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THE NATURE OF ALKALI CARBONATE APATITES

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ABSTRACT

Apatite has been formed by the interaction of both sodium and potassium phosphate solutions with calcite. The alkali content and to a lesser extent the carbon dioxide content of the apatite is dependent on the pH of the solution from which it formed with the highest contents in crystals formed in the most basic solutions. Under nearly the same conditions of formation, sodium carbonate apatite contains approximately twice as much carbon dioxide and five times as much alkali as potassium carbonate apatite.

The apatite has a continuous weight loss from room temperature to 900° C. of more than 11 per cent. Mean index of refraction, crystallinity, and carbon dioxide content systematically change with heat treatment of the apatite.

Of the 11 per cent volatiles in the apatite less than half can be accounted for by carbon dioxide in the samples. Water forms the other volatile released when the apatite is heated. This water probably is present in the crystals as hydronium ions and $(H_4O_4)^{4-}$ substituting for Ca^{2+} and $(PO_4)^{3-}$ respectively.

INTRODUCTION

The nature of carbonate-bearing apatite has been a subject of much discussion and controversy for many years. Evidence that the carbonate is contained in the apatite structure was presented by McConnell and others in 1937 and in subsequent publications. Other investigators, for example, Neuman and Neuman (1953), present evidence suggesting that the carbonate is adsorbed on the crystal surfaces. One author, Van Wazer (1958, p. 535), states "At present, this sorption theory appears to give the best explanation of the known facts." It is difficult to reconcile the *facts* presented in this report with any model based on the sorption theory.

It was the purpose of this study:

1) to establish the composition of apatite that was formed by the interaction of alkali phosphate solutions with calcite, 2) to evaluate the dependency of the carbonate substitution for phosphate on the alkali substitution for calcium, 3) to determine the effect of temperature on the composition and crystallinity of apatite containing an appreciable quantity of carbon dioxide, and 4) to relate these findings to data obtained on finely divided hydroxyl-apatite (reagent grade tricalcium phosphate).

FORMATION OF ALKALI CARBONATE APATITE

Experimental Method. In some of the early studies of phosphorite deposits it was suggested that the apatite may have formed by replacement of calcium carbonate minerals. In view of the phosphoritized fossils in some deposits, the replacement mechanism, for at least parts of the deposit, seems quite feasible. Ames (1959) presents experimental evidence showing that sodium phosphate solution reacts with aragonite and calcite to form apatite. He concludes that (p. 832) "phosphate reaction is a replacement process in the true sense, *i.e.*, the external morphology of the calcite is preserved in the resulting apatite." From chemical analysis, not given in the report, Ames (1959, p. 833) gives a structural formula for the apatite. The formula shows an appreciable amount of sodium and carbon dioxide in the apatite.

For the present study, alkali phosphate solutions were prepared from distilled water and analytical reagent grade chemicals. The solutions were made 0.3 molar in phosphoric acid and then sodium or potassium hydroxide was added to bring the solution to the desired pH value. Determination of pH was with a Beckman Model H-2 pH meter. Analytical reagent grade $CaCO_3$, listed as "low in alkali powder," was used. By *x*-ray the material was found to be calcite, and under the microscope it appears as rhombohedral crystals less than one micron in diameter.

The solutions were stored in glass bottles, and the interaction of the solution was carried out in pyrex test tubes. Even though some of the solutions were as basic as pH 10.6, there was no evidence, after a period of more than one year, that the solutions had attacked the bottles or the test tubes. After the solutions had been stored for a period of about a month, some small acicular crystals could be found in the basic solution. Presumably these crystals are alkali phosphate compounds, and consequently the solutions departed very slightly from the original 0.3 molar phosphate mixture.

In his experiments, Ames passed the sodium phosphate solutions through a column containing crushed or precipitated calcite. The time in which the calcite was in contact with the flowing solution was not reported by Ames; however, he does report an experiment in which the apatite formed was in contact with solution for a period of two weeks.

The flowing solution method has two disadvantages. First, if the experiment is conducted for a long period of time, for example, 100 days, an excessive quantity of solution is required. Second, and more important, it is likely that the solution would seek passageways through the calcite bed, and consequently there would not be a complete or efficient interchange of the interstitial fluid. Because of these disadvantages a different method was used by the writer.

About 3 grams of calcite and 40 ml of solution were put into test tubes. All work was at room temperature. These test tubes were violently agitated at least twice a day and the solutions were replaced once a week during a period of 105 days. Despite violent agitation lumps of crystals formed during the early stages of the reaction. Because these lumps could be a source of unreacted calcite as they are abraded during the agitation, they were removed after two months by screening the sample. These lumps were not present in the reagent calcite, and they must have formed during the early stages of the reaction. After their removal, no other lumps formed.

The reacting materials were periodically sampled and examined under the microscope. It was found that even after 105 days there were traces of calcite in the apatite formed in the two most basic sodium phosphate solutions! Generally this calcite was present as discrete crystals, and only rarely was it found as cores within apatite crystals. The reason for the persistence of traces of calcite is unknown; however its presence points out that such reactions must be conducted over a long period of time and the product carefully examined under the microscope. These traces of calcite, less than one per cent, were undetectable in *x*-ray diffraction patterns.

Experimental Results

(a) Interaction of potassium phosphate solutions and calcite

Brushite ($CaHPO_4 \cdot 2H_2O$) formed by reaction of a potassium phosphate solution and calcite at a pH of 6.1. A small quantity of a gel-like material coexists with the brushite at this pH. At a pH of 7.2 only the gel-like material formed through the interaction of the solution and calcite. This gel-like material is flocculent and has about a 20-fold volume increase over the original calcite. When *x*-rayed wet it gives a very poor apatite pattern. On air drying at temperatures up to 120° C. there is an increase in intensity of the major apatite reflections. This gel-like apatite showed no volume decrease for the duration of the experiment.

The coexistence of brushite and apatite at pH 6.1 indicates that this pH is the boundary between the stability fields of brushite and apatite in the potassium phosphate solutions under the conditions of the experiments. Monetite ($CaHPO_4$) was not found in any of the samples; however, it is found in nature with brushite and apatite.

Crystals of apatite averaging 1–2 microns in size formed by the interaction of potassium phosphate solutions and calcite at a pH of 8.2 and 10.1. These crystals are roughly equant and are very rarely rhombohedral shape. The crystals appear isotropic between crossed nicols, and consequently only a single index of refraction could be determined. Hereafter this is referred to as the mean index of refraction. Apatite formed in a potassium phosphate solution at pH 8.2 has a mean index of 1.584 ± 0.002; whereas that formed in a solution at pH 10.1 has a mean index of 1.582 ± 0.002. No calcite or aragonite was found in the products from all the potassium phosphate solutions.

(b) Interaction of sodium phosphate solutions and calcite

At pH values of 4.5, 5.7, and 6.2 brushite formed by interaction of sodium phosphate solutions and calcite. Gel-like apatite was not present with the brushite. However, at pH 6.8 a gel-like apatite did form. This indicates that the boundary between the field of formation of brushite and gel-like apatite lies between pH values of 6.2 and 6.8 under the experimental conditions used. The findings suggest that this boundary occurs at a slightly higher pH when the products form in a sodium phosphate solution than when they form in a potassium phosphate solution.

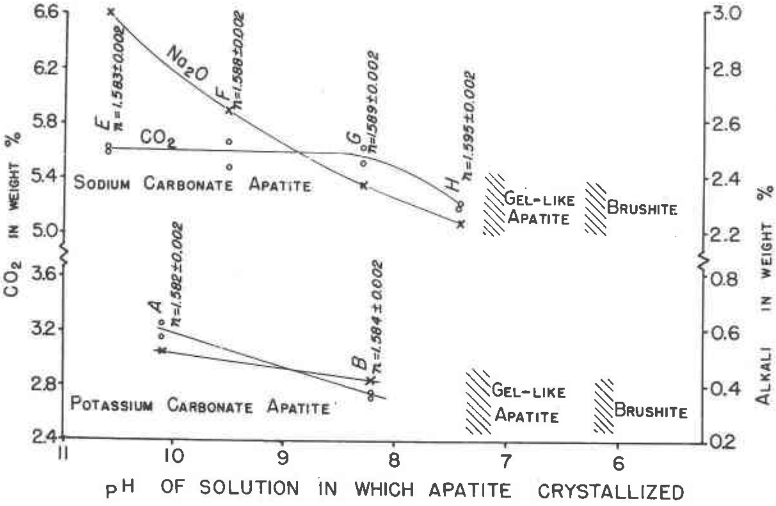

FIG. 1. Alkali and carbon dioxide content and mean index of apatite formed in 0.3 molar alkali phosphate solutions at different pH values. The letters refer to samples.

Good crystals of apatite, equant and averaging 1–2 microns, formed in sodium phosphate solutions at pH values of 7.4, 8.3, 9.5, and 10.6. The reaction products from these solutions appeared similar in size and habit, but they differ in mean index of refraction. Apatite formed in the most basic solution has a mean index of 1.582 ± 0.002; whereas that formed in a solution at a pH of 7.4 has a mean index of 1.595 ± 0.002. The other values are shown in Fig. 1.

(c) Chemical data

Apatites thus formed were analyzed for soda, potash, and carbon dioxide. Alkali analysis was by flame photometry using a Beckman DU spectrophotometer. Because the phosphate ion interferes, standards were prepared containing approximately the same concentrations of phosphate and calcium ions as the unknown. To remove any traces of alkali phosphate salts from the unknowns, each sample, about 0.3 gram, was washed with 300 ml of distilled water eight times and then examined under the microscope for foreign material. The samples of apatite formed in the two most basic solutions of sodium phosphate contained traces of calcite. To determine the quantity of calcite in the two samples, linear traverses were made across five different grain mounts of each sample. A total of more than 2000 grains was counted for each sample. It was found that the apatite formed in sodium phosphate solution at pH 10.6 contained 0.70 per cent calcite and the apatite formed at pH 9.5 contained 0.34 per cent calcite. Calcite or other foreign material was not found in other samples.

TABLE 1. PARTIAL CHEMICAL ANALYSES OF APATITE

Sample	Solution in which apatite formed	pH of Solution	Partial analyses of apatite		
			Na_2O	K_2O	CO_2
A	0.3 Molar Potassium Phosphate	10.1	0.14%	0.52%	3.35% 3.15%
B	0.3 Molar Potassium Phosphate	8.2	0.14%	0.42%	2.76% 2.72%
E	0.3 Molar Sodium Phosphate	10.6	3.00%	0.08%	5.62% 5.58%
F	0.3 Molar Sodium Phosphate	9.5	2.64%	0.08%	5.66% 5.47%
G	0.3 Molar Sodium Phosphate	8.3	2.37%	0.08%	5.50% 5.61%
H	0.3 Molar Sodium Phosphate	7.4	2.24%	0.08%	5.20% 5.17%

All samples of apatite, except the gel-like apatite were analyzed for both sodium and potassium and the values of the analyses are recorded in Table 1 and the values are plotted in Fig. 1.

Carbon dioxide content of the samples was determined by dissolving the sample in phosphoric acid and collecting the liberated CO_2 in a weighing tube containing ascarite-magnesium perchlorate. The system was flushed with nitrogen that was passed through an ascarite trap and then bubbled into the acid solution through a fritted glass filter. The carrier gas and liberated CO_2 passed through magnesium perchlorate before being carried to the weighing tube. The system was flushed for one-half hour during which time the acid solution was heated to boiling in order to reduce the solubility of gases in the solution. Samples of apatite of at least 0.5 gram and generally about 1 gram were used. The results of duplicate analyses of all the apatite samples, except the gel-like apatite, are listed in Table 1 and the values are plotted in Fig. 1. The carbon dioxide contents of the two samples containing calcite have been corrected for the carbon dioxide present in the calcite.

Even though the carbon dioxide contents of the apatites differ by more than a factor of two and the alkali contents by a factor of five, no consistent differences could be detected in the *x*-ray diffraction patterns.

The apatite which formed in the most basic solutions was found to contain the greatest quantity of carbon dioxide. It was further found that apatite that formed in the sodium phosphate solutions contained nearly twice as much carbon dioxide as the apatite that formed in potassium phosphate solutions. The highest carbon dioxide content of any sample was about 5.6 and the lowest was about 2.7 weight per cent.

The soda content of the apatite also shows a systematic decrease from about 3.0 to 2.2 weight per cent under the more acid conditions.

Similarly the highest potash content, about 0.5 per cent, was found in the apatite formed in the most basic solution. The lowest potash content, about 0.4 per cent, is for apatite formed at pH 8.2.

The corresponding decrease in the alkali content and the carbon dioxide content with decreasing pH is suggestive of a coupled substitution in the mineral. Such substitutions would involve sodium ions for calcium ions and carbonate ions for phosphate ions. However, there is insufficient alkali to compensate for the molar concentration of carbonate in the mineral. Possibly the hydronium ion makes up the deficit of monovalent ions.

Assuming a coupled substitution it is not surprising that the higher carbon dioxide content accompanies sodium rather than potassium inasmuch as substitution of sodium for calcium is well known in minerals and is quite understandable because of their similar ionic radii. Potassium ions, however, are about 30 per cent larger than sodium or calcium ions, and consequently less substitution for calcium would be expected. The analyses show that the cation substitution is important in controlling the carbonate substitution under the experimental conditions used.

The apatite did not form simple pseudomorphs after the calcite. Furthermore, the apatite grains formed are roughly twice the size of the original calcite grains. Possibly the reaction is one of pseudomorphic replacement and overgrowth, or it may be simply slow crystallization with the necessary ions being supplied from the solution and replenished by the slow dissolution of calcite.

THERMO-GRAVIMETRIC ANALYSIS OF CARBONATE

Apatite. Samples of sodium-carbonate apatite, potassium-carbonate apatite, and hydroxyl-apatite were analyzed by thermo-gravimetric analysis to determine whether chemical composition had a marked effect on the thermal stability of the crystals. Sodium carbonate apatite, sample G, was heated from room temperature to 900° C. in steps of less than 50° C. After raising the temperature by each successive increment the sample was allowed 6 to 8 hours to equilibrate before the weight was determined. Tests showed that holding the sample at a constant temperature for a longer period of time than 6 hours resulted in no further loss of weight. A sample of about 0.25 gram was used. Sodium-carbonate apatite showed a continuous weight loss from room temperature, 30° C., to about 800° C., with a linear relation for the range of about 200° C. to 750° C. The weight loss-temperature curves are shown in Fig. 2. The total volatiles lost from the sample by heating to 900° C. was more than 11.5 weight per cent, although by chemical analysis there is only about 5.5 per cent carbon dioxide in the material. After heating to 900° C., the material gave a well defined *x*-ray diffraction pattern of apatite. Whitlockite was not found either by *x*-ray or by optical examination. A sample of the

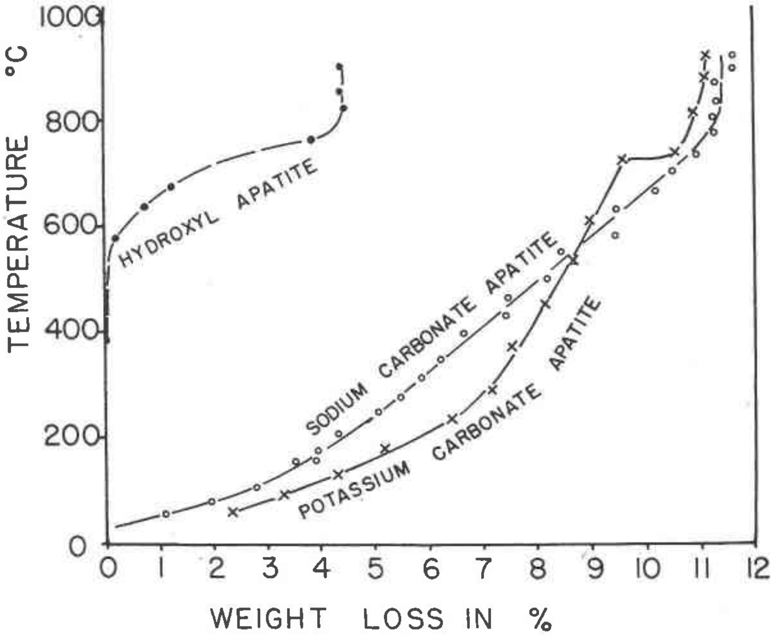

FIG. 2. Thermo-gravimetric analysis curves of apatite.

same material was heated above 1063° C. and the final product was merely apatite.

A sample of potassium-carbonate apatite was heated in a similar manner. The results are shown in Fig. 2. This apatite also shows a continuous weight loss from 30° C. to 900° C. At temperatures below 300° C. there is a greater weight loss per degree than for the sodium-carbonate apatite. The weight loss is linear through the temperature range of 300° C. to 720° C., but the rate was less than one-half of that found for sodium-carbonate apatite. At 725° C. there is an abrupt change in the slope of the curve toward a greater rate of weight loss. *X*-ray examination showed that materials heated above 725° C. contained whitlockite in addition to apatite and that the proportion of apatite decreased at higher temperatures. Below 720° C. only apatite is present. This formation of whitlockite from potassium-carbonate apatite is in marked contrast to the sodium-carbonate apatite which is stable to at least 1063° C. Total volatiles lost from the potassium-carbonate apatite were 11.2 per cent, although the carbon dioxide content of the original sample was only 2.75 per cent.

Finely divided hydroxyl-apatite, reagent grade tricalcium phosphate, was heated in steps to 905° C. during 142 days. After raising the temperature for each step, the sample was allowed 20 to 30 days to equilibrate. The sample first showed weight loss at 550° C. with some of the apatite going to whitlockite. Weight losses continued up to about 800° C., and further heating resulted in no more weight loss. The sample showed a total weight loss of 4.3 per cent with the product, at 905° C. being whitlockite and apatite.

In other experiments with the same finely divided hydroxyl-apatite, it is found that some apatite persists when the sample is heated in an open crucible to 1070° C. However, when a layer of the sample about 5 mm thick was heated in an open boat to 880° C., the only product is whitlockite and the total weight loss is 4.5 per cent. These findings suggest that the vapors liberated during the partial dehydration cause a recrystallization of the remaining apatite. It seems that the apatite recrystallizes to a more stable form or that larger crystals are formed resulting in a decrease in surface energy.

The thermo-gravimetric analyses show that the alkali-carbonate apatites have less thermal stability than finely divided hydroxyl-apatite, and that fewer volatiles contribute to greater stability.

PHYSICAL CHANGES IN APATITE EFFECTED BY HEAT TREATMENT

The mean index of refraction was determined for both the alkali-carbonate apatites, samples B and G, after the material had been heat treated. For this study the sample was held at one temperature for at least a day before the index was determined. The values determined, accurate to 0.002, are plotted in Fig. 3. Unheated potassium-carbonate apatite has a mean index of 1.584±0.002 and with heat treatment the mean index systematically increases. At 855° C. the mean index of this apatite is 1.635±0.002. Sodium-carbonate apatite yields similar results.

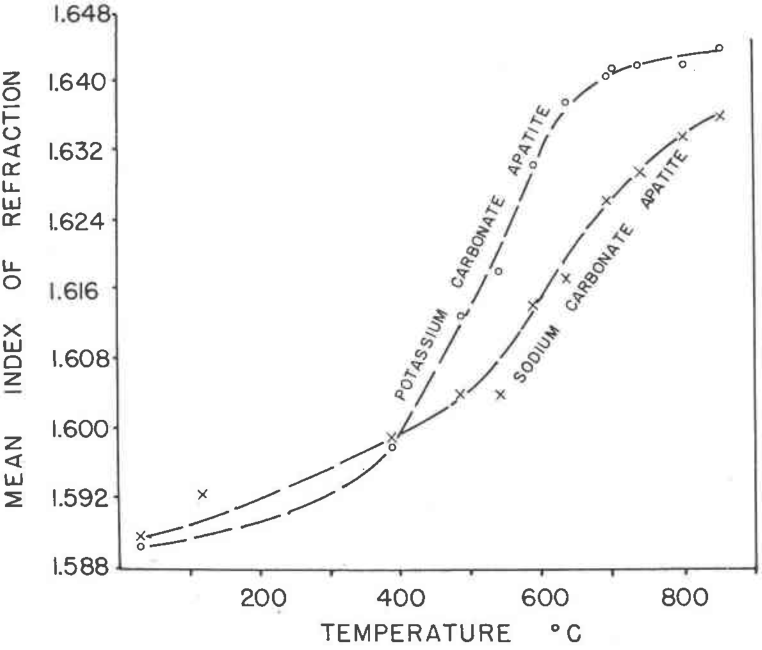

FIG. 3. Mean index of refraction of heated apatite.

The index is 1.588±0.002 prior to heating, and after heating to 855° C. it is 1.643±0.002.

Weight loss data shown in Fig. 2 compared to the mean index of refraction shows that the major change in index occurs only after 7 per cent of the volatiles are lost from the material. An additional loss of 3 per cent causes an index change from about 1.598 to more than 1.636. This major index change occurs after the sample has been heated to 400° C.

Hydroxyl-apatite synthesized under hydrothermal conditions has $\epsilon = 1.648 \pm 0.002$ and $\omega = 1.652 \pm 0.002$. Thus, with heat treatment the mean index of the alkali-carbonate apatite increases about 0.048 to a value that approaches the indices of pure hydroxyl-apatite. A similar increase in mean index is found for the finely divided hydroxyl-apatite (reagent tri-calcium phosphate). Unheated, this material has a mean index of 1.616±0.002 and after heating at 640° C. the mean index is 1.636±0.002.

X-ray patterns of the unheated alkali-carbonate apatite show broad, poorly defined reflections. With heat treatment, there was a notable increase in resolution of the *x*-ray diffraction patterns. To determine whether the change was systematic, the total width of both the diffraction peaks {211} and {112} at their half height divided by the greatest height of the two peaks was determined for material heated to different temperatures. Because these individual peaks could not be resolved until the sample had been heated to a moderate temperature, it was necessary to use the total width of the two peaks. This width-height relationship, hereafter referred to as crystallinity index, is shown plotted against temperature in Fig. 4. At temperature below 200° C. there are minor and contradictory changes in the crystallinity index. The potassium-carbonate apatite show a slightly improved crystallinity by heating to 200°C.; whereas the sodium-carbonate apatite show a decrease in crystallinity over the same temperature range. These differences are probably a result of sample preparation or machine variation. From about 300° C. to 700° C. there is a marked increase in the crystallinity; from 700° C. to

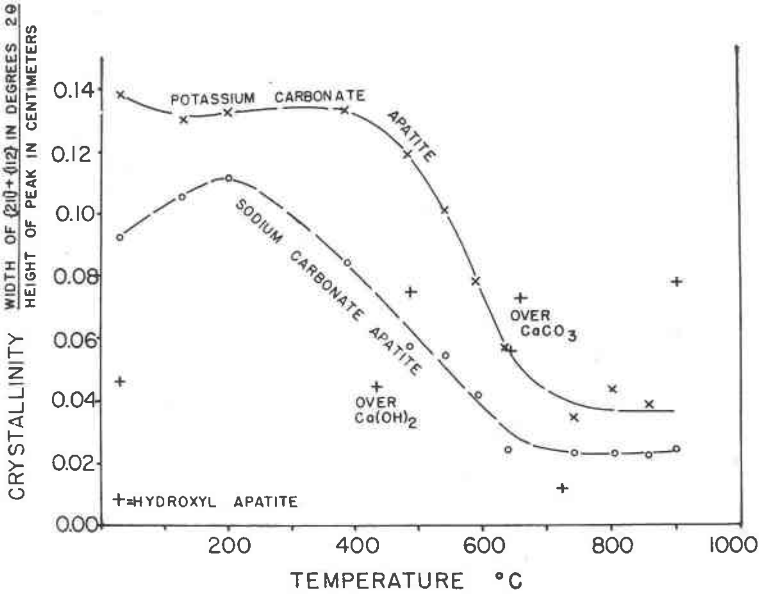

Fig. 4. Crystallinity of heated apatite.

900° C. there is little change. Thus within the same temperature range there is a direct relationship between the mean index and the crystallinity of the alkali-carbonate apatite.

Finely divided hydroxyl-apatite (reagent tri-calcium phosphate) was heat-treated to determine the effect on the crystallinity. Even though the material was heated to 900° C. there was no improvement in crystallinity. To determine whether volatiles have any effect on crystallinity by promoting recrystallization, samples were subjected to low partial pressures of water and carbon dioxide vapors. A low, but constant, partial pressure of water vapor was maintained by packing the finely divided hydroxyl-apatite over calcium hydroxide. The sample was heated to 420° C. at which temperature the calcium hydroxide slowly decomposed to lime and water vapor. This partial pressure of water vapor was maintained for 6 days after which the crystallinity of the hydroxyl-apatite was determined. A low partial pressure of carbon dioxide was maintained for 19 days by the slow decomposition of calcite in the temperature range of 628 to 652° C. The crystallinity of these samples of hydroxyl-apatite were not significantly different from samples not subjected to the vapors (see Fig. 4). The mean index of the sample heated over calcium hydroxide is 1.622±0.002 and that heated over calcite is 1.636±0.002. This change in index is explainable by the difference in temperature of the heat treatment.

TABLE 2

Temperature of Heat Treatment	Weight Per Cent CO_2 in Sample
Unheated	5.55
120° C.	4.89
120° C.	4.57
291° C.	4.22
423° C.	2.96
554° C.	1.58
710° C.	0.37

CHEMICAL CHANGES EFFECTED BY HEAT TREATMENT

Sample G, the sodium-carbonate apatite was analyzed for carbon dioxide after it had been heat treated at five different temperatures. The results of these analyses are given in Table 2 and plotted in Fig. 5.

Nearly one per cent carbon dioxide is lost by heating the material to 120° C. However, the major loss of carbon dioxide occurs in the temperature range of 300° C. to 700° C. In this temperature range the loss shows a linear relationship with temperature. It is important to note that it is in this range of temperature that the sample showed the major changes in mean index of refraction and in crystallinity.

Unheated sample G was placed under a vacuum to determine whether any of the volatiles lost at low temperatures were loosely adsorbed on the crystal surfaces. A nearly new Cenco vacuum pump originally rated to give a vacuum of 0.3 micron was used. Although the vacuum was maintained for three hours, there was no weight loss of the sample indicating that neither carbon dioxide nor water are loosely absorbed on the crystal surfaces.

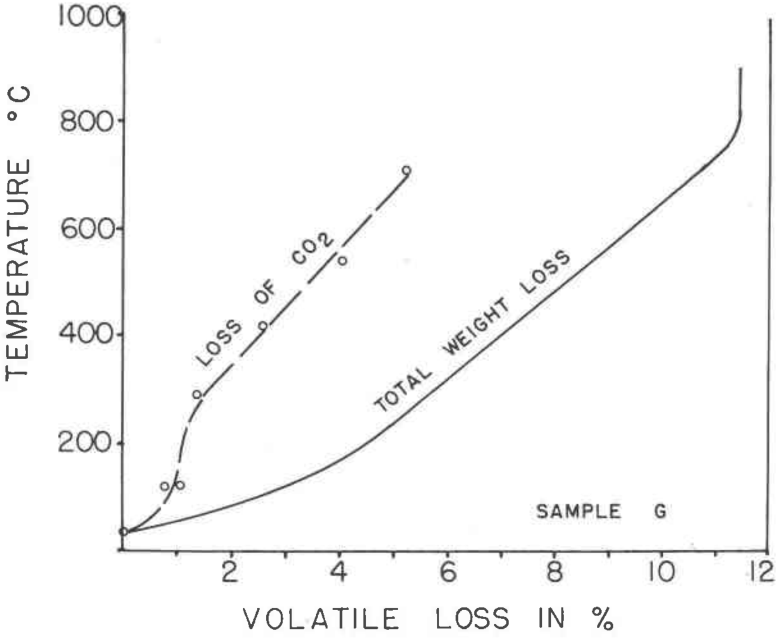

FIG. 5. Relation of loss of carbon dioxide to total weight loss of heated sodium-carbonate apatite.

SUMMARY AND CONCLUSIONS

Chemical analysis shows that there is a coupled substitution of alkali and carbon dioxide in apatite. However, the quantity of alkali is insufficient to compensate for the charge difference resulting from the substitution of carbonate for phosphate. Hydronium ion with a single plus charge may also substitute for calcium ions. The maximum carbon dioxide content of any sample was about 5.6 per cent and ranges as low as 2.75 per cent. But both from the sample containing 5.6 per cent carbon dioxide and the one containing 2.75 per cent, more than 11 per cent total volatiles can be expelled by heating the material to 900° C. Analysis of heated material showed that most of the carbon dioxide was expelled between 300° C. and 700° C. For the same temperature range there was a major increase in the mean index of refraction and the crystallinity of the apatite. Thus as carbon dioxide is expelled from the sample, the mean index and crystallinity approach the values for pure hydroxyl-apatite. Such changes can only be accounted for if the carbon dioxide is contained in the crystal structure! Any adsorption theory is wholly inadequate to explain the observations and chemical analyses. Furthermore, if much carbon dioxide or water were adsorbed on crystal surfaces, it should be possible to partially remove these volatiles under reduced pressure, but no such losses were observed.

The carbon dioxide content of these apatites can only account for about one-half of the weight lost during heating to 750° C. (Fig. 5). There is insufficient alkali to compensate for the charge difference caused by the carbonate substitution, and it is concluded that hydronium ion also substitutes for calcium. If the necessary quantity of hydronium ion is added to the quantity of carbon dioxide, the sum is still insufficient to account for the total weight loss of the heated material. Clearly, there also must be some other manner in which water can enter the crystal structure. McConnell (1962, p. 262) proposes that $(H_4O_4)^{4-}$ may substitute for $(PO_4)^{3-}$. Such a substitution could easily account for the volatiles in excess of the carbon dioxide that are lost from both the sodium and potassium carbonate apatities when heated.

Because of the dependence of carbon dioxide content, mean index, and crystallinity of apatite on temperature, it seems likely that the maximum temperature to which some phosphorite rocks and other rocks containing apatite were subjected may be deduced from the chemical composition and physical nature of apatite. The many complexities of apatite suggest that it will be a storehouse of geological information when such complexities are completely understood. The author is currently investigating the application of these findings to natural materials.

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