Chemical composition and evolution of tourmaline-supergroup minerals from the hydrothermal veins in Gemeric Superunit, Western Carpathians, Slovakia

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Tourmaline-supergroup minerals are common gangue minerals on many hydrothermal veins in the Gemeric Superunit, Eastern Slovakia. They were described from many occurrences of Sb hydrothermal veins (Klimko et al. 2009; Bačík et al. 2017a), siderite-quartz-sulphide hydrothermal veins (Bačík et al. 2017b) and also from a magnesite-talc deposit (Bačík et al. 2011).

Tourmalines are abundant in the Betliar – Straková, Čučma – Gabriela and Rožňava – Peter-Pavol Sb vein deposits in the Rožňava area, Slovakia. They form relatively large prismatic to radial aggregates of parallel black to greyish-black crystals. Tourmaline-supergroup minerals from Betliar – Straková and Rožňava – Peter-Pavol are compositionally almost homogeneous with intermediate schorl-dravite composition. Čučma – Gabriela tourmalines have distinct zoning with massive cores of schorl-to-feruvite shifting to schorl-to-dravite composition, and dravite to magnesio-foitite rim. The tourmaline composition is influenced by two main substitutions, namely $Ca(Mg,Fe)Na_{-1}Al_{-1}$ and $^{X}\square AlNa_{-1}(Mg,Fe)_{-1}$. Betliar – Straková and Rožňava – Peter-Pavol tourmaline-supergroup minerals exhibit only small extents of the $^{X}\square AlNa_{-1}(Mg,Fe)_{-1}$ substitution. In Čučma – Gabriela tourmalines, this substitution is more extended and shifts its composition to magnesio-foitite. In contrast, extensive $Ca(Mg,Fe)Na_{-1}Al_{-1}$ substitution results in the decrease of Al in the core of Čučma – Gabriela tourmalines. The unit-cell dimensions of all investigated tourmaline-supergroup minerals indicate an octahedral disorder with the $^{Z}(Fe^{3+}+Mg)$ proportion calculated from empirical equations varying between 0.85 and 0.87 apfu (atoms per formula unit). Based on Mössbauer spectra, the $^{Z}Fe^{3+}$ content varied between 0.25 apfu in Betliar – Straková tourmalines and 0.45 apfu in Čučma – Gabriela samples. Based on the Fe/(Fe+Mg) ratios, Betliar – Straková tourmalines are slightly enriched in Fe compared to Rožňava – Peter-Pavol, suggesting the impact of the host-rock composition; the former grew in Fe-richer acidic metarhyolitic rocks, the latter in metapelites. In Čučma – Gabriela tourmalines, the variations in Fe/(Fe+Mg) very likely reflect the change in fluid composition. Magnesio-foitite is the product of second-stage crystallization forming rims and crack fillings. The relatively low Fe^{3+}/Fe^{2+} ratio indicates only minor proportions of meteoric fluids in tourmaline crystallization.

Tourmalines occur in a large number of Cretaceous siderite-quartz-sulphide hydrothermal veins in the Gemeric Unit, Slovak Ore Mountains, Slovakia, such as Dobšiná, Vlachovo, Rožňavské Bystré, Hnilčík, Rakovnica, Novoveská Huta, Gretla, Rudňany, and Bindt. Tourmalines form selected deposits belong mostly to the alkali group, schorl-dravite series, whereas foitite (Vlachovo and Bindt) and oxy-dravite compositions (Hnilčík) occur only rarely. Rim zones of some schorlitic tourmalines show high concentrations of Ti (up to 2.35 wt. % TiO_2, 0.30 apfu; Rožňavské Bystré). The chemical composition is mostly controlled by alkali-deficient $^{X}\square AlNa_{-1}(Mg,Fe)_{-1}$ and proton-deficient $AlO(Mg,Fe^{2+})_{-1}(OH)_{-1}$ substitutions. Titanium is incorporated into the structure by $^{Y}Ti^{Y}(Mg,Fe)^{Y}Al_{-2}$, $^{Y}Ti^{Z}Mg^{Y}Al_{-1}{}^{Z}Al_{-1}$, $^{Y}TiO^{Y}Al_{-1}(OH)_{-1}$, and $^{X}Ca^{Y}Ti^{Z}MgO_{2}{}^{X}\square_{-1}{}^{Y,Z}Al_{-2}(OH)_{-2}$ substitutions.. The unit-cell parameter *a* varies between 15.960 and 15.985 Å; variations in *c* are larger, between 7.177 and 7.236 Å, indicating the presence of Fe^{3+} and Mg^{2+} at the *Z* site. Mössbauer spectroscopy has shown variable Fe^{3+} proportions (0.17-0.55 apfu) in all samples. The highest Fe^{3+} concentrations occur in samples from Rudňany and Gretla in the external part of the Gemeric unit, suggesting higher oxidation and greater impact of meteoric fluids during longer fluid transport. The determined X_{Mg} ratios in the samples are correlated with the compositions of the host rocks; schorl to foitite occurs in veins located in the meta-rhyolites host, while tourmalines with the highest Mg contents occur in metabasalts.

Brown tourmalines were found in the Gemerská Poloma talc-magnesite deposit. Acicular tourmalines form aggregates along with talc on the slip surface of carbonate rock consisting of dolomite and magnesite. The tourmalines are almost unzoned and have compositions corresponding to dravite with very high X_{Mg} (0.95 – 0.96). In contrast, samples have very low *X*-site vacancies (up to 0.17) and Ca contents (up 0.05 apfu). The Fe contents are also very low (up to 0.14 apfu) and the contents of Al variy between 5.97 and 6.27 apfu. The calculated $^{W}O^{2-}$ contents correlate with that of Al, which suggests a quite significant role of the $AlOMg_{-1}(OH)_{-1}$ substitution. Other substitutions are negligible, tourmaline compositions are very uniform. However, the dravite studied is significantly Al-Mg disordered with $^{Z}Mg/(^{Z}Mg+^{Y}Mg)$ = 0.45-0.50, as suggested by distribution of Al and Mg among octahedral sites calculated from lattice parameters [*a* = 15.9289(7) Å; *c* = 7.2132(17) Å]. Dravite from Gemerská Poloma was likely a side-product of talc formation from original carbonate rock during the Permian granite intrusion. Dravite formed from granite-derived Si- and B-bearing fluids on the slip surface during/after brittle deformation of carbonate which results in its finely acicular habitus. Its high-magnesian composition is controlled by the geochemical properties of the host rock.

Based on crystal-chemical data from various hydrothermal-tourmaline occurrences, it is possible that the factors influencing the evolution of tourmaline include the composition of the solutions, the origin of the fluid, the length of their transport and the host-rock environment in which the tourmaline crystallizes.

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