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

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

Introduction and Previous Work

The tourmaline group minerals are complex borocyclosilicates that occur in a wide variety of igneous, metamorphic, and sedimentary environments. The structure is characterized by groups of XO\textsubscript{6}, YO\textsubscript{6}, TO\textsubscript{6}, and BO\textsubscript{3} polyhedra connected to each other through ZO\textsubscript{6} octahedra. The latter are arranged in a 3-D framework and are linked to the YO\textsubscript{6} octahedron through the O3-O6 edge. The structural formula of tourmaline group minerals is formalized as XY\textsubscript{2}Z\textsubscript{2}YO\textsubscript{6}(BO\textsubscript{3})\textsubscript{2}V\textsubscript{4}W and, according to several authors (Fortier and Donnay 1975; MacDonald and Hawthorne 1995; Hawthorne and Henry 1999; Hughes et al. 2004), the following ions fit into the following structural sites: X = Na, Ca, \square (vacancy), K; Y = Al, Fe\textsuperscript{3+}, Cr\textsuperscript{3+}, V\textsuperscript{3+}, Mg, Fe\textsuperscript{2+}, Mn\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn, Li, Ti\textsuperscript{4+}, \square; Z = Al, Fe\textsuperscript{3+}, Cr\textsuperscript{3+}, V\textsuperscript{3+}, Mg, Fe\textsuperscript{2+}; T = Si, Al, B, Be; B = B, (\square); W(O1) = OH, F, O; V(O3) = OH, O.

Since 1975, when the first schorl structural refinement was reported by Fortier and Donnay, it has been suggested that Fe\textsuperscript{2+} may occur at the both Y and Z sites of tourmaline. In the following years, Grice and Robinson (1989) reported a structural formula with Fe\textsuperscript{2+} at Y and Z, adding, however, that it was not possible to verify its amount in both the octahedral sites. On the basis of structural data, small amounts of Fe\textsuperscript{2+} at Z (ca. 1% atoms/site) were also reported in Francis et al. (1999) and Ertl and Hughes (2002). Independent indication of the presence of some Fe\textsuperscript{2+} in the Z site have been obtained in Mössbauer and optical studies, e.g., Burns (1972), Mattson and Rossman (1984), Ferrow et al. (1988), Ferrow (1994), Foit et al. (1989), and Fuchs et al. (1995, 1998). Recently, using an unconstrained model for the assignment of Fe over the octahedral sites of tourmaline, Bosi and Lucchesi (2004) and Bosi et al. (2005b) optimized structural formulae with amounts of Fe\textsuperscript{2+} at Z up to ca. 4% atoms/site. On the bases of the latter structural formulae and the relative peak areas associated with the Mössbauer spectra of the same samples, Andreozzi et al. (2008) found a close match between the amount of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} in Y and Z derived from the structural data and from Mössbauer spectroscopy. Finally, Bosi and Lucchesi (2007) re-examined previously published tourmaline structural formulae using site optimization and found the models are consistent with Fe\textsuperscript{2+} at the Z site.

Nevertheless, the assignment of Fe\textsuperscript{2+} at the Z site still appears controversial. For example, Grice and Ercit (1993) consider only the possibility of Fe\textsuperscript{2+} at the Z site and not Fe\textsuperscript{2+}. However, the amounts of Fe\textsuperscript{2+} reported for their samples 43167, 43293, Cross, 32008, and 43873 corresponds in fact to Fe\textsuperscript{2+}. This is verified easily by comparing total Fe\textsuperscript{2+} and Fe\textsuperscript{2+} atoms per formula unit (apfu) from chemical analyses (Table 2 of Grice and Ercit, 1993) with the cation distribution shown in Table 5. Bloodaxe et al. (1999) did not observe the presence of Fe\textsuperscript{2+} at the Z site, and their results are often extrapolated to other Fe-tourmalines (e.g., Oliveira et al. 2002; Pieczka and Kraezka 2004). However, it should be noted that the samples of Bloodaxe et al. (1999) pos-