Tourmaline as a recorder of magmatic-hydrothermal evolution: In-situ elements and boron isotope analysis of tourmaline from the Qinghe pegmatite, NW China

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Abstract

We conducted systematic elements and boron isotope studies on the tourmalines from a single pegmatite vein of the Qinghe pegmatite field (NW China), aiming to reveal its magmatic-hydrothermal evolution and implications for Li mineralization. The pegmatite vein is barren, intruded into the Paleozoic mica schists, and texturally divided into a border zone, a transition zone and a core zone. Tourmalines occur in all these zones, and they commonly have late-stage hydrothermal tourmaline overgrowths. All tourmalines belong to the alkali group, but show varied Mg/(Mg+Fe) ratios (0.39-0.66), with the border and transition zone tourmalines belonging to schorl, while the core zone and hydrothermal tourmalines to dravite. Most tourmalines follow the (Na+Mg) (Al+Xvac)-1, FeMg-1 and MnMg-1 exchange vectors. The core zone tourmalines, however, show positively correlated FeOt and MgO, and negatively correlated FeOt and Al2O3, suggesting a Fe3+Al-1 substitution for them, which could be related to a rise of fO2. Thus, tourmaline FeAl-1 correlation could be reflective of the redox state of pegmatite system. The elevated fO2 can be linked to concentration of aqueous fluid during pegmatite evolution. Moreover, the core zone tourmalines differ from other tourmalines by their positive Eu anomalies, reflecting an increased polymerization of Eu2+-Al-Si complexing in the zone. The border zone tourmalines have δ11B = -14.0 ˜ -12.7˜ -12.1show slightly lower δ11B values (-14.4commonly light B, along with low Li (<120 ppm), of the tourmalines from barren pegmatite are in contrast to the relatively heavy B (-6.0 ˜ -9.0ppm) of tourmalines from global Li-mineralized pegmatite, which is significant in Li mineralization prospect.

Tourmaline as a recorder of magmatic-hydrothermal evolution: In-situ major, trace element and boron isotope analysis of tourmaline from Qinghe pegmatite in Altay, China

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Abstract

. The studied pegmatite intruded into the Paleozoic mica schists, and texturally divided into a border zone, a transition zone and a core zone. Tourmalines occur in all these zones, and they commonly have late-stage hydrothermal tourmaline overgrowths. All tourmalines belong to the alkali group, but show varied Mg/(Mg+Fe) ratios. The border and transition zone tourmalines belong to schorl, while the core zone and hydrothermal tourmalines belong to dravite. Most tourmalines follow the (Na+Mg) $(Al+X_{vac})_{-1}$, $FeMg_{-1}$ exchange vectors. The core zone tourmalines, however, show positively correlated FeO_t and MgO, and negatively correlated FeO_t and Al_2O_3, suggesting a rise of f_{O2} which linked to concentration of aqueous fluid during pegmatite evolution. The border zone tourmalines have $\delta^{11}B$ = -14.0 ~ -12.7‰, similar to the transition zone (-13.9 to -12.1‰). The core zone and hydrothermal tourmalines show slightly lower $\delta^{11}B$ values (-14.4‰ to -13.3‰). The Rayleigh fractionation model calculates the significantly light B cause by a 10% late-stage fluid exsolution. Along with low Li (<120 ppm), of the tourmalines from barren pegmatite are in contrast to the relatively heavy B (-6.0 to -9.0‰) and high Li (>6000 ppm) of tourmalines from global Li-mineralized pegmatite, which is significant in Li mineralization prospect.

Introduction

Evolution of pegmatite magma is the fundamental and key question in pegmatite research. Volatile content and its evolution detail is another focus issue for the petrogenesis of pegmatite. the degree of water saturation remains a subject of debate. Because of incorporation a large variety of cations in terms of size and charge, tourmaline has manifested to provide valuable information on the evolution of pegmatite system (Jolliff et al., 1987; Drivenes et al., 2015)

Geologic setting

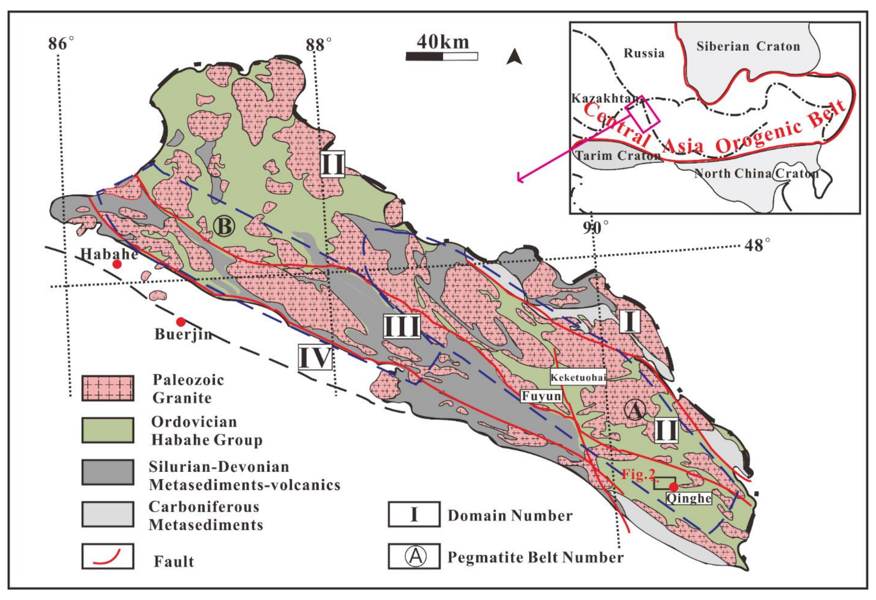

Figure 1. (a) Sketch geological map of the Central Asia Orogenic Belt (CAOB); (b) Geologic map of the Altay orogen (modified from Windley et al., 2002). Code: I: North Altay domain; II: Central Altay domain; III: Qiongkuer domain; IV: Erqis domain. A: Halong-Qinghe pegmatite belt; B: Jiamanheba-Xiaokalasu pegmatite belt.

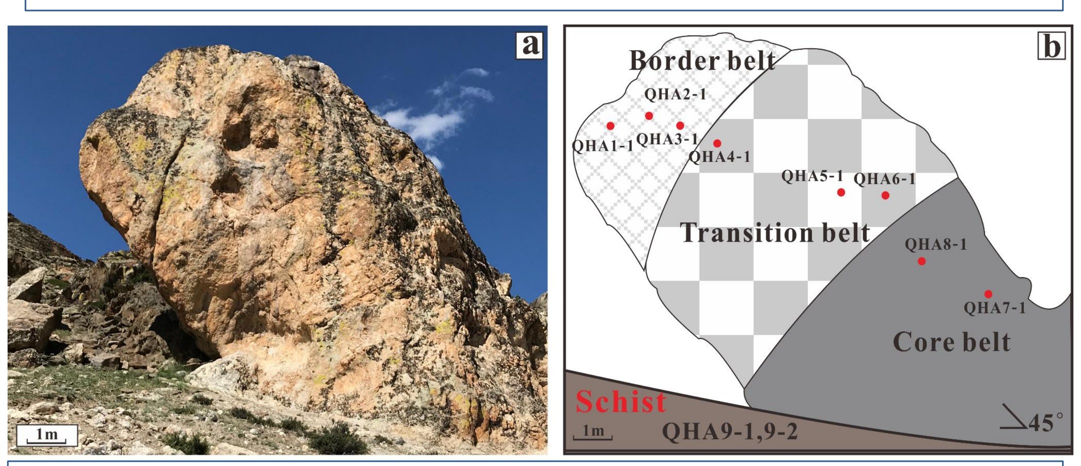

Figure 2. (a) Field photograph of the pegmatite vein of this study; (b) Sketch of the pegmatite vein with textually three zones (border zone, transition zone and core zone) from rim to core. Also shown are the sampling localities of tourmaline samples.

Sample descriptions

Tourmalines from the border zone are 1-2mm in length (Fig. 3a), while those from the transition (Fig. 3b). Some mega crystals (> 20mm) in the core zone were observed (Fig. 3c). All the tourmalines are subhedral to euhedral and transparent to semi-transparent, showing light blue to dark blue and almost patchy zoning. Compositional zoning is common in tourmalines from the border zone (Fig. 3a), transition zone (Fig. 3b) and core zone (Fig. 3c). Late-stage hydrothermal tourmalines (yellow in colour) are observed either as fillings in the fractures or as overgrowth around (Fig. 3b,c) early-formed tourmalines from the aforementioned three zones.

Metamorphic tourmalines from mica schistare euhedral and relatively small in size (2-3mm), and are characterized by dark green cores and light brownish rims.

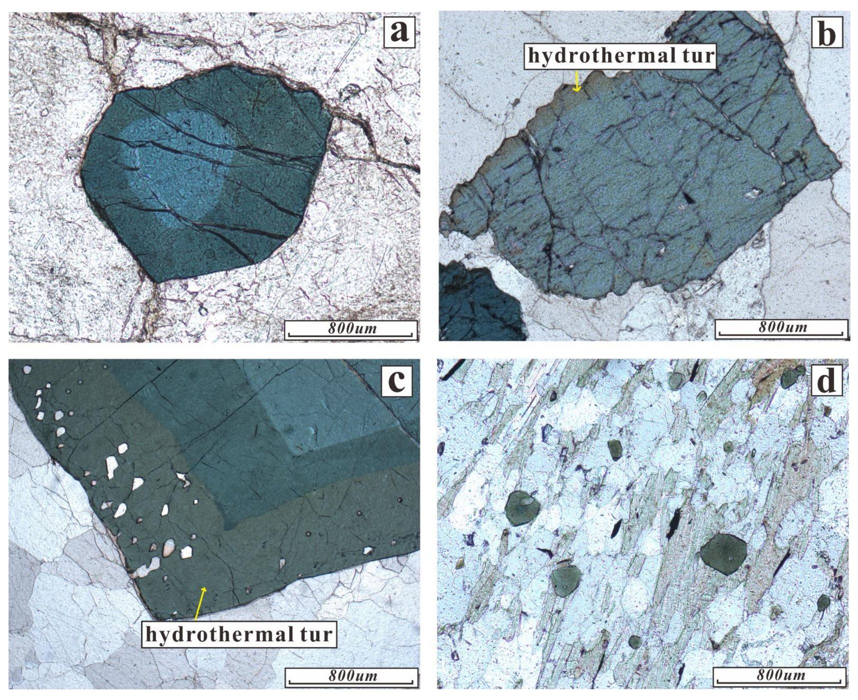

Figure 3. (a) Border zone tourmaline, (b) Transition zone tourmaline, (c) Core zone tourmaline with hydrothermal tourmaline overgrows, (d)) Euhedral tourmalines in the mica schist

Results

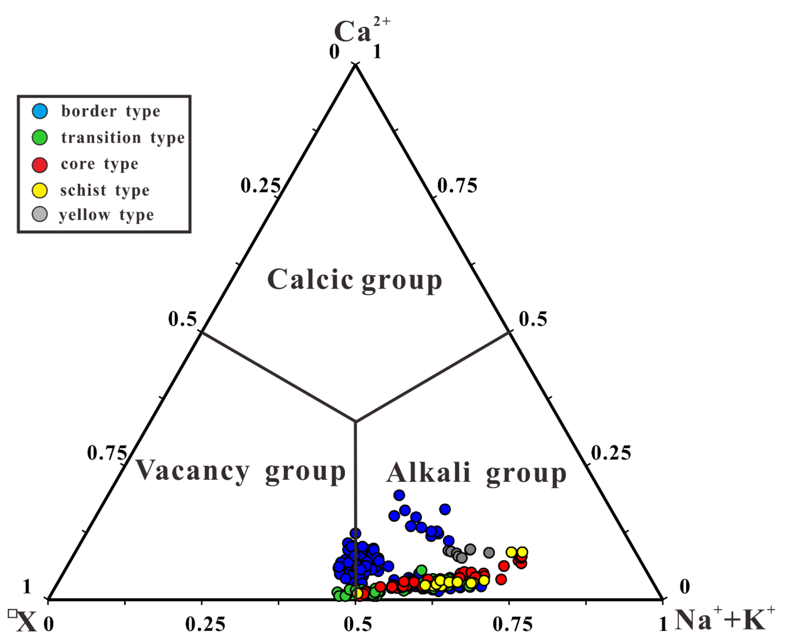

Figure 4. Classification diagram for tourmalines based on X-site occupancy (Henry et al., 2011)

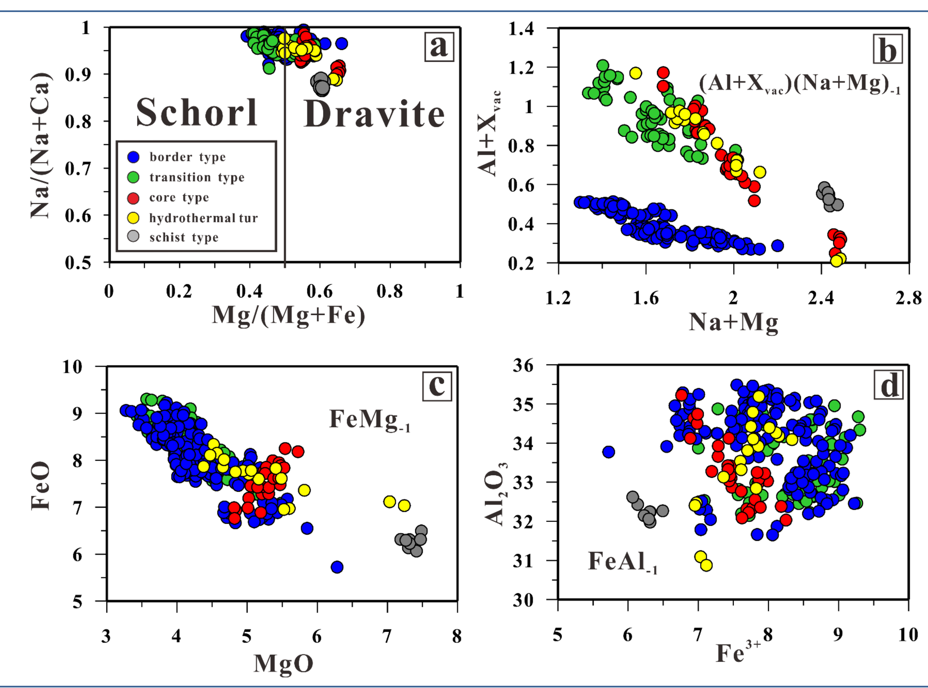

Figure 5. (a) Mg/(Fe+Mg) vs Na/(Na+Ca); (b) (Na+Mg) vs (Al+□X); (c) MgO vs FeO; (d) Fe^{3+} vs Al_2O_3.

Discussion

Border and transition zones (Fig. 5a) were crystallized under water-deficient conditions (Scaillet et al., 1991). The absence of Fe-Mg substitution in the core zone tourmalines may be ascribed to a change of oxygen fugacity (f_{O2}) (Fig. 5c,d). The elevation of f_{O2} in the core zone could be linked to concentration of aqueous fluid during pegmatite evolution (London, 2018).

The tourmalines from the border and transition zones of the pegmatite vein show comparable $\delta^{11}B$ values (-14.0‰ ~ -12.7‰ versus -13.9‰ ~ -12.1‰), whereas the core zone tourmalines have slightly lower $\delta^{11}B$ values (-14.4‰ ~ -13.3‰) (Fig. 6). Tourmalines from the Qinghe pegmatite have B isotope compositions similar to those from the surrounding biotite-quartz-tourmaline schist (-13.2 ‰ ~ -12.2‰), implying negligible B isotopic fractionation during melting of the schist under amphibolite facies conditions.

We suggest that the slightly lighter B isotopes of the core zone tourmalines could be ascribed to a process of fluid exsolution in the core zone, because heavy B would be preferentially partitioned into aqueous fluid in equilibrium with a melt (e.g., Meyer et al., 2008), and fluid exsolution is thus expected to deplete the residual melt in heavy B. By establishing a Rayleigh model, less than 10% boron should be removed from the magma into an escape fluid phase. It is noticed that the fluid exsolution in the Qinghe pegmatite of the Altay orogen is insignificant, which may characterize the barren pegmatite.

Some workers have proposed that evaporate interlayers in the source could be crucial to Li mineralization (Simmons and Webber 2008; Chen et al. 2020), because evaporate is expected to contain large amounts of fluxing components such as Li, alkalis (Na and K), carbonate anions, etc., which are common in Li-mineralized pegmatite (Li and Chou, 2016; Zhang et al. 2021). Generally, evaporate possesses heavy B isotopic compositions (Trumbull et al., 2020). Therefore, the typically heavy B signature of pegmatite with Li-mineralization could be ascribed to more involvement of evaporate interlayers (including carbonate and claystone, etc.) in the source.

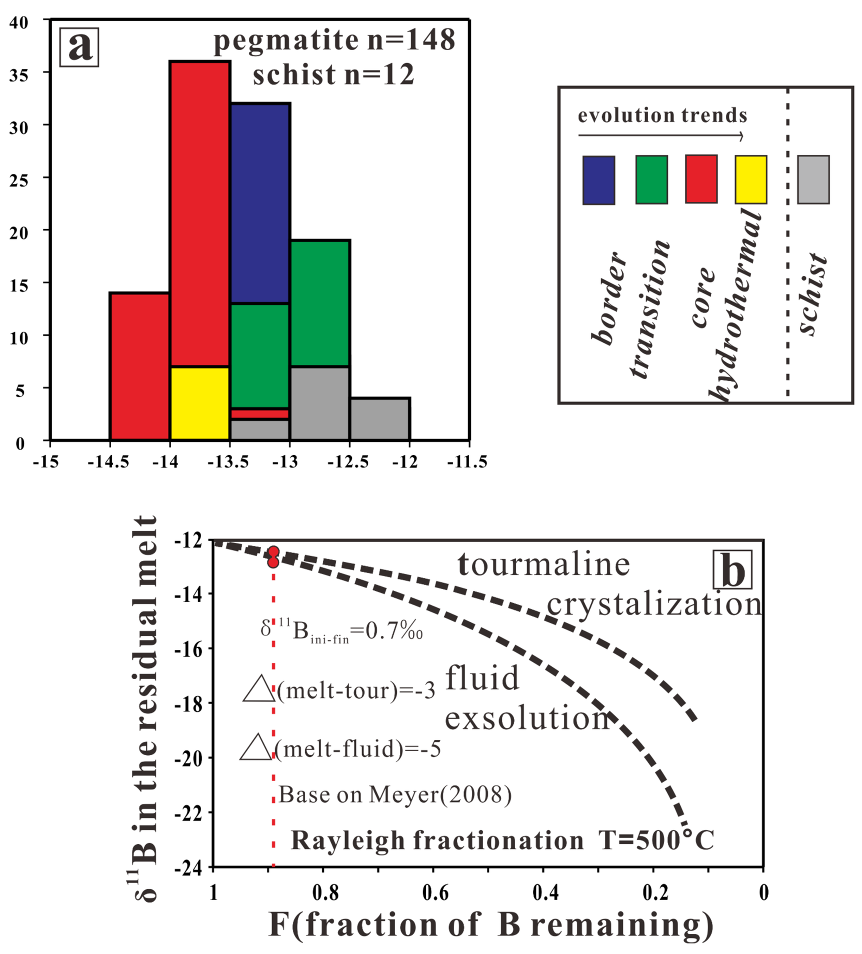

Figure 6. (a) Histogram of $\delta^{11}B$ values of Qinghe pegmatite and schist; (b) Modeling the B isotopic variation of the core zone pegmatite-forming magma after fluid exsolution using the Rayleigh fractionation model.

Conclusions

(1) Tourmaline evolve chemically from schorl in early-formed border and transition zone to dravite in the late-stage aqueous fluid-rich core zone. The evolution of pegmatite-forming magma is controlled mainly by aqueous fluid activity and oxygen fugacity (f_{O2}).

(2) Fluid exsolution from the core zone caused slight B isotopic fractionation, with heavy B preferentially partitioned in exsolved fluid. Boron isotopes could be used to infer the scale of fluid exsolution during pegmatite-forming magmatic evolution.

(3) A comparison between barren and fertile pegmatite worldwide suggest that pegmatite with spodumene mineralization basically show heavier $d^{11}B$ values than barren pegmatite, which could be ascribed to more involvement of evaporate interlayers in the source of the former.

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