The crystal structure of an aluminum-rich schorl overgrown by boron-rich olenite from Koralpe, Styria, Austria

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With 1 Figure

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Summary
The first natural tourmaline (because tourmaline with $^{[4]}$B has also been synthesized, we distinguish here between natural and synthetic tourmaline) that has been unequivocally demonstrated to contain B as a substituent at the T sites was described from Koralpe, Styria, Austria. This colourless B-rich olenite occurs as rims overgrowing schorl (black crystals up to a few cm) that has not yet been structurally characterized. A crystal structure refinement ($R = 0.019$) of this Al-rich schorl shows that $^{[4]}$B occurs in the overgrown schorl: the optimized occupants of the atomic positions yield $X$(Na$_{0.64}$Ca$_{0.10}$K$_{0.06}$$\square_{0.20}$) $^Y$(Fe$_{1.72}$Al$_{1.08}$Ti$_{0.11}$Zn$_{0.03}$$\square_{0.06}$) $^Z$(Al$_{1.70}$Mg$_{0.20}$Fe$_{0.08}$Mn$_{0.02}$) ($^{[4]}$BO$_3$)$_{3.00}$ $^7$(Si$_{5.76}$$^{[4]}$B$_{0.24}$)O$_8$ [F$_{0.11}$OH$_{3.31}$O$_{0.58}$]. This is the first known (Al-rich) schorl where a structure refinement has detected $^{[4]}$B. Comparing the structure refinements and the chemical composition of the Koralpe schorl and other $^{[4]}$B-bearing tourmalines with tourmalines which contain no $^{[4]}$B, it is of interest that only structure refinements of tourmalines which are low in magnesium and with a higher component of olenite show substantial amounts of $^{[4]}$B; the role of Mg in controlling the amount of $^{[4]}$B is not known, but it seems that an Al-component on the Y site (olenite-component), a boron-enriched environment and special P-T-t conditions are necessary to get tourmaline with substantial amounts of $^{[4]}$B.

Introduction
There has long been conjecture that B could enter the T site in tourmaline, but until recently no structural study has unequivocally shown B to occur in amounts greater than 3 $apfu$ (atoms per formula unit) in tourmaline (e.g., Burns et al., 1994; Hawthorne, 1996; Bloodaxe et al., 1999). In contrast to the commonly-accepted
lack of $^{10}$B, Ertl et al. (1997) reported an oleneite from Stoffhütte, Koralpe with significant excess B as determined by electron-microprobe analysis. Their structure study, which was done on an unanalyzed crystal, confirmed a significant level of B at the T site, although there was a large disparity (nearly a factor of 2) between the amount established by chemical analysis and that inferred from the structure analysis. As previous studies had not demonstrated that B substitutes for Si to any significant degree at the T site in “natural” tourmaline, Hughes et al. (2000) undertook a new single-crystal structure study on this oleneite and analyzed the structure crystal by electron and ion-microprobe. This study confirmed all aspects of the Ertl et al. (1997) study, and optimization of their structure and chemical data (Wright et al., 2000) showed that the oleneite from the Koralpe locality contains approximately one $^{10}$B at the T site.

The oleneite with excess-B occurs in an eo-Alpine pegmatitic rock (~90 Ma, pers. comm. R. Schuster) which discordantly intruded along the mylonitic foliation of the country rocks (mica schists) (Ertl and Brandstätter, 1998). B-rich oleneite forms rims on large grains of schorl. This schorl is of interest, as Wodara and Schreyer (1997), Schreyer et al. (2000) and Tagg et al. (1999) showed by MAS-NMR (Magic Angle Spinning–Nuclear Magnetic Resonance) that synthetic and natural tourmaline can indeed contain $^{10}$B. Contemporaneously with the study on the natural material (Ertl et al., 1997), the synthesis of oleneite with excess-boron was reported (Wodara and Schreyer, 1997); this study confirmed for the first time $^{10}$B in synthetic oleneite by MAS NMR. Here, we report the chemical composition and structure of the schorl that is overgrown by the B-rich oleneite, and comment on the relations between the two phases.

**Experimental**

**Chemical composition**

The chemical composition of the black schorl from Koralpe was analyzed with a wavelength-dispersive ARL SEMQ electron microprobe (EMP) (Table 1). The operating conditions were 15 kV accelerating voltage, beam current 10 nA, and spot size 5 µm. Natural silicates and oxides were used as standards. B$_2$O$_3$ was calculated as B + Si = 9 by assuming that there is no $^{10}$Al in the crystal structure (this assumption is a result of the structure refinement, see below). Hughes et al. (2000) also reported only small amounts of Al at the T site in the overgrowing much more Al-rich tourmaline (oleneite). H$_2$O has been calculated by difference to 100%. The formula calculated from the mean of several analyses (Table 1) is $^Y$(Na$_{0.65}$Ca$_{0.19}$K$_{0.01}$) $^Z$(Fe$^{2+}_{1.80}$Al$_{0.96}$Ti$_{0.10}$Zn$_{0.02}$Mn$_{0.01}$) $^Y$(Al$_{5.81}$Mg$_{0.19}$) $^Y$(BO$_{3.00}$) $^Y$(Si$_{5.80}$BO$_{2.00}$)O$_{18}$ [F$_{0.11}$]$_{3.31}$O$_{0.58}$. Small amounts of Li (up to about 0.1 Li apfu) cannot be excluded because Li has not been determined. Using the method of Wright et al. (2000) for optimizing chemical and structure data, we obtained an optimized formula of $^Y$(Na$_{0.58}$Ca$_{0.16}$K$_{0.06}$) $^Y$(Fe$^{2+}_{2.72}$Al$_{1.08}$Ti$_{0.11}$Zn$_{0.03}$) $^Z$(Al$_{5.70}$Mg$_{0.20}$Fe$^{2+}_{0.08}$Mn$_{0.02}$) $^Y$(BO$_{3.00}$) $^Y$(Si$_{5.76}$BO$_{2.24}$)O$_{18}$ [F$_{0.11}$]$_{3.31}$O$_{0.58}$.

Comparable oleneite-components with 1.10–1.28 Al at the Y site were determined for Fe-rich tourmalines by Bloodaxe et al. (1999) (tourmalines with a