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New mineralogical and paragenetic knowledge about siderite veins in the vicinity of Vyšná Boca, Nízke Tatry Mts.

DANIEL OZDÍN[1], MARTIN CHOVAN[2]

[1] Geological Survey of Slovak Republic, Mlynská dolina 1, 817 04 Bratislava 1
[2] Department of mineralogy and petrology, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava 4

Abstract. Siderite vein mineralization occurs near tectonic contact of the Tatricum and Veporicum in eastern part of the Ďumbier Nízke Tatry Mts. The most intensive exposure of the mineralization is in Tatricum tectonic unit in the Vyšná Boca area. The area is composed of regionally metamorphosed rocks of the Mesozoic envelope. We have studied two vein systems: southern (Paurovská, Kliesňová, Helena, Rovienky) and northern (Pod Štefanom, Kumštová, Králička) and several independent occurrences. Veins occur in mylonite zones and have WSW - ENE strike (250°), about 75° southward dip, and their average thickness is 0.5 m. Silification, presence of pyrite and arsenopyrite is characteristic for hydrothermal changes of surrounding rocks. The main vein minerals are siderite, barite and quartz. Pyrite, tetrahedrite and chalcopyrite are dominant sulphide minerals. Sphalerite, arsenopyrite and hematite from oxide minerals are rear. Occurrences of Ni-Co-bearing minerals and sulphosalts of aikinite isotype series are characteristic. Presence of Ag-Bi-bearing sulphosalts and carrollite are exceptional. Ankerite, galenite and tennantite are abundant in some veins only. Oxidized zone is developed mainly in northern vein systems where Fe-hydroxides and Ca-carbonates are the most abundant minerals. Siderite, quartz and sulphide form several generations. After carbonate stage, there was quartz-sulphide stage and then sulphosalt mineralization stage at the locality Paurovská. The latest generation of siderite and hematite veins penetrates into rocks of Mesozoic envelope.

Key words: Mineralogy, siderite veins, carbonates, Cu-Pb-Bi sulphosalts, Western Carpathians.

Introduction

An old mining village Vyšná Boca is located at the end of Bocianska dolina valley, between Ďumbier and Kráľová hoľa parts of Nízke Tatry Mts., 2.5 km NNE from the Čertovica saddle. Numerous tailing piles, feighs, discovery claim and mine galleries, some of them still accessible, are witnesses of the mining activities around the dwelling. According to Bergfest (1952), gold, silver, copper, antimony and later also iron were mined in this area in the past. The oldest records of mining activities near Boca (there is no distinction between Nižná and Vyšná Boca in older literature) are from 1271, when the King Štefan V. confirmed privileges for mining in Boca again (Bergfest, 1952). In 13-th century, gold was cradled in Boca stream, later it was also mined from ore veins. After 1955 (Bergfest, 1952), when the gold mining was on the top, the gold mining started to decline because of discord of mine owners and mine superintendents, low productivity and flooding of some mines. The last reports about gold mining are from the second half of 19-th century, when the mining was definitely over. Maderspach (1880) reports mining of gold, copper and silver and later also limonite and Fe-bearing carbonates in a mine Pod Štefanom. Papp (1919) evaluated this area as perspective for Fe-ore mining because only top horizons of the veins had been mined, and thus there was a significant amount of high quality ore in deeper parts. During the World War II., Kuthan (1941) again confirmed occurrences of gold, antimony, galenite and gold-bearing pyrite in the area SW from Vyšná Boca. During 50s a prospecting for iron ores took place, the emphasise was put on Fe-ore reserves (Zoubek, 1951; Zoubek and Rus, 1951; Čillík, 1955). The results from two galleries at the deposit Paurovská and Kliesňová dolina valley were encouraging, however, the mining was terminated earlier than the ore vein was reached. The mineralogy of the ore deposits Kliesňová and Pod Štefanom was described by Juriga (1958). Zoned arsenopyrite from the Vyšná Boca area was described by Stankovič and Siman (1992). Beside mentioned works, the complete mineralogy of the Vyšná Boca area was described by Koděra et al. (1990, 1990a), Slavkay et al. (1988), Slavkay and Chovan (1990) and Chovan et al. (1996). In mineralogical exposition of Natürhistorische Museum in Vienna, there are two several centimetres large strontianite minerals with radiated structure from the locality "Bocza, Ungarn". It is no doubt, that these samples were found in Austrian – Hungarian Monarchy (the name Bocza was used for today villages Vyšná and Nižná Boca).

Geological characteristics of the area.

Carbonate-quartz-sulphide ore mineralization occurs in the vicinity of Vyšná Boca, dominantly in rocks of crystalline complexes of Tatricum, northward of the Čertovica tectonic lineament. Biotite to two-mica paragneisses with banded structure are the most common metamorphic rocks of crystalline complexes. Garnet-biotite and other types of paragneisses and metaquartzite are less common. Westward of Vyšná Boca Maheľ (1986) describes also light-grey orthogneisses with quartz and microcline porphyroblast. In addition to acidic metamorphic rocks, there are also thin layers of amphiboles. Two types of granitoid rocks represent the rocks of the studied area: Ďumbier and Králička type. Ďumbier type, represented by biotite tonalite to granodiorite, is the most common granitoid rock in the eastern part of the Ďumbier crystalline complex (Biely et al., 1992). Petrík et al. (1993) classified this type of metaaluminous granitoid rocks to I-type granitoid. Cambel et al. (1990) concluded that the temperature of crystallisation was 670 - 700 °C and the age was 368±22 Ma (Rb/Sr method). Králička granite is less abundant (Biely et al., 1992). Peraluminous biotite to two-mica granite to granodiorite (Králička type) (Dupej and Siegl, 1984) forming 9.5 km long and max. 800 width strip from Veľký Gápeľ to Vyšná Boca was classified by Petrík et al. (1993) to S-type granitoid. Cambel et al. (1990) concluded that the temperature of crystallisation was 670-690 °C and the age of the granite was 365±17 Ma (Rb/Sr method). Granitoid and also metamorphic rocks are sometimes transected by up to several tens centimetres thick pegmatite and apatite veins. The Mesozoic envelope rocks composed mainly of low Triassic quartz of Lúžňan formation, sandstone and greywackes are rare, they occur mainly in eastern part of the studied area (at the end of the Kumštová and Starobocianska dolina valley). Rauwackes (at the end of the Starobocianska dolina valley under the Bocianske sedlo pass) and mottled shales and sandstones of Verfen formation are rare.

Mineral deposit characteristics of the area

There are two main types of ore mineralization in the studied area: siderite and gold. Siderite mineralization occurs mainly in mylonite zones within metamorphic rocks WSW to SWS-ward of Vyšná Boca. Gold mineralization is represented by quartz veins with sulphides and gold, which occurs in granitoid rocks westward and north-westward of Vyšná Boca. More detail division is the object of the ongoing research.

The two main vein bodies south-westward and westward of the village Vyšná Boca (Fig. 1) were subjected to the field, economic geological and mineralogical research:

1. The southern vein system is represented by mineral deposit Paurovská - Kliesňová - Helena and occurrence Rovienky. Old mining works are located along mylonite zone that is developed in high-rank metamorphic rocks of crystalline complex (mainly gneisses) in that beds of medium-rank metamorphic amphibolite and pegmatite veins occur. The mining strike is 250°. Individual deposits are separated from each other with tectonic failures (Zoubek, 1951, Čillík, 1955, and others). Originally uniform vein is gradually branched from ENE to WSW. The vein branching has always direction toward SW. The vein is formed by numerous small veins at its SW end in Rovienky. The general vein strike in Kliesňová is from 245° to 270°, most often 250°. The vein dip is very variable and steep. The dip range is from 45° to 80° toward S to SE or SW (for example, the gallery Kliesňová kutacia; Juriga, 1958), the most dominant dip is 75° toward S (Čillík, 1955), the dip in the gallery Helena is 75° - 80°. The thickness of the vein Kliesňová is in a range from several ten centimetres to two meters (exceptionally up to 3 m). It is wavy vein with frequent broadening and tailing off. The depth reach of the Kliesňová vein is 150 m at least (Čillík, 1955). Cocarde, brecciated and combed structures are characteristic for this southern vein system.

The oxidised zone is almost not developed on this vein system. Small occurrences of iron hydroxides and goethite are in tailing pile of the Vyšná Helena gallery, Fe-baring arsenic minerals (pharmacosiderite, ferisymplesite) occur near the Čertovica pass on the mountain ridge Rovienka.

Significant galleries of the Paurovská area are Kutacia Paurovská, Stará Paurovská and Vyšná Paurovská; in the Kliesňová area there are galleries Vyšná and Nižná Prozretelnosť Božia, Kliesňová kutacia and Leopold; and in the Helena dolina valley there are galleries Nižná Helena, Vyšná Helena and Helena. These galleries are also centres of mining areas with the same names. In southern part of the mining area Helena there is also buried mine Zubau with Ni-Co mineralization.

2. The Northern vein system includes mineral deposits Pod Štefanom - Kumštová dolina valley (the mining area Eduard) - Králička. The veins have the same trend and position as veins from the southern vein system. For example, the length of the vein Pod Štefanom (Pod István) is 1.4 km, Fe-ore mining was in western part, Cu mineralization dominated in eastern part (Zoubek, 1951). There are dominantly siderite and barite, less dominantly quartz in the vein rock. Sulphide and hematite are disseminated in the vein rock. Pyrite and arsenopyrite are abundant in altered silicified zones. Oxidized zone is more developed than in the southern vein system, and Cu-bearing (malachite, azurite) and Fe-bearing (goethite, hematite) secondary minerals are abundant in this zone.

The locality **Bruchatý Grúnik** is located on southern slope of the Rovná hoľa Mts. in altitude 1435 m. above see level about 1.5 km north-westward of mineral deposit Pod Štefanom and about 3.5 km WNW from Vyšná Boca. According to Zoubek and Rus (1951) and also according to map by Biely et al. (1992), the vein is located in granodiorite to tonalite of the Ďumbier type, however, it is not excluded that it is located at the contact of gneisses with granodiorite rocks. The vein has brecciated structure and it is characteristic by presence of abundant medium-grained ankerite and sulphides (galenite and tetrahedrite). Ni-Co mineralization is also abundant.

On the southern slopes of the **Chopec Mt.** there is large amount of mining-works with Sb-Au mineralization that is not subjected to our ongoing research. About 1200 m westward of Vyšná Boca in the Králička type granites, there are tailing pile and old collapsed gallery. Its vein

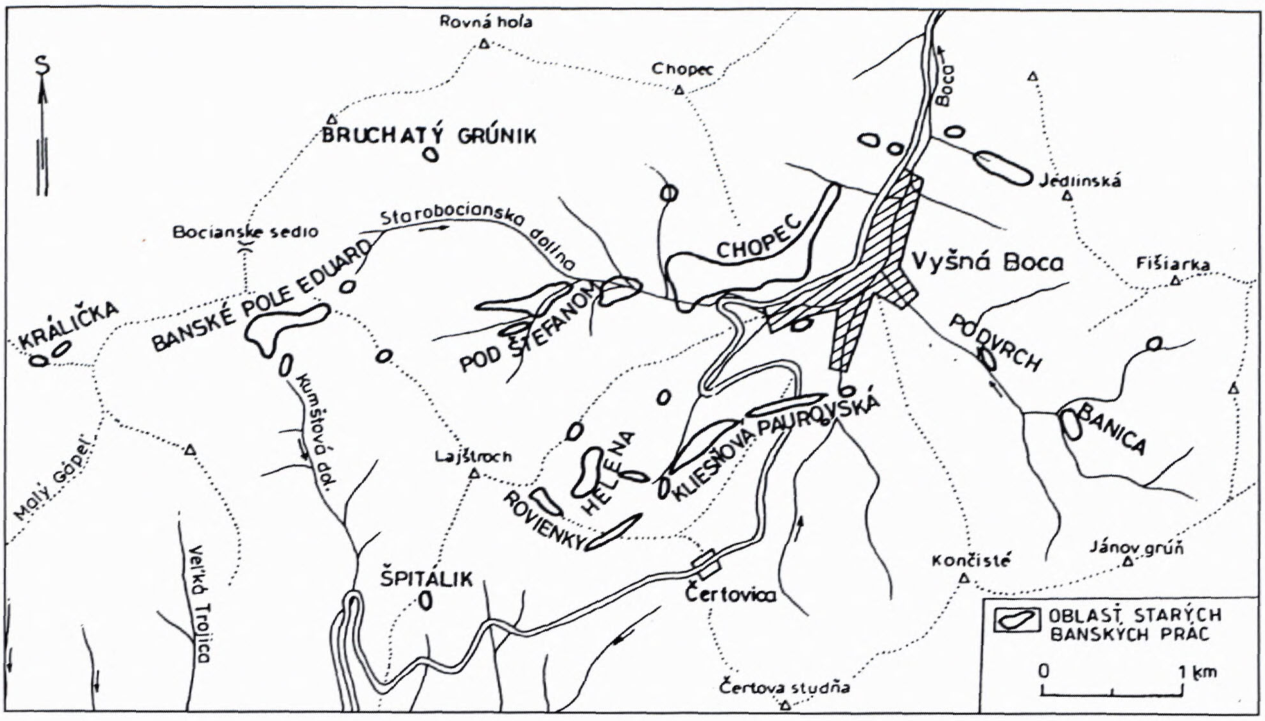

Fig. 1. Map of old mining activities in the vicinity of Vyšná Boca

rock contains large amount of sulphides (pyrite, galenite and tennantite). Its most abundant carbonate mineral is ankerite, however, siderite is also very common. Surrounding granitoid rocks are extensively altered, silicated and have extensive impregnation of pyrite and arsenopyrite. With respect to mineral parageneses and quantitative abundance of main minerals, we have classified the ankerite veins among carbonate mineralization.

All minor occurrences (**Banica, Fišiarka, Podvrch, Končistá**) mentioned in older references (Papp, 1919) are and were south-eastward to north-eastward of Vyšná Boca. Small carbonate lenses are in granodiorite to tonalite of the Ďumbier type or in gneisses of the Nízke Tatry crystalline complex. They are composed dominantly of weathered siderite, quartz and micas. Sulphides are represented by mostly strongly weathered pyrite. Most of the small mining activities (mainly feigh with little tailing piles) has already vanished.

Methodology of the research works

Majority of tested samples was picked up from tailing piles. 123 polished-sections and micro-sections had been made from the samples after their visual inspection and inspection under UV radiation (UVSL-58 lamp with wavelength of UV radiation, 254 - 366 nm). Microscopes Jenapol and Amplival made by Zeiss were used for microscopic studies. Immersion method of measurement of refractive index was used for initial identification of carbonates and barite. Reflectance of selected ore minerals was measured in Department of mineralogy ELTE in Budapest (microscope Leitz, standard: basal cat SiC, step 10 nm, wavelength 400-700 nm). Identification and initial analyses of chemical composition of carbonates was made by manometric and differential thermal analysis (DTA) (derivatograph MOM, type OD-102; conditions: charge 525 mg, TG 200 mg, DTA 0.5 V, DTG 2.5 V, temperature 1000 °C, rate of heat increase 10 °C/min.). RTG diffraction analyses of aragonite was made by Geologic Institute of Faculty of Natural Sciences of Comenius University with device DRON-3 under the following conditions: Cu/Ni, 20 kV, 40 mA, speed of arm advance 1°/min. Primary minerals were analysed by wave-dispersion (WDS) and energy-dispersion electron microprobe in GS SR Bratislava, device Jeol Superprobe 733 was used under conditions: 20 kV, 15-20 nA, beam diameter 3-5 μm, standards - arsenopyrite, pyrite, galenite, cinnabarite, Cu, Bi, Fe, Zn, Sb, Ag, Au, Co, Ni. The photographic pictures of compositions were taken with Jeol JSM-840 with 20-25 kV in GS SR Bratislava. All other analyses not mentioned in these papers are in papers by Ozdín (1996) or are in archives of both authors.

The results of the mineralogical research

The minerals are ordered according to mineralogical system (Strunz, 1982), except minerals of tetrahedrite group that are classified among sulphosalts (Makovický and Karup Möller, 1994). All sulphosalts are classified according the classification by Moëlo ed. (1994).

Primary minerals

Sphalerite, ZnS occurs only auxiliary in form of tiny, mostly microscopic allotriomorphic grains in association with tetrahedrite, chalcopyrite, pyrite, galenite, arsenopy-

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rite and hematite within milky-white quartz (Fig. 2) in siderite veins in the vicinity of Vyšná Boca. Sphalerite is more abundant in centre part of tailing pile at Kliesňová and mainly at Bruchatý Grúnik where sphalerite forms up to 5 mm large clusters within carbonate-sulphide vein rock. Larger grains of allotriomorphic sphalerite sometimes contain higher amounts of inclusions of chalcopyrite. Sphalerite was identified with reflected light and preliminary by EDS analysis.

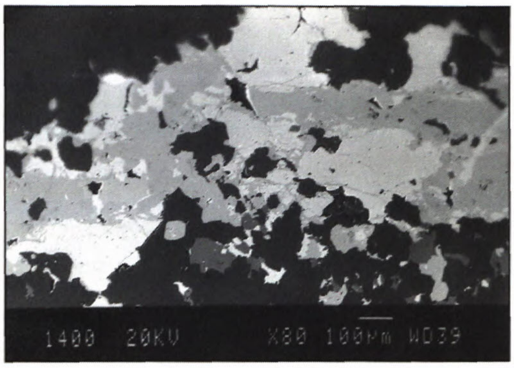

Fig. 2. Sphalerite (black-grey; in lower part) with tetrahedrite (light-grey) and chalcopyrite veins (dark grey) within quartz (black) from the mineral deposit Kliesňová.

Chalcopyrite $CuFeS_2$ belongs among main sulphide minerals in majority of siderite deposits, however, its quantity is variable from locality to locality. It is in association with tetrahedrite, pyrite, galenite, arsenopyrite, sulphosalts of bismuthite series and sphalerite, less with Ni-bearing diarsenides and Ni-Co-bearing sulphoarsenides within carbonate-quartz-sulphide veins where it forms small veins in hydrothermal milky-white quartz (for example Kliesňová, Helena etc.), less in siderite (Bruchatý Grúnik), or it is disseminated mainly in barite (Pod Štefanom). Small chalcopyrite veins (sometimes with pyrite) intersecting tetrahedrite can be often observed with help of reflected light. Sometimes it forms inclusions within tetrahedrite or skirts its allotriomorphic grains. Chalcopyrite itself contains inclusions of tetrahedrite, galenite, pyrite, sulphosalts of bismuthite-aikinite series and pavonite group. In samples from Kumštová dolina valley chalcopyrite forms filling of enclaves in metacrysts of pyrite. Chalcopyrite has sometimes optic zoning. It is locally intensively replaced with Fe-bearing hydroxides. It was preliminary identified by EDAX.

Cubanite (?), $CuFe_2S_3$ was sporadically found at the deposit Kliesňová, where it forms up to 2 mm long lamellas within chalcopyrite in association with tetrahedrite, sphalerite, and pyrite in quartz. In comparison to chalcopyrite, cubanite is more anisotropic and intensively laminated in reflected light. It was identified optically with reflected light.

Galena PbS usually occurs as inclusions in tetrahedrite and chalcopyrite, however, its occurrence with chalcopyrite, tetrahedrite, sphalerite and pyrite in siderite veins are rare. Sometimes it is more abundant in veins with barite (for example locality Pod Štefanom).

Samples of vein rock with abundant presence of galenite, tetrahedrite and another sulphides occur at locality Bruchatý Grúnik. They form several millimetres thick veins, nests with area up to several square centimetres and clusters within carbonate-quartz vein rock with brecciated structure. Mostly fine-grained idiomorphic galenite (grain size up to 1 mm) occurs in association with tetrahedrite, chalcopyrite, sphalerite, pyrite, arsenopyrite, tennantite, cobaltine and Ag-Pb-Bi- bearing sulphosalts. According to spectral analysis, the sample with high concentration of galenite from the locality Bruchatý Grúnik contains 89.2 ppm Ag and 0.06 ppm Au.

Galenite, together with tennantite and pyrite (Fig. 10), occur also on southern and eastern slopes of Chopok Mt. in rocs from tailing piles as noddles in quartz-ankerite vein rocks or as individual veins in granite. It occurs in association with quart-gold mineralization. Galenite was identified with reflected light and its chemical composition was studied by EMPA. The galenite from the locality Bruchatý Grúnik contains these accessory minerals: Bi 0 - 0.23, Ag 0 - 0.66, Sb 0 - 1.21, Cu 0.17 - 0.79, Fe 0 - 0.54 wt.%.

Carrollite $Cu(CoNi)_2S_4$ occurs only exclusively in the mining area Helena, where it is in association with cobaltine, gersdorffite, galenite, pyrite and minerals of tetrahedrite-tennantite series in arsenopyrite veins. It was preliminary identified by EDS analyses (Cu 13.82, Co 42.68, Ni 6.94, Fe 1.09, S 35.47, 100.00 wt.%).

Bismuthinite Bi_2S_3 occurs in siderite veins only rarely, but regularly in form of individual grains intergrowing with chalcopyrite (Fig. 3) and exceptionally also with tetrahedrite, or in form of allotriomorphic or hypidiomorphic grains freely occurring in quartz and exclusively also in siderite. It forms tiny needles and short-columnar crystals. At the locality Paurovská it occurs together with Ag-Bi-bearing sulphosalts (pavonite homoseries) and Cu-Pb-Bi- bearing sulphosalts (pecoite) into which it is gradually converted. Exceptionally it also contains inclusions of tetrahedrite. It is often chemically inhomogeneous. It was identified optically with reflected light and by WDS analysis (Fig. 7).

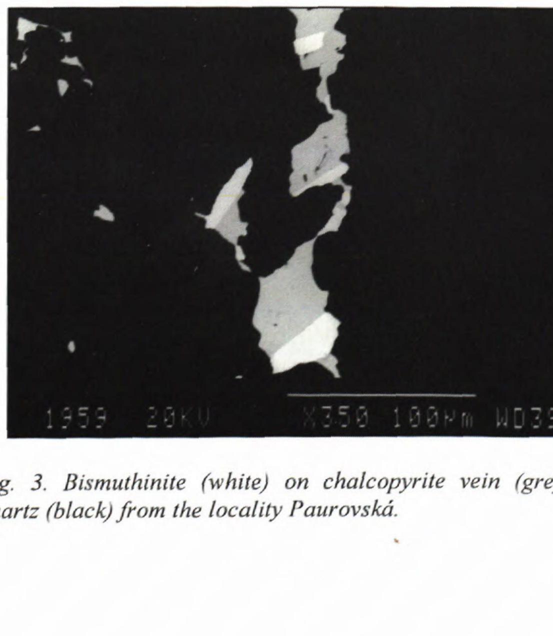

Fig. 3. Bismuthinite (white) on chalcopyrite vein (grey) in quartz (black) from the locality Paurovská.

Pyrite FeS_2 (cubic) is very abundant in silicified hydrothermal alteration zones in rock surrounding ore veins, where it occurs in two formations: 1. in intensively silicified zones in close proximity of ore vein, where more or less crushed and cataclastic pyrite rarely occurs in arsenopyrite veins. 2. in greater distances from ore veins, where alteration of rocks surrounding ore veins is weak. Pyrite is there abundantly disseminated and arsenopyrite does not occur there. Freely disseminated fine-grained pyrite is the main sulphide mineral disseminated in older fine-grained siderite in siderite veins. It often occurs together with chalcopyrite, sphalerite, galenite, arsenopyrite, and with another sulphides and Cu-Pb-Bi-bearing sulphosalts in siderite or ankerite in quartz veins.

At the deposit Pod Štefanom, pyrite, together with chalcopyrite and tetrahedrite, occurs in form of idiomorphic crystals or very tiny allotriomorphic crystals in pyrite-chalcopyrite veins transecting tetrahedrite. Pyrite also is abundant in thin, up to 3 mm thick arsenopyrite veins with Ni-Co mineralization at the locality Helena. Up to 2.5 mm large pyrite metacrystals with abundant inclusions of chalcopyrite, tetrahedrite, and galenite often occur at the Kumštová dolina valley and at the deposit Pod Štefanom. Pyrite itself forms inclusions within chalcopyrite and tetrahedrite. Sometimes it is recrystallised and replaced with marcasite. Freely disseminated fine-grained pyrite is the main ore mineral in one type of grey-white quartz at the locality Bruchatý Grúnik. It occurs here in association with galenite that often growth over the pyrite, forms network of veins within it, penetrates along fractures, fills open fractures and voids or it grow around individual pyrite grains. In zones rich in microlaminated hematite, the pyrite forms max. 2 mm large idiomorphic crystals with prevailing pentagonal dodecahedron shape. It is often chemically zoned. It posses sector (Chopec), concentric (Helena, Bruchatý Grúnik, Paurovská) or irregular (Chopec, Helena) zoning. It was identified optically with reflected light, with help of reflection curves, and by EMPA (Tab. 1). Gold bearing pyrite occurs in several quartz-sulphide veins. In some types of pyrite, it is the crystal cores that are enriched with the gold. (Tab. 1, Analyses No. 13-15). These parts are also characteristic with increased concentration of As. In the veins with sulphosalts at the locality Paurovská, it is the core of pyrite grains with concentric zoning, which are enriched with Au, Sb, Cu, As and also Se. According to spectral analyses, the sample of ore rocks with abundant pyrite from the Bruchatý Grúnik contains 0.18 ppm Au.

Chopec: Analyses No. 1-4 from the lightest phase to the darkest; pyrite in association with galenite, tennantite, quartz, ankerite, siderite and barite.

Helena: Analyses No. 5, 6 - light zones, 7, 8 - dark zones, 9 - very dark pyrite. Analyses No. 5-8 represents relatively large pyrite grains in arsenopyrite veins, analysis No. 9 represent pyrite that is part of Ni-Co-bearing mineral paragenesis.

Bruchatý Grúnik: Analyses No. 10, 11 - light zones, 12 - dark zone, idiomorphic pyrite in paragenesis with genetically younger galenite in quartz.

Paurovská: Analyses No. 13 - 15 of the zoned pyrite are ordered from the lightest phase to the darkest. Analysis No. 13 is the core of the grain and Analysis No. 15 is the edge of the grain. The pyrite originates from the quartz-sulphosalt phase of the mineralization.

Krutovite (?) $NiAs_2$ have been identified on the base of the optical properties and preliminary chemical analysis in association with galenite, tetrahedrite, arsenopyrite, chalcopyrite, Ni-Co-bearing minerals and pyrite on the sample from the locality Bruchatý Grúnik (Fig. 4).

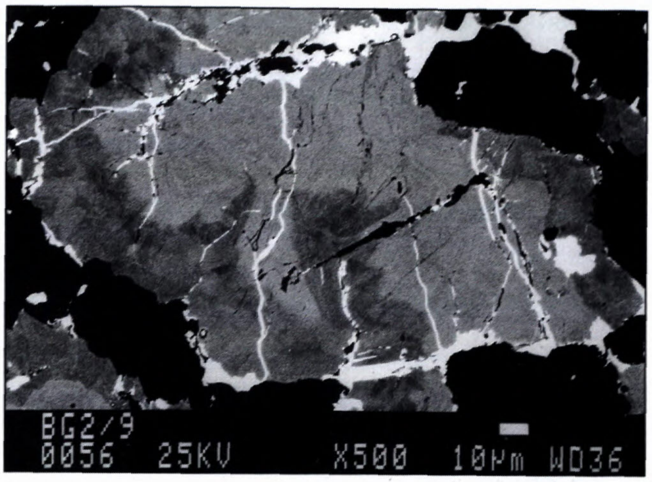

Fig. 4. Zoned krutovite (?) with galena veins (white) from the locality Bruchatý Grúnik.

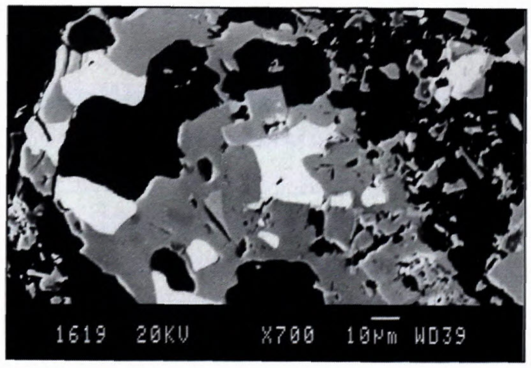

Fig. 5. Idiomorphic crystals of gersdorffite-(Co), (light-grey, cubic in centre), with galenite (white), tennantite (dark-grey) and tetrahedrite (light-grey, inclusion in the middle of the tennantite grain) from the locality Vyšná Boca - Helena.

Gersdorffite NiAsS, together with arsenopyrite, cobaltite, galenite, tetrahedrite, pyrite and Ni-bearing diarsenate, occur in carbonate-quartz-sulphide vein at the locality Bruchatý Grúnik. In SE part of the mining area Helena, the gersdorffite occurs in probably high-thermal arsenopyrite veins in association with cobaltite, arsenopyrite, pyrite, galenite, tennantite, carrollite and rare tetrahedrite. It creates idiomorphic crystals large up to 13 µm and with square or rectangular cross-section. Sometimes it forms hem around arsenopyrite aggregates. According to its chemical composition it resemble to gersdorffite-(Co) (Fig. 5). The average WDS analyses of gersdorffite-

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Tab. 1. Electron microprobe analyses of pyrite from the Vyšná Boca area.

Σ	Starobocianska dolina - Chopec				Helena					Bruchatý grúnik			Paurovská		
wt. %.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Fe	45,37	45,4	45,63	45,44	45,62	45,61	44,76	44,48	39,26	44,96	45,58	46,06	44,67	46,61	46,27
As	0	0	0	0,55	1,04	1,19	1,17	1,31	0,4	1,24	1,41	0,47	2,13	0,78	0,22
Sb	0	0	0	0	0	0	0	0	0	0	0	0	0,37	0	0
Cu	0	0	0	0	0	0	0	0	0	0	0	0	0,15	0,06	0,07
Co	0	0	0	0	0	0,04	0,16	0,11	4,81	0	0	0	0	0	0
Ni	0,01	0	0,02	0,01	0,12	0,15	0,35	0,38	1,55	0,04	0,24	0	0,01	0,05	0
Au	0	0,01	0	0,19	0	0,08	0,18	0	0	0	0	0,03	0,14	0	0
S	53,22	53,15	52,92	52,39	52,98	52,86	52,65	52,16	52,1	52,65	51,84	51,51	52,34	53,83	53,89
Se	0	0	0	0	0	0	0	0	0	0	0	0	0,15	0,02	0
Σ	98,6	98,56	98,57	98,58	99,76	99,93	99,27	98,44	98,12	98,89	99,07	98,07	99,96	101,35	100,45
atom. %.															
Fe	32,86	32,9	33,11	33,13	32,87	32,87	32,47	32,52	28,8	32,67	33,24	33,83	32,4	33,04	32,96
As	0	0	0	0,3	0,56	0,64	0,63	0,71	0,22	0,67	0,76	0,26	1,15	0,41	0,11
Sb	0	0	0	0	0	0	0	0	0	0	0	0	0,12	0	0
Cu	0	0	0	0	0	0	0	0	0	0	0	0	0,1	0,04	0,05
Co	0	0	0	0	0	0,03	0,11	0,08	3,35	0	0	0	0	0	0
Ni	0	0	0,01	0,01	0,08	0,1	0,24	0,27	1,08	0,03	0,16	0	0,01	0,04	0
Au	0	0	0	0,04	0	0,02	0,04	0	0	0	0	0,01	0,03	0	0
S	67,14	67,1	66,88	66,52	66,49	66,35	66,52	66,43	66,56	66,63	65,84	65,9	66,13	66,46	66,88
Se	0	0	0	0	0	0	0	0	0	0	0	0	0,07	0,01	0
Σ	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

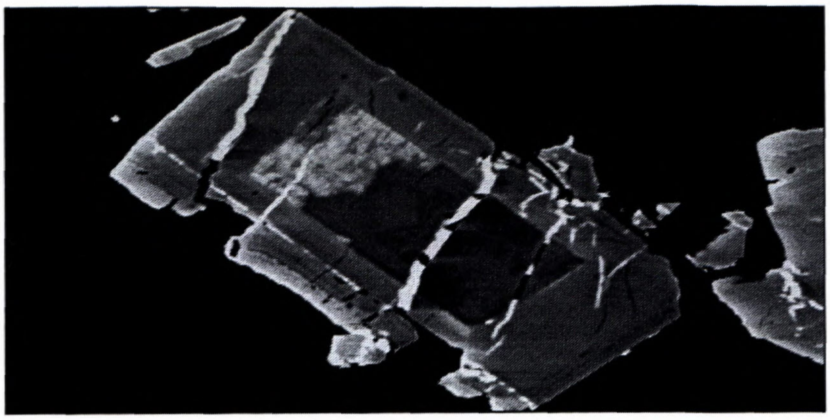
Tab. 2a. Electron microprobe analyses of arsenopyrite from the Vyšná Boca area.

	Bruchatý grúnik												
wt. %.	1	2	3	4	5	6	7	8	9	10	11	12	13
S	20,97	21,52	21,41	19,58	20,06	21,65	21,13	21,16	19,42	16,7	19,92	19,61	20,79
Fe	33,83	34,08	34,81	33,86	33,59	34,45	33,72	34,36	34,05	33,17	34,74	33,73	34,5
As	43,13	43,95	43,58	45,18	45,17	43,71	41,44	44,94	47,26	50,28	45,24	45,41	42,93
Co	0	0	0,01	0	0	0	0	0	0	0	0	0	0
Ni	0	0	0	0,03	0,01	0,005	0,003	0,13	0,28	0,26	0,18	0,02	0
Sb	0	0	0	0,9	0,21	0	1,34	0	0	0	0	0	0
Au	0	0	0	0,07	0,03	0	0	0,02	0	0	0	0	0,01
Cu	0,77	0,37	0,39	0	0	0	0	0	0,06	0,06	0	0	0
Σ	98,7	99,92	100,2	99,62	99,07	99,82	97,63	100,61	101,07	100,47	100,08	98,77	98,23
atom. %													
S	35,39	35,82	35,54	33,4	34,15	36	36,07	35,15	32,7	29,08	33,57	33,57	35,25
Fe	32,79	32,57	33,17	33,16	32,83	32,89	33,05	32,77	32,93	33,16	33,63	33,15	33,59
As	31,16	31,3	30,96	32,99	32,91	31,106	30,28	31,95	34,06	37,47	32,63	33,26	31,16
Co	0	0	0,01	0	0	0	0	0	0	0	0	0	0
Ni	0	0	0	0,03	0,01	0,005	0,003	0,12	0,25	0,25	0,17	0,02	0
Sb	0	0	0	0,4	0,09	0	0,6	0	0	0	0	0	0
Au	0	0	0	0,02	0,01	0	0	0	0	0	0	0	0
Cu	0,66	0,31	0,32	0	0	0	0	0	0,05	0,05	0	0	0
Σ	100	100	100	100	100	100	100	100	100	100	100	100	100

Tab. 2b. (continued)

	Bruchatý grúnik									Helena		
wt. %.	14	15	16	17	18	19	20	21	22	23	24	25
S	20,87	18,25	20,29	18,69	20,13	17,69	19,25	19,05	18,57	19,28	19,05	19,51
Fe	34,13	33,54	33,34	33,7	33,85	32,77	32,56	32,14	32,03	34,43	33,59	34,33
As	45,21	46,09	44,6	46,56	45,86	36,94	37,12	37,38	36,18	46,47	46,93	46,93
Co	0	0,01	0	0	0	0	0	0	0	0,08	0,11	0,08
Ni	0,07	0	0	0,02	0,02	0,02	0,02	0	0,04	0,06	0,03	0,02
Sb	0	0	0,13	0,78	0	11,59	10,49	10,6	11,81	0	0	0
Au	0	0,004	0	0	0,03	0	0	0,18	0	0,04	0	0
Cu	0	0	0	0	0	0	0	0	0	0	0,01	0
Σ	100,28	97,89	98,36	99,75	99,89	99,01	99,44	99,34	98,63	100,36	99,72	100,87
atom. %												
S	34,87	31,89	34,66	32,12	33,99	31,95	34,01	33,82	33,411	32,67	32,57	32,86
Fe	32,73	33,64	32,68	33,26	32,83	33,98	33,02	32,76	33,092	33,49	32,96	33,21
As	32,33	34,46	32,6	34,25	33,15	28,55	28,07	28,41	27,861	33,7	34,33	33,84
Co	0	0,01	0	0	0	0	0	0	0	0,08	0,1	0,07
Ni	0,07	0	0	0,02	0,02	0,01	0,02	0	0,042	0,05	0,03	0,02
Sb	0	0	0,06	0,35	0	5,51	4,88	4,96	5,594	0	0	0
Au	0	0	0	0	0,01	0	0	0,05	0	0,01	0	0
Cu	0	0	0	0	0	0	0	0	0	0	0,01	0
Σ	100	100	100	100	100	100	100	100	100	100	100	100

Fig. 6. Zoned arsenopyrite (magnification 2400x) with galenite veins from the locality Bruchatý Grúnik. Dark zones (Tab. 2a, Analyses No. 14-18), light zone in the middle of the grain - arsenopyrite-(Sb), (Tab. 2b, Analyses No. 19-22).



(Co) (5 measurements): Ni 14.988, Co 13.104, Fe 6.538, Sb 0.004, Au 0.035, Cu 1.136, As 43.588, S 19,442, 98.835 wt.%.

Cobaltite CoAsS, together with pyrite, galenite, minerals of isomorphous tetrahedrite-tennantite series and another Ni-Co-bearing minerals, is rarely found in arsenopyrite veins at the Bruchatý Grúnik and tailing pile of the Zubau gallery. It is usually idiomorphic or hypidiomorphic and it has chemical zonality. It was identified optically and preliminary by EDAX (Co 27.25, Ni 5.27, Fe 7.89, As 35.76, S 23.82, 100.00 wt.%).

Marcasite FeS_2 (rhombohedron) occurs rarely in siderite mineralization in a form of very tiny grains in quartz. Sometimes it replaces pyrite, or it comes into existence by its recrystallisation. It was identified optically and preliminary by EDS analysis.

Arsenopyrite FeAsS, together with pyrite and Fe-To-bearing oxides is abundant in altered, strongly silicified zones, where it forms several mm thick veins and impregnation composed of heavily cataclastic, less idiomorphic grains at the edges of hydrothermal siderite veins. It is exceptional in siderite veins with quartz-sulphide mineral association, where it occurs as individual idiomorphic grains or in clusters in quartz together with chalcopyrite, tetrahedrite, pyrite, galena and sulphosalts. Ni-Co mineralization occurs in arsenopyrite veins with pyrite at the mining area Helena. Arsenopyrite sometimes has optical zoning, the most common zoning is the hourglass and sector zoning. At Bruchatý Grúnik, where it, together with Ni-bearing diarsenides, tetrahedrite and galenite, occurs in quartz-carbonate vein rocks it forms idiomorphic crystals with characteristic oscillate zoning. Later galenite veins often penetrate into idiomorphic arsenopyrite grains. Tiny inclusions of galenite are also often, mostly in centre of arsenopyrite crystals. It was identified optically with reflected light and by WDS (Tab. 2a, 2b). In Tab. 2a. (Analyses No. 1-3), there is idiomorphic zoned arsenopyrite within tetrahedrite. The measured zones are from the lightest (increased concentration of As) to the darkest phase (increased concentration of S). Similar zoning has arsenopyrite grains from the Analyses No. 4-6. The Analyses No. 14-22 (Tab. 2b) are analyses of very fine zoned arsenopyrite that is scattered in block quartz from brecciated fragments of a carbonate-sulphide vein. The lightest phase in the crystal centre is formed with arsenopyrite - Sb (the Analyses No. 19-22, Fig. 6). Arsenopyrite from the locality Bruchatý Grúnik contains up to 0.28 wt.% Ni, Co is not present at all. Arsenopyrite from the locality Helena contains up to 0.11 wt.% Co; Ni is presented only in 0.0X wt.%. In some cases we have measured increased concentration of Au by EDS (see Tab. 2).

Sulphosalts are represented in siderite veins by minerals of pavonite homologous series and isotype series of aikinite.

Sulphosalts of pavonite homologous series are represented by *benjaminite* ($Ag_3Bi_7S_{12}$) that exceptionally occurs together with chalcopyrite in veins within quartz. It forms segregate inclusions up to 10 μm large in sulphosalts, which are with their chemical composition similar to bismuthite and members of aikinite isotype series. Benjaminite is chemically homogeneous. It was identified by WDS analysis. Sulphosalts, according to their chemical composition resemble probably to *borodaevite* (?), were found at the locality Bruchatý Grúnik, where they form up to 1 mm large needle-shaped crystals within ankerite together with galena, chalcopyrite, tetrahedrite and another sulphosalts. Allotriomorphic grains are homogeneous. Mainly the needle-shaped crystals intergrow with galenite and another sulphosalts. These sulphosalts sometimes contains very tiny inclusions of galenite. They have been identified by electron microprobe. Their chemical composition is subject of next research.

Typical and for siderite veins of this area characteristic sulphosalts of aikinite isotype series are represented mainly by *lindströmite* ($Cu_3Pb_3Bi_7S_{18}$), *hammarite* ($Cu_2Pb_2Bi_{11}S_{18}$), *friedrichite* ($Cu_5Pb_5Bi_7S_{18}$), less *pecoite* (?) ($CuPbBi_{11}S_{18}$), *krupkaite* ($CuPbBi_3S_6$) and *aikinite* (?) ($CuPbBiS_3$). They are extended almost at all siderite or siderite-barite deposits between Vyšná Boca and Jarabá, however, mostly in microscopic sizes. Only in one tailing pile at the vein system Paurovská these sulphosalts occur also in form of individual needles, clusters and bush like formation that is large up to several cm and composed of light-grey needles. Sulphosalts occur in white-grey quartz in association with disseminated siderite crystals or small siderite clusters, pyrite, tetrahedrite and minerals of chalcopyrite group. Sulphosalts are the main ore minerals. At the other localities, the sulphosalts of aikinite isotype series occur usually in association with chalcopyrite, tetrahedrite and pyrite within white quartz or exclusively within barite as well (Kumštová dolina valley). The needles of the sulphosalts are up to 2 mm large, 0.5 mm thick and they are variably folded. Some of them form small inclusions in chalcopyrite or tetrahedrite, which are result of magmatic segregation. They have been identified with reflected light and by EMPA (Fig. 7).

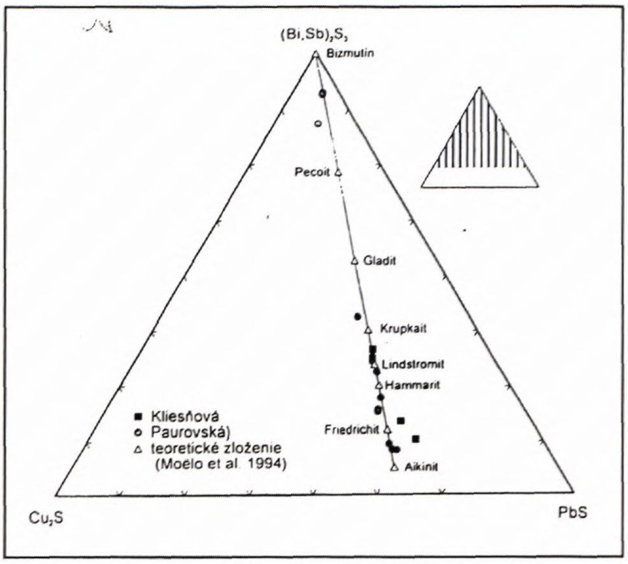


Fig. 7. Sulphosalts of aikinite isoseries from Vyšná Boca deposit..

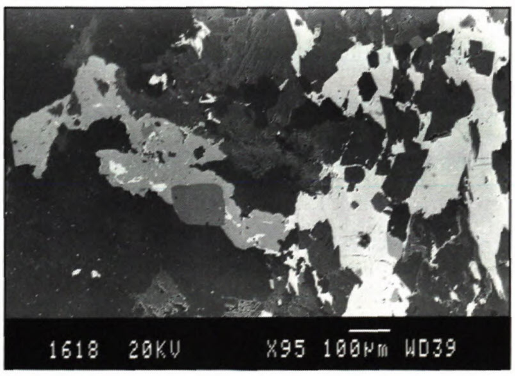


Fig. 8. Sulphosalts of bismuthite-aikinite series (light; in right half) with tetrahedrite (grey), pyrite (dark-grey, idiomorphic) and siderite (black-grey, allotriomorphic) in a quartz (black) from the locality Paurovská.

Tetrahedrite $Cu_{12}Sb_4S_{13}$ is the main ore mineral of the quartz-sulphide mineral association. It occurs in form of allotriomorphic, exclusively also as hypidiomorphic or idiomorphic aggregates, mainly in cracks and weakened zones within white quartz, rarely within carbonates and barite. It occurs individually or in clusters or grains together with chalcopyrite, pyrite, less with galena, sphalerite, arsenopyrite and Cu-Pb-Bi sulphosalts. Bruchatý Grúnik, the tetrahedrite forms compact mass large up to several cm^2. They are often intergrowth with galenite, sphalerite, less with Ni-bearing diarsenides. Sometimes it is replaced by chalcopyrite. On some aggregates of tetrahedrite oscillate chemical zoning can be observed. This is caused mainly by content of Sb, less by content of As, Cu and S. It contains inclusions of chalcopyrite, sphalerite, pyrite and galena, and it itself forms inclusions in metacrystals of pyrite. It has been identified optically with reflected light and by electron microprobe (Tab. 3a, 3b), and with help of reflectance curves (Fig. 9). In comparison to tetrahedrite from the Kumštová dolina valley (see Tab. 3a, analyses 1-3 and 9-11), the higher reflectance in tetrahedrite from the locality Paurovská is caused mainly by higher concentration of Bi, less by higher ratio of Sb:As with advantage to antimony. In Tab. 3b, there are analyses of zoned tetrahedrite (Analyses No. 16-22). They are ordered from the lightest to the darkest phase. The zoning is caused by variation of Sb and As concentration.

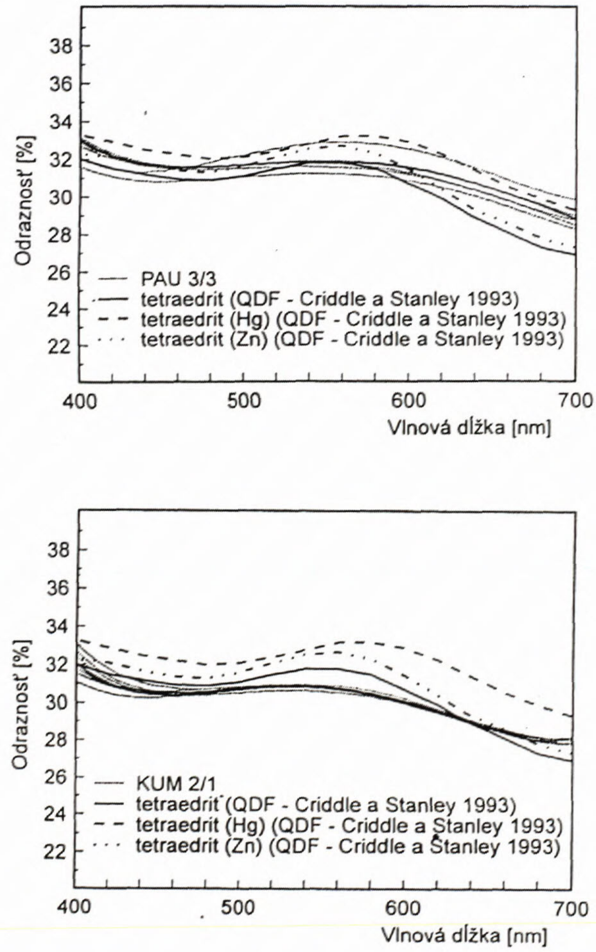


Fig. 9. Reflectance curves of tetrahedrite from the Vyšná Boca area (PAU 3/3 - Paurovská, KUM 2/1 - Kumštová dolina valley).

Tennantite $Cu_{12}As_4S_{13}$ occurs in the vicinity of Vyšná Boca only in arsenopyrite veins in the mining area Helena (Fig. 5), where it is in association with Ni-Co-bearing minerals, pyrite, galena, quartz and carbonates, and in the mineral deposit Chopec (Fig. 10). At Chopec, tennantite, together with siderite, barite and galena, is the most

Tab. 3a. Point electron microprobe analyses of tetrahedrite from the Vyšná Boca area.

	Paurovská			Kliesňová					Kumštová dolina			Králička			
wt. %	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Cu	37,74	37,72	37,72	41,84	39,77	39,27	39,64	39,05	40,6	40,36	40,89	39,35	39,77	39,15	38,88
Ag	1,6	1,35	1,05	1,2	1,04	1,21	1,03	1,25	1,49	1,38	1,22	0,05	0,3	0,69	0,35
Fe	2,52	2,7	2,17	3,17	2,79	2,74	2,86	2,77	3,25	3,26	3,35	3,21	3,17	3,3	3,34
Zn	4,27	3,98	4,39	4,04	4,48	4,37	4,47	4,34	3,34	3,27	3,35	3,68	3,76	3,6	3,65
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sb	25,72	25,37	25,75	19,12	18,57	18,64	19,28	19,19	19,4	19,62	19,04	23,14	22,79	22,84	22,3
As	0,75	0,89	0,8	5,37	6,9	6,64	6,13	6,44	6,05	6,48	6,44	4,7	4,79	4,73	5,07
Bi	3,16	3,21	2,64	1,24	0,53	0,49	0,41	0,97	0,44	0,2	0,59	0	0	0	0
S	24,99	25,04	24,97	22,82	26,17	26,27	25,96	24,6	25,86	26,21	26,32	25,55	24,96	24,91	24,72
Σ	100,8	100,26	99,49	98,8	100,3	99,63	99,78	98,61	100,4	100,8	101,2	99,68	99,54	99,22	98,31
atom. %.															
Cu	34,23	34,28	34,46	37,95	34,44	34,17	34,57	34,96	35,28	34,85	35,13	34,73	35,31	34,93	34,91
Ag	0,86	0,72	0,56	0,64	0,53	0,62	0,53	0,66	0,76	0,7	0,62	0,03	0,16	0,36	0,19
Fe	2,61	2,8	2,25	3,28	2,75	2,72	2,84	2,82	3,22	3,2	3,27	3,23	3,21	3,34	3,41
Zn	3,77	3,51	3,9	3,58	3,77	3,7	3,79	3,78	2,82	2,75	2,8	3,15	3,25	3,12	3,19
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sb	12,17	12,03	12,28	9,05	8,39	8,46	8,77	8,97	8,8	8,84	8,54	10,66	10,56	10,64	10,45
As	0,57	0,69	0,62	4,13	5,07	4,9	4,53	4,89	4,46	4,75	4,69	3,52	3,61	3,58	3,86
Bi	0,87	0,89	0,73	0,34	0,14	0,13	0,11	0,26	0,12	0,05	0,15	0	0	0	0
S	44,92	45,086	45,2	41,02	44,91	45,3	44,86	43,66	44,54	44,86	44,8	44,69	43,91	44,04	43,99
Σ	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Tab. 3b. (continued)

	Bruchatý grúnik									Pod Štefanom				
wt. %	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Cu	37,15	37,78	37,88	38,75	37,95	38,42	38,83	32,9	32,48	34,09	39,15	39,22	39,27	42,4
Ag	2,04	1,37	1,76	1,57	1,71	1,79	1,46	7,38	7,79	6,41	0,8	1,04	1,17	1,85
Fe	2,2	2,2	3,03	3,38	2,84	3,32	3,51	2,42	1,9	1,94	3,34	3,33	3,25	3,42
Zn	4,95	5	4,26	3,74	4,28	3,67	3,71	5,25	5,32	5,5	3,23	3,23	3,37	2,82
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sb	27,84	25,63	21,92	23,67	22,4	22,7	19,89	27,67	28,2	25,64	21,53	21,94	21,61	21,76
As	1,87	2,9	4,81	4,83	4,97	4,51	6,38	1,03	1,11	2,36	5,11	5,16	4,92	3,46
Bi	0	0	0	0	0	0	0	0	0	0	0,84	1,04	0,84	0,85
S	24,51	25,15	25,29	24,59	25,51	25,31	25,59	24,03	23,97	23,57	25,6	25,79	25,52	25,35
Σ	100,6	100	98,95	100,5	99,66	99,72	99,37	100,7	100,8	99,51	99,6	100,8	99,95	101,9
atom. %														
Cu	33,67	33,84	33,77	34,49	33,64	34,11	34,13	30,45	30,2	31,7	34,61	34,4	34,69	36,89
Ag	1,09	0,72	0,93	0,82	0,9	0,93	0,75	4,02	4,27	3,51	0,42	0,54	0,61	0,95
Fe	2,26	2,25	3,07	3,43	2,87	3,36	3,51	2,54	2,01	2,05	3,36	3,32	3,26	3,39
Zn	4,36	4,36	3,69	3,23	3,69	3,17	3,17	4,73	4,8	4,97	2,77	2,75	2,9	2,39
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sb	13,17	11,98	10,2	10,99	10,36	10,52	9,12	13,37	13,68	12,45	9,93	10,04	9,96	9,88
As	1,44	2,2	3,64	3,64	3,74	3,39	4,75	0,81	0,88	1,86	3,83	3,84	3,69	2,55
Bi	0	0	0	0	0	0	0	0	0	0	0,23	0,28	0,23	0,23
S	44,01	44,65	44,69	43,39	44,81	44,52	44,56	44,09	44,16	43,45	44,85	44,83	44,66	43,72
Σ	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Crystallochemical formula of tetrahedrite (recalculated to 16 cations)

1. $(Cu_{9.75}Ag_{0.25})_{10}(Cu_{0.19}Fe_{0.76}Zn_{1.09})_{2.04}(Sb_{3.54}As_{0.17}Bi_{0.25})_{3.96}S_{13.05}$
2. $(Cu_{9.79}Ag_{0.21})_{10}(Cu_{0.20}Fe_{0.82}Zn_{0.82})_{2.04}(Sb_{3.50}As_{0.20}Bi_{0.26})_{3.96}S_{13.14}$
3. $(Cu_{9.84}Ag_{0.16})_{10}(Cu_{0.22}Fe_{0.66}Zn_{1.14})_{2.02}(Sb_{3.59}As_{0.18}Bi_{0.21})_{3.98}S_{13.20}$
4. $(Cu_{9.83}Ag_{0.17})_{10}(Cu_{0.47}Fe_{0.89}Zn_{0.97})_{2.33}(Sb_{2.46}As_{1.12}Bi_{0.09})_{3.67}S_{11.13}$
5. $(Cu_{9.85}Ag_{0.15})_{10}(Cu_{0.15}Fe_{0.80}Zn_{1.10})_{2.05}(Sb_{2.44}As_{1.47}Bi_{0.04})_{3.95}S_{13.04}$
6. $(Cu_{9.82}Ag_{0.18})_{10}(Cu_{0.18}Fe_{0.80}Zn_{1.08})_{2.06}(Sb_{2.48}As_{1.43}Bi_{0.04})_{3.95}S_{13.25}$
7. $(Cu_{9.85}Ag_{0.15})_{10}(Cu_{0.18}Fe_{0.82}Zn_{1.10})_{2.10}(Sb_{2.55}As_{1.32}Bi_{0.03})_{3.90}S_{13.02}$
8. $(Cu_{9.81}Ag_{0.19})_{10}(Cu_{0.12}Fe_{0.80}Zn_{1.07})_{1.99}(Sb_{2.55}As_{1.39}Bi_{0.07})_{4.01}S_{12.40}$
9. $(Cu_{9.78}Ag_{0.22})_{10}(Cu_{0.40}Fe_{0.93}Zn_{0.81})_{2.14}(Sb_{2.54}As_{1.29}Bi_{0.03})_{3.86}S_{12.85}$
10. $(Cu_{9.80}Ag_{0.20})_{10}(Cu_{0.32}Fe_{0.93}Zn_{0.80})_{2.05}(Sb_{2.57}As_{1.38}Bi_{0.01})_{3.96}S_{13.01}$
11. $(Cu_{9.82}Ag_{0.18})_{10}(Cu_{0.36}Fe_{0.95}Zn_{0.81})_{2.12}(Sb_{2.48}As_{1.36}Bi_{0.04})_{3.88}S_{12.99}$
12. $(Cu_{9.99}Ag_{0.01})_{10}(Cu_{0.06}Fe_{0.93}Zn_{0.91})_{1.90}(Sb_{3.08}As_{1.02})_{4.10}S_{12.93}$
13. $(Cu_{9.96}Ag_{0.04})_{10}(Cu_{0.11}Fe_{0.91}Zn_{0.93})_{1.95}(Sb_{3.01}As_{1.03})_{4.04}S_{12.53}$
14. $(Cu_{9.90}Ag_{0.10})_{10}(Cu_{0.08}Fe_{0.96}Zn_{0.89})_{1.93}(Sb_{3.04}As_{1.02})_{4.06}S_{12.59}$
15. $(Cu_{9.95}Ag_{0.05})_{10}(Cu_{0.02}Fe_{0.97}Zn_{0.91})_{1.90}(Sb_{2.99}As_{1.10})_{4.09}S_{12.57}$
16. $(Cu_{9.62}Ag_{0.31})_{9.93}(Fe_{0.65}Zn_{1.24})_{1.89}(Sb_{3.76}As_{0.41})_{4.18}S_{12.58}$
17. $(Cu_{9.78}Ag_{0.21})_{9.99}(Fe_{0.65}Zn_{1.26})_{1.91}(Sb_{3.46}As_{0.64})_{4.10}S_{12.92}$
18. $(Cu_{9.73}Ag_{0.27})_{10}(Cu_{0.04}Fe_{0.89}Zn_{1.07})_{2.00}(Sb_{2.95}As_{1.05})_{4.00}S_{12.93}$
19. $(Cu_{9.75}Ag_{0.23})_{9.98}(Fe_{0.97}Zn_{0.91})_{1.88}(Sb_{3.11}As_{1.03})_{4.14}S_{12.27}$
20. $(Cu_{9.74}Ag_{0.26})_{10}(Cu_{0.01}Fe_{0.83}Zn_{1.07})_{1.91}(Sb_{3.00}As_{1.09})_{4.09}S_{12.99}$
21. $(Cu_{9.73}Ag_{0.27})_{10}(Cu_{0.11}Fe_{0.97}Zn_{0.91})_{1.99}(Sb_{3.03}As_{0.98})_{4.01}S_{12.84}$
22. $(Cu_{9.78}Ag_{0.22})_{10}(Cu_{0.07}Fe_{1.01}Zn_{0.92})_{2.00}(Sb_{2.63}As_{1.37})_{4.00}S_{12.86}$
23. $(Cu_{8.71}Ag_{1.15})_{9.86}(Fe_{0.73}Zn_{1.35})_{2.08}(Sb_{3.83}As_{0.23})_{4.06}S_{12.62}$
24. $(Cu_{8.65}Ag_{1.22})_{9.87}(Fe_{0.58}Zn_{1.38})_{1.96}(Sb_{3.92}As_{0.25})_{4.17}S_{12.65}$
25. $(Cu_{8.97}Ag_{0.99})_{9.96}(Fe_{0.58}Zn_{1.41})_{1.99}(Sb_{3.52}As_{0.53})_{3.85}S_{12.30}$
26. $(Cu_{9.88}Ag_{0.12})_{10}(Cu_{0.16}Fe_{0.97}Zn_{0.81})_{1.94}(Sb_{2.88}As_{1.11}Bi_{0.07})_{4.06}S_{13.01}$
27. $(Cu_{9.84}Ag_{0.16})_{10}(Cu_{0.13}Fe_{0.96}Zn_{0.80})_{1.89}(Sb_{2.91}As_{1.11}Bi_{0.08})_{4.10}S_{13.00}$
28. $(Cu_{9.82}Ag_{0.18})_{10}(Cu_{0.21}Fe_{0.94}Zn_{0.84})_{1.99}(Sb_{2.88}As_{1.07}Bi_{0.07})_{4.02}S_{12.92}$
29. $(Cu_{9.73}Ag_{0.27})_{10}(Cu_{0.76}Fe_{0.96}Zn_{0.68})_{2.40}(Sb_{2.81}As_{0.72}Bi_{0.07})_{3.60}S_{12.43}$

abundant ore mineral in the ankerite-quartz vein rock. In this vein, pyrite and exclusively also sphalerite and chalcopyrite are also present. Here the tennantite forms very tiny grains within quartz, or on the contrary, it forms large aggregates (up to 4 mm) and clusters together with idiomorphic pyrite, sometimes also with galenite within car bonates. It contains inclusions of pyrite and galena, and it itself forms inclusions and smaller rounded aggregates in galena. In the mining area Helena, the tennantite seldom contains inclusions of tetrahedrite. It has been identified optically with reflected light and by WDS analyses (Tab. 4).

Tab. 4 The electron microanalyses of tennantite from the Vyšná Boca area.

	Helena						Starobocianska dol.-Chopec				
wt. %.	1	2	3	4	5	6	7	8	9	10	11
Cu	43,23	42,36	42,72	41,87	41,81	42,09	42,51	42,38	42,62	43,1	42,5
Ag	0	0,23	0,17	0	0	0	0,3	0,16	0,26	0,11	0,23
Fe	6,01	5,84	5,92	6,12	6,11	6,09	3,14	3,27	3,28	3,34	3,26
Zn	0,24	0,19	0,3				4,54	4,43	4,59	4,38	4,4
Hg	0	0	0				0	0	0	0	0
Co				0,1	0,08	0,14					
Ni				0,08	0,07	0,11					
Au				0,17	0	0					
Sb	4,7	4,64	4,64	4,31	4,18	3,87	4,64	4,06	4,58	3,18	3,57
As	16,8	17,05	16,61	18,17	18,33	18,14	17,31	18,39	17,41	18,38	18,43
Bi	0	0	0				0	0	0	0	0
S	28,44	28,31	28	28,4	28,58	28,32	25,93	27,82	28,06	28,2	25,7
Σ	99,42	98,62	98,36	99,22	99,16	98,76	98,37	100,51	100,8	100,69	98,09
	atom. %.										
Cu	35,04	34,63	35,06	34,04	33,91	34,27	35,68	34,36	34,45	34,65	35,7
Ag	0	0,11	0,08	0	0	0	0,15	0,08	0,12	0,05	0,11
Fe	5,54	5,43	5,53	5,66	5,64	5,64	3	3,02	3,01	3,06	3,11
Zn	0,19	0,15	0,24				3,7	3,49	3,61	3,53	3,6
Hg	0	0	0				0	0	0	0	0
Co				0,09	0,07	0,12					
Ni				0,07	0,06	0,1					
Au				0,04	0	0					
Sb	1,99	1,98	1,99	1,83	1,77	1,64	2,03	1,72	1,93	1,34	1,57
As	11,55	11,83	11,56	12,53	12,61	12,53	12,32	12,64	11,93	12,53	13,13
Bi	0	0	0				0	0	0	0	0
S	45,69	45,87	45,54	45,75	45,93	45,7	43,12	44,7	44,94	44,94	42,78
Σ	100	100	100	100	100	100	100	100	100	100	100

Crystallochemical formula of tennantite: (recalculated to 16 cations).

1. $Cu_{10}(Cu_{0.32}Fe_{1.63}Zn_{0.06})_{2.01}(As_{3.40}Sb_{0.59})_{3.99}S_{13.46}$
2. $(Cu_{9.97}Ag_{0.03})_{10}(Cu_{0.27}Fe_{1.61}Zn_{0.04})_{1.92}(As_{3.50}Sb_{0.58})_{4.08}S_{13.56}$
3. $(Cu_{9.98}Ag_{0.02})_{10}(Cu_{0.33}Fe_{1.62}Zn_{0.07})_{2.02}(As_{3.40}Sb_{0.58})_{3.98}S_{13.38}$
4. $Cu_{10}(Cu_{0.04}Fe_{1.67}Co_{0.03}Ni_{0.02}Au_{0.01})_{1.77}(As_{3.69}Sb_{0.54})_{4.23}S_{13.49}$
5. $Cu_{10}(Cu_{0.04}Fe_{1.67}Co_{0.02}Ni_{0.02})_{1.75}(As_{3.73}Sb_{0.52})_{4.25}S_{13.60}$
6. $Cu_{10}(Cu_{0.10}Fe_{1.66}Co_{0.04}Ni_{0.03})_{1.83}(As_{3.69}Sb_{0.48})_{4.17}S_{13.47}$
7. $(Cu_{9.96}Ag_{0.04})_{10}(Cu_{0.08}Fe_{0.84}Zn_{1.04})_{1.96}(As_{3.47}Sb_{0.57})_{4.04}S_{12.13}$
8. $(Cu_{9.94}Ag_{0.02})_{9.96}(Fe_{0.87}Zn_{1.01})_{1.88}(As_{3.66}Sb_{0.50})_{4.16}S_{12.93}$
9. $(Cu_{9.97}Ag_{0.03})_{10}(Cu_{0.05}Fe_{0.87}Zn_{1.05})_{1.97}(As_{3.47}Sb_{0.56})_{4.03}S_{13.06}$
10. $(Cu_{9.99}Ag_{0.01})_{10}(Cu_{0.08}Fe_{0.89}Zn_{1.00})_{1.97}(As_{3.64}Sb_{0.39})_{4.03}S_{13.06}$
11. $(Cu_{9.97}Ag_{0.03})_{10}(Cu_{0.01}Fe_{0.87}Zn_{1.01})_{1.89}(As_{3.67}Sb_{0.44})_{4.11}S_{11.96}$

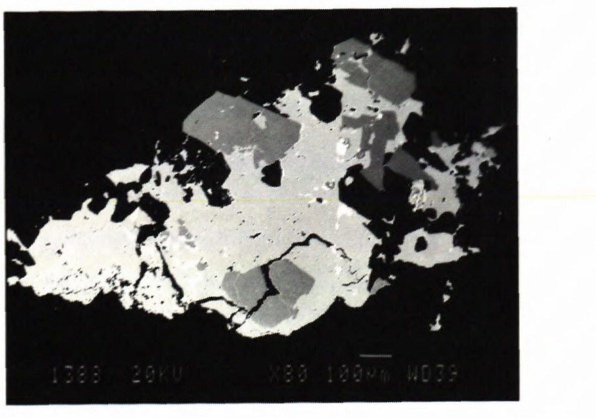


Fig. 10. Tennantite (grey) with galenite (white) and pyrite (dark-grey) from the deposit Chopec

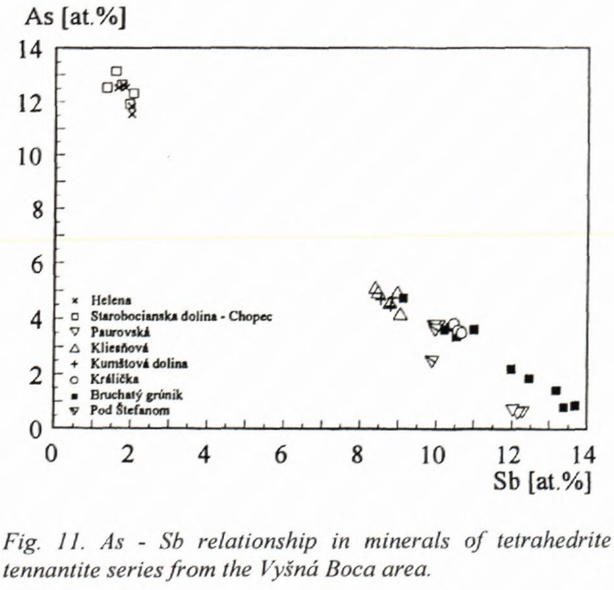


Fig. 11. As - Sb relationship in minerals of tetrahedrite - tennantite series from the Vyšná Boca area.

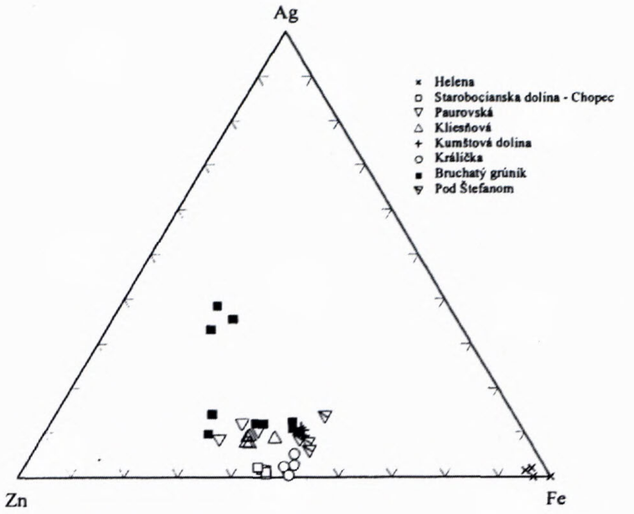


Fig. 12. Triangular diagram of Ag-Zn-Fe-bearing tetrahedrite-tennantite from the Vyšná Boca area.

Hematite Fe_2O_3 usually occurs in thin, practically monomineralic little veins composed of fine flaky variety of specularite. Specularite forms flakes and lamellas large 13 mm. The little veins are abundant in surrounding rocks and in ore vein where they transect all other types of mineral associations. Hematite is more abundant in barite-rich veins then in typical siderite-quartz veins with sulphide. In the locality Bruchatý Grúnik it forms little black veins composed of very tiny hematite micro-crystals in association with idiomorphic pyrite with hexahedron habit. The hematite was identified optically with reflected light and by EDAX.

Quartz (SiO_2) is abundant mineral in all mineral deposits in vicinity of Vyšná Boca. In siderite ore veins with quartz-sulphide mineralization it forms two generations: the older quartz is subtranslucent and forms up to 5 mm large mineral fragments in fine-grained siderite. The younger quartz is usually milky-white, more idiomorphic then the older and has sulphide mineralization in cracks (mainly tetrahedrite, chalcopyrite and pyrite). It forms veins usually 15 mm thin in coarse-grained siderite with which it often form combed intergrowth. At the siderite-barite deposit Pod Štefanom it often forms two generations. The older is coarse-grained quartz and the younger is fine-grained inlaid quartz that is intergrowing with carbonates. At the end of Kumštová dolina valley the quartz often forms idiomorphic hexahedral up to 4 cm long and 8 mm thick white crystals grown perpendicularly on base rock. Quartz is also a main mineral containing sulphosalt-carbonate fill on locality Paurovská. In quartz-carbonate-sulphide veins with abundant ankerite (the locality Bruchatý Grúnik and deposit Chopec) quartz forms several generations. The different quartz generations mutually differ not only by structure features, but also by content and quality of different sulphide and sulphosalts, colour, light transmissivity, mineral morphology etc. The quartz was identified optically and by X-ray diffraction analyses as subsidiary mineral during analyses for carbonate and barite.

Siderite ($FeCO_3$) is very abundant and dominant carbonate in most of carbonate-quartz-sulphide veins. Siderite has light brown to dark-brown colour, it is opaque with dull luster and fine to coarse-grained. The grain size is in range from 0.X - 18 mm. Siderite, together with quartz, barite, pyrite, chalcopyrite, tetrahedrite and sulphosalts of aikinite isoseries, occur in siderite veins. In ankerite veins it forms up to 1.5 cm thick veins filling and noddles and is associated with ankerite, quartz, galena, pyrite and tennantite. Siderite usually contains only very little sulphide relatively to content of quartz and barite. The highest concentration of disseminated sulphide is in fine-grained siderite (Bruchatý Grúnik, Pod Štefanom). There is almost none disseminated sulphide in coarse-grained siderite vein (Paurovská-Rovienky vein system). Sometimes, in fine-grained siderite, there is usually almost monomineralic idiomorphic pyrite (hexahedron, pentagonal dodecahedron). Siderite often cements rock and mica fragments at smaller occurrences (Nižná Helena, Banica, Podvrch). In siderite-barite deposits (Pod Štefanom, Kumštová dolina valley, Králička) siderite is often oxidised. Siderite was identified optically with transmitting and reflected light and also by DTA, X-ray diffraction analyses and manometry analyses (Tab. 5). These analyses suggest that more abundant members of siderite-magnesite isomorphous series are those with higher content of iron (siderite, sideroplesit). Tab. 5 does not include percentage content of CaO and MnO, because the contents were under the detection limit of the used manometry analyses and thus they are included into content of FeO. In insoluble residue of manometry analyses of carbonates we have identified mainly quartz (about 99 % in average), and accessory amounts of various micas (mostly muscovite), chlorites, rock fragments and unidentified grains, which proves that siderite veins have brecciated structure where framework of small siderite veins cements fragments of rocks and minerals. In samples No. 7, 8, 9 and 11 there was increased amount of grains of ore minerals (about 0,5 - 3 %). In the insoluble residue there were these ore minerals: chalcopyrite, tetrahedrite and pyrite that was dominant over other minerals in the sample No. 9.

Calcite $CaCO_3$ was found only in one sample from Bruchatý Grúnik, where it forms up to 1.4 mm large grains composed of white to grey-white rhombohedron crystals. The calcite, together with dolomite, form clusters in siderite, which are intersected with ankerite veins. It was identified optically with transmitting light and by EDS analysis.

Ankerite, $CaFe(CO_3)_2$, occurs rarely in studied area. It is abundant at Bruchatý Grúnik, where often coarse-grained white ankerite forms up to 3 cm thick veins penetrating through siderite and quartz veins. In most siderite veins the ankerite occurs in–rare small veins within siderite and quartz. At the locality Chopec, there are quartz-ankerite veins, where ankerite occurs in association with siderite, galena, tennantite and pyrite. In places coarse-grained ankerite dominates over quartz. In such places the hypidiomorphic ankerite phenocrysts are up to 2 cm large. The ankerite was preliminary identified by

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Tab. 5. The results of manometry analyses of siderite from the Vyšná Boca area.

	Kliesňová		Helena	Paurovská				Kum. dol.	Pod Štefanom		Chopec
Analysis No.	1	2	3	4	5	6	7	8	9	10	11
FeO	52,27	55,66	58,02	60,71	54,97	59,54	57,66	62,01	46,62	51,44	55,72
MgO	6,12	3,73	3,08	1	5,43	1,91	3,36	0	8,23	5,86	4,85
CO_2	41,61	40,61	38,9	38,29	39,6	38,55	38,98	37,99	45,15	42,7	39,43
$(Fe,Mg)CO_3$	91,95	96,18	96,58	96,48	75,4	92,1	69,77	78,6	95,2	95,55	96,3
Insoluable r.	8,05	3,82	3,42	3,52	24,6	7,9	30,23	21,4	4,8	4,45	3,7
Carbon.mem.	sidpl.	sidpl.	sid.	sid.	sidpl.	sid.	sid.	sid.	pis.	sidpl.	sidpl.

measurement of refractive index, and by DTA and manometry analyses (locality Pod Štefanom: CaO 14.78, (FeO+MnO) 25.99, CO_2 40.81, $CaFe(CO_3)_2$ 92.97 wt.%, insoluble residue 8.03 wt. %).

Dolomite $CaMg(CO_3)_2$ is very rare in siderite deposits. It was found only in one sample from the locality Bruchatý Grúnik where 2 mm large black-grey dolomite crystals form grains with calcite and tiny ankerite veins within siderite. Part of the dolomite has increased concentration of FeO, which classifies it among Fe-bearing dolomite members. The dolomite is probably coloured with graphite pigment. The dolomite was identified by EDAX.

Kutnohorite (?) $CaMn(CO_3)_2$ was found only in one sample from the locality Kliesňová, where it forms 4 mm thick vein within siderite. It was identified by X-ray diffraction analysis (Tab. 6.). The table shows up, that it is carbonate from dolomite isomorphous series. The values of interlamellar distance (b) do not match the table values of dolomite, ankerite or kutnohorite, however, they are very close to them. This means, that it is member with strong isomorphism, and according to JCPDS tables (Berry ed., 1974) the values of interlamellar distances are nearest to member kutnohorite-(Mg).

Barite $BaSO_4$ is abundant mainly in northern vein area (end of the Kumštová dolina valley, Králička and the deposit Pod Štefanom), where it often intergrow with oxidised siderite and less often with quartz in association with chalcopyrite, tetrahedrite, pyrite and galena. It is rare in the southern vein system Paurovská - Rovienky and at Bruchatý Grúnik, where white barite forms mostly thin and short veins within gneisses, or it intersects older coarse-grained siderite and milky-white quartz with sulphides. Barite occurs as tiny grains in quartz-ankerite veins with galenite and tennantite (± pyrite, chalcopyrite) at the deposit Chopec in Starobocianska dolina valley. Macroscopically it is usually fine-grained, only in Kumštová dolina valley and Králička it is also compact. The colour of the barite is white, only at localities where it is abundant it has also pink, grey, brownish and yellowish colour. Barite from Králička and Paurovská has sometime bright-green luminescence under a ultraviolet lamp. The luminescent colours form streak and diffusion structures. It was identified by X-ray diffraction analysis (locality Pod Štefanom: 4.34 (33), 3.90 (40), 3.579 (40), 3.442 (100), 3.3198 (85), 3.103 (98), 2.839 (45), 2.731 (50), 2.122 (83), 2.109 (83)) and with help of refraction index. (Np = 1.623, Ng = 1.643; Paurovská).

Tab. 6. X-ray powder diffraction analyses of kutnohorite-(Mg) from the Vyšná Boca area.

dtab	Itab	d	I
5,41	2		
		4,267	2 Q
3,73	8	3,722	7
		3,349	8 Q
2,91	100	2,91	100
2,701	2	2,696	2
2,564	2		
2,423	6	2,421	5
2,209	10	2,205	11
2,031	6	2,026	7
1,862	4	1,858	3
1,823	10	1,82	12
1,804	12		
1,8	10	1,799	12
1,578	2		
1,556	4	1,552	4
1,512	2	1,507	1
1,477	4	1,474	3
1,457	2	1,454	3
1,445	2		
1,398	2	1,396	3
		1,348	3
1,309	2		
1,2816	2	1,2799	2
		1,2456	2
1,2071	2		
1,1799	2	1,1776	2
1,1524	2		
1,1328	2		
1,1176	4	1,1149	3

Schorl (?), $NaFe_3Al_6Si_6O_{18}(BO_3)_3(OH)_4$ was found only in one sample from Čertovica (under Rovienky), near a place where siderite veins crop out. About 2 cm large black tourmaline with vertical striation was embayed into white quartz. It was identified only visually.

Secondary minerals

Covellite CuS occurs in siderite veins rarely, but regularly. It is more common at the locality Pod Štefanom, where it occurs in chalcopyrite and tetrahedrite together with galenite and secondary Cu and Fe-bearing minerals (Fig. 13). It forms only very tiny, microscopic grains usually in chalcopyrite or tetrahedrite. It was identified with reflected light and preliminary by EDAX.

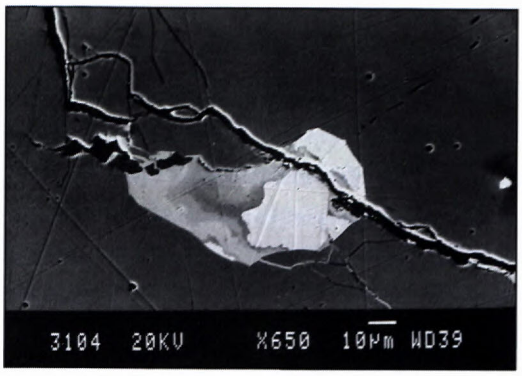

Fig. 13. Covellite (the darkest zone) with secondary Cu-bearing minerals and galena (white) in tetrahedrite (black-grey) from the deposit Pod Štefanom.

Goethite α-FeO(OH), together with another Fe-bearing oxides and hydroxides, is omnipresent mineral in siderite deposits and occurrences. It is part of oxidised zones, where it is product of weathering of carbonates, mainly siderite. Crystalline crust up to 0.8 mm thick occurs mainly on tailing pile of the gallery Vyšná Helena at the end of Kumštová dolina valley. It often has film, mamillary, radiolitic and crustal forms. It was identified optically with transmitted and reflected light.

Fe-bearing hydroxides are very abundant and regular companion of Fe-bearing carbonates in ore veins. They intensively replace mainly siderite, but also ankerite, pyrite, chalcopyrite (Fig. 14) and less tetrahedrite. They often penetrate along planes of cleavage of siderite and often fill narrow fissures and cracks in quartz. Skeleton, netted, bushy, finger-like and film structures are the most abundant grain shapes of all they have. They were identified optically with reflected light and by EDS analyses.

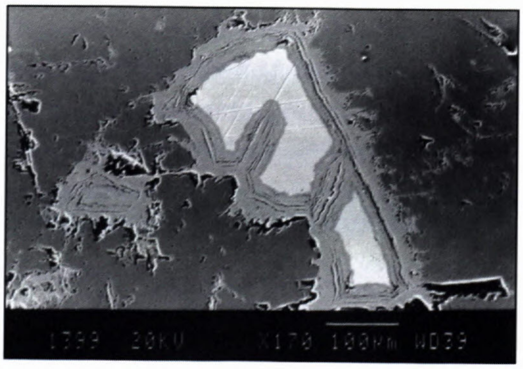

Fig. 14. Hydroxides of iron intensively replacing chalcopyrite, the Vyšná Boca area.

Aragonite $CaCO_3$ was found in the gallery Helena, where it forms clusters of tiny crystals spread over area several cm^2. Up to 1 mm large transparent crystals of aragonite have glassy luster, needle-shaped habit and usually grow on coarse-trained siderite. At the other siderite localities the aragonite is abundant and forms thick milky-white to pinkish-white film and thin crusts. It was identified optically and by X-ray diffraction analyses (Tab.7). In reaction with HCl it fizzles and dissolves.

Tab. 7. X-ray powder diffraction analyses of aragonite from the Vyšná Boca area.

dtab*	Itab*	d	I
4,212	2	4,29	17
		4,27	19
3,396	100	3,36	100
		3,33	52
3,273	52	3,28	42
		3,03	7
2,871	4	2,88	18
2,73	9	2,81	10
2,7	46	2,71	43
2,481	33	2,49	35
2,409	14	2,41	9
2,372	38	2,37	32
2,341	31	2,34	34
2,328	6	2,33	34
2,188	11	2,19	19
2,106	23	2,1	44
1,977	65	1,981	68
1,882	32		
1,877	25	1,877	31
1,814	23	1,824	11
1,759	4	1,755	15
1,742	25	1,738	16
1,728	15		
1,698	3	1,701	4

**-Berry (ed.)(1974)*

Azurite $Cu_3(CO_3)_2(OH)_2$ occurs together with malachite and another yet not identified secondary Cu-bearing minerals and Fe-bearing hydroxides in oxidised zone of siderite deposits. It occurs relatively more often at the deposit Pod Štefanom and in the lowest levels of the end of Kumštová dolina valley. Usually it occurs in a form of thin firm and crystalline crusts, rarely it forms 0.8 mm large translucent deep-blue crystals freely grown on weathered siderite or in voids in limonite. Sometimes it forms fluidic crystalline structure. It was identified optically and by morphology of the crystals.

Malachite $Cu_2(CO_3)(OH)_2$ often occurs together with another secondary Cu- and Fe-bearing minerals in oxidised zone of iron ore deposits and occurrences of the Vyšná Boca area. It forms usually thin firms or pulverulent aggregates. Malachite from these localities has characteristic green colour without significant light- or deep-green shade. It was identified optically and by EDAX.

Pharmacosiderite $KFe_4(AsO_4)_3(OH)_4.6H_2O$ is very rare. It was found near the surface where mylonite zone crops out of the mountain ridge Rovienky. Here farmakosiderite forms very tiny grey-green to yellow-green crystals grown on goethite. It occurs in voids and cracks of yellow-brown to brown quartz together with ferisymplezite and Fe-bearing hydroxides. It was identified by EDAX.

Ferisymplesite $Fe_3(AsO_4)_2(OH)_3.5H_2O$ is rarely found on the mountain ridge Rovienky in the crops out of mylonite zones. It forms film, collomorph and colloidal brown aggregates grown on goethite, less on farmakosiderite. It occurs in voids and cavities of limonite. It is similar to opal, evansite or metahalloysite. X-ray amorphous ferisymplesite was identified by EDS analysis.

In the Kumštová dolina valley we have found malachite and azurite together with olive-green firms and crystalline earthly aggregates containing Cu, Sb, Fe and less As. This miscellany of minerals comes to existence probably as secondary products of weathering of tetrahedrite. It was identified by EDAX.

Ore textures

Cocarde and mainly brecciated textures are the most common in siderite mineral deposits with quartz-sulphide mineral association. The genetically oldest quartz is disseminated in fine to medium-grained siderite, together with pyrite and another sulphides, muscovite (sericite) and chlorite. Siderite often cements rock fragments, as well as pieces of altered rocks. Coarse-grained siderite, together with younger quartz, has combed textures. In a sulphosalt vein at the locality Paurovská, rarely grey-white quartz containing disseminated siderite, sulphides and mainly sulphosalts envelope and enclose fragments of altered rocks as well as coarse-grained siderite that is combed intergrown with black-white quartz. Several mm-large clusters of often idiomorphic siderite crystals disseminated in quartz gives to veins here and there noddle character. Finger-like intergrowth of siderite and barite can be observed at the mineral deposit Pod Štefanom. In Kumštová dolina valley, sometimes barite, together with hematite, siderite, rarely also with quartz, form banded textures. At Králička and at mining area Eduard, barite is often massive and compact. Barite from monomineral barite vein at Chopec has coarse-crystal character. Quartz-ankerite vein with galenite and tennantite from the mineral deposit Chopec has brecciated textures at the places where fragments of siderite, ankerite and sometimes also altered rocks are enclosed in quartz. Galena with tennantite forms disseminated textures here. Quartz of several generations can be observed here. Cavities with tiny quartz crystals in the gallery Helena and barite in access gallery SW from the cottage Barbora at Vyšná Boca have drusy character. Sulphides in siderite deposits and occurrences occur in a form of veins and impregnation or they are einsprengled into carbonates, quartz and barite. Sometimes they form skin around quartz and ankerite grains.

The Mineralization Development

Several mineral paragenetic associations are distinguished within the siderite mineralization. They are ordered from the oldest to youngest ones, however, their age relations are not always proved enough.

1. The oldest evidence of hydrothermal mineralization in the studied area is the intensively silicified zones with arsenopyrite veins and disseminated pyrite. The siderite veins are strictly delimited from the hydrothermal altered zones or the thin siderite veins penetrate more or less into the silicified rocks. We incorporate into this phase the arsenopyrite veins with pyrite and Ni-Co-(Cu) mineralization of the adjacent rocks of siderite veins from the locality Helena. The position of quartz-tourmaline mineral association (Čertovica) has not been solved yet. With respect to the fact that it occurs in siderite deposits or in their neighbourhood, for instance Mýto pod Ďumbierom – Hviezda south (Majzlan and Chovan, 1997), it is probable that it is one of the siderite mineralization phase.

2. The siderite phase is represented by siderite veins with younger quartz-sulphide mineral association. The sulphides (pyrite, chalcopyrite, and tetrahedrite) form the thin veins in the milky-white quartz. Typical characteristics of the veins are coarse-grained and medium-grained siderite, thin oxidation zone (sometimes is missed) and the typical comb intergrowth of quartz and siderite. The three characteristic generation are distinguished: the oldest fine crystalline siderite I cementing the quartz fragments (probably rocky one) and the fragments of the altered rock. The main mass of siderite II is formed by coarse-grained and medium-grained, less fine-grained siderite. The youngest siderite III forms less occurred short thin veins that cross the previous two generations of siderite. These thin veins themselves can form several generations.

3. In the second phase the quartz-sulphosalt vein (Paurovská) was probably formed. The typical properties of this vein are sulphosalts and carbonates occurrences in the scattered form (disseminated textures) in grey-white and grey quartz. Except of the typical mineral composition some minerals have the specific chemical composition (for instance – tetrahedrite) that is different from minerals occurred in other carbonate-quartz-sulphide veins. Breccia fragments of quartz and siderite comb intergrowth from the previous phase are in the main quartz vein rocks.

4. In the third phase the younger siderite-barite veins were formed that are different from siderite ones of the first phase because of having more of barite component and sulphides occur more-less in noddle forms. Siderite form two main generations: siderite I is older than all other types and barite generations, and siderite II forming thin veins is younger than all barite types. The age relation between older and younger siderite veins in the Nízke Tatry Mts. was pointed out by Turan (1962) who distinguished the different concentrations of Sr in barite of various veins.

5. In the fourth phase the quartz-ankerite vein was probably formed with the younger galena-tennantite paragenesis in Chopec. This vein is characterised by plenty of quartz and pyrite types. It is younger than siderite veins because it encloses the fragments of older siderite. It occurs in granitoid rocks.

6. The youngest one in the area, in accordance with the present knowledge (Chovan et al., 1995 etc.), is the hematite mineralization where the hematite veins intersects all the previous types of ore mineralization. The similarities in age have the thin siderite veins interfering into Lower Triassic Lužnianske layers near Kumštové sedlo pass.

7. In the supergene phase were formed mainly Fe-bearing hydroxides for instance goethite (Helena, Kumštová dolina valley, Králička), less the Cu-bearing secondary minerals - malachite and azurite (Pod Štefanom, Kumštová dolina valley, Králička) and rarely Fe-bearing arsenates (Rovienky). The most abundant carbonate is the supergene aragonite that forms films in all the siderite deposits.

Discussion

Papp (1919) collected the first complete data about the iron ore in the Vyšná Boca area. By field and laboratory investigation we have found that the data about iron ore occurrences in the Vyšná Boca area (names, location and characteristics of the old mine works) as well as the analyses published in Papp´s work do not correspond with the present knowledge, Zoubek (1951) noted already that fact.

From the carbonates on hydrothermal veins siderite is the most abundant one (variety sideroplesite, pistomesite) that significantly prevails in the majority of deposits and occurrences over carbonates of dolomite-ankerite series. From the chemical composition of the carbonates of siderite-magnesite series of the different phases of siderite mineralization is obvious that in all types of siderite veins the quantitative composition of individual members of the series is almost the same. The calcite almost does not occur in siderite veins. It was found just in one sample in Bruchatý Grúnik in paragenetic association with dolomite, ankerite and siderite. The quantitative occurrence of the various carbonates and their chemical composition is very similar to the carbonates of siderite ore mineralization in the Spišsko-gemerské rudohorie Mts. (Cambel and Jarkovský, ed., 1985).

The gold presence in siderite veins was not confirmed (Maderspach, 1880; Toth, 1982). The occurrence of the free gold is not supposed in this type of mineralization.

The chemical composition of arsenopyrite from Vyšná Boca is the same as in other hydrothermal deposits in the Západné Karpaty Mts. (see Stankovič, 1998 etc.). At the locality Bruchatý Grúnik the arsenopyrite occurs rarely, it contains up to 11,6 wt. % Sb (Tab 1, analysis no 19-22). Similar type of arsenopyrite is sometimes gold bearing. The gold is probably fixed in lattice of arsenopyrite (Andráš et al., 1993). According to our investigation its distribution is random in arsenopyrite crystals. The connection of the "invisible" gold with zones rich in As and poor in S and Sb was not confirmed (Andráš et al. 1993).

The pyrites from the various veins have in siderite mineralization almost the same chemical composition. However, many of pyrite grains have chemical zoning. The zoning is caused by variation of Fe and S concentrations, sometimes by addition of subsidiary elements, mostly As. Central parts of concentric zoned grains exposed to reflected electrons have the lightest colours of all zones because they are enriched with subsidiary elements (Ni, Co, As, Cu, Sb, Au). Papers concerning the presence of "invisible" gold in zoned crystals of pyrite and arsenopyrite with Sb content in general was published by Andráš and Ragan (1994).

The chemical composition of tetrahedrite from carbonate-quartz-sulphide veins is relatively stabile. Different chemical composition has tetrahedrite from quartz - sulphosalt vein at Paurovská (it contains up to 3,21 wt. % Bi and max. 0,89 wt. % As). Tetrahedrite found in Rišianka in the Nízke Tatry Mts. (Majzlan et al. 1998) has similar Sb/As ratio. From the other localities the zero content of Bi in tetrahedrite (with typical intensive chemical zoning) from the locality Bruchatý Grúnik is exceptional. The contents of Ag in tetrahedrite from various veins are relatively stabile and vary in range 0,80 – 2,04 wt. % , average 1,38 wt. %. It is similar like in the Magurka deposit (Chovan et al., 1995). Higher concentration of silver in Ag-bearing tetrahedrite we have found only in one sample from the locality Bruchatý Grúnik (Tab. 6b, analyses no 23-25). This type of tetrahedrite contains 7,79 wt. % Ag.

By investigating the chemical composition of tennantite from two localities in the Vyšná Boca area (locality Helena – arsenopyrite veins with Ni-Co mineralization and locality Chopec–south – quartz-ankerite vein with galena and tennantite) we have found out that tennantite of both generations have practically identical chemical composition. The difference is only in Fe and Zn ratio. Tennantite from Ni-Co mineralization is characterised by intensive deficit of Zn due to Fe enrichment (average content of Fe 5,92 wt. %). Tennantite from both sites contain up to 0,3 wt. % Ag, zero content of Bi is typical for them. The whole area is characterised by absolute absence of Hg in minerals, which was expressed mainly in minerals of tetrahedrite group in which Hg does not occur even in trace amounts. Bi occurrences are interesting. In hydrothermal veins where galena, beside tetrahedrite or tennantite, is the main sulphide mineral, minerals of the tetrahedrite group do not contain Bi.

The comparisons of chemical composition of galena in association with arsenopyrite and with galena in association with tetrahedrite and sphalerite have revealed that the chemical compositions of both galenas of siderite mineralization are identical.

From the secondary minerals except of hydroxides of iron abundant crystalline films of aragonite were formed. Secondary minerals of copper are relatively rare comparing to amount and size of siderite localities. Forming of thin oxidised zones that are even missed on some localities probably causes their rare occurrence.

In altered zones that have not been deeply studied yet, the silicification, less sericitication and chloritization are extensive around quartz-sulphide veins. Close to ore veins there are almost totally silicified zones, in which arsenopyrite veins, rarely little grains of pyrite and sometimes plentiful Fe-Ti-bearing oxides occur. Gradually with increasing distance from an ore vein content of arsenopyrite decreases and content of free disseminated pyrite and other minerals increases. In the neighbourhood of siderite veins the close-ore metamorphosis reach max. first decades of cm, usually the thickness of altered rocks is lower.

On the base of mineralization development investigation we suppose that the oldest siderite veins are of Variscian age, while some, mainly younger generations of siderite (Černyšev et al., 1984; Chovan et al., 1996), could be the products of Alpine remobilisation. While in other parts of the Nízke Tatry Mts. the galena ore mineralization is related to barite rich ore veins (Jasenie – Soviansko, Malužiná – Olovienka etc.), in the Vyšná Boca area it is related to carbonate-quartz-sulphide veins where ankerite is the main or prevailing mineral. According to the fact, that siderite ore mineralization reaches Triassic members (Lúžnianské layers) near Kumštové sedlo pass, similarly as in Mýto pod Ďumbierom (Majzlan & Chovan, 1997) we suppose that siderite veins were formed still in Upper and Middle Triassic.

Topomineral influence of rock environment was manifested by presence of siderite veins in high-rank metamorphic rocks and ankerite veins in granitoid rocks. That proves also predominance of ankerite over siderite in other Nízke Tatry deposits and presence of Au or Au-Sb mineralization (Magurka, Rišianka, Malé Železné, Nižná Boca, Vyšná Boca - Chopec) that occur in granitoid rocks (Majzlan et al., 1998; Ozdín, 1997). Siderite veins are on the other hand situated only in highly metamorphic rocks of crystalline complex – for instance Jarabá, Mýto pod Ďumbierom – Mlynná dolina valley, Bystrá etc. (Majzlan & Chovan, 1997, Majzlan & Chovan, 1998). At Bruchatý Grúnik carbonates of siderite isomorphous series and carbonates of ankerite-dolomite series occur about in the same ratio. The influence of the rock environment can be explained here so, that the ore mineralization is probably developed on discontinuity zone between Králička type granite and high-rank metamorphic gneisses and migmatites. In contradiction with our results there is the presence of carbonates in the Jasenie-Soviansko deposit where ankerite prevails siderite in high-rank metamorphic rocks (Pouba & Vejnar, 1955).

The highest amount of siderite occurs with quartz-sulphide mineralization, if barite content increases than hematite content increases as well. In ankerite veins there is less siderite and galenite is the main ore mineral.

The occurrences of siderite mineralization and mineral filling of veins is very similar to ore mineralization in the Spišsko-gemerské rudohorie Mts. (for instance Cambel & Jarkovský, ed. 1985). The development of mineralization is in accordance with the present knowledge about mineralisations in Ďumbier part of the Nízke Tatry Mts. (Chovan et al., 1996, Chovan et al., 1998).

Conclusion

Siderite veins occur in intensive mylonite zones almost exclusively in metamorphic rocks of crystalline complex. They are sharply delimited from the surrounding rocks. The prevailing directions of these veins are ENE-WSW. The inclination varies very much, but in studied area the siderite veins incline predominantly to south. The thickness of veins vary, the average thickness is up to 0.5 m. The veins wedge out quickly or gain on thickness, brecciated textures and also noddle and cocarde structures are characteristic.

We have found out the following primary minerals by mineralogical research: aikinite, ankerite, arsenopyrite, barite, benjaminite, bismuthinite, carrollite, friedrichite, galena, gersdorffite, hammarite, hematite, chalcopyrite, cobaltite, quartz, krupkaite, cubanite (?), kutnohorite (?), lindströmite, marcasite, pecoite, pyrite, sphalerite, siderite, schorl (?), tennantite a tetrahedrite. We have described following secondary minerals: aragonite, azurite, covellite, pharmacosiderite, ferisymplesite, goethite, hematite and malachite. In hydrothermally altered rocks at siderite veins vicinity occur: arsenopyrite, biotite, quartz, muscovite, pyrite, rutile and Fe-Ti-bearing oxides.

During investigation of carbonates we have determined that carbonates of siderite series usually predominate in metamorphic rocks on hydrothermal ore veins over the carbonates of isomorphous ankerite-dolomite series. That is opposite in granitoid rocks. The most abundant is siderite with sideroplesite and pistomesite varieties. Dolomite, kutnohorite and calcite were found only in one sample. Aragonite occurs as the secondary mineral in siderite veins.

The mains of sulphide minerals are chalcopyrite and minerals from tetrahedrite and pyrite groups, which are abundant in all of the investigated localities. The subsidiary minerals are arsenopyrite, galena, sphalerite and sulphosalts of aikinite series. Arsenopyrite (max 0,04 wt. % Au) and pyrite (up to 0,19 wt. % Au) are locally gold bearing.

Quartz is the main non-metallic mineral that is the main mineral everywhere. However, in various deposits and occurrences it is present in various forms and it forms at least two generations everywhere. For each ore vein or vein system a specific type of quartz is characteristic that differs by colour, level of crystallisation, light transmissivity, and presence, quantity and form of sulphide, carbonate and barite occurrences in it.

From the mineralogical viewpoint the typical signs of siderite mineralization in the vicinity of Vyšná Boca are: the presence of sulphosalts of aikinite isotype series in all the siderite veins, relatively monotone mineralization and absence of gold and mercury bearing minerals.

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