

Leguernite, $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$, a new Bi oxysulfate from the fumarole deposit of La Fossa crater, Vulcano, Aeolian Islands, Italy

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ABSTRACT

Leguernite, ideally $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$, is a new mineral found in high-temperature fumarolic assemblages at La Fossa crater, Vulcano, Aeolian Islands, Italy. It occurs as aggregates of needle-shaped crystals associated strictly with anglesite, baličžuničite and an unknown Bi sulfate. Leguernite is colourless to white, transparent, non-fluorescent, has a sub-adamantine lustre and a white streak. Electron microprobe data led to the chemical formula (on the basis of 34 anions p.f.u.) $(\text{Bi}_{12.40}\text{Pb}_{0.15})_{\Sigma=12.55}\text{S}_{5.08}\text{O}_{34}$. The calculated density is 7.375 g cm^{-3} . A Raman spectrum collected on a single crystal of leguernite confirmed the anhydrous nature of the mineral.

Leguernite is monoclinic, space group $P2_1$, with $a = 11.2486(11)$, $b = 5.6568(6)$, $c = 11.9139(10) \text{ \AA}$, $\beta = 99.177(7)^\circ$, $V = 748.39(12) \text{ \AA}^3$ and $Z = 1$. The crystal structure is built up of Bi–O blocks of a fluorite-like structure with $\text{Bi}_{12}\text{O}_{14}$ composition separated by a single sulfate ion along [100] and by $\text{Bi}(\text{SO}_4)_4^{5-}$ groups along [101]. It can also be described as composed of (001) layers with composition $[\text{Bi}_{12}\text{O}_{14}(\text{SO}_4)^{6+}]_n$ alternating with layers of composition $[\text{Bi}(\text{SO}_4)_4]_n^{5-}$ along [001]. Leguernite shows significant similarities with the synthetic $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ compound.

The eight strongest reflections in the powder X-ray diffraction data [d in Å (hkl)] are: 3.220 (100) (013), 3.100 (95) ($\bar{3}11$), 2.83 (30) (020), 2.931 (25) (302), 2.502 (25) ($\bar{3}04$), 2.035 (20) (322), 1.875 (20) ($\bar{3}24$) and 5.040 (15) (110).

The name is in honour of François “Fanfan” Le Guern (1942–2011), who was a very active volcanologist and specialist in volcanic gases and sublimates. Both the mineral and the mineral name have been approved by the IMA-CNMNC (2013–051).

KEYWORDS: leguernite, Bi oxysulfate, new mineral, fumarole sublimates, Vulcano, fluorite-related crystal structure, Aeolian Islands, Italy.

Introduction

LEGUERNITE, ideally $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$, is the second Bi oxysulfate after baličžuničite, $\text{Bi}_2\text{O}(\text{SO}_4)_2$ (Pinto *et al.*, 2013, 2014), which forms as a high-temperature sublimate at La Fossa crater, Vulcano, Aeolian Islands, Italy. The

finding of these Bi sulfates represents a novelty in the mineralogy of high-temperature sublimates of La Fossa crater, which is mainly characterized by Pb–Bi sulfide and sulfosalt assemblages. Along with baličžuničite $\text{Bi}_2\text{O}(\text{SO}_4)_2$ (Pinto *et al.*, 2013, 2014), cannonite $\text{Bi}_2(\text{SO}_4)\text{O}(\text{OH})_2$ (Stanley *et al.*, 1992; Capitani *et al.*, 2013) and riomarinaite $\text{Bi}(\text{SO}_4)(\text{OH})\cdot\text{H}_2\text{O}$ (Graunar and Lazarini, 1982; Rögner, 2005), leguernite represents the fourth Bi sulfate (without additional cations) found in

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nature and, after baličžunicite, the second one completely lacking water molecules or (OH)⁻ groups. Additional Bi sulfates with still uncertain composition have been characterized recently by Capitani *et al.* (2014) with automatic electron diffraction tomography.

Synthetic bismuth oxide phases containing tetrahedral groups such as sulfate are of interest as potential oxide ion conductors (Smirnov *et al.*, 2003; Crumpton and Greaves, 2004). A number of investigations in the Bi₂O₃–SO₃ system have shown the existence of more than 10 different bismuth oxysulfates (Jones, 1984; Aurivillius, 1987, 1988; Francesconi *et al.*, 1998; Smirnov *et al.*, 2003; Crumpton and Greaves, 2004), with a Bi₂O₃:SO₃ ratio ranging from 2:3 to 14:1. These materials have structures often related to that of fluorite and some of them exhibit relatively high ionic-conducting properties (Smirnov *et al.*, 2003; Crumpton and Greaves, 2004). Aurivillius (1987) described two bismuth oxysulfates with compositions Bi₂₆O₂₇(SO₄)₁₂ and Bi₁₄O₁₆(SO₄)₅, respectively, which were prepared from the pyrolysis of Bi(SO₄)₃. Both compounds contain free (SO₄)²⁻ ions and fluorite-related regions: (Bi₂O₂)²⁺ layers in Bi₂₆O₂₇(SO₄)₁₂ and isolated (Bi₁₄O₁₆)¹⁰⁺ blocks extended infinitely along [010] in Bi₁₄O₁₆(SO₄)₅.

Several synthetic bismuth oxysulfates exhibiting a fluorite-related superstructure have been described recently: Francesconi *et al.* (1998) reported the synthesis and structure of a new Bi oxysulfate with composition Bi₁₄O₂₀(SO₄); Smirnov *et al.* (2003) described two Bi oxysulfates with composition Bi₉SO_{16.5} and Bi₁₅SO_{25.5}, respectively, and investigated some of their chemical and physical properties; Crumpton and Greaves (2004) investigated the structural chemistry and oxide ion-conducting properties of synthetic Bi₈O₁₁(SO₄).

The new mineral, leguernite, Bi_{12.67}O₁₄(SO₄)₅, described here, does not correspond to any synthetic phase but has a structure characterized by extensive fluorite-related regions.

The mineral and its name were approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2013-051; Garavelli *et al.* 2013a).

The name honours François Le Guern (1942–2011), better known as “Fanfan”. With a large number of publications under his belt, Fanfan Le Guern was a very active volcanologist, and an expert on volcanic gases and sublimates. He was the first to develop an entirely original

method for the collection and analysis of high-temperature gases and condensates – based on the introduction of silica tubes into fumarole vents – which is still applied in volcanology and industry. We were lucky to meet and to work with him in 1993 on Vulcano island, where we arrived independently to sample crater sublimates. His enthusiastic way of working, his extensive knowledge, and his friendship remain as our best memories of Fanfan.

The holotype of leguernite is deposited in the mineral collection of the Museum “C.L. Garavelli”, Dipartimento di Scienze della Terra e Geoambientali, Università di Bari, Italy, under the catalogue number 18/nm-V28.

Occurrence and physical properties

Leguernite was found in a cavity of a volcanic rock sample. The specimen was collected at Vulcano in 1990 from the walls of the high-temperature fumarole FF ($T = 600^{\circ}\text{C}$, direct measurement), which was sited on the inner slope of the crater (Fig. 1). Geological and metallogenic data for this area are given by Garavelli *et al.* (1997).

Leguernite occurs as needle-shaped crystals up to 0.4 mm long and 0.01 mm across, which form fibrous aggregates (Fig. 2) associated closely with anglesite, baličžunicite and one other unknown Bi sulfate still under investigation. Additional minerals present in the same specimen are: lillianite, galenobismutite, bismoclite, Cd-rich sphalerite, Cd-rich wurtzite, pyrite and pyrrhotite.

Leguernite is colourless to white in colour, with a white streak and a sub-adamantine lustre. Minute crystals are transparent to translucent. No twinning was observed. Leguernite is brittle and no cleavage, parting or fractures were observed.

The very small dimensions, as well as the rarity of the crystals, precluded direct measurements of the refractive index and physical properties such as density and micro-hardness. The calculation of the mean refractive index was performed using the Gladstone–Dale constants of Mandarino (1976, 1981). Taking into account the empirical formula, the mean refractive index of leguernite is 2.040. The calculated density is 7.375 g cm^{-3} .

Chemical data

Electron microprobe analyses of leguernite were obtained using a JEOL JXA 8200 Superprobe at

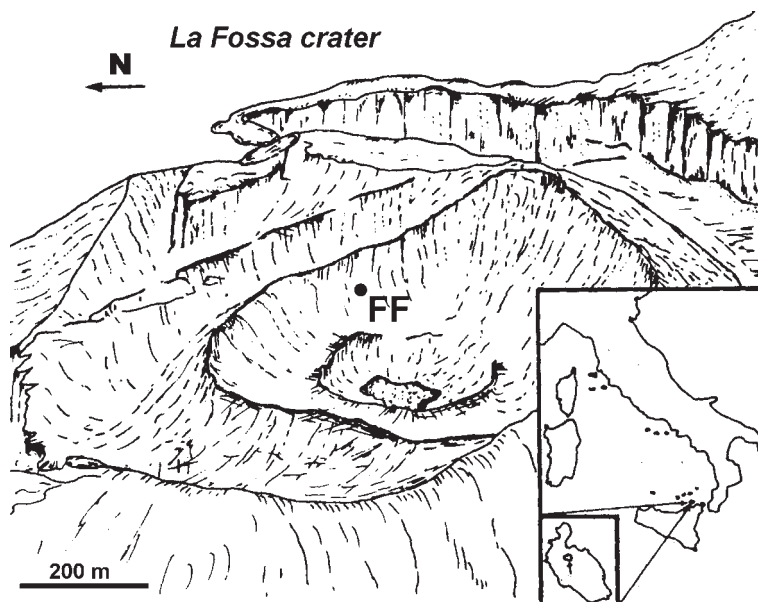


FIG. 1. Location of the sampling site (FF) for leguernite in La Fossa crater, Vulcano, Aeolian Islands, Italy.

the Dipartimento di Scienze della Terra “Ardito Desio”, Università degli Studi di Milano. Operating conditions were: accelerating voltage 15 kV, beam current 5 nA and beam diameter of 1 μm ; standard (element, emission line): metallic Bi ($\text{BiM}\alpha$), celestine ($\text{SK}\alpha$) and galena ($\text{PbM}\alpha$). The analytical results (mean of nine analyses) obtained on different crystals belonging to the same needle aggregate, are reported in Table 1. Low totals, as well as the slight overestimation of sulfur and the slight underestimation of bismuth, may be related to the very small thickness of the

analysed fibres (<10 mm) as well as to the different behaviour under the electron beam of the sulfate sample with respect to the standards. Similar analytical problems were also outlined by Capitani *et al.* (2013) for microprobe analysis of the Bi-sulfate cannonite. With the exception of small amounts of Pb (Table 1), no other elements substituting for Bi were detected by energy dispersive spectroscopy analyses. The empirical formula, calculated on the basis of 34 anions per formula unit (p.f.u.), is $(\text{Bi}_{12.40}\text{Pb}_{0.15})_{\Sigma=12.55}\text{S}_{5.08}\text{O}_{34}$. The ideal formula of leguernite is $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$, which requires Bi_2O_3 88.07, SO_3 11.93, total 100.00 wt.%.

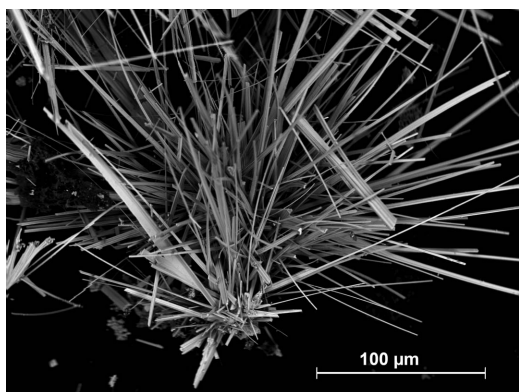


FIG. 2. Scanning electron image of leguernite crystals (SEM-QBSD image).

Raman data

The micro-Raman spectrum of leguernite (Fig. 3) in the region 100–4000 cm^{-1} was

TABLE 1. Chemical composition of leguernite.

Constituent	wt.%	Range	SD
SO_3	11.06	10.76–11.29	0.21
Bi_2O_3	78.57	75.80–80.03	1.53
PbO	0.91	0.36–1.63	0.38
Total	90.54		

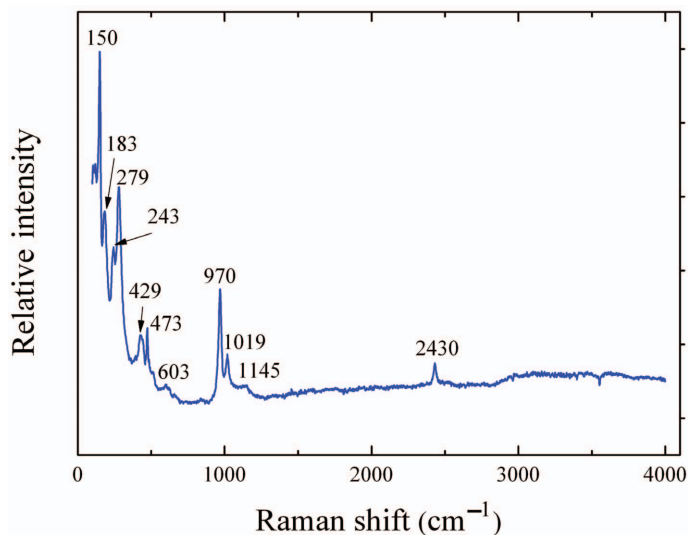


FIG. 3. Raman spectrum (unoriented crystal, cotype specimen) of leguernite in the 100–4000 cm^{-1} region.

collected at the Dipartimento di Chimica, Università degli Studi di Bari “A. Moro”, using an unoriented crystal exhibiting acicular morphology (leguernite cotype specimen). An Xplora (Horiba Jobin Yvon) instrument equipped with three lasers ($\lambda_0 = 532, 638$ and 785 nm) was used. Sample irradiation was accomplished with the $\lambda_0 = 532$ nm laser using the $50\times$ microscope objective of an Olympus BX41 microscope. The exposure time was set at 2 s and 30 accumulations were selected. The beam power was ~ 1.4 mW and the laser spot size was adjusted between 1 and 3 μm . Raman scattering was filtered by a double holographic notch filter system and collected by an air-cooled CCD detector. The wavelength scale was calibrated using a Si(111) standard (520.5 cm^{-1}).

The Raman spectrum of leguernite closely resembles that of the mineral cannonite (Capitani *et al.*, 2013). Most of the bands in the region $100\text{--}400$ cm^{-1} are due to the Bi–O lattice vibrations whereas the remaining bands are due to the SO_4 bending modes (region $400\text{--}600$ cm^{-1}) and SO_4 stretching modes (region $600\text{--}1200$ cm^{-1}), respectively. The peak at 2430 cm^{-1} remains unassigned. It is remarkable that there is an absence of peaks in the region $3000\text{--}3500$ cm^{-1} (O–H stretching modes) and $1400\text{--}1600$ cm^{-1} (H–O–H bending modes), thus confirming the anhydrous nature of leguernite and corroborating the structural results presented below.

X-ray data

Powder X-ray diffraction

Powder X-ray diffraction (XRD) data (Table 2) were obtained using the diffraction rings from a few powdered crystal aggregates of leguernite collected with a CCD-equipped Xcalibur PX Ultra diffractometer using $\text{CuK}\alpha$ radiation. The rings were then converted into a conventional XRD pattern. Data were processed using the *CrysAlis* software package version 1.171.31.2 (Oxford Diffraction, 2006) running on the Xcalibur PX control PC. Indexing of the reflections was performed on the basis of the calculated powder pattern obtained by the structural model described below, using the software *POWDERCELL* (Kraus and Nolze, 2000). The unit-cell parameters, $a = 11.250(5)$, $b = 5.654(2)$, $c = 11.906(5)$ Å, $\beta = 99.13(5)^\circ$ and $V = 747.8(5)$ Å³, were obtained by least-squares refinement using the program *CELREF* (Laugier and Bochu, 2003).

Single-crystal X-ray diffraction

Single-crystal XRD data were collected from a selected crystal fragment (0.260 mm \times 0.034 mm \times 0.016 mm) using a Bruker AXS X8 APEX2 CCD-automated diffractometer equipped with a k -geometry goniometer and graphite monochromated $\text{MoK}\alpha$ radiation (50 kV and 30 mA operating conditions). The Miracol fibre optics

TABLE 2. Powder X-ray diffraction data for leguernite.

I_{rel}	d_{meas} (Å)	d_{calc} (Å)*	h	k	l
5	5.870	5.878	0	0	2
5	5.360	5.361	$\bar{2}$	0	1
5	5.090	5.096	0	1	1
15	5.040	5.039	1	1	0
5	3.960	3.962	2	1	0
100	3.220**	3.221	0	1	3
95	3.100	3.098	$\bar{3}$	1	1
10	2.991	2.991	1	1	3
25	2.931	2.930	3	0	2
30	2.830	2.827	0	2	0
5	2.785	2.787	$\bar{2}$	0	4
25	2.502	2.503	$\bar{3}$	0	4
5	2.191	2.192	$\bar{2}$	2	3
20	2.035	2.035	3	2	2
5	1.960	1.959	0	0	6
20	1.875	1.874	$\bar{3}$	2	4
5	1.851	1.852	$\bar{6}$	0	2
5	1.820	1.822	$\bar{5}$	1	4
5	1.763	1.763	3	1	5
10	1.703	1.703	6	1	1
5	1.679	1.680	$\bar{3}$	3	1
5	1.622	1.621	$\bar{6}$	1	4
5	1.613	1.613	$\bar{2}$	1	7
5	1.566	1.566	$\bar{3}$	1	7
5	1.524	1.523	$\bar{6}$	1	5

* Calculated from the unit cell with $a = 11.250(5)$, $b = 5.654(2)$, $c = 11.906(5)$ Å and $\beta = 99.1(5)^\circ$, obtained from least-squares refinement of the data using the program *CELREF* (Laugier and Bochu, 2003). Indexing was performed following the crystal structure. **Coincides with a strong peak of anglesite, $d = 3.223$ Å.

capillary collimator (0.3 mm in size) was used to enhance the intensity of the MoK α radiation and to reduce X-ray beam divergence. The collection strategy was optimized by the *Apex* suite of programs (Bruker, 2003a). A total of 1230 frames (step = 0.5°, step/time = 180 s) were collected. Details of data collection and refinement are summarized in Table 3. The monoclinic orientation of the crystal lattice was determined from 416 reflections distributed evenly in reciprocal space and used for a subsequent integration of all collected intensities. The latter was accomplished by the software package *SAINT-IRIX* (Bruker, 2003b) which also performed L_p correction and calculation of the final unit-cell parameters. A semi-empirical absorption correction (Blessing,

1995) was applied using the *SADABS* program (Sheldrick, 2008a). The minimum and maximum X-ray transmission-factors were 0.5331 and 0.7457, respectively. No systematic absences were observed and the statistical tests on the distribution of $|E|$ values indicated the presence of an inversion centre ($|E^2 - 1| = 0.952$). The structure solution was then initiated in the space group $P2_1/m$. The position of most of the atoms (Bi and S) was determined from the three-dimensional Patterson synthesis (Sheldrick, 2008b). A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an R_1 factor of ~23%. Three-dimensional difference Fourier synthesis yielded the position of the O atoms. The full-matrix least-squares program *SHELXL-97* (Sheldrick, 2008b) was used for the refinement of the structure. A better solution was found ($R_1 = 16\%$), but with numerous partially occupied sites and very large atomic displacement parameters. Looking for an ordered model, we tried to solve the structure in the $P2_1$ subgroup by removing the mirror symmetry element of the $P2_1/m$ space group. The reflection and atomic position data sets were then adapted to the $P2_1$ space group and the structure refined.

After several cycles, an ordered solution with full site occupations was determined by carefully removing atoms with low site occupations and/or unrealistic distances with neighbouring atoms and adding significant positions found in the difference Fourier syntheses. The structure could be refined smoothly in $P2_1$ without any damping factor or restrictions.

Neutral scattering factors for Bi, S and O were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). The solution revealed 13 Bi, 5 S and 34 O sites in the unit cell, thus suggesting that $\frac{1}{3}$ Bi atoms must be missing for charge-balance requirements. Because in the isotropic least-squares refinement, Bi(7) had the largest displacement parameter among the Bi atoms, it was assumed to host only $\frac{2}{3}$ Bi in the final refinement. This choice appears further justified by the peculiar position of Bi(7) in the structure with respect to the other Bi sites which belong to the fluorite-like blocks (see the paragraph "Description of the structure" for more details). At the last stage, with anisotropic atomic displacement parameters for the Bi atoms and restraints to S–O distances of sulfate groups, the residual value settled at $R_1 = 7.66\%$ for 2372 observed reflections [with $I > 2\sigma(I)$] and 139

TABLE 3. Summary of parameters describing data collection and refinement for leguermite.

Empirical structural formula	Bi _{12.67} O ₁₄ (SO ₄) ₅
Crystal dimensions (mm)	0.260 × 0.034 × 0.016
Crystal system, space group	Monoclinic, <i>P</i> 2
<i>a</i> (Å)	11.2486(11)
<i>b</i> (Å)	5.6568(6)
<i>c</i> (Å)	11.9139(10)
β (°)	99.177
<i>V</i> (Å ³)	748.39(12)
<i>Z</i>	1
Temperature (K)	293
<i>D</i> _{calc} (g cm ⁻³)	7.375
X-ray conditions (kV, mA)	50, 30
Wavelength of radiation (Å)	0.71073
Detector to sample distance (mm)	40
Number of frames	1230
Rotation width per frame (°)	0.5
Measuring time (s)	180
Maximum covered 2θ (°)	56.58 (<i>d</i> = 0.75 Å)
Independent reflections	3162
Reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	2372
<i>R</i> _{int}	0.0624
<i>R</i> _σ	0.0890
Ranges of <i>h</i> , <i>k</i> , <i>l</i>	-14 ≤ <i>h</i> ≤ 14 -7 ≤ <i>k</i> ≤ 5 -15 ≤ <i>l</i> ≤ 15
<i>R</i> [<i>F</i> _o > 4σ(<i>F</i> _o)]	0.0766
<i>R</i> (all data)	0.1064
w <i>R</i> [<i>F</i> _o > 4σ(<i>F</i> _o)]	0.1863
w <i>R</i> (all data)	0.2060
Gof	1.044
Refined parameters	139
Weighting scheme	w = 1/[σ ² (<i>F</i> _o ²) + (0.1276 <i>P</i>) ² + <i>P</i>] where <i>P</i> = [max(<i>F</i> _o) ² + 2(<i>F</i> _c) ²]/3
Δρ _{min} , Δρ _{max} (e/Å ³)	-4.32, 15.82

parameters, and *R*₁ = 10.64% for all the 3162 equivalent reflections.

Final atom coordinates and displacement parameters are reported in Table 4. Selected interatomic distances and angles are given in Table 5.

Structure factors (Table 6) have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Description of the structure

The crystal structure of leguermite is built up of blocks of Bi and O atoms extending infinitely in the **b** direction, but separated from each other in the **a** and **c** directions (Fig. 4). The Bi–O blocks of composition (Bi₁₂O₁₄)⁸⁺ have a fluorite-like

structure and contain five rows of infinite OBi₄ edge-sharing tetrahedral chains, plus additional oxygen atoms O(17) and O(18), which do not occupy 'CaF₂' positions (Fig. 5). Each Bi–O block is thus formed by a central row, comprising the edge-sharing tetrahedra around O(15) and O(16), surrounded by four edge-sharing tetrahedral chains, in a cross-like arrangement along the planes (101) and (1̄02). All atoms within each Bi–O block are related by the 2-fold axes passing through O(15) and O(16). Projections of rows on (101) and (1̄02), respectively, are reported in Fig. 6. Neighbouring rows are joined to each other by renewed edge-sharing and form infinite [010] columns with composition [(Bi₁₂O₁₄)⁸⁺]_n, by including the four additional 'non-fluorite' oxygen atoms (Fig. 5*b*). Adjacent columns are related by the 2-fold axes passing through S(3)

TABLE 4. Fractional atomic coordinates and displacement parameters for leguernite.

Site	x/a	y/b	z/c	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq}
Bi(1)	0.33418(18)	0.2978(3)	0.01006(15)	0.0173(9)	0.0110(9)	0.0101(7)	0.0019(7)	0.0065(6)	-0.0035(7)	0.0123(4)
Bi(2)	0.53822(17)	0.7996(3)	0.15842(15)	0.0163(9)	0.0132(9)	0.0095(7)	0.0080(7)	0.0068(6)	0.0049(7)	0.0125(4)
Bi(3)	0.21076(15)	0.7118(6)	0.19423(14)	0.0175(8)	0.0135(8)	0.0160(7)	-0.003(1)	0.0083(6)	-0.0019(10)	0.0151(4)
Bi(4)	0.40591(15)	0.2143(5)	0.32991(12)	0.0225(8)	0.0126(8)	0.0086(6)	0.0036(10)	0.0068(6)	0.0006(11)	0.0141(4)
Bi(5)	0.25801(14)	0.2204(5)	0.69433(12)	0.0144(7)	0.0109(8)	0.0063(6)	-0.001(9)	0.0009(5)	-0.0033(9)	0.0106(4)
Bi(6)	0.13281(16)	0.7240(5)	-0.13890(14)	0.0178(8)	0.0146(10)	0.0170(8)	0.0043(10)	0.0056(6)	-0.009(1)	0.0161(4)
Bi(7)	0	0.7366(12)	$\frac{1}{2}$	0.017(2)	0.037(4)	0.044(2)	0.00000	0.0180(18)	0.00000	0.0315(13)
S(1)	0.3263(9)	0.697(3)	0.5350(8)	0.015(2)						
S(2)	0.072(10)	0.217(4)	0.3548(9)	0.020(2)						
S(3)	0	0.198(5)	0	0.015(3)						
O(1)	0.214(2)	0.692(10)	0.587(3)	0.029(8)						
O(2)	0.398(4)	0.915(6)	0.564(4)	0.041(13)						
O(3)	0.392(5)	0.483(7)	0.582(5)	0.063(17)						
O(4)	0.298(5)	0.737(13)	0.409(2)	0.068(16)						
O(5)	0.009(3)	0.446(5)	0.343(3)	0.028(9)						
O(6)	0.118(3)	0.176(11)	0.477(2)	0.045(10)						
O(7)	0.165(3)	0.233(10)	0.281(3)	0.044(11)						
O(8)	-0.019(4)	0.029(7)	0.316(4)	0.046(13)						
O(9)	0.112(4)	0.063(11)	0.031(5)	0.09(2)						
O(10)	-0.014(6)	0.344(11)	0.09(4)	0.09(2)						
O(11)	0.269(3)	0.46918(16)	-0.169(3)	0.006(6)						
O(12)	0.266(3)	-0.030(6)	-0.164(3)	0.004(6)						
O(13)	0.353(3)	0.468(7)	0.201(3)	0.012(7)						
O(14)	0.353(3)	0.966(6)	0.200(3)	0.008(7)						
O(15)	$\frac{1}{2}$	0.489(10)	0	0.013(11)						
O(16)	$\frac{1}{2}$	-0.008(9)	0	0.006(9)						
O(17)	0.554(2)	1.18126	0.235(2)	0.015(6)						
O(18)	0.233(3)	0.655(7)	0.021(2)	0.021(7)						

 Site occupancy for Bi(7) is $\frac{2}{3}$; 1.00 for the rest of the atoms.

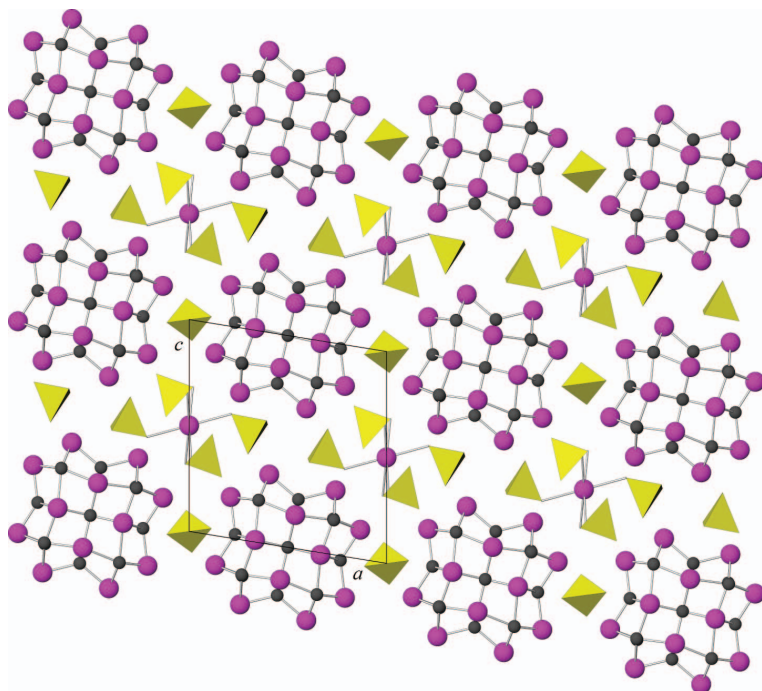


FIG. 4. A projection along $[010]$ showing Bi–O blocks with composition $(\text{Bi}_{12}\text{O}_{14})^{8+}$ and SO_4^{2-} tetrahedra in the crystal structure of leguernite. Yellow polyhedra: SO_4^{2-} groups, pink circles: Bi, dark circles: O.

and Bi(7) (Wyckoff position $1a$ and $1b$, respectively) and hence joined to each other by isolated sulfate tetrahedra around S(3) along $[100]$, and by $\text{Bi}(\text{SO}_4)_4^{5-}$ groups along $[101]$ and $[\bar{1}01]$ (Fig. 4). The $\text{Bi}(\text{SO}_4)_4^{5-}$ group, which is formed by Bi(7), and the four SO_4 -tetrahedra around S1 and S2, extend within a plane parallel to (001) , thus forming infinite $[\text{Bi}(\text{SO}_4)_4^{5-}]_n$ layers. The latter alternate along the $[001]$ direction with (001) layers of composition $[\text{Bi}_{12}\text{O}_{14}(\text{SO}_4)^{6+}]_n$, which are formed by infinite $[010]$ columns of edge-sharing tetrahedral chains and isolated tetrahedra around S(3) (Fig. 5b).

As is typical in Bi compounds, the coordination environment of Bi atoms is very irregular and distorted, thus indicating the presence of the stereochemically active Bi^{3+} lone pair of electrons. Interatomic distances summarized in Table 5 were selected by choosing an arbitrary limit of 3.0 for Bi–O bonds. In it can be seen that Bi atoms in the inner part of Bi–O blocks (Fig. 4), namely Bi(1) and Bi(2), have eight-fold and seven-fold coordination, respectively. The environment of Bi(1) is characterized by four nearest neighbour oxygen atoms which form a

square on one side of the Bi atoms [Bi–O distances from 2.18(3) to 2.45(4) Å] completed by four more distant oxygen atoms also in a square arrangement [Bi–O distances from 2.56(3) to 2.92(4) Å]. Bi(2) shows four closest oxygens at distances from 2.16(3) to 2.41(4) Å and three much more distant oxygens at distances from 2.56(4) to 2.91(4) Å. The Bi atoms in the external portions of the Bi–O blocks, Bi(3), Bi(4), Bi(5) and Bi(6), are in three-fold coordination with the closest oxygen atoms [Bi–O = 2.09(3)–2.19(3) Å], occupying the top of a trigonal pyramid with 3 O making a base. The full coordination environment of these cations includes several neighbour sulfate oxygens and varies from six-fold to eight-fold in a very irregular arrangement (Table 5).

Bi atoms of the $[\text{Bi}(\text{SO}_4)_4^{5-}]_n$ layers form very irregular eight-fold coordination polyhedra with sulfate oxygens of the neighbouring SO_4^{2-} groups. Considering the six closest sulfate oxygen atoms only, the coordination of Bi(7) approaches a distorted octahedron with bond distances ranging from 2.48(2) to 2.73(5) Å (Fig. 7a). The shortest Bi–O distances of Bi(7) are significantly longer

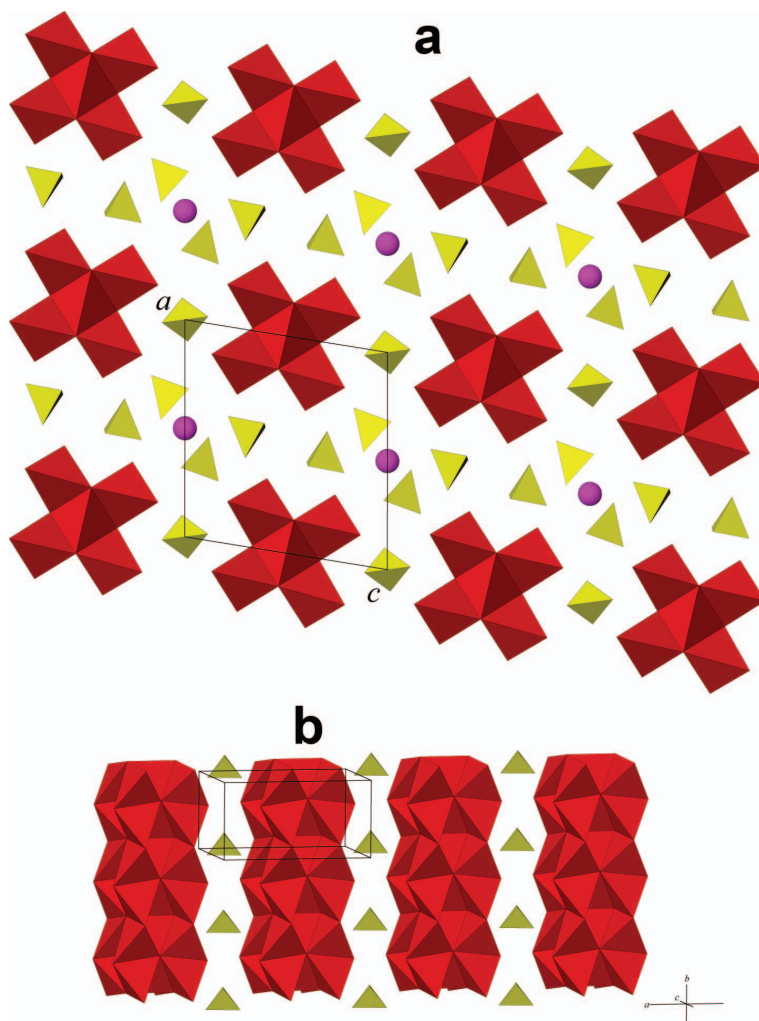


FIG. 5. Columns of OBi_4 edge-sharing tetrahedra in the crystal structure of leguernite. (a) Projection along $[010]$ showing cross-like portions formed by five rows of edge-sharing tetrahedral chains; (b) infinite $[010]$ columns of edge-sharing tetrahedral chains and isolated tetrahedra in the layer $[\text{Bi}_{12}\text{O}_{14}(\text{SO}_4)_6]_n$.

than those of the other Bi atoms. These anomalous bond-length values might be related to the peculiar position of Bi(7) in the crystal structure, at the centre of a cavity formed by six sulfate groups in a so-called pinwheels coordination, which represents a common feature in sulfate phases (Moore, 1973; Mills *et al.*, 2011). Under these circumstances, the Bi–O distances are expected to be longer due to the repulsion effect of neighbouring sulfur cations. On the contrary, all the other Bi sites of the leguernite structure belong to the compact fluorite groups and are thus

characterized by very strong cation-oxygen-cation interactions. On the other hand, we suppose that these relatively long Bi–O distances can also be related to the occurrence of minor Pb substituting for Bi at Bi(7). This hypothesis is further confirmed by the occurrence of Pb atoms coordinated octahedrally with oxygens of six neighbouring sulfate groups in the structure of $\text{PbMn}_5(\text{SO}_4)_6$ (West *et al.*, 2009) (Fig. 7b). Interestingly, the Pb–O distances in $\text{PbMn}_5(\text{SO}_4)_6$ range from 2.66 to 2.77 Å, significantly longer than those generally observed

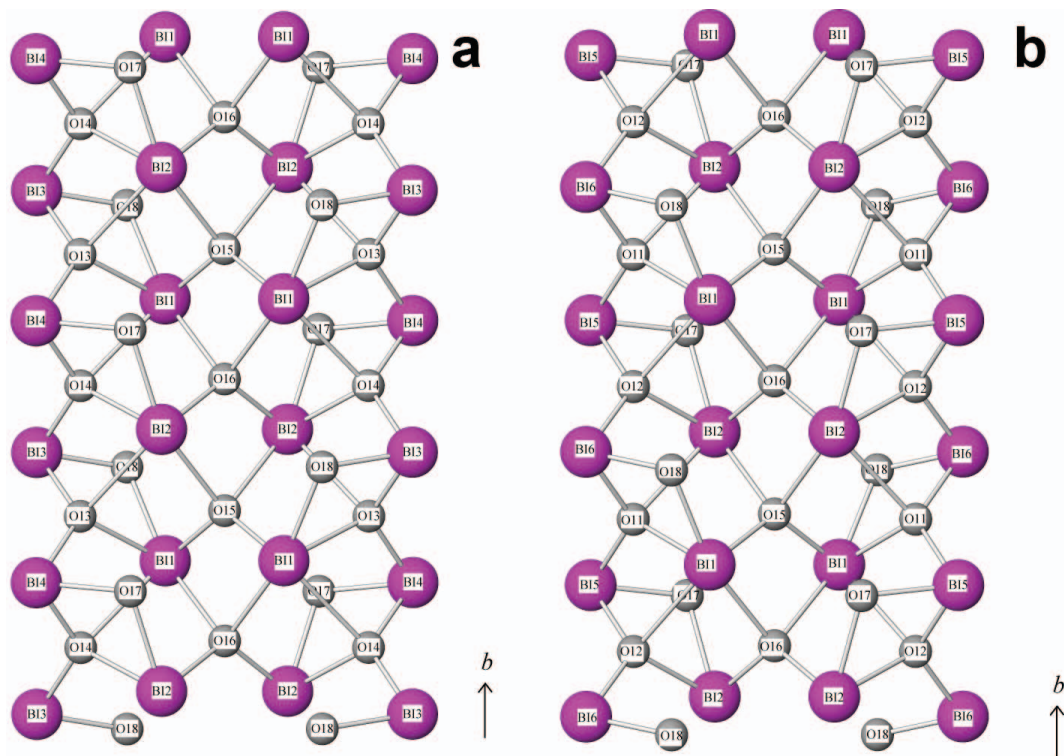


FIG. 6. Projection of the $(\text{Bi}_{12}\text{O}_{14})^{8+}$ block on (a) plane (101) and (b) plane $(\bar{1}02)$. The central row formed by edge-sharing tetrahedra around O(15) and O(16) is common in the two projections; O(17) and O(18) does not belong to the fluorite framework.

in other Pb-oxide or Pb-oxysulfate compounds, analogous to what is observed for the $\text{Bi}(\text{SO}_4)_4^{5-}$ groups of leguernite. The amount of Pb calculated from microprobe analyses varies from 0.06 to 0.27 anions p.f.u., thus suggesting up to 40% of

Pb-for-Bi substitution in the partially occupied Bi(7) site.

Efforts were made to rationalize the coordination of Bi atoms in the crystal structure of leguernite according to the Valence Shell

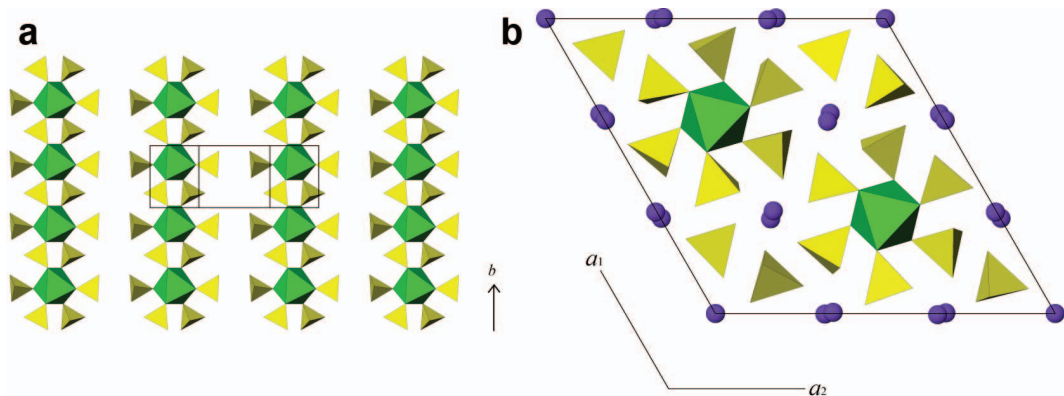


FIG. 7. Sixfold-coordination polyhedra (green) $\text{Me}(\text{SO}_4)_6$ ($\text{Me} = \text{Bi}, \text{Pb}$) in the crystal structure of (a) leguernite and (b) synthetic $\text{PbMn}_5(\text{SO}_4)_6$. Sulfate tetrahedra are yellow.

Electron Pair Repulsion (VSEPR) model (Gillespie and Nyholm, 1957; Gillespie 1963*a,b*; Gillespie, 2008 and references therein), which may help to predict the stereochemical influence of $6s^2$ lone electron pairs of Bi^{3+} ions. The VSEPR model has been used largely to explain and predict the geometry of molecules based upon the extent of electron-pair electrostatic repulsion. The general idea of this concept is to handle the free electron pairs of the central atom of a molecule as ligands. The geometry of a molecule is thus dependent on the relative numbers of bonding pairs (m) and lone pairs (n) on the central atom and can be represented by the general formula AX_mE_n where E denotes a lone electron pair. Extensions of the VSEPR model have been made by Andersson, Galy and coworkers (Andersson *et al.*, 1973; Galy *et al.*, 1975). They

used a hard-sphere model in which the inert electron pair is assumed to act as if it were an oxygen atom; it has a measurable distance to the central atom and occupies a volume in the crystal structures equal to that of an oxygen atom.

According to the VSEPR model the coordination of $\text{Bi}(3)$, $\text{Bi}(4)$, $\text{Bi}(5)$ and $\text{Bi}(6)$ atoms of the leguerrite structure can be described as BiO_3E tetrahedral (also denoted as Ψ -tetrahedral) with the lone pair of electrons at one corner and the three closest non-sulfate oxygens at the other corners of each tetrahedron (Fig. 8). $\text{Bi}(1)$ and $\text{Bi}(2)$ atoms have four close oxygen neighbours at distances less than 2.50 Å, with O–Bi–O angles between pairs of closest opposite oxygens of $90.2(12)$ and $130.5(12)^\circ$ for $\text{Bi}(1)$ and $82.4(11)$ and $131.2(11)^\circ$ for $\text{Bi}(2)$ (Table 5). These values are comparable with those observed in BiO_4E

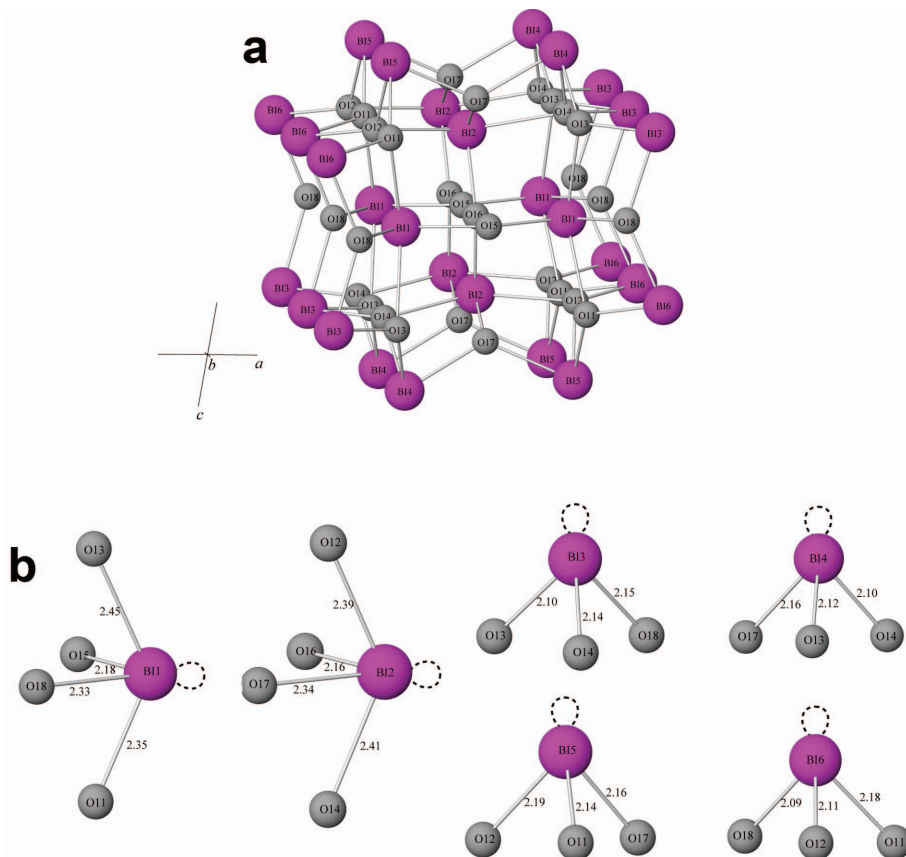


FIG. 8. Bismuth coordinations within the $(\text{Bi}_{12}\text{O}_{14})^{8+}$ fluorite-related blocks (a) and their description (b) according the VSEPR model: BiO_4E trigonal bipyramid coordination for $\text{Bi}(1)$ and $\text{Bi}(2)$, BiO_3E tetrahedral coordination for $\text{Bi}(3)$, $\text{Bi}(4)$, $\text{Bi}(5)$ and $\text{Bi}(6)$. Hatching indicates the volume of lone pair of electrons.

trigonal bipyramids in a number of Bi compounds (see Aurivillius, 1988). Hence, the coordination environment of Bi(1) and Bi(2) can be described as a distorted BiO_4E trigonal bipyramid (also denoted as a Ψ -trigonal bipyramid) (Fig. 8), which means that there are two oxygens along the axis of the bipyramid (axial) and that two corners of the equatorial triangle are occupied by oxygen atoms (equatorial), the third corner being occupied by the electron pair E (Galy *et al.*, 1975). The axial Bi–O bonds are generally longer than the corresponding equatorial distances (Fig. 8b, Table 5) in good agreement with the ratio $r_{\text{ax}}/r_{\text{eq}}$ ranging from 1.1 to 1.2 observed in a number of crystal structures with Ψ -trigonal bipyramids (Gillespie, 1963b).

Sulfur atoms show almost regular tetrahedral coordinations with S–O distances ranging from 1.452(39) Å to 1.501(24) Å (Table 5) and average values comparable with those commonly found in most sulfates (Palmer *et al.* 1972, and references therein).

Discussion

Leguernite was found as a new sublimate mineral from high-temperature fumaroles at La Fossa crater, Vulcano, Aeolian Islands, Italy. In spite of the relative abundance of sulfate species among volcanic sublimates from all over the world, leguernite is just the second Bi sulfate, together with baličžuničite (Pinto *et al.*, 2013, 2014), to be found in high-temperature fumarole environments. As a matter of fact, the occurrence of Bi sulfates (without additional cations) in nature is very rare, so that only two other hydrate Bi sulfate minerals, namely cannonite, $\text{Bi}_2(\text{SO}_4)\text{O}(\text{OH})_2$ (Stanley *et al.*, 1992; Capitani *et al.*, 2013) and riomarinaitite, $\text{Bi}(\text{SO}_4)(\text{OH})\cdot\text{H}_2\text{O}$ (Rögner, 2005; Graunar and Lazarini, 1982), were known before the discovery at Vulcano of baličžuničite and leguernite, and neither of them is a fumarole mineral.

Since 1990, a large variety of Bi-bearing phases were deposited in and around the high-temperature fumarole vent where leguernite and baličžuničite were found. During this time the “La Fossa” crater fumaroles produced a high-temperature sublimate deposition characterized by complex Pb–Bi sulfosalts and halogen sulfosalts (Borodaev *et al.*, 1998, 2000, 2001, 2003; Vurro *et al.*, 1999; Garavelli *et al.*, 2005; Pinto *et al.*, 2006a,b,c; 2008, 2011; Mitolo *et al.*, 2011; Garavelli *et al.*, 2013b). Notwithstanding

the limitations imposed by thermodynamic simulators, which operate only with very simple species, thermo-chemical calculations (Garavelli *et al.*, 1997, Cheynet *et al.*, 2000) suggest that the complex Pb–Bi sulfosalts which were found at Vulcano were deposited by the gas–solid reaction of simple binary MeS or MeX (Me = metal, X = halogen) compounds or complex MeSX species, which condensed forming simple or complex solids depending on the conditions of the system (i.e. temperature, partial pressure of S, O and halogens, and the presence of trace elements).

Highly oxidized, high-temperature conditions of the vent play an important role in converting gaseous volcanic species (e.g. H_2S , HCl , HBr or N_2) into reactive species, such as SO_3 , Cl , Br and NO . In the fumarolic depositional environment of Vulcano, the general reducing conditions of the gaseous steam at the time of sampling prevented the formation of oxidized phases like the two recently discovered Bi oxysulfates, with the exception of small local areas and short times in which the presence of SO_3 and O_2 , connected to the mixing of atmospheric and magmatic gases, made the processes possible. Like baličžuničite, the same MeX gaseous compounds involved in the complex sulfosalts condensation, mainly BiCl , contributed to the leguernite deposition at Vulcano. Possible reactions could be the following: $12.67\text{BiCl}_{(\text{g})} + 5(\text{SO}_3)_{(\text{g})} + 12.67/2\text{H}_2\text{O} + 12.67/2\text{O}_2 \rightarrow \text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_{5(\text{s})} + 12.67\text{HCl}_{(\text{g}/1)}$. The incorporation of small amounts of Pb substituting for Bi is a common occurrence for sublimate deposition at Vulcano and can be ascribed easily to the presence of this element in the fluids discharging from the “La Fossa” crater fumaroles. Moreover, the close association between leguernite and anglesite indicates the particular abundance of Pb in the gaseous steam at the time of deposition.

Apparently, leguernite shows no strict relationships with all the other natural Bi sulfates or structural similarity with other valid or invalid minerals. Furthermore, it has no analogues among synthetic phases. Nevertheless, the structure of leguernite shows strong similarities with that of the synthetic phase $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ described by Aurivillius (1987), in which similar fluorite-like blocks extended infinitely along the **b** direction can be observed. The **b** period in these two phases is the same, whereas the other lattice parameters are different (Table 7). This is related mainly to the different size of the Bi–O blocks in their structures: the natural phase have Bi–O blocks

TABLE 7. Comparison of leguernite with other natural and synthetic fluorite-related Bi compounds.

Compound	Chemical formula	Lattice parameters (Å)			β	V	Z	Space group	D (g cm ⁻³)	Reference
Leguernite	(Bi _{12.40} Pb _{0.15}) _{2-12.55} S _{5.08} O ₃₄	<i>a</i> 11.2486(11)	<i>b</i> 5.6568(6)	<i>c</i> 11.9139(10)	β 99.177(7) ^o	<i>V</i> 748.39(12) Å ³	Z 1	P2	7.375	This work
Synthetic	Bi ₂₈ O ₃₂ (SO ₄) ₁₀	<i>a</i> 21.638(7)	<i>b</i> 5.657(2)	<i>c</i> 15.087(8)	β 119.1(4) ^o	<i>V</i> 1614(1) Å ³	Z 1	C2/m	7.54	Aurivillius (1987)
Synthetic	Bi _{347/2} O ₃₆ (SO ₄) ₁₆	<i>a</i> 24.67(2)	<i>b</i> 5.650(3)	<i>c</i> 15.139(7)	β 97.67(5) ^o	<i>V</i> 2091(2) Å ³	Z 1	C2/c	7.43	Aurivillius (1987)
Synthetic	Bi ₂ O ₂ (SeO ₄)·H ₂ O	<i>a</i> 7.92	<i>b</i> 14.04	<i>c</i> 5.64	β 108.8 ^o	<i>V</i> 593.69 Å ³	Z 4	P2 ₁ /c	6.834	Aurivillius <i>et al.</i> (1960)
Synthetic	Bi ₂ O ₂ (SO ₄)·H ₂ O	<i>a</i> 7.641	<i>b</i> 13.857	<i>c</i> 5.694	β 108.82 ^o	<i>V</i> 570.66 Å ³	Z 4	P2 ₁ /c	6.542	Aurivillius (1964)
Synthetic	[Bi ₂ O(OH) ₂]SO ₄	<i>a</i> 7.692(3)	<i>b</i> 13.87(1)	<i>c</i> 5.688(2)	β 109.01(3) ^o	<i>V</i> = 573.75 Å ³	Z 4	P2 ₁ /c	6.507	Golič <i>et al.</i> (1982)
Cannonite	Bi ₂ O(SO ₄)(OH) ₂	<i>a</i> 7.7196(5)	<i>b</i> 13.8856(9)	<i>c</i> 5.6980(4)	β 109.174(1) ^o	<i>V</i> = 576.89 Å ³	Z 4	P2 ₁ /c	6.494	Capitani <i>et al.</i> (2013)
		<i>a</i> 7.7100(8)	<i>b</i> 13.8717(14)	<i>c</i> 5.6939(6)	β 109.155(2) ^o	<i>V</i> = 575.25 Å ³	Z 4	P2 ₁ /c	6.513	Capitani <i>et al.</i> (2013)

with composition $\text{Bi}_{12}\text{O}_{14}^{8+}$, whereas blocks of composition $\text{Bi}_{14}\text{O}_{16}^{10+}$ are present in the structure of synthetic $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ (Aurivillius, 1987). Characteristic structural elements within these blocks are the chains of edge-sharing OBi_4 tetrahedra, which are infinite in the **b** direction. Infinite [010] columns formed by five rows of such chains with a cross-like arrangement along the planes (101) and ($\bar{1}$ 02) were described in the structure of leguernite, while six rows are present in the structure of the synthetic $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ (Aurivillius, 1987). However, chains of edge-sharing OBi_4 tetrahedra are also present in a number of synthetic and natural phases. Among these are the synthetic compounds $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$ (Aurivillius, 1987), $\text{Bi}_2\text{O}_2(\text{SO}_4)\text{H}_2\text{O}$ and $\text{Bi}_2\text{O}_2(\text{SeO}_4)\text{H}_2\text{O}$ (Aurivillius *et al.*, 1960; Aurivillius, 1964), as well as the mineral cannonite, $\text{Bi}_2\text{O}(\text{SO}_4)(\text{OH})_2$ (Golič *et al.*, 1982; Capitani *et al.*, 2013). Common to all these phases is the presence of a short fluorite-like period of ~ 5.7 Å (Table 7), corresponding to the *b* axis of leguernite and $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$.

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