Hydrothermal siderite – basemetals vein mineralization in the vicinity of Čavoj, Suchý Mts.

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Abstract. Detailed mineralogical and paragenetical research distinguished several stages of the hydrothermal mineralization at the Čavoj deposit. The first stage is Ni-Co assemblage in the siderite veins, with arsenopyrite, gersdorffite and $NiAs_2$ phase. The second is quartz-carbonate-sulphide stage with Ag-mineralization (silver, freibergite, Ag-tetrahedrite, pyrargyrite, argentite, polybasite). Tetrahedrite with high Ag content (up to 35 wt. %) is unique in the Tatric tectonic unit. The youngest stage is represented by barite mineralization with hematite.

Key words: Western Carpathians, siderite mineralization, Pb-Zn-Ag mineralization, freibergite, Ag-sulphosalts

Introduction

The first report about mining activities in the Čavoj is from years 1568–1569, however in the year 1589, mines were destroyed. Renewal of mining was in the first half of 17th century. According to archive reports in the year 1609. 60 tons of lead from Čavoj was exported to Silesia. In the year 1613 it was only 45 tons. During Rakoczy uprising, the mines were closed and since ninetieth years of 17th century the baron Schmidegg reopen mines. Čavoj and Valaská Belá mines were reopen in the 1724, but in the 1746 following bad results mining activities were stopped. Mining company from Banská Štiavnica repurchased Čavoj deposit in the 1783. However, the unprofitable exploitation was stopped in the 1795 (Holec, 1968). In period 1941–1944 were rejected 270 m in the Eleonora adit (Mikoláš et al., 1993).

Čillík & Polák in Slávik et al. (1967) described mineralization in the Čavoj. Ore mineralization occurs in tiny ore veins in the crystalline schists. Veins generally have direction SW-NE with steep dip to SE and thickness up to 2 m. Two generations of minerals were distinguished by Kantor (1977): older – quartz, calcite, barite, siderite and younger – galena, sphalerite, pyrite and arsenopyrite. Šlepecký et al. (1992) described from the Čavoj deposit gersdorffite and Ag minerals as: Ag-tetrahedrite, freibergite, argentite, polybasite, stephanite, pyrargyrite and native silver.

Variscan age of Pb-Zn mineralization supports lead isotopes investigations: 240-250 Ma (Kantor & Rybár, 1964) (sample of galena from Temeš), 240-270 Ma (Černyšev et al., 1984) (sample of galena from Čavoj - Mendel adit).

Sulphur isotopic composition of barite is $\delta^{34}S = +23.7$ ‰ (Kantor, 1977). Repčok et al. (1993) provided isotopic analyses of oxygen and carbon in calcite (Čavoj, Baniská and Geschenk localities): $\delta^{13}C_{PDB}$ from –5.44 to –8.79 ‰, $\delta^{18}O_{SMOW}$ from +14.68 to +20.48 ‰.

After expansive drill-hole prospecting, reserves were calculated and ores were classified to rank P1 and Z3 (Mikoláš et al., 1995).

Low attention of mineralogists was paid to mineralization at the Čavoj deposit. No publication in periodical mineralogical magazines was published up to this time; results of mineralogical – geochemical investigations could be found in manuscripts and proceedings. During our mineralogical study we have reconstructed development of mineralization and correctly determined minerals by microprobe analysis.

Methods of study

Samples for mineralogical study were taken from old dumps in the vicinity of Čavoj village. A Carl Zeiss Jena – Jenapol microscope was used for microscopic studies. Sulphides and sulphoarsenides were analysed by a wave-dispersion (WDS) electron microprobe and photographed by back-scattered electron (BSE) at Faculty of Natural Sciences, Comenius University Bratislava; using a JEOL JXA 840A probe under following conditions: 20kV, 15nA, beam diameter 2-5 μm, standards – arsenopyrite, pyrite, sphalerite, cinnabar, chalcopyrite, GaAs, Fe, Ni, Co, Sb, Cu, Cd, MnO.

Ag minerals and Ag-tetrahedrites were analysed in the Geologisk Institut University of Kobenhagen in Danmark; using a JEOL SUPERPROBE 733 probe under following conditions: 15kV, 10nA, beam diameter 5 μm, standards – Sb_2Se_3, Ag, Cu_3AsS_4 for Ag minerals and 20kV, 20nA, standards ZnS, HgS, Ag, CdS, Cu_3AsS_4, Cu_3SbS_4, $CuFeS_2$ for tetrahedrite.

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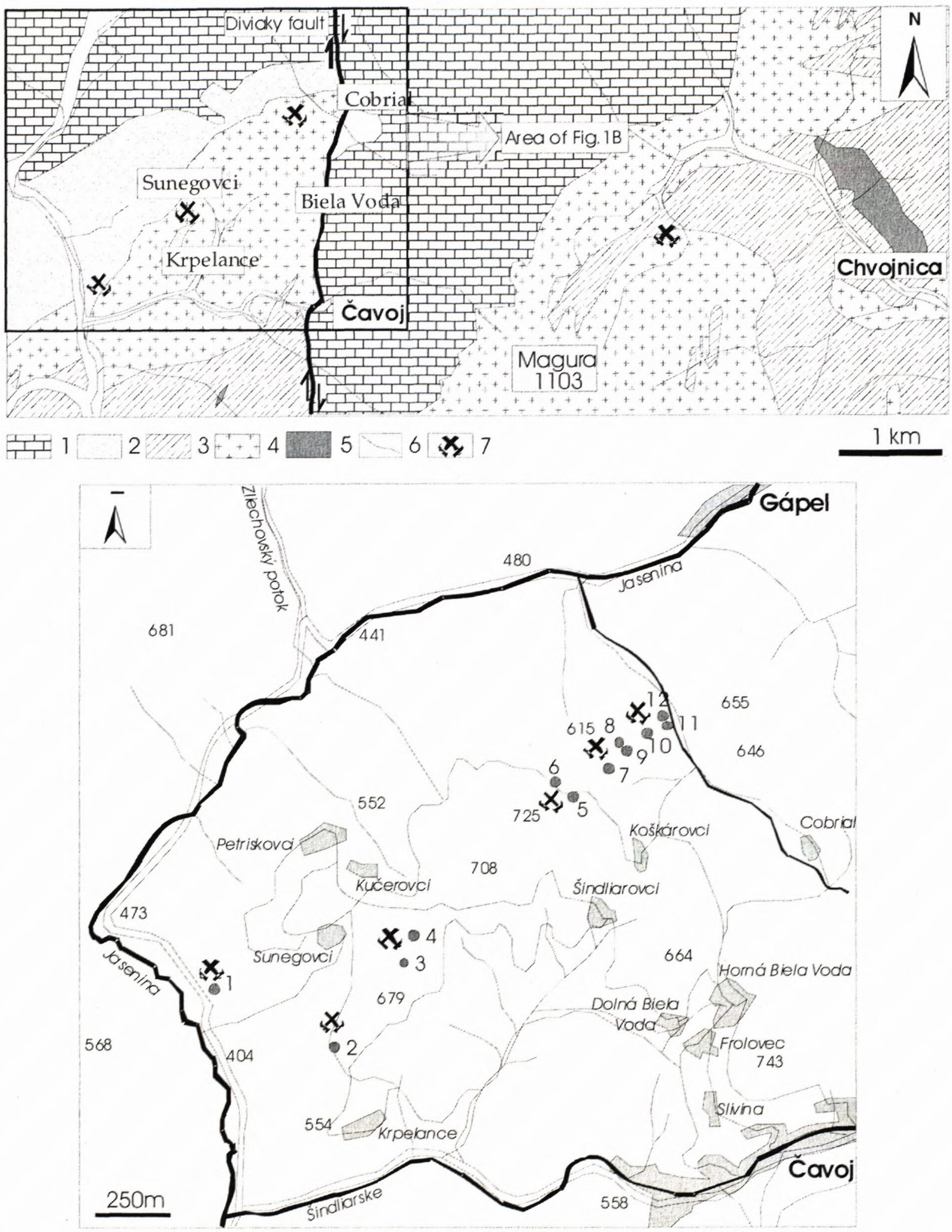

Fig. 1A: Schematic geological map of vicinity of Čavoj (according to Mahel', 1985). 1 - undivided Mesozoic (Krížna nappe and sedimentary Mesozoic cover), 2 – quartz biotitic paragneisses, 3 – ribbed migmatites and migmatized micaschists, 4 – leucocratic granites, biotitic granites, granodiorites and quartz diorites, 5 – amphibolites, 6 – quaternary delluvial and alluvial sediments, 7 – old mine entrances.

Fig. 1B: Schematic sketch of mining field between Čavoj and Gápel' with names of old adits and shafts: 1) Strieborná adit, 2) Alte adit, 3) Geschenk shaft, 4) Pingové pole field, 5) Ferdinand shaft, 6) Mendel adit, 7) Trojičná shaft, 8) Nepomuk adit, 9) Kormendi adit, 10) Jozef adit, 11) Eleonóra adit, 12) Kaiser adit.

Carbonates were analysed by an energy-dispersion (EDS) KEVEX at Geological Survey of Slovak Republic Bratislava, using a JEOL SUPERPROBE 733.

Geological settings and ore mineralization

The Pb-Zn-Ag deposit Čavoj is located in the Suchý Mts. The crystalline complexes of the Suchý Mts. are separated from Malá Magura Mts. by the Paleogene Diviaky fault (Fig. 1A). The crystalline core of the Suchý Mts. is mainly composed of granitoid rocks, paragneisses and migmatite complexes. The metamorphic rocks correspond to high-grade paragneisses. Granitic rocks (tonalites, granodiorites, granites) belong to the S-type group (Hovorka & Fejdi, 1983).

The age of granitoidic rocks from the Suchý and Malá Magura Mts. was determined by Rb-Sr isochron at 393 ± 6 Ma (Kráľ et al., 1987). Variscan tectonogenesis is dominant in both cores. The Alpine restructuring of the crystalline complex is relatively poor and did not change the older tectonic pattern substantially (Maheľ, 1985). P-T-X parameters of metamorphic processes indicate differences in their progressive and retrogressive metamorphic evolution in the crystalline cores of Suchý and Malá Magura Mts. The metamorphic temperatures and pressures are as follows: Suchý Mts: 540 - 560° / 4 - 5 Kbar, XH_2O = 0.6 - 0.8, Malá Magura Mts: 620-640° / 4.5 - 5.5 Kbar, XH_2O = 0.8-1.0 (Dyda, 1994).

Investigated hydrothermal siderite - basemetal (Pb-Zn-Ag) mineralization occurrences are situated 2 km NW and from the village Čavoj between settlements Krpeľanci, Sunegovci, Kučerovci, Šindliarovci and Koškárovci in the crystalline complex of the Suchý Mts (Fig. 1B). Mining field generally has direction NE-SW, length approximately 3.25 km and width in average about 50 m. It is situated in biotitic gneisses, paragneisses, granodiorites, granites, ribbed migmatites and migmatized paragneisses. Veins of pegmatites 50 cm thick are often situated in the migmatites. Samples were taken from old dumps shafts and adits Strieborná, Alte, Geschenk, Pingové pole, Ferdinand, Mendel, Trojičná, Jozef, Nepomuk, Eleonóra (Fig. 1B).

Mineralogy

Ore minerals

Acanthite is relatively rare on the Pingové pole locality. It forms anhedral grains and admixtures within galena large up to 0.05 mm in size (Fig. 2). Its characteristic feature is instability under the reflected polarised light (corrosion and colour changes). Acanthite is one of the youngest sulphide minerals at the deposit. WDS analyses are presented in Table 1 and in Fig. 3.

Arsenopyrite occurs commonly in the form of euhedral grains in large up to 1 mm in size or in form of impregnations in quartz I, mainly at the Jozef locality. It sometimes forms anhedral aggregates. Arsenopyrite occurs with pyrite I and pyrrhotite. Euhedral crystals are

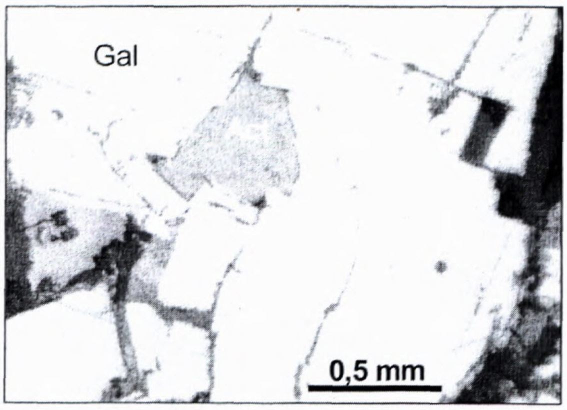

Fig. 2 Anhedral grains of acanthite (Act) up to 0,05 mm in galena (Gal). Reflected polarized light.

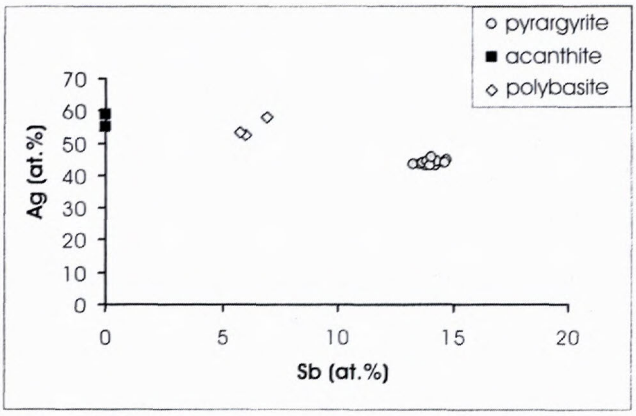

Fig. 3. The relationship between Ag and Sb content in the Ag sulphides and sulphosalts from the Čavoj deposit.

often crushed and cracks are filled by chalcopyrite, galena and sphalerite.

Bournonite is rare at the Jozef and Eleonóra localities. Bournonite forms anhedral agregates up to 0.02 mm in size. At the Jozef locality, it occurs with arsenopyrite and replace chalcopyrite I. On the Eleonóra locality bourno nite occurs with galena. Bournonite was identify by microscopic study by its greyish white colour with a distinct blue tint and very rare was observed weak anisotropy on twin lamellae.

Galena is one of the major sulphide minerals at the Čavoj deposit. It is usually medium to fine-grained, rarely forms individual crystals up to 0.5 cm in diameter. Galena creates veins in the quartz and carbonates up to few cm in thick. It accompanies sphalerite. Galena replaces chalcopyrite and is replaced by tetrahedrite and pyrite II. The fissures are often filled by Ag-sulphosalts and sulphides (Fig. 2). Secondary minerals from the grain-margins and through fissures corrode galena.

Gersdorffite is very abundant at the Jozef locality. It forms aggregates of euhedral crystals or impregnations in the quartz I and in the siderite. It occurs with arsenopyrite and pyrite I, replacing these minerals. Other association is with tetrahedrite, chalcopyrite and sphalerite. Gersdorffite create atolls structures with galena and rarely forms ske-

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leton aggregates (Fig. 4). Gersdorffite is heterogeneous and is oscillatory zoned (Fig. 5). Content of As and S is changing in the zones. The black zones have the highest content of S, while the lightest *phase* with diameter 10 μm (Fig. 6) correspond to *$NiAs_2$*. It is possible that it is one of these minerals: *rammelsbergite, pararammelsbergite* or *krutovite*. WDS analyses are presented in Table 2 (Fig. 7).

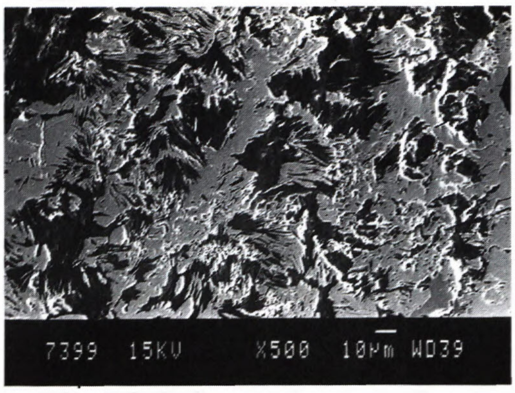

Fig. 4. Skeleton aggregates of gersdorffite. SEM-BEI.

Fig. 5. Oscillatory zoned gersdorffite crystals with changing content of As and S. The black zones have the highest content of S, while the lightest zones have the highest As content. SEM-BEI.

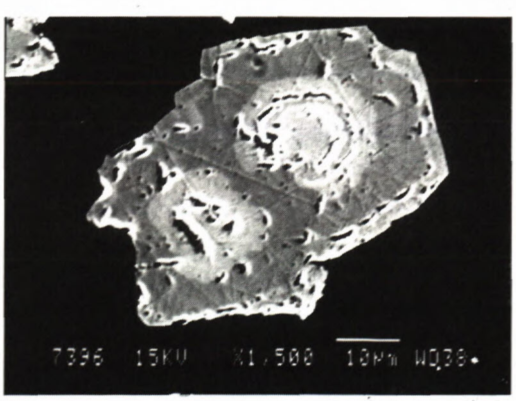

Fig. 6. Detailed view of gersdorffite grain. Darkest zones correspond to gersdorffite; white zones correspond to $NiAs_2$ phase. SEM-BEI.

Gold was found only exclusively at the Strieborná locality in the form of anhedral grain (0.0X mm) in the quartz vein. It occurs in the fragments of quartz, that cements veins of secondary Pb minerals in the galena. Its position within the succession scheme is uncertain.

Hematite is relatively rare and occurs at the Ferdinand locality in the barite. Hematite forms lamellar crystals up to 1 mm in size. It occurs in association with barite and replaces pyrite III and barite. The youngest mineral assemblage is consisting of hematite with barite and pyrite III. Hematite was identified by microscopic study. It has grey-white colour with a bluish tint and deep-red internal reflections.

Chalcopyrite is abundant at the all localities in the Čavoj deposit. It forms anhedral grains in two different associations and generations:

1. as inclusions in sphalerite up to 100μm in size forming blebs, dots, minute particles and vermicular structures in intimate chalcopyrite-sphalerite intergrowth.
2. in association with carbonate, pyrite I, galena or tetrahedrite.

Veins of chalcopyrite penetrate tetrahedrite and sphalerite and replace galena from margins. Furthermore, chalcopyrite replaces gersdorffite.

Marcasite is relatively abundant at the locality Baniská in the quartz I in the form of lamellar crystals up to 2 mm in size. It occurs with pyrite I and is replaced by quartz II. Its relation to other ore minerals is unclear. Marcasite was identified by optical properties. It has yellowish white colour and strong white bireflectance with brownish tint. Its anisotropy is strong with blue and green-yellow colour.

Native silver occurs only exclusively at the localities Strieborná and Geschenk. It forms admixtures, inclusions and veins (up to 10 μm) in the galena. Its relation to other ore minerals is unclear. WDS analyses are given in Table 1.

Pyrargyrite is abundant mineral at the localities in the Čavoj deposit. It forms dark-red anhedral aggregates (up to 0.5 cm) in the quartz and galena. Pyrargyrite occurs with galena and tetrahedrite. Fissures in galena are often filled by pyrargyrite (Fig. 8). Together with other Ag sulphosalts and sulphides, it is one of the youngest minerals at the deposit. WDS analyses are given in Table 3, and their plot in Fig. 3. In reflected polarized light it has bluish grey colour with strong anisotropy masked by intense carmine-red internal reflections.

Polybasite is rare and it forms anhedral grains and admixtures in the galena (up to 0.2 mm) (Fig. 9). Fissures in galena are filled by polybasite. WDS analyses are in Table 1 and their plot in Fig. 3. In reflected polarized light it has grey colour with a greenish tint. The anisotropy is very weak. A deep-red internal reflections are nearly always visible.

Pyrite is very abundant in silicified hydrothermal alteration zones in wallrock and also in hydrothermal veins. It forms euhedral crystals up to 3 mm in size. Pyrite occurs in several generations:

1. pyrite I forms euhedral grains and impregnations in the quartz and carbonates. Euhedral crystals are some-

Table 1. Representative electron microprobe analyses of ore minerals from the Čavoj deposit

	*	1	2	3	4	5	6	7
wt. %	Cu	0.57	2.53	0.03	1.63	0.01	0.01	
	S	16.43	18.11	13.49	15.26	0.47	0.01	
	As	0.10	0.02	-	-	0.07	0.01	
	Ag	81.22	79.12	0.01	70.74	95.59	102.5	
	Sb	0.01	0.01	0.01	8.56	0.01	0.01	
	Se	0.02	0.01	-	-	0.01	0.01	
	Fe	-	-	0.01	0.01	-	-	
	Pb	-	-	86.24	0.47	-	-	
	Bi	-	-	0.01	0.01	-	-	
	Σ	98.36	99.80	99.80	96.12	96.68	96.16	102.6
at. %	Cu	0.70	2.97	0.06	2.16	2.08	0.02	0.02
	S	40.16	42.20	50.22	39.45	38.69	1.63	0.03
	As	0.10	0.02	-	-	-	0.10	0.01
	Ag	59.01	54.79	0.01	52.26	53.31	98.23	99.89
	Sb	0.01	0.01	0.01	6.01	5.76	0.01	0.01
	Se	0.02	0.01	-	-	-	0.01	0.04
	Fe	-	-	0.02	0.01	0.01	-	-
	Pb	-	-	49.68	0.09	0.18	-	-
	Bi	-	-	0.01	0.00	0.00	-	-

* 1, 2 – acanthite, 3 – galena, 4, 5 – polybasite, 6, 7 – native silver

Table 2. Representative electron microprobe analyses of gersdorffite (1-8) and $NiAs_2$ phase (9-15) from the Čavoj deposit.

	Jozef adit														
wt. %	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ni	27.96	28.34	27.97	28.76	28.64	28.06	29.00	28.89	23.42	22.56	23.48	23.47	23.12	21.67	21.67
As	53.84	50.34	49.34	52.28	51.61	54.48	52.91	52.26	67.44	68.96	66.63	66.16	66.31	68.02	67.57
S	11.96	13.58	14.94	13.43	13.86	11.55	12.59	13.00	3.36	4.26	4.84	5.10	4.04	4.31	4.55
Co	2.85	3.05	3.17	3.33	3.32	2.87	2.91	2.90	3.10	3.44	3.51	3.51	3.69	3.53	3.53
Fe	2.21	2.77	2.41	2.60	2.59	2.22	2.13	2.12	1.33	1.74	1.77	1.77	1.60	1.72	1.72
Cu	0.15	0.56	0.56	0.46	0.46	0.15	0.25	0.25	0.10	0.30	0.08	0.08	0.09	0.14	0.14
Σ	98.97	98.65	98.39	100.87	100.47	99.32	99.79	99.41	98.74	101.26	100.32	100.09	98.86	99.40	99.18
	at. %														
Ni	28.72	28.59	27.91	28.53	28.38	28.86	29.33	29.18	26.92	25.09	26.09	26.06	26.30	24.53	24.51
As	43.34	39.80	38.59	40.64	40.08	43.91	41.93	41.37	60.75	60.09	58.02	57.55	59.09	60.35	59.90
S	22.50	25.08	27.30	24.39	25.14	21.76	23.31	24.05	7.06	8.66	9.85	10.36	8.41	8.94	9.42
Co	2.92	3.07	3.15	3.30	3.28	2.94	2.94	2.92	3.55	3.81	3.89	3.88	4.18	3.98	3.98
Fe	2.39	2.94	2.53	2.72	2.70	2.40	2.27	2.25	1.61	2.04	2.07	2.07	1.92	2.05	2.05
Cu	0.14	0.52	0.52	0.42	0.42	0.14	0.23	0.23	0.11	0.30	0.08	0.08	0.10	0.15	0.15

Table 3. Representative electron microprobe analyses of pyrargyrite from the Čavoj deposit.

		Eleonóra adit		Strieborná adit		Eleonóra adit							
		1	2	3	4	5	6	7	8	9	10	11	12
wt. %	Cu	0.07	0.01	0.01	0.18	0.21	0.16	0.09	0.10	0.21	0.16	0.42	0.01
	S	17.58	17.77	16.97	16.90	17.11	16.77	17.21	16.29	17.73	16.79	17.87	16.49
	As	0.49	0.02	0.08	0.01	0.13	0.01	0.04	0.01	0.01	0.09	0.07	0.08
	Ag	60.59	59.70	60.61	60.68	60.20	60.93	61.28	60.71	60.17	60.09	61.39	62.45
	Sb	21.40	22.46	22.72	22.19	21.74	21.57	21.66	22.61	22.10	22.68	21.15	21.83
	Se	0.01	0.01	0.01	0.04	0.03	0.06	0.01	0.07	0.01	0.01	0.01	0.01
	Σ	100.15	99.98	100.4	100.0	99.41	99.51	100.25	99.79	100.23	99.82	100.29	100.87
at. %	Cu	0.09	0.01	0.01	0.22	0.26	0.20	0.11	0.12	0.25	0.20	0.51	0.01
	S	42.39	42.88	41.38	41.33	41.83	41.24	41.78	40.35	42.67	41.21	42.62	40.37
	As	0.51	0.02	0.08	0.01	0.14	0.01	0.04	0.01	0.01	0.09	0.07	0.08
	Ag	43.42	42.81	43.93	44.11	43.75	44.53	44.21	44.69	43.04	43.83	43.51	45.44
	Sb	13.59	14.27	14.59	14.29	14.00	13.97	13.85	14.75	14.01	14.66	13.28	14.07
	Se	0.01	0.01	0.01	0.04	0.03	0.06	0.01	0.07	0.01	0.01	0.01	0.01

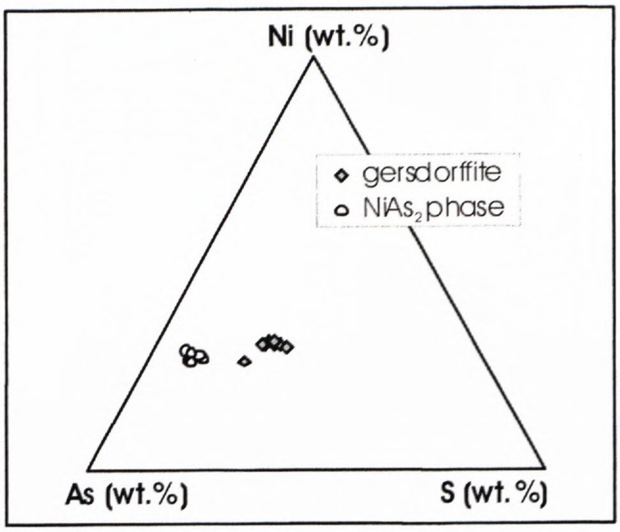

Fig. 7. The ternary diagram of WDS electron microanalyses of gersdorffite and $NiAs_2$ phase from Čavoj.

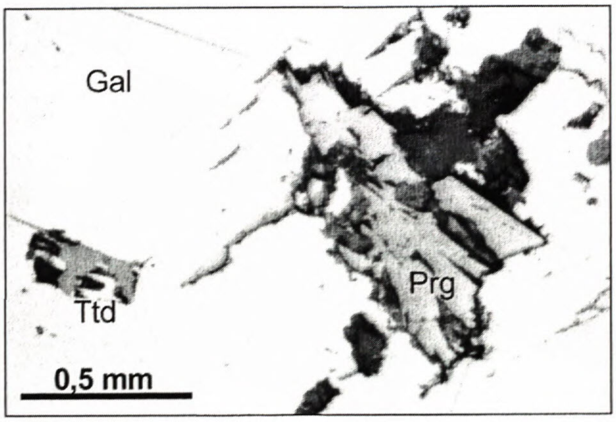

Fig. 8. Anhedral grain of pyrargyrite (Prg) and tetrahedrite (Ttd) in galena (Gal). Reflected polarized light.

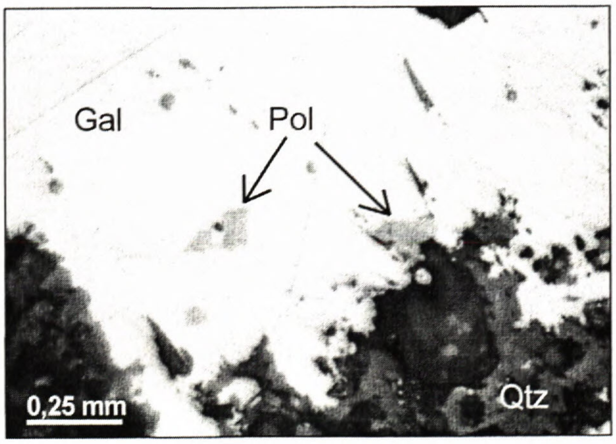

Fig. 9. Anhedral grains of polybasite (Pol) in galena (Gal). Reflected polarized light.

times crushed. Fissures are filled by secondary Fe-minerals. Pyrite I occurs in association with arsenopyrite, gersdorffite and marcasite. Sphalerite, galena and chalcopyrite intensive replace pyrite I from grain margins.

2. pyrite II occurs in form of tiny grains (up to 0.5 mm). Sphalerite, galena and chalcopyrite are replaced by pyrite II.

3. pyrite III is associated with barite and hematite.

Pyrrhotite was sporadically found at the Strieborná adit locality. Pyrrhotite forms anhedral grains in quartz I. It is replaced by galena and sphalerite. Pyrrhotite was identifying by microscopic properties: its colour is cream with a faint pinkish brown tint. It tarnishes slowly on air. Bireflectance is very distinct – brownish creamy. Anisotropy is very strong with yellow-grey, greenish grey or greyish blue colour.

Sphalerite is the prevailing ore mineral together with galena. It forms veins several cm thick, rarely 30 cm, in the quartz and carbonate at locality Eleonóra adit. In this locality, sphalerite occurs in two generations. The older sphalerite I has red-brown colour and is impregnated by pyrite. Younger sphalerite II is dark and it forms veins in the older one. Sphalerite II is enclosed by galena. Sphalerite is mostly replaced by galena and often contains chalcopyrite inclusions and admixtures. Sphalerite with „chalcopyrite disease" is enriched in Fe (3.59 wt. %, Table 4). Sphalerite is penetrated by chalcopyrite and tetrahedrite. Sphalerite is from the grain-margins and through fissures intensely corroded by secondary minerals. WDS analyses of sphalerite are given in Table 4.

Stephanite? occurs only rarely in the form of tiny, mostly anhedral grains in association with galena. It was identified only on the base of the optical properties: its colour is grey with pinkish tint. Bireflectance is weak, but distinct: grey with a brownish pink tint.

Tetrahedrite and Freibergite are relatively abundant in the all studied localities. Tetrahedrites from the Čavoj deposit have the high content of Ag (Fig. 10). Two types of „tetrahedrites" were distinguished. The 1st type - Ag-tetrahedrite contains 8.63-12.51 wt. % Ag (Table 5). The 2nd type - freibergite contains up to 35.52 wt. % Ag (Table 6). Both types occur with galena, sphalerite, chalcopyrite and Ag sulphosalts. Tetrahedrites are younger than sphalerite and galena. The contents of As and Sb range 0.44-2.94 wt. % and 24.05-26.96 wt. %, respectively. Relation Fe-Zn shows complementary substitution. In reflected polarized light they have grey colour, tetrahedrite with olive tint and freibergite with faint yellowish brown tint.

Gangue minerals

Barite forms veins, lenses and tabular crystals up to 4 cm in diameter. The colour of barite is withe, pink and brownish. It occurs together with calcite, quartz III, hematite and pyrite III. Barite was identified on the base of the optical properties.

Carbonates are very abundant in the Čavoj deposit. Carbonate I - *siderite* (Fig. 11) occurs with quartz I, arsenopyrite, pyrite, and gersdorffite. Siderite replaces quartz I and it is heterogeneous. Carbonate II - *Fe-dolomite* (Fig. 11), occurs with carbonate III - *calcite* (Fig. 11). *Fe-dolomite* and *calcite* are associated with

Table 4. Representative electron microprobe analyses of sphalerite from the Čavoj deposit.

Pingy shafts			Eleonóra adit						Alte adit			
		1	2	3	4	5	6	7	8	9	10	11
wt. %	Zn	63.20	68.96	69.36	67.80	64.71	65.27	63.81	68.13	66.96	66.73	66.85
	Cu	0.12	0.07	0.09	0.07	0.23	0.13	0.05	0.00	0.00	0.13	0.01
	Fe	3.59	0.82	0.68	0.51	0.75	0.88	0.72	1.48	1.47	1.42	1.49
	Mn	0.08	0.00	0.00	0.00	0.00	0.06	0.11	0.03	0.03	0.00	0.14
	Hg	0.10	0.17	0.00	0.16	0.03	0.00	0.04	0.04	0.04	0.05	0.18
	S	35.32	30.55	29.98	30.31	34.78	33.58	34.68	30.88	30.63	31.77	31.31
	Cd	0.46	0.20	0.11	0.19	0.14	0.21	0.16	0.15	0.14	0.23	0.22
	Σ	102.8	100.7	100.2	99.34	100.6	100.1	99.56	100.7	99.28	100.3	100.2
at. %	Zn	45.17	52.06	52.78	51.84	47.29	48.31	47.04	51.24	51.01	50.01	50.35
	Cu	0.09	0.06	0.07	0.06	0.17	0.10	0.04	0.00	0.00	0.10	0.01
	Fe	3.01	0.73	0.60	0.73	0.64	0.77	0.62	1.31	1.31	1.24	1.32
	Mn	0.07	0.00	0.00	0.00	0.00	0.06	0.09	0.03	0.03	0.00	0.12
	Hg	0.02	0.04	0.00	0.04	0.01	0.00	0.01	0.01	0.01	0.01	0.04
	S	51.46	47.02	46.51	47.25	51.82	50.68	52.13	47.35	47.57	48.53	48.06
	Cd	0.19	0.09	0.05	0.09	0.06	0.09	0.07	0.06	0.06	0.10	0.10

Table 5. Representative electron microprobe analyses of Ag-tetrahedrite from the Čavoj deposit.

		Jozef adit											
		1	2	3	4	5	6	7	8	9	10	11	12
wt. %	Fe	3.42	3.65	3.41	3.85	3.28	3.73	3.39	3.26	3.58	3.59	3.55	3.41
	S	24.4	24.27	24.25	24.91	24.03	24.98	23.88	24.1	23.81	23.89	24.26	23.75
	Cu	31.18	30.36	30.09	32.3	29.97	32.32	30.2	30.78	32.14	32.29	32.04	30.42
	Sb	25.26	25.82	26.21	22.75	26.26	23.06	27.26	27.9	25.62	25.7	25.85	27.76
	As	2.34	1.3	1.29	4.14	1.25	3.8	0.33	0.18	1.59	1.61	1.75	0.08
	Cd	0.11	0.22	0.18	0.13	0.2	0.14	0.16	0.18	0.21	0.18	0.06	0.18
	Hg	0.01	0.05	0.27	0.01	0.01	0.01	0.47	0.01	0.01	0.06	0.2	0.01
	Bi	0.29	0.45	0.19	0.28	0.68	0.41	0.21	0.14	0.6	0.08	0.36	0.45
	Zn	3.68	3.8	3.76	3.46	3.85	3.65	3.68	3.87	3.62	3.62	3.69	3.76
	Ag	9.88	11.56	12.2	9.58	12.51	9.56	11.17	10.26	8.91	8.68	8.63	10.82
	Σ	100.72	101.48	101.84	101.42	102.04	101.66	100.56	100.67	100.09	99.7	100.39	100.64
	Fe	3.60	3.85	3.60	3.96	3.47	3.83	3.63	3.47	3.80	3.81	3.74	3.65
	S	44.72	44.55	44.55	44.64	44.29	44.72	44.50	44.67	44.02	44.14	44.52	44.33
	Cu	28.83	28.12	27.89	29.20	27.87	29.19	28.39	28.79	29.98	30.10	29.66	28.64

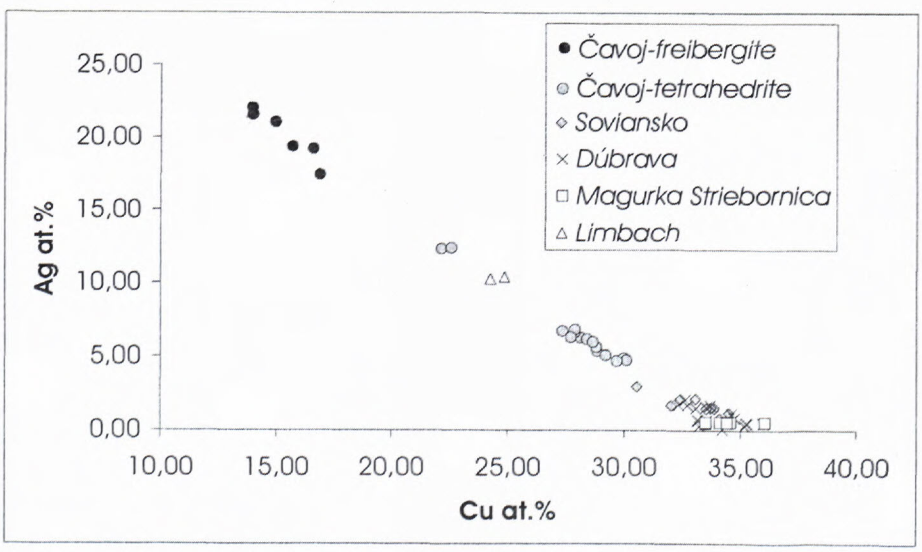

Fig.10. The relationship between Ag and Cu content in the tetrahedrites from Čavoj in comparison with Ag-tetrahedrites from the Tatric tectonic unit. Limbach - Andráš et al. (1990), Soviansko - Luptáková (1999), Dúbrava - Chovan et al. (1998), Magurka-Striebornica - Chovan et al. (1995).

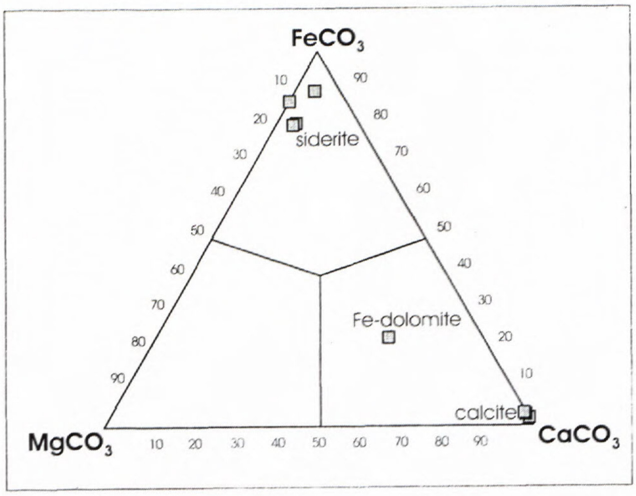

Fig. 11. The ternary diagram of EDS electron microprobe analyses of carbonates from the Čavoj deposit.

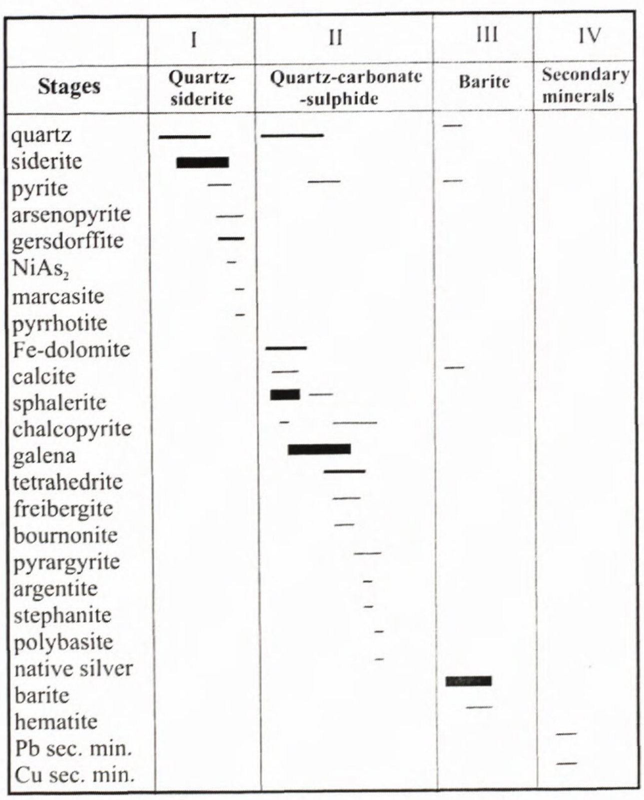

Fig. 12. Paragenetic sequence of the Čavoj deposit.

quartz II, III and other younger sulphide minerals (sphalerite, galena, tetrahedrite, chalcopyrite and Ag-sulphosalts). Galena often fills cavities and fissures in *Fe-dolomite*. *Fe-dolomite* and *calcite* are homogeneous. The chemical composition of carbonates is listed in Table 7.

Quartz is prevailing gangue mineral in the Čavoj. It occurs in three generations. Quartz I occurs with arsenopyrite, pyrite I, gersdorffite, pyrrhotite and marcasite. It is usually white, mainly massive. Quartz I is replaced by carbonates. Quartz II is milky-white, coarse-grained to massive. It is associated with carbonates II and III and intensely replaces quartz I. It occurs together with sphalerite, galena and Ag-sulphosalts. Quartz III occurs together with barite, calcite, hematite and pyrite III.

Development of mineralization

The following mineralization stages were distinguished at localities with base-metal mineralization in the vicinity of Čavoj (Fig. 12). The first mineral assemblage forms veins few cm thick in hydrothermally altered rocks. Siderite is prevailing gangue mineral; quartz is less common. Aggregates of arsenopyrite and pyrite are often. Ni-Co minerals are close with siderite. Other minerals are relatively rare.

The second mineral assemblage forms veins up to 30 cm, composed of milky-quartz and carbonates with sphalerite and galena. Ag-minerals are accompanied by galena. Sphalerite locally forms accumulations up to 25 cm in size.

The third mineral assemblage forms veins up to 10 cm in size.

Discussion

We consider mineralization at the Čavoj locality as carbonate-sulphide, which belongs to the siderite type of mineralization. This type is described from many localities in Tatric, Veporic and Gemeric tectonic Units of Western Carpathians.

Development of mineralization is similar to that in Spišsko Gemerské Rudohorie Mts. (Varček, 1976; Grecula (ed.), 1995), and Nízke Tatry Mts. (Ozdín & Chovan, 1999; Pršek & Chovan, 2001).

Siderite is one from the oldest minerals. Its chemical composition is characteristic by low content of Mg, whereas Ca and mainly Mn contents are increased. High content of Mn is characteristic also for siderite from Bacúch locality (Veporic Unit) (Pršek & Chovan, 2001).

As-Ni mineralization is younger than siderite. Main mineral is gersdorffite, which proceeded sometimes to Ni diarsenides similarly at another occurrences of siderite mineralization in Western Carpathians (Halahyová-Andrusovová, 1972; Chovan et al., (eds.) 1994; Ozdín & Chovan, 1999 and others).

Quartz-carbonate-sulphide mineralization is younger than siderite; carbonate is mainly represented by Fe-dolomite and calcite. Galena prevails over sphalerite and tetrahedrite in sulphide mineral assemblage. In that case, with these amounts of specific sulphide minerals, mineralization at the Čavoj locality could be compared with Bruchatý grúnik occurrence (Ozdín & Chovan, 1999) or Soviansko deposit (Luptáková et al., 2001). However, chalcopyrite or tetrahedrite prevails; galena is rare in Spišsko-Gemerské Rudohorie Mts. (Grecula (ed.), 1995). Chalcopyrite prevails and galena is abundant at the Bacúch locality in Northern Veporic (Pršek & Chovan, 2001). Tetrahedrite and chalcopyrite prevail; galena is presented rarely in the Vyšná Boca area (Ozdín & Chovan, 1999).

Barite, as a youngest mineral is usually presented at the prevalence of localities of siderite mineralization.

Occurrence of freibergite, Ag-tetrahedrite and other Ag sulphosalts is characteristic for Čavoj locality. Silver minerals in abundant amounts were not found at any other locality of siderite mineralization in Western Carpathians. Tetrahedrite with Ag ≥ 4 in the M^{+} position in the tetrahedrite formula $M^{2+}{}_2M^{+}{}_{10}M^{3+}{}_4S_{13}$ is consider to freibergite (Mozgova & Tsepin, 1983). Freibergit from Čavoj has more than 5 apfu of Ag. Silver rich tetrahedrite occurs on several others localities in the crystalline basement at the Western Carpathians. Tetrahedrite from the Bruchatý grúnik (Nízke Tatry Mts.) locality has content up to 7.79 wt. % Ag (Ozdín & Chovan, 1999). Tetrahedrite contains 5.65 wt. % Ag in the Jasenie-Soviansko (Luptáková, 1999), locally freibergite was observed with more than 31 wt. % (Pršek unpublished data). Ag-tetrahedrite with 17.98 wt. % Ag occurs together with electrum, polybasite, galena and sphalerite in the Pezinok – Staré mesto (Andráš et al., 1990). Futhermore, freibergite containing up to 26 wt. % of Ag and Ag-tetrahedrite containing up to 5 wt. % was observed together with stephanite and argentite near Margecany village in the Veporic Unit (Baláž, 1992).

Ag-sulphosalts are in the Tatric relatively rare; from the base-metals mineralization Pod Babou (Malé Karpaty Mts.) are mentioned Ag-Pb-Sb sulphosalts by Cambel (1959). Polybasite occurs at the locality Pezinok-Staré mesto (Malé Karpaty Mts.) (Andráš et al., 1990). Complex Ag-Bi-Pb sulphosalts are presented at several localities of siderite mineralization. Lillianite homologues are presented in Bacúch (Pršek & Chovan, 2001) and Bruchatý grúnik, pavonite homologues in Vyšná Boca (Ozdín & Chovan, 1999).

Silver free sulphosalts are rarely present in Čavoj locality and are represented by bournonite only. Association of bournonite with galena is characteristic. On the other side, Bi (Pb, Cu) sulphosalts are typical for sulphide mineralization at the siderite veins; bournonite and other Sb (Pb, Cu) sulphosalts are rare.

Conclusions

We consider mineralization at the Čavoj locality as carbonate-sulphide, which belongs to the siderite type of mineralization.

Chemical composition of siderite is characteristic by low content of Mg, and increased Ca and Mn contents. As, Ni and quartz-carbonate-sulphide assemblages are present, galena prevail over others sulphides.

Occurrence of freibergite, Ag-tetrahedrite and other Ag sulphosalts is characteristic for Čavoj locality. Silver minerals in abundant amounts were not found at any other locality of siderite mineralization in Western Carpathians. Freibergit from Čavoj has more than 5 apfu of Ag and Ag tetrahedrite has approximately 10 wt.% of Ag.

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References

Andráš, P., Jeleň, S. & Caño, F., 1990: Paragenetic relations between gold-quartz ore mineralization and antimonite ores of the Pezinok deposit, Western Slovakia. *Mineralia Slovaca*, 22, 429-435 (in Slovak).

Baláž, B., 1992: Ag-mineralization in Čierna hora in Margecany area. In: *Ag associations in Czechoslovakia, Donovaly*. DT Ústí nad Labem, ČSVTS, 1-6 (in Slovak).

Cambel, B., 1959 : Hydrothermal deposits in the Malé Karpaty Mts., mineralogy and geochemistry of their ores. *Acta geol. geogr. Univ. Comen.* 3, 338. (In Slovak).

Chovan, M., Háber, M., Jeleň, S. & Rojkovič, I. (eds) 1994: Ore textures in the Western Carpathians. *Slovak Academic Press*, 219p.

Chovan, M., Majzlan, J., Ragan, M., Siman, P. & Krištín, J., 1998: Pb-Sb and Pb-Sb-Bi sulfosalts and associated sulphides from Dúbrava antimony deposit, Nízke Tatry Mts. *Acta Geol. UC*, 53, 37-49.

Chovan, M., Póč, I., Jancsy, P., Majzlan, J. & Krištín, J., 1995: Ore mineralization Sb-Au (As-Pb) at the Magurka deposit, Nízke Tatry Mts. *Mineralia Slovaca*, 27, 397-406 (In Slovak)

Černyšev, I., Cambel, B., Koděra, M., 1984: Lead isotopes in galenas of the Western Carpathians. *Geol. Zbor. Geol. Carpath.* 35, 3, 307-327.

Dyda, M., 1994 : Geothermobarometric charakteristics of some Tatric crystalline basement units (Western Carpathians). *Mitt. Österr. Ges.*, 86, 45-59.

Grecula, P. (ed.) 1995: Mineral deposits of the Slovak Ore Mountains Volume 1. *Geocomplex*, Bratislava. 834p.

Halahyová-Andrusovova, G., 1972: Reflectivity of gersdorffite from Dobšiná. *Geol. Zbor. Geol. Carpath.* 23,1, 55-68.

Holec, G., 1968: Report about literary-historic research of the ore-mining in the Upper Nitra. *MS, Banský výskumný ústav*, Prievidza, 47 (in Slovak).

Hovorka, D. & Fejdi, P., 1983 : Garnets of peraluminous granites of the Suchý and Malá Magura Mts. (the Western Carpathians) - their origin and and petrological significance. *Geol. Zbor. Geol. Carpath.*, 34, 1, 103-115.

Kantor, J. & Rybár, M., 1964: Isotopes of ore - lead from several deposits of West Carpathian crystalline. *Geol. Sbor. Slov. Akad. Vied*, 15, 2, 285-297.

Kantor, J., 1977: Isotopes of sulphur on the barite deposits of the Western Carpathians. *MS, Geofond*, Bratislava, 72.

Kráľ, J., Goltzman, Y. & Petrík, I., 1987: Rb-Sr whole rock isochron data of granitic rocks from the Strážovské vrchy Mts.: the preliminary report. *Geol. Zbor. Geol. carpath.*, 38, 171-179.

Luptáková, J., 1999: Pb, Zn, Cu, Sb hydrothermal mineralization at the locality Jasenie-Soviansko (Nízke Tatry Mts.), *Unpublished diploma thesis, PriFUK*, Bratislava, 1-74 (in Slovak).

Luptáková, J., Chovan, M. & Huraiová, M., 2001: The base metal deposit of Jasenie-Soviansko (Nízke Tatry Mts., Slovakia): A fluid inclusion study. In: Mineral Deposits at the beginning of the 21th Century, Piestrzyński et al (eds), *Balkema*, Netherlands, 297-298.

Maheľ, M., 1985: Geological building of the Strážovské vrchy Mts. *GÚDŠ Bratislava*, 221 (in Slovak).

Mikoláš, S., Šlepecký, T., Sandanus, M., Komora, J. & Januš J., 1993: Malá Magura and Suchý Mts, Au -W prognoses source of mineral raw materials. *MS, Geofond*, Bratislava, 1-365 (in Slovak).

Mikoláš, S., Komora, J., Kandera, K., Sandanus, M., Šlepecký, T., Januš, J., Staňa, Š., Očenáš, D. & Stupák, J., 1995: Čavoj – Gápeľ – Ag, Pb, Zn ores – VP, *MS, Progeo*, Žilina, 114 (in Slovak).

Mozgova, N. N. & Tsepin, A. I., 1983: Fahlores (Peculiarity of the chemical compositions and properties). Moscow, *Nauka*, 280p. (In Russian).

Ozdín, D. & Chovan, M., 1999: New mineralogical and paragenetic knowledge about siderite veins in the vicinity of Vyšná Boca, Nízke Tatry Mts. *Slovak Geological Magazine*, 5, 4, 255-271.

Pršek, J. & Chovan, M., 2001: Hydrothermal Carbonate and Sulphide Mineralization in the Late Paleozoic Phyllites (Bacúch, Nízke Tatry Mts.). *Geolines* 13, 27-34.

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Repčok, I., Ferenčíková, E., Eliáš, K., Rúčka, I., Kovářová, A., Sládková, M. & Wiegerová, V., 1993: Isotope and thermometric study of Pb-Zn mineralization in the surrounding of Čavoj locality. *Mineralia Slovaca,* 25, 362-364 (in Slovak).

Slávik, J. & (EDS.) 1967: Raw materials of Slovakia. *SVTL,* Bratislava, 510 (in Slovak).

Šlepecký, T., Sandanus, M. & Krištín, J., 1992: Pb-Zn-Ag mineralization in the Čavoj-Gápeľ in the crystalline of Suchý Mts. *Ag associations in Czechoslovakia, Donovaly.* DT Ústí nad Labem, ČSVTS, 149-157 (in Slovak).

Varček, C., 1976: Main lines of metalogenetic development of the Spišsko-gemerské rudohorie Mts.. In: Geológia, metalogenéza a prognózy surovín SGR. *Zborník referátov,* Košice, 163p.