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SUBSTITUTIONS IN APATITE:
I. POTASSIUM-BEARING APATITE

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ABSTRACT

Apatites with good crystallinity can be synthesized at about 100°C by the slow release of calcium from EDTA into a phosphate-bearing solution. All apatites formed by this method have an enlarged *a*. Analyses show some of the apatites to be deficient in calcium even when the alkali is summed with calcium; however, all apatites crystallized contained an excess of water.

The enlarged *a* is principally accounted for by substitution of H_2O in the hydroxyl position. Substitution of H^+ for calcium is proposed on the basis of charge balance, lattice dimensions, and density. Such substitution causes a reduction in both *a* and *c*. The proposed substitutions are related to conditions of formation.

INTRODUCTION

Apatite is found in nearly all types of rocks and is the major mineral constituent of phosphate rock, phosphatic tests, teeth, and bone. Nonetheless, the chemical variations in the mineral are poorly understood. Much of the data, and interpretations of the data, are in conflict because many conclusions have been based on inadequate chemical analyses and mineralogical descriptions. However, because of wide variations in composition and nearly ubiquitous occurrence, apatite could prove to be a useful environmental indicator, when its variations are understood. The purpose of this paper is to relate unit-cell dimensions to pH of formation, and chemical composition of the apatites.

It is not the purpose of this paper to review the voluminous literature on apatites. The general structure of apatite was reported by Náray-Szabó (1930) and Mehmel (1930). McConnell (1938) presented results of a study of isomorphism of the apatite group. A general summary of the chemistry and artificial preparation of apatites is found in Van Wazer (1958).

Synthetic apatites formed under hydrothermal conditions give well defined X-ray diffraction patterns and have Ca/P ratios close to 1.67. However, hydroxyapatites formed in the temperature range of 4°C to 103°C under one atmosphere pressure commonly (1) contain considerable excess water and carbonate, (2) have a low mean index of refraction, and (3) have a Ca/P ratio that departs from 1.67 (Simpson, 1964, 1966a, 1967). Additionally, the crystallinity of such apatites decreases with decreasing temperature of formation. Because apatites formed at low temperatures, under conditions perhaps somewhat representative of those producing phosphorite formation, are markedly different from apatite formed under hydrothermal conditions, it is convenient experimentally to consider apatites as forming a low temperature series and a high temperature series. The laboratory conditions to effect the merger of the two series can be likened to a wide spectrum of natural conditions.

EXPERIMENTS

General statement. Apatites formed by direct precipitation characteristically are very fine-grained and give poor X-ray diffractograms. Analyses of such fine-grained apatites show excess water and commonly carbon dioxide. However, because of the minute grain size, and the absence of useful X-ray data, it is difficult to determine whether the water and carbon dioxide is sorbed on the surfaces or actually in the structure.

Ames (1959) described a method of formation of apatite involving the reaction of calcium carbonate with a sodium phosphate solution. The method is important because it may be a reasonably good model for the formation of some phosphorite deposits. Further, the study presented strong evidence concerning the nature of carbonate apatite. The method was slightly modified by Simpson (1964, 1966a, 1966b) and data were presented on the chemical and physical nature of the apatites as a result of changes in conditions of formation. Even with variations in the method of synthesis, the formed apatites lacked sufficient crystallinity for precise lattice measurements. Maintaining the apatites under their mother liquor for more than a year resulted in little improvement in crystallinity. A further limitation to this method of synthesis is that carbon dioxide is a component of the system, and consequently the apatites formed are carbonate bearing.

Le Geros (1965) described a method of synthesis involving the dropwise addition of a calcium acetate solution to mixtures of sodium phosphate and sodium bicarbonate at 100°C. The method had the advantage of giving a product of sufficient crystallinity for precise lattice determinations, and it served to demonstrate a relationship between carbonate content of apatite and an axial dimension.

Method. Apatites of good crystallinity can be formed at moderately low temperatures in a system that can accommodate wide variations in chemical composition. Basically this method involves the slow release of calcium from EDTA to a phosphate-bearing solution. Most crystallization was at approximately 100°C and chemicals used were analytical reagent grade. The procedure was as follows:

A. Acid EDTA (60 grams) and 60 grams of either $CaHPO_4$ or $Ca_3(PO_4)_2$ were mixed in 1800 cc. of water. The solution was brought to the desired pH with the addition of the hydroxide of an alkali, usually KOH.

B. The solution was stirred for six hours in order to saturate the solution with Ca EDTA. Phosphate goes into solution as calcium is chelated by the EDTA.

C. Suspended solids were filtered from the supernate.

D. The solution was then boiled at atmospheric pressure. This resulted in a release of calcium from the EDTA and permitted combination with the phosphate in the solution. During the boiling, nitrogen was bubbled through the solution in order to reduce the carbonate content of the system.

E. After a reduction of the solution by evaporation to one-sixth of its volume, the crystals were separated from the remaining hot liquor.

F. The crystals were washed, and then a portion of the sample was X-rayed while still moist, the remainder was dried at 110°C for 12 hours.

G. After cooling to 27°C, pH was determined on the residual liquor.

A reaction temperature near 100°C is necessary for the formation of good crystals. Experiments at 50°C and 80°C yielded a poorly crystallized product, even when maintained at these temperatures for several days.

Below a pH of 6, apatite fails to form, and no experiments were conducted above a pH of 13.38.

Results. Twenty samples of apatite were formed from potash-bearing solutions by the described method, over a pH range of 6.4 to 13.38. These apatites were X rayed, *a* and *c* were calculated, and the results are shown in Figure 1. All of these apatites have an *a* greater than normal hydroxyapatite with the largest value being greater than 9.45 Å. The *c* values of the apatites seem to be related to pH of formation; but there are many exceptions to a simple trend. In general, there is a group of samples formed at $\text{pH} < 7$, which have a smaller *c* and larger *a* than normal hydroxyapatite. Those samples formed under basic conditions, however, are enlarged both in *a* and *c*.

Because the lattice dimensions must be related to either substitutions or defects in the compound, the composition of the solution was varied in an attempt to determine a relation between solution composition and properties of the formed apatites. Four solutions were enriched in phosphate and potassium ions by the addition of phosphoric acid and potassium hydroxide. Material formed in these solutions is indicated in Figure 1 by the notation "PO_4" and can be related to apatite from the unspiked mother liquor of the same number. One sample (8) was crystallized rapidly, over a period of about one hour, by using fast flow aerating nitrogen. This sample gave a slightly larger *a* than a slowly crystallized equivalent (9). Spiking solutions with calcium ions increased *a* for sample 9 and decreased it for sample 10. Three samples, K-1, K-2, and K-3 were crystallized during more than 12 hours.

Nine samples were analyzed chemically after air drying at 110°C. The results of these analyses are shown in Table 1. Potassium was determined by flame photometry and calcium by EDTA titration. Carbon dioxide was determined with a Beckman Infrared analyzer. Phosphorus was determined gravimetrically as the quinolinium salt of molybdophosphoric acid. Three water analyses were by a modified Penfield method.

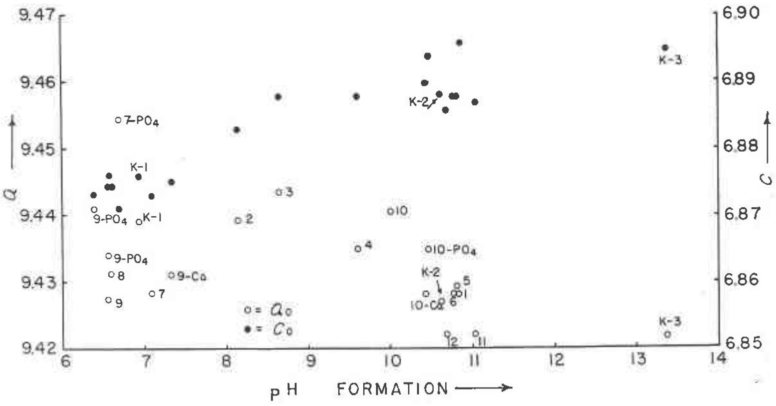

FIG. 1. Unit-cell dimensions of apatite formed in a potassium-bearing system. Samples undried. PO_4 indicates apatite formed in solutions enriched in $PO_4^{=}$, and Ca indicates that the solution was enriched in Ca^{+2}. K-1, K-2, and K-3 are samples frequently referred to in the text.

Samples K-1, K-2, and K-3 were crystallized during a 12-hour period; whereas all other samples indicated in Table 1 were formed in 1 to 6 hours.

In general, the analyses show phosphate to decrease with decreasing pH of formation of the samples; whereas potash tends to increase. The calcium to phosphate ratio shows a general increase with increasing pH of formation; although there appear to be differences between the rapidly and slowly crystallized groups. The sample from the phosphate spiked solution (10-PO_4 spike) has a low calcium to phosphate ratio, even though it formed in a more basic solution than the other samples. If potassium is summed with calcium, the calcium to phosphate ratios range from 1.53 to 1.72.

To determine whether the nitrogen gas had any effect on crystallinity or lattice dimensions, one solution was split, and half boiled down with nitrogen gas, the other split boiled down with oxygen gas. Within the limits of observational and experimental error, the products were identical. When CO_2 was used as the gas, with the pH maintained at 10.6, no precipitate formed until the solution had been reduced to a third of its initial volume. Recovery of the precipitate was poor, and it gave a very poor X-ray diffractogram of apatite.

Density. Density is difficult to determine accurately on samples composed of very small crystals; however, a knowledge of the density is critically important in establishing the correct structural formula for a complex compound. Attempts at determining density of the samples by the pycnometer method were unsuccessful. Consequently, a sink-float

TABLE 1. ANALYSES OF APATITE FORMED IN POTASSIUM-BEARING SOLUTIONS

Sample	pH formation		K_2O	CaO	P_2O_5	CO_2	H_2O^a	Ca/P	Ca+K/P
			0.76	51.49	43.24				
K-1	6.96		0.68	51.32	43.31	0.04			
			0.60	51.59	43.08				
		Avg.	0.68	51.47	43.21	0.04	4.60	1.51	1.53
			0.93	51.48	40.84				
K-2	10.65		0.82	51.33	40.94	0.58			
			0.78	50.98	40.82				
		Avg.	0.84	51.26	40.87	0.58	6.45	1.59	1.62
			0.94	53.68	40.46				
K-3	13.38		0.95	53.59	40.38	0.74			
			1.02	53.38	40.38				
		Avg.	0.97	53.55	40.41	0.74	4.33	1.68	1.72
9	6.6		0.2	53.3	42.9			1.57	1.58
7	7.1		0.3	53.2	42.9			1.57	1.58
2	8.1		0.8	52.6	42.2			1.58	1.61
4	9.6		0.8	53.3	41.8		4.2	1.61	1.54
10-Ca (spike)	10.4		1.3	52.3	40.7		5.2	1.63	1.68
$10\text{-}PO_4$ (spike)	10.4		1.7	51.4	41.3		5.1	1.58	1.64

[a] By difference.

method using methylene iodide was used. A centrifuge was used because of the crystal size. The samples, K-1, K-2, and K-3, were redried at 110°C immediately before putting in the methylene iodide. Because of the method of determination the densities of the samples were established as being in the ranges shown in Table 2.

As a result of the crystal size, birefringence is rarely observed. Therefore a mean index of refraction measured in sodium light was determined (Table 2). For comparison, the density of hydroxylapatite is greater than 3.1 and the lowest index is greater than 1.64. Thus these apatites have large differences in composition, density, unit cell dimensions, and index of refraction compared to normal hydroxyapatite.

Lattice periodicities of hydroxyapatite. Many values have been reported

TABLE 2. DENSITY OF POTASSIUM-BEARING APATITE

Sample	Density		Mean index ± 0.002
K-1	>2.945	<3.016	1.618
K-2	>2.868	<2.959	1.615
K-3	>3.055	>3.107	1.616

for the *a* and *c* dimensions of hydroxyapatite. McConnell (1960) records fifteen such reported values and concludes the note with the statements: "Thus the question remains: What are the lattice periodicities of pure hydroxyapatite?" In 1962, McConnell presented a listing of four reported values that range from 9.418–9.432 for *a* and 6.881–6.885 for *c*, and he states, "Almost certainly, these differences are produced by variation in the combined water contents, if not the carbon dioxide contents, of these precipitates." Simpson (1965) reported *a* and *c* for a hydrothermally synthesized hydroxyapatite as 9.42_6 and 6.88_5 respectively, and McConnell (1965) reported synthetic hydroxyapatite as $a=9.416\pm0.002$ and $c=6.883\pm0.002$.

It is highly desirable to relate reported axial dimensions to the chemical composition of the apatite; however, very few reports list a *complete* chemical analysis for the material on which the lattice dimensions were determined. Because no method of synthesis can guarantee a stoichiometric apatite, such analyses are necessary.

For the purpose of this paper, McConnell's (1965) value for hydroxyapatite is used for reference. The conclusions would remain unchanged had any other recently reported values been used.

DISCUSSION

General statement. Any model considering substitutions and their effect in low temperature apatites must be consistent with the following:

1) Apatites formed by the described method have enlarged *a*'s; and if formed under acid conditions, *c* is smaller than normal hydroxyapatite. If such apatite formed under basic conditions, *c* is larger than normal hydroxyapatite. Also, the Ca/P ratio tends to increase with increasing pH of formation; thus apatite formed under acid conditions, but at pH above 6, tends to be phosphorus-rich.

2) These apatites contain more than twice as much water as normal hydroxyapatite.

3) Density and mean index of the formed apatite is significantly less than normal hydroxyapatite.

4) Lattice dimensions are aberrant for this apatite.

Substitutions in apatites are many, and they are further complicated because one component such as water and its various ionic species can occupy several structural sites. However, some generalizations concerning substitutions can be drawn. On the basis of data presented by Mooney and Aia (1960) on calcium, strontium, and barium apatites, it appears certain that the substitution of an increasingly large cation in the calcium position causes about an equal increase in *a* and *c* of the apatite. The same reference also shows that in calcium apatites the substitution of an anion of increased size such as a halogen in the hydroxyl position results in a marked increase in *a* and, surprisingly, a diminution of *c*. The effects of substitutions in the phosphate position are more speculative. Data are available on the structurally similar pyromorphite series; however, these are lead chloride compounds of phosphate, arsenate, or vanadate and consequently reservation must be exercised in applying these trends to apatite. On the basis of Baker's (1966) data on the pyromorphite series, it is found that substitution of a larger ion for phosphorus results in an enlargement of both *a* and *c*. However, the increase in *a* is roughly two times the increase in *c*. The trends resulting from substitutions in the various positions are schematically shown in Figure 2.

Thus, a substitution in the hydroxyl position in apatite can probably cause only enlargement of *a* and reduction of *c*. Substitution of H_3O^+ in the calcium position, would be substitution of a larger ion like strontium and barium and should result in roughly an equal increase in *a* and *c*. The effect of an $H_4O_4^{4-}$ substitution for phosphate is not known with certainty. Presumably $H_4O_4^{4-}$ is considerably larger than PO_4^{3-}, because of likely repulsion of the hydrogens, and this should cause an enlargement in unit cell dimensions.

A plot of *a vs c* for all apatites synthesized for this study is shown in Figure 3. These lattice dimensions were determined on material dried at 110°-120°C in contrast to the data obtained on undried material shown in Figure 1. Also shown are the dimensions for hydroxyapatite as given by McConnell (1965), and the trends that would result from the substitution of a larger ion such as strontium for calcium and of chloride for hydroxyl (Mooney and Aia, 1960). The group of apatites formed under neutral or acid conditions clearly plots below the chloride substitution curve (group 1). Thus their dimensions cannot be explained *simply* by the substitution of a larger ion in the hydroxyl position. Nevertheless, substitution in the hydroxyl position must account for some enlargement of *a* and a reduction of *c*, remembering that substitution of H_3O^+ for Ca^{++} and $H_4O_4^{-4}$ for PO_4^{-3} will most likely result in an increase in both *a* and *c*. It seems likely that the substitution of H_2O for OH^- as

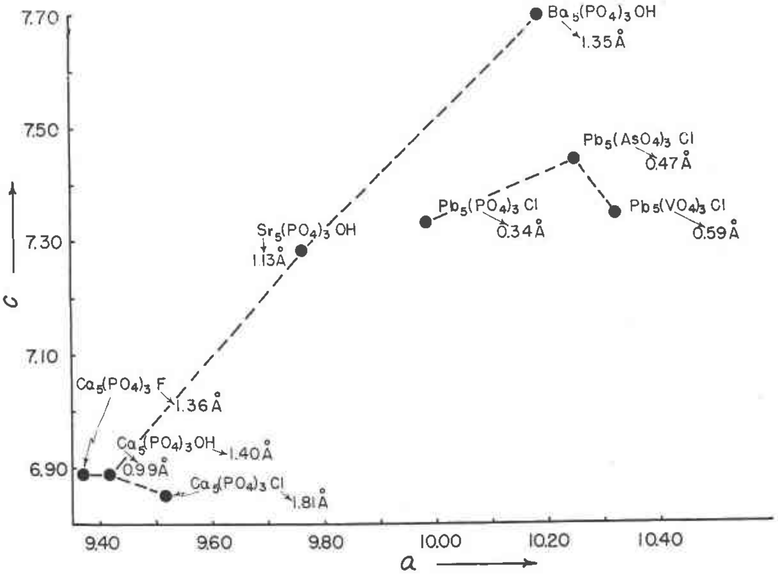

FIG. 2. Relation of *a* and *c* for the apatite and pyromorphite series. Pauling's ionic radius data shown under the various ions. Hydroxylapatite dimensions from McConnell (1965), other apatites data from Mooney and Aia (1960). Pyromorphite series data from Baker (1966).

proposed by McConnell (1965) may account for the large *a* and some reduction in *c*.

Apatite formed at pH∼7. Three analyses of the group 1 apatites indicate that the Ca/P ratio is 1.51–1.57 compared to that in normal apatite of 1.667. Thus this group of apatites is calcium deficient or phosphorus-rich, and, as such, extensive substitutions involving additions to an already overfilled phosphate position are unlikely. Also unlikely is substitution of any ion larger than calcium, such as H_3O^+, in the calcium position, because this would result in an increase in *a* and *c*. The following are possible conclusions:

1. Some of the calcium sites are truly vacant.
2. A small ion occupies some calcium sites.
3. There is more than one phase present in the sample.
4. The substitutions are complex and simply not understood.

Both optical and X-ray diffraction failed to show a second phase in the sample. Careful examination of X-ray diffractograms failed to show any peak that could not be attributed to apatite. This does not exclude the possibility of an amorphous phase, but none was found optically.

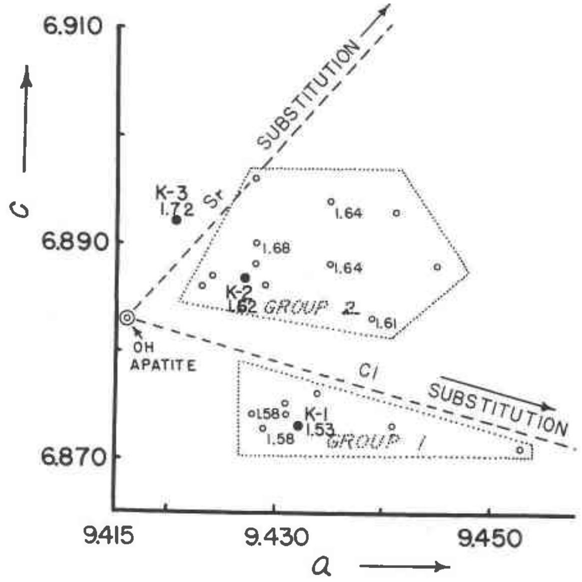

Fig. 3. Relation of $a-c$ for apatite synthesized under different conditions. Groups 1 and 2 formed under acid and basic conditions respectively.

Monetite and brushite admixed with apatite could account for the high water and phosphate content of the samples; however, these compounds have distinctive morphologies and optical properties. Admixed whitlockite could account for the high phosphate content, but being anhydrous it could not account for the high water content. Normal hydroxyapatite has a Ca/P ratio of 1.667; whereas whitlockite's ratio is 1.500. Sample K-1 has a Ca+K/P ratio of 1.53. If admixed whitlockite is proposed to account for the ratio, it would mean that most of the sample was whitlockite. X-ray and optics failed to show any whitlockite. Both monetite and brushite have a Ca/P ratio of 1.00. A mixture of roughly 15–20 percent monetite or brushite and 80–85 percent apatite could have a Ca/P ratio of roughly 1.53. Again, this quantity of brushite or monetite should be easily detectable, and it was not detected. Thus it is concluded that the sample is apatite, and if a second phase is present it occurs in minute, undetectable quantities and as such would have an insignificant effect.

Judgment between the first and second possibility rests on the development of a structural formula consistent with the presented physical and chemical data. The developed structural formula for K-1 is based on the following assumptions:

1) The 10/6/2 calcium/phosphate/water sites respectively must be accounted for.

2) Ionic charges should sum to 0.

3) The analysis must be accounted for, and that it is sufficiently accurate for the purpose.

4) Calculated density of the material should be consistent with observed density.

5) Hydrogen can occur in the crystals in any of the following species: H^+, H_3O^+, $H_4O_4^{-4}$, HPO_4^{-2}, OH^-, H_2O°.

6) Proposed substitutions must be reconcilable with the lattice dimensions.

On the basis of these assumptions, the only structural formula that can be derived for K-1 is:

$$(Ca_{8.81}K_{0.13}H_{1.06})[(PO_4)_{5.84}(CO_3)_{0.01}(H_4O_4)_{0.14}][(OH)_{0.68}(H_2O)_{1.32}]$$

The calculated density is 3.009 compared to an observed density between 2.945–3.016. With this formula there are no true vacancies or holes; however, there are calcium sites that contain only a proton.

It has been observed by TGA analysis of many low temperature apatites that there is a continuous weight loss from 23°C to high temperatures (700–800°C). Furthermore, there is no significant deflection in such weight loss curves in the region of 100–120°C. TGA was not performed on samples K-1, K-2, and K-3, but presumably they show the same pattern. However, lattice dimensions were determined by X-ray immediately after formation while the sample was still moist and also after drying in air at 120°C for 12 hours. The values for undried K-1 are $a=9.439$ and $c=6.876$, and for dried K-1 $a=9.432$ and $c=6.873$, all ± 0.002. Unit-cell volume goes, with drying, from 530.5 to 529.5 Å^3. Exposure of dried K-1 to water vapors at 110°C for 12 hours resulted in lattice dimension values about midway between the dried and undried material.

In view of the above consideration, the proposed structural formula must also account for a give and take of volatiles with a concomitant change in lattice dimensions, especially a, in the temperature range of 23–120°C. The proposed structural formula can accommodate such changes. Namely, a hydrogen ion occurs in a calcium site. When the crystals formed and before drying they likely contained hydronium ions (H_3O^+). With drying, H_2O from the hydronium is released with a hydrogen ion remaining in the structure and still balancing the charge. In the presence of steam, some water again enters the sites. Loss of a molecule, H_2O, with a radius of 1.4 Å from a calcium site would cause a diminution in a and c, exactly as observed. It is possible that with even the mild heating and loss of volatiles, a second phase formed and is then destroyed by hydration. However, there is no optical or X-ray evidence of such a phase. Additionally, such a phase would have to have cell dimensions such that apatite plus this phase would give an apparent change in the lattice dimensions of apatite.

All substitutions in the structures will have an effect on the lattice dimensions. Because potassium, carbonate, and $H_4O_4^{-4}$ ions are present at very low levels, the effect of these substitutions will be very small. More than half of the OH^- positions are filled with water. Because water is slightly larger, such substitution should effect a slight decrease in *c* and an enlargement of *a*. This is consistent with the lattice dimensions of K-1.

Apatite formed under basic conditions. Apatite in group 2 (figure 3) formed under basic conditions. Analyses show differences between K-2, a sample crystallized during 12 hours, and others in the group, samples crystallized from 1 to 6 hours. The details of the chemical variation are not understood, but they simply mean that there are factors other than pH of formation that have an effect on the composition of apatite. Even though there are chemical variations in the group, a characteristic of the group 2 apatites is that they have higher Ca/P ratios than group 1 apatites.

A structural formula for K-2 based on the same assumption as K-1 is the following:

$$(Ca_{8.60}K_{0.17}H_{1.24})[(PO_4)_{5.42}(CO_2)_{0.12}(H_4O_4)_{0.46}][(OH)_{0.26}(H_2O)_{1.73}]$$

Calculated density of this compound is 2.949 compared to observed density in the range of 2.868–2.959.

Similarly, the structural formula of K-3, formed at pH = 13.38 and having a Ca/P ratio of 1.68, is:

$$(Ca_{9.91}K_{0.21}H_{0.48})[(PO_4)_{5.55}(CO_3)_{0.17}(H_4O_4)_{0.29}][(OH)_{1.16}(H_2O)_{0.84}]$$

Observed density was in the range of 3.055–3.107, and the calculated density is 3.049.

Sample K-3 has an enlarged *c* and *a*. Because potassium is present in all samples in roughly the same concentration, 0.13–0.21 moles, its effect will be ignored in discussing differences in lattice dimensions among samples K-1, K-2, and K-3. Substitutions of water for OH^- has been discussed. Because the difference in size of OH^- and H_2O is small, the effect of differences in mole concentration of H_2O in the OH^- position for K-1 and K-2 is deemed to be minor relative to other substitutions.

The major difference between K-1 and K-2 is the larger *c* dimension of K-2; and, in composition, K-2 contains 0.11 moles more carbonate and and 0.32 moles more $H_4O_4^{4-}$. It is probable that the enlargement of *c* is principally a result of the combined effect of these substitutions for phosphate.

K-3 has an enlarged *c* and decreased *a* relative to K-1 and K-2. The principal compositional difference is a large decrease of hydrogen ions in calcium sites. This should yield an increase in *a* and *c*. The decreased *a* of K-3 relative to K-2 may result from the decreased water substituting for OH^-, 1.73 moles in K-2 to 0.84 moles in K-3.

The scheme of substitutions proposed is shown diagrammatically in Figure 4.

Comments. The many recent studies on apatite only confirm that the mineral deserves the meaning of its name, that is "to deceive." It still has defied a simple unified explanation for its strange properties and behavior, and the conclusions drawn from many careful studies are quite different. In this study apatites were synthesized under unusual conditions, and the conclusions at this time are necessarily limited to the products of these experiments. Their general applicability remains to be tested. The fact that low temperature apatites contain excess volatiles and are variable in composition, indicates that they will be especially

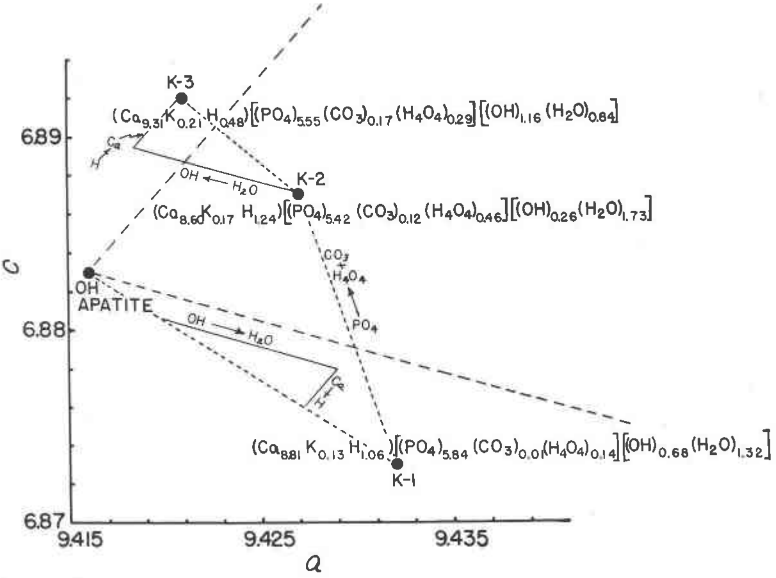

FIG. 4. Schematic showing effects on *a* and *c* by substitutions in apatite on the basis of samples K-1, K-2, K-3.

important as pressure and temperature indicators of a wide spectrum of natural conditions as the storehouse of information is slowly opened.

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