An experimental approach to quantify the effect of tetrahedral boron in tourmaline on the boron isotope fractionation between tourmaline and fluid

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**ABSTRACT**

This study investigates the effect of tetrahedral B ($^{11}$B) in synthetic tourmaline on the B-isotope fractionation between tourmaline and fluid. This is important for the correct interpretation of B-isotope variations in natural tourmalines containing “excess” B (greater than three atoms per formula unit), which substitutes for Si at tetrahedral sites. Such tourmalines commonly occur in Li, Al-rich pegmatites and have been reported from glaucophane schists that formed at high pressures during subduction.

Tourmaline synthesis experiments were performed in a piston-cylinder apparatus in the system SiO$_2$-Al$_2$O$_3$-B$_2$O$_3$-NaCl-H$_2$O at 4 GPa and 700 °C using different run durations, starting from quartz-$\gamma$-Al$_2$O$_3$-H$_2$BO$_3$ solid mixtures and NaCl-solutions. We were able to produce “olenitic” tourmaline with excess B between 1.2 and 2.5 $^{10}$B per formula unit. The B-isotope compositions of the olenitic tourmaline and coexisting fluids were determined by secondary ion mass spectrometry and multi-collector plasma source mass spectrometry to derive isotope fractionation coefficients. The results indicate that for every 10 mol% of total B in tourmaline in tetrahedral coordination, the value of $\Delta^{11}$B$_{tour\text{-}fluid}$ is shifted to more negative values by about 1‰ at 700 °C. This is in good agreement with published ab initio calculations and corresponds to an intracrystalline fractionation of B-isotopes between the trigonal B and tetrahedral T sites of tourmaline on the order of 8 ± 5‰, whereby $^{11}$B partitions to the T site.

**Keywords:** SIMS, experimental geochemistry, fluid, matrix effect, mass spectrometry

**INTRODUCTION**

The use of boron isotopes as a tracer of fluid-rock interaction is well established. Depending on the mineralogical, chemical, and isotopic composition of the B source, fluid-rock ratios, prevailing P-T and closed vs. open system conditions, the B-isotope ratios of natural fluids vary significantly (e.g., van Hinsberg et al. 2011). Because in situ sampling of (paleo) fluids is impossible in most cases, the isotopic composition must be determined indirectly through the analysis of hydrothermal minerals containing boron. Tourmaline is by far the most commonly used mineral for this purpose because it is stable over a wide range of P-T conditions (up to 7 GPa, 900 °C, Krosse 1995), it occurs in a large variety of magmatic, metamorphic, and sedimentary rocks, and it is chemically and physically robust (e.g., Henry and Dutrow 1996).

The use of tourmaline as a fluid monitor requires knowledge about the equilibrium B-isotope fractionation between tourmaline and fluid ($\Delta^{11}$B$_{tour\text{-}fluid}$). Experimental studies of tourmaline-fluid fractionation have so far addressed common tourmaline compositions where boron is exclusively in trigonal coordination (Meyer et al. 2008; Palmer et al. 1992). These results are applicable to most natural tourmalines but there are other cases where boron also occupies tetrahedral T-sites (e.g., Ertl et al. 1997, 2005, 2006, 2007; Hughes et al. 2000, 2004; Kalt et al. 2001; Schreyer et al. 2002; Tagg et al. 1999). In those tourmalines, $^{11}$B is incorporated in exchange for Si (Kutzschbach et al. 2016; Schreyer et al. 2000) and this seems to be favored in very Al-rich tourmaline with a large olenite component [NaAl$_3$Al$_2$Si$_6$O$_{18}$]$(BO_3)_3(OH)$ at high pressures and low temperatures (Ertl et al. 2008). Examples are known from granitic pegmatites with up to 0.83 $^{10}$B pfu (Ertl et al. 2008) and from blueschist facies glaucophane-schists with up to 0.26 $^{10}$B pfu (Marschall et al. 2004).

The driving force for B-isotope fractionation is the bonding environment, with the light $^{11}$B isotope preferring the higher coordination number or more precisely longer bonds (Kowalski et al. 2013; Kowalski and Wunder 2017; MacGregor et al. 2013). Thus it is expected that the presence of tetrahedral boron in tourmaline will affect the tourmaline-fluid fractionation. The magnitude of this effect was predicted by ab initio calculations (Kowalski et al. 2013), which suggest that for every 10 mol% $^{10}$B$_{tot}$, the $\Delta^{11}$B$_{tour\text{-}fluid}$ value is shifted by 0.9‰ toward more negative values (for olenitic compositions at 700 °C). However, the effect has so far not been experimentally studied, mainly due to the difficulty in synthesizing $^{10}$B-bearing tourmaline large enough for in situ B-isotope analysis. Kutzschbach et al. (2016, 2017) were able to produce crystals up to 30 × 100 μm of olenitic tourmaline containing up to 45 mol% $^{10}$B$_{tot}$. Based on these materials, we set out to evaluate the effect of $^{10}$B in tourmaline on isotopic fractionation with aqueous fluid.