STUDIES OF URANIUM MINERALS (XII): THE STATUS OF BILLIETITE AND BECQUERELITE*

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ABSTRACT

Billietite ($BaO \cdot 6UO_3 \cdot 11H_2O$), originally described from Katanga by Vaes (1947), is a valid species isostructural with becquerelite ($7UO_3 \cdot 11H_2O$).

New chemical analyses and Weissenberg *x*-ray studies on two specimens of billietite from Katanga gave: (1) BaO 6.88, UO_3 82.76, H_2O 8.97, SiO_2 0.76, CaO 0.30, total 99.67; a_0 14.25 Å, b_0 12.04, c_0 15.06, with four formula units per unit cell; α 1.730, β 1.810, γ 1.815; sp. gr. 5.32 (meas.), 5.33 (calc.); (2) BaO 7.41, UO_3 84.39, H_2O 8.68, total 100.48; a_0 13.98 Å, b_0 12.08, c_0 15.06; α 1.725, β 1.780, γ 1.790; sp. gr. 5.36 (meas.), 5.40 (calc.). Space group *Pmma*. Billietite is orthorhombic with 2V $(-)\sim 35°$; X pale yellow, Y and Z deep golden yellow. The unit cell differs from that of Brasseur (1949) in that the a-axis is doubled.

A new analysis and *x*-ray study of becquerelite from Katanga gave UO_3 89.53, H_2O 8.95, SiO_2 1.82, total 100.30; a_0 13.92 Å, b_0 12.45, c_0 15.09; α 1.730, β 1.805, γ 1.820; sp. gr. ~ 5.3 (meas.), 5.60 (calc.). From this new analysis the old formula for becquerelite ($2UO_3 \cdot 3H_2O$) has been revised to $7UO_3 \cdot 11H_2O$, analogous to the formula for billietite, and there are four formula units per unit cell. Space group *Pmma*. Becquerelite is orthorhombic, 2V $(-)\sim 30°$; X yellow, Y and Z deep golden yellow.

BILLIETITE

New chemical analyses and Weissenberg *x*-ray studies indicate that the hydrated barium uranium oxide, billietite, is a valid mineral species isostructural with the hydrated uranium oxide, becquerelite.

In the original description of becquerelite (Schoep, 1922) the chemical analysis showed about 5.25 per cent of PbO, which at that time was considered an impurity. Later, Schoep and Stradiot (1948) described becquerelite without lead and suggested that in the lead variety there was a substitution of some Pb for U. Vaes (1949), however, considered the original analyses to be in error in that the Pb was actually Ba. He believed that the original becquerelite actually was the more recently described mineral, billietite (Vaes, 1947), a hydrated barium-uranium oxide. He proposed that the name becquerelite be retained for the mineral without lead or barium and that the name billietite be reserved for the mineral with barium. There exist, then, to date, no authenticated specimens of lead-becquerelite.

Optically billietite and becquerelite are very similar (Table 1), except that twinning, common in billietite, has not been observed in becquerelite. Both minerals are orthorhombic and are holohedral. They are yellow to golden yellow and have a distinct pleochroism, with X colorless or pale yellow, and Y and Z deep golden yellow. The 2V of becquerelite is

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TABLE 1. OPTICS OF BILLIETITE AND BECQUERELITE

	Billietite			Becquerelite	
	1	2	3	4	5
	(Na)				
α	1.730	1.730	1.725	1.725	1.730
β	1.822	1.810	1.780	1.82	1.805
γ	1.829	1.815	1.790	1.83	1.820
2V	~47°	~35°	~35°	~30°	~30°
X	Colorless	Pale yellow	Pale yellow	Colorless	Pale yellow
Y	Greenish yellow	Deep golden yellow	Deep golden yellow	Yellow	Deep golden yellow
Z	Deep yellow	Deep golden yellow	Deep golden yellow	Yellow	Deep golden yellow

1. Brasseur (1949).
2. No. 104456, Katanga specimen from Spence collection of uranium minerals at Harvard University.
3. No. 104455, Katanga specimen sent by Vaes to Harvard University.
4. Brasseur (1949).
5. No. 104454, Katanga specimen obtained from Trace Elements Section Washington Laboratory, U. S. Geological Survey.

TABLE 2. CHEMICAL ANALYSES OF BILLIETITE AND BECQUERELITE

	Billietite				Becquerelite		
	1	2	3	4	5	6	7
UO_3	83.86	82.76	84.39	83.08	90.09	89.53	89.66
BaO	6.95	6.88	7.41	7.38			
H_2O	10.49	8.97	8.68	9.54	9.91	8.95	10.34
SiO_2		0.76				1.82	
CaO		0.30					
Total	101.30	99.67	100.48	100.00	100.00	100.30	100.00

1. Vaes (1949).
2. No. 104456. Analyst, Frank Cuttitta.
3. No. 104455. Analyst, Frank Cuttitta.
4. $BaO \cdot 6UO_3 \cdot 11H_2O$.
5. Schoep and Stradiot (1948).
6. No. 104454. Analyst, Frank Cuttitta.
7. $7UO_3 \cdot 11H_2O$.

about 30° and of billietite about 35°. The reported indices of refraction of the two minerals overlap. Both billietite and becquerelite have a perfect cleavage on (001) and their optic orientation is the same. The plane of the optic axes is (100), with Y=a, Z=b, and X=c. In Vaes' original description of billietite (1947) he made the cleavage plane (010). Thoreau (1948) reoriented the mineral, with his *abc*=Vaes' *cab*. This orientation was followed by Brasseur (1949) and is used in the present study. The distinction of billietite and becquerelite is difficult; it is best to use *x*-ray powder photographs together with qualitative chemical tests for Ba and Pb.

Table 3. Cell Constants[1] and Specific Gravities of Billietite and Becquerelite

	Billietite			Becquerelite
	Brasseur (1949)	No. 104456	No. 104455	No. 104454
a_0	7.11	14.25	13.98	13.92
b_0	12.08	12.04	12.08	12.45
c_0	15.09	15.06	15.06	15.09
sp. gr. (meas.)	5.28	5.32[2]	5.36[2]	5.3 (approx.)[3]
sp. gr. (calc.)	—	5.33	5.40	5.60

[1] All measurements are ±0.005 Å.

[2] Specific gravities determined with Berman balance on 10 to 12 mg. of sample.

[3] Sample too small for accurate determination of specific gravity.

In the past two years the Harvard University mineral collection acquired two specimens of billietite from Katanga. One was sent by Vaes. The other was in the Spence collection of uranium minerals. Both specimens have been analyzed chemically, and the results agree closely with those of Vaes' analysis (Table 2). Vaes proposed the formula $BaO \cdot 6UO_3 \cdot 10H_2O$. The new chemical analyses are represented better by the formula $BaO \cdot 6UO_3 \cdot 11H_2O$, suggested by Brasseur (1949). A Weissenberg *x*-ray study, using copper radiation ($\lambda = 1.5418$ Å), was made of both analyzed specimens. The unit cell differs from that of Brasseur (1949) in that the a-axis is doubled (Table 3). It is possible that Brasseur missed the odd orders in his rotation photograph about the a-axis, as he used molybdenum radiation and the unit cell is large. There are, then, four formula units per unit cell, rather than two. Plots of the zero, first, and second layer Weissenberg photographs about all three axes gave:

(hkl) all orders present,
(hk0) present only with h=2n,

(h0l) all orders present,
(0kl) all orders present.

The space group, therefore, is *Pmma*. The crystal forms observed by Thoreau (1948) as referred to the unit of the *x*-ray cell are given in table 4, and show that billietite is holohedral. The calculated specific gravities, 5.33 and 5.40, are close to the two measured values, 5.32 and 5.36, respectively. The specific gravities were measured with a Berman balance on about 10 to 12 milligrams of sample.

Table 4. Crystallographic Forms of Billietite

Thoreau (1948)			J. W. Frondel		
Form	ϕ	ρ	Form	ϕ*	ρ*
001	0°	0°	001	0°	0°
011	0°	51°48′45″	011	0°	51°16′
021	0°	68°31′52″	021	0°	68°12′
010	0°	90°00′	010	0°	90°
101	90°00′	—	201	90°	64°41′
110	58°55′10″	90°00′	210	59°22′	90°
111	58°55′10″	—	211	59°22′	67°50′
223	58°55′10″	58°39′18″	423	59°22′	58°35′
			New Forms Observed		
			232	29°23′	65°06′
			212	59°22′	50°55′

* Angles calculated from cell constants $a_0=14.25$ Å, $b_0=12.04$, and $c_0=15.06$, giving $a=1.184$, $c=1.251$, $p_0=1.057$, and $q_0=1.251$.

BECQUERELITE

A new chemical analysis and a Weissenberg *x*-ray study were made on a Katanga specimen of becquerelite obtained several years ago by the Trace Elements Section Washington Laboratory of the U. S. Geological Survey. The analysis agrees closely with that of Schoep and Stradiot (1948) on lead-free material (Table 2). The old formula of becquerelite ($2UO_3 \cdot 3H_2O$) is here replaced by $7UO_3 \cdot 11H_2O$, as this formula fits the analysis quite well and is analogous to the billietite formula. The cell constants are close to those of billietite (Table 3), and there are, similarly, four formula units per unit cell. The space group is *Pmma*. The calculated specific gravity is 5.60; the measured value is approximately 5.3. The measurement was made with a micropycnometer on a very small sample and may be in error. The attempt to make the two formulas analogous is justified because the near coincidence in dimensions and

Table 5. Interplanar Spacings of Billietite and Becquerelite from *X*-ray Powder Patterns (Å) Cu/Ni Radiation = 1.5418 Å

Billietite No. 104455		Becquerelite No. 104454	
d	I*	d	I*
—	—	8.51	1
7.53	10	7.50	10
—	—	6.63	2
—	—	6.24	1
—	—	5.63	1
4.59	2	4.71	6
—	—	4.31	1
3.77	9	3.75	8
3.54	5	3.56	8
—	—	3.48	2
—	—	3.39	2
3.17	8	3.22	9
3.02	1	3.13	1
2.89	1	2.97	2
2.79	2	2.88	3
—	—	2.73	1
2.56	3	2.58	7
2.49	4	2.47	2
—	—	2.44	2
—	—	2.38	2
2.30	2	2.31	3
2.19	1	2.21	1
2.10	3	2.11	2
—	—	2.07	3
2.03	6	2.04	4

* Intensities estimated visually.

intensities of the single crystal and powder photographs (Table 5) of billietite and becquerelite indicates that these minerals are isostructural. It is presumed that one Ba^{2+} substitutes for one U^{6+}. If the role of water in the structure were understood, it might be possible to explain the necessary valence compensation for such a substitution by the O to (OH) ratio in each mineral. Though no specimen of lead-bearing becquerelite is at hand, the authors believe that for crystallo-chemical reasons such a mineral may exist. It also may be noted that the closely related hydrous uranium oxide, schoepite ($UO_3 \cdot 2H_2O$), can contain up to 4.56 per cent PbO (Schoep, 1924). Should re-examination and chemical analyses of museum specimens indicate the presence of such a mineral, or if the original analyses of becquerelite containing lead are presumed to be correct, then a general formula for becquerelite, lead-becquerelite, and billietite might be written:

$$[U^{6+}_{1-x}(Ba, Pb)^{2+}_{x}]U^{6+}_{6}O_{20-4x}(OH)_{2+4x}\cdot(10\text{-}2x)H_2O$$

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