Experiments reveal enrichment of $^{11}$B in granitic melt resulting from tourmaline crystallisation

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Abstract

Tourmaline is the most common boron-rich mineral in magmatic systems. In this study, we determined experimentally the fractionation of boron isotopes between granitic melt and tourmaline for the first time. Our crystallisation experiments were performed using a boron-rich granitic glass ($\text{B}_2\text{O}_3 \approx 8 \text{ wt. }\%$) at 660–800 °C, 300 MPa, and $\alpha_{\text{B,O}} \approx 1$, in which tourmaline occurs as the only boron-hosting mineral. Our experimental results at four different temperatures show a small and temperature-dependent boron isotope fractionation between granitic melt and tourmaline ($\Delta^{11}\text{B}_{\text{melt-Tur}} = +0.90 \pm 0.05 \text{‰} \text{ at } 660 \degree \text{C and } +0.23 \pm 0.12 \text{‰} \text{ at } 800 \degree \text{C}$), and the temperature dependence can be defined as $\Delta^{11}\text{B}_{\text{melt-Tur}} = 4.51 \times (1000/T[K]) − 3.94$ ($R^2 = 0.96$). Using these boron isotope fractionation factors, tourmaline can serve as a tracer to quantitatively interpret boron isotopic ratios in evolved magmatic systems. Our observation that $^{11}$B is enriched in granitic melt relative to tourmaline suggests that the $^{8}$B of late-magmatic tourmaline should be higher than tourmaline that crystallised at an early stage, if B isotope fractionation is not affected by other processes, such as fluid loss.

Introduction

Boron is an incompatible trace element that can be highly enriched in granitic melts and aqueous fluids (London et al., 1996). The large difference in atomic mass by 10 % between the two stable isotopes of boron, $^{10}$B and $^{11}$B, results in significant variations in $\delta^{11}$B of natural rocks that can be up to ca. 100 ‰. The separation of B-rich phases such as tourmaline and aqueous fluid from silicate melt is expected to produce B isotope fractionation due to the different B coordination ($^{11}$B at trigonal site and $^{10}$B at tetrahedral site) in coexisting B-bearing phases (e.g., Trumbull et al., 2013; Siegel et al., 2016). Thus, B isotopes are a sensitive tool to trace magmatic–hydrothermal processes (such as fractional crystallisation, degassing, ore formation) and metamorphic fluid source, and tourmaline, as the most common B-hosting mineral in granitic magma, can serve as a useful tracer for such processes. The negligible intra-crystalline diffusion rate leads to the consequence that B isotopic composition of tourmaline is not easily overprinted by late magmatic or hydrothermal events and therefore ideal to record the evolution history of magmas (e.g., Marschall and Jiang, 2011). B isotope fractionation factors ($\Delta^{11}\text{B}_{\text{melt-Tur}}$) between silicate melt and tourmaline are a prerequisite to quantitatively interpret the B isotope composition of tourmaline in granitic systems. To our knowledge, so far, B isotopic fractionation between granitic melt and tourmaline has not been directly determined by experiments. In previous studies (e.g., Trumbull et al., 2013; Siegel et al., 2016), $\Delta^{11}\text{B}_{\text{melt-Tur}}$ values were indirectly calculated from the combination of experimental results on B isotope fractionation between hydrous melt and aqueous fluid ($\Delta^{11}\text{B}_{\text{melt-fluid}}$) (Hervig et al., 2002; Maner and London, 2018) and between tourmaline and aqueous fluid ($\Delta^{11}\text{B}_{\text{Tur-fluid}}$) (Palmer et al., 1992; Meyer et al., 2008). However, these experimental studies differ in the experimental and analytical methods, the P-T conditions, and the fluid compositions. Such discrepancies can lead to great uncertainties if these experimental results are used to calculate $\Delta^{11}\text{B}_{\text{melt-Tur}}$ values. In addition, theoretical studies have suggested that the magnitude of $\Delta^{11}\text{B}_{\text{Tur-fluid}}$ depends on the composition of tourmaline, with a larger fractionation for dravite than for schorl (Li et al., 2020), which further increases the uncertainty for indirectly calculated $\Delta^{11}\text{B}_{\text{melt-Tur}}$ values.

In this paper, we report results of tourmaline crystallisation experiments conducted for B-rich granitic systems in the temperature range of 660 to 800 °C and at 300 MPa. The analytical data of the B isotopic distribution between the experimental glasses and tourmalines provide direct constraints on the B isotope fractionation between granitic melt and tourmaline at magmatic temperatures.

Methods

Five tourmaline crystallisation experiments were performed at 660–800 °C, 300 MPa, $\text{O}_2 \approx \text{NNO}$ for ~15–30 days in waterpressurised, cold-seal pressure vessels. A B-rich peraluminous granitic glass ($\text{B}_2\text{O}_3 \approx 8.8 \text{ wt. }\%$), which was synthesised by melting mixed powders of a B-free glass (BDG-1) and

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boric acid powder, was used as starting material. Four water-saturated experiments (αH₂O = 1) and one water-undersaturated experiment (αH₂O ≈ 0.7) were conducted. The activity of water was decreased by adding a fluid composed of mixed H₂O and CO₂ (added as silver oxalate). Major element compositions of the starting glass and experimental products were measured by electron microprobe analyser (EMPA) using a Cametta SX-100 microprobe. Boron isotope compositions of the starting glass and experimental products were measured in situ using a Thermo Scientific Neptune Plus, which was connected to a Spectra-Physics Solstis femtosecond laser ablation system. Details on the experimental and analytical methods are reported in Supplementary Information (SI).

**Results**

Experimental conditions and products are listed in Table 1. Tourmaline was observed in all experiments and homogeneously distributed in melts as dark-green euhedral and columnar crystals, with a common size of ~100 μm in length and ~50 μm in width (Fig. 1). In back-scattered electron (BSE) images, most tourmalines show a variation in darkness even within one crystal (Fig. 1b), and some grains are characterised by faceted hourglass sector zoning (see details in SI) (Fig. 1e, f). The Mg/[Mg + Fe] ratio is 0.35–0.55 (Fig. S-2), which is typical for schorl and consistent with that of common igneous tourmalines in nature. Minor amounts of magnetite are evenly distributed in experiments. Bubbles were found in runs DC-28 and DC-87. Experimental melts (quenched as glasses) are peraluminous (ASI ≈ 1.1–1.4) and show a narrow range in B₂O₃ content (~7.7–8.0 wt. %). Additional details about experimental products and phase compositions are given in SI.

Boron isotopic compositions of the experimental tourmalines and glasses, as well as the calculated isotopic fractionation factors between them, are listed in Table 1. The starting glass lines and glasses, as well as the calculated isotopic fractionation factors between them, are listed in Table 1. The starting glass but displays a positive trend with temperature, increasing from −0.11 ± 0.04 ‰ at 660 °C to +0.86 ± 0.10 ‰ at 800 °C (Table 1). The calculated B isotope fractionation factors between melt and tourmaline (Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅) show a positive correlation with temperature, increasing from +0.23 ± 0.12 ‰ at 800 °C to +0.90 ± 0.05 ‰ at 660 °C (Table 1), and data regression indicates that the temperature dependence on Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅ can be described as Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅ = 4.51 × (1000/T [K]) − 3.94 (R² = 0.96) (Fig. 2a). In addition, the two experiments performed at 800 °C with different water activities (DC-27 and DC-28) show identical Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅ values within uncertainties.

**Discussion**

Several lines of evidence suggest that near equilibrium conditions in terms of both major elements and B isotopes were reached between melt and tourmaline in our experiments: (1) microscopic observation shows that tourmaline is evenly distributed within the glass matrix for all experiments (Fig. 1a); (2) the major element compositions (seven to ten analytical points for each run) and B isotopic compositions (more than five analytical points) of experimental glasses from each experiment collected at different locations are identical within error (Tables S-2 and S-6); (3) apart from the hourglass sector zoning, no compositional zoning is observed in tourmaline; (4) no variation in B isotope composition is observed in experimental glasses next to the contact with tourmaline and far from the crystals (two or three points).

Our experimental data reveal a small and temperature-dependent B isotopic fractionation between granitic melt and tourmaline at magmatic temperatures. The degree of B isotopic fractionation between different phases at given P-T conditions is considered to be mainly controlled by the coordination of B in each phase, with trigonal site favouring ¹¹B and tetrahedral site favouring ¹⁰B (Kowalski and Wunder, 2018). B in tourmaline is almost exclusively coordinated at the trigonal site (¹³B); ¹⁰B is expected in very Al-rich tourmaline (>1.2 atoms Al per formula unit at the Y site) and at high pressures (>1000 MPa) and low temperatures (Ertl et al., 2018). Our experimental tourmaline is thus assumed to contain negligible amounts of tetrahedrally coordinated B. However, the Δ₁¹Bₘₕₑₙₜ values show a systematic partitioned into fluid relative to granitic melt (Maner and London, 2018). The B isotopic compositions of the experimental tourmaline (Δ₁¹Bₘₕₑₙₜ) show a positive correlation with temperature, increasing from −0.11 ± 0.04 ‰ at 660 °C to +0.86 ± 0.10 ‰ at 800 °C (Table 1). The calculated B isotope fractionation factors between melt and tourmaline (Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅) increase from +0.23 ± 0.12 ‰ at 800 °C to +0.90 ± 0.05 ‰ at 660 °C (Table 1), and data regression indicates that the temperature dependence on Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅ can be described as Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅ = 4.51 × (1000/T [K]) − 3.94 (R² = 0.96) (Fig. 2a). In addition, the two experiments performed at 800 °C with different water activities (DC-27 and DC-28) show identical Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅ values within uncertainties.

**Table 1** Experimental conditions and boron isotopic fractionation factors and partition coefficients.

<table>
<thead>
<tr>
<th>Run</th>
<th>B₂O₃ content (wt. %)</th>
<th>T (°C)</th>
<th>P (kbar)</th>
<th>α_H₂O</th>
<th>Duration (days)</th>
<th>Phases</th>
<th>ASI</th>
<th>Δ₁¹Bₘₕₑₙₜ (‰)</th>
<th>s.d. (‰)</th>
<th>n</th>
<th>Δ₁¹Bₘₙₑₜ (‰)</th>
<th>s.d. (‰)</th>
<th>n</th>
<th>Δ₁¹Bₘₕₑₙₜ-Tₐₐ₅ (‰)</th>
<th>s.d. (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC-27</td>
<td>7.8</td>
<td>800</td>
<td>3</td>
<td>1.0</td>
<td>15</td>
<td>Tur (6.7), oxi (tr)</td>
<td>1.37</td>
<td>+1.10</td>
<td>0.07</td>
<td>5</td>
<td>+0.86</td>
<td>0.10</td>
<td>4</td>
<td>+0.23</td>
<td>0.12</td>
</tr>
<tr>
<td>DC-28</td>
<td>8.0</td>
<td>800</td>
<td>3</td>
<td>0.7</td>
<td>15</td>
<td>Tur (7.4), oxi (tr), fl</td>
<td>1.23</td>
<td>+1.10</td>
<td>0.02</td>
<td>5</td>
<td>+0.85</td>
<td>0.08</td>
<td>5</td>
<td>+0.25</td>
<td>0.09</td>
</tr>
<tr>
<td>DC-10</td>
<td>8.0</td>
<td>750</td>
<td>3</td>
<td>1.0</td>
<td>20</td>
<td>Tur (9), oxi (tr)</td>
<td>1.10</td>
<td>+0.96</td>
<td>0.08</td>
<td>6</td>
<td>+0.42</td>
<td>0.11</td>
<td>4</td>
<td>+0.54</td>
<td>0.13</td>
</tr>
<tr>
<td>DC-11</td>
<td>7.8</td>
<td>700</td>
<td>3</td>
<td>1.0</td>
<td>25</td>
<td>Tur (8.8)</td>
<td>1.20</td>
<td>+0.93</td>
<td>0.03</td>
<td>5</td>
<td>+0.31</td>
<td>0.11</td>
<td>4</td>
<td>+0.62</td>
<td>0.12</td>
</tr>
<tr>
<td>DC-87</td>
<td>7.7</td>
<td>660</td>
<td>3</td>
<td>1.0</td>
<td>30</td>
<td>Tur (10.8), oxi (tr), fl</td>
<td>1.24</td>
<td>+0.78</td>
<td>0.04</td>
<td>7</td>
<td>−0.11</td>
<td>0.04</td>
<td>4</td>
<td>−0.90</td>
<td>0.05</td>
</tr>
</tbody>
</table>

* Starting glass of all experiments was B10 glass.
* Boron contents of experimental glasses were measured by EMPA and calibrated based on data for synthesised glasses with different boron contents (B4, B6, and B10).
* Initial water activity in the experimental runs, α_H₂O = H_2O(H_2O + CO_2) on a molar basis.
* Numbers in parentheses represent phase abundances in wt. %, which were calculated by mass balance; tr, trace amount, but abundance not determined. Phase abbreviations: Tur, tourmaline; oxi, oxide; fl, fluid.
* Aluminium saturation index in the experimental glass; ASI = Al_2O_3/(Na_2O + K_2O + CaO) on a molar basis.
increase with increasing temperature, which could be interpreted as a positive temperature effect on stabilising $^{11}$B at the T-site of tourmaline (Ertl et al., 2018). In hydrous silicate glasses, B occupies both trigonally and tetrahedrally coordinated sites, and the proportions of $^{11}$B and $^{12}$B depend on melt composition (especially on B content), temperature, and pressure (Dingwell et al., 1996). Previous spectroscopic measurements indicate that the amount of $^{12}$B in both natural and synthetic glasses is minor and probably negligible (Tonarini et al., 2003). Since most B in magmatic tourmaline is at trigonal sites, the small $\Delta^{11}$B$_{\text{melt-Tur}}$ value implies that B should also be predominantly at 3-fold coordinated sites in the peraluminous B-rich granitic melts of this study. The slight increase in $\delta^{11}$B$_{\text{melt}}$ with increasing temperature in our experiments may be interpreted as the effect of temperature promoting the reaction $[\text{BO}_4] \rightarrow [\text{BO}_3] + \text{NBO}$ in silicate melts (Wu and Stebbins, 2013). It is noteworthy that some previous experimental studies observed a large B isotope fractionation between granitic melt and aqueous fluid, and interpreted it as an indication of a large proportion of $^{12}$B in the melt (Hervig et al., 2002; Maner and London, 2018). This interpretation is inconsistent with both the result of this study and the spectroscopic studies.

This study provides a direct constraint on the B isotope fractionation between silicate melt and tourmaline and indicates a slightly positive value of $\Delta^{11}$B$_{\text{melt-Tur}}$. The $\Delta^{11}$B$_{\text{melt-Tur}}$ estimated from fluid-melt and fluid-tourmaline fractionation factors indicate a slight fractionation between granitic melt and tourmaline, but the sign of $\Delta^{11}$B$_{\text{melt-Tur}}$ is controversial (Fig. 2b). A $\Delta^{11}$B$_{\text{melt-Tur}}$ of $-3 \%$ at 500 °C was applied by Trumbull et al. (2013) and Siegel et al. (2016), whereas Ribeiro da Costa

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**Figure 1** Representative images of experimental products. (a) Tourmaline is evenly distributed in melts (run DC-11, plane-polarised). (b, c, d) Representative BSE images of runs DC-10, DC-28, and DC-11, respectively, showing the positions of analysed areas with laser-ablation. (e) BSE image of a tourmaline grain with hourglass sector zoning from DC-87, section nearly parallel to the c-axis. Three zones can be recognised in this crystal: c+, c−, and a sectors (see details in SI). (f) BSE image of a tourmaline grain from DC-11 with hourglass sector zoning, section perpendicular to the c-axis. The image shows faceted compositional sector zoning splitting the crystal into light and dark areas.
We determined the temperature-dependent equilibrium B isotope fractionation between peraluminous granitic melt and tourmaline at 660 to 800 °C and 300 MPa, which can be expressed as Δ11B_{melt-Tur} = 4.51 × (1000/T [K]) − 3.94 (R² = 0.96). Our experiments, for the first time, provide direct measurements of the fractionation factors that can be used for tracing B isotopes of granitic melt from the records in tourmaline.

Conclusions

Boron isotope fractionation is expected to occur during magmatic-hydrothermal processes due to the difference in coordination of B between melt, fluid, and B-bearing minerals. As the most common B-rich mineral in granite and pegmatite, tourmaline is widely studied to trace processes at the magmatic-hydrothermal transition by measuring its B isotope composition. The results of this study show small slightly positive temperature-dependent Δ11B_{melt-Tur} values. Thus, the B isotope composition of tourmaline crystallising from a granitic melt could approximately reflect that of the silicate melt, especially at high temperatures (~700–800 °C). However, since the residual melt will be progressively enriched in 11B with ongoing crystallisation of tourmaline in a closed system, as indicated by the Rayleigh fractionation model (Fig. 3a), the δ11B of late-magmatic tourmaline should be higher than that of tourmaline crystallising at an early stage. Such an increasing trend of δ11B values from early- to late-stage tourmaline has been observed in pegmatite (Mikova et al., 2010; Siegel et al., 2016), based on the analysis of δ11B in core and rim of tourmalines, reflecting the evolution from early- to late-stage crystallisation. Our calculation applying a Rayleigh fractionation model and the new fractionation factors show that the consumption of ~62–78 % B in melt (as a result of tourmaline crystallisation) could explain the observed B isotopic variation of tourmaline between core and rim (Fig. 3b).

Differently, some other studies reported a decrease of δ11B from early- to late-stage tourmaline in granites and pegmatites (Trumbull et al., 2013; Drivenes et al., 2015; Zhao et al., 2019), which were ascribed to the preferential partitioning of 11B in tourmaline relative to the coexisting melt because negative Δ11B_{melt-Tur} values were assumed for the modelling (Fig. 3a, coloured lines). However, such an explanation is inconsistent with the positive Δ11B_{melt-Tur} value determined in this study. Alternatively, a kinetically driven B isotope fractionation during fluid exsolution is a potential interpretation for the decrease of δ11B observed in these studies (Kowalski and Wunder, 2018).

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2206.

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Figure 3 (a) Modelled curves illustrating the change in δ^{11}B values for residual melt after crystallisation of tourmaline, assuming a Rayleigh fractionation. Grey solid curves represent the evolution in δ^{11}B assuming tourmaline crystallisation, the starting δ^{11}B values of the melt are set as −13 ‰ and the fractionation factors are based on the result of this study. The coloured lines are calculated δ^{11}B variation trends of residual melts based on the δ^{11}B analyses of zoned tourmalines and negative Δ^{11}B_{melt-Tur} fractionation factors applied in the studies of Trumbull et al. (2013), Drivenes et al. (2015), and Zhao et al. (2019) (see data in Table S-8). Note the discrepancy between the grey solid lines and the coloured lines. (b) Rayleigh fractionation model illustrating the variation of δ^{11}B of residual melt with ongoing tourmaline crystallisation using tourmaline data from Mikova et al. (2010) and Siegel et al. (2016) and the positive fractionation factors from this study. The black dots in both figures represent δ^{11}B values of melt at the end of tourmaline crystallisation, calculated from the δ^{11}B values determined at the rim of the tourmalines. The δ^{11}B values at F = 1.0 are calculated from δ^{11}B values determined in the core of the tourmalines. Data used to draw the coloured lines are listed in Table S-8, and the detailed calculation process is given in SI.

References


