

Lead-antimony sulfosalts from Tuscany (Italy). X. Dadsonite from the Buca della Vena mine and Bi-rich izoklakeite from the Seravezza marble quarries

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Abstract - two very rare Pb sulfosalts, dadsonite and izoklakeite, discovered in the apuan alps, represent the first italian occurrence and were characterized by electron probe microanalysis and X-ray diffraction. dadsonite from the Buca della vena Ba-Fe deposit (two samples) has formula $Pb_{22.64}sb_{24.90}S_{60}Cl_{1.12}$ and $(Pb_{22.90}Cu_{0.01})sb_{25.12}S_{60}Cl_{1.07}$, in fair agreement with the ideal formula $Pb_{23}sb_{25}S_{60}Cl$. XRPD gives the monoclinic unit cell a 19.058(3), b 8.234(2), c 17.352(3) Å, β 96.33(2)°. dadsonite, with both pillaitite and pellouxite, is the third chloro-sulfosalts from Buca della vena, that reveals a high chlorinity of mineralizing solutions. izoklakeite from seravezza has the mean composition (wt.%) Pb 45.69, Bi 24.89, sb 8.16, Cu 1.08, ag 0.74, Hg 0.29, s 15.43, se 2.86, sum 99.14, with structural formula $Cu_{1.92}[ag_{0.77}Hg_{0.16}Pb_{24.49}(Bi_{13.23}sb_{7.44})_{\Sigma=20.67}]_{\Sigma=46.09}(S_{53.43}se_{4.02})_{\Sigma=57.45}$. it is a Bi-rich izoklakeite, close to the ideal Fe- and ag-free formula, $Cu_2Pb_{26}(Bi, sb)_{20}S_{57}$. significant se and Hg contents constitute chemical peculiarities of this occurrence. XRPD gives the orthorhombic unit cell a 34.272(4), b 38.351(5), c 4.098(1) Å.

Riassunto - viene descritto il primo ritrovamento italiano di due solfosali di Pb molto rari, dadsonite e izoklakeite; essi sono stati identificati sulle alpi apuane e caratterizzati mediante analisi in microsonda

elettronica e diffrazione di raggi X. La dadsonite, rinvenuta nel deposito a Ba-Fe di Buca della vena, ha mostrato, nei due campioni analizzati, formula chimica $Pb_{22.64}sb_{24.90}S_{60}Cl_{1.12}$ e $(Pb_{22.90}Cu_{0.01})sb_{25.12}S_{60}Cl_{1.07}$, in buon accordo con la formula ideale $Pb_{23}sb_{25}S_{60}Cl$. gli studi diffrattometrici mostrano una cella monoclinica con parametri a 19.058(3), b 8.234(2), c 17.352(3) Å, β 96.33(2)°. assieme a pillaitite e pellouxite, la dadsonite è il terzo cloro-solfosale osservato a Buca della vena, rivelando un alto contenuto in Cl delle soluzioni idrotermali. l'izoklakeite, rinvenuta a seravezza, ha composizione media (wt.%) Pb 45.69, Bi 24.89, sb 8.16, Cu 1.08, ag 0.74, Hg 0.29, s 15.43, se 2.86, totale 99.14, con formula strutturale $Cu_{1.92}[ag_{0.77}Hg_{0.16}Pb_{24.49}(Bi_{13.23}sb_{7.44})_{\Sigma=20.67}]_{\Sigma=46.09}(S_{53.43}se_{4.02})_{\Sigma=57.45}$. si tratta di una izoklakeite ricca in Bi, vicina alla formula ideale, priva di ag e Fe, $Cu_2Pb_{26}(Bi, sb)_{20}S_{57}$. la presenza di significativi contenuti di se e Hg costituisce una peculiarità chimica di questo nuovo ritrovamento. i parametri di cella raffinati sono a 34.272(4), b 38.351(5), c 4.098(1) Å.

Key words: dadsonite, izoklakeite, lead sulfosalts, Buca della Vena, Seravezza, Apuan Alps.

introduction

Hydrothermal ores from apuan alps, closely

related to the evolution of northern apennines, have been studied for over two centuries due to the occurrence of rare and well crystallized species, representing high scientific and museologic interest. Kerndt (1845) studied for first a sulfosalt from apuan alps, describing geocronite crystals found at valdicastello. since then, 37 sulfosalts from apuan alps were identified, nine of which were discovered for the first time in this area: meneghinite (Bechi, 1852), garavellite (gregorio *et al.*, 1979), grumiplucite (orlandi *et al.*, 1998), scainiite (orlandi *et al.*, 1999), pillaitite (orlandi *et al.*, 2001), moëloite (orlandi *et al.*, 2002), pellouxite (orlandi *et al.*, 2004), rouxelite (orlandi *et al.*, 2005), and marrucciite (orlandi *et al.*, 2007).

in the last years, the systematic studies of the apuan hydrothermal systems allow identification of other very rare sulfosalt species, like guettardite (Bracci *et al.*, 1980), robinsonite (Franzini *et al.*, 1992), baumhauerite (orlandi *et al.*, 1996), sartorite (orlandi and Criscuolo, 2009), sterryite (orlandi *et al.*, in preparation), and rathite (unpublished data), in addition to the identification of jamesonite (orlandi *et al.*, 2008). This paper describes the occurrence of two very rare sulfosalts, dadsonite and Bi-rich izoklakeite.

Geological setting

apuan alps are a “tectonic window” that allows the study of the deepest portions of northern apennines. The metamorphic units belong to the so-called “nucleo Metamorfico apuano”, formed by the autoctono Unit, Massa Unit, and the Fornovolasco-Panie Unit. The basement of these three units is very similar and is composed by silicoclastic and volcanic rocks of Cambrian-triassic age metamorphosed to greenschist facies. according to Carmignani and Kligfield (1990), apuan alps are affected by two main tectonic phases: a first compressional d₁ phase, dated to 27 My, followed by an

extensional d₂ phase, dated by Kligfield *et al.* (1986) to 12-8 My.

The studied specimens were found at Buca della vena mine (dadsonite) and in the cavities of seravezza marbles (izoklakeite). The specimens are deposited in the mineralogical collection of the Museo di storia naturale e del territorio of University of Pisa, with catalogue numbers 19301, 19303 (dadsonite from Buca della vena), and 19302 (izoklakeite from seravezza).

Buca della vena mine is located on the northern slope of Monte di stazzema; it exploited a strata-bound baryte - iron oxides deposit at the contact between Paleozoic schists and triassic carbonatic rocks of the Fornovolasco-Panie Unit. Benvenuti *et al.* (1986) interpreted the ore body as an original sedimentary-diagenetic ore, subsequently deformed and recrystallized by the alpine metamorphism. Lenses of carbonatic rocks are embedded in the baryte - iron oxides ore; these lenses are affected by fracture and vein formation, with the crystallization, inside the vugs, of a great number of mineralogical species, some of which are very rare in nature (orlandi and Checchi, 1986; orlandi and dini, 2004).

seravezza quarries exploited Triassic marbles belonging to autoctono Unit. since the beginning of 1980's, with the identification of guettardite (Bracci *et al.*, 1980), the attention of mineralogists was focused on the rare sulfosalts occurring in the marble cavities. These studies led to the description of a new mineral species, moëloite (orlandi *et al.*, 2002). orlandi *et al.* (1996), taking into account the unusual abundance of acicular Pb sulfosalts at this locality, hypothesized a genetic relationship with the nearby Pb-Zn-ag ores from the Bottino mine, embedded in the Paleozoic basement. This assumption was confirmed by the study of Costagliola *et al.* (1999); fluid inclusions in minerals from the Carrara marble show mixing phenomena between meteoric and deep syn-

metamorphic fluids, originating from the Paleozoic basement. This conclusion can be extended also to the hydrothermal veins in the seravezza marble basin.

Therefore, the Buca della vena mine and the seravezza marble quarries are important sites for the study of hydrothermal sulfosalts associations in a metamorphic setting.

Dadsonite and izoklakeite from apuan alps

Dadsonite and izoklakeite samples were studied by chemical and X-ray diffraction techniques. Crystallographic studies were performed using weissenberg technique and collecting X-ray powder data with a 114.6 mm gandolfi camera, using a ni-filtered Cu K α radiation; the cell parameters of dadsonite and izoklakeite were refined using the Unit Cell program (Holland and Redfern, 1997). Chemical analyses were carried on with a CaMeBaX SX 50 electron microprobe (BrgM-Cnrs-University common laboratory, orléans, France). analytical conditions were: accelerating voltage 20 kv, specimen current 20 na. the following standards were used: galena (Pb M α), pyrite (S K α), stibnite (sb L α), cinnabar (Hg M α), pyromorphite (Cl K α), pure elements (Cu K α , Ag L α , Bi M α , Se L α).

Dadsonite

Dadsonite was defined by Jambor (1969), studying samples coming from four different localities, as a monoclinic sulfosalt with chemical composition Pb₁₁Sb₁₂S₂₉. Then, new samples found at saint-Pons (France) allowed Moëlo (1979) to identify the presence of small quantities of Cl (~0.4 wt.%) and a superstructure doubling the **b** axis (2 x 4.11 Å). Based on these data, Moëlo (1979) proposed the new formula Pb₂₃Sb₂₅S₆₀Cl (Z = 1), with a new unit cell refined by Cervelle *et al.* (1979). After determination of the sub-cell crystal structure (Makovicky and Mumme, 1984), Makovicky *et al.* (2006) solved the true crystal structure of triclinic dadsonite, confirming the structural formula proposed by Moëlo (1979). Table 1 shows the cell parameters reported by different authors. Until now, dadsonite is a very rare mineral, being found in less than ten localities world-wide.

Dadsonite from Buca della Vena

Dadsonite was identified in only four specimens at the Buca della vena mine. It forms very thin acicular crystals, up to 2 mm in length, striated parallel to the elongation. The color is grey and the luster is metallic. It is associated with sphalerite and cerussite. In the same occurrence, two other chloro-sulfosalts were

Table 1
Dadsonite unit cell parameters.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	s.g.
Coleman (1953)	19.06	4.11	17.26		95.83		P2, Pm or P2/m (1)
Jambor (1969)	19.05	4.11	17.33		96.67		P2, Pm or P2/m (2)
Cervelle <i>et al.</i> (1979)	19.041	8.226	17.327		96.30		(3)
Makovicky and Mumme (1984)	17.33	4.11	19.05	90.0	96.3	90.4	P-1 or P1 (3)
Makovicky <i>et al.</i> (2006)	8.276	17.392	19.505	83.527	77.882	89.125	P-1 (4)
this study	19.058(3)	8.234(2)	17.352(3)		96.33(2)		(5)

(1) Yellowknife Bay ("Mineral Q"); (2) wolfsberg; (3) saint-Pons; (4) Klačianka; (5) Buca della vena.

identified, pillaitite (orlandi *et al.*, 2001) and pellouxite (orlandi *et al.*, 2004).

Table 2 reports the X-ray powder diffraction data of dadsonite from the Buca della venamine; cell parameters, refined on 29 unequivocally indexed reflections on the basis of monoclinic symmetry, are given in Table 1. This unit cell fully agrees with that proposed by Cervelle *et al.* (1979), with a slightly higher volume ($v = 2706(2) \text{ \AA}^3$ against $2697(3) \text{ \AA}^3$; $v = 2727.2(9) \text{ \AA}^3$ for dadsonite from Klačianka according to Makovicky *et al.*, 2006).

Chemical data are shown in Table 3; crystal chemical formulas for the two samples, based on 60 s atoms per formula unit (*apfu*), are $\text{Pb}_{22.64}\text{sb}_{24.90}\text{S}_{60}\text{Cl}_{1.12}$ (sample 19301) and $(\text{Pb}_{22.90}\text{Cu}_{0.01})\text{sb}_{25.12}\text{S}_{60}\text{Cl}_{1.07}$ (sample 19303), in good agreement with the theoretical formula $\text{Pb}_{23}\text{sb}_{25}\text{S}_{60}\text{Cl}$.

Izoklakeite

izoklakeite is a homeotypic derivative of giessenite, with which it forms a series with the general formula $(\text{Cu}_{2-x}\text{Fe}_x)[\text{Pb}_{26-2z+x}(\text{ag,Cu})_z(\text{sb}_{1-y}\text{Bi}_y)_{20+z-x}]_{\Sigma=46\text{S}57}$, with $0 \leq x \leq 1$, $0.44 \leq y \leq 0.85$, and $0 \leq z \leq 2.2$ (Moëlo *et al.*, 1995). izoklakeite is the orthorhombic phase of this series (space group *Pnmm*, with a 34.07(1), b 37.98(1), c 4.072(1) Å; Zakrzewski and Makovicky, 1986) whereas giessenite is the monoclinic phase (space group $P2_1/n$, with a 34.51(3), b 38.18(5), c 4.080(8) Å, $\beta \approx 90^\circ$;

graeser and Harris, 1986). These two species belong to the kobellite homologous series (Zakrzewski and Makovicky, 1986; Makovicky and Mumme, 1986).

giessenite was originally described as orthorhombic (graeser, 1963), like izoklakeite. so the distinction between these two mineral species was based upon the sb/Bi ratio ($\text{Bi} > \text{sb}$):

Table 2

X-ray powder diffraction data of dadsonite from the Buca della Vena mine.

d_{obs}	I_{obs}	hkl	d_{obs}	I_{obs}	hkl	d_{obs}	I_{obs}	hkl
8.6	3	0 0 2	3.126	11	-4 1 4	2.138	9	
7.5	3	1 0 2	3.086	8	1 1 5	2.121	6	
6.7	3	-2 0 2	3.026	33	4 0 4	2.107	6	
6.1	3	-3 0 1	2.959	5	-6 1 1	2.070	30	
5.71	4	2 1 1	2.888	18	-1 0 6	2.020	7	
4.77	4	4 0 0	2.851	43	6 1 1	1.995	17	
4.32	5	0 0 4	2.799	54	1 0 6	1.966	5	
4.12	19	0 2 0	2.729	31	-1 1 6	1.932	27	
4.03	9	3 0 3	2.650	27	6 0 3	1.890	62	
3.97	10	4 0 2	2.572	9		1.867	5	
3.89	7	1 2 1	2.517	15		1.857	10	
3.79	31	5 0 0	2.480	9		1.820	17	
3.69	11	-1 2 2	2.458	8		1.793	21	
3.63	31	3 1 3	2.391	17		1.760	6	
3.57	6	4 1 2	2.362	17		1.731	26	
3.446	25	-5 1 1	2.331	8		1.700	9	
3.384	100	-4 0 4	2.265	21	-7 2 0	1.680	5	
3.250	12	1 2 3	2.220	39		1.650	7	
3.158	16	-6 0 1	2.167	8				

Table 3
Chemical analyses of dadsonite from the Buca della Vena mine.

	19301 (n = 5)				19303 (n = 5)			
	wt. %	range	e.s.d.	structural formula (s=60 apfu)	wt. %	range	e.s.d.	structural formula (s=60 apfu)
Pb	48.08	47.79 – 48.23	0.18	22.64	48.79	48.32 – 49.09	0.29	22.90
Cu	-	-	-	-	0.005	0.00 – 0.02	0.01	0.01
sb	31.07	30.69 – 31.29	0.25	24.90	31.44	31.07 – 31.84	0.31	25.12
s	19.72	19.56 – 19.94	0.17	60.00	19.78	19.65 – 19.85	0.08	60.00
Cl	0.41	0.39 – 0.43	0.02	1.12	0.39	0.38 – 0.40	0.01	1.07
total	99.28	98.56 – 99.61	0.51		100.40	100.34 – 100.48	0.05	

giessenite; sb > Bi: izoklakeite; Harris *et al.*, 1986). The detection of the true monoclinic symmetry of giessenite (Makovicky and Karup-Møller, 1986) and the description of orthorhombic phases with Bi > sb (armbruster and Hummel, 1987), led these authors to distinguish the two sulfosalts taking into account their symmetry. Until now, the most Bi-rich izoklakeite was described from the otome mine (Japan; ozawa *et al.*, 1998), with Bi/(Bi+sb)_{at.} = 0.684, whereas the most Bi-poor giessenite, found at giessen (switzerland), has Bi/(Bi+sb)_{at.} = 0.805 (graeser and Harris, 1986).

Izoklakeite from Ceragiola (Seravezza)

The only known specimen of izoklakeite was found in the marble cavities from Ceragiola, in the seravezza basin. The studied sample showed 3-4 mm long acicular crystals, thin and curved, with a typical metallic luster and black in color. izoklakeite is associated with pyrite. Table 4 shows its X-ray powder diffraction data. its cell parameters, refined on the basis of 27 unequivocally indexed reflections, are a 34.272(4), b 38.351(5), c 4.098(1) Å.

The cell parameters of izoklakeite and giessenite are very similar; it is thus very difficult to distinguish these two mineral species using X-ray powder diffraction patterns. only

single-crystal studies allow the distinction between these two phases, in particular through the examination of the 0 k l reflections.

Makovicky and Karup-Møller (1986) observed the presence of 0 8 1, 0 10 1, 0 26 1, 0 28 1, 0 9 2, and 0 27 2 reflections, based on a cell with 4 Å c periodicity, in giessenite from Bjørkåsen (norway). Careful examination of hk

Table 4
X-ray powder diffraction data for izoklakeite from Seravezza.

<i>d</i> _{obs}	<i>I</i> _{obs}	<i>h k l</i>	<i>d</i> _{obs}	<i>I</i> _{obs}	<i>h k l</i>
5.73	vw	6 0 0	2.632	w	9 5 1
4.560	vw	4 7 0	2.518	w	8 8 1
4.285	w	8 0 0	2.337	mw	9 9 1
4.145	vw		2.169	ms	13 10 0, 13 4 1
					0 15 1
3.927	w	5 8 0	2.134	m	13 5 1
3.806	mw	4 9 0	2.104	w	13 11 0
3.634	w	3 10 0	2.066	w	14 10 0
3.491	w	4 10 0	2.030	mw	0 0 2, 14 5 1
3.429	s	10 0 0	1.968	w	13 9 1
3.334	w	4 5 1	1.915	w	16 9 0
3.188	mw	6 10 0	1.869	w	3 18 1
3.054	w	2 8 1, 6 5 1	1.833	mw	10 15 1
3.025	mw	7 10 0	1.810	w	16 6 1
2.912	m	7 5 1	1.761	mw	10 0 2
2.867	mw	3 9 1	1.719	w	6 10 2
2.756	w	2 10 1			

1 reflections, and in particular of 0 k 1, in single-crystal photographs taken on the sample from seravezza do not allow the observation of reflections with $k + 1 = 2n + 1$, characteristic of giessenite. in addition, oscillation crystal photographs show very weak reflections that double the *c* periodicity, as noted in izoklakeite from vena (sweden; Zakrzewski and Makovicky, 1986) and the otome mine (ozawa *et al.*, 1998) but not in giessenite from norway (Makovicky & Karup-Møller, 1986). thus the sample from seravezza appears to crystallize in the orthorhombic system and must be classified as izoklakeite.

Chemical data of izoklakeite from seravezza are reported in **Table 5**. the chemical formula, based on 48 cations, is $Cu_{1.92}[(ag_{0.77}Hg_{0.16})_{\Sigma=0.93}Pb_{24.49}(Bi_{13.23}sb_{7.44})_{\Sigma=20.67}]_{\Sigma=46.09}(s_{53.43}se_{4.02})_{\Sigma=57.45}$; it is in good agreement with the structural formula of izoklakeite-giessenite series, with $x = 0$, $z \sim 1$, and $y \sim 0.64$. the latter value corresponds to the atomic ratio $Bi/(Bi+sb)_{at.} = 0.640$, a little lower than the value measured in izoklakeite from the otome mine (0.684; ozawa *et al.*, 1998). Because of this high Bi content, the specimen from seravezza could be classified as a Bi-rich izoklakeite.

Compared to the previous chemical analyses of izoklakeite and giessenite (Moëlo *et al.*, 1995;

ozawa *et al.*, 1998), the sample from seravezza shows some chemical peculiarities. in fact, it is Fe-free, whereas it has a significant ag content, within the compositional range of previous analyses. Cu content (1.92 *apfu*) is close to the ideal one (2 *apfu*) and only a small fraction (0.08 *apfu*) of total ag (0.77 *apfu*) could be added to it by substitution. if the remaining ag content (0.69 *apfu*) is subtracted according to the rule $ag^{+} + (Bi, sb)^{3+} \rightarrow 2 Pb^{2+}$, then there are 25.87 Pb *apfu*, in agreement with the ideal value (26 *apfu*) of the structural formula with $x = z = 0$.

the microprobe analysis reveals two other minor components. First, there is a relatively high se content (~ 3 wt.%), substituting for s [$se/(s+se)_{at.} = 0.07$]. secondly, Hg, never reported in previous analyses of izoklakeite or giessenite, is significantly present (~ 0.3 wt.%).

Conclusions

dadsonite from the Buca della vena mine is the first well characterized italian occurrence of this rare chloro-sulfosalt. the association of dadsonite with two other chloro-sulfosalts, pillaitite and pelloxite, suggests a high chlorinity of hydrothermal solutions. the presence of high-salinity fluids (from 29.5 up to 37.0 wt.% naCl equiv.) in the metamorphic complex of the apuan alps during the tectono-metamorphic alpine events was described by some authors (Hodgkins and Stewart, 1994; Iattanzi *et al.*, 1994; Costagliola *et al.*, 1999; Montomoli *et al.*, 2005). in particular, Montomoli *et al.* (2005) suggest that the original metamorphic fluids interacted with evaporitic levels at the base of tuscan nappe overlying apuan alps metamorphic units. therefore, it is possible that chloro-sulfosalts, or Cl-bearing sulfosalts, could be present also in other tuscan hydrothermal deposits; for example, small Cl concentrations were detected in jamesonite from Fornovolasco (0.04 wt.%; orlandi *et al.*, 2008) and in boulangerite from seravezza (0.05 wt.%;

Table 5
Chemical analyses of izoklakeite from Seravezza.

	average (n=9) wt.%	range	e.s.d.	structural formula (Me=48 apfu)
Cu	1.08	1.06 – 1.12	0.02	1.92
ag	0.74	0.64 – 0.87	0.07	0.77
Hg	0.29	0.24 – 0.34	0.04	0.16
Pb	45.69	45.06 – 46.67	0.60	24.49
Bi	24.89	24.13 – 25.17	0.36	13.23
sb	8.16	7.87 – 8.40	0.15	7.44
s	15.43	15.22 – 15.61	0.14	53.43
se	2.86	2.58 – 3.07	0.18	4.02
total	99.14	97.96 – 100.38	0.78	

Table 6
Bi sulphides and sulfosalts from Apuan Alps.

	Chemical formula	Localities	ref.
aikinite	CuPbBiS ₃	Carrara	(1)
Bismuthinite	Bi ₂ S ₃	Miniera del Frigido	(2)
		seravezza	(3)
Cosalite	Pb ₂ Bi ₂ S ₅	Carrara	(1)
garavellite	FesbBiS ₄	Miniera del Frigido	(4)
grumiplucite	HgBi ₂ S ₄	Ievigliani	(5)
izoklakeite	(Cu,Fe) ₂ Pb _{26.4} (sb,Bi) _{19.6} S ₅₇	seravezza	(6)
Jaskólskiite	Cu _x Pb _{2+x} (sb,Bi) _{2-x} S ₅	Fornovolasco	(7)

(1) orlandi and Criscuolo, 2009; (2) Carrozzini *et al.*, (1993); (3) orlandi *et al.*, 1996; (4) gregorio *et al.* (1979); (5) orlandi *et al.*, (1998); (6) this study; (7) Biagioni *et al.*, (2008).

unpublished data).

Bi-rich izoklakeite from seravezza marble quarries is the first Italian occurrence of this very rare Pb-Bi-sb sulfosalt, until now described from about fifteen localities world-wide. In the metamorphic complex of Apuan Alps, Bi sulphides and sulfosalts are rather rare and have been identified till now only in a few localities (Table 6).

Chemically, izoklakeite from seravezza is interesting for its Hg and striking Se contents. In hydrothermal veins from the metamorphic complex of Apuan Alps, Hg minerals were frequently identified in some localities. In fact, Hg is a mobile element under metamorphic conditions and this behavior explains the diffusion of this chemical species in hydrothermal ores: the greenschist facies metamorphism overprinting the rocks of the Apuan Alps offered ideal conditions for transport and redeposition of Hg (Dini *et al.*, 2001). Supporting this, two new Hg sulfosalts were recently described from the Buca della Vena mine, rouxelite, Cu₂HgPb₂₂Sb₂₈S₆₄(O,S)₂ (Orlandi *et al.*, 2005), and marrucciite, Hg₃Pb₁₆Sb₁₈S₄₆ (Orlandi *et al.*, 2007), and exceptional Hg content were detected in andorite from the Monte Arsiccio mine (up to 2.8 wt.%; unpublished data). Unlike Hg, Se, detected in

significant concentrations in izoklakeite from seravezza, is a rare element in hydrothermal veins from Apuan Alps; up to now, the only Se mineral identified in this area is tiemannite (Biagioni and Orlandi, 2009) whereas small quantities of this element were detected in Zn-rich metacinnabar and Hg-rich sphalerite from the Ievigliani mine (around 0.2 wt.%; Dini, 1995) and in Jamesonite from Fornovolasco (0.02 wt.%; Orlandi *et al.*, 2008).

The discovery of rare sulfosalts in the Apuan Alps and their precise chemical analysis with electron microprobe allow to emphasize the geochemical and metallogenic continuity between various hydrothermal sulphide deposits of this region, despite their differences considering the main metals as well as their geological environments. The diversity of these ores is the result of the variability of local thermo-chemical conditions of deposition, although they all result from the same alpine large-scale hydrothermal processes.

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