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

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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 Fe2+ and Fe3+, it is not always useful in determining their site distribution. In particular, both for Fe3+ and for (Fe2+-Fe3+) interactions structural information is still essential. Fe3+ MS doublets were identified and assigned to iron in Y and Z sites on the basis of structural information. In a few spectra, Fe3+ doublets with very low parameters (δ ~ 0.2 mm/s) were observed and, in contrast with the T-site assignment of previous works, were assigned to Fe3+ in octahedral coordination. Electron delocalization between Fe2+ and Fe3+ was observed and related to three different interactions (Y-Y, Y-Z, and Z-Z). Notably, MS hyperfine parameters of Fe2+ were self-consistent and particularly reliable in determining Fe2+ site partitioning. Fe2+ at Y was modeled by three doublets (ΔE0 = 2.45, 2.19, and 1.72 mm/s). The sum of their absorption areas perfectly matches the 1Fe2+ populations derived from structural data (r2 = 0.97). The fourth doublet observed (ΔE0 = 1.38 mm/s) is consistent with Fe2+ at Z, which is an octahedron smaller and less distorted than Y (λZ = 1.014, λZ = 1.024). The absorption area of this doublet is highly correlated with the amount of 2Fe2+ obtained from site-occupancy refinement (r2 = 0.95).

For 1Fe3+, a link between the quadrupole splitting parameter ΔE0 and variations in the chemical/structural environment surrounding Fe nucleus was observed. The ΔE0 of 1Fe3+ increases with ZO6 volume (r2 = 0.84) and is linked to the variation of electrical field gradient generated by the 6R2+ → 2Al substitution. Since the Z skeleton completely surrounds Y islands, ΔE0 of 1Fe3+ shows much more susceptibility to inductive effects from the second rather than the first coordination sphere.

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

INTRODUCTION

Minerals of the tourmaline group are cyclosilicates that crystallize in the space group R3m and show complex crystal chemistry, due to the presence of many sites occupied by different ions. The crystal chemistry of tourmaline is characterized by several solid solutions, of which the elbaite-schorl and schorl-dravite series are most important. A standard structural formula may be written as: XY3Zr2(Ti,Fe)6(O3)3V6, where X = Ca, Na, K; Y (vacancy); Z = Mg, Fe2+, Mn2+, Al, Li, Fe3+, Cr3+, V3+; Z = Al, Mg, Fe2+, Fe3+, Cr3+, V3+; T = Si, Al, B; B = B; V = OH, O; W = OH, F, O. The above structural formula shows that both Y and Z sites can be occupied by Fe2+ and Fe3+, as reported in many structural (Table 1) and Mössbauer spectroscopy studies (Table 2).

Both quantification and site distribution of Fe2+ and Fe3+ are crucial points to properly define mineral structural formula.

Conventional electron microprobe analysis (EMPA), generally used to investigate chemical composition, cannot determine Fe2+ and Fe3+ separately (e.g., Sobolev et al. 1999). Mössbauer spectroscopy has been used to determine both Fe valence state and coordination number in tourmaline (see for example Dyar et al. 1998; Fuchs et al. 1998; Ferrow 1994). By using MS, most workers reported at least two doublets that are related to Fe2+ in octahedral coordination; at issue is the assignment of these doublets to the Y and Z sites. These doublets were generally interpreted on the basis of quadrupole splitting (ΔE0) to represent Fe2+ in Y (ΔE0 ~ 2.2 mm/s) and Z (ΔE0 ~ 1.7 mm/s) sites. However, other works (Pieczka and Krawczyk 1997a, 1997b, 2004; Pieczka et al. 1997; Dyar et al. 1998; Oliveira et al. 2002; Ertl et al. 2006; Castañeda et al. 2006) suggested that Fe2+ occupies only the Y site in the structure. They interpreted the multiple doublets previously attributed to Fe2+ in Y and Z as various combinations of nearest and next nearest neighbors to the Y site only and attributed the gradual decrease in quadrupole splitting (also accompanied by line broadening) to the decreasing contributions of ionic bonds.