Article

Princivalleite, Na(Mn₂Al)Al₆(Si₆O₁₈)(BO₃)₃(OH)₃O, a new mineral species of the tourmaline supergroup from Veddasca Valley, Varese, Italy

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Abstract

Princivalleite, Na(Mn₂Al)Al₆(Si₆O₁₈)(BO₃)₃(OH)₃O, is a new mineral (IMA2020-056) of the tourmaline supergroup. It occurs in the Veddasca Valley, Luino area, Varese, Lombardy, Italy (46°03’30.74”N, 8°48’24.47”E) at the centre of a narrow (2–3 cm wide) vertical pegmatitic vein, a few metres long, crosscutting a lens of flaser gneiss. Crystals are subhedral (up to 10 mm in size), azure with a vitreous lustre, conchoidal fracture and white streak. Princivalleite has a Mohs hardness of ~2, a calculated density of 3.168 g/cm³ and is uniaxial (−). Princivalleite has trigonal symmetry, space group R₃m, a = 15.9155(2) Å, c = 7.11660(10) Å, V = 1561.15(4) Å³ and Z = 3. The crystal structure was refined to R₁ = 1.36% using 1758 unique reflections collected with MoKα X-ray intensity data. Crystal-chemical analysis resulted in the empirical crystal-chemical formula

\[
X(Na^{0.54}Ca^{0.11})_{1}^{[\square]} (Al^{1.82}Mn^{2+}^{0.35})^{[\square]} (Zn^{0.07}Mg^{0.02}Li^{0.08})_{0.08} (SB_{1.00})_{1.00} (BO_{3})_{3} (OH)_{3} [\Theta] = 0.66 \frac{F_{0.25}(OH)_{1.22}}{1.21} \frac{1}{0.01} \frac{1.00}{1.00}
\]

which recast in its ordered form for classification purposes is:

\[
X(Na^{0.54}Ca^{0.11})_{1}^{[\square]} (Al^{1.82}Mn^{2+}^{0.35})^{[\square]} (Zn^{0.07}Mg^{0.02}Li^{0.08})_{0.08} (SB_{1.00})_{1.00} (BO_{3})_{3} (OH)_{3} [\Theta] = 0.66 \frac{F_{0.25}(OH)_{1.22}}{1.21} \frac{1}{0.01} \frac{1.00}{1.00}
\]

Princivalleite is an oxy-species belonging to the alkali group of the tourmaline supergroup. The closest end-member compositions of valid tourmaline species are those of oxy-schorl and darrellhenryite, to which princivalleite is related by the substitutions Mn²⁺ ↔ Fe²⁺ and Mn²⁺ ↔ 0.5Al³⁺ + 0.5Li⁺, respectively. Princivalleite from Veddasca Valley is a geochemical anomaly, originated in a B-rich and peraluminous anatectic pegmatitic metasedimentary in situ, poor in Fe and characterised by reducing conditions in the late-stage metamorphic fluids derived by the flaser gneiss. The Mn-enrichment in this new tourmaline is due to absence of other minerals competing for Mn such as garnet.

Keywords: princivalleite, new mineral species, crystal-structure refinement, electron microprobe, Mössbauer spectroscopy, infrared spectroscopy, optical absorption spectroscopy, micro-laser induced breakdown spectroscopy

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Introduction

Tourmalines are complex borosilicates that have been studied extensively in terms of their crystal structure and crystal chemistry (e.g. Foit, 1989; Hawthorne, 1996; Hawthorne and Henry, 1999; Ertl et al., 2002; Novák et al., 2004; Bosi and Lucchesi, 2007; Bosi, 2013, 2018; Henry and Dutrow, 2011; Cempírek et al., 2013; Bačík and Fridrichová, 2020). In accordance with Henry et al. (2011), the general chemical formula of tourmaline is written as: XY₃Z₂T₄O₁₈(BO₃)₃V₃W, where X = Na⁺, K⁺, Ca⁺, □ (= vacancy); Y = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg²⁺, Fe²⁺, Mn²⁺, Li⁺; Z = Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Mg²⁺, Fe²⁺; T = Si⁴⁺, Al³⁺, B³⁺; B = B³⁺; V = (OH)⁻, O²⁻; and W = (OH)⁻, F⁻, O²⁻. Note that the non-italicised letters X, Y, Z and B represent groups of cations hosted in the [⁰X][⁶Y][⁴Z]T and [⁰T and [⁰B] crystallographic sites (letters italicised). As for the letters V and W, they represent groups of anions accommodated at the [3]-coordinated O₃ and O₁ crystallographic sites, respectively. The dominance of specific ions at one or more sites of the structure gives rise to a range of distinct mineral species.

A formal description of the new tourmaline species princivalleite is presented here. The mineral is named after Francesco
of these small veins (2 to 3 cm wide and a few metres long), vertically crosscutting the flaser gneiss at Curiglia, there are some quite common occurrences of dispersed grains and crystals up to 1 cm long, of azure princivalleite and oxy-schorl. The pegmatitic vein is composed of muscovite aggregates, with blades mostly oriented perpendicular to the walls, with quartz, albite plagioclase and minor K-feldspar. In addition to tourmaline, other accessories are rare small pyrite crystals and violet glassy cordierite grains.

Appearance, physical and optical properties

The princivalleite crystals show subhedral habits, up to ∼10 mm and are azure with a vitreous lustre (Fig. 1). It has a white streak and shows no fluorescence. It has a Mohs hardness of ∼7 and is brittle with a conchoidal fracture. The calculated density, based on the empirical formula and unit-cell volume refined from single-crystal X-ray diffraction (XRD) data, is 3.168 g/cm³. In thin section, princivalleite is transparent; in transmitted light, pleochroism was not visible in the thin-section fragment investigated. Princivalleite is uniaxial (+) with refractive indices ω = 1.650(5) and ε = 1.635(5) measured by the immersion method using white light from a tungsten source. The mean index of refraction, density, and chemical composition led to an excellent compatibility index (1 – Kp/Kc = 0.024) (Mandarino, 1981).

Experimental methods and results

General comment

The present crystal structure refinement (SREF), electron microprobe (EMP) and μ-laser induced breakdown spectroscopy (μ-LIBS) data were all obtained from the same crystal fragment. However, complementary experimental data were recorded from coexisting crystals. Small differences in composition occur between these princivalleite crystals (see text).

Microprobe analysis

Electron microprobe analysis was obtained using a wavelength dispersive spectrometer (WDS mode) with a Cameca SX50 instrument at the "Istituto di Geologia Ambientale e Geoingegneria" (Rome, Italy), CNR, operating at an accelerating potential of 15 kV, a sample current of 15 nA and 10 μm beam diameter. Minerals and synthetic compounds were used as standards: wollastonite (Si and Ca), magnetite (Fe), rutile (Ti), corundum (Al), vanadinite (V) fluorophlogopite (F), periclase (Mg), jadeite (Na), orthoclase (K), sphalerite (Zn), rhodonite (Mn) and metallic Cr and Cu. The PAP routine was applied (Pouchou and Pichoir, 1991). The composition (mean of 6 spot analyses) is given in Table 1. Titanium, V, Cr and K were below detection limits (<0.03 wt.%).

Micro-laser induced breakdown spectroscopy

Lithium analysis was performed using 110 mJ of energy per pulse by a double pulse Q-Switched (Nd-YAG, λ = 1064 nm) laser with a 1 μs delay between the two pulses. The small spot size (7–10 μm) was obtained using a pетrographic optical microscope (objective lens = 10X, NA = 0.25 and WD = 14.75 mm). The μ-LIBS spectra were acquired using an AvaSpec Fiber Optic Spectrometer (390–900 nm with 0.3 nm resolution) with a delay of 2 μs after the second pulse.
Table 1. Electron microprobe data (WDS mode) and atoms per formula unit
(apfu) normalised to 31 anions for princivalleite.

| Wt.% | Mean (6 spots) | Range | Stand. Dev. | apfu |
|------|---------------|-------|-------------|------|
| SiO₂ | 33.71         | 33.21–34.10 | 0.37     | 5.60 |
| B₂O₃* | 10.46         |       | 3.00        |     |
| Al₂O₃ | 41.19         | 39.32–42.82 | 1.20 | 8.07 |
| FeO   | 2.29          | 1.85–2.69  | 0.36 | 0.32 |
| MnO   | 5.96          | 5.46–6.00  | 0.43 | 0.84 |
| MgO   | 0.08          | 0.04–0.12  | 0.03 | 0.02 |
| ZnO   | 0.55          | 0.43–0.61  | 0.08 | 0.07 |
| CaO   | 0.60          | 0.50–0.75  | 0.12 | 0.11 |
| Na₂O  | 1.68          | 1.59–1.78  | 0.08 | 0.54 |
| Li₂O  | 0.12          | 0.11–0.13  | 0.02 | 0.08 |
| F     | 0.42          | 0.35–0.63  | 0.13 | 0.22 |
| H₂O²⁻ | 2.55          |       | 2.83        |     |
| O = F | –0.18         |       |             |     |
| Total | 99.45         |       |             |     |

*Calculated by stoichiometry, [Y+Z+T] = 15.00 apfu.
*bFe oxidation state determined by Mössbauer spectroscopy.
*cLi Determined by μ-Laser Induced Breakdown Spectroscopy.

and were integrated for 1 ms. Quantitative data were obtained by generating a linear regression using the main Li emission line intensity (670.706 nm corresponding to resonance transition 1s² 2s > 1s² 2p) particularly sensitive to Li amounts. The linear fit was made according to Bosi et al. (2021) and revealed amounts of Li₂O = 0.12 wt.% (Table 1) in line with that estimated by the Pesquera et al. (2016) approach (0.18 Li₂O wt.%).

Mössbauer spectroscopy

To determine the Fe³⁺/ΣFe ratio of princivalleite, a crystal fragment was ground under acetone and analysed using ⁵⁷Fe Mössbauer spectroscopy with a conventional spectrometer system equipped with a 10 mCi point source and operated in constant acceleration mode. Data were collected over 1024 channels and were folded and calibrated against the spectrum of an α-Fe foil. The spectrum (Fig. 2) was fitted using the software MassA (Prescher et al., 2012) with three absorption doublets consistent with Fe²⁺ (Table 2). No indications of absorption due to Fe³⁺ was observed.

Single-crystal infrared spectroscopy

Polarised Fourier-transform infrared (FTIR) absorption spectra were measured on a 35 μm thick doubly polished single-crystal section oriented parallel to the c-axis. A Bruker Vertex spectrometer attached to a Hyperion 2000 microscope and equipped with a halogen lamp source, a CaF₂ beamsplitter, a ZnSe wiregrid polariser and an InSb detector was used to collect spectra in the range 2000–13000 cm⁻¹ at a resolution of 2 cm⁻¹. Spectra recorded in polarised mode parallel to the crystallographic c-axis show a significant band at 3365 cm⁻¹, a very intense band around 3500 cm⁻¹, two weaker bands at 3632 and 3644 cm⁻¹, and two very weak bands at 3662 and 3671 cm⁻¹ (Fig. 3). As observed typically for tourmaline spectra in the (OH) range, the main band is off-scale for the E[ei] direction due to excessive absorption. Spectra obtained perpendicular to the c-axis show considerably weaker bands.

Note that the band at 3365 cm⁻¹ is consistent with the presence of minor Al along with Si in [4]-fold coordination (Nishio-Hamane et al., 2014), whereas the comparatively weak bands above 3600–3650 cm⁻¹, which is the region where bands due to (OH) at the W position (≡ O1 site) are expected (e.g. Gonzalez-Carreño et al., 1988; Bosi et al., 2015b), indicate small amounts of W(OH). On the basis of previous investigations of Bosi et al. (2012, 2016, 2021) and Watenphul et al. (2016), the main broad FTIR band at ~3500 cm⁻¹ is probably caused by the occurrence of the atomic arrangements ([Li₂⁺,Fe²⁺,Mn²⁺](Mn²⁺,Al)₂(Al²⁺,Al)₃O₃(OH)₃, whereas the bands above 3600 cm⁻¹ may be caused by the arrangements [(Li₂⁺,Fe²⁺,Mn²⁺)(Mn²⁺,Al)Al]O₃(OH)≡O(□), where □ = vacancy.

Optical absorption spectroscopy (OAS)

Polarised optical absorption spectra of princivalleite (Fig. 4) were acquired at room temperature on the same polished crystal that was used for the collection of infrared spectra. An AVASPEC-ULS2048X16 spectrometer, connected via a 400 μm UV fibre cable to a Zeiss Axiositron UV-microscope, was used. A 75 W Xenon arc lamp was used as the light source and Zeiss Ultrafluar 10× lenses served as objective and condenser. An UV-quality Glan-Thompson prism, with a working range from 40000 to 3704 cm⁻¹ was used as a polariser.

The recorded spectra show two broad absorption bands at 13500 and 8900 cm⁻¹. The weak polarisation of these bands is explained by the absence of Fe³⁺ (e.g. Mattson and Rossman, 1987) in the sample and consequently the bands mark pure d-d transitions in [6]-coordinated Fe²⁺. This assignment agrees with the Fe valency and site distribution observed from Mössbauer spectra of the sample. Additional sharp absorption bands observed in the E[ei]-spectrum in the range 6700–7000 cm⁻¹ mark overtones of the fundamental (OH)-stretching modes. Weak and relatively sharp absorption bands at ~18000, ~22500, ~24000 and ~27500 cm⁻¹ are related to spin-forbidden electronic transitions in [6]-coordinated Mn²⁺ (e.g. Hålenius et al., 2007).

Single-crystal structure refinement

A representative azure crystal of princivalleite from Veddasca Valley was selected for X-ray diffraction measurements on a Bruker KAPPA APEX-II single-crystal diffractometer (Sapienza University of Rome, Earth Sciences Department), equipped with...
A CCD area detector (6.2 × 6.2 cm active detection area, 512 × 512 pixels) and a graphite-crystal monochromator, using MoKα radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. A total of 1621 exposures (step = 0.4°, time/step = 20 s) covering a full reciprocal sphere with a redundancy of ~12 was collected using 00 and φ scan modes. Final unit-cell parameters were refined using the Bruker AXS SAINT program on reflections with I > 10 σ(I) in the range 5° < 2θ < 75°. The intensity data were processed and corrected for Lorentz, polarisation and background effects using the APEX2 software program of Bruker AXS. The data were corrected for absorption using a multi-scan method (SADABS, Bruker AXS). The absorption correction led to an improvement in R_int. No violation of R3m symmetry was detected.

Structure refinement was done using the SHELXL-2013 program (Sheldrick, 2015). Starting coordinates were taken from Bosi et al. (2015a). The variable parameters were: scale factor, extinction coefficient, atom coordinates, site-scattering values (for X, Y and Z sites) and atomic-displacement factors. The fully ionised-oxygen scattering factor and neutral-cation scattering factors were used. In detail, the X site was modelled using the Na scattering factor. The occupancy of the Y site was obtained considering the presence of Al versus Mn, and the Z site with Al versus Fe. The T, B and anion sites were modelled, respectively, with Si, B and O scattering factors and with a fixed occupancy of 1, because refinement with unconstrained occupancies showed no significant deviations from this value. The position of the H atom bonded to the oxygen at the O3 site in the structure was taken from the difference-Fourier map and incorporated into the refinement model; the O3 bond length was restrained (by DFIX command) to be 0.97 Å with the isotropic displacement parameter constrained to be equal to 1.2 times that obtained for the O3 site. There were no correlations greater than 0.7 between the parameters at the end of the refinement. Table 3 lists crystal data, data-collection information, and refinement details; Table 4 gives the fractional atom coordinates, equivalent isotropic-displacement parameters and Table 5 shows selected bond lengths. The crystallographic information file has been deposited with the Principal Editor of Mineralogical Magazine and is available as Supplementary material (see below).

### Powder X-ray diffraction

A powder X-ray diffraction pattern for princivalleite was collected using a Panalytical X’pert powder diffractometer equipped with an X’celerator silicon-strip detector. The range 5–80° (2θ) was scanned with a step-size of 0.017° with the sample mounted on a background-free Si holder using sample spinning. The diffraction data (for CuKα = 1.54059 Å), corrected using Si as an internal standard, are listed in Table 6. The program UnitCell (Holland and Redfern, 1997) was used to refine unit-cell parameters in the trigonal system: a = 15.8851(3) Å, c = 7.1041(2) Å and V = 1522.46(5) Å³.

### Determination of number of atoms per formula unit (apfu)

In agreement with the structure-refinement results, the boron content was assumed to be stoichiometric (B³⁺ = 3.00 apfu). Both the site-scattering results and the bond lengths of B and T are consistent with the B site being fully occupied by boron and no amount of B³⁺ at the T site (e.g. Bosi and Lucchesi, 2007). The iron oxidation state was determined by Mössbauer spectroscopy. In accordance with these results, together with results from optical absorption spectroscopy and Fe and Mn redox potential arguments, all Mn was considered as Mn⁴⁺. Lithium was determined by µ-LIBS. The (OH) content and the formula were then calculated by charge balance with the assumption (T + Y + Z) = 15 apfu and 31 anions. The excellent agreement between the number of electrons per formula unit (epfu) derived from EMP data and SREF (223.2 and 223.0 epfu, respectively) supports the stoichiometric assumptions.

### Site populations

The princivalleite site populations at the X, B, T, O3 (≡ V) and O1 (≡ W) sites follow the standard site preference suggested for tourmaline (e.g. Henry et al., 2011) and are coherent with the information from FTIR absorption spectra (Fig. 3). In particular, the presence of 0.40 Al apfu at the T site is consistent with observed <$T–O_3$> = 1.624 Å, which is larger than the expected value for <$Si–O_3$> = 1.619(1) Å (Bosi and Lucchesi, 2007). The site populations at the octahedrally coordinated Y and Z sites were optimised according to the procedure of Bosi et al. (2017), and by fixing the minor elements Zn and Li at the Y site.
The resulting empirical crystal-chemical formula is:

$$\text{Formula} = X(\text{Na}_{0.34} \text{Ca}_{0.11} \text{Mn}_{0.01} \text{Fe}_{0.13} \text{Zn}_{0.17} \text{Li}_{0.08} ) [\text{Si}_{1.00} \text{Al}_{0.50} \text{OH}_{0.50} ]$$

A comparison between the values of refined site-scatterings and those calculated from this site population is reported in Table 7.

### Table 4. Fractional atom coordinates, isotropic (*) or equivalent-isotropic displacement parameters (in Å²) and site occupancy factors (s.o.f.) for princetonville.

| X     | y/a | z/c | Mr(s.o.f.) |
|-------|-----|-----|------------|
| Na(1) | 0   | 0   | 0.85(3)   |
| Na(2) | 0.1317(3) | 0.62913(8) | 0.00924(12) |
| Z      | 0.2967(4) | 0.60857(7) | 0.00545(9) |
| B      | 0.1097(1) | 0.4520(3) | 0.00623(1) |
| T      | 0.1919(7) | 0.1899(6) | 0.00496(7) |

### Table 5. Selected bond lengths (Å) for princetonville.

| X-O2 | B-O2 | Z-O6 | Z-O7 | Z-O8 | Z-O9 |
|------|------|------|------|------|------|
| 2.533(2) | 1.362(2) | 1.865(1) | 1.875(1) | 1.885(1) | 1.915(1) |

### Table 7. The agreement between the refined and calculated values is very good, and validates the distribution of cations over the X, Y, Z and T sites in the empirical structural formula of princetonville. This site population is also supported by the comparison of weighted bond valence sums and mean formal charge calculated from the empirical structural formula (Table 8).

For classification purposes, the empirical crystal-chemical formula was recast in its ordered form following Henry et al. (2011): $X(\text{Na}_{0.50} \text{Ca}_{0.10} \text{Mn}_{0.02} \text{Fe}_{0.18} \text{Zn}_{0.08} \text{Li}_{0.08}) [\text{Si}_{0.50} \text{Al}_{0.50} \text{OH}_{0.50} ]$.

### End-member formula and relation to other species

The composition of the present sample is consistent with an oxy-tourmaline belonging to the alkali group (Henry et al., 2011); it is Na-dominant at the X position of the general formula of tourmaline, oxy-dominant at W with O²⁻ > (F + OH) and Al³⁺ dominant at Z.

With regard to the Y position, the formula electroneutrality requires that the total charge at Y is +7 in the end-member formula: $\text{Na}(Y_3)[\text{Si}_{1.00} \text{Al}_{0.50} \text{OH}_{0.50} ]$. In accord with the dominant-valency rule and the valency-imposed double site-occupancy (Bosi et al., 2019a, 2019b), the possible charge and atomic arrangements compatible with the Y-site population in the ordered formula are:

$$\text{Na}(Y_3)[\text{Si}_{1.00} \text{Al}_{0.50} \text{OH}_{0.50} ]$$
Y(2+) 3 → Y(2+) 0.0625 → (21+ 2 Al) 0.0625 = 1.875 apfu (limited by 2+ contents)
Y(3+) 3 → Y(3+) 0.080 = (Al21+ 3 Li) 0.080 = 0.240 apfu (limited by Li contents)

As a result, and in accordance with the dominant-valency rule, the proportion of the arrangement (21+ 2 Al) 0.0625 is greater than the proportion of (Al21+ 3 Li) 0.080. In accordance with the dominant-constituent rule, Mn2+ prevails among the 2+-cations (0.84 Mn apfu > 0.32 Fe > 0.07 Zn > 0.02 Mg). Thus, the atomic arrangement (Mn2+Al3+) is the dominant one: (Mn2+Al3+)0.42 = 1.26 apfu. The end-member composition may hence be represented as Na(Mn2Al)Al6(Si6O18)(BO3)3(OH)3O. As no tourmalines are currently approved with this composition, it can be identified as a new species.

Princivalleite is related to oxy-schorl and darrellhenryite by the substitutions Mn2+ ↔ Fe2+ and 2Mn2+ ↔ Al3+ + Li+. The properties of these three tourmalines are compared in Table 9, whereas the position of the princivalleite holotype sample in the ternary diagram for the (Fe2+Al)–(Mn2+Al)–(Al3Li) subsystem is displayed in Fig. 5. This figure also shows the chemical variability of princivalleite to oxy-schorl and darrellhenryite by the occurrence of two additional samples from the same batch of tourmalines from the Veddasca rock sample (Fig. 1) and samples from Uvildy, Chelyabinsk region, Russia, and Pikárec, Czech Republic (Cempírek et al., 2015; Bosi et al., 2022). The chemical composition of these four samples is reported in Table 10. Moreover, the chemical composition of the yellow Mn-tourmaline identified as tsilaisite by Nuber and Schmetzer (1984) is WO-dominant; thus, it corresponds to princivalleite (Fig. 5). It is most likely that the locality of this yellow tourmaline should be the Canary mining area in the Lundazi District of eastern Zambia (for details, see Laurs et al., 2007), although it is important to point out that other tourmalines from this locality are actually Mn-rich elbaite or fluor-elbaite samples (Laurs et al., 2007; Simmons et al., 2011).

**Petrogenesis of princivalleite**

Formation of Mn-dominant tourmalines (e.g. tsilaisite, fluor-tsilaisite and cellerite; Bosi et al., 2012, 2015a, 2022) requires specific geochromical conditions that are rare in nature: ideally, high activity of Al and Mn combined with low activity of Fe, Li and Mg. For example, Simmons et al. (2011) suggested that the original pegmatite-forming melt (preferably a B-rich peraluminous melt) of tsilaisitic and Mn-rich elbaite tourmalines...
must be relatively low in Fe and enriched in Mn and B, moreover, during the early stages of crystallisation Fe must be removed, but abundant B and Mn must still be available when tourmaline crystallises.

The system, at the stage of growth of princivalleite, must be also depleted in F; this condition is not commonly achieved as Mn-enrichment in pegmatites is typically followed by an increase of F content in the system and in the Mn-rich tourmalines formed (e.g. Novák and Povondra, 1995; Novotný and Cempírek, 2021; Bosi et al., 2022) that, compared to lepidolite-subtype (Selway et al., 1999) or transitional pegmatites (Dixon et al., 2014; Roda-Robles et al., 2015), contain lower amounts of F. The latter typically remains below 0.5 apfu in tourmaline until the hydrothermal-metasomatic stage of pegmatite crystallisation, which is characterised by fluor-elbaite to fluor-liddicoatite compositions (e.g. Novotný and Cempírek, 2021; Zahradníček, 2012; Flégr, 2016). This is the case of the princivalleite occurrences in the Uvildy and Pikárec pegmatites (Table 10), whereas F in princivalleite from Veddasca valley could have been limited by the abundant crystallisation of muscovite in the pegmatitic vein.

Fig. 5. Plot of princivalleite compositions on the \((\text{Fe}^{2+}_n\text{Al})-(\text{Mn}^{2+}_n\text{Al})-(\text{Al}_{2}\text{Li})\) diagram. Black circles represent the coexisting samples from same batch of tourmalines from the Veddasca rock sample (Italy); black triangle and black diamond represent princivalleite samples from Uvildy (Russia) and Pikárec (Czech Republic), respectively; black star is the yellow Mn-tourmaline from Zambia (Nuber and Schmetzer, 1984) identified as princivalleite in this study.

Table 9. Comparative data for princivalleite, oxy-schorl and darrellhenryite.

|                      | Princivalleitea | Oxy-schorlb | Darrellhenryitec |
|----------------------|-----------------|------------|------------------|
| \(a\) (Å)            | 15.9155(2)      | 15.916(3)  | 15.809(2)        |
| \(c\) (Å)            | 7.1166(1)       | 7.107(1)   | 7.089(1)         |
| \(V\) (Å\(^3\))     | 1561.15(4)      | 1559.14(4) | 1534.4(4)        |
| Space group          | \(R\bar{3}m\)   | \(R\bar{3}m\) | \(R\bar{3}m\)    |
| Optic sign           | Uniaxial (−)    | Uniaxial (−)| Uniaxial (−)     |
| \(e\)               | 1.650(5)        | 1.663(2)   | 1.636(2)         |
| \(e'\)              | 1.641(2)        | 1.619(2)   |                  |
| Streak               | White           | Pale gray  | White            |
| Colour               | Azure           | Greenish black | Pink             |
| Pleochroism in thin section | Colourless | Colorless |                |
| Strong lines in the powder XRD pattern \(d\) (Å) (I, %) | 2.567 (100) | 3.466 (100) | 2.925 (100) |
|                     | 2.934 (78)      | 2.955 (79) | 2.555 (90)       |
|                     | 3.441 (67)      | 3.634 (75) | 3.431 (73)       |
|                     | 2.028 (51)      | 2.583 (65) | 3.952 (54)       |
|                     | 3.974 (50)      | 3.997 (52) | 1.901 (50)       |
|                     | 4.198 (43)      | 4.225 (48) | 1.643 (49)       |
| Reference            | This work       | Bačík et al. (2013) | Novák et al. (2013) |

\(^{a}\) Na(Mn_{2}\text{Al})Al_{6}(Si_{6}\text{O}_{18})(BO_{3})_{3}(OH)_{3}O

\(^{b}\) Na(\text{Fe}_{2}\text{Al})Al_{6}(Si_{6}\text{O}_{18})(BO_{3})_{3}(OH)_{3}O

\(^{c}\) Na(Li_{2}\text{Al})Al_{6}(Si_{6}\text{O}_{18})(BO_{3})_{3}(OH)_{3}O

The Mn-enrichment in tourmaline was allowed by the lack of formation other minerals competing for this element such as garnet.

The Mn-enrichment is unusual for anatectic pegmatites (cf. Cempírek and Novák 2006, Cempírek et al. 2006); we therefore assume that micas (especially biotite) in the protolith metapelitic were enriched in Mn, possibly due to admixture of volcanosedimentary component; this might also be indicated by relatively elevated ZnO contents in princivalleite (Tables 1 and 10). Another explanation might be an unexposed magmatic source of melt as in the case of (apparently anatectic) kyanite-bearing Li-rich pegmatites at Vitorco, Argentina (Galliski et al. 2012).
Table 10. Chemical composition of princivalleite (Prn) and oxy-schorl (Osch)
from: Veddasca Valley, Varese, Lombardy, Italy; Uvildy, Chelyabinsk region, Russia; and Pikárec, Czech Republic.

|       | Veddasca (n = 4) | Veddasca (n = 7) | Osch Veddasca (n = 13) | Uvildy (n = 8) | Pikárec (n = 4) |
|-------|-----------------|-----------------|------------------------|---------------|----------------|
| Wt.%  |                 |                 |                        |               |                |
| SiO₂  | 34.32(64)       | 34.41(46)       | 32.86(70)              | 34.44(28)     | 35.38(9)       |
| B₂O₃  | 10.53           | 10.60           | 10.33                  | 10.64         | 10.61          |
| Al₂O₃ | 42.19(79)       | 41.46(27)       | 39.73(41)              | 42.97(44)     | 39.64(11)      |
| FeO   | 2.71(12)        | 3.79(12)        | 6.63(28)               | 1.29(12)      | 1.37(31)       |
| MnO   | 4.43(24)        | 5.28(14)        | 4.29(19)               | 4.36(41)      | 7.36(15)       |
| MgO   | 0.22(24)        | 0.08(3)         | -                      | 0.15(11)      | -              |
| ZnO   | 0.415           | 0.22(6)         | 0.44(5)                | -             | 0.22(4)        |
| CaO   | 0.51(11)        | 0.72(6)         | 0.59(4)                | 0.10(3)       | 0.04(3)        |
| Na₂O  | 1.74(11)        | 1.71(5)         | 1.78(3)                | 1.73(7)       | 1.84(16)       |
| Li₂O  | 0.12(12)        | 0.11(6)         | -                      | 0.43(5)       | 0.48(6)        |
| F     | 0.40(13)        | 0.40(11)        | 0.50(7)                | 0.40(11)      | 0.46(7)        |
| TSi   | 0.36            | 0.25            | 2.69                    | 2.73          | 2.95           |
| XNa   | 0.55            | 0.54            | 0.58                    | 0.55          | 0.58           |
| XCa   | 0.09            | 0.13            | 0.11                    | 0.02          | 0.01           |
| XAl   | 1.83            | 1.63            | 1.40                    | 1.90          | 1.49           |
| XFe²⁺ | 0.37            | 0.52            | 0.93                    | 0.18          | 0.19           |
| XMn²⁺ | 0.62            | 0.73            | 0.61                    | 0.60          | 1.02           |
| XMg   | 0.05            | 0.02            | 0.02                    | 0.04          | 0.00           |
| XZn   | 0.05            | 0.03            | 0.06                    | 0.00          | 0.03           |
| XLi   | 0.08            | 0.07            | 0.00                    | 0.29          | 0.32           |
| XΣ    | 3.00            | 3.00            | 3.00                    | 3.00          | 3.00           |
| XCa   | 0.09            | 0.13            | 0.11                    | 0.02          | 0.01           |
| XNa   | 0.55            | 0.54            | 0.58                    | 0.55          | 0.58           |
| XD    | 0.36            | 0.33            | 0.32                    | 0.43          | 0.41           |
| XΣ    | 1.00            | 1.00            | 1.00                    | 1.00          | 1.00           |
| X(Oh) | 2.67            | 2.81            | 3.00                    | 2.98          | 3.00           |
| XO    | 0.33            | 0.19            | 0.00                    | 0.02          | 0.00           |
| XD    | 3.00            | 3.00            | 3.00                    | 3.00          | 3.00           |
| XΣ    | 1.00            | 1.00            | 1.00                    | 1.00          | 1.00           |
| XΣF   | 0.21            | 0.21            | 0.28                    | 0.20          | 0.24           |
| XΣO   | 0.79            | 0.79            | 0.71                    | 0.80          | 0.51           |
| XΣ(Oh)| 0.00            | 0.00            | 0.01                    | 0.00          | 0.25           |
| XΣW   | 1.00            | 1.00            | 1.00                    | 1.00          | 1.00           |

Atoms per formula unit (apfu) normalised to 31 anions. Standard deviations for oxides and F are in brackets.

*Calculated by stoichiometry (see text). #Determined by µ-LIBS. $Determined by LA-ICP-MS. ± = below detection limits

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Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2022.3

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