The incorporation of Li in the tourmaline structure

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Using natural and synthetic samples, it was investigated which Li-containing short-range orders can occur in Li-bearing Al-rich tourmalines. The investigated samples have lattice parameters from a = 15.72, c = 7.07 Å to a = 15.84, c = 7.10 Å. The general tourmaline formula is $XY_3Z_6(BO_3)_3[T_6O_{18}]V_3W$, where the *X* site is usually occupied by Na, Ca or is vacant. The *Y* site is in such tourmalines usually occupied by Al and Li, and the *Z* site is only occupied by Al. The *T* site can be occupied by Si and by minor amounts of B and Al. The *V* site is usually occupied by OH and the *W* site by OH, O or F.

It is still not clear how Li enters the *Y* site in Li-rich tourmalines. Until now, syntheses have not been successful in producing Li-rich tourmalines (>0.5 apfu ^{Y}Li). It therefore makes sense to take a closer look at which short-range orders Li can be built into. Synthetic Al-rich and Li-bearing tourmalines with no F, but with $^{[4]}$B and $^{[4]}$Al are of special interest, because they contain no Ca, only Na and vacancies (□) at the *X* site and mainly Al and Li at the *Y* site (Ertl et al., 2012). Since these tourmalines (synthesized by David London) do not have such a complex composition, relationships are easier to recognize. In Tab. 1 all short-range orders are listed which can contribute to these synthetic samples (*Z* site is always occupied by Al).

Table 1. Short-range orders in synthetic tourmaline

Number	*X* site	*Y* site	*T* site	*W* site
1.1	Na	Al_2Li	Si_5B	OH
1.2	Na	Al_2Li	Si_5Al	OH
1.3	Na	Al_3	Si_4B_2	O
2.1	□	Al_2Li	Si_6	OH
2.2	□	Al_3	Si_5B	O
2.3	□	Al_3	Si_5Al	O

Short-range order 2.1 is related to the rossmanite end-member. Short-range order 2.3 is related to the alumino-oxy-rossmanite end-member (Ertl et al., 2022), while 2.2 is related to the B-analogue of this tourmaline. It seems confirmed that the short-range order 1.3 is an essential component. Without it, it is not possible to explain the crystal chemical formulae of these synthetic tourmaline samples. The combination of these different short-range orders makes it clear that the Li content in such a tourmaline containing only Na and vacancies at the *X* site will be in the range of 0–1 apfu Li. When correlating the component of the different short-range orders in the examined tourmalines, which were synthesized at different temperatures, it can be recognized that with decreasing temperature the component of 2.1 increases, while it decreases with increasing temperature. This explains why the content of the tetrahedrally coordinated B towards lower temperatures significantly increases. There is no evidence that in these synthetic tourmalines a short-range order occurs, where the *X* and *Y* sites are occupied as in 1.1, but exclusively Si occupies the *T* site and only O occupies the *W* site. Such a short-range order may not be favourable at such pressure/temperature conditions or perhaps even unstable.

A natural Al-rich and Li-bearing tourmaline sample with a vacancy-dominant *X* site (rossmanite; Selway et al., 1998) with the updated crystal chemical formula $^{X}(\square_{0.6}Na_{0.4})$ $^{Y}(Al_{2.2}Li_{0.7}\square_{0.1})$ $^{Z}Al_6$ $(BO_3)_3$ $[Si_{5.6}B_{0.4}O_{18}]$ $^{V}(OH)_3$ $^{W}[(OH)_{0.6}O_{0.3}F_{0.1}]$ seems to consist of the same short-range orders. A minor component may occur additionally: a short-range order with ^{X}Na, $^{Y}(Al_2\square)$, ^{T}Si and ^{W}(OH) (see also Ertl, 2023). However, the dominant component is short-range order 2.2 (Tab. 1), which is not surprising.

There occur natural Al- and Li-rich tourmalines with Li >1.0 apfu. Such tourmalines contain additionally some Ca and significant amounts of F (*e.g.*, Ertl et al., 2006, 2010). The short-range orders occurring in such samples are already listed in Tab. 1, but additional short-range orders might also occur, which are listed in Tab. 2.

Table 2. Additional theoretical short-range orders in natural Al- and Li-rich samples

Number	*X* site	*Y* site	*T* site	*W* site
1.4	Na	Al_2Li	Si_5B	F
1.5	Na	Al_2Li	Si_5Al	F
2.4	□	Al_2Li	Si_6	F
3.1	Ca	Li_2Al	Si_6	F
3.2	Ca	Li_2Al	Si_6	OH
3.3	Ca	$Al_2\square$	Si_5Al	OH
3.4	Ca	$Al_2\square$	Si_5B	OH

Short-range orders 3.1 and 3.2 have (Li_2Al) at the *Y* site. The combination of these components together with short-range orders 1.1, 1.2, 1.4, 1.5, 2.1 and 2.4 produces Li contents in the range 1-2 apfu Li. However, the 2.4 short-range order does not appear to occur, as a summary of approximately 9000 tourmaline analyses from different lithological environments show that for tourmaline with an average *X*-site charge of <+0.5, the maximum F amounts are <0.2 apfu (Henry & Dutrow, 2011). These chemical data of natural tourmalines indicate crystallographic influences. Natural tourmaline with relatively high Li contents always contains relatively high F contents. It seems that the contents of Li and the F are positively correlated (Ertl, 2021). It is therefore possible that short-range orders with Li and F (1.4, 1.5, 3.1; Table 2) are crystal-chemically more favourable than orders with Li and OH (1.1, 1.2, 2.1; Tab. 1; 3.2; Tab. 2). However, further investigations seem to be necessary.

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