

SHORT COMMUNICATIONS

EXCESS CALCIUM FLUORIDE IN FLUORAPATITE

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Naturally occurring fluorapatites are known to be able to accommodate more fluoride than is required by the stoichiometric formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. The excess fluoride in these apatites has usually been assumed to be present as fluorite (CaF_2) crystals too small to be detected petrographically or by X-rays.¹ Clinical studies^{2,3} on hydroxyapatite in tooth enamel have shown CaF_2 to be a principal product of the application of topical fluoride solutions to intact tooth enamel surfaces. In neither of these fields has any detailed structural information regarding the mode or extent of incorporation of excess fluoride into the apatite structure been obtained.

Berak,⁴ in the course of an investigation on the $\text{CaO-P}_2\text{O}_5\text{-CaF}_2$ system, described a new high temperature fluorapatite phase, $2\text{Ca}_3(\text{PO}_4)_2\cdot\text{CaF}_2$ ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2\cdot\frac{1}{2}\text{CaF}_2$), which was reported to undergo "polymorphic transformations" at lower temperatures. Chlorapatite, by comparison, has been shown⁵ to have at low temperatures a structure field with CaCl_2 which extends to $\text{Ca}_2\text{PO}_4\text{Cl}$ ($\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2\cdot 2\text{CaCl}_2$) which is an incongruently melting compound corresponding to the mineral spodiosite. This paper presents the results of some electron diffraction, X-ray powder, and single-crystal diffraction investigations of fluorapatite samples containing excess calcium fluoride.

Experimental

Samples of fluoride-rich fluorapatite were prepared by solid state reaction of CaF_2 (>99% purity, chloride content <0.005%), and $\beta\text{-Ca}_3(\text{PO}_4)_2$ (reprecipitate,⁶ analysed at 99.7% purity). The manually mixed powders were sealed into 4-mm diameter platinum tubes and heated to 1040–1110°C for periods of 7–9 days; tubes were returned to room temperature over periods of approximately 12–14 hr.

X-ray powder diffraction examination of specimens was performed with a Hägg-Guinier focusing camera (8 cm diameter) using $\text{Cu K}\alpha_1$ radiation; Ceria ($a = 5.4109 \text{ \AA}$) was used as an internal standard for film shrinkage corrections. Single crystal diffraction patterns were obtained with a Nonius goniometer operating in the equi-inclination Weissenberg mode and with $\text{Cu K}\alpha$ radiation. An AEI EM802 metallurgical microscope fitted with high tilt cartridge and operated at 100 kV was used for electron diffraction experiments.

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¹ McLellan, G. H., and Lehr, J. R., *Am. Miner.*, 1969, **54**, 1374.

² Wei, S. H. Y., and Forbes, W. C., *J. dent. Res.*, 1968, **47**, 471.

³ Leach, S. A., *Br. dent. J.*, 1959, **106**, 133.

⁴ Berak, J., *Roczn. Chem.*, 1970, **44**, 1339.

⁵ Nacken, R., *Zentbl. Miner. Geol. Paläont.*, 1912, 545.

⁶ Trapp, H., *J. prakt. Chem.*, 1935, **144**, 93.

Lattice parameters for the fluorapatite phases were obtained by computer-programmed least-squares refinement of calculated $\sin^2\theta$ values against observed $\sin^2\theta$ values. In all cases, the reported⁷ cell parameters $a = 9.364 \text{ \AA}$, $c = 6.89 \text{ \AA}$ for fluorapatite, space group $P 6_3/m$ (hexagonal), were used as an initial basis for refinement.

Results

Seven samples, including stoichiometric fluorapatite (fap), $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, were prepared and examined. The approximate molar ratios, the chemical formulae, and X-ray powder data for these samples are shown in Table 1.

TABLE 1
PHASE DATA FOR FLUORAPATITE + CaF_2 SAMPLES
Lattice parameters are $\pm 0.002 \text{ \AA}$

Molar ratio $\text{CaF}_2/\text{Ca}_3(\text{PO}_4)_2$	Formula ($\pm 0.01 \text{ CaF}_2$)	Observed phases	Lattice parameters a (\AA) c (\AA)	
1.00/3	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	fap	9.384	6.876
1.20/3	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot \frac{1}{3}\text{CaF}_2$	fap'	9.384	6.879
1.50/3	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot \frac{1}{2}\text{CaF}_2$	fap''	9.384	6.880
3.00/3	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot 2\text{CaF}_2$	fap'''	9.386	6.880
4.00/3	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot 3\text{CaF}_2$	fap''' + CaF_2	—	—
5.00/3	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot 4\text{CaF}_2$	fap''' + CaF_2	—	—
6.00/3	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot 5\text{CaF}_2$	fap''' + CaF_2	—	—

Samples with molar ratios ($\text{CaF}_2/\text{Ca}_3(\text{PO}_4)_2$) of 1.00/3, 1.20/3, 1.50/3, and 3.00/3 are monophasic and their diffraction patterns are all very similar; the latter three samples appear to contain variants of stoichiometric fluorapatite (1.00/3 molar ratio) phase but with excess calcium fluoride incorporated. These variants are designated fap', fap'', and fap'''. Variations in lattice parameters a and c , for the fluorapatite-type unit cell, across the solid solution range are not beyond the limit of experimental error. It is perhaps for this reason that previous workers have failed to recognize the rather large solubility of CaF_2 in fluorapatite which, from the results above, is in excess of two moles of CaF_2 per mole of fluorapatite. In the diphasic mixtures formed at higher mole fractions of CaF_2 (i.e. samples with molar ratios 4.00/3, 5.00/3, and 6.00/3) the fluorapatite-type variant fap''' is, even with focused X-ray diffraction, indistinguishable from stoichiometric fluorapatite.

A validity check, to ensure sensibility of the powder diffraction equipment to small amounts of CaF_2 was carried out. To a sample of annealed fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, some annealed CaF_2 was added to simulate a physically admixed diphasic sample with an overall composition corresponding to the formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot \frac{1}{2}\text{CaF}_2$. Reflections due to fluorite (CaF_2) were clearly evident in the resulting diffraction pattern.

The similarity of the variants of fluorapatite, fap', fap'', and fap''' to stoichiometric fluorapatite, fap, was further verified by single crystal X-ray diffraction (on samples with molar ratios 1.00/3 and 1.50/3) and by electron diffraction (on samples with molar ratios 3.00/3 and 5.00/3). In all cases it was concluded that the true

⁷ Prener, J. S., *J. electrochem. Soc.*, 1967, **114**, 77.

space group symmetry was $P6_3/m$, that of fluorapatite; no reflections, other than those due to a simple fluorapatite-type cell, were evident on any of the diffraction patterns. In particular, reflections indicating doubling of the a -axis of the apatite unit cell as evidenced in the case of chlorapatite^{7,8} were not apparent. Widths of Bragg diffraction peaks from all samples were also inspected, and in no case was any significant "streaking" or "spiking" of diffraction spots due to disorder within the crystal apparent.

Discussion

The results indicate fluorapatite to be capable of accommodating large amounts of CaF_2 with virtually no change in symmetry or dimensions of the unit cell. A closer estimate of the upper limit of CaF_2 solubility in fluorapatite was obtained by comparing intensities of CaF_2 reflections (relative to fap) in the sample with molar ratio 4.00/3, with those in the validity check sample; the proportion of CaF_2 present in each case appeared to be similar. The upper limit to solubility of CaF_2 in fluorapatite is then close to 0.5 mol CaF_2 (per mol of fap) less than that in $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot 3\text{CaF}_2$, i.e. the limit of CaF_2 solubility is close to the composition of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \cdot 2\frac{1}{2}\text{CaF}_2$.

Locations for calcium and phosphate ions in the network of stoichiometric fluorapatite structure are well established.^{9,10} The exact positioning of charge-neutralizing anions, fluoride, chloride, or hydroxide has however been the matter for some conjecture. There seems little doubt that these anions are situated within the large channels which exist parallel to the c axis of the structure and which are formed by the surrounding calcium and phosphate network. There is also little doubt that large spaces exist within the channels; the positions for larger chloride ions in the channels of chlorapatite are significantly different from those of $z = 1/4$, $z = 3/4$ for fluoride and hydroxide in fluor- and hydroxy-apatites. Ordering of the excess CaF_2 in the present study between channels (e.g. as for chloride ions in chlorapatite) would create additional diffraction spots in samples at some, if not all, excess compositions. Coherent and specifically oriented CaF_2 precipitates could similarly be expected to produce diffraction effects and/or a change of symmetry. It seems likely, in the absence of all such effects, that the additional CaF_2 is incorporated randomly, and either non or only partially coherently in the fluorapatite matrix.

In fluorapatite the minimum diameter of the channels (which extend infinitely in the $[001]$ direction) has been estimated¹⁰ as 4.7 Å. It is interesting to note that, after allowing for the presence of two fluoride ions, the free volume of a channel per unit cell length is 98 Å.³ Using our figure of 2.5 molecules of excess CaF_2 per fluorapatite unit cell, and ionic radii $r(\text{Ca}^{++}) = 0.99$ Å, $r(\text{F}^-) = 1.36$ Å, the packing factor for the CaF_2 in the channels at saturation is 0.64. The packing factor for the fluorite (CaF_2) structure, calculated using the same ionic radii, is 0.65. It appears, if the fluorite (CaF_2) structure is taken as an acceptable criterion for "space filling" calcium and fluoride ions, that the channels of fluorapatite are close to being exactly "filled" with calcium fluoride at the limit of its solubility in fluorapatite.

⁸ Young, R. A., and Elliott, J. C., *Archs oral Biol.*, 1966, **11**, 699.

⁹ Náray-Szabó, S., *Z. Kristallogr. Kristallgeom.*, 1930, **75**, 387.

¹⁰ Kay, M. I., Young, R. A., and Posner, A. S., *Nature*, 1964, **204**, 1050.