1   **Revision-1**

2   **A spreadsheet for calculating normative mole fractions of end-**

3   **member species for Na-Ca-Li-Fe^{2+}-Mg-Al tourmalines from electron**

4   **microprobe data**

5   George B. Morgan VI

6   Electron Microprobe Laboratory, University of Oklahoma

7   100 East Boyd Street, SEC 710

8   Norman, OK 73019

9

10   **Abstract**

11   This work presents a spreadsheet that calculates the mole fractions of end-member components

12   for simple Na-Ca-Li-Mg-Fe^{2+}-Al tourmalines from electron microprobe data. The input includes

13   the B$_2$O$_3$ concentration obtained either from direct analysis or by estimation on the basis of

14   stoichiometry. The concentration of Li$_2$O can either be input from other analysis or estimated by

15   the spreadsheet. The spreadsheet does not address the mole fractions of Cr, V, oxidized or

16   deprotonated tourmaline species, nor account for species involving tetrahedral boron or

17   aluminum. Therefore, the spreadsheet is not a comprehensive tool that includes all IMA

18   approved tourmaline species, and so is not intended for naming tourmalines according to IMA

19   convention. The present method includes a useful subset of end-member species that can be

20   described simply from electron microprobe data and so, akin to a normative mineralogical

21   analysis for rock composition, the calculations are intended to provide a normative result that

22   serves as simple basis for comparing tourmalines that is more direct than names derived from the

23   most abundant species present.

24

25   Keywords: tourmaline, formula, mole fractions, end-members, electron microprobe analysis

26

Introduction

27

28   Tourmaline is by far the most important mineral phase in the earth's crust that contains

29   boron as an essential structural component. A complex borosilicate, the general formula for

30   tourmaline can be expressed as $XY_3Z_6(BO_3)_3(T_6O_{18})V_3W$, where most commonly X = (Na, Ca,

31   K, or vacancy), Y = (Mg, Fe^{2+}, Al, Li, Mn, Ti, Cr^{3+}, V^{3+}, Z = Al, Fe^{3+}, Cr^{3+}, V^{3+}, Fe^{2+}, Mg, or

32   vacancy), T = (Si, Al, or B), B = (B or vacancy), V = (OH, O), and W = (OH, O, F, Cl)

33   (Hawthorne and Henry 1999; Filip et al. 2012; Henry et al. 2011; Bosi et al. 2012). Simple, yet

34   informative, description of tourmaline composition is hindered by naming the mineral for the

35   most abundant end-member species present - with or without other compositional modifiers. A

36   more direct approach for tourmaline description would result from presentation of the mole

37   fractions of end-member species, similar to methods used for other mineral groups such as the

38   feldspars and pyroxenes. Despite considerable previous efforts toward calculating tourmaline

39   chemical formula, a mole fraction approach has been hindered by the complexity of tourmaline

40   crystal chemistry and resultant lack of a simple tool for calculation.

41   Calculating a chemical formula for tourmaline from an electron microprobe analysis

42   (EMPA) is complicated by the incorporation of up to three elements (B, H, and Li) that are

43   difficult or impossible to analyze using fluorescent X-rays. Moreover, the stoichiometric

44   abundance of hydrogen can vary due to several coupled substitutions and, thus, change the total

45   charge basis that provides the normalizing factor for calculating the chemical formula. Several

46   methods and spreadsheets for recalculating composition and formula from EMPA previously

47   have been discussed and distributed (e.g., Henry and Dutrow 2002; Selway and Xiong 2002;

48   Yavuz et al. 2006; Clark 2007), and these are useful for naming a tourmaline species and/or

49   classifying composition using a series of ternary and quaternary diagrams (e.g., Selway and

50   Xiong 2002; Hawthorne and Henry 1999; Henry et al. 2011). The program of Yavuz et al. (2006)

51   calculates the structural formula, including estimation of oxidized species, and provides the

52   relative percentages (mole fractions) of tourmaline types based on X site speciation (sodic,

53   calcic, and vacancy series), but the program does not estimate mole fractions of any tourmaline

54   end-member species. The TOURCOM program of Pesquera et al. (2008) calculates mole

55   fractions of tourmaline species, albeit using a somewhat outdated list of species, but does so

56   from a tourmaline formula as input rather than from compositional (oxide weight percent) data.

57   Hence, to date none of these approaches easily furnish mole fractions of end-member

58   components from an oxide weight fraction analysis, which is unfortunate because component

59   mole fractions would more instructive for conveyance of tourmaline composition in text than a

60   simple name, and so would be more useful for comparing tourmaline compositions and relating

61   those compositions to chemical environment of formation. For example, consider the

62   hypothetical tourmaline composition shown in Table 1. This composition was calculated from a

63   formula corresponding to 40% schorl, 25% dravite, 20% foitite, and 15% olenite on a molar

64   basis. Use of spreadsheets like that of Selway and Xiong (2002) does a fine job of calculating the

65   atomic formula and assigns the name "schorl" to the phase. Although "schorl" is the correct

66   name for this mineral according to the present rules (e.g., Henry et al. 2011), the name does not

67   convey a compositional difference relative to a mineral that is pure schorl. The use of other

68   descriptive or Schaller modifiers along with species name (cf. Henry et al. 2011) can provide

69   more compositional information, but typically yield convoluted names that provide at best a

70   qualitative description of composition. For example "dravitic-foititic-olenitic- schorl" requires

71   about the same number of characters to print, but provides less direct information than

72   Shl(40)Drv(25)Ftt(20)Oln(15)xF(0), where xF represents the mole fraction of F in the W site.

73   To date, the lack of use of tourmaline end-member components likely stems from the

74   complexity of tourmaline crystal chemistry and resultant lack of a simple tool for calculation.

75   This work describes a spreadsheet (Morgan_ProportionalTourmalineFormula_09July2015.xls)

76   that calculates the mole fractions of end-member components for Na-Ca-Li-Mg-Fe^{2+}-Al

77   tourmalines from electron microprobe data that includes TiO_2 and MnO. The compositional

78   input also includes the B_2O_3 concentration either obtained by direct analysis (e.g., by SIMS or

79   EMPA) or estimated from stoichiometry. The method utilized is based upon a 31 anion formula

80   calculation as discussed by Clark (2007). Although knowledge or estimation of the actual H (i.e.,

81   H_2O) concentration is commonly helpful for accurate calculation of formulae (e.g., Clark 2007;

82   Henry et al. 2011), it is not necessary for the present purpose as the H_2O concentration is used as

83   a variable in the present spreadsheet to optimize the cation formula based upon either or both

84   filling the Y site at 3 atoms per formula unit and/or estimation of the OH site occupancy. It is re-

85   emphasized here that the calculations in this spreadsheet do not include all IMA approved

86   tourmaline species, and that the spreadsheet is not intended to produce a species name according

87   to IMA conventions. Rather, this spreadsheet contains a subset of what are considered to be

88   useful tourmaline end-members that are easily applicable to electron probe data, intended for the

89   simple purpose of normative comparison of composition.

90

Methods

92   **Calculational Approach**

93   The approach to calculation was to first develop a spreadsheet (in Microsoft Excel) that

94   calculates a chemical formula based upon a 31 anion normalization (default 62^- total anionic

95   charge) from electron microprobe data that includes wt% B_2O_3 (e.g., Clark 2007). The decision

96   to include B_2O_3 concentration in the input was based on several factors: (1) addition of boron

97   reduces unconstrained components to two (Li, H); (2) boron can be analyzed directly by EMPA

98   or SIMS; (3) in cases where boron cannot, or is not, analyzed directly, the B_2O_3 concentration

99   can be estimated by the assumption of stoichiometric abundance (Selway and Xiong 2002; Clark

100   2007); and (4) the desire to accommodate tourmaline compositions that contain boron at the T

101   site. The latter desire partly stems from application to experimental tourmaline synthesis at the

102   University of Oklahoma, of which some products have been shown by both EMPA and other

103   methods (e.g., SIMS, ^{11}B NMR) to contain tetrahedrally-coordinated boron in excess of that

104   required to fill the trigonally-coordinated boron site, along with a concomitant Si deficiency

105   (e.g., London 2011; Guttery 2012).

106   Once a chemical formula is derived from the compositional data, atoms are assigned to

107   structural sites according to current tourmaline nomenclature (e.g., Henry et al. 2011). The moles

108   and subsequent mole fractions of components are then derived using a series of simple "IF" or

109   "IF/AND" logical statements that progressively calculate the moles of end-member species and

110   subtract the associated number of atoms associated with each from the starting stoichiometry,

111   ideally to arrive at a zero residual sum for all elements in the formula. Because they were

112   developed separately, but from a common root file, calculations for lithium-free and lithium-

113   bearing tourmalines are performed on separate sheets that draw their compositions by link to the

114   "front-end" sheet (Sheet 1) on which the user enters the composition and sample name for

115   calculation. Following entry of the composition, the user simply adjusts the water content of the

116   phase to optimize the sums of the Y site and OH site in the field (Li-free or Li-bearing) that is

117   appropriate for the mineral being considered; if necessary, the oxygen (anion) basis also can be

118   adjusted to provide an optimization of ΣYZTB cations (ideal = 18.000) but this is typically only

119   needed in the case of complex, oxidized (deprotonated) compositions. If the Li_2O content is

120   initially unknown, as is usually the case for minerals analyzed by electron probe, the Li-bearing

121   sub-sheet will calculate the approximate Li apfu allowing the user to refine the formula by

122   adjusting the Li_2O concentration on the front-end sheet; in such cases several subtle adjustments

123   of Li_2O and H_2O concentrations may be necessary to optimize the Y and OH site totals. The

124   atoms of Ti in the formula are added to Fe for the mole fraction calculations, and thus are added

125   to the schorl component. This does not produce a large error because Ti typically is present only

126   at trace levels (<0.5 wt%) in reduced tourmalines. A concentration of 0.5 wt% TiO_2 corresponds

127   to only a 2 mol% fictive schorl component in dravite, the Li-free tourmaline for which

128   stoichiometry would be most strongly affected by Ti(Y) substitution because of its low average

129   atomic number. All Ca in lithium tourmaline is calculated as a "hydroxy-liddicoatite" component

130   (not an IMA approved species). The calculations do not distinguish between "fluor-" or

131   "hydroxy-" end-members of relevant species, but do provide the mole fractions of F and Cl in

132   the W site (cells K32 & K33) for comparison; because F and Cl are believed not to enter the V

133   site (e.g., Henry et al. 2011), this value is not allowed to exceed 1.00.

134   Performing a normalization series that identifies the dominant species, based upon the

135   most abundant component (cation or vacancy) in the X site and most abundant cation in the Y

136   site (e.g., Henry et al. 2011), and then subtracts its associated cations from the bulk formula

137   would be most in line with the convention used for naming tourmalines (e.g., Henry et al. 2011).

138   Because ratios among Na, Ca, and vacancy in the X site, and among Fe, Mg, Al, and Li in the Y

139   site vary among different tourmaline species, however, such an approach would require a

140   procedure in which the order of calculation of the amounts of different tourmaline species is

141   variable dependent upon bulk composition. Moreover, attempts at such a simple, directly

142   "subtractive" approach commonly run into calculational difficulties involving balance of Mg and

6

143   Fe with Al in the Y site for tourmalines with significant X site vacancy. A way found to

144   circumvent these issues is to perform calculations for group based upon X site components

145   (sodic, calcic, and vacancy series), and to derive the abundances of Fe and Mg species within

146   these groups according to the Fe/Mg ratio of the bulk composition. Although this approach tends

147   to slightly reduce the calculated norm for the more abundant Fe or Mg species in each group

148   (e.g., schorl versus dravite, foitite versus magnesio-foitite), it typically does not decrease the

149   dominant species enough to affect naming the tourmaline for the most abundant species as

150   derived from simple consideration of chemical formula.

151

152   **End-Members Included**

153   The end-member components included in the calculations are listed in Table 2. End-

154   members represented among the common tourmaline species include all except Cr-rich, V-rich,

155   and Fe^{3+}-bearing compositions. Although Cr- and V-rich members should be easy enough to

156   accommodate, they are comparatively rare and were not considered a high priority for the

157   present spreadsheet. Calculation of ferric iron species was neglected because of multiple

158   substitution mechanisms that accommodate trivalent cations at the Y crystallographic site, and so

159   results would not be conclusive without direct analysis of Fe^{3+} and/or Li and H that are not

160   amenable to analysis by electron probe. Lithium-rich tourmaline species included in the

161   calculations are elbaite, rossmanite, and (hydroxy-) liddicoatite. Although darrellhenryite,

162    $Na(LiAl_2)Al_6(BO_3)_3Si_6O_{18}(OH)_3O$, has recently been accepted as a tourmaline species (Novak et

163   al. 2013), it was not included in the present calculations because it would be impossible to

164   resolve from a combination of elbaite and olenite using electron microprobe data.

165

Results

Example of calculation for a nominally Li-Free tourmaline

166

167

168   As a starting point, consider calculating the end member mole fractions for the

169   tourmaline composition shown in Table 1. The user enters the known, and/or estimated,

170   concentrations of oxide components and the name of the sample in the blue cells of Sheet 1 of

171   the spreadsheet (Fig. 1a: name in cell C3, oxides in cells B7-B20). After data entry (Fig 1a), note

172   an analytical total less than 100 wt%, calculated sums at the Y crystallographic site (red cells) for

173   both Li-free and Li-bearing tourmalines significantly in excess of 3, and a poor match to the

174   ideal stoichiometry of the phase (40-25-0-0-0-20-0-15, listed in the mole percent sequence

175   schorl-dravite-tsilaisite-uvite-feruvite-foitite-magnesio-foitite-olenite that is used by convention

176   for Li-free tourmalines hereafter). Excesses at the Y site and errors in the end-member

177   components at this stage are due to an incorrect number of cations to charge balance the oxygen

178   (anion) basis of the calculation, so is due to the absence of hydrogen. The easiest logical

179   adjustment to make at this point is to add water by difference, in the amount of 100-(Total),

180   which is 3.18 wt%. The Li-free calculations show that addition of this concentration of water

181   (Fig. 1b) yields a 3.00 apfu sum at the Y site and a sum of YZBT cations of 18.0005, indicating

182   that the calculations are complete. Note that whereas calculation of the mole fractions of species

183   by the Li-free sheet does not exactly reproduce the theoretical stoichiometry used for calculating

184   the tourmaline composition, the Li-bearing sheet does. This is because the Li sheet performs a

185   strictly progressive subtractive calculation routines whereas the Li-free sheet uses a proportional

186   normalization based upon the bulk Mg/Fe ratio for each of the tourmaline groups based upon X

187   site occupancy. Although the Li-bearing sheet performs well for this particular sodium-dominant

188   composition, the simple subtractive method fails for tourmalines with dominant X site vacancy,

189   as discussed above.

190   Discrimination of the Table-1 tourmaline composition from a Li-bearing tourmaline is

191   indicated by the 100 wt% analytical total obtained with added water and a zero estimated Li

192   content from the Li-bearing calculation routine. Note that the OH site total, $=\Sigma V+W$, is 3.55 (Fig

193   1b); this value is correct given the presence of 15 mol% olenite, each mole of which removes 3

194   moles of H. Calculated residuals from the sheet making the Li-Free calculations (Table 5) are

195   very low and essentially represent rounding errors in the calculations.

196

197   **Example of calculation for a Li-bearing tourmaline**

198   For a lithium-bearing tourmaline, consider calculation for a 50-50 molar mixture of

199   elbaite and rossmanite. As in the example above, the weight percent values for known oxide

200   components (excluding Li_2O) are entered in the blue cells (Fig. 2a: name in cell C3, oxides in

201   cells B7-B20). Note that in this example, a MgO concentration of 0.001 wt% was added to avoid

202   a division by zero error in the Li-Free sheet (sum of FeO+MgO=0); this addition is not necessary

203   for calculation of Li-bearing tourmalines. After data entry, again the analytical total is

204   significantly less than 100 wt% and the Y site sum for Li-free calculation is significantly

205   different than 3.00 (Fig. 2a). Identification as a Li-rich tourmaline is apparent from the

206   aluminous nature of the tourmaline, the positive estimated Li content from the Li-bearing

207   calculation, and the Y site sum for the Li-free calculation being much less than 3.00. Among the

208   remaining calculations, the addition of water to the analysis would only decrease the Y site sum

209   further and, hence, the calculations fail for a Li-absent composition. Note at this point that the Y

210   site sum for the Li-bearing calculation is 3.00 because Li is calculated by difference at this site,

9

211   but that the amount of Li calculated is underestimated. Similar to the previous example, the

212   easiest second step is to add water to obtain the proper OH site total (full at ~3.79 wt% H_2O for

213   this case: Fig. 2b). With the addition of water, note that the cations of Li calculated by the

214   spreadsheet increases, but is less than the ideal value, and that analytical total is still significantly

215   less than 100 wt%. The next step will be to add Li to the analysis. An initial estimate based on

216   difference of the analytical total from 100 wt%, =2.08 wt% Li_2O yields the correct mole

217   fractions of end-members, but provides slightly more Li to the formula (1.29 apfu) than is

218   calculated by the Li-bearing sheet (1.25 apfu), and yields a slightly deficient OH site sum as well

219   (Fig. 2c). Therefore, slight iterative adjustments to both Li_2O and H_2O (Fig. 2d) eventually

220   provide agreement between added and calculated Li, and better sums at the OH site (3.996) and

221   total of YZBT sites (18.002). Upon conclusion of calculation, the sheet performing the Li-

222   bearing calculations again shows zero or near-zero residuals for all components except

223   cumulative Li (which is correct) (Table 5).

224

225   **Compositions tested**

226   To test the spreadsheet, the chemical formulae of selected tourmaline stoichiometries

227   were converted to weight percent oxides using a spreadsheet that derives the oxide (and

228   elemental) weight fractions for a phase based upon the numbers of cations and anions in its

229   chemical formula unit. The compositions of Li-absent tourmalines tested include all of the end-

230   members in the calculation (tsilaisite not shown in table), 50-50 molar mixtures of dravite-schorl,

231   dravite-uvite, uvite-foitite, and schorl-foitite, a limited number of ternary compositions, and a

232   variety of more complicated 4- and 5-component theoretical phases plus some natural complex

233   compositions. The compositions and results from calculation for the simple Li-absent phases are

234   provided in Table 4, and those for the more complex Li-absent compositions in Table 5. The

235 residuals resulting from all Li-absent calculations are provided in Table 6. As can be seen, the

236 spreadsheet exactly reproduced the mole fractions of simple unary and binary compositions. As

237 compositions become more complex, there is slightly poorer agreement between theoretical and

238 calculated mole fractions due primarily to the effect of Fe/Mg proportionation among members

239 of the various X-site compositional groups. For example, note that the 50-30-0-20-0-0-0

240 composition yielded 40-40-0-10-10-0-0 because Na and Fe from the schorl component are re-

241 distributed toward dravite and feruvite components. Note that the solution obtained, 40-40-0-10-

242 10-0-0, represents a schorl-dravite that is just as consistent with the stoichiometry of the mineral

243 as the formula used to calculate the composition. This demonstrates a complication with

244 calculating tourmaline mole fractions: a single composition may be described algebraically by

245 more than one combination of accepted tourmaline species. Among the compositions tested

246 (Tables 3 and 4), however, this is one of only two cases noted where the mole fraction

247 calculations made naming the tourmaline for the most abundant species ambiguous or inaccurate

248 in comparison to the mole fractions used to calculate it.

249   Compositions input for Li-bearing tourmalines were calculated in the same manner as for

250 Li-free tourmalines. The compositions tested included elbaite, rossmanite, liddicoatite, a 50-50

251 molar mixture of elbaite-rossmanite, an elbaite(50)foitite(25)olenite(25) molar mixture, and

252 natural elbaitic tourmalines from the Little Three pegmatite (Morgan and London 1999) and

253 Elba, Italy. The results, residuals, and calculated Li atoms per formula unit are shown in Table 6.

254 Again, the spreadsheet faithfully reproduced the ideal mole fractions, and independently

255 calculated the cations of Li present to within 0.01 apfu of the ideal mineral formulae for the

256 calculated compositions. Calculations from the natural "elbaites" shows olenitic, rossmanitic,

257 and even tsilaisite –dominated results, consistent with the observation of Guttery (2012) that no

258 reported natural elbaite has been found to contain more than about 67 mole% of the elbaite end-

259 member.

260

261

Discussion

263   The present spreadsheet faithfully reproduces the formulae and mole fractions of the ideal

264 Li-absent end-members and their simple solid solutions tested here (Table 3). Reproduction of

265 mole fractions for more complex, quaternary and higher, calculated compositions (Table 4)

266 shows less perfect agreement with norms used to calculate the compositions for two reasons: (1)

267 not all compositions have a unique solution (e.g., a mixture of schorl and magnesio-foitite can

268 have an identical composition to a mixture of dravite and foitite); and (2) calculation of Fe and

269 Mg species among the different X site groups according to bulk Fe/Mg ratio can yield a

270 decrease in the mole fraction of the dominant component versus increase in that of the less

271 dominant one (e.g., schorl versus dravite; foitite versus magnesio-foitite). Both of these factors

272 are exacerbated for compositions with intermediate proportions of X site vacancy, and such

273 compositions can result in a dominant species mole fraction that is inconsistent with the species

274 name based upon simple consideration of the most abundant components in the X and Y sites.

275 An example of this is the 50-30-0-20-0-0-0-0 composition in Table 3 that yielded a 40-40-0-10-

276 10-0-0-0 norm, so would be named schorl-dravite even though the formula used for calculating

277 composition was schorl-dominant. As mentioned above, the solution obtained is correct for the

278 atomic proportions obtained from the composition, and highlights the problem that all

279 compositions may not have a unique solution with respect to mole fractions. This apparently

280 indicates that at least some of the accepted tourmaline species do not represent algebraically

12

281   discrete end-members. Such cases appear to be rare, however, and in some cases the calculated

282   mole fraction of the dominant species is greater than that of the theoretical formula used to

283   calculate the composition (e.g., the 40-25-0-0-0-20-0-15 composition yielded 44-21-0-0-0-14-6-

284   15, and the 40-30-0-0-10-0-10 composition yielded 46-27-0-4-6-6-4-7: Table 4).

285   Among the admittedly few calculated Li tourmaline compositions tested, the spreadsheet

286   accurately reproduced the ideal mole fractions and calculated cations of Li to within 0.01 apfu of

287   the ideal mineral formulae. Because the Li content is calculated by difference at the Y site, Li

288   can be slightly overestimated for crystals having significant vacancy at that site. There is,

289   however, no way to determine such vacancy from electron probe data: other methods are needed

290   (e.g., Filip et al. 2012). Because such vacancy cannot be evaluated from microprobe data, and

291   because tourmalines that contain appreciable Li commonly are Li-rich (i.e., elbaite-rossmanite-

292   liddicoatite solid solutions), this uncertainty is not considered an important (or addressable)

293   source of error for the mole fraction calculations presented here.

294   Noting reproduction of the mole fractions for calculated compositions within the limits

295   discussed, application can be turned to natural compositions. A dravite-uvite composition taken

296   from Deer, Howie, and Zussman (1982), DHZ, was indicated in its reference to have 4.40 wt%

297   H_2O, but the Li-free calculations yielded both an analytical total in excess of 100 wt% and

298   significantly more than four OH radicals per formula unit using that concentration. Lowering the

299   water content to 3.72 wt% (Table 4) yields 4.005 OH per formula unit, consistent with zero

300   olenite and ferric iron components, and lowers the analytical total to slightly less than 100 wt%.

301   Calculation by the Li-absent spreadsheet yields the result of 0-53-0-40-2-0-0-0 identifying this

302   tourmaline as dravite (dravite-uvite), consistent with Na>Ca and Mg>Fe. The DHZ composition

303   is notable in having 3.288 Mg apfu – a number greater than can be accommodated by the Y site

13

304   in tourmaline. The spreadsheet handles this by allocating Mg to the Z site, in agreement with

305   formulae for uvite and feruvite in which Mg^{2+} at the Z site provides charge compensation for

306   Ca^{2+} at the univalent X site (e.g., Hawthorne and Henry, 1999), although the presence of Mg in

307   the Z site led to slightly larger negative residuals at the T and Y sites than other compositions

308   tested (Table 5).

309   The mole fraction calculations for the L35f, HGTR40, BMR-CT, and India Dravite

310   tourmalines analyzed in our lab at Oklahoma (Table 4) all produce low residuals (Table 5) and

311   would yield names based on most abundant component consistent with the convention based

312   upon bulk X site occupancy and Mg/Fe ratio. The discussed uncertainties in formulae and

313   naming for tourmalines having intermediate values of X site occupancy, however, are

314   particularly notable for the Bačík -1 and Bačík -2 compositions (from Bačík et al. 2015) in Table

315   4. For the Bačík-1 composition, Na has slightly greater abundance than both vacancy and

316   calcium in the X site, and Fe>Mg in the Y site; by convention this species would be named

317   "schorl". The most abundant species calculated by the spreadsheet, however, is foitite at 22% as

318   compared to schorl at 19%. The result is similar, but slightly better, for the Bačík-2 composition

319   for which the two most abundant calculated species are schorl (22%) and foitite (19%). These

320   results show the uncertainty for naming tourmaline species with intermediate X site occupancies

321   from mole fraction calculations. Given that both tourmalines contain <0.44 apfu Na and have

322   Fe/(Fe+Mg)~0.6, it is suggested here that the name "schorl" is perhaps no less misleading than

323   "foitite" or "schorl-foitite-feruvite". Regardless of species name derived, however, the relative

324   fractions of sodic, calcic, and vacancy species produced by the spreadsheet are correct. In these

325   latter cases, the relative fractions of sodic species (schorl, dravite, olenite) are greater than that of

326   the other X-site groups (calcic, vacancy). Hence, although such compositions provide the

14

327   greatest uncertainty for naming a tourmaline species from mole fractions, the conveyance of

328   mole fractions provides more information about the true chemical nature of the mineral than

329   naming for the dominant species.

330   As discussed above, the spreadsheet does not address the abundances of oxidized species

331   containing trivalent cations in the Y crystallographic site. Although reasons have been presented

332   for not considering the abundances of oxidized atoms of Fe or other multivalent transition

333   metals, there is an additional complicating factor that is not yet well addressed by present

334   tourmaline nomenclature - namely the coupled substitution of trivalent cations in the Y and T

335   crystallographic sites. Boron can substitute for Si in the T site with charge balance mostly

336   maintained by the substitution of Al at the Y site (e.g., Hughes et al. 2009; Lussier et al. 2009).

337   Because significant tetrahedral boron is rare in natural tourmaline, and because there is no end-

338   member species named for this substitution, it does not affect mole fraction calculations (or

339   naming). Perhaps the most common trivalent ion substituting in the T site of tourmaline is

340   aluminum (e.g., Lussier et al. 2009), yielding a net substitution of the form: $M^{3+}(Y) + Al^{3+}(T) =$

341    $M^{2+}(Y) + Si^{4+}(T)$. Tourmaline is commonly formed in aluminous schists and in association with

342   highly-fractionated peraluminous granitic magmas, the latter of which become more aluminous

343   and transition metal-depleted with fractionation (London 2011). Tourmalines produced in both

344   environments often are more aluminous than ideal formulae, and often appear to involve the

345   operation of a "Tschermak"-like substitution of the form $Al(Y)Al(T) = M^{2+}(Y)Si(T)$ that could

346   progress toward a hypothetical hyper-aluminous tourmaline similar to

347    $NaAl_3Al_6(BO_3)_3(Si_3Al_3)O_{18}(OH)_4$. This substitution (with lesser $Al(Y)B(T)$) appears to lie at the

348   heart of hyper-aluminous, but Li-poor, tourmalines produced by experimental synthesis at the

349   University of Oklahoma (e.g., Guttery 2012; London 2011). Even though aluminum in the T site

15

350   is recognized to be common in natural tourmaline (Lussier et al. 2009), to date only one species

351   has been named that is distinctive for T-site Al: adachiite, $CaFe_3Al_6(Si_5Al)O_{18}(BO_3)_3(OH)_3(OH)$

352   (Nishio-Hamane et al. 2013). At present, however, there is no Mg-analog of this mineral, and

353   definition as a Ca- and Fe-rich tourmaline makes it of little application to hyper-aluminous

354   tourmalines from evolved pegmatite systems that tend to be depleted in both Ca and Fe and, as

355   discussed above, could potentially contain more than one Al in the T site. Therefore, even though

356   an approved species, adachiite was not considered an algebraically useful end-member for the

357   present calculations, and T site substitution of Al is omitted from the present calculation of end-

358   member mole fractions. Fortunately this is not a significant concern for mole fraction

359   calculations (or naming) for most natural tourmaline compositions, but it does complicate

360   estimating the abundances of other trivalent cations and lithium at the Y site as well as the

361   abundance of "oxy"-tourmaline species including olenite. With respect to "oxy-" tourmalines,

362   oxy-dravite $[Na(Al_2Mg)(Al_5Mg)(Si_6O_{18})(BO_3)_3(OH)_3O]$ (Bosi and Skogby 2013) and oxy-schorl

363   $[Na(Fe_2Al)(Al_6)(Si_6O_{18})(BO_3)_3(OH)_3O]$ (Bačík et al. 2013) are both approved tourmaline species

364   that are not addressed in the present calculations. Not only is the deprotonation in these minerals

365   not determinable from microprobe data, but at least algebraically both of these minerals represent

366   a combination of the root minerals (dravite and schorl) with olenite. Comparing the formula for

367   oxy-dravite, above, with that of olenitic-dravite, $Na(Mg_2Al)Al_6(Si_6O_{18})(BO_3)3(OH)_3O$, shows

368   the main distinction between phases to be disordering of Mg between the Y and Z sites in oxy-

369   dravite. Such disorder cannot be evaluated from electron probe data. Because of a lack of

370   algebraic uniqueness and inability to discern from electron probe data, the "oxy-" tourmaline

371   species are not addressed in the present spreadsheet; oxidized species in the present calculations

372   will at least partly be reflected by the olenite mole fraction, which represents a discrete

16

373   calculable component. If, however, a true Tschermak-like tourmaline end-member is ever

374   adopted as an approved end-member, then the present spreadsheet likely should be revised to

375   include that species – perhaps at the expense olenite. In that way, the aluminous component

376   reflected by Al(Y) would be treated in an equal manner to other tourmaline species without

377   regard to oxidation state or water activity.

378

379   **Implications**

380   Potential users should bear in mind that this spreadsheet is directed at simple normative

381   calculations from electron probe data for Na-Ca-Li-Fe^{2+}-Mg-Al tourmalines. For reasons

382   outlined previously, it does not address the mole fractions of Cr-rich, V-rich, or Fe^{3+}-rich

383   tourmalines, does not include calculation for K-rich tourmaline (although K is included in

384   calculating X site occupancy), and does not include deprotonated "oxy"-tourmalines other than

385   olenite. Some of these components, such as Cr and V, should be comparatively easy to address in

386   calculation whereas some, especially Fe^{3+} and deprotonated species, may be impractical unless

387   analyses in addition to EMPA are performed. The incorporation of Fe^{3+} species likely would

388   require a significant re-working of the spreadsheet which was deemed unnecessary given its

389   primary application for calculating tourmaline formula from EMPA data. Because not all IMA

390   approved tourmaline species are included, nor can even be distinguished on the basis of electron

391   probe data alone, this spreadsheet cannot be used to definitively name or classify a tourmaline

392   according to IMA rules and accepted species. Rather, this spreadsheet is intended to fill a niche

393   similar to that of a mineralogical norm for rock composition by providing a tool for direct

394   comparison of tourmalines from different deposits according to a common standard. Even if this

395   particular spreadsheet does not prove to be the accepted tool for such comparison, it is my hope

396   that other researchers will either improve upon this work or develop and distribute a more

397   comprehensive and user-friendly tool for calculating tourmaline mole fractions. In this way we

398   can move past the vague "(species)-itic" procedure of describing tourmaline towards a method

399   with more chemical specificity.

400

Acknowledgements

411

412

References Cited

413

414 Bačík P., Cempírek, J., Uher, P., Novák, M., Ozdín, D., Filip, J., Škoda, R., Breiter, K.,

415 Klementová, M., Ďuda, R., and Groat, L.A. (2013) Oxy-schorl,

416 $Na(Fe^{2+}_2,Al)Al_6Si_6O_{18}(BO_3)_3(OH)_3O$, a new mineral from Zlatá Idkam Slovak Republic and

417 Přibyslavice, Czech Republic. American Mineralogist, 98, 485-492.

418

419 Bačík P., Koděra P., Uher P., Ozdín D., Jánošík M. (2015) Chlorine-enriched tourmalines in

420 hydrothermally altered diorite porphyry from the Biely Vrch porphyry gold deposit (Slovakia).

421 Can. Mineral., in press.

422

423 Bosi, F. and Skogby, H. (2013) Oxy-dravite, $Na(Al_2Mg)(Al_5Mg)(Si_6O_{18})(BO_3)_3(OH)_3O$, a new

424 mineral species of the tourmaline supergroup. American Mineralogist, 98, 1442-1448.

425

426 Bosi F., Skogby H., Agrosì G., Scandale E. (2012) Tsilaisite,

427 NaMn3Al6(Si6O18)(BO3)3(OH)3OH, a new mineral species of the tourmaline supergroup from

428 Grotta d'Oggi, San Pietro in Campo, island of Elba, Italy. American Mineralogist, 97, 989-994.

429

430

431 Clark, C.M. (2007) Tourmaline structural formula calculations. Canadian Mineralogist, 45, 229-

432 237.

433

434 Deer, W.A., Howie, R.A., and Zussman, J. (1982) An Introduction to the Rock Forming

435 Minerals. Longman Group Limited, Essex, England, pp 92.

436   Dunn, P.T., Appleman, D., Nelen, J.A., and Norberg, J. (1977) Uvite, a new calcium member of

437   the tourmaline group, and its implications for collectors. American Mineralogist, 62, 1121-1124.

438

439   Filip, J., Bosi, F., Novák, M., Skogby, H., Tuček, J., Čuda, J., and Wildner, M. (2012) Redox

440   processes of iron in the tourmaline structure: example of the high-temperature treatment

441   of Fe^{3+}-rich schorl. Geochimica et Cosmochimica Acta, 86, 239–256.

442

443   Grice, J.D., and Robinson, G.W. (1989) Feruvite, a new member of the tourmaline group, and its

444   crystal structure. Canadian Mineralogist, 27, 199-203.

445

446   Guttery, B.G. (2012) The stability field and conditions of formation of elbaite. MS Thesis,

447   University of Oklahoma, Norman, 74pp.

448

449   Hawthorne, F.C., and Henry, D.J. (1999) Classification of the minerals of the tourmaline group.

450   European Journal of Mineralogy, 11, 201-215.

451

452   Henry, D.J., and Dutrow, B.L. (2002) Metamorphic tourmaline and its petrologic applications.

453   In: Boron Mineralogy, Petrology, and Geochemistry, Mineralogical Society of America,

454   Reviews in Mineralogy, 33, 503-557.

455

456   Henry, D.J., Novák, M., Hawthorne, F.C., Ertl, A., Dutrow, B.L., Uher, P., and Pezzotta, F.

457   (2011) Nomenclature of the tourmaline-supergroup minerals. American Mineralogist, 96, 895-

458   913.

459

460 Hughes, J.M., Ertl, A., Dyer, M.D., Grew, E.S., Shearer, C.K., Yates, M.G., and Guidotti, C.V.

461 (2009) Tetrahedrally coordinated boron in tourmaline: Boron-rich olenite from Stoffhütte,

462 Koralpe, Austria. Canadian Mineralogist, 38, 861-868.

463

464 London, D. (2011) Experimental synthesis and stability of tourmaline: a historical overview.

465 Canadian Mineralogist, 49, 117-136.

466

467 Lussier, A.J., Aguiar, P.M., Michaels ,V.K., Kroeker, C., and Hawthorne, F.C. (2009) The

468 occurrence of tetrahedrally coordinated Al and B in tourmaline: An ^{11}B and ^{27}Al MAS NMR

469 study. American Mineralogist, 94, 785-792.

470

471 Nishio-Hamane, D., Minakawa, T., Yamaura, J., Oyama, T., Ohnishi, M. and Shimobayashi, N.

472 (2013) Adachiite, IMA 2012-101. Mineralogical Magazine, 77, 2695-2709.

473

474 Novák, M., Ertl, A., Povondra, P., Vašinová Galiová, M., Rossman, G.R., Pristacz, H., Prem, M.,

475 Giester, G., Gadas, P., and Škoda, R. (2013) Darrellhenryite, $Na(LiAl_2)Al_6(BO_3)_3Si_6O_{18}(OH)_3O$,

476 a new mineral from the tourmaline supergroup. American Mineralogist, 98, 1886-1892.

477

478 Selway, J.B., and Xiong, J. (2002) Tourmaline recalculation software (quoted in Tindle AG,

479 Breaks, F.W., and Selway, J.B. (2002) Tourmaline in petalite-subtype granitic pegmatites:

480 evidence of fractionation and contamination from the Pakeagama Lake and Separation Lake

481   areas of northwestern Ontario, Canada. Canadian Mineralogist, 40, 753-788);

482   http://www.open.ac.uk/earth-research/tindle/

483

484   Yavuz, F., Yavuzm V., and Sasmaz, A. (2006) *WinClastour* – a Visual Basic program for

485   tourmaline formula calculation and classification. Computer and Geosciences, 32, 1156-1168.

486

487

488   Table 1. Hypothetical tourmaline composition

Oxide	Wt.%
SiO_2	35.84
B_2O_3	10.38
Al_2O_3	33.70
FeO*	11.43
MgO	3.01
Na_2O	2.46
H_2O	3.18
Total	100.00

489

490

491

492   Table 2. Tourmaline end-members included in the calculations; □ denotes a site vacancy.

Phase	Abbreviation	Formula
Common tourmalines		
Schorl	Shl	$NaFe_3Al_6(BO_3)_3Si_6O_{18}(OH)_3OH$
Dravite	Drv	$NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_3OH$
Tsilaisite	Tsl	$NaMn_3Al_6(BO_3)_3Si_6O_{18}(OH)_3OH$
Feruvite	Fuv	$CaFe_3(Al_5Mg)(BO_3)_3Si_6O_{18}(OH)_3OH$
Uvite	Uvt	$CaMg_3(Al_5Mg)(BO_3)_3Si_6O_{18}(OH)_3OH$
Olenite	Oln	$NaAl_3Al_6(BO_3)_3Si_6O_{18}((OH)O_2)O$
Foitite	Ftt	$□(Fe_2Al)Al_6Si_6(BO_3)_3Si_6O_{18}(OH)_3OH$
Magnesio-foitite	Mft	$□(Mg_2Al)Al_6Si_6(BO_3)_3Si_6O_{18}(OH)_3OH$
Lithium tourmalines		
Elbaite	Elb	$Na(Li_{1.5}Al_{1.5})Al_6(BO_3)_3Si_6O_{18}(OH)_3OH$
Rossmanite	Rss	$□(LiAl_2)Al_6(BO_3)_3Si_6O_{18}(OH)_3OH$
Liddicoatite-OH	Ldd	$Ca(Li_2Al_1)Al_6(BO_3)_3Si_6O_{18}(OH)_3OH$

493

494

495

496

23

497   Table 3. Simple theoretical Li-free compositions tested

	Shorl	Dravite	Uvite	Feruvite	Foitite	Mg-Foitite	Olenite	Shl(50)-Drv(50)	Drv(50)-Uv(50)	Uv(50)-Mft(50)	Shl(50)-Oln(50)	Shl(50)-Ftt(50)	50,30,0, 20,0, 0,0,0	0,20,0, 40,40, 0,0,0	0,0,0, 30,40, 0,0,30
Wt%															
SiO$_2$	34.23	37.60	37.04	33.76	36.00	38.42	37.41	35.83	37.32	37.68	35.75	35.09	35.73	35.76	35.76
B$_2$O$_3$	9.92	10.89	10.73	9.78	10.43	11.13	10.84	10.38	10.81	10.92	10.36	10.17	10.35	10.36	10.35
Al$_2$O$_3$	29.04	31.90	26.19	23.87	35.63	38.02	47.60	30.40	29.02	34.64	37.91	32.25	29.30	26.29	31.35
FeO	20.46			20.19	14.35			10.71			10.69	17.48	10.68	8.55	8.55
MgO		12.62	16.57	3.78		8.59		6.01	14.61	10.54			6.79	10.40	6.40
CaO			5.76	5.25					2.90	2.93			1.11	4.45	3.89
Na$_2$O	2.94	3.23					3.22	3.08	1.60		3.07	1.51	2.46	0.62	0.92
H$_2$O	3.42	3.76	3.70	3.37	3.60	3.84	0.93	3.58	3.73	3.30	2.23	3.51	3.57	3.57	2.77
Total	100.00	100.00	99.99	100.00	100.01	100.00	100.00	99.99	99.99	100.01	100.01	100.01	99.99	100.00	100.01
Results															
APFU (#Ox)	31	31	31	31	31	31	31	31	31	31	31	31	31	31	31
Si	6.000	6.000	6.000	6.000	6.000	6.001	6.001	6.000	6.001	5.999	6.000	5.999	6.001	6.001	6.000
Ti															
B	3.001	2.999	3.000	3.000	3.000	3.000	3.001	3.000	3.000	3.000	3.001	3.001	3.000	3.000	3.000
Al	6.000	6.000	5.000	5.001	6.999	6.999	9.000	6.001	5.500	6.500	7.500	6.499	5.800	5.200	6.200
Fe	2.999		0.000	3.001	2.000			1.500			1.501	2.500	1.500	1.200	1.200
Mg		3.001	4.000	1.001		2.000		1.500	3.501	2.501			1.700	2.601	1.600
Ca			1.000	1.000					0.500	0.500			0.200	0.800	0.699
Na	0.999	0.999					1.001	1.000	0.499		0.999	0.501	0.801	0.202	0.299
[ ]$_x$	0.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000	0.000	0.001	0.499	0.000	0.000	0.000
OH	3.999	4.002	3.998	3.995	4.002	4.001	0.995	3.999	4.000	3.504	2.497	4.003	3.999	3.996	3.100
Mole Fraction															
Schorl	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.50	0.50	0.40	0.08	0.10
Dravite	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.50	0.50	0.00	0.00	0.00	0.40	0.12	0.13
Tsilaisite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Uvite	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.50	0.50	0.00	0.00	0.10	0.48	0.40
Feruvite	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.32	0.30
Foitite	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00
Mg-Foitite	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.00	0.00
Olenite	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.07

24

498   Table 4. Complex theoretical and natural Li-free compositions tested (*-value calculated for microprobe analysis)

	40,25,0, 0,0, 20,0,15	30,10,0, 10,10, 30,10,0	40,30,0, 0,10, 10,0,10	10,40,0, 20,20, 0,0,10	DHZ[1]	Băćik-1[2]	Băćik-2[2]	L35f	HGTR-40	BMR-CT	India Dravite	Uvite C5212[3]	Feruvite[4]
Wt. %													
SiO$_2$	35.84	35.64	35.61	36.05	35.96	34.77	35.45	35.61	35.39	37.73	36.64	35.96	32.33
TiO$_2$					0.14	0.30	0.20	0.24	0.20	0.45	0.42	0.62	2.19
B$_2$O$_3$	10.38	10.33	10.32	10.45	10.73	10.37	10.31	*10.53	*10.61	*10.97	10.84	11.49	11.25
Al$_2$O$_3$	33.70	32.25	31.73	31.09	30.85	34.08	32.81	34.64	35.18	33.27	34.28	26.80	23.38
FeO	11.43	12.79	12.07	7.90	0.76	10.26	10.56	13.57	6.96	5.79	0.74	0.41	13.56
MnO						0.02	0.01	0.18	0.06	0.03	0.30		0.07
MgO	3.01	3.19	3.98	7.26	13.67	3.70	3.82	1.62	5.76	8.64	10.30	15.20	7.80
CaO		1.11	0.55	2.24	2.41	1.41	1.46	0.21	0.14	0.86	0.32	5.50	3.30
Na$_2$O	2.46	1.23	2.45	1.86	1.63	1.16	1.32	1.72	1.68	2.22	2.47	0.13	1.16
K$_2$O					0.09	0.03	0.00	0.05	0.07	0.01	0.00	0.00	0.05
H$_2$O	3.18	3.47	3.29	3.15	3.72	3.21	3.45	*3.56	*3.56	*3.49	*3.57	2.74	3.48
F						0.00	0.00	0.13	0.18	0.65		1.49	
Cl						0.11	0.05						
Total	100.00	100.01	100.00	100.00	99.96	99.37	99.43	102.01	99.71	103.85	99.88	99.71	99.57
Results													
APFU (#Ox)	31	31	31	31	31	31	31.2	31.13	31	31.08	31	31.13	30.98
Si	6.000	6.000	6.000	6.000	5.803	5.840	5.986	5.896	5.799	5.957	5.872	5.877	5.745
Ti					0.017	0.038	0.025	0.030	0.025	0.053	0.051	0.076	0.284
B	2.999	3.000	3.001	3.002	2.988	3.006	3.004	3.009	3.000	2.989	2.998	3.240	3.346
Al	6.650	6.400	6.301	6.100	5.869	6.747	6.530	6.671	6.795	6.192	6.475	5.162	4.750
Fe	1.600	1.800	1.701	1.100	0.103	1.441	1.491	1.879	0.954	0.765	0.099	0.056	1.955
Mn						0.003	0.001	0.025	0.008	0.004	0.041	0.000	0.010
Mg	0.751	0.800	0.999	1.801	3.288	0.926	0.961	0.400	1.407	2.033	2.460	3.702	2.004
Ca		0.200	0.099	0.400	0.417	0.254	0.264	0.037	0.025	0.146	0.055	0.963	0.610
Na	0.799	0.400	0.800	0.600	0.510	0.378	0.432	0.552	0.534	0.680	0.768	0.041	0.388
K					0.019	0.006	0.000	0.011	0.015	0.002	0.000	0.000	0.011
[ ]$_x$	0.201	0.400	0.100	0.000	0.055	0.362	0.304	0.400	0.427	0.173	0.178	0.000	0.000
OH	3.551	3.900	3.697	3.497	4.005	3.596	3.886	3.932	3.891	3.676	3.816	2.987	4.001
F								0.068	0.093	0.324		0.770	
Cl						0.020	0.009						
Mole Fraction													
Schorl	0.44	0.28	0.46	0.22	0.00	0.19	0.22	0.39	0.20	0.19	0.04	0.00	0.29
Dravite	0.21	0.12	0.27	0.35	0.53	0.12	0.14	0.08	0.29	0.49	0.66	0.04	0.10
Tsilaisite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
Uvite	0.00	0.06	0.04	0.25	0.40	0.10	0.10	0.01	0.01	0.10	0.05	0.92	0.15
Feruvite	0.00	0.14	0.06	0.15	0.02	0.16	0.16	0.03	0.01	0.04	0.00	0.04	0.45
Foitite	0.14	0.28	0.06	0.00	0.00	0.22	0.19	0.33	0.18	0.05	0.01	0.00	0.00
Mg-Foitite	0.06	0.12	0.04	0.00	0.00	0.14	0.12	0.07	0.25	0.12	0.17	0.00	0.00
Olenite	0.15	0.00	0.07	0.03	0.00	0.08	0.07	0.09	0.06	0.00	0.06	0.00	0.00

499

500   1 – Deer et al. (1982); 2 – Băćik et al. (2015); 3 – Dunn et al. (1977); 4 – Grice et al. (1989)

501

502 Table 5. Residuals from calculation of Li-absent tourmalines

503

504

Composition Tested:	Shl	Drv	Uvt	Fuv	Ftt	Mft	Oln	Drv50-Shl50	Drv50-Uv50	Uvt50-Mft50	Shl50-Oln50	Shl50-Ftt50
Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mg(Y)	0.0000	0.0017	0.0013	0.0000	0.0000	-0.0005	0.0000	0.0000	0.0022	0.0009	0.0000	0.0000
Fe+Ti	0.0001	0.0000	0.0000	0.0029	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Na	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0016	0.0000	0.0000	0.0000	0.0000	0.0004
□x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Al(Y)	-0.0007	-0.0006	-0.0002	-0.0002	-0.0007	-0.0007	0.0000	0.0001	-0.0016	-0.0015	0.0004	-0.0002
T	0.0001	0.0000	0.0002	0.0001	0.0000	0.0007	0.0015	-0.0005	0.0005	0.0000	0.0003	0.0024
Y	-0.0006	0.0011	0.0011	0.0027	-0.0005	-0.0012	0.0000	0.0001	0.0007	-0.0006	0.0003	-0.0002
Z	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0008	-0.0006	0.0000	0.0000	0.0000	0.0023
X	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0016	0.0000	0.0000	0.0000	0.0000	0.0004

Composition Tested:	50,30,0 20,0, 0,0,0	0,20,0, 40,40, 0,0,0	0,0,0, 30,40, 0,0,30	40,25,0, 0,0, 20,0,15 Table 1	30,10,0 10,10, 30,10,0	40,30,0 0,10, 10,0,10	10,40,0 20,20, 0,0,10	Băćik -1	Băćik -2	DHZ	Little 3 5f	BMR CT
Ca	0.0002	0.0015	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mg(Y)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0672	0.0000	0.0000
Fe+Ti	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0668	0.0000	0.0279
Mn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Na	0.0008	0.0002	0.0000	0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
□x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Al(Y)	0.0000	0.0000	0.0005	0.0014	0.0000	0.0012	-0.0003	0.0014	0.0006	-0.0546	0.0002	-0.0241
T	0.0015	-0.0002	0.0002	0.0001	0.0003	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Y	0.0000	0.0000	0.0000	0.0014	0.0000	0.0012	-0.0003	0.0014	0.0006	0.0794	0.0002	0.0037
Z	0.0010	-0.0007	0.0002	0.0000	-0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X	0.0010	0.0017	0.0000	0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

26

505   Table 6. Li-bearing compositions tested

Composition Tested:	Elb	Rss	LDD	Elb50-Rss50	Elb50-Ftt25-Oln25	Little 3 059B Pocket	Elbaite Elba
Wt%							
SiO_2	38.49	39.03	38.57	38.76	37.57	37.55	37.89
B_2O_3	11.15	11.31	11.17	11.23	10.88	*10.83	10.28
TiO_2						0.07	0.04
Al_2O_3	40.82	44.15	38.17	42.47	41.17	39.50	43.85
FeO					3.74	0.02	0.11
MnO						6.68	0.11
MgO						0.00	
Li_2O	2.39	1.61	3.20	2.00	1.17	*0.99	1.66
CaO			6.00			0.05	0.07
Na_2O	3.31	0.00	0.00	1.67	2.42	2.38	2.43
H_2O	3.84	3.90	2.89	3.87	3.05	*2.70	3.47
F						1.11	0.10
Cl							
Total	100.00	100.00	100.00	100.00	100.00	101.41	99.97
RESULTS							
APFU							
Si	6.001	6.000	6.001	6.000	6.001	6.004	5.942
B	3.000	3.001	2.999	3.000	2.999	2.989	2.782
Ti							
Al	7.501	8.001	7.000	7.750	7.751	7.445	8.106
Fe					0.500	0.003	0.014
Mn						0.905	0.014
Mg						0.000	
Ca			1.000			0.009	0.012
Li*	1.499	0.996	2.000	1.252	0.752	0.637	1.047
Na	1.001	0.000	0.000	0.501	0.750	0.738	0.739
OH	3.993	3.999	2.999	3.996	3.249	2.989	3.680
F						0.561	0.050
Mole Fractions							
Liddicoatite	0.00	0.00	1.00	0.00	0.00	0.01	0.01
Elbaite	1.00	0.00	0.00	0.50	0.50	0.25	0.44
Rossmanite	0.00	1.00	0.00	0.50	0.00	0.25	0.24
Tsilaisite	0.00	0.00	0.00	0.00	0.00	0.30	0.00
Schorl	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dravite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Foitite	0.00	0.00	0.00	0.00	0.25	0.01	0.01
Mg-foitite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Olenite	0.00	0.00	0.00	0.00	0.25	0.19	0.30
Residuals							
Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mg	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
FeTi	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mn	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Na	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
□x	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Al(Y)	-0.0019	0.0005	-0.0007	0.0000	0.0000	0.0000	0.0000
T	-0.0029	0.0004	-0.0007	0.0003	0.0006	0.0044	0.0000
Li apfu[#]	1.4987	1.0000	2.0004	1.2502	0.7499	0.6392	0.9180

554   *- Li calculated by manual refinement from microprobe data; # - Li calculated by spreadsheet

27

Figure Captions

555

556   Figure 1. Li-free tourmaline calculations for the Li-absent tourmaline of Table 1: (a) initial data

557   entry into blue cells (B7-B20) of Sheet1; (b) addition of water concentration (cell B18).

558

559   Figure 2. Li-bearing tourmaline calculations for Elb(50)Rss(50) composition: (a) initial data

560   entry into blue cells (B7-B20) of Sheet1; (b) first addition of water concentration (cell B18) in

561   Sheet1; (c) first addition of Li_2O concentration by difference (cell B14); (d) final calculation

562   after optimizing H_2O (cell B18) and Li_2O (cell B14).

563

564   Figure 1. Li-Free calculation

565

29

566   Figure 2. Li-bearing calculation

567