

Crystal structures and crystal chemistry of the uranyl oxide hydrates becquerelite, billietite, and protasite

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ABSTRACT

The related crystal structures of three uranyl oxide hydrate minerals, becquerelite, billietite, and protasite, have been determined by single-crystal X-ray diffraction. The chemical formulae have been determined by electron-microprobe analyses. Becquerelite, $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O}$, is orthorhombic, $Pn2_1a$, $a = 13.8378(8)$, $b = 12.3781(12)$, $c = 14.9238(9)$ Å, $Z = 4$, $R(F_{\text{obs}}) = 0.083$ (2853 reflections). Billietite, $\text{Ba}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 4\text{H}_2\text{O}$, is orthorhombic, $Pbn2_1$, $a = 12.0720(22)$, $b = 30.167(4)$, $c = 7.1455(5)$ Å, $Z = 4$, $R(F_{\text{obs}}) = 0.139$ (4104 reflections). Protasite, $\text{Ba}[(\text{UO}_2)_3\text{O}_3(\text{OH})_2] \cdot 3\text{H}_2\text{O}$, is monoclinic, Pn , $a = 12.2949(16)$, $b = 7.2206(10)$, $c = 6.9558(8)$ Å, $\beta = 90.401(15)^\circ$, $Z = 2$, $R(F_{\text{obs}}) = 0.073$ (2505 reflections). Each uranyl ion is coordinated to five other oxygen atoms in a plane nearly perpendicular to the uranyl axis forming infinite sheets that resemble those of $\alpha\text{-U}_3\text{O}_8$ in projection. The sheets are bonded together by large interlayer cations and water molecules.

INTRODUCTION

The uranyl oxide hydrates are a mineral group which has O^{2-} and $(\text{OH})^-$ as the only anionic species and U^{6+} in the form of uranyl ions, $(\text{UO}_2)^{2+}$, as the major cation. Other large cations such as K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , and possibly Bi^{3+} may be present in varying amounts. Many of the minerals are hard to distinguish from one another because of similarities in color and habit. They occur, often intermixed, as thin coatings on primary U-bearing minerals in the oxidization zone of uranium deposits. Becquerelite crystals (NMNH 106033)¹ are solitary yellow rectangular plates flattened on {001}, striated parallel to [010]. Billietite crystals (NMNH 160496) are rectangular, yellow tabular plates flattened on {010}; sector twinning is common. Protasite crystals (NMNH 150832) are bright orange pseudo-hexagonal plates flattened on {010}. All specimens are from Shaba, Zaire; the billietite and protasite are from the Shinkolobwe Mine and the specific locality for the becquerelite is unknown. Maximum plate diameter of the crystals used for structure analysis is 0.3 mm (becquerelite, billietite); 0.2 mm (protasite).

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¹ Specimens with NMNH museum numbers are in the collections of the Smithsonian National Museum of Natural History; those with HM are in the Harvard Museum.

EXPERIMENTAL DETAILS

In all cases, separate crystals from the same cluster, checked by precession photographs, were used for structure determination and electron-microprobe chemical analysis. The minerals were analyzed chemically with a modified ARL-SEM-Q microprobe using a beam approximately 25 μm in diameter at 15 kV and a current of 0.15 μA (Table 1). The standards were synthetic uraninite for U, benitoite for Ba, celestite for Sr, Corning glass C for Pb, microcline for K, and Kakanui hornblende for Si, Al, Mg, Fe, and Ca (Jarosewich et al., 1980).

Precession photographs of becquerelite confirmed the orthorhombic diffraction aspect Pn^*a as proposed by Protas and Rérat (1962). The space group $Pn2_1a$ was chosen and later confirmed by structure refinement. Precession photographs of billietite NMNH 160496 showed weak but distinct supercell reflections doubling b . The orthorhombic diffraction aspect is Pbn^* ; space group $Pbn2_1$ was confirmed. Precession photographs of the new mineral protasite (Pagoaga et al., 1986) showed monoclinic diffraction aspect P^*/n . Space group Pn was confirmed.

Intensity data for each crystal were collected by θ - 2θ scan on a Krisel-automated Picker diffractometer (Finger and Hadidiacos, 1982) with $\text{MoK}\alpha$ radiation (Zr filter). The measurements were collected using a constant precision scan, scan width = $1.5 + 0.7 \tan \theta$, maximum counting time 4 min. The collection range was 5° - $70^\circ 2\theta$, becquerelite yielding 5090 reflections [2237 with $I < 2.5\sigma(I)$], billietite yielding 6148 reflections [2040 with $I < 3.0\sigma(I)$], and protasite yielding 2913 reflections [408 with $I < 2.5\sigma(I)$]. Multiple standard reflections did not vary significantly during the data collection. The symmetry of all crystals

TABLE 1. Microprobe analyses of uranyl oxide hydrate minerals

Oxides (wt%)				Atomic proportions			
CaO	BaO	UO ₃	H ₂ O	Ca (Ba)	U	H	O
Becquerelite, NMNH 106033, Ca[(UO ₂) ₆ O ₄ (OH) ₆]·8H ₂ O							
3.3		86.4	10.3	1.2	6.0	22.7	30.5
3.1		86.4	10.5	1.1	6.0	23.2	30.7
Billietite, HM 104455, Ba[(UO ₂) ₆ O ₄ (OH) ₆]·4H ₂ O							
8.4	85.7	5.9	1.1	6.0	13.2		25.7
8.2	85.7	6.1	1.1	6.0	13.6		25.8
Billietite, NMNH 160496, Ba[(UO ₂) ₆ O ₄ (OH) ₆]·3-5H ₂ O							
8.3	84.6	7.0	1.1	6.0	15.8		27.0
8.3	86.0	5.7	1.1	6.0	12.7		25.4
Protasite, NMNH 150732, Ba[(UO ₂) ₃ O ₃ (OH) ₂]·3H ₂ O							
15.3	77.9	6.8	1.1	3.0	8.3		14.2
14.7	78.0	7.3	1.1	3.0	8.9		14.5

Note: Water content in the analyses is calculated by difference since spectral scanning and structure analyses detected no other elements in significant amounts. Atomic proportions are based on 6U (becquerelite and billietite) and 3U (protasite). Accuracy of the analyses in atomic proportions is to the nearest integer.

was confirmed by collecting multiple data sets. Cell dimensions were obtained from single-crystal data using the method of Hamilton (Ibers and Hamilton, 1974; Finger and Hadidiacos, 1982) and refined with the program of Appleman and Evans

(1973). The number of reflections used was 40 for becquerelite, 19 for billietite, and 37 for protasite; the 2θ range was 50° – 60° . Since linear absorption coefficients were high (becquerelite, 362 cm^{-1} ; billietite, 369 cm^{-1} ; protasite, 404 cm^{-1}), corrections for absorption were applied using the program ABSORB from XTAL83 (Stewart, 1983). All the other programs used in the solution and refinement of the structures were from XRAY76 (Stewart, 1976). Atomic scattering factors for oxygen, Ca, Ba, and U and anomalous-dispersion corrections were obtained from the *International Tables*, volume IV (Ibers and Hamilton, 1974).

STRUCTURE REFINEMENT

For all three structures, the U atoms were found from the largest peaks on Patterson maps, and all other atoms except H were located from difference Fourier syntheses. Least-squares refinements converged at $R(F_{\text{obs}}) = 0.083$ (becquerelite), 0.139 (billietite), and 0.073 (protasite). For billietite, refinement of the structure was started using the average subcell with cell parameters reported by Christ and Clark (1960) and verified in this study for specimen HM 104455 (Table 1). The space group for the subcell is $P2nn$. This refinement led to initial positions for the U atoms and the Ba atom in the supercell, which were then used in difference Fourier syntheses.

TABLE 2. Atomic parameters for becquerelite

Atom	X	Y	Z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
U(1)	0.08927(27)	0.5587(6)	0.25794(18)	0.66(13)	0.24(20)	0.21(8)	-0.11(15)	-0.05(8)	-0.13(10)
U(2)	0.12835(17)	0.2467(7)	0.24753(12)	0.80(7)	0.77(11)	0.36(6)	0.05(24)	0.03(5)	-0.01(12)
U(3)	0.09471(28)	0.9402(6)	0.25081(16)	0.41(12)	1.27(22)	0.30(9)	-0.15(17)	0.07(8)	-0.17(10)
U(4)	0.37304(14)	0.75 (od)	0.27802(10)	0.61(7)	0.52(11)	0.26(6)	-0.06(23)	-0.05(5)	-0.27(12)
U(5)	0.34222(27)	0.4404(7)	0.29160(21)	0.42(12)	1.10(23)	0.40(9)	-0.10(14)	-0.14(8)	-0.22(12)
U(6)	0.34898(30)	0.0690(7)	0.28840(20)	0.68(14)	0.34(21)	0.28(9)	-0.27(15)	0.06(7)	-0.22(10)
Ca	0.0429(12)	0.5735(17)	0.5341(8)	2.1(7)	2.2(10)	0.7(4)	-0.1(7)	-0.2(4)	0.4(5)
O(101) u	0.053(3)	0.537(5)	0.3728(27)	0.4(8)					
O(102) u	0.138(4)	0.590(4)	0.1414(26)	0.4(8)					
O(201) u	0.0739(28)	0.225(4)	0.3603(24)	0.4(8)					
O(202) u	0.1747(26)	0.260(5)	0.1352(22)	0.4(8)					
O(301) u	0.0641(34)	0.978(5)	0.3618(28)	0.4(8)					
O(302) u	0.1081(33)	0.914(4)	0.1368(27)	0.4(8)					
O(401) u	0.3861(27)	0.756(6)	0.3960(21)	0.4(8)					
O(402) u	0.3488(30)	0.763(4)	0.1583(23)	0.4(8)					
O(501) u	0.340(4)	0.452(6)	0.4059(33)	0.4(8)					
O(502) u	0.354(3)	0.417(4)	0.1736(26)	0.4(8)					
O(601) u	0.333(4)	0.050(6)	0.4095(33)	0.4(8)					
O(602) u	0.375(4)	0.099(4)	0.1686(27)	0.4(8)					
O(1) h	0.014(5)	0.384(7)	0.204(4)	1.5(12)					
O(2) o	0.178(4)	0.416(5)	0.287(3)	1.5(10)					
O(3) o	-0.072(5)	0.583(7)	0.224(4)	1.5(10)					
O(4) h	0.052(3)	0.738(7)	0.2767(27)	1.5(12)					
O(5) h	0.245(6)	0.617(9)	0.304(5)	1.5(12)					
O(7) w	0.112(5)	0.389(5)	0.510(4)	1.7(13)					
O(8) w	-0.121(5)	0.579(6)	0.477(4)	1.7(13)					
O(9) w	0.057(4)	0.754(9)	0.4755(28)	1.7(13)					
O(10) w	0.227(5)	0.607(7)	0.504(4)	1.7(13)					
O(11) h	0.309(3)	0.248(11)	0.3159(27)	1.5(12)					
O(12) h	0.011(5)	0.112(7)	0.191(4)	1.5(12)					
O(13) o	0.190(4)	0.068(5)	0.262(4)	1.5(10)					
O(14) o	0.438(4)	0.923(7)	0.267(4)	1.5(10)					
O(15) h	0.247(6)	0.873(9)	0.307(5)	1.5(12)					
O(16) w	0.305(4)	0.230(6)	0.504(3)	2.0(12)					
O(17) w	0.063(5)	0.089(6)	0.025(4)	2.0(12)					
O(19) w	0.469(5)	0.894(6)	0.517(4)	2.0(12)					
O(20) w	0.213(5)	0.871(7)	0.495(4)	2.0(12)					

Note: The thermal parameters are listed as $\text{\AA}^2 \times 100$, od = origin defining; u = uranyl, o = O²⁻, h = hydroxyl, and w = water. Anisotropic temperature factors have the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$.

TABLE 3. Atomic parameters for billietite

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(1)	0.44426(21)	0.25322(8)	0.0045 (od)	0.44(9)	0.23(8)	0.30(12)	0.11(8)	-0.04(10)	0.11(13)
U(2)	0.25251(26)	0.26419(8)	0.4376(6)	0.64(10)	0.39(10)	0.51(9)	-0.06(11)	0.23(11)	0.01(8)
U(3)	0.06112(22)	0.25716(8)	0.0075(8)	0.57(10)	0.19(9)	0.29(12)	-0.02(9)	-0.11(11)	-0.18(12)
U(4)	0.43954(27)	-0.00465(11)	-0.0141(6)	0.58(10)	0.59(9)	0.39(14)	0.06(10)	-0.01(10)	-0.03(12)
U(5)	0.06074(25)	-0.00560(10)	-0.0081(6)	0.53(10)	0.62(8)	0.34(13)	-0.01(10)	-0.07(10)	0.03(13)
U(6)	0.25071(26)	-0.01161(8)	0.5291(6)	0.44(9)	0.39(9)	0.67(10)	0.01(10)	0.09(12)	0.06(8)
Ba	0.3628(4)	0.12391(17)	-0.3120(10)	1.33(17)	1.13(18)	1.61(20)	-0.06(18)	0.06(19)	0.19(19)
O(101) u	0.468(4)	0.3084(17)	0.026(10)	0.6(9)					
O(102) u	0.416(4)	0.1949(18)	-0.004(9)	0.6(9)					
O(201) u	0.255(5)	0.3248(16)	0.423(8)	0.6(9)					
O(202) u	0.255(5)	0.2046(17)	0.460(7)	0.6(9)					
O(301) u	0.031(4)	0.3116(18)	0.023(10)	0.6(9)					
O(302) u	0.075(5)	0.1997(17)	-0.007(9)	0.6(9)					
O(401) u	0.387(5)	0.0519(19)	-0.031(8)	0.6(9)					
O(402) u	0.494(5)	-0.0633(20)	-0.021(8)	0.6(9)					
O(501) u	0.109(4)	0.0504(17)	0.041(8)	0.6(9)					
O(502) u	0.014(5)	-0.0626(20)	-0.050(9)	0.6(9)					
O(601) u	0.258(5)	-0.0449(17)	0.438(8)	0.6(9)					
O(602) u	0.240(5)	-0.0672(17)	0.561(8)	0.6(9)					
O(1) h	0.391(5)	0.2682(20)	0.703(10)	1.0(10)					
O(2) o	0.411(4)	0.2520(19)	0.349(7)	0.4(8)					
O(3) o	0.095(4)	0.2479(18)	0.309(8)	0.4(8)					
O(4) h	0.118(5)	0.2698(19)	0.691(11)	1.0(10)					
O(5) h	0.270(4)	0.2571(18)	0.017(10)	1.0(10)					
O(11) o	0.418(4)	-0.0144(17)	0.676(8)	0.4(8)					
O(12) h	0.394(5)	-0.0268(22)	0.326(10)	1.0(10)					
O(13) h	0.104(5)	-0.0275(22)	0.326(10)	1.0(10)					
O(14) o	0.090(4)	-0.0051(17)	0.695(9)	0.4(8)					
O(15) h	0.252(6)	-0.0259(18)	-0.082(8)	1.0(10)					
O(16) w	0.230(4)	0.1221(20)	-0.008(9)	0.7(8)					

Note: The thermal parameters are listed as $\text{\AA}^2 \times 100$, od = origin defining; u = uranyl, o = O^{2-} , h = hydroxyl, and w = water. Anisotropic temperature factors have the form $\exp[-2\pi^2(h^2a^2U_{11} + \dots + 2klb^*c^*U_{23})]$.

Refinement for all three structures consisted of a constrained step-wise full-matrix least-squares procedure designed to minimize the extraordinarily large effects of very strong absorption coupled with poor crystallinity due to omnipresent layer disorder. Scale, positional, and thermal parameters were alternately fixed and refined in

groups using unit weights until final convergence was achieved. The data did not permit anisotropic refinement of the oxygen atoms, and their isotropic temperature factors were refined in chemical groups (uranyl oxygens, O^{2-} , hydroxyl oxygens, and water oxygens) according to the method of Piret-Meunier and Piret (1982). Two types of

TABLE 4. Atomic parameters for protasite

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(1)	1.0000	-0.02314(20)	0.0 (od)	0.56(4)	0.60(5)	0.01(4)	-0.02(7)	0.06(4)	0.02(8)
U(2)	0.81983(15)	-0.01959(20)	0.45837(25)	0.27(5)	0.59(5)	0.26(4)	-0.05(8)	-0.02(4)	0.19(8)
U(3)	1.11859(16)	-0.01512(19)	0.52145(26)	0.32(5)	0.57(5)	0.08(5)	-0.04(8)	-0.13(4)	-0.01(8)
Ba	0.97749(24)	0.51175(33)	0.3285(4)	1.30(9)	0.62(9)	0.88(9)	0.10(9)	-0.07(7)	0.09(9)
O(101) u	1.0170(29)	-0.278(5)	-0.027(6)	1.2(6)					
O(102) u	0.9897(28)	0.231(5)	0.056(5)	1.2(6)					
O(201) u	0.8096(32)	-0.267(5)	0.504(6)	1.2(6)					
O(202) u	0.8418(28)	0.224(5)	0.399(5)	1.2(6)					
O(301) u	1.1337(28)	-0.264(5)	0.558(5)	1.2(6)					
O(302) u	1.1034(28)	0.233(5)	0.462(5)	1.2(6)					
O(1) o	0.9794(25)	-0.092(4)	0.318(4)	0.8(5)					
O(2) o	0.9540(24)	0.005(4)	-0.308(5)	0.8(5)					
O(3) h	0.8086(27)	-0.074(4)	0.072(5)	1.1(5)					
O(4) h	1.1938(26)	-0.072(4)	0.203(5)	1.1(5)					
O(5) o	1.1505(24)	0.025(4)	-0.163(4)	0.8(5)					
O(6) w	1.187(4)	0.545(8)	0.156(8)	4(1)					
O(7) w	0.802(5)	0.534(7)	0.062(8)	4(1)					
O(8) w	0.934(4)	0.442(7)	0.722(8)	4(1)					

Note: The thermal parameters are listed as $\text{\AA}^2 \times 100$, od = origin defining; u = uranyl, o = O^{2-} , h = hydroxyl, and w = water. Anisotropic temperature factors have the form $\exp[-2\pi^2(h^2a^2U_{11} + \dots + 2klb^*c^*U_{23})]$.

TABLE 6. Interatomic distances in becquerelite

Bonded atoms	Distance (Å)	Bonded atoms	Distance (Å)
U(1)–O(101)	1.81(4)	U(2)–O(201)	1.86(4)
U(1)–O(102)	1.91(4)	U(2)–O(202)	1.80(3)
U(1)–O(1)	2.53(8)	U(2)–O(1)	2.42(8)
U(1)–O(2)	2.20(6)	U(2)–O(2)	2.28(6)
U(1)–O(3)	2.31(7)	U(2)–O(11)	2.70(4)
U(1)–O(4)	2.29(8)	U(2)–O(12)	2.47(8)
U(1)–O(5)	2.38(9)	U(2)–O(13)	2.39(7)
U(3)–O(301)	1.77(4)	U(4)–O(401)	1.77(3)
U(3)–O(302)	1.74(4)	U(4)–O(402)	1.83(3)
U(3)–O(4)	2.61(8)	U(4)–O(3)	2.20(8)
U(3)–O(12)	2.58(8)	U(4)–O(4)	2.61(4)
U(3)–O(13)	2.06(6)	U(4)–O(5)	2.45(10)
U(3)–O(14)	2.20(6)	U(4)–O(14)	2.33(8)
U(3)–O(15)	2.42(9)	U(4)–O(15)	2.35(10)
U(5)–O(501)	1.71(5)	U(6)–O(601)	1.83(5)
U(5)–O(502)	1.79(4)	U(6)–O(602)	1.86(4)
U(5)–O(1)	2.47(7)	U(6)–O(11)	2.32(14)
U(5)–O(2)	2.29(5)	U(6)–O(12)	2.32(7)
U(5)–O(3)	2.14(8)	U(6)–O(13)	2.23(6)
U(5)–O(5)	2.58(10)	U(6)–O(14)	2.21(8)
U(5)–O(11)	2.45(14)	U(6)–O(15)	2.82(11)
Ca–O(101)	2.45(4)	Ca–O(7)	2.51(7)
Ca–O(201)	2.94(4)	Ca–O(8)	2.42(7)
Ca–O(301)	2.45(5)	Ca–O(9)	2.41(11)
Ca–O(602)	2.33(5)	Ca–O(10)	2.62(7)
Ca–U(1)	4.18	Ca–U(4)	5.54
Ca–U(2)	4.56	Ca–U(5)	5.74
Ca–U(3)	4.08	Ca–U(6)	4.08
Some possible bonds to interlayer water molecules			
O(7)–O(101)	2.87(8)	O(8)–O(101)	2.91(8)
O(7)–O(402)	2.76(7)	O(8)–O(301)	2.82(8)
O(7)–O(9)	2.89(10)	O(8)–O(20)	2.90(11)
O(9)–O(4)	2.97(6)	O(10)–O(501)	2.87(10)
O(9)–O(20)	2.61(11)	O(10)–O(602)	2.84(8)
		O(10)–O(5)	2.99(10)
		O(10)–O(17)	2.94(10)
O(16)–O(102)	2.79(7)	O(17)–O(302)	2.80(9)
O(16)–O(601)	2.67(9)	O(17)–O(401)	2.91(9)
O(16)–O(11)	2.82(6)	O(17)–O(501)	2.80(9)
		O(17)–O(12)	2.60(9)
		O(17)–O(19)	2.81(10)
O(19)–O(401)	2.74(8)	O(20)–O(202)	2.95(8)
O(19)–O(501)	2.98(8)	O(20)–O(502)	2.87(8)
O(19)–O(1)	2.80(8)	O(20)–O(15)	2.85(10)

TABLE 7. Interatomic distances in billietite

Bonded atoms	Distance (Å)	Bonded atoms	Distance (Å)
U(1)–O(101)	1.70(5)	U(2)–O(201)	1.83(5)
U(1)–O(102)	1.79(5)	U(2)–O(202)	1.80(5)
U(1)–O(1)	2.29(7)	U(2)–O(1)	2.53(7)
U(1)–O(2)	2.49(5)	U(2)–O(2)	2.05(5)
U(1)–O(3)	2.29(5)	U(2)–O(3)	2.17(5)
U(1)–O(4)	2.57(6)	U(2)–O(4)	2.44(7)
U(1)–O(5)	2.11(5)	U(2)–O(5)	3.02(7)
U(3)–O(301)	1.69(5)	U(4)–O(401)	1.82(6)
U(3)–O(302)	1.74(5)	U(4)–O(402)	1.89(6)
U(3)–O(1)	2.60(6)	U(4)–O(11)	2.25(6)
U(3)–O(2)	2.15(5)	U(4)–O(11)	2.26(5)
U(3)–O(3)	2.21(6)	U(4)–O(12)	2.50(7)
U(3)–O(4)	2.40(8)	U(4)–O(12)	2.58(7)
U(3)–O(5)	2.52(5)	U(4)–O(15)	2.40(7)
U(5)–O(501)	1.82(5)	U(6)–O(601)	1.83(5)
U(5)–O(502)	1.83(6)	U(6)–O(602)	1.70(5)
U(5)–O(1)	2.52(6)	U(6)–O(11)	2.28(5)
U(5)–O(13)	2.53(7)	U(6)–O(12)	2.31(7)
U(5)–O(14)	2.15(6)	U(6)–O(13)	2.34(7)
U(5)–O(14)	2.34(6)	U(6)–O(14)	2.29(5)
U(5)–O(15)	2.45(7)	U(6)–O(15)	2.81(6)
Ba–O(102)	3.14(6)	Ba–O(401)	2.97(6)
Ba–O(202)	3.20(6)	Ba–O(402)	2.93(6)
Ba–O(301)	3.05(6)	Ba–O(601)	3.24(6)
Ba–O(16)	2.70(6)		
Ba–U(1)	4.62	Ba–U(4)	4.52
Ba–U(2)	4.78	Ba–U(5)	5.77
Ba–U(3)	4.50	Ba–U(6)	4.45
Some possible bonds to interlayer water molecules			
O(16)–O(102)	3.14(8)	O(16)–O(401)	2.85(8)
O(16)–O(302)	3.00(8)	O(16)–O(501)	2.63(8)

water were distinguished in becquerelite. The final atomic coordinates and temperature factors are given in Tables 2 to 4. Observed and calculated structure factors are given in Table 5.²

The structure determined here for becquerelite agrees well with that of Piret-Meunier and Piret (1982), who obtained $R(F_{\text{obs}}) = 0.070$. We feel that the close agreement between these completely independent structure determinations, on different specimens, confirms the structure proposed for becquerelite despite rather large variations in the appearance of crystals from different sources. This agreement also validates the procedures used in this study, even though the R values obtained are relatively large.

² To obtain copies of Tables 5, 10, and 11, order Document AM-87-361 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

Disorder is observed for all three minerals as moderate to intense streaking in the diffraction patterns, primarily perpendicular to the plates. Compared to synthesized mineral-analogue structures reported recently (Mereiter, 1979), the natural minerals may not seem well refined. However, the final R values for becquerelite and protasite are comparable to the “ R ” values calculated between symmetrically equivalent data sets from the initial intensity measurements. Since care was taken in collecting and reducing the data, we conclude that the precision of the refinements reflects the poor crystallinity of the naturally occurring minerals as well as the difficulty of making accurate absorption corrections on irregular samples.

CRYSTAL CHEMISTRY

All three structures contain quasi-linear $(\text{UO}_2)^{2+}$ groups coordinated by five $(\text{O}^{2-}, \text{OH}^-)$ to form pentagonal bipyramids $[(\text{UO}_2)\text{O}_2(\text{OH})_3]$ (becquerelite and billietite) and $[(\text{UO}_2)\text{O}_3(\text{OH})_2]$ (protasite). These polyhedra share pentagon edges to form sheets of $[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]_n^{2n-}$ (becquerelite and billietite) and $[(\text{UO}_2)_3\text{O}_3(\text{OH})_2]_n^{2n-}$ (protasite). The sheets are parallel to $\{001\}$ (becquerelite) and $\{010\}$ (billietite and protasite) and are bonded together by interlayer cations and water molecules. Selected bond lengths and uranyl bond angles are listed in Tables 6, 7, 8, and 9. Complete bond valences and bond angles are listed in Tables 10 and 11, respectively (see footnote 2).

Our results confirm the prediction of Evans (1963) that the uranyl oxide hydrates would show mainly pentagonal

TABLE 8. Interatomic distances in protasite

Bonded atoms	Distance (Å)	Bonded atoms	Distance (Å)
U(1)–O(101)	1.86(3)	U(2)–O(201)	1.82(4)
U(1)–O(102)	1.88(3)	U(2)–O(202)	1.82(3)
U(1)–O(1)	2.28(3)	U(2)–O(1)	2.26(3)
U(1)–O(2)	2.22(3)	U(2)–O(2)	2.31(3)
U(1)–O(3)	2.44(3)	U(2)–O(3)	2.72(3)
U(1)–O(4)	2.78(4)	U(2)–O(4)	2.40(4)
U(1)–O(5)	2.21(3)	U(2)–O(5)	2.24(3)
U(3)–O(301)	1.83(3)	Ba–O(101)	2.95(4)
U(3)–O(302)	1.84(3)	Ba–O(102)	2.78(4)
U(3)–O(1)	2.28(3)	Ba–O(201)	2.89(4)
U(3)–O(2)	2.36(3)	Ba–O(202)	2.71(4)
U(3)–O(3)	2.45(3)	Ba–O(301)	2.97(4)
U(3)–O(4)	2.44(4)	Ba–O(302)	2.70(3)
U(3)–O(5)	2.24(3)	Ba–O(1)	2.86(3)
Ba–U(1)	4.07	Ba–O(6)	2.86(6)
Ba–U(2)	4.01	Ba–O(7)	2.84(6)
Ba–U(3)	4.06	Ba–O(8)	2.84(6)
Some possible bonds to interlayer water molecules			
O(6)–O(101)	2.76(7)	O(7)–O(301)	2.84(6)
O(6)–O(201)	2.73(7)	O(7)–O(3)	2.83(6)
O(6)–O(4)	2.78(6)	O(7)–O(8)	2.95(8)
O(8)–O(101)	2.85(7)		
O(8)–O(102)	2.86(7)		
O(8)–O(202)	2.97(7)		

coordination around the uranyl ion. This allows the coordinating oxygen atoms to remain in a plane perpendicular to the uranyl ion without crowding.

Structure of the uranyl oxide sheet

The uranium-oxygen sheet found in the uranyl oxide hydrate minerals is similar to the sheets in α - and β - U_3O_8 (Loopstra, 1964, 1970; Hoekstra et al., 1955). In α - U_3O_8 , each of the quasi-uranyl ions is coordinated to five oxygen atoms in a plane perpendicular to the uranyl axis. Triangular shaped “holes” (Fig. 1a) in the sheet are bounded by the edges of three uranyl pentagonal bipyramids. This is the simplest structure because all uranyl environments are the same and there are only two different sheet-oxygen environments. In β - U_3O_8 , on the other hand, two of the quasi-uranyl ions are each coordinated to five oxygen atoms, but one uranyl ion is coordinated to only four oxygen atoms. Triangular “holes” in this structure (Fig. 1b) are bounded by the edges of two uranyl pentagonal bipyramids and one uranyl tetragonal bipyramid. This structure is more complex since it has two different uranyl-ion environments and two dif-

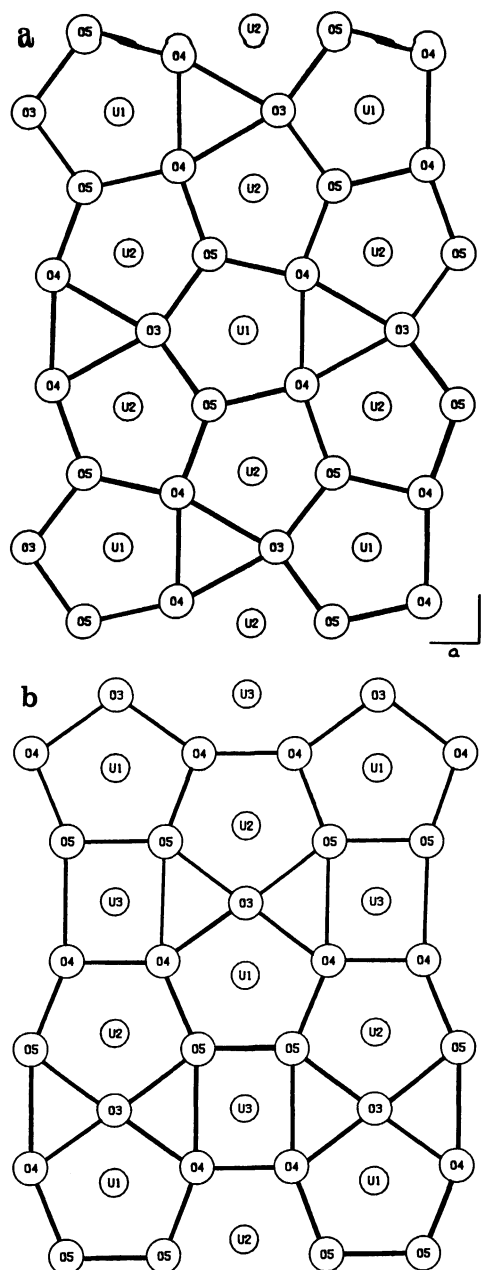


Fig. 1. Projections of two uranium-oxygen sheets. (a) α - U_3O_8 . (b) β - U_3O_8 . “Uranyl” oxygen atoms are not shown (see text).

TABLE 9. Uranyl bond angles in becquerelite, billietite, and protasite

Becquerelite				Billietite				Protasite			
Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
O(101)	U(1)	O(102)	174(2)	O(101)	U(1)	O(102)	177(3)	O(101)	U(1)	O(102)	173(2)
O(201)	U(2)	O(202)	176(2)	O(201)	U(2)	O(202)	177(3)	O(201)	U(2)	O(202)	174(2)
O(301)	U(3)	O(302)	171(2)	O(301)	U(3)	O(302)	173(2)	O(301)	U(3)	O(302)	175(2)
O(401)	U(4)	O(402)	171(2)	O(401)	U(4)	O(402)	175(2)				
O(501)	U(5)	O(502)	174(3)	O(501)	U(5)	O(502)	178(3)				
O(601)	U(6)	O(602)	174(3)	O(601)	U(6)	O(602)	167(3)				

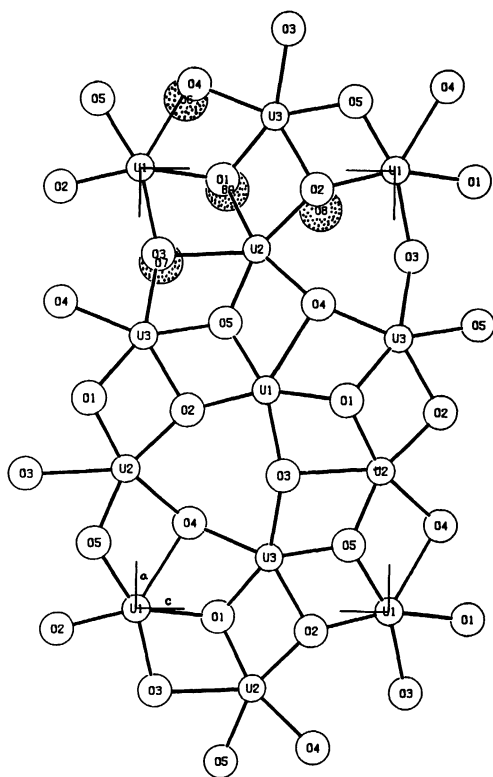


Fig. 2. Protasite sheet near $y = 0.0$. Stippled Ba atom and H_2O molecules are near $y = -0.5$. Uranyl oxygen atoms are not shown.

ferent sheet-oxygen environments. The arrangement of the atoms in the sheets of becquerelite, billietite, and protasite is most similar to the $\alpha-U_3O_8$ structure.

The sheet arrangement is simplest in protasite, with one $\alpha-U_3O_8$ repeat unit in one kind of sheet (Figs. 2, 3). Billietite has two crystallographically distinct sheets, each with one $\alpha-U_3O_8$ repeat unit (Fig. 4). Becquerelite has one distinct sheet with a double $\alpha-U_3O_8$ repeat unit (Fig. 5). This sheet is the most puckered of the three, perhaps because of the small size of the interlayer Ca atom. Protasite and billietite sheets are more nearly planar. The billietite sheets depart farthest from the $\alpha-U_3O_8$ model. Atoms U(2) and U(6) have such long bonds to O(5) and O(15), respectively, that the coordination around these two uranyl ions is almost fourfold. Thus, the billietite sheets, though still closer to $\alpha-U_3O_8$, are distorted toward the $\beta-U_3O_8$ arrangement (Fig. 1b).

Interlayer structure

In becquerelite, the uranyl sheets are bonded together by interlayer Ca atoms and water molecules. Each Ca is coordinated by four water molecules and four uranyl oxygens. The four water molecules not coordinated to the Ca occupy the remaining interlayer bonding sites. Possible hydrogen bonds are shown in Tables 6, 7, and 8.

In the interlayer region of billietite, there are ten pos-

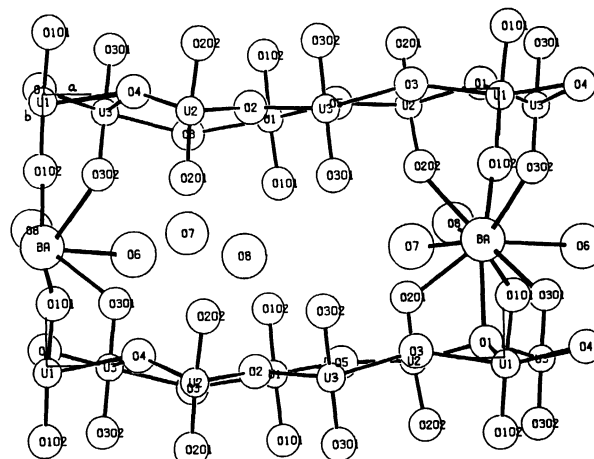


Fig. 3. Protasite viewed down c^* , approximately parallel to the sheets, near $z = 0.25$. Large oxygen atoms are H_2O molecules.

sible sites large enough to accommodate a cation or water molecule. One Ba and only one water molecule were located in this study, although microprobe analysis (Table 1) suggests that three additional water molecules are present. Ordering of the Ba atom and water molecule probably accounts in large part for the observed supercell. Billietites such as HM 104455 (Table 1) that lack supercell reflections must have disordered Ba occupancy. The three water molecules not located in this structure refinement are assumed to be disordered over the eight remaining interlayer sites. This random partial occupancy may contribute to the streaking observed in the diffraction pattern. A completely disordered arrangement would have an occupancy of 0.375 water molecules in each of the eight sites. Inclusion of these disordered water molecules in the refinement produced an insignificant decrease in R and no observable change in difference Fourier maps. With the quality of the data gathered from this crystal, it is apparently not possible to determine the position of water molecules with such a low site occupancy.

Previous analyses (Protas and Rérat, 1962; Protas, 1959; Brasseur, 1949) show formulae for billietites containing between three and six more molecules of water than our specimens. Such billietites might be better crystallized.

In protasite, one Ba atom is located between the U sheets and, along with the three water molecules, bonds the sheets together (Fig. 3). Each Ba atom is coordinated to ten oxygen atoms, of which six are uranyl oxygens, three are water oxygens, and one is an O^{2-} . All water molecules are bonded to Ba. All but one of the possible interlayer sites are occupied in this mineral.

One significant difference between the uranyl oxide hydrate and U_3O_8 sheets is the uranyl ion distances. In a sense the two forms of U_3O_8 have no "uranyl" oxygen atoms. There are no interlayer cations; each "uranyl" oxygen is shared between two U atoms in adjacent sheets. The result is a longer "uranyl" bond distance, 2.07 Å in

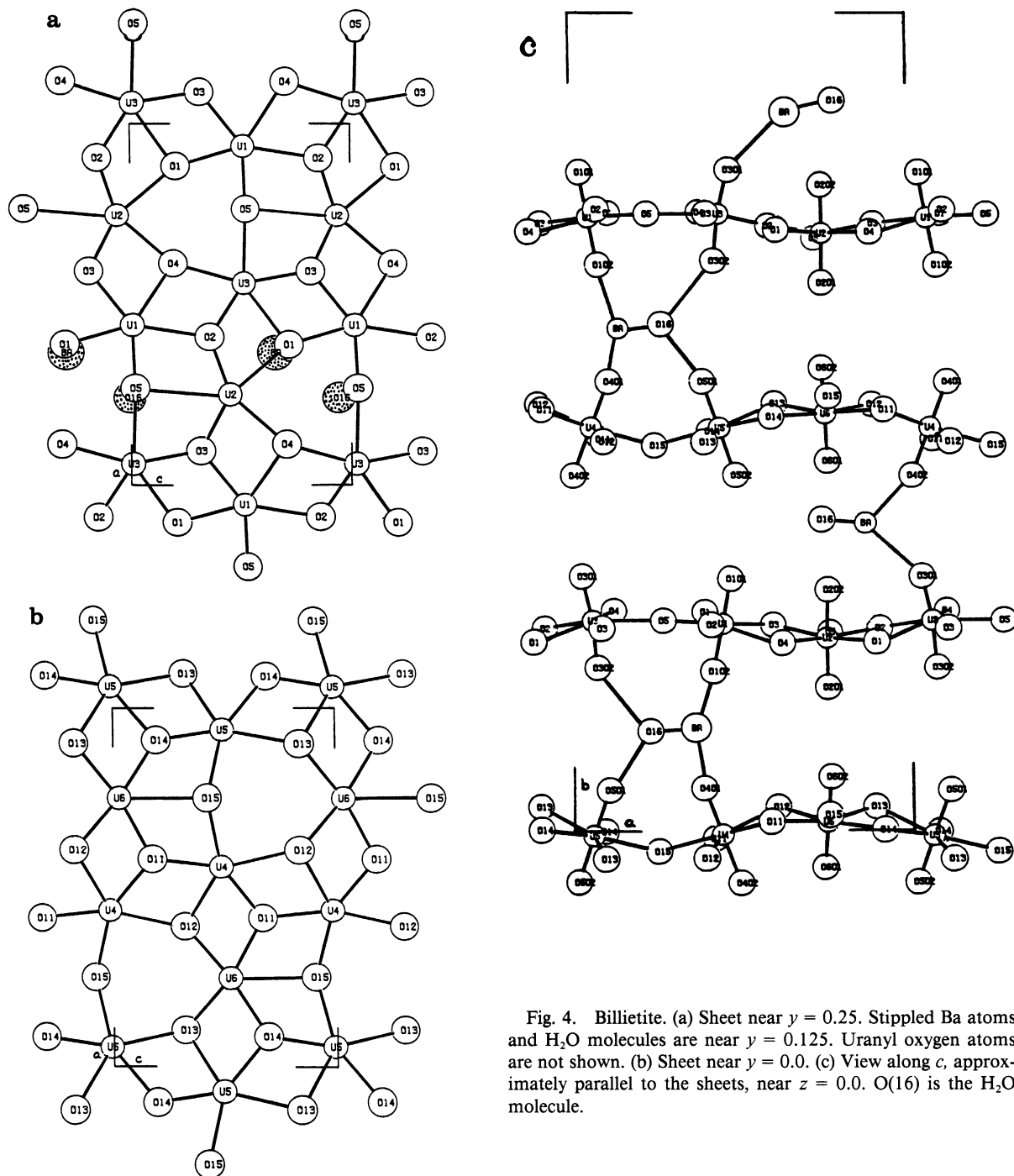


Fig. 4. Billietite. (a) Sheet near $y = 0.25$. Stippled Ba atoms and H₂O molecules are near $y = 0.125$. Uranyl oxygen atoms are not shown. (b) Sheet near $y = 0.0$. (c) View along c , approximately parallel to the sheets, near $z = 0.0$. O(16) is the H₂O molecule.

α -U₃O₈ and 1.89–2.28 Å in β -U₃O₈, compared to an average distance of 1.81 Å for the three structures determined in this study.

Bond strength–bond length comparisons

Assignment of O²⁻ and (OH)⁻ oxygen atoms was made following the method for bond length–bond strength calculations described by Brown and Wu (1976) and Don-

ay and Allmann (1970); the results are summarized in Table 12. This table shows that the valences from our study are comparable with those for curite (Mereiter, 1979), fourmarierite (Piret, 1985), and sayrite (Piret et al., 1983), three other uranyl oxide hydrate minerals whose structures are well determined. The wide variability in bond-strength sums indicates that the calculations of bond strengths for individual atoms should be used with cau-

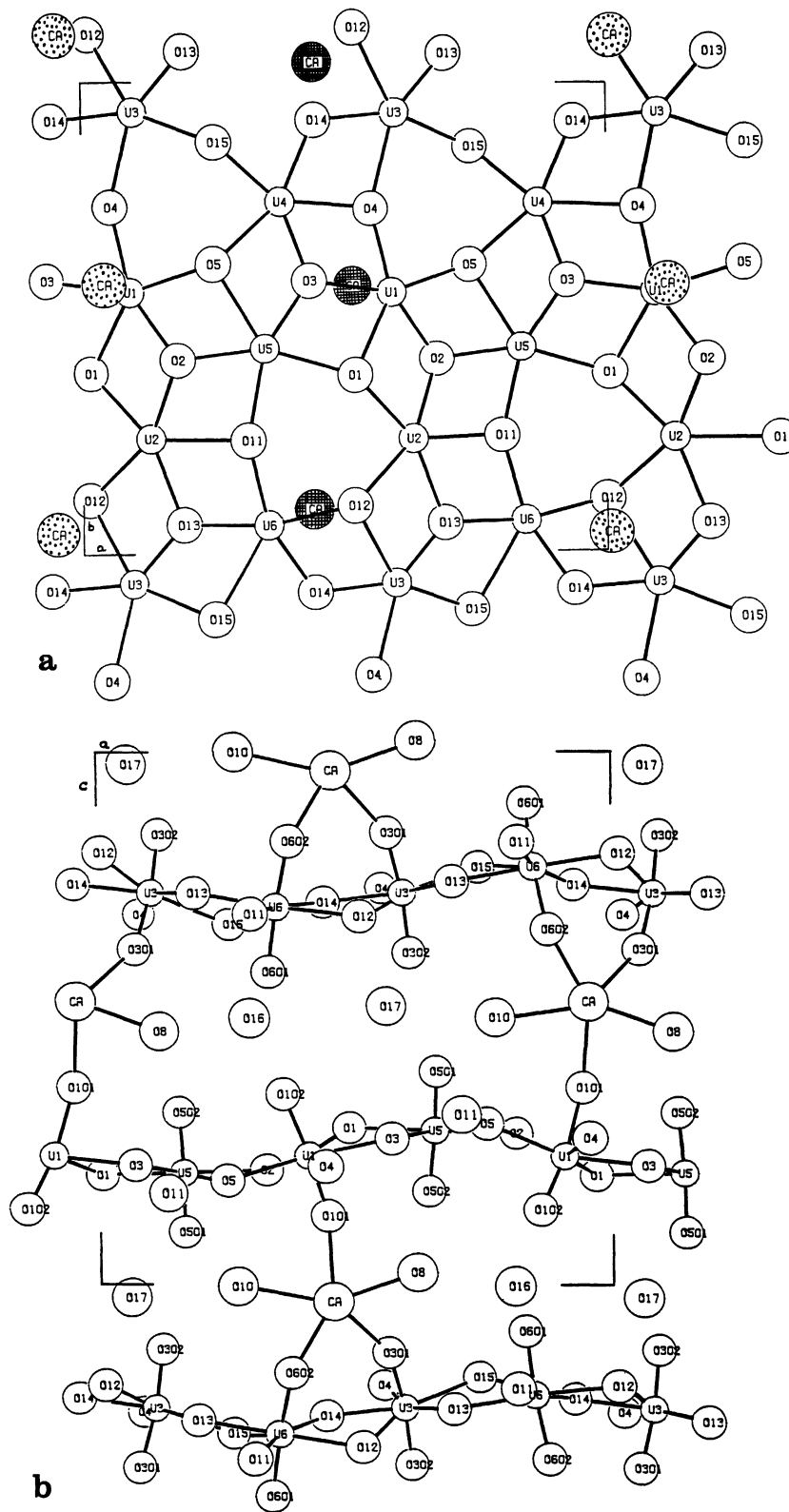


Fig. 5. Becquerelite. (a) Sheet near $z = 0.25$. Cross-hatched Ca atoms are near $z = 0.0$ and stippled Ca atoms are near $z = 0.5$. Uranyl oxygen atoms are not shown. (b) View along b , approximately parallel to the sheets, near $y = 0.0$. Large oxygen atoms are H_2O molecules.

TABLE 12. Bond-strength sums to oxygen atoms

Structure	Uranyl	O ²⁻	(OH) ⁻	Water	R
Protasite (this study)	1.72–2.01 1.9	1.89–2.19 2.1	1.25–1.27 1.3	0.22–0.23 0.2	7.3
Becquerelite (this study)	1.55–2.22 1.9	2.03–2.24 2.1	1.33–1.44 1.4	0.18–0.28 0.2	8.3
Billietite (this study)	1.63–2.48 1.9	2.00–2.29 2.1	1.25–1.51 1.4	0.32 0.3	13.9
Curite (Mereiter, 1979)	1.82–2.09 2.0	2.02–2.22 2.1	1.15–1.35 1.3	0.56 0.6	4.3
Sayrite (Piret et al., 1983)	1.81–2.05 1.9	2.00–2.07 2.0	1.31 1.3	0.21–0.28 0.2	10.5
Fourmarierite (Piret, 1985)	1.89–2.14 2.0	2.04–2.12 2.1	1.25–1.70 1.4	0.18–0.50 0.3	4.6

Note: The first line for each mineral represents the range of calculated bond-strength values, the second line, the average value for the specific oxygen atom type. The conventional R for each structure solution has been included to give a relative measure of the disorder in the structures. Hydrogen-bond distances to water molecules have been included for the uranyl oxygen atoms only. The bond strengths for water are derived from water-cation bonds.

tion in structures that are poorly crystallized. In structures like billietite, only an average bond strength for a group of structurally equivalent bonds is meaningful; e.g., uranyl U–O bonds.

CONCLUSIONS

The three minerals described here form a crystal-chemical group with very similar structures closely based on an α -U₃O₈ sheet. Other uranyl oxide hydrates, especially those containing Pb as an interlayer cation, show somewhat different sheet arrangements with elements of both the α -U₃O₈ and β -U₃O₈ structures (Mereiter, 1979; Taylor et al., 1981; Piret, 1985; Piret et al., 1983). This relationship to the U₃O₈ polymorphs thus provides a useful way to classify uranyl oxide hydrate structures. The type and arrangement of U₃O₈ repeat units in their sheets are the fundamental principles of such a classification (Pagoaga, 1983), which will be described in a forthcoming paper (Pagoaga et al., in prep.).

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