MONTETRISAITE, A NEW HYDROXY-HYDRATED COPPER SULFATE SPECIES FROM MONTE TRISA, VICENZA, ITALY

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ABSTRACT

Montetrisaite, a new hydroxy-hydrated copper sulfate mineral species from Monte Trisa, Torrebelvicino, Vicenza, in Italy, has chemical formula $Cu_6(SO_4)(OH)_{10} \cdot 2H_2O$. It is associated with galena, sphalerite, chalcopyrite, cerussite, anglesite, goethite, langite, posnjakite, linarite and redgillite. The crystals are blue, vitreous, transparent, striated vertically, with a cleavage, {001}. The diffraction pattern shows strong reflections pointing to an orthorhombic unit-cell with a 2.989(2), b 16.970(5), c 14.812(4) Å, space group $Cmc2_1$, $Z = 2$. The strongest reflections [d in Å(I_{rel})(hkl)] are: 7.45(100)(002), 3.73(35)(004), 2.788(18)(061), 2.503(14)(132) and 1.595(20)(175). In addition, very weak and diffuse reflections occur, which point to a monoclinic cell with a doubled a parameter. The crystal structure is built up of layers of edge-sharing Jahn–Teller-distorted Cu-centered octahedra, to which single SO_4 groups are connected on one side. Between the layers, H_2O molecules are located, and the layers are connected through hydrogen bonds. The refined average structure shows sulfate groups and H_2O molecules in both their statistically possible positions; in the real structure, however, only one half of those positions can be really occupied. The new mineral is structurally related to posnjakite, wroewolfeite, langite, and spangolite. On the other hand, its structure is significantly different from that of redgillite $Cu_6(SO_4)(OH)_{10} \cdot H_2O$, which has a very similar chemical formula.

Keywords: montetrisaite, hydroxy-hydrated copper sulfate, average structure, Mount Trisa, Vicenza, Italy.

SOMMAIRE

La montetrisaïte, nouvelle espèce minérale découverte à Monte Trisa, Torrebelvicino, Vicenza, en Italie, est un sulfate de cuivre hydroxy-hydraté ayant la formule chimique $Cu_6(SO_4)(OH)_{10} \cdot 2H_2O$. Lui sont associé galène, sphalérite, chalcopyrite, cérussite, anglésite, goethite, langite, posnjakite, linarite et redgillite. Les cristaux sont bleus, d'aspect vitreux, transparents, avec stries verticales et un clivage, {001}. Le spectre de diffraction X montre des réflexions intenses indiquant une maille orthorhombique, a 2.989(2), b 16.970(5), c 14.812(4) Å, groupe spatial $Cmc2_1$, $Z = 2$. Les raies les plus intenses [d en Å(I_{rel})(hkl)] sont: 7.45(100)(002), 3.73(35)(004), 2.788(18)(061), 2.503(14)(132) et 1.595(20)(175). De plus, nous observons des réflexions floues de très faible intensité qui semblent indiquer une maille monoclinique ayant un paramètre a doublé. La structure contient des couches d'octaèdres à Cu à arêtes partagées, rendus difformes à cause de l'effet de Jahn–Teller, auxquelles sont rattachées d'un côté des groupes isolés de SO_4. Les molécules de H_2O logent entre ces couches, qui sont alors liées par liaisons hydrogène. La structure moyenne affinée montre des groupes sulfate et des molécules de H_2O occupant deux positions statistiquement possibles, quoiqu'en réalité, seulement la moitié de ces positions ne pourrait être occupée. Du point de vue structural, la nouvelle espèce a des points communs avec posnjakite, wroewolfeite, langite, et spangolite. En revanche, sa structure diffère de façon importante de celle de la redgillite, $Cu_6(SO_4)(OH)_{10} \cdot H_2O$, qui possède une formule chimique très semblable.

(Traduit par la Rédaction)

Mots-clés: montetrisaïte, sulfate de cuivre hydroxy-hydraté, structure moyenne, mont Trisa, Vicenza, Italie.

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INTRODUCTION

Montetrisaite, a new hydroxy-hydrated oxysalt of copper having the chemical formula $Cu_6(SO_4)(OH)_{10} \cdot 2H_2O$, is a recently discovered mineral found at Monte Trisa, Vicenza, Italy, and named after the type locality. Both the mineral and the mineral name have been approved by the Commission on New Mineral, Nomenclature and Classification of the IMA (No. 2007–009). The type material is deposited at the Museo di Storia Naturale e del Territorio of the University of Pisa at Calci, Pisa, Italy, catalogue no. 18900. According to the Dana classification (Gaines *et al.* 1997), the mineral belongs to type 31.2 [hydrated sulfates containing hydroxyl or halogen, general formula $(A^+, B^{2+})_6(XO_4)Z_q \cdot x(H_2O)$]. According to the Strunz classification (Strunz & Nickel 2001), it belongs to the 7.DD subgroup (sulfates with additional anions, with H_2O, with only medium-sized cations, and sheets of edge-sharing octahedra).

Montetrisaite occurs within old drifts of the mining concession Lombardo, near the Veneziana mine, at Monte Trisa, within a porous altered basic volcanic rock associated with kaolinite. Other associated minerals are galena, sphalerite, chalcopyrite, cerussite, anglesite, goethite, langite, posnjakite, linarite and redgillite. Montetrisaite appears to be a product of oxidation of sulfide minerals such as chalcopyrite, pyrite, sphalerite and galena.

APPEARANCE AND PHYSICAL PROPERTIES

The morphology of the montetrisaite crystals is evident in the SEM photograph (Fig. 1). They are minute ($0.2 \times 0.015 \times 0.003$ mm), striated vertically, with a tabular (001) and elongate [100] habit. Owing to the thinness of the crystals, only {010} striated faces were observed. Macroscopically, the crystals are blue, vitreous, and transparent. Montetrisaite is brittle, with a conchoidal fracture, and shows Mohs hardness of 2 to 3.

Optical data were collected on a very small platy (001) crystal only. During the optical determination, the crystal split into many very thin fibers, too small to be used again for other measurements. Montetrisaite is biaxial, with α 1.584(4) parallel to *a*, and γ 1.65 parallel to *b*. The axial plane is orthogonal to *c*. It shows pleochroism, very pale blue parallel to *b* and blue parallel to *a*.

CHEMICAL DATA

The chemical analyses of montetrisaite were carried out with an ARL–SEMQ electron microprobe (WDS–EPMA) at the University of Modena and Reggio Emilia (Italy). The results for five analyzed points are reported in Table 1. The operating conditions were as follows: voltage 15 kV, beam current 20 nA, beam diameter 20 μm. We used as standards: brass for Cu and Zn, $Cu_{94}Sn_6$ for Cu, cerussite for Pb, and synthetic barite $BaSO_4$ for S. The SEM–EDS qualitative chemical analyses showed the absence of other elements with an atomic number greater than 4; the absence of CO_3 groups was confirmed also by IR spectroscopy. The H_2O content was calculated by assuming ten hydroxyl groups and two H_2O molecules per formula unit, as indicated by the structural refinement. The empirical formula, calculated on the basis of 6 (Cu + Zn), is $Cu_{5.97}Zn_{0.03}(SO_4)_{0.93}(OH)_{10.00} \cdot 2H_2O$, which can be simplified to $Cu_6(SO_4)(OH)_{10} \cdot 2H_2O$. This formula is very similar to
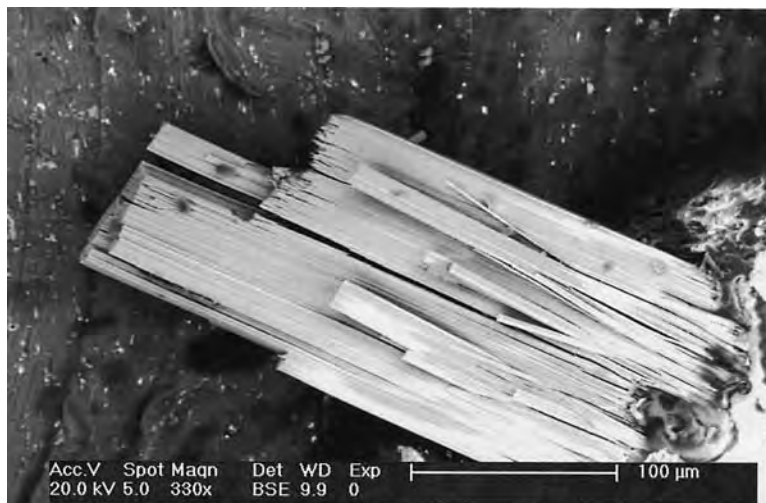

FIG. 1.   SEM photograph of montetrisaite.

the chemical formula of redgillite $Cu_6(SO_4)(OH)_{10} \cdot H_2O$ (Pluth *et al.* 2005).

X-RAY CRYSTALLOGRAPHY

Rotation and Weissenberg photographs indicated that montetrisaite is orthorhombic, with cell dimensions $a \approx 2.95$ Å, $b \approx 16.95$ Å, $c \approx 14.80$ Å; they suggest a C-centered lattice. The a parameter is shorter than any cell parameter of other hydroxyl-hydrated copper sulfates, and could suggest that the proposed unit-cell is actually a subcell; however, no superstructure reflections were observed, even in long-exposure rotation and Weissenberg photographs.

Powder-diffraction data collected with a Gandolfi camera (diameter 114.6 mm, Cu$K\alpha$ radiation, $\lambda = 1.54178$ Å) are presented in Table 2. The unit-cell parameters refined from the powder data are: a 3.010(4) Å, b 17.04(2) Å, c 14.91(1) Å, $V = 764(1)$ Å^3. The indices have been assigned taking into account the intensities recorded in the structural study.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Owing to the very minute size of the crystals and to their acicular morphology (Fig. 1), it was impossible to select a single needle suitable for a conventional collection of intensity data. Therefore, a very small single crystal of montetrisaite (Table 3) was used to collect the intensity data at the X-ray Diffraction Beamline of the Elettra Synchrotron facility (Trieste, Italy). The data collection was performed by rotating the crystal by steps of $\Delta\varphi = 3°$ and recording the diffracted beams by means of a 165 mm MarCCD detector. Data were integrated and corrected for Lorentz, polarization, and background effects using the HKL package (Otwinowski & Minor 1997). The data were corrected for absorption effects with the program MULTISCAN in WINGX (Farrugia 1999) on the basis of the intensities of equivalent reflections. Additional information on the data collection and structure refinement can be found in Table 3. In the observed diffraction pattern, reflections point to an orthorhombic C-centered cell with $a \approx 2.98$, $b \approx 16.9$, $c \approx 14.8$ Å. Moreover, very weak and diffuse additional reflections were observed, suggesting that the real a parameter is actually doubled (Fig. 2). However, because of the weakness and extreme diffuseness of these superstructure reflections, the diffraction pattern recorded was finally indexed on the basis of the cell with $a = 2.98$ Å, neglecting the weak and streaked reflections. The systematic absences confirm that the lattice is C-centered, and strongly suggest a c glide perpendicular to b; a sound structural model was finally obtained through the application of the direct methods (SHELXS–97, Sheldrick 1997) in the space group $Cmc2_1$.

The positions of three independent Cu cations and of six oxygen atoms were found; they form a continuous layer of octahedra perpendicular to c (Fig. 3). The Cu–O distances range from nearly 1.9 to 2.7 Å, featuring a typical Jahn–Teller (4 + 2) distorted octahedral coordination (Burns & Hawthorne 1996). Successive Fourier syntheses showed, as expected, a high degree of disorder with regards to the interlayer content. We interpret the electron-density maxima (S, O8, O9, O5) as due to a sulfate group and to a molecule of H_2O, both of them with half occupancy and statistically distributed in two

TABLE 1. THE COMPOSITION OF MONTETRISAITE

Oxides	wt.%	Range	esd	Probe standard	Atoms	*apfu*
CuO	71.66	76.41 - 67.69	1.95	Brass; Cu$_{94}$Sn$_6$	Cu	5.97
ZnO	0.33	0.20 - 0.50	0.33	Brass	Zn	0.03
PbO	0.11	0.00 - 0.18	0.10	Cerussite	Pb	0.00
SO$_3$	11.17	9.65 -12.29	0.14	Barite	S	0.93
Σ'	83.27					
H$_2$O*	19.00				H	14.00
Σ	102.27					

Results of electron-microprobe analyses (average of five points). The H$_2$O content was calculated by assuming ten hydroxyl groups and two H$_2$O molecules per formula unit, as indicated by the structure refinement.

TABLE 2. POWDER-DIFFRACTION PATTERN OF MONTETRISAITE

h k l	*d* obs.	*d* calc.	I_{rel}	*h k l*	*d* obs.	*d* calc.	I_{rel}
0 0 2	7.45	7.45	100	0 6 4	2.264	2.259	1
0 0 4	3.73	3.73	35	1 5 1	2.234	2.231	2
0 4 3	3.23	3.23	5	1 3 4	2.166	2.165	9
0 6 1	2.788	2.790	18	0 2 7	2.064	2.066	4
0 6 2	2.654	2.654	8	1 3 5	1.991	1.985	6
1 3 1	2.615	2.619	4	0 2 8	1.820	1.821	8
1 3 2	2.503	2.505	14	1 5 6	1.672	1.670	2
1 3 3	2.341	2.345	9	1 7 5	1.595	1.598	20
				1 3 8	1.526	1.526	8

The *d* values, obtained with a Gandolfi camera, are expressed in Å.

TABLE 3. INFORMATION ON THE CRYSTAL AND THE REFINEMENT OF THE STRUCTURE OF MONTETRISAITE

Empirical formula	$Cu_6(SO_4)(OH)_{10} \cdot 2H_2O$
Formula weight	683.44
Wavelength (Å)	1.0
Crystal system	Orthorhombic
Space group	$Cmc2_1$
Unit-cell dimensions	
a (Å)	2.988(2)
b (Å)	16.970(5)
c (Å)	14.812(4)
Volume (Å^3)	751.1(6)
Z	2
Density (calculated) (g/cm^3)	3.023
Crystal size (mm)	0.10 × 0.02 × 0.01
Theta range for data collection (°)	3.89 to 27.03
Index ranges	$-2 \le h \le 2, -15 \le k \le 14, -13 \le l \le 13$
Refinement method	Full-matrix least-squares on F^2
Independent reflections	716
Refined parameters	55
Goodness-of-fit on F^2	0.997
R indices (all data)	$R1 = 0.0787, wR2 = 0.2071$
Largest diff. peak and hole	0.729 and -1.051 e.Å^{-3}

positions within the interlayer space. The occupancy of the S site, as well as the occupancy of the O5, O8 and O9 sites, was held fixed to 0.5, in agreement with both the results of chemical analyses (which indicate approximately one SO_4 group per unit cell) and the measured electron-density at the sites. The refinement of the positions of the oxygen atoms O8 and O9, which
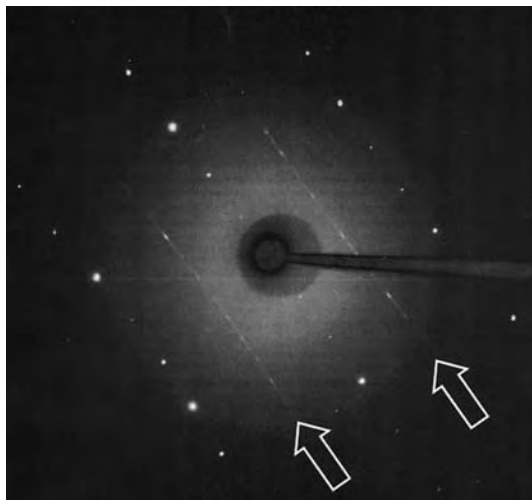
belong to the sulfate group only, resulted in unrealistic S–O distances, larger than 1.7 Å. Geometrical restraints were then applied to the S–O bond distances. The oxygen atoms O1 and O3, both of them belonging to the layer of octahedra, show relatively high displacement parameters and are split in two slightly displaced sites, O1–O1b and O3–O3b, respectively.

Refinement was continued with anisotropic displacement factors for Cu cations, and after several least-square refinement cycles, it converged to R = 0.079 for 716 unique reflections. The reliability index R reflects the poor quality of the crystal, and the difficulties in modeling the disordered structure. The refined coordinates and displacement parameters of the atoms are reported in Table 4; selected bond-distances are listed in Table 5. The anisotropic displacement parameters for the copper atoms and the structure factors are available from the Depository of Unpublished Data on the MAC website [document Montetrisaite CM47_143]. The bond-valence calculation (Brese & O'Keeffe 1992)

FIG. 2. Low-resolution portion of a diffraction pattern of montetrisaite, collected with a 165 mm MarCCD detector at the Elettra synchrotron facility. The white arrows indicate rows of very weak and streaked reflections, which cannot be indexed on the basis of the orthorhombic unit-cell with a = 2.98 Å.
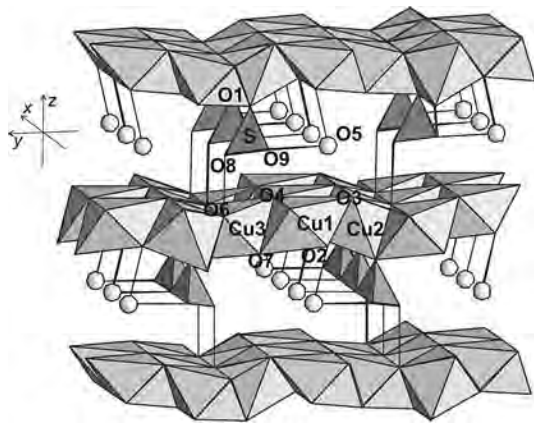

FIG. 3. Average structure of montetrisaite. The Cu-centered distorted octahedra are light gray, the sulfate tetrahedra are dark gray, and the H_2O molecules are indicated by circles.

TABLE 4. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR MONTETRISAITE

Site	Site multiplicity	Occupancy	x	y	z	U_{eq}
Cu1	4	1 Cu	0	0.0363(2)	0.5369(2)	0.033(2)
Cu2	4	1 Cu	0.5	0.8685(2)	0.5133(2)	0.027(1)
Cu3	4	1 Cu	0.5	0.2006(2)	0.4950(2)	0.024(2)
O1	4	0.5 O	0	0.818(2)	0.403(1)	0.044(9)
O1b	4	0.5 OH	0	0.840(2)	0.445(3)	0.041(9)
O2	4	1 OH	0.5	0.980(1)	0.472(2)	0.052(5)
O3	4	0.5 OH	0	0.883(2)	0.592(3)	0.078(1)
O3b	4	0.5 H_2O	0	0.902(3)	0.651(4)	0.089(1)
O4	4	1 OH	0.5	0.0852(9)	0.594(1)	0.046(5)
O5	4	1 H_2O	0.5	0.982(2)	0.789(2)	0.038(9)
O6	4	1 OH	0.5	0.752(1)	0.557(1)	0.037(4)
O7	4	1 OH	0	0.148(1)	0.434(1)	0.049(5)
O8	4	0.5 O	0	0.750(2)	0.253(3)	0.09(1)
O9	4	1 O	0.5	0.851(2)	0.284(3)	0.08(1)
S	4	0.5 S	0	0.8273(9)	0.302(1)	0.079(6)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The general multiplicity of the space group is 8. The chemical content of the anionic sites was obtained from bond-valence calculations (see text).

TABLE 5. BOND LENGTHS [Å] FOR MONTETRISAITE

Cu1	–O4	1.91(1)	Cu2	–O1b	1.86(2)*
	–O4	1.91(1)		–O1b	1.86(2)*
	–O2	2.01(1)		–O2	1.99(2)
	–O2	2.01(1)		–O6	2.08(2)
	–O7	2.43(2)		–O3	1.92(3)*
	–O3	2.72(4)*		–O3	1.92(3)*
	–O3b	2.85(4)*		–O1	2.37(2)*
				–O1	2.37(2)*
				–O3b	2.59(4)*
Cu3	–O7	1.96(1)		–O3b	2.59(4)*
	–O7	1.96(1)			
	–O6	1.96(1)			
	–O6	1.96(1)	S2	–O1	1.50(1)
	–O4	2.45(2)		–O8	1.51(1)
	–O1	2.41(3)*		–O9	1.57(1)
	–O1b	2.49(3)*		–O9	1.57(1)

* Bonds that occur with 50% of probability, depending on the occupancy of the sites O1–O1b and O3–O3b.

reported in Table 6 gives some information about the nature of the anions. The occurrence of relatively short O…O distances (Table 7) leads us to suppose the existence of hydrogen bonds, even though the hydrogen atoms were not located experimentally. One of the possible hydrogen-bonding schemes is reported in Figure 4. The bond-valence sums for the anionic sites were corrected by taking into account the system of hydrogen bonds reported in Figure 4, using the quantitative correlation between bond valence and bond length in O...O hydrogen bonds given in Ferraris & Ivaldi (1988). For the oxygen atoms O8 and O9, the sum of valences is less than the expected value of 2.00 *vu*. It is worth noting that both these anions are affected by disorder, and the determination of their real positions would require the measurement of the weak and diffuse reflections shown in Figure 2.

The relatively poor quality of the available crystal, indicated by the broadness of the reflections, as well as its stacking disorder, resulting in continuously streaked superstructure reflections (Fig. 2), prevented us from refining the structure at high resolution.

By taking into account the weak intensity of maxima along the streaked rows, a possible unit-cell of the ordered structure was found by the indexing program DENZO (Otwinowski & Minor 1997). This supercell is monoclinic, with parameters a_m 5.98, b_m 14.56, c_m 8.56 Å, β 99.9°; it can be obtained from the orthorhombic subcell by applying the transformation matrix $200/00\bar{1}/\frac{1}{2}\frac{1}{2}0$. On the basis of this unit cell and of crystal-chemical considerations, a structural model for the ordered superstructure was constructed, starting

from the layer shown in Figure 5a, and assuming that the adjacent layers are stacked along [010] as shown in Figure 5b. The ordered structure shown in Figure 5 presents space group $P2_1$, a maximal non-isomorphic subgroup of the space group $Cmc2_1$ of the average structure. However, probably because the superstructure reflections could not be reliably measured, the structural refinement of this structural model resulted in unreasonable Cu–O and S–O distances, and we abandoned it. New studies on more ordered crystals are therefore necessary to reveal the structural details of the actual distribution of sulfate groups and H_2O molecules in montetrisaite.

DESCRIPTION OF THE STRUCTURE

The refined crystal structure (Fig. 3) consists of layers of edge-sharing Cu-centered octahedra, to which single SO_4 groups are connected from one side. Between the layers, H_2O molecules are located, and the layers are connected to each other through hydrogen bonds.

The oxygen atoms O1 and O3 are split in two slightly displaced sites, O1–O1b and O3–O3b, respectively, as suggested by their high displacement-parameters. The
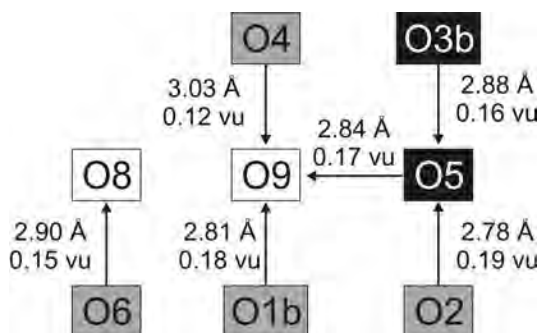

FIG. 4. Hydrogen bonding scheme for montetrisaite. The arrows point toward the acceptor oxygen atoms. Black, gray and white backgrounds indicate, respectively, H_2O molecules, hydroxyl groups, and oxygen atoms (see Table 6).

TABLE 6. BOND-VALENCE CALCULATION FOR MONTETRISAITE

	Cu1	Cu2	Cu3	S	Σ_{anions}	Σ'_{corr}	species
O1*		0.15 0.15	0.14	1.62	2.07		O
O1b*		0.61 0.61	0.11		1.34	1.16	OH
O2	0.40 0.40	0.43			1.25	1.15	OH
O3*	0.06	0.52 0.52			1.10		OH
O3b*	0.04	0.09 0.09			0.21	0.05	H_2O
O4	0.54 0.54		0.12		1.20	1.07	OH
O5					0	0.18	H_2O
O6		0.34	0.47 0.47		1.27	1.12	OH
O7	0.13		0.47 0.47		1.06		OH
O8				1.58	1.58	1.73	O
O9				1.34 1.34	1.34	1.64	O
$\Sigma_{cations}$	2.07	2.14	2.12	5.88			

The anionic bond valence sums, expressed in valence units (*vu*) were corrected following Ferraris & Ivaldi (1988) and by taking into account the hydrogen bonds system reported in Figure 4. * As these sites are only half-occupied, the corresponding Cu–O bond strengths were divided by two in the average bond valence sum for the Cu cations.

TABLE 7. O...O DISTANCES BETWEEN OXYGEN ATOMS INVOLVED IN HYDROGEN BONDS AND CORRESPONDING BOND-VALENCES

Donor → acceptor	O...O (Å)	*vu*
O2 (OH) → O5 (H_2O)	2.78	0.19
O4 (OH) → O9 (O)	3.03	0.12
O5 (H_2O) → O9 (O)	2.84	0.17
O3b (H_2O) → O5 (H_2O)	2.88	0.16
O6 (OH) → O8 (O)	2.90	0.15
O1b (OH) → O9 (O)	2.81	0.18

The arrows point toward the acceptor oxygen atoms. Bond valences are expressed in valence units (*vu*).

occupancy of the O1 site corresponds to the occurrence of a sulfate group, which shares a corner with the layer of octahedra through the O1 oxygen atom. The occupancy of the O1b site, therefore, is related to the presence of a H_2O molecule in the O5 site; the hydroxyl group at O1b forms a relatively strong hydrogen bond with the nearby O9 oxygen atom. On the other hand, the occupancy of the O5 site by a H_2O molecule is related to the presence of another H_2O molecule at the O3b site, with the formation of a relatively strong hydrogen bond between them. Therefore, the sites O1 and O3 are occupied where a sulfur atom occurs in the vicinity, whereas O1b and O3b are occupied where

a H_2O molecule is present. This atomic distribution affects the coordination of the Cu cations. As observed in redgillite (Pluth *et al.* 2005), there are three different Cu-centered octahedra, where the Cu atom coordinates, respectively, six hydroxyl groups, five hydroxyl groups plus a H_2O molecule, or five hydroxyl groups plus an oxygen atom (shared with the sulfate group). In greater detail, the Cu1 polyhedron is either a $Cu(OH)_6$ or a $Cu(OH)_5(H_2O)$ octahedron, whereas Cu2 and Cu3 are either a $Cu(OH)_5O$ or a $Cu(OH)_5H_2O$ octahedron; such different coordination depends on whether either O1, O3 or O1b, O3b sites are occupied (Tables 4, 5).

In Figure 3, the refined average structure is represented with sulfate groups and H_2O molecules in both their statistically possible positions. The half occupancy of the S site implies that only every second site in the continuous chain is filled. As a consequence, in the real structure, the orientation in the (001) plane of the single sulfate groups can be slightly different, modifying the hydrogen-bonding scheme within the layers. The ordered distribution of the sulfate groups along *a* could give rise to the observed doubling of the short *a* parameter, from 2.98 Å to 5.96 Å. The weakness and diffuseness of the superstructure reflections observed in the X-ray diffraction patterns (Fig. 2), on the other hand, indicate that each ordered mono-dimensional arrangement along the *a* direction could be only short-range-related to the others, both in the same layer along *b*, and in different layers stacked along *c*.

The new mineral belongs to the hydroxy-hydrated copper oxysalt minerals, as classified by Eby & Hawthorne (1993) and Hawthorne & Schindler (2000). Following the notation of Eby & Hawthorne (1993), it is formed of *M*=*M*–*T* sheets and represents a new member of the series $^{[6]}M_nT_N\varphi_{2n-N}$, with $n = 6$, $N = 1$, where in this case *M* represents copper as octahedrally coordinated cations, *T* is the sulfate group, φ represents OH⁻, H_2O, plus an interlayer H_2O molecule. Among all the possible layered structures listed in Eby & Hawthorne (1993), montetrisaite is structurally related to posnjakite (Mellini & Merlino 1979), wroewolfeite (Hawthorne & Groat 1985) and langite (Gentsch & Weber 1984), which have all $n = 4$, $N = 1$, and spangolite (Merlino *et al.* 1992, Hawthorne *et al.* 1993; $n = 7$, $N = 1$). All these phases, in fact, show sulfate groups connected only to one side of the layers of octahedra. On the contrary, the crystal structure of the mineral redgillite, despite the similarity of its chemical formula to that of montetrisaite, is substantially different. The sulfate decoration of the layer surfaces in redgillite, in fact, is two-sided, as in schulenbergite (Mumme *et al.* 1994), and the layers of octahedra are corrugated, as observed in the synthetic compound $Mg_6SO_2(OH)_{14}$ (Hamada *et al.* 1996). Structures of some of the listed phases are compared to that of the new mineral in Figures 6 and 7.
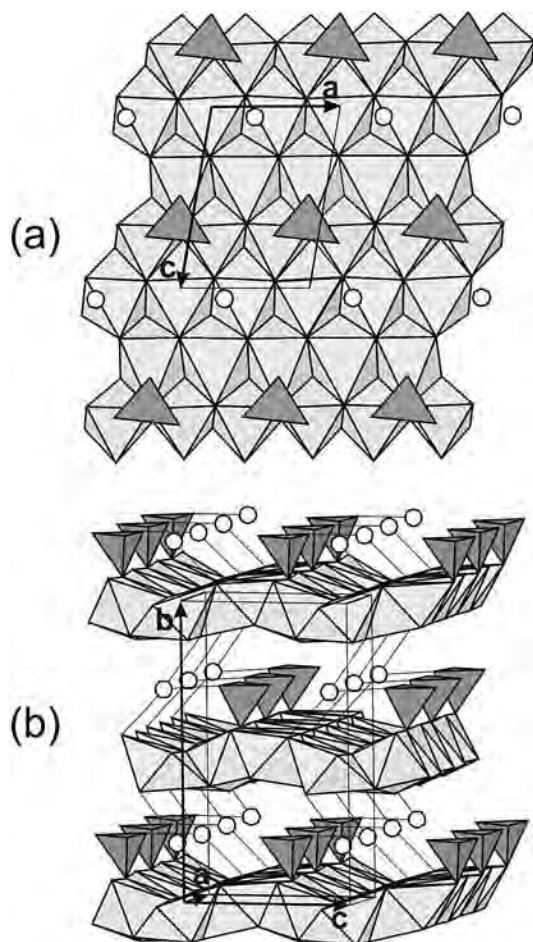

FIG. 5.   Structural model for ordered montetrisaite, with the indication of the monoclinic unit-cell. (a) One of the possible ordered layers; (b) ordered stacking of the layers along [010]. Dark gray triangles represent sulfate tetrahedra, which share an oxygen atom with the Cu-centered distorted octahedra (light gray), whereas white circles indicate H_2O molecules located within the layers.
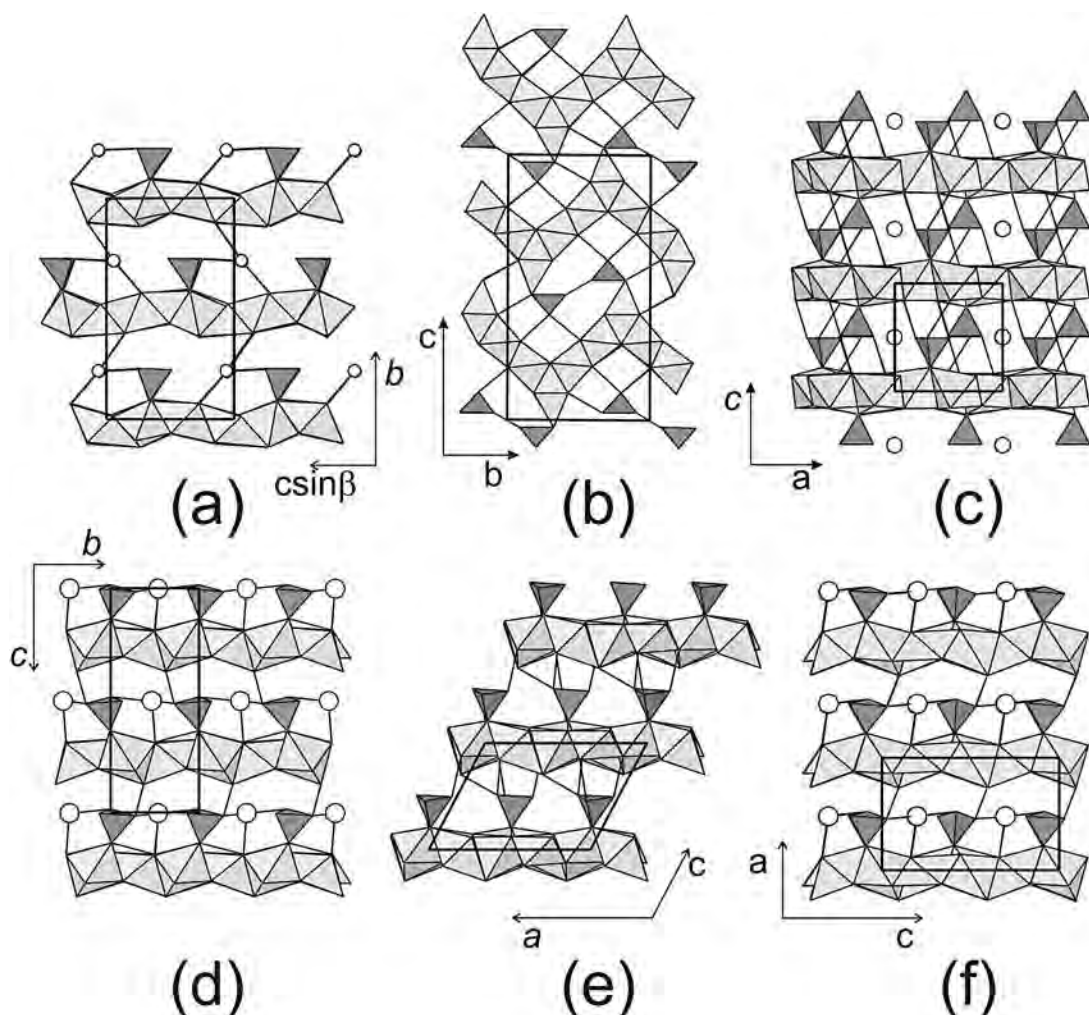
FIG. 6. Comparison of (a) montetrisaite $Cu_6(SO_4)(OH)_{10}(H_2O) \cdot (H_2O)$ and other copper sulfates, as seen along the $[6]M_nT_N\varphi_{2n-N}$ sheets: (b) redgillite $Cu_6(SO_4)(OH)_{10}(H_2O)$, (c) schulenbergite $(Cu,Zn)_7(SO_4)_2(OH)_{10} \cdot 3H_2O$, (d) wroewolfeite $Cu_4(SO_4)(OH)_6(H_2O) \cdot (H_2O)$, (e) posnjakite $Cu_4(SO_4)(OH)_6(H_2O)$, and (f) langite $Cu_4(SO_4)(OH)_6(H_2O) \cdot H_2O$. Dark gray triangles represent sulfate tetrahedra, which share an oxygen atom with the Cu-centered distorted octahedra (light gray).

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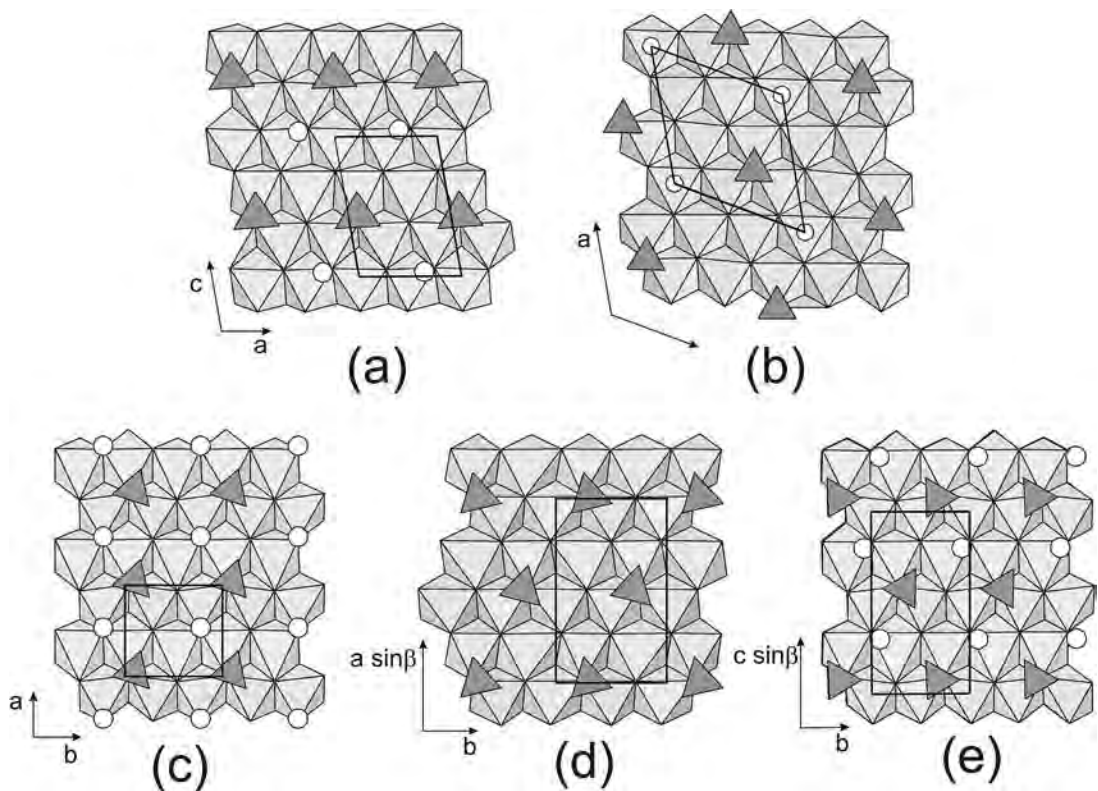
FIG. 7.   Comparison of (a) montetrisaite $Cu_6(SO_4)(OH)_{10}(H_2O) \cdot H_2O$ (ordered model) with other copper sulfates having a similar structure, as seen perpendicularly to the $^{[6]}M_nT_N\varphi_{2n-N}$ sheets: (b) schulenbergerite $(Cu,Zn)_7(SO_4)_2(OH)_{10} \cdot 3H_2O$, (c) wroewolfeite $Cu_4(SO_4)(OH)_6(H_2O) \cdot H_2O$, (d) posnjakite $Cu_4(SO_4)(OH)_6(H_2O)$; (e) langite $Cu_4(SO_4)(OH)_6(H_2O) \cdot H_2O$. Dark gray triangles represent sulfate tetrahedra, which share an oxygen atom with the Cu-centered distorted octahedra (light gray). In schulenbergite (b), sulfate groups are attached to the layer of octahedra also on the other side. White circles represent H_2O molecules located within the layers.

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