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Inclusive chemical characterization of tourmaline: Mössbauer study of Fe valence and site occupancy

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ABSTRACT

We report here the results of a series of inclusive chemical characterizations, including all elements except oxygen, for a suite of 54 tourmaline samples. A combination of analytical techniques was used to analyze for major and light elements (electron microprobe), Fe^{3+} and Fe^{2+} (Mössbauer spectroscopy), H (U extraction), and B, Li, and F (ion microprobe, or SIMS). The B content of the tourmalines studied ranges from 2.86 to 3.26 B per formula unit (pfu) with 31 anions; excess boron is believed to reside in the Si site. Li ranges from 0.0 to 1.44 Li pfu and F contents are 0.0–0.91 pfu. H contents range from nearly anhydrous up to 3.76 H pfu and do not correlate simply with Fe^{3+} content.

Mössbauer results show that tourmaline exhibits the entire range of $Fe^{3+}/\Sigma Fe$ from 0.0–1.0. Fe^{2+} is represented in the spectra by three doublets, with occupancy in at least three distinct types of Y sites (with different types of nearest and next nearest neighbors). Fe^{3+} was found in 26 of the 54 samples studied. Although Mössbauer data do not allow the distinction between $^{[Y]}Fe^{3+}$ and $^{[Z]}Fe^{3+}$ site occupancies to be made, XRD data on these samples suggest that the majority of Fe^{3+} is also in Y. Of the samples studied, $^{[4]}Fe^{3+}$ occurs in nine; five of those were either olenite or uvite with extensive Na substitution. A mixed valence doublet corresponding to delocalized electrons shared between adjacent octahedra was observed in 14 of the samples studied. Projection pursuit regression analysis shows that distribution of Fe among doublets is a function (albeit a complex one) of bulk composition of the tourmaline and supports the interpretation of doublets representing different populations of neighbors. Variations in Fe^{3+}/Fe^{2+} ratio cannot be directly related to variations in charge in any single site of the structure. Fe^{3+}/Fe^{2+} ratio is probably controlled by the prevailing oxidation state in the bulk rock assemblage, rather than by any particular crystal chemical substitution.