Contribution to Understanding of Ore Fluids in the Zletovo Mine Based on Fluid Inclusion Data

Raziskave Rudnih Fluidov v Rudniku Zletovo s Pomočjo Tekočinskih Vključkov

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Abstract

The Zletovo is lead–zinc (Pb–Zn) deposit, adjacent to the Plavica volcanic centre (R. Macedonia) with high-sulphidation and porphyry mineralisation. The analysis of fluid inclusions showed homogenisation temperatures in the range 335–145°C, which reflects phases of pulsation of hydrothermal solutions and defined into four groups from the lowest to the highest temperatures. The frequency of the homogenisation temperatures ranged from 265 to 125°C and with the most dominant from 245 to 225°C, from 225 to 205°C and from 145 to 125°C. Also, it was confirmed that hydrothermal ore-bearing solutions were defined as NaCl-type with range from 4.4 to 8.6 wt% NaCl equivalent. The latest stage salinities ranged from 3 to 12 wt% NaCl equivalent, where those from 10 to 12 wt% and from 6 to 8 wt% NaCl equivalent, prevailed. This suggests that hydrothermal solutions within analysed quartz grains were at final mineralizing phase. Density of fluid inclusions ranged from 0.7 to 0.95 g/cm³. Calculated pressures and paleo-depths of mineralisation ranged from 14 to 130 bar and from 0.6 to 0.8 km.

Key words: lead–zinc, quartz, fluid inclusions, temperature, salinity, Zletovo mine.

Izvleček

Svinčevo cinkovo (Pb-Zn) rudišče Zletovo z bogato sulfidno in porfirsko mineralizacijo leži v bližini vulkanskega centra Plavica (R. Makedonija). Analiza tekočinskih vključkov je pokazala, da so se homogenizacijske temperature gibale od 335 do 145°C, kar odraža različne faze prisotnosti hidrotermalnih raztopin. Frekvence homogenizacijskih temperatur so se gibale od 265 do 125°C, z najbolj prevladujočimi od 245 do 225°C, od 225 do 205°C in od 145 do 125°C. Z raziskavami smo potrdili, da so bile hidrotermalne rudonosne raztopine tipa NaCl, in sicer z razponom od 4,4 do 8,6 ut.% ekviv. NaCl. Slanost v zadnjih fazah prisotnosti raztopin je znašala od 3 do 12 ut.% ekviv. NaCl. Podatki tako kažejo na to, da so bile hidrotermalne raztopine znotraj analiziranih kremenovih zrn v zadnji fazi mineralizacije. Gostota tekočinskih vključkov je znašala od 0,7 do 0,95 g/cm³. Tlaki in paleo-globine pojava mineralizacije so znašali od 14 do 130 barov in od 0,6 do 0,8 km.

Ključne besede: svinec-cink, kremen, tekočinski vključki, temperatura, slanost, rudnik Zletovo.

Introduction

Research and exploitation of lead–zinc ore from Zletovo mine have recorded history of nearly a century, but detailed studies of ore fluids, as presented in this paper, are very rare. Namely, the Zletovo lead–zinc deposit has been the subject of exploitation since 1941. After the end of the Second World War, a modern mine with an annual production capacity of 400,000 t of ore was built at the Zletovo ore deposit. Thus, the Zletovo mine has been in continuous production for more than 75 years, with an average content of 8% of Pb + Zn within the ore.

During the exploration of the Zletovo deposit, numerous detailed and special mineralogical and geochemical studies on evolution and lead–zinc mineralisation were performed. The most complex and complete published materials are as follows [1, 3, 4, 5–10].

The aim of this paper is to investigate the fluid inclusions in quartz samples taken from the ore parageneses in order to define the ore deposit origin through values of homogenisation temperature, salinity and pressures.

Materials and methods

Geological setting and mineralisation

The Zletovo lead–zinc deposit, located in the east of the Kratovo–Zletovo volcanogenic complex, occupies the central parts of the Kratovo–Zletovo ore district or the south-eastern parts of the Zletovo ore field. The Zletovo lead–zinc deposit was formed by hydrothermal activity intimately associated with tertiary volcanism along the active continental margin. The major rock types in the area are andesite, dacite, dacitic ignimbrite and volcanic tuff [1, 3, 11]. Dacitic ignimbrite is the most common volcanic unit. The Pb–Zn mineralisation at Zletovo is spatially and genetically related to fracture zones in the NW, NNW and ENE directions, which have served as the main conduits and depositional sites for hydrothermal fluids.

Ore bodies occur as veins, accompanied by impregnation and stockwork-disseminated ore mineralisation, most commonly in the selvage parts of the mineralized vein structures. The ore bodies are of variable dimensions in terms of strike, dip and size. Vein-type ore bodies have been determined to be 100–300 m in length (depending on the length of veins), and rarely over 5 km (the vein no. 10), whereas they have been traced as over 500 m in dip, and according to the data available so far, no change in continuity has been noticed with depth, which is very important fact for the deposit reserve potential. The ore veins are also variable, ranging from several centimetres to 2 m and rarely over 5 m in size. Thickening of veins occurred at places with great changes in their direction in both strike and dip. Investigations done so far have determined about 16 veins from NW–SE to NNW–SSE and ENE–WSW to E–W extension, most commonly subparallel to each other. Occasionally they bend and intersect (commonly under a sharp angle) such as ore veins 2, 3, 4, 6 and 7 (Figure 1). Termi-
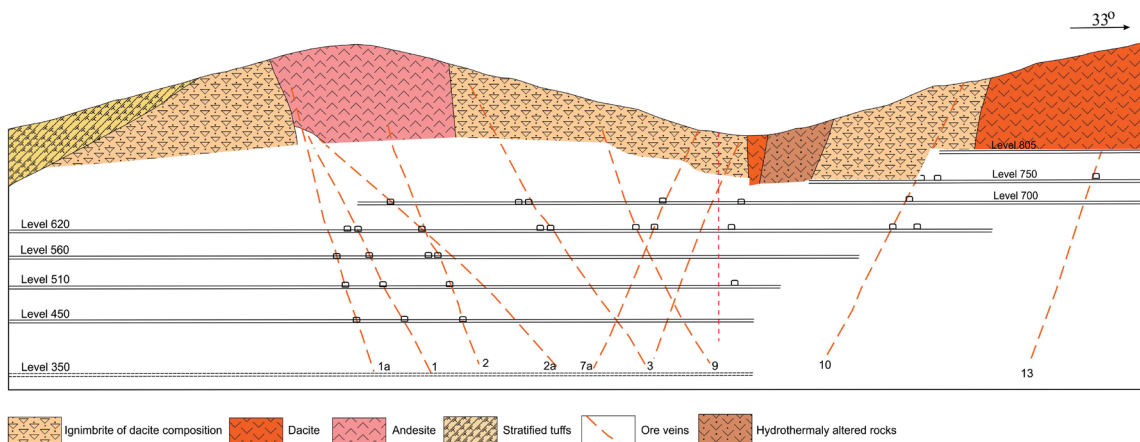

Figure 1: *Geological cross section through the Zletovo Mine.*

nal branching of the main ore veins is common (ore vein 1) and results in the formation of apophyses of small dimensions.

The ore mineral association comprises galena as the principal ore mineral together with sphalerite and subordinate pyrite, siderite and chalcopyrite and rare pyrrhotite, marcasite and magnetite [12, 13]. Veins typically contain large clasts or screens of altered dacitic and andesitic wall rocks. The altered clasts are weakly mineralized or barren.

Analysis

Fluid inclusion studies were conducted on doubly polished thin sections, made of six quartz samples (S1–S7, omitting S2) from the Zletovo mine, in which more than 130 separate fluid inclusions were investigated. Transparent, 150 μm thick, polished plates were utilised, in which fluid inclusions (5–40 μm in size) in quartz were analysed. Fluid inclusions were almost evenly distributed in the studied quartz grains and only those with strong indications of primary origin [14], and thus interpreted as having been trapped during the mineralising event, were taken into account during the microthermometric studies; however, the possibility that some secondary inclusions have also been investigated cannot be excluded [15]. The study was performed using Nikon and Olympus BX51 optical microscopes, and at least 20 inclusions were found and defined in each analysed sampleQQ. Microthermometric data were obtained using a Linkam THMSG600 heating–freezing stage (with temperature range from −196 to +600°C) and TMS 90 controller attached to a conventional petrographic microscope. The stage was calibrated using the Synflinc set of synthetic fluid inclusions and revealed a precision of ±0.1°C for the freezing runs and ±5°C for temperatures near to or higher than 360°C. Salinities were expressed as weight percent NaCl equivalent and were estimated from the melting temperatures of the last crystal of ice for two-phase fluid inclusions [16, 17]. Eutectic temperatures were used to estimate the overall composition of the studied fluid inclusions by comparison with published data for different salt–water systems [15, 18]. The pressure of heterogeneous fluids was de-
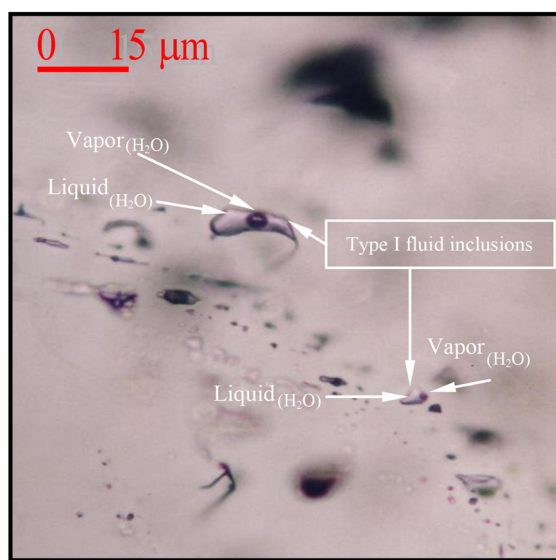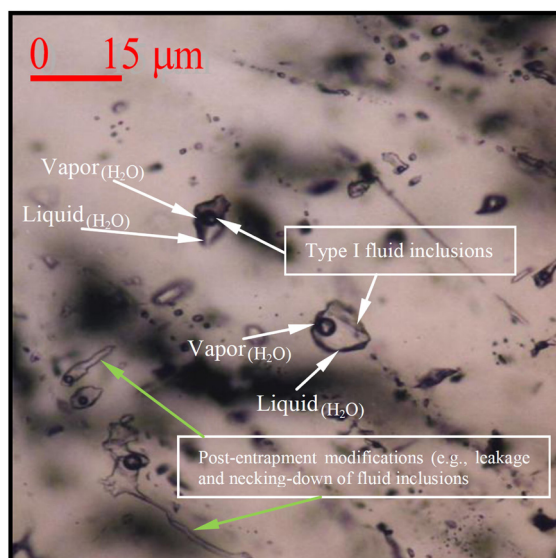

Figure 2: a) Large primary type I (V+L) fluid inclusions; b) Large and minute primary type I (V+L) fluid inclusions.

termined using the method of sections of isochors and isotherms [19].

As mentioned above, the fluid inclusions as remnants of ancient ore-bearing solutions from the Zletovo deposit were analysed by the analytical facilities of the Geological Department of Royal Holloway University in London, Egham, UK.

During the analysis, the following phenomena were analysed and interpreted: the homogenisation temperature (T_h), the temperature of melting of the last ice crystal (T_m), salinity (wt% NaCl equivalent), density, pressure and determination of the primary or secondary ori-

Table 1: *Microthermometry data of studied fluid inclusions from the Zletovo deposit (R. Macedonia).*

Locality and sample label	Mineral	Fluid inclusion type	Salinity (wt% NaCl equivalent)		Homogenisation temperature (°C)	
			Range	Average	Range	Average
Zletovo (*S*-1)	Quartz	P	3.1–11.8	8.6	137.8–265.4	196.2
Zletovo (*S*-2)	Quartz	P	1.7–5.4	4.4	233–285	251.2
Zletovo	Quartz	P	–	–	304.0–368.0	335.0
Zletovo	Quartz	Ps	–	–	210.0–265.0	235.0
Zletovo	Quartz	P	–	–	109.0–163.0	145.0

Note: *P—Primary fluid inclusions; Ps—Pseudosecondary fluid inclusions; samples S-1 and S-2 are from [11] and others are from [8].*

gin of inclusion (Table 1). At least 20 inclusions were taken into account in each specimen, which should provide sufficient data to ensure the reliability of the parameters mentioned above. All the studied fluid inclusions were colourless. The analysed fluid inclusions were mainly of two phases type (L + V, where L is liquid and V is vapour; see Figures 2a and 2b), or liquid phase (L) and vapour phase (V), without the presence of CO_2.

Results and discussion

Primary fluid inclusions in quartz vary in size from 3 to 7 μm and locally up to 12–13 μm (Figure 2). Some secondary liquid-rich inclusions occur along healed fractures that cut across different quartz grains and range from 1 to 5 μm and typically have irregular shapes (Figure 2a, green arrows). The degree of fill of the fluid inclusions was calculated by the following equation:

$$D_f = \frac{L}{L + V}$$

where D_f stands for degree of fill of the inclusion, L for liquid phase and V for vapour phase. The degree of fill of the studied fluid inclusions was high, ranging from 0.70 to 0.95. They consist of two phases (L + V) with 5–30 vol.% vapour. This gave us a basis for calculation of fluid inclusions densities later on. All the studied fluid inclusions were homogenized into a liquid phase. The salinity of solutions, in general, was low,

ranging from 1.7 to 11.8 wt% NaCl equivalent, with an average of 4.4–8.6 wt% NaCl equivalent. In more than 120 individual fluid inclusions, in six quartz samples from Zletovo deposit, homogenisation temperatures (T_h) were within the range of 109–368°C. This range of homogenisation temperatures showed high consistency, bearing in mind the range of 150–350°C determined by former studies [6, 20]. The T_h range given above is characterised by two peak values of 130–180°C and 200–275°C, which can be easily related to the polymetallic stage characterised by the assemblages of sphalerite–galena–pyrite–chalcopyrite and less abundant pyrite–galena–quartz. This is very similar to the data of [21] for the Maouduan deposit, where sulphides followed the sequence pyrite–sphalerite–chalcopyrite–galena. The capture temperatures of inclusions can be determined as medium to high. Here, it is necessary to point out that the homogenisation temperatures define the lowest temperature of mineralisation, while the temperatures determined by stable sulphur isotope geothermometers define the "real" temperatures of mineralisation [22–25]. For all of the studied fluid inclusions, temperatures of first ice melting (T_m) within the range of –26 to –20°C were determined, which suggests temperatures close to the eutectic temperature of the system H_2O–NaCl (–20.8°C), or the solution NaCl with (±K), while Ca and Mg are absent since their eutectic temperature is significantly lower.

In accordance with data obtained from micro-thermometric analyses, diagrams show relations between parameters of the fluid in-
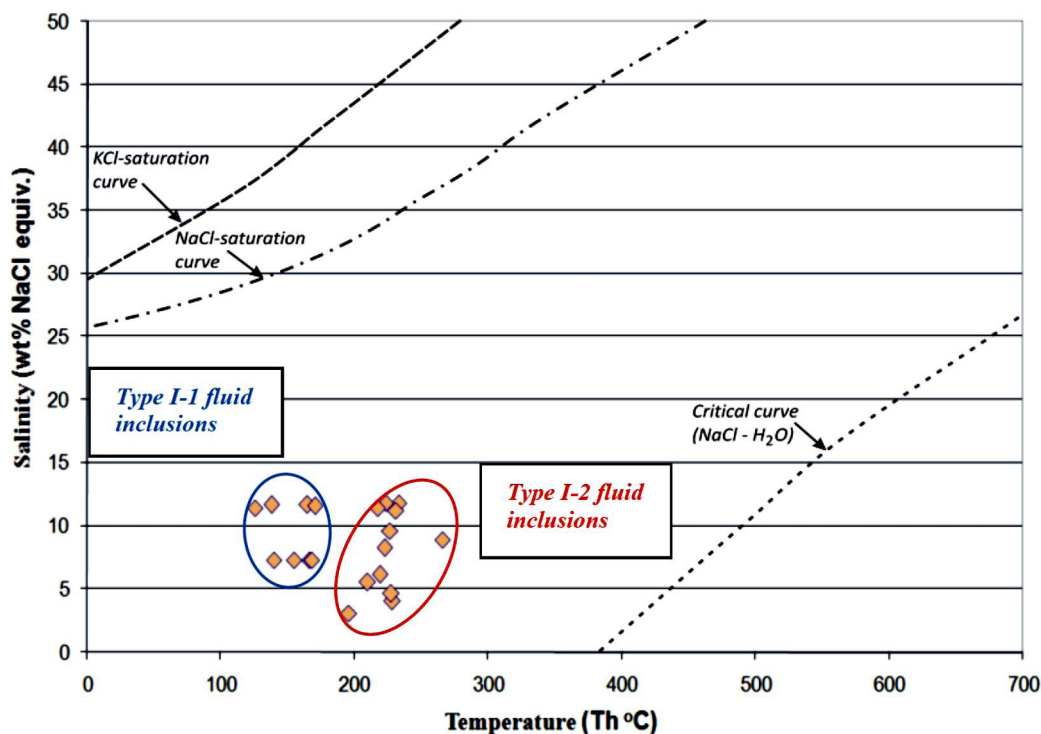
Figure 3: *Relations of homogenization temperatures and salinities in fluid inclusions from Zletovo deposit.*

clusions: salinity (wt% NaCl equivalent) versus homogenisation temperature (Figure 3).

It points to a wide temperature range of fluid inclusions capture, indicating a long process of new material deliveries, which is supported by a salinity difference of up to 10 wt% NaCl equivalent units. Such occurrences are very indicative of mineralisations with multiple pulsations and phase deposition of mineralisations. Fluid inclusion studies of ore-related minerals (in our case, quartz) constrain the fluid evolution in the later stages of development of the hydrothermal system. Homogenisation temperatures plotted against bulk salinity values clearly separate two types of fluid inclusions into two distinct groups, which strongly suggests the involvement of two distinct fluid types in the Pb–Zn mineralisation event: a higher temperature (>200°C), low-to-medium salinity (>7.5 wt% NaCl equivalent) brine, represented by type I-2 fluid inclusions, and a lower temperature (<200°C), low salinity (<5.5 wt% NaCl equivalent) type I-1 fluid inclusion (Figure 3). Post-entrapment modifications (e.g., leakage and necking-down; Figure 2a) could be invoked

to explain the broad and contrasting range of homogenisation temperatures and salinities displayed by types I-1 and I-2 fluid inclusions. Data on the melting temperatures of the last ice crystal and homogenisation temperatures, as expected, have shown the very same grouping as in the Figure 3.

Also, that data shows that there is no direct relation between the melting temperature of the last ice crystal and the homogenisation temperature. Ice melting temperatures ranging from −5.5 to −8.18°C yield salinities between 7.2 and 11.8 wt% NaCl equivalent for type I-1 inclusions. In contrast, ice melting of type I-2 inclusions invariably takes place at temperature values ranging from −1.8 to −8.3°C, indicating a broader range of salinities (3.0–11.8 wt% NaCl equivalent). Upon heating, total homogenisation of type I-1 fluid inclusions invariably occurred via the disappearance of vapour into the liquid phase between 130 and 180°C. Fluid inclusions of type I-2, on the other hand, show vapour disappearance within the interval of 200–275°C. Probably, type I-2 is representative of mixing of less saline and colder (probably
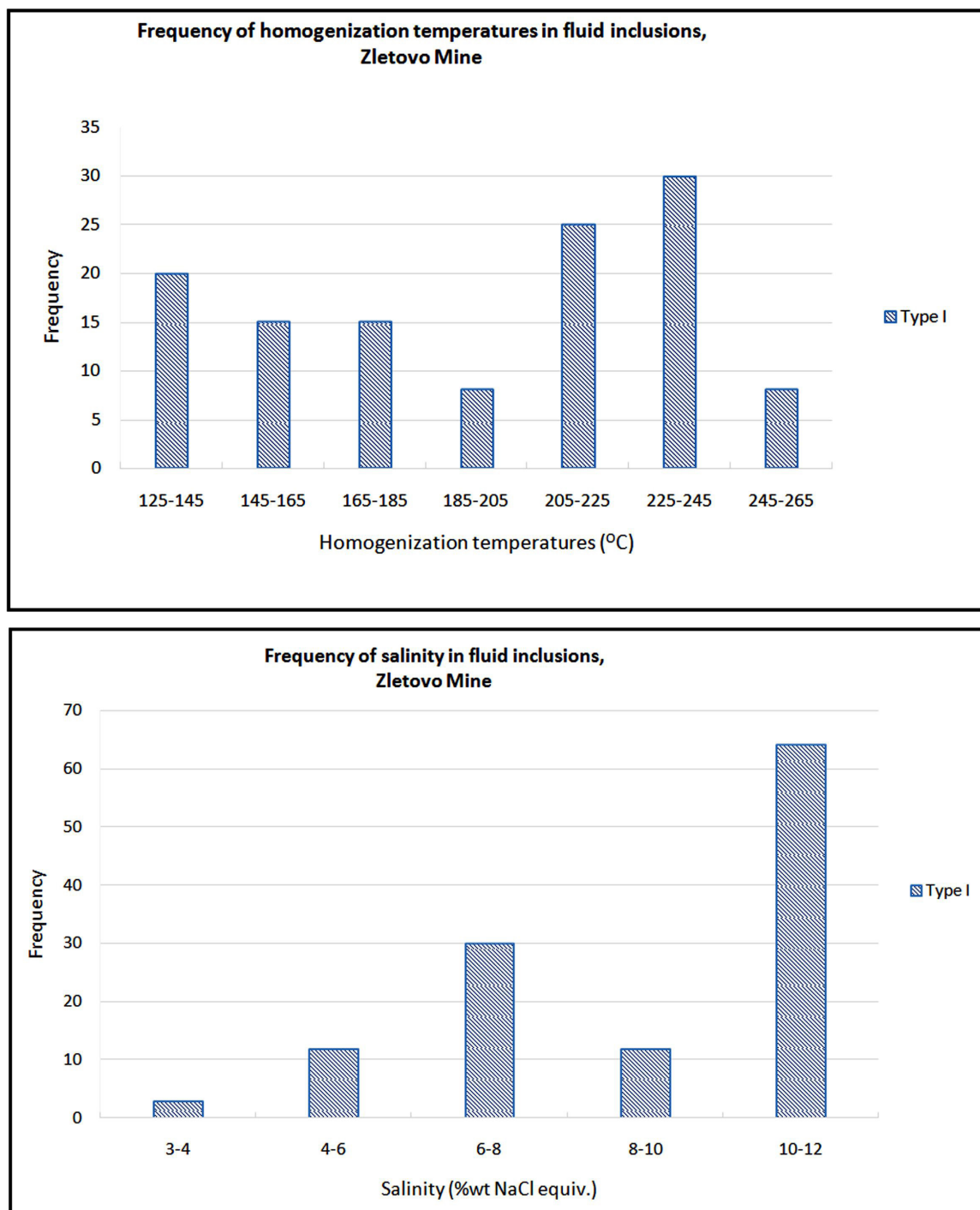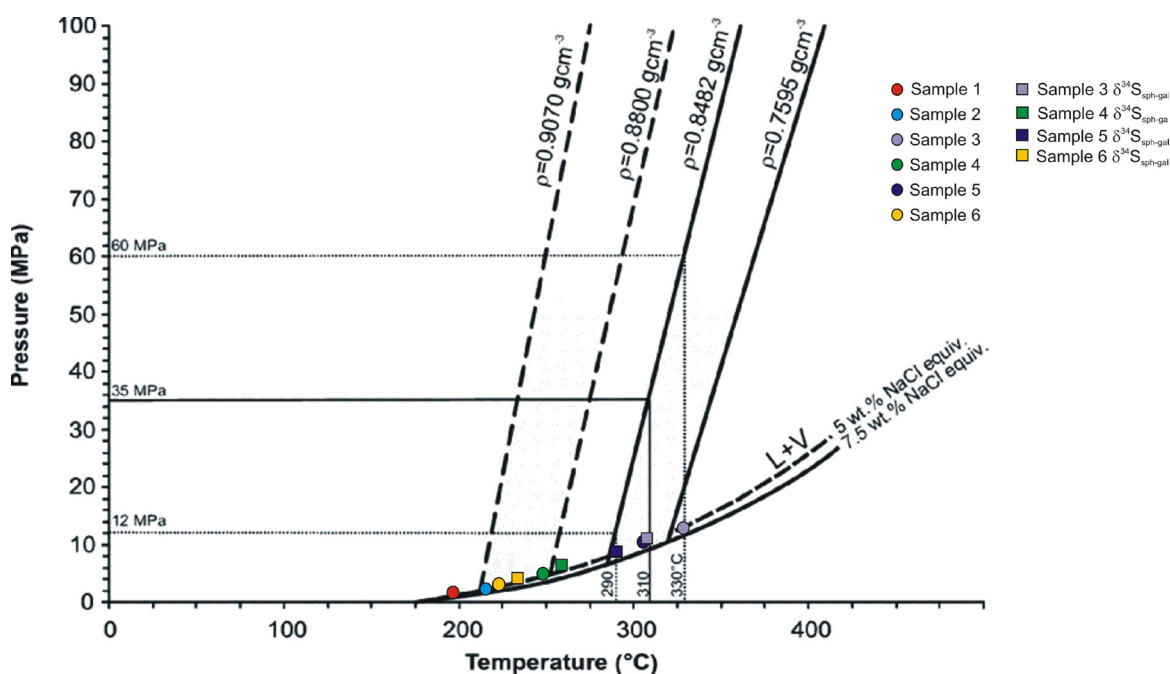
Figure 4: *Relations of homogenization temperature vs. last ice crystal melting temperature in fluid inclu¬sions from the Zletovo deposit [9].*

meteoric water) with magma water. Type I-1 shows a clear connection to I-2, that are inclusions with cooler fluid that survived the "leakage" and their T_h increased significantly.

However, the most common were inclusions with homogenisation temperatures within the ranges of 225–245°C and 205–225°C, while salinities showed the highest frequencies within the ranges of 10–12 wt% and 6–8 wt% NaCl

Table 2: *Several the most crucial fluid inclusion parameters calculated from ours fluid inclusions study.*

	x (NaCl)	w% (NaCl)	Molar volume (cm³/mol)	Density (g/cm³)	Temperature homogenisation (°C)	Pressure (MPa)
Sample 1	0.0282	8.6	20.490	0.93	198.2	1.41
Sample 3	0.0183	5.7	26.155	0.72	334.1	13.14
Sample 4	0.0220	6.8	21.779	0.87	244.5	3.48
Sample 5	0.0187	5.8	24.760	0.76	312.8	9.94
Sample 6	0.0155	4.9	21.099	0.88	217.9	2.16
Sample 7	0.0224	6.9	20.890	0.91	213.1	1.94

Figure 5: *Histograms of a) homogenization temperatures and b) salinities of fluid inclusions in ore associated quartz samples from the Zletovo Mine.*

equivalent (Figure 4). According to eutectic temperatures, solutions were probably of Na–Cl$^{\pm}$ Cl composition.

Calculations all fluid inclusions data from ours latest study, made in FLINCORE and AqCl following instructions [22], yielded the following parameters (Table 2).

Several findings emerged during the data processing from this study. Densities ranged from 0.72 to 0.93 g/cm³. Here, we would like to remind that at high pressures the supercritical fluid has a density similar to liquid water at the Earth's surface (1 g/cm³), while at low pressures and high temperatures its density differs significantly from 1 g/cm³. Low densities resulted in low solubility of ion materials, leading to relatively low mineralizing capacity of the ore-bearing solution [15]. Combining microthermometric data for the majority of fluid inclusions from the quartz (4.9–8.6 wt% NaCl equivalents, T_h = 198–334°C) with P-T stability field limits maximum formation temperature

at 334°C and total fluid pressure at 13.14 MPa. The data above (temperature of homogenisation, salinity, molar volume and density) gave us an opportunity to determine the pressures of formation of these particular parageneses (Figure 5, circles).

As it can be seen from the plot, the pressures ranged from 1.41 to 13.14 MPa. Based on this information, the palaeo-depths of mineralisation (during the capture of fluid inclusions [15]) ranged between 0.6 and 0.8 km [23], which is largely consistent with the depths around 1 km in data given by [2] and indicates that the deposit was generated at subvolcanic levels and under strong influence of lithostatic and explosive pressures. Additionally, the spatial coexistence of types I-1 and I-2 fluid inclusions within the same assemblage also suggest that both fluids may have been present during the precipitation of the ore-related quartz within the timeframe of the Pb–Zn mineralizing episode.

Studied fluid inclusions in quartz samples taken from the ore veins no. 2, 3 and 12, Zletovo mine, were also followed by analysis of the sulphur isotopic compositions in galenite and sphalerite, as basic ore minerals in the paragenesis in which the treated quartz is located. The results of the isotopic analyses of sulphur in the main sulphide minerals were used for calculation of geothermometer temperatures and comparison with the values obtained from fluid inclusions in quartz. After that those values were used to obtain the pressures at which these parageneses had been deposited. Temperatures calculated from sulphur stable isotopes for sulphide–sulfide mineral pairs from the Zletovo deposit, followed directions given in representative literature [24–28]. Namely, our recent stable sulphur isotope data (d34S; see Table 2) in samples from the Zletovo deposit have shown strong value compatibility with some of the previous researchers [29, 12]. In regards to sulphur stable isotopes geothermometers, we would like to stress out that a number of experimental studies have been performed to determine the temperature (in degrees Kelvin) dependence of equilibrium fractionation factors of sulphur isotopes between coexisting galena and sphalerite [30]. Through the years several equations occurred in literature. Some

of the most common examples were those given below:
Some of the earliest equations addressing sulphur stable isotopes thermometers [31], it was found that:

$$\Delta_{ZnS - PbS} = (0.63/T^2) \cdot 10^6. \tag{1}$$

Certain researchers [32] later have proposed the equation:

$$\Delta_{ZnS - PbS} = (0.80/T^2) \cdot 10^6. \tag{2}$$

While particular variation of the equation was suggested some other authors too [33]:

$$\Delta_{ZnS - PbS} = (0.70/T^2) \cdot 10^6. \tag{3}$$

Detailed study of equations above has shown good agreement between values calculated from Equation (3) and filling temperatures of fluid inclusions from several ore deposits [34]. One of the most preferred equations was the one given below [24]:

$$\Delta_{ZnS - PbS} = (0.73/T^2) \cdot 10^6. \tag{4}$$

Authors of this paper, based on numerous references, have decided to use Equation (4) to calculate temperatures (Table 3). We have used sphalerite–galena (in paragenesis with quartz from which originated measured fluid inclusions), as the most commonly used pair that in many cases yields temperatures consistent with those obtained from fluid inclusion data, which suggests that sphalerite and galena in numerous deposits are precipitated by similar mechanisms and under similar conditions [35] while eventual inconsistent temperatures obtained from this geothermometer in some studies elsewhere has been attributed to isotopic disequilibrium [36, 30].

The isotopic sphalerite–galena geothermometer yielded temperatures ranging from 154 to 309°C according to Equation (4) already mentioned above. Temperatures for the Zletovo deposit estimated with the sulphur isotope sphalerite–galena geothermometer are plotted versus fluid inclusion homogenisation temperatures in Figure 6.

Table 3: *Analytical data for coexisting sphalerite and galena crystallized during simultaneous mineralisation within the same ore vein, distribution, sulphur isotope fractionation and estimated mineralisation temperatures.*

| No.	Sample No.		Mineral	No. of vein or horizon	$^{34}S/^{32}S$	$\delta^{34}S‰$	$\delta A - \delta B$	Pair	1000 lnα	T (Kelvin)	T (°C)
1	69 z	δ A	Sphalerite	vein 3,h-625	22.231110	0.5	−2.3	69z-70zA	-2.29621226	563.8394	290.6894
2	70zA	δ B	Galena	vein 3,h-625	22.282216	2.8					
3	12 z	δ A	Sphalerite	vein 2,h-510	22.224444	0.2	2.9	12zs-12zg	2.903631577	501.4073	228.2573
4	12z	δ B	Galena	vein 2,h-510	22.160006	−2.7					
5	M 71	δ A	Sphalerite	vein 12,h-490	22.155562	−2.9	−4	M71s-M71g	-4.003608591	427.0076	153.8576
6	M 71	δ B	Galena	vein 12,h-490	22.244442	1.1	−2.5	M71s-M76g	-2.504133126	539.9241	266.7741
7	M 76	δ B	Galena	vein 12,h-490	22.211112	−0.4					
8	M 39	δ A	Sphalerite	vein 3,h-700	22.225545	0.3	2	M39s-M39g	2.156966909	581.7544	308.6044
9	M 39	δ B	Galena	vein 3,h-700	22.177657	-1.7					
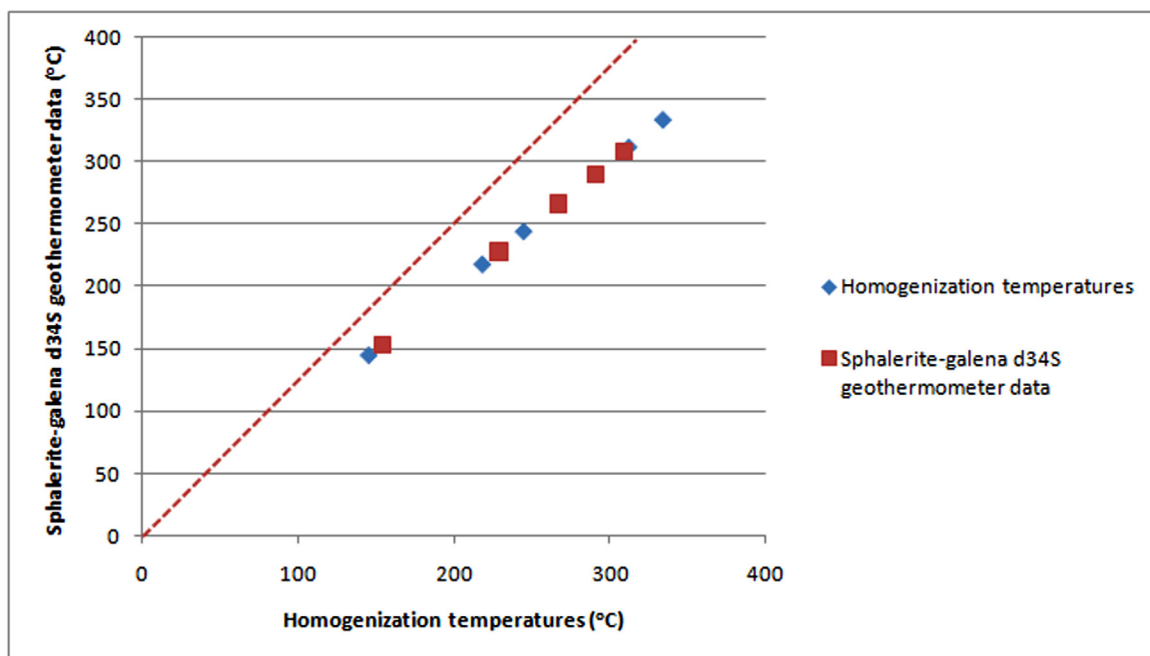
Figure 6: *Changes in density and gas pressure of the liquid water [24, 9].*
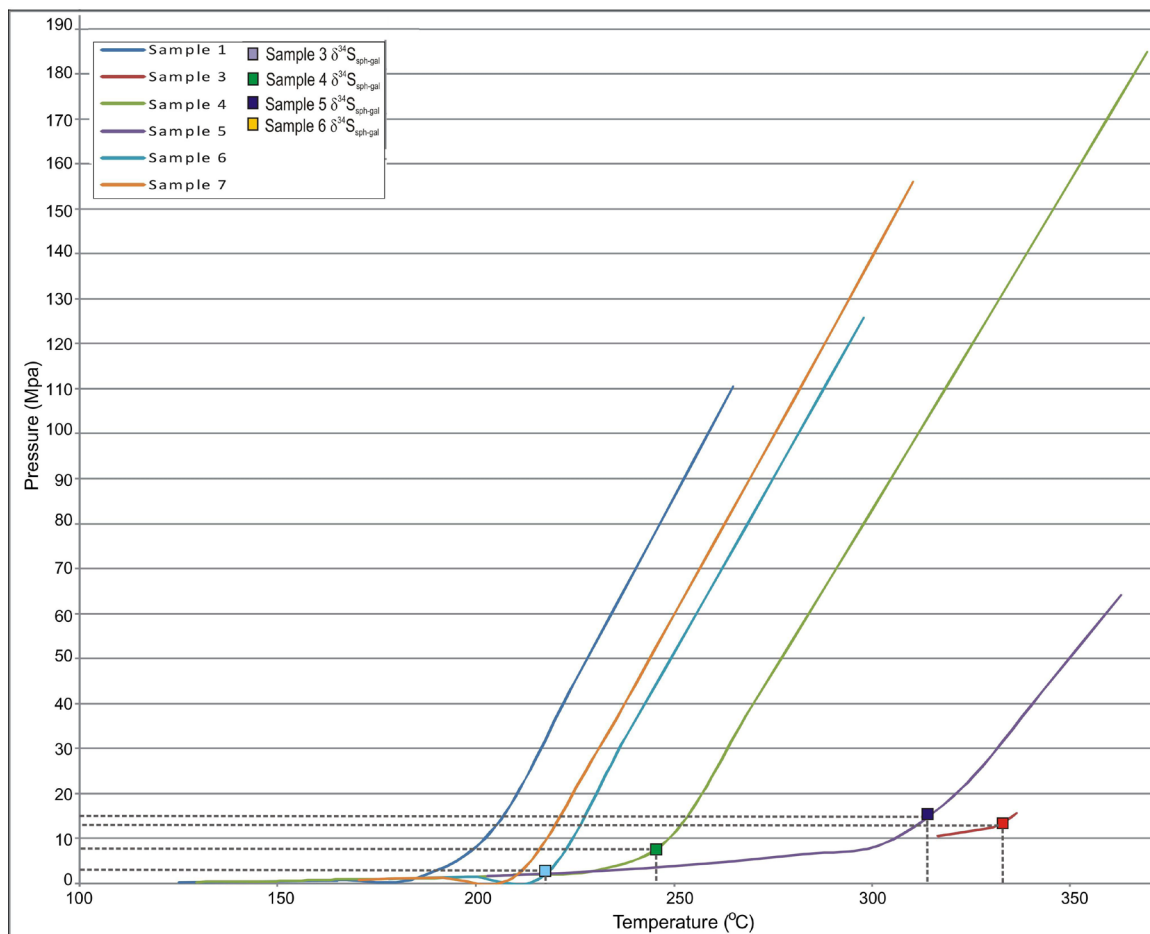
Figure 7: *Density changes of supercritical fluid as a function of pressure and temperature (basic plot data [25] and [9]).*

The majority of sulphur isotope mineral pair (sphalerite–galena) data yield isotopic temperatures (154–309°C ±6°C) in general agreement with fluid inclusions data. This suggests that isotopic equilibrium was established between the sphalerite and galena and was not affected by an eventual re-equilibration. Thus, the sphalerite–galena geothermometer, along with fluid inclusion results, appears to give correct temperatures for ore formation. Here, we would like to stress out that Equation (4) yielded values are in good agreement with homogenisation temperatures (Figure 6).

Using solely the data from our research (fluid inclusions and sulphur stable isotopes), as well as their compilation in Excel, an isochore diagram was constructed (Figure 7).

From the plot above (Figure 7), we obtained confirmation of the data obtained from the

similar diagram above (Figure 5). As it can be seen, these pressures only slightly or not at all differ from the pressures determined solely based on fluid inclusions data, which point out to an equilibrium of the system at the moment of paragenesis deposition.

Conclusions

The main ore parageneses in the Zletovo mine are galena–sphalerite ones, usually followed by quartz, pyrite and chalcopyrite, which determines the hydrothermal nature of this famous vein type of lead–zinc deposit. The selected quartz grains, where fluid inclusions have been identified and measured originates from the main ore parageneses with galena and sphalerite prevailing, followed by pyrite, chal-

copyrite, calcite, kaolinite and others. Homogenisation temperatures were within the range of 335–145°C and reflect phases of pulsation of hydrothermal solutions that have been classified into four separate and consecutive groups from the highest temperature down to the lowest. Also, it was confirmed that the hydrothermal ore-bearing solution was of NaCl-type with salinity ranging from 4.4 to 8.6 wt% NaCl equivalent. Density or fulfilment of fluid inclusions with liquid phase was within the range of 0.7–0.95 g/cm³. Calculated pressures and paleo-depths of mineralisation were probably within the range of 1.41–313.14 MPa and 0.6–0.8 km, respectively. The latest data obtained with the study of fluid inclusions within the quartz from ore veins from the Zletovo mine are quite similar to some older data [6], with certain differences in the concentration of NaCl (10–25 wt% NaCl equivalent), which is probably due to analysis of fluid inclusions from cleophane varieties of sphalerite and barites in former studies. Calculation of the homogenisation temperature frequencies and salinities clearly points to the productive solutions from which the primary parageneses were deposited.

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