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Distal johannsenite-hedenbergite skarns at Madan, Bulgaria and their link to Pb-Zn mineralization: constraints from trace element analyses in skarn silicates

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Madan ore field represents one of the most significant manifestations of vein-type Pb- Zn mineralization in Europe. The ore filed occupies the southwestern part of the Central Rhodopean polymetallic district in south Bulgaria. The mineralization is controlled by six large, up to 10-15 km long, NNW-SSE trending subvertical major fault zones and is mainly hosted by the Madan allochton unit, which overlies tectonically the Arda unit. The Madan unit consists of alternation of gneisses, schists, amphibolites and marbles. Marbles are the main host for large replacement Pb-Zn metasomatic ore bodies (Ivanov et al. 2000). Rhyolitic dikes pre-dating the polymetallic mineralization intruded group of non-mineralized faults with WNW-ESE direction in the northern part of the ore field (Ivanov et al. 2000; Marchev et al. 2005; Vassileva et al. 2009; Kaiser-Rohrmeier et al. 2013).

The aim of this study is to establish a genetic model for the distal skarn formation and its role in the subsequent polymetallic mineralization. This work focuses on three deposits from the Madan ore field, namely (from north to south): Kroushev Dol, Petrovitsa, and Gjudjurska. The deposits are characterized by the occurrence of distal johannsenite-hedenbergite skarn bodies, formed by the interaction of hydrothermal fluids with marbles along lithological contacts and faults. Simultaneously to the early clinopyroxene formation within the marble, a syngenetic hydrothermal alteration dominated by epidote ± titanite affected the gneiss in contact with the marble horizons.

Electron microprobe analyses on clinopyroxenes yield dominantly johannsenite compositions, typical of distal Zn skarns (Meinert et al., 2005). LA-ICP-MS analyses reveal anomalously high Zn concentrations in the clinopyroxenes – as much as 250 ppm, while Cu and Pb rarely exceed 1 ppm. Optical cathodoluminescence followed by selective carbonate dissolution and textural SEM study along the skarn front show the presence of a few-mm to a centimeter-thick layer dominantly made of recrystallized fine-grained Mn-rich calcite. At the boundary between the skarn association and the marble the bladed shape of the pyroxene turns into a hairy-like texture made by an intergrowth of pyroxene and amphiboles, as confirmed by Raman microspectroscopy. BSE imaging on samples from Kroushev Dol shows sharp changes of the clinopyroxene blade close to the contact with the marble consisting of significant change in chemical composition and growth direction of the crystal. These features are indicative of a complex late-stage skarn formation with multiple dissolution-replacement reactions.

Neoformed titanites appear to be an important part of the skarn assemblage affecting the gneiss, along the contact with marbles, forming euhedral crystals elongated in the foliation plan of the host. Euhedral titanites from the Petrovitsa and Gjudjurska deposits display constant major element composition in the core and Nb-rich rim as confirmed by LA-ICP-MS analyses. Common sector zoning, as illustrated by BSE images, is due to zonal distribution of trace elements. REE spectra of titanite are consistent within single samples; however titanites from different lithologies display rather significant differences in light and/or heavy REE patterns, thus indicating that the environment of skarn formation, the skarn mineral paragenesis and the composition of the protolith strongly influence the partitioning of various elements between the different calc-silicates.

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