REVISION 1

Vanadio-oxy-dravite, $NaV_3(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$, a new mineral species of the tourmaline supergroup

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ABSTRACT

Vanadio-oxy-dravite, $NaV_3(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$, is a new mineral of the tourmaline supergroup. It is found in metaquartzites of the Pereval marble quarry (Sludyanka, Lake Baikal, Russia) in association with quartz, Cr-V-bearing tremolite and mica, diopside – kosmochlor – natalyite, Cr-bearing goldmanite, escolaite – karelianite, dravite – oxy-vanadium-dravite, V-bearing titanite and rutile, ilmenite, oxyvanite – berdesinskiite, shreyerite, plagioclase, scapolite, zircon, pyrite and an unnamed oxide of V, Cr, Ti, U and Nb. Crystals are green, transparent with a vitreous luster, pale green streak and conchoidal fracture. Vanadio-oxy-dravite has a Mohs hardness of approximately 7½, and a calculated density of 3.14 g/cm^3. In plane polarized light, vanadio-oxy-dravite is pleochroic (O = yellow green and E = pale olive green) and uniaxial negative: ω = 1.693(5), ε = 1.673(5) Vanadio-oxy-dravite is rhombohedral, space group *R*3*m*, with the unit-cell parameters *a* = 16.0273(3), *c* = 7.2833(1) Å, *V* = 1620.24(5) Å^3, *Z* = 3. Crystal-chemical analysis resulted in the empirical structural formula:

$^{X}(Na_{0.70}Ca_{0.23}\square_{0.05}K_{0.02})_{\Sigma 1.00}\ ^{Y}(V^{3+}_{1.39}Mg_{1.16}Al_{0.35}Fe^{3+}_{0.04}Ti^{4+}_{0.04}\ Fe^{2+}_{0.02})_{\Sigma 3.00}$
$^{Z}(Al_{3.74}Mg_{1.28}V^{3+}_{0.78}Cr^{3+}_{0.20})_{\Sigma 6.00}\ ^{T}(Si_{6.00}O_{18})\ ^{B}(BO_3)_3\ ^{V}(OH)_3\ ^{W}[O_{0.74}(OH)_{0.26}]_{\Sigma 1.00}$.

The crystal structure of vanadio-oxy-dravite was refined to an *R*1 index of 1.70% using 1800 unique reflections collected with Mo*K*α X-radiation. Ideally, vanadio-oxy-dravite is related to oxy-dravite and oxy-vanadium-dravite by the homovalent substitution $V^{3+} \leftrightarrow Al^{3+}$. Tourmaline with chemical compositions classified as vanadio-oxy-dravite can be either Al-dominant or V-dominant as a result of the compositional boundaries along the solid solution between Al and V^{3+} that are determined at $^{Y+Z}(V_{1.5}Al_{5.5})$, corresponding to $Na^{Y}(V_{1.5}Al_{1.5})^{Z}(Al_4Mg_2)Si_6O_{18}(BO_3)_3(OH)_3O$, and $^{Y+Z}(V_5Al_2)$, corresponding to $Na^{Y}(V_3)^{Z}(V_2Al_2Mg_2)Si_6O_{18}(BO_3)_3(OH)_3O$.

INTRODUCTION

The tourmaline supergroup minerals are widespread, occurring in sedimentary, igneous and metamorphic rocks (Dutrow and Henry 2011). They are important indicator minerals that can provide information on the compositional evolution of their host rocks, chiefly due to their ability to incorporate a large number of elements (e.g., Novák et al. 2004; Agrosì et al. 2006; Lussier et al. 2011a; Novák et al. 2011; van Hinsberg et al. 2011; Bačík et al. 2012). However, the chemical composition of tourmalines is also controlled by short-range and long-range constraints (e.g., Hawthorne 1996, 2002a; Bosi and Lucchesi 2007; Bosi 2010, 2011; Henry and Dutrow 2011; Skogby et al. 2012; Bosi 2013) as well as by temperature (van Hinsberg and Schumacher 2011). Tourmaline supergroup minerals are complex borosilicates and their crystal structure and crystal chemistry have been extensively studied (e.g., Foit 1989; Hawthorne and Henry 1999; Bosi and Lucchesi 2007; Lussier et al. 2008; Bosi 2008; Bosi et al. 2010; Lussier et al. 2011b; Filip et al. 2012). In accordance with Henry et al. (2011), the general formula of tourmaline may be written as: $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, where X (≡ $^{[9]}X$) = Na^{+}, K^{+}, Ca^{2+}, □ (=vacancy); Y (≡ $^{[6]}Y$) = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Li^{+}; Z (≡ $^{[6]}Z$) = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}; T (≡ $^{[4]}T$) = Si^{4+}, Al^{3+}, B^{3+}; B (≡ $^{[3]}B$) = B^{3+}; W (≡ $^{[3]}O1$) = OH^{1-}, F^{1-}, O^{2-}; V (≡ $^{[3]}O3$) = OH^{1-}, O^{2-} and where, for example, T represents a group of cations (Si^{4+}, Al^{3+}, B^{3+}) accommodated at the [4]-coordinated *T* sites. The dominance of these ions at one or more sites of the structure gives rise to a range of distinct mineral species.

Recently, several new minerals of the tourmaline supergroup were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the

International Mineralogical Association (IMA). Among these are a number of oxy-tourmalines related by complete solid solution in the Al^{3+}-Cr^{3+}-V^{3+} subsystem: oxy-dravite, end-member formula $NaAl_3(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$ (IMA 2012-004a; Bosi and Skogby 2013), oxy-chromium-dravite, $NaCr_3(Cr_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$ (IMA 2011-097; Bosi et al. 2012a); oxy-vanadium-dravite, $NaV_3(V_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$ (IMA 11-E; Bosi et al. 2013a).

A new species of oxy-tourmaline, vanadio-oxy-dravite, has been approved by the IMA-CNMNC (proposal no. 2012-074). The holotype specimen (sample PR73) is deposited in the collections of the Museum of Mineralogy, Earth Sciences Department, Sapienza University of Rome, Italy, catalogue number 33068. A formal description of the new species vanadio-oxy-dravite is presented here, including a full characterization of its physical, chemical and structural properties.

OCCURRENCE, APPEARANCE AND PHYSICAL AND OPTICAL PROPERTIES

The crystals of vanadio-oxy-dravite are green and occur in metaquartzites in the Pereval marble quarry, Sludyanka crystalline complex, Southern Baikal region, Russia (51°37'N 103°38'E). The Pereval quarry is the type locality (see Bosi et al. 2012a for a more detailed description) for natalyite, florensovite, kalininite, magnesiocoulsonite, oxy-vanadium-dravite, oxy-chromium-dravite, vanadio-oxy-chromium-dravite, chromo-alumino-povondraite, batisivite, oxyvanite and cuprokalininite. Minerals associated with the holotype specimen are: quartz, Cr-V-bearing tremolite and muscovite-celadonite, diopside – kosmochlor – natalyite, Cr-bearing goldmanite, escolaite – karelianite, dravite, V-bearing titanite and rutile, ilmenite, oxyvanite – berdesinskiite, shreyerite, plagioclase, scapolite, zircon, pyrite and an unnamed oxide of V, Cr, Ti, U and Nb, The host rocks (quartz-diopside) are Cr-V-bearing carbonate-siliceous sediments, metamorphosed to granulite facies and partly diaphtorized (Salnikova et al. 1998) to amphibolite facies (retrograde stage). Vanadio-oxy-chromium-dravite was formed in the prograde stage (granulite facies). The crystals are euhedral, reaching up to 0.3 mm in length, and may be chemically zoned (for details, see Figure 3 of Bosi et al. 2013a), but homogeneous crystals also occur.

The morphology of vanadio-oxy-dravite consists of elongated $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ prisms terminated by a prominent {0001} pedion and small, minor $\{10\bar{1}1\}$ pyramidal faces.

Crystals are green, with pale green streak, transparent and display vitreous luster. They are brittle and show conchoidal fracture. The Mohs hardness is approximately 7½ (Reznitsky et al. 2001). The calculated density is 3.14 g/cm^3. In transmitted light, vanadio-oxy-dravite is pleochroic with O = yellow green and E = pale olive green. Vanadio-oxy-dravite is uniaxial negative with refractive indices, measured by the immersion method using white light from a tungsten source, of ω = 1.693(5), ε = 1.673(5). The mean index of refraction, density and chemical composition lead to excellent compatibility indices ($1 - K_p/K_c = 0.026$) (Mandarino 1976, 1981)

METHODS

Single-crystal structural refinement

A representative fragment of the type specimen was selected for X-ray diffraction measurements on a Bruker KAPPA APEX-II single-crystal diffractometer, at Sapienza University of Rome (Earth Sciences Department), equipped with a CCD area detector (6.2 × 6.2 cm^2 active detection area, 512 × 512 pixels) and a graphite crystal monochromator, using Mo*K*α radiation from a fine-focus sealed X-ray tube. The sample-to-detector distance was 4 cm. A total of ca. 3265 exposures (step = 0.2°, time/step = 20 s) covering a full reciprocal sphere with a redundancy of about 8 was used. Final unit-cell parameters were refined by means of the Bruker AXS SAINT program using reflections with $I > 10\ \sigma(I)$ in the range $5° < 2\theta < 73°$. The intensity data were processed and corrected for Lorentz, polarization, and background effects with the APEX2 software program of Bruker AXS. The data were corrected for absorption using the multi-scan method (SADABS). The absorption correction led to a significant improvement in R_{int}. No violations of *R*3*m* symmetry were noted.

Structural refinement was done with the SHELXL-97 program (Sheldrick 2008). Starting coordinates were taken from Bosi et al. (2004). Variable parameters were: scale factor, extinction coefficient, atomic coordinates, site scattering values and atomic-displacement factors. To obtain the best values of statistical indexes (*R*1, *wR*2), a fully ionized scattering curve for O was used, whereas neutral scattering curves were used for the other atoms. In detail, the occupancy of the *X* site was modeled by using the sodium scattering factor, the *Y* site vanadium and magnesium scattering factors, and the *Z* site using vanadium and aluminum factors. The *T* and *B* sites were modeled, respectively, with Si and B scattering factors and with a fixed occupancy of 1, because refinement with unconstrained occupancies

showed no significant deviations from this value. Three full-matrix refinement cycles with isotropic-displacement parameters for all atoms were followed by anisotropic cycles until convergence was attained. No significant correlations over a value of 0.7 between the parameters were observed at the end of refinement. Table 1 lists crystal data, data-collection information and refinement details; Table 2 gives the fractional atomic coordinates and site occupancies; Table 3 gives the displacement parameters; Table 4 gives selected bond distances.

X-ray powder diffraction

Powder X-ray data were was derived from the single-crystal structural refinement since the available sample material was not sufficient for X-ray powder diffraction measurements. Data are listed in Table 5.

Electron-Microprobe analysis

Electron-microprobe analyses of the crystal used for X-ray diffraction refinement were obtained by 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 and a sample current of 15 nA, 10 μm beam diameter. Minerals and synthetic compounds were used as standards: wollastonite (Si, Ca), magnetite (Fe), rutile (Ti), corundum (Al), vanadinite (V) fluorphlogopite (F), periclase (Mg), jadeite (Na), K-feldspar (K), sphalerite (Zn), metallic Cr, Mn and Cu. The overlap corrections and the PAP routine were applied (Pouchou and Pichoir 1991). The results (Table 6) represent mean values of 10 spot analyses. In accord with the very low concentration of Li in dravitic samples (e.g., Henry et al. 2011), the Li_2O content was assumed to be insignificant. Manganese, Zn, Cu and F were below their respective detection limits (0.03 wt%) in the studied sample.

Infrared spectroscopy

A homogeneous vanadio-oxy-dravite crystal was measured by Fourier transform infrared (FTIR) absorption spectroscopy to characterize (OH) absorption bands in the wavenumber range 2000-5000 cm^{-1} using a Bruker Equinox 55 spectrometer equipped with a NIR source, a CaF_2 beam-splitter, a wire-grid polarizer and an InSb detector. Polarized spectra with a resolution of 4 cm^{-1} were acquired parallel and perpendicular to the crystallographic **c**-

axis direction using a circular measurement area of 100 μm diameter on a 36 μm thick doubly-polished crystal plate that had been oriented parallel the **c**-axis by morphology and optical microscopy. As often observed, fundamental (OH) absorption bands polarized parallel to the **c**-axis direction of tourmalines are exceptionally intense, and it was not possible to thin the sample sufficiently to avoid off-scale absorption intensity for the strongest band (Fig. 1).

Optical absorption spectroscopy

Polarized, room-temperature optical-absorption spectra were recorded on the same 36 μm thick crystal platelet used for the FTIR measurements. The spectra were measured in the range 270-1100 nm (37037-9091 cm^{-1}) at a resolution of 1 nm using an AVASPEC-ULS2048X16 spectrometer attached via a 400 μm UV optical fiber to a Zeiss Axiotron UV-microscope. A 75 W Xenon arc lamp served as illuminating source and Zeiss Ultrafluar 10x lenses served as objective and condenser. A UV-quality Glan-Thompson prism with a working range from 250 to 2700 nm (40000 to 3704 cm^{-1}) was used as polarizer. The size of the circular measure aperture was 64 μm in diameter. The wavelength scale of the spectrometer was calibrated against Ho_2O_3 doped and Pr_2O_3/Nd_2O_3 doped standards (Hellma glass filters 666F1 and 666F7) with an accuracy better than 15 cm^{-1} in the wavelength range 300-1100 nm. Recorded spectra were fitted using the Jandel PeakFit 4.12 software assuming Gaussian peak shapes.

RESULTS AND DISCUSSION

General comment

The present crystal-structure refinement and electron-microprobe analyses were obtained from the same single crystal. However, complementary optical and spectroscopic data were recorded from coexisting crystals. Small differences in composition are likely to occur between these crystals.

Determination of atomic proportions

In agreement with the structural-refinement results, the boron content was assumed to be stoichiometric in the vanadio-oxy-dravite sample (B^{3+} = 3.00 apfu). Both the site-scattering results and the bond lengths of *B* and *T* are consistent with the *B* site fully occupied by boron and no amount of B^{3+} at the *T* site (e.g., Hawthorne 1996; Bosi and Lucchesi 2007). In line

with the optical absorption results, which show the occurrence of both Fe^{2+} and Fe^{3+} (see below), the Fe contents were calculated on the basis of $Fe^{3+}/\Sigma Fe = 0.68$, measured by Mössbauer spectroscopy (Bosi et al. 2013b) for a Fe-bearing chromo-alumino-povondraite coming from the same locality as the present sample. Note that due to the relatively low concentrations of Fe, uncertainty on its oxidation state has little influence on the overall charge calculations. The (OH) content can then be calculated by charge balance with the assumption $T + Y + Z = 15.00$. The atomic proportions were calculated on this assumption (Table 6). The excellent match between the number of electrons per formula unit (epfu) derived from chemical and structural analysis supports this procedure, respectively: 251.2 epfu and 251.3 epfu.

Site populations

The anion site populations in the studied sample follow the general preference suggested for tourmaline (e.g., Grice and Ercit 1993; Henry et al. 2011): the O3 site (V position in the general formula) is occupied by (OH), and the O1 site (W position in the general formula) is occupied by O^{2-} and (OH). The cation distribution at the *T*, *Y* and *Z* sites was optimized by using a quadratic program to minimize the residuals between calculated and observed data (based on the chemical and structural analysis). Site-scattering values, octahedral and tetrahedral mean bond-distances (i.e., <*Y*-O>, <*Z*-O> and <*T*-O>) were calculated as the linear contribution of each cation multiplied by its ideal bond-distance (Table 7). More details about the ideal distances as well as about the optimization procedure may be found in Bosi et al. (2004) and Bosi and Lucchesi (2004; 2007). The robustness of this approach was confirmed by another optimization procedure (Wright et al. 2000), which led to very similar cation distributions (Table 7). This result represents another example of convergence of these two procedures to similar solutions for tourmaline (e.g., Bosi and Lucchesi 2007; Filip et al. 2012; Bosi et al. 2012a, 2013a).

The final structural formulae are as follows:

$^{X}(Na_{0.70}Ca_{0.23}\square_{0.05}K_{0.02})_{\Sigma 1.00}\ ^{Y}(V^{3+}_{1.39}Mg_{1.16}Al_{0.35}Fe^{3+}_{0.04}Ti^{4+}_{0.04}\ Fe^{2+}_{0.02})_{\Sigma 3.00}$

$^{Z}(Al_{3.74}Mg_{1.28}V^{3+}_{0.78}Cr^{3+}_{0.20})_{\Sigma 6.00}\ ^{T}(Si_{6.00}O_{18})\ ^{B}(BO_3)_3\ ^{V}(OH)_3\ ^{W}[O_{0.74}(OH)_{0.26}]_{\Sigma 1.00}$.

The bond-valence analysis is consistent with the optimized structural formulae. Bond-valence calculations, using the formula and bond-valence parameters from Brown and Altermatt (1985), are reported in Table 8.

Name and crystal chemistry

The chemical composition of sample PR73 is consistent with tourmalines belonging to the alkali group, oxy-subgroup 3 (Henry et al. 2011). They are Na-dominant at the *X* site, oxygen-dominant at W with $O^{2-} > (OH+F)^{1-}$. As V^{3+} is the dominant cation at *Y* and Al^{3+} is the dominant cation at *Z*, its end-member composition may be represented as $NaV_3(Al_4Mg_2)Si_6O_{18}(BO_3)_3(OH)_3O$. This is in accord with the dominant-valency rule (Hatert and Burke 2008) for which the dominant ion of the dominant valency at one site becomes the basis for naming the species. As no tourmalines have yet been reported with V^{3+}- and Al^{3+}-dominant at *Y* and *Z*, respectively, this tourmaline can be classified as a new species. The closest end-member composition of a valid tourmaline species is that of oxy-dravite. The name vanadio-oxy-dravite may hence be assigned for the chemical composition, following Henry et al. (2011). The prefix *vanadio* represents the substitution of $3V^{3+}$ for 3Al in the root composition of oxy-dravite.

Although there exists a significant degree of V^{3+}, Al and Mg disorder over the *Y* and *Z* sites, the structural formula of sample PR73 indicates a clear preference of V^{3+} for the *Y* site and Al for the *Z* site, while Mg shows only a slight preference for the *Z* site. Chromium, on the other hand, seems completely ordered at the *Z* site. The O1 site is dominated by O^{2-} with a relatively minor concentration of (OH). The presence of only minor concentrations of (OH) at O1 (~ 0.26 apfu) are consistent with both the observation of weak absorption bands at 3761 and 3732 cm^{-1} in the infrared spectrum (Fig. 1), i.e. the area typically ascribed to the O1 site (see below), and the equation proposed by Bosi (2013) to estimate the (OH) contents in tourmaline: $^{W}(OH) = [2 - 1.01 \cdot BVS(O1) - 0.21 - F] = 0.27$ apfu.

End-member formula

Although the amount of Mg at *Z* is larger than that at *Y* (1.28 and 1.16 apfu, respectively), the formula of vanadio-oxy-dravite may also be approximated as $Na^{Y}(V^{3+}{}_2Mg)^{Z}(Al_4MgV^{3+})(Si_6O_{18})(BO_3)_3(OH)_3O$. Such a formula could represent the structural formula for vanadio-oxy-dravite, but is not an end-member formula. In fact, this composition has multiple cations at more than one site (i.e., V^{3+} and Mg over *Y* and *Z*), and hence is inconsistent with the characteristics of an ordered end-member formula as defined by Hawthorne (2002b). The most ordered site allocation of V^{3+}, Al and Mg consistent with the empirical formula and the end-member definition is $Na^{Y}(V_3)^{Z}(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$.

Note that the difference between these two formulae is solely in V^{3+}-Mg order-disorder; no difference occurs in chemical composition.

Infrared spectroscopy

Spectra recorded in polarized mode perpendicular and parallel to the crystallographic **c** axis show an intense broad band around 3550 cm^{-1} and two weaker bands at 3732 and 3761 cm^{-1}, all strongly polarized in the **c** direction (Fig. 1). As it was not possible to thin the sample sufficiently to avoid off-scale absorption for the main band, any possible fine structure cannot be discerned. However, in line with previous studies (Bosi et al. 2012b; Bosi et al. 2013b), the band can be related to the local arrangement ($^{Y}V^{3+}\,^{Z}R\,^{Z}R$)-O3, i.e., to the occurrence of (OH) at the V position of the tourmaline general formula (O3 site in the structure). The two weaker bands at ca. 3732 and 3761 cm^{-1} are consistent with the minor concentrations of (OH) (ca. 0.3 apfu) assigned to the W position (O1 site in the structure), and may be related to the local arrangements ^{Y}(Mg Mg Mg) and ^{Y}(Mg Mg R) (cf. Gonzalez-Carreño et al. 1988; Bosi et al. 2012b; Bosi et al. 2013b).

Optical-absorption spectroscopy

The optical spectra of vanadio-oxy-dravite show two broad absorption bands at ca. 432 and 609 nm, superimposed on an intense UV absorption edge (Fig. 3). These absorption bands are ascribed to spin-allowed *d*-*d* transitions in octahedrally coordinated V^{3+}, in accord with similar bands observed for vanadio-oxy-chromium-dravite (Bosi et al. 2012c) at ca. 440 and 610 nm. In addition to the dominant V^{3+}-bands, two broad but weak absorption bands at ca. 765 and 1100 nm are observed in the **E**||**a**-spectrum. They are in accord with previous studies on the optical spectra of tourmaline (e.g., Smith 1978; Taran et al. 1993; Mattson and Rossman 1987) and are ascribed to electronic transitions in Fe^{2+}-Fe^{3+} pairs. Consequently, the appearance of these absorption bands suggests that a small fraction of the total iron in the present sample occurs in the divalent state.

COMPOSITIONAL BOUNDARIES OF VANADIO-OXY-DRAVITE

The plot of the *Z*- and *Y*-site cations in the ternary diagram for the Al-Cr-V^{3+} subsystem show, of course, that vanadio-oxy-dravite is ^{Z}Al-dominant and $^{Y}V^{3+}$-dominant.

More interesting, however, is the triangular plot in terms of Al-Cr-V^{3+} at *Y* and *Z*, showing that vanadio-oxy-dravite can be either Al-dominant or V^{3+}-dominant (Fig. 3). This latter plot type displays the occurrence of three end-members along the full solid solution between the Al^{3+} and V^{3+} apices: oxy-dravite, vanadio-oxy-dravite and oxy-vanadium-dravite. These end-members are related by the substitution $V^{3+} \leftrightarrow Al^{3+}$ at the Y position (vanadio-oxy-dravite ↔ oxy-dravite) and $V^{3+} \leftrightarrow Al^{3+}$ at the Z position (oxy-vanadium-dravite ↔ vanadio-oxy-dravite), while their compositional boundaries are at: (1) $^{Y+Z}(V_5Al_2)$, corresponding to $Na^{Y}(V_3)^{Z}(V_2Al_2Mg_2)Si_6O_{18}(BO_3)_3(OH)_3O$; (2) $^{Y+Z}(V_{1.5}Al_{5.5})$, corresponding to $Na^{Y}(V_{1.5}Al_{1.5})^{Z}(Al_4Mg_2)Si_6O_{18}(BO_3)_3(OH)_3O$. Consequently, oxy-dravite is characterized by V^{3+} contents less than 1.5 apfu, vanadio-oxy-dravite is characterized by V^{3+} contents between 5 and 1.5 apfu, and oxy-vanadium-dravite is characterized by V^{3+} contents larger than 5 apfu.

The discovery of the new mineral vanadio-oxy-dravite provides new information on the crystal chemistry of the tourmaline supergroup. The current chemical data supports complete exchange of V^{3+}, Cr^{3+} and Al in species of the tourmaline supergroup (Reznitsky et al. 2001; Bosi et al. 2004, 2013a,b), and it shows that vanadio-oxy-dravite can be either V^{3+}-dominant or Al-dominant.

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Table 1. Single-crystal X-ray diffraction data: details for vanadio-oxy-dravite

Sample	PR73
Crystal size (mm)	$0.10 \times 0.16 \times 0.24$
a (Å)	16.0273(3)
c (Å)	7.2833(1)
V (Å^3)	1620.24(5)
Range for data collection, 2θ (°)	5 - 73
Reciprocal space range *hkl*	$-21 \le h \le 25$
	$-23 \le k \le 26$
	$-12 \le l \le 11$
Total number of frames	3265
Set of measured reflections	7988
Unique reflections, R_{int} (%)	1800, 2.10
Redundancy	8
Absorption correction method	SADABS
Refinement method	Full-matrix last-squares on F^2
Structural refinement program	SHELXL-97
Extinction coefficient	0.00007(1)
Flack parameter	0.06(2)
*wR*2 (%)	3.81
*R*1 (%) all data	1.70
*R*1 (%) for $I > 2\sigma(I)$	1.65
GooF	1.060
Largest diff. peak and hole (±e$^-$/Å^3)	0.40 and –0.30

Notes: R_{int} = merging residual value; *R*1 = discrepancy index, calculated from *F*-data; *wR*2 = weighted discrepancy index, calculated from F^2-data; GooF = goodness of fit; Diff. Peaks = maximum and minimum residual electron density. Radiation, Mo*K*α = 0.71073 Å. Data collection temperature = 293 K. Space group *R*3*m*; *Z* = 3.

TABLE 2. Fractional atom coordinates and site occupancy for vanadio-oxy-dravite

Site	*x*	*y*	*z*	Site occupancy
X	0	0	0.22772(15)	$Na_{1.137(6)}$
Y	0.12347(2)	0.061737(12)	0.63625(6)	$V_{0.513(4)}$ $Mg_{0.487(4)}$
Z	0.29820(2)	0.26190(2)	0.61148(6)	$Al_{0.852(3)}V_{0.148(3)}$
B	0.11004(6)	0.22007(12)	0.4539(2)	$B_{1.00}$
T	0.191020(18)	0.189344(19)	0.000	$Si_{1.00}$
O1 (≡W)	0	0	0.7691(3)	$O_{1.00}$
O2	0.06078(4)	0.12157(8)	0.48340(16)	$O_{1.00}$
O3 (≡V)	0.26119(9)	0.13059(4)	0.51120(17)	$O_{1.00}$
O4	0.09258(4)	0.18516(8)	0.07085(16)	$O_{1.00}$
O5	0.18236(8)	0.09118(4)	0.09011(16)	$O_{1.00}$
O6	0.19403(5)	0.18472(5)	0.77971(12)	$O_{1.00}$
O7	0.28367(5)	0.28332(5)	0.07786(11)	$O_{1.00}$
O8	0.20860(5)	0.26946(6)	0.44063(12)	$O_{1.00}$
H3	0.2565(16)	0.1283(8)	0.393(3)	$H_{1.00}$

TABLE 3. Displacement parameters ($Å^2$) for vanadio-oxy-dravite

Site	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq}/U_{iso}*
X	0.0149(4)	0.0149(4)	0.0158(5)	0.000	0	0.00743(18)	0.0152(3)
Y	0.00704(16)	0.00604(13)	0.00951(17)	-0.00095(5)	-0.00189(10)	0.00352(8)	0.00742(10)
Z	0.00619(13)	0.00663(13)	0.00729(12)	0.00037(9)	-0.00002(9)	0.00314(10)	0.00673(8)
B	0.0075(4)	0.0083(6)	0.0088(6)	0.0008(5)	0.0004(2)	0.0041(3)	0.0081(3)
T	0.00521(12)	0.00494(11)	0.00708(12)	-0.00055(9)	-0.00045(9)	0.00252(9)	0.00575(6)
O1	0.0104(5)	0.0104(5)	0.0077(8)	0.000	0	0.0052(2)	0.0095(3)
O2	0.0088(3)	0.0052(4)	0.0120(5)	0.0014(3)	0.00071(17)	0.0026(2)	0.0091(2)
O3	0.0179(5)	0.0139(4)	0.0061(5)	0.00053(19)	0.0011(4)	0.0089(3)	0.0122(2)
O4	0.0084(3)	0.0162(5)	0.0094(5)	-0.0009(4)	-0.00045(19)	0.0081(3)	0.0104(2)
O5	0.0158(5)	0.0078(3)	0.0097(5)	0.00071(19)	0.0014(4)	0.0079(3)	0.01019(19)
O6	0.0102(3)	0.0085(3)	0.0068(3)	-0.0014(2)	-0.0008(2)	0.0053(3)	0.00825(13)
O7	0.0079(3)	0.0069(3)	0.0101(3)	-0.0008(2)	-0.0028(3)	0.0014(3)	0.00929(14)
O8	0.0045(3)	0.0097(3)	0.0178(4)	0.0025(3)	0.0009(3)	0.0029(3)	0.01094(15)
H3							0.018*

Notes: Equivalent (U_{eq}) and isotropic (U_{iso}) displacement parameters; H-atom was constrained to have a U_{iso} 1.5 times the U_{eq} value of the O3 oxygen.

TABLE 4. Selected bond distances (Å) for vanadio-oxy-dravite

B-O2	1.384(2)	*Y*-O1	1.9682(10)
B-O8^{A} ($\times$ 2)	1.3715(11)	*Y*-O2^{B} ($\times$ 2)	2.0327(8)
<*B*-O>	1.376	*Y*-O3	2.1174(12)
		Y-O6^{C} ($\times$ 2)	2.0066(8)
T-O4	1.6292(5)	<*Y*-O>	2.027
T-O5	1.6453(5)		
T-O7	1.5995(7)	*Z*-O3	2.0164(6)
*T**-O6	1.6080(9)	*Z*-O6	1.9374(8)
<*T*-O>	1.620	*Z*-O8^{E}	1.9178(8)
		Z-O7^{E}	1.9349(8)
X-O2^{B,F} ($\times$ 3)	2.5129(13)	*Z*-O7^{D}	1.9836(8)
X-O4^{B,F} ($\times$ 3)	2.8126(13)	*Z*-O8	1.9492(8)
X-O5^{B,F} ($\times$ 3)	2.7223(12)	<*Z*-O>	1.957
<*X*-O>	2.683	O3-H	0.86(2)

Notes: Standard uncertainty in parentheses. Superscript letters: A = (*y* – *x, y, z)*; B = (*y* – *x*, – *x, z*); C = (*x, x* – *y, z*); D = (*y* – *x* + 1/3, – *x* + 2/3, *z* + 2/3); E = (–*y* + 2/3, *x* – *y* + 1/3, *z* + 1/3); F = (–*y, x* – *y, z*). Transformations relate coordinates to those of Table 2.

* Positioned in adjacent unit cell.

TABLE 5. Simulated X-ray powder diffraction data for vanadio-oxy-dravite (λ = 1.5418 Å)

I_{calc} > 9 (%)	d_{calc} (Å)	*h*	*k*	*l*
37	6.4467	1	0	1
19	5.0153	0	2	1
19	4.6185	3	0	0
52	4.2606	2	1	1
66	4.0041	2	2	0
47	3.5221	0	1	2
10	3.0317	4	1	0
67	2.9928	1	2	2
100	2.5958	0	5	1
15	2.3970	2	3	2
15	2.3594	5	1	1
13	2.2091	5	0	2
12	2.1500	0	3	3
11	2.0763	2	2	3
43	2.0573	1	5	2
28	1.9340	3	4	2
20	1.6756	0	6	3
13	1.6520	2	7	1
17	1.6025	5	5	0
15	1.5226	0	5	4
15	1.4704	5	1	4
10	1.4232	4	3	4

Notes: *I* = calculated intensity, *d* = calculated interplanar spacing; *hkl* = reflection indices.

TABLE 6. Chemical composition of vanadio-oxy-dravite

	Weight %		apfu
SiO_2	35.34(17)	Si	6.00(3)
TiO_2	0.29(4)	Ti^{4+}	0.037(5)
B_2O_3*	10.23	B	3.00
Al_2O_3	20.36(37)	Al	4.08(6)
Cr_2O_3	1.48(28)	Cr^{3+}	0.20(4)
V_2O_3	15.97(39)	V^{3+}	2.18(5)
Fe_2O_3†	0.34	Fe^{3+}	0.044(4)
FeO†	0.15	Fe^{2+}	0.021(3)
MgO	9.65(10)	Mg	2.44(3)
CaO	1.24(7)	Ca	0.23(1)
Na_2O	2.11(6)	Na	0.70(2)
K_2O	0.09(1)	K	0.019(2)
H_2O*	2.86	OH	3.26
Total	100.12		

* Calculated by stoichiometry.

† Calculated as $Fe^{3+}/\Sigma Fe$ ratio = 0.68 (see text); measured FeO = 0.45(4).

Notes: Errors for oxides are standard deviations (in brackets) of 10 spot analyses. Standard errors for the atomic proportions (in brackets) were calculated by error-propagation theory; apfu = atoms per formula unit.

TABLE 7. Cation site populations (apfu), mean atomic numbers and mean bond lengths (Å) for vanadio-oxy-dravite

Site	Site population	Mean atomic number		Mean bond length	
		refined	calculated	refined	calculated*
X	0.70 Na + 0.23 Ca + 0.05 □ + 0.02 K	12.51(8)	12.52		
Y	1.39 V^{3+} + 1.16 Mg + 0.35 Al + 0.04 Fe^{3+} + 0.04 Ti^{4+} + 0.02 Fe^{2+}	17.64(7)	17.65	2.027	2.032
	(1.39 V^{3+} + 1.20 Mg + 0.30 Al + 0.04 Fe^{3+} + 0.04 Ti^{4+}+ 0.02 Fe^{2+})†				
Z	3.73 Al + 1.28 Mg + 0.78 V^{3+} + 0.20 Cr^{3+}	14.48(4)	14.46	1.957	1.955
	(3.77 Al + 1.24 Mg + 0.79 V^{3+} + 0.20 Cr^{3+})†				
T	6.00 Si	14‡	14.00	1.620	1.620
B	3 B	5‡	5		

Notes: apfu = atoms per formula unit;
* Calculated using the ionic radii of Bosi and Lucchesi (2007).
† Site populations optimized by the procedure of Wright et al. (2000).
‡ Fixed in the final stages of refinement

TABLE 8. Bond-valence calculations (valence unit) for vanadio-oxy-dravite.

Site	*X*	*Y*	*Z*	*T*	*B*	Σ
O1		$0.51^{\times 3}\rightarrow$				1.51
O2	$0.17^{\times 3}\downarrow$	$0.42^{\times 2}\downarrow\rightarrow$			0.96	1.98
O3		0.34	$0.40^{\times 2}\rightarrow$			1.13
O4	$0.07^{\times 3}\downarrow$			$0.99^{\times 2}\rightarrow$		2.05
O5	$0.10^{\times 3}\downarrow$			$0.94^{\times 2}\rightarrow$		1.98
O6		$0.45^{\times 2}\downarrow$	0.49	1.04		1.99
O7			0.49	1.07		1.99
O8			0.43 0.48 0.52		$1.00^{\times 2}\downarrow$	2.00
Σ	1.02	2.59	2.81	4.04	2.96	
MFV	1.17	2.62	2.79	4.00	3.00	

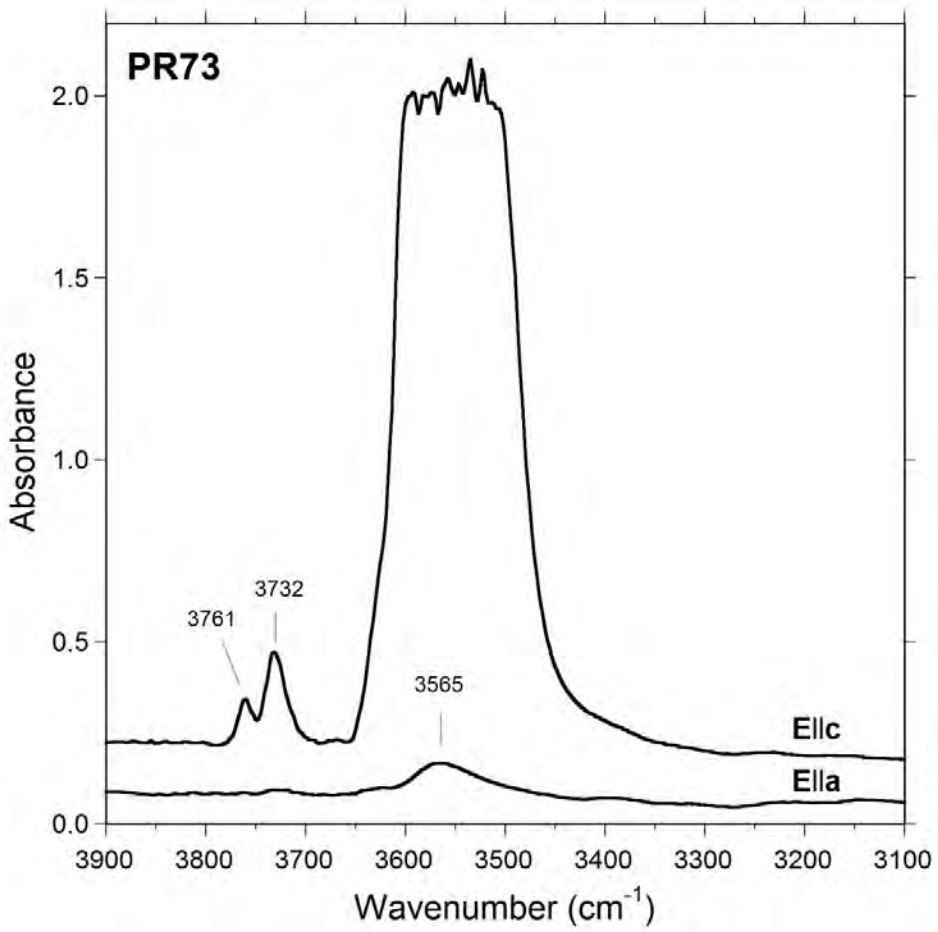
*MFV = mean formal valence from site populations.

TABLE 9. Selected properties of oxy-dravite, vanadio-oxy-dravite and oxy-vanadium-dravite.

	Oxy-dravite	Vanadio-oxy-dravite	Oxy-vanadium-dravite
a (Å)	15.9273(2)	16.0273(3)	16.1908(4)
c (Å)	7.2001(1)	7.2833(1)	7.4143(2)
V (Å^3)	1581.81(4)	1620.24(5)	1683.21(7)
Space group	*R*3*m*	*R*3*m*	*R*3*m*
Optic sign	Uniaxial (–)	Uniaxial (–)	Uniaxial (–)
ω	1.650(5)	1.693(5)	1.786(5)
ε	1.620(5)	1.673(5)	1.729(4)
Colour	Dark red	Green	Black
Pleochroism	O = orange E = pink	O = yellow green E = pale olive green	O = deep brownish green E = yellow green
Reference	(1)	(2)	(3) and (4)

*(1) Bosi and Skogby (2013); (2) this study; (3) Reznitskii et al. (2001); (4) Bosi et al. (2013a).

FIGURE 1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1.0
0.5
0.0
3761
3732
3565
Ellc
Ella
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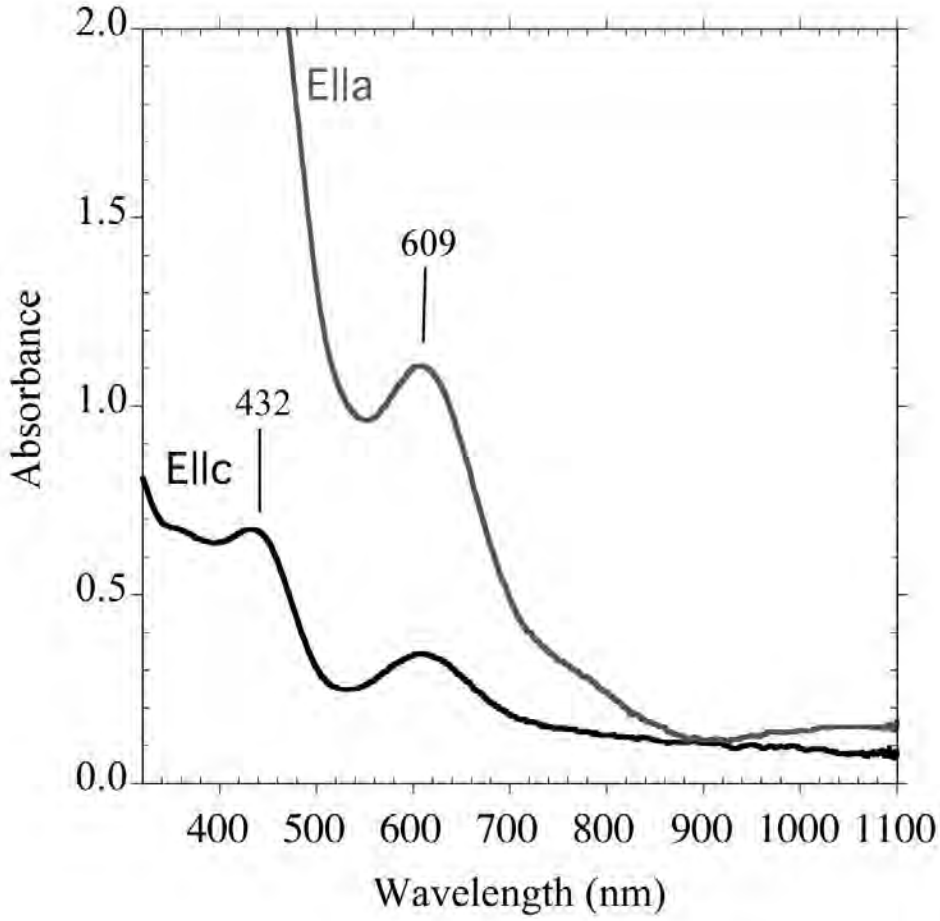
3800
3700
3600
3500
3400
3300
3200
3100
Wavenumber (cm-1)

FIGURE 2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Absorbance
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Ellc
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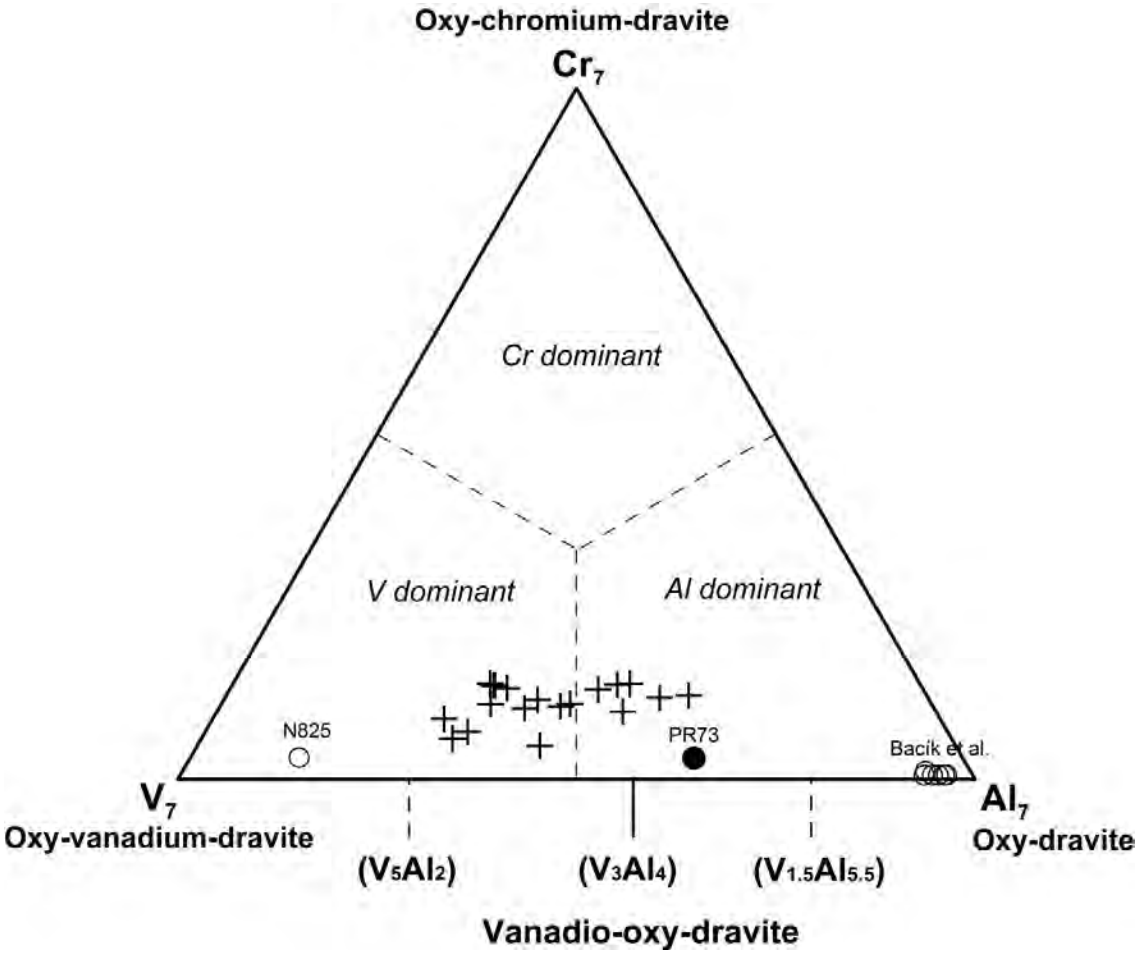
700
800
900
1000
1100
Wavelength (nm)

FIGURE 3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Cr7
Cr dominant
V dominant
Al dominant
N825
PR73
Bacik et al.
V7
Oxy-vanadium-dravite
Al7
Oxy-dravite
(V5Al2)
(V3Al4)
(V1.5Al5.5)
Vanadio-oxy-dravite