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FERUVITE FROM LEPIDOLITE PEGMATITES AT RED CROSS LAKE, MANITOBA

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ABSTRACT

Feruvite occurs in the Ca-rich exocontacts of lepidolite-subtype granitic pegmatites in the Red Cross Lake pegmatite field, northeastern Manitoba. The pegmatites intrude meta-andesitic to metabasaltic host-rocks. In addition to tourmaline, exocontacts contain Cs- and Rb-rich biotite, Fe-rich muscovite, epidote, apatite, Ca-rich garnet, titanite, calcite, quartz and arsenopyrite. The tourmaline is commonly zoned, with a core of feruvite surrounded by schorl or dravite, and rimmed by uvite. The most extreme composition of feruvite analyzed is $(Ca_{0.56}Na_{0.39})_{\Sigma 0.95}$ $(Fe^{2+}_{1.96}Mg_{0.81}Li_{0.18}Ti_{0.04}Mn_{0.01})_{\Sigma 3.00}(Al_{5.31}Mg_{0.69})_{\Sigma 6.00}(BO_3)_3Si_{6.07}O_{18}$ $[(OH_{3.51})F_{0.49}]_{\Sigma 4.00}$; the *X*, *Y*, and *Z* sites are dominated by Ca, Fe and Al, respectively. Magnesium is a significant component at the *Y* and *Z* sites. In plane-polarized light, uvite and dravite are mainly pale blue or blue, and feruvite and schorl are mainly dark blue. Brown schorl and feruvite tend to be rich in Ti. The meta-andesitic and metabasaltic wallrocks provided the Fe and Ca for contact-metasomatic reactions between the wallrocks and the intruding pegmatite to produce feruvite.

Keywords: feruvite, tourmaline, granitic pegmatite, exocontact, Red Cross Lake, Manitoba.

SOMMAIRE

Nous avons découvert la feruvite dans l'exocontact calcique de pegmatites granitiques de type lépidolite dans le champ de pegmatites du lac Red Cross Lake, dans le nord-est du Manitoba. Ces pegmatites ont été mises en place dans une séquence de roches encaissantes méta-andésitiques et métabasaltiques. En plus de la tourmaline, ces zones d'exocontact contiennent une biotite riche en Cs et en Rb, une muscovite ferrifère, épidote, apatite, un grenat calcique, titanite, calcite, quartz et arsénopyrite. Les cristaux de tourmaline sont généralement zonés, avec un noyau de feruvite entouré d'une zone de schorl ou de dravite, et une bordure d'uvite. La composition la plus extrême de feruvite est $(Ca_{0.56}Na_{0.39})_{\Sigma 0.95}(Fe^{2+}_{1.96}Mg_{0.81}Li_{0.18}Ti_{0.04}Mn_{0.01})_{\Sigma 3.00}$ $(Al_{5.31}Mg_{0.69})_{\Sigma 6.00}(BO_3)_3Si_{6.07}O_{18}$ $[(OH_{3.51})F_{0.49}]_{\Sigma 4.00}$; les sites *X*, *Y*, et *Z* sont occupés surtout par Ca, Fe et Al, respectivement. Le Mg est un occupant important des sites *Y* et *Z*. En lumière polarisée en plan, l'uvite et la dravite sont généralement bleu pâle ou bleu, tandis que le schorl et la feruvite sont surtout bleu foncé. Le schorl et la feruvite bruns ont tendance à être enrichis en Ti. Les méta-andésites et les métabasaltes des parois ont fourni le Fe et le Ca nécessaires aux réactions métasomatiques dans l'exocontact entre les roches encaissantes et les pegmatites pour produire la feruvite.

(Traduit par la Rédaction)

Mots-clés: feruvite, tourmaline, pegmatite granitique, exocontact, lac Red Cross, Manitoba.

INTRODUCTION

Feruvite is a rare calcic Fe-rich tourmaline having the end-member formula $CaFe^{2+}_3(Al_5Mg)(BO_3)_3(Si_6O_{18})(OH)_4$. It was first identified in a pegmatitic tourmalinized rock and in quartz – tourmaline veins associated with a diorite intrusion on Cuvier Island, New Zealand (Grice & Robinson 1989). The term "pegmatitic" applied to the Cuvier Island locality refers to the coarse-grained texture of the hydrothermal tourmalinized rocks, and is not meant to imply that they are igneous. Recently, feruvite was found in tourmalinites and quartz – tourmaline veins associated with a gabbro intrusion in the footwall of the Sullivan Pb–Zn–Ag deposit, British Columbia (Jiang *et al.* 1996). At both localities, feruvite formed by hydrothermal replacement and tourmalinization of Ca- and Al-rich host rocks. Calcic Fe-rich tourmaline occurs in hydrothermal tourmaline breccia in an aureole at St. Austell, southwestern England, in metasedimentary rocks in St. Lawrence County, New York and Broken Hill, Australia, and in a granitic pegmatite dike in the Inner Piedmont belt, South Carolina (Plimer 1983, Mittwede 1984, Brown & Ayuso 1985, Manning 1991).

Here, we report the first occurrence of feruvite in association with rare-element-enriched granitic pegmatites, specifically in the Ca-rich exocontacts of lepidolite-subtype pegmatites at Red Cross Lake, Manitoba (Selway *et al.* 1996). Feruvite has also been found in a tourmaline-rich granitic pegmatite dike that intrudes a biotite – quartz augen gneiss from the Inner Piedmont belt, South Carolina (Mittwede 1984), but

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this pegmatite is more primitive in composition than the lepidolite pegmatites of Red Cross Lake, as it is composed of quartz, microcline, calcic plagioclase and tourmaline.

LOCALITY

The Red Cross Lake pegmatite field is located in the Oxford Lake greenstone belt of the Sachigo Subprovince, in the northwestern part of the Archean Superior Province of the Canadian Shield (Potter 1962, Jambor & Potter 1967, Trueman 1982, Chackowsky *et al.* 1985). The field consists of highly evolved pegmatitic leucogranites and a progressively fractionated suite of tourmaline-, spodumene- and lepidolite-bearing pegmatites. All of the pegmatitic rocks are mylonitized (Eby 1986), but the primary compositional features of virtually all minerals are well preserved (Černý *et al.* 1994), and the exocontacts are surprisingly well preserved.

Dikes of the lepidolite subtype are the most fractionated pegmatites known to date (Černý *et al.* 1994). In addition to dominant albite, quartz, lepidolite and K-feldspar, the pegmatites may carry subordinate spodumene + quartz pseudomorphs after petalite, and accessory tourmaline, pollucite, beryl, amblygonite, apatite, cassiterite, manganotantalite, wodginite, microlite, monazite and hafnian zircon. All internal units of the Red Cross Lake lepidolite pegmatites contain tourmaline, but the occurrence of feruvite is restricted to the exocontact assemblage that separates the pegmatites from their meta-andesitic to metabasaltic host-rocks.

The exocontacts consist dominantly of Cs- and Rb-rich biotite and tourmaline with subordinate to minor Fe-rich muscovite, epidote, apatite, garnet, titanite, calcite, quartz and arsenopyrite. The strongly zoned grains of trioctahedral mica are mainly ferroan, but locally show a slight dominance of Mg; commonly, their outer rims are highly enriched in Rb and Cs. The Al-rich garnet has Ca:Fe^{2+}:Mn (at.%) ~1:1:1 and only 0.02–0.03 atoms per formula unit (*apfu*) of Mg (unpubl. data of D.K. Teertstra). The exocontact tourmaline is fine grained, ranges in habit from euhedral to subhedral, and contains minor inclusions of primary apatite, quartz, titanite and garnet. Arsenopyrite has euhedral contacts with tourmaline, with which it may be in equilibrium. Cesium-rich biotite is interstitial to and locally fills fractures in euhedral prisms of tourmaline. Secondary calcite also is interstitial to prismatic tourmaline. Tourmaline commonly contains anhedral grains of epidote and quartz, and is strikingly zoned.

METHODS

Electron-microprobe analysis was done on a CAMECA SX–50 instrument in wavelength-dispersion mode. The beam voltage for all elements was 15 kV, with a spot diameter of 1 μm. Beam current was 20 nA for Na, Fe, Ca, Al, Si and Mg, and 30 nA for F, Mn, Zn, K, Ti and P. Counting times for peak and background determinations for all elements were 20 s and 10 s, respectively. The analytical data were reduced and corrected by the $\phi(\rho z)$ method (Pouchou & Pichoir 1984, 1985). Crystals were analyzed using $K\alpha$ lines from the following standards: albite (Na), fayalite (Fe), diopside (Si, Ca), kyanite (Al), spessartine (Mn), olivine (Mg), orthoclase (K), fluor-riebeckite (F), titanite (Ti), apatite (P) and gahnite (Zn).

TABLE 1. REPRESENTATIVE COMPOSITIONS OF FERUVITE FROM RED CROSS LAKE

	1	2	3	4
SiO_2, wt%	35.30	34.90	35.70	34.90
TiO_2	0.35	0.44	0.27	0.07
Al_2O_3	26.20	27.10	27.60	27.00
B_2O_3*	10.11	10.09	10.26	10.08
MgO	5.84	5.27	5.89	6.20
CaO	3.01	2.76	2.80	2.88
MnO	0.09	0.10	0.07	0.05
FeO	13.60	13.60	12.30	12.90
Li_2O*	0.26	0.16	0.31	0.07
Na_2O	1.18	1.25	1.29	1.25
H_2O*	3.06	3.12	3.06	3.20
F	0.90	0.76	1.02	0.58
O=F	-0.38	-0.32	-0.43	-0.24
Total	99.52	99.23	100.13	98.94
Cell contents normalized to 31 anions				
Si, *apfu*	6.07	6.01	6.05	6.02
Al	5.31	5.50	5.51	5.49
Mg	0.69	0.50	0.49	0.51
$\sum Z$	6.00	6.00	6.00	6.00
Ti	0.04	0.06	0.03	0.01
Mg	0.81	0.86	1.00	1.08
Mn	0.01	0.01	0.01	0.00
Fe	1.96	1.96	1.74	1.86
Li	0.18	0.11	0.21	0.05
$\sum Y$	3.00	3.00	2.99	3.00
Ca	0.56	0.51	0.51	0.53
Na	0.39	0.42	0.42	0.42
$\sum X$	0.95	0.93	0.93	0.95
OH	3.51	3.59	3.45	3.68
F	0.49	0.41	0.55	0.32
$\sum OH$	4.00	4.00	4.00	4.00

not detected = P, Zn, and K; detection limits: P_2O_5 = 0.02(4), ZnO = 0.09(1), K_2O = 0.01(6) wt%. * calculated from stoichiometry: B = 3, OH+F = 4, Li = 3-$\sum Y$, anions = 31. (1) sample 14-2T, (2) sample 14-2T, (3) sample 8-19T, (4) sample A4.

The analytical data are summarized in Table 1; structural formulae are calculated on the basis of 31 anions, assuming stoichiometric amounts of B_2O_3 (B = 3 *apfu*), H_2O as $(OH)^-$ (*i.e.*, OH + F = 4 *apfu*), and Li_2O (as Li) at the *Y* site (MacDonald *et al.* 1993). Wet-chemical analysis of the tourmaline for the light elements and Mössbauer spectrometry for Fe^{2+}/Fe^{3+} are bulk methods that are inappropriate for these fine-grained strongly zoned crystals of tourmaline.

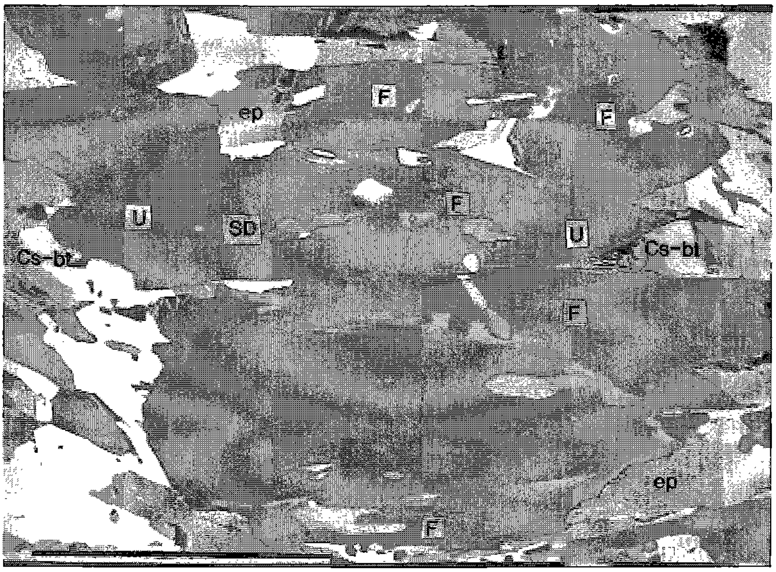

FIG. 1. Back-scattered electron image of zoned tourmaline from the exocontact of the lepidolite pegmatites at Red Cross Lake. Symbols: U: uvite, F: feruvite, SD: schorl – dravite, ep: epidote, Cs-bt: cesium-bearing biotite. The central grain contains inclusions of epidote (pale grey) and quartz (black). Scale bar: 100 μm.

Crystal-structure refinement and bond-valence calculations indicate that B = 3 *apfu* in all tourmalines structurally analyzed to date (Hawthorne 1996). In the absence of an analysis for H_2O, OH + F is assumed to be equal to 4 *apfu*. The pegmatites contain abundant lepidolite, subordinate spodumene + quartz after petalite, and accessory elbaite and amblygonite. Analyses by atomic absorption spectrometry indicate that there is 0.76–1.27 wt% Li_2O in the exocontact biotite associated with tourmaline. Morgan & London (1987) noted that appearance of metasomatic tourmaline and biotite in amphibolitic host-rocks may be associated with an influx of Li from the intruding pegmatite, as indicated by the common occurrence of holmquistite in amphibolite exocontacts of LCT pegmatites (London 1986). The amount of Li assigned to the *Y* site is the ideal cation sum for the *Y* site minus the amount of other cations occupying this site $[Li = 3 - (Ti + {}^{Y}Mg + Fe + Mn)]$, and the calculation was iterated to self-consistency (Burns *et al.* 1994). If OH + F is less than 4 *apfu*, then the estimated Li contents will be too high (Taylor *et al.* 1995). All Mn and Fe are assumed to be divalent for the structural-formula calculation; if Fe^{3+} is present, then the calculated Li will be higher than the values given in Table 1. The presence of epidote in the exocontact suggests that some of the total Fe may be Fe^{3+}.

CHEMISTRY OF EXOCONTACT TOURMALINE

The tourmaline is commonly concentrically zoned, with a feruvite core surrounded by schorl or dravite and rimmed by uvite. One tourmaline grain (0.22 × 0.05 mm in size) consists of a zoned core of dark blue feruvite and schorl – dravite surrounded by a rim of pale blue uvite (Fig. 1). Another much smaller grain (0.07 × 0.05 mm) consists of a core of green feruvite surrounded by a zone of blue schorl and a rim of blue uvite (Fig. 1). The color of the tourmaline refers to that parallel to the ω index in plane-polarized light (PPL).

An electron-microprobe traverse along the length of the larger (0.22 × 0.05 mm) grain (Fig. 1) shows antipathetic relations between Na and Ca at the *X* site and between Fe and Mg at the *Y* site (Figs. 2a, b). A dravite zone interrupts the uvite rim. The tourmaline shows F–Fe^{2+} avoidance (Rosenberg & Foit 1977), as the uvite tends to be more F-rich than the feruvite and schorl – dravite (Fig. 2b). Uvite and feruvite are slightly more Ti-rich relative to schorl – dravite (Fig. 2c).

The most extreme composition of feruvite recorded is $(Ca_{0.56}Na_{0.39})_{\Sigma 0.95}(Fe^{2+}_{1.96}Mg_{0.81}Li_{0.18}Ti_{0.04}Mn_{0.01})_{\Sigma 3.00}$ $(Al_{5.31}Mg_{0.69})_{\Sigma 6.00}(BO_3)_3Si_{6.07}O_{18}[(OH_{3.51})F_{0.49}]_{\Sigma 4.00}$ (Table 1). The *X*, *Y* and *Z* sites in feruvite are dominated by Ca, Fe and Al, respectively. Note that Mg is a significant

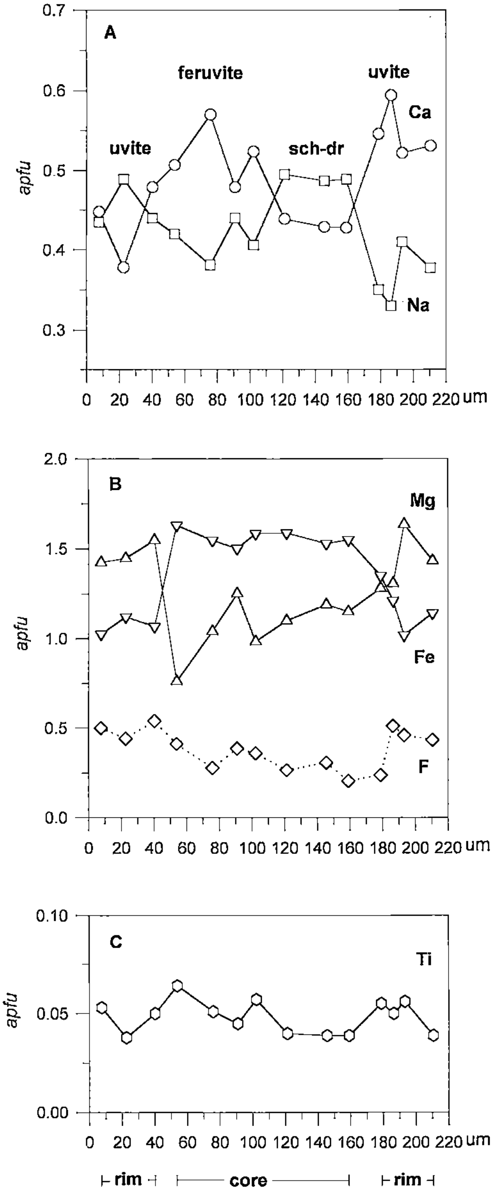

FIG. 2. Compositional variations for the traverse along the length of the 0.22 × 0.05 mm grain shown in Figure 1; sch–dr: schorl – dravite.

component at the *Y* and *Z* sites. The ~5.5:0.5 ratio for Al:Mg at the *Z* site is intermediate between the 5:1 ratio for end-member feruvite and 6:0 ratio for end-member schorl.

A wide range in Na and Ca contents is observed, with limited *X*-site vacancy; all compositions plot in the uvite – dravite – schorl – feruvite region (Fig. 3). Tourmaline compositions from the exocontact cluster in the center of this graph, and all four of the tourmaline species on this plot are represented (Fig. 3). Compositional zones in the exocontact tourmaline reflect solid solutions between Na-rich schorl and dravite, and between Ca-rich feruvite and uvite. The negative slope for the graph of Ca *versus* Na at the *X* site and the negative correlation between Mg and Al at the *Z* site indicate that the coupled substitution between feruvite and schorl is ^{X}Ca + ^{Z}Mg = ^{X}Na + ^{Z}Al [CaMg(NaAl)$_{-1}$] (Fig. 4a). The –1 slope for the graph of Fe *versus* Mg at the *Y* site indicates that the solid solution between feruvite and uvite is ^{Y}Fe^{2+} = ^{Y}Mg [Fe^{2+}Mg$_{-1}$] (Fig. 4c) and verifies the assignment of Mg rather than Fe to the *Z* site.

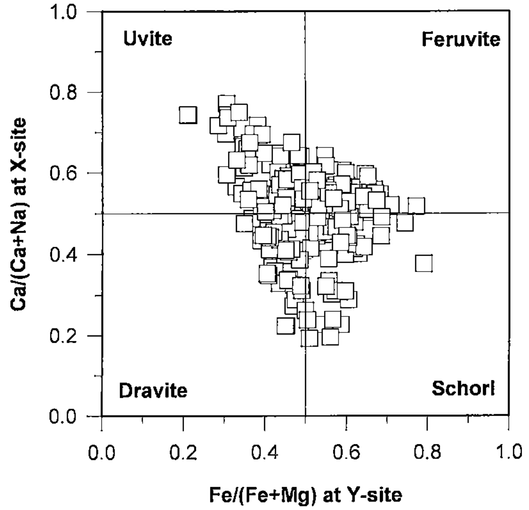

FIG. 3. Plot of Ca/(Ca + Na) at the *X* site *versus* Fe/(Fe + Mg) at the *Y* site in tourmaline from the exocontact of the lepidolite pegmatite. Quadrants are labeled according to the dominant tourmaline end-members.

Compositions of exocontact tourmaline for which PPL information is available on color are shown as a function of color in Figure 5a. The Mg-rich species are pale blue or blue, whereas Fe-rich species are dark blue. Uvite is dominantly blue to pale blue, and only rarely is green. Dravite is mainly blue, and rarely pale blue, dark blue or green. Feruvite is dominantly dark blue, brown and green, and rarely blue. Schorl is mainly dark blue and brown, and rarely blue and green. The rare colors observed for each species may reflect uncertainties in assignment of color due to the difficulty in correlation of PPL and BSE images. The green color spans a wide range of compositions, but is dominant in Fe-rich species.

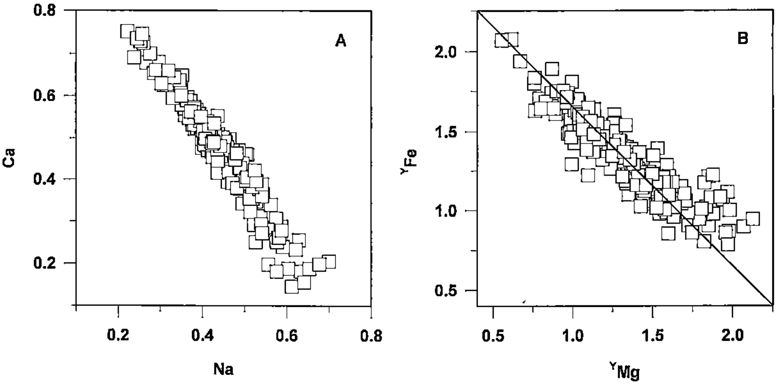

FIG. 4. A. Ca *versus* Na (*apfu*). B. ^{Y}Fe *versus* ^{Y}Mg (*apfu*) for tourmaline in the exocontact of the lepidolite pegmatites. The line represents a slope of –1.

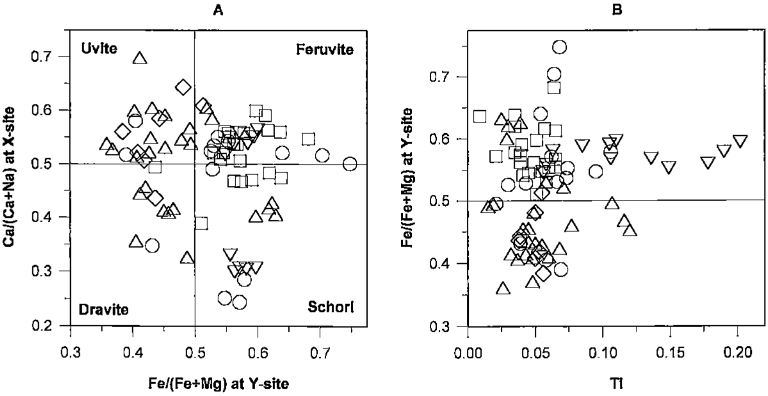

FIG. 5. Color *versus* composition of tourmaline from the exocontacts of the lepidolite pegmatites. A. Ca/(Ca + Na) at the *X* site *versus* Fe/(Fe + Mg) at the *Y* site. B. Fe/(Fe + Mg) *versus* Ti (*apfu*). Circles represent green tourmaline, squares represent dark blue tourmaline, triangles represent blue tourmaline, diamonds represent pale blue tourmaline, and inverted triangles represent brown tourmaline.

Brown tourmaline shows a very narrow range in Fe/(Fe + Mg) ratio (0.55–0.60), and brown schorl (1.09–1.61 wt% TiO_2) is more Ti-rich than brown feruvite (0.45–0.87 wt% TiO_2) (Fig. 5b). Dark blue feruvite and blue uvite are relatively Ti-poor (<0.59 wt% TiO_2). A review of the literature shows that brown feruvite from other localities commonly is enriched in Ti (>0.88 wt% TiO_2) and that blue feruvite is depleted in Ti (<0.29 wt% TiO_2) (data from Black 1971, Grice & Robinson 1989, Jiang *et al.* 1996).

CONCLUDING REMARKS

Feruvite can be expected to occur at other localities where granitic pegmatites intrude meta-igneous rocks of basic to intermediate composition. Metagabbros, metabasalts and meta-andesites of upper greenschist to amphibolite facies are very common wallrocks of B-bearing granitic pegmatites of the rare-element class, and provide a ready source of Ca and Fe.

In addition to Al and Si, the occurrence of feruvite is presumably controlled partly by the relative activities of Mg and Fe^{2+}. These activities are influenced by the chemical composition of the wallrocks and are reflected in partitioning of these elements among coexisting phases of the exocontacts, most commonly trioctahedral mica, holmquistite, garnet and tourmaline (Henry & Guidotti 1985, Morgan & London 1987, Henry & Dutrow 1990).

In the amphibolite wallrock of the Newry pegmatites, Maine, Mg is preferentially partitioned into tourmaline (dravite) rather than other mafic phases, with Mg/(Mg + Fe) values decresing in the sequence tourmaline (0.86–0.88) > amphibole (0.77–0.87) >

chlorite (0.81–0.82) > biotite (0.79) (Henry & Dutrow 1990). The amphibolite wallrock contains tourmaline porphyroblasts with grains of amphibole, chlorite and biotite present in the matrix and as inclusions in the tourmaline (Henry & Dutrow 1990). The Newry amphibolite is in an Al-rich environment, and the Ca-substitution in the tourmaline is $^{X}Ca + {}^{Y}Mg + {}^{O(1)}O \rightarrow {}^{X}\square + {}^{Y}Al + {}^{O(1)}OH$ [$CaMgO(\square AlOH)_{-1}$], whereas the Ca-substitution in the tourmaline in the exocontact at Red Cross Lake is $^{X}Ca + {}^{Z}Mg = {}^{X}Na + {}^{Z}Al$ [$CaMg(NaAl)_{-1}$].

In the staurolite-grade metapelites of northwestern Maine, Mg is preferentially partitioned into tourmaline (dravite) over the other mafic minerals (Henry & Guidotti 1985). The Mg/Fe values in the minerals are: tourmaline rim > cordierite > chlorite > biotite > staurolite > garnet > ilmenite. The role of Fe^{3+} was minimized by analyzing mafic minerals associated with graphite in a reducing environment.

In the proximal amphibolite host-rock of the Tanco pegmatite, Mg is preferentially partitioned into biotite rather than tourmaline, with Mg/(Mg + Fe) values of 0.45 and 0.05–0.44, respectively (Morgan & London 1987). The exocontact of the Tanco pegmatite contains members of the schorl–dravite series with minor components of uvite and feruvite (Morgan & London 1987, Černý *et al.* 1996). This reversal in Mg partitioning could be due to more oxidizing conditions, as partitioning of Fe^{3+} differs from partitioning of Fe^{2+}.

The distribution of feruvite is also controlled by the relative activities of Ca and Na due to partitioning of these elements among coexisting phases of the exocontact, most commonly tourmaline and plagioclase. In metabasalts and amphibolites, the plagioclase tends to be andesine or labradorite, which provides an *in situ* source for Ca. Thus exocontact tourmaline will tend to be Ca-rich.

In the staurolite-grade metapelites of northwestern Maine, Ca is preferentially partitioned into plagioclase over tourmaline (Henry & Guidotti 1985). A similar trend occurs in the proximal amphibolite host for the Tanco pegmatite, with Na/(Na + Ca) values in the range 0.49–0.55 for plagioclase and 0.55–0.98 for tourmaline (Morgan & London 1987).

At Red Cross Lake, the tourmaline rims (uvite and dravite) are in equilibrium with Cs-rich biotite. Magnesium is preferentially partitioned into tourmaline rims rather than biotite, with Mg/(Mg + Fe) ratios of 0.49–0.81 and 0.39–0.52, respectively. For tourmaline, the average Mg/(Mg + Fe) ratio is 0.61 for 64 compositions. Garnet shows a very strong preference for Fe, with Mg/(Mg + Fe) of 0–0.03, but plays a relatively minor role because of its low abundance. Epidote does not enter the partitioning process, as it is a late Fe^{3+}-rich Mg-free phase; it postdates biotite and tourmaline. For tourmaline rims, the Na/(Na + Ca) values from 0.25 to 0.78, with an average of 0.48 for 64 compositions. The high activity of Ca is evident from the abundance of epidote and local Ca-rich garnet (35–40 mole % grossular component), titanite and calcite.

In view of the extremely high degree of fractionation of the Red Cross Lake pegmatites and their almost total depletion in Fe and Ca, the meta-andesitic and metabasaltic wallrocks undoubtedly provided Ca and Fe (± Mg) for contact metasomatic reactions between the wallrocks and the intruding pegmatite to produce cores of feruvite, schorl or dravite in intermediate zones, and uvite in the rims.

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