

Versiliaite and apuanite, two new minerals from the Apuan Alps, Italy

MARCELLO MELLINI, STEFANO MERLINO AND PAOLO ORLANDI

Istituto di Mineralogia e Petrografia dell'Università di Pisa
C.N.R., Centro di Studio per la Geologia Strutturale e Dinamica dell'Appennino
Via S. Maria 53, 56100 Pisa, Italy

Abstract

Two new minerals, versiliaite and apuanite, were found in the Buca della Vena mine on the Apuan Alps (Italy). The minerals generally occur as massive black aggregates in veinlets within layers of dolomite.

Versiliaite, $(\text{Fe}_{4.65}^{2+}\text{Zn}_{1.04}\text{Fe}_{2.43}^{3+})(\text{Fe}_{2.90}^{3+}\text{Sb}_{11.76}^{3+}\text{As}_{1.34}^{3+})\text{O}_{32}\text{S}_{1.33}$, has space group *Pbam* or *Pba2*, $a = 8.499(2)$, $b = 8.326(2)$, $c = 11.935(2)\text{Å}$, density 5.12 g cm^{-3} . The strongest lines in the powder pattern are: 3.196(100), 3.167(97), 2.972(81), 2.682(40), 1.946(40), 1.652(33).

Apuanite, $(\text{Fe}_{4.15}^{2+}\text{Zn}_{0.32}\text{Fe}_{7.40}^{3+})(\text{Fe}_{6.87}^{3+}\text{Sb}_{15.64}^{3+}\text{As}_{1.49}^{3+})\text{O}_{48}\text{S}_{3.57}$, has space group *P4₂/mbc*, $a = 8.367(2)$, $c = 17.959(6)\text{Å}$, density 5.33 g cm^{-3} . The strongest lines in the powder pattern are 3.168(100), 2.957(43), 2.646(23), 2.434(17), 1.922(47), 1.647(30). The chemical, crystallographic, and structural data indicate a close relationship of the new minerals with schafarzikite.

Introduction

Within the program of a thorough reexamination of the Tuscan mineralogy, a careful study of the numerous minerals found in various mineral deposits of the Apuan Alps was undertaken. In the course of the study two new mineral phases were found in samples from the Buca della Vena mine.

The aim of this paper is to define the new mineral phases, which were called versiliaite and apuanite from the locality where the samples were found. Both minerals and their names were approved by the Commission on New Minerals and Mineral Names of IMA.

Paragenesis

The Buca della Vena mine is a small mineral deposit which outcrops north of Stazzema, in the upper Versilia valley, and contains iron ores (magnetite, hematite, and minor pyrite) within a microcrystalline mass of barite. The mineralization took place by metasomatic process at the contact between phyllites and dolomites ("grezzoni" of the Tuscan metamorphic core; Carmignani *et al.*, 1977).

The new minerals were generally found as massive black aggregates in veinlets within thin layers of dolomite, which are relics of the metasomatic proc-

ess. Associated with the black minerals in the veinlets is spathic barite.

X-ray crystallography and physical properties

Powder diffraction patterns of specimens from the black aggregates differ from each other in minor details, with good agreement with the X-ray powder pattern reported for ZnSb_2O_4 (JCPDS 15-802).

The specimens were then examined by single-crystal techniques. Rotation and Weissenberg photographs revealed three distinct mineral phases: the first, with tetragonal unit cell, $a \approx 8.5$, $c \approx 6.0\text{Å}$, was easily identified as schafarzikite, a mineral previously found only in the antimonian deposits of Pernek (Czechoslovakia) by Krenner (1921); the second, with orthorhombic cell, $a \approx 8.5$, $b \approx 8.3$, $c \approx 12.0\text{Å}$ and the third, with tetragonal unit cell and $a \approx 8.4$, $c \approx 18.0\text{Å}$, were new minerals closely related to schafarzikite and were named *versiliaite* and *apuanite* respectively, from the locality. Whereas the three minerals most frequently appear as massive aggregates, apuanite was also found as very rare well-crystallized tabular prisms.

Crystals of versiliaite are black, with metallic luster, platy on (001) and with perfect (110) cleavage. The density determined by the torsion balance was 5.12 g cm^{-3} . Weissenberg and precession photo-

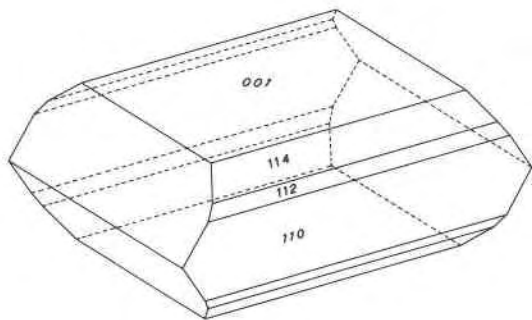


Fig. 1. Habit of a well-formed crystal of apuanite.

graphs indicated Laue symmetry mmm . The systematic absences ($0kl$ absent for $k = 2n + 1$ and $h0l$ absent for $h = 2n + 1$) gave $Pbam$ and $Pba2$ as possible space groups.

Crystals of apuanite are black, with metallic luster, platy on (001) and with perfect (110) cleavage. The density, determined by the torsion balance, was 5.33 g cm^{-3} . The habit of a well-developed crystal, which is characterized by the forms $\{001\}$, $\{110\}$, $\{112\}$, and $\{114\}$, is illustrated in Figure 1. Weissenberg and precession photographs indicated Laue symmetry $4/mmm$. The systematic absences ($0kl$ reflections absent for $k = 2n + 1$ and hhl absent for $l = 2n + 1$) gave $P4_2/mbc$ as the only possible space group.

The VHN microhardnesses of versiliaite and apuanite were determined with a load of 20 g as 330 and 240–480 respectively. Larger loads led to unsatisfactory indentations with concave borders and fractures. Reflectivities, obtained using SiC as standard, are given in Table 1.

Table 2 gives the X-ray powder patterns of versiliaite and apuanite. The powder data were obtained by means of a Philips diffractometer, scanning speed $0.5^\circ 2\theta$ per min, Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54178\text{\AA}$). The patterns were indexed using the single-crystal photographs as a check; as the powder

diffraction pattern of schafarzikite has never been published before, it is reported in Table 2 for comparison. Because the diffraction powder pattern revealed that the specimen of schafarzikite was mixed with versiliaite, we checked the powder data for schafarzikite by means of a Gandolfi camera, using a fragment which was previously tested by single-crystal techniques.

The three patterns have common features, which indicate that versiliaite and apuanite have a subcell corresponding to the cell of schafarzikite. The new minerals, however, can be easily differentiated from schafarzikite not only by the shifting of some reflections but also by the presence of additional weak supercell reflections. The distinction between versiliaite and apuanite can be easily made on the basis of the splitting in the orthorhombic versiliaite of peaks which are single in the tetragonal apuanite.

The unit-cell parameters, derived from the single-crystal photographs, were refined by a least-squares method, using the powder lines whose indices were unambiguously determined (Table 3).

Chemical composition

Three crystal fragments, previously identified as schafarzikite, versiliaite, and apuanite, were analyzed by electron microprobe. Because qualitative X-ray fluorescence analyses excluded the presence of elements other than iron, zinc, antimony, arsenic, and sulphur, several analyses on each specimen were made using Fe_3O_4 , ZnS , Sb_2S_3 , and As_2S_3 as standards. The analyses were then repeated using metallic Fe, Zn, Sb, and As_2S_3 as standards, with very similar results. The electron probe analyses of each specimen were then averaged and the elemental weight percents obtained are reported in Table 4; the oxide contents were recalculated taking account of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios indicated by the structural data discussed in the following paragraph.

Table 1. Reflectivities of versilianite and apuanite

Phase		wavelength (nm)			
		470	546	589	* 650
Versiliaite	in air	18.5–19.4	18.5–17.8	18.3–16.9	17.7–16.2
	in oil (Cargille D/A 58884)	4.7–6.5	5.9–5.3	6.0–5.0	5.2–4.4
Apuanite	in air	19.1–20.8	21.9–19.6	21.6–18.4	19.6–16.9
	in oil (Cargille D/A 58884)	6.5–6.8	7.3–5.9	7.8–5.6	6.4–4.8

Table 2. X-ray powder diffraction data for schafarzikite, versiliaite, and apuanite

Schafarzikite				Versiliaite				Apuanite			
d _{obs}	d _{calc}	I/I ₀	hkl	d _{obs}	d _{calc}	I/I ₀	hkl	d _{obs}	d _{calc}	I/I ₀	hkl
6.04	6.059	21	110	5.94	5.947	25	110	5.90	5.916	15	110
4.28	4.285	59	200	4.24	4.249	17	200	4.18	4.183	15	200
				4.16	4.164	12	020				
				3.782	3.785	4	210	3.782	{ 3.792		202
				3.729	3.738	4	120		{ 3.742	5	210
				3.603	3.608	4	211	3.658	3.663	12	211
				3.562	3.567	4	121				
3.209	3.210	100	211	3.196	3.196	100	212	3.168	3.173	100	213
3.031	3.030	55	220	3.167	3.168	97	122	3.059	3.061	3	204
2.937	2.937	10	002	2.972	{ 2.974	81	220	2.991	2.993	15	006
					{ 2.983		004	2.957	2.958	43	220
2.708	2.710	50	310	2.682	2.682	40	310	2.668	2.671	13	116
2.640	2.643	5	112	2.637	2.638	24	130	2.646	2.646	23	310
								2.591	2.591	2	215
								2.536	2.538	4	312
2.422	2.423	9	202	2.442	2.442	14	204	2.434	2.434	17	206
				2.425	2.425	10	024				
				2.341	{ 2.343		214				
2.330	2.331	3	212		{ 2.342	4	320	2.338	2.337	3	216
				2.333	2.332	9	124				
								2.320	2.320	3	320
2.138	2.142	3	400					2.279	2.279	3	314
2.021	2.020	13	330	1.982	1.982	10	330	1.973	1.972	10	330
1.960	1.959	29	411	1.946	1.946	40	412	1.922	1.922	47	413
				1.915	1.915	29	142				
1.915	1.916	12	420	1.892	1.892	7	420	1.871	1.871	10	420
				1.870	1.869	9	240				
1.744	1.744	5	213	1.762	1.761	10	216	1.762	1.761	10	219
				1.757	1.756	14	126				
1.731	1.731	4	402	1.731	1.731	6	404	1.716	1.714	7	406
				1.707	1.707	6	044				
1.665	1.664	11	332	1.652	1.651	33	334	1.647	1.647	30	336
				1.521	1.522	5	522				
1.537	1.536	4	521	1.501	1.500	7	252	1.505	1.504	10	523
1.516	1.515	3	440	1.487	1.487	7	440				
				1.455	1.454	5	514	1.440	1.439	7	516
1.471	1.470	16	530	1.449	1.449	12	530	1.437	1.435	12	530
				1.436	1.436	5	350				
1.428	1.428	15	600	1.432	{ 1.433		154	1.424	1.423	8	419
					{ 1.430	12	416				
				1.416	{ 1.418	12	146	1.396	1.394	7	600
					{ 1.416		600				
1.306	{ 1.306	7	304								
	{ 1.305		541								

As regards the relatively low totals of the three analyses, we can exclude, on the basis of qualitative X-ray fluorescence analyses and the results of the structural investigation, the presence of other ions or water molecules. Thus we think that the low totals may be due to the matrix effects between the specimens and the standards used in the microprobe analyses, effects not completely emended in the raw data correction procedure.

Structural and crystal-chemical considerations

The crystal structure of schafarzikite was determined by Zemann (1951) and refined by Fischer and Pertlik (1975). It is built up by chains of edge-sharing Fe^{2+}O_6 octahedra connected with chains of corner-sharing Sb^{3+}O_3 pyramids: these last units can also be called ψ -tetrahedra, where ψ indicates that a vertex is occupied by an electron lone pair. The crystal-chem-

Table 3. X-ray crystallographic data of schafarzikite, versiliaite, and apuanite (A)

	Schafarzikite (Fischer and Pertlik, 1975)	Schafarzikite	Versiliaite	Apuanite
Space group	$P4_2/mbc$	$P4_2/mbc$	$Pbam$	$P4_2/mbc$
<i>a</i>	8.590(5)	8.568(4)	8.499(1)	8.367(2)
<i>b</i>			8.326(1)	
<i>c</i>	5.913(5)	5.957(10)	11.935(2)	17.959(6)

ical formula for the cell content of schafarzikite can be expressed as $Fe_4^{2+}Sb_8^{3+}O_{16}$.

The crystal structure of versiliaite (Mellini and Merlino, 1979) can be derived from that of schafarzikite by substituting every fourth Sb^{3+} cation in the pyramidal chains by a Fe^{3+} cation and introducing a sulphide anion between pairs of Fe^{3+} cations of different chains: the sulphide anions complete the tetrahedral coordination around the two Fe^{3+} cations and connect them to give rise to double-chain ribbons. The four negative charges introduced with the two sulphide anions in the unit cell are balanced by substituting four Fe^{3+} cations to four divalent cations in octahedral coordination, thus obtaining the ideal formula:



Similarly the crystal structure of apuanite (Mellini and Merlino, 1979) can be derived from that of schafarzikite by substituting every third Sb^{3+} cation in the pyramidal chains by an Fe^{3+} cation. The connections by means of the sulphide anions which complete the coordination about the Fe^{3+} cations build layers par-

allel to (110). The eight negative charges introduced with four sulphide anions in the unit cell are balanced by substituting eight Fe^{3+} cations for eight divalent cations in octahedral coordination, thus obtaining the ideal formula:



The structural data, which impose the presence of four Fe^{3+} cations for every sulphide anion, were taken into account in recalculating the oxide contents from the electron microprobe analyses data (columns *b* in Table 4). Assuming 16, 32, and 48 oxygen atoms in the unit cells of schafarzikite, versiliaite, and apuanite respectively, the unit-cell contents given in columns *c* of Table 4 can be calculated and the following formulas obtained:

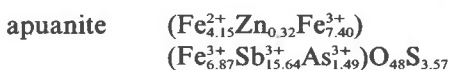
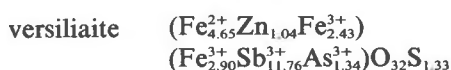


Table 4. Electron microprobe analytical data and unit cell contents for schafarzikite (1), versiliaite (2), and apuanite (3)

	Elemental weight percent			Oxide weight percent			Unit cell content				
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)		
				FeO	17.58	11.70	7.04	Fe^{2+}	3.54	4.65	4.15
Fe	13.67	19.53	24.28	Fe_2O_3	-	14.92	26.88	Fe^{3+}	-	5.33	14.27
Zn	0.89	2.38	0.50	ZnO	1.10	2.96	0.62	Zn^{2+}	0.20	1.04	0.32
Sb	56.74	50.22	44.96	Sb_2O_3	67.95	60.12	53.82	Sb^{3+}	6.75	11.76	15.64
As	7.36	3.51	2.64	As_2O_3	9.72	4.63	3.48	As^{3+}	1.42	1.34	1.49
S	-	1.50	2.70	S	-	1.50	2.70	S^{2-}	-	1.33	3.57
					96.35	95.83	94.54				
				-O=S		0.75	1.35				
						95.08	93.19				

where the first parentheses in each formula enclose the cations in octahedral coordination, and the second parentheses enclose the cations in tetrahedral or ψ -tetrahedral coordination. The crystal-chemical formulas just given for versiliaite and apuanite correspond to calculated densities of 5.20 and 5.32 g cm⁻³ respectively, in fair agreement with the measured values. Both the incomplete occupancy of the sulphide site and the cation distribution in versiliaite and apuanite were amply confirmed by the structural investigation.

These considerations indicate the close relationship of the two new minerals with schafarzikite. However it should be observed that, from the chemical point of view, the new minerals can be classified as oxide-sulphide compounds, which are quite rare in nature, and the only other mineral phases being kermesite and sarabauite (Nakai *et al.*, 1978).

Acknowledgments

The first samples with apuanite and versiliaite were kindly provided by Dr. F. Checchi. Dr. G. Duchi is thanked for his assistance in determining the reflectivity and microhardness values. The Consiglio Nazionale delle Ricerche, Roma, Italy, is acknowledged for financing the installation and the maintenance, for the use of

all scientists affiliated with the Committee 05 of the CNR, of an electron microprobe laboratory at the Istituto di Mineralogia e Petrologia dell'Università di Modena, whose facilities were used in the present work, with the kind assistance of Dr. M. G. Vezzalini.

References

- Carmignani, L., G. Dessau and G. Duchi (1977) I giacimenti a barite, pirite e ossidi di ferro delle Alpi Apuane. Studio mineralogico e strutturale. *Boll. Soc. Geol. Ital.*, 95, 1009-1061.
- Fischer, R. and F. Pertlik (1975) Verfeinerung der Kristallstruktur des Schafarzikits, FeSb₂O₄. *Tschermaks Mineral. Petrogr. Mitt.*, 22, 236-241.
- Krenner, J. A. (1921) Schafarzikite, ein neues Mineral. *Z. Kristallogr.*, 56, 198-200.
- Mellini, M. and S. Merlino (1979) Versiliaite and apuanite: derivative structures related to schafarzikite. *Am. Mineral.*, 64, 1235-1242.
- Nakai, I., H. Adech, S. Matsubara, A. Kato, K. Masutomi, T. Fujiwara and K. Nagashima (1978) Sarabauite, a new oxide sulphide mineral from the Sarabau Mine, Sarawak, Malaysia. *Am. Mineral.*, 63, 715-719.
- Zemann, J. (1951) Formel und Kristallstruktur des Schafarzikits. *Tschermaks Mineral. Petrogr. Mitt.*, 2, 166-175.

Manuscript received, April 24, 1979;
accepted for publication, June 29, 1979.