FLINKITE AND ATELESTITE

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ABSTRACT

Flinkite, $Mn_2''Mn'''(AsO_4)(OH)_4$ is orthorhombic, spacegroup *Pnna* (52), with $a = 9.55$, $b = 13.11$, $c = 5.25$ Å, $Z = 4$ and calculated specific gravity 3.73.

Atelestite, $Bi_8(AsO_4)_3O_5(OH)_5$ is monoclinic, space group $P2_1/a$ (14) with $a = 10.88$, $b = 7.42$, $c = 6.98$ Å, $\beta = 107°13$, $Z = 1$ and calculated specific gravity 6.95.

INTRODUCTION

Flinkite and atelestite are basic arsenates of manganese and bismuth, respectively, which have been grouped (Dana, 1951) in Type 3 of Class 41 together with clinoclase $Cu_3AsO_4(OH)_3$ and cornetite $Cu_3PO_4(OH)_3$. The latter minerals (Palache & Berry, 1946, Berry, 1950), although analogous in chemical composition, are crystallographically dissimilar. Flinkite and atelestite have a metal to arsenate ratio which is similar to clinoclase but the hydroxyl content differs. In both cases the formulae are open to question. The minerals are of very rare occurrence, only one chemical analysis is on record for flinkite, and two for atelestite. The lack of x-ray data on these minerals has hindered a thorough crystallographic comparison with the copper minerals.

The writers wish to thank Professor C. Frondel of Harvard University for the loan of specimens of these scarce minerals on which the present studies were performed. Acknowledgments are also due to the National Research Council and the Committee on Scientific Research of Queen's University for grants (L. G. B.) in support of x-ray crystallographic studies.

FLINKITE

Flinkite, $Mn_2^2Mn^3(AsO_4)(OH)_4$ was described by Hamberg (1889) from the Harstig mine at Pajsberg near Persberg, Sweden. It occurs as feather-like and small bladed aggregates, greenish brown in colour, in veinlets in magnetite ore.

Two small specimens (Numbers 471 and 3728) were made available from the A. F. Holden collection at Harvard University. A small fragment, broken from a bladed aggregate, oriented optically, yielded an x-ray rotation film with smeared diffractions. This crystal was broken again and a smaller fragment yielded sharp rotation and Weissenberg films, using filtered copper radiation (λ = 1.5418). The films indicated orthorhombic symmetry with the following lattice dimensions:

$$a = 9.55 \quad b = 13.11 \quad c = 5.25 \text{ Å}$$
$$a{:}b{:}c = 0.728{:}1{:}0.400$$
Space group: *Pnna* (52)

Only three weak reflections, 031, 051, 421, among those indexed on the first layer Weissenberg film, *hkl*, are inconsistent with a *B*-centred lattice. The ratio of lattice dimensions is in fair agreement with the morphological axial ratio when the latter is reoriented with $c < a < b$:

$$c'{:}b{:}a' = 0.7386{:}1{:}0.4131 \text{ (Hamberg, 1889, Dana, 1951)}$$

TABLE 1. FLINKITE: *X*-RAY POWDER DATA
(Fe*K*, MnO filter, λ = 1.9373, Diameter 114.59 mm, no correction for film shrinkage)

d (meas)	*I*	*hkl*	*d* (meas)	*I*	*hkl*
4.733 Å	100	200, 101	2.183 Å	5	060, 222
4.386	100 B	111, 210	2.082	5	341, 042
3.815	30	220, 121	1.969	5	161
3.179	80	131	1.729	5	
2.710	10	240, 301	1.711	5	
2.662	100	141, 311	1.650	10	
2.570	5	103	1.625	5	
2.506	30	321	1.565	5	
2.392	10	400, 122	1.538	20	
2.271	5	151	1.471	5	
2.214	5	132			

Composition and Cell Content

The only available analysis of flinkite (Table 2) combined with the cell volume (669.8 Å^3) and measured specific gravity (3.78) lead to the

TABLE 2. FLINKITE: ANALYSIS AND CELL CONTENT

	1	2		3	4	
CaO	0.4	0.11	Ca	0.11		
MgO	1.7	0.64	Mg	0.64	Mn^{2+}	8
MnO	35.8	7.79	Mn^{2+}	7.79		
Mn_2O_3	20.2	1.97	Mn^{3+}	3.94	Mn^{3+}	4
$(Fe,Al)_2O_3$	1.5	0.17	(Fe,Al)	0.34		
As_2O_5	29.1	1.98	As	3.96	As	4
Sb_2O_5	2.5	0.11	Sb	0.22		
H_2O	9.9	8.46	H	16.92	H	16
	101.1		O	33.76	O	32

1. Flinkite, Harstig mine, Sweden (Hamberg, 1889).
2. Unit cell content (oxides).
3. Atomic content of unit cell.
4. Ideal unit cell content $4[Mn_2Mn(AsO_4)(OH)_4]$.

cell content $4[Mn_2^{2+}Mn^{3+}(AsO_4)(OH)_4]$ with a calculated specific gravity of 3.73.

The unit cell content confirms the previously accepted formula which led Dana (1951) to classify flinkite with clinoclasite. The (OH) content of the formula differs from clinoclasite and cornetite and no crystallographic similarity between these minerals is apparent from this study.

Atelestite

Atelestite, $Bi_3(AsO_4)O_2(OH)_2$?, was first described in crystals and crystalline aggregates by Breithaupt (1832) from the Neuhilfe mine, Schneeberg, and later as rhagite in mammillary material from the Weisser Hirsch mine near Schneeberg by Weisbach (1874). Frondel (1943) concluded from an *x*-ray powder study of several specimens of both materials from the original locality, that rhagite is identical with atelestite. Two specimens of atelestite from Schneeberg, Saxony, were available for this study from the Holden collection of Harvard University (numbers 1659 and 7115).

Atelestite occurs on the above specimens as subspherical aggregates with a maximum dimension of one millimetre and individual crystal faces of one fifth mm. or less. Single crystals are not present but fragments showing one or two crystal faces are obtainable from the aggregates. A tiny crystal fragment of atelestite, showing the faces ($\bar{1}11$) and ($\bar{1}\bar{1}1$) in the setting adopted here, was oriented for single crystal study. Precession and Weissenberg films yielded the following lattice dimensions:

$$a = 10.88 \qquad b = 7.42 \qquad c = 6.98\ \text{Å} \qquad \beta = 107°\ 13'$$

The observed diffractions, conforming to the conditions ($h0l$) present only with h even and ($0k0$) present with k even, lead to the space group $P2_1/a$ (14).

Comparison of the lattice elements determined by *x*-ray methods with the morphological ratio of Busz (1889) as given by Dana (1951)

$$a:b:c = 1.466:1:0.941, \qquad \beta = 107°\ 13'\ (x\text{-ray})$$

$$c':b':a' = 1.5051:1:0.9334, \qquad \beta = 109°\ 17'\ (\text{Busz, 1889})$$

reveals good agreement between $b:c$ and $b':a'$ but poor agreement between $a:b$ and $c':b'$, and between the β angles. Examination of the morphological unit reveals a less oblique unit with:

$$a:b:c = 1.4855:1:0.9334, \ \beta = 107°\ 05'\ (\text{morphology})$$

which compares more favourably with the structural unit. The old morphological setting is related to the structural setting by the reversible transformation:

Busz to structure	$101/010/\bar{1}00$
Structure to Busz	$00\bar{1}/010/101$

In Table 3 the indices of the observed crystal forms, as listed in Dana, are tabulated with their indices in the structural setting and the standard φ and ρ angles calculated from the structural lattice elements.

TABLE 3. ATELESTITE, CRYSTAL FORMS AND CALCULATED ANGLES, $a:b:c = 1.466:1:0.941$, $\beta = 107°13'$

Busz	Structure	ϕ	ρ
c 001	100	90°00′	90°00′
b 010	010	0°00′	90°00′
a 100	$10\bar{1}$	−90°00′	19°54′
m 110	$11\bar{1}$	−20°59 1/2′	45°18′
l 310	$31\bar{3}$	−49°01′	25°37′
e 011	110	35°31 1/2′	90°00′
d 101	$20\bar{1}$	−90°00′	45°57 1/2′
g $\bar{1}01$	001	90°00′	17°13′
o 111	$21\bar{1}$	−47°42′	54°25 1/2′
q 313	$61\bar{3}$	−73°07′	47°12′

The interfacial angles calculated from the axial elements for the structural lattice are tabulated in Table 4 with the measured and calculated angles given by Busz (1889). The differences between the original

TABLE 4. ATELESTITE: MEASURED AND CALCULATED INTERFACIAL ANGLES

Busz (1889) $c':b':a' = 1.5051:1:0.9334$ $\beta = 109°17'$				Structural lattice $a:b:c = 1.466:1:0.941$ $\beta = 107°13'$		
	Measured	Calculated	Δ		Calculated	Δ
$100 \wedge 10\bar{1}$	36°21′30″	*	0	$\bar{1}01 \wedge 001$	37°07′	+ 36′
$100 \wedge 001$	70°43′	*	0	$10\bar{1} \wedge 100$	70°06′	− 37′
$110 \wedge 1\bar{1}0$	82°45′45″	*	0	$\bar{1}11 \wedge \bar{1}\bar{1}1$	82°46′	0′
$001 \wedge \bar{1}01$	72°57′	72°55′30″	− 1 1/2′	$100 \wedge 001$	72°47′	− 10′
$100 \wedge 101$	25°30′ †	25°53′32″	+ 23 1/2′	$\bar{1}01 \wedge \bar{2}01$	26°03 1/2′	+ 33 1/2′
$100 \wedge 110$	41°22′30″	41°22′52″	+ 1/2′	$\bar{1}01 \wedge \bar{1}11$	41°34′	+ 11 1/2′
$110 \wedge 001$	75°07′	75°39′09″	+ 32′	$11\bar{1} \wedge 100$	75°14′	+ 7′
$110 \wedge 10\bar{1}$	52°55′	52°49′30″	− 5 1/2′	$\bar{1}11 \wedge 001$	53°24′	+ 29′
$011 \wedge 001$	54°39′30″	54°51′28″	+ 12′	$110 \wedge 100$	54°28 1/2′	− 11′
$011 \wedge 100$	78°53′30″	79°28′36″	+ 35′	$110 \wedge 10\bar{1}$	78°35′	− 19′
$011 \wedge \bar{1}01$	80°16′30″	80°16′11″	− 1/2′	$110 \wedge 001$	80°14′	− 2 1/2′
$011 \wedge 110$	46°48′30″	46°54′19″	+ 6′	$110 \wedge 11\bar{1}$	46°31′	− 17 1/2′
$100 \wedge 111$	41°16′30″	41°16′40″	0	$10\bar{1} \wedge 21\bar{1}$	41°17′	+ 1/2′
$111 \wedge 1\bar{1}1$	66°28′	66°41′20″	+ 13 1/2′	$\bar{2}11 \wedge \bar{2}\bar{1}1$	66°24′	− 4′
$111 \wedge 110$	22°05′	21°58′17″	− 6 1/2′	$\bar{2}11 \wedge \bar{1}11$	22°16′	+ 11′
$111 \wedge 011$	37°37′	38°11′56″	+ 35′	$21\bar{1} \wedge 110$	37°22 1/2′	− 14 1/2′
$110 \wedge 310$	24° †	25°00′53″	+ 61′	$11\bar{1} \wedge 31\bar{3}$	25°09′	+ 69′
$111 \wedge 313$	20°30′ †	20°58′25″	+ 28 1/2′	$21\bar{1} \wedge 61\bar{3}$	20°59′	+ 29′
$313 \wedge 3\bar{1}3$	25°30′ †	24°44′30″	− 45 1/2′	$61\bar{3} \wedge 6\bar{1}\bar{3}$	24°36′	− 54′
		Σ + Δ	247′		Σ + Δ	226 1/2′
		Σ − Δ	59 1/2′		Σ − Δ	169 1/2′
		Σ	+ 187 1/2′		Σ	+ 47′
		ΣΔ	306 1/2′		ΣΔ	396′

*Used to calculate axial ratio.
†Schimmer.

measured angles and those calculated from the new and old axial ratios are also shown. The angles calculated from the structural elements show a somewhat larger total difference, but lower net difference, from the

TABLE 5. ATELESTITE: *X*-RAY POWDER DATA
$a = 10.88$ $b = 7.42$ $c = 6.98$Å $\beta = 107°13'$
(corrected for film shrinkage)

Frondel (1943 CuK, filtered		This study CoK, Fe filter		Calculated	
I	*d* (meas)	*I*	*d* (meas)	*hkl*	*d* (calc)
20	6.798	20	6.62	001	6.65
20	6.098	10	6.03	110	6.03
60	4.221	20	4.233	210	4.241
—	—	5	3.326	002	3.325
100	3.234	100 B	3.239	$\bar{2}02$, $\bar{1}21$	3.272, 3.228
70	3.115	40	3.116	310	3.126
20	2.939	10	2.940	$\bar{2}21$	2.944
70	2.720	30	2.725	$\bar{1}12$	2.721
50	2.522	20	2.526	$\bar{4}11$, 320	2.533, 2.526
—	—	2	2.469	022	2.477
—	—	2	2.406	$\bar{4}02$, 130	2.418, 2.406
20	2.305	2	2.316	031, $\bar{1}31$	2.319, 2.314
—	—	5	2.287	$\bar{1}22$, $\bar{4}12$	2.297, 2.299
—	—	2	2.260	$\bar{3}22$	2.261
60	2.200	20	2.201	$\bar{2}31$, 401	2.202, 2.201
50	2.121	20	2.124	013, 420	2.124, 2.122
60	2.033	15	2.040	231	2.039
—	—	5	2.015	$\bar{3}12$, $\bar{1}32$	2.023, 2.016
50	1.973	20	1.968	$\bar{5}12$	1.976
50	1.885	15	1.878	$\bar{3}23$	1.881
10	1.831	5	1.826		
40	1.803	20	1.802		
20	1.733	2	1.741		
—	—	5	1.721		
40	1.685	5	1.681		
—	—	2	1.653		
60	1.641	10	1.637		
30	1.575	2	1.574		
30	1.548	5	1.554		
—	—	2	1.538		
40	1.511	5	1.515		
20	1.468	—	—		
20	1.447	5	1.450		
40	1.416	5	1.420		
—	—	5	1.408		
10	1.373	—	—		
40	1.290	5	1.293		
10	1.264	5	1.264		
10	1.229				
30	1.201				
(19 additional lines)					

measured angles than do the calculated angles of Busz. If the poor measurements are neglected the total and net differences are reduced to 210 1/2′, 20 1/2′ (*x*-ray) and 148′, 120′ (Busz). The low net difference between the measured angles and those calculated from the *x*-ray measurements indicate that the structural lattice elements are closer to the true crystallographic constants of atelestite than the elements derived by Busz. The present specimens did not include crystals suitable for accurate measurement on a two-circle optical goniometer; therefore Busz' data remain the only published morphological measurements.

X-ray Powder Pattern

In Table 5 the observed spacings and intensities obtained from an *x*-ray powder film are compared with the data published by Frondel (1943). The probable indices of the reflecting planes together with the calculated interplanar spacings are also given.

Composition and Cell Content

The two available analyses are listed in Table 6. The first represents the well crystallized material studied by Busz (1889). The second represents mammillary material originally described as rhagite but shown to

TABLE 6. ATELESTITE: ANALYSES AND CELL CONTENT

I	*a*	*b*	*c*	*d*	*e*	*f*	*g*
Bi_2O_3	82.41	82.87	.1778	3.69	Bi 7.38	8.00	8
As_2O_5	14.12	14.20	.06767	1.40	As 2.80	3.04	3
H_2O	1.92	1.93	.10712	2.22	H 4.44	4.81	5
Remainder	0.51	0.00			O 20.29	21.99	22
Total	98.96	100.00					
G	6.4						6.95
M	2074.91						2253.77
II	***a***	***b***	***c***	***d***	***e***	***f***	
Bi_2O_3	72.76	79.45	.1705	3.77	Bi 7.54	8.00	
As_2O_5	14.20	15.51	.07392	1.63	As 3.26	3.46	
H_2O	4.62	5.04	.27975	6.18	H 12.36	13.11	
Remainder	6.85	0.00			O 25.64	27.20	
Total	98.43	100.00					
G	6.82						
M	2211.07						

I—Neuhilfe mine, Schneeberg (crystals) Dana (1951) from Busz (1889), remainder is Fe_2O_3.

II—"Rhagite" Weisser Hirsch mine, Schneeberg (mammillary) Dana (1951) from Winkler (1874), remainder is CoO 1.47, CaO 0.50, $(Fe,Al)_2O_3$ 1.62, gangue 3.26. *a*—analysis, *b*—analysis corrected to 100%, *c*—molecular proportions, *d*—oxide content of unit cell, *e*—atomic content, *f*—atomic content adjusted to 8 Bi atoms, *g*—ideal atomic content.

be identical with atelestite by Frondel (1943). The measured values for the specific gravity are given for both materials, but it is unlikely that these values are accurate. The higher value was obtained on the mamillary material with a lower bismuth content and higher water content. The data here quoted can be considered as representing a rough approximation to the true composition and specific gravity.

In Table 6 the molecular weight of the cell content *M* is given for both analyses using the measured unit cell volume and the specific gravity. For each analysis the cell content is computed in terms of oxides and elements. The most reasonable cell content is represented by the formula $Bi_8(AsO_4)_3O_5(OH)_5$ which gives a calculated specific gravity of 6.95, not far different from the higher measured value. Formulae derived for the cell content II *f* give higher calculated specific gravities. The nature of material II indicates that much of the water shown is probably part of the impurities. Thus more weight should be given to analysis I especially with respect to the water content. Formulae with 7 Bi give calculated specific gravities appreciably below 6.4.

In spite of the doubts expressed above regarding the reliability of the chemical data, the calculations in Table 6 clearly indicate a cell content of:

$$Bi_8(AsO_4)_3O_5(OH)_5$$

The contents of Bi and As are well established unless the analysis is grossly in error. The content of O and OH is less certain. The most serious objection to the above formula lies in the content of 3 As since the space group found for atelestite has no one-fold atomic positions. The correct answer to the composition of this mineral must await new analyses on pure material or a study of the synthetic phases in the system $Bi_2O_3-As_2O_5-H_2O$.

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