

Geochemistry of beryl from the granitic pegmatite at Namivo, Alto Ligonha, Mozambique

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A geochemical evolution was found in beryl from an elongated, concentrically zoned granitic pegmatite from Namivo, Mozambique. The crystalchemical evolution is marked by an increase in Al, Li, Na, Cs, Al/(Fe+Mn+Mg), Σ REE and a decrease in Be, Fe, Mg, Be/Li, Be/(Na+Cs), Be/(Li+Na+Cs), Na/Li and Li/Cs from the green and bluish green beryls of the outer zone to the pink beryls of the inner and core zones and is caused by magma fractionation. Beryl has low REE contents, a negative Eu anomaly and enrichment of the middle REE. The colour change in beryl from the outer zone to the core zones is attributed to an increase in the Mn/Fe ratio and a possible decrease in the Fe^{3+}/Fe^{2+} ratio. The octahedral substitution of Fe^{2+} , Mg^{2+} and Mn^{2+} for Al^{3+} predominates in green beryl from the outer zone, while the tetrahedral substitution of Li for Be mainly takes place in pink beryl from the other more fractionated zones. Na^+ and Cs^+ in channels are important for the charge balance of both substitutions, but $Cs \geq 0.009$ apfu is only important in beryls from the inner and core zones.

The crystalchemical substitutions in beryl cause an increase in unit-cell dimension c , cell volume and c/a ratio in beryl from the outer zone to beryls of the inner and core zones. The unit-cell parameter c correlates positively with volume, c/a ratio and Li and negatively with Be. Two trends are defined at c 9.210 Å and Be 2.75 apfu, one for the beryls from the outer zone with the predominately octahedral substitution and the other for the beryls from the inner and core zones with mainly tetrahedral substitution.

A single zoned crystal from the outer zone has a core of primary beryl, while the rim has a composition similar to that of beryls from the inner and core zones of the pegmatite. Li, Na, Cs, Al/(Fe+Mn+Mg), unit-cell dimension c , cell volume and c/a ratio increase and Be, Be/Li, Na/Li, Li/Cs, Be/(Na+Cs) and Be/(Li+Na+Cs) decrease from core to rim of this single zoned crystal. Li increases by a factor of two from core to rim. This is approximately half of the increase in Li from beryl of the outer zone to beryl of the other more fractionated zones, suggesting that in the outer zone beryl composition was significantly affected during the crystallization of the inner and core zones.

Structural state of Th in fluoroapatite determined by single crystal XRD and EXAFS

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Thorium in apatite has been used extensively in geochronologic and petrogenetic studies for decades. Because of its high affinity for Th and other radionuclides and its thermal annealing behaviour, there is also great interest in apatite as a solid nuclear-waste form and an engineered contaminant barrier. Fundamental to our understanding of thorium retention and release by apatite are crystal chemical parameters such as site occupancy and structural distortions created by this substituent. Despite the interest in Th in apatite, the basic crystal chemistry of its substitution in the structure is still unknown. We present the first direct evidence of the site of incorporation and the response of the structure to Th. Single crystal X-ray diffraction data were used to refine the structure and site occupancies of a synthetic fluorapatite with approximately 2 wt% Th in the structure. Extended X-ray absorption fine structure (EXAFS) was used to probe the local structure of Th within a natural fluorapatite from Mineville, NY with a Th concentration of approximately 2000 ppm.

Structure refinements of three separate crystals of the synthetic Th doped fluorapatite ($R=0.0167-0.02167$) indicate that Th partitions almost exclusively into the Ca2 site. EXAFS results also indicate that Th substitutes into the Ca2 site and yield Th specific bond distances not obtainable from XRD data.