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MAGNESIOFOITITE FROM THE URANIUM DEPOSITS OF THE ATHABASCA BASIN, SASKATCHEWAN, CANADA

Philip E. ROSENBERG[§] and Franklin F. FOIT, Jr.

Department of Geology, Washington State University, Pullman, Washington 99164, U.S.A.

Abstract

Two generations of tourmaline have been observed in the matrix of altered breccias associated with the uranium deposits of the Athabasca Basin, Saskatchewan, Canada. The earlier tourmaline occurs as isolated crystals, whereas the later stage is represented by radial (or spherulitic) aggregates of fibrous crystals or overgrowths on earlier tourmalines. Tourmaline in associated veins closely resembles the late-stage tourmaline in the matrix of brecciated rocks. Atom proportions (based on electron-microprobe data) normalized to 15 $Y + Z + T$ cations suggest that the earlier tourmaline is partially deprotonated, whereas the late-stage tourmaline is highly alkali-deficient. Assuming a stoichiometric content of boron, the structural formulas calculated for early and late-stage tourmalines from Rabbit Lake (sample R81) are: $Na_{0.48}K_{0.01}Ca_{0.51}$ $(Mg_{2.48}{Fe^{3+}}_{0.21}Mn_{0.01}Ti_{0.24})$ $Al_{5.34}{Fe^{3+}}_{0.66}$ $(Si_{6.06})O_{18}(BO_3)_3(OH)_{2.68}$ and $\square_{0.76}Na_{021}K_{0.01}Ca_{0.02}$ $(Mg_{2.15}{Fe^{3+}}_{0.05}Al_{0.80})$ $Al_{6.00}$ $(Si_{5.89}Al_{0.11})O_{18}(BO_3)_3(OH)_{4.01}$. Similar compositions have been observed at the Second Link Lake and Key Lake uranium deposits. Early-stage tourmalines consist of proton-deficient dravite, whereas the late-stage tourmalines are close to the magnesiofoitite end-member of the tourmaline group.

Keywords: tourmaline, dravite, magnesiofoitite, electron-microprobe data, Athabasca Basin, Saskatchewan.

Sommaire

Il y a deux générations de tourmaline dans la matrice des brèches altérées associées aux gisements d'uranium du bassin d'Athabasca, au Saskatchewan, Canada. La tourmaline précoce se présente en cristaux isolés, tandis que les cristaux tardifs sont représentés par des aggrégats fibroradiés (ou sphérulitiques) de cristaux ou des surcroissances sur les cristaux précoces. La tourmaline dans les veines associées ressemble étroitement à la tourmaline de la matrice des roches bréchifiées. La proportion des atomes, calculée à partir de données obtenues avec une microsonde électronique normalisées sur une base de 15 cations $Y + Z + T$, montre que la tourmaline précoce est partiellement dépourvue de protons, tandis que la tourmaline tardive est fortement dépourvue d'alcalins. Si on suppose une proportion stoechiométrique de bore, les formules structurales calculées pour les deux générations de tourmaline au gisement de Rabbit Lake (échantillon R81) sont: $Na_{0.48}K_{0.01}Ca_{0.51}$ $(Mg_{2.48}{Fe^{3+}}_{0.21}Mn_{0.01}Ti_{0.24})$ $Al_{5.34}{Fe^{3+}}_{0.66}$ $(Si_{6.06})O_{18}(BO_3)_3(OH)_{2.68}$ et $\square_{0.76}Na_{021}K_{0.01}Ca_{0.02}$ $(Mg_{2.15}{Fe^{3+}}_{0.05}Al_{0.80})$ $Al_{6.00}$ $(Si_{5.89}Al_{0.11})O_{18}(BO_3)_3(OH)_{4.01}$. Des compositions semblables ont été observées aux gisements d'uranium de Second Link Lake et Key Lake. Les tourmalines précoces correspondent à une dravite déficitaire en protons, tandis que les tourmalines tardives se rapprochent du pôle magnésiofoïtite du groupe des tourmalines.

(Traduit par la Rédaction)

Mots-clés: tourmaline, dravite, magnésiofoïtite, données de microsonde électronique, bassin d'Athabasca, Saskatchewan.

Introduction

Dravitic tourmaline has been reported at several unconformity-type uranium deposits within the Athabasca Basin, Saskatchewan, Canada (Kotzer & Kyser 1995, Wilson & Kyser 1987, Hoeve & Sibbald 1978). Bulk analyses of these altered rocks by Hoeve & Sibbald (1978) show low concentrations of Na, K and Ca cations, which normally occupy the alkali site in dravite. Therefore, it seemed likely that the tourmaline in these rocks might be alkali-deficient. Five samples were obtained for this study, two from the deposit at Rabbit Lake, two from Second Link Lake and one from Key Lake.

Two generations of dravitic tourmaline were first reported from the Rabbit Lake uranium deposit by

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[§] *E-mail address*: rosenberg@wsu.edu

Hoeve & Sibbald (1978) and later studied by Rosenberg & Foit (1986). The earlier tourmaline was found to be only slightly alkali-deficient, but the later generation of tourmaline that occurs as radial or spherulitic aggregates of very fine fibrous crystals were found to have about two-thirds of the alkali sites vacant. Since then, Hawthorne *et al.* (1999) have described a similar, highly alkali-deficient dravite from Japan as a new mineral species, magnesiofoitite, with a theoretical end-member composition $\square(Mg_2Al)Al_6Si_6O_{18}(BO_3)_3(OH)_4$.

This investigation represents a further, more detailed study of dravitic tourmaline from the Rabbit Lake, the adjacent Second Link Lake and the Key Lake deposits in the Athabasca Basin.

OCCURRENCE

The Rabbit Lake, Second Link Lake and Key Lake uranium deposits are located at the eastern edge of the Athabasca Basin (Fig. 1), close to the unconformity between metamorphosed Precambrian basement and the overlying unmetamorphosed Proterozoic Athabasca Formation. Uranium mineralization occurs in brecciated meta-arkose within the Wollaston Lake fold belt on the

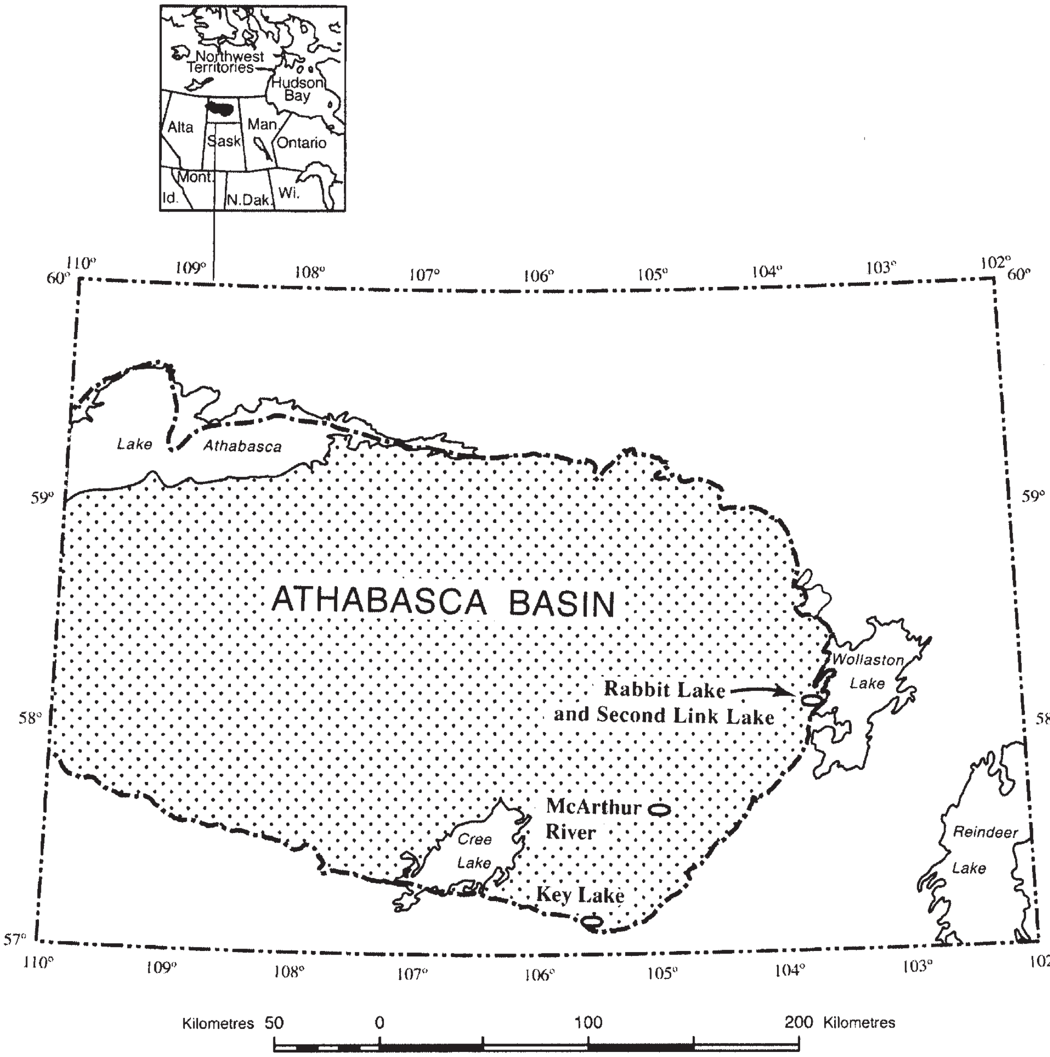

FIG. 1. Map of the Athabasca Basin. Two generations of dravite occur at the Rabbit Lake deposit, the immediately adjacent Second Link Lake deposit, and at the Key Lake deposit, as well as in the McArthur River District. The map is modified after Kotzer & Kyser (1995) and Denner (1978).

hanging wall of a thrust fault near the unconformity (Hoeve & Sibbald 1978). Two major episodes of alteration, an earlier "red alteration" and a later "pale green alteration", separated by a brecciation event and by the emplacement of euhedral quartz veins, accompanied the mineralization. Both episodes of alteration involved chloritization and crystallization of tourmaline, which may comprise up to 20% of the matrix in brecciated rocks (Hoeve & Sibbald 1978). Red, altered, chloritized breccias are composed essentially of Mg-rich, nearly colorless chlorite, which replaces both feldspars and mafic minerals. The chlorite is accompanied by small amounts of epidote, quartz and brown tourmaline that commonly are surrounded by oriented overgrowths of colorless tourmaline. Dravitic tourmaline also occurs in very fine radiating spherulitic aggregates, which tend to be concentrated in clusters (Hoeve & Sibbald 1978). The complex mineralogy and paragenesis of these deposits have been described in detail by Hoeve & Sibbald (1978).

Two apparent generations of dravitic tourmaline have also been recognized in the McArthur River District (Fig. 1), an altered detrital dravite and an "alkali-free" dravite (Quirt *et al.* 1991). These dravitic tourmalines are associated with hydrothermal alteration in areas of intense fracturing (Kotzer & Kyser 1995). They occur in a mineral assemblage of illite, euhedral quartz, Mg,Al chlorite and hematite containing varying amounts of uranium minerals. Two types of tourmaline were recognized: (1) tourmaline intergrown with euhedral quartz in the matrix of the altered breccias, and (2) late tourmaline infilling fractures and pore spaces. Electron micrographs of radial to spherulitic aggregates of late-stage tourmaline are shown in Kotzer & Kyser (1995). These tourmalines are thought to have formed at temperatures ≤200°C in the Athabasca Basin (Wilson & Kyser 1987, Kotzer *et al.* 1993, Kotzer & Kyser 1995). In a recent paper, Kister *et al.* (2005) considered thermodynamic constraints on fluid composition in the Athabasca Basin deposits and further constraints on the crystallization of alkali-deficient tourmaline to 150–180°C and 0.6–1.4 kbar based on fluid-inclusion data. They noted that alkali-deficient tourmaline was probably generated during the mixing of fluids associated with the deposition of U ore.

MINERALOGY AND TEXTURAL RELATIONS OF THE SAMPLES

Five hydrothermally affected tourmaline-bearing rock samples were studied, two from the Rabbit Lake (R81 and R77) deposit, two from the Second Link Lake (SL 23 and SL35) deposit and one from the Key Lake (K79) deposit. The Rabbit Lake and Second Link Lake samples are associated with the red alteration zone in a massive meta-arkose (Hoeve & Sibbald 1978), which is characterized by the presence of hematite and high Fe^{3+}/Fe^{2+} values. Hematite also is associated with dravitic tourmaline in the Key Lake deposit (Wilson & Kyser 1987). Under the microscope, the appearance of the late-stage tourmaline is very similar to that described by Hawthorne *et al.* (1999) from the Kyonosawa area, Honshu, Japan.

Sample R81

Highly altered (chloritized), fine-grained granite (pale green alteration partially superimposed on pervasive red alteration) is transected by a very fine-grained tourmaline-rich vein composed almost entirely of colorless late-stage tourmaline occurring as radiating, spherulitic and fibrous aggregates. Individual crystals of late-stage tourmaline average ~3 μm in width and 30 μm in length in all samples. Quartz, hematite and subhedral, early-stage tourmaline are accessory minerals in the vein.

Sample R77

Highly altered (chloritized), hematite-pigmented granite (red alteration) is transected by tourmaline-rich veinlets mainly composed of very fine, radial aggregates of colorless tourmaline. Earlier crystals of brown tourmaline up to 0.1 mm in diameter, overgrown by later tourmaline, are a minor component of the veins.

Samples SL23 and SL35

Hematite-pigmented, altered breccia has a tourmaline-rich matrix (Fig. 2). Two generations of tourmaline are evident. The earlier, subhedral, brown tourmaline (~0.1 mm) is surrounded by later aggregates of radial or fibrous tourmaline, commonly occurring in clusters, which comprise up to 85% of the matrix (SL35, Fig. 3). The remainder of the matrix is composed of the earlier brown tourmaline, chlorite, hematite and epidote transected by quartz veinlets.

Sample K 79

Altered (pale green superimposed on pervasive red alteration), medium-grained sandstone is transected by a fine-grained, tourmaline-rich vein. The sandstone consists of subhedral quartz with accessory subhedral brown tourmaline and zircon, which occupy interstitial spaces between quartz grains. The tourmaline-rich vein contains fine-grained (<2 μm), radiating spherulitic and unoriented aggregates of colorless tourmaline.

CHEMICAL COMPOSITION OF THE SAMPLES

Partial electron-microprobe analyses (Na, K, Ca, Mg, Mn, Fe, Ti, Al, Si; F not observed) and calculated structural formulas of early and late tourmaline from the Rabbit Lake, Second Link Lake and Key deposits are given in Tables 1, 2 and 3, respectively. Oxide totals of the late tourmaline are slightly low in some cases owing to voids in the aggregates of spherulitic and fibrous tourmaline. Only one acceptable composition could be obtained for late tourmaline from Key Lake owing to the extremely small size of the aggregates. Inasmuch as rocks subjected to red alteration are highly oxidized and have high Fe^{3+}/Fe^{2+} values (Hoeve & Sibbald 1978), iron has been calculated as Fe^{3+}. Early tourmaline is significantly lower in Al and higher in Na, K and Ca than late tourmaline, reflecting the change in bulk composition of the host rocks due to alteration (Hoeve & Sibbald 1978).

FIG. 2. Altered breccia, sample SL 35. Dravitic tourmaline comprises as much as 20% of the matrix. Marked divisions are centimeters.

Structural formulas were calculated from these analytical data by assuming that: a) Al supplements Si to fill the tetrahedral site, b) the remaining Al preferentially fills the smaller Z octahedral site, c) excess Al occupies the larger *Y* octahedral site that is usually filled by Mg, Fe and other cations, and d) excess Mg (if any) enters the alkali site along with all available Na, K and Ca.

Calculation of atomic proportions assuming stoichiometric B and (OH) contents (31 anions O, OH) gave structural formulas that are alkali-site-deficient. Samples of late-stage tourmaline have a high Al-content and are highly alkali-deficient. However, in some cases, significant numbers of Ca ions are required to fill the *Y* sites, an unlikely scenario. To restrict Ca to its usual occupancy in the *X* site and to test the possibility of deprotonization, atomic proportions have been recalculated on the basis of 15 (Si, Ti, Al, Fe^{3+}, Mg, Mn) cations in the $Y + Z + T$ sites. Site assignments now suggest that the early tourmaline from Rabbit Lake and Second Link Lake (Tables 1, 2) is deprotonated but not alkali-deficient, whereas all late-stage tourmaline appears to be fully protonated but highly alkali-deficient (Tables 1, 2 and 3), approaching the composition $\square_{0.79}Na_{0.21}(Mg_{1.44}Al_{1.42}Fe_{0.23})Al_6Si_6(BO_3)_3(OH)_4$ reported by Hawthorne *et al.* (1999), that suggested the existence of the magnesiofoitite end-member $\square(Mg_2Al)Al_6Si_6$

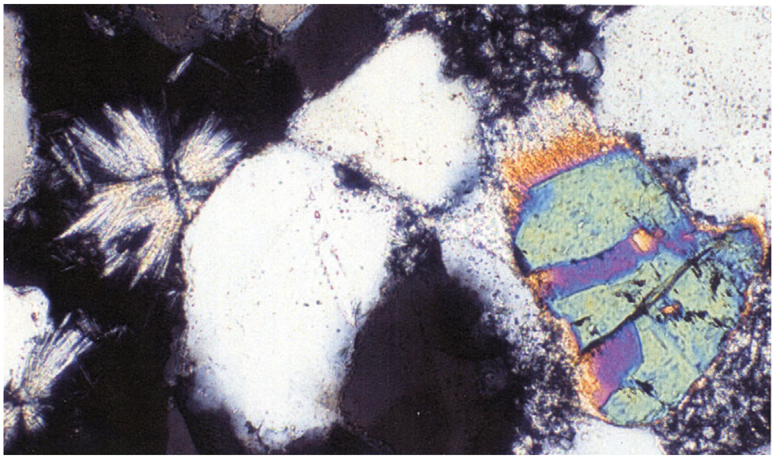

FIG. 3. Thin section, sample SL 23, 100×, crossed polars. There are two generations of tourmaline. The early grain (0.15 mm) has a high birefringence; the late tourmaline (~3 μm) is developed in radial, felted aggregates and as oriented overgrowths on partially resorbed, early tourmaline. Clusters of fine-grained aggregates of late tourmaline are present in the lower right corner and along the upper margin. The remaining grains are quartz.

$O_{18}(BO_3)_3(OH)_4$. Early-stage tourmaline from Key Lake (Table 3) is both deprotonated and somewhat alkali-site-deficient. Inasmuch as the calculated atomic proportions are not very precise, owing to the small size of individual crystals of the late-stage tourmalines and the assumption that all iron is in the ferric state, atom proportions based on 15 $Y + Z + T$ cations are believed to give a more accurate estimate of the structural formulas of tourmalines in the Athabasca Lake suite.

DISCUSSION

Substitutional relations in the tourmaline from the Rabbit Lake, Second Link Lake and Key Lake deposits are analogous to those in the foitite from the tourmaline–dumortierite deposits of Jack Creek, Montana and Ben Lomond, Australia, described by Foit *et al.* (1989). There, three substitutions, 1) $R^+ + R^{2+} = R^{3+} + {}_X\square$, 2) $Si^{4+} + R^{2+} = {}_YR^{3+} + {}^{IV}Al^{3+}$, and 3) $Si^{4+} + {}_X\square = R^+ +$

TABLE 1. CHEMICAL COMPOSITIONS OF TOURMALINE FROM RABBIT LAKE, SASKATCHEWAN

Sample No. of anal.	R81: Early 10	R81: Late 14	R77: Early 19	R77: Late 16
SiO_2 wt. %	36.64 (0.27)	36.97 (0.76)	36.92 (0.52)	35.98 (1.26)
TiO_2	1.91 (0.16)	0.03 (0.04)	2.33 (0.62)	0.01 (0.02)
Al_2O_3	27.39 (0.15)	36.81 (0.83)	28.44 (0.89)	38.77 (0.78)
Fe_2O_3	6.97 (0.16)	0.39 (0.14)	3.14 (0.22)	0.36 (0.10)
MgO	10.05 (0.10)	9.04 (0.22)	11.26 (0.16)	9.84 (0.47)
MnO	0.05 (0.09)	0.02 (0.03)	0.01 (0.12)	0.03 (0.04)
CaO	2.86 (0.11)	1.73 (0.04)	1.73 (0.29)	0.12 (0.06)
Na_2O	1.48 (0.11)	0.68 (0.08)	2.15 (0.24)	0.74 (0.07)
K_2O	0.06 (0.02)	0.03 (0.04)	0.02 (0.02)	0.01 (0.01)
Anal. total	87.41 (0.38)	84.07 (1.44)	86.00 (0.87)	85.86 (1.91)
B_2O_3*	10.78	11.03	10.78	11.10
H_2O*	3.72	3.81	3.72	3.83
Total	101.91	98.91	100.49	100.79

		R81 Early	R81 Late	R77 Early	R77 Late	R81 Early	R81 Late	R77 Early	R77 Late
		Atom proportions based on 31 anions (O, OH)				based on 15 cations[§] at $Y + Z + T$ sites			
T:	Si	5.91	5.82	5.96	5.63	6.06	5.89	6.06	5.58
	Al	0.09	0.18	0.04	0.37	0.00	0.11	0.00	0.42
ΣT		6.00	6.00	6.00	6.00	6.06	6.00	6.06	6.00
	B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z:	Al	5.11	6.00	5.32	6.00	5.34	6.00	5.50	6.00
	Fe^{3+}	0.85	0.00	0.38	0.00	0.66	0.00	0.39	0.00
	Mg	0.04	0.00	0.30	0.00	0.00	0.00	0.11	0.00
ΣZ		6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y:	Al	0.00	0.66	0.05	0.79	0.00	0.80	0.00	0.67
	Ti	0.23	0.00	0.28	0.00	0.24	0.00	0.29	0.00
	Mg	2.37	2.13	1.77	2.17	2.48	2.15	2.65	2.28
	Mn	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	Fe^{3+}	0.00	0.05	0.00	0.04	0.21	0.05	0.00	0.04
	Ca	0.39	0.16	0.30	0.00				
ΣY		3.00	3.00	3.00	3.00	2.94	3.00	2.94	2.99
X:	Ca	0.10	0.13	0.00	0.02	0.51	0.02	0.30	0.02
	Mg	0.00	0.00	0.00	0.13				
	Na	0.46	0.21	0.67	0.23	0.48	0.21	0.68	0.22
	K	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00
ΣX		0.57	0.35	0.67	0.38	1.00	0.24	0.98	0.24
	□	0.43	0.65	0.33	0.62	0.00	0.76	0.02	0.76
	OH	4.00	4.00	4.00	4.00	2.68	4.01	3.11	4.43
Total charge						50.32	48.99	49.89	48.57

[§] Atom proportions based on 15 (Si, Ti, Al, Fe^{3+}, Mg, Mn) cations at $Y + Z + T$ sites.
* The amount of B_2O_3 and H_2O is calculated by stoichiometry.

TABLE 2. CHEMICAL COMPOSITIONS OF TOURMALINE FROM SECOND LINK LAKE, SASKATCHEWAN

Sample No. of anal.	SL23: Early 29	SL23: Late 10	SL35: Early 20	SL35: Late 17
SiO_2 wt. %	37.34 (0.29)	35.85 (0.68)	37.68 (0.38)	37.15 (1.34)
TiO_2	1.64 (0.32)	0.04 (0.05)	0.81 (0.30)	0.02 (0.03)
Al_2O_3	28.06 (0.70)	36.72 (1.19)	30.05 (0.97)	37.44 (0.99)
Fe_2O_3	3.12 (0.49)	0.31 (0.13)	2.68 (0.37)	0.43 (0.19)
MgO	11.46 (0.25)	9.55 (0.64)	11.34 (0.49)	9.39 (0.39)
MnO	0.02 (0.03)	0.04 (0.03)	0.03 (0.05)	0.02 (0.04)
CaO	1.78 (0.38)	0.10 (0.06)	1.95 (0.55)	0.08 (0.06)
Na_2O	2.10 (0.24)	0.75 (0.06)	2.09 (0.30)	0.74 (0.09)
K_2O	0.02 (0.02)	0.01 (0.01)	0.02 (0.02)	0.02 (0.03)
Anal. total	85.54 (0.67)	83.37 (1.36)	86.65 (0.57)	85.29 (2.06)
B_2O_3*	10.71	10.80	10.90	11.06
H_2O*	3.70	3.73	3.76	3.81
Total	99.95	97.89	101.32	100.16

		SL23 Early	SL23 Late	SL35 Early	SL35 Late	SL23 Early	SL23 Late	SL35 Early	SL35 Late
		Atom proportions based on 31 anions (O, OH)				based on 15 cations[§] at $Y + Z + T$ sites			
T:	Si	6.05	5.77	6.00	5.84	6.15	5.74	6.10	5.83
	Al	0.00	0.23	0.00	0.16	0.00	0.26	0.00	0.17
ΣT		6.05	6.00	6.00	6.00	6.15	6.00	6.10	6.00
	B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Z:	Al	5.36	6.00	5.64	6.00	5.45	6.00	5.73	6.00
	Fe^{3+}	0.38	0.00	0.32	0.00	0.39	0.00	0.27	0.00
	Mg	0.26	0.00	0.04	0.00	0.16	0.00	0.00	0.00
ΣZ		6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Y:	Al	0.00	0.74	0.00	0.78	0.00	0.67	0.05	0.75
	Ti	0.20	0.01	0.10	0.00	0.20	0.00	0.10	0.00
	Mg	2.50	2.20	2.66	2.17	2.65	2.28	2.74	2.20
	Mn	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00
	Fe^{3+}	0.00	0.04	0.00	0.05	0.00	0.04	0.06	0.05
	Ca	0.30	0.00	0.24	0.00				
ΣY		3.00	3.00	3.00	3.00	2.85	3.00	2.95	3.00
X:	Mg	0.00	0.09	0.00	0.03				
	Ca	0.01	0.02	0.09	0.01	0.32	0.02	0.34	0.01
	Na	0.67	0.23	0.65	0.23	0.67	0.23	0.66	0.23
	K	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00
ΣX		0.68	0.35	0.74	0.27	0.99	0.26	1.00	0.24
	□	0.32	0.65	0.26	0.73	0.01	0.74	0.00	0.76
	OH	4.00	4.00	4.00	4.00	3.16	4.27	3.20	4.11
Total charge						49.84	48.73	49.80	48.89

[§] Atom proportions based on 15 (Si, Ti, Al, Fe^{3+}, Mg, Mn) cations at $Y + Z + T$ sites.
* The amount of B_2O_3 and H_2O is calculated by stoichiometry.

$^{IV}Al^{3+}$, were found to account for the deviation from ideal end-member schorl, $NaFe_3Al_6(Si_6O_{18})(BO_3)_3(OH)_4$. Substitution 1) represents the solid solution between schorl and foitite, $\square Fe_3Al_6(Si_6O_{18})(BO_3)_3(OH)_4$. Substitutions 2 and 3 represent replacement of Si^{4+} by Al^{3+} in the ring of tetrahedra, with charge balance maintained by substitution of trivalent for divalent cations in the octahedral sites (2) or an increased occupancy of the alkali site (3). To these may be added the deprotonation reaction, 4) $R^{2+} + (OH)^- = R^{3+} + O^{2-}$ (Foit & Rosenberg 1977).

Early tourmaline from the Rabbit Lake and Second Link Lake deposits shows little or no deficiency in alkalis, whereas late-stage tourmaline from all deposits is highly alkali-deficient. Inasmuch as ^{IV}Al and alkali deficiency are not observed in the early tourmalines, the principal substitution involves deprotonation (4). However, the late magnesiofoitite with large alkali-site deficiencies (average = 0.76) and some tetrahedrally coordinated Al (average = 0.26 *apfu*) must involve substitutions (1) and (2). Early tourmaline from the Key Lake deposit, which is both proton- and alkali-deficient and contains significant amounts of ^{IV}Al, illustrates the effects of substitutions (1), (2) and (4).

Magnesiofoitite from Honshu, Japan, occurs as felted or radial needle-like aggregates of fibrous crystals (Hawthorne *et al.* 1999) apparently similar to those observed in the Athabasca basin uranium deposits. In order to provide a more direct comparison of the Athabasca Basin magnesiofoitite material with that from the type locality, the atomic proportions of the latter have been recalculated on the basis of 15 $Y + Z + T$ cations (Table 4). Since the associated rocks are goethite-stained, highly altered porphyritic andesite to dacite that lie along a shear zone characterized by intense acid hydrothermal alteration, iron has been recalculated as Fe^{3+}. The alkali-site deficiency is identical to that reported by Hawthorne *et al.* (1999), but the calculation of total charge suggests a slight deficiency in protons.

Although magnesiofoitite has been synthesized in alkali-free systems (Rosenberg & Foit 1979), substitution (3) may serve to stabilize compositions close to the alkali-free end-member in nature by partially mitigating the effects of substitution (1). Substitution of ^{IV}Al for Si creates valence undersaturation in the alkali cation's coordination sphere, which is compensated by increased occupancy of the alkali site (Foit *et al.* 1989), thus stabilizing the structure. Inasmuch as the magnesiofoitite reported by Hawthorne *et al.* (1999) is only slightly more alkali-site deficient than that from the Athabasca Basin, their assumption of 6 Si *apfu* is open to question. Although the ideal composition of magnesiofoitite may serve as a hypothetical end-member of the tourmaline group, the stabilizing effect of the opposing reaction, substitution (3), may preclude its existence in nature. If the hypothetical end-member composition does exist as a mineral, then it probably forms at temperatures considerably higher than the dravitic tourmaline of the Athabasca Basin. Tourmalines synthesized at higher temperatures are more alkali-site-deficient and have less substituted ^{IV}Al than those synthesized at lower temperatures (Rosenberg & Foit 1979, 1985).

TABLE 3. CHEMICAL COMPOSITIONS OF TOURMALINE K79, KEY LAKE DEPOSIT

Sample No. of anal.	Early 20		Late 1
SiO_2 wt.%	35.50	(0.43)	34.53
TiO_2	0.67	(0.16)	0.00
Al_2O_3	34.25	(0.53)	38.42
Fe_2O_3	7.77	(1.42)	0.88
MgO	5.29	(0.78)	7.63
MnO	0.03	(0.03)	0.04
CaO	1.14	(0.27)	0.20
Na_2O	1.44	(0.14)	0.62
K_2O	0.04	(0.02)	0.01
Anal. total	86.13	(0.79)	82.33
B_2O_3*	10.77		10.66
H_2O*	3.72		3.68
Total	100.62		96.67

		Early 31 anions	Late 31 anions	Early 15 cations	Late 15 cations
T:	Si	5.73	5.63	5.91	5.64
	Al	0.27	0.37	0.09	0.36
Σ*T*		6.00	6.00	6.00	6.00
	B	3.00	3.00	3.00	3.00
Z:	Al	6.00	6.00	6.00	6.00
Σ*Z*		6.00	6.00	6.00	6.00
Y:	Al	0.24	1.02	0.63	1.03
	Ti	0.08	0.00	0.08	0.00
	Mg	1.27	1.86	1.31	1.86
	Mn	0.00	0.01	0.00	0.01
	Fe^{3+}	0.94	0.11	0.97	0.11
	Ca	0.20	0.00		
Σ*Y*	2.73	3.00	2.99	3.00	
X:	Ca	0.00	0.04	0.20	0.04
	Na	0.45	0.20	0.46	0.20
	K	0.01	0.00	0.01	0.00
Σ*X*	0.46	0.24	0.67	0.24	
	□	0.54	0.76	0.33	0.76
	OH	4.00	4.00	2.44	3.96
Total charge				50.56	49.04

□: alkali (*X*)-site vacancy. Atom proportions are first calculated on the basis of 15 anions (O +OH), then on 15 (Si, Ti, Al, Fe^{3+}, Mg, Mn) cations at $Y + Z + T$ sites.
* The amount of B_2O_3 and H_2O is calculated by stoichiometry.

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TABLE 4. ATOM PROPORTIONS IN TOURMALINE* FROM HONSHU, JAPAN, ON THE BASIS OF 15 CATIONS AT THE $Y + Z + T$ SITES

T:	Si	6.00	*Y*:	Al	1.43
Σ*T*		6.00		Mg	1.44
				Fe^{3+}	0.13
	B	3.00	Σ*Y*		3.00
Z:	Al	6.00	*X*:	Na	0.21
Σ*Z*		6.00	Σ*X*		0.21
				□	0.79
				OH	3.22
			Total charge		49.78

□: Alkali (*X*)-site vacancy. * After Hawthorne *et al.* (1999).

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