Spectroscopic and crystal-chemical study of Mg-dominant tourmalines

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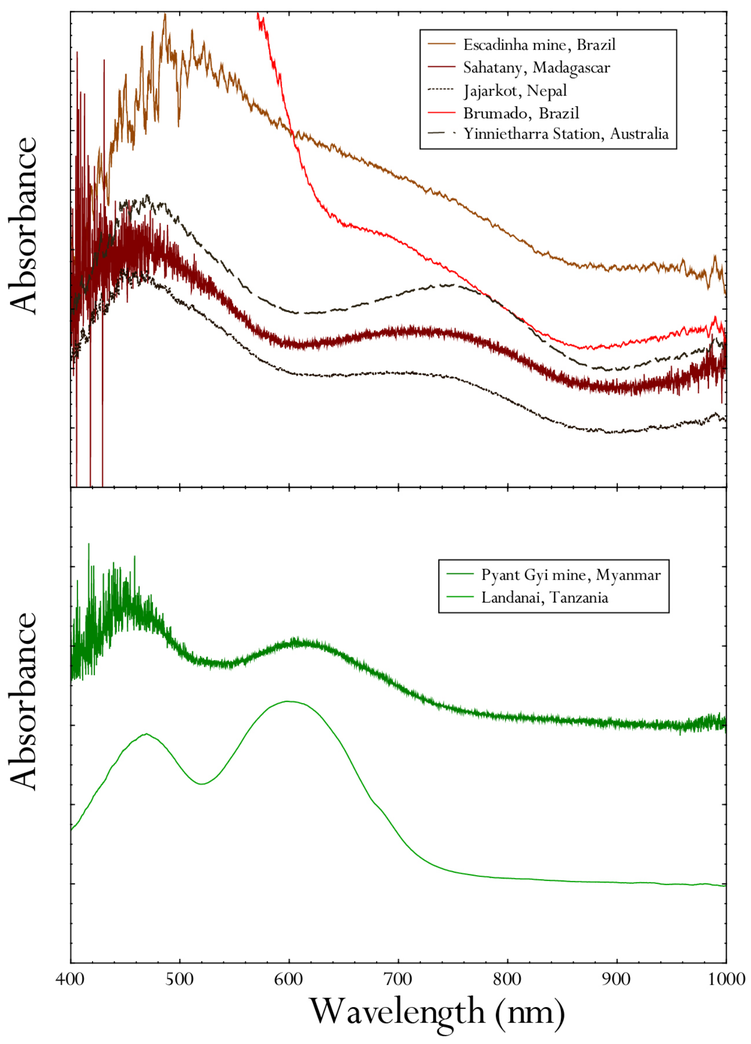
Dravitic and uvitic tourmalines display relatively large colour variability if their Fe content is limited. Brown dravite was found in the Gemerská Poloma, Slovakia, Yinnietharra Station, Australia, Jajarkot district, Nepal, Escadinha mine, Minas Gerais, Brazil, Sahatany Pegmatite Field, Madagaskar. Red (along with green and brown) uvite occurs on its type locality at Brumado mine, Bahia, Brazil. Specific colour varieties typical for Mg-rich tourmalines is a shades of green. Green tourmalines can be divided to two groups according to their chemical composition – V- and Cr-enriched (with typical emerald green colour) and V- and Cr-poor (greyish green to green colour) toumalines. Emerald-green tourmalines, often named as "chrome-dravite", occur e.g. in Landanai, Arusha Region, Tanzania, and Pyant Gyi mine, Mandalay Division, Myanmar. Green to brown-green tourmalines occur in Lengenbach quarry, Switzerland. Green-to-grayish green tourmaline crystals occur in the Forshammar pegmatite, Sweden. Tourmaline from Gemerská Poloma is almost homogenous and has a composition of dravite with very high X_{Mg} (0.95 – 0.96), and a very low *X*-site vacancy (up to 0.17) and Ca content (up 0.05 *apfu*). The Fe content is also very low (up to 0.14 *apfu*), the content of Al varies between 5.97 and 6.27 *apfu*. Dravite from Yinnietharra Station is magnesium-dominant (2.74 Mg *apfu*, 0.06 Fe *apfu*) with a relatively high content of Ti (0.13 *apfu*). Dravite from Jajarkot district is also strongly magnesium-dominant (2.52 Mg *apfu*, 0.05 Fe *apfu*) and slightly enriched in Al (total Al 6.34 *apfu*). Brown dravites found in Escadinha mine (2.47 Mg *apfu*, 0.04 Fe *apfu*, total Al 6.41 *apfu*), and in the Sahatany Pegmatite Field (2.46 Mg *apfu*, 0.07 Fe *apfu*, total Al = 6.45 *apfu*), are chemically very similar to the occurences above. In comparison to the other studied Mg-dominant tourmalines, red uvite from the Brumado mine, Bahia, Brazil has an increased content of Fe (0.50 *apfu*), Mg attains 2.92 *apfu*. Interestingly, a part (at least 0.03 *apfu*) of iron might be trivalent according to the calculation of charge-balanced formula, which along with slightly increased content of Ti (0.06 *apfu*) could have an impact on the colour of uvite. Although markedly green colour of tourmalines from Landanai and Pyant Gyi mine suggest the presence of Cr, in fact, it is only a minor element attaining max. 0.03 *apfu* in Pyant Gyi mine and 0.04 *apfu* in Landanai. The content of V is more significant – 0.04 *apfu* in Pyant Gyi mine and 0.14 *apfu* in Landanai. Thus, this composition is very far from "chrome-dravite" or "vanadium-dravite". Moreover, none of tourmalines from both localities is dravite at all because their composition (studied only on one sample for each locality) correspond to uvite (Ca = 0.76 *apfu* in Pyant Gyi mine and 0.57 *apfu* in Landanai). Both uvites are strongly Mg-dominant (3.58 Mg *apfu*, Fe below detection limit in Pyant Gyi mine and 3.31 Mg *apfu*, 0.002 Fe *apfu* in Landanai). Green to brown-green tourmaline from Lengenbach contains 2.82 Mg *apfu*, 0.09 Fe *apfu*, 0.07 Ti *apfu*, and 0.02 V *apfu*. Tourmaline from Forshammar displays chemical zoning with the high Mg/(Mg+Fe) value which decreases from core (~0.85) to intermediate zone (0.76-0.79) but increases in the rim and vein dravite (0.93). The core has the highest proportion of *X*-site vacancy and Al content, while the intermediate zone is the most enriched in Fe and Na. The rim is slightly depleted in Al and has the highest content Na compared to inner zones. Tourmaline veins crosscut the pre-existing tourmaline and are relatively more enriched in Na and Ca.

Based on the powder XRD and structure refinement, uvitic samples from Brumado mine and Landanai along with dravitic sample from Yinnietharra Station has *c* parameter higher than 7.20 Å which indicates a significant proportion of Mg at *Z* site. However, all the samples have $c > 7.17$ Å, therefore, some proportion of ^{Z}Mg is very likely in all samples.

The optical spectra of the studied samples clearly manifested their division into two groups. Brown and red tourmalines had a strong absorption (absorption edge?) in blue and green regions, in red uvite from Brumado it spreads to yellow region. This results from Fe^{2+}–Ti^{4+} IVCT (intervalence charge transfer) at around 470 nm (21,200 cm^{-1}). In the Brumado sample, which contains around ten times higher amount of Fe, the Fe^{2+}–Fe^{3+} IVCT band at around 525 nm (ca. 19,000 cm^{-1}) shifts the absorption edge to yellow region. Additional band at around 730-750 nm (13,300-13,700 cm^{-1}) results from $^{5}T_{2g} \rightarrow {}^{5}Eg$ electronic transition on $^{Y}Fe^{2+}$ or $^{Y}Fe^{2+}$-$^{(Y,Z)}Fe^{3+}$exchange-coupled pair. The optical spectra of green tourmalines have similar features with two distinct bands at 600-614 nm and 445-469 nm. These can be assigned to $^{4}A_{2g}(^{4}F) \rightarrow {}^{4}T_{1g}(^{4}F)$ a $^{4}A_{2g}(^{4}F) \rightarrow {}^{4}T_{2g}(^{4}F)$ electronic transitions in Cr^{3+} and $^{3}T_{1g}(^{4}F) \rightarrow {}^{3}T_{2g}(^{4}F)$ and $^{3}T_{1g}(^{4}F) \rightarrow {}^{3}T_{1g}(^{4}F)$ in V^{3+}. The colour of dravite, just like the colour of other minerals, is the result of a combination of structural properties and chemical composition – the presence of typical chromophores. The low content of iron and titanium is typical for coloured dravite. High Fe^{3+} and Ti^{4+} contents cause dark (macroscopically black) colour of Fe-rich tourmalines. Therefore, most of the tourmaline with the intermediate composition between schorl and dravite is macroscopically black. However, although the content of the above-mentioned elements may be low, it could influence the dravite colour. It has been shown that blue colour in tourmaline is related to the spin-allowed crystal field transitions of Fe^{2+} in deformed octahedral sites while usual IVCT transitions (Fe^{2+}-Ti^{4+}, Fe^{2+}-Fe^{3+}) are responsible for brown and red-brown colour. Brown tourmalines from Gemerská Poloma, Jajarkot, Escadinha mine, Yinnietharra, Sahatany and Brumado are relatively richer in Ti (0.05-0.13 *apfu*), thus their colour may be the result of Fe^{2+}-Ti^{4+} (and in Brumado also Fe^{2+}-Fe^{3+}) IVCT transitions. The reason of greyish green colour of dravite from Forshammar is yet unknown and cannot be estimated from the data available. Intensely green colour of dravite, as in Pyant Gyi Mine and Landanai, can be caused by the presence of vanadium and/or chromium, as in other silicates such as beryl (variety emerald), and uvarovite and goldmanite from the garnet group. The colour of dravite from Lengenbach is probably the result of slightly increased Ti (Fe^{2+}-Ti^{4+} IVCT transitions responsible for brown shades) as well as V content (green shades).

Optical absorption spectroscopy



Studied samples

Escadinha mine
Minas Gerais Brazil

Brumado mine
Bahia Brazil

Pyant Gyi mine
Myanmar

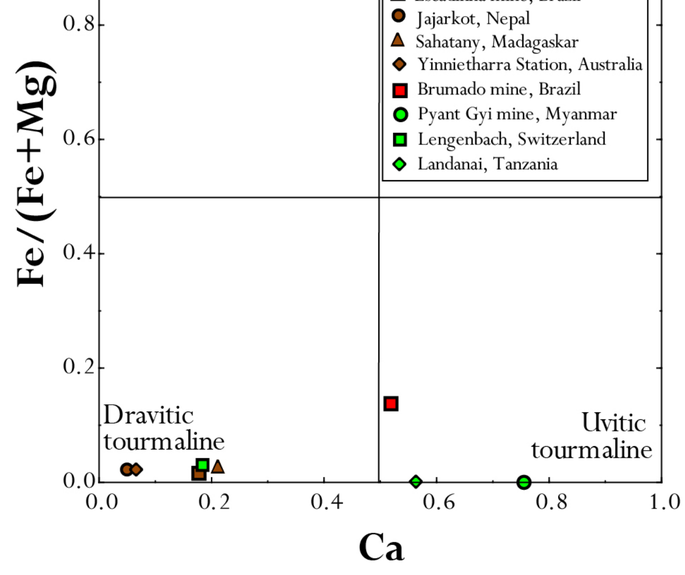
Yinniethara Station
Australia

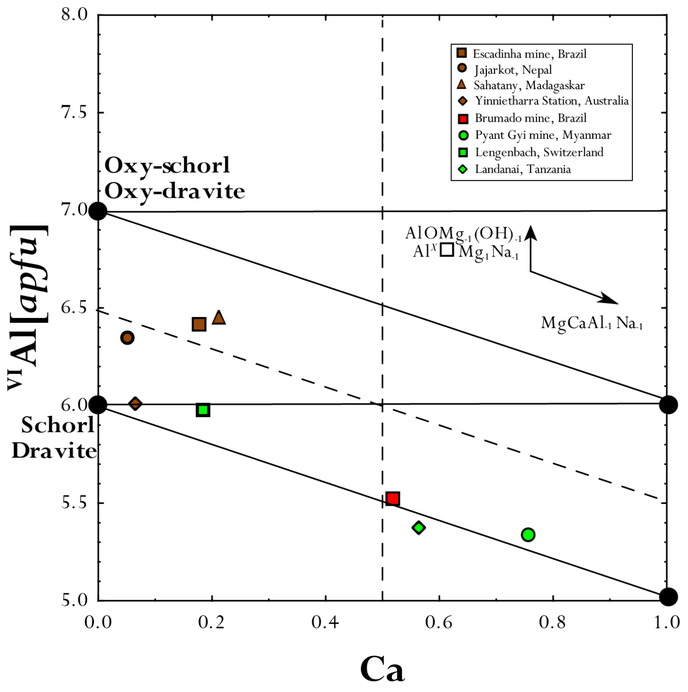
Landanai
Tanzania

Jajarkot district
Nepal

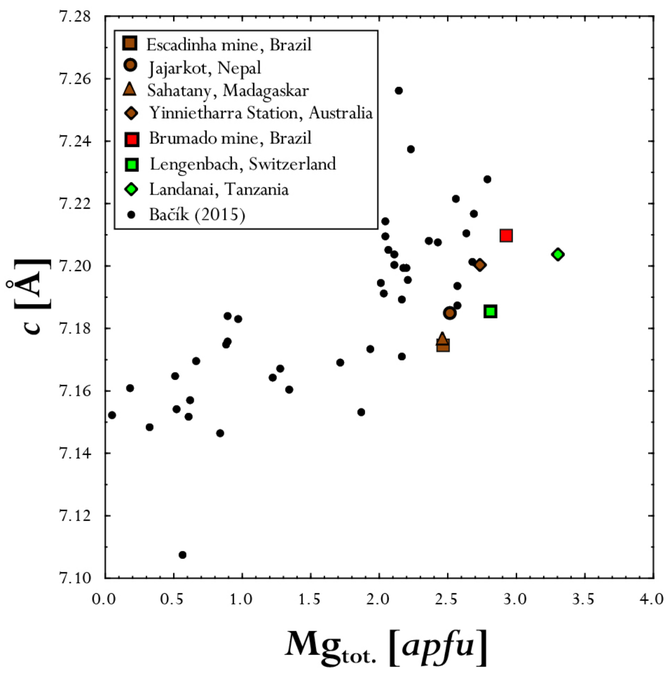
Sahatany Pegmatite Field
Madagascar

Chemical composition





XRD



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