

## CHEMICAL COMPOSITION OF TOURMALINE; A SIGNIFICANCE OF CRYSTAL-STRUCTURAL CONSTRAINTS

NOVÁK, M.<sup>1</sup> & CEMPÍREK, J.<sup>2</sup>

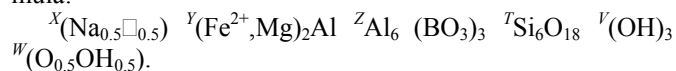
<sup>1</sup> Institute of Geological Sciences, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

E-mail: mnovak@sci.muni.cz

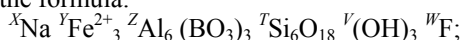
<sup>2</sup> Department of Mineralogy and Petrography, Moravian Museum, Zelný trh 6, 659 37 Brno, Czech Republic

Tourmaline is a common accessory to minor mineral in many magmatic and metamorphic rocks. General formula of tourmaline is:  $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ , where  $X = Na, Ca, \square, K$ ;  $Y = Mg, Fe^{2+}, Li, Al, Fe^{3+}$ ;  $Z = Al, Mg, Fe^{3+}, Cr^{3+}, V^{3+}$ ;  $T = Si, Al, B$ ;  $B = B$ ;  $V = OH, O$ ;  $W = OH, F, O$ ; 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:

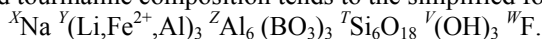
a) (Ca, F)-poor peraluminous system (e.g., primitive barren pegmatites with the assemblage Qtz + Ab + Kfs + Ms + Bt + Tur; e.g., NOVÁK *et al.*, 2004) with tourmaline showing  $X_{Fe} < \sim 0.80$ , a simple compositional trend was recognized showing increase  $X_{Fe}$  and  $^YAl$  during fractionation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



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,  $X_{Fe} > \sim 0.90$  and low  $^YAl$ ; tourmaline composition tends very well to the formula:



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:



c) F-poor,  $Fe^{3+}$ -rich alkaline system (metaevaporites with the assemblage Dol + Mgs + Kfs + Gp + Anh, Alto Chapare, Cochabamba, Bolivia; ŽÁČEK *et al.*, 2000) with tourmaline showing high K, very low X-site vacancy, high  $^YFe^{3+}$  and very low  $^ZAl$ ; tourmaline composition tends to the simplified formula:



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  $R^{2+}-R^{2+}-Al^{3+}$  in the Y-site and disorder of Mg and Al between Y- and Z-site is the most suitable; this configuration controls 0.5 *pfu* vacancy in the X-site and 0.5 *apfu* 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 ( $Fe^{2+}-Fe^{2+}-Fe^{2+}$  in Li-poor system) or (Li- $Fe^{2+}$ -Al 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,  $Fe^{3+}$ -rich alkaline system, high K in the X-site is controlled by high ( $Fe^{3+}$ ) 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.

This research was supported by the research projects MSM0021622412 to MN and MK00009486201 to JC.

### References

- HAWTHORNE, F.C. (1996): Canadian Mineralogist, 34: 123–132.  
 HAWTHORNE, F.C. (2002): Canadian Mineralogist, 40, 789–797.  
 NOVÁK, M. & TAYLOR, M.C. (2000): Canadian Mineralogist, 38: 1399–1408.  
 NOVÁK, M., SELWAY, J.B. & HOUZAR, S. (1998): Journal of the Czech Geological Society, 43: 37–44.  
 NOVÁK, M., POVONDRA, P. & SELWAY, J.B. (2004): European Journal of Mineralogy, 16: 323–333.  
 ŽÁČEK, V., FRÝDA, J., PETROV, A. & HYRŠL, J. (2000): Journal of the Czech Geological Society, 45: 3–12.