

## **Tourmaline chemical and boron isotopic constraints on the magmatic-hydrothermal transition and rare-metal mineralization in alkali granitic systems**

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### **ABSTRACT**

The magmatic-hydrothermal transition in granite-related, rare-metal metallogenic systems has received great attention as economic rare metal (including rare earth) minerals reach saturation and trigger mineralization at this stage. However, deciphering the details of the melt-fluid evolution process and the distribution behavior of rare metals remains difficult. Here, we applied tourmaline chemistry and B isotopes to unravel processes at the magmatic-hydrothermal transition that are responsible for rare-metal partitioning in the Huoshibulake (HS) and Tamu (TM) REE-Nb-mineralized intrusions in Southern Tianshan, SW Central Asian Orogenic Belt. Three types of tourmaline are identified in the plutons: (1) disseminated tourmaline in the granite, with a brown-yellow core (HS-DB) and blue-green rim (HS-DG); (2) orbicular tourmaline, with a brown-yellow core (HS-OB and TM-OB) and blue-green rim (HS-OG and TM-OG); and (3) vein tourmaline (HS-V and TM-V). Compositionally, all these tourmalines exhibit extremely low Ca and Mg contents and are classified as schorl. The substitution processes of major-element variations are dominantly caused by  $(\text{Al}, \square)(\text{Fe}, \text{Na})_{-1}$  exchange vectors. Four generations of tourmaline crystallization are established based on the petrographic, compositional, and B isotopes evolution of the tourmaline. First, the HS-DB crystals crystallized from the highly evolved residual melt, and then HS-OB and TM-OB precipitated from immiscible B-rich aqueous melts during the magmatic-hydrothermal transition. Subsequently, the blue-green overgrowths (HS-DG, HS-OG, and TM-OG) crystallized from exsolved hydrothermal fluids. Finally, the formation of HS-V and TM-V resulted from another melt pulse from a deeper magma chamber. The magmatic tourmaline exhibits a narrow range of  $\delta^{11}\text{B}$  values between  $-12.6$  to  $-10.0\%$ , while the hydrothermal tourmaline shows significantly heavier and variable  $\delta^{11}\text{B}$  values ranging from  $-10.2$  to  $-4.9\%$ . The fractionation of B isotopes is reproduced by Rayleigh fractionation modeling. Lower Nb and Sn contents in the orbicular tourmaline relative to those precipitated from the residual melt, along with the lack of rare-metal minerals in the orbicules, indicate that B-rich melt/fluid exsolution does not necessarily contribute to the rare-metal mineralization. In comparison, the veins contain abundant rare-metal and REE minerals in close paragenesis with fluorite, and the vein tourmaline shows high-Nb and -Sn contents. These observations suggest that saturation of fluorite triggered the precipitation of rare metals, and fluorine played a critical role in rare metal concentration and mineralization. This study highlights the potential of tourmaline to trace the magmatic-hydrothermal transition and provide insights into rare-metal mineralization in the granitic systems.

**Keywords:** Multi-generation tourmaline, boron isotopes, magmatic-hydrothermal transition, rare-metal mineralization