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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"

Ferdinando Bosi* and Giovanni B. Andreozzi

Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro, 5, I-00185 Rome, Italy

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 $^{Y}Mn^{2+}$ 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.

Keywords: Tourmaline, order-disorder, inductive effects, iron