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Site preference of rare earth elements in fluorapatite: Binary (LREE+HREE)-substituted crystals

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ABSTRACT

Crystals of binary (LREE+HREE)-bearing fluorapatite [La,Gd-FAp, Ce,Dy-FAp, Pr,Er-FAp, Eu,Lu-FAp; $Ca_{10-x-2y}Na_yREE_{x+y}(P_{1-x}Si_xO_4)_6A_2$, with $x = 0.12$–0.20, $y = 0.26$–0.42; $P6_3/m$] have been grown from H_2O-rich phosphate-fluoride melts, and their structures refined at room temperature with single-crystal X-ray intensities to $R = 0.017$–0.022. These binary-REE-substituted fluorapatite samples have REE site-occupancy ratios (REE-Ca2/REE-Ca1) of 2.32, and 2.32, 2.03, 1.71, respectively, which are 0.47–0.16 smaller than corresponding ratios calculated using data for reference single-REE-substituted fluorapatite. Discrepancies in intracrystalline partitioning between multiple-REE-substituted apatites and single-REE-substituted fluorapatite decrease with a decrease in REE concentration, becoming negligible at 0.2–0.3 total REE cations pfu in synthetic binary-REE-substituted fluorapatite and at trace abundances of REE in natural apatites. However, quantitative transference of laboratory REE site preferences to natural apatites is frustrated by the compositional complexity in nature. In the synthetic fluorapatite, there is a profound change in the spatial accommodation of REE in the apatite structure at about the position of Nd in the 4f transition-metal series, corresponding to the peak in the experimental uptake curve. Discrepancies in intracrystalline partitioning between binary-REE- and single-REE-substituted fluorapatite are attributed to non-ideal mixing of LREE and HREE that results in contraction of the Ca1 coordination sphere.