

## Versiliaite and apuanite: derivative structures related to schafarzikite

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### Abstract

Schafarzikite,  $\text{FeSb}_2\text{O}_4$ , is tetragonal, space group  $P4_2/mbc$ , with  $a = 8.59$ ,  $c = 5.91\text{\AA}$ . The crystal structure is characterized by the presence of edge-sharing iron octahedra connected with corner-sharing antimony  $\psi$ -tetrahedra (Fischer and Pertlik, 1975).

Versiliaite is orthorhombic, space group  $Pbam$ ,  $a = 8.492$ ,  $b = 8.326$ ,  $c = 11.938\text{\AA}$ . Its crystal structure is related to that of schafarzikite in the following manner: every fourth  $\text{Sb}^{3+}$  ion in the  $\psi$ -tetrahedral chains is substituted by a  $\text{Fe}^{3+}$  ion and a sulphide anion is added between two  $\text{Fe}^{3+}$  cations in adjacent chains. The corner-sharing  $\text{Fe}^{3+}$  tetrahedra connect the chains to build double-chain ribbons. The charge balance, altered by the insertion of sulphide anions, is restored by the substitution of  $\text{Fe}^{2+}$  cations in the octahedral chains by  $\text{Fe}^{3+}$  cations.

Apuanite is tetragonal, space group  $P4_2/mbc$ ,  $a = 8.372$ ,  $c = 17.974\text{\AA}$ . Its crystal structure can be derived from that of schafarzikite by substituting every third  $\text{Sb}^{3+}$  ion in the  $\psi$ -tetrahedral chains with an  $\text{Fe}^{3+}$  cation and adding sulphide anions which connect adjacent chains to build infinite layers. As in versiliaite the charge balance is restored by substitution of  $\text{Fe}^{2+}$  cations in octahedral chains with  $\text{Fe}^{3+}$  cations.

The crystal chemistry of these minerals is clarified and the vacancies in sulphide sites as well as the incompleteness in cationic substitutions are explained. The lines for a systematic derivation of possible, yet unknown, related structures are developed.

### Introduction

Versiliaite and apuanite were described by Mellini *et al.* (1979); they showed the close chemical, physical, and crystallographic relationships of the two minerals with schafarzikite,  $\text{FeSb}_2\text{O}_4$ , from which versiliaite and apuanite can be derived by a concerted mechanism of insertion, substitution, and oxidation.

The aim of this paper is to describe and discuss the main features of their crystal structures and to develop a comprehensive crystal chemistry for the schafarzikite group of minerals.

### Structure determination

The experimental parameters characterizing the intensity data collection step are summarized in Table 1. Two equivalent sets were collected for both crystals; the diffraction intensities were corrected for the usual geometrical factors, as well as for absorption by the semiempirical method of North *et al.* (1968); symmetry-related reflections were thereafter checked for equivalence and averaged to pro-

duce the unique sets. In the subsequent structure-factor calculations, all the scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography, or calculated from them when a hybrid curve was used.

### Versiliaite

The structure determination was undertaken in the centrosymmetric space group  $Pbam$ , indicated by the statistical averages and distribution of  $E_{hkl}$  values; the choice appeared correct in the subsequent refinement stage. A trial model was built, starting from the parameters given by Fischer and Pertlik (1975) for schafarzikite and taking account of the doubled  $c$  parameter. The use of the scattering factors of antimony for atoms at  $z = 0.0$  and  $z = 0.25$  and of arsenic for an atom at  $z = 0.5$  led to the doubling of the  $c$  translation. Moreover we used the full reflections set, including the weakest ones corresponding to  $l = 2n + 1$ . The refinement was led by Fourier syntheses and least-squares cycles for all the three-coordinated and

Table 1. Crystal data and experimental details

	Versiliaite	Apuanite
Crystal dimensions	0.16x0.16x0.07 mm <sup>3</sup>	0.26x0.13x0.10 mm <sup>3</sup>
a	8.492(5) Å	8.372(5) Å
b	8.326(5)	
c	11.938(7)	17.974(10)
Space group	Pbam	P4 <sub>2</sub> /mbc
Radiation	Mo Kα	Mo Kα
Monochromator	graphite	graphite
Scan mode	θ-2θ	θ-2θ
Scan width	2.20°	2.00°
Scan speed	0.10° sec <sup>-1</sup>	0.10° sec <sup>-1</sup>
Scan range	2-30° in θ	2-30° in θ
Independent diffractions	1289	942

six-coordinated cations and the oxygen atoms. At this point a sulphur atom was introduced in the structure-factor calculations; it corresponded to a maximum located at 1/2, 1/2, 1/2, between two symmetry-related Fe(1) "arsenic" atoms at bond distances of nearly 2.1 Å. On the basis of the chemical data (Mellini *et al.*, 1979) and crystallographic and structural evidence, such as bond distances, thermal parameters, occupancy factors, and local valence balance, we obtained the cation distribution in the various sites (Table 2), from which we calculated the corresponding hybrid scattering curves. At the end of the isotropic refinement we obtained a reliability index  $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.08$ . The introduction of anomalous dispersion and anisotropic thermal parameters led to  $R_1 = 0.072$  and  $R_2 = 0.08$ , with  $R_2 = (\sum w |F_o| - |F_c|)^2 / \sum w |F_o|^2)^{1/2}$ , for all the reflections, including the 210 weakest ones with  $I_{obs} < 3\sigma(I_{obs})$ . The weight  $w$  was assigned as the reciprocal of the variance, estimated from counting statistics.

The final atomic positional and thermal parameters are reported in Table 3. Observed and calculated structure factors for versiliaite, as well as for apuanite, are deposited at the Business Office of the Mineralogical Society of America.<sup>1</sup>

#### Apuanite

The structural analysis was carried out by the same procedure previously described for versiliaite. First we built a model with six- and three-coordinated cations, then introduced oxygen atoms, and eventually we located the sulphur atom. As for versiliaite we

found the cation distribution in the various sites on the basis of chemical, crystallographic, and structural data (Table 2).

The refinement converged to  $R_1 = 0.068$ ; the introduction of anomalous dispersion and anisotropic thermal parameters led to  $R_1 = 0.051$  and  $R_2 = 0.058$  for all reflections, including 267 reflections with  $I_{obs} < 3\sigma(I_{obs})$ .

The final atomic positional and thermal parameters are reported in Table 4.

#### Description of the structures

The crystal structure of schafarzikite (Zemann, 1951; Fischer and Pertlik, 1975) is illustrated in Figures 1 and 6. It is built up by columns, running along [001], of edge-sharing Fe<sup>2+</sup> octahedra; parallel to these are chains of corner-sharing Sb<sup>3+</sup>  $\psi$ -tetrahedra, namely trigonal pyramids with a lone pair as fourth ligand (Cotton and Wilkinson, 1966, p. 461, 487).

All the oxygen atoms of each tetrahedral chain lie on one plane, parallel to (110); successive antimony atoms of the chain are located on opposite sides of this plane. The connection between chains and octahedral columns builds up a framework with open channels parallel to [001]. The diameter of the channels is related to the distance (4.1 Å) between antimony atoms lying on opposite sides of the channels and pointing their lone pairs one toward the other.

#### Versiliaite

The structural units in the structure of schafarzikite, namely chains and columns, are preserved in

Table 2. Sulphide occupancies and mixed scattering curves in the various cationic sites of the crystal structures of versiliaite and apuanite

Atom site	Versiliaite		Occupancy
	Distribution		
Fe(1)	0.75 Fe	0.25 Sb	1.0
Fe(2)	1.00 Fe		1.0
Fe(3)	0.75 Fe	0.25 Zn	1.0
Sb(1)	0.90 Sb	0.10 As	1.0
Sb(2)	0.90 Sb	0.10 As	1.0
S	1.00 S		0.8
Atom site	Apuanite		Occupancy
	Distribution		
Fe(1)	0.88 Fe	0.12 Sb	1.0
Fe(2)	1.00 Fe		1.0
Fe(3)	0.90 Fe	0.10 Zn	1.0
Sb	0.90 Sb	0.10 As	1.0
S	1.00 S		0.84

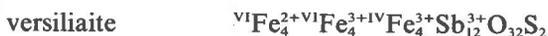
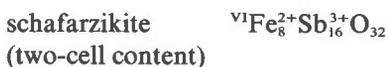
<sup>1</sup> To obtain a copy of these data, order Document AM-79-112 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, NW, Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 3. Atomic coordinates and thermal anisotropic parameters of versiliaite

Atom site	x	y	z	B <sub>eq.</sub>	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>
Fe(1) 4(g) m	0.3084(4)	0.3193(4)	0	1.20	42(4)	54(4)	15(2)	21(3)	0	0
Fe(2) 4(f) 2	0	1/2	0.3752(3)	0.32	7(4)	13(4)	7(2)	0(3)	0	0
Fe(3) 4(f) 2	0	1/2	0.1239(3)	0.36	10(3)	10(3)	9(2)	3(3)	0	0
Sb(1) 8(i) 1	0.1711(1)	0.1671(1)	0.2450(1)	0.23	6(1)	5(1)	7(1)	3(1)	-2(1)	0(1)
Sb(2) 4(h) m	0.3303(2)	0.3292(2)	1/2	0.38	6(2)	15(2)	10(1)	4(1)	0	0
S 2(a) 2/m	1/2	1/2	0	1.15	19(13)	32(14)	35(7)	-5(11)	0	0
O(1) 4(h) m	0.3610(19)	1.0993(20)	1/2	0.30	16(19)	15(19)	22(9)	7(15)	0	0
O(2) 8(i) 1	0.4003(13)	1.1350(13)	0.2438(9)	0.27	21(12)	13(13)	19(6)	5(10)	-1(8)	7(7)
O(3) 8(i) 1	0.3234(15)	0.8176(15)	0.3764(11)	0.93	30(15)	29(15)	20(7)	-4(13)	-8(9)	11(9)
O(4) 8(i) 1	0.1855(13)	0.3428(15)	0.1357(10)	0.72	16(13)	32(15)	15(7)	21(12)	-1(8)	-4(9)
O(5) 4(g) m	0.6070(20)	0.8915(21)	0	0.66	15(19)	20(20)	17(10)	11(16)	0	0

versiliaite, but every fourth  $\psi$ -tetrahedral cation is substituted by an Fe<sup>3+</sup> cation [Fe(1) in Figs. 2 and 3], whose coordination is enhanced to tetrahedral by insertion of a sulphide anion in the open channels between two Fe<sup>3+</sup> cations facing each other: the tetrahedral and  $\psi$ -tetrahedral chains are thus connected to build ribbons, two chains wide (Fig. 3). The charge balance, which is altered by the insertion of two sulphide anions in the unit cell, is restored by the oxidation of half the octahedral Fe<sup>2+</sup> cations to Fe<sup>3+</sup> cations: as required to have local charge balance, the octahedral cations in the highest oxidation state are those sharing vertices with the tetrahedrally-coordinated Fe(1) cations and correspond to Fe(3) sites in Figure 2.

From these insertions and substitutions, the following ideal cell content can be derived for versiliaite and compared with that of schafarzikite:



In versiliaite the structural layer between  $z = 1/4$

and  $z = 3/4$  is closely similar to the corresponding layer in schafarzikite.

#### Apuanite

Similarly the crystal structure of apuanite can be derived from that of schafarzikite by substituting every third  $\psi$ -tetrahedral cation by an Fe<sup>3+</sup> cation [Fe(1) in Figs. 4 and 5] and inserting sulphide anions in the open channels between pairs of Fe<sup>3+</sup> cations facing each other: the chains are thus connected to build sheets (Fig. 5). Two series of interlaced sheets parallel to (110) and ( $\bar{1}10$ ) are present in the structure, as described in Figure 6.

As in versiliaite the charge imbalance, due to the insertion of four sulphide anions in the unit cell, is compensated by the oxidation of eight Fe<sup>2+</sup> cations to Fe<sup>3+</sup> cations, located in Fe(3) site in Figure 4.

The following ideal cell content can be derived for apuanite and compared with that of schafarzikite:

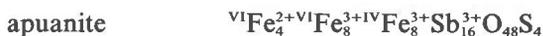


Table 4. Atomic coordinates and thermal anisotropic parameters of apuanite

Atom site	x	y	z	B <sub>eq.</sub>	β <sub>11</sub>	β <sub>22</sub>	β <sub>33</sub>	β <sub>12</sub>	β <sub>13</sub>	β <sub>23</sub>
Fe(1) 8(h) m	0.3098(3)	0.3179(3)	0	1.22	48(4)	49(4)	7(1)	12(2)	0	0
Fe(2) 4(d) 222	0	1/2	1/4	0.80	30(2)	30(2)	5(1)	15(7)	0	0
Fe(3) 8(f) 2	0	1/2	0.0829(1)	0.71	27(5)	25(4)	5(1)	4(4)	0	0
Sb 16(i) 1	0.1677(1)	0.1706(1)	0.1638(1)	0.52	18(1)	21(1)	4(1)	2(1)	1(1)	1(1)
S 4(a) 2/m	1/2	1/2	0	1.36	44(4)	35(13)	14(2)	31(7)	0	0
O(1) 16(i) 1	-0.0987(8)	0.3624(8)	0.1628(4)	0.52	18(9)	15(9)	5(2)	-1(7)	2(4)	-4(4)
O(2) 8(h) m	-0.1067(13)	0.3915(13)	0	0.76	39(17)	15(14)	6(3)	-4(12)	0	0
O(3) 16(i) 1	-0.1853(9)	0.6574(9)	0.0899(4)	0.71	30(10)	27(9)	4(2)	12(9)	3(4)	-1(4)
O(4) 8(g) 2	-0.1779(8)	0.6779	1/4	0.90	45(9)	45(9)	1(2)	-29(14)	3(4)	-3(4)

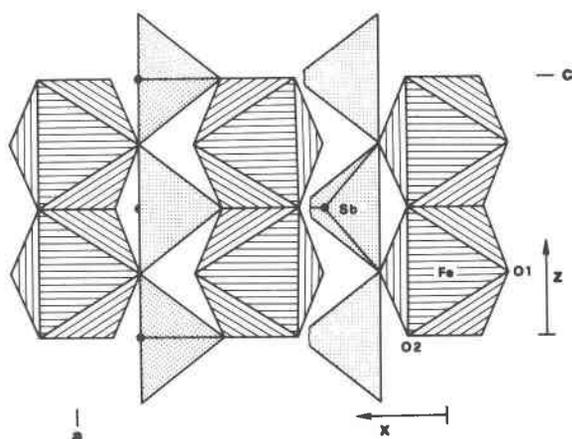


Fig. 1. Crystal structure of schafarzikite, as seen along [010].

### Bond lengths

Bond lengths and angles in versiliaite and apuanite are given in Tables 5 and 6 respectively. The mean bond lengths in Fe(2) and Fe(3) octahedral sites are 2.107 and 2.008 Å in versiliaite and 2.110 and 2.006 Å in apuanite; these values compare very well with the corresponding values 2.130 and 2.005 Å, obtained from the effective crystal radii given by Shannon and Prewitt (1969) for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  octahedrally coordinated by three-coordinated oxygen anions.

The Fe(1) tetrahedral sites, which are coordinated

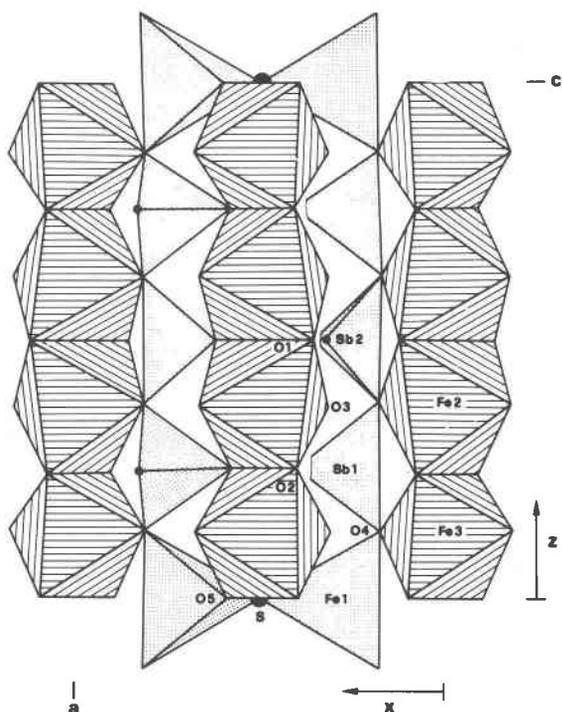


Fig. 2. Crystal structure of versiliaite, as seen along [010].

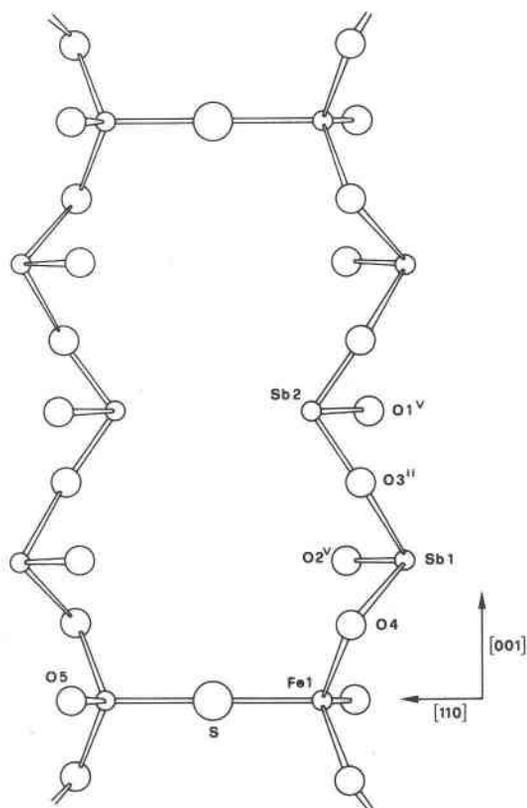


Fig. 3. Tetrahedral ribbon in versiliaite, as seen along  $[\bar{1}10]$ .

by three oxygen and one sulphide anions, present Fe(1)-O mean bond lengths of 1.92 Å in both compounds; this value appears larger than the value 1.85 Å corresponding to the effective crystal radius of  $\text{Fe}^{3+}$  in tetrahedral coordination, which can be accounted for by the partial substitution of  $\text{Sb}^{3+}$  in this site.

The Sb sites in both compounds present the well-known  $\psi$ -tetrahedral coordination, with three corners occupied by oxygen anions and the lone pair at the fourth corner. The mean bond lengths in the Sb site of apuanite and Sb(1) and Sb(2) sites of versiliaite are 1.981, 1.978, and 1.959 Å respectively. The same Sb coordination, with similar bond lengths, is also found in cubic  $\text{Sb}_2\text{O}_3$  (Svensson, 1975), in  $\text{Sb}_4\text{O}_5\text{Cl}_2$  (Sarnstrand, 1978), as well as in the minerals valentinite (Buerger and Hendricks, 1938; Svensson, 1974), sarabauite (Nakai *et al.*, 1978), schafarzikite (Zemann, 1951; Fischer and Pertlik, 1975), and derbylite (Moore and Araki, 1976).

### Crystal chemistry

The crystal-chemical formulae calculated from the microprobe data on the basis of 32 and 48 oxygen atoms in the unit cell were:

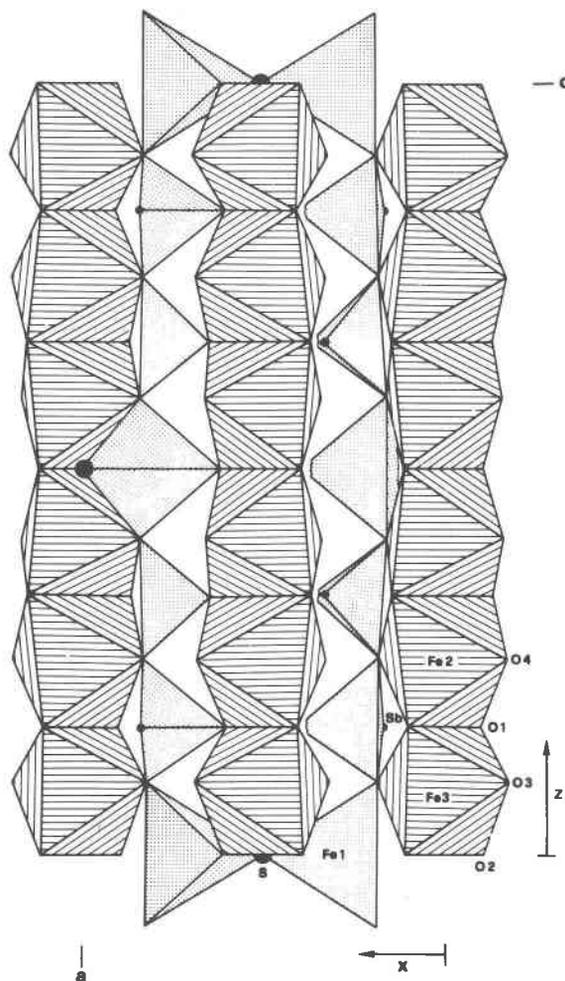
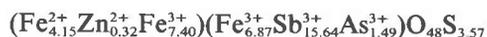
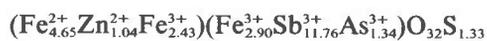


Fig. 4. Crystal structure of apuanite, as seen along [010].



for versiliaite and apuanite respectively (Mellini *et al.*, 1979). The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio was derived by taking into account the structural data, which indicated the presence of four  $\text{Fe}^{3+}$  cations for each sulphide anion. The values obtained for the cationic contents, namely 24.12 and 35.87, compare well with the theoretical values 24 and 36 for versiliaite and apuanite respectively. For both compounds the unit-cell contents give similar amounts of  $\text{Fe}^{3+}$  cations in octahedral and tetrahedral coordinations, which indicate the correctness of our structural considerations. The partial occupancies indicated by the crystal-chemical formulae were confirmed by the values of the final occupancy factors, which were 0.79 with  $B_{\text{eq}} = 1.15\text{Å}^2$  for versiliaite and 0.84 with  $B_{\text{eq}} = 1.36\text{Å}^2$  for apuanite. Moreover, according to our structural discussion

the vacancies in the sulphide sites should be reflected in a lower substitution of tetrahedral  $\text{Fe}^{3+}$  cations to  $\psi$ -tetrahedral cations relative to the theoretical formulae. In fact the cell contents for  $\psi$ -tetrahedral cations are 13.10 and 17.13 as compared with the theoretical values 12 and 16 for versiliaite and apuanite respectively.

Two further problems deserve consideration, namely the distribution of  $\text{Zn}^{2+}$  cations among octahedral sites and of  $\text{Sb}^{3+}$  and  $\text{As}^{3+}$  cations among tetrahedral and  $\psi$ -tetrahedral sites. As regards the first point, the chemical data (Mellini *et al.*, 1979) indicate a low zinc content in schafarzikite, where all the iron is present as  $\text{Fe}^{2+}$  cations, and in apuanite where the Fe(3) site is nearly fully occupied by  $\text{Fe}^{3+}$  cations, whereas the zinc content is high in versiliaite where the  $\text{Fe}^{3+}$  content is well below that required to fully occupy the Fe(3) sites. This indicates, in our view, that  $\text{Zn}^{2+}$  cations are preferred to  $\text{Fe}^{2+}$  cations in Fe(3) sites, which is in keeping with the indications which can be derived from the comparison of the effective crystal radii of  $\text{Zn}^{2+}$  (0.745Å) and  $\text{Fe}^{2+}$  (0.770Å) with the effective crystal radius of  $\text{Fe}^{3+}$

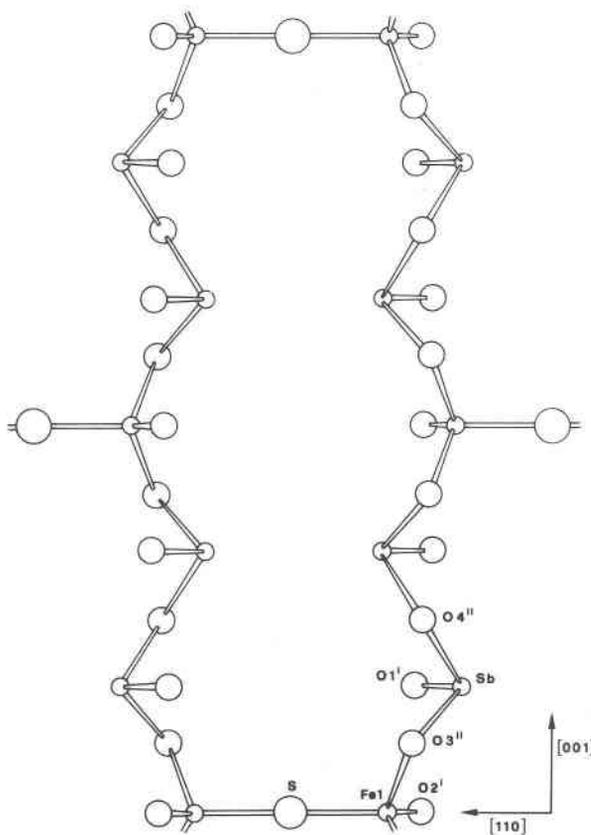


Fig. 5. Tetrahedral sheet in apuanite, as seen along [110].

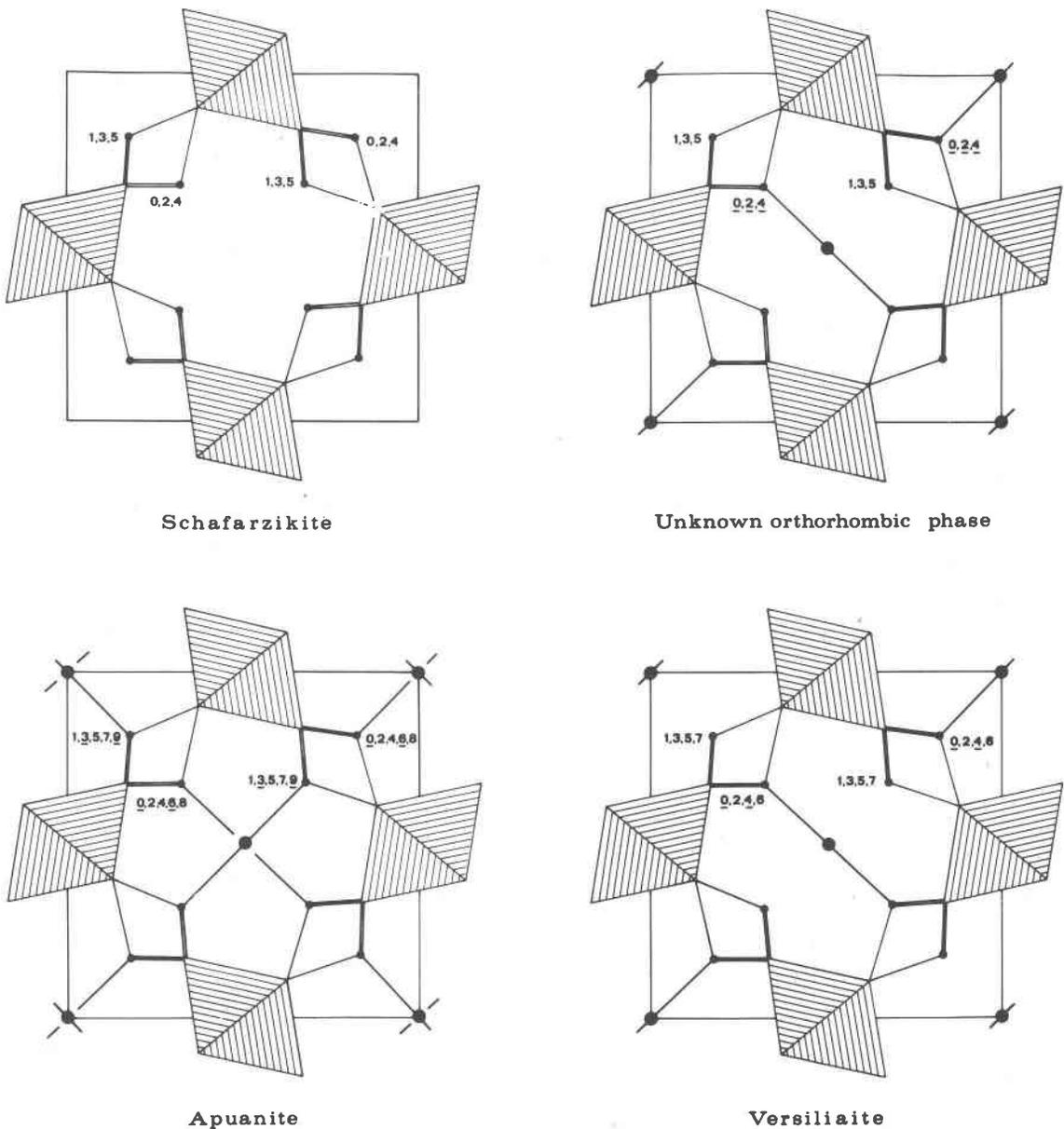


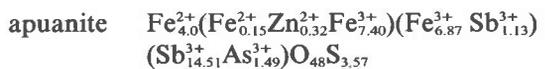
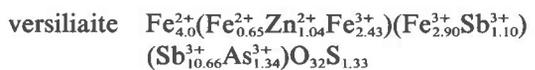
Fig. 6. Schafarzikite-like structures, as seen along [001].

(0.645A) (Shannon and Prewitt, 1969), and from the results obtained during the refinement stage.

As regards the second point, the heights of the maxima in the Fourier syntheses and the least-squares refinement strongly indicated a substantial substitution of  $\text{Fe}^{3+}$  cations by  $\text{Sb}^{3+}$  cations in Fe(1) sites in both compounds; therefore scattering factors ( $0.75f_{\text{Fe}} + 0.25f_{\text{Sb}}$ ) and ( $0.88f_{\text{Fe}} + 0.12f_{\text{Sb}}$ ) were assumed for Fe(1) site in versiliaite and apuanite respectively.

Thus the crystal chemical formulae which better

summarize the structural as well the chemical indications are:



It cannot be excluded, on the basis of the chemical and structural data at our disposal, that some arsenic follows antimony into the Fe(1) site.

Table 5. Bond distances and angles in versiliaite

Fe(1)-0(5) <sup>i</sup>	1.897(18) Å	0(5) <sup>i</sup> -Fe(1)-0(4)	107.3(5)x2°
-0(4)	1.936(12)x2	0(5) <sup>i</sup> -Fe(1)-S	110.5(5)
-S	2.216(3)	0(4)-Fe(1)-0(4) <sup>vi</sup>	113.5(5)x2
		0(4)-Fe(1)-S	109.1(4)
Fe(2)-0(1) <sup>iii</sup>	2.073(11)x2	0(2) <sup>v</sup> -Sb(1)-0(4)	91.8(5)
-0(2) <sup>ii</sup>	2.112(12)x2	0(2) <sup>v</sup> -Sb(1)-0(3) <sup>ii</sup>	93.7(5)
-0(3) <sup>iii</sup>	2.135(13)x2	0(4)-Sb(1)-0(3) <sup>ii</sup>	93.1(5)
average	2.107	average	92.9
Fe(3)-0(5) <sup>iv</sup>	1.957(11)x2	0(1) <sup>v</sup> -Sb(2)-0(3) <sup>ii</sup>	92.3(5)
-0(2) <sup>ii</sup>	2.013(11)x2	0(3) <sup>ii</sup> -Sb(2)-0(3) <sup>iii</sup>	96.8(5)
-0(4)	2.053(11)x2	average	93.8
average	2.008		
Sb(1)-0(2) <sup>v</sup>	1.963(11)		
-0(4) <sup>ii</sup>	1.964(12)		
-0(3)	2.008(13)		
average	1.978		
Sb(2)-0(1) <sup>v</sup>	1.932(16)		
-0(3) <sup>ii</sup>	1.972(13)x2		
average	1.959		

In Table 5 and in Figs. 2 and 3 the atoms of the different asymmetric units are related to the symmetry equivalent atoms of the fundamental unit as follows:

i	atom at	1-x	1-y	-z
ii	" "	1/2-x	-1/2+y	z
iii	" "	1/2-x	-1/2+y	1-z
iv	" "	1/2-x	-1/2+y	-z
v	" "	x	-1+y	z
vi	" "	x	y	-z

### Systematics of the schafarzikite group

Figure 6 gives a schematic representation of the crystal structures of schafarzikite, versiliaite, and apuanite, as viewed along [001]. As was previously described, four chains of corner-sharing tetrahedra or  $\psi$ -tetrahedra run in each unit cell, with subsequent cations in each chain at levels 0,  $c_o$ ,  $2c_o$ , ...  $nc_o$ , with  $c_o = 1/2 c_{schaf} \approx 3\text{Å}$ . The levels  $nc_o$ , at which substitutions of the  $\psi$ -tetrahedral  $\text{Sb}^{3+}$  cations by the tetrahedral  $\text{Fe}^{3+}$  cations occur, are indicated by the corresponding  $n$  values. The figure clearly shows that whereas isolated chains are found in the structure of schafarzikite, double-chain ribbons and interlaced layers are present in the structure of versiliaite and apuanite respectively.

To describe conveniently all the structures in the group, let us indicate with  $n$  and italic  $n$  respectively the level of  $\psi$ -tetrahedral and tetrahedral cations. A sequence of numbers and italic numbers thus indicates a kind of chain characterized by definite substitutions of  $\text{Sb}^{3+}$  by  $\text{Fe}^{3+}$  cations. The sequence (0,1),2,3, ..., for example, symbolizes the chain of schafarzikite, whereas the chains of versiliaite and apuanite are symbolized by the sequences (0,1,2,3),4,5 ... and (0,1,2,3,4,5),6,7 ... . In all the sequences the parentheses enclose tetrahedra and  $\psi$ -tetrahedra within a unit translation parallel to the  $c$  axis; odd- and even-numbered cations point toward opposite sides relative to the plane defined by the basal oxygen atoms.

Table 6. Bond distances and angles in apuanite

Fe(1)-0(2) <sup>i</sup>	1.887(16) Å	0(2) <sup>i</sup> -Fe(1)-0(3) <sup>iii</sup>	107.2(4)x2°
-0(3) <sup>ii</sup>	1.934(12)x2	0(2) <sup>i</sup> -Fe(1)-S	112.4(6)
-S	2.204(3)	0(3) <sup>iii</sup> -Fe(1)-0(3) <sup>iii</sup>	114.3(6)
		0(3) <sup>i</sup> -Fe(1)-S	107.9(3)
Fe(2)-0(4)	2.106(10)x2	0(3) <sup>ii</sup> -Sb-0(1) <sup>i</sup>	91.3(4)
-0(1)	2.113(11)x4	0(3) <sup>i</sup> -Sb-0(4) <sup>ii</sup>	93.2(5)
average	2.110	0(1) <sup>i</sup> -Sb-0(4) <sup>ii</sup>	93.1(3)
		average	92.5
Fe(3)-0(2)	1.960(13)x2		
-0(1)	2.018(11)x2		
-0(3)	2.039(9) x2		
average	2.006		
Sb-0(3) <sup>ii</sup>	1.964(11)		
-0(1) <sup>i</sup>	1.975(9)		
-0(4) <sup>ii</sup>	2.004(8)		
average	1.981		

In Table 6 and in Figs. 4 and 5 the atoms of the different asymmetric units are related to the symmetry equivalent atoms of the fundamental unit as follows:

i	atom at	1/2+x	1/2-y	z
ii	" "	-x	1-y	z
iii	" "	-x	1-y	-z

The chains are repeated in [100] and [010] directions by  $a$  and  $b$  glide planes: within this condition, each sequence represents not only a kind of chain, but also a complete structure, because all the structural features, such as insertion of sulphide anions and substitution of  $\text{Fe}^{2+}$  by  $\text{Fe}^{3+}$  cations in octahedral columns, are strictly related to the substitutions in the chains. Assuming this condition and the further condition of regularly spaced substitutions in the chains, the simplest possible structures are those reported in Table 7, together with the corresponding  $c$  value and space group. Table 7 shows that when the levels at which substitution of  $\text{Sb}^{3+}$  by  $\text{Fe}^{3+}$  cations occur are all even (or all odd), two-chain ribbons are formed, in orthorhombic structures with space group  $Pb\bar{m}$ , whereas when the substitutions occur in each chain at even as well at odd levels, with subsequent substitutions at a distance  $c/2$ , interlaced layers are formed, in tetragonal structures with space group  $P4_2/mbc$ .

The general crystal-chemical formula for all the minerals of the group can be easily derived. Let us call  $2n$  the number of tetrahedra or  $\psi$ -tetrahedra and  $2m$  the number of tetrahedra within a unit cell. The

Table 7. Possible structures in the schafarzikite group

Sequence	$c$	Space group	Phase
(0,1),2...	$2c_o$	$P4_2/mbc$	Schafarzikite
(0,1),2...	$2c_o$	$Pb\bar{m}$	Unknown
(0,1,2,3),4...	$4c_o$	$Pb\bar{m}$	Versiliaite
(0,1,2,3,4,5),6...	$4c_o$	$P4_2/mbc$	Apuanite
(0,1,2,3,4,5),6...	$6c_o$	$Pb\bar{m}$	Unknown

cell content for each mineral of the group can then be written as:



The formula indicates that  $m \leq n/2$ , which clearly shows the impossibility of the hypothetical structure  $(0,1), 2, \dots$  as in this case  $n = 2$  and  $m = 2$  and the charge balance cannot be obtained. Moreover, that structure is impossible also for structural reasons, since the interlacing of the sheets parallel to  $(110)$  and  $(\bar{1}10)$  would require sulphide anions at too small a distance  $c_0$ .

If we compare the ideal formulae for versiliaite and apuanite with those obtained for the actual structures, we observe that, apart from minor substitutions of  $\text{Fe}^{2+}$  by  $\text{Zn}^{2+}$  and of  $\text{Sb}^{3+}$  by  $\text{As}^{3+}$ , the most important differences lie in a deficiency of sulphide ions in the actual structures, together with a degree of substitution of  $\text{Sb}^{3+}$  by  $\text{Fe}^{3+}$  cations and of  $\text{Fe}^{2+}$  by  $\text{Fe}^{3+}$  cations, which appears incomplete relative to the theoretical values.

The deficiency of sulphide anions and the incompleteness in substitutions by  $\text{Fe}^{3+}$  cations appear relevant in versiliaite. This could be related, in our opinion, to the presence in this mineral, from  $z = 1/4$  to  $z = 3/4$ , of structural layers corresponding to the cell content  ${}^{\text{VI}}\text{Fe}_4{}^{2+} {}^{\text{III}}\text{Sb}_8\text{O}_{16}$ , strictly similar in all the chemical and structural features to the cell content of schafarzikite. In versiliaite such layers, which can be conveniently called schafarzikite-like or *S*-layers, alternate with layers  ${}^{\text{VI}}\text{Fe}_4{}^{3+} {}^{\text{IV}}\text{Fe}_4{}^{3+} \text{Sb}_4\text{O}_{16}\text{S}_2$ , strictly similar in chemistry and structure to those that make up the unknown structure of Figure 6 and which can be called *U*-layers. Similarly all the possible orthorhombic structures are ordered sequences of *S*- and *U*-layers, with *U*-layers regularly spaced in the sequence.

As both *S*- and *U*-layers would fit either with similar layers, as in schafarzikite (*SS* ... ) and in the unknown phase (*UU* ... ), or with different layers, as in versiliaite (*SUSU* ... ), the possibility arises of crystals growing as successions of various well-fitted domains. In this context we should interpret the sul-

phide deficiency as evidence for the presence of schafarzikite-like domains beside domains of ideal versiliaite: in other words single *S*-layers would act as seeds on which a whole schafarzikite-like domain could develop. Obviously more research with a powerful technique such as transmission electron microscopy coupled with X-ray crystallography is necessary to confirm or reject such a hypothesis.

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