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Manganoquadratite, $AgMnAsS_3$, a new manganese-bearing sulfosalt from the Uchucchacua polymetallic deposit, Lima Department, Peru: Description and crystal structure

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ABSTRACT

Manganoquadratite, ideally $AgMnAsS_3$, is a new mineral from the Uchucchacua polymetallic deposit, Oyon district, Catajambo, Lima Department, Peru. It occurs as dark gray, anhedral to subhedral grains up 0.5 mm across, closely associated with alabandite, Mn-rich calcite, Mn-rich sphalerite, proustite, pyrite, pyrrhotite, tennantite, argentotennantite, stannite, and other unnamed minerals of the system Pb-Ag-Sb-Mn-As-S. Manganoquadratite is opaque with a metallic luster and possesses a reddish-brown streak. It is brittle, the Vickers microhardness (VHN_{10}) is 81 kg/mm^2 (range 75–96) (corresponding Mohs hardness of 2–2½). The calculated density is 4.680 g/cm^3 (on the basis of the empirical formula). In plane-polarized reflected light, manganoquadratite is moderately bireflectant and very weakly pleochroic from dark gray to a blue gray. Internal reflections are absent. Between crossed polars, the mineral is anisotropic, without characteristic rotation tints. Reflectance percentages ($R_{\min}$ and $R_{\max}$) for the four standard COM wavelengths are 29.5, 31.8 (471.1 nm), 28.1, 30.5 (548.3 nm), 27.3, 29.3 (586.6 nm), and 26.0, 28.2 (652.3 nm), respectively.

Manganoquadratite is tetragonal, space group $P4_322$, with unit-cell parameters: $a = 5.4496(5)$, $c = 32.949(1)$ Å, $V = 978.5(1)$ Å^3, $c:a = 6.046$, $Z = 8$. The structure, refined to $R1 = 0.0863$ for 907 reflections with $F_o > 4\sigma(F_o)$, consists of a stacking along [001] of alabandite-like Mn_2S_2 layers connected to each to other by a couple of $AgAsS_2$ sheets where As^{3+} forms typical AsS_3 groups, whereas Ag^+ cations are fivefold coordinated. The six strongest lines in the observed X-ray powder-diffraction pattern [d in Å (I/I_0) (hkl)] are: 3.14 (60) (116), 2.739 (50) (0 0 12), 2.710 (100) (200), 1.927(70) (2 0 12 + 220), 1.645 (25) (3 0 16), and 1.573 (20) (2 2 12).

Electron microprobe analyses gave the chemical formula (on the basis of six atoms) $(Ag_{0.95}Cu_{0.05})_{\Sigma=1.00}(Mn_{0.96}Pb_{0.04})_{\Sigma=1.00}(As_{0.87}Sb_{0.14})_{\Sigma=1.01}S_{2.99}$, leading to the simplified formula $AgMnAsS_3$.

The name was chosen to indicate the close analogy of the formula and unit-cell dimensions with quadratite, $Ag(Cd,Pb)(As,Sb)S_3$. The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA 2011-008.

Keywords: Manganoquadratite, new mineral, electron microprobe data, reflectance data, X-ray diffraction data, quadratite, Uchucchacua deposit, Peru

INTRODUCTION

For a long time, the only known sulfosalt of manganese was samsonite, $Ag_4MnSb_2S_6$ (Werner and Fraatz 1910); in the 1980s other sulfosalts of this element were found, i.e., benavidesite, $Pb_4(Mn,Fe)Sb_6S_{14}$ (Oudin et al. 1982), uchucchacuaite, $AgMnPb_3Sb_5S_{12}$ (Moëlo et al. 1984), and clerite, $MnSb_2S_4$ (Murzin et al. 1996), all of them being thioantimonites. Two of these, benavidesite and uchucchacuaite, were first discovered in samples from an Ag-Pb-Zn mine within the Uchucchacua polymetallic deposit (Peru). Recently, two other Mn-bearing sulfosalts were recognized from this deposit and approved as new minerals. The first one, menchettiite, ideally $AgPb_{2.40}Mn_{1.60}Sb_3As_2S_{12}$ (Bindi et al. 2012), exhibits the highest As contents (9.09–9.60 wt%) among the Sb-rich members of the lillianite homeotypic series (Moëlo et al. 2008). The second one, described in the present paper, ideally $AgMnAsS_3$, is the first sulfosalt of Mn with As largely dominant. The mineral has been named manganoquadratite to reflect the close similarity in chemistry and unit-cell dimensions with quadratite, $Ag(Cd,Pb)(As,Sb)S_3$ (Graeser et al. 1998). The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA 2011-008. 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 3108/I. After the approval of manganoquadratite by the IMA-CNMNC, additional data on the same mineral collected by J. Hyrsl in the Socorro section of the Uchucchacua deposit (Sejkora 2011) were reported on the RRUFF Project collection (rruff.info/R090021).

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OCCURRENCE AND PHYSICAL PROPERTIES

Manganoquadratite was found by one of the authors (F.N.K.) in a sample collected in October 2010 from the 890 level, Uchucchacua polymetallic deposit (Oyon Province, Catajambo Region, Lima Department, Peru), a complex vein-type deposit related to a dacitic intrusion cutting through Cretaceous and Tertiary formations on the West side of the Occidental Cordillera of Central Andes. According to Oudin et al. (1982), the Mn-sulfides present at the Uchucchacua deposit likely precipitated from Mn-rich hydrothermal fluids at unusually low-oxygen fugacity and relatively ordinary (pyrite to pyrrhotite equilibrium) sulfur fugacity.

The sample containing manganoquadratite mainly consists of alabandite, with associated Mn-rich calcite, Mn-rich sphalerite, proustite, pyrite, pyrrhotite, tennantite, argentotennantite, stannite, manganoquadratite, and other unnamed minerals of the system Pb-Ag-Sb-Mn-As-S. Minute veins of geocronite cut some grains of manganoquadratite (Fig. 1). Manganoquadratite occurs as very rare, subhedral to anhedral grains up to grain size of 0.5 mm. It does not show any obvious twinning, and no inclusions of, or intergrowths with other minerals, were noted.

Manganoquadratite is dark gray in color and has a reddish-brown streak. The mineral is brittle and opaque with a metallic luster. No evident cleavage was observed in our available minute grains; however, pseudocubic cleavage was noted on the centimetric crystals described by Sejkora (2011). Density could not be measured because it was difficult to separate a pure grain large enough for the measurement. The calculated density is 4.680 g/cm^3 (on the basis of the empirical formula). To measure Vickers hardness and reflectivity a grain was embedded in epoxy and polished using diamond pastes down to 0.25 μm.

The micro-indentation measurements carried out with a VHN load of 10 g gave a mean value of 81 (range: 75–96) kg/mm^2, corresponding to 2–2½ on the Mohs scale.

In plane-polarized reflected light, manganoquadratite is moderately bireflectant and very weakly pleochroic from dark gray to a blue gray. With crossed polars, 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 3350 K, approximately). An interference filter was adjusted, in turn, to select the following 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 29.5, 31.8 (471.1 nm), 28.1, 30.5 (548.3 nm), 27.3, 29.3 (586.6 nm), and 26.0, 28.2 (652.3 nm), respectively.

In Figure 2 the reflectance percentages obtained for manganoquadratite are plotted together with those measured by Graeser et al. (1998) for quadratite, $Ag(Cd,Pb)(As,Sb)S_3$. As expected on the basis of the more pronounced metallic character of Cd with respect to Mn, manganoquadratite exhibits a reflectivity lower than that of quadratite.

EXPERIMENTAL METHODS

Several crystals of manganoquadratite were selected from the rock sample and examined by means of a Bruker MACH3 single-crystal diffractometer using graphite-monochromatized Mo$K\alpha$ radiation. Unit-cell dimensions were determined by least-squares refinement of the setting angles of 25 high-θ reflections ($15 < \theta < 22°$). For all the crystals investigated, nearly identical values ($a \approx 5.45$, $c \approx 32.95$ Å) resembling those of quadratite (Graeser et al. 1998) were observed. 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, fitted with a Sapphire 2 CCD detector (see Table 1 for details). 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. The merging R for the data set decreased from 0.160 before absorption correction to 0.062 after this correction.

The diffraction rings from a few ground grains of manganoquadratite were collected with a CCD-equipped diffractometer Xcalibur PX Ultra using Cu$K\alpha$ radiation (50 kV and 40 mA) and then converted into a conventional XRD pattern. Crystal-to-detector distance was 7 cm. Data were processed using the CrysAlis software package version 1.171.31.2 (Oxford Diffraction 2006) running on the

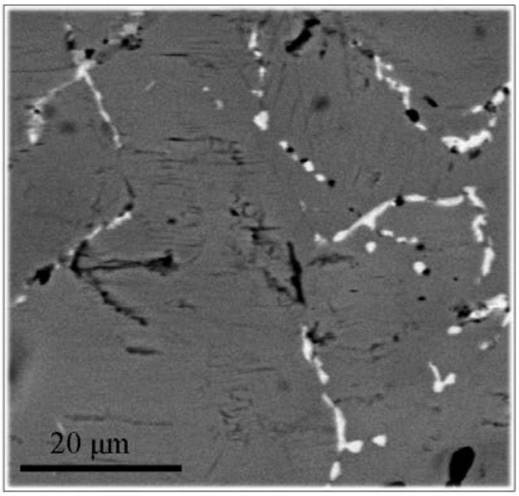

FIGURE 1. SEM-BSE image of a manganoquadratite. Brighter veins consist of geocronite.

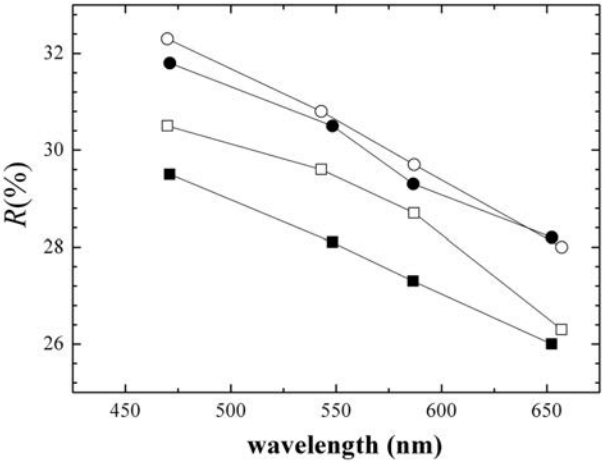

FIGURE 2. Reflectivity curves for manganoquadratite (filled symbols) compared with those of quadratite (open symbols; Graeser et al. 1998). Squares and circles refer to R_{max} and R_{min} values, respectively. Measures were done in air.

TABLE 1. Crystallographic data and refinement parameters for manganoquadratite

Crystal data	
Ideal formula	$AgMnAsS_3$
Crystal system	Tetragonal
Space group	$P4_322$
Unit-cell parameters *a*, *c* (Å)	5.4496(5), 32.949(1)
Unit-cell volume (Å^3)	978.5(1)
Z	8
Calculated density (g/cm^3)	4.680
Crystal size (mm)	0.055 × 0.065 × 0.095
Data collection	
Diffractometer	Oxford Diffraction Excalibur 3 (CCD)
Temperature (K)	298(3)
Radiation, wavelength (Å)	Mo*K*α, 0.71073
θ range for data collection (°)	4.17–31.75
h, *k*, *l* ranges	−4–6, −8–1, −46–38
Axis/frames/width (°)/time per frame (s)	ω/585/0.65/120
Total reflections collected	2939
Unique reflections (R_{int})	1532 (0.0624)
Unique reflections $F > 4\sigma(F)$	907
Data completeness to θ_{max} (%)	99.4
Absorption correction method	multiscan (ABSPACK Oxford Diff 2006)
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$1/\sigma^2(F)$
Flack parameter	0.08(3)
Data/restraints/parameters	2939/0/58
R_1 [$F > 4\sigma(F)$]	0.0863
R_1 all	0.1425
Largest diff. peak and hole (e$^-$/Å^3)	2.78, −1.73

Xcalibur PX control PC.

The same crystal fragment used for the structural study was analyzed by means of a Jeol JXA-8200 electron microprobe using WDS. Major and minor elements were determined at an accelerating voltage of 15 kV and 30 nA beam current with a counting time of 15 s. The following standards (and lines) were employed: Ag-pure element (Ag*L*α), Cu-pure element (Cu*K*α), galena (Pb*M*α), synthetic MnS (Mn*K*α), pyrite (Fe*K*α, S*K*α), synthetic ZnS (Zn*K*α), synthetic Sb_2S_3 (Sb*L*β), synthetic As_2S_3 (As*L*α), synthetic Bi_2S_3 (Bi*M*β), and synthetic $PtSe_2$ (Se*L*α). Iron, Zn, Cd, Se, and Bi were found to be equal or below the limit of detection (0.01 wt%).

The crystal fragment that was analyzed was found to be homogeneous within the analytical uncertainty. The chemical composition (nine analyses on different spots), together with the atomic ratios, is reported in Table 2. On the basis of six atoms, the formula is $(Ag_{0.95}Cu_{0.05})_{\Sigma=1.00}(Mn_{0.96}Pb_{0.04})_{\Sigma=1.00}(As_{0.87}Sb_{0.14})_{\Sigma=1.01}S_{2.99}$. The simplified formula is $AgMnAsS_3$, which requires: Ag 32.31, Mn 16.45, As 22.44, S 28.80, Total 100.00 wt%.

CRYSTAL-STRUCTURE DETERMINATION

Refined unit-cell parameters [*a* = 5.4496(5), *c* = 32.949(1) Å] and analysis of intensity data indicated the Laue group 4/*mmm* and *E*-statistics strongly indicated the structure to be centrosymmetric ($|E^2 - 1| = 0.943$). However, systematic absences gave contradictory information due to extreme weakness of the *hkl* reflections with $h + k + l = 2n + 1$, and the first attempts to solve the structure by standard methods [Patterson and direct methods in the SHELX package (Sheldrick 1997)] did not lead to reliable solutions.

A starting model was first obtained by refining the average *I*4 substructure (subcell $a_{sub} = a$, $c_{sub} = 1/3\ c$), which incorporated a *ccp* array of sulfur atoms with metals located within the octahedral interstices. The obtained atomic coordinates were then transformed for the unit-cell having $c = 3c_{sub}$ and the model slowly achieved convergence in the triclinic *P*1 space group [*R*1 = 0.093 for 1622 $F_o > 4\sigma(F_o)$ and 0.15 for all 2939 data]. At this stage, an analysis of the structure with the ADDSYMM routine of the PLATON program (Spek 2003) revealed the real symmetry to be $P4_322$. The site occupancies of all the metal positions were allowed to vary using different combinations of the scattering curves for neutral Ag, Mn, Sb, and As (Ibers and Hamilton 1974). At the last stage, which involved refinement of the anisotropic atomic-displacement parameters for all atoms and no constraints, the residual value converged to *R*1 = 0.0863 for 907 observed reflections [$F_o > 4\sigma(F_o)$] and 58 parameters and *R*1 = 0.1425 for all 1532 independent reflections. The Flack parameter of 0.08(3) (Flack 1983) indicated the orientation to be correct. Inspection of the difference Fourier map revealed maximum positive and negative peaks of 2.78 and 1.73 e$^-$/Å^3, respectively. Fractional atomic coordinates and anisotropic-displacement parameters are given in Table 3 and bond distances in Table 4. The calculated X-ray powder pattern is given in Table 5 together with the measured pattern. Table 6[1] lists the observed and calculated structure factors. Bond-valence sums calculated from the curves of Brese and O'Keeffe (1991) are reported in Table 7.

TABLE 2. Electron microprobe analyses (means, ranges, and standard deviations in wt% of elements) and atomic ratios (on the basis of six atoms) for manganoquadratite

	Mean*	Range	σ	Atomic ratios	
Ag	29.69	28.77–30.44	0.20	Ag	0.95
Cu	0.91	0.70–1.06	0.06	Cu	0.05
Pb	2.37	2.08–2.50	0.03	Pb	0.04
Mn	15.28	15.05–15.44	0.14	Mn	0.96
Sb	4.89	4.60–5.11	0.04	Sb	0.14
As	18.91	18.01–19.23	0.15	As	0.87
S	27.67	27.40–28.10	0.19	S	2.99
Total	99.72	99.30–100.05		Σ_{atoms}	6.00

* Nine analyses on different spots.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of manganoquadratite is a galena-derivative framework, with a cubic closest-packing array of S atoms arranged in layers stacked along the [66$\bar{1}$] axis with metals occupying all available octahedral interstices. However, only the Mn^{2+} cations adopt an octahedral coordination; Ag^+ and As^{3+} are located outside the center of cavities, occurring in asymmetrical coordination polyhedra, AgS_5 and AsS_3, respectively. The asymmetry of these polyhedra thus causes a strong distortion of the S close-packing. Alternatively, the structure can be described as a series of square-net layers of S atoms (S-S = $2^{1/2}a/2$ = 3.85 Å) each offset from the adjacent one by ~½*a* with respect to the adjacent one (Fig. 3). With this arrangement, cations are located at the center of the S_4 square-nets to form two unique layers: Mn_2S_2 (A) and $AgAsS_2$ (B). In the succession, one A layer is stacked by two B layers thus determining the tripling of the two-layers sequence leading to a sixfold translation along [001] with respect to the basic unit cell of alabandite, MnS (Fig. 4). The layers containing Mn^{2+}, located at *z* = ⅛, ⅜, ⅝, and ⅞, are rather regular (Fig. 5a), while those containing As^{3+} and Ag^+ (approximately located at *z* ≈ 0 ± 1/24, ¼ ± 1/24, ½ ± 1/24, and ¾ ± 1/24) are more irregular (Fig. 5b), mostly due to the lone-pair-bearing As^{3+} cation, which is asymmetrically located within the S_4 squared net to bond two sulfur atoms within the layer (S2 and S3). As^{3+} ion occurs in threefold coordination, which is achieved by linking a S atom (S1) belonging to the A layer. Although As-S1 (2.377 Å) is the longest As-S distance, it is still shorter than the A-B separation, corresponding to the Mn1-S3 (2.563 Å) and Mn2-S2 (2.512 Å) bonds, thus causing the puckering of the B layer. In turn, to compensate the differences between As-S and Mn-S interlayer bond lengths, both the MnS_6-octahedra are compressed along [001]. The two B layers are joined together through the linkage between Ag and S3 atoms (2.768 Å), which alternates between the apex and basal vertices of the AgS_5 square pyramids in adjacent B layers. The two B layers are combined to form a slab con-

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[1] Deposit item AM-12-047, Table 6. 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 3. Atoms, site occupancy, fractional atom coordinates (Å), and atomic displacement parameters (Å^2) for manganoquadratite

Atom	Site occupancy	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{iso}
Ag	$Ag_{1.00}$	0.7366(3)	0.2344(3)	0.03502(4)	0.035(1)	0.034(1)	0.0373(7)	–0.0071(6)	0.0089(6)	–0.0037(8)	0.0353(4)
Mn1	$Mn_{1.00}$	0.2153(6)	0.2153(6)	1/8	0.027(2)	0.027(2)	0.012(1)	–0.0016(8)	0.0016(8)	0.006(2)	0.023(1)
Mn2	$Mn_{1.00}$	0.7105(6)	0.7105(6)	1/8	0.032(2)	0.032(2)	0.016(1)	0.001(1)	–0.001(1)	–0.002(3)	0.027(1)
As	$As_{0.81(1)}Sb_{0.19}$	0.2381(3)	0.7380(3)	0.04808(4)	0.0173(9)	0.025(1)	0.0207(6)	–0.0014(6)	0.0037(6)	–0.0047(7)	0.0209(5)
S1	$S_{1.00}$	0.1959(9)	0.7002(9)	0.11962(9)	0.026(3)	0.034(3)	0.014(1)	0.002(2)	0.006(2)	–0.007(2)	0.0252(9)
S2	$S_{1.00}$	0.6671(9)	0.709(1)	0.0491(1)	0.025(2)	0.046(3)	0.018(2)	0.001(2)	0.001(2)	–0.006(2)	0.030(1)
S3	$S_{1.00}$	0.211(1)	0.1633(9)	0.0477(1)	0.042(3)	0.024(2)	0.020(2)	0.001(2)	–0.001(2)	–0.005(2)	0.029(1)

TABLE 4. Selected bond distances (Å) for manganoquadratite

Ag-S3	2.645(6)	Mn2-S2 (x2)	2.511(4)
Ag-S2	2.656(6)	Mn2-S1 (x2)	2.652(5)
Ag-S3	2.769(4)	Mn2-S1 (x2)	2.810(5)
Ag-S3	2.923(6)	mean	2.658
Ag-S2	2.924(6)	V_p	24.76
mean	2.783	σ^2_{oct}	21.02
		λ_{oct}	1.0098
Mn1-S3 (x2)	2.561(4)		
Mn1-S1 (x2)	2.650(6)	As-S3	2.322(5)
Mn1-S1 (x2)	2.815(6)	As-S2	2.343(5)
mean	2.675	As-S1	2.377(3)
V_p	25.21	mean	2.347
σ^2_{oct}	27.31		
λ_{oct}	1.0104		

Note: the octahedral angle variance (σ^2) and the octahedral quadratic elongation (λ) were calculated according to Robinson et al. (1971).

TABLE 5. X-ray powder diffraction patterns for manganoquadratite

	1		2	
hkl	d_{calc} (Å)	I_{calc}	d_{obs} (Å)	I_{meas}
004	8.2373	7.58	–	–
105	4.1996	3.07	–	–
008	4.1186	3.42	–	–
112	3.7522	7.51	3.74(1)	10
107	3.5622	9.73	3.54(1)	10
116	**3.1543**	**76.69**	**3.14(1)**	**60**
0 0 12	**2.7458**	**51.86**	**2.739(5)**	**50**
200	**2.7248**	**100.00**	**2.710(4)**	**100**
201	2.7155	13.03		
1 1 10	2.5043	7.32	2.508(6)	10
1 0 13	2.2981	4.25	2.281(5)	5
217	2.1642	4.66	2.162(5)	5
2 0 11	2.0156	3.46	2.010(5)	5
2 0 12	**1.9341**	**53.49**	**1.927(3)**	**70**
220	**1.9267**	**26.67**		
221	1.9234	5.91		
2 0 13	1.8558	3.45	–	–
1 0 17	1.8261	4.30	–	–
2 1 13	1.7567	3.51	1.755(4)	5
1 1 18	1.6534	7.32	–	–
1 0 19	1.6525	4.01	–	–
3 0 16	**1.6443**	**27.98**	**1.645(2)**	**25**
2 2 12	**1.5772**	**20.77**	**1.573(2)**	**20**
2 1 17	1.5170	3.19	–	–
2 1 19	1.4130	3.96	–	–
400	1.3624	4.73	–	–
3 1 18	1.2547	6.35	–	–
336	1.2507	5.44	–	–
2 0 24	1.2260	4.60	–	–
4 0 12	1.2204	4.99	–	–
420	1.2186	5.39	–	–
421	1.2177	3.02	–	–
4 2 12	1.1138	6.33	–	–
516	1.0491	6.72	–	–
5 1 18	0.9230	3.38	–	–
536	0.9214	5.11	–	–
5 3 18	0.8324	3.69	–	–

Notes: 1 = calculated powder pattern and indexing for manganoquadratite on the basis of $a = 5.4496(5)$ Å, $c = 32.949(1)$ Å, and with the atomic coordinates and occupancies reported in Table 3. Intensities calculated using XPOW software version 2.0 (Downs et al. 1993). 2 = observed powder pattern for manganoquadratite obtained with a CCD-equipped single crystal diffractometer (Cu*K*α radiation). The refined unit-cell parameters are $a = 5.4458(3)$ Å, $c = 32.804(3)$ Å, $V = 972.85(9)$ Å^3. The strongest reflections are indicated in bold.

TABLE 7. Bond-valence (v.u.) sums for manganoquadratite

	Ag	Mn1	Mn2	As*	Σ S
S1		$0.28^{x2\downarrow x1\rightarrow}$, $0.18^{x2\downarrow x1\rightarrow}$	$0.28^{x2\downarrow x1\rightarrow}$, $0.18^{x2\downarrow x1\rightarrow}$	0.86	1.78
S2	0.23, 0.11		$0.41^{x2\downarrow x1\rightarrow}$	0.94	1.69
S3	0.24, 0.17, 0.11	$0.36^{x2\downarrow x1\rightarrow}$		0.99	1.87
	0.86	1.64	1.74	2.79	

* Calculated assuming a refined site occupancy of $As_{0.81}Sb_{0.19}$.

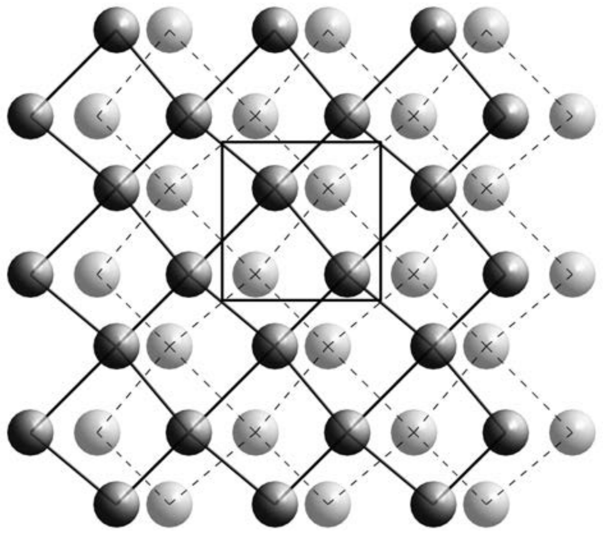

FIGURE 3. Two superimposed square-net layers of S atoms shifted of ½*a* with respect to the adjacent one ([010] projection). The S atoms belonging to adjacent layers are depicted with dark and light gray, respectively. The unit cell is outlined.

taining two sets of AgS_5 pyramids whose apices alternatively point upward and downward (Fig. 6b). In terms of modular units, these pyramidal slabs, which also include AsS_3 groups, are interconnected by slabs of edge-sharing MnS_6 octahedra (Fig. 6a), which can be described as alabandite modules. In manganoquadratite, however, the mean octahedral distances (<Mn1-S> = 2.675; <Mn2-S> = 2.658 Å) are the largest with respect to those observed in the other Mn-bearing sulfides and sulfosalts including alabandite (2.612 Å; McCammon 1991), hauerite (2.59 Å; Offner 1934), clerite (2.605 Å; Bente and Edenharter 1989), samsonite (2.6172 Å; Bindi and Evain 2007); menchettiite (2.64 Å; Bindi et al. 2012), and uchucchacuaite [2.650 Å (site occupancy: 0.902 Mn + 0.049 Ag + 0.049 Sb) and 2.654 Å (site occupancy: 0.918 Mn + 0.041 Ag + 0.041 Sb); Yang et al. 2011].

The Ag atom exhibits a distorted square-pyramidal coordination with three shorter bond distances at 2.645, 2.656, and

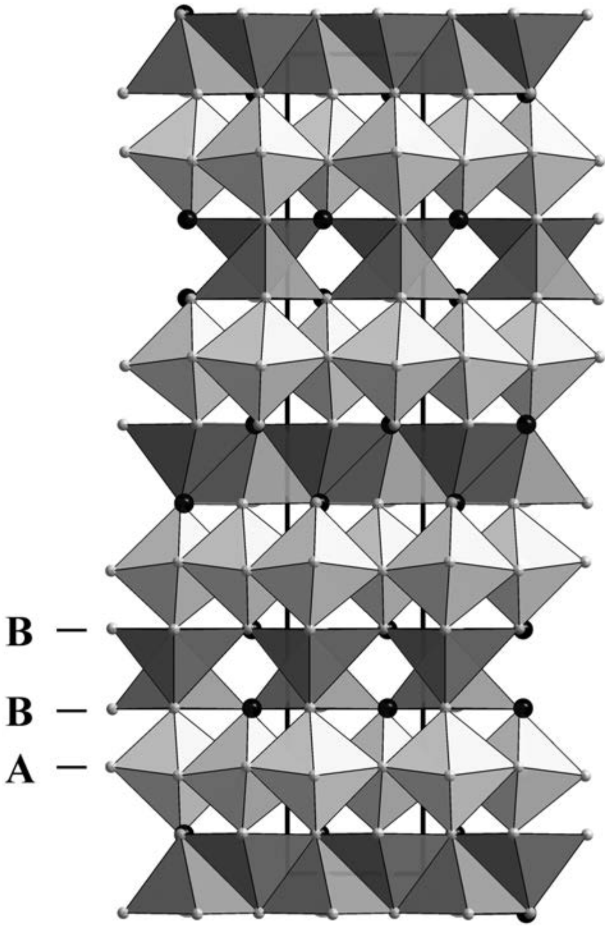

FIGURE 4. The crystal structure of manganoquadratite projected down [010] showing the succession of Mn_2S_2 (A) and $AgAsS_2$ (B) layers stacked along [001]. Mn-octahedra and Ag square-pyramids are depicted in dark gray and white, respectively; As atoms as black circles.

2.769 Å and two longer additional bonds at 2.923 and 2.924 Å (Table 4). This kind of coordination is quite rare and, to the authors' knowledge, there are no minerals reported in the literature with AgS_5 square pyramids. Indeed, Ag has a strong preference for lower coordination environments, including linear, triangular, and tetrahedral configurations. However, it is well known that both Ag^+ and Cu^+, d^{10} cations, can adopt various complex asymmetric coordinations. It has been shown (Gaudin et al. 2001 and references therein) that those particular coordinations are due to *s*/*d* orbital mixing and/or polarization factors.

Finally, the choice of the name manganoquadratite deserves a remark. As shown in Table 8, manganoquadratite shows strong similarities with the mineral quadratite Ag(Cd,Pb)$(As,Sb)S_3$ (Graeser et al. 1998). The slight differences observed in the unit-cell parameters, as well as the values of reflectance and hardness, are in keeping with the differences in chemical composition. Although a precise determination of the crystal structure of quadratite has not yet been obtained, an approximate model was obtained by Berlepsch et al. (1999) by assuming the apparent $I4_1/amd$ crystal symmetry of quadratite (Graeser et al. 1998) as the result of the superposition of two enantiomorphic structures, having space groups $P4_12_12$ and $P4_32_12$, respectively. As in manganoquadratite, quadratite can be described as a galena-based derivative framework composed of warped layers parallel to (001) with cations located in distorted octahedral coordinations. Possibly owing to twinning or order-disorder in quadratite crystals, S atoms are disordered on split positions. The disorder observed in quadratite could be a function of difficulties associated with linking the A and B layers. Substitution of $^{[6]}Mn^{2+}$ (ionic radius = 0.83 Å; Shannon 1976) in manganoquadratite by 0.80 Cd^{2+} + 0.20 Pb^{2+} (mean ionic radius = 1.00 Å; Shannon 1976) in quadratite would

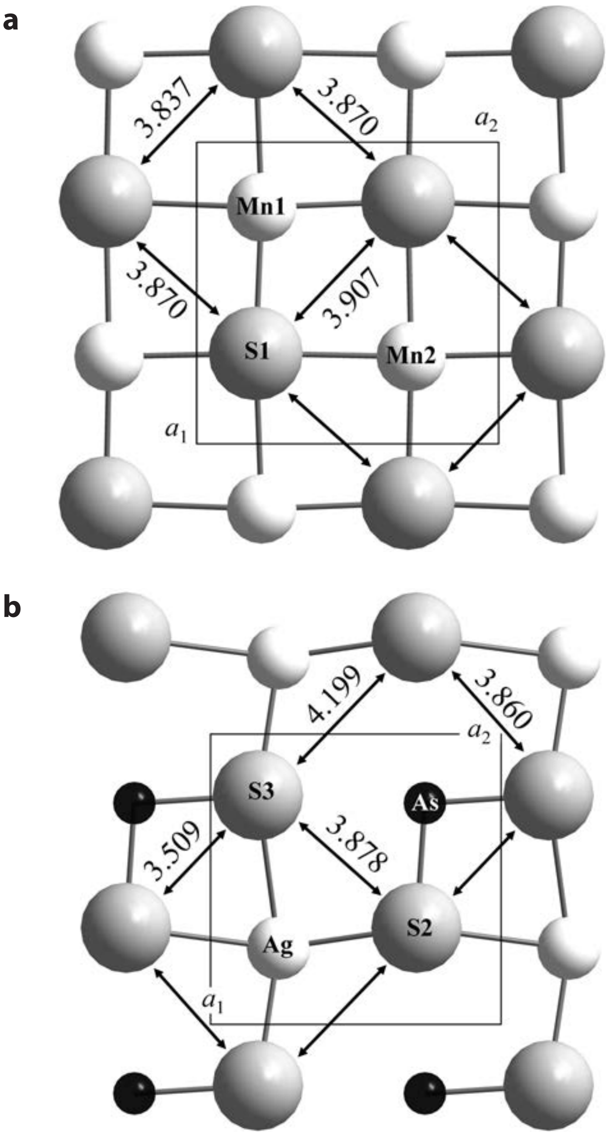

FIGURE 5. Projection down [001] of layers containing Mn^{2+} located at z = ⅛, ⅜, ⅝, and ⅞ (**a**) and layers containing As^{3+} and Ag^+ approximately located at z = 0 ± 1/24, ¼ ± 1/24, ½ ± 1/24, and ¾ ± 1/24 (**b**).

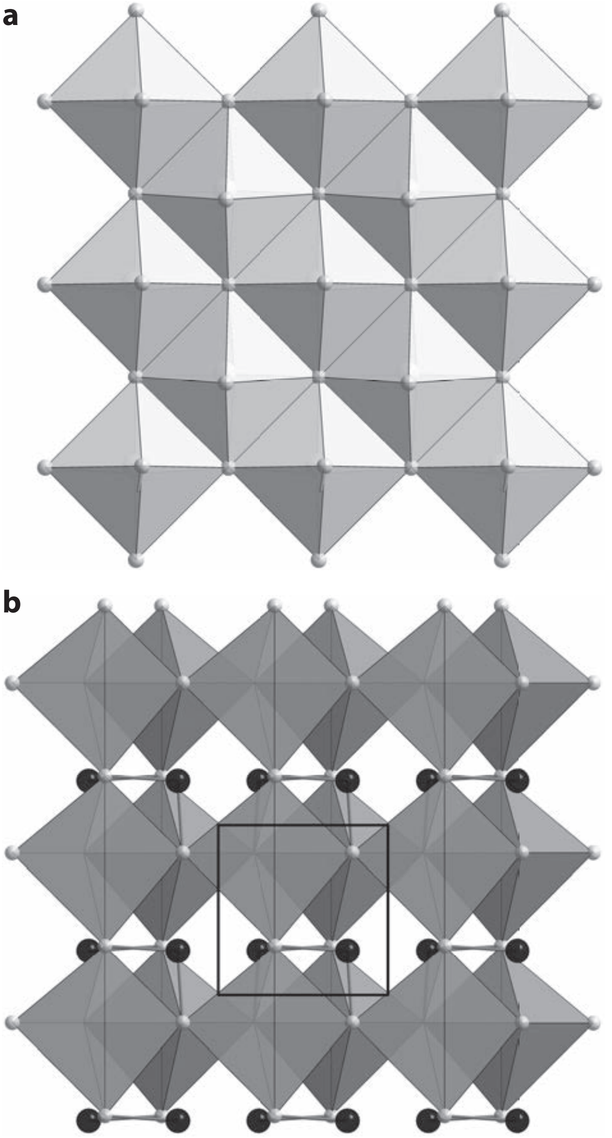

FIGURE 6. Alabandite-like slab consisting of edge-sharing MnS_6 octahedra (**a**) and two $AgAsS_2$ layers forming a double pyramidal slab (**b**) projected down [001].

cause a lengthening of Mn-S and As-S bonds directed along [001] [i.e., $M^{2+}(1)$-S3 and $M^{2+}(2)$-S2]. Correspondingly, a further puckering of the B layer would be required to preserve the As-S1 bond, which in turn, would result in a contraction of the unit cell along [100] and [010]. Thus, the increase of the unit cell due to incorporation of octahedral (Cd, Pb) in the structure could reasonably be smoothed along [100] and [010] with respect to [001]. This hypothesis is in keeping with the different increments observed for the *a* (0.9%) and *c* (2.9%) parameters (Table 8). Whether the supposed, more pronounced puckering of B layers, in turn, involves a different distribution of the metals within the sulfur close packing and a different symmetry needs to be further substantiated by a re-investigation of the crystal structure of quadratite.

TABLE 8. Relationships between manganoquadratite and quadratite

	Manganoquadratite (this study)	Quadratite (Graeser et al. 1998)
Formula	$AgMnAsS_3$	$Ag(Cd,Pb)(As,Sb)S_3$
Color	dark gray	gray
Streak	reddish-brown	reddish-brown
Hardness (kg/mm^2)	VHN_{10} = 75–96 (mean 81)	VHN_{10} = 52–72 (mean 63)
Density (g/cm^3)	4.68	5.31
Reflectance values (in air)	29.5–31.8 (471.1 nm)	30.5–32.3 (470 nm)
	28.1–30.5 (548.3 nm)	29.6–30.8 (543 nm)
	27.3–29.3 (586.6 nm)	28.7–29.7 (587 nm)
	26.0–28.2 (652.3 nm)	26.3–28.0 (657 nm)
a (Å)	5.4496(5)	5.499(5)
c (Å)	32.949(1)	33.91(4)
V (Å^3)	978.5(1)	1025(2)
Z	8	8
Space group	$P4_322$	$I4_1/amd$ [$P4_12_12$ (or $P4_32_12$)]*
hkl, *d* (*I*)†	1 1 6, 3.14 (60)	1 1 6, 3.19 (50)
	0 0 12, 2.739 (50)	
	2 0 0, 2.710 (100)	2 0 0, 2.77 (100)
	2 0 12 + 2 2 0, 1.927 (70)	2 0 12, 1.960 (80)
	3 0 16, 1.645 (25)	2 0 16, 1.679 (70)
	2 2 12, 1.573 (20)	2 2 12, 1.598 (70)

* The $I4_1/amd$ (Graeser et al. 1998) symmetry was interpreted by Berlepsch et al. (1999) as due to superposition of two $P4_12_12$ (or $P4_32_12$) acentric structures.
† Strongest lines in the observed diffraction patterns of manganoquadratite and quadratite, respectively.

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REFERENCES CITED

Bente, K. and Edenharter, A. (1989) Roentgenographische Strukturanalyse von $MnSb_2S_4$ und Strukturverfeinerung von Berthierite, $FeSb_2S_4$. Zeitschrift für Kristallogrographie, 186, 31–33.

Berlepsch P., Balić-Žunić, T., and Makovicky, E. (1999) The superposition structure of quadratite $Ag(Cd,Pb)AsS_3$. 1s. Det 30. Danske Krystallografmøde, Forskningscenter Risø 1999. Abstract 30.

Bindi, L. and Evain, M. (2007) Gram-Charlier development of the atomic displacement factors into mineral structures: The case of samsonite, $Ag_4MnSb_2S_6$. American Mineralogist, 92, 886–891.

Bindi, L., Keutsch, F.N., and Bonazzi, P. (2012) Menchettiite, $AgPb_{2.40}Mn_{1.60}Sb_3As_2S_{12}$, a new sulfosalt belonging to the lillianite series from the Uchucchacua polymetallic deposit, Lima Department, Peru. American Mineralogist, 97, 440–446.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Downs, R.T., Bartelmehs, K.L., Gibbs, G.V., and Boisen, M.B. Jr. (1993) Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. American Mineralogist, 78, 1104–1107.

Flack, H.D. (1983) On enantiomorph-polarity estimation. Acta Crystallographica, A39, 876–881.

Gaudin, E., Boucher, F., and Evain, M. (2001) Some factors governing Ag^+ and Cu^+ low coordination in chalcogenide environments. Journal of Solid State Chemistry, 160, 212–221.

Graeser, S., Lustenhouwer, W., and Berlepsch, P. (1998) Quadratite, Ag(Cd,Pb)$(As,Sb)S_3$—a new sulfide mineral from Lengenbach, Binntal (Switzerland). Schweizer Mineralogische und Petrographische Mitteilungen, 78, 489–494.

Ibers, J.A. and Hamilton, W.C. (1974) International Tables for X-ray Crystallography, vol. IV, 366p. Kynock, Dordrecht, The Netherlands.

McCammon, C.A. (1991) Static compression of alpha-MnS at 298 K to 21 GPa. Physics and Chemistry of Minerals, 17, 636–641.

Moëlo, Y., Makovicky, E., Mozgova, N.N., Jambor, J.L., Cook, N., Pring, A., Paar, W., Nickel, E.H., Graeser, S., Karup-Møller, S., Balić-Žunić, T., Mumme, W.G., Vurro, F., Topa, D., Bindi, L., Bente, K., and Shimizu, M. (2008) Commission on Ore Mineralogy of the International Mineralogical Association: Report of the Sulfosalt Subcommittee. European Journal of Mineralogy, 20, 7–46.

Moëlo, Y., Oudin, E., Picot, P., and Caye, R. (1984) L'uchucchacuaite,

$AgMnPb_3Sb_5S_{12}$, une nouvelle espece minerale de la serie de l'andorite. Bulletin de Minéralogie, 107, 597–604.

Murzin, V.V., Bushmakin, A.F., Sustavov, S.G., and Shcherbachev, D.K. (1996) Clerite, $MnSb_2S_4$—a new mineral from the Vorontsovskoye gold deposit in the Urals. Zapiski Vsesoyuznogo Mineralogicheskogo Obshchvestva, 124, 95–101 (in Russian).

Offner, F. (1934) A redetermination of the parameter for hauerite, MnS_2. Zeitschrift für Kristallographie, 89, 182–184.

Oudin, E., Picot, P., Pillard, F., Moëlo, Y., Burke, E., and Zakrzewski, A. (1982) La benavidesite, $Pb_4(Mn,Fe)Sb_6S_{14}$, un nouveau mineral de la serie de la jamesonite. Bulletin de Minéralogie, 105, 166–169.

Oxford Diffraction (2006) CrysAlis RED (Version 1.171.31.2) and ABSPACK in CrysAlis RED. Oxford Diffraction, Abingdon, Oxfordshire, England.

Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation; A quantitative measure of distortion in coordination polyhedra. Science, 172, 567–570.

Sejkora, J. (2011) Hyrslite (manganoquadratite) from Uchucchacua. RRUFF Document, R, 090021, 1–5.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Sheldrick, G.M. (1997) SHELXS-97. A program for automatic solution of crystal structures. University of Göttingen, Germany.

Spek, A.L. (2003) PLATON, A multipurpose crystallographic tool. Journal of Applied Crystallography, 36, 7–13.

Werner, S. and Fraatz, A. (1910) Samsonit, ein manganhaltiges Silbermineral von St. Andreasberg im Harz. Zentralblatt für Mineralogie, Geologie und Paläontologie 1910, 331–335 (in German).

Yang, H., Downs, R.T., Evans, S.H., Feinglos, M.N., and Tait, K.T. (2011) Crystal structure of uchucchacuaite, $AgMnPb_3Sb_5S_{12}$, and its relationship with ramdohrite and fizélyite. American Mineralogist, 96, 1186–1189.

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