Structural Interactions of F, Cl and OH in Apatites

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Structural interactions of F, Cl, and OH ions accompany their mutual substitutions on the 6_3 axis of calcium apatites $Ca_5(PO_4)_3X$, where $X =$ F, Cl and OH, with space group $P6_3/m$. These interactions have been studied by means of crystal structural refinements for six mineral and synthetic specimens of differing X-ion contents, plus reported results for the end-members. The z positional parameters of both Cl and OH positions are primarily sensitive to and depend roughly linearly on the fractional amount of chlorine present. The pattern found leads to a predicted z positional parameter of 0·36 to 0·37 for the Cl in human tooth enamel, contrasting with 0·44 in chlorapatite. The dominance of Cl over F in affecting the OH ion positions correlates with the observed infrared spectral effect of greater perturbation of the OH stretch frequency by Cl. As the relative Cl content decreases, the Cl ions move closer to the planes of the associated Ca triangles, which expand to maintain the normal Ca–Cl distance while the Ca triangles associated with other X ions remain relatively unchanged.

1. Introduction

Fluorine, chlorine, and hydroxyl ions substitute readily for one another in apatites. When they do, they interact with each other to produce effects not predictable from the knowledge of the detailed structures of the end-member compounds alone. One of the reasons for interest in this interaction is that both fluorine and chlorine are present in human tooth enamel as minor substituents, a few hundred to a few thousand p.p.m. in the inorganic portions modeled by multiply substituted and somewhat hydroxyl-deficient hydroxyapatite. Another reason for interest is the role the minor substituents play in the properties of apatites used as phosphors in the lighting industry and those used in catalysis.

Although Cl is present in essentially all human tooth enamel to the extent of a few tenths of 1 wt%, in the literature there is very little attention given to its possible role. Shannon (1958) reported increased caries incidence with salivary chloride level. Esposito (1971) noted that dietary NaCl with sucrose led to fewer cavities while NaCl without sucrose led to more. Dykes & Elliott (1971) showed that Cl present in the apatitic structure of tooth enamel (on the hexad axis) interacts strongly enough with OH to perturb the OH stretch frequency from 3572 to 3495 cm^{-1} (*vs* 3540 cm^{-1} for F perturbation of OH).

Fluorine is present in lesser amounts (*e.g.* 30 to 3000 p.p.m.) than is chlorine in human tooth enamel. Because fluorine, however, has long been known to increase resistance to caries attack, a substantial amount of information has been developed about the location and role of F occurring as a minor substituent in hydroxyapatite (*e.g.* Sudarsanan & Young, 1969; Young, van der Lugt & Elliott, 1969; van der Lugt, Knottnerus & Young, 1970). When F ions substitute for OH ions in hydroxyapatite they tend to locate at the
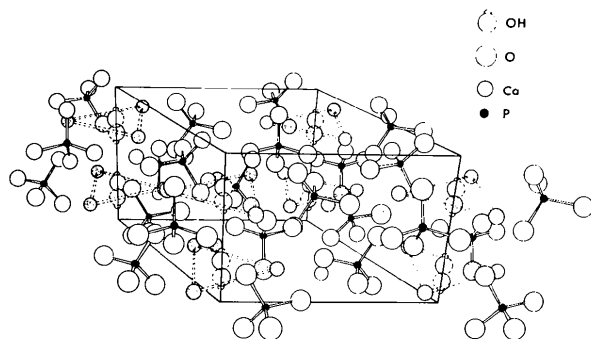

Fig. 1. 'Hexagonal' OHAp. **a** is directed to the right, **c** upward and **b** into the page. The fact that each OH$^-$ position is statistically only 50% occupied is indicated by the dotted outline of half of each OH group.
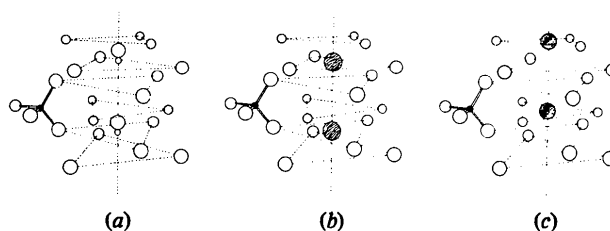

Fig. 2. X-ion location and environment in (*a*) OHAp, (*b*) ClAp, and (*c*) FAp. Ion identity is presented as in Fig. 1 with H$^+$ indicated by small open circles, Cl$^-$ by large circles filled with wavy lines and F$^-$ by vertically striped circles.

sites normal for them in fluorapatite $(0,0,\frac{1}{4})$. But when fluorine is partially substituted for chlorine in chlorapatite the interactions between the F and Cl ions result in a trimodal distribution of fluorine ions (Mackie & Young, 1974).

The structural differences among the three apatites, fluorapatite (FAp), hydroxyapatite (OHAp) and chlorapatite (ClAp), are seemingly rather small. PO_4 groups and Ca ions occupy much the same structural locations in all three (Fig. 1). The principal differences are indicated in Fig. 2. FAp crystallizes in the hexagonal system in space group $P6_3/m$ with F at the site $(0,0,\frac{1}{4})$ at the centers of Ca triangles (Náray-Szabó, 1930; Sudarsanan, Mackie & Young, 1972). In OHAp the oxygen of the OH group is either above or below the Ca triangle by 0·3 Å at $(0,0,0·196)$ and symmetry-related sites (Kay, Young & Posner, 1964; Sudarsanan & Young, 1969). Except for a short-range ordering requirement, the choice is statistical in most hydroxyapatites of record, which leads to $P6_3/m$. In nearly stoichiometric hydroxyapatite prepared under favorable thermal conditions, the hydroxyl ions become ordered over long ranges and the space group becomes $P2_1/b$ (Elliott, 1971; Elliott, Mackie & Young, 1973; Elliott & Mackie, 1974). The monoclinic structure is strongly pseudo-hexagonal ($b = 2a$, $\gamma = 120°$ within experimental error). In stoichiometric ClAp the chlorine ion occurs at $(0,0,0·444)$ and the space group is $P2_1/b$. But, as for OHAp, departure from stoichiometry leads to twofold statistical disordering about the Ca triangle and to space group $P6_3/m$ (Mackie, Elliott & Young, 1972).

Detailed precision structure refinement results have been previously reported for synthetic and mineral fluorapatite (Sudarsanan, Mackie & Young, 1972), for mineral hydroxyapatite with 0·3 wt% F (Sudarsanan & Young, 1969), for synthetic chlorapatite (Mackie, Elliott & Young, 1972), and for synthetic (F,Cl)Ap of compositions ~14% and ~34% substitution of F for Cl (Mackie, 1972; Mackie & Young, 1974).

2. Experimental

2.1. Techniques

The intensity data were collected either with a computer-controlled four-circle single-crystal X-ray diffractometer (for specimens A, C and F) or with a punched-tape-controlled diffractometer (for specimens B, D and E) and Mo $K\alpha$ radiation. The basic experimental conditions have been described elsewhere (Sudarsanan & Young, 1969; Sudarsanan & Young, 1974). Spherical single-crystal specimens of $<0·2$ mm radius (except for C, see § 2.3.2) were used for measurement of intensities. A balanced-filter (Zr and Y) ω-scan technique was used for low-angle reflections

for which the absorption edge of Zr fell within the scanning range for peak-plus-background. Zr-filtered Mo $K\alpha$ radiation and the 2θ-scan method were employed for the other reflections. When the computer-controlled instrument was used, simultaneous diffraction effects were assessed by remeasurement of each reflection intensity after the specimen was rotated about the diffraction vector by 1°. Those measured reflection intensities which, for the two settings of the crystal, differed by more than three times the expected standard deviation (on the basis of counting statistics) were not used in the refinement. When the punched-tape-controlled instrument was used, no assessment of simultaneous diffraction was made.

Absorption corrections were based on the tabular data in *International Tables for X-ray Crystallography* (1967) for four of the spherical specimens (B, D, E and F, with $\mu R = 0·54, 0·46, 0·54$, and 0·56 respectively). No absorption correction was made for specimen A ($\mu R = 0·28$ for the maximum dimension of the irregular chip used) and for specimen C absorption corrections were applied by the method of Busing & Levy (1957) (*ORABS*-2 by H. A. Levy and R. D. Ellison was used). The calculated transmission coefficients ranged from 0·57 to 0·70.

2.2. Structure-refinement procedures

Full-matrix least-squares refinements of all variable positional, temperature, site occupancy, and isotropic secondary extinction parameters were carried out with the *ORXFLS*3 program of Busing, Johnson, Ellison, Thiessen & Levy (1973). The sources of atomic scattering factors used were Cromer & Waber (1965) for Ca^{2+}, F^- and Cl^-, *International Tables for X-ray Crystallography* (1968) for O^- and, for P^+, values graphically extrapolated from those for P^0 with the help of the Si^0, Si^+ difference, all as given in *International Tables for X-ray Crystallography* (1968). Anomalous dispersion corrections were made with the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer (1965).

In the least-squares refinements, the weights used were reciprocal estimated variances, σ^{-2}, for the individual reflections. The estimated variance for each observation was revised according to

$$\sigma^2 = \sigma_c^2 + \sigma_x^2$$

where $\sigma_x = k|F|^2$ and σ_c is the standard deviation estimated from counting statistics. Normal probability plots (∂R type, Abrahams & Keve, 1971) and correlation plots $\Delta|F|^2/\sigma$ vs $(\sin \theta)/\lambda$ (Sudarsanan & Young, 1974) were used to check the distribution of random errors corresponding to different values for k. The value of k which straightened the normal probability plot bringing its best straight line slope to about 1·0 was used in calculating σ. The best value of k was ~0·05.

2.3. Specimens

Six specimens from four sources were specifically analyzed, *via* crystal structure refinement, for the present study which also utilized the previously published results for four others.

2.3.1. (Cl,OH) Apatite – mineral.
The source of this material is a sample from the Smithsonian Institution (Washington, DC) labeled USNM113977. McConnell (1960) has described this mineral sample, 'post-Wisconsin fossilized dental enamel from a mastodon found near Bluffton, Ohio', as containing or being dahllite, a carbonate-bearing hydroxyapatite. The off-white polycrystalline matrix contained particles of mm size which proved to be single crystals. A spherical specimen ground to 0·18 mm radius from a darker portion and an irregular chip (maximum dimension 0·2 mm) from a clearer portion were used to collect X-ray intensities. They are designated as B and A, respectively, in the tables.

Since the lattice parameters did not agree with those given by McConnell ($a = 9·454$, $c = 6·892$ Å), it was concluded that the particular portions used of the Smithsonian specimen might be not the fossilized dental enamel he described but an associated mineral. The refractive indices (1·662 and 1·663 for the darker portion), the low (0·001) birefringence, and the value of the c parameter indicated that the specimens used could be apatite with a partial substitution of chlorine. The material is probably best characterized by the successful refinement of the structure. Successive refinements of a (F,Cl,OH)Ap model (with positional parameters, site-occupancy factors and the anisotropic temperature parameters of all atoms as variables) indicated that the site $(0,0,\frac{1}{4})$ of F in FAp was vacant in both specimens. The positional parameters of Ca ions and PO_4 groups agreed well with those of apatites. Site-occupancy factors indicated that both specimens were fairly stoichiometric with respect to Ca ions and PO_4 groups. Further, the lattice parameters of the two specimens agreed with those to be expected by Vegard's law (Cullity, 1956) for a (Cl,OH)Ap with Cl and OH contents indicated by the site-occupancy factors obtained (see § 3). The specimens were thus identified as (Cl,OH)Ap.

2.3.2. (Cl,OH) Apatite – synthetic.
A single crystal of (Cl,OH) apatite grown hydrothermally by Ruszala & Kostiner (1975) and characterized by them as $Ca_{10}(PO_4)_6Cl_{0.8}(OH)_{1.2}$ was used for collection of the X-ray intensities. The specimen is designated C in the tables. It was an irregular hexagonal prism 0·24 mm long with prism-face dimensions ranging from 0·12 to 0·24 mm.

2.3.3. (F,Cl,OH,O) Apatite.
Young & Manson (1966) have characterized a mineral from Crystal Lode pegmatite near Eagle, Colorado, as fluorchlorhydroxy-oxyapatite. They suggested a partial substitution of oxygen for halogen. From chemical analysis results they suggested $Ca_{9.81}Na_{0.06}Mn_{0.02}RE_{0.11}(PO_4)_{5.90}$ $(SO_4)_{0.01}(CO_3)_{0.01}F_{1.29}Cl_{0.26}(OH)_{0.14}O_{0.32}$, where RE means rare earth, which gives F:Cl:OH:O 1·0: 0·26:0·10:0·25. Two spherical specimens, here designated as D and E, were used for this study.

In least-squares structure refinement, the site-occupancy factor at $0,0,\frac{1}{4}$, the site of F in FAp, was found to be more than could be accounted for by the F found in the reported chemical analysis. This excess could be attributed to the substitution of oxygen suggested by Young & Manson (1966), so their identification was accepted.

2.3.4. (F,Cl,OH) Apatite.
P. G. Cooray (1970) described a mineral apatite from Metale, Ceylon (now Sri Lanka), containing roughly similar amounts of F, Cl and OH (F:Cl:OH 1·0:1·17:1·36). From chemical analysis results Cooray proposed the formula $Ca_{9.93}(PO_4)_{5.81}(CO_3)_{0.27}(OH)_{0.76}F_{0.56}Cl_{0.66}$. A spherical specimen, designated F, was used in data collection.

3. Results and discussion

The lattice parameters of the crystals involved, six of which were herein initially studied, are given in Table 1.

Table 1. *Lattice parameters*

Apatite type	Crystal Designation	a (Å)	c (Å)	Reference
		Parameters (standard deviations)		
ClAp		9·6418 (8)	6·7643 (5)	Mackie & Young (1974)
(Cl,F)Ap I		9·6205 (9)	6·7761 (6)	Mackie & Young (1974)
(Cl,F)Ap II		9·5485 (10)	6·8237 (7)	Mackie & Young (1974)
(Cl,OH)Ap	A	9·564 (2)	6·816 (2)	Present work, §2.3.1
(OH,Cl)Ap	B	9·488 (1)	6·855 (1)	Present work, §2.3.1
(OH,Cl)Ap	C	9·541 (1)	6·838 (1)	Present work, §2.3.2
(F,Cl,OH,O)Ap	D	9·4215 (4)	6·8739 (4)	Present work, §2.3.3
(F,Cl,OH,O)Ap	E	9·419 (1)	6·872 (1)	Present work, §2.3.3
(OH,Cl,F)Ap	F	9·483 (2)	6·780 (3)	Present work, §2.3.4
OHAp		9·422 (3)	6·883 (3)	Young & Elliott (1966)
FAp		9·367 (1)	6·884 (1)	Mackie & Young (1974)

The final R factors are in Table 2. The various structural parameters are given in Table 3.*

All the refined site-occupancy factors for F, OH and Cl (Table 3) correlate reasonably well with the lattice-parameter differences from those for stoichiometric FAp, OHAp, and ClAp (Fig. 3).

In all these compounds, Ca ions and PO_4 groups occupy more or less the same structural locations as they do in stoichiometric apatites (Table 3). In every case, in the initial refinements, β_{22} of the Ca(2) atom was found to be much larger than normal in apatites, in some cases two or three times larger (Table 3). This suggested possible disorder in the y parameter of the

Ca(2) atom. Elliott, Young & Mackie (1975) found that in $CaCl_2$-deficient chlorapatite the Ca(2) atoms fell into two distinguishable sites according to whether or not a Cl ion was nearby. Their finding raised the possibility that a similar two-site distribution of Ca(2) might be occurring in the present cases. Difference

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*Lists of structure factors for all six specimens and those aniso-tropic thermal parameters not shown in Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33227 (63 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *R factors*

Crystal	Number of independent reflections	R_1 (%)	R_2 (%)	WR_2 (%)
A	1449	4·1	5·8	9·2
B	2035	4·9	5·3	9·4
C	1577	3·4	4·0	9·8
D	1190	2·6	2·7	6·5
E	1265	2·9	3·4	7·4
F	1986	3·1	3·4	7·8

$$R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|, \quad R_2 = \Sigma(||F_o|^2 - |F_c|^2|)/\Sigma|F_o|^2,$$
$$WR_2 = \{\Sigma W(|F_o|^2 - |F_c|^2)^2/\Sigma W|F_o|^4\}^{1/2}.$$

Table 3. *Atom parameters with standard deviations (all $\times 10^4$ except for fractions)*

Apatite type	Crystal designation	Atom*	Site-occupancy factor	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(Cl,OH)Ap	A	Ca(2)	10239 (31)	14 (1)	2570 (1)	$\frac{1}{4}$	31 (1)	53 (1)	30 (1)	17 (1)	0	0
		Ca(2A)	4453 (35)	4 (1)	2462 (1)	$\frac{1}{4}$	29 (1)	30 (1)	32 (1)	9 (1)	0	0
		Ca(2B)	5339 (36)	29 (1)	2656 (1)	$\frac{1}{4}$	31 (1)	32 (1)	26 (1)	17 (1)	0	0
		Cl	5870 (85)	0	0	4209 (5)	36 (1)	36	174 (6)	18	0	0
		O_H	5023 (190)	0	0	1767 (20)	23 (3)	23	244 (28)	11	0	0
		P	10073 (41)	4041 (1)	3722 (1)	$\frac{1}{4}$	26 (1)	23 (1)	26 (1)	15 (1)	0	0
		O(1)	10007 (82)	3375 (2)	4887 (2)	$\frac{1}{4}$	60 (1)	43 (1)	51 (1)	42 (2)	0	0
		O(2)	10075 (85)	5904 (1)	4653 (2)	$\frac{1}{4}$	27 (1)	41 (1)	105 (3)	16 (1)	0	0
		O(3)	9840 (70)	3513 (2)	2640 (1)	680 (1)	112 (2)	56 (1)	63 (2)	61 (1)	−56 (1)	−39 (1)
(OH,Cl)Ap	B	Ca(2)	9847 (36)	48 (1)	2552 (1)	$\frac{1}{4}$	26 (1)	61 (1)	33 (1)	15 (1)	0	0
		Ca(2A)	6948 (25)	44 (2)	2488 (1)	$\frac{1}{4}$	27 (1)	29 (1)	32 (1)	13 (1)	0	0
		Ca(2B)	2921 (17)	60 (5)	2748 (3)	$\frac{1}{4}$	27	29	32	13	0	0
		Cl	2970 (96)	0	0	3723 (15)	29 (3)	29	350 (25)	15	0	0
		O_H	8362 (260)	0	0	1955 (14)	33 (3)	33	218 (20)	16	0	0
(OH,Cl)Ap	C	Ca(2)	9659 (28)	33 (1)	2577 (1)	$\frac{1}{4}$	26 (1)	66 (1)	29 (1)	18 (1)	0	0
		Ca(2A)	5553 (32)	10 (1)	2474 (1)	$\frac{1}{4}$	24 (1)	26 (1)	28 (1)	9 (1)	0	0
		Ca(2B)	3973 (20)	66 (1)	2733 (1)	$\frac{1}{4}$	24	26	28	9	0	0
		Cl	3996 (66)	0	0	3897 (16)	29 (1)	29	249 (8)	15	0	0
		O_H	6851 (180)	0	0	1820 (8)	24 (2)	24	130 (8)	12	0	0
(F,Cl,OH, O)Ap	D	Ca(2)	9779 (26)	65 (1)	2502 (1)	$\frac{1}{4}$	20 (1)	32 (1)	25 (1)	9 (1)	0	0
		Ca(2A)	8615 (28)	61 (1)	2483 (1)	$\frac{1}{4}$	21 (1)	22 (1)	27 (1)	9 (1)	0	0
		Ca(2B)	1263 (15)	79 (4)	2769 (4)	$\frac{1}{4}$	21	22	27	9	0	0
		Cl	1131 (96)	0	0	3765 (24)	26 (2)	26	309 (108)	13	0	0
		O_H	874 (92)	0	0	1905 (87)	17 (15)	17	363 (100)	9	0	0
		F + O	7659 (121)	0	0	$\frac{1}{4}$	28 (2)	28	312 (16)	14	0	0
(F,Cl,OH, O)Ap	E	Ca(2)	10007 (36)	63	2506 (1)	$\frac{1}{4}$	22 (1)	37 (1)	27 (1)	10 (1)	0	0
		Ca(2A)	9035 (38)	64 (1)	2488 (1)	$\frac{1}{4}$	20 (1)	21 (1)	25 (1)	8 (1)	0	0
		Ca(2B)	885 (28)	80 (4)	2802 (6)	$\frac{1}{4}$	20	21	25	8	0	0
		Cl	1031 (54)	0	0	3674 (28)	24 (6)	24	333 (38)	10	0	0
		O_H	835 (13)	0	0	1954 (76)	19 (15)	19	290 (120)	10	0	0
		F + O	7500 (63)	0	0	$\frac{1}{4}$	25 (2)	25	263 (9)	13	0	0
(OH,Cl,F) Ap	F	Ca(2)	9971 (35)	46 (1)	2540 (1)	$\frac{1}{4}$	26 (1)	57 (1)	30 (1)	14 (1)	0	0
		Ca(2A)	6289 (25)	39 (1)	2464 (1)	$\frac{1}{4}$	25 (1)	25 (1)	29 (1)	10 (1)	0	0
		Ca(2B)	3283 (83)	59 (1)	2705 (1)	$\frac{1}{4}$	25	25	29	10	0	0
		Cl	3406 (90)	0	0	4072 (6)	31 (2)	31	221 (10)	15	0	0
		O_H	4118 (220)	0	0	1891 (16)	23 (6)	23	251 (86)	12	0	0
		F	2887 (146)	0	0	$\frac{1}{4}$	30 (3)	30	193 (19)	15	0	0

* Values for Ca(2) are from the least-squares refinements made with only one Ca(2) in the model; those for Ca(2A) and Ca(2B) and all other atoms are from the later refinements in which two sites for Ca(2) were permitted. Parameter values for Ca(1), P, O(1), O(2) and O(3) are similar for all specimens.

syntheses also indicated a possible second position for the Ca(2) atom. Further least-squares refinements indicated that there are, indeed, two distinct positions for the Ca(2) atoms, here designated A and B (Table 3). Because of strong correlation, the site-occupancy factors at the two Ca(2) positions and the two sets of thermal parameters could not all be refined simultaneously. Thus, to find the distribution of Ca(2) atoms at the two sites, the two sets of thermal parameters were first set equal to those in stoichiometric end-member compounds. Refinements were then carried out

Fig. 3. Lattice parameter vs Cl content (% of maximum). Linear interpolations are shown for $Ca_5(PO_4)_3(Cl,OH)$ (dashed line) and for $Ca_5(PO_4)_3(Cl,F)$ (solid line). Specimens containing no F are indicated by O, no OH by ●, and the others by ★.

Table 4. Ca(2) *and* Cl *spatial correlations*

		Triangle side lengths (Å)		z(Cl)	Ca(2B)—Cl
Crystal	Cl(%)	Ca(2A)	Ca(2B)	($\times 10^4$)	distance (Å)
A	59	4·08	4·38	4209	2·77
B	29	4·09	4·47	3723	2·71
C	40	4·08	4·46	3897	2·75
D	11	4·00	4·46	3765	2·72
E	10	4·01	4·51	3674	2·73
F	34	4·01	4·40	4072	2·75

Fig. 4. Side length of the Ca(2B) triangle as a function of Cl content. See Table 4. The point at 95% Cl was deduced from Mackie, Elliott & Young (1972).

for crystal A with first one and then the other set of thermal parameters held fixed. For the other crystals, the thermal parameters for Ca(2B) were held fixed while first one and then the other Ca(2A,B) site-occupancy factor was held fixed, as all other variables were refined (Table 3).

The occurrence of the two sites for Ca(2) is taken to indicate two types of Ca(2) triangles around the sixfold axis. The end-member studies showed that the presence of F or OH at or near the center of the Ca(2) triangles results in triangles smaller than those associated with Cl, which occurs not at the center of the Ca(2) triangle but > 1 Å away. The correlation between the Cl z positions and the Ca(2B) positions with changing Cl content (Table 4 and Fig. 4) identifies the Ca(2B)
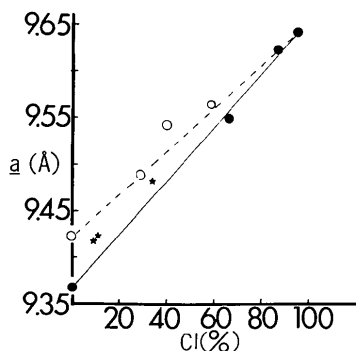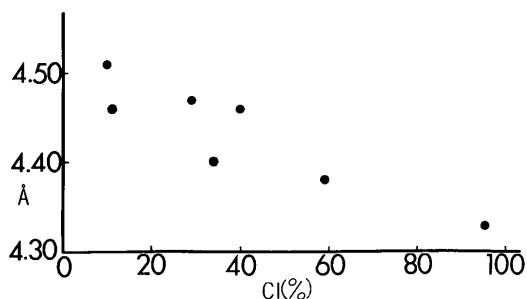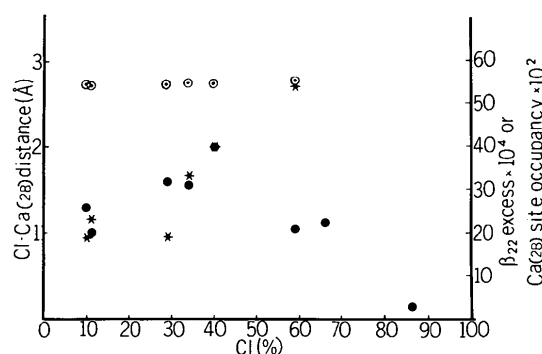

Fig. 5. Correlation of Ca(2B)—Cl distance (O), β_{22} excess for Ca(2) (●) and Ca(2B) site occupancy (★) with Cl content. Data for 'excess β_{22}' (see text) extracted from (Cl,F)Ap I and (Cl,F)Ap II results have been added to the figure. They show that the decrease of 'excess β_{22}' at 59% Cl is part of an expected trend: In a simple two-site model, the disorder contribution to β_{22} evaluated for a single, 'average' site should be maximized when the two sites are equally filled, *e.g.* at 50% Cl in this case.
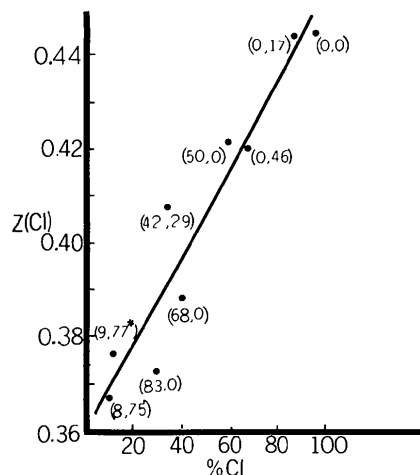

Fig. 6. Dependence of z(Cl) on Cl content irrespective of OH and F content (%OH,%F). Asterisk (*) means percentage is for (F + O) at (0,0,$\frac{1}{4}$).
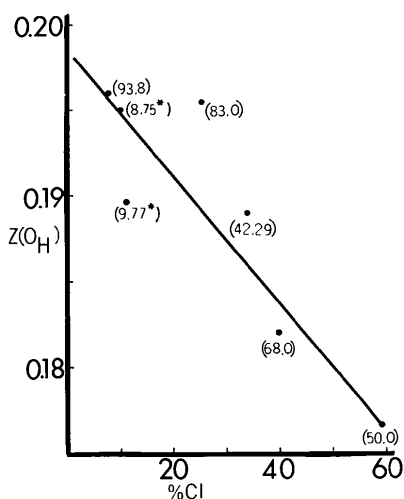
Fig. 7. Dependence of $z(O_H)$ on Cl content irrespective of OH and F content (%OH,%F). Asterisk (*) means percentage is for (F + O) at $(0,0,\frac{1}{4})$.

triangles as being those associated with Cl. Further, as Cl ions move closer to their associated Ca(2B) triangles, the triangles expand such that the same Ca(2B)–Cl distance, similar to that in nearly stoichiometric ClAp (2·80 Å, Mackie, Elliott & Young, 1972), is maintained (Table 4; Fig. 5). The Ca(2A) triangles, on the other hand, being not associated with Cl, do not change size significantly with variation in Cl content. [The contraction of the Ca(2A) triangles in D, E, and F can probably be ascribed to the effect of fluorine at the triangle centers.] As it must on this model, a strong correlation also exists between the site-occupancy factors of chlorine and of Ca(2B) (Fig. 5). Since the Ca(2B) site occupancies were obtained by setting the thermal parameters, specifically β_{22}, to normal values, it is of interest that the excess in the initial [one site for Ca(2)] β_{22} values also correlates well with the Cl content (Fig. 5). These last two correlations further confirm the identification of Ca(2B) as being associated

with the Cl ions. Thus, the association of Ca(2B) with Cl and not with Ca(2A) has been reliably deduced from X-ray diffraction data with the help of composition as a variable.

One effect of the interaction between ions on the six-fold axis is indicated in part by the increases in the temperature factors β_{33} of Cl and O_H atoms for the different specimens as compared to the end members. Strong interaction effects are also shown by the compositional dependence of the positions of the O_H and Cl atoms (Table 5, Figs. 6 and 7).

As Fig. 6 shows, the Cl-ion position depends almost solely on Cl-ion content, even though the F content may be 35% of maximum. It is therefore possible to extrapolate to very small Cl-ion content and to obtain the important result that in human tooth enamel the Cl ion should be found at about $z = 0.36$ to 0.37 (0.2 to 0.3 wt% Cl in tooth enamel translates to ~5 to 9% Cl in Fig. 1), rather than at $z = 0.44$ as would be expected from the examination of nearly stoichiometric ClAp alone. This change of position moves the Cl out of the plane of an O(3) triangle [which is ~5 Å on a side and at the same z level as the Cl ion ClAp (Mackie, Elliott & Young, 1972)] about one third of the way to the plane of the nearest Ca(2) triangle. Presumably, the particular O(3) triangle will contract somewhat, the repulsive Cl ion having been moved out (Mackie, Elliott & Young 1972), while the particular Ca(2B) triangle expands to maintain the normal Ca–Cl distance (Young & Elliott, 1966).

As can be seen from Table 5, the position of the hydroxyl oxygen, O_H, does not correlate well with the OH content. Yet, as Fig. 7 shows, it does correlate well with the Cl content. It is thus evident that both O_H and Cl positions depend strongly on Cl content and rather little on F or OH content (Table 5, Figs. 6 and 7), even if the F content is 35% of maximum.

The dominance of Cl is thought probably to be due to the large size of the Cl ion or to its hydrogen bonding to O_H, or both. The large size tends to produce crowding in stoichiometric ClAp (the sum of 'normal'

Table 5. O_H and Cl parameters vs X-ion composition

Crystal		Cl (%)	F (%)	OH (%)	$z(O_H)$	$\beta_{33}(O_H)$	$z(Cl)$	$\beta_{33}(Cl)$	Reference
ClAp		95 (1)	–	–	–	–	0·4439 (2)	0·0091 (1)	Mackie, Elliott & Young (1972)
(Cl,F)Ap I		86 (1)	17 (2)	–	–	–	0·4432 (2)	0·0200 (3)	Mackie & Young (1974)
(Cl,F)Ap II		66 (1)	46 (2)	–	–	–	0·4203 (5)	0·0142 (3)	Mackie & Young (1974)
OHAp		–	8	93 (1)	0·1960 (8)	0·0102 (8)	–	–	Sudarsanan & Young (1969)
(Cl,OH)Ap	A	59 (1)	–	50 (2)	0·1767 (20)	0·0244 (28)	0·4209 (4)	0·0174 (6)	Present work
(OH,Cl)Ap	C	40 (2)	–	68 (2)	0·1820 (8)	0·0130 (8)	0·3897 (6)	0·0264 (9)	Present work
(OH,Cl,F)Ap	F	34 (1)	29 (1)	42 (2)	0·1891 (16)	0·0251 (84)	0·4072 (6)	0·0221 (10)	Present work
(OH,Cl)Ap	B	29 (1)	–	83 (3)	0·1955 (14)	0·0218 (20)	0·3723 (15)	0·0350 (25)	Present work
(F,Cl,OH,O)Ap	D	11 (1)	77 (1)	9 (1)	0·1905 (87)	0·0363 (100)	0·3765 (24)	0·0309 (108)	Present work
(F,Cl,OH,O)Ap	E	10 (1)	75 (1)	8 (1)	0·1954 (76)	0·0290 (120)	0·3674 (28)	0·0333 (38)	Present work

Cl-ion diameters exceeds the c-axis length into which they are – or would have to be – packed by 5 to 10%) and encourages crystallization with a Cl-ion deficiency of a few per cent (Sudarsanan, Young & Wilson, 1977; Wilson, Sudarsanan & Young, 1977). In infrared spectra, the presence of some Cl occurring along with OH in apatites perturbs the OH stretch frequency from 3572 cm^{-1} to 3495 cm^{-1} (Dykes & Elliott, 1971), whereas F perturbs it only to ~ 3540 cm^{-1} (Young, van der Lugt & Elliott, 1969). It has also been noted (Bartlett & Young, 1972) that the IR oscillator strength of OH is significantly decreased by the presence of Cl but not so by F. A full exposition of the mechanism by which Cl produces these effects on OH, however, awaits further analysis, probably primarily of IR band shifts and broadening.

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