

New data on sulphosalt assemblages at Vulcano (Italy)

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ABSTRACT. — Original samples of the «cannizzarite» collected in 1927 among the sublimation products from Vulcano's fumaroles were re-examined. Five minerals belonging to the Pb-Bi-S(Se) system were identified by microprobe and X-ray diffraction methods: Se-goongarrite (Se-heyrovskite), Se-lillianite, Se-galenobismutite, Se-cannizzarite and Se-bearing galena. The cannizzarite composition is rather variable, ranging from $Pb_4S_4(S,Se)_{11.5}$ with $PbS : Bi_2S_3 = 1.6$ to $Pb_4Bi_{14.5}(S,Se)_{10.75}$ with $PbS : Bi_2S_3 = 1.8$ and $Me : S = 0.79$. These ratios are closer to the structural formula $Pb_{10}Bi_{14}S_{127}$ ($PbS : Bi_2S_3 = 1.7$ and $Me : S = 0.787$) than to those corresponding to the cannizzarite formula $Pb_3Bi_5S_{11}$ ($PbS : Bi_2S_3 = 1.2$ and $Me : S = 0.73$) reported in handbooks. The cannizzarite from Vulcano may thus be described by the formula $Pb_4Bi_{14-x}(S,Se)_{11.5-1.5x}$, where x varies from 0 to 0.5.

Key words: Se-goongarrite, Se-heyrovskite, Se-lillianite, Se-galenobismutite, Se-cannizzarite, Se-galena, Vulcano, fumaroles.

RIASSUNTO. — Sono stati riesaminati campioni originali di «cannizzarite» raccolti nel 1927 fra i prodotti delle fumarole di Vulcano.

Per mezzo di indagini con la microsonda elettronica e diffrazione di raggi X sono stati identificati cinque minerali appartenenti al sistema Pb-Bi-S(Se): Se-goongarrite, (Se-heyrovskite), Se-lillianite, Se-galenobismutite, Se-cannizzarite e galena selenifera. La composizione della cannizzarite è piuttosto variabile, da $Pb_4S_4(S,Se)_{11.5}$ con $PbS : Bi_2S_3 = 1,6$ e $Me : S = 0,781$ a $Pb_4Bi_{14.5}(S,Se)_{10.75}$ con $PbS : Bi_2S_3 = 1,8$ e $Me : S = 0,79$. Questi rapporti sono più vicini alla formula strutturale $Pb_{10}Bi_{14}S_{127}$ ($PbS : Bi_2S_3 = 1,7$ e $Me : S = 0,787$) piuttosto che alla formula $Pb_3Bi_5S_{11}$ riportata nei testi.

La cannizzarite di Vulcano può essere rappresentata con la formula $Pb_4Bi_{14-x}(S,Se)_{11.5-1.5x}$, con x variabile da 0 a 0,5.

Parole chiave: Se-goongarrite, Se-heyrovskite, Se-lillianite, Se-galenobismutite, Se-cannizzarite, Se-galena, Vulcano, fumarole.

Introduction

Vulcano (Lipari Islands, Italy) is known as the first occurrence of cannizzarite $Pb_3Bi_5S_{11}$, discovered by ZAMBONINI, DE FIORE and CAROBBI (1925).

The mineral was found irregularly distributed as a product of a group of fumaroles aligned along a N-S fissure cutting the north rim of the 1890 crater and along a nearby fissure directed E-W on the inner north slope of the crater. ZAMBONINI et al. believe that the formation of the cannizzarite started from 1921 but only in september and october 1924 field studies and samples collection took place.

Cannizzarite occurs in the deepest part of the fumaroles, in which temperatures of 550°C to 615°C were measured. In the outer parts in contact with the atmospheric gases, alteration products were observed, followed by salammuniac, realgar and sulphur. It is worth noting that in the same fumaroles as early as in 1916 some crusts

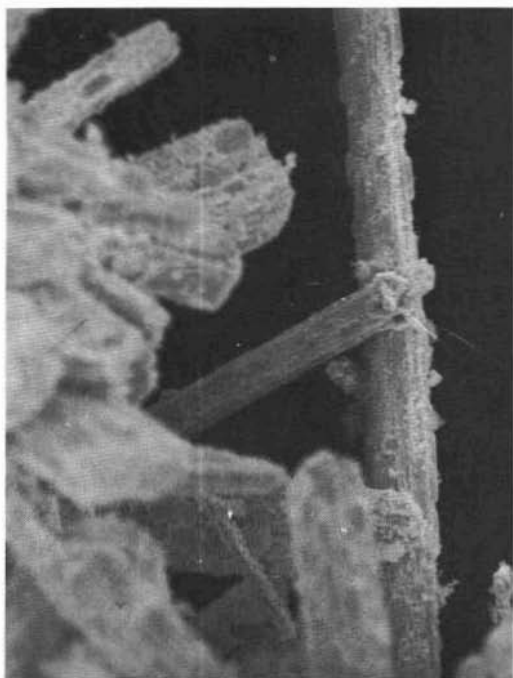


Fig. 1-2. — General view of the Se-bearing Pb-Bi sulphosalt druse from Vulcano, 150 x. Scanning microscope J.S.M. - T - 20.

made up of black sulphur containing tellurium and selenium were collected and analyzed. ZAMBONINI et al. (1925) conclude that cannizzarite forms in CO_2 and SO_2 fumaroles, in absence of air and in a temperature range between 550° and 615°C , in presence of salamoniac, realgar and sulphur, probably containing selenium, tellurium and arsenic.

No other sulphosalts were described in this deposit by these authors. C. WOLFE (1938) re-examined two specimens of cannizzarite from Vulcano. One (loose acicular crystals) proved to be bismuthinite. The data obtained for minute, flattened crystals from the second specimen (crystal measurements, cell dimensions, new chemical analysis and specific gravity) were ascribed by WOLFE to cannizzarite for which the formula $\text{Pb}_3\text{Bi}_5\text{S}_{11}$ was proposed. Later on M.A. PEACOCK pointed out (DANA, 1946) that all these cell dimensions and physical properties were identical to those reported for galenobismutite by BERRY (1940). Thus in DANA (1946) cannizzarite was considered to be identical with galenobismutite and hence discredited.

GRAHAM et al. (1953), operating under hydrothermal conditions in the system Pb-Bi-S, synthesized different crystalline phases, one of them, named phase 2, consisting in bundles of leafy blades, gave an X-ray pattern identical with that given by the thin flattened plates from the WOLFE's specimen of cannizzarite. A single leafy crystal from another type specimen of cannizzarite from Vulcano yielded rotation and Weissenberg X-ray data nearly identical to those shown by the mentioned phase 2. GRAHAM et al. (1953) concluded that the leafy mineral was apparently a component, along with galenobismutite and bismuthinite of the mineral originally described as « cannizzarite ». Therefore they proposed to retain the old name « cannizzarite » for this mineral even if they were not able to obtain a pure sample for chemical analysis.

It is worth noting that as early as 1933 F. BERNAUER (in HERRMANN, 1933) stated that « cannizzarite » was a mixture of bismuthinite and a platy, metallic mineral not further investigated.



Fig. 3. — Shape of the cannizzarite crystals. 750 x. Scanning microscope J.S.M. - T - 20.

After the paper of GRAHAM et al. (1933) cannizzarite was listed again in handbooks as a valid mineral species (STRUNZ, 1978) but its formula was considered as doubtful, and only galenobismutite and bismuthinite were reported in its association (VV.AA., 1960). As we know, no new analysis of type cannizzarite are available.

In the course of a study on the type specimen of cannizzarite collected by O. DE FIORE in 1927 (as in the original label) and provided by the Institute of Geochemistry of the Rome University, we could characterize the composition of the original cannizzarite from Vulcano and obtain new data on its assemblage.

General description

Two samples of cannizzarite were studied, one of which was a choice of loose tiny acicular, thin tabular and leafy crystals; the other was an aggregate of such crystals growing in a small wug of andesite rock having about 1 cm in diameter. The individual crystal size is 0.07-0.5 mm in length

and 0.01-0.07 mm in width; they are extremely thin and fragile. The different crystal habitus is well observed under the scanning microscope (J.S.M.-T-20, « Joel ») (fig. 1-2).

The method of investigation was the following. First of all each crystal was studied with a GANDOLFI camera. Then, the crystal prepared as a polished section and studied by microprobe. At least, a small quantity of material was extracted from the crystal and analysed for X-ray powder data and electron micro-diffraction.

Five opaque minerals: Se-göongarrite (Se-heyrovskyite), Se-lillianite, Se-galenobismutite, Se-cannizzarite and Si-Se-bearing galena were identified in these specimens by microprobe and X-ray diffraction methods.

All minerals are silvery gray with metallic luster. Some of them are covered by a small crust of white tiny crystals.

Cannizzarite crystals are thin platy and leafy, usually strongly striated parallel to their elongation (fig. 3). They are easily twisted, bent and split up in small thin bright plates, which fray out at their ends. Three other sulphosalts show a long thin prismatic and acicular habitus. Bi-Se bearing galena was observed only in polished sections. Its grains are of irregular form and very small (about 10 μ in diameter).

In reflected light, the color of all minerals is white; sulphosalts acquire a slightly gray-greenish tint when in contact with galena

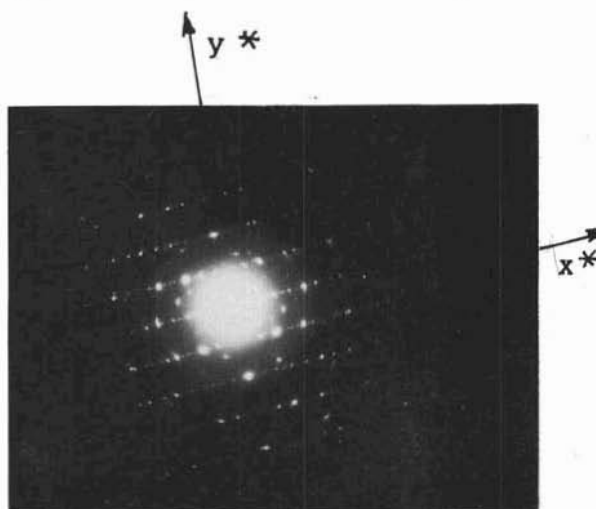


Fig. 4. — Electron microdiffraction pattern of cannizzarite.

TABLE 1
Composition of Pb-Bi-sulphosalts from Vulcano (microprobe data)

N of grain	Mineral	Wt%						Atomic ratios					Me:S	PbS (Bi,Sb) ₂ S ₃
		Pb	Bi	Sb	S	Se	Total	Pb	Bi	Sb	S	Se		
1	Se-galenobismutite	26.29	53.43	-	16.16	3.31	99.19	0.96	1.93	-	3.78	0.32	0.72	1.48
2	Se-cannizzarite	34.5	45.61	0.08	14.3	3.88	98.5	4	5.33	0.02	10.81	1.19	0.78	1.50
3	" "	35.0	45.26	0.07	13.8	5.25	99.47	4	5.13	0.02	10.19	1.57	0.78	1.55
4	" "	34.69	44.81	-	13.66	5.20	98.52	4	5.12	-	10.18	1.57	0.78	1.56
5	" "	36.10	46.20	-	14.1	3.6	100.00	3.97	5.03	-	9.91	1.03	0.82	1.58
6	" "	36.2	45.0	-	14.1	4.98	100.35	4	5.04	-	10.07	1.44	0.79	1.59
7	" "	37.6	43.3	-	14.4	4.1	99.4	4	4.57	-	9.90	1.14	0.78	1.75
8	" "	37.84	43.22	-	14.2	4.49	99.75	4	4.53	-	9.70	1.25	0.79	1.77
9	" "	37.77	43.13	-	14.0	4.98	99.87	4	4.53	-	9.58	1.38	0.78	1.77
10	Se-lillianite	47.1	35.6	-	13.5	3.1	99.3	2.92	2.18	-	5.40	0.50	0.86	2.68
11	" "	49.0	36.2	-	13.8	2.8	101.8	2.98	2.18	-	5.40	0.44	0.85	2.73
12	Se-goongarrite	59.8	24.0	-	13.3	3.0	100.1	5.73	2.28	-	8.23	0.75	0.90	5.03
13	" "	62.1	21.2	-	13.2	2.5	99.0	6.02	2.04	-	8.30	0.64	0.93	5.90
14	" "	63.6	21.1	-	12.9	2.8	100.4	6.16	2.02	-	8.09	0.72	0.93	6.10
15	Bi-Se-galena	80.3	4.4	-	12.2	2.5	99.4	0.94	0.05	-	0.93	0.08	0.98	37.6
16	" "	79.7	4.4	-	12.4	1.8	98.3	0.94	0.05	-	0.95	0.05	0.99	37.6
17	" "	80.0	6.1	-	12.5	2.0	100.6	0.93	0.07	-	0.94	0.06	1	26.57
18	" "	80.54	4.04	-	13.06	2.16	99.8	0.92	0.05	-	0.97	0.06	0.94	38.80

N.os 1-4, 6-9, 18 = analyst I.P. LAPUTINA; 5, 10-17 = analyst YU.S. BORODAEV.

and show a noticeable anisotropy in air. Unfortunately the extremely small size of the crystals did not allow to investigate the optical properties of these sulphosalts in more detail.

Chemical composition

The minerals were analysed on a «Cameca» MS-46 electronprobe microanalyser (analyst I.P. LAPUTINA) and on a «Jeol» JXA-5 (analyst YU. S. BORODAEV). Analytical conditions were as follows: accelerating voltage 20 KV, spectral lines (standards) PbL_α and SK_α (PbS), BiL_α (Bi₂S₃), SeK_α (PbSe), SbL_α (pure metal) on a «Cameca»; accelerating voltage 25 KV, spectral lines (standards) PbM_α and SK_α (PbS), BiM_α, SbL_α (pure metals) on a JXA-5; probe diameter ≈ 1 μ in both cases.

ZAF - correction was used. The X-ray intensity data were processed using a PUMA computer programme (BORONIKHIN, TSEPIN, 1980).

Ag was not detected. The results are listed in table 1. It is of interest to note that all the minerals studied have a rather high Se content (2-5 wt%), although Se was never so far detected in Vulcano sulphosalts. Ga-

lena is characterized by a high Bi-content (4-6 wt%) which is unusual in natural samples. The analytical values of Se-galenobismutite and Se-lillianite closely correspond to the stoichiometric formulas PbBi(S,Se)₄ and Pb₃Bi₂(S,Se)₆, respectively. The composition of Se-cannizzarite and Se-goongarrite, as table 1 shows, varies noticeably. Se-goongarrite is characterized by an interval of the ratio PbS: (Bi,Sb)₂S₃ from 5 to 6; Se-cannizzarite 1.5-1.8. It evidently indicates the non-stoichiometry of the sulphosalts (MOZGOVA, 1979). For goongarrite, this conclusion corresponds to the existence of solid solutions fields, which was established in the system PbS-Bi₂S₃ at high temperature by B. SALANCI and H. MOH (1969) (phase II according to these authors).

The analytical values of Se-cannizzarite are subdivided into two groups: the first (N 2-5) corresponds to the ideal formula Pb₄Bi₅(S,Se)_{11.5} with PbS: Bi₂S₃ = 1.6 and Me: S = 0.78 and the second (N 7-9) to PbBi_{4.5}(S,Se)_{10.75} with PbS: Bi₂S₃ = 1.8 and Me: S = 0.79. These ratios are closer to those of the structural formulas Pb₄₆Bi₅₄S₁₇₂ (PbS: Bi₂S₃ = 1.7 and Me: S = 0.787) calculated by E. MATZAT in his analysis of cannizzarite structure (MATZAT, 1972, 1979) than to those obtained from the cannizzarite

TABLE 2

X-ray powder diffraction data of Se-galenobismutite and Se-cannizzarite from Vulcano

Galenobismutite				Cannizzarite							
1a		2		1a		1b		2			
l	d	l	d	l	d	l	d	l	d	l	d
				3spl	7.74			1	7.38		
				3spl	5.12	1	5.12	2	5.13		
0.5	4.58	1	4.55	6spl	4.17	1	4.21				
1	4.01	0.5	3.93	10	3.88	6	3.84	10	3.82		
1	3.84										
2	3.65	3	3.65	1	3.62	2	3.64				
				2	3.53	2	3.53	2	3.43		
10	3.49	10	3.45	2	3.42	5	3.40	3	3.38		
4	3.37	0.5	3.36	1	3.37	2	3.32	1	3.29		
2	3.27	0.5	3.27	1	3.23						
				2	3.20	2	3.195				
8	3.05	4	3.03	9	3.04	0.5	3.14	6	3.01		
1w	2.90			6spl	2.95	10	3.02				
3	2.78	3	2.76	3	2.89	10	2.90	5	2.87		
				2	2.81	2	2.79	2	2.76		
0.5	2.74			5	2.72	5	2.70	6	2.68		
1	2.66	2	2.65	2	2.59	1	2.60				
5	2.494	4	2.46	1	2.50	1	2.48	2	2.54		
2	2.448										
4	2.409	2	2.39	1	2.42	2	2.41	0.5	2.39		
0.5	2.340										
0.5	2.296										
6	2.262	1	2.24	7	2.25	5	2.25	5	2.22		
2	2.217	1	2.20								
1	2.178										
3	2.083	4	2.05	0.5	2.13	1	2.20				
3	2.033	0.5	2.01	8	2.05	9	2.05	5	2.03		
9	1.976	5	1.961	5	1.937	1	1.914	4	1.91		
4	1.897	2	1.881								
5	1.817	0.5	1.848								
1	1.792	0.5	1.794	4	1.807	5	1.807	3	1.791		
4	1.769	3	1.762			1	1.774				
3	1.741	1	1.734	4w	1.759	1	1.715	1	1.734		
2	1.723	0.5	1.704	2	1.707	1	1.689	2	1.684		
1w	1.670	0.5	1.642			1	1.638	0.5	1.618		
1	1.620										
2	1.575	0.5	1.566			1	1.580	1	1.573		
1spl	1.532							0.5	1.526		
2	1.470	1	1.514			1	1.499	1	1.488		
4	1.428	2	1.455			1	1.439	0.5	1.441		
3	1.391	1	1.415								
1	1.383	1	1.382			1	1.381	1	1.384		
2	1.368	1	1.357								
2	1.342	0.5	1.334								
3	1.325	0.5	1.321			2	1.333	1	1.326		
1	1.299	0.5	1.305			2	1.298	1	1.295		
						2	1.266	1	1.274		
								0.5	1.232		
								1	1.201		
						1	1.90	2	1.172		
						1	1.160				

1 = this study: 1a GANDOLFI camera; 1b DEBYE camera; 2 = after BERRY and THOMPSON, 1962.

formula $Pb_3Bi_5S_{11}$ ($PbS : Bi_2S_3 = 1.2$ and $Me : S = 0.73$) reported in handbooks as doubtful (STRUNZ, 1978; VV.AA., 1960).

It should be also pointed out that the cannizzarite composition range according to our analyses, is more larger than that suggested by E. MAKOVICKY (1981) from MATZAT's structural data $Pb_{12}Bi_{14}S_{33} - Pb_{17}Bi_{20}S_{47}$. The ratios $PbS : Bi_2S_3$ and $Me : S$ for the first formula are 1.70 and 0.788 respectively; for the second one they

are 1.714 and 0.787. Thus, the composition range of the cannizzarite from Vulcano which we studied is described by the formula $Pb_4Bi_{5-x}(S,Se)_{11.5-1.5x}$, where x varies from 0 to 0.5.

Diffraction data

The X-ray diffraction data obtained by using GANDOLFI's camera and a 57.3 mm dia. camera (DEBYE-SCHERRER method, unfiltered Fe-radiation) are displayed in tables 2 and 3. The data for Se-cannizzarite and Se-galenobismutite (table 2) are practically identical to those for cannizzarite and galenobismutite reported by BERRY and THOMPSON (1962). The data for Se-lillianite and Se-goongarrite are similar to those published for these pure minerals and synthetic compounds (without Se) (table 3).

The small observed differences can be interpreted as due to non stoichiometric nature of these minerals and to their rather large compositional range.

The diffraction data for the minerals studied were also obtained by using electron microdiffraction (microscope JEM-100C with X-ray spectrometer Kevex 5100). The electron diffraction images for cannizzarite revealed two sublattices (fig. 4). One of them is a pseudotetragonal subcell with $a = 4.12$ and $b = 4.1 \text{ \AA}$; the other one (more intense) is pseudohexagonal with $a = 7.03$ and $b = 4.1 \text{ \AA}$. The subcells have a common parameter b . This cannizzarite is one of the representatives of the very interesting family of minerals with incommensurate structures (MAKOVICKY, 1981; ORGANOVA, 1984; MOZGOVA et al., 1984). The incommensuration is evident along axis X (fig. 4), where reflections appear to be irregular. The data obtained agree with those published for cannizzarite by GRAHAM et al. (1953) and by MATZAT (1979), and for wittite (cannizzarite with high selenium content, about 8 wt%) by MUMME (1980) (table 4).

This allows us to conclude that the crystals of Se-cannizzarite studied represent intermediate members of the cannizzarite-wittite series.

The electron diffraction data derived by us for the Se-galenobismutite and Se-lillianite are poorer. From them, we could determine

TABLE 3

X-ray diffraction data for Se-lillianite and Se-goongarrite from Vulcano in comparison with published data on lillianite and goongarrite

LILLIANITE										GOONGARRITE							
NATURAL				SYNTHETIC						NATURAL				SYNTHETIC, PHASE II			
This study An. No 11	Ontoev, 1959	Godovikov, 1972 Phase III		Sugaki et al. 1974 Pb _{2.92} Bi _{2.05} Se		Craig, 1967 Pb _{2.84} Bi _{1.20} Se				This study An. No 13	Mozgova et al. 1976			Godovikov, 1972	Otto and Strunz, (*) 1968		
1	d	1	d	1	d	1	d	1	d	1	d	1	d	1	d	1	d
4	9.69			3	10.3					7	5.03	1	4.48				
				2	5.16					7	4.05	2	3.98				
				13	4.10	2	4.10			7	3.74	2	3.91	5	3.71	10	3.93
8	3.68			27	3.68	0.5	3.92			2	3.67	4	3.74			20	3.75
10	3.41	4	3.50	100	3.52	10	3.52	4	3.56	3	3.71	3	3.71	4	3.51	30	3.54
		8	3.36	7	3.36	60	3.419	4	3.42	10	3.43	8	3.38	10	3.38	100	3.41
				30	3.387	3	3.39	3	3.39	4	3.34	2	3.33	5	3.33	30	3.35
9	3.09	5	2.97	3	3.08	2	3.06	5	3.12	4	3.08	3	3.08	3	3.08	15	3.11
				3	3.02	3	3.00	3	3.00	4	3.00	4	3.00	4	2.98	15	3.01
				5	2.97	3.5	2.91	8	2.95	6	2.94	9	2.93	9	2.93	30	2.94
8	2.78	10	2.89	8	2.88	1	2.85	6	2.86	5	2.85			9	2.84	30	2.85
		7	2.76	5	2.75	2	2.77	6	2.75								
6	2.68			3	2.67			6	2.67					6	2.61		
1	2.56																
2	2.39	2	2.35	4	2.33	15	2.359	1	2.36					1	2.40		
												2	2.30	2	2.31		
1	2.23	1	2.22									1	2.22	2	2.22		
6	2.15	9	2.13	9	2.13	45	2.156	3	2.15	2	2.15	5	2.17	7	2.17	20	2.18
						35	2.150			5	2.10	4	2.14	5	2.14	10	2.14
						40	2.070	3.5	2.06	5	2.07	7	2.09	5	2.09	40	2.09
						45	2.066										
10	2.07	10	2.03	10	2.04	50	2.060			3	2.05	3	2.07	7	2.06	20	2.07
						21	1.980	1	1.98	5	2.03	5	2.03	8	2.03	10	2.06
5	1.958	3	1.946	8	1.956	16	1.966	1	1.96	0.5W	1.961	2	1.942	4	1.95	10	1.961
												1	1.909	4	1.893	15	1.896
1	1.894			6	1.871			1	1.89			3	1.884				
												0.5	1.862	4	1.842	10	1.846
1	1.851							1	1.83			3	1.843				
				6	1.814							2W	1.801	5	1.827	25	1.810
3	1.781					35	1.777			0.5W	1.781			6	1.780	30	1.783
										5	1.767	10	1.768	9	1.762	40	1.767
		4	1.757	5	1.760	17	1.759									10	1.758
				5	1.742									3	1.740	10	1.743
2	1.743			1	1.707					4	1.717	2	1.716	4	1.717	10	1.720
														4	1.701		
				2	1.685					3	1.693	3	1.690	4	1.682		
										2	1.572	2	1.671	1	1.625		

(*) Reflections with $1 < 10$ were omitted.

TABLE 4

Published crystallochemical data for cannizzarite and wittite

Mineral Formula	Space Group	a, Å	b, Å	c, Å	β	References
Synth. Phase 2 (1) Pb ₃₈ Bi ₂₈ S ₈₀	T:P2/m H:C2/m	4.09 7.00	4.06 4.06	15.39 15.39	99°00 99°00	Graham et al., 1953
Cannizzarite (1) Pb ₄₆ Bi ₅₄ S ₁₂₁	P2 ₁ /m (*) T:P2 ₁ /m H:A2 ₁ /m	189.8 (*) 4.13 7.03	4.09 (*) 4.09 4.09	74.06 (*) 15.48 15.46	11.93 (*) 98.56 98.00	Matzat, 1979
Wittite Pb _{0.354} Bi _{0.347} Se _{0.203} S _{0.797} (2)	T:P2 /m H:C2 /m	4.19 7.21	4.08 4.08	15.56 15.56	101.4 98.8	Mumme, 1980

(1) The compositions are derived from the crystal structure. (2) Microprobe data. (*) For true cell.

$a \approx 11.3$, $b \approx 14$, $c \approx 4$ Å for Se-galenobismutite and $a \approx 13.6$, $b \approx 20.8$ and $c \approx 4$ Å for Se-lillianite. These data are rather consistent with those known for these minerals without Se-admixture. Small size of Bi-Se-bearing galena did not allow to obtain reliable diffraction values.

Conclusions

Among the sublimation products of the Vulcano's fumaroles (Italy) 5 minerals belonging to the Pb-Bi-S(Se) system were identified. These minerals grew together and formed very small microdruses. This evidence probably indicates the absence of equilibrium during the mineral formation process.

It should be stressed that the temperature measured on the fumaroles of 550-615° C (ZAMBONINI et al., 1925) corresponds to the temperature stability interval of the phases: 400-830° C - phase II, the synthetic analogue of goongarrite; 320-816° C - phase III, synthetic lillianite; 340-750° C - phase IV, synthetic galenobismuthite, established by experimental study of the system $\text{PbS-Bi}_2\text{S}_3$ (GODOVIKOV, 1972). The close temperature conditions of stability of these phases were also established by SALANCI and MOH (1969).

Acknowledgements. — The authors are indebted to Dr. A.I. GORSHKOV and A.V. SIVTsov (I.G.E.M. Moscow) for their assistance in electron microdiffraction investigation.

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