

SUBSTITUTION IN APATITE:

II. LOW TEMPERATURE FLUORIDE-HYDROXYL APATITE

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ABSTRACT

Alkali-bearing apatite was synthesized at 25°C and 100°C in solutions bearing a wide range of alkali and fluoride concentration. For apatite synthesized at 100°C in the pH range of 7.4-8.1, CaO, P<sub>2</sub>O<sub>5</sub>, and CO<sub>2</sub> content failed to show a relationship to fluoride concentration; however, the alkali concentration increased with increasing fluoride concentrations. These crystals have a low cation to anion ratio and a low mean index of refraction relative to stoichiometric apatite. Apatite synthesized in very basic solutions contains more alkali, lime, and carbon dioxide, and less P<sub>2</sub>O<sub>5</sub>, and thus has a high cation to anion ratio relative to crystals formed under less basic conditions.

Increasing fluoride concentration in the crystals results in a reduced *a* lattice parameter; whereas an increased cation to anion ratio results in an increased *c*.

Apatite formed at 25°C by reaction of calcite with a sodium phosphate solution (pH 7.06-8.27), bearing 10<sup>-1</sup> M. fluoride, contains an average 3.7 percent fluoride and 4.6 percent water. The cation/anion ratio of these crystals averages 1.69; and *a* averages 9.35 Å, a value significantly less than found for apatite synthesized at 100°C.

Balanced structural formula require the incorporation of water in various combinations of H<sub>3</sub>O<sup>+</sup>, H<sub>4</sub>O<sub>4</sub><sup>4-</sup>, and H<sub>2</sub>O° in the calcium, phosphate, and hydroxyl site respectively. Some crystals also require a reduction of charge of the phosphate site, a requirement that can be satisfied by substitution of PO<sub>3</sub>F<sup>2-</sup> for PO<sub>4</sub><sup>3-</sup>.

INTRODUCTION

Low-temperature apatite of nodules and phosphorite deposits differs markedly from apatite in igneous rocks. Specifically, low-temperature apatite can vary widely in composition, especially with respect to volatiles such as water and carbon dioxide. It is because of these low-temperature chemical variants of the mineral, that it should be useful as an indicator of diagenetic conditions.

The literature on apatite is voluminous. It is the purpose of this paper to report the effect of fluoride substitution in apatite in systems that contain potassium or sodium ions, and not to review the literature. Prior to rigorous application of solubility studies of apatite, the nature of the chemical variants of the mineral must be established. It was toward this end that this study was conducted.

PREVIOUS STUDIES

Results of a study on isomorphism of the apatite group was reported by McConnell (1938), and in subsequent papers the substitution of carbonate and various ions of water were considered (McConnell, 1952, 1962a, 1965). A general summary of the chemistry and artificial prepara-

tion of apatite is found in Van Wazer (1958). Nacken (1912) reports high-temperature studies of the fluor-chlor-apatite join; however, he did not study the fluor-hydroxyl apatite join. Prener (1967) reports the formation at high temperatures of fluor- and chlor-apatite and gives lattice parameters of the products.

In general, there is a scarcity of papers on the fluor-hydroxyl substitution in apatite. Interestingly, more than a century ago it was proposed that the uptake of fluoride by fossil bone could be used to determine the age of the bone (Middleton, 1844). This method was used subsequently; however, McConnell (1962b) pointed out serious problems and untenable assumptions in various principles other workers had adopted in applying the method.

#### EXPERIMENTS

*General statement.* Apatite can be formed by the release of calcium, from EDTA, to a phosphate bearing solution. Unfortunately crystallization must be at about 100°C, a temperature that is unrealistically high for direct comparison of conditions of formation to phosphorite deposits. Even with formation at about 100°C, the crystals contain more than 1.8 percent water, hereafter referred to as excess volatiles. Because low-temperature synthetic and natural apatites inevitably contain excess volatiles, the products of the described synthesis at about 100°C are referred to as low-temperature apatite. This term is used as a convenience and to emphasize the fact that there is a group of apatites that are nonstoichiometric, have a low mean index of refraction, and contain excess volatiles. As such, they contrast to the more ideal apatite of igneous and metamorphic rocks.

*Method.* A solution is prepared of suspension free liquor containing Ca EDTA and ions of phosphate and potassium or sodium. Small quantities of NaF are added to this stock solution. The solution is boiled for about 12 hours in a Teflon coated beaker. This results in a precipitation of apatite. The pH of the residual solution is measured after cooling to 25°C.

Calcium analysis was by EDTA, and phosphate was determined gravimetrically as the quinolinium salt of molybdophosphoric acid. Potassium and sodium were determined by flame photometry, and carbon dioxide was determined with a Beckman infrared analyzer. Fluoride was determined by an Orion fluoride ion activity electrode using a Keithley electrometer. For the fluoride analysis, crystals of apatite were dissolved by using cation exchange resin, a method that has the advantage of eliminating cation-fluoride complexes.

*Results.* Nineteen samples of apatite were synthesized by the described method over a pH range of 7.4 to 14.2. Fluoride activities, reported as weight percent, ranged from 0.14 to 3.93. There were three series of samples formed. In two series, one formed in a pH range of 7.4–8.1 and the other in a system more basic than pH=12.5, the dominant alkali in the system was potassium. Sodium was the alkali in the third series, and the pH range was 7.6–8.1. All samples were X-rayed, *a* and *c* were calculated, and the results are shown in Figure 1. Also shown are K-1 and K-3 as reported by Simpson (1968). As was previously found, apatite formed under strongly basic conditions has a significantly larger *c* than apatite formed from near neutral solution. Samples of each series fail to show a linear relation.

Lattice dimensions are related to composition and structure. To determine compositions, all samples were analyzed chemically, and the results are shown in Table 1. With the method of synthesis, atmospheric CO<sub>2</sub> was not excluded from the system. However, the maximum concentration of carbonate ions in crystals formed at pH<8.1 is 0.13

TABLE 1. ANALYSES OF APATITES (WEIGHT PERCENT)

Potassium-Fluoride Apatite										
Sample	pH fm.	K <sub>2</sub> O	Na <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	CO <sub>2</sub>	F	H <sub>2</sub> O <sup>a</sup>	Ca+K+Na/ P+CO <sub>2</sub>	Mean Index <sup>b</sup>
K-1B	7.4	0.33	0.25	52.99	43.25	0.06	0.42	2.88	1.58	1.619
K-1C	7.4	0.45	0.25	53.28	43.30	0.11	1.30	1.86	1.58	1.612
K-1D	7.4	0.37	0.23	53.59	42.86	0.12	2.27	1.51	1.60	1.611
K-1E	7.6	0.30	0.30	53.64	42.63	0.01	2.78	1.51	1.62	1.609
K-1F	8.0	0.33	0.46	53.45	42.19	0.00	3.01	1.83	1.64	1.606
K-1G	7.9	0.36	0.83	52.89	42.72	0.00	3.00	1.42	1.63	1.605
K-1A	8.1	0.10	1.32	52.47	42.42	0.00	3.93	1.43	1.64	1.602
K-3A	13.7	1.06	0.28	54.22	39.78	0.83	0.15	3.74	1.72	1.627
K-3B	13.6	1.05	0.29	54.08	39.16	1.06	0.14	4.28	1.73	1.626
K-3C	14.2	0.73	0.24	53.70	38.91	1.60	0.77	4.37	1.68	1.626
K-3D	13.6	0.92	0.37	54.21	39.32	1.50	1.03	3.08	1.70	1.623
K-3E	12.5	0.41	0.42	53.74	39.35	1.85	1.70	3.25	1.65	1.623
K-3F	13.7	0.75	0.75	52.85	39.58	1.67	2.28	3.08	1.65	1.619
K-3G	13.5	0.60	1.34	53.27	40.31	1.46	3.18	1.18	1.67	1.611
Sodium-Fluoride Apatite										
Na-1A	7.6		2.10	51.34	43.26	<0.01	1.00	2.71	1.62	nd
Na-1B	7.6		2.45	50.84	42.80	<0.01	1.30	3.15	1.64	nd
Na-1C	7.6		2.45	50.84	42.72	0.00	2.06	2.80	1.64	1.613
Na-1D	7.8		2.60	50.49	42.85	0.00	2.54	2.59	1.63	1.614
Na-1E	8.1		2.60	50.60	41.98	0.00	2.68	3.27	1.67	1.614

<sup>a</sup> By difference after correction of O=F.

<sup>b</sup> Mean index of refraction =0.002.

nd=Not determined.

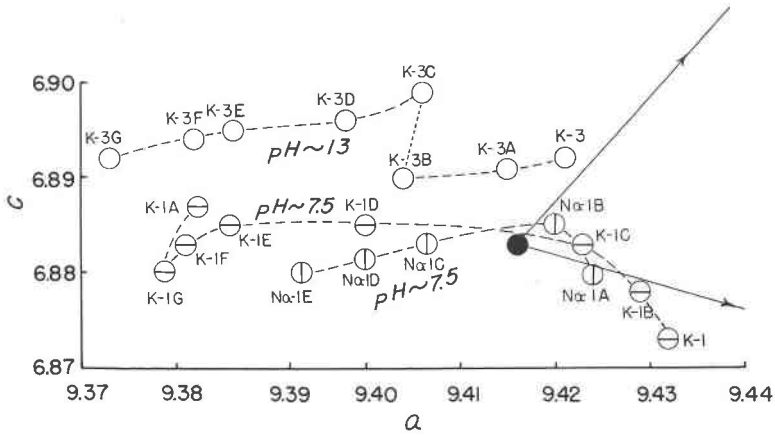


FIG. 1. Unit-cell parameters of apatite formed in systems containing sodium, potassium, and fluoride. The solid circle indicates lattice parameters for hydroxyl-apatite as given by McConnell (1965). Solid lines from hydroxylapatite indicate trends to strontium apatite (upper right) and chlor-apatite (lower right).

weight percent  $\text{CO}_2$ . Thus the effect of carbonate on the lattice parameters of these crystals is deemed insignificant. Samples formed at  $\text{pH} > 12.5$  contain roughly 1–2 percent  $\text{CO}_2$ . Work by Le Geros (1965) indicates that carbonate substitution in apatite causes a reduction in  $a$ . Thus all  $a$  values shown for the K-3 series, Figure 1, probably have some displacement toward small values, compared to ideal apatite, as a result of carbonate substitution. However, the major cause of the decreased  $a$  is not carbonate substitution, because of: (1) the low carbonate concentration and (2) the similarity of carbonate content among the samples within a series.

Apatite formed in a potassium-rich system under slightly basic conditions contains less than 0.5 weight percent  $\text{K}_2\text{O}$ ; however, some apatite formed at  $\text{pH} 12.5$  contains more than twice that amount. In both series, K-1 and K-3, the soda content ranges from roughly 0.25 to 1.34 percent. Calcium oxide and phosphorous pentoxide fail to show any obvious trend, but fluoride shows a general increase from less than 0.5 to greater than 3 percent.

If alkali are summed with calcium, and carbonate is summed with phosphate, the K-1 series has a  $(\text{Ca} + \text{Na} + \text{K})/(\text{PO}_4 + \text{CO}_3)$  ratio less than the 1.667 of ideal apatite. In contrast, the K-3 series has a higher ratio, and for most samples exceeds the 1.667. Hereafter the ratio of ions in the calcium site to ions in the phosphate site will be referred to as the cation/anion ratio.

Apatite formed in a sodium-rich system, and in the absence of potas-

sium, contains from 2.1 to 2.6 percent soda. Fluoride content of the samples ranged from 1.00 to 2.68 percent. These samples (Na-1 series) have a cation/anion ratio < than 1.667 (Table 1).

In general, apatite formed at pH 7-8 by the Ca EDTA method, in either a sodium or potassium bearing solution, has a low cation/anion ratio. In contrast, apatite formed by the same method, but in a very basic solution, has a ratio nearly equal or greater than 1.667. A crystallographic expression of this difference in ratio is most likely the enlarged *c* for the K-3 series relative to the K-1 series, and *a* reflects principally the difference in fluoride content of the crystals.

Mean index of refraction was determined for the synthesized crystals. For both the K-1 and K-3 series there is a consistent decrease of mean index with an increase in fluoride content of the crystals (Table 1). Three values listed for the Na-1 series are identical within observational error. The difference in indices between hydrothermally synthesized hydroxylapatite and well crystallized natural fluorapatite is consistent with the range found for both the K-1 and K-3 series. However, the mean index of all the low temperature apatite is significantly lower than the natural or hydrothermally synthesized crystals. This low mean index is likely the result of the high water content of the apatite.

#### FLUORAPATITE FORMED AT 25°C

A method for formation of apatite involving reaction of a sodium phosphate solution with calcite was described by Ames (1959). A modification of the method was used to form fluorapatite. As modified, several grams of calcite reacted with about 200 ml of 0.2 molar phosphate solution, some of which contained  $10^{-1}$ ,  $10^{-2}$ , or  $10^{-3}$  M fluoride. The initial pH was controlled by the addition of NaOH, and the reactions were carried out in plastic flasks. The experiment was maintained for several months during which time the solution was frequently changed. Because of the frequent changing of the solutions over the reaction product in the flask, the fluoride and phosphate over the final solid product was that originally in the stock solution. There is no guarantee that the crystals were in equilibrium with the solution; however, the final solid was entirely apatite.

Apatite formed by the calcite-solution reaction method was analyzed by the method described previously except for the following: (1) Phosphate was determined spectrophotometrically, and (2) carbonate was determined by absorption of evolved gas on ascarite.

Fourteen samples of this apatite, formed under a solution of  $10^{-1}$  M fluoride, were analyzed. Different samples in this series formed at pH values in the range of 7.06 to 8.27; however, no consistent compositional

trends were found that could be related to pH of formation. Average values (in weight percent) and standard deviations for all the analyses are listed below. The large standard deviation among the fourteen samples illustrates the variability in composition of low temperature apatite. Major differences of these analyses, compared to analyses reported in Table 1, are: (1) lower phosphate values, (2) higher CO<sub>2</sub> values, (3) fluoride values greater than 3.3 percent, and (4) high water values.

	Na <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>	CO <sub>2</sub>	F	H <sub>2</sub> O	Cation/Anion
	3.5	49.6	38.6	2.0	3.7	4.6	1.69
S.D.	0.9	1.2	1.1	0.6	0.2	0.8	0.04

Fluoride values range from 3.3 to 4.1 percent, averaging 3.7 percent, a values close to that of ideal fluorapatite, 3.8 percent. Although the amount of fluoride in the apatite is close to ideal, the analyses show 3.1 to 5.6 percent H<sub>2</sub>O, with the average being 4.6 percent. This indicates that some ion of water, or fluoride, occurs in the structure in some site other than the OH<sup>-</sup> site.

The ratio of cations to anions ranges from 1.63 to 1.78. The average value is 1.69 and thus greater than the ideal 1.667, in contrast to the generally low values for the sodium fluoride apatites formed by the EDTA method at about 100°C.

Fluoride was determined on 13 other samples formed by the reaction of calcite and a fluoride-phosphate solution. Phosphate concentration was maintained at 0.2 M level; however, for one series the fluoride concentration was 10<sup>-2</sup> M and for the other series 10<sup>-3</sup> M. Apatite formed in a solution containing 10<sup>-2</sup> M fluoride contains an average of 2.57 weight percent fluoride with a standard deviation of 0.17; whereas apatite formed under 10<sup>-3</sup> M fluoride contains an average of 1.29 weight percent fluoride, with a standard deviation of 0.08.

Lattice parameters were determined for these fluorapatites and are shown in Figure 2. Also shown are the trends for the K-1 and K-3 series. In general, apatite formed at 25°C lacks the crystallinity of apatite formed at 100°C, and this is reflected in the precision of the lattice determination.

Even with the relatively large error in *a* and *c* determinations the composite grouping can be separated into groups related to cell parameters and fluoride content of the crystals. The group having an average fluoride content of 3.7 percent has a much smaller *a*-axis dimension than the most fluoride-rich sample of the K-1, K-3, or Na-1 series or pub-

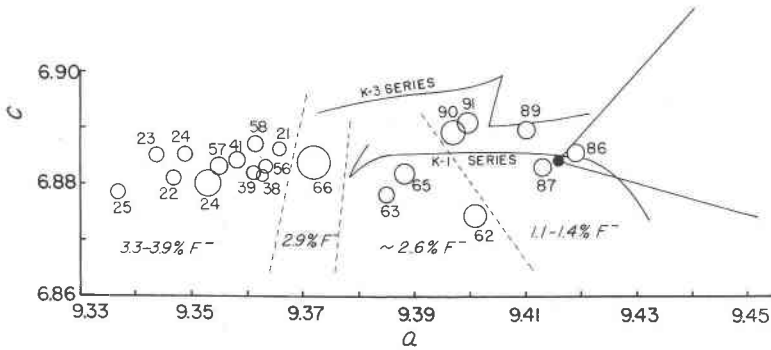


Fig. 2. Unit-cell parameters for sodium-fluor-apatite formed at 25°C.  
Trend lines as shown in Figure 1.

lished values for fluorapatite. The difference is about 0.02 to 0.04 Å. Carbon dioxide content, averaging about 2 percent, may account for some of this diminution. Using data presented by Le Geros (1965), the diminution of  $a$  and  $\text{CO}_2$  content of the crystals are of the right order; however, the substitutions in these crystals are many, and it is premature to relate one variable of many to a single parameter. Additionally, the  $\text{CO}_2$  content of different samples in the cluster (Fig. 2) vary by a factor of three, and the location of the plotted point in the cluster appears unrelated to such differences.

#### SUBSTITUTION AND STRUCTURAL FORMULAS

*General consideration.* There are many substitutions in apatite, and any structural formula developed on the basis of chemical analysis involves certain assumptions. Some of the assumptions were tabulated by Simpson (1968), and an additional assumption is that only a single phase is present in the analyzed material. In the material used in this study, only apatite was found by X-ray and optical examination.

In numerous papers evidence has been presented that sodium and potassium can substitute for calcium in apatite, and it has been shown that carbonate can substitute for phosphate. Substitution of fluoride for hydroxyl is also well established. Such substitution will be assumed in the following consideration.

All analyses of low temperature apatite indicate more than the ideal 1.8 percent  $\text{H}_2\text{O}$  as is obtained if all the hydroxyl sites are filled with hydroxyl ions. The manner of incorporation of excess water in apatite is a subject of some controversy. Various methods of incorporation of water in apatite are summarized in Table 2. The various ions of water are incorporated in the following structural formulas in a manner (1)

TABLE 2. EFFECT OF VARIOUS IONS OF WATER

Ion	Position of the Substitution	Charge	Ca site/PO <sub>4</sub> site ratio	Efficiency for incorporation of H <sub>2</sub> O
1. H <sub>3</sub> O <sup>+</sup>	Ca Site	+1	increases	good
2. H <sub>4</sub> O <sub>4</sub> <sup>4-</sup>	PO <sub>4</sub> Site	-4	decreases	good
3. 1.667 H <sub>3</sub> O <sup>+</sup> + 1 H <sub>4</sub> O <sub>4</sub> <sup>4-</sup>	Ca & PO <sub>4</sub> Sites	-2.33	no or very small change	excellent
4. PO <sub>3</sub> F <sup>-2</sup> for PO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> Site	+1	no change	no effect
5. H PO <sub>4</sub> <sup>2-</sup> for PO <sub>4</sub> <sup>3-</sup>	PO <sub>4</sub> Site	+1	no change	poor
6. OH <sup>-</sup> for F <sup>-</sup>	Hydroxyl Site	no change	no change	poor
7. H <sub>2</sub> O for F <sup>-</sup>	Hydroxyl Site	+1	no change	good
8. H <sub>2</sub> O for OH <sup>-</sup>	Hydroxyl Site	+1	no change	fair
9. OH <sup>-</sup>	Hydroxyl Site	-1	no change	poor

to yield a 10:6:2 ratio for the calcium sites, phosphate sites, and hydroxyl sites respectively; (2) such that the charges of the ions sum to zero; and (3) to account for the water values shown in the analyses.

The possibility of PO<sub>3</sub>F<sup>2-</sup> replacing PO<sub>4</sub><sup>3-</sup> must be considered because it is one of the few substitutions that will effect a reduction in minus charges for fluorapatite. Shifting of fluoride from the hydroxide site to the PO<sub>3</sub>F<sup>2-</sup> arrangement effects a reduction of -2 charges because: (1) fluoride no longer contributes the minus charge it had in the hydroxyl site, and (2) it displaces a O<sup>2-</sup> and introduces only a -1.

*Substitutions in the K-3 series.* Considering substitutions of Table 2, one can draw conclusions concerning the introduction of water in samples of the K-3 series. Series K-3 apatites were synthesized under very basic conditions. Samples with a cation/anion ratio near 1.667, abundant water in the analysis, and a need for a negative charge, must incorporate some water by process 3, Table 2. Namely, 1.667 H<sub>3</sub>O<sup>+</sup> and H<sub>4</sub>O<sub>4</sub><sup>4-</sup> would introduce a negative charge, cause no change in ratio, and would account for considerable water in the analysis. Additional water could be accommodated by process 8 or 9 (Table 2); namely, completing the filling of the hydroxyl site which may be only partially filled with fluoride. This is only a general pattern of the substitution.

Sample K-3G, can serve as an example of the above model. The actual structural formula is presented in Table 3, and it is found to be consistent with the model.

A cation/anion ratio greater, or less, than 1.667 and a crystal requiring minus charges can be satisfied by the above substitutions, but in a dif-



TABLE 3. STRUCTURAL FORMULAS FOR APATITE

	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	H <sub>3</sub> O <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	CO <sub>3</sub> <sup>2-</sup>	H <sub>4</sub> O <sub>4</sub> <sup>4-</sup>	PO <sub>3</sub> F <sup>2-</sup>	OH <sup>-</sup>	F <sup>-</sup>	H <sub>2</sub> O
K-3G	0.129	0.422	9.402	0.049	5.620	0.327	0.053		—	1.653	0.347
K-3D	.194	.116	9.399	.292	5.386	.331	.283		0.923	0.528	0.549
K-1B	.069	.083	9.301	.550	5.990	.010	—		.762	0.217	1.020
K-1F	.069	.147	9.458	.326	5.973	.000	.026	.110		1.463	0.537
K-1A	.020	.422	9.264	.296	5.483	.000	.083	.434	—	1.616	0.386

ferent ratio. The structural formula of K-3D (Table 3) is another example.

Water analyses were determined by differences, and such values are subject to greater error than other oxide determinations. However, a greater or lesser quantity of water is simply partitioned to the various structural sites, provided there is more water than the hydroxyl sites can accommodate, and the error is therefore inconsequential.

Samples K-3B and K-3C have roughly the same *a*, but they differ by nearly 0.01 Å in *c* with K-3C being the larger. The cause for this is not obvious, and it is further complicated by the *a* dimension of K-3B indicating that the sample should contain more fluoride than was found in the analysis. Differences shown in the analysis may be sufficient to account for the differences in lattice dimensions. In an earlier study, Simpson (1968) presented evidence indicating that H<sub>2</sub>O can easily be lost from the H<sub>3</sub>O<sup>+</sup> ion in potassium hydroxylapatite. With the loss of such water, a hydrogen ion occurs in the calcium site. Such loss of water in the previous study was effected simply by drying samples at 110°C. It seems likely that the discontinuity in the K-3 trend for lattice parameters reflects retention of hydronium and the loss of water from hydronium as a result of drying, at 110°C, samples rich and poor in fluoride respectively.

*Substitutions in the K-1 series.* Series K-1 apatites were synthesized in a pH range of 7.4 to 8.1, a range close to that of many natural systems. Apatites of this series have a cation/anion ratio <1.667; and as such, they appear cation deficient. Substitutions in the K-1 series must balance this deficiency and introduce predominantly plus charges. Process 1, Table 2, would satisfy the requirements. Additional processes of water introduction would be some combination of 8 and 9. Thus ions of water added to the K-1 series will be principally H<sub>3</sub>O<sup>+</sup> in calcium sites and some combination of OH<sup>-</sup> and H<sub>2</sub>O in the hydroxyl sites unoccupied by fluoride. The structural formula developed for K-1B (Table 3) is an example of such substitutions.

Sample K-1A is also deficient in plus charges, and the analysis shows that it contains more fluoride than can occupy the hydroxyl site. In addition, it contains nearly 1.5 percent water. In contrast to K-1B which has a cation/anion ratio of 1.58, the ratio in K-1A is 1.64. Because of the 1.64 ratio only a small quantity of water can be introduced in the structure as  $\text{H}_3\text{O}^+$ . The introduction of the  $\text{H}_3\text{O}^+$  to yield a cation/anion ratio of 1.667 still leaves a deficiency of plus charges and fails to account for significant water in the analysis. For these reasons it is proposed that  $\text{PO}_3\text{F}^{2-}$  occurs in some of the phosphate sites instead of  $\text{PO}_4^{3-}$ . This removes a fluoride from its considered position in the hydroxyl site. If the site vacated by the fluoride is filled by a hydroxyl, there is no change in charge; however, if filled by  $\text{H}_2\text{O}^\circ$ , there is in effect a gain of +1 charge and a process for the incorporation of a significant quantity of water in the crystals. The structural formula derived for K-1B is given in Table 3. The formula accounts for 1.3 percent  $\text{H}_2\text{O}$ , 1.4 percent is reported in the analysis. A structural formula for K-1F is also listed in Table 4, and again it is found that  $\text{PO}_3\text{F}^{2-}$  is necessary.

The incorporation of  $\text{PO}_3\text{F}^{2-}$  in an apatite crystal containing 3.8 percent fluoride, or less, has broad implication. It means that fluoridation of apatite can in part result from necessity to satisfy the charge of the crystal, and it does not necessarily involve a simple occupation of a hydroxyl site by fluoride.

*Substitution in other series.* The Na-1 series of samples (Table 1) was synthesized in a sodium-rich solution in the pH range 7.6–8.1. This series has similarities to the K-1 series in that the cation/anion ratio is equal to or slightly less than 1.667; and the crystals, excluding water from consideration, require a plus charge. Thus the dominant substitution will be  $\text{PO}_3\text{F}^{2-}$  for  $\text{PO}_4^{3-}$  with minor  $\text{H}_3\text{O}^+$  added to the calcium sites. Additional water can be incorporated in the structure as  $\text{OH}^-$  and  $\text{H}_2\text{O}^\circ$  in the hydroxyl site. Addition of minor  $\text{H}_4\text{O}_4^{4-}$  to the phosphate site is not precluded.

Analyses of apatite formed by reaction of calcite at 25°C (see above) show a high cation/anion ratio, and all contain a high percentage of water, even though they have nearly the ideal 3.8 percent fluoride. Excluding water, the components of all these samples sum to essentially zero charge. Thus it is required that water be introduced so that it contributes to the phosphate site and with additional substitution a zero charge is maintained. The only mechanism for doing this is to introduce water as  $\text{H}_4\text{O}_4^{4-}$  in the phosphate site and to substitute  $\text{PO}_3\text{F}^{2-}$  for  $\text{PO}_4^{3-}$  so as to maintain zero charge. Such substitution vacates a hydroxyl site which in turn can be filled with  $\text{H}_2\text{O}^\circ$ .

## SUMMARY AND CONCLUSIONS

The substitution of fluoride in apatite has been considered to be a simple process. Namely, a fluoride ion displaces a hydroxyl ion. However this is not the case. The processes for the incorporation of fluoride in apatite are exceedingly complex and have a direct dependence on the total chemistry and physical nature of the system.

Lattice parameters show a decrease in  $a$  with increasing fluoride content, a conclusion consistent with many previous reports. Also, the general pattern is for  $c$  to increase and then decrease with increasing fluoride. Even these simple trends indicate complexities in the incorporation of fluoride in the crystals, for, if the substitution is ideal, there should be a linear relation in molar volume. It is obvious from the trends shown (Fig. 1) that lattice parameters alone are insufficient to characterize apatite. The general pattern that has evolved is one of increasing  $c$  with an increasing  $(\text{Ca} + \text{Na} + \text{K})/(\text{PO}_4)$  ratio which in turn is related to pH of formation.

It is possible for several structural formulas to be consistent with a chemical analysis. In this study the existence of a  $\text{PO}_3\text{F}^{2-}$  ion was assumed because (1) it is a mechanism for the incorporation of more than the ideal 3.8 percent fluoride in apatite, (2) it preserves the calcium/phosphorous ratio, (3) it reduces negative charges, and (4) it permits a concomitant substitution that is efficient in the incorporation of water in the structure. A  $\text{HPO}_4^{2-}$  substitution for  $\text{PO}_4^{3-}$  is not disproven; however, it is unnecessary for the analyses reported in this study, and it fails on several of the above points.

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