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Chemical and boron isotopic compositions of tourmaline from the Paleoproterozoic Houxianyu borate deposit, NE China: Implications for the origin of borate deposit

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ABSTRACT

The Houxianyu borate deposit in northeastern China is one of the largest boron sources of China, hosted mainly in the Paleoproterozoic meta-volcanic and sedimentary rocks (known as the Liaohe Group) that are characterized by high boron concentrations. The borate ore-body has intimate spatial relationship with the Mg-rich carbonates/silicates of the Group, with fine-grained gneisses (meta-felsic volcanic rocks) as main country rocks. The presence of abundant tourmalinites and tourmaline-rich quartz veins in the borate orebody provides an opportunity to study the origin of boron, the nature of ore-forming fluids, and possible mineralization mechanism. We report the chemical and boron isotopic compositions of tourmalines from the tourmaline-rich rocks in the borate deposit and from the tourmaline-bearing fine-grained gneisses.

Tourmalines from the fine-grained gneisses are chemically homogeneous, showing relatively high Fe and Na and low Mg, with $\delta^{11}B$ values in a narrow range from +1.22‰ to +2.63‰. Tourmalines from the tourmaline-rich rocks, however, commonly show compositional zoning, with an irregular detrital core and a euhedral overgrowth, and have significantly higher Mg, REE (and more pronounced positive Eu anomalies), V (229–1852 ppm) and Sr (208–1191 ppm) than those from the fine-grained gneisses. They show varied B isotope values ranging from +4.51‰ to +12.43‰, which plot intermediate between those of the terrigenous sediments and arc rocks with low boron isotope values (as represented by the $\delta^{11}B$ = +1.22‰ to +2.63‰ of the fine-grained gneisses of this study) and those of marine carbonates and evaporates with high boron isotope values. In addition, the rim of the zoned tourmaline shows notably higher Mg, Ti, V, Sn, and Pb, and REE (particularly LREEs), but lower Fe, Co, Cr, Ni, Zn, Mn, and lower $\delta^{11}B$ values than the core. These data suggest that (1) the sources of boron of the borate ore-body are mainly the Paleoproterozoic meta-volcanic and sedimentary rocks, and (2) the ore-forming fluids should be the high temperature metamorphic fluids related to the amphibolite-facies metamorphism of the Paleoproterozoic foldbelt, which leach boron from the boron-rich meta-volcanic and sedimentary rocks of the Liaohe Group, and the boron-rich metamorphic fluids subsequently interacted with the marine Mg-rich carbonates and evaporates, forming borate deposit, the tourmaline overgrowth in the rim and the tourmaline-rich rocks.

1. Introduction

Boron is not a major element in the earth's crust and waters, averaging only 3–20 ppm in the upper continental crust and is a minor component in seawater (Garrett, 1998). However, boron tends to accumulate in the last phase of magmatic flows or geothermal fluids due to its mobile and volatile features. Most economically exploited borate deposits are formed by leaching of hydrothermal waters circulating through boron-rich lithologies, and subsequent evaporation of surface and near-surface waters in volcanic terrains characterized by active geothermal springs (Warren, 2006). Most borate deposits are commonly situated in active volcanic terrains, and have a close relationship with tuff, basalts and volcanic sediments. In these areas, the subduction processes may have played an important role in the formation of borate-rich series (Floyd et al., 1998). Boron is enriched in continental crust, clastic sediments, and seawater-altered oceanic crust (Leeman and Sisson, 1996). Thus, the initial source and enrichment of boron was likely in a subduction environment via

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metasomatism of lithosphere by boron-rich fluids released from down-going altered oceanic slabs (Palmer, 1991; Ryan and Langmuir, 1993) and possible boron-rich pelagic sediments (You et al., 1993).

The Houxianyu borate deposit of northeastern China is one of the major boron sources in China. The borate deposits in China are unusually hosted in the Palaeoproterozoic metamorphic volcanic-sedimentary rocks (known as the Liaohe Group; Zhang, 1984), while most other major economic borate deposits on Earth are contained in Cenozoic (or younger) sediments (Kistler and Helvaci, 1994). Origin of the Chinese borate deposits remains controversial, focusing on three issues: (1) the source of ore-forming fluids, (2) the origin of boron, and (3) the mechanism of borate formation. The Houxianyu borate deposit is one of the largest borate deposits in the Liaohe Group of northeastern China. It has experienced the most extensive hydrothermal alteration, and resulted in the formation of a complex borate–silicate–carbonate assemblage (Jiang et al., 1997), in which tourmaline-rich rocks are ubiquitous.

Tourmaline has received great interest in recent years and is believed to be a useful petrogenetic indicator for ore genesis (Henry and Dutrow, 1996; Slack, 1996; Jiang, 2001; Jiang et al., 1999, 2004;Marschall and Jiang, 2011; Slack and Trumbull, 2011). Tourmaline-rich rocks have a close spatial relationship with the borates ore bodies, providing an opportunity to study the origin of boron, the nature of ore-forming fluids, and possible mineralization mechanism (Marschall and Jiang, 2011; Slack et al., 1993; Slack and Trumbull, 2011). However, few studies have been done on the origin and significance of tourmaline-rich rocks in the Houxianyu borate ores (Jiang et al., 1997; Peng and Palmer, 2002; Xu et al., 2004). In this paper, we present new mineralogical and geochemical data of the tourmalines from the borate ores, particularly, the in situ analyses of boron isotopic and chemical compositions of tourmalines from different rock types, in an attempt to clarify the origin of the borate ores.

2. Geological setting

The borate deposits are hosted in the Paleoproterozoic Jiao-Liao-Ji Belt (JLJB) that lies between two Archean cratons, the Longgang Block to the north and the Nangrim Block to the south (Bai, 1993; Fig. 1a). The two Archean blocks are largely made up of granitoids and greenstone belts. The NE-trending 300 km-long Paleoproterozoic belt consists mainly of volcanic sedimentary rocks and associated granitic and mafic intrusions of greenschist to lower amphibolite facies (Zhang, 1984, 1988; Fig. 1b). The Li'eryu Formation, being at the lower part of the Paleoproterozoic Liaohe Group, is made up of meta-volcanic sedimentary rocks, and is characterized by high boron concentration (known as boron-bearing sequence; Zhang, 1988), in which several borate deposits are found (Fig. 1b). The Li'eryu Formation is overlain by graphitic gneiss of the Gaojiayu Formation, magnesium marbles of the Dashiqiao Formation, and metamorphosed clastic sediments of the Gaixian Formation. Several Paleoproterozoic granitic plutons (known as the Liaoji granites) occur in the Liaohe Group, including the deformed gneissic granites (~2.16 Ga; Li et al., 2005; Lu et al., 2006; Li and Zhao, 2007) and un-deformed post-collisional granites (~1.85 Ga; Li et al., 2005; Lu et al., 2006; Li and Zhao, 2007).

The dynamic setting and tectonic evolution of the JLJB remain controversial (e.g., Zhao et al., 2011; Zhao and Zhai, 2013). Some workers believe that the Paleoproterozoic fold-belt represents a sequence of volcanic-sedimentary rocks (and associated granite intrusions) in a continental rifting setting, which finally were metamorphosed and folded due to the collision between the Longgang and Nangrim blocks at ca. 1.9 Ga (Li et al., 2001, 2004; Luo et al., 2004; Li and Zhao, 2007; Li et al., 2012; Tam et al., 2011, 2012). Others suggest that the belt represented Paleoproterozoic continental arc series, and was finally metamorphosed during an arc-continent collisional process (Bai, 1993; Peng and Palmer, 1994, 1995; He and Ye, 1998; Faure et al., 2004; Lu et al., 2006; Wang et al., 2011; Zhao et al., 2011; Zhao and Zhai, 2013).

3. Geological features of the Houxianyu borate deposit

The Houxianyu borate deposit is one of the three main borate deposits hosted in the Li'eryu Formation (boron-bearing sequence) of the Paleoproterozoic rocks. Four main rock units are present in the Houxianyu borate deposit (Fig. 2), including: (1) fine-grained gneisses; (2) tourmalinite and tourmaline-rich quartz veins (tourmalite); (3) magnesium-rich series; and (4) borate ore bodies.

(1) Fine-grained gneisses.

The fine-grained gneisses show banding structures with foliated biotite and amphibole (Fig. 3a), being in conformable contact with the borate-hosting rocks. They are mainly composed of quartz (40 vol.%), microcline (25 vol.%) and plagioclase (10 vol.%), and small amounts of hornblende, biotite, magnetite and tourmaline (Fig. 3b), etc., representing metamorphosed felsic volcanic rocks (Peng and Palmer, 1995). Tourmaline is minor (less than 10 vol.%) in the rock, and appears to have formed during the metamorphism as indicated by the mosaic contact with quartz and feldspar (Fig. 3b).

(2) Tourmaline-rich rocks.

The tourmaline-rich rocks include tourmalinites and tourmaline-rich quartz (±amphibole) veins (tourmalite). Tourmalinites occur as stratiform (Fig. 3c), being the direct hanging walls of the borate ore bodies. Tourmalinite contains more than 90 vol.% of the tourmaline and minor quartz, feldspar, diopside, muscovite, magnetite and zircon (Fig. 3d). Tourmaline appears as both euhedral and subhedral crystal, ranging from 0.1 to 3 mm in diameter. Most tourmaline grains show compositional zoning, with either a yellow brown rim on a dark green/yellowish brown core or a greenish blue rim on a yellowish core (Fig. 3d). The boundary between core and rim is sharp. The tourmaline core is characterized by the presence of many tiny detrital phases such as quartz, tourmaline and zircon, which contrasts with the scarcity of such detrital grains in the rim. Tourmaline-rich quartz (±amphibole) veins are generally restricted to the borate bodies or their stratigraphic hanging wall (Fig. 3e), being made up mainly of quartz (40 vol.%), and tourmaline (40 vol.%), amphibole (15 vol.%), and minor feldspar (Fig. 3f).

(3) Magnesium-rich series

The borate ore bodies are exclusively hosted in the magnesium-rich series (Fig. 4a and b) that consist mainly of Mg-silicate (forsterite–diopside–phlogopite–tremolite rocks) and subordinate magnesium-rich carbonate. The peridotite is variedly serpentinized, and comprises more than 90 vol.% forsterite (Fig. 4c and d). Forsterite (olivine) occurs in two forms. The smaller forsterite grains (about 50–500 μm in diameter) suffered no alteration, commonly coexisting with szaibelyite and ludwigite (Fig. 4e and f). The larger forsterite grains (up to >2 mm) show mosaic textures, generally being altered to serpentine and tremolite, and coexist with apatite and magnetite (Fig. 4c and d). Phlogopite is present in carbonates and Mg-silicate rocks.