

Disordering of Fe²⁺ over octahedrally coordinated sites of tourmaline

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ABSTRACT

The partitioning of iron among octahedrally coordinated sites in tourmaline, and its stereochemical consequences, were investigated in a Fe-rich dravite in a skarn rock from Utö, Sweden. A multi-analytical approach using structure refinement (SREF), electron microprobe analysis (EMPA), and Mössbauer spectroscopy (MS) established the chemical and structural nature of the tourmaline. A structural formula obtained by optimization procedures indicates disordering of Al, Mg, and Fe²⁺ over the *Y* and *Z* sites, and ordering of Fe³⁺ at the *Y* site. Two Fe-rich tourmalines from the literature, re-examined with the optimizing site assignment procedure, appear to have iron partitioning comparable to that of the Utö tourmaline with Fe²⁺ disordered over the octahedral sites. This is best explained by disordered Fe²⁺ distributions that minimize the strain state of the *Y*-O bonds and provide a shielding effect reducing *Y*-*Z* repulsion. This is consistent with predictions from bond-valence theory and Pauling's rules.

An indication of *Z*-site occupancy by Fe²⁺ in tourmaline may be signaled by a significant correlation between $\langle Z-O \rangle$ and the *c* lattice parameter ($r^2 = 0.96$). The *c* value for a very Fe²⁺-rich tourmaline and an ideal end-member schorl, with Fe²⁺ and Al ordered at *Y* and *Z* (respectively), yielded $\langle Z-O \rangle$ values larger than 1.907 Å (the likely bond length for $\langle Z-Al-O \rangle$). These large $\langle Z-O \rangle$ lengths indicate that Fe²⁺ occurs at the *Z* site. The hypothesis of a dragging effect from $\langle Y-O \rangle$ to explain lengthening of $\langle Z-Al-O \rangle$ is not supported by experimental evidence.

Keywords: Chemical analysis, tourmaline, crystal structure, Mössbauer spectroscopy, order-disorder, XRD data