STUDIES OF URANIUM MINERALS: THE STATUS OF BILLIETITE AND BECQUERELITE

By Judith W. Frondel and Frank Cuttitta

Trace Elements Investigations Report 309

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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Division of Raw Materials
U. S. Atomic Energy Commission
P. O. Box 30, Ansonia Station
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Dear Phil:

Transmitted herewith are six copies of TEI-309, "Studies of uranium minerals: The status of billietite and becquerelite," by Judith W. Frondel and Frank Cuttitta, February 1953.

We plan to publish this report in American Mineralogist and are asking Mr. Hosted to approve this plan.

Sincerely yours,

O. E. McKelvey

for W. H. Bradley
Chief Geologist

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UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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THE STATUS OF BILLIETITE AND BECQUERELITE *

By

Judith W. Frondel and Frank Cuttitta

February 1953

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* This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission

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R. J. Roberts, Salt Lake City	1
TEPCO, Washington (Including master)	5
	62

CONTENTS

TABLES

STUDIES OF URANIUM MINERALS: THE STATUS OF BILLIETITE AND BECQUERELITE

by

Judith W. Frondel and Frank Cuttitta

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_o 14.25Å, b_o 12.04, c_o 15.06, with $4(BaO \cdot 6UO_3 \cdot 11H_2O)$ per unit cell; nX 1.730, nY 1.810, nZ 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_o 13.98Å, b_o 12.08, c_o 15.06; nX 1.725, nY 1.780, nZ 1.790; sp. gr. 5.36 (meas.), 5.40 (calc.). Space group <u>Pmma</u>. 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_o 13.92Å, b_o 12.45, c_o 15.09; nX 1.730, nY 1.805, nZ 1.820; sp. gr. $\sim$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 $4(7UO_3 \cdot 11H_2O)$ per unit cell. Space group <u>Pmma</u>. Becquerelite is orthorhombic, 2V(-) $\sim$30°; X yellow, Y and Z deep golden yellow.

The near coincidence in dimensions and intensities of the single crystal and powder photographs of billietite and becquerelite indicates that these minerals are isostructural. There is some question as to the existence of a lead-bearing becquerelite, but if the original analyses of becquerelite containing Pb are presumed to be correct, then a serial relation between becquerelite, lead-becquerelite, and billietite might be written:

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

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 percent 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, therefore, the original becquerelite actually was the more recently described mineral, billietite (Vaes, 1947), a hydrated barium-uranium oxide. He proposed the name becquerelite be retained for the mineral without lead or barium, and the name billietite be reserved for the mineral with barium. There exists, 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 probably 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 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, interchanging b and c. 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.

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 better represented by the formula $BaO \cdot 6UO_3 \cdot 11H_2O$, suggested by Brasseur (1949). A Weissenberg X-ray study, using copper radiation, was made of both analyzed specimens. The unit cell differs from that of Brasseur (1949) in that the a-axis is doubled (table 3). There are, then, four formula units per unit cell, rather than two. The space group is Pmma. 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. The crystal forms observed by Thoreau (1948) as referred to the unit of the X-ray cell are given in table 4.

BECQUERELITE

A new chemical analysis and 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 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 <u>Pmma</u>. The calculated specific gravity is 5.50; the measured value is approximately 5.3. The measurement was made with a micropycknometer 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 intensities of the single crystal and powder photographs (table 5) of billietite and becquerelite indicate 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 for crystallo-chemical reasons that 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 percent PbO (Schoep, 1924). Should reexamination 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:

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

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This work was completed as a part of a program undertaken by the U. S. Geological Survey on behalf of the Atomic Energy Commission. The authors wish to thank Dr. Clifford Frondel, of Harvard University, for his assistance in the interpretation of results.

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Table 1.--Optics of billietite and becquerelite

	Billietite			Becquerelite	
	Brasseur (1949)	Frondel and Cuttitta 1/	Frondel and Cuttitta 2/	Brasseur (1949)	Frondel and Cuttitta 3/
nX	1.730	1.730	1.725	1.725	1.730
nY	1.822	1.810	1.780	1.82	1.805
nZ	1.829	1.815	1.790	1.83	1.820
2V	36°	35°	35°	30°	30°
X	Colorless	Pale yellow	Pale yellow	Colorless	Pale yellow
Y	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/ No. 104456, Katanga specimen from Spence collection of uranium minerals at Harvard University.
2/ No. 104455, Katanga specimen sent by Vaes to Harvard University.
3/ 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	
	Vaes (1949)	Frondel and Cuttitta 1/ No. 104456	Frondel and Cuttitta 1/ No. 104455	Schoep and Stradiot (1948)	Frondel and Cuttitta 1/ No. 104454
UO_3	83.86	82.76	84.39	90.09	89.53
BaO	6.95	6.88	7.41		
H_2O	10.49	8.97	8.68	9.91	8.95
SiO_2		0.76			1.82
CaO		0.30			
Total	101.30	99.67	100.48	100.00	100.30

1/ Analyst, Frank Cuttitta, U. S. Geological Survey.

Table 3.--Cell constants and specific gravities of billietite and becquerelite.

	Billietite			Becquerelite
	Brasseur (1949)	Frondel and Cuttitta No. 104456	Frondel and Cuttitta No. 104455	Frondel and Cuttitta No. 104454
a_o	7.11	14.25	13.98	13.92
b_o	12.08	12.04	12.08	12.45
c_o	15.09	15.06	15.06	15.09
sp gr (meas.)	5.28	5.32 1/	5.36 1/	5.3 (approx.) 2/
sp gr (calc.)	--	5.33	5.40	5.60

1/ Specific gravities determined with Berman balance on 10 to 12 mg of sample.
2/ Sample too small for accurate determination of specific gravity.

Table 4.--Crystallographic forms of billietite.

Thoreau (1948)	Frondel and Cuttitta
001	001
011	011
021	021
010	010
101	201
110	210
111	211
223	423

Table 5.--Interplanar spacings of billietite and becquerelite from X-ray powder patterns (Å).

Cu/Ni radiation = 1.5418 Å

Billietite		Becquerelite		Billietite		Becquerelite	
d	I*	d	I*	d	I*	d	I*
---	---	8.51	1	1.46	2	1.45	2
7.53	10	7.50	10	1.43	1	1.41	3
---	---	6.63	2	1.38	2	1.38	3
---	---	6.24	1	1.36	1	---	---
---	---	5.63	1	---	---	1.33	1
4.59	2	4.71	6	1.31	2	---	---
---	---	4.31	1	1.28	2	1.29	1
3.77	9	3.75	8	---	---	1.27	1
3.54	5	3.56	8	1.25	1	1.24	1
---	---	3.48	2	1.23	1	1.22	1
---	---	3.39	2	1.21	1	1.21	1
3.17	8	3.22	9	1.19	1	1.19	1
3.02	1	3.13	1	1.16	1	1.17	1
2.89	1	2.97	2	---	---	1.15	1
2.79	2	2.88	3	1.14	2	1.13	1
---	---	2.73	1	1.12	1	1.12	1
2.56	3	2.58	7	1.10	1	1.11	1
2.49	4	2.47	2	1.07	2	---	---
---	---	2.44	2	1.06	1	1.05	1
---	---	2.38	2	1.04	1	---	---
2.30	2	2.31	3	1.03	1	1.03	1
2.19	1	2.21	1	1.01	1	---	---
2.10	3	2.11	2	1.00	1	---	---
---	---	2.07	3	.987	1	.987	1
2.03	6	2.04	4	.981	1	---	---
1.97	4	1.99	4	---	---	.967	1
1.94	2	1.94	5	---	---	.955	1
1.90	1	1.89	2	.944	3	.944	1
1.87	3	1.88	2	.931	1	.933	1
---	---	1.85	2	.914	1	.914	1
1.81	1	1.81	1	.898	1	---	---
1.79	2	1.77	3	.884	2	.887	1
---	---	1.72	3	.871	2	---	---
1.68	3	1.68	2	.858	1	.859	1
1.65	4	---	---	.852	1	---	---
---	---	1.61	2	.843	2	.842	1
1.60	1	1.60	2	.831	2	.836	1
1.57	2	1.56	2	.824	1	---	---
1.53	1	1.54	1	.783	4	---	---
1.50	2	---	---	.776	2	---	---

* Intensities estimated visually.