Tourmaline is a common accessory to minor mineral in many magmatic and metamorphic rocks. General formula of tourmaline is: \(XY_2ZnT_jO_{18} (BO_3)_j(F,W)\), where \(X = \text{Na, Ca, } \Box, \) \(Y = \text{Mg, Fe}^{2+}, \) \(Z = \text{Al, Mg, Fe}^{3+}, \) \(V^{3+}; T = \text{Si, Al, B}; B = B; V = \text{OH, } F; W = \text{OH, } F, \) O; chiefly heterovalent substitutions operate in the tourmaline group minerals. Tourmaline is widely used as an indicator of various processes. However, its chemical composition is controlled, besides external factors (e.g., PT conditions, chemical potentials and competition with associated minerals) also by internal factors (crystal structural constraints – short-range ordering); consequently, using chemical composition of tourmaline as a strict indicator of geochemical processes might be misleading. We will focus on several examples of tourmaline from different geological and geochemical environments where short-range ordering play principal role on chemical composition of the relevant tourmaline. The following systems are discussed:

a) (Ca, F)-poor peraluminous system (e.g., primitive barites with the assemblage Qtz + Ab + KFs + Ms + Bt + Tur; e.g., NOVÁK et al., 2004) with tourmaline showing \(X_{Fe} < -0.80, \) a simple compositional trend was recognized showing increase \(X_{Fe}\) and \(\Delta Al\) during fractionation and tourmaline composition commonly tends to the simplified formula:

\[\frac{1}{2}(\text{Na}_{0.5-1.3}) \quad (\text{Fe}^{2+}, \text{Mg})_2 \text{Al}_6 (\text{BO}_3)_3 \quad \text{Si}_6 \text{O}_{18} \quad (\text{OH})_3 \quad (\text{F})_{\#} \]

b) Ca-poor, F-rich peraluminous system (e.g., Li-poor tourmaline-muscovite granite with the assemblage Qtz + Ab + KFs + Ms + Tur; e.g., NOVÁK et al., 1998) with tourmaline showing high Na and low vacancy in the X-site, \(X_{Na} > 0.90\) and low \(\Delta Al; \) tourmaline composition tends very well to the formula:

\[3\text{Na}^{\#} \quad \text{Fe}^{3+}\] 

or Li-rich peraluminous system (complex pegmatite with the assemblage Qtz + Ab + Elb + Ms + Lpd; e.g., NOVÁK & TAYLOR, 2000) with tourmaline showing high Na and F, and tourmaline composition tends to the simplified formula:

\[3\text{Na}^{\#} (\text{Li,Fe}^{2+})_2 \quad \text{Al}_6 (\text{BO}_3)_3 \quad \text{Si}_6 \text{O}_{18} \quad (\text{OH})_3 \quad (\text{F})_{\#} \]

c) F-poor, Fe\(^{3+}\)-rich alkaline system (metakaolinite with the assemblage Dol + Mgs + KFs + Gp + Anh, Alto Chapare, Cochabamba, Bolivia; ZÁČEK et al., 2000) with tourmaline showing high K, very low X-site vacancy, high \(\text{Fe}^{3+}\) and very low \(\Delta Al; \) tourmaline composition tends to the simplified formula:

\[3\text{K}\] 

These well-defined distinctive trends in tourmaline strongly suggest significant role of crystal-structural constraints on the tourmaline composition. In F-poor peraluminous rocks with variable \(X_{Fe}\) in tourmaline, the composition is characterized by high vacancy in the X-site, and significant amount of O in the W-site (NOVÁK et al., 2004). The occupation of the Y-site, Z-site and O(1) site is controlled by short-range requirements (HAWTHORNE, 1996, 2002) and the configuration \(R^{2+}=R^{3+}\) which is the Y-site and disorder of Mg and Al between Y- and Z-site is the most suitable; this configuration controls 0.5 \(\text{pfu}\) vacancy in the X-site and 0.5 \(\text{pfu}\) O in the W-site. In F-rich peraluminous rocks high amount of F in the W-site controls, high Na and low vacancy in the X-site. The occupation of the Y-site is controlled by short-range requirements and the configuration with lowest charge of 3Y sites (\(\text{Fe}^{2+}=\text{Fe}^{3+}\) in Li-poor system) or (\(\text{Li}=\text{Fe}^{2+}\) in Li-rich system) in tourmaline is the most suitable; this configuration is compensated best by the low valence of W-site (high F) and it controls the low vacancy in the X-site. In F-poor, \(\text{Fe}^{3+}\)-rich alkaline system, high K in the X-site is controlled by high \(\text{Fe}^{3+}\) in the Y-site and especially by the network of the Z-site octahedra, built up by Fe\(^{3+}\) and Mg. Enlarged unit cell, due to Fe\(^{3+}\) dominant in the Z-site and rather small Fe\(^{3+}\) cation relative to Fe\(^{2+}\) in the Y-site, enables entering of large cation of K into the X-site; K is typically very low (commonly below the detection limit of electron microprobe) in tourmaline from K-rich peraluminous systems (e.g., blocky K-feldspar unit in granitic pegmatites). Presence of O\(^2\) in the W-site is necessary due to very high total charge of the Y-site.

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