

Accommodation of the carbonate ion in fluorapatite synthesized at high pressure

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ABSTRACT

Sodium-bearing, type A-B carbonate fluorapatites $\{\text{Ca}_{10-1.5y}\text{Na}_y\text{F}_{0.5y}[(\text{PO}_4)_{6-2y}(\text{CO}_3)_{2y}][\text{F}_{2-2x}(\text{CO}_3)_x]\}$, with $x \approx y \approx 0.1$; CFAP} have been synthesized at 1150–1300 °C and 1.0 GPa, and investigated by single-crystal X-ray diffraction and FTIR spectroscopy. Typical crystal and compositional data are $a = 9.3659(3)$, $c = 6.8901(4)$ Å, space group $P6_3/m$, $R = 0.023$, $R_w = 0.021$, $x = 0.14(3)$, and $2y = 0.23(1)$. Crystal-chemical features and FTIR spectra are similar to Na-bearing, type A-B carbonate hydroxyapatites (CHAP) reported recently. However, uptake of carbonate is significantly lower in CFAP than in CHAP for similar conditions of crystal synthesis. Structural accommodation of the substitutions requires local coupling of the Na cation and channel (type A) and phosphate (type B) carbonate ion defects, as in CHAP but now in the approximate ratio 1:1:2. The type B carbonate ion is located on the sloping faces of the substituted phosphate group, and tilted only 3.5° from the mirror plane. The presence of weak electron density in the outer wall of the c -axis channel of apatite and in triangular coordination with one Ca1 and two Ca2 cations appears to represent a trace amount of excess fluoride, the controversial crystal-chemical feature of francolite.

Keywords: Apatite structure, fluorapatite, carbonate ion, biomineralization, dental enamel, crystallography