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RARE SULFOSALTS FROM VULCANO, AEOLIAN ISLANDS, ITALY. V. SELENIAN HEYROVSKÝITE

YURI S. BORODAEV

Department of Geology, Moscow State University, Moscow, 119992, Russia

ANNA GARAVELLI

Dipartimento Geomineralogico, University of Bari, Via E. Orabona 4, I-70125 Bari, Italy

CARLO GARBARINO AND SILVANA M. GRILLO

Dipartimento di Geoingegneria e Tecnologie Ambientali, University of Cagliari, Piazza d'Armi, I-09123 Cagliari, Italy

NADEZHDA N. MOZGOVA

IGEM RAS, Staromonetny 35, Moscow, 109017, Russia

WERNER H. PAAR AND DAN TOPA

Institute of Mineralogy, University of Salzburg, Hellbrunnerstr. 34, A-5020 Salzburg, Austria

FILIPPO VURRO[§]

Dipartimento Geomineralogico, University of Bari, Via E. Orabona 4, I-70125 Bari, Italy

ABSTRACT

Heyrovskýite, a rare Pb–Bi sulfosalt, was found around a fumarole of *ca.* 500°C at the La Fossa crater, Vulcano Island, Italy. The mineral occurs in the thin sulfosalt-rich crust covering the brecciated altered rocks of fumaroles, mainly admixed with selenian varieties of lillianite and cannizzarite, with subordinate galenobismutite and galena. Heyrovskýite occurs as thin needle-like crystals up to 300 μm in length and less than 1 μm in width. No traces of a breakdown texture have been noticed in any of the crystals studied. Electron-microprobe analyses show that the heyrovskýite from Vulcano has a composition close to the ideal Pb-rich composition of synthetic Phase II, $Pb_6Bi_2S_9$, obtained by Salanci & Moh in 1969. Particularly interesting is the absence of Ag and Cu, which makes the heyrovskýite from Vulcano unique, with respect to cations; only a minor amount of a Cd impurity is present. Like in other sulfosalts from Vulcano, significant Se concentrations are invariably present (0.9–2.5 wt.%). The compositional field of heyrovskýite from Vulcano, expressed in terms of the mol.% Bi_2S_3, ranges from ~14.23% (the most Pb-rich composition) up to 15.24% (the most Bi-rich), averaging 14.73 mol.%. This very narrow compositional spread (~1 mol.%) is in the range attributable to analytical error; the composition of heyrovskýite from Vulcano is thus quite constant in terms of Pb-for-Bi substitution. The calculated average composition corresponds to the empirical formula $(Pb_{5.95}Cd_{0.02})_{\Sigma 5.97}Bi_{2.06}(S_{8.53}Se_{0.44})_{\Sigma 8.97}$, which is close to the ideal end-member, $Pb_6Bi_2S_9$. The cell parameters, resulting from an X-ray powder-diffraction study, are: *a* 13.734(7), *b* 31.28(3), *c* 4.135(3) Å. The reflections having $h + l = 2n$ are indicative of space group *Bbmm*. The cell parameters of heyrovskýite from Vulcano have been compared with those in the literature for heyrovskýite from various deposits and with those of synthetic Phase II. There is no general agreement among the data reported by different authors. These data, together with the compositional differences, in terms of mol.% Bi_2S_3, among various natural and synthetic products, suggest that the range occupied by synthetic Phase II consists of many chemically and structurally very similar compounds. In particular, the Pb-rich part of the compositional field of the Phase II might be considered as the synthetic analogue of heyrovskýite from Vulcano.

Keywords: selenian heyrovskýite, Pb–Bi sulfosalts, fumarole, Vulcano Island, Italy.

[§] *E-mail address*: f.vurro@geomin.uniba.it

SOMMAIRE

Nous décrivons un exemple de heyrovskýite, sulfosel de Pb–Bi assez rare, comme produit de cristallisation autour d'une fumerolle à environ 500°C au cratère La Fossa, île de Vulcano, en Italie. Le minéral fait partie d'une mince croûte de sulfosels recouvrant les roches hôtes altérées le long des parois, en mélanges avec des variétés sélénifères de lillianite et de cannizzarite, avec galénobismutite et galène accessoires. La heyrovskýite se présente en cristaux aciculaires atteignant 300 μm, avec une largeur de moins de 1 μm. Aucune trace de déstabilisation n'est développée. Les analyses à la microsonde électronique montrent que la heyrovskýite de Vulcano a une composition proche de la composition idéale riche en Pb de la phase synthétique II, $Pb_6Bi_2S_9$, telle qu'obtenue par Salanci et Moh en 1969. Nous signalons l'absence ici de Ag et de Cu, ce qui en fait un exemple unique par rapport au contenu de cations; seul un peu de Cd est présent comme impureté. Comme dans les autres sulfosels à Vulcano, des teneurs importantes de Se sont présentes (0.9–2.5%, poids). Le champ de compositions de la heyrovskýite à Vulcano, exprimé en termes de la teneur en Bi_2S_3 (en pourcentage molaire), va d'environ 14.23% (la composition la plus riche en Pb) jusqu'à 15.24% (la plus riche en Bi), en moyenne 14.73%. Cet intervalle très étroit (~1%) est d'un ordre de grandeur attribuable aux erreurs analytiques; la composition de l'heyrovskýite de Vulcano est donc assez constante en termes du taux de substitution de Pb pour Bi. La composition moyenne calculée correspond à la formule empirique $(Pb_{5.95}Cd_{0.02})_{\Sigma 5.97}Bi_{2.06}(S_{8.53}Se_{0.44})_{\Sigma 8.97}$, qui se rapproche du pôle idéal, $Pb_6Bi_2S_9$. Les paramètres réticulaires, obtenus suite à une étude du spectre de diffraction X, méthode des poudres, sont: a 13.734(7), b 31.28(3), c 4.135(3) Å. Les réflexions de type $h + l = 2n$ sont indicatives du groupe spatial *Bbmm*. Les paramètres de la heyrovskýite de Vulcano sont comparés avec ceux pris de la littérature pour l'heyrovskýite provenant de divers gisements et avec ceux de la phase synthétique. Il n'existe aucun consensus parmi les données des différents auteurs. Ces données, de même que les différences en composition en termes de proportion de Bi_2S_3 parmi les divers produits naturels et synthétiques, font penser que l'intervalle de composition de la phase synthétique II est fait de plusieurs composés très semblables. En particulier, la partie riche en Pb de cet intervalle pourrait bien représenter l'analogue synthétique de la heyrovskýite de Vulcano.

(Traduit par la Rédaction)

Mots-clés: heyrovskýite sélénifère, sulfosels de Pb–Bi, fumerolle, île de Vulcano, Italie.

INTRODUCTION

Heyrovskýite, with a composition $6[Pb_{0.86}Bi_{0.08}(Ag,Cu)_{0.04}]S\bullet Bi_2S_3$, was first described by Klomínský *et al.* (1971) from Hůrky, in the Czech Republic, and considered by these authors as an Ag-bearing natural analogue of the synthetic Phase II in the system PbS–Bi_2S_3. Other occurrences of the mineral have been described, but there is as yet no general agreement on the chemical formula describing the observed compositions (Klomínský *et al.* 1971, Takéuchi & Takagi 1974, Large & Mumme 1975, Mozgova *et al.* 1976, Paar *et al.* 1980, Karup-Møller & Makovicky 1981, Getmanskaja *et al.* 1984, Moëlo *et al.* 1987, Vinogradova *et al.* 1992).

Natural heyrovskýite usually contains appreciable amounts of silver and additional metals, and the presence of these elements is considered to stabilize the structure, according to a coupled substitution Ag(Cu) + Bi = 2Pb (Makovicky & Karup-Møller 1977a). The structure of heyrovskýite (orthorhombic) was determined both on synthetic Ag-free crystals (Otto & Strunz 1968, Takéuchi & Takagi 1974) and natural Ag–Bi-bearing crystals (Makovicky *et al.* 1991). It consists of polysynthetically twinned slabs of galena occurring on the (311) plane. Taking into account the frequent occurrence of Ag in natural heyrovskýite, Makovicky & Karup-Møller (1977b) described the mineral as the seventh member of the lillianite homologous series (LHS), $Pb_{N-1-2x}Bi_{2+x}Ag_xS_{N+2}$, where N is the order of the homologue, and x is the coefficient of the Ag + Bi ⟶ 2Pb substitution. Taking into account the order of the homologue, the general structural formula describing heyrovskýite is $Pb_{6-2x}Bi_{2+x}Ag_xS_9$.

The N value may be calculated directly from the chemical data (N_{chem}) with the formula $N_{chem} = -1 + \{Bi_i + (Pb_i-1)/2\}^{-1}$, where $Bi_i + Pb_i = 1$ (Makovicky & Karup-Møller 1977a, Takéuchi 1997). Alternatively, N value may be determined crystallographically (N_{cryst}).

The synthetic analogue of heyrovskýite, Phase II of the system Pb–Bi–S (Van Hook 1960, Salanci 1965, Craig 1967, Otto & Strunz 1968, Godovikov 1972), has a compositional field ranging from 14.3 to 21.0 mol.% Bi_2S_3 (Salanci & Moh 1969), with the Bi content decreasing from 800 to 450°C. The variation of the composition of the Phase II is generally ascribed to the well-known substitution in sulfosalts $3Pb^{2+} \longrightarrow 2Bi^{3+} + \square$ ($\square$: vacancy), that is reflected by the general structural formula for Phase II: $6Pb_{1-x}Bi_{2x/3}S\bullet Bi_2S_3$ (Otto & Strunz 1968). According to Salanci & Moh (1969), values of the coefficient x range between 0 and 0.166. In addition, the reported compositional variation could also be attributed to the existence of disordered intergrowths of structural blocks of varying sizes, as documented by HRTEM studies on both synthetic material (Tilley & Wright 1982, Skowron & Tilley 1986) and natural species (Pring *et al.* 1999) belonging to the lillianite homologous series.

Heyrovskýite is chemically and structurally related to the Pb–Bi sulfosalt aschamalmite (Mumme *et al.* 1983), which differs from heyrovskýite by the absence of silver and other metals in the structure and a slight departure from orthorhombic symmetry (β = 91°).

Here, we describe Ag-free selenium-bearing heyrovskýite from high-temperature fumaroles located along the northern rim of the "La Fossa" crater at Vulcano Island, in the Aeolian Archipelago, Italy; there the mineral grew, was quenched, and thus remains homogeneous. Thirteen of the fourteen samples studied were collected in June 1994 from the deepest part of the fumarole FA (T = 510°C, direct measurement). In addition, one sample, previously described as "goongarrite" (Mozgova *et al.* 1985), has been re-examined. This latter sample was collected in 1927 along a N–S fissure cutting the north rim (T = 550°C). It is remarkable that fumarole FA is located on the same fracture where the 1927 samples were collected. The geological settings of the sampling area have been previously described (Borodaev *et al.* 1998, 2000, 2001, Vurro *et al.* 1999). Some natural samples of heyrovskýite from Moaralm and Sedl, Salzburg Province, Austria (Paar *et al.* 1980) have been re-examined for purposes of comparison.

Occurrence, Morphology and Paragenesis of Selenian Heyrovskýite

Selenian heyrovskýite from Vulcano was found in the thin sulfosalt-rich crust covering the rocks around the outlet of fumaroles, mainly admixed with selenian lillianite and cannizzarite, and subordinate galenobismutite and galena (Fig. 1a). All the sulfosalt minerals are silvery gray in color, with a metallic luster and, as noted in previous papers (Borodaev *et al.* 1998, 2000, 2001, Vurro *et al.* 1999), they cannot be macroscopically distinguished with certainty in hand specimens. In polished sections, selenian heyrovskýite occurs as long and thin needle-like crystals up to 300 μm in length and to 0.7 μm in width. The crystals differ distinctly from larger lath-like crystals of lillianite and fan-like grains of cannizzarite (Fig. 1b). In some cases, the shorter platy crystals of selenian heyrovskýite are split at one end (Fig. 1c), which is a rather typical feature for some sulfosalts from Vulcano. The crystals typically join each other at an angle of 90° or form more complex aggregates (Fig. 1d). The most intimate intergrowth is noted between selenian heyrovskýite and galena (Fig. 1e), which is more clearly evident under crossed polars (Fig. 1f). It should be stressed that there are no traces of a breakdown texture in any of the crystals studied.

Optical Properties

Under the ore microscope, the mineral has a creamy white reflection color without discernible pleochroism in air and in oil. Between crossed polars, the anisotropism is moderate, with colors changing from gray to red-brown.

Reflectances were measured in air using a Leitz MPV SP with Grid Monochromator. The field of measurement is approximately 5 × 5 μm. The data were processed using the program Spectra 2.11 (Leica Mikroskopie und Systeme GmbH, Wetzlar, Germany), with WTiC as the standard. The reflectances of heyrovskýite from Moaralm and of aschamalmite from Aschamalm (type specimen) were measured under the same conditions for comparison.

Since no properly oriented crystals were available, R_1 (~R_{max}) and R_2 (~R_{min}) were determined on fragments showing maximum anisotropism. The reflectance values (in air) are presented in Table 1.

Chemical Data

Fourteen electron-microprobe analyses of heyrovskýite from Vulcano fumaroles were made on polished sections in different laboratories. Eight analyses were obtained with a ARL–SEMQ–95 electron microprobe at the Centro Studi Geominerari e Mineralurgici, CNR, Cagliari. Operating conditions were as follows: voltage 20 kV, beam current 20 nA; standards (emission lines): PbS (Pb*M*α, S*K*α), CdS (Cd*L*α), Bi_2S_3 (Bi*M*α, S*K*α), metallic Ag (Ag*L*α), CuS (Cu*K*α); $FeAsS_2$ (As*L*α), metallic selenium (Se*L*α), KCl (Cl*K*α). Detection limits are: Pb 0.10, Cd 0.14, Bi 0.10, As 0.08, S 0.02, Se 0.04, Cl 0.03, Ag 0.05, Cu 0.04 wt.% at a confidence level of 99%. Analytical errors, at the same level of confidence, are as follows: Pb 0.85, Cd 0.18, Bi 0.67, S 0.23, Se 0.10. Four analyses were carried out at the Institute of Mineralogy, University of Salzburg, using a JEOL–8600 instrument equipped with Link EXL software, which includes on-line ZAF correction (20 kV, 30 nA, synthetic and natural standards). A re-examination of the 1927 material (Mozgova *et al.* 1985) was performed at the Moscow State University (one analysis) with a JEOL JXA–5 (25 kV, 30 nA, standards PbS

TABLE 1. REFLECTANCES OF SELENIAN HEYROVSKÝITE FROM VULCANO, HEYROVSKÝITE FROM MOARALM, AND ASCHAMALMITE FROM ASCHAMALM

λ, nm	Heyrovskýite Vulcano		Heyrovskýite Moaralm		Aschamalmite Aschamalm	
	R_1	R_2	R_1	R_2	R_1	R_2
400	49.6	40.7	50.6	46.3	48.8	44.1
420	48.6	40.0	49.9	45.6	48.2	43.5
440	47.9	39.5	49.7	44.9	47.5	43.0
460	47.0	39.0	49.4	44.4	46.7	42.5
470	46.5	38.6	49.2	43.9	46.4	42.1
480	46.0	38.4	48.9	43.6	45.8	41.7
500	45.4	37.7	48.3	42.9	44.8	41.1
520	44.5	37.0	47.6	42.3	44.3	40.5
540	44.2	36.4	46.9	41.4	44.0	40.1
546	44.1	36.3	46.6	41.3	43.9	40.0
560	43.8	36.0	46.4	40.9	43.8	39.7
580	43.7	35.5	46.2	40.6	43.5	39.4
589	43.6	35.4	46.0	40.7	43.5	39.4
600	43.6	35.2	45.9	40.5	43.5	39.3
620	43.4	35.1	45.7	40.2	43.3	39.0
640	43.4	35.0	45.6	39.9	43.2	38.8
650	43.3	34.8	45.6	39.9	43.1	38.7
660	43.2	34.7	45.5	39.9	43.0	38.7
680	42.9	34.6	45.3	39.7	42.9	38.5
700	42.6	34.5	45.2	39.6	42.9	38.4

Reflectances are expressed in %.

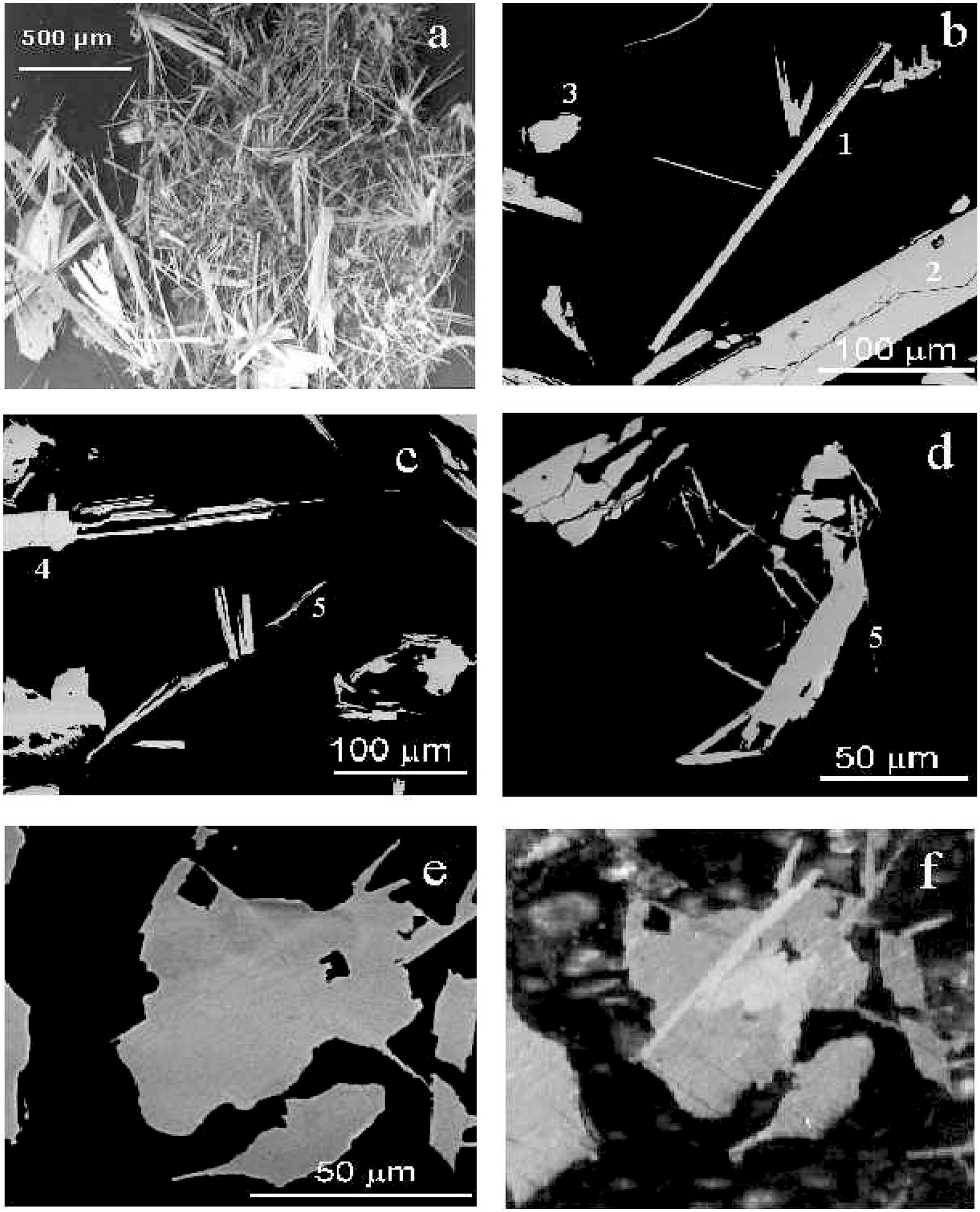

FIG. 1. Typical selenian heyrovskýite aggregates and assemblages. Back-scattered electron images (photos a–e) and photomicrograph under crossed polars (f). a. Typical assemblage containing selenian heyrovskýite. b. Long and thin needle-like crystals of selenian heyrovskýite (1), associated with larger lath-like crystals of lillianite (2) and fan-like grains of cannizzarite (3). c. Lath-like crystals of selenian heyrovskýite split from one end (4) surrounded by crystals and grains of lillianite. d. Complex aggregate of selenian heyrovskýite crystals (5) with irregular isometric galena grains. e. Intergrowth of selenian heyrovskýite with galena. f. Photomicrograph (crossed polars) of the same assemblage of selenian heyrovskýite with galena as represented in Figure 1e. The intergrowth is here more clearly visible.

and pure metals with the same lines as above). Twelve analyses were made on material from Salzburg Province, Austria (eight from Moaralm, and four from Sedl). These were conducted for comparison in the Salzburg laboratories under the same conditions as those described above.

Results of the analyses obtained on Vulcano heyrovskýite with the different instruments are quite comparable. Silver, which is a common constituent in heyrovskýite from other localities, was sought, but it invariably was below the detection limit (0.05 wt.%).

The electron-microprobe results obtained are summarized in Table 2, and compared with the theoretical composition $Pb_6Bi_2S_9$. All the individual crystals of heyrovskýite are chemically homogeneous, and the ranges of concentrations of the main components are as follows (in wt.%): Pb: 61.1–63.4 (average 62.2, $\sigma = 0.8$), Bi: 21.2–22.4 (average 21.7, $\sigma = 0.4$), S: 13.2–14.3 (average 13.8, $\sigma = 0.3$), Se: 0.9–2.5 (average 1.7, $\sigma = 0.5$). Cadmium is present in only six cases, and ranges between 0.1 and 0.4 wt.%.

The compositional field of heyrovskýite from Vulcano, expressed in terms of the mol.% Bi_2S_3, ranges from ~14.23 mol.% (the most Pb-rich composition) up to 15.24 mol.% (the most Bi-rich) averaging at 14.73 mol.%. The corresponding compositional spread (~1 mol.% Bi_2S_3) does not exceed the analytical error (~1.1 mol.% Bi_2S_3), confirming the quite constant composition of this mineral in terms of Pb-for-Bi substitution.

TABLE 2. SELENIAN HEYROVSKÝITE FROM VULCANO: CHEMICAL DATA, N_{chem} VALUES AND CHEMICAL FORMULAE

No.	Pb	Cd	Bi	S	Se	Total	N_{chem}	$\frac{Pb(+Cd)}{Bi}$	$\frac{cat.}{(S+Se)}$	Bal. val.	Bi_2S_3 mol.%
1	63.4	n.d.	21.5	13.5	2.2	100.6	6.9	2.97	0.91	2.5	14.39
2	63.2	n.d.	21.3	14.1	0.9	99.5	7.0	2.99	0.90	1.5	14.32
3	63.0	0.2	21.2	14.1	1.9	100.4	7.0	3.01	0.88	-1.3	14.23
4	62.6	n.d.	21.9	14.3	0.9	99.7	6.8	2.88	0.89	0.4	14.78
5	62.6	n.d.	21.3	13.9	1.0	98.8	6.9	2.96	0.91	2.0	14.43
6	62.5	n.d.	21.8	14.2	1.0	99.5	6.8	2.89	0.89	0.6	14.74
7	62.3	n.d.	21.8	13.6	2.1	99.8	6.8	2.88	0.90	1.4	14.78
8*	62.1	n.d.	21.2	13.2	2.5	99.0	6.9	2.95	0.90	1.9	14.47
9	62.0	0.3	22.0	13.7	1.7	99.7	6.7	2.87	0.91	2.4	14.85
10	61.7	0.1	21.6	13.6	1.9	98.9	6.8	2.89	0.90	1.2	14.75
11	61.3	n.d.	21.5	13.6	2.0	98.4	6.8	2.88	0.89	0.1	14.81
12	61.2	0.4	22.4	14.0	2.0	100.0	6.6	2.79	0.88	-0.5	15.20
13	61.2	0.3	22.4	13.6	2.1	99.6	6.6	2.78	0.90	1.8	15.24
14	61.1	0.2	22.3	13.8	2.1	99.5	6.6	2.78	0.88	-0.1	15.24
Av.	62.2	0.3	21.7	13.8	1.7	99.7	6.8	2.89	0.90	1.0**	14.73
Th.	63.76	-	21.44	14.80	-	100.0	7.0	3.00	0.89	0.0	14.29

n.d.: not detected. * 1927 sample. ** calculated from the average empirical formula. Balance of valences (Bal. val.) has been calculated from the empirical formulae.

	Empirical formulae based on 17 atoms	*Structural formulae based on S = 9*
1.	$Pb_{6.06}Bi_{2.04}(S_{8.35}Se_{0.55})_{\Sigma 8.90}$	$Pb_{6.13}Bi_{2.06}(S_{8.44}Se_{0.56})_{\Sigma 9.00}$
2.	$Pb_{6.04}Bi_{2.02}(S_{8.71}Se_{0.23})_{\Sigma 8.94}$	$Pb_{6.08}Bi_{2.03}(S_{8.77}Se_{0.23})_{\Sigma 9.00}$
3.	$(Pb_{5.93}Cd_{0.03})_{\Sigma 5.96}Bi_{1.98}(S_{8.58}Se_{0.47})_{\Sigma 9.05}$	$(Pb_{5.90}Cd_{0.03})_{\Sigma 5.93}Bi_{1.97}(S_{8.53}Se_{0.47})_{\Sigma 9.00}$
4.	$Pb_{5.94}Bi_{2.06}(S_{8.77}Se_{0.22})_{\Sigma 8.99}$	$Pb_{5.94}Bi_{2.06}(S_{8.78}Se_{0.22})_{\Sigma 9.00}$
5.	$Pb_{6.04}Bi_{2.04}(S_{8.67}Se_{0.25})_{\Sigma 8.92}$	$Pb_{6.09}Bi_{2.06}(S_{8.74}Se_{0.26})_{\Sigma 9.00}$
6.	$Pb_{5.95}Bi_{2.06}(S_{8.74}Se_{0.25})_{\Sigma 8.99}$	$Pb_{5.96}Bi_{2.06}(S_{8.75}Se_{0.25})_{\Sigma 9.00}$
7.	$Pb_{5.97}Bi_{2.07}(S_{8.43}Se_{0.53})_{\Sigma 8.96}$	$Pb_{6.00}Bi_{2.08}(S_{8.47}Se_{0.53})_{\Sigma 9.00}$
8.	$Pb_{6.03}Bi_{2.04}(S_{8.29}Se_{0.64})_{\Sigma 8.93}$	$Pb_{6.08}Bi_{2.06}(S_{8.36}Se_{0.64})_{\Sigma 9.00}$
9.	$(Pb_{5.94}Cd_{0.05})_{\Sigma 5.99}Bi_{2.09}(S_{8.49}Se_{0.43})_{\Sigma 8.92}$	$(Pb_{6.00}Cd_{0.05})_{\Sigma 6.05}Bi_{2.11}(S_{8.57}Se_{0.43})_{\Sigma 9.00}$
10.	$(Pb_{5.95}Cd_{0.02})_{\Sigma 5.97}Bi_{2.07}(S_{8.48}Se_{0.48})_{\Sigma 8.96}$	$(Pb_{5.98}Cd_{0.02})_{\Sigma 6.00}Bi_{2.08}(S_{8.52}Se_{0.48})_{\Sigma 9.00}$
11.	$Pb_{5.93}Bi_{2.06}(S_{8.50}Se_{0.51})_{\Sigma 9.01}$	$Pb_{5.92}Bi_{2.06}(S_{8.49}Se_{0.51})_{\Sigma 9.00}$
12.	$(Pb_{5.78}Cd_{0.07})_{\Sigma 5.85}Bi_{2.10}(S_{8.55}Se_{0.50})_{\Sigma 9.05}$	$(Pb_{5.75}Cd_{0.07})_{\Sigma 5.82}Bi_{2.09}(S_{8.51}Se_{0.49})_{\Sigma 9.00}$
13.	$(Pb_{5.87}Cd_{0.05})_{\Sigma 5.92}Bi_{2.13}(S_{8.42}Se_{0.53})_{\Sigma 8.95}$	$(Pb_{5.90}Cd_{0.05})_{\Sigma 5.95}Bi_{2.14}(S_{8.47}Se_{0.53})_{\Sigma 9.00}$
14.	$(Pb_{5.83}Cd_{0.04})_{\Sigma 5.87}Bi_{2.11}(S_{8.50}Se_{0.53})_{\Sigma 9.03}$	$(Pb_{5.81}Cd_{0.04})_{\Sigma 5.85}Bi_{2.10}(S_{8.48}Se_{0.52})_{\Sigma 9.00}$
Av.	$(Pb_{5.95}Cd_{0.02})_{\Sigma 5.97}Bi_{2.06}(S_{8.53}Se_{0.44})_{\Sigma 8.97}$	$(Pb_{5.97}Cd_{0.02})_{\Sigma 5.99}Bi_{2.07}(S_{8.56}Se_{0.44})_{\Sigma 9.00}$
Th.	$Pb_6Bi_2S_9$	$Pb_6Bi_2S_9$

Av.: average formula, Th.: theoretical formula.

In Table 2, the empirical formulae, calculated from the analytical data on the basis of 17 atoms, and the structural formulae, based on ΣS atoms = 9 (Otto & Strunz 1968), are also given. The balance of valences is rather good: deviations do not exceed about 2.5% in absolute value. The calculated average composition (Table 2) corresponds to the empirical formula $(Pb_{5.95}Cd_{0.02})_{\Sigma 5.97}Bi_{2.06}(S_{8.53}Se_{0.44})_{\Sigma 8.97}$, which is close to the ideal one. Analogously, using the structural formula $6Pb_{1-x}Bi_{2x/3}S{\bullet}Bi_2S_3$ proposed for the Phase II by Otto & Strunz (1968) and normalizing the average composition to nine atoms of sulfur plus selenium, we represent the same average composition with the formula $6Pb_{0.99}Bi_{0.01}S{\bullet}Bi_2S_3$, in which $x = 0.01$. The atomic ratios (Pb + Cd) / Bi (Table 2) and (Pb + Cd + Bi) / (S + Se) range from 3.01 to 2.78 and from 0.88 to 0.91, respectively.

N_{chem} values, which have been calculated for each composition, are also reported in Table 2. Most of the values are non-integral and extend from 6.6 to 7.0, averaging 6.8.

X-RAY-DIFFRACTION DATA

A crystal of heyrovskýite that has been previously analyzed (Table 2, No. 8) was extracted from a polished section under the microscope and was used to obtain the X-ray powder-diffraction data. A Debye–Scherrer camera (57.3 mm in diameter, unfiltered Fe-radiation) was used; the relative intensities of reflections were estimated visually.

The results are given in Table 3 in comparison with a selection of lines from the powder diagram of synthetic Phase II with 17.6 mol.% Bi_2S_3 (Otto & Strunz 1968). The cell parameters were calculated by the least-squares method on the basis of 17 reliable lines indexed according to the powder diagram of Phase II (one reflection with double indexes) reported by Otto & Strunz (1968). The cell constants thus determined are: *a* 13.734(7), *b* 31.28(3), *c* 4.135(3) Å; the $h + l = 2n$ reflections are diagnostic of the space group *Bbmm*.

The strong similarity of the X-ray data and the space group between the Ag-free heyrovskýite from Vulcano and the synthetic Phase II allows us to conclude that in spite of the closeness of their chemical composition, the mineral investigated cannot be aschamalmite, $Pb_{5.9}Bi_{2.9}S_9$, which is monoclinic.

DISCUSSION

Heyrovskýite from Vulcano has been identified on the basis of its chemical composition and the X-ray powder-diffraction data. Unlike other occurrences of

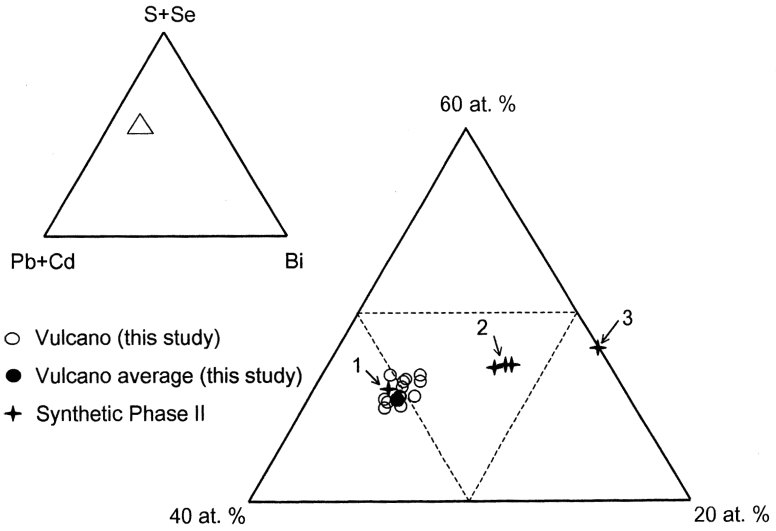

FIG. 2. Composition of heyrovskýite from Vulcano and synthetic Phase II (at.%) in the system Bi–Pb(Cd)–S(Se). Increment: 5 at.%. Ideal compositions: 1 $Pb_6Bi_2S_9$ (Salanci & Moh 1969), 2 $Pb_9Bi_4S_{15}$ (Craig 1967, Otto & Strunz 1968, Salanci & Moh 1969, Godovikov 1972, Sugaki *et al.* 1974, Chang *et al.* 1988, Liu & Chang 1994), 3 $Pb_{15}Bi_8S_{27}$ (Salanci & Moh 1969).

this species, the Vulcano material is homogeneous, it displays no traces of a breakdown texture, it has a constant Ag- and Cu-free composition, and it is characterized by the presence of selenium substituting for sulfur. Particularly interesting is the absence of monovalent cations like Ag and Cu, which allows us to consider the heyrovskýite from Vulcano as unique owing to its relative purity with respect to cations (except for the minor incorporation of Cd). The crystals investigated show a quite constant composition, with only a very narrow compositional range caused by slight variation of the main elements, Pb and Bi (Fig. 2). In any case, the compositional spread does not exceed the analytical error. The general chemical formula, which has been obtained by averaging the results of 14 analyses, is: $(Pb_{5.95}Cd_{0.02})_{\Sigma 5.97}Bi_{2.06}(S_{8.53}Se_{0.44})_{\Sigma 8.97}$. If we consider the general structural formula used by various authors to describe natural occurrences of Ag-free heyrovskýite and synthetic Phase II, $6Pb_{1-x}Bi_{2x/3}S \bullet Bi_2S_3$, or $Pb_{6-6x}Bi_{2+4x}S_9$ with $0 \leq x \leq 0.166$ (Otto & Strunz 1968, Salanci & Moh 1969, Takéuchi & Takagi 1974), the heyrovskýite from Vulcano shows a value of x equal to 0.01, which indicates a composition very close to the ideal Pb-rich end-member of synthetic Phase II: $Pb_6Bi_2S_9$ (Salanci & Moh 1969). Because of the very narrow compositional spread observed in the samples, which is very close to the analytical error at a confidence level of 99%, the average composition reported above may be considered representative of the material

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR HEYROVSKÝITE FROM VULCANO AND SYNTHETIC PHASE II

Heyrovskýite*			Phase II **			
I/I_0	d_{meas}	d_{calc}	I/I_0	d_{meas}	d_{calc}	*h k* l
7	5.03	5.1599			5.1572	2 4 0
7	4.05	4.1523			4.1545	2 6 0
7	3.74	3.7454	2	3.751	3.7488	2 7 0
4	3.56	3.5324	3	3.537	3.5336	1 4 1
10	3.43	3.4335	10	3.409	3.4237	4 0 0
4	3.34	3.3457	3	3.348	3.3475	1 5 1
5	3.12	3.1280	0.1	3.138	3.1358	0 10 0
3	3.00	3.0112	1.5	3.007	3.0077	3 2 1
8	2.95	2.9437	3	2.942	2.9409	3 3 1
6	2.86	2.8565	3	2.854	2.8543	3 4 1
6	2.75	2.7550	0.2	2.754	2.7535	3 5 1
6	2.61	2.6067	0.3	2.614	2.6132	0 12 0
2	2.15	2.1488	1	2.145	2.1457	551
5	2.10	2.0959	4	2.092	2.0917	6 6 0
5	2.07	2.0675	2	2.069	2.0675	0 0 2
3	2.05	2.0562	1	2.060	2.0598	1 13 1
0.5b	1.961	1.9550	1	1.9608	1.9599	0 16 0
0.5b	1.781	1.7824	3	1.7833	1.7842	4 15 0
5	1.767 {	1.7683	4	1.767 {	1.7670	4 1 2
		1.7662			1.7668	2 8 2
4	1.717 {	1.7195	1	1.7202 {	1.7195	5 12 1
		1.7168			1.7119	8 0 0
3	1.693 {	1.6939	0.7	1.6885 {	1.6894	8 3 0
		1.6847			1.6883	2 18 0
2	1.572	1.5719			1.5688	8 8 0

a (Å)	13.734(7)	*a* (Å)	13.695
b (Å)	31.28(3)	*b* (Å)	31.358
c (Å)	4.135(3)	*c* (Å)	4.135
α = β = γ = 90°		α= β = γ = 90°	
Space group:	*Bbmm*		*Bbmm*

* with 14.47 mol% Bi_2S_3; anal. no. 8 in Table 2.
** selection from the powder diagram of synthetic Phase II, containing 17.6 mol.% Bi_2S_3 (Otto & Strunz 1968).

from Vulcano. The values of chemical N, calculated for the fourteen compositions presented in this work, range from 6.6 to 7 and are mostly not integral and less than the theoretical crystallographic value (N = 7). Makovicky (1981) noted that differences between non-integral values for N, generally smaller than the theoretical one, may be due either to vacancies in the metal positions, created by substitution $3Pb^{2+} \rightarrow 2Bi^{3+} + \square$ ($\square$: vacancy), or to the errors in the frequency of "chemical twinning". Defect structures and disordered intergrowth were first reported from studies based on high-resolution transmission electron microscopy (HRTEM) of synthetic members of the LHS (Tilley & Wright 1982, Skowron & Tilley 1986). Stacking disorder and disordered intergrowth have been recently confirmed also in natural LHS (Pring *et al.* 1999). HRTEM investigations have not been carried out on the material discussed in this paper. Taking into account the high speed of crystallization at the interface between fumarole fluids and atmosphere, which characterizes the conditions of sulfosalt formation at Vulcano, it is reasonable to suppose that disorder in the stacking of the slabs greatly contributes to the nonstoichiometry of the heyrovskýite studied.

In Figure 3, the composition of heyrovskýite from Vulcano is compared with that from other occurrences (Table 4). In spite of the absence of Ag, Cu and Sb, the mineral from Vulcano shows strong similarities to the compositions of heyrovskýite from Sedl and, to a lesser extent, Moaralm. Moreover, the composition of heyrovskýite from Vulcano differs significantly from that of the Ag- and Cu-free mineral from Juno mine (Australia), which was described by Large & Mumme (1975) as heyrovskýite. This last-named mineral, on the basis of its $N_{chem} = 5$, could represent another lillianite homologue, not heyrovskýite. But in the absence of structural data, it is difficult to provide a more accurate identification of this phase. A similar discrepancy in the chemical composition, although not as striking, can be noted with the minerals from Yakuki (Takéuki & Takagi 1974), Spokoinoe and Vaskö (Mozgova *et al.* 1976), whose N_{chem} values (~6) fall close to but not along the heyrovskýite line.

Thus the heyrovskýite from Vulcano is the first truly Ag-free end member of the series of the natural lillianite homologues with N = 7. This evidence confirms that monovalent cations (Ag, Cu and others) are not necessary to stabilize the structure of heyrovskýite. On the other hand, heyrovskýite from Vulcano shows a slight surplus of bismuth if compared with the theoretical $Pb_6Bi_2S_9$. As suggested by Liu & Chang (1994), a certain amount of Bi is required to fill the Pb sites in the absence of additional cations, to stabilize the slab-twinning structures of lead and bismuth sulfosalts.

All analyzed grains of heyrovskýite from Vulcano display significant concentrations of Se, ranging between 0.9 and 2.2 wt.%. These concentrations correspond to an atomic ratio Se/(S + Se) of 0.02 and 0.07,

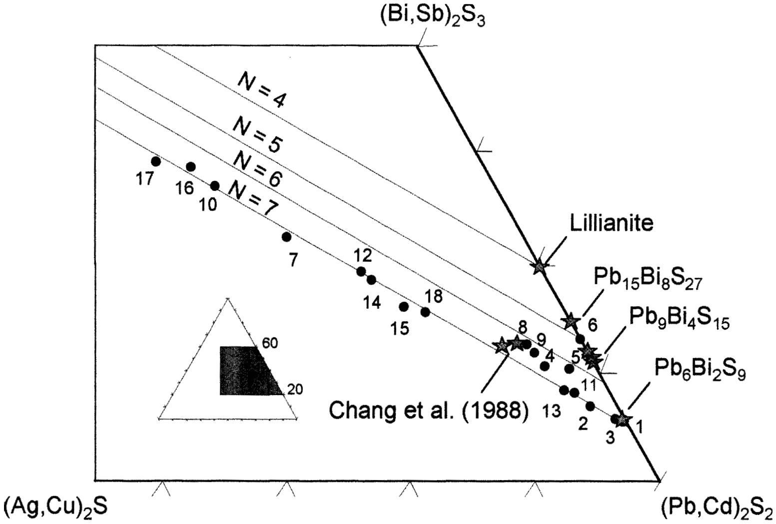

FIG. 3. Composition of heyrovskýite from various occurrences and synthetic phases (mol.%) in the system $(Pb,Cd)_2S_2$ – $(Bi,Sb)_2S_3$ – $(Ag,Cu)_2S$. Filled circles: natural phases described as heyrovskýite (this study and literature data, figures refers to Table 4); stars: lillianite, synthetic Phase II (ideal composition) and synthetic heyrovskýite (literature data).

TABLE 4a. HEYROVSKÝITE FROM VARIOUS OCCURRENCES: CHEMICAL DATA AND N_{chem} VALUES

No.	*n*	Pb	Cd	Fe	Cu	Ag	Bi	Sb	S	Se	Te	total	*Me*/ *ΣMe*	N_{chem}	Bi_2S_3 mol.%
1	14	62.2	0.3		-	-	21.7	-	13.8	1.7	-	99.7	2.9	6.8	14.63
2	8	60.9	-	-	0.1	0.8	23.3	-	14.9	-	-	100.0	2.7	7.1	15.74
3	4	62.7	-	-	-	0.2	21.8	0.2	14.7	-	-	99.6	2.9	6.9	14.86
4	5	56.5	-	-	-	1.7	26.6	-	14.5	-	-	99.3	2.3	6.5	18.49
5		57.9	-	-	-	1.0	26.2	-	14.9	-	-	100.0	2.3	6.1	18.08
6	4	55.1	-	-	-	-	27.2	-	11.1	6.8	-	100.2	2.0	5.1	19.66
7	1	33.2	-	-	-	8.4	36.5	-	11.9	7.4	0.75	98.15	1.4	7.5	30.48
8	1	56.1	-	-	0.1	1.9	28.3	0.5	15.6	-	-	102.5	2.1	6.1	19.93
9	1	54.4	-	-	-	1.8	27.2	-	14.0	-	-	97.40	2.15	6.2	19.37
10	1	28.2	-	-	n.d.	10.5	44.1	n.d.	16.6	-	-	99.40	1.1	7.0	36.14
11	1	59.3	-	-	0.2	0.9	23.8	0.2	14.7	-	-	99.10	2.6	6.9	16.52
12	5	41.24	0.27	-	n.d.	6.73	35.52	0.04	15.96	0.03	-	99.79	1.55	7.0	26.79
13	12	58.55	-	-	-	1.62	24.08	0.18	15.25	-	-	99.68	2.55	7.1	16.52
14	1	41.90	-	-	-	6.42	33.99	0.05	14.96	1.97	0.15	99.44	1.61	7.2	26.01
15	1	44.28	-	0.14	-	5.72	31.59	-	14.47	2.01	-	98.21	1.78	7.6	23.74
16	1	25.60	-	-	-	11.09	45.21	-	15.56	1.42	-	98.88	1.05	6.8	38.20
17	1	23.38	-	-	0.18	12.41	46.89	0.06	15.46	1.81	0.13	100.32	1.03	7.5	39.56
18	1	46.90	-	-	0.17	4.77	31.47		13.52	3.13	0.36	100.32	1.81	7.2	23.16

n: number of analyses. *Me*/Σ*Me* = (Pb + Ag + Cu + Cd + Fe) / (Bi + Sb), at.% .

TABLE 4b. EMPIRICAL CH7EMICAL FORMULAE FOR HEYROVSKÝITE FROM VARIOUS OCCURRENCES

No.	Empirical chemical formulae calculated on the basis of 17 atoms	Structural formulae ($Pb_{6-2x}Ag_xBi_{2+x}S_9$) calculated on the basis of (S + Se + Te) = 9 *apfu*
1	$(Pb_{5.95}Cd_{0.02})_{\Sigma 5.97}Bi_{2.06}(S_{8.53}Se_{0.44})_{\Sigma 8.97}$	$Pb_{5.97}Cd_{0.02}Bi_{2.07}(S_{8.56}Se_{0.44})_{\Sigma 9.00}$
2	$(Pb_{5.35}Ag_{0.30})_{\Sigma 5.65}Bi_{2.50}S_{8.85}$	$Pb_{5.44}Ag_{0.31}Bi_{2.54}S_{9.00}$
3	$(Pb_{5.68}Ag_{0.14}Cu_{0.03})_{\Sigma 5.85}Bi_{2.16}S_{8.99}$	$Pb_{5.69}Ag_{0.14}Cu_{0.03}Bi_{2.16}S_{9.00}$
4	$(Pb_{5.92}Ag_{0.04})_{\Sigma 5.96}(Bi_{2.04}\,Sb_{0.02})_{\Sigma 2.06}S_{8.97}$	$Pb_{5.94}Ag_{0.04}Bi_{2.05}Sb_{0.02}S_{9.00}$
5	$(Pb_{3.63}Cd_{0.04}Ag_{1.14})_{\Sigma 4.81}(Bi_{3.10}Sb_{0.01})_{\Sigma 3.11}(S_{9.08}Se_{0.01})_{\Sigma 9.09}$	$Pb_{3.60}Cd_{0.04}Ag_{1.13}(Bi_{3.07}Sb_{0.01})_{\Sigma 3.08}(S_{8.99}Se_{0.01})_{\Sigma 9.00}$
6	$(Pb_{2.40}Ag_{1.72})_{\Sigma 4.12}Bi_{3.73}S_{9.15}$	$Pb_{2.37}Ag_{1.69}Bi_{3.67}S_{9.00}$
7	$(Pb_{5.58}Ag_{0.16}Cu_{0.06})_{\Sigma 5.80}(Bi_{2.22}Sb_{0.03})_{\Sigma 2.25}S_{9.08}$	$Pb_{5.62}Ag_{0.16}Cu_{0.06}(Bi_{2.24}Sb_{0.03})_{\Sigma 2.27}S_{9.00}$
8	$(Pb_{5.40}Ag_{0.29})_{\Sigma 5.69}(Bi_{2.20}Sb_{0.03})_{\Sigma 2.23}S_{9.08}$	$Pb_{5.35}Ag_{0.28}(Bi_{2.18}Sb_{0.03})_{\Sigma 2.21}S_{9.00}$
9	$(Pb_{5.40}Ag_{0.18})_{\Sigma 5.68}Bi_{2.42}S_{9.00}$	$Pb_{5.40}Ag_{0.18}Bi_{2.42}S_{9.00}$
10	$Pb_{5.46}Bi_{2.67}(S_{7.10}Se_{1.77})_{\Sigma 8.87}$	$Pb_{5.54}Bi_{2.71}(S_{7.21}Se_{1.79})_{\Sigma 9.00}$
11	$(Pb_{5.02}Ag_{0.33}Cu_{0.03})_{\Sigma 5.38}(Bi_{2.51}Sb_{0.08})_{\Sigma 2.59}S_{9.03}$	$Pb_{5.01}Ag_{0.33}Cu_{0.03}(Bi_{2.50}Sb_{0.08})_{\Sigma 2.58}S_{9.00}$
12	$(Pb_{5.28}Ag_{0.34})_{\Sigma 5.62}Bi_{2.62}S_{8.77}$	$Pb_{5.41}Ag_{0.34}Bi_{2.68}S_{9.00}$
13	$(Pb_{3.75}Ag_{1.10})_{\Sigma 4.85}(Bi_{3.01}Sb_{0.01})_{\Sigma 3.02}(S_{8.65}Se_{0.46}Te_{0.02})_{\Sigma 9.13}$	$(Pb_{3.69}Ag_{1.09})_{\Sigma 4.78}(Bi_{2.97}Sb_{0.01})_{\Sigma 2.98}(S_{8.52}Se_{0.46}Te_{0.02})_{\Sigma 9.00}$
14	$(Pb_{4.05}Fe_{0.05}Ag_{1.00})_{\Sigma 5.10}Bi_{2.86}(S_{8.55}Se_{0.48})_{\Sigma 9.03}$	$(Pb_{4.03}Fe_{0.05}Ag_{1.00})_{\Sigma 5.08}Bi_{2.85}(S_{8.52}Se_{0.48})_{\Sigma 9.00}$
15	$(Pb_{2.22}Ag_{1.85})_{\Sigma 4.07}Bi_{3.89}(S_{8.72}Se_{0.32})_{\Sigma 9.04}$	$(Pb_{2.21}Ag_{1.84})_{\Sigma 4.05}Bi_{3.87}(S_{8.68}Se_{0.32})_{\Sigma 9.00}$
16	$(Pb_{1.99}Ag_{2.03}Cu_{0.05})_{\Sigma 4.07}(Bi_{3.97}Sb_{0.01})_{\Sigma 3.98}(S_{8.52}Se_{0.41}Te_{0.02})_{\Sigma 8.95}$	$(Pb_{2.01}Ag_{2.05}Cu_{0.05})_{\Sigma 4.11}(Bi_{3.99}Sb_{0.01})_{\Sigma 4.00}(S_{8.57}Se_{0.41}Te_{0.02})_{\Sigma 9.00}$
17	$(Pb_{3.08}Ag_{1.50})_{\Sigma 4.58}Bi_{3.36}(S_{7.14}Se_{1.80}Te_{0.11})_{\Sigma 9.05}$	$(Pb_{3.06}Ag_{1.49})_{\Sigma 4.55}Bi_{3.34}(S_{7.10}Se_{1.79}Te_{0.11})_{\Sigma 9.00}$
18	$(Pb_{4.33}Ag_{0.85}Cu_{0.05})_{\Sigma 5.23}Bi_{2.88}(S_{8.07}Se_{0.76}Te_{0.05})_{\Sigma 8.88}$	$(Pb_{4.39}Ag_{0.86}Cu_{0.05})_{\Sigma 5.30}Bi_{2.92}(S_{8.18}Se_{0.77}Te_{0.05})_{\Sigma 9.00}$

Samples: 1 Vulcano, Aeolian Islands, Italy (this study); 2 Moaralm, Province of Salzburg, Austria (this study); 3 Sedl, Province of Salzburg, Austria (this study); 4 Hůrky, Stredocesky kraj, Cechy (Bohemia), Czech Republic (Klomínský *et al.* 1971); 5 Yakuki, Fukushima Prefecture, Japan (wt.% calculated from formula, Takéuchi & Takagi 1974); 6 Juno mine, Northern Territory, Australia (Large & Mumme 1975); 7 Darwin, Inyo County, California ("Type IV sulfosalt", Czamanske *et al.* 1975); 8 Spokoinoe, Siberia, Russia (Mozgova *et al.* 1976); 9 Vaskö, old name for Ocna de Fier, Banat, Romania (Mozgova *et al.* 1976); 10 Castlegar, British Columbia (Karup-Møller & Makovicky 1981); 11 Shumilovskoe, western Transbaikal, former USSR (Getmanskaja *et al.* 1984); 12 La Roche-Balue, Loire Atlantique, France (Moëlo *et al.* 1987); 13 Spokoinoe (Vinogradova *et al.* 1992); note that some compositions contain Cu, Fe, Se and Te in traces; 14–17 Biuţ deposit, Romania (Cook 1998); 18 Darwin (Dunning *et al.* 2000).

respectively. Liu & Chang (1994) have experimentally examined the phase relationships of Pb–Bi chalcogenides and showed that heyrovskýite forms a complete solid-solution with the seleniferous analogue. Totally Se-substituted heyrovskýite has never been found in nature. The maximum Se concentrations reported for this mineral correspond to the occurrence described by Large & Mumme (1975) for the Juno mine deposit (Se ranging between 6.7 and 7.1 wt.%), and by Czamanske & Hall (1975) for the Darwin deposit (Se ranging between 7.2 and 10.3 wt.%). Concentrations of Se in the heyrovskýite from Vulcano are highly comparable with the selenium content reported by Cook (1998) for heyrovskýite from the Băiuţ epithermal deposit in Romania and by Dunning *et al.* (2000) for heyrovskýite from the Darwin deposits. In all these cases, Se content is less than 3.13 wt.%.

No reliable X-ray data are available for natural Ag-free selenian heyrovskýite. Likewise, selenium-bearing synthetic phases with $N_{chem} = 7$ have not been structurally investigated. The only unit-cell parameters available for synthetic selenian heyrovskýite were obtained by Liu & Chang (1994), but their products have $N_{chem} \approx 5.5$. In addition, a comparison between cell parameters reported by these authors for their synthetic phases and those reported in literature for natural and synthetic examples of heyrovskýite displays some general disagreements. The parameters *b* and *c* are not comparable with the corresponding unit-cell parameters reported for natural and synthetic samples (Table 5). No explanation can be offered for this disagreement. In spite of this, no strong discrepancies can be noted for the cell parameter *a*. The data reported by Liu & Chang (1994) suggest a significant positive change in the unit-cell parameter *a* with increasing Se-for-S substitution in Ag-free synthetic selenian heyrovskýite. The parameter *a* obtained in this work for the Ag-free selenian heyrovskýite from Vulcano conforms to such a line (Fig. 4).

The relation between heyrovskýite from Vulcano and Phase II, *i.e.*, its synthetic homologue, is also interesting. According to Salanci & Moh (1969), the composition of Phase II ranges from 14.3 to 21.0 mol.% Bi_2S_3, and this compositional variation is related to the temperature variation (Bi content increases with an increase in temperature from 500 to 800°C). The empirical chemical formulae of the terminal members ideally correspond to $Pb_6Bi_2S_9$ and $Pb_{15}Bi_8S_{27}$, with Pb/Bi ranging from 3 to 1.88, respectively (Table 6a). These terminal members fix the boundaries of the compositional field generally ascribed to Phase II, which covers intermediate compositions like $Pb_9Bi_4S_{15}$ (Craig 1967, Otto & Strunz 1968, Salanci & Moh 1969, Godovikov 1972, Chang *et al.* 1988, Liu & Chang 1994).

TABLE 5. COMPARISON OF CELL PARAMETERS OF HEYROVSKÝITE AND SYNTHETIC PHASE II

a, Å	*b*, Å	*c*, Å	N_{chem}	Cu_2S	Ag_2S	PbS	PbSe	Bi_2S_3	Ref.
13.734(7)	31.28(3)	4.135(3)	6.9	-	-	76.5	9.0	14.5	1
13.72	31.04	4.14	7.7	0.2	0.8	84.7	-	14.3	2
13.712(2)	31.210(5)	4.131(1)	6.1	-	1.3	80.6	-	18.1	3
13.697	31.069	4.112	7.2	-	2.2	81.1	-	16.7	4
13.705	31.194	4.12	6.5	-	2.3	79.2	-	18.5	5
13.71	31.24	4.10	6.1	0.22	2.52	77.33		19.93	6
13.61	30.47	4.08	7.1	-	9.8	63.3	0.1	26.8	7
13.583	30.533	4.129	7.0	-	17.0	46.9	-	36.1	8
13.666(3)	30.778(5)	4.1403(5)	7.5	-	13.6	21.2	34.8	30.4	9
13.70	31.35	4.14	5.6	-	-	82.0	-	18.0	10
13.695	31.358	4.135	5.7	-	-	82.4	-	17.6	11
13.87	31.79	4.15	5.5			81.8		18.2	12
13.695	31.68	4.135	5.6	-	-	82.0	-	18.0	13
13.68	32.57	4.23	5.6	-	-	82.0	-	18.0	14
13.90	32.75	4.23	5.6	-	-	55.0	27.0	18.0	15
13.96	32.90	4.23	5.6	-	-	40.0	42.0	18.0	16

Samples 1–9: natural heyrovskýite: 1 Vulcano, Aeolian Islands, Italy (this study); 2 Moaralm, Province of Salzburg, Austria (Paar *et al.* 1980); 3 Yakuki, Fukushima Prefecture, Japan (Takéuchi & Takagi 1974); 4 Spokoinoe (Vinogradova *et al.* 1992); 5 Hůrky, Stredocesky kraj, Cechy (Bohemia), Czech Republic (Klomínský *et al.* 1971); 6 Spokoinoe, Siberia, Russia (Mozgova *et al.* 1976); 7 La Roche-Balue, Loire Atlantique, France (Moëlo *et al.* 1987); 8 Castlegar, British Columbia (Karup-Møller & Makovicky 1981); 9 Darwin, Inyo County, California ("Type IV sulfosalts", Czamanske *et al.* 1975). Samples 10–16: synthetic phase II: 10 Sugaki *et al.* (1974); 11 Otto & Strunz (1968); 12 Godovikov (1972); 13 Chang *et al.* (1988); 14–16 Liu & Chang (1994).

It should be noted that $N_{chem} = 7$ occurs only in synthetic members of the series compositionally close to the ideal formula $Pb_6Bi_2S_9$, which were synthesized by Salanci & Moh (1969) at about 500°C. All the other compositions display N_{chem} values less than the theoretical value, all of them ranging between 4.8 and 5.7. Thus we speculate that only the Pb-rich part of the compositional field of the Phase II, in absence of monovalent cations, may be considered as the synthetic analogue of heyrovskýite. The members with a higher concentration of Bi evidently need additional presence of Ag or Cu or both to stabilize the structure with N = 7, as we can see in Tables 4 and 6b, as well as in Figure 3. In addition, we cannot exclude the possibility that these members in the system Pb–Bi–S correspond to some questionable minerals previously described in this system (Godovikov 1972, Mozgova 1985).

The Ag-free heyrovskýite from Vulcano investigated in this study is compositionally very close to the Pb-rich end-member of Phase II (Figs. 2, 3). It was collected from fumarole FA at a temperature (500°C), which is very close to the temperature of formation of the Pb-rich synthetic products (Salanci & Moh 1969). Unfortunately, X-ray-diffraction data and the cell parameters of heyrovskýite from Vulcano and those for the synthetic Pb-rich homologue cannot be compared, because of the absence of relevant X-ray data regarding the Pb-rich members of Phase II. Cell parameters given

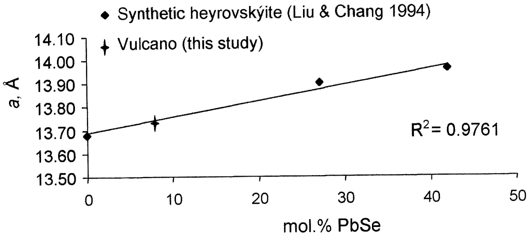

FIG. 4. The cell parameter *a* (Å) increases with an increase in Se content in selenian synthetic heyrovskýite (Liu & Chang 1994). The cell parameter *a* (Å) in selenian heyrovskýite from Vulcano (this study) is well located along the alignment.

TABLE 6a. CHEMICAL COMPOSITION OF SYNTHETIC PHASE II

Ideal composition	Formula based on S = 9 *apfu*	x ¶	Bi_2S_3 mol.%	(Pb+Bi) /S	Pb / Bi	N_{chem}	T °C	Ref.
$\mathit{Pb_6Bi_2S_9}$	$\mathit{Pb_6Bi_2S_9}$	*0.00*	*14.3*	*0.89*	*3.00*	*7.0*		
	$Pb_6Bi_2S_9$	0.00	14.3	0.89	3.00	7.0	450	1
$\mathit{Pb_9Bi_4S_{15}}$	$\mathit{Pb_{5.40}Bi_{2.40}S_9}$	*0.100*	*18.2*	*0.87*	*2.25*	*5.5*		
	$Pb_{5.48}Bi_{2.34}S_9$	0.086	17.6	0.87	2.34	5.7	650	2
	$Pb_{5.43}Bi_{2.38}S_9$	0.095	18.0	0.87	2.28	5.6	≥400	3
							500	4
							500	5§
							650	1
							750	6
	$Pb_{5.40}Bi_{2.40}S_9$	0.100	18.2	0.87	2.25	5.5	500	7
$\mathit{Pb_{15}Bi_8S_{27}}$	$\mathit{Pb_5Bi_{2.67}S_9}$	*0.167*	*21.0*	*0.85*	*1.88*	*4.8*		
	$Pb_5Bi_{2.66}S_9$	0.166	21.0	0.85	1.88	4.8	805	1

¶ x in the structural formula $6Pb_{1-x}Bi_{2/3x}S{\bullet}Bi_2S_3$ (Otto & Strunz 1968). § Synthetic heyrovskýite: forms a complete solid-solution with the seleniferous analogue. References: 1 Salanci & Moh (1969), 2 Otto & Strunz (1968), 3 Craig (1967), 4 Chang *et al.* (1988), 5 Liu & Chang (1994), 6 Sugaki *et al.* (1974), 7 Godovikov (1972).

TABLE 6b. CHEMICAL COMPOSITION OF SYNTHETIC Cu- AND Ag-BEARING HEYROVSKÝITE*

T °C	Formula based on S = 9 *apfu*	Bi_2S_3 mol.%	(Pb+Bi) / S	Pb / (Pb+Bi)	N_{chem}	Label
500	$Pb_{4.90}Cu_{0.47}Bi_{2.57}S_9$	20.0	0.88	2.09	6.6	Cu-rich heyrovskýite
500	$Pb_{4.95}Ag_{0.38}Bi_{2.57}S_9$	20.0	0.88	2.07	6.2	Ag-rich heyrovskýite
500	$Pb_{3.18}Ag_{0.76}Cu_{1.31}Bi_{3.18}S_9$	27.4	0.94	1.65	14.2	Ag-,Cu-rich heyrovskýite

* Chang *et al.* (1988).

by different authors on synthetic Phase II (Table 5) pertain only to Bi-rich compositions, characterized by a N_{chem} value lower than the theoretical one (Table 6a).

The Ag-free orthorhombic heyrovskýite from Vulcano is very close in chemical composition to aschamalmite, $Pb_{5.9}Bi_{2.1}S_{9.0}$ (known only from the type locality), but differs from it in the absence of the slight monoclinic distortion, with β = 91° (Mumme *et al.* 1983). This is considered as evidence of Pb–Bi cation ordering (Makovicky *et al.* 1991). Taking into account the conditions of formation of sulfosalts in the fumaroles of Vulcano (rapid drop in the temperature taking place at the fumaroles, similar to the quenching procedure in laboratory experiments), it is difficult to expect cation ordering in their structures. Moreover, according to Liu & Chang (1994), aschamalmite is not a stable phase in the system $PbS–PbSe–Bi_2S_3–Bi_2Se_3$ at 500°C, which is very close to the temperature directly measured in fumarole FA at the time of collection of the heyrovskýite samples. On the other hand, the temperature of formation of aschamalmite is unknown. The sulfosalt was formed during the retrograde stage of the Alpine episode of metamorphism, but we could not establish the temperature of formation of aschamalmite from the associated phases (the holotype material was found associated with chlorite only).

Finally, we note that heyrovskýite occurs at Vulcano owing to peculiarities of the depositional environment in fumaroles, with no relevant paragenetic sequence with other sulfosalts. The crystals of selenian heyrovskýite are commonly admixed with selenian lillianite and selenian cannizzarite, with subordinate selenian galenobismutite and selenian galena, but no traces of exsolution, as is commonly encountered in other deposits, or ordering in the sequence of deposition have been noted. The crystals formed very quickly, and the mineralization occurred as thin crusts and aggregates of tiny sulfosalt crystals covering fragments of wallrocks. At the La Fossa crater, the deposition of the sulfosalt assemblage occurs in non-equilibrium conditions. This fact is demonstrated by the great amount of simultaneously crystallized phases (seven or eight minerals from four main components: Pb, Bi, S and Se) and by the simultaneous formation of morphological varieties of the same mineral (lillianite as laths, long prismatic crystals and whiskers; cannizzarite as flakes, whiskers and prismatic crystals, for example).

In the actual epithermal deposit of Vulcano, the deposition of sulfosalts is mainly controlled by the chemical composition, temperature and flux rates of the fumarole fluids, which have been found to change instantaneously. An important role in the depositional processes is played by the simultaneous abundance of HCl, H_2S and SO_2 in the gaseous vapors discharging from the fumaroles. Chlorine, in particular, plays an important role as carrier of the metals and catalyst for the reaction involving the deposition of sulfosalts (Garavelli *et al.* 1997, Cheynet *et al.* 2000). All the ore-forming elements (Pb, Bi, Cd, but also S and Se) are transported in the steam. A high $f(S_2)$ is suggested by the absence of native Bi among the products of the deposition. The absence of Ag and Cu in heyrovskýite, and also in the associated Pb–Bi sulfosalts, is due to the low activity of Ag and Cu at the time of the mineralization, according to the low concentrations of these elements in the hydrothermally altered rocks of the high-temperature fumarole field of the La Fossa volcano (Fulignati & Sbrana 1998).

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