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A STRUCTURAL INVESTIGATION OF THE ISOMORPHISM OF THE APATITE GROUP

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INTRODUCTION

A mineral name has never been more appropriately selected than that of apatite, which is from ἀπατάω (I deceive). Nor has this deception been limited to elementary students: indeed, the variability of the properties and modes of occurrence of the members of the apatite group are so great as to have resulted in the failure to refer certain of them to the apatite group even since the beginning of the twentieth century. In other studies the manner of substitution of some of the ions, commonly present, has been poorly understood or wholly misunderstood.

This study cannot hope to treat the subject exhaustively, because there are not sufficient data available to do so. The optical properties of these minerals will not be considered in the present work, except as they may have a bearing upon the identification of the materials studied. The optical properties have been discussed in some detail by Hausen (1) who also gives an extensive bibliography to 1929. The identification of the several members of the apatite group on the basis of their refractive indices is probably fully as unreliable as the determination of the various garnets by this means. The properties reported for various synthetic apatites are not consistent, and several of these also are inconsistent with the data on natural materials.

Some new chemical data have been obtained, however, and more than thirty *x*-ray powder diagrams have been examined. The more important of these were measured and the dimensions of the unit cells have been determined and compared with one another and with fluor-apatite. This has led to several entirely new conclusions concerning the isomorphism of the group and has verified some of the ideas previously held. This is also a justifiable basis on which to assume that certain substances bearing different names are identical, and an attempt is made to remove some of the confusion regarding the nomenclature of these minerals.

There are many analyses of the various members of the apatite group on record, but most of these antedate the more reliable methods for the determination of some of the constituents which are reported. The analytical difficulties encountered among these materials are so great as to cast serious doubt upon the reliability of any analyses made prior to 1910, as well as those which were not made by analysts with considerable experience in mineral analysis. The rather arbitrary deduction of supposed "impurities" and the failure to test for all of the probable constituents has greatly added to the difficulties in interpreting some of the analyses.

The apatite group [exclusive of pyromorphite, svabite, mimetite and vanadinite] may contain significant amounts of the following metals: Ca, Mg, Mn, Sr, K and Na. In addition to these a number of analyses report BaO, CrO, FeO, Fe_2O_3, Cr_2O_3, Al_2O_3, et al., but these constituents were not investigated in the present work and it is questionable whether or not these can enter the apatite lattice in significant amounts. Cerium and the rare earths also occur, according to Starynkevič-Borneman (2), but no specimens known to contain these elements were examined by the writer. A number of negative ions and groups may be expected also: PO_4^{-3}, AsO_4^{-3}, VO_4^{-3}, SiO_4^{-4}, SO_4^{-2}, CO_3^{-2}, F^-, Cl^-, OH^- and O^{-2}.

The writer is indebted to Dr. J. W. Gruner for his interest in this problem and for numerous valuable suggestions. He is further indebted to Dr. R. B. Ellestad, of the Laboratory for Rock Analysis, for a number of valuable analytical determinations and for helpful suggestions. A number of individuals and institutions have generously contributed the specimens used in this study. The following materials were examined:

Apatite

I. Fluor-apatite, from Faraday Township, Hastings County, Ontario. Kindly furnished by Mr. A. S. Dadson, Toronto, Ontario. (3)[1]

II. Labelled "Apatite, from Nishiyamanashigun, Kai, Japan." This apparently is not an ordinary fluor-apatite and no reliable analysis is available.

III. Fluor-apatite, locality unknown.

Francolite

IV. Labelled "Apatite, var. staffelite, from Staffel on Lahn, Nassau." Purchased from Ward's Natural Science Establishment, Rochester, N. Y. (4)

V. Labelled "Grodnolite, from Raków, near Grodno, Poland." Kindly furnished by Dr. J. Morozewicz, Director of the Geological Survey of Poland. (5)

Dahllite

VI. No. 106,181, Museum of Natural History, Paris. Dahllite, from Mouillac, Quercy, France. Kindly furnished by Dr. A. Lacroix. (6)

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[1] The numbers following the descriptions of the specimens refer to the bibliography. In many cases a number of descriptions are on record, but usually only the most recent or most complete description is given for reference.

VII. Dahllite, from near Ishawooa, Wyoming. Kindly furnished by Mrs. F. C. Sayles, Jr., Ishawooa, Wyoming. (7)

VIII. Dahllite, from near Junction City, Ky. Kindly furnished by Dr. Raymond Edmundson, Cornell University, Ithaca, N. Y. (8)

IX. Labelled "Podolite, from Podolien, Fluss Uschiza, Zurzewka." Kindly furnished by Dr. V. Chirvinsky, Ukrainian Geol. Research Trust, Kiev, U. S. S. R. (9 and 10)

Dehrnite

X. No. R5590, U. S. National Museum. Dehrnite (Kalkwavellite), part of type specimen, from Dehrn, Nassau. Kindly furnished by Dr. W. F. Foshag. (11 and 12)

XI. Labelled "Dehrnite, not analyzed, Utah." Kindly furnished by Dr. E. S. Larsen, Harvard University, Cambridge, Mass. (11 and 12)

XII. Labelled "Dehrnite, from Utah." Kindly furnished by Dr. F. H. Pough, American Museum of Natural History, New York, N. Y.

Lewistonite

XIII. Lewistonite, from Utah. Kindly furnished by Dr. F. H. Pough. (12)

Fermorite

XIV. No. 326, Geological Survey of India. Fermorite, from Sitapar Manganese Mine, Sausar Tehsil, Chhindwara District, Central Provinces, India. Kindly furnished by the Director at the request of Dr. M. S. Krishnan, Calcutta, India. (14)

Ellestadite

XV. Ellestadite, from Crestmore, Riverside County, California. Kindly furnished by Dr. Adolf Pabst, University of California, Berkeley, California. (15)

Wilkeite

XVI. Wilkeite, from Crestmore, Calif. Purchased from Mr. R. M. Wilke, Palo Alto, California. (15)

XVII. Wilkeite, from Crestmore, Calif. Purchased from Ward's Natural Science Establishment, Rochester, N. Y. (15)

Mangan-apatite

XVIII. No. 86,790, Harvard University Collection. Manganapatite, from Buckfield, Maine. Kindly furnished by Dr. Harry Berman, Cambridge. Mass. (16)

Collophane and various mixtures

XIX. No. 80,177, Museum of Natural History, Paris. Labelled "Quercyite, Castillo de Belmez, Espagne." Kindly furnished by Dr. A. Lacroix. (17)

XX. Labelled "Sandy phosphorite, from Kursk" [kurskite]. Kindly furnished by Dr. V. Chirvinsky, Ukrainian Geol. Research Trust, Kiev, U. S. S. R.

XXI. Podolian phosphorite, Uschiza River, Zurzewka, Podolia. Kindly furnished by Dr. V. Chirvinsky.

XXII. Labelled "Dahllite, from Ochotnikov, near Kiev, Ukrainia." Purchased from Mr. R. M. Wilke, Palo Alto, California.

The Structure of Fluor-Apatite

In the pages that follow, the isomorphous substitutions have been discussed in terms of the structure of fluor-apatite and, for this reason, it is essential to discuss this structure briefly at this point.

Náray-Szabó (18) and Mehmel (19 and 20) have shown that the structure contains the following ions: 10 Ca, 6 P, 2 F, and 24 O. The positions of these ions are given in Fig. 1, slightly modified according Mehmel (20).

Because these authors have arrived at similar conclusions working independently, it seems almost conclusive that this structure is essentially correct. The calculations of Náray-Szabó have been extremely useful as a check in the present work.

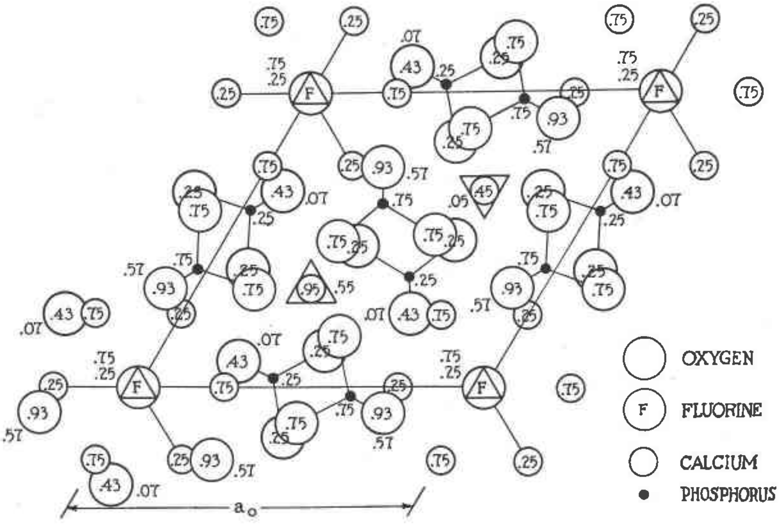

FIG. 1. Projection of the unit cell of fluor-apatite on (0001). The heights of the various ions are indicated as fractions of c_0.

The interplanar distances for fluor-apatite, from Ontario (specimen I), with unfiltered iron radiation are given in Table 1, column 1. The calculation of the unit cell for this material is comparable with the results of Náray-Szabó and Mehmel, as follows:

	a_0	c_0	c/a	Vol.
fluor-apatite, Ontario, I	9.36 ± .01	6.88 ± .01	.7350	522
fluor-apatite (Náray-Szabó)	9.37 ± .01	6.88 ± .01	.7342	523
fluor-apatite (Mehmel)	9.36 ± .02	6.85 ± .02	.7318	520

If it is assumed that each of these specimens represents pure fluor-apatite and the theoretical densities are calculated on the basis of the molecular weight of the theoretical fluor-apatite (1008.9), the results show only slight differences. The values thus calculated are, respectively:

TABLE 1. COMPARISONS OF POWDER DIAGRAMS OF VARIOUS MINERALS OF THE APATITE GROUP. (Unfiltered Fe Radiation—$r=57.3$ mm.)

		Fluor-apatite		Francolite		Dahllite		Mangan-apatite		Fermorite		Dehrnite		Lewistonite		Wilkeite	
No.	Indices	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
1	111	—		—		—		—		3.952	0.5	—		—		—	
2	002	3.432	2	3.431	2	3.437	2	3.386	2	3.494	3	3.432	1	3.449	1	3.452	2
3	102	—		3.157	0.5	—		3.134	0.5	—		3.160	0.5	3.169	0.5	—	
4	120, 210	3.060	3	3.044	2	3.077	3	3.050	2	3.143	1	3.044	3	3.068	2	3.109	3
5	300β	2.975	0.5	2.957	0.5	2.990	1	2.967	0.5	3.052	0.5	2.960	0.5	2.982	0.5	3.026	0.5
6	202β	2.884	0.5	2.844	0.5	—		—		—		—		—		—	
7	121, 211	2.798	>10	2.765	>10	2.811	>10	2.784	10	2.866	>10	2.765	>10	2.798	>10	2.830	>10
8	112	2.769	4			2.778	3	2.750	3	2.824	5			2.771	4	2.795	4
9	300	2.702	6	2.683	7	2.712	6	2.694	8	2.769	8	2.685	6	2.700	6	2.731	6
10	202	2.616	3	2.618	4	2.628	1	2.599	4	2.675	2	2.613	3	2.622	2	2.642	3
11	301	2.517	0.5	2.508	0.5	2.524	0.5	—		—		2.507	0.5	—		—	
12	130β	2.477	0.5	2.462	0.5	2.493	0.5	—		—		2.462	0.5	—		—	
13	122, 212	2.289	0.5	2.277	1	—		—		—		2.281	0.5	—		—	
14	130, 310	2.248	2	2.238	3	2.256	4	2.240	6	2.306	1	2.234	4	2.247	2	2.276	3
15	131, 311	2.135	1	2.127	2	2.145	2	2.128	2	2.191	1	2.124	2	2.134	1	2.157	1
16	222β	—		—		—		—		—		—		—			
17	113	2.057	1	2.060	1	—		2.042	0.5	—		2.054	0.5	2.058	0.5	—	
18	123β	2.026	0.5	2.020	1	2.031	0.5	2.012	0.5	2.063	1	2.020	0.5	2.020	0.5	2.030	0.5
19	203	2.001	0.5	1.996	1	—		1.977	0.5	—		—		—		2.007	0.5
20	231β	—		1.967	0.5	1.993	0.5	—		2.031	0.5	—		—		—	
21	222	1.937	3	1.928	3	1.941	4	1.925	6	1.980	5	1.926	6	1.934	3	1.956	4
22	132, 312	1.883	1	1.876	1	1.888	1	1.872	3	1.926	1	1.877	2	1.880	1	1.902	1
23	123, 213	1.838	6	1.835	3	1.840	2	1.820	8	1.873	8	1.831	6	1.833	5	1.849	4
24	231, 321	1.795	3	1.788	2	1.805	1	1.790	3	1.840	2	1.788	2	1.795	2	1.818	1
25	140, 410	1.769	3	1.762	2	1.778	1	1.764	3	1.814	2	1.759	2	1.768	2	1.792	1
26	402	1.745	3	1.740	2	1.753	1	1.738	3	1.788	2	1.742	2	1.745	2	1.766	1
27	004	1.720	3	1.720	2	1.721	1	1.703	3	1.749	3	1.719	2	1.721	2	1.727	2
28	232, 322	1.637	1	1.631	0.5	1.645	0.5	1.629	2	1.675	1	1.631	1	1.635	1	1.655	0.5
29	133, 313	1.605	0.5	1.601	0.5	—		—		1.641	0.5	—		—		—	
30	240, 420	1.533	0.5	1.525	0.5	1.538	1	1.531	1	1.574	0.5	1.527	0.5	—		—	
31	331	1.521	0.5	1.515	0.5	1.502	1	1.517	1	1.560	0.5	1.516	0.5	—		—	
32	124, 214	1.498	1	1.496	0.5			1.488	1	1.531	1	—		—		1.511	0.5
33	502	1.468	2	1.462	1	1.473	1	1.462	2	1.504	1	1.464	2	1.466	1	1.486	1
34	304	1.452	1	1.453	1	1.455	1	1.439	2	1.478	2	—		—		1.467	1
35	233, 323	1.445	1	1.441	1	1.434	2	1.421	3			—		—			
36	151, 511	1.424	1	1.419	1					1.462	1	—		—		1.439	0.5

3.187, 3.180 and 3,201. Actually, the differences are probably due to differences in the chemical compositions of the apatites examined, but, because the theoretical density is one of the fundamental considerations in several instances below, this uniformity of results is emphasized here.

In the sections to follow, the isomorphism is discussed under the headings of substitutions for: (1) calcium, (2) phosphorus, (3) fluorine and (4) oxygen.

TABLE 2. CHEMICAL ANALYSES OF VARIOUS MINERALS OF THE APATITE GROUP

	1	2	3	4	5	6	7	8	9
CaO	55.16	51.02	53.65	47.33	44.34	50.88	46.78	54.88	55.47
MgO		0.47						0.31	
MnO	0.12			8.67					0.06
SrO					9.93				
Na_2O		0.7				7.11	4.34		
K_2O		0.57				1.20	1.36		
CO_2	0.50	5.79	5.30			1.49		3.36	
P_2O_5	41.30	33.01	38.40	41.43	20.11	37.12	37.92	37.71	42.19
SiO_2		trace							
SO_3		1.77						none	
Al_2O_3	0.24	0.20	0.57	0.55		trace	2.53		
Fe_2O_3	0.63	0.66							
F	3.67	3.55	trace	3.80	0.83	none		4.11	
Cl	0.09	trace				none		none	
H_2O+	0.01	3.16	2.10	0.06	trace	1.52	7.69	1.14	1.73
H_2O-		0.54				0.16		0.04	0.00
Others	0.42	0.77			25.31	0.12		0.24	0.60
	102.14	102.22	100.02	101.84	100.52	99.60	100.62	101.79	100.05
Less O	1.56	1.49		1.60	0.35			1.73	
	100.58	100.73	100.02	100.24	100.17	99.60	100.62	100.06	100.05

1—Fluor-apatite, Faraday Township, Hastings Co., Ontario. A. S. Dadson, analyst. Others = 0.14 FeO + 0.28 insol.

2—Francolite [grodnolite], near Grodno, Poland. W. Wawryk, analyst. Others = 0.47 organic C + 0.30 insol. [Possibly the value for Na_2O should be 0.71 (instead of 0.7), in which case the sum would be correct as given.]

3—Dahllite, Mouillac, Quercy, France. F. Pisani, analyst.

4—Mangan-apatite, Buckfield, Maine. H. E. Vassar, analyst.

5—Fermorite, Sausar Tehsil, India. G. T. Prior, analyst. Others = 25.23 As_2O_5 + 0.08 insol.

6—Dehrnite, Dehrn, Nassau. E. V. Shannon, analyst. Others = 0.12 insol.

7—Lewistonite, near Fairfield, Utah. F. A. Gonyer, analyst.

8—Francolite [staffelite], Staffel on Lahn, Nassau, Germany. R. B. Ellestad, analyst. Others = 0.24 V_2O_5.

9—Hydroxy-apatite, Kemmleten, near Hospenthal. J. Jakob, analyst. Others = 0.60 insol

SUBSTITUTIONS FOR CALCIUM

FRANCOLITE AND DAHLLITE

Some of the substitutions for calcium have been surmised for many years, such as the substitution of small amounts of magnesium, manganese and strontium. The substitution of carbon for calcium is rather surprising, however. Apparently this type of substitution takes place to a limited extent in all carbonate-apatites, but it has been definitely shown only in ellestadite (15) and francolite (4). By analogy C-ions also substitute for Ca in dahllite, dehrnite and lewistonite and, possibly, in merrillite.

The demonstration of the substitution of carbon for calcium requires a rather detailed discussion of the analysis give in Table 2, column 8, and, because Gruner and McConnell (4) have considered these data in considerable detail, their results will receive only brief mention here. It was found that CO_3-groups could not occur in the positions to which they had been previously assigned for several reasons:

(1) The CO_3-group, being much larger than the F-ion, would require that the size of the unit cell of francolite be larger than that of fluor-apatite. On the contrary it was found to be slightly smaller.

(2) The theoretical density of a carbonate-apatite in which CO_3-groups substitute for fluorine is greater than the density of fluor-apatite but the calculation of the theoretical density of francolite (specimen IV) gives the following:

$$\frac{993.19\times 1.649}{519.77}=3.151$$

and this is considerably less than the density of fluor-apatite (3.18). The theoretical density is in excellent accord, however, with an experimental value, which is 3.147 (4°C.).

(3) If CO_3-groups were assumed to occupy F-positions the F-ions would have to occupy other positions in the structure; because there is an excess of fluorine above the amount of the theoretical fluor-apatite; and, furthermore, it would not be possible to reconcile the analysis with the proportion Ca:P::10:6. A statistical distribution of the carbon ions between the P-positions and the Ca-positions was accepted as the most probable explanation. The distribution was found to be as follows:

$$\begin{array}{rl}
10\ \mathrm{Ca} & =9.810\ \mathrm{Ca}+.077\ \mathrm{Mg}+.113\ \mathrm{C} \\
6\ \mathrm{P} & =5.322\ \mathrm{P}+.026\ \mathrm{V}+.652\ \mathrm{C} \\
2\ \mathrm{F} & =2.000\ \mathrm{F} \\
\underline{24\ \mathrm{O}} & =23.732\ \mathrm{O}+.100\ \mathrm{OH}+.168\ \mathrm{F} \\
42 & =\text{number of ionic positions of fluor-apatite}
\end{array}$$

This distribution indicates that C-ions replace Ca-ions, but this can take place only in those Ca-positions which are located on three-fold axes (Fig. 1). Figure 2 is an illustration of the supposed manner of this substitution. If this represents a true picture of the manner of introduction of carbon into the structure—and there is every indication that it is the correct one—nitrogen might be expected to enter the structure in the same way if it were available in the proper state of oxidation. The fact that a nitrate-apatite is not known does not weaken the hypothesis, because NO_3-groups are probably not available in the environment in which most of these minerals form and, in most cases, there has probably not been an attempt to ascertain the presence or absence of NO_3-groups by analysis.

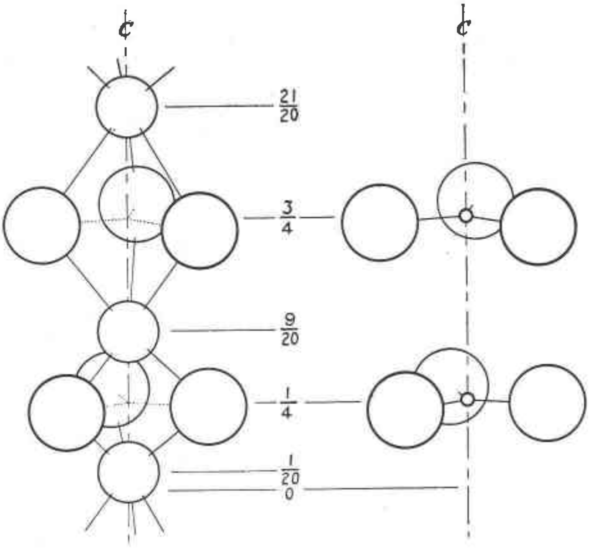

FIG. 2. Clinographic projection of the ions immediately adjacent to the three-fold axes on which the Ca-ions are located, showing the hypothetical manner of the displacement of Ca-ions by C-ions with the formation of CO_3-groups. The circles represent oxygen, calcium and carbon in order of decreasing sizes.

Two specimens of francolite were examined and they compare with each other, and with fluor-apatite as follows:

	a_0	c_0	c/a	Vol.
fluor-apatite, I	9.36 ± .01	6.88 ± .01	.7350	522
francolite, IV	9.34 ± .01	6.88 ± .01	.7366	520
francolite, V	9.32 ± .01	6.88 ± .01	.7382	518

The interplanar distances for francolite [grodnolite] are given in Table 1, column 2. Although a chemical analysis of this material has been recently reported by Tokarski (5) it seems highly improbable that the results are representative of the phosphate mineral which is the chief constituent of a rather complex sedimentary rock. For this reason it seems inadvisable to base calculations upon this analysis, but it is noteworthy that 3.55 per cent fluorine was found (Table 2, column 2). The interplanar distances for francolite [staffelite] have been given (4).

Francolite is a suitable name for an apatite which contains an appreciable amount of CO_2 but which also contains more than one per cent of fluorine. It many or may not contain OH-ions, depending upon the various amounts of other ions present. Francolite should include both a carbonate-fluor-apatite and a carbonate-hydroxy-fluor-apatite (where $F > 1\%$). Grodnolite is identical with francolite, as shown by Tokarski (5) and confirmed in this work. Staffelite is also identical as has been previously indicated by numerous authors.[2]

The essential difference between dahllite and francolite is the presence of appreciable amounts of fluorine in the latter compound and the absence of appreciable amounts in the former. Dahllite, as it is here defined contains less than one per cent of fluorine, but this limit is arbitrary and probably of no structural significance. It is noticeable however, that most apatite analyses indicate considerably less than one per cent of fluorine or considerably more than this amount. Dahllite is a carbonate-hydroxy-apatite.

Dahllite from Quercy has been analyzed by Pisani (6, p. 1390) with the results shown in Table 2, column 3. The CO_2-content of specimen VI was determined as 4.35% by Dr. R. B. Ellestad and the fluorine was found to be 0.19% by Dr. W. D. Armstrong, so it may be concluded that this material is essentially similar to the dahllite from the same locality which Pisani analyzed. The interplanar distances obtained for this material are given in Table 1, column 3.

The dimensions of the unit cells of several dahllite specimens are comparable with fluor-apatite and with each other as follows:

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[2] Since going to press a personal communication has been received from Mr. M. H. Hey, of the British Museum, and it states in part: "I . . . do not agree that Schaller's conclusion [regarding the identity of staffelite and francolite (*U. S. Geol. Surv., Bull.* **509,** pp. 89–95, 1912)] is proven—only that it is probable. The name francolite undoubtedly belongs to the material collected from the mine Wheal Franco, Buckland Monachorum, Travistock, Devon, and nobody knows just what this material is."

Mr. Hey kindly called attention also to the fact that neither the material analyzed by Henry (*Phil. Mag.*, vol. **36,** p. 134, 1850) nor the material analyzed by Maskelyne and Flight (*Jour. Chem. Soc.*, vol. **24,** p. 3, 1871) was from the Wheal Franco mine.

Under these circumstances a definite choice between the names francolite and staffelite cannot be made until the material from the Wheal Franco mine has been analyzed. Mr. Hey has indicated that microchemical methods would be required.

	a_0	c_0	c/a	Vol.
fluor-apatite, I	9.36 ± .01	6.88 ± .01	.7350	522
dahllite, Quercy, VI	9.41 ± .01	6.88 ± .01	.7311	528
dahllite, Wyoming, VII	9.39 ± .01	6.88 ± .01	.7329	525
dahllite [podolite], IX	9.41 ± .01	6.89 ± .01	.7322	528

It seems reasonable to assume in the case of specimen VI, that carbon replaces both calcium and phosphorus because this was the condition encountered in francolite (specimen IV), but there is need of further theoretical justification for the substitution of carbon for calcium in view of the fact that only a small amount of carbon has been shown to substitute for calcium in this compound.

This justification seems evident in the case of the alkali-apatites (dehrnite and lewistonite), because here an excess of negative charges would occur if substitution of OH-groups for O-ions did not tend to decrease the negative charges. As CO_2 is also present in these compounds it becomes necessary to assume that the carbon substitutes for calcium rather than phosphorus as the former substitution would also decrease the number of negative charges, whereas substitution of carbon for phosphorus would increase the negative charges. The analyses of these materials which are available hardly show sufficient water to produce electrostatic neutrality if carbon substitutes for calcium, and the substitution of carbon for phosphorus would require a considerably greater number of hydroxyl ions to produce electrostatic neutrality.

A more detailed investigation of the composition of dahllite seems necessary to establish conclusively that there is a significant amount of calcium replaced by carbon and this investigation is now in progress.

Fermorite and Mangan-Apatite

During the time this work was in progress only one specimen of mangan-apatite was available. This specimen (XVIII) is probably quite similar to the material studied by Landes (16) and analyzed by H. E. Vassar (Table 2, column 4). Dr. S. S. Goldich kindly determined the manganese content of this material. Based upon his manganese determination alone, the following composition has been assumed for the purpose of calculations:

	Computed wt. of oxides	No. of ions	M. W.
CaO	46.3	Ca = 8.50	340.6
MnO	10.3 ± .2	Mn = 1.50	82.4
P_2O_5	41.3	P = 6	186.2
F	3.7	F = 2	38.0
	101.6	O = 24	384.0
Less O	1.6	42	1,031.2
	100.0		

If the molecular weight is taken as 1031, the theoretical density becomes 3.317 for the lattice dimensions given below. This is comparable with the measured density which is 3.301 (4°C.). The density of mangan-apatite is appreciably greater than that of the ordinary fluor-apatite because the lattice dimensions are smaller and the molecular weight is greater. The lattice dimensions are comparable with fluor-apatite as follows:

	a_0	c_0	c/a	Vol.
fluor-apatite, I	$9.36 \pm .01$	$6.88 \pm .01$	.7350	522
mangan-apatite, XVIII	$9.33 \pm .01$	$6.80 \pm .01$	.7288	513

Fermorite is an example of the substitution of Sr for Ca but this mineral also shows an appreciable substitution of As for P. Specimen XIV has the largest unit cell observed for any of the materials examined, and it compares with fluor-apatite as follows:

	a_0	c_0	c/a	Vol.
fluor-apatite, I	$9.36 \pm .01$	$6.88 \pm .01$	.7350	522
fermorite, XIV	$9.60 \pm .01$	$7.00 \pm .01$	.7292	559

The interplanar distances for fermorite from Sausar Tehsil, India, are given in Table 1, column 5.

The original analysis (Table 2, column 5) cannot be entirely reconciled with the structure of fluor-apatite, as it is now understood, because the constituents of the F-positions have not been accounted for in a satisfactory manner. For this reason the theoretical density has not been calculated.

DEHRNITE, LEWISTONITE AND MERRILLITE

The powder diagrams indicate that dehrnite is a member of the apatite group, and, although it was not referred to this group in the original description (11), Larsen and Shannon state in a later paper (12) that it may be a member of the apatite group. Their supposition has been confirmed, and the lattice dimensions are as follows:

	a_0	c_0	c/a	Vol.
fluor-apatite, I	$9.36 \pm .01$	$6.88 \pm .01$	.7350	522
dehrnite, X	$9.31 \pm .01$	$6.87 \pm .01$	.7379	516
dehrnite, XI	$9.34 \pm .01$	$6.89 \pm .01$	.7377	521
dehrnite, XII	$9.35 \pm .01$	$6.89 \pm .01$	.7369	522

The interplanar distances obtained for the specimen from Dehrn, Nassau (X) are given in Table 1, column 6. An analysis by Shannon is shown in Table 2, column 6.

If Na-ions take the place of some Ca-ions of ordinary fluor-apatite, there is an appreciable decrease in positive charges in the structure which must be taken into account. This is probably accomplished by the substitution of monovalent negative ions for oxygen or the substitution of carbon for calcium, resulting in addition of positive charges. However, this structure has not been given detailed consideration because more accurate chemical data would be required for this work, and a suitable specimen was not available. This type of substitution is considered further below.

The name dehrnite is considered proper for an apatite containing a significant amount of sodium replacing calcium, and also containing CO_2, a sodium carbonate-hydroxyl-apatite.

The specimen of lewistonite examined in this work indicates that this mineral is also a member of the apatite group, although this view has not been previously advanced. The physical and optical properties of lewistonite are quite similar to those of apatite, according to Larsen and Shannon (12), except the lewistonite is considered biaxial with $2V = 42°$. Another specimen (an amygdule) is described as uniaxial and negative (12).

This specimen gave the following dimensions for the unit cell:

	a_0	c_0	c/a	Vol.
fluor-apatite, I	$9.36 \pm .01$	$6.88 \pm .01$	.7350	522
lewistonite, XIII	$9.35 \pm .01$	$6.89 \pm .01$	.7369	522
"kurskite," XX	$9.33 \pm .01$	$6.89 \pm .01$	.7385	519

These data are based upon the interplanar distances given in Table 1, column 7. Both of the specimens of dehrnite, from Utah, produce diagrams more closely resembling lewistonite than the dehrnite from Dehrn (specimen X). This would suggest that these dehrnites contain a greater amount of K- or OH-ions than the specimen from Dehrn. Shannon's analysis (12, p. 325) indicates that there are greater amounts of both of these ions in the material from Utah. Apparently the Utah material is intermediate between lewistonite and dehrnite. The unit cell of lewistonite is somewhat larger than that of dehrnite as would be expected from a comparison of the radii of K and Na, but the relative abundance of OH-ions in the two compounds is a complicating factor which prevents a direct comparison.

Lewistonite is considered a suitable name for an apatite containing an appreciable amount of potassium, regardless of the presence or absence of CO_2. Lewistonite is a potassium carbonate hydroxyl-apatite or a potassium-hydroxyl-apatite.[3]

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[3] Hintze's *Handbuch der Mineralogie*, V. 1, Abt. 4, p. 1036, gives dehrnite and lewistonite as varieties of collophane, but this hardly seems justifiable because both of these substances are distinctly crystalline.

Kurskite (specimen XX) produced a pattern quite similar to lewistonite, with which it is compared above. Apparently kurskite should be more closely associated with lewistonite and dehrnite than francolite, but this supposition would be difficult to confirm because it would seem almost impossible to separate this highly contaminated mineral in sufficient amounts for analytical purposes. A qualitative examination with a direct vision spectroscope, however, showed the presence of very strong Na-lines and weak K-lines.

Merrillite, which has been reported as occurring only in meteorites, was not examined because no specimen was available. However, in view of the rather broad limits of the isomorphism in apatite, and the marked similarity between this mineral and dehrnite [previously mentioned by Larsen and Shannon (11)], there can be little doubt that, if this mineral differs from dehrnite, the difference apparently lies in the absence of CO_2 in merrillite. Merrillite may tentatively be considered as a name applicable to a sodium hydroxyl-apatite.

If the statements regarding these minerals do not seem conclusive it is because the recorded chemical data cannot be reconciled with the x-ray data, and it was not possible to obtain sufficient material to check the recorded analytical results. It is to be remembered, however, that the specimens were obtained from the most reliable sources.

In each case (except "kurskite") only one substance appeared to be present and this substance produced a diffraction pattern with intensities similar to those of fluor-apatite but with slightly different values for θ.

Substitutions for Phosphorus

Ellestadite and Wilkeite

Before discussing an entirely new type of substitution, it is well to recall two types which have already been mentioned above. In fermorite there is a substitution of As-ions for P-ions, and in francolite a very small amount of vanadium substitutes for phosphorus. This sort of substitution involves no difference in valence and has been recognized for many years. The second type of substitution, carbon for phosphorus, however, involves a difference in valence and has not been previously brought to light in compounds of this sort. Here there is an increase in the negative charges associated with each tetrahedron which has carbon at its center instead of phosphorus, and this increase of negative charges must be compensated by other constituents of the structure.

The case would not be nearly so conclusive if it were not for the substitution of Si-ions for P-ions which occurs in wilkeite and ellestadite (15). Here there is an increase of the negative charges associated with those tetrahedra which have Si-ions at their centers, but the electrostatic neutrality of the structure is produced by the compensating effect of the substitution of sulfur for phosphorus.

The interplanar distances for wilkeite (XVI) are shown in Table 1, column 8, and those for ellestadite have been given elsewhere (15). The lattice dimensions for these materials compare with fluor-apatite as follows:

	a_0	c_0	c/a	Vol.
fluor-apatite, I	9.36 ± .01	6.88 ± .01	.7350	522
wilkeite, XVII	9.40 ± .01	6.89 ± .01	.7330	527
wilkeite, XVI	9.48 ± .01	6.91 ± .01	.7289	538
ellestadite, XV	9.53 ± .01	6.91 ± .01	.7251	544

The apatite-ellestadite series is the only series of the apatite group (as limited above) showing substitutions for phosphorus in which both end-members are known. With the exception of the fluorapatite-hydroxylapatite series it is the only one in which both end-members are known.

SUBSTITUTIONS FOR FLUORINE

In this investigation it was found that CO_3-groups do not substitute for fluorine in the apatite structure, but occupy other positions as mentioned above. The CO_3-groups had been relegated to the F-positions or to positions intermediate between the two F-positions on the three-fold axes, but the occurrence of CO_3-groups in these positions is not possible, as has been shown by Gruner and McConnell (4).

As early as 1856, Damour (21) recognized that OH-ions replaced fluorine in apatite, but his conclusions were not generally accepted until comparatively recently. As shown above, OH-ions occupy the fluorine positions in a number of minerals. Natural hydroxy-apatite has recently been described by Burri, Jakob, Parker and Strunz (22) and compares with fluor-apatite as follows:

	a_0	c_0	c/a	Vol.
fluor-apatite, Ontario, I	9.36 ± .01	6.88 ± .01	.735	522
hydroxy-apatite, Hospenthal	9.42	6.935	.736	533

The most poorly understood substitution for fluorine is oxygen. In 1912 Rogers (23) set down the formula $Ca_{10}O\,(PO_4)_6$, assuming that one O-ion replaces two F-ions. If this assumption were correct it would require that the O-ions occupy half of the positions intermediate between two F-positions or half of the F-positions, because the space group C_{6h}^2 requires reflection planes at $\frac{1}{4}$ and $\frac{3}{4}$ c. One of these assumptions would require a most peculiar type of coordination—an O-ion at the center of a distorted octahedron surrounded by 6 Ca-ions. Either assumption would require vacancies in half of the ionic positions of a particular sort. These conditions are objectionable and have been rejected in this work.

To account for oxy-apatite it is necessary to assume that the formula is $(Ca, X)_{10}\ O_2(PO_4)_6$ or $Ca_{10}\ O_2[(P, X)O_4]_6$. In the former case X represents a trivalent metal or carbon (15) or, possibly, nitrogen. In the latter case X represents a hexavalent ion, such as, sulfur. Sulfur and carbon are both present in ellestadite and other analyses of materials supposedly containing the oxy-apatite molecule report CO_2. More analytical data are necessary to establish which of these formulas is the correct one because some of the constituents reported in the older analyses were determined prior to the development of reliable methods for these constituents.

The substitution of chlorine for fluorine is well known but was not further investigated in this study. Mehmel (20) has based several calculations on the data supplied by Nacken (24), but it would seem that synthetic chlor-apatite should be investigated further, as his value for the specific gravity (3.17) is not consistent with the values reported for most apatites containing a large amount of chlorine. Nor is it comparable with the results of Hendricks, Jefferson and Mosley (25) who give a calculated value 3.20 and measured value 3.25. Cameron and McCaughey (26) obtained 3.010 for synthetic chlor-apatite.

Pehrman (27) has suggested that miscibility of the fluor-, chlor- and oxy-apatite molecules is not complete. He plotted the analyses available in 1925 on a ternary diagram and obtained an apparent hiatus. Hydroxy-apatite was not included in these computations, however, and other rather broad assumptions were required, such as, the validity of the fluorine determinations. Nevertheless, his conclusions seem plausible in view of the significant difference between the radius of chlorine and the radii of fluorine, oxygen and the OH-group.

SUBSTITUTIONS FOR OXYGEN

Gruner and McConnell (4) have found definite evidence of the substitution of fluorine for oxygen in francolite. The amount of fluorine present exceeds that of the theoretical fluor-apatite by only 0.34 weight per cent, to be sure, but this represents an amount about six times as great as the probable error of the method used to determine the fluorine. This mineral also suggests the substitution of OH-ions for oxygen, because 0.90 weight per cent of water was not removed during twenty-four hours at 300°C. However, this cannot be accepted as absolute evidence of the presence of OH-groups substituting for oxygen. The manner of liberation of the water in these compounds requires further investigation. Several dehydration curves have been obtained using a vacuum apparatus [a so-called tensi-eudiometer (28)] but a satisfactory interpretation of the dehydration curves has not been obtained.

In dehrnite, lewistonite and merrillite there is a strong indication that monovalent negative groups (OH) substitute for oxygen in order to compensate the substitution of monovalent positive ions (alkalies) for the bivalent positive ions (Ca) of fluor-apatite, and thus produce electrostatic equilibrium. As mentioned above, these structures have not been investigated in an exhaustive manner and substitutions of this sort have not been demonstrated beyond doubt, but they represent the only plausible explanation for these compounds which can be based on the data now available.

SUMMARY AND CONCLUSIONS

All of the minerals examined in this work are structurally similar to apatite, i.e. they have the space group, C_{6h}^2, as indicated by the similarities of the spacing and intensities of their powder diagrams. There is every indication that the structure assigned to fluor-apatite by Náray-Szabó and by Mehmel is essentially correct.

The formulas, lattice dimensions and densities of certain representative specimens are given in Table 3. These are mostly isomorphous members of several complex series and the properties of the end-members are not known, except in fluor-apatite, ellestadite and hydroxy-apatite. Four of these apatites are carbonate-apatites and the *c*-dimension of each of these is similar to that of fluor-apatite within the limits of accuracy for the method used. Considerably greater differences were found in the *a*-dimensions, but it is probably not possible to distinguish between the various members of this group by means of *x*-ray measurements alone. In favorable cases it may be possible to distinguish the different members by combining a few qualitative tests with *x*-ray measurements.

The structure of apatite seems to be remarkably stable, permitting a number of rather unusual types of substitution and involving a considerable number of ions. Several different ions apparently substitute for each of the four ions of fluor-apatite.

(1) Calcium is replaced by sodium, potassium, manganese, strontium, magnesium and carbon.

(2) Phosphorus is replaced by sulfur, silicon, arsenic, vanadium and carbon.

(3) Fluorine is replaced by chlorine and oxygen ions and by hydroxyl groups, but not by CO_3-groups.

(4) Oxygen is replaced by fluorine ions and hydroxyl groups. These substitutions involve differences in valency as well as differences in ionic radii. The most surprising is the substitution of carbon for calcium and for phosphorus, and fluorine for oxygen in one particular instance but oxygen for fluorine in another.

TABLE 3. SUMMARY OF STRUCTURAL DATA FOR VARIOUS MINERALS OF THE APATITE GROUP

Mineral	Structural Composition	a_0	c_0	c/a	Vol.[1]	Calc. D[2]	Meas. D
Fluor-apatite	$(Ca_3F)_2(PO_4)_6Ca_4$	9.36	6.88	.735	522	3.187	3.176^3
Dahllite	$Ca_6(OH)_2(P, C)_6O_{24}$ $(Ca, C)_4$	9.41	6.88	.731	528	—	2.93
Dehrnite	$(Ca, Na)_6(OH)_2(PO_4)_6$ $(Ca, C)_4$	9.31	6.87	.738	516	—	3.04^4
Lewistonite	$(Ca, K, Na)_6(OH)_2(PO_4)_6$ $(Ca, C)_4$	9.35	6.89	.737	522	—	3.08^4
Francolite	$(Ca_3F)_2(P, C)_6$ $(O, OH, F)_{24}(Ca, C)_4$	9.34	6.88	.737	520	3.151	3.147
Hydroxy-apatite	$(Ca_3OH)_2(PO_4)_6Ca_4$	9.42^5	6.935^5	$.736^5$	533^5	3.109	3.067^5
Wilkeite	$Ca_6(Cl, F, OH, O)_2$ $(P, S, Si, C)_6O_{24}(Ca, C)_4$	9.48	6.91	.729	538	—	3.120
Fermorite	$(Ca, Sr)_6(F, OH, O)_2$ $(P, As)_6O_{24}Ca_4$	9.60	7.00	.729	559	—	3.518^6
Mangan-apatite	$(Ca, Mn)_6F_2(PO_4)_6Ca_4$	9.33	6.80	.729	513	3.317^7	3.301
Ellestadite	$Ca_6(Cl, F, O, OH)_2$ $(S, Si, P, C)_6O_{24}(Ca, C)_4$	9.53	6.91	.725	544	3.046	3.068

[1] Vol. $= a^2c \sin 60° \times 10^{24}$ cm³.

[2] Calc. density $= M\ W \times 1.649/\text{Vol.}$

[3] According to A. S. Dadson (3).

[4] According to Larsen and Shannon (12).

[5] According to Burri, Jakob, Parker, and Strunz (22). The density measurement is for 18° C. and the calculated value of D was not given by these authors but is based on their data.

[6] According to Smith and Prior (14).

[7] This calculated value of D was not based upon a complete analysis but upon a determination of MnO, as mentioned above.

The substitution of monovalent positive ions for bivalent positive ions, compensated by a substitution of monovalent negative ions for bivalent negative ions, is the only plausible explanation for certain alkali-apatites.

The isomorphism of this group is considerably more complicated than has been previously recognized. The value of accurate and complete analyses cannot be overemphasized in connection with any further investigations of these minerals. Analyses which are incomplete or which were made by methods now obsolete, or were made on heterogeneous materials, are almost valueless for this work in view of the complexity of the isomorphism.

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