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Ludwigite-group minerals and szaibelyite: rare borate minerals from Vysoká – Zlatno skarn, Štiavnica stratovolcano, Slovakia

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Beside of sedimentary evaporitic rocks, borate minerals occur also in some high temperature contact-metamorphic rocks, especially in skarns, locally in association with Fe and Sn ore minerals (e.g., Anovitz & Grew 1996). The borate minerals are generally associated with the post-magmatic processes which occur in the contact aureoles of intrusive, acid to intermediary, calc-alkaline rocks (Pertsev 1991). Borate minerals of the ludwigite group and szaibelyite were identified from the Mg-skarn in the R-20 drilling core in depth of 1172 m during geological exploration for Cu-Au porphyry-skarn ores in the Vysoká – Zlatno area near Banská Štiavnica, in the Štiavnica Neogene stratovolcano, central Slovakia (Koděra et al. 2010).

Ludwigite-group minerals (LGM) form massive black aggregates (>5 cm large) of numerous acicular, euhedral to subhedral prismatic crystals (usually 0.2–3 mm long). Ludwigite associates with clinohumite, szaibelyite, clinochlore, serpentine-group mineral, magnesite, dolomite, hematite, rarely valeriite, chalcopyrite, and sphalerite. Under transmitted light, LGM crystals are mostly opaque; locally they are translucent with strong pleochroism in sections parallel to Z-axis (deep green – dark reddish brown). In BSE, LGM crystals show regular concentric, rarely oscillatory or irregular zoning caused by distinct element variations during their growth or partial alteration: the dark zones show enrichment in Mg, Al and Ti, in contrast to the pale zones which reveal larger amounts of Fe. The electron-microprobe analyses reveal growth evolution of LGM crystals from Al-rich azoproite with ≤79 mol.% of $Mg_2(Mg_{0.5}Ti_{0.5})(BO_3)O_2$ end-member] to Al±Ti-rich ludwigite and Al-dominant LGM phase ["aluminoludwigite" with ≤53 mol.% of $Mg_2Al(BO_3)O_2$ end-member] in central zones, whereas rim zones of the crystals and secondary veinlets attain nearly pure ludwigite composition [87–99 mol.% of $Mg_2Fe^{3+}(BO_3)O_2$ end-member]. Consequently, LGM from the Vysoká – Zlatno skarn show the largest compositional variations ever known from one occurrence and they reach the highest contents of Ti (≤17.4 wt.% TiO_2, 0.39 *apfu*) and Al (≤14.4 wt.% Al_2O_3, 0.53 *apfu*) ever reported in LGM (Schaller & Vlisidis 1961, Marincea 2000, Pertsev et al. 2004, Aleksandrov & Troneva 2008, 2011).

The compositional variations indicate the following substitution mechanisms in the studied LGM: $Mg^{2+} = Fe^{2+}$ for the all compositions, $Fe^{3+} = Al^{3+}$ for samples without higher amount of Ti, and $2Al = Mg^{2+} + Ti^{4+}$ or $2Fe^{3+} = Mg^{2+} + Ti^{4+}$ for analyses including high Ti content.

Szaibelyite $MgBO_2(OH)$ occurs as aggregates of fibrous crystals, up to 0.5 mm in size, replacing LGM. Zoning in szaibelyite was not observed. The amounts of Mg are uniform (0.98 to 0.99 *apfu*), content of Fe^{2+} oscillates from 0.2 to 1.2 wt.% FeO (0.002–0.014 *apfu*) and indicates the $Mg^{2+} = Fe^{2+}$ substitution. Szaibelyite also contains small admixtures of Mn (0.1–0.4 wt.% MnO), Al and Cr (≤0.3 wt.% Al_2O_3 or Cr_2O_3).

The skarn mineralization originated as a result of contact thermal metamorphism of Miocene

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calc-alkaline granodiorite intrusion on host Middle to Upper Triassic limestones, dolomites, shales and evaporitic anhydrite beds (the Veľký Bok Group, Veporicum Unit). The evaporites were most likely the primary source of boron, whereas Ti was probably derived from the granodiorite. Clinohumite and LGM (azoproite to Al±Ti-rich ludwigite and "aluminoludwigite") precipitated during the high-temperature contact metamorphic event at ~700°C and ≤100 MPa, whereas the youngest Al,Ti-poor ludwigite veinlets, szaibelyite, serpentine-group mineral, clinochlore, magnesite, dolomite, hematite and probably also sulfide minerals were formed during younger, lower-temperature hydrothermal-metasomatic event.

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