Eur. J. Mineral.
1999, **11**, 949-954

Lead-antimony sulfosalts from Tuscany (Italy). I. Scainiite, $Pb_{14}Sb_{30}S_{54}O_5$, the first Pb-Sb oxy-sulfosalt, from Buca della Vena mine

PAOLO ORLANDI [1] *, YVES MOËLO [2]**, ALAIN MEERSCHAUT [2]
and PIERRE PALVADEAU [2]

[1] Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53,
I-56126 Pisa, Italy

[2] Laboratoire de Chimie des Solides, Institut des Matériaux J. Rouxel, UMR CNRS 6502,
2, rue de la Houssinière, 44 322 Nantes Cedex 3, France

Abstract: The new mineral scainiite, $Pb_{14}Sb_{30}S_{54}O_5$, the first lead oxy-sulfosalt, has been found at Buca della Vena mine in the Apuan Alpes, northern Tuscany, Italy. Scainiite occurs as black acicular crystals with bluish metallic lustre, elongated [010], up to 2 mm long and 0.2 mm thick. The mineral is brittle, opaque; $VHN_{20} = 192$ kg/mm², $d_{calc.} = 5.56$ g/cm³. In reflected light it shows a low anisotropy and bireflectance, and rare red internal reflections. Its ideal chemical formula, derived from electron-microprobe data and from crystal structure refinement, is $Pb_{14}Sb_{30}S_{54}O_5$. Scainiite is monoclinic, space group *C2/m*, *a* = 52.00(2), *b* = 8.148(2), *c* = 24.31(6) Å, *β* = 104.09(4)°, *Z* = 4. The strongest five lines of the X-ray powder diffraction pattern are [d in Å(I)(hkl)]: 3.472(100)($\overline{14}$ 0 4), 2.956(54) (6 2 4, $\overline{12}$ 2 1), 2.052(46)($\underline{14}$ 0 8, $\underline{24}$ 0 1), 3.041(35)($\overline{4}$ 0 8), 2.228(22)($\underline{22}$ 0 1, $\overline{22}$ 0 6, $\overline{8}$ 2 9). Scainiite is a structural derivative of synthetic hexagonal $Ba_{\sim12}Bi_{\sim24}S_{48}$, a member of cyclically twinned sulfosalt structures (zinkenite group). Scainiite crystallized in small fractures of dolomitic lenses in massive Fe-Ba ore, together with many Pb-Sb sulfosalts. The formation of this unique lead oxy-sulfosalt is related to narrow $fO_2 - fS_2$ conditions, corresponding to the magnetite-hematite-pyrite buffer at relatively high temperature (> 300°C).

Key-words: scainiite, new mineral species, sulfosalt, lead, antimony, oxy-sulfide, Tuscany, Italy.

Introduction

The Buca della Vena mine is a small iron and barite deposit, located in the southern part of the Apuan Alps, near Pietrasanta (Tuscany, Italy), at 2° 09' 31" longitude east, 43° 59' 55" latitude north, and an altitude of 479 m. During a general mineralogical study (Orlandi & Checchi, 1986), two unknown acicular lead sulfosalts were discovered. The reexamination of these sulfosalts, together with the resolution of their crystal structure, permitted to define them as new mineral species, approved by the Commission of the I.M.A. (CNMMN). This first paper presents the definition of one of these two species, scainiite, the first known lead oxy-sulfosalt, with the formula $Pb_{14}Sb_{30}S_{54}O_5$ (CNMMN vote n° 96-014, accepted 30 April 1997). The other species, a chloro-sulfosalt, will be presented in a separate paper (Orlandi *et al.*, in prep.).

The name of scainiite is in memory of the late Dr. Giuseppe Scaini (Milano, 1906 - Piacenza, 1988), engineer and skilful investigator of systematic and Italian mineralogy. The type material has been deposited at Museo di Storia Naturale e del Territorio (Università di Pisa, Via Roma 103,

---

*e-mail: orlandi@dst.unipi.it
**e-mail: moelo@cnrs.imn.fr

0935-1221/99/0011-0949 $ 1.50

I-56011 Calci (PI), Italy; catalogue numbers: 15521, 15522, 15523) and at the Musée de l'Ecole des Mines de Paris, France.

1. Occurrence, paragenesis and geological setting

Scainiite was found at the Buca della Vena mine, a small Fe-Ba deposit in the Apuan Alps (northern Tuscany), where many rare minerals were recently found, like apuanite, versiliaite, schafarzikite, derbylite and stibivanite (Mellini *et al.*, 1979, 1986; Orlandi & Checchi, 1986). The Ba-Fe deposit of Buca della Vena mine, exploited for barite and iron oxides up to 1988, consists of a fine-grained mixture of barite, iron oxides (magnetite and hematite), minor pyrite, and various sulfides and sulfosalts. The mineralization is hosted within two carbonate lenses of dolomite limestones of Upper Triassic age (Grezzoni) and marble, interbedded with lenses of phyllite (Benvenuti *et al.*, 1986). The ore body and the hosted rocks show evident deformation features, which have been referred to a first compressive tectonic phase dating back 26 m. y. (Kligfield *et al.*, 1986). Measured homogenization temperatures in beryl crystals from the ore body (Duchi *et al.*, 1993) ranged from 250°C to 340°C, in good agreement with the metamorphic grade of the area, referred to the greenschist facies.

Carmignani *et al.* (1972, 1975, 1976) considered this ore deposit to be a metasomatic replacement of carbonate rocks, genetically connected to a hypothetical synkinematic intrusive body. On the other hand Cortecci *et al.* (1985), on the basis of isotope analysis of sulfates and sulfides, concluded that the deposit is sedimentary in origin, and was subsequently metamorphosed and partly remobilized during the Tertiary Apenninic orogeny.

Scainiite occurs in late extensional calcite veins that cut the Ba-Fe ore body as well as the phyllites and the dolomitic limestones. In these calcite veins, scainiite is associated with many other lead-antimony acicular sulfosalts like zinkenite, boulangerite, robinsonite, tintinaite, sorbyite, the new chloro-sulfosalt referred in the introduction, and other compounds not yet fully characterized. All these acicular sulfosalts are morphologically very similar to each other; a distinction between them is not possible macroscopically but only by testing every crystal with X-ray diffraction methods. Other minerals associated with scainiite are sphalerite, cinnabar, galena, andorite, bournonite, tetrahedrite, chalcostibite, gersdorffite, barite, cerussite and stibiconite.

2. Appearance and physical properties

Crystals of scainiite are acicular, elongated [010] up to 2 mm long and 0.2 mm thick (Fig. 1), black in colour with bluish metallic lustre. The bluish colour apparently arises from a superficial, very low hydrothermal alteration of the crystals. In the same veins where scainiite occurs, bluish acicular crystals of stibnite were also found. Scainiite is opaque, non-fluorescent, brittle and shows an irregular fracture. Calculated density is 5.56 g/cm^3; micro-hardness VHN$_{20}$ is close to 192 kg/mm^2. In reflected light scainiite shows low anisotropy, and low bireflectance values (Table 1). Pleochroism was not observed, and red internal reflections are rare.

According to Fig. 2, the reflectance curves of scainiite in air and oil are very close to (but a little bit lower than) the minimum curves of zinkenite (Criddle & Stanley, 1993). This great similarity is due firstly to the Pb/Sb atomic ratios of these two sulfosalts (~ 0.47 for scainiite, ~ 0.41 for zinken-

Fig. 1. Acicular scainiite crystals (Scanning electron microscope; scale bar = 1 mm).

Table 1. Reflectance (%) of scainiite (basal section) from 400 to 800 nm in air and oil. Data for the four COM wavelengths are interpolated.

λ (nm)	R_{air}	R_{oil}	λ (nm)	R_{air}	R_{oil}	λ (nm)	R_{air}	R_{oil}	λ (nm)	R_{air}	R_{oil}
400	37.5	22.1	500	36.6	20.3	600	34.1	17.8	700	31.1	15.3
410	38.3	21.7	510	36.3	20.0	610	34.0	17.5	710	30.9	15.6
420	38.0	21.8	520	36.2	19.7	620	33.4	17.7	720	30.9	15.0
430	38.1	22.3	530	36.2	19.3	630	33.0	16.9	730	30.7	14.7
440	37.6	21.6	540	35.6	19.2	640	32.8	16.8	740	30.2	14.6
450	37.6	21.4	550	35.4	19.2	650	32.8	16.5	750	30.2	14.4
460	37.6	21.0	560	35.4	18.8	660	32.4	16.1	760	29.8	14.8
470	37.3	19.9	570	35.2	18.9	670	31.7	16.4	770	29.9	14.3
480	37.0	20.7	580	34.7	18.5	680	32.0	15.9	780	29.2	13.8
490	36.7	20.6	590	34.4	18.3	690	31.4	16.0	790	29.6	14.5
									800	29.8	12.3
470	37.3	*19.9*	***546***	35.5	*19.2*	***589***	34.4	*18.3*	***650***	32.8	16.5

Polishing method : 600/1200 mesh carborundum (paper) ; 6, 3, 1 and ¼ diamond on cloth ; final buffing with Cr_2O_3 on cloth. LEICA DMR microscope with objectives FLUOTAR 20x/0.50 POL (air) and OEL 50x/0.85 (oil). Microscope photometer : Leica MPV-SP , monochromator : λ = 2 nm. Standard : SiC (NPL n°50).

ite), and secondly to the relationship between the crystal structures (Moëlo *et al.*, submit.). The highest Pb/Sb ratio of scainiite would normally increase the mean reflectance, as observed in the group of acicular Pb-Sb sulfosalts (boulangerite family), but this tendency is largely compensated by the oxygen content, which lowers this reflectance (compare for instance the reflectance data of stibnite, Sb_2S_3, and kermesite, Sb_2S_2O – Criddle & Stanley, 1993).

3. Crystallography

X-ray single-crystal study (Weissenberg, precession and image-plate technique) indicated that scainiite is monoclinic with space group *C2/m*. Cell parameters obtained from image-plate technique are: a = 51.996(8), b = 8.148(1), c = 24.311(4) Å, β = 104.09(1)°, V = 9991(10) Å^3, Z = 4. The X-ray powder diffraction pattern of scainiite, collected with a Gandolfi camera of 114.6 mm in diameter and Cu$K\alpha$ radiation, is reported in Table 2. Due to the high number of atoms in the unit cell, an attempt to compute the X-ray powder pattern from the crystal structure was unsatisfactory. Finally, the measured powder pattern was indexed after selection of the main diffraction intensities of the crystal structure study. On this basis, the calculated unit cell from the powder pattern gives a = 52.01(3), b = 8.13(1), c = 24.34(2) Å, β = 104.03(7)°, $V_{calc.}$ = 9985 Å^3, in good agreement with the data from the crystal-structure study (Moëlo *et al.*, submit.).

4. Chemistry

Electron microprobe analyses were carried out in two steps (Table 3).

- First with an ARL-SEMQ apparatus at Modena University (operating conditions: 20 kV accelerating voltage, 20 nA sample current, 5 µm beam size). Standards used were (elements, emis-

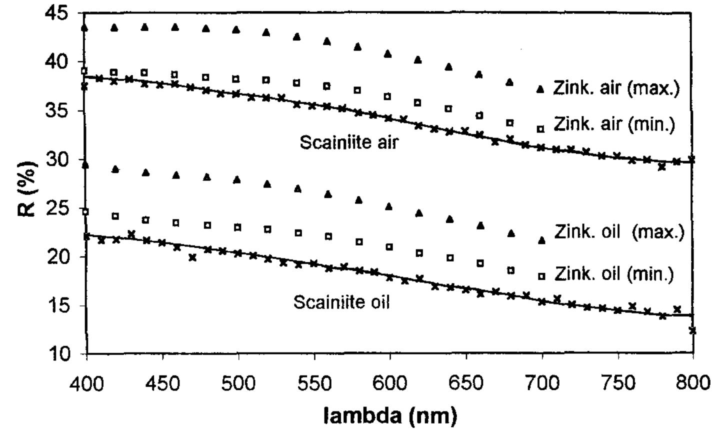

Fig. 2. Reflectance curve of scainiite in air and oil from 400 to 800 nm (basal section). Comparison with the two reflectance curves of zinkenite from 400 to 700 nm (Criddle & Stanley, 1993).

Table 2. X-ray powder pattern of scainiite.

I obs	d meas	d calc	*h*	*k*	*l*
13	4.039	4.0405	$\bar{2}$	0	6
		3.7750	$\bar{8}$	0	6
11	3.773	3.7730	4	2	1
4	3.706	3.7070	$\overline{14}$	0	2
		3.6318	$\bar{2}$	2	3
11	3.622	3.6264	$\overline{14}$	0	3
		3.4758	$\bar{4}$	0	7
100	3.472	3.4731	$\overline{14}$	0	4
18	3.441	3.4452	10	0	4
		3.0526	$\bar{6}$	2	5
35	3.041	3.0423	$\bar{4}$	0	8
		2.9615	$\overline{12}$	2	1
54	2.956	2.9551	$\overline{12}$	2	2
		2.9471	10	2	2
		2.8330	$\bar{6}$	2	6
20	2.827	2.8272	0	2	6
		2.8142	$\overline{12}$	2	4
		2.7168	$\overline{18}$	0	5
8	2.706	2.7078	18	0	1
		2.7026	$\bar{4}$	0	9
		2.6965	$\overline{12}$	2	5
8	2.628	2.6259	14	2	1
		2.6237	0	0	9
		2.6218	$\bar{6}$	2	7
5	2.441	2.4403	$\overline{14}$	2	6
		2.3613	0	0	10
5	2.356	2.3548	$\overline{18}$	2	2
		2.3486	16	2	2
		2.3014	10	2	6
7	2.296	2.2999	2	0	10
		2.2934	22	0	0
		2.2313	22	0	1
		2.2306	$\overline{22}$	0	6
22	2.228	2.2269	$\bar{8}$	2	9
		2.1039	18	2	3
2	2.100	2.1023	24	0	0
		2.0964	2	0	11
		2.0540	8	0	10
46	2.052	2.0526	14	0	8
		2.0506	24	0	1
		2.0096	$\overline{16}$	2	9
8	2.006	2.0002	$\overline{26}$	0	3
8	1.973	1.9687	6	0	11
		1.9678	0	0	12
12	1.947	1.9520	4	2	10
9	1.898	1.8968	26	0	1
		1.8962	8	0	11
6	1.867	1.8673	24	2	0
4	1.827	1.8316	14	2	8

Gandolfi camera, diameter 114.6 mm, Fe *K*α radiation, $\lambda = 1.93728$ Å. Indexed with $a = 52.01(3)$, $b = 8.13(1)$, $c = 24.34(2)$ Å, $\beta = 104.03(7)°$, V = 9985 Å^3.

sion lines): "546-PbS (GC)" (Pb*M*α and S*K*α), "531 chalcopyrite chgo/31 st. block" (Cu*L*α), "568-Sb_2S_3 syn J.C.-30" (Sb*L*α), and a natural albite for oxygen (O*K*α, with PbSD (lead stearate) wavelength dispersive spectrometer).

- A new set of microprobe analyses was performed after the resolution of the crystal structure, in order to confirm the oxygen content, and to determine the chemistry of the single crystal used for this crystal structure study. For this, the second half part of the studied acicular crystal was mounted in epoxy perpendicularly to its elongation, and then carefully polished until the appearance of a rectangular section under the metallographic microscope. Microprobe analysis was performed with a Cameca SX 50 apparatus (Common Analytical Laboratory of BRGM - CNRS - University of Orléans). Analytical conditions: accelerating voltage of 20 kV for all elements, oxygen excepted (10 kV); beam current, 20 nA; counting time for each spot analysis, 10 s; standards (elements, emission lines), PbS (Pb*M*α), Sb_2S_3 (Sb*L*α), FeS_2 (S*K*α), Cu (Cu*L*α), SnO_2 (O*K*α, with PC1-type wavelength dispersive spectrometer). Simultaneously with this scainiite crystal, natural stibnite, galena, boulangerite, zinkenite and füloppite were analysed, in order to control the concentration of major elements (Pb, Sb and S).

Copper was not detected in this crystal of scainiite, while the oxygen peak was clearly apparent: peak = 139(19) c/s; background = 35(2) c/s (mean of 10 analyses), corresponding to 0.87(15) wt.% oxygen, with a detection limit of 0.05 wt.%. Nevertheless, analysis of the other sulfides and sulfosalts shows systematically a small oxygen content: galena and boulangerite 0.22(3), zinkenite 0.22(4), füloppite 0.27(2) and stibnite 0.20(4) wt.%. This very probably indicates a small oxide film at the surface of the polished samples (a very old polished section of zinkenite showed a higher oxygen

Table 3. Microprobe analyses of scainiite.

a – Weight %

Probe	Pb	Sb	Cu	S	O	Total
ARL	36.31	42.38	0.12	19.72	(1.9)*	99.49**
Range	36.20/36.74	41.91/42.57	0.06/0.43	19.61/19.93		
SX 50***	36.99(33)	41.80(37)	n. d.	20.39(20)	0.65(15)	99.83(64)
Theor.	34.68	43.67	---	20.67	0.96	100

b – Structural formula (basis : Pb + Sb = 44 at.)

		Pb/Sb (at.)
ARL	$Pb_{14.7}Cu_{0.2}Sb_{29.3}S_{51.7}O_x$	0.502
SX 50	$Pb_{15.05}Sb_{28.95}S_{53.62}O_{3.43}$	0.520
Theor.	$Pb_{14}Sb_{30}S_{54}O_5$	0.467

* albite std. – overestimated . ** without O. ***Mean of 10 spot analyses

content, around 0.5 wt.%). Thus an oxygen content of 0.22 wt.% has been subtracted for this second set of analyses of scainiite (Table 3); the final result (0.65(15) wt.%) is a little bit lower, but close to the theoretical one given by the crystal structure analysis (0.96 wt.% – Moëlo *et al.*, submit.).

In the two microprobe analyses, the Pb/Sb ratio is significantly higher than that of the structural formula (Table 3b – see discussion below).

5. Crystal chemistry

Due to its complexity and relationship to other compounds, the crystal structure of scainiite will be presented in a separate paper (Moëlo *et al.*, submit.). It is an expanded derivative of synthetic hexagonal $Ba_{\sim 12}Bi_{\sim 24}S_{48}$ (Aurivillius, 1983), by insertion of a kermesite-type rod, where the oxygen atoms are located. Thus scainiite is a derivative of cyclically twinned sulfosalt structures (zinkenite group), as defined by Makovicky (1985).

A full-site model gives the structural formula $Pb_{14}Sb_{30}S_{54}O_5$; nevertheless, one must point out that this structural formula has a Pb/Sb ratio significantly lower than those obtained by microprobe analysis (Table 3). One explanation could be the incorporation of a minor amount of copper through the heterovalent substitution $Sb \rightarrow Pb + Cu$, as in zinkenite (Moëlo, 1983). The general structural formula would become: $Cu_xPb_{14+x}Sb_{30-x}S_{54}O_5$. For Pb/Sb = 0.50, one has x = 0.67, *i.e.* 0.50 wt.% Cu; for Pb/Sb = 0.52, x = 1.05, *i.e.* 0.78 wt.% Cu. These Cu contents largely exceed those obtained by microprobe analysis, ruling out such a substitution mechanism.

A second possible substitution could be chlorine incorporation (Breskovska *et al.*, 1982; Kostov & Macicek, 1995): $Sb + S \rightarrow Pb + Cl$. The structural formula $Pb_{14+x}Sb_{30-x}S_{54-x}Cl_xO_5$ gives the same *x* values, and Cl close to 0.30 and 0.43 wt. %. However, Cl was not detected. Another substitution, $3\,Pb \rightarrow 2\,Sb + \square$, would decrease the Pb/Sb ratio. Thus the discrepancy between the microprobe and crystallographic formulas remains unexplained, and the stoichiometric formula given by the crystal structure study is proposed for the time being as the ideal one for scainiite.

6. Conditions of formation of scainiite

The geological history of the Ba-Fe deposit of Buca della Vena is very complex, and its genesis always debatable: metasomatic replacement of carbonate rocks according to Carmignani *et al.* (1976) and Checchi (1978), or metamorphosed syn-sedimentary (Cortecci *et al.*, 1985). However that may be, scainiite has crystallized together with other sulfosalts in the latest hydrothermal stage, in narrow fractures cutting the dolomitic lenses.

The numerous rare minerals described by Orlandi & Checchi (1986) in carbonate vugs are probably related to the same mineralizing process. According to these authors, the minor (Pb, Sb, Cu...) or rare elements (Be, Ti, V) forming these species would have been leached from the surrounding rocks, especially the carbonate lens. At a regional scale, the Pb-Sb stage of deposition must be related to similar Pb-Sb concentrations in the same district, for instance the well known deposit of Bottino (type locality for meneghinite – Bechi, 1852), or the Pb-Sb-(As) sulfosalts in the Seravezza and Carrara marble quarries (Orlandi & Franzini, 1994; Orlandi *et al.*, 1996).

The original formation of scainiite implies very specific geochemical conditions. In nature, there are very few oxy-sulfides, always very rare. Kermesite, Sb_2S_2O, is the most frequently encountered, and reflects narrow fO_2/fS_2 conditions, permitting the partial oxidation of antimony by oxygen. As kermesite is generally formed in the supergene oxidation of stibnite ores, in very strong disequilibrium conditions, its specific fO_2/fS_2 conditions of formation are relatively constrained, favouring the direct formation of antimony oxides and hydroxides. Sometimes, the formation of well-crystallized kermesite is related to a hydrothermal process, with relative stability of fO_2/fS_2 conditions. In a similar way, the formation of well-crystallized scainiite must indicate relatively stable fO_2/fS_2 conditions. At Buca della Vena mine, these conditions were apparently assumed by the buffer effect of the massive iron ore, with the equilibrium between pyrite, hematite and magnetite. This buffer effect is also illustrated by the formation of rare minerals of the oxysulfide type (apuanite, $Fe^{2+}_4Fe^{3+}_{16}Sb^{3+}_{16}O_{48}S_4$, and versiliaite, $Fe^{2+}_4Fe^{3+}_8Sb^{3+}_{12}O_{32}S_2$; Mellini *et al.*, 1979), as well as minerals where the two oxidation states of iron coexist (apuanite, versiliaite and derbylite, $Fe^{2+}_{0.45}Fe^{3+}_{2.90}Ti^{4+}_{3.66}Sb_{0.99}O_{13.11}OH$; Mellini *et al.*, 1986).

The role of temperature is not known. One must point out that the formation of robinsonite, associated with scainiite, implies a relatively high temperature (over 318°C), according to experimental data (Craig *et al.*, 1973). This is in accordance with the upper range of homogenization temperatures measured in beryl crystals (from 250°C to 340°C; Duchi *et al.*, 1993).

Among Pb-Sb acicular sulfosalts, scainiite has a low Pb/Sb ratio, between those of zinkenite and robinsonite, and its optical properties are quite dull (like zinkenite). Thus the presence of scainiite in a Pb-Sb ore may easily go unnoticed. The best way to detect it is to perform an X-ray study on selected single crystals, when possible; in massive ore, that is the general case, the only way for its detection would be the systematic microprobe analysis with oxygen programming, on very freshly polished sections.

Acknowledgements: We sincerely thank Franco Jarnò, mineral amateur of the Gruppo Ricerche Geologiche di Prato, who kindly gave us the first samples of scainiite for study. Drs. C. J. Stanley and C. Chopin are thanked for there helpful comments and careful revision of the manuscript. We greatly appreciate the assistance of Prof. G. Vezzalini and Dr. S. Bigi (Dipartmento di Scienze della Terra, Modena) for ARL-SEMQ microprobe analysis, and O. Rouer (CNRS Orléans) for CAMECA microprobe analysis.

References

Aurivillius, B. (1983): The crystal structure of two forms of $BaBi_4S_2$. *Acta Chemica Scandinavia*, **A 37**, 399-407.

Bechi, E. (1852): Intorno a un nuovo minerale (meneghinite). *Atti Acc. Georgofili*, **XXX**, 84.

Benvenuti, M., Lattanzi, P., Tanelli, G., Cortecci, G. (1986): The Ba-Fe-pyrite deposit of Buca della Vena, Apuan Alps, Italy. *Rend. Soc. Ital. Mineral. Petr.*, **41**, 347-358.

Breskovska, V.V., Mozgova, N.N., Bortnikov, N.S., Gorshkov, A.I., Tsepin, A.I. (1982): Ardaite – a new lead-antimony chlorosulphosalt. *Mineral. Mag.*, **46**, 357-361.

Carmignani, L., Dessau, G., Duchi, G. (1972): I giacimenti minerari delle Alpi Apuane e loro correlazioni con l'evoluzione del gruppo montuoso. *Mem. Soc. Geol. Ital.*, **11**, 417-431.

—, —, — (1975): Una mineralizzazione sintettonica: il giacimento di Valdicastello (Alpi Apuane). Rapporti tra tettonica e minerogenesi in Toscana. *Boll. Soc. Geol. Ital.*, **94**, 725-758.

—, —, — (1976): I giacimenti a barite, pirite e ossidi di ferro delle Alpi Apuane. Studio minerogenetico e strutturale. *Boll. Soc. Geol. Ital.*, **95**, 1009-1061.

Checchi, F. (1978): Studio strutturale e giacimentologico della zona compresa tra Pontestazzemese e Foce di Mosceta, Alpi Apuane. Thesis, University of Pisa.

Cortecci, G., Lattanzi, P., Tanelli, G. (1985): Barite-iron-oxide-pyrite deposits from Apuane Alps (Northern Tuscany, Italy). *Geol. Zborn.-Geol. Carpath.*, **36**, 347-357.

Craig, J.R., Chang, L.L.Y., Lees, W.R. (1973): Investigations in the Pb-Sb-S system. *Can. Mineral.*, **12**, 199-206.

Criddle, A.J. & Stanley, C.J. (1993): Quantitative data file for ore minerals (QDF3, COM-IMA). Chapman & Hall ed., London, 700 p.

Duchi, G., Franzini, M., Giamello, M., Orlandi, P., Riccobono F. (1993): The iron-rich beryls of Alpi Apuane. Mineralogy, chemistry and fluid inclusion. *N. Jb. Miner. Mh.*, **1993/5**, 193-207.

Kligfield, R., Hunziker, J., Dallmeyer, R.D., Schamel, S. (1986): Dating of deformation phases using K-Ar and $^{40}Ar/^{39}Ar$ techniques: Results from the northern Apennines. *J. structural Geol.*, **8**, 781-798.

Kostov, V.V. & Macicek, J. (1995): Crystal structure of synthetic $Pb_{12.65}Sb_{11.35}S_{28.35}Cl_{2.65}$ – A new view of the crystal chemistry of chlorine-bearing lead-antimony sulphosalts. *Eur. J. Mineral.*, **7**, 1007-1018.

Makovicky, E. (1985): Cyclically twinned sulphosalt structures and their approximate analogues. *Z. Kristallogr.*, **173**, 1-23.

Mellini, M., Merlino, S., Orlandi, P. (1979): Versiliaite and apuanite, two new minerals from the Apuan Alps, Italy. *Am. Mineral.*, **64**, 1230-1234.

Mellini, M., Orlandi, P., Vezzalini, G. (1986): V-bearing derbylite from the Buca della Vena mine, Apuan Alps, Italy. *Mineral Mag.*, **50**, 328-330.

Moëlo, Y. (1983): Conditions naturelles de formation des sulfosels de Pb/Sb. In *Documents du BRGM*, BRGM ed., Orléans, **55**, 624 p.

Orlandi, P. & Checchi, F. (1986): The Buca della Vena mine, Tuscany, Italy. *The Mineralogical Record*, **17**, 261-268.

Orlandi, P., Del Chiaro, L., Pagano, R. (1996): Minerals of the Seravezza marble, Tuscany, Italy. *The Mineralogical Record*, **27**, 47-58.

Orlandi, P. & Franzini, M. (1994): I minerali del marmo di Carrara. Cassa di Risparmio di Carrara ed., 109 p.

Received 12 February 1999
Modified version received 8 July 1999
Accepted 12 July 1999