

# MINERALOGICAL, FLUID INCLUSION AND STABLE ISOTOPE STUDIES OF THE BANSKA ŠTIAVNICA EPITHERMAL PRECIOUS AND BASE METALS DEPOSIT IN THE CENTRAL SLOVAKIA

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**Abstract:** The results of scientific investigations of mineralogy, fluid inclusions and stable isotopes of epithermal precious and base metals ores at Biber, Rozalia and Terezia vein systems and subepithermal gold-quartz ores at Svetozar vein system are discussed. The main physico-chemical parameters of ore-forming process and the factors of metal concentration in ore determined.

**Key words:** stable isotopes, fluid inclusions, minerals, epithermal, gold, ore, base metals, mineral assemblage

## Introduction

The problems of the origin of epithermal precious and base metals ores during many decades are in the center of attention of ore geologists dealing both with elaboration of ore-formation theory and prospecting of deposits. However in spite of many investigations during last years many questions concerning regularities of evolution of ore-forming process, factors and mechanisms remain disputable. Therefore the detail study of the peculiarities of mineral-forming process in typical epithermal deposits using modern methods are actual.

The deposits of precious and base metals of Štiavnica-Hodruša ore field have many centuries history of extraction and geologic investigations. During last years owing to the works of slovakian specialists many questions concerning interrelations of metallogenesis and magmatism, the stages and zonality of ores were determined, the models of developing of ore-forming systems, which have formed mineralization in this ore field were proposed (Burian et al., 1985; Konečný et al., 1995; Haber et al., 2001; Lexa et al., 1999; Maťo et al., 1996; Štohl et al., 1994).

In this report we accent the attention on epithermal vein mineralization with discussion of the results of detail investigations of mineralogy, fluid inclusions and stable isotopes which were performed last ten years in the frames of scientific cooperation between Academies of Sciences of Slovakia and Russia.

## Geologic setting

The Štiavnica-Hodruša ore field is situated in Neogene volcanic belt of inner arc of West Carpathians. It is placed in Central zone of one of grades in Europe Štiavnica stratovolcano. In the limits of Štiavnica-Hodruša ore field are developed some types of hydrothermal deposits (magnetite skarn; porphyry/skarn and porphyry Cu±Mo, Au; intrusion related base metals stockwork/disseminated; base metal replacement and vein subepithermal gold-quartz) associated with subvolcanic granodiorite complex and having also the main economic value low sulphidation Au-Ag-base metal epithermal vein, which are connected to the system of extended faults tied with the horst elevation, and sulfide-poor Au-Ag-quartz mineralization, associating closely in space and time with emplacement of rhyolite ( Lexa et al., 1999). In the limits of ore field are known more than 120 epithermal ore veins extended from 1-3 to 5-7 km with overage thickness 0.8-1.1 m and in places up to 10-15 m, and with vertical extend from 200-300 m up to 700-900 m.

The epithermal vein ores are distributed in the limits of ore field zonality: in the inner zone are situated Au-Ag-Bi-Cu-base metals ores, in the intermediate - Au-Ag- base metals (Au : Ag ~ 1:100), in the external – Au-Ag-quartz (Au : Ag ~ 1:10). In the same order take place the change of the types of mineralization in direction from the deep to the surface parts of the veins (Burian et al., 1985; Štohl et al., 1994). The spatial extend of epithermal veins and their zonality correspond roughly to the extend of granodiorite bell-jar complex ( Lexa et al., 1999).

## Mineralogy and parageneses

In the difference from many low-sulphidation type of epithermal deposits, the epithermal ores of Banská Štiavnica are characterized by extraordinary variety of mineralogy. In this ores beside wide-spread sphalerite, galena, pyrite, chalcopryrite and hematite was established great number of ore minerals, including of pyrrotite, bornite, calcocite, sulfides, selenides and tellurides of Ag, sulphosalts of systems Ag-Cu-Pb-Bi-S and Ag-Cu-Sb-As-S, native gold, silver, electrum, etc.

On the base of structural investigations in the history of formation of the Banská Štiavnica epithermal ores we distinguish some distinctly manifested stages, the number of which could vary from 4 to 6 in dependence from spatial place in mineralogical zonality and type of ores. In particular we have should (Haber et al., 2001; Kovalenker et al., 1991), that epithermal vein ores of the štiavnica type were formed during five mineralization stages: **I** -Hematite-quartz (with rhodonite, rodochrosite, minor sulfides ); **II**-Sphalerite (with galena, chalcopryrite, pyrite, quartz); **III** – Rhodonite –carbonate – quartz (with minor sulfides); **IV** – Galena- chalcopryrite (with sphalerite, hematite, pyrite, native gold, Ag-Cu-Pb-Bi-sulphosalt, Ag-Cu-Sb-As-sulphosalt, sheelite, quartz) and **V** –Sulphosalt- barite (with quartz, , carbonates, pyrite, kleiofan, chalcopryrite, acantite, Ag-Sb-sulphosalt, fluorite).

### Fluid inclusion studies

By the methods thermo- and cryometry ( THMSG-600 Linkam) in quartz, sphalerite, barite and fluorite were studied individual fluid inclusions ( FI, total >2700 FI from 95 samples characterizing the ores of vein systems Biber, Rozalia, Špitaler, Terezia, Terzia-Waiden and Svetozar). The pressure were evaluated mainly by the pressure of water steam (the pressure of CO<sub>2</sub> don't extend 4.5-0.5 bar). The results of investigation are summarized in the table 1. By the methods of gas and ion chromatography in 35 samples of quartz and sphalerite from the ores of vein systems Biber, Špitaler, Terezia and Terzia-Waiden is studied the gas phase of FI (H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>) and is determined the anion composition of solutions (Cl<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), and by the methods of flame spectrometry – also concentration of Na<sup>+</sup> и K<sup>+</sup>.

The received data show that deposition of minerals of subepithermal and epithermal ores of all investigated types took place from heated boiling solutions of chloride Mg- Na composition. The temperatures of formation of Au-Ag-Bi-Cu-base metals ores were in the interval 347-145 °C, salinity varied from 11.6 to 0.5 wt.% eq.. NaCl, and maximal pressure reached 247 bar. Close parameters were in solutions deposited the minerals of Au-Ag- base metals (accordingly 353-145 °C and 12.1-0.2 wt.% eq.. NaCl), and Au-Ag-quartz ores (accordingly 310-151 °C and 10.4-0.4 wt.% eq.. NaCl), but the pressure reached only 90-100 bar.. The solutions deposited subepithermal Au-quartz ores had the temperatures from 348 to 162 °C, varying in not great limits of salts concentration (6.5-0.5 wt.% eq.. NaCl) by maximal pressure up to 156 bar.

In the composition of gas phase of oreforming fluids main component is vaporlike H<sub>2</sub>O (80.16-99.89 mol.%), constantly are present varying quantities of CO<sub>2</sub> ( 0.11-19.34 mol.%) and, rarely, - CH<sub>4</sub> (0.00-0.11 mol.%), N<sub>2</sub> (0.00-0.69 mol.%). Among anions the main role have chlorine (0.02 –1.39 m/kg H<sub>2</sub>O) and fluor ( 0.02-0.57 m/kg H<sub>2</sub>O), rarely is present SO<sub>4</sub><sup>2-</sup> (0.00-0.09 m/kg H<sub>2</sub>O). Na<sup>+</sup> (0.02-0.65 m/kg H<sub>2</sub>O) usually prevail over K<sup>+</sup> (0.01-0.20 m/kg H<sub>2</sub>O).

### Stable isotope studies

Were performed 370 determinations of δ<sup>34</sup>S in all main sulfide minerals and barite, about 100 determinations δ<sup>18</sup>O в quartz, barite, carbonate, sheelite and hematite, and more than 20 determinations δ<sup>13</sup>C in carbonates composing epithermal ores at Biber, Rozalia, Spitaler and Terezia vein systems (table 2). These data show, that isotope composition of sulfur of sulfides of different types of Banska Štiavnica epithermal ores are characterized by significant variations of δ<sup>34</sup>S. But average values of δ<sup>34</sup>S in similar minerals from different vein systems are enough similar, particularly in sphalerites, galenas and chalkopyrites (table 2). Calculated values of δ<sup>34</sup>S<sub>H<sub>2</sub>S</sub> of fluids which have deposited sulfides in different vein systems are also practically constant (vary from 5 to 6‰). However, the sulfides of subepithermal ores of Svetozar vein system as a whole

have more narrow (from -1.0 to 6.7 ‰) interval of  $\delta^{34}\text{S}$  variations, which show the relatively constant and low  $\text{SO}_2/\text{H}_2\text{S}$  in solutions (Mat'o et al., 1996).

The values of  $\delta^{18}\text{O}$  in gangue minerals (table 2), and their calculated values in the water of ore-forming solutions (from -8.1 to 5.9 ‰) varied greatly, testifying both the changing of physico-chemical parameters of ore-forming process and the mixing of different types fluids.

### **Conclusion**

The dynamics of change of the parameters of fluid is good traced on mineral assemblages of productive stages II, IV и V. The mineralization of stage II was forming under decrease of the temperature from 380 to 240 °C, and the variation of fluid salinity from 11.6 to 0.5 wt. % eq. NaCl. An important peculiarity is periodical boiling of fluid, preceding the deposition of sulfides. By similar feature is characterised mineral formation of the stage IV: decrease of the temperature from 310 to 190 °C and waveform change of salinity from 9 to 0.5 wt. % eq. NaCl. In the same time the formation of mineral associations of stage V is in relatively low temperature region 225-220 °C in the beginning and some greater than 100 °C at the end. The fluid here also retains its Cl-Mg-Na composition and its salinity is regularly decreasing by the lowering of the temperature. Only individual inclusions contain Ca-Na chloride solutions of raised salinity. Often were found evidences of formation of ores from heterogeneous (boiling) fluids.

The data for epithermal vein systems studied in significant vertical interval (800-900 m) show the presence of two principal different trends of the change of salinity in dependence of the temperature: the increase with the decrease of the temperature characteristic for upper level of the veins, and reverse tendency on the lower level. The first trend testifies the mixing of the earlier mineral-forming fluids with cold weakly mineralized waters coming in hydrothermal system on later stages of its developing. The second trend is connected with the boiling effect. Similar regularities are established also for subepithermal ores from Svetozar vein system. The considered data show that: 1) all investigated vein systems were formed in the frames of evolution of single epithermal ore-forming system, and 2) the main factors of depositing of precious and base metals were boiling and mixing of fluids.

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**Table 1.** Summary of microthermometric data of fluid inclusions for quartz, sphalerite, barite and fluorite from the epithermal vein ores at the Banska Štiavnica deposit\*

Type of ore vein mineralization	Ore vein systems	n	Th, °C	C, wt.% eq. NaCl	P, bar
Subepitermal Au-quartz	Svetozar	453	348- 162	6.5- 0.5	156- 60
Au-Ag-Bi-Cu-sulfide-quartz	Biber	842	378- 145	11.6- 0.5	245- 7
	Rozalia	70	313- 147	8.0- 1.7	10- 5
Au-Ag-Pb-Zn-sulfide-quartz	Terezia	635	353-138	12.1- 0.2	90- 15
	Špitaller	355	295- 150	8.9- 1.4	60-20
Au-Ag-quartz	Terezia- Waiden	363	310- 151	10.4- 0.4	100- 20

- n – number of fluid inclusions; Th –homogenisation temperature; C- salinity; P- pressure

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**Table 2.** Summary of stable isotope data ( ‰ ) of minerals from the epithermal vein ores at the Banská Štiavnica deposit

Iso- tope	Min- eral	Biber	Rozalia	Terezia	Špitáler	Terezia- Waiden
$\delta^{34}\text{S}$	Py	0.44÷6.07 (2.43)* [5]**		4.44÷11.35 (6.24) [24]	7.01÷8.99 (8.00) [2]	5.47÷7.08 (6.53) [3]
	Sp	2.65÷8.42 (5.60) [22]	0.66÷6.86 (5.08) [5]	3.00÷9.67 (5.48) [58]	3.00÷8.33 (5.91) [14]	3.09÷7.30 (5.33) [7]
	Ga	-4.88÷10.72 (2.61) [27]	-1.28÷6.89 (3.02) [5]	-1.91÷10.72 (2.53) [57]	-1.78÷6.06 (3.09) [14]	1.20÷4.54 (3.01) [5]
	Cp	-6.71÷8.45 (5.42) [14]	3.57÷6.09 (5.21)[3]	-0.65÷11.72 (5.49) [40]	-6.71÷8.37 (3.23) [7]	5.41
	Mrc	-11.62÷-10.19 (-10.90) [2]		-9.80÷ -1.2 (-5.93) [4]	-3.41	
	Ba	20.36		17.26÷22.22 (18.88) [11]	6.04	
$\delta^{18}\text{O}$				0.16÷15.24 (4.64) [9]	4.20	
	Hm		5.02÷12.96 (9.36) [6]		8.23÷8.31 (8.27) [2]	
	She			-3.29÷-0.59 (-1.65) [6]	-4.04	
	Q	7.76÷13.50 (9.90) [8]	2.37÷10.85 (6.55) [5]	0.00÷10.28 (7.59) [26]	4.75÷13.63 ( 8.56) [8]	6.38÷8.83 (7.61) [2]
	Carb	18.49÷23.11 (20.80)[2]	3.53÷11.46 (6.65) [3]	11.92÷25.12 (16.67) [12]	23.90	13.68÷16.77 (14.73) [3]
$\delta^{13}\text{C}$						
		-1.48÷-0.29 (-0.89) [2]	-5.83÷-1.92 (-4.20) [3]	-13.25÷-5.00 (-9.04) [12]	0.22	-3.51÷2.05 (-0.41) [3]

Minerals: Py-pyrite, Sp-sphalerite, Ga- galena, Cp- chalcopyrite, Mrc-marcasite, Ba- barite, Hm- hematite, Q- quartz,

Carb- carbonite. \* -average; \*\*- number of sample