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AUTHOR

L. L. Ames, Jr.

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HW-5A-2

THE GENESIS OF CARBONATE APATITES*

L. L. Ames, Jr.

CONTENTS

ABSTRACT

A portion of the system Na_3PO_4-$CaCO_3$-H_2O was investigated at low temperatures. The formation of a carbonate apatite by phosphate replacement of calcite in alkaline solutions and the structural positions of the carbonate groups are discussed. Data indicate calcite replacement by low concentrations of phosphate to be the principal mechanism of formation of marine phosphorite deposits.

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HW-5A

INTRODUCTION

During the course of soil studies at Hanford, it was found that the presence of phosphate ion enhanced the removal of Sr^{90} from waste solutions (26). The soils that exhibited this enhanced Sr^{90} removal were calcareous. Consequently the calcite-phosphate-strontium reaction was investigated to ascertain its value as a Sr^{90} extraction mechanism (1). The portion of the study that concerns carbonate apatite genesis is presented here.

LITERATURE REVIEW

The literature concerning carbonate apatites (phosphorites) is voluminous. No attempt will be made to review it in detail. Summaries of the literature on apatites and phosphorite genesis are presented by Jaffe (15), Dietz, et al.,(7), McConnell (21, 22, 23), Hutchinson (13), Hendricks, et al. (12), Pettijohn (28), Arnold (2), Clark (6), and Eisenberger, et al. (8).

Mineralogists appear to be in essential agreement that phosphorites are carbonate-bearing apatites. Beyond this point, however, there is little agreement. Hendricks (11) is of the opinion that the carbonate is present outside of the apatite lattice as adsorbed or non-crystalline carbonate. Gruner and McConnell (10), on the other hand, presented optical and XRD data to substantiate the location of CO_3^{-2} groups within the apatite lattice. Posner (29) has presented XRD and infrared spectroscopic data that show the carbonate to be present as a separate, admixed phase. Romo (32) demonstrated the absence of hydroxyl groups in a product resulting from the reaction of calcite with alkaline phosphate solutions, and postulated the substitution of CO_3^{-2} groups for OH^- in this product. McConnell and Gruner (25) consider the carbonate to be substituting for phosphate groups, or water and carbonate for calcium along the threefold axes of francolite.

The literature, then, concerning the carbonate of carbonate-apatite appears to be in disagreement on three points; 1) whether the carbonate is present within or outside of the apatite lattice, or as a separate phase, 2) if within the lattice, in what structural position or positions, and, 3) wherever the carbonate is located, how it got there.

To briefly summarize the literature on phosphorite genesis, Murray and Renard (27) postulated the local concentration of phosphate by the catastrophic destruction of phosphatic marine organisms. Blackwelder (3) and Krumbein and Garrels (18) favored low pH (7.0-7.5), restricted basins for phosphorite precipitation. Mansfield (20) emphasized the role of fluorine in phosphorite deposition, Kazakov (16) the role of CO_2, and Cayeux (5) the concentration of phosphates from sea water by micro-organisms. Dietz, Emery, and Shepard (7) pointed out that the offshore nodular phosphorite deposits of California are found in a highly oxidizing environment. Clark (6) mentioned the origin of phosphorite deposits by the mechanism of differential solution of admixed calcite and calcium phosphates. Bushinsky (4) reported the replacement of calcite and aragonite by phosphate solutions, and the effect of carbonate grain size on the relative rate of replacement. Limestone replacement as a mechanism for the formation of biochemical phosphates was discussed by Hutchinson (12). Irvine and Anderson (13) first demonstrated the replacement of $CaCO_3$ by alkaline phosphate solutions in the laboratory.

The work of Klement, et al. (17) on the non-existence of carbonate apatite precipitated from aqueous solutions, and Riviere (31) on calcite replacement by low concentrations of PO_4^{-3} are especially pertinent to this study.

METHODS OF INVESTIGATION

The calcite-phosphate mechanism was studied under equilibrium and non-equilibrium (column) conditions at 28° C. The column setup is shown in Figure 1. This apparatus allows the collection of column effluent fractions at controlled flow rates. Equilibrium results were obtained by shaking aliquots of traced influent solutions in lusteroid tubes along with blank or control solutions, which minimized errors arising from adsorption and decay of tracers. The difference in activity between equivalent volumes of influent and effluent solutions is a measure of the amount of radioisotope removed. It was assumed that there were no differences between the chemical properties of tracers and corresponding non-radioactive ions. High-salt solutions were sampled and counted on stainless steel plates at secular equilibrium. Calculations were based on differential counting rates to minimize corrections for back-scatter, self-adsorption, and other factors that introduce counting errors between influent and effluent solutions. An open-end, mica-window GM tube, along with appropriate scaling apparatus, was used for sample counting. C^{14} was counted in a proportional gas flow unit.

A Norelco X-ray diffraction unit was used to identify unknown materials.

Types of calcite used included precipitated, optical grade, marble, travertine, and limestone. Except for the physical differences in the above types, their chemical behavior was the same, and they are all referred to in this paper as calcite.

High-purity radioisotopes from Oak Ridge were added to certain of the influent solutions in amounts convenient for counting purposes. All other chemicals were reagent grade.

RESULTS

A column containing 10 g. of precipitated calcite was constructed (Figure 1) and a $0.3\underline{M}$ Na_3PO_4 solution passed over this calcite at a flow rate of 7 ml/hr/cm^2 and a pH of 12.4. Samples of the calcite were removed at intervals, washed with distilled water, air-dried, and X-ray diffraction patterns obtained. These patterns showed the simultaneous disappearance of calcite and appearance of an apatite (Figure 2), corresponding to the idealized reaction -

$$NaOH + 3Na_3PO_4 + 5CaCO_3 \longrightarrow Ca_5(PO_4)_3OH + 4Na_2CO_3.$$

Table I lists the X-ray diffraction data for the air-dried carbonate apatite of this study.

TABLE I

X-ray Diffraction Powder Data for the Air-dried Compound

$$\left[\mathrm{Ca}_{9.01}\ \mathrm{Na}_{1.07}\right]\left[(\mathrm{PO}_4)_{5.46}\ (\mathrm{CO}_3)_{1.36}\right]\left[(\mathrm{OH})_{0.67}\ (\mathrm{H}_2\mathrm{O})_{1.33}\right]$$

d (Å)	I	d (Å)	I
4.116	W	1.931	M
3.694	VW	1.880	VW
3.402	M	1.834	M
3.138	VW	1.795	VW
2.768	S	1.763	VW
2.687	M	1.721	W
2.607	M	1.500	VW
2.505	VW	1.447	VW
2.232	W	1.371	VW
2.127	VW	1.258	VW
2.055	VW	1.232	VW
		1.216	VW

The phosphate reaction with calcite is a replacement process in the true sense, i.e., the external morphology of the calcite is preserved in the resulting apatite. With the replacement of a synthetic $\mathrm{Ca}^{45}\mathrm{CO}_3$, the quantitative retention of the Ca^{45} within the resulting apatite was confirmed.

To substantiate the assumption that CO_3^{-2} was being replaced by PO_4^{-3} during the calcite-phosphate reaction, a synthetic $\mathrm{CaC}^{14}\mathrm{O}_3$ was replaced under the conditions of the original calcite column. X-ray diffraction patterns were made from this calcite at intervals (a procedure allowed by the comparatively soft radiation of C^{14}) in addition to C^{14} counting. At approximately 10 per cent by weight $\mathrm{C}^{14}\mathrm{O}_3^{-2}$ in the resulting apatite, the main "d" spacing of calcite at 3.04 Å was no longer discernible. The pattern was entirely that of an apatite. The structural formula calculated from a chemical analysis of this "apatite" was -

$$\left[\mathrm{Ca}_{9.01}\ \mathrm{Na}_{1.12}\right]\left[(\mathrm{PO}_4)_{5.26}\ (\mathrm{CO}_3)_{1.68}\right](\mathrm{H}_2\mathrm{O})_{2.00}$$

Na^+ in Ca^{++} positions balance the apatite electrostatically by compensating for CO_3^{-2} in PO_4^{-3} positions.

A digestion of this same apatite at room temperature in a 0.3$\underline{M}$ Na_3PO_4 solution for two weeks resulted in an apatite with the formula -

$$\left[Ca_{9.35}\;Na_{1.07}\right]\left[(PO_4)_{5.46}\;(CO_3)_{1.36}\right]\left[(OH)_{0.67}\;(H_2O)_{1.33}\right]$$

The mean refractive index of the above, air-dried sample, was 1.61 to 1.62.

A kinetic study of phosphate removal (Figure 3) gave a velocity constant, k, of 3×10^{-4} per hour per cm^2 under the experimental conditions indicated in Figure 3. Below a concentration of 5×10^{-4} $\underline{M}$, phosphate removal was no longer first order. This lower limit is in doubt, however, as influent solutions were not carbonate-free. Under the above conditions, the reaction ceases at concentrations of less than 0.09 ppm (10^{-6} $\underline{M}$) PO_4^{-3}.

Certain cations that fit into the apatite lattice were also removed by first order reactions (1). These cations may be used to trace the relative rate of apatite formation (the formation of the apatite itself is certainly not a first order reaction). Tracing the rate of apatite formation with Sr^{90}, and adding various concentrations of $NaHCO_3$ to a Na_3PO_4 influent (Figure 4), demonstrated the influence of bicarbonate concentration on the calcite reaction at 28°C. The HCO_3^- content of the solution affects the solubility of the calcite and, hence, the calcite replacement rate. An increase in temperature from 15°C to 65°C, by lowering the CO_2 content of the system, increased the relative rate of apatite formation by a factor of approximately three. An apatite column, after contact with solutions containing 0.4 $\underline{M}$ $NaHCO_3$ or greater, and no Ca^{++} or PO_4^{-3}, yielded an initial calcite that was rapidly dissolved in the same solution. At less than 0.4 $\underline{M}$ $NaHCO_3$ in the system, apatite was a stable phase.

Calcite replacement by phosphate proceeds when the system is Ca-saturated in relation to its HCO_3^- content, or the degree of undersaturation does not exceed a definite HCO_3^-/PO_4^{-3} molar ratio. The data given in Figure 4 are applicable only for those conditions that are listed there.

The calcite replacement was found to proceed in a 3.0 $\underline{M}$ $NaNO_3$ - 0.05 $\underline{M}$ Na_3PO_4 (pH = 11.1) solution with the same velocity as in a 0.05 $\underline{M}$ Na_3PO_4 solution, when adjusted for pH differences (1). The replacement is little affected by large concentrations of alkalies.

Sr^{90} was also used to show the effect of pH on the relative rate of apatite formation (Figure 5), and the effect of calcite grain size on relative rate of apatite formation (Table II). Abrasion of the larger calcite grain sizes during shaking caused considerable deviation from the grain size ranges as listed in Table II. However, with equal weights of calcite, the relative rates of apatite formation were roughly proportional to calcite surface areas.

TABLE II

Effect of calcite grain size on the relative rate of apatite formation

Calcite grain size range (mm)	Relative rate of apatite formation (as per cent Sr90 removed)
1.0 to 2.0	33.9
0.25 " 1.0	36.8
0.05 " 0.25	69.2
0.01 " 0.05	80.0

Solution-calcite contact time (hrs)	1.0
Calcite weight (mg)	400.0
Influent solution pH	11.1
Influent solution:	3$\underline{M}$ $NaNO_3$, 0.05$\underline{M}$ $Na_3PO_4 \cdot 12H_2O$, 2 mg $Sr(NO_3)_2$/liter, 100,000 d/m/ml Sr90-Y90; 40 ml solution per sample.

Table III gives the relative rates of apatite formation for other carbonates. Note that both the calcite and aragonite type lattices are involved.

TABLE III

Relative rates of apatite replacement of some other carbonates

Carbonate	Relative rate of "apatite" formation (as per cent Sr^{90} removed)
$SrCO_3$	98.5
$BaCO_3$	96.6
$MgCO_3$	94.8 (wagnerite)
$CaCO_3$ (calcite)	94.4

Carbonate-solution contact time (hrs)	2.0
Carbonate weight (mg)	400.0
Carbonate grain size (mm)	0.01
Solution volume (ml)	40.0
Solution pH	11.1

Influent solution: 3M $NaNO_3$, 0.05M $Na_3PO_4 \cdot 12H_2O$, 2 mg per liter $Sr(NO_3)_2$, 100,000 d/m/ml Sr^{90}-Y^{90}.

Calcite had no appreciable ion exchange capacity for Sr^{90} as illustrated by Table IV. The exchangeability of Sr^{90} for Ca in $CaCO_3$ was investigated to insure that the Sr^{90} used here as a tracer was not removed to any large extent in this manner.

TABLE IV

Strontium exchange capacity of calcite in the absence of phosphate

Column volumes	Removal of Sr^{90} (%)
0.98	32.7
1.96	22.1
2.61	10.8
3.92	6.6

Column: 150g of 1.0 to 0.25 mm calcite, volume = 102.3 cc
Flow rate: 7 ml/cm^2/hr
Influent solution: 3M $NaNO_3$, 100,000 d/m/ml Sr^{90}-Y^{90}, pH adjusted to 11.8 with NaOH.

It was also proved that the Sr^{90} and phosphate were not removed from the system as a strontium-phosphate precipitate (1).

As further substantiation that the equilibrium, illustrated by the idealized equation -

$$NaOH + 3Na_3PO_4 + 5CaCO_3 \rightleftharpoons Ca_5(PO_4)_3OH + 5Na_2CO_3,$$

apparently lies far toward the apatite side, 150 ml of $0.3\underline{M}$ Na_3PO_4 solution containing 100,000 d/m/ml $C^{14}O_3^{-2}$ as the sodium salt was passed through 5g of precipitated $CaCO_3$ at a flow rate of 10 ml/cm^2/hr. The resulting apatite contained 1,000 d/m/g, or a total of 0.033 per cent of the $C^{14}O_3^{-2}$. This small amount of $C^{14}O_3^{-2}$ was probably surface-adsorbed rather than present in the apatite lattice.

Sodium metaphosphate ($NaPO_3$), containing PO_3^{-1} groups linked to form chains by the sharing of two oxygens by each group, was tried as a phosphorus source. No calcite replacement occurred. Discrete PO_4^{-3} tetrahedra were required for the replacement to proceed.

DISCUSSION

The calcite replacement results in a carbonate apatite due to incomplete replacement of CO_3^{-2} with PO_4^{-3}. The reaction equilibrium data and structural formulae indicate that this carbonate can be entirely present in the apatite lattice when the apatite contains less than 10 per cent by weight CO_3^{-2}. Above 10 per cent by weight CO_3^{-2}, it is at least partly present as a separate carbonate phase. Structural formulae, equilibrium data, and C^{14} tracing show no indications of the carbonate being present in Hendricks' "voids" (11), or adsorbed to any great extent on apatite surfaces during calcite replacement. $C^{14}O_3^{-2}$ exhibits little tendency for surface removal on apatite in the presence of phosphate concentrations greater than 10^{-6} M, and no tendency to substitute in the apatite for phosphate or any other lattice position. The CO_3^{-2} contained in the apatite was present in the original calcite. Apatites precipitated from aqueous solution contained adsorbed $C^{14}O_3^{-2}$ only, as was previously reported by Klement (17), in amounts that were proportional to the $C^{14}O_3^{-2}$ added to the original solution. There is no evidence that an apatite containing structural CO_3^{-2} can be synthesized except by phosphate replacement of a carbonate.

Romo's assumption (32) that CO_3^{-2} groups were substituting for OH^- groups in a carbonato-apatite synthesized under similar circumstances is without foundation in the absence of a chemical analysis. As previously presented results show, it is possible to obtain a carbonate apatite without OH^-. Romo has not shown that CO_3^{-2} groups occupy OH^- positions in his synthetic apatite.

It is entirely possible that Posner (29) has found admixed $CaCO_3$ in a francolite sample, probably representing incomplete calcite replacement.

The variable composition of the apatite phase, even in this relatively simple system, shows the fallacy of attempting to apply the laws of sparingly soluble compounds to apatite. Levinskas (19) also reported that apatites are "solid solutions" and not stoichiometric compounds as evidenced by their highly variable solubility products. The term "carbonate apatite" is used in this paper to designate an apatite that contains 10 per cent or less CO_3^{-2} within its lattice, and does not imply an invariant apatite composition. The term "phosphorite" is used to designate a sedimentary phosphate deposit primarily composed of carbonate apatite.

This investigation has clearly established that the deposition of phosphorite can occur in calcium-free solutions as a carbonate replacement. Furthermore, phosphate is removed from solution by this mechanism at a relatively rapid rate. It is highly improbable that the concentration of PO_4^{-3} could, even locally, rise sufficiently to produce a relatively unadulterated phosphorite deposit _ the presence of calcite. Because field studies of phosphorites have shown them to be commonly associated with limestones (7, 9, 12) or limy sediments, the phosphate replacement of these carbonates is considered to be the principal mechanism of phosphorite formation.

The differential solution of limestones, leaving an apatite residue after dissolving $CaCO_3$, is an unlikely source of phosphorites. The average PO_4^{-3} content of limestone is given as 400 ppm by Rankama and Sahama (30), or approximately 720 ppm apatite. Considering a thousand foot column of limestone (density = 174.7 lbs/ft^3) one foot square, containing the above amount of apatite (0.072 per cent), the resulting phosphorite residue would be 0.65 ft^3 in volume. It is impossible to accept differential solution as a phosphorite source when attempting to account for 14-foot beds such as occur in the Phosphoria formation.

Apatite replacement of $CaCO_3$, on the other hand, occurs under conditions that fit the field occurrences and laboratory investigations of phosphorites. These conditions are:

1) a non-depositional environment,
2) limy sediments or limestone, available for replacement,
3) sea water Ca-saturated, or nearly so, in order that the limestone present be in near-equilibrium with the sea water,
4) pH = 7.0 or greater,
5) PO_4^{-3} concentration of 0.1 ppm or greater.

Limestone replacement also can occur during diagenesis of phosphatic shales that contain calcite nodules or layers, or are adjacent to limestones in the sedimentary sequence.

Cyclic replacement of limestone and limy sediments is implied by the results of this investigation. Interrupted limestone replacement, along with the facility of the growing apatite for including other cations such as Mn^{++} or Fe^{++}, can result in agate-like banding characteristic of many nodular phosphorites (4, 7, 22). Replacement, of course, proceeds from the surface of the limy nodule towards the nodule center. The vitreous appearance of certain of the bedded phosphorites (4) was noted on the larger apatite-replaced calcite grains. Fine-grain size calcite cements are more rapidly replaced, due to their larger surface areas per unit weight than are larger $CaCO_3$ crystals. Quartz sand grains and other extraneous material included in the original limy sediments are ordinarily not replaced.

Changes in the chemical composition and crystal size of the apatite do not terminate after limestone replacement is completed. Continued CO_3^{-2} loss and gain in OH^- and/or F are indicated over a period of time.

SUMMARY

Alkaline phosphate solutions were found to replace calcite with a carbonate apatite of variable composition. Relative replacement rates were a function of solution pH, PO_4^{-3} content in relation to HCO_3^- concentration, and calcite grain size (surface area). The carbonate can be present within the apatite lattice, and as a separate phase at greater than 10 per cent by weight CO_3^{-2}. There was no evidence for the adsorption of relatively large amounts of CO_3^{-2} by the crystallizing apatite during replacement. Precipitated apatites contain $C^{14}O_3^{-2}$,

probably adsorbed, in amounts that are proportional to $C^{14}O_3^{-2}$ concentration in the original solutions. Stability relations in the system Na_3PO_4 [illegible] $CaCO_3 - H_2O$ indicate that apatite replacement of carbonates is the most probable mode of formation of large marine phosphorite deposits [illegible] due to the operation of the replacement mechanism with PO_4^{-3} and Ca^{++} concentrations far below those required for apatite precipitation [illegible]

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The author wishes to acknowledge the able assistance and helpful suggestions of Olevia C[illegible] Sterner in the laboratory work [illegible]

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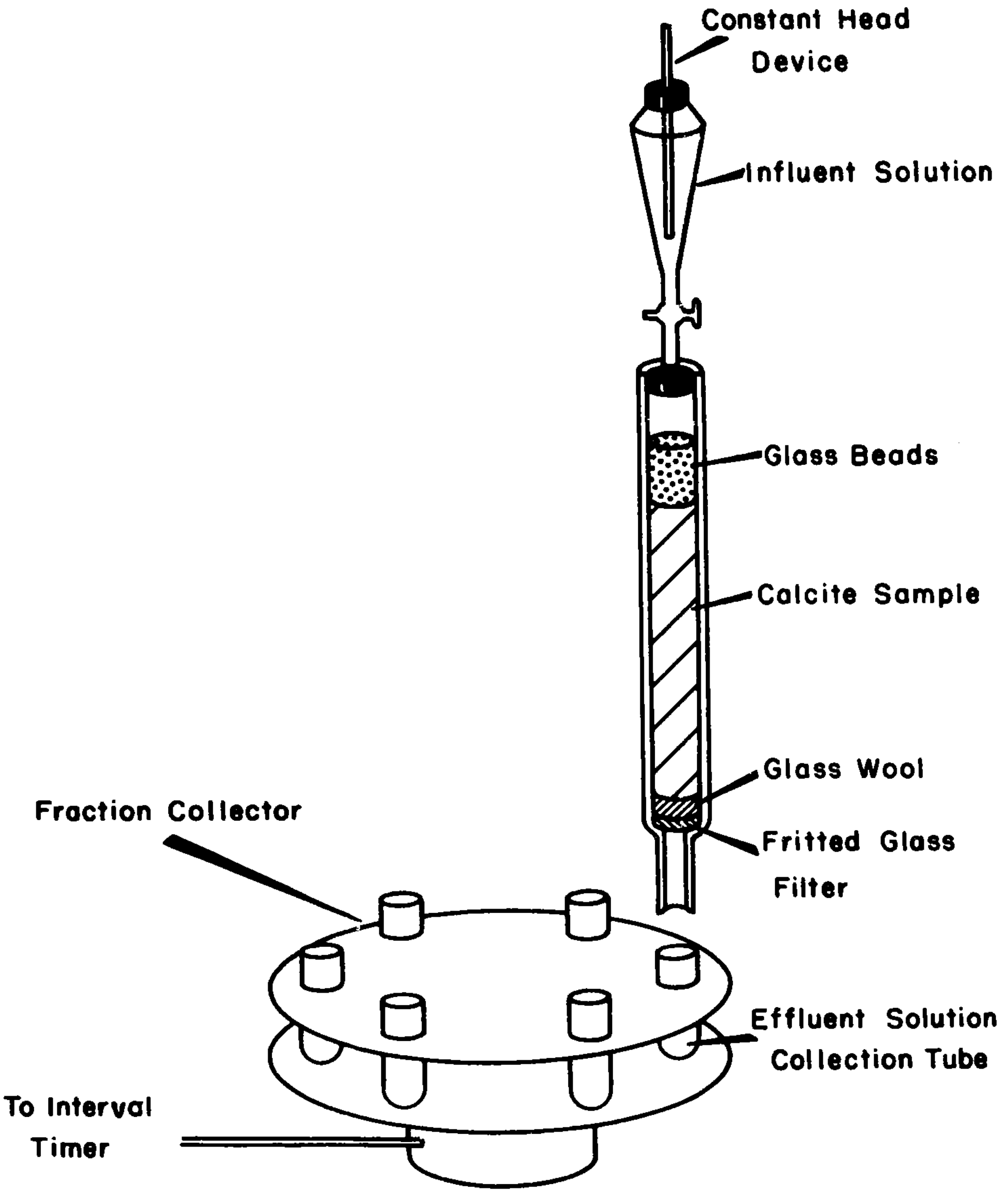
Figure 1. Sketch of column and collection apparatus used in column studies.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Influent Solution
Glass Beads
Calcite Sample
Glass Wool
Fraction Collector
Fritted Glass Filter
Effluent Solution Collection Tube
To Interval Timer

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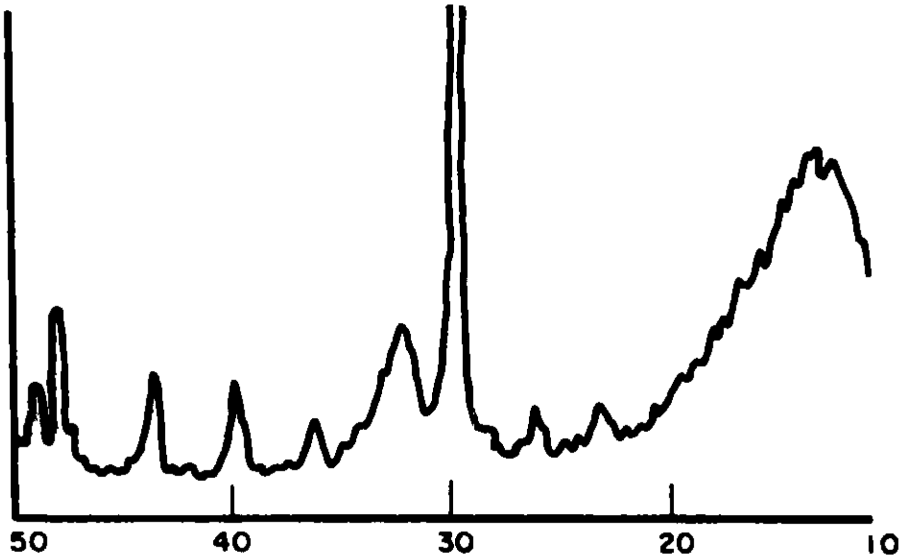
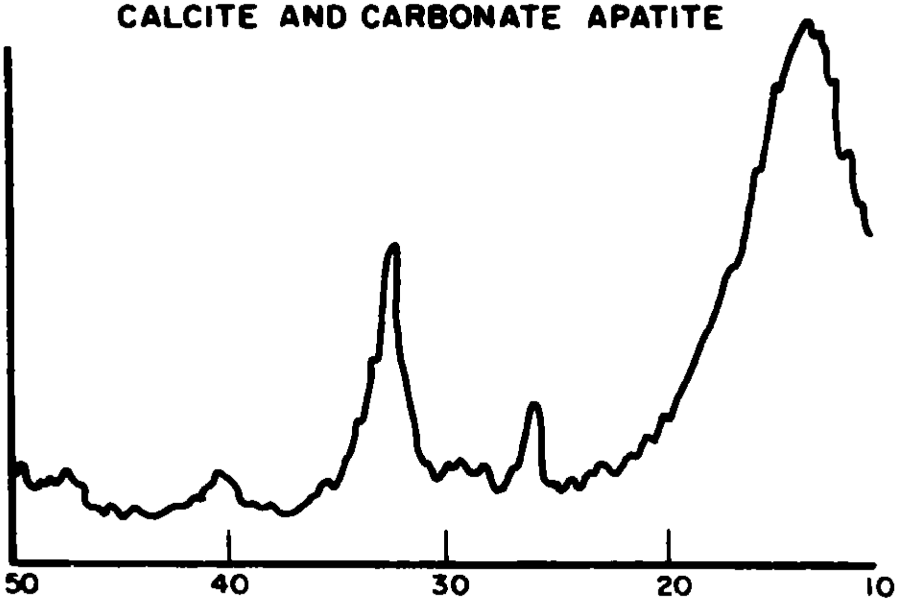
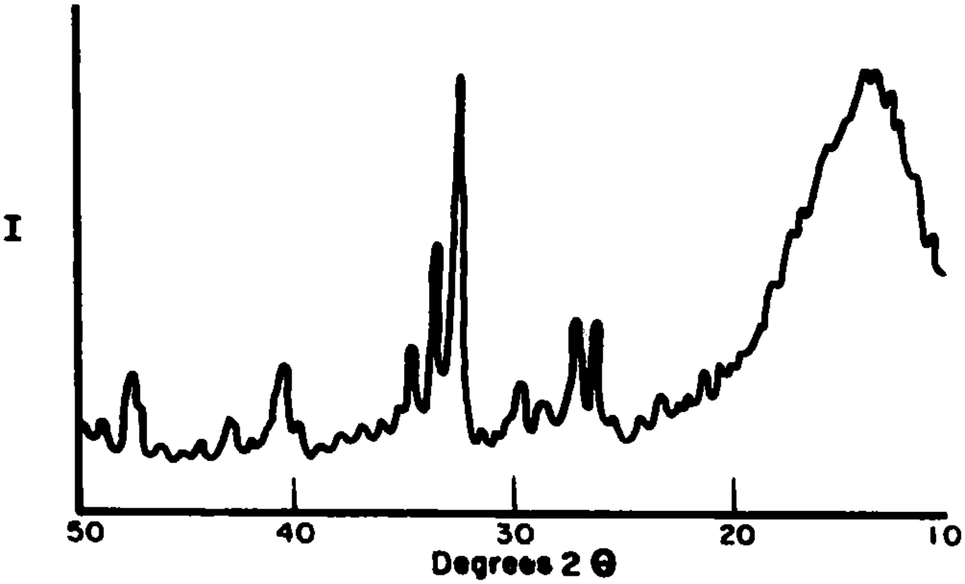
Figure 2. X-ray diffraction pattern tracings of a calcite-carbonate apatite mixture, carbonate apatite, and phosphorite rock. These samples were air-dried, but otherwise untreated.



CALCITE AND CARBONATE APATITE



CARBONATE APATITE



PHOSPHORITE, PHOSPHORIA FORMATION

Figure 2
The Genesis of Carbonate Apatites
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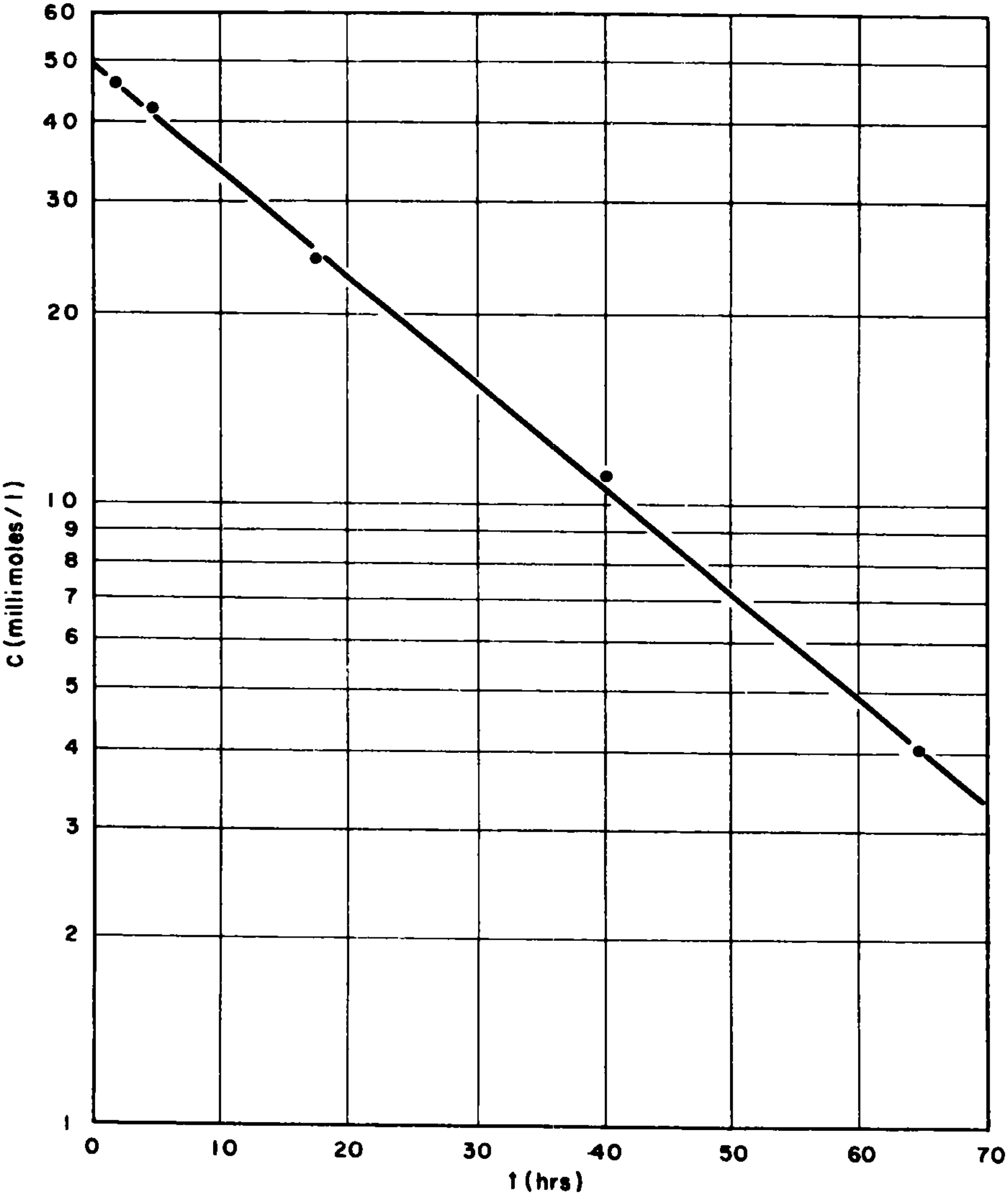
Figure 3. The removal of phosphate with time during the replacement of calcite by carbonate apatite.

Influent solution: 0.05 $\underline{M}$ $Na_3PO_4 \cdot 12H_2O$, 100,000 d/m/ml P^{32}.

Influent solution pH	11.8
Calcite weight (mg)	500
Calculated calcite surface area (cm^2)	14.4 ± 1.0
Calcite grain size (mm)	0.077
Temperature (°C)	28


60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
C (millimoles / l)
0
10
20
30
40
50
60
70
t (hrs)

[illegible]

The Genesis of Carbonate Apatites

L. L. Ames Jr.

GENERAL ELECTRIC
PHOTOGRAPHY OPERATION
700 AREA, BLDG. 717
HANFORD ATOMIC PRODUCTS OPERATION
REQUEST NO. 02403-5

Figure 4. The relative rate of apatite formation by replacement of calcite as a function of the molar ratios of bicarbonate and phosphate in the influent solution. The replacement rate was measured as the amount of Sr^{90} removed by the replacement process at a fixed flow rate through the calcite column.

Influent solution: HCO_3^- and PO_4^{-3} as above, 100,000 d/m/ml Sr^{90}-Y^{90}

Calcite column weight (g)	50
Calcite column volume (cc)	34
Calcite column cross section (cm^2)	2.83
Calcite grain size (mm)	1.0-0.25
Flow rate	7 cc/cm^2/hr
Influent solution pH	8-9

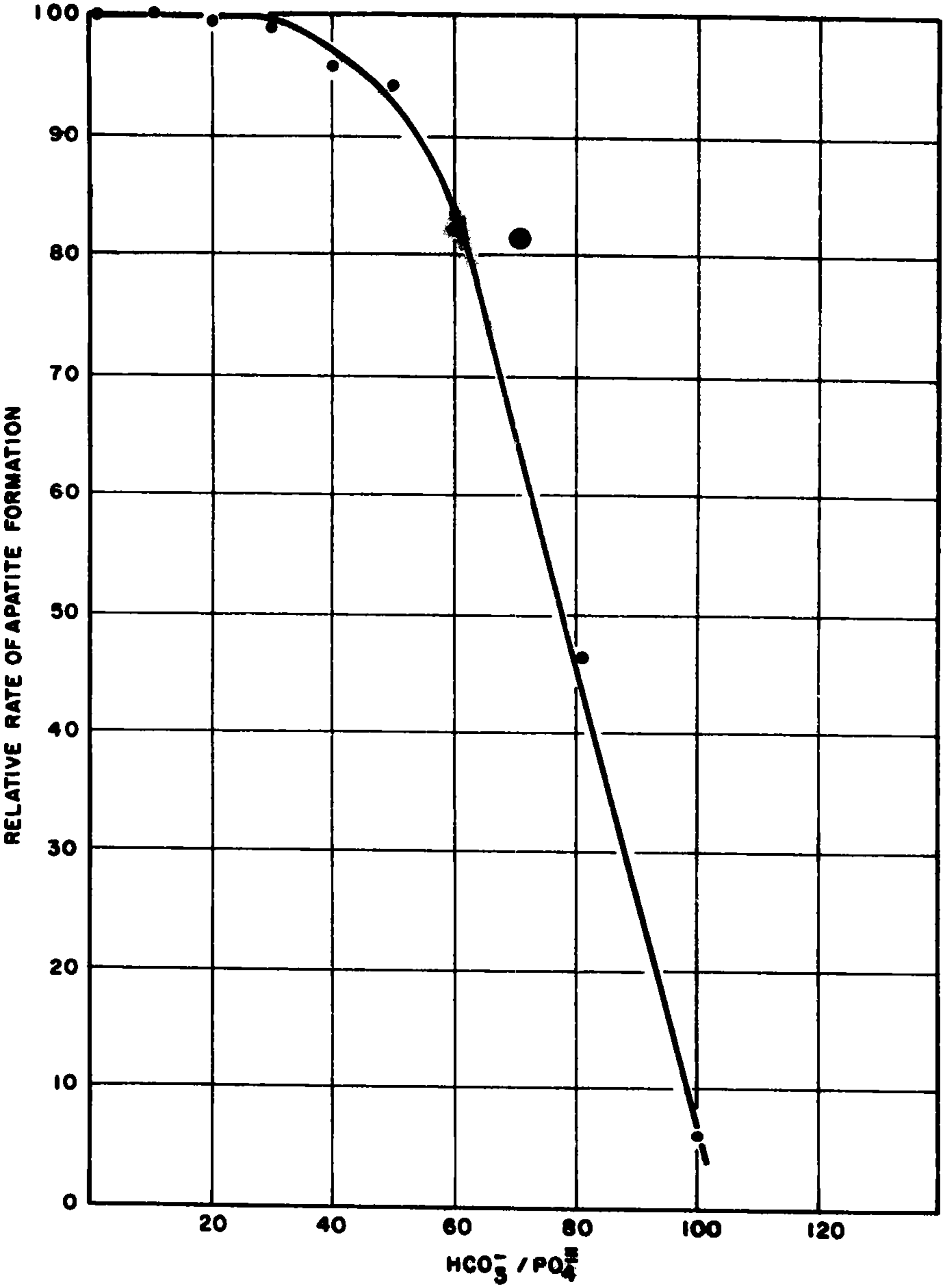

RELATIVE RATE OF APATITE FORMATION
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
120
$HCO_3^- / PO_4^{\equiv}$

Figure 4

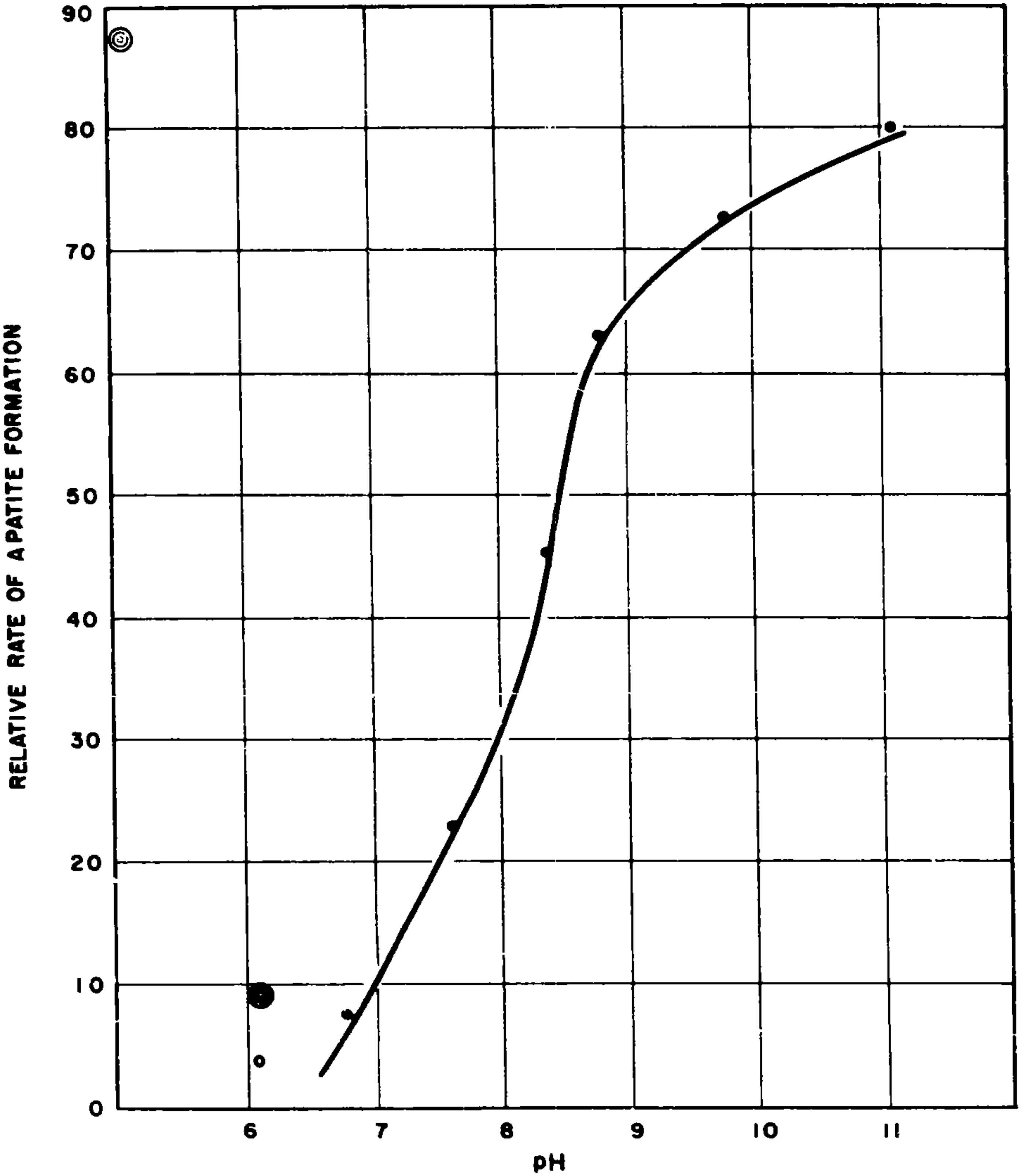
[illegible]

GENERAL ELECTRIC
PHOTOGRAPHIC [illegible]ION
700 AREA, B[illegible] 717-A
HANFORD ATOMIC PRODUCTS OPERATION
REQUEST NO. 02403-1

Figure 5. The effect of pH on the relative rate of apatite formation by replacement of calcite. The replacement rate was measured by the amount of Sr^{90} removed per unit time.

Influent solution: 0.05 M $Na_3PO_4 \cdot 12H_2O$, 10,000 d/m/ml Sr^{90}-Y^{90}.

Calcite grain size (mm)	0.077
Calcite weight (mg)	500
Calcite-solution contact time (hrs)	1.0


RELATIVE RATE OF APATITE FORMATION
90
80
70
60
50
40
30
20
10
0
6
7
8
9
10
11
pH

GENERAL ELECTRIC
PHOTOGRAPHY OPERATION
700 AREA, BLDG. 717-A
HANFORD ATOMIC PRODUCTS OPERATION
REQUEST NO. 02403-x

Figures
The Genesis of Carbonate apatites
F L Ames, Jr.