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THE CRYSTAL CHEMISTRY OF APATITE: STRUCTURE FIELDS OF FLUOR- AND CHLORAPATITE[1]

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ABSTRACT

A comparative study of the crystal chemistry of synthetic fluor- and chlorapatites was carried out. The common apatites prepared may be represented by the general formula $A_{10}(XO_4)_6Z_2$ where $A=$Cd, Ca, Sr, Pb, or Ba; $X=$P, As, or V; and $Z=$F or Cl. All combinations formed apatites except $Cd_{10}(AsO_4)_6F_2$ and $Cd_{10}(VO_4)_6F_2$. The existence of unusual apatites of composition $Mn_{10}(PO_4)_6Cl_2$, $Na_6Ca_4(PO_4)_6F_2$, and $Ca_{10}(SiO_4)_3(SO_4)_3F_2$ was confirmed, and some new analogues of the latter two compounds were discovered.

The structure fields of fluorapatite and chlorapatite were determined, and from them, the size limitations on ions capable of totally occupying the calcium and phosphorus positions were deduced. The size limits for substitutions in fluorapatite were $0.29\ \text{Å} \leq R_p \leq 0.60\ \text{Å}$ and $0.95\ \text{Å} \leq R_c \leq 1.35\ \text{Å}$ where R_p and R_c represent the radii of ions occupying the phosphorus and calcium positions respectively. The size limits for substitutions in chlorapatite were $0.29\ \text{Å} \leq R_p \leq 0.60\ \text{Å}$ and $0.80\ \text{Å} \leq R_c \leq 1.35\ \text{Å}$ (based on Ahrens' radii).

The compounds, $Cd_{10}(PO_4)_6F_2$, $Ca_{10}(AsO_4)_6F_2$, and $Ca_{10}(VO_4)_6F_2$ did not have hexagonal symmetry, but may be regarded as distorted apatites. The solid solubility of divalent Mg and Ni and of pentavalent V in $Ca_{10}(PO_4)_6F_2$ was investigated. The lattice parameters of about thirty-five apatites were determined, some for the first time.

INTRODUCTION

The crystal chemistry of apatite is complex and it is the purpose of this study to examine some of the crystal chemical limitations on the apatite structure. It was thought that the most systematic way to approach this objective was to determine the relevant structure fields. Ito (1968) determined the structure fields of the silicate oxy- and hydroxyapatites, but such determinations have not been made for other classes of apatite. The complete structure field diagram of apatite would be a three-dimensional plot since crystal chemical substitutions can occur on the calcium, phosphorus, and fluoride sites. The present investigation was, however, limited to the fluorapatite and chlorapatite sections through the three-dimensional structure field.

Most of the compounds prepared in this study have been previously reported in the literature. However, in a number of cases no characteristics, by which the reported compounds could be identified, were

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given. In other instances, isolated reports of the syntheses of various apatite compounds were found, but subsequent, independent confirmations were not found. In view of this, further objectives of the study were to confirm or reject the reported synthesies of varous unusual apatites and to provide a complete set of lattice parameters for the more common fluor- and chlorapatites.

EXPERIMENTAL

The compounds for this work were prepared by heating stoichiometric mixtures of alkaline earth halides and pre-reacted intermediates for 0.5 to 24 hours at temperatures in the range 350–1250°C depending upon composition. In essence the method is based on solid state reactions of the type:

$$3Ca_3(PO_4)_2 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2$$

which have been previously studied (Montel, 1958; Wallaeys 1952; and Akhavan-Niaki, 1961) and found to proceed rapidly at moderately high temperatures. In the present study, a single 60 minute heat treatment was usually sufficient to produce apatites which were well crystallized and phase pure insofar as could be determined by X-ray diffraction analysis.

The intermediate materials contained everything to be present in the finished apatites except the halides, and were prepared by reacting mixtures of chemically pure reagents such as alkaline earth carbonates, alkaline earth sulfates, alkali sulfates, silicic acid, ammonium orthophosphate, arsenic acid, and ammonium metavanadate in the solid state. To ensure homogeneity, the intermediates were subjected to three heat treatments of 15 hours duration—each of which was followed by thorough grinding under acetone. The temperatures of the heat treatments were typically 500°C, 800°C, and 800–1000°C. The purpose of the pre-reacted intermediates was to eliminate halogen losses due to side reactions such as (a) pyrohydrolysis of the halides by water present in the starting materials and (b) formation of volatile phases such as POF_3 as observed by Montel (1958).

Phase analyses were accomplished by use of a Norelco diffractometer set at maximum counting sensitivity and scanned at $\theta = 1.0°/\text{min}$. Nickel filtered copper radiation was used except for materials containing high concentrations of manganese. Such materials were examined on a General Electric diffractometer using vanadium filtered chromium radiation. For lattice parameter determinations, the samples were back-packed into aluminum holders, and the diffractometer was scanned at $\theta = 0.125$ degree per minute. A sample of fluorapatite, measured on four different occasions, gave theta values which were reproducible to ± 0.005 degree. The positions of the reflections were corrected by reference to an external silicon standard. The lattice parameters were reproducible to ± 0.002 Å, but since only forward reflections were used in the calculations, the parameters were probably accurate to only ± 0.01 Å.

A few samples were examined under a Leitz petrographic microscope, but most of the products (not having been melted) were too fine grained for precise optical measurements.

RESULTS AND DISCUSSION

Syntheses Attempted. The synthesis of apatites having the compositions given in Tables 1 and 2 was attempted. The phase purity of each sample was ascertained by X-ray diffraction analysis and in some cases by examination under a petrographic microscope. The lattice parameters of most of the apatites were measured and (with the exception of data reported by Klement *et al.*) found to be in good agreement with previously published values (Table 3).

TABLE 1. APATITE SYNTHESES ATTEMPTED

Composition	Synthesis conditions[a] (°C/hr)	Phases present
$Cd_{10}(PO_4)_6F_2$	1100/1 P	Ap
$Ca_{10}(PO_4)_6F_2$	920/1	Ap
$Sr_{10}(PO_4)_6F_2$	1230/0.3	Ap+tr. $Sr_3(PO_4)_2$
$Pb_{10}(PO_4)_6F_2$	900/1 S	Ap
$Ba_{10}(PO_4)_6F_2$	1100/1 S	Ap
$Ca_{10}(AsO_4)_6F_2$	860/1.2 S	Ap
$Sr_{10}(AsO_4)_6F_2$	860/1.2 S	Ap
$Pb_{10}(AsO_4)_6F_2$	860/1.2 S	Ap
$Ba_{10}(AsO_4)_6F_2$	860/1.2 S	Ap+tr. $Ba_3(AsO_4)_2$
$Ca_{10}(VO_4)_6F_2$	970/1	Ap
$Sr_{10}(VO_4)_6F_2$	970/1	Ap
$Pb_{10}(VO_4)_6F_2$	630/6 S	Ap
$Ba_{10}(VO_4)_6F_2$	970/1	Ap
$Mn_{10}(PO_4)_6Cl_2$	850/1 S	Ap+tr. Mn_2PO_4Cl
$Cd_{10}(PO_4)_6Cl_2$	770/1	Ap+tr. $Cd_3(PO_4)_2$
$Ca_{10}(PO_4)_6Cl_2$	770/1	Ap
$Sr_{10}(PO_4)_6Cl_2$	820/1	Ap
$Pb_{10}(PO_4)_6Cl_2$	320/23	Ap
$Ba_{10}(PO_4)_6Cl_2$	930/0.7	Ap
$Cd_{10}(AsO_4)_6Cl_2$	770/1	Ap+tr. $Cd_3(AsO_4)_2$
$Ca_{10}(AsO_4)_6Cl_2$	930/0.5	Ap+tr. $Ca_3(AsO_4)_2$
$Sr_{10}(AsO_4)_6Cl_2$	820/1	Ap+tr. $Sr_3(AsO_4)_2$
$Pb_{10}(AsO_4)_6Cl_2$	800/0.3	Ap
$Ba_{10}(AsO_4)_6Cl_2$	930/0.7	Ap+$Ba_3(AsO_4)_2$
$Cd_{10}(VO_4)_6Cl_2$	550/1	Ap
$Ca_{10}(VO_4)_6Cl_2$	900/1	Ap+tr. $Ca_3(VO_4)_2$
$Sr_{10}(VO_4)_6Cl_2$	970/1	Ap
$Pb_{10}(VO_4)_6Cl_2$	550/1	Ap
$Ba_{10}(VO_4)_6Cl_2$	900/1	Ap
$Ca_{10}(SiO_4)_3(SO_4)_3F_2$	1000/2	Ap
$Sr_{10}(SiO_4)_3(SO_4)_3F_2$	1000/2	Ap+tr. Sr_2SiO_4 +tr. $SrSO_4$
$Pb_{10}(SiO_4)_3(SO_4)_3F_2$	675/1	Ap+tr. unidentified phase
$Na_6Ca_4(SO_4)_6F_2$	800/1	Ap
$Na_6Pb_4(SO_4)_6F_2$	570/2	Ap+tr. $PbSO_4$
The following syntheses were unsuccessful.		
$A_{10}(SiO_4)_3(SO_4)_3F_2$	A = Cd or Ba	
$Ca_{10}(GeO_4)_3(SO_4)_3F_2$		
$Na_6B_4(SO_4)_6F_2$	B = Cd, Sr, or Ba	
$K_6B_4(SO_4)_6F_2$	B = Cd, Ca, Sr, Pb, or Ba	
$K_6Pb_4(XO_4)_6F_2$	X = Mo or W	
$A_{10}(SbO_4)_6F_2$	A = Ca or Pb	
$A_{10}(XO_4)_6F_2$	A = Pb or Ba; X = Ta or Nb	

[a] P = platinum capsule, S = evacuated silica capsule, tr. = trace, and Ap = apatite.

The synthesis of fluor- and chlorapatites presented no problems when the calcium positions were occupied by Ca, Sr, Pb, or Ba and when the phosphorus positions were occupied by P, As, or V. The manganese and cadmium apatites were more difficult to synthesize and will be dealt with in the next section of the paper.

A few apatites involving charge compensated substitutions were prepared in order to obtain more data for the construction of the structure field diagrams. A synthetic apatite of composition $Ca_{10}(SiO_4)_3(SO_4)_3F_2$ which involves the substitution $2P_5^+ = Si_4^+ + S_6^+$ was reported by Klement (1939a). The existence of this compound was confirmed and the strontium and lead analogues were also successfully prepared—apparently for the first time. The strontium silico-sulfate apatite was not stable, and when heated at 1130°C for thirty minutes it decomposed to a mixture of strontium silicate and strontium sulfate. High temperatures must therefore be avoided when synthesizing this compound. Several attempts to prepare cadmium and barium silico-sulfate apatites were unsuccessful, and a silicocarnotite-like phase was obtained from a mixture of composition $Ca_{10}(GeO_4)_3(SO_4)_3F_2$, rather than apatite.

Klement (1939b) prepared an all-sulfate apatite of composition $Na_6Ca_4(SO_4)_6F_2$ in which charge compensation involved both the "calcium" and "phosphorus" positions. The preparation of this and other $A_6B_4(SO_4)_6F_2$ compounds in which A = Na or K and B = Cd, Ca, Sr, Pb, or Ba was studied. Of the ten compositions thus generated, only $Na_6Ca_4(SO_4)_6F_2$ and $Na_6Pb_4(SO_4)_6F_2$ yielded apatites. The chloride analogue of $Na_6Pb_4(SO_4)_6F_2$ occurs na-

TABLE 2. SYNTHESIS OF MANGANESE AND CADMIUM APATITES

Composition	Synthesis conditions[a] (°C/hr)	Phases present
$Mn_{10}(PO_4)_6Cl_2$	850/1 S	Ap+tr. Mn_2PO_4Cl
$Mn_{10}(PO_4)_6Cl_2+0.1\ MnCl_2$	850/1 S	Ap+Mn_2PO_4Cl
Mn_2PO_4Cl	850/1 S	Mn_2PO_4Cl
$Mn_{10}(PO_4)_6F_2+0.1\ MnF_2$	800/1 S	$Mn_3(PO_4)_2+Mn_2PO_4F$
$Mn_{10}(PO_4)_6F_2+0.10\ MnF_2$	1000/1 S, G	$Mn_3(PO_4)_2+Mn_2PO_4F$
$Mn_7(PO_4)_4F_2$	800/1 S	$Mn_2PO_4F+Mn_3(PO_4)_2$
$Mn_7(PO_4)_4F_2$	1000/1 S, G	$Mn_2PO_4F+Mn_3(PO_4)_2$
$Mn_2PO_4F+XMnF_2$	800/1 S, G	$MnF_2+Mn_2PO_4F$
$Mn_2PO_4F+XMnF_2$	900/0.5 P, G	$MnF_2+Mn_2PO_4F$
$Cd_{10}(PO_4)_6F_2$	900/1 A	$Cd_3(PO_4)_2$
	900/1 S, G	Ap+$Cd_3(PO_4)_2$
	1100/1 P, G	Ap

Optical Properties:

$Mn_{10}(PO_4)_6Cl_2$	uniaxial (−)	$n \approx 1.76$	irregular grains
Mn_2PO_4Cl	biaxial (+)	$n \approx 1.72$	well defined prismatic crystals
Mn_2PO_4F	biaxial (−)	$n \approx 1.68$	irregular grains
$Cd_{10}(PO_4)_6F_2$	biaxial (?)	$n \approx 1.79$	very fine grained

[a] S = evacuated silica capsule, A = air, G = gas emitted when tube opened and P = platinum capsule.

turally as the mineral coracolite (Schneider, 1967), but the fluoride compound has not been previously reported. Chromate apatites such as $K_6Pb_4(CrO_4)_6F_2$ which are analogous to the sulfate apatites were synthesized by Pascher (1963), but present attempts to go one step further and prepare molybdate and tungstate analogues were unsuccessful. Apparently the MoO_4^{2-} and WO_4^{2-} ions are either too large or too greatly distorted from a tetrahedral configuration to be incorporated in the apatite structure.

As a further check on the size limit for ions occupying the tetrahedral (or phosphorus) positions, the possibility of preparing antimonate, tantalate, and niobate apatites was examined. The failure to obtain such apatites was not surprising since from radius ratio arguments, pentavalent Sb, Nb, and Ta are somewhat too large for tetrahedral coordination by oxygen, and these ions apparently prefer octahedral coordination as found in the pyrochlor and perovskite structures (Aleshin and Roy, 1962 and Roy, 1954).

Manganese and Cadmium Apatites. The synthesis of manganese fluor- and chlorapatite was reported by Klement and Haselbeck (1965) wherein the apatites were obtained by heating mixtures of $Mn_3(PO_4)_2$ and $MnCl_2$ or MnF_2 in sealed silica tubes at 1000°C for several hours. Duplication of these experiments confirmed the existence of manganese chlorapatite, but no evidence for the existence of manganese fluorapatite was found.

A compound having optical properties similar to those of high-manganese triplites (Palache *et al.* 1951), and tentatively identified as Mn_2PO_4F, was found in the MnF_2—$Mn_3(PO_4)_2$ system. The X-ray pattern of the compound did not resemble that of fluorapatite and could not be indexed on the basis of a hexagonal unit cell. The coexistence of

TABLE 3. UNIT CELL DIMENSIONS OF SYNTHETIC APATITES

Formula	This Study				Former Studies		
	a(Å)	c(Å)	V(Å^3)	c/a	a(Å)	c(Å)	References
$Mn_{10}(PO_4)_6Cl_2$	9.54	6.20	489	0.650	(9.30)	(6.20)	Klement & Haselbeck (1965)
$Cd_{10}(PO_4)_6F_2$	9.30	6.63	497	0.713	9.32	6.61	Engel (1965)
$Cd_{10}(PO_4)_6Cl_2$	9.67	6.50	526	0.672	9.67	6.46	Engel (1965)
$Cd_{10}(AsO_4)_6Cl_2$	10.03	6.53	569	0.651	10.04	6.51	Engel (1965)
$Cd_{10}(VO_4)_6Cl_2$	10.13	6.55	582	0.646	10.11	6.52	Engel (1965)
$Ca_{10}(PO_4)_6F_2$	9.36	6.88	522	0.735	9.352	6.871	Wallaeys (1952)
$Ca_{10}(AsO_4)_6F_2$	9.63	6.99	561	0.726			
$Ca_{10}(VO_4)_6F_2$	9.68	7.01	569	0.724	9.67	7.01	Aia & Lublin (1966)
$Ca_{10}(PO_4)_6Cl_2$	9.63	6.78	544	0.704	9.610	6.763	Wallaeys (1952)
$Ca_{10}(AsO_4)_6Cl_2$	10.04	6.83	596	0.680			
$Ca_{10}(VO_4)_6Cl_2$	10.18	6.77	608	0.665	10.16	6.79	Aia & Lublin (1966)
$Ca_{10}(SiO_4)_3(SO_4)_3F_2$	9.43	6.93	533	0.735	(9.54)	(6.99)	Klement & Dihn (1941)
$Ca_4Na_6(SO_4)_6F_2$	9.39	6.89	525	0.734	(9.49)	(6.87)	Klement & Dihn (1941)
$Ca_9Mg(PO_4)_6F_2$	9.355	6.867	520	0.734			
$Ca_9Ni(PO_4)_6F_2$	9.364	6.870	522	0.734			
$Sr_{10}(PO_4)_6F_2$	9.71	7.28	594	0.750	9.719	7.276	Akhavan Niaki (1961)
$Sr_{10}(AsO_4)_6F_2$	9.99	7.40	640	0.741			
$Sr_{10}(VO_4)_6F_2$	10.01	7.43	645	0.742			
$Sr_{10}(PO_4)_6Cl_2$	9.87	7.19	607	0.728	9.874	7.184	Akhavan Niaki (1961)
$Sr_{10}(AsO_4)_6Cl_2$	10.18	7.28	653	0.715	(10.12)	(7.50)	Klement & Harth (1961)
$Sr_{10}(VO_4)_6Cl_2$	10.21	7.30	659	0.715			
$Pb_{10}(PO_4)_6F_2$	9.75	7.30	603	0.749	9.76	7.29	Merker & Wondratschek (1959)
$Pb_{10}(AsO_4)_6F_2$	10.08	7.42	653	0.736	10.07	7.42	Merker & Wondratschek (1959)
$Pb_{10}(VO_4)_6F_2$	10.11	7.34	650	0.726	10.10	7.34	Merker & Wondratschek (1959)
$Pb_{10}(PO_4)_6Cl_2$	9.99	7.34	634	0.735	9.97	7.32	Merker & Wondratschek (1959)
$Pb_{10}(AsO_4)_6Cl_2$	10.24	7.44	676	0.726	10.25	7.46	Merker & Wondratschek (1959)
$Pb_{10}(VO_4)_6Cl_2$	10.32	7.36	679	0.713	10.32	7.33	Merker & Wondratschek (1959)
$Pb_{10}(SiO_4)_3(SO_4)_3F_2$	9.88	7.41	627	0.750			
$Pb_4Na_6(SO_4)_6F_2$	9.63	7.11	571	0.738			
$Ba_{10}(PO_4)_6F_2$	10.16	7.69	687	0.757	(10.220)	(7.665)	Akhavan Niaki (1961)
$Ba_{10}(AsO_4)_6F_2$	10.41	7.83	735	0.752			
$Ba_{10}(VO_4)_6F_2$	10.44	7.86	742	0.753			
$Ba_{10}(PO_4)_6Cl_2$	10.26	7.65	697	0.746	10.275	7.647	Akhavan Niaki (1961)
$Ba_{10}(AsO_4)_6Cl_2$	10.54	7.73	744	0.733	(10.44)	(7.59)	Klement & Harth (1961)
$Ba_{10}(VO_4)_6Cl_2$	10.55	7.75	747	0.734			

Mn_2PO_4F with either MnF_2 or $Mn_3(PO_4)_2$ depending upon the initial composition (Table 2) was additional evidence against the existence of manganese fluorapatite. Tubes containing mixtures of manganese orthophosphate and manganese fluoride evolved a pungent gas when opened. This gas smelled somewhat like HCl and formed a white smoke upon contact with the atmosphere. The gas is thought to consist of POF_3 or PF_5 which hydrolyzes in the presence of water vapor to form HF and a smoke of "P_2O_5". Montel (1958) observed the formation of POF_3 and PF_5 when acidic calcium phosphates (molar ratio of $Ca/P < 1.5$) were heated with calcium fluoride.

Manganese chlorapatite was made by heating a stoichiometric mixture of $MnCl_2$ and $Mn_3(PO_4)_2$ in a sealed silica tube. Compositions having excess manganese chloride yielded a second compound which was tentatively identified as Mn_2PO_4Cl (Table 2). The powder pattern of $Mn_{10}(PO_4)_6Cl_2$ resembled that of cadmium chlorapatite and was successfully indexed on the basis of a hexagonal unit cell. Optically, manganese chlorapatite was uniaxial negative which was expected for a compound having the apatite structure. Manganese chlorapatite must be prepared in a protective atmosphere to prevent the oxidation of di-

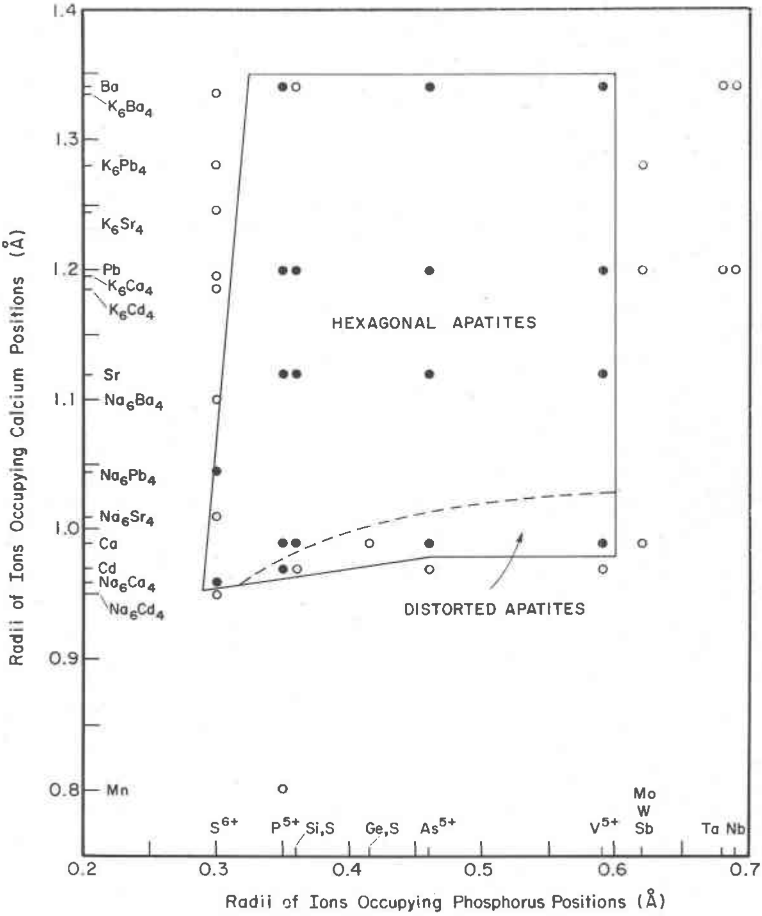

FIG. 1. The structure field of fluorapatite. (Filled circles = apatite, open circles = no apatite, Ahrens' radii.)

valent manganese. This may be accomplished by use of sealed tubes as in the present study, or by use of a stream of nitrogen which has been passed over ammonium chloride at 300°C (Parodi, J., General Electric Co., personal communication).

The cadmium chlorapatites formed readily when stoichiometric mixtures of $CdCl_2$ and $Cd_3(PO_4)_2$, $Cd_3(AsO_4)_2$, or $Cd_3(VO_4)_2$ were heated in air at 770°C for one hour. Attempts to prepare cadmium flourapatite in air were unsuccessful, for the reason that, as in the MnF_2—$Mn_3(PO_4)_2$ system, gaseous phosphorus fluorides were formed which escaped the system and prevented the formation of apatite. The use of sealed silica or platinum tubes was sufficient to suppress the gas forming reactions and prevent drastic changes in composition. Under these conditions, cadmium fluorapatite could be prepared by heating a mixture of cadmium fluoride and cadmium orthophosphate. Attempts to prepare the cadmium arsenate and vanadate fluorapatites were unsuccessful. Engel (1965) was also unable to prepare these compounds and the synthesis of $Cd_{10}(AsO_4)_6F_2$ reported by Klement and Haselbeck (1965) is questionable.

The Structure Fields of Fluorapatite and Chlorapatite. The observation on the synthesis of apatite were used to construct the structure field diagrams in Figures 1 and 2. The radii of ions occupying the calcium (R_c) and phosphorus (R_p) positions in apatite were plotted along the ordinate and abscissa respectively. In cases where more than one kind of ion occupied a set of positions, the average radius was plotted. The boundaries of the structure fields were determined by observing which compositions produced apatites and which did not (see Tables 1 and 2).

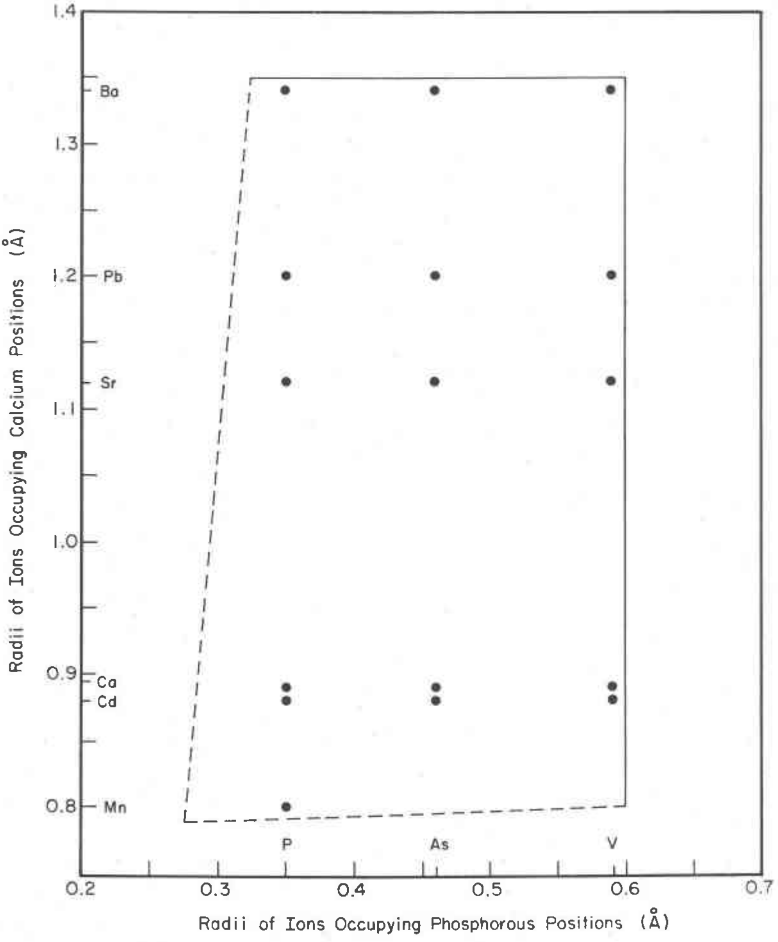

FIG. 2. The structure field of chlorapatite. (Ahrens' radii.)

The structure field of fluorapatite was well defined as a function of R_p and had the limits $0.29\ \text{Å} \leq R_p \leq 0.60\ \text{Å}$. The size limitations of ions occupying the calcium positions were less well defined because (a) an upper limiting radius was not found (the only divalent cation larger than Ba^{+2} is Ra^{2+}) and (b) near the lower limit the apatites tended to have distorted structures which no longer possessed hexagonal symmetry. For practical purposes the upper limit of R_c was set at 1.35 Å which is slightly greater than the ionic radius of barium. The lower limit of R_c was set at 0.95 Å so that both the normal and distorted phases were included in the fluorapatite structure field. In other words the limits on R_c were $0.95\ \text{Å} \leq R_c \leq 1.35\ \text{Å}$.

The chlorapatite structure field, having boundaries of $0.29\ \text{Å} \leq R_p \leq 0.60\ \text{Å}$ and $0.80\ \text{Å} \leq R_c \leq 1.35\ \text{Å}$ differed from that of fluorapatite in two respects. First, structurally distorted chlorapatites did not occur near the lower limit of R_c, and second the chlorapatite structure could tolerate much smaller cations on the calcium sites than could the fluorapatite structure. Both of these differences are probably related to the difference in position of the halide ions in the fluor- and chlorapatite structures (Prener, 1967 and Young and Elliott, 1966), but a detailed explanation of how the structural difference enables chlorapatite to accept smaller cations without distortion will not be attempted.

Solid Solubility of Mg *and* Ni *in* $Ca_{10}(PO_4)_6F_2$. The structure field diagrams of fluor- and chlorapatite were constructed on the basis of complete replacement of calcium or phosphorus by the substituting ions. However it should not be concluded that ions whose radii are outside the size limitations for complete replacement, play no role in the crystal chemistry of apatite. The extent to which the small divalent cations, Mg (0.67 Å) and Ni (0.69 Å), could be substituted for calcium in fluorapatite was examined. The compositions in Table 4 were prepared by heating stoichiometric mixtures of calcium fluoride and $(Ca, Mg)_3(PO_4)_2$ or $(Ca, Ni)_3(PO_4)_2$ at 920°C for one hour. The magnesium series was prepared in air, but in order to prevent the oxidation or vaporization of NiF_2, the nickel series was prepared in evacuated silica capsules. The nickel doped fluorapatites were light green in color. The lattice parameters of the solid solutions were determined and plotted as a function of composition in Figure 3. The *c*-parameters decreased slightly and then remained constant with increasing Mg or Ni concentration. The changes in the *a*-parameters were rather erratic, and for this reason only the *c*-axis plots were used in fixing the solubility limits of Mg and Ni in fluorapatite at 9.0 and 7.5 mole percent respectively. As may be seen in Table 4, large amounts of secondary phases appeared in the samples

TABLE 4. SOLID SOLUTION OF MAGNESIUM AND NICKEL IN $CA_{10}(PO_4)_6F_2$

$Ca_{10-x}Mg_x(PO_4)_6F_2$	Phases Present[a]
$x=0.0$	Ap
0.5	Ap+tr. $\beta-Ca_3(PO_4)_2$
1.0	Ap+tr. $\beta-Ca_3(PO_4)_2$+tr. CMP
1.5	Ap+CMP+tr. $\beta-Ca_3(PO_4)_2$
2.0	Ap+CMP+tr. $\beta-Ca_3(PO_4)_2$
3.0	Ap+CMP
4.0	Ap+CMP
$Ca_{10-x}Ni_x(PO_4)_6F_2$	
$x=0.0$	Ap
0.5	Ap
1.0	Ap+tr. $Ni_3(PO_4)_2$
1.5	Ap+$Ni_3(PO_4)_2$
2.0	Ap+$Ni_3(PO_4)_2$
3.0	Ap+$Ni_3(PO_4)_2$

[a] CMP = $Ca_3Mg_3(PO_4)_4$

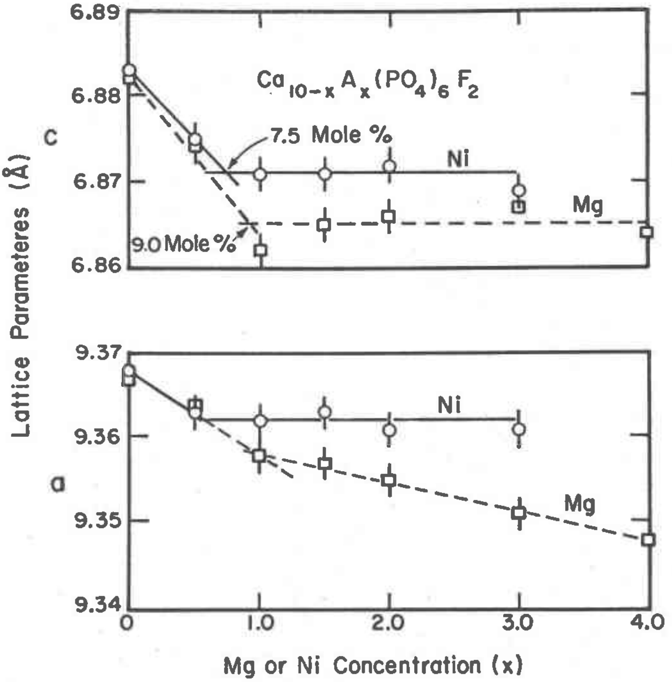

FIG. 3. Solid solution limits of Mg and Ni in $Ca_{10}(PO_4)_6F_2$.

when these limits were exceeded. Klement and Haselbeck (1965) found that about 30 percent of the calcium in chlorapatite could be replaced by Mg or Ni. This is about three times the solubility in fluorapatite, but the results are consistent with the observation that chlorapatite more readily accepts small cations into its structure than does fluorapatite.

Just as Mg and Ni can to some extent replace calcium, cations whose radii are outside the limits on R_p, can to some extent replace phosphorus in the apatite structure. Bauer (1959) and Ito (1968) have, for example, reported the existence of boron containing apatites such as $Ba_{10}(PO_4)_5(BO_4)V_2$, where V = fluoride vacancy, and $Y_{10}(SiO_4)_4(BO_4)_2O_2$.

Structurally Distorted Apatites. The X-ray diffraction patterns of most of the compounds in Table 1 could be rigorously indexed on the basis of a hexagonal unit cell, and yielded lattice parameters of the correct magnitude for apatite structures. The X-ray patterns of $Cd_{10}(PO_4)_6F_2$, $Ca_{10}(AsO_4)_6F_2$, and $Ca_{10}(VO_4)_6F_2$, however, could not be rigorously indexed on the basis of a hexagonal unit cell since certain lines such as (111), (211), (202), and (213) were split into several components. If mean d-values were used for the split lines (as in Table 5, for example), the patterns could be approximately indexed on the basis of a hexagonal unit cell. The "pseudohexagonal" lattice parameters of the three compounds seemed to be in line with the lattice parameters of other apatites (Table 3), and for this reason, the compounds were regarded as distorted apatites. An approximate boundary was placed in the fluorapatite structure field to distinguish the distorted apatites from the normal apatites.

Banks and Jaunarajs (1965) observed a structural distortion in $Ca_{10}(CrO_4)_6F_2$ which was apparently the same as that observed in the present study. Since the analogous compound, $Ca_{10}(CrO_4)_6(OH)_2$, was not distorted, the distortion in fluorochromate apatite was attributed to a slight difference in size between the fluoride and hydroxide ions. However, it seems more likely that the distortion occurs as a result of the unique location of the fluoride ions in the apatite structure. In fluorapatite the fluoride ions are located at the centers of triangular groups of Ca_{II} ions, but in chlorapatite and hydroxyapatite the "halide" ions are located above or below the planes defined by the triangular Ca_{II} groups. It is reasonable to assume that upon contracting to accommodate the smaller cations, the fluorapatite structure might undergo distortions which the chlor- and hydroxyapatite structures do not undergo. The failure to observe distorted chlorapatites near the lower limit of the structure field is further evidence that the distortion is related to the position or type of ion occupying the halide sites. Unfortunately, the structures of the distorted apatites are unknown, and it is not pos-

TABLE 5. POWDER PATTERN OF $Ca_{10}(VO_4)_6F_2$

I/I_0	d(obs.)Å	d(calc.)Å	*hkl*
11	4.832	4.838	110
6	4.189	4.190	200
17	4.002 (3.985)[a]	3.980	111
23	3.969		
6	3.609	3.596	201
70	3.506	3.507	002
6	3.232	3.236	102
25	3.167	3.168	210
62	2.903 (2.889)	2.887	211
100	2.876		
19	2.823	2.837	112
89	2.793	2.794	300
16	2.706 (2.692)	2.691	202
17	2.678		
8	2.589	2.595	301
24	2.325	2.325	310
9	2.289	2.287	221
5	2.219 (2.210)	2.206	311
10	2.200		
12	2.000 (1.991)	1.992	222
17	1.982		
5	1.925	1.923	320
14	1.891 (1.880)	1.882	213
20	1.870		
12	1.850	1.854	321
11	1.830	1.828	410
6	1.789	1.793	303
22	1.753	1.753	004

[a] Numbers in parentheses give mean values of split lines.

sible to give a detailed description of the distortion or of the factors operating to produce it.

Solid Solubility of $Ca_{10}(VO_4)_6F_2$ *in* $Ca_{10}(PO_4)_6F_2$

The solid solubility of $Ca_{10}(VO_4)_6F_2$ in $Ca_{10}(PO_4)_6F_2$ was studied in order to more conclusively establish the structural similarity of the two compounds. The compositions in Table 6 were prepared by heating stoichiometric mixtures of CaF_2 and $Ca_3(P, V)_2O_8$ in air at 950°C for one hour. The refractive indices and lattice parameters of the samples were measured and both sets of data (Fig. 4 and Table 6) indicated the existence of a continuous solid solution series between the end member compounds. This conclusion was supported by microscopic observations showing the samples to consist of only one phase. The distortion charac-

TABLE 6. SOLID SOLUBILITY OF $Ca_{10}(VO_4)_6F_2$ IN $Ca_{10}(PO_4)_6F_2$

$Ca_{10}(PO_4)_{6-x}(VO_4)_xF_2$	Phases Present	Refractive Index[a]
$x=0.0$	Ap	1.63 ± 0.01
1.0	Ap	—
2.0	Ap	1.71
3.0	Ap	1.75
4.0	Ap	1.79
5.0	Ap (distorted)	—
6.0	Ap (distorted)	1.87[b]

[a] Average refractive index, birefringence was low.

[b] Extrapolated value, a calculated value of 1.90 was obtained by applying the Gladstone-Dale rule (Jaffe, 1956).

teristic of pure calcium fluorovanadate did not appear in the solid solutions until the composition $Ca_{10}(PO_4)(VO_4)_5F_2$ was reached. The profiles of the (213), (222), and (202) diffraction peaks (Fig. 5) indicate that

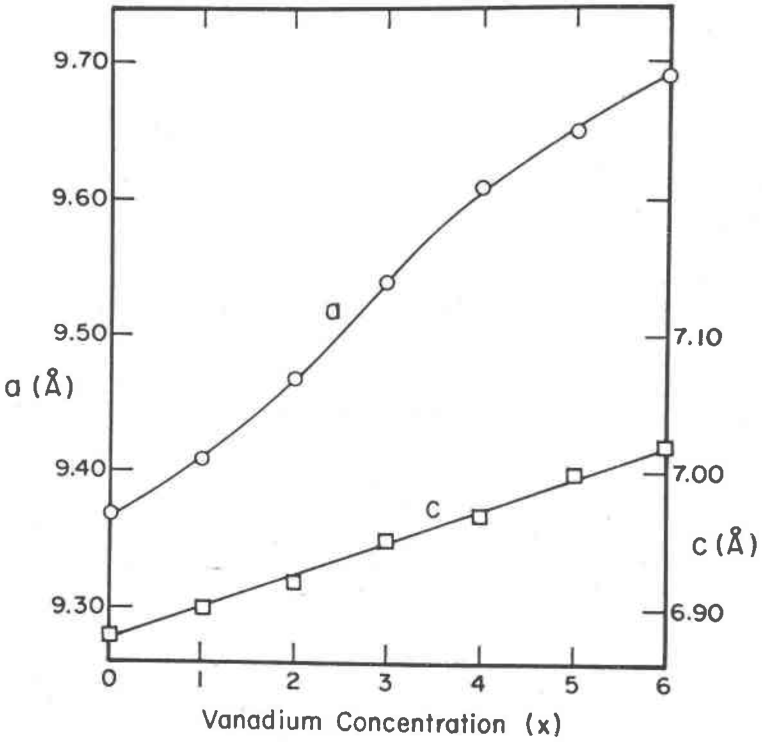

FIG. 4. Lattice parameters for the solid solutions $Ca_{10}(PO_4)_{6-x}(VO_4)_xF_2$.

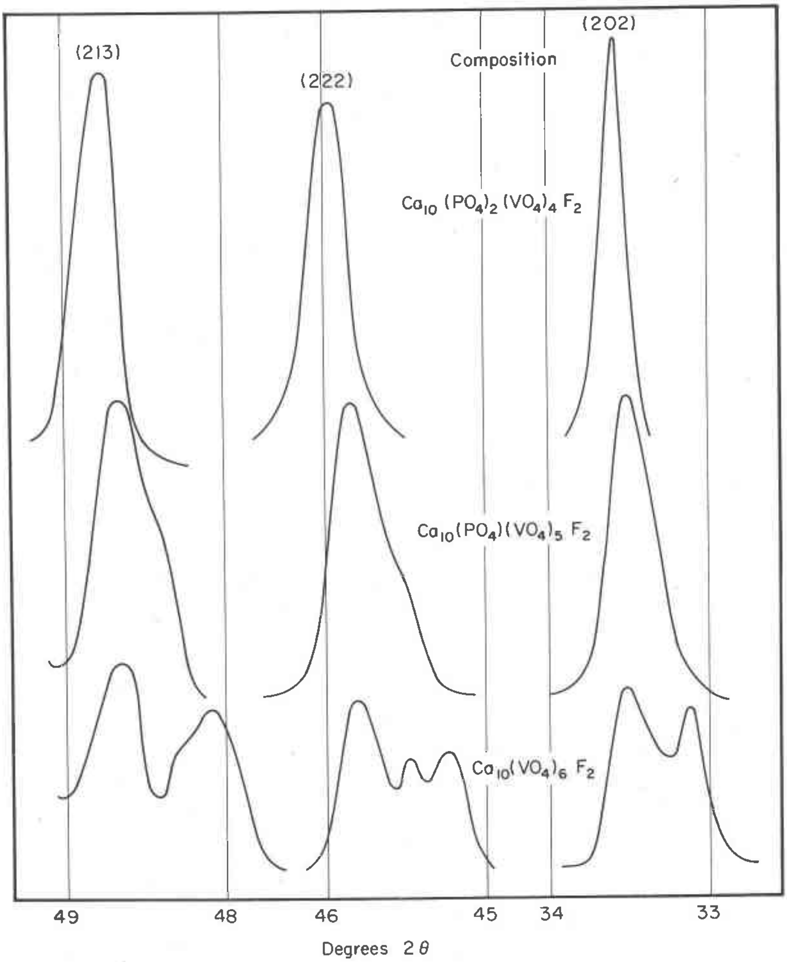

FIG. 5. X-ray line profiles of distorted vanadate apatites.

hexagonal apatites gradually become distorted as the composition nears that of $Ca_{10}(VO_4)_6F_2$. The absence of a miscibility gap in the $Ca_{10}(PO_4)_6F_2$—$Ca_{10}(VO_4)_6F_2$ system shows that the vanadate compound is structurally similar to $Ca_{10}(PO_4)_6F_2$ and justifies the viewpoint that $Cd_{10}(PO_4)_6F_2$, $Ca_{10}(AsO_4)_6F_2$, and $Ca_{10}(VO_4)_6F_2$ may be regarded as distorted apatites.

CONCLUSIONS

The determination of the structure fields has led to the assignment of size restrictions for ions *completely* replacing calcium or phosphorus in the fluor- and chlorapatite structures. Ions which fall outside these restrictions can be partially but not completely substituted for ions normally present in the structure. Thus, nickel and magnesium, which are outside the restrictions for complete replacement of calcium can occupy 7–9 percent of the calcium sites in fluorapatite. It was somewhat surprising to find that rather slight differences between the fluor- and chlorapatite structures were reflected in rather great differences in crystal chemical behavior. The differences noted were (a) the chlorapatites could tolerate smaller cations on the calcium sites than could the fluorapatites and (b) the fluorapatites tended to be distorted when the calcium sites were occupied by small cations whereas no such distortions were observed among the chlorapatites.

Although some progress has been made in determining the crystal chemical limitations on the apatites, our understanding of this group of materials is far from complete. For one thing, relatively little is known about the size restrictions for ions occupying the halide positions. Another problem is interpreting and evaluating reports of various kinds of "massively defective apatites." Two examples of such materials are $La_8(SiO_4)_6$ and $Pb_{10}(BO_3)_4(SiO_4)_2$ both of which have been reported to have the apatite structure (Cockbain and Smith, 1967 and Moore and Eitel, 1957). Additional structural and chemical information is needed before these materials can be unequivocally accepted as defective apatites.

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