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Diversity of potassium-bearing tourmalines in diamondiferous Kokchetav UHP metamorphic rocks: A geochemical recorder from peak to retrograde metamorphic stages

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ABSTRACT

Chemical variations and inclusion mineralogy of tourmaline in diamond-bearing ultrahigh-pressure (UHP) gneisses and related siliceous rocks from the Kokchetav Massif, Kazakhstan are extensively investigated, in conjunction with a review of previously discovered K-bearing tourmaline with microdiamond inclusions. Tourmalines in these Kokchetav UHP rocks have a wide compositional range (dravite – "potassium-oxy-dravite" – schorl – uvite – feruvite – foitite, and some of their oxy-variants) with potassium content ranging from 0 to 0.576 atoms per formula unit (apfu, based on Y + Z + T cations = 15) (or 0–2.76 wt.% K_2O) and decreasing from core to rim. The variation in potassium is spatially related to the inclusion mineralogy and is attributed to changes in metamorphic grade. Four stages of tourmaline growth in the Kokchetav UHP rocks are recognized based on the potassium contents and occurrences; in order of decreasing *P* and *T*: (1) K-dominant tourmaline (K > Na, Ca, and X-vacancy) with microdiamond and high-Si—Ti phengite inclusions and without quartz inclusions; (2) K-rich tourmaline (K: 0.2–0.05 apfu) with graphite, phengite, kyanite and quartz inclusions; (3) K-poor tourmaline (K: 0.05–0.01 apfu) with matrix quartz and biotite; and (4) K-free anhedral or overgrown tourmaline associated with low-*P*–*T* minerals such as amphibole or chlorite. Several lines of evidence also suggest that K-dominant tourmaline crystallized in the diamond stability field. Tourmalines in the Kokchetav UHP rocks recorded multi-stage growth history from peak UHP conditions through a granulite facies overprint event including partial melting and ultimately to the latest retrograde metamorphism during exhumation.

1. Introduction

Tourmaline is a common accessory mineral in various rock types and is the most important boron-carrying mineral in high grade metamorphic rocks (e.g., Henry and Dutrow, 1996). Tourmaline-supergroup minerals are complex solid solutions with the general formula of $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, where X = Na, Ca, K, □ (vacancy); Y = Li, Fe^{2+}, Mn^{2+}, Al, Cr^{3+}, V^{3+}, Fe^{3+}, Ti^{4+}; Z = Mg, Al, Fe^{3+}, V^{3+}, Cr^{3+}; T = Si, Al, (B); B = B, (□), V = OH, O; W = OH, F, O (Hawthorne and Henry, 1999; Henry et al., 2011). Because of its chemical diversity and refractory nature, metamorphic tourmaline is expected to retain information from multiple metamorphic events in compositionally zoned domains (e.g., Dutrow and Henry, 2011; van Hinsberg et al., 2011b). Thus tourmaline has been used as an excellent geochemical recorder of metamorphic conditions. Moreover, since tourmaline contains boron and other volatile elements as essential components, it can also serve as a powerful tracer for the chemical environment in deeper parts of the earth.

Dravitic tourmalines coexisting with the ultrahigh-pressure (UHP) index mineral coesite were first found from the Western Alps (Reinecke, 1991; Schertl et al., 1991). Later on, several studies have reported occurrences of tourmaline in diamond-bearing rocks from the Kokchetav Massif, Kazakhstan (Shatsky et al., 1995; Zhang et al., 1997; Massonne, 2003). In the latter cases, tourmalines have all been regarded as retrograde minerals, which probably crystallized after deformation at the exhumation stage based on textures and the absence of UHP indicator minerals. However, Shimizu and Ogasawara (2005) discovered extraordinarily potassium-rich dravitic tourmaline ("potassium-dravite") with microdiamond inclusions in a quartzofeldspathic rock. Ota et al. (2008b) obtained unusually heavy isotopic ratios of boron ($\delta^{11}B$) from the "potassium-dravite" and concluded that this rock may have been formed by the partial melting of pelitic rocks due to the infiltration of boron-bearing fluid from the underlying mantle in the diamond stability field.

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After the discovery of microdiamond in "potassium-dravite" in the Kokchetav tourmaline-bearing UHP rock, occurrences and compositions (both chemical and isotopic) of tourmalines from various UHP and HP terranes were studied and reviewed (Marschall et al., 2009; Ertl et al., 2010). As a result, coesite-bearing tourmaline was found from the Erzgebirge Massif, Germany. In spite of careful examination, however, neither tourmaline with microdiamond inclusion nor potassium-rich tourmaline has been observed. Marschall et al. (2009) postulated that the scenario of UHP origin for "potassium-dravite" (Shimizu and Ogasawara, 2005; Ota et al., 2008b) is controversial for several reasons; for example, they described diamond-bearing tourmaline coexisting with quartz, but they did not show any photomicrographs of this.

To settle the controversy and to establish the genesis of potassium-rich tourmalines, we present detailed information on the occurrences and chemical compositions of tourmalines in Kokchetav UHP gneisses and associated siliceous rocks. We investigate compositional zoning of various tourmalines as a function of *P–T* conditions and in particular, related type of mineral inclusion in tourmalines to their chemical zoning.

2. Geological background and sample description

2.1. The Kumdy-Kol area, Kokchetav Massif

All rock samples investigated in the present study were collected from the Kumdy-Kol area of the Kokchetav Massif, northern Kazakhstan. The area has been mapped in detail by Kaneko et al. (2000) and is characterized by abundant pelitic–psammitic gneisses with small amounts of lenses of eclogite (with a partial overprint at amphibolite-facies), Ti-clinohumite-garnet rock, orthogneiss, and marbles (e.g., Zhang et al., 1997; Ogasawara et al., 2000, 2002; Okamoto et al., 2000). The Kumdy-Kol area is characterized by abundant occurrence of microdiamond and some very high pressure indicator minerals such as coesite, potassium-rich clinopyroxene and supersilicic titanite. Peak metamorphic conditions are estimated at: >6 GPa and >1000 °C (Ogasawara et al., 2000, 2002; Okamoto et al., 2000; Katayama et al., 2001).

2.2. Tourmaline-bearing rocks from the Kumdy-Kol area, Kokchetav Massif

Tourmaline-bearing siliceous metasedimentary rocks in the present study include pelitic gneisses, tourmaline–K-feldspar–quartz rock and tourmaline-phengite gneiss. Sample locality map is given as a Supplementary material (Fig. S-1).

2.2.1. Pelitic gneisses

Pelitic gneisses are the most ubiquitous tourmaline-bearing rock in the Kumdy-Kol area, and have porphyroblastic textures and various mineral assemblages (see Supplementary material, Table S-1). Major constituent minerals are garnet, clinopyroxene, kyanite, biotite, phengite, K-feldspar, plagioclase and quartz. Minor constituent minerals are zircon, tourmaline, rutile, titanite, apatite, zoisite, calcite, amphibole, chlorite, prehnite, and graphite. The diamond-bearing gneisses are classified into the following six types based on mineral assemblages (Table S-1): (1) pyroxene–garnet–biotite gneiss; (2) garnet–biotite gneiss; (3) garnet-two-mica gneiss; (4) garnet–phengite gneiss; (5) kyanite–garnet–phengite schist; and (6) titanite–garnet–biotite gneiss. The peak *P–T* mineral assemblages based on textures and phase-relations are garnet, coesite, clinopyroxene, kyanite, phengite, K-feldspar, zircon, rutile, apatite, and diamond. Phengite, biotite and some secondary minerals often show preferred orientation. Porphyroblastic garnet (usually 1–2 mm in diameter) is common and sometimes is elongated to the direction of the preferred orientation. Some UHP indicator minerals such as diamond, coesite and potassium-bearing clinopyroxene were observed. Diamond occurs as micrometer-scaled inclusion (microdiamond) mainly in garnet, zircon, and kyanite, and sometimes in clinopyroxene. Diamond also occurs in some secondary minerals such as chlorite, biotite, amphibole rimming garnet, muscovite replacing kyanite, and even in quartz. Coesite is extremely rare in the gneisses but one grain of coesite was confirmed in zircon. Clinopyroxene shows exsolution textures (phlogopite and quartz lamellae) implying high-K precursor compositions. Leucocratic veins composed of quartz, K-feldspar, plagioclase, and occasional tourmaline are often observed in the gneisses. These veins are usually centimeter-sized and concordant with the preferred orientation. Anti-perthite is often observed in plagioclase.

2.2.2. Tourmaline–K-feldspar–quartz rock (A6)

The other diamond- and tourmaline-bearing rock is a tourmaline-rich quartzofeldspathic rock (sample A6) reported by Shimizu and Ogasawara (2005) and Ota et al. (2008b). The tourmaline–K-feldspar–quartz rock (also could be considered as a tourmalinite) occurs as thin layers in diamond-bearing pelitic gneiss with thicknesses on the order of a few mm to several cm (Ota et al., 2008b).

This rock shows a granoblastic texture with variable grain sizes (Fig. 1A) and consists mainly of quartz (45–55 vol.%), K-feldspar (5–25 vol.%) and tourmaline (20 vol.%). Minor constituents in matrix are goethite, titanite, zircon, phengite, phlogopite, apatite, chlorite, zoisite, pumpellyite and graphite. Diamond occurs only as inclusions in cores of tourmaline and in zircon.

Tourmaline in this rock occurs as euhedral to subhedral large crystal (ca. 1 mm), and shows pleochroism and color zoning from very light to dark brown. Quartz and K-feldspar occur as anhedral coarse grain (ca. 1 mm). K-feldspar has almost pure orthoclase composition. Titanite does not contain coesite or excess silica (cf. Ogasawara et al., 2002). Graphite occurs as both matrix mineral and inclusions. In the matrix, graphite displays a platy shape and is about 0.5 mm in long dimension, and accompanies pumpellyite or chlorite. Such graphite also occurs in the mantles and the rims of diamondiferous tourmaline and in fractures in tourmaline. In the cores of tourmaline and in zircon, graphite occurs as fine-grained aggregates (<20 μm), and is associated with microdiamond.

2.2.3. Tourmaline-phengite gneiss (ZG10)

This rock is fine-grained with gneissose texture (Fig. 1B) and consists mainly of quartz, tourmaline, phengite, and chlorite, with minor amounts of zircon, pumpellyite, and graphite. The modal fraction of tourmaline is more than 10%. Tourmaline occurs as relatively fine-grained euhedral crystals (<0.2 mm). Inclusion minerals in tourmaline are quartz, kyanite, phengite, K-feldspar, zircon, rutile, and fine-grained massive graphite. A CO_2-rich fluid inclusion in tourmaline was confirmed by laser Raman spectroscopy. UHP indicator minerals such as microdiamond have not been identified in tourmaline.

Coarse-grained leucocratic veins composed of quartz, K-feldspar, and tourmaline similar to those in the diamond-bearing gneisses also occur in the tourmaline-phengite gneiss. Tourmaline crystals in the veins are coarse-grained euhedral prisms (up to 2 mm) and contain quartz inclusions.

2.3. Occurrences of tourmalines

Tourmalines in the Kokchetav UHP rocks show several occurrences: (1) euhedral to subhedral crystal in the tourmaline-rich rocks (tourmaline–K-feldspar–quartz rock and tourmaline-phengite gneiss) as described above; (2) subhedral to euhedral porphyroblast in gneisses; (3) well-developed prismatic crystals