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The Crystal Structures of some Natural and Synthetic Apatite-Like Substances.

By

S. B. Hendricks, M. E. Jefferson and V. M. Mosley in Washington.

(With 2 figures and 1 plate.)

We recently have had occasion, while investigating the compositions of some western phosphate rocks¹⁾ to make a number of observations on the unusual group of compounds structurally similar to apatite. The work was simplified by the determination of the crystal structure of apatite²⁾.

Apatite, $Ca_{10}F_2(PO_4)_6$, later referred to as fluor-apatite, in order to avoid confusion, chlor-apatite, $Ca_{10}Cl_2(PO_4)_6$, pyromorphite, $Pb_{10}Cl_2(PO_4)_6$, mimetite, $Pb_{10}Cl_2(AsO_4)_6$, and vanadinite, $Pb_{10}Cl_2(VO_4)_6$, all have atomic arrangements derivable from space group $C_{6h}^2 - C_{6h}/m$. It is probable that the mineral svabite and the synthetic substances $Ca_{10}Br_2(PO_4)_6$, $Ca_{10}I_2(VO_4)_6$, $Cd_{10}Cl_2(VO_4)_6$, etc., are isomorphous with point group $C_{6h} - 6/m$. The results of published chemical analyses indicate that mimetite, pyromorphite, and vanadinite, from extensive if not complete series of solid solutions, of which the described minerals polysphaerite, kampylite, hedyphane, and endlichite are representative members. Chlor- and fluor-apatite³⁾, as well as fluor- and hydroxy-apatite (4) form complete series of solid solutions.

The "apatite group" of minerals is usually considered to include, in addition to the compounds mentioned above, various poorly defined substances some of which occur as components of phosphate rock. The exact compositions of these substances have been obscured since they

1) Hendricks, Hill, Jacob and Jefferson, Ind. eng. Chem. (in press).

2) St. N'aray-Szabó, Z. Krist. 75, 387, 1930; M. Mehmél, Z. Krist. 75, 323, 1930.

3) R. Nacken, Ctbl. Min. 1912, 545.

usually occur as submicroscopic crystals admixed with difficulty separable impurities. Some of the described minerals are¹⁾:

Voelkerite	$Ca_{10}O(PO_4)_6$
Wilkeite	$3 Ca_3(PO_4)_2 \cdot CaCO_3 \cdot 3 Ca_3((SiO_4)(SO_4)) \cdot CaO$
Dahlite	$3 Ca_3(PO_4)_2 \cdot 2 CaCO_3 \cdot H_2O$
Podolite	$3 Ca_3(PO_4)_2 \cdot CaCO_3$
Staffelite	$3 Ca_3(PO_4)_2 \cdot CaCO_3 \cdot CaF_2 \cdot H_2O$, also known as Francolite, Merrillite
Collophanite	$(3 Ca_3(PO_4)_2)_x \cdot (2 CaF_2CO_3)_y \cdot 2 H_2O$, also known as Pyroclaspite, Nauruite, Pyroguanite, Sombrierite, Monite, Fluo-collophanite, Dehrnite, Lewistonite.

The compositions of these minerals and of some artificial products supports the concept that fluorine in fluor-apatite can isomorphously be replaced by carbonate, sulfate, silicate, or hydroxy groups and by oxygen, chlorine, bromine, or iodine ions.

A hydrate of tricalcium phosphate, $Ca_3(PO_4)_2 \cdot xH_2O$ is known to form a complete series of solid solutions with hydroxy-apatite²⁾. The results of numerous biological experiments indicate that the inorganic compound of bone proximates the composition, $Ca_{10}CO_3(PO_4)_6 \cdot xH_2O$, and that it forms solid solutions with hydroxy apatite. The atomic arrangement of $Ca_3(PO_4)_2 \cdot xH_2O$ and $Ca_{10}CO_3(PO_4)_6 \cdot xH_2O$, and of many of the compounds mentioned above, cannot be derived from space group $C6_3/m$, and indeed it is improbable that they are isomorphous with point group $6/m$. The powder diffraction patterns of the various calcium compounds, nevertheless, are closely similar both in the intensities and the positions of the interference maxima.

The compounds $Ca_{10}O(PO_4)_6$, $Ca_{10}CO_3(PO_4)_6 \cdot xH_2O$, $Ca_{10}(OH)_2(PO_4)_6$, $Ca_3(PO_4)_2 \cdot xH_2O$, $Ca_{10}Cl_2(PO_4)_6$, and $Ca_{10}F_2(PO_4)_6$, the probable end members of many of the series of solid solutions, can either be prepared synthetically as pure compounds or obtained as macroscopically crystalline minerals. Our observations upon the structural characteristics of these compounds and of the "apatite-group" of minerals are given below.

Sources of the Materials.

We are indebted to Dr. W. F. Foshag of the United States National Museum for specimens of the various minerals examined. Mr. K. D. Jacob

1) Hintze, »Handbuch der Mineralogie«, I pt. 4, Leipzig 1924.

2) Bassett, J. chem. Soc. London III, 620. 1917; Lorah, Tartar and Wood, J. Am. chem. Soc. 51, 1097. 1929.

and Mr. W. L. Hill kindly prepared and analyzed the synthetic materials described below.

Chlor-*x*-Apatite. Bamle Mines, Kragerö, Norway.

Fluor-Apatite. Quebec Province, Canada.

Vanadinite. U. S. Nat. Museum No. 48793, Yuma Co., Arizona.

Mimetite. U. S. Nat. Museum No. 95811, Velardena Mine, Santa Eulalia District, Chihuahua, Mexico.

Pyromorphite. U. S. Nat. Museum No. 48590, Hunter Min. Dist., Shoshone Co., Idaho.

Table I.

Analyses of Some Apatite-Like Substances.

Type of Material Con- stituent	Fluor- Apatite %	Chlor- X- Apatite %	Mime- tite ¹ %	Vana- dinite ¹ %	Steamed Bone %	Naphtha Extd. Bone %	Ca ₃ (PO ₄) ₂ · xH ₂ O %	Hy- droxy- Apatite %
CaO	52.40	52.97	1.27	0.26	50.96	34.40	47.76	49.99
MgO	0.46	0.29			0.67	0.32		0.11
P ₂ O ₅	40.30	40.50	1.62	0.00	38.47	26.13	40.48	38.68
As ₂ O ₅			21.72	3.17				
V ₂ O ₅				16.20				
F	3.26	0.17						
C ₁	1.16	4.13						
CO ₂	1.51	0.00			1.50	3.09		0.12
Na ₂ O	0.00	0.22			0.69	0.54	0.56	1.01
K ₂ O		0.10						
SiO ₂	3.08	1.16			0.00	0.09	0.00	0.54
Fe ₂ O ₃	0.60	0.18			0.13	0.09		0.13
(Total Fe)								
Ignition loss at 1000° C	1.95	0.48			8.30	37.61	10.97	8.56
Total	103.72	101.18			100.72	102.18	99.77	99.14
CO ₂ , oxy- gen equiv. of F and Cl	2.92	0.98			1.50	3.09	0.00	0.12
Total cor- rected	100.20	100.80			99.22	99.09	99.77	99.02

1) We are indebted to Miss Ellen Z. Kibbe for the partial analyses of mimetite and vanadinite.

Table II.

Dimensions of the Units of Structure and Densities of Some Apatite-Like Substances

Substance	Formula	<i>a</i>	<i>c</i>	<i>a</i> : <i>c</i> obs.	<i>a</i> : <i>c</i> calc.	<i>ρ</i> abs.	<i>ρ</i> calc.	Vol. calc. cm ³	<i>M. W.</i>
Apatite	$Ca_{10}F_2(PO_4)_6$	$9.37 \pm .01$	$6.88 \pm .01$	0.7346	0.734	3.19	3.18	317	1008.9
Chlor-X-Apatite	$Ca_{10}(Cl \cdot X)_2(PO_4)_6$	$9.52 \pm .03$	$6.85 \pm .03$	—	0.719	3.25	3.20	326	1041.8
Pyromorphite	$Pb_{10}Cl_2(PO_4)_6$	$9.95 \pm .02$	$7.31 \pm .02$	0.7293—0.7354	0.735	7.04 ± 0.04	7.14	380	2713.1
Mimetite	$Pb_{10}Cl_2(AsO_4)_6$	$10.24 \pm .02$	$7.43 \pm .02$	0.7224—0.7315	0.725	$7.23 - 7.24$	7.19	414	2976.7
Vanadinite	$Pb_{10}Cl_2(VO_4)_6$	$10.31 \pm .02$	$7.34 \pm .02$	0.7122	0.712	6.86	6.92	409	2832.6
Hydroxy-Apatite	$Ca_{10}(OH)_2(PO_4)_6$	$9.40 \pm .03$	$6.93 \pm .03$	—	0.737	3.08	3.13	321	1004.9
Tricalcium Phosphate hydrate	$Ca_9(H_2O)_2(PO_4)_6$	$9.25 \pm .03$	$6.88 \pm .03$	—	0.744	3.01	3.13	309	966.8
Oxy-Apatite	$Ca_{10}O(PO_4)_6$	$9.38 \pm .03$	$6.93 \pm .03$	—	0.739	$3.17 - 3.20$	3.09	320	986.9
Bone (Naphtha Extracted)	$Ca_{10}CO_3(H_2O)(PO_4)_6$	$9.27 \pm .03$	$6.95 \pm .03$	—	0.750	3.25	3.35	313	1048.9
or	$Ca_{10}CO_3(PO_4)_6$						3.29		1030.9

Bone. Diffraction photographs were obtained from commercial naphtha-extracted bone and from naphtha-extracted bone that had been steamed under approximately 40 lb. pressure for about 225 hours.

Tricalcium Phosphate Hydrate. A solution of pure trisodium phosphate was slowly added to a solution containing an excess of calcium nitrate. The precipitate was washed with a saturated solution of tricalcium phosphate, until the filtrate was free of nitrates. The salt was then dried at 50° C.

Hydroxy-Apatite. This compound was prepared by hydrolyzing tricalcium phosphate with neutral ammonium citrate solution¹).

Oxy-Apatite was made by igniting hydroxy-apatite or bone to constant weight at 900° C.

Chlor-Apatite. Calcium chloride and anhydrous tricalcium phosphate, in proportions corresponding to the formula $Ca_{10}Cl_2(PO_4)_6$, were fused together in a platinum crucible²). Dr. F. C. Kracek of the Geophysical Laboratory, Carnegie Institution of Washington, kindly carried out the fusion in one of his furnaces.

Analyses of some of the compounds described above are listed in Table I. It was not convenient to make complete analyses of mimetite and vanadinite. In these cases determinations were made for those constituents the replacement of which would cause the greatest changes in the diffraction patterns. The composition of the pyromorphite specimen was assumed to approximate that of the pure compound $Pb_{10}Cl_2(PO_4)_6$.

Lattice Dimensions and Densities.

Dimensions of units of structure and densities for the various compounds examined are listed in Table II. The listed values of a and c for apatite are those given by Náráy-Szabó³). The lattice dimensions of pyromorphite, mimetite, and vanadinite, were determined from spacing measurements for ($h00$) and ($00l$) on single crystals against ($00l$) of βAl_2O_3 as reference. The accuracy of the measurements was considerably enhanced by the high absorption coefficients of the various crystals for the CuK radiation used. The value of c for mimetite was also determined from ($00l$) reflections of high orders on the Weissenberg photographs. In these cases it is estimated that the probable error does not exceed ± 0.02 Å. The lattice dimensions of the other com-

1) Jacob, Hill and Rader, Ind. eng. Chem. 22, 1385. 1930.

2) R. Nacken, loc. cit.

3) Náráy-Szabó, loc. cit.

pounds examined were each determined from powder photographs with $NaCl$ present as a reference substance, CuK radiation being used. The large dimensions of the lattice vitiated somewhat the accuracy of the measurements; we give as an outside limit $\pm 0.03 \text{ \AA}$.

The densities of pyromorphite, mimetite, and vanadinite, are those listed by Leitz¹⁾ as are also the observed values of the axial ratios for these substances. The densities of the other substances examined were determined by a modified Retgers suspension method. Finely divided samples were placed in methylene iodide, shaken well, and then boiled at room temperature for several minutes in order partially to expel occluded air. The mixtures were then centrifuged and acetone added until a considerable part of the solids remained suspended after prolonged centrifuging. Such a method obviates the usual sources of error but for synthetic compounds of very small particle size the determined values of the densities are somewhat low, probably on account of occluded air.

The Structure of Mimetite, Pyromorphite and Vanadinite.

The structure of fluor-apatite, as determined by N  ray-Szab  ²⁾ is summarized below.

Atomic Positions

$$\begin{aligned}
 &2 F (a) 00\frac{1}{4}, 00\frac{3}{4} \\
 &4 Ca_I (f) \frac{1}{3}, \frac{2}{3}, u; \frac{2}{3}, \frac{1}{3}, \bar{u}; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-u; \frac{2}{3}, \frac{1}{3}, u+\frac{1}{2}. \\
 &6 Ca_{II}, 6 P, 6 O_I, 6 O_{II} (h), uv\frac{1}{4}, \bar{u}\bar{v}\frac{3}{4}; \bar{v}, u-v, \frac{1}{4} \\
 &\quad v-u, \bar{u}\frac{1}{4}; v, v-u, \frac{3}{4}; u-v, u, \frac{3}{4} \\
 &12 O_{III} (i) xyz; \bar{x}\bar{y}\bar{z}; x-y, x, \bar{z}; \bar{y}, x-y, z \\
 &\quad x, y, \frac{1}{2}-z; \bar{x}, \bar{y}, \frac{1}{2}+z; x-y, x, \frac{1}{2}+z; \bar{y}, z-y, \frac{1}{2}-z \\
 &\quad y, y-x, \frac{1}{2}+z; y-x, \bar{x}, z \\
 &\quad y, y-x, \bar{z}; y-x, \bar{x}, \frac{1}{2}-z
 \end{aligned}$$

Parameter Values

	θ_1	θ_2	θ_3
2 F	0°	0°	90°
4 Ca _I	120	240	0
6 Ca _{II}	90	0	90
6 P	150	130	90
6 O _I	120	180	90
6 O _{II}	216	168	90
12 O _{III}	120	90	22½

1) Leitz, Z. Krist. 77, 437. 1931.

2) St. N  ray-Szab  , loc. cit.

In the structure of fluor-apatite suggested by Mehmél¹⁾ the fluorine atoms are $\frac{1}{4}c$ from the reflection planes; positions; 000, 00 $\frac{1}{2}$. Such an arrangement, if packing is to obtain, would require parameter values differing considerably from those given by Náray-Szabó. The choice between the two structures for fluor-apatite is difficult to make, even on the basis of absolute intensity measurements. For pyromorphite, however, it is a relatively simple matter to settle this question.

The predominant effect of the lead ions upon the intensities of reflections from pyromorphite allow their ready allocation in the unit of

Table III.

Weissenberg Photographic Data for Pyromorphite with A/F_{Pb} Values.

(a) (004) Axis of Rotation, Equatorial Zone. *CuK* Radiation.

	<i>h</i> 00		<i>h</i> 10		<i>h</i> 20		<i>h</i> 30		<i>h</i> 40		<i>h</i> 50	
	Int.	A/F_{Pb}	Int.	A/F_{Pb}	Int.	A/F_{Pb}	Int.	A/F_{Pb}	Int.	A/F_{Pb}	Int.	A/F_{Pb}
1 <i>k</i> 0	0	0	20	2								
2 <i>k</i> 0	40	—4		2) ²⁾	40	2						
3 <i>k</i> 0	100	6	0	0		2) ²⁾	10	2				
4 <i>k</i> 0	35	4	80	6	40	—4	0	0	100	10		
5 <i>k</i> 0	0	0	15	—4	10	2	0	0	0	0		
6 <i>k</i> 0	5	2	15	—4	15	—4	3	2	15	—4	5	2
7 <i>k</i> 0	0	0	30	6	15	—4	10	—4	30	6	20	—4
8 <i>k</i> 0	15	4	0	0	3	2	3	0 ³⁾	15	4		
9 <i>k</i> 0	20	6	15	—4	20	—4	40	6				
10 <i>k</i> 0	15	—4	5	2								
11 <i>k</i> 0	0	0										
12 <i>k</i> 0	100	10										

structure. The parameter values for the lead ions were determined from Weissenberg photographic data listed in part in Table III. Since the intensities of (*hik*0) and (*kīh*0) were approximately the same, data for (*hik*0) only are listed. The maximum differences in relative intensities noted for planes of this class were

$$\begin{array}{ll} (6, 4, \bar{1}0, 0) & 15; \quad (7, 3, \bar{1}0, 0) & 10 \\ (10, \bar{6}, \bar{4}, 0) & 20; \quad (10, \bar{7}, \bar{3}, 0) & 8 \end{array}$$

1) M. Mehmél, loc. cit.

2) Observations on (240) and (320) are not included since, for instrumental reasons, they were missing from the photograph used in estimation of the intensities of reflections.

3) (11, $\bar{3}$, 0), Int. 0.

The intensities of reflections are to be explained only if the lead ions are at $4(f)$ and $6(h)$ above with $(6h)\theta_1 = 90^\circ$, $(6h)\theta_2 = 0^\circ$, and $(4f)\theta_3 = 0^\circ$. It is improbable that these values are in error by as much as 3° . The differences in intensities between planes $(hik0)$ and $(kiz0)$ can be explained as arising from unsymmetrical contributions of the lighter atoms in the structure. However, an analysis of the intensity differences of this type indicates that they are best to be explained if θ_2 ($6h$ for Pb) differs from zero by $\pm 1^\circ$ — 2° .

Three lead ions on the reflection planes approach to within $2.49 \text{ \AA}$ of the hexagonal screw axes, a value markedly smaller than $3.02 \text{ \AA}$, the sum of the ionic radii of lead ($1.21 \text{ \AA}$) and chlorine ($1.81 \text{ \AA}$)¹. It

Table IIIa.

(b) (100) Axis of Rotation, Equatorial Zone, CuK Radiation.

	00		11		22		33		44	
	Int.	A/F_{Pb}	Int.	A/F_{Pb}	Int.	A/F_{Pb}	Int.	A/F_{Pb}	Int.	A/F_{Pb}
$hh0$			20	2	10	2	10	2	100	10
$hh1$					0	0	20	4	0	0
$hh2$	10	— 2					30	6	5	— 2
$hh3$							15	— 4	0	0
$hh4$	100	10					1	2	80	5
$hh6$	3	— 2								
$hh8$	60	10								
$hh10$	2	— 2								

is therefore most probable that in pyromorphite the chlorine atoms are at $\frac{1}{4}c$ on each side of the reflection planes. The chlorine-lead distance is $3.09 \text{ \AA}$, in agreement with the calculated value.

If it is assumed that the configuration of the phosphate groups are the same as found by J. West²) in KH_2PO_4 and that the $Pb-O$ and $Cl-O$ distances are the same as the sum of the appropriate ionic radii, $2.56 \text{ \AA}$ and $3.16 \text{ \AA}$, respectively, there are several possible atomic arrangements compatible with the arrangement of the lead and chlorine ions determined above. Since the arrangement of the lead and chlorine ions satisfactorily accounts for the intensities of reflection, it is not possible to differentiate among the several possible arrangements for the phosphate groups on the basis of such data alone.

1) The ionic radii used throughout this paper are those listed by L. Pauling, J. Am. chem. Soc. 49, 765, 1927.

2) J. West, Z. Krist. 74, 306, 1930.

The parameter values in Table IV are for phosphate groups arranged in the manner suggested by Mehmél for apatite. The values of A/F_{Pb} for $(hk0)$ and (hhl) are in part given in Table III, together with the observed relative intensities of reflections visually estimated in comparison with a standard scale.

In mimetite the intensities of reflections are, for the greater part, determined by the arrangement of the lead and the arsenic ions. This permits of a choice among various arrangements that are structurally reasonable. The intensities of $(h00)$ and $(h\bar{h}0)$, note Table V, without reference to probable atomic arrangements are only to be accounted for if the lead ions are at 4 (f) and 6 (h) with $\theta_1(Pb) = 90^\circ$, $\theta_2(Pb) = 0^\circ$,

Table IV.
Parameter Values.

	Pyromorphite			Mimetite			Chlor-x-Apatite		
	θ_1	θ_2	θ_3	θ_1	θ_2	θ_3	θ_1	θ_2	θ_3
2 $Cl \cdot X$	0°	0°	0°	0°	0°	0°	0°	0°	0°
4 Ca_I, Pb_I	120	240	0	120	240	0	120	240	0
6 Ca_{II}, Pb_{II}	90	1	90	90	0	90	90	0	90
6 P, As, V	150	133	90	148	141	90	150	130	90
6 O_I	124	173	90	114	165	90	120	180	90
6 O_{II}	216	167	90	232	181	90	216	168	90
12 O_{III}	126	90	23	121	98	22	120	90	23

and arsenic ions at 6 (h) with θ_1 or $\theta_2(As) = 148^\circ$, θ_2 , or $\theta_1(As) = 141^\circ$ if it is assumed that the F curves for lead, chlorine, and arsenic are approximately those listed by James and Brindley¹). The intensities of hhl require $\theta_3(Pb \text{ at } 4f) = 0^\circ$. The intensities of $(hi0)$ and $(k\bar{i}0)$ require $(6h) \theta_1^{(As)} = 148^\circ$, $\theta_2^{(As)} = 141^\circ$.

If it is assumed that the $Pb-Cl$ distance is at least 3.0 Å, then the chlorine ions must be at $\frac{1}{2}c$ on each side of the reflection planes. The $Pb-Cl$ distance is 3.16 Å, which is somewhat greater than the sum, 3.02 Å, of the ionic radii. With such an arrangement of lead, chlorine, and arsenic ions if AsO_4 groups are preserved, and if packing is to obtain, the arsenate groups must be arranged according to Mehmél's structure for apatite. The approximate values of the oxygen parameters given in Table IV are based upon the further assumptions that the arsenate groups are regular tetrahedral ones with the $As-O$ distance = 1.82 Å. The intensities of various reflections as estimated from Weissenberg photo-

1) R. W. James and G. W. Brindley, Z. Krist. 78, 470. 1931.

graphs are listed in Table V together with the values of $A/F(Pb)$. For the sake of simplicity in calculating these values possible contributions due to oxygen ions were neglected and it was assumed that $F_{As} = .35 F_{Pb}$ and $F_{Cl} = .2 F_{Pb}$ throughout the region involved.

Table V.

A Partial Summary of Weissenberg Photographic Data from Mimetite with Calculated A/F_{Pb} Values, CuK Radiation.

Plane	Observed Intensity	A/F_{Pb}	Plane	Observed Intensity	A/F_{Pb}
(100)	0	— 0.04 ¹⁾	(002)	20	— 3.7
(200)	15	— 1.5	(004)	80	+ 12.5
(300)	75	+ 7.5	(006)	10	— 3.7
(400)	15	+ 3.9	(008)	30	+ 12.5
(500)	5	+ 2.3	(331)	60	+ 4.7
(600)	0	+ 1.8	(332)	80	+ 6.6
(700)	0	+ 1.2	(333)	30	— 4.7
(800)	20	+ 5.2	(441)	15	— 1.4
(900)	15	+ 5.6	(442)	10	— 1.0
(10, 0, 0)	0	+ 2.2	(443)	2	+ 1.4
(11, 0, 0)	0	— 0.34	(444)	70	+ 9.8
(110)	15	+ 1.5	(551)	40	— 4.0
(220)	20	+ 2.3	(552)	40	+ 4.8
(330)	15	+ 2.2	(553)	40	+ 4.0
(440)	100	+ 9.8	(554)	35	+ 4.0
(550)	35	+ 3.9	(510)	15	— 4.3
(660)	15	+ 2.1	(610)	7	— 3.6
			(720)	4	— 3.6
			(920)	10	— 4.1

Extensive observations were not made upon vanadinite. It is probable, however, that its structure closely simulates that of mimetite since the units of structures for the two substances differ but slightly in dimensions. The presence of the larger V^{+5} , in comparison with As^{+5} , results in a slight increase in the value of a .

Structural Characteristics of the "Apatite" Group.

The analyses of the crystal structures of pyromorphite and mimetite clearly show that these substances have structures similar to the one suggested by Mehmel for fluor-apatite. Since they are supposed to be isomorphous with fluor-apatite it might be thought that Náray-Szabó's

1) F_{As} is assumed to be $.35 F_{Pb}$, $F_{Cl} = .2 F_{Pb}$ within the region considered.

structure for fluor-apatite is incorrect. An examination of his table of absolute intensity measurements for $(00l)$, $(h00)$ and $(hh0)$, however, indicates that his structure must be approximately correct. In particular the agreement between observed and calculated F values for (002) and (006) are decidedly best if the fluorine ions are on the reflection planes. Although there are some discrepancies between observed and calculated F values for $(hh0)$ the high intensities of (800) , (1200) , and (440) , leave but little doubt that the parameter values of the calcium ions are correctly determined. A structure simulating that of mimetite gives pronounced disagreement between observed and calculated F values for $(hh0)$. Irrespective then of the positions of the fluorine ions, Náray-Szabó's parameter values for the other atoms are probably correct. The distances of the calcium ions from the hexagonal screw axes, more-

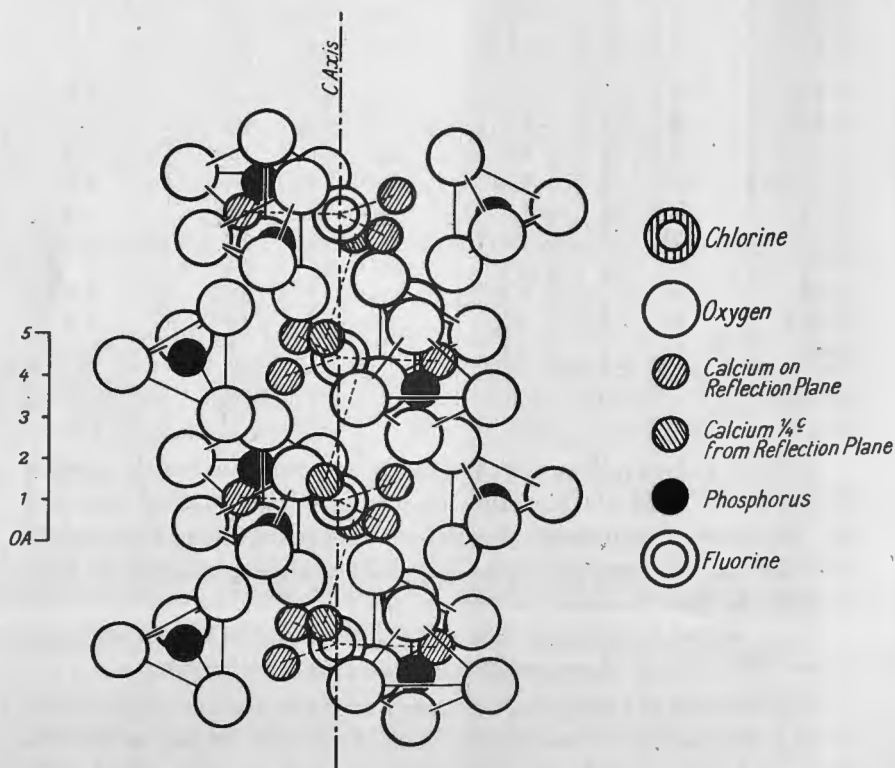


Fig. 1a. A partial representation of the structure of fluorapatite showing surroundings of the halogen atoms.

over, are approximately the same as the sum of the ionic radii of calcium and fluorine.

For the sake of clarity, it perhaps is best to discuss at this juncture the structural characteristics of the "apatite group", anticipating certain results obtained from examinations of chlor-, oxy-, and carbonate apatites. The atomic arrangements in mimetite and fluor-apatite are shown in part as Figure 1. The atomic surroundings are:

Fluor-Apatite	Mimetite
F^- or Cl^- 3 Ca^{+2}	Octahedron of 6 Ca^{+2}
P^{+5} tetrahedron of 4 O^{-2}	Tetrahedron of 4 O^{-2}
Ca_I^{+2} (on three fold axis) 9 O^{-2}	9 O^{-2}
Ca_{II}^{+2} (on reflection planes) 6 O^{-2}	6 O^{-2} and 2 Cl^-
and 1 F^-	Tetrahedron of 1 P^{+5} and 3 Ca^{+2} .
O^{-2} tetrahedron of 1 P^{+5} and 3 Ca^{+2}	

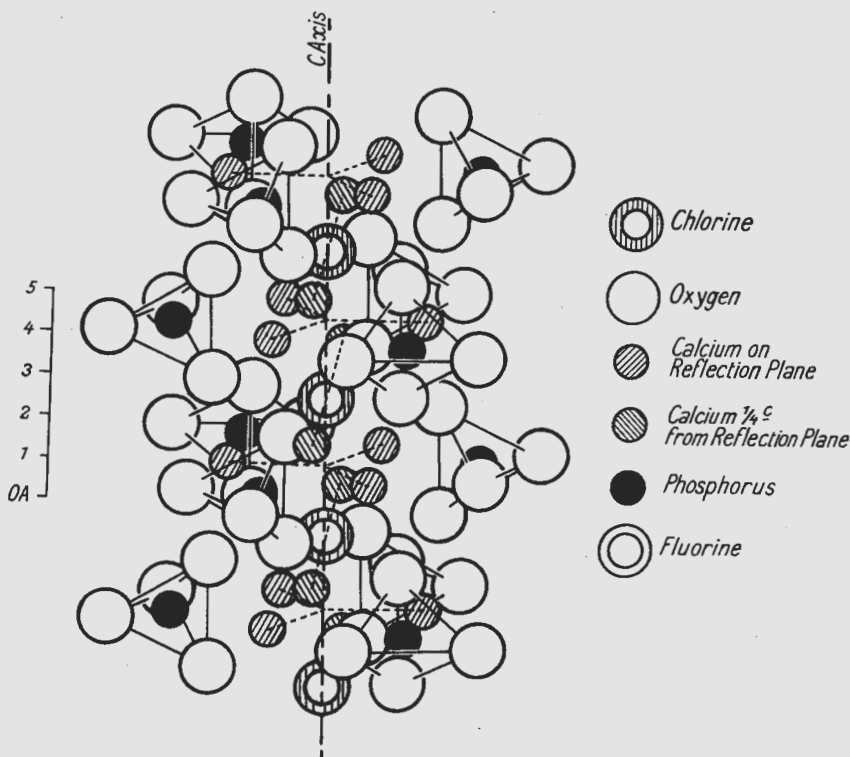


Fig. 1b. A partial representation of the structure of chlorapatite showing surroundings of the halogen atoms.

Microscopic neutrality is attained equally well by both structures, as it also is by the possible structure for a compound $Ca_{10}X^{-2}(PO_4)_6$ shown in part as Figure 2. Replacement in the mimetite structure of two uni-

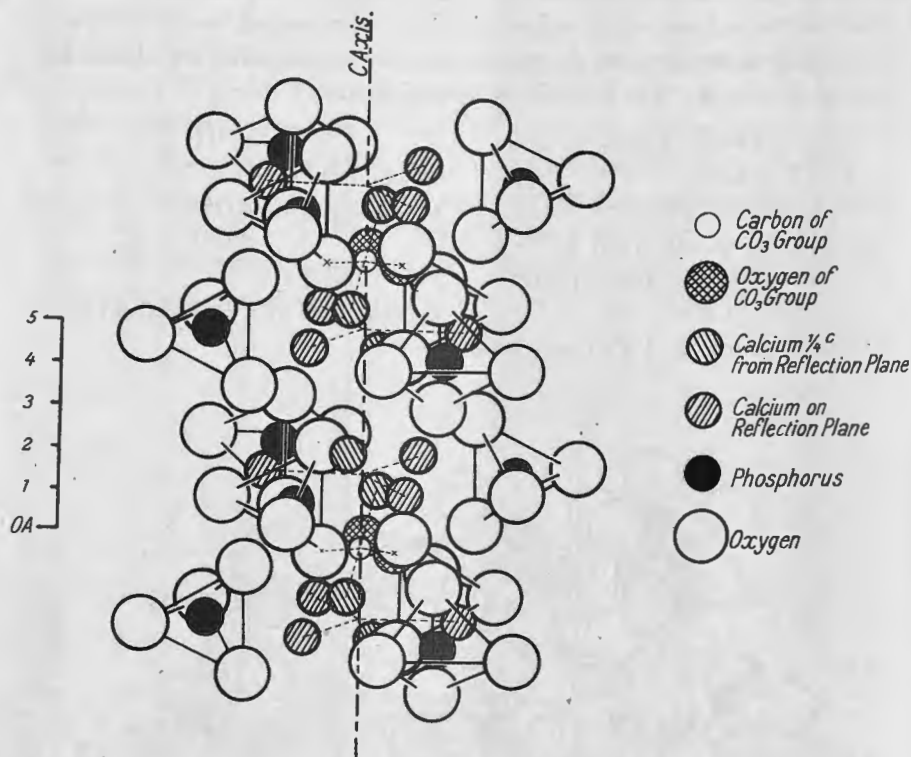


Fig. 2. A partial representation of the structure of $Ca_{10}CO_3(PO_4)_6$.

valent chlorine ions by a bivalent ion is accomplished by the filling of only half the available positions, 000, $00\frac{1}{2}$. The remaining positions can be occupied by uncharged groups, especially water molecules.

In no case is pronounced cleavage to be expected but compounds with the fluor-apatite structure or the structure of $Ca_{10}X^{-2}(PO_4)_6$ would be expected to give some indication of cleavage parallel to (001). Mimetite, vanadinite, and pyromorphite have no pronounced cleavage while fluor-apatite and dahllite each has moderate cleavage parallel to (001)¹⁾.

1) C. Hintze, »Handbuch der Mineralogie«, I Pt. 4, p. 494, 4024, Leipzig 1924.

The Structure of Chlor-Apatite.

Chlor- and fluor-apatite are known to form a complete series of solid solutions¹⁾. In natural products, however, it is seldom that more than half of the fluorine is replaced by chlorine²⁾. Goniometric measurements upon natural products show that the axial ratio, $a:c$, decreases with increase in chlorine content. The observed limits of variation are $a:c = 1:0.7346$, for fluor-apatite, and $a:c = 1:0.7246$ for a specimen containing 2.06% *Cl* and 4.18% *Fl*³⁾. X-ray diffraction measurements⁴⁾ upon a mixed chlor-, fluor-apatite from Jumilla, Spain, containing about 0.6% *Cl*, gave $a = 9.41 \text{ \AA}$, $c = 6.88 \text{ \AA}$, in agreement with the above measurements.

The X-ray powder diffraction data obtained from one mixed chlor-apatite, containing 4.13% *Cl* and 0.17% *F*, are in part listed in Table VI. The dimensions of the unit of structure containing $2Ca_{10}(Cl \cdot X)_2(PO_4)_6$, *X* being possibly oxygen, or hydroxyl, are $c = 6.85 \pm 0.03 \text{ \AA}$, $a = 9.52 \pm 0.03 \text{ \AA}$. The intensities of the various interference maxima are best to be accounted for by an arrangement of the calcium and phosphate ions simulating that found by Náray-Szabó for fluor-apatite. In such an atomic arrangement the calcium ions on the reflection planes are $2.38 \text{ \AA}$ from hexagonal screw axes. Since this value is markedly smaller than $2.80 \text{ \AA}$, the sum of the ionic radii of Ca^{++} and Cl^- , it is extremely improbable that the chlorine ions are on the reflection planes. If the atomic arrangement is similar to that of mimetite the Ca^{++} to Cl^- distances are $2.93 \text{ \AA}$, slightly greater than the expected values. That the latter indeed is the correct arrangement is rather strikingly shown by the type of intensity differences between fluor- and chlor-*x*-apatite, note Table VI. The replacement of fluorine at $00\frac{1}{2}$, $00\frac{3}{4}$ by chlorine at 000 and some unknown, but light, group at $00\frac{1}{2}$, most markedly affects the intensities of (hkl) with l even but not a multiple of four. The F values for various reflections of chlor-*x*-apatite listed in Table VI were calculated from the corresponding values for fluor-apatite as calculated by Náray-Szabó, introducing the changes caused by the differences in the positions of the halogen atoms.

It is to be noted that the value of c , $6.85 \text{ \AA}$, does not change upon replacement of fluorine in fluor-apatite by chlorine. Since the two

1) R. Nacken, loc. cit. See also, C. Doelter, »Handbuch der Mineralchemie«, 3 Pt. 1, Leipzig, 1918.

2) C. Hintze, loc. cit., p. 488.

3) P. Ramdohr, Jahrb. der Preuss. Geol. Landesanst. 40, 284. 1919.

4) H. Hentschel, Ctbl. Min. 1923, 600 Nr. 20.

Table VI.

Powder Photographic Data for Chlor-X-Apatite.

$$\sin^2 \theta = .00870 (h^2 + k^2 + hk) + .0126 l^2. (CuK\alpha_1.)$$

Chlor-X-Apatite					Fluor-Apatite			
Plane	$\sin^2 \theta$ exp.	$\sin^2 \theta$ calc.	Int. est.	F calc.	Number of planes	F calc.	Int., est. Náray- Szabó	Int., est. H, J, M.
101		.02130			12			
110		.02610		+ 14	6	+ 7	0	
200		.03480		— 36	6	— 42	1	.5
111	.0385	.03870	.5	— 30	12	— 30	1	.5
201		.04740		+ 17	12	+ 17	—	—
002	.0505	.05040	2.5	— 86	2	— 124	4.5	4
102		.05910		+ 24	12	— 12	1.5	1
120	.0625	.06090	1.5	— 18	6	— 23	2	1.5
210				— 52	6	— 57		
121	.0728	.07350	10	— 62	12	— 62		
211				— 92	12	— 92	> 10	> 10
112	.0775	.07650	> 10	+ 121	12	+ 87		
300		.07830		+ 126	6	+ 121	6	5
202	.0849	.08520	2.0	+ 3	12	— 30	4	4
301	.0912	.09090	1.5	+ 39	12	+ 39	1.5	1
220		.10440		— 15	6	— 20	—	
122	.1113		3.5	+ 61	12	+ 32	1.5	1
212				— 3	12	— 32		
130		.11310		+ 123	6	+ 118		
310				+ 3	6	— 2	4.5	3.5
221		.11700		— 22	12	— 22	—	
103		.12310		— 28	12	— 28	—	
131	.1265	.12570	.5	+ 24	12	+ 24	1	1.—.5
311				—	12	—		
302		.12870		+ 56	12	+ 28	—	
400		.13920		— 27	6	— 32	—	
113	.1415	.13950	.5	+ 25	12	+ 25	1	1.—.5
203		.14820		+ 30	12	+ 30	1	1.—.5
401		.15180		+ 12	12	+ 12	—	
222	.1551	.15480	5	+ 135	12	+ 108	4.5	4.5
132		.16350		— 16	12	— 43	3	2
312	.1632		2	— 25	12	— 52		
230		.16530		— 60	6	— 64	—	
320				—	6	—		
123	.1750	.17430	5	+ 42	12	+ 42	5	5
213				+ 60	12	+ 60		
231		.17790		+ 45	12	+ 45		
321				+ 38	12	+ 38	3	2.5

Table VI (continuation).

Chlor-X-Apatite					Fluor-Apatite			
Plane	$\text{Sin}^2 \theta$ exp.	$\text{Sin}^2 \theta$ calc.	Int. est.	F calc.	Number of planes	F calc.	Int., est. Náray- Szabó	Int., est. <i>H, J, M.</i>
140	.1810	.18270	2	+ 76	6	+ 71	3	2
410				+ 80	6	+ 75		
402	.1897	.18960	1.5	— 45	12	— 70	3	2
303		.19170		— 19	12	— 19	—	
411		.19530		+ 13	12	+ 13	—	
141				— 9	12	— 9	—	
004	.2068	.20160	2.5	+ 208	2	+ 204	3.5	3
104		.21030		+ 10	12	+ 6	—	
223		.21380		+ 12	12	+ 12	—	
322		.21570		— 14	12	— 38	1.5	1.5
232				— 2	12	— 26		
500		.21750		+ 14	6	+ 10	—	
133	.2280	.22650	1.—.5	— 20	12	— 20	1	1.—.5
313				— 36	12	— 36		
114		.22770		+ 29	12	+ 25	—	
204		.23640		— 11	12	— 15	—	

halogen atoms are at $00u, 00u + \frac{1}{2}$, the value of c must be at least twice the diameter of the halogen atoms. For chlor-apatite, $\text{Ca}_{10}\text{Cl}_2(\text{PO}_4)_6$, or for a mixed chlor-apatite containing much more than 3.5% chlorine the value of c would be expected to be at least 7.24 Å, as it is observed to be for pyromorphite, mimetite, and vanadinite.

Pure chlor-apatite was prepared as microscopic hexagonal crystals by heating CaCl_2 with $\text{Ca}_3(\text{PO}_4)_2$, in proportions corresponding to the formula to about 1400° C. The diffraction data obtained from this material indicate that the dimensions of the unit of structure differ but slightly from those of chlor-*x*-apatite, $c = 6.85$ Å, $a = 9.52$. The structure, as shown by the intensities of reflections, is similar to that of mimetite. It would thus seem that the chlorine ions, in chlor-apatite, either occupy somewhat less than their normal volumes, or are somewhat displaced from the hexagonal screw axes of the remainder of the structure.

It is probable that a compound, chlor-fluor-apatite, $\text{Ca}_{10}\text{ClF}(\text{PO}_4)_6$, can be considered as existing with an ordered arrangement of the chlorine and fluorine atoms. The relationship of chlor-fluor-apatite, chlor- and fluor-apatite is similar to that of dolomite, magnesite, and calcite. The appearance of such compounds in series of solid solutions can be explained as arising from the large differences in the radii of the varying ions;

the radii for the above cases being Cl^- , 1.81 Å; F^- , 1.36 Å; Mg^{++} , 0.65 Å; Ca^{++} , 0.99 Å. If the varying ions differ but slightly in radii, their distribution is probably a random one among the positions available. Such a case, the usual solid solution in which ions of equal charge vary, is but a special case of the more general principle of "variate atom equi-points" recognized by Barth and Posnjak¹).

The Structure of Hydroxy-Apatite, Oxy-Apatite, Tricalcium Phosphate Hydrate, and the Apatite-Like Compound of Bone.

Powder diffraction photographs of the substances listed in the title are reproduced in Figure 3, together with that of fluor-apatite. The lattice dimensions, Table II, are approximately the same for all of these compounds as also are the intensities of reflections. Nevertheless, each diffraction pattern is sufficiently distinctive to permit its use for the identification of the various substances in mixtures and natural products. (Note differences in relative positions of the two most intense reflections (112) and (214) (121).)

It is to be expected that the diffraction patterns of hydroxy- and fluor-apatite should be closely similar since the ionic radii of F^- and OH^- are approximately the same. The other compounds, however, are indeed strange bedfellows whose compatibility is to be explained only by the structural peculiarities of the apatite group discussed above. Their formulas can be written as:

$Ca_{10}O(PO_4)_6$	Oxy-apatite
$Ca_{10}(CO_3)(H_2O)(PO_4)_6$	Bone
$Ca_9(H_2O)_2(PO_4)_6$	Tricalcium phosphate hydrate
$Ca_{10}(OH)_2(PPO_4)_6$	Hydroxy-apatite.

Oxy-apatite and bone have structures simulating that of $Ca_{10}X^{-2}(PO_4)_6$ shown as Figure 2. Since bone is formed in aqueous systems at low temperatures it is probable that one molecule of water of hydration is present in the unit of structure. Microscopic neutrality and close packing can attain if the plane of the CO_3^{--} ion is perpendicular to the hexagonal screw axis at 000. Such an arrangement, of course, lowers the crystal symmetry.

Tricalcium phosphate hydrate can be considered as formed from fluor-apatite by replacement of fluorine ions at $00\frac{1}{2}$, $00\frac{3}{2}$, by the larger H_2O molecules at 000, $00\frac{1}{2}$. In order for the structure to remain neutral

1) J. Wash. Acad. Sci. 21, 255. 1931. We gratefully acknowledge the privilege of having been allowed to read in manuscript, "The Crystal Structure of Lithium Ferrite", by Drs. Posnjak and Barth.

it is necessary for one-tenth of the calcium ions to be removed. It would be improbable that water molecules could be in the positions thus left vacant since their apparent diameters are much greater than that of Ca^{++} . For this reason it is probable that the composition of the hydrate of tricalcium phosphate which forms solid solutions with hydroxy-apatite can best be represented by the formula $Ca_9(H_2O)_2(PO_4)_6$ or $Ca_3(PO_4)_2 \cdot 2/3 H_2O$. This hydrate upon heating to constant weight at $900^\circ C$ loses water, yielding an anhydrous substance whose diffraction pattern is markedly different from that of apatite. This anhydrous material, probably $Ca_3(PO_4)_2$, gives the same diffraction pattern as the mineral martinite previously described as $Ca_5H_2(PO_4)_4 \cdot 3/2 H_2O$.

We do not consider it possible, on the basis of our diffraction data, to decide whether the structure of hydroxy-apatite is similar to that of apatite or of mimetite.

Summary.

A study has been made of the crystal structures of the compounds forming the "apatite-group". Structural reasons have been deduced accounting for the apparent isomorphous replacement of fluorine ions by carbonate, hydroxy, sulphate, and silicate groups and by oxygen, chlorine, bromine, or iodine ions. A rational explanation is thus possible for the occurrence of the various poorly defined mineral components of phosphate rock.

The probable existence of a compound $Ca_{10}ClF(PO_4)_6$ is pointed out and the structure of a compound approximating this composition is deduced. A structural reason is given for the limited replacement of fluorine by chlorine in natural fluor-apatite.

Pyromorphite, $Pb_{10}Cl_2(PO_4)_6$, mimetite, $Pb_{10}Cl_2(AsO_4)_6$, vanadinite, $Pb_{10}Cl_2(VO_4)_6$, and chlor-apatite, $Ca_{10}Cl_2(PO_4)_6$ have crystal structures similar to that suggested by Mehmél for fluor-apatite. The structure of fluor-apatite and possibly hydroxy-apatite is that determined by Náray-Szabó for fluor-apatite.

The X-ray powder diffraction photographs of oxy-apatite, $Ca_{10}O(PO_4)_6$ a hydrate of tricalcium phosphate, $Ca_9(H_2O)_2(PO_4)_6$, and a phosphate compound of bone, $Ca_{10}(CO_3)(H_2O)(PO_4)_6$ differ but slightly from those of hydroxy- and fluor-apatite. It is probable, however, that these compounds more closely simulate pyromorphite in structure. There are structural reasons for supposing that the hydrate of tricalcium phosphate has the composition indicated above and that the phosphate compound of bone is hydrated.

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