

Tourmaline-fluid interactions: Fluorine monitor and the role of tourmaline crystallography

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Tourmaline effectively partitions F relative to many hydrous minerals and can be a monitor of the F in coexisting fluids. However, F contents in tourmaline are a function of external factors such as the F concentrations in the coexisting fluid and, probably, PT conditions and internal factors such as crystallographic surface energy constraints. The proper interpretation of the relation between tourmaline chemistry and fluid compositions depends on the relative influences of both factors.

The general formula of tourmaline is $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$; with the most common site occupancies being: X = Ca, Na, K, ^X□ (vacancy); Y = Li, Mg, Fe²⁺, Mn²⁺, Al, Cr³⁺, Fe³⁺; Z = Al, Mg, Fe³⁺, Cr³⁺; T = Si, Al; B = B; V = OH, O; W = OH, F, O. Of particular importance is that F occurs at a single anion site, the W site. Incorporation of F in this site is influenced by the occupancy of the X site. The X-site is generally occupied by cations of variable charge (Na¹⁺ or Ca²⁺) and/or is vacant (zero charge). Because of local bonding of the W site anion to three neighboring Y-site cations and the X-site cation, the charge of the X-site cation affects the F occupancy in the W site. Infrared and Raman spectroscopy measurements and local charge balance considerations establish that F for OH substitution will be favorable where the Y site charge of 6+ such as where the X-site is occupied by Na¹⁺ or Ca²⁺. However, F substitution will be unfavorable where there is a 7+-charge (or more) environment such as proximal to the three Y sites in ^X□ tourmaline. Natural tourmaline data verifies the antipathetic relationship between the magnitude of ^X□ and concentration of F. A summary of >600 tourmaline analyses from different tourmaline varieties illustrates that in tourmalines not dominated by ^X□, F concentrations range from 0-1.0 apfu. However, tourmalines with more than 0.5 ^X□ there is little or no F present in the tourmaline. In addition to the crystallographic factors, F concentrations are also a function of the F concentrations in the coexisting fluid phase. This influence can be illustrated from a study of fibrous tourmaline replacing preexisting tourmaline in a pegmatite pocket that apparently has undergone rupture. Change in the tourmaline fiber compositions reflect that of a varying infiltrating fluid. Empirical calibrations of HF contents in the fluid are being correlated against fluid-biotite systematics.