

CRYSTAL CHEMICAL INVESTIGATION OF NATURAL APATITES¹

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ABSTRACT

Studies were made of the mineralogy and composition of the apatite fractions of 110 phosphate ores that represent nearly all the economically important deposits in the world. Most of the samples represent sedimentary deposits, and their apatites are the carbonate-substituted variety, francolite, but some igneous and metamorphic deposits were included. All the apatites showed the same correlations of crystallographic properties with chemical composition. Values of a ranged from 9.322 to 9.409 Å, and those of c from 6.876 to 6.901 Å; the standard error for both parameters was 0.003 Å or less. Isomorphous substitution of carbonate for phosphate in the apatite structure results in a non-linear decrease of a with increasing substitution of CO_3 for PO_4 , and calculations of unit-cell contents show that substitution of CO_3 for PO_4 is practically one for one.

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Apatite, the tenth most abundant mineral, occurs in sedimentary, igneous, and metamorphic rocks; its physical, chemical, and crystallographic properties vary considerably. The natural apatites are usually designated as fluor-, chlor-, or hydroxyapatites on the basis of the principal anion that occupies the channels through the structure parallel to c that result from the packing arrangement of the calcium, oxygen, and phosphorus atoms. Fluorapatite, the principal igneous and metamorphic apatite, occurs in massive, well-formed crystals with compositions close to that of the ideal $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$; its structure was determined independently by Náráy-Szabó (1930) and Mehmel (1930). Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and chlorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$, occur only rarely in nature. Posner, Perloff, and Diorio (1958) and Skinner and Burnham (1966) determined the structure of hydroxyapatite from synthetic preparations; Kay, Young, and Posner (1964) refined the structure by X-ray and neutron diffraction studies on natural crystals. Young and Elliott (1966) described in detail the differences between the structures of the three apatites.

Sedimentary apatites are microcrystalline and differ considerably in composition from pure fluor- and hydroxyapatites because of extensive substitution of carbonate for phosphate and of other metals for calcium. The minerals in which this substitution has occurred and which have fluorine contents higher than one percent are designated as francolites

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(McConnell, 1938). The X-ray patterns are typically apatitic with slight positional shifts of the X-ray maxima that indicate changes in the cell parameters.

The literature on carbonate apatites has been reviewed by Silverman *et al.* (1952), Ames (1959), and Elliott (1964). The contributions of McConnell (1938, 1952, 1959, 1965) to this field are especially noteworthy. Carbonate apatites are now recognized as a true mineral species, and it is generally agreed that carbonate can substitute for phosphate in the structure, although there is still disagreement on the details of the substitution. Changes in the *a* axis with changes in the carbonate content have been reported (Maslennikov and Kavitskaya, 1956), but no satisfactory correlation has been made between the unit-cell dimensions of the apatites and their carbonate contents.

Sedimentary apatites almost always contain more fluorine than is required by the empirical formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, and the excess fluorine usually has been assumed to be present as fluorite in crystals too small to be detected petrographically or by X-ray. From a chemical study of sedimentary apatites, Borneman-Starinkevich and Belov (1953) suggested that when a planar carbonate ion substitutes for a tetrahedral phosphate ion the vacant oxygen site is occupied by a fluorine ion. This unusual carbonate-fluorine arrangement would have no mutual bonding, but it would preserve electroneutrality and complete the coordination of the cations in the structure. Elliott (1964) considers this substitution the most logical explanation of the composition of carbonate apatites that has been advanced, and Smith and Lehr (1966), Trueman (1966), and Gulbrandsen (1966) support this substitution with mineralogical data.

In the apatite structure, two faces of the phosphate tetrahedron are parallel to the *c* axis, and two are mutually inclined to the *c* axis. From microscopic studies, Trautz (1960) concluded that the birefringence of apatite indicated that the carbonate occupied one of the planes inclined to the *c* axis. Subsequent polarized infrared studies of single crystals led Elliott (1964) to the same conclusion.

Hendricks and Hill (1950) were unable to distinguish the X-ray diffraction patterns of francolite from those of fluorapatite, even in high orders of diffraction, but they indicated that substitution of carbonate for phosphate would cause minor changes in the intensities of certain reflections. These suggested variations in intensity had been reported previously by Gruner and McConnell (1937). The precise measurements of X-ray intensities which would be required to distinguish between the structure of francolite and that of unsubstituted apatite are difficult to make from powder patterns.

This paper presents the results of examinations of apatite concentrates

from 110 phosphate rocks that represent almost all the commercial phosphate deposits in the world. The examinations were made in a continuing attempt to correlate the crystallographic properties of the phosphates with their chemical compositions. Results of statistical treatment of the data are compatible with the isomorphous substitution of carbonate for phosphate and of sodium and magnesium for calcium.

EXPERIMENTAL PROCEDURE

X-ray Methods. The powder diffraction data were obtained with a Norelco diffractometer and nickel-filtered $\text{CuK}\alpha$ radiation from a tube operated at 40 kv and 18 ma. The divergence and scatter slits were 1° wide and the receiving slit was 0.003" wide, conditions chosen to permit both maximum resolution of the peaks and sufficient peak intensity for accurate measurements. The goniometer was aligned so that the errors in 2θ for silicon or quartz peaks scanned at 0.125° 2θ /minute and a chart speed of 30 inches/hr were 0.005° or less. The apatites examined were the minus 200-mesh concentrates that had been prepared for chemical characterization.

The line profiles of back-loaded samples were recorded at a scanning rate of 0.25° 2θ /minute over the angular range 25° to 54° 2θ with a time constant of 4 sec and a chart speed of 30 inches/hr. Continuous check of the goniometer alignment was obtained by measuring a series of α -quartz (sample impurities) and spinel (MgAl_2O_4 , internal standard) lines and preparing correction graphs for the range recorded.

Determination of Lattice Constants. Interplanar spacings (d_{obs}) of the line profiles were calculated in the usual manner from Bragg's equation for 2θ values measured to 0.01° with a maximum error of 0.005° . The crystallites usually were so small that the $\text{CuK}\alpha_1\alpha_2$ doublet was not resolved, and a weighted average of the two wavelengths was used, $\lambda = 1.54178 \text{ \AA}$. For well-crystallized samples, the $\text{CuK}\alpha_1$ value, $\lambda = 1.54050 \text{ \AA}$, was used.

The lattice constants for each sample were calculated by an iterative least-squares computer program (Moore and Ziegler, 1960) that solves a truncated Taylor series by the Newton-Raphson method for two unknowns. The relationship for this problem is

$$d_{\text{obs}}(a_0, c_0) = d_{\text{calc}}(a_{n+1}, c_{n+1}) + \frac{\partial d}{\partial a_0} \Delta a + \frac{\partial d}{\partial c_0} \Delta c \quad (1)$$

where the d_{obs} are the values from the Bragg equation produced by the lattice constants of the sample (i.e., a_0, c_0), and the d_{calc} are the values calculated from the general expression for hexagonal crystals [equation (2)] from a first approximation value for the unit-cell constants (i.e., a_{n+1}, c_{n+1}) and the Miller indices (hkl) corresponding to each d_{obs} .

The d_{calc} were obtained from the equation

$$d_{hkl} = \frac{1}{\sqrt{\frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}}} \quad (2)$$

where the Miller indices were 002, 300, 202, 310, 222, 312, 213, 321, 410, 402, and 004 and the first approximation of the lattice constants were those of unsubstituted fluorapatite, $a = 9.3700$ and $c = 6.8800$, reported by Naray-Szabo (1930).

The differences, Δd , between the observed d -values and the calculated d -values are minimized in the computer program by determining the increment by which the first approximation values of a_{n+1} and c_{n+1} must be changed to make Δd approach zero. These incre-

ments are the Δa and Δc terms of equation 1. The solution of the problem is

$$\begin{bmatrix} \Delta a \\ \Delta c \end{bmatrix} = \frac{\begin{bmatrix} \sum_1^N \left(\frac{\partial d}{\partial a_0} \cdot \Delta d \right) \\ \sum_1^N \left(\frac{\partial d}{\partial c_0} \cdot \Delta d \right) \end{bmatrix}}{\begin{bmatrix} \sum_1^N \left(\frac{\partial d}{\partial a_0} \right)^2 & \sum_1^N \left(\frac{\partial d}{\partial a_0} \cdot \frac{\partial d}{\partial c_0} \right) \\ \sum_1^N \left(\frac{\partial d}{\partial a_0} \cdot \frac{\partial d}{\partial c_0} \right) & \sum_1^N \left(\frac{\partial d}{\partial c_0} \right)^2 \end{bmatrix}} \quad (3)$$

where N is the number of reflections used to evaluate a_{n+1} and c_{n+1} . In a computer program for minimizing Δa and Δc by the least-squares technique, a_1 is replaced by $(a_1 + \Delta a)$ or a_2 and c_1 by $(c_1 + \Delta c)$ or c_2 , and the calculation is repeated. When Δa and Δc decrease to less than the standard error of a_{n+1} and c_{n+1} (usually in 3 cycles), the calculation is stopped. The maximum standard error in a_{n+1} and c_{n+1} values reported here is 0.002 Å; the usual error is 0.001 Å or less.

The standard errors are calculated by the statistical approach presented by Box (1960): Standard error in the observed d values (SD) =

$$\sqrt{\frac{\sum_1^N (\Delta d)^2 - \Delta a \cdot \sum_1^N \left(\Delta d \frac{\partial d}{\partial a_0} \right) - \Delta c \cdot \sum_1^N \left(\Delta d \cdot \frac{\partial d}{\partial c_0} \right)}{N - 2}} \quad (4)$$

$$\text{Standard error in } a = \text{SD} \sqrt{\sum_1^N \left(\frac{\partial d}{\partial a_0} \right)^2} \quad (5)$$

$$\text{Standard error in } c = \text{SD} \sqrt{\sum_1^N \left(\frac{\partial d}{\partial c_0} \right)^2} \quad (6)$$

Each of these standard errors is at the 68 percent confidence level.

A multiple-precision computer program is used to evaluate these constants and their standard errors. The advantage of the program is that the computer can carry a large number of significant figures and so remove the influence of computer truncation (usually at seven to nine decimals). The application of such a program decreases the standard errors produced by our conventional Fortran program by an average of 30 percent.

A weighting scheme of $1/d^2$ was used in calculating the unit-cell data presented in Table 1 to place the emphasis on the reflections at the high angles. This method of determining lattice constants has four advantages. First, it produces reliable results for non-cubic materials whose diffraction is recorded at values of θ less than 30° . Thus, it is particularly useful for diffractometer studies as well as for camera work. Tests have shown that this method produces results with much smaller standard errors than those produced by other methods.

Second, the technique uses all the recorded planes in its cell refinements instead of only a few arbitrarily selected planes.

Third, this method makes unnecessary the use of predetermined values for calculation of the cell constants. In our application we used the cell constants of unsubstituted fluorapatite as a first approximation, but we have obtained the same result with any integer from 1 to 10 as the first approximation for a and c , although a few more cycles were required to decrease the standard errors to acceptable values than when the initial values were those known for fluorapatite.

TABLE 1. COMPOSITION OF PHOSPHATE ROCKS AFTER EXTRACTION WITH SILVERMAN SOLUTION

No.	Source	Composition, weight percent						Unit-cell dimensions, Å		Crystallite size, Å	
		CaO	P ₂ O ₅	F	CO ₂	Na ₂ O	MgO	a	c	a	c
2B	Florida	50.65	34.51	4.10	3.30	0.65	0.17	9.333	6.890	450	725
12	Quebec, Canada,	54.90	40.57	3.40	0.20	.25	.20	9.385	6.891	2000	2000
17	Morocco	53.70	37.90	4.30	2.30	.28	.80	9.344	6.894	450	650
21B	North Carolina	47.50	30.56	3.76	4.90	.96	.46	9.327	6.890	275	475
22	South Carolina	42.90	27.74	3.92	4.70	1.20	.33	9.322	6.900	625	700
26B	Ocean Island	53.60	40.24	3.01	1.10	.13	.14	9.377	6.885	550	800
44	Australia	52.00	39.20	3.81	0.30	.13	.80	9.366	6.883	2000	2000
46	Peru	46.10	31.00	2.80	4.10	1.40	.53	9.337	6.886	225	575
85	Senegal	52.42	37.46	3.83	1.65	.17	.30	9.352	6.891	450	700
93	Tennessee	48.50	34.90	3.68	1.40	.31	.10	9.358	6.890	475	750
105	Kola, USSR	52.40	38.30	3.18	0.40	.36	.40	9.378	6.891	800	2200
113	Idaho	47.40	33.00	3.43	1.80	.81	.17	9.354	6.890	400	625
114	California	47.40	36.14	3.87	4.40	.87	.59	9.335	6.886	250	425
125	Israel	52.10	35.00	3.83	3.30	.48	.28	9.340	6.891	350	600
129	Florida	50.90	33.10	3.90	3.60	.60	.30	9.333	6.893	350	475
221	Sweden	53.40	38.60	4.30	0.10	.14	.25	9.377	6.886	2000	2000

Finally, mensuration errors can be detected and removed by comparing the Δd values with the standard error in the observed d values determined for each set of data. The limiting factors are the number of reflections considered and the statistical validity of the data if the incorrect reflections are removed rather than changed. This method of calculation is not recommended for less than six reflections, but natural apatites rarely present this limitation.

Approximate crystallite sizes were determined by the line-broadening technique of Rau (1962). The line profiles of the 002 and 300 reflections were obtained by scanning at a rate of $0.125^\circ 2\theta/\text{min.}$, with a time constant of 8 and a chart speed of 30 inches/hr. These results are included in Table 1.

Chemical Characterization. Most of the apatite samples were high-grade commercial concentrates; some samples were concentrated by hand sorting of washed ore. Igneous and metamorphic apatites were upgraded by hand sorting and heavy-liquid separation. None of the apatites had had any thermal treatment.

A representative sample of each apatite was obtained by quartering and grinding to minus 200 mesh. Free carbonate materials were removed by extraction with Silverman's solution (1952) by a modified procedure (Smith and Lehr, 1966); the extraction was repeated if residual free carbonates (usually coarse dolomite or ankerite) were detected petrographically. The extracted apatites were washed repeatedly with water, dried at 105°C , and submitted for chemical analysis. The principal residual minerals usually were siliceous.

Although more than 25 elements have been reported in igneous and metamorphic apatites, the compositions of sedimentary apatites can be closely approximated by their contents of CaO, P₂O₅, F, CO₂, Na₂O, and MgO. To determine the composition of the apatite portions of the samples and to minimize the contributions of minor amounts of clays, feldspars, and other accessory minerals sometimes present, the samples were dissolved rapidly in warm dilute (3*N*) HCl and the filtrates were analyzed for the acid-soluble

constituents. Determinations of CO_2 and F, however, required treatment of the entire samples. The compositions of some representative samples in terms of these major constituents are shown in Table 1.²

Calculation of the contents of the unit-cell appeared to be the best approach for placing all the data on a uniform basis. This approximation ignores minor substitutions of rare earths for calcium, and of sulfur, silicon, and vanadium for phosphorus, but these omissions contribute no significant errors in the statistical correlations of a large number of samples. A statistical approach is necessary because samples of pure sedimentary apatites are very rare. All the samples for this study were examined petrographically, and only those that were mostly apatite are included. The principal diluent was quartz or chalcedony; silicates, iron oxides, and heavy minerals were present as minor constituents. Calcite, dolomite, and other rhombohedral carbonates were common impurities in unextracted samples. Samples of phosphate rocks, such as those from Curacao and Senegal, that contained significant amounts of non-apatitic phosphates were omitted from the series.

Isomorphous substitutions of carbonate for phosphate and of sodium and magnesium for calcium produce significant decreases in the formula weight of apatite. To approximate the influence of the substitutions on the molecular weight the general formula for sedimentary apatites was idealized as



on the assumptions that the basic substitution is CO_3 for PO_4 and that electroneutrality must be maintained. In the samples examined, x varied from near zero to 1.5. The values of y and b varied widely, but the average values were $y = 0.4x$ and $b = 0.4x$. Electroneutrality is preserved when $a = x - y$. A plot of these data describes the linear relationship:

$$\text{Formula weight} = 1008.64 - 7.75 (\text{wt. } \% \text{ CO}_2 \text{ in apatite})$$

1008.64 is the formula weight of unsubstituted fluorapatite, and the CO_2 is contributed by apatite alone and by no other carbonate-containing mineral.

For each sample, a correction was made for the non-apatitic minerals in which the amounts of the seven constituents were adjusted by a common factor to total 100 percent after allowance for the oxygen equivalent of fluorine. The adjusted weight fractions were then divided by their respective molecular or equivalent weights and multiplied by the calculated formula weight to obtain the moles or equivalents per unit cell.

The sum of the cations (Ca, Na, and Mg) plus the anions (PO_4 and CO_3) obtained by these calculations averages 16.084, which is close to that of the ideal apatite structure of 10 cation and 6 anion sites per unit cell. To facilitate the comparison of the data with the actual apatite structure and to minimize the effect of analytical errors, the cations and anions were adjusted by a common factor to total 16.000. Some representative results are shown in Table 2.¹

The adjusted values closely approach electroneutrality, and the near agreement of the cation sums with 10 and of the anion sums with 6 indicates the agreement of our statistical model with that of the apatite structure. There are, of course, small errors resulting from minor anion and cation substitutions that are known to take place in this structure, from

² To obtain a copy of tables listing the analyses of samples, order NAPS Document 0535 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting in advance \$1.00 for microfiche or \$3.00 for photocopies, payable to ASIS/NAPS.

TABLE 2. ADJUSTED COMPOSITIONS OF PHOSPHATE ROCKS

No.	Adjusted composition, weight percent								Moles/formula weight						Molar sums		Mole ratio		Sum of charges				
	CaO		P ₂ O ₅		F		CO ₂		Na ₂ O		MgO		Ca	PO ₄	F	CO ₂	Na	Mg	Cations	PO ₄ + CO ₃	CO ₃ : PO ₄	Pos.	Neg.
	CaO	P ₂ O ₅	F	CO ₂	Na ₂ O	MgO	Ca	PO ₄	F	CO ₂	Na	Mg											
2B	55.18	37.59	4.47	3.59	0.71	0.19	9.701	5.223	2.318	0.805	0.225	0.045	9.972	6.028	0.154	19.72	19.60						
12	55.95	41.35	3.47	0.20	.25	.20	9.988	5.832	1.826	.046	.082	.051	10.121	5.879	.008	20.16	19.42						
17	55.07	38.87	4.41	2.36	.29	.82	9.742	5.433	2.303	.532	.092	.202	10.036	5.964	.098	19.98	19.66						
21B	54.74	35.22	4.33	5.65	1.11	.53	9.468	4.813	2.212	1.245	.346	.128	9.942	6.058	.259	19.54	19.14						
22	53.98	34.90	4.93	5.91	1.51	.42	9.347	4.775	2.521	1.305	.473	.100	9.920	6.080	.273	19.37	19.46						
26B	55.26	41.49	3.10	1.13	.13	.14	9.832	5.832	1.630	.257	.043	.036	9.911	6.089	.044	19.78	19.64						
44	54.90	41.38	4.02	0.32	.14	.84	9.822	5.851	2.124	.072	.044	.210	10.077	5.923	.012	20.11	19.82						
46	54.28	36.50	3.30	4.83	1.65	.62	9.326	4.955	1.672	1.057	.513	.149	9.988	6.012	.213	19.46	18.65						
85	55.58	39.72	4.06	1.75	.18	.32	9.885	5.582	2.132	.396	.058	.079	10.022	5.978	.071	19.99	19.67						
93	55.41	39.87	4.20	1.60	.35	.11	9.878	5.616	2.212	.363	.114	.028	10.020	5.980	.065	19.93	19.79						
105	55.87	40.84	3.39	0.43	.38	.43	9.936	5.738	1.780	.097	.124	.106	10.165	5.835	.017	20.21	19.19						
113	55.52	38.65	4.02	2.11	.95	.20	9.789	5.385	2.091	.474	.303	.049	10.141	5.859	.088	19.98	19.19						
114	51.65	39.38	4.22	4.79	.95	.64	9.033	5.442	2.177	1.068	.300	.156	9.490	6.510	.196	18.68	20.64						
125	55.73	37.44	4.10	3.53	.51	.30	9.782	5.192	2.123	.789	.163	.073	10.018	5.982	.152	19.87	19.28						
129	55.99	36.41	4.29	3.96	.66	.33	9.795	5.033	2.215	.883	.209	.080	10.084	5.916	.175	19.96	19.08						
221	56.17	40.60	4.52	0.11	.15	.26	10.096	5.766	2.400	.024	.048	.066	10.210	5.790	.004	20.37	19.75						

traces of non-apatitic phosphates, from sodium and magnesium in the silicate minerals, and from other minor discrepancies. The model, however, is as reliable as the chemical and X-ray data, and it is suitable as a basis for the interpretation of the composition and structure of the sedimentary apatites.

CORRELATION OF DATA

This study was mainly an exploration of the correlations of the cell constants of apatites with their chemical compositions. The values of a range from 9.322 to 9.392 Å and those of c range from 6.877 to 6.900 Å. The standard error for these values is 0.002 Å or less, usually 0.001 Å at the 68 percent confidence level. The greater range of a than of c indicates that the substitutions have a greater effect in the a direction, and the tests of the correlation with the chemical data were based largely on the values of a , although several models were tested with the values of c also.

The ranges in composition of the apatites, expressed as moles per formula weight, were Ca 9.326 to 10.102, PO₄ 4.610 to 5.872, CO₂ 0.024 to 1.347, F 1.210 to 2.858, Na 0.041 to 0.513, and Mg 0.021 to 0.253. Of the 110 samples examined, only 22 contained less than 2 moles F per formula weight; these samples were either igneous apatites, apatites from Pacific Islands, or apatites that had been formed in fresh-water lakes (Sechura, Peru) instead of in the ocean. Infrared examination showed that all these apatites contained hydroxyl which apparently had substituted for part of the fluorine.

Mathematical models were set up to determine the effects of several parameters on the correlations of the cell constants with the chemical compositions of the apatites. Smith and Lehr (1966) made a similar study with a smaller number of samples, but they assumed that there had been no significant isomorphous substitution for calcium. More recent work (Lehr *et al.*, 1967), however, shows that the substitution of sodium and magnesium for calcium has a significant effect, and the models should be modified to allow for the effects of other substitutions on the properties of the unit cell and for the larger number of samples studied.

The mathematical models that were tested by least-squares regression analysis are shown in Table 3. For all samples the values of a and c were correlated with the unit-cell chemical constituents. The constants of all the models were calculated by a multiple-precision computer program, and the standard errors are calculated at the 68 percent confidence level.

The standard error of the observed values of a (a_0) minus those calculated (a_c) from the model is considered to be the best measure of the agreement of the calculated values with the observed values. Model 1, in which fluorine is the only parameter considered, extrapolates to $a = 9.431$ Å which is close to the value of $a = 9.427$ Å reported for fluorine-free hydroxyapatite (Posner *et al.*, 1958). The relatively large standard errors

TABLE 3. MATHEMATICAL CORRELATION OF AXIS LENGTHS WITH CHEMICAL COMPOSITION^a

Model	Constants				Standard error					
	$a(c)$	b	e	f	$a(c)$	b	e	f	$a_0 - a_c$ or $e_0 - e_c$	R
1. $a_0 = a + bF$	9.4311	-0.0400			0.0130	0.0061			0.0152	0.57
2. $a_0 = a + b(F + CO_2)$	9.4368	-0.0321			0.0040	0.0014			0.0072	0.92
3. $a_0 = a + bF + eCO_2$	9.4170	-0.0205	-0.0389		0.0055	0.0027	0.0019		0.0064	0.94
4. $a_0 = a + bF + eCO_2 / (F \times CO_2)$	9.4436	-0.0332	-0.0899	0.0238	0.0100	0.0048	0.0164	0.0076	0.0061	0.94
5. $a_0 = a + bCO_2$	9.3769	-0.0439			0.0018	0.0023			0.0082	0.90
6. $a_0 = a + bCO_2 + e(CO_2)^2$	9.3842	-0.0737	0.0214		0.0027	0.0089	0.0062		0.0077	0.91
1c. $e_0 = c + bF$	6.8755	0.0074			0.0034	0.0016			0.0043	0.41
2c. $e_0 = c + b(F + CO_2)$	6.8801	0.0039			0.0024	0.0008			0.0043	0.44

^a $a_0(e_0)$ = observed length, \bar{A} , of $a(c)$ axis. $a(c)$ = limiting length, \bar{A} , of $a(c)$ axis. $a_e(e_c)$ = length, \bar{A} , of $a(c)$ axis calculated from model. R = correlation coefficient. Compositions of F and CO_2 are in moles per formula weight.

of this model indicate, however, that the correlation of the length of the a axis with fluorine alone is poor.

The combined effects of fluorine and carbonate are tested in model 2. This model predicts the observed value for the a axis with half the standard error of the model based on fluorine alone. The value for a predicted when $(F + CO_3) = 0$ is 9.436_8 \AA which is close to the values reported in the literature for hydroxyapatite. In model 3, treatment of the effects of carbonate and fluorine separately improves the correlation further. The ratio of the coefficient of the carbonate term to that of the fluorine term indicates that a change in the carbonate content causes twice as much change in the value of a as the same change in the fluorine content. The addition of a fluorine-carbonate interaction term in model 4 further improves the correlation, and the presence of a statistically significant ($d/\sigma = 3.10$) interaction term must not be ignored in considerations of proposed substitution systems.

Model 3 shows that carbonate has a greater effect on the value of a than does fluorine, and in model 5 the effect of carbonate alone is tested. This model extrapolates to a value of a of 9.377 \AA for carbonate-free apatites which is close to that of 9.370 \AA reported by Naray-Szabo (1930) for fluorapatite. The plot of a vs. CO_3 , however, is not the straight line predicted by model 5. Although addition of a second-degree term to model 5, as in model 6, improves the correlation of a with the carbonate content, the correlation is poorer than that of model 4.

The models tested for correlation of the values of a were tested also with the values of c . These correlations were poorer than those with the values of a because of the small range of c , 0.023 \AA , and only the two best models are reported here.

Model 1c predicts a linear relation between c and the fluorine content that extrapolates to a limiting value of 6.876 \AA . Model 2c shows that the relation between c and the sum of fluorine plus carbonate also is linear, but its slope is only about half that of model 1c and it extrapolates to a limiting value of 6.880 \AA . These models correlate the observed changes in c to approximately the same extent. In the absence of other criteria, model 1c is preferred because of its simplicity and its closer approach to the observed minimum value of c of 6.877 \AA .

DISCUSSION OF RESULTS

The statistical models suggest several meaningful relationships of unit-cell constants to chemical composition. The most important of these is the statistically significant interaction between carbonate and fluorine shown in model 4. This interaction is helpful in a purely mathematical correlation of the data, but it also is fundamental to any consideration of

the substitution mechanism involved in carbonate-substituted fluorapatites. The interaction term is statistical evidence in support of the substitution of $(\text{CO}_3^{2-} \cdot \text{F}^{1-})$ for PO_4^{3-} as proposed by Borneman-Starinkevich and Belov (1953), and this substitution explains why many sedimentary apatites contain more fluorine than can be incorporated on the hexad sites in the structure. The presence of fluorine at some of the oxygen sites that are left vacant by substitution of the planar carbonate groups for the tetrahedral phosphate groups thus is compatible with the chemical data and helps to preserve the integrity of the structure by maintaining electroneutrality and cation coordination. It should be noted, however, that the interaction term does not show the ratio of fluorine to carbonate involved in the substitution. The mean value of the mole ratio of excess fluorine (i.e., all the fluorine in excess of two atoms per formula weight) to carbonate calculated from all the data is about 0.4. In more general terms, assuming that all six-fold-axis sites are occupied by fluorine atoms, almost half of the carbonate that has substituted for phosphate is accompanied by fluorine to complete the pseudotetrahedral group, and the remaining oxygen sites are not necessarily filled.

A schematic representation of model 4 is shown in Figure 1. The compositions of all the samples examined in this study fall on the planes LMQR and MNPQ which are curved because of the interaction term ($F \times \text{CO}_3$). In model 6 (Figure 2) also the change in a with increasing carbonate substitution is curvilinear because of the diminishing effect of the

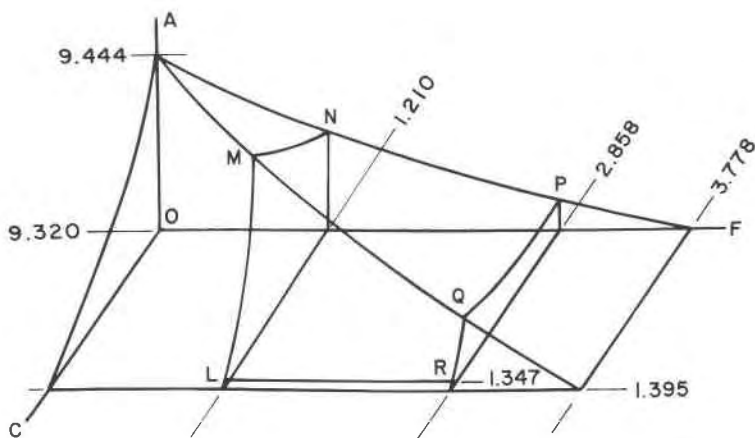


FIG. 1. Correlation of length of a axis with carbonate and fluorine contents by model 4. OA = length of a axis, Å; OC = moles CO_3 /formula weight; OF = moles F/formula weight. Observed values fall on curved planes LMQR and MNPQ.

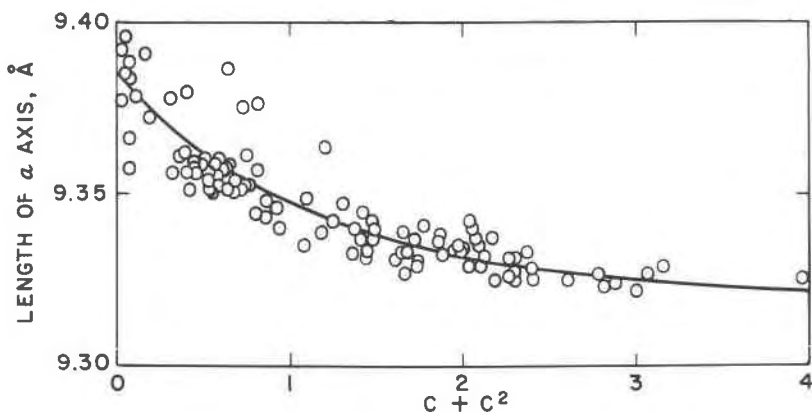


FIG. 2. Correlation of length of a axis with carbonate content by model 6. C = moles CO_3 /formula weight.

substitution of carbonate for phosphate as the substitution increases. Thus the initial carbonate substitution causes proportionately a greater change in a than does addition to an already highly substituted structure. These curvilinear relationships show also that there are limits to the amount of substitution that is possible without disrupting the apatite structure.

To determine the minimum values of a that correspond to these limits of substitution it is necessary to set the partial derivatives with respect to fluorine and carbonate in models 4 and 6 equal to zero and solve for the limiting substitution values. For model 4, the limiting values are 3.777 atoms of fluorine per formula weight, 2 atoms of which are on the hexad sites, and 1.395 carbonate groups per formula weight, corresponding to a minimum value of a of 9.318 Å. For model 6 the limiting value is 1.722 carbonate groups per formula weight, corresponding to a minimum value of a of 9.321 Å. These predicted values are in good agreement with the minimum observed value of a of 9.322 Å. Smaller values of a that have been reported in the literature (Whippo and Murowchick, 1967) are suspect because of the experimental methods that were used in their determination. The highest observed carbonate content is 1.347 moles per formula weight which is close to the maximum value predicted by model 4. The difference between the maximum carbonate substitutions predicted by the two models is caused by the magnitude of the values of b for each model and re-emphasizes the greater effect of carbonate than of fluorine on the length of the a axis. A physical indication of a limiting value of the substitution of carbonate for phosphate is shown by the general decrease in crystallite size with increasing substitution (Table 1), an observation

reported also by LeGeros *et al.* (1967). This decrease in crystallite size with increasing substitution of carbonate for phosphate may indicate the development of structural incompatibilities between substituting groups and the PO_4 framework which limit the number of unit-cell repetitions that are possible before the misfit of the structural units prevents further growth of the individual crystallite.

The changes in the value of a thus correlate well with the variations in chemical composition. It seems probable that the substitution of anions is coupled with that of cations to preserve the electroneutrality of the structure. Examples of this effect are discussed below.

Two statistical models for correlating c with the chemical composition are presented in Table 3. The models correlate the data about equally well, and the positive slopes of both models are interpreted to indicate that the value of c increases as the structure adjusts to incorporate fluorine at oxygen sites in addition to the fluorine on the hexad channel sites. This "excess fluorine" becomes more significant as the substitution of carbonate for phosphate increases. The resultant increase in c , which is in contrast to the decrease in a with increasing substitution, probably is a function of the extent to which fluorine is associated with the carbonate in the structure. The observation that the average mole ratio of "excess fluorine" to carbonate is about 0.4 might indicate that only part of the possible sites are filled, and the models indicate that these sites may be only those that cause an increase in the value of c of the unit-cell.

The mathematical models that correlate the changes in unit-cell constants with changes in chemical composition are useful in examining different combinations of substitutions. It should be noted that the intercept values of a for the models involving only carbonate are close to the value of a of fluorapatite reported in the literature, 9.3700 Å (Náray-Szabó, 1930). In the samples examined in this study, the decrease in the value of a with increasing carbonate substitution must involve a substitution site other than that in the hexad channel, since Elliott (1964) has demonstrated that carbonate substitutions on the hexad sites cause marked increases in the value of a of the unit cell.

The initial correlations by Smith and Lehr (1966) were based on the relation $(\text{CO}_3 + \text{F})/10\text{Ca}$ on the assumption that there was little isomorphous substitution of cations for calcium in the apatite structure. More recent work by Lehr *et al.* (1967), however, has shown this to be only an approximation, and the more recent chemical data show that almost 10 percent of the calcium can be replaced by sodium and magnesium. The amounts of sodium and magnesium increase regularly with increasing carbonate substitution, and the amount of sodium increases about 2.5 times as fast as that of magnesium (Figures 3 and 4). The solid symbols

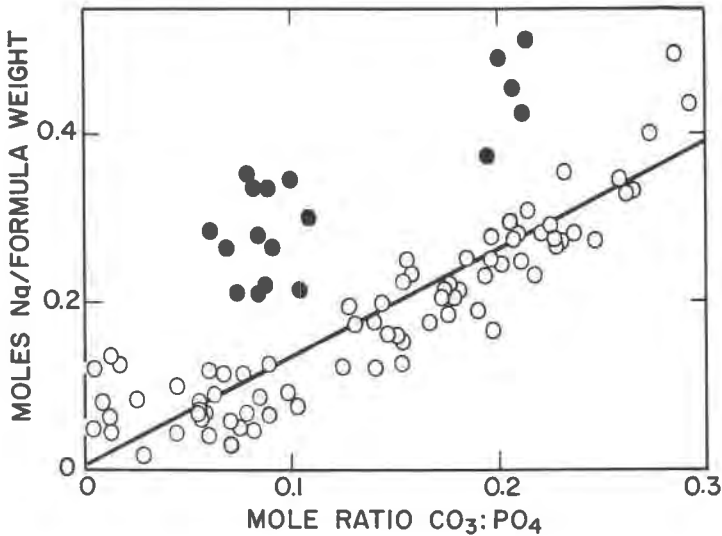


FIG. 3. Sodium contents of apatites.

in Figures 3 and 4 are those of samples in which accessory minerals such as sodium montmorillonite and basic volcanic glasses contribute to the gross composition without participating in the substitutions in the apatite structure.

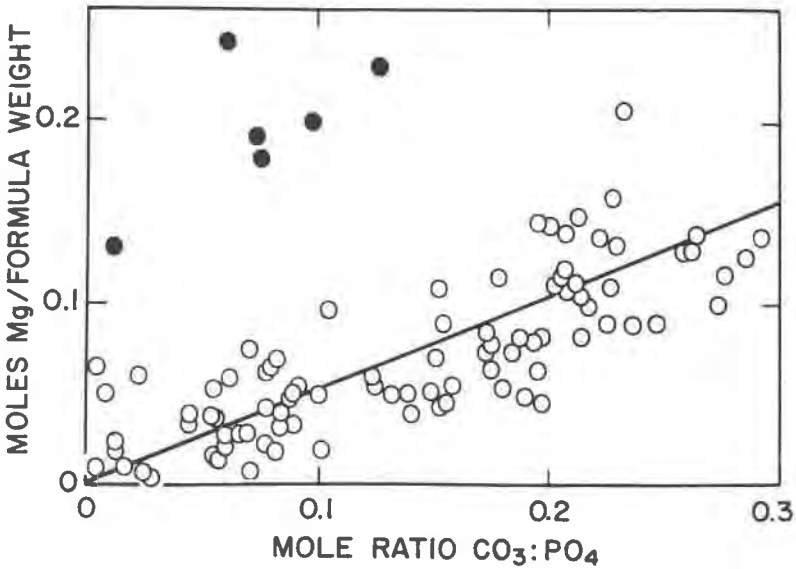


FIG. 4. Magnesium contents of apatites,

One interpretation of the presence of sodium is that it is a compensating cation in a coupled substitution pair of Na^{1+} for Ca^{2+} with CO_3^{2-} for PO_4^{3-} to preserve the electroneutrality of the structure. It is also possible that part of the Na^{1+} is compensating for a trivalent rare earth (RE^{3+}) which has replaced part of the calcium. Although both of these coupled substitutions probably occur, the data indicate that the coupling with the carbonate is the more important because there is much more substitution of carbonate for phosphate than of rare earths for calcium in most apatites. The substitution of magnesium for calcium could result from the presence of magnesium as a major divalent cation in marine systems in which apatites are thought to form, or from a structural adjustment resulting from the substitution of carbonate for phosphate, or a combination of these factors.

Gulbrandsen (1966) found in several samples of the Phosphoria formation that the atomic ratio Na:S was nearly 1:1. He suggested that there could be a coupled substitution of Na^{1+} or RE^{3+} and S^{6+} for Ca^{2+} and P^{+5} in the apatite structure and that it would preserve electroneutrality. Seventeen of the apatites examined in this study, however, had mole ratios Na: SO_4 of about 4.5, and these apatites covered wide ranges of both geographical source and degree of substitution. As shown in Table

TABLE 4. SODIUM AND SULFATE CONTENTS OF REPRESENTATIVE PHOSPHATE ROCKS

No.	Adjusted compn., weight percent		Moles per formula weight		Mole ratio Na: SO_4
	Na_2O	SO_3	Na	SO_4	
8	0.58	0.36	0.184	0.044	4.2
17	0.29	0.17	0.092	0.021	4.4
19	0.36	0.28	0.118	0.035	3.3
49	0.40	0.23	0.130	0.028	4.5
69	0.79	0.37	0.250	0.045	5.5
70	1.14	0.59	0.356	0.072	5.0
83	0.86	0.45	0.271	0.056	4.9
101	0.90	0.45	0.281	0.054	5.2
102	0.74	0.44	0.234	0.054	4.3
103	1.40	0.84	0.438	0.101	4.3
109	0.67	0.28	0.212	0.034	6.2
113	0.95	0.58	0.303	0.071	4.2
124	0.99	0.44	0.311	0.053	5.8
134	0.86	0.49	0.270	0.059	4.5
138	1.05	0.70	0.337	0.087	3.9
139	0.66	0.64	0.212	0.080	2.7
140	1.11	0.76	0.357	0.094	3.8

4, the largest amount of SO_4 in any apatite was 0.101 mole per formula weight, an amount almost insignificant in comparison with the amounts of carbonate in the highly substituted apatites. Thus the contribution of SO_4 , which was ignored in our calculations, is slight. It should be noted also that most of the high sodium contents, shown as solid circles on the left in Figure 3, were those of francolites from the Phosphoria formation. The grouping of these points significantly above the trend for all samples suggests that the sodium is associated with an accessory mineral rather than with the apatite itself. Further study is being made of the sodium and sulfate contents of the apatite concentrates and their association with the accessory minerals and the organic matter.

It is apparent that a number of minor constituents other than those considered here can and probably do substitute to small extents in the apatites. The most notable minor constituents are potassium, rare earths, strontium, and barium as cations, and silicon and sulfur as anions. The seven major constituents, on which we have concentrated, are Ca, P, C,

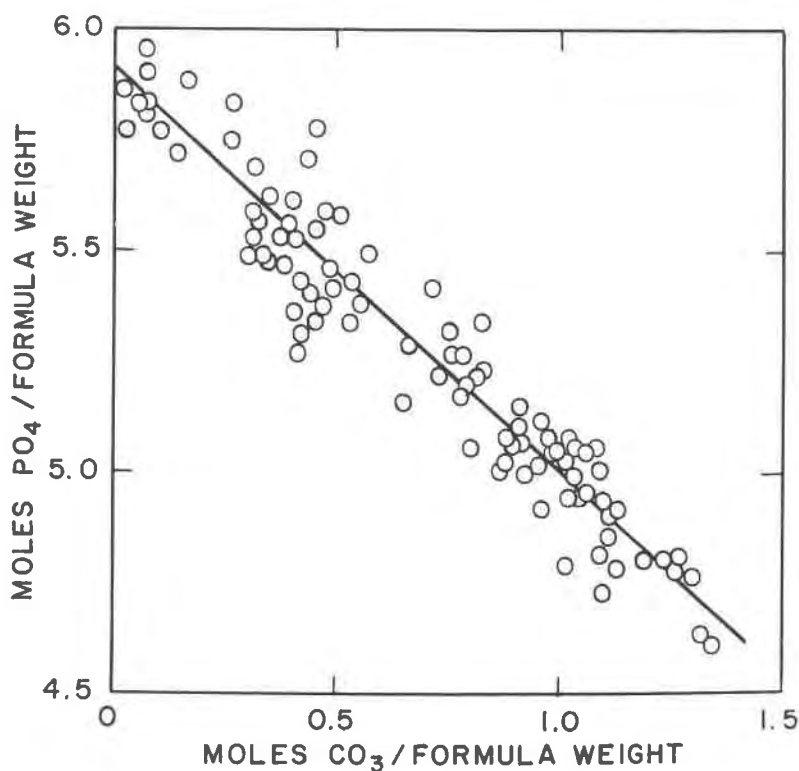


FIG. 5. Relation between carbonate and phosphate contents of apatites.

F, Na, Mg, and S; they occur in nearly all commercial apatites and account for the major effects on the crystallographic parameters of the apatites.

The mathematical correlations of the unit-cell constants with chemical composition show that the most significant effects result from the substitution of carbonate for phosphate. Although the degree of this substitution has been measured, the ratio of the constituents involved in the substitution has not been established. McConnell (1952) suggested that 4CO_3^{2-} substitutes for 3PO_4^{3-} to preserve the oxygen framework of the structure. If this were the correct substitution, the plot of moles PO_4 vs. moles CO_3 would have a slope of -0.75 . The plot of the data shown in Figure 5, however, is a straight line with a PO_4 intercept of 5.929 and a slope of -0.919 with a correlation coefficient of 97 percent and a standard error of observation of 0.083. In the 110 samples examined in this study, therefore, one carbonate substituted for one phosphate.

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