

## STUDIES OF URANIUM MINERALS (IV): JOHANNITE\*

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### ABSTRACT

X-ray Weissenberg study of johannite gave the following dimensions for the triclinic face-centered cell corresponding to the pseudo-monoclinic morphological cell of Peacock (1935):  $a_0=16.51$  kX,  $b_0=17.98$ ,  $c_0=6.83$  with  $\alpha=90^\circ 54'$ ,  $\beta=90^\circ 38'$ ,  $\gamma=110^\circ 37'$  (from morphology). Cell contents  $\text{Cu}_4\text{U}_8(\text{SO}_4)_8(\text{OH})_{40}\cdot 8\text{H}_2\text{O}$ . Specific gravity 3.32 (meas.), 3.27 (calc.). Transformation, face-centered to primitive triclinic cell:  $\frac{1}{2}0\frac{1}{2}/0\frac{1}{2}\frac{1}{2}/001$ . Elements of the primitive cell:  $a_0:b_0:c_0=0.9382:1:0.7143$ ,  $\alpha=108^\circ 50'$ ,  $\beta=112^\circ 3'$ ,  $\gamma=64^\circ 52'$ .

### INTRODUCTION

Johannite,  $\text{CuU}_2(\text{SO}_4)_2(\text{OH})_{10}\cdot 2\text{H}_2\text{O}$ , long known as a mineral species, has been studied by several investigators during the past 120 years. The latest work was by Peacock (1935). Peacock summarizes the previous crystallographic work as follows: "Haidinger (1830) regarded johannite as monoclinic. Ježek (1916) likewise found the crystals he studied to be morphologically monoclinic, although they appeared to be optically triclinic. In order to reconcile the morphology of johannite with its optical behavior Larsen and Berman (1926) proposed a triclinic orientation for the mineral, taking the prismatically developed orthodome zone of Ježek as prism zone and Ježek's  $x(011)$  as base." From careful goniometric measurements of crystals of johannite from Joachimsthal, the type locality, Peacock confirmed the triclinic character of the mineral and determined the following morphologic elements:

Johannite: Triclinic— $F$  (after Peacock)

$a=0.9182$	$p_0'=0.442$	$p_0=0.4419$
$c=0.3799$	$q_0'=0.406$	$q_0=0.4059$
$\alpha=90^\circ 54\frac{1}{2}'$	$x_0'=0.011$	$\lambda=88^\circ 48'$
$\beta=90^\circ 38'$	$y_0'=0.021$	$\mu=88^\circ 59'$
$\gamma=110^\circ 37'$		$\nu=69^\circ 22'$

From the above elements one can see the pseudo-monoclinic nature of johannite and understand why the early workers considered it monoclinic.

### X-RAY DATA

The present investigation was undertaken to determine both the constants of the unit cell, and the contents of the unit cell in the light of the available chemical analyses. Using the same material on which Peacock

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had worked (Harvard specimen no. 89613), a rotation photograph and zero, first and second layer Weissenberg photographs were taken with the  $c$ -axis as the axis of rotation. It was impossible to find a suitable untwinned crystal, so the photographs were made on a twin composed of two individuals 0.5 mm. long and 0.1 mm. across. Because of this, the first and second layer line photographs showed double diffraction spots, one set from each lattice. These spots on the first layer photograph were so close together that they merged into one large spot; on the second layer line photograph they were resolved and a projection of the photograph gave two interpenetrating nets. An attempt was made to rotate the crystals about another axis, but because of their elongated habit this proved to be impractical.

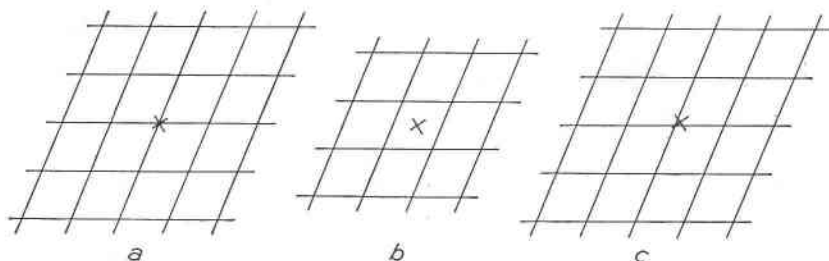


FIG. 1. Projections of Weissenberg photographs of johannite taken with  $c$  the axis of rotation. (a) zero layer. (b) first layer. (c) second layer.

When the projections of the three Weissenberg photographs about  $c$  were compared with one another, that of the first layer line showed an apparent exact centering of the zero layer, and the second layer line projection appeared to superimpose on that of the zero layer. These three projections are shown in Fig. 1 with the center of each marked with a cross. Such a centering indicates a multiple cell of an  $F$ -centered lattice. Careful inspection, however, shows that the second layer projection does not quite superimpose on the zero layer projection but is offset slightly with a small  $x_0'$  and  $y_0'$  and thus showing the triclinic character. This then is the pseudo-monoclinic cell, the constants of which as determined directly from the Weissenberg and rotation photographs are:

$$c_0 = 6.84 \text{ kX}, d(100) = 15.48, d(010) = 16.76, \nu = 69^\circ 30'$$

Reducing Peacock's geometrical values for  $p_0'$  and  $q_0'$  to  $c_0 = 6.84$  we obtain:  $c_0/p_0 = 6.84/0.442 = 15.47$  for  $d(100)$ ,  $c_0/q_0 = 6.84/0.406 = 16.85$  for  $d(010)$ . Taking 6.83 as an average value for  $c_0$ , we find the following remarkably good agreement between the geometrical and  $x$ -ray data:

	Peacock	Hurlbut
$c$	6.83	6.84
$d_{(100)}$	15.46	15.48
$d_{(010)}$	16.82	16.76

For the calculations of the dimensions of the unit cell it seems wise to use the angles determined graphically by Peacock. Since they were the result of the measurement of 12 crystals projected on a 10 centimeter scale, they are no doubt more accurate than those obtained from the graphical solution of one x-ray projection on less than  $\frac{1}{4}$  the scale. Using his angles, the dimensions of the  $F$ -cell are:

$$\begin{array}{ll} a_0 = 16.51 \text{ kX} & \alpha = 90^\circ 54' \\ b_0 = 17.98 & \beta = 90^\circ 38' \\ c_0 = 6.83 & \gamma = 110^\circ 37' \end{array}$$

Using the above dimensions of the  $F$ -cell, the following elements were determined for the triclinic  $P$ -cell.

JOHANNITE: TRICLINIC- $P$

$$\begin{array}{lll} a = 0.9382 & p_0' = 0.884 & p_0 = 0.7962 \\ c = 0.7143 & q_0' = 0.812 & q_0 = 0.7314 \\ \alpha = 108^\circ 50' & x_0' = 0.425 & \lambda = 78^\circ 9' \\ \beta = 112^\circ 03' & y_0' = 0.228 & \mu = 73^\circ 22' \\ \gamma = 64^\circ 52' & & \nu = 110^\circ 37' \end{array}$$

The relation of the  $F$ -cell and  $P$ -cell is shown in Fig. 2. The transformation formula  $F$  to  $P$  is  $\frac{1}{2}0\frac{1}{2}/0\frac{1}{2}\frac{1}{2}/001$ . It seems best, however, to retain

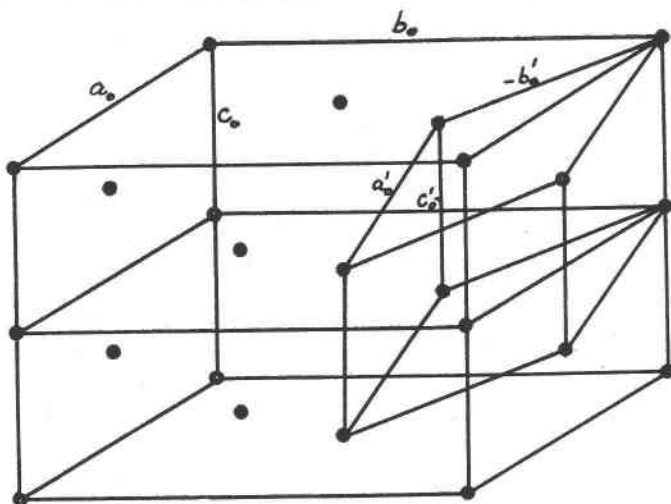


FIG. 2. Relation between the pseudomonoclinic triclinic  $F$ -cell and the triclinic  $P$ -cell of johannite. Primed letters are on axes of primitive cell.

for johannite the *F* setting of Peacock. In so doing the geometrical crystallography remains unchanged and the pseudo-monoclinic nature of both the morphology and the optics is preserved.

X-RAY POWDER DATA FOR JOHANNITE  
Cu radiation, Ni filter

Line No.	<i>d</i>	<i>I</i>	Line No.	<i>d</i>	<i>I</i>
1	7.83	6	21	2.09	3
2	6.15	9	22	2.05	1
3	5.57	5	23	2.01	3
4	4.90	1	24	1.929	4
5	4.40	4	25	1.899-1.838	3 (very broad)
6	3.82	10 (broad)	26	1.801	1
7	3.53	2	27	1.765	2
8	3.41	8	28	1.710-1.647	3 (very broad)
9	3.23	1	29	1.595	3
10	3.10	7 (broad)	30	1.563	2
11	2.94	3	31	1.549	2
12	2.80	2 (broad)	32	1.526	3
13	2.67	3	33	1.484	2
14	2.59	4	34	1.459	2
15	2.44	2	35	1.433	1
16	2.38	1	36	1.412	1
17	2.32	1	37	1.375	1
18	2.24	3	38	1.351	1
19	2.19	2	39	1.326	1
20	2.13	3			

UNIT CELL CONTENTS

Three chemical analyses of johannite are available: (1) Johannite from Joachimsthal analyzed by A. Lindacker in 1856, (2) "Gilpinite" from Gilpin County, Colorado, analyzed by G. V. Brown on 0.22 gram (Larsen and Brown, 1917), (3) Johannite from Joachimsthal; the reported data are the results of duplicate microanalyses on 0.035 gram made by R. Nováček (cited in Peacock, 1935). This last analysis is given below:

JOHANNITE: ANALYSIS AND CELL CONTENTS

	1	2	3	4	5	6	7
UO <sub>3</sub>	61.34	61.44	.2148	.2148	8.20	8	61.00
CuO	8.07	8.08	.1012	.1012	3.87	4	8.48
SO <sub>3</sub>	16.59	16.62	.2075	.2075	7.92	8	17.07
H <sub>2</sub> O	13.84	13.86	.7610	1.5220	58.0 (H)	56	13.45
	99.84	100.00		2.1291	81.1 (O)	80	100.00

1. Analysis by R. Nováček.
2. Analysis (1) reduced to 100%.
3. Molecular quotients.
4. Atomic quotient of the metals.
5. Measured cell contents.  $M=3,817$ .
6. Ideal unit cell content.
7. Theoretical composition of  $\text{CuU}_2(\text{SO}_4)_2(\text{OH})_{10} \cdot 2\text{H}_2\text{O}$ .

The specific gravity of johannite is 3.32—an average of five new measurements on the Berman balance. Using this as the density and the volume of the multiple  $F$ -cell as 1897.1, the molecular weight of the unit cell was found to be 3,817. Assuming the integers given in column 6 above as correct, the formula for johannite can be written  $\text{CuU}_2(\text{SO}_4)_2(\text{OH})_{10} \cdot 2\text{H}_2\text{O}$ . There are four of these formula units in the  $F$ -cell and one in the  $P$ -cell. The calculated specific gravity is 3.27.

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