

STUDIES OF MINERAL SULPHO-SALTS:
XVII—CANNIZZARITE

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ABSTRACT

Cannizzarite, a lead, bismuth sulphosalt, from Vulcano, Lipari Islands, is redefined as a mineral species. Crystals are thin leafy blades, monoclinic, showing two lattices:

A;	$P2/m$,	$a=4.13$,	$b=4.10$,	$c=15.5A$,	$\beta=99^{\circ}00'$
B;	$C2/m$,	$a=7.07$,	$b=4.10$,	$c=15.5A$,	$\beta=99^{\circ}00'$

Hydrosynthetic experiments in the system Pb-Bi-S lead to the production of crystals of cannizzarite essentially similar to the natural material. Sufficient material, certainly free from bismuthinite and other Pb-Bi-S materials, was not available for quantitative chemical analysis.

Cannizzarite, occurring as a sublimation product in fumaroles on Vulcano, Lipari Islands, Italy was first described by Zambonini, de Fiore & Carobbi (1925). It is noted by Wolfe (1938) that Professor F. Bernauer found cannizzarite to be a mixture of bismuthinite and a platy, metallic mineral. Wolfe re-examined two specimens of cannizzarite from the type locality, available in the Harvard Mineralogical Museum collections. One, a bottle of loose acicular crystals, proved to be bismuthinite; minute, prismatic crystals from the second specimen yielded crystal measurements, structural cell dimensions, a new chemical analysis and a specific gravity which Wolfe ascribes to cannizzarite. Professor M. A. Peacock pointed out (Dana, 1944, 472) that these structural lattice dimensions and physical properties are identical with those reported for type galenobismutite by Berry (1940). Thus, in Dana, cannizzarite is reported to be identical with galenobismutite.

In the course of a study² of the synthesis of Pb-Bi-S compounds commenced at Queen's University in 1947 and continued at the University of Toronto in 1947-49 the first author synthesized, under hydrothermal conditions in a bomb, galena, galenobismutite and four other crystalline phases with probable compositions in the Pb-Bi-S system. One of these phases (Phase 2) gave an x-ray powder pattern identical with that given by thin leafy crystals from Wolfe's specimen of cannizzarite. This leafy material is probably the same as the platy mineral referred to by

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² Described fully in a thesis accepted for the degree Ph.D. *Synthesis and x-ray study of compounds in the systems Pb-Bi-S, Ag-Bi-S and Ag(Bi, Sb)S₂*, A. R. Graham, University of Toronto, 1950.

Professor Bernauer. The leafy material was exhausted in preparing the powder sample. In 1951 the latter authors examined a fine specimen of cannizzarite from the type locality which had been acquired from Ward's Natural Science Establishment by The University of British Columbia. A single leafy crystal from this specimen yielded rotation and Weissenberg x -ray films nearly identical with those given by the artificial crystals. This leafy mineral was apparently a component, along with galenobismutite and bismuthinite, of the material originally described as cannizzarite; therefore it is proposed that the old name be retained for this mineral. This present description is incomplete, lacking quantitative chemical data, but will serve to characterize the mineral as a crystalline phase in the system Pb-Bi-S and to ensure its future identification.

SYNTHESIS OF CANNIZZARITE

The methods of synthesis follow closely those used successfully by Robinson (1948) for compounds in the system Pb-Sb-S. This method utilizes a graphite-lined steel bomb fully described by Smith (1947) and Béland (1948). The details of charges and heating procedures for 30 experiments in the Pb-Bi-S system are given in Table 1. Crystals of phase 2 (=cannizzarite) were obtained in 8 experiments. In all cases phase 2 and artificial bismuthinite are intimately associated, but experiment 17 yielded the largest quantity of fairly pure material. The material occurs as felted masses, bundles of crystals loosely arranged in radial groups, and occasionally as stellate trillings made up of three doubly terminated individuals.

PHYSICAL PROPERTIES

The leafy blades are silvery grey and strongly striated parallel to their elongation. The individual crystals occasionally reached 2 mm. in length by $\frac{1}{4}$ to $\frac{1}{2}$ mm. in width, but they are extremely thin and fragile, twist and bend very easily and fray out at the ends and along their edges at the least touch. They appear friable rather than malleable but are difficult to crush to equidimensional fragments. The effects of preferred orientation in the powder sample are noticeable in the x -ray patterns.

Material from experiment 17 showed only traces of the bismuthinite pattern in powder photographs. Microchemical tests on clean crystals showed the presence of lead, bismuth and sulphur. Three specific gravity determinations, using a 10 cc. pycnometer and about 1.5 gms. of material give 6.64, 6.71, 6.75, average 6.7. The accuracy is not great because of the proven presence of bismuthinite (G (calc) 6.81).

TABLE 1. HYDROSYNTHETIC EXPERIMENTS IN THE SYSTEM Pb-Bi-S

Exp.	Na ₂ S · 9H ₂ O				Pb	Bi	Heated		Cooled to		Products
	S	H ₂ O	NaOH	g.			g.	°C.	Hours	°C.	
1	30	20	15	—	6	1	380	12	180	22	P, B, S, 1, N, L, H
									20	14	
2	30	20	15	—	4	2	400	12	180	9	P, B, S, 2, N, L, H
									20	12	
3	30	15	15	—	3	3	375	24	20	44	P, B, S, 3, N, L, H
4	30	20	15	—	2	4	410	26	210	72	
									20	12	P, B, S, 2, N, L, H
									20	12	
5	30	20	12	—	1	6	395	12	20	72	P, B, S, 3, N, L, H
					PbCl ₂	BiCl ₃					
6	25	15	17	—	1.8	9.3	395	24	190	36	P, B, S, 2, 4, N, L, H
									20	12	
7	20	10	20	—	2.7	6.0	405	30	260	60	P, B, S, 2, N, L, H
									20	24	
8	20	10	20	—	4.0	4.5	400	30	20	100	P, B, S, G, 2, N, L, H
9	20	10	20	—	5.4	3.0	400	30	20	48	
10	20	10	20	—	6	1.5	410	48	20	100	
					Pb	Bi					
11	30	20	20	—	1	0.2	400	86	20	16	P, S, N, H
12	20	—	25	15	1	2					
13	20	3	30	15	1	2					A, P, B, N, C
14	20	15	15	—	3	1					
15	40	15	15	—	2	1					A, P, B, S, Ph, N, L, H
16	40	15	15	—	1	6	400	54	20	16	
											P, B, S, 2, N, L, H
				NaCl							
17	40	15	15	5	1	4					P, B, S, 2, N, L, H
18	40	15	15	5	1	3					
19	35	15	15	5	1	3.5	400	54	20	8	P, B, S, N, L, H, C
20	35	15	15	2	1	5	450	32	40	7	
21	35	15	15	2	1	5					P, B, S, N, L, H, C
22	35	15	15	2	1	7	400	54	chilled in air		
23	35	15	10	—	1	7					
24	35	15	15	—	1	8					
25	35	15	15	—	1	8	400	30	300	48	P, B, S, N, L, H, C
									220	3	
									quenched		
26	35	15	15	—	1	8	400	24	210	54	
									chilled in air		
27	35	20	10	—	1	20					A, B, N, C, and Bi oxide crystals
28	35	2	15	—	1	8	400	6	maintained at 400 for 48 hrs.		
29	35	4	15	—	1	8					
30	45	6	—	—	1	6			chilled in air		

Abbreviations: A, Pb/Bi shot. P, PbS. 1, Phase 1. 2, Phase 2. 3, Phase 3. 4, Phase 4. B, Bi₂S₃. S, Sulphur. N, Soluble Na salt. H, Hydrogen sulphide. G, galenobismutite. Ph, pyrrhotite. L, yellow or brown oily liquid. C, black colloidal matter.

Note: Phases 1 and 4 are fine grained materials represented by certain x-ray powder lines in patterns of mixed materials. They could not be purified nor did they occur as single crystals.

The natural material from Vulcano (1927), Lipari Islands, consists of a single specimen about $1\frac{1}{2} \times 1 \times 1$ in. in size. The porous lower portion of the specimen is composed of a dark substance intimately associated with a white granular powder which gave an x -ray powder pattern identical with that of apthitalite from Vesuvius. This material grades upward into a dark gray, fine-grained, vuggy rock with an irregular surface. Implanted on this surface and in the many vugs and cracks are small metallic lusted leaves which have a marked bluish to iridescent tarnish.

Under the binocular microscope, crystals with several different habits may be observed. Some are single straight laths with occasional frayed ends; some are twinned exhibiting a simple V shape; others composed of three blades show an open trigonal pyramidal shape; a few are triangular; and others occur as felted masses or loosely arranged stellate groups. All crystals are exceedingly thin and are often warped; many are striated parallel to their elongation. The individual crystals rarely reach 2 mm. in length by $\frac{1}{2}$ mm. in width; they are slightly elastic and are difficult to crush, suggesting that they are somewhat malleable.

Bismuthinite needles are present in small amounts.

STRUCTURAL LATTICE

Good signals were not observed on the optical goniometer from single terminated blades, but the crystals were readily oriented about their axes of elongation by using a strong train of signals from their striated surfaces. Rotation and zero and first-layer Weissenberg films about this axis using copper radiation showed the presence of two distinct lattices with the following characteristics.

Lattice A	Symmetry	<i>a</i>	<i>b</i>	<i>c</i>	β
Artificial	<i>P2/m</i>	4.09A	4.06A	15.39A	99°00'
Natural	<i>P2/m</i>	4.13	4.10	15.5	99°00'
Lattice B					
Artificial	<i>C2/m</i>	7.00	4.06	15.39	99°00'
Natural	<i>C2/m</i>	7.07	4.10	15.5	99°00'

The rotation axis is the monoclinic symmetry axis, *b*, for both lattices, and the period of this axis compares well with those of the elongation axis of a large number of mineral sulphosalts. The *c*-axis direction and period are also shared, the plane (001) is the plane of platy development in the crystals. The *a* axes of the two lattices, while coincident in direction have periods in the complex but rational ratio of 7 to 12. The zero and first layer of the reciprocal lattices, as plotted from the Weissenberg films are shown in Figure 1. The films from the artificial and natural crystals are essentially identical although the spots are large and

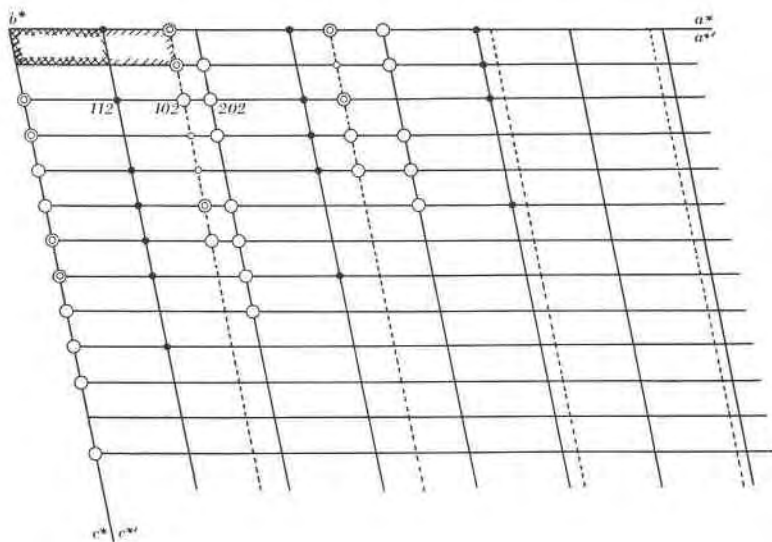


FIG. 1. Diagram of zero and first layers of the reciprocal lattice of phase 2 (=cannizzarite) plotted from Weissenberg photographs about the b axis. Large open circles are zero layer diffractions; small filled circles are first layer diffractions (of lattice B); small open circles represent maxima of smeared first layer diffractions (of lattice A).

generally diffuse on films from the natural material. On the films from artificial material all spots are sharp except for pronounced smearing in the $11l$, $21l$, and $31l$ festoons for lattice A on the first layer Weissenberg film. This suggests a partial disorder in the stacking of layers parallel to (001). This effect is not noticeable in a corresponding film from a natural crystal. Both lattices must be used to fully index the powder pattern measured on films from natural material given in Table 2.

The x-ray powder data given by Harcourt (1942) for "cannizzarite (=galenobismutite) from fumeroles, Lipari Islands, Italy H-89262" agree very closely with the data given in Table 2 for our natural material. These data are distinctly different from those for galenobismutite (Berry, 1940). Thus Harcourt's powder data (1942) represent the material described here as cannizzarite while Wolfe's crystal data (1938) refer to galenobismutite from the same locality.

The stellate trillings of artificial cannizzarite are due to the familiar twin law found in pseudo-hexagonal, monoclinic platy crystals. In such crystals when $b:a$ approaches $1:\sqrt{3}$ the angle $(100) \wedge (110)$ approaches 30° and twinning takes place on (110) as the twin axis with composition plane (001). In lattice B of these crystals, $b:a = \tan 30^\circ 07'$, twinning on (110) is therefore to be expected. Lattice A is evidently not responsible for the twinning.

TABLE 2. CANNIZZARITE—Pb, Bi, S—X-RAY POWDER DATA
 Monoclinic—A: C_{2h}^1-P2/m ; $a=4.09$, $b=4.06$, $c=15.39$, $\beta=99^\circ00'$
 B: C_{2h}^3-C2/m ; $a=7.00$, $b=4.06$, $c=15.39$, $\beta=99^\circ00'$

<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas)	<i>hkl</i>	<i>d</i> (calc)	<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas)	<i>hkl</i>	<i>d</i> (calc)
1	6.0°	7.38A	002	7.60	6	16.7°	2.68A	114B	2.68A
2	8.65	5.13	003	5.07					203B
10	11.65	3.82	102A	3.82	2	17.65	2.54	006	2.53
			004	3.80	$\frac{1}{2}$	18.8	2.39	115B	2.39
			101A	3.76	5	20.35	2.22	115B	2.21
110B	3.50	115A	2.21						
3	12.75	3.49	201B	3.49	5	22.35	2.03	201A	2.04
			102A	3.36				202A	2.03
3	13.2	3.38	111B	3.35	5	22.35	2.03	200A	2.02
			202B	3.35				312B	2.01
1	13.55	3.29	112B	3.28	4	23.8	1.910	311B	2.00
			201B	3.26				008	1.900
6	14.85	3.01	104A	3.01	3	25.5	1.791	312B	1.876
			113B	2.99				122A	1.793
5	15.6	2.87	202B	2.98	1	26.4	1.734	121A	1.787
			111A	2.87				313B	1.783
2	16.2	2.76	110A	2.86	2	27.25	1.684	122A	1.737
			112A	2.78				222B	1.736
			111A	2.76				025	1.688

<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas)	<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas)	<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas)	<i>I</i>	$\theta(\text{Cu})$	<i>d</i> (meas)
$\frac{1}{2}$	28.45	1.618	1	31.2	1.488	1	35.55	1.326	1	38.75	1.232
1	29.35	1.573	$\frac{1}{2}$	32.35	1.441	1	36.55	1.295	$\frac{1}{2}$	39.95	1.201
$\frac{1}{2}$	30.35	1.526	1	33.85	1.384	$\frac{1}{2}$	37.25	1.274	2	41.15	1.172

The thin leafy character of cannizzarite and the constant association with bismuthinite and galenobismutite make the preparation of a suitable sample for quantitative analysis very difficult, and this has still to be done. The existing analyses were certainly made on mixed material and are therefore not representative of cannizzarite.

PHASE 3

This crystalline phase, designated here as phase 3 in the Pb-Bi-S system, possesses a powder pattern which found no exact counterpart in the patterns available from mineral specimens suspected of containing lead-bismuth sulphides. One powder pattern closely resembles that of phase 3; it represents a component of webullite from Falun, Sweden, reproduced in Berry (1941). However the cell dimensions¹ given for this

¹ Quoted in another paper appearing in this number, page 526.

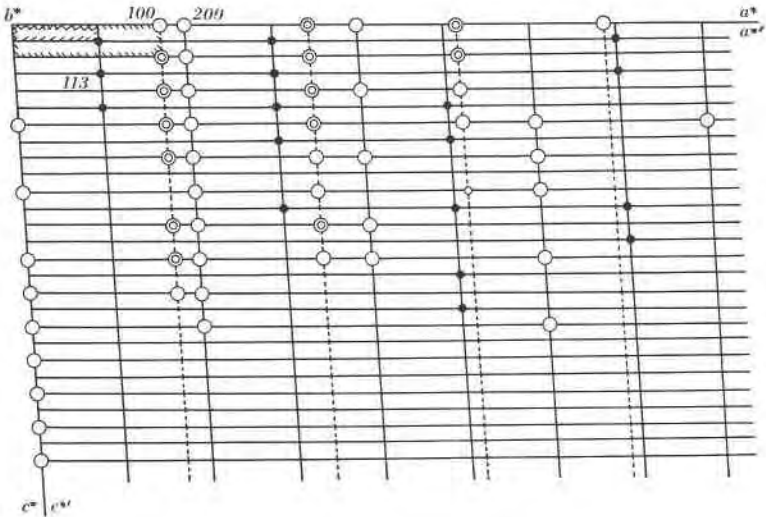


FIG. 2. Diagram of zero and first layers of the reciprocal lattice of phase 3 Pb-Bi-S system, plotted from Weissenberg photographs about the b axis. Large open circles are zero layer diffractions; small filled circles are first layer diffractions (of lattice B); small open circles represent maxima of smeared first layer diffractions (of Lattice A).

fibrous component of weibullite (Peacock & Berry, 1940, p. 68)—show very little similarity with those of phase 3 presented here.

Phase 3 resembles phase 2 (=cannizzarite) in habit; it occurs in typically thin, leafy crystals which bend easily and are so fragile that a touch causes fraying of the edges and splitting of the blades parallel to the lengthwise striations. As this habit is possible in bismuthinite, galenobismutite and cosalite, as well as in phase 2, only powder photographs can differentiate among the products of the experiments. The crystals reach about $1\frac{1}{2}$ mm. in maximum length, and a breadth of about $\frac{1}{4}$ mm.; they are extremely thin. No stellate trillings of phase 3 were observed although in individual habit and colour phase 2 and phase 3 are indistinguishable by inspection.

The crystals of phase 3 were sparser than phase 2, and insufficient could be obtained for tests requiring more than a few blades. Micro-chemical tests on clean blades were positive for lead, bismuth and sulphur, while no other elements were detected. The quantity of material was insufficient for specific gravity tests.

A single crystal was oriented to rotate about the elongation on the optical goniometer. Rotation and Weissenberg films about this axis show interpenetrating monoclinic lattices somewhat analogous to those of phase 2, with the following characteristics.

Lattice A: $P2/m$ $a=4.11$, $b=4.08$, $c=18.58A$; $\beta=93^\circ35'$
 Lattice B: $F2/m$ $a=7.03$, $b=4.08$, $c=37.16A$; $\beta=93^\circ35'$

Like phase 2, phase 3 has the three axial directions in common, with equal periods for the rotation axis b , and the peculiar ratio of 7:12 for the lengths of the a -axis. Phase 3 differs from phase 2 in β -angle, in the F -centering of lattice B, and in the length of the c axes. The relationship of the A and B lattices of phase 3 is shown in Figure 2, a reciprocal lattice projection of the zero and first layer Weissenberg films. Smears on the first layer Weissenberg photograph show a condition of partial disorder in the stacking of the basal layers in lattice A. The disorder is more marked than in phase 2.

The observed intensities and spacings of the powder pattern lines are given in Table 3.

TABLE 3. PHASE 3—Pb-Bi-S—X-RAY POWDER DATA

Monoclinic, A: $P2/m$; $a=4.11$, $b=4.08$, $c=18.58A$, $\beta=93^\circ35'$

B: $F2/m$; $a=7.03$, $b=4.08$, $c=37.16A$, $\beta=93^\circ35'$

I	$\theta(\text{Cu})$	$d(\text{meas})$	hkl	$d(\text{calc})$	I	$\theta(\text{Cu})$	$d(\text{meas})$	hkl	$d(\text{calc})$
1	7.05°	6.32A	003A	6.18A	3	20.5°	2.20	1.1.13B	2.18
			006B	6.18				020A	2.04
			012A	3.74	8	22.15	2.04	020B	2.04
10	11.85	3.75	014B	3.74				202A	2.03
			005A	3.71				201A	2.02
			0.0.10B	3.71				024A	1.867
$\frac{1}{2}$	12.55	3.55	103A	3.52				028B	1.867
			200B	3.52	1	24.3	1.873	317B	1.862
3	13.2	3.38	113B	3.37				319B	1.862
			204B	3.36				0.0.10A	1.855
$\frac{1}{2}$	13.95	3.20	204B	3.22				0.0.20B	1.855
			104A	3.17				025A	1.787
7	14.9	3.00	117B	2.98	1	25.45	1.794	0.2.10B	1.787
			206B	2.97				213A	1.782
			208B	2.92				3.1.11B	1.780
1	15.45	2.89	111A	2.89	$\frac{1}{2}$	26.15	1.749		
2	16.35	2.74	015A	2.74	$\frac{1}{2}$	27.05	1.698		
$\frac{1}{2}$	17.95	2.50	1.1.11B	2.51	$\frac{1}{2}$	32.45	1.437		
			2.0.10B	2.47	$\frac{1}{2}$	33.95	1.380		
			008A	2.32	$\frac{1}{2}$	35.55	1.326		
$\frac{1}{2}$	19.35	2.33	0.0.16B	2.32	$\frac{1}{2}$	36.35	1.301		
			107A	2.29					

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