

## Fluorine-Chlorine Interaction in Fluor-Chlorapatite

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When fluorine is partially substituted for chlorine in chlorapatite, steric interactions between the F and Cl ions produce effects not directly predictable from the properties of the end members, fluorapatite and chlorapatite, alone. The proximity of the remaining chlorine ions causes some of the substituting fluorine ions to be located  $\sim 0.6 \text{ \AA}$  from their normal sites (0, 0,  $\frac{1}{2}$  and 0, 0,  $\frac{3}{2}$ ) on the halogen ion column. Some of the chlorine ions are similarly shifted  $>0.2 \text{ \AA}$  farther away from 0, 0,  $\frac{1}{2}$ . The details of the displacements have been determined from least-squares analyses of X-ray data from synthetic single crystals. Two fluor-chlorapatite compositions were used,  $\sim 14\%$  and  $\sim 34\%$  substitution of  $F^-$  for  $Cl^-$  with excess halogen becoming incorporated to raise the  $F/(F + Cl)$  ratios to 0.17 and 0.41, respectively. The substitution models developed are capable of explaining (i) the nonlinear effects of the fluorine-chlorine substitution, and (ii) the initial stabilization and later inhibition of the monoclinic phase, with respect to the hexagonal phase, with increasing substitution of fluorine into the chlorapatite structure, and (iii) in part, the occurrence of halogens in excess of the stoichiometric 2 per unit cell.

### Introduction

Since the properties of apatites are important to many diverse fields (e.g., those of phosphor chemistry, biological hard tissue, mineralogy, fertilizers, and catalysis), the development of an understanding of the atomic details which may affect those properties is of value. One formula unit of a calcium phosphate apatite is  $Ca_5(PO_4)_3X$ , where  $X$  may be any of several ions including OH, Cl, and F. The structures of hydroxyapatite (OHAp) (1)-(3) chlorapatite (ClAp) (4), and fluorapatite (FAP) (5) are well known. A stereographic view of the FAp structure is reproduced in Fig. 1.

A wide variety of substitutions for each ion, Ca,  $PO_4$ , and  $X$ , are also known. Solid solutions of fluor-chlorapatite ( $X$  ion = F, Cl) are technologically important to the lighting industry as a source of phosphors which are often activated with 1 or 2 wt. % of manganese and antimony. Explanation, in part, of the fluorescence properties of these phosphors has been given (e.g., (6)) in terms of manganese-chlorine-vacancy complexes which may form along the halogen chains. Another field in

which the F, Cl "doping" effects and possible interactions may have particular importance is that of dental research. Since both F and Cl ions are present at once in tooth enamel, partially replacing OH ions, it is important to know whether mutual interaction should be expected and, if so, just what its structural mechanisms and implications are.

Interactions between mutually substituting ions, such as F, Cl, and OH, do produce solid solutions with properties not predictable from the study of the end members alone. Fluor-hydroxyapatite was the first apatite in which such a "nonlinear" phenomenon was understood in terms of atomic-scale mechanisms (7); fluor-chlorapatite is believed to be the second and, of course, the interaction phenomena are different. The presence of some F, Cl interaction was indicated by an apparent shift of the Cl position (from  $z = 0.44$  to  $z = 0.41$ ) in an apatite containing F and OH as well as Cl in the  $X$ -ion positions (8). The curious fact that a small amount of F substitution for Cl in ClAp raises the monoclinic-hexagonal phase transition temperature while

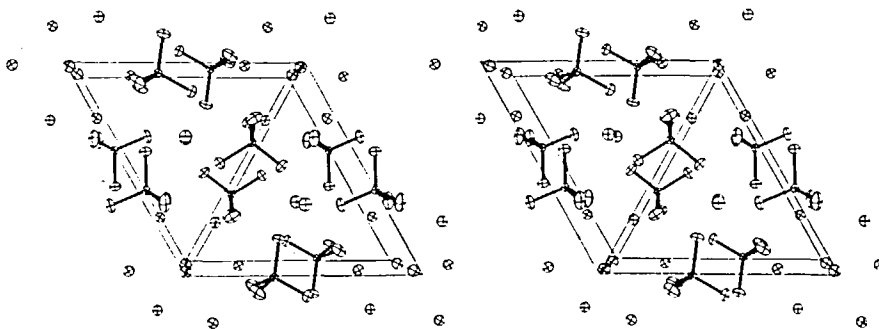


Fig. 1. Stereographic view of the fluorapatite structure. Fluorines atoms are located on the vertical edges (out of the plane of the page) of the unit cell as drawn. The atoms shown connected by bonds are  $\text{PO}_4$  groups. All other atoms are calciums. The ellipsoids represent rms thermal vibrational amplitudes, not ion sizes.

a greater substitution stabilizes the hexagonal phase even at room temperature (9) also suggested an  $X$ -ion interaction phenomenon. Single-crystal  $X$ -ray diffraction structure-refinement studies were therefore initiated to obtain direct atomic-scale knowledge of the distribution and mutual interactions of the  $X$  ions along the hexad axis in the mixed fluor-chlorapatite systems (10).

### Materials and Procedures

As finally determined with the help of the  $X$ -ray analyses, the atomic ratios  $F/(F + \text{Cl})$  of the apatites studied were 0,  $\sim 3/20$ ,  $\sim 8/20$ , and 1, that is, from stoichiometric ClAp [ $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ ] to stoichiometric FAp [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ] with 2 intermediate compositions. All 4 specimen materials were prepared by the method of growth from the flux used

by Prener (9). Starting materials were  $\text{CaF}_2$  or dry  $\text{CaCl}_2$  and fluorapatite or chlorapatite prepared by high-temperature methods in R. L. Hickock's laboratory at the General Electric Co., Cleveland, OH.

The chemical analyses (11), lattice parameters, and indices of refraction (sodium D) for the 4 apatite samples are presented in Table 1. The fluorine determination was by the Willard-Winter steam distillation method followed by titration with thorium nitrate. The experimental error in this method of fluorine analysis was estimated to be 10% for sample A ( $F/(F + \text{Cl}) \approx 3/20$ ) and 2-4% for sample B ( $F/(F + \text{Cl}) \approx 8/20$ ) (11).

The structures were refined from single-crystal  $X$ -ray diffraction data ( $|F^2|$ ) with the full-matrix least-squares technique. The Busing-Martin-Levy ORFLS program (12), modified to include anomalous dispersion and

TABLE I  
SPECIMEN CHARACTERISTICS

Specimen No.	Type	Chemical analyses (wt %) <sup>a</sup>				Lattice parameters		Refractive indices	
		Ca	$\text{PO}_4$	Cl	F	$a$ (Å)	$c$ (Å)	$n_o$	$n_e$
C	ClAp	38.5	54.2	6.72	—	9.6418 (8)	6.7643 (5)	1.668	1.669
A	(F, Cl) Ap	38.65	54.46	6.44	0.40	9.6205 (9)	6.7761 (6)	1.646	1.646
B	(F, Cl) Ap	38.81	54.76	5.13	1.29	9.5485 (10)	6.8237 (7)	1.652	1.650
D	FAp	39.7	56.5	—	3.73	9.3666 (12)	6.8839 (10)	1.633	1.629

<sup>a</sup> Analyses made by N. M. Braun, General Electric Co., Cleveland, OH.

anisotropic extinction correction and called ORXFLS3, was used (13). The data<sup>1</sup> were collected from fractional mm spheroids with MoK $\alpha$  radiation ( $\lambda = 0.70926$  Å) and a computer-controlled X-ray diffractometer. The atomic scattering factors for Ca<sup>2+</sup>, F<sup>1-</sup>, and Cl<sup>1-</sup> were obtained from Cromer and Waber (14), O<sup>2-</sup> from Tokonami (15), and P<sup>5+</sup> from Fukamachi (16). Anomalous dispersion corrections  $\Delta F'$  and  $\Delta F''$  (17) were made to the scattering of the Ca<sup>2+</sup>, P<sup>5+</sup>, and Cl<sup>1-</sup> ions. The data collection strategy included data collection to 1% statistical counting error in most cases and experimental identification and rejection of reflections compromised significantly ( $\geq 3\sigma$ ) by simultaneous diffraction. The procedures have been described in more detail by Mackie (10). For sample A, data for 1512 reflections were collected, of which 1190 were kept as usable. The corresponding numbers for sample B were 1508 and 1129. Data were corrected for extinction by Zachariasen's (18) method and for absorption with use of the tables for spherical specimens given in the "International Tables for X-ray Crystallography" (19). In the worst case, sample A, the absorption correction factor  $A^*$  changed by 27% over the angular range for which data were collected ( $0.365 \leq \sin\theta/\lambda \leq 0.998$ ). The maximum extinction correction to any one  $|F|^2$  value was approx. 26% for both samples A and B.

Before the single-crystal Bragg-intensity data were collected with the diffractometer, long-exposure ( $\sim 120$ -hr) upper-layer Weissenberg photographs were obtained of samples A and B, both fluor-chlorapatite. These photographs did not show evidence of twinning nor the presence of any "extra" reflections (i.e., from doubling of the  $b$  axis) indicative of the monoclinic,  $P2_1/b$ , form (4, 3). Thus, the structures were refined in the

space group  $P6_3/m$ .<sup>2</sup> (Later attempts at refinement of Sample A in  $P2_1/b$  were not successful.) The final refined parameters of ClAp (4), transformed to the hexagonal space group, were used as the starting point for the refinements of the fluor-chlorapatites. Details of the electron distribution along the hexad axis were determined both from least-squares structure refinements and from electron-density difference maps.

## Results and Discussion

In the least-squares refinements, the structure parameters converged rapidly to "normal" values with the exceptions that the particular anisotropic thermal parameter,  $\beta_{33}$ , of fluorine (i.e., the component of thermal motion perpendicular to the mirror plane of the apatite structure with space group  $P6_3/m$ ) was unusually large and that the chlorine atom was shifted along the  $c$  axis from the position normally found for chlorine in nearly stoichiometric chlorapatites. It is this apparent chlorine-fluorine interaction which is the subject of the remainder of this paper.

The unusually large size of  $\beta_{33}$  of the fluorine atom suggested that not all of the fluorine was located precisely on the mirror planes. Difference syntheses were prepared with chlorine placed in the model at its refined position ( $z = 0.4432$  for sample A and  $z = 0.4203$  for sample B) and the fluorine atom omitted. Figures 2 and 3 show the isodifference-electron-density contours for a cross section of the unit cell which contains the screw axis. Positive difference densities, in units of electron charge, are represented by solid curves and the negative difference densities

<sup>1</sup>A table of observed and calculated Bragg intensities has been deposited as Document No. NAPS 02372 with the ASIS National Auxiliary Publications Service, c/o Microfiche Publications, 305 E. 46th St., New York, NY 10017. A copy may be secured by citing the document number and by remitting \$5.00 for photocopies of \$1.50 for microfiche. Advance payment is required. Make check or money order payable to Microfiche Publications.

<sup>2</sup>The question of whether the space group for the intermediate compositions could be  $P6_3$  rather than  $P6_3/m$  was raised by a referee. It has been presumed throughout that the space group of the intermediate composition would be that of one of the other of the end members, both of which are reported to be centrosymmetric. In the absence of anomalous dispersion the space groups  $P6_3$  and  $P6_3/m$  are not directly distinguishable from X-ray data. As nothing in the detailed structural results or models cast doubt on the presence of a center of symmetry, no direct physical tests for it were undertaken.

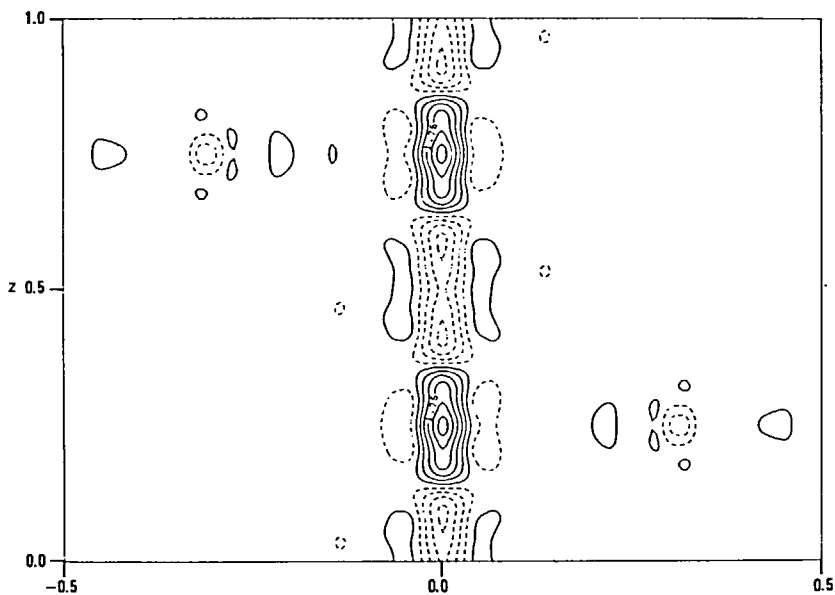


FIG. 2. Difference electron density synthesis at  $y = 0$  for sample B ( $F/(F + Cl) = 0.41$ ). No fluorines have been included in the model. Contour interval is  $0.5e/\text{\AA}^3$ , and first positive contour is at  $0.25e/\text{\AA}^3$ . Negative difference electron density is indicated by the broken contours.

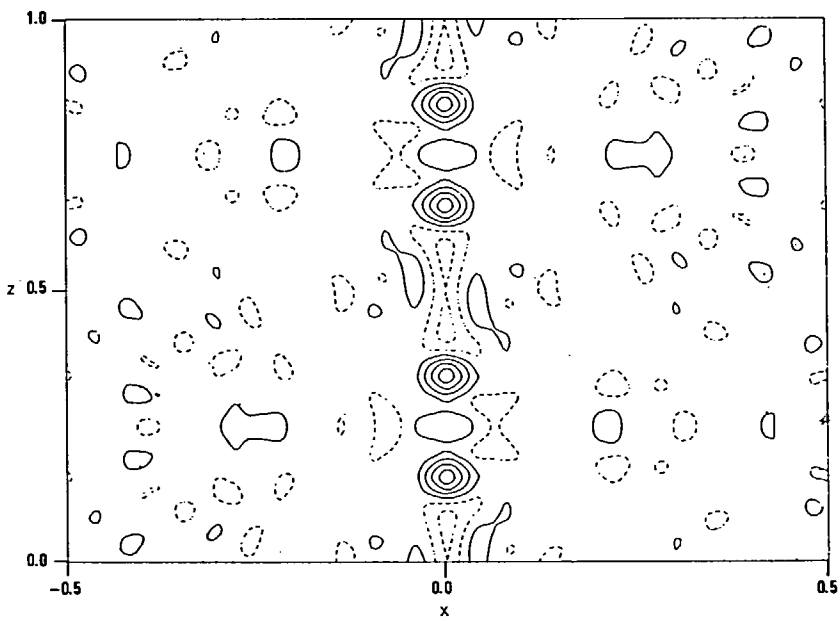


FIG. 3. Difference electron density synthesis at  $y = 0$  for sample A ( $F/(F + Cl) = 0.17$ ). No fluorines have been included in the model. Contour interval is  $0.25e/\text{\AA}^3$  and the first positive contour is at  $0.125e/\text{\AA}^3$ . Negative difference electron density is indicated by the broken contours.

by dashed curves. Centered at  $x = 0$ ,  $y = 0$ ,  $z = \frac{1}{4}$ , an apparent trimodal distribution of scattering density can be discerned in both structures. The question of the physical significance of this distribution was approached separately for the 2 structures.

*Fluor-chlorapatite with  $F/(F + Cl) = 0.41$*

Fluorine atoms were next introduced into the structural model at 2 locations, F(1) at 0, 0,  $\frac{1}{4}$  and F(2) at 0, 0, 0.17, to fit the trimodal distribution. Least-squares structure refinements,<sup>3</sup> which included adjustments of the site occupancy factors<sup>4</sup> but not the locations of F(1) and F(2), then led to  $wR_2 = 4.34\%$ ,<sup>5</sup> which compared to 6.3% obtained without F atoms in the model. A subsequent difference synthesis was featureless when contours were drawn at the same intervals as those used in Fig. 2; all residual difference peaks were less than  $0.2e/\text{\AA}^3$ . At the fluorine sites the residual difference-electron density was reduced to less than  $0.1e/\text{\AA}^3$ .

*Fluor-chlorapatite with  $F/(F + Cl) = 0.17$*

In the electron density difference synthesis (Fig. 3) initially made to verify the correctness of the structural model, the structural details

<sup>3</sup> The close proximity of the 3 fluorine ions (F(1) and 2 F(2)) in the structure model prohibited the simultaneous least-squares adjustment of all of the fluorine variables. The fluorine thermal parameters, site occupancy factors, and the  $z$  parameter of F(2) were refined in a stepwise iterative procedure; that is, one member of each highly correlated pair of parameters was held constant in each cycle of the refinement. On alternate cycles of refinement, the set of parameters held constant in the previous cycle was allowed to vary while that set previously allowed to vary was now held constant.

<sup>4</sup> The term "site occupancy factor" is here used to mean the fractional occupancy of that subset of space group equivalent positions which can actually be occupied in any 1 unit cell (e.g., for F(2) and Cl at type  $4e$  sites of space group  $P6_3/m$  there are only 2 sterically possible positions per unit cell, not 4). This definition is employed so that the site occupancy factor will always be unity for stoichiometric conditions.

<sup>5</sup>  $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2]^{1/2} / [\sum w|F_o|^4]^{1/2}$ , where  $w$  is the reciprocal of the variance for each observation and the summations are carried out over all observations.

were partially masked by large termination-of-series effects. The problem was more serious with this specimen than with specimen B because of the smallness of the amount of fluorine for which structural data were being sought. The approach taken was based on the truism that termination-of-series effects will be completely eliminated in a difference map if all of the scattering density is accounted for correctly in the scattering model, i.e., the difference map is everywhere zero. Centers of scattering density which appeared in the difference synthesis were, therefore, added to the scattering model (in the form of fractional F atoms). As each bit of scattering density was placed in the scattering model, the termination-of-series effects became smaller; observation of even smaller residual electron densities was then possible and the model was further improved. This procedure was continued toward the ultimate goal of construction of an optimized model indicated by a completely zero electron density difference synthesis. (While a model so optimized is not necessarily correct in all degrees of detail for the material, it is indistinguishable from the "correct" one on the basis of the data in hand. Stated another way, this procedure for optimizing the model assures that all of the information in the data has been utilized.)

Fluorine was introduced into the structural model for this material at 0, 0, 0.16. (Initially, no fluorine was placed at 0, 0,  $\frac{1}{4}$  for it was felt that this central peak in the difference density distribution might be due to a termination-of-series effect; this central peak as shown in Fig. 3 does appear to be smaller than the negative termination-of-series peaks at 0, 0,  $0.25 \pm 0.15$ ). The resulting difference synthesis showed that a substantive difference peak did indeed exist on the mirror plane at  $x = 0$ ,  $y = 0$  and that this peak was at least as strong as the off-mirror-plane peaks (Fig. 4). For subsequent refinements, therefore, a fluorine atom was also incorporated into the model on the mirror plane at the screw axis location (i.e., at 0, 0,  $\frac{1}{4}$ ). Again, as in the refinements of sample B, only a stepwise iterative refinement procedure could be followed in varying the fluorine parameters. A third difference synthesis (Fig. 5) showed that minor site-occupancy

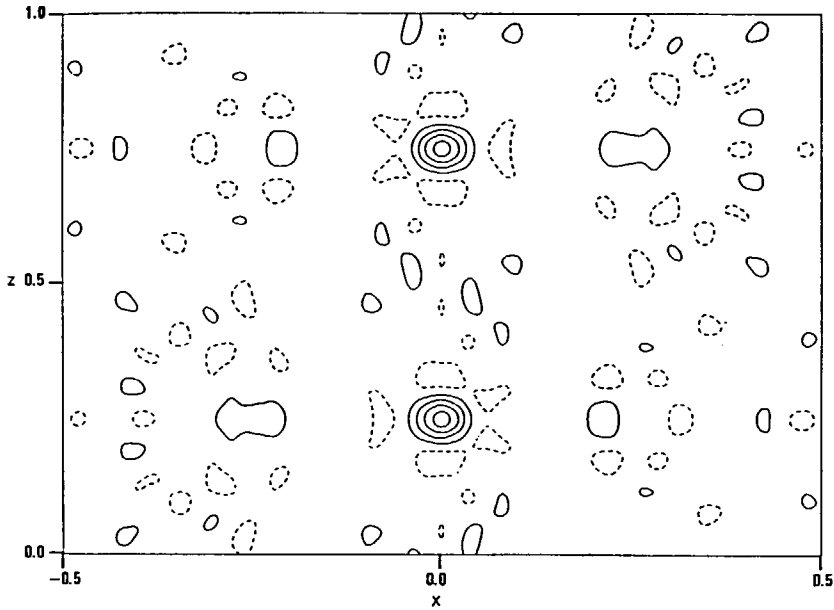


FIG. 4. Difference electron density synthesis at  $y=0$  for sample A ( $F/(F+Cl)=0.17$ ). No fluorine has been included in the model at  $z=\frac{1}{4}$ . Contour interval is  $0.25e/\text{\AA}^3$  and the first positive contour is at  $0.125e/\text{\AA}^3$ . Negative difference electron density is indicated by the broken contours.

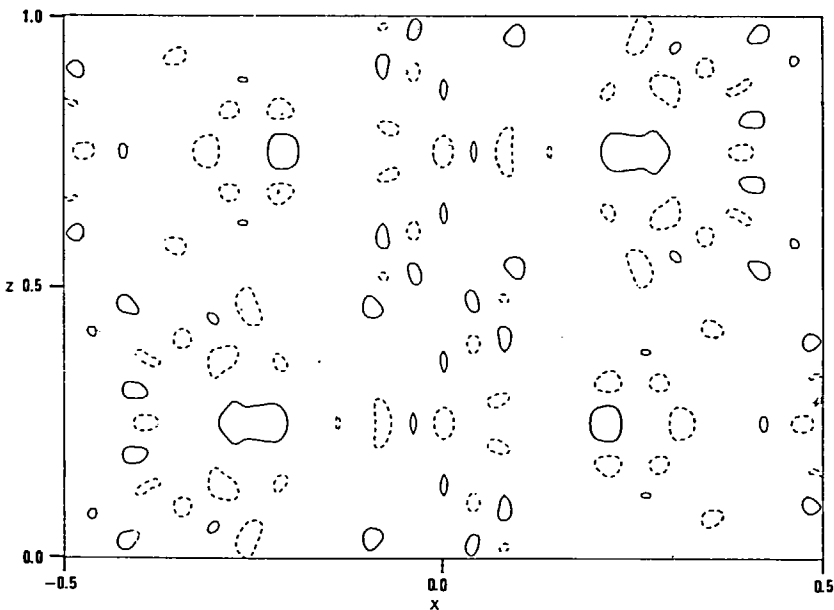


FIG. 5. Final difference electron density synthesis at  $y=0$  for sample A ( $F/(F+Cl)=0.17$ ). Fluorine ions have now been included in the model at  $z=\frac{1}{4}$  and  $z=0.09$ . Contour interval is  $0.25e/\text{\AA}^3$  and the first positive contour is at  $0.125e/\text{\AA}^3$ . Negative difference electron density is indicated by the broken contours.

TABLE II

FINAL PARAMETER VALUES FOR FLUOR-CHLORAPATITE SAMPLES A AND B (F/(F + Cl) = 0.17, 0.41)

ATOM	PARAMETER <sup>a</sup>	PARAMETER VALUE (STD. ERROR)		ATOM	PARAMETER	PARAMETER VALUE (STD. ERROR)			
		SAMPLE A	SAMPLE B			SAMPLE A	SAMPLE B		
O(1)	x	0.3417(1)	0.3366(1)	Ca(1)	x	1/3	1/3		
	y	0.4911(1)	0.4894(1)		y	2/3	2/3		
	z	1/4	1/4		z	0.0033(0)	0.0025(0)		
	B <sub>11</sub>	0.0055(1)	0.0051(1)		B <sub>11</sub>	0.0035(0)	0.0036(0)		
	B <sub>22</sub>	0.0037(1)	0.0037(1)		B <sub>22</sub>	0.0035	0.0036		
	B <sub>33</sub>	0.0046(1)	0.0043(1)		B <sub>33</sub>	0.0021(0)	0.0021(0)		
	B <sub>12</sub>	0.0038(1)	0.0036(1)		B <sub>12</sub>	0.0017	0.0018		
	B <sub>13</sub>	0	0		B <sub>13</sub>	0	0		
	B <sub>23</sub>	0	0		B <sub>23</sub>	0	0		
	S	0.996(8)	1.016(8)		S	1.001(3)	0.950(3)		
	O(2)	x	0.5920(1)		0.5906(1)	Ca(2)	x	0.2594(0)	0.2545(0)
		y	0.4651(1)		0.4657(1)		y	0.0027(0)	-0.0019(0)
		z	1/4		1/4		z	1/4	1/4
B <sub>11</sub>		0.0020(1)	0.0025(1)	B <sub>11</sub>	0.0030(0)		0.0052(0)		
B <sub>22</sub>		0.0027(1)	0.0039(1)	B <sub>22</sub>	0.0033(0)		0.0030(0)		
B <sub>33</sub>		0.0092(2)	0.0104(2)	B <sub>33</sub>	0.0030(0)		0.0032(0)		
B <sub>12</sub>		0.0009(1)	0.0016(1)	B <sub>12</sub>	0.0014(0)		0.0015(0)		
B <sub>13</sub>		0	0	B <sub>13</sub>	0		0		
B <sub>23</sub>		0	0	B <sub>23</sub>	0		0		
S		1.001(8)	1.017(8)	S	0.994(2)		0.938(2)		
O(3)		x	0.3534(1)	0.3502(1)	F(1)		x	0	0
		y	0.2661(1)	0.2632(1)			y	0	0
		z	0.0671(1)	0.0665(1)			z	1/4	1/4
	B <sub>11</sub>	0.0096(1)	0.0111(2)	B <sub>11</sub>		0.0036(25)	0.0040(7)		
	B <sub>22</sub>	0.0049(1)	0.0052(1)	B <sub>22</sub>		0.0036	0.0040		
	B <sub>33</sub>	0.0062(1)	0.0058(1)	B <sub>33</sub>		0.0096(52)	0.0131(22)		
	B <sub>12</sub>	0.0053(1)	0.0060(1)	B <sub>12</sub>		0.0018	0.0020		
	B <sub>13</sub>	-0.0055(1)	-0.0055(1)	B <sub>13</sub>		0	0		
	B <sub>23</sub>	-0.0037(1)	-0.0037(1)	B <sub>23</sub>		0	0		
	S	1.010(6)	0.981(6)	S		0.051(6)	0.204(6)		
	P	x	0.4063(0)	0.4037(0)		F(2)	x	0	0
		y	0.3741(0)	0.3721(0)			y	0	0
		z	1/4	1/4			z	0.1595(45)	0.1745(18)
B <sub>11</sub>		0.0019(0)	0.0023(0)	B <sub>11</sub>	0.0033(19)		0.0029(7)		
B <sub>22</sub>		0.0016(0)	0.0019(0)	B <sub>22</sub>	0.0033		0.0029		
B <sub>33</sub>		0.0021(0)	0.0021(0)	B <sub>33</sub>	0.0118(33)		0.0101(21)		
B <sub>12</sub>		0.0011(0)	0.0014(0)	B <sub>12</sub>	0.0016		0.0015		
B <sub>13</sub>		0	0	B <sub>13</sub>	0		0		
B <sub>23</sub>		0	0	B <sub>23</sub>	0		0		
S		0.992(4)	0.987(2)	S	0.119(12)		0.258(12)		
Cl		x			Cl		x	0	0
		y					y	0	0
		z					z	0.4432(3)	0.4203(5)
	B <sub>11</sub>			B <sub>11</sub>		0.0034(1)	0.0034(1)		
	B <sub>22</sub>			B <sub>22</sub>		0.0034	0.0034		
	B <sub>33</sub>			B <sub>33</sub>		0.0200(3)	0.0142(3)		
	B <sub>12</sub>			B <sub>12</sub>		0.0017	0.0017		
	B <sub>13</sub>			B <sub>13</sub>		0	0		
	B <sub>23</sub>			B <sub>23</sub>		0	0		
	S			S		0.858(6)	0.664(6)		

<sup>a</sup> S = SITE OCCUPANCY FACTORTABLE III  
TOTAL HALOGEN CONTENT AND DEGREE  
OF F SUBSTITUTION IN TWO FLUOR-  
CHLORAPATITES

Sample	X-ray diffraction	Chemical analysis
A	2.06	2.09
B	2.25	2.19
	F/(F + Cl)	
A	0.17	0.10
B	0.41	0.32

factor adjustments could usefully be made for the fluorine and chlorine atoms. After these

adjustments had been made, the difference electron density reduced to less than  $0.1e/\text{\AA}^3$  everywhere, including the fluorine sites.

The final refined parameters for both fluor-chlorapatite samples are presented in Table II. The values of F/(F + Cl) for samples A and B were, respectively, 0.17 and 0.41, in fair agreement with the chemical analysis results (Table III). The final agreement factors,  $wR_2$ , were 4.2% for sample A and 4.0% for sample B.

### Substitution Models

Several plausible substitution models can be devised for the assimilation of the fluorine ion into the chlorapatite structure accompanied by changes in the chlorine ion position and site-occupancy factor. Each column in

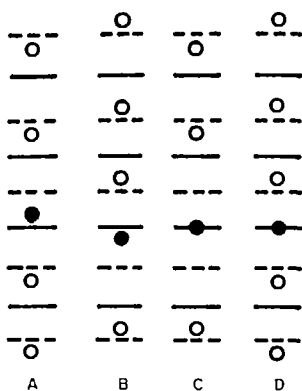


FIG. 6. Proposed substitution models; (F, Cl)Ap. O, Chlorine; ●, fluorine; —, edge view of Ca(2) triangles, also mirror planes at  $z = \frac{1}{4}, \frac{3}{4}$ ; ----, planes (mid way between the mirror planes) at  $z = 0, \frac{1}{2}$ .

Fig. 6 is a schematic representation of a possible configuration of fluorine and chlorine ions along the screw axis of the apatite structure (20). Each of the 4 models (A, B, C, and D) is for a stoichiometric apatite (no vacancies and 2 halogen ions/unit cell). (That this is so can be seen if one associates each halogen ion with the nearest calcium triangle and continues the motif indefinitely. Each calcium triangle will have 1, and only 1 halogen ion associated with it.) Substitution models with X-ion vacancies can readily be devised for defect-apatite structures. For those fluor-chlorapatites used in this work, however, no halogen deficiency was indicated; in fact, an excess of halogens was indicated by both X-ray and chemical analyses (Table III). Possible models to accommodate the excess will be discussed after the stoichiometric models have been exploited.

In each of the 4 (stoichiometric) models in Fig. 6 a single chlorine ion has been removed and a fluorine ion placed on the screw axis. In each case, the substitution is not isostructural; in fact, the fluorine ion not only occurs at positions different from those of the chlorine ion but the positions of the adjacent chlorine ions also differ from those in pure chlorapatite. Furthermore, some of the fluorine ion positions, those for F(2), differ from those in pure fluorapatite.

Substitution models A and B, which are

equivalent, maintain the ordered arrangements of the chlorine ions required in the monoclinic form of chlorapatite (4). These 2 substitutions can be thought of as occurring in 2 steps; (i) the removal of a chlorine ion from  $z = 0.44$  (the position found in pure chlorapatite) with an accompanying general relaxation of the remaining chlorine ions on the column toward the vacancy, and (ii) the placement of a fluorine ion at  $z = \frac{1}{4}$  (the ideal position for F in fluorapatite) with the relaxation of the fluorine ion away from the mirror plane toward the chlorine ion vacancy and away from the nearest, negatively charged, chlorine ion. Thus, although the ordered displacements of the chlorine ions are maintained, those chlorine ions nearest the substituting fluorine ions are shifted, with the result that the average Cl ion position, averaged over both perturbed and unperturbed positions, is shifted ( $\Delta z_{Cl} = 0.0010_3$  and  $0.0236_5$  for Samples A and B, respectively) from the position in pure chlorapatite. Furthermore, the fluorine ion is in an off-mirror-plane position. Thus, models A and B do permit at least a semiquantitative explanation of the effect of substituting F ions on the observed Cl-ion position and, conversely, the occurrence of some of the substituting F ions at other than their "normal" positions.

An acceptable substitutional model, however, must also provide explanation of the curious fact that small amounts of fluorine stabilize the monoclinic phase against the hexagonal phase, whereas larger amounts of fluorine have quite the opposite effect (9). In models A and B it can be perceived that the effect of small amounts of fluorine would be to reinforce the ordered displacements of the chlorines with a concomitant increase in the monoclinic-hexagonal transition temperature. For example, in model A the F-Cl distances would be 4.10 and 2.78 Å if there were no relaxation from the F and Cl positions in FAp and ClAp, respectively. Since the sum of the F and Cl radii is  $1.35 + 1.81 = 3.17$  Å, it is clear that an F ion on or near the mirror plane at  $z = \frac{1}{4}$  repels the lower Cl ion but permits the upper Cl ion to relax toward it, the F ion. Both Cl ions are thus moved farther away from 0, 0,  $\frac{1}{2}$ . Model B is simply model A



inverted. In model C, both F-Cl distances would be 4.61 Å if the F<sub>Ap</sub> and Cl<sub>Ap</sub> positions were maintained, which distances permit both the upper and lower Cl ions to relax toward the F ion and, hence, to move away from 0, 0,  $\frac{1}{2}$  (or the corresponding crystallographically equivalent position). In model D, the F-Cl distances based on the positions in F<sub>Ap</sub> and Cl<sub>Ap</sub> are both 2.27 Å, which is much too close for a normal F-Cl distance, so much so as to suggest that case D effectively does not occur. Thus, the effects of all cases expected to occur, A, B, and C, are to move the Cl ion farther from 0, 0,  $\frac{1}{2}$  than it is in pure Cl<sub>Ap</sub>. In order for the structure to become hexagonal, either the Cl ions must all move to 0, 0,  $\frac{1}{2}$  or a statistically selected one-half of them must pass over to symmetrically related positions on the other side of 0, 0,  $\frac{1}{2}$  (e.g., from  $z = 0.42$  to  $z = 0.58$ ). Thus, by moving the Cl ions farther away from 0, 0,  $\frac{1}{2}$  (and equivalent positions) the substituting F ions inhibit the monoclinic-hexagonal phase transition.

The introduction of still more F ions eventually leads to the destruction of the intercolumn ordering necessary for the monoclinic phase to occur and the crystalline phase becomes hexagonal. To see how this might occur, one needs to understand how the glide plane ordering arises in the first place (4). Each phosphate group contributes to 2 oxygen triangles approximately (monoclinic case) or exactly (hexagonal case) centered on the Cl-ion column ( $2_1$  or  $6_3$  axis, respectively). Coincidentally, in maintaining normal Cl-Ca distances the Cl ion occurs essentially at the center of one or the other but, because of its large size, not both of the 2 oxygen triangles. Mutual Cl-O repulsion enlarges the Cl-containing triangle somewhat, tilting the attached PO<sub>4</sub> groups and thus setting off a rumple that can propagate throughout the structure carrying information about which of the 2 different oxygen triangles has a Cl ion in it. When all Cl ions are present, they are in "contact" along the columns and there is no opportunity for any to pass over into the "other" oxygen triangle. But the occurrence of a vacancy does permit the adjacent Cl ion, being repulsed by the Cl ion next in turn to it, to relax into the

second choice of oxygen triangle. This tilts the attached PO<sub>4</sub> groups in a sense opposite to that imposed by the general monoclinic ordering. The structure can tolerate only a limited occurrence (e.g., 10-15%) of such "mistakes" before the ordering information is no longer propagated effectively and the selection of the oxygen triangle to be occupied in a given column or column segment becomes a local statistical choice. The introduction of increasingly larger amounts of F (a) leaves more and more oxygen triangles empty and, thus, eventually inhibits the propagation of the ordering information from column to column of the Cl ions and (b) enhances reversal of the ordering sense within a (Cl, F) column. As a result, the monoclinic ordering is lost and the crystalline phase becomes hexagonal.

#### Occurrence of Excess Halogen

Up to this point, it has been assumed that the sites occupied by fluorine and chlorine are distinct. Both X-ray and chemical analyses (Table III) indicate in sample B a halogen content significantly in excess of the stoichiometric 2 halogens/unit cell. While the chemical analyses could be explained by the occurrence of excess halogen anywhere in the structure—or the sample—the X-ray results place the excess, or the bulk of it, on the hexad axis. An explanation of this anomaly requires (i) a stereochemically acceptable packing sequence which permits up to one extra halogen to occur on the screw axis in every 5 unit cells, and (ii) a mechanism for charge compensation. Plausible packing sequences with some new features have been developed but the charge compensation mechanisms that come most readily to mind seem not to apply.

A number of criteria were used to govern the selection of plausible packing sequences: (i) The interatomic distances must exceed certain minimum values, e.g., (F-F)  $\geq 0.35c$ , (Cl-Cl)  $\geq 0.50c$ , and (F-Cl)  $\geq 0.44c$ , (where  $c$  is the magnitude of the  $c$  axis). (ii) The only valid atomic sites (as determined by electron density maps) occur in 2 restricted ranges of  $z$ ,  $0.42 \leq z \leq 0.58$  (site R) and  $0.18 \leq z \leq 0.32$  (site Q). (Valid ranges of sites also occur at  $z \pm n/2$ , where  $n = 0, 1, 2, \dots$ ) (iii) Either F or

Cl may occur at R sites but only F can occupy a Q site, because the Ca-Cl distance would be much too short to accommodate Cl at this site. Following these guidelines, one can easily find packing sequences for F and Cl which yield values of  $(F + Cl)$  and  $F/(F + Cl)$  in close agreement with the observed values. A typical sequence would have F at  $z = 0.18, 0.56, 1.94, 2.32,$  and  $2.70$  and Cl at  $z = 1.00$  and  $1.50$ . A common feature of all of these sequences is the occurrence of a fluorine ion in an R site, heretofore thought to be occupied only by Cl ions.

An unusually large Ca-F distance would result from this F placement at R sites. There is, however, some precedent for packing sequences, in structural channels such as the X-ions occupy in apatite, in which the normal ion-ion distance along the column is maintained at the expense of impaired coordination with the surrounding ions. The usual case in such chain-packing sequences is that the sequence continues only until the steric strain, produced by the impaired coordination with surrounding ions, reaches some maximum limit, at which point a vacancy occurs and the packing sequence then starts over. Examples are iodine in dextran iodide (21, 22), Ce in cerium-plutonium-cobalt (23), Co in  $Pr_2Co_{1.7}$  (24), and halogens in several cadmium apatites (25). In each of those examples, however, the interrupted chain-packing sequence provides accommodation for oversize ions. Charge balance, it is thought, is then preserved by omission of the required number of coordinating cations (e.g., Cd(2) in the case of the Cd apatites).

In the present case, however, the hypothetical chain packing accommodates an excess of halogen ions which, on the average, are small enough to fit in in excess numbers. No interruption of the chain sequence would then seem to be needed. However, the required analog of the cation vacancy in the oversize-anion chain case would seem to be either an extra, interstitial cation (e.g.,  $Ca^{2+}, Na^+$ , etc.) or replacement of a  $Ca^{2+}$  ion by one of higher valence. Alternatively, charge balance might conceivably be maintained through replacement of  $PO_4^{3-}$  groups by some of lower valence, e.g.,  $CO_3^{2-}$ . Finally, the occurrence of an

unidentified heavier univalent anion on the hexad axis and the accompanying occurrence of F or Cl elsewhere in the sample could explain both the X-ray and the chemical analysis results.

It is thought that most of the above possibilities are rendered improbable by the fact that the specimens were synthesized from starting materials of sufficiently high purity to exclude the required amounts of foreign ions. Furthermore, the chemical analyses of synthesized fluor-chlorapatite crystals from the same crystal-growth batches as those crystals used for the X-ray studies (Table I) did not show a lack of materials balance sufficient for trivalent cations to be the means of charge balance. Since care was taken to exclude  $CO_2$  from the reaction vessel during the crystal growth runs (the chamber was flushed and a slight positive pressure of nitrogen was maintained whenever the chamber was heated above room temperature), the  $CO_2^{2-}$  for  $PO_4^{3-}$  substitution should be ruled out. Since the reaction vessel was made entirely of platinum, no opportunity was provided for foreign ions, such as Na, to be introduced from the reaction vessel in the amounts required for them to be the means of charge balance. Thus, at this point, it appears that none of the foreign-ion hypotheses (substitution for  $Ca^{2+}$  by a higher valence ion, interstitial univalent ions, heavier anions on the hexad axis,  $CO_2^{2-}$  for  $PO_4^{3-}$ ) are probable and that the charge balance mechanism, which apparently must involve only the elements present in pure fluor-chlorapatite, has not yet been perceived.

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