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INDICE - CONTENTS

<p>C. BIAGIONI, Y. MOËLO, F. ZACCARINI, Ferdowsiite from the Monte Arsiccio mine, Apuan Alps, Tuscany (Italy): occurrence and crystal structure. <i>Ferdowsiite della miniera di Monte Arsiccio, Alpi Apuane, Toscana (Italia): giacitura e struttura cristallina.</i></p>	<p>pag. 5</p>	<p><i>Broadkill Beach Delaware: caso di studio di un progetto per un uso vantaggioso di materiale dragato.</i></p>	<p>» 83</p>
<p>C. BIAGIONI, S. MUSETTI, M. PASERO, New data on metacinnabar from Tuscany (Italy). <i>Nuovi dati sul metacinnabro toscano.</i></p>	<p>» 13</p>	<p>J. GUILLÉN, G. SIMARRO, A. CORAL, Morphological changes in the artificially embayed beaches of the Barcelona City (Spain). <i>Variazioni morfologiche delle spiagge artificiali della città di Barcellona (Spagna).</i></p>	<p>» 93</p>
<p>P. BILLI, Quantification of bedload flux to beaches within a global change perspective. <i>Stima degli apporti solidi fluviali alle spiagge in una prospettiva di cambiamento globale.</i></p>	<p>» 19</p>	<p>M. LUPPICHINI, M. BINI, R. GIANNECCHINI, Evoluzione temporale del sedime edilizio nella Versilia pre-alluvione 1996 in rapporto alle mappe di pericolosità idraulica e da frana mediante <i>software GIS open source e open data.</i></p>	<p>» 101</p>
<p>P. BILLI, Hydro-morphology of discontinuous gullies: an Ethiopian example. <i>Idromorfologia dei solchi d'erosione discontinui: un esempio Etiopico.</i></p>	<p>» 31</p>	<p>F. RAPETTI, Tendenze attuali della temperatura dell'aria presso i laghi artificiali di Chiotas, Serrù, Goillet e Gabiet, nella media montagna delle Alpi Marittime, Graie e Pennine Italiane. <i>Air temperature trends by the artificial lakes of Chiotas, Serrù, Goillet and Gabiet, in a medium-altitude mountain environment in the Maritime, Graian and Pennine Alps, in Italy.</i></p>	<p>» 115</p>
<p>M. BOSSELAERS, F. VAN NIEULANDE, A. COLLARETA, A new record of <i>Cetopirus complanatus</i> (Cirripedia: Coronulidae), an epibiont of right whales (Cetacea: Balaenidae: <i>Eubalaena</i> spp.), from a beach deposit of Mediterranean Spain. <i>Nuova segnalazione di Cetopirus complanatus (Cirripedia: Coronulidae), un epibionte delle balene franche (Cetacea: Balaenidae: Eubalaena spp.), da un deposito di spiaggia della costa Mediterranea della Spagna.</i></p>	<p>» 43</p>	<p>G. SARTI, D. BERTONI, M. CAPITANI, A. CIAMPALINI, L. CIULLI, A. C. FERONI, S. ANDREUCCI, G. ZANCHETTA, I. ZEMBO, Facies analysis of four superimposed Transgressive-Regressive sequences formed during the two last interglacial-glacial cycles (central Tuscany, Italy). <i>Analisi di facies di quattro sequenze trasgressivo-regressive (T-R) sovrapposte, formate durante gli ultimi due cicli interglaciale-glaciale (Toscana centrale, Italia).</i></p>	<p>» 133</p>
<p>A. COLLARETA, S. CASATI, A. DI CENCIO, A pristinid sawfish from the lower Pliocene of Lucciolabella (Radicofani basin, Tuscany, central Italy). <i>Un pesce sega della famiglia Pristidae dal Pliocene inferiore di Lucciolabella (Bacino di Radicofani, Toscana, Italia centrale).</i></p>	<p>» 49</p>	<p>M. SIMONETTI, R. CAROSI, C. MONTOMOLI, Variscan shear deformation in the Argentera Massif: a field guide to the excursion in the Pontebernardo Valley (Cuneo, Italy). <i>Deformazione non coassiale Varisca nel Massiccio dell'Argentera: guida all'escursione nel Vallone di Pontebernardo (Cuneo, Italia).</i></p>	<p>» 151</p>
<p>G. CRUCIANI, D. FANCELLO, M. FRANCESCHELLI, G. MUSUMECI, The Paleozoic basement of Monte Grighini Unit, a deep view in the nappe structure of Variscan belt in Sardinia. Synthesis of geological data and field guide. <i>Il basamento Paleozoico dell'Unità del Monte Grighini, uno sguardo approfondito nella struttura delle falde della catena Varisca Sarda. Sintesi dei dati geologici e guida all'escursione.</i></p>	<p>» 57</p>	<p>Processi Verbali - http://www.stsn.it</p>	<p>» 171</p>
<p>S. DOHNER, A. TREMBANIS, Broadkill Beach Delaware: case study of a beneficial use of dredged material project.</p>			

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FERDOWSIITE FROM THE MONTE ARSICCIO MINE, APUAN ALPS, TUSCANY (ITALY): OCCURRENCE AND CRYSTAL STRUCTURE

Abstract - C. BIAGIONI, Y. MOËLO, F. ZACCARINI, *Ferdowsiite from the Monte Arsiccio mine, Apuan Alps, Tuscany (Italy): occurrence and crystal structure.*

A new finding of ferdowsiite, ideally $\text{Ag}_8\text{Sb}_5\text{As}_3\text{S}_{16}$, from the Monte Arsiccio mine, Apuan Alps, Tuscany (Italy) is reported. Ferdowsiite occurs as black euhedral crystals, up to 0.3 mm in size, associated with arsiccioite, boscardinite, and chabournéite in small vugs of baryte + dolomite veins embedded in the pyrite-rich metadolostone close to the contact with the baryte + pyrite ore body. Electron microprobe data gave (wt% - mean of nine spot analyses): Ag 39.03(36), Pb 0.24(3), As 10.63(18), Sb 26.57(9), S 23.71(14), Cl 0.04(1), total 100.22(41). On the basis of $\Sigma\text{Me} = 16$ apfu, the chemical formula is $\text{Ag}_{8.01(5)}\text{Pb}_{0.03(1)}\text{Sb}_{4.83(2)}\text{As}_{3.14(4)}\text{S}_{16.36(15)}\text{Cl}_{0.03(1)}$. The crystal structure of ferdowsiite has been refined in the space group $P2_1/n$, with unit-cell parameters $a = 8.6573(4)$, $b = 5.7896(3)$, $c = 13.7866(7)$ Å, $\beta = 96.122(2)^\circ$, $V = 687.08(6)$ Å³, $Z = 1$. The R_1 factor converged to 0.024 on the basis of 1898 reflections with $F_o > 4\sigma(F_o)$ and 75 parameters.

Key words - ferdowsiite, crystal structure, sulfosalt, silver, antimony, arsenic, Monte Arsiccio mine, Apuan Alps, Tuscany, Italy

Riassunto - C. BIAGIONI, Y. MOËLO, F. ZACCARINI, *Ferdowsiite della miniera di Monte Arsiccio, Alpi Apuane, Toscana (Italia): giacitura e struttura cristallina.*

Viene descritto un nuovo ritrovamento di ferdowsiite, idealmente $\text{Ag}_8\text{Sb}_5\text{As}_3\text{S}_{16}$, dalla miniera di Monte Arsiccio, Alpi Apuane, Toscana (Italia). La ferdowsiite si presenta in cristalli euedrali neri, grandi fino a 0.3 mm, associati ad arsiccioite, boscardinite e chabournéite, all'interno di piccole cavità delle vene di dolomite e barite incassate nelle dolomie ricche in pirite, vicino al contatto con il corpo mineralizzato a barite e pirite. La media di nove analisi chimiche puntuali, condotte con microsonda elettronica, è (in wt%): Ag 39.03(36), Pb 0.24(3), As 10.63(18), Sb 26.57(9), S 23.71(14), Se 0.03(4), Cl 0.04(1), totale 100.24(40). Sulla base di $\Sigma\text{Me} = 16$ apfu, la formula chimica è $\text{Ag}_{8.01(5)}\text{Pb}_{0.03(1)}\text{Sb}_{4.83(2)}\text{As}_{3.14(4)}\text{S}_{16.36(15)}\text{Cl}_{0.03(1)}$. La struttura della ferdowsiite è stata raffinata nel gruppo spaziale $P2_1/n$, con parametri di cella $a = 8.6573(4)$, $b = 5.7896(3)$, $c = 13.7866(7)$ Å, $\beta = 96.122(2)^\circ$, $V = 687.08(6)$ Å³, $Z = 1$. Il fattore di accordo R_1 converge a 0.024 sulla base di 1898 riflessi con $F_o > 4\sigma(F_o)$ e 75 parametri.

Parole chiave - ferdowsiite, struttura cristallina, solfosale, argento, antimonio, arsenico, miniera di Monte Arsiccio, Alpi Apuane, Toscana, Italia

INTRODUCTION

Ferdowsiite, ideally $\text{Ag}_8\text{Sb}_5\text{As}_3\text{S}_{16}$, is a recently described mineral belonging to the ABX_2 series of sulfosalts. It was first described from the Barika gold deposit, north-western Iran, by Makovicky *et al.* (2013), in association with sterryite, arsenquatrandorite, bournonite, guettardite, barikaite, tetrahedrite, and smithite, in a gangue of baryte and quartz. Its crystal structure, solved by Makovicky & Topa (2014), can be described as a superstructure of a PbS -like motif. Later, other occurrences of ferdowsiite were reported from the Pollone mine, Apuan Alps, Italy (D. Topa, personal communication), and the Uchucchacua mine, Oyon Province, Lima Department, Peru (F. Keutsch, personal communication) but no data have been published so far. According to Makovicky *et al.* (2013), a further occurrence of ferdowsiite could be the unnamed mineral UM2000-45:AgAsSb from Jas Roux, Hautes-Alpes, France (Johan & Mantiene, 2000; Smith & Nickel, 2007).

The occurrence of Ag-Sb-As sulfosalts in the Monte Arsiccio baryte + pyrite ore deposit was first reported by Biagioni *et al.* (2013) as μm -sized anhedral grains occurring in the interstices of the baryte + pyrite ore body or in veinlets embedded within pyrite-rich metadolostone, and intimately intergrown with Tl-bearing sulfosalts (*e.g.*, boscardinite, protochabournéite). Recently, new samples of an unknown Ag-Sb-As sulfosalt were collected in small vugs of baryte + dolomite veins close to the contact between pyrite-rich metadolostone and the baryte + pyrite ore body. The quality of these samples allowed their crystallographic investigation and their identification with the very rare mineral ferdowsiite. The aim of this paper is the description of the new occurrence of this rare Ag sulfosalt together with the results of its crystal-structure refinement.

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MINERALOGICAL CHARACTERIZATION

Ferdowsiite was identified on a specimen collected in the Sant'Olga level. It occurs as black euhedral crystals, up to 0.3 mm in size (Fig. 1), associated with arsenicite, boscardinite, and chabournéite (the latter here reported for the first time from the Monte Arsiccio mine), in small vugs of a baryte + dolomite vein hosted within pyrite-rich metadolostone, close to the contact with the microcrystalline baryte + pyrite ore body. In the same occurrence, realgar was observed. This is a very unusual occurrence, because at the Monte Arsiccio mine thallium minerals have been usually observed as compact aggregates filling the interstices of the microcrystalline baryte + pyrite ore bodies or as veinlets within the pyrite-rich metadolostone. Only in very few cases, euhedral crystals of Tl minerals (parapierrrotite, routhierite, and an unknown Tl-Sb sulfosalt), up to 30-40 μm in size, have been observed in small vugs of metadolostone, associated with senarmontite, hörnseite, realgar, stibnite, and miargyrite. Finally, a crystal of routhierite, 3 mm in size, was identified in a quartz vein embedded in the metadolostone, in association with boscardinite, stibnite, tetrahedrite, and andradinite.

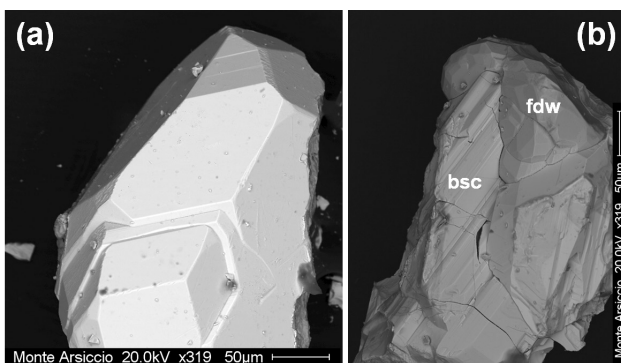


Fig. 1 - Ferdowsiite from the Monte Arsiccio mine (SEM images). (a) Euhedral crystal, 0.3 mm in length; (b) equant crystals (fdw) associated with prismatic crystals of boscardinite (bsc).

Chemical data

The identification of ferdowsiite was done through qualitative EDS chemical analysis, carried out with a Philips XL30 scanning electron microscope equipped with an EDAX DX4 system, and single-crystal X-ray diffraction. Qualitative chemical analysis showed the presence of Ag, Sb, As, and S as the only elements with $Z > 8$. Quantitative chemical data were collected with a Superprobe JEOL JXA 8200 electron microprobe at the Eugen F. Stumpfl laboratory (Leoben University, Austria). The operating conditions were: accelerating voltage 20 kV, beam current 10 nA, beam size 1 μm .

Standards (element, emission line) were: AgBiSe₂ (Ag *La*, Se *La*), galena (Pb *Ma*, S *K α*), Sb₃Te₂ (Sb *La*), GaAs (As *La*), and atacamite (Cl *K α*). Counting times were 20 s on the peak and 10 s on the right and left backgrounds. The studied grain proved to be very homogeneous. The average of nine spot analyses is (in wt%): Ag 39.03(36), Pb 0.24(3), As 10.63(18), Sb 26.57(9), S 23.71(14), Se 0.03(4), Cl 0.04(1), total 100.24(40).

On the basis of $\Sigma Me = 16$ atoms per formula unit, the empirical formula of ferdowsiite from the Monte Arsiccio mine is $\text{Ag}_{8.01(5)}\text{Pb}_{0.03(1)}\text{Sb}_{4.83(2)}\text{As}_{3.14(4)}\text{S}_{16.36(15)}\text{Cl}_{0.03(1)}$, in agreement with the ideal chemical formula $\text{Ag}_8\text{Sb}_5\text{As}_3\text{S}_{16}$. Such a chemical composition can be compared with that reported by Makovicky *et al.* (2013) for type ferdowsiite, *i.e.* $\text{Ag}_{7.97}\text{Pb}_{0.08}\text{Sb}_{4.75}\text{As}_{3.15}\text{Bi}_{0.01}\text{S}_{16.04}$.

Crystallographic data

Single-crystal X-ray diffraction study revealed the monoclinic unit-cell of ferdowsiite and allowed the refinement of its crystal structure. Intensity data were collected using a Bruker Smart Breeze diffractometer equipped with an air-cooled CCD detector, with graphite-monochromatized Mo *K α* radiation. The detector-to-crystal distance was 50 mm. A total of 1664 frames were collected using ω and ϕ scan modes in 0.5° slices, with an exposure time of 5 s per frame. Data were corrected for Lorentz and polarization factors, and absorption using the package of software Apex2 (Bruker AXS, 2004). Unit-cell parameters are $a = 8.6573(4)$, $b = 5.7896(3)$, $c = 13.7866(7)$ Å, $\beta = 96.122(2)^\circ$, $V = 687.08(6)$ Å³. The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 1.035$) and the systematic absences agree with the space group $P2_1/n$. The crystal structure of ferdowsiite was refined starting from the atomic coordinates given by Makovicky & Topa (2014) using Shelxl-2014 (Sheldrick, 2015). Four independent cation sites and four S positions occur. Scattering curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson, 1992). The following curves were used: Ag vs \square for Ag1 and Ag2 sites; Sb vs As for Sb1 and As sites; S for S sites. Ag sites were found fully occupied by Ag, and their site occupancy factors (s.o.f.) were fixed to 1. Similarly, Sb1 was found fully occupied by Sb, whereas the As site shows a mixed (As,Sb) occupancy. After several cycles of anisotropic refinement, the refinement converged to $R_1 = 0.0242$ for 1898 reflections with $F_o > 4\sigma(F_o)$ and 0.0256 for all 1967 independent reflections and 75 parameters. The chemical formula of ferdowsiite, as obtained through the crystal structure refinement, is $\text{Ag}_8(\text{Sb}_{5.19}\text{As}_{2.81})\text{S}_{16}$, in agreement with the ideal formula $\text{Ag}_8\text{Sb}_5\text{As}_3\text{S}_{16}$. Details of the intensity data collection and crystal structure refinement are given in Table 1. Atomic coordinates and

equivalent isotropic displacement parameters are given in Table 2, whereas selected bond distances are shown in Table 3.

The structural features of ferdowsiite from the Monte Arsiccio mine (Fig. 2) agree with those described by Makovicky & Topa (2014) for the Iranian sample. Ag1 and Ag2 sites are characterized by a distorted tetrahedral coordination (close to eccentric triangular – average bond distances of 2.675 and 2.669 Å, respectively). The coordination is completed by two longer bonds, with Ag-S distances in the range 3.17-3.28 Å. The bond-valence sums (BVS), calculated using the bond parameters of Brese & O’Keeffe (1991), are 1.14 and 1.10 valence unit (v.u.), respectively. Sb1 site displays the typical trigonal pyramidal coordination, with three Sb-S distances shorter than 2.70 Å (average distance 2.542 Å). Three additional bonds complete its coordination sphere, with Sb-S bonds between 2.86 and 3.39 Å. The BVS at the Sb1 site is 2.94 v.u.

Finally, the As site is a mixed (As,Sb) site. Makovicky & Topa (2014) refined the fractional atomic coordinates of the As and Sb sub-positions. On the contrary, in the present study As and Sb were refined at a single atom position, having three distances shorter than 2.70 Å (average distance 2.323 Å) and three long distances, ranging from 3.21 and 3.48 Å. The BVS, at this site, is 3.25 v.u. The bond-valence sums at the S sites are 2.03, 2.24, 2.08, and 2.08 v.u. for S1, S2, S3, and S4 sites, respectively.

Taking into account the shortest (= the strongest) Sb-S bonds, zig-zag chains formed by Sb1 trigonal pyramids and running along **b** are shown (Fig. 3). These chains are decorated on both sides by AsS₃ trigonal pyramids to form infinite [(As,Sb)₂(Sb1)₂S₈]_∞ ribbons.

In inter-spaces, lone electron pairs and the Ag atoms are accommodated. Considering also the three shortest Ag-S distances, the projection of the structure along **b** reveals a layered organization parallel to (001) (Fig. 4). These layers correspond to a (140) slice of the galena structure. The weak inter-layer bonding may favor a (001) cleavage plane.

Table 1 - Details of data collection and structure refinement for ferdowsiite.

Crystal data	
Crystal size (mm)	0.20 x 0.12 x 0.08
Cell setting, space group	Monoclinic, $P2_1/n$
a (Å)	8.6573(4)
b (Å)	5.7896(3)
c (Å)	13.7866(7)
β (°)	96.122(2)
V (Å ³)	687.08(6)
Z	1
Data collection and refinement	
Radiation, wavelength (Å)	Mo K α , 0.71073
Temperature (K)	293
$2\theta_{\max}$ (°)	60.03
Measured reflections	7413
Unique reflections	1967
Reflections with $F_o > 4\sigma(F_o)$	1898
R_{int}	0.0278
$R\sigma$	0.0225
Range of h, k, l	$-12 \leq h \leq 12,$ $-8 \leq k \leq 8,$ $-18 \leq l \leq 19$
$R [F_o > 4\sigma(F_o)]$	0.0242
R (all data)	0.0256
wR (on F_o^2)	0.0735
Goof	1.294
Number of least-squares parameters	75
Maximum and minimum residual peak ($e \text{ \AA}^{-3}$)	1.75 (at 0.69 Å from Ag2) -1.68 (at 0.86 Å from Sb1)

Table 2 - Atoms, site occupancy factors (s.o.f.), fractional atomic coordinates, and equivalent isotropic displacement parameters (in Å²) for ferdowsiite.

Site	s.o.f.	x/a	y/b	z/c	U_{eq}
Ag1	Ag _{1.00}	0.57666(6)	0.74085(7)	0.71113(3)	0.02948(12)
Ag2	Ag _{1.00}	0.52217(4)	0.22339(7)	0.92452(4)	0.02975(12)
Sb1	Sb _{1.00}	0.28388(3)	0.20959(5)	0.64400(2)	0.01439(10)
As	As _{0.703(5)} Sb _{0.297(5)}	0.66932(4)	0.23095(6)	0.54302(3)	0.01454(15)
S1	S _{1.00}	0.57659(12)	0.6687(2)	0.89488(8)	0.0174(2)
S2	S _{1.00}	0.56986(11)	0.1953(2)	0.69472(8)	0.0155(2)
S3	S _{1.00}	0.25082(11)	0.1305(2)	0.82897(7)	0.0132(2)
S4	S _{1.00}	0.31784(12)	0.3700(2)	0.45150(7)	0.0152(2)

Table 3 - Selected bond distances (in Å) and calculated bond-valences (BV, in valence unit) for ferdowsiite.

		d (Å)	BV			d (Å)	BV
Ag1	- S1	2.568(1)	0.32	Ag2	- S4	2.604(1)	0.29
	- S4	2.590(1)	0.30		- S3	2.624(1)	0.28
	- S2	2.641(1)	0.27		- S1	2.660(1)	0.25
	- S3	2.901(1)	0.13		- S1	2.788(1)	0.18
	- S2	3.167(1)	0.06		- S2	3.242(1)	0.05
	- S2	3.205(1)	0.06		- S1	3.278(1)	0.05
		Sum			1.14		Sum
Sb1	- S3	2.488(1)	0.90	As	- S1	2.302(1)	1.07
	- S2	2.501(1)	0.87		- S4	2.314(1)	1.04
	- S3	2.636(1)	0.60		- S2	2.354(1)	0.93
	- S4	2.856(1)	0.33		- S3	3.208(1)	0.09
	- S1	3.118(1)	0.16		- S4	3.268(1)	0.08
	- S3	3.390(1)	0.08		- S4	3.482(1)	0.04
		Sum			2.94		Sum

Note: for the As site, having a mixed (As,Sb) site occupancy, BV has been weighted.

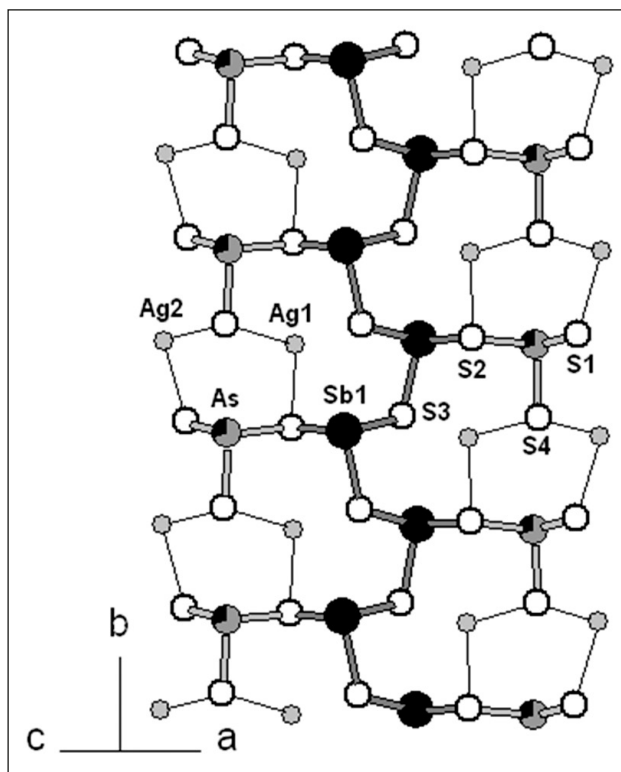
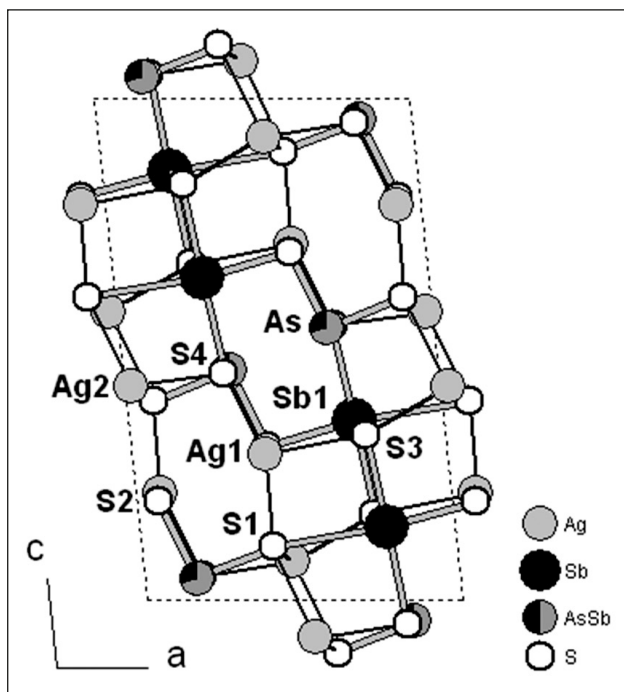


Fig. 2 - Projection along **b** of the crystal structure of ferdowsiite from Monte Arsiccio. Sb₁-S and (As,Sb)-S bonds have been thickened.

Fig. 3 - Fish-bone organization along **b** of the $[(As,Sb)_2(Sb_1)_2S_8]_{\infty}$ ribbon.

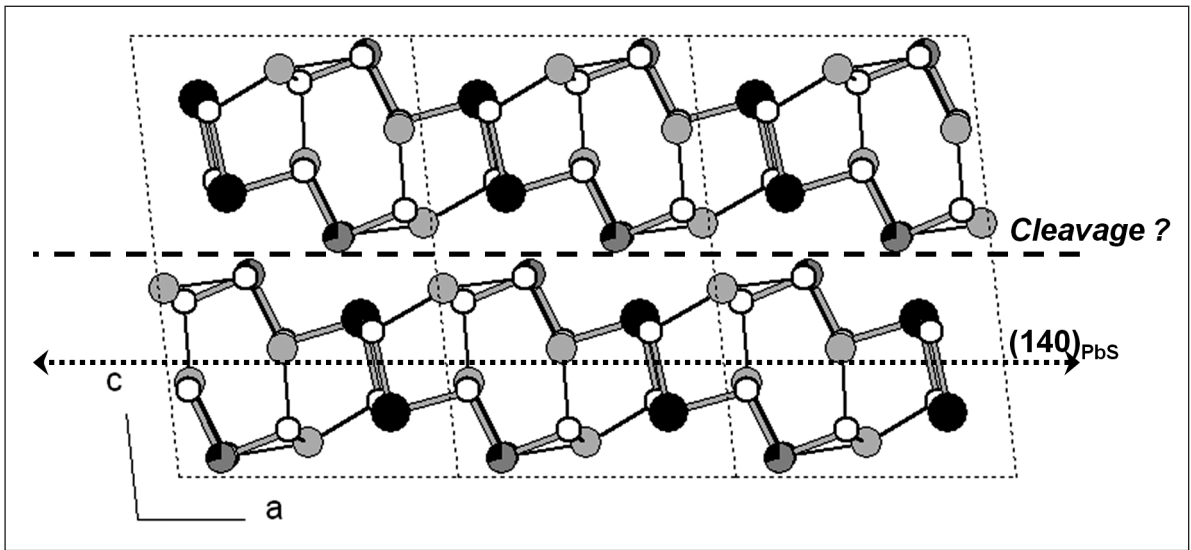


Fig. 4 - The (001) layered organization, parallel to $(140)_{\text{PbS}}$, of the crystal structure of ferdowsiite, selecting the strongest Me-S bonds (the three shortest for Ag).

DISCUSSION

Ferdowsiite is a new addition to the series of sulfosalts found in the hydrothermal veins from southern Apuan Alps. It is noteworthy that the findings of ferdowsiite from this area occur in assemblages similar to those reported from other localities. Indeed, ferdowsiite from Monte Arsiccio occurs in an assemblage similar to those reported from Jas Roux, where the unnamed mineral UM2000-45:AgAsSb is associated with routhierite and smithite (Johan & Mantiene, 2000). The other occurrence from the Pollone mine (D. Topa, personal communication) is similar to that from the type locality.

On the basis of chemical data, ferdowsiite from the Monte Arsiccio mine has the same $\text{As}/(\text{As}+\text{Sb})$ atomic ratios of the type specimen, i.e. ~ 0.39 . Moreover, ferdowsiite from Monte Arsiccio is virtually Pb-free. This agrees with the slightly smaller unit-cell volume of ferdowsiite from Monte Arsiccio, with $\Delta V = -0.75\%$ with respect to type ferdowsiite.

The Ag-rich nature of some ore deposits from Apuan Alps is well-known since long time. Indeed, the ore deposits of the Bottino-Valdicastello area had been exploited for silver since Middle Age. Pilla (1845) described the finding of an Ag-rich mineral in the Valdicastello mines, whereas Sagui (1924) reported the presence of acanthite from the Bottino mine. Menchetti (1970) detailed the finding of “arsenopolybasite”, first reported by Amodio Morelli & Menchetti (1969), from the Valdicastello area; however, the description of its mineral assemblage raises some doubts about the actual provenance of the sample studied by these authors.

Thus, the very first description of Ag ore minerals can be attributed to Carmignani *et al.* (1976), who gave chemical data of owyheite and Ag-rich tetrahedrite from the Pollone mine. Later, Brizzi & Olmi (1989), Benvenuti (1991), Benvenuti *et al.* (1993a, b), Frizzo & Simone (1995), and Costagliola *et al.* (2003) reported the occurrence of some Ag minerals (acanthite, argentopentlandite, diaphorite, “electrum”, proustite, pyrrgryrite, and Ag-rich tetrahedrite) from the Bottino – Valdicastello ore district. A further report of acanthite was given by Carrozzini *et al.* (1993) from the Cu-Fe ore deposit of the Frigido mine.

In the last decade, the mineralogical investigation of the baryte + pyrite \pm iron oxide ore deposits allowed to ascertain that Ag ore minerals are widespread as rare accessory phases in this kind of occurrence. As pointed out by several authors (*e.g.*, Hammerli *et al.*, 2016), Ag is a mobile element in metamorphic conditions; consequently, the greenschist facies metamorphism affecting the rocks of the Apuan Alps did represent ideal conditions for the transport of this element and the subsequent crystallization of Ag phases. Table 4 summarizes the distribution of Ag-bearing ore minerals reported from the Apuan Alps. It is noteworthy that in addition to mineral species belonging to the simple ternary system $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{As}_2\text{S}_3$ (*e.g.*, the proustite-pyrrgryrite series, $\text{Ag}_3\text{AsS}_3-\text{Ag}_3\text{SbS}_3$), the geochemical complexity of the hydrothermal solutions favored the crystallization of compounds characteristic of more complex chemical systems, *e.g.* sterryite, belonging to the pseudosenary system $\text{PbS}-\text{Sb}_2\text{S}_3-\text{As}_2\text{S}_3-\text{Ag}_2\text{S}-\text{CuS}-\text{AsS}$ (Moëlo *et al.*, 2011), or andrea-diniite, which can be described in the quinary system

Table 4 - Distribution of Ag sulfides and sulfosalts in the hydrothermal veins from the Apuan Alps.

Baryte ± pyrite ± iron oxides ore deposits	
Buca della Vena mine	“andorite” ¹ , pellouxite ² , Ag-bearing tetrahedrite ¹
Monte Arsiccio mine	andreadiniite ³ , arsiccioite ⁴ , boscardinite ^{5,6} , ferdowsiite ⁷ , laffittite ⁸ , miargyrite*, Ag-bearing rouxelite ⁹
Pollone mine	acanthite ¹⁰ , billingsleyite ¹¹ , carducciite ¹² , diaphorite ¹³ , ferdowsiite ¹⁴ , fettelite ¹¹ , meerschautite ¹⁵ , owyheeite ¹⁶ , parasterryite ¹⁷ , polloneite ¹⁸ , proustite ¹⁰ , pyrargyrite ^{10,13} , sterryite ¹⁷ , Ag-bearing tennantite ¹⁰ , xanthoconite ¹⁰
Pb-Zn-Ag ore deposits	
Argentiera di Sant’Anna mine	acanthite ¹⁹
Bottino mine	acanthite ²⁰ , argentopentlandite ²¹ , pyrargyrite ^{22,23} , Ag-bearing tetrahedrite ²⁰
Cu-Fe ore deposits	
Frigido mine	acanthite ²⁴
Marble quarries	
Seravezza quarries	senandorite*, Ag-bearing izoklakeite ²⁵

¹ Orlandi & Dini, 2004; ² Orlandi *et al.*, 2004; ³ Biagioni *et al.*, 2014a; ⁴ Biagioni *et al.*, 2014b; ⁵ Orlandi *et al.*, 2012; ⁶ Biagioni & Moëlo, 2017; ⁷ this work; ⁸ Biagioni *et al.*, 2014c; ⁹ Biagioni & Moëlo, 2014; ¹⁰ Biagioni *et al.*, 2012; ¹¹ Biagioni *et al.*, 2014d; ¹² Biagioni *et al.*, 2014e; ¹³ Frizzo & Simone, 1995; ¹⁴ D. Topa, personal communication; ¹⁵ Biagioni *et al.*, 2016; ¹⁶ Carmignani *et al.*, 1976; ¹⁷ Moëlo *et al.*, 2011; ¹⁸ Topa *et al.*, 2015; ¹⁹ Biagioni, 2009; ²⁰ Benvenuti *et al.*, 1993a; ²¹ Benvenuti, 1991; ²² Benvenuti *et al.*, 1993b; ²³ Biagioni *et al.*, 2008; ²⁴ Carrozzini *et al.*, 1993; ²⁵ Orlandi *et al.*, 2010. * Unpublished data.

PbS-CuS-Ag₂S-HgS-Sb₂S₃ (Biagioni *et al.*, 2014a). Probably, it is the coexistence of Ag with various metals (Pb, Cu, Hg, Tl), together with Sb and As, and the occasional occurrence of minor anions (O, as in meerschautite; Biagioni *et al.*, 2016) which gave rise to the complexity of the ore mineral assemblages of the baryte + pyrite ± iron oxide ore deposits from southern Apuan Alps. These geochemical features favoured the description of several new mineral species. Indeed, seven new Ag minerals have been described so far from these deposits: carducciite, meerschautite, parasterryite, and polloneite from the Pollone mine, and andreadiniite, arsiccioite, and boscardinite from the Monte Arsiccio mine. Accordingly, the hydrothermal ore deposits of southern Apuan Alps can be considered as reference localities for the study of Ag ore mineralogy in low-grade metamorphic environments.

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