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Nonstoichiometry in Calcium Chlorapatite

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Some properties dependent on deviations from ideal stoichiometry in $Ca_{10}(PO_4)_6Cl_2$ have been studied. By vacuum annealing chlorapatite, up to 23 % of the $CaCl_2$ content can be lost without the appearance of a second phase. Measurements of lattice constants and density indicate the formation of Ca and Cl vacancies. Changes in the optical properties, color centers, and structure have been observed upon loss of $CaCl_2$.

Introduction

The compound whose ideal stoichiometry is represented by $Ca_{10}(PO_4)_6Cl_2$ is a member of an important class of natural and synthetic solids referred to as apatites. Included, among others, are fluorapatite $Ca_{10}(PO_4)_6F_2$, a major ore of phosphorus; hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, the major inorganic component of the bones and teeth of animals; and the synthetic mixed fluor-chlorapatites which constitutes the major fluorescent lamp phosphors. Single crystals of both calcium fluor- and chlorapatite have been grown from the melt (*1*) and from calcium halide fluxes (*2*) and the optical properties of both pure and doped crystals have been studied (*1–4*). Young and Elliot (*5*) were able to convert flux grown chlorapatite crystals into hydroxyapatite crystals by heating in steam. Optical and EPR studies of fluor- and chlorapatite doped with small amounts of OH^- and O^{2-} have been carried out (*6*). Point defects in apatites can, upon X-ray irradiation, capture electrons and holes and give rise to color and paramagnetic centers. These have been investigated by optical and EPR techniques (*7*, *8*). Mazelsky et al. (*9*) have observed laser action in Nd-doped fluorapatite crystals grown from a melt.

All of these studies indicate the large variety of properties exhibited by apatites and the wide interest in these materials shown by workers in many diverse fields (*10*). Unfortunately, many of the apatite materials studied have not been well characterized with respect to purity, defect structure and stoichiometry. In this paper we consider the problem of the nonstoichiometry in chlorapatite and its effect upon some physical properties. This study may have some bearing on the question of the nature of the inorganic portion of bones and teeth, since this appears to be a low Ca/P form of hydroxyapatite (*11*). Posner and Perloff (*12*) have studied the divalent cation deficiency in microcrystaline calcium and lead hydroxyapatites. Chlorapatite appears to us to be an excellent model compound for studying the nonstoichiometry of apatites for a number of reasons:

(1) Well-crystallized, stoichiometric, large particle size (up to 60 μ), chlorapatite powders can be prepared.
(2) Chlorapatite can also be prepared as macroscopic single crystals.
(3) The stoichiometry can be easily controlled and measured.
(4) Chlorapatite may be converted to hydroxypatite by heating in steam.

Properties of Synthetic Chlorapatite Crystals

Single crystals of chlorapatite grown from a melt at 1650°C differ from crystals grown from a $CaCl_2$ flux at 1050–1200°C. Melt grown crystals have a low chloride content, are optically uniaxial negative, have a structure based on a hexagonal unit cell (space group $P6_3/m$) and exhibit a strong optical absorption band at 200 nm (*1*, *2*). Flux grown crystals, on the other hand, have a composition very close to the ideal stoichiometry, are optically

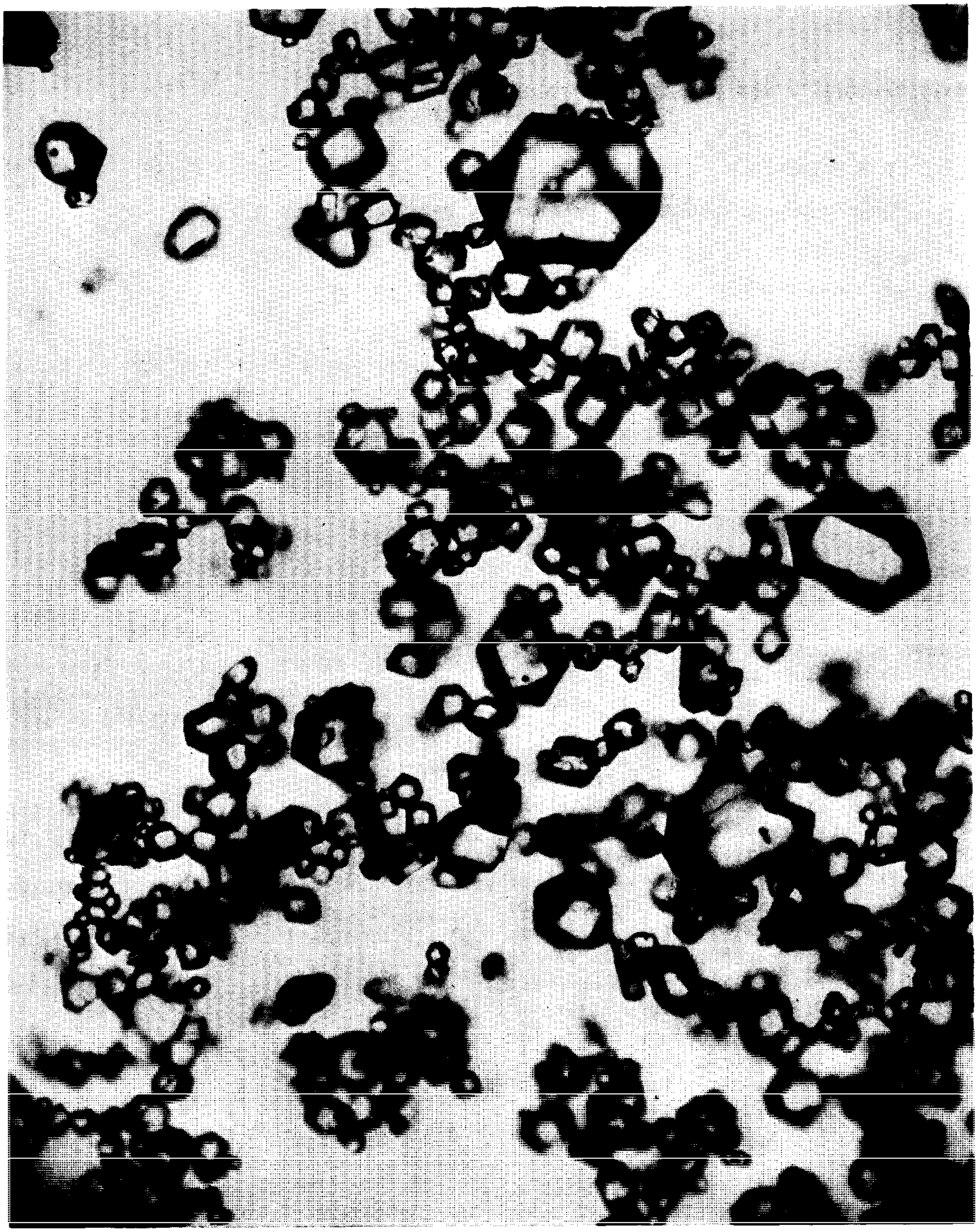

FIG. 1. Photomicrograph of $Ca_{10}(PO_4)_6Cl_2$ crystallites prepared by the thermal decomposition of Ca_2PO_4Cl. The largest crystallites are about 60 μ.

biaxial, have a monoclinic unit cell ($P2_1/b$) and only a weak absorption at 200 nm (*2*).[1]

As described in a previous paper (*2*), monoclinic chlorapatite could be converted into the hexagonal material, by heating in vacuum at temperatures near 1000°C. It was simply assumed at that time that $CaCl_2$ was lost during the vacuum anneal resulting in a nonstoichiometric solid. This loss of $CaCl_2$ is considered further below.

Materials

We have used single crystals grown both from the melt and from a $CaCl_2$ flux, and well crystallized stoichiometric Cl-apatite powder consisting of 10–60 μ crystallites. To prepare the powder, $Ca_4P_2O_9$ was synthesized by a solid phase reaction at 1100°C between $CaHPO_4$ and $CaCO_3$. The product was then heated in anhydrous HCl at 800°C and thereby converted to Ca_2PO_4Cl. The phase diagram of the system $Ca_3(PO_4)_2$–$CaCl_2$ shows that Ca_2PO_4Cl melts incongruently at 1040°C to give $Ca_{10}(PO_4)_6Cl_2$ and $CaCl_2$ (*13*). Accordingly, the synthetic $Ca_2(PO_4)Cl$ was annealed in argon at 1200°C for several hours and then cooled rapidly. The fluxing action of the $CaCl_2$ formed in situ produced extremely well-formed, stoichiometric crystallites of chlorapatite free of flux inclusions and extraneous phases (Fig. 1).[2]

Composition of Vacuum Annealed Chlorapatite

The chlorapatite powders were annealed in vacuum for 16 hr at various temperatures (900–1200°C). A white powdery film, readily soluble in water formed on the surface of the clear fused silica heating tube just outside the hot zone of the furnace. Microscopic examination of the annealed samples showed their appearance to be unchanged from that shown in Fig. 1. The chlorapatite and the white deposit were analyzed for Cl by the Volhard method and for Ca by an EDTA titration. A qualitative test showed no PO_4 in the white deposit.

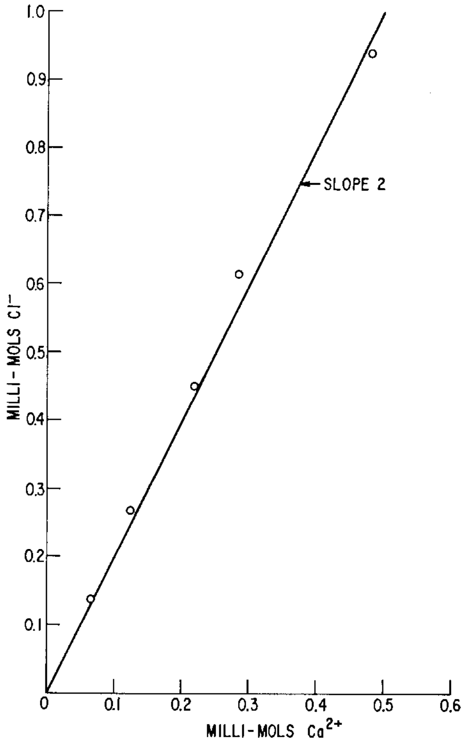

FIG. 2. Plot of the number of millimoles of Cl against the number of millimoles of Ca found in the white deposit after the vacuum heat treatment of $Ca_{10}(PO_4)_6Cl_2$.

The result of the analysis of the white deposit on a series of samples is shown in Fig. 2. Since the molar ratio of Cl/Ca is 2, the white deposit is $CaCl_2$. The Cl mass balance results shown in Fig. 3, indicate that all the Cl lost from the sample was recovered in the white deposit. No Cl was lost, for example, through the formation of $POCl_3$ which would not deposit as a recoverable solid on the walls of the silica tube. On the basis of these analytical results

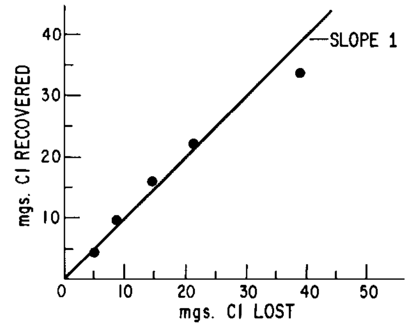

FIG. 3. Plot of the number of milligrams of Cl found in the white deposit against the number lost from the solid during the vacuum heat treatment.

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[1] Although the term apatite refers strictly to those compounds with the ideal composition, $Ca_5(PO_4)_3X$ which crystallize in a structure having the symmetry of the hexagonal space group $P6_3/m$, we shall refer to the Cl compound as chlorapatite. The structures are very similar, involving only slight displacements of the atoms. The monoclinic cell is derived from the hexagonal cell by doubling one of the "*a*" direction while maintaining the 120° angle (*2*, *5*).

[2] I am indebted to R. Hickock of the General Electric Company's Lighting Research Laboratory for this method of synthesizing chlorapatite.

TABLE I

Composition of Chlorapatite Annealed for 16 Hr in Vacuum

Number	Firing temp (°C)	wt% Cl	wt% Ca	x (calcd.)
1	Starting material	6.81	38.5	0.000
2	900	6.37	38.5	0.071
3	1000	6.08	38.6	0.118
4	1100	5.75	38.6	0.171
5	1200	4.86	38.6	(0.310) 0.23

we may write the composition of the vacuum annealed material as $Ca_{10-x}(PO_4)_6Cl_{2(1-x)}$. In Table I are listed the vacuum annealing temperature, the Cl and Ca contents and the values of x as calculated from the Cl content for a series of samples.

The sample fired at 1200°C was found to be a two-phase material as evidenced by the appearance of lines of α-$Ca_3(PO_4)_2$ in the X-ray diffraction pattern. Using a series of synthetic mixtures we measured the ratio of the intensity of the 441 reflection ($2\theta = 20.8°$) of α-$Ca_3(PO_4)_2$ to that of the 211 reflection ($2\theta = 31.4°$) of chlorapatite. This ratio varied linearly with the α-$Ca_3(PO_4)_2$ content from 0 to 15 wt%. The 1200°C annealed sample was thereby found to contain 9.0 wt% of the orthophosphate phase. Correcting for this, we calculated a value of $x = 0.23$. This value then fixes the limit of the off-stoichiometric composition of chlorapatite at 1200°C; within the one phase region chlorapatite can exist with a 23% deficiency of $CaCl_2$.

If vacuum annealed chlorapatite is reheated in $CaCl_2$ vapor for a sufficiently long time, the lost $CaCl_2$ in the solid can be largely replaced. For example, we reheated sample number 4 (Table I) in saturated $CaCl_2$ vapor at 1000°C for 16 hr. Analysis of the thoroughly washed product indicated a Cl content of 6.44% corresponding to $x = 0.06$.

Lattice Constants and Density of Vacuum Annealed Chlorapatite

The lattice constants of chlorapatite (based on a hexagonal cell) were determined from powder diffraction data using a least-squares analysis of ten lines. The results are shown in Fig. 4. Only lines in the forward reflection region could be used and there is some scatter in the data. Assuming a linear dependence of the lattice constants on the x values, we determined the relationship by a least-squares fit using the four sets of constants. The results with a mean deviation of ±0.002 Å are

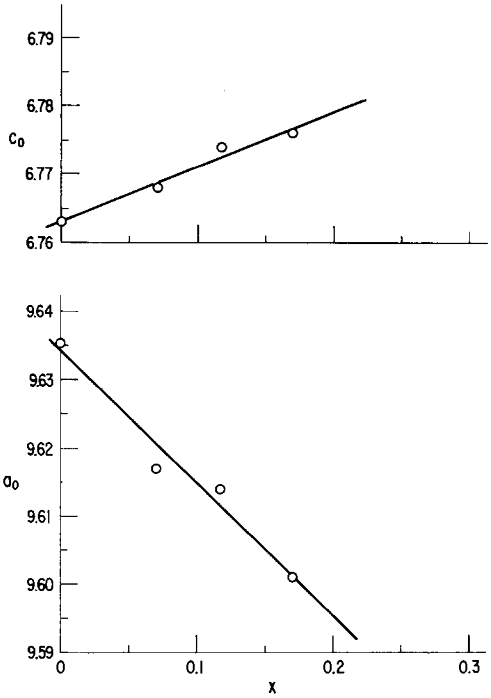

Fig. 4. The variation of the hexagonal unit cell dimensions of chlorapatite with the composition given by $Ca_{10-x}(PO_4)_6$-$Cl_{2(1-x)}$.

$$a_0 = 9.634 - 0.1934x$$

and

$$c_0 = 6.763 + 0.0802x.$$

By comparing the density of nonstoichiometric chlorapatite as calculated from the unit cell mass and volume with the measured bulk density, we were able to confirm the presence of xCa and $2x$Cl vacancies per unit cell.

For the density measurement, we used a polished piece of a melt grown crystal, which when examined under high magnification while immersed in an index matching fluid, was found to be free of internal bubbles or precipitates. The x value as determined from a Cl analysis was 0.173. The lattice constants as determined from the equation given above were $a_0 = 9.601$ and $c_0 = 6.777$ Å giving a unit cell volume of 541.0×10^{-24} cm^{-3}. The unit cell mass assuming 0.173 Ca vacancies and 0.346 Cl vacancies is 169.7×10^{-23} g. The calculated density is then 3.13_7 g/cm^3. For comparison, stoichiometric

Cl apatite has a calculated density of 3.18_1 g/cm^3. The bulk density of the crystal was determined by a flotation method. The composition of an aqueous solution of thallium formate and thallium malonate, thermostated at 26.7 ± .01°C, was adjusted until the crystal chip neither rose nor fell when placed in the center of a column of the liquid. The density of the liquid was then determined using a bicapillary pyknometer calibrated with distilled water at the same temperature. The bulk density at 26.7°C was found to be 3.14_1 g/cm^3. The difference between the two density values of 1.2 ppt can arise from the uncertainty in the lattice constants or in the analysis. The close agreement between the calculated and measured density indicates the formation of Ca and Cl vacancies in the chlorapatite structure when $CaCl_2$ is lost from the structure. It says nothing, of course, as to whether these vacancies are isolated or clustered.

Optical Properties of Vacuum Annealed Chlorapatite

Stoichiometric, pure chlorapatite should exhibit no optical absorption down to about 150 nm where intrinsic absorption begins (*1*). Carefully prepared polycrystalline chlorapatite heated in anhydrous HCl at 1000°C to remove traces of OH^- and O^{2-} impurities shows no evidence of optical absorption down to 190 nm as measured by diffuse reflectance (*6*). After heating in vacuum at 900°C for 16 hr a strong broad absorption band is observed starting at about 240 nm, see (Fig. 5).[3] Excitation in this band leads to very weak yellow fluorescence. Reheating in $CaCl_2$ vapor results in a marked decrease in the intensity of this band and the disappearance of the fluorescence. It seems reasonable, therefore, to assume that this band is associated with the formation of vacancy defects in the crystal.

Absorption bands in the same spectral region are known in the alkali halides containing halogen vacancies (*14*). In particular, the α band has been attributed to the excitation of a p electron in the valence shell of one of the halide ions neighboring a halide ion vacancy. Both the excited electron and the hole produced in the p shell are trapped in the vicinity of the vacancy. In other words, an exciton is produced; this exciton being trapped at the halide ion vacancy. The recombination of the electron and hole also produces fluorescence in the alkali halides.

In addition to the appearance of an ultraviolet absorption band upon loss of $CaCl_2$ a marked increase in the birefringence is observed in the plane containing the pseudohexagonal c axis. Stoichiometric chlorapatite is optically biaxial; the structure being based upon a monoclinic unit cell. However, the birefringence perpendicular to the pseudohexagonal c axis (the unique axis of the monoclinic cell) as well as parallel to this axis is extremely small being 0.0002–0.0003. These values were measured on relatively thick crystals using a quartz wedge. In other words the stoichiometric compound is close to being optically isotropic. After heating a flux grown, stoichiometric crystal of Cl-apatite for 32 hr at 1000°C in vacuum the crystal became uniaxial negative, the birefringence disappearing in plane perpendicular to the c axis [see also Ref. (*2*)]. The birefringence in a plane contain the c axis, however, increased by a factor of 10 to 0.0030. The change in optical character from biaxial to uniaxial

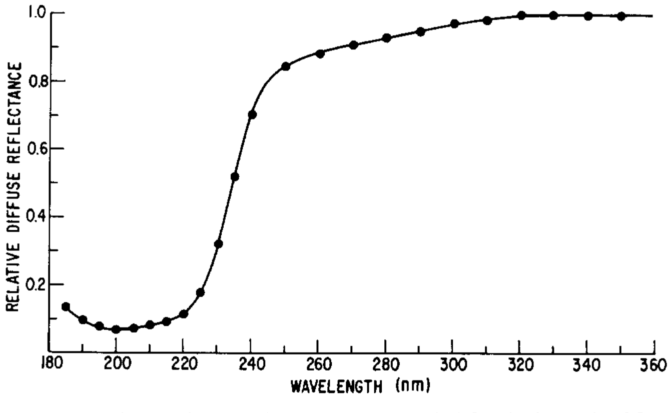

FIG. 5. The diffuse reflectance of chlorapatite powder vacuum annealed for 16 hr at 900°C. The reflectance is measured relative to that of freshly smoked MgO taken as unity at all wavelengths.

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[3] In Ref. (*6*) it was stated that no changes in optical absorption were observed after a vacuum heat treatment. This observation was due to the short heating time of 1 hr that was used.

negative upon loss of $CaCl_2$ is, as already mentioned, accompanied by a change in crystal symmetry from monoclinic $P2_1/b$ to hexagonal $P6_3/m$. The uniaxial character of melt grown crystals (*1*) is due to their departure from stoichiometry. The same may be true of uniaxially negative mineralogical specimens although impurities such as F^-, OH^- and O^{2-} at Cl^- sites can also change the optical character of chlorapatite (*2*, *5*).

Color Center Formation in Vacuum Annealed Chlorapatite

In his study of color centers formed in calcium fluor- and chlorapatite upon X-ray irradiation, Swank (*7*) found a number of absorption bands in the visible and near ultraviolet region of the spectrum. He was able to relate, in a reasonable way, some of the absorption bands observed in chlorapatite with similar bands in fluorapatite. The defects responsible for the color center absorption bands in fluorapatite are known from EPR studies (*6*, *8*, *10*) and one can assume that similar defects occur in chlorapatite. In this way, the isolated Cl^- ion vacancy (*A* band) and associated complexes of an O^{2-} ion impurity at a Cl^- site with two Cl^- ion vacancies (*B* band) are probable defects in chlorapatite. Swank found in addition strong color center absorption bands at 486 nm ($E \| C$) and at 380 nm ($E \perp C$) in chlorapatite which he labelled *X* bands because they did not correspond closely to any of the bands seen in fluorapatite. These two bands probably arise from the same defect, since all the other color center bands in the apatites are dichroic. We measured the diffuse reflectance spectra of the five samples listed in Table I after irradiation by 50 kV X rays from a tungsten target for 15 min at room temperature. The most significant changes in the observed spectra produced by X-ray irradiation was the continuous growth in the intensity of the *X* bands as $CaCl_2$ was lost from the structure (see Fig. 6). Without detailed study we cannot, of course, give a model for those defects responsible for the *X* bands. A not unreasonable defect, however, may be an associate of a Ca^{2+} ion vacancy with a Cl^- ion vacancy. Such associates are to be expected at the high concentration of vacancies in chlorapatite and the coulombic attraction between the effective positive charge of the Cl^- vacancy and the effective double negative charge of the Ca^{2+} ion vacancy. An associate of this sort would still have an effective single negative charge and be capable of trapping a hole in the same way as an O^{2-} impurity at a halide site. The latter defects are known to act as hole traps in fluorapatite although no optical absorption has been associated with them after hole trapping. We have already noted that the effective singly positively charged associates consisting of one O^{2-} ion and two Cl^- ion vacancies act as electron traps and give rise, after trapping, to absorption bands.

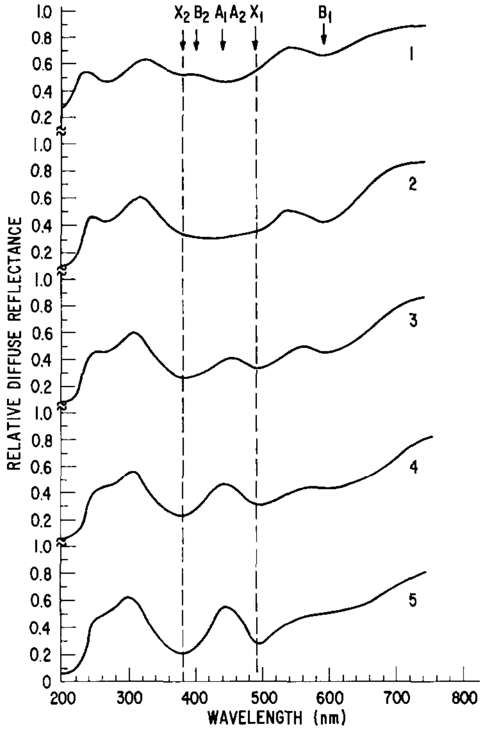

FIG. 6. The diffuse reflectance of chlorapatite powders after X-ray irradiation at room temperature for 15 min. The five samples are those listed in Table I.

Some Structural Considerations in Nonstoichiometric Chlorapatite

The large concentration of both Ca and Cl vacancies possible in chlorapatite raises the question as to whether or not the vacancies occupy random positions in the structure.

The change in crystal symmetry of chlorapatite from monoclinic ($P2_1/b$) to hexagonal ($P6_3/m$) with loss of $CaCl_2$ has been discussed in a previous paper (*2*). The monoclinic form of stoichiometric chlorapatite undergoes a reversible phase transition at about 200°C to the hexagonal form. With loss of $CaCl_2$ the transition temperature is lowered until a composition is reached at which the hexagonal phase becomes stable at all temperatures. No transition to a monoclinic phase was observed down to liquid He temperatures. Although the value of x at which the hexagonal phase is stabilized has not been determined, it is probably lower than 0.07 (Table I, Sample 2), since a small single crystal exhibited a hexagonal structure after a 15-hr anneal in vacuum at only 830°C. We also indicated that the hexagonal structure may arise from a one-dimensional disorder in the columns of chloride ions parallel to the c axis; this disorder arising from the presence of chloride ion vacancies. The monoclinic phase is then an ordered phase and the nonstoichiometric hexagonal phase with a range of composition is a disordered one. As Wadsley (*15*) has pointed out, however, short-range order may be retained as microscopic blocks or domains, perhaps only a few unit cells in dimension, within a disordered phase of variable composition. In Ref. (*2*) we presented evidence for the existence of such ordered monoclinic domains in nonstoichiometric hexagonal chlorapatite. This conclusion was arrived at from measurements of the fluorescence spectrum of both fluorapatite and chlorapatite doped with a small amount of MnO_4^{3-} impurities at PO_4^{3-} sites (*4*). The ion MnO_4^{3-} introduces a number of broad absorption bands in the near ultraviolet, visible and near infrared. By excitation in these bands, at low temperatures, a sharp fluorescence line was observed in fluorapatite at 1.58 μ. In stoichiometric chlorapatite, three closely spaced lines of equal intensity were observed near 1.163 μ. These three lines were interpreted as arising from the substitution of MnO_4^{3-} at the three crystallographically inequivalent PO_4^{3-} sites of the monoclinic ($P2_1/b$) structure (*2*). The crystal mentioned above heated at 830°C in vacuum still showed the three closely spaced fluorescence lines when measured at liquid He temperatures. At higher temperatures the lines were broadened so as to be unresolvable. This broadening probably is due to the small size of the monoclinic domains and the consequent strains and distortion in the ion positions around the MnO_4^{3-} ions. We have looked for a similar effect in a crystal of chlorapatite doped with MnO_4^{3-} but heated at 1100°C in a vacuum for 16 hr. This crystal had lost considerable amounts of $CaCl_2$. The infrared emission lines were so broadened, even at liquid He temperatures that no structure could be resolved. We cannot be certain therefore that the monoclinic domain structure present at low values of x is maintained at larger values of x. Careful X-ray diffraction studies of nonstoichiometric chlorapatite over the composition range might reveal some interesting structural features and might very well have some bearing on the problem of the nature of the inorganic phase in bones and teeth.

Acknowledgments

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