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HYDROTHERMAL Sb-Au MINERALIZATION IN THE STRÁŽOVSKÉ VRCHY MOUNTAINS (MALÁ MAGURA, WESTERN CARPATHIANS)

TOMÁŠ MIKUŠ[1] and MARTIN CHOVAN[2]

[1]Geological Institute, Slovak Academy of Sciences, Severná 5, 974 01 Banská Bystrica, Slovak Republic; mikus@savbb.sk
[2]Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republic; chovan@fns.uniba.sk

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Abstract: Sb-Au mineralization in the Malá Magura mountain group of the Strážovské vrchy Mts was found in the vicinity of the Chvojnica village. Mineralization occurs in quartz-carbonate veins and disseminated zones in the Variscan granitoids and highly-metamorphosed rocks. Paragenetic associations of Sb-Au mineralization are close to other deposits of this type in the Tatric Superunit (Malé Karpaty Mts, Nízke Tatry Mts etc.). The mineralization was formed during three stages. The pyrite-arsenopyrite-gold mineral stage is the oldest one. The arsenopyrite geothermometer gives a temperature range of 385–465 °C. Younger stages are the sphalerite-galena-tetrahedrite (2nd) and stibnite-sphalerite-sulphosalts (3rd) mineral stages. A substantial part of the sphalerite of the 2nd mineralization stage shows "chalcopyrite disease". Common association of pyrrhotite and native antimony observed in the 3rd mineralization stage indicates low aS_2 and fO_2 values of the ore-forming fluid. Furthermore, the 3rd mineralization stage comprises Fe-bearing minerals (jamesonite, pyrrhotite and berthierite), which indicate Fe-rich environment. Primary gold occurs in two generations differring in Ag content.

Key words: Western Carpathians, Variscan basement, Sb (Pb, Zn, Cu, Fe) sulphides and sulphosalts, gold.

Introduction

Sb-Au mineralization in the Tatric Superunit (Western Carpathians) is known mainly from numerous occurrences in the Ďumbierske Tatry Mts (Chovan et al. 1996 a.o.). Deposits such as Magurka, Dúbrava, Medzibrod, Lom, Dve Vody and Boca were important sources of gold and later on antimony. Localities in the past in the Malé Karpaty Mts — Kolársky vrch, Limbach (Au), Pernek and Kuchyňa (Cambel 1959; Chovan et al. 1992) were of economic importance. Gold was also extracted from the small Sb-Au mineralization deposit on Kriváň in the High Tatra Mts (Bakos 2000). Occurrences in the Malá Fatra Mts (Bystrička and Trebostovo) were without economic importance and have been insufficiently studied (Varček 1963). The geochemical indices of Sb mineralization in the crystalline basement in the Považský Inovec and Tribeč Mts were noted by Polák & Rak (1980).

A rich gold-field was known and mined in the Malá Magura mountain group of the Strážovské vrchy Mts, in the vicinity of Chvojnica and Malinová villages from the 14th century. The mining continued in the 16th and 17th century, (e.g., in the year 1614, 700 g Au), (Janczy 1973). However the primary sources of the gold remain unknown (Böhmer & Hvožďara 1980). Up to now, occurrences of ore mineralization in the vicinity of Chvojnica village were ascribed to base metal hydrothermal mineralization in the Tatric Superunit (Zelný & Uher 1988; Mikoláš et al. 1993 a.o.).

During our research in the past few years, we have identified primary mineralization in the Chvojnica — Partizánska dolina Valley. This mineralization shows similarities with Sb-Au mineralization in other mountains of the Tatric Superunit.

Geological setting and mineralization

Tatric Superunit

The Western Carpathians belong to a collisional Alpine Orogen, which arose from the closure of the Tethys Ocean. The Western Carpathians can be subdivided into the Outer-, Central- and Inner Western Carpathians (Plašienka et al. 1997). The Tatric Superunit is an extensive thick-skinned crustal sheet composed of a pre-Alpine (generally Variscan) crystalline basement and its sedimentary cover. The Tatric basement generally shows well-preserved Variscan structures without a significant Alpine overprint.

The Tatric basement is built up of large Variscan granitoid plutons located within medium to high-grade metamorphic rocks such as gneisses, anatectic migmatites and amphibolites. Low to medium-grade shales and mafic rocks of Devonian to Early Carboniferous age are less abundant (Malé Karpaty Mts). The Tatric cover comprises the following lithological units: Upper Carboniferous and Permian molasse sediments, bimodal volcanics and Lower Triassic-mid-Cretaceous sedimentary rocks. A few Mesozoic nappes were thrust from the S and overlie the Tatric basement and cover series.

The formation of the most important Sb-Au hydrothermal mineralizations is believed to be linked either to Variscan

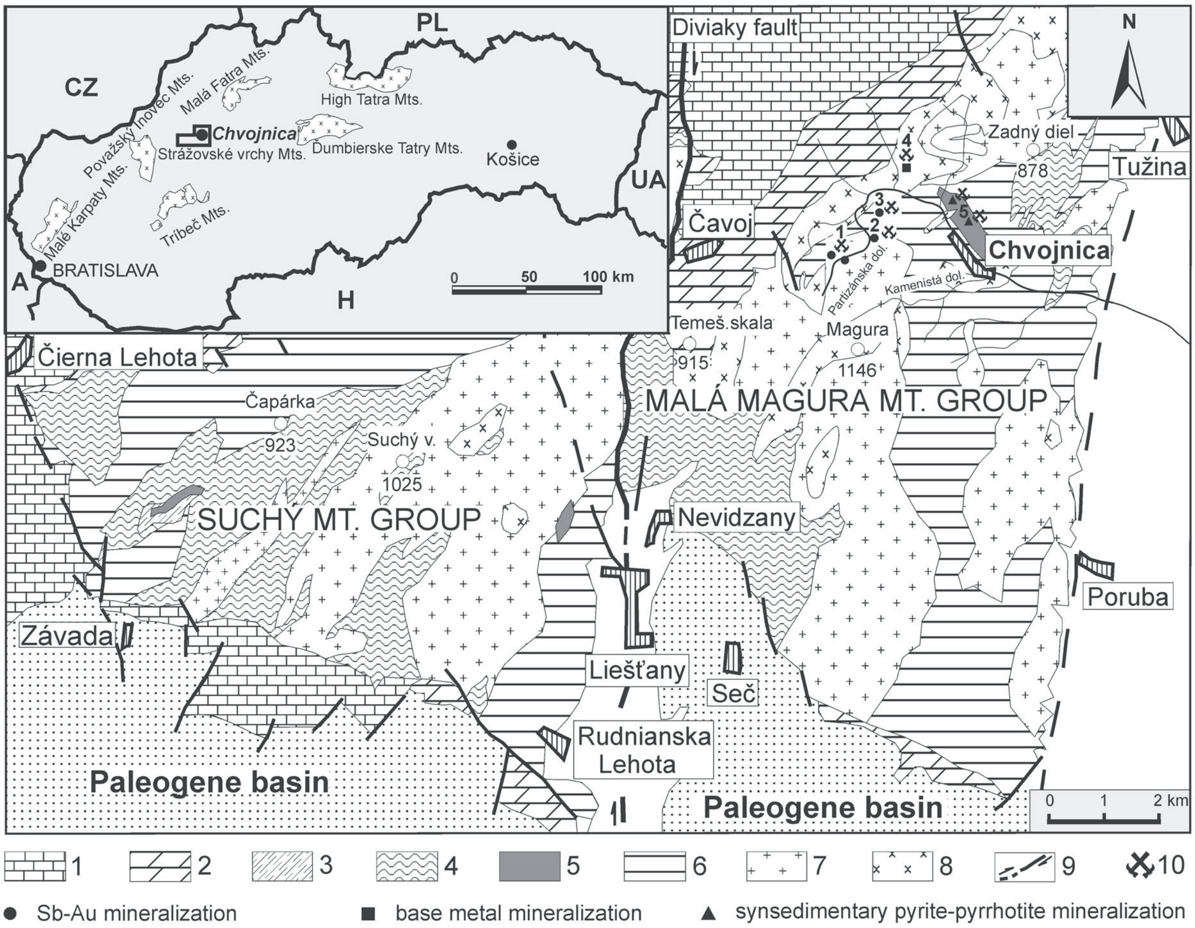

Fig. 1. Schematic geological map of crystalline of Suchý and Malá Magura mountain groups (according to Maheľ 1985) with localization of various types mineralization. **1** — Krížna Nappe, **2** — Mesozoic sedimentary cover, **3** — graphitic black-shales, **4** — biotitic micaschists, **5** — amphibolites, **6** — ribbed migmatites and migmatized micaschists, **7** — leucocratic granites and biotite-bearing granites, **8** — medium-grained granites and granodiorites, **9** — faults, **10** — old mines (1,2 — Partizánska dolina Valley, 3 — Trausementz dolina Valley, 4 — Kňažia štôlňa adit, 5 — synsedimentary pyrite-pyrrhotite mineralization).

granitoids or metamorphism. Particular results about mineralogy and fluid inclusions study in the Sb-Au mineralization in the Tatric Superunit are reported by many authors (e.g., Chovan et al. 1992, 1995, 1996, 1999; Majzlan et al. 2001; Hurai 1988 a.o.).

The Suchý and Malá Magura mountain groups

The crystalline complexes of Suchý and Malá Magura mountain groups of the southernmost part of Strážovské vrchy Mts are situated in two areas separated by the Paleogene Diviaky fault. They are similar with respect to their magmatic, metamorphic and tectonic evolution. Both complexes are composed mainly of granitoid rocks and paragneisses. Migmatites become dominant towards the periphery of the core areas. The crystalline basement is rather homogeneous without any remnants of Mesozoic and younger Tertiary units.

In the Malá Magura mountain group the metamorphic rocks are mainly high-temperature paragneisses and quartz-rich paragneisses. Granitic rocks (tonalites, granodiorites, granites) belong to common differentiation series. They belong to peraluminous S-type granite suite (Hovorka & Fejdi 1983). The radiogenic $^{207}Pb/^{206}Pb$ zircon age of 356±9 Ma from a granite and coexisting diorite at the Kamenistá dolina Valley (Malá Magura mountain group) indicates the granite intrusion close to the Devonian/Carboniferous boundary (Kráľ et al. 1997). The core of the Malá Magura mountain group displays a reduced amount of cover rocks, due probably to a more important uplift. The pre-Alpine, Variscan tectonics is dominant in both cores. The Alpine restructuring of the crystalline basement is relatively poor and did not substantially change the older tectonic pattern (Maheľ 1985).

The P-T-X parameters of metamorphic processes within crystalline cores of the Suchý and Malá Magura indicate differences in their progressive and retrograde metamorphic evolution. The metamorphic temperatures and pressures of these particular crystalline complexes are as follows: Suchý mountain group: 540–560°/4–5 kbar, XH_2O = 0.6–0.8 and Malá Magura mountain group: 620–640°/4.5–5.5 kbar, XH_2O = 0.8–1.0 (Dyda 1994).

The P-T-X uplift trajectories in the Suchý paragneisses indicate their isothermal decompression and display several uniform trajectories influenced by decompression during cooling of the Malá Magura paragneisses (Dyda 1994).

Two types of mineralization were described N and NW from the village of Chvojnica (Fig. 1):

1. syngenetic primary exhalation-sedimentary pyrite-pyrrhotite mineralization (Fig. 1, locality 5) located in an amphibolite body (Böhmer & Hvožďara 1980),

2. base metal mineralization (Fig. 1, locality 4) considered as continuation of veins from Čavoj (Mikoláš et al. 1993).

The investigated hydrothermal Sb-Au mineralization occurrences (Fig. 1, localities 1–3) in the Malá Magura mountain group are situated 2 km W and NW from the village of Chvojnica in the Partizánska and Trausementz dolina Valleys within the crystalline complex of the Malá Magura mountain group. These occurrences of generally SW–NE direction are located in fine-grained biotitic granodiorites, granites, ribbed migmatites and migmatitic paragneisses.

Methods of study

Samples for mineralogical study were collected at old mine dumps in the Partizánska dolina Valley. Sulphides, sulphosalts and native elements were analysed by wave-dispersion (WDS) analysis and photographed in back-scattered electrons (SEM–BEI) at Faculty of Natural Sciences, Comenius University in Bratislava; a JEOL JXA 840A probe was used with operating conditions: 20kV, 15nA, beam diameter 2–5 μm, standards — pyrite, galena, cinnabarite, sphalerite, chalcopyrite, arsenopyrite, Fe, Ag, Cu, Bi, Sb, Au, Cd, MnO, GaAs, Ni, Co. Carbonates were analysed by an energy-dispersion system (EDS) KEVEX in the Geological Survey of the Slovak Republic, Bratislava.

The results of mineralogical research

Jamesonite, sphalerite, pyrite, arsenopyrite, quartz, carbonates, boulangerite are the most abundant in the Partizánska dolina Valley. Berthierite, bournonite, galena, gold and tetrahedrite are less abundant. Pyrrhotite, native antimony, stibnite and chalcopyrite were found only sporadically. In the Trausementz dolina Valley, only berthierite and gold were identified.

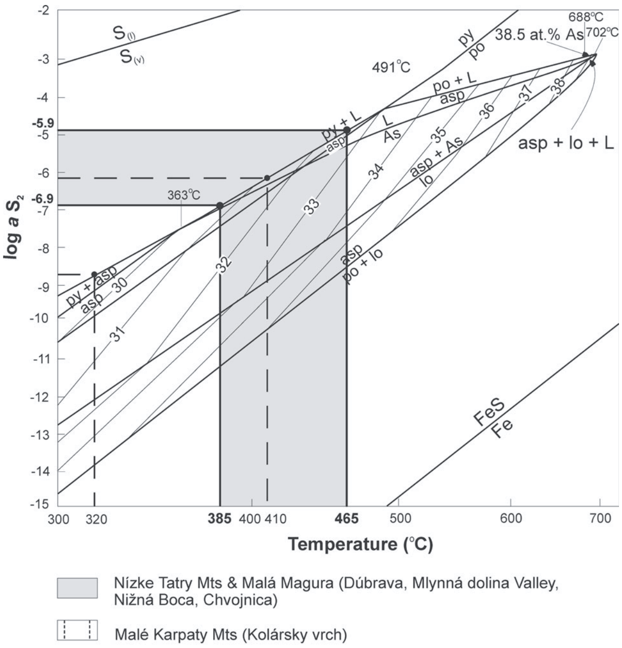

Fig. 2. Log aS versus crystallization temperature (°C) of arsenopyrite as determined according to As content (in at. %) in arsenopyrite (Kretschmar & Scott 1976). *Symbols:* **asp** — arsenopyrite, **py** — pyrite, **po** — pyrrhotite, **lo** — löllingite.

Primary minerals

Arsenopyrite is abundant; associated with quartz I and pyrite, and in silicified hydrothermal wall-rock alteration zones. Euhedral grains, anhedral aggregates and several mm thick veinlets occur in quartz. Aggregates are often crushed. The relationship between arsenopyrite and Pb-Sb, Fe-Sb sulphosalts was not observed. Arsenopyrite is not Au-bearing (Mikoláš et al. 1993). The arsenopyrite geothermometer (Kretschmar & Scott 1976) was applied to calculate the crystallization temperature from equilibrium arsenopyrite+pyrite association, taking into account all limiting conditions (Fig. 2) (Table 2). The temperature of arsenopyrite precipitation ranges from 385 to 465 °C, and log aS_2 = –5.9 to –6.9 (Fig. 2).

Table 1: Selected WDS analyses of sulphides and sulphosalts from the Partizánska dolina Valley.

wt. %	Stb	Stb	Brt[2]*	Brt	Blg[2]*	Blg[2]*	Blg	Bnt	Bnt	Ant	Jms[4]*	Jms[4]*	Jms	Po
Sb	73.08	73.27	57.22	54.98	24.98	26.10	25.31	20.76	25.69	99.98	35.69	36.13	32.60	0.19
Pb	2.15	0.00	0.00	0.03	55.36	55.90	53.41	43.53	42.43	0.77	40.34	37.81	43.16	0.63
Fe	0.26	0.41	15.00	15.10	0.15	0.27	0.27	0.14	0.34	0.10	3.50	3.42	3.21	65.03
S	23.37	25.56	27.36	29.61	19.68	17.44	19.58	20.03	19.25	0.09	20.94	22.29	21.16	34.69
Cu	0.17	0.00	0.05	0.13	0.00	0.04	0.13	14.22	12.47	0.03	0.08	0.11	0.13	0.14
Ag	0.07	0.03	0.00	-	-	0.07	0.03	0.14	0.00	0.02	0.03	-	0.02	0.04
Bi	0.00	0.11	0.06	0.10	0.16	0.07	0.27	1.90	0.00	0.00	0.15	0.06	0.00	0.12
Σ	99.09	99.39	99.70	99.95	100.33	99.89	98.99	100.72	100.18	101.0	100.73	99.82	100.28	100.84
	atomic %													
Sb	44.55	42.76	29.54	27.40	18.82	20.71	19.17	13.73	17.31	98.92	24.32	23.97	22.40	0.07
Pb	0.77	0.00	0.00	0.01	24.52	26.09	23.76	16.92	16.81	0.45	16.21	14.74	17.43	0.13
Fe	0.34	0.52	16.92	16.41	0.24	0.48	0.44	0.20	0.50	0.21	5.19	4.94	4.80	51.66
S	54.10	56.65	53.46	56.03	56.32	52.57	56.30	50.29	49.27	0.33	54.09	56.14	55.19	48.00
Cu	0.19	0.00	0.05	0.12	0.00	0.06	0.19	18.03	16.10	0.06	0.10	0.14	0.17	0.10
Ag	0.05	0.02	0.00	-	-	0.06	0.02	0.11	0.00	0.03	0.02	-	0.02	0.02
Bi	0.00	0.04	0.02	0.03	0.07	0.03	0.12	0.73	0.00	0.00	0.06	0.02	0.00	0.02

Stb – stibnite, Brt — berthierite, Blg — boulangerite, Bnt — bournonite, Ant — antimony, Jms — jamesonite, Po — pyrrhotite; [2]* — average of 2 analyses, [4]* – average of 4 analyses

Table 2: Selected WDS analyses of arsenopyrite from the Partizánska dolina Valley.

	weight %								atomic %						
	Fe	**As**	**S**	**Sb**	**Ni**	**Co**	**Au**	**Total**	**Fe**	**As**	**S**	**Sb**	**Ni**	**Co**	**Au**
1	34.24	43.34	21.61	0.63	0.03	0.00	0.00	99.87	32.76	30.93	36.01	0.28	0.03	0.00	0.00
2	33.96	42.56	22.02	0.61	0.03	0.00	0.00	99.17	32.54	30.40	36.76	0.27	0.03	0.00	0.00
3	34.33	43.21	22.30	0.66	0.02	0.03	0.07	100.61	32.47	30.46	36.73	0.28	0.02	0.03	0.02
4	34.62	44.02	21.87	0.68	0.02	0.03	0.07	101.32	32.68	30.98	35.97	0.29	0.02	0.03	0.02
5	33.10	45.63	21.57	0.73	0.01	0.02	0.01	101.07	31.51	32.38	35.76	0.32	0.00	0.02	0.00
6	32.83	44.80	22.01	0.71	0.01	0.02	0.01	100.38	31.29	31.83	36.54	0.31	0.00	0.02	0.00
7	34.21	44.10	22.07	0.82	0.00	0.02	0.00	101.22	32.30	31.03	36.29	0.36	0.00	0.02	0.00
8	33.93	43.27	22.49	0.80	0.00	0.02	0.00	100.50	32.09	30.51	37.04	0.35	0.00	0.02	0.00
9	33.31	45.45	21.52	0.22	0.00	0.01	0.00	100.51	31.79	32.33	35.77	0.10	0.00	0.01	0.00
10	33.04	44.61	21.95	0.21	0.00	0.01	0.00	99.83	31.58	31.78	36.54	0.09	0.00	0.01	0.00
11	33.74	44.18	22.92	0.23	0.00	0.01	0.01	101.09	31.62	30.86	37.41	0.10	0.00	0.00	0.00
12	34.02	45.03	22.49	0.24	0.00	0.01	0.00	101.80	31.83	31.40	36.66	0.10	0.00	0.00	0.00
13	33.77	43.31	22.28	0.30	0.00	0.08	0.00	99.74	32.13	30.72	36.94	0.13	0.00	0.08	0.00
14	33.49	45.64	21.24	0.05	0.00	0.04	0.00	100.46	32.03	32.53	35.37	0.02	0.00	0.04	0.00
15	33.22	44.80	21.67	0.05	0.00	0.04	0.00	99.79	31.82	31.98	36.14	0.02	0.00	0.04	0.00

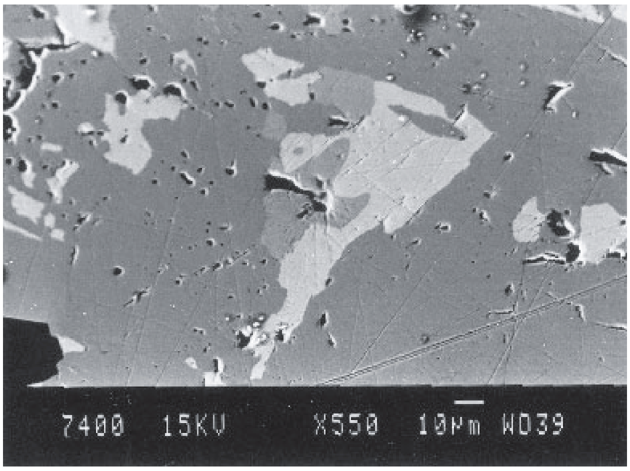

Fig. 3. Berthierite (**dark-grey**) associated with jamesonite (**white**) and stibnite (**light-grey**) inclusion within the jamesonite grain. Back-scattered electrons (SEM-BEI).

Berthierite forms needle-shaped and stalk-like crystals up to 0.2 cm in size or anhedral aggregates in quartz and carbonates. Berthierite is one of the youngest minerals associated with stibnite, jamesonite (Fig. 3) and boulangerite. It replaces quartz of the arsenopyrite stage. Identification of berthierite was confirmed by WDS analysis (Table 1).

Boulangerite is commonly associated with galena, bournonite and jamesonite in quartz and carbonate, forming needle-shaped crystals and anhedral grains up to 0.1 cm in size. Two different forms of boulangerite can be distinguished: 1) needle-shaped crystals and grains (max. 100 μm) enclosed in galena and 2) anhedral and needle-shaped grains associated with jamesonite (Fig. 4) and bournonite (Fig. 5) in cleavage planes and cavities of ankerite. Boulangerite replaces carbonates, bournonite and galena. WDS analyses of boulangerite are given in Table 1, (Fig. 6).

Bournonite occurs with tetrahedrite, chalcopyrite, galena and boulangerite (Fig. 5). It is one of the oldest sulphosalts, forming anhedral grains up to 5 mm in size. It is replaced by galena and boulangerite, and replaces tetrahedrite, chalcopy-

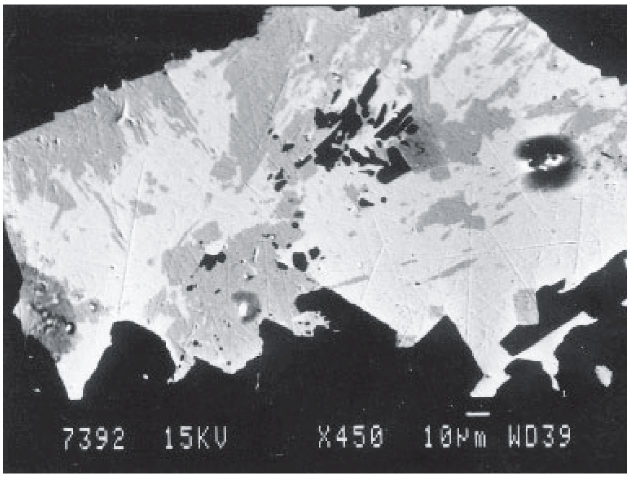

Fig. 4. Boulangerite (**white**) associated with jamesonite (**grey**); (SEM-BEI).

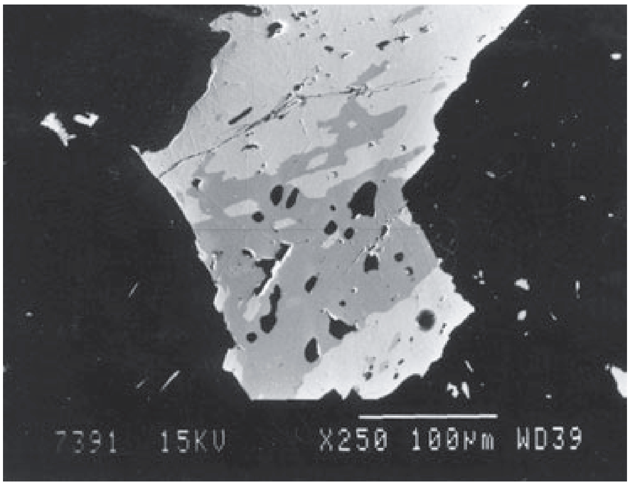

Fig. 5. Boulangerite (**white**) associated with bournonite (**grey**); (SEM-BEI).

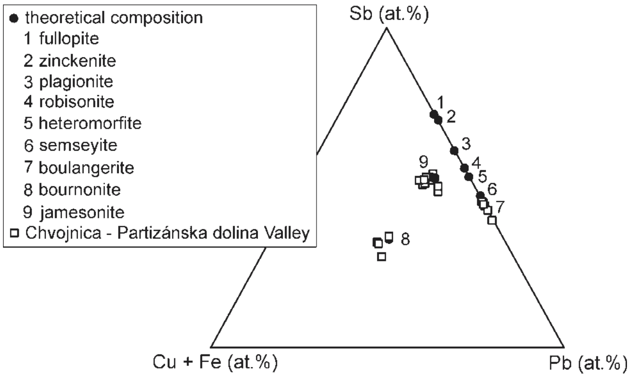

Fig. 6. Ternary plot of electron probe microanalyses of Pb-Sb-(Cu) sulphosalts from Chvojnica.

rite and sphalerite I. WDS analyses of bournonite are given in Table 1 and depicted in Fig. 6.

Galena forms irregular aggregates and grains as big as 5 mm in quartz and in younger Fe-bearing carbonate. It usually fills cavities and fissures in quartz belonging to the older arsenopyrite stage. It is most commonly associated with sphalerite I, tetrahedrite, bournonite and chalcopyrite.

Gold was observed in two generations at the Partizánska dolina Valley locality: 1) anhedral grains in the arsenopyrite stage quartz, up to 10 μm in size. Gold is younger than rutile. Its relationship with other ore minerals was not observed. This type of gold is characterized by higher purity (14.27 wt. % Ag in average). We presume this is the 1st generation gold (Fig. 7). 2) anhedral grains (inclusions) up to 10 μm enclosed in sphalerite belonging to the 2nd mineral stage. The relationship of gold with sphalerite is unclear. The average silver content is 23.12 wt. %. We propose that it is the younger gold (2nd generation) (Fig. 7).

Colluvial gold from exploratory pits in the Trausementz dolina Valley occurs in the form of grains overgrown with quartz. The size of gold particles is up to 1.5 mm.

Some gold grains exhibit a gold-rich rim (Fig. 8) with characteristic spongy structure. The thickness of rims ranges from 10 to 20 μm; silver contents does not exceed 2 wt. %. High purity gold veinlets penetrate the core of gold grains, whose composition ranges from 10.31 to 28.37 wt. % Ag (Table 3). An inclusion rich in Ag was observed (up to 42 wt. % Ag) (Fig. 8). This gold could be a result of a late mobilization process. In the quartz-gold overgrowth thin gold veinlets (up to 1 μm) were observed in quartz interstices. Sporadically, gold is enclosed in grains of arsenopyrite. In total, 27 WDS analyses of gold were carried out (Table 3).

Chalcopyrite forms anhedral grains in two different associations and generations:

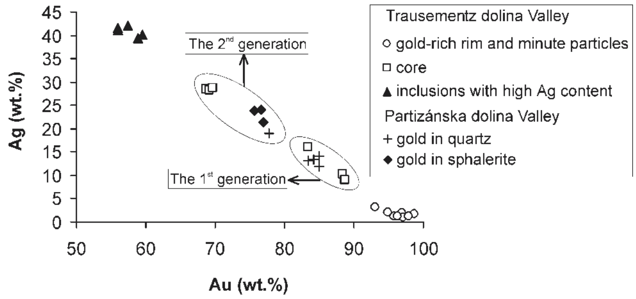

Fig. 7. Au/Ag plot in different types of gold from the vicinity of the Chvojnica village.

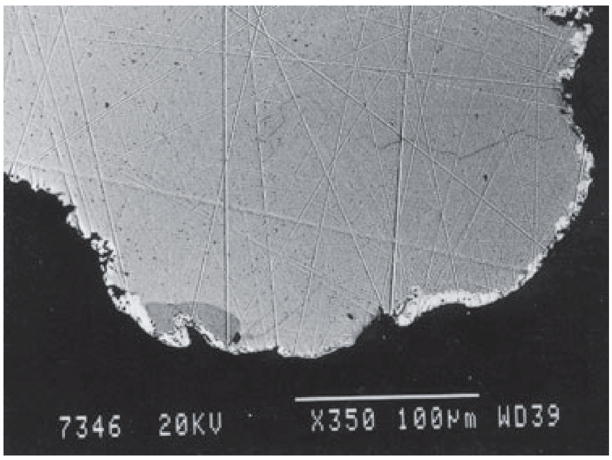

Fig. 8. Gold-rich ream (**white**) on a gold grain (**grey**). The phase with high Ag content (**dark-grey**) is in the down-left corner; (SEM-BEI).

Table 3: Selected WDS analyses of gold from the Partizánska and Trausementz dolina Valley.

		1	2	3	4	5	6	7	8	9	10	11	12
wt. %	Au	98.69	96.90	69.13	83.41	88.45	95.33	58.92	57.39	85.02	84.25	76.96	75.68
	Ag	1.69	1.99	28.32	15.97	10.31	2.06	39.29	41.99	14.04	13.40	21.50	23.82
	Hg	0.58	1.09	0.73	0.78	0.83	1.21	0.76	0.77	0.64	0.94	0.63	0.65
	Bi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Sb	0.06	0.08	0.01	0.36	0.04	0.16	0.76	0.67	0.37	0.17	0.01	0.01
	Cu	0.00	0.05	0.17	0.00	0.00	0.03	0.10	0.13	0.11	0.28	0.00	0.00
	Σ	101.02	100.11	98.36	100.52	99.63	98.79	99.83	100.95	100.18	99.04	99.10	100.16
at. %	Au	96.33	95.10	56.62	73.22	81.78	94.72	44.40	42.10	75.76	76.06	65.86	63.16
	Ag	3.01	3.57	42.34	25.60	17.41	3.74	54.06	56.25	22.85	22.08	33.59	39.29
	Hg	0.56	1.05	0.59	0.67	0.75	1.18	0.56	0.56	0.56	0.83	0.53	0.54
	Bi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Sb	0.10	0.13	0.01	0.51	0.06	0.26	0.75	0.80	0.53	0.24	0.02	0.02
	Cu	0.00	0.14	0.44	0.00	0.00	0.09	0.23	0.30	0.29	0.78	0.00	0.00

Colluvial primary gold from the Trausementz dolina Valley, analyses number: 1,2 — gold-rich rim, 3,4,5,6 — core, 7,8 — admixtures and inclusions; Primary gold from Partizánska Valley, analyses number: 9,10 — generation I (gold with quartz), 11,12 — generation II (gold with sphalerite)

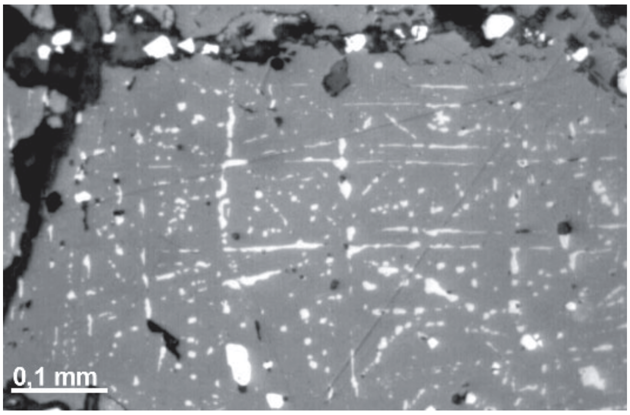

Fig. 9. Chalcopyrite inclusions in sphalerite (texture "chalcopyrite disease"). Reflected light.

1) as inclusions in sphalerite (up to 100 μm) forming blebs, dots, minute particles and vermicular structures in intimate chalcopyrite-sphalerite intergrowth (Fig. 9).

2) in association with tetrahedrite and bournonite. Chalcopyrite replaces tetrahedrite and bournonite.

Jamesonite is usually medium to fine-grained, sometimes forming needle-shaped crystals in quartz and carbonates up to several cm in size. Needle-shaped crystals of jamesonite cement carbonates and quartz of the 3rd mineralization stage. Furthermore, jamesonite fills fissures in carbonates. Its anhedral grains are often overgrown with other Pb-Sb sulphosalts and berthierite. Quartz relicts belonging to the arsenopyrite mineralization stage are common. Jamesonite is replacing bournonite and boulangerite (Fig. 4) and is replaced by berthierite (Fig. 3). Moreover, jamesonite is associated with pyrrhotite, native antimony and sphalerite II, replacing these minerals. WDS analyses of jamesonite are in Table 1 and Fig. 6.

Native antimony occurs together with jamesonite, pyrrhotite and sphalerite II. Fine isometric grains of antimony are up to 0.01 mm in size, forming anhedral aggregates up to 1×1.5 cm in size. It is replaced by pyrrhotite and jamesonite. It is chemically pure without any distinct impurities (Table 1).

Pyrite is very abundant in silicified hydrothermal alteration wall-rock zones and also in hydrothermal veins. It occurs in several generations. Pyrite I forms massive irregular aggregates and crystals of euhedral shape, forming up to 2 cm thick veins in quartz of the arsenopyrite stage. Pyrite I is mostly associated with arsenopyrite and is often cataclastically deformed. Rarely, it is replaced by sphalerite and Fe-oxyhydroxides. Pyrite II forms crystals up to 0.05 mm in size enclosed in galena and bournonite. It impregnates the oldest quartz. Pyrite III occurs with ankerite and it is enclosed in Pb-Sb sulphosalts.

Pyrrhotite is found in paragenetic association with jamesonite and native antimony. It forms irregular aggregates evolving into veinlets several mm thick. Lamellar crystals up to 0.05 mm in size are commonly present. They cement aggregates of native antimony and are replaced by jamesonite. Identification of pyrrhotite was confirmed by WDS analysis (Table 1).

Sphalerite forms aggregates composed of anhedral grains mainly located in quartz (up to 2 cm), more rarely in carbonates. It has a black or brown-black colour and occurs in two generations: Sphalerite I (the most frequent) contains numerous chalcopyrite inclusions ("chalcopyrite disease") (Fig. 9). It is enriched in Fe (3.41 wt. %), whereas sphalerite without "chalcopyrite disease" contains only up to 1.95 wt. % Fe (Table 4) and (Fig. 10). Sphalerite I also occurs associated with galena and tetrahedrite and is intensively replaced from rims by the latter. Sphalerite I encloses gold grains up to 10 μm in size. The gold grains are probably younger than sphalerite I.

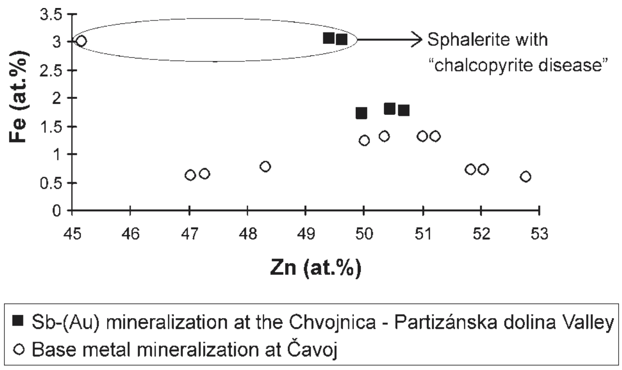

Fig. 10. The relationship between Fe and Zn content in sphalerite with and without "chalcopyrite disease".

Sphalerite II occurs together with stibnite, jamesonite, native antimony and pyrrhotite.

Stibnite occurs as anhedral grains in quartz or in jamesonite (up to 0.04 mm), associated with berthierite (Fig. 3). Stibnite is replaced by berthierite. Identification of stibnite was confirmed by WDS analyses (Table 1).

Tetrahedrite occurs with sphalerite I, bournonite, chalcopyrite and galena. It is older than sulphosalts, replacing sphalerite and quartz belonging to the arsenopyrite stage. It rarely encloses and replaces pyrite I.

Table 4: Selected WDS analyses of sphalerite from the Partizánska dolina Valley.

		1	2	3	4*	5*
wt. %	Zn	66.47	65.33	67.17	65.28	64.18
	Cu	0.03	0.03	0.10	0.52	0.52
	Fe	1.99	1.98	1.97	3.41	3.38
	Mn	0.09	0.09	0.00	0.05	0.05
	Hg	0.10	0.10	0.06	0.00	0.00
	S	30.37	30.13	31.68	30.03	29.80
	Cd	0.43	0.41	0.34	0.69	0.67
	Σ	99.48	98.07	101.32	99.98	98.60
at. %	Zn	50.69	50.46	49.98	49.64	49.42
	Cu	0.02	0.02	0.08	0.41	0.41
	Fe	1.78	1.79	1.72	3.03	3.05
	Mn	0.08	0.09	0.00	0.04	0.04
	Hg	0.03	0.02	0.01	0.00	0.00
	S	47.21	47.44	48.06	46.56	46.78
	Cd	0.19	0.18	0.15	0.31	0.30

*The analyses 4 and 5 are from sphalerite with "chalcopyrite disease"

Gangue minerals

Carbonates are abundant in Sb-Au veins. The oldest is *siderite* occurring with quartz, arsenopyrite, pyrite. Its grains are inhomogeneous in chemical composition and its position within the succession scheme is uncertain. *Calcite* (Fig. 12) is enclosed by *dolomite* and *ankerite*. The chemical composition of calcite is homogeneous but its position in the succession of crystallization remains unclear. Dolomite is often brecciated. Fissures in dolomite are filled by ankerite (Fig. 12), showing a compositional zoning with some zones corresponding to Fe-dolomite. Dolomite and ankerite occur together with quartz II and III. Furthermore, dolomite is associated with sphalerite, chalcopyrite, tetrahedrite, bournonite and galena. Ankerite occurs with pyrite III, stibnite, native antimony, pyrrhotite, jamesonite and berthierite. Sulphosalts often fill cavities and fissures in ankerite. Both ankerite and dolomite are affected by "overprinting" tectonic processes. The chemical composition of carbonates is given in Table 5 and in Fig. 11.

Quartz appears in 3 generations:

Quartz I occurs in association with arsenopyrite, pyrite I and gold. Quartz I is replaced by carbonates, quartz II with younger mineralization (quartz III, ankerite etc.) and is fine-grained. It sporadically occurs in quartz I gold grains. Quartz II is coarse-grained to massive. It occurs associated with dolomite, sphalerite, chalcopyrite, tetrahedrite, bournonite, galena and intensively replaces quartz I. Quartz III occurs with ankerite, stibnite, native antimony, pyrrhotite, jamesonite and berthierite. Quartz II (the sphalerite-galena-tetrahedrite stage of Sb-Au mineralization) and quartz III (the stibnite-sphalerite-sulphosalts stage of Sb-Au mineralization) are devoid of fluid inclusions.

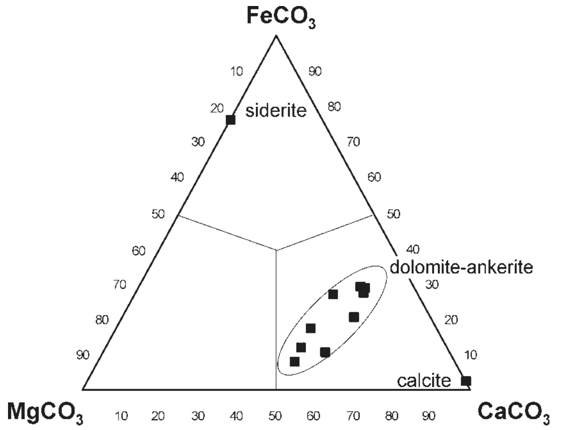

Fig. 11. Ternary diagram of carbonates from the vicinity of the Chvojnica village.

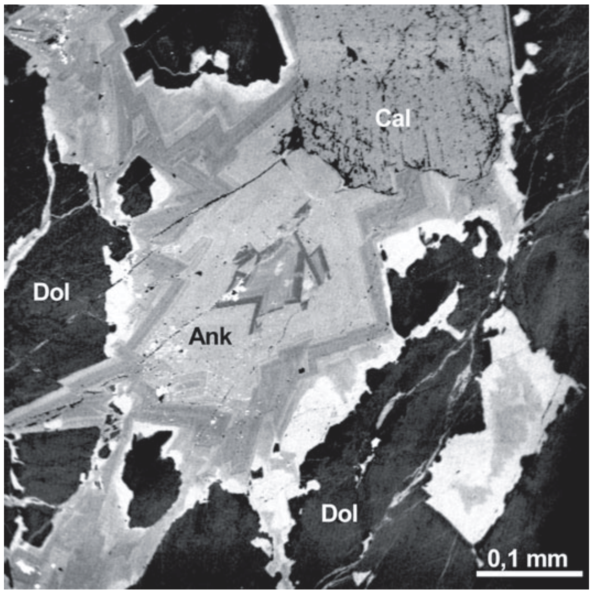

Fig. 12. Grain of calcite (**Cal**) enclosed in ankerite (**Ank**) displaying compositional zoning. Younger ankerite veins replace older dolomite (**Dol**) veins.

Development of mineralization

Paragenetic associations were distinguished by mineralogical study and are also supported by analogy with previously investigated Variscan Sb-Au deposits in the Western Carpathians (Chovan 1990; Chovan et al. (Eds.) 1994). In the Malá Magura mountain group, at localities with Sb-Au mineralization in the vicinity of the Chvojnica village the following mineralization stages were distinguished:

I. quartz I–**pyrite,** arsenopyrite–**gold I**

II. quartz II–dolomite–**sphalerite I,** (chalcopyrite I), gold II–tetrahedrite–bournonite–chalcopyrite II, **galena, boulangerite**, pyrite II

III. quartz III–ankerite–pyrite III–stibnite–sphalerite II, pyrrhotite, antimony, **jamesonite, berthierite**

Discussion

The Sb-Au type of mineralization, reported in the Tatric by Chovan et al. (1996) was found in the vicinity of the

Table 5: Selected EDS analyses of carbonates from the Partizánska dolina Valley.

	1	2	3	4	5	6	7	8	9	10	11
MgO	4.78	5.22	8.30	4.87	7.59	13.06	13.13	17.40	15.55	0.00	8.40
CaO	30.60	30.86	27.62	28.98	31.71	32.40	28.54	29.86	29.37	53.85	0.16
MnO	2.86	2.92	2.15	4.74	3.34	2.21	0.98	0.50	0.70	1.04	3.10
FeO	19.05	18.32	18.48	18.77	14.36	7.66	12.35	5.81	8.64	1.44	48.18
Total	57.29	57.32	56.55	57.36	57.00	55.33	55.00	53.57	54.26	56.33	59.84
$MgCO_3$	10.00	10.92	17.36	10.19	15.88	27.32	27.47	36.40	32.53	0.00	17.57
$CaCO_3$	54.61	55.08	49.30	51.72	56.60	57.83	50.74	53.29	52.42	96.11	0.29
$MnCO_3$	4.63	4.73	3.48	7.68	5.41	3.58	1.59	0.81	1.13	1.69	5.02
$FeCO_3$	30.72	29.54	29.80	30.27	23.16	12.35	19.92	9.37	13.93	2.32	77.69
Total	99.97	100.28	99.94	99.86	101.04	101.08	99.91	99.87	100.02	100.12	100.57

Analyses number: 1,2,3,4,5,6 — ankerite, 7,8,9 — dolomite, 10 — calcite, 11 — siderite

Chvojnica village, in the Partizánska and Trausementz dolina Valleys.

The mineralization in the vicinity of Chvojnica, including occurrences in the Partizánska dolina Valley was identified by Zelný & Uher (1988) as a low- to moderate-temperature polymetallic association (Cu, As, Pb, Zn, Sb) with crystallization of sulphosalts at the end of the hydrothermal process.

The oldest paragenesis of Sb-Au mineralization is quartz–pyrite–arsenopyrite with frequent occurrence of native gold. The temperature of arsenopyrite–pyrite association (Chvojnica) ranges from 385 to 465 °C according to the arsenopyrite geothermometer of Kretschmar & Scott (1976). This temperature corresponds to that calculated for other localities in the Tatric Superunit of the Western Carpathians for equilibrium assemblage arsenopyrite+pyrite (Fig. 2): the Dúbrava deposit — 395–430 °C (Sachan & Chovan 1991); Mlynná dolina Valley — 393 °C (Majzlan & Chovan 1997); the Nižná Boca deposit — 445 °C (Smirnov 2000) and the Pezinok-Kolársky vrch deposit in the Malé Karpaty Mts — 320–410 °C (Andráš et al. 1999).

The presence of primary gold is described for the first time in the Partizánska dolina and Trausementz dolina Valleys. The gold occurs in two generations: I) 1st generation gold — has higher Ag content in comparison with the 1st generation gold from Magurka (Bakos & Chovan 1999) and II) 2nd generation gold with high Ag content, which occurs together with Sb, Pb, Cu sulphides; this association is also known from other Sb-Au mineralization localities in the Ďumbierske Tatry Mts, such as Magurka and Nižná Boca (Chovan et al. 1995; Bakos & Chovan 1999; Smirnov 2000).

Colluvial gold from the Trausementz dolina Valley exhibits three different chemical compositions: the core of gold grains is formed by gold of the 1st and the 2nd generation. Gold with high Ag content (Fig. 8) forms admixtures and inclusions within the core. The 3rd composition corresponds to the gold-rich rim, which can be produced by a combination of self-electrorefining and cementation processes in streams, or stream sediments where the Ag-dissolution process and subsequent Ag-complexation can take place (Groen et al. 1990).

The presence of Au in the Partizánska dolina Valley and Chvojnica occurrences, was suggested by Mikoláš et al. (1993). It was detected by quantitative spectral analyses of quartz veins with pyrite and arsenopyrite. The Au content ranges from 0.1 g/t to 13.10 g/t. Mikoláš et al. (1993) suggest that gold occurs in pyrite, mainly because analyses of arsenopyrite were not shown to be Au-bearing and free native gold grains were not observed.

The occurrence of primary gold at the Partizánska dolina and Trausementz dolina Valleys was expected because a) the primary Sb-Au mineralization is located in the drainage area of rivers flowing through these valleys, and b) the existence of an important alluvial gold deposit located between the villages of Chvojnica and Malinová.

Several opinions exist regarding the formation of chalcopyrite inclusions in sphalerite, known as the "chalcopyrite disease" (Barton 1978 in Barton & Bethke 1987). Until the last two decades, all these textures were thought to be formed by exsolution from solid solution. Barton & Bethke (1987) interpreted the formation of chalcopyrite blebs by a replacement processes. These authors supported their argument by the fact, that chalcopyrite inclusions mostly result from replacement of a Fe-rich sphalerite. Chalcopyrite inclusions were formed by a reaction of iron from the sphalerite with copper ions transported in hydrothermal solutions. The studies of Bortnikov et al. (1991) showed that chalcopyrite inclusions were found in sphalerite with different iron content: both Fe-poor varieties (0.5 to 2 wt. %) and Fe-rich (8 to 14 wt. %). They suggested that chalcopyrite inclusions are produced by a replacement process resulting from the interaction of sphalerite with fluids, which transport both Cu and Fe. A co-precipitation of sphalerite and chalcopyrite was suggested as an alternative mechanism.

Sphalerite from the Partizánska dolina Valley (Chvojnica) contains 3.41 wt. % Fe. It is questionable in this case, if chalcopyrite inclusions in sphalerite (Fig. 9) resulted from co-precipitation or replacement processes. Chalcopyrite inclusions in sphalerite occur at moderate temperatures (between 200 and 400 °C). The metamorphism homogenizes the sphalerite banding, re-crystallizes both chalcopyrite and its host sphalerite and coarsens the textures — thereby masking its heritage (Barton & Bethke 1987). This investigation supports Variscan age for the Sb mineralization, knowing that the Variscan metamorphosis reached the amphibolite grade. The Alpine metamorphosis of the crystalline basement was not recognized in these areas (Dyda 1994).

The prevailing sulphosalts in the investigated mineralization are jamesonite and boulangerite. Jamesonite occurs in the Sb-assemblage, representing sulphosalts with low Pb/Sb ratio and Fe content. In many occurrences, zinckenite is abundant and the presence of jamesonite is restricted to local environments with increased Fe content (e.g., Dúbrava) (Chovan 1990). A high Pb/Sb ratio and occurrence of boulangerite is typical for the association with galena. It is characteristic for the Kľačianka and Magurka (Chovan et al. 1995) or the Jasenie-Soviansko deposit (Luptáková 1999). Bournonite is typical for the tetrahedrite-bearing mineral assemblage of Sb-Au mineralization in the Nízke Tatry Mts and occurs at most localities: Mlynná dolina Valley (Majzlan & Chovan 1997), Veľké Oružné, Kľačianka, Krámec (Bakos et al. 2000), Dúbrava (Chovan et al. 1998), Magurka (Chovan et al. 1995), Rišianka, Malé Železné (Majzlan et al. 1998) a.o. Berthierite is a major representative of Fe-Sb sulphosalts. It occurs in association with stibnite and gudmundite at Hviezda in the Mlynná dolina Valley in the Nízke Tatry Mts (Majzlan & Chovan 1997), and is abundant associated with stibnite, gudmundite, native antimony and kermesite in Sb mineralizations of the Malé Karpaty Mts (Chovan et al. 1992).

Studied assemblage of native antimony, pyrrhotite, berthierite and stibnite can be compared with the experimental data of Williams-Jones & Normand (1997). The crystallization of native antimony is limited by aS_2 and fO_2. The stability field of native antimony is defined by low fO_2 and aS_2. Therefore, in nature, stibnite occurs more frequently as a result of a wider stability field.

The common association of pyrrhotite and native antimony observed in studied deposits indicates low aS_2 and fO_2 values. Resulting from increase in aS_2 during crystallization, berthierite is also present, compared to gudmundite-pyrrhotite association in the Malé Karpaty Mts. With increasing fO_2 senarmontite appears and with increasing aS_2, kermesite and stibnite associated with pyrite are stable.

At higher aS_2 and fO_2, the characteristic paragenesis is stibnite–senarmontite and (pyrite) observed at the Dúbrava deposit. By increasing aS_2 and fO_2, an association with native antimony and pyrrhotite appears, occasionally with gudmundite (Malé Karpaty Mts a.o.). Seinäjokite and magnetite which could have formed, were not discovered in the Western Carpathians.

Dolomite is a characteristic gangue mineral of the sphalerite–galena–(Cu)-Pb-Sb sulphosalts assemblage with ankerite being a common carbonate of stibnite-bearing assemblage, in which also Fe-bearing sulphides are present.

As in other localities with Sb-Au mineralization in the Tatric Superunit of the Western Carpathians, an older, higher temperature mineral assemblage was found at Chvojnica. It consists of quartz, arsenopyrite, pyrite and gold. The temperature of arsenopyrite crystallization (385–465 °C) corresponds to the temperatures determined for this mineral assemblage in other localities within the Tatric Superunit.

Younger sulphide mineralization developed at lower temperatures (about 200 °C). Two stages can be distinguished:

(1) *sphalerite-galena-tetrahedrite,*

(2) *stibnite-sphalerite-sulphosalts.*

The common mineralization stages in the Sb-Au mineralization of the Tatric Superunit are: stibnite Sb-Pb(Zn, Fe) and tetrahedrite-bournonite Cu-Sb(Pb, Zn, Fe). Independent of local conditions, the stibnite mineralization stage can comprise abundant Fe-bearing minerals: berthierite, gudmundite, pyrrhotite (Malé Karpaty Mts) or with Pb content zinckenite (Dúbrava). Galena and sphalerite are abundant in the tetrahedrite–bournonite assemblage (Chvojnica, Jasenie-Soviansko?) or sulphosalts Pb-Sb-Bi (tintinaite) at the Dúbrava deposit.

The succession relations of sulphide assemblages in various localities are different. At the Dúbrava deposit (Chovan 1990) the stibnite mineralization stage is considered older than the tetrahedrite, and the stibnite assemblage is younger than the sphalerite–zinckenite. However, at: Kľačianka, Krámec, Veľké Oružné (Bakos et al. 2000) and Nižná Boca (Smirnov 2000) the stibnite-bearing assemblage is older than the sulphosalts–zinckenite assemblage. At the Pezinok deposit, the stibnite assemblage with native antimony is younger than the sphalerite–sulphosalts assemblage (Andráš 1983 in Chovan et al. 1992).

The Sb-Au mineralization hosted in crystalline basement of the Malá Magura mountain group was generated during the Variscan tectonometamorphic events, characterized by amphibolite metamorphic grade. The Alpine remodelling of the crystalline basement is relatively poor (Maheľ 1985). Ore veins did not interact with Mesozoic sedimentary cover and the Krížna Nappe. The presence of chalcopyrite inclusions in sphalerite indicates that the temperature of Alpine overprint did not exceed ~200 °C; otherwise these two usual phases would form a homogeneous solid solution. The last known tectonometamorphic event recognized in the crystalline basement of the Malá Magura mountain group reached about 200 °C, being of the Variscan age, which attained the amphibolite metamorphic grade (620–640 °C/4.5–5.5 kbar, XH_2O = 0.8–1.0 (Dyda 1994).

Summary

Sb-Au mineralization was discovered in the Malá Magura mountain group, at the Chvojnica — Partizánska and Trausementz dolina Valley localities (Fig. 1B). This discovery increased the number of known Sb-Au mineralization occurrences in the Tatric Superunit (Western Carpathians). Furthermore, the origin of geochemical anomalies and the existence of Au placer deposits between the Chvojnica and Malinová villages, were explained. The occurrence of primary gold is reported for the first time in the Chvojnica — Partizánska dolina Valley.

The oldest high-temperature mineral paragenesis is represented by quartz–pyrite–arsenopyrite with frequent occurrence of gold. The younger sulphide mineralization was formed at considerably lower temperatures. Two stages of mineralization were distinguished: sphalerite-galena-tetrahedrite and stibnite-sphalerite-sulphosalts, consistent with other Sb-Au occurrences in the Tatric Superunit (Western Carpathians).

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