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Retrograde skarn formation and polymetallic mineralization in the Petrovitsa deposit, Madan district, South Bulgaria

Ретроградни скарни и полиметална минерализация в находище Петровица, Мадански район, Южна България

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Introduction

Petrovitsa is a Pb-Zn distal skarn deposit, located in the Madan district in South Bulgaria. The district is situated in the Central Rhodopes, which are part of the Alpine-Balkan-Carpathian-Dinaride province of the Alpine-Himalayan metallogenic belt (Burg, 2011). The region was one of the most important Pb-Zn producers in Europe in the past. The base-metal mineralization is hosted by a metamorphic core complex, consisting of gneisses, amphibolites, mica schists and three major marble horizons (labelled I to III) (Vassileva et al., 2009 and references therein). The deposits are structurally controlled by six large, up to 10–15 km long, NNW-SSE-striking faults. Two main morphological types of ore bodies occur in the district: polymetallic veins (1–3 m wide; up to 7 km long) and skarn-sulfide bodies formed at the intersections of ore-controlling faults with marble lenses/layers (Vassileva et al., 2009 and references therein). Sulfide mineralization in the veins and in the metasomatic bodies is dominated by galena, sphalerite, pyrite and chalcopyrite, associated with quartz and carbonate-rich gangue. Both mineralization styles, veins and metasomatic replacement bodies, were studied in the Petrovitsa deposit to compare the geochemical characteristics, mineralogy and alteration styles of the polymetallic mineralization.

Analytical techniques

A detailed field mapping alongside with a large set of analytical techniques (optical petrography, cold-CL, SEM-CL, X-ray computed tomography, QEMSCAN, EPMA and LA-ICP-MS) have been used to study the main ore-forming processes leading to the formation of the veins (as feeders for the skarn-hosted mineralization) and the metasomatic bodies. Two mine levels (668 and 845) at Petrovitsa were studied. Significant difference in terms of sulfide distribution, Pb/Zn ratio, mineral textures, temperature of formation, major and trace elements concentrations in main sulfide minerals between vein and metasomatic mineralization were noted (Milenkov, 2019).

Results and discussion

Statistical analysis of a large dataset reveals that the Pb/Zn metal ratio is systematically higher in the veins compared to the metasomatic bodies (Milenkov, 2019). Generally, the metasomatic ore bodies in the Petrovitsa deposit have higher metal concentrations than the veins, however both become richer at depth. The Pb/Zn distribution in the different ore bodies is valid not for Petrovitsa deposit only, but for the Madan district as a whole. We believe that both mineralization styles are formed from the same hydrothermal fluids during a single major hydrothermal event. The main difference results from the fact that in order to produce the metasomatic replacement bodies, the fluid interacts with the pyroxenes from the prograde skarn assemblage already formed during the early stage of mineralisation, whereas the formation of sulfides in the vein is due to precipitation related to the cooling of the

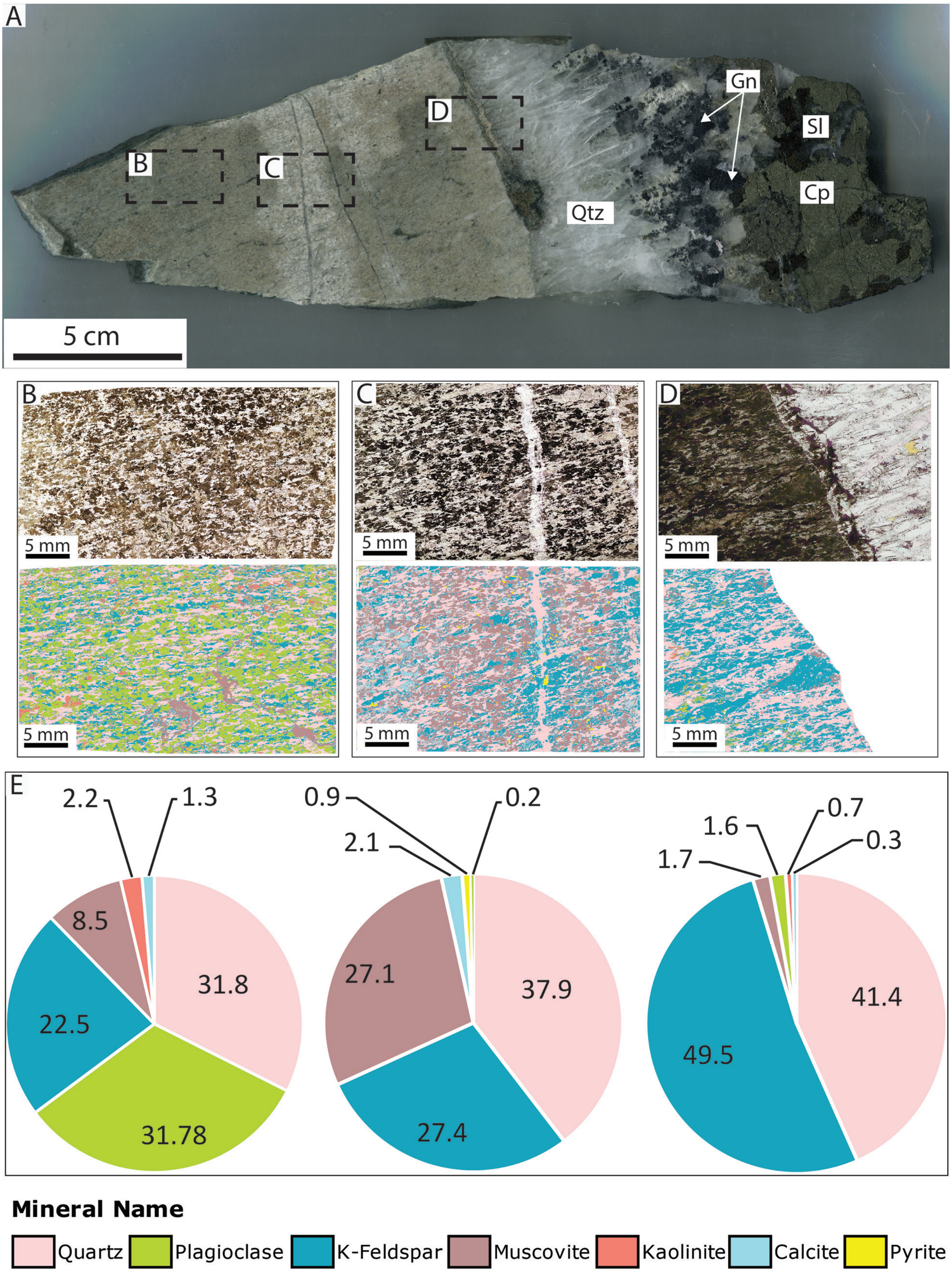

Fig. 1. Profile on sample 17-MN-74 consisting of three sections which represent the alteration of the host rock (gneiss): *A)* Polished slab from sample 17-MN-74; *B)* Scan section (plane-polarized light) and QEMSCAN mineralogical map of sample 17-MN-74_a; *C)* Scan section (plane-polarized light) and QEMSCAN mineralogical map of sample 17-MN-74_b; *D)* Scan section (plane-polarized light) and QEMSCAN mineralogical map of sample 17-MN-74_c; *E)* Mineral relative abundances in the three sections

fluid in an open space (Kostova et al., 2004). The most significant feature, which can explain the Zn enrichment in the metasomatic ore bodies, is the fact that the primary skarn pyroxene is enriched in Zn, reaching concentrations between 100 and 250 ppm (Bovay et al., 2015). During the interaction with the skarn minerals, the fluid leaches Zn from the pyroxene structure. In combination with the Zn already available in the fluid the quantity of sphalerite precipitating in the metasomatic bodies is higher than galena, compared to the veins.

Mineral geochemistry of ore and alteration minerals reveal that the sulfide precipitation temperature at level 845 was higher compared to level 668. Sphalerite geothermometry based on the Fe/Zn ratio shows crystallization temperature of ca. 330 °C at the upper level and ~280 °C at the lower one. Minor and trace element contents in minerals like epidote, chlorite, chalcopyrite and pyrite are also higher in the metasomatic body at level 845 (Milenkov, 2019).

The hydrothermal alteration associated with the vein mineralization at level 668 has been characterized using a combination of analytical techniques (Fig. 1). The wall rock is gneiss, which consists mainly of a K-feldspar-plagioclase-quartz-mica assemblage plus minor quantities of apatite and zircon. Along the contact with the main or satellite veins hydrothermal K-feldspar replaces metamorphic feldspars (plagioclase and K-feldspar), which is the reason of plagioclase absence in sections C and D. This K-metasomatism in the gneiss along the vein contact temporally corresponds to the prograde skarn stage in the marble. There is no mineral precipitation in the vein at this stage. Due to cooling of the system quartz, epidote and chlorite start to precipitate in the vein corresponding to the earliest stage of vein infill (Fig. 1A). The following sulfide precipitation lowers the pH of the fluid enough to produce sericitic alteration. The alteration is weak in section B where it is associated with kaolinite occurring at lower temperature and/or lower pH, compared to the sericite and therefore further away from the fluid source. Sericitization is well preserved in section C along a secondary quartz-sulfide veins subparallel to the main one where it destroys partially the hydrothermal K-feldspar and the relictic plagioclase in the gneiss. This alteration occurs sporadically along the main structure in section D.

The carbonates associated with the alteration and the infill of the vein precipitate late in the sequence. They occupy voids of secondary porosity, produced by the sericitization, resulting in a late carbonate-sericite association. Kostova et al. (2004) have reported high to moderate temperature (T from 320 to 260 °C) and moderate- to low-salinity (3 to 6 wt% NaCl equiv.) of the mineralizing fluids at Petrovitsa.

This study demonstrates that the earliest mineralization stage in the veins consists of a quartz-epidote-chlorite-adularia assemblage. These minerals are associated with minor quantity of hematite, indicative of oxidizing conditions during the early stages of vein formation, in contrast to the reduced nature of mineralizing fluids responsible for the prograde skarn assemblage.

A genetic model summarizing the relationships between fluid processes responsible for vein and metasomatic mineralization at levels 668 and 845 at Petrovitsa is proposed. Mixing between magmatic and meteoric fluids was probably a major factor for sulfide precipitation.

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