Abstract: A detailed investigation was conducted on high-pressure (~1.4 GPa) tourmaline from an Eoalpine mafic eclogite, which occurs in the Kreuzeck Mountains, Eastern Alps, Austria. Tourmaline from this locality contains the highest amount of Sr2+ (up to 0.68 wt% SrO) known to date. The space group is R3m with unit-cell parameters \(a = 15.944(1)\), \(c = 7.202(1) \text{\AA}\), \(V = 1585.5(3) \text{\AA}^3\). Analyses by a combination of electron microprobe, optical absorption spectroscopy and crystal-structure refinement showed that this high-pressure tourmaline crystallized under oxidizing conditions. It has a significant oxy-dravite component. A near-rim zone contains 0.6 wt% Cr2O3, 0.5 wt% PbO2, 0.2 wt% NiO and 0.1 wt% V2O3. Only a small F content was found by structure refinement (\(\text{F}_{\text{tot}} = 0.45\)). The \(\text{Sr}^{2+}\) site contains mainly Si and additionally small amounts of B and Al. According to optical absorption spectroscopy (using the band near 1120 nm), the \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio is 79 ± 2%, suggesting that this high-pressure tourmaline crystallized under oxidizing conditions. It has a significant oxy-dravite component. A near-rim zone contains 0.6 wt% Cr2O3, 0.5 wt% PbO2, 0.2 wt% NiO and 0.1 wt% V2O3. Only a small F content was found by structure refinement. There is no evidence for significant \(\text{Si}^{4+}\) vacancy in the investigated tourmaline zones. We assume that the original boron source for tourmaline crystallization in the eclogite, i.e. tourmaline-bearing pegmatites in the country-rock, were influenced by a Sr-bearing marble.

Key-words: high-pressure tourmaline; oxy-dravite; Kreuzeck Mountains; Eastern Alps; crystal structure; optical absorption spectroscopy.

1. Introduction and previous work

The general chemical formula of the tourmaline-supergroup minerals can be written as \(X_y Z_z [\text{T}_6\text{O}_{18}] (\text{BO}_3)_3 V_3 W\), as proposed by Henry et al. (2011). These authors and Hawthorne (1996, 2002) suggest occupancies by the following most common constituents:

- \(X = \text{Na, K, Ca}\), □ (vacancy),
- \(Y = \text{Mg, Fe}^{2+}, \text{Mn}^{2+}, \text{Al, Li, Fe}^{3+}, \text{Cr}^{3+}, \text{V}^{3+}\),
- \(Z = \text{Al, Mg, Fe}^{3+}, \text{V}^{3+}, \text{Cr}^{3+}\),
- \(T = \text{Si, Al, B}\),
- \(V = \text{OH, O}\), \(W = \text{OH, F, O}\).

Substantial research efforts have been devoted to analytical work and interesting crystal-chemical relationships between structural features and site-occupancies have been established (e.g. Bosi & Lucchesi, 2004, 2007; Lussier et al., 2009; Ertl et al., 2010b and c; Bosi, 2018).

A variety of substituents for Si at the tetrahedral site have been described. A substitution of Al3+ for Si4+ was first proposed by Buerger et al. (1962). Foit (1989) described a positive correlation between \(^{\text{Al}}\) and the \(<\text{T-O}>\) distance. MacDonald & Hawthorne (1995) have shown by crystal-structure analyses in combination with chemical analyses that Mg-rich tourmaline can contain significant amounts of \(^{\text{Al}}\) and that there is a good linear positive correlation between \(<\text{T-O}>\) and \(\text{Al}^{3+}\).

Structure studies showed that B substitutes for Si in significant amounts at the tetrahedral site in natural tourmaline (Ertl et al., 1997, 2007, 2008; Lussier et al., 2008). Structure studies by Hughes et al. (2004) and Ertl & Hughes (2002) on Fe-bearing olenite and on Al-rich schorl also showed substantial amounts of \(^{\text{B}}\). “Oxy-rosmite”, with a \(T\)-site occupancy of \((\text{Si}_{0.51} \text{Al}_{0.25} \text{B}_{0.24})\), gave for the first time a clear indication that it is possible to have significant amounts of both \(^{\text{B}}\) and \(^{\text{Al}}\) in an Al-rich tourmaline (Ertl et al., 2005). Although the structure refinements showed significant amounts of \(^{\text{B}}\), the \(<\text{T-O}>\) bond-lengths (~1.620 Å) masked the incorporation of \(^{\text{B}}\) because of the concomitant incorporation of \(^{\text{Al}}\) (Ertl et al., 2005).

Chromium- and Mg-rich green tourmaline from Outokumpu, Finland, with 0.34 wt% SrO was described by Peltola et al. (1968). This tourmaline with unit-cell...
parameters $a = 15.96$, $c = 7.22$ Å contains 10.6 wt% MgO, 9.6 wt% Cr$_2$O$_3$, 0.6 wt% V$_2$O$_3$, 2.0 wt% Na$_2$O and 1.0 wt% CaO. In the Outokumpu area, Cr-rich tourmaline is associated with other Cr-bearing minerals which frequently occur in contact skarns between serpentinites and quartzites.

A high-pressure tourmaline formation resulting from a saline aqueous fluid activity in mafic eclogites from the Kreuzeck Mountains (Austroalpine basement), Eastern Alps, Austria, was described by Konzett et al. (2012). These authors described tourmaline samples with 7.9 wt% Cr$_2$O$_3$, 0.6 wt% V$_2$O$_3$, 2.0 wt% Na$_2$O and 1.0 wt% CaO. In the Outokumpu area, Cr-rich tourmaline is associated with other Cr-bearing minerals which frequently occur in contact skarns between serpentinites and quartzites.

A reinvestigation of this eclogitic tourmaline was carried out to obtain further data, in particular on the cation occupation of the individual atomic positions.

### 2. Petrological setting

The tourmaline-bearing eclogite sample was collected from an eclogite lens of ~50 m in diameter enclosed in metapelitic gneisses of the Polinik Unit, the latter forming part of the Austroalpine basement units of the Eastern Alps within the Kreuzeck Mountains (46°53′32″N, 13°10′19″E) in the state of Carinthia, Austria. The brown coloured tourmaline investigated in this study is part of an eclogite assemblage comprising garnet + omphacite + quartz + epidote-group phases + calcic amphibole + K-feldspar + rutile + apatite + zircon that formed under peak metamorphic $P$–$T$ conditions of ~2.1 GPa and ~650 °C during Eo-Alpine metamorphism (Konzett et al., 2012). Tourmaline inclusions in garnet and omphacite + K-feldspar inclusions in tourmaline are most consistent with a high-pressure origin of the tourmaline, however, with a possible continuation of tourmaline growth during uplift and decompression. Secondary ion mass spectrometry (SIMS) U–Pb isotopic dating by using eight data points (zircon) yielded a well-constrained intercept age of 90 ± 9 Ma (Konzett et al., 2012). These authors suggested as possible source of B the metapelitic country rocks that were pre-enriched in B by the intrusion of tourmaline-bearing pegmatites during Permian metamorphism. Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis of primary aqueous saline fluid inclusions trapped in quartz coexisting with tourmaline under eclogite-facies conditions show high concentrations of Ca (1.6–2.7 wt%), K (3500–4900 µg/g), B (250–370 µg/g), Sr (490–1080 µg/g) and Pb (8–16 µg/g) with total solute concentrations of up to 9.3 wt% (Konzett et al., 2012).

The eclogite suite to which the tourmaline-bearing sample belongs is characterized by bulk compositions rich in Fe, Ti, P, Zr and Sr relative to MOR basalts and by compositional variations indicating progressive differentiation of a mafic magma with Fe–Ti oxides and apatite as important igneous phases and metasomatic addition of K and Sr. The systematics of bulk Ti–V–Zr–P–Nb–Y contents of the eclogites points to a within-plate rather than MORB-type environment of protolith formation (Konzett et al., 2012).

### 3. Experimental details

#### 3.1. Crystal-structure refinement

A fragment of a rock-forming tourmaline crystal (from zone 1, which is relatively homogeneous and significantly enriched in Sr; see details in Table 1 and Fig. 1) was separated and subsequently studied on a Bruker AXS Kappa APEXII single-crystal diffractometer equipped with a charge-coupled device (CCD) area detector and an Incoatec Microfocus Source (30 W, multilayer mirror, MoKα). Redundant data were collected at room temperature (up to 80° 20) for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors, and absorption correction by evaluation of partial multiscans, using the Bruker programs SaintPlus and SADABS (Bruker AXS Inc., 2001). The structure was refined with SHEXL97 (Sheldrick, 1997, 2008) using scattering factors for neutral atoms and a tourmaline starting model from Ertl et al. (2010b). The H atom bonded to the O3 atom was located from a difference-Fourier map and subsequently refined. Refinement was done with anisotropic displacement parameters for all non-H atoms. Table 1 provides crystal data and details of the structure refinement. The refinement converged to an $R1(F)$ value of ~1.3% (Table 1). In Table 2, the atomic parameters and equivalent isotropic-displacement parameters are listed, and in Table 3 selected interatomic distances are presented.

#### Table 1. Crystallographic data and refinement details for high-pressure tourmaline from the Kreuzeck Mountains, Eastern Alps, Austria.

| Parameter          | Value       |
|--------------------|-------------|
| $a$, $c$ (Å)       | 15.944(1), 7.202(1) |
| $V$ (Å$^3$)        | 1585.5(3)   |
| Crystal size (mm$^3$) | 0.15 x 0.13 x 0.10 |
| Collection mode, $2\theta_{\text{max}}$ (°) | Full sphere, 79.98 |
| $h$, $k$, $l$ ranges | 28/28, 28/28, 13/12 |
| Number of frames   | 728         |
| Total reflections measured | 31855      |
| Unique reflections | 2351        |
| $R1(F)$            | 1.31%, 3.59%, 1.68% |
| $R$ parameter      | 0.046(18)   |
| Goodness-of-Fit$^d$| 1.115       |
| $\Delta\sigma_{\text{min}}$, $\Delta\sigma_{\text{max}}$ (e/Å$^3$) | $-0.47$, 0.69 |

$^d$Note: X-ray radiation: MoKα ($\lambda = 0.70735$ Å); Z = 3; space group $R3m$ (no. 160); multi-scan absorption correction; refinement on $F^2$. Frame width, scan time, detector distance: 2°, 35 s, 35 mm. Scan mode: sets of $\eta$ and $\delta$ scans.

#### Table 2. Atomic parameters for high-pressure tourmaline from the Kreuzeck Mountains, Eastern Alps, Austria.

| Atom  | $x$, $y$, $z$ | $U_{\text{iso}}$ (Å$^2$) |
|-------|---------------|--------------------------|
| O     |               |                          |
| P     |               |                          |
| Na    |               |                          |
| K     |               |                          |
| Ti    |               |                          |
| V     |               |                          |
| Cr    |               |                          |
| Sr    |               |                          |
| Eu    |               |                          |

The systematics of bulk Ti–V–Zr–P–Nb–Y contents of the eclogites points to a within-plate rather than MORB-type environment of protolith formation (Konzett et al., 2012).
3.2. Chemical analyses

Crystal fragments of the same tourmaline crystal that was used for the structure refinement were prepared as a section (polished on one side) for chemical analysis. The composition of the high-pressure tourmaline was determined on a JXA-8530F "HyperProbe" field-emission electron-probe microanalyzer equipped with five wavelength-dispersive spectrometers (Naturhistorisches Museum, Vienna). The operating conditions were: 15 kV accelerating voltage, 20 nA beam current, 5–10 μm (defocused) beam diameter, 10 s counting time for peak, and 5 s for background intensities for all major and minor elements. The trace elements (K, V, Ni, Zn, Sr and Pb) were counted for 200 s on peak and 70 s on background positions. Natural and synthetic standards were used. Data reduction was done with an online JEOL ZAF correction program. The mean values for the detection limits (in ppm) of mentioned trace elements (same order as above) are: 20(1), 69(3), 103(14), 154(7), 67(2) and 84(11), respectively. Table 4 contains the analytical data of the different zones of the high-pressure tourmaline. The crystal-chemical formulae were calculated on the basis for 31 (OH,O,F). The amount of B2O3 for zone 1 was calculated using the structure refinement (SREF) data.

Table 2. Atomic parameters for tourmaline from the Kreuzeck Mountains, Eastern Alps, Austria.

| Site | x | y | z | Ueq |
|------|---|---|---|-----|
| X    | 0 | 0 | 0.22936(12) | 0.0179(2) |
| Y    | 0.12512(2) | 0.06256(1) | 0.63163(4) | 0.00719(8) |
| Z    | 0.29822(1) | 0.26173(1) | 0.61154(3) | 0.00539(5) |
| B    | 0.10995(3) | 0.21990(7) | 0.45452(13) | 0.0057(2) |
| T    | 0.19188(1) | 0.19000(1) | 0.61154(3) | 0.00539(5) |
| H3   | 0.261(2) | 0.1305(11) | 0.61154(3) | 0.00539(5) |
| O1   | 0  | 0  | 0.77347(18) | 0.0146(3) |
| O2   | 0.06097(3) | 0.12193(5) | 0.48397(1) | 0.0107(1) |
| O3   | 0.26576(6) | 0.13288(3) | 0.51107(10) | 0.0124(1) |
| O4   | 0.09279(3) | 0.18556(8) | 0.06948(10) | 0.0096(1) |
| O5   | 0.18378(6) | 0.09189(3) | 0.09053(10) | 0.0096(1) |
| O6   | 0.19604(3) | 0.18620(4) | 0.77725(6) | 0.00809(7) |
| O7   | 0.28485(3) | 0.28478(3) | 0.07901(7) | 0.00787(7) |
| O8   | 0.10942(3) | 0.20942(3) | 0.44112(7) | 0.00891(7) |
| Note: For the definition of Ueq see Fischer & Tillmanns (1988). |

3.3. Optical and near-infrared absorption spectroscopy

Tourmaline sample GRR 3534 was extracted from the same zone and the same single crystal as the sample that was used for the structure refinement and was prepared for optical absorption spectroscopy as a doubly polished section, 0.156 mm thick, oriented with the c-axis in the plane of the section. Plane-polarized optical and near-IR absorption spectra in the 390–1660 nm range were obtained on a homemade diode array spectrometer described in Taran & Rossman (2001). Optical absorption spectroscopy was used to estimate the percentage of Fe2+. For this purpose the band near 1120 nm was used, because it is the band that is best separated from other bands (Fig. 2). We conclude that this tourmaline contains 79 ± 2% Fe3+. Usually Mössbauer
4. Results

4.1. Optical and near-infrared absorption spectra

The optical spectrum is typical of iron-containing tourmalines showing prominent Fe$^{2+}$ absorption bands near 1120 and 720 nm and Fe$^{2+}$–Ti$^{4+}$ intervalence charge-transfer absorption near 460 nm, which accounts mainly for the brown bulk colour of the tourmaline. Of particular note is the fact that the iron bands are much more intense in the $E\perp c$ direction than in the $E||c$ direction. This is an indication that the Fe$^{2+}$ is interacting with a significant amount of Fe$^{3+}$ (Mattson & Rossman, 1987). To estimate the proportion of the two oxidation states, the intensity of the Fe$^{2+}$ bands in the dravite was compared to the intensity of the Fe$^{3+}$ bands in two zones (HIM1, HIM2) of a previously very well characterized Fe-bearing elbaite from the Himalaya Mine (Ertl et al., 2010c) assuming that a Beer-Lambert Law calibration applies.

4.2. Crystal chemistry and structure analysis

Analyses by a combination of electron microprobe (based on an average of 10 analyses), spectroscopic data and crystal-structure refinement result in the structural formula

$$\text{X}(\text{Na}_{0.85}\text{Ca}_{0.08}\text{Sr}_{0.06}\text{K}_{0.01})_{2}\text{Al}_{11}\text{Al}_{0.70}\text{Fe}_{0.37}\text{Ti}_{0.10}\text{Fe}_{0.11}$$

Table 3. Selected interatomic distances in tourmaline from the Kreuzeck Mountains, Eastern Alps, Austria.

| X- | T- |
|----|----|
| O2 × 3 | 2.4894(10) | O6 | 1.6006(5) |
| O5 × 3 | 2.7274(8) | O7 | 1.6042(5) |
| O4 × 3 | 2.8093(9) | O4 | 1.6271(3) |
| Mean | 2.6751(1) | O5 | 1.6421(3) |
| Y- | Mean | 1.6185(4) |
| O1 | 2.0071(7) | B- |
| O6 × 2 | 2.0089(5) | O2 | 1.3693(12) |
| O2 × 2 | 2.0104(5) | O8 (×2) | 1.3769(7) |
| O3 | 2.1272(9) | Mean | 1.3744(9) |
| Mean | 2.0288(6) |
| Z- |
| O6 | 1.8865(5) |
| O8 | 1.8945(5) |
| O7 | 1.9020(5) |
| O8$'$ | 1.9285(6) |
| O7$'$ | 1.9602(5) |
| O3 | 1.9871(4) |
| Mean | 1.9269(5) |

Standard deviation in brackets.

Table 4. Compositions (wt% and apfu) of high-pressure tourmaline from the Kreuzeck Mountains, Eastern Alps, Austria.

| Constit. | Zone 1 | Zone 2 | Zone 3 | Zone 4 |
|----------|--------|--------|--------|--------|
| SiO2 | 35.52(31) | 34.42(20) | 35.30(6) | 34.54(12) |
| TiO2 | 0.82(6) | 1.40(8) | 0.99(8) | 0.87(2) |
| Al2O3 | 30.71(23) | 30.34(6) | 30.85(18) | 30.04(1) |
| Cr2O3 | 0.08(3) | 0.11(3) | 0.10(3) | 0.59(2) |
| V2O3 | 0.04(1) | 0.07(1) | 0.05(1) | 0.10(1) |
| FeO | 3.87(6) | 5.19(15) | 5.28(4) | 3.63(5) |
| FeO | 0.81 | 1.09 | 1.11 | 0.76 |
| Fe3+ | 3.40 | 4.56 | 4.64 | 3.19 |
| MgO | 10.14(18) | 9.08(13) | 8.87(7) | 9.92(3) |
| CaO | 0.63(3) | 1.48(5) | 0.70(1) | 0.61(1) |
| SrO | 0.59(5) | 0.20(1) | 0.37(2) | 0.64(2) |
| ZnO | 0.04(1) | 0.03(1) | 0.04(3) | 0.02(0) |
| NiO | 0.04(1) | 0.03(1) | 0.01(0) | 0.21(5) |
| PbO | 0.02(1) | 0.03(1) | 0.06(4) | 0.54(4) |
| Na2O | 2.69(6) | 2.21(11) | 2.68(2) | 2.66(2) |
| K2O | 0.06(1) | 0.02(1) | 0.04(1) | 0.06(1) |
| B2O3 | 10.95 | n.c. | n.c. | n.c. |
| H2O*** | 3.07 | n.c. | n.c. | n.c. |
| F** | 0.38 | n.c. | n.c. | n.c. |
| O=|F | 0.16 | n.c. | n.c. | n.c. |
| Sum | 99.83 | 85.04 | 85.82 | 84.75 |

Note: n.c., not calculated. Zone 1, 10 analyses in the core region (crystal structure see Tables 1–3); Zone 2, 5 analyses (core region); Zone 3, 5 analyses (rim region); Zone 4, 2 analyses (rim region). Li (16–30 ppm) was determined on a bulk sample by ICP-MS (Konzett et al., 2012). Manganese and Cl are below detection limit.

*The proportions of Fe$^{2+}$ and Fe$^{3+}$ are calculated on the basis of optical spectroscopic investigation.

**B2O3 and F calculated according to SREF data (details in text);

[4]$^4$B

Fixed at 0.10 apfu in zone 2–4, based on SREF data of zone 1.

[4]**H2O was calculated for a charge-balanced formula and to minimize the errors of the cation occupancies compared to the structure refinement (details see text). The formula of zone 1 was also calculated for 31 (O,OH,F). As no evidence was found for vacancies at any site in zone 1, the other zones were calculated for 21 ± 2% of the total iron is in the 2+ oxidation state.
Ca_{0.03}Cr_{0.01}^{3+}\Sigma_{3.00}^{\infty}(Al_{15.15}Mg_{0.80}Fe_{0.03}^{3+})_{2.60}^{\infty}(Si_{5.82}B_{0.10}Al_{0.08}O_{18})(BO_{3})_{3}\Sigma_{0.01}^{\infty}[O_{(OH),F}]_{\Sigma_{0.01}^{\infty}}[O_{(OH),F}].

Fig. 2. Optical absorption spectra of tourmaline (sample GRR 3534) from the Kreuzeck Mountains, Eastern Alps, Austria.

Table 5. Refined site-scattering values (SREF; epfu), assigned site-populations (apfu) and equivalent site-scattering values (EMPA; epfu) for tourmaline from the Kreuzeck Mountains, Eastern Alps, Austria.

| Site | SREF | Site population | EMPA |
|------|------|----------------|------|
| X    | 12.9(5)* | 0.85 Na + 0.08 Ca + 0.06 | 13.4 |
| Y    | 44.2(4) | 1.68 Mg + 0.70 Al + 0.48 | 44.8 |
| Z    | 77.9(4)** | 5.15 Al + 0.80 Mg + 0.05 Fe | 77.9 |

Note: *Refining Na ↔ Ca at the X site by using the same X-ray data gave the value 13.4(1) epfu.

**This value was estimated by releasing the Z-site occupancy in a preliminary refinement.

It was still too high if the OH content was increased further and Y-site vacancies were all allowed. Therefore we checked the possibility that each cation, which usually occupies the [9]-coordinated X site, could also occupy another atomic position. It is unlikely that Sr^{2+} and K^{+} occupy a site other than the X site, because of their relatively large effective ionic radii. Compared to Na^{1+} (1.24 Å), Ca^{2+} (1.18 Å) has a significantly smaller ionic radius (Shannon, 1976). Hence, the likelihood for Ca to occupy a [6]-coordinated position is the highest among all these cations. At the [6]-coordinated Y site Ca would have an effective ionic radius of 1.00 Å, which would be 20% higher than the ionic radius of Mn^{2+} (0.83 Å). The tourmaline structure is known to be very flexible and therefore we assigned small amounts of Ca (≤0.04 apfu) to the Y site of this high-pressure tourmaline, so as not to exceed the 1.00 apfu at the X site. Another explanation for this observation might be analytical errors.

Zone 4 contains additionally 0.02 Pb apfu. Because in this tourmaline ~80% of the total Fe is oxidized, it is likely that also Pb is oxidized to Pb^{4+}. In a [6]-coordination Pb^{4+} has an effective ionic radius of 0.78 Å (Shannon, 1976), which is very similar to Fe^{2+} (0.78 Å) and Mg (0.72 Å). Therefore we assigned these small amounts of Pb to the Y site and not to the X site.

It is important to note that significant amounts of Sr were verified to occupy the X site in the tourmaline structure for the first time. Refining Na ↔ Sr gave a very similar result to what was found with microprobe analysis (Table 5). This is the highest amount of Sr (up to 0.68 wt% SrO) in any tourmaline structure. By refining Na ↔ Ca at the X site (all other sites were refined as before) in a preliminary refinement, the refined site-scattering value increases slightly, but gives also a very similar result. Such slight differences are within errors of the refinements.

4.3. X-site occupancy

The X site in all zones is mainly occupied by Na (~0.7–0.9 apfu). Additionally minor amounts of Ca (0.08–0.27 apfu) and Sr (0.02–0.06 apfu) and traces of K (≤0.01 apfu) occupy this site. When the (OH) content was calculated for (Y + Z + T) = 15 atoms per formula unit (apfu), the sum of (Na + Ca + Sr + K) was exactly 1.00 apfu for one sample (zone 2), but >1.00 apfu for the other three zones.

4.4. Y- and Z-site occupancy

The Y site is in all zones dominantly occupied by Mg (1.4–1.7 apfu). But not all Mg is ordered into the Y site (based on the structure refinement). Because of a significant disorder some Mg (0.8 apfu) occupies also the Z site. Aluminium is the second most abundant cation at the Y site
Further cations with significant amounts at the Y site are Fe$^{3+}$ (0.4–0.5 apfu), Ti$^{3+}$ and Fe$^{2+}$ (both 0.1–0.2 apfu). Very small amounts of Cr$^{3+}$, V$^{3+}$; Ni$^{2+}$, Zn$^{2+}$, Ca$^{2+}$ and Pb$^{2+}$ may also occur at this site. The assigned Z-site occupancy with ($\text{Al}_{5.15}\text{Mg}_{0.80}\text{Fe}_{3.12}^3\text{O}_{10}^-$) is in good agreement with the refined site-scattering values (Table 5) and with the enlarged <$Z$–O$>$ distance of 1.927 Å (Table 3) as compared to <$Z$–O$>$.

4.5. T-site occupancy

The <$T$–O$>$ distance of ~1.6185 Å (Table 3) is also in good agreement with a T-site occupied by ($\text{Si}_{5.82}\text{Al}_{0.18}$). To fill the T site after considering the refined [4]B value of 0.10(2) apfu (Table 2), small amounts of [4]Al seem also to occupy this site. Tourmalines with such T-site occupancies including Si and small amounts of [4]B and [4]Al have already been described (Ertl et al., 2005, 2010c; Lussier et al., 2009). A T-site occupancy assigned with ($\text{Si}_{5.82}\text{Al}_{0.18}$) would produce a <$T$–O$>$ distance between 1.621 and 1.622 Å (Ertl et al., 2016). This would be significantly higher than the observed <$T$–O$>$ distance. Hence, a mixed occupation with Si and small amounts of [4]B and [4]Al seems to be likely.

4.6. V- and W-site occupancy

An H atom (H3) at the site associated with O3 was easily located in the refinement. Ertl et al. (2002) showed that the bond-angle distortion ($\sigma_{\text{ve}}^2$) of the $Z\text{O}_6$ octahedron in a tourmaline is largely a function of the <$Y$–O$>$ distance in that tourmaline, although the occupant of the O(3) site (V site in the general formula) also affects that distortion. The correlation coefficient, $r$, of <$Y$–O$>$ and $\sigma_{\text{ve}}^2$ of the $Z\text{O}_6$ octahedron is $-0.99$ (Fig. 2 in Ertl et al., 2005) for all investigated tourmalines whose V site is occupied by three (OH) groups.

The high-pressure tourmalite (with $Z\text{O}_6$) was iteratively calculated for a charge-balanced formula. Another interesting possibility for a calculation of the OH content is reported by Bosi (2013): $W$(OH) = [$2 - 1.01$ BVS(O1) – $0.21$ \text{F}]$^\text{gg}$, where BVS(O1) is the bond-valence sum at O1 (W and F is in apfu). For the studied tourmaline this calculation yields for a BVS(O1) of 1.35 valence units and for a F content of 0.20(5) apfu (Table 2) a $W$(OH) content of -0.23(5) apfu. Considering the errors both values are in good agreement with each other.

It is not surprising that the W site contains a relatively high amount of oxygen, because ~80% of the Fe content is oxidized to Fe$^{3+}$. To produce a charge-balanced formula H atoms have to be released. Because of the relatively large error of the estimated amount of (OH), the classification of the studied tourmaline sample is problematic, but it seems that it belongs to the dravite–oxy-dravite–buferite series.

5. Discussion and conclusion

How can the relatively high Sr content, with up to 0.68 wt% SrO and the significant Pb content, with up to 0.54 wt% PbO$^2$, in the tourmaline structure be explained? Primary aqueous saline fluid inclusions trapped in quartz coexisting with tourmaline under eclogite-facies P–T conditions show relatively high concentrations of Sr, B and also of some Pb (Konzett et al., 2012). The Sr content is the highest observed in tourmaline to date. A possible source of B is the metapelitic country rocks with tourmaline-bearing pegmatites, which intruded during Permian times. A crustal source of B would be consistent with relatively high Li concentrations of 5–8 μg g$^{-1}$ Li in zircon, intergrown with the tourmaline (Konzett et al., 2012). The tourmaline itself is enriched in Mg and Fe (Table 4).

Commonly, tourmaline-bearing pegmatites of the Austroalpine basement units and many other occurrences are in contact with marbles (Beck, 1936; Höller, 1959; Esterlus, 1983; Bernhard, 2009; Ertl et al., 2010a; Pfaffl, 2012). A pegmatite from the Austroalpine basement, in contact to mylonitic garnet micaschist and to marble, which was found at the Koralpe, Eastern Alps, Styria, Austria, contains Al-rich tourmaline with 189 ppm Sr (Ertl et al., 2006).

Magnesium-rich tourmalines from the contact zone of Permian pegmatites to mica schists and marbles from different localities of the Austroalpine basement units (Rappold Complex) in Styria, Austria, contain up to 142 ppm Sr (Ertl et al., 2010a). These authors concluded that the pegmatites were formed by anatectic melting of mica schists and paragneisses in Permian time and that they crystallized from the pegmatitic melt, and were influenced by the metacarbonate and metapelitic host rocks (Ertl et al., 2010a). Another tourmaline (fluor-liddicoatite) was found at the border zone of a pegmatite of the Austroalpine basement units, near Altes Almhaus, Stubalpe, Styria. The tourmaline- and spodumene-bearing pegmatite crosses a marble from where Ca was mobilized, which is also responsible for the crystallization of this Ca-dominant tourmaline (Ertl et al., 2013).

More than 60 samples of calcitic and a few dolomitic marbles of the greenschist- to eclogite-facies Austroalpine basement (Eastern Alps) were investigated by Pühr et al. (2008). These authors further described some marbles containing up to 1300 ppm Sr. Carbonate is generally known to be the most important carrier rock of Sr.

In plagioclase–muscovite–scapolite metaevaporite layers in dolomite marble near Prosetín (Moravicum, Czech Republic), blue-grey Mg-rich tourmalines were found to contain up to 337 ppm Sr (Bačík et al., 2012). These authors found a positive correlation between Sr and Ca in tourmaline ($r^2 = 0.77$). Some tourmaline analyses correspond to
oxy-dravite and some others to magnesio-foitite. The unit-cell parameters \( [a = 15.912, c = 7.199 \text{ Å}] \) and the calculated average bond lengths \( (<Y-O> = 1.995 \text{ Å}; <Z-O> = 1.929 \text{ Å}) \) indicate also a relatively high Al–Mg disorder (Bačík et al., 2012).

The Anjanabonoina pegmatites in Madagascar are famous for their large and multicoloured Ca-rich tourmalines (liddicoatite). These pegmatite dikes are emplaced in a complex environment characterized by gneisses and marbles of medium metamorphic grade (De Vito et al., 2006). The metasedimentary rocks hosting the pegmatitic dikes locally show extensive contact-metasomatic phenomena. Veins of quartz and tourmaline occur in metasedimentary rocks close to the pegmatites, and marble is transformed into skarn (De Vito et al., 2006). An Al-rich tourmaline from such a pegmatite contains 273 ppm Sr (Ertl et al., 2006).

As mentioned, Mg-rich tourmaline from Outokumpu, Finland, contains 0.34 wt% SrO (Peltola et al., 1968). This tourmaline contains 10.6 wt% MgO, 9.6 wt% Cr₂O₃ and 0.6 wt% V₂O₃. It occurs in contact skarns between serpentinites and quartzites. The authors described indications that this tourmaline is a product of an interaction of serpentinites with metasomatic dolomitic marble and quartzite (Peltola et al., 1968). The unit-cell parameters of this Sr-bearing, Mg-rich tourmaline from Outokumpu are very similar to the unit-cell parameters of the tourmaline investigated here (Table 1), which contains a similar amount of Mg (8.9–10.1 wt% MgO), much lower amounts of Cr³⁺ (0.1–0.6 wt% Cr₂O₃) and V³⁺ (≤0.1 wt% V₂O₃; Table 4), and an amount of Sr²⁺ that can be twice as high as from Outokumpu. The investigated tourmaline zones exhibit a significant CaO content (0.6–1.5 wt% CaO; Table 4).

The possibility should also be considered that the original boron sources for tourmaline crystallization in the eclogite from the Kreuzeck Mountains, namely Permian tourmaline-bearing pegmatites, were influenced by a Sr-enriched metacarbonate, maybe by a dolomitic marble. In the eclogite, Sr and Ca concentrations of fluid inclusions in quartz (coexisting with tourmaline) show a nearly linear positive correlation (Konzett et al., 2012). In such fluid inclusions, calcite daughter crystals were also identified by these authors.

In a “mushroom” tourmaline from Myanmar, which is enriched in Al and B, a significant amount of Pb (0.18 wt% PbO) was reported (Ertl et al., 2007). In that work also tourmaline samples with a significant amount of Pb from other localities were discussed. In absence of any other data, we assumed that in our investigated tourmaline Pb is in a 4+ oxidation state, because ~80% of the Fe is oxidized to Fe³⁺. Hence, we assign the small Pb amount of 0.02 apfu to the Y site rather than the X site (Table 4).

Because only a small amount of F (0.20 apfu; Table 2) was estimated by refinement, and the amount of (OH) was only estimated to 0.35 apfu, the W site seems to be dominated by oxygen. Therefore the composition of this high-pressure tourmaline has a significant oxy-dravite component, which would be in agreement with a significant amount of oxidized Fe in our sample. Oxy-dravite was approved as a new species by theIMA in 2012 and described by Bosi & Skoghy (2013). A further investigation of the exact location of the two proton sites was done by Gatta et al. (2014).

Based on this data review, we recommend for tourmalines with MgO > 8 wt% and which contain significant Ca amounts (notably when the tourmaline-bearing rock is in contact with a carbonate) that analyses be obtained also for Sr and Pb. Especially tourmalines from metamorphic rocks or from contact skarns could be of particular interest. Sometimes such Sr-bearing tourmalines can also contain significant amounts of Cr, V and Ni.

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