

# Tavagnascoite, $\text{Bi}_4\text{O}_4(\text{SO}_4)(\text{OH})_2$ , a new oxyhydroxy bismuth sulfate related to klebelsbergite

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## ABSTRACT

The new mineral tavagnascoite,  $\text{Bi}_4\text{O}_4(\text{SO}_4)(\text{OH})_2$ , was discovered in the Pb-Bi-Zn-As-Fe-Cu ore district of Tavagnasco, Turin, Piedmont, Italy. It occurs as blocky, colourless crystals, up to 40  $\mu\text{m}$  in size, with a silky lustre. In the specimen studied, tavagnascoite is associated with other uncharacterized secondary Bi-minerals originating from the alteration of a bismuthinite  $\pm$  Bi-sulfosalt assemblage. Electron microprobe analyses gave (average of three spot analyses, wt.%)  $\text{Bi}_2\text{O}_3$  85.32,  $\text{Sb}_2\text{O}_3$  0.58,  $\text{PbO}$  2.18,  $\text{SO}_3$  8.46,  $\text{H}_2\text{O}_{\text{calc}}$  1.77, sum 98.31. On the basis of 10 O apfu, the chemical formula is  $(\text{Bi}_{3.74}\text{Pb}_{0.10}\text{Sb}_{0.04})_{\Sigma=3.88}\text{O}_{3.68}(\text{SO}_4)_{1.08}(\text{OH})_2$ , with rounding errors. Main calculated diffraction lines are [ $d$  in  $\text{\AA}$  (relative intensity)  $hkl$ ] 6.39 (29) 012, 4.95 (19) 111, 4.019 (32) 121, 3.604 (28) 014 and 3.213 (100) 123. Unit-cell parameters are  $a = 5.831(1)$ ,  $b = 11.925(2)$ ,  $c = 15.123(1)$   $\text{\AA}$ ,  $V = 1051.6(3)$   $\text{\AA}^3$ ,  $Z = 4$ , space group  $Pca2_1$ . The crystal structure was solved and refined from single-crystal X-ray diffraction data to  $R_1 = 0.037$  on the basis of 1269 observed reflections. It consists of Bi–O polyhedra and  $\text{SO}_4$  tetrahedra. Bismuth polyhedra are connected each to other to form Bi–O sheets parallel to (001). Successive sheets are linked together by  $\text{SO}_4$  groups and hydrogen bonds. Tavagnascoite is the Bi-analogue of klebelsbergite,  $\text{Sb}_4\text{O}_4(\text{SO}_4)(\text{OH})_2$ , and it is the fifth natural known bismuth sulfate without additional cations. The mineral and its name have been approved by the IMA CNMNC (2014-099).

**KEYWORDS:** tavagnascoite, new mineral, bismuth, sulfate, klebelsbergite, Tavagnasco, Piedmont, Italy.

## Introduction

THE occurrence of natural Bi sulfates is quite rare and few such mineral species have been described. Taking into account the Bi sulfates with no additional cations, four species are known: cannonite,  $\text{Bi}_2\text{O}(\text{SO}_4)(\text{OH})_2$  (Stanley *et al.*, 1992; Capitani *et al.*, 2013), riomarinaite,  $\text{Bi}(\text{SO}_4)(\text{OH})\cdot\text{H}_2\text{O}$  (Rögner, 2005), baličžuničite,  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  (Pinto *et al.*, 2014) and leguernite,  $\text{Bi}_{12.67}\text{O}_{14}(\text{SO}_4)_5$  (Garavelli *et al.*, 2014). If Bi sulfates containing additional cations are considered, the list includes aiolosite,  $\text{Na}_4\text{Bi}(\text{SO}_4)_3\text{Cl}$  (Demartin *et al.*, 2010), atlasovite,  $\text{K}(\text{BiO})\text{Cu}_6\text{Fe}^{3+}(\text{SO}_4)_5\text{O}_3\text{Cl}$  (Popova *et al.*, 1987),

campostriniite,  $(\text{Bi}_{2.5}\text{Na}_{0.5})(\text{NH}_4)_2\text{Na}_2(\text{SO}_4)_6\cdot\text{H}_2\text{O}$  (Demartin *et al.*, 2014) and markhininite,  $\text{TlBi}(\text{SO}_4)_2$  (Siidra *et al.*, 2014). Finally, additional potential new Bi sulfates have been reported by Capitani *et al.* (2014) and Pinto *et al.* (2014). These species are typically found in oxidizing environments, being formed as supergene products of bismuthinite  $\pm$  Bi sulfosalts assemblages or in high-temperature fumaroles.

Mineralogical studies of the Pb-Bi-Zn-As-Fe-Cu ore district from Tavagnasco, Turin, Piedmont, Italy, allowed the identification of other potential new Bi sulfates. The primary ore mineral assemblage is composed of sulfides (sphalerite, galena, arsenopyrite, with minor pyrrhotite, pyrite, chalcopyrite and bismuthinite), accessory sulfosalts (bourmonite, tennantite), and native gold. Gangue minerals are represented by quartz and siderite (Mastrangelo

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*et al.*, 1983). In addition, minor amounts of acicular Pb-Bi sulfosalts, mainly cosalite and a kobellite-like sulfosalts, have been identified recently. This sulfide assemblage is altered locally, with the occurrence of Cu-Bi-Pb secondary minerals (anglesite, azurite, langite and several Bi compounds). During a preliminary check of a suite of specimens from the Espérance supérieure tunnel (45.5416N 7.8134E) with a scanning electron microscope, energy dispersive spectra showed the presence of some phases characterized by Bi and S as the only elements with  $Z > 9$ . In order to identify these minerals, fragments were examined using single-crystal X-ray diffraction methods. One of these grains showed a klebelsbergite-like unit cell, thus suggesting that the phase under investigation was the Bi analogue of klebelsbergite,  $\text{Sb}_4\text{O}_4(\text{SO}_4)(\text{OH})_2$  (Menchetti and Sabelli, 1980; Nakai and Appleman, 1980; Roper *et al.*, 2015). The solution of its crystal structure (see below) confirmed this hypothesis.

The new mineral species has been named tavagnascoite, from the type locality, Tavagnasco, Turin, Piedmont, Italy. The mineral and its name have been approved by the IMA CNMNC (2014-099; Bindi *et al.*, 2015). Holotype material is deposited in the mineralogical collection of the Museo di Storia Naturale, Università degli Studi di Firenze, Florence, Italy, catalogue number 3149/I. This paper reports the description and characterization of tavagnascoite, together with a discussion of the structural relationships with the Sb analogue klebelsbergite.

## Occurrence and mineral description

The Tavagnasco Pb-Bi-Zn-As-Fe-Cu hydrothermal ore district is located ~50 km north of Turin, in the Alto Canavese region, Piedmont, Italy. Ore bodies were exploited intermittently from the second half of the nineteenth century (Jervis, 1873) until the 1950s (Matteucci and Zucchetti, 1962). They are embedded in the Eclogitic Micaschist Complex, belonging to the Sesia Zone, one of the innermost units of the Western Alps, located between the Southern Alps (part of the Austroalpine domain) and remnants of the Piemontese-Ligurian ocean. This tectonic unit is interpreted as a slice of continental crust composed of a pre-Hercynian metasedimentary basement intruded by Variscan metagranitoids. These rocks suffered an Eo-Alpine metamorphism to eclogite facies (Liermann *et al.*, 2002). Ore bodies are related to a system of fractures having NE to E strike, dipping NW to N, with dips to 60°; a second vein system, oriented NW, dipping NE up to 40°, intersects the first one, giving rise to a

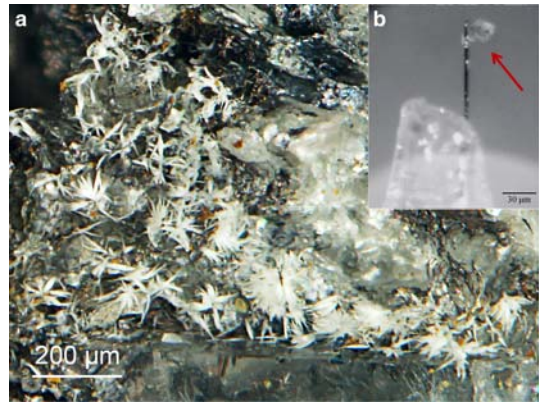


FIG. 1 The secondary mineral assemblage resulting from the alteration of bismuthinite  $\pm$  Pb-Bi sulfosalts (a). Tavagnascoite [in (b), mounted on a 0.005 mm diameter carbon fibre, which was in turn attached to a glass rod] occurs in this secondary assemblage.

stockwork deposit (Matteucci and Zucchetti, 1962; Mastrangelo *et al.*, 1983). The origin of the Tavagnasco ore district could be related to the intrusion of the Oligocene Traversella pluton, causing remobilization of syngenetic proto-ores hosted in metasedimentary rocks (Mastrangelo *et al.*, 1983).

Tavagnascoite occurs as brittle, colourless, blocky crystals, transparent to translucent, up to 40  $\mu\text{m}$  in size, with a silky lustre (Fig. 1a). No cleavage or parting was observed. Owing to the very small crystal size and their rarity (only two grains were available for the mineralogical study), microhardness and density were not measured. Calculated density, based on the ideal formula, is 6.505  $\text{g cm}^{-3}$ ; on the basis of the empirical formula, the calculated density is 6.334  $\text{g cm}^{-3}$ . The mean refractive index of tavagnascoite, obtained from the Gladstone-Dale relationship (Mandarino, 1979, 1981) using the ideal formula and the calculated density, is 2.00. In the specimen studied, tavagnascoite occurs within vugs of quartz veins, associated with other still poorly-characterized Bi oxides and sulfates (Fig. 1b), originating from the supergene alteration of the bismuthinite  $\pm$  Pb-Bi sulfosalts assemblage.

## Chemical composition

Quantitative chemical data for the crystal fragment used for the structural investigation were collected using a JEOL JXA-8200 electron microprobe operating in wavelength dispersive spectrometry mode. The following analytical conditions were

TABLE 1. Electron microprobe analysis of tavagnascoite.

Oxide	Wt.%	Range ( $n = 3$ )	e.s.d.	Standard
Bi <sub>2</sub> O <sub>3</sub>	85.32	84.09–87.11	0.21	Bi <sub>2</sub> O <sub>3</sub>
Sb <sub>2</sub> O <sub>3</sub>	0.58	0.36–1.08	0.04	Sb <sub>2</sub> O <sub>3</sub>
PbO	2.18	1.71–2.86	0.09	PbS
SO <sub>3</sub>	8.46	7.44–9.05	0.14	PbS
Sum	96.54	96.01–97.85	1.00	
H <sub>2</sub> O <sub>calc</sub>	1.77			
Total	98.31			

e.s.d. – estimated standard deviation.

used: accelerating voltage 20 kV, beam current 30 nA, beam size 1  $\mu\text{m}$ , counting times 15 s for peak and 20 s for background. Standards (element, emission line) were Bi<sub>2</sub>O<sub>3</sub> (BiM $\alpha$ ), Sb<sub>2</sub>O<sub>3</sub> (SbL $\alpha$ ), PbS (PbM $\alpha$ , SK $\alpha$ ). The crystal fragment was found to be homogeneous within analytical error. Chemical data are given in Table 1. The H<sub>2</sub>O content was calculated assuming two OH groups per formula unit. The low analytical total could be related to the small size of the polished grain, in particular to the small thickness of the sample analysed (<10  $\mu\text{m}$ ). The empirical formula, based on 10 O apfu is (Bi<sub>3.74</sub>Pb<sub>0.10</sub>Sb<sub>0.04</sub>) $\Sigma$ <sub>3.88</sub>O<sub>3.68</sub>(SO<sub>4</sub>)<sub>1.08</sub>(OH)<sub>2</sub>, with rounding errors. The slight overestimation of sulfur, as well as the underestimation of Bi, has also been reported for leguermite by Garavelli *et al.* (2014) and related both to the small thickness of the analysed sample and to the behaviour of sulfates with respect to the standard under the electron beam. The simplified chemical formula is Bi<sub>4</sub>O<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>2</sub>, which requires Bi<sub>2</sub>O<sub>3</sub> 90.48, SO<sub>3</sub> 7.77, H<sub>2</sub>O 1.75, total 100.00 wt.%.

### X-ray crystallography

Single-crystal X-ray diffraction data were collected using an Oxford Diffraction Xcalibur 3 diffractometer equipped with a Sapphire 2 CCD area detector with graphite-monochromatized MoK $\alpha$  radiation. A one-minute frame-time and 0.3° frame-width were used. A full theta Ewald sphere was collected to  $\theta_{\text{max}} = 35^\circ$ , giving a total of 18,423 reflections. Intensity integration and standard Lorentz polarization corrections were performed with the *CrysAlis RED* (Oxford Diffraction, 2006) software package. The program *ABSPACK* in *CrysAlis RED* (Oxford Diffraction, 2006) was used for the absorption

correction. Tests on the distribution of  $|E|$  values indicated the absence of an inversion centre ( $|E^2 - 1| = 0.811$ ). This information, coupled with that from systematic absences, suggested the choice of the space group *Pca2*<sub>1</sub>. Refined unit-cell parameters are  $a = 5.831(1)$ ,  $b = 11.925(2)$ ,  $c = 15.123(1)$  Å,  $V = 1051.6(3)$  Å<sup>3</sup>,  $Z = 4$ . The  $a:b:c$  ratio, using the single-crystal data, is 0.489 : 1:1.268.

The crystal structure was refined with *SHELXL-97* (Sheldrick, 2008) starting from the atom coordinates given by Menchetti and Sabelli (1980) for klebelsbergite, which represents the Sb-analogue of tavagnascoite. In the crystal structure, five cation and ten anion sites occur. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). The occupancies of the four independent Bi sites, namely Bi1, Bi2, Bi3 and Bi4, were refined initially by using the curve of Bi vs.  $\square$ . These sites were found to be fully occupied and their site occupancies were fixed to 1. Some S–O distances were found to be relatively short

TABLE 2. Crystal and experimental data for tavagnascoite.

<b>Crystal data</b>	
Crystal size (mm)	0.028 × 0.020 × 0.012
Cell setting, space group	Orthorhombic, <i>Pca2</i> <sub>1</sub>
$a, b, c$ (Å);	5.831(1), 11.925(2), 15.123(1)
$V$ (Å <sup>3</sup> )	1051.6(3)
$Z$	4
<b>Data collection and refinement</b>	
Radiation, wavelength (Å)	MoK $\alpha$ , $\lambda = 0.71073$
Temperature (K)	293
$2\theta_{\text{max}}$ (°)	70.00
Measured reflections	18,423
Unique reflections	2377
Reflections with $F_o > 4\sigma(F_o)$	1269
$R_{\text{int}}$	0.0325
$R\sigma$	0.0478
Range of $h, k, l$	$-9 \leq h \leq 9, -18 \leq k \leq 18,$ $-24 \leq l \leq 24$
$R [F_o > 4\sigma(F_o)]$	0.0370
$R$ (all data)	0.0399
$wR$ (on $F^2$ )	0.0573
Goof	0.573
Number of least-squares parameters	138
Max. and min. residual peak ( $e \text{ \AA}^{-3}$ )	3.23 (at 0.15 Å from Bi2) –5.22 (at 0.62 Å from Bi3)

(e.g. S–O1  $\approx$  1.40 Å) and consequently constraints were imposed. The target value (i.e. 1.47 Å) was chosen in agreement with the average  $\langle$ S–O $\rangle$  distance found by Roper *et al.* (2015) for klebelsbergite, i.e. 1.477 Å. The occurrence of a {001} twin was assumed, as in klebelsbergite (Menchetti and Sabelli, 1980; Nakai and Appleman, 1980; Roper *et al.*, 2015). The refined twin-component ratio is 23:77. After several cycles of anisotropic refinement,  $R_1$  converged to 0.037 for 1269 reflections with  $F_o > 4\sigma(F_o)$ . Table 2 reports details of the selected crystal, data collection and refinement. Final atom coordinates and displacement parameters are given in Table 3, whereas selected bond distances and bond-valence sums are shown in Tables 4 and 5, respectively. Bond-valence sums were calculated with the bond parameters given by Krivovichev (2012) and Brese and O’Keeffe (1991) for  $\text{Bi}^{3+}$ –O and  $\text{S}^{6+}$ –O bonds, respectively. Table 6 reports the calculated powder X-ray diffraction pattern of tavagnascoite on the basis of the structural model obtained through the single-crystal X-ray diffraction study.

## Description of the crystal structure

The crystal structure of tavagnascoite comprises Bi–O polyhedra and  $\text{SO}_4$  tetrahedra (Fig. 2). Bismuth polyhedra are connected through edge-sharing to form Bi–O sheets parallel to (001). Successive sheets are linked together by  $\text{SO}_4$  tetrahedra and H bonds. This structural arrangement is identical to that first described by Menchetti and Sabelli (1980) for klebelsbergite. Bismuth coordination is irregular, a common feature observed in other  $\text{Bi}^{3+}$  compounds related to the presence of stereochemically active  $6s^2$  lone-pair electrons (e.g. Aurivillius, 1988). Taking into account the shortest Bi–O distances, Bi atoms are three- and four- coordinate (Fig. 3), with distances ranging from 2.055 (Bi1–O7) to 2.510 Å (Bi2–O8). Average  $\langle$ Bi–O $\rangle$  bond distances vary between 2.19 (at the Bi1 site) and 2.36 Å (at the Bi3 site). These distances are longer than those observed in klebelsbergite (ranging between 2.10 and 2.15 Å; Menchetti and Sabelli, 1980; Roper *et al.*, 2015), in agreement with the larger ionic radius of  $\text{Bi}^{3+}$ . Additional longer distances (considering an arbitrary limit of 3.5 Å) increase the Bi coordination number to six (Bi1 and Bi2), seven (Bi4) and eight (Bi3). Bond-valence sums (BVS) at Bi1 and Bi4 are in quite good agreement with the expected value, i.e. 2.95 and 3.08 valence units (vu),

respectively. On the contrary, Bi2 and Bi3, having the largest average bond distances, are underbonded significantly, with BVS values of 2.35 and 2.39 vu, respectively. The possible substitution of  $\text{Bi}^{3+}$  by  $\text{Pb}^{2+}$  could only partially explain such low values, owing to the limited amount of Pb replacing Bi ( $\sim$ 0.10 apfu from electron microprobe data).

The geometry of the  $\text{SO}_4$  tetrahedra is almost regular, but is affected by the constraints on the S–O distances imposed during the refinement. The average  $\langle$ S–O $\rangle$  distance is shorter than the ideal one, resulting in the slight oversaturation of the S atom. Examination of the short O $\cdots$ O distances that are not polyhedral edges reveals the occurrence of some hydrogen bonds, in agreement with what is observed in klebelsbergite. Menchetti and Sabelli (1980) reported hydrogen bonds between O2 and O5 and between O3 and O9, later partially confirmed by the localization of the H atoms by Roper *et al.* (2015). Actually, these latter authors proposed a bifurcated H-bond system involving O5, O2 and a symmetry-related O5 position. In tavagnascoite, the H-bond system could be very similar to that proposed by Roper *et al.* (2015) for klebelsbergite. The O2 $\cdots$ O5 distance is 2.84(1) Å, similar to that reported in the crystal structure of klebelsbergite, 2.82 Å (Roper *et al.*, 2015); the O5 $\cdots$ O5 distance is 2.947(2) Å, to be compared with 3.00 Å given by Roper *et al.* (2015). By using the relation proposed by Ferraris and Ivaldi (1988), the O2 $\cdots$ O5 and O5 $\cdots$ O5 distances have a bond strength of 0.17 and 0.14 vu, respectively. Finally, O3 $\cdots$ O9 is longer [3.16(1) Å] than that observed in the Sb compound (2.96 Å), and the corresponding bond strength is 0.11 vu.

Oxygen atoms display different coordination environments. They can be distinguished between sulfate bonded and non-sulfate bonded. The former are represented by oxygen atoms at the O1, O2, O3 and O4 sites. The oxygen O1 site has a tetrahedral coordination, being bonded to S and three Bi atoms (Bi2, Bi3 and Bi4). Four coordination is also observed for the O2 site, but in this case the geometrical arrangement of cations is ‘one-sided’, with Bi–O distances longer than 2.50 Å. In this way, O2 can be an acceptor of a hydrogen bond from O5. The O3 site is three-coordinate, being bonded to S and two Bi atoms. In addition, it is an acceptor of a hydrogen bond from O9. Finally, O4 is three-coordinate, with an additional, very long Bi–O distance of 3.52(1) Å. The BVS values of the oxygen atoms bonded to the  $\text{SO}_4$  group range between 1.94 and 2.20 vu; these values are satisfactory considering the constraints on

TABLE 3. Fractional atom coordinates and displacement parameters ( $\text{\AA}^2$ ) for tavagnascoite.

Site	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Bi1	0.47170(7)	0.36213(4)	0.25326(3)	0.0235(1)	0.0246(2)	0.0243(2)	0.0215(2)	-0.0001(1)	0.0002(1)	0.0000(1)
Bi2	0.40043(8)	0.10158(3)	0.08473(2)	0.0209(1)	0.0214(1)	0.0215(2)	0.0199(1)	0.0007(1)	-0.0004(1)	0.0000(1)
Bi3	0.14881(6)	0.39878(2)	0.44242(2)	0.0189(1)	0.0194(2)	0.0200(2)	0.0174(1)	-0.0004(1)	-0.0006(1)	-0.0001(1)
Bi4	0.03080(6)	0.14153(3)	0.28524(3)	0.0250(1)	0.0247(2)	0.0252(2)	0.0251(1)	0.0001(1)	0.0000(1)	0.0003(1)
S	0.6897(5)	0.2634(2)	0.5110(3)	0.0272(5)	0.0300(11)	0.0290(12)	0.0228(9)	-0.0003(9)	-0.0030(8)	0.0002(10)
O1	0.8513(11)	0.2499(7)	0.4389(5)	0.0233(12)	0.016(2)	0.033(4)	0.021(2)	-0.003(2)	0.006(2)	-0.009(2)
O2	0.6406(14)	0.3821(4)	0.5188(5)	0.0212(13)	0.029(3)	0.014(2)	0.021(2)	0.008(2)	0.023(3)	0.011(2)
O3	0.4662(11)	0.2152(11)	0.4902(7)	0.0360(18)	0.025(3)	0.046(5)	0.037(4)	-0.011(4)	0.002(3)	-0.011(3)
O4	0.7784(14)	0.2117(8)	0.5935(7)	0.0303(16)	0.023(3)	0.032(4)	0.036(4)	0.007(3)	0.009(3)	0.003(3)
O5	0.2727(14)	0.4820(7)	0.1697(5)	0.0208(11)	0.026(3)	0.022(3)	0.015(2)	-0.005(2)	-0.001(2)	-0.007(2)
O6	0.2993(16)	0.2128(12)	0.1906(6)	0.0353(22)	0.033(4)	0.060(7)	0.013(2)	0.003(4)	-0.002(3)	0.012(4)
O7	0.4078(34)	0.4828(14)	0.3471(13)	0.0611(48)	0.072(10)	0.048(7)	0.063(10)	-0.021(8)	-0.027(8)	-0.011(7)
O8	0.6144(28)	-0.0021(14)	0.1808(12)	0.0526(36)	0.043(5)	0.053(7)	0.062(8)	-0.031(6)	-0.021(6)	-0.001(5)
O9	0.2748(12)	0.0425(6)	0.3497(5)	0.0182(11)	0.023(3)	0.019(3)	0.013(2)	-0.001(2)	-0.001(2)	0.003(2)
O10	0.1929(19)	0.2835(10)	0.3318(7)	0.0362(20)	0.040(4)	0.039(5)	0.029(4)	0.013(4)	0.005(4)	0.001(4)

TABLE 4. Selected interatomic distances (in Å) for tavagnascoite.

Bi1	–O7	2.055(16)	Bi2	–O6	2.161(11)
	–O10	2.221(10)		–O8	2.280(17)
	–O5	2.233(8)		–O4	2.291(8)
	–O6	2.254(14)	average		2.244
average		2.191	–O8	2.510(17)	
	–O5	2.852(8)	–O3	2.906(9)	
	–O4	3.343(11)	–O1	3.176(10)	
	–O7	3.450(19)			
Bi3	–O10	2.181(12)	Bi4	–O10	2.063(13)
	–O7	2.316(22)		–O9	2.091(7)
	–O7	2.459(14)		–O6	2.286(10)
	–O1	2.483(7)	average		2.196
average		2.360	–O9	2.827(7)	
S	–O2	2.857(5)	–O1	2.857(6)	
	–O3	2.957(13)	–O8	3.365(13)	
	–O2	3.098(9)			
	–O2	3.186(7)			
	–O2	1.449(5)			
	–O1	1.450(4)			
	–O3	1.459(4)			
	–O4	1.486(10)			
average		1.461			

 TABLE 6. Calculated powder X-ray diffraction data for tavagnascoite. Intensities and  $d_{hkl}$  values were calculated using *Powdercell 2.3* software (Kraus and Nolze, 1996) on the basis of the structural model given in Table 3; only reflections with  $I_{\text{calc}} > 5$  are listed.

$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$
6	7.56	0 0 2	5	2.614	1 4 1
<b>29</b>	<b>6.39</b>	<b>0 1 2</b>	10	2.520	0 0 6
15	5.24	1 1 0	17	2.469	2 1 3
<b>19</b>	<b>4.95</b>	<b>1 1 1</b>	7	2.309	2 0 4
<b>32</b>	<b>4.019</b>	<b>1 2 1</b>	5	2.084	2 4 0
8	3.781	0 0 4	7	2.065	2 4 1
12	3.651	1 2 2	7	2.017	0 5 4
<b>28</b>	<b>3.604</b>	<b>0 1 4</b>	7	2.009	2 4 2
15	3.284	1 3 0	9	1.997	1 1 7
<b>100</b>	<b>3.213</b>	<b>1 2 3</b>	11	1.925	0 4 6
17	3.210	1 3 1	5	1.922	0 6 2
6	3.013	1 3 2	5	1.918	1 2 7
17	2.981	0 4 0	9	1.834	3 2 1
12	2.863	2 0 1	6	1.805	1 3 7
13	2.801	1 2 4	9	1.762	1 6 3
5	2.739	0 3 4	7	1.733	2 5 3
10	2.720	2 0 2	6	1.577	3 2 5

The strongest reflections are given in bold.

the S–O distances imposed during the refinement of the crystal structure. Among the non-sulfate bonded oxygen positions, sites occupied by oxygen and by hydroxyl groups can be distinguished. The latter occur at the O5 and O9 sites, in agreement with their low BVS values (0.60 and 0.87 vu, after the

correction for the hydrogen bonds). The atoms hosted at these positions are two-coordinate by Bi; additional very long Bi–O distances occur (Bi–O > 3.60 Å). The four remaining anion positions are occupied by oxygen. O6 and O10 are three-coordinate,

TABLE 5. Bond-valence sums (BVS, in valence units, vu) for tavagnascoite.

	O1	O2*	O3*	O4	O5*	O6	O7	O8	O9*	O10	$\Sigma_{\text{cations}}$	Theor.
Bi1				0.06	0.60	0.58	0.87			0.62	2.95	3.00
					0.17		0.05					
Bi2	0.08		0.15	0.53		0.70		0.55			2.35	3.00
								0.34				
Bi3	0.36	0.16	0.13				0.51			0.67	2.39	3.00
		0.10					0.38					
		0.08										
Bi4	0.16					0.54		0.48	0.81	0.86	3.08	3.00
								0.06	0.17			
S	1.60	1.61	1.56	1.45							6.22	6.00
$\Sigma$ anions	2.20	1.95	1.84	2.04	0.77	1.82	1.81	1.43	0.98	2.15		
Theor.	2.00	2.00	2.00	2.00	1.00	2.00	2.00	2.00	1.00	2.00		

\*Atoms involved in hydrogen bonds.

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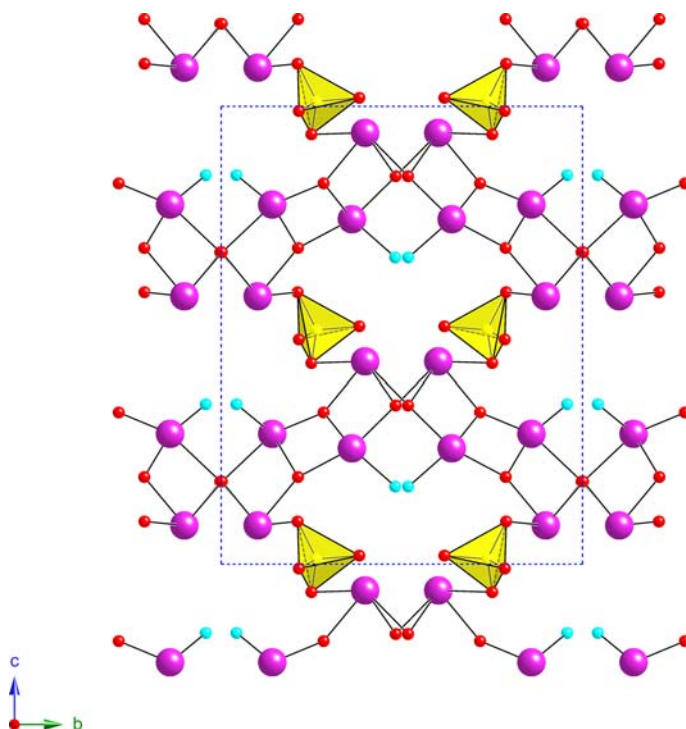


FIG. 2 Crystal structure of tavagnascoite as seen down [100]. Circles: violet = Bi sites; red = oxygen atoms; light blue = hydroxyl groups. Polyhedra = S site.

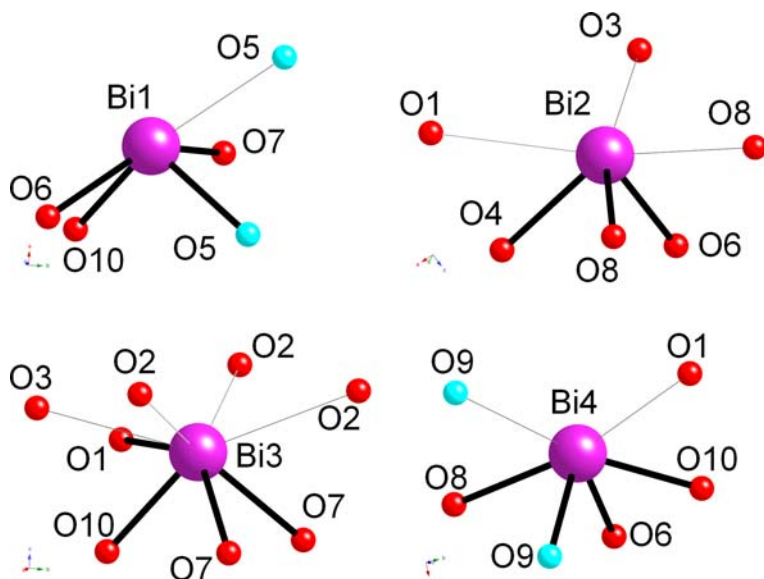
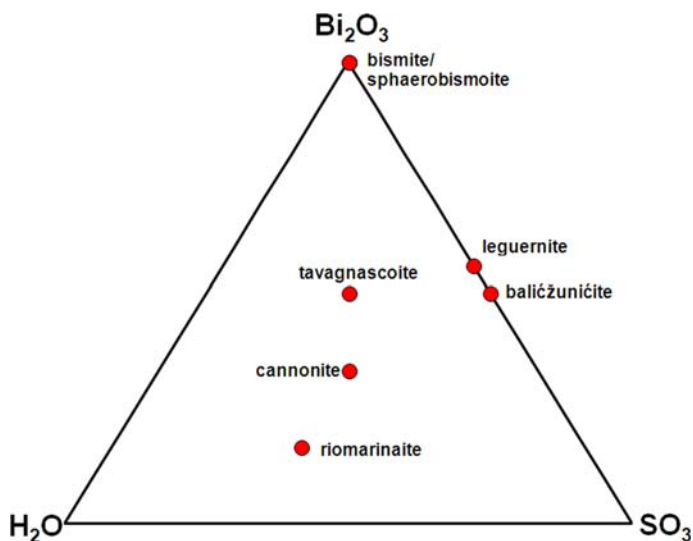


FIG. 3 Coordination environments of Bi atoms in tavagnascoite. Thick lines = Bi–O distances shorter than 2.50 Å; thin lines = Bi–O distances between 2.50 and 3.0 Å; dotted lines = Bi–O distances between 3.0 and 3.50 Å. Same symbols as in Fig. 2.


 FIG. 4 Minerals belonging to the ternary system  $\text{Bi}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ .

whereas the coordination of O7 and O8 increases to four if one considers Bi–O distances longer than 3.35 Å [i.e. Bi1–O7 = 3.45(2) Å; Bi4–O8 = 3.36(1) Å]. Bond-valence sum values of oxygen non-bonded to  $\text{SO}_4$  groups can be considered reasonable for O6, O7 and O10. On the contrary, the BVS value for the oxygen at the O8 position is very low (1.43 vu). Such undersaturation could be related to uncertainties in the determination of the oxygen position due to local structural disorder. Such a feature could be also the cause of the undersaturation observed at the Bi2 and Bi3 sites.

#### Relationships with other species and the role of $\text{Bi}^{3+}\text{--Sb}^{3+}$ substitution

Tavnascoite is a new oxyhydroxy bismuth sulfate fitting the 07.B group of the Strunz and Nickel (2001) classification, i.e. sulfates with additional anions, without  $\text{H}_2\text{O}$ . It belongs to the ternary system  $\text{Bi}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$ , in which seven mineral species are known. Indeed, in addition to the bismuth sulfates cited briefly above, this chemical system is completed by two dimorphs of  $\text{Bi}_2\text{O}_3$ , bismite and sphaerobismoite (Fig. 4). From a structural point of view, tavnascoite is the Bi analogue of klebelsbergite,  $\text{Sb}_4\text{O}_4(\text{SO}_4)(\text{OH})_2$  (Menchetti and Sabelli, 1980; Nakai and Appleman, 1980). The two mineral species form the new klebelsbergite group, in agreement with Mills *et al.* (2009). The replacement of  $\text{Sb}^{3+}$  by the

larger  $\text{Bi}^{3+}$  cation results in a significant increase in the unit-cell volume, 962.8 Å<sup>3</sup> for klebelsbergite (Roper *et al.*, 2015) compared with 1051.6 Å<sup>3</sup> for tavnascoite, an increase of +9.2%. A very small amount of  $\text{Sb}^{3+}$  replacing  $\text{Bi}^{3+}$  was detected during electron microprobe analysis of tavnascoite. The miscibility range between tavnascoite and klebelsbergite is unknown. Another chemical substitution occurring in tavnascoite is represented by the replacement of  $\text{Bi}^{3+}$  by  $\text{Pb}^{2+}$  related possibly to the mechanism  $\text{Bi}^{3+} + \text{O}^{2-} = \text{Pb}^{2+} + \text{OH}^-$ . Lead could be hosted at the larger Bi site (Bi3).

The pair tavnascoite–klebelsbergite is a rare example of isotypism between Bi and Sb compounds (Table 7). The Bi–Sb substitution occurs also in complex oxides of the cervantite group, but induces a structural transition from centrosymmetric space groups (e.g. *Pcnn* in bismuto-tantalite – Galliski *et al.*, 2001) for Bi-dominant phases to polar space groups (e.g. *Pc2<sub>1n</sub>* in stibiotantalite – Galliski *et al.*, 2001). Similarly, the pair russellite–tungstibite could be affected by structural changes induced by Bi–Sb substitution. The crystal structure of russellite was refined by Knight (1992) in space group *Pca2<sub>1</sub>* using the synthetic analogue  $\text{Bi}_2\text{WO}_6$ . On the contrary, synthetic  $\text{Sb}_2\text{WO}_6$  has a triclinic *P1* structure and structural changes in the  $\text{Bi}_{2-x}\text{Sb}_x\text{WO}_6$  series have been investigated by Castro *et al.* (1995). It should be stressed that the natural counterpart of  $\text{Sb}_2\text{WO}_6$ , tungstibite, was described by Walenta (1995) as



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TABLE 7. Structurally related Bi and Sb minerals: unit-cell parameters, space group (s.g.) symmetry, volume variation ( $\Delta V$ ) and CPI value.

Mineral	Ideal formula	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	s.g.	$\Delta V$ (%)	CPI
Bismutocolumbite <sup>1</sup>	BiNbO <sub>4</sub>	5.668	11.725	4.971	330.36	<i>Pnma</i>	+2.1	60
Stibiocolumbite <sup>1</sup>	SbNbO <sub>4</sub>	5.557	4.932	11.808	323.62	<i>Pna2</i> <sub>1</sub>		58
Bismutotantalite <sup>2</sup>	BiTaO <sub>4</sub>	4.965	11.7831	5.6462	330.32	<i>Pcnn</i>	+2.9	60
Stibiotantalite <sup>3</sup>	SbTaO <sub>4</sub>	4.916	5.542	11.78	320.94	<i>Pbn2</i> <sub>1</sub>		58
Perite <sup>4</sup>	PbBiClO <sub>2</sub>	5.627	5.575	12.425	389.78	<i>Bmmb</i>	+4.3	61
Nadorite <sup>5</sup>	PbSbClO <sub>2</sub>	5.603	12.245	5.448	373.78	<i>Cmcm</i>		61
Russellite <sup>6</sup>	Bi <sub>2</sub> WO <sub>6</sub>	5.437	16.430	5.458	487.63	<i>Pca2</i> <sub>1</sub>	-3.2	62
Tungstibite <sup>7</sup>	Sb <sub>2</sub> WO <sub>6</sub>	8.59	9.58	6.12	503.63	<i>P22</i> <sub>1</sub> 2 <sub>1</sub> (?)		n.a.
Tavagnascoite <sup>8</sup>	Bi <sub>4</sub> O <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>2</sub>	5.831	11.925	15.123	1051.6	<i>Pca2</i> <sub>1</sub>	+9.2	48
Klebsbergite <sup>9</sup>	Sb <sub>4</sub> O <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>2</sub>	5.756	11.254	14.863	962.8	<i>Pca2</i> <sub>1</sub>		48

<sup>1</sup>Zubkova *et al.* (2002); <sup>2</sup>Galliski *et al.* (2001); <sup>3</sup>Dihlström (1938); <sup>4</sup>Gillberg (1960); <sup>5</sup>Giuseppetti and Tadini (1973); <sup>6</sup>Knight (1992); <sup>7</sup>Walenta (1995); <sup>8</sup>this work; <sup>9</sup>Roper *et al.* (2015.); n.a. = not available.

having a hypothetical space-group symmetry *P22*<sub>1</sub>2<sub>1</sub>.

According to Galy *et al.* (1975), these structural changes related to Bi<sup>3+</sup>-Sb<sup>3+</sup> substitution may be attributed to the different stereochemical activities of the lone electron pairs associated with the two cations. Introduction of the more stereochemically active Sb<sup>3+</sup> ion in Bi<sup>3+</sup> sites gives rise to higher electrostatic repulsion between lone electron pairs and oxygen atoms, thus promoting structural changes. In our opinion, the more close-packed the atomic arrangement, the more important these stereochemical effects would be. An estimation of the atom close-packing could be obtained through the ratio between the volume occupied by the atoms within the cell and the unit-cell volume, here indicated as CPI. Ratios calculated using the ionic radii given by Shannon (1976) are reported in Table 7. Compounds characterized by structural changes induced by the Sb<sup>3+</sup>-for-Bi<sup>3+</sup> substitution are characterized by high CPI values; unfortunately no structural data for natural tungstibite are available but the high CPI of its Bi counterpart, russellite, is in agreement with the structural behaviour observed in synthetic Sb<sub>2</sub>WO<sub>6</sub>. A similar value of the CPI is shown by the pair nadorite-perite but available data show no evidence of a structural change. Actually, the synthetic equivalent of perite is reported to exhibit a tetragonal symmetry (Ketterer and Krämer, 1985) and Deschanvres *et al.* (1970) reported a change of symmetry in synthetic PbSbClO<sub>2</sub> by varying the Sb:Bi atomic ratio. Consequently, the pair

nadorite-perite deserves further structure investigations. Finally, klebsbergite-like structures show significant lower CPI values, indicating a less close-packed structure. In this way, the effects of the different stereochemical activity of the 5s<sup>2</sup> and 6s<sup>2</sup> electrons of Sb<sup>3+</sup> and Bi<sup>3+</sup>, respectively, could be incorporated without significant structural changes.

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