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Abstract. Six types of fluid inclusions were identified in three growth zones of hydrothermal quartz from the Rudnik skarn deposit. In the core zone, primary two-phase fluid inclusions of high (type 1) and moderate salinity (type 2) homogenized to liquid between 350-430 °C and 340-420 °C, respectively. Raman analysis revealed that the vapour phases are a CO_2-CH_4 gas mixture, with a predominance of CO_2. The core contains and dispersed vapour-rich fluid inclusions of low salinity (type 3) composed of CO_2-CH_4-H_2S gas mixture with significant amounts of H_2S, as well as liquid-rich fluid inclusions (type 4) predominantly composed of pure water and small vapour phase with lower homogenization temperatures between 174-284 °C. In the transition zone, primary fluid inclusions arranged perpendicular to the growth zone (type 5) homogenize over a wide range of temperatures between 235-401 °C. The vapour phase is a CO_2-CH_4 gas mixture additionally enriched in CH_4 compared to the other types. Fluid inclusions in paths of the rim zone of the quartz (type 6) have a homogenization temperature between 259-385 °C. The vapour phase is a CO_2-CH_4 mixture with reduced CH_4 content, while the liquid phase has a low salinity.

1 Introduction

The Rudnik deposit is located in central Serbia and present one of the most significant polymetallic skarn deposits in the Serbo-Macedonian metallogenic province (Figure 1). Over 13 Mt of polymetallic ore (Pb-Zn-Cu-Ag) was found in the Rudnik deposit so far. Ore bodies are hosted in the complex of contact-metasomatically altered areas of the Upper Cretaceous flysch units (Djoković 2013) (Figure 2). Genesis of the ore deposit is temporally associated with the formation of the Oligocene-Miocene volcanic-intrusive complex and results of subsequent hydrothermal activities (Cvetković et al. 2016).

Quartz is commonly associated with the ore mineralization in the deposit. According to field and petrographic observations, we can distinguish two generations of quartz. The first, syn-ore generation of quartz is characterised by well-developed prismatic crystals intergrowth with ore minerals. This generation of quartz commonly has well-developed oscillatory growth zoning. The second generation is primarily represented by anhedral or, less extent, small idiomorphic quartz crystals which are coevally with calcite filling the voids between ore mineralization.

Until now, there are only preliminary studies on the presence of fluid inclusions (Blečić 1974). The primary task of the study is to determine the characteristics of fluid inclusions hosted in syn-ore quartz and to provide a contribution to define the multiple events in the magmatic-hydrothermal system that led to the formation of the deposit.

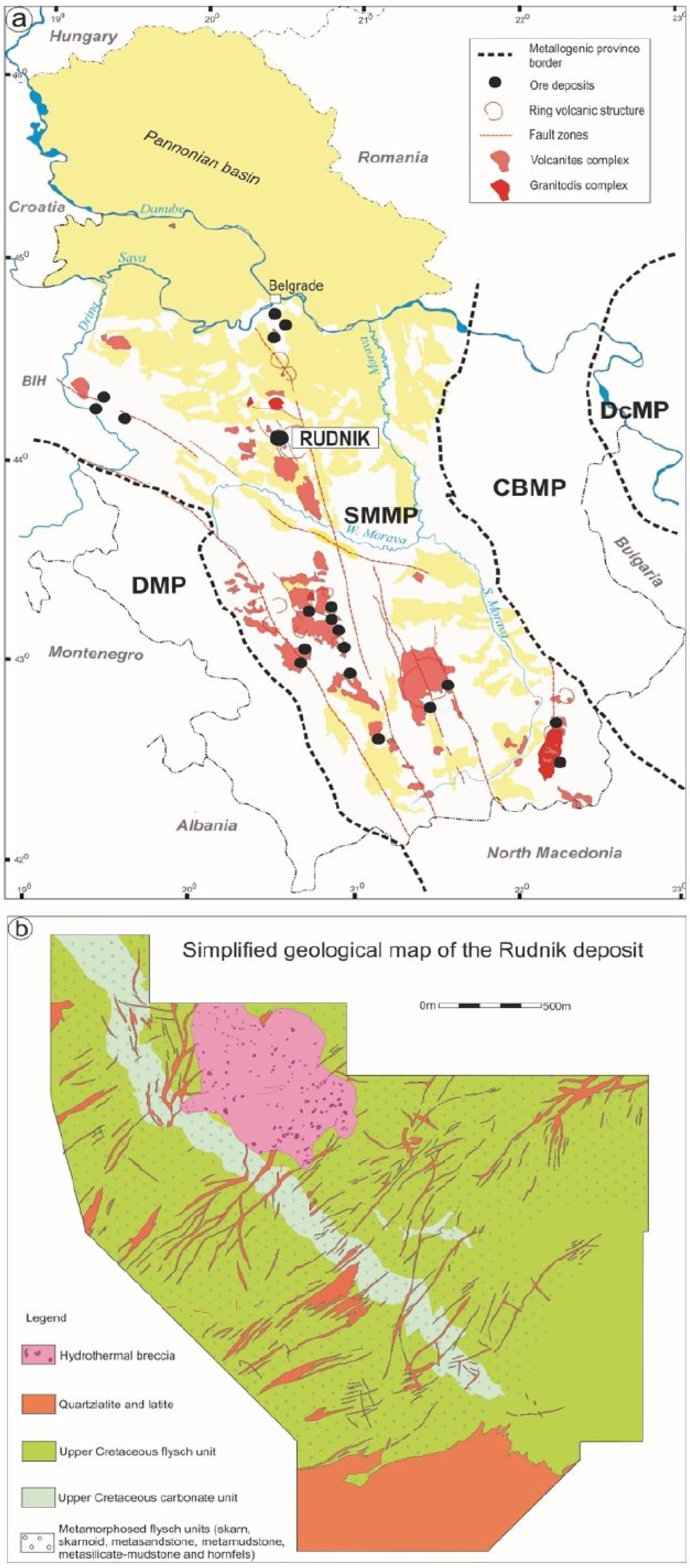

Figure 1. a Location of the Rudnik ore deposit in Serbo-Macedonian metallogenic province (adapted from Jelenkovic et al. 2008). **b** Simplified geological map of the Rudnik deposit (adapted from Djoković 2013)).

2 Methodology

Preparation of thick section was performed at the University of Belgrade, Faculty of Mining and Geology at the Department of Mineralogy, Crystallography, Petrology and Geochemistry and at the Department of Economic Geology. Fluid inclusions were studied from doubly polished thick sections of thickness ~150 μm.

Microthermometry of fluid inclusions was conducted at the Department of Applied Geosciences and Geophysics, chair of Resource Mineralogy at the University of Leoben in Austria and Fluid inclusion Laboratory at the Faculty of Mining and Geology at the University of Belgrade.

Microthermometry was carried out using a Linkam MDS 600 stage mounted on an Olympus BX 60 optical microscope in Leoben. Calibration of the Linkam stage was performed using synthetic fluid inclusion standards (pure H_2O, CO_2–H_2O mixtures) for the melting temperatures of CO_2 at -56.6 °C, of H_2O at 0.0 °C and the critical homogenisation temperature of H_2O at 374.0 °C. Microthermometry measurements at the Faculty of Mining and Geology in Belgrade were carried out on a THMSG600 heating stage connected to an Olympus BX51 microscope. The primary CO_2 standard WRECT-006160 was used for calibration. The reproducibility is ±0.1 °C between -60 °C and +100 °C and ±0.3 °C at higher temperatures.

Calculations of microthermometric parameters were performed using AqSo_NaCl software (Bakker 2018).

Raman spectroscopy was performed with a LabRAM (Department of Applied Geosciences and Geophysics, chair of Resource Mineralogy, Leoben) instrument, from the company Horiba Scientific, Jobin Yvon Technology. The LabRAM is operated with an Olympus microscope, and an LMPlanFI 100x/0.80 numerical aperture objective lens. A frequency-doubled 100 mW Nd-YAG laser with an excitation wavelength of 532.068 nm is used, with a laser power of about 1 to 2 mW at the sample surface. The scattered light is dispersed by 1800 grooves/mm gratings. The detector is an air-cooled (Peltier) CCD-3000 (1024 x 256 pixels) operating at -60 °C. Spectra are collected using multiple spectral windows between 100 to 3000 cm^{-1}, corresponding to a pixel resolution of about 1.64 cm^{-1} at relative low wave numbers, and 1.35 cm^{-1} at relative high wave numbers. A 100 μm slit combined with a 1000 μm confocal hole aperture is used to obtain the best resolved spectra.

3 Petrography

Colourless and transparent syn-ore quartz, in the form of idiomorphic crystals, has three visible crystal growth zones with fluid inclusions (Figure 2).

The core zone contains four types of fluid inclusions: 1) semi-irregular shaped fluid inclusions, up to 25 μm that occur in small groups. The volume fraction of the vapour phase varies between 20-30 vol. %. 2) fluid inclusions in trails that reflected partly healed cracks and internal growth zones. They have a regular locally negative-crystal shape, usually sizes up to 20 μm, and the volume fraction of the vapour phase varies between 50-60 vol. %. 3) regular, locally negative crystal shaped fluid inclusions, length up to 10 μm and extremely rich in vapour phase 90 vol. %. 4) elongated irregular shaped fluid inclusions liquid-rich to all-liquid, up to 40 μm in length, in trails (healed cracks) in the core.

The transition zone contains abundant fluid inclusions of irregular shape that are mainly elongated in an orientation perpendicular to growth-zone traces. These fluid inclusions have a length of 50-300 μm and the volume fraction of the vapour phase varies between 10-20 vol. %.

The rim contains traces of growth zones with fluid inclusions of regular shape, with an average length of 30 μm, and volume of the vapour phase varies between 20-30 vol. %.

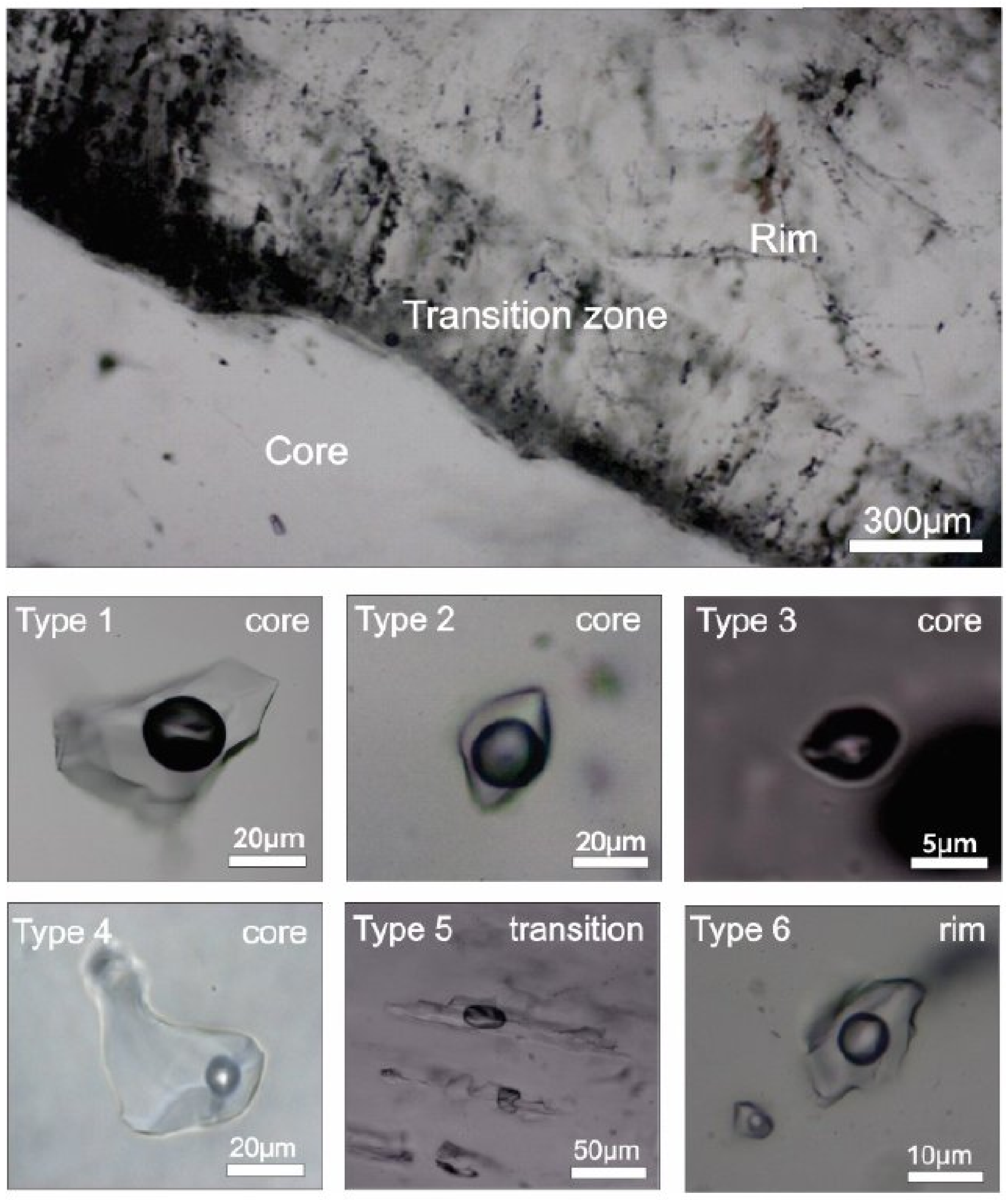

Figure 2. Photomicrograph of a piece of a quartz crystal with three visible growth zones and fluid inclusions. Below are the photomicrographs of single fluid inclusion types**.**

4 Raman spectroscopy

In the core, type 1 inclusions are characterised by a relatively high salinity of the liquid phase. The vapour phase is a gas mixture of CO_2-CH_4, with a predominance of CO_2. The relative low intensity of the CO_2 and CH_4 Raman spectra implies a low density of the vapour phase and high salinity.

Type 2 inclusions have an H_2O spectrum which corresponds to a moderate salinity, and the vapour phase is slightly enriched in CH_4 compared to type 1, but remains a CO_2-rich gas mixture. Some inclusions reveal minor amounts of additional H_2S.

Type 1 and 2 contain occasionally solid phases, i.e., accidentally trapped small crystals of calcite and mica.
Type 3 inclusions have a vapour phase consisting of a CO_2-CH_4-H_2S gas mixture that is enriched in CH_4 and with significant amounts of H_2S. The H_2O spectrum of the liquid phase reveals a relatively high shoulder at about 3200 cm^{-1}, which corresponds to low salinity.
Raman spectra of Type 4, liquid-rich to all-liquid fluid inclusions, reveal nearly pure CO_2 vapour and a H_2O liquid phase.
In the transitional zone, type 5 inclusions have a vapour phase that is relatively enriched in CH_4 in a mixture with CO_2. The Raman band of the liquid phase corresponds to a low salinity aqueous solution, similar to type 3.
Fluid inclusions in the rim zone, type 6, have a CO_2-enriched vapour phase with minor CH_4. The Raman spectrum of the liquid phase resembles a low salinity aqueous solution.

5 Microthermometry

Type 1 inclusions have a temperature of homogenization in the range of 350-430 °C with a mode at 380-390 °C. Ice melting temperatures are from -6 to -23 °C, corresponding to a calculated salinity between 9 and 24 wt.% NaCl eq., with a mode in the 12 to 16 wt.% NaCl eq..
Type 2 inclusions have relatively similar homogenization temperatures that range between 340 and 420 °C as type 1 inclusions and a slightly lower mode at 370-380 °C. Ice melting temperatures are in the range of -2 to -9 °C while salinity is from 4 to 12 wt.% NaCl eq. with a mode at 6-7 wt.% NaCl eq..
The low density of the vapour phase in type 3 does not allow any microthermometric analyses, i.e. homogenization or melting of CO_2 is not observed. Locally, the final ice melting temperature of the frozen aqueous phase occurs at temperatures of -1.0 to -4.0 °C, corresponding to a salinity of 1 to 6 wt.% NaCl eq..
Homogenization temperatures of type 4 inclusions are significantly lower than the previous types and are in the range of 148 to 245 °C. Ice melting temperatures occur from -0.7 to -4.9 °C while the salinity of this type varies between 1 and 8 wt.% NaCl eq..
Inclusion in the transition zone homogenize at a mode of 360 to 380 °C similar to type 2, but a wider range of 235-401 °C has been measured. Dissolution of ice occurs between -1 and -6 °C corresponding to a salinity of 2 to 8 wt.% NaCl eq..
Inclusions in the rim of quartz have homogenization temperatures between 259 and 385 °C with a mode at 340-360 °C. These temperatures are significantly lower than type 5 and higher than type 4. The melting temperature of ice ranges from -2 to -3 °C, which corresponds to a low salinity of 2 to 5 wt.% NaCl eq..

6 Conclusion

The different fluid inclusions from the quartz growth zones reveal that deposition of the ore mineralization was the result of a multiphase evolution of the hydrothermal ore-forming fluid, similar to skarn deposits worldwide (Kwak, 1986; Meinert et al., 2003).

These events are preserved in distinguished types of fluid inclusions and reflected through their varying temperature of homogenization, salinity, and fluid composition.
The study shows that the examination of fluid inclusions from quartz can considerably contribute to tracing the evolution of hydrothermal ore-bearing fluid, which is associated with the genesis of the Rudnik skarn deposit.

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