

STUDIES OF MINERAL SULPHO-SALTS: IV—GALENO-BISMUTITE AND "LILLIANITE"

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ABSTRACT

Single crystal x -ray measurements on galenobismutite from Nordmark Mines, Sweden (type specimen) give the following structural data: orthorhombic; space group, D_{2h}^{16} — $Pnam$ or C_{2v} — $Pna2$. Cell edges, a_0 11.72 ± 0.03 , b_0 14.52 ± 0.03 , c_0 4.07 ± 0.02 Å. Unit cell contains $Pb_4Bi_8S_{16} = 4[PbS \cdot Bi_2S_3]$. Specific gravity 7.04 (highest of three measurements), 7.18 (calculated). Polished sections, white, strongly anisotropic; etch-reactions: HNO_3 , at once effervesces violently, etches deeply and leaves yellow deposit; HCl, gives a slight brown stain; KCN, $FeCl_3$, KOH, $HgCl_2$, negative.

Galenobismutite from Cariboo Gold Quartz Mine, British Columbia, and 'lillianite' from Mt. Farrell, Tasmania, gave powder patterns identical with that of the type material. 'Lillianite' from Gladhammar is shown by polished sections and x -ray photographs to be a mixture of galena and galenobismutite. Flink's crystals of 'lillianite' evidently represent the only known occurrences of distinct crystals of galenobismutite. These observations confirm the individuality of Sjögren's galenobismutite and show that 'lillianite' has no standing as a mineral species.

Galenobismutite was first described from the Kogrufvan, Nordmark, Sweden, by Sjögren (1878) who derived the composition $PbS \cdot Bi_2S_3$. There appears to be no subsequent description of a homogeneous mineral with this composition. Weibull (1885) described a seleniferous material from Falun, Sweden, as *seleniferous galenobismutite*, later named *weibullite* by Flink (1910). Dana (1892) accepted this 'seleniferous galenobismutite' along with the *alaskaite* of Koenig (1881) as varieties of galenobismutite. Murdoch (1916, p. 130), Walker and Thomson (1921, p. 12) and Schneiderhöhn and Ramdohr (1931, p. 396) all worked with the seleniferous material, which had become known as galenobismutite, and found it to be a mixture; and thus the individuality of galenobismutite has been widely questioned. Specimens of this mixed mineral were examined and found to contain two minerals, neither of which is galenobismutite; these will be described on another occasion.

Lillianite, a new mineral with the composition $3PbS \cdot Bi_2S_3$, was described from the Lillian Mine, Leadville, Colorado by Keller and Keller (1885) and Keller (1889). Material from the type locality has since been shown to be a mixture, by Emmons, Irving and Loughlin (1927, p. 170). The name lillianite was later applied by Flink (1910) to a mineral from Gladhammar, Sweden, previously analyzed by Lindström (1889). Analyses of this material by Mauzelius, in Flink (1910), agreed well with the early analysis by Lindström (1889). The same material was again examined by Walker and Thomson (1921) and analyzed by Todd, who confirmed the previously reported composition. Walker and Thomson

concluded that this material is homogeneous; our specimens, however, prove to be a mixture of galena and galenobismutite, and therefore a description of this so-called 'lillianite' is appropriate in the present connection.

Professor G. Aminoff in Stockholm kindly supplied a fragment from the specimen of galenobismutite originally described and analyzed by Sjögren (1878), thus making it possible to re-examine this mineral and determine its specific properties. The specimens of 'lillianite' were made available by Professor A. L. Parsons. The material from British Columbia was received from Professor H. V. Warren, who will give further descriptive details elsewhere. Professor M. A. Peacock has given me some useful suggestions and has helped in the preparation of this paper.

MATERIALS

The following materials proved to be galenobismutite or to contain this mineral.

1. Galenobismutite, Kogrufvan, Nordmark Mines, Sweden (type material). "Naturhistoriska Riksmuseet, Stockholm, yellow 3987"; crystalline, indistinctly columnar aggregate. This is the material analyzed and named by Sjögren (1878).

2. 'Lillianite' (Royal Ontario Museum of Mineralogy, M/14076), Mt. Farrell, Tasmania; crystalline, indistinctly columnar aggregate with calcareous gangue.

3. 'Lillianite' (R.O.M.O.M., M/11826 and polished section A.2.3.2.), Gladhammar, Sweden; fibrous aggregate intimately intergrown with galena. Analyzed by Todd, in Walker and Thomson (1921).

4. Galenobismutite (R.O.M.O.M., M/19716), Cariboo Gold Quartz Mine, Barkerville, Cariboo District, British Columbia; Crystalline, indistinctly columnar aggregate with cosalite and gold in quartz.

The x-ray measurements were made on the type material; the identity of the remaining specimens was established by means of x-ray powder photographs.

PHYSICAL PROPERTIES

Galenobismutite forms indistinctly columnar aggregates showing poor longitudinal cleavage. It is tin-white in colour with metallic lustre. Specific gravity measurements on three different fragments from material 1 gave 7.04, 7.01, and 6.96 as compared with 6.88 noted by Sjögren. The published specific gravity of 'lillianite' from Gladhammar ranges from 7.00 to 7.14, due to the presence of more or less galena with specific gravity 7.5.

In polished sections galenobismutite is whiter than galena and strongly anisotropic, the polarization colours being yellow to dark brown. Standard etch-reactions: HNO_3 , immediately gives violent effervescence, leaving a deeply etched surface and a yellow deposit; HCl gives a slight

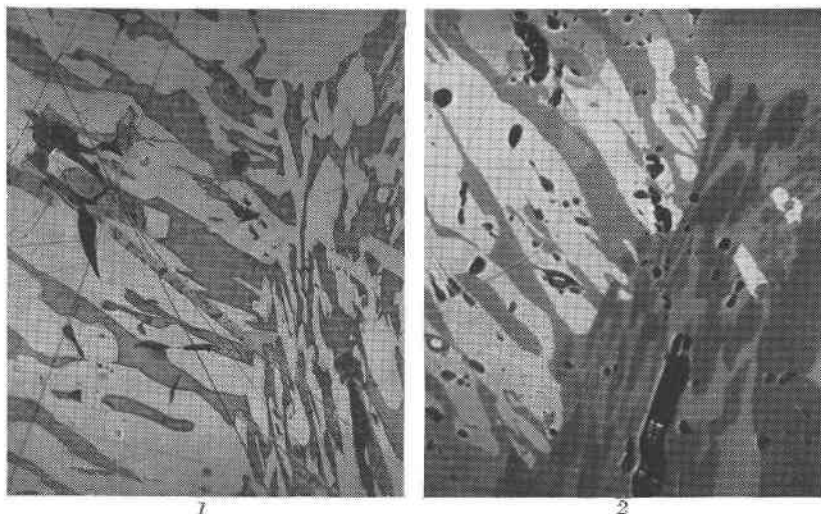


FIG. 1. Galenobismutite ('lillianite'), Gladhammar, Sweden (material 3); galenobismutite (light grey, unetched) intergrown with galena (darker grey, etched with FeCl_3). Vertical illumination; $\times 60$.

FIG. 2. The same; galenobismutite (light grey and dark grey) intergrown with galena (intermediate shade of grey). Unetched; crossed nicols; $\times 60$.

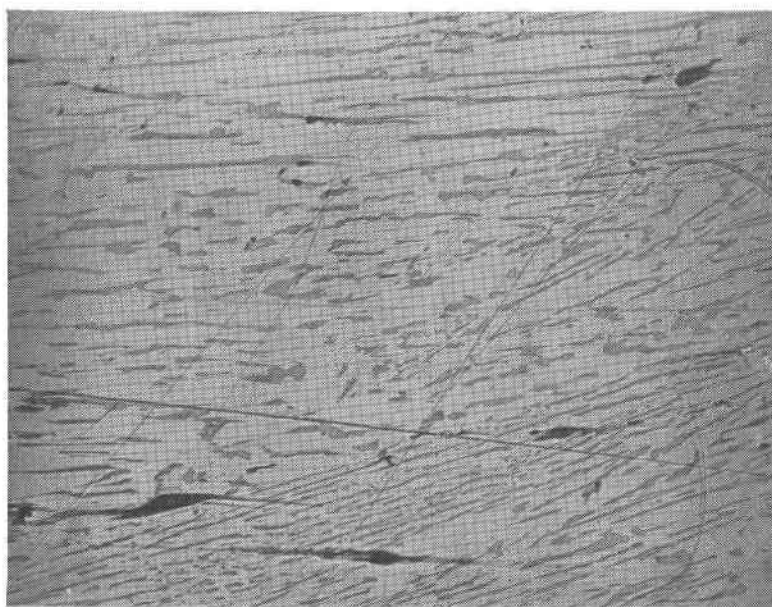


FIG. 3. Galenobismutite ('lillianite'), Gladhammar, Sweden (material 3); fine-grained intergrowth of galenobismutite (light grey, unetched) and galena (darker grey, etched with FeCl_3). Vertical illumination; $\times 90$.

brown stain; KCN, negative; FeCl₃, negative; KOH, negative; HgCl₂, negative. Hardness B, estimated by the steel needle. Published etch-reactions for galenobismutite (Short, 1934) are not reliable since they were made on the so-called 'seleniferous galenobismutite.'

Three polished sections of 'lillianite' from Gladhammar are shown in Figs. 1, 2, 3. Figure 1 shows galenobismutite (unetched) intergrown with galena (etched by FeCl₃). Figure 2, taken under crossed nicols, shows regular intergrowths of the strongly anisotropic galenobismutite with isotropic galena. Figure 3 shows elongated inclusions of galena oriented with the direction of elongation of the galenobismutite.

STRUCTURAL CRYSTALLOGRAPHY

A cleavage fragment about 0.4 mm. long by 0.08 to 0.1 mm. thick was obtained from material 1. The long edge of this fragment proved to be the shortest lattice period and therefore the properly chosen vertical axis. The cleavage or cleavages are therefore in the zone [001], but the indices could not be determined.

A rotation photograph (Fig. 4) about the axis of elongation of the fragment showed the zero, first and second layer lines, giving the lattice period:

$$c_0 = 4.07 \pm 0.02 \text{ \AA}$$

Weissenberg photographs (Figs. 5, 6) of the zero and first layer lines showed orthorhombic symmetry, with 14 orders of $h00$ and 18 orders of $0k0$ including the orders extinguished by the space group symmetry and the structure. Owing to the general weakness of the diffractions $h00$, three strong diffractions $3h \cdot 2h \cdot 0$ were taken into account in deriving the remaining lattice periods:

$$a_0 = 11.72 \pm 0.03 \text{ \AA}$$

$$b_0 = 14.52 \pm 0.03 \text{ \AA}$$

The systematically missing spectra conform to the conditions:

$$h0l \text{ present only with } h \text{ even}$$

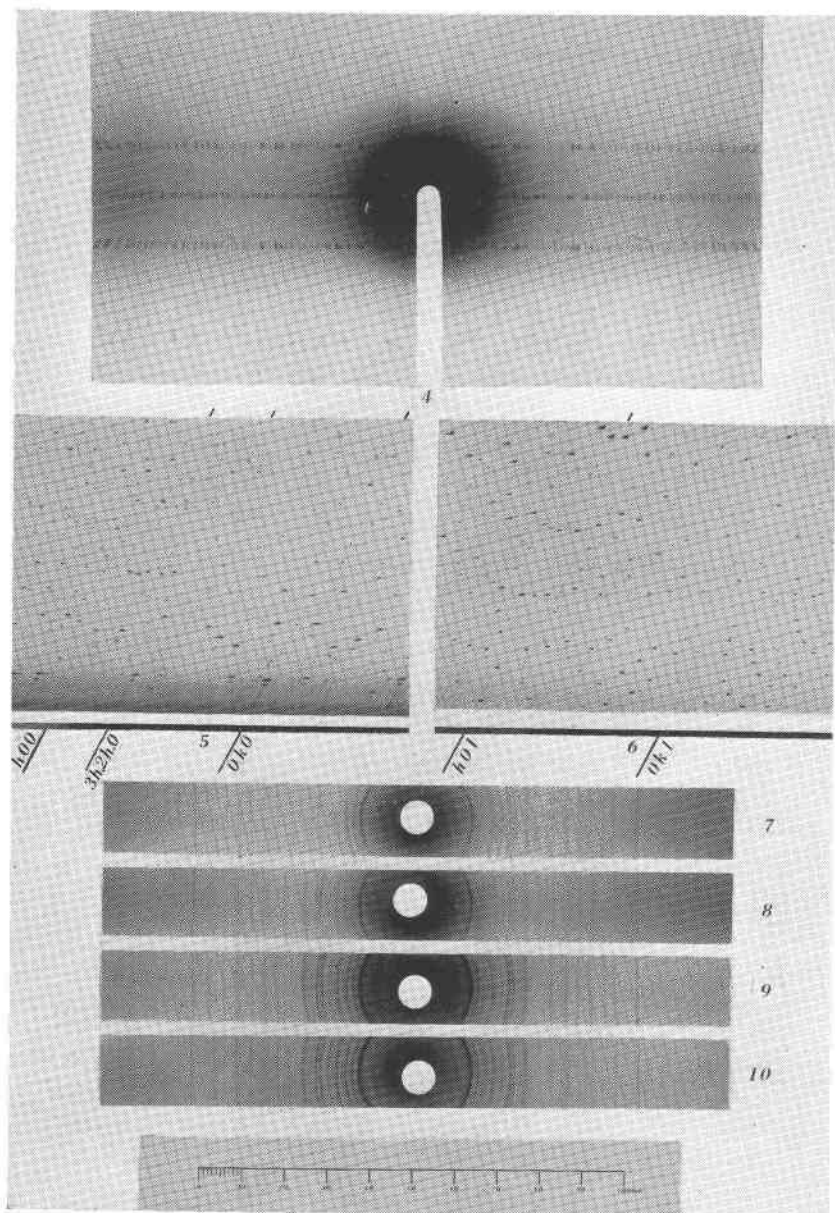
$$0kl \text{ present only with } k+l \text{ even}$$

These conditions are characteristic for the space groups:

$$D_{2h}^{16} - Pnam \text{ or } C_{2v}^9 - Pna2$$

The chosen orientation is the normal orthorhombic setting in which c_0 is the shortest and b_0 the longest edge of the rectangular lattice cell.

Flink (1910, p. 13) described and figured distinct orthorhombic crystals from the material called 'lillianite' from Gladhammar, which we have



(See opposite page for description of figures.)

shown to consist of a mixture of galena and galenobismutite. For these crystals Flink obtained the elements:

$$a:b:c=0.8002:1:0.5433$$

and noted the forms (100), (010), (110), (210), (011).

By halving Flink's *c*-axis the axial ratio:

$$a:b:c/2=0.8002:1:0.2717$$

agrees very fairly with the structural ratio for galenobismutite:

$$a_0:b_0:c_0=0.807:1:0.280$$

In the new setting Flink's forms become (100), (010), (110), (210), (021). There can be no question, therefore, that Flink's crystals of 'lillianite' were, in fact, galenobismutite and that they actually represent the only crystals of this mineral that have ever been measured.

POWDER PHOTOGRAPHS

Identical powder photographs (Figs. 7, 8, 9, 10) were obtained from materials 1, 2, 3 and 4. In the case of 'lillianite' from Gladhammer (material 3), the sample was obtained from the polished section by scraping the unetched portion of the intergrowth with galena.

Table 1 gives the *x*-ray powder spectrum of galenobismutite which has been indexed with reference to the cell elements already determined. A number of lines, with θ -values greater than 35° , although clearly visible on the films, were too indistinct to be measured accurately. The photographs and tabulated data will be sufficient for future identification of the species.

FIGS. 4-10. X-ray photographs of galenobismutite; copper radiation; radius of cameras, $360/4\pi$ mm.

FIG. 4. Rotation photograph about $c[001]$; 1.5 KWH (unfiltered).

FIG. 5. Weissenberg photograph of the zero layer line $/hk0/$, with some diffractions due to a sub-parallel individual; 23.0 KWH (unfiltered).

FIG. 6. Weissenberg photograph of the first layer line $/hk1/$; 21.5 KWH (unfiltered).

FIG. 7. Sweden (galenobismutite, material 1); powder photograph; 10.8 KWH (nickel filter).

FIG. 8. Tasmania ('lillianite,' material 2); powder photograph; 5.9 KWH (nickel filter).

FIG. 9. Sweden ('lillianite,' material 3); powder photograph; 4.6 KWH (nickel filter).

FIG. 10. British Columbia (galenobismutite, material 4); powder photograph; 3.4 KWH (nickel filter).

TABLE 1. GALENOBISMUTITE: X-RAY POWDER SPECTRUM

s_{Cu}	I_P	$d_{meas.}$	hkl	$d_{calc.}$	I_W
12.3	w	3.67	040	3.84	vvs
13.0	vvs	3.47	{140	3.47	vs
			{320	3.44	vvs
13.3	vw	3.39	{121	3.40	vvs
			{201	3.34	vs
13.9	vw	3.25	211	3.26	m
14.9	s	3.03	{330	3.04	m
			{131	3.02	vs
16.2	w	2.79	311	2.77	s
17.0	vw	2.66	{420	2.72	s
			{340	2.66	m
18.3	s	2.47	241	2.46	s
19.0	m	2.38	401	2.38	vvs
20.1	vw	2.26	260	2.24	vs
20.7	vw	2.19	251	2.19	s
22.1	s	2.06	360	2.06	vs
22.6	vw	2.02	511	2.01	vs
			{441	1.989	s
23.1	s	1.975	{112	1.986	—
			{261	1.960	s
			{521	1.958	vs
24.0	vw	1.905	212	1.906	—
24.3	m	1.882	{531	1.874	vs
			{460	1.866	vs
25.9	s	1.772	{232	1.787	—
			{042	1.775	—
26.6	vw	1.729	640	1.720	vs
			{242	1.699	—
27.1	vw	1.699	{461	1.696	w
			{470	1.693	m
			{740	1.520	s
30.8	vw	1.510	{442	1.518	—
			{721	1.514	s
			{651	1.506	m
			{291	1.453	m
32.2	m	1.451	{571	1.452	m
			{0.10.0	1.452	s
33.1	m	1.415	{2.10.0	1.410	s
34.1	m	1.378	{801	1.378	s
			{811	1.372	vs

s_{Cu} —Semi-diameter of powder ring as measured on the film (mm.). I_P —Intensity estimated visually. $d_{meas.}$ —Corrected planar spacing (Å), using $\theta = s - 0.2$ mm. hkl —Indices of the powder ring. $d_{calc.}$ —Planar spacing (Å) calculated from the cell dimensions. I_W —Intensity of the corresponding Weissenberg spot, if in the range of the photographs taken.

COMPOSITION AND CELL CONTENT

The cell dimensions of galenobismutite (material 1) combined with the highest measured specific gravity $G = 7.04$, give the molecular weight of the cell content, $M_0 = 2957$. Applying this number to the better of the two original analyses of the type material we obtain the atomic content shown in Table 2.

TABLE 2. GALENOBISMUTITE: ATOMIC CONTENT OF UNIT CELL

	1	2	3	4	5
Pb	27.65	0.2773	0.001338	3.96	4
Bi	54.69	0.5486	0.002625	7.76	8
S	17.35	0.1714	0.005429	16.05	16
	99.69	1.0000			

1. Analysis by Sjögren (1878). 2. Analysis reduced to the sum of unity. 3. Atomic proportions. 4. Numbers of atoms in unit cell, obtained by multiplying the values under 3 by the molecular weight 2957. 5. Ideal cell content of galenobismutite.

As shown in column 4, the cell content of galenobismutite closely approaches $Pb_4Bi_8S_{16} = 4[PbS \cdot Bi_2S_3]$ thus confirming the empirical formula found by Sjögren. For a cell containing $Pb_4Bi_8S_{16}$ the calculated gravity is 7.18, in fair agreement with the measured value of 7.04.

The analyses of 'lillianite' from Gladhammar are useless to confirm the composition of galenobismutite, since they represent mixtures with galena. The analyses show that the intergrowth consists of about 37 per cent of galena and 63 per cent of galenobismutite by weight.

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