Structural variations along the apatite F-OH join

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ABSTRACT

The atomic arrangements of eight synthetic samples along the fluorapatite-hydroxylapatite join were examined using X-ray crystallographic techniques; the results of those refinements demonstrate that the incorporation of both F and OH in the apatite anion column, mimicking the human apatite system as modified by fluoridation, is complex. The compositions of the anion columns in the phases ranged from [F0.06(OH)0.60] to [F0.67(OH)0.33], and the high-precision structure refinements yielded R1 values from 0.0116 to 0.0140. The apatite structure responds to the variable content of the anion columns. Counterintuitively, the OH groups in the anion column move monotonically closer to the mirror planes at z = ¼, ¾ with increasing F content, despite the decreasing size of the triangle of Ca2 atoms to which the column anions bond and the increasing overbonding of the hydroxyl oxygen. In the structure the F atoms are underbonded and have zero degrees of positional freedom in the (0,0,½) special position to relieve that underbonding; the bonding deficiency of the anion column is relieved by the overbonding of the O(H) atom in the anion column, overbonding that increases with increasing content of underbonded F in the anion column. Together the underbonded F and the overbonded OH meet the formal bond valence (1.0 v.u.) required by the anion column occupants. The changes in bonding from the individual anion column occupants to the surrounding Ca2 atoms with composition induce bond length changes principally in the irregular Ca2 polyhedron and also affect the a lattice parameter in the apatites. The bond valence values imparted on the F, OH column anions, when extrapolated to end-member compositions, suggest that different column anion arrangements may exist near the F and OH end-member compositions, as is also seen along the apatite Cl-OH join. These values have implications for the incorporation of fluoride in human teeth during the fluoridation process.

Keywords: Apatite, fluorapatite, hydroxylapatite, crystal structure

INTRODUCTION

Apatite sensu lato is the most abundant phosphate mineral on Earth and is fundamentally important in geology, materials science, biology, medicine, agriculture, and dentistry. The mineral serves as the base of the phosphorus cycle on our planet. Apatite is employed in many geological applications, including several different geochronology and thermochemistry techniques (Chew and Spikings 2015). Apatite is also a major repository of halogens in rocks of the Earth’s crust and mantle (Piccoli and Candela 2002; Harlov and Aranovich 2018). Because of its robust atomic arrangement, apatite is also host to many substituents (Hughes and Rakovan 2015), making it an oft-used tool in geochemical studies.

Apatite has many industrial applications as well. The phase has emerged as an important tool in environmental remediation through phosphate induced metal stabilization (PIMS; Wright and Conca 2002). Apatite is also used in radionuclide sequestration, as its Ca1 and Ca2 sites serve as a solid-state repository for radioactive substituents (Ewing and Wang 2002; Rakovan and Pasteris 2015). Apatite was historically heavily used in the fluorescent lighting industry (Hughes 2015). Apatite is also used as a lasing material; through co-doping of substituents in the Ca1 and Ca2 sites, “designer” apatite lasers can be manufactured with desirable optical properties (Payne et al. 1994). Each Li-Fe-phosphate battery in an electric car consumes 60 kg of P mined principally from apatite (Elser et al. 2012). In addition, approximately 80 million metric tons of phosphoric acid worldwide are produced annually for many industrial uses.

The most important use of apatite is as a source of phosphorus for fertilizer. The dramatic rise in world population in the twentieth century was enabled by a parallel dramatic rise in apatite mining for fertilizer manufacturing to feed the growing world population; the coincidence of world population and “phosphate rock” (apatite) production is illustrative of the societal importance of apatite (Hughes 2015). Worldwide, apatite consumption, dominantly for use as fertilizer, is approximately 20 kg apatite/yr per capita (Etter et al. 2011).

Except for small portions of the inner ear, all hard tissue of the human body is formed of apatite materials, indicating the remarkable link between geology and biology for the mineral; apatite is among the most common biominerals on Earth. Sig-