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B and Li in Proterozoic metapelites from the Black Hills, U.S.A.: Implications for the origin of leucogranitic magmas

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ABSTRACT

The abundance and distribution of B and Li in metasedimentary rocks and in the Harney Peak Granite (HPG) in the Black Hills, South Dakota, U.S.A., elucidate the behavior of these two elements during (1) regional metamorphism that began at ~1760 Ma; (2) subsequent contact metamorphism associated with emplacement of the HPG and associated pegmatites at ~1715 Ma; and (3) anatexis leading to production of the granite. There is no clear evidence for changes in B and Li concentrations with progressive regional metamorphism of the metapelites from chlorite-biotite grade up to staurolite grade. Rocks outside the pegmatite aureole that surround the HPG have average B contents of ~80 ppm. There is no correlation of B with other elements in the pelitic schists, which indicates that none of the major phases is the dominant host for B. Boron content is mainly controlled by small amounts of randomly distributed tourmaline that was identified in alpha-track maps of thin sections. In the aureole of the granite, B concentrations are depleted in many samples. The depletion is attributed to consumption of tourmaline during interaction of the rocks with alkalic fluids. The average Li contents in metapelites far away from the HPG are also ~80 ppm. Near the HPG, Li concentrations reach roughly 190 ppm, indicating significant metasomatism by fluids that emanated from the granite and pegmatites.

The concentrations of B and Li in the low-grade metapelites are sufficient to explain their abundances in the HPG, if the granite formed by partial melting of the metapelites and if there was total breakdown of tourmaline. Stabilization of tourmaline in leucogranites is not necessarily related to sources enriched in B, but may be related to its competition for Fe and Mg with biotite.

INTRODUCTION

The chemical differentiation of the upper crust is, to a large degree, related to partial melting of metapelitic rocks. A consequence of partial melting of metapelites is the production of leucogranites and pegmatites, which may be highly enriched in B, Li, Cs, Be, and other large-ion-lithophile (LIL) elements. Elevated concentrations of B and Li lead to stabilization of tourmaline, spodumene, lepidolite, and other B- and Li-containing minerals. In addition, these elements can affect the physical properties of magmas and their liquidus relationships (Pichavant 1987; Holtz et al. 1993; Dingwell et al. 1996). However, the source of these elements and their solubility in granitic melts are still controversial. For example, experiments suggest a broad range of concentrations (~0.5–2.5 wt% in B_2O_3) for saturation of silicate melts in tourmaline (e.g., Bénard et al. 1985; London et al. 1994; London and Manning 1995; Wolf and London 1997), and Holtz and Johannes (1991) dissolved up to 6 wt% of tourmaline during experimental melting of a natural biotite-bearing gneiss. Thus, some of these studies appear to imply that the saturation levels of B before tourmaline becomes stable are exceedingly high, even in peraluminous granites (e.g., London 1999). Yet, metapelitic rocks, which are regarded as the most plausible source rocks for leucogranites, contain on average only ~100 ppm of B (Harder 1970). Therefore, partial melts should not have much more than 1000 ppm B, assuming 10% partial melting. Thus, a contribution of B from evaporites or other B-enriched rocks into partial leucogranite melts may seem to be required if B saturation levels are higher than that (London et al. 1996). However, evaporites are not very likely to reach anatectic metamorphic conditions, and B and O isotopic compositions of granitic rocks usually do not indicate any contribution from evaporites (Palmer and Swihart 1996; Nabelek et al. 1992b). Alternatively, Scaillet et al. (1995) and Pichavant et al. (1996) suggested that an increase in f_{O_2} during crystallization of leucogranitic magmas may lead to stabilization of tourmaline relative to biotite.

In this paper, we use bulk B and Li contents and alpha-track images of their distribution in a suite of Proterozoic metapelites and metagraywackes in the Black Hills, South Dakota, to determine the fate of these elements during regional metamorphism and subsequent contact-metamorphic overprint by the Harney Peak Granite (HPG). The HPG is a leucogranite located in the southern, highest-grade part of the Proterozoic metamorphic terrane (Fig. 1). It is surrounded by an extensive field of rare-element-bearing pegmatites (Norton and Redden

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1990). Of particular significance in the HPG is the distribution of biotite and tourmaline: biotite is the predominant ferromagnesian mineral in the core of the main pluton, whereas tourmaline predominates along the perimeter and in satellite intrusions (Nabelek et al. 1992a). Both granite suites have the same average alumina saturation index (ASI) of 1.2. Therefore, this parameter did not play a significant role in the relative stability of the two ferromagnesian minerals, in contrast to the proposal of London (1999) that ASI may influence the stability of tourmaline. Nabelek and Bartlett (1998, 2000) were able to model, using mass-balance approaches, the trace-element characteristics of the tourmaline-bearing granites by assuming that the granite formed by partial melting of deeper equivalents of the surrounding metapelites. In a similar manner, we show that B and Li contents in the metapelites are sufficient to yield the observed B concentrations in the tourmaline-bearing HPG. Based on evidence from this and previous studies on the Harney Peak Granite, we explore the possibility that stabilization of tourmaline in leucogranitic magmas is related more to its competition for Mg and Fe with biotite than other compositional parameters or intensive variables that were proposed by others (cf., Pichavant et al. 1996; London 1999).

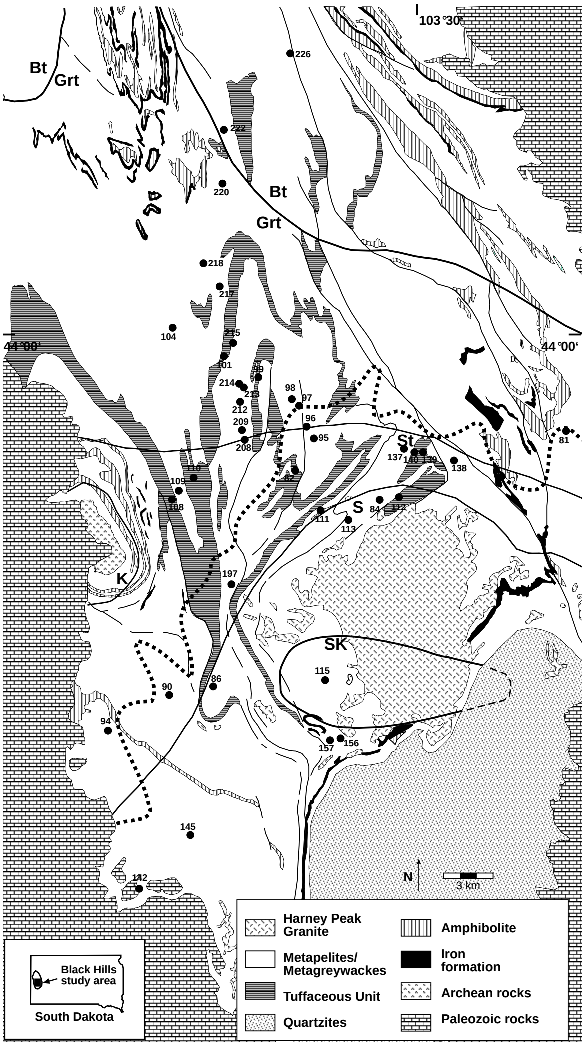


FIGURE 1. Geological map of the Precambrian terrane of the southern Black Hills. Thin lines, including dashed lines, are faults. Heavy lines are isograds: Grt = garnet, S = sillimanite, SK = second sillimanite. A tuffaceous shale unit is shown to highlight the major fold structures. The heavy dashed line outlines a region of abundant pegmatites surrounding the Harney Peak Granite. Location of samples used in this study is shown by black circles.

GEOLOGICAL SETTING

The Middle Proterozoic and minor Archean metamorphic and granitic rocks in the Black Hills were uplifted during the Laramide orogeny and subsequently exposed by erosion (Redden et al. 1990). The HPG consists of a large central pluton that is surrounded by smaller satellite plutons, dikes, sills, and an extensive field of pegmatites. The Proterozoic metasedimentary rocks consist mainly of quartzites and quartz-muscovite-biotite-plagioclase metapelites and metagraywackes. The metapelites have higher ratios of muscovite to plagioclase than the metagraywackes (Nabelek and Bartlett 2000). Rare amphibolites, iron formations, and marbles also occur. The originally sedimentary and mafic igneous rocks were metamorphosed during syntectonic regional metamorphism (M1), which began at 1760–1770 Ma during the late Trans-Hudson orogeny (Dahl and Frei 1998). The HPG complex was emplaced in the exposed part of the crust during late stages of the orogenic cycle at ~1715 (Dahl et al. 2000; Nabelek et al. 2001a) and imposed a thermal overprint (M2). The overprinting may have been coeval with bowing-up of isograds, as the second-sillimanite isograd is not concentric around the HPG pluton. The dominant Trans-Hudson-related structures in the metasedimentary rocks are NNW-trending folds with steeply dipping foliations, which were reoriented near the HPG during emplacement of the magma.

CONDITIONS OF METAMORPHISM

A comprehensive summary of the current knowledge of the conditions of metamorphism in the southern Black Hills is given by Nabelek et al. (1999) and Dahl et al. (1999). Therefore, only a brief overview is given here, with the addition of some new information for the lower-grade rocks in the northern part of the Proterozoic terrane.

The approximate location of isograds is shown in Figure 1. Minerals in the metapelites below the staurolite isograd consist mainly of biotite, chlorite, muscovite, garnet and accessory minerals, including tourmaline, monazite, zircon, apatite, xenotime, sulfides, and graphite. Graphite can reach considerable abundance, over 1% in some formations, giving many of the rocks a dark-gray appearance. The abundance of garnet decreases from the staurolite isograd northward into lower-grade rocks. In the lowest-grade rocks, garnet is mostly confined to dark, sulfide-rich bands. Assemblages in the metapelites and metagraywackes in the staurolite zone include staurolite, garnet, biotite, muscovite, quartz, plagioclase, and accessory phases. The relative proportion of the micas does not appreciably change with grade.

Until recently, the staurolite isograd was considered to be the result of chlorite breakdown during M1 metamorphism (Redden et al. 1990; Helms and Labotka 1991; Dahl and Frei 1998). However, Dahl et al. (2000) have shown that monazite within garnet inside the staurolite isograd north of the HPG formed at ~1715 Ma, which suggests that this isograd and the higher-grade, first- and second-sillimanite isograds are related to emplacement of the HPG (M2). Chlorite within the staurolite zone generally forms pseudomorphs after staurolite and garnet, and therefore can be ascribed to fluid-present retrograde metamorphism (Nabelek et al. 1999).

The first-sillimanite isograd can be described by the reaction

$$\text{st} + \text{ms} + \text{qtz} \rightarrow \text{grt} + \text{bt} + \text{sil} + H_2O. \quad (1)$$

The second-sillimanite isograd corresponds to migmatization of the schists by partial melting (Shearer et al. 1987; Nabelek 1997, 1999). Leucosomes have either granite mineralogy or mostly quartz plus sillimanite. Mesosomes contain quartz, biotite, sillimanite, and plagioclase. Conditions in this zone are estimated to have been 670–700 °C (Nabelek 1999). Garnet-sillimanite-plagioclase-quartz barometry using cores of monazite-bearing garnets that grew during the regional M1 metamorphism indicates a pressure of ~7 kbar at the time of growth (Terry and Friberg 1990; Dahl and Frei 1998), whereas HPG emplacement occurred at ~3.5 kbar (Helms and Labotka 1991). This change in pressure implies decompression of the terrane between the times of regional metamorphism and emplacement of the HPG.

ANALYTICAL PROCEDURES

Alpha-track mapping

Alpha-track mapping utilizes the nuclear reactions

$$^{10}B(n, \alpha)^{7}Li \quad (2)$$

and

$$^{6}Li(n, \alpha)^{3}H. \quad (3)$$

Uncovered polished thin sections of the samples were irradiated at the 10 MW University of Missouri Research Reactor for 1s with thermal neutrons at a flux of 4×10^{13} n/cm^2·s. Alpha particles produced during irradiation were recorded on a cellulose nitrate film (Kodak-LR115), which was attached to the surface of the thin sections. The alpha particles produced images of the B and Li distribution in the samples. After irradiation, the detector films were etched in a NaOH solution. The resulting track density on the film is proportional to the B plus Li content in each mineral. In general, the sensitivity of B to neutron flux is approximately ten times greater than that of Li.

Whole-rock analysis

Boron concentrations were analyzed by prompt gamma neutron activation (PGNAA) and by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer Optima 3300 instrument. Lithium concentrations were determined only by ICP-OES. PGNAA was performed using a thermal neutron flux of 5×10^8 n/cm^2·s following the method of Hanna et al. (1981). Further details of the technique are described in Nabelek et al. (1990). For the analysis of B and Li by ICP-OES, duplicate aliquots of the samples were dissolved in a mixture of 48% HF and concentrated H_2SO_4 using autoclave vessels in a microwave oven. To avoid loss of B during the procedure, orthophosphoric acid was added to the acid mix (Li-Qiang and Zhu 1986). Boron concentrations were determined with the 249.678 nm emission line. Interference by a minor Fe peak at 249.653 nm was avoided using the background subtraction procedure of Li-Qiang and Zhu (1986). Lithium concentrations were determined using the emission line at 670.784 nm. Agreement of resulting B contents with results from PGNAA is better than 10% (relative). Analysis of USGS standard AGV-1 is in agreement with the recommended value (8 ppm vs. 8.6 ppm), whereas the USGS standard GSP-1 is below the detection limit (0.9 ppm). The Li concentration for the AGV-1 of 14 ppm is in good agreement with the recommended value of 12 ± 2 ppm. Deviation of the Li concentration in GSP-1 is slightly larger (40 ppm vs. 31 ± 4 ppm).

RESULTS AND DISCUSSION

Localization of B and Li in metamorphic rocks

Alpha-track images were recorded for two samples of biotite schists from different metamorphic grades, a metagraywacke, and a migmatite. The alpha-track images are shown in Figure 2. All images have small, dark spots of very high track density, which can be related to tourmaline crystals. In fine-grained samples, crystal shapes are not resolvable from the alpha-tracks, whereas in coarser-grained samples the tracks define shapes of tourmaline crystals. Other phases that produced alpha-tracks are the micas.

In the fine-grained sample (below the garnet isograd) shown in Figure 2a, the foliation of micas is clearly visible, whereas individual crystals are not distinguishable. In this sample, it is difficult to assign individual alpha-track regions to particular minerals because the detector film cannot be matched with sufficient accuracy to the thin sections. Thus, any difference in track density produced by muscovite and biotite is difficult to determine. Another possible carrier of B in this sample could be graphite. However, it is rarely exposed on the surface of the thin sections, and therefore does not contribute alpha-tracks significantly. However, graphite could contribute some B to the overall rock budget. Areas with low or no track densities correspond to quartz and feldspar.

In the sillimanite-bearing biotite schist (Fig. 2b), the alpha-tracks from micas outline a network around quartz and feldspars. In addition, lenses of fibrous, fine-grained sillimanite in this sample produced considerable track densities. The tracks are probably produced almost exclusively by B because Li content in sillimanite is negligible (Pereira and Shaw 1996; Grew et al. 1990). Pereira and Shaw (1996) report similar B concentrations for muscovite and sillimanite from migmatites in the Peña Negra complex, Spain, based on both alpha-track and laser-ablation ICP-MS techniques. Alpha-track densities for biotite in our sample are significantly higher than for the micas in the low-grade sample. The higher densities may be related to Li enrichment near the HPG, as this sample was collected inside the pegmatitebearing aureole (see below).

The alpha-track image of the metagraywacke sample (Fig. 2c) shows contributions from small tourmaline grains and from micas, which form a network around quartz and feldspar. Tourmaline is randomly dispersed throughout the sample and carries most of the B in the rock. Its distribution suggests that it (or its precursor) had a detrital origin.

In the migmatitic sample (Fig. 2d), both sillimanite and micas carry considerable concentrations of B and Li. Among the micas, biotite, found mostly in mesosome and melanosome, produced high alpha-track densities. Fibrolitic sillimanite is found in the leucosomes and as lenses in mesosomes, where it is sometimes intergrown with tiny tourmaline crystals. Large tourmaline crystals are mostly confined to the leucosomes, whereas tourmaline is rare in the mesosomes.

Variations in whole rock B and Li concentrations and their causes

Previous studies of the behavior of B with increasing metamorphic grade have given somewhat contradictory results. For example, Moran et al. (1992), Leeman and Sisson (1996), and Bebout et al. (1999) documented progressive loss of B from subduction-related schists with increasing grade, which they attributed to dissolution of B in evolving metamorphic fluids. However, the authors did not report a consumption of a borosilicate mineral that could explain the loss. Nabelek et al. (1990) reported progressive B depletion with grade in contact metamorphosed calc-silicates in the Notch Peak aureole, Utah. They attributed the depletion to loss of micas during prograde reactions. In contrast, Woodford et al. (2001) reported an increase in B in high-grade rocks in the dolomitic Alta contact-aureole, Utah. The increase in B concentrations can be related to the

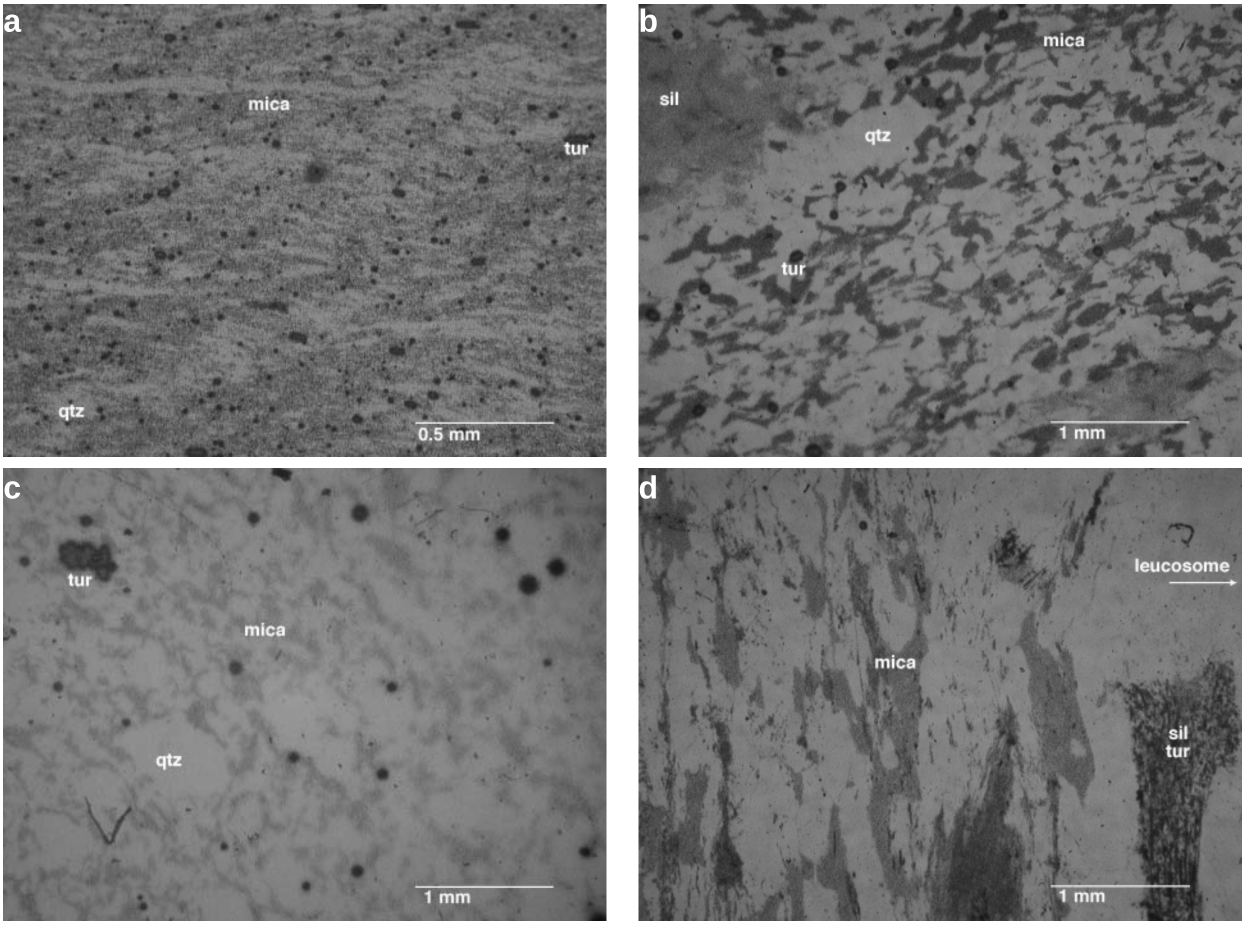


FIGURE 2. Alpha-track images of metasedimentary samples. (**a**) Pelite from biotite-chlorite zone (biotite, muscovite, chlorite, quartz, graphite, tourmaline). Dark spots from B in tourmaline are prominent. Tracks delineating micas are from both Li and B (the whole rock contains 79 ppm B and 85 ppm Li). (**b**) Pelite from first-sillimanite zone and inside the pegmatite area outlined in Figure 1 (biotite, quartz, muscovite, sillimanite, tourmaline). In addition to tourmaline and micas, sillimanite is also a carrier of B (the whole rock contains 111 ppm B and 184 ppm Li). (**c**) Graywacke from first sillimanite zone and inside the pegmatite area (quartz, feldspar, biotite, muscovite, tourmaline). Dark spots from B in tourmaline are prominent. Tracks delineating micas between quartz and feldspar grains are from Li and B. (**d**) Migmatite from second-sillimanite zone (mesosome: biotite, quartz, sillimanite, muscovite; leucosome: quartz, feldspar, sillimanite, tourmaline). The photograph shows a portion at the rim of the leucosome. Tracks delineating micas (mostly biotite) are from Li and B. Sillimanite also carries significant amounts of B. Intergrowths of sillimanite with tourmaline are found in the leucosome.

growth of new borosilicates that formed by reaction between dolomite and aqueous B complexes in fluids emanating from the Alta stock. Similarly, B was retained in several granulite-facies terranes due to growth of borosilicate minerals (Grew 1996). Thus, the presence of a borosilicate mineral during metamorphism may control retention of B. Lithium, however, seems to be retained in micas up to high metamorphic grades (Bebout et al. 1999).

In the Black Hills, there are no systematic variations in B or Li concentrations with metamorphic grade (Figs. 3a and 3b; Table 1). Instead, significant changes in B and Li concentrations occur within the pegmatite aureole, irrespective of metamorphic grade (Figs. 3c and 3d). Far away from the HPG, B and Li are variable, but on average, concentrations of both elements are ~80 ppm. Close to the HPG, Li concentrations are considerably elevated. Duke (1995) also observed significant increases in Li concentrations near quartz veins related to HPG intrusion that cut through metasedimentary rocks north of the pluton, and Redden and Norton (1992) reported elevated Li concentrations in samples collected in a grid-pattern in the same area. In contrast, B concentrations near the HPG are mostly lower, except for a few samples in which B is elevated. The pegmatite field follows the shape of the sillimanite isograd relative to the HPG, although the isograd is closer to the main pluton of the HPG. If the isograd is related to the M2 contact metamorphism (Dahl et al. 1999, 2000), then the observed changes in B and Li concentrations are probably related to metasomatism associated with granite and pegmatite emplacement.

Mechanism of lithium exchange. Outside of the pegmatite aureole, Li contents do not show a clear correlation with any major oxide, for example Al_2O_3 (Fig. 4a), indicating that Li abundances cannot be related simply to the amounts of biotite and muscovite in the samples. There is also no correlation between Li and B (Fig. 4c), which suggests that the two elements reside primarily in different host phases, even though Li could potentially be incorporated by tourmaline in significant amounts or both elements could reside in muscovite (e.g., Henry and Dutrow 1996). Multiple regressions of Li with various combinations of oxides and B give poor fits. Thus, pre-metamorphic and low-grade processes must have influenced the concentrations of Li in the rocks.

Within the pegmatite aureole, increases in Li concentrations can be attributed to interaction of the metapelites with Li-rich fluids that emanated from the crystallizing granitic magmas. Lithium is highly soluble in Cl-rich aqueous fluids at elevated temperatures (Webster et al. 1989). The increases appear to have been accommodated mostly by micas, as indicated by positive correlation of Li with Al_2O_3 in the enriched rocks (Fig. 4). Absorption of Li from fluids into micas is favored by relatively high mica/fluid partition coefficient for Li (Volfinger and Robert 1980).

TABLE 1. Chemical composition of metapelitic samples

Sample no.	Grade	SiO_2 wt%	TiO_2 ppm	Al_2O_3	FeO_t	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	B	Li
81-1	grt	59.9	0.66	19.4	7.16	0.08	2.5	0.33	0.95	5.61	0.12	2.3	99.01	73	95
82-1	stau	61.1	0.62	15.9	9.39	2.09	2.68	1.01	1.44	3.60	0.16	1.1	99.09	290	87
84-1	sil	69.3	0.70	14.7	5.14	0.06	1.75	0.65	1.73	3.57	0.17	1.4	99.17	70.3	252
84-2	sil	77.3	0.51	11.0	3.31	0.04	1.14	0.59	1.84	2.37	0.16	1.2	99.46	40	167
90-1	sta	64.9	0.77	16.8	6.61	0.08	2.25	0.22	0.40	5.56	0.17	1.9	99.66	125	65
95-1	grt	59.3	0.67	17.0	9.17	0.09	3.36	0.91	2.09	4.48	0.08	1.5	98.65	52	324
96-1	grt	61.6	0.72	18.0	7.5	0.50	2.65	0.64	2.35	4.18	0.13	0.8	99.07	44	93
97-1	grt	60.9	0.65	16.9	8.73	0.23	3.17	0.38	1.27	5.03	0.13	1.6	98.99	27	119
98-1	grt	62.8	0.69	16.3	7.55	0.26	2.52	0.70	2.11	4.41	0.04	1.4	98.78	98	74
99-1	grt	59.4	0.70	18.4	7.67	0.33	2.91	0.31	2.14	4.32	0.14	2.4	98.72	109	84
101-1	grt	61.3	0.70	17.5	7.62	0.58	2.38	0.76	3.74	3.02	0.13	1.5	99.23	70	71
108-1	sta	63.8	0.65	16.6	7.16	0.67	2.82	0.48	1.34	4.15	0.12	1.8	99.59	90	90
109-2	sta	62.8	0.74	16.7	6.25	0.06	2.84	0.66	1.84	5.39	0.18	1.6	99.06	118	104
110-1	sta	60.5	0.66	17.2	9.46	0.42	2.77	0.49	1.53	4.55	0.12	1.6	99.30	87	93
111-1	sta	59.3	0.79	19.7	8.04	0.10	2.94	0.41	1.17	4.66	0.15	1.7	98.96	116	125
112-1	sil	73.2	0.58	13.2	4.43	0.03	1.67	0.58	1.17	2.97	0.18	1.4	99.41	111	184
137-1	sta	61.9	0.64	18.1	6.97	0.17	2.74	0.50	1.31	4.79	0.11	1.9	99.13	74	93
138-1	sta	59.6	0.66	18.7	7.27	0.07	2.39	0.26	0.50	7.40	0.14	2.2	99.19	30	235
139-1	sta	61.3	0.67	18.1	7.21	0.15	2.83	0.46	1.13	5.08	0.11	1.9	98.94	71	103
140-1	sta	57.0	0.75	22.0	6.99	0.17	2.5	0.69	1.75	4.95	0.11	2.2	99.11	92	99
156-2	sil	56.0	0.70	23.0	7.28	0.09	2.55	0.26	0.74	5.92	0.16	2.1	98.80	52	187
157-1	sil	63.9	0.80	17.4	6.14	0.08	2.15	0.76	1.90	4.30	0.17	1.4	99.00	51	72
197-1	sta	59.5	0.81	19.7	6.87	0.15	2.71	0.64	1.03	5.33	0.16	2.8	99.70	99	131
208-1	sta	60.6	0.68	16.8	9.65	0.59	3.28	0.62	1.26	3.90	0.14	2.3	99.82	52	87
208-2	sta	59.5	0.67	17.6	8.76	0.49	2.87	0.93	2.33	3.50	0.13	2.8	99.58	73	76
209-1	grt	56.3	0.77	19.6	9.26	0.32	3.36	0.52	1.06	4.72	0.15	3.3	99.36	65	115
212-1	grt	59.7	0.75	17.9	7.78	0.66	2.56	0.58	1.43	4.55	0.13	3.7	99.74	82	88
213-2	grt	59.5	0.73	17.7	8.88	0.27	2.66	0.69	1.86	4.62	0.14	2.4	99.45	90	89
214-1	grt	61.3	0.69	15.3	10.00	1.47	2.79	1.51	1.99	2.91	0.18	1.7	99.84	58	64
215-4	grt	59.7	0.71	16.7	9.80	0.18	3.12	0.32	1.78	3.85	0.14	3.4	99.70	70	80
217-3	grt	64.7	0.75	16.3	6.12	0.09	2.38	0.34	1.31	4.38	0.04	3.3	99.71	91	68
218-1	grt	58.7	0.70	18.5	7.09	0.08	2.58	0.24	0.80	4.90	0.17	5.9	99.66	59	70
220-1	grt	65.0	0.68	16.3	5.30	0.07	2.25	0.27	1.07	4.65	0.13	3.8	99.52	93	69
222-1	bt	63.9	0.54	12.9	10.37	0.79	2.36	0.37	0.50	3.60	0.17	3.9	99.40	47	75
226-1	bt	64.5	0.64	15.6	5.80	0.39	1.44	0.14	0.46	4.36	0.14	6.0	99.47	79	85

Note: Abbreviations for metamorphic grades are: bt = below garnet-in isograd; grt = above garnet-in isograd; sta = above staurolite-in isograd; sil = above sillimanite-in isograd.

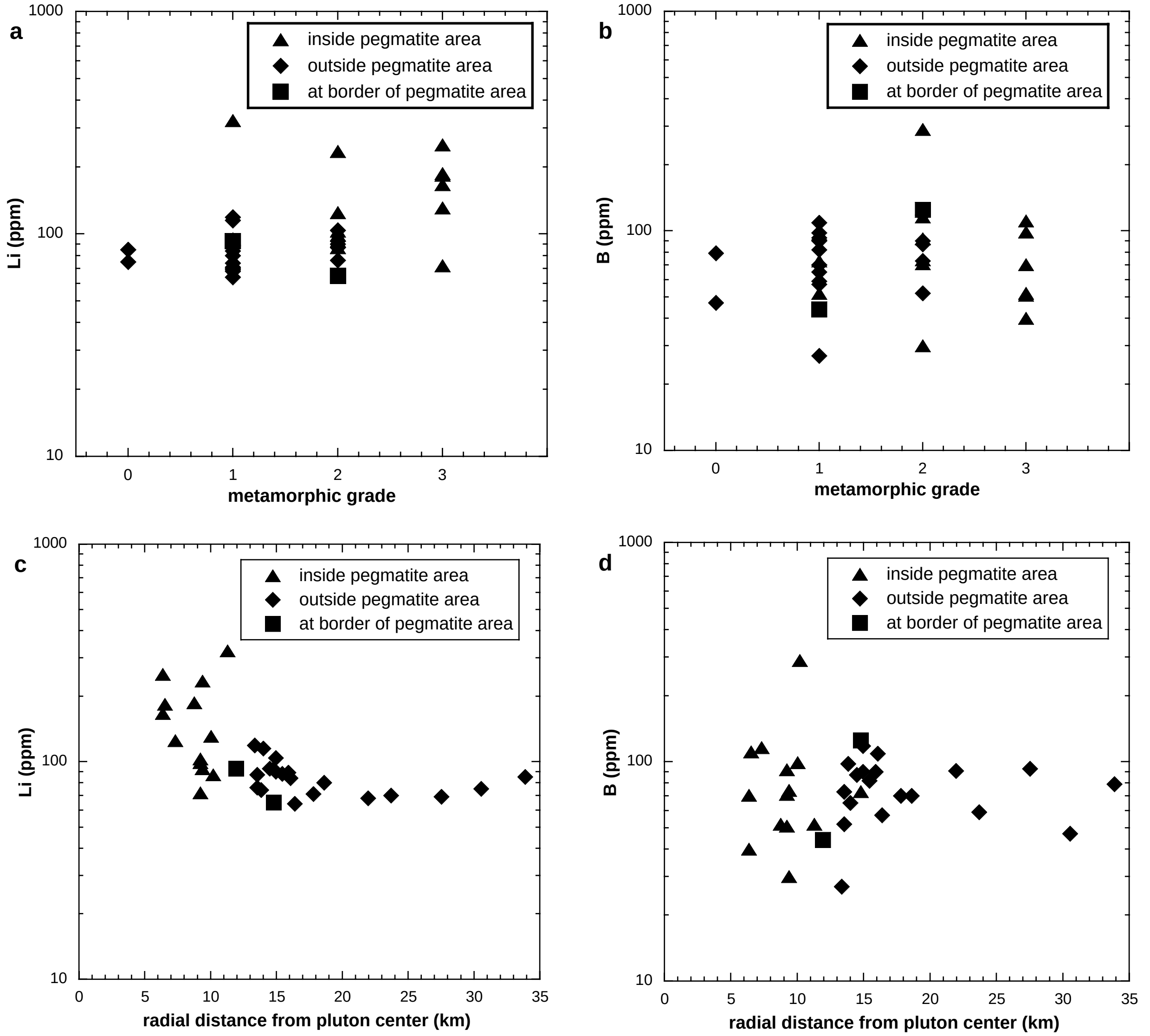
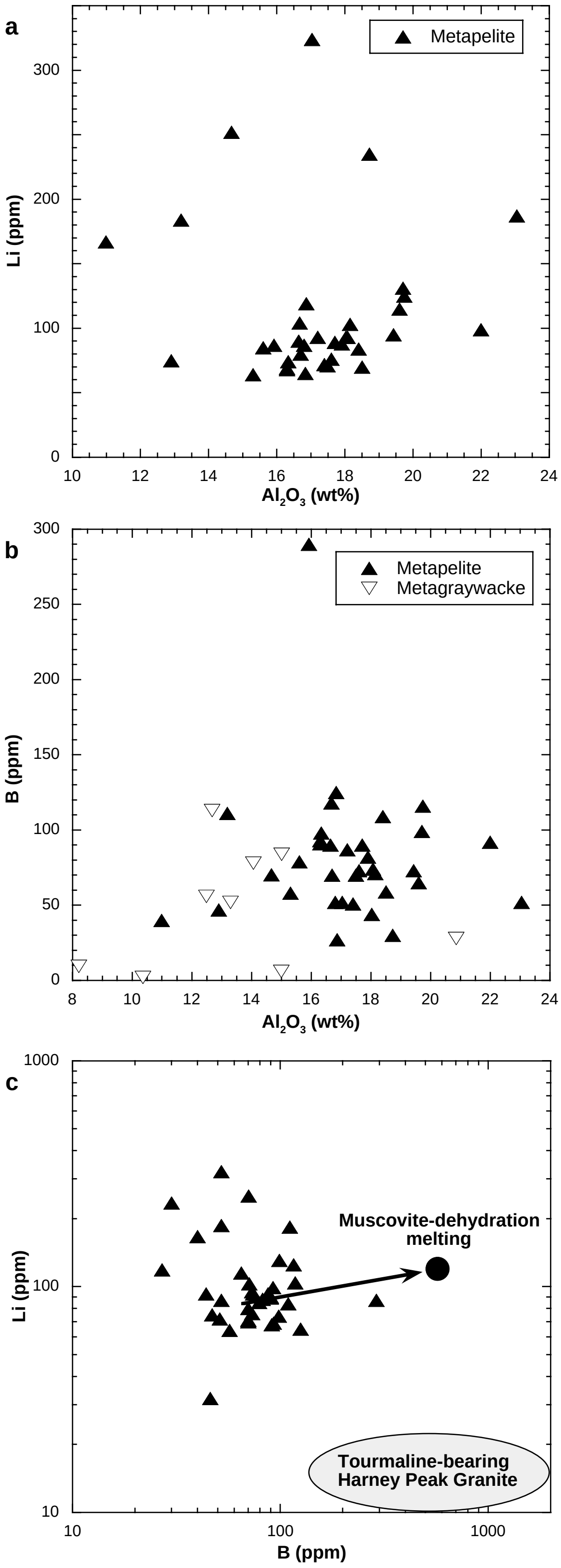


FIGURE 3. Contents of Li (**a**) and B (**b**) in metapelites plotted as a function of metamorphic grade of the samples. 0 = below garnet isograd, 1 = above garnet isograd, 2 = above staurolite isograd, 3 = above first sillimanite isograd. Contents of Li (**c**) and B (**d**) metapelites plotted as a function of the radial distance to the center of the main HPG pluton.

Mechanisms of boron exchange. In rocks outside the pegmatite field, there is no correlation of B with any major oxide, for example Al_2O_3 (Fig. 4b), indicating that none of the major phases is a significant carrier of B. Instead, the B budget of these rocks appears to be controlled by tourmaline. As shown by the alpha-track maps and optical examination, tourmaline occurs in almost all metasedimentary rocks throughout the metamorphic terrane. It may have formed during diagenesis or during incipient metamorphism from the breakdown of clay minerals or may be detrital. The random distribution of tourmaline suggests that it may be detrital.

The enrichment of B in several samples from the granite-pegmatite zone (Fig. 3) is expected, because B is also quite soluble in aqueous fluids that emanate from granite melts (Pichavant 1981). However, the length-scale of B mobility through metapelites is much shorter than that of Li (Duke 1985), perhaps because introduction of B into biotite-containing wall rocks leads to tourmalinization, whereas no mineral in which Li is an essential structural constituent crystallizes in metapelites. Thus, the gain of B in a few of the analyzed samples may be related to tourmalinization, which is commonly observed in aureoles of pegmatites (e.g., Galbreath et al. 1988). Tourmalinization generally occurs in the presence of neutral to acidic solutions (Morgan and London 1989). A plausible tourmalinization reaction is

$$\begin{gathered}K(Fe, Mg)_3AlSi_3O_{10}(OH)_2 + 1.67\ KAl_2AlSi_3O_{10}(OH)_2 \\ + NaCl(aq) + 1.67\ HCl(aq) + 3\ B(OH)_3(aq) \rightarrow \\ Na(Fe,Mg)_3Al_6B_3O_9Si_6O_{18}(OH)_4 + 2\ SiO_2 + 2.67\ KCl(aq) \\ + 6\ H_2O. \qquad (4)\end{gathered}$$



◀**FIGURE 4.** (**a**) A plot of whole-rock values of Li vs. Al_2O_3 in metasedimentary rocks. (**b**) A plot of whole-rock values of B vs. Al_2O_3 in metasedimentary rocks. (data for metagraywackes from Nabelek and Bartlett 1998). (**c**) A plot of whole-rock concentrations of Li vs. B indicating the lack of correlation of the two elements. Also shown is the B and Li content of a model melt calculated assuming muscovite-dehydration melting of the average Black Hills metapelite. For comparison, the range in the Harney Peak Granite is also shown (B contents in granite from Nabelek et al. 1992a).

However, most rocks in the granite-pegmatite aureole appear to have lost B (Fig. 3). Although Tawakami (2001) ascribed disappearance of tourmaline in the Ryoke metamorphic belt, Japan, to a melt-forming reaction, in the Black Hills, the decrease in B already occurs outside the second-sillimanite zone and, therefore, is probably not related to partial melting. It is more likely that tourmaline was consumed during interaction of the rocks with alkalic fluids (cf., Morgan and London 1989). Raman-spectroscopic analysis of daughter minerals in fluid inclusions in some pegmatites and quartz veins in the Black Hills high-grade metamorphic rocks indicates the presence of sodium carbonate minerals, including dawsonite [$NaAlCO_3(OH)_2$] and nahcolite ($NaHCO_3$) (Sirbescu and Nabelek 2001; Huff and Nabelek, unpublished data). The presence of these minerals suggests that in some cases, fluids emanating from the pegmatites and flowing through the high-grade metamorphic rocks may have been alkalic. Thus, tourmaline may have become unstable, perhaps due to a reaction such as

$$2\ Na(Fe,Mg)_3Al_6B_3O_9Si_6O_{18}(OH)_4 + K_2CO_3(aq) + 6\ H_2O \rightarrow 2\ K(Fe,Mg)_3AlSi_3O_{10}(OH)_2 + 5\ Al_2SiO_5 + SiO_2 + Na_2CO_3(aq) + 6\ B(OH)_3(aq). \quad (5)$$

This reaction produces sillimanite, which, as was demonstrated using alpha-track imaging, contains significant B concentrations above the first-sillimanite isograd. Boron may have been incorporated into the sillimanite directly from the tourmaline or from the aqueous fluid. Rocks within the pegmatite aureole also lost significant amounts of graphite due to interaction with aqueous fluids that emanated from the intrusions (Nabelek et al. 2001b). The loss of graphite may have contributed to the loss of B, if it was a significant host for B.

Origin of B and Li in the Harney Peak Granite

The measured B and Li contents in the metapelites permit calculation of B and Li concentrations in melts produced by dehydration-melting reactions. The best evidence linking the metasedimentary rocks to the granites comes from major, trace element, and isotopic data (Nabelek and Bartlett 1998, 2000). The tourmaline- and biotite-bearing HPG suites have distinct isotopic ratios of O, Pb, and Nd (Nabelek et al. 1992b; Krogstad et al. 1993; Krogstad and Walker 1996); therefore, the two suites cannot be related by fractional crystallization, as has been proposed for other similar biotite and tourmaline-bearing leucogranite suites (Scaillet et al. 1990).

Aside from the difference in isotopic ratios, a major difference between the tourmaline-bearing and biotite-bearing HP granites is their contrasting B/TiO_2 ratios (Nabelek et al. 1992a).

Higher ratios in the tourmaline-bearing suite are thought to indicate that it was generated by the muscovite-dehydration melting reaction only. In contrast, lower B/TiO_2 ratios in the biotite-bearing suite, partially due to significantly higher TiO_2 concentrations, are thought to indicate melting reactions that also involved biotite, the primary host for Ti in high-grade metapelites (Nabelek et al. 1992a). Muscovite-dehydration melting of metapelites leads to low degrees of partial melting, which is necessary to reach enrichment of B that is consistent with the B concentrations in the tourmaline-bearing suite.

The calculation of B and Li contents in a partial melt formed by muscovite-dehydration melting can be estimated using mass-balance approaches (Nabelek and Bartlett 2000). The B content of the average metapelite is taken to be 80 ppm, with tourmaline the dominant host phase. During the muscovite-dehydration melting reaction

$$KAl_2AlSi_3O_{10}(OH)_2 + NaAlSi_3O_8 + SiO_2 \rightarrow \text{melt} + Al_2SiO_5 \quad (6)$$

tourmaline is also assumed to break down. Breakdown of tourmaline during melting is supported by its confinement to leucosomes in migmatites above the second-sillimanite isograd. The melt fraction produced by reaction 6 from the average Black Hills metapelite is 14 wt% (Nabelek and Bartlett 2000). Even though residual biotite and sillimanite could retain some B, it has much higher solubility in the melt (Wolf and London 1997). Therefore, the residue/melt partition coefficient for B can be assumed to be much less than 1 and the concentration of B in the partial melt is given by C_0/F, where C_0 is the initial B concentration and F is the fraction of melting. The calculated B concentration in the model melt is 570 ppm. Comparison of the calculated B concentration with the B contents in the tourmaline-bearing HPG suite (Fig. 4c) shows that it is possible to produce similar concentrations by the low degrees of melting that is allowed by the mineralogy of the metapelites. A value of 570 ppm B is equivalent to about 2 wt% of tourmaline in the rock, which is a substantial amount. Some rocks in the tourmaline-bearing suite have higher modal proportions. They reflect fractional crystallization of the magma.

The only feasible Li-bearing mineral in the residue after muscovite-dehydration melting is biotite (Nabelek and Bartlett 2000). The average residue after melting of the Black Hills schists would have contained 36% biotite. The distribution coefficient of Li between biotite and a peraluminous melt (D_{Li}) ranges from 1.0 to 1.6 (Icenhower and London 1995). The concentration of Li in the partial melt (C_{l}) is given by

$$C_{\mathrm{l}} = \frac{C_o}{X_{\mathrm{bt}} D_{\mathrm{Li}} (1 - F) + F} \quad (7)$$

where X_{bt} is the proportion of biotite. Therefore, assuming that the initial concentration of Li in the source rocks was 80 ppm, the partial melt should contain between 120 to 180 ppm. Li concentrations in the tourmaline-bearing HPG are an order of magnitude smaller than this amount (Fig. 4c). Thus, the metapelites in the Black Hills have more than sufficient amounts of Li to explain its concentration in the granite. A reason for the low abundance in the tourmaline-bearing suite may be that no major Li-hosting phase was stable during crystallization of the magma. The amount of crystallized tourmaline was apparently insufficient to retain all the Li in the rocks. Much of the Li was apparently lost to the surrounding country rocks as evident in the elevated Li concentrations within the pegmatite aureole. It is noted, however, that local metasomatic Li haloes also occur near spodumene-bearing pegmatites in the Black Hills (Galbreath et al. 1988).

Stability of tourmaline in leucogranites

The results of the calculations show that it is possible to produce B and Li contents of the tourmaline-bearing HPG during partial melting of metapelites. However, our interpretation that the calculated amount of B is sufficient for crystallization of tourmaline in the leucogranite magma seems to disagree with some experimental studies, which appear to imply at least one order-of-magnitude higher B concentrations in melts than we have calculated are necessary to induce crystallization of tourmaline.

There are two potential problems with application of experimental results to natural leucogranites and pegmatites. First, Scaillet et al. (1995) observed that in their experiments, tourmaline never crystallized spontaneously unless the experimental charges were seeded with tourmaline. Thus, the inability of tourmaline to nucleate easily may lead to misleading results. Indeed, in leucogranite-pegmatite systems, tourmaline primarily occurs either in aplitic layers, which probably represent strongly undercooled magmas after intrusion into host rocks, or in pegmatitic sills, in which it nucleates heterogeneously on wall rocks or other substrates to form radiating spherulitic crystals.

The second, and potentially more serious problem is that in most experimental studies on tourmaline saturation, there was another mineral, usually biotite, competing for Fe and Mg (Holtz and Johannes 1991; London et al. 1994; London and Manning 1995; Wolf and London 1997). Bénard et al. (1985) found that saturation of felsic peraluminous magmas in tourmaline in the absence of other ferromagnesian minerals occurred at levels significantly below 1 wt% B_2O_3. Therefore, competition with biotite seems to be a crucial parameter for controlling the stability of tourmaline. As demonstrated by Patiño-Douce (1993), the stability of biotite is considerably enhanced by Ti, which was the case for the biotite-bearing HPG suite that has TiO_2 concentrations relative to FeO + MgO + Al_2O_3 higher than the tourmaline-bearing suite, in which TiO_2 concentrations are <0.04 wt% (Nabelek et al. 1992a). There is no other Ti-bearing mineral in either granite suite besides biotite. Because there was lack of competition for Fe and Mg in the tourmaline-bearing suite, tourmaline was free to crystallize. The relationship between TiO_2 concentration of whole rocks and the relative stability of biotite and tourmaline is illustrated well by an ATF diagram (Fig. 5a), which shows that biotite-bearing HP granites fall close to the Ti apex between the projected position of muscovite and biotite, whereas the tourmaline-bearing rocks fall closer to the A-F join between the projected position of muscovite and tourmaline. The same relationship between TiO_2 and the relative abundance of biotite and tourmaline exists in the High Himalayan Gangotri leucogranite (Scaillet et al. 1990). The biotite- and tourmaline-bearing suites have similar A/F ratios, suggesting that the ratio

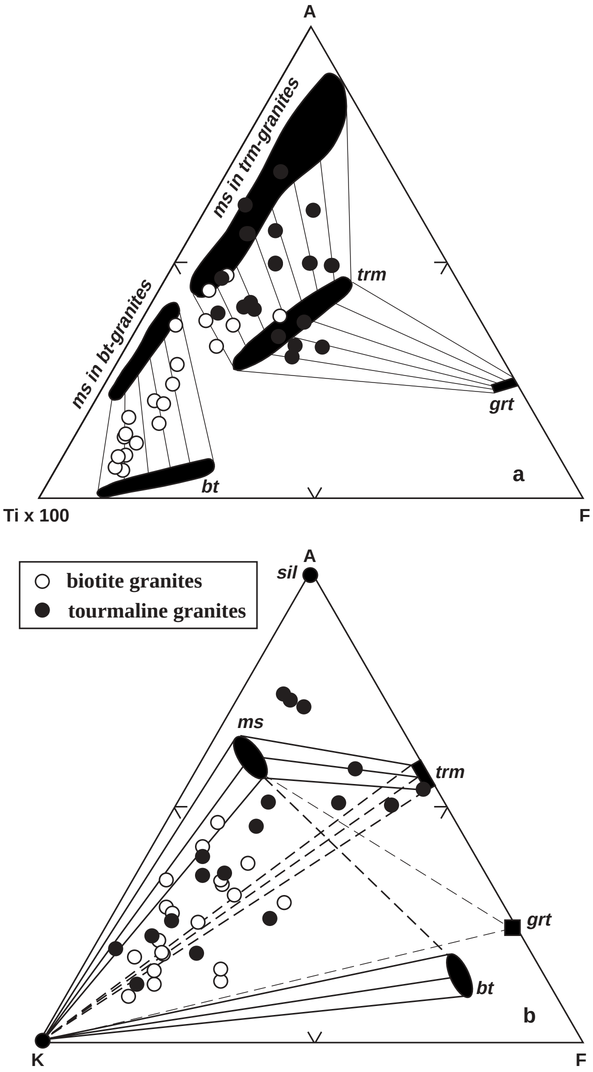


FIGURE 5. ATF and AKF diagrams showing the compositions of biotite- and tourmaline-bearing HPG whole-rock samples and constituent minerals (after Nabelek et al. 1992a). (**a**) The components in the diagram are, on molar basis, A = Al_2O_3-CaO-Na_2O-K_2O, T = $TiO_2 \times 100$, F = FeO_{tot} + MgO + MnO. The tourmaline-bearing granites have lower concentrations of TiO_2 and are bounded by low-Ti muscovite found in these granites, tourmaline, and, in high-Mn samples, almandine-spessartine garnet. The biotite-bearing granites have overall higher proportion of TiO_2 and most are bounded by biotite and high-Ti muscovite that occurs in these samples. Only a few biotite-containing samples contain low-Ti muscovite and biotite. (**b**) The components in the diagram are A = Al_2O_3-CaO-Na_2O-K_2O, K = K_2O, F = FeO_{tot} + MgO + MnO. The majority of the tourmaline and biotite-bearing samples define the same field in this diagram. The four samples falling near tourmaline have accumulations of tourmaline and the three samples above the muscovite and tourmaline join contain sillimanite.

is not a major factor in controlling the stability of the two phases. On the basis of their experiments, Wolf and London (1997) and London (1999) suggested that the ASI may play a role in controlling the stability of tourmaline. That was not the case in the HPG where both suites have virtually the same range of ASI (biotite suite: 1.08–1.31; tourmaline suite: 1.09–1.42) and have the same range of projected AKF compositions (Fig. 5b).

Scaillet et al. (1995) and Pichavant et al. (1996) suggested that an increase in f_{O_2} during crystallization of a magma may promote stabilization of tourmaline relative to biotite. Although this alternative may be feasible in some cases, it is inconsistent with field evidence from the Black Hills where tourmaline co-exists in many cases with massive graphite in fracture-filling veins cutting through the granites, and the tourmaline-bearing suite is surrounded by the graphitic metapelites. There is no evidence for a difference in the oxidation state of the biotite- and tourmaline-bearing suites and no reason why a difference should exist.

Isotopic evidence against an evaporitic or other similar high-B sources and lack of a significant amount of tourmalinization in the aureole of the HPG, which would indicate a massive loss of B, lead us to conclude that the amount of B incorporated into the magma during partial melting of metapelites was sufficient to induce crystallization of tourmaline. In the biotite-bearing suite, crystallization of biotite instead of tourmaline was promoted by higher TiO_2 concentrations in the melt.

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