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FERDOWSIITE: A NEW MINERAL FROM THE BARIKA ORE DEPOSIT, IRAN

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Abstract

Ferdowsiite is a member of a mineral association subsidiary to the principal metamorphic minerals of the Barika ore deposit in NW Iran. The empirical formula of ferdowsiite (based on 32 *apfu*, 16Me + 16S) is $Ag_{7.97}Pb_{0.08}\,Sb_{4.75}As_{3.15}Bi_{0.01}S_{16.04.}$ The crystal-structure formula is $Ag_8(Sb_{5.49}As_{2.51})_{\Sigma 8}S_{16}$; the simplified formula is $Ag_8(Sb_5As_3)_{\Sigma 8}S_{16}$. The slightly plumbian variety of ferdowsiite has the idealized formula $Pb_{2x}Ag_{4-x}Sb_{3-x}AsS_8$ with x =~0.2. Ferdowsiite is monoclinic, space group $P2_1/n$, *a* 8.677(2) Å, *b* 5.799(1) Å, *c* 13.839(3) Å, β 96.175(4)° , *V* 692.28(10) Å^3, *Z* = 1 for the formula $Ag_8(Sb_5As_3)_{\Sigma 8}S_{16}$. Calculated powder X-ray data are listed; main diffraction lines are [d_{calc} (I_{rel}) (*hkl*)]: 3.225 (96)(113); 3.205 (100)($\bar{2}$12); 2.8995 (78)(020); 2.7559 (90)(301); 2.7073 (79)($\bar{1}$05); 1.9401 (22)(206); 1.9226 (22)($\bar{4}$04). Plumbian ferdowsiite has the same space group, $P2_1/n$. It has *a* 8.746(7) Å, *b* 5.805(4) Å, *c* 13.929(10) Å, β 96.236(11)°, unit cell volume 703.05 Å^3. The mineral is greyish black, opaque, with dark grey streak and metallic luster. It is brittle with irregular fracture; no cleavage or parting was observed. Calculated density is 5.3 g/cm^3. In reflected light ferdowsiite is greyish white. Internal reflections are not observable. Pleochroism is distinct, white to grey. Bireflectance is distinct; reflectance values are [λ(nm), R_{min},R_{max}]: 470, 34.9, 37.3; 546, 33.4, 35.9; 589, 32.4, 35.1; 650, 30.7, 33.5. Anisotropism is distinct and rotation tints vary between dark brown and bluish grey. Ferdowsiite is associated with large corroded crystals of arsenquatrandorite and is partly replaced by guettardite. It also corrodes smithite. Ferdowsiite is often associated with tetrahedrite/tennantite and forms worm-like symplectites with it. This symplectite is partly replaced on the surface by guettardite. Ferdowsiite is one more member of the group of ABX_2-type sulfosalts of silver, combining antimony and arsenic, with a crystal structure different from other members of this group. The closest crystallographic and structural affinity is to the ternary sulfosalt diaphorite.

Introduction

The A_3BX_3 and ABX_2 type sulfosalts of silver, which combine antimony and arsenic (eventually also with bismuth) and display frequent cases of dimorphism, attracted the attention of classical mineralogists. The prominent dimorphic pairs (Strunz & Nickel 2001) are: proustite (defined by Beudant in 1832) – xanthoconite (Breithaupt in 1840), pyrargyrite (by Glocker in 1831) – pyrostilpnite (by Dana in 1868), as well as trechmannite (described by Solly in 1904) – smithite (by the same author in 1905). Miargyrite was described by Rose in

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1829, whereas the isochemical cubic cuboargyrite was redefined by Walenta (1998); matildite was recognized by D'Achiardi in 1883, whereas the controversial cubic schapbachite was relegated to a ternary system by Walenta *et al*. (2004) because it includes Pb (Moëlo *et al*. 2008). The proof that mixed-cation sulfosalts of these groups can deviate crystallographically and structurally from the simple endmembers appeared with the description of aramayoite by Spencer in 1926; this problem, complicated by the existence of baumstarkite, which is close to a pure Sb-endmember composition, was treated recently by Effenberger *et al*. (2002).

The present contribution adds one more member of this group, ferdowsiite, which is an ABX_2-type sulfosalt of silver combining antimony and arsenic, with a crystal structure different from the above quoted examples. This sulfosalt is a member of a mineral association subsidiary to the principal metamorphic minerals of the Barika ore deposit in NW Iran. This association is without economic importance but of great mineralogical interest (*e.g*., Topa *et al*. 2013a,c). In the first find, ferdowsiite was practically lead-free, but a variety with a modest lead substitution was found in the same deposit soon after the original, nearly lead-free ferdowsiite.

Mineral name and type material

The name is for one of the greatest Persian personalities, Ferdowsi Tousi (935–1020), one of the greatest Persian poets to have ever lived. His life-long endeavor to preserve the national identity, language and heritage of his homeland, especially through one of the greatest poetic masterpieces, the *Shahnameh,* won him lasting fame and honor. Ferdowsiite was approved as a new mineral by IMA, under no. 2012-062 (Topa *et al*. 2013b). The holotype specimen of ferdowsiite is deposited in the mineral collection of the Natural History Museum-Vienna, Austria, with specimen number N 9604.

Occurrence

The locality at which the new mineral occurs is the Barika gold deposit, located in the west of Iran, 17 km E of Sardasht (West Azerbaijan province). The gold mineralization district lies between latitudes 36°10 N and 36° 13 N, and between longitudes 45° 37 E and 45° 41 E. The Barika ore deposit is a gold-rich volcanogenic massive sulfide deposit of Cretaceous age, situated in the metamorphic Sanandaj-Sirjan Zone. Greenschist metamorphism and deformation in shear zones overprint the original synvolcanic stratiform mineralization (Khodaparast *et al*. 2010).

The lens-like deposit consists of massive to semi-massive banded pyrite and baryte ores, accompanied by locally developed silica bands. Pyrite, sphalerite, galena, tetrahedrite-tennantite, and stibnite were deposited during synvolcanogenic hydrothermal activity (Khodaparast *et al*. 2010). Brittle deformation fractures host veinlets that contain a number of Ag-As-Sb-Pb-rich sulfosalts (Makovicky *et al*. 2012) including tetrahedrite-tennantite, stephanite, pyrargyrite, trechmannite, smithite, miargyrite, andorite, geocronite, seligmannite, guettardite, sterryite, realgar, as well as the new minerals barikaite (Topa *et al*. 2013a) and arsenquatrandorite (Topa *et al*. 2013c), pyrite, and Au-Ag alloys. Remobilization of the components leading to these minerals, originally housed in the stratiform ores, took place at the margins of the orebody.

Associations

In the Barika deposit, ferdowsiite is involved in a number of associations. In one of them, needle-like sterryite lies among aggregates of barite. The needle-like sulfosalt is embedded in a ferdowsiite matrix which shows zoning: the higher-lead ferdowsiite matrix has polyhedrally outlined portions with lower Pb contents, oriented towards baryte. They are indistinctly zoned. Besides sterryite, the matrix contains an irregular patch of bournonite. It is possible that sterryite is partly corroded by ferdowsiite matrix.

In other ferdowsiite-containing samples, arsenquatrandorite forms large, partly corroded crystals (Fig. 1a,d). Guettardite is present everywhere that arsenquatrandorite has been corroded. Barikaite (Topa *et al*. 2013a) is present as well. Irregular replacement bodies in arsenquatrandorite contain ferdowsiite and tetrahedrite. Ferdowsiite heavily and irregularly corrodes a large crystal of smithite (Fig. 1b). All this is included in a gangue of quartz and baryte. In one sample of arsenquatrandorite, parallel linear replacement veins of ferdowsiite are observed, cut perpendicularly by Pb-containing ferdowsiite which forms irregular veins (Fig. 1c). Before these replacement processes, arsenquatrandorite underwent brecciation.

An irregular remnant of arsenquatrandorite, with the highest arsenic contents in the center, was found in an envelope of ferdowsiite, surrounded in turn by guettardite, which partly replaces ferdowsiite (Fig. 1a). Boundaries between arsenquatrandorite and guettardite are often straight, but ferdowsiite and Pb-zoned ferdowsiite have irregular boundaries with guettardite. Fahlerz (inhomogeneous and irregular in detail) partly replaces guettardite. Guettardite will eventually replace arsenquatrandorite, but ferdowsiite was often observed as imperfect crystals or a regular layer on the arsenquatrandorite surface (partly replacing it), mostly situated under guettardite, which replaces ferdowsiite as well.

In one sample, ferdowsiite forms worm-like symplectites with ferroan tetrahedrite-tennantite with the Sb:As ratio about 1:1 (Fig. 2), probably produced by replacement processes. This symplectite is replaced partly by guettardite, coarsening and half-destroying the texture of symplectite in the process. Guettardite

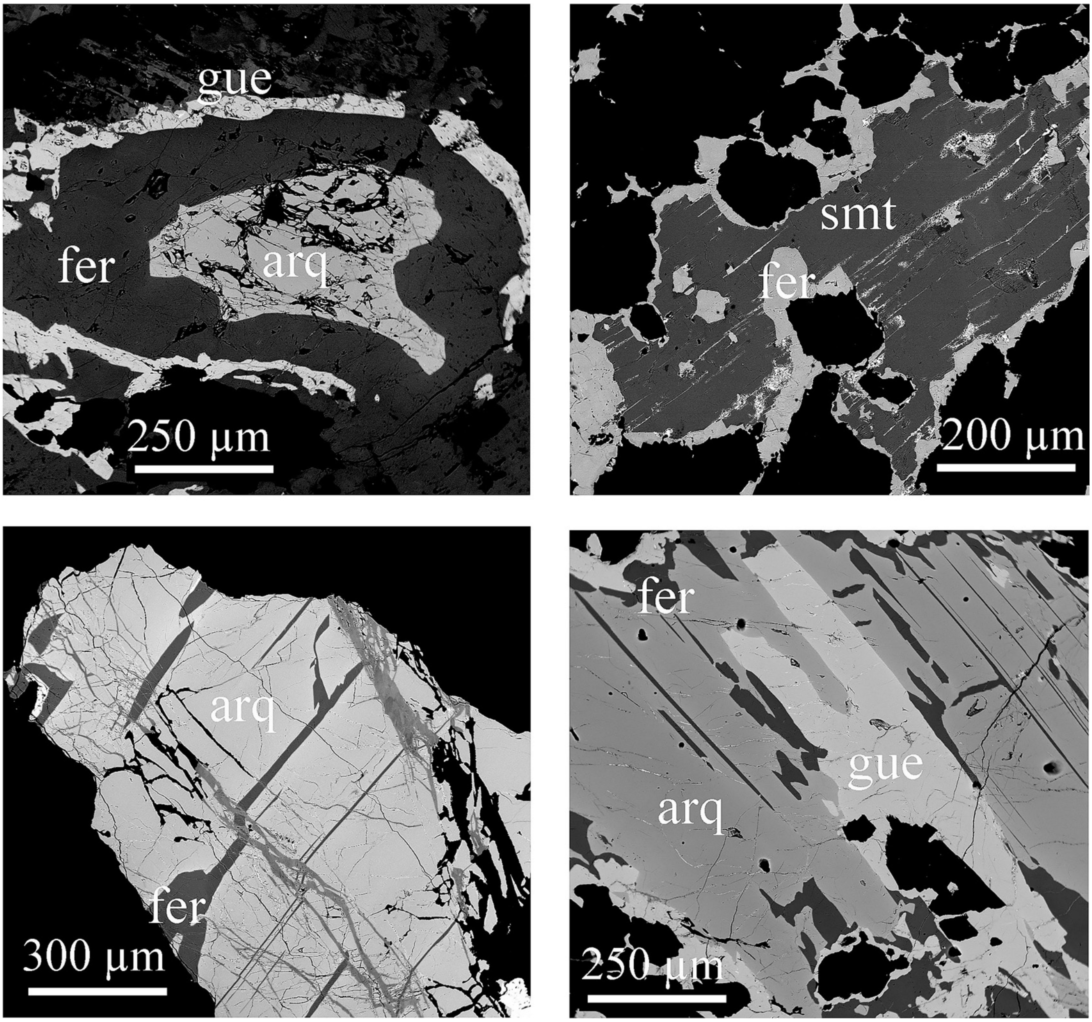

FIG. 1. (a) Irregular remnant of arsenquatrandorite (*arq,* center) surrounded and replaced by ferdowsiite (*fer*), which in turn is enveloped and partly replaced by guettardite (a thin envelope). Size of the aggregate: 2 mm. (b) A crystal of smithite (*smt*, center) replaced from the margins by ferdowsiite (*fer*). Accumulations of very fine-grained silver-rich material (white). Gangue (black) has been corroded as well. (c) A large grain of arsenquatrandorite (*arq*) with two generations of ferdowsiite (*fer*). Darker and older straight veins (or exsolution lamellae?) of Pb-free ferdowsiite are crossed by medium grey, irregular veins of later, plumbian ferdowsiite. (d) A crystal of arsenquatrandorite (*arq*) with oriented replacements and overgrowths of ferdowsiite (dark, *fer*). Later guettardite (light, *gue*) replaces arsenquatrandorite and overgrows and corrodes ferdowsiite. Black: gangue.

replaces the solid ferdowsiite surrounding these aggregates, as well. Other samples from Barika contain boulangerite replaced by geocronite. The boundary between geocronite and tetrahedrite is replaced by an interrupted layer of bournonite with symplectitic galena. Pure bournonite is developed towards tetrahedrite.

Although the available material is too limited for elucidating the deposition and replacement sequence of ore minerals, we can postulate that arsenquatrandorite and smithite are older mineral phases. They are partly or fully replaced (after some brecciation) by ferdowsiite and plumbian ferdowsiite, followed by arsenian tetrahedrite and frequent guettardite. Although disconnected in the sample set, boulangerite, geocronite, bournonite, and galena appear to belong to a later association, whereas a possible number of tetrahedrite generations remains undefined. The tetrahedrite/tennantite-ferdowsiite and galena-bournonite symplectites are most probably products of decomposition and replacement processes.

APPEARANCE AND PHYSICAL PROPERTIES

Ferdowsiite selected for the present study occurs as rare, elongated crystals in baryte. No crystal forms were observed. The maximum grain size of ferdowsiite is about 400 μm. The mineral is greyish black, opaque, with a dark grey streak and metallic luster. It is brittle with irregular fracture; neither cleavage nor parting were observed. Density could not be measured because of the paucity of available material. Calculated density is 5.3 g/cm^3 using the simplified chemical formula. Pure ferdowsiite areas were too small for indentation hardness measurements; the estimated Mohs hardness is 2½–3.

In reflected light ferdowsiite is greyish white. Internal reflections are not observable. Pleochroism is distinct, white to grey. Bireflectance is distinct, as illustrated in Table 1. Under crossed nicols, anisotropism is distinct in air, and further enhanced in oil. Rotation tints vary between dark brown and bluish grey. Reflectance values (WTiC standard in air) decrease monotonously from 400 to 700 nm. Measured difference is about 7%, ΔR is about 3% at any wavelength.

CHEMICAL COMPOSITION

Chemical analyses of ferdowsiite (10 points on one grain) were carried out using an electron microprobe apparatus (JEOL Superprobe JXA-8600, controlled by the *Probe for Windows* system of programs) in WDS mode (acceleration voltage 25 kV, sample current 20 nA, 5 μm beam diameter, on-line ZAF correction procedure). No elements with atomic number greater than 11, other than those indicated in Table 2, were detected. The empirical formula of ferdowsiite (based on 32 *apfu*, 16Me + 16S) is $Ag_{7.97}Pb_{0.08}Sb_{4.75}As_{3.15}Bi_{0.01}S_{16.04}$, or $Ag_{8.01}(Sb_{4.79}As_{3.15}Bi_{0.01})_{\Sigma 7.95}S_{16.04}$ after correction for the 2Pb-for-Ag+Sb substitution. The crystal-structure formula is $Ag_8(Sb_{5.49}As_{2.51})_{\Sigma 8}S_{16}$ and the simplified formula is $Ag_8(Sb_5As_3)_{\Sigma 8}S_{16}$. Based on 32 *apfu*, plumbian ferdowsiite (Table 3) has the formula $Cu_{0.11}Ag_{7.63}Pb_{0.76}Sb_{5.03}As_{2.43}S_{16.03}$, which gives the idealized formula $Pb_{2x}Ag_{4-x}Sb_{3-x}AsS_{16}$ with x ~0.2.

CRYSTALLOGRAPHY

A Bruker AXS three-circle diffractometer equipped with a CCD area detector was used to perform the single-crystal study. Cell parameters were refined from single-crystal data. Ferdowsiite is monoclinic, space group $P2_1/n$, a 8.677(2) Å, b 5.799(1) Å, c 13.839(3) Å, β 96.175(4)°, V 692.28(10) Å^3, and Z = 1 for the formula $Ag_8(Sb_5As_3)_{\Sigma 8}S_{16}$. Twinning is absent; the a:b:c ratio calculated from the unit-cell parameters is 1.0573 : 1 : 3.0911. Powder X-ray data were not collected (due to intimate mixture with a similar Pb-rich phase), but were calculated on the basis of the results of the single-crystal structure results. Data are listed in Table 4. Plumbian ferdowsiite has the same space group, $P2_1/n$. It has a 8.746(7) Å, b 5.805(4) Å, c 13.929(10) Å, β 96.236(11)°, V 703.05 Å^3. All parameters are perceptibly larger for the plumbian variety.

The structure of ferdowsiite is a superstructure of a PbS-like motif. It was solved by direct methods and difference Fourier syntheses. In the final stage of

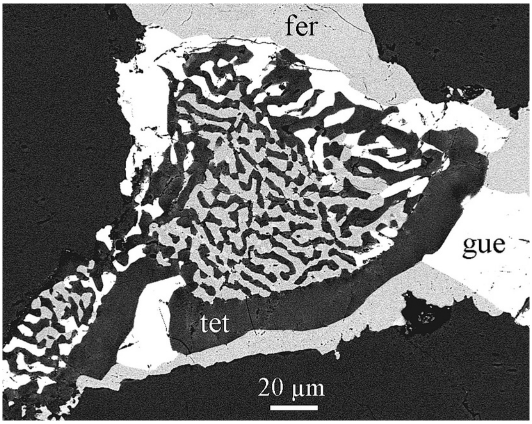

FIG. 2. Symplectite of ferdowsiite (grey, *fer*) with tetrahedrite (dark, *tet*). Guettardite (*gue*) partly replaces ferdowsiite, while coarsening and partly destroying the symplectite texture.

TABLE 1. REFLECTANCE VALUES FOR FERDOWSIITE

l (nm)	Rmin	Rmax
400	32.3	37.4
420	36.1	38.5
440	35.7	37.8
460	35.1	37.3
470	**34.9**	**37.3**
480	34.9	37.4
500	34.3	37.1
520	34.1	36.7
540	33.5	36.3
546	**33.4**	**35.9**
560	33.3	35.9
580	32.4	35.3
589	**32.4**	**35.1**
600	32.3	35.1
620	31.8	34.4
640	31.0	33.8
650	**30.7**	**33.5**
660	30.4	33.0
680	29.8	32.6
700	29.2	31.9

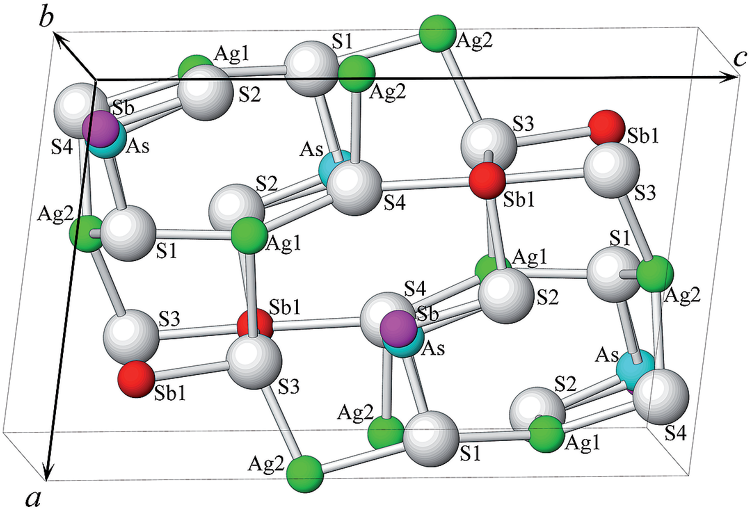

FIG. 3. The crystal structure of ferdowsiite viewed along [010]. White: S; light blue: As; red: Sb; light blue and magenta: As and Sb, respectively, at a split site; green: Ag.

TABLE 2. ELECTRON MICROPROBE DATA FOR FERDOWSIITE

Constituent	wt.%	Range		SD	Standards and lines
		Min	Max		
Ag	38.81	37.99	39.33	0.70	metal (syn.) Ag$L\alpha$
Pb	0.76	0.51	1.19	0.08	galena (nat.) Pb$M\alpha$
Sb	26.06	25.23	27.84	0.81	stibnite(nat.) Sb$L\alpha$
As	10.64	9.23	11.56	0.70	InAs (syn.) As$L\alpha$
Bi	0.11	0.00	0.22	0.08	bismuthinite (syn.) Bi$L\alpha$
S	23.21	22.68	23.75	0.13	stibnite(nat.) S$K\alpha$
Total	99.59				

10 measured points

TABLE 3. ELECTRON MICROPROBE DATA FOR PLUMBIAN FERDOWSIITE

Element	wt.%	Range		SD
		Min	Max	
Cu	0.31	0.26	0.40	0.05
Ag	35.70	35.51	36.00	0.16
Pb	6.87	6.36	7.09	0.26
Sb	26.55	26.15	26.92	0.31
As	7.90	7.64	8.10	0.16
S	22.29	22.14	22.38	
Total	99.62			

6 measured points, Cu$K\alpha$ standard:. nat. $CuFeS_2$, for other standards see Table 2

refinement all positions were treated anisotropically, except for one split cation site. For ferdowsiite, final $R_1 = 0.0282$ for 626 X-ray reflections with $F_O > 4\sigma(F_O)$. The asymmetric unit contains four independent cation and four anion sites, all in general positions, giving 32 sites for the unit cell, on which the above empirical formula is based. Besides two Ag sites and one Sb site, the crystal structure contains one mixed As–Sb coordination polyhedron (Fig. 3). The two silver sites show a very distorted tetrahedral coordination, with additional long interatomic distances to the remaining octahedral ligands. The Sb1 site has three short Sb–S bonds, 2.503–2.645 Å. As and Sb in the mixed site (0.63 As and 0.37 Sb) were refined separately. As has typical bond length values of 2.248–2.354 Å, whereas Sb–S bonds are a bit short, indicating that the observed ligand positions are adjusted to the predominant arsenic. In the lead-enriched variety, about 0.1 Pb substitutes at the Sb1 site and one of the silver sites; both display increased cation–ligand distances.

The {100} planes of the PbS-like substructure are the $(10\bar{5})$, (301), and (010) planes in terms of the ferdowsiite lattice. The structure contains zig-zag chains of Sb1 connected via short Sb–S bonds and flanked by $(Sb,As)S_3$ groups and Ag polyhedra. A detailed description of the crystal structure and its comparison with other ABX_2 structures will be the topic of an upcoming publication (Makovicky & Topa, *in prep.*).

RELATION TO OTHER MINERAL SPECIES

Ferdowsiite is a new As-Sb sulfosalt of silver, and a new addition to the spectrum of complex ABX_2 sulfides. As with many of these compounds, the crystal structure of ferdowsiite can be interpreted as a complex superstructure of the cubic PbS archetype. Distribution of Ag and semi-metals in the structure of ferdowsiite differs from that in all the other known Ag-As-Sb sulfosalts. Although selected local configurations in smithite, freieslebenite, and sicherite can be found in ferdowsiite, the only phase with geometric features and structural configurations comparable to ferdowsiite is diaphorite, $Pb_2Ag_3Sb_3S_8$ (Armbruster *et al.* 2003). In agreement with the more complicated chemical composition of diaphorite, however, the distribution of cations over structure sites and the resulting unit cell of diaphorite are not in a simple relation to those of ferdowsiite (details in Makovicky & Topa, *in prep.*). Thus, the low Pb concentrations in Pb-bearing ferdowsiite do not represent a solid-solution ferdowsiite-diaphorite.

Ferdowsiite might potentially be identical with the valid unnamed mineral UM2000-45-S:AgAsSb (Johan

TABLE 4. CALCULATED X-RAY POWDER DIFFRACTION DATA FOR FERDOWSIITE*

I_{rel}	d_{calc} (Å)	*h*	*k*	*l*	I_{rel}	d_{calc} (Å)	*h*	*k*	*l*
3	7.69	$\bar{1}$	0	1	**22**	**1.9401**	**2**	**0**	**6**
1	4.46	1	1	1	**22**	**1.9226**	$\bar{\mathbf{4}}$	**0**	**4**
3	4.43	0	1	2	2	1.9184	2	2	4
4	4.24	$\bar{1}$	0	3	4	1.9178	3	2	2
8	3.880	1	0	3	3	1.8892	3	0	5
1	3.597	0	1	3	3	1.8591	$\bar{1}$	1	7
3	3.461	2	1	0	3	1.7912	$\bar{1}$	2	6
3	3.440	0	0	4	3	1.7598	2	2	5
2	3.424	$\bar{1}$	1	3	1	1.7594	$\bar{2}$	3	1
96	**3.225**	**1**	**1**	**3**	2	1.7446	4	0	4
100	**3.205**	$\bar{\mathbf{2}}$	**1**	**2**	1	1.7355	4	2	1
2	2.9898	2	1	2	19	1.7302	1	3	3
78	**2.8995**	**0**	**2**	**0**	19	1.7271	$\bar{2}$	3	2
18	2.8372	0	2	1	2	1.7199	0	0	8
90	**2.7559**	**3**	**0**	**1**	3	1.6996	3	2	4
79	**2.7073**	$\bar{\mathbf{1}}$	**0**	**5**	11	1.6707	4	1	4
3	2.5829	$\bar{1}$	2	2	2	1.6672	$\bar{4}$	2	3
1	2.5775	$\bar{3}$	1	1	13	1.6622	$\bar{5}$	1	1
3	2.5584	2	0	4	8	1.6489	0	1	8
5	2.5523	$\bar{2}$	1	4	9	1.6408	$\bar{3}$	1	7
2	2.5226	1	2	2	14	1.6124	2	2	6
5	2.4508	0	2	3	1	1.6094	$\bar{5}$	1	3
3	2.3940	$\bar{1}$	2	3	15	1.6023	$\bar{4}$	2	4
1	2.3446	$\bar{3}$	1	3	2	1.5984	$\bar{4}$	1	6
2	2.3294	1	1	5	1	1.5828	3	2	5
2	2.3227	1	2	3	1	1.5254	$\bar{4}$	2	5
6	2.1840	$\bar{1}$	2	4	1	1.4949	4	2	4
2	2.1566	4	0	0	1	1.4947	3	1	7
7	2.1325	0	1	6	1	1.4794	2	2	7
5	2.0417	3	2	0	2	1.4498	0	4	0
41	**1.9975**	**3**	**2**	**1**	3	1.4418	0	4	1
36	**1.9788**	$\bar{\mathbf{1}}$	**2**	**5**	1	1.4407	$\bar{2}$	2	8
6	1.9781	$\bar{3}$	1	5	4	1.3779	6	0	2

*The theoretical pattern was calculated using PowderCell 2.3 (Kraus & Nolze 1999) in Debye-Scherrer configuration employing Cu*K*α radiation (l = 1.540598 Å), fixed slit, no anomalous dispersion. Cell parameters, space group, atom positions, site occupancy factors and isotropic displacement factors from the crystal structure determination were used

TABLE 5. COMPARATIVE DATA FOR FERDOWSIITE AND RELATED MINERALS

Mineral	ferdowsiite[1]	miargyrite[2]	smithite[3]	aramayoite[2]	baumstarkite[2]
Formula	$Ag_8(Sb_5As_3)_{\Sigma 8}S_{16}$	$Ag_8Sb_8S_{16}$	$Ag_6As_6S_{12}$	$Ag_6Sb_4(Sb,Bi)_2S_{12}$	$Ag_6(Sb,As)_4Sb_2S_{12}$
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
Cell parameters (Å)					
a (Å)	8.677(2)	12.862(3)	15.19	7.813(2)	7.766(2)
b (Å)	5.799(1)	4.409(1)	7.78	8.268(2)	8.322(2)
c (Å)	13.839(3)	13.218(3)	17.23	8.880(2)	8.814(2)
α (°)	90	90	90	100.32(2)	100.62(2)
β (°)	96.175(4)	98.48(2)	101.2	104.07(2)	104.03(2)
γ (°)	90	90	90	90.18(2)	90.22(2)
Z	1	1	4	1	1
R_1 (%)	2.8	3.1	10.3	3.4	5.7

*[1]: this work; [2]: Effenberger *et al.* 2002; [3]: Hellner & Burzlaff 1964

& Mantienne 2000, Smith & Nickel 2007). However, because of a paucity of material (which was present as a symplectitic intergrowth with routhierite at the contact with smithite) for this UM, only qualitative optical data (strong bireflectance in white to grey; strong anisotropy with polarization colors partly coinciding with our case; reflectivity close to stibnite) were given, together with a chemical formula from electron microprobe data, quoted as $Ag_{1.13}Sb_{0.47}As_{0.40}S_{2.00}$. No X-ray diffraction data were obtained. The anisotropy appears distinctly stronger for UM, and the Sb:As ratio in it is distinctly closer to 1:1 than in our case. Experience shows that the changes in the Sb:As ratio may have a pronounced influence on the resulting structure and crystallography [*e.g.*, the guettardite–twinnite pair (Makovicky *et al.* 2012 and Makovicky & Topa 2012)], and the miargyrite–baumstarkite–smithite example of chemically closest minerals in Table 5). Thus, this potential identity needs crystallographic confirmation.

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