

Evolution of borate minerals from contact metamorphic to hydrothermal stages: Ludwigite-group minerals and szaibélyite from the Vysoká – Zlatno skarn, Slovakia

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Borate minerals of the ludwigite group and szaibélyite [MgBO₂(OH)] in association with hydroxylclinohumite, clinochlore, a serpentine mineral, magnesian magnetite, spinel, magnesite, dolomite and sulphide minerals, occur in a magnesian exoskarn in the R-20 borehole at the depth of 1174 m, located in the Vysoká – Zlatno Cu-Au porphyry-skarn deposit, located within the Štiavnica Neogene stratovolcano, Western Carpathians, central Slovakia. The skarn is developed along the contact of Miocene (~13 Ma) granodiorite to quartz-diorite porphyry and a Middle-Upper Triassic dolomite-shale-psammite-anhydrite sedimentary sequence (Koděra et al. 2010). The boron minerals were investigated by electron probe micro-analyser (EPMA) and micro-Raman techniques. Based on textural and compositional data, the skarn minerals originated during two stages.

Stage 1: An early high-temperature, contact-metamorphic and metasomatic stage comprises coarse-crystalline aggregate of ludwigite-group minerals (LGM) (types 1 to 3) in association with hydroxylclinohumite, magnetite, and rarely spinel inclusions in ludwigite. The LGM form massive black aggregates (>5 cm across) of numerous acicular, euhedral to subhedral prismatic crystals (usually 0.2 to 3 mm long). In BSE images, LGM crystals show regular concentric, rarely oscillatory or irregular zoning caused by distinct compositional variations during their growth or partial alteration: the dark zones show enrichment in Mg, Al and Ti, in contrast to the pale zones which have larger amounts of Fe. Compositional variations of LGM show a crystallization sequence from early azoproteite with ≤17 wt% TiO₂ (~0.40 apfu Ti), which correspond to ≤79 mol% of the Mg₂(Mg_{0.5}Ti_{0.5})O₂(BO₃) end-member, Ti-Al-rich members of LGM, “aluminoludwigite” with ≤14 wt% Al₂O₃ [≤0.53 apfu Al and ≤53 mol% of Mg₂AlO₂(BO₃) end-member] and Al-rich ludwigite [Mg₂Fe³⁺O₂(BO₃)] in the central zone of crystals, to Ti-Al-poor ludwigite in outer parts of crystals. The contents of other constituents in LGM attain elevated concentrations in some cases: 2.5 to 3.2 wt% SnO₂ (0.03–0.04 apfu Sn), 0.4 to 1.0 wt% ZrO₂ (0.01–0.02 apfu Zr), and 0.2 to 0.5 wt% V₂O₃ (≤0.01 apfu V) in Ti-Al-rich LGM compositions of type 1; Sn-enriched analyses were locally documented also in ludwigite of type 3. The compositional variations indicate the following main substitution mechanisms in the studied LGM: Fe²⁺ = Mg²⁺ in M1-3 sites for all compositions, Mg²⁺ + Ti⁴⁺ (Sn⁴⁺, Zr⁴⁺) = 2(Fe³⁺, Al) in M4 site mainly for analyses including high Ti contents (type 1), and Al³⁺ (V³⁺) = Fe³⁺ in M4 site for compositions with a small amount of Ti but moderate to high Al contents (types 2 and 3).

Stage 2: Minerals of the late retrograde serpentinization and hydrothermal stage of the skarn form irregular veinlets and aggregates, including partial alteration of hydroxylclinohumite to the serpentine-group mineral and clinocllore, replacement of LGM by szaibélyite, formation of the latest generation of Fe-rich, Ti-Al poor ludwigite in veinlets (type 4), and precipitation of dolomite, magnesite and sulphide minerals (valleriite, sphalerite, chalcopyrite).

The distinct compositional zoning of the LGM documents a complex evolution of the skarn beginning with a high-temperature stage 1 and ending with a low-temperature overprint, stage 2. The source of boron in the skarn could have been originated from the granodiorite/quartz diorite intrusion; however some supply of B from adjacent evaporite-bearing sediments is also possible. Conditions for the precipitation of borates and associated minerals could be estimated at ~600–700 °C and 50–70 MPa for the stage 1, and ~320 to 370 °C for the stage 2 of the Vysoká – Zlatno skarn mineralization (cf. Koděra et al. 2010).

***Acknowledgments:** Authors thank L. Rojkovičová for mineral samples. The present work was supported by the Slovak Research and Development Agency under the projects APVV-0537-10 and APVV-15-0050, as well as the VEGA-1/0560/15 project of Ministry of Education, Slovak Republic.*

References:

Koděra P, Lexa J, Fallick AE (2010) Formation of the Vysoká-Zlatno Cu-Au skarn-porphyry deposit, Slovakia. *Mineral Depos* 45:817–843