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STRUCTURE REFINEMENT OF AN UNTWINNED SINGLE CRYSTAL OF Ag-EXCESS FIZÉLYITE, $Ag_{5.94}Pb_{13.74}Sb_{20.84}S_{48}$

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Abstract

The crystal structure of Ag-excess fizélyite from the Van Silver mine, just north of Squamish, British Columbia, Canada, was studied on the basis of X-ray-diffraction data collected from an untwinned single crystal. The structure was refined to R_1 = 0.041 in space group $P2_1/n$, with unit-cell parameters a 19.2767(6), b 13.2345(4), c 8.7230(3) Å, β 90.401(2)°, and V 2225.3(1) Å^3. The chemical composition of the sample, determined by electron-microprobe analysis, is $Ag_{5.94}Pb_{13.74}Sb_{20.84}S_{48}$, which reveals nearly one more Ag atom per formula unit than in the ideal composition, $Ag_5Pb_{14}Sb_{21}S_{48}$, presently proposed by the IMA for fizélyite. Except for an additional partially occupied Ag site (Ag2) and two split cation sites (Ag1 and $M2$) in our sample, fizélyite is isostructural with ramdohrite, $CdAg_{5.5}Pb_{12}Sb_{21.5}S_{48}$. The structure of fizélyite contains chains of edge-sharing SbS_6 octahedra connected by chains of alternating $M1S_6$ ($M1$ = Pb + Sb) and SbS_6 octahedra, forming slabs parallel to (100). The slabs of octahedra are linked by distorted AgS_4 tetrahedra, $M2S_6$ octahedra, and PbS_8 polyhedra. The excess Ag in our fizélyite is mostly situated at the Ag2 site, and is likely responsible for the splitting of the Ag1 and $M2$ sites.

Keywords: fizélyite, ramdohrite, andorite, sulfosalt, crystal structure, single-crystal X-ray diffraction, Ag excess.

Sommaire

Nous avons étudié la structure cristalline de la fizélyite contenant un excédent de Ag par diffraction X sur monocristal; l'échantillon non maclé provient de la mine d'argent Van, au nord de Squamish, en Colombie-Britannique, Canada. L'affinement a atteint un résidu R_1 de 0.041 dans le groupe spatial $P2_1/n$, et les paramètres réticulaires sont: a 19.2767(6), b 13.2345(4), c 8.7230(3) Å, β 90.401(2)°, et V 2225.3(1) Å^3. La composition chimique de l'échantillon, déterminée par analyse avec une microsonde électronique, est $Ag_{5.94}Pb_{13.74}Sb_{20.84}S_{48}$, ce qui révèle un excédent de presque un atome de Ag par rapport à la composition idéale, $Ag_5Pb_{14}Sb_{21}S_{48}$, présentement adoptée par l'IMA. Mis à part le site Ag2 à occupation partielle et deux sites dédoublés (Ag1 et $M2$) dans notre échantillon, la fizélyite serait isostructurale avec la ramdohrite, $CdAg_{5.5}Pb_{12}Sb_{21.5}S_{48}$. La structure contient des chaînes d'octaèdres SbS_6 à arêtes partagées, connectées par des octaèdres $M1S_6$ ($M1$ = Pb + Sb) et SbS_6 en alternance, pour former des dalles parallèles à (100). Ces dalles d'octaèdres sont interliées par des tétraèdres AgS_4 difformes, des octaèdres $M2S_6$, et des polyèdres PbS_8. L'excédent en Ag dans notre échantillon est surtout sur le site Ag2, et serait responsable pour le dédoublement des sites Ag1 et $M2$.

(Traduit par la Rédaction)

Mots-clés: fizélyite, ramdohrite, andorite, sulfosel, structure cristalline, diffraction X sur monocristal, excédent de Ag.

Introduction

Fizélyite, ideally defined as having the stoichiometry $Ag_5Pb_{14}Sb_{21}S_{48}$ by the International Mineralogical Association (IMA), is a member of the lillianite group of Pb–Ag–Sb–Bi sulfosalts and can be classified as a member of the Sb-rich andorite subgroup, which has a general chemical formula $Ag_xPb_{3-2x}Sb_{2+x}S_6$ (Moëlo *et al.* 2008). The classification of member minerals within the andorite subgroup can be indicated by the percentage of the andorite component And_m, where m = 100x (Moëlo *et al.* 2008). In addition to fizélyite ($And_{62.5}$), there are five other structurally related minerals with either orthorhombic or monoclinic (pseudo-orthorhombic) symmetry in the andorite subgroup, including andorite VI, $AgPbSb_3S_6$ (And_{100}), andorite IV, $Ag_{15}Pb_{18}Sb_{47}S_{96}$ ($And_{93.75}$), ramdohrite, $CdAg_{5.5}Pb_{12}Sb_{21.5}S_{48}$ ($And_{68.75}$), uchucchacuaite, $MnAgPb_3Sb_5S_{12}$ (And_{50}), and roshchinite, $(Ag,Cu)_{19}Pb_{10}Sb_{51}S_{96}$ ($And_{118.75}$). Depending on chemical composition, the c dimension of minerals in

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the andorite subgroup varies by an integral number: $c = (4.36 \times n)$ Å, where $n = 2$, 4, or 6. In fizélyite and ramdohrite (Mackovicky & Mumme 1983), n is equal to 2, whereas n is equal to 4 in andorite IV (Moëlo *et al.* 1984) and roshchinite (Spiridov *et al.* 1990), and equal to 6 in andorite VI (Sawada *et al.* 1987).

Fizélyite was formally described by Krenner & Loczka (1923). Its physical and chemical properties were investigated by Nuffield (1945), Williams (1968), Kašpar *et al.* (1983), and Weiner & Hochleitner (1984), and its ideal chemical formula was redefined by Moëlo *et al.* (1984). A subcell ($c' = c/2$ with the A-centered lattice) structural model of fizélyite was proposed by Hellner (1958). From single-crystal X-ray photographs, Moëlo *et al.* (1984) noted that whereas the intensities of the X-ray reflections of the fizélyite subcell are nearly identical to those of the ramdohrite subcell, the intensities of reflections of the true primitive lattice ($P2_1/n$) differ from the corresponding ones of $P2_1/n$ ramdohrite. The unit-cell parameters reported by Moëlo *et al.* (1984) for fizélyite are a 13.21, b 19.27, c 8.68 Å, and $\alpha = 90.4°$ (non-standard setting). Previous examination of fizélyite and the structurally related ramdohrite revealed that both minerals are ubiquitously twinned on the (100) plane (Kašpar *et al.* 1983, Makovicky & Mumme 1983, Moëlo *et al.* 1984). The twinning has so far prevented satisfactory solutions of their structures. For instance, an investigation of the ramdohrite structure based on a twinned crystal yielded an R value of ~20% (Makovicky & Mumme 1983). No detailed structural study has been reported for fizélyite thus far. In this study, we describe the structure of fizélyite structure determined using single-crystal X-ray-diffraction data collected from an untwinned crystal.

EXPERIMENTAL

The fizélyite crystal used in this study comes from the Van Silver mine, just north of Squamish, British Columbia, Canada (Woodside *et al.* 2000) and was kindly supplied by Ty Balacko (RRUFF project collection, R060175; http://rruff.info). Its composition was established with a Cameca SX50 electron microprobe run at an accelerating potential of 15 kV and a beam current of 20 nA. Standards include chalcopyrite, galena, Ag metal, and Sb metal. Online reduction of raw data was done using the ZAF matrix correction. The resultant chemical formula, calculated from the average composition of 12 analysis points (Table 1), is $Ag_{5.94}Pb_{13.74}Sb_{20.87}S_{48}$.

On the basis of an optical examination and peak profiles, a nearly equi-dimensional crystal (0.05 × 0.05 × 0.04 mm) was selected and mounted on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized Mo$K\alpha$ radiation. The X-ray-diffraction data were collected with frame widths of 0.5° in ω and 30 s counting time per frame. The unit-cell refinement, data reduction, and multi-scan absorption correction were performed with the SAINT software (Bruker 2005). All reflections with $I > 2\sigma(I)$ were indexed on the basis of a monoclinic unit-cell (Table 2). It should be pointed out that we decided to choose a unit-cell setting that is different from the one previously reported (*e.g.*, Moëlo *et al.* 1984) to maintain consistency with the ramdohrite structure (Makovicky & Mumme 1983). No satellite or superlattice reflections were observed. Observed systematic absences of reflections suggest the unique space-group $P2_1/n$. The structure was solved and refined using the program SHELX97 (Sheldrick 2008; see Table 2 for additional experimental details). Our fizélyite is isostructural with ramdohrite (Makovicky & Mumme 1983), except for (1) the presence of an additional Ag2 site, and (2) the splitting of the $M2$ site into $M2$ and $M2$' and the Ag1 site into Ag1 and Ag1' (Table 3). A preliminary refinement revealed that these five sites ($M2$, $M2$', Ag1, Ag1', and Ag2) are all partially occupied, with $M2$ occupied by (Pb + Sb) and the other four sites occupied by Ag. By assuming that the splitting of the $M2$ and Ag1 sites is due partly or completely to the presence of Ag at the Ag2 site (see the discussion below), we subsequently attempted to refine the structure in two slightly different ways while constraining the chemical composition of the crystal to that determined from the electron-microprobe data. In model A, the occupancies of five partially occupied sites were refined independently, yielding [0.556(2) Pb + 0.095(2) Sb], 0.330(3) Ag, 0.75(4) Ag, 0.19(4) Ag, and 0.209(3) Ag for $M2$, $M2$', Ag1, Ag1', and Ag2,

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF A FIZÉLYITE CRYSTAL

Spots	1	2	3	4	5	6	7	8	9	10	11	12	Ave.	StDev
Pb wt.%	37.60	37.85	37.74	36.97	37.97	37.35	37.18	37.20	37.18	37.17	37.27	36.90	37.37	0.35
Sb	33.60	32.89	32.88	33.78	33.07	33.29	33.71	33.64	33.61	33.43	33.77	33.64	33.44	0.33
S	20.60	20.34	20.19	20.13	20.25	20.19	20.33	20.08	20.10	20.09	20.03	20.09	20.20	0.16
Ag	8.28	8.56	8.59	8.36	8.25	8.39	8.44	8.20	8.34	8.43	8.53	8.63	8.42	0.14
Total	100.08	99.64	99.40	99.24	99.54	99.22	99.66	99.12	99.23	99.12	99.60	99.26	99.43	0.29

Chemical formula calculated based on 48 S: $Ag_{5.94}Pb_{13.74}Sb_{20.86}S_{48}$.

respectively. In model *B*, only the site occupancies of *M*2 and Ag1 were allowed to vary freely, whereas the Ag contents in *M*2', Ag1', and Ag2 are constrained to be equal. The resultant occupancies are [0.586(2) Pb + 0.065(2) Sb] for *M*2, 0.694(3) Ag for Ag1, and 0.263(1) Ag for *M*2', Ag1', and Ag2. For reasons discussed below, model *A* was adopted in this paper. No significant twin components were detected during the refinement. All atoms were refined with anisotropic displacements. Final refined coordinates and displacement parameters of the atoms are listed in Table 3, and selected bond-lengths are shown in Table 4. A table of structure factors is available from the Depository of Unpublished Data on the MAC website [document Fizélyite CM47_1257].

TABLE 2. SUMMARY OF CRYSTAL DATA AND REFINEMENT RESULTS FOR Ag-EXCESS FIZÉLYITE

Ideal chemical formula				$Ag_5Pb_{14}Sb_{21}S_{48}$	
Empirical chemical formula				$Ag_{5.94}Pb_{13.74}Sb_{20.87}S_{48}$	
Space group				$P2_1/n$ (no. 14)	
Unit-cell parameters					
a (Å)	19.2767(6)	*b* (Å)	13.2345(4)	*c* (Å)	8.7230(3)
β (°)	90.401(2)	*V* (Å^3)	2225.3(1)	*Z*	1
ρ_{calc} (g/cm^3)	5.644	λ (Å)	0.71069	μ (mm^{-1})	34.49
θ range for data collection				1.87 to 29.57	
Number of reflections collected				31150	
Number of independent reflections				6237	
Number of reflections with I > 2σ(I)				4272	
Number of parameters refined				236	
R(int)				0.068	
Final R factors [I > 2σ(I)]				R_1 = 0.041, wR_2 = 0.076	
Final R factors (all data)				R_1 = 0.068, wR_2 = 0.084	
Goodness-of-fit				1.064	

RESULTS AND DISCUSSION

Chemical composition

Compared to the ideal chemical formula adopted by the IMA for fizélyite, $Ag_5Pb_{14}Sb_{21}S_{48}$ (Moëlo *et al.* 1984, 2008), our sample apparently contains excess Ag (5.94 Ag atoms per formula unit), though its Pb and Sb contents are very close to the ideal values. In fact, the Ag content of our sample is even significantly higher than that for ramdohrite, which has an ideal value of 5.5 Ag *apfu*. This raises an interesting question regarding the classification of our sample: is it fizélyite or ramdohrite, ($CdAg_{5.5}Pb_{12}Sb_{21.5}S_{48}$)? Fizélyite and ramdohrite exhibit the same symmetry ($P2_1/n$) and comparable unit-cell dimensions [*a* 19.24, *b* 13.08, *c* 8.73 Å, β 90.28° for ramdohrite (Makovicky & Mumme 1983) *versus a* 19.27, *b* 13.21, *c* 8.68 Å, β 90.40° for fizélyite (Moëlo *et al.* 1984)], but they appear to have distinct chemical compositions. According to Moëlo *et al.* (1989), ramdohrite from the type locality (Potosí,

TABLE 3. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN FIZÉLYITE

Atom	Atom in Rdr*	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq} (Å^2)
Pb1	*Me*8 Pb	0.25336(3)	0.90335(4)	0.39489(6)	0.0336(3)	0.0338(3)	0.0292(3)	-0.0029(2)	0.0020(2)	-0.0077(2)	0.0322(1)
Pb2	*Me*3 Pb	0.25021(3)	0.91738(4)	-0.09877(6)	0.0332(3)	0.0274(3)	0.0340(3)	0.0020(2)	-0.0036(2)	-0.0022(2)	0.0316(1)
*M*1	*Me*5 Pb	0.04887(3)	0.88423(4)	0.63069(6)	0.0245(3)	0.0261(3)	0.0241(3)	-0.0008(2)	-0.0015(2)	0.0011(2)	0.0249(1)
*M*2	*Me*9 Pb+Ag	0.12809(7)	0.1488(1)	0.1164(1)	0.0248(5)	0.0188(5)	0.0275(5)	0.0000(4)	0.0021(4)	0.0005(4)	0.0237(2)
*M*2'		0.1180(5)	0.1501(5)	0.055(1)	0.106(6)	0.021(3)	0.167(9)	0.015(5)	0.038(6)	-0.009(3)	0.098(3)
Sb1	*Me*1 Sb	0.34866(4)	0.12667(6)	0.64208(9)	0.0255(4)	0.0215(4)	0.0200(4)	0.0007(3)	-0.0013(3)	0.0026(3)	0.0224(2)
Sb2	*Me*2 Sb	0.44284(4)	0.88187(6)	0.62540(9)	0.0187(4)	0.0210(4)	0.0270(4)	0.0009(3)	-0.0036(3)	0.0000(3)	0.0222(2)
Sb3	*Me*6 Sb	0.12784(4)	0.64666(6)	0.38066(9)	0.0221(4)	0.0201(4)	0.0227(4)	0.0002(3)	0.0000(3)	-0.0002(3)	0.0216(2)
Sb4	*Me*7 Sb	-0.05363(4)	0.63074(6)	0.63687(9)	0.0218(4)	0.0243(4)	0.0220(4)	-0.0015(3)	-0.0015(3)	-0.0011(3)	0.0227(2)
Sb5	*Me*10 Sb	0.05207(4)	0.87500(6)	0.14416(9)	0.0202(4)	0.0222(4)	0.0225(4)	0.0014(3)	0.0002(3)	-0.0033(3)	0.0216(2)
Ag1	*Me*4 Ag	0.1437(4)	0.1799(4)	-0.3927(13)	0.038(2)	0.051(2)	0.051(2)	0.010(2)	-0.002(2)	0.022(1)	0.046(1)
Ag1'		0.1334(9)	0.1690(16)	-0.347(4)	0.017(4)	0.024(6)	0.043(9)	-0.012(4)	-0.002(4)	0.010(3)	0.028(5)
Ag2		0.1733(3)	0.1154(4)	0.3388(7)	0.033(3)	0.022(3)	0.067(4)	-0.015(2)	0.027(3)	-0.011(2)	0.040(2)
S1	S1	0.3946(2)	0.0041(2)	-0.1648(3)	0.026(2)	0.024(2)	0.018(1)	0.000(1)	-0.001(1)	0.001(1)	0.0230(6)
S2	S2	-0.0003(2)	0.7256(3)	0.8477(4)	0.033(2)	0.041(2)	0.023(2)	-0.005(1)	0.000(1)	-0.011(2)	0.0322(8)
S3	S3	0.2305(2)	0.0465(2)	-0.3553(3)	0.022(2)	0.023(2)	0.027(2)	-0.001(1)	-0.003(1)	0.005(1)	0.0229(6)
S4	S4	0.3364(2)	0.7851(2)	0.6266(3)	0.023(2)	0.024(2)	0.025(2)	0.004(1)	-0.001(1)	-0.004(1)	0.0241(6)
S5	S5	0.0996(2)	0.9692(3)	0.9308(4)	0.028(2)	0.037(2)	0.026(2)	0.006(1)	-0.003(1)	-0.010(1)	0.0302(7)
S6	S6	0.1661(2)	0.7576(2)	0.5875(3)	0.021(2)	0.024(2)	0.023(1)	0.000(1)	0.002(1)	-0.002(1)	0.0226(6)
S7	S7	0.3973(2)	0.0031(2)	0.4333(3)	0.026(2)	0.024(2)	0.018(1)	0.002(1)	0.000(1)	-0.001(1)	0.0224(6)
S8	S8	-0.0200(2)	0.7515(2)	0.4316(3)	0.021(2)	0.034(2)	0.020(1)	0.002(1)	0.000(1)	0.000(1)	0.0252(7)
S9	S9	0.2586(2)	0.0602(2)	0.1372(4)	0.024(2)	0.022(2)	0.031(2)	0.000(1)	0.003(1)	-0.005(1)	0.0255(7)
S10	S10	-0.1686(2)	0.7059(3)	0.6486(4)	0.017(1)	0.034(2)	0.028(2)	0.004(1)	0.001(1)	-0.002(1)	0.0264(7)
S11	S11	0.0870(2)	0.9905(2)	0.3488(4)	0.038(2)	0.026(2)	0.024(2)	-0.004(1)	-0.001(1)	-0.001(1)	0.0293(7)
S12	S12	0.1577(2)	0.7673(2)	0.1685(3)	0.025(2)	0.025(2)	0.022(1)	0.002(1)	0.000(1)	-0.001(1)	0.0237(6)

* Rdr: ramdohrite; see Makovicky & Mumme (1983). Note: Site occupancies are [0.880(2) Pb + 0.120(2) Sb] for *M*1, [0.556(2) Pb + 0.095(2) Sb] for *M*2, 0.330(3) Ag for *M*2', 0.75(4) Ag for Ag1, 0.19(4) Ag for Ag1', and 0.209(3) Ag for Ag2.

Bolivia) contains a significant amount of Cd, whereas fizélyite from the type locality (Kisbanya, Romania), shows exsolution-induced domains of a (Mn,Fe)-rich variety of ramdohrite. For the following reasons, we have chosen to categorize our sample as fizélyite in this study: (1) its crystal structure, if compared to that of ramdohrite (Makovicky & Mumme 1983), contains an extra cation site (Ag2) to account for excess Ag (see below); (2) if the additional Ag2 site in our sample is excluded (discussed below), then we have $x = 0.6465$ or $\text{And}_{64.65}$, which corresponds more closely to the value of $x = 0.625$ for ideal fizélyite, rather than to the ideal value of $x = 0.6875$ for ramdohrite; (3) the Pb content in our sample (13.74 *apfu*) is also rather close to that (14 *apfu*) for ideal fizélyite, but markedly greater than that (12 *apfu*) for ideal ramdohrite.

Crystal structure

Fizélyite is isotypic with ramdohrite (Makovicky & Mumme 1983), except for the additional Ag2 site and the splitting of the *M*2 and Ag1 sites (Table 3). For comparison, we list in Table 3 the corresponding atomic sites for ramdohrite as given by Makovicky & Mumme (1983). The structure of fizélyite contains 25 symmetrically nonequivalent atomic sites, 12 occupied by S, two by Pb, five by Sb, four by Ag, and two (*M*1 and *M*2) that are mixed, with (Pb + Sb). The five sites that exclusively contain Sb are all in distorted octahedral coordination, with each formed by three short and three long Sb–S bonds (Table 4). Among these five SbS_6 octahedra, four (Sb1, Sb2, Sb3, and Sb4) share edges with one another to form chains (designated as the A chain for simplicity hereafter, Fig. 1, outline A) extending along the *c* axis, whereas the Sb5 octahedra alternate, by sharing edges, with the *M*1 octahedra to form another type of chain (designated as the B chain, Fig. 1, outline B) running parallel to the *c* axis. Note that the *M*1 site in ramdohrite is solely occupied by Pb. The A and B chains are linked together through shared edges and corners to form slabs parallel to (100) (Fig. 1). Bond-valence sums calculated for Sb1, Sb2, Sb3, Sb4, and Sb5 from parameters given by Brese & O'Keeffe (1991) are 3.20, 3.21, 2.85, 3.03, and 3.15 valence units (*vu*), respectively, if six bonds are considered, and 2.99, 2.95, 2.35, 2.65, and 2.79 *vu* if only the three shortest bonds are taken into account. These results suggest that the three short Sb–S bonds contain most of the valence-electron density, characteristic of the SbS_3 trigonal–pyramidal configuration. The three longer Sb–S bonds within each SbS_6 octahedron are primarily due to the presence of lone pairs of electrons, resulting in so-called "lone-electron-pair micelles" (Makovicky & Mumme 1983, Makovicky 1997), as indicated in Figure 2.

TABLE 4. SELECTED BOND-LENGTHS (Å) IN FIZÉLYITE

Pb1		Pb2		*M*1		*M*2	
S3	2.923(3)	S9	2.798(3)	S8	2.799(3)	S9	2.780(3)
S10	3.002(3)	S3	2.839(3)	S6	2.840(3)	S4	2.869(3)
S4	3.009(3)	S5	2.996(4)	S11	2.931(3)	S10	2.914(3)
S9	3.061(3)	S1	3.070(3)	S2	2.986(3)	S5	2.926(3)
S6	3.068(3)	S10	3.118(3)	S5	3.007(3)	S2	2.990(4)
S7	3.088(3)	S4	3.409(4)	S11'	3.106(4)	S11	3.025(4)
S12	3.239(3)	S6	3.812(4)	<*M*1–S>	2.945	<*M*2–S>	2.917
S11	3.429(3)	S12	3.553(4)				
<Pb1–S>	3.103	<Pb2–S>	3.199				

Sb1		Sb2		Sb3		Sb4		Sb5	
S1	2.496(3)	S4	2.418(3)	S6	2.437(3)	S10	2.432(3)	S5	2.425(3)
S3	2.514(3)	S7	2.477(3)	S9	2.477(3)	S2	2.447(3)	S11	2.441(3)
S7	2.626(3)	S1	2.618(3)	S12	2.514(3)	S8	2.489(3)	S12	2.493(3)
S6	2.942(3)	S2	3.021(3)	S1	3.147(3)	S7	3.279(3)	S8	3.308(3)
S2	3.204(3)	S8	3.277(3)	S8	3.203(3)	S1	3.327(3)	S2	3.403(3)
S12	3.288(3)	S7'	3.479(3)	S7	3.365(3)	S1'	3.500(3)	S5'	3.634(3)
<Sb1–S>	2.845	<Sb2–S>	2.882	<Sb3–S>	2.857	<Sb4–S>	2.912	<Sb5–S>	2.951

Ag1		Ag1'		*M*2'		Ag2	
S3	2.452(6)	S3	2.48(2)	S4	2.546(8)	S11	2.348(6)
S8	2.573(7)	S8	2.53(2)	S5	2.649(8)	S10	2.369(6)
S4	2.732(8)	S4	2.52(2)	S2	2.934(9)	S9	2.524(6)
S10	2.741(12)	S10	3.19(3)	S9	3.042(9)	S3	3.021(7)
<Ag1–S>	2.624	<Ag1–S>	2.68	<Ag2–S>	2.793	<Ag3–S>	2.565

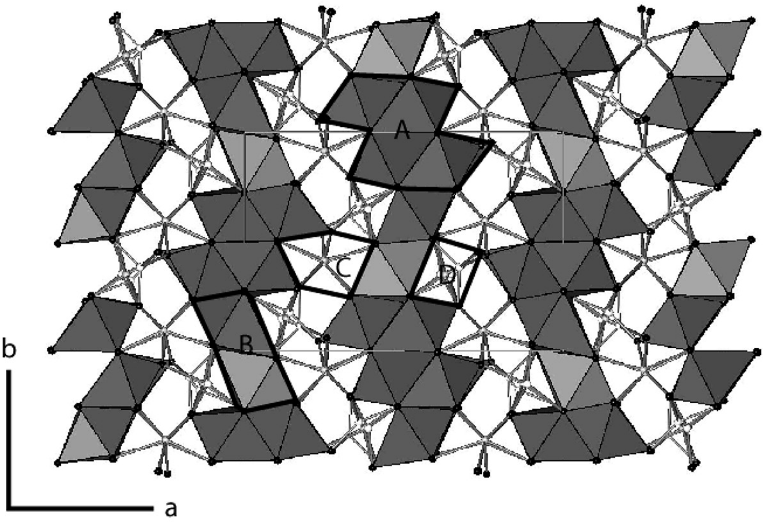


FIG. 1. Representation of chains of polyhedra extending along the *c* axis in fizélyite. Outline A: chains of edge-shared SbS_6 octahedra; outline B: alternating chains of Sb5 and *M*2 octahedra; outline C: chains of PbS_8 polyhedra, and outline D: location of Ag tetrahedra.

The lone-electron-pair micelles are a distinctive feature in many sulfosalts containing As, Sb, and Bi atoms, and their sizes may vary significantly (see review by Makovicky 1997). There are two sorts of micelles in fizélyite, as also found in ramdohrite (Makovicky & Mumme 1983). The larger micelles, confined within the A chain, contain four lone pairs of electrons similar to those in lillianite (Takagi & Takéuchi 1972), whereas the smaller micelles within the B chain contain two lone pairs of electrons and resemble those in andorite IV (Kawada & Hellner 1971). The two kinds of micelles alternate *en échelon* along the *c* axis within the slabs of octahedra.

Sandwiched between the slabs of octahedra are four nonequivalent Ag sites (Ag1, Ag1', Ag2, and *M*2'), two 8-coordinated Pb sites (Pb1 and Pb2), and an octahedrally coordinated *M*2 site. The weak bonds holding the slabs of octahedra together explain the good (100) cleavage in this mineral (see Anthony *et al*. 1990). An outstanding structural feature of our fizélyite, if compared to the structure of ramdohrite (Makovicky & Mumme 1983), is the presence of the Ag2 site and the splitting of the Ag1 and *M*2 sites. The corresponding Ag1 and *M*2 sites in the ramdohrite structure are not split, and the Ag2 position is unoccupied (Makovicky & Mumme 1983). The distance between the Ag1 and Ag1' sites in our sample is 0.473 Å, and that between *M*2 and *M*2' is 0.572 Å. Another notable structural feature of our sample is the occupancy and content of the *M*2 site which, together with the *M*2' site, has a total refined occupancy of 0.99 (0.56 Pb + 0.10 Sb + 0.33 Ag). In contrast, the corresponding site in ramdohrite contains (0.50 Sb + 0.50 Ag) and a mixed occupancy of (0.50 Pb + 0.25 Sb + 0.25 Ag) in ideal fizélyite (Makovicky & Mumme 1983).

Similar to the two Pb sites in ramdohrite, the $Pb1S_8$ and $Pb2S_8$ polyhedra in fizélyite share their trigonal faces and alternate along the *c* axis, forming chains of PbS_8 polyhedra. The individual Pb–S interatomic distances within the Pb1 and Pb2 polyhedra vary appreciably, from 2.798 to 3.812 Å (Table 4). All four nonequivalent Ag sites are in characteristic, irregular tetrahedral coordination, with the average Ag1–S, Ag1'–S, Ag2–S, and *M*2'–S bond lengths being 2.624, 2.680, 2.565, and 2.793 Å, respectively. These Ag tetrahedra also form chains extending along *c* through shared corners and edges. It is these chains of polyhedra (the A, B, PbS_8, and AgS_4 chains) in the fizélyite structure that determine its morphology, which is usually elongate along the *c* axis (see http://rruff.info/fizélyite).

Compared to the ramdohrite structure, the Ag2 site in our sample is an additional one (Fig. 3), with a site occupancy of 0.209(3) Ag, which corresponds to 0.836 Ag *apfu*. Because this number is close to the excess Ag amount determined by electron-microprobe analysis (0.94 Ag *apfu*), we propose that the excess Ag in our sample is principally concentrated at the Ag2 site. Given the short distances between Ag2 and Ag1 (2.561 Å) and that between Ag2 and *M*2 (2.167 Å), we therefore attribute the site splitting of Ag1 (into Ag1 and Ag1') and *M*2 (into *M*2 and *M*2') to the presence of the Ag2 site so as to minimize the cation–cation repulsion. The resultant distance between Ag2 and Ag1' is 2.943 Å, and that between Ag2 and *M*2' is 2.731 Å. The similar amounts of Ag in the Ag2 and Ag1' sites [0.209(3) *versus* 0.19(4)] may lend support to our inference. Nonetheless, owing to the size and charge differences between Ag^+ and ($Pb^{2+} + Sb^{3+}$), the splitting of *M*2 into the *M*2 and *M*2' sites in fizélyite may also be further enhanced by the fact that Ag can achieve a better environment for bonding in a four-coordinated *M*2' site than a six-coordinated *M*2 site. This may explain why the amount of Ag at the *M*2' site (0.330) is slightly greater than that in Ag2. Without detailed structural data for fizélyite without excess Ag and high-quality data for ramdohrite for comparison, it is difficult for us to rule out the possibility that the splitting of the *M*2 site might exist even without excess Ag. On the basis of the above discussion, we present a structural formula for our fizélyite as follows: $^{Ag2}(Ag_{0.21})\ ^{(Ag1+Ag1')}Ag\ ^{(M2+M2')}(Ag_{0.33}Pb_{0.57}Sb_{0.10})\ ^{M1}(Pb_{0.88}Sb_{0.12})Pb_2Sb_5S_{12}$.

For ideal fizélyite, the Ag2 site should be unoccupied, and the occupancy at (*M*2 + *M*2') and *M*1 should change accordingly to maintain charge neutrality. Moreover, the above structural formula should be compared to that given by Makovicky & Mumme (1983) for ramdohrite: $^{Ag1}Ag\ ^{M2}(Sb_{0.5}Ag_{0.5})Pb_3Sb_5S_{12}$. However, as ramdohrite from the type locality invariably contains a significant amount of Cd with the IMA-defined chemical formula $CdAg_{5.5}Pb_{12}Sb_{21.5}S_{48}$ (Moëlo *et al.* 1989, 2008), we can suggest the following structural formula for ideal ramdohrite: $^{Ag1}Ag\ ^{M2}(Sb_{0.375}Ag_{0.375}Cd_{0.25})Pb_3Sb_5S_{12}$. It appears, therefore, that it is the makeup of the *M*2 (or *M*2 + *M*2') site that defines the chemical and structural difference between fizélyite and ramdohrite. It, then, begs the question: is ramdohrite a Cd-rich variety of

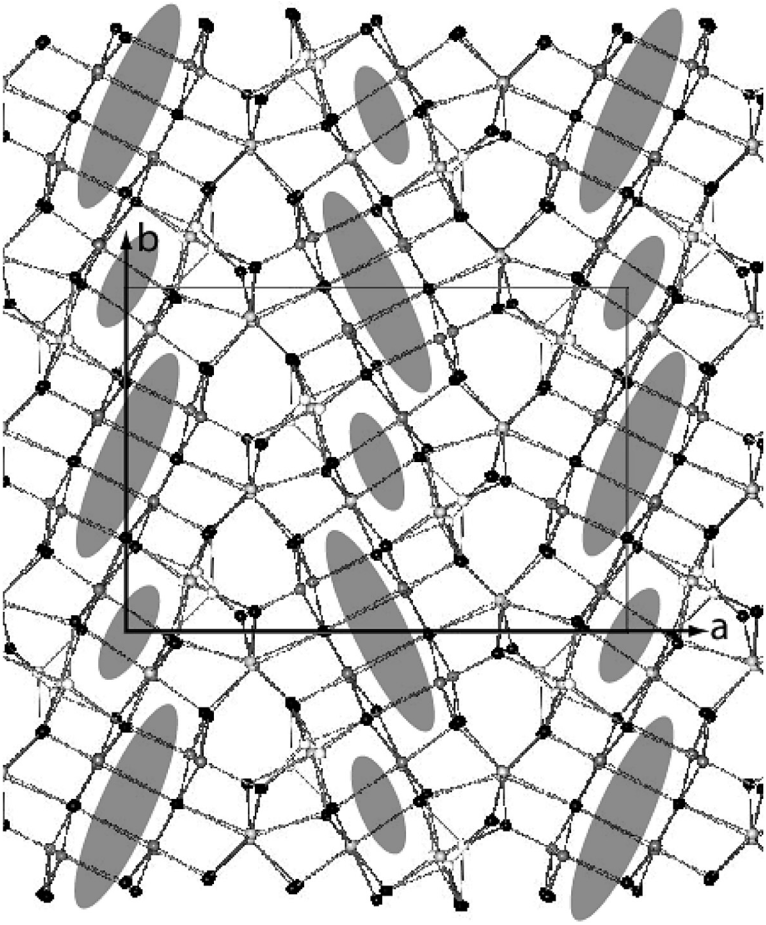
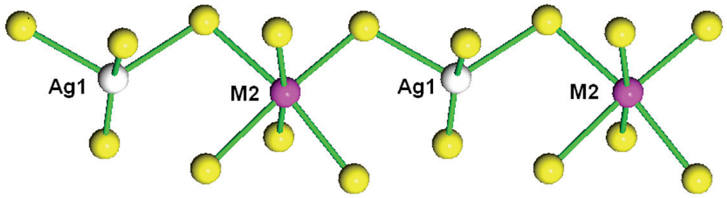
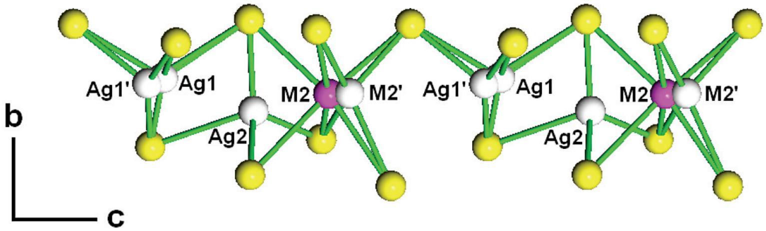


FIG. 2. View of fizélyite down [001] with alternating large and small lone-electron-pair micelles, which are located within the A and B chains, respectively.



(a) Ideal fizelyite or ramdohrite



(b) Ag-excess fizelyite

FIG. 3. Comparison of a portion of the structures. (a) Ideal fizélyite with the *M*2 site occupied fully by 50% Pb + 25% Sb + 25% Ag; (b) Ag-excess fizélyite containing five partially occupied cation sites: Ag1, Ag1', Ag2, *M*2 and *M*2'.

fizélyite (Moëlo *et al*. 2008)? Evidently, more detailed analyses of the structure of ramdohrite and fizélyite from the type localities are needed to establish the real distinction between these two minerals.

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