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EFFECT OF pH AND SOLUTION CONCENTRATION ON THE
COMPOSITION OF CARBONATE APATITE

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INTRODUCTION

Carbonate substitutions for phosphate in the apatite structure have been indicated by many investigations (McConnell, 1952; Ames, 1959; Le Geros, 1965; Simpson, 1964, 1965). The reported quantities of carbonate substituting in natural and synthetic apatite range from a fraction of a percent to more than 22 weight percent. Because many of the experiments were performed under conditions conducive to the formation of metastable crystals, the effect of extrinsic variables on carbonate substitution in apatite cannot be gleaned from the studies. It is the purpose of this study to present data on the effects of pH and concentration of other ions on the composition of apatite.

EXPERIMENTS

Apatite can be formed by the slow interaction between sodium phosphate solution and calcite, as described by Ames (1959). Although it takes from several months to a year for the reaction to go to completion,

control on the solution composition can be maintained by frequent replenishment. The long duration of the experiment is advantageous in approaching equilibrium. An additional advantage of this method for the formation of apatite is that sodium is the only foreign ion involved, and because sodium is ubiquitous in nature, its presence in a system modeling nature is advantageous.

In one group of experiments at 25°C, a 3 cm-thick bed of fine-grained calcite was inundated in a column of 0.2 M sodium phosphate solution of pH = 7.5. The solution was replaced several times without disturbing the bed of calcite. The gaseous phase in the system was restricted; consequently, with time and reaction the CO₂ content of the gaseous phase and the CO₂-derived species in the solution increased. After several months, at which time the top of the calcite bed appeared cemented, the system was sealed and left for an additional 9 months. After a total time of 11 months the system was opened, the pH of the solution measured as 9.16 ± 0.02, and successive horizontal layers in the original calcite bed were removed and analyzed by X-ray diffraction to determine the nature of the reaction product. Because several of the possible reaction products easily lose water of hydration, all material was moist when X-rayed. At the interface with the solution, the solid material was found to be only apatite. At a depth of 5 mm apatite and calcite were found, and at greater depths the abundance of apatite decreased and calcite increased. Below 15 mm only calcite was found. Octa-calcium phosphate (OCP) was not found at any level in the sample.

Even though the quantity of apatite decreased with depth in the undisturbed bed, the crystallinity, as shown by X-ray diffractograms, increased (Fig. 1). These differences in crystallinity are likely the result of formation of apatite in environments of differing phosphate concentration. At the top of the material the phosphate concentration of the solution is 0.2 M; however, at depths in the material the phosphate ion concentration in the solution is a function of the rate of diffusion of phosphate ions through the interstitial fluid and the rate of reaction of the solution with calcite. At the reaction front, a depth of roughly 15 mm, the phosphate ion concentration must be extremely low.

In repeated experiments of 15-day duration, OCP was found at the top of the bed, and apatite was found at depths of about 1.5 and 3 mm. This suggests that OCP is formed by rapid reaction in rather concentrated solution. A comparison with the previous experiment indicates that OCP, under these conditions, recrystallizes to apatite with time.

Because of the indication that crystallinity of apatite increases with decreasing phosphate concentration of the reacting solution, a series of experiments was conducted specifically to investigate this effect. About 4

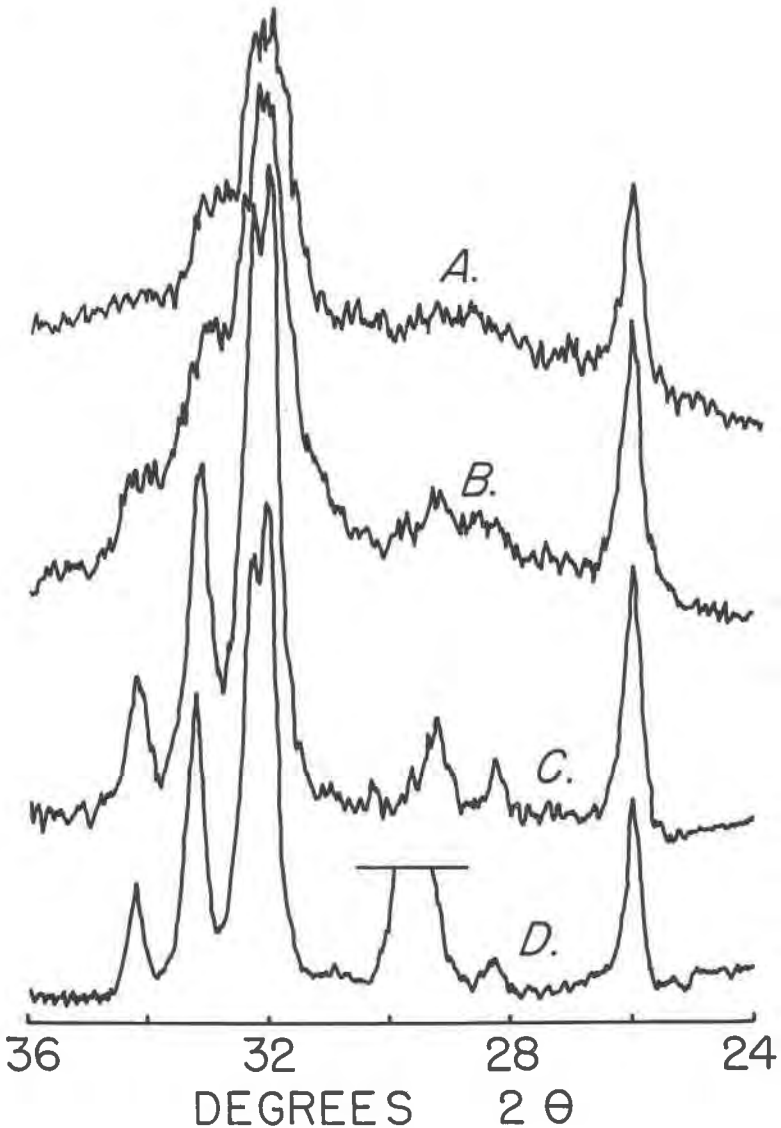


FIG. 1. X-ray diffractograms of apatite formed by reaction of calcite and sodium phosphate solution Cu radiation, Ni filter.

- A. Pattern from top surface of the undisturbed bed.
- B. Pattern from horizontal surface 15 mm. below top of bed.
- C. Pattern from horizontal surface 3 mm. below top of bed.
- D. Pattern from horizontal surface 5 mm. below top of bed.

Truncated peak is an off-scale calcite reflection.

g of fine-grained calcite reacted under 150 ml of solution at 25°C in a system vented to air. Solutions were replaced 18 times over two months. One month after the start of the experiment, the material in the solution was ball-milled to liberate any unreacted cores of calcite. Phosphate concentrations ranging from 0.4 to 0.01 M were used in two series of six samples each. In one series the pH was about 8 and in the other series the pH was about 9.

In both series it was found that the crystallinity, as shown by resolu-

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF LOW-TEMPERATURE APATITE

Sample	Solution		Crystals			
	M, PO ₄ ⁴⁻	pH	CO ₂	Mean <i>n</i>	Wt. Loss ¹	Heated Product ²
C-1	0.4	7.96	1.82	1.56	9.1	W>>A
C-2	0.3	8.05	2.25	1.58	9.2	W>A
C-3	0.2	7.98	2.38	1.59	10.2	W>A
C-4	0.1	7.99	2.90	1.59	8.7	W~A
C-5	0.05	8.08	3.38	1.59	9.0	A
C-6	0.01	9.44	7.26 ³	1.56	14.0 ³	A
C-7	0.4	9.04	2.15	1.56	5.9	A
C-8	0.3	9.10	2.44	1.56	10.0	A
C-9	0.2	9.02	2.62	1.55	9.7	A
C-10	0.1	9.13	3.09	1.57	9.8	A
C-11	0.05	8.85	3.43	1.58	9.6	A
C-12	0.01	8.66	3.62	1.59	9.6	A

¹ 30°-900°C.

² W = whitlockite, A = apatite, Identification by X-ray.

³ Sample contains unreacted calcite.

tion of X-ray diffractograms, increased with decreasing concentration of phosphate in the solution. Although the formed crystals X ray as apatite, and not OCP, they have unusual physical and chemical properties (Table 1). All material was examined microscopically for residual calcite and, with the exception of sample C-6, none was found. Carbon dioxide content of the crystals shows a systematic increase, for both series, with decreasing concentration of the solution in which they formed. Crystals formed under the more basic conditions consistently contain greater amounts of CO₂. This pH effect is less for crystals formed in dilute systems (Fig. 2). It is significant that the increase in carbon dioxide content and the increase in crystallinity follow the same trend.

Weight loss, or total expellable volatile, H₂O plus CO₂, was determined

by vacuum drying the crystals over calcium chloride and then heating to 900°C. With the exception of C-6 for which the determination would be meaningless because the sample contained calcite, the total expellable volatiles ranged from 5.9 to 10.2 weight percent. This volatile content did not show a systematic trend nor could it be related to the CO₂ content of the crystals. Unfortunately, precise values for total expellable volatiles

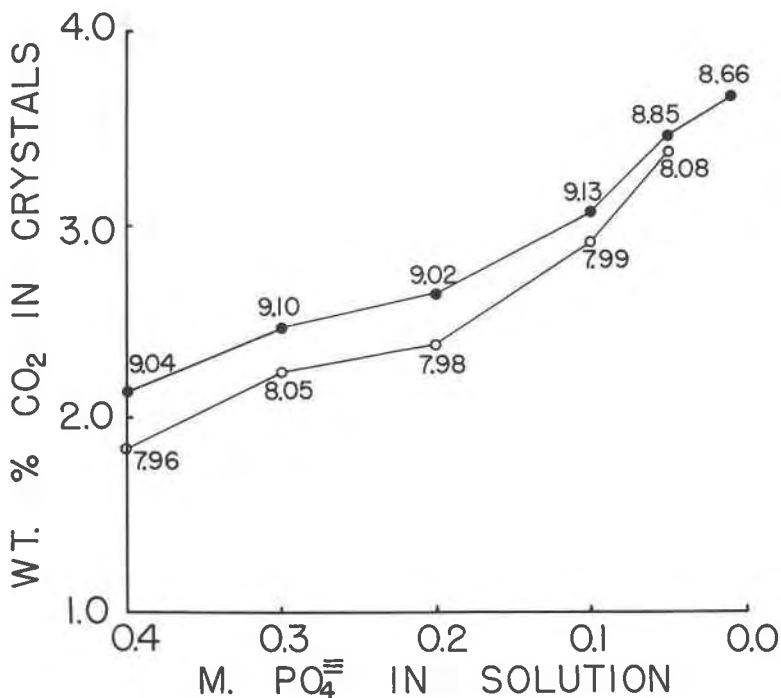


FIG. 2. CO₂ content of apatite relative to phosphate concentration of the solution in which the crystals formed. Numbers at the data points indicate the final pH of the solution.

are difficult to measure because there is no lower temperature reference point (*e.g.* 110°C) at which the crystals can be effectively dried without losing significant quantities of structural water. The total volatile content is far in excess of the CO₂ content of the crystals. Probably the excess volatiles over those accountable for as CO₂ are present in the crystal structure as H₂O or H₄O₄⁴⁻, a substitution indicated by McConnell (1965). Such substitution would tend to balance a charge difference resulting from the substitution of a carbonate ion for a phosphate ion in the crystal structure.

Mean index of refraction was determined on the crystals and found to

range from 1.56 to 1.59. This value is strikingly lower than the $\omega \approx 1.642$ and 1.637 measured by Simpson (1965) on hydrothermally-synthetic hydroxylapatite and carbonate hydroxylapatite containing 2.29 weight percent CO_2 . The low mean index of refraction can also be accounted for by the substitution of H_2O or $\text{H}_4\text{O}_4^{\equiv}$ in the crystal.

With heating to 900°C some crystals decomposed to whitlockite whereas others remained as apatite. Reaction to whitlockite was never complete in 9 hours. Whitlockite was found only in the heated product of material formed at a $\text{pH} \sim 8$ in solution concentrations of 0.1 M or greater. Furthermore, the amount of whitlockite showed a systematic increase with increasing solution concentration. The crystals going in part to whitlockite as a result of heat treatment are those formed at a $\text{pH} \sim 8$, which show the poorest crystallinity, and the lowest CO_2 content.

On the basis of the heating experiments it appears that low temperature apatite can be divided into two series. One series remains apatite after heating even though a large quantity of volatiles is expelled. The other series has a heated product of whitlockite plus apatite. Because whitlockite is phosphorus-rich relative to apatite, the one series can be classified as phosphorus-rich and the other series as apatite with a normal Ca/P ratio. The presence or absence of whitlockite in the heated product is the basis for the distinction of the two series. Because X-ray diffraction was the means of identifying the presence of whitlockite, a sample containing a few percent whitlockite may escape detection.

CONCLUSIONS

The CO_2 content of apatite is found to increase with increasing pH and decreasing phosphate concentration. In very dilute solution the carbon dioxide content of apatite is less dependent on pH of formation than when apatite forms in a concentrated solution. With $\text{pH} \sim 8-9$, a range of both geological and biological interest, apatite formed in dilute solutions had a carbon dioxide content of about 3.5 weight percent.

Some natural systems, geological and biological, are reported to be saturated or supersaturated with respect to "apatite". The concentration or activity products of calcium and phosphate in many natural systems is comparable to the reported solubility data for hydroxylapatite or carbonate hydroxylapatite. Such a comparison has real significance only if the solubility product of the apatite in equilibrium with the solution is indeed identical to the solubility product used in the comparison. This study suggests that a better comparison to a natural system would be obtained by using solubility data for low temperature apatite containing about 3.5 percent CO_2 and 6 percent excess H_2O in the structure.

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Fe/(Fe+Mg) RATIO IN BIOTITE FROM GEORGIA GRANITIC ROCKS

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INTRODUCTION

Preliminary observation of samples from quarries in the Elberton granite district, Georgia, revealed that biotite in gneiss and schist inclusions had a different refractive index than biotite in adamellite taken from the same quarry; whereas biotites in adamellite taken from scattered quarries had similar refractive indices.

Uncertainties in the determination of the refractive indices of biotite have been reported; Engel and Engel (1960) comment extensively on this, but Peikert (1963) implies that the determination is not particularly difficult. Because of absorption in the biotite, a match with the oil is difficult to tell unless the grain size is very fine. Due to these uncertainties $d(060)$ was determined in addition to $\beta(\approx\gamma)$ refractive index on biotite from 45 specimens of Elberton adamellite and one specimen each of Gray granodiorite, Stone Mountain adamellite, Danburg porphyritic adamellite, Columbia County adamellite, and a gneiss and a schist inclusion in Elberton adamellite.

GEOLOGY AND PETROLOGY OF ROCKS

The Elberton Granite District (Ramspott, 1964a), from which most of the samples came, extends over 200 square miles in Elbert, Oglethorpe, and Madison Counties, Georgia. Fine- to medium-grained adamellite bodies cross-cut the surrounding sillimanite-grade gneiss and schist, but are themselves faintly metamorphosed (retrograde and dynamic), as shown by microscopic metamorphic textures, chlorite-sericite alteration,

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