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Insights from the compositional evolution of a multi-coloured, zoned tourmaline from the Cruzeiro pegmatite, Minas Gerais, Brazil

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S1. Mössbauer data and Fe speciation

Room temperature ^{57}Fe Mössbauer spectra of the four tourmaline samples are typical of paramagnetic silicates and show two main absorptions in the region from -1 to +3 mm/s. The spectra were deconvoluted using Lorentzian doublets based on previous experience and in agreement with models already used in the existing literature (e.g., Andreozzi et al., 2008; Bosi et al., 2015). Quantification of Fe^{3+}/Fe_{Tot} ratios was obtained through evaluation of the absorption area of the refined doublets. The four doublets assigned to Fe^{2+} have δ values in the range 1.0÷1.1 mm/s and are distinguished by their quadrupole splitting values: $\Delta E_Q \sim 2.6$, 2.3, 2.0 and 1.4 mm/s (Table S1).

The first three doublets, conventionally labelled *Y*1, *Y*2 and *Y*3 are interpreted as Fe^{2+} at the *Y* sites with different nearest and next-nearest neighbour coordination environments and may represent up ~100% of Fe_{Tot} (Fig. S1). The fourth Fe^{2+} doublet, required to satisfactorily model the absorption for T2, T3 and T4 samples, is interpreted as Fe^{2+} at a different crystallographic site of area up to 29% of the Fe_{Tot} (in T4). According to the multianalytical approach results, this doublet is compatible with Fe^{2+} at the *Z* site. An additional, low intensity doublet –centred at $\delta \leq 0.3$ mm/s and assigned to $^{Y}Fe^{3+}$– was introduced to improve the fit for samples T3 and T4, but its absorption was too low ($\leq$ 4% of the Fe_{Tot}) for its hyperfine parameters to be reliable.

Table S1. Room temperature ^{57}Fe Mössbauer parameters and Fe site assignment for the selected fragments of a multi-coloured, zoned tourmaline single crystal from the Cruzeiro pegmatite (Minas Gerais, Brazil)

Sample	δ	ΔE_Q	Γ	Assignment	Area (%)
T1	1.08	2.53	0.28	Fe^{2+} (*Y*1)	35
	1.10	2.31	0.26	Fe^{2+} (*Y*2)	37
	1.16	1.98	0.56	Fe^{2+} (*Y*3)	28
T2	1.09	2.49	0.28	Fe^{2+} (*Y*1)	39
	1.10	2.21	0.36	Fe^{2+} (*Y*2)	44
	1.04	1.41	0.56	Fe^{2+} (*Y*3)	17
T3*	1.10	2.51	0.38	Fe^{2+} (*Y*1)	34
	1.10	2.25	0.28	Fe^{2+} (*Y*2)	24
	1.10	1.90	0.38	Fe^{2+} (*Y*3)	16
	1.00	1.38	0.68	Fe^{2+} (*Z*)	23
	0.30	0.50	0.60	Fe^{3+} (*Y*)	3
T4	1.10	2.56	0.24	Fe^{2+} (*Y*1)	23
	1.09	2.34	0.24	Fe^{2+} (*Y*2)	27
	1.07	2.07	0.29	Fe^{2+} (*Y*3)	17
	1.07	1.47	0.63	Fe^{2+} (*Z*)	29
	0.19	0.12	0.22	Fe^{3+} (*Y*)	4

Note: errors were estimated at about ± 0.02 mm/s for isomer shift (δ), quadrupole splitting (ΔE_Q) and peak width (Γ), and about ± 3 % for doublets areas.
*Data from Bosi et al. (2015)

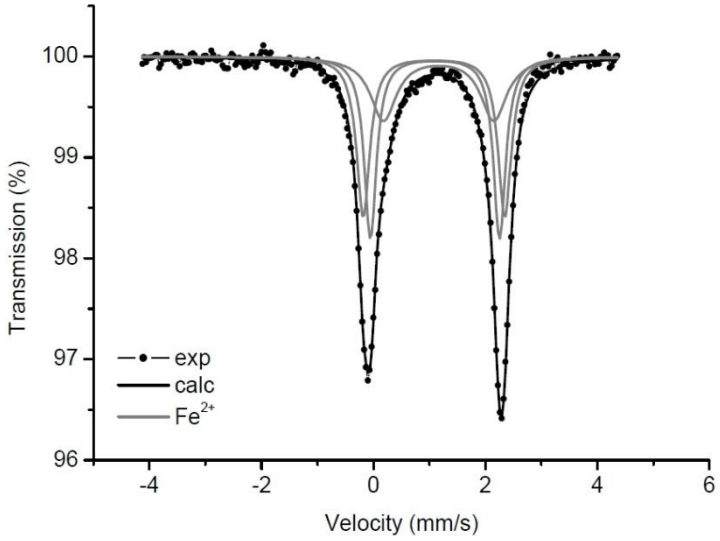

Figure S1: Tourmaline sample T1 Mössbauer spectrum at room temperature

S2. Single-crystal X-ray diffraction data

Table S2. Single-crystal X-ray diffraction data for the selected fragments of a multi-coloured, zoned tourmaline from the Cruzeiro pegmatite (Minas Gerais, Brazil)

Sample	T1	T2	T3*	T4
Crystal size (mm)	0.25 × 0.30 × 0.40	0.30 × 0.40 × 0.40	0.20 × 0.20 × 0.20	0.20 × 0.25 × 0.30
a (Å)	15.8984(2)	15.9315(3)	15.9801(2)	15.9688(3)
c (Å)	7.1226(1)	7.1286(1)	7.1577(1)	7.1698(1)
V (Å^3)	1559.11(4)	1566.92(6)	1582.93(5)	1583.37(6)
Reciprocal space range *hkl*	$-26 \le h \le 24$	$-22 \le h \le 26$	$-19 \le h \le 26$	$-19 \le h \le 26$
	$-26 \le k \le 19$	$-25 \le k \le 23$	$-25 \le k \le 18$	$-26 \le k \le 26$
	$-11 \le l \le 19$	$-6 \le l \le 11$	$-8 \le l \le 11$	$-11 \le l \le 12$
Number reflections	7503	7519	7626	7532
Unique reflections	1683	1431	1565	1771
R_{int} *(%)*	1.44	1.45	1.74	1.41
Extinction coefficient	0.0020(2)	0.0067(3)	0.0032(2)	0.0038(3)
Flack parameter	0.21(2)	0.165(19)	0.021(17)	0.052(16)
*wR*2 (%)	4.47	4.13	3.94	3.68
*R*1 (%) all data	1.80	1.62	1.60	1.34
GooF	1.061	1.073	1.118	1.097

Notes: R_{int} = merging residual value for equivalents; *R*1 = discrepancy index, calculated from *F*-data; *wR*2 = weighted discrepancy index, calculated from F^2-data; GooF = goodness of fit; Radiation, Mo*K*α = 0.71073 Å. Data collection temperature = 293 K. Range for data collection, 2θ = 5-74°. Space group *R*3*m*; *Z* = 3. Absorption correction method: SADABS; Refinement method: Full-matrix last-squares on F^2; Structural refinement program: SHELXL-2013

*Data from Bosi et al. 2015

Table S3. Fractional atom coordinates (*x, y, z*) and equivalent isotropic displacement parameters (U_{eq} in Å^2) for the selected fragments of a multi-coloured, zoned tourmaline from the Cruzeiro pegmatite (Minas Gerais, Brazil)

		T1	T2	T3*	T4
X	*x*	0	0	0	0
	y	0	0	0	0
	z	0.2367(4)	0.2343(4)	0.2283(4)	0.2303(3)
	U_{eq}	0.0232(7)	0.0242(8)	0.0244(8)	0.0234(7)
Y	*x*	0.12397(5)	0.12469(4)	0.12476(3)	0.12464(2)
	y	0.06198(3)	0.06235(2)	0.06238(2)	0.06232(2)
	z	0.62798(12)	0.62660(11)	0.62790(8)	0.62917(7)
	U_{eq}	0.00894(18)	0.00910(14)	0.00854(10)	0.00865(10)
Z	*x*	0.29763(4)	0.29803(3)	0.29854(3)	0.29842(2)
	y	0.26077(4)	0.26118(3)	0.26169(3)	0.26171(3)
	z	0.61149(10)	0.61134(9)	0.61082(8)	0.61110(7)
	U_{eq}	0.00593(10)	0.00579(9)	0.00571(11)	0.00577(10)
T	*x*	0.10950(9)	0.10976(8)	0.19196(2)	0.11008(6)
	y	0.21899(18)	0.21953(16)	0.18998(3)	0.22016(13)
	z	0.4557(4)	0.4556(3)	0	0.4553(3)
	U_{eq}	0.0063(3)	0.0066(3)	0.00515(9)	0.0066(3)
B	*x*	0.19197(3)	0.19200(3)	0.11019(7)	0.19185(2)
	y	0.18997(3)	0.18999(3)	0.22038(15)	0.18990(2)
	z	0	0	0.4551(3)	0
	U_{eq}	0.00481(8)	0.00501(8)	0.0070(3)	0.00513(8)
O1	*x*	0	0	0	0
	y	0	0	0	0
	z	0.7857(6)	0.7840(6)	0.7813(5)	0.7790(4)
	U_{eq}	0.0574(16)	0.0531(14)	0.0343(8)	0.0273(6)
O2	*x*	0.06081(7)	0.06116(6)	0.06170(5)	0.06159(5)
	y	0.12162(14)	0.12232(12)	0.12340(11)	0.12317(9)
	z	0.4843(3)	0.4843(3)	0.4859(2)	0.4862(2)
	U_{eq}	0.0165(4)	0.0165(4)	0.0153(3)	0.0139(3)
O3	*x*	0.26888(14)	0.26917(13)	0.26830(12)	0.26730(11)
	y	0.13444(7)	0.13459(7)	0.13415(6)	0.13365(6)
	z	0.5096(3)	0.5093(3)	0.5095(2)	0.5101(2)
	U_{eq}	0.0094(3)	0.0096(3)	0.0121(3)	0.0128(2)
O4	*x*	0.09310(7)	0.09313(6)	0.09322(5)	0.09324(5)
	y	0.18621(13)	0.18626(12)	0.18644(11)	0.18648(10)
	z	0.0715(2)	0.0703(2)	0.0683(2)	0.06897(19)
	U_{eq}	0.0077(3)	0.0083(3)	0.0099(2)	0.0098(2)
O5	*x*	0.18644(13)	0.18670(12)	0.18710(11)	0.18628(10)
	y	0.09322(6)	0.09335(6)	0.09355(6)	0.09314(5)
	z	0.0936(2)	0.0927(2)	0.0913(2)	0.09127(19)
	U_{eq}	0.0078(3)	0.0086(3)	0.0102(2)	0.0101(2)
O6	*x*	0.19715(8)	0.19758(8)	0.19793(7)	0.19737(7)
	y	0.18698(8)	0.18730(8)	0.18757(7)	0.18712(7)
	z	0.77587(18)	0.77556(18)	0.77571(15)	0.77653(14)
	U_{eq}	0.00701(19)	0.00708(18)	0.00864(17)	0.00872(16)

O7	*x*	0.28560(8)	0.28551(8)	0.28511(7)	0.28501(6)
	y	0.28572(8)	0.28578(7)	0.28568(7)	0.28545(6)
	z	0.08051(17)	0.08023(16)	0.07932(14)	0.07930(13)
	U_{eq}	0.00609(18)	0.00650(17)	0.00805(17)	0.00814(15)
O8	*x*	0.20993(8)	0.20989(8)	0.20980(7)	0.20973(6)
	y	0.27047(9)	0.27052(8)	0.27062(8)	0.27052(7)
	z	0.44158(18)	0.44135(18)	0.44085(15)	0.44107(15)
	U_{eq}	0.0073(2)	0.00780(19)	0.00931(18)	0.00938(16)
H3	*x*	0.258(3)	0.258(3)	0.268(2)	0.260(2)
	y	0.1290(14)	0.1291(13)	0.1341(12)	0.1298(11)
	z	0.380(3)	0.381(3)	0.389(5)	0.381(3)
	U_{iso} [a]	0.011	0.012	0.015	0.015

[a] isotropic (U_{iso}) displacement parameters for H3-atom was constrained to have a U_{iso} 1.2 times the U_{eq} value of the O3 oxygen.
*Data from Bosi et al. (2015)

Table S4. Selected mean bond distances (Å) and mean atomic numbers (m.a.n.) for the selected fragments of a multi-coloured, zoned tourmaline from the Cruzeiro pegmatite (Minas Gerais, Brazil)

Sample	T1	T2	T3*	T4
<*X*-O>	2.672	2.681	2.702	2.697
X-m.a.n.	10.42(13)	9.47(10)	7.70(1)	8.43(7)
<*Y*-O>	2.035	2.041	2.045	2.039
Y-m.a.n.	13.90(4)	16.57(5)	20.90(1)	19.76(8)
<*Z*-O>	1.907	1.909	1.917	1.920
Z-m.a.n.	13[a]	13[a]	13.50(1)	13.34(4)
<*B*-O>	1.376	1.376	1.375	1.374
B-m.a.n.	5[a]	5[a]	5[a]	5[a]
<*T*-O>	1.619	1.620	1.622	1.620
T-m.a.n.	14[a]	14[a]	14[a]	14[a]

[a] Fixed in the final stages of refinement

**Data from Bosi et al. (2015)

S3. FTIR and OAS data

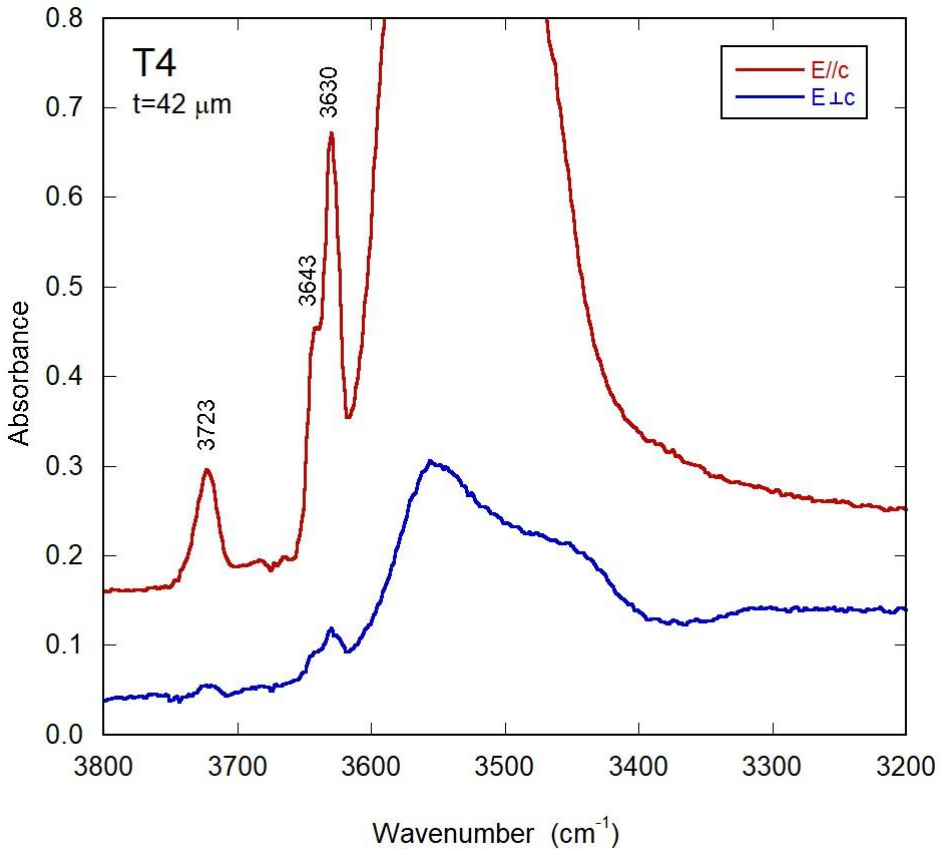

Figure S2: Polarized FTIR spectra perpendicular (E⊥c) and parallel (E||c) to the c-axis direction of the T4 crystal fragment (sample thickness 42 μm) of a colored, zoned tourmaline from the Cruzeiro pegmatite (Minas Gerais, Brazil). Peak positions are indicated.

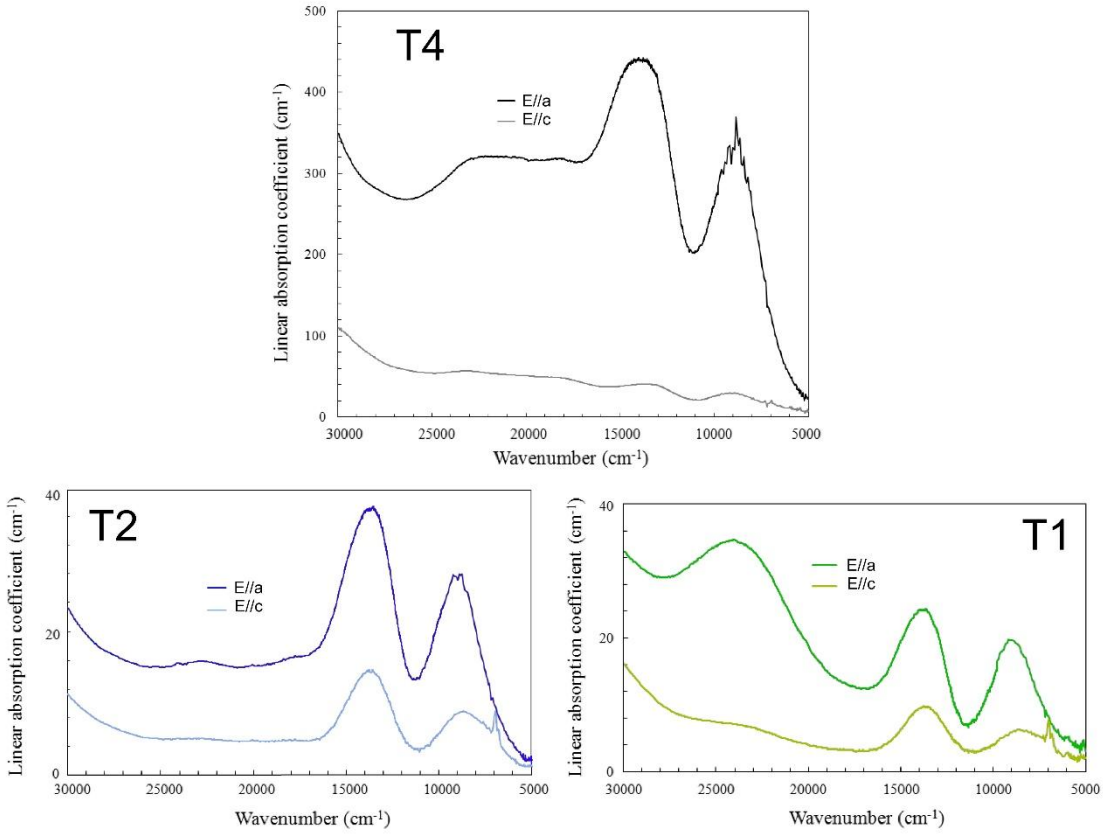

Figure S3: Optical absorption spectra polarized perpendicular (E||a) and parallel (E||c) to the c-axis direction of the T1, T2 and T4 crystal fragments of a colored, zoned tourmaline from the Cruzeiro pegmatite (Minas Gerais, Brazil). Thickness of all samples: 100 µm.