

The site occupancy assessment in tourmaline-supergroup minerals based on bond-length constraints

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Theoretical bond-length calculation from ideal bond valences for each ion and coordination can predict ion site preference in the structure. It revealed that *T* site can freely accommodate Si⁴⁺ and Be²⁺; B³⁺ and Al³⁺ substitution requires compression or expansion of *TO*₄ tetrahedron, respectively. The *B*-site occupancy is strictly limited to B³⁺. Proper bond lengths for octahedral sites were calculated for Al³⁺ (*Z*-site preference), Ti⁴⁺, Mn³⁺, Ga³⁺, V³⁺, Fe³⁺ (mixed preference), Mg²⁺, Fe²⁺, Li⁺, Mn²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Sc³⁺ and Zr⁴⁺ (*Y*-site preference). Another group of cations including U⁴⁺, Th⁴⁺, Y³⁺ and lanthanoids from Tb³⁺ to Lu³⁺ and Ce⁴⁺ have significantly longer bonds than typical *Y*-O, but they form too short bonds for the *X* site. Therefore, they probably prefer octahedron. The usual empirical bond length for the *X* site is met with Na⁺, Ca²⁺, Sr²⁺, Pb²⁺ and lanthanoids from La³⁺ to Gd³⁺, while K⁺, Rb⁺ and Cs⁺ bond lengths are unbearably large for tourmaline *X* site.

For every structural site, the “Goldilocks zone” of bond lengths can be assumed. This defines the range of bond length, which does not induce large structural tension and distortion. It is quite narrow in small sites such as *B* and *T* in tourmaline, but larger in sites with higher coordination number. This is the case of Al and B at *T* site – they substitute for Si but only in a limited proportion. Similarly, the proportion of REE in tourmaline is limited, although these can be abundant in the environment. It results from the deviation from the “Goldilocks zone” for both *X* and *Y* site and also relatively high charge for the *X* site. However, based on the present data, if present, REE likely partition between the *Y* (HREE) and *X* (LREE) site. However, the final tourmaline composition results from interaction of structure with the genetic environment. The proportion of REE in tourmaline is structurally limited, while e.g. Zr⁴⁺, Sc³⁺, Sr²⁺, Pb²⁺ have only geochemical limits with no obvious structural limit.

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