A critical comment on Ertl et al. (2012): “Limitations of Fe$^{2+}$ and Mn$^{2+}$ site occupancy in tourmaline: Evidence from Fe$^{2+}$- and Mn$^{2+}$-rich tourmaline”

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ABSTRACT

In this paper we have presented a detailed response to Ertl et al. (2012a) who, in a paper in volume 97 (year 2012), pages 1402–1416, this journal, claim evidence for limitations of Fe$^{2+}$ and Mn$^{2+}$ occupancy at the Z site of the tourmaline structure. They also propose a model by which the $<Z-O>$ distance of tourmaline varies as a function of its $<Y-O>$ and $<T-O>$ bond lengths. We have examined their conclusions and find that a different distribution of cations over the Y and Z sites gives better agreement with the extensive experimental information available. In fact, on the basis of crystal-structure refinements, Mössbauer spectroscopy, optical absorption spectroscopy, bond-valence theory, ionic radius concept and literature, the occurrence of Fe$^{2+}$ at the Z site of tourmaline is well supported. Conversely, existing experimental data does not provide indisputable evidence for the occurrence of Mn$^{2+}$ at the Z site. Despite this, there is no evidence for inductive effects of $^{57}$Mn$^{2+}$ on $<Z-O>$, and the proposed effects must be regarded as speculative. Statistical analysis shows that the $<Z$-Al-O$>$ average value is 1.906(2) Å, which is consistent with the observed values of $<Z$-Al-O$>$ at the 99% confidence limit (within 3σ) in tourmalines with the Z site fully occupied by Al. Consequently, the proposed inductive effect of $<Y-O>$ and $<T-O>$ on $<Z-O>$ can be ruled out.

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