Gold incorporation into sulphide minerals from the Tatric Unit, the Western Carpathians, with respect to their chemical composition

Väzba zlata v sulfidikých mineráloch Tatrika (Západné Karpaty) v závislosti na ich chemickom zložení

(21 figs, 6 tabs)

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Numerous Sb-Au mineralization occurrences and deposits containing gold-bearing sulphides are described from an area of the Tatric Unit in Western Carpathians e.g.: Pezinok, Dúbrava, Jasenie, Nižná Boca, Vyšná Boca etc. It was shown, that arsenopyrite is the main sulphide mineral incorporating invisible gold in its crystal structure. Concentrations of invisible gold in pyrite are not as high as in arsenopyrite. Only if arsenic is present in pyrite in amounts greater than 0.2 wt %, there is significant incorporation of Au in its crystal structure. Gold content in these sulphides ranges from zero up to several hundred ppm. The fine-grained types contain Au concentrations higher by as much as an order of magnitude. This work has demonstrated that Au co-precipitated together with Fe, As and S during the arsenopyrite and pyrite crystallization and was incorporated in sulphide mineral crystals both as native gold and as chemically bound gold. Although As and Au contents in arsenian pyrites and arsenopyrites vary from sample to sample, there is a positive correlation between Au and As. The covariance in As and Au indicates that they were transported by the same solutions and that the same geochemical processes led to their removal from solution. Au is predominantly concentrated within As-rich zones of gold-bearing sulphides.

Key words: gold-bearing sulphides; arsenopyrite; pyrite; Mössbauer spectroscopy; Western Carpathians

Introduction

Wagner et al. (1989a) demonstrated that gold in pyrite, arsenopyrite or in tetrahedrite-tennantite may occur either in the metallic form or structurally bound in the lattice. Korobushkin (1970) assumed that submicroscopic gold is situated in lattice deformation sites, while other autors (e.g. Wagner et al. 1989 a, b, Cathelineau et al. 1989) published opinion that gold is incorporated in sulphides in the "non-metallic" anion form. Wagner et al. (1989 b), Cabri et al. (2000), Schoonen et al. (2002), Vaughan – Kyin (2004), Reich et al. (2005) and others have shown that the refractory character of the ore is caused by the chemical bonding of gold rather than by physical inclusion of small, discrete metallic particles in the matrix of sulphides.

The incorporation of Au into sulphides is dependent on a number of factors, such as the stoichiometry, temperature and pressure changes, pH of ore-forming fluids in which Au was transported in the form of sulphide and chloride complexes or Au-colloids (Roedder 1984, Arehart et al. 1993). Important for the processes of precipitation is the charge and stability of the aqueous complexes, the surface charge on the sulphide substrate, and the availability of suitable bonding sites in the sulphides (Vlassopoulos – Wood 1990).

Arsenopyrite is characterized by a significant nonstoichiometry (Kostov 1981). Boyle (1979) assumed that similarity in ionic radii in the covalent bonding, which are in aurostibite AuSb$_2$ 1.40 Å for Au and in arsenopyrite 1.39 Å for As, enable Au substitution for As in the structure. According to Arehart et al. (1993), the covariance of Au and As in individual crystals suggests that Au enters the structure as a coupled substitution with As. Trend to a positive As:Au correlation in sulphide minerals containing invisible gold was described, e.g., by Fleet et al. (1993), Andráš (1995), Cook – Chryssoulis (1990) and Ashley et al. (2000).

Johan et al. (1989) used electron microprobe data from gold-rich arsenopyrite and stoichiometric calculations to propose that Au is substituting for the excess As, which actually is present in Fe sites: 2As(Fe) → (Au, Sb) + (Fe), where As(Fe) = As at the Fe sites.

Wagner et al. (1989a, b) published an opposite opinion. The Mössbauer spectroscopy study shows that Sb occurs in arsenopyrite in the form of Sb^{3+}. Sb^{5+} has practically a null isomer shift with respect to the source of Ca^{121}SnO$_3$, in which the ^{121}Sn decays to ^{121}Sb in the pentavalent state. The small component at null velocity in the gudmundite spectrum is Sb^{5+}, but this data cannot identify the mineral present.

According to Cook – Chryssoulis (1990) in arsenopyrite, which can be expressed as [Fe]$^{3+}$ [AsS]$^{3-}$, it is easier for trivalent Sb^{3+}, Au^{3+} cations to substitute for Fe^{3+} than in pyrite. Schoonen et al. (1992), Fleet et al. (1993), Ashley et al. (2000) show the importance of adsorption-redox reactions on surface of the sulphide growth zones in the gold-bearing sulphides ore-forming process. The Au transport is possible in form of miscellaneous fluids and Au is not incorporated in sulphide structure but deposited in pores, vacancies and on surface of mineral growth-zones. According to this assumption, pyrite and arsenopyrite contain oxidizable S-H and S$_x$-H surface groups (≡SSH), so they can reduce AuOH(H$_2$O)^0 ligands and form Au-S complexes on surface of arsenopyrite and pyrite crystals (Vlassopoulos – Wood 1990).

Andráš et al. (1993), Andráš et al. (1995), Ozdín – Chovan (1999) and others described the presence of "invisible gold" in pyrite and arsenopyrite from several Western Carpathian deposits: Pezinok, Dúbrava, Vyšná Boca, Nižná Boca, Jasenie etc. (Fig. 1).

Study of fluid inclusions in quartz associated with the gold-bearing arsenopyrite enable characterization of the gold-bearing ore-forming fluids. They are essentially CO_2-rich ones and have low salinities: 0.4–15.4 equiv wt. percent NaCl (Table 1). Gold-bearing arsenopyrite from the Tatric Unit crystallized at temperatures of 320 to 450 °C (Sachan – Chovan 1991, Majzlan et al. 2001, Andráš et al. 1999). Isotope composition of oxygen from Pezinok-Kolársky Vrch deposit ($\delta^{18}O_{(SMOW)}$ –10.01 to –16.46) and $\delta^{18}O$ 5.5 to 8.5 $‰_{(SMOW)}$ from Dúbrava deposit represents predominantly meteoric (± metamorphogenous) fluids (Andráš et al. 1999, Chovan et al. 1995, 1999).

These data correspond with those of Boiron et al. (1989) and Cathelineau et al. (1989). from the Massif Central in France and other data from similar gold mineralizations.

The topic of the article is the investigation of gold incorporation into the gold-bearing sulphides from selected deposits of the Tatric Unit. The study is focused, on the one hand, on gold determination and location, and on the other hand, on the estimation of factors controlling the coprecipitation of Au and As within arsenopyrite and pyrite.

Regional geology

The Tatric Unit is an extensive thick-skinned crustal sheet consisting of the pre-Alpine (generally Variscan) crystalline basement and its sedimentary cover. The Tatric sheet is approximately 10 km thick, upward convex tabular body rooted in the lower crust below the southward located Veporic wedge. The Tatric basement has a generally well-preserved Variscan structures without significant Alpine overprint. The basement is mainly composed of crystalline rocks: medium- to high-grade Early Palaeozoic volcano-sedimentary complexes and several suites of Variscan granitoids intruding mostly the high-grade gneiss-migmatitic complexes. The crystalline basement complexes are incorporated into several thick-skinned Variscan nappe structures (Plašienka et al. 1997).

The Tatric Unit comprises the following core mountains: Malé Karpaty Mts., Tríbeč Mts., Považský Inovec Mts., Žiar Mts., Strážovské Vrchy Mts., Malá Fatra Mts., Veľká Fatra Mts., Nízke Tatry Mts. and Tatry Mts. The present study is focused on the Sb-Au mineralization, including former mining areas: Malé Karpaty Mts. and Nízke Tatry Mts.

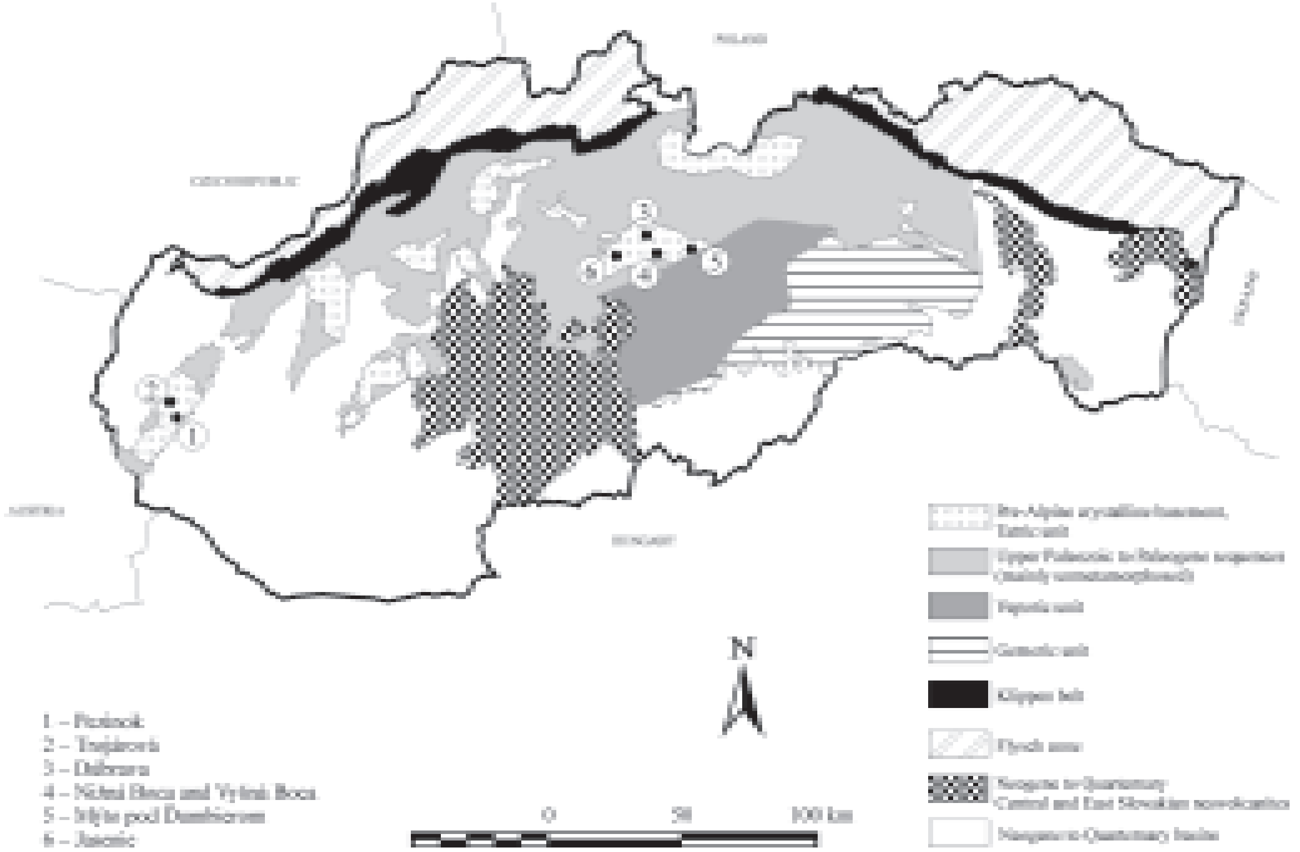


Fig. 1 Localization of investigated gold-bearing sulphides occurrences and deposits in the Tatrikum Unit, Western Carpathians.

Table 1 Characteristics of the ore forming fluids.

Deposit/occurrence	Salinity (wt. % NaCl equiv.)	Chemical composition of fluids	Homogenization temperature of fluids (°C)	Crystallization temperature (°C)
Pezinok*	6 ± 2	CO_2-NaCl-(KCl)-H_2O	180–275	425–450
Dúbrava**	0.4–5.1	CO_2-NaCl-KCl-H_2O ± CH_4 ± N_2	232–349	350–400
Mýto pod Ďumbierom and Mlynná Dolina Valley***	1.2–15.4	CO_2-NaCl-H_2O	281–365	320–380

* Andráš et al. (1998)
** Chovan et al. (1995, 1999)
*** Majzlan et al. (2001)

The Malé Karpaty Mts.

The geological structure of the Malé Karpaty Mts. consists of a pre-Alpine basement, Mesozoic cover and higher nappes (Plašienka et al. 1991). The crystalline complex developed from Silurian – Devonian volcano-sedimentary formations consisting of pelitic-psammitic flyschoid sequences overlain by black-shale-carbonate and uppermost volcano-sedimentary sequences (Planderová – Pahr 1983).

The whole complex was subjected to a low-grade regional metamorphism in the Devonian times (380 ± 20 Ma, Rb-Sr data). It was later subjected to a deeper periplutonic and/or shallower contact metamorphism during intrusions of Variscan granitoids (348 ± 4 Ma, or 320 ± 3 Ma, Rb-Sr and U-Pb data, respectively: Cambel et al. 1990; 355 ± 18 Ma and 345 ± 22 Ma, EMPA monazite dating: Finger et al. 2003).

Several Sb-deposits (Pezinok-Kolársky Vrch and Pernek) and numerous Sb-occurrences (such as Kuchyňa and Trojárová) have been described from the Malé Karpaty Mts.

The Nízke Tatry Mts.

The Nízke Tatry Mts. crystalline complex is built by Variscan granitoids penetrating MP-HP rocks (migmatites, gneisses and amphibolites). The autochthonous Mesozoic cover and the crystalline complex are overlapped by Mesozoic nappes (Chovan et al. 1996). Most of the vein deposits are situated in regionally mylonitized Variscan zones (about 330 Ma old, ^{40}Ar/ ^{39}Ar dating on muscovite: Dallmeyer et al. 1996) developed both in granitoids and metamorphic rocks.

Biotite tonalites to granodiorites (the Ďumbier type) prevail in the eastern part of the granitoid complex (crystallization temperature is 690–730 °C), while muscovite-biotite granodiorites to granites (the Prašivá type) predominate in the west (crystallization temperature was estimated to 670–700 °C). Both granitoid types were dated by the Rb/Sr method at 369 ± 22 Ma (Cambel et al. 1990). The EMPA monazite dating of S type biotite granite from the Nízké Tatry Mts. yielded 362 ± 27 Ma and of I type biotite granodiorite 326 ± 31 Ma (Finger et al. 2003).

Similarly young age for I type granitoid magmatism has been obtained also from the High Tatra Mts. (314 ± 4 Ma, single grain CLC zircon dating of Poller – Todt 2000 In the nearby Velká Fatra Mountains the intense Variscan granitoid magmatism was dated at 315.8 ± 2.7 Ma (I-type tonalites), 304.4 ± 7.5 Ma (S-type Lipová two mica granites) and 305 ± 17 Ma (S-type Kornietov granodiorite) (single grain CLC zircon dating of Poller et al. 2005).

Metavolcanic and metasedimentary rocks were transformed into amphibole gneisses and amphibolites. The metamorphic conditions were estimated by Janák et al. (1993) at 700–750 °C and 1000–1400 MPa. Metavolcanic and metasedimentary rocks with metaantracite to semigraphite of organic origin are according to fossil microflora of Lower to Middle Devonian age (Planderová 1986).

The most common metamorphic rock types in the areas of Sb-mineralization (Ďumbier part of the Nízke Tatry Mts.) are biotite and two-mica gneisses with banded texture, often plastically deformed (Chovan et al. 1996). Biotite gneisses were metamorphosed at 610–690 °C and 400–470 MPa. Regional metamorphism of the calc-silicate rocks produced calc-silicate gneisses ("erlans") (Krist et al. 1992) and skarnoids (Pitoňák – Spišiak 1992).

Several economic Sb-deposits (e.g., Dúbrava, Magurka, Medzibrod and Lom) and numerous Sb-occurrences (Vyšná Boca, Mýto pod Ďumbierom and Mlynná Dolina Valley) were studied.

Mineral deposits

The Pezinok–Kolársky Vrch deposit is situated along a tectonic fault-zone trending NW-SE, about 3500 m long. The mineralized zone is 25–70 m wide at the surface and about 430 m long (Chovan et al. 1992). About 20 000 t of antimony was exploited from this deposit (Uher et al. 2000). Identified resources of antimony are 5000 t and 5.5 t of gold. The average Au content in ore is 3.60 ppm (Mikula 1992).

The Trojárová adit is situated to the N of the Pezinok-Kolársky Vrch deposit (Fig. 1). The mineralized structure of NW-SE direction is 1200 m long (Chovan et al. 1994). Estimated and identified resources of antimony ores at the Trojárová deposit are summarized at 2 700 kt (49 274 t of Sb). Gold resources represent 3 t of metal. The Sb content in ores is 2 % and the Au content varies from 1.2 to 1.7 ppm (Tréger et al. 1989, Mikula 1992).

At the Pezinok deposit and in the Trojárová adit we can distinguish two types of ore mineralization: 1 – metamorphosed, primarily exhalatory-sedimentary pyrite mineralization genetically related to the Devonian basaltic volcano-sedimentary cycle, which was subsequently metamorphosed and 2 – hydrothermal Sb-Au-As mineralization of epigenetic character which is most frequently located in layers of tectonically deformed black schists (Chovan et al. 1992). Ore elements could have been mobilized from the black schists by the circulation of fluids released during regional metamorphism and periplutonic metamorphism associated with the intrusion of Bratislava granite body (348 ± 4 Ma; Cambel et al. 1990).

The Dúbrava deposit is situated on northern slopes of the Nízke Tatry Mts. (Fig. 1) The deposit is structure-controlled and the diastrophism belts are in a transversal position to the mountains axis. The ore field is 4000 m long and 1000 m wide. The antimony was the only exploited metal at the deposit. Locally, the ore was enriched in precious metals (Au 20–70 ppm, Ag up to 500 ppm). During the last 40 years the gold content in the ore was only 0.5 ppm. The gold content in the concentrate was 4 ppm (Michálek 1984).

The ore field consists of a swarm of quartz-sulphide veins, veinlets and impregnations developed in mylonite zones and open fractures in the granodiorite-tonalite massif, less frequently in gneisses and migmatites Chovan (1990). Chovan et al. (1996) distinguished two mineralization stages: an earlier scheelite phase and later sulphide phase. The younger sulphide phase consists of four mineralization stages. The quartz-stibnite veins reach to the depth of 350 m. From the view of the gold content the most important is the first gold-bearing arsenopyrite-pyrite stage. According to Michálek (1984) the gold content in this ore type ranges from 1 to 5 ppm. Arsenopyrite represents locally, in the southern part of the deposit, the most common ore mineral of the quartz veins.

The Vyšná Boca deposit is situated on northern slopes of Nízke Tatry Mts. (Fig. 1) in the mylonitized zones of highly metamorphosed crystalline rocks. The quartz-siderite veins are developed in biotite and two-mica gneisses as well as in granitoids. The ore field is about 2 000 m long. Two main types of epigenetic mineralization can be distinguished at the deposits. The first one is the siderite mineralization represented by carbonate-quartz-sulphide veins. The dominant minerals are: siderite, quartz, pyrite, chalcopyrite and tetrahedrite. Barite, ankerite, hematite, galena, arsenopyrite, sulphosalts and Ni-Co minerals are less abundant. The second type of mineralization is represented by quartz veins with gold (Chopec occurrence) in granitoids. Gold and sulphides (arsenopyrite, pyrite, galena, Cu-Pb-(Sb,Bi) sulphosalts) form impregnations in quartz. Ankerite is rare. The main gold-bearing minerals are pyrite and arsenopyrite ± cobaltite, gersdorffite, carrolite (Ozdín – Chovan 1998).

The Mýto pod Ďumbierom – Mlynná Dolina Valley is located on the southern slopes of the Ďumbier part of the Nízke Tatry Mts. (Fig. 1). The studied veins and less frequent impregnation mineralization type are hosted by gneisses and migmatites of crystalline complex. The ore mineralization is accompanied by an intensive wall rock alteration, especially by the sericitization of plagioclase and chloritization of biotite, silicification and tectonic deformation (Chovan et al. 1996). Two mineral associations were distinguished: the gold–pyrite–arsenopyrite and the stibnite (Sb-Au). The first one occurs in white quartz with abundant patches of K-feldspar and it is characterized by gold grains of high fineness (95.7 wt. % Au, 2.3 wt. % Ag) enclosed in large subhedral to euheral homogeneous arsenopyrite crystals (Majzlan et al. 2001). The second one is dominated by stibnite that intersects older quartz or cements quartz fragments. Stibnite is intergrown with pyrite or rare berthierite and is intersected by veinlets of chalcopyrite and zinckenite. Gold occurs in stibnite, arsenopyrite and pyrite. Its average composition is 88.6 wt. % Au, 9.4 wt. % Ag (Chovan et al. 1996). The tungsten-gold mineralization in the region of the ore field Jasenie – Kyslá (Fig. 1) at the southern slopes of Nízke Tatry Mts. is both of vein and disseminated character. Minerallized zone is 15 000 m long and 1000 m wide (Pulec et al. 1983). Predominant quartz veins and less common carbonate veins have N-S direction with dip to the E. Their thickness ranges from several tens of cm to 10 m. Scheelite mineralization is highly irregular. The average gold content in the ore is 1.15 ppm. The mineralization is situated in migmatites containing intercalated layers of amphibolites and amphibole gneisses.

Gold of the Hercynian age occurs: a) in association with scheelite mineralization, b) with arsenopyrite, pyrite, chalcopyrite, pyrhotite and galena, c) with Sb-minerals (gudmundite, boulangerite, jamesonite), kobellite, bismuthinite and löllingite. Gold of the Alpine age is relatively rare and associated with carbonate-sulphide mineralization (Chovan et al. 1992). The total gold resources are estimated at 1.4 t (Tréger – Baláž 1999).

Experimental

The first step of the research was realized by the study of polished sections in reflected light. The distribution of As, Fe, S, Sb and several other elements was investigated by WDS analyses using EMPA Jeol 840 A and Jeol Superprobe JCXA 733 (Geological Survey of Slovak Republic, Bratislava) and CLEOM laboratory (Faculty of Natural Sciences, Comenius University, Bratislava). Analytical conditions 20 kV, 17 nA, beam diameter 3–5 µm.

Monomineral samples of euhedral arsenopyrite and pyrite of limited grain size (not powdered), 2 to 5 g in weigh, were transferred to a glass beaker and gradually corroded under unceasing control in 1 M nitric acid or in 1 M aqua regia mixture until approximately one third of crystals dissolved. The insoluble residue was weighted and separately dissolved. Then both the solutions were separately evaporated to dry consistency. After the dissolution in a dionized water the solutions were collected in a 100/ml volumetric flask and diluted to volume. Gold was extracted from environment of 3M hydrochloric acid to Fluka Amberlite IRA-400 basic ion exchanger (20–50 mesh, Cl^- form and determined using OES analysis in both parallel samples and calculated for the both partial weights to get bulk-analyses of the crystal rims and cores). The measurements were made with the PGS-2 Carl-Zeiss Jena spectrograph. Experimental conditions: excitation A.C. arc, 7A, electrodes SU-308/SG-359 Elektrocarbon Topoľčany, exposition 120 s, photographic emulsion: WU-3 (ORWO), developing: ORWO R 09, 1:20 5 min, 20 °C. Analyses were realized at the Geological Institute of Slovak Academy of Sciences in Banská Bystrica.

The atom absorption spectrometric (AAS) Au determination in bulk analyses of gold-bearing sulphides was realized from 1g sample after its dissolution in 3M hydrochloric acid and Au enrichment to 5 ml dibutylsulphide using atom absorption spectrometer PU-9000 (Pye-Unicam/Philips) and PU 9095 furnace in Ar atmosphere; wavelength: 242.8 nm, 20 mA.

The character of Fe, Au and Sb bonding in sulphides was studied by the Mössbauer spectroscopy using ^{197}Pt (obtained by irradiation of ^{196}Pb metal) as the source isotope. Samples were analysed at Physik-Department E-15 Technische Universität in München (Germany).

The same samples as studied by the Mössbauer spectroscopy, were used for a detailed laser ablation ICP-MS analysis of Au, Sb and Co in sulphides (analysed at BRGM, Orléans, France).

Results

Arsenopyrite zonality and chemistry

Gold-bearing arsenopyrite occurs in the Tatric Unit along with pyrite and forms impregnations in black quartz and in altered rocks (Figs 2, 3). Disseminated textures are the most common. Characteristic feature is the distinct inhomogeneity of Sb and As contents in the individual euhedral crystals. Some large, often fractured grains, up to 4 mm in size, represent a very porous core zone with abundant gangue inclusions (Figs 4, 5) of various silicate minerals as quartz, rutile, monazite, titanite etc. The irregular zonality (Fig. 6) is less abundant than the concentric peripheral band zoning of the grains (Figs 2, 7).

In gold-bearing arsenopyrite from the Malé Karpaty Mts. (Pezinok – Kolársky Vrch and Trojárová adit), as well as in that from Dúbrava deposit, gudmundite inclusions are common (Fig. 6). The chemical composition of arsenopyrite from Pezinok – Kolársky Vrch is presented in Table 2. Whereas the crystal cores are usually enriched in Sb (up to 1.24 wt. % in spot analyses), the rims are As-rich (in arsenopyrite up to 44.76 wt. %; Table 2, Figs 2, 4).

Unlike the As-rich rims and Sb-rich cores of gold-bearing sulphides from the Malé Karpaty Mts., the As-distribution in arsenopyrites from Nízke Tatry Mts. is not uniform. The irregular sector zonality and hourglass zonality are typical (Fig. 8) at the Dúbrava deposit. The most common concentric growth-zonality shows variation both in As-rich cores (Fig. 7) and As-rich rims (Fig. 9).

Arsenopyrite from Vyšná Boca deposit is often cataclastic and carries numerous holes and fractures as well as galena and sphalerite inclusions (Fig. 10). The irregular and sector zonality are most common. Frequent is the hourglass zonality (Fig. 10). Concentric oscillatory growth zonality

Table 2 Electron microprobe analyses (wt. %; at. %) of gold-bearing arsenopyrite and atomic absorption bulk analyses of Au from Pezinok – Kolársky Vrch deposit.

	Fe	As	Sb	Co	Ni	Cu	S	Total	Au	Fe	As	Sb	Co	Ni	Cu	S	Total
				wt.%					ppm				at.%				
AU-6	35.71	40.11	0.48	0.01	0.02	0.01	23.65	99.99	120	33.36	27.93	0.21	0.01	0.02	0.01	38.48	100.00
AU-7	35.88	38.90	0.34	0.01	0.02	0.01	24.20	99.36	74	33.46	27.04	0.15	0.01	0.02	0.01	39.31	100.00
AU-8	35.12	40.76	0.42	0.01	0.04	0.01	23.64	100.00	78	32.85	28.41	0.18	0.01	0.04	0.01	38.51	100.00
AU-9	34.67	41.20	0.67	0.01	0.04	0.01	23.40	100.00	74	32.55	28.84	0.29	0.01	0.04	0.01	38.27	100.00
RB-49	35.23	41.48	1.04	0.00	0.01	0.01	23.12	100.89	79	32.95	28.92	0.45	0.00	0.01	0.01	37.66	100.00
	35.15	41.63	1.24	0.00	0.00	0.01	23.23	101.26		32.78	28.94	0.53	0.00	0.00	0.01	37.74	100.00
	34.66	41.05	0.18	0.01	0.01	0.00	24.05	99.96		32.32	28.53	0.08	0.01	0.01	0.00	39.06	100.00
	34.43	43.92	0.15	0.01	0.03	0.01	21.35	99.90		32.96	31.34	0.07	0.01	0.03	0.01	35.60	100.00
	35.19	41.00	1.01	0.00	0.00	0.00	23.75	100.95		32.71	28.41	0.43	0.00	0.00	0.00	38.45	100.00
	35.11	41.49	0.68	0.00	0.00	0.01	23.48	100.77		32.74	28.84	0.29	0.00	0.00	0.01	38.13	100.00
	34.57	44.76	0.16	0.00	0.00	0.01	21.19	100.69		32.95	31.80	0.07	0.00	0.00	0.01	35.18	100.00
	34.14	44.19	0.12	0.04	0.00	0.00	31.08	99.57		32.86	31.71	0.05	0.04	0.00	0.00	35.34	100.00
RB-50	35.43	39.80	0.47	0.01	0.02	0.00	23.48	99.21	122	33.35	27.93	0.20	0.01	0.02	0.00	38.49	100.00
	34.59	44.74	0.17	0.00	0.00	0.00	21.30	100.80	155	32.91	31.73	0.07	0.00	0.00	0.00	35.29	100.00
RB-51	35.05	43.47	0.32	0.10	0.00	0.00	22.01	100.95	74	33.06	30.56	0.14	0.09	0.00	0.00	36.16	100.00
RB-53	34.79	40.80	0.41	0.01	0.04	0.01	23.58	99.64	78	32.66	28.55	0.18	0.01	0.04	0.01	38.56	100.00

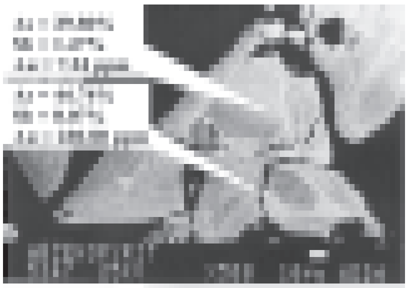


Fig. 2

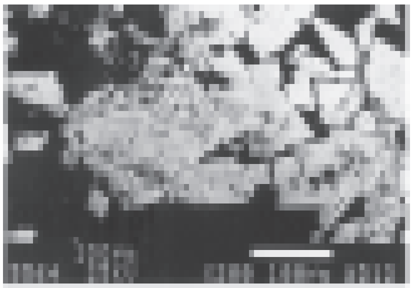


Fig. 3

Fig. 4

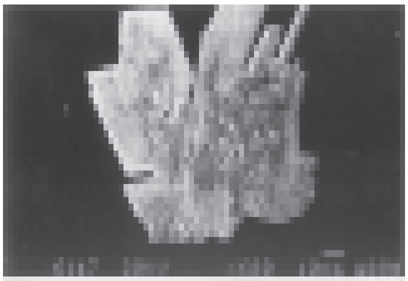


Fig. 5

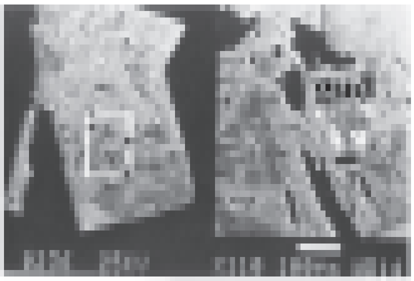


Fig. 6

Fig. 7

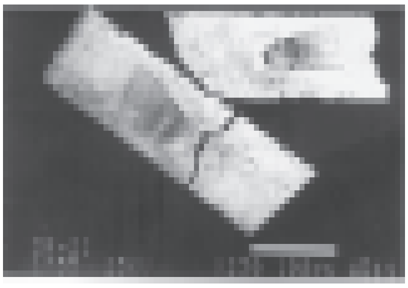


Fig. 8

Fig. 9

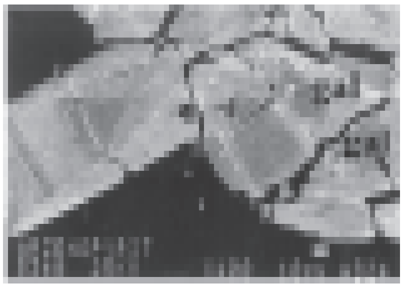


Fig. 10

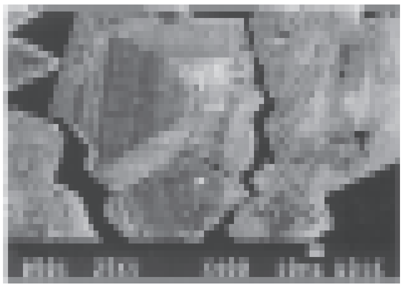
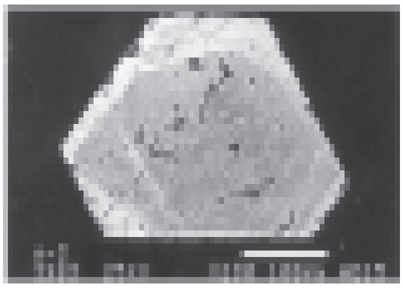


Fig. 11

Fig. 12



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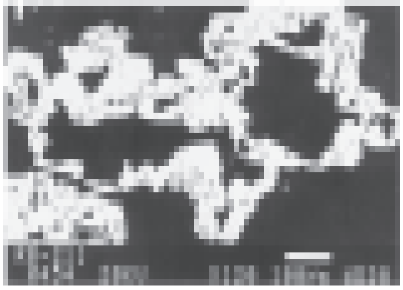

Fig. 14

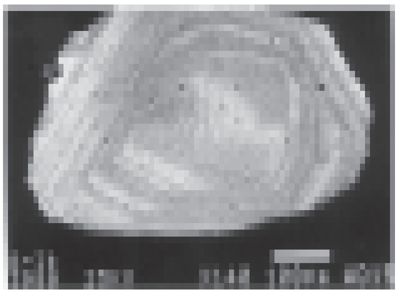

Fig. 15

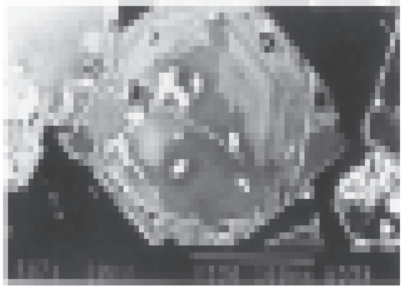

Fig. 16

Table 3 Electron microprobe analyses (wt. %; at. %) of gold-bearing pyrite and atomic absorption bulk analyses of Au from Pezinok – Kolársky Vrch deposit.

	Fe	As	Sb	Co	Ni	Cu	S	Total	Au	Fe	As	Sb	Co	Ni	Cu	S	Total
				wt.%					ppm				at.%				
AU-2	44.98	3.60	0.04	0.02	0.05	0.09	51.22	100.00	42	32.82	1.96	0.01	0.01	0.03	0.06	65.10	100.00
AU-3	47.58	5.37	0.09	0.18	0.13	0.38	46.28	100.01	36	35.81	3.01	0.03	0.13	0.09	0.25	60.67	100.00
RB-48	46.30	1.58	0.01	0.04	0.00		51.26	99.19	25	33.84	0.86	0.00	0.03	0.00	0.00	65.26	100.00
	46.30	1.05	0.00	0.04	0.00		52.00	99.39		33.63	0.57	0.00	0.03	0.00	0.00	65.78	100.00
RB-50	46.18	1.19	0.00	0.00	0.05		52.28	99.70	55	33.42	0.64	0.00	0.00	0.03	0.00	65.90	100.00
RB-52	46.40	0.00	0.00	0.01	0.00		53.80	100.21	62	33.12	0.00	0.00	0.01	0.00	0.00	66.88	100.00
	46.50	0.08	0.00	0.00	0.00		53.73	100.31		33.18	0.04	0.00	0.00	0.00	0.00	66.78	100.00
	46.63	0.04	0.00	0.00	0.01		53.51	100.19		33.34	0.02	0.00	0.00	0.01	0.00	66.63	100.00
PA-73	46.76	0.14	0.00		0.00	0.00	52.90	99.80	26	33.64	0.08	0.00	0.00	0.00	0.00	66.29	100.00
	45.43	4.32	0.02		0.00	0.04	49.54	99.35		33.66	2.39	0.01	0.00	0.00	0.03	63.92	100.00
	45.51	3.97	0.00		0.00	0.01	50.35	99.84		33.42	2.17	0.00	0.00	0.00	0.01	64.40	100.00
	45.96	2.80	0.00		0.00	0.00	51.51	100.27		33.36	1.52	0.00	0.00	0.00	0.00	65.12	100.00
	45.66	3.56	0.00		0.00	0.03	50.64	99.89		33.44	1.94	0.00	0.00	0.00	0.02	64.60	100.00
	48.03	0.19	0.00		0.16	0.00	51.62	100.00		34.75	0.10	0.00	0.00	0.11	0.00	65.04	100.00
	46.90	2.61	0.00		0.36	0.00	50.13	100.00		34.36	1.43	0.00	0.00	0.25	0.00	63.97	100.00

is rare (Fig. 11). The combined type of zonality in some distinct grains was also described. The grain size of the chemically homogeneous euhedral and subhedral arsenopyrite ranges up to 2 mm. At the Mýto pod Ďumbierom – Mlynná Dolina Valley occurrence arsenopyrite often has As-rich rims (Fig. 5). Euhedral arsenopyrite from the Jasenie deposit is homogeneous (Fig. 12) or with a distinct zoning, both irregular and with concentric band zoning. Arenopyrite often contains inclusions of gold (Fig. 12).

Pyrite zonality and chemistry

Gold-bearing arsenian pyrite from the Pezinok deposit (average gold content is 50 ppm; Table 3) and from Trojárová adit commonly nucleates around earlier As-poor pyrite and forms porphyroblastic grains with inclusions of non-ore minerals (Fig. 13) and of arsenopyrite. Disseminated textures and relic textures are common (Fig. 14). The concentric oscillatory zoning of the grains (Fig. 15) is characteristic.

Gold-bearing pyrite at Dúbrava deposit forms predominantly euhedral grains with a distinct inhomogeneity caused mainly by different As-contents (Fig. 16). Gudmundite inclusions are common.

Gold content of arsenopyrites

The gold contents in gold-bearing arsenopyrite from Pezinok – Kolársky Vrch deposit are presented in Table 2 and in Fig. 17a. The average gold content is about 100 ppm. The gold is preferentially enriched to As-rich rim parts of the crystals (Tables 4 a, b). The opposite trend was described only in three samples of homogeneous arsenopyrite (RB-22, RB-204, RB-243) from Pezinok-Kolársky Vrch. In two samples of homogeneous arsenopyrite crystals from Trojárová adit the gold contents are below the detection limit.

Both ICP/MS spot analyses and microprobe analyses of gold-bearing arsenopyrite from Pezinok – Kolársky Vrch deposit prove neither Au : Sb (Fig. 18 a) nor Au : Co

⇦

Fig. 2 – Pezinok – Kolársky Vrch deposit: concentric peripheral band-zoning of arsenopyrite grains (light: As-rich zones), SEM image.
Fig. 3 – Dúbrava deposit: zoned aggregate of arsenopyrite. The zoning is caused mainly by variations in As (light zones are As-rich) arsenopyrite.
Fig. 4 – Trojárová adit: disseminated structure of zonal brecciated gold-bearing arsenopyrite with As-rich crystal-rims (lighter zones) and gudmundite inclusion (gud).
Fig. 5 – Mýto pod Ďumbierom – Mlynná Dolina Valley: porous gold-bearing arsenopyrite with As-rich rim (light zone).
Fig. 6 – Pezinok – Kolársky Vrch deposit: porous arsenopyrite with irregular sector zonality and gudmundite inclusions (gud).
Fig. 7 – Dúbrava deposit: gold-bearing arsenopyrite with porous As-rich core (light zone).
Fig. 8 – Dúbrava deposit: SEM image of zoned arsenopyrite crystals showing hour-glass texture (As- rich light zones and Sb-rich dark zones).
Fig. 9 – Dúbrava deposit: gold-bearing arsenopyrite aggregate with As-rich rims (light zones) is cemented by gudmundite (white).
Fig. 10 – Vyšná Boca: hour-glass zonality in brecciated arsenopyrite (As- rich light zones and Sb-rich dark zones) with galena inclusion (gal).
Fig. 11 – Vyšná Boca: concentrically zoned euhedral brecciated gold-bearing arsenopyrite.
Fig. 12 – Jasenie deposit: SEM image of arsenopyrite with gold inclusions (Au).
Fig. 13 – Pezinok – Kolársky vrch: gold-bearing pyrite with central homogeneous porous As-poor core and peripheral As-rich overgrowth.
Fig. 14 – Trojárová adit: relic texture of pyrite.
Fig. 15 – Pezinok – Kolársky Vrch: pyrite with concentric oscillatory zonality (As- rich light zones).
Fig. 16 – Dúbrava deposit: inhomogenous pyrite (As-rich light zones) with gudmundite inclusions (white).

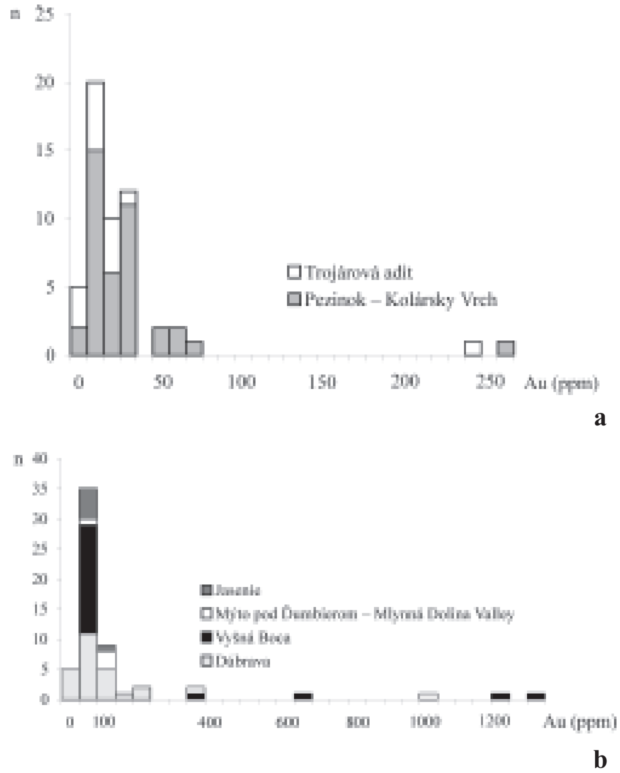

Fig. 17 Histogram showing the gold distribution in cores and rims of gold-bearing arsenopyrite (a – Malé Karpaty Mts.; b – Nízke Tatry Mts.).

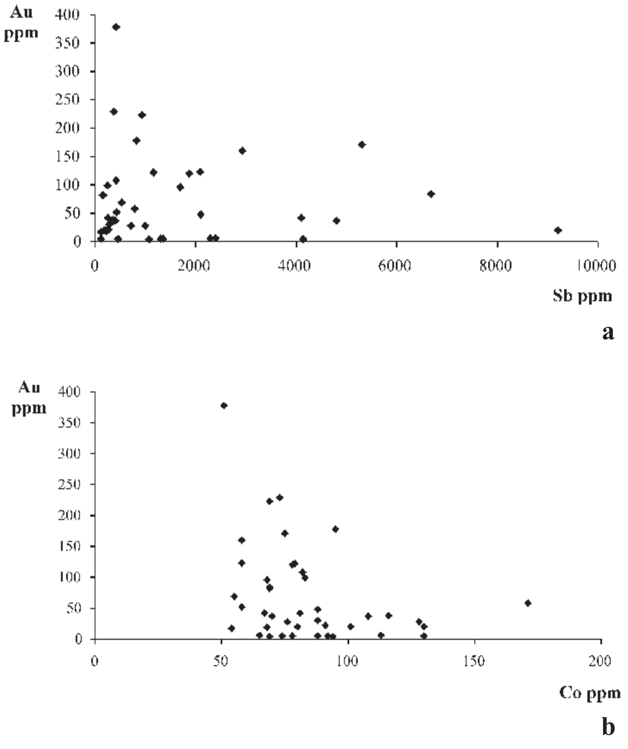

Fig. 18 Pezinok deposit – correlation of: a – Au : Sb; b – Au : Co in gold-bearing arsenopyrites (ICP/MS analyses).

(Fig. 18 b) correlation. A similar situation has been found with the arsenopyrite from the Trojárová adit (Fig. 19).

The very irregular Au-distribution in arsenopyrite from the Nízke Tatry Mts. is documented in Fig. 17 b. Most numerous are the contents from null to 100 ppm Au. The present study at Dúbrava and Vyšná Boca deposits ascertained, regardless of the zonality type, trend to concentration of Au in arsenopyrite As-rich zones: within twenty-three investigated samples in seventeen cases there are Au-enriched crystal-cores, in two samples the gold contents are below the detection limit and only in four samples it is possible to find enrichment of crystal-rims in gold (Tables 5 a, b). However, Au is concentrated mainly in the core region, which is surrounded by an Au-poor rim. The microprobe spot analyses do not prove a positive Au : As correlation.

Detailed investigation was done using a single arsenopyrite sample from Mýto pod Ďumbierom – Mlynná Dolina Valley without visible gold. Three grain-size fractions of the sample were analysed. Analyses confirmed preferential Au-incorporation to the crystal-rims, whereas the Au content is unambiguously rising from the coarse-grained fraction towards the fine-grained one (Table 5 c).

The investigated samples of predominantly euhedral arsenopyrite from the Jasenie deposit (Fig. 12) show that gold is incorporated in the crystals in the final stages of precipitation (Table 5 d). Rims of the crystals are Au-rich. Gold forms small inclusions.

Gold content of pyrites

The chemical composition and the gold contents in gold-bearing pyrite from Pezinok-Kolársky Vrch deposit are presented in Table 2. The diagram (Fig. 20) of Au-distribution in arsenian pyrites from the Malé Karpaty Mts. using OES analyses (Table 4) shows Au-contents in the range from 0.01 to 2.00 ppm. The preference of Au for the core or the rim parts of pyrite crystals is equivocal, based on the available data (Table 4 a). This is probably caused by a statistically insufficient data set of only five samples. Crystal cores are usually enriched in Sb (up to 0.09 wt. % in spot analyses). In sample RB-104 we can see the preferential incorporation of Au in the fine-grained crystals.

The investigated gold-bearing pyrite collection from Trojárová adit consists of fourteen samples. Au- and As-rich crystal rims were determined in ten samples, in four samples there was no difference between gold content in grain cores versus their rims (Table 4 b). Various grain-size fractions of pyrite were analysed. Analyses confirmed that the gold content is rising from coarse grains towards the fine-grained fractions.

Mössbauer spectroscopy

The ^{197}Au Mössbauer spektroscopy proved in gold-bearing samples from Pezinok – Kolársky Vrch only chemically bound “non-metallic gold”. The ^{121}Sb Mössbauer spektroscopy showed that the Sb bonding in arsenopyrite is of a gudmundite type (Figs 21 a, b). Locally elevated Sb content, however, may give rise to individual phases of Sb-minerals. They were identified as gudmundite inclusions. The similarity in structure of arsenopyrite and gudmundite allows to suggest that Au can be incorporated also in gudmundite. Andráš et al. (1993) proved the existence of Au-enriched gudmundite from the Pezinok deposit (3.83 ppm Au).

The ^{197}Au Mössbauer spectroscopy proved in gold-bearing arsenopyrite and pyrite from the Dúbrava deposit predominantly chemically "isomorphous" bound gold and unbalanced but small portion of metallic gold. Sb in arsenopyrite and pyrite is of the *gudmundite bounding type* also (Fig. 21 c).

According to the results of the Mössbauer spectroscopy gold at the Jasenie deposit forms small inclusions in gold-bearing sulphides (Fig. 21 d). Invisible gold was not described. Mössbauer spectroscopy proved exclusively metallic (visible) gold and gudmundite bonding type of Sb in gold-bearing sulphides at the deposit.

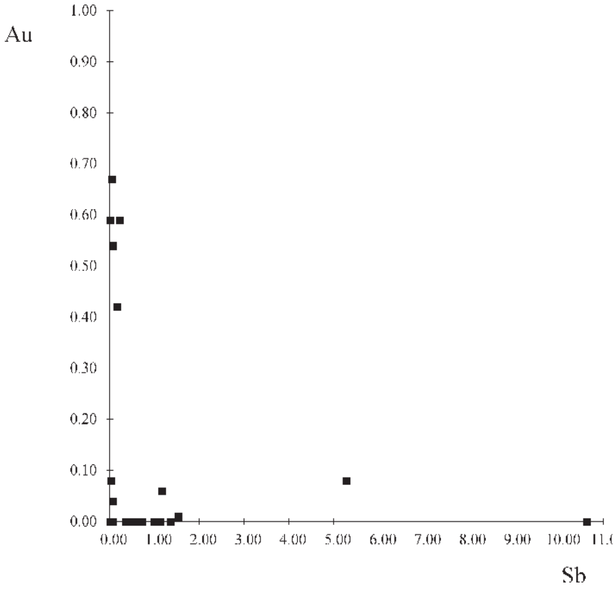

Fig. 19 Pezinok – Trojárová adit: correlation of Au : Sb in gold-bearing arsenopyrites (ICP/MS analyses).

Discussion

The presented analytical data are of a variable reliability. Electron microprobe spot analyses as well as ICP/MS laser ablation spot analyses are compared with AAS bulk analyses and OES analyses (both in monomineral arsenopyrite and pyrite samples and of the rim- or core-portions of gold-bearing sulphides). The OES analyses are not of exact character because of the different ratio of the analysed crystal parts but they can show trends of gold enrichment in analysed crystal fractions. Unfortunatelly, the authors do not dispose with data about the localization of ICP/MS-analysed spots within studied crystals.

The gold content in gold-bearing sulphide minerals from several deposits varies in a very wide range from null up to 1250 ppm in spot analyses. Its uneven distribution is shown in diagrams (Figs 17, 20). Distinct heterogenities characterize the gold distribution. The Au-enriched zones usually correlate with the As-enriched ones. Such zones usually occur either at the periphery of sulphide grains (Pezinok – Kolársky Vrch deposit, Trojárová adit, Mýto pod Ďumbierom) or in their cores (Dúbrava deposit, Vyšná Boca) of arsenopyrite and pyrite crystals. According to Michel et al. (1994), from the mineralogical point of view there are more possibilities how to explain the origin of As-rich growth zones in arsenopyrite/pyrite: 1) the presence of As-bearing minerals as cryptoinclusions. 2) the second possibility is the presence of As and Co substituting for S and Fe, respectively, in the pyrite lattice, based on the inverse correlation of As/S and Co/Fe.

According to Marion et al. (1991) Au-As rich zones in arsenopyrite may be formed by overgrowth, dissolution-recrystallization and Au-As diffusion from the mineral boundaries into the crystal. Most models for deposition of gold are based on the assumption that Au is transported as $AsHS_2^-$ or $Au(HS)^{2-}$ and deposited as free gold $(Au)^0$ (Arehart et al. 1993).

Although study of gold distribution in gold-bearing sulphides of the Tatric Unit proved that the preferential gold-binding in individual growth zones of arsenopyrite and pyrite crystals is different at various deposits, the available data suggest that within each single deposit the trend of gold-incorporation in rims or cores of crystals is relatively constant. In general it is possible to state that in inhomogeneous crystals Au is preferentially bound in As-rich zones of Sb-containing arsenopyrite and pyrite. The rare exceptions from this rule are not significant. They are usualy connected with chemically homogeneous sulphide samples.

At the investigated deposits of the Malé Karpaty Mts. (Pezinok-Kolársky Vrch and Trojárová), preferential Au-bounding in rim growth-zones of gold-bearing sulphide crystals was found (Tables 3, 4), whereas in the Nízke Tatry Mts. deposits (Dúbrava and Vyšná Boca) Au is incorporated in the crystals in the early As-excess stage of crystallization (Tables 5 a, b). Only a single arsenopyrite sample from the Mlynná Dolina Valley shows the opposite tendency (Table 5c).

Analyses of various grain-size fractions both from the Malé Karpaty Mts. and the Nízke Tatry Mts. (Tables 4–6) proved more or less unambiguous trend of increasing gold content from coarse-grained to fine-grained arsenopyrite.

The mechanism described by Schoonen et al. (1992) and Fleet et al. (1993) is the most probable one for the investigated Western Carpathian deposits. They assume that Au from gold-bearing fluids is not incorporated in sulphide structure but as a consequence of adsorption-redox reactions it is deposited at pores, vacancies and on

Table 4 Optical emission epectroscopic analyses of gold-bearing arsenopyrite from deposits of the Malé Karpaty Mts. region.

a) Pezinok – Kolársky Vrch

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
RB-1		6.56	7.10	□
RB-2		< DL	0.11	□
RB-4		1.10	28.80	□
RB-22		4.71	2.30	◆
RB-23		0.42	55.18	□
RB-24		22.61	256.69	□
RB-25		15.41	57.19	□
RB-26		19.50	5.00	◆
RB-107		0.42	0.91	□
RB-200	f	2.07	27.14	◆ □
RB-200	m	14.90	22.80	◆ □
RB-202		20.60	25.80	◆ □
RB-204		13.30	2.80	◆
RB-206		23.66	26.05	□
TR-206		23.66	42.00	□
RB-210	m	10.52	21.00	◆
RB-210	c	14.70	24.19	◆ □
RB-240		42.70	65.60	□
RB-243		5.57	0.79	◆
LB-300		< DL	0.11	◆

b) Trojárová adit

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
TR-139		1.40	2.31	□
RB-201		0.13	< DL	◆
RB-211		10.50	21.00	◆
RB-217		18.05	13.86	◆
TR-228		< DL	< DL	◆
T-24		7.23	230.80	□
T-27		16.12	3.08	□

Explanations to Tables 4, 5 and 6

● – concentric growth zonality with As-rich crystal cores
□ – concentric growth zonality with As-rich crystal rims
⅄ – irregular sector zonality
◆ – homogenic crystals
f – fine grained crystals (< 0.1 mm)
m – middle grained crystals (0.1–1 mm)
c – coarse grained crystals (> 1 mm)
n.d. – not determined

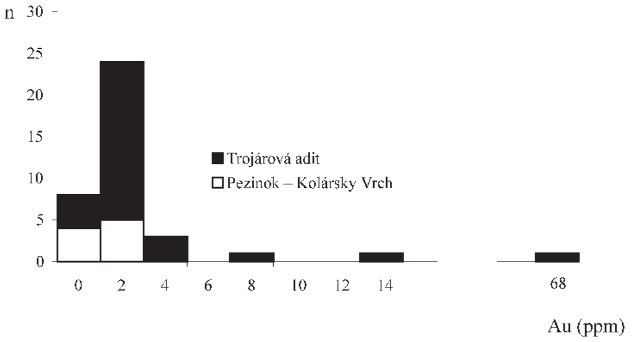

Fig. 20 Histogram showing the gold distribution in cores and rims of gold-bearing pyrite from Malé Karpaty Mts.

Table 5 Optical emission epectroscopic analyses of gold-bearing arsenopyrite from deposits of the Nízke Tatry Mts. region.

a) Dúbrava

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
RB-1		92.63	29.76	◆
RB-2		173.65	29.70	(◆) ●
RB-3		53.32	12.40	●
RB-4		< DL	< DL	(□) ⅄
RB-5		1.12	2.09	◆
RB-6		51.11	70.13	●
RB-7		< DL	< DL	◆
RB-8		19.23	4.25	●
RB-9		64.30	29.72	●
RB-10		0.64	0.30	◆ ●
RB-18		101.00	170.25	◆
RB-32		0.58	< DL	●

b) Vyšná Boca

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
VB-1		5.40	0.45	□
VB-2		8.10	2.90	⅄
VB-3		12.98	10.35	◆ ⅄
VB-4		0.45	0.86	□
VB-5		15.20	0.75	◆
VB-6		332.43	4.50	●
VB-7		602.00	3.04	◆ ⅄ ●
DE-21		1250.30	26.47	□
AN-2		8.10	2.90	◆
AN-3		1153.00	15.60	□
AN-6		13.18	11.50	◆

c) Mýto pod Ďumbierom-Mlynná Dolina Valley

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
ML-20	c	55.00	55.60	
ML-20	m	13.20	343.60	
ML-20	f	56.10	966.80	

d) Jasenie

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
SP-2		17.50	61.10	◆
SP-3		6.30	16.40	◆
SP-5		1.90	2.95	◆

Table 6 Optical emission epectroscopic analyses of gold-bearing pyrite from deposits of the Malé Karpaty Mts. region.

a) Pezinok – Kolársky Vrch

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
RB-104	f	0.09	0.22	◆ □
RB-104	c	0.62	< DL	◆
RB-201	f	0.22	67.90	◆
RB-209	f	0.56	< DL	◆ □ (●)
RB-209	m	< DL	< DL	◆ □

b) Trojárová adit

Sample No.	**grain size**	**crystal cores (Au ppm)**	**crystal rims (Au ppm)**	**zonality type**
RB-211	f	0.25	2.50	◆
RB-211	m	0.05	0.05	◆
RB-223		< DL	3.20	□
RB-224	f	0.34	1.50	□ ⅄
RB-224	m	0.04	0.17	□
RB-212		0.30	0.40	□
RB-213		0.71	6.13	□
RB-215		< DL	12.05	□
RB-223	f	0.42	3.10	□
RB-223	m	0.04	0.04	⅄
RB-223	c	0.01	0.01	⅄
RB-228	f	0.40	1.30	◆ □
RB-228	m	0.30	1.30	◆ □
RB-228	c	< DL	< DL	◆

surface of mineral growth-zones. Such an assumption could explain the absence of As:Au correlation in ICP/MS-laser ablation and microprobe spot analyses (Andráš 1995), and on the other hand, important As:Au correlation in bulk-analyses of distinct growth zones of gold-bearing sulphide minerals.

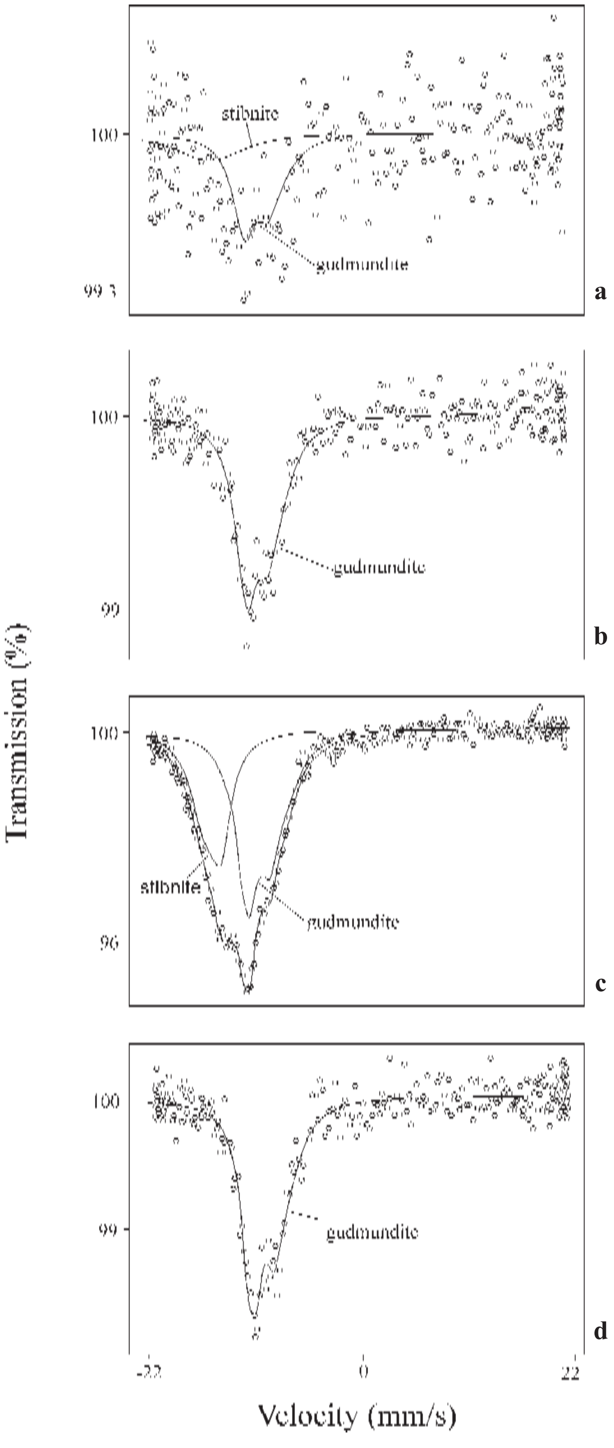

Fig. 21 ^{151}Sb Mössbauer spectra of gold-bearing arsenopyrite-pyrite mixture (a, b – Pezinok; c – Dúbrava; d – Jasenie).

Conclusion

The main gold-bearing sulphides of the Tatric Unit are arsenopyrite and pyrite (the arsenopyrite is usually Sb-enriched, up to 1.24 wt. % in spot analyses). Their characteristic feature is the distinct inhomogeneity caused mainly by negative As-Au vs. S-(Sb, Fe) correlation (Tables 4–6; Figs 2, 7). The Au content of arsenopyrite is up to 1 250 ppm (Vyšná Boca) and null to 67.90 ppm in pyrite. Mössbauer spectroscopy proved that the dominant part of the Au content in gold-bearing sulphide minerals is (with the exception of the Jasenie deposit) represented by chemically-bounded gold (Fig. 21). Au contents in gold-bearing sulphides depend neither on the mineralization type nor on the character of the wall rocks. The gold content in the gold-bearing sulphides is higher in fine-grained aggregates in comparison with the coarse-grained ones.

The crystals of arsenopyrite and arsenian pyrite from the studied deposits exhibit distinct zonation patterns. Growth zones characterized by two different trace/major element behaviour can be found: i) simultaneous enrichment in Sb and Fe, and ii) enrichment in As coupled with low Sb content. The progressive enrichment in As correlates generally with a decrease in the S and Sb content. As and S are negatively correlated in all cases.

Despite the fact that the incorporation of Au in the crystals of pyrite/arsenopyrite shows numerous exceptions and hampers thus simple generalization, three relatively well-defined trends can be observed: 1) more or less homogeneous distribution of Au in As-homogeneous sulphides; 2) Au-enriched crystal cores; and 3) Au-enriched crystal rims. The cases 2 and 3 are further characterized by significant positive Au–As correlation.

Au-As enrichment of crystal rims was described from the Malé Karpaty Mts. region (Pezinok – Kolársky Vrch and Trojárová adit) and from some occurrences in the Nízke Tatry Mts. (Mýto pod Ďumbierom – Mlynná Dolina Valley). An opposite trend was ascertained at the Dúbrava and Vyšná Boca deposits: Au-As enrichment of crystal cores.

The sharp compositional changes across zones in gold-bearing sulphides reflect rapid, non-equilibrium conditions of their crystallization. The co-precipitation of Fe, As, S, Sb with Au usually follows the temporary increase of the As-content during the dynamic, varying conditions of deposition, the suitable temperature and pH conditions. Stable crystallization conditions are probably not suitable for Au-incorporation.

The ^{121}Sb Mössbauer spectra of Sb-bearing arsenopyrite from the Pezinok, Dúbrava and Jasenie deposits allow to suggest presence either of separate microinclusions of gudmundite crystals, or residence of Sb at As sites in arsenopyrite.

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Väzba zlata v sulfidikých mineráloch Tatrika (Západné Karpaty) v závislosti na ich chemickom zložení

V Tatriku Západných Karpát sú známe početné Sb-Au výskyty a ložiská so zlatonosnými sulfidickými minerálmi: napríklad Pezinok, Dúbrava, Jasenie, Nižná Boca, Vyšná Boca a ďalšie. Hlavným zlatonosným sulfidickým minerálom je arzenopyrit. Obsahy zlata v pyrite bývajú nižšie ako v arzenopyrite. Zlato vstupuje do pyritu spravidla len pri obsahoch arzénu nad 0.2 váh. %. Obsah zlata v zlatonosných sulfidických mineráloch kolíše od 0 do n. 100 ppm. Jemnozrné kryštály obsahujú aj viac než o poriadok vyššie koncentrácie zlata.

Prezentovaná práca poukazuje na súčasnú precipitáciu Au s Fe, As a S v arzenopyrite a pyrite, pričom Au do týchto minerálov vstupuje jednak vo forme metalického a jednak vo forme chemicky viazaného zlata. Obsahy As a Au v jednotlivých vzorkách zlatonosného arzenopyritu a pyritu značne kolíšu, existuje však medzi nimi pozitívna korelácia.

As a Au boli transportované v tých istých roztokoch a ich vypadávanie z roztokov spôsobili totožné geochemické procesy. Au sa prednostne viaže na As bohaté zóny zlatonosných sulfidov.