

Structural variations along the apatite F-OH join: II. The role of hydrogen bonding in fluoridated teeth

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ABSTRACT

Fluoride is one of the most consumed pharmaceuticals in the world, and its facility in preventing dental caries is recognized as one of the top 10 public health achievements of the 20th century. Although hydroxylapatite is often used as an analog of dental enamel, the details of the substitution of F for OH in the apatite anion column are not well known. Using new synthesis techniques, this study extends the structure work on $P6_3/m$ apatites along the middle portion of the F-OH apatite join to compositions near that of fluoridated human teeth. The first F substituent in hydroxylapatite, near fluoridated dental enamel compositions, is dramatically underbonded by the surrounding Ca2 atoms (0.72 v.u.) in a hydroxylapatite matrix. However, the hydroxyl hydrogen can contribute 0.20 or 0.10 v.u. in hydrogen bonding to the F, depending on whether the substitution creates a reversal site in the anion column; this hydrogen bonding alleviates the bonding requirements of the substituent F. As F concentrations increase along the join, the average hydroxyl contributes increasing amounts of hydrogen bonding to the F column anions; to mitigate the loss of its hydrogen bonding, the hydroxyl oxygen migrates toward the adjacent mirror plane that contains the bonded Ca2 atoms, and the triangle of bonded Ca2 ions concomitantly contracts. These two mechanisms increase bonding to the column hydroxyl oxygen from the adjoining Ca2 atoms to balance the loss of hydrogen bonding that stabilizes the substituent F column anion and the increasing concentration of underbonded F.

Keywords: Hydroxylapatite, fluoridation, crystal structure, teeth