Tourmaline Chemistry and the Flexible *B*-site

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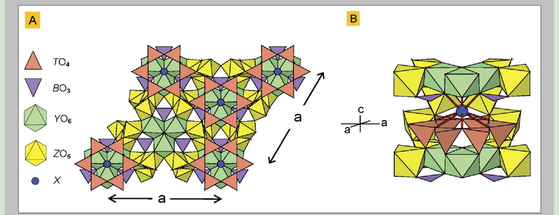
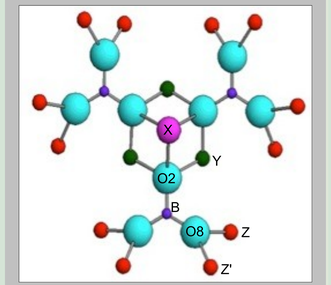
Abstract

Tourmaline is a complex borosilicate mineral group with over 30 species currently approved by the IMA. Due to its complex chemistry and difficulties with full chemical analysis, assumptions are commonly made during formulae normalizations, often with little corroborative support. This include Fe^{2+}/Fe^{3+} ratios and amounts of the light elements Li, B and H. These assumptions can lead to misidentification of tourmaline species and resulting interpretation of geochemical environment of formation. Past research has shown the stereochemistry of the *B*-site to be sensitive to variations in chemistry, responding to the occupancy of the *Y*- and *Z*-sites in particular. We are further investigating this relationship to better understand why the (BO_3) triangle responds to the chemistry of the octahedral sites, and what has the strongest effect. This will allow crystallographic data to support assumptions made during the tourmaline normalizations. This information can also be used to validate, identify, and differentiate similar species among the tourmaline group.

Tourmaline Structure



Structure Fragment



Statement of Problem

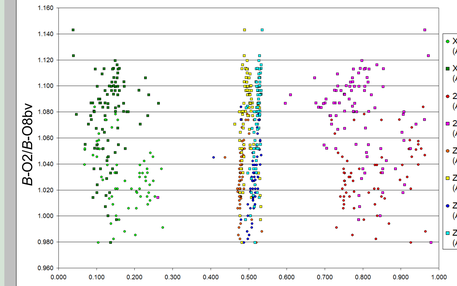
- Previous studies suggest the octahedral *Z*-site greatly influences the stereochemistry of the BO_3 triangle. Multiple new tourmaline species have been discovered recently, and this trend has not yet been confirmed in them
- It is unclear how the variation in the *B*-site stereochemistry is geometrically accommodated in the rest of the tourmaline structure

Methods

- Compile a database of tourmalines, including chemistry and crystal structure
- Create two subsets from the database, one with *Z*≥5.00 *apfu* Al, and one with *Z*=6.00 *apfu* Al
- Run statistical analysis on the above data subsets to better understand how *Z*-site occupancy is responsible for fluctuations in *B*-site bond-lengths

Bond-valence Relationships and Statistics

X-O2bv, 2*(*Y*-O2bv), *Z*-O8bv, *Z'*-O8bv VS *B*-O2/*B*-O8bv



Analysis of all samples with *Z*-site occupancy of 5.00 *apfu* or more aluminum

Model		Unstandardized Coefficients B	Unstandardized Coefficients Std. Error	Standardized Coefficients Beta	t	Sig.
1	(Constant)	.371	.149		2.497	.014
	X-O2bv	-.130	.061	-.179	-2.125	.035
	2*(Y-O2bv)	.042	.033	.102	1.264	.208
	Z-O8bv	.344	.181	.149	1.904	.059
	Z'-O8bv	1.100	.182	.426	6.053	.000

a. Dependent Variable: *BO2/BO8bv

Analysis of all samples with *Z*-site occupancy of 6.00 *apfu* aluminum

Model		Unstandardized Coefficients B	Unstandardized Coefficients Std. Error	Standardized Coefficients Beta	t	Sig.
1	(Constant)	-.545	.255		-2.137	.035
	X-O2bv	.198	.072	.246	2.744	.007
	2*(Y-O2bv)	.073	.036	.212	2.045	.044
	Z-O8bv	.419	.227	.183	1.846	.068
	Z'-O8bv	2.544	.329	.693	7.727	.000

a. Dependent Variable: *BO2/BO8bv

Results and Conclusions

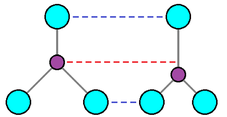
- Statistical analyses show that even when the *Z*-site occupancy is uniform across multiple samples, the *Z'*-bond is still the bond most responsible in influencing the *B*-site's bond-lengths
- A potential explanation is that the bond-angles/geometry are responsible for this occurrence, where the *Z'*-O8 bond has a straighter alignment to, and therefore greater effect on, the BO_3 stereochemistry

Future Work

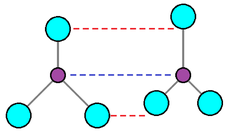
- Determine which of the possible geometry scenarios is occurring in and around the boron triangle
- Continue running statistical analysis on new tourmaline species as they are discovered/more data becomes available
- Further develop our understanding of the relationship between tourmaline's chemistry and crystal structure

Possible Geometries

Scenario 1: The boron shifts, and the oxygen remain fixed.



Scenario 2: The oxygen shift, and the boron remains in place.



Scenario 3: Both the boron *and* oxygen shift.

References & Acknowledgements

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