

Variscan granitoid hosted hydrothermal gold deposit Pezinok-Staré Mesto (Malé Karpaty Mts., Western Carpathians): Mineralogy, paragenesis, fluid inclusions study

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Abstract: Pezinok-Staré Mesto gold deposit is hosted by a small massif of Variscan granodiorites, leucocratic granites and pegmatites. It is formed by several parallel NW-SE and transversal E-W veins, veinlets and impregnation bodies bounded on mylonitized granitoids. According to the area of old mining works, the length of mineralization can reach more than 1 km, vertical extent is unknown. The thickness of veins varied from 0.0X to 0.X m, max. 1 m. Quartz dominates from gangue minerals, carbonates are very rare. The content of gold varied from 0.X to X0 ppm Au, locally with bonanza accumulations. Au/Ag ratio is 5, the content of sulphides in vein filling is less than 1 %. Mineralization originated in several stages. The oldest one is characterized by arsenopyrite, pyrite and visible gold. Fineness of gold reaches values from 792 to 909. Minerals of later mineral stage (Cu, Pb, Sb, Ag sulphides and sulphosalts) are rare at the deposit. They fill thin cracks and form small grains and inclusions in quartz. This stage is characterised by remobilization of gold (684 - 753). In the quartz of the first mineral stage 3 types of fluid inclusions (1. $\text{CO}_2 \pm \text{CH}_4(?)$, 2. $\text{H}_2\text{O}-\text{CO}_2 \pm \text{NaCl}$, 3. $\text{H}_2\text{O}-\text{NaCl} \pm \text{KCl}$, $\text{CaCl}_2(?)$) have been. The mineralization originated from fluids with high salinity (17 - 25 wt. % NaCl eq.). Homogenization temperatures vary from 100 to 350 °C.

There is an anomal content of gold grains in the alluvial sands and gravels in the vicinity of occurrences of Au-Ag mineralization. Gold placers were mined in Middle Ages. Nowadays content of gold in alluvial placers of Limbašský potok brook is max. 0.221 g/m³. Gold occurs mostly in the form of nuggets, less in the form of flakes up to 1 mm in size.

Key words: quartz veins, gold, sulphosalts, Slovakia

Introduction

Sb-As-Fe-Au mineralization in the Pezinok area is the most important type of mineralization in Malé Karpaty Mts. mined until the beginning of 1990's. The largest is the Pezinok - Kolársky vrch deposit. In the vicinity of the deposit, in a distance less than 2 km, several occurrences of Au-mineralization are hosted by a small massif of Variscan granitoids (fig. 1). The largest occurrence, the Pezinok-Staré mesto deposit, used to be mined with alternating successes. It has been abandoned several times. The first written note about the mining activity comes from the year 1339. Archive information about the deposit was used by Cotta & Fellenberg (1862) and Döll (1899) in Bergfest (1952), Dubovský (1990), Michal & Uher (1999) and Wittgrüber et al., (2001). In the 19th century the mining profit per one year was about 5-10 kg Au. The highest profit – 21 kg Au was achieved in 1826-1827. Small amounts of silver were mined, too. The site was abandoned in 1872 for the last time. Information from the 20th century about the mineralization in the studied area can be found in Cambel (1959), Polák & Rak (1979) and Chovan et. al. (1992). One of two archive samples was mineralogically investigated by Andráš et.

al. (1990). Despite of this fact, mineralogical and paragenetical relations of the deposit have up been unclear till now and there have been just guesses about its characteristics. This paper brings new results about the Au-mineralization from the Pezinok-Staré Mesto location.

Geological setting and deposit structure

The Pezinok-Staré Mesto deposit is situated on the southeastern slope of Malé Karpaty Mts., between Hrubá dolina and Slnčné údolie valleys, 380 to 500 m above the sea level (fig. 2). The gold deposit is hosted by a small massif (fig. 1) of variscan Bratislava granitoides (S-type) represented by two mica granodiorites, leucocratic granites and pegmatites. Geological structure of Malé Karpaty Mts. is characterized by several superimposed nappes – Prealpine crystalline Tatric basement, Mesozoic cover and upper nappes (Plašienka et. al. (1991). Tatric fundament is divided into the Harmónia series and Pezinok – Pernek series (Cambel, 1954). Plašienka et. al. (1991) distinguishes these units: Pezinok Sequence (metamorphic cover of the Bratislava granitoid massif), Pernek and Harmónia Sequence (metamorphic cover of the Modra granitoid massif) and Dolný Se-

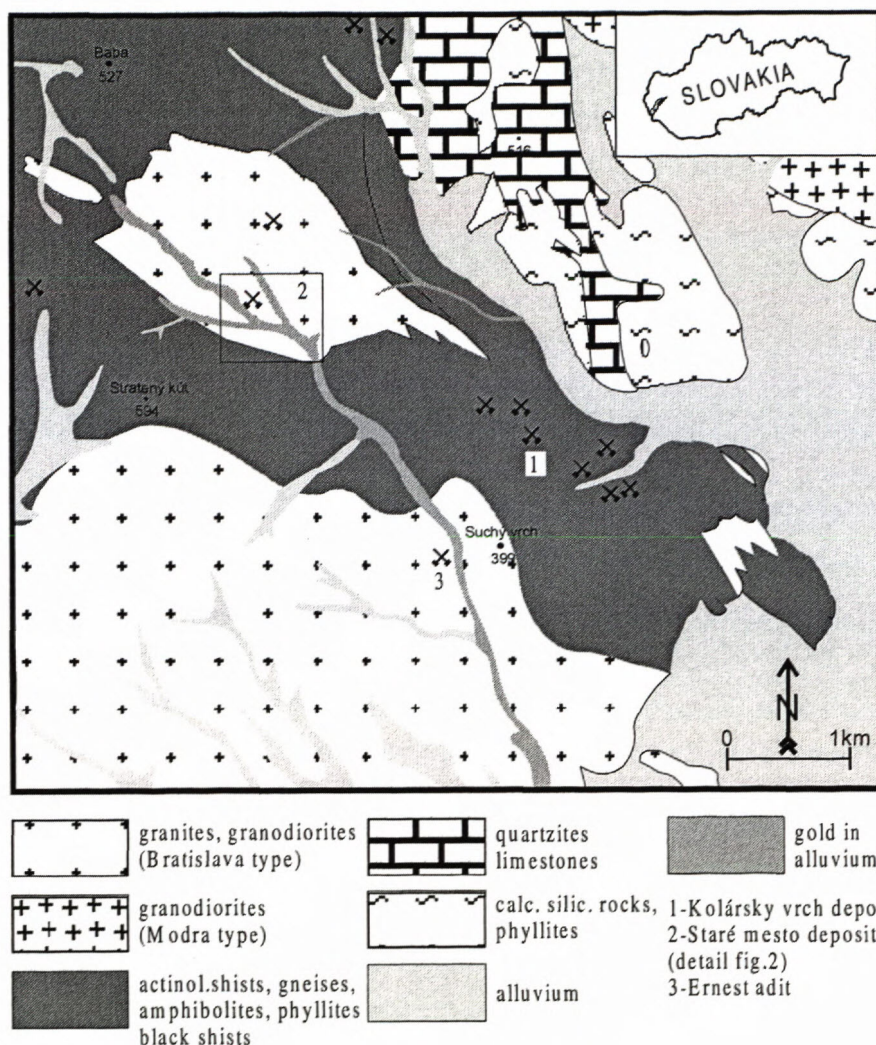


Fig. 1 Geological map of the vicinity of Pezinok – Staré Mesto deposit (according to Mahel' & Cambel eds., 1972)

g/t), 0.3–0.45 m (3 g/t), 0.01–0.15 m (32–50 g/t), 0.3 m (63–78 g/t). The highest content of gold, were in intersections of veins (Polák, 1970).

Three large and several small occurrences of Sb mineralizations are known in the Malé Karpaty Mts. More than 10 000 tons of Sb have been produced from the Pezinok – Kolársky vrch deposit in period until 1990. It is situated about 2 km SE from Pezinok-Staré Mesto deposit. The deposit is hosted by volcano-sedimentary Pezinok – Pernek crystalline formation. Strata-bound type mineralization, represented mainly by stibnite, arsenopyrite with „refractory gold“ and other Sb, Fe-sulphides and sulphosalts, is associated with a large tectonic zone and located in the so-called productive zones in black shists and phyllites (Chovan et al., 1994).

Small occurrence of Sb-mineralization (Ernest adit) is situated cca 3 km SSE from Pezinok – Staré Mesto deposit in Slnčné údolie valley (fig.1). Mineralization is hosted by granitoides of Bratislava type (Andráš et al., 1999).

quence (Lower Silurian to Lower Devonian – of flysch character) and upper volcano – sedimentary formations (lower to middle Devonian).

The vein system is formed by the main Terézia vein of the general NW-SE direction steeply dipping to W and by several small combed veins (Plochá, Strmá, Pavol) of small thickness and length (Cambel, 1959). Veins are formed in mylonite zones. They often fork and thin out. The Terézia vein is an ore structure with the maximum thickness of 0.9 m with short productive areas. The Plochá vein is of E-W direction with the inclination 20°–45° to S and the thickness 0.1–0.2 m. The length of the productive area is about 100 m. The Pavol vein is approximately parallel to the Plochá vein. According to the location of the old mining sites the total length of the ore zone is even 1 km. The depth of the ore zone is not known. According to the archive information the number of „unknown Fe-sulphides“ increases with depth. In the NE part of small Staré Mesto granitoid massif there are some unclear trails of a small old mining work. Vein filling is formed by quartz and mylonite, rarely pyrite, markacite and visible gold. In an archive sample of quartz veinstone electrum, galena, sphalerite, chalcopyrite, Ag-tetrahedrite and polybasite was found (Andráš et al., 1990). The content of Au in the ore was very variable: thickness 0.3–0.45 m (2.5–8

Methods

Concentrates of heavy minerals (28 samples) and the samples of large volume (5 samples of 0.1 m³) from the alluvium and the elluvium were taken by standard method (obtaining heavy minerals concentrates in a pan, using a sieve with 3 mm mesh) and processed in the laboratory of Comenius University Bratislava. Heavy minerals concentrates were evaluated using binocular magnifying. 0.653 g of the alluvial gold and 0.487 g of the elluvial gold were mineralogically evaluated. The weight of gold was set by weighting of separated gold flakes and of gold obtained by amalgamation of samples of large volume.

The majority of tested samples (more than 150 samples of visible gold and other minerals) were picked up from old dumps material and from a shallow prospect pit (down to 0.5 m) in the area of the old mining activities. Polished samples were studied using the Jenapol and Amplival (Zeiss) microscopes. Ore minerals were analyzed by wave-dispersion (WDS) and energy-dispersion electron microprobe at Geological Survey of the Slovak Republic Bratislava, at CLEOM – Comenius University Bratislava and at Geology Institute University of Copen-

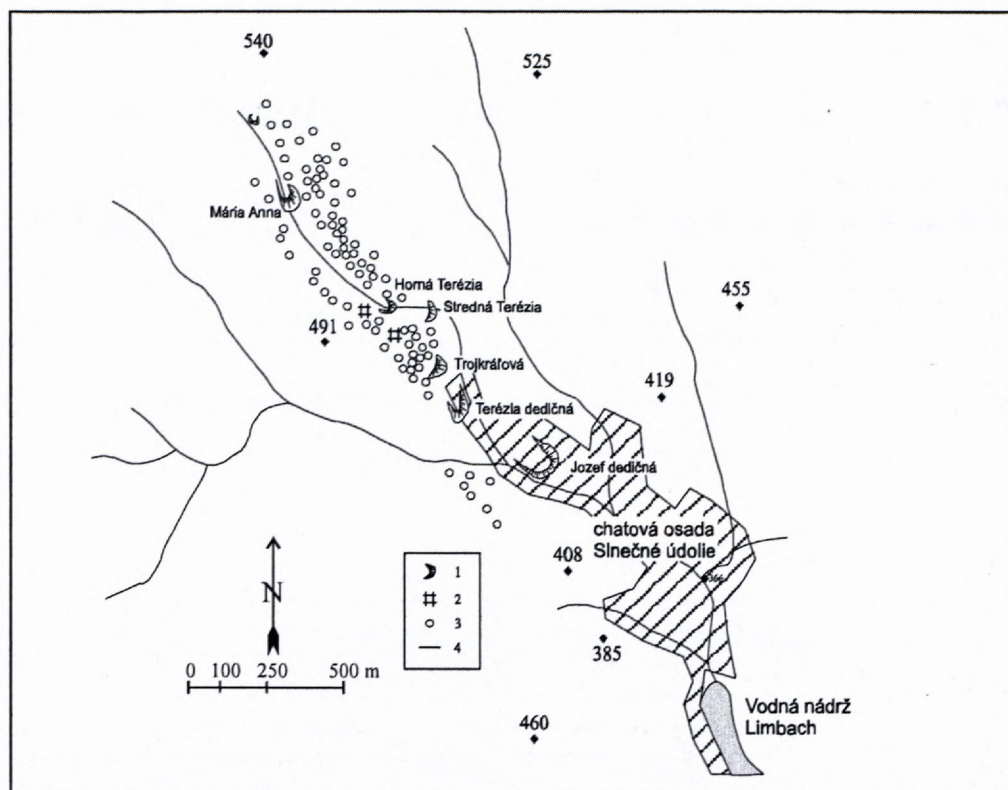


Fig. 2 Old miner works in the Pezinok - Staré Mesto deposit (modified by Cambel, 1959).

1 - mine dumps, 2 - shafts, 3 - slumps, 4 - brooks

hagen, Denmark (JEOL Superprobe 733). The operating conditions were 20kV and 20 nA. Natural (n) and synthetic (s) standards for unnamed mineral: Ag (AgL α) s, Sb (SbL α) s, PbS (PbL α) s, Bi₂S₃ (BiL α) s, CuFeS₂ (CuK α , FeK α , SK α) n and for tetrahedrite: Ag (Ag) s, Pb (PbS) s, Bi (Bi₂S₃) s, Cd (CdS) s, As (Cu₃As₄) s, Hg (HgS) s, Zn (ZnS) s, Sb (Sb) s, Cu, S (CuFeS₂) n. Operating conditions of Jeol Superprobe 733 and JXA 840A device (Geological Survey of the Slovak Republic Bratislava, CLEOM - Comenius University Bratislava): 20 kV, 15 - 20 nA, beam diameter 3 - 5 μ m. Standards: n FeS₂, FeAsS, HgS, PbS, Te, Sb, Ag, Bi, Cu, Au. SEM images were taken by JXA 840A device (Comenius University Bratislava). Fluid inclusions were analyzed by LINKAM THMS 600 heating-freezing stage (Comenius University Bratislava). Salinity was calculated according to the equation of Bodnar (1992).

Ore mineralization

Mineralization in the Pezinok-Staré Mesto deposit originated during several stages. The origin of wallrock alteration along tectonic zones preceded formation of Au-mineralization. Leucocrate granitoides forming near surroundings of exploited veins were struck by extensive silicification. The silicification zones gradually replace quartz veins and veinlets. They are characterised by the predominance of quartz and the presence of new-formed white mica. Feldspars were almost entirely replaced by fine-grained white mica and quartz. The presence of chlorite, as a desintegration product of biotite, is characteristi-

cal in more basic varieties of granitoids struck by alterations. It can also appear in areas of foliation of mylonitized rocks and it is abundant in hydrothermal quartz. Wallrock alteration out of tectonic zones did not appear in the vicinity of thin veins and veinlets. Carbonates were not found in altered zones. It is not possible to comment the zoning and the extent of altered zones associated with Au-mineralization are to the fact that there is no access to the old mines.

The main mass of the ore originated in the **oldest stage**. It is represented by quartz veins, veinlets and silicified zones with of pyrite, arsenopyrite and visible gold impregnations. However, usually there are no ore minerals in quartz veins. According to the archive information the maximum thickness of veins was 0,9 m (Cambel, 1959). However, usually the mineralization was formed by a group of several veins from 0,5 to 5 cm, or maximum 15 cm thick, located mostly in altered zones in mylonite granitoids. The content of Au in hydrothermal quartz (5 kg of quartz from the mine dump material samples) is 31.5 ppm. Even 204 ppm Au were found in one of the samples. The Au/Ag ratio in ores is 5. The deposit is strongly faulted according to findings of the cataclastic textures of vein filling (fig. 3). Quartz veins often join and thin out. It is often possible to see continuous changes of veins into quartz zones. The vein margins are closely associated with Fe-oxides and hydroxides (often even tectonically) of the thickness of several tenths of millimeter. Vein and veinlets type of mineralization is accompanied by impregnations of pyrite and arsenopyrite in altered zones. Extensively silicified zones are characterized also by the presence of gold.

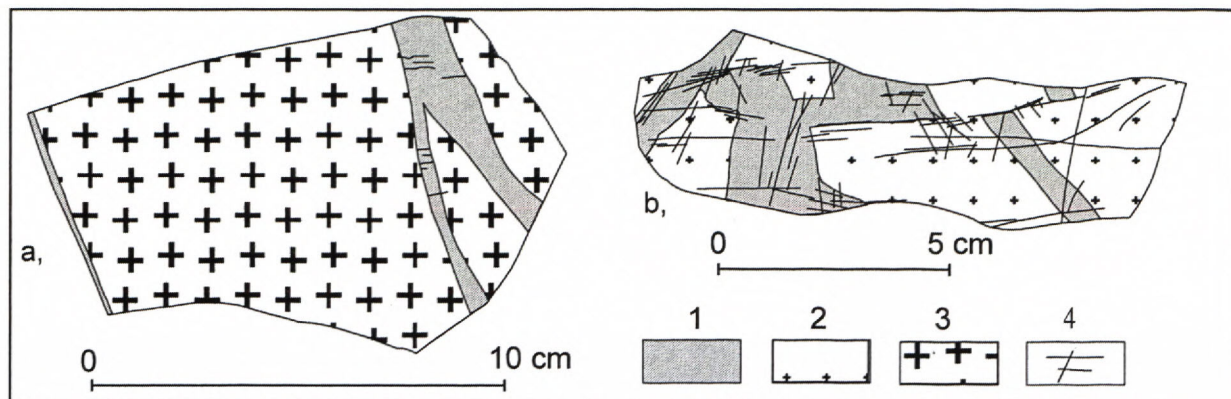


Fig. 3 Examples of auriferous quartz vein morphology (1 – quartz, 2 – silicified granite, 3 – unaltered granite, 4 – meso - micro faults). a: the veinlets of auriferous quartz in unaltered granite, b: strongly faulted auriferous quartz veinlets in silicified granite with impregnations of arsenopyrite and high finess gold.

Tab. 1 Selected electron microprobe analyses of gold

	1	2	3	4	5	6	7	8	9	10	11
Au	91,67	89,93	88,74	82,63	78,64	74,20	68,76	57,16	80,95	87,84	87,91
Ag	9,18	9,48	10,79	17,21	20,02	24,25	29,35	40,71	17,70	11,15	11,97
Hg	0,00	0,00	0,00	0,00	1,14	0,84	1,04	1,45	0,00	0,00	0,00
Cu	0,02	0,02	0,00	0,00	0,64	0,06	0,00	0,43	0,00	0,00	0,00
Sb	0,03	0,09	0,00	0,00	0,10	0,01	1,00	0,11	0,16	0,02	0,07
Bi	0,03	0,00	0,01	0,01	n.a.	n.a.	n.a.	n.a.	0,00	0,00	0,00
Fe	0,00	0,03	0,00	0,00	0,15	0,12	0,71	0,15	0,01	0,00	0,00
Σ	100,94	99,55	99,54	99,84	100,68	99,49	100,85	100,01	98,82	99,01	99,95

anal. 1, 2, 3, 4, 5, 6, 7, 8 – prim. Gold; anal. 9, 10, 11 – alluv. Gold; n.a. – not analysed; anal. 1, 2, 3, 4, 9, 10, 11 – ŠGUDŠ Bratislava; anal. 5, 6, 7, 8 – CLEOM Comenius University, Bratislava

Gold occurs most often as isometric grains, dendrites and flakes in quartz. Crystals of gold are rare. Sometimes two crystals, octahedral and hexahedral joined together, 0.1 mm in size were found (fig. 4f). Gold is relatively coarse-grained, more than 40 wt. % occurs in the fraction 0.5 – 2 mm (fig. 5a). More than 50 % of gold grains in polished samples are concentrated in fraction – 0.16 mm (fig. 5b). It fills the spaces among the quartz grains in the form of isolated grains of the size 0.0X – 5 mm. Locally it forms rich impregnations that often change continuously into veinlets of the maximum width 1 mm. There are several tens of 0.05 – 0.2 mm flakes in a 15 cm² area. The most of flakes are found on the margins of quartz veins on the contact zone with altered granitoid rock. There are clusters of small flakes on the margins of quartz veins and tectonically smoothed surfaces. They form almost continuous surface (a gold film) of up to 40 mm² in size. Gold along with pyrite and arsenopyrite is concentrated also in quartz from altered silicified granitoids (fig. 3). It dominates mostly at the margins, less in the cracks (fig. 4a). It is often joined together by Fe-secondary minerals (pyrite relicts), rarely with micas. According to the chemical composition and paragenetic relations it is possible to assign two generations of gold on the deposit (fig. 6, tab. 1). The older gold I, with the fineness of 792 – 909 associate with pyrite and arsenopyrite (fig. 4a). The younger gold II is accompanied by Cu, Sb, Pb, Ag sulfides and sulphosalts (fig. 4b) with lower fineness (684 – 753). Gold II with a high content of Ag

(fineness 584) was found as thin veins and margins penetrating and dominating over flakes of gold I (fig. 4c).

Pyrite and arsenopyrite are the most common minerals at the deposit. Despite of this fact, their volume in vein-stones is relatively low and it usually does not exceed 1 %. Most often they form 0.2 – 2 mm, often cataclased, well-terminated and subhedral grains in quartz and silicified granitoid rock. Rarely they form 5 mm big nests in quartz. Pyrite and arsenopyrite very often occur along with gold, which dominates and encloses them in cracks and in direction from margins. 0.0X flakes are often enclosed by pyrite and arsenopyrite. The content of As (tab. 2) varies from 26.29 to 31.99 at. %. The content of other elements (Sb, Au, Cu, Ni, Co) in arsenopyrite is lower than 0.5 at. %. Higher content of Au was found in arsenopyrite aggregates. These enclose visible gold or penetrate it.

Based on the presence of arsenopyrite - pyrite assemblage, arsenopyrite geothermometer (Kretschmar & Scott, 1976) was applied to determine the formation temperature of the first mineral stage. Considerable variation of As content in arsenopyrite resulted in large-scale crystallization temperature. The determination of the lower limit of the crystallization temperature was not possible because the arsenopyrite geothermometer is not calibrated for such low temperature values. According to the geothermometer, arsenopyrite have crystallized at 340 – 360 °C, upper limit for crystallization temperature is 445 °C.

In the younger stage of the mineralization origin, after ore tectonic event, the new structures were filled

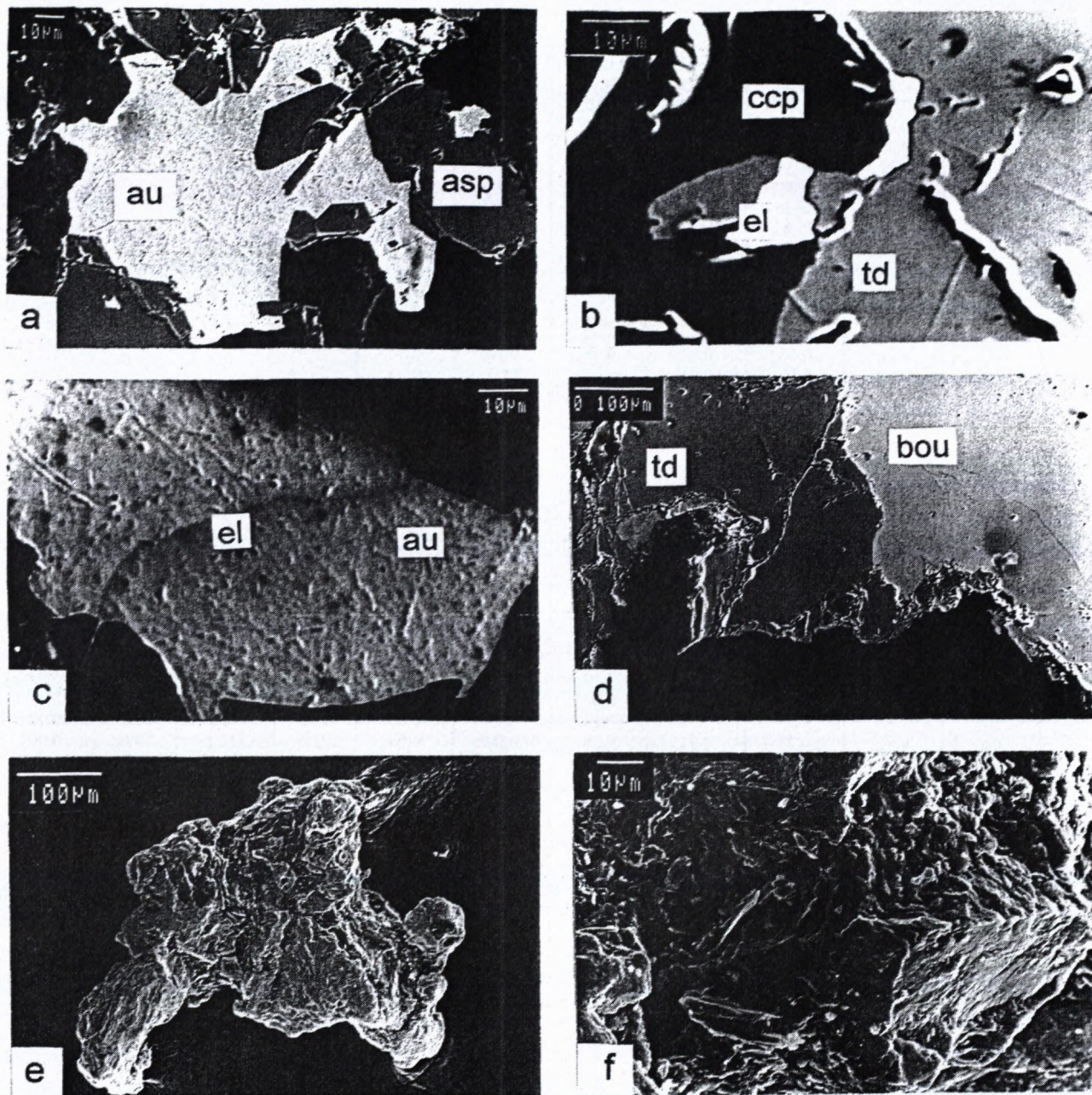
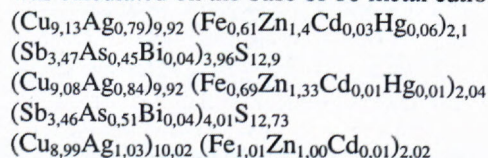


Fig. 4a: high finess gold (au) replacing arsenopyrite (asp), b: an intergrowth of low finess gold (el) with tetrahedrite (td) and chalcopyrite (ccp), c: the veinlet of low finess gold (el) in high finess gold (au), d: tetrahedrite (td) is affected by bournonite (bou), e: typical alluvial gold particle from Limbašský potok brook, f: crystal of gold isolated from the eluvial sediments on the deposit Pezinok – Staré Mesto.

with younger generation of quartz II, which is the bearer of the Cu, Sb, Pb, Ag mineralization. This mineralization is not evolved much at the deposit and its extent is only local. From ore minerals, pyrite II, tetrahedrite and chalcopyrite, occasionally also bournonite and unnamed Pb-Sb-Cu sulphosalt are present. Tetrahedrite and chalcopyrite occur in grains 0,0X – 5 mm and veinlets along with quartz II in quartz I. They penetrate each other, enclose crystals of pyrite II and grains of gold II (fig. 4b). Gold II has higher content of Ag instead of gold I. They were mostly found as inclusions in pyrite I and arsenopyrite. Locally chalcopyrite dominates over tetrahedrite. Chalcopyrite also forms 0,02 mm inclusions and veinlets in

tetrahedrite. We distinguished tetrahedrite in two paragenetic associations. Association with chalcopyrite and gold II is the most wide-spread. Rarely, tetrahedrite occurs together with bournonite, galena and unnamed sulphosalt. Tetrahedrite in association with Pb-Sb minerals has higher content of Ag (up to 7 wt. %) and Zn (more than 8 wt. %), (tab. 3). Crystallochemical formula of tetrahedrite was calculated on the base of 16 metal cations:



Tab. 2 Selected electron microprobe analyses of arsenopyrite

		1	2	3	4	5	6
wt. %	Fe	35,04	35,91	35,13	34,44	34,66	35,61
	Sb	0,34	0,46	0,12	0,15	0,16	0,15
	Co	0,00	0,00	0,00	0,00	0,00	0,29
	Ni	0,00	0,00	0,00	0,00	0,00	0,00
	Cu	0,32	0,08	0,16	0,21	0,20	0,05
	Au	0,00	0,00	0,18	0,25	0,27	0,00
	As	38,50	39,88	41,61	41,99	45,42	42,31
	S	25,82	23,88	21,74	21,52	21,24	20,95
at. %	Σ	100,02	100,21	98,95	98,56	101,94	99,36
	Fe	32,10	33,40	33,70	33,26	32,75	34,23
	Sb	0,14	0,20	0,05	0,07	0,07	0,06
	Co	0,00	0,00	0,00	0,00	0,00	0,26
	Ni	0,00	0,00	0,00	0,00	0,00	0,00
	Cu	0,26	0,06	0,13	0,18	0,16	0,04
	Au	0,00	0,00	0,05	0,07	0,07	0,00
	As	26,29	27,65	29,75	30,23	31,99	30,32
	S	41,21	38,69	36,32	36,20	34,95	35,07

anal. – CLEOM Comenius University, Bratislava

Tab. 3 Selected electron microprobe analyses of tetrahedrite

		1	2	3	4	5	6	7	8	9	10
wt. %	Cu	35,11	35,06	34,06	33,78	34,76	34,55	32,79	34,67	33,32	35,23
	Sb	25,59	25,62	25,54	26,25	24,16	24,68	25,85	24,90	25,32	24,39
	S	25,02	24,79	24,46	24,38	24,44	24,42	25,36	25,82	24,03	23,93
	As	2,06	2,33	1,84	1,55	2,05	1,96	0,38	0,37	2,07	1,94
	Cd	0,19	0,07	0,07	0,13	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Ag	5,17	5,53	6,62	7,12	6,67	6,72	5,61	5,51	6,21	6,35
	Zn	5,57	5,29	3,91	4,14	5,27	4,53	7,43	8,35	4,89	5,93
	Fe	2,06	2,35	3,37	3,09	3,33	3,32	1,60	1,57	3,42	3,23
	Bi	0,53	0,57	0,39	0,63	0,25	0,00	0,25	0,22	0,02	0,00
	Hg	0,75	0,20	0,01	0,18	0,00	0,08	0,00	0,00	0,00	0,00
	Σ	102,05	101,89	100,47	100,25	100,93	100,26	99,26	101,41	99,28	100,99
at. %	Cu	31,60	31,62	31,32	30,30	31,47	31,51	30,00	30,86	30,79	31,97
	Sb	12,02	12,06	12,22	12,67	11,41	11,74	12,34	11,57	12,21	11,55
	S	44,63	44,31	44,33	44,67	43,85	44,13	45,99	45,53	44,00	43,03
	As	1,57	1,78	1,43	1,22	1,57	1,52	0,29	0,28	1,62	1,49
	Cd	0,01	0,04	0,04	0,07	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Ag	2,74	2,94	3,57	3,88	3,56	3,61	3,03	2,89	3,38	3,39
	Zn	4,87	4,64	3,48	3,72	4,63	4,02	6,61	7,23	4,39	5,23
	Fe	2,11	2,41	3,51	3,25	3,43	3,45	1,67	1,59	3,59	3,34
	Bi	0,15	0,16	0,11	0,18	0,07	0,00	0,07	0,06	0,01	0,00
	Hg	0,21	0,06	0,00	0,05	0,00	0,02	0,00	0,00	0,00	0,00

anal.1, 2, 3, 4 – Copenhagen, Denmark; anal.5,6,7,8,9,10 – CLEOM Comenius University, Bratislava; n.a. – not analysed

Tab. 4 Selected electron microprobe analyses of Pb-Sb-Cu sulphosalts

		1	2	3	4	5	6	7	8
wt. %	Pb	39,66	40,04	42,84	42,92	43,09	46,18	44,26	45,95
	Sb	23,64	24,68	26,30	23,97	24,23	27,67	26,70	26,75
	Cu	13,83	13,99	11,62	13,54	13,48	1,96	2,76	2,23
	Bi	0,00	0,00	0,00	0,01	0,34	0,00	0,00	0,00
	Ag	0,09	0,06	0,02	0,01	0,01	0,00	0,00	0,00
	Fe	0,25	0,14	0,18	0,02	0,01	0,14	0,21	0,21
	Zn	0,00	0,00	0,08	n.a.	n.a.	0,01	0,01	0,01
	S	21,51	20,47	20,52	19,85	19,72	23,93	24,00	23,32
	As	0,39	0,35	0,38	n.a.	n.a.	0,50	0,49	0,47
	Σ	99,37	99,74	101,95	100,31	100,88	100,40	98,43	98,90
at. %	Pb	14,90	15,31	16,47	16,75	16,82	18,02	17,29	18,27
	Sb	15,12	16,06	17,21	15,92	16,10	18,38	17,75	18,07
	Cu	16,94	17,44	14,57	17,23	17,16	2,05	3,51	2,90
	Bi	0,00	0,00	0,00	0,01	0,13	0,00	0,00	0,00
	Ag	0,06	0,05	0,01	0,01	0,01	0,00	0,00	0,00
	Fe	0,35	0,20	0,25	0,03	0,01	0,20	0,30	0,31
	Zn	0,00	0,00	0,09	n.a.	n.a.	0,01	0,02	0,01
	S	52,22	50,57	50,99	50,06	49,76	60,35	60,60	59,92
	As	0,40	0,37	0,40	n.a.	n.a.	0,54	0,53	0,52

anal.: 1, 2, 3, 4, 5 – bounonite; anal.: 6, 7, 8 – unnamed mineral; n.a. – not analysed; anal. 1, 2, 3, 6, 7, 8 – CLEOM Comenius University, Bratislava; anal. 4, 5 – Copenhagen, Denmark

$(\text{Sb}_{3,52}\text{As}_{0,41}\text{Bi}_{0,03})_{3,96}\text{S}_{12,79}$
 $(\text{Cu}_{8,88}\text{Ag}_{1,1})_{9,98}(\text{Fe}_{0,92}\text{Zn}_{1,06}\text{Cd}_{0,02}\text{Hg}_{0,01})_{2,01}$
 $(\text{Sb}_{3,6}\text{As}_{0,35}\text{Bi}_{0,05})_{4,00}\text{S}_{12,71}$
 $(\text{Cu}_{8,97}\text{Ag}_{1,01})_{9,98}(\text{Fe}_{0,98}\text{Zn}_{1,32})_{2,3}(\text{Sb}_{3,25}\text{As}_{0,45}\text{Bi}_{0,02})_{3,72}\text{S}_{12,5}$
 $(\text{Cu}_{9,02}\text{Ag}_{1,03})_{10,05}(\text{Fe}_{0,99}\text{Zn}_{1,15})_{2,14}(\text{Sb}_{3,36}\text{As}_{0,43})_{3,79}\text{S}_{12,64}$
 $\text{Cu}_{8,89}\text{Ag}_{0,89})_{9,78}(\text{Fe}_{0,49}\text{Zn}_{1,96})_{2,45}(\text{Sb}_{3,66}\text{As}_{0,09}\text{Bi}_{0,02})_{3,77}\text{S}_{13,63}$
 $(\text{Cu}_{9,07}\text{Ag}_{0,85})_{9,92}(\text{Fe}_{0,47}\text{Zn}_{2,12})_{2,59}(\text{Sb}_{3,4}\text{As}_{0,08}\text{Bi}_{0,02})_{3,5}\text{S}_{13,38}$
 $(\text{Cu}_{8,8}\text{Ag}_{0,97})_{9,77}(\text{Fe}_{1,03}\text{Zn}_{1,25})_{2,28}(\text{Sb}_{3,49}\text{As}_{0,46})_{3,95}\text{S}_{12,58}$
 $(\text{Cu}_{8,98}\text{Ag}_{0,95})_{9,93}(\text{Fe}_{0,94}\text{Zn}_{1,47})_{2,41}(\text{Sb}_{3,24}\text{As}_{0,42})_{3,66}\text{S}_{12,09}$

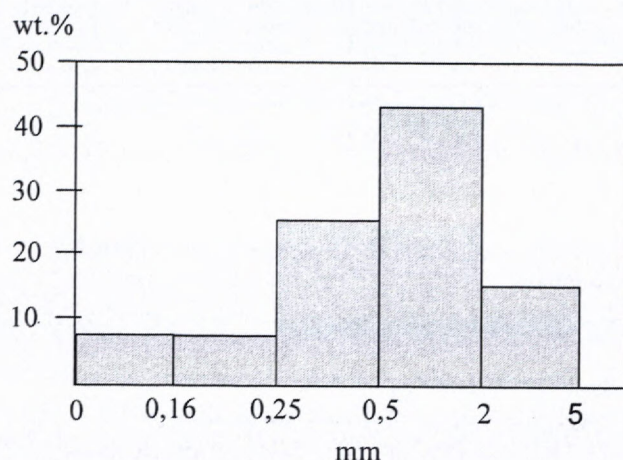


Fig. 5a Histogram of primary gold grain size from Pezinok – Staré Mesto deposit

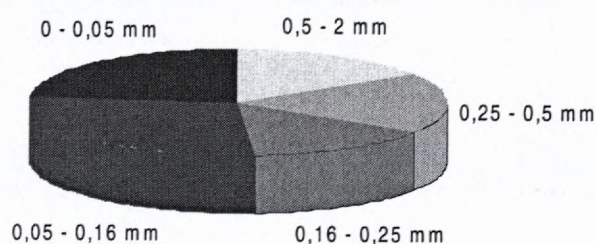


Fig. 5b Histogram of gold grain size measured in polished samples

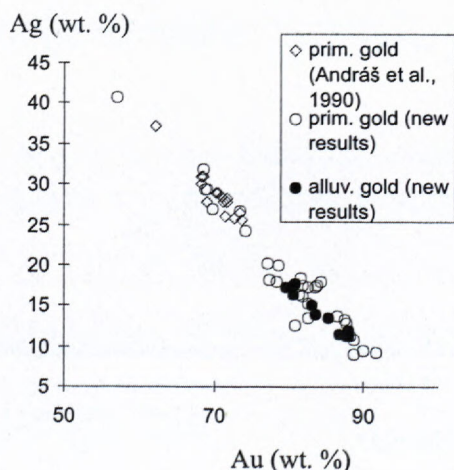


Fig. 6 Plot of Au vs. Ag content (wt. %) in gold from the Pezinok – Staré Mesto deposit

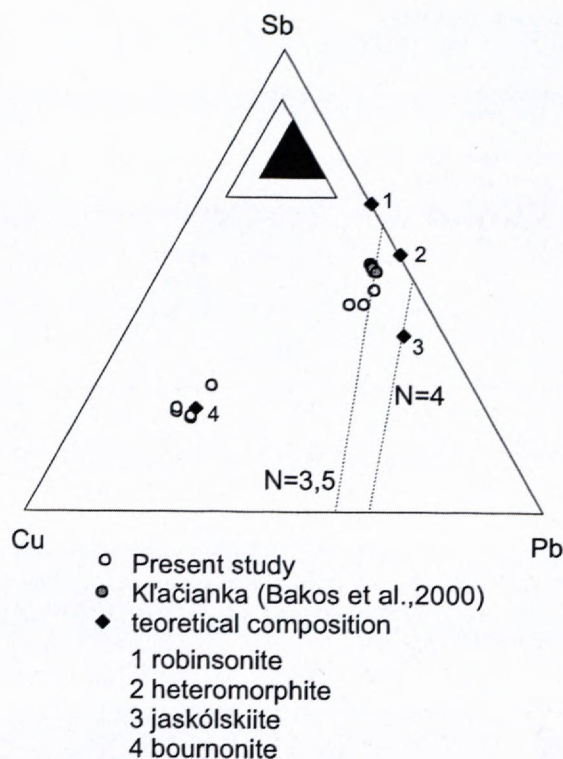


Fig. 7 Triangular diagram of Pb-Sb-Cu tetrahedrite (at. %)

Tetrahedrite accompanied by chalcopyrite is strongly replaced by secondary minerals. We can see two groups of points from microprobe analyses (fig. 7). Bournonite, galena and unnamed Pb-Sb-Cu sulphosalt (tab. 4) were found in one sample, where quartz II, tetrahedrite and chalcopyrite form an aggregate approximately 5 mm in size. They replace tetrahedrite from the margins (fig. 4d). Unnamed Pb-Sb-Cu sulphosalt (fig. 8) has the reflectance very similar to that of bournonite, it is greyish-white and strong anisotropic. Bireflectance and internal reflects were not observed. Unnamed mineral from Pezinok-Staré Mesto deposit contains 2-3,5 at. % Cu and no Ag, Bi (tab. 4). The Fe content is ~ 0,2 - 0,3 at. % and As content ~ 0,5 at. %.

The latest stage is characterized by nests and veinlets of calcite. They cement cataclased vein filling. This type of mineralization is very rare and evolved only locally.

Fluid inclusions

Fluid inclusions appropriate for the microthermometry were found in quartz of first generation. Fluid inclusions were not found in darker varieties of quartz. Measurements were performed in 3 different quartz samples with pyrite-arsenopyrite mineralization with visible gold. The size of inclusions was 1 – 10 µm, in the mostly 5 µm. Three types of inclusions were found. The most of the inclusions had of one phase at the room temperature, lower amount had two phases and contained liquid and gaseous CO₂. We expect presence of another compounds (CH₄?) in the inclusions based on the shift of the melting point of CO₂ rich inclusions (fig. 10) towards lower temperatures. The second type of inclusions was found only rarely and the microthermometry was not possible due to

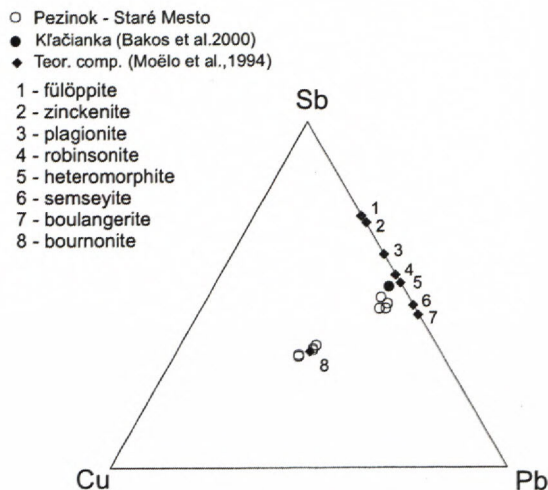


Fig. 8 Triangular diagram of X-ray electron microanalyses of Pb-Sb-Cu sulphosalts (at. %). Teoretical composition of sulphosalts are after Makovický (1989) for 1,2,4 and after Makovický & Nørrestam (1985) for 3.

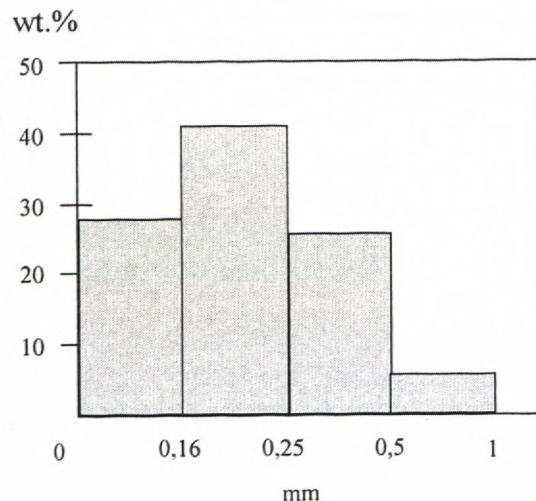


Fig. 9 Histogram of alluvial gold grain size from Limbašský potok brook

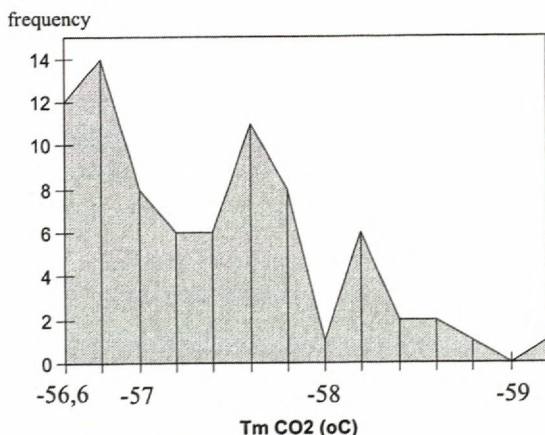


Fig. 10 Histogram of melting temperatures for the CO₂ – rich fluid inclusions from quartz

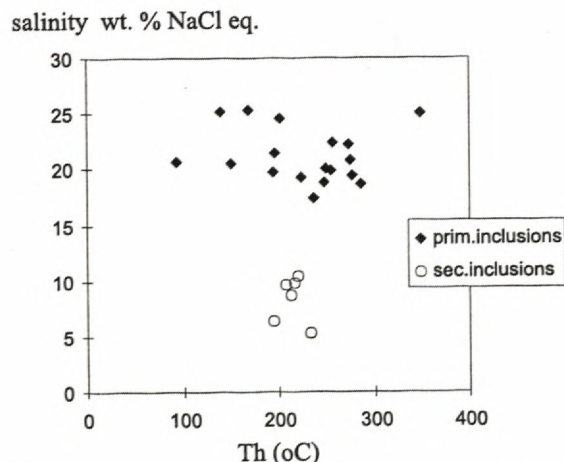


Fig. 11 Plot of homogenization temperature vs. salinity for fluid inclusions from quartz

their small dimensions. They had of two and three phases and contained liquid – gaseous CO₂ and a small amount of aqueous phase (H₂O – electrolytes). The third type of inclusions had two phases, rarely three phases and contained aqueous phase, small amount of vapour. There were also cubes of halite in the three-phased inclusions. Except for the primary inclusions several secondary inclusions were found (fig. 11). According to the melting point shift of the last solid H₂O rich inclusions towards lower temperatures (down to –24,9 °C) we deem that except for NaCl, there is also CaCl₂ or KCl. It was not possible to measure the eutectic temperatures due to the small dimensions of inclusions. The salinity of H₂O – NaCl ± KCl(?), CaCl₂(?) inclusions was from 17 to 25 wt. % NaCl eq. and salinity of the secondary inclusions was from 5 to 10 wt. % NaCl eq. (fig. 11). Homogenization temperatures of these inclusions were between 100 and 350 °C with the maximum at around 225 °C (fig. 12). Temperatures of homogenization of some of the secondary inclusions were around 210 °C.

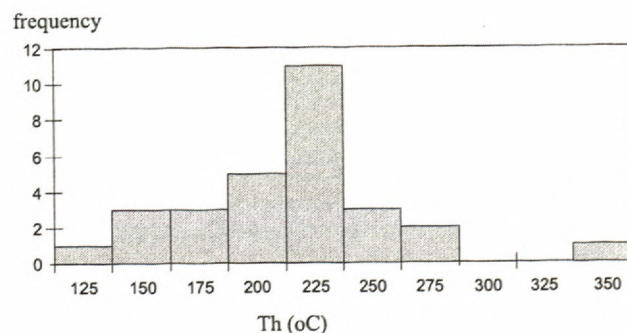


Fig. 12 Histogram of homogenization temperatures for fluid inclusions from quartz

Alluvial sediments

In heavy minerals concentrates of alluvial sediments, mostly garnets, ilmenite, magnetite, zircon, apatite, micas, monazite, xenotime and gold, less pyrite, epidote and rutile are present. We investigated mostly the distri-

bution, size, shape and the chemical composition of gold. The majority of gold from the alluvium occurs as small bunches and thick flakes (fig. 4e). It is modified to a relatively small extent, just sharp edges are-shaped deformed. Even in the distance of more than 4 km from the source, there are relatively abundant flakes with the shape similar to that of gold grains on the primary mineralization. Only about 50 % of grains are deformed. Grains deformed into thin plates by a mechanic pressure are rare. The most abundant are bunch grains with smooth surface. Dendritic grains are rare. More than 30 % of grains are penetrated with quartz or they enclose small grains of quartz. They form almost 100 % of the fraction exceeding 0,5 mm. Occasionally they are penetrate by Fe-oxides. Alluvial gold is relatively small-grained. There are more than 40% of flakes in the fraction from 0,16 to 0,25 mm. Almost 95 % of flakes are smaller than 0,5 mm (fig. 9). As for heavy minerals concentrates, gold exceeding 1 mm occur only rarely (the maximum is 4 mm).

The Au content of alluvial sediments in the lower part of Slnéčné údolie valley (in the depth of 0-0,4 m) is from 0,094 g.m⁻³ to 0,221 g.m⁻³. We found the biggest number of flakes in heavy minerals concentrates from this area (138 grains per heavy minerals concentrate at the most). Either upstream or downstream, the amount of gold is small in the area (up to ten grains per heavy minerals concentrate).

Interestingly there is a large amount of monazite in the vicinity of the primary location of the Au-mineralization (maximum 70 % in the heavy minerals concentrate). Monazite can be found as clear honey-yellow, yellow-and-brown and brown crystals and subhedral and xenomorphic grains up to 3 mm in size.

Discussion

Au mineralization at the Pezinok-Staré Mesto deposit is related to tectonic zones in Staré Mesto granitoid massif. According to the heavy minerals concentrates (Polák and Hanas, 1981, present study) the mineralization is spread in the whole massif. The mineralization is represented mostly by arsenopyrite, pyrite and visible gold and is related to the quartz veins, veinlets and impregnation zones in altered granitoides. Gold bearing „pyrites“ described by Döll (1899) and gold bearing pyrite described by Andráš et. al. (1990) are probably arsenopyrite and pyrite with 0,0X gold inclusions. Higher amounts of gold in arsenopyrite were found in grains in which free gold occurred. The occurrence of the secondary gold that originates from weathering of sulfides was not found, although Döll (1899) supposed so. Archive information about the occurrence of „gold bearing stibnite“ (Cotta & Fellenberg, 1862) at the deposit was not proved.

Younger base metal mineralization at the deposit is rare and occurs only locally. typical is higher amount of Ag in the hydrothermal solutions because of which more Ag minerals and Ag-rich tetrahedrite (Andraš et. al., 1990) originated. Higher amount of Ag in the younger stage of mineralization caused also the transport of gold of high fineness. It also caused the origin of the Ag - rich rims and veinlets and also the origin of gold of low fine-

ness. Newly found sulphosalts (bournonite and unnamed Pb-Sb-Cu sulphosalt) contribute to the paragenetic association of minerals of younger base metal period described by Andráš et. al. (1990). Microprobe analyses of tetrahedrites form three distinct group of points. Inter-growths of polybasite with Ag-rich tetrahedrite explain higher content of Ag in tetrahedrites described by Andráš et al. (1990). Two another groups of analyses vary in Zn and As contents while Ag content is nearly constant. We suppose that zonal tetrahedrite has two different phases. Older tetrahedrite with lower content of Zn originated together with chalcopyrite. Association of Pb-Sb minerals caused partial remobilization of tetrahedrite, which can be demonstrated by a phase with higher content of Zn. Higher content of Zn is typical for tetrahedrites from Sb mineralizations (Chovan, 1990). This paragenetic association of minerals conspicuously resembles the mineralization described from Ernest adit in Slnéčné údolie valley (Andraš et. al., 1999). Mineralizations at Ernest adit and Pezinok-Staré Mesto deposit differ by the absent stibnite mineralization with gudmundite, berthierite and other Pb-Sb sulphosalts at Pezinok-Staré Mesto deposit. Association of Pb-Sb minerals can be considered as an example of stibnite mineralization at the Pezinok-Staré Mesto deposit. Tetrahedrites from Ernest adit are not known to have higher Cu content and Ag content (Andraš et al., 1999). Furthermore, tenantite with As content 10 wt. % and Fe 6 wt.% was also described. Fe-As rich tetrahedrites are typical for siderite mineralization (Cambel & Jarkovský 1985). Quartz veins with stibnite at the deposit were not present in granitoid massive Staré mesto, described by Polák and Rak (1980).

Very rare is the occurrence of the unnamed Pb-Sb-Cu sulphosalt that probably belongs to the meneghinite homologue series. Its first finding in Western Carpathians was described from Kľačanka NE of Magurka (Nízke Tatry Mts.). Several occurrences of Sb-Au mineralization are known from this area there with a rich sulphosalt paragenetic association (Bakos et. al., 2000). Unnamed sulphosalt occurs here together with bournonite, heteromorphite, robinsonite and galena in younger period of the base metal mineralization. Compared to the theoretical composition of heteromorphite it contains about 1.8 at. % Cu and 0.2 at. % Ag. Cu and Ag can be introduce into the structure by the following possible substitutions: $Ag + Sb = 2 Pb$, $Cu + Pb = Sb + vac.$, which is a typical form of substitution in sulphosalts. The order number N is ~ 3.5 which corresponds to the hypothetical new member of meneghinite homologue series. Unnamed Pb-Sb-Cu sulphosalt from the Pezinok-Staré Mesto deposit contains 2 - 3.5 at. % Cu and no Ag and the order number N is ~ 3.5. Balance charge valence of analyses is wrong. Analyses points on the line for the hypothetical N ~ 3,5 rather than jaskolskiite which is N = 4. It seems to be a similar sulphosalt like the one from the Kľačanka occurrence.

Fluid inclusion study showed that the quartz from the arsenopyrite-pyrite-gold mineralization originated from CO₂ - rich (CO₂ - H₂O - NaCl ± KCl, CaCl₂(?) - CH₄(?)), fluids with salinity 17 - 25 wt. % NaCl eq. The fluid separation could be one of the reasons for the gold deposition. This can be proved by a presence of CO₂-CH₄(?)-

rich inclusions and by the presence of high salinity H_2O inclusions. In the mineralized bodies gold is located at the margins of the quartz veins. The fluid - rock interaction is considered to be the most important mechanism of gold deposition at deposits of this type (Pirajno, 1992, McCuaig & Kerrich, 1998). In the first stages of fluid penetration through rocks there sulphidic reactions occur. Here the altered zones with Fe-sulphidic impregnations originate. Under favourable conditions a chemical absorption occurs resulting in the origin of sulfides and „refractory gold“ (Pezinok-Kolársky vrch deposit - Andráš et al., 1995). Due to a high occurrence of free gold it is not possible to exactly find the presence of „refractory gold“ in arsenopyrites and pyrites from the Pezinok-Staré mesto deposit. Homogenization temperatures of fluid inclusions in studied samples are from 100 °C to 350 °C. Th around 225 °C had most of the inclusions. As for the adjacent Pezinok deposit, homogenization temperatures of the first stage of mineralization (pyrite – arsenopyrite with „refractory gold“) are from 300 °C to 320 °C (Chovan et al., 1992). Arsenopyrite mineralization (\pm visible and refractory gold) in Ďumbierske Nízke Tatry Mts. originated at temperatures from 315 °C to 355 °C (Dúbrava deposit - Chovan et al., 1995) or from 280 °C to 360 °C (Mlynná dolina deposit - Majzlan et al., 2001). Temperature of origin of the orogenic type Au mineralization ranges from 150 °C to 700 °C, but most often from 250 °C to 400 °C (Kerrich & Cassidy, 1994, Groves et al., 1998 and others). Conditions of origin of the younger base metal mineralization were not determined from the studied samples. Homogenization temperatures (180 °C to 255 °C) of inclusions from younger stages from Pezinok-Kolársky vrch deposit mineralization (Chovan et al., 1992) are very similar to that secondary aqueous inclusions of Pezinok-Staré mesto deposit (Th 210 °C, salinity 5-10 wt. % NaCl eq.). CO_2 - rich fluid inclusions were found in arsenopyrite – pyrite mineralizations at Dúbrava (Chovan et al., 1995), Mlynná dolina (Majzlan et al., 2001) and Kriváň (Bakos, 2000) deposits too.

It was not possible to find out the power limit of the formation temperature of arsenopyrite using the arsenopyrite geothermometer (Kretschmar & Scott, 1976). The formation temperature is 340 – 360 °C, max. 445 °C. Such values fully correspond to temperature values determined from other localities of arsenopyrite mineralization in Western Carpathians. Temperature values at Dúbrava deposit vary from 395 to 430 °C (Sachan & Chovan, 1991), 320 – 380 °C at Mlynná dolina valley (Majzlan et al., 2001), 445 °C at Nižná Boca (Smirnov, 2000) and 350 – 410 °C at Pezinok - Kolársky vrch deposit (Andraš, et al., 1998).

Very high amounts of monazite in dry heavy minerals concentrates from the vicinity of Au-Ag mineralization do not correlate with accessory amounts of monazite in granitoids of Bratislava massif. This refers to a likelihood that the origin of a part of monazite is joined with the origin of the Au mineralization.

Au mineralization at the Pezinok-Staré Mesto deposit represents typical Au deposits of orogenic type (depth of formation 2 – 5 km, compressional/transpressional

environments), described in Groves et. al. (1998). The deposit is a part of Sb-Au formation, that is developed in crystalline basements of Tatric unit and it is abundant mainly in Nízke Tatry and Malé Karpaty Mts. Three sub-groups of Sb-Au mineralizations it are possible to assign in Western Carpathians: 1. Sb-As-Au (\pm Pb,Cu, Zn), 2. Sb-Au (\pm Pb,Cu,Zn) and 3. Au (Ag \pm Sb,Cu,Pb) mineralization. Dúbrava and Pezinok-Kolársky vrch deposits are typical representants of the first type mineralizations, which are characteristic by the presence of „refractory gold“ fixed mainly in the arsenopyrite. Magurka, Nižná Boca, Mlynná dolina, Dve Vody and Chvojníka deposits belong to the second sub-group, where mainly „visible gold“ and Sb-sulphide/sulphosalt mineralization is present. Third sub-group is characterised by „visible gold“ with a very low content of sulphides (less than 1 % in ores) and the presence of Ag-minerals. This sub group was distinguished according to the similarity of mineral assemblages, paragenesis and the character of mineralization on the Pezinok - Staré Mesto and Kriváň deposits. These deposits are so similar, that it is possible to assign an Au mineralization sub-group on the basis of similarity/dissimilarity compared to other Sb-Au deposits described in Western Carpathians. Noteworthy at Pezinok - Staré Mesto deposit compared to other „visible gold“ deposits in Western Carpathians is the absence of stibnite mineralization in ore bodies and presence of Ag-minerals. Cambel & Khun (1979) and Chovan et al. (1992) showed evidence about genetic relationship of Au and Sb mineralizations at Kolársky vrch and Pezinok - Staré Mesto deposits located at the structural continuation of the Kolársky vrch deposit. Based on the knowledge about other similar deposits (Kriváň deposit, Bakos (2000)) it is very probable that Sb-As-Au ore-like mineralization at Pezinok-Kolársky vrch deposit, mineralization in Ernest adit and gold mineralization at Pezinok-Staré Mesto deposit are genetically related. Some differences can occur due to the different rock composition and other conditions of mineral deposition which have a considerable influence to the deposition of minerals. Various mineralization stages at adjacent deposits did not have to occur at all, or only to a small extent.

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