

## The occurrence of tetrahedrally coordinated Al and B in tourmaline: An $^{11}\text{B}$ and $^{27}\text{Al}$ MAS NMR study

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### ABSTRACT

Considerable uncertainty has surrounded the occurrence of tetrahedrally coordinated Al and B at the *T* site in tourmaline. Although previously detected in several tourmaline specimens, the frequency of these substitutions in nature, as well as the extent to which they occur in the tourmaline structure, is not known. Using  $^{11}\text{B}$  and  $^{27}\text{Al}$  MAS NMR spectroscopy, we have investigated the presence of B and Al at the *T* site in 50 inclusion-free tourmaline specimens of low transition-metal content and different species (elbaite, “fluor-elbaite,” liddicoatite, dravite, uvite, olenite, and magnesiofoitite) from different localities worldwide. Chemical shifts of  $^{14}\text{B}$  and  $^{13}\text{B}$  in  $^{11}\text{B}$  spectra, and  $^{4}\text{Al}$  and  $^{6}\text{Al}$  in  $^{27}\text{Al}$  spectra, are well resolved, allowing detection of even small amounts of *T*-site constituents. In the observed spectra,  $^{14}\text{B}$  and  $^{13}\text{B}$  peaks are located at 0 and 18–20 ppm, respectively, with the greatest intensity corresponding to  $^{13}\text{B}$  (=3 apfu). In  $^{27}\text{Al}$  spectra,  $^{4}\text{Al}$  and  $^{6}\text{Al}$  bands are located at 68–72 and 0 ppm, respectively, with the greater intensity corresponding to  $^{6}\text{Al}$ . However, inadequate separation of  $^{\text{V}}\text{Al}$  and  $^{\text{Z}}\text{Al}$  precludes resolution of these two bands. Simulation of  $^{11}\text{B}$  MAS NMR spectra shows that tetrahedrally and trigonally coordinated B can be readily distinguished at 14.1 T and that a  $^{14}\text{B}$  content of 0.0–0.5 apfu is common in tourmaline containing low amounts of paramagnetic species.  $^{27}\text{Al}$  MAS NMR spectra show that Al is also a common constituent of the *T* site in tourmaline. Determination of  $^{4}\text{Al}$  content by peak-area integration commonly shows values of 0.0–0.5 apfu. Furthermore, the chemical shift of the  $^{27}\text{Al}$  tetrahedral peak is sensitive to local order at the adjacent *Y* and *Z* octahedra, where  $^{4}\text{Al}-^{\text{Y}}\text{Mg}_3$  and  $^{4}\text{Al}-^{\text{Y}}(\text{Al,Li})_3$  arrangements result in peaks located at ~65 and ~75 ppm, respectively. Both  $^{11}\text{B}$  MAS NMR and  $^{27}\text{Al}$  MAS NMR spectra show peak broadening as a function of transition-metal content (i.e.,  $\text{Mn}^{2+} + \text{Fe}^{2+} = 0.01\text{--}0.30$  apfu) in the host tourmaline. In  $^{11}\text{B}$  spectra, broadening and loss of intensity of the  $^{13}\text{B}$  signal ultimately obscures the signal corresponding to  $^{14}\text{B}$ , increasing the limit of detection of  $^{14}\text{B}$  in tourmaline. Our results clearly show that all combinations of Si, Al, and B:  $T = (\text{Al}, \text{Si})_6$ ,  $T = (\text{B}, \text{Si})_6$ ,  $T = (\text{Al}, \text{B}, \text{Si})_6$ , and  $T = \text{Si}_6$  apfu, are common in natural tourmalines.

**Keywords:** Tourmaline,  $^{11}\text{B}$  and  $^{27}\text{Al}$  MAS NMR, tetrahedrally coordinated B and Al