

## Linking Mössbauer and structural parameters in elbaite-schorl-dravite tourmalines

GIOVANNI B. ANDREOZZI,<sup>1,\*</sup> FERDINANDO BOSI,<sup>2</sup> AND MICAELA LONGO<sup>3</sup>

<sup>1</sup>Dipartimento di Scienze della Terra, Università di Roma “La Sapienza,” Piazzale Aldo Moro 5, 00185, Roma, Italy

<sup>2</sup>Department of Mineralogy, Swedish Museum of Natural History, Box 50007, 10405 Stockholm, Sweden

<sup>3</sup>Bayerisches Geoinstitut, Universität Bayreuth, D95440 Bayreuth, Germany

### ABSTRACT

Accurate crystal-chemical analysis of complex minerals such as tourmalines belonging to the elbaite-schorl-dravite series was obtained by combining Mössbauer spectroscopy (MS) and structural information. Well-defined relationships were established between the two approaches, leading to a close match of results obtained and a strong link between observed parameters.

Although MS information is a powerful tool for quantifying the amount of Fe<sup>2+</sup> and Fe<sup>3+</sup>, it is not always useful in determining their site distribution. In particular, both for Fe<sup>3+</sup> and for (Fe<sup>2+</sup>-Fe<sup>3+</sup>) interactions structural information is still essential. Fe<sup>3+</sup> MS doublets were identified and assigned to iron in *Y* and *Z* sites on the basis of structural information. In a few spectra, Fe<sup>3+</sup> doublets with very low parameters ( $\delta \sim 0.2$  mm/s) were observed and, in contrast with the *T*-site assignment of previous works, were assigned to Fe<sup>3+</sup> in octahedral coordination. Electron delocalization between Fe<sup>2+</sup> and Fe<sup>3+</sup> was observed and related to three different interactions (*Y*-*Y*, *Y*-*Z*, and *Z*-*Z*). Notably, MS hyperfine parameters of Fe<sup>2+</sup> were self-consistent and particularly reliable in determining Fe<sup>2+</sup> site partitioning. Fe<sup>2+</sup> at *Y* was modeled by three doublets ( $\Delta E_Q = 2.45, 2.19,$  and  $1.72$  mm/s). The sum of their absorption areas perfectly matches the <sup>57</sup>Fe<sup>2+</sup> populations derived from structural data ( $r^2 = 0.97$ ). The fourth doublet observed ( $\Delta E_Q = 1.38$  mm/s) is consistent with Fe<sup>2+</sup> at *Z*, which is an octahedron smaller and less distorted than *Y* ( $\lambda_Z = 1.014, \lambda_Y = 1.024$ ). The absorption area of this doublet is highly correlated with the amount of <sup>57</sup>Fe<sup>2+</sup> obtained from site-occupancy refinement ( $r^2 = 0.95$ ).

For <sup>57</sup>Fe<sup>3+</sup> a link between the quadrupole splitting parameter  $\Delta E_Q$  and variations in the chemical/structural environment surrounding Fe nucleus was observed. The  $\Delta E_Q$  of <sup>57</sup>Fe<sup>3+</sup> increases with  $ZO_6$  volume ( $r^2 = 0.84$ ) and is linked to the variation of electrical field gradient generated by the <sup>27</sup>R<sup>2+</sup> → <sup>27</sup>Al substitution. Since the *Z* skeleton completely surrounds *Y* islands,  $\Delta E_Q$  of <sup>57</sup>Fe<sup>3+</sup> shows much more susceptibility to inductive effects from the second rather than the first coordination sphere.

**Keywords:** Tourmaline, Mössbauer spectroscopy, structural formula, Fe disorder