CANNIZZARITE AND BISMUTHINITE FROM VULCANO

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Cannizzarite was described from the deeper parts of fumaroles on Vulcano, Lipari Islands, by Zambonini, De Fiore, and Carobbi (1925), who pointed out the similarity between their chemical formula for the new mineral ($Pb\ Bi_4\ S_7$) and that of livingstonite ($Hg\ Sb_4\ S_7$). A prominent prism at about 45° to (010) suggested a similarity between cannizzarite and stibnite, which is pseudo-tetragonal and very like bismuthinite in form. Since livingstonite was early described as resembling stibnite in form, a relation between cannizzarite, livingstonite, stibnite, and bismuthinite seemed to be established. Recently, however, Richmond (1936) has shown that livingstonite is monoclinic and quite unrelated to stibnite. Furthermore, the pseudo-tetragonal prism noted on cannizzarite appears actually to have been measured on bismuthinite. Consequently, the suggested relations of cannizzarite are without foundation.

In his study of the structure of bismuthinite, Hofmann (1933) used crystals from Vulcano supplied by Professor F. Bernauer, who had found cannizzarite to be a mixture of bismuthinite and a platy, metallic mineral, which he did not investigate further. Hintze (1936, p. 105), therefore, doubts the validity of the species.

CANNIZZARITE

Material. The specimens described as cannizzarite in the Harvard Mineralogical Museum were supplied by R. Palumbo of Naples. They are of two types, both from Vulcano. One sample consists of a bottle of loose, acicular crystals, 1 cm. or more in length, deeply striated and, in a few cases, well terminated. These prove to be bismuthinite, which will be described later. The other specimen consists of minute, prismatic crystals attached to a mass of dense, gray, perlitic andesite. Many of the crystals show an iridescent tarnish; others have a splendent, metallic luster. Measurement of the terminal planes proved difficult because of the minute size of the faces and the resulting poor reflections; the results show, however, that cannizzarite, although orthorhombic, is not homeomorphous with the stibnite group.

Morphology. The crystals are minute, flattened, orthorhombic prisms, plates, or laths less than $1.0\times0.3\times0.1$ mm. in size. The axis of elongation is taken as $c[001]$; the plane on which all of the crystals are more or less flattened becomes $a(100)$. The main zone is rarely free from vertical striations which give trains of weak reflections, only a few of which were observed repeatedly on several crystals. Of the many forms noted on the twenty-four measured crystals only those observed repeatedly in good position are considered as certain; forms observed but once in good position are retained subject to confirmation; the remaining forms, mostly in the striated zone, are uncertain.

In the adopted notation, which gives geometrical elements corresponding to the structural cell, the certain forms, in order of decreasing importance, are:

a{100}, *m*{110}, *w*{011}, *Q*{210}, *y*{810}, *d*{201}, *p*{111}, *G*{211}, *h*{140}, *S*{410}, *x*{031}.

The forms requiring confirmation are:

c{001}, *b*{010}, *o*{190}, *i*{130}, *j*{120}, *k*{230}, *l*{560}, *O*{430}, *N*{750}, *P*{320}, *R*{310}, *T*{920}, *U*{510}, *V*{11.2.0}, *W*{610}, *Y*{15.2.0}, *Z*{16.1.0}, *e*{232}, *f*{121}, *g*{311}.

The uncertain forms, for which letters are unnecessary, are:

{1.12.0}, {1.10.0}, {2.13.0}, {160}, {150}, {250}, {670}, {760}, {650}, {540}, {530}, {740}, {021}, {052}, {403}, {133}, {182}, {263}, {544}, {361}.

The best mean measured angles: (100):(110) = 38°50′; (001):(011) = 15°47½′ give the geometrical elements: $a:b:c = 0.8050:1:0.2828$.

TABLE 1. CANNIZZARITE: MEASURED AND CALCULATED ANGLES

Form	No. xls.	No. times	Measured Range		Weighted Mean		Calculated	
			φ	ρ	φ	ρ	φ	ρ
100	24	48	90°00′–	90°00′–	90°00′	90°00′	90°00′	90°00′
140	5	5	15 58 –18°00′	90 00 –	17 06	90 00	17 15	90 00
110	15	22	47 40 –54 14	90 00 –	51 10	90 00	51 10	90 00
210	6	7	66 32 –70 00	90 00 –	68 15	90 00	68 04½	90 00
410	7	8	78 56 –77 37	90 00 –	78 23	90 00	78 37½	90 00
810	9	9	84 05 –84 55	90 00 –	84 14	90 00	84 15	90 00
011	10	17	0 00 –	15 16 –16°40′	0 00	15 47½	0 00	15 47½
031	4	5	0 00 –	39 30 –40 34	0 00	40 21	0 00	40 18½
201	5	7	90 00 –	33 19 –36 42	90 00	35 00	90 00	35 05½
111	4	7	48 56 –54 38	23 02 –25 42	51 05	24 13	51 10	24 16½
211	6	7	67 24 –72 36	35 38 –38 19	68 43	37 47	68 04½	37 08½

Due to the imperfection of the crystals the measured angles in Table 1 agree only moderately well with the calculated values.

Table 2 gives a formal angle table for the certain forms. Figure 1 represents a typical crystal flattened on *a*{100}.

X-ray measurements. The following *x*-ray photographs were taken of

TABLE 2. CANNIZZARITE: ANGLE TABLE

Cannizzarite—$Pb_3Bi_5S_{11}$
Orthorhombic; dipyramidal: $2/m\ 2/m\ 2/m$
$a:b:c=0.8050:1:0.2828;\ p_0:q_0:r_0=0.3513:0.2828:1$
$q_1:r_1:p_1=0.8050:2.8463:1;\ r_2:p_2:q_2=3.5359:1.2423:1$

Forms		ϕ	ρ	ϕ_1	ρ_1	ϕ_2	ρ_2
a	100	90°00′	90°00′	—	0°00′	0°00′	90°00′
h	140	17 15	90 00	90°00′	72 45	0 00	17 15
m	110	51 10	90 00	90 00	38 50	0 00	51 10
Q	210	68 04½	90 00	90 00	21 55½	0 00	68 04½
S	410	78 37½	90 00	90 00	11 22½	0 00	78 37½
y	810	84 15	90 00	90 00	5 45	0 00	84 15
w	011	0 00	15 47½	15 47½	90 00	90 00	74 12½
x	031	0 00	40 18½	40 18½	90 00	90 00	49 41½
d	201	90 00	35 05½	0 00	54 54½	54 54½	90 00
p	111	51 10	24 16½	15 47½	71 19½	70 38½	75 03½
G	211	68 04½	37 08½	15 47½	55 56½	54 54½	76 58½

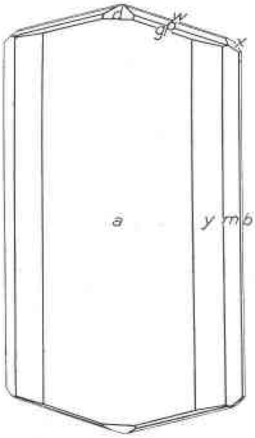

FIG. 1. Cannizzarite from Vulcano.

cannizzarite, using copper radiation: Laue, normal to (100); rotation about [001]; zero- and first-layer Weissenberg about [001]; and zero-layer Weissenberg about [010]. The photographs gave an orthorhombic lattice with the cell edges:

$$a_0 = 11.73\text{Å},\ b_0 = 14.47\text{Å},\ c_0 = 4.076\text{Å}$$
$$a_0 : b_0 : c_0 = 0.8106 : 1 : 0.2817$$

These results are in good agreement with the morphological ratio:

$$a : b : c = 0.8050 : 1 : 0.2828$$

Combining the cell volume with the measured specific gravity, 4.8, we obtain the molecular weight of the unit cell:

$$M_0 = 2012$$

The following reflections were present on the Weissenberg photographs:

(hkl)—all orders
$(hk0)$—all orders
$(0kl)$—$k+l$, even
$(h0l)$—h, even

Since the same forms were observed on both ends of doubly terminated crystals, the symmetry is holohedral. This, together with the above space group criteria, establishes the space group as D_{2h}^{16}–*Pnam*.

Morphological development is in agreement with the space group requirements, according to the Donnay rule (1937). According to these requirements, systematic omissions occur only in the $\{0kl\}$ and $\{h0l\}$ forms. {011}, {031}, and {201} are the only certain forms in these categories which are listed in the angle table, and the indices of these forms conform to the criteria for the space group.

Physical properties. Cannizzarite has a good cleavage parallel to {110}. The hardness is probably between 2 and 3. The luster is metallic on untarnished surfaces. The specific gravity, 4.8, was obtained with the micro-pyknometer; the value calculated from the cell volume and theoretical composition is 4.82. A sample of bismuthinite accompanying the cannizzarite gave the specific gravity 6.46. Zambonini gave the value 6.54 for cannizzarite which was evidently measured on material consisting largely of bismuthinite.

Composition. On a carefully separated sample of cannizzarite F. A. Gonyer obtained the values given in column 1 of Table 3.

The new analysis gives the cell formula $Pb_3Bi_5S_{11}$ and compares well with the percentage weights calculated for this composition. Carobbi's analysis differs widely from the newly found composition, due no doubt to admixture with bismuthinite.

TABLE 3. ANALYSES OF CANNIZZARITE AND BISMUTOPLAGIONITE

	1	2		3	4	5
Pb	31.33	3.05		15.79	33.02	30.79
Bi	51.25	4.90		66.00	46.83	51.75
			5.00			
Fe	0.27	0.10		0.51	...	...
Cu	0.00	—		trace	...	...
As	0.00	—		—	...	...
Sb	0.19	0.04		—	3.05	...
			10.79			
S	17.16	10.75		17.70	17.10	17.46
	100.20			100.00	100.00	100.00

1. Cannizzarite, Vulcano, Lipari Islands; analyst F. A. Gonyer.
2. Number of atoms in the unit cell ($M_0=2012$).
3. Cannizzarite, Vulcano, Lipari Islands; analyst Carobbi, in Zambonini, De Fiore and Carobbi (1925).
4. Bismutoplagionite, Montana; analyst Shannon (1920). Reduced to 100 per cent after deducting 18.8 per cent insoluble and 1.25 per cent FeS.
5. Theoretical values for formula $Pb_3Bi_5S_{11}$.

IDENTITY OF CANNIZZARITE AND BISMUTOPLAGIONITE

Shannon (1920) described a new mineral from Montana, having the composition $Pb_5Bi_8S_{17}$, for which he proposed the name bismutoplagionite, indicating a relation to plagionite with the composition $Pb_5Sb_8S_{17}$. Since the proportions as indicated in Shannon's formula $Pb_5Bi_8S_{17}$ are close to those found for cannizzarite $Pb_3Bi_5S_{11}$, as shown; also as the similarity between Shannon's analysis (column 4, Table 3) and the new analysis of cannizzarite is rather striking, further observations were made on the type bismutoplagionite.

The crystals are minute and very imperfect. Five very poor crystals were finally measured on the goniometer, and only one of these gave fair reflections from the terminal planes. The crystals proved to be orthorhombic, as suggested by Shannon, with approximate polar elements close to those of cannizzarite:

Bismutoplagionite: $p_0:q_0:r_0=0.342:0.267:1$
Cannizzarite: $p_0:q_0:r_0=0.351:0.282:1$

A rotation photograph about [001] gave a lattice period identical with the corresponding period in cannizzarite. A zero-layer Weissenberg photograph about [001] did not give closely comparable values for the reciprocal lattice periods.

Bismutoplagionite: $a^*=0.115$; $b^*=0.100$ (Cu)
Cannizzarite: $a^*=0.132$; $b^*=0.105$ (Cu)

The discrepancy in a^* may be due to the fact that the crystal used was, in reality, a sub-parallel aggregate.

The physical properties of bismutoplagionite, as given by Shannon, agree with those of cannizzarite, except for the specific gravity, for which Shannon obtained 5.35 as against 4.8 found for cannizzarite. A second test on Shannon's material is impossible with the limited material available.

Bismutoplagionite and cannizzarite, thus, have essentially identical properties. Although the name bismutoplagionite has priority, it seems unwise to retain it since the implied relation to plagionite is not well founded. It seems better to adopt the name cannizzarite for the species in spite of the fact that the original description was made on a mixture of two minerals.

BISMUTHINITE

Two samples from Vulcano were studied, both labeled cannizzarite. Both proved to be bismuthinite; and it is probable that all bottled samples of cannizzarite are, likewise, bismuthinite. The second lot of material, purchased for this study, consists of well terminated crystals, giving good measurements which permitted exact determination of the elements. Many of the crystals are hollow prisms on which almost every face consists of two parts giving coincident reflections. In some cases the termination is unbroken, and excellent reflections are obtained.

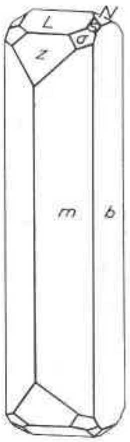

FIG. 2. Bismuthinite from Vulcano.

The proper setting of bismuthinite corresponds to the structural lattice determined by Hofmann (1933). This setting is related to the classical setting, used by Dana (1892), by the transformation:

Dana to Hofmann: 300/030/001

In the new setting, the propriety of which was recognized by Peacock (1933) and Ungemach (1934), the principal forms observed on the Vulcano bismuthinite are, in order of decreasing importance:

b{010}, *m*{110}, *z*{301}, *σ*{211}, *s*{111}, *L*{101}.

These determine the common habit illustrated in Fig. 2. The following known forms were, also noted:

t{150}, *q*{130}, *x*{250}, *o*{120}, *d*{230}, *g*{450},
n{210}, *h*{310}, *f*{410}, *N*{021}, *u*{221}, λ{311}.

In addition to these, the following new forms were observed. All except *w*{121}, noted four times, require confirmation. The majority of the new forms are based on single reflections from the trains of signals given by the striated vertical zone.

{180}, {3.10.0}, {370}, {470}, {10.7.0}, {730}, {20.7.0}, {610},
{10.1.0}, {12.1.0}, {023}, {504}, {904}, {502}, {601}, {377},
w{121}, {955}, {16.3.6}, {12.1.2}, {631}.

TABLE 4. BISMUTHINITE: MEASURED AND CALCULATED ANGLES

Form	No. xls.	No. times	Measured Range		Weighted Mean		Calculated	
			φ	ρ	φ	ρ	φ	ρ
121	4	4	27°08′–27°17′	38°02′–39°05′	27°10′	38°20′	26°53′	38°06½′

In Table 4 the measured angles are compared with those calculated from Peacock's elements on bismuthinite from Tasna, Bolivia, transformed to the new setting by dividing the *c*-axis by three:

$$a:b:c = 0.9862:1:0.3498$$

A determination of elements for the Vulcano bismuthinite, in the old setting, gave values closely similar to those recently obtained by Bianci

(1924), Peacock (1933), and Carpanese (1936). The variations are probably due to slight variations in composition.

TABLE 5. BISMUTHINITE: COMPARISON OF ELEMENTS

	$a:b:c$	(010):(110)	(001):(101)	
Crodo	0.9844:1:1.0447	45°27′	46°42′	Bianci
Tasna	0.9862:1:1.0493	45 24	46 46½	Peacock
Artificial	0.9879:1:1.0660	45 21	47 11	Carpanese
Vulcano	0.9820:1:1.0548	45 31½	47 03	Wolfe

A measurement of the specific gravity gave 6.46, which is normal for the species but lower than the value 6.81 calculated from structural data.

An analysis gave the composition listed below:

TABLE 6. BISMUTHINITE ANALYSIS

	1	2
Bi	80.29	81.3
Fe	0.38	...
Pb	0.00	...
Sb	0.00	...
As	0.00	...
S	19.48	18.7
	100.15	100.0

1. Bismuthinite, Vulcano, Lipari Islands; anal. F. A. Gonyer.
2. Theoretical values for Bi_2S_3.

The Vulcano bismuthinite is, therefore, an unusually pure occurrence; the slight deficiency in bismuth might account for the discrepancy in specific gravity.

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