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Cation partitioning based on bond-length constraints in beryl

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The site preference for each cation and site in beryl based on the bond-length calculations was determined and compared with analytical data.

Tetrahedral SiO_4 six-membered rings normally have no substitutions which results from very compact Si-O bonds in tetrahedra. Any substitution except Be would require significant tetrahedral ring distortion.

The Be tetrahedron should also be negligibly substituted based on the bond-valence calculation; the tetrahedral Li-O bond length is almost 20 % larger than Be-O. Similar or smaller bond lengths were calculated for Cr^{3+}, V, Fe^{3+}, Fe^{2+}, Mn^{3+}, Mg^{2+} and Al^{3+}, which can substitute for Be but also can occupy neighboring tetrahedrally coordinated site which is completely vacant in the full Be occupancy.

The octahedral site is also very compressed due to dominant Al with short bond lengths; any substitution of other tetravalent (Ti^{4+}), trivalent (Fe^{3+}, Mn^{3+}, Cr^{3+}, V^{3+}, Sc^{3+}), and divalent (Mg^{2+} and Fe^{2+}) cations results in the octahedron expansion.

There are two channel sites in beryl, one smaller in the center of each tetrahedral ring and one larger between the pair of rings. Bond-length calculations revealed that from the cations usually occurring in beryl, only Na^+, Ca^{2+} and Li^+ have proper ionic radii to occupy 2*b* site, Fe^{2+} and Fe^{3+} are too small, K^+, Cs^+, Rb^+ and Ba^{2+} are too large. Interestingly, if any REE^{3+} are in the beryl structure, these would be located here.

The 2*a* site has the maximal bond length of 3.38 Å. This is a very large distance, larger than calculated $d(Cs^+–O)$ (3.31 Å). This allows the presence of simple molecules including H_2O, CO_2 or NH_4. Among cations, the large size of the site results in preferring Cs^+ at this site, which is in fact the most abundant cation at this site in natural samples. Among others, Rb^+, K^+ and Ba^{2+} have calculated ionic radii within the 15% range for free substitution, all other including Na^+, Ca^{2+}, Li^+, REE^{3+}, Fe^{2+} and Fe^{3+} are too small for the 2*a* site.

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