

МАКЕДОНСКО ГЕОЛОШКО ДРУШТВО

ВТОР КОНГРЕС

на

Геолозите на Република Македонија

ЗБОРНИК НА ТРУДОВИ



Уредници:

Јовановски, М. & Боев, Б

Крушево, 2012

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FLUID INCLUSIONS STUDY IN THE QUARTZ FROM THE ZLETOVO MINE

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Abstract

The latest studies of fluid inclusions in Zletovo Mine were performed on quartz samples from the ore veins No. 2, 3 and 8. The quartz samples were selected from main ore parageneses where have dominated galena and sphalerite, followed by pyrite, chalcopyrite, calcite, kaolinite etc. Homogenization temperatures were within the range of 335÷145°C and they reflect phases of pulsation of hydrothermal solutions, which have been defined into four groups going from the highest temperatures down to the lowest temperatures ones. Also, it was confirmed the hydrothermal ore-bearing solutions were of a NaCl-type where concentration of components was within the range 4.4÷8.6 % wt NaCl equiv. This points out that hydrothermal solutions at the moment of formation of the analyzed quartz already have been within the final mineralizing phase. Density of fluid inclusions with liquid phase were within the range 0.7÷0.95 g/cm³. Calculated pressures and paleo-depths of mineralization ranged from 200÷250 bar and 1.0÷1.5 km, respectively.

Key words: homogenization, quartz, fluid inclusion, Zletovo Mine

INTRODUCTION

The lead-zinc deposit Zletovo has been subject of exploitation even back to the medieval time while its official exploitation have started in 1941, but for a short period because the Second World War started and the mine worked under the occupation. After the end of the war at the Zletovo deposit was built modern mine with an annual production capacity of 400 000 t of ore. The Zletovo mine is in continuous production for more than 70 years, mainly as state owned, while at 2006 there was a transformation of ownership into a private one as an associate branch of the company Indo Minerals and Metals. An average content of metals within the ore is around 8% Pb+Zn.

Along to the exploration of the Zletovo deposit were performed detailed and special studies of the lead-zinc mineralizations as well as the settings where it has been deposited. Within the important published and fund materials here we would like to stress out that the most complex and complete one were workings of Петковиќ и др. (1982), Блечик (1983), Serafimovski (1990, 1993), Ефремов (1993), Serafimovski and Aleksandrov (1995), Serafimovski et al., (2005), Serafimovski et al., (2006), etc..

GEOLOGICAL SETTING AND MINERALIZATION

The Zletovo lead and 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 has been formed during hydrothermal activity that was intimately associated with Tertiary volcanism along an active continental margin. The major rock types in the area are andesite, dacite, dacitic ignimbrite and volcanic tuff (Serafimovski 1990; Serafimovski and Aleksandrov 1995; Tasev 2003). Dacitic ignimbrite is the most common volcanic unit. Pb-Zn mineralization at Zletovo is spatially and genetically related to fracture zones that trend NW, NNW and ENE. These fractures appear to have served as the main conduits and depositional sites for hydrothermal fluids.

Ore bodies occur as veins, accompanied by impregnation and stockwork-disseminated ore mineralization, most commonly in the selvage parts of the mineralized vein structures. The ore bodies are of variable dimensions in strike, dip and size. Vein type ore bodies have been determined 100 to 300 m in length (depending on the vein), rarely over 5 km (vein no 10), whereas they have been traced over 500 m in

dip and according to data available so far no change in continuity has been noticed to depth which is very important for the potential of the deposit.

The ore veins are also variable, ranging from several centimeters up to 2 m, and rarely over 5 m in size. Thickening of veins occurred in places where there are great changes in their direction both in strike and dip. Investigations

done so far have determined about 16 veins of 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). Flank branching of main ore veins is common (ore vein 1) which results in formation of apophyses of small dimensions.

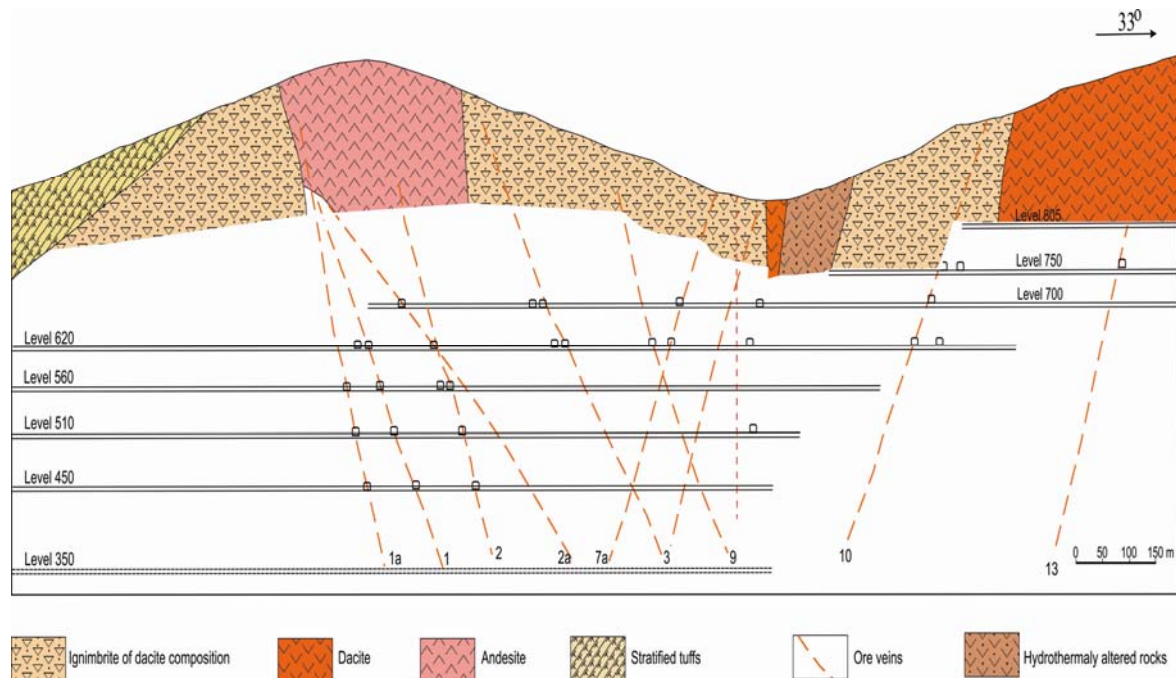


Figure 1. Geological cross section through the Zletovo Mine

The ore mineral association comprises galena as the principal ore mineral together with sphalerite and subordinate pyrite, siderite and chalcopryite, and rare pyrrhotite, marcasite, and magnetite. Minor occurrences of U-mineralization (pitchblende) have also been discovered. Detailed information about the mineral parageneses and geochemical features of the major minerals in ore veins is provided in Mudrinic and Serafimovski (1991) and Serafimovski and Tasev (2003). The veins typically contain large clasts or screens of altered dacitic and andesitic wallrocks. The altered clasts are weakly mineralized or barren.

METHODOLOGY

The study of numerous transparent quartz wafers, made of 6 quartz samples (S1-S7, there is not S2) from the Zletovo mine, polished on both sides (with a thickness of 150 μm), was performed under the optical microscopes Nikon and Olympus BX51,

equipped with high quality lenses capable of studying the fluid inclusions (whose dimensions are varied in the range from 5-40 μm) and photographic cameras for photographing the fluid inclusions. In each analyzed sample were analyzed by at least 20 inclusions, which guarantees the reliability of results obtained for several parameters assessed.

Detailed investigations at Royal Holloway, University of London, were performed using the Linkam heating stage THM 600 (temperature range -196°C to $+600^{\circ}\text{C}$) and controller TMS 90, which was possible to be programmed for number of phases and temperature changes over the time

The accuracy of the apparatus was controlled by measuring the temperature of melting and homogenization of "artificial" standards of pure substances. The calibration was performed using water fluid inclusion in synthetic quartz crystal, but we will still have an error of $\pm 1^{\circ}\text{C}$.

RESULTS AND DISCUSSION

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

During the analysis were analyzed few parameters of the fluid inclusions, such are: T_h -homogenization temperature, T_m -temperature of melting of last ice crystal, salinity (%NaCl), density, pressure, determination of

the primary or secondary origin of the inclusion etc. (Table 1).

In each analyzed sample were taken into account at least 20 inclusions, which should provide sufficient data that will ensure reliability of the parameters mentioned above.

All the studied fluid inclusions were colorless. Analyzed fluid inclusions were mainly of two phases type (L+V where L-Liquid; V-Vapour; see Figure 2a and 2b), or liquid phase (L) and vapour phase (V), without presence of CO₂.

Table 1. Microthermometry data data of studied fluid inclusions from the Zletovo deposit, Macedonia

Locality and sample label	Mineral	Tip na fluidni inkluzii	Salinity (wt% NaCl equiv.)		Homogenization temperature (°C)	
			Range	Average	Range	Average
Zletovo (S-1)	Kvarc	P	3.1÷11.8	8.6	137.8÷265.4	196.2
Zletovo (S-2)	Kvarc	P	1.7÷5.4	4.4	233÷285	251.2
Zletovo	Kvarc	P	-	-	304.0÷368.0	335.0
Zletovo	Kvarc	Ps	-	-	210.0÷265.0	235.0
Zletovo	Kvarc	P	-	-	109.0÷163.0	145.0

Note: P-Primary fluid inclusions; Ps-Pseudoprimary fluid inclusions; samples S-1 and S-2 are from (Tasev, 2003), other are from Efremov (1993)

Primary fluid inclusions in quartz varied 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 had irregular shapes (Figure 2a lower left area-green arrows).

The degree of fulfillment of the fluid inclusions has been calculated by the formula below:

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

where: Df – degree of fulfillment of the inclusion

L – liquid phase

V – vapor phase

The degree of fulfillment of the studied fluid inclusions was high, ranging from 0.7 up to 0.9. They consist of two phases (L+V) with 10 to 15 vol.% vapor. All the studied fluid inclusions homogenized into a liquid phase. The salinity of solutions, in general, was low, ranging from 1.7 to 11.8 wt% NaCl equiv, in average 4.4-8.6 wt% NaCl equiv.

In more than 120 individual fluid inclusions in six quartz samples from Zletovo Mine,

homogenization temperatures (T_h) were within a range from 109 up to 368°C. This range of homogenization temperatures have shown high consistency bearing in mind range of 150÷350 °C determined by former studies (Blečić, 1983). Also here we would like to stress out that T_h range given above is characterized with two peak values of 130–180°C and 200–275°C, which easily can be related to the polymetallic stage that is characterized by the assemblages of sphalerite–galena–pyrite–chalcopryrite, and less abundant pyrite–galena–quartz. This is very similar to the data of Li et al., (2011) for the Maouduan deposit where sulfides followed the sequence pyrite → sphalerite → chalcopryrite → galena. The temperatures of capture of the inclusions can be determined as medium to high ones. Here it is necessary to point out that the homogenization temperatures are defining the lowest temperature of mineralization while the temperatures determined by sulfur stable isotope geothermometers are defining “real” temperatures of mineralization (Ohmoto and Rye, 1979; Ohmoto, 1986; Rye et al., 1974; Shelton and Rye, 1982).

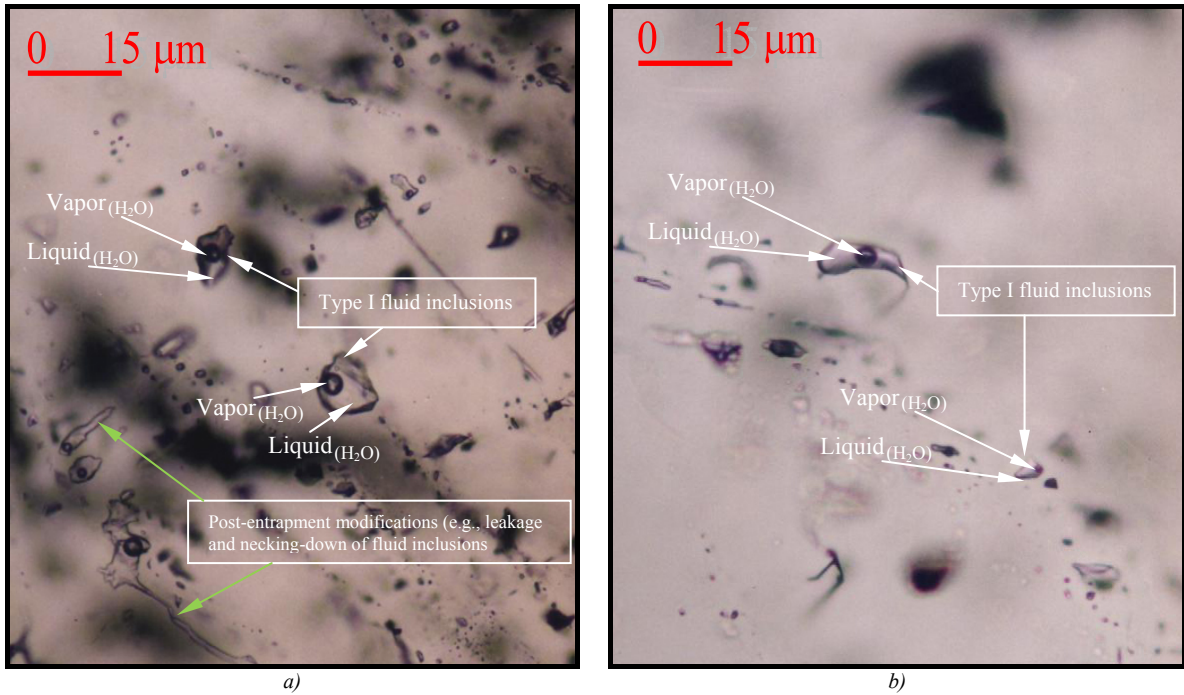


Figure 2. a) Large primary type I (V+L) fluid inclusions; b) Large and minute primary type I (V+L) fluid inclusions

For all of the studied fluid inclusions were determined temperatures of first ice melting (T_m) within the range from -26°C up to -20°C , which points out to a temperatures close the eutectic temperature of the eutectic system $\text{H}_2\text{O}-\text{NaCl}$ (-20.8°C), or within the solution are present Na, Cl and H_2O ($\pm\text{K}$) while Ca and Mg

are absent since their eutectic temperature is significantly lower.

In accordance with data obtained from micro thermometric analyses were plotted a few diagrams that are showing certain relations of certain parameters of the fluid inclusions: salinity (wt% NaCl equiv.) vs. homogenization temperature (Figure 3).

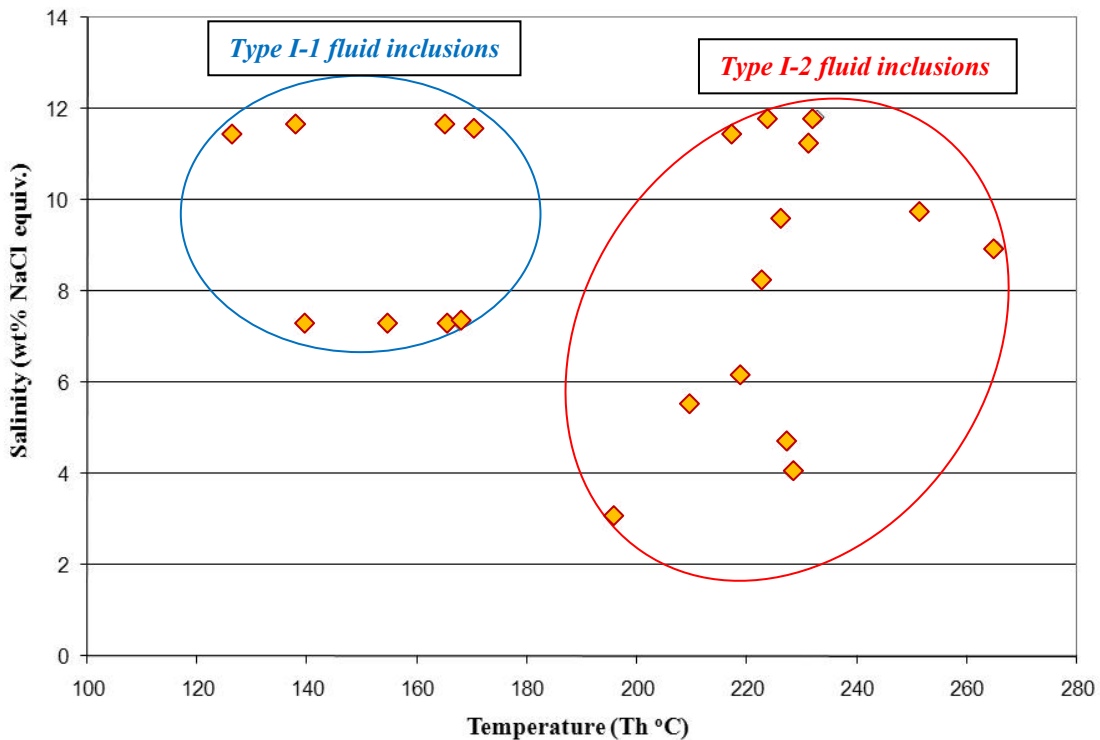


Figure 3. Relations of homogenization temperatures and salinities in fluid inclusions from Zletovo deposit

From the plot can be concluded that was a wide temperature range of fluid inclusions capture, which indicates a long process in which there were deliveries of new material that is supported by salinity difference of up to 10 wt% NaCl equiv., units.

Such an occurrences are very indicative of mineralizations with multiple pulsations and phase deposition of mineralizations.

Fluid inclusion studies of ore-related minerals (in ours case-quartz) constrain the fluid evolution in the later stages of the hydro-thermal system development. Homogenization temperatures plotted against bulk salinity values clearly separate two types of fluid inclusions into two distinct groups which strongly suggest involvement of two distinct fluid types in the Pb-Zn mineralization event: a higher temperature (>200°C), low to medium

saline (>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 inclusions (Figure 3).

Post-entrapment modifications (e.g., leakage and necking-down; Figure 2a) could be invoked to explain the broad and contrasting range of homogenization temperatures and salinities displayed by types I-1 and I-2 fluid inclusions.

Also, we have used data of temperatures of melting of last ice crystal and homogenization temperatures to plot respective diagram (Figure 4).

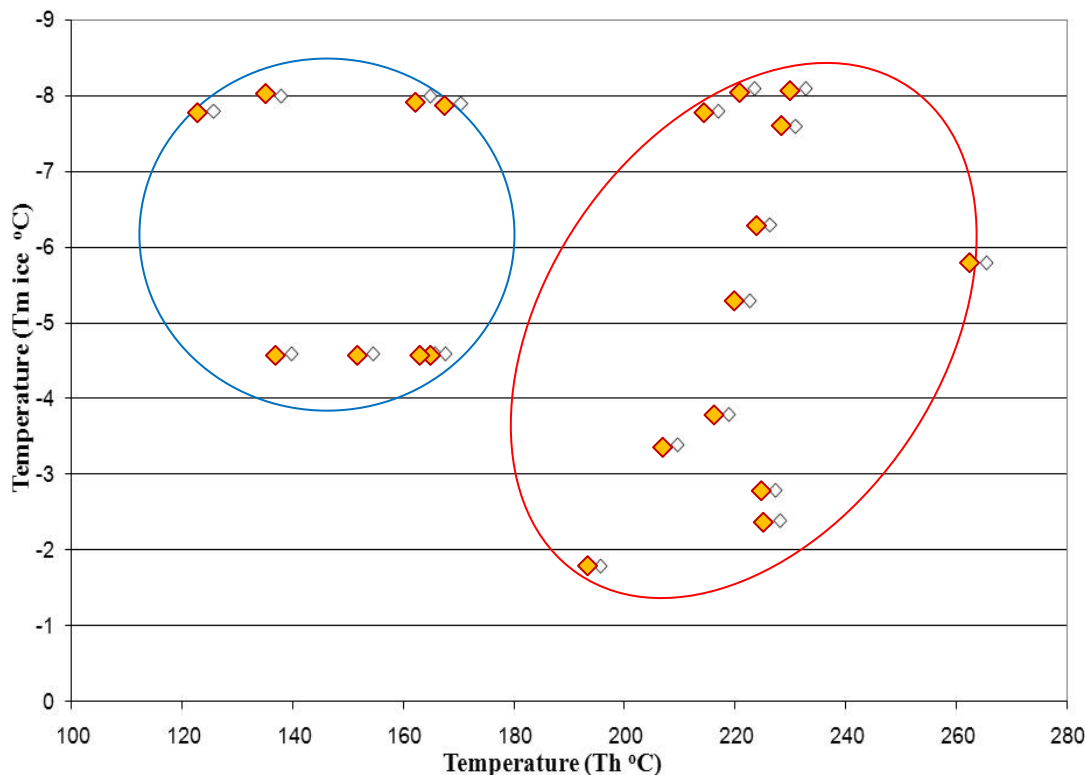


Figure 4. Relations of homogenization temperature vs. last ice crystal melting temperature in fluid inclusions from the Zletovo deposit (Tasev, 2003)

From the diagram above it can be seen that there is not any direct relation between the last ice melting temperature and homogenization temperature.

Ice melting temperatures ranging from -5.5°C to -8.18°C yield salinities between 7.2 and 11.8 wt.% NaCl equivalent for type I-1

inclusions in the ore related quartz. As a contrast, ice melting of type I-2 inclusions invariably takes place under temperature values, ranging from -1.8°C and -8.3°C , indicating broader range of salinities ($3.0 \div 11.8$ wt.% NaCl equivalent).

Upon heating, total homogenization type I-1, fluid inclusions invariably occurred via the disappearance of vapor into the liquid phase between 130–180°C. Fluid inclusions of type I-2, on the other hand, show vapor disappearance within the interval of 200–275°C.

For the Zletovo ore deposit, obtained temperatures calculated from sulfur stable isotopes for sulfide-sulfide and sulfide-sulphate mineral pairs (Ohmoto and Rye, 1979; Ohmoto, 1986; Rye et al., 1974; Shelton and Rye, 1982; Brownlow, 1996), were within the range 134 ÷ 307 °C, which closely corresponds to the temperature ranges obtained by the fluid inclusions studies. That fact points out to an isotopic equilibrium during the genesis of

sulfide/sulphate minerals with the hydrothermal solutions, which is by the way the basic requirement for the accuracy of the isotope thermometers. According to the eutectic temperatures, solutions probably were of Na-K-Cl composition.

Data obtained during the fluid inclusions studies were used to plot diagram of relations between temperatures, pressures and densities (Figure 5). Pressures during the formation of analyzed fluid inclusions used to be quite high, ranging from 175 up to 240 bars.

Due to such setting of physical and chemical conditions fluid densities also were in upper part of the scale or within the range 0.7 ÷ 0.95 g/cm³.

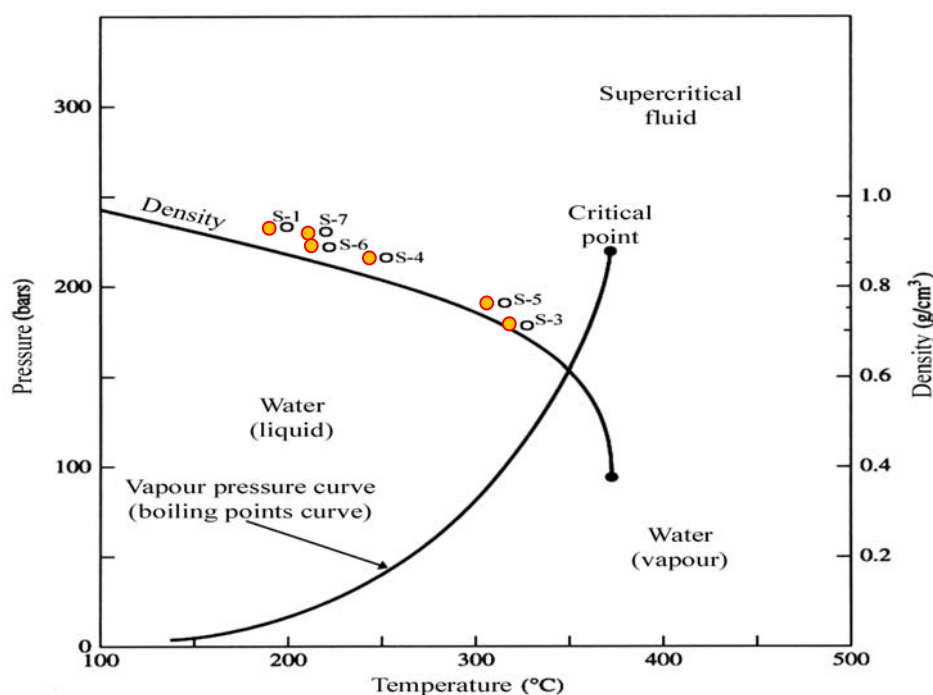


Figure 5. Changes in density and gas pressure of the liquid water (Verhoogen et al., 1974; Tasev, 2003)

Also, we would like to stress out that at high pressures the supercritical fluid have density similar to the liquid water at the Earth's surface (1 g/cm³) while at low pressures and high temperatures density significantly differs from 1 g/cm³.

Low densities resulted in low solubility of ion materials leading to relatively low mineralizing capacity of the ore bearing solution (Roedder, 1984). In direct correlation to the data above was plotted diagram relating temperatures, pressures and depths (Figure 6).

As can be seen from the diagram, below, the paleodepths of mineralization (during the capture of fluid inclusions; Roedder, 1984) ranged between 1.0 and 1.5 km (Figure 6), which is largely consistent with the depths above 1 km in data given by Blečić (1983) and indicating that the deposit was generated at sub-volcanic levels and under strong influence of lithostatic and explosive pressures.

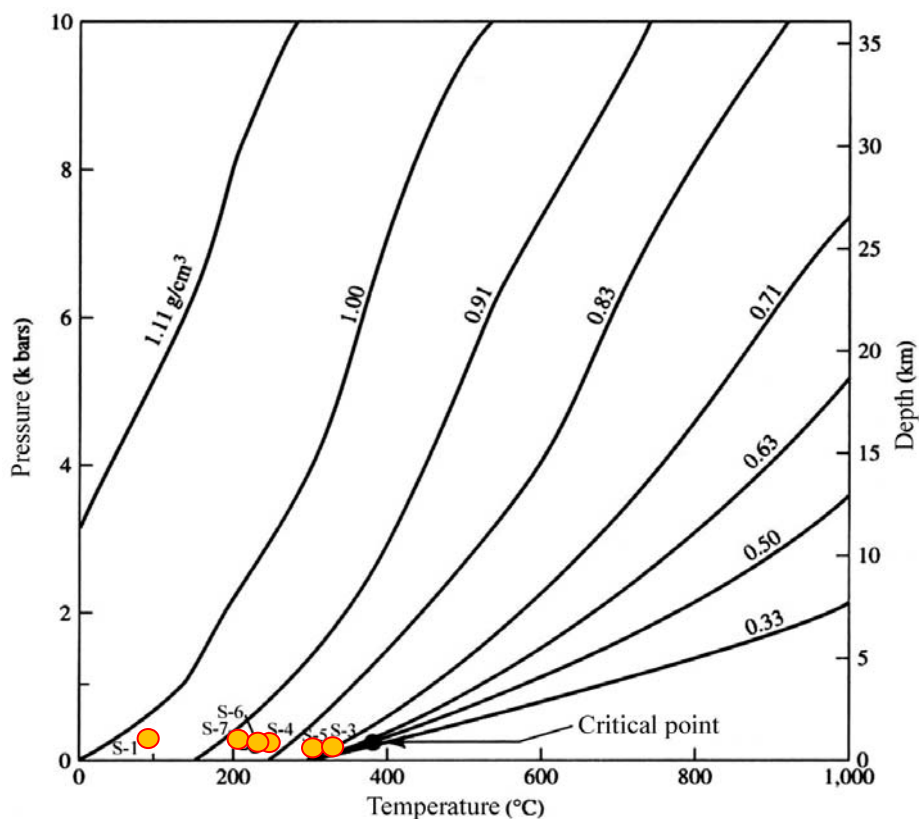


Figure 6. Density changes of supercritical fluid as a function of pressure and temperature (Best, 2002; Tasev, 2003).

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.

CONCLUSION

The lead-zinc deposit Zletovo is a very characteristic representative of the vein type sub-volcanic hydrothermal deposits related to the Tertiary volcanic complex of the famous Kratovo-Zletovo volcanic area.

Selected quartz where has been identified and measured fluid inclusions originate from the main ore parageneses where prevailed galena and sphalerite followed by pyrite, chalcopyrite, calcite, kaolinite etc.

Homogenization temperatures were within the range 335–145°C and they reflect phases of pulsation of hydrothermal solutions that have been defined into four separate and consecutive groups from the highest temperature down to the lowest temperatures ones.

Also, it was confirmed that the hydrothermal ore-bearing solution were of NaCl-type where

the salinity ranged 4.4–8.6 %wt NaCl equiv. Density or fulfillment of fluid inclusions with liquid phase was within the range from 0.7 up to 0.95 g/cm³. Calculated pressures and palodepths of mineralization probably were within the range 200–250 bar and 1.0–1.5 km respectively.

The latest data obtained with study of fluid inclusions within the quartz from ore veins from the Zletovo Mine are quite similar to the data presented in Blečić (1983) with certain differences in concentration of NaCl (10–25 %wt NaCl equiv.), which is probably due to analysis of fluid inclusions from cleophane varieties of sphalerite and barites in former studies.

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