Formation of metasomatic tourmalinites in reduced schists during the Black Hills Orogeny, South Dakota

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ABSTRACT

Tourmaline is a common mineral in granites and metamorphic rocks in collisional orogens. This paper describes graphite-bearing, metasomatic tourmalinites in sillimanite-zone schists of the Proterozoic Black Hills Orogen, South Dakota. The tourmalinites bound quartz veins and beyond about 1 m grade into schists with disseminated tourmaline, and ultimately tourmaline becomes only a trace, intrinsic phase in the schists. Next to the quartz veins tourmaline has almost completely replaced schist minerals, including biotite, muscovite, and plagioclase. The tourmaline is generally anhedral and follows the original foliation direction of the schist. However, tourmaline is euhedral in quartz veinlets cutting through the tourmalinites. Tourmaline is compositionally zoned from having about 22% to 2% of apparent Al occupancy on the Y sites. There are very good negative correlations of \( \frac{\text{Y}}{\text{Al}^{3+}} \), X\( \text{Ca}^{2+} \), and Y\( \text{Ti}^{4+} \) with Y\( \text{Al}^{3+} \), and a very good positive correlation of X-site vacancies with Y\( \text{Al}^{3+} \). Mg# \([\text{molar} \text{Mg}^{2+} / (\text{Mg}^{2+} + \text{Fe}^{2+})]\) is fairly invariant at approximately 0.5, which is somewhat higher than that in the precursor biotite. This is in contrast to tourmaline in the neighboring peraluminous Harney Peak leucogranite where the range of Y site occupancy of Al is small at about 20%, but the Mg# ranges from 0.12 to 0.5.

The compositional trends in the metasomatic tourmaline are dominated by the exchange \( X^{\square} + 4 \text{YAl}^{3+} = X\text{Ca}^{2+} + 3 \text{Y(Fe}^{2+} + \text{Mg}^{2+}) + \text{YTi}^{4+} \). Mass-balance calculations suggest the metasomatizing fluid brought in H\(^+\) and B(OH\(_3\)) and removed K\(^+\), SiO\(_2\), and some Fe\(^{2+}\) during tourmalinization. Other elements in the tourmaline largely reflect the bulk composition of the replaced schist. The calculations show that silica in the quartz veins was locally derived, not brought in by the metasomatizing fluid. Interstitial graphite in the tourmalinites shows
precipitation of carbon from the methane-bearing fluid. The study demonstrates an important
effect of boron transfer by fluids during metamorphism and magmatism in the Earth's crust.

**Keywords:** Tourmaline, tourmalinite, metasomatism, schist, fluid, Black Hills

**INTRODUCTION**

Relatively high abundances of boron and its common mineral host, tourmaline, are
frequent features of collisional granites and metapelites (Henry and Guidotti 1985; Nabelek et al.
1992a; Guillot and Le Fort 1995; Nabelek and Bartlett 1998; Nabelek 2019). High abundances of
B in metapelites stem from its incorporation into ocean floor sediments (Leeman and Sisson
1996). Boron may be conserved in metapelites during prograde metamorphism if it is contained
by tourmaline (Henry and Dutrow 1996; Wilke et al. 2002), but if instead bulk of it resides in
micas, some of it may be lost from rocks by aqueous fluids produced by mica-consuming
metamorphic reactions (Nabelek et al. 1990; Moran et al. 1992; Leeman and Sisson 1996).
Ultimately, when all muscovite is consumed from schists during partial melting, most B is
incorporated into the melts, although a portion may be retained in residual sillimanite (Grew and
Hinthorne 1983). An important feature of B is that it is highly mobile in aqueous fluids as is
evident by experiments (Pichavant 1981), frequent association of tourmaline with veins of
hydrothermal origin, either as a replacement mineral or a primary mineral (Slack 1996), and by
frequent enrichments of B in aureoles of granitic pegmatites, either within micas or in newly-
formed tourmaline (Shearer et al. 1984; Shearer et al. 1986; Duke 1995; Wilke et al. 2002).

This contribution describes a tourmalinite next to a quartz vein in a sillimanite-grade
schist in the aureole of the Harney Peak Granite (HPG) in the Black Hills, South Dakota, USA
(Figs. 1, 2). The granite, associated pegmatites, schists, and metagraywackes occur within the
Proterozoic core of the Black Hills. The core is a classic orogenic sedimentary wedge that became deformed and metamorphosed during the Proterozoic Black Hills orogeny that was a consequence of the collision of the Archean Wyoming and Superior cratonic blocks. Tourmaline characterizes large portions of the HPG and some pegmatites and is a common metasomatic phase in the metamorphic aureoles that affect the surrounding metapelitic rocks. Although Slack (1996) defined tourmalinites as a metasomatized rock with more than 15% tourmaline, at the locality described here metasomatism was unusually intense with tourmaline effectively completely replacing a quartz-mica schist. Such tourmalinites also occur at other localities in the western aureole of the HPG. The tourmalinites include interstitial graphite and occur next to quartz veins.

The focus of this contribution is on the crystal-chemistry of tourmaline as a recorder of the tourmalinization process and composition of the metasomatizing fluid. Compositions of tourmaline and micas reveal the solutes that were in the metasomatizing fluid and the ion-exchange reactions that were responsible for the tourmalinization reactions. Such fluids are likely to exist in deep orogenic wedges undergoing metamorphism during continental collisions, and therefore are an important part of the crustal boron cycle.

**Geologic Background**

Metamorphism and magmatism in the Black Hills were previously described in several papers (e.g., Norton and Redden 1990; Helms and Labotka 1991; Nabelek et al. 1992a, b, 2006; Nabelek and Chen 2014). The Proterozoic core of the Black Hills was exposed by late-Mesozoic to early-Tertiary Laramide uplift and erosion (Redden et al. 1990). Protoliths of the metamorphic rocks were shales with variable amounts of organic components, graywackes, mafic sills, and to
the southeast of the HPG a sandstone (Fig. 1). Metamorphism occurred during a polyphase
deformational history. Evidence for the earliest metamorphism (M₁) and deformation (D₁)
appears to be restricted to the western margin of the terrane. They were attributed to a regional
thrusting related to Yavapai arc accretion from the south between 1790 and 1750 Ma (Dahl et al.
1999, 2005). However, metamorphism (M₂) and deformation (D₂) that dominate the structure of
the Proterozoic terrane are related to east-west shortening during the Black Hills Orogeny
beginning at c. 1750 Ma (Redden et al. 1990; Chamberlain et al. 2003; Dahl et al. 2005).

Late-orogenic intrusion of the HPG in the southern Black Hills superimposed contact
metamorphism (M₃) and associated deformation (D₃) on the regionally metamorphosed rocks.
Intrusion of the granite occurred at c. 1715 Ma (Redden et al. 1990). The HPG pluton and a large
pegmatite field are the dominant geologic features of the southern Black Hills (Norton and
Redden, 1990). The HPG was built-up by intrusion of many thousands of leucogranite sills and
dikes. Most pegmatite intrusions occur in schists and metagraywackes. In close proximity to the
HPG, the intrusion of magma transposed the regional S₂ foliation in metamorphic rocks into S₃,
which is more horizontal and generally concordant with granite sills that constructed the HPG
(Duke et al. 1988, 1990b). The M₂ and M₃ metamorphic events probably overlapped in time
(Redden and DeWitt 2008). Maximum metamorphic pressures in the aureole of the HPG were at
least 6 kbar but the aureole appears to have decompressed to about 3 kbar as the granite was
being emplaced, probably due to buoyancy (Nabelek and Chen 2014).

Fluids were present in the metamorphic rocks during the M₂ and M₃ metamorphic events.
Compositions of fluid inclusions in quartz veins show that reducing conditions prevailed (Huff
and Nabelek, 2007). During M₂, the fluids were dominated by variable proportions of CH₄, CO₂
and N₂. Application of the Andersen and Lindsley (1988) oxygen barometer to Mn-bearing
ilmenite and magnetite-ulvöspinel pairs in some garnet-grade samples suggests that fO$_2$ was $4.6 \pm 1.1$ log units below the fayalite-magnetite-quartz oxygen buffer. Graphite in the schists ranges from poorly ordered in the garnet zone to well-ordered within the sillimanite zone in the HPG contact aureole (Huff and Nabelek 2007). Fluids in the aureole of the HPG had ~25% of carbonic components. Well-ordered graphite commonly occurs along margins of quartz veins and host rocks to the veins (Duke et al. 1990a). In the samples described here, graphite is highly ordered with area ratios of “disordered/ordered” Raman peaks between 0 and 0.1, and fluid inclusions in the quartz vein have >90% CH$_4$ (Huff and Nabelek 2007).

A large portion of fluids in the HPG aureole and aureoles of pegmatite intrusions was magmatic. The fluids caused alkali (Na, K, Li) and B metasomatism of schists and graywackes on various scales (Duke 1995; Wilke et al. 2002; Nabelek et al. 2006; Teng et al. 2006). Fluid flow was probably preferentially concentrated on and near faults that bound the HPG as most intense metasomatism appears to have occurred there. Moreover, tourmalinites described here come from a locality that may have beneath it a portion of the Harney Peak Granite (Duke et al., 1990b), from which the metasomatizing fluid may have emanated.

The HPG in its outer portions contains abundant tourmaline. The inner portions tend to have biotite instead of tourmaline as the dominant ferromagnesian mineral. Tourmaline ranges from the millimeter scale in aplitic granite layers, in which it may define color banding (often called "line rock"), to the decimeter scale in pegmatitic layers (Rockhold et al., 1987, Duke et al., 1988). In pegmatite sheets, both within the granite and the wall rocks, it is oriented almost invariably with the long c-axis perpendicularly to the contacts between the sheets and intruded rocks. Tourmaline's orientation within the intrusive sheets follows the probable direction of heat loss from the crystallizing sheets.
Tourmaline, biotite, and muscovite in tourmalinites were analyzed for major elements by a JEOL JXA-8200 electron microprobe at Washington University, St. Louis, Missouri. The operating conditions were 15 keV accelerating voltage, 25 nA specimen current, 5-10 µm beam diameter, and 11 mm working distance. The Mean Atomic Number correction method of Donovan et al. (2016) was used to calculate wt.% of oxides in the minerals. For tourmaline, Si, Ti, Al, Fe, Mn, Mg, Zn, Ca, Na, and K were sought, but Zn was below the detection limit and K\textsubscript{2}O was always <0.02 wt.%. F was analyzed in only a subset of tourmaline.

Atomic site assignments in tourmaline, given its formula XY\textsubscript{3}Z\textsubscript{6}(T\textsubscript{6}O\textsubscript{18})(BO\textsubscript{3})\textsubscript{3}V\textsubscript{3}W, followed the scheme recommended by Henry et al. (2011). Thirty-one oxygens per formula unit were assumed. The weight percents of H\textsubscript{2}O and B\textsubscript{2}O\textsubscript{3} were iteratively adjusted to obtain 3 B atoms and 15 other cations in Y+Z+T sites. Vacancies can exist on the X sites. The V and W sites are filled by either OH\textsuperscript{−}, F\textsuperscript{−}, or O\textsuperscript{2−}, but here for simplicity, it is assumed that F\textsuperscript{−} and O\textsuperscript{2−} occur only on the W sites. Given the reducing conditions of the environment in which the tourmalinites formed, all Fe was assumed to be ferric. Compositions of tourmaline with minimum and maximum amounts of apparent YAl\textsuperscript{3+} in each sample are given in Table 1. Site assignments for biotite and muscovite were calculated by assuming 12 O\textsuperscript{2−} anions and two H\textsuperscript{+} cations. All mineral analyses are given in Supplementary Material.

**Petrography of Tourmalinite**

Tourmalinites described here replaced schists and occur next to quartz veins. This style of occurrence differs from tourmalinites that occur as breccia tourmaline-quartz veins at relatively
low-pressure localities (e.g., Dini et al. 2008) or gold-bearing tourmaline-quartz veins (e.g., Olivo and Williams-Jones 2002). Samples 195-1, 195-3A, B, and 195-5 represent the metasomatic progression from nearly wholly replaced schist to one with only disseminated tourmaline. Sample 195-3A is a 7 mm thick quartz-tourmaline vein that cuts through sample 195-3B. In samples 195-1 and 195-3B, interstices between tourmaline grains are mostly filled with graphite (Fig. 3a, c). There are occasional interstitial quartz grains, but most quartz occurs as rounded, anhedral inclusions within tourmaline. Tourmaline within 195-3A is euhedral (Fig. 3b). A few grains of pyrrhotite occur in 195-3B. Foliated muscovite, biotite, and quartz dominate sample 195-5, and graphite is much less abundant in it than in the other samples. Plagioclase and minor ilmenite also occur in the sample. Tourmaline is generally euhedral (Fig. 3d).

Petrography of samples 195-1 and 195-3B shows apparent alignment of tourmaline grains that corresponds with the local foliation direction in unmetasomatized schist (Fig. 3c). It is unclear whether the tourmaline foliation is due to compression of the tourmaline itself, or whether the tourmaline merely mimics the foliation direction of replaced micas. Tourmaline within 195-3A (quartz vein) and 195-5 appears to be randomly oriented (Fig. 3b, d). The random orientation of tourmaline in sample 195-5 suggests that the bulk of its crystals grew after the development of foliation. Because intrusion of the HPG and pegmatites was the last major event of the Black Hills Orogeny, and some minerals, particularly staurolite, in the aureole of the HPG overgrew the D3 foliation, the metasomatism at location 195 appears to have been related to the late-orogenic magmatism in the region.

Zoning of tourmaline in sample 195-5 is not apparent by either petrography and backscatter electron (BSE) imaging. On the other hand, zoning of tourmaline is revealed by both techniques in samples 195-1, 195-3A, and 195-3B. In BSE images, most tourmaline grains in
195-1 and 195-3 have fairly bright, broad cores that trend outward toward even brighter zones (Fig. 4a). The shapes of the brighter zones are not well defined. The rims of the grains are gray. In sample 195-3A, the zoning is more pronounced and the shape of zoning is consistent with the euhedral crystal shapes. The cores are gray but become brighter outward. The rims of the grains are again gray. The brightness of the zones correlates mostly with Fe concentration. There is no obvious evidence for detrital grains in any of the tourmaline images. Petrographically in plain light, the most intense zoning of tourmaline appears in 195-3A where it ranges from green in cores to brown outward toward rims (Fig. 3b). However, the very rims have less intense brown color.

**COMPOSITIONAL ZONING IN TOURMALINE**

Chemical variations in the metasomatic tourmaline are best considered in view of the formula \( XY_3Z_6(T_6O_{18})(BO_3)_3V_3W \). In the stoichiometric schorl end-member, the X site is filled with \( Na^+ \), the Y sites are filled with \( Fe^{2+} \), the Z sites are filled with \( Al^{3+} \), the T sites are filled with \( Si^{4+} \), the V sites are filled with \( OH^- \) or \( O^{2-} \), and the W site is filled with \( OH^- \), \( O^{2-} \), or \( F^- \) (Henry et al. 2011). In the dravite end-member, the Y sites are filled with \( Mg^{2+} \) instead of \( Fe^{2+} \). When \( Al^{3+} \) partially occupies the Y sites, it is frequently assumed that its charge is balanced by \( Li^+ \) also in the Y sites, which makes up the elbaite component. Although \( Li \) was not measured in the metasomatic tourmaline, analysis of schorl-dravite tourmaline in high-Li pegmatites shows that \( Li \) concentrations are only up to \( \sim 1000 \) ppm by weight (Maloney et al. 2008). Published data suggests that there is only a limited solubility of the elbaite component in dravite-bearing tourmaline, such that there appears to exist a complete solution only between dravite-poor

The metasomatic tourmaline in the Black Hills has sub-equal proportions of schorl and dravite components with up to 22% Al$^{3+}$ in the Y site (Fig 5a). The highest Mg$^{2+}$/Fe$^{2+}$ is in tourmaline 195-5, probably due to the preferential partitioning of Mg over Fe into tourmaline relative to biotite (Henry and Guidotti, 1985). The Mg$^{2+}$/Fe$^{2+}$ ratios in the metasomatic tourmaline are on the high end of the tourmaline composition trend in the HPG (Fig. 5a), but the HPG tourmaline (Supplementary Material) does not trend toward zero Y Al$^{3+}$. There is no correlation of Mg$^{2+}$/Fe$^{2+}$ with Y Al$^{3+}$ in the metasomatic tourmaline. The Mg# of all metasomatic tourmaline is higher than that of biotite in sample 195-5 and in most analyzed metapelites in the Black Hills (Fig. 5b). The correspondence of major element biotite compositions in 195-5 with compositions of biotite in other metapelites shows that its composition was not affected by metasomatism to any significant extent.

The metasomatic tourmaline shows remarkably good negative correlations of Y(Fe$^{2+}$+ Mg$^{2+}$), XCa$^{2+}$, and XTi$^{4+}$ with Y Al$^{3+}$ (Fig. 6a, b; Table 2). There is also a very good positive correlation of X-site vacancies with Y Al$^{3+}$. Tourmaline within 195-3A (thin quartz vein) occupies the whole compositional trend from Y Al$^{3+} = 0.07$ to 0.66, which is also exhibited by optical and BSE zoning (Figs. 3, 4). Only portions of the trend are occupied by tourmaline in the other samples, which is also reflected in less pronounced optical and BSE zoning. The tight negative correlation of Y(Fe$^{2+}$+Mg$^{2+}$) with Y Al$^{3+}$ is largely driven by Fe$^{2+}$ as the correlation of Mg$^{2+}$ with Y Al$^{3+}$ is weak (Fig. 6b, Table 2). There are no significant correlations of Na$^+$ and O$^{2-}$ with Y Al$^{3+}$ (Fig. 6c). There is only very minor apparent substitution of Al$^{3+}$ in the T sites (Table 1;
Supplementary Material), on average 0.08 atoms per formula unite (apfu) that is ignored in the
substitution relationships below.

Intercepts of regressions (Table 2) and consideration of errors on the intercepts, suggest
that if the tourmaline compositions extended to $Y\text{Al}^{3+} = 0$, the substitution relative to a
stoichiometric dravite-schorl solution would be:

$$2X\text{Na}^+ + Y(\text{Fe}^{2+}+\text{Mg}^{2+}) + 2\text{OH}^- \rightarrow X\text{Ca}^{2+} + X\square + Y\text{Ti}^{4+} + 2\text{O}^{2-} \quad (1)$$

At the high end of the $Y\text{Al}^{3+}$ spectrum, at approximately $Y\text{Al}^{3+} = 0.66$ where both $\text{Ca}^{2+}$ and $\text{Ti}^{4+}$
have zero concentrations, the substitution relative to a stoichiometric dravite-schorl solution is:

$$X\text{Na}^+ + 2Y(\text{Fe}^{2+}+\text{Mg}^{2+}) + \text{OH}^- \rightarrow X\square + 2Y\text{Al}^{3+} + \text{O}^{2-} \quad (2)$$

Both of these substitutions require deprotonation on the W site and existence of vacancies on the
X site. These two substitutions produce theoretical tourmaline compositions that describe the
ends of the compositional trend (Table 3). Thus, along the trend of decreasing $Y\text{Al}^{3+}$ the
substitution is:

$$0.03X\text{Na}^+ + 0.66Y\text{Al}^{3+} + 0.15X\square + 0.03\text{OH}^- =$$

$$0.18X\text{Ca}^{2+} + 0.48Y(\text{Fe}^{2+}+\text{Mg}^{2+}) + 0.18Y\text{Ti}^{4+} + 0.03\text{O}^{2-} \quad (3)$$

Because the participation of $\text{Na}^+$, $\text{OH}^-$, and $\text{O}^{2-}$ in the substitution is minor and none of them
shows a significant correlation with $Y\text{Al}^{3+}$, the substitution is dominated by:

$$4Y\text{Al}^{3+} + X\square = X\text{Ca}^{2+} + 3Y(\text{Fe}^{2+}+\text{Mg}^{2+}) + Y\text{Ti}^{4+}. \quad (4)$$

This substitution effectively represents zoning from green to brown color seen in plain light in
195-3A (Fig. 3b) and from dark to bright portions of the metasomatic tourmaline in BSE images
(Fig. 4).
DISCUSSION

Tourmaline-producing reactions

Zoning in tourmaline within the tourmalinites in the aureole of the HPG, from cores with elevated $^Y\text{Al}^{3+}$ toward rims with less $^Y\text{Al}^{3+}$ but higher $^Y\text{Fe}^{2+}$ and $^Y\text{Ti}^{4+}$ concentrations, suggests that the replacement of muscovite occurred preferentially over the replacement of biotite during early stages of metasomatism. This is not surprising because of the peraluminous compositions of both tourmaline and muscovite. On the other hand, the nearly 1:1 correlation of $^Y\text{Ti}^{4+}$ and $^X\text{Ca}^{2+}$ substitution in tourmaline is surprising. Such a correlation has also been noted in metasomatic tourmaline on the island of Elba, Italy (Dini et al. 2008) and at various localities on the margins of the Leinster Granite, Ireland (Gallaher and Kennan 1992). The correlation between the two elements exists in spite of the probability that in the tourmaline studied here, most $\text{Ti}^{4+}$ came from biotite in the unmetasomatized schists, whereas $\text{Ca}^{2+}$ probably came from plagioclase. The correlation can be explained by preferential partitioning of both elements into tourmaline over the metasomatizing fluid. Experiments have shown that above $500^\circ\text{C}$, $\text{Ca}^{2+}$ is partitioned preferentially into tourmaline over a Cl-bearing fluid (von Goerne and Franz 2000; von Goerne et al. 2011). The average $\text{Ca}#$ [molar $\text{Ca}^{2+}/(\text{Na}^{+}+\text{Ca}^{2+})$] of 0.22 ratio in the low-Al metasomatic tourmaline corresponds closely to the average $\text{Ca}#$ of 0.20 in plagioclase in Black Hills schists (unpublished data), and in all likelihood the composition of plagioclase in the metasomatized schist. A correspondence of the $\text{Ca}#$ between coexisting tourmaline and plagioclase has been noted by von Goerne et al. (2011). The solubility of $\text{Ti}^{4+}$ in hydrothermal fluids is generally low, usually only tens to hundreds of ppm when saturated with rutile (Manning et al. 2008). Instead, $\text{Ti}^{4+}$ usually prefers to partition into minerals, including silicates.
Figure 5b shows that tourmaline has a higher Mg/Fe ratio than the replaced biotite, which implies that some Fe was lost into the metasomatizing fluid or incorporated into pyrrhotite. Dissolution of a significant amount of Fe in the metasomatizing fluid has probably occurred given the very low-fO₂ conditions in the system. Fe loss to the fluids is suggested by low-Fe rims on most tourmaline grains (Fig. 4). Two ion-exchange reactions can be written, one for the initial growth of tourmaline that preferentially replaced muscovite (Reaction 5) and one for the latter growth that that involved a progressively increasing amount of reactant biotite (Reaction 6):

\[
\begin{align*}
\text{Reactions:} \\
1.36 \text{Bt} + 1.54 \text{Ms} + 3.00 \text{B(OH)}_3 + 0.31 \text{Na}^{+}_{\text{aq}} + 3.90 \text{H}^{+}_{\text{aq}} & \rightarrow \\
\text{Tur}(^{3+}\text{Al} = 0.66) + 0.17 \text{Ilm} + 2.46 \text{SiO}_2{\text{aq}} + 7.53 \text{H}_2\text{O} + 0.88 \text{Fe}^{2+}_{\text{aq}} + 2.44 \text{K}^{+}_{\text{aq}} & \text{ (5)} \\
1.47 \text{Bt} + 0.92 \text{Ms} + 0.85 \text{Pl(An}_{20} + 3.00 \text{B(OH)}_3 + 3.85 \text{H}^{+}_{\text{aq}} & \rightarrow \\
\text{Tur}(^{3+}\text{Al} = 0.1) + 0.02 \text{Ilm} + 3.22 \text{SiO}_2{\text{aq}} + 6.99 \text{H}_2\text{O} + 0.78 \text{Fe}^{2+}_{\text{aq}} + 2.04 \text{K}^{+}_{\text{aq}} + 0.26 \text{Na}^{+}_{\text{aq}} & \text{ (6)}
\end{align*}
\]

Mineral compositions that were used to compute these reactions are given in Table 4. Tourmaline compositions corresponding to those at $^{3+}\text{Al} = 0.1$ and 0.66 as given by the ends of regressed compositional zoning (Fig. 6; Table 2). Biotite and muscovite compositions are averages in sample 195-5. Ilmenite is added as a possible source or sink for Ti⁴⁺.

The reactions show the addition of B(OH)₃ and H⁺ by the fluid and dissolution of Fe²⁺, K⁺, and an aqueous SiO₂ species. The reactions imply that the main quartz vein (Fig. 2) and thin quartz veinlets within the tourmalinites (Fig. 3b) are products of the metasomatic reaction, not the cause of it. The SiO₂ is deemed to have been an aqueous species so it could accumulate to make the veins. The apparent dissolution of quartz from the schist during tourmalinization, as is evident by occurrences of round quartz inclusions in tourmaline, suggests that there was a chemical potential gradient of Si between the schist and the metasomatizing fluid into which the
Si must have transferred and where quartz has ultimately precipitated. Cl\(^-\) was probably the
dominant anion in the fluid to which Na\(^+\), K\(^+\), H\(^+\), and Fe\(^{2+}\) were bonded. F\(^-\) was probably a
minor component as it does not exceed 0.1 apfu in the tourmaline. In biotite in sample 195-5, F\(^-\)
concentration is <0.07 apfu, which is somewhat less than the average amount in biotite in other
schists in the Black Hills (Supplementary Material). Reaction 6 shows that there was a sufficient
amount of Ti\(^{4+}\) in biotite to explain the amount in the low-Al tourmaline as ilmenite appears as a
product of the reaction. Na\(^+\) as a reactant is needed to balance reaction 5, but is a product in
reaction 6, in which Na\(^+\) is coming from plagioclase. Nevertheless, the small amount of Na\(^+\)
involved is consistent with the precursor plagioclase largely controlling the Ca\# of the low-Al
tourmaline. It is thus apparent that the tourmalinite largely reflects the bulk composition of the
replaced schist, except for lost K\(^+\) and some Si\(^{4+}\), Fe\(^{2+}\), and H\(_2\)O.

Graphite and methane

Graphite occurs in interstices of the tourmalinites. The graphite apparently precipitated
from the CH\(_4\)-bearing fluid that is evident in microthermometric and Raman spectroscopic
analyses of fluid inclusions in the main quartz vein (Huff and Nabelek 2007). A combination of
CH\(_4\) and H\(_2\)O is predicted to dominate a fluid at the very reduced fO\(_2\) conditions indicated by Fe-
Ti oxides in the schists (Nabelek et al., 2006) and will cause precipitation of graphite (Ohmoto
and Kerrick 1977). Well-ordered graphite is seen not only in the tourmalinites described here,
but also in other quartz veins in the high-grade metamorphic rocks of the Black Hills (Duke et al.
1990a). Thus, along with components that were needed to replace silicate minerals by
tourmaline, the metasomatizing fluid must have contained abundant CH\(_4\) to cause precipitation
of the graphite.
The tourmalinites described here and abundant metasomatic tourmaline in the aureoles of the Harney Peak Granite and pegmatites in the Black Hills (Shearer et al. 1984, 1986; Duke 1995) demonstrate a high mobility of boron through metamorphic rocks in collisional orogens. In the case presented here, the activity of boron in the fluid was sufficiently high to cause an effectively complete replacement of muscovite, biotite, quartz, and feldspar in schists. Because oceanic sediments that are protoliths to orogenic schists commonly contain organic components, the metamorphic environment was highly reducing. Thus, methane is likely to accompany boron in the fluid and ultimately cause precipitation of graphite along with tourmaline. In a way, tourmalinites in collisional orogens are reflections of the end of a boron cycle that begins with absorption of boron from seawater into clays on the ocean floor, continues with its incorporation into partial melts that mark the limit of metamorphism of oceanic sediments, and ends with expulsion of boron from the crystallizing melts back into the metamorphic aureoles of plutons.

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**Figure Captions**

**Figure 1:** Map showing the location of station 195 in the western aureole of the Harney Peak Granite (HPG). Thin solid lines are formation boundaries and thick solid lines are recognized faults. Thick dashed lines are isograds. Metamorphic zones are Grt = garnet, St = staurolite, Sil = sillimanite, and 2\textsuperscript{nd} Sil = second sillimanite where partial melting has occurred.

**Figure 2:** An image showing a quartz vein that is bounded by tourmalinite. A schist into which the tourmalinite grades is not shown in this image.

**Figure 3:** Thin-section images of (a) 195-1, (b) 195-3A, (c) 195-3B, and (d) 195-5. All images are in plain light and each field of view is 1 mm. (a) and (c) show tourmaline and graphite and some remnant anhedral quartz (white spots). (b) shows tourmaline within a 7 mm thick quartz vein cutting through 195-3B. (d) shows a biotite-muscovite schist with randomly-oriented tourmaline.

**Figure 4:** Back-scatter electron images of (a) sample 195-1 and (b) 195-3A. Each scale-bar represents 100 µm. Grey areas in tourmaline contain relatively low Fe/Al ratios. The ratio increases with brightness. Interstitial black patches are graphite. Quartz, also black, occurs as rounded inclusions in tourmaline.

**Figure 5:** (a) Relative occupancies of Al\textsuperscript{3+}, Fe\textsuperscript{2+}, and Mg\textsuperscript{2+} on tourmaline's Y sites in tourmalinite and HPG. Compositions of tourmaline in the HPG are given in Supplementary Material. (b) Average molar proportions of Al\textsubscript{2}O\textsubscript{3}, FeO, and MgO in individual grains of

**Figure 6:** Variations of selected ions and X-site vacancies with $\text{YAl}^{3+}$ in metasomatic tourmaline. Lines through data are linear regressions given in Table 2. $\text{Fe}^{2+}$ contributes more than $\text{Mg}^{2+}$ to a tight combined correlation of $\text{Y(Fe}^{2+}+\text{Mg}^{2+})$ with $\text{YAl}^{3+}$. $\text{Na}^+$ and $\text{O}^{2-}$ do not show significant correlations with $\text{YAl}^{3+}$. 
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<th>195-1 max. $^\text{Y} \text{Al}$</th>
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<th>195-3B min. $^\text{Y} \text{Al}$</th>
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**Site occupancies**

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$^a$ Assumed occupancy.

$^b$ Calculated by assuming 3 boron atoms and 15 Y+Z+T cations.

$^c$ Fluorine was analyzed in only a subset of samples (see Supplementary Materials).
**Table 2.** Regressions of element occupancies with $^\gamma$Al

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<td>Fe + Mg</td>
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<td>$-0.65 \times ^\gamma$Al + 1.49</td>
<td>0.55</td>
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<td>Mg</td>
<td>$-0.12 \times ^\gamma$Al + 1.33</td>
<td>0.04</td>
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<tr>
<td>Ti</td>
<td>$-0.24 \times ^\gamma$Al + 0.17</td>
<td>0.74</td>
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<tr>
<td>Ca</td>
<td>$-0.31 \times ^\gamma$Al + 0.20</td>
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<tr>
<td>Na</td>
<td>$-0.04 \times ^\gamma$Al + 0.66</td>
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<td>Vacancies X</td>
<td>$0.36 \times ^\gamma$Al + 0.13</td>
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**Table 3.** Tourmaline compositions (apfu) used in computing substitution 3

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<td>$^\gamma$YAl</td>
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<td>$^\gamma$(Fe+Mg)</td>
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*Because there is no significant correlation of these cations with $^{1}$Al in tourmaline, average concentrations were used to calculate reactions.*
Figure 4
Ions or vacancies pfu

(a) Fe$^{2+}$+Mg$^{2+}$
(b) Mg$^{2+}$ vacancies X
(c) Na$^+$

YAl$^3+$

YAl$^3+$