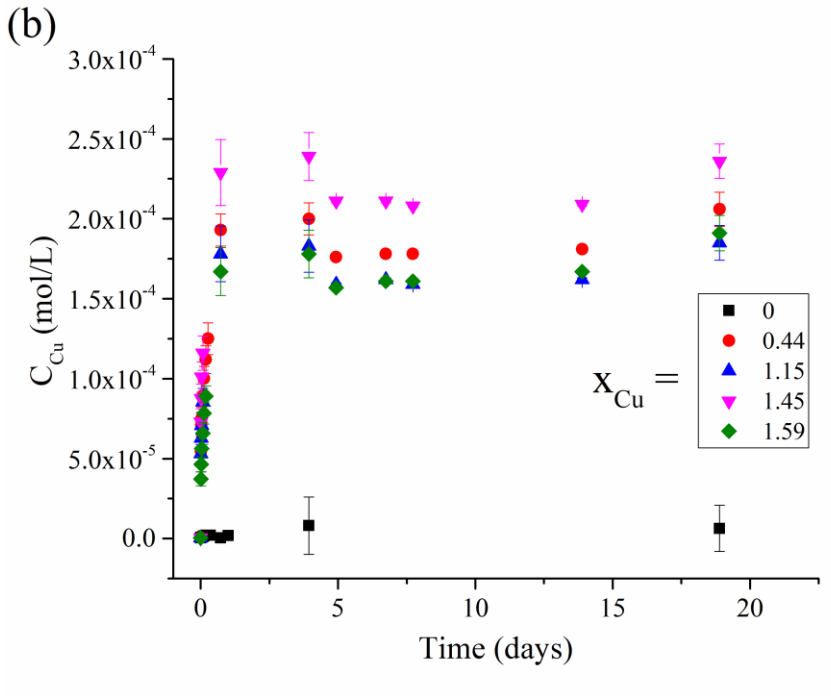


Figure S3. Evolution of the P (a); Cu (b) and Ca (c) elemental concentrations in BD200 mining waters when contacting with the different prepared Cu-Hap samples.


(a)
8.0x10-5
6.0x10-5
4.0x10-5
2.0x10-5
0.0
Cp (mol/L)
0
5
10
15
20
Time (days)
xCu =
0
0.44
1.15
1.45
1.59


(b)
3.0x10-4
2.5x10-4
2.0x10-4
1.5x10-4
1.0x10-4
5.0x10-5
0.0
CCu (mol/L)
0
5
10
15
20
Time (days)
xCu =
0
0.44
1.15
1.45
1.59

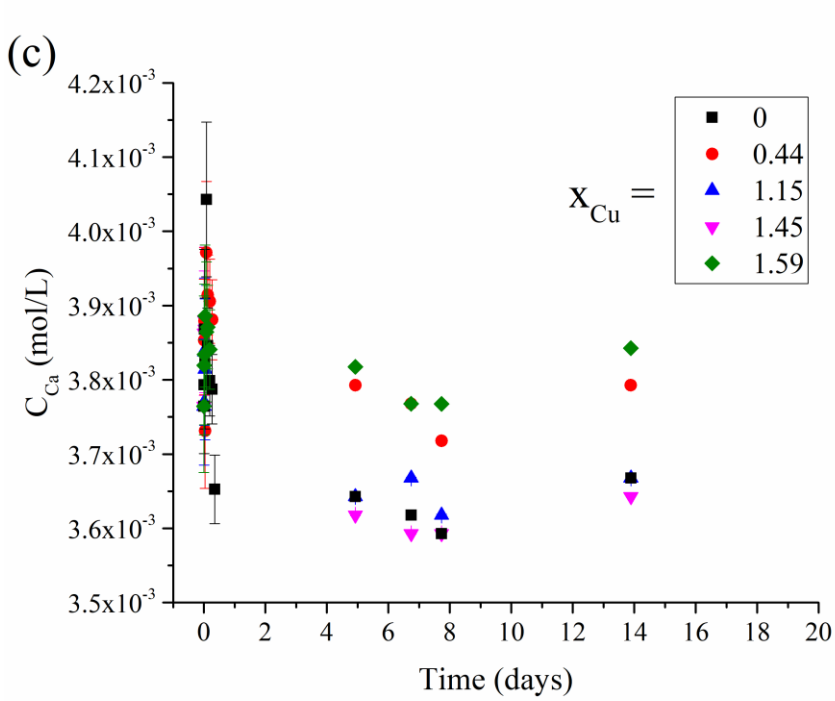
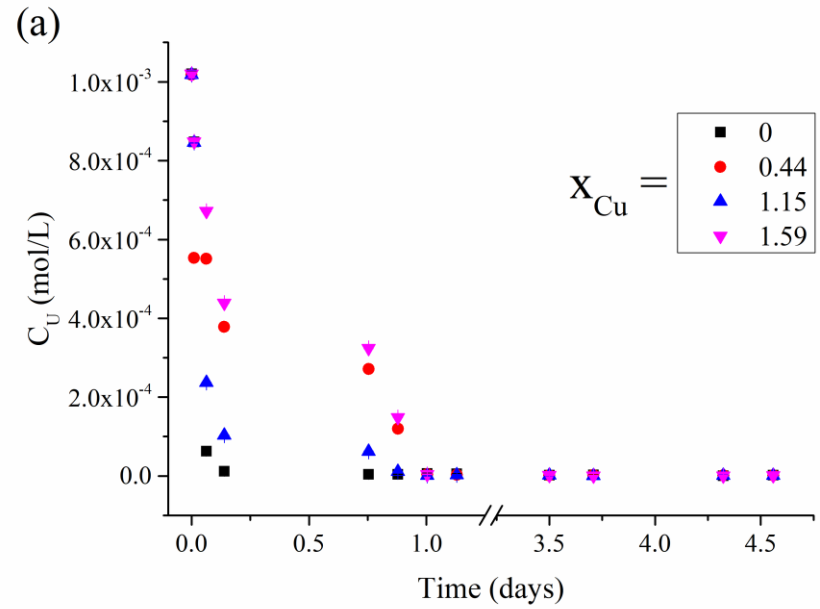
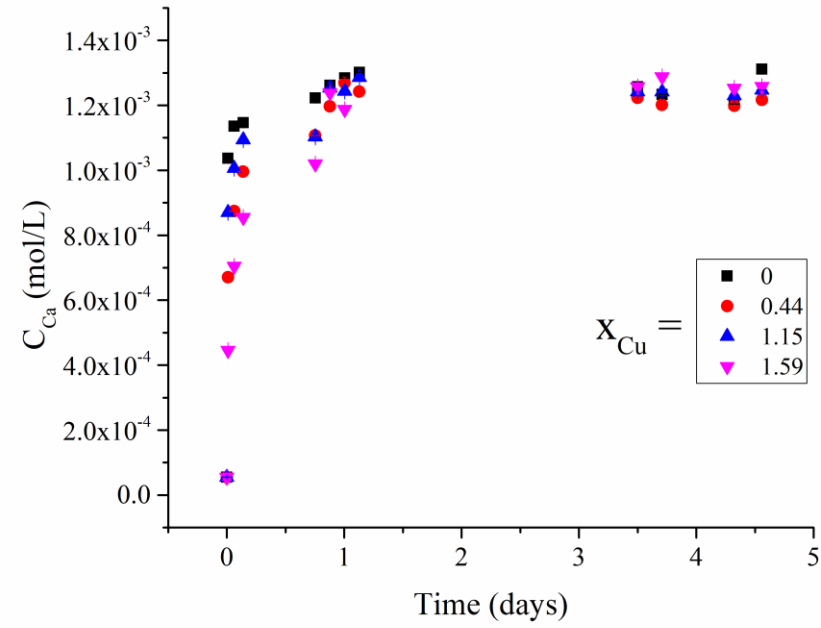


Figure S4. Evolution of the P (a), Cu (b) and Ca (c) elemental concentrations in V105 mining waters when contacting with the different prepared Cu-Hap samples. Ca elemental concentration were

(a)


1.0x10-3
8.0x10-4
6.0x10-4
4.0x10-4
2.0x10-4
0.0
CU (mol/L)
0.0
0.5
1.0
3.5
4.0
4.5
Time (days)
xCu =
0
0.44
1.15
1.59

(b)


1.4x10-3
1.2x10-3
1.0x10-3
8.0x10-4
6.0x10-4
4.0x10-4
2.0x10-4
0.0
CCa (mol/L)
0
1
2
3
4
5
Time (days)
xCu =
0
0.44
1.15
1.59

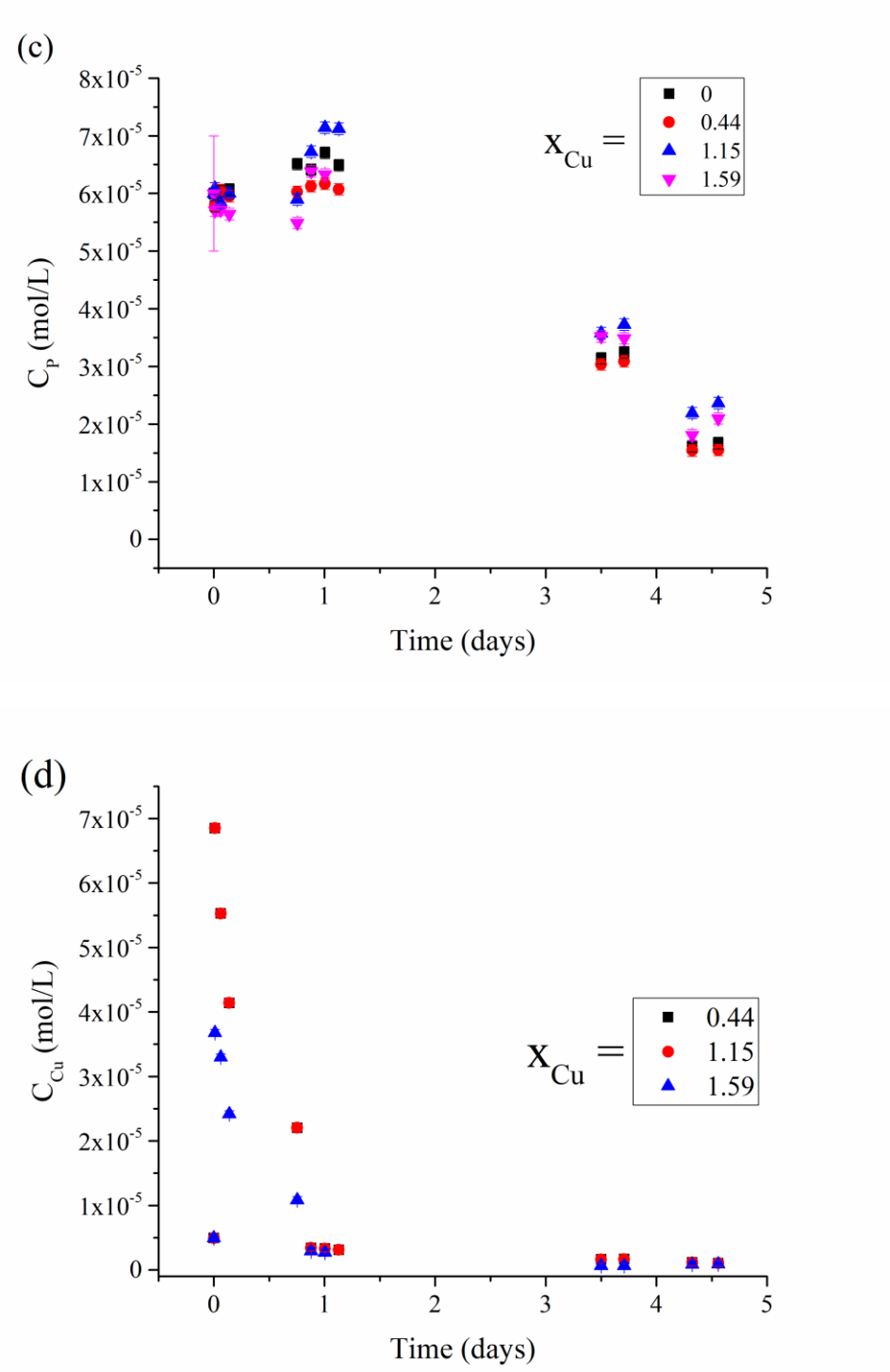
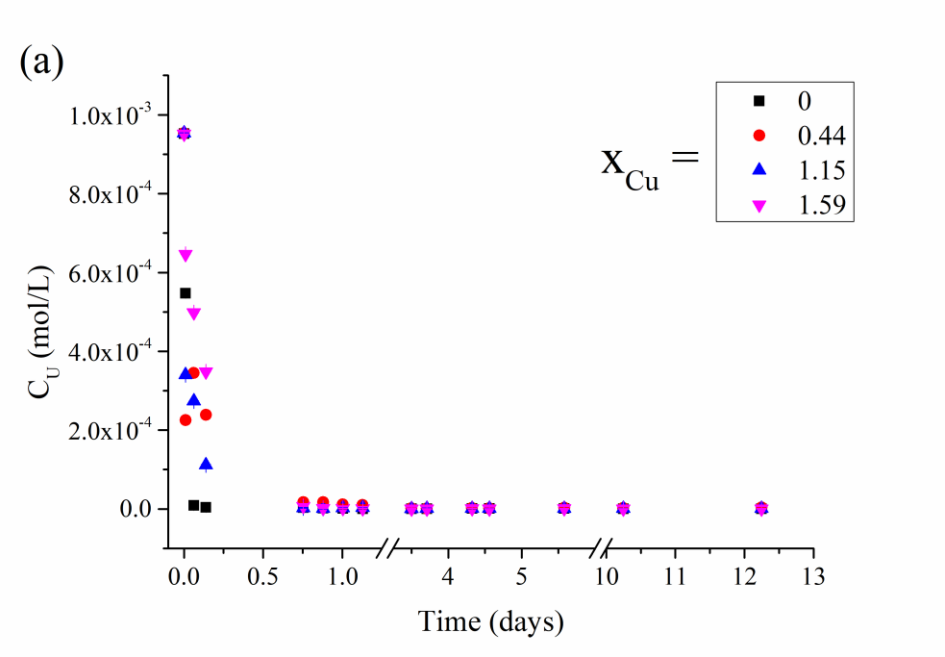
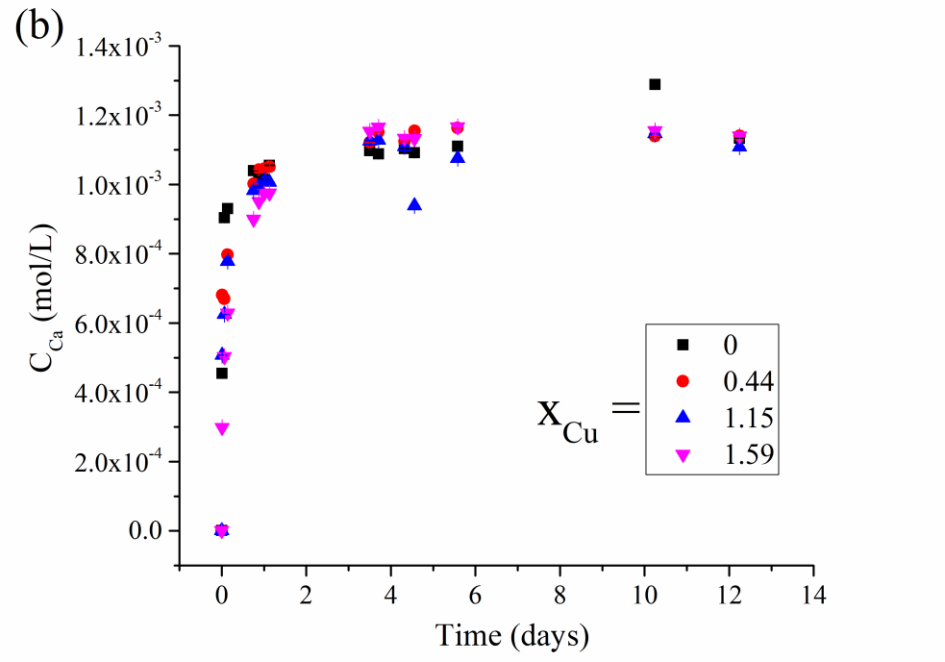


Figure S5. Evolution of the U (a); Ca (b); P (c) and Cu (d) elemental concentrations in spiked synthetic solution of 0.02 mol/L $NaNO_3$ in contact with the prepared Cu-HAP with various Cu content at near-neutral pH and 25°C.


(a)
1.0x10-3
8.0x10-4
6.0x10-4
4.0x10-4
2.0x10-4
0.0
CU (mol/L)
0.0
0.5
1.0
4
5
10
11
12
13
Time (days)
xCu =
0
0.44
1.15
1.59


(b)
1.4x10-3
1.2x10-3
1.0x10-3
8.0x10-4
6.0x10-4
4.0x10-4
2.0x10-4
0.0
CCa (mol/L)
0
2
4
6
8
10
12
14
Time (days)
xCu =
0
0.44
1.15
1.59

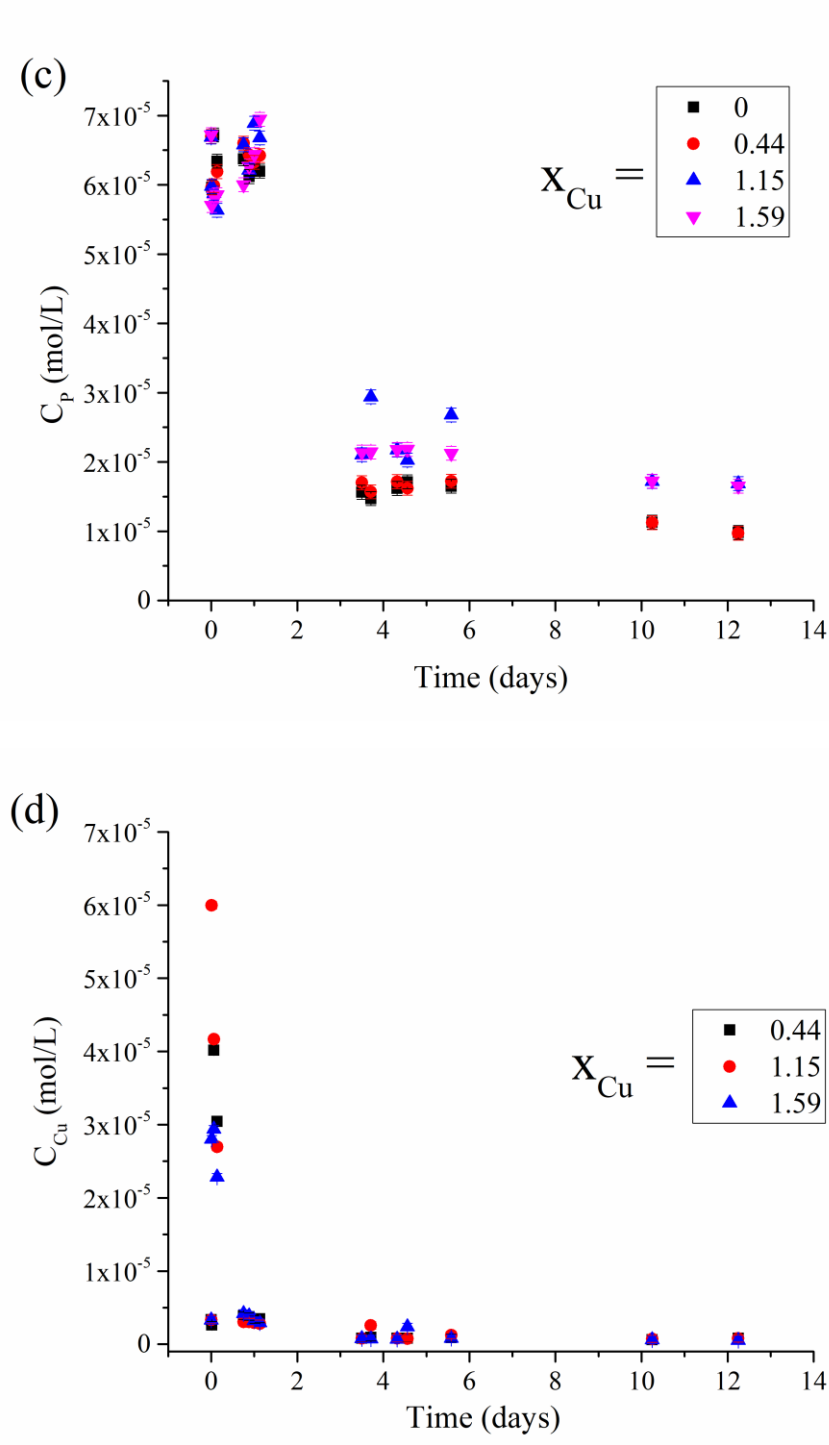
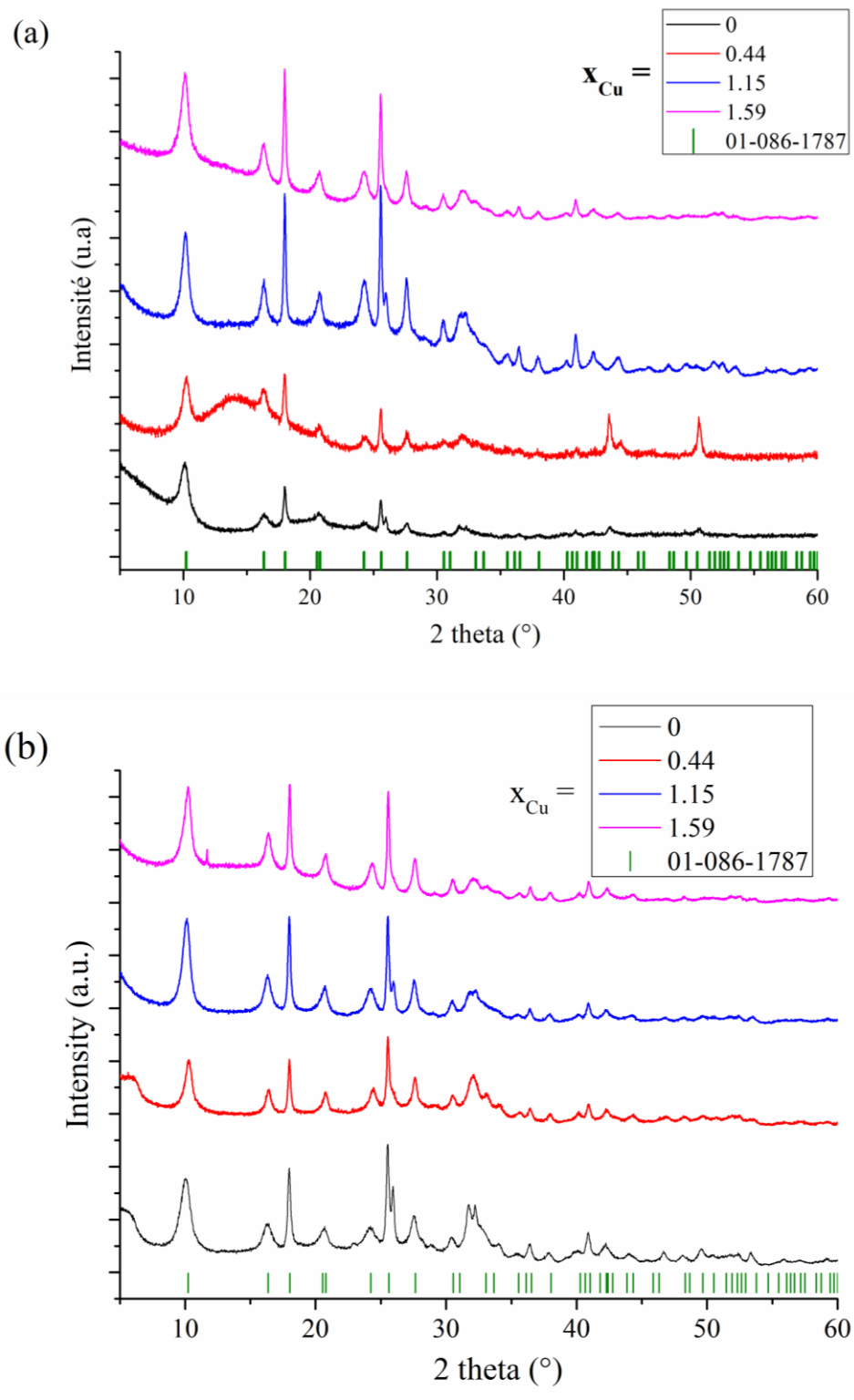


Figure S6. Evolution of the U (a); Ca (b); P (c) and Cu (d) elemental concentrations in uranium spiked synthetic solution of 0.02 mol/L Na_2SO_4 in contact with the prepared Cu-HAP with various Cu content at near-neutral pH and 25°C.


(a)
x_{Cu} =
0
0.44
1.15
1.59
01-086-1787
Intensité (u.a)
10
20
30
40
50
60
2 theta (°)
(b)
x_{Cu} =
0
0.44
1.15
1.59
01-086-1787
Intensity (a.u.)
10
20
30
40
50
60
2 theta (°)

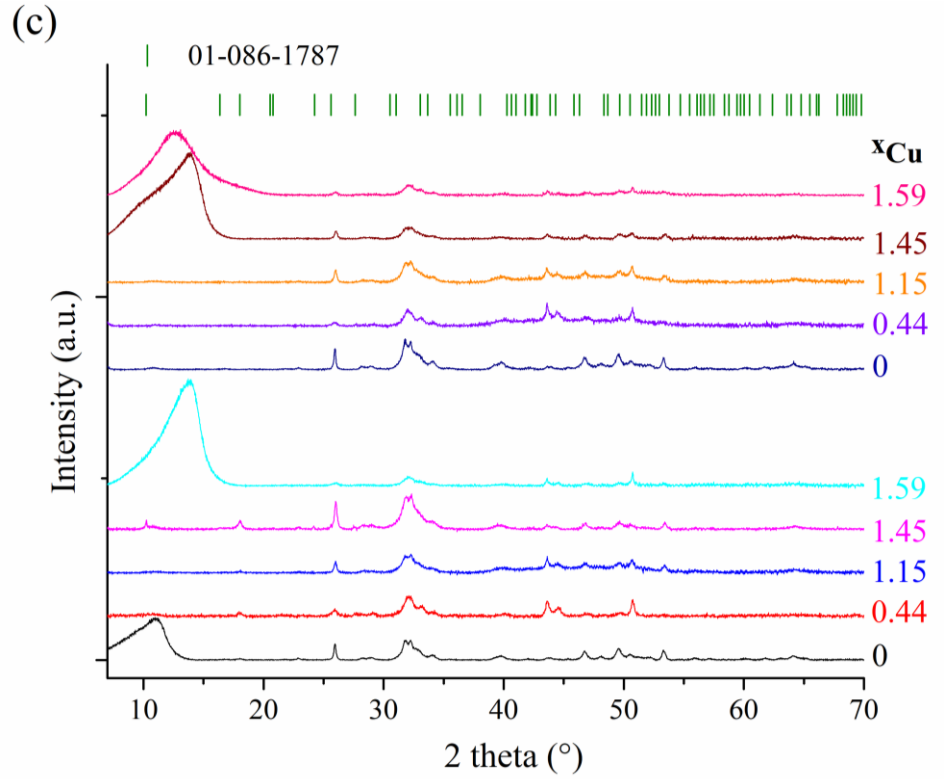


Figure S7. PXRD patterns of Cu-HAP sample after contact with U-spiked (C_U = 10^{-3} mol/L) solution of 0.02 mol/L $NaNO_3$ (a); Na_2SO_4 (b); V105 and BD200 mining waters (C_U ~10^{-6} mol/L) (c). The green bars correspond the Bragg positions of the peaks for meta-torbernite (PDF: 01-086-1787).

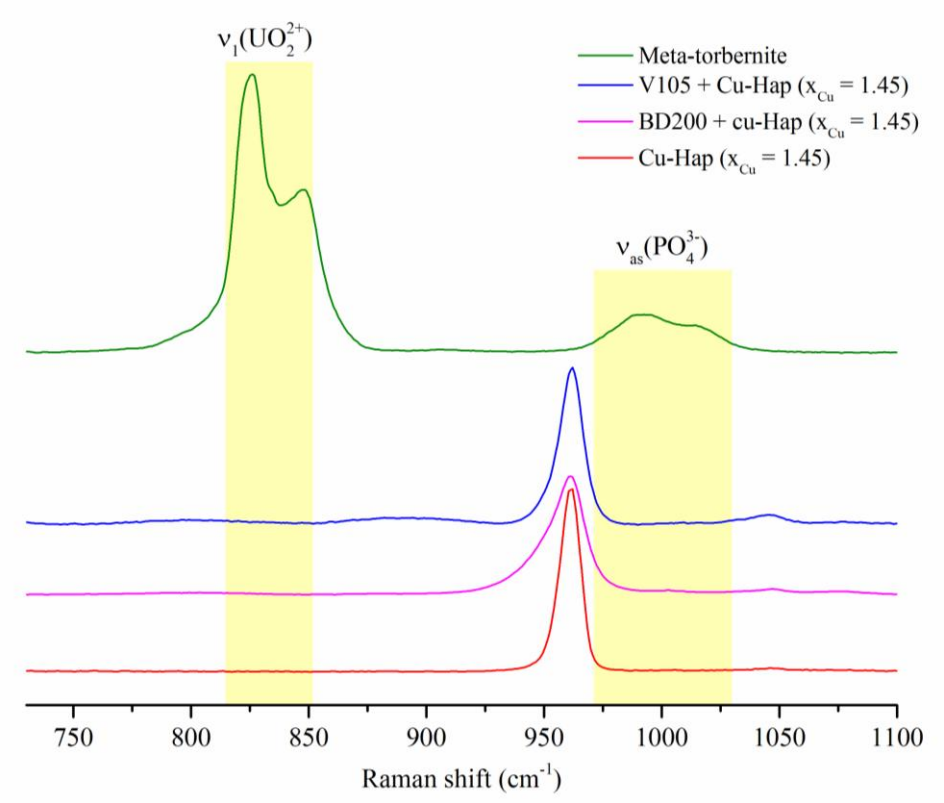
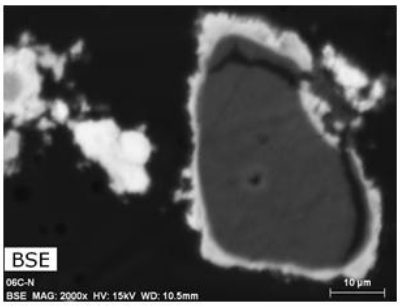
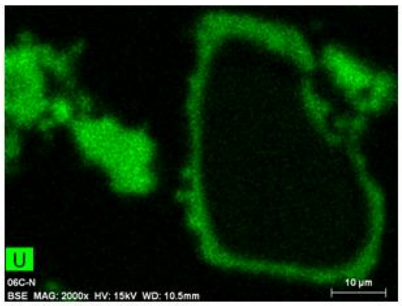


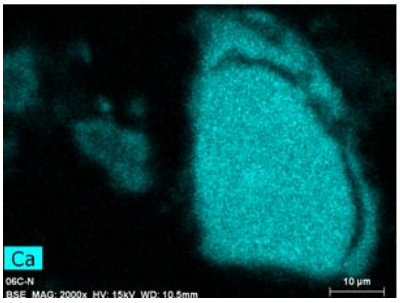
Figure S8. Raman spectra of the Cu-Hap sample (x_{Cu} = 1.45) contacted with BD200 and V105 mining waters compared to the spectrum of the Cu-Hap sample before experiment and with the spectrum of a sample of synthetic meta-torbernite[5]. Attribution of the bands were based on the results obtained by Frost for a natural sample of meta-torbernite[6].

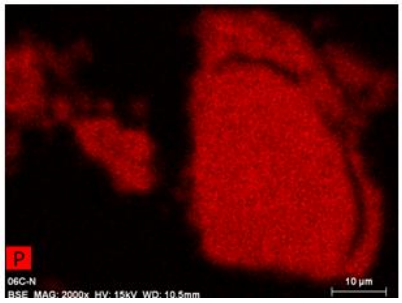
(a)

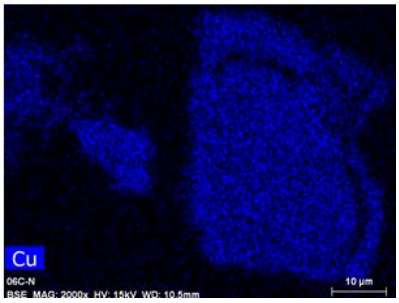
x_{Cu} = 1.59
0.02 M $NaNO_3$





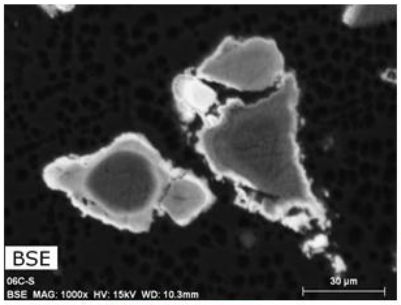


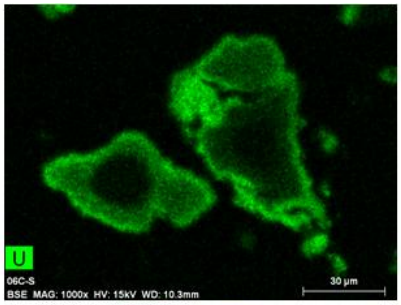


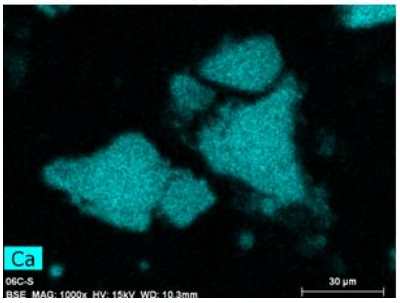


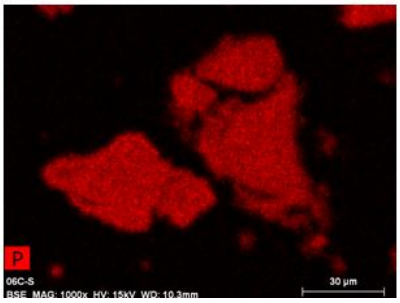
(b)

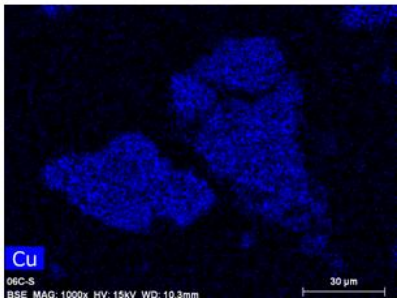
x_{Cu} = 1.59
0.02 M Na_2SO_4











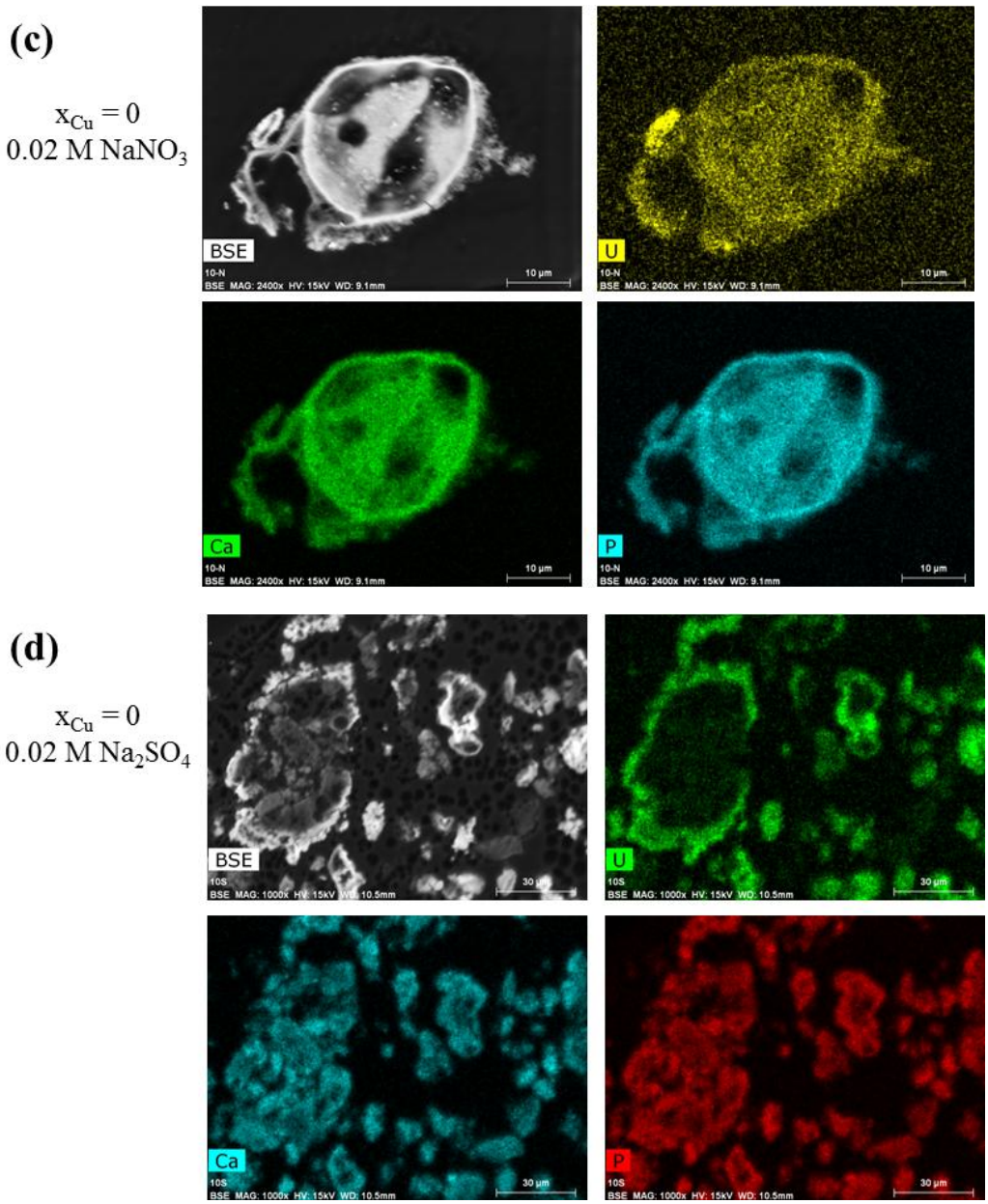


Figure S9. SEM micrograph in backscattered electron mode, U, Ca, Cu and P X-EDS maps determined for Cu-HAP with x_{Cu} = 1.59 contacted with the 0.02 M $NaNO_3$ solution spiked with uranium (a); with the 0.02 M Na_2SO_4 solution spiked with uranium (b); for Cu-HAP with x_{Cu} = 0 contacted with the 0.02 M $NaNO_3$ solution spiked with uranium (c); with the 0.02 M Na_2SO_4 solution spiked with uranium (d).

Table S1. Position of the maximum and full width half maximum of TRFLS peaks for Cu-Hap samples contacted with uranyl synthetic solutions and mining waters. Comparison with uranium-bearing synthetic phases of the autunite family.

x_{Cu}	Peak position λ_{max} (nm)				FWHM (nm)
0.02 M Na_2SO_4					
0	502	523	547	572	13
1.15	503	524	547	573	13
1.59	503	524	547	573	13
0.02 M $NaNO_3$					
0	502	524	547	573	12
1.15	502	524	547	572	14
1.59	502	524	547	572	14
V105					
0	498	519	543	567	13
1.15	497	519	542	567	14
1.45	497	519	542	567	14
BD200					
0	500	521	545	568	15
References	**Peak position λ_{max} (nm)**				**FWHM (nm)**
meta-torbernite	502	524	547	573	7
chernikovite	502	524	548	574	7
meta-autunite	502	524	548	573	10

References

1. Karpov, A. S.; Nuss, J.; Jansen, M.; Kazin, P. E.; Tretyakov, Y. D., Synthesis, crystal structure and properties of calcium and barium hydroxyapatites containing copper ions in hexagonal channels. *Solid State Sciences* **2003,** *5*, (9), 1277-1283.
2. Li, C.; Ge, X.; Zhao, J.; Li, G.; Bai, J.; Du, Q.; Ding, R., Preparation and characterization of novel hydroxyapatite/copper assemblies with well-defined morphologies. *Solid State Sciences* **2014,** *29*, 66-74.
3. Shanmugam, S.; Gopal, B., Copper substituted hydroxyapatite and fluorapatite: Synthesis, characterization and antimicrobial properties. *Ceramics International* **2014,** *40*, (10), 15655-15662.
4. Stanic, V.; Dimitrijevic, S.; Antic-Stankovic, J.; Mitric, M.; Jokic, B.; Plecas, I. B.; Raicevic, S., Synthesis, characterization and antimicrobial activity of copper and zinc-doped hydroxyapatite nanopowders. *Applied Surface Science* **2010,** *256*, (20), 6083-6089.
5. Cretaz, F.; Szenknect, S.; Clavier, N.; Vitorge, P.; Mesbah, A.; Descostes, M.; Poinssot, C.; Dacheux, N., Solubility properties of synthetic and natural meta-torbernite. *Journal of Nuclear Materials* **2013,** *442*, (1-3), 195-207.

6. Frost, R. L., An infrared and Raman spectroscopic study of the uranyl micas. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy* **2004,** *60*, (7), 1469-1480.