

Column anion arrangements in chemically zoned ternary chlorapatite and fluorapatite from Kurokura, Japan

SEAN R. KELLY^{1,*}, JOHN RAKOVAN¹, AND JOHN M. HUGHES²

¹Department of Geology and Environmental Earth Science, Miami University, Oxford, Ohio 45056, U.S.A.

²Department of Geology, University of Vermont, Burlington, Vermont 05405, U.S.A.

ABSTRACT

The substitution of F, OH, and Cl in apatite has recently gained increased attention due to the complex nature of incorporation of these three constituents and the implications of apatite column anion chemistry, such as apatite's contribution to the water budget of the Moon and Mars and the use of apatite anion chemistry as an indicator of halogen and water activities. The solid solutions among F, OH, and Cl are complex because the end-member atomic arrangements cannot fully explain the ternary and binary substitutions of these constituents due to differing atomic radii and the resulting steric constraints in the structure. Three structural variations have recently been reported for the OH-Cl binary solid solution in synthetic samples. This study elucidates column anion arrangements in a chemically zoned ternary apatite from Kurokura, Japan. The structures of the compositionally different core and rim were solved ($R1 = 0.0158$ and $R1 = 0.0143$, respectively) in space group $P6_3/m$ using single-crystal X-ray diffraction data. The chemistry of these apatites was analyzed using electron microprobe analysis and crystal structure refinement. The core of the Kurokura crystal is a naturally occurring example of the $\text{OH} \approx \text{Cl}$ apatite structural variation in a ternary chlorapatite, with four column anion sites (one for F, two for Cl and one for *both* OH and Cl). The rim exhibits a previously unseen apatite structural variation in a ternary OH-rich fluorapatite (with only a trace Cl component) with three column anion sites (one each for F, OH, and Cl). Both structural variations show a splitting of the Ca2 site that enables reasonable column anion bond distances with Ca2 atoms. A sequence of anions that provides reasonable anion-anion distances while simultaneously enabling reversal of the anion sites relative to the mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ exists for both structure variations. This study demonstrates the structural complexity of natural ternary apatites, and that a structural variety of OH-Cl apatite occurs over a wider range of chemistry than initially anticipated. The results have implications regarding the poorly understood (and potentially complex) crystallization history of apatite from Kurokura, Japan.

Keywords: Apatite, ternary solid solution, chlorapatite, Kurokura, Japan