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Balićžunićite, $Bi_2O(SO_4)_2$, a new fumarole mineral from La Fossa crater, Vulcano, Aeolian Islands, Italy

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ABSTRACT

Balićžunićite, ideally $Bi_2O(SO_4)_2$, is a new mineral found as a high-temperature fumarole sublimate (T = 600ºC) at La Fossa crater, Vulcano, Aeolian Islands, Italy. It occurs as aggregates of μm-sized prismatic and elongated crystals (~50 μm across and up to 200 μm long) associated with anglesite, leguernite, one other potentially new Bi-oxysulfate mineral, lillianite, galenobismutite, bismoclite, Cd-rich sphalerite, wurtzite, pyrite and pyrrhotite. Balićžunićite is colourless to white or pale brown, transparent and non-fluorescent. It has a vitreous lustre and a white streak. Electron microprobe analysis gives the following average chemical composition (wt.%): Bi_2O_3 68.68 and SO_3 23.73, total 92.41. The empirical chemical formula, calculated on the basis of 9 anions p.f.u., is $Bi_{1.99}S_2O_9$. The calculated density is 5.911 g/cm^3.

Balićžunićite is triclinic, space group $P\bar{1}$, with a 6.7386(3), b 11.1844(5), c 14.1754(7) Å, α 80.082(2)º, β 88.462(2)º, γ 89.517(2)º, V = 1052.01(8) Å^3 and Z = 6. The six strongest reflections in the X-ray powder-diffraction data [d in Å (I) (hkl)] are: 3.146 (100) (033), 3.486 (21) (004), 3.409 (12) ($0\bar{3}1$), 3.366 (7) (200), 5.562 (4) (111), 5.433 (4) ($\bar{1}11$). Balićžunićite is the natural analogue of the stable low-temperature α form of synthetic $Bi_2O(SO_4)_2$. The name is in honour of Tonci Balić-Žunić (born 1952), Professor of Mineralogy at the Natural History Museum of the University of Cophenagen. Both the mineral and the mineral name have been approved by the IMA-CNMNC Commission (IMA2012-098).

Keywords: balićžunićite, Bi-sulfates, new mineral, sublimates, fumaroles, Vulcano, Aeolian Islands, Italy.

Introduction

Since the last explosive eruption which occurred in the years 1888–1890, La Fossa crater of Vulcano has remained in a dormant state characterized by fumarolic activity of varying intensity. Fumarole temperatures and the thermodynamic conditions of the fluids emitted have shown large fluctuations during this time (Garavelli, 1994; Garavelli and Vurro, 1994; Garavelli *et al.*, 2013*a*). This has contributed to the deposition of numerous and varied mineralogical phases, a number of which have been identified as new minerals (Zambonini *et al.*, 1924; Garavelli and Vurro, 1994; Vurro *et al.*, 1999; Garavelli *et al.*, 2005, 2012, 2013*a*,*b*; Campostrini *et al.*, 2008, 2011; Demartin *et al.*, 2008*a*,*b*,*c*, 2009*a*,*b*,*c*,*d*, 2010*a*,*b*,*c*,*d*, 2011*a*,*b*, 2012, 2013; Mitolo *et al.*, 2013*a*). The depositional period around 1987–1993 was interesting particularly from a mineralogical point of view. Fumarole temperatures increased rapidly from 1987 onwards and important variations in the flow rate and chemical composition of the fluids emitted from crater fumaroles were also recorded. In 1987 (Tmax ≈ 330ºC) sulfur, salammoniac and sassolite were the only minerals deposited in the fumaroles of La Fossa crater, whereas from 1990 onwards the mineralogy of the crater fumaroles began to be dominated by sulfides and sulfosalts (Garavelli *et al.*,1997). These are

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interesting classes of minerals, which are very rare in fumarole environments. At Vulcano the deposition of sulfides and sulfosalts is due to a sublimate formation under high-temperature reducing conditions, as was also identified by thermodynamic modelling (Cheynet *et al.*, 2000). Hence, from 1990 onwards, galena, cannizzarite, wittite, galenobismutite, bismuthinite, lillianite, heyrovskýite, kirkiite, mozgovaite and vurroite (Garavelli *et al.*,1997; Borodaev *et al.*, 1998, 2000, 2001, 2003; Vurro *et al.*, 1999; Garavelli *et al.*, 2005; Pinto *et al.*, 2006*a*,*b*,*c*, 2008, 2011; Mitolo *et al.*, 2009, 2011) were the main sublimate minerals from the high-temperature Vulcano fumaroles (T >450ºC) and Pb and Bi were the major metals contributing to the high-temperature sublimate formation. The abundance of these elements was related to the magmatic component of the mixing feeding the fluids emitted from La Fossa crater fumaroles, as well as to their presence in lavas through which the high-temperature and reactive fumarole fluids made their way to the surface (Garavelli, 1994; Ferrara *et al.*, 1995). In the areas characterized by temperature values <450ºC, sulfur, salammoniac, barberiite and sassolite were the only mineral phases found as sublimates (Garavelli *et al.*, 1997) and it is remarkable that no oxidized phases, i.e. sulfates, were found before now among high- or low-temperature sublimates collected in the period 1987–1993. This fact, which represents a very rare event in fumarole environments, was explained at Vulcano as a consequence of the peculiar chemistry of the fluids discharging from the area and of the reducing thermodynamic conditions at the time of deposition (Garavelli et *al.*, 1997; Cheynet *et al.*, 2000). These conditions were, and still are, highly variable, as temperature and gas composition may change considerably even in a very brief span of time (Mitolo *et al.*, 2013*a*). In addition, the intense and highly irregular fracturing and permeability of La Fossa crater fumarolized area might further contribute to the variability of the thermodynamic parameters, thus allowing the existence of specific, small depositional environments with thermochemical characters totally different from the surroundings. In particular, the existence of this variability could be the cause of the sporadic formation of very rare individual crystals of the new Bi-sulfate minerals discovered recently in the high-temperature sublimate assemblages of Vulcano: balićžunićite, $Bi_2O(SO_4)_2$ (this work), leguernite, $Bi_{12.67}O_{14}(SO_4)_5$ (IMA2013-51, Garavelli *et al.*, 2013*b*; Garavelli *et al.*, 2014) and a third potentially new Bi-oxysulfate with probable composition $Bi_{14}O_{16}(SO_4)_5$, which is still under investigation. These phases have been found in small cavities on sample rocks on which reduced phases like lillianite and galenobismutite are the main sublimate minerals deposited on the surface, thus indicating the simultaneous existence of small areas of oxidizing conditions near to reducing environments.

Along with cannonite, $Bi_2(SO_4)O(OH)_2$ (Stanley *et al.*, 1992; Capitani *et al.*, 2013) and riomarinarite $Bi(SO_4)(OH){\cdot}H_2O$ (Rögner, 2005), balićžunicite represents the third Bi-sulfate found in nature and the first one completely lacking water molecules or $(OH)^-$ groups.

Synthetic Bi sulfates isochemical with balićžunicite were obtained and investigated by Jones (1984). Two different synthetic phases were identified: α-$Bi_2O(SO_4)_2$ stable at low temperature and β-$Bi_2O(SO_4)_2$, which is stable at temperatures >535ºC. Aurivillius (1988) synthesized and described the crystal structure of a compound with composition $Bi_2O(SO_4)_2$, but the Jones phases were not mentioned in his work. Hence, no clear relationships among the Jones and the Aurivillius phases exist in the literature up to now. The discovery of balićžunićite, which the present investigation proves to be the natural analogue of synthetic α-$Bi_2O(SO_4)_2$ (Jones, 1984), improves the knowledge of synthetic $Bi_2O(SO_4)_2$ phases (Jones, 1984; Aurivillius, 1988) and their reciprocal relationships.

The new mineral balićžunicite and its name were approved by the IMA Commission on New Minerals, Nomenclature and Classification, CNMNC (IMA2012-098; Pinto *et al.*, 2013). It is named after Tonci Balić-Žunić (born 1952), Professor of Mineralogy at the Natural History Museum of the University of Copenhagen, in recognition of his important contribution to several aspects of mineralogy and crystallography (i.e. crystal-structure determination from single-crystal and powder techniques and the theoretical crystal-chemistry of minerals) including applications in material science, nano-science, minerogenesis and petrogenesis, research into environmental hazards and biomineralogy. His particular interest in volcanic sublimates led him to contribute to the discovery of a number of new mineral species from fumarole deposits: kudriavite (Chaplygin *et al.*, 2005), mutnovskyite (Zelenski *et al.*, 2006), eldfellite (Balić-Žunić *et*

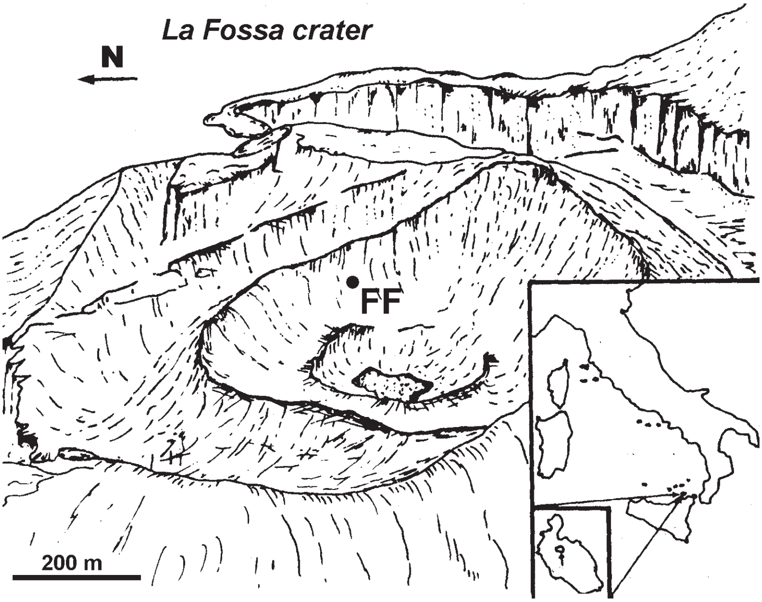

FIG. 1. Location of the sampling site for balićžunićite in La Fossa crater, Vulcano, Aeolian Islands, Italy.

al., 2009), heklaite (Garavelli *et al.*, 2010), jakobssonite (Balić-Žunić *et al.*, 2012), leonardsenite (Mitolo *et al.*, 2013*b*) and oskarssonite (Jacobsen *et al.*, 2013).

The holotype of balićžunićite 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 17/nm-V28.

Occurrence and physical properties

Balićžunićite was found as a fumarole mineral deposited in the surface cavities on one hand specimen of volcanic rock. The sample was collected at Vulcano in 1990 from the high-temperature fumarole FF (T = 600ºC, direct measurement), which was sited on the inner slope of the crater (Fig. 1). Balićžunićite forms transparent and minute, elongated, prismatic crystals associated closely with anglesite $PbSO_4$, the new Bi-sulfate leguernite, $Bi_{12.67}O_{14}(SO_4)_5$ (Garavelli *et al.*, 2013*b*; Garavelli *et al.*, 2014) and one other unknown Bi-sulfate still under investigation. Additional minerals present on the same hand specimen from which balićžunićite was identified, but not associated closely with it, are: lillianite, galenobismutite, bismoclite, Cd-rich sphalerite, wurtzite, pyrite and pyrrhotite.

Balićžunićite occurs as aggregates of µm-sized elongated prismatic crystals (Figs 2 and 3) ~50 µm across and up to 200 µm long; the elongation direction is [100]. No twinning was observed. Balićžunićite is colourless to white or pale brown in colour, with a white streak and a vitreous lustre. The origin of the colour changes is not yet known. Minute crystals are transparent to translucent. Balićžunićite is brittle and no cleavage, parting or fracture were observed.

The very small dimensions, as well as the rarity of the crystals, precluded direct measurements of

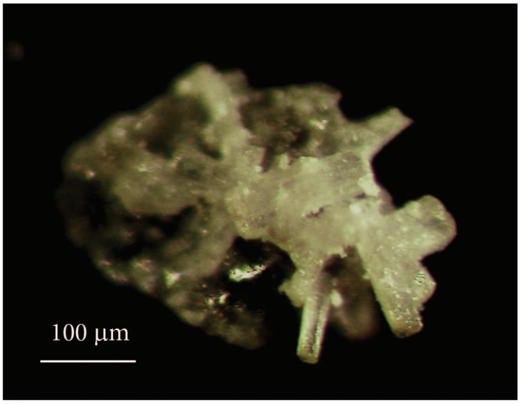

FIG. 2. Photomicrograph of balićžunićite crystals.

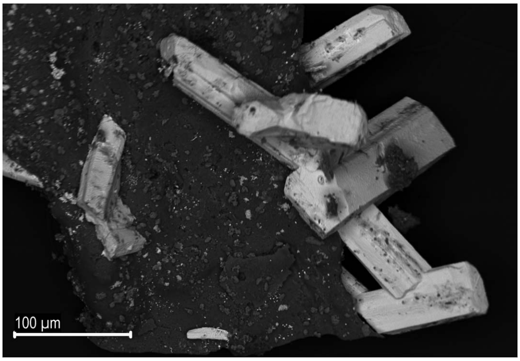

FIG. 3. Scanning electron photomicrograph of balićžunićite crystals (SEM-QBSD image).

physical properties such us the refractive index, density and the Mohs 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 balićžunićite is 2.09. The calculated density is 5.911 g/cm^3.

Chemical composition

Seventeen chemical analyses of balićžunićite were made on polished sections using different analytical devices. Seven analyses were first obtained by scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) using a S 360 Cambridge SEM coupled with an Oxford-Link Ge ISIS EDS equipped with a Super Atmosphere Thin Window©, as this allows better detection of light elements. The SEM was operated at 15 kV accelerating potential, 500 pA probe current, 2500 cps as the average count rate for the whole spectrum and 100 s counting time. X-ray intensities were converted to wt.% by the *ZAF4/FLS* quantitative analysis software of Oxford-Link Analytical (UK). The standards employed were: metallic bismuth (Bi) and baryte (S). The presence of other elements in addition to Bi, S and O was investigated, but none was detected at significant levels. Ten electron microprobe analyses were performed using a JEOL JXA 8200 Superprobe at the Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano. The operating conditions were: accelerating voltage 15 kV, beam current 5 nA, beam focus 1 μm; standards (element, emission line): metallic Bi (Bi$M\alpha$), celestine (S$K\alpha$). The results of chemical analyses and the calculated empirical formulae based on 9 anions per formula unit (p.f.u.) are reported in Table 1. Low totals may be related to the different behaviour under the electron beam of the sulfate sample with respect to the standards. Similar analytical problems were outlined by Capitani *et al.* (2013).

The chemical compositions obtained using the SEM and microprobe devices, $Bi_{2.1}O(SO_4)_{1.95}$ and $Bi_{1.99}O(SO_4)_2$, respectively, are comparable and very close to the ideal theoretical formula $Bi_2O(SO_4)_2$ (Table 1).

X-ray diffraction study

Samples of balićžunićite were investigated by single-crystal and powder diffraction techniques. A selected crystal fragment of balićžunićite (50 μm × 110 μm × 150 μm) was measured using a Bruker AXS X8 APEX2 CCD automated single-crystal diffractometer equipped with a k-geometry goniometer and graphite-monocromated Mo$K\alpha$ radiation. Single-crystal data

TABLE 1. Chemical composition of balićžunićite.

	SEM-EDS			Microprobe			Theoretical composition
	Wt.%	Range	St. dev.	Wt.%	Range	St. dev.	Wt.%
Bi_2O_3	75.86	74.24–76.86	0.9	68.68	67.85–69.78	0.6	74.43
SO_3	24.19	21.76–25.21	1.2	23.73	23.17–24.45	0.4	25.57
Total	100.05			92.41			100.00
Chemical formula (9 anions p.f.u.)		$Bi_{2.1}S_{1.95}O_9$			$Bi_{1.99}S_2O_9$		$Bi_2S_2O_9$
Bi/S		1.08			1.00		1.00

show that balićžunićite crystallizes in the space group $P\bar{1}$, with unit-cell parameters *a* 6.7386(3) Å, *b* 11.1844(5) Å, *c* 14.1754(7) Å, α 80.082(2)°, β 88.462(2)° and γ 89.517(2)°. The resulting unit-cell volume is 1052.01(8) Å^3 with *Z* = 6. The triclinic symmetry was validated with the software routine *ADDSYM* implemented in *PLATON* (Spek, 2005), while the presence of the inversion centre was indicated by statistical tests on the distributions of |E| values. The crystal structure of balićžunićite was solved by direct methods (*SHELXS-97*; Sheldrick 1997*a*) and least squares refinement of the structure (*SHELXL-97*; Sheldrick 1997*b*) resulted in the final residual value *R* of 5.07% for 3856 observed reflections ($F > 4\sigma_F$).

The crystal structure of balićžunićite (Fig. 4) consists of clusters of five Bi atoms, which form nearly planar $Bi_5O_3^{9+}$ groups with an almost regular trapezoidal shape and oxo O atoms situated at the trigonal holes of the Bi_5 trapezoids (Bi–O = 2.08–2.33 Å). Along the [100] direction, trapezoidal-shaped $Bi_5O_3^{9+}$ groups are joined to SO_4^{2-} ions by means of strong Bi-to-sulfate O bonds (Bi–O = 2.32–2.48 Å), thus forming infinite [100] columns with composition $Bi_5O_3(SO_4)_5^-$. Due to the symmetry centre, couples of opposite columns displaced with respect to each other by ½ along the [100] direction can be observed in the three-dimensional network. The sixth Bi atom (Bi6) occurs as an isolated atom in a large cavity between adjacent $Bi_5O_3^{9+}$ groups and is joined to a sulfate tetrahedron along the [100] direction, the same as observed for $Bi_5O_3(SO_4)_5^-$ columns (Bi–O = 2.34 – 3.02 Å). Therefore, two symmetrically related [100] columns with composition $BiSO_4^+$ occupy large channels formed by six adjacent $Bi_5O_3(SO_4)_5^-$ columns. The structure can be also described as consisting of infinite layers with composition $[Bi_5O_3(SO_4)_5^-]_n$ extending parallel to the crystal plane (010) with [100] columns of composition $BiSO_4^+$ located on the irregular surface of contact between adjacent layers. Experimental details of the structure determination on balićžunićite and a detailed discussion of the crystal structure will be given in a forthcoming paper (D. Pinto, A. Garavelli and T. Balić-Žunić, unpublished data).

A selection of the most intense reflections of the theoretical powder-diffraction pattern of balićžunićite calculated from the single-crystal structure data using the program *POWDERCELL* (Kraus and Nolze, 2000) is reported in Table 2 and compared with measured X-ray powder-diffraction data. The latter were obtained using a PANalytical X'Pert Pro MPD diffractometer (Bragg–Brentano geometry) equipped with

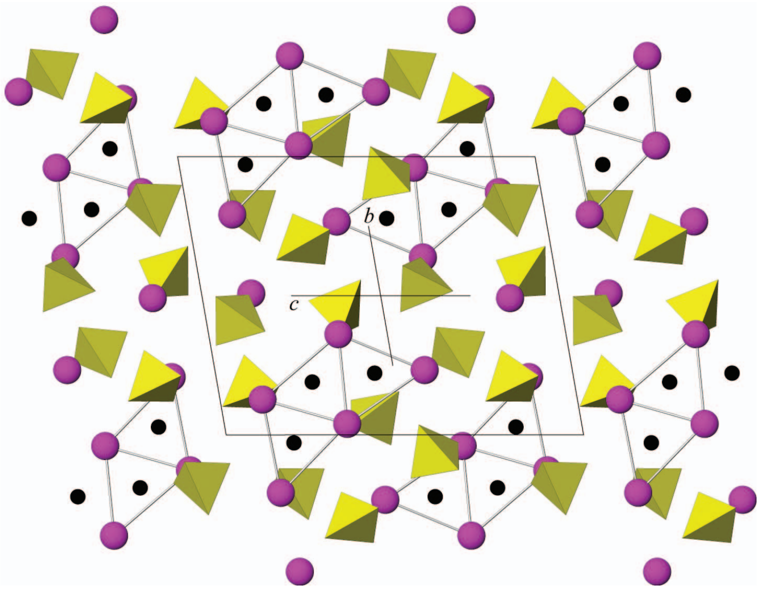

FIG. 4. The crystal structure of balićžunićite projected along [100]. SO_4 tetrahedra are yellow, pink circles are Bi atoms, dark circles are O atoms. Nearly planar trapezoidal-shaped $Bi_5O_3^{9+}$ groups are shown.

TABLE 2. X-ray powder-diffraction data for balićžunićite[a] and synthetic α-$Bi_2O(SO_4)_2$. The strongest reflections are reported in bold.

			— Natural $Bi_2O(SO_4)_2$ – Balićžunićite (this study) —				Syn α-$Bi_2O(SO_4)_2$ (Jones, 1984)		
h	*k*	*l*	I_{calc}[b]	I_{obs}	d_{obs} (Å)	d_{calc} (Å)[c]	I_{obs}	d_{obs} (Å)	d_{calc} (Å)[d]
0	1	1	2	3	9.398	9.474			
1	0	1	20	3	6.112	6.123	18	6.117	6.121
$\bar{1}$	0	1	20				17	5.978	5.995
1	$\bar{1}$	0	29	3	5.749	5.754	41	5.726	5.728
1	**1**	**1**	**49**	**4**	**5.562**	**5.542**	**46**	**5.53**	**5.537**
$\bar{1}$	**1**	**1**	**46**	**4**	**5.433**	**5.433**	**43**	**5.417**	5.428
1	$\bar{1}$	1	5				6	5.169	5.178
$\bar{1}$	$\bar{1}$	1	5				5	5.113	5.114
1	0	2	5				5	4.897	4.905
$\bar{1}$	0	2	3				5	4.769	4.777
1	1	2	11				14	4.693	4.701
$\bar{1}$	1	2	4				4	4.571	4.578
1	$\bar{2}$	0	9	3	4.259	4.252	16	4.257	4.250
$\bar{1}$	$\bar{1}$	2	11				9	4.205	4.207
0	$\bar{2}$	2	11				7	3.993	3.996
1	2	2	11				10	3.904	3.909
1	1	3	9	1	3.834	3.832	13	3.826	3.830
$\bar{1}$	1	3	8				10	3.727	3.733
0	3	0	8	1	3.656	3.67	10	3.66	3.666
0	**0**	**4**	**100**	**21**	**3.489**	**3.486**	**100**	**3.485**	**3.485**
1	$\bar{2}$	2	12				4	3.45	3.454
0	**$\bar{3}$**	**1**	**78**	**12**	**3.409**	**3.407**	**89**	**3.403**	**3.404**
2	**0**	**0**	**74**	**7**	**3.366**	**3.365**	**82**	**3.358**	3.362
0	$\bar{2}$	3	1				9	3.282	3.282
0	**3**	**3**	**91**	**100**	**3.146**	**3.142**	**100**	**3.151**	**3.154**
2	$\bar{1}$	1	9				7	3.124	3.113
$\bar{1}$	3	2	6				10	3.079	3.085
$\bar{1}$	0	4	13	2	3.068	3.064			
2	0	2	28	1	3.057	3.061	48	3.058	3.060
1	$\bar{3}$	1	21				33	3.038	3.041
$\bar{2}$	0	2	23	2	2.998	3.001	20	2.996	2.997
1	$\bar{1}$	4	3				2	2.894	2.893
2	2	0	3				3	2.874	2.873
0	1	5	4	1	2.824	2.822	4	2.822	2.821
1	$\bar{3}$	2	15				18	2.774	2.776
$\bar{2}$	2	2	2				1	2.714	2.714
$\bar{2}$	1	3	2				1	2.673	2.674
1	1	5	10				4	2.629	2.627
0	$\bar{4}$	1	5				4	2.618	2.614
1	3	4	3				11	2.589	2.588
$\bar{1}$	1	5	13	1	2.574	2.578	13	2.579	2.576
$\bar{2}$	$\bar{2}$	2	2	1	2.563	2.56			
$\bar{1}$	0	5	9				17	2.552	2.552
$\bar{1}$	4	0	1	1	2.546	2.544			
1	2	5	5	2	2.516	2.514			
2	3	1	15				14	2.505	2.503
$\bar{2}$	3	1	13				12	2.477	2.478
2	0	4	15				16	2.453	2.451
1	$\bar{4}$	1	4				6	2.438	2.438
$\bar{2}$	3	2	2				4	2.411	2.407
$\bar{2}$	$\bar{3}$	1	15	1	2.393	2.392	44	2.39	2.389
2	3	3	8				5	2.326	2.325
$\bar{2}$	3	3	15				11	2.277	2.278

Table 2 (*contd.*)

— Natural $Bi_2O(SO_4)_2$	– Balićžunićite (this study) —				Syn α-$Bi_2O(SO_4)_2$ (Jones, 1984)		
h k l	I_{calc} [b]	I_{obs}	d_{obs} (Å)	d_{calc} (Å) [c]	I_{obs}	d_{obs} (Å)	d_{calc} (Å) [d]
$\bar{1}$ $\bar{3}$ 4	4	1	2.197	2.197			
$\bar{1}$ 2 6	6	2	2.148	2.148			
3 $\bar{2}$ 0	8	2	2.075	2.074			
1 4 5	5	2	2.062	2.065			
0 $\bar{3}$ 5	8	1	2.054	2.056			
0 $\bar{2}$ 6	7	1	2.019	2.02			
0 3 7	15	2	1.894	1.893			
0 6 2	8	4	1.856	1.855			
3 4 2	2	1	1.745	1.745			
$\bar{1}$ $\bar{6}$ 1	5	1	1.721	1.721			
1 $\bar{6}$ 3	6	1	1.571	1.571			

[a] Owing to the small amount of pure material available and the predominant prismatic habit of the crystals, it was impossible to prepare a sample for X-ray powder diffraction with no preferential orientation and this influences strongly the measured intensities of the balićžunićite powder pattern.
[b] Calculated from X-ray single-crystal structure determination (D. Pinto, A. Garavelli and T. Balić-Žunić, unpublished data).
[c] Calculated from the unit cell with a = 6.739(4), b = 11.184(7), c = 14.176(9) Å, α = 80.06(5), β = 88.47(8), γ = 89.46(7)º, obtained from least-squares refinement of balićžunićite powder-diffraction data.
[d] Calculated from the unit-cell with a = 6.733(3), b = 11.174(7), c = 14.168(9) Å, α = 80.08(5), β = 88.42(5), γ = 89.53(4)º, obtained from least-squares refinement of α-$Bi_2O(SO_4)_2$ powder-diffraction data of Jones (1984), using the program *CELREF* (Laugier and Bochu, 2003).

graphite-monochromated Cu$K\alpha$ radiation and using a Si zero-background plate (analytical conditions: 40 kV and 40 mA, step size 0.02º2θ and step-counting time of 25 s). Indexing of reflections was performed on the basis of the single-crystal structural study (D. Pinto, A. Garavelli and T. Balić-Žunić, unpublished data). The unit-cell parameters of balićžunićite obtained by least-squares refinement of powder X-ray diffraction (XRD) data using the program *CELREF* (Laugier and Bochu, 2003) are a 6.739(4) Å, b 11.184(7) Å, c 14.176(9) Å, α 80.06(5)º, β 88.47(8) and γ 89.46(7)º. Despite the measured powder XRD pattern being affected by preferential orientation effects related to the predominant prismatic habit of crystals, its correspondence with the powder pattern calculated from the structure is reasonably good, as testified by the excellent agreement between unit-cell parameters of balićžunićite obtained from the single-crystal data and those refined from the measured powder XRD data.

Relation to other species

Balićžunicite represents the first natural Bi-sulfate not containing water or hydroxyl. From a chemical and structural point of view it does not show relationships with the other known natural Bi-sulfates, or with other valid or invalid minerals. Compositionally it corresponds to synthetic $Bi_2O(SO_4)_2$ obtained by thermal decomposition of $Bi_2(SO_4)_3$ (Jones, 1984; Aurivillius, 1988). Jones (1984) reported two different $Bi_2O(SO_4)_2$ polymorphs, the low-temperature α-$Bi_2O(SO_4)_2$ and the high-temperature β-$Bi_2O(SO_4)_2$. The latter is stable above 535ºC and transforms very slowly to the α form at lower temperatures. Jones gives only X-ray powder patterns (PDF 38-506, PDF 38-507), with no symmetry or unit-cell parameters. Aurivillius (1988) described and determined the crystal structure of a synthetic monoclinic phase $Bi_2O(SO_4)_2$ obtained as a pyrolysis product of $Bi_2(SO_4)_3$ in the temperature range 560–720ºC. Aurivillius (1988) does not mention the results of Jones (1984) but the powder diffraction pattern of his compound corresponds to the pattern of the β phase given by the latter author. A summary of some crystallographic data of the synthetic $Bi_2O(SO_4)_2$ compounds is reported in Table 3 in comparison with structural data of balićžunićite. From this comparative table we observe that: (1) the powder XRD pattern of balićžunićite (both

TABLE 3. Relationship of balićžunićite with synthetic $Bi_2O(SO_4)_2$ phases.

	Balićžunićite		α-$Bi_2O(SO_4)_2$	Syn β-$Bi_2O(SO_4)_2$	Syn, monoclinic phase (stable at T ranging from 560 to 720°C)		
Chemical formula	$Bi_2O(SO_4)_2$		$Bi_2O(SO_4)_2$	$Bi_2O(SO_4)_2$	$Bi_2O(SO_4)_2$		
Crystal system	Triclinic		not determined	not determined	Monoclinic		
Space group	$P\bar{1}$				$C2/c$		
Unit-cell parameters	a = 6.7386(3) Å b = 11.1844(5) Å c = 14.1754(7) Å α = 80.082(2)° β = 88.462(2)° γ = 89.517(2)° V = 1052.01(8) Å^3 Z = 6	a = 6.739(4) Å b = 11.184(7) Å c = 14.176(9) Å α = 80.06(5)° β = 88.47(8)° γ = 89.46(7)° V = 1052(1) Å^3 Z = 6			a = 32.160(9) Å b = 6.7606(25) Å c = 22.612(16) Å α = 90.00° β = 119.55° γ = 90.00° V = 4277(4) A^3 Z = 24	a = 32.2150 Å b = 6.7522 Å c = 22.6560 Å α = 90.00° β = 119.52° γ = 90.00° V = 4288.42 A^3 Z = 24	a = 32.1600 Å b = 6.7606 Å c = 22.612 Å α = 90.00° β = 119.55° γ = 90.00° V = 4276.83 A^3 Z = 24
Strongest lines [d in Å (I_{rel}) (hkl)]	5.545 (49) (111) 5.437 (47) ($\bar{1}$11) 3.490 (100) (004) 3.410 (78) (0$\bar{3}$1) 3.368 (74) (200) 3.159 (91) (033) 3.064 (28) ($\bar{1}$04)	5.562 (4) 5.433 (4) 3.489 (21) 3.409 (12) 3.366 (7) 3.146 (100)	5.530 (46) 5.417 (43) 3.485 (100) 3.403 (89) 3.358 (82) 3.151 (100) 3.058 (48)	5.763 (28) 5.456 (100) 3.653 (92) 3.373 (72) 3.307 (79) 3.124 (65) 2.480 (29) 2.370 (30)		5.78978 (75) ($\bar{1}$12) 5.48384 (100) (310) 3.66426 (75) ($\bar{7}$11) 3.38933 (75) (020) 3.33021 (75) (404) — 2.48452 (75) ($\bar{6}$26) 2.37161 (75) (424)	5.78222 (32.2) ($\bar{1}$12) 5.47358 (100) ($\bar{4}$04) 3.66351 (76) ($\bar{6}$06) 3.38030 (59.5) (020) 3.32467 (64) (021) 3.12724 (55.7) ($\bar{7}$16) 2.48433 (29.0) ($\bar{6}$26) 2.37032 (23.0) (424)
Reference	This work[(a)]	This work[(b)]	PDF 38-506[(c)] (Jones, 1984)	PDF 38-507[(d)] (Jones, 1984)	Aurivillius (1988)	PDF 41-686[(e)]	PDF 78-2087[(f)]

[(a)] Unit cell from X-ray single-crystal data; strongest lines of the powder pattern calculated from the crystal structure (D. Pinto, A. Garavelli and T. Balić-Žunić, unpublished data). [(b)] Unit cell refined from X-ray powder-diffraction data; strongest lines of the measured X-ray powder pattern. [(c)]Marked as deleted (replaced by 41-686). [(d)] Marked as doubtful because unindexed. [(e)] PDF 41-686 refers to Aurivillius (1988) and Aurivillius (pers. comm., 1989); note that the diffraction data given in the PDF file are lacking in Aurivillius (1988) and the cell parameters in the PDF file differ from those in the paper. [(f)] Calculated from the monoclinic crystal structure (ICSD 63292) determined by Aurivillius (1988).

the measured and the calculated pattern from the triclinic structure) matches the powder XRD data of the α-$Bi_2O(SO_4)_2$ phase (PDF 38-506) described by Jones (1984) very well, whereas a poorer match is observed for the powder pattern of the β-$Bi_2O(SO_4)_2$ phase (PDF 38-507) described by the same author; (2) the powder XRD pattern of balićžunićite shows very poor agreement with the powder XRD data of monoclinic $Bi_2O(SO_4)_2$ (PDF 41-686 and PDF 1-78-2087) described by Aurivillius (1988), the latter being very similar to that of β-$Bi_2O(SO_4)_2$ described by Jones (1984).

Thus, taking into account the characteristics of the powder diffraction patterns (Table 3) it is possible to assert that balićžunićite represents the natural analogue of the synthetic α-$Bi_2O(SO_4)_2$ described by Jones (1984), whereas the monoclinic phase described and investigated structurally by Aurivillius corresponds to the high-temperature form of $Bi_2O(SO_4)_2$ stable over 535ºC. The unit-cell parameters obtained from the least-squares refinement of α-$Bi_2O(SO_4)_2$ powder-diffraction data of Jones (1984) indexed according to the balićžunićite structural model are *a* 6.733(3), *b* 11.174(7), *c* 14.168(9) Å, α 80.08(5), β 88.42(5) and γ 89.53(4)º, in good agreement with those of balićžunićite, thus further confirming the correspondence between this natural phase and α-$Bi_2O(SO_4)_2$ of Jones (1984). Hence, despite the absence of information about the symmetry and the crystal structure of synthetic α-$Bi_2O(SO_4)_2$, the available data allow us to consider balićžunićite as the low-temperature form of $Bi_2O(SO_4)_2$, stable at temperatures <535ºC.

The crystal structure of balićžunićite shows strong similarities with that of the monoclinic (*C*2/*c*) synthetic phase $Bi_2O(SO_4)_4$ described by Aurivillius (1988) corresponding to the high-temperature form of $Bi_2O(SO_4)_2$ as described above. As a matter of fact, the arrangement of Bi and S atoms in both the triclinic and the monoclinic structures show a very similar general scheme and the structural axes of these two structures appear related to each other, i.e. the monoclinic unit-cell setting of the synthetic phase (Aurivillius 1988) can be obtained from that of balićžunićite by means of the transformation matrix [0$\bar{2}$2/100/020]. The lowering of symmetry from the high-temperature to the low-temperature phase might be related to an orientation ordering of sulfate groups.

A detailed description of the relationships between the crystal structure of balićžunićite and that of the monoclinic synthetic phase $Bi_2O(SO_4)_2$ (Aurivillius 1988), together with a comprehensive description and comparison of Bi coordinations in both these two structures will be the subject of future work (D. Pinto, A. Garavelli and T. Balić-Žunić, unpublished data).

Conclusion

Balićžunicite is a new Bi sulfate which was discovered in one small cavity on the surface of a rock sample collected from the walls of a high-temperature (T = 600ºC) fumarole from La Fossa crater at Vulcano. In the small area where balićžunicite was deposited, this new mineral was found associated closely with anglesite $Pb(SO)_4$, one other Bi oxysulfate approved recently as a new mineral, leguernite, $Bi_{12.67}O_{14}(SO_4)_5$ (Garavelli *et al.*, 2013*b*; Garavelli *et al.*, 2014) and a third unknown Bi-oxysulfate still under investigation. On the surface of the same hand specimen from which balićžunićite was identified, other minerals such as sulfides and sulfosalts like lillianite, galenobismutite, Cd-rich sphalerite, wurtzite, pyrite and pyrrhotite are present, but not in close association with the new mineral.

Balićžunicite and associated sulfates represent an exceptional occurrence for the site, of which the mineralogy at the time of sampling was dominated by sulfides and sulfosalts owing to the peculiar reducing thermodynamic conditions of the fluid phase emitted from Vulcano fumaroles (Garavelli *et al.*, 1997; Cheynet *et al.*, 2000).

At Vulcano, an important role in the sublimate depositional processes is played by the simultaneous presence of HCl and H_2S in the gaseous vapours discharging from fumaroles. Chlorine plays the important role of carrier for the mineral-forming elements. Bismuth, in particular, is transported mainly in the gaseous steam as $BiCl_3$, which reacts with H_2S to form sublimates (gas-solid reaction) (Garavelli *et al.*, 1997; Cheynet *et al.*, 2000). In the absence of O, as it happens deep inside the high-temperature fumarole vents and/or in that proportion of volcanic rocks exposed directly to the fumarole flux, the deposition of Bi-sulfides like bismuthinite (Bi_2S_3) and Bi-sulfosalts takes place. In the presence of O, e.g. near the interface with the atmosphere and/or in small cavities isolated from the surrounding environment, the fumarole steam phase can meet cold air, condense and the H_2S undergo oxidation. The O involved in the reaction with the other components is due to atmospheric contamination processes related to the intense fracturing and permeability of La Fossa crater fumarolized area. The hand specimen on which balićžunićite was identified was sampled directly from the inner walls of the FF fumarole vent; it was taken manually from the inside of the hole. If part of the rock sample was exposed directly to the flux of the volcanic vapours (i.e. where sulfides and sulfosalts were deposited) and the other part was outside the vent and involved in local processes of atmospheric contamination then this could be the environment in which balićžunicite formed and it could explain the simultaneous existence of small areas of oxidizing conditions near to reducing environments. A possible reaction explaining the balićžunićite formation is: $2BiCl_3(g) + 2H_2S(g) + H_2O(aq) + 4O_2(g) \rightarrow 6HCl(g) + Bi_2O(SO_4)_2(s)$

Naturally occurring Bi-sulfate minerals are very rare. To date the only natural pure Bi-sulfate minerals approved by the IMA-CNMNC are cannonite, $Bi_2(SO_4)O(OH)_2$ (Stanley *et al.*, 1992; Capitani *et al.*, 2013) and riomarinarite $Bi(SO_4)(OH)\cdot H_2O$ (Rögner, 2005). Additional Bi-sulfates have been characterized recently by Capitani *et al.* (2014) with automatic electron diffraction tomography, but they are not listed as either valid or invalid unnamed minerals. One other sulfate containing Tl in addition to Bi is markhininite, $TlBi(SO_4)_2$ (Filatov *et al.*, 2013), whereas atlasovite, $Cu_6Fe^{3+}Bi^{3+}O_4(SO_4)_5\cdot KCl$ (Popova *et al.*, 1987) and aiolosite, $Na_2(Na_2Bi)(SO_4)_3Cl$ (Demartin *et al.*, 2010*d*), are two complex Bi sulfates also containing Cl and other metals. The latter has Vulcano as the type locality.

Thus, balićžunicite represents the first anhydrous Bi sulfate discovered in nature. From a chemical and structural point of view it was found to be related to the synthetic compounds described by Jones (1984) and then by Aurivillius (1988). In particular, powder-diffraction data indicate that balićžunićite corresponds to the synthetic low-temperature α-$Bi_2O(SO_4)_2$ described by Jones (1984). This correspondence is further supported by the fumarole temperatures measured during the balićžunićite sampling. At Vulcano, balićžunićite crystals were found on a rock sample taken from the FF fumarole vent, where a temperature of 600ºC was measured directly by a thermocouple inserted deep in the fumarole hole. However, the measured value corresponds to the temperature of the inner part of fumarole vent and it is very likely that the temperature in the small cavity on the surface of the rock sample in which balićžunićite was found was less than the value measured directly with the thermocouple. Taking into account the temperature value of 535±3°C measured by Jones (1984) for the $\alpha-\beta$ transition of $Bi_2O(SO_4)_2$ the temperature of formation of balićžunićite at Vulcano was estimated as <535°C.

A transformation from the high-temperature to the low-temperature phase cannot be ruled out but seems unlikely given the morphology of the balićžunićite crystals, which is consistent with a direct gas-solid deposition process as described previously. In addition, Jones (1984) observed that the β phase transforms very slowly to the low-temperature phase but was not able to obtain it in the pure form.

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