

Rare-earth elements in chlorapatite [Ca₁₀(PO₄)₆Cl₂]: Uptake, site preference, and degradation of monoclinic structure

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ABSTRACT

Differences in the inter- and intracrystalline partitioning behavior of rare earth elements (REE) between chlorapatite (ClAp), fluorapatite (FAP), and hydroxylapatite (OHAp) are directly or indirectly related to substitution mechanism and spatial accommodation. The substitution of REE for Ca is charge compensated by Na in ClAp, Na and Si in FAp, and Si in OHAp. Twinned crystals of REE-substituted ClAp [La-ClAp, Nd-ClAp, Sm-ClAp, Dy-ClAp; Ca_{10-2y}Na_yREE_y(PO₄)₆Cl₂, with $y = 0.05$ – 0.09 ; space group $P2_1/b$] have been grown from SiO₂-bearing, H₂O- and Na-rich phosphate-chloride melts, and their hexagonal ($P6_3/m$) subcell structures refined at room temperature with single-crystal X-ray intensities to $R = 0.020$ – 0.023 . The crystal/melt partition coefficients for La, Nd, Sm, and Dy are 0.073, 0.128, 0.122, and 0.101. Thus, uptake of REE is up to two orders of magnitude lower in ClAp than in REE-substituted FAp and OHAp crystallized under equivalent conditions, but remains peaked at Nd. REE site occupancy ratios [(REE-Ca2)/(REE-Ca1)] obtained from direct refinement of electron densities are 0.71, 1.11, 0.21, and 0.09 for La-, Nd-, Sm-, and Dy-ClAp, respectively, and are consistent with relative change in Ca-O bond distances and sizes of Ca polyhedra. Thus, La, Sm, and Dy favor the Ca1 position of ClAp, not Ca2, as in FAp and OHAp; this unusual site preference is attributed to the large increase in size (6–8%) and distortion of the Ca₂O₆X polyhedron on substitution of Cl for (F,OH). The slight preference of Nd for Ca2 and the peaking of REE uptake at Nd are attributed to a $4f$ crystal-field contribution, which is revealed by an anomalous decrease in the Ca2-O1 bond length and volume of the Ca₂O₆X polyhedron in Nd-ClAp, Nd-Fap, and Nd-OHAp. The $P2_1/b$ structure of La-ClAp has been refined by detwinning the diffraction pattern, confirming that this monoclinic superstructure largely represents ordering of Cl atoms displaced along [001]. The $P2_1/b$ structure of Dy-OHAp has been refined similarly. The intensity of superstructure reflections decreases abruptly with increasing substitution of REE for Ca, showing that REE cations interfere with ordering of Cl atoms (and OH⁻ groups) during the $P6_3/m \rightarrow P2_1/b$ transition.