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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 $[F_{0.40}(OH)_{0.60}]$ to $[F_{0.67}(OH)_{0.33}]$, 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 (0,0,¼) 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