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Rare-Earth-Substituted Chloro-Phosphate Apatites

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Compositions with the general formula $Ln_xM_{10-2x}Na_x(PO_4)_6Cl_2$ (Ln = Pr, Nd, Sm, Eu, Dy, Ho and Y; M = Ca, Sr, Ba, and Pb) have been prepared and studied by X-ray diffraction methods. The limited extent of rare earth substitution observed in chlorapatites in comparison to fluorapatites is attributed to the structural differences of the two systems.

Introduction

Compounds of apatite have been studied extensively because of their biological and industrial importance. The major inorganic component of bone and teeth is basically "impure" hydroxyapatite $Ca_5(PO_4)_3OH$; calcium fluorapatite $Ca_5(PO_4)_3F$ is found in phosphate deposits, and apatites activated with Sn, Sb, Mn, or rare earths are useful phosphor and laser materials (*1, 2*).

Both synthetic and naturally occurring apatites form in a large variety of compositions with the general formula $M_5(XO_4)_3Y$, where M can be Ca, Sr, Ba, Pb, or almost any divalent ion; X = P, As, V, Mn, Cr, or Si; and Y = F, Cl, or OH.

The crystal structure of apatites has been extensively studied (*1, 3–6*). Apatites crystallize in the hexagonal ($P6_3/m$) structure with two $M_5(XO_4)_3Y$ formula units per unit cell. In $M_{10}(PO_4)_6Y_2$ the 10 metal ions are distributed among two nonequivalent crystallographic sites. The lattice position of the chloride ion (Y = Cl) is significantly different from that of the fluoride (Y = F) and hydroxide (Y = OH) ions. $Ca_5(PO_4)_3Cl$ and $Ca_5(PO_4)_3OH$ also occur in a monoclinic (pseudo-hexagonal) form, which is very similar to the hexagonal structure involving only slight displacement of the atoms (*7–9*).

The presence of metal ions in two crystallographically different sites and differences in the position of the Y^- ions in the apatite structure becomes of special interest in the study of substituted apatites as the structural and physical properties of these materials are extremely sensitive to even small changes in composition (*3*). Partial or complete substitution of the alkali earths by Na and rare earth ions in apatites is of great biological interest (*10, 11*) because of the possible role of substitutions in dental caries and bone.

In a recent investigation of fluoro-phosphate apatites with the alkali earth cations partially substituted by rare earth and sodium ions Mayer *et al.* (*12*) found stable hexagonal apatite phases of up to $Ln_4M_2Na_4(PO_4)_6F_2$ composition in Ca and Sr apatites. A maximum composition of

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$Ln_{3.5}Ba_3Na_{3.5}(PO_4)_6F_2$ and $Ln_3Pb_4Na_3(PO_4)_6F_2$ single phases formed in the Ba and Pb apatites (*13, 14*). No phases of $Ln_5Na_5(PO_4)_6F_2$ could be prepared. On the basis of single-crystal data it was established that the substitution of the rare earth–sodium couple is statistically disordered in Ca- and Sr–F apatite but ordered in the Ba- and Pb–F apatites (*13, 14*).

In this work we have conducted a systematic investigation of the substitution of mixed rare earth sodium ions in the chloro-phosphate apatites $M_{10}(PO_4)_6Cl_2$ with M = Ca, Sr, Ba, and Pb to determine (a) the structural fields of substituted chloro-phosphate apatites and (b) the effect of the position of the Cl^- ion on the substitution process.

Experimental

For each sample preparation the rare earth ion was coupled with a monovalent sodium ion to replace two divalent metal ions making the general formula for substitution: $Ln_x^{3+}M_{10-2x}^{2+}Na_x(PO_4)_6Cl_2$. The rare earth ions used were: Pr, Nd, Sm, Eu, Dy, Ho, and Y.

All substitutions were deemed possible based on the structure field boundaries of the M^{2+} ion, $0.8\ \text{Å} \leq M^{2+} \leq 1.47\ \text{Å}$, as determined by Kreidler and Hummel (*15*). The "effective ionic radii" (*16*) for all substitutional rare earths fall within this limit, as shown in Table I. The starting materials, reagent-grade $LnPO_4$, $M_3(PO_4)_2$, MCl_2, and Na_3PO_4, were all mixed in stoichiometric amounts and ground thoroughly in a mortar, then transfered into either Pt or quartz tubes. Reaction temperatures varied according to the particular M series: Pb 600°C, Sr 1024°C, Ba and Ca 1100–1200°C. Due to the low melting point of $PbCl_2$ (501°C), the Pb apatite mixtures were heated to 450°C overnight, then the temperature was increased to 600°C. Compounds were usually reground and reheated to assure single-phase products. Reaction times varied from 19 hr to several days. Samples were weighed before and after heat treatment. No significant weight losses were observed. Reaction products were analyzed by X-ray powder diffraction patterns on a Norelco Electronic Diffractometer with nickel-filtered Cu$K\alpha$ radiation. Silicon powder was used as an internal standard, and X-ray lines were measured to $2\theta = 90°$. Single-phase products were assumed to form when no additional X-ray lines appeared, corresponding to any of the starting materials or other possible phases, besides the somewhat shifted parent $M_{10}(PO_4)_6Cl_2$ X-ray pattern. The hexagonal unit cell parameters were obtained by least-squares refinement of 12–15 strong X-ray diffraction peaks for each specimen.

TABLE I

EFFECTIVE IONIC RADII OF SUBSTITUENT AND SUBSTITUTING IONS IN 7 AND 9 COORDINATION

	r(Å)			r(Å)	
M^{2+}	7CN	9CN	*Ln*	7CN	9CN
Ca	1.06	1.18	Pr	~1.06	1.18
Sr	1.21	1.31	Nd	~1.04	1.16
Pb	1.23	1.35	Sm	1.02	1.13
Ba	1.38	1.47	Eu	1.01	1.12
			Dy	0.97	1.08
			Ho	~0.96	1.07
Na^+	1.12	1.24	Y	0.96	1.02

The densities of selected single-phase compounds were measured as a check on the assumed stoichiometry, using a 2-ml pycnometer bottle with CCl_4 as the liquid. Reagent-grade ZrO_2 powder was used as a standard to determine the accuracy of density measurements.

Results

The resulting lattice parameters calculated on the basis of a hexagonal unit cell are listed in Tables II–V.

TABLE II

LATTICE PARAMETERS OF RARE EARTH–LEAD–SODIUM CHLORAPATITES[a]

	a (Å)	c (Å)
$Pb_{10}(PO_4)_6Cl_2$	9.987	7.330
$PrPb_8Na(PO_4)_6Cl_2$	9.934	7.286
$Pr_2Pb_6Na_2(PO_4)_6Cl_2$	9.940	7.282
$Pr_3Pb_4Na_3(PO_4)_6Cl_2$	9.906	7.233
$Pr_4Pb_2Na_4(PO_4)_6Cl_2$[b]	9.86	7.15
$NdPb_8Na(PO_4)_6Cl_2$	9.938	7.298
$Nd_2Pb_6Na_2(PO_4)_6Cl_2$	9.934	7.292
$Nd_3Pb_4Na_3(PO_4)_6Cl_2$	9.884	7.259
$Nd_4Pb_2Na_4(PO_4)_6Cl_2$[b]	9.788	7.137
$SmPb_8Na(PO_4)_6Cl_2$	9.951	7.314
$Sm_2Pb_6Na_2(PO_4)_6Cl_2$	9.918	7.255
$Sm_3Pb_4Na_3(PO_4)_6Cl_2$[b]	9.821	7.162
$EuPb_8Na(PO_4)_6Cl_2$	9.928	7.276
$Eu_2Pb_6Na_2(PO_4)_6Cl_2$	9.923	7.269
$Eu_3Pb_4Na_3(PO_4)_6Cl_2$[b]	9.811	7.164
$DyPb_8Na(PO_4)_6Cl_2$	9.960	7.316
$Dy_2Pb_6Na_2(PO_4)_6Cl_2$	9.925	7.272
$Dy_3Pb_4Na_3(PO_4)_6Cl_2$	9.868	7.195
$HoPb_8Na(PO_4)_6Cl_2$	9.953	7.313
$Ho_2Pb_6Na_2(PO_4)_6Cl_2$	9.922	7.286
$Ho_3Pb_4Na_3(PO_4)_6Cl_2$[b]	9.845	7.200
$YPb_8Na(PO_4)_6Cl_2$	9.930	7.292
$Y_2Pb_6Na_2(PO_4)_6Cl_2$	9.860	7.231
$Y_3Pb_4Na_3(PO_4)_6Cl_2$	9.821	7.182
$Y_4Pb_2Na_4(PO_4)_6Cl_2$	9.742	7.103

[a] Standard deviations in lattice parameters are all about ±0.002 Å except for Pr with $x = 4$.

[b] Strongest lines of $LnPO_4$ are present in addition to apatite pattern.

The most extensive substitution occurred in the lead series where some of the rare earth ions attempted, substituted up to $x = 4$ in the $Ln_xPb_{10-2x}Na_x(PO_4)_6Cl_2$ composition. Most of the compounds in the Ba and Sr phases accommodated a maximum of two rare earth ions. In the Ca series only $x = 1$ rare earth substitution produced single phases and in most cases weak lines of the rare earth starting materials could be seen in the apatite X-ray pattern indicating only partial substitution. To account for the extra X-ray lines observed, attempts were made to index the powder patterns on the basis of a monoclinic unit cell with $b = 2a$ and $\gamma = 120°$ in analogy with $Ca_5(PO_4)_3Cl$ (*7*) without success. In general the limit of rare earth ion substitution in a particular apatite series was determined by the appearance of the strongest X-ray lines of the rare earth phosphates in addition to the apatite pattern. Footnoted compounds, in Tables II–V indicate partially substituted phases, in which the number of rare earth ions shown is more than the structure can apparently accommodate (e.g., $Ln_4 \simeq Ln_{3<x<4}$). Apatite samples with the composition $Ln_5Na_5(PO_4)_6Cl_2$, could not be prepared.

In a given series of the same alkali earth ions the lattice parameters *a* and *c* decrease with increasing substitution of the rare

TABLE III

LATTICE PARAMETERS OF RARE EARTH–STRONTIUM–SODIUM CHLORAPATITES[a]

	a (Å)	c (Å)
$Sr_{10}(PO_4)_6Cl_2$	9.950	7.175
$PrSr_8Na(PO_4)_6Cl_2$	9.843	7.169
$Pr_2Sr_6Na_2(PO_4)_6Cl_2$[b]	9.822	7.150
$NdSr_8Na(PO_4)_6Cl_2$[b]	9.833	7.163
$SmSr_8Na(PO_4)_6Cl_2$	9.835	7.165
$Sm_2Sr_6Na_2(PO_4)_6Cl_2$	9.741	7.100
$EuSr_8Na(PO_4)_6Cl_2$	9.833	7.151
$Eu_2Sr_6Na_2(PO_4)_6Cl_2$	9.753	7.114
$DySr_8Na(PO_4)_6Cl_2$	9.821	7.150
$Dy_2Sr_6Na_2(PO_4)_6Cl_2$	9.769	7.140
$HoSr_8Na(PO_4)_6Cl_2$[b]	9.835	7.165
$YSr_8Na(PO_4)_6Cl_2$	9.817	7.150
$Y_2Sr_6Na_2(PO_4)_6Cl_2$	9.785	7.139

[a] Standard deviations in the lattice parameters are all about ±0.002 Å.

[b] Strongest lines of $LnPO_4$ are present in addition to apatite pattern.

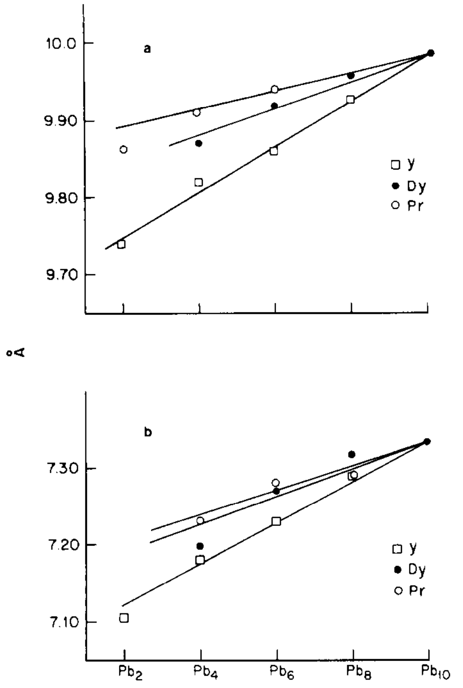

FIG. 1. (a) Lattice parameter *a* vs lead content in the $Ln_xPb_{10-2x}Na_x(PO_4)_6Cl_2$ system. (b) Lattice parameter *c* vs lead content in the $Ln_xPb_{10-2x}Na_x(PO_4)_6Cl_2$ system.

earth alkali metal couple, as shown in Fig. 1. This is to be expected since the effective cation radii of the divalent ions (M^{2+}) are larger than the Ln^{3+}–Na^+ couple (Table I). In general, the lattice parameters of the different rare earth phases in a given alkali earth metal series decrease in order of decreasing radius of the rare earth ion (this trend is particularly well behaved in the $Ln_4Pb_2Na_4(PO_4)_6Cl_2$ compounds).

Densities measured for a selected number of apatites (Table VI) show fairly good agreement between the calculated and measured values, confirming the indicated stoichiometries of the prepared phases.

Discussion

The results indicate that substantial rare earth–alkali (Ln^{3+}–Na^+) coupled substitutions occur in chloro-phosphate apatites with the general formula $Ln_xM_{10-2x}Na_x(PO_4)_6Cl_2$. The powder diffraction patterns of all the compounds were similar, characteristic of the hexagonal apatite structure.

Similar results were obtained for substituted fluoro-phosphate apatites (*12*), $Ln_xM_{10-2x}Na_x(PO_4)_6F_2$, but there are significant differences in the extent of substitution between rare-earth-substituted F and Cl apatites. In the case of $Ln_xPb_{10-2x}Na_x(PO_4)_6F_2$ only $x \leq 2$ rare-earth substitution produced single phases (*14*). In contrast, the Pb–Cl apatite can accommodate up to $x \sim 4$ rare earth ions, as shown in Table II. Mayer *et al.* (*14*) report on similar Pb–Cl preparations but with only $2x \leq 2$ compositions. The 850–900°C temperature of preparation used by them may have re-

TABLE IV

LATTICE PARAMETERS OF RARE EARTH–BARIUM–SODIUM CHLORAPATITES[a]

	a (Å)	*c* (Å)
$Ba_{10}(PO_4)_6Cl_2$	10.26	7.64
$PrBa_8Na(PO_4)_6Cl_2$	10.236	7.629
$NdBa_8Na(PO_4)_6Cl_2$	10.225	7.627
$SmBa_8Na(PO_4)_6Cl_2$	10.183	7.590
$Sm_2Ba_6Na_2(PO_4)_6Cl_2$	10.105	7.517
$Sm_3Ba_4Na_3(PO_4)_6Cl_2$[b]	10.066	7.494
$EuBa_8Na(PO_4)_6Cl_2$	10.203	7.603
$Eu_2Ba_6Na_2(PO_4)_6Cl_2$	10.115	7.566
$DyBa_8Na(PO_4)_6Cl_2$	10.189	7.589
$Dy_2Ba_6Na_2(PO_4)_6Cl_2$	10.118	7.539
$Dy_3Ba_4Na_3(PO_4)_6Cl_2$[b]	10.068	7.512
$HoBa_8Na(PO_4)_6Cl_2$	10.230	7.626
$Ho_2Ba_6Na_2(PO_4)_6Cl_2$	10.144	7.539
$YBa_8Na(PO_4)_6Cl_2$	10.161	7.588
$Y_2Ba_6Na_2(PO_4)_6Cl_2$	10.103	7.527

[a] Standard deviations in the lattice parameters are all about ±0.002 Å.

[b] Strongest lines of $LnPO_4$ are present in addition to apatite pattern.

TABLE V

Lattice Parameters of Rare Earth–Calcium–Sodium Chlorapatites[a]

	a (Å)	c (Å)
$Ca_{10}(PO_4)_6Cl_2$	9.642	6.764
$PrCa_8Na(PO_4)_6Cl_2$	9.558	6.851
$Pr_2Ca_6Na_2(PO_4)_6Cl_2$	9.507	6.862
$NdCa_8Na(PO_4)_6Cl_2$	9.581	6.825
$Nd_2Ca_6Na_2(PO_4)_6Cl_2$[b]	9.53	6.82
$EuCa_8Na(PO_4)_6Cl_2$	9.555	6.802
$Eu_2Ca_6Na_2(PO_4)_6Cl_2$	9.475	6.853
$SmCa_8Na(PO_4)_6Cl_2$	9.546	6.797
$Sm_2Ca_6Na_2(PO_4)_6Cl_2$[b]	9.47	6.84
$DyCa_8Na(PO_4)_6Cl_2$	9.498	6.843
$YCa_8Na(PO_4)_6Cl_2$	9.572	6.797

[a] Standard deviation in lattice parameters are all about ±0.002Å except for Nd^{2+} Sm^{2+} with $x = 2$.

[b] Strongest lines of $NdPO_4$ and $SmPO_4$ respectively are present besides apatite pattern.

sulted in chloride-deficient phases. This is also suggested by the lattice parameter values they report, which are smaller than the lattice parameters we have found for analogous phases.

In the Sr–Cl apatites compositions with $x \leq 2$ occurred in some cases (Table III) compared to $x \leq 3$ in the Sr–F apatites (*12*). The Ba–F apatite phases with rare earth ions smaller than Sm are unstable $x = 3.5$ is possible with the larger rare earth ions. In Ba–Cl apatite, all rare earth ions investigated substitute but up to $x \leq 3$ only (Table IV) yield single-phase compounds. The fluorapatite phases $Ln_4Ca_2Na_4(PO_4)_6F_2$ (*12*) are stable for most rare earth ions studied. Single-phase compositions with only $LnCa_8Na(PO_4)_6Cl_2$ (i.e., $x = 1$) are possible in the analogous chlorapatites (Table V). Thus a greater amount of rare-earth alkali metal substitutions are tolerated by Ca, Sr, and Ba fluorapatite than the analogous chlorapatite systems. In contrast, in the Pb apatites the extent of rare earth–alkali metal substitution appears to be larger in the Cl than the F apatite.

In hexagonal $M_{10}(PO_4)_6Y_2$ the 10 M ions occupy two crystallographically nonequivalent positions; four M_I ions at the $4f$ site (in $6_3/m$) along a threefold axis, with ninefold coordination, and six M_{II} ions in the $6h$ site, around a sixfold screw axis, with sevenfold coordination. The six phosphorus are located in crystallographically equivalent sites. When Y^- is fluoride, it is situated at the center of a triangle of M_{II} ions at $z = \frac{1}{4}, \frac{3}{4}$. If Y^- is OH^- the oxygens are slightly displaced from the mirror plane of M_{II} triangles along z. The larger Cl^- ions are located at approximately $z = 0, \frac{1}{2}$ between planes of M_{II} triangles (*5*).

The basic difference between the structures of fluoro- and chloro-phosphate apatites is in the relative position of the F^- and Cl^- ions. As a result of the differences in ionic interactions the edge length of the Ca_{II} triangle is 3.975 and 4.290 Å in Ca–F apatite and Ca–Cl apatite, respectively. This suggests that larger ions might substitute more easily in the triangular site in Cl than in F apatite. The smaller, highly charged rare earth ions experience less repulsion (Ln^{3+}–Ln^{3+}, Ln^{3+}–M^{2+}, and Ln^{3+}–Na^+ interactions) in F apatite in the M_I site, (where the M_I ions are arranged in a column at $z = 0, \frac{1}{2}$) as there is a small decrease in the c parameter in going from fluorapatite to

TABLE VI

Densities of Selected Substituted Apatites[a]

Compound	ρ_{calc}	ρ_{exp}
$PrPb_8Na(PO_4)_6Cl_2$	6.55	6.50
$Pr_2Pb_6Na_2(PO_4)_6Cl_2$	5.91	6.00
$EuSr_8Na(PO_4)_6Cl_2$	4.19	4.12
$Sm_2Sr_6Na_2(PO_4)_6Cl_2$	4.31	4.25
$SmPb_8Na(PO_4)_6Cl_2$	6.54	6.39
$Y_3Pb_4Na_3(PO_4)_6Cl_2$	4.96	4.98
$DySr_8Na(PO_4)_6Cl_2$	4.24	4.25
$YBa_8Na(PO_4)_6Cl_2$	4.53	4.60

[a] Standard deviation in ρ_{exp} is ±0.05.

chlorapatite (a = 9.367, c = 6.884 in F apatite (*17*) and a = 9.642, c = 6.764 in Cl apatite (*17*)). Thus one possible difference in the substitution of cations in F or Cl apatites may be the different sites where the substituent enters. Mathew *et al.* (*12*) found that in $Nd_3Ba_4Na_3(PO_4)_6F_2$ the smaller Nd–Na ions ordered in the column sites presumably, because of the increased coordination (9 vs 7) at that site. In chlorapatites at least *Ln* might be at the triangular sites. This is consistent with the larger cation–cation separation of the triangular sites and smaller cation–cation separation at the column sites (associated with a decrease in c).

In *Ln*–Na-substituted Ca apatites the substituent and substituting cation sizes are similar. The very limited rare earth substitution observed in Ca–Cl apatite vs that in Ca–F apatite is indicative of the large differences in cation–anion interactions in the two compounds.

The unique behavior of Pb apatites may be due to polarization effects. The Pb bonds are more covalent and Pb is more polarizing than the alkali earths. In Pb–Cl apatite the cations may be statistically distributed at each of the cation sites of the apatite structure allowing the greater amount of rare earth substitution.

Results of this work indicate large differences in the nature of cation substitution in Cl vs F apatites, which are attributed primarily to the structurally different locations of F^- and Cl^- anions. Comparison of the two systems can only be made in a limited manner without more detailed structural information on substituted apatites.

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