

Original paper

Sn-rich tourmaline from the Land's End granite, SW England

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Multiple generations and growth stages of tourmaline from a hydrothermal quartz-tourmaline rock from the Land's End granite, SW England, were investigated by Electron Probe MicroAnalyzer (EPMA) to reveal details of the variation in tourmaline composition with emphasis on the distribution of Sn. Tourmaline shows a large range in chemical composition, mostly on the dravite–schorl solid solution and towards more Fe-rich compositions. Several growth zones have very high Fe levels (>3.5 apfu) with a significant amount of Fe^{3+} coupled with low Al. The main substitution vectors controlling the major element composition are $\text{Fe}^{2+}\text{Mg}_{-1}$ and $\text{Fe}^{3+}\text{Al}_{-1}$. The Fe–Mg exchange is the main substitution in the earlier growth stages, whereas the Fe–Al substitution becomes more important towards the end of the crystallization sequence. Tin is commonly associated with the high-Fe zones, but all Fe-rich zones do not necessarily have elevated Sn content. Octahedral sites in tourmaline, most likely the Y-site, host Sn through the proposed coupled substitution $^{1/2}\text{Sn}^{4+} + 2^{1/2}\text{Fe}^{2+} + 5^{1/2}\text{Fe}^{3+} + \text{O}^{2-} \leftrightarrow 2^{1/2}\text{Mg}^{2+} + 6^{1/2}\text{Al}^{3+} + \text{OH}^-$. The thin Sn-rich zones, hosting up to 2.53 wt. % SnO_2 , are interpreted to coincide with the onset of cassiterite crystallization, and the lower Sn content in subsequent growth zones reflects the fluid chemistry and Sn solubility in a cassiterite-buffered hydrothermal system. This study demonstrates the suitability of quantitative X-ray mapping in identifying and quantifying minor elements in finely-spaced growth zones.

Keywords: Tourmaline, tin, trace elements, EPMA

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1. Introduction

Tourmaline is widely used as a petrogenetic indicator mineral (e.g., Henry and Guidotti 1985; van Hinsberg et al. 2011) and has been effectively utilized in provenance studies (Kowal-Linka and Stawikowski 2013; Farnsworth-Pinkerton et al. 2018; Guo et al. 2021) and mineral exploration (Clarke et al. 1989; Galbraith et al. 2009; Baksheev et al. 2012). The tourmaline crystal structure can accommodate a large range of elements (e.g., Vereshchagin et al. 2018, 2021) distributed over seven crystallographic sites described by the general formula $XY_3Z_6T_6O_{18}(\text{BO}_3)_3V_3W$ (Hawthorne and Henry 1999). The most common substitutions are Na, Ca, K, and $\square$ (vacancy) in the [9]-coordinated X-site; Fe^{2+} , Mg, Al, Mn^{2+} , Li, Fe^{3+} , and Ti in the [6]-coordinated Y-site; Al, Fe^{3+} , and Mg in the [6]-coordinated Z-site; Si, Al, and B in the [4]-coordinated T-site; B in the [3]-coordinated B-site; OH^- and O^{2-} in the [3]-coordinated V-site; and OH^- , F, and O^{2-} in the [3]-coordinated W-site. Order-disorder substitutions are common across the Y- and Z-sites. These are controlled by short-range structural constraints depending on the anion occupancy of the V- and W-sites, and long-range structural constraints depending on the ionic radii of the cations (Bosi 2018). Despite occurring as a major or accessory mineral in the ore-bearing rocks of various deposit types (Slack 1996), the economic element(s) of deposits are not necessarily

incorporated into the tourmaline structure in significant amounts, and studies comparing tourmaline compositions from different ore deposit types have mostly used other elements as distinguishing features (e.g., Sr, V and Ni in orogenic gold deposits and Fe^{3+} in Mo–Sn deposits) (Baksheev et al. 2020; Sciuba et al. 2021). Tourmaline is particularly common in granite-related Sn mineralizations, and many studies have used it as an indicator for Sn mineralization, with reported Sn concentrations in tourmaline typically in the 10s–1000s $\mu\text{g/g}$ range (Drivenes et al. 2015; Duchoslav et al. 2017; Hong et al. 2017; Harlaux et al. 2020; Codeço et al. 2021; Zhang et al. 2021). The highest values reported from natural tourmaline are around 1 wt. % SnO_2 (Baksheev et al. 2012; Baksheev et al. 2020), and several studies have described tourmaline with SnO_2 contents ~ 0.5 wt. %, commonly coupled with high Fe (Slack et al. 1999; Williamson et al. 2000; Jiang et al. 2004; Mlynarczyk and Williams-Jones 2006). In a recent study, Vereshchagin et al. (2022) synthesized tourmaline with up to 1.77 wt. % SnO_2 . The fine growth zoning commonly found in tourmaline poses a challenge when analyzing trace elements. The most common method for trace element analyses is Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), which typically operates with a spot size of 10s of μm . Such spot size may not be small enough to resolve growth zones, resulting in chemical information from the adjacent zones being

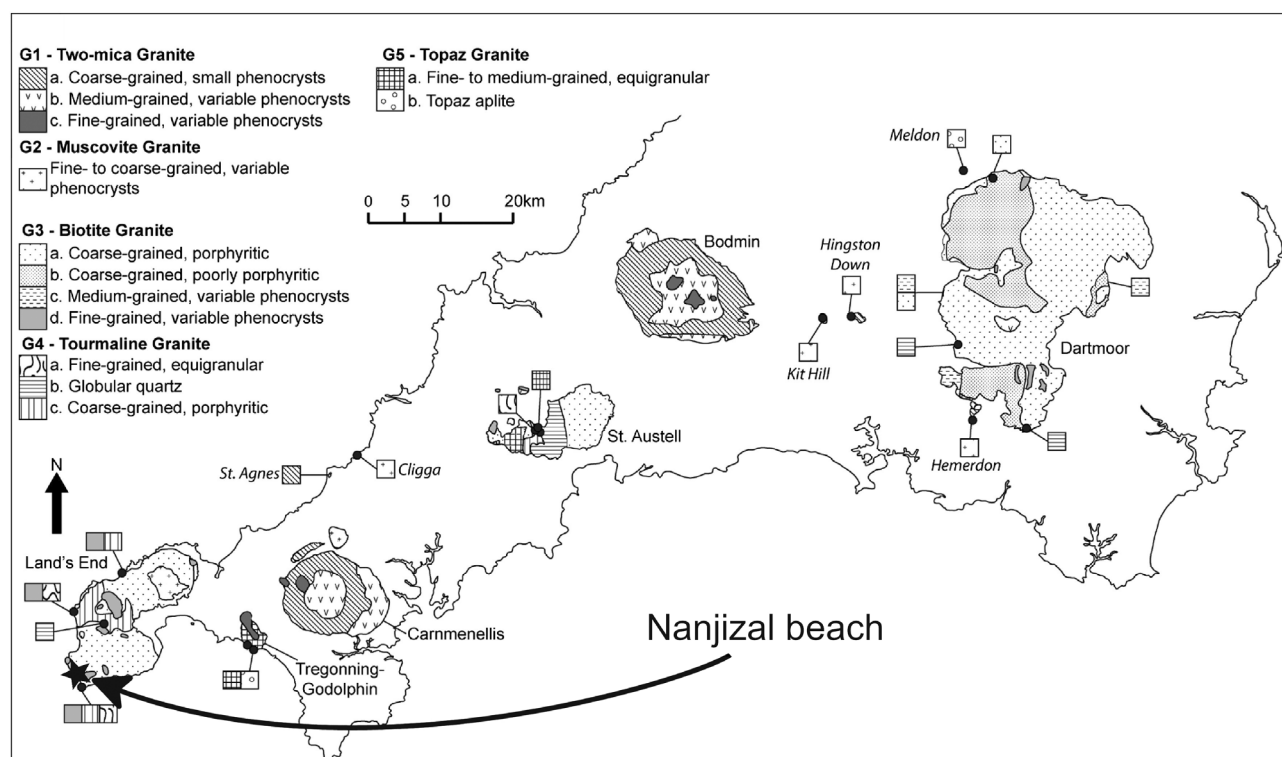


Fig. 1 Map of the granite petrology of the Cornubian Batholith from Simons et al. (2016).

mixed. The highest SnO_2 values listed above are from studies using electron microprobe (EPMA), which allows a much smaller analytical spot size (typically 1–3 μm in tourmaline with standard analytical settings) compared to LA-ICP-MS. In this study, EPMA spot analyses and quantitative mapping were used to investigate Sn-rich zones in tourmaline from a Sn-mineralized quartz-tourmaline rock from Nanjizal in the Land's End granite, SW England, and present, to my knowledge, the highest Sn concentrations in tourmaline yet observed.

2. Geological settings

2.1. The Land's End Granite

The Land's End granite (LEG) is the youngest of five onshore granitic complexes comprising the Cornubian Batholith. The batholith is continuous at depth (Bott et al. 1958), but surface exposure is limited to six major complexes and numerous smaller stocks (Fig. 1) spanning ca. 250 km from Devon (Dartmoor granite) throughout Cornwall (Bodmin, St. Austell, Carnmenellis, Land's End), and continuing offshore (Isles of Scilly). The batholith intruded sub-lower greenschist grade metasediments over a ca. 20 Ma period, from ca. 294 to 274 Ma, based on U–Pb dating of xenotime, monazite and zircon (Chen et al. 1993; Chesley et al. 1993; Tapster and Bright 2020). The peraluminous LEG comprises mostly porphyritic,

coarse-grained biotite granite (G3 in the classification of Simons et al. 2016), with dikes and larger sheets of tourmaline granite (G4) intruding the G3 granite. The G4 granites are interpreted to be a result of increased fractionation of the magmas that produced the predominant G3 granites (Simons et al. 2016, 2017). The LEG was emplaced by multiple magma pulses as several sub-horizontal granite sheets (Müller et al. 2006; Pownall et al. 2012; Drivenes et al. 2016), and the matrix grain size as well as the size and amount of K-feldspar phenocrysts vary between and across sheets. In the Cornubian Batholith, tourmaline occurs as an accessory mineral in G3 granites, and a minor mineral in G4 granites. In addition, it is an important mineral in hydrothermal vein systems in the granite and the surrounding aureole, breccia pipes (Müller and Halls 2005), and in obscure rock-types comprising quartz and tourmaline $\pm$ K-feldspar (Lister 1978; Müller et al. 2006; Drivenes et al. 2015).

2.2. Nanjizal beach tourmaline occurrences

At Nanjizal beach, three sub-horizontal sheets of granites are observed (bottom to top): non-megacrystic fine-grained, poorly-megacrystic medium to coarse-grained, and megacrystic coarse-grained (Fig. 2a). Along the footpath above the beach, two major tourmaline bodies can be observed within the megacrystic coarse-grained granite: a ca. 30 cm wide lode and a ca. 5 $\times$ 2 m massive quartz-tourmaline rock

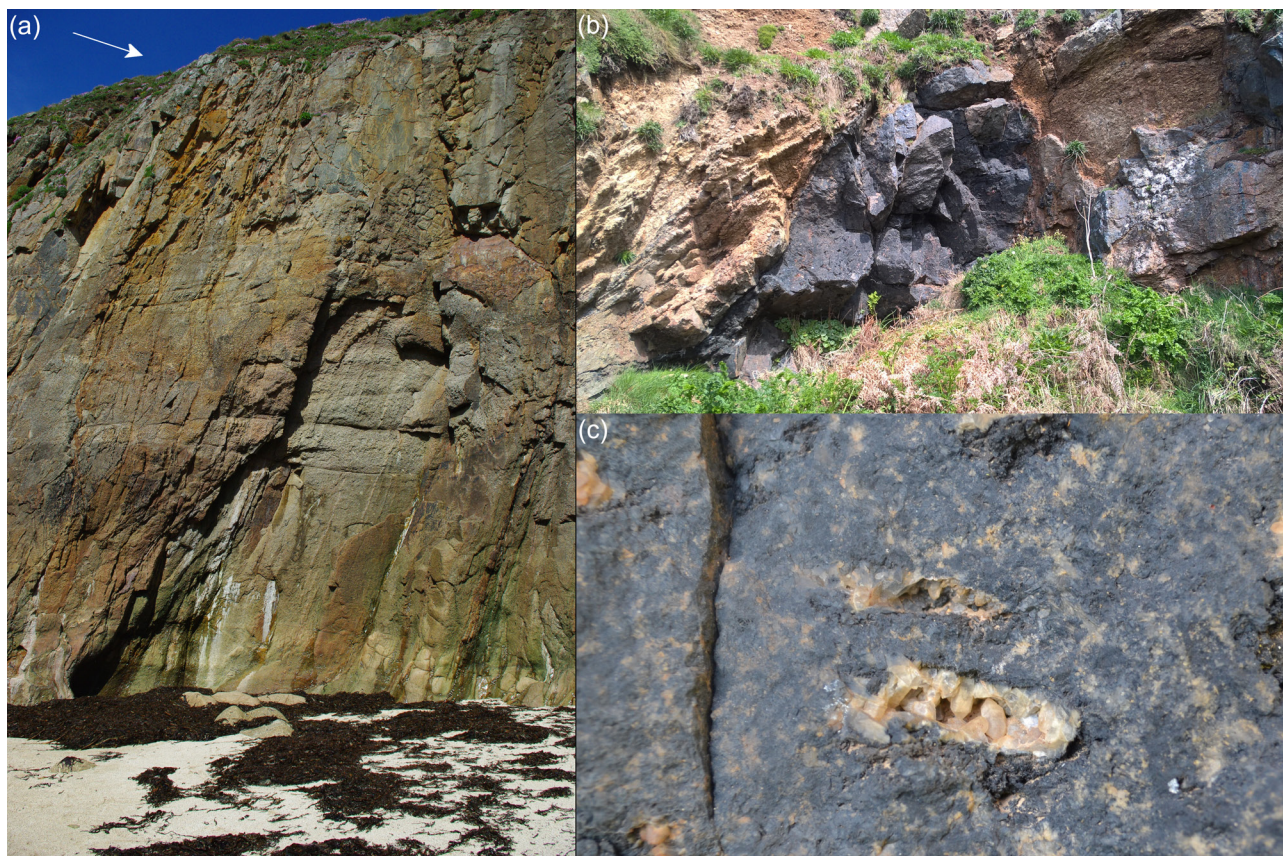


Fig. 2 Field photographs of the outcrop. **a** – Variations of granite sheets comprising the Nanjizal beach granites. White arrow indicates the location of the MQT. **b** – The outcrop from where the samples in this study were collected. The field of view is ca. 5 m. **c** – Close-up of the typical texture of the quartz-tourmaline rock. The field of view is ca. 10 cm.

(MQT) (Figs 2b–c). The former was mined for cassiterite in the mid-1800s, and the latter was blasted, but likely abandoned, in the same period (LeBoutillier 2002). The quartz-tourmaline rock does not crop out further down the cliff (Fig. 2a) and is limited to the exposure in the pit. It has mostly sharp contacts towards the granite, but sprays of mm-thick tourmaline veins originating from the MQT cut into the granite. K-feldspar phenocrysts are only observed in a limited patch, and K-feldspar is replaced by quartz and tourmaline. On the surface, euhedral quartz crystals grow into cavities from former K-feldspar phenocrysts (Fig. 2c).

3. Methods

Quantitative spot analyses were performed at the Norwegian Laboratory for Mineral and Material Characterization, Department of Geosciences and Petroleum, Norwegian University of Science and Technology, using a JEOL 8530FPlus electron microprobe. Acceleration voltage and beam current were set to 15 kV and 10 nA, respectively, and the defocused beam diameter was 1 μm . Peak and background counting times were 20 and 10 s,

respectively, for F, Mg, Na, Si, Al, Fe, Ca, Ti, Cl, K, and Mn, and 70 and 35 s, respectively, for Sn. In a second run targeting Sn-rich zones, V, Zn and Sr were added to the element list, and peak and background counting times for Sn were decreased to 40 and 20 s, respectively. This increased the detection limit (3σ) of Sn from $\sim 215 \mu\text{g/g}$ to $\sim 320 \mu\text{g/g}$. Other typical detection limits were around $150 \mu\text{g/g}$ for K and Cl, $250 \mu\text{g/g}$ for Al, Fe, and Ti, $300 \mu\text{g/g}$ for Na, $400 \mu\text{g/g}$ for Ca, $350 \mu\text{g/g}$ for Si, $500 \mu\text{g/g}$ for Mg, V, Mn, and Sr, $700 \mu\text{g/g}$ for Zn, and $1400 \mu\text{g/g}$ for F. Reference materials were albite (NaK_a), diopside (MgK_a , CaK_a), sanidine (AlK_a , SiK_a , KK_a), fluorite (FK_a), magnetite (FeK_a), rutile (TiK_a), tugtupite (ClK_a), rhodnite (MnK_a), cassiterite (SnL_a), SrF_2 (SrL_a) and pure metal standards (VK_a , ZnK_a) from Astimex Standards Ltd. A schorl from a previously analyzed sample (Drivenes et al. 2015) was analyzed between runs and sessions to monitor consistency. The raw data were processed using the $\rho\phi(z)$ matrix correction (Armstrong 1995). Uniform amounts of 10.5 wt. % B_2O_3 and 3.3 wt. % H_2O were added manually to the correction procedure for more accurate results.

Numerous low-resolution ($70 \times 50 \text{ px}$) combined energy-/wavelength-dispersive spectroscopy (EDS/

WDS) maps of zoned tourmaline were collected using the settings 20 kV, 200 nA, 4 μm defocused beam and 4 μm step size. Areas where Sn was detected were subsequently selected for high-resolution mapping. The high-resolution X-ray maps were collected at 12 kV and 120 nA, using a 0.3 μm step size and equally defocused beam. The elements B, F, Ca, Ti, and Sn were analyzed by WDS, and Na, Mg, Fe, Al, and Si were simultaneously collected by EDS. Boron was not quantified but was used to monitor for potential inclusions. Dwell time varied between 500 ms (Fig. 6a) and 750 ms (Fig. 6b). The resulting maps were imported as text images into the software package ImageJ-Fiji (Schindelin et al. 2012), and the X-ray intensities of all elements in spots with known compositions were measured. Linear regression of the X-ray intensities and elemental composition of 20 and 31 spots in maps in Fig. 6a and 6b, respectively, provided calibration lines to convert mapped intensities to wt. %. The calibration equations were applied to the images using the image expression parser function in ImageJ, converting each pixel from X-ray intensity to wt. %. The elements mapped with EDS have no significant peak overlaps with the other mapped elements, and EDS can sufficiently resolve these peaks. Thus, the conversion of mapped X-ray intensities to wt. % works for elements mapped by EDS and WDS. The maps in the electronic supplementary material (ESM 1b–e) were collected using the same settings as Fig. 6a, and the conversion factors used in Fig. 6a were used in the quantification routine. The map in ESM 1f was quantified using the data from the analyzed profile. The maps in Fig. 3 and ESM 1a and 2 were recorded using different acceleration voltages (7–10 kV) and/or crystal configuration compared to the setup used for the maps in Fig. 6 and are not quantified. The data from the quantified maps in Fig. 6 and ESM 1b–e were plotted as scatter plots using the ScatterJn and ScatterJ plugins (Zeitvogel and Obst 2016; Zeitvogel et al. 2016) in ImageJ-Fiji, providing a total of ca. 1.5 million point analyses. Some maps include areas of quartz and, rarely, cassiterite and Fe-oxides. These spots were filtered out based on unrealistic concentrations of Si, Al, Sn or Fe, or a combination of these elements, leaving 820,000 analyses considered as representative compositions of the mapped tourmaline crystals.

Tourmaline structural formula calculations were calculated based on $T+Z+Y=15$ cations or $\text{Si}=6$ if the first calculation resulted in more than 6 atoms per formula units (apfu) Si. Minimum Fe^{3+} contents were calculated by charge balance for 24.5 O. Boron was fixed at 3 apfu, and OH was calculated for 31 anions. In tourmaline with $\text{Al} < 6$ apfu, the Z-site was filled in the order Mg, Fe^{3+} , Fe^{2+} , as recommended by Henry et al. (2013). Atoms per formula units of cations from quantified maps were calculated by normalizing $\text{Si}+\text{Al}+\text{Fe}+\text{Mg}+\text{Ti}+\text{Sn}$ to 15.

4. Results

4.1. Tourmaline textures

The tourmaline crystals investigated here are strongly zoned, both optically and chemically, and the width of growth zones vary from $\sim 100\ \mu\text{m}$ (Figs 3a–d) to $\sim 0.05\ \mu\text{m}$ (Fig. 3e). Most tourmaline crystals in the sample are acicular with strong pleochroism from colorless to blue-green. Throughout SW England, this type of tourmaline has been classified as metasomatic and hydrothermal in origin (London and Manning 1995; Drivenes et al. 2015; Duchoslav et al. 2017; Drivenes et al. 2020) and is commonly associated with cassiterite mineralization (London and Manning 1995; Drivenes et al. 2015). A few large grains have a central light brown zone with light and dark blue, brown, green, and colorless overgrowths (See Fig. 3a for identification and numbering of zones). The central brown (zone 1) and light blue (zone 2) zones are likely remnants of early magmatic-hydrothermal tourmaline. The crystallization order of the late-stage tourmaline generations and growth zones is not straightforward, and particularly the colorless and darker brown tourmaline is observed at different growth stages in different crystals. However, from looking at grains cut normal to the *c*-axis and overgrowth patterns on crystals cut parallel to the *c*-axis, a general crystallization order can be established from colorless (zone 3) $\rightarrow$ dark brown (zone 4a) $\rightarrow$ colorless (zone 3) $\rightarrow$ dark blue (zone 4) $\rightarrow$ colorless (zone 3) $\rightarrow$ green (zone 5) (Figs 3a, b). All growth zones are not always present in the tourmaline crystals, and commonly, only the latter three (dark blue; zone 4 $\rightarrow$ colorless; zone 3 $\rightarrow$ green; zone 5) are observed. Cassiterite is syngenetic with the green acicular tourmaline. This tourmaline type is found as inclusions in cassiterite, with large cassiterite grains also nucleating on clusters of green tourmaline (Fig. 3a).

4.2. Tourmaline chemistry

A total of 477 spot analyses of tourmaline were analyzed by EPMA. In addition, 820,000 point analyses from the quantitative maps were used to establish compositional trends. Tourmaline analyses plot predominantly in the alkali and hydroxy fields based on *X*- and *W*-site occupancies, respectively (Figs 4a, b). Thirty analyses plot in the fluor field, and 33 analyses plot in the oxy-field. Examples of tourmaline compositions are listed in Tab. 1, all individual EPMA analyses can be found in ESM 3, and additional scatterplots of mapped compositions are displayed in ESM 4. The dominant cation in the Z-site is always Al^{3+} , and most of the analyzed tourmaline are classified as schorl and dravite and their oxy- and fluor-

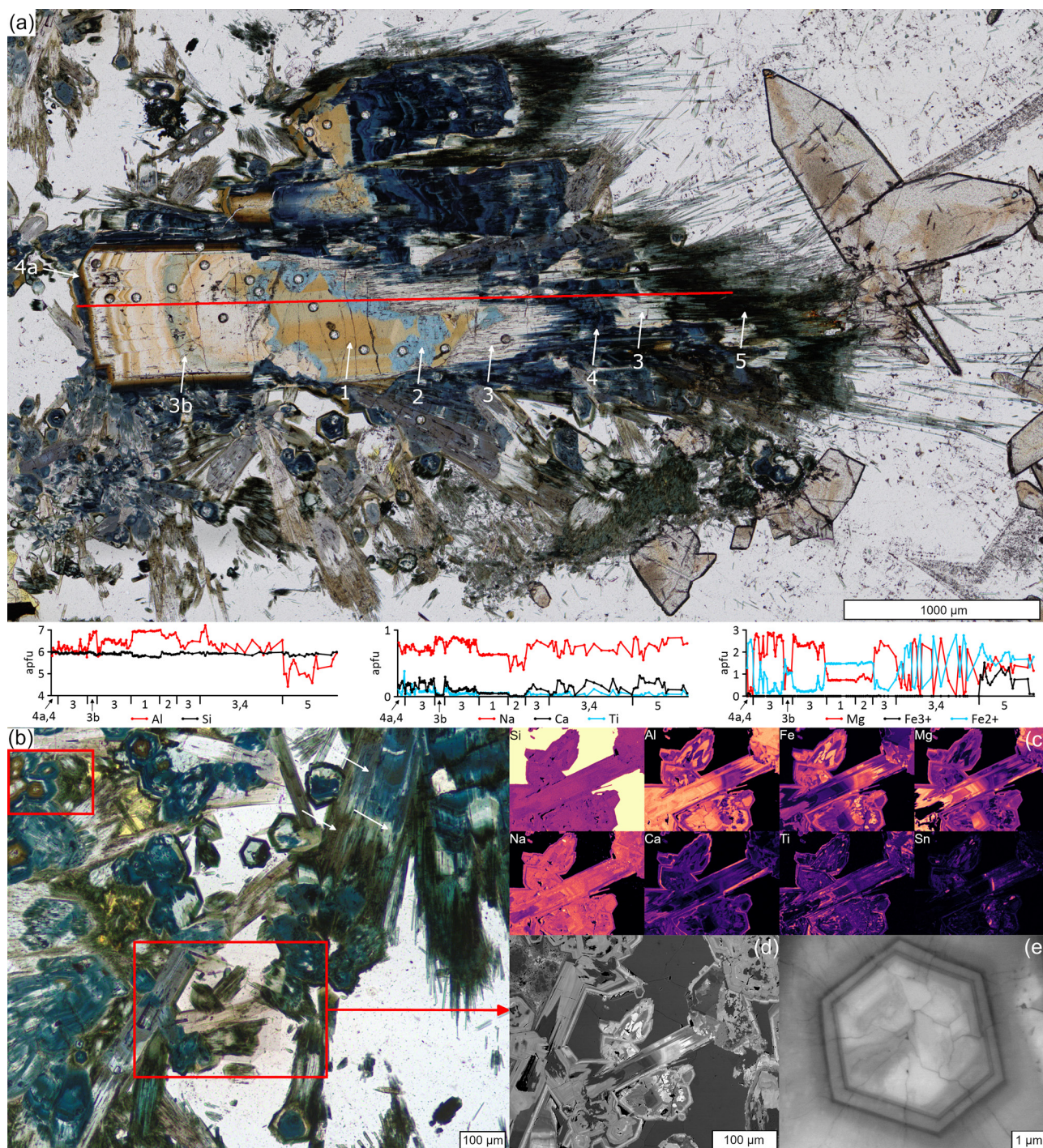


Fig. 3 Micrographs of typical tourmaline from the samples. **a** – Plane polarized optical image showing all tourmaline types and the textural relationship with cassiterite. Cassiterites are the euhedral, pale brown crystals growing on the green tourmaline. The colorless matrix is quartz. The inserts show the chemical variations in *apfu* along the profile indicated by the red line. See ESM 1f for an X-ray map of the large tourmaline crystal. Growth zones mentioned in the text are indicated by arrows. **b** – Plane polarized optical image of zoned, late-stage tourmaline. The area mapped in **c** is indicated by the red rectangle in the center. Growth zones mentioned in the text are marked by arrows and the red rectangle in the upper left corner. The yellow areas are porosity filled with colored epoxy. **c** – X-ray maps showing very fine zoning typical for tourmaline in this study. **d** – Backscatter electron image of the area marked in **b**. **e** – Example of extremely fine growth zones in tourmaline. The innermost growth zone has a double band, each band ~50 nm wide.

counterparts for oxy- and fluor species, respectively. Six analyses plotting in the vacancy field (Fig. 4a) are classified as foitite and oxy-foitite.

The different zones in Fig. 3a can be distinguished based on the major element composition (Figs 4c–g) in addition to the color in the optical microscope. The

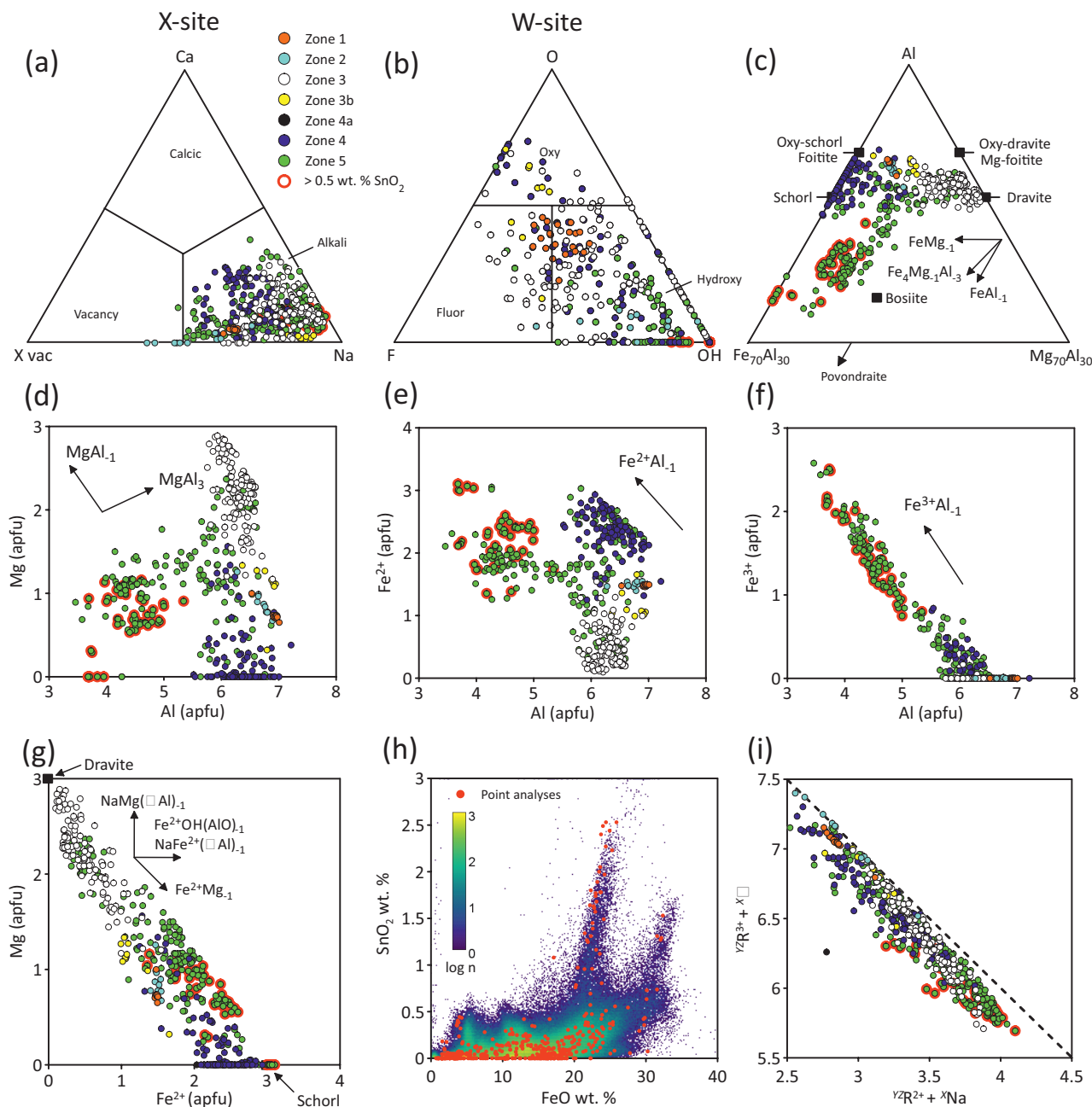


Fig. 4 Classification diagrams and compositional plots of tourmaline. The colors of the symbols indicate tourmaline groups equivalent to the different zones in Fig. 3a, and Sn-rich (> 0.5 wt. % SnO_2) tourmaline analyses are indicated by red circles around the dots. See **a** for legend. Relevant substitution vectors are indicated in the plots. **a** – Classification diagram based on *X*-site occupancy. **b** – Classification diagram based on *W*-site occupancy. **c** – Apfu normalized Al–Mg–Fe diagram. **d** – Al vs. Mg. **e** – Al vs. Fe^{2+} . **f** – Al vs. Fe^{3+} . **g** – Fe^{2+} vs. Mg. **h** – Plot of FeO vs. SnO_2 . The red dots are single EPMA analyses. The blue to yellow dots are compositions derived from the quantitative maps. Each axis was divided into 256 bins, and the color scale indicates the number of analyses ($1-10^3$) with the same composition. **i** – Plot of divalent cations in the *Y*- and *Z*-sites + Na vs. trivalent cations in the *Y*- and *Z*-sites + *X*-vacancies. The dashed line represents $\frac{1}{2}\text{R}^{3+} + \text{X}\square + \frac{1}{2}\text{R}^{2+} + \text{XNa} = 10$.

early tourmaline generations (zones 1 and 2) have similar Al, Fe and Mg contents, but the light blue tourmaline (zone 2) has more vacancies in the *X*-site and accounts for all analyses classified as foitite. This zone is also very low in Ti (Fig. 3a, ESM 1f). The colorless tourmaline (zone 3) is dravitic, and the deep blue (zone 4) is Fe-rich schorl, with some of the analyses from tourmaline

equivalent to zone 4 in Fig. 3a having a minor Fe^{3+} component (Fig. 4f). The colorless zones on the left side of the large crystal in Fig. 3a may represent two separate growth stages divided by the greenish zone (zone 3b in Fig. 3a), but for the sake of simplification, these are grouped together in Figs 4c–g. The pleochroic green tourmaline (zone 5) is strongly zoned (Fig. 3c) and is the group that shows the

Tab. 1 Selected EPMA analyses of tourmaline from the sample. All analyses are available in ESM 3.

	Group 1	Group 2	Group 3	Zone 1	Zone 2	Zone 3	Zone 4	Zone 4	Zone 5	Zone 5	Zone 5	
SiO ₂	32.01	31.36	32.05	34.44	34.76	36.60	33.58	35.00	35.71	33.68	32.48	
TiO ₂	0.12	b.d.l.	0.18	0.44	b.d.l.	0.29	b.d.l.	0.26	0.30	0.19	0.14	
SnO ₂	2.53	1.53	0.54	b.d.l.	b.d.l.	0.05	0.04	0.03	0.16	0.15	0.73	
Al ₂ O ₃	20.62	16.32	16.73	34.71	33.59	32.15	30.64	30.57	31.72	21.71	17.13	
V ₂ O ₃	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	
MgO	2.03	b.d.l.	3.36	2.82	3.43	10.35	b.d.l.	2.78	3.70	5.27	1.14	
MnO	b.d.l.	0.12	b.d.l.	b.d.l.	0.07	b.d.l.	0.08	0.07	b.d.l.	b.d.l.	0.10	
FeO _{tot}	25.89	32.36	27.49	10.34	10.25	2.70	19.28	14.19	11.97	20.49	30.12	
ZnO	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	
CaO	0.39	0.28	0.59	0.27	0.00	1.05	0.22	1.01	0.31	1.29	0.65	
Na ₂ O	2.38	2.40	2.07	1.90	1.44	2.46	2.20	2.04	2.12	1.96	2.18	
K ₂ O	0.07	0.08	0.08	0.03	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.03	0.05	
F	b.d.l.	b.d.l.	0.20	0.55	0.42	0.61	b.d.l.	0.72	b.d.l.	b.d.l.	b.d.l.	
Cl	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.04	b.d.l.	b.d.l.	b.d.l.	
O=F	0.00	0.00	-0.09	-0.23	-0.18	-0.26	0.00	-0.30	0.00	0.00	0.00	
O=Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	
B ₂ O ₃ [*]	9.51	9.08	9.28	10.26	10.21	10.71	9.95	10.14	10.34	9.79	9.41	
Fe ₂ O ₃ [*]	10.53	14.41	15.44	0.00	0.00	0.00	1.03	0.00	0.00	9.33	18.05	
FeO [*]	16.41	19.40	13.60	10.34	10.25	2.70	18.35	14.19	11.97	12.09	13.87	
H ₂ O [*]	3.28	3.13	3.11	2.89	3.28	3.18	3.43	2.95	3.52	3.38	3.24	
Total	99.88	98.11	97.15	98.41	97.27	99.89	99.53	99.48	99.85	98.87	99.17	
Calculated structural formula. See text for normalization procedure												
T-site	Si	5.849	6.000	6.000	5.835	5.919	5.940	5.864	6.000	6.000	5.981	6.000
	Al	0.151			0.165	0.081	0.060	0.136			0.019	
B-site	B	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Z-site	Al	4.290	3.680	3.691	6.000	6.000	6.000	6.000	6.000	6.000	4.525	3.729
	Mg	0.553		0.938							1.395	0.313
	Fe ³⁺	1.157	2.074	1.371							0.080	1.958
	Fe ²⁺		0.246									
Y-site	Fe ²⁺	2.508	2.858	2.129	1.465	1.460	0.366	2.680	2.034	1.682	1.796	2.144
	Mg				0.712	0.871	2.504		0.710	0.927		
	Mn		0.019			0.011		0.012	0.011			0.015
	Al				0.767	0.659	0.090	0.170	0.176	0.281		
	Fe ³⁺	0.292		0.804				0.135			1.168	0.552
	Ti	0.016		0.025	0.056		0.036		0.033	0.038	0.026	0.019
	Sn	0.184	0.117	0.041			0.003	0.003	0.002	0.011	0.011	0.054
X-site	Ca	0.076	0.057	0.118	0.049	0.000	0.182	0.040	0.186	0.055	0.246	0.128
	Na	0.843	0.890	0.751	0.624	0.475	0.774	0.745	0.678	0.691	0.675	0.781
	K	0.017	0.020	0.019	0.006	0.000	0.000	0.000	0.000	0.000	0.006	0.011
	vac.	0.064	0.033	0.111	0.320	0.525	0.044	0.215	0.136	0.254	0.073	0.081
V-site	OH	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
W-site	F			0.121	0.294	0.225	0.312		0.390			
	Cl								0.012			
	OH	1.000	1.000	0.879	0.263	0.722	0.441	1.000	0.368	0.943	1.000	1.000
	O				0.443	0.053	0.247		0.229	0.057		

*Calculated

b.d.l. – analysis was below the detection limit of the corresponding element.

most scatter in the chemical plots in Figs. 4c–g. Some analyses overlap with those from the colorless (zone 3) and dark blue (zone 4) tourmaline. However, most of the analyses plot as a separate group characterized by low Al, high Fe_(tot), high Fe³⁺, and low to moderate Mg (Figs 4c–f). This is the group that hosts the high-Sn tourmaline. The high Fe³⁺ content is calculated based on stoichiometry. Such estima-

tions of Fe²⁺/Fe³⁺ are semiquantitative at best. However, the incorporation of divalent cations at the Y- and Z- sites is restricted to maximum 3 *apfu* in Na-tourmalines, and 4 *apfu* in Ca-tourmalines (Vereshchagin et al. 2018). The highest analyzed Ca concentration was 0.40 *apfu*, but Ca typically varies from 0 to 0.2 *apfu*. Thus, it is assumed that at least some Fe in the Fe-rich zone is ferric. The Fe-rich tourmalines

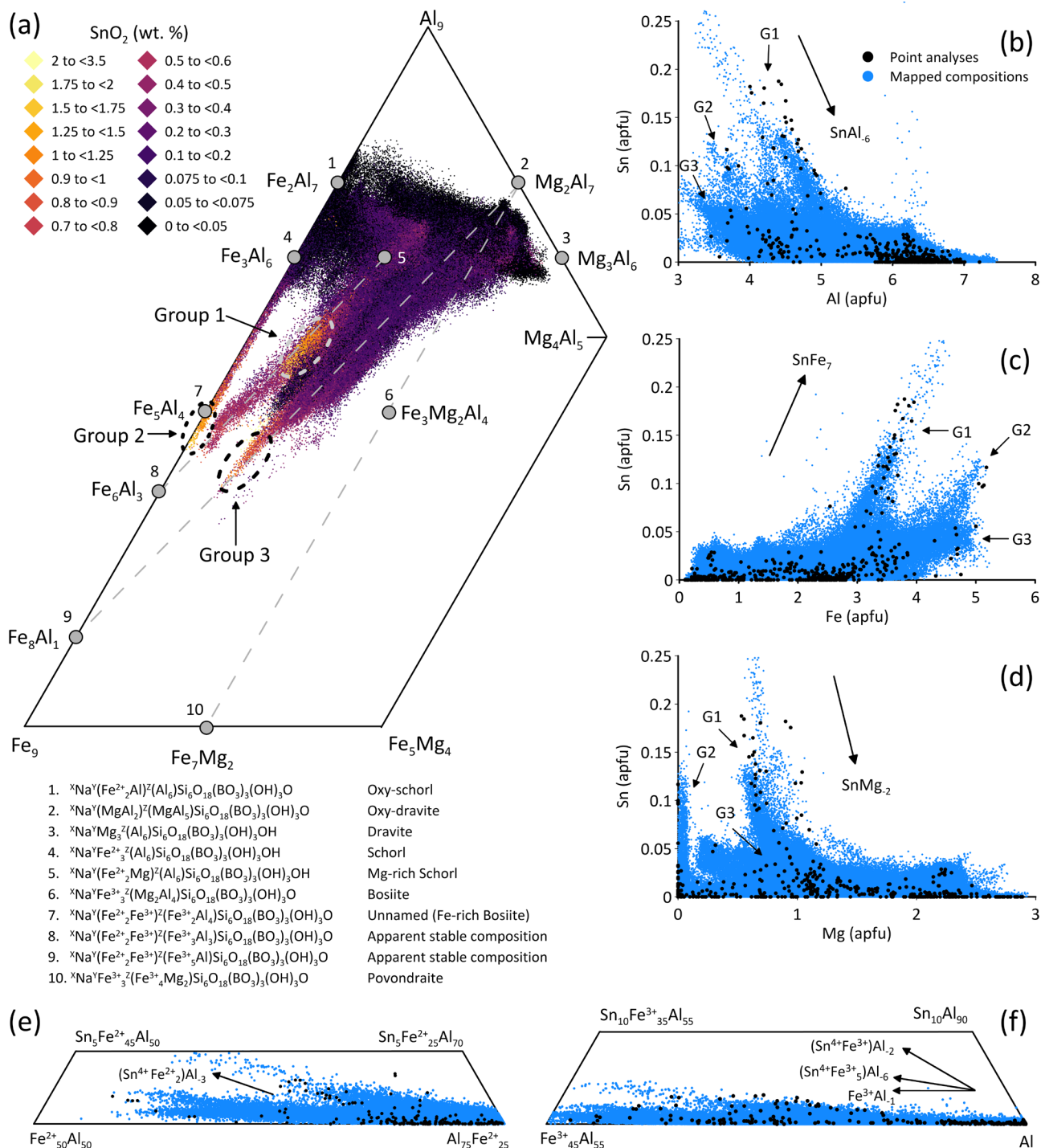


Fig. 5 a – Ternary plot of Al, Mg and Fe. Compositions are derived from the quantified maps. Abbreviated formulas indicating the occupancy of (Y + Z) are marked on the diagram. Full formulas of corresponding Na-tourmalines are listed below the diagram. The color scale indicates the Sn-content as wt. % oxide. The Sn-rich tourmaline groups mentioned in the text are indicated by dashed ellipses. Plots of **b** – Al vs. Sn, **c** – Fe vs. Sn, **d** – Mg vs. Sn. Blue dots are mapped compositions. Black dots are single EPMA analyses. The large arrows indicate correlation vectors fitting the major trends in the plots, and the Sn-rich tourmaline groups mentioned in the text are indicated (G1–3). **e** – *Apfu* normalized ternary plot of Sn–Al–Fe²⁺. The substitution vector fitting the trend towards higher Sn content is indicated by the arrow. **f** – *Apfu* normalized ternary plot of Sn–Al–Fe³⁺. Relevant substitution vectors are indicated by arrows.

plot between bosiite and schorl in the Al–Fe–Mg diagram (Fig. 4c). Zone 4a in Fig. 3a is characterized by high Ti and very low Mg (see also ESM 1f).

The X-site in all analyzed tourmaline is mainly occupied by Na or vacancies (Tab. 1, ESM 3). A 1–2 μm Ca-rich growth zone is commonly observed as the second

to last growth zone towards the quartz contact (Figs. 3c, 6, ESM 1, 2). This zone has ca. 2 wt. % CaO and ca. 1 wt. % Na₂O. Other major elements vary in this zone, but Mg is typically ~5 wt. % MgO, FeO is typically 10–15 wt. %, and Al is ~30 wt. %. TiO₂ is generally <0.5 wt. % in all growth zones but is slightly concentrated (1–3 wt. %) in late, oscillatory growth zones (Figs 3a, c, 6, ESM 1). The Na and vacancy contents in the X-site are correlated with the divalent and trivalent cations, respectively, in the Y- and Z-sites, and $X\Box + YZR^{3+}$ vs. $XNa + YZR^{2+}$ plot on a linear trendline (Fig. 4i).

Tin occurs as concentrated growth zones in the center of late tourmaline grains. Commonly, a central zone with up to ca. 2.53 wt. % SnO₂ (0.19 apfu Sn) is followed by a zone with lower Sn-content, typically around 1 wt. % SnO₂ (Figs 6a, b). This zoning pattern is evident in grains cut normal to the c-axis. In grains cut (sub-)parallel to the c-axis, the Sn-rich zones are elongated (Fig. 3c, ESM 1b). Figure 6a shows two Sn-rich zones with sharp contacts to an Sn-free tourmaline generation, which may represent the nucleation of two separate Sn-rich tourmaline grains. Two bright spots in the Sn-map in Fig. 6a (arrows) are submicron cassiterite. These can be clearly distinguished from the Sn-rich tourmaline zones. Also, SnO₂-concentrations of around 2.5 wt. % were observed in several spot analyses, and the Sn-concentrations derived from maps from different grains plotted on consistent trends up to 0.26 apfu Sn (~3.55 wt. % SnO₂) (Figs 5b–d). Therefore, Sn is interpreted to be incorporated in the tourmaline structure and not cassiterite inclusions.

The high-Sn zones occur in zones with high Fe and low Al. The relationship is not exclusive, and not all analyses with high Fe have high Sn (Figs 4h, 5c). Three groups of Sn-rich tourmaline are recognized based on Al, Fe and Mg contents. The group with the highest concentrations of Sn (group 1) has ca. 3–4 apfu Fe_(tot), ca. 4–5 apfu Al, and ca. 1 apfu Mg. Group 2 is characterized by no or very low Mg. Spot analyses of tourmaline in this group showed above 0.1 apfu Sn. Group 3 tourmalines have Sn up to ca. 0.05 apfu and have the lowest Al (<4 apfu), Fe similar to group 2 (4–5 apfu), and Mg similar to group 1 (Figs 5a–d, 6, Tab. 1, ESM 3). There is no obvious relationship between Sn and X-site occupancy.

5. Discussion

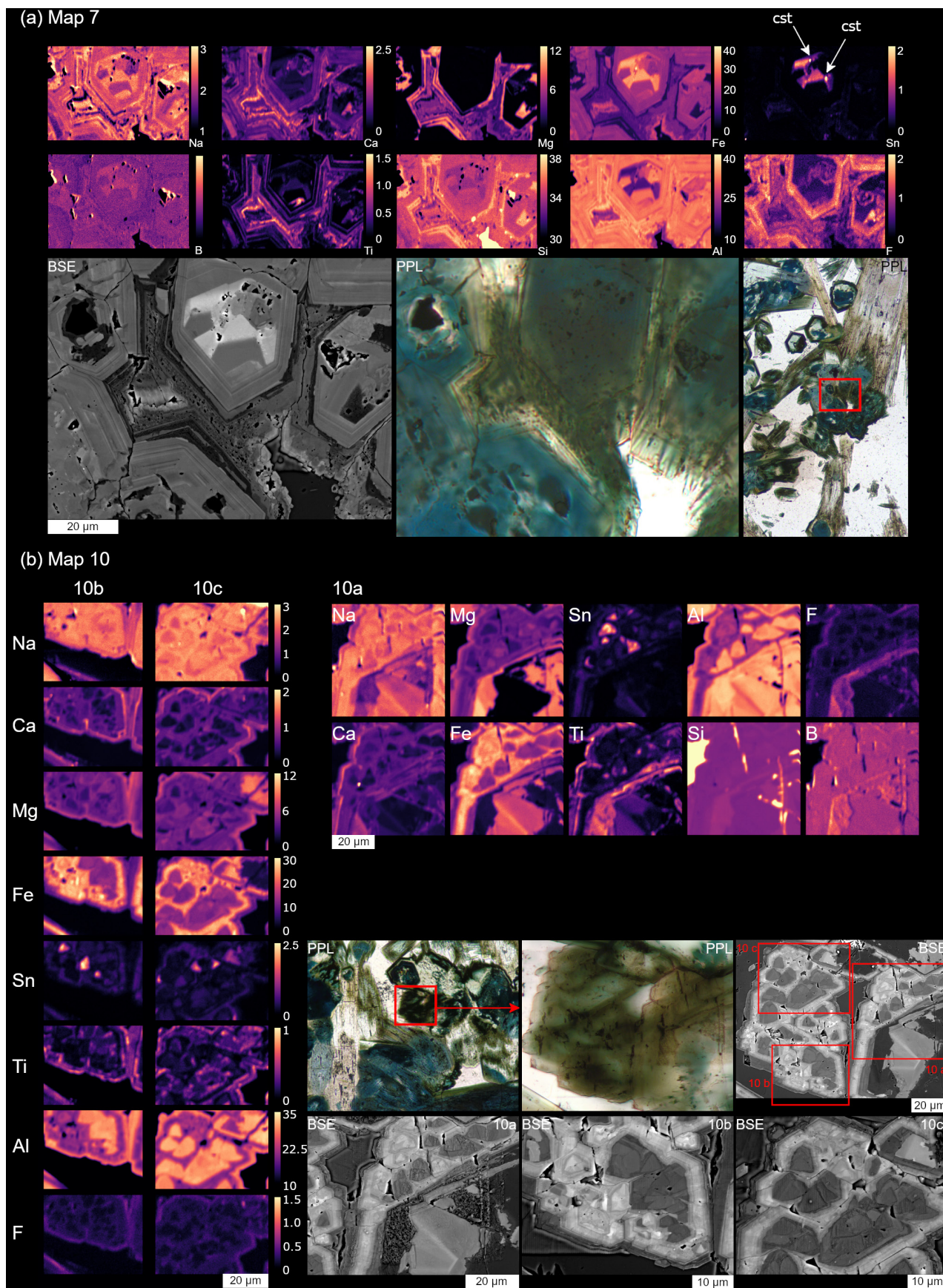
5.1. Sn in mineral-melt-fluid systems

In minerals where Sn is a major element, such as cassiterite (SnO₂), stannite (Cu₂FeSnS₄), malayaite (CaSnSiO₅), colusite (Cu₁₃V[As,Sb,Sn,Ge]₃S₁₆), and mawsonite (Cu₆Fe₂SnS₈), Sn typically occurs as Sn⁴⁺ in octahedral coordination bonding to oxygen or tetrahedral coordina-

tion bonding to sulfur (Higgins and Ribbe 1977; Cheng et al. 2019; Hausmann et al. 2020; Guélou et al. 2021). Sn has also been shown to substitute for Al³⁺, Fe³⁺, and Ti⁴⁺ in octahedral coordination in the structures of rutile, magnetite, ilmenite, garnet, biotite, muscovite, amphibole, and epidote (e.g., Müller and Halls 2005; Chen et al. 2021). Stannous tin is rare in common natural minerals, but Sn²⁺ has been reported from oxides, sulfides, and sulfosalts such as foordite (SnNb₂O₈), herzenbergite (SnS), and franckeite ([Pb,Sn]₆FeSn₂Sb₂S₁₄) (Černý et al. 1988; Smeds 1993; Makovicky et al. 2011). Badullovich et al. (2017) used lattice strain modeling to show that Sn²⁺ may partition into the Ca-bearing [8]-coordinated sites in clinopyroxene and plagioclase. Similarly, Weck and Kim (2016) predicted that Sn²⁺ may be substituted for Ca as a major element in hydroxylapatite. Contrary to the theoretical studies mentioned above, experiments trying to incorporate Sn²⁺ into carbonates were unsuccessful (Junio et al. 2021), and feldspars from tin granites have very low Sn contents (Müller et al. 2006; Chen et al. 2021).

In reduced, peraluminous granitic melts, Sn²⁺ is the dominant species and Sn behaves incompatibly (Ishihara 1977; Linnen et al. 1996; Bhalla et al. 2005; Farges et al. 2006). If an aqueous fluid is exsolved, Sn may be partitioned into the fluid, depending particularly on the HCl content of the fluid and the aluminosity of the melt (Duc-Tin et al. 2007; Schmidt et al. 2020). Magmatic and early hydrothermal tourmaline from the Cornubian batholith is low in Sn, less than 100 µg/g in early hydrothermal tourmaline, and typically <20 µg/g in magmatic tourmaline (Drivenes et al. 2015; Duchoslav et al. 2017; Drivenes et al. 2020). Tourmaline is not a natural host for Sn under these conditions despite being a late-forming mineral in the crystallization sequence.

In hydrothermal fluids, Sn is predominantly transported as various Sn(II)Cl_x^{(2-x)-} ± (H₂O) complexes and the dominant complex varies with temperature and phase state of the fluid phase (i.e., liquid, vapor, supercritical) (Wang et al. 2021). However, Sn(IV)Cl-species have been reported in Sn solubility experiments (Schmidt 2018) and may play a significant role in the transport of Sn in hydrothermal fluids. Such complexes may be particularly important in the leaching of Sn⁴⁺ from early-forming minerals (e.g., ilmenite and biotite) and cassiterite enrichment during progressive greisenization (Heinrich 1990; Schmidt et al. 2020). The samples from this study are rich in cassiterite. The mechanisms required to precipitate cassiterite from an ore fluid involve fluid oxidation, dilution of the magmatically derived hydrothermal fluid by mixing with meteoric water, or HCl consuming fluid-rock reactions (Heinrich 1990; Lehmann 2021). Due to the close association between the Sn-rich tourmaline generations and cassiterite, and the inferred Fe³⁺ content in the Sn-rich tourmaline, it is likely that at the time of



crystallization, the available tin of Sn-rich tourmaline was in the form Sn^{4+} , either through oxidation of $\text{Sn}(\text{II})$ Cl-complexes, or existing $\text{Sn}(\text{IV})\text{Cl}$ -complexes.

5.2. Incorporation of Sn into the tourmaline structure

The ionic radius of Sn^{4+} in tetrahedral coordination (0.55 Å; Shannon 1976) is too large to fit in the tetrahedral *T*-site as a substitution for Si (0.26 Å; Shannon 1976), and since Sn typically substitutes for octahedrally coordinated Al^{3+} , Fe^{3+} , and Ti^{4+} in silicates, the *Y*- and *Z*-site are the likely locations for Sn^{4+} . The ionic radius of Sn^{4+} in octahedral coordination is 0.69 Å, similar to Fe^{3+} (0.675 Å) and Mg^{2+} (0.72 Å) (Shannon 1976; Bosi 2018). Fe and Mg are allocated to the *Y*-site in an ordered structure, but in alkali tourmalines with $\text{Al} < 6 \text{ apfu}$, both Fe^{3+} and Mg^{2+} can be major cations at the *Z*-site (Ertl et al. 2016; Bosi et al. 2017). The lack of structural data on tourmaline from this sample, and the common disordering across the *Y*- and *Z*-sites, makes it difficult to determine the exact site where Sn is located. However, Vereshchagin et al. (2018) showed that transition metals are preferably incorporated into the *Y*-site at low (e.g., $< 0.3 \text{ apfu}$ for V^{3+} and $< 1.6 \text{ apfu}$ for Ni^{2+}) concentrations. These elements have similar ionic radii as Sn, and if Sn follows the same trend, the *Y*-site is the most likely site for Sn.

The major element composition of tourmaline in these samples is mainly controlled by the $\text{Fe} \leftrightarrow \text{Mg}$ and $\text{Fe} \leftrightarrow \text{Al}$ substitutions (Figs 4c, e, f, g, ESM 4). Figure 6b (Map10a) shows how different growth zones are controlled by the two main substitutions. In the lower right half of the map, the Mg and Fe maps are negatively correlated, with Al being more or less constant. In the upper left half, Mg is more or less constant, whereas Al and Fe are negatively correlated. Similar relationships can be observed in the maps in ESM 1–2. Typically, the FeMg_{-1} exchange is dominant in the earlier tourmaline growth stages towards the center of the grains, whereas the FeAl_{-1} exchange represents the main substitution in the outer growth zones (Figs. 6a, b, ESM 1, 2). However, there are examples where the FeMg_{-1} exchange is the main substitution in growth zones overgrowing the high Fe, and low Al zones (lower part of ESM 2c). The Al vs. Mg plot in ESM 4 shows trends with both positive and negative slopes. The positive Al–Mg relationship is only observed in green (the equivalent of zone 5 in Fig. 3a) tourmaline (Fig. 4d) with a slope of ca. 0.33. In

tourmaline equivalent to zones 1–3 (Fig. 3a), Al and Mg are negatively correlated, indicating the exchange vector MgAl_{-1} . Clusters of colorless tourmaline plot in vertical trends in the Fe–Mg plot (Fig. 4g), and the Mg–Al trend is likely a result of the coupled substitution $^{\text{X}}\text{Na} + ^{\text{Y}}\text{Mg} \leftrightarrow ^{\text{X}}\square + ^{\text{Y}}\text{Al}$. The relationship between Al and Fe depends on the oxidation state of Fe. The green tourmaline shows no correlation between Al and Fe^{2+} , but plots nicely along the $\text{Fe}^{3+}\text{Al}_{-1}$ exchange vector (Figs 4e–f). The dark blue tourmaline shows a negative correlation between Al and Fe^{2+} corresponding to the $\text{Fe}^{2+}\text{Al}_{-1}$ exchange vector, and a weaker negative correlation between Al and Fe^{3+} indicating some involvement of the $\text{Fe}^{3+}\text{Al}_{-1}$ exchange vector. Similar to tourmaline from zones 1–3, which had a negative correlation between Mg and Al, the tourmaline group showing a negative relationship between Fe^{2+} and Al has between 6 and 7 *apfu* Al, meaning that Al also occupies the *Y*-site. For most of the analyses, the sum of divalent cations in the *X*- and *Y*-sites and Na in the *X*-site plot on a linear trend with a slope of -1 against the sum of trivalent cations and vacancies in the *X*-site (Fig. 4i). However, some analyses of dark blue tourmaline (around 7 on the *y*-axis) show a horizontal trend. Most of the dark blue tourmaline is very low in Mg and plot along a horizontal line in Fig. 4g. Thus, it is likely that the $\text{Fe}^{2+}\text{Al}_{-1}$ relationship in the dark blue tourmaline is a result of the $\text{NaFe}^{2+}(\square\text{Al})_{-1}$ or $\text{Fe}^{2+}\text{OH}(\text{AlO})_{-1}$ exchange vectors. Sn is predominantly hosted by the green (zone 5) tourmaline, in which the major element composition is mainly controlled by the povondraite substitution ($\text{Fe}^{3+}\text{Al}_{-1}$). The green tourmalines plot along the FeMg_{-1} vector in Fig. 4g, and in the Al–Mg–Fe ternary plot (Fig. 4c), it is clear that the high-Fe tourmalines plot on a trend away from the Al and Mg apices, and that the exchange vector for the Sn-rich tourmalines includes Fe, Al and Mg (e.g., $\text{Fe}_4\text{Mg}_{-1}\text{Al}_{-3}$).

The three main groups of Sn-rich tourmaline (orange-yellow dots in Fig. 5a) are most easily distinguished in the ternary Al–Mg–Fe diagram (Fig. 5a): one with normalized Fe–Mg–Al composition ($\text{Fe} + \text{Mg} + \text{Al} = 9 \text{ apfu}$) of ca. $\text{Fe}_{3.5}\text{Mg}_{0.75}\text{Al}_{4.75}$ (group 1); an Mg-free group around Fe_5Al_4 (group 2), a composition corresponding to the Fe-equivalent of bosiite; and a group with slightly lower Sn-content with normalized Fe–Mg–Al composition around $\text{Fe}_{4.75}\text{Mg}_{0.75}\text{Al}_{3.5}$ (group 3). Ordered structural formulas, assuming alkali tourmaline, of the referred tourmaline compositions are listed below Fig. 5a. Calculated average formulas of groups of individual EPMA analyses corresponding to groups 1–3 are listed in Tab. 2. The three analyses representing group 3 all have lower Sn content compared to the mapped compositions. Thus, Sn is slightly underestimated in the calculated formula. Currently approved compositions of Fe-rich alkali end-members have O^{2-} as the dominant anion in the *W*-site

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Fig. 6 X-ray maps, backscatter electron and plane polarized optical images **a** – of map 7. **b** – of map 10. The quantitative scale is given in wt. % oxide and is identical for all three maps. See text for quantification procedure and EPMA settings.

Tab. 2 Calculated average formulas for Sn-rich tourmaline groups

Group 1 ($n = 11$)	$^{X}(\text{Na}_{0.82}\text{Ca}_{0.08}\square_{0.08}\text{K}_{0.02})^{Y}(\text{Fe}^{2+}_{2.41}\text{Fe}^{3+}_{0.39}\text{Sn}_{0.16}\text{Ti}_{0.01})^{Z}(\text{Al}_{4.43}\text{Fe}^{3+}_{0.95}\text{Mg}_{0.63})\text{Si}_{5.99}\text{Al}_{0.01}\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH})$
Group 2 ($n = 4$)	$^{X}(\text{Na}_{0.88}\text{Ca}_{0.05}\square_{0.04}\text{K}_{0.02})^{Y}(\text{Fe}^{2+}_{2.84}\text{Sn}_{0.10}\text{Ti}_{0.02}\text{Mn}_{0.02})^{Z}(\text{Al}_{3.72}\text{Fe}^{3+}_{2.07}\text{Fe}^{2+}_{0.20})\text{Si}_{5.99}\text{Al}_{0.01}\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.98}\text{F}_{0.02})$
Group 3 ($n = 3$)	$^{X}(\text{Na}_{0.79}\text{Ca}_{0.11}\square_{0.07}\text{K}_{0.02})^{Y}(\text{Fe}^{2+}_{2.12}\text{Fe}^{3+}_{0.84}\text{Sn}_{0.03}\text{Ti}_{0.01})^{Z}(\text{Al}_{3.54}\text{Fe}^{3+}_{1.57}\text{Mg}_{0.89})\text{Si}_{5.93}\text{Al}_{0.07}\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.96}\text{F}_{0.04})$

(Henry and Dutrow 2018). Stoichiometric calculations of the V - and W -sites include high degrees of uncertainty and vary depending on the normalization procedure. It can be questioned whether the hydroxy-classification is real or if the tourmalines are oxy-species. Fluorine was below the detection limit in most analyses with $\text{Sn} > 0.05$ apfu, and the W -site is dominated by OH^- and/or O^{2-} .

None of the three groups of Sn-rich tourmaline appear to be related to each other through direct substitutions, and trails of Sn-bearing tourmaline (purple dots in Fig. 5a) surrounding each of the Sn-rich groups are separated by low-Sn analyses or compositional gaps. These trails can be used to assess the involved exchange vectors. Group 2 does not include Mg and is related to endmember schorl by the operation FeAl_{-1} , most likely the povondraite substitution ($\text{Fe}^{3+}\text{Al}_{-1}$). Groups 1 and 3 plot on parallel trendlines controlled by $\text{Fe}_4\text{Mg}_{-1}\text{Al}_{-3}$. This operation relates Mg-bearing schorl (Fe_2MgAl_6 ; Point 5 in Fig. 5a) and a hypothetical composition (Fe_6Al_3 ; Point 8 in Fig. 5a), with the Sn-rich tourmalines in group 1 plotting along the trendline. The same operation relates oxy-dravite (Mg_2Al_7) to another hypothetical composition (Fe_8Al_1) with group 3 tourmaline plotting along the trendline. There are currently no approved tourmaline species with the compositions of the hypothetical compositions, but tourmaline plotting on a trend similar to that of group 1 was reported from the Julianna pegmatite, Piława Górna, Poland (Pieczka and Sek 2017).

Fe-rich oxy-tourmalines are related through a series of substitutions mainly involving Al, Fe and Mg, from oxy-schorl through oxy-dravite and bosite towards povondraite. The data in Fig. 5a share similarities to the literature values compiled by Bosi et al. (2017) in Fig. 2. The trend of the Sn-bearing tourmalines in group 1 can be extended through point 5 in Fig. 5a towards slightly higher Mg and Al contents ($\sim \text{Fe}_{1.25}\text{Mg}_{1.25}\text{Al}_{6.5}$), then towards oxy-schorl. The data in Bosi et al. (2017) plot from oxy-schorl towards dravite composition, concerning Al–Fe–Mg, until it reaches the line connecting oxy-dravite and povondraite, which the data plot neatly along towards povondraite. The data in this study differ from those reviewed in Bosi et al. (2017) in that the change in the direction of the trend towards Fe-rich compositions happens before the oxy-dravite–povondraite line and that the exchange vector controlling the composition with increasing Fe involves Mg, although as Bosi et al. (2017) concluded, there is no evidence for a direct solid solution between oxy-schorl and bosite or povondraite (e.g., a $\text{Mg}_2\text{Fe}_1\text{Al}_{-3}$ exchange vector)

Previously suggested substitution schemes for Sn in tourmaline include $^X\text{Na}^+ + ^Y\text{Fe}^{2+} + ^Z\text{Sn}^{4+} \leftrightarrow ^X\text{Ca}^{2+} + ^Y\text{Mg}^{2+} + ^Z\text{Al}^{3+}$, $2^X\text{Al}^{3+} \leftrightarrow ^Y\text{Sn}^{4+} + ^Z\text{Mg}^{2+}$, $^Y\text{Al}^{3+} + ^W\text{OH}^- \leftrightarrow ^Z\text{Sn}^{4+} + ^W\text{O}^{2-}$, and $2^Y\text{Mg}^{2+} \leftrightarrow ^Y\text{Sn}^{4+} + ^Z\square$ (Baksheev et al. 2020; Vereshchagin et al. 2022). The Sn-rich tourmalines in this study are Fe-rich, and the latter three substitution reactions were derived from synthesized dravite. The first is derived from analyses of natural schorl and may be relevant for the tourmaline studied here. However, no correlation between the X -site and Sn is observed. An overall quantitative correlation between Sn and the major elements can be proposed by plotting Sn against the other major elements in the Z - and Y -sites (Figs 5b–d). The slopes of the trendlines of Sn vs. Al, $\text{Fe}_{(\text{tot})}$, and Mg are -6 , 7 , and -2 , respectively, for group 1, which is the main group of Sn-rich tourmaline. The trends in the ternary plots of Sn–Al– Fe^{2+} and Sn–Al– Fe^{3+} (Figs 5e, f) indicate the exchange vectors $(\text{Sn}^{4+}\text{Fe}^{2+}_2)\text{Al}_{-3}$ and $(\text{Sn}^{4+}\text{Fe}^{3+}_5)\text{Al}_{-6}$. By combining the trends in the ternary and binary plots (Figs 5b–f), the major coupled substitution involving Sn in the Sn-rich tourmalines in this study is $^Y\text{Sn}^{4+} + ^Z2\text{Fe}^{2+} + 5^Y\text{Fe}^{3+} + ^W\text{O}^{2-} \leftrightarrow 2^Y\text{Mg}^{2+} + 6^Y\text{Al}^{3+} + ^W\text{OH}^-$. This complex exchange reaction represents a combination of $\text{SnO}(\text{AlOH})_{-1}$, $\text{Fe}^{2+}\text{Mg}_{-1}$, and $\text{Fe}^{3+}\text{Al}_{-1}$ substitutions in the ratio of $1:2:5$.

5.3. Crystallization of Sn-rich tourmaline

The texture and zoning patterns of tourmaline observed in the studied samples span the entire range from patchy and erratic dissolution-reprecipitation of former tourmaline generations, to fine oscillatory zoning, indicating numerous episodes of tourmaline crystallization. The sharp contacts to the granite and the restricted volume of the massive quartz-tourmaline (MQT) body indicate that the tourmalinization of the granite protolith was structurally controlled, possibly a fault jog causing a local low-pressure zone. The tourmalinization likely happened over a short time period with a high fluid-rock ratio. Initially, the tourmaline composition was to a certain degree buffered by the granite mineral assemblage, but as metasomatism progressed, the tourmaline composition was increasingly fluid-controlled.

Since tourmaline composition evolves from mineral- to fluid-buffered, the question may be raised whether Sn is solely derived from the fluid or if the Sn-rich zones might result from tourmalinization of Sn-bearing granite minerals. The bulk Sn-content of the host granite is low (~ 10 $\mu\text{g/g}$) (Müller et al. 2006; Drivenes et al. 2015; Simons et al. 2017), and as discussed in Section 5.1, there are only a

few natural hosts for Sn. Ilmenite is a common accessory mineral in the Land's End granite, but during hydrothermal alteration, ilmenite is altered to rutile, which is unlikely to release Sn to the fluid (Müller and Halls 2005). A subsequent alteration of rutile to tourmaline is also unlikely, and the Sn-rich zones are low in Ti. The average Sn-concentration in biotite from G3 granites from Land's End is 66 µg/g Sn (Simons et al. 2017). Thus, *in-situ* replacement of granite minerals is most likely not a significant contributing factor to the Sn-content of tourmaline.

The coexistence of the green acicular tourmaline and cassiterite indicates that the fluid was saturated with respect to SnO₂ during late-stage tourmaline crystallization. Quartz, tourmaline and cassiterite are the only available minerals for Sn to partition into, and cassiterite is the primary sink for Sn. Some of the Sn-rich zones (Fig. 6, ESM 1a, c, 2a, b, e, g, m) occur as central zones, with surrounding oscillatory zones with no or trace level Sn. These grains have nucleated on existing tourmaline clusters and represent a new tourmaline growth stage. The elongated tourmaline grain in the center of Fig. 3c is cut parallel to the *c*-axis. By looking closely at the Mg zoning, it appears that the Mg-rich zone defines a euhedral terminal edge of the crystal just to the left of the elongated Sn zone. This adds to the observations that the Sn-rich zones represent the initiation of a new tourmaline growth stage. It is very difficult to pinpoint exactly when in the tourmaline growth history cassiterite started to crystallize, but I speculate that the Sn-rich tourmaline represents the point where the fluid became supersaturated with respect to Sn, and cassiterite started to crystallize together with Sn-rich tourmaline. Vereshchagin et al. (2022) found that tourmaline which crystallized at low pressure may incorporate more Sn compared to tourmaline produced in high-pressure experiments. An alternative explanation for the Sn-rich tourmaline may be a drop in pressure. A sudden pressure drop may also provoke phase separation of the fluid and, consequently, a decrease in Sn solubility. A scenario in which a drop in pressure (e.g., by going from lithostatic to hydrostatic pressure and/or opening of the fault jog) caused phase separation of the fluid and, at the same time, increased the ability for tourmaline to accommodate Sn, is possible. Subsequent growth zones may have trace levels of Sn, and this likely reflects variation in the fluid chemistry and Sn solubility (Dutrow and Henry 2016). Cassiterite also shows growth zoning (Drivenes et al. 2018, ESM 2h), and the coexisting cassiterite-tourmaline pair may record the fluctuating fluid composition.

5.4. Mapping as a quantitative tool

X-ray mapping provides a greater overview compared to scattered point analyses, particularly for minerals with such complex zoning as tourmaline where it is difficult or

impossible to assign a chemical composition to a specific backscatter brightness or color in the optical microscope. All postprocessing steps of the X-ray maps produced in this paper use free, open-source software. An additional advantage is that all the points used to create the multi-point calibration curve can be selected manually. Obvious outliers can be removed and minor spatial offsets between the backscattered electron image used to identify the position of quantitative spots in the calibration and the exact position of the spot can be compensated. This is more accurate and flexible compared to the two-point calibration available in the built-in map quantification function in the JEOL software used in this study. Once a set of images are converted to wt. %, each pixel provides a chemical composition. All elements can easily be viewed or measured by stacking the 32-bit images in ImageJ. A general expression converting X-ray intensity (counts/s/nA) to wt. % can be derived, excluding the need to collect maps at identical conditions other than the same acceleration voltage and crystal configuration. However, this general equation does not consider potentially variable X-ray adsorption with different counting times and probe currents. In this study, the maps were quantified separately for the two different counting times used.

Producing phase maps or element maps of larger areas or thin sections is a common step in the analytical protocol for identifying and quantifying rare-earth or platinum-group minerals (Osbaht et al. 2015; Allaz et al. 2020), which are typically very small or time-consuming to locate in samples. The lack of a distinct backscatter brightness necessary for thresholding in automatic mineralogy systems (e.g., QEMSCAN, Mineralogic), short counting times (<1 ms), or large defocus or step size necessary to avoid long analysis times for full sample element scans, makes detection of micron-size zones with less than a few wt. % SnO₂ challenging. As shown, it is impossible to recognize Sn-rich zones in tourmaline optically (Fig. 6), and the bright backscatter signal is mostly due to high Fe content and is not strictly correlated with Sn. Therefore, it is difficult to detect Sn-rich zones prior to detailed EPMA work, or an LA-ICP-MS study. The latter method is by far the most common method to analyze trace elements in minerals. However, the typical laser spot size (30–50 µm) would be too large to get an accurate composition of the fine growth zones in the samples from this study, the result being an underestimation of the Sn content. This may explain why Sn is rarely reported as a minor element in tourmaline.

6. Conclusions

Tourmaline from a hydrothermal quartz-tourmaline rock from SW England is shown to contain up to 2.53 wt. % SnO₂. Sn-rich tourmaline is found as small (<10 µm)

growth zones in late-stage tourmaline. The composition is characterized by low Al and high Fe contents, with a significant proportion of ferric iron. Tin is incorporated into octahedral sites (most likely the Y-site) in the tourmaline structure mainly by the coupled substitution $^{YZ}\text{Sn}^{4+} + 2^{YZ}\text{Fe}^{2+} + 5^{YZ}\text{Fe}^{3+} + {}^W\text{O}^{2-} \leftrightarrow 2^{YZ}\text{Mg}^{2+} + 6^{YZ}\text{Al}^{3+} + {}^W\text{OH}^-$. The Sn-rich zones likely correspond to the onset of cassiterite crystallization, and the trace level Sn content in subsequent growth zones reflects the variation in fluid chemistry and Sn solubility.

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Electronic supplementary material. Additional quantitative and qualitative X-ray maps, all EPMA spot analyses, and chemical scatterplots are available online on the Journal website (<http://dx.doi.org/10.3190/jgeosci.351>).

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