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MINERAL ASSEMBLAGES AND PHYSICAL-CHEMICAL MODEL OF THE FORMATION OF GOLD-SILVER-POLYMETALLIC MINERALIZATION ON THE DEPOSIT BANSKÁ ŠTIAVNICA (CENTRAL SLOVAKIA)

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Abstract: The authors distinguished 5 stages of the mineralization process which took place in the depth range of 0.5–1.5 *km* and has been characterized by cyclicity of periods of deposition of ore and vein minerals. Thermo- and cryometric study of fluid inclusions in 102 samples of quartz, sphalerite, barite and fluorite has shown that the formation of minerals occurred at a decrease of temperatures from 380 to 100 *°C* and lower, at pressures of 125 to 15 *bar* and salinity varying from 0.5 to 11.5 *wt%* equiv. NaCl, at periodical thermobarometric inversions, with phenomena like boiling and fluid-mixing. On the basis of thermodynamic calculations it has been determined that ore-stage minerals deposited at $a_{S_2} = 10^{-11} - 10^{-12}$, $a = 10^{-34} - 10^{-36}$ (Stage IV) and $a_{S_2} = 10^{-16} - 10^{-17.5}$, $a_{O_2} = 10^{-44} - 10^{-46}$ (Stage V). It has been demonstrated that the principal factors of the deposition of early-stage ore associations were temperature decrease and pH increase, and in the late stages additionally the decrease of a_{O_2}.

Key words: precious and base metal, stages of mineralization, fluid inclusions, thermodynamics.

Introduction

The problems of the origins of anomalous accumulations of ore matter, in other words – the problems of ore formation are exceptionally varied and their more or less acceptable solution is directly related to the development of the ore-formation theory in general as well as to the results of prognostics and prospection geology. In the last years, thanks to the application of modern research methods, substantial progress has been made in the study of the nature of many types of ore deposits in neovolcanic regions (Ahmad and Solomon 1987, Barton et al. 1977, Hayba et al. 1985, Kamilli and Ohmoto 1977). At the same time, not all regions of epithermal mineralization and not all of its types have been studied to the same extent. Actually, data on the physical-chemical conditions of the formation of Au-Ag-polymetallic epithermal deposits of neovolcanic regions in the Carpathian branch of the Mediterranean orogenic belt remains up to now isufficient.

In this context the focusing of our studies on the controls of the formation of Au-Ag-polymetallic mineralization of the deposit Banská Štiavnica (Central Slovak neovolcanic region of the Western Carpathians – see Fig. 1) appears to be fully justified. This deposit represented by numerous sulphidic-carbonatic-quartz veins in propyllitized andesites, dacites and diorites, in endo- and exocontact zones of an intrusive massif, is a classical example of epithermal mineralization in a caldera structure with elevated central block.

The features of geological structure and metallogenic development of Central Slovak volcanics, including the largest region of the Štiavnica stratovolcano, which has been exploited for centuries, have been widely explained in numerous publications and scientific-economic reports of M. Kuthan, J. Šalát, M. Böhmer, L. Rozložník, M. Koděra, J. Burian, J. Štohl, A. Brlaj, F. Zabranský, J. Pastor, J. Smolka, J. Michalenko, J. Konečný, J. Lexa and many others. New data on the conditions of occurrence of gold and silver minerals in the ores of the deposit Banská Štiavnica, the characteristics of their chemistry have been recently discussed by the authors on the example of the vein Terézia (Jeleň et al. 1987). This allows to devote special attention in the presented paper to the problems immediatelly related to the clarification of the laws controlling the formation of ore mineralization of the deposit, studied on the presently exploited veins Terézia, Bieber, Rozália, Bakali, William and Špitáler.

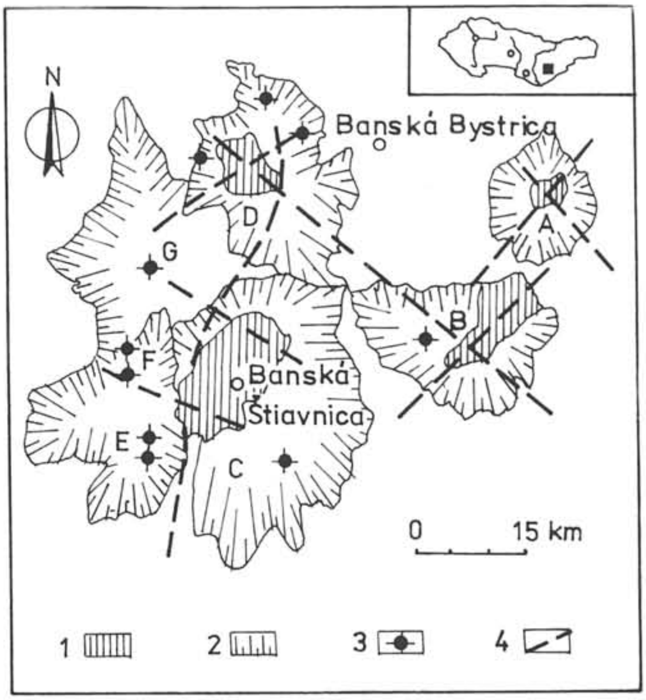

Fig. 1. Distribution scheme of volcanic centres in Central Slovakian neovolcanites.
Legend: 1 – central volcanic zone with ore mineralization of various meaning and hydrothermal alteration; 2 – mantle facies prevailingly in stratovolcanic structures; 3 – less significant volcanic centres; 4 – faults. Volcanic centres: A – Poľana, B – Javorie, C – Banská Štiavnica, D – Kremnica, E – Rudno-Brehy-Pukanec, F – Župkov, G – Prochoť (according to Burian et al. 1985).

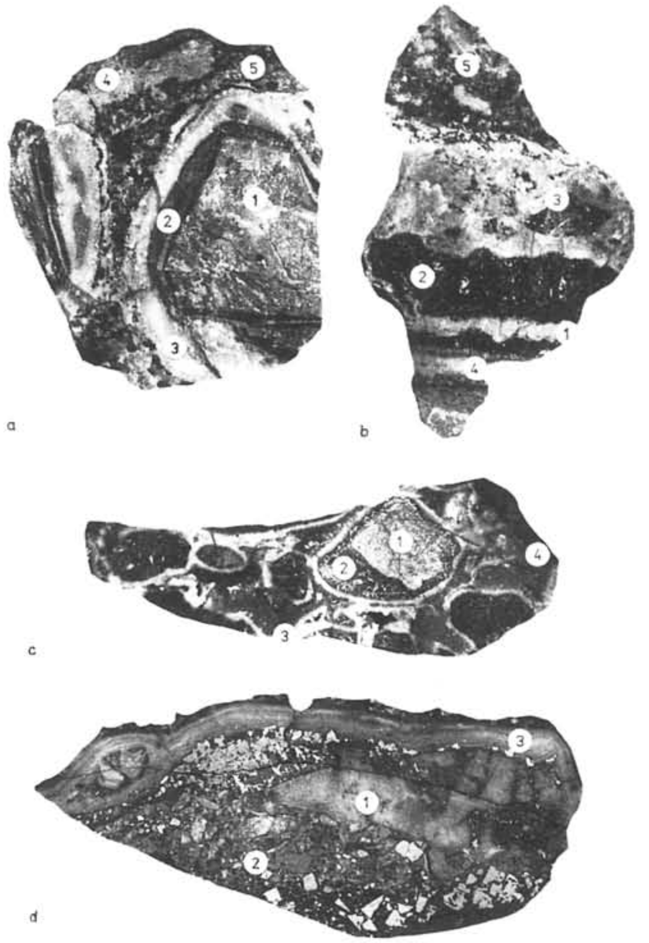

Fig. 2. Typical ore structures in Banská Štiavnica deposit.
a – *Breccia-rimmed structure:* rock fragments are replaced by the assemblage quartz + hematite (1) and are rimmed by several thin bands of hematite + quartz (2) of the Stage I, which are in turn surrounded by milk-white quartz (3) of the Stage II. Interstitions between fragments are filled with rhodonite (4) and minerals of the pyrite-galena-chalcopyrite assemblage (5) of the Stage III (2/3 of – natural size).
b – *Banded structure:* 1 – assemblage quartz + carbonate of the Stage III; 2 – thin band of galena-sphalerite of the Stage II; 3 – fragment of altered rock; 4 – the assemblage rhodonite-rhodochrosite-quartz of the Stage I; 5 – the assemblage chlorite-quartz of the Stage V (2/3 of a natural size).
c – *Breccia structure:* rock fragments (1), replaced partly or entirely by sulphide assemblage of the II stage (2) and surrounded by rims of milk-white quartz with needle-like rhodochrosite crystals (3). Fragments are cemented by grey quartz with inclusions of Mn-carbonates of the III stage (4) (3/4 of a natural size).
d – *Relations between minerals of Stages IV and V:* 1 – grey, fine-grained quartz; 2 – assemblage quartz-sphalerite-chalcopyrite of the Stage IV; 3 – thin banded quartz of the Stage V with fragments of mineral aggregates of the Stage IV in it; 4 – quartz with barite of the Stage V (natural size).

Succession of the formation of mineral assemblages of Au-Ag-polymetallic ores

The problems of the succession of mineral formation at the deposits of the Štiavnica-Hodruša ore field have been tackled since the last century (studies of G. Fessl, J. Szabo, M. Lipold, J. Hettler and others), however, this problem has been dealt with in greatest detail in the works of M. Koděra (Koděra 1963, 1956, 1959).

The above cited author observed on the vein Terézia, on its southern (shaft Maximilian) and northern (shaft Ferdinand) flank, substantial differences in the products of deposition and he suggested for them different stage schemes. For the deeper (180–250 *m*) southern flank he distinguished 6 stages (from early to late ones): hematite-quartz I, hematite-quartz II, quartz, chalcopyrite, carbonate, barite. For the near-surface (50–100 *m*) northern flank he suggested 7 stages: rhodonite I, rhodonite II, ore, cocarde-texture, quartz-dolomite, dolomite and barite. According to Koděra (l. c.), the ore-forming process in the whole deposit (including the veins Terézia, Medená and Rozália) can be generally divided into 6 periods, two of them being ore-productive ones, alternating with non-ore periods.

Our studies of the central parts of the vein Terézia, and of the veins Bieber and Špitáler allowed to conclude that the

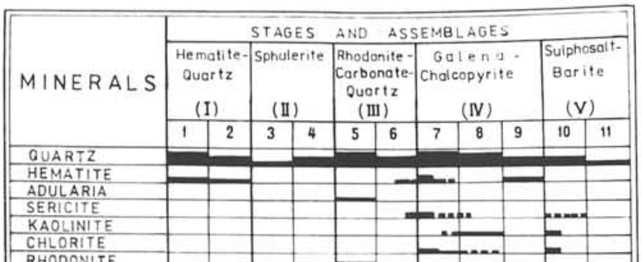

Fig. 3. Generalised scheme of the sequence of the formation of silver-base metal ores in Banská Štiavnica deposit (made by Jeleň and Kovalenker using data of M. Koděra (Koděra 1956, 1959, 1963).

structural features of Au-Ag-polymetallic ores of Banská Štiavnica are determined above all by the high permeability – "cavernosity" – of the ore-deposit zone, caused by the opening of fissures and widespread crushing and brecciating of rocks and early-stage mineralization products. It can be assumed that the deposition of mineral matter occurred here to a great extent by the process of filling of open space and only early periods of the ore-forming process are characterized by the formation of a part of mineral associations by metasomatic replacement of host rocks.

The most typical structural features of the ores which illustrate the above mentioned conclusions, are presented on Fig. 2. The in the veins observed relationships between ore and vein mineral aggregates, host rocks and mineral components of the veins are an evidence of irregular distribution of various associations, cyclic, multistage deposition of ore and vein mineralization, frequent spatial relationships of temporally different formations, intensive intramineralization tectonics. The mentioned facts as well as the results of previous studies (Böhmer and Štohl 1971; Burian et al. 1985; Koděra 1956, 1959, 1963) have been applied in the reconstruction of the succession of the formation of mineral assemblages of the Štiavnica ores. The generalized scheme of such a succession reflecting the basic trends of ore-forming processes is presented on Fig. 3. In accordance with this scheme the mineralization process is subdivided into 5 stages, each of which includes 2–3 successively formed associations.

The deposition of quartz-hematite (I) stage was preceded by regional (post-volcanic) propyllitization and berezitization of the vein-surrounding rocks. Two successive parageneses can be distinguished among the products of this stage: hematite-quartz (1) and rhodonite-rhodochrosite-quartz (2), the characteristic feature of which is the practically simultaneous deposition of manganese carbonate and silicate with quantitative predominance of rhodonite.

The sphalerite (II) stage reflects the period of the appearance of first industrial concentration of base metals, above all zinc. Two paragenetic associations have been distinguished here as well. The relatively earlier one, galena-chalcopyrite-sphalerite (3), occurs predominantly on the upper horizons and the later one, quartz-rhodochrosite (4), represented by fine-grained intergrowths of milky-white quartz with needle-like rhodochrosite, on upper and middle horizons of the deposits.

The products of the rhodonite-carbonate-quartz (III) stage, which is interproductive, are related to the formations of the rhodonite-adularia-carbonate-quartz (5) and pyrite-galena-chalcopyrite-sphalerite (6) paragenetic assemblages. They occur most frequently on the upper levels of the deposit within vein material cementing the fragments of mineral formations of the stages I and II in an ore breccia. At the same time, the quantitative role of the assemblage 6, represented by interrupted zones of fine sulphide impregnations around fragments, is inferior.

The galena-chalcopyrite stage (IV) (the principal ore stage) is composed of three (7, 8 and 9) assemblages, which are irregularly and with variable intensity represented in the ore veins. In general, the mineralization of this stage trends towards deeper horizons of the deposit. In comparison with other sulphidic ore assemblages, the role of chalcopyrite is here increased, especially on lower levels of the veins. The early, gold-silver-copper-bismuth (7) assemblage of this stage, including native gold, various minerals of the system Au-Cu-Pb-Bi-S, hematite and chalcopyrite, occur locally on the veins Bieber and Rozália in deep horizons. This assemblage reflects the first appearance of interesting Au and Ag concentrations in the Štiavnica ores. The position of bismuth mineral assemblage is ambiguous. Some observations suggest that it could be formed after the deposition of the galena, sphalerite and chalcopyrite assemblage (8) – see Fig. 3. The principal quantitative importance among the products of the stage IV has the assemblage scheelite-pyrite-sphalerite-galena-chalcopyrite (8), to the final stages of which is added the deposition of small amounts of Ag-tetrahedrite and polybasite (3) (Jeleň et al. 1987). Mineral formation of the stage IV is concluded by the development of the minerals of hematite-quartz assemblage (9).

The characteristic feature of this period of mineralization is the presence of tungsten. According to the data of M. Kalinaj (personal communication), the generally high contents of this element (up to 3.5 *wt%*), except scheelite, are present in coarse-crystalline hematite. However, this problem deserves special attention and it will not be discussed in the presented paper.

The latest formation of the Štiavnica ores are the widespread assemblages of the sulphosalt-barite (V) stage, even though generally they do not play a leading role in the ore veins. The earlier one, quartz-barite (10) assemblage of this stage, contains in a number of cases a small amount of cleophane, pyrite, marcasite, galena and chalcopyrite, and the later one, carbonate-sulphosalt (11), is practically interesting due to its content of electrum, acanthite, polybasite, pyrargyrite and other silver minerals (Jeleň et al. 1987).

Following from the above mentioned facts it is necessary to mention that our studies of the ore-forming processes and mineral composition of the ores principially correspond with the studies of Koděra. According to our observations of spatial and temporal relationships of mineral aggregates in the studied parts of ore bodies, the galena-chalcopyrite (IV) stage includes the hematite-quartz (9) assemblage, corresponding to Period 5 in the sense of Koděra (1963). The last, sulphosalt-barite (V) stage thus corresponds to Period 6 after Koděra (1963).

When generally characterizing the ore-forming process it is necessary above all to mention its cyclicity, the alternating of the periods of deposition of sulphidic and vein mineral associations, the gradual increase of the role of lead, copper, gold and silver minerals with the development of ore processes. It is also necessary to point out the widespread development of breccia, crustification, cocarde and druse structures which are typomorphic for epithermal ores and show that ore formation took place at active dilatation, multistage opening of fissures in a zone highly permeable for circulating fluids.

Evolution of chemical composition of sphalerite and native gold

Sphalerite, which is one of the most widespread ore minerals, is in variable amounts present in mineral associations of practically all stages. In mineral aggregates there are fine as well as coarse grains of the mineral as well as its isomorphic crystalls, occurring in druse-like cavities of the veins.

The composition of sphalerite from assemblages of different ages has been studied in samples representing various depth levels of the veins Terézia and Bieber. In all, about 50 grains of this mineral have been analysed by microprobe (analysts V. S. Malov and S. M. Sandomirskaya), representing the mineralization of the stages II–V. On Fig. 4 are presented data on the variation of the contents of FeS, CdS and MnS in the studied sphalerites, from which it can be concluded that increased Fe and Mn contents are typical for minerals of the basically sulphidic stages II and IV. At the same time the contents of Cd do not correlate with the concentrations of other elements. The studies by microprobe allowed to determine that in some cleophane crystals from the mineralization stage V, from center toward peripheral parts, a regular decrease of Fe and Mn contents can be observed simultaneously with an increase of Cd content. Thus, in one of the grains, the following contents have been determined (from center to periphery, in *wt*%): Fe – 3.15, 2.65, 1.09 and 0.19, Mn – 0.29, 0.34, 0.24 and 0.09, Cd – 0.31, 0.38, 0.32 and 0.51.

In contrast to sphalerite, native gold from the Štiavnica ores does not belong to widespread minerals. Its principal amounts belong to the gold-silver-copper-bismuth assemblage of the Stage IV and carbonate-sulphosalt assemblage of the Stage V. The analysis of the composition of gold grains from this associations from the veins Rozália, Bieber and Terézia using microprobe (analysts V. S. Malov, S. M. Sandomirskaya, in all about 27 determinations) shows that native gold from assemblage 7 is more pure – the content of silver in it varies from 13 (vein Rozália) to 29–36*wt* % (vein Bieber). At the same time, in association with sulphides and sulphoantimonites of silver (Stage V), less pure gold can be found (electrum), with Ag contents reaching 41–51*wt* %.

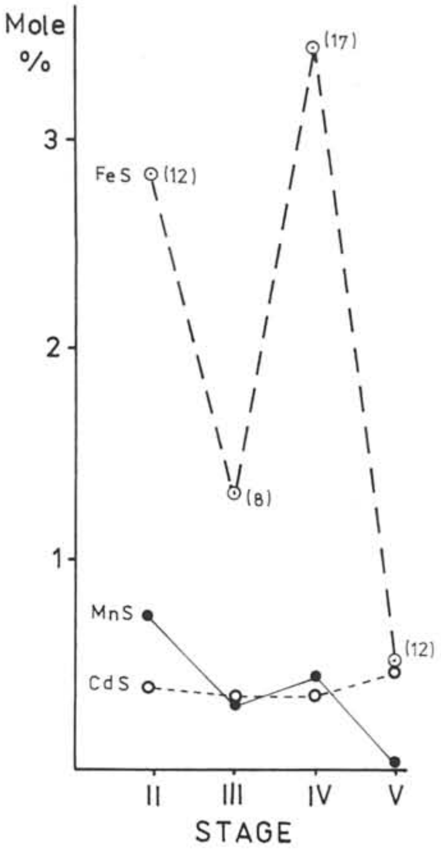

Fig. 4. Variations of FeS, MnS and CdS content in sphalerites of ore assemblages from different stages (figures in brackets – number of analysed samples).

P-T regime and composition of mineral-forming fluids

The compositon, salt concentration in fluids and P-T regime of mineral-forming processes in the veins Terézia, Bieber, William, Špitáler and Rozália have been studied using the methods of thermo- and cryometry in individual fluid inclusions in transparent minerals of the ores. The precision of the determination of homogenization temperature (T_H) was ± 22 *°C*, of eutectic temperature (T_E) and CO_2-escape temperature ± 1.5 *°C*, of CO_2-melting ± 0.5 *°C*, of CO_2-homogenization and melting of ice and hydrous gas ±0.2 *°C*.

Fluid inclusions found in quartz, sphalerite, barite and fluorite from ore-stage assemblages are as a rule large (up to 150 *μm*), they often have the form of negative crystal, frequently they are associated with zones of crystal growth of the host mineral, which indicates their primary character. Among the studied inclusions noteworthy are the groups of syngenetic inclusions in quartz (sometimes in sphalerite), there are pure gaseous as well as gas-liquid inclusions with

Table 1. Parametric characteristics of ore-forming fluid on the deposit Banská Štiavnica according to data obtained by the study of individual fluid inclusions.

Mineral	n	Temperature, °*C*		C *wt%* NaCl equiv.	d *g/cm³*	Pressure *bar*	
		of homogenization	eutectic			H_2O	CO_2
Quartz	1268	378–155	−38/−29	11–0.5	0.95–0.75	100–15	4–3
Sphalerite	540	336–133	−48/−29	11.5–3	0.96–0.76	100–75	–
Barite	28	205–50	−33/−29	4–1	1.01–0.90	–	–
Fluorite	8	204–150	−36/−33	2–1.5	0.93–0.87	–	–

Note: C – concentration (salinity) of fluid, d – density of fluid, n – number of studied inclusions

various ratio of the phases. As a rule, T_H of both inclusion types are similar, which is usually interpreted as an evidence of fluid heterogenization (boiling).

Parametric characteristics of ore-forming fluids, obtained from thermobarometric study of almost 1850 individual fluid inclusions, are listed in Tab. 1. These data indicate that the deposition of minerals took place from hot aqueous solutions with chloride-magnesium-sodium composition, with salt concentrations varying from 0.5 to 11.5 *wt%* NaCl equiv. As a result of low pressure, no substantial correction of T_H is necessary and thus it is very similar to fluid-capture temperature.

The observed cases of fluid heterogenization (boiling) allow to determine the pressure at ore deposition: maximal pressure (200 *bar*) has been noted in a sample of Stage II quartz collected on horizon 12 of the vein Bieber (T_H = 378 *°C*,

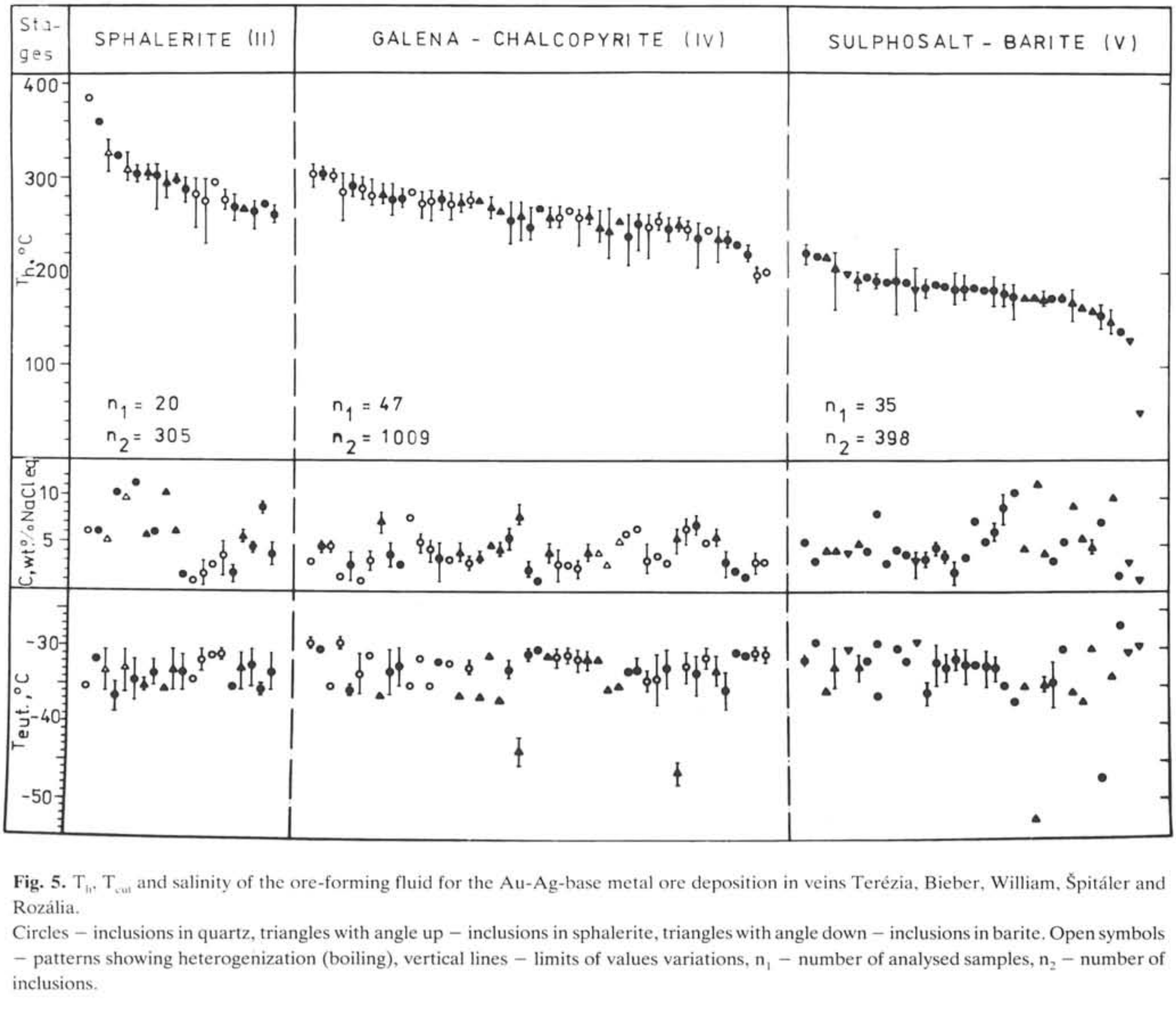

Fig. 5. T_h, T_{eut} and salinity of the ore-forming fluid for the Au-Ag-base metal ore deposition in veins Terézia, Bieber, William, Špitáler and Rozália.

Circles – inclusions in quartz, triangles with angle up – inclusions in sphalerite, triangles with angle down – inclusions in barite. Open symbols – patterns showing heterogenization (boiling), vertical lines – limits of values variations, n_1 – number of analysed samples, n_2 – number of inclusions.

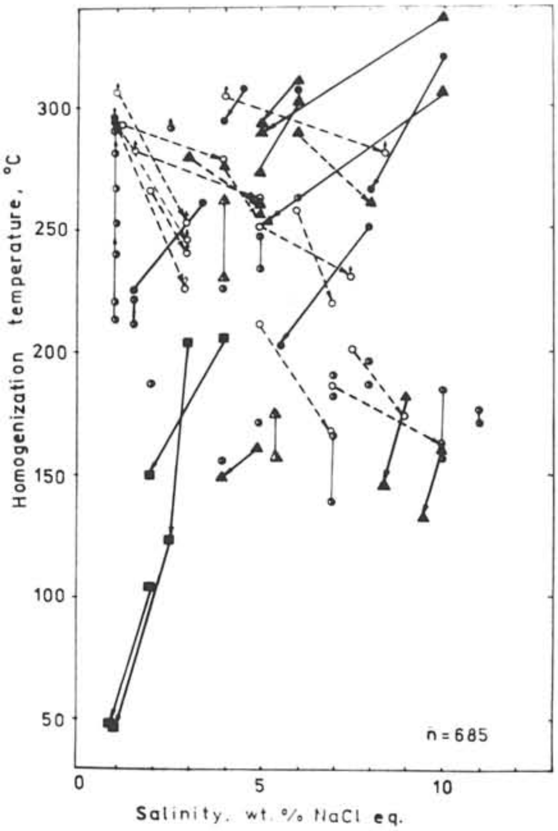

Fig. 6. T−C parameters of ore-forming fluids in the Terézia vein. Explanations see Fig. 5.
Arrows − main trends in variation of the fluid salinity, n − number of analysed inclusions.

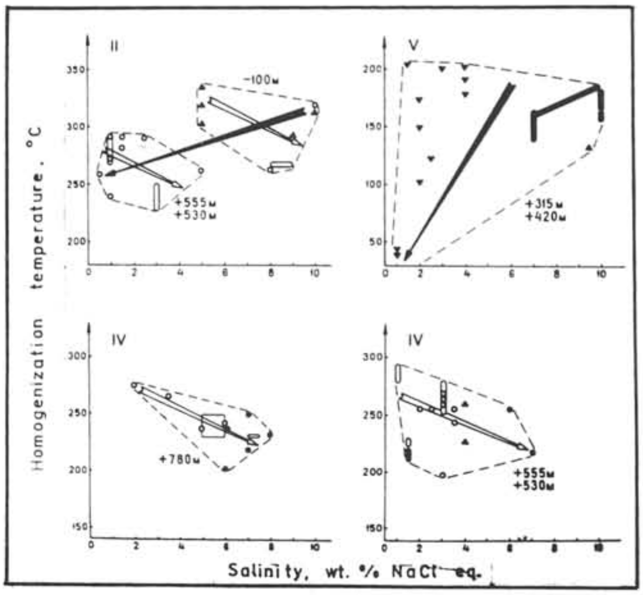

Fig. 7. T−C parameters of ore-forming fluids in the Terézia vein (see Fig. 6): related to different stages (II, IV and V) and depth levels. Arrows show prevailing trends of variation in salinity due to boiling (open arrows) and to dilution (mixing) (closed ones) of the fluid. Explanations see Fig. 5.

n = 5). However, a great part of the studied inclusions displays in the temperature range 336−198 °C pressures varying from 100 to 15 *bar*, i. e. usual pressures for epithermal conditions (Hayba et al. 1985; Heald et al. 1987). It is important to point out that in pure gaseous inclusions ($T_H \approx 300$ °C) cryometric studies yielded the presence of CO_2 of uncommonly low density, which escapes at −73/−77 °C. At the indicated temperature this corresponds to P_{CO_2} = 3−4 *bar*.

The dynamics of the change of TCX-parameters of fluids at the deposition of mineral assemblages of ore stages II, IV and V is shown on Fig. 5. It can be seen that mineralization of the Stage II formed on the background of temperature decrease from 380 to 240 °C. The composition of fluid appears to be here chloride-magnesia-sodium (T_H = −30/−39 °C) and its salinity varies freely between 0.5 and 11.5 *wt*% NaCl equiv. An important feature of the ore-forming process in this time span appears to be periodic boiling of the fluid, preceding, as a rule, the deposition of sulphides. The same features characterize the mineral deposition of Stage IV: temperature decrease from 310 to 190 °C and free variation of the salinity of chloride-magnesia-sodium fluid from 0.5 to 9 *wt*% NaCl equiv. Only in two sphalerite samples from this mineralization stage there are sporadic inclusions containing fluid of chloride-calcite-magnesium composition (T_E = −43/−48 °C). At the same time, the formation of mineral assemblages of Stage V falls into a relatively low-temperature region- 225−220 °C at the beginning and slightly higher than 100 °C at the conclusion of this stage. It is characteristic that the fluid preserves here wholly its chloride-magnesia-sodium character and its salinity, in contrast to the fluids of the preceding stages, displays regular decrease proportional to temperature decrease. Only in a few inclusions Ca-Na-Cl solutions with increased salinity have been found here (7−11 *wt*% NaCl equiv.).

Since statements about the relationships of temperature and fluid salinity are very important for the explanation of the dynamics of ore-forming processes, we shall deal with this problem in detail. On Fig. 6 there are data on T_H and C obtained by thermo-cryometric studies of 685 individual fluid inclusions in quartz, sphalerite and barite from the vein Terézia, the samples of which characterize the whole vertical span of mineralization, from the surface (abs. elevation +790 *m*) to the horizon V (−110 *m*). We can see three trends of the change of fluid salinity with temperature decrease: **1.** concentration increase from 1 to 11 *wt*% NaCl equiv.; **2.** its decrease from 11.5 to 0.5 *wt*% NaCl equiv.; **3.** independence of C on T_H. At the same time, although there are exceptions, the solutions behaving according to the first relationship occur to a great extent in the upper part of the vein, those behaving according to the second rule are more characteristic for deep horizons and the third trend is related to middle depth levels.

The determined trends are preserved also when we order the studied values of T_H and C in time (according to the stages of the process) and space (according to depth levels), which can be seen on Fig. 7. Thus, in the second stage, in the direction from lower (−110, +95 *m*) towards upper (+555, +580 *m*) horizons of the deposit, the distribution of the sudied parameters of fluid inclusions is completely controlled by the second type of relationships. Apparently this can be interpreted as an evidence in favour of a dilution of relatively concentrated hot fluids by cold, weakly mineralized meteoric waters, these being mixed in the upper part of the ore-forming system. At the same time, another trend can be observed within the individual horizons (−110 *m*, less markedly at +555 *m*) – certain increase of salinity proportional to cooling of the fluid, which could have been caused by concentration due to ebulition, since, especially on the mentioned horizons, intensive boiling of ore-forming solution of Stage II has been determined. During Stage IV mineralization the level of fluid boiling corresponded to horizons with absolute elevations +315, +555 and +790 *m*. However, the influence of ebulition in the form of an increase of salinity of the fluid with temperature decrease is clearly recorded only on the uppermost level of the ore deposit. This effect, but already somewhat "eroded" by the opposite process of dilution, can be observed on the level of the horizon +555 *m*. In the concluding, fifth stage of the process, when the formation of minerals occurs without phenomena of fluid heterogenization, there is very markedly manifested the second type of T_H – C relationship, related to dilution effects. Most demonstrative of this is an example observed in inclusions in barite. It has been suggested that solution mixing is an especially important factor for mineral deposition (Hayba et al. 1985).

The above discussed results of thermobarometric studies of representative material show that the formation of Au-Ag-polymetallic ores in Banská Štiavnica took place at PT-parameters consistent with conditions of ore deposition in such typical representatives of epithermal quartz-adularia-sericite mineralization type as the deposits Creede, Tonopah, Colqui (Hayba et al. 1985; Heald et al. 1987). The determination of the phenomena of recycling, periodic boiling, mixing of deep, relatively hot fluids with weakly mineralized cold meteoric waters of near-surface zones strenghtens the mentioned similarity and are the evidence of Banská Štiavnica being, similarly as the above cited deposits, an example of an old, meteoric-hydrothermal convective system.

Estimation of the depth of the formation of ore mineralization

Two basic methods of estimation of the depth of the formation of mineralization are the methods of geological reconstructions and the method based on the study of the P-T-C relationships in fluids at vapour separation in the moment of their heterogenization (boiling) in hydrostatic conditions. It is assumed that maximal paleodepth corresponds to highest T_H and P values for the observed case (Haas 1971; Albinson 1988). Broad development of heterogenization phenomena in ore-forming fluids in the period of deposition of ore assemblages in Banská Štiavnica allowed to use this method for the estimation of possible depths of ore formation at the studied deposit.

On Fig. 8 there are presented data characterizing basic parameters of ore forming solution of stages II and IV, corresponding to the early moments of heterogenization. It can be well seen that all observed points are distributed between boiling curves of pure H_2O and 10% solution of NaCl, which reflect the limits of salinity variation of fluids in Banská Štiavnica. This means that during the capture of fluids in the moment of their boiling the pressure approached hydrostatic pressure, i. e. it is most probable that ore-containing fissures were filled by a solution and they could in this period communicate with the surface. In this case the obtained estimates of the depth of ore-formation which vary between 0.4−0.6 and 1.6 *km* (Fig. 8) can be considered very reasonable, especially since they are consistent with data on such typical epithermal gold-silver deposits of the quartz-adularia-sericite formation like Tonopah, Comstock, Colqui, Creede, Eureka (Hayba 1985; Heald 1987).

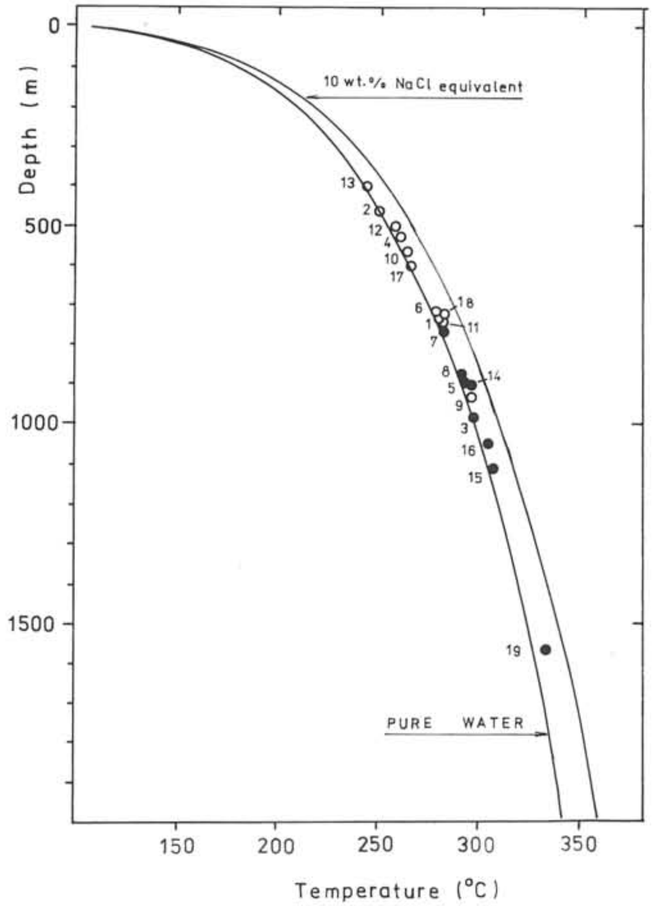

Fig. 8. T−P parameters of the fluids captured in time of boiling. Boiling curves are shown after Haas (1971).
Closed symbols – fluids of the II stage, open ones – fluids of the IV stage. 1−2 – present surface (+790 *m*); 3−8 – abs. level +555 *m*; 9−10 – abs. level +535 *m*; 11−12 – abs. level +490 *m*; 13 – abs. level +420 *m*; 14−16 – abs. level +315 *m*; 17 – abs. level +240 *m*; 18 – abs. level +95 *m*; 19 – abs. level −110 *m*.

At the same time, from an analysis of data presented on Fig. 8 it can be seen that mineral formation during Stage II took place in substantially greater depths (0.75−1.6 *km*) from the paleosurface than in Stage IV (0.4−1.1 *km*). This would indicate that in the period between the stages the block of rocks with ore structures underwent noticeable displacement towards the surface. In the opposite case it would be difficult to explain the fact that in the present position, as a rule, mineral assemblages of both stages are related in space and in a number of cases mineralization of Stage IV occupies even relatively deeper levels of the deposit. Evidence of notable vertical displacement is known in many caldera structures, including the Štiavnica stratovolcano (Burian et al. 1985).

Physical-chemical conditions of the formation of gold-silver-polymetallic ores

The above discussed data characterizing the PTCX-parameters of the ore-forming fluid and their evolution in the process of mineral formation allow to proceed to the estimation of physical-chemical conditions of ore deposition corresponding to average parameters of mineral assemblages 3−11 successively formed during the ore-forming stages (Fig. 3.)

The activities of sulphidic sulphur and oxygen have been determined on the basis of data for the equilibria of sulphide and oxide minerals (Fig. 9). The values of a_{S_2} for the conditions of the deposition of mineral assemblages 3−11 have been determined on the basis of the content of the pyrrhotite molecule in sphalerites (Fig. 5), according to the equation

$$\lg a_{S_2} = 13.3 - 14680/T - 21g\, Xp_o \qquad (1)$$

(according to /I/, T. K)

For the assemblages 7 and 11 the activity of sulphidic sulphur has been calculated as well on the basis of Ag content in electrum in equilibrium with acanthite (in accordance with the equation of Barton and Toulmin 1964). These estimates obtained by independent methods correspond mutually very

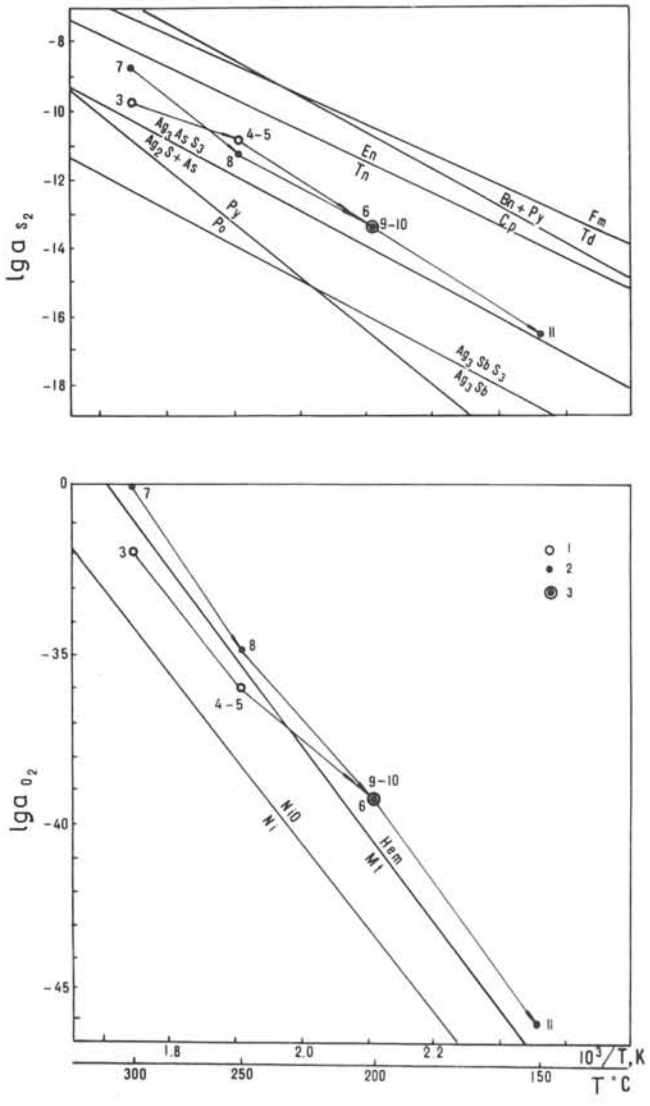

Fig. 9. Dependence between a_{S_2} and a_{O_2} of T during formation of parageneses of the first (1) and the second (2, 3) cycles of mineral deposition.
Figures corresponds to the numbers of assemblages in Fig. 3. *Abbreviations:* Py − pyrite, Po − pyrrhotite, Cp − chalcopyrite, Bn − bornite, En − enargite, Fm − famatinite, Td − tetrahedrite, Tn − tennantite, Hem − hematite, Mt − magnetite. Arrows − trends of variations in thermodynamic parameters.

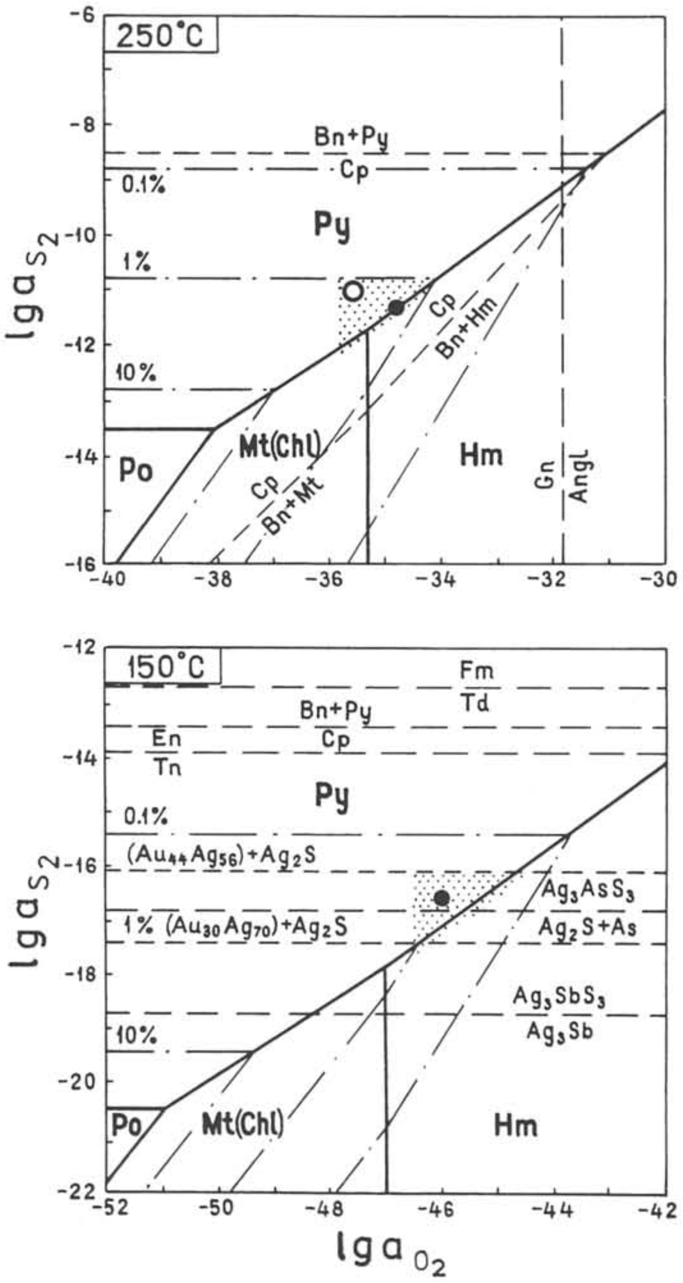

Fig. 10. $\lg a_{S_2} - \lg a_{O_2}$ plots for 250 and 150 °C.
Explanations see Fig. 9. Chl − chlorite. Dot-dashed lines − lines of equal content of FeS (in mol.%) in sphalerite. Dotted area − see text, open symbol − first cycle, solid symbol − second cycle.

well. Generally said, a_{s_2} and a_{o_2} were apparently during the whole process near to the triple point Py-Hm-Mt (Fig. 10), with some upward displacement along the line Py-Hm and shifting into the field of pyrite or hematite. This is supported by practically constant presence of these minerals in ore assemblages of all stages (Fig. 4). The most probable fields of the values a_{s_2} and a_{o_2} for the parageneses 4 and 8 (250 *°C*) and 11 (150 *°C*) are on Fig. 10 marked by dots. In general, the characteristic feature of ore formation in Banská Štiavnica, as it follows from the discussed data, is the decrease of the activities of sulphur and oxygen proportional to temperature decrease which is common in ephithermal deposits and geothermal fluids.

The active part of ore-forming solutions, as it has been shown above, contains carbon dioxide, the parcial pressure of which is 3–4 *bar*. This corresponds to $m_{H_2CO_3} = 0.03-0.04$ at 300 and 250 *°C*, respectively. Carbon dioxide could buffer the acidity of the solution during the deposition of the Stage II parageneses, according to the equation

$$H_2CO_3 = H^+ + HCO_3^- \qquad (2)$$

This means that the most probable pH values of the fluid in the conditions of mineral deposition of the assemblages 3 (300 *°C*) and 4 (250 *°C*) corresponded to 4.7 and 5.4. The deposition of adularia in the beginning of Stage III and of sericite at the end (Fig. 3) allows to estimate approximately, according to the equilibrium Ad/Ser, the acidity of the fluid in this mineral-forming period:

$$pH = -\lg m_{\Sigma k} - 2.22 + 3280/T - \lg \gamma_H^+ \qquad (3)$$

(modified from Redkin 1983).

Since cryometric data on fluid inclusions have not shown any noteworthy amounts of potassium in the ore-forming solution, for the calculations was used the value 0.1 $m_{\Sigma k}$. In this case, at 250 *°C* (conditions of the assemblage 5) pH ≥ 5.47 (sericite is missing) and at 200 *°C* (assemblage 6) pH ≤ 6.12 (adularia is missing). According to Rafalski (1987), the equilibrium value of pH for 1 M NaCl at 200 *°C* is 5.35, i. e. near to neutral. For the determination of the conditions of ore formation in stages IV and V, pH has been estimated on the basis of the equilibrium Kaol/Ser according to the equation (modified after Redkin 1983):

$$ph = -\lg m_{\Sigma k} - 6.89 + 5150/T - \lg \gamma_{H+} \qquad (4)$$

At $m_{\Sigma k} = 0.1$, pH of the fluid in the conditions of the formation of the assemblage 7 (300 *°C*) is 3.6, for assemblage 8 (250 *°C*) 4.4, for assemblages 9, 10 (200 *°C*) it is 5.4, in assemblage 11 (150 *°C*) over 6.6 (kaolinite is missing).

On the basis of calculated values of a_{s_2} and a_{o_2} we have estimated the limits of concentration variation of sulphidic and sulphatic sulphur during the ore-forming process. It has been determined that proportionally to temperature decrease a marked decrease of m_{H_2S} is observed and, on the contrary, an increase of m_{SO_4} to such an extent that at 200 *°C* the concentrations become equal, but with further temperature decrease sulphidic sulphur becomes again prevalent in the solution.

The above mentioned parameters of the conditions of the formation of mineral parageneses in the Štiavnica ores are listed in Tab. 2. An analysis of the trends of their changes shows that the ore-forming process can be divided into two cycles which are separated above all by the temperature inversion at the beginning of Stage IV. The first cycle includes stages II and III, the second one the stages IV and V. Monotonous decrease of temperature, with corresponding changes of such parameters as the activities of sulphur and oxygen, pH and m_{H_2S}, takes place from the beginning to the end of each cycle. Noteworthy is the marked similarity of physical-chemical parameters at the formation of some assemblages: 4 and 5, 9 and 10, which are for this reason, and for the convenience of the reader, presented in Tab. 2 in one column (4–5 and 9–10).

Table 2. Average parameters of the physical-chemical conditions of formation of mineral assemblages of gold-silver-polymetallic ores on the deposit Banská Štiavnica.

Parameters	Mineral assemblages						
	3	(4–5)	6	7	8	(9–10)	11
T °*C*	300	250	200	300	250	200	150
$\lg_\Sigma a_{S_2}$	−8.8	−11.3	−13.5	−16.6	−9.8	−11.0	−13.5
pH	4.7	5.5	5.5	3.6	4.4	5.4	6.6
$\lg_\Sigma m_{H_2S}$	−2.8	−3.4	−4.7	−2.8	−3.8	−4.7	−5.4
$\lg_\Sigma m_{Cl^-}$	0.8	0.4	0.4	0.5	0.6	0.6	1.0

Factors of transport and deposition of ore components

As a result of the calculations and alternative estimation of equilibrium solubilities of minerals of gold, silver, lead, zinc and copper in the form of chloride, hydrosulphide and hydroxide complexes, we have determined equilibrium solubilities of Au, Ag, Pb, Zn and Cu for the conditions of the formation of asseblages 3–11 (Tab. 3). The dynamics of the changes of solubilities of the studied metals during the ore-forming process from assemblage 3 to assemblage 11 is shown on Fig. 11.

What is noteworthy when comparing the physical-chemical conditions of the first (Stage II-III) and second IV–V) cycle? The regimes of sulphur and oxygen in both cycles are practically the same, apparently, this is also an explanation of the great similarity of the mineral composition of the ores in stages II an IV. Similar are salinities of the solutions, their cation and anion composition, characterized by a high ratio of m_{Cl}/m_{H_2S}, which is connected also with the same form of transport – chlorocomplexes for Ag, Pb, Zn, Cu and hydrocomplex for Au. The principal differences lie in the regime of acidity and the duration of temperature interval of ore deposition.

The calculations have shown that cooling of the solution in the interval 300 – 150 *°C* at each 50° decreases the solubility of ore components: Pb 80 times, Ag 25 times, Cu 3–10 times, Au 1.1–1.7 times. Analogous is the increase of pH: an increase of one unit decreases the solubility of lead and zinc 100 times, of copper and silver 10 times. At the same time the deposition of gold from the complex $AuOH^\circ$ does not depend on acidity.

The deposition of ore assemblages of the first cycle took place at cooling and alkalization of the solution, which, as it follows from the previous paragraph, decreases most rapidly the solubility of Pb and Zn. Indeed, galena and sphalerite are

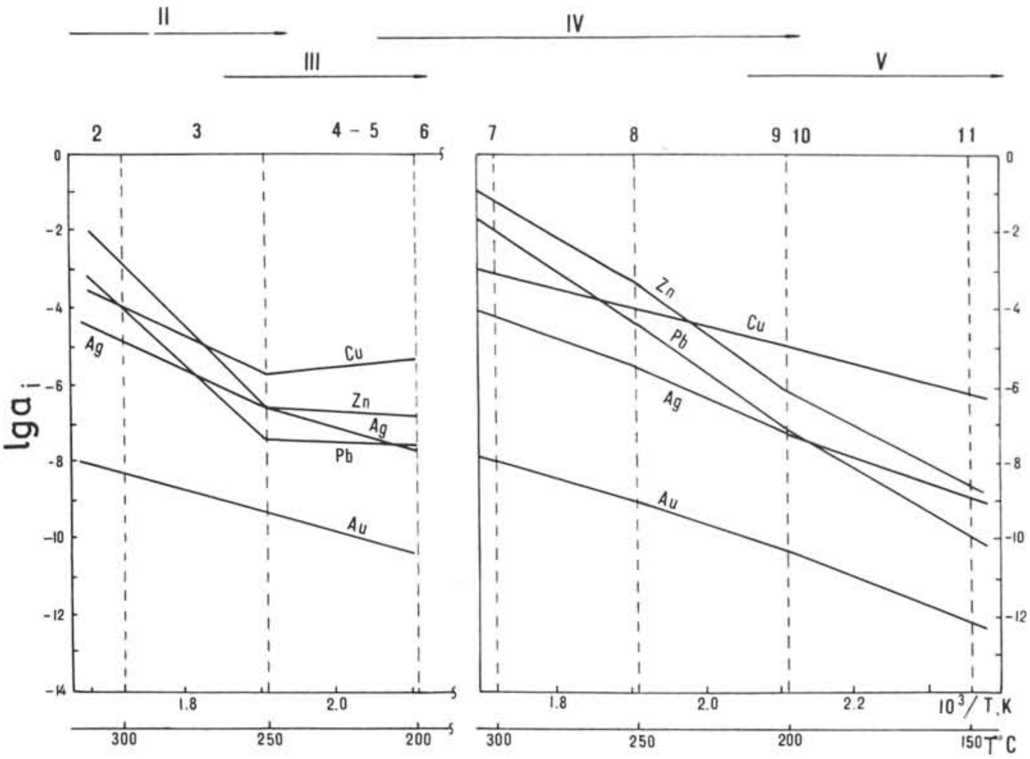

Fig. 11. Variations in equilibrium solubility value of minerals of gold, silver and base metals during a formation of assemblages (2−11) of the first cycle (stages II−III) and the second one (stages IV−V) of mineral deposition in ore veins of Banská Štiavnica deposit.

the predominant minerals of assemblage 3. A small amount of chalcopyrite can be added here too – the decrease of the solubility of copper is caused by additional (besides temperature and pH) influence of the decrease of a_{O_2}. Further on, the equilibrium concentrations of Pb, Zn and Cu in assemblages (4−5) and 6 change only slightly which also explains the limited occurrence of ore minerals at the end of the first cycle (assemblages 4−6 – see Fig. 4). At the same time the solubilities of silver and gold continue to decrease and, even though in negligible amounts, their minerals (electrum, acanthite, polybasite) appear at the end of each cycle (assemblage 6).

The second cycle of ore formation begins by the deposition of the Au-Ag-Bi containing assemblage 7. In relation with the still stronger dependence of the solubility of Bi from temperature than it is the case for Ag, Pb and Zn (thus, e. g. cooling from 300 to 200 °C decreases the solubility of bismuth by 6 orders), minerals of this assemblage are deposited earlier than other ones even at slight temperature decrease (below 300 °C). Since neutralization of solutions also strongly decreases Bi solubility, an additional factor of the deposition of Bi is here the alkalization of the originally acid (pH 3.6) solutions.

Cooling by 50 °C (from 300 to 250 °C) and alkalization by 1.1 pH units (from 3.6 to 4.7) towards the conditions of assemblage 8 caused a strong decrease of the solubility of Zn, Pb, and to a several times lesser extent that of Cu and Ag, which led to mass deposition of sphalerite, galena, chalcopyrite as well as noteworthy amounts of silver sulphoantimonites. Since this deposition began already at negligible cooling of the fluid (to 280 – 270 °C), it is probable that at the very beginning of the second cycle the solutions were sufficiently near to saturation with Pb, Zn and Cu. Thus we can conclude that in connection with higher acidity, the primary concetrations of metals in fluids of the second cycle were markedly (by up to 1 order) higher than in the first one.

Table 3. Calculated values of equilibrium solubilities of Au, Ag and other metals in the conditions of formation of mineral asseblages of the Štiavnica ores.

Parameters	Mineral assemblages						
	3	(4–5)	6	7	8	(9–10)	11
$\lg_{\Sigma}a_{Au}$	−8.3	−9.2	−10.4	−8.0	−9.0	−10.3	−12.2
$\lg_{\Sigma}a_{Ag}$	−4.9	−6.6	−7.7	−4.2	−5.5	−7.2	−8.9
$\lg_{\Sigma}a_{Zn}$	−2.9	−6.6	−6.8	−1.2	−3.3	−6.1	−8.6
$\lg_{\Sigma}a_{Pb}$	−4.0	−7.4	−7.6	−2.0	−4.3	−7.1	−9.9
$\lg_{\Sigma}a_{Cu}$	−4.0	−5.6	−5.3	−3.1	−4.0	−4.9	−6.2

The further development of the ore-forming process led to the formation of minerals of the assemblages 9−11, the principal factors of their deposition having been, as it follows from the above discussed data, cooling and alkalization of the solution, and for Au, Cu and Ag minerals also a decrease of a_{O_2}. Ore deposition of the second cycle ended at substantially lower temperatures (up to 150−100 °C) and higher pH (up to 6.6) than in the first cycle.

Thus, concentration decrease of ore components (Δm_i) from the beginning to the end of the second cycle was by 1.5−4 orders higher than during the first cycle (Fig. 11). This is in our opinion connected also with the fact that the richest Au-Ag mineralization formed during the stages IV and V of the second cycle. The markedly more substantial decrease of the solubility of Pb and Zn at the beginning stages of ore-forming cycles caused the enrichment of the mineral assemblages 3 and 8 by polymetals. At the same time, the principal factors of the deposition of ore components in both cycles are temperature decrease and alkalization of the solution, caused above all by developed phenomena of heterogenization and dilution of ore-forming fluid due to mixing with meteoric waters during convective circulation.

Conclusions

1. Five stages have been distinguished in the history of the formation of the gold-silver-polymetallic mineralization on the deposit Banská Štiavnica, during which the deposition of vein, sulphidic, and precious-metal mineral assemblages took place: hematite-quartz, sphalerite, rhodonite-carbonate-quartz, galena-chalcopyrite and sulphosalt-barite. The deposition of ores took place in depths of 0.5 to 1.5 *km* from the syn-ore paleosurface, in the conditions of active stretching, multi-stage opening of fissures, in an environment highly permeable for solution circulation, with predominant deposition of mineral matter by the process of filling of free space. The mineral-forming process can be characterized by cyclicity, alternation of periods with deposition of sulphidic and vein minerals, by gradual increase of the role of the minerals of Cu, Bi, Au, Sb and Ag in ore assemblages from early to late stages.

2. On the basis of highly detailed and precise thermo- and cryometric studies of more than 1850 individual fluid inclusions in transparent minerals from ore veins Terézia, Bieber, Bakali, William, Špitáler and Rozália, the controls on the variation of PT-parameters of ore mineral formation and the composition of ore-forming solutions have been determined. It has been determined that the deposition of ore and vein mineral assemblages in all stages took place from genetically identical hot aqueous solution with chloride-magnesia-sodium composition, primarily containing small amounts ($m_{H_2CO_3} = 0.03-0.04$) of carbon dioxide, which developed on the background of temperature decrease (from 380 to 100 *°C* and less), periodic thermobarometric inversions, phenomena of boiling and mixing of fluids.

3. The estimation of the values of sulphur and oxygen activities, pH, of chlorine, sulphidic and sulphatic sulphur concentrations has shown that these parameters were during the ore-forming process controlled by temperature. Two large cycles of such changes have been observed, the earlier of which is connected with the formation of above all polymetallic mineral assemblages enriched by zinc and the later one with the formation of relatively lead-, copper-, bismuth- and antimony-rich ores including assemblages of gold and silver minerals.

4. On the basis of thermodynamic calculations and alternative estimation of equilibrium solubilities of Au, Ag, Zn, Pb and Cu minerals in the form of chloride, hydrosulphide and hydroxide complexes, a physical-chemical model has been suggested for the transport and deposition of the these metals in the conditions of the formation of the Štiavnica ores. It has been demonstrated that the principal factors of the deposition of ore assemblages of the first cycle were cooling and alkalization of the ore-forming solution, and for the mineralization of the second cycle, besides these, also the decrease of a_{O_2}, controlling the deposition of Cu, Ag and Au minerals. At the same time, base metals and silver were transported mostly in the form of chlorocomplexes and gold in the form of hydrocomplex.

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