

## Disordering of Fe<sup>2+</sup> over octahedrally coordinated sites of tourmaline

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### ABSTRACT

The partitioning of iron among octahedrally coordinated sites in tourmaline, and its stereochemical consequences, were investigated in a Fe-rich dravite in a skarn rock from Utö, Sweden. A multi-analytical approach using structure refinement (SREF), electron microprobe analysis (EMPA), and Mössbauer spectroscopy (MS) established the chemical and structural nature of the tourmaline. A structural formula obtained by optimization procedures indicates disordering of Al, Mg, and Fe<sup>2+</sup> over the Y and Z sites, and ordering of Fe<sup>3+</sup> at the Y site. Two Fe-rich tourmalines from the literature, re-examined with the optimizing site assignment procedure, appear to have iron partitioning comparable to that of the Utö tourmaline with Fe<sup>2+</sup> disordered over the octahedral sites. This is best explained by disordered Fe<sup>2+</sup> distributions that minimize the strain state of the Y-O bonds and provide a shielding effect reducing Y-Z repulsion. This is consistent with predictions from bond-valence theory and Pauling's rules.

An indication of Z-site occupancy by Fe<sup>2+</sup> in tourmaline may be signaled by a significant correlation between <Z-O> and the *c* lattice parameter ( $r^2 = 0.96$ ). The *c* value for a very Fe<sup>2+</sup>-rich tourmaline and an ideal end-member schorl, with Fe<sup>2+</sup> and Al ordered at Y and Z (respectively), yielded <Z-O> values larger than 1.907 Å (the likely bond length for <Z-Al-O>). These large <Z-O> lengths indicate that Fe<sup>2+</sup> occurs at the Z site. The hypothesis of a dragging effect from <Y-O> to explain lengthening of <Z-Al-O> is not supported by experimental evidence.

**Keywords:** Chemical analysis, tourmaline, crystal structure, Mössbauer spectroscopy, order-disorder, XRD data

### INTRODUCTION AND PREVIOUS WORK

The tourmaline group minerals are complex borocyclosilicates that occur in a wide variety of igneous, metamorphic, and sedimentary environments. The structure is characterized by groups of XO<sub>9</sub>, YO<sub>6</sub>, TO<sub>4</sub>, and BO<sub>3</sub> polyhedra connected to each other through ZO<sub>6</sub> octahedra. The latter are arranged in a 3-D framework and are linked to the YO<sub>6</sub> octahedron through the O3-O6 edge. The structural formula of tourmaline group minerals is formalized as XY<sub>3</sub>Z<sub>6</sub>(T<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>V<sub>3</sub>W and, according to several authors (Fortier and Donnay 1975; MacDonald and Hawthorne 1995; Hawthorne and Henry 1999; Hughes et al. 2004), the following ions fit into the following structural sites: X = Na, Ca, □ (= vacancy), K; Y = Al, Fe<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, Mg, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Zn, Li, Ti<sup>4+</sup>, □; Z = Al, Fe<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, Mg, Fe<sup>2+</sup>; T = Si, Al, B, Be; B = B, (□); W(O1) = OH, F, O; V(O3) = OH, O.

Since 1975, when the first schorl structural refinement was reported by Fortier and Donnay, it has been suggested that Fe<sup>2+</sup> may occur at the both Y and Z sites of tourmaline. In the following years, Grice and Robinson (1989) reported a structural formula with Fe<sup>2+</sup> at Y and Z, adding, however, that it was not possible to verify its amount in both the octahedral sites. On the basis of structural data, small amounts of Fe<sup>2+</sup> at Z (ca. 1% atoms/site) were also reported in Francis et al. (1999) and Ertl and Hughes (2002). Independent indication of the presence of some Fe<sup>2+</sup> in

the Z site have been obtained in Mössbauer and optical studies, e.g., Burns (1972), Mattson and Rossman (1984), Ferrow et al. (1988), Ferrow (1994), Foit et al. (1989), and Fuchs et al. (1995, 1998). Recently, using an unconstrained model for the assignment of Fe over the octahedral sites of tourmaline, Bosi and Lucchesi (2004) and Bosi et al. (2005b) optimized structural formulae with amounts of Fe<sup>2+</sup> at Z up to ca. 4% atoms/site. On the bases of the latter structural formulae and the relative peak areas associated with the Mössbauer spectra of the same samples, Andreozzi et al. (2008) found a close match between the amount of Fe<sup>2+</sup> and Fe<sup>3+</sup> in Y and Z derived from the structural data and from Mössbauer spectroscopy. Finally, Bosi and Lucchesi (2007) re-examined previously published tourmaline structural formulae using site optimization and found the models are consistent with Fe<sup>2+</sup> at the Z site.

Nevertheless, the assignment of Fe<sup>2+</sup> at the Z site still appears controversial. For example, Grice and Ercit (1993) consider only the possibility of Fe<sup>3+</sup> at the Z site and not Fe<sup>2+</sup>. However, the amounts of <sup>57</sup>Fe<sup>3+</sup> reported for their samples 43167, 43293, Cross, 32008, and 43873 corresponds in fact to Fe<sup>2+</sup>. This is verified easily by comparing total Fe<sup>2+</sup> and Fe<sup>3+</sup> atoms per formula unit (apfu) from chemical analyses (Table 2 of Grice and Ercit, 1993) with the cation distribution shown in Table 5. Bloodaxe et al. (1999) did not observe the presence of Fe<sup>2+</sup> at the Z site, and their results are often extrapolated to other Fe-tourmalines (e.g., Oliveira et al. 2002; Pieczka and Kraczka 2004). However, it should be noted that the samples of Bloodaxe et al. (1999) pos-

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sess an electron occupancy at the *Z* site between 12 and 13  $e^-$ , in agreement with Al and Mg occupancy. Assuming their cation distribution scheme to be “definitive” is hazardous, since not all Fe-tourmalines have less than 13  $e^-$  in *Z*. In fact, other alternatives could be considered rather than make the assumption of  $Fe^{2+}$  exclusively at the *Y* site. Therefore, it is important to stress the point about the site occupancy of  $Fe^{2+}$ . After Hawthorne et al. (1993) had shown the presence of Mg at the *Z* site of tourmaline, it was clear that the  $ZO_6$  octahedron could enlarge to host non-Al cations. This result was important, because it highlights the fact that the usual assumption—that Al completely fills the *Z* site before occupying any other site—is not correct. Consequently, it should be not surprising if other divalent cations, such as  $Fe^{2+}$ , may occur at the *Z* site, in proportions related to *Z*-site cation size mismatch.

This study presents chemical and structural data of a single crystal of Fe-bearing tourmaline. These data in conjunction with literature data are used to clarify the crystal-chemical mechanisms for which  $Fe^{2+}$  may be disordered over the octahedrally coordinated sites of tourmaline.

## OCCURRENCE

The tourmaline crystal under investigation is from the Swedish Museum of Natural History (collection number 19980432). It occurs in a skarn rock from the island of Utö (south of Stockholm, Sweden). The bedrock of Utö is mainly characterized by Proterozoic metatuffitic rocks, gabbro-granitic intrusions, layered quartz porphyry intrusions, a banded iron formation, and metasedimentary rocks with associated marbles, and skarns (Stålhös 1982). Several granitic pegmatite dikes transect the Utö rocks, and tourmaline frequently occurs in the classic petalite-subtype pegmatites (e.g., Selway et al. 2002). An unusual black tourmaline, associated with tennantite as the dominant phase, with minor chalcopyrite and bornite, was found in a small cavity filled with calcite in an iron mine on Utö. Therefore, this sample is not the typical Utö tourmaline, but rather represents a late skarn-forming phase (Dan Holtstam, pers. comm.).

## ANALYTICAL AND CRYSTAL STRUCTURAL PROCEDURES

### Single-crystal structural refinement (SREF)

After preliminary optical examination, one representative crystal fragment was selected for X-ray data collection with a four-circle Siemens P4 automated diffractometer. Unit-cell parameters were measured by centering 52 reflections (13 independent reflections and their Friedel pairs, on both sides of the direct beam) in the range  $85-95^\circ 2\theta$ , with  $MoK\alpha_1$  radiation (0.70930 Å). X-ray data were collected in the  $3-70^\circ 2\theta$  range with the  $\omega$ -scan method. Scan speed was variable, depending on reflection intensity, estimated with a pre-scan. Background was measured with a stationary crystal and counter at the beginning and end of each scan, in both cases for half the scan time. Preliminary full exploration of reciprocal space was carried out, and no violations of  $R3m$  symmetry were noted. Data reduction was performed with the SHELXTL-PC program package. Intensities were corrected for polarization and Lorentz effects. An absorption correction was accomplished with a semi-empirical method (North et al. 1968). Structure refinement was carried out with the SHELXL-97 program (Sheldrick 1997). Starting coordinates were taken from Foit (1989). Variable parameters were scale factor, extinction coefficient, Flack parameter, atomic coordinates, site scattering values expressed as mean atomic number of *X*, *Y*, and *Z* sites, and atomic displacement factors. The *X* site was modeled using Na scattering factors. The occupancies of the *Y* site were obtained considering the presence of Mg vs. Fe, and the occupancy of *Z* site considering Al. The *T* and *B* sites were modeled with Si and B scattering factors, respectively, and with fixed occupancy of 1, because refinement with unconstrained multiplicity showed the *T* and *B* sites to be fully occupied by Si and B, respectively. The H atom associated with O3 (H3) was found by difference Fourier synthesis, and

subsequently refined. Three isotropic, full-matrix, refinement cycles were followed by anisotropic cycles until convergence was attained. No correlation between scale factor and site occupancy was observed. Table 1 lists crystal data, data-collection information and refinement details, and Table 2 gives the fractional atomic coordinates and equivalent isotropic displacement parameters. Table 3<sup>1</sup> contains anisotropic displacement parameters for non-hydrogen atoms. Relevant bond lengths, octahedral and tetrahedral distortions (expressed as mean quadratic elongation; Robinson et al. 1971), and mean atomic number are listed in Table 4.

### Electron microprobe analysis (EMPA)

After X-ray data collection, the same crystal was mounted on a glass slide, polished and carbon-coated for electron microprobe analysis (WDS-EDS method) on a CAMECA SX50 electron microprobe, operating at 15 kV, sample current of 15 nA, and with a beam diameter of 5  $\mu$ m. For raw data reduction, the PAP computer

**TABLE 1.** Miscellaneous X-ray data of the refinement of the Utö tourmaline

Crystal data	
Space group	<i>R3m</i>
<i>Z</i>	3
<i>a</i> (Å)	15.9875(8)
<i>c</i> (Å)	7.2372(5)
<i>V</i> (Å <sup>3</sup> )	1602.0(2)
Crystal size (mm)	0.12 × 0.11 × 0.13
Diffraction intensity collection	
Radiation	$MoK\alpha$ (0.71073 Å)
Monochromator	High-crystallinity graphite crystal
Range	$3-70^\circ 2\theta$
Reciprocal space range	$0 \leq h, k \leq 26, -12 \leq l \leq 12$
Scan method	$\omega$
Scan range	$2.4^\circ$
Scan speed	Variable 1.5–14.6°/min
Temperature	296 K
Data reduction	
Program	SHELXTL-PC
Corrections	Lorentz, Polarization
Absorption correction	Semi-empirical, 13 $\Psi$ scans ( $10-70^\circ 2\theta$ )
Set of measured reflections	1711
Refinement	
Program	SHELXL-97
<i>wR2</i> (%)	5.01
<i>R1</i> (%) for $I_o > 2\sigma(I_o)$	2.26
Goof	1.056
Extinction coefficient	0.0039(2)
Flack parameter	0.02(2)
Largest diff. peak and hole ( $e/\text{Å}^3$ )	0.40 and -0.37

**TABLE 2.** Fractional coordinates and equivalent displacement factor ( $\text{Å}^2$ )

Site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
<i>X</i>	0	0	0.22803(21)	0.0121(4)
<i>Y</i>	0.12314(4)	<i>x</i> /2	0.63654(8)	0.0072(1)
<i>Z</i>	0.29818(3)	0.26182(3)	0.61179(8)	0.0054(1)
<i>B</i>	0.11004(8)	2 <i>x</i>	0.45391(32)	0.0067(3)
<i>T</i>	0.19155(3)	0.18979(3)	0	0.00500(8)
O1 ( <i>W</i> )	0	0	0.77405(41)	0.0118(5)
O2	0.06076(6)	2 <i>x</i>	0.48109(24)	0.0099(3)
O3 ( <i>V</i> )	0.26447(13)	<i>x</i> /2	0.51197(24)	0.0115(3)
O4	0.09254(6)	2 <i>x</i>	0.07090(23)	0.0098(3)
O5	0.18277(12)	<i>x</i> /2	0.09062(23)	0.0099(3)
O6	0.19543(8)	0.18604(8)	0.77857(16)	0.0084(2)
O7	0.28443(8)	0.28420(8)	0.07916(16)	0.0087(2)
O8	0.20917(8)	0.26991(8)	0.44095(18)	0.0102(2)
H3	0.2510(30)	<i>x</i> /2	0.3888(57)	0.04(1)

<sup>1</sup> Deposit item AM-08-051, Table 3 and CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

**TABLE 4.** Relevant bond lengths (Å), mean quadratic elongation ( $\langle\lambda\rangle$ ) for the octahedra and tetrahedron, and mean atomic number (m.a.n.)

B-O2	1.379(3)	Y-O1	1.974(2)
B-O8 (×2)	1.376(2)	Y-O2 (×2)	2.033(1)
<B-O>	1.377(2)	Y-O3	2.154(2)
m.a.n. B	5	Y-O6 (×2)	2.013(1)
		<Y-O>	2.037(1)
T-O4	1.6296(6)	<λ> <sub>Y</sub>	1.0218
T-O5	1.6445(8)	m.a.n. Y	17.81(8)
T-O7	1.603(1)		
T-O6	1.606(1)	Z-O3	1.9969(9)
<T-O>	1.621(1)	Z-O6	1.906(1)
<λ> <sub>T</sub>	1.0030	Z-O8	1.938(1)
m.a.n. T	14	Z-O7E*	1.915(1)
		Z-O7D*	1.971(1)
X-O2 (×3)	2.487(2)	Z-O8E*	1.904(1)
X-O4 (×3)	2.803(2)	<Z-O>	1.938(1)
X-O5 (×3)	2.719(2)	<λ> <sub>Z</sub>	1.0134
<X-O>	2.670(2)	m.a.n. Z	13.56(4)
m.a.n. X	13.1(1)		
		O3-H	0.91(4)

\* According to labels reported in Foit (1989).

**TABLE 5.** Chemical composition of the present Utö tourmaline

	wt%		apfu
SiO <sub>2</sub>	36.7(2)	Si	6.00(5)
TiO <sub>2</sub>	0.07(2)	Ti <sup>4+</sup>	0.009(3)
B <sub>2</sub> O <sub>3</sub> *	10.63	B	3.00
Al <sub>2</sub> O <sub>3</sub>	27.48(5)	Al	5.30(4)
FeO	10.5(4)	Fe <sup>3+</sup>	0.85(3)
MnO	0.17(3)	Fe <sup>2+</sup>	0.59(2)
MgO	9.18(5)	Mn <sup>2+</sup>	0.023(4)
CaO	1.63(4)	Mg	2.24(2)
Na <sub>2</sub> O	2.01(5)	Ca	0.286(8)
K <sub>2</sub> O	0.07(1)	Na	0.64(2)
F	0.15(4)	K	0.014(2)
H <sub>2</sub> O*	3.24	F	0.08(2)
O = F	-0.065	OH	3.54
Total	101.7	OH + F	3.62
Fe <sub>2</sub> O <sub>3</sub> †	6.88	Sum Y + Z‡	9.00
FeO†	4.30	X-vacancy	0.06

Notes: Number of ions calculated on basis of 31 (O, OH, F). Uncertainties for oxides (in parentheses) are standard deviation of repeated analyses. B<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O uncertainty assumed at 5%. Standard uncertainty for ions was calculated by uncertainty-propagation theory.

\* Calculated by stoichiometry.

† From MS data (Table 6).

‡ Using three decimals.

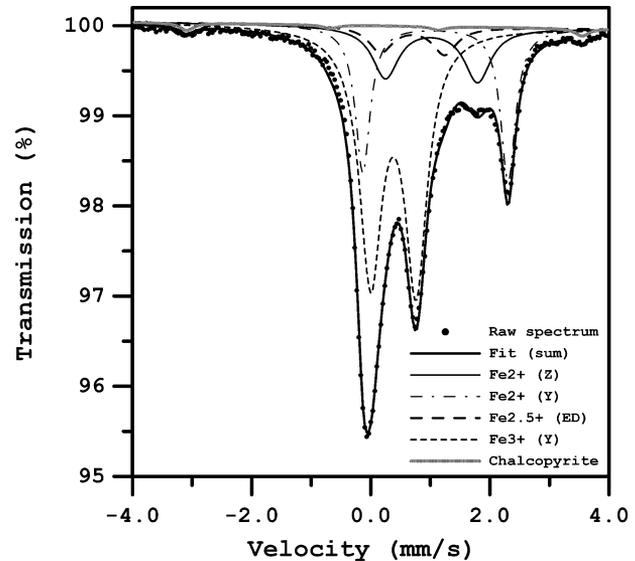
program was applied (Pouchou and Pichoir 1984). Natural and synthetic standards were used: anorthite (Al), rutile (Ti), olivine (Si, Fe), rhodonite (Mn), diopside (Mg, Ca), sphalerite (Zn), orthoclase (Na, K), fluorite (F), synthetic metals (Cr, V, Cu). Each element determination was accepted after checking that the intensity of the analyzed standard before and after each determination was within 1%. The chemical composition data are the average of 10 spot analyses, performed along two orthogonal traverses, and their standard deviations indicate compositional homogeneity (Table 5). In accordance with the documented very low concentration of Li in dravitic samples (Dyar et al. 1998) and the absence of Li-enriched minerals, the Li<sub>2</sub>O content was assumed to be insignificant. ZnO, CuO, V<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub> were not detected, with their concentrations being below the minimum detection limits of 0.03 wt%.

### Mössbauer spectroscopy (MS)

A Mössbauer spectrum was collected at 25 °C using a conventional spectrometer system operating in constant acceleration mode with a <sup>57</sup>Co point-source of 10 mCi in a rhodium matrix. The absorber consisted of 1.6 mg powdered tourmaline placed between mylar windows in an aperture (1 mm diameter) in a lead metal disk. The Fe thickness of the absorber was ca. 7 mg/cm<sup>2</sup>. Data collection time was about one week for robust statistics. Spectral data for the velocity range -4 to +4 mm/s were recorded on a multichannel analyzer using 1024 channels. After velocity calibration against a spectrum of high-purity α-iron foil (0.25 mm thick),

the raw data were reduced to 512 and then folded to 256 channels. The folded spectrum showed very weak peaks at about -3.1 and +3.6 mm/s indicating the presence of small amounts of a magnetic phase in the spectrum. Consequently, a second spectrum was recorded in the range -10 to +10 mm/s to assess the amount and identity of this impurity. Inspection of this Mössbauer spectrum indicated the presence of strong non-magnetic absorption (tourmaline) and very weak magnetic absorption, which according to Mössbauer parameters is chalcopyrite (Table 6). Because the chalcopyrite absorption is a sextet, its contribution to the central part of the spectrum (from -2 to 3 mm/s) is below 1%. Hence, the chalcopyrite contamination of the tourmaline spectrum is considered negligible.

The original spectrum was fitted assuming Lorentzian peak shape, using a



**FIGURE 1.** Room-temperature Mössbauer spectrum of the Utö tourmaline. Spectral data were recorded in the velocity range -10 to 10 mm/s to evaluate the chalcopyrite contribution to the tourmaline spectrum. Because this contribution is very weak, in figure displays only the spectrum recorded in the velocity range -4 to 4 mm/s. ED = electron delocalization.

**TABLE 6.** Mössbauer parameters of the Utö tourmaline

Fe valence	Parameter	Value	Amount of Fe in tourmaline sites (pfu)	Assignment
Fe <sup>2+</sup>	δ	1.02	0.21	Z site
	ΔE <sub>Q</sub>	1.55		
	Γ	0.53		
	% Area	14 ± 3		
Fe <sup>2+</sup>	δ	1.09	0.32	Y site
	ΔE <sub>Q</sub>	2.44		
	Γ	0.29		
	% Area	22 ± 1		
Fe <sup>2.5+</sup>	δ	0.70	0.08	Z site
	ΔE <sub>Q</sub>	1.08		
	Γ	0.49		
	% Area	6 ± 2		
Fe <sup>3+</sup>	δ	0.38	0.79	Y site
	ΔE <sub>Q</sub>	0.76		
	Γ	0.44		
	% Area	56 ± 1		
Chalcopyrite	δ	0.23		
	ΔE <sub>Q</sub>	0		
	Γ	0.28		
	H*	35.6		
	% Area	2 ± 1		

Notes: δ, ΔE<sub>Q</sub>, and Γ are in mm/s. Errors on these parameters are ±0.02 mm/s.

\* H = Hyperfine magnetic field (Tesla), error is ±1 (T).

least squares fitting program (Jernberg and Sundqvist 1983). Reduced  $\chi^2$  was considered as a parameter to evaluate statistical best fit. Four doublets and a sextet were used as a fitting strategy (Fig. 1), and the  $\chi^2$  was 1.41. The addition of another doublet yielded slight reduction in  $\chi^2$ , but some refined hyperfine parameters were unrealistic and, therefore, the above strategy was preferred. Errors were estimated at  $\pm 0.02$  mm/s for isomer shift ( $\delta$ ), quadrupole splitting ( $\Delta E_Q$ ) and peak width ( $\Gamma$ ), and  $\pm 1$ –3% for absorption areas due to doublet overlap (Table 6). Figure 1 shows that  $\text{Fe}^{3+}$  is the principal oxidation state, followed by  $\text{Fe}^{2+}$  and  $\text{Fe}^{2.5+}$  (electron delocalization), and that all iron is in octahedral coordination. Contents of FeO and  $\text{Fe}_2\text{O}_3$  (Table 5) were obtained from  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios measured by MS.

## RESULTS AND DISCUSSION

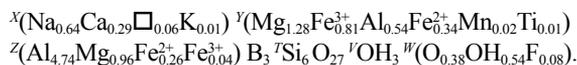
### Determination of atomic proportions

Structure refinement shows that the *B* and *T* sites are filled by B and Si, respectively. The latter information is consistent with EMPA data. Consequently, atomic proportions were calculated assuming stoichiometric B. All Mn was assumed to be divalent, as not all iron was oxidized, and crystal-structure studies have shown that this is the most common valence state of Mn in tourmaline (Bosi et al. 2005a). In this way, the OH content can be calculated by charge balance with the assumption  $Y + Z = 9.00$  apfu. It is possible to verify the amount of OH by considering the F content and the bond valence sum at O1 (Grice and Ercit 1993). Because bond lengths reflect bond valence values, the latter can be evaluated by a first approximation of the atomic distribution. For the Utö tourmaline, the bond-valence sum at O1 is 1.44 valence units (calculated according to Brown and Altermatt 1985), which yields an OH amount of 3.5 apfu in excellent agreement with the inferred by stoichiometry (Table 5).

According to the classification of Hawthorne and Henry (1999), this skarn tourmaline belongs to the alkali group: the *X* site is dominated by Na, with 0.64 apfu. The amount of Mg (2.24 apfu) is larger than Fe (1.44 apfu), with  $\text{Fe}^{3+}$  (0.85 apfu) larger than  $\text{Fe}^{2+}$  (0.59 apfu). Consequently, the Utö sample may be classified as a Fe-rich dravite.

### Determination of site population

To convert crystal chemical and structure-refinement results into accurate site populations, optimization between experimental and calculated data from atomic distribution should be achieved. Bosi and Lucchesi (2007) used a quadratic program approach to minimize the residuals between calculated and observed data from chemical analysis and structure refinement to re-examine the cation distributions of several tourmaline specimens. They showed that a self-consistent set of ionic radii fits the *T*-, *Y*-, and *Z*-mean bond lengths of most of the refined tourmaline specimens in the literature. This approach was employed for obtaining the cation distribution of the *Y* and *Z* sites in the Utö sample. All residuals between calculated and observed data (such as mean atomic number, mean bond lengths, atomic proportions) are within analytical error (two standard deviations). The final structural formula of the Utö tourmaline is



This formula shows a clear disordering of Al, Mg, and  $\text{Fe}^{2+}$  over the *Y* and *Z* sites, and strong ordering of  $\text{Fe}^{3+}$  at the *Y* site. Although  $\text{Fe}^{2+}$  seems to prefer the *Y* site, a significant amount

of  $\text{Fe}^{2+}$  is found in *Z*. This iron partitioning is also in accordance with that reported by Fortier and Donnay (1975) and by Bosi and Lucchesi (2004).

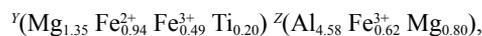
### Mössbauer data

Mössbauer spectra of tourmaline are often complex and their interpretation is not straightforward. As a rule, Mössbauer data used to characterize relative site-occupancies for Fe, when combined with chemical analysis results, should provide absolute occupancies in agreement with those derived from structure refinement. In the Utö tourmaline, the assignment of the Fe doublets to the *Y* or *Z* sites is not possible solely on the basis of Mössbauer parameters because several models may be assumed. However, taking into account the areas of the  $\text{Fe}^{2+}$ ,  $\text{Fe}^{2.5+}$ , and  $\text{Fe}^{3+}$  doublets, only one model is consistent with the structural data: that is the model reported in Table 6. The case of  $\text{Fe}^{3+}$  nicely illustrates this. Assignment of the absorption areas of the  $\text{Fe}^{3+}$  doublet (56% of  $\text{Fe}_{\text{tot}}$ ) to the *Z* site will yield a residual between calculated and observed site scatterings at the *Y* and *Z* sites much larger ( $>1.10 e^-$ ) than their analytical error (Table 4). In contrast, the assignment of this  $\text{Fe}^{3+}$  doublet to the *Y* site fits significantly better with the site-occupancy refinement (residuals  $<0.12 e^-$ ). Hence, the  $\text{Fe}^{3+}$  doublet is consistent with assignment to the *Y* site. The two doublets assigned to  $\text{Fe}^{2+}$ , distinguished by their  $\Delta E_Q$  values, represent  $\text{Fe}^{2+}$  in different structural environments: because the  $\text{YO}_6$  distortion ( $\langle\lambda_y\rangle = 1.0218$ ) is larger than the  $\text{ZO}_6$  distortion ( $\langle\lambda_z\rangle = 1.0134$ ), the former is reflected in the larger  $\Delta E_Q = 2.44$  mm/s (assigned to *Y*, in accordance with the optimized structural formula) and the latter in the smaller  $\Delta E_Q = 1.55$  mm/s (assigned to *Z*, in accordance with the optimized structural formula). The positive correlation between  $\Delta E_Q$  for  $\text{Fe}^{2+}$  and octahedral distortion is consistent with published results for  $\text{Fe}^{2+}$  in weakly distorted ( $\langle\lambda\rangle \leq 1.02$ ) octahedra (Zhe and De Grave 1998). The  $\text{Fe}^{2.5+}$  doublet is related to interaction between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  located in *Z*-*Z* (although a minor interaction *Y*-*Z* might occur, which is within analytical error); this assignment is also supported by the results of Farrow (1994) and Andreozzi et al. (2008).

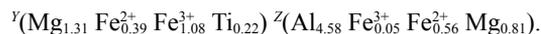
### Reconsideration of previously published crystal-chemical formulae

Because the Utö sample is most consistent with  $\text{Fe}^{3+}$  at *Y* and  $\text{Fe}^{2+}$  at *Z*, it is worth considering whether other Fe-bearing tourmaline specimens from the literature, for which  $\text{Fe}^{2+}$  at the *Z* site is not reported, also have similar iron partitioning. Samples drv18 of Cámara et al. (2002) and GRAS1 of Ertl et al. (2006) illustrate this possibility. The cation distributions of drv18 and GRAS1 were re-examined using the same procedure adopted for the Utö sample.

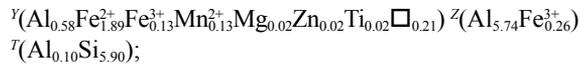
For sample drv18, the original cation distribution (Cámara et al. 2002) was reported as



and the newly optimized one is



For sample GRAS1, the original cation distribution (Ertl et al. 2006) was reported as



and the new one is

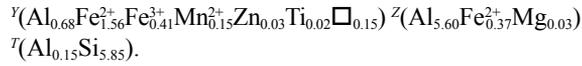


Figure 2 displays the optimization residuals between observed and calculated data from the original and new cation distributions in the two cases. There is a clear improvement in the new site assignment, with a better distribution of minimal residuals over the whole structure. For example, the site scattering residuals retrieved from the original cation distributions for the *Y* and *Z* sites (ca.  $-0.33$  and  $0.23$   $e^-$  in drv18 and GRAS1, respectively) are much greater than their uncertainties ( $0.10$  and  $0.04$   $e^-$ , respectively). In contrast, the optimized parameters in the new cation distributions are within analytical error. Notably, the main difference between the original and new cation distribution of the drv18 and GRAS1 is the presence of significant amounts of  $\text{Fe}^{2+}$  at the *Z* sites (ca. 9 and 6% atoms/site, respectively).

#### STERIC REASONS FOR IRON PARTITION BETWEEN BOTH OCTAHEDRAL SITES

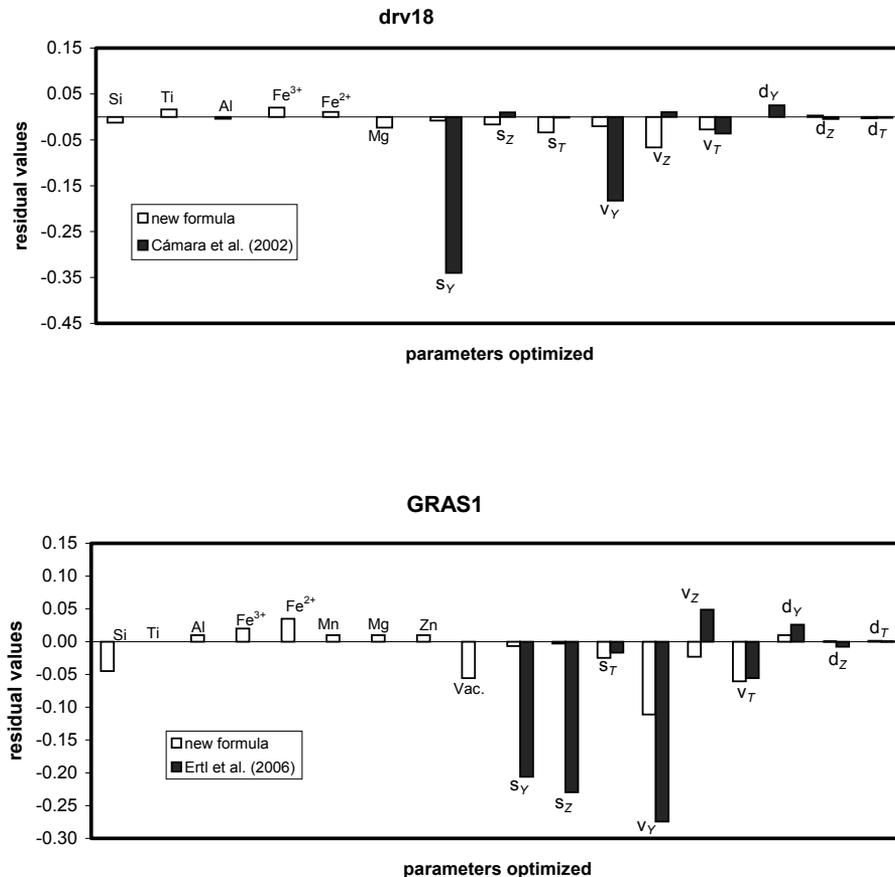
##### Bond valence approach

The preference of  $\text{Fe}^{2+}$  over  $\text{Fe}^{3+}$  at the *Z* site and, conversely  $\text{Fe}^{3+}$  over  $\text{Fe}^{2+}$  at the *Y* site, may be explained by considering

the difference between mean atomic valence (MAV) and bond valence sum (BVS) at the *Y* site: i.e., *Y*-site valence residuals in Figure 2. Using the original cation distributions of drv18 and GRAS1, this difference is larger than  $-0.18$  valence unit (v.u.). This suggests an underbonded state in the *Y* site because the MAV obtained from the original cation distribution does not match the BVS obtained by the experimental *Y*-O bond lengths. According to the bond valence theory, there is a tendency for experimental bond valences around each atom to approach atomic valence (equal-valence rule). Large mismatches between MAV and BVS are indicative of strained bonds, which may lead to instabilities in the structure. Consequently, any structure tends to relax its bonds to minimize the strain (Brown 2002). Incorporating  $\text{Fe}^{3+}$  (instead of  $\text{Fe}^{2+}$ ) into the *Y* site, *Y*-O bond lengths decrease and *Y* MAV increases. As a result, the deviation from the equal-valence rule decreases and the *Y*-O bonds tend to relax. This is consistent with the new cation distributions (Fig. 2).

##### Structural constraints

The preference of  $\text{Fe}^{2+}$  over  $\text{Fe}^{3+}$  at *Z* and, conversely,  $\text{Fe}^{3+}$  over  $\text{Fe}^{2+}$  at *Y* appears to be a function of size and charge required at the *Y* site. Relationships between structural parameters and compositional parameters illustrate how the tourmaline structure exerts constraints on its own chemical composition, i.e., maintaining the difference between  $\langle Y-O \rangle$  and  $\langle Z-O \rangle$  ( $\Delta_{YZ}$ ) smaller than ca.  $0.15$  Å (Bosi and Lucchesi 2007). A substitution like  ${}^Y\text{Al} + {}^Z\text{R}^{2+} \rightarrow {}^Y\text{R}^{2+} + {}^Z\text{Al}$  increases the structural stability because it decreases  $\Delta_{YZ}$  ( $\langle Y-O \rangle$  decreases and  $\langle Z-O \rangle$  increases).



**FIGURE 2.** Plot of residuals (calculated – observed) for optimized parameters:  $s_Y$ ,  $s_Z$ , and  $s_T$  = site scattering;  $v_Y$ ,  $v_Z$ ,  $v_T$  = site valence;  $d_Y$ ,  $d_Z$ ,  $d_T$  = mean bond length.

This mechanism is further supported by the observed positive correlation between the O3-Z-O6 angle, which is opposite to the O3-O6 edge shared between *Y* and *Z*, and  $\Delta_{YZ}$  (Fig. 3). For the tourmaline structure, this correlation represents a strong constraint whereby  $\langle Y-O \rangle$  maintains dimensions commensurate with  $\langle Z-O \rangle$ . If the O3-Z-O6 angle becomes larger, the shielding effect of the anions is weakened and the repulsive force between *Y* and *Z* becomes greater. This may lead to instabilities in the structure (Pauling's rules). Incorporating  $Fe^{3+}$  into *Y* and  $Fe^{2+}$  into *Z* (for example by  ${}^YFe^{3+} + {}^ZFe^{2+} \rightarrow {}^YFe^{2+} + {}^ZFe^{3+}$ ), both  $\Delta_{YZ}$  and O3-Z-O6 decrease. In this way, the shielding effect needed to reduce the *Y-Z* repulsion is provided, and the structural state moves toward a free energy minimum.

According to the ionic radii reported by Bosi and Lucchesi (2007), the  $\Delta_{YZ}$  values calculated for the ideal schorl ( $\dots {}^YFe_3^3 {}^ZAl_6 \dots$ ) and dravite ( $\dots {}^YMg_3 {}^ZAl_6 \dots$ ), yield large O3-Z-O6 values. The model of Bosi and Lucchesi (2007) indicates that these ordered schorl and dravite end-members should be unstable (Fig. 3). Stability of schorl and dravite may increase by disordering of Mg, Fe and Al over the octahedral sites, which yields decreasing  $\Delta_{YZ}$  as well as O3-Z-O6. As a consequence, the absence of ordered schorl and dravite end-members in nature may be ascribed to crystal-chemical constraints rather than to petrologic conditions.

Variations in mean bond length due to constituent anions are very small compared to those due to constituent cations in tourmaline, therefore anions could take part in the above-mentioned disordering scheme.

#### Use of the *c* lattice parameter to evaluate $\langle Z-O \rangle$

A plot of  $\langle Z-O \rangle$  vs. *c* for 129 crystal-structural refinements of tourmaline samples spanning the whole tourmaline group shows a positive correlation (Fig. 4). The following quadratic fit is obtained:

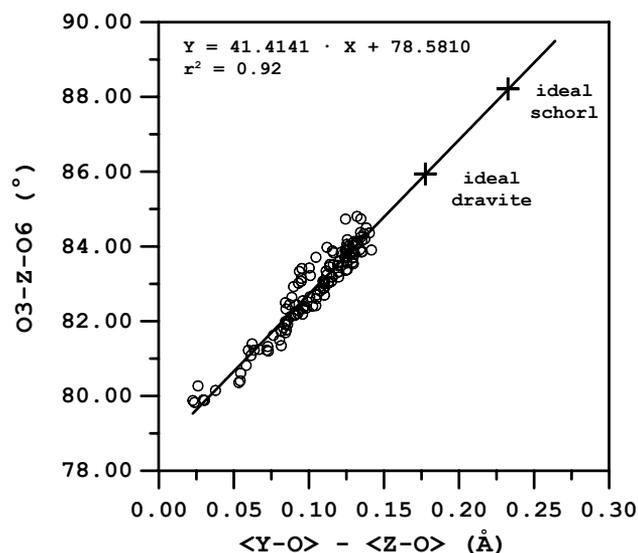


FIGURE 3. Variation in the O3-Z-O6 angle as a function of the difference between  $\langle Y-O \rangle$  and  $\langle Z-O \rangle$  in tourmaline. Plot obtained using 129 samples: 127 from literature (see references in Bosi and Lucchesi 2007) plus the Utö and GRAS1 samples.

$$\langle Z-O \rangle = 0.47467 \times c^2 - 6.5626 \times c + 24.5720.$$

This relation can be used to predict  $\langle Z-O \rangle$  values from lattice parameter measurements and obtain information on *Z*-site occupancy. For example, the schorl reported in JCPDF (number 43-1464) shows very high amounts of  $Fe^{2+}$  (2.48 apfu) and the *c*-lattice parameter is 7.172 Å. The ideal end-member schorl ( $\dots {}^YFe_3^3 {}^ZAl_6 \dots$ ) reported by Pieczka (2000), has a *c*-lattice parameter of 7.206 Å. Replacing these two *c* values in the above quadratic fit,  $\langle Z-O \rangle$  values of 1.921 and 1.930 Å, respectively, are obtained. However, in the ideal end-member schorl, with  $Fe^{2+}$  and Al ordered at the *Y* and *Z* sites, respectively, the most reasonable bond length for  $\langle {}^ZAl-O \rangle$  is 1.907 Å. In fact, this bond length is consistent with: (1)  $\langle Z-O \rangle$  average calculated from 35 tourmalines from the literature, in which the *Z* site is only occupied by Al (Fig. 5); (2)  $\langle {}^ZAl-O \rangle$  bond length refined by Bosi et al. (2005a, 2005b) in tourmaline with  $\Sigma R^{2+} < 0.40$  apfu; and (3)  $\langle {}^ZAl-O \rangle$  calculated on the basis of the bond valence constant and coordination number related to  ${}^VIAl^{3+}$ : i.e.,  $1.651 - 0.37 \times \ln(3/6) = 1.907$  Å. To explain the larger  $\langle Z-O \rangle$  values (1.921 and 1.930 Å) obtained by using the data of JCPDS and Pieczka (2000), we may assume a dragging effect of  $\langle Y-O \rangle$  that lengthens  $\langle {}^ZAl-O \rangle$ ; alternatively, significant amounts of  $Fe^{2+}$  may be present at the *Z* site. In the former hypothesis, a direct proportionality relation between  $\langle Y-O \rangle$  and  $\langle {}^ZAl-O \rangle$  should exist. However, the plot of  $\langle Y-O \rangle$  vs.  $\langle Z-O \rangle$  in 35 tourmalines with  ${}^ZAl = 6$  apfu shows no such correlation (Fig. 5). Furthermore, any polyhedron with fixed composition should exhibit an increase in size with increasing distortion (e.g., Brown 2002). Consequently, if  $\langle Y-O \rangle$  and  $\langle Z-O \rangle$  are linked by a direct proportionality relation,  $\langle Y-O \rangle$  should be positively correlated with  $ZO_6$  distortion. In contrast, a strong negative correlation ( $r^2 = 0.92$ ) exists between  $\langle Y-O \rangle$  and  $ZO_6$  distortion (Bosi and Lucchesi 2007). This inverse proportionality relation indicates that, when  $\langle Y-O \rangle$  increases, the  $ZO_6$  polyhedron becomes more regular. As a result,  $\langle Z-O \rangle$  tends to decrease, as expected from the tendency of *Y* to compress *Z* (Foit 1989; Bosi and Lucchesi 2007). In the tourmaline group, it makes no crystal-chemical sense to explain a  $\langle Z-O \rangle$  variation by

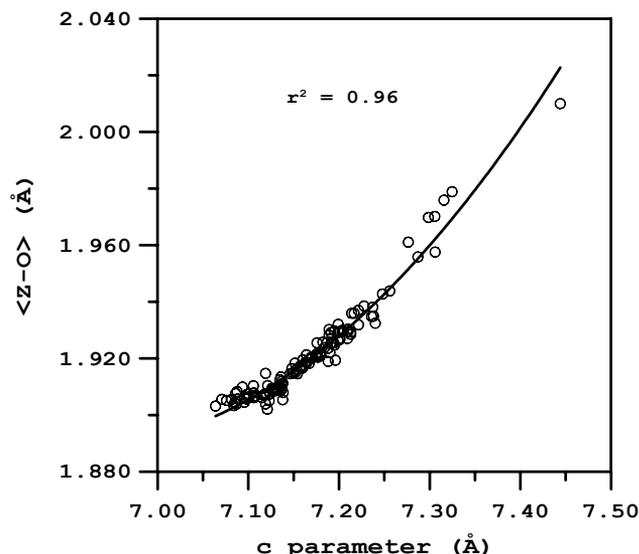
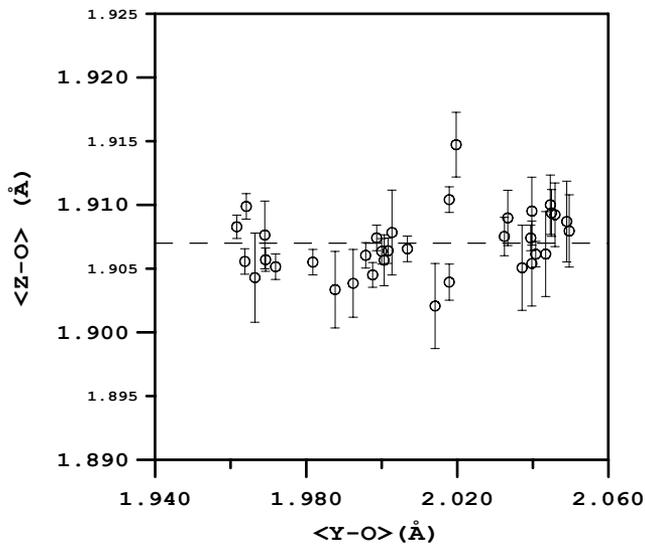


FIGURE 4.  $\langle Z-O \rangle$  vs. *c*-cell edge, showing strong dependence of these structural parameters. Plot obtained using the same as in Figure 3.



**FIGURE 5.** Plot of 35 tourmalines with Al = 6 apfu from literature (see references in Bosi and Lucchesi 2007), showing that no correlation of direct proportionality exists between Z and Y mean bond lengths ( $r^2 < 0.06$ ). Dotted horizontal line: average of  $\langle Z-O \rangle = 1.907(2)$  Å. Vertical bars: average estimated standard deviation ( $\pm 1\sigma$ ).

direct proportionality with  $\langle Y-O \rangle$ , when it may be explained by a compositional variation of the Z population. Larger  $\langle Z-O \rangle$  values obtained for the very Fe<sup>2+</sup>-rich schorl reported in JCPDS and the ideal end-member schorl of Pieczka (2000) strongly suggest the presence of Fe<sup>2+</sup> (associated with Al) at the Z site.

In conclusion, a careful examination of some Fe-tourmalines demonstrates that limited, but significant, amounts of Fe<sup>2+</sup> are required at the Z site. This is consistent with analytical data, the bond-valence theory, and Pauling's rules.

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