Influence of the octahedral cationic-site occupancies on the framework vibrations of Li-free tourmalines

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ABSTRACT

Tourmalines, $XY_3Z_6T_{14}O_{18}(BO_3)_3V_3W$, are excellent petrogenetic indicators as they capture the signature of the host rock bulk composition. Raman spectra of tourmalines can be used as fingerprints for species identification and crystal chemical analysis. While Li-bearing species are directly distinguishable by the shape of the OH-stretching vibrations, the discrimination of Mg- and Fe-dominant species can be hindered by the coexistence of at least 2 types of octahedrally coordinated $R^{3+}$ cations.

Thirty Li-free tourmaline samples comprising fourteen different species were studied by Raman spectroscopy and electron microprobe. All nine Fe$^{3+}$-bearing samples were analyzed also by single-crystal X-ray diffraction and Mössbauer spectroscopy. The Raman scattering analysis shows that Mg-dominant species can be immediately distinguished from Fe-dominant species by the shape of the vibrational modes at ~200-240 cm$^{-1}$ arising from the $YO_6$ vibrations. Trivalent Fe can be observed and quantified by shifts of the framework vibrations towards lower wavenumbers. The position of the main $ZO_6$ vibrational mode (275-375 cm$^{-1}$) can be used to determine the $ZFe^{3+}$ content, while the $YFe^{3+}$ content can be inferred from the position of the peak at ~315 cm$^{-1}$. Fits to the data points indicate that the homovalent substitution of Fe$^{3+}$ for Al$^{3+}$ leads to a considerably larger downward shift of the $ZO_6$ vibrational mode than the heterovalent substitution Mg$^{2+}$ for Al$^{3+}$. The intensity ratio of the two major $YO_6$ vibrational modes (200-240 cm$^{-1}$) of the fully characterized Fe$^{3+}$-bearing samples reflects the amount of Y-site Mg and thus can be used to deduce the site-occupancy disorder of Mg over the Y and Z site for tourmaline species with Mg $\leq$ 2 apfu.

By combining the information from framework and OH-stretching vibrations, Raman spectroscopy alone can be used as a, micrometer-scale sensitive non-destructive method for the analysis of tourmaline crystal chemistry including trivalent Fe, which is the major tracer for oxygen fugacity and central for intersite geothermometry.

Keywords: tourmaline, Raman spectroscopy, framework vibrations, trivalent iron
Tourmaline supergroup minerals are common cyclosilicates that occur in a wide range of igneous, metamorphic, and sedimentary environments (e.g., van Hinsberg et al. 2011 and references therein). Being very useful petrogenetic indicators, the complex crystal chemistry of tourmalines has been extensively studied (e.g., Grice et al. 1993; Hawthorne et al. 1993; Hawthorne 2002; Pieczka and Kraczka 2004; Bosi and Lucchesi 2007; Henry and Dutrow, 2011; Bosi 2011; Bosi et al. 2015a, b). The generalized formula can be expressed as $XY_3Z_6(T6O18)(BO3)3V3W$ with $X = Na^+$, $Ca^{2+}$, $(\square =$ vacancy), $K^+$, $Y = Fe^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Al^{3+}$, $Li^+$, $Fe^{3+}$, $Cr^{3+}$, $Ti^{4+}$, $Zn^{2+}$, $Cu^{2+}$, $V^{3+}$; $Z = Al^{3+}$, $Fe^{3+}$, $Mg^{2+}$, $Fe^{2+}$, $Cr^{3+}$, $V^{3+}$; $T = Si^{4+}$, $Al^{3+}$, $B^{3+}$; $B = B^{3+}$; $V = (OH)^-$, $O^2-$; and $W = F^-$, $(OH)^-$, $O^2-$ being the most common cations and anions at each site (Henry et al. 2011). The crystal structure has $R3m$ space group symmetry and consists of puckered 6-membered rings of corner-sharing TO$_4$ tetrahedra as well as of units of edge-sharing YO$_6$ and ZO$_6$ octahedra further connected by isolated BO$_3$ triangles (see Fig. 1). The X-site cations and W-site anions are located on the three-fold axis of symmetry, on both sides of the ring plane. The W-site anions are shared between three YO$_6$ octahedra, whereas the V-site anions are shared between one YO$_6$ and two ZO$_6$ octahedra (see Fig. 1).

The flexibility of the crystal structure is demonstrated by the occurrence of a large variety of possible major, minor, and trace elements occupying the different crystallographic sites. This has the following implications: (1) the tourmaline supergroup currently consists of thirty-four species approved by the International Mineralogical Association (IMA); (2) solid solutions between different end members are common, including dravite–schorl, schorl–elbaite, dravite–uvite, fluor-buergerite–schorl, povondraite–bosite–oxydravite–dravite (e.g., Donney and Barton 1972; Bloodaxe et al. 1999; Žáček et al. 2000; Bosi et al. 2005; Ertl et al. 2016); and (3) there exists occupancy disorder between the Y and Z sites, i.e., elements are distributed across both sites regardless of the ordered end-member formula. The Y-Z occupancy disorder occurs to release short- and long-range structural strains and it is very typical of Mg-Al as well as of Fe$^{3+}$-Al pairs and to a considerably lesser extent of Fe$^{2+}$-Al pairs (e.g., Hawthorne 1996; Bosi et al. 2010). Thus the identification of tourmaline species requires not only knowledge of the major-element contents, but also of the valence states of certain cations (Fe, Mn) and their site occupancies. While the chemical composition is usually determined by electron microprobe analysis, commonly under the assumption of a stoichiometric boron content ($B = 3$ apfu) and fully occupied anionic sites ($V$+$W = 4$), the valence state of Fe can be most precisely analyzed by Mössbauer spectroscopy, and site occupancies can be refined from single-crystal X-ray diffraction data. All of these
techniques require different sample preparations and high analytical expenses. Hence, it would be beneficial to
gather all the information by a single non-destructive, easy-to-perform analytical technique.

The advantages of Raman spectroscopy for studying the crystal chemistry of complex silicates have
been demonstrated among others for feldspars (Mernagh 1991), garnets (Hofmeister and Chopelas 1991),
pyroxenes (Wang et al. 2001), amphiboles (Leißner et al. 2015), and tourmalines (Watenphul et al. 2016). In the
case of tourmalines, several studies suggest to use the spectral region of the framework vibrations (Alvarez and
Coy-Yll 1977; Gasharova et al. 1997; McKeown 2008; Hoang et al. 2011) as well as of the OH-stretching
vibrations as fingerprints for the discrimination of different tourmaline species (Fantini et al. 2014; Berryman et
al. 2015; Watenphul et al. 2016). In particular Li-rich tourmalines such as elbaite or fluor-liddicoatite can be
immediately distinguished from Mg- and Fe-dominant species, e.g., dravite and schorl, by the shape of the OH-
stretching modes (Fantini et al. 2014; Watenphul et al. 2016). The shape of the OH-stretching Raman scattering
is also quite efficient to discriminate X-site vacant \(Y(\text{R}^{2+}, \text{R}^{3+})\)-dominant species from the corresponding alkali
and calcic species, e.g., foitite vs. schorl (Watenphul et al. 2016) or magnesio-foitite vs. dravite and uvite
(Berryman et al. 2015). Alkali/calcic Fe- or Mg-dominant tourmaline species exhibit OH-stretching Raman
scattering of similar shape (see Fig.2), but their crystal chemistry can still be determined by the \(Y\text{OH}-\text{stretching}
peak positions and relative intensities if only one type of impurity element at the Y site is present (Watenphul et
al. 2016). However, if there are at least two extra types of octahedrally coordinated \(R^{n+}\) cations coexisting along
with the end-member Y-site element, the species identification based only on the shape and position of the OH-
stretching vibrations can be rather ambiguous. This is due to the inverse correlation between the OH-stretching
wavenumber and the average charge of the octahedrally coordinated cations that coordinate the OH group
(Gonzalez-Carreño et al. 1988; Martínez-Alonso et al. 2002). Similar behavior is also known for other hydrous
minerals, e.g., amphiboles, micas, and staurolite (Leißner et al. 2015; Robert et al. 1989; Koch-Müller et al.
1997). For example, additional non-negligible amounts of octahedrally coordinated Al and/or Fe\(^{3+}\), i.e., larger
than 0.1 atoms per formula unit (apfu), shifts the \(Y\text{OH}-\text{vibrational modes toward lower wavenumbers, whereas}
the presence of extra Mg and Li leads to a peak shift toward higher wavenumbers. Therefore, the corresponding
effects may compensate each other in the case of tourmaline samples with coexisting heterovalent substitution
elements on the octahedrally coordinated sites.

The aim of this study is to analyze in detail the Raman scattering generated by the framework vibrations
of various, mostly Li-free, natural tourmaline species, focusing on the vibrational modes of the \(YO_6\) and \(ZO_6\)
octahedra. Special emphasis is thereby placed on Fe$^{3+}$-containing samples as an easy and reliable identification of Fe$^{3+}$ allows for important inferences on the host rock compositions. The Raman spectroscopic results on the Y- and Z-site occupancies are correlated with data from complementary electron microprobe analysis, single-crystal X-ray diffraction, and Mössbauer spectroscopy to establish a more reliable approach for non-destructive tourmaline species identification and crystal-chemistry analysis, combining the information from the Raman spectra of framework and OH-stretching vibrations.

**MATERIALS AND METHODS**

**Samples**

Thirty natural tourmaline samples from worldwide localities are examined in this study. Table 1 gives the structural formulae and references to previous studies, when applicable. Sample S59 (H-rich “buergerite”) was annealed for 110 h at 700 °C and sample S51 (oxy-dravite) was kept at 800 °C for 20 h to oxidize Fe$^{2+}$ to Fe$^{3+}$ as described by Filip et al. (2012). Sample S57 was analyzed by single-crystal X-ray diffraction, electron microprobe (WDS mode) and optical absorption spectroscopy in order to determine the site populations and the Fe$^{2+}$/Fe$^{3+}$ and Mn$^{2+}$/Mn$^{3+}$ ratio (work in progress).

**Raman spectroscopy**

Raman scattering experiments were conducted in backscattering geometry with a Horiba Jobin-Yvon T64000 triple-monochromator spectrometer (holographic gratings of 1800 grooves/mm) equipped with an Olympus BX41 confocal microscope (Olympus LM Plan FLN 50x objective with a numerical aperture of 0.5) and a Symphony liquid-N$_2$-cooled charge-coupled device detector. Raman spectra of all samples were excited either by the 488.0 or 514.5-nm line of a Coherent 90C Fred Ar$^+$ laser. For both laser lines the laser power on the sample surface was approximately 14 mW to ensure no sample overheating during the experiment. The achieved spectral resolution was $\sim$2 cm$^{-1}$ and the accuracy in determining the peak positions was $\sim$0.35 cm$^{-1}$. The spectrometer was calibrated to the silicon Raman peak at 520.5 cm$^{-1}$. Further experimental and analytical details are given by Watenphul et al. (2016).

Polarized Raman spectra in $\bar{y}(zz)y$ scattering geometry (Porto’s notation; Porto and Scott 1967) were collected for all samples in the spectral range 15-4000 cm$^{-1}$. The acquisition time was chosen to yield a
satisfactory signal-to-noise ratio, thus most spectra were collected for 20 s averaging over 10 accumulations. The OriginPro® 9.1 software package was used for data evaluation. The collected spectra were baseline corrected for the continuum luminescence background when necessary, temperature-reduced to account for the Bose-Einstein occupation factor (Kuzmany 2009), and normalized to the acquisition time. Peak positions, full widths at half maximum (FWHMs), and integrated intensities were determined from fits with pseudo-Voigt functions (\( PV = (1-q) \star \text{Lorentz} + q \star \text{Gauss} \), \( q \) is the weight coefficient). The criterion for the maximum number of fitted peaks was \( \Delta I < I/2 \), where \( I \) and \( \Delta I \) are the calculated magnitude and uncertainty of each peak intensity, respectively.

Electron microprobe analysis (EMPA)

Chemical analyses of polished specimens of the samples first studied here were obtained using a Cameca SX-100 SEM system with a wavelength-dispersive detector. The energy of the electron beam was 15 keV and the beam current was 20 nA. The following standards were used: LiF for F, albite for Na, MgO for Mg, Al\(_2\)O\(_3\) for Al, andradite for Si, Ca, and Fe, vanadinite for Cl and V, orthoclase for K, MnTiO\(_3\) for Ti and Mn, Cr\(_2\)O\(_3\) for Cr, olivenite for Cu, SrTiO\(_3\) for Sr, and Ba-glass for Ba. The acquisition times were 20 s for Na, K, Mg, Ca, Mn, Fe, Al, Ti, and Si, 60 s for Ba, Sr, Cu, Cr, and Cl, and 120 s for F. The acquisition time to collect the background level on both sides of the corresponding peak was a half of the peak acquisition time. The program WinTcac (Yavuz et al. 2014) was used to calculate the chemical formulae and also to classify the tourmaline species. The latter was additionally verified by the spreadsheet in the supplement of Henry et al. (2011). About 25 to 50 spot analyses were carried out for each sample to achieve statistical standard deviations allowing for a compositional precision of about 0.02 apfu for each element in the calculated chemical formulas.

RESULTS AND DISCUSSION

Polarized \( \gamma(zz) \) Raman spectra of selected tourmaline samples in the spectral region of the framework and OH-stretching vibrations are shown in Figure 2. Four main ranges of framework vibrations are identified that, according to lattice dynamics calculations (Mihailova et al. 1996; McKeown 2008), can be attributed to the following vibrating groups: (i) the range \( \sim 200-240 \text{ cm}^{-1} \) is dominated by YO\(_6\) vibrations; (ii) the strongest Raman peak that appears in the range \( \sim 360-375 \text{ cm}^{-1} \) for \( ^2 \)Al-dominant species is generated by ZO\(_6\) vibrations.
and it considerably shifts toward lower wavenumbers (~277 cm$^{-1}$) for $^{2}\text{Fe}^{3+}$-rich species; (iii) the range ~650-720 cm$^{-1}$ is dominated by breathing modes of bridging oxygen atoms of TO$_4$ rings; and (iv) the range ~960-1120 cm$^{-1}$ arises predominantly from TO$_4$ stretching modes. Note that the TO$_4$ ring and stretching vibrations in $^{2}\text{Fe}^{3+}$-rich species also exhibit significant shifts toward lower wavenumbers (~450-550 cm$^{-1}$), which is most probably related to the overall expansion of the unit cell upon the incorporation of Fe$^{3+}$ at the Z site (Grice et al. 1993) and overall weakening of the metal-oxide interactions.

Magnesium- and Fe-dominant tourmalines can be immediately discriminated by the spectral shape of the YO$_6$ vibrations. All Mg-dominant tourmalines exhibit a clearly resolved peak doublet, labeled as P$_1$ and P$_2$ in Fig. 2, with a subtle shoulder at higher phonon energies and an intensity ratio I$_1$/I$_2$ ~ 1. In contrast, Fe-dominant species show mostly one well-defined peak with sometimes less-resolved shoulders on either side (Fig. 2).

**The behavior of the ZO$_6$ vibration**

For all tourmaline species the dominant ZO$_6$ vibrational mode produces a strong well-resolved Raman peak, which is marked by a line in Figure 2. Therefore, even small shifts in its position due to changes in the crystal chemistry can be experimentally well detected. Figure 3a-c shows the fitted peak position in dependence of the total octahedral contents of $^{\text{Y-}Z}\text{Al}$, $^{\text{Y-}Z}(\text{Fe}^{2+}+\text{Fe}^{3+})$, and $^{\text{Y-}Z}\text{Mg}$ for all studied samples. As it can be clearly seen, Mg- and Fe$^{2+}$-dominant tourmalines are practically indistinguishable by the position of the ZO$_6$ vibration for all octahedral elements. The small spread in the data of ±6 cm$^{-1}$ (see supplemental table 1) originates most likely from additional minor and trace elements. It should be noted that no influence of the X-site occupancy on the spectra is experimentally observed, although such has been predicted by lattice dynamics calculations (McKeown 2008). Likewise, Y-/Z-site occupancy disorder of Mg and Al typical of dravite, fluor-dravite, oxy-dravite, and uvite (e.g., Hawthorne et al. 1993; Clark et al. 2011; Bosi and Skogby 2013) is difficult to determine from the position of the main ZO$_6$ vibration, as the spread in the peak positions for Mg-dominant tourmaline species amounts only to ±3.5 cm$^{-1}$. This indicates that either the degree of Y-/Z-site disorder is similar for all studied samples or that the shift of $\omega(\text{ZO}_6)$ due to $^{2}\text{Mg}$ replacing $^{2}\text{Al}$ is small and possibly also masked by other factors, i.e. Fe$^{3+}$ and/or trace elements.

Some samples that are rich in Fe$^{3+}$ clearly exhibit a lower wavenumber of the ZO$_6$ vibration than the rest of the samples. In particular, the position of the dominant ZO$_6$ vibration of povondraite is shifted by almost a hundred wavenumbers to 277 cm$^{-1}$. However, the mode can still be identified by being the dominant vibration in...
the Raman spectrum, although its intensity in comparison with the other modes in this spectral region is lower compared to other tourmaline species shown in Figure 2, which is due to the different dominant element at the Z site, i.e. $^{2}\text{Fe}^{3+}$ instead of $^{2}\text{Al}^{3+}$, and differences in the ratios of the Z-site element contents. To study whether the peak shift is entirely a unit-cell-volume effect or whether it also provides information about the site occupancy, we considered the dependence of $\omega(\text{ZO}_6)$ on the content of Y-site Al, Fe$^{3+}$, and Mg (Figs 3d,e,f) as well as on the content of Z-site Al, Fe$^{3+}$, and Mg (Figs 3g,h,i) for all Fe$^{3+}$-containing samples with site occupancies derived from single-crystal X-ray diffraction.

As can be expected, no dependence of $\omega(\text{ZO}_6)$ at the Y-site contents of Al, Fe$^{3+}$, and Mg can be observed (Fig. 3d,e,f). In strong contrast, $\omega(\text{ZO}_6)$ gradually increases with increasing $^{2}\text{Al}$ content (Fig. 3g), and decreases with increasing $^{2}\text{Fe}^{3+}$ content (Fig. 3h). $\omega(\text{ZO}_6)$ also decreases with increasing $^{2}\text{Mg}$ content (Fig. 3i), although the data are more dispersed. Fits with 2nd-order polynomial functions indicate that $^{2}\text{Fe}^{3+}$ and $^{2}\text{Mg}$ are complementary to each other in substituting Al at the Z site, with $^{2}\text{Mg}$ having a maximum of about 2 apfu and $^{2}\text{Fe}^{3+}$ having a maximum of about 4 apfu. Note that the linear term in the 2nd-order polynomial fits is $\omega(\text{ZO}_6)$ vs. $^{6}\text{ZAl}$, $\omega(\text{ZO}_6)$ vs. $^{2}\text{Fe}^{3+}$ and $\omega(\text{ZO}_6)$ vs $^{2}\text{Mg}$ dataset is zero within the uncertainties. The goodness of fit $R^2$ for $\omega(\text{ZO}_6)$ vs. $^{2}\text{Fe}^{3+}$ ($R^2 \sim 0.97$) almost equals that of $\omega(\text{ZO}_6)$ vs. $^{2}\text{Al}$ ($R^2 \sim 0.99$), whereas the data points for $\omega(\text{ZO}_6)$ as a function of $^{2}\text{Mg}$ are significantly more dispersed ($R^2 \sim 0.74$) (Table 2). This indicates that the homovalent Fe$^{3+}$-Al substitution is the major reason for the downward wavenumber shift of the ZO$^6$ vibrational mode. However, the minor effect of Mg cannot be entirely neglected although it is difficult to quantify.

The dependence of $\omega(\text{ZO}_6)$ on $^{6}\text{ZAl}$, which gives the content of non-aluminum Z-site cations, allows for the unambiguous determination using the relation, $6 - ^{2}\text{ZAl} = \sqrt{[(371 \pm 1) - \omega(\text{ZO}_6)]/(3.1 \pm 0.1)}$. For samples that contain none or very little $^{2}\text{Fe}^{3+}$, this content typically equals the content of Z-site Mg. The content of Fe$^{3+}$ at the Z site can be reliably determined using the relation $^{2}\text{Fe}^{3+} = \sqrt{[(367 \pm 2) - \omega(\text{ZO}_6)]/(6 \pm 1)}$. Generally, the quantification of $^{2}\text{Mg}$ and $^{2}\text{Fe}^{3+}$ contents requires to combine the information provided by the OH stretching and the framework vibrations as discussed below for the showcase.

In addition to the dependence of the position of the ZO$^6$ vibration on the octahedrally coordinated metal cation contents there should also be a dependence of the full width at half maximum (FWHM) of this vibration. The analysis of these data indicates similar trends as observed for $\omega(\text{ZO}_6)$, but the datasets exhibit larger errors. Besides, the analysis of the FWHMs as well as of the integrated peak intensities strongly depends on the chosen baseline and the weight coefficient $q$ determining the ratio of Gaussian and Lorentzian component. The proper
determination of the former might be difficult if the sample shows considerable photoluminescence due to high amounts of incorporated trace elements. The latter might vary due to occupancy disorder on the corresponding crystallographic site. Therefore, it is advisable to use the trends in the peak positions rather than the FWHMs.

The behavior of the peak P₃ near 315 cm⁻¹

The comparison of the framework vibrational modes of different tourmaline species showed that the vibrational mode, labeled as P₃ in Figure 2, exhibits a shift from ~315 cm⁻¹ to ~ 300 cm⁻¹ for all YFe³⁺-rich samples except for povondraite (see supplemental table 1). The corresponding peak for povondraite appears either at significantly lower wavenumber ~ 230 cm⁻¹ due to the large unit-cell volume or it is also near 300 cm⁻¹, but it is overlapped by the stronger ZO₆ peaks. Because of the uncertainty in the peak assignment, povondraite will be excluded from this analysis. Lattice dynamics calculations of fluor-buergerite (McKeown 2008) suggest that the Raman peak near 315 cm⁻¹ is predominantly associated with bending vibrations of the YO₆ octahedra and secondary contributions from deformation vibrations of the ZO₆ octahedra, external modes of the BO₃ and TO₄ groups, and displacements of X-site cations along the c axis. The analysis of the experimental Raman data reveals that there is no detectable influence of the X-site occupancy on the position of P₃. Thus, variations in the position of P₃ can be indeed attributed mainly to changes in the Y-site occupancy.

A thorough analysis of the Fe³⁺-bearing tourmaline samples shows that the position of P₃ linearly decreases with increasing Fe³⁺ content at the Y site (Fig. 4e), whereas there is no clear dependence on YAl and YMg, as revealed by the considerably worse goodness of fit R² (Fig. 4d, f). The absence of correlated trends of the P₃ peak position with YAl and YMg most probably stems from the larger structural flexibility of the Y site as suggested by its larger chemical variability, including minor and trace elements. Nevertheless, the goodness of fit for YFe³⁺ clearly shows that the position of P₃ is a good indicator for Fe³⁺ at the Y site and the equation of the fitting can be used for simple determination of the YFe³⁺ content.

The behavior of the P₁-P₂ doublet

The spectral region of the YO₆ vibration shows multiple, partly overlapping peaks (Fig. 2). For Mg-dominant species there are two very well resolved Raman signals at 215 and 243 cm⁻¹, labeled in Figure 2 as P₁ and P₂, while the spectral shape of Fe-dominant species is more complex. If one considers the main peak as P₂ and the shoulder on the lower-energy side as P₁, the difference Δω = (ω₂ − ω₁) and the intensity ratio I₁/I₂ can be
calculated for all samples. \( \Delta \omega \) is about 25-30 cm\(^{-1}\) for all Mg-dominant species and decreases significantly to about 10-18 cm\(^{-1}\) for the Fe\(^{2+}\)-dominant species (see supplemental table 1). There is no distinct trend for the Fe\(^{3+}\)-dominant samples. The wavenumber difference \( \Delta \omega \) slightly increases with the total Mg content, while there seem to be no dependencies on \(^{1}\)Y\(^{2+}\)Al and \(^{1}\)Y\(^{2+}\)Fe. A detailed analysis of the dependence of \( \Delta \omega \) on the Y-site Mg and Al was not possible due to the absence of enough samples on hand with refined site occupancies. If only the Fe\(^{3+}\)-bearing samples previously studied by single-crystal X-ray diffraction are considered, no distinct trends are observed.

The intensity ratio \( I_1/I_2 \) ranges between 0.7 and 1.3 for the Mg-dominant species. The spread is considerably larger for the Fe\(^{2+}\)- and Fe\(^{3+}\)-dominant samples spanning almost the complete range between 0 and 1. One might assume a linear negative correlation between the content of \(^{1}\)YFe\(^{3+}\) and \( I_1/I_2 \) (Fig. 5b), but a few data points considerably deviate from this trend and therefore the intensity ratio could be used only as a secondary indicator for the presence of \(^{1}\)YFe\(^{3+}\), along with the primary indicator: the wavenumber of peak P\(^3\) ranging from \( \sim 315 \) cm\(^{-1}\) to \( \sim 300 \) cm\(^{-1}\) with the increase of \(^{1}\)YFe\(^{3+}\). There is also no clear dependence on the content of Y-site Al (Fig. 5a). However, there is an apparent stepwise trend between \( I_1/I_2 \) and the content of \(^{1}\)YMg, with an inflection point corresponding to \(^{1}\)YMg ~ 0.55 apfu (Fig. 5c). The \(^{1}\)YMg content vs. \( I_1/I_2 \) can be nicely fitted with a growth function, e.g., Boltzmann function of the type

\[
^{1}\text{YMg} = \frac{(1.02 \pm 0.05) - (1.02 \pm 0.05)}{1 + \exp[(I_1/I_2 - (0.55 \pm 0.04)) / (0.10 \pm 0.03)]} 
\]

and this dependence can be used to determine Y-site Mg content in tourmaline species with total Mg \( \leq 2 \) apfu. The latter restriction is related to the fact that the data presented in Figure 5b have such compositions. It should be however emphasized that all studied dravitic and uvitic samples exhibit intensity ratio \( I_1/I_2 \sim 1 \) and therefore the framework vibrations should be analyzed in combination with the OH stretching modes (Watenphul et al. 2016) to obtain quantitative information about the total amount of Mg. The quantitative distinction between \(^{1}\)YMg and \(^{2}\)Mg via Raman scattering still remains an open issue for tourmalines with total Mg > 2 apfu.

It should be underlined that sample S57 contains a substantial amount of Mn\(^{3+}\) (see Table 1). Our previous studies on amphiboles (Leißner et al. 2015) and tourmalines (Watenphul et al. 2016) indicated that Mn\(^{2+}\) can hardly be distinguished from Fe\(^{2+}\) by Raman spectroscopy. This is also supported by nearly the same wavenumbers of the WOH-stretching bands observed in infrared spectra of Fe\(^{2+}\)-rich elbaite and tsilaisite samples (Bosi et al. 2012; 2015b). Hence, we considered the amount of (Mn\(^{3+}\) + Fe\(^{3+}\)) for sample S57 rather than only the amount of Fe\(^{3+}\), and the corresponding data points matched very well the trends shown in Figures 3-5, when only
Mn-free samples are considered. This result indicates that one cannot distinguish Mn\(^{3+}\) from Fe\(^{3+}\) in tourmalines by Raman spectroscopy. However, from the point of view of oxygen fugacity, only the valence state matters (Mn\(^{3+}\) + Fe\(^{3+}\) vs. Mn\(^{2+}\) + Fe\(^{2+}\)), i.e. the discrimination of Mn\(^{3+}\) from Fe\(^{3+}\) is insignificant.

**CONCLUSIONS**

The study of thirty tourmaline samples encompassing fourteen different species showed that Raman spectroscopy is a suitable tool to analyze the crystal chemistry of tourmaline. Even samples with complex Y- and Z-site chemistry, i.e., with impurity element contents larger than 0.1 apfu, can be clearly identified by combining the information from the framework and OH-stretching vibrations. In particular, the incorporation of Fe\(^{3+}\) can be identified by downward shifts of the framework vibrational modes. The trends of the positions of the dominant \(\text{ZO}_6\) vibrational mode, the position of the peak \(P_1\) near 315 cm\(^{-1}\), and the intensity ratio of the \(\text{YO}_6\) vibrational modes \(P_1 \sim 215\) cm\(^{-1}\) and \(P_2 \sim 243\) cm\(^{-1}\) with the content of Fe\(^{3+}\) can be used to quantify the contents at the Y and Z sites.

The crystallochemical analysis of an Fe\(^{3+}\)-bearing tourmaline sample combining the information from the framework and OH-stretching vibrations is illustrated for sample S50 as a showcase (Fig. 6). Note that the \(\nu\text{OH}\)-stretching modes of this sample, as observed by infrared spectroscopy, have been already assigned to various \(\text{YZZ-YZZ-YZZ}\) chemical species that contain Mg, Al, and Fe\(^{3+}\), after precisely determining the structural formula by a combination of analytical methods (Bosi et al. 2016b). In the following discussion we are going to try to solve the reverse problem: to identify the tourmaline species and to determine the crystallochemical formula only on the basis of the Raman scattering in the entire spectral range.

First, the inspection of the shape of Raman scattering in the range \(~200-240\) cm\(^{-1}\) consists of a well-resolved \(P_1\)\(-P_2\) doublet, i.e., the sample is a Mg-dominant tourmaline species. Further on, the region of the \(\nu\text{OH}\)-stretching vibrations shows four peaks (3776\(\pm2\) cm\(^{-1}\), 3738\(\pm1\) cm\(^{-1}\), 3674\(\pm6\) cm\(^{-1}\), 3642\(\pm1\) cm\(^{-1}\)), which correspond within errors well to that of dravite and uvite (Watenphul et al. 2016).

Second, the range 3300-3615 cm\(^{-1}\) reveals three \(\nu\text{OH}\) modes at 3567\(\pm1\) cm\(^{-1}\), 3529\(\pm2\) cm\(^{-1}\), and 3480\(\pm7\) cm\(^{-1}\), which according to Watenphul et al. (2016) are assigned to \(3\nu\text{Mg}^2\text{Al}^2\text{Al}\), \(2\nu\text{Mg}^2\text{Al}^2\text{Al}-\nu\text{Al}^2\text{Al}^2\text{Al}\), and \(\nu\text{Mg}^2\text{Al}^2\text{Al}-2\nu\text{Al}^2\text{Al}^2\text{Al}\), correspondingly. The \(\nu\text{OH}\) peak positions are shifted towards lower wavenumbers by 5-16 cm\(^{-1}\) compared to dravite (Watenphul et al. 2016), which indicates an additional incorporation of significant amount of trivalent elements such as Fe\(^{3+}\) and/or variations in the X-site occupancy. The former should have a...
stronger effect than the latter, since in general the H3-X distances in tourmalines are rather large (~ 3.60 Å, Gatta et al. 2014) and hence, the H3-X interactions are weak (Hawthorne 2016) and have only a secondary effect on the \( ^5\text{OH} \) vibrations (Watenphul et al. 2016). However, the \( ^5\text{OH} \)-stretching modes associated with possible additional trivalent elements at the Y or Z sites should overlap with the corresponding modes of dravite so that the additional elements cannot be identified nor quantified. Therefore, there are two effects on the \( ^5\text{OH} \) stretching: an additional type of octahedrally coordinated trivalent cations and X-site vacancy, which cannot be separated from each other. Thus, the X-site content calculated from the equation \( x_{(\text{Na+Ca})} = \left[ \omega(\text{VOH}) - 3547 \right]/30 \) for the \( ^3\text{YMgZAlZAl} \) peak (Watenphul et al. 2016) gives only the X-site occupancy minimum. For sample S50 \( \omega(\text{VOH}) = 3567 \) cm\(^{-1}\) and therefore the obtained minimum value of \( ^3\text{(Na+Ca)} \) is 0.67 apfu. Assuming disorder of Mg and Al over the Y and Z sites, the integrated intensities of the \( ^5\text{OH} \) modes (Watenphul et al. 2016) give \( ^{\text{Y+ZMg}} = 2.34 \pm 0.09 \) apfu and \( ^{\text{YAl + ZAl}} = (0.66 \pm 0.06) + 6 \) apfu.

Third, the dominant \( ^6\text{ZO} \) vibration is observed at 368±0.1 cm\(^{-1}\). Thus, the calculated content \( ^6\text{Fe}^{3+} = \sqrt{(367 - 368)/6} \) amounts to 0 apfu, whereas the content of non-aluminum Z-site cations \( 6 - ^6\text{Al} = \sqrt{(371 - 368)/3.1} \) is calculated to 0.98 apfu. Assuming that only Mg and \( ^6\text{Fe}^{3+} \) can replace Al at the Z site, it follows that \( ^6\text{Mg} = 0.98 \) apfu. From the value of \( \omega_3 = 312\pm0.1 \) cm\(^{-1}\) the Y-site \( ^6\text{Fe}^{3+} \) content is calculated to \( ^6\text{Fe}^{3+} = (314 - \omega_3)/7 = 0.29 \) apfu and the intensity ratio \( I_1/I_2 \) of 1.1 indicates a \( ^6\text{Mg} \) content of 1.02 apfu. Therefore, the framework vibrations reveal a total amount of Mg equal to 2 apfu, which is slightly lower than that calculated from the \( ^5\text{OH} \) stretching modes. The discrepancy is related to the neglected additional types of cations occurring predominantly at the Y site, whose influence is commonly strong on the OH-stretching vibrations. Then, the Al contents can be calculated as \( ^6\text{Al} = (3 - 1.02^6\text{Mg} - 0.29^6\text{Fe}^{3+}) \) and \( ^6\text{Al} = (6 - 0.98^6\text{Mg} - 0.29^6\text{Fe}^{3+}) \).

Finally, assuming stoichiometric amounts of Si and B, the chemical formula of this tourmaline sample is \( x_{(\text{Na+Ca})_{0.7},(\text{K})_{0.3}}[^6\text{Mg}_{1.02}\text{Al}_{0.68}\text{Fe}^{3+}_{0.29}]^6\text{Al}_{1.02}\text{Mg}_{0.08}\text{Si}_{6}\text{O}_{18}(\text{BO}_3)_3(\text{OH})_2(\text{O}_{0.7}\text{OH}_{0.3}), \) which is in a good agreement with \( x_{(\text{Na+K})_{0.85}}[^6\text{Mg}_{1.44}\text{Al}_{1.34}\text{Fe}^{3+}_{0.38}\text{Fe}^{2+}_{0.02}\text{Ti}_{0.03}]^6\text{Al}_{1.44}\text{Mg}_{1.03}\text{Fe}^{3+}_{0.03}\text{Fe}^{2+}_{0.03}\text{Si}_{5.98}\text{Al}_{0.02}\text{Si}_{5}\text{O}_{18}(\text{BO}_3)_3(\text{OH})_2(\text{O}_{0.69}\text{F}_{0.24}\text{OH}_{0.07}), \) calculated from EMPA, single-crystal X-ray diffraction, and Mössbauer spectroscopy (Table 1). The sample can be classified as \( ^6\text{Fe}^{3+} \)-bearing oxy-dravite. Certainly the use of combined EMPA, single-crystal X-ray diffraction and Mössbauer spectroscopy can provide more precise chemical formula, but the approach presented here demonstrates the ability of Raman spectroscopy to be used as a sole, fast, non-destructive method with micrometer-scale length sensitivity for crystallochemical analyses of tourmalines.
The complex crystal chemistry and zonation of tourmalines allows for recording the geologic evolution of the host rock environment (e.g., van Hinsberg et al. 2011). Several studies have focused on potential geothermometers based on the Mg-Fe exchange between tourmaline and biotite (e.g., Blamart et al. 1992; Henry and Dutrow 1996). In a more rigorous study, the geothermobarometric potential of tourmaline was explored by studies of element exchange among tourmaline and coexisting minerals in metamorphosed rocks and also through experimental exchange between tourmaline and biotite by van Hinsberg and Schumacher (2009). However, they observed considerable spread in $K_D$-values versus temperature, which was ascribed to intersite partitioning of elements over the Y and Z sites in tourmaline, and concluded that the promising potential of tourmaline geothermobarometry cannot be fulfilled until effects of intersite partitioning and non-ideal interactions are better understood. The current knowledge regarding intersite partitioning is limited and predominantly based on structure refinement and spectroscopic methods, but indicates substantial intersite partitioning coupled to short-range ordering. Recent findings obtained on Fe$^{3+}$-bearing oxy-dravite (Bosi et al., 2016b) demonstrate that Fe progressively disorders over the Y and Z sites with increasing temperature, whereas Mg orders at the Y site according to the order-disorder reaction $^Y$Fe + $^Z$Mg $\leftrightarrow$ $^Z$Fe + $^Y$Mg. As a consequence, a geothermometer may be developed by thermal calibration of this Mg-Fe order-disorder reaction, and thus providing means for more accurate estimates of formation temperatures. Our findings here show that such order-disorder processes may be studied by Raman spectroscopy, which is a relatively easily applied technique. The incorporation of Fe$^{3+}$ and in some cases Mn$^{3+}$ is also of particular interest as it points to the oxygen activity during the formation. Thus, zoned tourmaline samples with different Fe$^{3+}$/Fe$_{\text{total}}$ ratios provide the information on the oxidation history on the host rocks. The valence state of Fe is most precisely studied by Mössbauer spectroscopy, which however typically requires a relatively large amount of sample for standard spectrometer systems. This study showed that Raman spectroscopy is also a suitable tool to detect Fe$^{3+}$ in tourmaline and study its zonation. By comparison with complementary analyses by electron microprobe, Mössbauer spectroscopy and X-ray diffraction, trends between peak positions and octahedrally coordinated Fe contents have been established and proposed to be used for quantification. Such dependencies of Raman peak positions with Fe$^{3+}$ contents should also exist in other complex hydrous silicates like e.g. amphiboles and layered silicates.
Acknowledgements. Financial support by the Deutsche Forschungsgemeinschaft DFG (MI 1127/7-1 and SCHL 549/6-1) and Sapienza University of Rome (Prog. Università 2015 to F.B.) are gratefully acknowledged. The authors thank P. Stutz for sample preparation, S. Heidrich for conducting electron microprobe analysis, M. Lensing-Burgdorf for parts of the Raman spectroscopic measurements, as well as M. Ciriotti and I. Baksheev for providing sample S57 and the bosite sample, respectively. We also thank M. Koch-Müller and J. Cempírek for their constructive reviews and G.D. Gatta for the editorial handling of the manuscript.
References


Bosi, F., Babić-Žunić, T., and Surour, A.A. (2010) Crystal structure analyses of four tourmaline specimens from the Cleopatra’s Mines (Egypt) and Jabal Zalm (Saudi Arabia), and the role of Al in the tourmaline group. American Mineralogist, 95, 510-518.


Figure captions

Figure 1. Crystal structure of tourmaline, space group $R3m$, with X-site cations shown in yellow, $YO_6$ octahedra in brown, $ZO_6$ octahedra in light blue, $TO_4$ tetrahedra in dark blue, and $BO_3$ groups in green. Oxygen atoms are depicted by red balls, hydrogen atoms by pink balls. The structural data were taken from Ertl et al. (2006), the software package VESTA (Momma and Izumi 2011) was used for figure preparation.

Figure 2. Polarized $\bar{Y}(zz)y$ Raman spectra of representative tourmaline samples: dravite (S2), uvite (S39), foitite (S45), schorl (S7), $Fe^{3+}$-rich schorl (S49), fluor-buergerite (S36), lucchesite (S47), oxy-dravite (S50), bosiite (S48), and povondraite (S33). For better comparison spectra are normalized to the intensity of the $ZO_6$ vibration and vertically offset for clarity.

Figure 3. Position of the $ZO_6$ vibration $a_d(ZO_6)$ in dependence of (a-c) the total octahedral contents of Al, ($Fe^{2+}$+$Fe^{3+}$), and Mg in all samples, (d-f) the Y-site and (g-i) the Z-site contents of Al, $Fe^{3+}$, and Mg in all $Fe^{3+}$-containing samples (S33, S36, S47, S48, S49, S50, S51, S57, S59). If not shown error bars are within the symbol size. Data points with yellow contours refer to sample S52 for which the shown $Fe^{3+}$ content is the sum of $Fe^{3+} + Mn^{3+}$. Solid gray lines indicate 2nd-order polynomial fits to the corresponding sets of data points (see Table 2), dashed gray lines in (h) depict the fitting functions to $a_d(ZO_6)$ vs. $ZMg$ [$f(ZMg)$] and for $a_d(ZO_6)$ vs. $6-ZAl$ [$f(6-ZAl)$], respectively.

Figure 4. (a-c) Position of the peak P3 (as labeled in Fig. 2) in dependence of the total octahedral contents of Al, ($Fe^{2+}$+$Fe^{3+}$), and Mg. Symbol shape and color indicate the dominant octahedral cation. (d-f) Position of P3 of all $Fe^{3+}$-bearing samples in dependence of the $YAl$, $YFe^{3+}$, and $YMg$ contents. Gray lines indicate linear fits of the data points excluding those with yellow contours.

Figure 5. Intensity ratio $I_1/I_2$ of the two main $YO_6$ peaks in the range 195 to 243 cm$^{-1}$ for all $Fe^{3+}$-bearing samples in dependence of the Al, $Fe^{3+}$, and Mg content in the Y site. The gray line in (b) indicates the linear fit of the data points excluding those with yellow contours. The gray line in (c) depicts a Boltzman fit $y = c_1 + (c_0 - c_1)/(1 + \exp[(x-x_0)/dx])$. 
Figure 6. Raman spectrum of the oxy-dravite showcase sample S50 in the spectral region of the framework and OH-stretching vibrations. Peak positions and selected integrated intensities are given above the peaks. Gray lines illustrate the fit functions; integrated intensities used for chemical quantification are highlighted.
Table 1. Structural formula of the studied tourmaline samples; the site populations of samples marked by * has been derived by single-crystal X-ray diffraction.

<table>
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<th>#</th>
<th>species</th>
<th>general formula XY3Z6(T6O18)(BO3)3V3W</th>
<th>reference</th>
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<td></td>
<td></td>
<td>X</td>
<td>Y</td>
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<td>0.05K0.02</td>
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<td>Sample</td>
<td>Mineral Name</td>
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</table>

Notes: The total amount of boron is assigned to the B site and assumed to be 3 apfu. The occupancy disorder of Y- and Z-site cations was not studied for the samples considered by Watenphul et al. (2016) except for samples S33 and S36. The symbol 
refers to X-site vacancies. Manganese is always considered to be divalent, except for sample S57. The errors in the element contents due to chemical variations amount to 0.1 apfu in maximum. 
* In addition to the chemistry determination by EMPA in Watenphul et al. (2016), the Fe2+/Fe3+ ratio was determined by Mössbauer spectroscopy. 
# annealed samples.
Table 2. Parameters of the 2nd order polynomial fits $\omega (Z\text{O}_6) = c_0 + c_1 x + c_2 x^2$ to the experimental data sets $\omega (Z\text{O}_6)$ versus the contents $x$, $x = Z\text{Al}, Z\text{Fe}^{3+}, Z\text{Mg}$, and $(6-Z\text{Al})$. The goodness of fit is given by the coefficient of determination $R^2$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$Z\text{Al}$</th>
<th>$Z\text{Fe}^{3+}$</th>
<th>$Z\text{Mg}$</th>
<th>$(6-Z\text{Al})$</th>
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<tr>
<td>$c_0$</td>
<td>262 ± 2</td>
<td>367 ± 2</td>
<td>375 ± 8</td>
<td>371 ± 1</td>
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<tr>
<td>$c_1$</td>
<td>34 ± 1</td>
<td>-2 ± 5</td>
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<td>0</td>
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<tr>
<td>$c_2$</td>
<td>-2.5 ± 0.2</td>
<td>-6 ± 1</td>
<td>-23 ± 5</td>
<td>-3.1 ± 0.1</td>
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<td>$R^2$</td>
<td>0.99</td>
<td>0.97</td>
<td>0.74</td>
<td>0.99</td>
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</table>

Note: $c_1$ for $Z\text{Fe}^{3+}, Z\text{Mg}$, and $(6-Z\text{Al})$ is 0 within the uncertainties.
Figure 2

The figure shows Raman spectra for various minerals, including dravite, uvite, foitite, schorl, Fe³⁺-rich schorl, F-buergerite, lucchesiite, oxy-dravite, bosiite, and povondraite. The x-axis represents the Raman shift in cm⁻¹, ranging from 100 to 3800, and the y-axis represents the normalized intensity (arb. units). The spectrum features SiO₄ ring vibrations, SiO₄ stretching, and OH stretching.
Figure 3

(a) Mg-dominant
(b) Fe$^{2+}$-dominant
(c) Fe$^{3+}$-dominant
(d) Fe$^{3+}$-rich schorl
(e) lucchesite
(f) F-buergerite
(g) oxy-dravite
(h) bosite
(i) povondraite

Z$^{2+}$Al content (apfu) vs. $\omega$ (ZAl) (cm$^{-1}$)
Z$^{2+}$(Fe$^{2+}$+Fe$^{3+}$) content (apfu) vs. $\omega$ (Z(Fe$^{2+}$+Fe$^{3+}$)) (cm$^{-1}$)
Z$^{2+}$Mg content (apfu) vs. $\omega$ (ZMg) (cm$^{-1}$)
Z$^{2+}$Al content (apfu) vs. $\omega$ (ZAl) (cm$^{-1}$)
Z$^{2+}$Fe$^{3+}$ content (apfu) vs. $\omega$ (ZFe$^{3+}$) (cm$^{-1}$)
Z$^{2+}$Mg content (apfu) vs. $\omega$ (ZMg) (cm$^{-1}$)
Z$^{2+}$Al content (apfu) vs. $\omega$ (ZAl) (cm$^{-1}$)
Z$^{2+}$Fe$^{3+}$ content (apfu) vs. $\omega$ (ZFe$^{3+}$) (cm$^{-1}$)
Z$^{2+}$Mg content (apfu) vs. $\omega$ (ZMg) (cm$^{-1}$)
Figure 4

(a) Mg-dominant
(b) Fe²⁺-dominant
(c) Fe³⁺-dominant

(y = (-7±1)x + (314±2) 
R² = 0.81)

(y = (8±3)x + (300±2) 
R² = 0.51)

(y = (8±2)x + (302±3) 
R² = 0.38)
Figure 5

(a) Fe$^{3+}$-rich schorl
lucchesiite
F-buergerite
oxy-dravite
bosiite
povondraite

(b) $y = (-1.7 \pm 0.1)x + (2.6 \pm 0.1)$
$R^2 = 0.98$

(c) $\gamma$ content (apfu)

intensity ratio $I_1/I_2$
Figure 6

[Graph showing Raman shift vs. intensity for oxy-dravite S50 with peaks at 217, 312, 368, 3529, 3567, 3480, 3674, and 3738 cm\(^{-1}\) with corresponding intensities of 0.09, 0.09, 0.37, 0.53, and 0.05, 0.05, 0.05, and 0.05, respectively.]