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

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. Introduction

Tourmaline and Sn-W mineralizations are closely associated. However, the commodity of a deposit is not necessarily reflected by the chemical composition of tourmaline. Sn-rich tourmalines have been observed in Sn-mineralizations throughout the world, whereas W-content in tourmaline is typically very low, even in mineralized areas. Tourmaline from a Sn-bearing hydrothermal quartztourmaline rock at Nanjizal, Land's End, was investigated in order to understand how Sn is distributed in tourmaline. It is located 10s-100 meters from two small, formerly worked lodes, and comprises almost exclusively quartz and tourmaline, with minor K-feldspar, apatite and cassiterite. Tourmaline occurs as replacements of former granite minerals and as overgrowths on former tourmaline generations. The relationship with cassiterite is not straightforward, but typically, cassiterite nucleates on clusters of late-stage tourmaline, and tourmaline, cassiterite and quartz crystallized simultaneously. The tourmaline generation coexisting with cassiterite is acicular with strong green/bluecolorless pleochroism. This association is recognized throughout the Land's End granite, but the Sn-content of rocks including this tourmaline generation may vary from a few 100 ppm to several wt%, the quartz-tourmaline rock at Nanjizal being an example of the latter. Tourmaline is strongly zoned, both optically and chemically. Homogenous zones in the tourmaline generation associated with cassiterite rarely exceed 10 µm, and high-resolution BSE imaging revealed distinct growth zones less than 50 nm wide.



Figure 1. Geological map, field appearance, and examples of optical and chemical zoning of tourmaline in the analysed sample.





3. Representative EPMA analyses and correlation with mapped intensities

| Point ID | SiO ₂ | TiO ₂ | Al ₂ O ₃ | FeO | MgO | CaO | Na ₂ O | SnO ₂ | SrO | F | Cl | Total | Si | Ti | Sn | Al | Fe ³⁺ | Fe ²⁺ | Mg | Са | Na | Name |
|----------|------------------|------------------|--------------------------------|-------|---|------|-------------------|------------------|------|---|---|-------|------|------|------|------|------------------|------------------|------|------|------|------------|
| 10a-9 | 32.01 | 0.11 | 20.62 | 25.89 | 2.03 | 0.39 | 2.38 | 2.53 | 0.07 | <d.l.< td=""><td><d.l.< td=""><td>86.13</td><td>5.85</td><td>0.02</td><td>0.18</td><td>4.44</td><td>1.43</td><td>2.52</td><td>0.55</td><td>0.08</td><td>0.84</td><td>Oxy-Schorl</td></d.l.<></td></d.l.<> | <d.l.< td=""><td>86.13</td><td>5.85</td><td>0.02</td><td>0.18</td><td>4.44</td><td>1.43</td><td>2.52</td><td>0.55</td><td>0.08</td><td>0.84</td><td>Oxy-Schorl</td></d.l.<> | 86.13 | 5.85 | 0.02 | 0.18 | 4.44 | 1.43 | 2.52 | 0.55 | 0.08 | 0.84 | Oxy-Schorl |
| 10b-113 | 32.24 | 0.03 | 18.93 | 25.61 | 3.38 | 0.72 | 2.19 | 0.08 | 0.13 | 0.19 | 0.02 | 83.65 | 5.96 | 0.02 | 0.03 | 4.13 | 1.75 | 2.21 | 0.93 | 0.14 | 0.79 | Oxy-Schorl |
| 10c-4 | 35.74 | 0.17 | 30.52 | 11.22 | 4.52 | 0.24 | 2.14 | 0.31 | 0.04 | 0.19 | <d.l.< td=""><td>85.21</td><td>6.08</td><td>0.02</td><td>0.02</td><td>6.12</td><td>0.00</td><td>1.60</td><td>1.15</td><td>0.04</td><td>0.71</td><td>Schorl</td></d.l.<> | 85.21 | 6.08 | 0.02 | 0.02 | 6.12 | 0.00 | 1.60 | 1.15 | 0.04 | 0.71 | Schorl |
| 10c-6 | 34.52 | 0.06 | 20.91 | 22.98 | 2.54 | 0.51 | 2.35 | 1.77 | 0.10 | 0.08 | 0.01 | 85.90 | 6.24 | 0.01 | 0.13 | 4.46 | 1.06 | 2.41 | 0.69 | 0.10 | 0.82 | Schorl |
| 7-2 | 31.46 | 0.20 | 16.49 | 32.04 | <d.l.< td=""><td>0.22</td><td>2.39</td><td>1.27</td><td>0.05</td><td>0.14</td><td>0.01</td><td>84.59</td><td>6.01</td><td>0.03</td><td>0.10</td><td>3.71</td><td>2.07</td><td>3.05</td><td>0.00</td><td>0.05</td><td>0.89</td><td>Schorl</td></d.l.<> | 0.22 | 2.39 | 1.27 | 0.05 | 0.14 | 0.01 | 84.59 | 6.01 | 0.03 | 0.10 | 3.71 | 2.07 | 3.05 | 0.00 | 0.05 | 0.89 | Schorl |
| 7-3 | 31.78 | 0.09 | 19.20 | 29.67 | <d.l.< td=""><td>0.38</td><td>2.37</td><td>0.42</td><td>0.04</td><td>0.10</td><td>0.01</td><td>84.27</td><td>5.99</td><td>0.01</td><td>0.03</td><td>4.27</td><td>1.60</td><td>3.08</td><td>0.00</td><td>0.08</td><td>0.87</td><td>Oxy-Schorl</td></d.l.<> | 0.38 | 2.37 | 0.42 | 0.04 | 0.10 | 0.01 | 84.27 | 5.99 | 0.01 | 0.03 | 4.27 | 1.60 | 3.08 | 0.00 | 0.08 | 0.87 | Oxy-Schorl |
| 7-5 | 34.26 | 0.11 | 31.56 | 15.34 | <d.l.< td=""><td>0.70</td><td>1.78</td><td>0.02</td><td>0.05</td><td>0.86</td><td>0.03</td><td>84.81</td><td>6.09</td><td>0.01</td><td>0.00</td><td>6.61</td><td>0.00</td><td>2.28</td><td>0.00</td><td>0.13</td><td>0.61</td><td>F-Schorl</td></d.l.<> | 0.70 | 1.78 | 0.02 | 0.05 | 0.86 | 0.03 | 84.81 | 6.09 | 0.01 | 0.00 | 6.61 | 0.00 | 2.28 | 0.00 | 0.13 | 0.61 | F-Schorl |

5. Quantitative maps





10a



20 µm



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4. Mapping

Numerous low-resolution combined EDS/WDS maps of zoned areas were collected, and areas where Sn was detected were selected for high-resolution mapping. The maps were imported into ImageJ, and the x-ray intensities of all elements in spots with known compositions were measured. Linear regression of 31 (maps 10a-c) and 20 (map 7) spots was used to convert mapped x-ray intensities to mass% (Section 3) This method worked for both EDS and WDS analyses, since there are no major overlaps between the analysed elements. The maps were collected using a JEOL 8530FPlus at 12 kV, 120 nA, 300 nm step size, and 500 (map 7) or 750 (maps 10a-c) ms dwell time, respectively. Maps 10a-c have identical element scales, showing mass% oxide. B, F, Ca, Ti, and Sn were collected by WDS, and Na, Mg, Fe, Al, and Si were simultaneously collected by EDS.

6. Sn-distribution in tourmaline

Sn-rich zones are patchy or concentric. The highest recorded value in a quantitiative analysis was 2.53 wt% SnO₂, and a few zones in the quantmaps show values around 2.5 wt%. This appears to the the maximum level in the sample. Several zones with >1 wt% SnO2 were observed, either as zones surrounding higher Sn-levels, or as separate zones. The high Sn-levels are typically found in the center of tourmaline grains forming rims on former tourmaline generations (e.g. map 10a-c). Submicron inclusions of cassiterite, Fe- and Ti-oxides are easily distinguished in the BSE and x-ray maps (Sn, Fe and BSE in map 7). Also, Sn-rich tourmaline is not necessarily observed close to cassiterite grains. Thus, the high Snvalues are not due to cassiterite inclusions, but structurally bound in tourmaline. High Sn-values (>0.4 wt% SnO₂) are associated with a substantial substitution of Fe for Al (Figure 2, maps 7 and 10) in the Z-site, and in analyses with more than ca. 20 wt% FeO, structural formula calculation indicate that some Fe is present as Fe^{3+} . However, the Fe-Al substitution is not limited to the Snrich zones (map 10). Trends between Sn and other elements are erratic, except for a weak positive correlation with Sr.

The fluid precipitating tourmaline was, at least periodically, saturated with respect to Sn, but Sn-rich zones in tourmaline are rare compared to cassiterite. This may indicate that co-precipitation of tourmaline and cassiterite was limited, or that Sn-content of the fluid is not the only parameter controlling the incorporation of Sn in tourmaline. Cassiterite precipitation from granite-derived fluids typically requires oxidation, and combined with the inferred Fe³⁺ in the Sn-rich zones this may indicate that oxidation of the ore fluid caused cassiterite precipitation and the Sn-rich tourmaline zones. Alternatively, the Sn-rich zones may be the result of local redistribution of Sn from granite minerals by dissolution-reprecipitation processes.

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