Low-Sulfidation Type of Epithermal Au-Ag Mineralization Near Pukanec (Central Slovakia Neogene Volcanic Fields)

Branislav BAHNA and Martin CHOVAN

Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University, Bratislava, Slovak republic

ABSTRACT: Precious metal Au-Ag vein type (low-sulfidation) is the youngest epithermal mineralization in the Pukanec ore district. This mineralization is represented by electrum in quartz veinlets intersected in boreholes. Supergene-enriched zones that contain quartz and clay debris, secondary Mn (Fe) oxides and electrum are developed in the near-surface level of Au-Ag mineralization. These zones which were the main object of mining in Middle Ages are enriched in Au, Ag and Mn.

KEY WORDS: epithermal ore deposit, supergene enrichment, electrum.

Introduction

The Pukanec ore district is situated in the Central Slovakia Neogene Volcanic Field in the SW part of the Banská Štiavnica stratovolcano. Beginning of mining was in the 14th century. Maximum of exploitation was in the 15th and the 16th century and the real end of mining was in the last century. Large ancient remnants after the mining indicate significant gold and silver production in Middle Ages.

During the last decades several geological explorations were realized in the Pukanec area. Geologic and paragenetic conditions of ore veins were studied by Harman (1959). In the 60's, the geological mapping on scale of 1:25000 was realized (Brlay, 1965). In the 70's, a complex geological exploration started. Hydrothermal rock alteration was studied by Forgáč and Kupčo (1977), later on by Harman and Forgáč (1988). Geophysical exploration was realized by Filo et al., (1981 and 1983), precious and base metal reserves were assessed by Brlay et al., (1982), the ore mineralization genesis was evaluated by Štohl et al., (1994). Further exploration for Au-Ag mineralization was undertaken by Argosy company in 1995-1997, however borehole did not confirm perspective results from surface exploration (Smolka, 1998). Mineralogy of alluvial gold was investigated by Bahna and Chovan (1999).

Methods

Microscopic study of polished sections, thin sections and double polished sections were done by Zeiss Jena Jenapol microscope. X-ray analyses of powder samples were realized by device DRON-3 (Geological Institute, Faculty of Natural Sciences ips PW 1710 (Geological Institute of Slovak Academy of Science, Bratislava). Conditions: Cu lamp, voltage 35 kV, intensity 20 mA, step 0,02 °2 Θ / 0,8s. Electron microanalysis was realized by device JEOL SUPERPROBE 733, WDS system, ZAF correction (Geological Institute of Dionýz Štúr, Bratislava). Conditions: 20kV, 15nA, beam 5µm, standards: FeAsS-Fe, S, As; HgS-Hg; Ag-Ag; Co-Co; Ni-Ni; PbS-Pb; Cu-Cu; Bi-Bi; Zn-Zn; Sb-Sb; Au-Au; $CaSiO_3$-Ca; MgO-Mg $MnSiO_3$-Mn; $SrTiO_3$-Sr. Standardized EDS analyses were used for carbonates and non-standardized EDS analysis for Mn oxides. Microanalysis of gold was realized by device JEOL JXA 840A, WDS system, ZAF correction (CLEOM, Faculty of natural sciences UK, Bratislava). Conditions: 20kV, 12-15nA, standards: HgS-Hg; Ag-Ag; CuFeS-Cu, Fe; Bi-Bi; Te-Te, Sb-Sb; Au-Au. Au, Ag and Mn contents in samples were determined by AAS analysis (Au and Ag in Geological and Ecological Laboratories, Spišská Nová Ves, Mn in Geological Institute of Slovak Academy of Science, Banská Bystrica). The properties of fluid inclusions were studied by microthermometric device LINKAM THMS 600 (Faculty of Natural Sciences UK, Bratislava). We obtained electrum by panning method from supergene-enriched zones from outcrops and old mining works.

Geologic setting

Pukanec ore district is separated from central volcanic zone by younger caldera and horst volcano-tectonic structures. The Tatiar complex intruded into Badenian pyroxenic andesites and their porphyries. It is formed by north-south dikes of intermediary composition (granodiorite, quartzdiorite and diorite porphyres) (Fig. 1). These intrusions are connected with intensive hydrothermal and metasomatic alteration (silicification, sericitization, chloritization). The end of intrusive activity belongs to rhyolite porphyry dikes (12,1-12,3 Ma) (Štohl et al. 1994).

Characteristic hydrothermal wall-rock alterations and geochemical anomalies accompany various types of mineralization. (Štohl et al. 1994; Filo et al. 1981; Filo et al. 1983). Cu porphyry mineralization stage (considered as the oldest) is spatially overlapped by younger intrusion-related base metal stockwork Pb-Zn mineralization stage. Both types are probably spatially and genetically bounded to the Tatiar intrusive complex (Štohl et al. 1994).

The youngest gold-silver vein stage (low-sulfidation type) created individual vein zones. According to Štohl et al., (1994) it is younger than dikes of rhyolites. Supergene zones enriched in Au, Ag and Mn are developed in the near-surface levels. These zones (exploited in Middle Ages) have north-south direction and occupy a 4×3 km area on the surface (Fig.1). Intensively altered (silicified) andesites form their immediate environment and the intensity of alteration is gradually decreases away from secondary quartzite (adularization, sericitization and propylitization).

The continuation of precious metal mineralized zones were detected (boreholes) under the supergene-enrichment level (cca 40–50 m), but with markedly lower contents of Au and Ag (Smolka 1998). We found quartz veinlets with rare occurrence of gold (electrum) in these boreholes.

Mineral assemblages of primary mineralization

Gold-quartz assemblage we discovered in borehole AP-27 in depth 142–145 m. It is represented by electrum with Ag content about 30 wt. % (Tab. 6), creating wire and flake form (up to

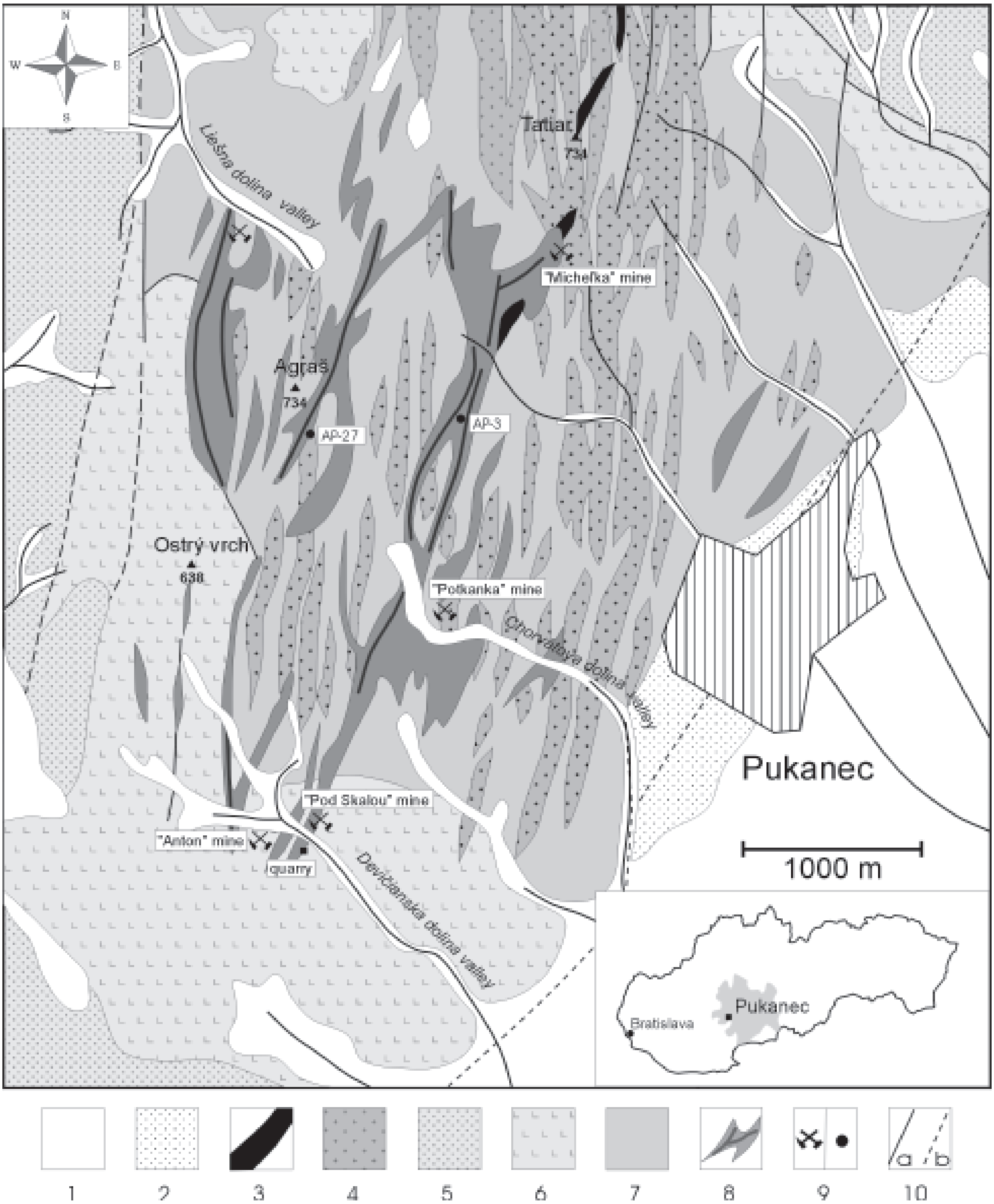

Fig. 1. Geological map of the Pukanec area (based on map compiled by Konečný et al. 1998).
1 – deluvial-proluvial formations of loams and screes, 2 – deluvial sediments (slope loams), 3 – rhyolite and rhyolite porphyries, 4 – pyroxene andesite, 5 – Tatiar intrusive complex (diorite, quartz-diorite and granodiorite porphyry), 6 – leucocrate to pyroxene andesite, 7 – complex of propylitized andesites, 8 – argillites and main ore veins, 9 – studied mines and boreholes, 10 – faults: a) observed, b) hidden.

1 mm in size) in drusy cavities of quartz. Silicificated, sericitized and pyritized clasts of andesites are cemented by quartz with breccia texture. Adularia is rarely present in quartz veinlets (up to 1 cm in size). Because the core recovery was very low in the section 142–145 m, it is not possible to characterize this mineralization in detail. However, it is the first description of primary gold in quartz from the Pukanec area. Gold in quartz gangue from old mine dumps has not been found.

	PU-111	PU-112	PL-29a1	PL-29a2	PL-29a3
			weight %		
S	53.96	52.54	51.63	53.97	52.86
Fe	46.26	45.89	45.46	47.10	46.83
As	0.00	0.00	1.30	0.00	1.18
Cu	0.00	0.00	0.03	0.00	0.00
Ni	0.00	0.01	0.02	0.00	0.01
Total	100.31	98.43	98.44	101.07	100.88
			atomic %		
S	66.97	66.60	65.93	66.62	65.87
Fe	33.03	33.40	33.32	33.38	33.50
As	0.00	0.00	0.71	0.00	0.63
Cu	0.00	0.00	0.01	0.00	0.00
Ni	0.00	0.00	0.02	0.00	0.00

Sb, Au and Co = 0

Tab. 1. Chemical composition of pyrite from quartz-carbonate gangue.

	1	2	1	2
	wt. %		at. %	
S	11.77	12.30	46.37	47.22
Pb	86.59	87.47	52.77	51.96
Fe	0.12	0.12	0.27	0.27
Cu	0.30	0.29	0.59	0.55
Total	98.78	100.18	100.00	100.00

Sb, Ag and Bi = 0

Tab. 2. Chemical composition of galena from quartz-carbonate gangue.

Chalcopyrite-galena-sphalerite assemblage belongs to primary mineralization. This assemblage was found in samples from old mine dumps (Liešna dolina valley) and in borehole AP-3 at depth of 151 m. Ore minerals are represented by chemically pure pyrite without significant content of Cu, Ni, Co, Sb, Au and in 3 analyses also As (Tab. 1). Higher content of Fe and Cu in galena (Tab. 2) connected with intergrowth of chalcopyrite and galena. Sphalerite belongs to major minerals of this assemblage. Grain size of sulphides is up to 5 mm. Gangue minerals are coarse-grained quartz and calcite (Tab. 3). Wallrock alterations are silicification and sericitization. Altered clasts of andesites are cemented by quartz and calcite with brecciated texture.

Rhodonite-Mn carbonate assemblage we have assigned to primary hydrothermal mineralization. Minerals of this assemblage were identified on old dumps around the Micheľka shaft (Fig. 1). Mn and Mn-Ca silicates, Mn carbonates, calcite and quartz are in fragments of vein filling. Pink Mn mineral phases correspond to silicates: rhodonite (Tab. 4, anal.1,2, Fig. 3) and with increased Ca content to bustamite (Tab. 4, anal. 3,4,5, Fig. 3). White colored carbonates have chemical composition similar to calcite with increased content of manganese, phases are changing from manganocalcite to pinkish rhodochrosite (Tab. 5). Pyrite and chalcopyrite represent rare ore minerals. Altered andesite clasts are cemented by quartz, rhodonite and Mn carbonates with breccia texture. Somewhere the texture is colloform and concentrically zoned. Younger minerals are manganese oxides that replace primary minerals along fissures. In this secondary Mn minerals the content of MnO_2 is 76,5–82,8; CaO is 2,9–3,1; SiO_2 is 0,5–1,8 wt. % (EDS). Contents of K_2O and MgO are 0,X wt. %. Occurrence of this mineral assemblage has not been observed in Pukanec area until now.

	$CaCO_3$	$MnCO_3$	$FeCO_3$	Total
PU-111	97.97	1.13	0.66	99.76
PU-112	100.29	0.00	0.00	100.29
PU-113	98.34	1.69	0.00	100.03
PU-114	100.39	0.00	0.00	100.39
PU-115	99.06	1.15	0.00	100.21
PU-151	98.88	1.78	0.00	100.66
PU-152	98.73	1.13	0.50	100.37
PU-153	99.75	0.44	0.00	100.29
PU-154	99.06	0.91	0.00	99.97
PL-19c1	99.43	0.66	0.00	100.09
PL-19c2	97.63	1.96	0.61	100.20
PL-19c3	98.11	1.44	0.00	99.55

Tab. 3. Chemical composition of calcite from quartz-carbonate gangue (weight %).

	1	2	3	4	5
SiO2	44.90	44.67	48.10	48.58	47.98
MnO	43.73	47.55	26.89	26.15	27.56
CaO	8.70	6.33	20.21	19.72	20.43
FeO	1.28	1.67	1.06	1.84	1.64
Al2O3	0.19	0.25	0.46	0.42	0.30
MgO	0.00	0.00	3.06	3.40	2.66
Cr2O3	0.21	0.26	0.00	0.00	0.00
Total	99.01	100.73	99.78	100.11	100.57

Tab. 4. Chemical composition of rhodonite and bustamite (EDS).

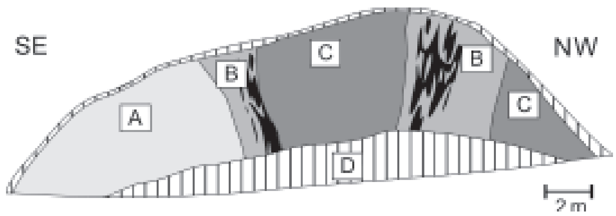

Fig. 2. Schematic sketch of quarry in Devičianska dolina valley. A – argillitized andesites, B – intensively altered andesites (sericitization, adularization) and supergene-enriched zones (black), C – secondary quartzites, D – debris.

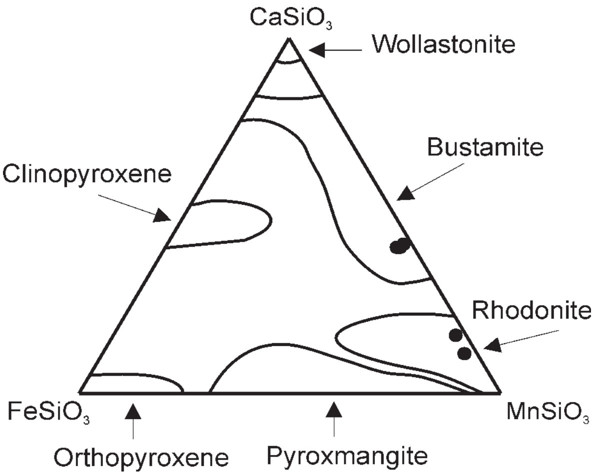

Fig. 3. Projection of chemical composition of rhodonite and bustamite from Pukanec in ternary diagram of $CaSiO_3$, $MnSiO_3$ and $FeSiO_3$ (atomic proportions). Fields after Brown et al. 1980.

	$CaCO_3$	$MnCO_3$	$FeCO_3$	Total
1	100.29	0.00	0.00	100.29
2	100.39	0.00	0.00	100.39
3	99.06	1.15	0.00	100.21
4	98.34	1.69	0.00	100.03
5	97.97	1.13	0.66	99.76
6	90.02	10.41	0.00	100.43
7	83.38	16.32	0.00	99.70
8	78.76	19.69	0.81	99.26
9	22.24	75.77	1.45	99.46
10	22.15	75.82	1.71	99.68

Tab. 5. Chemical composition of calcite and Mn carbonates from the rhodonite assemblage (WDS) – weight %.

	PŠ-231	PŠ-233	PŠ-263	PŠ-261	PŠ-262	AP27/145
Au	62.48	62.58	54.55	62.63	61.34	69.62
Ag	37.06	36.59	43.27	34.53	37.21	30.35
Bi	0.16	0.34	0.21	0.43	0.44	0.00
Hg	0.14	0.48	0.21	0.37	0.37	n.a.
Fe	0.19	0.18	0.21	0.25	0.26	0.24
Te	0.13	0.07	0.07	0.27	0.29	n.a.
Cu	0.11	0.07	0.11	0.12	0.12	0.09
Sb	0.00	0.09	0.05	0.07	0.08	0.14
Tot.	100.26	100.40	98.69	98.66	100.11	100.42
F	628.00	631.00	558.00	645.00	622.00	696.00

F fineness, n.a. – not analysed

Tab. 6. Selected electron microanalysis of electrum from supergene-enriched zones samples PŠ 23, PŠ 26 and from gold – quartz assemblage sample AP 27/145 (weight %)

Localization	Au (ppm)	Ag (ppm)	Mn (%)
Potkanka adit	1.17	32.30	1.82
quarry	2.51	86.00	1.92
Pod Skalou adit	15.40	134.00	4.10

Tab. 7. Au, Ag and Mn contents in supergene-enriched zones.

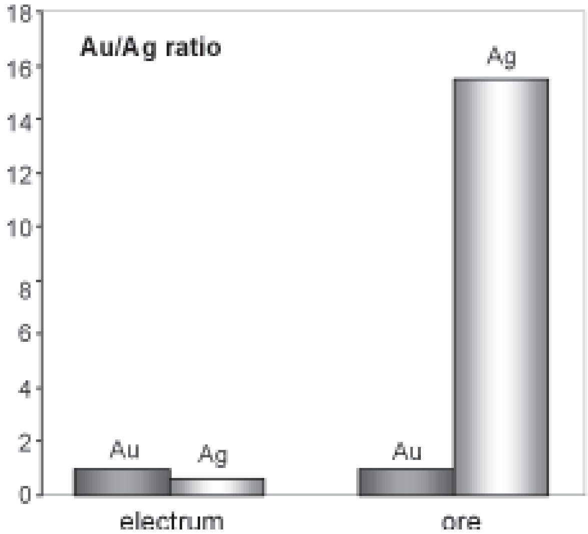

Fig. 4. Average Au/Ag ratio in electrum grains and in filling of enriched zones (ore), calculated on 1 Au.

Mineral assemblage of supergene-enriched zones

Supergene-enriched zones in near-surfaces levels of primary precious metal mineralization have the character of tectonic breccias. These zones we identified in old quarry in Devičianska dolina valley (Fig. 1), they are located on interfaces of silicificated andesites and less altered andesites (adularized and sericitized) (Fig. 2). Silicified rocks are intensively pyritized. In pyrite grains we detected high content of gold (296–1100 ppm) by quantitative spectrochemical analysis.

Mineralized zones we identified also in the Potkanka adit (Chorvátova dolina valley), Anton adit and Pod Skalou adit (Devičianska dolina valley) (Fig. 1). These zones have north-south direction, dipping 40–70° to the east, their thickness is 0.5–2 m.

The filling of mineralized zones is formed by tectonic breccia. Fragments of leached vuggy quartz and altered andesites are cemented by mixture of clay minerals (montmorillonite) and secondary Mn(Fe) oxides (X-ray – amorphous) which black-colourize these zones. In these secondary Mn minerals the content of MnO_2 is 27.1–86.2; Fe_2O_3 is 0–51.6; SiO_2 is 1.6–4.1 wt.% (EDS). Contents of K_2O, CaO and BaO are 0,X wt.%. Limonitized grains of pyrite are also present. Locally pyritized rocks are altered to mixture of jarosite, gypsum and clay minerals (X-ray). In clay filling contains electrum wires, flakes and skeletal grains (up to 0,2 mm in size) (Bahna and Chovan 1999). The chemical composition of electrum is relatively uniform and contains 34,5–43,3 wt. % of Ag (WDS) (Tab. 6).

Analyses (AAS) of enriched-zone filling showed contents of Au 1.17–15.4 ppm and Ag 32.3–134.0 ppm. Mn content was 1.8–4.1% (Tab. 7). Au/Ag ratio in electrum grains differs from that in clayey filling (ore) (Fig. 4). Argentiferous minerals, on which Ag content might be fixed were not found in these zones. It is likely that Ag is adsorbed on Mn oxides.

Fluid inclusions

Microthermometric study was carried out on samples from outcrops, boreholes and old miner works. Using the criteria of Bodnar (1992); Ďurišová and Hurai (1991), the heating and freezing measurements were selectively conducted on primary fluid inclusions trapped in the quartz and calcite. All the fluid inclusions are two-phase (L+V) with prevalence of liquid phase at room temperature and they were homogenized to liquid phase at heating runs. No daughter minerals, other phases (clathrate e. g.) and no presence of CO_2 were observed.

The fluid inclusions in both quartz and calcite displayed high melting temperatures between −0.1 and −1.6 °C that is indicative of apparent salinites ranging from 0.2 to 3.0 wt.% NaCl equivalent (Bodnar 1992). Temperatures of homogenization range from 140 to 270 °C (quartz) and from 200 to 310 °C (calcite) (Tab. 8, Fig. 5).

The salinity of inclusions from calcite decreases from 1.8 to 0.2 wt.% NaCl equivalent with decreasing homogenization temperature (from 310 to 200 °C) (Fig. 5A). We interpret this trend as an effect of diluting fluids due to mixing with meteoric water.

	Homogenization (Th)			Melting of ice (Tm)			Salinity NaCl eq. (wt.%)			Size (mm)		
	range (°C)	avg.(°C)	n	range (°C)	avg.(°C)	n	range	avg.	n	range	avg.	n
quartz												
AP – 27/144	140 to 248	197	20	− 0.8 to − 0.2	− 0.4	20	0.4 to 1.5	0.7	20	9 to 34	15	22
AP – 27/145	164 to 276	206	24	− 1.3 to − 0.1	− 1.3	30	0.2 to 2.4	0.9	30	9 to 43	18	30
PU – 7	186 to 256	231	14	− 1.6 to − 1.0	− 1.2	13	1.8 to 3.0	2.2	13	11 to 31	21	14
DE – 28	202 to 215	208	13	− 0.5 to − 0.1	− 0.3	21	0.2 to 0.9	0.5	21	14 to 71	32	25
PM – 3	228 to 268	257	31	− 0.8 to − 0.1	− 0.4	31	0.2 to 1.5	0.8	31	9 to 51	20	31
calcite												
PU – 9	241 to 312	256	34	− 0.8 to − 0.4	− 0.6	22	0.7 to 1.5	1.1	22	6 to 57	20	34
PU – 15	202 to 268	240	24	− 1.0 to − 0.1	− 0.5	24	0.2 to 1.8	0.9	24	14 to 57	25	24
DE – 29	207 to 253	231	40	− 0.6 to − 0.1	− 0.4	15	0.2 to 1.1	0.7	15	7 to 61	21	40
PU – 11	218 to 268	253	15	− 0.6 to − 0.1	− 0.4	15	0.2 to 1.1	0.7	15	11 to 57	27	15

Tab. 8. Fluid inclusions data.

Discussion and Conclusions

In the last decades two genetic types of epithermal mineralization were identified during geological explorations in the Pukanec area. Cu porphyry mineralization together with overprinted intrusion-related base metal stockwork mineralization stage (high-sulfidation) are older than gold-silver vein stage (low-sulfidation) that was exploited in the Middle Ages (Štohl et al. 1994). Our research in outcrops, old miners works and boreholes showed that the main object of ancient exploitation was supergene zone enriched in Au, Ag and Mn.

The chalcopyrite – galena – sphalerite assemblage occurring in quartz-carbonate gangue probably belongs to precious metal stage determined by Petr in Smolka et al. (1988), Smolka et al. (1987).

The rhodonite-Mn carbonate assemblage we assigned to primary hydrothermal mineralization. Occurrence of this mineral assemblage in Pukanec area has not been observed yet. Koděra et al. (1986) describe rhodonite as the main component of gangue in the oldest mineralization periods in near-surface level of Terézia vein and Kovalenker et al. (1991) describe presence of rhodonite in quartz-hematite, sphalerite and rhodonite-carbonate-quartz stage in the Banská Štiavnica ore district. Mineral assemblage of primary mineralization (rhodonite-Mn carbonate-Cu, Pb, Zn sulphides-gold) observed in Pukanec is similar to the third mineral stage of the Banská Štiavnica deposit (Kovalenker et al. l.c.). The gold-quartz assemblage we discovered in a borehole.

In the archive records there are several references about gold occurrence in environment that correspond to our results (Zamboj 1975; Uher 1999). Gold origin in the supergene-enriched zones of the Pukanec area has not been exactly approved yet. We assume a secondary origin of electrum.

Webster and Mann (1984) and Webster (1986) describe the origin of secondary electrum in Mn enriched zones at Wau in Papua New Guinea. Primary ore comprise calcite with finely divided electrum (fineness 400–670), manganocalcite, quartz, pyrite and argentite that are in massive subhorizontal carbonate lodes. In the oxidized zone the coarse, crystalline secondary electrum (fineness 430–650) is concentrated in lenses and stockworks of residual lode of manganese dioxide at the water table. The enrichment relates to gold reprecipitation from the thiosulphate complex $Au(S_2O_3)_2^{3-}$, $Ag(S_2O_3)_2^{3-}$, eventually $(Au,Ag)\ (S_2O_3)_2^{3-}$ as weathering fluids mixing with ground water undergo dilution and significant change in pH and oxidation potential. This is possible only in neutral to alkali environment.

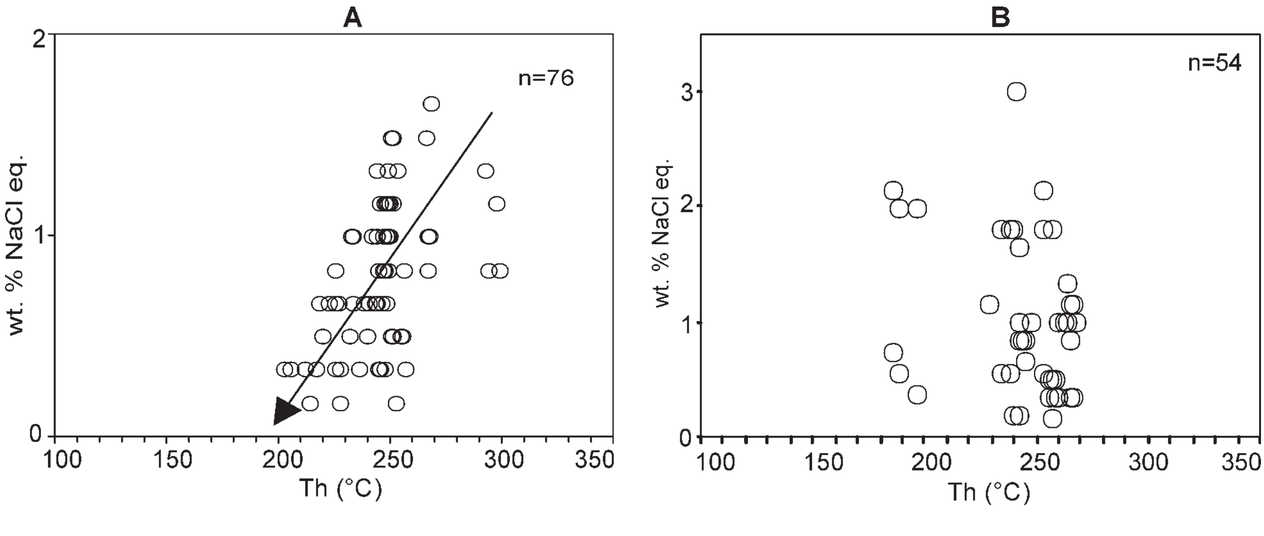

Fig. 5. Homogenization temperatures (Th) versus salinity for fluid inclusions from calcite (A) and quartz (B).

The high degree of gold remobilization and low fineness of the secondary electrum may also be interpreted in terms of thiosulphate complexing. Silver grades are high in both, the primary and oxidized ore, where mineralization includes electrum, argentite, rare native silver and secondary argentiferous manganese oxides (e. g., todorokite). Gold solubility in the weathering fluid may therefore be enhanced by the presence of dissolved silver generated by oxidation of co-existing silver mineralization (Webster 1986).

Electrum in supergene-enriched zones in Pukanec area could possibly have a similar genesis because electrum, carbonates and Mn minerals are present in primary mineralization. An open question is the existence of silver in enriched zones, where the Au/Ag ratio is different in electrum grains and in clayey Mn filling of enriched zones. In these zones individual argentiferous minerals were not found. Silver content is probably fixed in secondary Mn oxides.

Similar situation to Wau occurs also in the locality Pongkor (Indonesia) where primary rhodonite have been altered to Mn and Fe oxides forming coatings or interbeds between the quartz bands. These pockets with quartz and clay debris are rich in secondary electrum (Milési et al. 1999).

Gasparrini (1993) suggests for situations when it is not possible to determine the presence of Ag minerals by EDS-SEM analyses, and where a correlation between Mn and Ag content (determined by chemical analyses) is significant, that Ag is bound in manganese oxides.

Altered andesites in the quarry in Devičianska dolina valley are strongly pyritized. Separated pyrite is rich in gold (296–1100 ppm). Gold probably occurs in pyrite as metallic inclusions but have not observed them.

Thermometric study of fluid inclusions in quartz and calcite gives basic data about salinity and homogenization temperature of fluids. In inclusions from calcite the decreasing salinity was observed together with decreasing homogenization temperature. This trend according to Jeleň et al. (1987), Jeleň (1988), Bebej (1993), Jeleň in Chovan, Háber, Jeleň, Rojkovič, (eds.) (1994) suggests diluting fluids due to mixing with meteoric waters.

Character of wallrock alterations as well as other observed facts (mineral assemblages, fluid inclusions, etc.) point, according to several authors (e.g. Henley 1985; Hayba et al. 1985; Heald et al. 1987; White and Hedenquist 1990; Hedenquist 1995 and others), to low-sulfidation type of epithermal Au-Ag mineralization that has been already determined by Štohl et al. (1994) in the Pukanec area. The most important are supergene-enriched zones of near-surface levels of the deposit, that was almost completely exploited in the Middle Ages.

Acknowledgements

Research is part of project "Metalogenetic valuation of Slovak Republic" Geological Survey of Slovak Republic (GSSR). We would like to thank to B. Bartalský and Ľ. Ma•o (company Argosy s.r.o.) for co-operation. Our thanks are also due to J. Lexa and V. Hurai (GSSR), M. Huraiová (Comenius University) and to P. Andráš and Ľ. Puškelová (Geological Institute of Slovak Academy of Sciences) for analysis.

References

BAHNA B. and CHOVAN M., 1999. Morphology and chemical composition of gold from Pukanec. *Miner. slovaca*, 31: 259-262. (in Slovak)

BEBEJ J. 1993. Volatile components in hydrothermal systems and their significance for interpretation of the genesis of deposits. Part 1: Review. *Miner. slovaca*, 25: 292-300. (in Slovak)

BODNAR R.J., 1992. Revised equation and table for determinating the freezing point depression of H2O-NaCl solutions. *Geochim Cosmochim Acta*, 57: 683-684.

BRLAY A., 1965. Report about base geological exploration in Pukanec (year 1964). Manuskript-Geofond, Bratislava. (in Slovak)

BRLAY A., (ed), 1982. Determination of reserves of base and precious metal ores in Rudno, Brehy and Pukanec area. Manuskript-Geofond, Bratislava, 127. (in Slovak)

BROWN P. E., ESSENE E. J. and PEACOR D. R., 1980. Phase relations inferred from field data for Mn pyroxenes and pyroxenoids. *Contributions to Mineralogy and Petrology*, 74, 4, 417-425.

ĎURIŠOVÁ J. and HURAI V., 1991. Fluid inclusions in minerals. Academia Praha, 105. (in Czech)

FILO M., BLÁHA V. and STRÁNSKA M., 1981. Geophysical exploration of metalogenetic zone Rudno–Brehy–Pukanec. Manuskript-Geofond, Bratislava, 41. (in Slovak)

FILO M., KURKIN M. and LIZOŇ I., 1983. Partial final report for period 1981-1983. Investigation geophysical exploration, II. stage, Varta, Agraš-Tatiar, Šementlov area. Manuskript-Geofond, Bratislava, 42. (in Slovak)

FORGÁČ J. and KUPČO G., 1977. Hydrothermal alterations of rock in zone Rudno-Brehy-Pukanec-Nová Baňa (Partial final report). Manuskript-Geofond, Bratislava, 61. (in Slovak)

GASPARRINI C., 1993. Gold and other precious metals. Springer-Verlag Berlin, Heidelberg, 336.

HARMAN M., 1959. Review of geologic and paragenetic conditions of ore veins around the Pukanec. *Acta geol. geogr. Univ. Comen. Geol.*, 2, Bratislava, 34-47. (in Slovak)

HARMAN M. and FORGÁČ J., 1988. Geochemistry and mineralogy of altered rocks in Tatiar intrusive complex (Štiavnické vrchy Mts.). *Geol. Carpathica*, 39: 437-453. (in Slovak)

HAYBA D.O., BETHKE P.M., HEALD P. and FOLEY N.K., 1985. The geological, mineralogical and geochemical characteristics of volcanic-hosted epithermal deposits. In: Berger B.R. and Bethke P.M., (eds), Geology and Geochemistry of Epithermal Systems. Soc. Econ. Geol., *Rev. Econ. Geol.*, 2: 129-168.

HEALD P., FOLEY N.K. and HAYBA D.O., 1987. Comparative anatomy of volcanic-related epithermal deposits: acid-sulfate and adularia-sericite types. *Econ. Geol.*, 82: 1-26.

HEDENQUIST J.W., 1995. Origin of and exploration for epithermal gold deposits. Dept. of Mineralogy, Eötvös Loránd University, Budapest.

HENLEY R.W., 1985. The geothermal framework of epithermal deposits. In: BERGER B.R. and BETHKE P.M., (Editors), Geology and geochemistry of epithermal systems, Society of Economic Geology, *Rev. Econ. Geol.*, 2: 1-24.

CHOVAN M., HÁBER M., JELEŇ S. and ROJKOVIČ I. (eds.), 1994. Ore textures in the Western Carpathians, Slovak Academic Press, Bratislava.

JELEŇ S., 1988. Mineral assemblages and formation conditions of ores in the Banská Štiavnica deposit. PhD Thesis, GÚSAV, Banská Bystrica. (in Russian)

JELEŇ S., GENKIN A. D., KOVALENKER V. A., LAPUTINA I. P., SANDOMIRSKAYA S. M. and GAZDÍK R. 1987. Au-

Ag mineralization of the Terézia vein in the Banská Štiavnica deposit. *Geol. Zborník Geol. Carpath.*, 38, 615-640. (in Russian)
KODĚRA M. (ed), 1986. Topographic mineralogy of the Slovakia I., Veda, Bratislava, s. 1590. (in Slovak)
KONEČNÝ V. (ed), 1998. Geological map of the Štiavnické vrchy Mts. (1:50000). Publishing house of Dionýz Štúr, GSSR, Bratislava. (in Slovak)
KOVALENKER V.A., JELEŇ S, LEVIN K.A., NAUMOV V.B., PROKOFYEV V.Yu. and RUSINOV V.L., 1991. Mineral assemblages and physical-chemical model of the formation of gold – silver – polymetallic mineralization on the deposit Banská Štiavnica (Central Slovakia). *Geol. Carpathica*, 42: 291-303.
MILÉSI J.P., MARCOUX E., SITORUS T., SIMANDJUNTAK M., LEROY L. and BAILLY L., 1999. Pongkor (West Java, Indonesia): a Pliocene supergene-enriched epithermal Au-Ag-(Mn) deposit. *Mineral. Deposita*, 34: 131-149.
SMOLKA J., 1998. Pukanec, Au-Ag, VP. Final report. Manuskript-Geofond, Bratislava, 31. (in Slovak)
SMOLKA J., DAUBNER J., KÁMEN M. and PETR K., 1987. Prospect of the Pukanec ore district from the point of view of realized prospecting works, Central Slovakia. *Miner. slovaca*, 19, 6. (in Slovak)
SMOLKA J., (ed), 1988. The final report Rudno-Brehy-Pukanec (Pb-Zn-Cu). Manuskript-Geofond, Bratislava, 108. (in Slovak)
ŠTOHL J., LEXA J., KALIČIAK M. and BACSÓ Z., 1994. Genesis of stockwork base metal mineralizations in the Neogene volcanics of West Carpathians. *Miner. slovaca*, 26, 2: 75-118. (in Slovak)
UHER P., 1999: A scientific tour of Edward Daniel Clark, an English mineralogist, to the Middle Slovak gold and silver deposits in 1802. *Miner. slovaca*, 31: 425-428. (in Slovak)
WEBSTER J.G., 1986. The solubility of gold and silver in the system Au-Ag-S-O2-H2O at 25 °C and 1 atm. *Geochim. Cosmochim. Acta*, 50: 1873-1845.
WEBSTER J.G. and MANN A.W., 1984. The influence of climate, geomorphology and primary geology on the supergene migration of gold and silver. *J. Geochem. Explor.*, 22: 21-42.
WHITE N.C. and HEDENQUIST J.W., 1990. Epithermal environment and styles of mineralization: variations and their causes, and guidelines for their exploration. In: Hedenquist, J.W., White, N. C. and Siddeley, G., (eds), Epithermal gold deposits of Circum-Pacific: Geology, Geochemistry, Origin and Exploration, II. *J. Geochem. Explor.*, 36: 445-474.
ZAMBOJ J., 1975. Pukanec. Osveta, Martin, 329. (in Slovak)

Chemical Evolution of Volcanic Rocks in the Altenberg - Teplice Caldera (Eastern Krušné Hory Mts., Czech Republic, Germany)

Karel BREITER[1], Jiří K. NOVÁK[2] and Marta CHLUPÁČOVÁ[3]

[1] *Czech Geological Survey, Geologická 6, CZ-152 00 Praha 5,Czech Republic*
[2] *Institute of Geology, Academy of Sciences of the CR, Rozvojová 135, CZ-16502 Praha 6, Czech Republic*
[3] *PETRAMAG, Boháčova 866/4, CZ-14900 Praha 4, Czech Republic*

ABSTRACT: The volcanic sequence of the Altenberg-Teplice caldera (ATC) in the Eastern Krušné Hory Mts./Erzgebirge, was studied at the pilot borehole of Mi-4 (Mikulov) using lithogeochemical data, petrological methods and magnetic susceptibility measurements. The dacitic and rhyolitic ignimbrites and tuffs, as well as shallow subvolcanic rhyolite and post-caldera dykes of granite porphyry are products of a fractionated, zonally arranged magma chamber. Two older units (basal rhyolite-BR and dacite-DC are calc-alkaline in character. Three younger units, traditionally termed as the Teplice rhyolite (TR1-TR3) have high-K calc-alkaline to A-type chemistry. The vertical compositional zoning and the reverse geochemical evolution within the three youngest volcanic phases (TR1-TR3) is confirmed. The successive cycles are shifted from more evolved (acid) types at the basis toward less fractionated (more basic), cumulate-rich magmas at the top of each unit. It is likely the result of a combination of the step-by-step exhausting of stratified magma reservoir.

KEY WORDS: rhyolite, dacite, magma evolution, caldera, Krušné Hory Mts.

Introduction

In 1928, Moesta first interpreted large complex of volcanic and subvolcanic rocks in the Eastern Krušné Hory Mts. (the Teplice Rhyolite -TR) as remnants of a late Variscan caldera, now termed the Altenberg-Teplice caldera (ATC).

Purpose of this contribution is to present basic data of evolution of the magma produced from the Teplice volcano obtained during new processing of the deep borehole Mi-4 (drilled in 1983–84) and of lithogeochemical data sets gathered by the Czech Geological Survey in the seventies.

Geological settings

The Altenberg–Teplice Caldera (ATC) is situated in the Eastern Krušné Hory Mts. (Osterzgebirge) between towns of Teplice (Czech Republic) in the south and Dippoldiswalde (Saxony) in the north (Hoth et al. 1995).

The ATC is 18×35 km (500 km^2) in area. Country rocks of the ATC consist mainly of Proterozoic polyphase metamorphosed granitoids and paragneisses intruded by Carboniferous monzogranites of the pre-caldera Fláje pluton (G1). The crystalline footwall of the caldera dips at an angle of c. 20° east-