Rare-earth elements in chlorapatite [Ca$_{10}$(PO$_4$)$_6$Cl$_2$]: 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$_{10-3y}$Na$_y$REE$_y$(PO$_4$)$_6$Cl$_2$, with y = 0.05–0.09; space group P$2_1/ b$] have been grown from SiO$_2$-bearing, H$_2$O- and Na-rich phosphate-chloride melts, and their hexagonal (P$6/m$) 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 CaO$_6X$ 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 Ca2O$_6X$ polyhedron in Nd-ClAp, Nd-Fap, and Nd-OHAp. The P$2_1/ b$ 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 P$2_1/ b$ 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 P$6/m$ → P$2_1/ b$ transition.

INTRODUCTION

Stoichiometric and near-stoichiometric chlorapatite [Ca$_{10}$(PO$_4$)$_6$Cl$_2$; ClAp] is monoclinic at room temperature with space group P$2_1/ b$, $a = 9.642$ Å, $b = 19.273$ Å ($=2a$), $c = 6.766$ Å, $\gamma = 120.02^\circ$ (Mackie et al. 1972; Elliott 1994, 1998; Bauer and Klee 1993). The monoclinic structure is very similar to the hexagonal P$6/m$-type structure of apatite, but has an ordered arrangement of Cl atoms above and below z = 1/4 on the pseudohexagonal axis. Hexagonal ClAp is formed when either a flux of molten CaCl$_2$, where CaCl$_2$ is present to excess (Prener 1967; Bauer and Klee 1993), or from hydrothermal solution, where the heating is confined in a vessel (Argiolas and Baumer 1978; Baumer et al. 1995). The hexagonal (P$6/m$) crystal structures of natural fluorapatite (FAp), hydroxylapatite (OHAp), and ClAp were compared in Hughes et al. (1989).

Rare earth elements (REE) substitute differentially for Ca in the apatite structure, with uptake being highest in the range Nd–Gd for natural apatite and near Nd for synthetic FAp (Fleet and Pan 1995, 1997a) and OHAp (Fleet et al. 2000), and being lowest for Lu (Fig. 1). The overall consistency of this behavior for rocks, melts, and solvents of widely different composition points to crystal-chemical control(s) on REE uptake. The two Ca positions (Ca1, Ca2) in the apatite structure offer quite different stereochemical environments. The nearest-neighbor environment of the Ca1 position (site symmetry 3) is a CaO$_9$ tricapped trigonal prism, which also can be regarded as 6 + 3 coordination. The environment of Ca2 (site symmetry m) is a CaO$_6X$ irregular polyhedron formed by a hemisphere of 6 oxygen atoms capped by the volatile anion component (Fig. 2; see

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