

Original paper

# Marrucciite, a rare Hg-sulfosalt from the Gelnica ore deposit (Slovak Republic), and its comparison with the type occurrence at Buca della Vena mine (Italy)

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The rare Hg-sulfosalt, marrucciite, with ideal formula  $\text{Hg}_3\text{Pb}_{16}\text{Sb}_{18}\text{S}_{46}$ , was found in the Gelnica ore deposit (Spišsko-Gemerské Rudohorie Mts., Slovak Republic). It occurs as acicular crystals up to 0.5 mm in length and fine-grained aggregates up to 1 mm in quartz (+siderite/dolomite) gangue in association with other sulfosalts (zinkenite, scainiite, boulangerite, chalcostibite, bournonite) and cinnabar. It is opaque, dark steel grey to greyish black, sometimes tarnished to a bronze-brown tint, has a dark grey streak with a very weak reddish tint and a metallic luster. Marrucciite is very brittle but thin acicular crystals are flexible. One good cleavage parallel to the elongation of the crystals was observed. The VHN<sub>20g</sub> microhardness is 85 (69–101) kp/mm<sup>2</sup> and corresponds to a Moh's hardness of *c.* 2; the calculated density is 6.00 g.cm<sup>-3</sup>. In reflected light, marrucciite is white to greyish white with a weak yellowish tint, distinct bireflectance and white–white grey pleochroism. Under crossed polars, it has distinct anisotropy, with rotation tints in shades of grayish brown and dark brown. Dark red internal reflections were observed only rarely. Marrucciite is monoclinic, space group *C2/m* with *a* 48.12(1), *b* 4.1083(2), *c* 23.990(5) Å,  $\beta$  118.76(2)°, *V* 4158.3(3) Å<sup>3</sup>. Its average composition (electron microprobe data in wt. %) is Cu 0.03, Hg 7.83, Cd 0.02, Fe 0.06, Zn 0.02, Pb 43.13, Sn 0.03, Sb 29.15, Bi 0.12, S 19.71, Cl 0.05, total 100.15. The empirical formula on the basis 83 of *apfu* is  $\text{Hg}_{2.93}(\text{Pb}_{15.63}\text{Fe}_{0.08}\text{Cu}_{0.04}\text{Cd}_{0.02}\text{Zn}_{0.02}\text{Sn}_{0.02}\text{S}_{15.81}(\text{Sb}_{17.97}\text{Bi}_{0.04})_{\Sigma 18.01}(\text{S}_{46.14}\text{Cl}_{0.11})_{\Sigma 46.25}$ . The crystal structure of marrucciite from Gelnica contains two Hg positions (6 atoms), 7 Pb positions (28 atoms), 8 Sb positions (32 atoms), two mixed Pb–Sb positions (refined as  $\text{Pb}_{0.39}\text{Sb}_{0.61}$  and  $\text{Pb}_{0.61}\text{Sb}_{0.39}$ ) and 23 S positions (46 atoms).

**Keywords:** marrucciite, Hg-sulfosalt, X-ray powder data, electron microanalyses, the Gelnica ore deposit, Slovak Republic

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## 1. Introduction

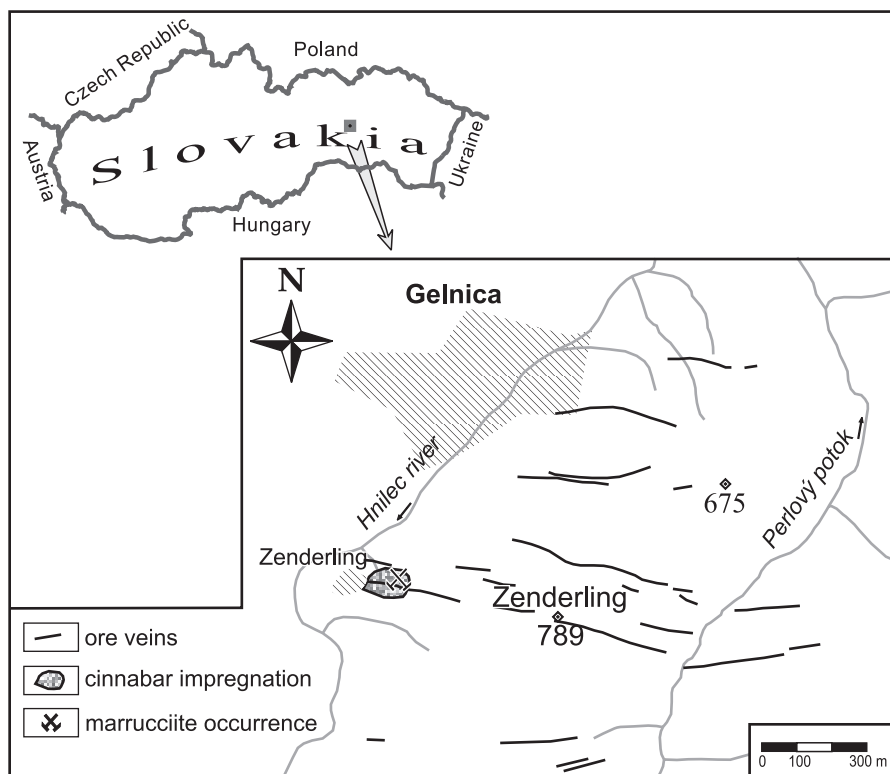
A Hg–Pb-sulfosalt from the Zenderling occurrence near Gelnica (Slovak Republic) was described for the first time (without a name for the mineral) by Háber and Babčan (1971) and later on (with proposed name gelnicite) by Háber (1980). Háber et al. (2004) again described the material in an abstract, under an unapproved mineral name “gelnicaitite?”. Descriptions of Hg–Pb-sulfosalts from Zenderling published in Háber's papers (especially optical properties, hardness and proposed unit-cell parameters) are problematic, confusion with other minerals in close association (namely boulangerite) cannot be excluded. Subsequently, this mineral phase was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA) as a new mineral – marrucciite – from the Fe–Ba deposit at Buca della Vena mine, Apuan Alps, Italy

(Orlandi et al. 2007). This mineral is identical with the Hg–Pb-sulfosalt from the Zenderling occurrence.

The present study concentrates on our new finds (2002–2004) of marrucciite at Zenderling, where this Hg–Pb-sulfosalt rarely occurs as well-formed crystals and their aggregates in close association with cinnabar and other sulfosalts. The results of a chemical study confirmed the identity of our mineral phase and the sample described by Háber. The aim of this work is detailed mineralogical characterization of the marrucciite from Zenderling and its comparison to the description of the same mineral from Buca della Vena.

## 2. Occurrence and associated minerals

Mine dumps of the Zenderling deposit (newly designated as the Háj settlement) are located about 1.5 km SW of



**Fig. 1** Topographic sketch of the Zenderling deposit near Gelnica (Slovak Republic) with marked ore veins and place of marrucciite occurrence.

Gelnica (30 km NW of Košice) in the eastern Slovakia, in the Spišsko–Gemerské Rudohorie Mountains (Fig. 1). Mining exploitation of mainly Ag, Hg and Cu ores began in the 13<sup>th</sup> century. The last mining, geological and metallogenetic research in this area was carried out in the 1960s and 1970s (Háber 1980).

The veinlets–disseminated type of hydrothermal mineralization occurs in porphyroids and rarely in graphite–sericite phyllites of the Drnava Complex in the Gelnica Group. The Drnava Complex is an upper lithostratigraphic unit of the Gelnica Group and includes two lydite horizons, volcanoclastic material and metabasalt bodies. The age of the Gelnica Group was determined as Late Cambrian to Early Devonian (Bajaník 1984; Slavkay et al. 2004) on the basis of microflora and acritarchs. The age of the Drnava Complex is considered as Early Devonian (Ivanička et al. 1989).

Hydrothermal veins trend W–E and dip 45–80° to the south. The zone of ore veins is 1 km long and maximum thickness of veins reaches several tens of cm (Koděra et al. 1986). According to the latest data by Hurai et al. (2002), the age of ore mineralization is Alpine.

The most abundant minerals in this hydrothermal deposit are quartz, siderite and cinnabar. Háber (1980) and Chovan et al. (1994) described also chlorite, rutile, dolomite, ankerite, magnetite, hematite, calcite, muscovite, barite, schorl, dravite, pyrite, chalcopryrite, stibnite, galena and native mercury. Among sulfosalts, the occurrences of tetrahedrite and its variety schwazite, bourno-

nite, boulangerite, jamesonite and “gelnicite” (= marrucciite) were described by Háber (1980). During our recent research scainiite, zinkenite, chalcostibite, jordanite and seligmannite were also identified.

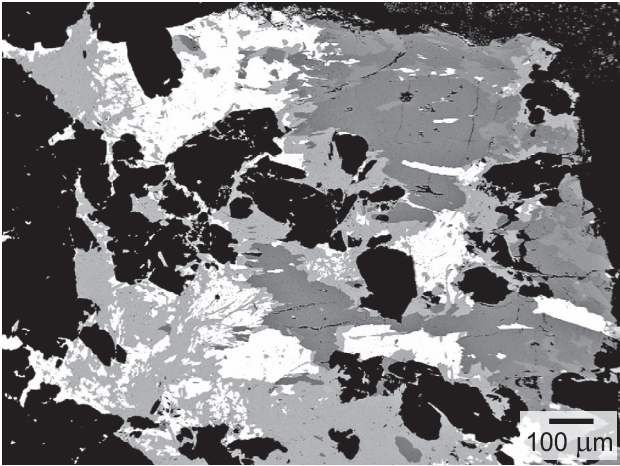
Hydrothermal marrucciite is one of the youngest primary minerals in siderite/dolomite–quartz–sulfide veins located in the tectonic zones. Marrucciite occurs in two characteristic mineral assemblages: zinkenite, scainiite, chalcostibite, cinnabar (Fig. 2) and bournonite, boulangerite (Figs 3–5).

### 3. Appearance and physical properties

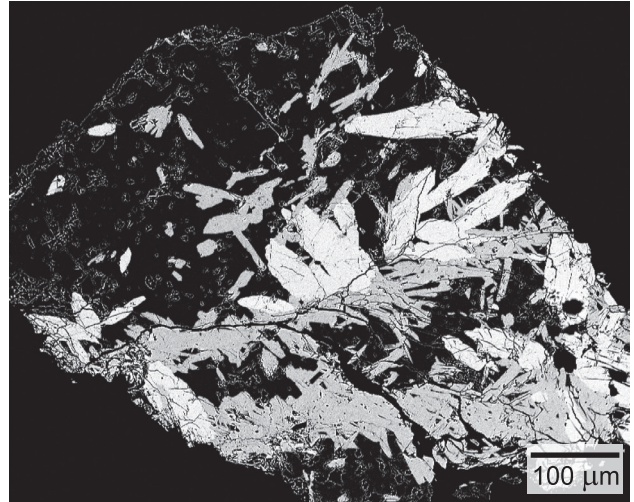
Marrucciite from Gelnica occurs as acicular crystals, up to 0.5 mm in length (Fig. 6), sometimes grouped in rich aggregates (Fig. 7); fine-grained aggregates up to 1 mm across in quartz (+siderite/dolomite) gangue in association with other sulfosalts were also observed (Figs 2–5). It is opaque, dark steel grey to greyish black, sometimes tarnished to a bronze-brown tint, has a dark grey streak with a very weak reddish tint, and a metallic luster. It is not fluorescent in short- or long-wave UV radiation.

Marrucciite is very brittle but the thin acicular crystals are flexible. One good cleavage parallel to the elongation of the crystals was observed. According to Orlandi et al. (2007), the cleavage plane would be (20–1). The fracture is uneven, the VHN<sub>20g</sub> microhardness is 85 (69–101) kp/mm<sup>2</sup> (30 indentations), corresponding to a Moh’s hardness

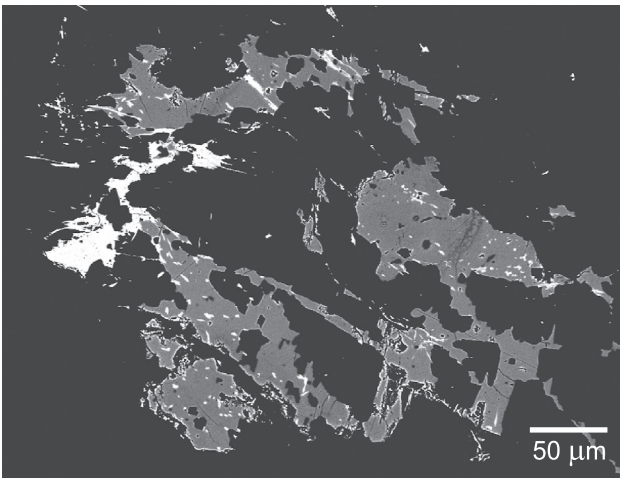




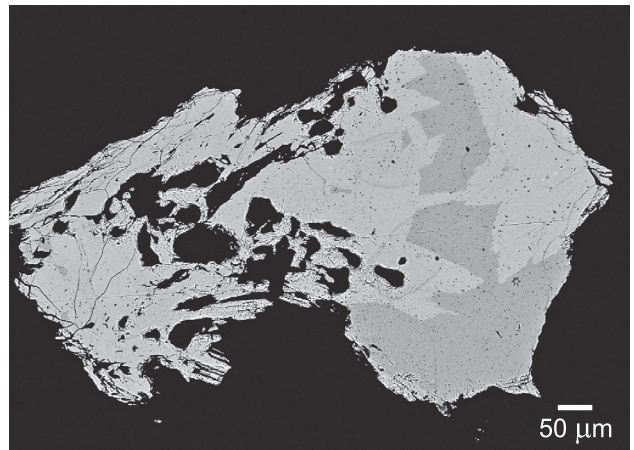
**Fig. 2** Marrucciite (light grey) in association with cinnabar (white), scainiite (grey) and zinkenite (dark grey); BSE photo.



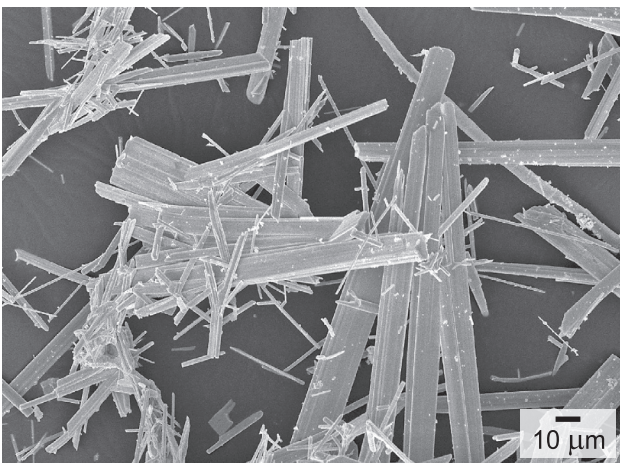
**Fig. 3** Thin veins of marrucciite (grey) grown on boulangerite (white) needles in bourmonite (dark); BSE photo.



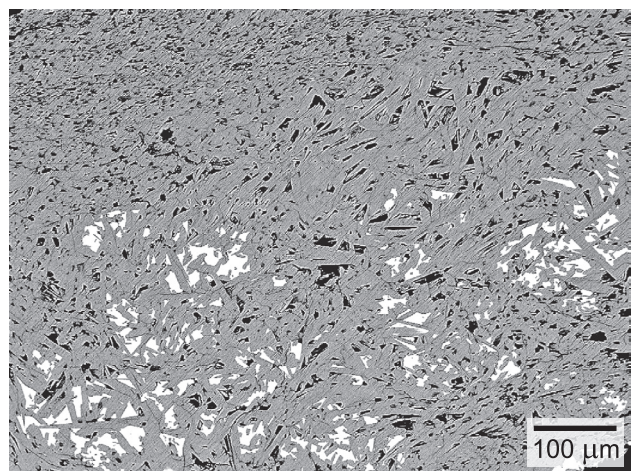
**Fig. 4** Bourmonite aggregates (grey) are crossed and overgrown by genetically younger marrucciite (white) in dolomite (black); BSE photo.



**Fig. 5** Boulangerite aggregate (light) with marrucciite relics (darker) in quartz gangue; BSE photo.



**Fig. 6** Group of acicular marrucciite crystals; SEM photo



**Fig. 7** Intergrowth of acicular marrucciite crystals (grey) with relict grains of cinnabar (white). BSE photo Cameca SX 100.

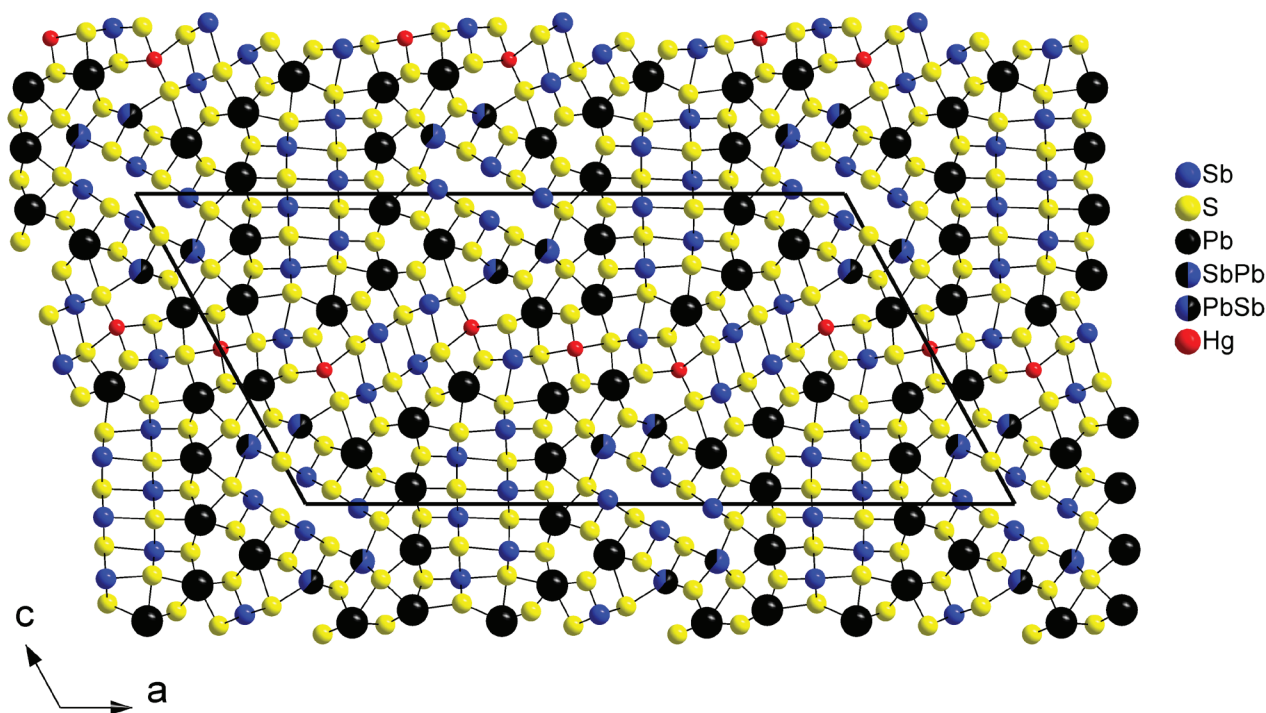


Fig. 8 Projection of the marrucciite crystal structure along *b* axis. Unit cell is outlined. Based on the data of Laufek et al. (2007).

of *c*. 2. Density could not be measured directly due to the small grain size; the value of  $6.00 \text{ g}\cdot\text{cm}^{-3}$  was calculated on the basis of the empirical formula and unit-cell parameters refined from X-ray powder data. This is very close to the calculated value  $6.01 \text{ g}\cdot\text{cm}^{-3}$  given for marrucciite from Buca della Vena mine by Orlandi et al. (2007).

The sample of marrucciite from Gelnica was prepared for optical investigation using standard diamond polishing techniques. In plane-polarized reflected light (from an unfiltered quartz-halogen lamp at about 3100 K), marrucciite is white to greyish white with a weak yellowish tint, distinct bireflectance and white–white grey pleochroism. Under crossed polars, marrucciite has a distinct anisotropy with rotation tints in shades of greyish brown and dark brown. Dark red internal reflections were observed only rarely. Orlandi et al. (2007) reported for marrucciite from Buca della Vena mine a light grey color without pleochroism and for sub-longitudinal sections a distinct anisotropy without marked polarization tints (dark blue to dark brown).

#### 4. Crystallography

The crystal structure of marrucciite from Buca della Vena was solved and refined to a R factor of 9.56% by Orlandi et al. (2007). Discovery of crystals of this sulfosalts in Gelnica allowed Laufek et al. (2007) a more precise structure refinement to a R factor of 2.46%.

The structure model proposed by Orlandi et al. (2007) was in principle confirmed. Marrucciite crystallizes in space group  $C2/m$ . The unit-cell of marrucciite (Fig. 8) contains two Hg positions (6 atoms), 7 Pb positions (28 atoms), 8 Sb positions (32 atoms), two mixed Pb–Sb positions (refined as  $\text{Pb}_{0.39}\text{Sb}_{0.61}$  and  $\text{Pb}_{0.61}\text{Sb}_{0.39}$ ) and 23 S positions (46 atoms). The crystal structure-derived formula, based on the refinement of Laufek et al. (2007), is  $\text{Hg}_3\text{Pb}_{16}\text{Sb}_{18}\text{S}_{46}$ .

The major difference between the two refinements of marrucciite from Gelnica and Buca della Vena is the absence of the rare and weak  $2b$  superstructure diffraction spots in the former. These weak reflections indicate a weak  $\sim 8 \text{ \AA}$  superstructure along the *b* direction in the Buca della Vena material, which modifies the  $4 \text{ \AA}$  submotif by split positions of some Sb sites. Splitting of adjacent S positions was also observed (Orlandi et al. 2007). As was mentioned above, no  $2b$  superstructure reflections were detected for marrucciite from Gelnica. Consequently, no split positions with a half-occupancy were determined in the crystal structure of marrucciite from Gelnica (Laufek et al. 2007). On the other hand, both marrucciite samples show two Pb–Sb mixed positions with approximately identical occupancy factors of Pb and Sb. Noteworthy is that many sulfosalts from Buca della Vena (e.g. scainiite, pillaitite, pelloxite) show very weak  $8 \text{ \AA}$  superstructure reflections. However, with the exception of scainiite (Mořlo et al. 2000), they are too weak to be fully exploited in the crystal structure analysis.



Tab. 1 X-ray powder diffraction pattern of marrucciite from Gelnica

$I/I_o$	$d_{obs.}$	$d_{calc.}$	h	k	l	$I/I_o$	$d_{obs.}$	$d_{calc.}$	h	k	l	$I/I_o$	$d_{obs.}$	$d_{calc.}$	h	k	l
2	20.90	21.07	2	0	0	1	3.080	3.080	7	1	-5	2	2.1805	2.1805	9	1	5
		21.02	0	0	1	11	3.056	3.057	8	0	4	5	2.1651	2.1655	18	0	-10
1	20.57	20.66	2	0	-1	3	3.022	3.015	5	1	3		2.1648		1	1	8
4	12.199	12.229	2	0	1	35	3.003	3.004	16	0	-4	1	2.1352	2.1362	17	1	-8
5	11.990	12.016	4	0	-1			3.001	1	1	-5	4	2.1267	2.1265	22	0	-3
1	10.518	10.537	4	0	0			3.000	7	1	2	7	2.1192	2.1192	15	1	-9
2	10.306	10.329	4	0	-2	11	2.9956	2.9964	8	0	-8	6	2.1013	2.1020	0	0	10
2	7.998	8.003	4	0	1	12	2.9803	2.9806	11	1	-2	3	2.0966	2.0963	15	1	2
13	7.825	7.836	6	0	-2	5	2.9619	2.9670	3	1	4	4	2.0692	2.0685	22	0	-2
		7.822	4	0	-3	6	2.9358	2.9382	11	1	-4	6	2.0659	2.0659	20	0	-10
2	7.017	7.025	6	0	0	15	2.9143	2.9146	11	1	-1		2.0617		3	1	8
		7.007	0	0	3	9	2.8952	2.8975	4	0	-8	4	2.0528	2.0534	0	2	0
1	6.883	6.886	6	0	-3	12	2.8636	2.8646	1	1	5	2	2.0302	2.0316	19	1	-8
1	6.112	6.115	4	0	2	11	2.8561	2.8543	7	1	-6	6	2.0282	2.0299	17	1	1
2	6.004	6.008	8	0	-2	3	2.8379	2.8369	11	1	-5	9	1.9976	1.9961	7	1	7
1	5.982	5.993	4	0	-4	11	2.8007	2.8017	11	1	0	0	1.9976	1.9968	22	0	-1
5	5.858	5.868	6	0	1	0	2.8007	2.7981	9	1	-6	2	1.9910	1.9900	21	1	-4
		5.858	2	0	3	2	2.7746	2.7730	7	1	3	4	1.9608	1.9616	22	0	-10
3	5.737	5.742	8	0	-3	1	2.7575	2.7598	5	1	4		1.9607		20	0	-11
1	5.246	5.255	0	0	4	2	2.7474	2.7479	13	1	-3		1.9607		19	1	-9
1	5.166	5.165	8	0	-4	2	2.7222	2.7235	1	1	-6	3	1.9532	1.9528	6	0	9
4	4.787	4.788	10	0	-2	6	2.7109	2.7123	10	0	4	2	1.9383	1.9375	24	0	-3
3	4.750	4.753	6	0	-5			2.7112	8	0	5	3	1.9313	1.9317	6	0	-12
1	4.606	4.605	2	0	4	5	2.6688	2.6686	13	1	-5		1.9319		17	1	2
5	4.578	4.579	10	0	-1	3	2.6645	2.6615	8	0	-9	1	1.9144	1.9139	13	1	-11
3	4.559	4.566	2	0	-5	3	2.6535	2.6574	11	1	1	2	1.9129	1.9113	18	0	-12
5	4.201	4.204	0	0	5			2.6548	10	0	-9	2	1.9051	1.9058	1	1	-10
21	4.075	4.076	6	0	3	2	2.6267	2.6275	0	0	8	3	1.8795	1.8797	14	0	6
26	3.997	4.005	12	0	-3	4	2.6020	2.6049	9	1	-7		1.8792		12	0	7
		4.002	8	0	2			2.6007	1	1	6	5	1.8717	1.8719	19	1	1
		3.997	4	0	4	1	2.5627	2.5611	3	1	-7		1.8712		21	1	-9
		3.995	6	0	-6			2.5621	18	0	-2	5	1.8618	1.8612	23	1	-6
2	3.970	3.978	1	1	1	2	2.5532	2.5545	4	0	-9	4	1.8489	1.8489	7	1	8
		3.973	3	1	-1			2.5525	7	1	4	3	1.8401	1.8405	14	0	-13
3	3.949	3.951	12	0	-2	4	2.5246	2.5251	14	0	-9	5	1.8336	1.8339	6	2	3
		3.942	3	1	0	1	2.4977	2.4974	11	1	2		1.8328		17	1	3
4	3.912	3.911	8	0	-6	1	2.4811	2.4814	15	1	-2	4	1.8253	1.8263	6	2	-6
2	3.867	3.871	1	1	-2	1	2.4717	2.4713	16	0	1		1.8257		2	0	11
		3.866	3	1	-2			2.4658	2	0	8	2	1.8180	1.8181	8	2	-6
7	3.795	3.796	10	0	1	2	2.4534	2.4542	2	0	-9	9	1.7925	1.7934	13	1	-12
5	3.786	3.783	3	1	1			2.4507	13	1	-7		1.7920		24	0	-11
1	3.759	3.761	2	0	-6	1	2.4439	2.4459	10	0	5	2	1.7691	1.7688	8	2	3
		3.751	1	1	2	4	2.3945	2.3920	5	1	-8	2	1.7640	1.7634	7	1	-12
17	3.712	3.714	12	0	-5			2.3939	20	0	-4	4	1.7609	1.7616	14	2	-3
5	3.691	3.692	5	1	0	1	2.3555	2.3558	9	1	4		1.7603		6	2	-7
4	3.650	3.653	3	1	-3			2.3546	20	0	-3		1.7598		14	2	-4
1	3.519	3.520	7	1	-2	7	2.3349	2.3367	3	1	-8	4	1.7418	1.7413	16	0	6
80	3.481	3.483	8	0	3	3	2.3157	2.3166	13	1	-8	2	1.7352	1.7357	25	1	-5

Tab. 1 – continued

$I/I_o$	$d_{obs.}$	$d_{calc.}$	h	k	l	$I/I_o$	$d_{obs.}$	$d_{calc.}$	h	k	l	$I/I_o$	$d_{obs.}$	$d_{calc.}$	h	k	l
26	3.428	3.428	14	0	-3	1	2.3091	2.3099	5	1	6			1.7340	21	1	1
100	3.415	3.419	6	0	-7	4	2.2952	2.2954	18	0	-9	3	1.7222	1.7216	24	0	-12
		3.415	14	0	-4	2	2.2804	2.2828	4	0	-10	3	1.7170	1.7181	25	1	-8
7	3.405	3.408	8	0	-7			2.2840	13	1	2			1.7166	28	0	-7
14	3.386	3.380	3	1	-4	2	2.2705	2.2698	17	1	-2	2	1.7034	1.7038	16	0	-14
10	3.376	3.374	5	1	-4	2	2.2466	2.2470	3	1	7			1.7046	8	2	4
19	3.356	3.353	14	0	-2	1	2.2332	2.2346	9	1	-9	2	1.6949	1.6952	16	2	-4
19	3.340	3.343	4	0	-7			2.2334	15	1	-8			1.6938	8	2	-8
21	3.316	3.317	14	0	-5	7	2.2059	2.2114	15	1	1	2	1.6800	1.6808	5	1	10
6	3.253	3.255	9	1	-2			2.2080	2	0	9	3	1.6767	1.6754	4	2	-8
		3.253	3	1	3			2.2045	17	1	-1	3	1.6750	1.6744	15	1	-13
4	3.193	3.195	2	0	-7			2.2049	20	0	-1	1	1.6577	1.6572	13	1	7
6	3.153	3.156	1	1	4	4	2.1978	2.1936	5	1	-9						
4	3.130	3.131	9	1	-4			2.1941	8	0	7						
2	3.085	3.088	9	1	0	2	2.1855	2.1844	22	0	-5						

Tab. 2 Unit-cell parameters of marrucciite (for monoclinic space group  $C2/m$ )

		$a$ [Å]	$b$ [Å]	$c$ [Å]	$\beta$ [°]	$V$ [Å <sup>3</sup> ]
powder	this paper	48.077(8)	4.1068(6)	23.976(3)	118.752(8)	4150.(1)
single	Laufek et al. (2007)	48.12(1)	4.1083(2)	23.990(5)	118.76(2)	4158.(1)
single	Orlandi et al. (2007)	48.32(1)	4.1170(8)	24.056(5)	118.84(3)	4192.(1)
powder	Orlandi et al. (2007)	48.32(1)	4.117(1)	24.056(5)	118.84(3)	4192.(3)

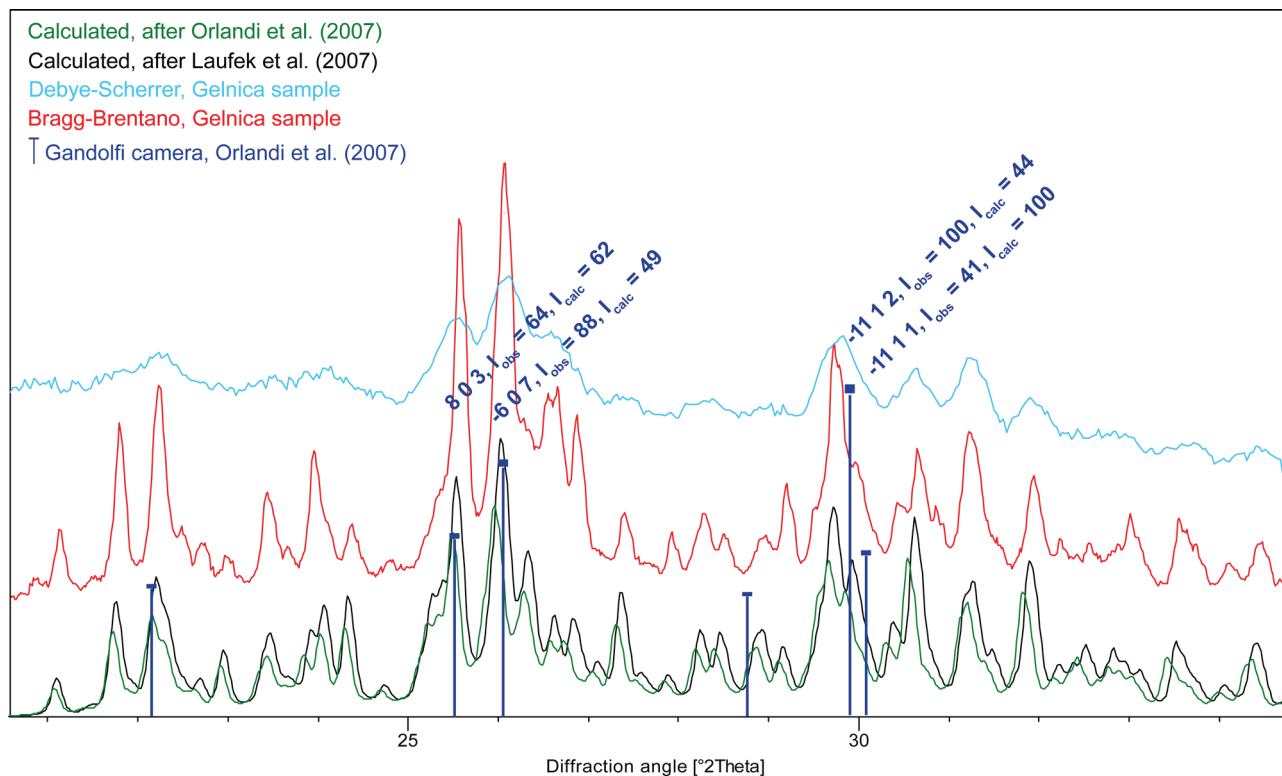


Fig. 9 A comparison of powder diffraction patterns of marrucciite from Gelnica with the previously published data. The values for the four diffractions of the highest intensity by Orlandi et al. (2007) are indicated.

A handpicked sample of marrucciite from Gelnica was used to collect the X-ray powder diffraction patterns. First, a PANalytical X'Pert Pro powder diffractometer (40 kV/30 nA) with X'Celerator solid-state detector operating in Bragg–Brentano geometry using monochromatic  $\text{CuK}_{\alpha 1,2}$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) was utilized. To minimize the complicated shape of the background, the powder sample was placed onto a flat low-background silicon wafer. The powder pattern was collected in the range from  $2$  to  $90^\circ 2\theta$  with a step size of  $0.017^\circ 2\theta$  and integrated exposure time of  $500 \text{ s}$  per step (total collection time  $\sim 10$  hours) (Tab. 1). The positions and intensities of diffractions were found and refined using the Pearson VII profile-shape function with the ZDS program package (Ondruš 1995) and the unit-cell parameters were refined by the least-squares algorithm implemented by Burnham (1962). Due to some obvious discrepancies between experimental data and powder pattern calculated by Laufek et al. (2007) from the crystal structure using Lazy Pulverix (Yvon et al. 1977) and PowderCell (Kraus and Nolze 2000), a second diffraction experiment involving a different geometry of the diffractometer (Debye–Scherrer) was carried out. For this purpose a PANalytical X'Pert Pro powder diffractometer was utilized. The small amount of marrucciite powder was placed onto a glass fiber, mounted on a goniometric head and scanned using a nearly linear X-ray beam, provided by a  $300 \text{ }\mu\text{m}$  capillary. In order to improve the counting statistics, the secondary monochromator was not used. The radiation was Ni-filtered. The powder pattern was collected in the range from  $3$  to  $90^\circ 2\theta$  with a step size of  $0.033^\circ 2\theta$  and a counting time  $3000 \text{ s}$  (yielding a total data collection time of  $\sim 3$  days).

An overview of the refined unit-cell parameters for marrucciite from both occurrences is given in Tab. 2. As has been mentioned above, there are considerable discrepancies between experimental and calculated powder patterns, namely between that from the refined structure by Laufek et al. (2007) and the experimental powder pattern reported by Orlandi et al. (2007). For clarity, all

data discussed are displayed in Fig. 9. First, the shift between patterns calculated from the structure data of Laufek et al. (2007) and Orlandi et al. (2007) is caused by different unit-cell volumes,  $4158.2(15)$  and  $4192(3) \text{ \AA}^3$ , respectively. Further, there are a few mismatches between the calculated intensities of some diffractions in the two powder patterns. The main discrepancy, as was mentioned above, is between the powder data reported by Orlandi et al. (2007), their own results of structural refinement (calculated powder pattern), results of Laufek et al. (2007) and currently presented experimental powder diffraction data. The diffraction with the highest intensity in the experimental powder pattern of Orlandi et al. (2007) is  $-11 \ 1 \ 2$  and a second one of high intensity is  $-6 \ 0 \ 7$  ( $I_{\text{rel}} = 88$ ). According to the structural model of Orlandi et al. (2007), the former should have an intensity of  $44$  and the latter of  $64$ . It is a question, why Orlandi et al. (2007) reported as the diffraction of the highest calculated intensity,  $-11 \ 1 \ 1$  at  $30.63^\circ 2\theta$ , because from their own structural model it should have  $I_{\text{rel}} = 89$ . Why there are such differences between the experimental powder pattern of Orlandi et al. (2007) and their own structural model on the one hand, and our data and calculated pattern on the other, is not clear. The currently presented powder diffraction data are quite homogeneous (overall intensity agreement of both diffraction geometries). Orlandi et al. (2007) suggested that these problems arose from various causes such as fibrous habit of the crystals, long-range disorder at the crystal scale, and consequently bad quality of the crystal structure refinement. Based on the current results, such explanations seem unlikely.

## 5. Chemical composition

Quantitative chemical analyses of marrucciite from Gelnica were carried out by means of a Cameca SX 100 electron microprobe in wavelength-dispersive mode (State Geological Institute of Dionýz Štúr, Bratislava), using an acceleration voltage of  $20 \text{ kV}$ , a sample current of  $15\text{--}20 \text{ nA}$  and a beam diameter of  $3\text{--}8 \text{ }\mu\text{m}$ . The following standards and spectral lines were employed: PbS (Pb  $M_{\alpha}$ ),  $\text{CuFeS}_2$  (Cu, Fe, S  $K_{\alpha}$ ), ZnS (Zn  $K_{\alpha}$ ),  $\text{Sb}_2\text{S}_3$  (Sb  $L_{\beta}$ ), Ag (Ag  $L_{\alpha}$ ), Cd (Cd  $L_{\alpha}$ ), Bi (Bi  $L_{\alpha}$ ), HgS (Hg  $L_{\alpha}$ ),  $\text{SnO}_2$  (Sn  $L_{\beta}$ ), FeAsS (As  $K_{\beta}$ ), PbSe (Se  $L_{\beta}$ ) and NaCl (Cl  $K_{\alpha}$ );  $\beta$  lines for Sb, Sn, As and Se were used to solve overlaps problems. The contents of Ag, As and Se were sought but not detected (detection limit close to  $0.01\text{--}0.05 \text{ wt. \%}$ ).

Representative analyses of marrucciite from Gelnica are given in Tab. 3,

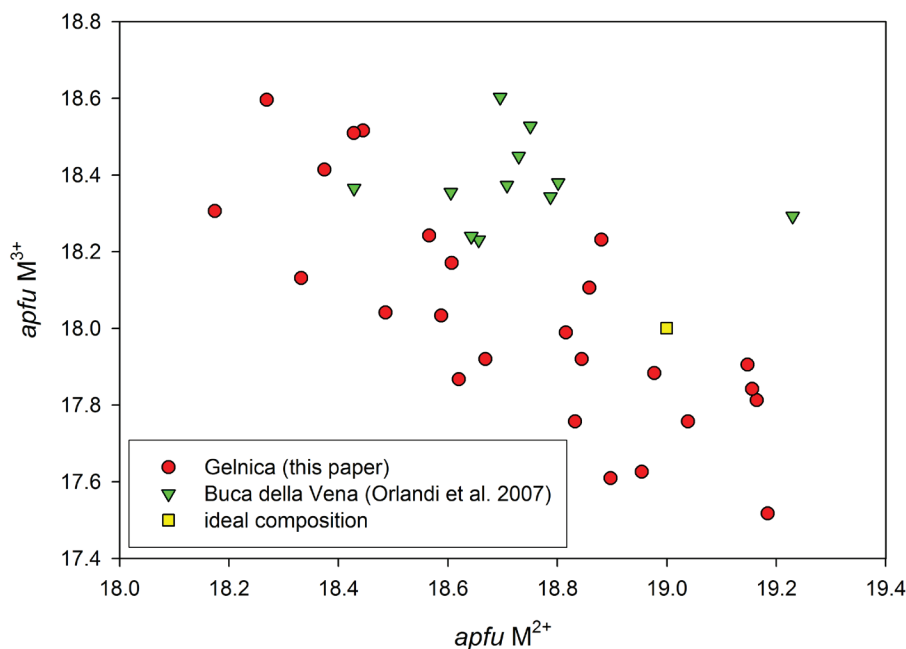
**Tab. 3** Representative electron microprobe analyses of marrucciite from Gelnica (wt. %)

Fe	0.38	0.41	0.05	0.07	0.33	0.00	0.01	0.01	0.15	0.02	0.00
Pb	43.42	43.24	43.37	42.99	43.08	43.24	43.13	44.24	44.15	44.33	43.01
Cd	0.01	0.00	0.00	0.05	0.07	0.06	0.05	0.00	0.02	0.05	0.01
Zn	0.03	0.00	0.07	0.00	0.00	0.00	0.00	0.02	0.05	0.00	0.00
Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.08	0.00	0.08
Hg	7.46	7.67	7.97	7.71	7.27	8.24	8.38	7.57	7.79	7.88	7.99
Cu	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.07	0.04	0.00	0.02
Sb	28.71	29.02	28.71	28.92	29.04	28.29	28.45	28.67	28.57	28.78	28.54
Bi	0.10	0.00	0.15	0.00	0.00	0.16	0.00	0.16	0.00	0.00	0.00
S	19.49	19.52	19.48	19.77	19.67	19.25	19.46	19.97	19.85	19.93	19.61
Cl	0.09	0.10	0.09	0.06	0.07	0.03	0.04	0.03	0.04	0.03	0.04
total	99.69	100.00	99.88	99.57	99.53	99.26	99.52	100.81	100.75	101.03	99.30

**Tab. 4** Comparison of chemical composition of marrucciite from Gelnica and Buca della Vena (wt. %)

	Gelnica <sup>1</sup>		Buca della Vena <sup>2</sup>		Buca della Vena <sup>3</sup>		ideal <sup>4</sup>
	mean	range	mean	range	mean	range	
Fe	0.06	0.00–0.41					
Pb	43.13	41.59–44.42	42.17	41.98–42.37	42.41	42.34–42.51	43.71
Cd	0.02	0.00–0.07					
Zn	0.02	0.00–0.07					
Sn	0.03	0.00–0.08					
Hg	7.83	7.27–8.38	7.73	7.25–8.29	7.90	7.78–7.98	7.94
Cu	0.03	0.00–0.31	0.09	0.00–0.27	0.18	0.08–0.34	
Sb	29.15	28.29–30.16	28.96	28.79–29.22	29.71	29.65–29.79	28.90
Bi	0.12	0.00–0.66					
S	19.71	19.25–20.06	19.00	18.85–19.33	19.47	19.22–19.64	19.45
Cl	0.05	0.03–0.10	0.06	0.00–0.15	0.02	0.04–0.08	
total	100.15	98.01–102.37	98.02	97.29–98.86	99.73	99.53–99.83	100.00

<sup>1</sup> 25 analyses in 7 independent samples (this paper); <sup>2</sup> 7 analyses in sample A (Orlandi et al. 2007); <sup>3</sup> 4 analyses in sample B (Orlandi et al. 2007); <sup>4</sup> ideal composition of marrucciite  $\text{Hg}_3\text{Pb}_{16}\text{Sb}_{18}\text{S}_{46}$ .



**Fig. 10** Contents of divalent (Pb + Hg + Cu + Cd + Fe + Zn + Sn) and trivalent (Sb + Bi) cations in marrucciite from Gelnica and Buca della Vena.

and a comparison with data published for the same mineral from Buca della Vena mine (Orlandi et al. 2007) is made in Tab. 4 and Fig. 10. The chemical composition of marrucciite from both localities is very similar. Marrucciite from Gelnica in addition contains minor amounts of Bi (up to 0.66 wt. %), Fe (0.41 wt. %), Sn (0.08 wt. %), Cd (0.07 wt. %) and Zn (0.07 wt. %). Interesting are regular minor contents of Cl (up to 0.15 wt. % corresponding to 0.32 apfu) in marrucciite from both occurrences (Fig. 11). This indicates the possible presence

of Cl in the crystal structure of marrucciite. Attempts to find its position in crystal structure using the single-crystal data collected by Laufek et al. (2007) were made, however no sensible solution was obtained. As indicated by recently published data, minor contents of specific elements (such as Cl or O) can play a critical role in mineral formation. Examples include dadsonite (with 0.2–0.4 wt.% Cl), scainiite (0.65 wt. % O – Orlandi et al. 1999), pellouxite (0.33 wt. % Cl and 0.39 wt. % O – Orlandi et al. 2004), pillaitite (0.98 wt. % Cl and 0.21 wt. % O – Orlandi et al. 2001), rouxelite (0.20 wt. % O – Orlandi et al. 2005) or chovanite (0.06 wt. % O – Topa et al. in print). The empirical formula of marrucciite from Gelnica, calculated from average compositions (Tab. 4) on the basis of 83 apfu is  $\text{Hg}_{2.93}(\text{Pb}_{15.63}\text{Fe}_{0.08}\text{Cu}_{0.04}\text{Cd}_{0.02}\text{Zn}_{0.02}\text{Sn}_{0.02})_{\Sigma 15.81}(\text{Sb}_{17.97}\text{Bi}_{0.04})_{\Sigma 18.01}(\text{S}_{46.14}\text{Cl}_{0.11})_{\Sigma 46.25}$ . This is in good agreement with the ideal formula  $\text{Hg}_3\text{Pb}_{16}\text{Sb}_{18}\text{S}_{46}$  derived from the crystal structure study.

## 6. Conclusions

This paper presents description and occurrence characteristics of marrucciite from Gelnica, Slovakia. Material from this locality was described some years ago under the unapproved names “gelnicite” or “gelnic-aite”. Mineralogical, chemical, physical and structural data for marrucciite from Gelnica and their comparison with published data for the same mineral phase from the type locality Buca della Vena mine (Italy) are given. At Gelnica, marrucciite belongs to the youngest primary mineral phases, which originated, together with cinnabar and bournonite, during hydrothermal re-mobilization accompanying a strong tectonic activity. Because marrucciite occurs in two distinct mineral assemblages of Pb–Sb sulfosalts, including both members with lower Pb con-



tents (zinkenite, scainiite) and Pb–Sb sulfosalts (boulangerite, bournonite), the determining factor for its origin was probably the presence of sufficient Hg in the source fluids.

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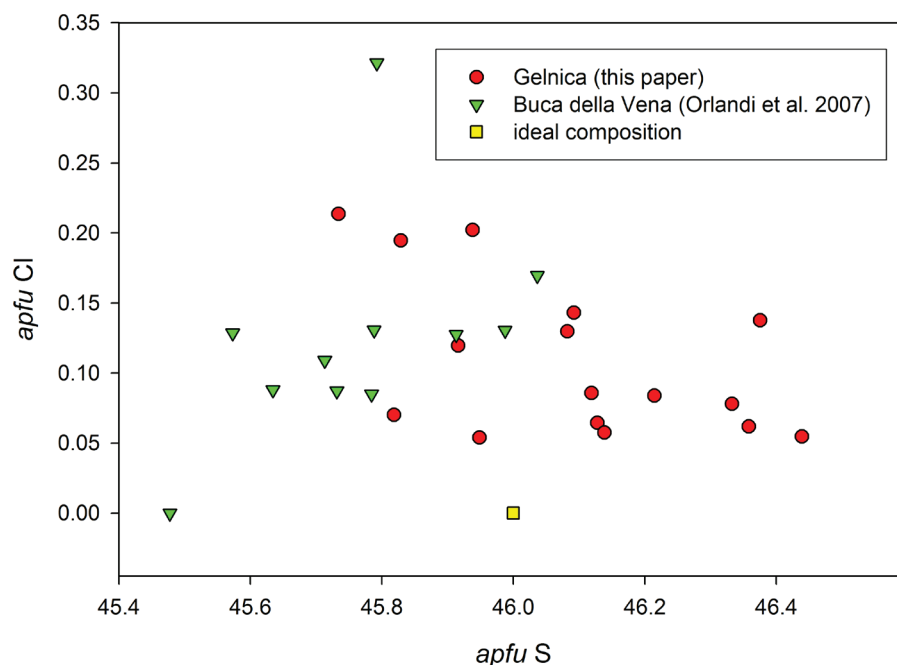


Fig. 11 Binary plot of S vs. Cl (apfu) in marrucciite from Gelnica and Buca della Vena.

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