

Menchettiite, $\text{AgPb}_{2.40}\text{Mn}_{1.60}\text{Sb}_3\text{As}_2\text{S}_{12}$, a new sulfosalt belonging to the lillianite series from the Uchucchacua polymetallic deposit, Lima Department, Peru

LUCA BINDI,¹ FRANK N. KEUTSCH,² AND PAOLA BONAZZI^{3,*}

¹Museo di Storia Naturale, sezione di Mineralogia e Litologia, Università degli Studi di Firenze, via La Pira 4, I-50121 Firenze, Italy

²Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706, U.S.A.

³Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4, I-50121 Firenze, Italy

ABSTRACT

Menchettiite, ideally $\text{AgPb}_{2.40}\text{Mn}_{1.60}\text{Sb}_3\text{As}_2\text{S}_{12}$, is a new mineral from the Uchucchacua polymetallic deposit, Oyon district, Catajambo, Lima Department, Peru. It occurs as black, anhedral to subhedral grains up to 200 μm across, closely associated with orpiment, tennantite/tetrahedrite, other unnamed minerals of the system Pb-Ag-Sb-Mn-As-S, and calcite. Menchettiite is opaque with a metallic luster and possesses a black streak. It is brittle, with uneven fracture; the Vickers microhardness (VHN_{100}) is 128 kg/mm^2 (range 119–136) (corresponding to a Mohs hardness of $2\frac{1}{2}$ –3). The calculated density is 5.146 g/cm^3 (on the basis of the empirical formula). In plane-polarized incident light, menchettiite is weakly to moderately bireflectant and weakly pleochroic from dark gray to a dark green. Internal reflections are absent. Between crossed polarizers, the mineral is anisotropic, without characteristic rotation tints. Reflectance percentages ($R_{\min}$ and $R_{\max}$) for the four standard COM wavelengths are 33.1, 39.8 (471.1 nm), 31.8, 38.0 (548.3 nm), 30.9, 37.3 (586.6 nm), and 29.0, 35.8 (652.3 nm), respectively.

Menchettiite is monoclinic, space group $P2_1/n$, with unit-cell parameters: $a = 19.233(2)$, $b = 12.633(3)$, $c = 8.476(2)$ Å, $\beta = 90.08(2)^\circ$, $V = 2059.4(8)$ Å³, $a:b:c = 1.522:1:0.671$, $Z = 2$, and it is twinned on {100}. The crystal structure was refined to $R = 0.0903$ for 2365 reflections with $F_o > 4\sigma(F_o)$ and it resulted to be topologically identical to those of ramdohrite, uchucchacuaite, and fizelyite. The six strongest X-ray powder-diffraction lines [d in Å (I/I_0) (hkl)] are: 3.4066 (39) ($\bar{3}12$), 3.4025 (39) (312), 3.2853 (100) (520), 2.8535 (50) ($\bar{2}32$), 2.8519 (47) (232), and 2.1190 (33) (004). Electron-microprobe analyses gave the chemical formula $\text{Ag}_{1.95}\text{Cu}_{0.01}\text{Pb}_{4.81}\text{Mn}_{3.20}\text{Fe}_{0.02}\text{Zn}_{0.01}\text{Sb}_{6.09}\text{As}_{3.94}\text{Bi}_{0.01}\text{S}_{23.95}\text{Se}_{0.01}$, on the basis of 44 atoms and according to the structure refinement results. Menchettiite can be classified among the Sb-rich members of the lillianite homeotypic series, which are described with the general formula $\text{Ag}_x\text{Pb}_{3-2x}\text{Sb}_{2+x}\text{S}_6$. Besides the heterovalent substitution $2\text{Pb}^{2+} \rightarrow \text{Ag}^+ + \text{Sb}^{3+}$ taken into consideration by the above formula, two isovalent substitutions relate menchettiite to the other lillianite homeotypes, i.e., $\text{Mn}^{2+} \rightarrow \text{Pb}^{2+}$ and $\text{As}^{3+} \rightarrow \text{Sb}^{3+}$. The name is after Silvio Menchetti (1937–), Professor of Mineralogy and Crystallography at the University of Florence. The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2011-009).

Keywords: Menchettiite; new mineral; electron microprobe data; reflectance data; X-ray diffraction data; ramdohrite; lillianite; Uchucchacua deposit, Peru

INTRODUCTION

The building principles ruling the chemistry and crystallography of the sulfosalts belonging to the lillianite homologous series were deeply examined by Makovicky (1977) and Makovicky and Karup-Møller (1977a, 1977b) who also provided a structural classification based on a modular description of their complex structures, which contain “galena-like” slabs of various thickness leading to variable metal/sulfur ratios and topologies. Among them, the Sb-rich members of the lillianite homeotypic series (⁴*L*) exhibit a general formula $\text{Ag}_x\text{Pb}_{3-2x}\text{Sb}_{2+x}\text{S}_6$ (Moëlo et al. 2008), where x represents the fraction of the andorite VI component, AgPbS_3S_6 (And_{100} ; $x = 1$).

In this paper we report the occurrence, physical properties, and crystal structure of a new Mn-bearing sulfosalt belonging to the Sb-rich members of the lillianite homeotypic series coming from the Uchucchacua polymetallic deposit, Oyon district, Lima Department, Peru. The mineral, ideally $\text{AgPb}_{2.40}\text{Mn}_{1.60}\text{Sb}_3\text{As}_2\text{S}_{12}$, was named menchettiite after Silvio Menchetti (1937–), Professor of Mineralogy and Crystallography at the University of Florence, in recognition of his recent contribution to systematics of sulfosalts. The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2011-009). Holotype material is deposited in the collections of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, via La Pira 4, I-50121, Firenze, Italy, catalog number 3109/I.

* E-mail: paola.bonazzi@unifi.it

OCCURRENCE AND PHYSICAL PROPERTIES

The sample studied here that contains menchettiite was not found in situ but originates from a sample given to one of the authors (F.N.K.) by the mineral dealer John Veevaert who recognized the specimen as something unusual. The material was found in October 2010 from the Nivel 890, Uchucchacua polymetallic deposit, Oyon district, Catajambo, Lima Department, Peru. This deposit is the type locality for three other Mn-bearing sulfosalts: uchucchacuaite, $\text{AgPb}_3\text{MnSb}_5\text{S}_{12}$ (Moëlo et al. 1984); benavidesite, $\text{Pb}_4\text{MnSb}_6\text{S}_{14}$ (Oudin et al. 1982); and the newly approved manganogaduate, AgMnAsS_3 (Bonazzi et al. in review). Geological and metallogenetic data concerning the Uchucchacua deposit district have been reported by Oudin et al. (1982).

The sample mainly consists of menchettiite with associated orpiment, quartz, tennantite/tetrahedrite, and other unnamed minerals of the system Pb-Ag-Sb-Mn-As-S in a calcite matrix (Fig. 1). Menchettiite occurs as rare, subhedral to anhedral grains, and it is found either as homogeneous grains or intergrown with other minerals. The maximum grain size of menchettiite is about 200 μm .

Menchettiite is black in color and shows a black streak. The mineral is opaque with a metallic luster. It is brittle, with uneven fracture. Density could not be measured because of the small grain size. The calculated density is 5.146 g/cm^3 (on the basis

of the empirical formula). The micro-indentation measurements carried out with a VHN load of 100 g gave a mean value of 128 kg/mm^2 (range: 119–136).

In plane-polarized incident light, menchettiite is weakly to moderately birefractant and weakly pleochroic from dark gray to a dark green. With crossed polarizers, the mineral is anisotropic, without characteristic rotation tints. Internal reflections are absent and no evidence of growth zoning is observed.

Reflectance measurements were performed in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages for $R_{\min}$ and $R_{\max}$ are 33.1, 39.8 (471.1 nm), 31.8, 38.0 (548.3 nm), 30.9, 37.3 (586.6 nm), and 29.0, 35.8 (652.3 nm), respectively.

In Figure 2, the reflectance percentages obtained for menchettiite are plotted together with those measured by Moëlo et al. (1984) for uchucchacuaite, $\text{Pb}_3\text{AgMnSb}_5\text{S}_{12}$. As expected on the basis of the higher Mn/Pb and As/Sb ratios, menchettiite exhibits a reflectivity lower than that of uchucchacuaite.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Several crystals of menchettiite were selected from the rock sample and examined by means of a Bruker MACH3 single-crystal diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation and unit-cell dimensions were determined by least-squares refinement of the setting angles of 25 high- θ reflections ($15 < \theta_{\text{MoK}\alpha} < 22^\circ$). For all the crystals investigated nearly identical values ($a \sim 19.23$, $b \sim 12.63$, $c \sim 8.45$ Å, $\beta \sim 90.1^\circ$) were found, closely resembling those of ramdohrite



FIGURE 1. Macroscopic image of the rock sample containing menchettiite (dark gray) together with quartz and orpiment in a calcite matrix (white bar corresponds to 4 mm). (Color online.)

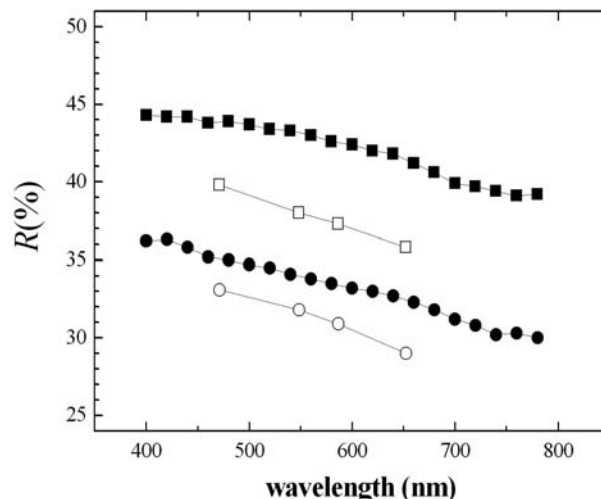


FIGURE 2. Reflectivity curves for menchettiite in air. Filled symbols refer to uchucchacuaite (Moëlo et al. 1984), open symbols refer to menchettiite (this study). Squares and circles refer to $R_{\max}$ and $R_{\min}$ values, respectively.

(Makovicky and Mumme 1983), fizélyite (Yang et al. 2009), and uchucchacuaite (Moëlo et al. 1984; Yang et al. 2011). Data collection was carried out on the crystal showing the best diffraction quality. The data collection was done with an Oxford Diffraction Xcalibur 3 diffractometer, equipped with a Sapphire 2 CCD detector (see Table 1 for details). Intensity integration and standard Lorentz-polarization correction 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. The merging R for the data set decreased from 0.182 before absorption correction to 0.070 after this correction. The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.866$), which indicated the presence of an inversion center, together with the observed systematic absences, led unequivocally to the choice of the space group $P2_1/n$ ($P2_1/c$ as standard).

The position of most of the atoms (all the metals and eight S-positions) was determined from the three-dimensional Patterson synthesis (Sheldrick 1997a). A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an $R1$ factor of 0.2432. Three-dimensional difference Fourier synthesis yielded the position of the remaining sulfur atoms. The full-matrix least-squares program SHELXL-97 (Sheldrick 1997b) was used for the refinement of the structure. The introduction of anisotropic temperature factors for all the atoms led to $R1 = 0.1966$. At this stage, the introduction of a twinning on $\{100\}$ dramatically lowered the R indices. The site occupancy of all the metal positions was allowed to vary using different combinations of neutral Pb, Ag, Mn, Sb, and As scattering curves (Ibers and Hamilton 1974). The corresponding site assignments were in turn evaluated on the basis of crystal-chemical criteria (see discussion). The final results are given in Table 2. At the last stage, with anisotropic atomic displacement parameters for all atoms and no constraints, the residual value settled at $R1 = 0.0903$ for 2365 observed reflections [$F_o > 4\sigma(F_o)$] and 205 parameters and at $R1 = 0.1359$ for all 3591 independent reflections. The inspection of the difference Fourier map revealed that maximum positive and negative peaks were 2.14 and 2.04 $e^-/\text{\AA}^3$, respectively. Fractional atom coordinates (atomic labeling according to the original description of ramdohrite structure, Makovicky and Mumme 1983), and anisotropic-displacement parameters are shown in Table 2. Bond distances are reported

TABLE 1. Crystallographic data and refinement parameters for menchettiite

Crystal data	
Ideal formula	AgPb _{2.40} Mn _{1.60} Sb ₃ As ₂ S ₁₂
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit-cell parameters	
a	19.233(2)
b	12.633(3)
c (Å)	8.476(2)
β (°)	90.08(2)
Unit-cell volume (Å ³)	2059.4(8)
Z	2
Calculated density (g/cm ³)	5.146
Crystal size (mm)	0.060 × 0.080 × 0.090
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3 (CCD)
Temperature (K)	298(3)
Radiation, wavelength (Å)	MoK α , 0.71073
θ range for data collection (°)	4.24–25.00
h, k, l ranges	–16–22, –12–15, –10–9
Axis, frames, width (°), time per frame (s)	ω , 425, 0.65, 100
Total reflections collected	7808
Unique reflections (R_{int})	3591 (0.0698)
Unique reflections $F > 4\sigma(F)$	2365
Data completeness to θ_{max} (%)	99.2
Absorption correction method	multiscan (ABSPACK Oxford Diff 2006)
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$1/\sigma^2(F)$
Twin matrix	[–100/010/001]
Twin volume fraction	0.505(4)
Data/restraints/parameters	7808/0/205
R_1 [$F > 4\sigma(F)$]	0.0903
R_1 all	0.1359
Largest diff. peak and hole ($e^-/\text{\AA}^3$)	2.14, –2.04

¹ Deposit item AM-12-009, Table 5. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 2. Atoms, site scattering, fractional atom coordinates (Å), and atomic displacement parameters (Å²) for menchettiite

Atom	Site scattering	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{iso}
M1	47.8(1)	0.1373(2)	0.3542(4)	0.1313(7)	0.059(3)	0.118(4)	0.056(3)	0.015(3)	0.013(3)	0.013(2)	0.078(2)
M2	40.7(1)	0.0605(2)	0.6271(3)	0.1220(6)	0.035(2)	0.026(2)	0.044(2)	–0.008(2)	0.005(2)	–0.006(1)	0.035(1)
M3	71.2(1)	0.2427(1)	0.5750(2)	0.3818(3)	0.056(2)	0.097(2)	0.064(2)	0.018(2)	0.010(2)	0.026(2)	0.072(1)
M4	47.0	0.3593(2)	0.3320(4)	0.1296(8)	0.074(3)	0.085(3)	0.074(3)	0.016(4)	0.024(3)	0.049(3)	0.078(1)
M5	58.1(1)	0.4529(1)	0.6006(2)	0.1302(4)	0.032(1)	0.046(2)	0.038(2)	–0.001(2)	–0.0007(15)	0.004(1)	0.039(1)
M6	51.0	0.1185(2)	0.3444(2)	0.6177(5)	0.056(2)	0.035(2)	0.046(2)	–0.002(2)	0.008(2)	–0.002(1)	0.0457(8)
M7	45.2(1)	0.0535(2)	0.6435(3)	0.6442(5)	0.026(2)	0.054(2)	0.058(3)	–0.023(2)	0.003(2)	0.005(2)	0.046(1)
M8	82.0	0.24490(8)	0.5865(1)	0.8809(2)	0.0331(9)	0.0354(9)	0.0497(9)	0.001(1)	–0.0058(13)	0.0022(8)	0.0394(5)
M9	25.0	0.3643(2)	0.3519(4)	0.623(1)	0.024(3)	0.024(3)	0.033(3)	0.006(4)	–0.001(4)	–0.003(3)	0.027(1)
M10	33.0	0.4377(2)	0.6106(3)	0.6362(5)	0.026(2)	0.015(2)	0.026(2)	0.004(2)	0.002(2)	0.001(2)	0.0224(9)
S1	16.0	0.1004(5)	0.5071(9)	0.331(1)	0.033(5)	0.043(6)	0.031(6)	0.016(5)	0.005(5)	0.005(5)	0.036(3)
S2	16.0	–0.0065(5)	0.2378(9)	0.157(1)	0.034(5)	0.033(6)	0.050(7)	0.006(6)	0.007(6)	0.006(5)	0.039(3)
S3	16.0	0.2553(5)	0.4399(7)	0.142(1)	0.041(5)	0.030(5)	0.034(6)	–0.002(5)	–0.002(7)	0.011(5)	0.035(2)
S4	16.0	0.1630(5)	0.7261(7)	0.102(1)	0.027(5)	0.025(5)	0.020(5)	–0.005(5)	0.004(5)	–0.004(4)	0.024(2)
S5	16.0	0.3916(6)	0.5128(9)	0.431(1)	0.042(6)	0.018(5)	0.067(8)	0.003(5)	0.010(6)	0.000(5)	0.042(3)
S6	16.0	0.3440(5)	0.7213(8)	0.109(2)	0.028(5)	0.032(6)	0.084(9)	0.005(8)	–0.001(8)	–0.009(5)	0.048(3)
S7	16.0	0.0927(5)	0.5105(8)	0.914(2)	0.033(5)	0.016(5)	0.073(9)	0.003(6)	0.005(6)	–0.005(5)	0.041(3)
S8	16.0	0.4838(6)	0.280(1)	0.076(1)	0.045(7)	0.053(8)	0.033(6)	0.007(5)	–0.002(5)	0.016(6)	0.044(3)
S9	16.0	0.2370(4)	0.4284(7)	0.619(2)	0.030(5)	0.022(5)	0.062(6)	0.008(6)	0.002(7)	0.005(4)	0.038(2)
S10	16.0	0.1650(5)	0.7242(8)	0.638(2)	0.033(5)	0.023(5)	0.079(8)	–0.019(8)	0.019(8)	0.008(5)	0.045(3)
S11	16.0	0.4005(5)	0.4954(9)	0.830(1)	0.034(5)	0.032(6)	0.030(6)	0.003(5)	–0.005(5)	0.008(5)	0.032(3)
S12	16.0	0.3429(5)	0.7300(8)	0.658(1)	0.026(5)	0.035(6)	0.019(5)	0.007(4)	–0.002(5)	–0.003(5)	0.027(2)

TABLE 3. Selected bond distances (Å) for menchettiite

M1-S3	2.52(1)	M6-S12	2.50(1)
M1-S1	2.67(1)	M6-S9	2.514(9)
M1-S6	2.79(2)	M6-S6	2.58(2)
M1-S7	2.84(1)	M6-S8	3.05(1)
M1-S12	2.94(1)	M6-S1	3.20(1)
M1-S2	3.14(1)	M6-S7	3.31(1)
M2-S4	2.34(1)	M7-S10	2.38(1)
M2-S7	2.38(1)	M7-S2	2.43(1)
M2-S1	2.46(1)	M7-S8	2.64(1)
M2-S2	3.09(1)	M7-S7	2.94(1)
M2-S8	3.32(1)	M7-S1	3.29(1)
M2-S7	3.43(1)	M7-S1	3.53(1)
M3-S3	2.67(1)	M8-S3	2.90(1)
M3-S9	2.74(1)	M8-S9	2.99(1)
M3-S1	2.90(1)	M8-S4	3.02(1)
M3-S5	3.00(1)	M8-S7	3.09(1)
M3-S10	3.24(1)	M8-S10	3.10(2)
M3-S4	3.41(1)	M8-S6	3.20(1)
M3-S6	3.55(1)	M8-S12	3.23(1)
M3-S12	3.61(1)	M8-S11	3.24(1)
M4-S3	2.43(1)	M9-S4	2.54(1)
M4-S8	2.53(1)	M9-S11	2.62(1)
M4-S4	2.68(1)	M9-S9	2.63(1)
M4-S10	2.69(2)	M9-S10	2.65(2)
M4-S11	3.37(1)	M9-S5	2.66(1)
M4-S5	3.48(1)	M9-S2	2.75(1)
M5-S6	2.60(1)	M10-S5	2.31(1)
M5-S8	2.62(1)	M10-S11	2.31(1)
M5-S2	2.71(1)	M10-S12	2.38(1)
M5-S5	3.02(1)	M10-S8	3.18(1)
M5-S11	3.04(1)	M10-S2	3.24(1)
M5-S11	3.09(1)	M10-S5	3.68(1)

in Table 3. The calculated X-ray powder pattern for menchettiite is given in Table 4. Table 5¹ lists the observed and calculated structure factors.

CHEMICAL COMPOSITION

The same crystal fragment used for the structural study was analyzed by means of a Jeol JXA-8200 electron microprobe. Major and minor elements were determined at 15 kV accelerating voltage and 30 nA beam current, with 10 s as counting time. For the WDS analyses the following lines were used: PbM α , AgL α , CuK α , MnK α , FeK α , ZnK α , SbL β , AsL α , BiM β , SK α , and SeL α . The estimated analytical precision was: ± 0.21 for Pb; ± 0.09 for Ag; ± 0.01 for Cu, Fe, Zn, and Bi; ± 0.07 for Mn; ± 0.18 for Sb; ± 0.10 for As; ± 0.16 for S; and ± 0.02 for Se. The standards employed were: galena (Pb), Ag-pure element (Ag), Cu-pure element (Cu), synthetic MnS (Mn), pyrite (Fe, S), synthetic ZnS (Zn), synthetic Sb₂S₃ (Sb), synthetic As₂S₃ (As), synthetic Bi₂S₃ (Bi), and synthetic PtSe₂ (Se); Cd was found below the detection limit.

The crystal fragment was found to be homogeneous within the analytical uncertainty. The chemical composition (12 analyses on different spots), together with the atomic ratios, is reported in Table 6. On the basis of 44 atoms, the formula of menchettiite is Ag_{1.95}Cu_{0.01}Pb_{4.81}Mn_{3.20}Fe_{0.02}Zn_{0.01}Sb_{6.09}As_{3.94}Bi_{0.01}S_{23.95}Se_{0.01}. The simplified formula is AgPb_{2.40}Mn_{1.60}Sb₃As₂S₁₂, which requires: Ag 6.77, Pb 31.22, Mn 5.52, Sb 22.93, As 9.41, S 24.15, Total 100.00 wt%.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Menchettiite is isostructural with ramdohrite (Makovicky and Mumme 1983), fizélyite (Yang et al. 2009), and uchucchacuaite (Yang et al. 2011). The crystal structure is based on “galena-like”

TABLE 4. Calculated X-ray powder-diffraction data for menchettiite

<i>l</i>	<i>d</i> _{calc}	<i>h k l</i>
6.72	9.6165	2 0 0
13.91	6.0011	1 2 0
4.17	5.7170	3 1 0
10.94	5.2795	2 2 0
7.32	4.0179	0 1 2
15.58	3.8259	4 2 0
18.33	3.7091	2 1 2
18.84	3.7056	2 1 2
38.80	3.4066	3 1 2
39.03	3.4025	3 1 2
100.00	3.2853	5 2 0
10.04	3.2055	6 0 0
15.33	3.1583	0 4 0
18.73	3.1165	1 4 0
7.40	2.9871	0 3 2
19.78	2.9522	1 3 2
21.24	2.9513	1 3 2
25.67	2.8585	6 2 0
49.05	2.8535	2 3 2
46.96	2.8519	2 3 2
20.01	2.7087	3 3 2
24.32	2.7066	3 3 2
4.79	2.4041	8 0 0
8.56	2.2694	7 1 2
10.38	2.2666	7 1 2
4.21	2.2497	6 4 0
33.01	2.1190	0 0 4
4.25	2.0729	7 4 0
19.52	2.0642	8 1 2
17.88	2.0618	8 1 2
10.16	2.0561	3 5 2
8.92	2.0552	3 5 2
14.01	1.9786	4 5 2
13.13	1.9775	4 5 2
17.15	1.9287	4 6 0
8.83	1.9233	10 0 0
9.72	1.8738	8 3 2
10.52	1.8720	8 3 2
6.58	1.8469	5 6 0
4.46	1.7977	6 5 2
5.32	1.7965	6 5 2
15.12	1.7817	5 2 4
15.21	1.7798	5 2 4
4.12	1.7699	9 4 0
7.46	1.7596	0 4 4
5.25	1.6851	11 2 0
6.12	1.6427	10 4 0
4.69	1.5738	1 8 0
5.26	1.4259	4 6 4
4.23	1.3877	13 1 2

Note: The calculated X-ray powder pattern was computed on the basis of $a = 19.233(2)$, $b = 12.633(3)$, $c = 8.476(2)$ Å, $\beta = 90.08(2)^\circ$, with the atomic coordinates reported in Table 2 and with occupancies given in Table 7, column ii.

TABLE 6. Electron microprobe analyses (means, ranges, and standard deviations in wt% of elements) and atomic ratios (on the basis of 44 atoms) for menchettiite

	wt%	Range	σ	Atom	Atomic ratios
Pb	31.27	30.01–32.15	0.21	Pb	4.81
Ag	6.59	6.20–6.88	0.09	Ag	1.95
Cu	0.02	0.00–0.06	0.01	Cu	0.01
Mn	5.52	5.19–5.77	0.07	Mn	3.20
Fe	0.03	0.00–0.12	0.01	Fe	0.02
Zn	0.02	0.00–0.07	0.01	Zn	0.01
Sb	23.26	23.08–23.55	0.18	Sb	6.09
As	9.27	9.09–9.60	0.10	As	3.94
Bi	0.03	0.00–0.08	0.01	Bi	0.01
S	24.09	23.55–24.30	0.16	S	23.95
Se	0.02	0.00–0.04	0.02	Se	0.01
Total	100.12	99.20–100.34		Σ_{atoms}	44.00

slabs parallel to (100) having a thickness of four octahedra. Slabs are linked together by flattened M4S₄ tetrahedra and M9S₆ octahedra and by alternating adjacent M3 and M8 polyhedra,

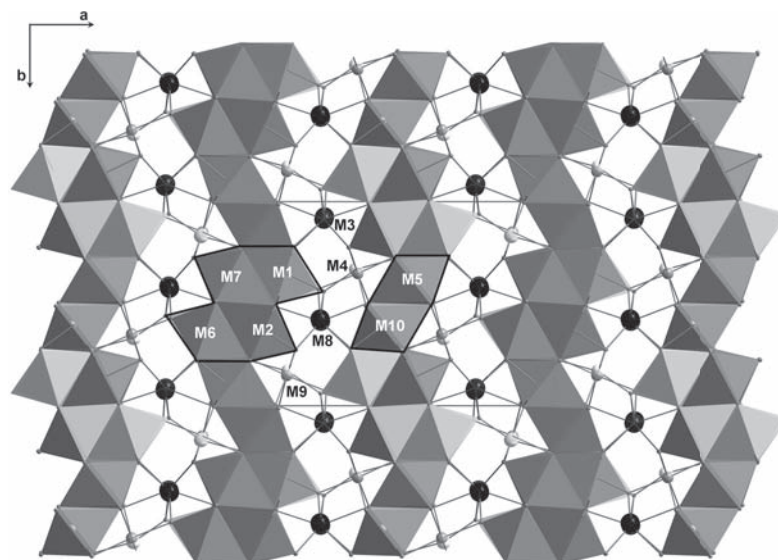


FIGURE 3. The crystal structure of menchettiite projected down [001]. Edge-sharing polyhedra belonging to the octahedral slabs (M1-M2-M5-M6-M7-M10) are depicted in gray. M3 and M8 are indicated with black circles, whereas white and gray circles represent M4 and M9, respectively.

which form chains running along [001]. As pointed out by Yang et al. (2009), the octahedral slabs are formed by two kinds of rods extending along [001], namely a four-sites (M1-M2-M6-M7) and a two-sites (M5-M10) rod (Fig. 3).

Taking into account the electron density obtained from the refinement (Table 2) and the crystal-chemical features the site assignment was done as follows. The M4 site is completely filled by Ag ($\langle M4-S \rangle = 2.58 \text{ \AA}$), like in all the ramdohrite-type minerals (Table 7). M9, which exhibits a regular octahedral coordination in all these minerals, is fully occupied by Mn^{2+} and shows a mean distance ($\langle M9-S \rangle = 2.64 \text{ \AA}$) very similar to those observed in both uchucchacuaite crystals (2.650 and 2.654 $\text{\AA}$) refined by Yang et al. (2011), where this octahedron is largely dominated by Mn^{2+} as well. On the other hand, the longer $\langle M9-S \rangle$ distances observed in ramdohrite (2.83 $\text{\AA}$; Makovicky and Mumme 1983) and in fizélyite (2.917 $\text{\AA}$; Yang et al. 2009) are in keeping with the incorporation of larger cations at this site (Table 7). Although in the ramdohrite crystal investigated by Makovicky and Mumme, the M9 site was considered to accommodate 0.50Ag+0.50Sb, these authors predicted the possibility of the structure of accommodate either smaller (i.e.,

Mn^{2+} , Fe^{2+} , and Cd^{2+}) or larger (Pb) divalent cations at this site.

Both M3 and M8 sites form large and irregular polyhedra, which were described as bi-capped trigonal prisms by Makovicky and Mumme (1983). In the M8 polyhedron, occupied by Pb alone, the range of these eight distances is from 2.90 to 3.24 $\text{\AA}$, whereas M3 shows a larger spread (from 2.67 to 3.61 $\text{\AA}$). The mean of the three shortest distances (2.77 $\text{\AA}$) in M3, where the site scattering indicates substitution of an element lighter than Pb, is slightly smaller than in other ramdohrite-type minerals where M3 is occupied by Pb alone (2.87 $\text{\AA}$ in ramdohrite, Makovicky and Mumme 1983; 2.878 $\text{\AA}$ in fizélyite, Yang et al. 2009; 2.853–2.851 $\text{\AA}$ in uchucchacuaite, Yang et al. 2011).

Among the sites belonging to the octahedral slab, M10, M2, M7, and M6, which are occupied by Sb alone in the homologous sites of the ramdohrite-type minerals, exhibit various electron counts between 33 to 51 in menchettiite, indicating variable amounts of As^{3+} and Sb^{3+} at these sites. Accordingly, they exhibit an asymmetrical coordination with three distances shorter than the others (Table 3). As shown in Figure 4, the mean $\langle M-S \rangle$ linearly increases as a function of the Sb content. For the remaining M1 and M5 sites, two possible cation populations

TABLE 7. Summary of site occupancy for the ramdohrite-type minerals

Site	Menchettiite (i)	Menchettiite (ii)	Ramdohrite (1)	Fizélyite (2)	Uchucchacuaite (3)
M1	$Sb_{0.77}Mn_{0.18}Pb_{0.05}$	$Mn_{0.60}Pb_{0.40}$	Sb	Sb	Sb
M2	$As_{0.57}Sb_{0.43}$	$As_{0.57}Sb_{0.43}$	Sb	Sb	Sb
M3	$Pb_{0.65}Sb_{0.35}$	$Pb_{0.65}Sb_{0.35}$	Pb	Pb	Pb
M4	Ag	Ag	Ag	Ag*	Ag
M5	$Mn_{0.58}Pb_{0.42}$	$Sb_{0.77}Pb_{0.23}$	Pb	Pb	Pb
M6	Sb	Sb	Sb	Sb	Sb
M7	$Sb_{0.68}As_{0.32}$	$Sb_{0.68}As_{0.32}$	Sb	Sb	Sb
M8	Pb	Pb	Pb	Pb	Pb
M9	Mn	Mn	$Sb_{0.5}+Ag_{0.5}$	$Pb_{0.56}Ag_{0.33}Sb_{0.10}$ *	$Mn_{0.90-0.92}Ag_{0.04-0.05}Sb_{0.04-0.05}$
M10	As	As	Sb	Sb	Sb

Note: Sites are labeled according to Makovicky and Mumme (1983); (i), (ii): two different hypotheses of site assignment for menchettiite (see text); (1) Makovicky and Mumme (1983); (2) Yang et al. (2009); (3) Yang et al. (2011).

* M4 and M9 occupancy sites are reported as the sum of occupancy of three and two split sites, respectively.

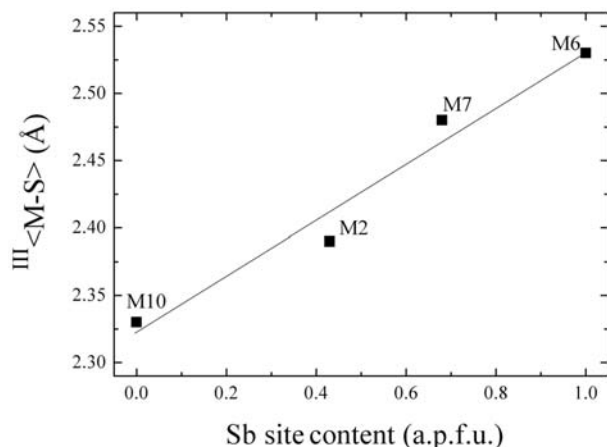


FIGURE 4. Variation of $^{III}\langle M-S \rangle$ as a function of the Sb content substituting for As.

were tentatively hypothesized (see Table 7, columns *i* and *ii*). On the basis of analogies with ramdohrite, fizélyite, and uchucchacuaite, the site assignment (*i*) provides dominance of Sb and Pb at M1 and M5, respectively, with the remaining Mn distributed on both sites. On the other hand, the same site electron number can be obtained with the assignment (*ii*), which provides dominance of Mn and Sb at M1 and M5, respectively, with the remaining Pb distributed on both sites. Figure 5 shows the linear increase of the mean of the three shortest distances ($^{III}\langle M-S \rangle$) as a function of the amount of Pb substituting for Mn (Fig. 5a) or Sb (Fig. 5b). For M1 and M5 sites, both the hypothesized cation populations are plotted. It can be noted that points referring to hypothesis (*ii*) match more closely the linear model observed. The assumption that M1 is occupied by $0.60\text{Mn} + 0.40\text{Pb}$ rather than by dominant Sb^{3+} is corroborated by the comparison with the other ramdohrite-type minerals where M1 is occupied by Sb alone: the gap between the fourth and third distance [$\Delta = (\text{M}-\text{S})^{\text{IV}} - (\text{M}-\text{S})^{\text{III}}$], indicating the typical pyramidal coordination of Sb^{3+} , is 0.25 Å in ramdohrite (Makovicky and Mumme 1983), 0.32 Å in fizélyite (Yang et al. 2009), and 0.29 Å in uchucchacuaite (Yang et al. 2011), whereas it is 0.05 Å in menchettiite. On the other hand, the same parameter obtained for the M5 site indicates dominance of Sb rather than Pb in the structure of menchettiite. Indeed, $\Delta = (\text{M}-\text{S})^{\text{IV}} - (\text{M}-\text{S})^{\text{III}} = 0.31$ Å in menchettiite, while

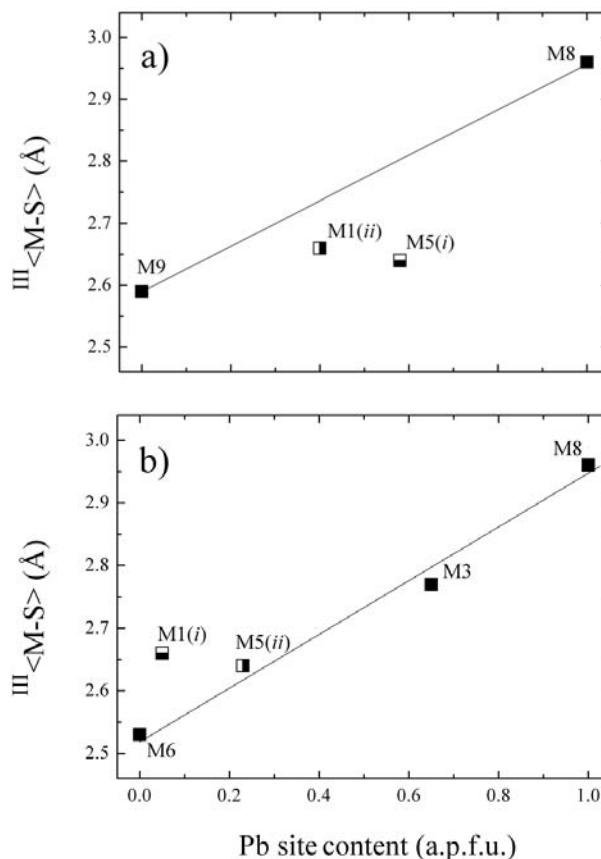


FIGURE 5. Variation of the mean of the three shortest distances ($^{III}\langle M-S \rangle$) as a function of the amount of Pb substituting for Mn (a) or Sb (b). For M1 and M5 sites, both the hypothesized cation populations [*i*) and (*ii*)] are plotted.

it is close to zero in the ramdohrite-type minerals where M5 is occupied by Pb alone: 0.03 Å in ramdohrite, 0.06 Å in fizélyite, and 0.06–0.07 Å in uchucchacuaite. For all the reasons explained above, the site-assignment reported in Table 7, column *ii*, was chosen for menchettiite and used for bond-valence calculations (Table 8).

Menchettiite can be classified among the Sb-rich members of the lillianite homeotypic series, which are described with the general formula $\text{Ag}_x\text{Pb}_{3-2x}\text{Sb}_{2+x}\text{S}_6$ (Moëlo et al. 2008). Besides the heterovalent substitution $2\text{Pb}^{2+} \rightarrow \text{Ag}^+ + \text{Sb}^{3+}$

TABLE 8. Bond-valence (v.u.) arrangement for menchettiite

	M1 Mn _{0.60} Pb _{0.40}	M2 As _{0.57} Sb _{0.43}	M3 Pb _{0.65} Sb _{0.35}	M4 Ag	M5 Sb _{0.77} Pb _{0.23}	M6 Sb	M7 Sb _{0.68} As _{0.32}	M8 Pb	M9 Mn	M10 As	ΣS
S1	0.44	0.79	0.36			0.14	0.10, 0.05			0.07	1.88
S2	0.12	0.14			0.55		0.97		0.21		2.06
S3	0.66		0.67	0.43				0.38			2.14
S4		1.09	0.09	0.22				0.27	0.38		2.05
S5			0.27	0.03	0.24				0.27	0.90, 0.02	1.73
S6	0.32		0.06		0.74	0.75		0.17			2.04
S7	0.28	0.98, 0.06				0.10	0.25	0.23			1.90
S8		0.08		0.33	0.70	0.21	0.55				1.97
S9			0.55			0.90		0.30	0.30		2.05
S10			0.14	0.21			1.12	0.22	0.28		1.97
S11				0.03	0.23, 0.20			0.15	0.30	0.90	1.81
S12	0.21		0.05			0.93		0.16		0.75	2.10
	2.03	3.14	2.19	1.25	2.66	3.03	3.04	1.88	1.74	2.74	

Note: Calculated from the bond-valence curves of Brese and O'Keeffe (1991).

taken into consideration by the above formula, however, two isovalent substitutions relate menchettiite to the others lillianite homeotypes, i.e., $\text{Mn}^{2+} \rightarrow \text{Pb}^{2+}$ (also working in uchucchacuaite) and $\text{As}^{3+} \rightarrow \text{Sb}^{3+}$. Moreover, M^{2+} cations other than Mn^{2+} were reported in these minerals. In particular, significant amounts of Cd (up to 1.6 wt%) were found in ramdohrite from the type deposit (Moëlo 1989), while a fizélyite sample from Bohemia (Kašpar et al. 1983) contains 0.43 wt% Fe. Therefore, a general formula working for all the Sb-rich members of the lillianite homeotypic series should be written as follows: $\text{Ag}_x\text{Pb}_{3-2x-y}\text{M}^{2+}_z\text{Sb}_{2+x-z}\text{As}_z\text{S}_6$ ($\text{M}^{2+} = \text{Mn}^{2+}, \text{Cd}^{2+}, \text{Fe}^{2+}$) with $x = 0.5$, $y = 0.8$, and $z = 1.0$ for menchettiite and $x = 0.5$, $y = 0.5$, $z = 0.0$ for uchucchacuaite. This formalism highlights the close similarity between menchettiite and uchucchacuaite, the only members of the series to have the same ratio between metallic and semi-metallic elements. For the other members, i.e., andorite VI, andorite IV, ramdohrite, fizélyite, and roshchinite (Moëlo et al. 2008), $0.69 \leq x \leq 1.19$, $0 \leq y \leq 0.125$, and $z = 0$.

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