



## Tetrahedral substitutions in tourmaline: a review

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**Abstract:** The Si<sup>4+</sup> cation, typically the overwhelming occupant of the tetrahedral site of the tourmaline structure, can be partially replaced by Al<sup>3+</sup>, B<sup>3+</sup>, and Be<sup>2+</sup>. Tetrahedrally coordinated Al (up to ~0.9 <sup>[4]</sup>Al atom per formula unit, apfu) has been found in different Mg- and/or Fe<sup>2+</sup>-rich tourmalines from high-temperature aluminous lithologies as well as in Li-rich pegmatites. It is relatively common for Li- and <sup>[4]</sup>Al-bearing tourmalines to also contain some <sup>[4]</sup>B. While the highest boron content (~0.8 <sup>[4]</sup>B apfu) in a natural tourmaline was found in an Al-rich tourmaline (olenite) from the Eastern Alps, Austria, much higher contents of up to ~2.8 apfu have been reported for synthetic Al-rich tourmalines. Natural tourmalines with a higher total Al content (> 7.2 Al apfu) can also contain significant <sup>[4]</sup>B. The highest verified beryllium content in a tourmaline is still below 100 ppm, but current data show that in pegmatitic tourmaline crystals the Be content is positively correlated with the overall Al content. Therefore Li-rich tourmalines can contain higher Be contents in pegmatites that originated from differentiated granitic magma, than in pegmatites that have evolved as granitic pegmatitic melts from the surrounding country-rocks during decompression.

**Key-words:** tourmaline; tetrahedral site; substitutions; boron; aluminium; beryllium; petrology.

### 1. Introduction

Tourmaline is an extremely important mineral because of its relevance in the geosciences and also for its technical applications (piezo- and pyroelectric material) and its use as gemstone. The tourmaline composition gives information on the thermal and fluid history of rocks in which it develops, is intimately associated with some of the world's premier metallic ore deposits and yields isotopic evidence for the environmental sources of the boron that is an essential constituent of all tourmalines. Thus tourmaline is an extremely critical link in the boron cycle on the Earth and has many other useful petrogenetic features (e.g., Dutrow & Henry, 2000). Varying chemical compositions of tourmaline reflect the chemical conditions of rocks where tourmaline forms and have been used as an important petrologic indicator of different geologic environments in previous investigations (e.g., Henry & Guidotti, 1985). Tourmaline can be stable in a wide range of pressure-temperature conditions (e.g., Ertl *et al.*, 2010).

The tourmaline group consists of more than 30 species, which occur in many different geological environments (Henry & Dutrow, 1996; Henry *et al.*, 2011). Tourmalines are complex aluminium-borosilicate minerals with strongly varying compositions related to isomorphous substitutions. The tourmaline mineral group is chemically one

of the most complicated groups of silicate minerals, with the general formula  $XY_3Z_6[T_6O_{18}](BO_3)_3V_3W$  (Henry *et al.*, 2011), with the most common site occupants:

$X = Ca^{2+}, Na^+, K^+, \square$  (vacancy)  
 $Y = Li^+, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, V^{3+}, Fe^{3+}, Ti^{4+}$   
 $Z = Al^{3+}, Mg^{2+}, Fe^{3+}, Mn^{3+}, V^{3+}, Cr^{3+}, Ti^{4+}, (Fe^{2+})$   
 $T = Si^{4+}, Al^{3+}, B^{3+}, Be^{2+}$   
 $V = OH^-, O^{2-}$   
 $W = OH^-, F^-, O^{2-}, (Cl^-)$ .

The structure is characterized by six-membered tetrahedral rings (*T* sites), whose apical oxygens point toward the (–) c-pole, producing the acentric nature of the structure. These planar rings of tetrahedra are linked by two types of octahedra, *Z* and *Y*, which share edges to form brucite-like fragments. Triangular BO<sub>3</sub> groups lie parallel to the (0001) plane. The *Z* octahedra are relatively small, somewhat distorted, and are usually occupied predominantly by trivalent Al.

### 2. Tetrahedral site occupants

The six *T* sites in tourmaline are typically occupied by Si. In tourmalines where the average *T* site is fully occupied by Si the  $\langle T-O \rangle$  bond-length is usually in the range 1.619–1.621 Å (e.g., MacDonald & Hawthorne 1995; Bloodaxe *et al.*, 1999; Bosi & Lucchesi, 2004). Because the effective ionic radius of Al is larger than the radius of Si, substitution

of Si by Al increases the  $\langle T-O \rangle$  bond-length. Substitution of Si by the smaller B would have the opposite effect and decrease the  $\langle T-O \rangle$  bond-length. The following updated formula to calculate the  $\langle T-O \rangle$  distance by using the different  $T$ -site occupants was given by Ertl *et al.* (2012a):

$$\langle T-O \rangle = \left( \frac{x_A * r_A + x_B * r_B + x_C * r_C + \dots}{6} - 0.26 \text{ \AA} \right) * 0.79 + 1.620 \text{ \AA}$$

where:

$r_A, \dots$  = effective ionic radius of atom  $^{[4]}A, \dots$ , in (Å) (Si, 0.26; Al, 0.39; B, 0.11; Shannon, 1976);

$x_A, \dots$  = concentration (apfu) of elements A, ... which occupy the  $T$  site of tourmaline (note that the sum of all element concentrations at the  $T$  site is 6.00 apfu);

$\langle T-O \rangle$  = average  $T-O$  bond length (Å) of tourmaline.

In most tourmalines, especially in Mg-bearing samples from non-pegmatitic environments, the substitution of Si at the  $T$  site is limited. In the following sections we discuss documented  $T$ -site cation occupants in addition to Si and consider the implications. To date, there is no conclusive evidence for the presence of either  $Ti^{4+}$  (Grice & Ercit, 1993) or  $Fe^{3+}$  (Dyar *et al.*, 1998) at the  $T$  site in significant amounts (Hawthorne, 1996; Andreozzi *et al.*, 2008; George Rossman, pers. comm., 2016).

## 2.1. Aluminium at the $T$ site

An effective way to incorporate Al in the tetrahedral sites of minerals is through a Tschermak-type substitution, *i.e.*  $[6]R^{2+} + [4]Si = [6]Al + [4]Al$ , where  $R^{2+}$  represents divalent cations. In general, operation of this type of substitution to enhance  $^{[4]}Al$  will be favoured by increasing temperature and by bulk compositions that are aluminous and, to a lesser extent, silica poor (*e.g.* Pattison, 1987; Padrón-Navarta *et al.*, 2013). Using a limited set of data, Henry & Dutrow (1996) described 0.25 apfu  $^{[4]}Al$  from tourmalines which have been crystallized above 750 °C. Such tourmalines from high-grade aluminous metapelites have relatively low vacancies ( $0.05 \pm 0.05$ ) at the  $X$  site when they crystallized above 750 °C (Henry & Dutrow, 1996). However, it is not uncommon for silica-undersaturated upper-amphibolite to granulite-facies rocks with corundum, kornepupine and/or grandierite to contain tourmaline with 0.3–0.4 apfu  $^{[4]}Al$  (*e.g.* Grew *et al.*, 1990, 1997).

The  $T$  sites can be occupied by significant amounts of Al (Povondra, 1981), especially in aluminous, high-grade metamorphic rocks (*e.g.* Cempírek *et al.*, 2006). The relationship between  $\langle T-O \rangle$  distances and Al occupancy in the ring was first defined by Foit & Rosenberg (1979) and Foit (1989). Subsequently, MacDonald & Hawthorne (1995) re-examined this relationship and found a linear relation between  $\langle T-O \rangle$  and the aggregate cation radius approximating hard-sphere behaviour.

Small, but significant amounts of tetrahedrally coordinated Al (0.15 apfu  $^{[4]}Al$ ,  $\langle T-O \rangle = 1.624(1) \text{ \AA}$ ) were described from a V-, Cr-, and Mg-bearing oxy-tourmaline from the Sludyanka crystalline complex, Lake Baikal, Russia, by Bosi *et al.* (2017). Even higher amounts of  $^{[4]}Al$  were found in Li-bearing schorl (0.17 apfu  $^{[4]}Al$ ,  $\langle T-O \rangle = 1.623(1) \text{ \AA}$ ) from the border zone of the Cruzeiro pegmatite, Minas Gerais, Brazil (Bosi *et al.*, 2005) and from a Mn- and Li-bearing schorl (0.24 apfu  $^{[4]}Al$ ,  $\langle T-O \rangle = 1.624(1) \text{ \AA}$ ) from a black nodule from the Alto Lighona pegmatite field, Zambezia, Mozambique (Cámara *et al.*, 2002). Similar amounts of  $^{[4]}Al$  are found in an Mg-rich tourmaline (0.19 apfu  $^{[4]}Al$ ,  $\langle T-O \rangle = 1.624(1) \text{ \AA}$ ; oxydravite) from a metapyroxenite from Jabal Zalm, Saudi Arabia, embedded in serpentinite, which derived from a dunite-peridotite protolith (Bosi *et al.*, 2010). Another tourmaline sample, a Mg-rich schorl (#108749) from a syenite pegmatite from the Raglan Township, Renfrew Co., Ontario, Canada, exhibits even higher amounts of  $^{[4]}Al$  (0.34 apfu  $^{[4]}Al$ ,  $\langle T-O \rangle = 1.625(1) \text{ \AA}$ ; Bloodaxe *et al.*, 1999). Manganese- and Al-rich, Li-bearing tourmaline (fluor-elbaite) from a pegmatite near village Eibenstein, Austria, can also contain significant amounts of  $^{[4]}Al$  (0.33 apfu  $^{[4]}Al$ ,  $\langle T-O \rangle = 1.626(1) \text{ \AA}$ ) as was shown by chemical analyses (including light elements) in combination with crystal-structure determination (Prowatke *et al.*, 2003). Similar amounts of  $^{[4]}Al$  were found in an Mn-bearing elbaite from Mogok, Myanmar (0.34 apfu  $^{[4]}Al$ ; Lussier *et al.*, 2008) and in  $Fe^{2+}$ -bearing olenite from an abyssal pegmatite at the locality Kuklík, near Kutná Hora, Czech Republic (0.40 apfu  $^{[4]}Al$ ,  $\langle T-O \rangle = 1.626(1) \text{ \AA}$ ; Cempírek *et al.*, 2006). Foit & Rosenberg (1979) and MacDonald & Hawthorne (1995) showed using crystal-structure analyses in combination with chemical analyses that Mg-rich and V-bearing tourmaline samples can also contain relatively high amounts of  $^{[4]}Al$  ( $\langle T-O \rangle = 1.625(1) \text{ \AA}$  for a tourmaline from a quartz-graphite schist from Silverknob, Mariposa County, California, USA, with  $\sim 0.37$  apfu  $^{[4]}Al$ ;  $\langle T-O \rangle = 1.627(2) \text{ \AA}$  for green fluor-uvite samples from East Africa (Landanai, Arusha Region, Tanzania) with  $0.45 \pm 0.04$  apfu  $^{[4]}Al$ ; MacDonald & Hawthorne, 1995; see also Lussier *et al.*, 2009). An Mg-bearing oxy-schorl from fracture fillings cutting altered metarhyolite pyroclasts near Zlatá Idka village, Slovak Ore Mountains, Slovak Republic, was described with a relatively high amount of  $^{[4]}Al$  ( $\sim 0.50$  apfu  $^{[4]}Al$ ;  $\langle T-O \rangle = 1.632(2) \text{ \AA}$ ) by Bačík *et al.* (2013). In the new Ca- and  $Fe^{2+}$ -rich tourmaline adachiite, which was found in a hydrothermal vein (with margarite and diaspore), crosscutting a lateritic metamorphic rock (mainly consisting of corundum and hercynite) near Saiki City, Oita Prefecture, Japan, Nishio-Hamane *et al.* (2014) described the highest amount of  $^{[4]}Al$  (0.85 apfu  $^{[4]}Al$ ;  $\langle T-O \rangle = 1.634(2) \text{ \AA}$ ). Adachiite is the first end-member of the tourmaline group formed via Tschermak-like substitution. The measured  $\langle T-O \rangle$  distance of this tourmaline is consistent with the calculated  $\langle T-O \rangle$  distance for such a high amount of  $^{[4]}Al$  (Ertl *et al.*, 2012a). Hence, a maximum amount of  $\sim 0.9$  apfu  $^{[4]}Al$ , which seems to be verified by single-crystal structure data, might be near the upper limit.

In sum, relatively high amounts of  $^{[4]}\text{Al}$  may be expected in Mg- and/or  $\text{Fe}^{2+}$ -rich tourmalines, especially when they are in aluminous bulk compositions and experienced high-temperature metamorphic conditions. Significant amounts of  $^{[4]}\text{Al}$  are also found in pegmatitic Al-rich and Li-bearing tourmaline species (elbaite, liddicoatite, olenite, “oxyrossmanite”). Quite commonly these  $^{[4]}\text{Al}$ - and Li-bearing tourmalines also contain significant amounts of  $^{[4]}\text{B}$  (Ertl *et al.*, 2005, 2009, 2010, 2012a, 2012b; Hughes *et al.*, 2000; Lussier *et al.*, 2009; Schreyer *et al.*, 2002).

## 2.2. Boron at the *T* site

Over the last 20 years many examples of substitution of Si by B have been found in natural and synthetic tourmalines (Ertl *et al.*, 1997, 2005, 2006, 2007, 2008, 2012a, 2012b, 2015; Hughes *et al.*, 2004; Kutzschbach *et al.*, 2016, 2017; Lussier *et al.*, 2008, 2009; Schreyer *et al.*, 2000, 2002). Using the crystallographic and analytical techniques that are most commonly employed today it is difficult to verify the presence of B at the *T* site. If analyses are done only with the electron microprobe, as is typical, tetrahedrally coordinated B goes unnoticed due to uncertainty of analyses and common site-assignment assumptions. However, it is important to determine the amount of B incorporation at the *T* site in tourmaline because it appears to be best expressed at lower temperatures of crystallization and likely reflects local petrologic environmental conditions (Schreyer *et al.*, 2000; Ertl *et al.*, 2008).

The initial report of natural Al-rich tourmaline with  $^{[4]}\text{B}$  was substantiated by Ertl *et al.* (1997) using single-crystal structure refinement and independently by chemical analysis (including the light elements B, Li, H). These authors reported the unit-cell parameters as  $a = 15.7395(2)$ ,  $c = 7.0656(2)$  Å (cell volume:  $1515.86(5)$  Å<sup>3</sup>) and a  $\langle T\text{--}O \rangle$  bond length of  $1.610(1)$  Å. This colourless tourmaline, identified as olenite, from the Koralpe, Eastern Alps, Styria, Austria, exhibits relatively high amounts of  $^{[4]}\text{B}$ . An updated formula of  $\text{X}(\text{Na}_{0.40}\text{Ca}_{0.29}\square_{0.31})\text{Y}(\text{Al}_{2.40}\text{Li}_{0.35}\square_{0.25})\text{ZAl}_6(\text{BO}_3)_3\text{T}[\text{Si}_{4.89}\text{B}_{0.83}\text{Al}_{0.27}\text{Be}_{0.01}]\text{O}_{18}\text{V}(\text{OH})_3\text{W}[\text{O}_{0.58}(\text{OH})_{0.36}\text{F}_{0.06}]$  was given by Ertl *et al.* (2007). This tourmaline was found in a pegmatite that intruded discordantly into mylonitic garnet–biotite schists (Hughes *et al.*, 2000; Kalt *et al.*, 2001). The mylonitization of the gneisses in the shear zone of the Koralpe Complex occurred during the eo-Alpine metamorphism. The peak conditions of the pressure–temperature (*PT*) path of the shear zone as reported by Stüwe & Powell (1995) involved decompression from  $>1800$  MPa to  $1400\text{--}1600$  MPa at temperatures above  $620^\circ\text{C}$  and reaching the peak conditions of  $1400\text{--}1600$  MPa and  $700^\circ\text{C}$ . The *PT* conditions of the tourmaline-bearing pegmatite were described with  $500\text{--}700$  MPa/ $\sim 630^\circ\text{C}$  (Ertl *et al.*, 2008). Even 20 years after the first publication, the  $^{[4]}\text{B}$  content in this olenite is still the highest known in natural tourmalines.

Another tourmaline with a relatively high amount of  $^{[4]}\text{B}$  was described by Ertl *et al.* (2007). This sample is an almost colourless olenite ( $a = 15.7561(6)$ ,  $c = 7.0703(5)$  Å) from a

“mushroom” tourmaline from Momeik Township, northeast of Mogok, Mandalay Division, Shan State, Myanmar. This tourmaline has the second highest amount of  $^{[4]}\text{B}$  ( $\sim 0.7$  apfu  $^{[4]}\text{B}$ ) with a  $\langle T\text{--}O \rangle$  distance of  $1.604$  Å, the shortest observed in natural tourmaline to date. This tourmaline was found in a pegmatitic pocket emplaced in a peridotite body. The olenite from Koralpe contains a greater amount of  $^{[4]}\text{B}$  than the olenite from Mogok, but the Koralpe olenite also contains a significant amount of  $^{[4]}\text{Al}$ , which enlarges the  $\langle T\text{--}O \rangle$  distance. “Mushroom” tourmalines from Mogok with larger unit-cell parameters ( $\langle T\text{--}O \rangle$  distances:  $1.609\text{--}1.614$  Å) and lower amounts of  $^{[4]}\text{B}$  were described by Lussier *et al.* (2008, 2009).

An Al-rich tourmaline with unit-cell parameters  $a = 15.777(1)$ ,  $c = 7.086(1)$  Å from the Sahatany Pegmatite Field at Manjaka, Sahatany Valley, Madagascar, contains also a significant amount of  $^{[4]}\text{B}$  ( $\sim 0.4$  apfu, no  $^{[4]}\text{Al}$ ;  $\langle T\text{--}O \rangle = 1.611(1)$  Å; Ertl *et al.*, 2008). A microthermometric study of fluid inclusions indicate *PT* conditions of  $200\text{--}300$  MPa/ $350\text{--}500^\circ\text{C}$  (Ranorosoa, 1986).

Elbaite samples from Li-pegmatites with small amounts of  $^{[4]}\text{B}$  were also described ( $\sim 0.1\text{--}0.2$  apfu  $^{[4]}\text{B}$ ; e.g., Ertl *et al.*, 2009, 2010; Lussier *et al.*, 2009). Most of these samples also contain small amounts of  $^{[4]}\text{Al}$ . Therefore, it is not very easy to prove the presence of  $^{[4]}\text{B}$  by crystal-structure refinements alone, but it requires allied evidence.

The first description of synthetic Al-rich tourmaline with verified  $^{[4]}\text{B}$  was by Schreyer *et al.* (2000). They successfully synthesized tourmaline in the range  $550\text{--}900^\circ\text{C}/1\text{--}5$  GPa. Similar tourmalines were synthesized later by different groups (e.g. Wodara & Schreyer, 2001; Schlager, 2003; Kempl, 2008; London, 2011; Berryman *et al.*, 2016; Kutzschbach *et al.*, 2016, 2017). A pronounced negative correlation ( $r^2 = 1.0$ ) between crystallization temperature (at constant pressure) and  $^{[4]}\text{B}$  (from refinement) in synthetic Al-rich tourmalines (synthesis by London, 2011) was found by Ertl *et al.* (2012a). Wodara & Schreyer (2001) and Marler *et al.* (2002) found an inverse correlation between the  $^{[4]}\text{B}$  content and the unit-cell volume. When plotting this relationship including recent data from structure refinements from Al- and  $^{[4]}\text{B}$ -rich tourmaline, a pronounced negative correlation ( $r^2 = 0.95$ ) is observed (Fig. 1). An extrapolation to an Al-rich tourmaline with 3 apfu  $^{[4]}\text{B}$  implies a hypothetical cell volume of  $\sim 1454$  Å<sup>3</sup> (corresponding to  $a = 15.48$ ,  $c = 7.00$  Å). A theoretical end-member with the highest possible amount of  $^{[4]}\text{B}$  and having the formula  $\text{CaAl}_3\text{Al}_6(\text{BO}_3)_3[\text{B}_4\text{Si}_2\text{O}_{18}](\text{OH})_4$  has a calculated cell volume of  $\sim 1425$  Å<sup>3</sup> and would have cell parameters of  $a = 15.36$ ,  $c = 6.97$  Å, *i.e.* smaller than observed in any tourmaline characterised to date. The relationship between temperature during crystal growth and the maximal possible amount of  $^{[4]}\text{B}$  in Al-rich tourmaline is plotted in Fig. 2. The amount of  $^{[4]}\text{B}$  was calculated (by using the correlation of Fig. 1) from synthetic tourmalines with the lowest cell volumes. Above a pressure of  $\sim 1000\text{--}1500$  MPa (depending on the temperature) the highest observed  $^{[4]}\text{B}$  content does not change significantly at a given temperature (Ertl *et al.*, 2008).

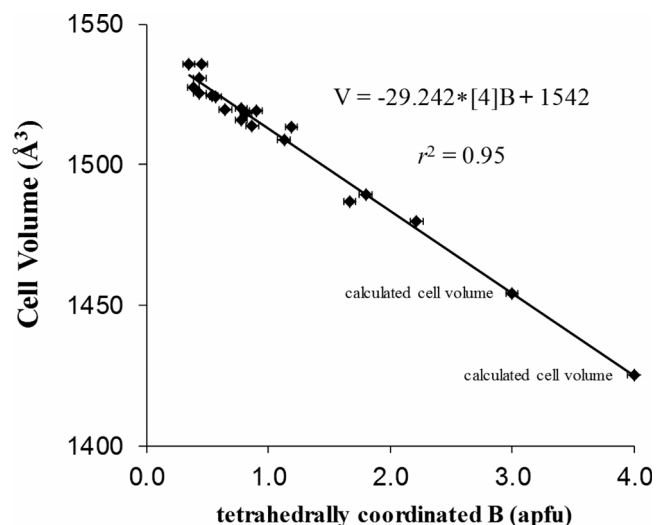


Fig. 1. Relationship between tetrahedrally coordinated boron (from structure refinements) in Al- and  $^{[4]}B$ -rich tourmaline and the unit-cell volume. *Note:* Natural and synthetic Al- and  $^{[4]}B$ -rich tourmaline samples (refined  $^{[4]}B \geq 0.4$  apfu; FeO + MnO < 2.0 wt %; cell volumes < 1536 Å<sup>3</sup>) are plotted (16 samples: Ertl *et al.*, 2006, 2007, 2008, 2012; Hughes *et al.*, 2004; Kutzschbach *et al.*, 2016, 2017; Lussier *et al.*, 2008; Marler *et al.*, 2002; Schreyer *et al.*, 2002; unpublished data)

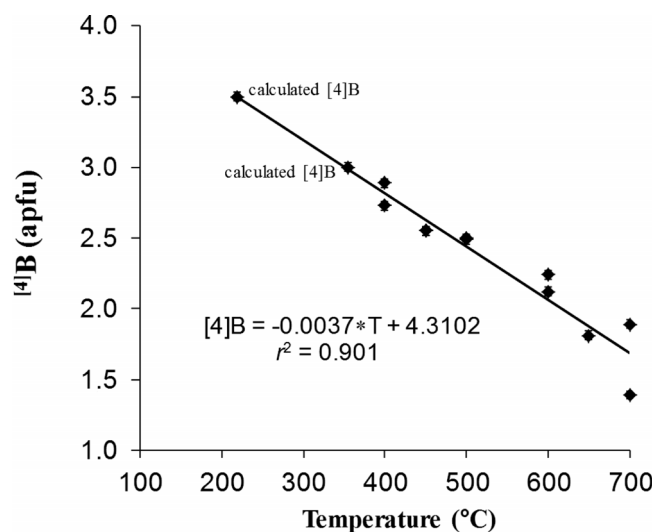


Fig. 2. Relationship between temperature during crystal growth and tetrahedrally coordinated boron (calculated by using the cell volume) in Al- and  $^{[4]}B$ -rich tourmaline. *Note:* Synthetic Al- and  $^{[4]}B$ -rich Li-bearing tourmaline samples are plotted (9 samples: Marler *et al.*, 2002; Schlager, 2003; Kutzschbach *et al.*, 2016)

Hence, the pressure conditions during the syntheses have only a minor influence on the amount of  $^{[4]}B$ , but at higher pressures larger crystals can be grown. The temperature (over a range of ~400–700 °C; see Fig. 3 in Ertl *et al.*, 2008) is the most important factor.

Very high  $^{[4]}B$  tourmalines appear to be most likely to occur in low-temperature environments. To generate tourmalines with a maximum content of 3 apfu  $^{[4]}B$  a

temperature of ~350 °C was extrapolated (Fig. 2). Such tourmalines could theoretically occur in distal contact metamorphic, hydrothermal and greenschist-facies rocks, and possibly in high-pressure metamorphic rocks associated with subduction zones (blueschist and eclogite facies). It only can be speculated that tourmalines with more than 50% B at the tetrahedral site occur. For a maximum content of 3.5 apfu  $^{[4]}B$  a temperature of ~220 °C was calculated. Tourmalines with even higher amounts of  $^{[4]}B$  might hypothetically occur as tiny crystals in diagenetic sediments.

### 2.3. Beryllium at the T site

Beryllium, which also occupies the T site, was found in a strongly zoned tourmaline from a Li-pegmatite from the Himalaya Mine, Mesa Grande, California. Beryllium is very low in the Fe<sup>2+</sup>-rich core (oxy-schorl; 7 ppm Be), but increases concomitantly with the Al content towards the fluor-elbaite rim zone (Ertl *et al.*, 2010). The zone with highest Al content also has the highest Be content (76 ppm Be). Liddicoatite samples from Li-pegmatites from Anjanabonoina, Madagascar, exhibit Be contents of 26–28 ppm (Ertl *et al.*, 2006). A  $^{[4]}B$ -bearing elbaite from the same locality has 19 ppm Be. An elbaite from Nuristan, Afghanistan, contains 20 ppm Be (Ertl *et al.*, 2006). Fluor-elbaites from pegmatites, which may have evolved from granitic pegmatitic melts during decompression from the surrounding country rocks during exhumation of the Moldanubian nappes (Lower Austria) after the peak of the Variscan metamorphism, exhibit lower Be contents of 5–13 ppm (Ertl *et al.*, 2012b). The  $^{[4]}B$ -rich olenite samples (with varying Fe<sup>2+</sup>-contents) from Koralpe contain up to 37 ppm Be and, similar to the zoned tourmaline from the Himalaya Mine, California, the Be content increases simultaneously with the Al content (Ertl *et al.*, 2006; Hughes *et al.*, 2004).

## 3. Summary and conclusions

In sum,  $^{[4]}B$  may be expected in Al-rich tourmalines with >7.2 apfu Al (>1.2 apfu Al the Y site and 6 apfu at the Z site), because short-range order configurations with  $^{[4]}B$  always include Al at the sixfold coordinated positions (Ertl *et al.*, 2007, 2010). Based on the correlation in Fig. 1 the unit-cell volume of  $^{[4]}B$ -bearing tourmalines should be smaller than ~1540 Å<sup>3</sup>. Especially colourless or pale coloured samples are candidates for such tourmalines. Petrologic environments with four-coordinated B in associated minerals, such as some of the borates in evaporites, may also be potential carriers of  $^{[4]}B$ -bearing tourmalines.

To date, the highest verified Be contents of tourmaline are still below 100 ppm. It might be possible to synthesize Al-rich tourmalines with higher Be contents. It can be concluded that in pegmatites that originated from differentiated granitic magma, Li-rich tourmalines can contain higher Be contents (~19–76 ppm) than in

pegmatites that have evolved as granitic pegmatitic melts from surrounding country-rocks during decompression (~5–13 ppm Be). In all investigated zoned tourmaline crystals, the Be content is positively correlated with the Al content.

Based on this review, future research might include (1) search for and evaluation of tourmalines that develop in low-temperature Ca-Al-rich environments and may have maximal levels of  $^{14}\text{B}$  and  $^{27}\text{Al}$ , (2) determination of the influence of temperature and pressure on  $^{14}\text{B}$  and  $^{27}\text{Al}$  in natural settings and (3) continued chemical investigation of Be-enriched tourmaline found in Be-rich environments such as beryl-bearing lithologies. Because of the difficulties in analyzing B and Be and in determining their crystallographic locations in tourmaline, improved determination techniques such as SIMS and NMR Magic Angle Spinning will be critical for proper characterization of these cations on tourmaline (e.g. Lussier *et al.*, 2008).

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## References

- Andreozzi, G.B., Bosi, F., Longo, M. (2008): Linking Mössbauer and structural parameters in elbaite-schorl-dravite tourmalines. *Am. Mineral.*, **93**, 658–666.
- Berryman, E.J., Wunder, B., Ertl, A., Koch-Müller, M., Rhede, D., Scheidl, K., Giester, G., Heinrich, W. (2016): Influence of the X-site composition on tourmaline's crystal structure: Investigation of synthetic K-dravite, dravite, oxy-uvite, and magnesio-foitite using SREF and Raman spectroscopy. *Phys. Chem. Minerals*, **43**, 83–102.
- Bačík, P., Cempírek, J., Uher, P., Novák, M., Ozdín D., Filip, J., Škoda, R., Breiter, K., Klementová, M., Duřa, R., Groat, L.A. (2013): Oxy-schorl,  $\text{Na}(\text{Fe}^{2+}_2\text{Al})\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$ , a new mineral from Zlatá Idka, Slovak Republic and Příbyslavice, Czech Republic. *Am. Mineral.*, **98**, 485–492.
- Bloodaxe, E.S., Hughes, J.M., Dyar, M.D., Grew, E.S., Guidotti, C. V. (1999): Linking structure and chemistry in the schorl-dravite series. *Am. Mineral.*, **84**, 922–928.
- Bosi, F. & Lucchesi, S. (2004): Crystal chemistry of the schorl-dravite series. *Eur. J. Mineral.*, **16**, 335–344.
- Bosi, F., Andreozzi, G.B., Federico, M., Graziani, G., Lucchesi, S. (2005): Crystal chemistry of the elbaite-schorl series. *Am. Mineral.*, **90**, 1784–1792.
- Bosi, F., Balić-Zunić, T., Surour, A.A. (2010): Crystal structure analysis of four tourmalines from the Cleopatra's Mines (Egypt) and Jabal Zalm (Saudi Arabia), and the role of Al in the tourmaline group. *Am. Mineral.*, **95**, 510–518.
- Bosi, F., Reznitskii, L., Hälenius, U., Skogby, H. (2017): Crystal chemistry of Al-V-Cr oxy-tourmalines from Sludyanka complex, Lake Baikal, Russia. *Eur. J. Mineral.*, **29**, 457–472.
- Cámara, F., Ottolini, L., Hawthorne, F.C. (2002): Chemistry of three tourmalines by SREF, EMPA, and SIMS. *Am. Mineral.*, **87**, 1437–1442.
- Cempírek, J., Novák, M., Ertl, A., Hughes, J.M., Rossman, G.R., Dyar, M.D. (2006): Fe-bearing olenite with tetrahedrally coordinated Al from an abyssal pegmatite of the Bohemian massif at Kutná Hora: Structure, crystal chemistry, and optical spectra. *Can. Mineral.*, **44**, 23–30.
- Dutrow, B. & Henry, D.J. (2000): Complexly zoned fibrous tourmaline: A record of evolving magmatic and hydrothermal fluids. *Can. Mineral.*, **38**, 131–143.
- Dyar, M.D., Taylor, M.E., Lutz, T.M., Francis, C.A., Robertson, J. D., Cross, L.M., Guidotti, C.V., Wise, M. (1998): Inclusive chemical characterization of tourmaline: Mössbauer study of Fe valence and site occupancy. *Am. Mineral.*, **83**, 848–864.
- Ertl, A., Pertlik, F., Bernhardt, H.-J. (1997): Investigations on olenite with excess boron from the Korpalpe, Styria, Austria. *Österr. Akad. Wiss., Math.-naturwiss. Kl., Abt. I, Anz.*, **134**, 3–10.
- Ertl, A., Rossman, G.R., Hughes, J.M., Prowatke, S., Ludwig, T. (2005): Mn-bearing “oxy-rossmanite” with tetrahedrally coordinated Al and B from Austria: structure, chemistry, and infrared and optical spectroscopy study. *Am. Mineral.*, **90**, 481–487.
- Ertl, A., Hughes, J.M., Prowatke, S., Ludwig, T., Prasad, P.S.R., Brandstätter, F., Körner, W., Schuster, R., Pertlik, F., Marschall, H. (2006): Tetrahedrally coordinated boron in tourmaline from the liddicoatite-elbaite series from Madagascar: structure, chemistry, and infrared spectroscopic studies. *Am. Mineral.*, **91**, 1847–1856.
- Ertl, A., Hughes, J.M., Prowatke, S., Ludwig, T., Brandstätter, F., Körner, W., Dyar, M.D. (2007): Tetrahedrally-coordinated boron in Li-bearing olenite from “mushroom” tourmaline from Momeik, Myanmar. *Can. Mineral.*, **45**, 891–899.
- Ertl, A., Tillmanns, E., Ntaflos, T., Francis, C., Giester, G., Körner, W., Hughes, J.M., Lengauer, C., Prem, M. (2008): Tetrahedrally coordinated boron in Al-rich tourmaline and its relationship to the pressure-temperature conditions of formation. *Eur. J. Mineral.*, **20**, 881–888.
- Ertl, A., Kolitsch, U., Meyer, H.-P., Ludwig, T., Lengauer, C.L., Nasdala, L., Tillmanns, E. (2009): Substitution mechanism in tourmalines of the “fluor-elbaite”-rossmanite series from Wolkenburg, Saxony, Germany. *N. Jb. Miner. Abh.*, **186**, 51–61.
- Ertl, A., Rossman, G.R., Hughes, J.M., London, D., Wang, Y., O'Leary, J.A., Dyar, M.D., Prowatke, S., Ludwig, T., Tillmanns, E. (2010): Tourmaline of the elbaite-schorl series from the Himalaya Mine, Mesa Grande, California, USA: A detailed investigation. *Am. Mineral.*, **95**, 24–40.
- Ertl, A., Giester, G., Ludwig, T., Meyer, H.-P., Rossman, G.R. (2012a): Synthetic B-rich olenite: Correlations of single-crystal structural data. *Am. Mineral.*, **97**, 1591–1597.
- Ertl, A., Schuster, R., Hughes, J.M., Ludwig, T., Meyer, H.-P., Finger, F., Dyar, M.D., Ruschel, K., Rossman, G.R., Klötzli, U., Brandstätter, F., Lengauer, C.L., Tillmanns, E. (2012b): Li-bearing tourmalines in Variscan pegmatites from the Moldanubian nappes, Lower Austria. *Eur. J. Mineral.*, **24**, 695–715.
- Ertl, A., Vereshchagin, O. S., Giester, G., Tillmanns, E., Meyer, H.-P., Ludwig, T., Rozhdestvenskaya, I.V., Frank-Kamenetskaya, O.V. (2015): Structural and chemical investigation of a zoned synthetic Cu-rich tourmaline. *Can. Mineral.*, **53**, 209–220.

- Foit, F.F.Jr. (1989): Crystal chemistry of alkali-deficient schorl and tourmaline structural relationships. *Am. Mineral.*, **74**, 422–431.
- Foit, F.F.Jr., & Rosenberg, P.E. (1979): The structure of vanadium-bearing tourmaline and its implications regarding tourmaline solid solutions. *Am. Mineral.*, **64**, 788–798.
- Grew, E.S., Chernosky, J.V., Werdling, G., Abraham, K., Marquez, N., Hinthorne, J.R. (1990): Chemistry of kornerupine and associated minerals, a wet chemical, ion microprobe, and X-ray study emphasizing Li-contents, Be-contents, B-contents and F-contents. *J. Petrol.*, **31**, 1025–1070.
- Grew, E.S., Yates, M.G., Shearer, C.K., Wiedenbeck, M. (1997): Werdingite from the Urungwe district, Zimbabwe. *Mineral. Mag.*, **61**, 713–718.
- Grice, J.D. & Ercit, T.S. (1993): Ordering of Fe and Mg in the tourmaline crystal structure: the correct formula. *N. Jb. Mineral. Abh.*, **165**, 245–266.
- Hawthorne, F.C. (1996): Structural mechanisms for light-element variations in tourmaline. *Can. Mineral.*, **34**, 123–132.
- Henry, D.J. & Guidotti, C.V. (1985): Tourmaline as a petrogenetic indicator mineral: an example from the staurolite-grade metapelites of NW Maine. *Am. Mineral.*, **70**, 1–15.
- Henry, D.J. & Dutrow, B. (1996): Metamorphic tourmaline and its petrologic applications. *Rev. Mineral.*, **33**, 503–557.
- Henry, D.J., Novák, M., Hawthorne, F.C., Ertl, A., Dutrow, B.L., Uher, P., Pezzotta, F. (2011): Nomenclature of the tourmaline-supergroup minerals. *Am. Mineral.*, **96**, 895–913.
- Hughes, J.M., Ertl, A., Dyar, M.D., Grew, E.S., Shearer, C.K., Yates, M.G., Guidotti, C.V. (2000): Tetrahedrally coordinated boron in a tourmaline: boron-rich olenite from Stoffhütte, Koralpe, Austria. *Can. Mineral.*, **38**, 861–868.
- Hughes, J. M., Ertl, A., Dyar, M. D., Grew, E. S., Wiedenbeck, M., Brandstätter, F. (2004): Structural and chemical response to varying  $^{14}\text{B}$  content in zoned Fe-bearing olenite from Koralpe, Austria. *Am. Mineral.*, **89**, 447–454.
- Kalt, A., Schreyer, W., Ludwig, T., Prowatke, S., Bernhardt, H.-J., Ertl, A. (2001): Complete solid solution between magnesian schorl and lithian excess-boron olenite in a pegmatite from Koralpe (eastern Alps, Austria). *Eur. J. Mineral.*, **13**, 1191–1205.
- Kempl, J. (2008): Synthese und Charakterisierung von Turmalin mit tetraedrischem Bor. Diploma Thesis, Technische Universität Berlin, 85p.
- Kutzschbach, M., Wunder, B., Rhede, D., Koch-Müller, M., Ertl, A., Giester, G., Heinrich, W., Franz, G. (2016): Tetrahedral boron in natural and synthetic high-pressure tourmaline: Evidence from Raman spectroscopy, EMPA, and single-crystal XRD. *Am. Mineral.*, **101**, 93–104.
- Kutzschbach, M., Wunder, B., Krstulovic, M., Ertl, A., Trumbull, R., Rocholl, A., Giester, G. (2017): First high-pressure synthesis of rossmanitic tourmaline and evidence for the incorporation of Li at the X-site. *Phys. Chem. Minerals*, **44**, 353–363.
- London, D. (2011): Experimental synthesis and stability of tourmaline: a historical overview. *Can. Mineral.*, **49**, 117–136.
- Lussier, A.J., Aguiar, P.M., Michaelis, V.K., Kroeker, S., Herwig, S., Abdu, Y., Hawthorne, F.C. (2008): Mushroom elbaite from the Kat Chay mine, Momeik, near Mogok, Myanmar: I. Crystal chemistry by SREF, EMPA, MAS NMR and Mössbauer spectroscopy. *Mineral. Mag.*, **72**, 747–761.
- Lussier, A.J., Aguiar, P.M., Michaelis, V.K., Kroeker, S., Hawthorne, F.C. (2009): The occurrence of tetrahedrally coordinated Al and B in tourmaline: An  $^{11}\text{B}$  and  $^{27}\text{Al}$  MAS NMR study. *Am. Mineral.*, **94**, 785–792.
- MacDonald, D.J. & Hawthorne, F.C. (1995): The crystal chemistry of Si  $\leftrightarrow$  Al substitution in tourmaline. *Can. Mineral.*, **33**, 849–858.
- Marler, B., Borowski, M., Wodara, U., Schreyer, W. (2002): Synthetic tourmaline (olenite) with excess boron replacing silicon in the tetrahedral site: II. Structure analysis. *Eur. J. Mineral.*, **14**, 763–771.
- Nishio-Hamane, D., Minakawa, T., Yamaura, J., Oyama, T., Ohnishi, M., Shimobayashi, N. (2014): Adachiite, a Si-poor member of the tourmaline supergroup from the Kiura mine, Oita Prefecture, Japan. *J. Mineral. Petrol. Sci.*, **109**, 74–78.
- Padrón-Navarta, J.A., Sánchez-Vizcaino, V.L., Hermann, J., Connolly, J.A.D., Garrido, C.J., Gómez-Pugnaire, M.T., Marchesi, C. (2013): Tschermak's substitution in antigorite and consequences for phase relations and water liberation in high-grade serpentinites. *Lithos*, **178**, 186–196.
- Pattison, D.R.M. (1987): Variations in Mg/(Mg + Fe), F, and (Fe, Mg)Si = 2Al in pelitic minerals in the Ballachulish thermal aureole, Scotland. *Am. Mineral.*, **72**, 255–272.
- Povondra, P. (1981): The crystal chemistry of tourmalines of the schorl-dravite series. *Acta Univ. Carol. Geol.*, **3**, 223–264.
- Prowatke, S., Ertl, A., Hughes, J.M. (2003): Tetrahedrally-coordinated Al in Mn-rich, Li- and Fe-bearing olenite from Eibenstein an der Thaya, Lower Austria: A chemical and structural investigation. *N. Jb. Miner. Mh.*, **2003**, 385–395.
- Ranoroosa, N. (1986): Étude minéralogique des pegmatites du champ de la Sahatany (Madagascar). Thèse de doctorat de l'Université Paul Sabatier, Toulouse 3, no. 86 TOU3 0210, Toulouse, 240 p.
- Schlager, O. (2003): Hochdruck-Niedertemperatursynthesen von extrem borreichen olenitischen Turmalinen. Diploma Thesis, Ruhr-Universität Bochum, 78 p.
- Schreyer, W., Wodara, U., Marler, B., van Aken, P.A., Seifert, F., Robert, J.L. (2000): Synthetic tourmaline (olenite) with excess boron replacing silicon in the tetrahedral site: I. Synthesis conditions, chemical and spectroscopic evidence. *Eur. J. Mineral.*, **12**, 529–541.
- Schreyer, W., Hughes, J., Bernhardt, H.-J., Kalt, A., Prowatke, S., Ertl, A. (2002): Tetrahedral boron in olenite from the type locality: A chemical and structural investigation. *Eur. J. Mineral.*, **14**, 935–942.
- Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.*, **A32**, 751–767.
- Stüwe, K. & Powell, R. (1995): PT Paths from modal proportions: application to the Koralm Complex, Eastern Alps. *Contrib. Mineral. Petrol.*, **119**, 83–93.
- Wodara, U. & Schreyer, W. (2001): X-site vacant Al-tourmaline: a new synthetic endmember. *Eur. J. Mineral.*, **13**, 521–532.

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