Chromium-rich vanadio-oxy-dravite from the Tzarevskoye uranium–vanadium deposit, Karelia, Russia: a second world-occurrence of Al–Cr–V–oxy-tourmaline

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Abstract

A green tourmaline sample from the Tzarevskoye uranium–vanadium deposit, close to the Srednaya Padma deposit, Lake Onega, Karelia Republic, Russia, has been found to be the second world-occurrence of Cr-rich vanadio-oxy-dravite in addition to the Pereval marble quarry, Studyanka crystalline complex, Lake Baikal, Russia. From the crystal-structure refinement and chemical analysis, the following empirical formula is proposed: 

\[ X(Na_{0.96}K_{0.02})_2[Al_{19.36}Cr_{13.6}V_{0.03}Mg_{0.03}Li_{0.07}]_2(Si_{0.15}O_{18})(BO_3)_3V_{0.03}W_{0.05}OH_{2.3}O_{17.2}F_{0.1}F_{0.02}Zn_{0.01}Th_{0.01}F_{0.01} \]

Together with the data from the literature, a compositional overview of Al–V–Cr–Fe3+-tourmalines is provided by using \[ [6]Al–V–Cr–Fe^{3+} \] diagrams for tourmaline classification. These diagrams further simplify the tourmaline nomenclature as they merge the chemical information over the octahedrally-coordinated sites (Y and Z) by removing the issues of uncertainty associated with cation order–disorder across Y and Z. Results show the direct identification of tourmalines by using the chemical data alone.

Keywords: tourmaline, crystal-structure refinement, electron microprobe, nomenclature

Introduction

The tourmaline-supergroup minerals are chemically complex borosilicates that are widespread in the Earth’s crust, occurring in sedimentary rocks, granites and granitic pegmatites and in low-grade to ultrahigh-pressure metamorphic rocks (e.g. Dutrow and Henry, 2011). In common with Henry et al. (2011), the general formula of tourmaline can be written as

\[ XY_3Z_6T_6O_{18}(BO_3)_3V_3W\]

where X = Na+, K+ , Ca2+ and \[ Y = Al^3+, Fe^3+, Cr^3+, V^3+, Mg^2+, Fe^2+, Mn^{2+}, Li^+ \]; Z = Al^3+, Fe^3+, Cr^3+, V^3+, Mg^2+, Fe^2+, Mn^2+, Mg^2+, Fe^2+, and T = Si^4+, Al^3+, B^3+, B = B^3+, V = OH^2-, and O^2- and W = OH^2-, F^− and O^2-. The (non-italicised) letters X, Y, Z, T and B represent groups of cations accommodated at the \([9]X\), \([6]Y\), \([6]Z\), \([3]T\) and \([3]B\) crystallographic sites (identified with italicised letters); the letters V and W represent groups of anions accommodated at the \([3]O(3)\) and \([3]O(1)\) crystallographic sites, respectively. The H atoms occupy the \(H(3)\) and \(H(1)\) sites, which are related to O(3) and O(1), respectively (e.g. Bosi, 2013; Gatta et al., 2014).

Due to their highly variable chemical composition and refractory behaviour, tourmaline is considered a very useful indicator of geological processes in igneous, hydrothermal and metamorphosed systems (Dutrow and Henry, 2011; van Hinsberg et al., 2011; Ahmadi et al., 2019; Sipahi, 2019) and able to record and preserve the chemical composition of their host rocks.

Vanadum and Cr-bearing hydroxyl- and oxy-tourmaline species have been described widely in the literature (Cossa and Arzruni, 1883; Badalov, 1951; Bassett, 1953; Snetsinger, 1966; Peltola et al., 1968; Jan et al., 1972; Dunn, 1977; Nuber and Schmetzer, 1979; Foit and Rosenberg, 1979; Rumyantseva, 1983; Gorskaya et al., 1984, 1987; Reznitskii et al., 1988; Hammarstrom, 1989; Kazachenko et al., 1993; Reznitskii and Sklyarov, 1996; Erli et al., 2008; Arif et al., 2010; Lupulescu and Rowe, 2011; Rozhdestvenskaya et al., 2011; Cempirek et al., 2013; Vereshchagin et al., 2014). Currently, they are known from several localities: Studyanka (Slyudyanka) crystalline complex, Lake Baikal, Russia; Onega region, Central Karelia, Russia; Primorye, Far eastern Russia; Balmat, St. Lawrence County, New York, USA; Silver Knob deposit, Mariposa County, California, USA; Nausahi deposit, Orissa, India; Outokumpu deposit, Finnish North Karelia, Finland; Mininga and Gujar Kili mines, Swat, Pakistan; Alpurai, Pakistan; Shabrovskoe ore deposit, Middle Ural, Russia; Syyserdax Dach, Ural Mountains, Russia; Umba Valley, Tanga Province, Tanzania; Kwal District, Kenya;
Amstall, Lower Austria, Austria; and Bitovánky, Czech Republic. Also, fluor-rich tourmalines characterised by V and Cr have been reported in the literature with a strong positive relation between F and Cr, but with F contents less than 0.5 atoms for formula unit (Bosi et al., 2017b).

Oxy-tourmalines rich in both V and Cr are unusual minerals and occur almost exclusively in metamorphosed V- and Cr-enriched host rocks such as sulfide-rich black shales, graphite quartzites and calcareous metasediments (Snetsinger, 1966; Kazachenko et al., 1993; Bačík et al., 2011; Cempírek et al., 2013). Most oxy-tourmalines with dominant V and/or Cr (V₂O₅ or Cr₂O₃ > 9 wt.%) were found in the Studyanka crystalline complex, Lake Baikal, Russia (Bosi et al., 2004, 2012, 2013a,b; Reznitskii et al., 2014; Bosi et al., 2014a,b, 2017a,b). Among these is a vanadio-oxy-dravite, ideally NaV₄(Al₆Mg₄)(Si₆O₁₈) (BO₃)₃(OH)₃O, a rare tourmaline recently described by Bosi et al. (2014a). The sample studied was found in the Tzarevskoye uranium–vanadium deposit, close to the Srednyaya Padma deposit, Zaonezhye Peninsula, Lake Onega, Karelia Republic, Northern Region, Russia. It is the first occurrence of V-dominant, Cr-rich oxy-tourmaline in Karelia and the second world-occurrence in addition to the Pervel marble quarry (Studyanka) type-locality. In this work, we describe this tourmaline and provide a compositional overview of Al–V–Cr–Fe³⁺-tourmalines.

Geological setting
The Srednyaya Padma mine is the largest of the deposits from vanadium, uranium and precious metals of the Onega region and has abnormally high concentrations of gold, palladium, platinum, copper and molybdenum. It is concentrated in the Onega epicratonic trough, which is filled with volcano–sedimentary rocks of Lower Proterozoic age (organic carbon-rich shists, sandstones, dolomites and tuffites prevail) (Boitsov, 1997). The ore mineralisation is located in the albite–mica–carbonate metasomatites upon the Proterozoic aleorolites and schists (Boitsov, 1997). The distribution of these ore-bearing metasomatites is controlled by axial faults and shear zones. In fact the Srednyaya Padma deposit is located in zones of fold-fracture dislocations, which are represented by systems of N–W oriented anticlines with interior portions of the anticlines composed of dolomites and exterior portions composed of schists. The orebodies are situated in steeply-dipping fracture zones in siltstones and in some wedge-shaped zones at the contact with the schungite schists.

The Srednyaya Padma deposit is 3 km long and consists of two orebodies with different amounts of V and U (Boitsov, 1997): the first orebody has a length of 1060 m, thickness 40–50 m, with an average V₂O₅ and UO₂ content of ~3 wt.% and 0.13 wt.%, respectively, whereas the second has a length of 1840 m, vertical size of 100–450 m and an average content of V₂O₅ and UO₂ of ~2.4 wt.% and 0.11 wt.%, respectively.

In accordance with Borozdin et al. (2014), the main minerals of the ore metasomatites are V- and Cr-micas (roscoelite, chromceladonite and Cr-bearing micas of the phengite series), which make up ~26% of all ores, carbonate marbles (dolomite and calcite), with ~21%, feldspars (albite, which usually prevails over other minerals with a mean content of ~37%), minor V–Cr alkaline pyroxenes (nabylite and Cr-bearing aegirine) and Cr-rich tourmalines.

The tourmaline studied was found in the Tzarevskoye uranium–vanadium deposit, ~14 km from the well-known Srednyaya Padma deposit. The Tzarevskoye deposit is situated in the anticline zone with cores of metamorphosed terrigenous–carbonate rocks in the cores and intensely brecciated, mylonitised and foliated metamorphosed siltstones at the margins of the folds. The tectonic activity was accompanied by hydrothermal–metasomatic and hypogene processes (Boitsov, 1997). The tourmaline sample occurs in micaceous metasomatites, associated with rosoelite, Cr-bearing phengite micas, quartz and dolomite. It forms dark-green to black pyramidal crystals up to 0.1 mm. A similar mineralogical association was observed for the chromium-dravite from the Velikaya Guba gold–copper–uranium occurrence (see below).

Experimental Methods

Electron-microprobe analysis
Electron-microprobe analyses of the present sample were obtained by a wavelength-dispersive spectrometer (WDS mode) using a CAMECA SX50 instrument at the Istituto di Geologia Ambientale e Geingegneria (CNR of Rome, Italy), operating at an accelerating potential of 15 kV and a sample current of 15 nA, with a 10 μm beam diameter. Minerals and synthetic compounds were used as standards as follows: wollastonite (Si and Ca), magnetite (Fe), rutile (Ti), corundum (Al), karelianite (V), fluorphlogopite (F), periclase (Mg), jadeite (Na), orthoclase (K), rhodonite (Mn), metallic Cr, Ni, Cu and Zn. Vanadium and Cr concentrations were corrected for interference from the TiKα and VKβ peaks, respectively. The PAP matrix correction procedure (Pouchou and Pichoir 1991) was applied to reduce the raw data. The results, which are summarised in Table 1, represent mean values of 4 spot analyses. In accordance with Pesquera et al. (2016), the Li₂O content was assumed to be insignificant as MgO > 2 wt.% is contained in the sample studied. Calcium, Mn, Fe and Ni were below the detection limits (0.03 wt.%).

Single-crystal structural refinement (SREF)
A pale green crystal fragment (0.037 mm × 0.042 mm × 0.052 mm) of the sample was mounted on an Oxford Gemini R Ultra diffractometer equipped with a Ruby CCD area detector at CrisDi (Interdepartmental Centre for the Research and Development of Crystallography, Turin, Italy) with graphite-monochromatised MoKα radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 5.3 cm. A total of 222 exposures (step = 1°, time/step = 48–478 s) with an average redundancy of ~6 was used. Data were integrated and corrected for Lorentz and polarisation background effects, using CrysAlisPro (Agilent Technologies, Version 1.171.36.20, release 27-06-2012 CrysAlisPro1.171.36.24). Refinement of the unit-cell parameters was based on 2304 measured reflections. The data were corrected for absorption using the multi-scan method (Scale3 ABSPACK). No violations of R3m symmetry were noted.

Structural refinement was done with the SHELXL-2013 program (Sheldrick, 2013). Starting coordinates were taken from Bosi et al. (2014a). Variable parameters were: scale factor, atomic coordinates, site scattering values and atomic-displacement factors. Attempts to refine the extinction coefficient yielded values within its standard uncertainty, thus it has not been refined. Neutral scattering factors were used for the cations and a fully
Table 1. Chemical composition for Cr-rich vanadio-oxy-dravite from the Tzarevskoye deposit, Russia.

| Element | wt.% | apfu |
|---------|------|------|
| SiO₂    | 34.58(39) | Si | 6.00 |
| TiO₂    | 0.11(6) | Ti³⁺ | 0.01 |
| B₂O₃*   | 10.02 | B | 3.00 |
| Al₂O₃   | 18.89(56) | Al | 3.86 |
| Cr₂O₃   | 9.93(68) | Cr³⁺ | 1.36 |
| V₂O₅    | 9.87(33) | V³⁺ | 1.37 |
| MgO     | 9.10(64) | Mg | 2.35 |
| CuO     | 0.18(13) | Cu²⁺ | 0.02 |
| ZnO     | 0.09(4) | Zn | 0.01 |
| Na₂O    | 2.85(5) | Na | 0.96 |
| K₂O     | 0.10(3) | K | 0.02 |
| F       | 0.31(14) | F | 0.17 |
| H₂O*    | 2.79 | OH | 3.23 |
| Total   | 98.66 |      | |

Notes: Errors for oxides are standard deviations (in parentheses) of 4 spot analyses; apfu = atoms per formula unit.

*Calculated by stoichiometry.

Results

Determination of atomic fractions

In agreement with the SREF results, the B content was assumed to be stoichiometric in the sample studied (B³⁺ = 3.00 atoms per formula unit, apfu). In fact, both the site-scattering results and the bond lengths of B and T are consistent with the B site fully occupied by B³⁺ and no amount of B³⁺ at the T site. The (OH) content can then be calculated by charge balance with the assumption (T + Y + Z) = 15.00 apfu and 31 anions. The atomic fractions were calculated on these assumptions (Table 1). The excellent match between the number of electrons per formula unit (epfu) derived from chemical and structural analysis supports this procedure: 268.90 and 267.95 epfu, respectively.

Determination of site populations and mineral formula

The anion site populations in the sample studied follow the general preference suggested for tourmaline (e.g. Henry et al., 2011): the O(3) site (Y position in the general formula) is occupied by (OH), while the O(1) site (W position in the general formula) can be occupied by O²⁻, (OH) and F. The T site is fully occupied by Si. The cation distribution at the Y and Z sites can be optimised according the procedure of Bosi et al. (2017b) and the ionic radii of Bosi (2018). In detail, the site distribution of Mg, Al, V³⁺ and Cr³⁺ was obtained by minimising the residuals between calculated and observed structural data (such as mean bond distance, site scattering expressed in terms of mean atomic number) by using a least-square approach. The minor amounts of Ti, Cu²⁺ and Zn were assumed fixed at the Y site. The resulting empirical crystal-chemical formula is

\[
X(N_0.96K_0.02) S_1.00 (V_{1.34Al_0.68Mg_0.09Cu_0.02Zn_0.01Ti_0.01})_S 23.00
\]

\[
Z(Al_{1.19}Cr_{1.36}V_{0.03}Mg_{0.12})_V S 5.60 (Si_{0.56}O_{1.39})_Y (BO_3)_3 V (OH)_3
\]  

\[
W(O_{0.60}(OH)_{0.23}F_{0.17})_W S 1.00
\]

The observed mean atomic number and mean bond length values and those calculated from the optimised site-populations are in excellent agreement (Table 5). This cation distribution is consistent with the studies of Bosi et al. (2017b) and Bosi (2018), which showed that the preference of Al³⁺, V³⁺ and Cr³⁺ for the Y and Z sites is controlled mainly by the cation size according to the sequence: \(X_{Y3+} > X_{Cr3+} > Al^{3+}\) and \(X_{Al3+} > Cr_{3+} > V_{3+}\). Because \(<Y-O>\) is always greater than \(<Z-O>\) in tourmaline, the Y site will in fact tend to incorporate relatively large cations, whereas the Z site will tend to incorporate relatively small cations. This trend is documented by the preference of V³⁺ over Cr³⁺ to dominate the Y site in the vanadio-oxy-chromium-dravite compositions. Compared to Al³⁺, V³⁺ prefers the Y site (and Al³⁺ the Z site) as observed in the vanadio-ox- oxy-dravite samples.

The optimised empirical formula can be recast in its ordered form for classification purposes (Henry et al., 2011) by ordering...
Table 3. Displacement parameters (Å²), fractional atom coordinates and site occupancy for Cr-rich vanadio-oxy-dravite from the Tzarevskoye deposit, Russia.

| Site  | x    | y    | z    | Site occupancy | U¹¹ | U¹² | U¹³ | U¹⁴ | U¹⁵ | U¹⁶ | U¹⁷/U¹⁶ | x     | y     | z    |
|-------|------|------|------|---------------|-----|-----|-----|-----|-----|-----|---------|-------|-------|------|
| X     | 0    | 0    | 0.2365(6) | Na⁹,bc,Mg³⁺⁰⁺ | 0.0921(26) | 0.0921(26) | 0.0226(2) | 0.0145(8) | 0.0281(14) |
| Y     | 0.1249(7) | 0.0624(8) | 0.6370(19) | M⁹,bc,Mg₂⁺⁺ | 0.0066(5) | 0.0058(4) | 0.0108(6) | -0.00061(18) | -0.0012(4) | 0.0033(2) | 0.0077(3) |
| Z     | 0.2383(5) | 0.2617(5) | 0.6113(18) | Al⁹,bc,Mg²⁺⁺ | 0.0055(3) | 0.0062(4) | 0.0073(4) | 0.0007(3) | -0.0001(3) | 0.0029(3) | 0.0063(2) |
| B     | 0.1093(18) | 0.2184(6) | 0.4562(7) | O     | 0.0052(13) | 0.0084(14) | 0.0032(19) | 0.0017(15) | 0.0008(8) | 0.0042(7) | 0.0052(8) |
| T     | 0.1309(5) | 0.1982(5) | 0.0724(8) | Si     | 0.0060(10) | 0.1220(12) | 0.4903(5) | 0.0085(10) | 0.0142(13) | 0.1036(16) | 0.0051(1) |
| O(1)  | 0.1728(5) | 0.2216(6) | 0.0724(8) | O     | 0.0060(10) | 0.1220(12) | 0.4903(5) | 0.0085(10) | 0.0142(13) | 0.1036(16) | 0.0051(1) |
| O(2)  | 0.1099(10) | 0.2681(14) | 0.4903(5) | O     | 0.0060(10) | 0.1220(12) | 0.4903(5) | 0.0085(10) | 0.0142(13) | 0.1036(16) | 0.0051(1) |
| O(3)  | 0.2599(2) | 0.1920(3) | 0.1120(3) | H     | 0.0060(10) | 0.1220(12) | 0.4903(5) | 0.0085(10) | 0.0142(13) | 0.1036(16) | 0.0051(1) |

*Equivalent (Ueq) and isotropic (Uiso) displacement parameters; H-atom was constrained to have a Uiso 1.2 times the Uiso value of the O(3) oxygen.

Discussion

Similar to other tourmaline groups, tourmaline from the Sludyanka crystalline complex (Lake Baikal), the vanadio-oxy-dravite sample studied is also strongly enriched in Cr. Karelia appears to be of major importance of the world in hosting tourmalines highly enriched in both Cr and V. In particular, the first description of chromium-dravite, ideally NaMg₃Cr₆(Si₆O₁₈)(BO₃)₃(OH)₃OH is from Karelia (Rumyantseva, 1983). More precisely, the holotype chromium-dravite specimen occurs in micaceous metasomatic clay-carbonate rocks from the Velikaya Guba gold–copper–uranium occurrence, Zaonezhye peninsula, Lake Onega, Karelia Republic, Northern Region, Russia. The Velikaya Guba occurrence is close to (~18 km) the Tzarevskoye deposit where the sample studied was found. The empirical formula of chromium-dravite (Rumyantseva, 1983) recast in its ordered form is as follows:

\[
\begin{align*}
X(Na⁹,bc,Mg³⁺⁰⁺) & \geq 0.03 \sum_{0.02}^{0.03} \times Y(Mg²⁺⁺,Ca²⁺,Zn⁰⁺⁺,Ti⁰⁺⁺) & \sum_{0.00}^{0.10} \\
Z(Al⁴⁺⁺₅⁺⁺,Cr⁴⁺⁺₅⁺⁺) & \geq 0.03 \sum_{0.00}^{0.03} \times Z(BO₃) & \sum_{0.00}^{0.03} \\
W(\text{O}⁺⁺,\text{OH}) & \geq 0.03 \sum_{0.01}^{0.03} \times F(\text{OH}) & \sum_{0.00}^{0.01} 
\end{align*}
\]

Both the empirical and ordered formulae are consistent with an oxy-tourmaline species belonging to the alkali group, subgroup 3 (Henry et al., 2011): Na-dominant at the X position of the tourmaline general formula and oxygen-dominant at the W position with O³⁺ > (OH⁺⁺). As V³⁺ is the dominant cation at Y and Al³⁺ is the dominant cation at Z along with relatively small amounts of Mg for formula electroneutrality (valency-imposed double-site occupancy; Bosi et al., 2019a), its end-member composition is NaV₅(SiAl₅O₁₈)(BO₃)₃(OH)₃O. As a result, the sample studied can be classified as Cr-rich vanadio-oxy-dravite.
(hydroxy-species) belonging to alkali subgroup 1. Compared to the sample studied, significant chemical differences at the octahedrally coordinated sites can be noted between the tourmalines from Karelia: the studied oxy-species \( (\text{WO} = 0.60 \text{ apfu}) \) has \( \text{Mg} = 2.05 \text{ apfu}, \text{Al} = 3.86 \text{ apfu}, \text{V} = 1.37 \text{ apfu} \) and \( \text{Cr} = 1.38 \text{ apfu} \), whereas the chromium-dravite hydroxy-species \( (\text{WOH} = 0.77 \text{ apfu}) \) has \( \text{Mg} = 2.57 \text{ apfu}, \text{Al} = 0.37 \text{ apfu}, \text{V} = 0.22 \text{ apfu}, \text{Cr} = 4.71 \text{ apfu} \) and \( \text{Fe}^{3+} = 1.18 \text{ apfu} \). These differences lead to the following \( (Y + Z) \) charge arrangements following Bosi et al. (2019b), \( Y^+Z(R^2^+_2R^3^+_7) \) for the oxy-species and \( Y^+Z(R^2^+_3R^3^+_6) \) for the hydroxy-species, which should be reflected in two different compositional diagrams for their classification. Recently, Henry and Dutrow (2018) proposed two ternary diagrams for the [6]Al–V–Cr subsystem and [6]Al–Cr–Fe\(^{3+}\) subsystem of the [6]Al–V–Cr–Fe\(^{3+}\) quaternary system to classify oxy-tourmalines \( (\text{WO}_{2} > 0.5 \text{ apfu}) \). It is worth noting that this diagram includes trivalent cations at both the \( Y \) and \( Z \) sites to remove issues of uncertainty associated with order–disorder across these sites.

In order to better show the chemical variability of oxy-tourmalines in the [6]Al–V–Cr–Fe\(^{3+}\) quaternary system, we have merged the diagrams [6]Al–Cr–V and [6]Al–Cr–Fe\(^{3+}\) through the edge [6]Al–Cr (Fig. 1). We made these ternaries because no tourmaline rich in both V and Fe\(^{3+}\) has been found so far.

With regard to the classification of hydroxy/fluor-tourmalines \( (\text{OH} + \text{F} > 0.5 \text{ apfu} \text{ at W}) \), the ternary diagram for the Al–Fe\(^{3+}\)–Cr subsystem (Fig. 2) of the Al–V–Cr–Fe\(^{3+}\) quaternary system is used (Henry et al., 2011). This diagram is based on occupancy of the Z site obtained from the tourmaline ordered formula, which also removes issues of uncertainty associated with order–disorder across the \( Y \) and \( Z \) sites as may occur for example between Fe\(^{2+}\)–Al in schorl (Andreozzi et al., 2020). In other words, the use of the diagrams in Figs 1 and 2 is equivalent to classifying tourmalines using only the chemical information of the \( Y \) and \( Z \) sites.

The plotted data in these diagrams (for a total 109 data sets) are from: Peltola et al. (1968); Foit and Rosenberg (1979); Nuber and Schmetzer (1979); Rumyantseva (1983); Gorskaya et al. (1987, 1989); Cavarretta and Puxeddu (1990); Grice et al. (1993); Grice and Ercit (1993); Žáček et al. 2000; Bosi et al. (2004, 2012, 2013a, b, 2014a, b, 2017a, b); Ertl et al. (2008, 2016); Arif et al. (2010), in which Fe was considered +3 as suggested by the authors; Baksheev et al. (2011); Lupulescu and Rowe (2011); Rozhdestvenskaya et al. (2011); Cempírek et al. (2013); Reznitskii et al. (2014) and Vereshchagin et al. (2014).

The position of Cr-rich vanadio-oxy-dravite from the Tzarëvskoye uranium–vanadium deposit close to the chromo-alumino-povondraite boundary is shown in Fig. 1.
Moreover, the complete chemical variability of the \([6]Al–Cr–V\) oxy-tourmalines can be compared to the only chemical variability of \(Fe^3+\) occurring along the oxy-dravite–bosite–povondraite series. From a nomenclature viewpoint, the range of the oxy-tourmaline compositions is valid for most of the oxy-tourmalines classified by considering the actual cation distributions over the \(Y\) and \(Z\) sites as overriding information for the definition of a tourmaline species (Henry et al., 2013). The only exception regards one of the two samples described by Bosi et al. (2012) as oxy-chromium-dravite, which falls in the chromo–alumino–povondraite field. Also note that the \(V\)-bearing tourmaline from Silver Knob, California, USA (Foit and Rosenberg, 1979) is classified as \(V\)-rich oxy-dravite (Fig. 1).

The position of the chromium-dravite from the Velikaya Guba gold–copper–uranium occurrence (Rumyantseva, 1983) with respect to the other \(Cr-Fe^{3+}\) hydroxy-tourmalines from the literature is shown in Fig. 2. This figure shows the occurrence of a complete chemical variability along the dravite–chromium–dravite series and a partial variability from dravite to the hypothetical end-member \(NaMg_3Fe_3^+(Si_6O_{18})(BO_3)_3(OH)_2OH\) of the samples from Larderello geothermal field, Italy (Cavarretta and Puxeddu, 1990). However, it should be noted that in all the oxy- and hydroxy-tourmalines plotted in Figs 1 and 2 the oxidation state of Fe has always been assumed to be +3 by the various authors, except for the \(Fe^2+\)–chromo–alumino–povondraite from the Studyanka crystalline complex, Russia (Bosi et al., 2013b). The latter was characterised by Mössbauer spectroscopy resulting in \(Fe^2+/Fe^{3+} = 2.49\) wt.% and \(FeO = 1.05\) wt.%. To date, this is the only experimental information confirming the presence of \(Fe^{3+}\) in \(Cr\)-tourmalines (at least the 80% of the \(Fe^{3+}/\Sigma Fe_{tot}\)).

**Conclusions**

A classification scheme that disregards details of ion ordering, which typically require techniques that are uncommonly realised in the geosciences community (e.g. crystal structure refinements) is desirable. In this regard, the tourmaline ordered formula would best assist mineralogists and petrologists in identifying tourmaline species. The tourmaline nomenclature can be simplified further by merging the chemical information over the \(Y\) and \(Z\) sites that results in \([6]Al–Cr–Fe^{3+}\) diagrams.

This study describes the second world-occurrence of the rare vanadio-oxy-dravite from the Tzarevskoye uranium–vanadium deposit, Lake Onega, Karelia Republic, Russia, along with the first world-occurrence of chromium-dravite from the relatively close Velikaya Guba gold–copper–uranium occurrence. These provided an excellent opportunity to use the new \([6]Al–V–Cr–Fe^{3+}\) diagrams for the tourmaline classification. This approach has also been successfully applied to other oxy- and hydroxy-Al-tourmalines rich in \(V–Cr–Fe^{3+}\) from the literature. Results show the robust classification of tourmalines by using only the chemical data.

**Supplementary material.** To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2020.77

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