

## The role of iron in Fe-rich tourmaline: results of high-temperature experiments

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Tourmaline is a typical accessory to minor and rather exceptionally also major mineral in rocks of highly variable origin and chemical composition. Although tourmalines serve as a very suitable indicator of compositional evolution of the host rocks chiefly due to its ability to incorporate large number of elements, the chemical composition of tourmaline is significantly controlled also by crystal-structural constraints. In order to better understand such constraints, tourmaline samples of rather simple chemical composition were heat-treated under various conditions to reveal role of Fe<sup>2+</sup>/Fe<sup>3+</sup> and their ordering in crystal structure of Mg-poor, Li-free and F-poor samples.

Black tourmaline forming fine-grained aggregates and individual grains of tourmaline, up to 5 mm in size, from irregular pegmatite patches enclosed in biotite-nepheline-plagioclase gneisses at the Cancrinite Hill, east of Bancroft, southern Ontario was predominantly used in this study. This tourmaline is homogeneous, Na-rich (0.91-1.00 apfu), Al-poor (5.55-5.68 apfu), Fe-rich (2.91-3.01 apfu Fe<sup>2+</sup><sub>tot</sub>), Mg-poor (0.28-0.35 apfu) and F-poor ( $\leq$  0.03 apfu) and along with the results of Mössbauer spectroscopy it could be classified as schorl. The results of high-temperature treatment of this schorl were compared with two other samples of Fe-rich tourmaline differing in their compositions and origin: fluorine-rich schorl from orthogneiss in Nedvědice, Czech Republic and foitite-olenite from abyssal anatectic pegmatite in Miskovice, Czech Republic. The tourmaline crystals (mm-sized fragments) were thermally treated in air and hydrogen atmospheres at 700, 800 and 900 °C for sufficient period of time to fully oxidize or reduce iron within the tourmaline structure. The process of oxidation/reduction of iron was monitored using Mössbauer and FTIR spectroscopy. Parts of the crystals were subsequently used for single-crystal X-ray diffraction study and magnetic measurements.

The possibility to fully oxidize the iron within the tourmaline structure but not to reduce the iron to higher extent that was the original value could indicate that the structure of almost pure end-member schorl would not be stable when all the iron atoms are in Fe<sup>2+</sup> form. This is supported by the fact that prior full reduction of the iron atoms the tourmaline decomposes and immediately appears the iron in metallic form. Therefore, the presented results imply that tourmaline structure of end-member schorl composition is not stable and must be stabilized by the presence of certain amount of ferric iron and/or disorder of Fe and Al over the Y- and Z-sites. Moreover, with respect to the ease of oxidation of iron in tourmaline structure this could be used, under some circumstances, to evaluate the post-crystallization history of both tourmaline and tourmaline host-rocks.