

## Site partitioning of Fe<sup>2+</sup> and Fe<sup>3+</sup> in tourmaline

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### ABSTRACT

Both quantification and site distribution of Fe<sup>2+</sup> and Fe<sup>3+</sup> are crucial points to properly define mineral structural formula. Electron microprobe (EMP), generally used to investigate chemical composition, cannot determine Fe<sup>2+</sup> and Fe<sup>3+</sup> separately. However, structural refinements (SREF) and Mössbauer spectroscopy (MS) have been successfully used to determine both Fe valence state and coordination number in several minerals, including tourmaline. In spite of this, the site assignment of Fe<sup>2+</sup> and Fe<sup>3+</sup> in tourmaline is still controversial, because no clear information comes from the literature and some misprints and misinterpretations contributed to entangle the question.

This study aims to understand crystal-chemical mechanisms of Fe<sup>2+</sup> and Fe<sup>3+</sup> order/disorder over the octahedrally-coordinated sites of tourmalines crystallized from late magmatic fluids.

Thirteen tourmaline crystals belonging to the series elbaite-schorl-dravite, mainly coming from Cruzeiro pegmatite (Brazil), which had been previously analyzed by SREF, EMP and ion microprobe, were studied by MS. Moreover, a single crystal of Fe-tourmaline, found in a skarn rock from Utö (Sweden), was studied by EMP and SREF. In the elbaite-schorl-dravite samples, the presence of Fe<sup>3+</sup> in tetrahedral coordination was excluded on basis of structural data, and MS doublets with very low isomer shift were assigned to Fe<sup>3+</sup> in octahedral coordination. The Fe<sup>2+</sup> content of the Y site obtained by structural approach was confirmed by MS ( $r^2 = 0.97$ ) adding the absorption areas of three Fe<sup>2+</sup> doublets, and Fe<sup>3+</sup> content of Y was satisfactorily reproduced by the area of the MS doublet assigned to Fe<sup>3+</sup> ( $r^2 = 0.99$ ). In seven samples structural data distinctively revealed Fe<sup>2+</sup> and Fe<sup>3+</sup> in the Z site. Their contents revealed to be highly correlated to the areas of a fourth Fe<sup>2+</sup> doublet ( $r^2 = 0.93$ ) and of a second Fe<sup>3+</sup> doublet ( $r^2 = 0.86$ ), respectively. Notably, such doublets were only observed in the Mössbauer spectra of the seven samples.

For the Utö sample, the optimized structural formula showed a disordering of Fe<sup>2+</sup> over the Y and Z sites, and an ordering of Fe<sup>3+</sup> at the Y site. Data of two Fe-tourmalines from the literature, in which Fe<sup>2+</sup> at the Z site were not mentioned by the authors, were re-examined by using of a well-tested site assignment procedure. Results showed that also for those samples Fe<sup>3+</sup> was almost ordered at the Y site and Fe<sup>2+</sup> was disordered over the octahedrally-coordinated Y and Z sites (up to 9% atoms/site in Z). It was demonstrated that disordered Fe<sup>2+</sup> distributions are needed (i.e., Fe<sup>2+</sup> is preferred to Fe<sup>3+</sup> at Z and Fe<sup>3+</sup> moves to Y) to minimize the strain state of Y-O bonds, as expected from the bond-valence theory.

**Keywords:** Tourmaline, crystal structure, crystal chemistry, Mössbauer spectroscopy, cation disorder, bond valence.