

# STUDIES OF URANIUM MINERALS (VI): WALPURGITE\*

HOWARD T. EVANS, JR., † *Massachusetts Institute  
of Technology, Cambridge, Mass.*

## ABSTRACT

Walpurgite, a hydrated bismuth uranium arsenate from Schneeberg, Saxony, has been studied by *x*-ray diffraction using the Buerger precession method. The lattice is triclinic with the following elements:  $a_0 = 7.13 \text{ \AA}$ ,  $b_0 = 10.44 \text{ \AA}$ ,  $c_0 = 5.49 \text{ \AA}$ ,  $\alpha = 101^\circ 40'$ ,  $\beta = 110^\circ 49'$ ,  $\gamma = 88^\circ 17'$ ;  $a:b:c = 0.683:1:0.525$ . The crystals are commonly elongated parallel to [001], flattened parallel to (010) and twinned on (010). The morphological data of Weisbach and Fischer are correlated with the *x*-ray data through the following transformations: Weisbach to *x*-ray  $x0\bar{1}/0x\bar{1}/001$  ( $x$  undetermined); Fischer to *x*-ray  $0\bar{1}\bar{1}/302/001$ . From the volume of the unit cell as determined by *x*-rays, it is concluded that available data on composition and density are unreliable because of the scarcity of pure material. The best formula is one proposed by Fischer:  $2\text{Bi}_2\text{O}_3 \cdot \text{UO}_3 \cdot \text{As}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ .

Walpurgite was described and named in 1871 by Weisbach (6) as a hydrated bismuth uranium arsenate from Schneeberg, Saxony. The crystals, yellow triclinic twins resembling gypsum crystals in shape, were partially described by Weisbach (7) in 1877. The crystal morphology was recently treated in detail by Fischer (4) on the basis of a study of twinned and untwinned crystals from Schneeberg and Joachimsthal. The present paper presents a complete determination of the unit cell on the basis of an *x*-ray study using the Buerger precession method. This information is used to redefine the results of Weisbach and Fischer and to attack the problem of composition.

## X-RAY STUDY

Small twinned crystals from Schneeberg were mounted in two positions and three intersecting reciprocal lattice planes were photographed with the Buerger precession camera. The  $[hk0]$  reciprocal lattice plane is shown in Fig. 1. In this photograph the composition plane is normal to the lattice plane, and, because of the high absorption in the crystal of the *x*-rays, the pattern on the left is mainly generated by one individual, while that on the right is due mainly to the other. From these films, the reciprocal elements were measured directly and the elements of the direct lattice were calculated therefrom. In the direct lattice, the three shortest axes were found and the new axial angles calculated. These axes were then finally oriented with  $c < a < b$  and with  $\alpha$  and  $\beta$  obtuse, according to the rules of convention proposed by Donnay (2). From these

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 321.

† Present address: Philips Laboratories, Inc., Irvington-on-Hudson, New York.

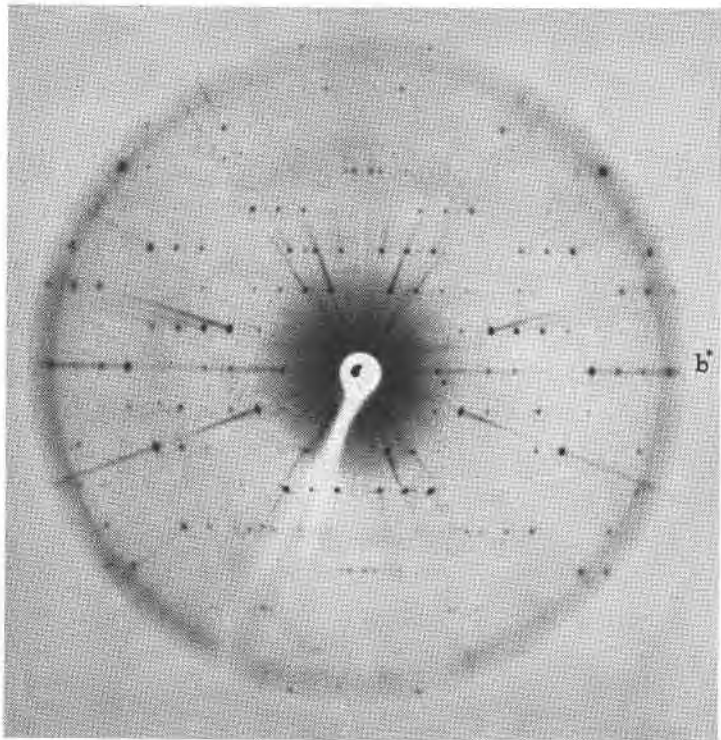


FIG. 1. Precession photograph of  $(hk0)$  plane, of walpurgite twin crystal (Mo  $K\alpha$  radiation).

final axial elements, the projection and polar elements were derived using the relations given by Evans (3). These results are given in Table 1. The twin plane is  $b(010)$ .

#### MORPHOLOGY

Walpurgite crystals are almost invariably twinned, and the habit described by Weisbach is very characteristic (Fig. 2). He listed four forms, which were not sufficient to give a complete morphological unit cell. Fischer lists fourteen forms found on twinned crystals and three single crystals from Schneeberg and Joachimsthal. These forms are listed in Table 2, with symbols and letters given by Weisbach, Fischer and the  $x$ -ray determination. The relationship between the  $x$ -ray lattice and the lattices of Weisbach and Fischer was found by the identification of the twinning plane and the direction of elongation, parallel to the  $c$  axis in all three settings. A gnomonic projection of the  $x$ -ray lattice was made, and the  $(001)$  pole of each of the other two settings was identified from the polar angles given by the respective authors. Thus,

Weisbach's (001) is equivalent to the  $x$ -ray  $(\bar{1}\bar{1}1)$ , and Fischer's (001) is the  $x$ -ray  $(\bar{1}21)$ . The gnomonic projection showing all reported forms and the three unit cells is shown in Fig. 3. From this projection, the following transformation matrices are derived:

$$\text{Weisbach to } x\text{-ray} \begin{pmatrix} \bar{x} & 0 & \bar{1} \\ 0 & \bar{x} & \bar{1} \\ 0 & 0 & 1 \end{pmatrix} \quad (x \text{ not determined})$$

$$\text{Fischer to } x\text{-ray} \begin{pmatrix} 0 & \bar{1} & \bar{1} \\ 3 & 0 & 2 \\ 0 & 0 & 1 \end{pmatrix}$$

Some of the angles reported by Weisbach and Fischer are listed in Table 3 for comparison.<sup>1</sup> Fischer's two single crystals are shown in Fig. 4 redrawn in the new orientation.

TABLE 1. CRYSTALLOGRAPHIC ELEMENTS OF WALPURGITE

Symmetry: Triclinic; space group prob. $P\bar{1}=C_i^1$ .	
Axial elements:	
$a_0 = 7.13 \text{ \AA}$	$\alpha = 101^\circ 40'$
$b_0 = 10.44 \text{ \AA}$	$\beta = 110^\circ 49'$
$c_0 = 5.49 \text{ \AA}$	$\gamma = 88^\circ 17'$
$a:b:c = 0.638:1:0.525$	
Polar elements:	
$a^* = 0.1502$	$\lambda = 78^\circ 10'$
$b^* = 0.0979$	$\mu = 69^\circ 10'$
$c^* = 0.1992$	$\nu = 87^\circ 22'$
$p_0:q_0:r_0 = 0.748:0.488:1$	
Projection elements:	
$x_0' = 0.380$	$p_0' = 0.824$
$y_0' = 0.224$	$q_0' = 0.537$
$\nu = 87^\circ 22'$	
Cartesian matrices:	
$v_1 = -0.0448$	$v_2 = 0.978$
Direct:	
$M = \begin{pmatrix} 6.667 & -0.468 & 0 \\ 0 & 10.217 & 0 \\ -2.535 & -2.112 & 5.487 \end{pmatrix} \quad (\text{in } \text{\AA})$	
Reciprocal:	
$\bar{M}^{-1} = \begin{pmatrix} 0.1500 & 0 & 0.0693 \\ 0.0069 & 0.0979 & 0.0408 \\ 0 & 0 & 0.1822 \end{pmatrix} \quad (\text{in } \text{\AA}^{-1})$	

<sup>1</sup> The axial elements are not compared for the following reasons: Weisbach's elements are incomplete; Fischer's axial elements cannot be reconciled with the polar angles which he observes (the latter agree well with the  $x$ -ray lattice, while no rational relationship can be found among the axial elements).

## COMPOSITION

Several analyses of walpurgite have been recorded in the literature, and these are shown in Table 4.

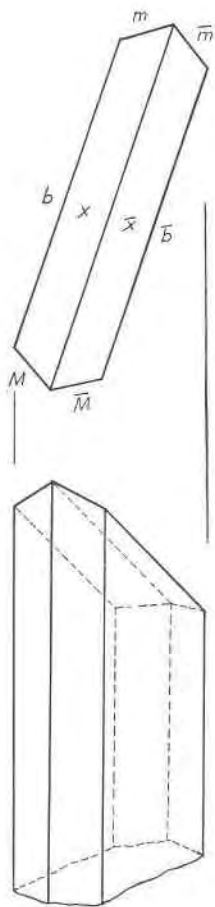


FIG. 2. Walpurgite twin, after Weisbach; Schneeberg (common habit).

Several different formulae have been proposed on the basis of these analyses, usually with a molecular weight roughly three times that corresponding to column 5 of Table 4. Because of the relatively small size of the unit cell,  $373.7 \text{ \AA}^3$ , none of these can be correct. But even the relatively simple formula given by Fischer's micro-analysis on 34 mg. is not compatible with the density of 5.76 given by Weisbach (7). The formula given demands a density of 6.69. A redetermination of the

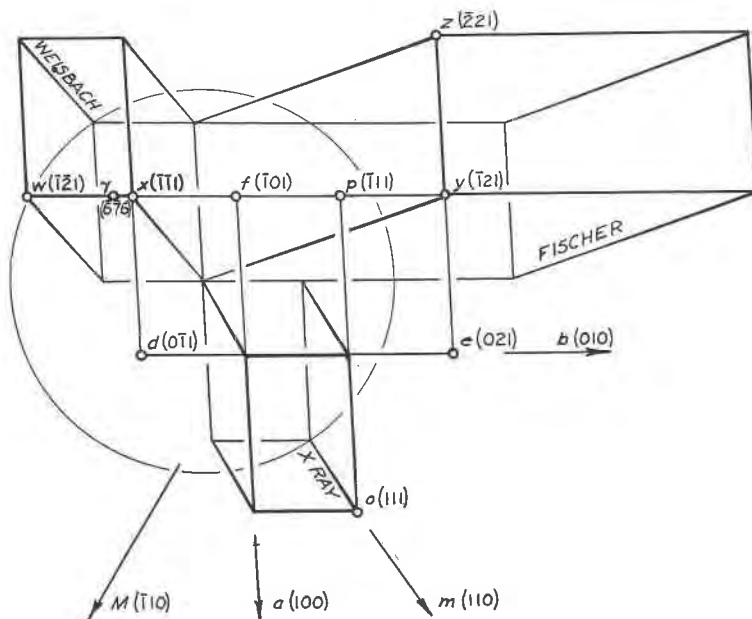


FIG. 3. Gnomonic projection for walpurgite showing unit cells of Weisbach (completed), Fischer and x-ray.

TABLE 2. WALPURGITE CRYSTAL FORMS

X-ray	Fischer, 1946	Weisbach, 1877
<i>b</i> 010	100	<i>b</i> 010
<i>a</i> 100	010	
<i>m</i> 110	130	<i>m</i> 110
<i>M</i> 110	130	<i>μ</i> 110
<i>e</i> 021	011	
<i>g</i> 011	111	
<i>h</i> 101	203	
<i>o</i> 111	121	
<i>p</i> 111	103	
<i>z</i> 221	011	
<i>x</i> 111	101	<i>c</i> 001
<i>y</i> 121	001	
<i>γ</i> 676	19.0.18	
<i>w</i> 121	403	

density by Miss Mary E. Mrose using the Berman balance gave a value of 5.95.

TABLE 3. SOME WALPURGITE ANGLES COMPARED

Angle (New setting)	X-ray (calc.)	Fischer (obs.)	Weisbach (obs.)
$(010) \wedge (1\bar{1}0)$	$58^{\circ}45'$	$58^{\circ}18' \pm 24'$	$59^{\circ} 2'$
$(010) \wedge (110)$	55 4	55 8	53 50
$(010) \wedge (\bar{1}\bar{1}1)$	72 13	72 29	70 52
$(100) \wedge (010)$	87 22	$88 23 \pm 47'$	86 6
$(100) \wedge (\bar{1}\bar{1}1)$	113 31		114 1
$(1\bar{1}0) \wedge (\bar{1}\bar{1}1)$	80 8		80 40
$(\bar{1}\bar{1}0) \wedge (\bar{1}\bar{1}1)$	70 36		82 59
$(010) \wedge (\bar{1}21)$	40 57	$40 29 \pm 13'$	
$(\bar{1}00) \wedge (\bar{1}21)$	76 40	$76 29 \pm 10$	
$(\bar{1}21) \wedge (\bar{1}\bar{1}1)$	66 50	$66 53 \pm 26$	
$(\bar{1}21) \wedge (\bar{2}21)$	13 52	$22 56 \pm 23$	
$(\bar{1}21) \wedge (021)$	28 29	$27 59 \pm 5$	
$(100) \wedge (0\bar{1}1)$	70 52	$72 15 \pm 14$	

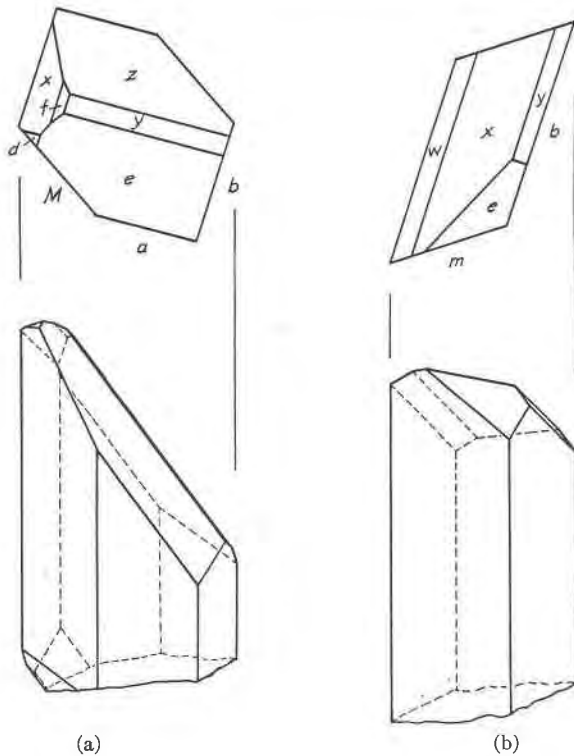


FIG. 4. Walpurgite single crystals, after Fischer: (a) Schneeberg; (b) Joachimsthal.

Walpurgite crystals are generally opaque yellow plates, sometimes with a clear zone at the termination. Fischer's analysis was made on the transparent terminations of the crystals. Gonyer's analysis and the other analyses together with the density measurements were made on samples consisting mostly of opaque material. According to Fischer the opaque parts contain disseminated basic bismuth carbonate. It appears

TABLE 4. WALPURGITE ANALYSES

	1	2	3	4	5
Bi <sub>2</sub> O <sub>3</sub>	61.43	59.34	61.8	61.87	62.1
UO <sub>3</sub>	20.29	20.54	18.7	16.16	19.0
P <sub>2</sub> O <sub>5</sub>			0.9	5.88	
As <sub>2</sub> O <sub>5</sub>	11.88	13.03	14.1	12.45	15.3
H <sub>2</sub> O	4.32	4.65	3.7	3.42	3.6
Total	97.92	97.56	99.2	99.78	100.0

1, 2. Weisbach, 1873(6).  
 3. Fischer, 1948 (5).  
 4. New analysis by Gonyer (1949) on Schneeberg material.  
 5. 2Bi<sub>2</sub>O<sub>3</sub> · UO<sub>3</sub> · As<sub>2</sub>O<sub>5</sub> · 3H<sub>2</sub>O.

likely that the opaque material contains finely disseminated impurities and air or minute open cavities, making these measurements unreliable. Because of the small quantity of clear material available, it has not been possible to improve the data on composition and density. It seems likely that Fischer's analysis gives the best information regarding composition.

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