

## **Unusual M<sup>3+</sup> cations in synthetic amphiboles with nominal fluoro-eckermannite composition: Deviations from stoichiometry and structural effects of the cummingtonite component**

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### **ABSTRACT**

Single-crystal structure-refinement and electron-microprobe analysis of synthetic amphiboles with nominal fluoro-eckermannite composition and different trivalent cations (Al, Sc, Ti<sup>3+</sup>, V<sup>3+</sup>, Cr<sup>3+</sup>, Ga,) show significant deviations from nominal stoichiometry. Synthetic Sc- and Cr-bearing fluoro-eckermannite are close to nominal stoichiometry, whereas the corresponding nominal Al-, V<sup>3+</sup>-, Ga-, and Ti-bearing species contain very few trivalent cations and approximate Na(NaMg)Mg<sub>5</sub>Si<sub>8</sub>O<sub>22</sub>F<sub>2</sub>, a composition that has not been found in natural systems. The presence of a significant cummingtonite component strongly affects unit-cell parameters, coordination geometry around the B-, C-, and T-group sites, and cation ordering at the A-group sites. The high-charge cations are completely ordered at the M2 site, and there is a well-developed linear relationship between <M2-O> and the constituent-cation radius at the M2 site. The synthetic fluoro-eckermannite structure is stabilized by large spherically symmetric trivalent cations at the M2 site; for small spherically symmetric trivalent cations, it is not stable (at least at the synthesis conditions used here). Synthetic chromium-fluoro-eckermannite is stabilized by the non-spherically symmetric 3d<sup>3</sup> electronic arrangement, whereas Ga and V<sup>3+</sup> (3d<sup>2</sup>) do not stabilize the fluoro-eckermannite structure.