

Supergene Uranyl Mineralization of the Rabejac Deposit, Lodève, France

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Table S1. Experimental details for the single-crystal X-ray diffraction study of becquerelite and billietite.

Sample	VC2134	U006
Mineral	Becquerelite	Billietite
Ideal structural formula	$\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8$	$\text{Ba}(\text{UO}_2)_6\text{O}_4(\text{OH})_6(\text{H}_2\text{O})_8$
<i>a</i> (Å)	13.8625(5)	30.1894(5)
<i>b</i>	14.9459(5)	12.08285(14)
<i>c</i>	12.3768(4)	7.15099(10)
<i>V</i> (Å ³)	2564.31(15)	2608.49(7)
Space group	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁
<i>Z</i>	4	4
Calculated density (g·cm ⁻³)	5.193	5.265
Absorption coefficient (mm ⁻¹)	38.450	38.710
<i>F</i> (000)	3392	3480
Radiation (Å)	MoKα, 0.71073	MoKα, 0.71073
Crystal size (mm)	0.15 × 0.13 × 0.05	0.26 × 0.23 × 0.09
Temperature (K)	293(2)	293(2)
θ range (°)	2.93 to 28.77 −16 ≤ <i>h</i> ≤ 17	3.15 to 28.78 −40 ≤ <i>h</i> ≤ 40
Reflection range	−16 ≤ <i>k</i> ≤ 19 −15 ≤ <i>l</i> ≤ 16	−16 ≤ <i>k</i> ≤ 16 −9 ≤ <i>l</i> ≤ 9
Total no. of reflections	8291	115043
Unique reflections	4538	6623
Observed reflections, <i>F</i> o ≥ 4σ <i>F</i>	3824	5610
Refined parameters	185	184
<i>R</i> ₁ , <i>F</i> o ≥ 4σ <i>F</i>	0.0565	0.0724
<i>R</i> ₁ , all data	0.0703	0.0886
<i>wR</i> ₂ (<i>F</i> ²), all data	0.1574	0.1393
GOF obs/all	1.060/1.060	1.251/1.250
Δσmin, Δσmax (e/Å ³)	3.07, −3.78	5.90, −5.78

Table S2. Atom fractional coordinates, isotropic and anisotropic atom displacement parameters (\AA^2) for becquerelite.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}		
Ca1	0.5430(4)	0.4655(4)	0.2334(5)	0.0269(12)		
U1	0.58967(8)	0.74194(8)	0.25146(8)	0.0178(3)		
U2	0.65169(8)	0.21110(8)	0.24444(8)	0.0173(3)		
U3	0.62664(5)	0.22199(6)	0.55925(14)	0.0173(2)		
U4	0.87177(6)	0.25240(6)	1.06289(14)	0.0186(2)		
U5	0.90591(8)	0.24896(7)	1.37090(8)	0.0176(3)		
U6	0.65734(8)	0.20897(9)	0.87263(8)	0.0190(3)		
O1	0.6040(11)	0.1051(11)	0.562(3)	0.030(4)		
O2	0.6654(12)	0.0897(13)	0.863(2)	0.021(4)		
O3	0.8197(10)	0.3631(10)	1.052(2)	0.022(4)		
O4	0.8204(12)	0.2180(12)	0.8967(15)	0.018(4)		
O5	0.5532(12)	0.6232(13)	0.2671(16)	0.021(4)		
O6 (OH)	0.9933(15)	0.3052(16)	0.9290(19)	0.026(5)		
O7 (OH)	0.9490(9)	0.2204(9)	1.556(2)	0.018(3)		
O8 (OH)	0.7574(13)	0.1892(14)	0.6883(17)	0.016(4)		
O9	0.5629(13)	0.2239(13)	0.7236(17)	0.016(4)		
O10	0.6568(10)	0.3393(10)	0.550(2)	0.020(4)		
O11	0.6463(15)	0.3277(17)	0.892(2)	0.032(5)		
O12	0.9266(11)	0.1424(12)	1.0765(17)	0.026(4)		
O13	0.6276(17)	0.8551(16)	0.228(2)	0.036(6)		
O14	0.5661(14)	0.2253(15)	0.393(2)	0.027(5)		
O15 (H ₂ O)	1.025(2)	0.517(2)	0.698(2)	0.068(9)		
O16	0.8063(12)	0.2441(11)	1.2294(15)	0.013(4)		
O17	0.8674(14)	0.3589(15)	1.4048(19)	0.025(5)		
O18 (OH)	0.9864(14)	0.3068(15)	1.1915(18)	0.021(5)		
O19	0.9430(14)	0.1368(14)	1.3395(16)	0.025(5)		
O20 (H ₂ O)	0.7257(17)	0.4963(16)	0.198(2)	0.036(6)		
O21 (OH)	0.7562(14)	0.1956(15)	1.4361(18)	0.020(5)		
O22 (H ₂ O)	0.6110(16)	0.4897(17)	0.416(2)	0.042(7)		
O23 (H ₂ O)	0.5535(10)	0.5230(11)	0.058(2)	0.031(4)		
O24 (H ₂ O)	0.3774(13)	0.5250(15)	0.222(2)	0.032(5)		
O25 (OH)	0.6946(9)	0.1826(9)	1.061(2)	0.016(3)		
O26	0.6672(14)	0.0935(15)	0.263(3)	0.036(6)		
O27 (H ₂ O)	0.9554(16)	0.4775(19)	0.902(2)	0.046(6)		
O28 (H ₂ O)	0.7997(13)	0.4988(13)	0.0571(3)	0.044(6)		
O29 (H ₂ O)	0.7157(15)	0.5060(15)	0.933(2)	0.034(6)		
O30	0.6295(16)	0.3295(15)	0.2141(19)	0.029(5)		
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ca1	0.032(3)	0.026(3)	0.023(3)	0.006(2)	0.006(2)	0.004(3)
U1	0.0167(6)	0.0271(6)	0.0096(6)	0.0010(5)	-0.0015(5)	0.0020(5)
U2	0.0162(6)	0.0248(6)	0.0110(7)	-0.0015(6)	0.0013(5)	0.0002(4)
U3	0.0183(4)	0.0262(5)	0.0074(4)	0.0000(7)	-0.0003(6)	-0.0001(3)
U4	0.0177(4)	0.0299(5)	0.0083(4)	-0.0010(6)	0.0000(6)	-0.0006(3)
U5	0.0159(6)	0.0282(7)	0.0088(6)	-0.0007(4)	0.0003(4)	-0.0005(5)
U6	0.0178(6)	0.0295(7)	0.0098(6)	0.000(6)	-0.0013(4)	-0.0013(5)

Table S3. Selected bond distances for becquerelite.

Bond	d, Å	Bond	d, Å	Bond	d, Å
U1–O5	1.855(19)	U2–O26	1.79(2)	U3–O1	1.775(17)
U1–O13	1.800(20)	U2–O30	1.83(2)	U3–O10	1.805(15)
U1–O4	2.217(18)	U2–O14	2.20(2)	U3–O14	2.609(13)
U1–OH6	2.650(20)	U2–O16	2.207(16)	U3–OH7	2.609(13)
U1–OH7	2.500(30)	U2–OH18	2.40(2)	U3–OH8	2.460(20)
U1–OH8	2.394(19)	U2–OH21	2.79(2)	U3–O9	2.220(20)
U1–O9	2.203(18)	U2–OH25	2.38(3)	U3–OH21	2.390(20)
<U1–O _{Ur} >	1.83	<U2–O _{Ur} >	1.81	<U3–O _{Ur} >	1.79
<U1–φ _{eq} >	2.39	<U2–φ _{eq} >	2.40	<U3–φ _{eq} >	2.38
U4–O3	1.810(15)	U5–O17	1.78(20)	U6–O2	1.791(19)
U4–O12	1.819(17)	U5–O19	1.800(20)	U6–O11	1.800(30)
U4–O4	2.237(19)	U5–OH7	2.400(30)	U6–O4	2.283(17)
U4–OH6	2.490(20)	U5–O14	2.270(20)	U6–OH6	2.390(20)
U4–O16	2.256(18)	U5–O16	2.231(17)	U6–OH8	2.690(20)
U4–OH18	2.390(20)	U5–OH18	2.603(20)	U6–O9	2.270(20)
U4–OH25	2.669(13)	U5–OH21	2.370(10)	U6–OH25	2.420(30)
<U4–O _{Ur} >	1.81	<U5–O _{Ur} >	1.79	<U6–O _{Ur} >	1.80
<U4–φ _{eq} >	2.41	<U5–φ _{eq} >	2.38	<U6–φ _{eq} >	2.39
Ca1–O5	2.40(2)				
Ca1–O12	3.00(2)				
Ca1–O19	2.45(2)				
Ca1–H ₂ O20	2.61(2)				
Ca1–H ₂ O22	2.47(3)				
Ca1–H ₂ O23	2.33(3)				
Ca1–H ₂ O24	2.47(2)				
Ca1–O30	2.37(2)				
<Ca1–φ>	2.51				

Table S4. The bond-valence analysis (vu) for becquerelite.

	Ca1	U1	U2	U3	U4	U5	U6	Σ	Species
O1				1.702				1.70	O
O2						1.650	1.65		O
O3					1.591			1.59	O
O4		0.726			0.699		0.640	2.06	O
O5	0.310	1.459						1.77	O
O6		0.315			0.429		0.520	1.26	OH
O7		0.421		0.341		0.510		1.27	OH
O8		0.516		0.455			0.292	1.26	OH
O9		0.746		0.722			0.656	2.12	O
O10				1.606				1.61	O
O11						1.622	1.62		O
O12	0.062				1.564			1.63	O
O13		1.622						1.62	O
O14			0.750	0.722		0.656		2.13	O
O15								0.00	H ₂ O
O16			0.740		0.674	0.707		2.12	O
O17						1.686		1.69	O
O18			0.510		0.520	0.328		1.36	OH
O19	0.271					1.622		1.89	O
O20	0.176							0.18	H ₂ O
O21			0.241	0.520		0.541		1.30	OH
O22	0.257							0.26	H ₂ O
O23	0.375							0.37	H ₂ O
O24	0.257							0.26	H ₂ O
O25			0.531		0.304		0.491	1.33	OH
O26			1.653					1.65	O
O27								0.00	H ₂ O
O28								0.00	H ₂ O
O29								0.00	H ₂ O
O30	0.336		1.531					1.87	O
Σ	2.04	5.81	5.96	6.07	5.78	6.05	5.87		

The crystal structure of becquerelite contains six symmetrically independent U⁶⁺ cations, which are forming typical nearly linear (UO₂)²⁺ uranyl ions. Each uranyl ion is additionally coordinated by five additional ligands, two O²⁻ anions and three OH⁻ groups, located at the equatorial vertices of the uranyl ions to form Ur ϕ_5 pentagonal bipyramids. The <U–O_{Ur}> and <U– ϕ_{eq} > mean bond lengths vary between 1.79 and 1.83 Å, and between 2.38 and 2.40 Å, respectively (Table S3). These values closely match the typical bond lengths observed for [7]-coordinated U⁶⁺ [1,2]. The structure contains also one symmetrically independent Ca cation that is coordinated by eight ligands ϕ : four O²⁻ anions belonging to the uranyl ions (O_{Ur}), and four H₂O water molecules, thus forming a CaO₄(H₂O)₄ polyhedron. The mean <Ca1– ϕ > bond length is 2.51 Å. In addition, four isolated water molecules (O15, O27–O29) are located in the interlayer space, increasing the connectivity of adjacent sheets through H-bonds. The structural formula of becquerelite is given by Ca[(UO₂)₃O₂(OH)₃]₂(H₂O)₈.

The structure of becquerelite is based upon infinite sheets parallel to (010), which are constituted by corner- and edge-sharing uranyl pentagonal bipyramids (Figure S1). The sheets show the α -U₃O₈ (protasite) anion topology [3]. The protasite anion topology is quite common among the uranyl oxide hydrate minerals, and is observable in the structure of billietite Ba[(UO₂)₃O₂(OH)₃]₂(H₂O)₈ [4], protasite Ba(UO₂)₃O₃(OH)₂(H₂O)₃ [5], compreignacite K₂[(UO₂)₃O₂(OH)₃]₂(H₂O)₇ [6], masuyite Pb(UO₂)₃O₃(OH)₂(H₂O)₃ [7], agrinierite K₂Ca[(UO₂)₃O₃(OH)₂]₂(H₂O)₅ [8], and richetite M_xPb_{8.57}[(UO₂)₁₈O₁₈(OH)₁₂]₂(H₂O)₄₁ [9,10].

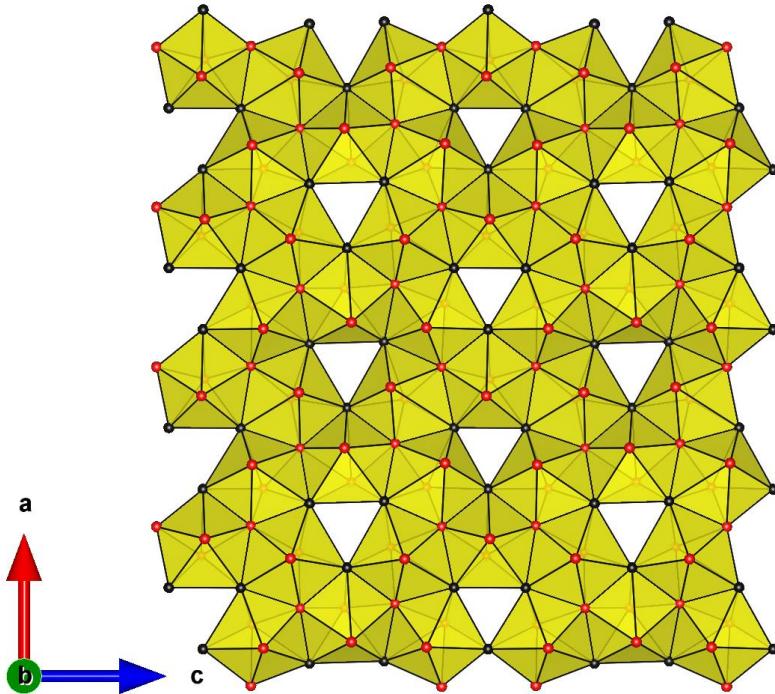


Figure. S1. Representation of the sheet of uranyl polyhedra ($\alpha\text{-U}_3\text{O}_8$) occurring in the structure of becquerelite. Yellow: UO_7 polyhedra, red: O^{2-} atoms, black: $(\text{OH})^-$ groups.

However, the distribution of anions (O^{2-} and OH^-) within the sheets based upon this anion topology is not identical in all these minerals. Actually the topology of the becquerelite sheet is only identical to that found in billietite and compreignacite. The distribution of O^{2-} and OH^- within the sheets is important because it modifies the charge of the sheets and their connectivity to the interlayer constituents through H bonding [11]. Adjacent infinite sheets of uranyl polyhedra are connected via the Ca cations which are bonded to four O_{ur} atoms, with three of which from the same sheet (Figure S2).

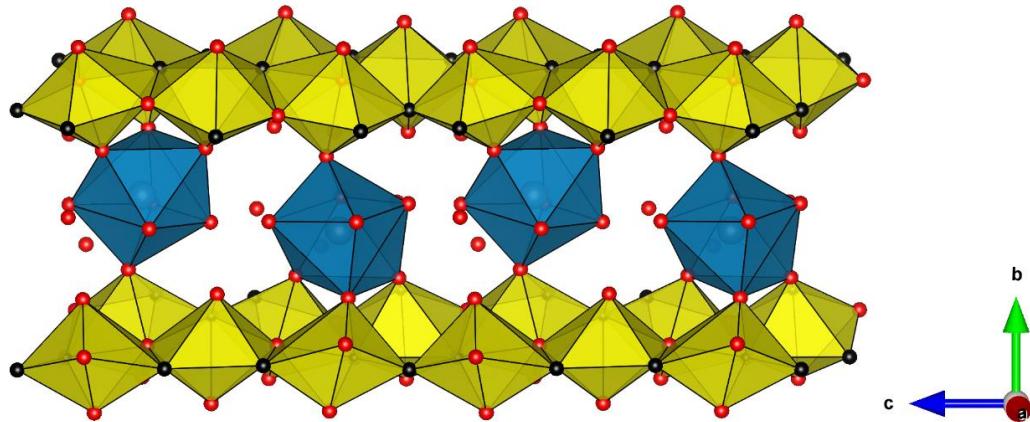


Figure. S2. Structure of becquerelite projected along [100] and showing the connectivity between the sheets and the $\text{Ca}\phi_8$ polyhedra. Yellow: UO_7 polyhedra, bleu: $\text{Ca}\phi_8$ polyhedra, red: O^{2-} atoms and H_2O groups, black: $(\text{OH})^-$ groups.

The structural data obtained on natural becquerelite from Rabejac are completely consistent with the data published on synthetic becquerelite [12]. The mean bond lengths for the Ca and U sites are exactly the same in natural and synthetic becquerelite samples. These distances are also in good agreement with the distances reported by Pagoaga et al. (1987) [5] for natural becquerelite from Shaba

region. Consequently this study confirms also the presence of six OH⁻ groups and eight water molecules *pfa* in the crystal structure of becquerelite.

Table S5. Atom fractional coordinates, isotropic and anisotropic atom displacement parameters (\AA^2) for billietite.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}		
Ba1	0.62538(6)	0.86308(16)	0.6424(4)	0.0230(4)		
U1	0.49428(4)	0.56022(10)	0.32715(17)	0.0134(3)		
U2	0.50484(4)	0.06005(10)	0.8319(2)	0.0151(3)		
U3	0.51187(4)	0.24981(8)	0.3694(2)	0.0149(3)		
U4	0.74654(4)	0.44433(9)	0.84694(18)	0.0116(2)		
U5	0.75678(4)	0.56264(9)	0.34421(18)	0.0135(3)		
U6	0.76376(4)	0.75268(9)	0.7791(2)	0.0140(3)		
O1	0.5500(9)	0.597(2)	0.381(4)	0.034(6)		
O2	0.4383(8)	0.526(2)	0.277(4)	0.030(6)		
O3	0.4484(6)	0.1006(15)	0.887(3)	0.012(4)		
O4	0.5628(6)	0.0228(16)	0.787(3)	0.011(4)		
O5	0.4538(8)	0.240(2)	0.279(4)	0.031(5)		
O6	0.5691(8)	0.2500(19)	0.426(4)	0.027(5)		
O7	0.6893(7)	0.4871(19)	0.856(4)	0.024(5)		
O8	0.8041(9)	0.396(2)	0.837(4)	0.039(6)		
O9	0.7000(7)	0.6071(18)	0.334(3)	0.024(5)		
O10	0.8147(8)	0.517(2)	0.355(4)	0.028(5)		
O11	0.8225(7)	0.7509(17)	0.763(4)	0.019(4)		
O12	0.7060(8)	0.757(2)	0.797(3)	0.031(6)		
O13 (OH)	0.7300(7)	0.3908(17)	0.520(3)	0.017(4)		
O14 (OH)	0.5279(7)	0.3896(17)	0.150(4)	0.022(5)		
O15	0.7593(7)	0.5821(19)	0.653(4)	0.029(5)		
O16 (H ₂ O)	0.6355(5)	0.6346(13)	0.684(2)	0.002(3)		
O17 (H ₂ O)	0.6234(10)	0.7279(18)	0.325(5)	0.036(5)		
O18	0.7595(6)	0.9183(16)	0.652(3)	0.019(4)		
OH19 (OH)	0.4755(9)	0.7501(19)	0.297(3)	0.028(6)		
O20	0.4961(5)	0.4083(12)	0.515(2)	0.000(3)		
O21	0.4994(8)	0.098(2)	0.523(3)	0.029(6)		
O22 (OH)	0.7720(7)	0.6174(17)	1.024(3)	0.016(4)		
O23 (OH)	0.7242(8)	0.2579(18)	0.900(3)	0.022(5)		
O24 (OH)	0.5271(6)	0.1028(14)	1.152(3)	0.010(4)		
O25 (H ₂ O)	0.3749(12)	0.742(2)	0.354(6)	0.051(7)		
O26 (H ₂ O)	0.3831(12)	0.135(3)	0.512(5)	0.060(9)		
O27 (H ₂ O)	0.6151(10)	0.430(2)	0.147(6)	0.045(7)		
O28 (H ₂ O)	0.3829(10)	-0.078(2)	0.625(6)	0.047(7)		
O29 (H ₂ O)	0.6362(9)	0.418(2)	0.527(4)	0.030(6)		
O30 (H ₂ O)	0.8653(11)	0.583(3)	1.020(4)	0.045(7)		
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ba1	0.0270(9)	0.0211(8)	0.0209(8)	-0.0030(8)	-0.0036(9)	0.0007(7)
U1	0.0246(5)	0.0102(5)	0.0055(6)	0.0012(4)	0.0009(5)	-0.0002(4)
U2	0.0244(5)	0.0087(5)	0.0122(6)	-0.0005(4)	-0.0009(6)	0.0004(4)
U3	0.0218(6)	0.0093(5)	0.0135(6)	0.0002(4)	-0.0004(5)	0.0001(4)
U4	0.0208(5)	0.0052(4)	0.0087(6)	-0.0038(5)	-0.0042(6)	-0.0017(4)
U5	0.0201(5)	0.0083(5)	0.0122(6)	-0.0054(5)	-0.0060(6)	0.0011(4)
U6	0.0225(6)	0.0056(5)	0.0138(6)	0.0047(4)	-0.0022(5)	-0.0027(4)

Table S6. Selected bond distances for billietite.

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
U1–O1	1.78(3)	U2–O3	1.815(18)	U3–O5	1.87(3)
U1–O2	1.78(3)	U2–O4	1.835(19)	U3–O6	1.77(2)
U1–OH14	2.48(3)	U2–OH19	2.38(2)	U3–OH14	2.36(2)
U1–OH14	2.62(2)	U2–O21	2.26(2)	U3–O20	2.231(15)
U1–OH19	2.37(2)	U2–O21	2.35(2)	U3–O21	2.17(3)
U1–O20	2.273(15)	U2–OH24	2.44(2)	U3–OH24	2.41(2)
U1–O20	2.286(15)	U2–OH24	2.542(19)	$\langle U3-O_{Ur} \rangle$	1.82
$\langle U1-O_{Ur} \rangle$	1.78	$\langle U2-O_{Ur} \rangle$	1.83	$\langle U3-\phi_{eq} \rangle$	2.29
$\langle U1-\phi_{eq} \rangle$	2.41	$\langle U2-\phi_{eq} \rangle$	2.39		
U4–O7	1.80(2)	U5–O9	1.80(2)	U6–O11	1.78(2)
U4–O8	1.83(3)	U5–O10	1.83(2)	U6–O12	1.75(3)
U4–OH13	2.48(2)	U5–OH13	2.56(2)	U6–OH13	2.41(2)
U4–O15	2.20(3)	U5–O15	2.22(3)	U6–O15	2.25(2)
U4–O18	2.21(2)	U5–O18	2.27(2)	U6–O18	2.20(2)
U4–OH22	2.56(2)	U5–OH22	2.43(2)	U6–OH22	2.41(2)
U4–OH23	2.38(2)	U5–OH23	2.46(2)	U6–OH23	2.74(2)
$\langle U4-O_{Ur} \rangle$	1.82	$\langle U5-O_{Ur} \rangle$	1.82	$\langle U6-O_{Ur} \rangle$	1.77
$\langle U4-\phi_{eq} \rangle$	2.37	$\langle U5-\phi_{eq} \rangle$	2.39	$\langle U6-\phi_{eq} \rangle$	2.40
Ba1–O3	2.915(19)	Ba1–O12	2.96(3)		
Ba1–O4	2.89(2)	Ba1–H ₂ O16	2.793(16)		
Ba1–O5	2.87(2)	Ba1–H ₂ O17	2.80(3)		
Ba1–O8	3.08(3)	Ba1–H ₂ O26	2.66(4)		
Ba1–O10	3.01(2)	Ba1–H ₂ O30	2.85(3)		
		$\langle Ba1-\phi \rangle$	2.88		

Table S7. The bond-valence analysis (*vu*) for billietite.

Ba1	U1	U2	U3	U4	U5	U6	Σ	Species	
O1	1.686						1.69	O	
O2	1.686						1.69	O	
O3	0.182		1.576				1.76	O	
O4	0.195		1.516				1.71	O	
O5	0.206			1.445			1.65	O	
O6				1.731			1.73	O	
O7					1.622		1.62	O	
O8	0.117				1.531		1.65	O	
O9						1.622	1.62	O	
O10	0.141					1.531	1.67	O	
O11							1.686	1.69	O
O12	0.161						1.786	1.95	O
O13				0.438	0.375	0.501	1.31	OH	
O14		0.438		0.597			1.37	OH	
	0.334								
O15					0.750	0.722	0.682	2.15	O
O16	0.253						0.25	H ₂ O	
O17	0.249						0.25	H ₂ O	
O18					0.736	0.656	0.750	2.14	O
O19		0.541	0.531				1.07	OH	
O20		0.652		0.753			2.04	O	

		0.636					
O21		0.669 0.562	0.841			2.07	O
O22			0.375	0.482	0.501	1.36	OH
O23			0.531	0.455	0.265	1.25	OH
O24		0.473 0.388	0.545			1.41	OH
O25						0.00	H ₂ O
O26	0.363					0.36	H ₂ O
O27						0.00	H ₂ O
O28						0.00	H ₂ O
O29						0.00	H ₂ O
O30	0.217					0.22	H ₂ O
Σ	2.08	5.97	5.71	5.91	5.98	5.84	6.17

The crystal structure of billietite contains six symmetrically independent U⁶⁺ cations, which are forming typical nearly linear (UO₂)²⁺ uranyl ions. Five of the six uranyl ions are additionally coordinated by five additional ligands ϕ ($\phi = \text{O}^{2-}$ or OH⁻) located at the equatorial vertices of the uranyl ions to form Ur ϕ_5 pentagonal bipyramids. The <U–O_{Ur}> and <U– ϕ_{eq} > mean bond lengths vary between 1.78 and 1.83 Å, and between 2.37 and 2.41 Å, respectively (Table S6). Like in becquerelite, all of the uranyl ions are coordinated by two O²⁻ anions and three OH⁻ groups. The sixth uranyl ion (U3) is additionally coordinated by four ligands ϕ arranged at the vertices of a distorted octahedron. This polyhedra can also be identified as a distorted square bipyramid. The <U–O_{Ur}> and <U– ϕ_{eq} > mean bond lengths are 1.82 and 2.29 Å, respectively. The structure contains also one symmetrically independent Ba cation that is coordinated by ten ligands ϕ : six O²⁻ anions belonging to the uranyl ions (O_{Ur}), and four H₂O water molecules, thus forming a BaO₆(H₂O)₄ polyhedron. The mean <Ba1– ϕ > bond length is 2.88 Å. In addition, four isolated water molecules (O25, O27–O29) are located in the interlayer space, increasing the connectivity of adjacent sheets through H-bonds. The structural formula of billietite is given by Ba[(UO₂)₃O₂(OH)₃]₂(H₂O)₈.

The structure of billietite is based upon two symmetrically and stereochemically distinct infinite sheets parallel to (100). The first sheet consists of corner- and edge-sharing uranyl pentagonal bipyramids (Figure S3a), and is identical to the sheet occurring in the structure of becquerelite and compreignacite. The second sheet is formed by chains of edge-sharing uranyl pentagonal bipyramids that extend parallel to the *c* crystallographic axis (Figure S3b). Adjacent chains are then connected by corner-sharing and edge-sharing via the U3 distorted square bipyramids.

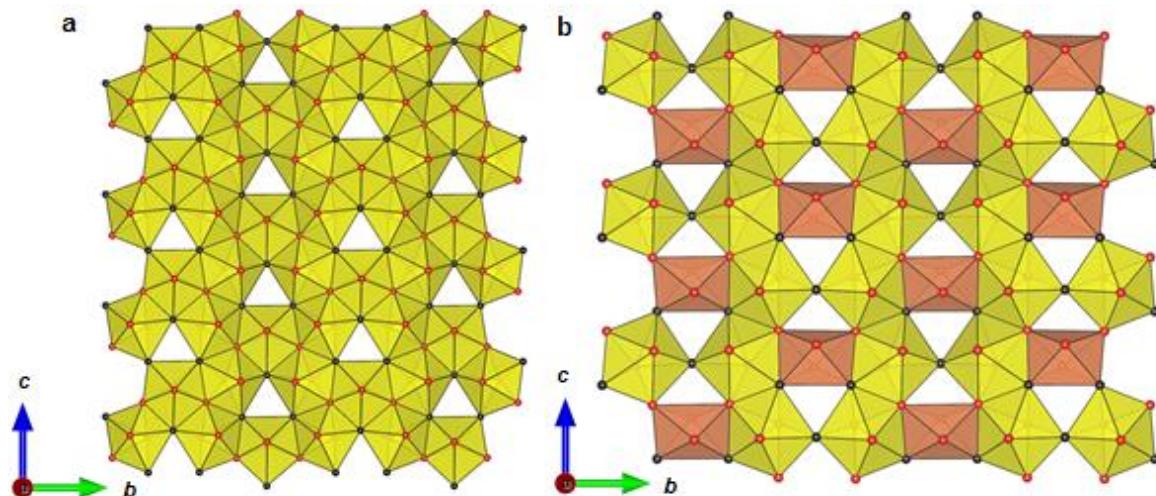


Figure S3. The structural sheets of uranyl polyhedra occurring in the structure of billietite: (a) α -U₃O₈ and (b) β -U₃O₈-type sheet. Yellow: UO₇ polyhedra, orange: UO₆ polyhedra, red: O²⁻ atoms, black: (OH)⁻ groups.

The anion topology of this second sheet is actually described as the β -U₃O₈ anion topology, which is also observed in the structure of minerals ianthinite [U⁴⁺₂(UO₂)₄O₆(OH)₄](H₂O)₅ [13], wyartite, and its dehydrated equivalent CaU⁵⁺[(UO₂)₂(CO₃)O₄(OH)](H₂O)₇₋₃ [14,15], spriggite Pb₃[(UO₂)₆O₈(OH)₂](H₂O)₃ [16], and rameauite K₂Ca[(UO₂)₃O₃(OH)₂]₂(H₂O)₆ [17]. Note that in spriggite, billietite and rameauite, the square sites contain U⁶⁺O₆ tetragonal bipyramids, while in wyartite and ianthinite the square sites are occupied by U⁵⁺O₇ polyhedra and U⁴⁺O₆ octahedra, respectively. Adjacent infinite sheets of uranyl polyhedra are connected via the Ba cations which are bonded to six O_{Ur} atoms, with three of which from the same sheet (Figure S4).

The structural data obtained on natural billietite from Rabejac are completely consistent with the data previously published [4]. As the work of Finch *et al.* (2006) [4], this study confirms the presence of six OH⁻ groups and eight water molecules *p*f_u for billietite, and disprove the structural model containing four water molecules *p*f_u proposed by Pagoaga *et al.* (1987) [5].

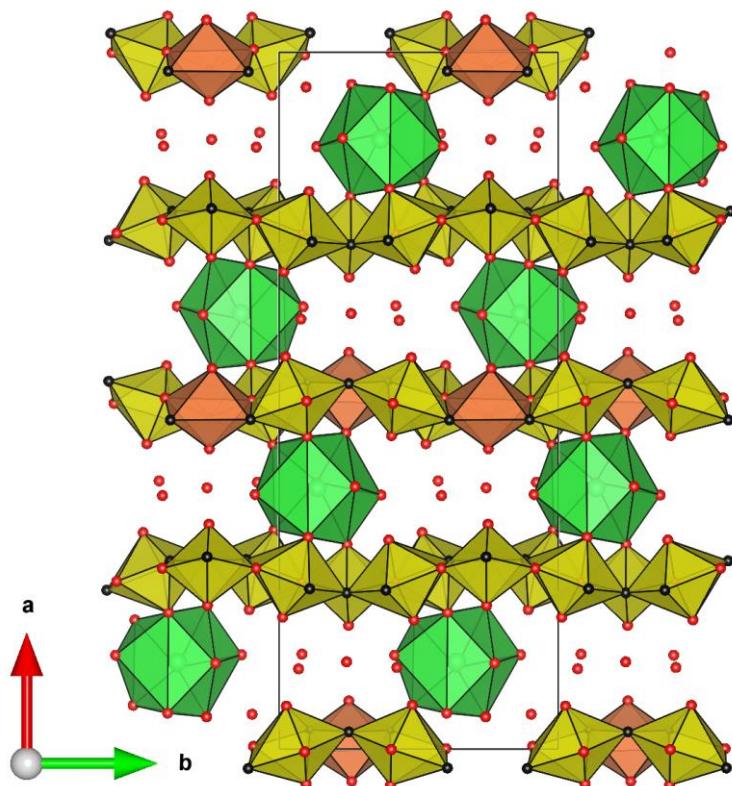


Figure S4. Structure of billietite projected along [001] and showing the connectivity between the sheets and the Ba ϕ_{10} polyhedra. Yellow: U ϕ_7 polyhedra, orange: U ϕ_6 polyhedra, green: Ba ϕ_{10} polyhedra, red: O²⁻ atoms and H₂O groups, black: (OH)⁻ groups.

Table S8. Experimental details for the single-crystal X-ray diffraction study of liebigite.

Sample	U016
Ideal structural formula	Ca ₂ [(UO ₂)(CO ₃) ₃](H ₂ O) ₁₁
<i>a</i> (Å)	17.5731(4)
<i>b</i>	16.7367(4)
<i>c</i>	13.7180(4)
<i>V</i> (Å ³)	4034.7(2)
Space group	<i>Aba</i> 2
<i>Z</i>	8.654

Calculated density (g·cm ⁻³)	2.398
Absorption coefficient (mm ⁻¹)	8.654
<i>F</i> (000)	3008
Radiation (Å)	MoK α , 0.71073
Crystal size (mm)	0.22 × 0.16 × 0.13
Temperature (K)	293(2)
θ range (°)	2.25 to 28.62 -23 ≤ <i>h</i> ≤ 21
Reflection range	13 ≤ <i>k</i> ≤ 21 -18 ≤ <i>l</i> ≤ 13
Total no. of reflections	6468
Unique reflections	3810
Observed reflections, <i>F</i> _o ≥ 4σ <i>F</i>	3504
Refined parameters	320
<i>R</i> ₁ , <i>F</i> _o ≥ 4σ <i>F</i>	0.0622
<i>R</i> ₁ , all data	0.0669
<i>wR</i> ₂ (<i>F</i> ²), all data	0.1678
GOF obs/all	1.033/1.038
Δσ _{min} , Δσ _{max} (e/Å ³)	1.47, -1.09

Table S9. Atom coordinates and isotropic displacement parameters (Å²) for liebigite.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ca1	0.5	0.5	0.3912(4)	0.0268(10)
Ca2	0.70640(19)	0.3138(2)	0.0879(3)	0.0300(7)
Ca3	0.5	0	0.3041(3)	0.0263(11)
U1	0.54415(3)	0.23821(3)	0.27860(11)	0.02234(18)
C1	0.6311(10)	0.1245(10)	0.1675(13)	0.028(3)
C2	0.5741(11)	0.4038(11)	0.2469(14)	0.035(4)
C3	0.5652(11)	0.3180(11)	-0.0839(15)	0.035(4)
O1	0.06166(9)	0.2371(9)	0.3715(2)	0.043(3)
O2	0.4731(8)	0.2380(9)	0.1845(12)	0.036(3)
O3	0.5214(8)	0.3795(7)	0.3058(10)	0.040(4)
O4	0.4785(8)	0.1347(7)	0.3638(10)	0.035(3)
O5	0.4478(9)	0.2574(8)	0.4033(15)	0.041(4)
O6	0.5808(7)	0.1038(7)	0.2302(9)	0.032(3)
O7	0.6086(8)	0.3490(8)	0.1997(11)	0.039(3)
O8	0.6392(8)	0.2012(7)	0.1576(11)	0.035(3)
O9	0.7661(19)	0.1903(14)	0.040(3)	0.120(13)
H9a	0.804(13)	0.19(2)	0.09(2)	0.137
H9b	0.792(18)	0.21(2)	-0.013(14)	0.137
O10	0.5030(10)	0.6017(9)	0.5157(11)	0.044(3)
H10a	0.510(12)	0.652(3)	0.495(10)	0.052
H10b	0.461(7)	0.607(8)	0.552(14)	0.052
O11	0.4115(8)	0.5227(7)	0.2378(11)	0.041(3)
O12	0.6151(9)	0.3466(9)	-0.0286(12)	0.049(4)
O13	0.8088(11)	0.3503(15)	-0.0133(15)	0.070(6)
H13a	0.842(12)	0.314(8)	-0.036(15)	0.084
H13b	0.803(10)	0.381(14)	-0.066(11)	0.084
O14	0.6320(8)	0.5076(9)	0.4418(10)	0.041(3)
H14a	0.655(7)	0.469(7)	0.407(12)	0.049
H14b	0.650(7)	0.552(6)	0.412(13)	0.049
O15	0.7110(8)	0.4583(8)	0.1093(14)	0.051(4)

H15a	0.756(4)	0.485(7)	0.111(17)	0.060
H15b	0.686(10)	0.483(7)	0.158(12)	0.060
O16	0.4109(8)	0.0618(7)	0.1858(10)	0.036(3)
H16a	0.382(9)	0.038(4)	0.140(11)	0.043
H16b	0.390(9)	0.111(5)	0.188(10)	0.043
O17	0.6713(7)	0.0752(8)	0.1217(9)	0.034(3)
O18	0.5977(8)	0.0090(8)	0.4297(11)	0.041(3)
H18a	0.588(5)	0.032(12)	0.487(7)	0.048
H18b	0.644(5)	0.029(12)	0.416(7)	0.048
O19	0.7832(11)	0.3244(14)	0.2366(14)	0.072(6)
H19a	0.803(13)	0.287(10)	0.197(10)	0.085
H19b	0.789(14)	0.369(6)	0.200(11)	0.085
O20	0.691(2)	0.684(2)	0.328(4)	0.19(3)
H20a	0.71(3)	0.634(16)	0.31(6)	0.264
H20b	0.73(2)	0.71(3)	0.31(6)	0.264
O21	0.7609(11)	0.523(2)	0.3339(19)	0.134(14)
H21a	0.812(4)	0.52(2)	0.33(3)	0.151
H21b	0.75(2)	0.55(2)	0.28(2)	0.151
O22	0.5839(15)	0.1087(13)	0.5943(17)	0.079(6)
H22a	0.543(11)	0.082(15)	0.57(2)	0.095
H22b	0.576(17)	0.156(8)	0.57(2)	0.095

Table S10. Atom anisotropic displacement parameters (\AA^2) for liebigite.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.030(2)	0.022(2)	0.028(2)	0.000	0.000	0.0046(17)
Ca2	0.0252(16)	0.0329(17)	0.0319(17)	0.0068(16)	-0.0002(14)	-0.0014(14)
Ca3	0.026(2)	0.0199(19)	0.033(3)	0.000	0.000	-0.0010(15)
U1	0.0251(3)	0.0175(3)	0.0244(3)	-0.0039(5)	0.0023(4)	-0.0009(2)
C1	0.032(8)	0.023(7)	0.028(8)	-0.002(7)	0.002(7)	0.005(6)
C2	0.036(9)	0.031(9)	0.038(10)	-0.003(7)	0.007(7)	0.003(7)
C3	0.042(10)	0.023(8)	0.039(10)	0.12(3)	0.12(4)	0.07(2)
O1	0.042(8)	0.047(9)	0.041(8)	-0.001(7)	-0.008(7)	-0.007(6)
O2	0.030(6)	0.042(9)	0.037(8)	0.008(6)	0.002(6)	0.014(6)
O3	0.039(7)	0.022(6)	0.059(11)	-0.011(6)	0.012(6)	0.003(5)
O4	0.044(7)	0.022(6)	0.038(7)	-0.004(6)	0.011(6)	0.000(5)
O5	0.053(10)	0.013(6)	0.058(11)	-0.006(6)	0.020(8)	-0.005(5)
O6	0.031(6)	0.028(6)	0.037(7)	-0.001(5)	0.013(5)	0.003(5)
O7	0.050(8)	0.022(6)	0.045(7)	-0.006(6)	0.026(7)	-0.001(5)
O8	0.040(7)	0.021(6)	0.043(7)	-0.002(5)	0.014(6)	0.002(5)
O9	0.14(3)	0.055(10)	0.16(3)	0.005(18)	0.09(2)	0.006(15)
O10	0.060(9)	0.033(7)	0.038(7)	-0.009(6)	0.006(7)	-0.002(7)
O11	0.045(7)	0.025(6)	0.054(8)	-0.008(6)	-0.008(7)	0.002(5)
O12	0.060(10)	0.035(7)	0.051(9)	0.006(7)	-0.028(8)	-0.008(7)
O13	0.055(11)	0.091(16)	0.063(12)	0.005(11)	0.035(10)	0.014(10)
O14	0.033(6)	0.048(8)	0.041(8)	-0.002(6)	0.000(6)	-0.004(6)
O15	0.040(8)	0.032(7)	0.080(12)	-0.008(7)	0.004(8)	-0.010(6)
O16	0.041(7)	0.027(6)	0.040(7)	-0.001(6)	-0.016(6)	0.001(5)
O17	0.027(6)	0.032(6)	0.044(8)	-0.005(6)	0.008(5)	0.001(5)
O18	0.046(8)	0.033(7)	0.044(8)	0.002(6)	-0.018(7)	-0.001(6)
O19	0.060(11)	0.093(14)	0.063(11)	0.022(10)	-0.026(9)	-0.020(10)
O20	0.17(3)	0.12(2)	0.29(6)	0.12(3)	0.12(4)	0.07(2)
O21	0.031(11)	0.30(5)	0.072(15)	0.04(2)	0.011(10)	-0.008(16)

O22	0.115(18)	0.066(12)	0.057(11)	-0.002(11)	0.004(13)	0.032(12)
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Table S11. Selected bond distances (\AA) in the structure of liebigite.

Bond	d, \AA	Bond	d, \AA	Bond	d, \AA
U1–O1	1.801(16)	Ca1–O3	2.362(12)	Ca2–O7	2.378(13)
U1–O2	1.796(16)	Ca1–O3	2.362(12)	Ca2–O8	2.422(13)
U1–O3	2.427(12)	Ca1–H ₂ O10	2.413(14)	Ca2–H ₂ O9	2.410(30)
U1–O4	2.387(13)	Ca1–H ₂ O10	2.413(14)	Ca2–O12	2.329(14)
U1–O5	2.428(17)	Ca1–O11	2.644(15)	Ca2–H ₂ O13	2.353(17)
U1–O6	2.433(12)	Ca1–O11	2.644(15)	Ca2–H ₂ O15	2.438(14)
U1–O7	2.427(13)	Ca1–H ₂ O14	2.425(14)	Ca2–H ₂ O19	2.453(19)
U1–O8	2.435(13)	Ca1–H ₂ O14	2.425(14)	<Ca2– ϕ >	2.40
<U1–O _u >	1.80	<Ca1– ϕ >	2.46		
<U1–O _{eq} >	2.42				
Ca3–O4	2.429(12)	C1–O6	1.28(2)		
Ca3–O4	2.429(12)	C1–O8	1.30(2)		
Ca3–O6	2.462(12)	C1–O17	1.25(2)	C3–O4	1.32(2)
Ca3–O6	2.462(12)	<C1–O>	1.28	C3–O5	1.30(2)
Ca3–H ₂ O16	2.481(13)			C3–O12	1.25(2)
Ca3–H ₂ O16	2.481(13)	C2–O3	1.30(2)	<C3–O>	1.29
Ca3–H ₂ O18	2.437(13)	C2–O7	1.28(2)		
Ca3–H ₂ O18	2.437(13)	C2–O11	1.26(2)		
<Ca3– ϕ >	2.45	<C2–O>	1.28		

Table S12. Hydrogen-bond geometry in the structure of liebigite.

Bond	O–H (\AA)	H···O (\AA)	O···O (\AA)	O–H···O ($^{\circ}$)
O9–H9a···O22	1.00(30)	2.40(30)	3.06(4)	126(15)
O9–H9b···O13	0.90(30)	2.40(30)	2.88(4)	115(15)
O9–H9b···O1	0.90(30)	2.30(30)	3.20(4)	164(15)
O10–H10a···O3	0.90(8)	2.71(14)	2.93(3)	95(13)
O10–H10a···O5	0.90(8)	2.11(11)	2.95(2)	156(11)
O10–H10b···O16	0.90(16)	2.17(18)	2.92(2)	140(12)
O13–H13a···O1	0.90(18)	1.95(18)	2.79(3)	156(3)
O13–H13b···O14	0.89(19)	2.40(20)	2.90(3)	115(13)
O14–H14a···O11	0.90(13)	2.60(16)	2.94(3)	103(15)
O14–H14a···O13	0.90(13)	2.36(13)	2.90(3)	119(14)
O14–H14a···O21	0.90(13)	2.30(13)	2.72(3)	108(9)
O14–H14b···O20	0.91(12)	2.59(13)	3.50(4)	176(14)
O14–H14b···O21	0.91(12)	2.28(14)	2.72(3)	110(9)
O15–H15a···O17	0.91(10)	1.98(10)	2.85(2)	160(11)
O15–H15b···O11	0.90(16)	2.04(17)	2.80(2)	142(14)
O16–H16a···O14	0.90(13)	2.83(15)	3.62(2)	146(19)
O16–H16a···O17	0.90(13)	2.13(10)	2.85(2)	136(10)
O16–H16b···O2	0.90(9)	2.58(11)	3.14(2)	121(13)
O16–H16b···O19	0.90(9)	2.27(14)	3.03(2)	142(12)
O18–H18a···O22	0.89(14)	1.95(15)	2.82(3)	163(11)
O18–H18b···O21	0.90(12)	2.02(10)	2.82(3)	148(15)
O19–H19a···O15	0.91(13)	2.38(13)	3.11(3)	138(19)
O19–H19a···O16	0.91(13)	2.40(20)	3.03(2)	122(17)
O19–H19b···O9	0.90(17)	2.77(16)	3.52(5)	142(3)
O19–H19b···O20	0.90(17)	2.49(16)	2.70(5)	94(14)

O20–H20a…O21	0.90(40)	2.10(30)	2.96(5)	155(5)
O20–H20b…O19	0.90(5)	2.20(60)	2.70(5)	120(3)
O21–H21a…O6	0.90(11)	2.70(30)	3.40(3)	134(3)
O21–H21a…O18	0.90(11)	2.10(30)	2.82(3)	136(4)
O21–H21b…O17	0.90(30)	2.60(30)	3.26(3)	131(3)
O21–H21b…O20	0.90(30)	2.60(30)	2.96(5)	109(3)
O22–H22a…O18	0.91(18)	2.50(30)	2.82(3)	103(19)
O22–H22b…O2	0.87(14)	2.50(20)	3.02(3)	117(1)

Table S13. Bond-valence table (vu) for liebigite from Rabejac, France.

	U1	C1	C2	C3	Ca1	Ca2	Ca3	Σ	Species
O1	1.61							1.61	O
O2	1.63							1.63	O
O3	0.47		1.28		0.34 × 2 ↓			2.09	O
O4	0.51			1.21		0.29 × 2 ↓	2.01		O
O5	0.47			1.28				1.75	O
O6	0.46	1.35				0.26 × 2 ↓	2.07		O
O7	0.47		1.35			0.33		2.15	O
O8	0.46	1.28				0.29		2.03	O
O9						0.30		0.30	H ₂ O
O10					0.30 × 2 ↓			0.30	H ₂ O
O11			1.42		0.16 × 2 ↓			1.58	O
O12				1.46		0.38		1.84	O
O13						0.35		0.35	H ₂ O
O14					0.29 × 2 ↓			0.29	H ₂ O
O15						0.28		0.28	H ₂ O
O16						0.25 × 2 ↓	0.25		H ₂ O
O17			1.46					1.46	O
O18						0.28 × 2 ↓	0.28		H ₂ O
O19						0.27		0.27	H ₂ O
O20								0.00	H ₂ O
O21								0.00	H ₂ O
O22								0.00	H ₂ O
Σ	6.06	4.08	4.04	3.94	2.19	2.20	2.16		

↓: Indicates the coordination.

Table S13. *Cont.* Bond-valence table (*vu*) for liebigite.

	H9a	H9b	H10a	H10b	H13a	H13b	H14a	H14b	H15a	H15b	H16a	H16b	H18a	H18b	H19a	H19b	H20a	H20b	H21a	H21b	H22a	H22b	H*	Cations	Σ					
O1		0.16			0.23																		0.39	1.61	2.00					
O2																							0.25	1.63	1.88					
O3					0.10																		0.10	2.09	2.19					
O4																							0.00	2.01	2.01					
O5					0.19																		0.19	1.75	1.94					
O6																							0.10	2.07	2.17					
O7																							0.00	2.15	2.15					
O8																							0.00	2.03	2.03					
O9	0.63	0.70			0.11																		0.10	1.54	0.30	1.84				
O10			0.70	0.70																				1.41	0.30	1.71				
O11						0.12																		0.21	0.32	1.58	1.90			
O12																									0.00	1.84	1.84			
O13		0.14				0.70	0.71	0.15																0.35	0.35	2.06				
O14						0.14	0.70	0.70																0.09	1.63	0.29	1.92			
O15									0.70	0.70														0.15	1.54	0.28	1.82			
O16										0.70	0.70													0.14	1.73	0.25	1.98			
O17											0.22													0.12	0.53	1.46	1.99			
O18													0.71	0.70										0.20	0.13	1.74	0.28	2.02		
O19														0.16											0.70	1.73	0.27	2.00		
O20															0.12										0.13	0.70	0.18	1.77	0.00	1.77
O21															0.16	0.16								0.21	0.70	0.12	2.14	0.00	2.14	
O22		0.14																							0.23	0.70	0.73	1.79	0.00	1.79
Σ	0.77	1.00	1.00	0.89	1.04	0.85	1.13	0.97	0.92	0.91	0.98	0.98	0.94	0.92	0.98	0.92	0.90	0.88	1.00	0.93	0.82	0.85	0.94	0.00	1.96					

The crystal structure of liebigite is composed by one symmetrically independent U^{6+} cation, which is forming a typical nearly linear UO_2^{2+} uranyl ion. This UO_2^{2+} uranyl ion is coordinated by six oxygen atoms arranged at the equatorial vertices in order to form UrO_6 hexagonal bipyramids. The mean $\langle \text{U}-\text{O}_{\text{U}} \rangle$ bond length is 1.80 Å and the mean $\langle \text{U}-\text{O}_{\text{eq}} \rangle$ bond length is 2.42 Å (Table S11). In addition to the UrO_6 polyhedra, three independent C^{4+} cations are occurring as typical CO_3 triangles. The $\langle \text{C}-\text{O} \rangle$ bond lengths vary between 1.25 and 1.32 Å. The structure also contains three independent Ca^{2+} atoms occurring either in 7- or 8-fold coordination to form the following polyhedra: $\text{Ca}(1)\text{O}_4(\text{H}_2\text{O})_4$, $\text{Ca}(2)\text{O}_3(\text{H}_2\text{O})_4$ and $\text{Ca}(3)\text{O}_4(\text{H}_2\text{O})_4$. Finally, three isolated water molecules ($\text{H}_2\text{O}20$, $\text{H}_2\text{O}21$ and $\text{H}_2\text{O}22$) are occurring in the interlayer space of the structure. The structural chemical formula of liebigite is given by $\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_{11}$.

The structure of liebigite is based upon the uranyl tricarbonate $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ clusters, which are constituted by one UrO_6 hexagonal bipyramid and three CO_3 triangles connected together by edge-sharing. These clusters are linked together by three independent Ca^{2+} polyhedra, and the connection between the clusters and the Ca polyhedra lead to the formation of layers perpendicular to the crystallographic a axis. (Figure S5). Each Ca polyhedron is differently connected to the $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ clusters: $\text{Ca}(1)\text{O}_4(\text{H}_2\text{O})_4$ shares one edge with two CO_3 triangles from two different clusters, $\text{Ca}(2)\text{O}_3(\text{H}_2\text{O})_4$ shares one edge with UrO_6 hexagonal bipyramidal and one vertex with CO_3 triangle, and $\text{Ca}(3)\text{O}_4(\text{H}_2\text{O})_4$ shares one edge with two different UrO_6 hexagonal bipyramids (Figure. S6). All the oxygen atoms from the Ca polyhedra which are not linked to the UrO_6 or CO_3 polyhedra are connected to hydrogen atoms to form water molecules.

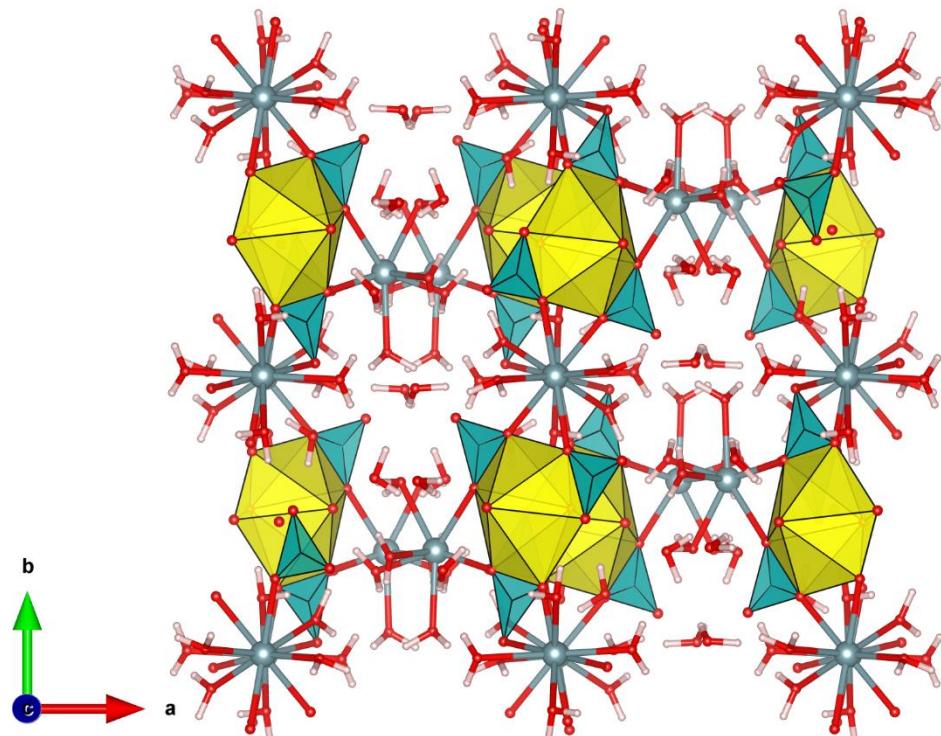


Figure S5. General view projected along the c axis of the structure of liebigite, showing the uranyl tricarbonate clusters connected together via the Ca polyhedra. Yellow: UO_6 , green: CO_3 , green: Ca atoms, red: O^{2-} atoms, white: H^+ atoms.

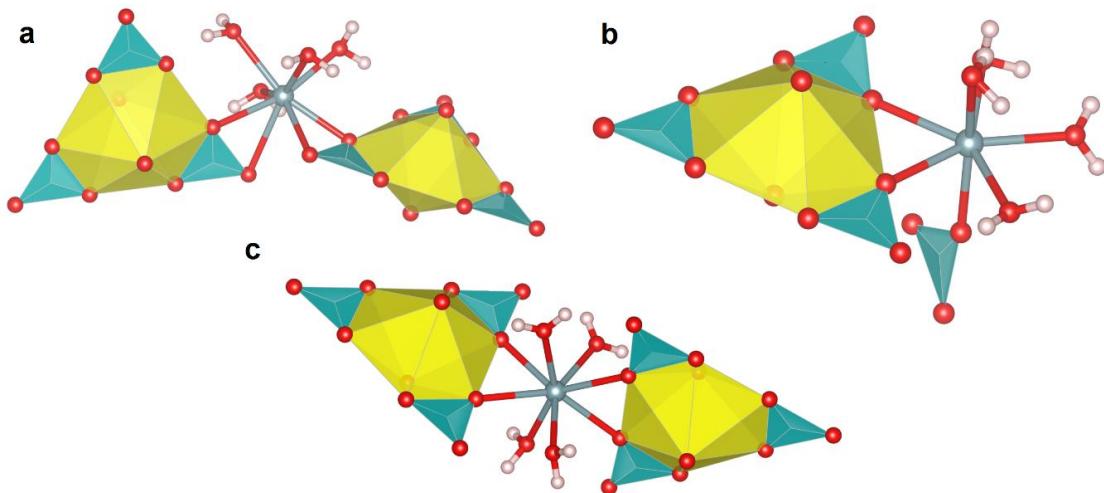


Figure S6. Detailed view of the connectivity around the Ca polyhedra: (a) $\text{Ca}(1)\text{O}_4(\text{H}_2\text{O})_4$, (b) $\text{Ca}(2)\text{O}_3(\text{H}_2\text{O})_4$ and (c) $\text{Ca}(3)\text{O}_4(\text{H}_2\text{O})_4$. Same legend as Figure S5.

The hydrogen bonds network is primordial to maintain the stability of the structure of liebigite. The connections between the $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$ clusters and the Ca polyhedra result in a loose framework, in which the H bonds strengthen the connectivity and the stability of the structure. On the eleven water molecules located in the structure of liebigite, eight are connected to the Ca polyhedra. These H_2O groups share twelve H-bonds with anions from other Ca polyhedra, seven H-bonds with oxygen atoms of the uranyl carbonate clusters, and seven H-bonds with isolated water molecules (Table S12). Four of the eight water molecules connected to the Ca polyhedra ($\text{H}_2\text{O}10$, $\text{H}_2\text{O}14$, $\text{H}_2\text{O}16$ and $\text{H}_2\text{O}19$) act as *bond-valence transformers*, transforming the bond valence received from the cation (Ca) into two separate bonds of lower valence towards neighboring anions [18–20]. Three water molecules ($\text{H}_2\text{O}9$, $\text{H}_2\text{O}13$ and $\text{H}_2\text{O}15$) act as *non-transformer* H_2O groups, receiving and giving the same number of bonds. The last water molecule ($\text{H}_2\text{O}18$) connected to the Ca polyhedra acts as *inverse-transformer* H_2O group, receiving more bonds than given [20]. Finally, the water molecules, which are not directly bonded to any cations, act as *non-transformer* H_2O groups ($\text{H}_2\text{O}21$ and $\text{H}_2\text{O}22$) or either as *inverse-transformer* H_2O group ($\text{H}_2\text{O}20$). They share three H-bonds with anions from the Ca polyhedra, three H-bond with the uranyl carbonate clusters, and two H-bonds with other isolated water molecules (Table S12). Hence, according to the method of Schindler & Hawthorne (2008) [20], the structural formula of the interstitial complex in liebigite can be given as $[\text{Ca}_2(\text{H}_2\text{O})_4(\text{H}_2\text{O})_2(\text{H}_2\text{O})_3(\text{H}_2\text{O})_2]^{4+}$.

The crystal structure of natural liebigite was firstly reported by Mereiter (1982) [21], from a natural sample of Joachimsthal. Later, Vochten *et al.* (1994) [22] solved the structure of a synthetic phase compositionally intermediate between liebigite and andersonite, $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_6$. The present study confirms that liebigite contains 11 water molecule *pfa*, as it was demonstrated by the previous structural data [21] and by the chemical analyses performed on synthetic compounds analogue to liebigite [23,24].

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