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Structure refinement of Ag-free heyrovskýite from Vulcano (Aeolian Islands, Italy)

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ABSTRACT

The first single-crystal structure refinement of Ag- and Cu-free heyrovskýite was performed in this study. Crystals investigated were sampled from the high-temperature fumaroles of La Fossa crater of Vulcano, Aeolian Islands, Italy. Electron microprobe analyses gave the average chemical formula $(Pb_{5.86}Cd_{0.03})_{\Sigma 5.89}Bi_{2.04}(S_{8.52}Se_{0.53}Cl_{0.03})_{\Sigma 9.08}$, which is very close to the ideal composition of heyrovskýite, $Pb_6Bi_2S_9$. Lattice parameters are a = 13.7498(4), b = 31.5053(8), c = 4.1475(1) Å, V = 1796.7(1) Å^3, space group *Bbmm*. The structure refinement converges to R = 4.17% for 1312 reflections with $F_o > 4\sigma(F_o)$.

In Ag-free heyrovskýite from Vulcano, as well as in the synthetic $Pb_6Bi_2S_9$, the trigonal prismatic coordinated position Me1, as well as the octahedrally coordinated position Me3 are occupied only by Pb. Me2, also octahedrally coordinated, is dominated by Pb, whereas the octahedra situated at the edges of the octahedral layers (Me4 and Me5) are centered around mixed (Pb,Bi) positions, with almost equal occupancy. The octahedrally coordinated site Me3 was found to incorporate vacancies (□), created by the substitution $3Pb^{2+} \rightarrow 2Bi^{3+} + \square$, which allows for the observed deviations from the ideal composition, $Pb_6Bi_2S_9$. Selenium is preferentially ordered at the fivefold-coordinated anionic sites. Taking into account vacancies, as well as Se for S substitutions the structural formula of Ag-free heyrovskýite from Vulcano is $Pb_{5.82}Bi_{2.12}\square_{0.06}S_{8.70}Se_{0.30}$.

Comparison with the Ag-bearing heyrovskýite structures shows that during the 2 Pb → Ag(Cu)+Bi substitution the increased content of Bi is incorporated preferentially in the Me5 site until 2/3 Bi occupancy and thereafter in the two central octahedrally coordinated sites (Me2 and Me3). Silver occupies exclusively marginal octahedrally coordinated Me4 site like in the other members of the lillianite homologous series. The observed crystal chemical characteristics of the Ag-free heyrovskýite are in accordance with a model suggested by Callegari and Boiocchi, which describes the monoclinic form, aschamalmite, as an ordered polymorph of $Pb_6Bi_2S_9$, and heyrovskýite as a fully disordered polymorph of the same compound. Ag incorporation is expected to increase the Pb/Bi disorder and to stabilize the orthorhombic heyrovskýite form.

Keywords: Ag-free heyrovskýite, crystal structure, Pb-Bi sulfosalts, lillianite series, Vulcano, Italy

INTRODUCTION

Heyrovskýite, ideally $Pb_6Bi_2S_9$, was described by Klominsky et al. (1971) and considered by these authors as the natural Ag-bearing analog of the synthetic Phase II of the system PbS-Bi_2S_3, which was synthesized and characterized by Otto and Strunz (1968). The compositional variation in Phase II is generally ascribed to the heterovalent substitution $3Pb^{2+} \rightarrow 2Bi^{3+} + \square$ (□ = vacancy) that is reflected by the general structural formula for Phase II: $Pb_{6-x}Bi_{2+2x/3}S_9$ (Otto and Strunz 1968). According to Salanci and Moh (1969) the coefficient x ranges from 0 to 0.166. The crystal structure of heyrovskýite was investigated by Takéuchi and Takagi (1974) and, subsequently, by Makovicky et al. (1991) on two natural Ag-bearing crystals with composition $Pb_{5.4}Ag_{0.18}Bi_{2.42}S_9$ and $Pb_{3.36}Ag_{1.32}Bi_{3.32}S_9$, respectively. It consists of alternating layers of PbS archetype, cut parallel to $(311)_{PbS}$, which also represent the reflection and contact planes of a unit-cell twinning (Takéuchi 1997). On these planes, the Pb atoms achieve a bi-capped trigonal prismatic coordination PbS_{6+2}. Heyrovskýite is considered as a 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 indicates the number of octahedra running diagonally across an individual layer of the archetype, whereas x is the coefficient of the Ag and Bi substitution with maximum value $x_{max} = (N - 2)/2$ (Makovicky and Karup-Møller 1977a, 1977b; Makovicky and Balić-Žunić 1993). The value of N can be determined crystallographically (N_{cryst}) or may be calculated from the chemical data (N_{chem}) using the formula $N_{chem} = -1 + [Bi_j + (Pb_j - 1)/2]^{-1}$, where Pb_j and Bi_j are the Pb and Bi contents in the samples, normalized to the formula Ag+Bi+Pb = 1 (Makovicky and Karup-Møller 1977a).

In the above classification each homologue is denoted as $^{N1,N2}L$ where N_1 and N_2 are the value of N for two alternating sets of layers. Heyrovskýite is the seventh-order member with equal thickness of all structural slabs and is indicated as $^{7,7}L$. The broader lillianite structural family includes also non-

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sulfides and, e.g., the so-called post-perovskite $MgSiO_3$ phase is actually the ^{1,1}L member of the family (Olsen et al. 2008). The same family includes also the members with two unequal slabs, like ^{4,7}L lillianite homologue vikingite (Makovicky et al. 1992). The largest so-far observed slab thickness is in ourayite (Makovicky and Karup-Møller 1984), the ^{11,11}L homologue. Recent investigations showed that under high pressures the crystals of lillianite and heyrovskýite undergo piezoplastic phase transitions to other structure types based on the modules built after the SnS-archetype instead of the PbS-archetype characteristic for this family (Olsen et al. 2008, 2011).

The invariable presence of Ag and/or Cu in all natural occurrences of heyrovskýite suggested that these monovalent cations may play a role in stabilizing the structure of this mineral according to the coupled substitution 2 Pb → Ag(Cu)+Bi (Makovicky and Karup-Møller 1977a). As a matter of fact, distribution of Ag in the LHS structures is believed to control the thickness of the galena-like slabs (Makovicky 1977), thus influencing the stability of the homologues (Price and Yeomans 1984; Skowron and Tilley 1990). According to Skowron and Tilley (1990) the incorporation of Ag may lead to changes in the relative stability of the LHS phases since this monovalent cation has not only a different valence but also a different size with respect to Pb, Bi, and S. This is supported by the results of some calculations of elastic strain energy in Pb-Bi sulfosalts (Aizawa et al. 1983), which suggest that the relative stability of the homologues in the LHS is critically dependent upon the distribution of the cations in the various sites available.

The discovery of the heyrovskýite polymorph aschamalmite, $Pb_6Bi_2S_9$ (Mumme et al. 1983), which shows evidence of cation ordering and ensuing change in symmetry from orthorhombic to monoclinic, suggested the possibility of Pb-Bi cation ordering in lillianite homologues as a possible means of stabilization at lower temperature in the absence of Ag(Cu) and Bi substitution (Makovicky et al. 1991). The recent structure refinement of aschamalmite (Callegari and Boiocchi 2009) showed that the monoclinic symmetry in the mineral forms because of an ordering between Pb and Bi on the margins of the two octahedral layers (i.e., sites Me4A and Me4B, Me5A and Me5B) that are symmetrically equivalent in heyrovskýite. The following couples of opposite sequences were suggested: $^{[Me4A]}$Bi-$^{[Me5A]}$Pb facing $^{[Me4B]}$Pb-$^{[Me5B]}$Bi in about 70% of the unit cells of the crystal and the opposite ordering scheme $^{[Me4A]}$Pb-$^{[Me5A]}$Bi facing $^{[Me4B]}$Bi-$^{[Me5B]}$Pb in the remaining unit cells (Callegari and Boiocchi 2009). According to Mumme et al. (1983), aschamalmite is not the heyrovskýite dimorph sensu stricto because the latter was supposed to always contain a significant amount of monovalent Ag(Cu) and a corresponding extra Bi content for charge balance. Nevertheless, crystals of heyrovskýite free of monovalent cations such as Ag and Cu were recently found around high-temperature fumarole deposit of Vulcano Aeolian Island, Italy (Borodaev et al. 2003). It represents the first natural occurrence of a truly Ag(Cu)-free end-member (with a slight surplus of bismuth) of the LHS with $N = 7$. According to Borodaev et al. (2003) the lack of the Ag and Cu in heyrovskýite, as well as in the other Pb-Bi sulfosalts from Vulcano, is connected to the absence of these monovalent cations in fumarole fluids from which the crystals form.

TEM investigations were recently performed on Ag-free lillianite homologues from Vulcano (Mitolo 2009; Mitolo et al. 2011). These studies showed that lillianite and heyrovskýite from this locality appear, generally as discrete phases, showing a perfectly ordered structure, with minor stacking faults and/or dislocations, in comparison with the corresponding natural Ag-bearing phases, which are much more defective, showing high density of stacking faults and intergrowths of different homologues (Makovicky et al. 1991; Pring et al. 1999; Pring and Etschmann 2002). Also, some nanometric lillianite/heyrovskýite intergrowths, as well as incommensurate structural modulations that make an angle of ~29° with **b*** in the *hk*0 plane and have a wavelength of ~75 Å, were found in Ag-free heyrovskýite from Vulcano. The origin of these modulations was tentatively explained either as the result of an ordering process of Pb and Bi cations in Me4 and Me5 sites within the PbS-like layer, or of the ordering of vacancies naturally present or induced by Bi_2S_3 sublimation phenomena during ion milling (Mitolo 2009; Mitolo et al. 2011).

In this paper, we present a detailed X-ray single-crystal study of the Ag-free heyrovskýite from Vulcano with the refinement of its crystal structure and comparison with the crystal structures of synthetic $Pb_6Bi_2S_9$ and natural Ag-bearing heyrovskýites.

EXPERIMENTAL METHODS

The sample of Ag-free heyrovskýite from Vulcano investigated in this work was collected in 1995 from a widespread fumarolic area in the inner walls of the "La Fossa" crater ($T = 410$ °C). Chemical composition was obtained by electron-microprobe analysis using an ARL-SEMQ-95 instrument at the Centro Studi Geominerari e Metalurgici, CNR, Cagliari. Operating conditions were as follows: voltage 20 kV, beam current 20 nA; standards (emission lines): PbS (Pb$M\alpha$, S$K\alpha$), Bi_2S_3 (Bi$M\alpha$), CdS (Cd$L\alpha$), metallic Ag (Ag$L\alpha$), CuS (Cu$K\alpha$), $FeAsS_2$ (As$L\alpha$), metallic selenium (Se$L\alpha$), KCl (Cl$K\alpha$). Detection limits were (in wt%): Pb 0.10, S 0.02, Bi 0.10, Cd 0.14, Ag 0.05, Cu 0.04, As 0.08, Se 0.04, Cl 0.03. The crystals were homogeneous within the analytical error. Electron microprobe results (wt%) are reported in Table 1. The empirical formulas and N_{chem} values (Makovicky and Karup-Møller 1977a, 1977b), calculated for each composition, are also given.

X-ray diffraction data were collected using a Bruker AXS X8 APEX2 CCD automated diffractometer equipped with a κ-geometry goniometer and graphite monochromatized Mo$K\alpha$ radiation (50 kV and 30 mA operating conditions). The Miracol fiber optics capillary collimator (0.3 mm size) was used to enhance the intensity of the Mo$K\alpha$ radiation and to reduce X-ray beam divergence. Three sets of 12 frames were used for initial cell determination, whereas complete data collection was accomplished by several φ and ω scans with 0.5° rotation, 20 s exposure time per frame and a crystal-to-detector distance of 45 mm. The collection strategy was optimized by the Apex suite program (Bruker 2003a). Details about data collection and refinement are summarized in Table 2. Data reduction including intensity integration, background, and Lorentz-polarization corrections, was carried out using the program SAINT (Bruker 2003b). Correction for absorption was performed by

TABLE 1. Chemical composition (in wt%) of Ag-free heyrovskýite from Vulcano

	Pb	Bi	Cd	S	Se	Cl	Sum	N_{chem}*
	62.67	22.04	0.28	14.19	2.26	0.04	101.49	6.78
	62.45	21.88	0.37	13.96	2.32	0.08	101.05	6.82
	61.66	21.35	0.05	14.01	1.85	0.08	99.00	6.84
	61.86	22.35	0.08	13.97	2.14	0.03	100.43	6.60
	62.43	21.53	0.09	13.91	2.06	0.05	100.08	6.86
Mean	62.21	21.83	0.17	14.01	2.13	0.06	100.41	6.78
St.dev.	0.43	0.40	0.14	0.11	0.18	0.02	0.96	

Empirical average formula† $(Pb_{5.86}Cd_{0.03})_{\Sigma 5.89}Bi_{2.04}(S_{8.52}Se_{0.53}Cl_{0.03})_{\Sigma 9.08}$
Theoretical formula based on N_{chem} $(Pb_{5.89}Cd_{0.03})_{\Sigma 5.92}Bi_{2.05}\square_{0.03}(S_{8.44}Se_{0.53}Cl_{0.03})_{\Sigma 9.00}$
Ideal formula $Pb_6Bi_2S_9$

* Calculated using the formula $N_{chem} = -1 + \{Bi_j + (Pb_j - 1)/2\}^{-1}$, where Pb_j and Bi_j are the Pb and Bi contents in the samples, normalized to Ag + Bi + Pb = 1 (Makovicky and Karup-Møller 1977a).

† Calculated on the basis of 17 atoms.

the numerical method implemented in the program SADABS (Sheldrick 2008). The relation between the minimum and the maximum X-ray transmission-factors estimated by the program was 0.2563.

The structure refinement was performed in the orthorhombic *Bbmm* space group using the program SHELXL-97 (Sheldrick 1997) starting from the atom coordinates of natural Ag-bearing heyrovskýite (Takéuchi and Takagi 1974). The refinement converged to an agreement *R* value 0.0417 for 1312 reflections with $F_o > 4\sigma(F_o)$ [0.0523 for all the 1566 unique reflections]. Neutral scattering factors for Pb, Bi, and S were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). In the final refinement anisotropic displacement factors were used for all the atoms. The refinement without any constrains of the occupancies for metal sites allowed us to investigate the distribution of potential vacancies among the cation positions in the structure of the Ag-free heyrovskýite (Table 3). It showed 97% occupancy in Me3 (specified as pure Pb) and no vacancies were found on the other positions specified as Me1 = 100% Pb, Me2 = 100% Pb, Me4 and Me5 fixed to 50Bi/50Pb.

As suggested by the results of the microprobe study, about 0.5 atoms per formula unit (apfu) of selenium are present in the measured crystals of heyrovskýite. Therefore, the distribution of this element among the non-metal positions of the structure was investigated. The occupancies of the S sites were kept free during the refinements, whereas the cation occupancies were fixed to the previously assumed values. This showed that the anion positions S1 and S4 yield slightly higher electron density than the other sites; no indication of a heavier element resulted for the position S2, S3, and S5. Consequently, the S1 and S4 sites in Ag-free heyrovskýite were refined as mixed (S,Se) positions (Table 3).

TABLE 2. Summary of parameters describing data collection and refinement for Ag-free heyrovskýite from Vulcano

Simplified structural formula	$Pb_{5.82}Bi_{2.12}\square_{0.06}S_{8.70}Se_{0.30}$
Crystal dimensions (mm)	0.07 × 0.01 × 0.14
Crystal system, space group	Orthorhombic, *Bbmm*
a (Å)	13.7498(4)
b (Å)	31.5053(8)
c (Å)	4.1475(1)
V (Å^3)	1796.7(1)
Z	4
Temperature (K)	293
D_x (Mg/m)	7.294
X-ray conditions (kV, mA)	50, 30
Wavelength of radiation (Å)	0.71073
Detector to sample distance (mm)	45
Number of frames	2118
Rotation width per frame (°)	0.5
Measuring time (s)	20
Maximum covered 2θ (°)	61 (*d* = 0.70 Å)
Reflections measured	15351
Independent reflections	1566
Reflections with $F_o > 4\sigma(F_o)$	1312
R_{int} (%)	6.54
R_σ (%)	3.87
Ranges of *h*, *k*, *l*	$-19 \le h \le 18$ $-44 \le k \le 45$ $-5 \le l \le 5$
$R\ [F_o > 4\sigma(F_o)]$ (%)	4.17
R (all data) (%)	5.23
$wR\ [F_o > 4\sigma(F_o)]$ (%)	0.1140
w*R* (all data) (%)	0.1203
Goof	1.066
Refined parameters	58
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.050\,P)^2+190.5054\,P]$ where $P = (F_o^2+2F_c^2)/3$
$D\rho_{min}$, $D\rho_{max}$ (e/Å^3)	−4.78, 4.02

Fractional atomic coordinates, occupancies, and anisotropic displacement parameters are presented in Table 3, whereas selected Me-S distances are in Table 4.

As the atomic displacement ellipsoid of Me1 was more anisotropic than for other structural sites (elongated along [010]), and the sum of valences for this site was lower than the expected value of 2 (Table 5), a refinement with Me1 placed out of the symmetry plane was tried (with an isotropic displacement parameter). The resulting *R* factor was almost identical to that of an anisotropic refinement, and the influence on other parameters was negligible. The obtained displacement of the two equivalent sites with half occupation from the mirror plane was 0.006 Å. However, the calculation of the valence sum for such a Pb site gave only a slight improvement over the site on the symmetry plane (1.82 instead of 1.79), which shows that the coordination change is not very significant. The above evidence suggests, as already observed in the structure of lillianite (Pinto et al. 2006a) that the large anisotropy of the displacement parameters can be caused by a dynamic disorder of the Me1 atom over the two close sites out of the symmetry plane, or be a consequence of large movements inside a large coordination polyhedron.

Owing to the negligible difference in the scattering power of Pb and Bi, no direct refinement of cation occupancies was attempted and site population was assigned on the basis of crystal-chemical considerations based on the refined bond lengths (Table 4), the polyhedron volume (V_p), the volume of circumscribed sphere (V_s), eccentricity (ECC), sphericity (SPH), and the volume distortion (υ) of the coordination polyhedra. V_p, V_s, ECC, SPH, and υ were defined by Balić-Žunić and Makovicky (1996) and Makovicky and Balić-Žunić (1998), and their use in distinguishing Pb and Bi coordinations is discussed in Makovicky et al. (2001) and

TABLE 4. Selected interatomic distances (Å) for Ag-free and Ag-bearing heyrovskýites

Cation	Anion	(1)	(2)	(3)	(4)
Me1	–S3 × 2	2.832(5)	2.8(2)	2.86(4)	2.837(9)
	–S/Se1 × 4	3.199(3)	3.21(1)	3.27(3)	3.167(7)
	–S/Se4 × 2	3.529(5)	3.43(2)	3.21(3)	3.51(1)
Me2	–S2 × 2	2.949(4)	2.93(2)	2.87(4)	2.922(7)
	–S5 × 4	2.940(3)	2.94(1)	2.91(2)	2.951(9)
Me3	–S5 × 2	2.935(3)	2.91(1)	2.92(2)	2.934(7)
	–S5	2.947(4)	2.93(2)	2.85(3)	2.94(1)
	–S2 × 2	2.965(3)	2.99(1)	2.90(2)	2.968(6)
	–S/Se4	3.071(5)	3.10(2)	3.06(3)	3.07(1)
Me4	–S3	2.728(3)	2.68(1)	2.48(3)	2.7010(6)
	–S/Se1 × 2	2.866(3)	2.85(1)	2.76(3)	2.875(6)
	–S/Se4 × 2	3.002(3)	3.03(1)	3.06(2)	2.983(7)
	–S2	3.100(4)	3.07(2)	3.04(4)	3.082(9)
Me5	–S/Se1	2.713(4)	2.66(2)	2.54(4)	2.696(9)
	–S/Se4 × 2	2.869(3)	2.83(1)	2.82(2)	2.865(7)
	–S2 × 2	2.952(3)	2.91(1)	2.97(3)	2.933(6)
	–S5	3.181(4)	3.19(2)	3.22(3)	3.17(1)

Note: (1) from Vulcano (this study); (2) Ag-poor heyrovskýite (Takéuchi and Takagi 1974); (3) Ag-Bi-rich heyrovskýite (Makovicky et al. 1991); (4) synthetic heyrovskýite (Olsen et al. 2011).

TABLE 3. Fractional atomic coordinates, anisotropic displacement factors (Å^2), and occupancies (s.o.f.) for Ag-free heyrovskýite from Vulcano

Multiplicity	Site	*x/a*	*y/b*	*z/c*	s.o.f.	U_{11}	U_{22}	U_{33}	U_{12}	U_{equiv}
4*c*	Me1	0.42053(11)	0.25	0	1	0.0366(8)	0.0807(11)	0.0329(7)	0	0.0501(4)
4*a*	Me2	0.5	0	0	1	0.0201(5)	0.0206(4)	0.0173(4)	0.0005(3)	0.0193(2)
8*f*	Me3	0.22858(5)	0.05814(2)	0	0.974(4)	0.0195(4)	0.0223(3)	0.0166(3)	0.0009(2)	0.0195(2)
8*f*	Me4	0.18197(5)	0.17479(2)	0.5	1	0.0253(4)	0.0214(3)	0.0203(3)	0.0003(2)	0.0223(2)
8*f*	Me5	0.45567(5)	0.11896(2)	0.5	1	0.0207(4)	0.0216(3)	0.0181(31)	−0.0004(2)	0.02011(18)
8*f*	S/Se1	0.0461(3)	0.19549(12)	0	1	0.028(3)	0.022(2)	0.025(2)	−0.0016(15)	0.0250(14)
8*f*	S2	0.0877(3)	0.08542(12)	0.5	1	0.021(2)	0.0173(17)	0.0160(18)	0.0010(15)	0.0180(8)
4*c*	S3	0.2803(5)	0.25	0.5	1	0.024(3)	0.023(3)	0.024(3)	0	0.0239(13)
8*f*	S/Se4	0.3254(4)	0.14598(15)	0	1	0.026(3)	0.037(3)	0.019(2)	0.0094(18)	0.0271(15)
8*f*	S5	0.3614(3)	0.02677(13)	0.5	1	0.015(2)	0.0251(2)	0.0133(17)	0.0001(15)	0.0180(8)

Notes: The anisotropic displacement parameters are defined as: $\exp\,[-2\pi^2\Sigma_i^3 = {}_1\Sigma_j^3 = {}_1U_{ij}a_i^*a_j^*h_ih_j]$, U_{equiv} according to Fischer and Tillmanns (1988). U_{23} and U_{13} are equal to 0. Me1 and Me3 are pure Pb sites; Me2 has 72% Pb and 28% Bi, Me4 and Me5 contain 54% Pb and 46% Bi each (Pb-Bi occupancies were obtained from the values reported in Table 5 renormalized for the factor 1.233; more explanations are the text). Site occupation factors assumed during the refinement were: Me1, Me2, and Me3 = 100% Pb; Me4 and Me5 = 50% Bi, 50% Pb. Refined ratios of scattering functions for sites S/Se1 and S/Se4 are 0.91(2)/0.09(2) and 0.94(2)/0.06(2), respectively. Formula from crystal structure: $Pb_{5.82}Bi_{2.12}\square_{0.06}S_{8.70}Se_{0.30}$.

TABLE 5. Coordination parameters* for cation sites in Ag-free and Ag-bearing heyrovskýites

Atom/Site	C.N.	<*d*>	d_{min}	d_{max}	V_s	ECC_v	SPH_v	V_p	υ	Valence	Pb† occ.	Bi† occ.	Ag‡ occ.
Ag-free heyrovskýite (this study)													
Me1	8	3.2(3)	2.832(5)	3.529(5)	135.887	0.0552	0.7577	56.2(1)	0.0458	1.79	1	0	
Me2	6	2.943(5)	2.940(3)	2.949(4)	106.771	0.0000	0.9953	33.99(7)	0.0000	2.08	0.78	0.22	
Me3	6	2.97(5)	2.935(5)	3.071(5)	109.883	0.0658	0.9702	34.88(7)	0.0028	1.98	0.94	0.03	
Me4	6	2.9(1)	2.728(3)	3.100(4)	104.932	0.2063	0.9882	33.24(6)	0.0048	2.35	0.59	0.37	
Me5	6	2.9(2)	2.713(4)	3.181(4)	104.691	0.2268	0.9825	33.20(7)	0.0036	2.41	0.6	0.38	
Ag-poor heyrovskýite (Takéuchi and Takagi 1974)													
Me1	8	3.167	2.822	3.431	132.94	0.1110	0.7944	55.209	0.0419	1.82	1	0	
Me2	6	2.940	2.933	2.944	106.484	0	0.9943	33.890	0.0001	2.09	0.77	0.23	
Me3	6	2.969	2.906	3.095	109.922	0.1018	0.9690	34.832	0.0045	1.96	0.96	0.04	
Me4	6	2.918	2.683	3.070	104.056	0.2290	0.9666	32.860	0.0079	2.49	0.51	0.4	0.09
Me5	6	2.887	2.662	3.190	101.080	0.2555	0.9713	31.987	0.0059	2.62	0.36	0.64	
Ag-Bi-rich heyrovskýite (Makovicky et al. 1991)													
Me1	8	3.153	2.859	3.269	130.867	0.2154	0.9024	54.974	0.0309	1.77	1	0	
Me2	6	2.898	2.867	2.913	101.920	0	0.9755	32.390	0.0016	2.35	0.44	0.56	
Me3	6	2.925	2.851	3.061	105.374	0.1066	0.9795	33.259	0.0084	2.21	0.63	0.37	
Me4	6	2.858	2.479	3.057	97.916	0.3363	0.9193	30.850	0.0102	2.35	0.04	0.31	0.65
Me5	6	2.889	2.541	3.218	101.515	0.3189	0.9866	32.019	0.0091	2.80	0.37	0.63	
Synthetic heyrovskýite (Olsen et al. 2011)													
Me1	8	3.8(3)	2.837(9)	3.51(1)	133.433	0.0353	0.7629	55.2 (3)	0.0456	1.83	1	0	
Me2	6	2.93(2)	2.922(7)	2.951(9)	105.571	0.0000	0.9846	33.6(2)	0.0000	2.14	0.70	0.30	
Me3	6	2.97(5)	2.934(7)	3.07(1)	109.882	0.0684	0.9722	34.9(26)	0.0028	1.95	0.94	0.03	
Me4	6	2.9(1)	2.710(6)	3.082(9)	103.955	0.1990	0.9816	32.9(1)	0.0055	2.34	0.55	0.45	
Me5	6	2.9(2)	2.696(9)	3.17(1)	103.439	0.2271	0.9851	32. 8(2)	0.0044	2.43	0.53	0.47	

Notes: <*d*> = average bond distance, V_s = volume of the circumscribed sphere, V_p = volume of the coordination polyhedron, υ = volume distortion, ECC_v = volume-based eccentricity of the coordination, SPH_v = volume-based sphericity of the coordination.

* The parameters for atom coordinations are defined in Balić-Zunić and Makovicky (1996) and Makovicky and Balić-Zunić (1998). Bond valence calculations were made using the parameters of Brese and O'Keeffe (1991). All calculations were done by IVTON (Balić-Zunić and Vicković 1996). For the mixed sites the calculated valences of individual species are multiplied by the fractional occupancies and summed.

† Based on V_p (see text).

‡ From the chemical analysis (Ag-poor) or structure refinement (Ag-rich).

Berlepsch et al. (2001). The results of these calculations are summarized in Table 5.

To check for the presence of satellite reflections at a short distance from the main reflections as observed in the HRTEM study (Mitolo 2009; Mitolo et al. 2011), a new data collection with an increased sample-to-detector distance up to 7.86 cm has been performed. The instrument used was a Bruker AXS four-circle diffractometer equipped with CCD 1000 area detector (6.25 × 6.25 cm active detection-area, 512 × 512 pixels) and a flat graphite monochromator (Mo$K\alpha$ radiation from a fine-focus sealed X-ray tube). A total of 2520 frames were collected with an exposure time of 60 s per frame and crystal rotation 0.2° per frame. No traces of satellite reflections could be observed from the measured diffraction pattern suggesting that the bulk crystal structure in the investigated crystal is not significantly influenced by modulations or that the structure modulations are not present at all in the crystal. The structure refinement produced results in full correspondence with those obtained from the previous refinement.

For comparison, a new refinement was attempted on data collected previously for a synthetic $Pb_6Bi_2S_9$ at atmospheric pressure in the course of the high-pressure study (Olsen et al. 2011) using the program JANA2006 (Petricek et al. 2006). The synthesis conditions are described by Elcoro et al. (2008). As already observed for the natural Ag-free heyrovskýite, all sites of the structure resulted fully occupied except Me3, which showed 0.966(7) occupancy.

The CIF-files with structure data of the natural Ag-free heyrovskýite from Vulcano and the synthetic heyrovskýite can be download from the Inorganic Crystal Structure Database at FIZ Karlsruhde, Germany (CSD numbers 422351 and 422352, respectively), or from the MSA Supplementary Data[1] site.

RESULTS AND DISCUSSION

The structure of Ag-free heyrovskýite from Vulcano (Fig. 1) contains five independent cation positions, four of which show octahedral coordination (Me2, Me3, Me4, and Me5) and form an octahedral chain Me4-Me5-Me3-Me2-Me3-Me5-Me4 running diagonally across the structural slabs. The Me1 site, which displays a standing bicapped trigonal-prismatic coordination when viewed along the **c**-axis, is situated on the mirror plane that connects the adjacent, mirror-related galena-type layers. The details of the crystal structure are the same as that of the natural Ag-bearing heyrovskýites described by Takéuchi and Takagi (1974) and Makovicky et al. (1991), except for quantitative differences in the atomic coordinations (Tables 4 and 5).

As mentioned earlier, the very small difference in the scattering power of Pb and Bi does not allow a direct refinement of their occupancies at cationic positions. One would expect that the bond valence calculations could give an easy evaluation of the distribution of Pb and Bi, because the Pb-S and Bi-S have the same bond valence parameters according to the best statistical analysis available (Brese and O'Keeffe 1991). However, as often observed in the applications of the simple bond-valence formalism, reliable quantitative results cannot be obtained in this way. It is illustrated also in Table 5, by a significant deficit of valence in the Me1 site and a significant deficit in the sum of Bi on other sites compared with the results of the chemical analyses. As shown in the analysis of the crystal structure of neyite (Makovicky et al. 2001) more reliable results can be obtained for the Pb/Bi substitutions in octahedral coordinations if the volumes of the coordination polyhedra or the volumes of the circumscribed spheres are used to quantify their contents. They are used also in this work, like in the analysis of the more ordered monoclinic polymorph ashamalmite (Callegari and Boiocchi 2009). We assume the following values for the pure Pb and Bi coordinations, respectively (V_p;V_s): 35.0 Å^3; 110.2 Å^3 and 30.3 Å^3; 95.6 Å^3. They are the same as obtained from the analysis of neyite and are confirmed by the excellent match to the values of coordinations in galena, PbS [34.84(5) Å^3; 109.5(1) Å^3; Noda et al. 1983] and the Bi octahedral

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[1] Deposit item AM-11-034, CIFs. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

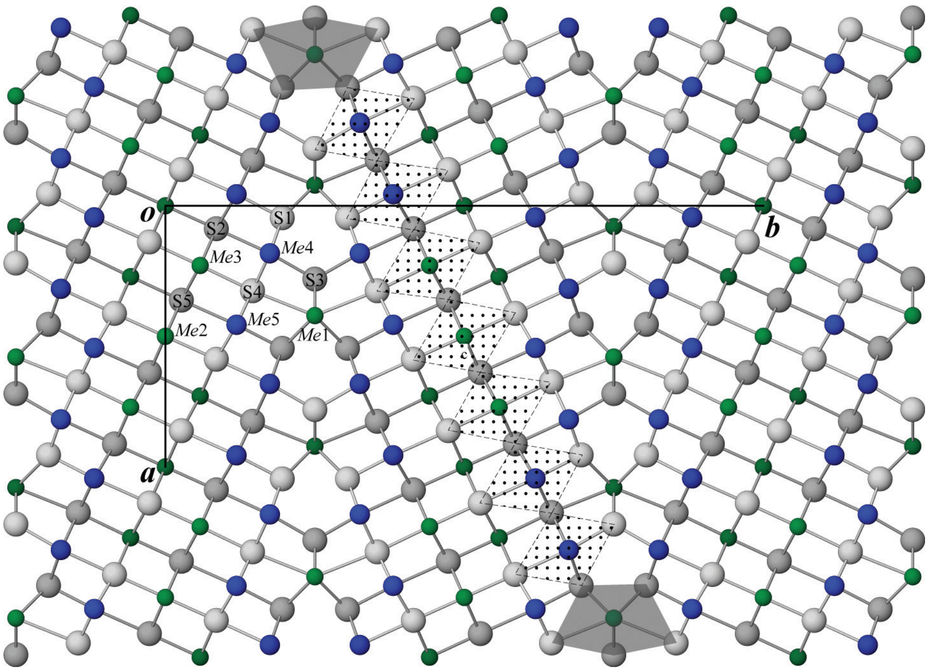

FIGURE 1. The crystal structure of Ag-free heyrovskýite from Vulcano. Projection on (001). In order of decreasing size, spheres represent S (gray), mixed (Pb,Bi) positions (dark blue), Pb-dominated positions (green). Lightly and darkly shaded circles indicate atoms at z = ½ and z = 0, respectively, along the ~4 Å axis. Stippled = chain of *N* octahedra running diagonally across an individual PbS-like layer; gray-shades = bicapped trigonal prisms around Me1. ATOMS program was used for drawing. (Color online.)

coordination in $Cu_4Bi_5S_{10}$ [30.4(2) $Å^3$; 95.8(6) $Å^3$; Mariolacos et al. 1975]. The relative amounts of Pb and Bi at octahedral sites are found assuming a linear dependence of the volume of the octahedron on the contents of Pb and Bi. Like in the case of neyite, the values obtained with polyhedral volumes do not differ significantly from those obtained with volumes of circumscribed spheres, but the former give sums closer to those of the chemical analyses and are therefore used in Table 5. Differences with the compositions obtained from chemical analyses can be explained for each case.

In the case of the sample from Vulcano, the underestimation of the Bi content is due to the presence of Se in the structure. As can be seen from the values of lattice parameters and the volume of the unit cell, the substitution of Se for S in our sample produces increase in the volume of the unit cell of 1% compared to the synthetic Se-free sample (Table 6). It can therefore be expected that the volumes of the coordination polyhedra are overestimated with respect to the reference [PbS_6] and [BiS_6] coordinations and this must produce an underestimation of the Bi content. We can try to renormalize the calculated amounts of Bi assuming that the sum pfu should correspond to the value obtained by the chemical analysis (2.12). The renormalization factor for the values from Table 5 is then 1.233, which gives the values used for the Table 3 as the most probable values of Pb/Bi occupancies. Note that we neglect the very small amount of Bi calculated for the Me3 site.

In the case of the synthetic sample, the structure refinement suggests a total of ~0.06 vacancies pfu concentrated in the Me3 site, in agreement with the result obtained on heyrovskýite from Vulcano. This evidence indicates that the cation population of synthetic heyrovskýite is practically the same as that of natural Ag-free species above described and that the differences between these two structures are only related to Se-for-S substitutions occurring in the natural phase. This conclusion is generally confirmed by comparison of coordination parameters and site occupancies calculated for the two structures (Table 5).

In the case of the Ag-rich heyrovskýite, the apparent deficit of Bi can be due to the calculation procedure applied for the Me4 site. The calculation of the Pb and Bi contents in the sites where Ag is present is accomplished by calculating the contribution

TABLE 6. Unit-cell parameters for Ag-free and Ag-bearing heyrovskýites

	Composition	*a* (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)	Space group	*Z*	Ref.
Ag-free heyrovskýite	$(Pb_{5.86}Cd_{0.03})_{Σ5.89}Bi_{2.04}(S_{8.52}Se_{0.53}Cl_{0.03})_{Σ9.08}$	13.7498(4)	31.5053(1)	4.1475(1)	1796.66(7)	*Bbmm*	4	(1)*
Ag-poor heyrovskýite from Yakuki mine	$Pb_{5.40}Ag_{0.18}Bi_{2.42}S_9$	13.712(2)	31.210(5)	4.131(1)	1767.9(6)	*Bbmm*	4	(2)*
	$Pb_{5.53}Ag_{0.20}Cu_{0.02}Bi_{2.24}S_9$	13.719	31.260	4.127	1769.888	*Bbmm*	4	(3)†
	$Pb_{5.15}Ag_{0.38}Bi_{2.44}S_9$	13.704	31.247	4.124	1765.933	*Bbmm*	4	
Ag-Bi-rich heyrovskýite	$(Pb_{3.67}Cd_{0.05})_{4.72}Ag_{1.15}Bi_{3.13}S_{9.19}$	4.110(1)	13.600(3)	30.485(12)	1704.0(9)	*CmCm*	4	(4)*
Synthetic heyrovskýite	–	13.719(4)	31.393(9)	4.1319(10)	1779.5(1.4)	*Bbmm*	4	(5)*

Note: (1) from Vulcano (this study); (2) Takéuchi and Takagi (1974); (3) Shimizu et al. (1993); (4) Makovicky et al. (1991); (5) Olsen et al. (2011).
* Obtained by X-ray single crystal data.
† Obtained by powder diffraction data.

of Ag to the volume of the polyhedron assuming 30.8 Å^3 as the volume of the pure [$\mathrm{AgS_6}$] octahedron (Makovicky et al. 2001). For Me4 in Ag-poor and Ag-rich heyrovskýite the calculation was done according to the formula $V_p = \mathrm{Ag}\cdot 30.8 + (1 - \mathrm{Ag})X$, where Ag is the content of Ag at the site (0.09 and 0.65, respectively) and X is the volume due to the Bi+Pb content. The relative contents of Pb and Bi are then calculated from X as for other sites. The estimation can be largely biased in the case of Ag-rich crystal where the site is dominated by Ag, due to increased distortion of the site (see later) and the (small) content of Pb might well be unrealistic. If only Bi is assumed together with Ag at this site, the obtained sum has a negligible difference to the one expected from a stoichiometric composition.

The main differences among various structures as regards the interatomic distances can be summarized as follows: in the case of Me1 it can be observed that the introduction of Ag equalizes the 6 longest bonds (Table 4). In the Ag-free heyrovskýite, on the contrary, the bonds to four S1 atoms are significantly shorter than the bonds to two S4 atoms. The crystal structure analysis of the Ag-rich sample (Makovicky et al. 1991) did not indicate any atomic substitution on this site and the differences should be considered as a consequence in changes in other coordinations. In particular, the S4 atoms are shared with the Me4 site, which houses Ag and the shortening of Me1-S4 bonds can thus be a consequence of the lack of the valence electrons at the Me4 site, which is compensated by a stronger bonding to Me1. It is accomplished by displacement of Pb atom from the center of the trigonal prism toward the S3 atoms and away from the S1 atoms, combined with the approach of the two S4 atoms toward the prism. It can be seen also in the distortion parameters where the eccentricity of the Me1 site and the sphericity of its coordination increase with the Ag content at Me4.

Me2, the symmetric octahedrally coordinated site in the center of the slab, shows a shortening of two bonds to S2 atoms with increased Ag+Bi substitution in heyrovskýite. In the Ag-rich sample they become even shorter than the four bonds to S5 atoms, contrary to the situation in the Ag-free sample. This might be a result of the increase of the Bi content at this site, but also of the increased Ag content at the Me4 site with which the S2 atoms are shared. As a consequence, the Me2 coordination, which is a practically perfect octahedron, with almost perfect sphericity and absence of any volume distortion, in Ag-free and Ag-poor heyrovskýite and in the synthetic sample, becomes slightly distorted with a lower sphericity in the Ag-rich sample.

The Me3 site occupies the largest of the octahedral coordinations and in Ag-free and Ag-poor crystals represents a practically pure Pb site. In the Ag-rich sample, however, it contains about 1/3 of Bi. This can be related to the general shortening of bonds and an increase in eccentricity and volume distortion.

The largest influence on the coordination parameters is seen, as can be expected, for the Me4 site in which Ag is incorporated. It shows the most pronounced shortening of the shortest bonds when compared with the Ag-free sample, together with a prominent increase in eccentricity and decrease in sphericity, which both can be connected to de-centrally placed Ag with significantly shorter bonds to S when compared to Pb or Bi. It is interesting that according to the present analysis this site contains some surplus of Pb over Bi in the Ag-free, but also in the Ag-poor sample, whereas in Ag-rich one it contains practically only Ag and Bi.

The Me5 site becomes Bi-dominated already in the Ag-poor crystal. The increase of the Bi content is characterized by the shortening of the shortest and lengthening of the longest bonds, which is also reflected in the increased eccentricity. It is interesting that the calculation shows that the Bi content does not increase in this site over ~2/3, even in the Ag-rich crystal. In it the surplus of Bi coming from the Ag+Bi substitution for Pb is incorporated in the central octahedra of the PbS-like slabs (Me2 and Me3).

Refinement of selenium occupancy showed incorporation of this element only in the anion sites S1 and S4, with S/Se ratios of scattering functions of 0.91(2)/0.09(2) and 0.94(2)/0.06(2), respectively. The former anion site has square pyramidal coordination, the latter octahedral coordination. No selenium was found in the octahedral anion sites S2 and S5, as well as in the tetrahedral anion site S3. This suggests that the distribution of Se among anion sites of heyrovskýite is connected not only to the coordination characteristics of the sites, but also to their position in the structure. The preference of Se for the square pyramidal anion site and the lack of this element in the tetrahedrally coordinated anion site are consistent with the results obtained for the structure of lillianite (Pinto et al. 2006a). Among the octahedrally coordinated anionic sites only the S4 site, which lies in the marginal portions of the PbS-like slabs, shows a preference for Se, whereas the two sites in the central portion of the slabs remain free of Se. The resulting total Se is 0.30(8) apfu, which is less than the amount of this element obtained by microprobe investigations [0.53(4) apfu]. The disagreement could be ascribed to the difficulty in refining such a low concentration.

The investigated sample of Ag-free heyrovskýite from Vulcano differs from the ideal composition, $\mathrm{Pb_6Bi_2S_9}$, by a slight surplus of bismuth. The value of chemical N calculated for the mean composition ($N_{\mathrm{chem}} = 6.78$) is less than the crystallographically defined theoretical value ($N = 7$). Makovicky (1981) points out that non-integral values of N, generally smaller than the theoretical one, may be due either to vacancies in the metal positions, created by the substitution $3\mathrm{Pb}^{2+} \rightarrow 2\mathrm{Bi}^{3+}+\square$, or to errors due to "chemical twinning," which introduces slabs of different thicknesses belonging to other homologues of the series. TEM investigations underline the presence of lillianite/heyrovskýite intergrowths in samples from Vulcano (Mitolo 2009; Mitolo et al. 2011). On the other hand, calculation of vacancies from the general formula of the lillianite homologous series, $\mathrm{Pb}_{N-1-2x}\mathrm{Bi}_{2+x}\mathrm{Ag}_x\mathrm{S}_{N+2}$, considering $x = 0$ and $N = 6.78$, suggests the presence of 0.03 vacancies per formula unit (pfu) in the investigated Ag-free heyrovskýite sample (Table 1). Although the number of calculated vacancies is very small, the good quality of the X-ray data allowed their direct refinement, giving ~0.03 $\square$ in the sole Me3 site. This calculates to a total of 0.06 vacancies pfu, which is a value just slightly higher than that suggested by the chemical composition. The discrepancy can be assumed as close to the resolution limits of the methods.

As suggested by the results of the electron microprobe study, Cl and Cd are present as traces in the investigated heyrovskýite in the amount of about 0.03 apfu each. While Cd-bearing heyrovskýites were already described by Borodaev et al. (2003)

and Moëlo et al. (1987), this is the first time that Cl is found in heyrovskýite although the occurrence of minor Cl substituting for S has been recently reported in several Pb-Bi sulfosalts, i.e., lillianite (Borodaev et al. 2001) and galenobismutite (Pinto et al. 2006a). In addition, this element was found to be an essential chemical component in the sulfosalts vurroite [$Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$; Garavelli et al. 2005; Pinto et al. (2008)], tazieffite [$Pb_{20}Cd_2(As,Bi)_{22}S_{50}Cl_{10}$; Zelenski et al. (2009)], ardaite [$Pb_{10}Sb_6S_{17}Cl_{l4}$; Breskovska et al. (1982)], dadsonite [$Pb_{23}Sb_{25}S_{60}Cl$; Moëlo (1979)], pillaite [$Pb_9Sb_{10}S_{23}ClO_{0.5}$; Orlandi et al. (2001)], and pellouxite [$(Cu,Ag)_2Pb_{21}Sb_{23}S_{55}ClO$; Orlandi et al. (2004)]. Several Cd-bearing phases are also known among natural sulfosalts. For instance, Pattrick (1978) reported Cd-rich varieties of tetrahedrite, ~$Cu_{10}Cd_2Sb_4S_{13}$, and, according to Moëlo et al. (1984, 1989), Cd is an essential component of ramdohrite, ideally $CdPb_{12}Ag_{5.5}Sb_{21.5}S_{48}$. Furthermore, Cd was found as essential chemical component in the Cd-Pb-Bi sulfosalts kudriavite $(Cd,Pb)Bi_2S_4$ (Chaplygin et al. 2005) and tazieffite (Zelenski et al. 2009) and as a minor chemical component in lillianite and mozgovate from "La Fossa" crater, Vulcano Island, Italy (Borodaev et al. 2001; Vurro et al. 1999), as well as in Ag-rich heyrovskýite, vikingite, and gustavite from La Roche-Balue (Moëlo et al. 1987).

Since the amounts of Cl and Cd detected in the investigated heyrovskýite samples are very small, no direct information can be obtained from the refinement about the distribution of these elements in the structure of Ag-free heyrovskýite from Vulcano. In the case of Cl, a further difficulty is the negligible difference between the scattering power of Cl and that of S. Previous investigations of the S-Cl substitutions in sulfosalts with more pronounced Cl content did not show some specific regularity or preference, which can be related to the case of heyrovskýite [see e.g., Pinto et al. (2006b, 2008)]. In the case of Cd, the previous investigations on sulfosalts show its preference for regular octahedral coordinations (Evstigneeva et al. 1973, Choe et al. 1997, Balić-Žunić and Makovicky 2007; Zelenski et al. 2009) and it can be supposed that this element preferentially occupies the octahedrally coordinated sites in the investigated structure of heyrovskýite.

CONCLUDING REMARKS

Our X-ray single-crystal study performed on a selected sample of Ag-free heyrovskýite from Vulcano [$(Pb_{5.86}Cd_{0.03})_{\Sigma5.89}Bi_{2.04}(S_{8.52}Se_{0.53}Cl_{0.03})_{\Sigma9.08}$, $N_{chem} = 6.78$], allowed to investigate the Pb-Bi ordering in the structure of heyrovskýite in the absence of Ag. The study of the distribution of Pb and Bi over the metal positions of the structure of heyrovskýites with varying content of Ag has been performed on the basis of the volumes of polyhedra. It generally confirms the previous conclusions about the preference of Pb for the trigonal-prismatic coordinated site at the border plane between the PbS-like slabs (Me1) and the two central octahedra of the slabs (Me2 and Me3), whereas Bi prefers the marginal octahedral coordinaed sites (Me4 and Me5) (Takéuchi and Takagi 1974; Makovicky et al. 1991). However, the present analysis suggests some modifications in the quantitative distribution of Pb and Bi among the octahedral sites compared to previous works on heyrovskýite. In their analysis of an Ag-rich heyrovskýite Makovicky et al. (1991) assumed Me4 and Me5 sites to be a Ag/Bi and a pure Bi site, respectively. They also assumed that the rest of Bi expected from stoichiometry is equally distributed in Me2 and Me3 sites (with 20% occupancy). We show that V_p values generally confirm their assumptions about the Bi content in Me4 and Me3, but also suggest that significantly more Bi enters Me2 site and that Me5 contains about 1/3 of Pb. This is in better accordance with the results obtained for the Ag-free and Ag-poor samples in, which the volume of Me2 is significantly smaller than that of Me3 (or the one characteristic for the pure Pb site) suggesting some Bi content in this site even without Ag+Bi substitution. An interesting result of the present analysis is also that the Me5 site does not become exclusively populated by Bi even in the Ag-rich sample, where the excess Bi starts to enter Me2 in larger quantities and even the Me3 site, which in the Ag-free and Ag-poor samples is a practically pure Pb-site.

The analysis of the distortion parameters of coordination polyhedra shows that the Ag+Bi substitution for Pb introduces more distortion to atomic coordinations. If this substitution has any at all stabilizing effect on the heyrovskýite structure, it would be connected to the distribution of chemical bonds and cannot be due to making more regular configuration of the PbS-like slabs.

The possible extent of the Ag incorporation in heyrovskýite is an interesting question. Based on the assumption that the trigonal prismatic coordinated site remains solely a Pb-site, whereas Ag could be substituted at all octahedral sites, the maximum possible substitution coefficient was defined as $x_{max} = (N - 2)/2$ (Makovicky and Karup-Møller 1977a, 1977b; Makovicky and Balić-Žunić 1993). For heyrovskýite this would lead to the formula $PbBi_{4.5}Ag_{2.5}S_9$. However, this would involve a full occupancy of Ag on Me4 site plus additional substitution on other sites. So-far known Ag-rich crystal structures from the homologous series have confirmed a 50% Ag occupancy in the marginal octahedral site in the Ag-rich end-member of the lillianite substitution series—gustavite (Bente et al. 1993), 50 and 40% substitutions in the lillianite-like and the heyrovskýite-like slabs, respectively of the $^{4,7}L$ homologue vikingite (Makovicky et al. 1992) and already mentioned 65% substitution in the Ag-rich heyrovskýite (Makovicky et al. 1991), all exclusively in the marginal octahedral sites of the slabs. As can be seen, none of the known structures exhibits a fully Ag-occupied marginal site or Ag at some other structural site, so the maximum Ag substitution in the series could be supposed never to exceed 2, which would correspond to the fully occupied marginal sites, even in heyrovskýite and higher homologues. According to the present observation of the naturally occurring Ag-free heyrovskýite and the continuous nature of the crystal-chemical characteristics of the Ag-substitution in the structure, the results support an existence of the solid-solution series between Ag-free heyrovskýite and the Ag-rich member, which can tentatively be defined with a composition $Pb_2Bi_4Ag_2S_9$ and thus would deserve a specific mineral name in accordance with the opinion from the review of sulfosalt systematics (Moëlo et al. 2008). The sample investigated by Makovicky et al. (1991) falls already inside the field of this end-member.

The equal populations of Pb and Bi in the marginal octahedral sites Me4 and Me5 in pure heyrovskýite are in accordance with the conclusions of Callegari and Boiocchi (2009) in their recent study of the crystal structure of aschamalmite, $Pb_6Bi_2S_9$. They ascribed the lowering of symmetry in aschamalmite to geometrical differences between the octahedral sites in the two pseudo-mirror related PbS-like slabs (the so called A- and B-type layers), which comprise an almost complete order of Pb and Bi among the octahedral sites. The inner octahedral coordinations of the slabs in aschamalmite, which correspond to the sites Me2 and Me3 of heyrovskýite contain dominantly Pb and pure Pb, respectively, whereas an alternation between Pb-dominated coordination octahedra and Bi coordination octahedra is present on the sites at the margin of the octahedral slabs corresponding to the sites Me4 and Me5 of heyrovskýite. The analysis suggests the following ordering sequences: $^{[Me4A]}$Bi-$^{[Me5A]}$Pb facing $^{[Me4B]}$Pb-$^{[Me5B]}$Bi in about 70% of the unit cells and the opposite ordering scheme $^{[Me4A]}$Pb-$^{[Me5A]}$Bi facing $^{[Me4B]}$Bi-$^{[Me5B]}$Pb in the remaining 30% of the unit cells. According to Callegari and Boiocchi (2009), it is expected that the two opposite ordering schemes occur in the same percentage statistically distributed in the crystal structure of heyrovskýite, resulting in its orthorhombic symmetry. The mixed (Pb,Bi) character of the Me4 and Me5 structure sites outlined in the present study for the pure heyrovskýite from Vulcano supports this conclusion. On the other hand, the solid solution with the Ag-Bi-rich end-member is expected to prevent completely the formation of a monoclinic analog with the aschamalmite-type structure, because Ag shows preference for exclusively Me4 site and thus prevents the Pb/Bi ordering of the same type.

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