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Disordering of Fe^{2+} over octahedrally coordinated sites of tourmaline

Ferdinando Bosi[1,2,*]

[1]Department of Mineralogy, Swedish Museum of Natural History, Box 50007, 10405 Stockholm, Sweden
[2]Dipartimento di Scienze della Terra, Università di Roma "La Sapienza," Piazzale Aldo.Moro 5, 00185 Roma, Italy

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 Fe^{2+} over the *Y* and *Z* sites, and ordering of Fe^{3+} 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 Fe^{2+} disordered over the octahedral sites. This is best explained by disordered Fe^{2+} 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 Fe^{2+} in tourmaline may be signaled by a significant correlation between <*Z*-O> and the *c* lattice parameter ($r^2 = 0.96$). The *c* value for a very Fe^{2+}-rich tourmaline and an ideal end-member schorl, with Fe^{2+} and Al ordered at *Y* and *Z* (respectively), yielded <*Z*-O> values larger than 1.907 Å (the likely bond length for $<^{Z}$Al-O>). These large <*Z*-O> lengths indicate that Fe^{2+} occurs at the *Z* site. The hypothesis of a dragging effect from <*Y*-O> to explain lengthening of $<^{Z}$Al-O> is not supported by experimental evidence.

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