

## VOLASCHIOITE, $\text{Fe}^{3+}_4(\text{SO}_4)\text{O}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ , A NEW MINERAL SPECIES FROM FORNOVOLASCO, APUAN ALPS, TUSCANY, ITALY

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### ABSTRACT

Volaschioite, ideally  $\text{Fe}^{3+}_4(\text{SO}_4)\text{O}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ , occurs in a small magnetite–pyrite orebody near Fornovolasco, in the Apuan Alps, Tuscany, Italy. The new mineral species is associated with pyrite and iron oxyhydroxides. In the same occurrence, other iron sulfates were identified, including alum-(K), “copiapite”, fibroferrite, halotrichite, melanterite, römerite, and voltaite. Volaschioite occurs as radial aggregates of bladed crystals, up to 100  $\mu\text{m}$  in length and less than 5  $\mu\text{m}$  across. The color is yellowish orange with an orange streak; the luster is vitreous to resinous. The mineral is transparent and strongly pleochroic. Electron-microprobe analyses lead to the empirical formula  $\text{Fe}_{4.16}(\text{SO}_4)_{0.92}\text{O}_{2.32}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ; the calculated density is 3.03  $\text{g}/\text{cm}^3$ . Volaschioite is monoclinic, with  $a$  16.068(4),  $b$  3.058(1),  $c$  10.929(2) Å,  $\beta$  93.82(3)°,  $V$  535.8(2) Å<sup>3</sup>,  $Z = 2$ , space group  $C2/m$ . The strongest three X-ray powder-diffraction lines [ $d$  in Å( $I$ )( $hkl$ )] are: 8.03(100)(200), 4.37(24)(202), 3.989(22)(400). The single-crystal X-ray diffraction pattern shows the presence of additional very weak and streaked reflections indicating a doubling of the  $b$  parameter. The average structure of volaschioite is composed of ribbons of edge-sharing Fe-centered octahedra running along  $\mathbf{b}$ , linked together by corner-sharing to form corrugated layers, decorated on both sides by sulfate groups. Additional H<sub>2</sub>O molecules are located between the layers. Volaschioite is the product of pyrite alteration in an oxidizing environment. The name of this new species refers to the ancient name of the type locality, *Forno de Volaschio*. This mineral and its name have been approved by the IMA–CNMNC (IMA2010–005).

*Keywords:* volaschioite, new mineral species, sulfate, iron, Fornovolasco, Apuan Alps, Tuscany, Italy.

### SOMMAIRE

La volaschioïte, de composition idéale  $\text{Fe}^{3+}_4(\text{SO}_4)\text{O}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ , a été découverte dans un petit gisement de magnétite–pyrite près de Fornovolasco, dans les Alpes Apuanes, en Toscane, Italie. La nouvelle espèce minérale est associée à la pyrite et à des oxyhydroxydes de fer. Au même endroit, on a pu identifier d’autres sulfates de fer, dont alum-(K), “copiapite”, fibroferrite, halotrichite, mélanterite, römerite, et voltaïte. La volaschioïte se présente en agrégats radiaires de cristaux lamellaires, atteignant 100  $\mu\text{m}$  en longueur et moins de 5  $\mu\text{m}$  en largeur. Ces cristaux sont orange jaunâtre avec une rayure orange; l’éclat est vitreux ou résineux. Le minéral est transparent et fortement pléochroïque. Les analyses, effectuées avec une microsonde électronique, ont mené à la formule empirique  $\text{Fe}_{4.16}(\text{SO}_4)_{0.92}\text{O}_{2.32}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ; la densité calculée est 3.03  $\text{g}/\text{cm}^3$ . La volaschioïte est monoclinique, avec  $a$  16.068(4),  $b$  3.058(1),  $c$  10.929(2) Å,  $\beta$  93.82(3)°,  $V$  535.8(2) Å<sup>3</sup>,  $Z = 2$ , groupe spatial  $C2/m$ . Les trois raies les plus intenses du spectre de diffraction X, méthode des poudres [ $d$  en Å( $I$ )( $hkl$ )] sont: 8.03(100)(200), 4.37(24)(202), 3.989(22)(400). La diffraction X sur monocristal confirme la présence de raies additionnelles très faibles et étirées indiquant un dédoublement du paramètre  $b$ . La structure moyenne de la volaschioïte contient des rubans d’octaèdres contenant le Fe à arêtes partagées le long de  $\mathbf{b}$ , rattachés par partage de coins pour former des couches ondulantes décorées de chaque côté par des groupes SO<sub>4</sub>. Des molécules de H<sub>2</sub>O se situent entre les couches. La volaschioïte serait un produit de l’altération de la pyrite dans un milieu oxydant. Le nom de cette nouvelle espèce rappelle l’ancien nom de la localité type, *Forno de Volaschio*. Ce minéral et son nom ont été approuvés par le comité IMA–CNMNC (IMA2010–005).

(Traduit par la Rédaction)

*Mots-clés:* volaschioïte, nouvelle espèce minérale, sulfate, fer, Fornovolasco, Alpes Apuanes, Toscane, Italie.

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## INTRODUCTION

In the Southern Apuan Alps, in Tuscany, Italy, small barite – pyrite – iron oxides deposits were exploited up to the end of the 1980s. The ores are embedded either in a metavolcanic – metasedimentary sequence (*Scisti di Fornovolasco* Formation) or at the contact between this formation and lenses of dolomitic marble of uncertain stratigraphic setting, known as *Grezzone metallifero*. In the area of Fornovolasco, the *Grezzone metallifero* hosts veins and lenticular bodies of magnetite ± pyrite ± sphalerite ± pyrrhotite ± iron hydroxides (Carmignani *et al.* 1976, Tanelli 1983, Ciarapica *et al.* 1985, Pandeli *et al.* 2004). The mineralogy of this ore was studied by Biagioni *et al.* (2008) and Orlandi *et al.* (2008). These authors described three different kinds of occurrence: i) dolomite ± siderite ± quartz veins embedded in dolomitic marbles and magnetite orebodies; ii) veins of quartz ± K-feldspar ± albite ± carbonates, embedded in phyllites and tourmaline-rich schists, and iii) lenses of altered pyrite.

In the first occurrence, Biagioni *et al.* (2008) identified some common sulfides and sulfosalts (chalcopyrite, jamesonite, pyrite, pyrrhotite, sphalerite, stibnite), together with products of their alteration (bindheimite, bottinoite, cerussite, erythrite, gypsum, hydrozincite, sulfur) and with other common phases (“apatite”, barite, “chlorite”). In the veins of quartz ± K-feldspar ± albite ± carbonates, other sulfosalts (boulangerite, jamesonite, jaskólskiite, meneghinite) and products of their alteration (mimetite and some Bi phases, such as beyerite, bismutite, and ximengite) were found, in some cases associated with anatase, rutile, and a tourmaline-supergrupp phase. Finally, some iron sulfates were identified in piles of altered pyrite; this kind of occurrence is particularly developed in the tunnels of the 740 m level, the oldest level of the Fornovolasco mines. Here, well-crystallized sulfates were found: alum-(K), “copiapite”, fibroferrite, halotrichite, melanterite, römerite, and voltaite. Volaschioite was found in this third kind of occurrence.

The new species and its name, volaschioite (pronounced *volaskioait*), have been approved by the CNMNC of the IMA (IMA 2010–005). It is named after the ancient name of the type locality, *Forno de Volas-*

*chio*. The origin of the name Fornovolasco is linked to the metallurgy of iron: *Forno* means “furnace”, whereas the word *Volaschio* is related to the presence, since the twelfth century, of a hospital, the *Hospitale de Volaschio* (Bonini & Biagioni 2007). However, according to another tradition, the word “*Volasco*” is linked to a man, Volasco from Brescia (Lombardy, Italy), who was the first to work iron at Fornovolasco (Raffaelli 1879). The type material is deposited in the mineralogical collections of Museo di Storia Naturale e del Territorio, University of Pisa, catalog number 19300.

## OCCURRENCE AND PARAGENESIS

Volaschioite was found in the old tunnels at the 740 m level of the Cava del Ferro mining complex, near Trimpello, a small locality near the town of Fornovolasco. This mining complex had been exploited since the 15<sup>th</sup> century and was finally abandoned in the late 1970s.

The first specimen of volaschioite was found in 2009 by Tiberio Bardi, amateur mineralogist, who provided us with the sample. In hand specimen, volaschioite occurs as radial aggregates of bladed crystals, elongate on [010], up to 100 µm long and less than 5 µm across (Fig. 1). Its origin is closely related to the alteration of pyrite. This process takes place with the first appearance of melanterite; in some cases, rare crystals of voltaite are present in the inner portions of the sulfate masses. In the outer portion of the altered piles, römerite and “copiapite” appear. These phases show both oxidation states of Fe. Halotrichite appears as hairy white crystals associated both with melanterite and with römerite. At the periphery of the pyrite-derived masses, in contact with air, Fe<sup>3+</sup>-dominant phases are predominant: goethite and fibroferrite are very common. Volaschioite was limited to a very restricted area under a fibroferrite layer. This mineralogical sequence (Fig. 2) is a typical product of pyrite alteration in an oxidizing environment, as described by Atencio & Hypolito (1993), with an increasing Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) value (atomic) from the core to the periphery of the piles of altered pyrite (Table 1).

## OPTICAL AND PHYSICAL PROPERTIES

Volaschioite is yellowish orange in color; it has an orange streak and vitreous to resinous luster. It is transparent. Volaschioite is brittle, and it shows a perfect cleavage on {100}. Its hardness could not be measured because of the small size of the crystals. It is not soluble in water. In plane-polarized transmitted light, volaschioite is strongly pleochroic, red along [010] and yellowish orange normal to this direction. Rossman (1975, 1976) pointed out that ferric iron hydroxy sulfates are strongly pleochroic, with the greatest absorption occurring where the electric vector is in the direction of the Fe<sup>3+</sup>–Fe<sup>3+</sup> chains. This statement is in agreement with the

TABLE 1. SEQUENCE OF IRON SULFATES FROM THE BOTTOM TO THE TOP OF THE PILES OF SULFATES

Mineral	Chemical formula	Fe <sup>3+</sup> /(Fe <sup>2+</sup> +Fe <sup>3+</sup> )
Melanterite	Fe <sup>2+</sup> (SO <sub>4</sub> )·7H <sub>2</sub> O	0
Halotrichite	Fe <sup>2+</sup> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·22H <sub>2</sub> O	0
Voltaite	KFe <sup>2+</sup> <sub>3</sub> Fe <sup>3+</sup> <sub>3</sub> Al(SO <sub>4</sub> ) <sub>12</sub> ·18H <sub>2</sub> O	0.375
Römerite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·14H <sub>2</sub> O	0.66
Copiapite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>4</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> ·20H <sub>2</sub> O	0.8
Volaschioite	Fe <sup>3+</sup> <sub>4</sub> (SO <sub>4</sub> )O <sub>2</sub> (OH) <sub>2</sub> ·2H <sub>2</sub> O	1
Fibroferrite	Fe <sup>3+</sup> (SO <sub>4</sub> )(OH)·5H <sub>2</sub> O	1

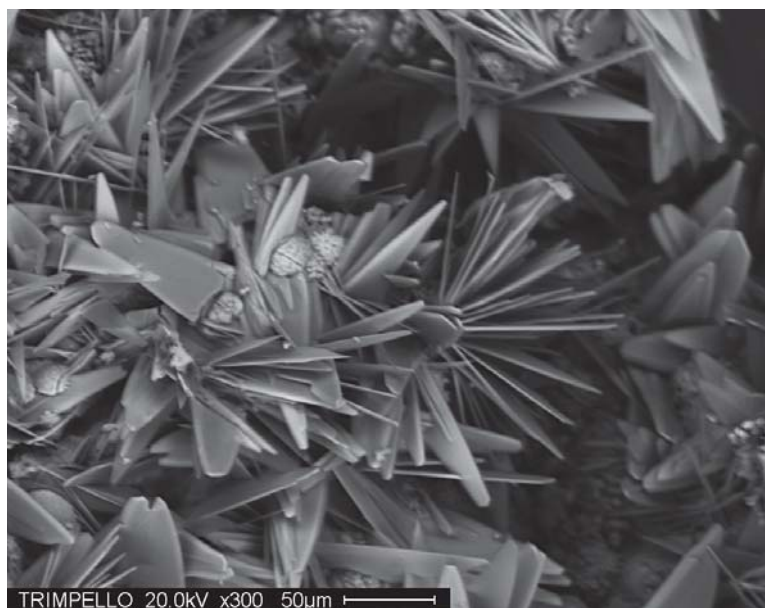


FIG. 1. Volaschioite, in bladed crystals of up to 50 micrometers.

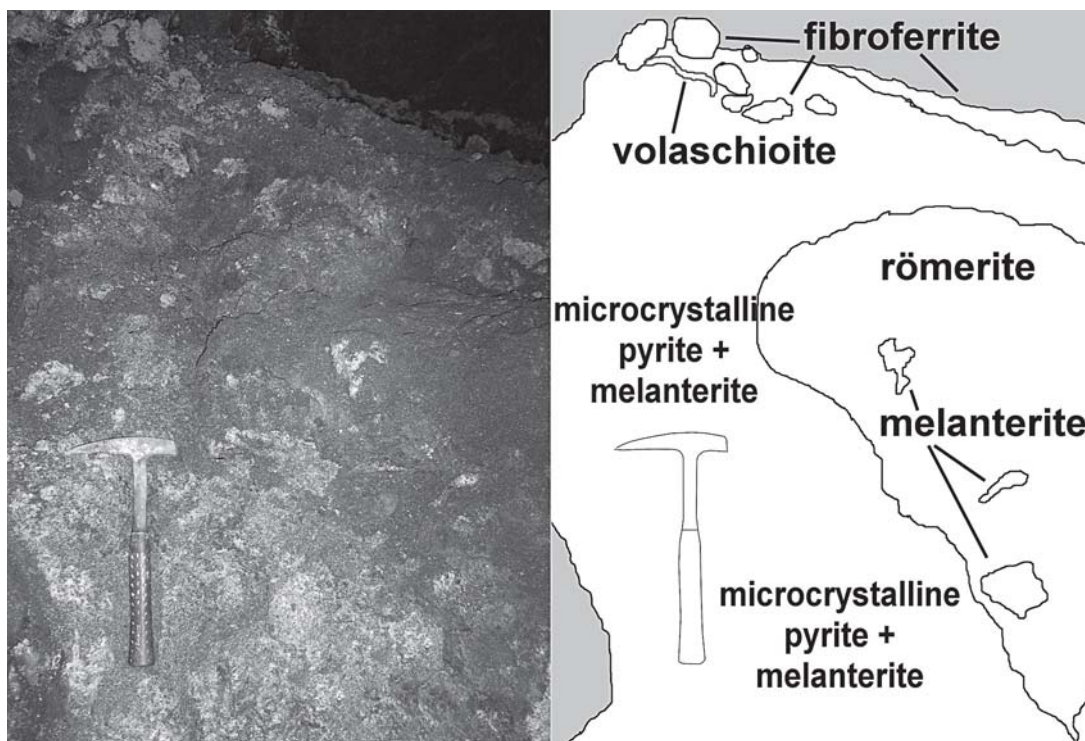


FIG. 2. The pile of altered pyrite in which volaschioite was found.

structural features shown by volaschioite (see below). The indices of refraction, measured using the Becke line method with liquids of known index, are greater than 1.68; the calculated mean index of refraction is 1.90. The extinction is parallel to [010]; on {100}, elongation is positive. Density was not measured because of the scarcity of available material and the small size of crystals; the calculated density is 3.03 g/cm<sup>3</sup>.

#### CHEMICAL AND SPECTROSCOPIC STUDIES

Results of preliminary EDS analyses showed the presence of Fe and S as the only elements with  $Z > 9$ . Volaschioite was analyzed using an ARL-SEMQ microprobe (University of Modena and Reggio Emilia, Italy) under the following operating conditions: accelerating voltage 15 kV, beam current 20 nA, beam size 6  $\mu\text{m}$ ; standards (element, emission line): BaSO<sub>4</sub> (SK $\alpha$ ), ilmenite (FeK $\alpha$ ). Table 2 shows the results of 11 analytical points. The H<sub>2</sub>O content was calculated by assuming six hydroxyl groups and two H<sub>2</sub>O molecules per formula unit, as suggested by the structure refinement (see below). The sum of the wt% of the oxides is low, even after the addition of 17.18 wt% of H<sub>2</sub>O. This may be the consequence of the very small size of the crystals, which have a thickness of less than 5  $\mu\text{m}$ , *i.e.*, close to the nominal value of the beam-spot diameter. Moreover, it may depend on the possible instability of volaschioite under the electron beam, with some of the sulfate volatilized along with H<sub>2</sub>O during analysis, as witnessed by the high (Fe:S)<sub>at</sub> ratio. The empirical formula of volaschioite, based on 14 anions per formula unit, is Fe<sub>4.16</sub>(SO<sub>4</sub>)<sub>0.92</sub>O<sub>2.32</sub>(OH)<sub>6</sub>•2H<sub>2</sub>O, in good agreement with the formula Fe<sup>3+</sup><sub>4</sub>(SO<sub>4</sub>)O<sub>2</sub>(OH)<sub>6</sub>•2H<sub>2</sub>O suggested by the structural study; that formula requires 65.24 Fe<sub>2</sub>O<sub>3</sub>, 16.36 SO<sub>3</sub>, and 18.40 wt.% H<sub>2</sub>O. A Fe:S ratio of 4:1 is known in the discredited mineral "glockerite" and in the synthetic phase B obtained by Walter Lévy & Quémeur (1966). As shown by X-ray powder diffraction (Table 3), volaschioite is the natural counterpart of the latter phase, which has a chemical composition Fe<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>10</sub>, as measured by wet-chemical analyses.

Raman spectra of volaschioite were obtained on an unpolished fragment in nearly back-scattered geometry with a Jobin-Yvon Horiba Labram apparatus, equipped

TABLE 2. CHEMICAL COMPOSITION OF VOLASCHIOITE

Constituent	wt%	Range	esd	Probe standard
Fe <sub>2</sub> O <sub>3</sub>	63.33	59.95 – 67.99	2.24	BaSO <sub>4</sub>
SO <sub>3</sub>	14.07	11.77 – 15.20	1.19	ilmenite
sum	77.40	74.23 – 79.90	1.47	
H <sub>2</sub> O*	17.18			
Total	94.58			

\* calculated from structural data.

with a motorized  $x$ - $y$  stage and an Olympus microscope with a 50 $\times$  objective. The 632.8 nm line of an He-Ne laser was used; laser power was controlled by means of a series of density filters. The system was calibrated using the 520.6 cm<sup>-1</sup> Raman band of silicon. Spectra were collected with multiple acquisitions (2 to 6) with single counting times, ranging between 20 and 180 s.

The Raman spectra of volaschioite show intense peaks in the region from 200 to 1200 cm<sup>-1</sup> (Fig. 3); the

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR VOLASCHIOITE, COMPARED WITH THOSE FOR SYNTHETIC Fe<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>10</sub>

$d_{\text{obs}}$	$l_{\text{obs}}$	Volaschioite			JCPDS 21-429		
		$d_{\text{calc}}$	$l_{\text{calc}}$	$h k l$	$d_{\text{hkl}}$	$l_{\text{hkl}}$	$h k l$
8.03	s	10.90	4.09	0 0 1	10.9	8	0 0 1
		8.02	100	2 0 0	8.03	100	2 0 0
		6.67	3.78	2 0 1	6.68	4	2 0 1
4.37	m	4.655	1.36	2 0 2	4.66	2	2 0 2
		4.375	24.46	2 0 2	4.38	25	2 0 2
		4.008	23.97	4 0 0	4.02	18	4 0 0
3.989	m	3.846	0.69	4 0 1	3.85	2	4 0 1
		3.683	0.09	4 0 1	3.69	2	4 0 1
		3.397	0.54	2 0 3	3.40	2	2 0 3
3.343	mw	3.337	15.48	4 0 2	3.34	10	4 0 2
		3.230	5.68	2 0 3	3.23	4	2 0 3
		3.131	4.88	4 0 2	3.14	2	4 0 2, 5 0 1
3.028	w	3.004	4.11	1 1 0	3.01	4	1 1 0
		2.905	0.18	1 1 1	2.913	2	1 1 1
		2.887	0.10	1 1 1	2.895	2	1 1 1
2.73	w	2.786	0.19	4 0 3	2.792	2	4 0 3, 2 1 1
		2.726	11.94	0 0 4	2.728	10	0 0 4
		2.654	0.88	3 1 0			
2.633	mw	2.645	11.96	1 1 2	2.651	8	1 1 2
		2.636	1.86	6 0 1			
		2.635	3.50	2 0 4	2.637	4	2 0 4, 6 0 1
2.548	w	2.617	11.02	1 1 2	2.623	8	1 1 2
		2.599	3.23	3 1 1	2.604	4	3 1 1
		2.560	4.23	3 1 1	2.566	2	3 1 1, 2 1 2
2.414	w	2.530	3.65	2 0 4	2.534	2	2 0 4
		2.465	3.17	6 0 2	2.466	2	6 0 2
		2.418	7.81	3 1 2	2.423	4	3 1 2
2.305	w	2.356	1.91	3 1 2	2.362	2	3 1 2, 4 1 1
		2.339	1.50	6 0 2	2.342	2	6 0 2, 0 1 3
		2.330	1.34	1 1 3	2.334	2	1 1 3, 5 0 3
2.213	w	2.327	0.16	4 0 4			
		2.301	4.19	1 1 3	2.307	4	1 1 3
		2.225	0.17	6 0 3	2.226	4	2 1 3, 6 0 3
2.099	w	2.213	6.80	5 1 0	2.217	2	7 0 1, 5 1 0
		2.188	1.47	5 1 1	2.189	4	4 0 4, 4 1 2
		2.187	2.01	4 0 4			
2.010	w	2.181	0.43	0 0 5	2.182	2	1 0 5, 3 1 3
		2.110	0.59	3 1 3	2.115	2	5 1 1, 5 0 4
		2.088	0.49	6 0 3	2.089	2	3 1 3
1.930	w	2.084	3.50	5 1 2			5 1 2, 6 0 3
		2.07	0.13	2 0 5	2.072	2	2 0 5, 3 0 5
		2.018	1.90	5 1 2	2.039	2	0 1 4
1.873	w	2.006	2.40	1 1 4	2.023	2	5 1 2
		2.004	0.54	8 0 0	2.010	2	1 1 4, 8 0 0
		1.995	1.52	8 0 1			
1.837	w	1.923	5.30	8 0 2			
		1.871	3.83	3 1 4			
		1.833	4.37	7 1 0			
1.760	w	1.824	3.32	7 1 1			
		1.758	3.60	5 1 4			

Peak intensity was visually estimated; s: strong, m: medium, mw: medium-weak, w: weak.

bands are rather broad, suggesting possible structural disorder. The bands observed are at the following frequencies (in  $\text{cm}^{-1}$ ): 250, 299 (shoulder), 319, 408, 453, 527, 698, 941, 1005, 1055, 1178. Two very weak additional bands are at 606 and 975  $\text{cm}^{-1}$ . A digital version of the spectrum presented in Figure 3 is available from the Depository of Unpublished Data on the MAC web site [document Volaschioite CM49\_605].

According to Nakamoto (1986), the  $\text{SO}_4$  tetrahedra exhibit symmetric stretching ( $\nu_1$ ) and bending ( $\nu_2$ ) modes, and antisymmetric stretching ( $\nu_3$ ) and bending ( $\nu_4$ ) vibrations at 983, 450, 1105, and 611  $\text{cm}^{-1}$ , respectively. Ling & Wang (2010) reported the Raman spectra of some ferric sulfates; according to these authors, the frequency range for the various vibrational modes are 989–1098  $\text{cm}^{-1}$  ( $\nu_1$ ), 415–514  $\text{cm}^{-1}$  ( $\nu_2$ ), 1066–1230  $\text{cm}^{-1}$  ( $\nu_3$ ), and 595–677  $\text{cm}^{-1}$  ( $\nu_4$ ). The interpretation of the micro-Raman spectra of volaschioite is rather speculative. The main features are related to the fundamental modes of  $\text{SO}_4$ ; some  $\text{SO}_4$  modes probably are split, and this could indicate a lower symmetry than the ideal. In addition, the intensity of the  $\nu_2$  modes (408 and 453  $\text{cm}^{-1}$ ) is higher than that of the  $\nu_1$  modes (probably those at 1005 and 1055  $\text{cm}^{-1}$ ); this unusual feature was observed also in the micro-Raman spectrum of schwertmannite by Mazzetti & Thistlethwaite (2002). Moreover, it is probable that Fe–O modes could contribute to the spectra; Mazzetti & Thistlethwaite (2002) attributed to Fe–O modes the bands at 294, 318, 350, and 544  $\text{cm}^{-1}$  observed in the spectra of schwertmannite.

In the region between 1500 and 1800  $\text{cm}^{-1}$ , there are very weak and broad bands, with a maximum at about 1530  $\text{cm}^{-1}$ , whereas in the region from 3000 to 3800  $\text{cm}^{-1}$ , only a weak and very broad band can be

observed. Therefore, the presence of  $\text{H}_2\text{O}$ , suggested by the structural studies and by the wet-chemical data on the synthetic compound (Walter Lévy & Quéméneur 1966), cannot be confirmed experimentally by Raman spectroscopy. It is possible that preferential orientation plays an important role in detecting the Raman signals from O–H bending and stretching modes; using a small crystal of volaschioite, flattened on (100), it was possible only to detect vibrations lying in this plane, whereas O–H bonds are out the plane (100). In addition, some experimental evidence shows that iron sulfates can dehydrate owing to heating by the He–Ne laser beam (Mazzetti & Thistlethwaite 2002), with the appearance of iron oxides.

### X-RAY DIFFRACTION STUDIES

#### *X-ray powder diffraction*

The X-ray powder-diffraction pattern for volaschioite was obtained using a Gandolfi camera, 114.6 mm in diameter, with Ni-filtered  $\text{CuK}\alpha$  radiation. Indexing of the reflections was done using the calculated powder-pattern conforming to the structural model described below, using the software POWDERCELL (Kraus & Nolze 2000). The unit-cell parameters refined through least-square methods of 17 reflections with CELREF (Laugier & Bochu 1999) are  $a$  16.086(1),  $b$  3.0654(3),  $c$  10.934(1) Å,  $\beta$  93.91(1)°,  $V$  537.90(8) Å<sup>3</sup>. Table 3 shows the X-ray powder-diffraction pattern of volaschioite; it is compared with that of the synthetic phase B described by Walter Lévy & Quéméneur (1966) and reported in the JCPDS, #21–429.

#### *Single-crystal X-ray diffraction*

Because of the very small size of the volaschioite crystals, even long-exposure oscillation photographs

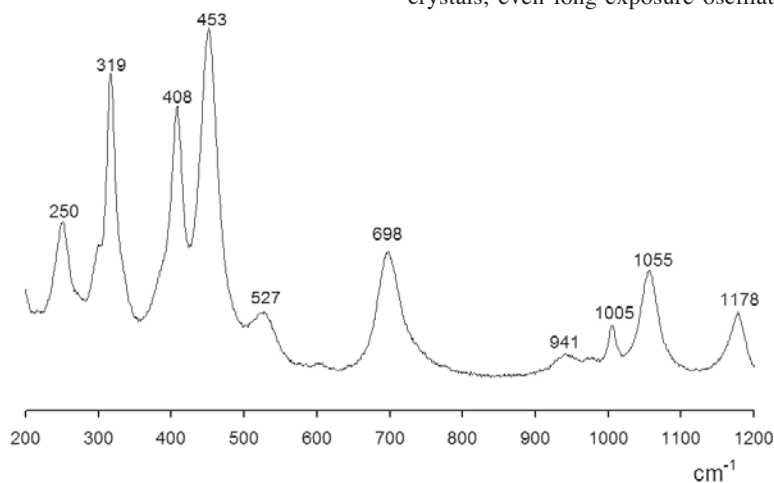


FIG. 3. Raman spectrum of volaschioite, in the region between 200 and 1200  $\text{cm}^{-1}$ .



show very weak reflections, pointing to a 3 Å periodicity on the elongation of the crystals. Therefore, intensity data were collected at the XRD1 beamline of the Elettra synchrotron facility of Basovizza, Trieste, Italy. The data collection was performed by rotating the crystal around one axis by angles  $\Delta\phi = 5^\circ$  and collecting the diffraction effects by means of a 165 mm MarCCD detector, placed 60 mm from the crystal. Reflections were integrated, and their intensities were corrected for Lorentz, polarization, and background effects using the HKL package of programs (Otwinowski & Minor 1997). The observed reflections pointed to a monoclinic *C*-centered cell with  $a$  16.068(4),  $b$  3.058(1),  $c$  10.929(2) Å,  $\beta$  93.82(3)°. The structure was solved by direct methods by using SHELXS-97 (Sheldrick 1997) in space group *C2/m*. This model was refined to  $R = 6.4\%$  for 246 reflections with  $F_o > 4\sigma(F_o)$ . Details of data collection and crystal-structure refinement are reported in Table 4. A table of structure factors and a cif file are available from the Depository of Unpublished Data of the MAC website [document Volaschioite CM49\_605].

#### DESCRIPTION OF THE CRYSTAL STRUCTURE

The structure of volaschioite (Fig. 4) is composed of ribbons of edge-sharing Fe-centered octahedra, running along **b**, linked together by corner-sharing to form corrugated layers. Each layer consists of two kinds of ribbons of octahedra: (a) a two-octahedron-thick ribbon, running along **b**, formed by edge-sharing Fe1 octahedra. Sulfate groups are connected to this ribbon at both sides, with half occupancy; (b) a two-octahedron-thick ribbon, running along **b**, formed by edge-sharing Fe2 octahedra.

An apparent disorder exists with regard to the position of the sulfate groups and the occurrence of one H<sub>2</sub>O molecule between the layers of octahedra, with the corresponding atom sites having 50% occupancy. However, as it is not possible that two sulfate groups be located in two adjacent sites at a distance of only 3 Å (*i.e.*, the periodicity along the **b** axis), it is highly probable that a regular alternation of (SO<sub>4</sub>) groups and H<sub>2</sub>O molecules occurs in volaschioite along the [010] direction. Such an ordered sequence would double the *b* translation, with the consequent occurrence of additional superstructure reflections. Actually, only continuous streaks of diffuse intensity, normal to the **b**\*

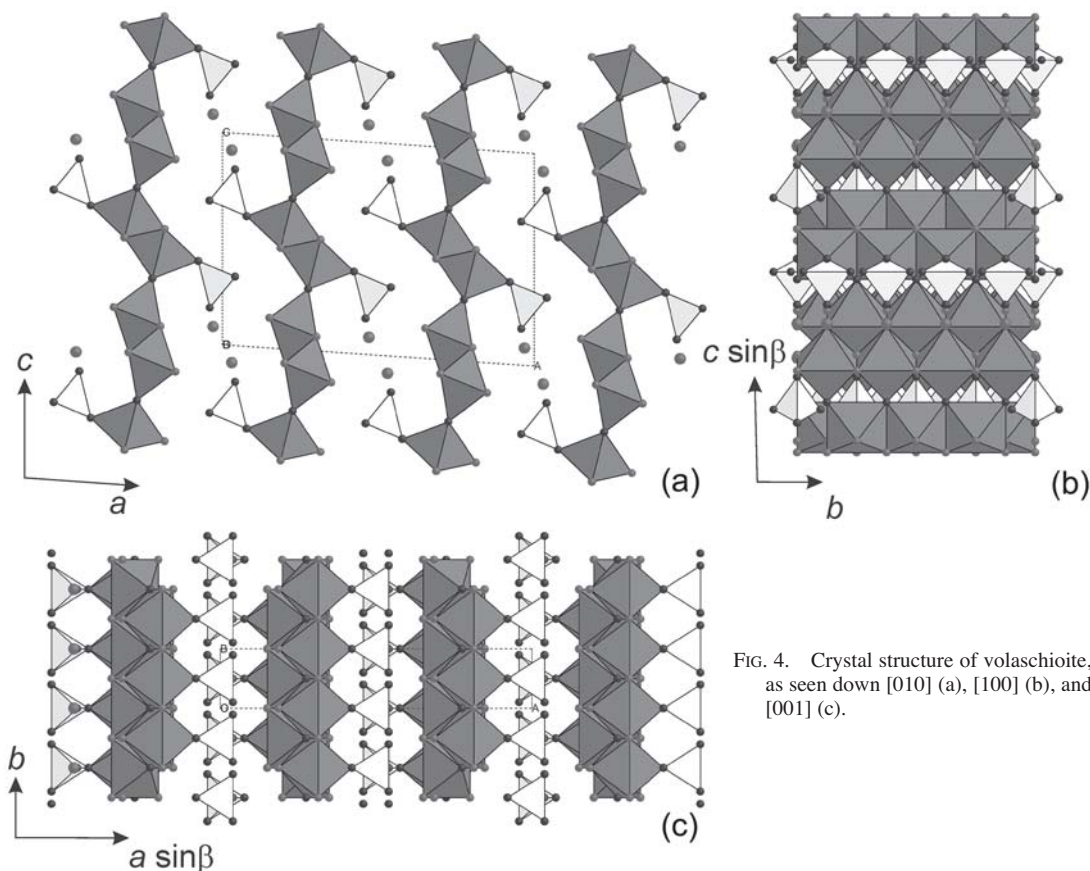


FIG. 4. Crystal structure of volaschioite, as seen down [010] (a), [100] (b), and [001] (c).

axis, at half-integral values of  $k$ , were detected in the diffraction patterns (Fig. 5), indicating that such ordered sequences of alternating (SO<sub>4</sub>) and H<sub>2</sub>O groups are not long-range-related in different parts of the crystal.

Refined positions of atoms and selected bond-distances are given in Tables 5 and 6. The occurrence of some relatively short O...O distances between oxygen atoms not belonging to the same coordination polyhedra suggests the presence of hydrogen bonds. Figure 6 shows the proposed scheme of hydrogen bonding. According to this scheme, the O5 atom corresponds to an oxygen atom wherever it is bonded to S, whereas it would correspond to a H<sub>2</sub>O molecule if the S site is vacant. In addition, W7 substitutes for O7 wherever the SO<sub>4</sub> is not present.

Table 7 shows the bond-valence balance for volaschioite (Brese & O'Keeffe 1991). The bond-valence sums of anions, corrected taking into account the system of hydrogen bonds in Figure 6, are reported in the second-to-last column. The two different cases (occurrence of either a sulfate group or a H<sub>2</sub>O molecule within the layers of octahedra) are indicated, respectively, by one and two asterisks. Table 8 reports the O...O distances and the corresponding bond-valence contributions (Ferraris & Ivaldi 1988). According to the structural refinement, the chemical formula of volaschioite may be written as Fe<sup>3+</sup><sub>4</sub>(SO<sub>4</sub>)O<sub>2</sub>(OH)<sub>6</sub>•2H<sub>2</sub>O.

## DISCUSSION

Volaschioite is the natural analogue of the phase B synthesized by Walter Lévy & Quéméneur (1966).

TABLE 4. VOLASCHIOITE: INFORMATION ON DATA COLLECTION AND STRUCTURAL REFINEMENT

Crystal data	
X-ray formula	Fe <sub>4</sub> (SO <sub>4</sub> )O <sub>2</sub> (OH) <sub>6</sub> •2H <sub>2</sub> O
Crystal size	0.07 × 0.01 × 0.005 mm <sup>3</sup>
Cell setting, space group	Monoclinic, C2/m
<i>a</i> , <i>b</i> , <i>c</i>	16.068(4), 3.058(1), 10.929(2) Å
β	93.82(3)°
<i>V</i>	535.8(2) Å <sup>3</sup>
<i>Z</i>	2
Data collection and refinement	
Radiation, wavelength	synchrotron, λ = 1 Å
Detector to sample distance	60 mm
Active detection-area	16.5 × 16.5 cm <sup>2</sup>
Number of frames	72
Rotation width per frame	5°
Maximum observed 2θ	53.09°
Measured reflections	1246
Unique reflections	249
Reflections <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )	246
<i>R</i> <sub>int</sub>	0.0485
<i>R</i> <sub>σ</sub>	0.0282
Range of <i>h</i> , <i>k</i> , <i>l</i>	-14 ≤ <i>h</i> ≤ 14, -2 ≤ <i>k</i> ≤ 2, -9 ≤ <i>l</i> ≤ 9
<i>R</i> [ <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )]	0.0641
<i>R</i> (all data)	0.0644
<i>wR</i> (on <i>F</i> <sub>o</sub> <sup>2</sup> )	0.1564
Goof	1.109
No. of least-squares parameters	36

These authors indicated a chemical formula of Fe<sub>4</sub>(SO<sub>4</sub>)(OH)<sub>10</sub> on the basis of wet-chemical analytical data. The crystal-structure refinement of volaschioite leads to an interpretation of the real nature of anionic species in this phase, represented by O<sup>2-</sup> and OH<sup>-</sup> anions in addition to H<sub>2</sub>O molecules.

Volaschioite belongs to the chemical system Fe<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O (Fig. 7), in which fourteen other natural ferric iron sulfates are known. All these phases are produced by the alteration of pyrite or, more rarely, in fumarolic conditions. Chemically, volaschioite is similar to "glockerite", an ill-defined and discredited phase having a Fe:S ratio of 4:1. This compound was found to be identical to lepidocrocite by Fojt (1975), whereas Bigham & Nordstrom (2000) pointed to the identity between "glockerite" and schwertmannite. This latter mineral is an iron oxyhydroxysulfate that occurs as an ochreous precipitate from acid, sulfate-rich waters (Bigham *et al.* 1994); it is a poorly known mineral phase, and its compositional range is still uncertain. Some authors have suggested that the crystal structure of schwertmannite resembles that of akaganeite (Bigham *et al.* 1990, Barham 1997, Waychunas *et al.* 2001, Fernandez-Martinez *et al.* 2010), which has edge-sharing Fe octahedra forming a hollandite-like structure with Cl ions hosted in the tunnels (Post & Buchwald 1991, Post *et al.* 2003); the SO<sub>4</sub> groups could occupy these positions in schwertmannite. The chemical composition proposed by Bigham *et al.* (1994) is Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>8-3x</sub>(SO<sub>4</sub>)<sub>x</sub>, with *x* varying from 1 to 1.75; Yu *et al.* (1999) estimated that the *x* value could vary from 1.74 to 1.86. Fernandez-Martinez *et al.* (2010)

TABLE 5. FINAL POSITIONS, OCCUPANCIES, AND ISOTROPIC DISPLACEMENT PARAMETERS (Å<sup>2</sup>) OF ATOMS IN VOLASCHIOITE

	Site population	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
Fe1	1 Fe <sup>3+</sup>	0.2971(1)	0	0.3927(2)	0.014(2)
Fe2	1 Fe <sup>3+</sup>	0.2264(1)	1/2	0.1251(2)	0.014(2)
S	0.5 S	0.4906(5)	0	0.2983(6)	0.022(3)
O1	1 O	0.2744(6)	1/2	0.2888(9)	0.019(3)
O2	0.5 O	0.5405(8)	0.605(5)	0.3245(11)	0.031(5)
O3	1 OH	0.1511(6)	0	0.1423(9)	0.020(3)
O4	1 OH	0.1860(6)	0	0.4732(9)	0.017(3)
O5	0.5 O, 0.5 H <sub>2</sub> O	0.4228(7)	0	0.3872(10)	0.034(4)
O6	1 OH	0.3014(6)	0	0.0670(8)	0.021(3)
O7	0.5 O	0.4599(14)	0	0.170(2)	0.031(6)
W7	0.5 H <sub>2</sub> O	0.4700(19)	0	0.081(3)	0.063(9)

TABLE 6. SELECTED BOND-DISTANCES (Å) IN VOLASCHIOITE

Fe1 - O1	1.924(6)	Fe2 - O1	1.902(10)	S - O7	1.45(3)
- O1	1.924(6)	- O3	1.966(6)	- O2	1.47(2)
- O5	2.024(12)	- O3	1.966(6)	- O2	1.47(2)
- O4	2.042(10)	- O6	2.072(7)	- O5	1.51(2)
- O4	2.123(7)	- O6	2.072(7)		
- O4	2.123(7)	- O6	2.117(10)		

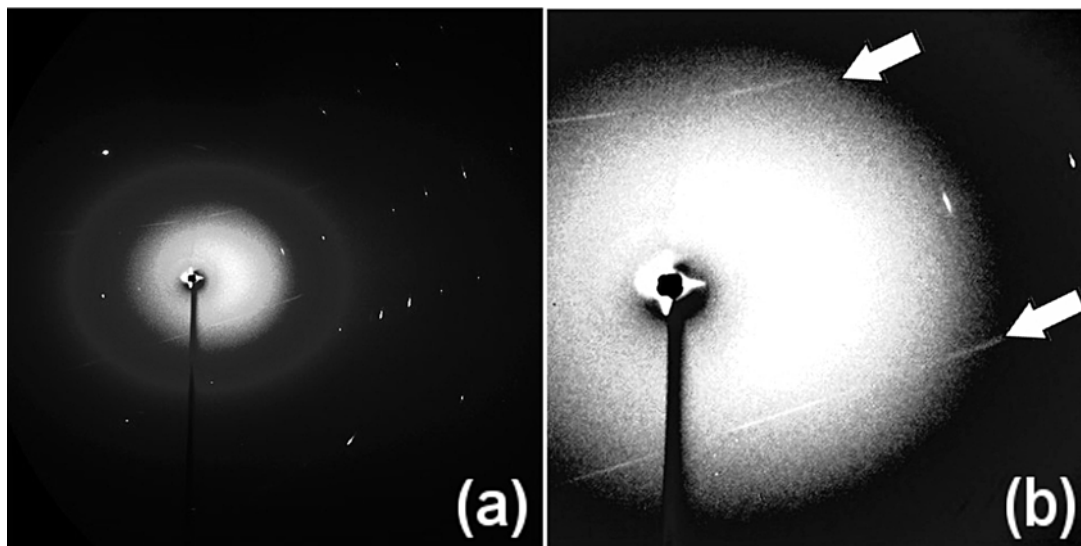


FIG. 5. (a) Diffraction pattern of volaschioite, collected with a 165 mm MarCCD detector at the Elettra synchrotron facility. In (b), the white arrows indicate rows of continuously streaked reflections, doubling the *b* periodicity.

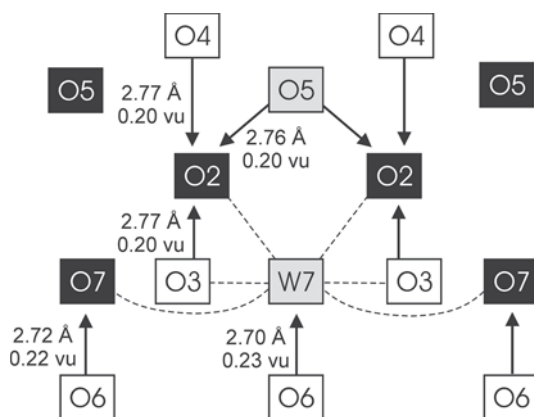


FIG. 6. Hydrogen-bond scheme in volaschioite. The type of anion is indicated by different colors (black for oxygen atoms, grey for H<sub>2</sub>O molecules, white for hydroxyl groups).

TABLE 7. BOND-VALENCE BALANCE IN VOLASCHIOITE

	Fe1	Fe2	S	$\Sigma_{\text{anions}}$	$\Sigma'_{\text{corr}}$	species
O1	0.64 0.64	0.68		1.96	1.96	O
O2			1.51 1.51	1.51	2.11	O
O3		0.57 0.57		1.14	0.94	OH
O4	0.47 0.37 0.37			1.21	1.01	OH
O5	0.49		1.37	1.86* 0.49**	1.86* 0.09**	O* H <sub>2</sub> O**
O6		0.43 0.43 0.38		1.24	1.02* 1.01**	OH
O7			1.6	1.60	1.94*	O
W7				0.00	0.11**	H <sub>2</sub> O
$\Sigma_{\text{cations}}$	2.98	3.06	5.99			

\* S and O7 sites are occupied, W7 is empty.

\*\* SO<sub>4</sub> group is replaced by H<sub>2</sub>O in W7 site (S, O7 sites are empty).

suggested, on the basis of data on pair-distribution function, a higher sulfate content ( $3.2 \pm 1$  sulfate groups on the basis of 8 Fe atoms). Therefore, it is possible that the compositional range of schwertmannite could extend toward the chemical composition of volaschioite. As a consequence, volaschioite could be a common mineral phase in acid mine-drainage systems, but it is possible that it has been overlooked owing to its schwertmannite-like chemical composition. However, further studies

will be needed to constrain the genesis of volaschioite. As pointed out by Jerz & Rimstidt (2003), the evolution from ferrous sulfates to iron oxyhydroxide minerals is related to a complex series of oxidation, dehydration, and neutralization reactions, strictly dependent on environmental conditions.

The crystal structure of volaschioite refined during this study can be considered an average structure. In fact, sulfate groups and H<sub>2</sub>O molecules are located in two statistically possible positions; their half-occupancy



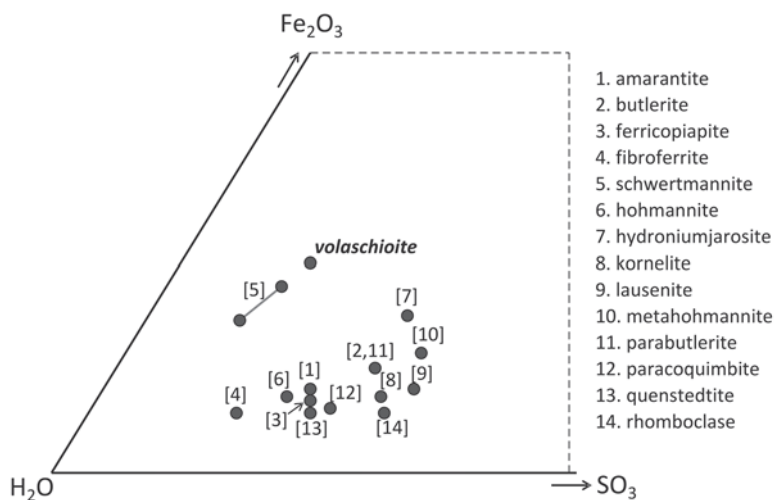


FIG. 7. Chemical composition of volaschioite, expressed as mol.%, in the ternary system  $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ .

TABLE 8. O...O DISTANCES AND CORRESPONDING BOND-VALENCE

Donor → acceptor	O ... O (Å)	<i>vu</i>	
O5 (H <sub>2</sub> O) → O2 (O)	O5 ... O2	2.76(2)	0.20
O3 (OH) → O2 (O)	O3 ... O2	2.77(1)	0.20
O4 (OH) → O2 (O)	O4 ... O2	2.77(2)	0.20
O6 (OH) → O7 (O)	O6 ... O7	2.72(2)	0.22
O6 (OH) → W7 (H <sub>2</sub> O)	W7 ... O6	2.70(3)	0.23
W7 (H <sub>2</sub> O) → O7 (O)	W7 ... O7	3.04(5)	0.12

Weaker hydrogen bonds may occur between the H<sub>2</sub>O molecule W7 and the atoms O2, O7, O3.

implies that only every second site in the [010] direction is occupied by S, whereas H<sub>2</sub>O is absent, and *vice versa*. As a consequence, in the real structure, the orientation of the sulfate groups can be slightly different, with a modification of the hydrogen-bonding scheme within the layers. The ordered distribution of SO<sub>4</sub> groups and H<sub>2</sub>O molecules along **b** could be the reason for the observed doubling of the short *b* parameter. It is important to stress that the superstructure reflections observed in X-ray diffraction patterns indicate that each ordered mono-dimensional sequences along [010] could be only short-range-related to the others, both in the same layers along **c**, and in different layers stacked along **a**. Orlandi & Bonaccorsi (2009) described identical structural features in the hydroxy-hydrated copper sulfate mineral montetrisaite.

Following the structural classification of sulfates suggested by Hawthorne *et al.* (2000), this mineral presents a new arrangement of octahedral and tetrahedral

units disposed in infinite sheets; no other natural sulfate is known so far with a crystal structure analogous to that of volaschioite.

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