TOURMALINE-BEARING QUARTZ VEINS IN THE BARABOO QUARTZITE, WISCONSIN: OCCURRENCE AND SIGNIFICANCE OF FOITITE AND “OXY-FOITITE”

L. GORDON MEDARIS JR.§ AND JOHN H. FOURNELLE

Department of Geology and Geophysics, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.

DARRELL J. HENRY

Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70808, U.S.A.

ABSTRACT

The alkali-deficient tourmaline, foitite \([\text{Fe}^{2+}2\text{Al}]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})]\), and associated hematite occur in quartz veins that cut the geon 17 Baraboo Quartzite in south-central Wisconsin. The bluish green prismatic crystals of tourmaline are chemically zoned from core to rim, with the cores being very aluminous, highly alkali-deficient and, in one sample, relatively magnesian. Electron-microprobe analyses demonstrate that the tourmaline has a prevailing alkali-deficiency in the X site, which ranges from 49 to 87%, with a mean of 73%, making this the most alkali-deficient tourmaline reported to date. In one sample, high contents of Al (up to 7.7 Al apfu) and high cation-charge excess demonstrate the likely existence of a dominant “oxy-foitite” component \([\text{Fe}^{2+}\text{Al}_2]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(O)\], which is the first recognition of such in a natural occurrence. The wide range of chemical zoning in the tourmaline is most consistent with substitutions represented by the \([\text{Al}(\text{NaR})^{-1}, \text{AlO}[\text{R(OH)}]^{-1}, \text{FeAl}^{-1}\text{ and MgFe}^{-1}\text{ exchanges, where R symbolizes Fe + Mg. The alkali-deficient character of the Baraboo tourmaline largely reflects the alkali-depleted and chemically mature composition of the host Baraboo Quartzite, but core-to-rim compositional variation in the tourmaline records the evolving nature of the attendant hydrothermal fluid, from a Na-poor, relatively alkaline early stage to a more sodic, acidic later stage.

Keywords: foitite, “oxy-foitite”, Baraboo Quartzite, Wisconsin, U.S.A.

SOMMAIRE

On trouve la foïtite \([\text{Fe}^{2+}2\text{Al}]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})]\), pôle du groupe de la tourmaline déficitaire en alcalins, en association avec l’hématite dans des veines de quartz recoupant la quartzite de Baraboo (géon 17) dans le centre-sud du Wisconsin. Les cristaux vert bleuâtre prismatiques de tourmaline sont zonés du cœur vers la bordure; le cœur est fortement alumineux, déficitaire en alcalins et, dans un échantillon, magnésien. Les analyses à la microsonde électronique montrent que la tourmaline accuse un déficit important au site X, entre 49 et 87%, en moyenne 73%, faisant de ce groupe de compositions le plus déficitaire en alcalins qui soit. Dans un échantillon, les teneurs élevées en Al (jusqu’à 7.7 Al atomes par unité formulaire) et l’excédent en charges positives démontrent l’existence probable d’une composante “oxy-foïtite” \([\text{Fe}^{2+}\text{Al}_2]\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(O)\], ce qui est en fait le premier exemple à être signalé dans la nature. On interprète l’étendue de la zonation chimique dans la tourmaline en termes de substitutions représentées par les échanges \([\text{Al}(\text{NaR})^{-1}, \text{AlO}[\text{R(OH)}]^{-1}, \text{FeAl}^{-1}\text{ et MgFe}^{-1}\text{; ici, R représente Fe + Mg. Le déficit en alcalins de la tourmaline de Baraboo témoigne surtout du déficit en alcalins et le caractère chimiquement mature de l’hôte, la quartzite de Baraboo. La zonation des cristaux résulterait de l’évolution du système hydrothermal, au départ à faible teneur en Na et relativement alcalin, et vers la fin plus sodique et plus acidique.

(Traduit par la Rédaction)


§ E-mail address: medaris@geology.wisc.edu
INTRODUCTION

Alkali-deficient tourmaline, in which the X site is incompletely filled by Na or Ca, occurs in alkali-poor and aluminum-rich geological settings, in rocks that have interacted with hydrothermal fluids. The geological settings include certain types of granitic pegmatites (Pezzotta et al. 1996, Aurisicchio et al. 1999, Selway et al. 1999, Dutrow & Henry 2000, Novák & Taylor 2000, Selway et al. 2000), hydrothermally altered volcanic and sedimentary rocks (Foit et al. 1989, Jiang et al. 1997, Hawthorne et al. 1999, Pesquera et al. 1999), hydrothermal quartz veins (Francis et al. 1999, Yavuz et al. 2002), and metakarstbauxite (Henry & Dutrow 2001). In these occurrences, three species of alkali-deficient tourmaline are important: foitite, magnesiofoitite, and “oxy-foitite” (Table 1). Foitite, which was formally described and named by MacDonald et al. in 1993, is the alkali-deficient analogue of schorl, the common tourmaline. A magnesian counterpart, magnesiofoitite, which was recognized by Hawthorne et al. in 1999, is the alkali-deficient analogue of dravite. There is also a theoretical X-site-vacant deprotonated end-member of the tourmaline group, “oxy-foitite”, which has been proposed by Hawthorne & Henry (1999).

During a comprehensive investigation of Proterozoic rocks in the Baraboo Range, Wisconsin, it was determined that highly alkali-deficient tourmaline is the characteristic tourmaline in quartz veins in the Baraboo Quartzite (Medaris & Fournelle 2000). Because of the relative chemical simplicity of the quartz veins, constituent tourmaline, and surrounding quartzite, it is feasible to evaluate the nature and range of substitutions that control X-site vacancies in tourmaline, to assess the possible existence of “oxy-foitite” in a natural setting, and to infer the nature of fluids associated with quartz veins in the Baraboo Quartzite.

OCCURRENCE

The geon-17 Baraboo Quartzite is a 1500-meter-thick sequence of supermature quartz arenite and subordinate siltstone and mudstone, which was transformed to quartzite, argillite, and phyllonite during 1.63 Ga low-grade metamorphism (Medaris et al. 2003). The Baraboo metasedimentary rocks, which are composed essentially of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, and H₂O, have a Chemical Index of Alteration (CIA) that ranges from 96.8 to 98.8, ranking them among the most chemically mature sedimentary rocks in the geological record [CIA is defined as 100*(molar Al₂O₃/(Al₂O₃ + K₂O + Na₂O + CaO)]. Such a mature chemical composition is reflected in the mineralogical composition of the metasedimentary rocks, which consist predominantly of quartz and pyrophyllite, accompanied by accessory hematite and rutile.

Quartz veins, which likely originated during the 1.63 Ga metamorphism and deformation, are relatively abundant and widely distributed in the Baraboo Quartzite. The quartz veins are composed almost entirely of quartz, except for local concentrations of tourmaline and specular hematite. In addition, quartz veins that cut a paleosol at the base of the Baraboo Quartzite contain muscovite, which was introduced after formation of the quartz veins by regionally extensive, but stratigraphically restricted, migration of brine at 1.45 Ga (Medaris et al. 1996, Aurisicchio et al. 1999, Yavuz et al. 2002). Sample 1 is a folded, 1.5-cm-thick quartz vein in the regolith of the paleosol underlying Baxter Hollow (NW¼, Sec33, T11N, R6E). Sample 2 is a 3-cm-thick quartz vein in quartzite in Baxter Hollow (SE¼, Sec29, T11N, R6E), and Sample 3 is a 3-mm-thick, tourmaline-rich quartz vein that cuts quartzite and metapelite in Pine Hollow (NW¼, Sec35, T11N, R6E).

The three samples analyzed are mineralogically simple, consisting of quartz, specular hematite, and tourmaline, which typically occurs in clusters of small (<1 mm), randomly oriented, prismatic crystals (Fig. 1). The tourmaline is strongly pleochroic, with O medium bluish green and E almost colorless. Tourmaline in Sample 3 is optically zoned, such that grain rims have a darker color than the cores.

TABLE 1 | TOURMALINE SPECIES OF SIGNIFICANCE IN THE BARABOO QUARTZ VEINS

<table>
<thead>
<tr>
<th>Species</th>
<th>(X)</th>
<th>(Y)</th>
<th>(Z)</th>
<th>(BO₃)</th>
<th>(PO₄)</th>
<th>(OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kelloi</td>
<td>Na</td>
<td>Fe³⁺</td>
<td>Al⁴⁺</td>
<td>Na₂O₃</td>
<td>BO₃</td>
<td>(OH)</td>
</tr>
<tr>
<td>Dravite</td>
<td>Na</td>
<td>Mg²⁺</td>
<td>Al⁴⁺</td>
<td>Na₂O₃</td>
<td>BO₃</td>
<td>(OH)</td>
</tr>
<tr>
<td>Foiite*</td>
<td>Fe³⁺</td>
<td>Al⁴⁺</td>
<td>SiO₂</td>
<td>BO₃</td>
<td>(OH)</td>
<td>(OH)</td>
</tr>
<tr>
<td><em>Oxy-foitite</em>*</td>
<td>Fe³⁺</td>
<td>Al⁴⁺</td>
<td>SiO₂</td>
<td>BO₃</td>
<td>(OH)</td>
<td>(OH)</td>
</tr>
</tbody>
</table>

* End-member formula modified from the initial formula (Hawthorne & Henry 1999).
** X-site vacancy.
*** Hypothetical species of tourmaline not currently approved by the CMMVN IMA.

IMAGING AND ANALYTICAL PROCEDURES

Imaging

The character of chemical zoning in the Baraboo tourmaline was revealed by back-scattered electron (BSE) images and element-distribution maps. Because compositional zoning in different samples involves distinct patterns of variation among the light elements, Na, Mg, and Al, BSE images alone are insufficient to portray the precise nature of zoning, and element-distribution maps are required. BSE images and element-distribution maps were acquired at 15 keV with 30 nA beam current. Element-distribution maps were acquired at 2000X magnification, 0.05 s dwell time per
pixel, and 2 μm/pixel spacing. We utilized a combination of WDS and EDS channels, and employed WinEDS hardware/software for acquisition of the energy-dispersion spectra (EDS) and MicroImage software to produce mosaics for the element-distribution maps.

Electron-microprobe (EMP) analysis and normalization procedures

Tourmaline was analyzed by wavelength-dispersion spectrometry (WDS) with a Cameca SX51 instrument, using a 15 kV accelerating voltage, a 10 nA beam (Faraday cup) current, a beam diameter of 1 μm. Probe for Windows software utilizing the matrix correction of Armstrong (1988), and a combination of natural and synthetic minerals as standards.

Analysis of tourmaline by electron microprobe (EMP) presents a challenge because of the inability to measure amounts of Li and H directly, the difficulty in determining amounts of B and O precisely, and the uncertainty in the valence of transition elements. We assumed that Li contents are minimal in the Baraboo tourmaline because of the paucity of other elements of Group Ia, as well as Group IIa, in the geochemical environment of the quartz veins. The preferred method for calculating cation proportions in Li-poor tourmaline is to normalize the sum of \( T + Z + Y \) cations to 15, assuming no vacancies (or deficiencies) in the \( T, Z, \) or \( Y \) sites (Henry & Dutrow 1996). Such a normalization procedure is effective because knowledge of B concentration, OH content, and oxidation state of Fe is unnecessary, and it allows an approximation of OH and oxidation state to be made, based on charge balance. The amount of \( \text{B}_2\text{O}_3 \) necessary to produce three B cations in the structural formula was calculated from stoichiometric constraints, because we do not expect \(^{4}\text{B}\) in these Fe-rich tourmaline samples. Fe is reported as \( \text{Fe}^{2+} \) in the representative EMP analyses (Table 2), but we recognize that tourmaline from these hematite-bearing samples may contain significant amounts of \( \text{Fe}^{3+} \). This possibility is examined further below. Finally, \( \text{O}^{2–} \) substitution for \( \text{OH}^{–} \) (deprotonation), calculated by charge balance, is assigned to the \( W \) site, owing to preferential incorporation of \( \text{O}^{2–} \) at the \( W \) site relative to the \( V \) site (Henry & Dutrow 1996, Hawthorne & Henry 1999).

RESULTS

BSE images and element-distribution maps

BSE images and element-distribution maps reveal the existence of discrete cores and rims of grains, as best illustrated in Samples 2 and 3 (Figs. 2, 3). The euhedral morphology of the core relative to the rim observed in the BSE image implies that the rim is an overgrowth on the precursor tourmaline core, rather than a replacement of that tourmaline (cf. Henry et al. 2002). However, the chemical variations that are responsible for the BSE zonning are better revealed by EMP spot analyses (below) and element-distribution maps (Fig. 3). Sample 2 is different from samples 1 and 3 in that it contains Mg-
Tourmaline composition and chemical zoning characteristics

The chemical composition of the Baraboo tourmaline reflects the chemical simplicity of the host quartz veins and surrounding quartzite. The tourmaline was analyzed for Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, F and Cl, but only Si, Al, Fe, Mg and Na were detected (Table 2). In all three samples, the T site of tourmaline is fully occupied by Si (6.02 ± 0.05, 6.07 ± 0.05, and 6.01 ± 0.04 atoms per formula unit [apfu]). The tourmaline is aluminous, with total Al ranging widely from 6.39 to 7.74 apfu. In terms of Fe and Mg contents, samples 1 and 3 are Fe-rich, with Fe/(Fe + Mg) values of 0.929 ± 0.01 and 0.999 ± 0.01, respectively. Sample 2 has a wider range of Fe/(Fe + Mg), with a mean of 0.761 ± 0.16. The fundamental alkali-deficient nature of the Baraboo tourmaline is demonstrated by less than 50% occupancy of the X site by Na in each sample, with mean occupancies being 0.31 ± 0.09, 0.25 ± 0.05, and 0.25 ± 0.08 apfu. Consequently, this tourmaline can be generally classed as a vacancy-group tourmaline (Hawthorne & Henry 1999). However, the specific classification and details of the controlling substitutions are best revealed by plotting results of individual EMP analyses on a series of compositional diagrams (Figs. 4–7).

Because all of the analyzed grains of tourmaline are aluminous (Al > 6 apfu), the optimal diagram for classification of the tourmaline species is one in which X vacancy/(Na + X vacancy) is plotted versus Fe/(Fe + Mg) (Fig. 4A). This diagram does not specifically take into account the W-site anion occupancy, and each of the fields may also represent fluor- or oxy-equivalents of the tourmaline species. However, F contents are below detection levels for all samples and, as noted below, W-site O²⁻ contents are only dominant in the core of Sample 3 tourmaline. Consequently, the foitite field in Figure 4A could also be considered an “oxy-foitite” field for those “O²⁻ dominant at the W site” compositions. The compositions of the three samples overlap in terms of X-site vacancy, with ranges of values of 0.49–0.80, 0.66–0.82, and 0.61–0.87. However, the three samples are distinct with respect to Fe/(Fe + Mg), which varies from 0.904 to 0.941 in Sample 1, varies widely from 0.347 to 0.876 in Sample 2, and is tightly constrained between 0.980 and 0.999 in Sample 3 (Table 2, Fig. 4A). Most of the tourmaline data fall within the foitite field, with the exception of the cores of Sample 2, which are best classified as magnesiofoitite, where the Fe/(Fe + Mg) value ranges from 0.3 to 0.5. By comparison with available compositions of alkali-deficient tourmaline from other localities and different geological settings (Fig. 4B), it is apparent that tourmaline in the Baraboo quartz veins represents the most strongly alkali-deficient variety recorded to date.

To evaluate the controlling substitutions in the tourmaline, a series of binary composition diagrams are employed, and the arrays of data are compared to reference exchange-vectors that represent hypothetical schemes of substitution (Table 3). In a plot of Fe versus Mg (Fig. 5), tourmaline data from samples 1 and 3 exhibit a distribution roughly parallel to the FeAl₁ and □Al(FeNa)₁ exchange vectors. For Sample 2, the only one containing appreciable amounts of Mg, a least-squares fit to the approximately linear data array yields the expression \( \text{Fe} = -0.895(\text{Mg}) + 2.053 \), with a correlation coefficient of -0.98. Based on a slope of -0.895, it can be argued that most of the Mg incorporation is explained by a simple homovalent MgFe₁ substitution. However, the minor deviation of the linear fit to the data from a slope of -1 suggests that other substitutions, such as □Al(FeNa)₁, □Al(FeNa)₁, and FeAl₁, contribute to the dispersion of the data, and likely result in a deviation from a slope of -1. If MgFe₁ is the predominant mechanism of substitution, this vector may be used to project to an Mg-free system simply by adding Mg to...
TABLE 2. REPRESENTATIVE COMPOSITIONS OF ALKALI-DEFICIENT TOURMALINE FROM QUARTZ VEINS IN THE BARABOO QUARTZITE

<table>
<thead>
<tr>
<th></th>
<th>Sample 1 (vein in paleosol)</th>
<th>Sample 2 (vein in Baxter Hollow)</th>
<th>Sample 3 (vein in Pine Hollow)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>max</td>
<td>min</td>
<td>mean</td>
</tr>
<tr>
<td>wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>35.09</td>
<td>35.14</td>
<td>35.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>31.49</td>
<td>34.00</td>
<td>32.91</td>
</tr>
<tr>
<td>FeO</td>
<td>15.63</td>
<td>13.98</td>
<td>14.96</td>
</tr>
<tr>
<td>MgO</td>
<td>0.93</td>
<td>0.49</td>
<td>0.64</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.51</td>
<td>0.62</td>
<td>0.92</td>
</tr>
<tr>
<td>Sum</td>
<td>84.66</td>
<td>84.23</td>
<td>84.45</td>
</tr>
</tbody>
</table>

Cations based on 15 Si₂+Zr²⁺ Y

|         |     |     |      |                 |     |     |     |     |      |                 |     |     |     |     |     |
|---------|     |     |      |                 |     |     |     |     |      |                 |     |     |     |     |     |
| Na      | 6.57 | 6.01 | 6.02 | 0.05 | 5.97 | 5.97 | 6.08 | 5.97 | 6.07 | 0.05 | 5.94 | 5.96 | 6.10 | 6.01 | 0.05 |
| Al      | 6.42 | 6.86 | 6.67 | 0.16 | 6.93 | 7.00 | 6.64 | 6.90 | 6.93 | 0.10 | 6.69 | 7.44 | 6.39 | 7.03 | 0.32 |
| Fe      | 2.26 | 2.00 | 2.15 | 0.12 | 1.52 | 1.75 | 0.79 | 1.87 | 1.53 | 0.34 | 2.37 | 1.28 | 2.51 | 1.96 | 0.32 |
| Mg      | 0.24 | 0.12 | 0.16 | 0.04 | 0.58 | 0.28 | 1.49 | 0.26 | 0.48 | 0.37 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| Na      | 0.51 | 0.20 | 0.31 | 0.10 | 0.34 | 0.18 | 0.26 | 0.20 | 0.25 | 0.03 | 0.39 | 0.13 | 0.36 | 0.25 | 0.08 |
| charge  | 49.08 | 49.09 | 49.01 | 0.10 | 49.21 | 49.12 | 49.06 | 49.03 | 49.31 | 0.10 | 48.96 | 49.79 | 48.94 | 49.29 | 0.26 |

Site occupancies based on 15 Si₂+Zr²⁺ Y

|         |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |     |
|---------|     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Na      | 0.49 | 0.80 | 0.69 | 0.09 | 0.66 | 0.82 | 0.74 | 0.80 | 0.75 | 0.05 | 0.61 | 0.87 | 0.64 | 0.75 | 0.08 |
| Al      | 0.51 | 0.20 | 0.31 | 0.09 | 0.34 | 0.18 | 0.26 | 0.20 | 0.25 | 0.05 | 0.39 | 0.13 | 0.36 | 0.25 | 0.08 |
| Fe      | 2.93 | 2.98 | 2.98 | 0.03 | 3.03 | 3.03 | 2.92 | 3.03 | 2.93 | 0.03 | 3.06 | 3.04 | 2.90 | 2.99 | 0.04 |
| Ti(Si)  | 6.07 | 6.01 | 6.02 | 0.03 | 5.97 | 5.97 | 6.08 | 5.97 | 6.07 | 0.05 | 5.94 | 5.96 | 6.10 | 6.01 | 0.04 |

Fe(Mg+Fe²⁺) = 0.904 0.941 0.929 0.014 0.724 0.861 0.347 0.876 0.761 0.164 0.998 0.90 0.999 0.010

* Where Ti(Si) < 6.00, it is likely that small amounts of Al occur at the Y site

Fig. 3. Element-distribution maps for selected elements in tourmaline in samples 2 and 3 (these are the same grains that appear in Figure 2). Brighter tones represent higher elemental concentrations. Scale bar is 20 μm for sample 2 and 50 μm for sample 3.
The value \( R \) is used to denote the sum of Mg and Fe, i.e., the vector projection associated with \( \text{MgFe}^{-1} \). We recognize that some of Fe is likely to be \( \text{Fe}^{3+} \); the attendant consequences will be examined further.

The \( R (\text{Fe} + \text{Mg}) \) versus \( \text{Al} \) diagram (Fig. 6A) illustrates the very large range of \( \text{Al} \) and \( R \), from almost schorl through foitite to “oxy-foitite” (Fig. 6A). A least-squares fit of these data produces a well-constrained line, \( R = -0.938(\text{Al}) + 8.568 \), with a correlation coefficient of -0.99. The slope of nearly -1 is consistent with \( \text{Al} \) variation being due to any or all of the following exchange vectors: \( \square \text{Al(\text{NaR})}^{-1} \), \( \square \text{AlO}[\text{R(OH)}]^{-1} \), and \( \text{FeAl}^{-1} \). However, to estimate the relative contribution of each of these substitutions to the range in \( \text{Al} \) and \( R \), it is useful to isolate the influence of the \( \square \text{Al(\text{NaR})}^{-1} \) exchange.

The \( X \) vacancy versus \( \text{Al} \) diagram (Fig. 6B) permits some separation of the influence of the \( \square \text{Al(\text{NaR})}^{-1} \) exchange.

### Table 3

<table>
<thead>
<tr>
<th>Size substitution*</th>
<th>Exchange vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \square \text{Fe}^{2+} = \text{Mg} )</td>
<td>( \text{MgFe}_4 )</td>
</tr>
<tr>
<td>( \square \text{Al} = \text{Fe}^{3+} )</td>
<td>( \text{FeAl}_4 )</td>
</tr>
<tr>
<td>( \square \text{Na} + \square \text{Mg} = \square \text{Al} )</td>
<td>( \square \text{Al(\text{NaMg})}_2 )</td>
</tr>
<tr>
<td>( \square \text{Na} + \square \text{Fe} = \square \text{Al} )</td>
<td>( \square \text{Al(\text{NaFe})}_2 )</td>
</tr>
<tr>
<td>( \square \text{Na} + \square \text{Fe} = \square \text{Al} + \square \text{Al}_2 )</td>
<td>( \square \text{Al(\text{NaFe})}_4 )</td>
</tr>
</tbody>
</table>

* Precursor substitutions do not specify specific sites in tourmaline.
** \( R \) represents the sum of \( \text{Fe} + \text{Mg} \).


![Fig. 5](image) Fe (total) versus Mg diagram for tourmaline data from all samples. The solid line represents a linear least-squares regression through the data for Sample 2. The directions of several selected exchange-vectors are shown for reference.
change from those of the AlO[R(OH)]$_{-1}$ and FeAl$_{-1}$ exchanges on the range of Al and R. If Al is incorporated into tourmaline exclusively via the $\square$Al(NaR)$_{-1}$ substitution, the slope of the data array in the plot will be +1, but if it is exclusively due to the AlO[R(OH)]$_{-1}$ or FeAl$_{-1}$ substitution, or both, the slope of the data array will be 0. The data from all three of the Baraboo samples generally have values for X-site vacancy greater than 0.5, and a least-squares linear fit to the data results in a rather poorly correlated regression expression for $X_{\text{vacancy}} = 0.195(\text{Al}) - 0.615$, with a correlation coefficient of 0.70. This relatively shallow slope implies that the range of Al associated with chemical zoning is a consequence of roughly 20% substitution of Al via the $\square$Al(NaR)$_{-1}$ exchange and 80% from that of the AlO[R(OH)]$_{-1}$ and FeAl$_{-1}$ exchanges. However, the influence of the $\square$Al(NaR)$_{-1}$ substitution remains important, because extrapolation of the least-squares fit to Al = 6 apfu still yields a highly alkali-deficient tourmaline. The original local chemical environment must have been Al-rich and Na-poor, resulting in tourmaline that reflects a significant amount of $\square$Al(NaR)$_{-1}$ exchange (e.g., von Goerne et al. 2001).

The (R [Fe + Mg] + $X_{\text{vacancy}}$) versus (Al – $X_{\text{vacancy}}$) diagram (Fig. 7A) strips out the influence of $\square$Al(NaR)$_{-1}$ by projecting down this vector to the Al–R compositional plane, yielding a rough indication of the relative importance of AlO[R(OH)]$_{-1}$ and FeAl$_{-1}$, and condensing the compositions of schorl and foitite to a common point. A linear least-squares fit to the transformed data has a slope close to −1, (Fe + Mg + X vacancy) = −0.932(Al – $X_{\text{vacancy}}$) + 8.578, with a correlation coefficient of −0.98, implying that most of the residual Al variation is due to a combination of the AlO[R(OH)]$_{-1}$ and FeAl$_{-1}$ exchanges. However, it is possible to establish the relative importance of each substitution. Those data points that plot to the left of the schorl–foitite point will represent a minimum contribution of the FeAl$_{-1}$ exchange (up to roughly 0.2 apfu), and those data to the right of the schorl–foitite point will represent a minimum contribution of the AlO[R(OH)]$_{-1}$ exchange (0–0.9 apfu). These are minimal contributions because they react to offset calculation effects (Henry & Dutrow 1996). Nonetheless, it is unlikely that the AlO[R(OH)]$_{-1}$ vector will extend beyond the “oxyfoitite” composition, so this will serve as a reasonable minimum estimate of the amount of deprotonation in the tourmaline, i.e., $O^2-$ for OH$^-$ at the W site. Of particular note is that five compositions of the core of Sample 3 tourmaline fall closer to the “oxy-foitite” end-member composition than the foitite–schorl point, and can be most reasonably classified as “oxy-foitite”, although H$_2$O has not been determined directly.

The (excess charge) versus (R[Fe + Mg] + $X_{\text{vacancy}}$) diagram (Fig. 7B) serves as a rough approximation of the amount of Fe as Fe$^{3+}$ and the amount of deprotonation. Because these two factors have offsetting effects on charge calculation, the calculated values of excess charge represent minima. However, a number of compositions have a charge deficiency (<0), which indicates that some Fe$^{3+}$ is present in portions of the tourmaline. The presence of Fe$^{3+}$ is also indicated by

**Fig. 6.** A). R(Fe + Mg) versus Al diagram for tourmaline data from all samples. R represents the sum of Fe(total) + Mg, i.e., the condensation of the data down the FeMg$_{-1}$ vector. The solid line represents a linear least-squares regression through the data from all samples. The directions of several selected exchange-vectors are shown for reference. The locations of end-member schorl, foitite and “oxy-foitite” are designated by the filled circles. B) Diagram showing Al versus $X_{\text{vacancy}}$ for tourmaline data from all samples. The solid line represents a linear least-squares regression through the data from all samples. The directions of several selected exchange-vectors are shown for reference. The location of the end-member schorl, foitite and “oxy-foitite” are designated by the filled circles.
the intense pleochroism of the Baraboo tourmaline, which reflects the interaction of Fe$^{3+}$ with Fe$^{2+}$. The tourmaline data in Figure 7B have a linear least-squares fit with a negative slope of ~1: (excess charge) \(= -0.974(\text{Fe} + \text{Mg} + \text{X vacancy}) + 2.931\), with a correlation coefficient of ~0.98. The relatively high excess charge for many compositions is further evidence for deprotonation at the W site, and several of the core compositions in Sample 3 extend very close to the hypothetical "oxy-foitite" end-member. It should be noted that the Baraboo tourmaline coexists with hematite, and experiments have demonstrated that tourmaline crystallized at high levels of \(f(\text{O}_2)\) can have a relatively high ratio of Fe$^{3+}$ to total Fe (Fuchs et al. 1998). A complete chemical characterization of the Baraboo tourmaline requires independent measurements of Fe$^{3+}$ and OH; thus, the calculated cation charges and estimated oxy-foitite contents given here may not be entirely accurate. Nevertheless, the high Al contents and the high calculated excess charges for the cores of tourmaline grains in Sample 3 require a substantial "oxy-foitite" component, on the order of 70 to 80 mol.%. 

**DISCUSSION**

Foitite from other occurrences differs from that at Baraboo in containing appreciable quantities of Ti, Mn, Ca, Li and F, depending on locality, and in being associated with a variety of silicate minerals, including albite, "adularia", micas and zeolites, among others. In contrast, the Baraboo foitite is chemically simple, containing only Si, Al, Fe, Mg, and Na (+ B+ O + H), and is accompanied solely by quartz and hematite.

Compositions of alkali-deficient tourmaline reported in the literature span the same range of Fe/(Fe + Mg) as that for the Baraboo tourmaline, but typically display a higher occupancy of the X site (Fig. 4B), with many samples having less than 50% vacancy, thus being Na-poor schorl and dravite, rather than true foitite. Among the various occurrences of alkali-deficient tourmaline, those from pegmatites have the highest X-site vacancies, comparable to those in the Baraboo tourmaline, although such tourmaline typically may contain significant amounts of Li.

In terms of geological occurrence, foitite from Copper Mountain, New Mexico (Francis et al. 1999) is most comparable to that at Baraboo. The Copper Mountain foitite occurs in a quartz vein that cuts the Ortega Quartzite, which is considered to be correlative with the Baraboo Quartzite (Medaris et al. 2003). With respect to mineral assemblage, the Copper Mountain foitite is associated with scheelite and “wolframite”, rather than hematite, and crystallized at relatively low oxygen fugacity, below that of the quartz – fayalite – iron buffer. The Copper Mountain foitite is compositionally similar to foitite in Baraboo Samples 1 and 2 (cf. Figs. 4A, B).
except for the presence of small amounts of Ti (0.35 wt% TiO₂) and F (0.20 wt%). The major compositional distinction in tourmaline from the two localities is the high aluminum content and presence of substantial “oxy-foitite” component in the cores of tourmaline grains in Baraboo Sample 3.

The composition of the Baraboo tourmaline reflects in large part its environment of formation within the chemically mature Baraboo metasedimentary rocks. However, the zoning characteristics of the tourmaline are the result of chemical changes in the hydrothermal fluids associated with quartz vein formation. During post-Penokean folding and low-grade metamorphism at 1.63 Ga, hydrothermal fluids migrated through the alkali-depleted Baraboo sequence, where they scavenged B and the other elements necessary to precipitate quartz, hematite, and foitite. The exceptionally mature Baraboo tourmaline demonstrates that the core-to-rim compositional variation in the Baraboo tourmaline mirrors the evolution of hydrothermal fluids as the system matured.

The composition of the Baraboo tourmaline reflects in large part its environment of formation within the chemically mature Baraboo metasedimentary rocks. However, the zoning characteristics of the tourmaline are the result of chemical changes in the hydrothermal fluids associated with quartz vein formation. During post-Penokean folding and low-grade metamorphism at 1.63 Ga, hydrothermal fluids migrated through the alkali-depleted Baraboo sequence, where they scavenged B and the other elements necessary to precipitate quartz, hematite, and foitite. The exceptionally mature Baraboo tourmaline demonstrates that the core-to-rim compositional variation in the Baraboo tourmaline mirrors the evolution of hydrothermal fluids as the system matured.

ACKNOWLEDGEMENTS

We thank Bruce Brown for providing access to the Baxter Hollow drill core, from which Sample 1 was obtained, and Paul Herr for contributing Sample 3. The Weeks Bequest of the Department of Geology and Geophysics provided funds for the electron-microprobe analyses and the acquisition of the images. We thank George Rossman and Andreas Erli for their constructive reviews, and Franklin F. Foit, Jr., for editorial handling of the manuscript.

REFERENCES


Received January 25, 2003, revised manuscript accepted April 12, 2003.