

AN ABSTRACT OF THE THESIS OF

Elliot Leonard Atlas for the degree of Doctor of Philosophy

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Title: PHOSPHATE EQUILIBRIA IN SEAWATER AND  
INTERSTITIAL WATERS

Abstract approved: Redacted for privacy  
Ricardo M. Pytkowicz

In this thesis, the chemistry of phosphate in seawater is examined in terms of solution and solubility equilibria. Extrapolations, based on experimental results, are made which provide a first approximation to the behavior of phosphate in interstitial waters. Such extrapolations are necessary to examine the formation and behavior of marine phosphorites.

Solution equilibria are described by an ion-pairing model. Measurements of the three dissociation constants of phosphoric acid were made in seawater and various NaCl-KCl-MgCl<sub>2</sub>-CaCl<sub>2</sub> solutions. From the shift in the acid dissociation constants measured in different solutions, association constants between Na<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>-2</sup>, and PO<sub>4</sub><sup>-3</sup> were calculated. The calculations were based on the assumption that K<sup>+</sup> association with phosphate is

negligible. It was found that, at pH = 8.0,  $\text{HPO}_4^{-2}$  and  $\text{Mg}^{++}\text{PO}_4^0$  species comprise 70% of the total inorganic phosphate in seawater.

The solubility behavior of apatite in seawater was found to be dominated by surface reactions. Nine different naturally occurring apatites were equilibrated in 33‰ seawater at 10°C. When equilibrated, the samples demonstrated a nearly reversible steady-state phosphate concentration which could be described by an expression of the type  $-\log \text{PO}_4^{-3} = K_1 + K_2 \text{ pH}$ .  $K_1$  ranged from 8.190 to 13.697;  $K_2$ , the pH dependence, ranged from -.047 to -.928. Experiments also demonstrated the uptake and release of alkalinity and  $\text{F}^-$  on the apatite surface. The results are interpreted in terms of a surface layer containing varying proportions of  $\text{F}^-$  and  $\text{HPO}_4^{-2}$  ions. Calculations using an average value of the solubility of marine apatites shows seawater to be very near apatite saturation.

The conditions of apatite formation are discussed, and it is concluded that interstitial waters in modern upwelling regions are the most favorable locations for phosphorite growth. Data on apatite precipitation kinetics shows that phosphorite formation will not occur in open seawater. Equilibrium and kinetic conditions for phosphorite growth are met, however, in the interstitial environment. Oceanographic conditions, also, make upwelling areas likely sites for phosphorite formation. The saturation state of interstitial waters is not well defined, though, because of compositional variations in the

fluid. Calculations are made which illustrate the dependence of apatite solubility on the concentration of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ . A decrease in  $\text{Mg}^{+2}$  decreases the solubility, whereas a decrease in  $\text{Ca}^{+2}$  increases the solubility.

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Professor of Oceanography in charge of major

Redacted for privacy

Dean of School of Oceanography

Redacted for privacy

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## TABLE OF CONTENTS

I. INTRODUCTION	1
II. PHOSPHATE ASSOCIATION WITH $\text{Na}^+$ , $\text{Ca}^{+2}$ , and $\text{Mg}^{+2}$ IN SEAWATER	6
Introduction	6
Theory	7
Experimental	11
Results	14
Discussion	14
Conclusions	31
III. SOLUBILITY BEHAVIOR OF APATITE IN SEAWATER	32
Introduction	32
Experimental	38
Results	40
Discussion	60
Conclusions	71
IV. FACTORS AFFECTING THE FORMATION OF MARINE PHOSPHORITES	74
Introduction	74
Equilibrium Considerations	79
Kinetic Considerations	89
Discussion	93
Oceanographic conditions relating to phosphorite formation	97
Synthesis: apatite formation in the ocean	102
BIBLIOGRAPHY AND RELATED REFERENCES	110
APPENDIX I	
Thermodynamic estimates of phosphate stability in seawater	125
APPENDIX II	
Methods and procedures for apatite solubility experiments	135
APPENDIX III	
Description of samples used in apatite solubility study	
Microprobe analysis of apatite sample	138
APPENDIX IV	
Data for apatite solubility studies	146

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1 Phosphate dissociation in distilled water, 0.68 KCl, and 34.8‰ SW	3
2.1 $pK^*$ ( $MgHPO_4^0$ , $CaHPO_4^0$ ) versus ionic strength	22
2.2 Temperature and salinity dependence of $K_2'$	26
2.3 Phosphate speciation in 34.8‰ seawater at pH = 8.0	29
3.1 Experimental flow-system for solubility studies	39
3.2 Time of equilibration in column experiments	41
3.3 Experimental results ( $TPO_4$ , F, pH) showing surface area effects	43
3.4 $HPO_4^{-2}$ and $PO_4^{-3}$ concentrations for surface area experiments	44
3.5 $pHPO_4^{-2}$ , $pPO_4^{-3}$ , and pH versus surface area	45
3.6 $\Delta F/\Delta TPO_4$ for surface area experiments	47
3.7 $TPO_4$ , $F^-$ , pH, and alkalinity variations versus time for beaker experiments	49
3.8 $TPO_4$ , $pPO_4^{-3}$ , and alkalinity for repeated equilibrations in column experiments	54
3.9 $pPO_4^{-3}$ versus pH for eight different apatites	55
3.10 $pPO_4^{-3}$ versus pH, showing effect of $CO_3^{-2}$ on solubility	59a
3.11 "Steady-state" interpretation of experimental results	67
3.12 Percent saturation with respect to oceanic apatites in the North Pacific	72



## LIST OF FIGURES CONTINUED

<u>Figure</u>	<u>Page</u>
4.1     Distribution of marine apatite deposits	76
4.2     Variation in the dissociation constants of $H_3PO_4$ with changes in $Ca^{+2}$ and $Mg^{+2}$	83
4.3     Effect of solution composition on apatite solubility	87
4.4     Time of precipitation of calcium phosphate in seawater at pH = 7.6 and pH = 8.2	91
4.5     Schematic of homogeneous and heterogeneous apatite formation	95
4.6     Model of phosphorite genesis in upwelling areas	107
A1.1    Stability of calcium phosphates in seawater	130
A3.1    Microvariation of Ca, P, and F in phosphorite sample	143
A3.2    Triangle plots of Ca, P, F variation in phosphorite sample	144

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
2.1    Activity coefficients of $H^+$ and $OH^-$ in phosphate-free salt solutions	13
2.2    First apparent dissociation constant of phosphoric acid in various media at 20°C	15
2.3    Second apparent dissociation constant of phosphoric acid in various media at 20°C	16
2.4    Third apparent dissociation constant of phosphoric acid in various media at 20°C	17
2.5    Association constants of orthophosphate with $Na^+$ , $Ca^{+2}$ , $Mg^{+2}$ at $\mu = 0.68$ and 20°C	21
2.6    Association constants in various media measured by other workers	23
2.7    Estimates of thermodynamic association constants	24
2.8    Total phosphate distribution at several pH's for 34.8‰ seawater	28
2.9    Distribution of free-ion and ion-pairs for the phosphate species in seawater	30
3.1    Solubility products of hydroxyapatite and fluorapatite in distilled water	34
3.2    pH dependence of $PO_4^{-3}$ and $F^-$ in column experiments	56
3.3    Comparison of measured versus predicted $TPO_4$ and $F^-$ for supersaturation experiments	58
3.4    Atoms/unit cell for apatite samples (based on $P+C = 6.0$ )	63
3.5    Summary of properties of marine apatites used in this study	71

# LIST OF TABLES CONTINUED

<u>Table</u>	<u>Page</u>
4.1 Apatite occurrences and associations	78
4.2 $\text{TPO}_4$ in equilibrium with apatite for varying levels of $\text{Ca}^{+2}$ and $\text{Mg}^{+2}$	82
4.3 Approximate changes in the various factors required to decrease $\text{TPO}_4$ in equilibrium with apatite by 10%	86
4.4 Chemical analysis of amorphous precipitates obtained from seawater	92
4.5 Prediction of effects of chemical factors on apatite formation rates	96
A1.1 Thermodynamic solubility products of calcium phosphates	127
A1.2 Equations and constants used in the estimation of total phosphate in equilibrium with various calcium phosphates	131
A3.1 Description of samples used in apatite solubility study	139
A3.2 Chemical composition of apatites used in solubility study	140
A3.3 X-ray data for apatites used in solubility study	141
A4.1 Data for experiment determining effect of surface area/solution ratio	146
A4.2 Final data for beaker experiments	147
A4.3 Representative values for repeated equilibrations at $\text{pH} \approx 8.2$	148
A4.4 Representative values for repeated equilibrations at $\text{pH} \approx 7.4$	149
A4.5 Representative values for repeated equilibrations at $\text{pH} \approx 7.0$	150

## LIST OF TABLES CONTINUED

<u>Table</u>	<u>Page</u>
A4.6    pH and $p\text{PO}_4$ for samples equilibrated at 25°C	151
A4.7    Data for experiments run from $\text{TPO}_4$ supersaturation	152
A4.8    Data for experiments using regular seawater and seawater with no alkalinity	153

# PHOSPHATE EQUILIBRIA IN SEAWATER AND INTERSTITIAL WATERS

## CHAPTER I

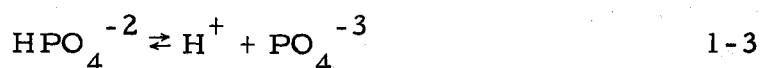
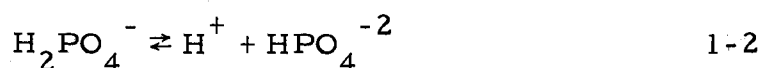
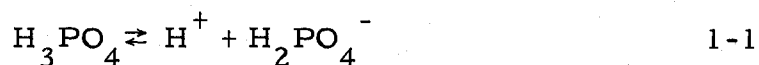
### INTRODUCTION

The importance of phosphate as a plant nutrient has led to a vast amount of descriptive information on the abundance of phosphate throughout the world's oceans (see, for example, Armstrong, 1963; Gulbrandsen and Roberson, 1974). The spatial variation and overall distribution of phosphate is, on the whole, quite well known. The variation in phosphate concentration in the ocean is related to the biological uptake and release of phosphate and to the general circulation of the oceans. It is through the biological cycle that phosphate is linked with oxygen (Redfield, 1934, 1948; Redfield, Ketchum and Richards, 1963). Indeed, some have suggested that phosphate levels in the ocean, by their influence on the oxygen cycle, are a key factor in the stability of atmospheric oxygen throughout geological time (Walker, 1974).

In addition to the biological cycle, phosphate enters into a geochemical cycle. Phosphate enters rivers as a product of weathering of rocks and is subsequently brought to the oceans. If the oceans are approximately at steady-state (Pytkowicz, 1975), an equivalent amount of phosphate leaves the oceans through the sediments. The

phosphate remains in the sediments as a biochemical precipitate (e.g., fish teeth), as phosphate adsorbed or bound to clays or metal hydroxides (Berner, 1973), or as a direct chemical precipitate (apatite) (Burnett, 1974).

Surprisingly little is known, however, of the chemistry of phosphate in seawater. In solution, phosphate occurs (inorganically) as phosphoric acid, which undergoes three dissociation steps, i.e.



The dissociation of phosphoric acid has been shown to be strongly influenced by the major cations in seawater (Kester and Pytkowicz, 1967). In effect, there are two major causes of the shift in phosphoric acid equilibria between distilled water solutions and seawater: ionic strength effects and ion association of phosphate with seawater cations (see Figure 1.1). The theoretical basis for these effects has been discussed by Kester (1970), Kester and Pytkowicz (1969), and Pytkowicz and Hawley (1974). Knowing the stability of individual phosphate ion-pairs can give one insight into the effect of changes in seawater composition on phosphoric acid dissociation and solubility equilibria.

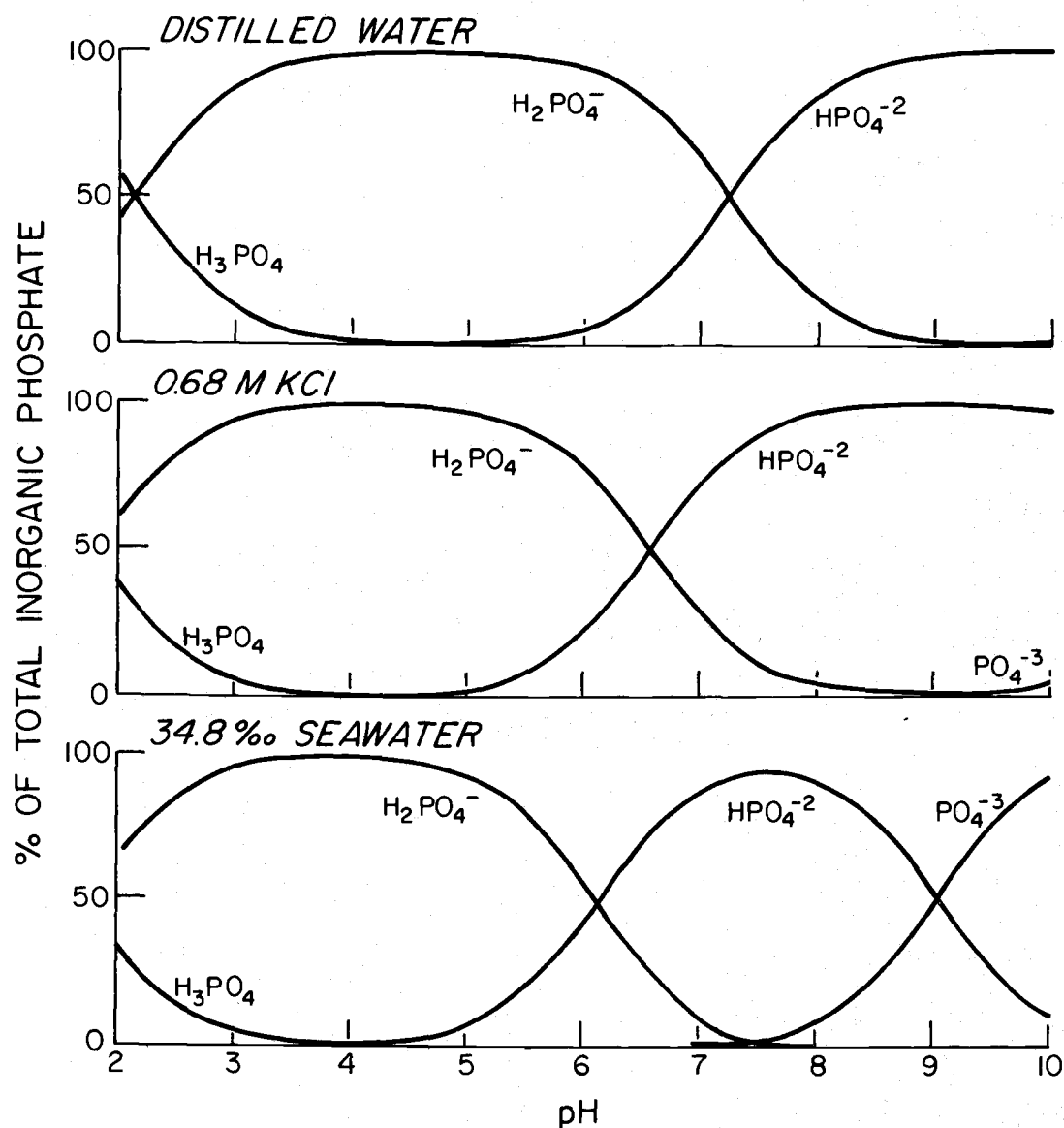


Figure 1.1. Dissociation of phosphoric acid in distilled water, 0.68 M KCl, and 34.8‰ seawater. The shift in dissociation is caused by ionic strength effects (illustrated by the distilled water-KCl shift) and specific ion effects (shown by the KCl-seawater shift). The data for this figure are from Chapter II.

Another aspect to the chemistry of phosphate in seawater involves the solubility of phosphate minerals. The phosphatic solid phase found in the ocean is apatite--specifically a substituted carbonate fluorapatite. The results of only two solubility studies of apatite in seawater have been reported (Kramer, 1964; Roberson, 1966). Insufficient precision was attained in the experiments to determine the saturation state of seawater with respect to a carbonate fluorapatite. Though theoretical calculations of phosphate solubility can be made (Appendix I), it is important to obtain experimental verification since such calculations often involve the use of quantities of unknown accuracy. Also, unexpected reactions may occur between the mineral and seawater which would not be predicted by existing theoretical relationships. The work in this thesis shows this to be the case for apatite behavior in seawater.

The objective of this thesis was to provide an experimental framework on which to base predictions of the chemical behavior of phosphate in seawater. The approach to this goal was basically twofold: 1) to investigate the solution (ion-pairing) equilibria of phosphoric acid, and 2) to examine the behavior of apatite in seawater. The investigation of solution equilibria was designed to answer the following questions: What are the relative stabilities of cation-phosphate ion-pairs? What are the major phosphate species in seawater? Can an ion-pairing model be used to estimate the dissociation



equilibria of phosphoric acid? Apatite behavior was examined with the following questions in mind: If apatite has a well-defined solubility in seawater, what is it? Are surface effects relevant to apatite-seawater equilibria? How does apatite solubility vary with changes in apatite composition? Finally, the results from the ion-pairing and solubility studies were used to examine theories of marine phosphorite formation in terms of apatite equilibria and kinetics.

Since the background material for each chapter in this thesis is considerably different, discussion of the literature on each topic is presented in the chapter on that topic. The thesis is divided into three main sections--ion-association of phosphate in seawater, solubility reactions of apatite, and factors controlling phosphorite genesis. Additional data and information are presented in appendices.

## CHAPTER II

PHOSPHATE ASSOCIATION WITH  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ , AND  $\text{Mg}^{+2}$   
IN SEAWATERIntroduction

Equilibrium calculations of the distribution of inorganic phosphate in aqueous solution requires knowledge of the dissociation constants of phosphoric acid in that medium. These constants can be directly measured in terms of "apparent" equilibrium constants. This was done by Kester and Pytkowicz (1967) for seawater. As they point out, the constants they measured are applicable to solutions of the same relative composition as seawater. Deviations in the major-ion concentrations will cause a shift in the apparent constants. This shift can be interpreted in terms of ion-association of the major ions with orthophosphate ion. Ion-association models have been successfully applied to seawater for the major-ion-sulfate system by Kester (1970) and Kester and Pytkowicz (1969) and for the major-ion-carbonate-bicarbonate system by Pytkowicz and Hawley (1974). One application of phosphate ion association measurements is to the study of apatite equilibria in interstitial waters (see Chapter IV).

Recent evidence suggests that sedimentary apatite forms in interstitial waters rather than directly in seawater (Burnett, 1974; Baturin, 1966). Apatite is also found in sediments as an organic

precipitate of teeth, bones, etc. Since the major-ion composition of interstitial waters can deviate significantly from seawater composition, saturation calculations cannot be performed using the seawater constants. Rather, dissociation constants can be derived from an ion-association model, and subsequent calculation of saturation states of phosphates can be made. All measurements were made at 20°C and ionic strength,  $\mu$ , = 0.68 in order for comparison with those obtained by other workers.

### Theory

A full discussion of ion-association models can be found in Kester and Pytkowicz (1969) and Pytkowicz and Hawley (1974). The derivation can be made as follows:

The total phosphate in a solution can be written as:

$$[\text{TPO}_4] = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{-2}] + [\text{PO}_4^{-3}] \quad 2-1$$

If ion-pairing occurs between  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Ca}^{+2}$  and the orthophosphate anions then:

$$[\text{H}_2\text{PO}_4^-] = (\text{H}_2\text{PO}_4^-) + (\text{MgH}_2\text{PO}_4^+) + (\text{CaH}_2\text{PO}_4^+) + (\text{NaH}_2\text{PO}_4^0) \quad 2-2$$

$$[\text{HPO}_4^{-2}] = (\text{HPO}_4^{-2}) + (\text{MgHPO}_4^0) + (\text{CaHPO}_4^0) + (\text{NaHPO}_4^-) \quad 2-3$$

$$[\text{PO}_4^{-3}] = (\text{PO}_4^{-3}) + (\text{MgPO}_4^-) + (\text{CaPO}_4^-) + (\text{NaPO}_4^{-2}) \quad 2-4$$

where [ ] refer to total and ( ) to free concentrations. The stoichiometric association constant,  $K^*$ , between a metal ion,  $M^{\nu+}$ , and an anion is: (using  $\text{HPO}_4^{-2}$  as an example)

$$K^*_{\text{MHPO}_4} = \frac{(\text{MHPO}_4^{(\nu+ - 2)})}{(M^{\nu+})(\text{HPO}_4^{-2})} \quad 2-5$$

so that

$$\begin{aligned} [\text{H}_2\text{PO}_4^-] = (\text{H}_2\text{PO}_4^-) \left\{ 1 + (\text{Mg}^{+2})K^*_{\text{MgH}_2\text{PO}_4^+} + \right. \\ \left. + (\text{Ca}^{+2})K^*_{\text{CaH}_2\text{PO}_4^+} + (\text{Na}^+)K^*_{\text{NaHPO}_4^0} \right\} \quad 2-6 \end{aligned}$$

$$\begin{aligned} [\text{HPO}_4^{-2}] = (\text{HPO}_4^{-2}) \left\{ 1 + (\text{Mg}^{+2})K^*_{\text{MgHPO}_4^0} + \right. \\ \left. + (\text{Ca}^{+2})K^*_{\text{CaHPO}_4^0} + (\text{Na}^+)K^*_{\text{NaHPO}_4^-} \right\} \quad 2-7 \end{aligned}$$

$$\begin{aligned} [\text{PO}_4^{-3}] = (\text{PO}_4^{-3}) \left\{ 1 + (\text{Mg}^{+2})K^*_{\text{MgPO}_4^-} + \right. \\ \left. + (\text{Ca}^{+2})K^*_{\text{CaPO}_4^-} + (\text{Na}^+)K^*_{\text{NaPO}_4^{-2}} \right\} \quad 2-8 \end{aligned}$$

It is assumed that  $[\text{H}_3\text{PO}_4] = (\text{H}_3\text{PO}_4)$  because it is not charged and it is not expected to associate. The apparent dissociation constants of phosphoric acid can be written as:

$$K'_1 = \frac{X[H_2PO_4^-]}{[H_3PO_4]} = k K^O_1 \frac{f_{H_3PO_4}}{f_{H_2PO_4}} \quad 2-9$$

$$K'_2 = \frac{X[HPO_4^{-2}]}{[H_2PO_4^-]} = k K^O_2 \frac{f_{H_2PO_4^-}}{f_{HPO_4^{-2}}} \quad 2-10$$

$$K'_3 = \frac{X[PO_4^{-3}]}{[HPO_4^{-2}]} = k K^O_3 \frac{f_{HPO_4^{-2}}}{f_{PO_4^{-3}}} \quad 2-11$$

where:  $X$  is the operational hydrogen ion activity which is related to  $a_H$  by  $X = ka_H$ ;  $K^O_i$  is the  $i$ th thermodynamic dissociation constant for phosphoric acid;  $f_i$  = total activity coefficient of  $i$  species. In a solution that is not ion-paired, the total activity coefficient,  $f_i$ , equals the free activity coefficient  $\gamma_i$ . I will make the assumption that potassium ion does not associate with orthophosphate ion. This assumption will be discussed later.

Combining equations 2-6 and 2-9, one gets

$$K'_1 (\text{salt}) =$$

$$\frac{X(H_2PO_4^-)(1+(Mg^{+2})K^*_{MgH_2PO_4} + (Ca^{+2})K^*_{CaH_2PO_4} + (Na^+)K^*_{NaH_2PO_4})}{(H_3PO_4)}$$

2-12

and

$$K'_1(\text{KCl}) = \frac{X(\text{H}_2\text{PO}_4^-)}{(\text{H}_3\text{PO}_4)} = k K_1^o \frac{\gamma_{\text{H}_3\text{PO}_4}}{\gamma_{\text{H}_2\text{PO}_4^-}} \quad 2-13$$

Assuming that the free-ion activity coefficients are independent of solution composition at constant ionic strength (Kester and Pytkowicz (1969); Pytkowicz and Hawley (1974)), and that  $k$ , a factor which takes into account liquid junction effects, is constant between solutions then,

$$\frac{K'_1(\text{salt})}{K'_1(\text{KCl})} = 1 + \Sigma K^*_{\text{MH}_2\text{PO}_4} (M_i^{\nu+}) \quad 2-14$$

Similarly, one can obtain:

$$\frac{K'_2(\text{salt})}{K'_2(\text{KCl})} = \frac{1 + \Sigma K^*_{\text{MHPO}_4} (M_i^{\nu+})}{1 + \Sigma K^*_{\text{MH}_2\text{PO}_4} (M_i^{\nu+})} \quad 2-15$$

and, finally,

$$\frac{K'_3(\text{salt})}{K'_3(\text{KCl})} = \frac{1 + \Sigma K^*_{\text{MPO}_4} (M_i^{\nu+})}{1 + \Sigma K^*_{\text{MHPO}_4} (M_i^{\nu+})} \quad 2-16$$

Thus, by measurements of the dissociation constants in mixed salt solutions at the same ionic strength one can obtain values for the association constants between cations and the various phosphate species.

## Experimental

In order to have an independent means of checking the dissociation constants, the method used by Kester and Pytkowicz (1967) was not followed. Determinations of  $K'_1$ ,  $K'_2$  and  $K'_3$  were done in NaCl-MCl<sub>2</sub> and KCl-MCl<sub>2</sub> mixtures or in the pure MCl<sub>2</sub> or NaCl or KCl solution ( $M = Ca^{+2}$  or  $Mg^{+2}$ ). The method used for  $K'_1$  was similar to that used by Elliot et al. (1958).  $K'_1$  can be computed from the pH and the ratio of  $[H_2PO_4^-]$  to  $[H_3PO_4]$  according to

$$-\log K'_1 = pK'_1 = pH - \log \frac{[H_2PO_4^-]}{[H_3PO_4]} . \quad 2-17$$

The  $H_2PO_4^-$  concentration in solution at a given pH can be calculated from

$$[H_2PO_4^-] = [H_2PO_4^-]_{\text{initial}} - [H_3PO_4] . \quad 2-18$$

The  $[H_3PO_4]$  concentration is determined from the amount of the HCl added to the cell, the cell volume, and the measured pH using the relation

$$[H_3PO_4] = [HCl] - [H^+] = [HCl] - a_H/\gamma_H \quad 2-19$$

$a_H$  was calculated from the pH by:

$$-\log a_H = pH = 4.002 + \frac{E_{\text{buff}} - E_{\text{sample}}}{58.165} \quad 2-20$$

where:  $E_{\text{buff}}$  = millivolt reading for buffer

$E_{\text{sample}}$  = millivolt reading for sample

58.165 = theoretical slope (mv/pH)

The measured slope was 0.9953 of the theoretical slope. A similar method was used for the determination of  $K'_3$  in some of the solutions.

$K'_3$  was computed from the relation

$$-\log K'_3 = \text{p}K'_3 = \text{pH} - \log \frac{[\text{PO}_4^{-3}]}{[\text{HPO}_4^{-2}]} \quad 2-21$$

Then,

$$[\text{HPO}_4^{-2}] = [\text{HPO}_4^{-2}]_{\text{initial}} - [\text{PO}_4^{-3}] \quad 2-22$$

and

$$[\text{PO}_4^{-3}] = [\text{NaOH}] - [\text{OH}] = [\text{NaOH}] - a_{\text{OH}}/\gamma_{\text{OH}} \quad 2-23$$

$a_{\text{OH}}$  was calculated from  $K_w$  and the pH by

$$-\log(a_{\text{OH}}/K_w) = -\log a_{\text{H}} = \text{pH} = 9.225 + \frac{E_{\text{buff}} - E_{\text{sample}}}{58.165} \quad 2-24$$

( $\text{p}K_w = 14.1669$ ).

Values of  $\gamma_{\text{H}}$  and  $\gamma_{\text{OH}}$  in the various media were measured by titration of the solution in the absence of phosphate. One obtains  $\gamma_{\text{H}}$ , for example, from

$$\gamma_{\text{H}} = a_{\text{H}}/[\text{H}^+] \quad 2-25$$



The results of the  $\gamma_H$  and  $\gamma_{OH}$  determinations are given in Table 2.1.

Table 2.1. Measured activity coefficients of  $H^+$  and  $OH^-$  in the phosphate-free salt solutions used in this work.

<u>Medium</u>	<u><math>\gamma_H</math></u>	<u><math>\gamma_{OH}</math></u>
0.68 NaCl	1.023	.452
0.68 KCl	.873	.673
0.2267 $CaCl_2$	.983	----
0.2267 $MgCl_2$	.997	----
0.68 $(Me)_4NCl$	.839	.77-.83*
0.68 $(Et)_4NBr$	.936	.98-1.03*
$CO_3$ -free seawater**	.790	----

\* Variable due to slight contamination with tri-alkyl amines.

\*\* Measured value is total activity coefficient.

$K'_2$  was estimated from the pH of maximum buffer capacity ( $= pK'_2$ ) from a titration of  $\sim 1-2$  mmoles of  $H_2PO_4^-$  in salt solution with  $CO_3$ -free NaOH. For NaCl- $MCl_2$  solutions and seawater,  $K'_3$  was estimated from the pH of minimum buffer capacity ( $= 1/2 (pK'_2 + pK'_3)$ ) in a titration of  $\sim 0.5$  mmoles total phosphate with  $CO_3$ -free NaOH.

All titrations were performed in a thermostated cell closed to the atmosphere. The cell volume was about 160 mls. Titrations were done with a Gilmont microburet (Model S1200A or S3200A).

The potential of a glass-calomel electrode pair (pH electrode-Sargent

Model S30050-15c; reference: calomel reference with asbestos fiber junction Corning Model 476002) was measured with an Orion Model 801 digital pH meter with a resolution of  $\pm 0.1$  mV. The temperature was held constant at  $20.0^{\circ}\text{C}$ .

### Results

The measured dissociation constants for the various media are listed in Tables 2.2, 2.3, 2.4. Also listed for comparison are determinations made by others.

### Discussion

As was shown above, the calculation of association constants depends on the comparison of the dissociation constants of  $\text{H}_3\text{PO}_4$  in two solutions--one in which ion-pairing occurs to some unknown extent versus one in which there is a known or negligible amount of ion-pairing. It has been assumed, for the purposes of calculation, that the extent of ion-pairing of orthophosphate with  $\text{K}^+$  ion is negligible compared to the other ions in solution. The reasons behind this assumption are discussed next.

First, a rough estimate can be made of the expected first dissociation constant of  $\text{H}_3\text{PO}_4$  in 0.68 KCl assuming no ion-pairing. Kester and Pytkowicz (1975) give approximate free activity-coefficients for dipolar uncharged species and negative univalent

Table 2.2. First apparent dissociation constant of phosphoric acid in various media at 20°C.

Medium (M)	$\text{pK}'_1 (= -\log K'_1)$	Reference
0.68 KCl	1.797	1
0.68 KCl	1.790	2
0.68 NaCl	1.719	1
0.68 NaCl	1.548	3
0.68 NaCl	1.734	2
0.2267 $\text{CaCl}_2$	1.654	1
0.2267 $\text{CaCl}_2$	1.623	2
0.2267 $\text{MgCl}_2$	1.612	1
0.2267 $\text{MgCl}_2$	1.665	2
34.8‰ SW	1.711	1
34.8‰ SW	1.642	3
0.68 $(\text{CH}_3)_4\text{NCl}$	2.022	1
0.68 $(\text{C}_2\text{H}_5)_4\text{NBr}$	2.148	1

1 = this work

2 = Lugg (1931), measured at 18°C,  $K'_1 = \frac{(\text{H}^+)_F (\text{H}_2\text{PO}_4)_T}{(\text{H}_3\text{PO}_4)}$

3 = Kester and Pytkowicz (1967)

Table 2.3. Second apparent dissociation constant of phosphoric acid in various media at 20°C.

Medium (M)	$pK'_2 (-\log K'_2)$	Reference
0.68 KCl	6.546	1
.17 $KH_2PO_4$ + .17 $K_2HPO_4$	6.53	4
0.68 NaCl	6.395	1
0.68 NaCl	6.387	3
0.68 NaCl	6.389	5
0.53 KCl + .05 $CaCl_2$	6.313	1
0.53 KCl + .05 $MgCl_2$	6.208	1
0.53 NaCl + .05 $CaCl_2$	6.241	1
0.53 NaCl + .05 $MgCl_2$	6.153	1
34.8‰ SW	6.107	1
34.8‰ SW	6.0	3
0.68 $(CH_3)_4NCl$	6.977	1
0.68 $(C_2H_5)_4NBr$	7.066	1

4 = Drozdov, N. S. and V. P. Krylov (1961)

5 = Sillen and Martell (1964)

Table 2.4. Third dissociation constant of phosphoric acid in various media at 20°C.

Medium (M)	$\text{pK}'_3$ ( $-\log K'_3$ )	Reference
0.68 KCl	11.455	1
0.68 NaCl	11.193	1
0.68 NaCl	11.23 (at 15°C)	6
0.68 NaCl	11.00	3
0.53 NaCl + .05 $\text{MgCl}_2$ *	9.482	1
0.53 NaCl + .05 $\text{CaCl}_2$ *	8.191	1
0.62 NaCl + .02 $\text{CaCl}_2$ *	8.443	1
.50 NaCl + .052 $\text{MgCl}_2$ + .01 $\text{CaCl}_2$ *	8.954	1
.62 NaCl + .01 $\text{MgCl}_2$ + .01 $\text{CaCl}_2$ *	8.890	1
34.8‰ SW *	8.999	1
34.8‰ SW *	8.889	3
0.68 $(\text{CH}_3)_4\text{NCl}$	11.935	1
0.68 $(\text{C}_2\text{H}_5)_4\text{NBr}$	11.914	1

\* calculation from  $1/2(\text{pK}'_2 + \text{pK}'_3)$

6 = Chambers and Whitely (1966)

dipolar species as 0.8 and 0.4, respectively. Using  $pK_1^0$  (20°) = 2.127, and the relation

$$pK_1' = pK_1^0 + \log \gamma_{H_2PO_4^-} / \gamma_{H_3PO_4} \quad 2-26$$

$pK_1'$  (KCl) = 1.825 is calculated. The experimental value was 1.797. This is good agreement and tends to support the assumption that the  $K^+$  ion associates only to a negligible extent, at least with  $H_2PO_4^-$ . Continuing with similar calculations and using Kester and Pytkowicz's estimated activity coefficients with  $pK_2^0 = 7.213$  and  $pK_3^0 = 12.42$ , it is computed that  $pK_2'$  (KCl) = 6.912, and  $pK_3'$  (KCl) = 11.55. The measured values were  $pK_2'$  (KCl) = 6.546 and  $pK_3'$  (KCl) = 11.455. The agreement in these cases is not as good, suggesting either the use of inappropriate activity coefficients, or some  $K^+$  ion association. If the reason for the discrepancy is  $K^+$  ion association, then the difference between the calculated and the measured dissociation constants should be larger for  $pK_3'$  than for  $pK_2'$ , as the error is cumulative. This is seen not to be the case. Therefore, it appears that activity coefficients were chosen which are not applicable. The assumption of no, or negligible,  $KHPO_4^-$  association can be tested by calculating a best value for  $K_{KHPO_4}^*$  from the measurements of  $K_2'$  in NaCl-KCl-MgCl<sub>2</sub>-CaCl<sub>2</sub> mixtures. Under the constraint that  $K^* \geq 0$ , it is found, using a least-squares

technique, that the best value for  $K_{\text{KHPO}_4}^*$  is 0. No similar check is available on  $K_{\text{KPO}_4}^*$  but for subsequent calculations it will be assumed that it, too, is zero. The effect of the assumption of no  $\text{K}^+$  ion-pairing is to generate a smaller  $K^*$  for the association of  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Ca}^{+2}$  with orthophosphate.

The assumption of no  $\text{K}^+$ -phosphate ion-pairing stands in contrast to the finding of Smith and Alberty (1954), who report an association constant for  $K_{\text{KHPO}_4}^*$  (= 3.1 at 25°C and  $\mu = 0.2$ ). They based their calculations on the assumption that propylammonium ion doesn't associate with orthophosphate. Otherwise, their calculations were essentially the same as those used here, although they assumed no ion-pairing with  $\text{H}_2\text{PO}_4^-$  ion. I measured the dissociation constants of  $\text{H}_3\text{PO}_4$  in methylammonium chloride and ethylammonium bromide at 0.68 M and verified the observation of Smith and Alberty that solutions of alkylammonium ion give a lower dissociation constant (higher  $\text{pK}'_1$ ) than in  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2$ , or  $\text{CaCl}_2$  solutions of the same ionic strength. I interpret these measurements to indicate that the large alkylammonium ions behave quite differently than  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  ions. Consider the first dissociation constant measured in the different solutions. It was calculated above that  $\text{pK}'_1$  should be approximately 1.82 if there were no ion-pairing. The  $\text{pK}'_1$  measured in  $(\text{Me})_4\text{NCl}$  and  $(\text{Et})_4\text{NBr}$  were 2.022 and 2.148, respectively. Recalling that  $K'_1 = K^0_1 (f_{\text{H}_3\text{PO}_4} / f_{\text{H}_2\text{PO}_4^-})$ , one

calculates that ( $f_{\text{H}_3\text{PO}_4} / f_{\text{H}_2\text{PO}_4^-}$ ) is about .95-1.25 in the alkylammonium ion solutions. This suggests a relatively small  $f_{\text{H}_3\text{PO}_4}$  compared to the one in  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Ca}^{+2}$  solutions. One might expect this behavior from data on the salting coefficient,  $K_s$ , (= ratio of solubility in salt solution to solubility in distilled water) of various ions in salt solutions. From the data in Masterton et al. (1971), it is found that, on the average,  $K_s$  in salt solutions behaves according to  $\text{NaCl} > \text{KCl} > \text{CaCl}_2 = \text{MgCl}_2 > (\text{Me})_4\text{NCl} > (\text{Et})_4\text{NBr}$ . If  $K_s$  in 0.7 NaCl is taken to range from 0.1-0.2, then one can calculate  $f_{\text{H}_3\text{PO}_4}$  from  $\log f_{\text{H}_3\text{PO}_4} = K_s(\mu)$ . The following results are found:

$(\mu = 0.7)$	NaCl	KCl	$\frac{\text{Mg}}{\text{Ca}}\text{Cl}_2$	$(\text{Me})_4\text{NCl}$	$(\text{Et})_4\text{NBr}$
$f_{\text{H}_3\text{PO}_4}$	1.17-1.36	1.14-1.29	1.10-1.21	1.00	.95-.91

Thus, the difference in activity coefficients of the alkylammonium ions versus  $\text{K}^+$  may exceed 30%, which indicates that the alkylammonium ions behave significantly differently from  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$  and  $\text{Ca}^{+2}$  ions in solution. For this reason, I choose to use  $\text{K}^+$  ion as a zero-association reference ion for subsequent calculations. Future data obtained on the extent of potassium-phosphate interactions in concentrated salt solutions can be used with the present data to revise the association constants found here. The results of the



calculations of association constants are given in Table 2.5.

Table 2.5. Association constants of  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ , and  $\text{Mg}^{+2}$  with orthophosphate at  $\mu = 0.68$  and  $20^\circ\text{C}$ . Calculations are based on the assumption of no association between  $\text{K}^+$  and orthophosphate.

M	$K^*_{\text{MH}_2\text{PO}_4}$	$K^*_{\text{MHPO}_4}$	$K^*_{\text{MPO}_4}$
$\text{Na}^+$	0.29	1.12	3.28
$\text{Mg}^{+2}$	2.34	29.8	$3.63 \times 10^3$
$\text{Ca}^{+2}$	1.72	17.7	$9.61 \times 10^4$

The association constants of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  with  $\text{HPO}_4^{-2}$  ion can be compared to values determined by others at various ionic strengths (Figure 2.1). Although most values in Figure 2.1 are obtained at  $25^\circ\text{C}$ , there is enough data to show that the values obtained here compare well with those of other workers. Data for comparison of the other association constants are relatively scarce. The following list (Table 2.6) is obtained from Sillen and Martell (1964); the original references were consulted to give error limits.

One can calculate activity coefficients for the various ions by the mean-salt method and assume activity coefficients for the ion-pairs in order to estimate thermodynamic association constants. The stoichiometric association constant is related to the thermo-

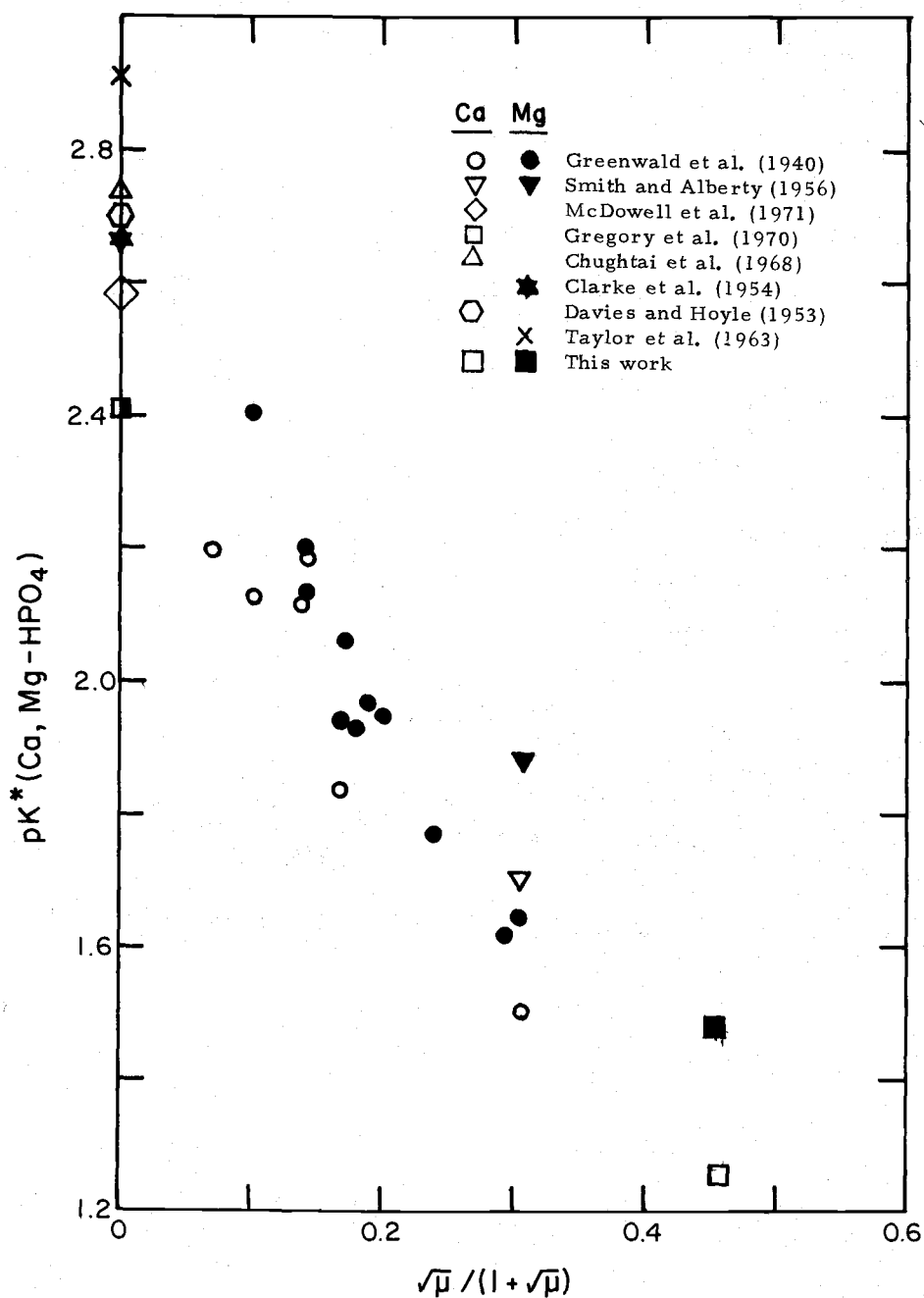


Figure 2.1.  $-\log K^*_{\text{MHPO}_4}$  ( $M = \text{Ca}^{+2}, \text{Mg}^{+2}$ ) versus  $\mu/(1 + \mu)$ .

$\mu$  = ionic strength. The open or half-filled symbols are for  $K^*(\text{CaHPO}_4^0)$ . The filled symbols are for  $K^*(\text{MgHPO}_4^0)$ .

Table 2.6. Association constants in various media measured by other workers.

<u>Ion-pair</u>	<u>Medium</u>	<u>Temp.</u>	<u>K*</u>	<u>Reference</u>
NaHPO <sub>4</sub>	Tetra 1-n propyl ammonium chloride 0.2	25°	4.0±0.4	1
KHPO <sub>4</sub>	"	25°	3.1±0.4	1
CaH <sub>2</sub> PO <sub>4</sub>	→ 0	25°	12.0±0.5	2
"	→ 0	25°	5.0±1	3
"	→ 0	25°	25.6±1.7	4
CaPO <sub>4</sub> <sup>-</sup>	→ 0	25°	2.9±.1x10 <sup>6</sup>	4
MgPO <sub>4</sub> <sup>-</sup>	0.16 KNO <sub>3</sub>	37°	2.5±0.5x10 <sup>3</sup>	5

1 = Smith and Alberty (1956) J. Phys. Chem. 60: 180

2 = Davies and Hoyle (1953) J. Chem. Soc. 4134.

3 = Gregory, Moreno, and Brown (1970) J. Res. NBS 74A: 461.

4 = Chughtai, Marshall, and Nancollas (1968) J. Phys. Chem. 72: 208.

5 = Childs (1970) Inorganic Chemistry 9: 2465

dynamic constant by:

$$K_{o\ MX}^* = K_{MX}^* \frac{\gamma_{MX}}{\gamma_M \gamma_X}$$

At 25°C and  $\mu = 0.7$  one obtains from the mean-salt method that

$\gamma_{Mg^{+2}} = 0.28$ ,  $\gamma_{Na^+} = 0.71$ ,  $\gamma_{Ca^{+2}} = 0.26$ ,  $\gamma_{H_2PO_4^-} = 0.36$ ,

$\gamma_{HPO_4^{2-}} = 0.12$ , and  $\gamma_{PO_4^{3-}} = 0.033$ . The activity coefficients of

ion-pairs are more difficult to estimate, and depend on the charge

distribution in the ion-pair as well as on the net charge (Pytkowicz and Kester, 1975). Pytkowicz and Kester estimate that the activity coefficient of an ion-pair can be assigned according to charge type. They estimate for a 1-1 ion pair  $\gamma = 1.0$ ; for a 1-2, 2-1 ion pair  $\gamma = 0.4$ , and for a 2-2 ion-pair  $\gamma = 0.8$ . In accordance with these estimates I assigned ion pairs of the 1-3 and 2-3 charge types activity coefficients of 0.1 and 0.2. These are purely arbitrary and were chosen to be intermediate to the activity coefficients of the constituent ions. Using the activity coefficients above, thermodynamic association constants were calculated (Table 2.7).

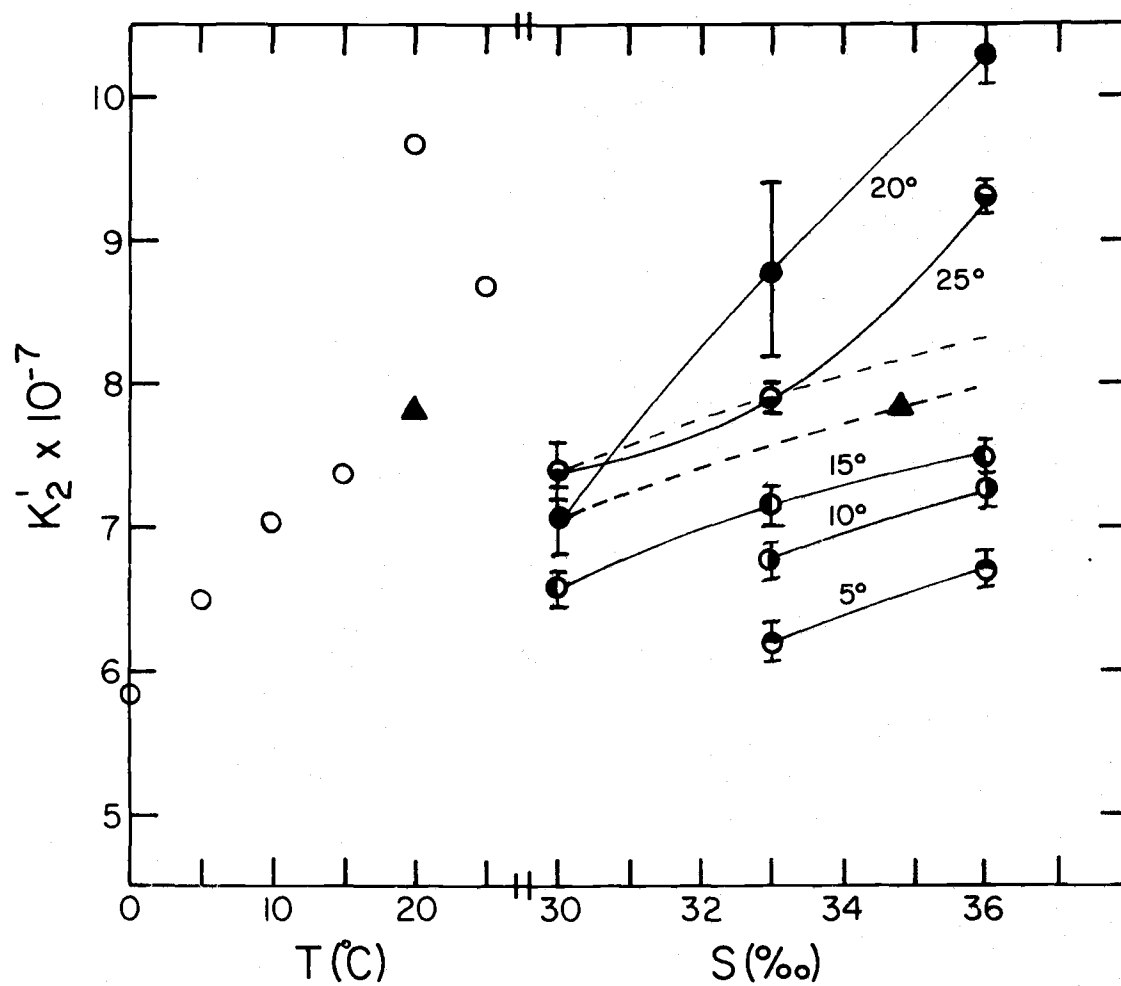
Table 2.7. Estimates of thermodynamic association constants.

M	$K^{\circ}_{\text{MH}_2\text{PO}_4}$	$K^{\circ}_{\text{MHPO}_4}$	$K^{\circ}_{\text{MPO}_4}$
Na <sup>+</sup>	1.13	4.79	14.0
Mg <sup>+2</sup>	9.29	722	$7.86 \times 10^4$
Ca <sup>+2</sup>	7.35	466	$2.24 \times 10^6$

The calculated results compare fairly well to those estimated by others (Table 2.6 and Figure 2.1), considering the uncertainties in the experimental method and in the estimation of activity coefficients.

Another comparison which can be made is between the measured apparent dissociation constants in seawater and those calculated using the association constants measured here. First, I remeasured the dissociation constants at 20°C and 34.8‰. There is a difference between values found in this work and those obtained by Kester and Pytkowicz (1967). The value of  $K'_3$  is dependent upon that of  $K'_2$ , so a difference in  $K'_3$  is expected if a difference in  $K'_2$  is found. Plotting the measured and interpolated data of Kester and Pytkowicz for  $K'_2$  versus temperature at 34.8‰ and versus salinity at various temperatures (Fig. 2.2), it appears that their value at 20°C and 34.8‰ is somewhat high, and that the value found here fits in more smoothly with their values at other temperatures. Considering also the salinity dependence at 5°, 10°, and 15°C and where our value lies, it is possible, though not necessary, that the values of  $K'_2$  determined by Kester and Pytkowicz at 20°, 33‰ and 20° and 25° at 36‰ are too high.

The dissociation constants  $K'_1$ ,  $K'_2$ ,  $K'_3$  in seawater can be calculated from equations (2-14)-(2-16) and the values of  $K'$  in KCl. Using the Cl‰ ratios in Pytkowicz and Kester (1971) and the % free-ion values at 25°C calculated by Hawley (1974) the following calculations are made:



	Measured - 34.8‰,* 20°C	Calculated Using Association Model
$pK'_1$	1.711	1.686
$pK'_2$	6.107	6.152
$(pK'_2 + pK'_2)$	(7.818)	(7.838)
$pK'_3$	8.999	8.938
$(pK'_1 + pK'_2 + pK'_3)$	(16.817)	(16.776)

\* 34.8‰ seawater has an effective ionic strength of 0.67

From the above list it is seen that the association constants measured here can be used to calculate the dissociation constants of phosphoric acid to within about 10%-15% of their measured values.

The values for the dissociation constants and the association constants given above can be used to estimate the phosphate speciation for seawater of a given composition. Such a procedure has been used by Garrels and Thompson (1964), Kester and Pytkowicz (1969), Pytkowicz and Hawley (1974) and others to compute the chemical species found in seawater. From equations 2-1 and 2-9 to 2-11 the following relations may be derived:

$$[PO_4^{-3}]_T = TPO_4 / (1 + \frac{X^3}{K'_1 K'_2 K'_3} + \frac{X^2}{K'_2 K'_3} + \frac{X}{K'_3}) \quad 2-27$$

$$[\text{HPO}_4^{-2}]_T = \text{TPO}_4 / (1 + \frac{K'_3}{X} + \frac{X}{K'_2} + \frac{X^2}{K'_1 K'_2}) \quad 2-28$$

$$[\text{H}_2\text{PO}_4^-]_T = \text{TPO}_4 / (1 + \frac{X}{K'_1} + \frac{K'_2}{X} + \frac{K'_2 K'_3}{X^2}) \quad 2-29$$

From these expressions and equations 2-6 to 2-8, one can compute the percentage of the total phosphate as each species. The results of these calculations for seawater of 34.8‰ are summarized below in three parts. Table 2.8 gives as a function of pH the percentage of the total phosphate as each acid-phosphate ion. Table 2.9 indicates how each phosphate species is divided according to free ion and metal-phosphate ion pair. Figure 2.3 combines the information to indicate how each free ion or ion-pair contributes to the total phosphate in solution at pH 8. The most abundant species in seawater at pH 8 is the  $\text{MgHPO}_4^0$  ion pair, followed by free  $\text{HPO}_4^{-2}$ . Speciation for pH's other than 8.0 can be calculated from Tables 2.7 and 2.8.

Table 2.8. Total phosphate distribution at various pH's for 34.8‰ seawater.

pH	% of total $\text{PO}_4$ as $[\text{H}_2\text{PO}_4^-]_T$	% of total $\text{PO}_4$ as $[\text{HPO}_4^-]_T$	% of total $\text{PO}_4$ as $[\text{PO}_4]_T$
8.5	0.3	75.4	24.3
8.0	1.1	89.8	9.1
7.5	3.8	93.0	3.1
7.0	11.2	87.9	1.0



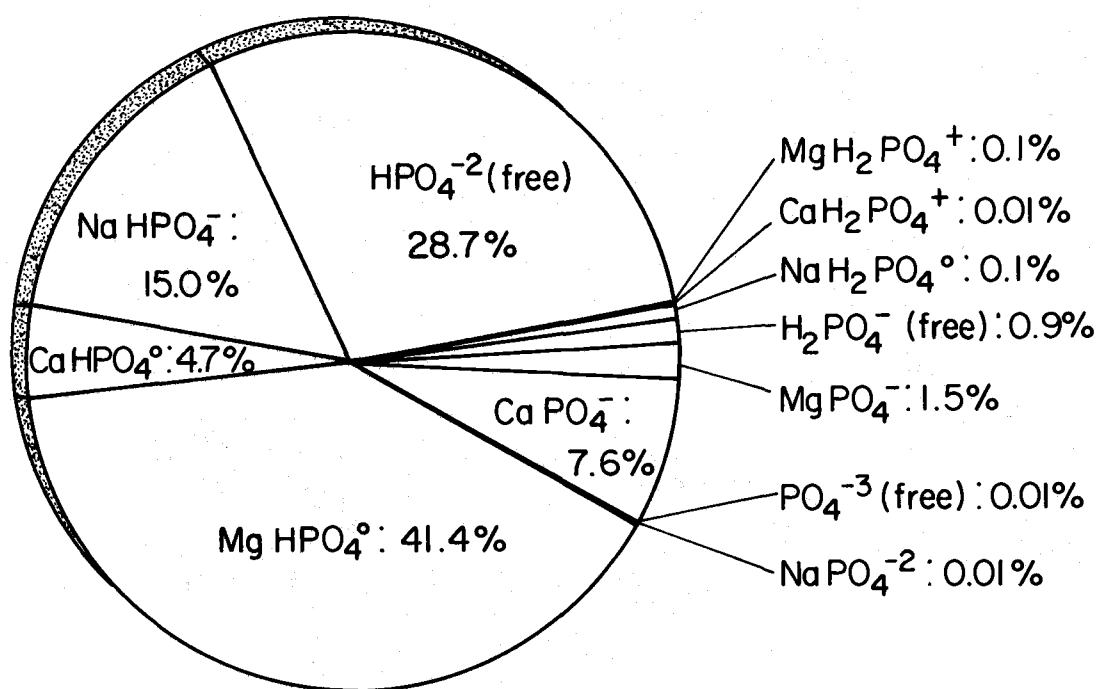


Figure 2.3. Speciation of phosphate in seawater at 34.8‰ S, 20°C, and pH = 8.0.

Table 2.9. Distribution of free ion and ion pairs for each phosphate species.

% of [ ] <sub>T</sub> as X-[ ] ion pair			
X	% of [H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ] <sub>T</sub>	% of [HPO <sub>4</sub> ] <sub>T</sub>	% [PO <sub>4</sub> ] <sub>T</sub>
free	79.1	32.0	0.1
Na <sup>+</sup>	10.7	16.7	0.1
Mg <sup>++</sup>	9.0	46.1	16.4
Ca <sup>++</sup>	1.3	5.2	83.3

There are several assumptions and restrictions which apply to the model developed above. First, it has been assumed in calculating the association constants that free-ion activity coefficients are independent of solution composition. This assumption has been shown to be applicable to sulfate ion in solution (Kester and Pytkowicz, 1969) and should not cause serious errors in this work. Secondly, it has been assumed that K<sup>+</sup>-phosphate association is negligible. In addition, although the constants were measured at 20°C, I have used in further derivations some calculations and constants which were measured or derived for 25°C. Thus it has been assumed that there is no significant error due to the temperature dependence of association constants over the range 20-25°C. The errors caused by the above assumptions, I feel, do not obscure the trends or invalidate the conclusions which have been presented. Clearly, more work on

phosphate association as functions of temperature and pressure would be valuable in understanding the processes affecting phosphate mineral equilibria in interstitial waters.

### Conclusions

From measurements of the dissociation constants of phosphoric acid in mixed salt solutions, the association constants of ortho-phosphate ion with  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ , and  $\text{Mg}^{+2}$  (assuming no  $\text{K}^+$ -phosphate ion association) were calculated. It was found, in agreement with others, that  $\text{MgHPO}_4^0$  ion pairs show a slightly stronger association than  $\text{CaHPO}_4^0$  pairs.  $\text{CaPO}_4^-$  ion-pairs, however, are about 25 times more strongly associated than  $\text{MgPO}_4^-$  ion-pairs.

Using the measured association constants the phosphate species existing in 34.8‰ seawater were computed.  $\text{MgHPO}_4^0$  and free  $\text{HPO}_4^{-2}$  comprise about 70% of the total dissolved inorganic phosphate in seawater at pH 8.0.

## CHAPTER III

## SOLUBILITY BEHAVIOR OF APATITE IN SEAWATER

Introduction

Sillen (1961) has suggested that hydroxyapatite controls the equilibrium concentration of phosphate in seawater. Kramer (1964) and Roberson (1966) pointed out that francolite, a carbonate fluor-apatite, rather than hydroxyapatite is the solid phase which occurs in seawater. Thus its solubility is the pertinent one to study (Appendix I). Differences in the results of the solubility studies of Kramer, Roberson, and Smirnov, Ivnitskaya, and Zalavina (1962), and the relatively poor precision in the study by Roberson, have made it impossible to accurately determine the saturation state of seawater with respect to apatite. It was the goal of this work to better define the solubility of apatite in seawater, and to examine the differences in solubility of apatites of different composition. It was found, though, that the solubility behavior is best described in terms of complex reactions on the apatite surface rather than by simple solubility theory.

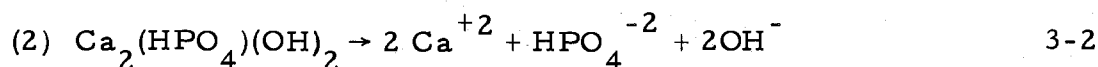
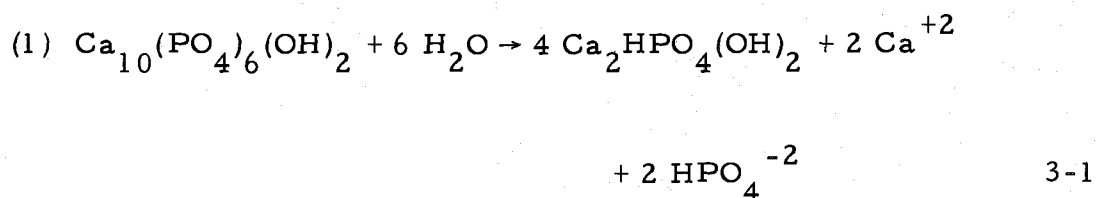
The apatite surface has been shown to be very susceptible to rearrangement or complex formation in distilled water solutions (Dietz, Rootore, and Carpenter, 1964; Smith, Posner, and Quirk,

1974). Some authors, though, argue that surface reactions do not prohibit the use of a conventional solubility product (Avnimelech, Moreno, and Brown, 1973). The solubility products of hydroxy- and fluor-apatites measured by various workers are presented in Table 3.1. The results show wide variation, some large deviations coming from sample treatment. Generally a lower solubility is found for fluorapatite than hydroxyapatite. Work by Duff (1971) showed that a relatively small mole-% of F in the solid solution  $\text{Ca}_{10}(\text{PO}_4)_3(\text{F},\text{OH})_2$  had a relatively large effect in decreasing the solubility.

As early as 1942, Greenwald reported surface area effects in his studies on the solubility of calcium phosphates, though he used a poorly defined solid phase in his work. Levinskas and Neumann (1955) found a decrease in the solubility of hydroxyapatite with a decrease in surface area of solid and an increasing pH. Rootare, Dietz and Carpenter (1962) presented experimental evidence suggesting that a surface complex with the formula  $\text{Ca}_2(\text{HPO}_4)(\text{OH})_2$  was formed on the surface of hydroxyapatite. This suggestion was supported by La Mer (1962), though later work by Dietz, Rootare, and Carpenter (1964) showed no evidence for the presence of a single solid phase corresponding to  $\text{Ca}_2(\text{HPO}_4)\text{OH}_2$ . They interpreted their results in terms of a two step process, the first of which does not reach equilibrium. The two step reaction they proposed is:

Table 3.1. Solubility products of hydroxyapatite and fluorapatite in distilled water.

	$K_{SP}^0$ (25°C)	Comments
<u>HYDROXYAPATITE</u>		
Clark (1955)	$2.07 \times 10^{-58}$	approach from under and over saturation heat-treated sample
Moreno et al. (1968)	$3.7 \times 10^{-58}$	1000°C steam-heated precipitate
"	$2.500 \times 10^{-58}$	air-heated precipitate
"	$0.8-251 \times 10^{-58}$	untreated precipitates
Avnimelech et al. (1973)	$0.63 \times 10^{-58}$	boiled precipitate, approach from under-saturation only
Wier et al. (1971)	$.54 \times 10^{-58}$	boiled with H <sub>2</sub> O
"	$.02-.006 \times 10^{-58}$	" " "
McDowell and Brown (1969)	$.26 \times 10^{-58}$	-----
<u>FLUORAPATITE</u>		
Farr and Elmore (1962)	$3.2 \times 10^{-61}$	measured in conc. solutions in pH range 0.8-1.76
McCann (1968)	$2.5 \times 10^{-60}$	calculated activity product using extended Debye-Hückel theory
Hagen (1975)	$1.2 \times 10^{-59}$ (37°C)	extrapolation of results to infinite dilution



They postulated that reaction (2) is at equilibrium and dominates the normal hydroxyapatite equilibrium.

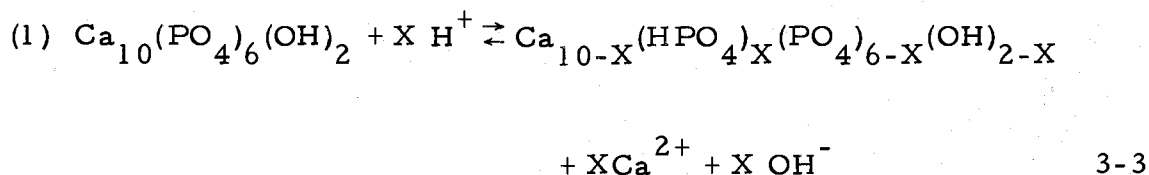
The evidence for a single, or any, surface complex on apatite is mixed. In the acid pH range 4-6, where  $\text{CaHPO}_4$  is more stable than  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , Francis (1965) has shown the  $\text{CaHPO}_4$  can precipitate on dissolving apatite surfaces and prevent further dissolution. Also,  $\text{CaF}_2$  is deposited on the surface of fluorapatite in the pH range 4-6. This can explain variations in Ca/P ratios with surface area and pH. Nancollas and Tomazic (1974) report the initial growth of unstable calcium phosphates on hydroxyapatite crystals. These unstable growths eventually convert to hydroxyapatite. Non-stoichiometric dissolution of apatite was noted by Avnimelech et al. (1973) and they attributed the variable Ca/P ratio in solution to surface reactions. They found, however, that equilibrium with the apatite lattice was finally obtained, and they did not need to refer to any surface complex in describing the solubility.

In all of the above cases it is suggested that a surface of excess

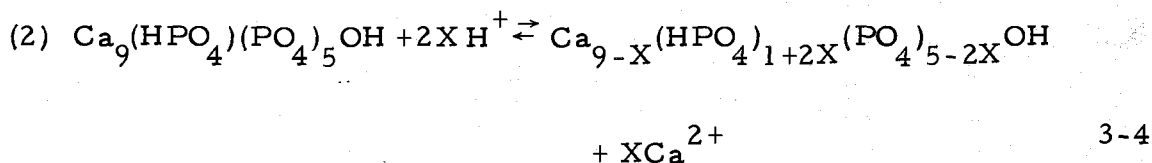
Ca (or P-deficiency) is formed relative to stoichiometric apatite. Radio-isotope measurements of the surface concentrations of Ca and P at the zero-point of charge of hydroxyapatite by Kukura, Bell, Posner, and Quirk (1972) suggested that there is no excess P or Ca (or deficiency) on the apatite surface, but this evidence has been questioned (Smith et al., 1974). Smith et al. postulated a variable surface layer formed during the preparation of the hydroxyapatite which can subsequently be dissolved exposing crystal units of normal composition beneath.

The apatites used in the studies above generally show a Ca/P solid ratio of 1.67, the theoretical ratio for pure apatite. Other ratios less than 1.67 are possible for calcium-deficient apatites. Two general formulations for calcium-deficient apatites have been given by Berry (1967) (the first originally proposed by Winand (1961)):

for Ca/P 1.5-1.67 ( $0 \leq X \leq 1$ )



for Ca/P 1.33-1.5 (continuing the series when  $X = 1$ )



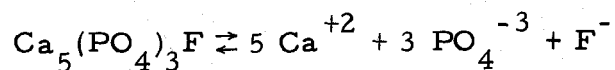


Stutman, Posner, and Lippincott (1962) favor a formulation  $\text{Ca}_{10-\text{X}}^- \text{H}_{2\text{X}}(\text{PO}_4)_6(\text{OH})_2$  for structure (1). No solubility studies that I am aware of have been performed with calcium-deficient apatites. It is possible, though, that some workers who thought they were using  $\text{Ca}_3(\text{PO}_4)_2$  ( $\text{Ca}/\text{P} = 1.5$ ) were actually using a calcium-deficient apatite ( $\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5\text{OH}$ ).

One such study may have been that reported by Riviere (1941) on the solubility of tricalcium phosphate in seawater. Significantly, he reported alkalinity changes similar to those found in the work presented here. He assumed, however, that a new phosphocarbonate phase was being formed.

Other studies of phosphate solubility in seawater have been made by Roberson (1966), Kramer (1964), and Smirnov et al. (1962). Kramer gives no account of his experimental work, and reports only his results. He concludes that seawater is slightly supersaturated with respect to carbonate fluorapatite. Smirnov et al. measured the final solution compositions in (assumed) equilibrium after apatite was precipitated from solution. The solutions he used, however, were not seawater composition, but rather  $\text{NaCl}-\text{CaCl}_2$  mixtures with additions of  $\text{F}^-$  and  $\text{CO}_2$ . Roberson dissolved natural apatites in a carbonate-free artificial seawater. Recalculating his results for  $25^\circ\text{C}$  and 35‰, using the dissociation constants of Kester and Pytkowicz (1967), an average ion-product of  $36.08 \pm 2.03$  (2  $\sigma$ ) for

$5 \text{ pCa} + 3 \text{ pPO}_4 + \text{pF}$  is computed. This  $\text{pK}_{\text{SP}}$  represents the equilibrium constant for the idealized solubility reaction:



Other studies of fluorapatite in the pH range of seawater are rare. One pertinent study is that of Simpson (1969), who found that a low-fluoride surface layer is formed on fluorapatite crystals in alkaline solutions.

Summarizing the observations on apatite behavior in solution:

- (1) Precise solubility measurements can be made, but inter-comparison between measurements is poor.
- (2) The surface of apatite is easily susceptible to alteration. This alteration may be in the form of a surface complex, a calcium-deficient apatite, and/or fluoride exchange reactions.
- (3) Kinetic factors are important in determining the reactions at the apatite-solution interface.
- (4) The formation of a surface-phase does not necessarily prohibit equilibrium between the bulk phase and the solution.

### Experimental

The basic experimental scheme was a flow-system shown in Figure 3.1. The pH was held nearly constant by bubbling an air-CO<sub>2</sub> mixture through the seawater reservoirs. For one series of

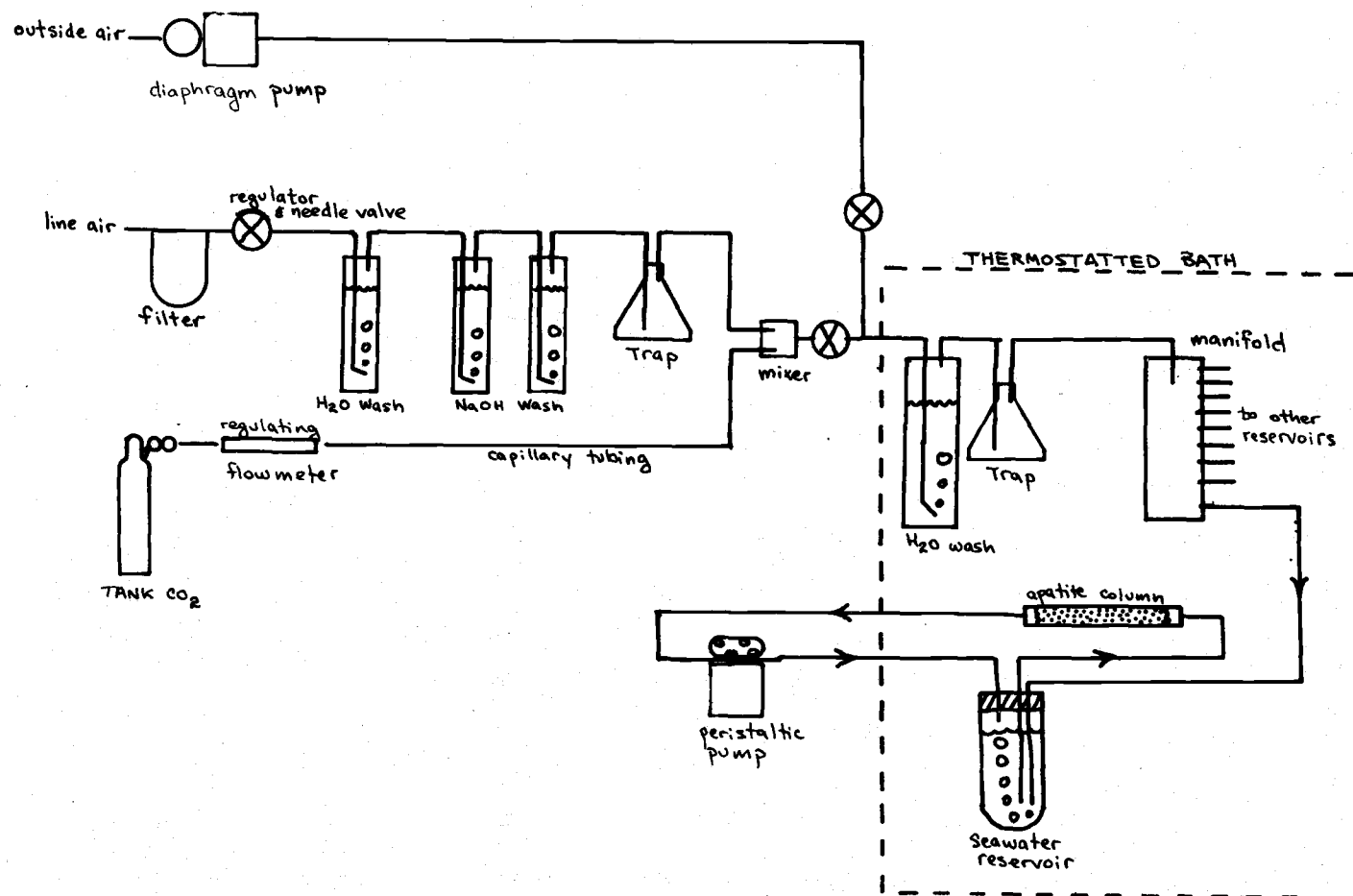


Figure 3.1. Experimental system for apatite solubility studies. For beaker experiments, column and pump were replaced by a single beaker which was stirred by a magnetic stirrer from below.

experiments the apatite columns and pumping system were replaced by a sample of apatite suspended in a nylon bag in a 1000 ml Berzelius beaker. A magnetic stir bar was used to stir the sample. Discrete samples placed in 100 ml ampoules were also used. Total phosphate, fluoride, pH, alkalinity, and calcium were measured using techniques and equipment outlined in Appendix 2. The seawater was 33.3‰ S and maintained at 10°C unless otherwise specified.

The samples used in the study are described in Appendix 3. They were obtained from land phosphate deposits as well as from sedimentary ocean environments.

## Results

Preliminary experiments showed that a steady value of phosphate was reached in a relatively short time in the column experiments (Figure 3.2), and unless otherwise specified, the column experiments were terminated at 48 hours. Beaker and ampoule experiments ran from 30-60 days, and their time behavior was generally monitored.

In the discussion to follow, the term  $\text{TPO}_4$  will be used to designate the total inorganic phosphate. It is defined by:

$$\text{TPO}_4 = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

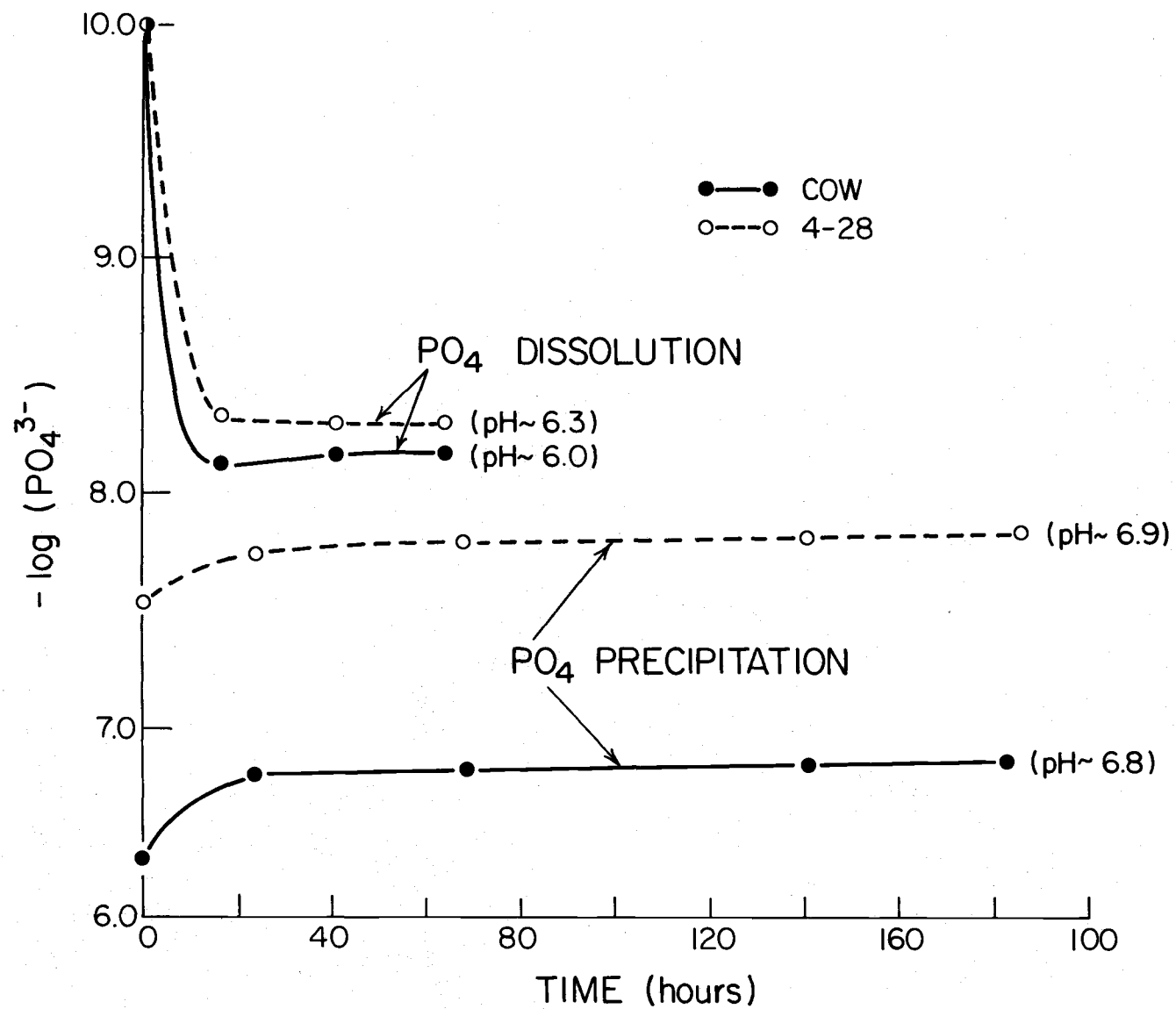


Figure 3.2. Time of equilibration for column experiments.

The individual ionic species will also be referred to. They can be calculated from the  $\text{TPO}_4$  by the following relations:

$$[\text{PO}_4^{-3}] = \text{TPO}_4 / (1 + \frac{X^3}{K'_1 K'_2 K'_3} + \frac{X^2}{K'_2 K'_3} + \frac{X}{K'_3}) \quad 3-5$$

$$[\text{HPO}_4^{-2}] = \text{TPO}_4 / (1 + \frac{K'_3}{X} + \frac{X}{K'_2} + \frac{X^2}{K'_1 K'_2}) \quad 3-6$$

$$[\text{H}_2\text{PO}_4^{-}] = \text{TPO}_4 / (1 + \frac{X}{K'_1} + \frac{K'_2}{X} + \frac{K'_2 K'_3}{X^2}) \quad 3-7$$

where  $K'_i$  = ith apparent dissociation constant of phosphoric acid

$X$  = operational hydrogen ion activity =  $10^{-\text{pH}}$

The effect of surface area and surface reactions are best exemplified in the results of a series of ampoule experiments. Weighed portions of a sample (COW) were placed in alkalinity free seawater. One sample was placed in seawater of normal alkalinity ( $\sim 2.2$  meq/l). The results are shown in Figures 3-3 and 3-4. (Data for the analyses is given in Appendix 4, Table A4.1). A good correlation is seen between the  $[\text{HPO}_4^{-2}]$  concentration and the amount of solid used (Figure 3.5). The  $[\text{PO}_4^{-3}]$  concentration showed an initial increase which was due to the rapid initial increase in the  $\text{TPO}_4$  in solution. This increase was followed by a slower decrease

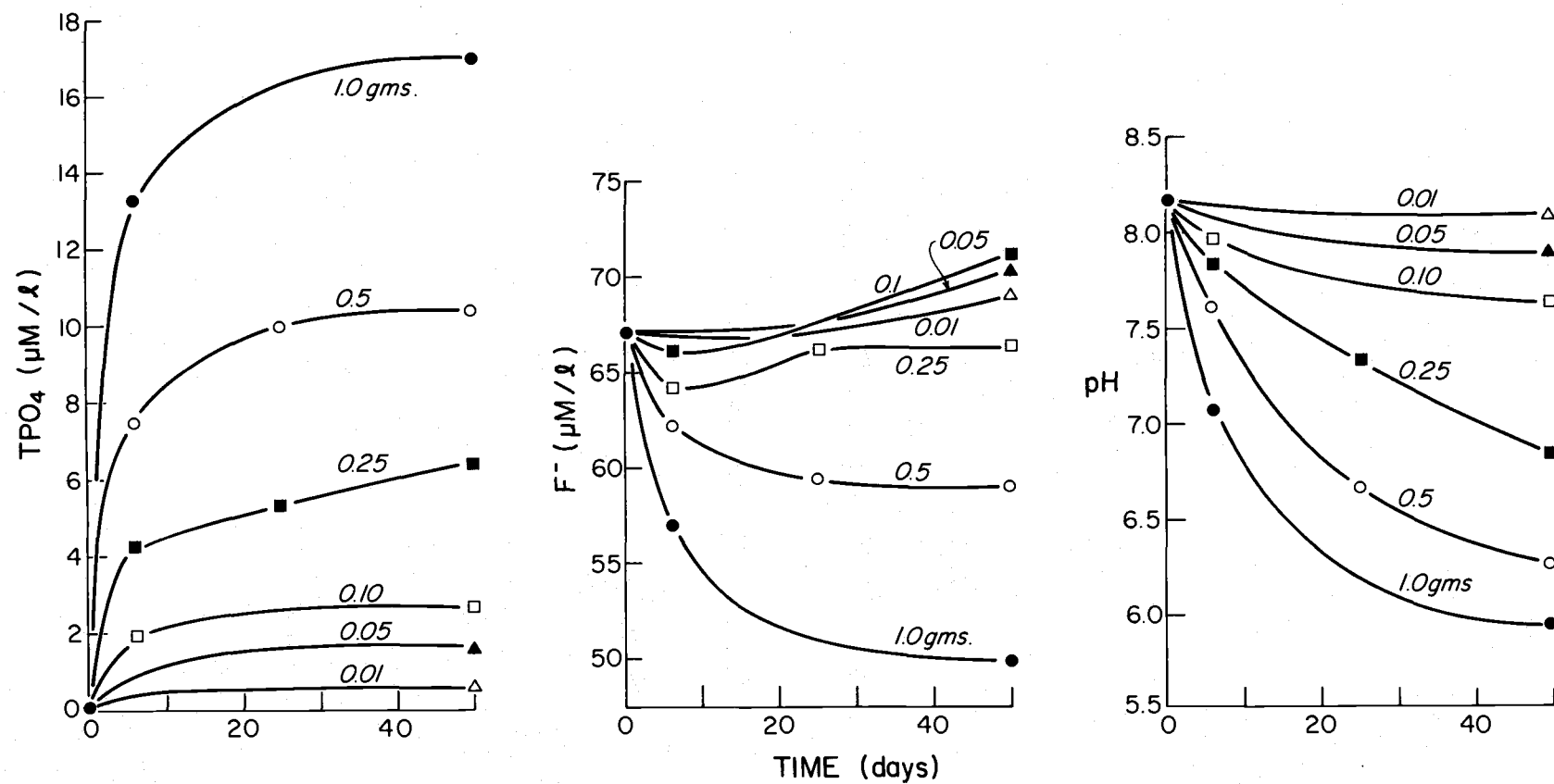


Figure 3.3. Experimental results showing the effect of surface area (solid/solution ratio) on TPO<sub>4</sub>, F<sup>-</sup>, and pH.

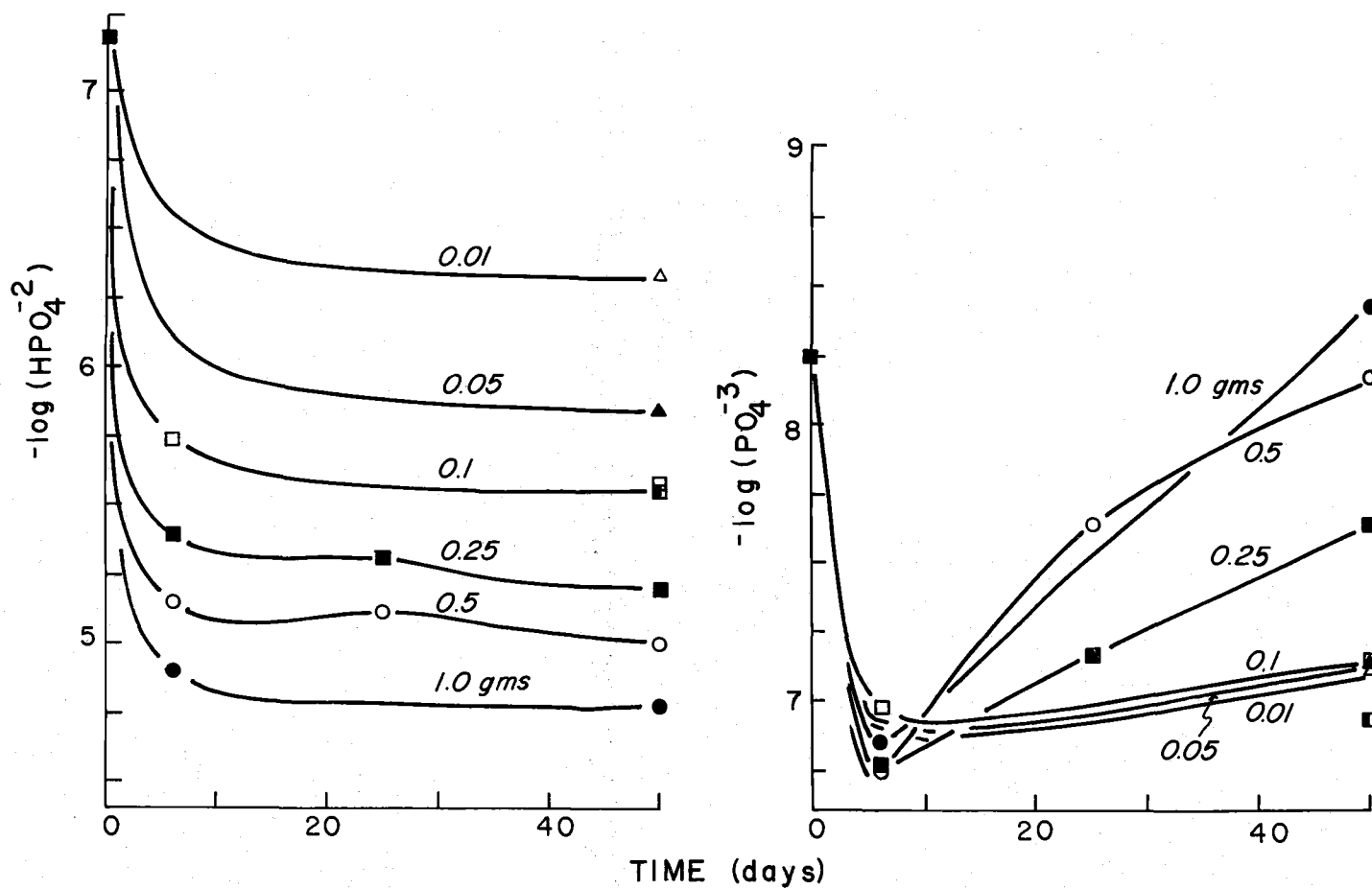


Figure 3.4. Calculated variables,  $\text{HPO}_4^{-2}$  and  $\text{PO}_4^{-3}$ , for surface area experiments versus time. Notice the regularity of the  $\text{HPO}_4^{-2}$  variation compared to the  $\text{PO}_4^{-3}$  variation.



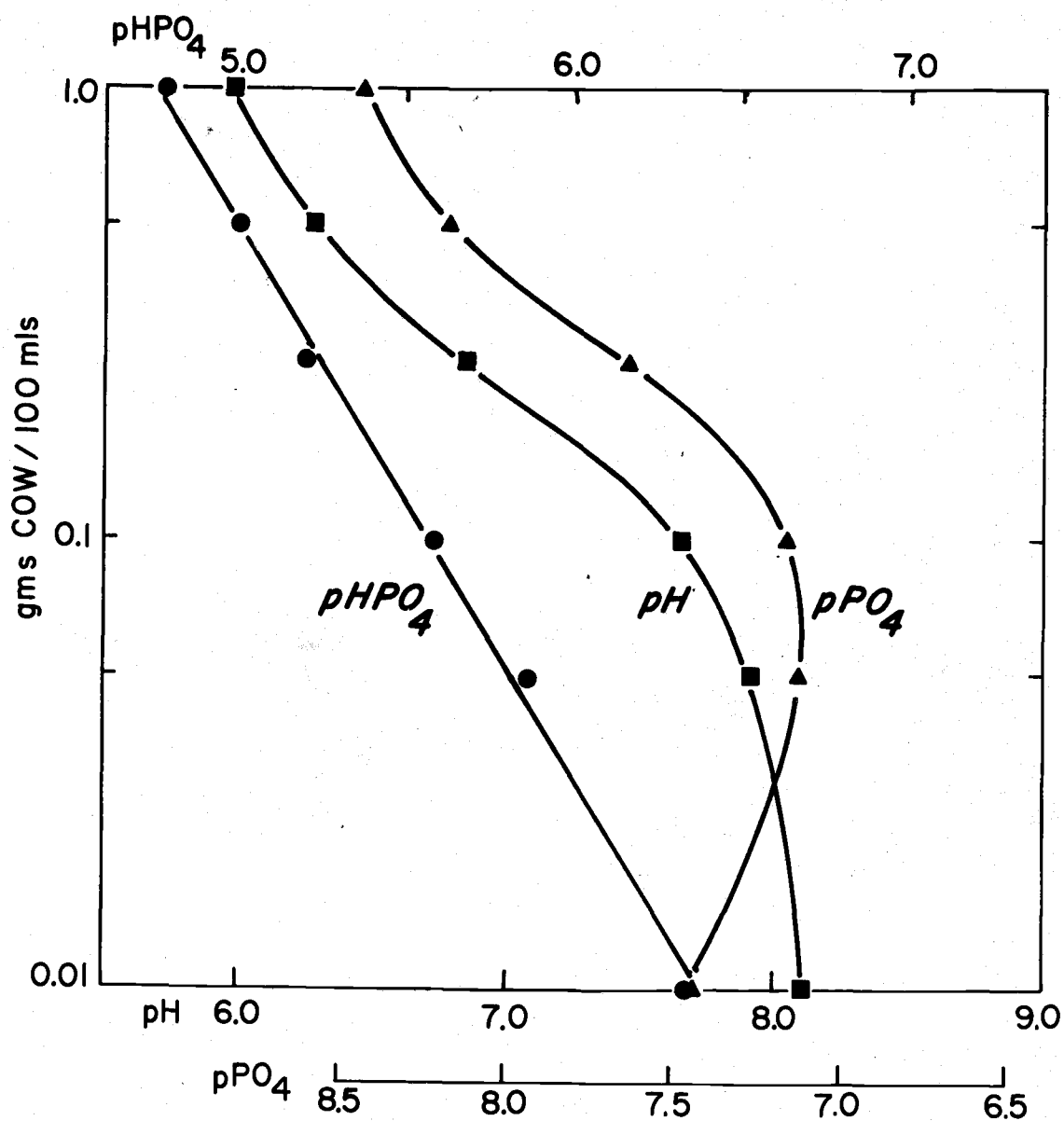


Figure 3.5.  $\text{pHPO}_4^{-2}$ ,  $\text{pPO}_4^{-3}$ , and pH versus log (solid/solution ratio). These data suggest a surface reaction involving  $\text{HPO}_4^{-2}$  ions.

in  $[\text{PO}_4^{-3}]$  caused by a slow decrease in pH which was not accompanied by the necessary increase in  $\text{TPO}_4$  to increase or even maintain a constant  $[\text{PO}_4^{-3}]$  concentration. This manner of  $[\text{PO}_4^{-3}]$  change versus time was typical of the behavior of the COW sample in other experiments.

The concentration of fluoride was a function of both pH and surface area (Figure 3.6). Most notably, it showed both increases and decreases in solution even though the  $\text{TPO}_4$  increased steadily. These data suggest that there is excessive  $\text{F}^-$  dissolution (relative to P) above  $\text{pH} \approx 7.1$  and excessive P dissolution (relative to F) below that pH for this sample. Thus, the apatite exhibited an ion-exchange type behavior with the  $\text{F}^-$  in solution. The magnitude of the  $\text{F}^-$  dependence on pH was different for other samples, though all showed the same trend. The behavior of the sample equilibrated in seawater of normal alkalinity ( $\sim 2.2$  meq/l) is somewhat different from the other samples. The final  $[\text{HPO}_4^{-2}]$  concentration is very near that of the sample with the same surface area ( $2.85$  vs.  $2.58 \times 10^{-6}$  M/l  $\text{HPO}_4^{-2}$ ) and this is consistent with the behavior of the other samples. The  $\text{F}^-$  concentration, however, is significantly higher than that in the other samples. This is true even considering the expected increase in  $\text{F}^-$  with increasing pH. This indicates that  $\text{CO}_3^{=}$  or  $\text{HCO}_3^-$  ion might also substitute for  $\text{F}^-$  ion on the apatite surface. Interaction of  $\text{CO}_3^{2-}$  and  $\text{F}^-$  is mentioned in the literature, but

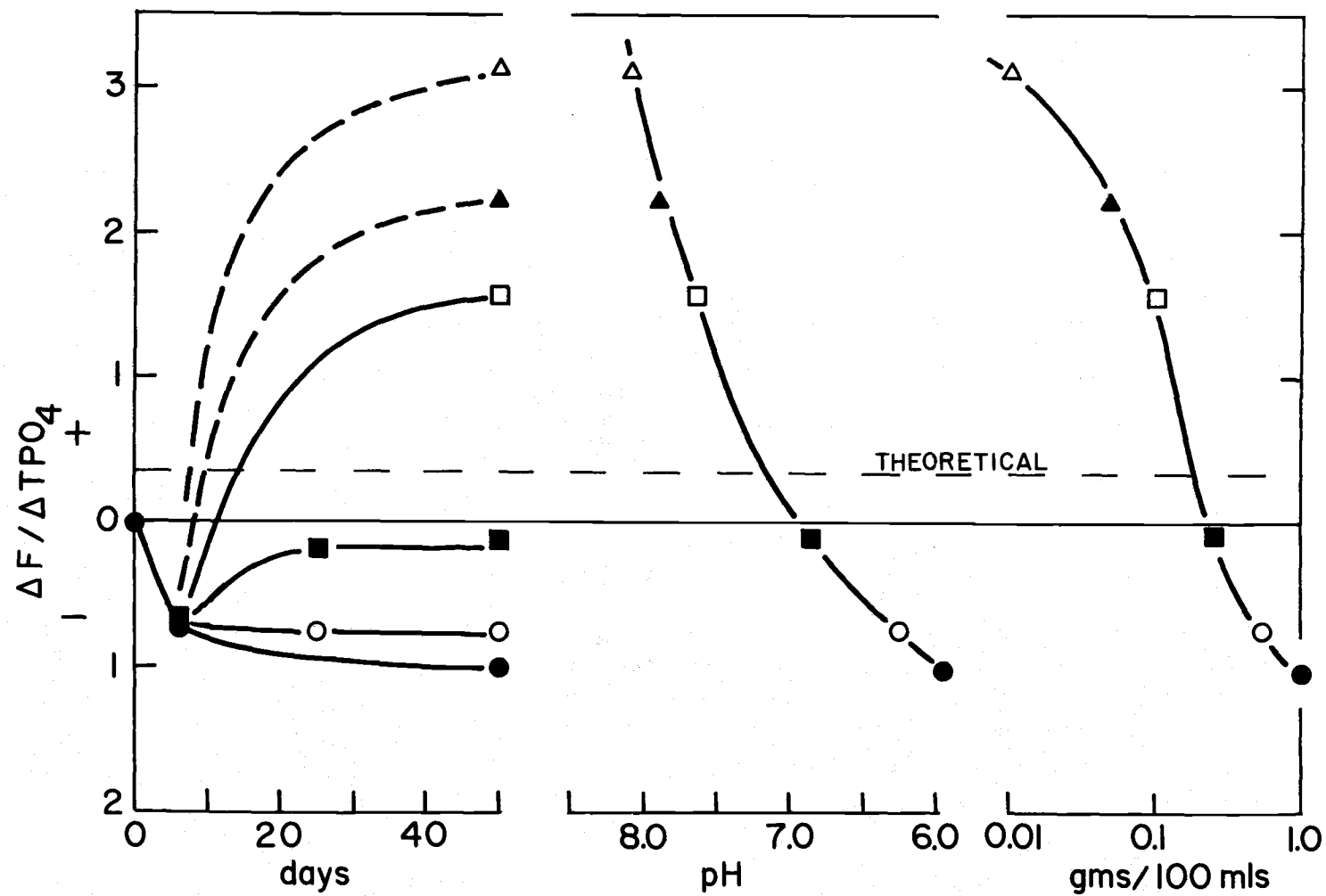


Figure 3.6. A comparison of  $\Delta F / \Delta TPO_4$  for surface area experiments versus time, pH, and surface area. Notice that  $F^-$  can decrease when  $TPO_4$  increases. This indicates a  $F^-$  exchange process on the apatite surface independent of the solubility reaction.

evidence is conflicting. Cook (1972) showed that an increase in  $\text{CO}_3^{-2}$  of apatites correlates with a decrease in  $\text{F}^-$ , however, the data of McClellan and Lehr (1969) show the reverse trend. Apatite precipitation studies by Legeros et al. (1968) showed no  $\text{CO}_3^{-2}/\text{F}^-$  interaction.

Further experiments were performed with samples of COW (5.5 g - 20 to 30 mesh), FAP (35 g - 50 to 100 mesh), and 4-28 (16.5 g - 18 to 30 mesh) suspended in nylon bags in ~700 mls of seawater. The samples were continuously bubbled with outside air or an air- $\text{CO}_2$  mixture. Approximately 50-ml aliquots were removed periodically for analysis of  $\text{F}^-$ ,  $\text{TPO}_4$ , and alkalinity. The results are illustrated in Figure 3.7, and the final data is given in Appendix 4, Table A4.2.

The striking feature of the first equilibration, notably with COW, is the difference in the rates of change of  $\text{TPO}_4$ ,  $\text{F}^-$ , and alkalinity. The comparison can only be qualitative since pH also is changing, and each of the processes changing  $\text{F}^-$ ,  $\text{TPO}_4$ , and alkalinity is likely pH dependent. Even so, the difference in rates indicates a different process dominating the concentration of these variables. Certainly, other processes than stoichiometric apatite solution and dissolution are operating here.

During the second equilibration, changes in alkalinity and  $\text{F}^-$  are virtually absent in 4-28 and FAP. The alkalinity loss in COW

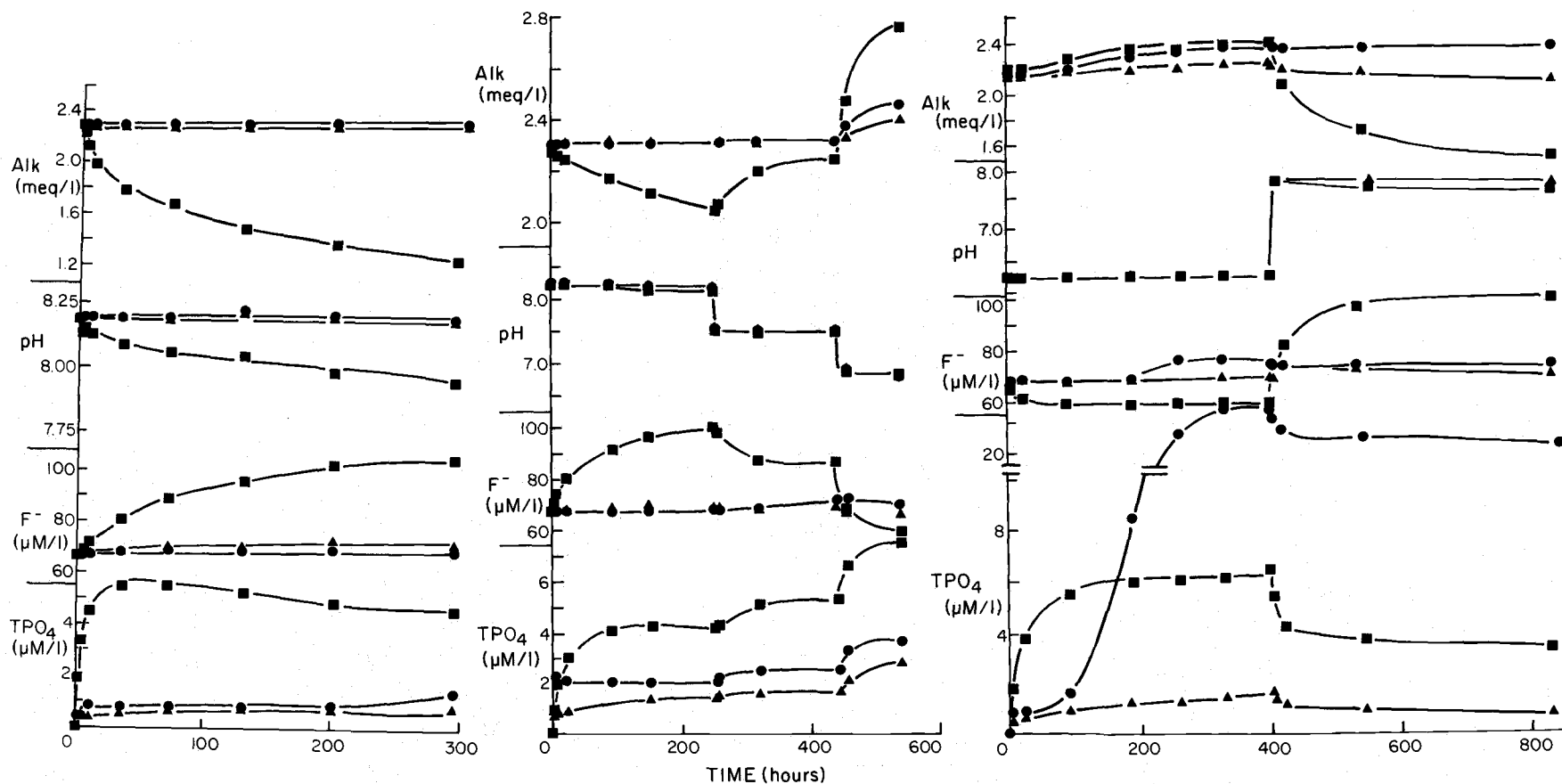


Figure 3.7.  $\text{TPO}_4$ ,  $\text{F}^-$ , pH and alkalinity variations versus time for beaker experiments. Note that there is a change in scale between separate graphs. o = FAP,  $\Delta$  = 4-28,  $\square$  = COW.

is only 1/3 of that in the first equilibration, indicating that certain sites on the apatite are being used up with each equilibration. The  $F^-$  concentration, however, is nearly as great as in experiment #1. This shows that the  $F^-$  reaction is not wholly tied to the alkalinity reaction. A drop in pH caused by  $CO_2$  addition is followed by a relatively small increase in  $TPO_4$ , a decreasing  $F^-$  concentration, and an increase in alkalinity. The third equilibration began at a low pH, and the pH was then raised. This made the system super-saturated with respect to  $PO_4$ . Decreases in  $TPO_4$  in this case were accompanied by decreasing alkalinity and increasing  $F^-$ .

The behavior of dissolved phosphate for these apatites can be summarized in equations of the form:  $-\log(PO_4^{-3}) = pPO_4^{-3} = \text{const}_1 + \text{const}_2 \cdot \text{pH}$ . For ideal behavior of apatite  $\text{const}_2 = 0$ . From beaker experiments 2 and 3, the following equations are found (by the method of least-squares):

COW	Expt 2	$pPO_4^{-3} = 13.46 - .857 \text{ pH}$	3-8a
	Expt 3	$= 13.41 - .835 \text{ pH}$	3-8b
4-28	Expt 2	$pPO_4^{-3} = 13.65 - .818 \text{ pH}$	3-9a
	Expt 3	$= 13.94 - .819 \text{ pH}$	3-9b
FAP	Expt 2	$pPO_4^{-3} = 13.74 - .851 \text{ pH}$	3-10a
	Expt 3	$= 13.74 - .975 \text{ pH}$	3-10b

Except for FAP (Expt 3), the pH dependence of the phosphate concentration going from low to high  $TPO_4$  is very close to that found when

approaching the final state from high to low  $\text{TPO}_4$ . During Expt 3, some of the fine mesh FAP escaped from the nylon bag and grinding by the stir bar caused enhanced solubility, which did not exhibit the degree of reversibility seen in the behavior of COW. In the equations above (3-8, -9, -10), a negative pH coefficient ( $\text{const}_2$ ) near unity indicates the influence of  $\text{HPO}_4^{-2}$  ion rather than  $\text{PO}_4^{-3}$  ion. This can be seen from the following derivation:

The definition of  $K'_3$  can be written as:

$$pK'_3 = \text{pH} + \log \frac{[\text{HPO}_4^{-2}]}{[\text{PO}_4^{-3}]} \quad 3-11$$

or

$$pK'_3 = \text{pH} + p\text{PO}_4^{-3} - p\text{HPO}_4^{-2} \quad 3-12$$

then

$$p\text{PO}_4^{-3} + \text{pH} = pK'_3 + p\text{HPO}_4^{-2} \quad 3-13$$

Equations 3-8, -9, -10 can be rearranged to the form:

$$(1 + \text{const}_2) p\text{PO}_4^{-3} - \text{const}_2 (\text{pH} + p\text{PO}_4^{-3}) = \text{const}_1 \quad 3-14$$

so, substituting from Eq. 3-13

$$(1 + \text{const}_2) p\text{PO}_4^{-3} - \text{const}_2 (p\text{HPO}_4^{-2}) = \text{const}_1 + \text{const}_2 pK'_3 \quad 3-15$$

or,

$$A \text{ pPO}_4^{-3} + B \text{ pHPO}_4^{-2} = C \quad 3-16$$

Thus  $\text{const}_2$  shows the influence of  $\text{HPO}_4^{-2}$  ion on the dissolution and precipitation behavior on apatite. Equations (3-8, -9, -10) can then be recast in the form of equation 3-16 ( $\text{pK}'_3 = 9.215$ ), which yields the following:

	<u>A</u>	<u>B</u>	<u>C</u>
COW 2	.143	.857	5.56
COW 3	.165	.835	5.72
4-28 2	.182	.818	6.11
4-28 3	.181	.819	6.39
FAP 2	.149	.851	5.89
FAP 3	.025	.975	4.76

The final constant, C, should be constant for each sample if there is a constant solubility product for a phase of constant relative  $\text{PO}_4^{-3} / \text{HPO}_4^{-2}$  composition. This comparison can be made not including the influence of  $\text{F}^-$  ion because  $\text{F}^-$  is approximately equal at corresponding pH's in experiments 2 and 3.

Since it was observed that the solubility of apatites depended to some extent on the  $\text{HPO}_4^{-2}$  concentration, a series of experiments was designed to examine the  $\text{HPO}_4^{-2}$  dependence for a range of apatite samples. Eight different apatites (described in Appendix 3) were simultaneously equilibrated in a column-flow apparatus.



Repeated equilibrations were performed, for the most part, at a single pH. Deviations in pH came from alteration of the alkalinity. The only sample pretreatment was in distilled water. After the initial distilled water wash, only seawater washes were used. In addition, some equilibrations were done at 25°C to measure the temperature effect on the solubility. The remainder were done at 10°C. The time of equilibration was approximately 48 hours. At the end of each equilibration, pH,  $\text{TPO}_4$ ,  $\text{F}^-$  and alkalinity were measured. Some results are illustrated in Figure 3.8. The data are compiled in Appendix 4, Tables A4.3-A4.5.

This series of experiments illustrates fairly well the diverse behaviors of apatite in seawater. Phosphate increase can be accompanied by either fluoride decrease or increase. Phosphate removal from solution can also be accompanied by either fluoride increase or decrease. Alkalinity changes depended on the pH of prior equilibration. Using the final two equilibrations at each pH (Figure 3.9), the following equations (Table 3.2) describing the experimental data can be calculated using the method of least-squares. They show the pH dependence of the solubility.

Two equilibrations were done at 25°C near pH = 7. (See Table A4.5.) The temperature dependence of the solubility of apatite is not constant from sample to sample, though a lower total phosphate is measured at 25° compared to 10° for all samples (Table A4.6). The

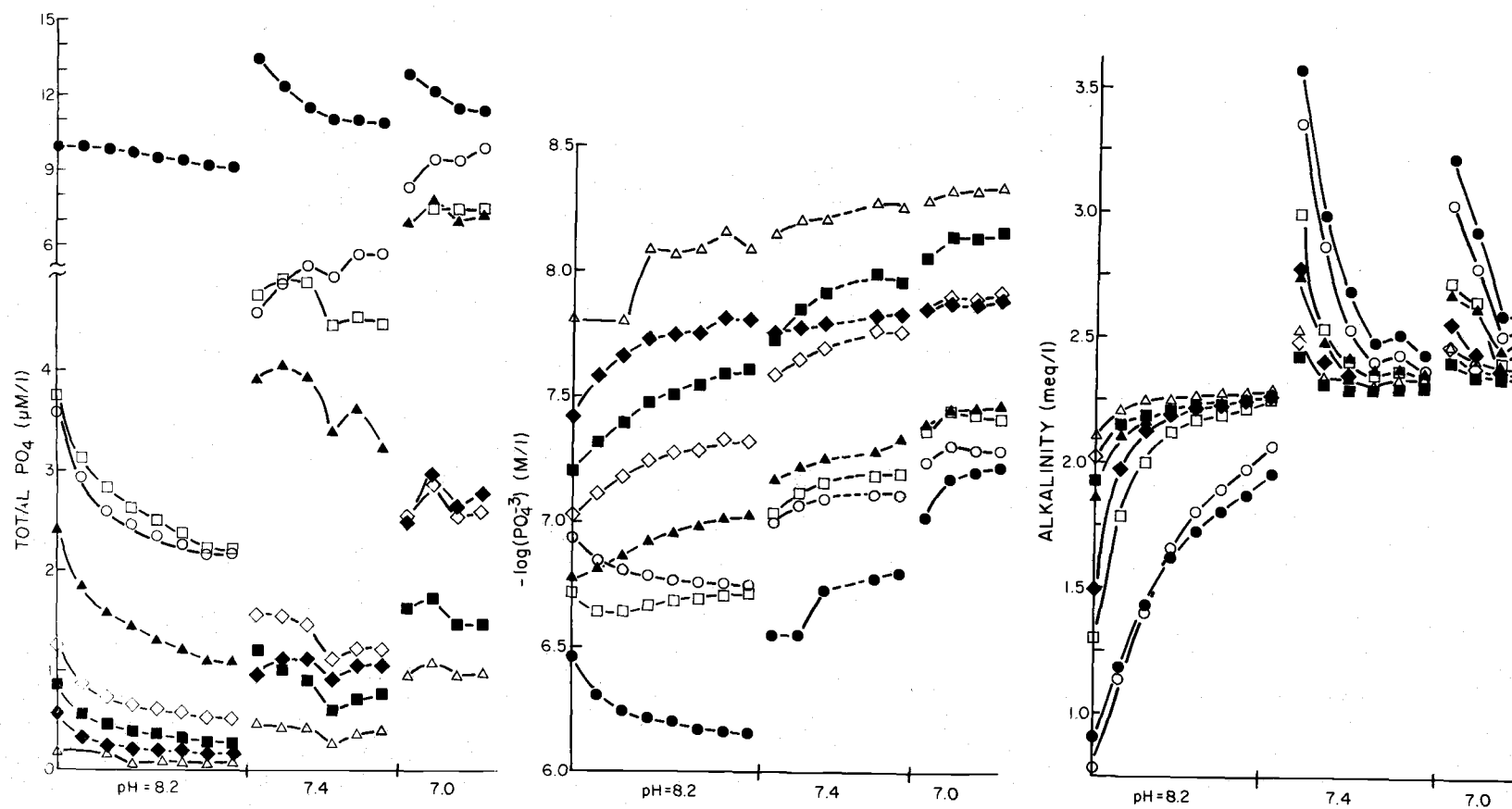


Figure 3.8. Variation in TPO<sub>4</sub>, pPO<sub>4</sub> and alkalinity for repeated 48-hour equilibrations of apatite at three pH's. There were eight equilibrations at pH 8.2, six at pH 7.4, and four at pH = 7. See Figure 3.9 for explanation of symbols.

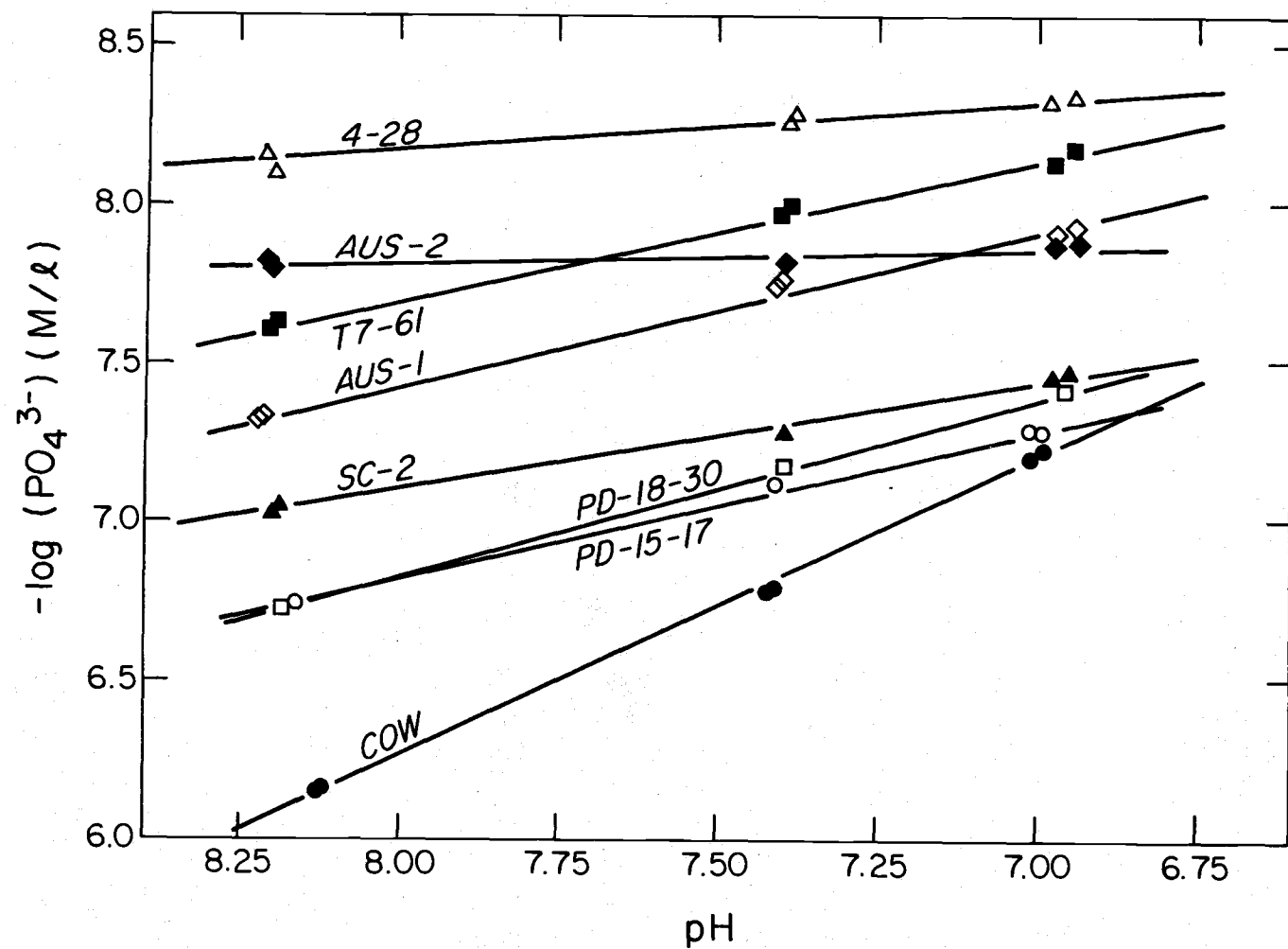


Figure 3.9.  $\text{pPO}_4$  versus pH for different apatites in column experiments. "Ideal" apatite solubility is a horizontal line on this type of graph.

Table 3.2. pH dependence of  $\text{PO}_4^{-3}$  and  $\text{F}^-$  in column experiments.

	$\text{pPO}_4^{-3} = A + B \text{ pH}$		correlation coefficient	standard error
	<u>A</u>	<u>B</u>		
PD-15-17	10.533	-.4625	-.9993	.0082
COW	13.697	-.9283	-.9991	.0186
4-28	9.518	-.1693	-.9729	.0208
SC-2	9.929	-.3550	-.9982	.0119
PD-18-30	11.470	-.5796	-.9988	.0144
T7-61	11.295	-.4495	-.9986	.0122
AUS-1	11.262	-.4777	-.9943	.0266
AUS-2	8.190	-.0466	-.8805	.0123
(A = 8.135 + 6.001 B      R = .97928      .3048)				
	$\text{pF} = C + D \text{ pH}$		correlation coefficient, R	standard error
	<u>C</u>	<u>D</u>		
PD-15-17	5.363	-.1484	-.9927	.0087
COW	6.518	-.3227	-.9981	.0092
4-28	4.342	-.0217	-.9035	.0053
SC-2	4.602	-.0548	-.9889	.0046
PD-18-30	4.684	-.0618	-.8841	.0166
T7-61	4.303	-.0142	-.9421	.0026
AUS-1	4.205	-.0031	-.1219	.0131
AUS-2	4.359	-.0210	-.5580	.0162
(C = 4.208 + 7.271 D      .9989      .0338 )				

reduction in  $\text{TPO}_4$  ranged from 30-50% for a 15°C temperature increase.

Two experimental runs approached equilibrium from

supersaturation with respect to phosphate. The final phosphate concentration of these equilibrations (Table A4.7) can be compared to the phosphate predicted using the equations presented in Table 3.2. The results are given in Table 3.3. A least-squares regression of the expected  $\text{TPO}_4$  versus the measured  $\text{TPO}_4$  (excluding 1 sample) gives  $\text{TPO}_4(\text{measured}) = 1.182 \text{ TPO}_4(\text{expected})$ . Thus, most samples remained  $\sim 18\%$  higher in  $\text{PO}_4$  than predicted. This discrepancy is somewhat lessened when one considers the effect of the relatively lower levels of  $\text{F}^-$  in these runs compared to the predicted  $\text{F}^-$ . The levels of phosphate for each sample were, however, reduced to close to the concentrations of phosphate approached from undersaturation.

Early experiments were done to estimate the effect of  $\text{CO}_3^{2-}$  levels on the apatite solubility. It was found that  $\text{CO}_3^{-2}$  had no appreciable effect on the final phosphate in solution (Figure 3.10). (See data in Table A4.8.) Greenwald (1945), on the other hand, reports an increase in phosphate solubility with an increasing solution carbonate content.

Riviere (1941) attributed alkalinity changes in his phosphate solubility experiments to the formation of a phosphocarbonate phase. I tested that hypothesis in a solubility experiment allowing no atmospheric  $\text{CO}_2$  exchange. If the alkalinity change observed in the experiment was due to carbonate dissolution or precipitation, the change would be reflected in the total carbon dioxide ( $\text{TCO}_2$ ). If

Table 3.3. Comparison of measured versus predicted  $\text{TPO}_4$  and  $\text{F}^-$  for supersaturation experiments

Sample	$\text{F}^-$ ( $\mu\text{M}$ )		$\text{TPO}_4$ ( $\mu\text{M}$ )	
	<u>expected</u>	<u>measured</u>	<u>expected</u>	<u>measured</u>
PD-15-17	68.4	70.8	2.39	2.88
	50.0	45.2	7.58	8.97
COW	112.9	107	9.48	7.27
	64.2	63.1	11.02	12.7
4-28	68.4	59.7	.09	.08
	64.6	53.3	.81	1.35
SC-2	69.9	63.6	1.18	1.17
	61.0	47.4	5.99	7.40
PD-18-30	66.1	55.4	2.29	2.59
	57.0	43.1	6.33	7.69
T7-61	65.0	59.7	.29	.19
	62.6	53.3	1.26	2.19
AUS-1	66.1	60.0	.53	.42
	65.6	48.6	2.13	3.02
AUS-2	65.0	55.1	.19	.10
	61.6	37.6	2.13	1.97

alkalinity was altered by  $\text{H}^+$  or  $\text{OH}^-$ , the  $\text{TCO}_2$  would remain constant.

It was found that the alkalinity removal was related to  $\text{H}^+$  -  $\text{OH}^-$  ions rather than  $\text{CO}_3^{2-}$ . The initial and final conditions are shown below:

	<u>Initial</u>	<u>Final</u>
pH	8.118	7.302
TPO <sub>4</sub> (μM)	0.02	10.2
Alk (meq/l)	2.27 <sub>1</sub>	2.03 <sub>8</sub>
TCO <sub>2</sub> (μM/l)	2.11	2.14

If there had been CO<sub>3</sub><sup>-2</sup> precipitation the final TCO<sub>2</sub> would have been 2.00 μM/l.

To summarize the experimental work, I will list the observed behavior of apatite in seawater:

(1) For the sample "COW," the amount of phosphate in solution was a function of the surface area of the solid material. The dissolution curves approached a constant [HPO<sub>4</sub><sup>-2</sup>]/sfc area ratio rather than a constant [PO<sub>4</sub><sup>-3</sup>] or [PO<sub>4</sub><sup>-3</sup>]/sfc area ratio.

(2) The rates of phosphate, fluoride, and alkalinity changes in solution indicate different processes acting to alter each component.

(3) A more soluble surface layer dissolved (or is replaced) upon successive equilibrations of apatites after washing in distilled water. The final equilibrations of packed columns of apatite exhibit a pH dependence ranging from nearly constant (PO<sub>4</sub><sup>-3</sup>) to nearly constant (HPO<sub>4</sub><sup>-2</sup>). The computed pH dependence shows a fair degree of reversibility when approached from under- or supersaturation with respect to phosphate.

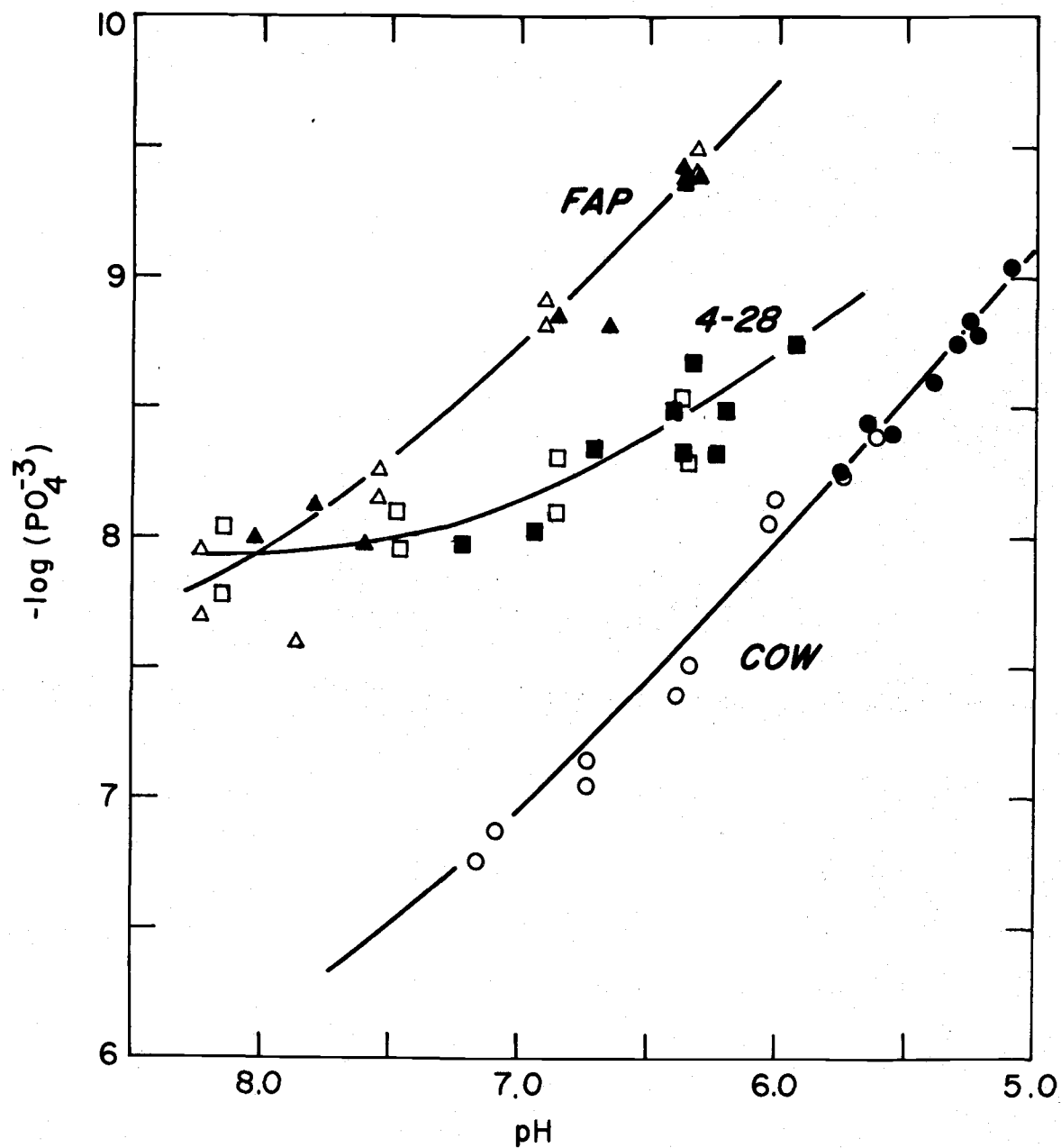


Figure 3.10.  $\text{pPO}_4$  versus pH for three apatite samples equilibrated in solutions of normal  $\text{CO}_2$  (unfilled symbols) and zero  $\text{CO}_2$  (filled symbols). Data show that there is no significant variation due to solution  $\text{CO}_2$  content.



(4) Fluoride concentrations are a function of pre-equilibration and pH. Final fluoride concentrations are increased with increasing pH. Alkalinity is a function of pre-equilibration and pH, also. A change from low to high pH will cause a decrease in alkalinity, and vice versa.

(5) Temperature affects the solubility of apatite as well as the fluoride and alkalinity reactions with apatite. Apatite becomes less soluble with increasing temperature.

(6) The presence or absence of dissolved  $\text{CO}_2$  has a relatively minor effect on the level of dissolved phosphate. Other factors predominate.

(7) The uptake (release) of alkalinity is not related to the precipitation (dissolution) of a carbonate mineral.

### Discussion

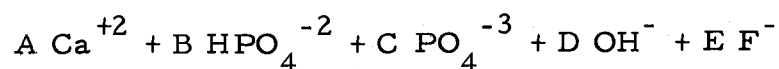
I have suggested that the apatite surface which equilibrates with seawater is different from the bulk apatite. Because data were obtained in a solution of constant Ca, however, the Ca/P ratio cannot be used to ascertain the nature of the equilibrating phase. The only means of analysis is through the pH-dependence of the solubility. A constant  $-\log(\text{PO}_4^{-3}) (= \text{pPO}_4^{-3})$  is the expected condition for equilibrium with a pure apatite. This is seen by the ideal dissolution reaction  $\text{Ca}_5(\text{PO}_4)_3\text{F} \rightleftharpoons 5 \text{Ca}^{+2} + 3 \text{PO}_4^{-3} + \text{F}^-$ . Rather, a constant  $\text{pPO}_4 + X\text{pH}$

was observed for each different apatite studied. This implies a solid phase containing  $\text{HPO}_4^{-2}$  ions, or a surface coating of some type containing  $\text{HPO}_4^{-2}$  ions. There is also some F/OH variation on the solid surface. Assuming that the F/OH variation is associated with the equilibrating phase, then a simplified representation of the surface can be given by:

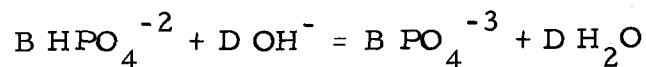


Other ions, such as  $\text{CO}_3^{-2}$  and  $\text{Na}^+$ , are likely involved on the surface; they are excluded because I am not trying to completely describe the surface but rather to simply illustrate the effect of pH on the solubility. The pH variation of the solubility of the hypothetical phase will be a function on the relative proportions of  $\text{HPO}_4^{-2}$ ,  $\text{PO}_4^{-3}$ , and  $\text{OH}^-$ . There are several possible cases:

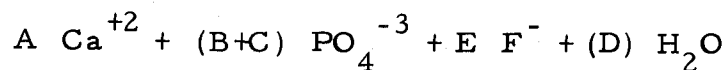
(1)  $B = D$  (see formula) From stoichiometric dissolution of the solid surface one writes:  $\text{Ca}_A(\text{HPO}_4)_B(\text{PO}_4)_C(\text{OH})_D(\text{F})_E \rightleftharpoons$



The reaction between  $\text{HPO}_4^{-2}$  and  $\text{OH}^-$  leads to

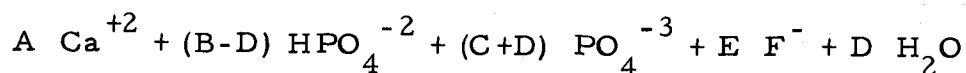


Therefore if  $B = D$ , the solubility is represented by



This leads to a constant  $\text{PO}_4^{-3}$  concentration and would be indistinguishable from equilibrium with a pure apatite under our experimental conditions.

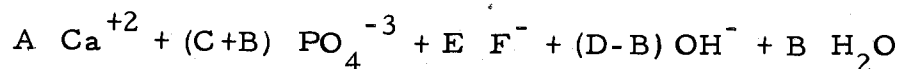
(2)  $B > D$ . If there is an excess of  $\text{HPO}_4^{-2}$  over  $\text{OH}^{-}$  with the magnitude of the excess =  $(B-D)$ , then one can write the net dissolution reaction as:



Therefore, this would give the appearance of the dissolution of a surface of the composition  $\text{Ca}_A \text{H}_{B-D} \text{PO}_4 \text{C}_{C+B} \text{F}_E$ . The solution would then show the property of a constant sum of

$$(B-D)\text{pH} + (C+B)\text{pPO}_4 [ (B-D) > 0 ].$$

(3)  $D > B$ . The excess of  $\text{OH}^{-}$  over  $\text{HPO}_4^{-2}$  would neutralize all  $\text{HPO}_4^{-2}$ , thus giving the net dissolution reaction of:



This would lead to a constant composition in the solution of

$$(C+B) \text{ pPO}_4^{-3} + (D-B) \text{ pOH}^{-} = \text{constant} [ (D-B) > 0 ]$$

Introducing  $\text{pH} + \text{pOH} = \text{pK}_w$ , then

$$(C+B)p\text{PO}_4^{-3} - (D+B)p\text{H} = \text{constant}$$

The second condition is observed for all of the samples. Therefore, if equilibration occurs with a phase represented as above, then for samples used in this study  $B \geq D$ .

Exact correlation of the pH dependence with composition is not possible for the several reasons discussed above: lack of quantitative information on admixed impurities; lack of quantitative information on ions which are substituted for Ca and  $\text{PO}_4$  and  $\text{F}^-$ ; some uncertainty as to composition of the solid relative to microvariations in the apatite composition (see Appendix 3). If one assumes that all Ca,  $\text{PO}_4$ ,  $\text{CO}_3^{-2}$  and  $\text{F}^-$  measured in the bulk sample belong to the apatite, then average compositions can be formulated. For bulk apatite, composition calculations are based on  $\text{PO}_4^{-3} + \text{CO}_3^{-2} = 6.0$  atoms/unit cell (McConnell, 1970). Using this procedure, the following data (atoms/unit cell) are computed (see also Table A3.2):

Table 3.4. Atoms/unit cell for apatite samples based on  $\text{P+C} = 6.0$ .

Sample	$\text{Ca}^{+2} /$	$\text{F}^- /$	$\text{PO}_4^{-3} /$	$\text{CO}_3^{-2} /$
PD-15-17	9.384	(2.440)	4.554	1.446
COW	9.346	1.658	5.148	.852
4-28	9.982	1.541	5.527	.473
SC-2	9.532	2.036	4.838	1.162
PD-18-30	9.489	1.860	4.738	1.262
T7-61	9.854	1.426	5.640	.360
AUS-1	9.897	1.963	5.651	.349
AUS-2	10.222	1.822	5.672	.328

Only in a very rough sense are the solubilities correlated with the bulk average composition. This is to be expected from general solubility considerations. The pH-dependence, though, is not apparently correlated with the bulk composition. Arbitrary assignment of  $\text{Ca}^{+2}$  to some other non-apatitic phase would be necessary to construct a bulk composition which would dissolve according to the measured pH-dependence.

One is left with the possibility that a surface reaction or complex controls the solubility behavior of apatite in seawater. Surface reactions seem to be a characteristic of apatite in aqueous solution. The exact nature of these reactions, however, has been elusive.

One reaction is apparently the dissolution of a more soluble surface coating formed during crystal preparation or, in our case, pretreatment. This was also observed by Smith et al. (1974). The behavior of 4-28 in the beaker experiments can be compared to its behavior in the column experiments. The sample showed a considerably higher solubility and greater dependence on  $\text{HPO}_4^{-2}$  in the beaker experiments. It is possibly this type of reaction which was observed in the experiment with COW on varying surface areas. The initial decrease in solubility in the column experiments may also be related to the dissolution of this coating. Roberson (1966) also remarked on the dissolution of a more soluble surface layer.

The second reaction is the formation of a surface material

containing relatively more  $H^+$  ion than the solid. This coating thus shows an apparent equilibrium with a surface of some proportion of  $HPO_4^{-2}$  to  $PO_4^{-3}$  ions. It may be qualitatively similar to the first layer, but acts as if it is more closely bound to the surface. The apparent relative proportions of  $HPO_4^{-2}$  and  $PO_4^{-3}$  show only slight correlation with the average composition. One would predict this behavior on the basis of a calcium-deficient apatite structure as described above. The magnitude of the  $HPO_4^{-2}$  dependence, however, cannot be predicted from the bulk composition. Using COW, for example, there is no apparent way to formulate (from the average composition) an apatite having a 9:1 ratio of  $HPO_4^{-2}$  to  $PO_4^{-3}$  ions. This is another indication that the surface of apatite has a different composition from the bulk apatite. This surface shows a fair degree of reversibility with respect to dissolved phosphate.

One should also consider that the pH-dependence and absolute level of solubility measured here does not represent true equilibrium. The final measured solubility could represent the balance between the reaction rates of the solubility of the bulk phase and the solubility reaction of the surface layer. An apparent equilibrium (steady-state) could be obtained which is intermediate between the true equilibrium for each reaction. Wollast (1974) discusses this concept in reference to the solubility of dissolved silica versus silica uptake by clay minerals. He shows that the rate of change of dissolved silica can

vary over a wide range of silica concentrations and, for many cases, can appear to be at equilibrium when, in fact, the relative kinetics of the two different processes are controlling the final state.

If this kind of process is translated to the solubility behavior of apatite, one would predict much of the same behavior which was observed. A hypothetical reaction diagram based on Wollast's (1974) is presented in Figure 3.11. Thus, if the precipitation reaction of apatite dominates, one finds a low solubility. If the surface layer controls the solubility a higher, but not necessarily equilibrium, solubility would be measured. As seen, this can roughly explain the observed behavior.

The kinetics of these reactions will be dependent on many factors. The pH, the surface area, the degree of crystallinity, the composition, and possibly other factors will all contribute to the rates of these two reactions - the surface layer reaction and the "true" solubility reaction.

Finally, an alternative way to explain the experimental results is to interpret the behavior totally in terms of ion-exchange rather than solubility processes. Because of the overwhelming amount of  $\text{Ca}^{+2}$  in seawater, there is no evidence here that the apatite is actually dissolving or precipitating. Or, the amount of actual dissolution may be so small as to be masked by other processes, such as ion-exchange, on an active apatite surface.

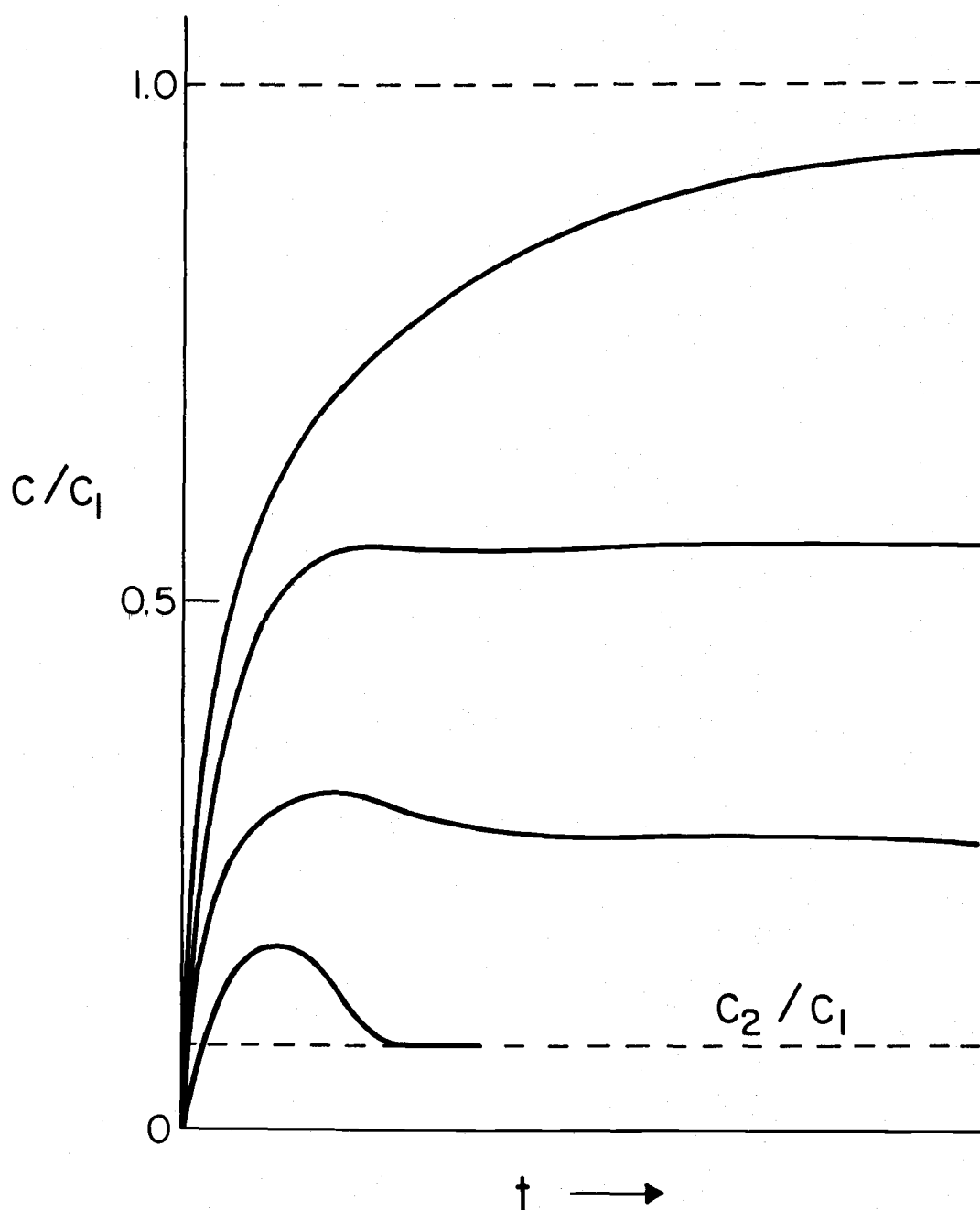


Figure 3.11. Possible "steady-state" interpretation of experimental results (after Wollast, 1974). Final steady concentration results from relative kinetics of reaction between more soluble surface layer (solubility =  $C_1$ ) and less soluble bulk material (solubility =  $C_2$ ).  $t$  = time.



The interaction and participation of  $F^-$  ion in the altered-surface apatite phase is undetermined and cannot be estimated from the data. There is a considerable amount of uptake and release of  $F^-$  by the apatite, but this can be easily accounted for by the normal apatite structure. In addition to the expected exchange at the normal hydroxyl position in the apatite structure, there is also the possibility that the reaction  $F^- + HPO_4^{-2} \rightleftharpoons FPO_3^{-2} + OH^-$  occurs on the apatite surface (Simpson, 1969). Ingram (1968) demonstrates the ability of apatite to incorporate  $FPO_3^{-2}$  ion. A difference in reaction rates of  $F^-$  and  $PO_4^{-3}$  has been found, which indicates the involvement of the ions in different reactions on the apatite. The extent of  $F^-$  reaction is a function of pretreatment of the apatite, and  $F^-$  uptake is enhanced at lower pH's. Assuming that the final  $F^-$  concentrations in the column experiments represent equilibrium values, we should be able to compute a constant for the exchange reaction. No such constant is found. Furthermore, the equations derived do not correlate with the average  $F^-$  on the samples. This could be due to micro-variation in F content of the apatite samples (see Appendix 3, Figure A3.1).

An estimate of stoichiometric apatite solubility can be made from a manipulation of equations in Table 3.2. If the constant A is related to B, the pH dependency, A can be extrapolated to  $B = 0$ . This was done for  $PO_4^{-3}$  and  $F^-$ , and the results are  $pPO_4 = 8.135$  and  $pF = 4.208$ . From the salinity,  $p(Ca^{+2})$  is found as 1.999. Thus,

a stoichiometric solubility product may be computed for  $5\text{pCa} + 3\text{pPO}_4 + \text{pF} = 9.995 + 24.405 + 4.208 = \text{pK}'_{\text{SP}} = 38.608$ . At 33.3‰,  $10^\circ\text{C}$ , and  $\text{pH} = 8$  this corresponds to approximately  $0.13 \mu\text{M TPO}_4$ . The same type of correlation for the change in solubility between  $10^\circ$  and  $25^\circ$  versus pH dependence can also be made. The correlation, however, is much poorer. At  $B = 0$ ,  $\Delta\text{pPO}_4$  is .322 (see Table A4.6). Using this value yields a stoichiometric  $\text{pK}'_{\text{SP}}$  (assuming the same pF) as above of 37.64 at  $25^\circ$ . A  $\text{pK}'_{\text{SP}}$  of this magnitude corresponds to an equilibrium value of  $\sim .075 \mu\text{M TPO}_4$  at  $\text{pH} = 8.0$ . This value can be compared to that obtained by Roberson (1966). An equivalent calculation of his results shows  $\text{pK}'_{\text{SP}} = 36.08 \pm 2.03$ . My value lies within his range, but, on the average, shows a considerably lower solubility, roughly 3 x in  $\text{TPO}_4$  at a given pH and salinity.

The exchange of alkalinity on the apatite surface was also observed. For some samples there was considerable exchange resulting in removal or addition of alkalinity amounting to 1-2 meq/l. This exchange on the apatite surface was found to be pH-dependent, and may be an important reaction in the buffering of pore waters of phosphatic sediments (Culberson et al., 1975). A change in pH is opposed by the uptake or release of  $\text{H}^+$  ions. The reaction likely occurs on the surface phosphate groups (Stumm and Morgan, 1970), but at least some of the changes in alkalinity will arise from reactions of the admixed impurities. The extent to which the changes in

alkalinity are affecting the crystal lattice, e.g. see Equation 3-3 for Ca-deficient apatites, cannot be estimated from the data. For those samples I measured, the change in alkalinity did not bring about any observable  $\text{Ca}^{+2}$  change. Thus, ions other than  $\text{Ca}^{+2}$  are involved in the exchange reaction.  $\text{Na}^{+}$  is a likely possibility (Neuman and Neuman, 1953; Bell, Posner, and Quirk, 1973).

Application of the present results to seawater conditions may best be made using those three samples which were formed and remained in seawater (until removed for examination and experimentation). Two (18-30 and 15-17) are relatively recent-formed apatites, and one (SC-2) was a coated relict-nodule found in a region where apatites are presently not forming. Compositionally, they are quite similar, and they show very similar solubility behavior. It should be noted that they contain the highest  $\text{CO}_3^{-2}$  content compared to those samples which were of marine origin but subsequently uplifted and exposed to weathering on land. A summary of their properties is shown below. Using an average of their measured solubilities and an estimate of the temperature dependence (between 30-50% in  $\text{TPO}_4$ ) the following equation was calculated:

$$\text{TPO}_4 \text{ } (\mu\text{M}) = (305.831 - 74.654 \text{ pH} + 4.583 \text{ pH}^2)(1 - (T-10)X) \quad 3-17$$

$$X = .0333 - .020$$

Table 3.5. Summary of properties of marine apatites used in this study.

<u>Sample</u>	<u>Solid molar ratios</u>			<u>Approximate solubility (<math>\text{TPO}_4</math>) <math>\mu\text{M}</math> at pH</u>		
	<u>P/Ca</u>	<u>(P+C)/Ca</u>	<u>C/Ca</u>	<u>8.2</u>	<u>7.4</u>	<u>7</u>
SC-2	.5076	.6295	.1219	1.1	3.2	7.0
15-17	.4853	.6394	.1541	2.1	5.3	9.4
18-30	.4993	.6323	.1329	2.2	4.5	7.0
range of all samples	.4853- .5710	.5870- .6394	.0321- .1541	.09- 9.2	.4- 11	.8- 12.2

This equation was applied to several stations in the North Pacific (Wyatt et al, 1971) and the percent saturation ( $\text{TPO}_4(\text{meas})/\text{TPO}_4(\text{calculated})$ ) was computed. The results (Figure 3.12) do not take into account pressure effects but do show that seawater is near or undersaturated with respect to oceanic apatites.

If one uses the solubility of apatite which behaved most ideally (AUS-2), one finds that the % saturation of seawater runs from 5 to 10 times supersaturated.

### Conclusions

A wide range of solubility behavior was observed for natural carbonate fluorapatites in seawater. This behavior included exchange reactions of  $\text{OH}^-$  and  $\text{F}^-$  ions, and  $\text{H}^+$  (or  $\text{OH}^-$ ) ion exchange on the

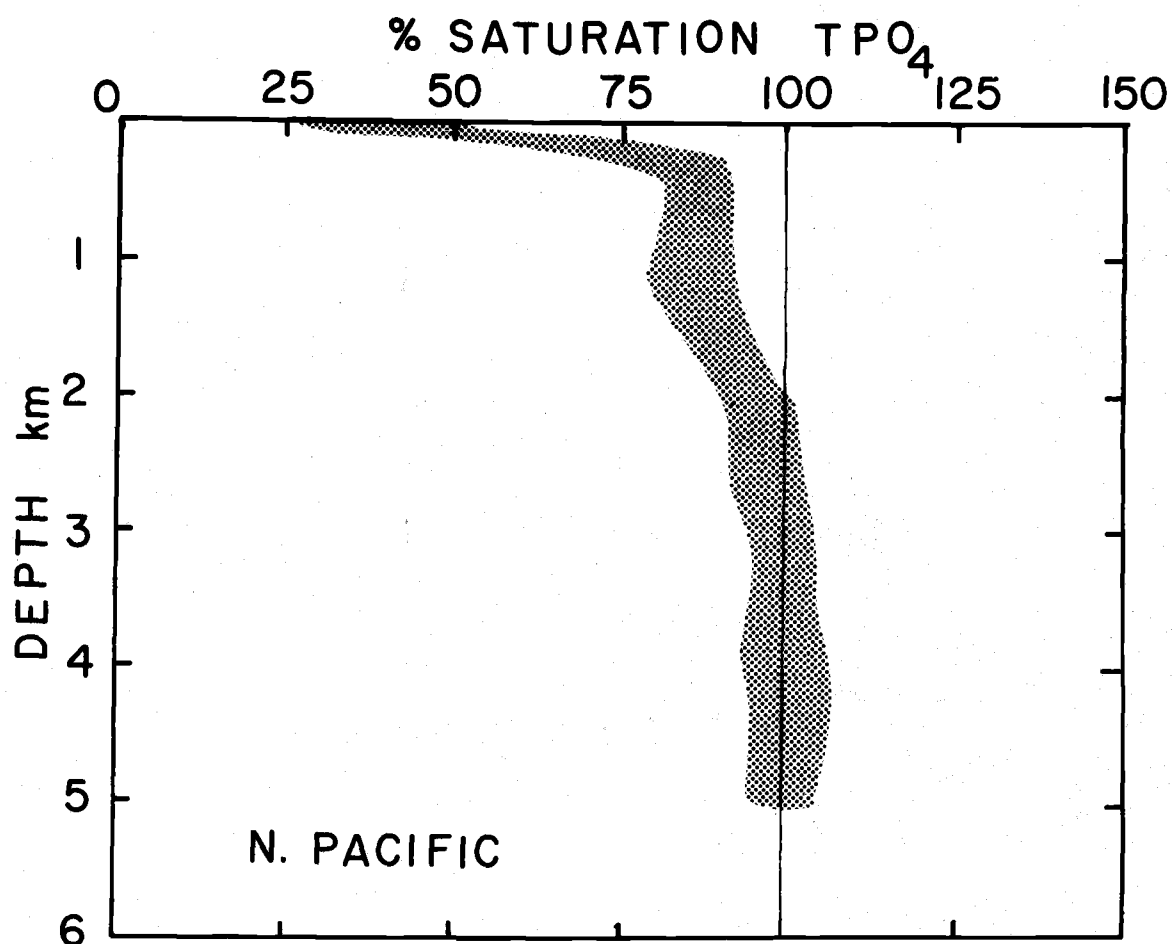


Figure 3.12. Calculation of apatite saturation (as  $\text{TPO}_4(\text{meas})/\text{TPO}_4(\text{calc.})$ ) versus depth for several stations in the North Pacific.

apatite surface with seawater ions. It is postulated that one, or possibly two, surface layers are involved when apatite reacts with seawater. The first is a disorganized, highly soluble layer. The second type of layer, possibly a reorganization of the first, is more closely bound to the bulk apatite. The exact nature of this layer could not be determined from the experimental data. The composition of the bulk phase is apparently one factor in determining the composition of the surface layer. One characteristic of the surface layer is its apparent  $\text{HPO}_4^{-2}$  content. The relative kinetics of apatite versus surface reactions may also be important in determining the steady-state values of phosphate in seawater equilibrated with apatite.

Further studies on the properties of the apatite surface in seawater and on the kinetics of apatite reactions in seawater would obviously be very useful in predicting the behavior of phosphate in seawater.

## CHAPTER IV

FACTORS AFFECTING THE FORMATION OF  
MARINE PHOSPHORITESIntroduction

The unique circumstances which combine to bring about the formation of sedimentary apatite in the oceans have long interested oceanographers and geologists. Since the early 1800's scientists have been describing and hypothesizing about various phosphatic deposits and formations around the world. Gulbrandsen (1969) gives a concise historical review of the significant geological work done during the 1800's and early 1900's, and references later papers (up to 1969) which discuss apatite formation. This chapter will concentrate on the work done after the 1930's and especially on recent findings pertaining to apatite formation. This will include some of my recent experimental work. In addition to the review by Gulbrandsen, Bushinskii (1966), Tooms, Summerhayes and Cronan (1969), and Burnett (1974) have also discussed factors influencing phosphorite formation. The terms apatite and phosphorite will be used interchangeably. Both of these terms will refer to francolite, the primary phosphate mineral of phosphorites. Francolite is a carbonate fluor-apatite, having a general composition of  $(\text{Ca}, \text{Na})_5(\text{PO}_4, \text{CO}_3)(\text{F}, \text{OH})$ . In this chapter, it will be demonstrated that kinetic factors, in

addition to equilibrium considerations, are required for any comprehensive explanation of phosphorite formation. The emphasis here will be on the chemistry of phosphorite formation, as others have presented comprehensive discussions of the geology of phosphorites.

Phosphorites are found only in limited areas of the present ocean (Figure 4.1). The primary locus of apatite deposits is the coastal zone in the low to mid-latitudes. Those are areas of high biological activity associated with upwelling. The phosphorite facies studied on land deposits also indicated that deposition took place in a near-shore, shallow environment. Kazakov (1938) was the first to combine relevant information on geology, oceanography, and the physical chemistry of apatites into an overall theory of phosphorite deposition in the oceans. His hypothesis has been the basis for much of the present understanding of apatite formation and has been widely accepted with only minor modifications since it was presented. Kazakov recognized the shallow, coastal nature of the deposits; he knew of the higher dissolved phosphate content of deep ocean water; he also knew that high pH and high temperature favored apatite precipitation. He concluded that phosphorites were precipitated from seawater when cold, phosphate-rich seawater was upwelled along the edge of a basin. As the water upwelled, the temperature rose and the pH rose (due to loss of  $\text{CO}_2$ ). This combination of relatively high temperature, high pH, and high phosphate induced the precipitation of apatite. The area of



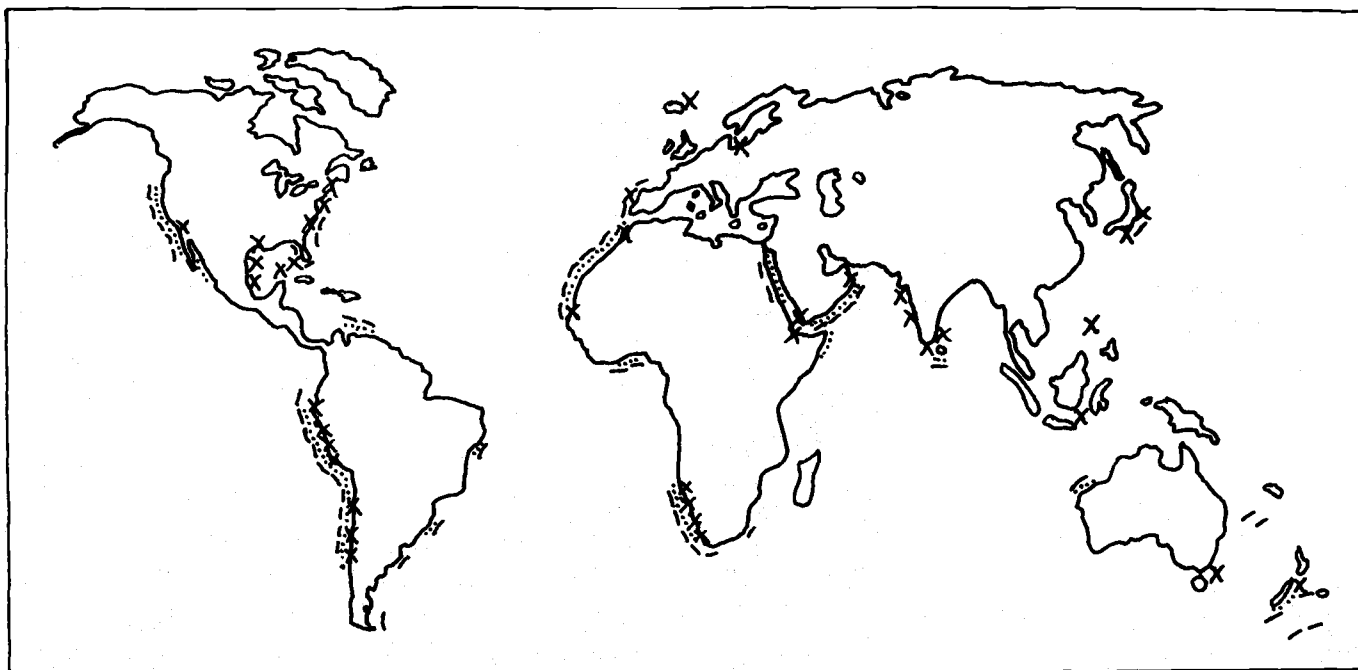


Figure 4.1. Distribution of phosphorite in relation to upwelling water and related phenomena. (Taken from Tooms, Summerhayes and Cronan, 1969). ..... upwelling water; ----- phosphorite deposits; xxxxxxxx phenomena caused by high biological productivity such as plankton concentrations (red water), mass mortalities of fish and other creatures, occurrences of diatom ooze.

phosphate deposition moved as the sea level fluctuated over time. It was a very elegant work which combined and explained many of the observed features of sedimentary apatite deposits. It will be shown, though, that Kazakov's main conclusion--that apatite is precipitated from open seawater--is incorrect.

First, I wish to emphasize that a single theory will not explain the several modes of occurrence of apatite. Rather, there will be several broad features in common for the formation of all apatite deposits, while details and mechanisms of apatite formation will vary from place to place. Gulbrandsen (1969) summarizes the various types of apatites and their geologic associations. These are reproduced in Table 4.1.

Basically, submarine apatite can be grouped into two main categories--biogenic apatite (hard parts of organisms) and inorganic apatite. Biogenic apatite occurs in sediments world wide, and rarely accounts for more than a percent or so of the bulk sediment. Even in small amounts, though, biogenic apatite can cause significant compositional variations in marine sediments (Dymond et al., 1973). Its origin, however, is clear, and it is the formation of inorganic apatite which has been the topic of much controversy.

The inorganic apatite may be subdivided into phosphate replacement of existing structures, relict phosphorites (phosphorites either not forming in the present ocean or reaching the ocean floor as

Table 4.1. Apatite occurrences and associations.

A. Forms in which apatite is commonly noted.	B. Geologic features, associations and factors.
1) Fish teeth, bones, scales 2) Reptile and mammal bones 3) Shells, e.g. <u>Lingula</u> 4) Carapaces of arthropods 5) Microcrystalline aggregates as nodules, pellets, oolites, shell casts, and spicular canal fillings. 6) Coprolites 7) Microcrystalline aggregates as laminae, lenses, beds, and cement 8) Macrocrystalline subhedra and euhedra (probably diagenetic) 9) Replacement of carbonate shells and bryozoa 10) Replacement of carbonate minerals 11) Replacement of wood	1) Organic matter and carbonaceous mudstone--high organic productivity--red tides--mass mortalities 2) Chert-porcellanite, and diatomite 3) Carbonate rock 4) Glauconite 5) Conglomerate-reworking--unconformity 6) Condensed section 7) Upwelling 8) Warm, arid climates--evaporites 9) Volcanism-bentonites and tuffs 10) Platform-miogeosyncline

weathering products of preexisting phosphate deposits) and recent phosphorites (those apatites apparently forming in the present ocean). Though relict apatites may be the source of much or most of the phosphate content of some sediments, for example off Northwest Africa (Summerhayes, Nutter, and Tooms, 1972). This work will concentrate on those deposits which are presently accumulating in the modern ocean. There has been considerable debate over the question of recent formation of phosphorites (Kolodny, 1969), but recent

radiometric and morphological evidence has clearly indicated that in some areas, e.g. off the coast of Chile and Peru (Burnett, 1974) and off the southwest coast of africa (Baturin, Kochenov, and Petelin, 1970; Baturin, Merkulova, and Chalov, 1972), phosphorites are currently accumulating.

### Equilibrium Considerations

For apatite to precipitate from solution, its solubility product must be exceeded, that is,

$$[\text{Ca}]_m^5 [\text{PO}_4^{-3}]_m^3 [\text{F}^-]_m > K'_{\text{SP}} \quad 4-1$$

where  $K'_{\text{SP}}$  = apparent solubility product =  $[\text{Ca}]^5 [\text{PO}_4^{-3}] [\text{F}]$  at saturation, at a given T and P;  $[\ ]_m$  = in situ concentration of element in brackets. Once the apparent dissociation constants of phosphoric acid are known, the  $[\text{PO}_4^{-3}]$  concentration can be calculated from

$$\text{PO}_4^{-3} = \text{TPO}_4 / (1 + \frac{X^3}{K'_1 K'_2 K'_3} + \frac{X^2}{K'_2 K'_3} + \frac{X}{K'_3}) \quad 4-2$$

where:

$$\text{TPO}_4 = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{-2}] + [\text{PO}_4^{-3}]$$

$$X = \text{operational hydrogen ion-activity} = 10^{-\text{pH}}$$

$K'_i$  = ith apparent dissociation constant of  $H_3PO_4$ .

Equation 4-2 shows that the quantity  $[PO_4^{-3}]$  is increased by either an increase in the total phosphate,  $TPO_4$ , or by an increase in pH (decrease in X). Given equations 4-1 and 4-2 several conditions which will increase the ion-product of apatite beyond its solubility product can be listed. These are:

1. increase total dissolved phosphate,
2. increase pH,
3. increase  $Ca^{+2}$ , and
4. increase  $F^-$ .

The  $K'_{SP}$  as described above is valid only for seawater of normal composition since it is measured in normal seawater. Interstitial waters can have its relative major-ion composition significantly altered from that of seawater. Deviations from normal composition will set different conditions for apatite precipitation. This can be illustrated using an ion-pairing model (Garrels and Thompson, 1962; Pytkowicz and Hawley, 1974). Ben-Yaakov and Goldhaber (1973) discuss how deviations from normal composition affect the carbonate system.

The total concentration of an ion in solution may be expressed as the sum of its free plus ion-paired concentrations. The relevant sums in this case(not including carbonate) are:

$$[Ca^{+2}]_T = (Ca^{+2})_F + (CaSO_4^0) + (CaHPO_4^0) + (CaPO_4^-) \quad 4-3$$

$$[PO_4^{-3}]_T = (PO_4^{3-})_F + (CaPO_4^-) + (MgPO_4^-) + (NaPO_4^{-2}) \quad 4-4$$

$$[F^-]_T = (F)_F + (CaF^+) + (MgF^+) \quad 4-5$$

Rewriting these expressions in terms of free-ion concentrations and association constants,  $K^*$ , one finds:

$$[Ca^{+2}]_T = (Ca^{+2})_F \left\{ 1 + (SO_4^{-2})_F K^*_{CaSO_4} + (HPO_4^{-2})_F K^*_{CaHPO_4} + (PO_4^{-3})_F K^*_{CaPO_4} \right\} \quad 4-3a$$

$$[PO_4^{-2}]_T = (PO_4^{-3})_F \left\{ 1 + (Ca^{+2})_F K^*_{CaPO_4} + (Mg^{+2})_F K^*_{MgPO_4} + (Na^+)_F K^*_{NaPO_4} \right\} \quad 4-4a$$

$$[F^-]_T = (F^-)_F \left\{ 1 + (Ca^{+2})_F K^*_{CaF} + (Mg^{+2})_F K^*_{MgF} \right\} \quad 4-5a$$

$K'_{SP}$  may then be rewritten in terms of free concentrations and association constants as

$$K'_{SP} = (Ca^{+2})_F^5 (PO_4^{-3})_F^3 (F)_F (1 + \sum A_i K^*_{CaA})^5 (1 + \sum M_i K^*_{MPO_4})^3 (1 + \sum M_i K^*_{Mg}) \quad 4-6$$

From these equations, one can see that  $(\text{Mg}^{+2})$  and  $(\text{SO}_4^{-2})$  concentrations will affect the free concentrations of  $\text{Ca}^{+2}$ ,  $\text{PO}_4^{-3}$  and  $\text{F}^-$ . This means that the concentration of  $\text{Mg}^{+2}$  and, to a lesser extent,  $\text{SO}_4^{-2}$  can affect the equilibrium conditions under which apatite will precipitate. Examination of equations 4-2 and 4-4a shows that the  $[\text{PO}_4^{-3}]$  concentration is a function of  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ , and the apparent constants of phosphoric acid. The apparent constants, in turn, are also dependent upon  $\text{Mg}^{+2}$  and  $\text{Ca}^{+2}$ . One can calculate this dependence using the association constants measured in Chapter II of this work (Figure 4.2). The changes in the apparent dissociation constants can be used along with the simplifying assumption that  $(\text{Ca})_{\text{F}}/(\text{Ca})_{\text{T}}$  is constant to show how the  $\text{TPO}_4$  in equilibrium with apatite at constant  $\text{F}^-$  (total) varies with changes in  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  concentrations (Table 4.2).

Table 4.2.  $\text{TPO}_4$  ( $\times 10^7$ ) M/l in equilibrium with apatite for varying levels of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ .  $\text{pK}'_{\text{SP}}(25^\circ) = 37.64$ .  $\text{F}^-_{\text{T}} = 80 \mu\text{M}$ ,  $\text{pH} = 8.0^*$ .

$\text{Ca}_{\text{F}} \backslash \text{Mg}_{\text{F}}$	0	.01	.02	.03	.04	.05
.001	37.3	40.5	43.6	46.7	49.6	52.4
.002	12.1	13.0	14.0	15.0	15.9	16.7
.005	2.8	3.0	3.2	3.4	3.6	3.8
.010	.98	1.04	1.10	1.16	1.22	1.27
.015	.55	.57	.60	.63	.66	.69

\* Association constants from Elgquist (1970), Kester and Pytkowicz (1969) and Chapter II of this work.

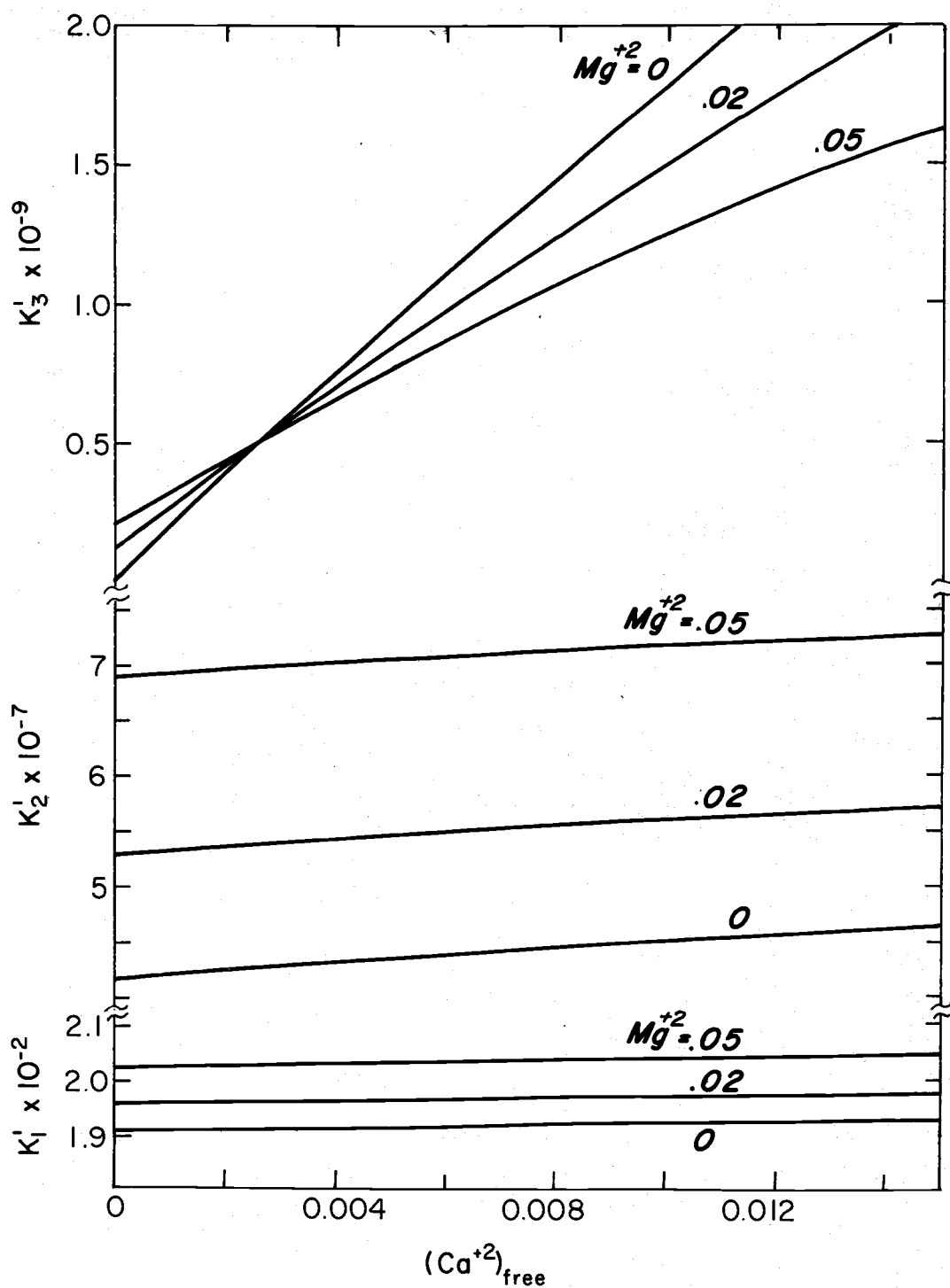


Figure 4.2. Variation in the dissociation constants of  $\text{H}_3\text{PO}_4$  in solutions of varying  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  at  $\mu = 0.68$  and  $T = 20^\circ\text{C}$ . Ionic strength is held constant in these calculations by addition or removal of  $\text{Na}^+$  ion.



Table 4.2 shows that the net effect of reducing the  $(\text{Mg}^{+2})_F$  in solution is to decrease the solubility of apatite in terms of  $\text{TPO}_4$ . This net effect due to lower  $\text{Mg}^{+2}$  ion represents a balance between the reduction in  $(\text{TPO}_4)_{eq}$  due to decreased ion-pairing (Eq. 4-4) and an increase in  $(\text{TPO}_4)_{eq}$  due to the smaller dissociation constants of  $\text{H}_3\text{PO}_4$  in media with lower  $\text{Mg}^{+2}$ . The increase in  $(\text{TPO}_4)_{eq}$  would come from a change in  $(\text{PO}_4^{-3})_T$  (Eq. 4-2); a reduction in  $(\text{TPO}_4)_{eq}$  arises from a change in  $(\text{PO}_4^{-3})_F$  (Eq. 4-4a). Of course, these two effects cannot be separated or operate independently of each other.

I present these two effects to contrast to the case where an acid dissociation is unaffected, for example the  $\text{F}^-$  species. The change in solubility is a direct function of the amount of  $\text{F}^-$  which is ion-paired (Eq. 4-5a). Because  $\text{Ca}^{+2}$  ion enters into the computation of the solubility product as  $(\text{Ca}^{+2})^5$ , changes in its concentration cause the most significant changes in the equilibrium  $\text{TPO}_4$ . In addition to its effect on  $\text{TPO}_4$  as a constituent ion of apatite (mass-action principle),  $\text{Ca}^{+2}$  ion also acts to change  $(\text{TPO}_4)_{eq}$  by the same mechanisms as described for  $\text{Mg}^{+2}$ . Changes in the major ion composition of seawater can alter the  $\text{TPO}_4$  in equilibrium with apatite in three ways:

- a) the direct effect of ion-pairing on the free-ion concentration of a constituent ion (Eq. 4-5a);
- b) the direct effect plus the indirect effect of ion-pairing on the dissociation of  $\text{H}_3\text{PO}_4$  (Eq. 4-4a); and
- c) the direct effect of  $\text{Ca}^{+2}$  ion on the solubility according to the solubility

product (Eq. 4-1).

The above conclusions allow additional equilibrium considerations to be added to the list of factors which will promote apatite precipitation.

5. Factors which reduce the  $(\text{Mg}^{+2})_F$  ion concentration and do not reduce the  $(\text{Ca}^{+2})_F$  ion concentration significantly.
6. Indirect (ion-pairing) reactions which will increase the  $(\text{Ca}^{+2})_F$  or  $(\text{PO}_4^{-3})_F$  concentrations.

Temperature is another important equilibrium factor which must be considered. The experiments described in Chapter III showed that a temperature increase of  $15^\circ\text{C}$  ( $10$ - $25^\circ\text{C}$ ) could decrease the solubility of apatite by up to 50%. Assuming that the solubility is a linear function of temperature, then approximately a  $1.5^\circ\text{C}$  temperature increase would decrease the solubility of apatite as much as a decrease of .01 M/l of  $\text{Mg}^{+2}$ .

The effect of pressure on apatite solubility has not yet been measured. Pressure effects would play only a very minor role in phosphate deposition, since phosphorites are formed in shallow waters. If apatite behaves as other minerals, then an increase in pressure will increase the solubility of apatite. It is possible that pressure effects are dominant in determining the saturation state of deep ocean waters with respect to apatite.

The relative importance of the factors mentioned above can be

compared by estimating the change in that factor required to change the  $\text{TPO}_4$  in equilibrium with apatite by a given percentage (Table 4.3). Figure 4.3 illustrates the changes in ideal apatite solubility which can be caused by compositional changes and changes in pH and temperature. A factor of 5 increase in  $\text{F}^-$  decreases the equilibrium solubility by approximately 40%; a factor of 5 decrease in  $\text{Mg}^{+2}$  decreases the solubility by 20-25%. The solubility is most sensitive to  $\text{Ca}^{+2}$ .

Table 4.3. Approximate changes in various factors required to decrease  $\text{TPO}_4$  in equilibrium with apatite by 10%.

Factor	Approximate Change Required to Decrease Equilibrium $\text{TPO}_4$ by 10%	% Change from Normal Seawater Composition
1) $\text{Ca}^{+2}$	+ .0008 M/l	+ 8%
2) $\text{F}^-$	+ 25 $\mu\text{M/l}$	+ 35%
3) pH	+ .04 pH units	9%
4) $\text{Mg}^{+2}$	- .02 M/l	- 35%
5) Temperature	+ 3°C	50% **
6) Pressure	Unknown	---
7) $\text{SO}_4^{-2}$	- .02 M/l *	- 80%

\* Calculated from ion-pairing model of Pytkowicz and Hawley (1974).

\*\* Estimated from maximum temperature change between glacial and interglacial periods (J. Thiede, pers. comm.).

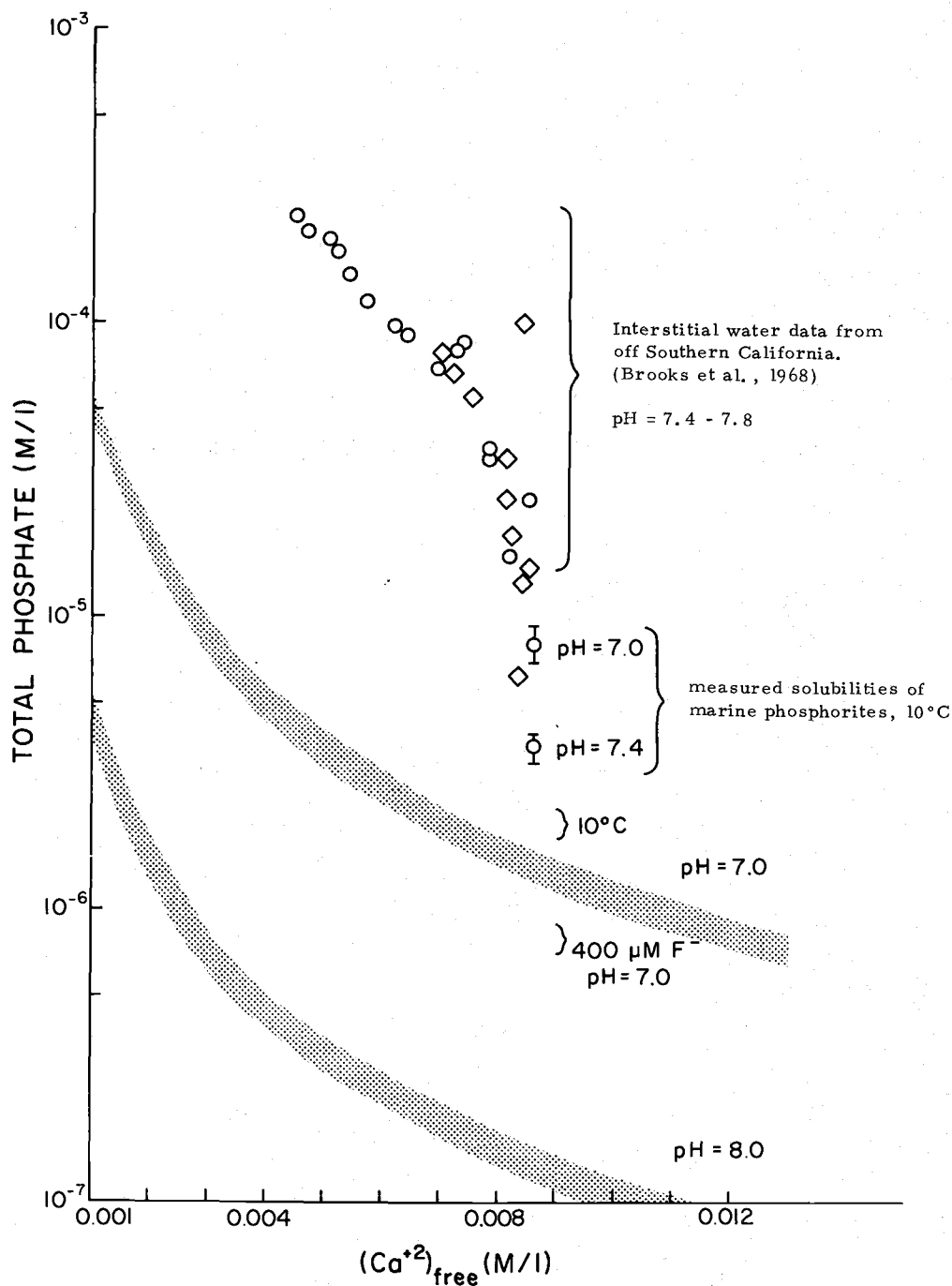
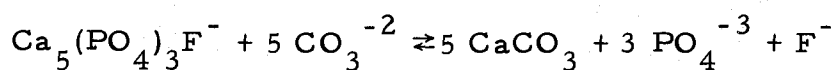


Figure 4.3. Solution composition effects on  $\text{TPO}_4$  in equilibrium with apatite at  $\text{pH} = 8.0$  and  $7.0$ . Stippled areas for "ideal" apatite solubility at  $25^\circ\text{C}$ ,  $80 \mu\text{M/l F}^-$ . Upper boundary of curve =  $.05 \text{ M Mg}^{+2}$ ; lower boundary =  $0.0 \text{ M Mg}^{+2}$ . Parentheses indicate shift in solubility with temperature and  $\text{F}^-$  changes. Measured solubility at  $10^\circ\text{C}$  (see Chapter III) and interstitial water data are also presented. Interstitial waters are supersaturated with respect to apatite.

The calculations above assume that the solution is in equilibrium with an ideal apatite whose solubility can be represented by the ion-product  $[Ca]^5[PO_4^{-3}]^3[F]$ . Changes in the composition of the bulk apatite due to substitution reactions will alter the computed saturation state by a factor approximately equal to the change in the activity of the solid. No quantitative information is available as yet to determine the effect of heteroionic substitution on the activity of apatite.

The experimental evidence presented in the previous chapter suggested that a surface reaction controlled, or moderated, the solubility of apatite, at least over short time periods. The surface reaction was characterized by a constant product  $[HPO_4]^X[PO_4]^Y$  rather than by  $[PO_4^{-3}]^3$ , and by a variable rather than constant  $F^-$  content. No information was obtained on the  $Ca^{+2}$  content of the surface. Thus, the effect on the solubility due to changes in solution composition cannot be quantitatively estimated.

Gulbrandsen (1969) discusses the equilibria of the apatite-calcite-seawater system and shows, to a first approximation, the factors which will promote precipitation of either apatite or calcite. He notes that the calcite equilibria should control the  $Ca^{+2}$  in solution, making apatite equilibrium dependent on it. Replacement of calcite by apatite has been shown to be a widespread mechanism for producing phosphorite (D'Anglejan, 1968; Ames, 1959; Parker and Siesser, 1972). The ideal equilibrium which needs to be considered is:



which has an equilibrium constant, assuming unit activity for the solids, of:

$$K'_{\text{eq}} = \frac{[\text{PO}_4]^{-3} [\text{F}]}{[\text{CO}_3^{-2}]^5}$$

or, multiplying both numerator and denominator by  $[\text{Ca}^{+2}]^5$ , one gets:

$$K'_{\text{eq}} = \frac{[\text{Ca}^{+2}]^5 [\text{PO}_4^{-3}]^3 [\text{F}]}{[\text{Ca}^{+2}]^5 [\text{CO}_3^{-2}]^5} = \frac{K'_{\text{SP}} (\text{apatite})}{K'_{\text{SP}}^5 (\text{calcite})}$$

Using the apatite solubility at 25°C estimated in the previous chapter, and the calcite solubility measured by Ingle et al. (1973), it is calculated that  $K'_{\text{eq}} = (10^{-37.64}) / (4.6 \times 10^{-7})^5 = 1.113 \times 10^{-6}$ . A rough calculation for seawater shows that  $[\text{PO}_4^{-3}]^3 [\text{F}] / [\text{CO}_3^{-2}]^5$  for typical seawater values is near  $0.8 \times 10^{-6}$  indicating that seawater is very close to equilibrium with respect to the calcite-apatite transformation.

### Kinetic Considerations

In this section the various kinetic factors which pertain to the formation of apatites in the oceans will be discussed. Pytkowicz (1975) suggested that calcium phosphate precipitation in the oceans

may behave in a similar manner to calcium carbonate. That is, the time of (homogeneous) nucleation of calcium carbonate in surface waters at that present state of supersaturation is very much longer than the replacement time of these waters. Experiments were performed to measure the time of onset of calcium phosphate precipitation. Samples were adjusted to a specified total phosphate concentration, and the pH was adjusted with a small quantity of sodium borate solution. The two series of sealed vials, one at  $\text{pH} \approx 8.2$  and the other at  $\text{pH} \approx 7.6$ , were observed, and the time of appearance of a visible precipitate was recorded. The results are shown in Figure 4.4. If the data can be extrapolated to low concentrations, they indicate that precipitation at  $30 \mu\text{M/l}$  of phosphate would take on the order of  $2 \times 10^6$  years at  $\text{pH} = 8.2$  and  $\sim 2 \times 10^9$  years at  $\text{pH} = 7.6$ . Therefore, inorganic homogeneous precipitation of a calcium phosphate from normal seawater is not a viable alternative for phosphorite formation.

Larger volumes of seawater treated in a similar manner to the samples just described in order to obtain a larger amount of precipitate. One sample was precipitated from a carbonate-free seawater, and two other seawater samples were spiked to obtain 5 and 10 mM/l of fluoride. The precipitate which was obtained was kept in contact with the supernatant solution for 3-5 days. In all cases, the precipitate was found to be amorphous. The high  $\text{F}^-$

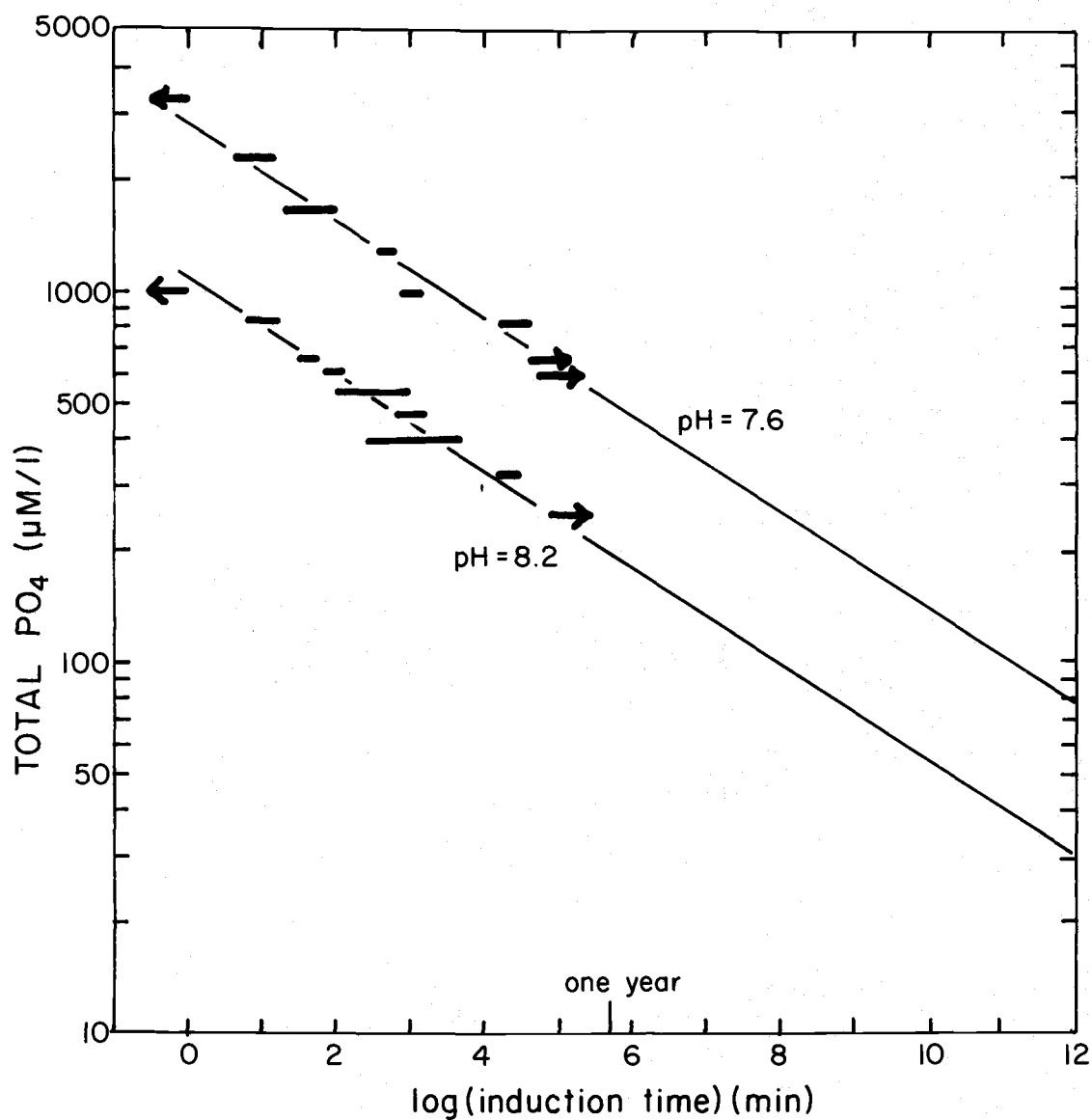


Figure 4.4. Time of homogeneous precipitation of calcium phosphate from seawater at pH 8.2 and 7.6. Temperature  $\approx 22^{\circ}\text{C}$ . Bars indicate uncertainty in recognition of precipitate.



samples were calculated to be about 1.2 and 2.5 times supersaturated with respect to  $\text{CaF}_2$ , but no  $\text{CaF}_2$  could be observed by x-ray diffraction. The samples obtained from normal  $\text{F}^-$  seawater were chemically analyzed. The results are given in Table 4.4. Two samples which were obtained in the time of precipitation experiment were removed from the precipitating solution after nine months at room temperature. The initial  $\text{TPO}_4$  in each was 3.3 and 1.0 mM; the initial pH was 7.6 and 8.2, respectively. After nine months, the both had a pH of approximately  $7.3 \pm 0.05$ . These were examined under a transmission electron microscope. The low phosphate sample was amorphous, while sample exposed to the higher phosphate solution showed signs of some degree of crystallinity. The diffraction pattern obtained was quite irregular, though, when compared to a well-crystallized apatite.

Nucleation experiments were also conducted using calcite and quartz as seeding material. 100 to 800 mg of -400 mesh calcite or

Table 4.4. Chemical analysis of amorphous precipitates obtained from seawater.

<u>pH of Precipitation</u>	<u>Ca : P : F (molar ratio)</u>
8.2	2.06 : 1 : .05
8.0-8.2	2.02 : 1 : .06
8.2 (no alkalinity)	1.92 : 1 : .06
7.6	1.97 : 1 : .08

quartz were added to 100 mls of seawater containing from 10-500  $\mu\text{M/l}$  of  $\text{PO}_4$ . The pH of the calcite ampoules was approximately 7.6 and about 8.0 for the quartz samples. The samples were kept at room temperature and were checked periodically over a nine-month period. A maximum uptake of  $\text{PO}_4$  of only 3-5  $\mu\text{M/l}$  was measured in the 500  $\mu\text{M}$  sample after nine months. One quartz-seeded sample was also seeded with amorphous calcium phosphate. No apparent crystallization occurred over the nine-month period.

### Discussion

These experiments show that, in addition to a time factor which prevents calcium phosphate precipitation in the ocean, apatite formation is inhibited by the formation of a metastable amorphous precursor. Recrystallization of the amorphous material can apparently occur to some extent in normal seawater at very high levels of dissolved phosphate. The experiments also demonstrate the very slow kinetics of the heteronucleation of calcium phosphate and the calcite-apatite replacement reaction. Martens and Harriss (1970) demonstrated that  $\text{Mg}^{+2}$  ion was an important factor in stabilizing the amorphous phosphate precipitate obtained from seawater. Only scattered data are available to estimate the kinetics of  $\text{Mg}^{+2}$  ion inhibition of apatite formation. Eanes and Posner (1968) found a 4-5 fold increase in the conversion time of amorphous calcium phosphate to apatite when the

solution Mg:Ca ratio was raised from 0 to 1:25.

In addition to  $\text{Mg}^{+2}$ ,  $\text{CO}_3^{-2}$  and  $\text{F}^-$  ions also affect apatite precipitation (Bachra, 1963, 1965a, b). Bachra and his co-workers found that increased  $\text{CO}_3^{-2}$  and  $\text{Mg}^{+2}$ , and very high  $\text{Ca}^{+2}$ , stabilized amorphous Ca-phosphate precipitates. The crystallinity of precipitates was enhanced by increasing  $\text{F}^-$  ion. Newesley (1967) also found that  $\text{F}^-$  improved the crystallinity of apatitic precipitates.

The homogeneous precipitation of apatite from solution occurs in three stages (Figure 4-5): 1) the induction period; 2) the formation of an amorphous Ca-phosphate (or Ca- $\text{CO}_3$ -phosphate); 3) the transformation of amorphous material to crystalline apatite (Eanes and Posner, 1968). The solution composition can affect the kinetics of each of these stages. Insufficient data have been obtained to make quantitative estimates applicable to seawater conditions. Qualitative information on the effects of various ions allow us to predict the probable behavior in seawater. The predictions are shown in Table 4.5.

Heterogeneous nucleation of apatite should occur more readily than homogeneous nucleation (Wollast, 1971; Stumm and Morgan, 1970). This is because of the generally lower energy barrier associated with the formation of a nucleus on a solid substrate compared to the homogeneous formation of a nucleus. Heterogeneous formation of apatite can occur by epitaxial growth of apatite and by

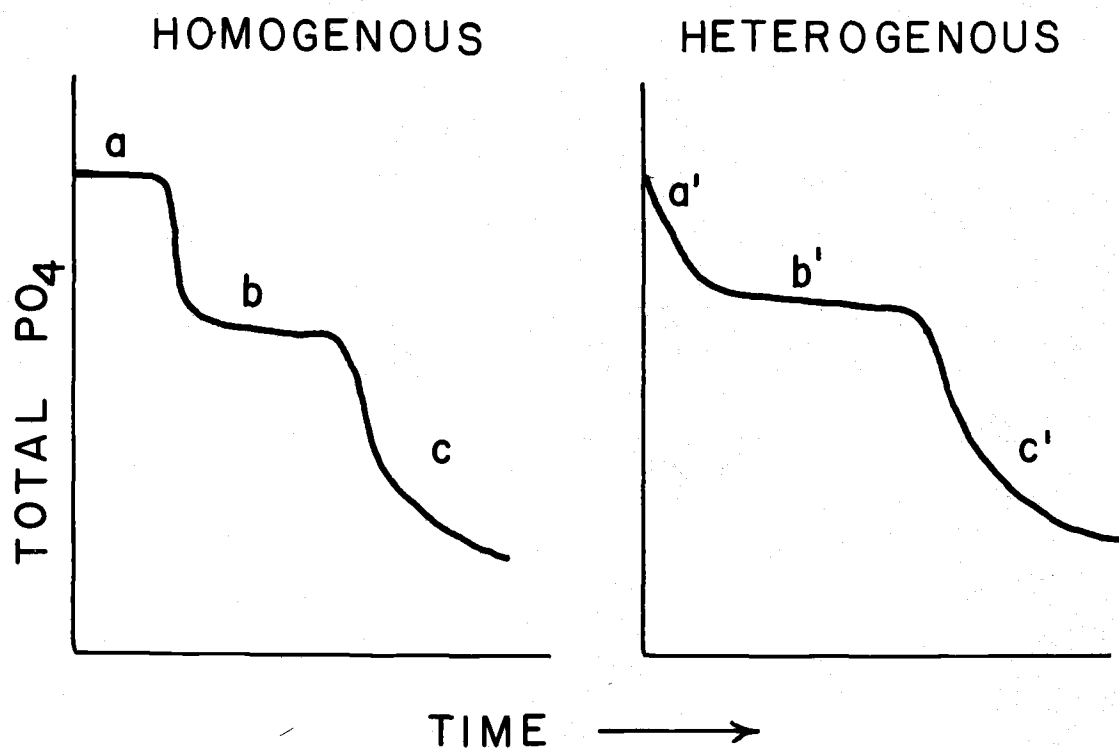


Figure 4.5. Schematic of heterogeneous and homogeneous precipitation of calcium phosphates (see Eanes and Posner, 1968 and Leckie, 1969). For homogeneous formation: a = induction time; b = metastable amorphous calcium phosphate; c = apatite formation. For heterogeneous formation: a' = chemisorption; b' = inhibited crystal growth; c' = normal crystal growth. Solution composition can effect the kinetics at all stages of apatite formation.

Table 4.5. Prediction of effects of chemical factors on apatite formation rates. (+ indicates acceleration or stabilization, - indicates retardation. Those estimates in parentheses are assumed.)

	<u>Induction</u>	<u>Amorphous</u>	<u>Amorphous to Crystalline</u>
Increase pH	+		(+)
Increase $\text{HCO}_3^-$	(-)	+	(-)
Increase $\text{Ca}^{+2}$ (moderate)	(+)		+
(high)	(+)	+	
Increase $\text{Mg}^{+2}$	(-)	+	-
Increase $\text{TPO}_4$	+	-	+
Increase $\text{F}^-$	(+)	-	+

replacement reactions of apatite. Leckie (1969) observed epitaxial growth of apatite on calcite crystals and characterized the heterogeneous reaction by three stages: i) chemisorption, ii) inhibited crystal growth, and iii) normal growth (Figure 4.5). He also reported the inhibitory effect of carbonate and the enhancing effect of fluoride and increased pH on apatite formation. Replacement rates of calcite by apatite has been shown to be affected by the same factors which alter epitaxial growth rates (Ames, 1959; Simpson, 1966a, b, 1968, 1969). Simpson also showed that a 14 mole % Mg-calcite could be replaced by apatite, but that pure dolomite was not

replaced. Simpson further demonstrated that the fluorine content of replaced calcites varied with the  $F^-$  content of the replacing solution. To obtain fluorapatites similar to those found in the ocean, fluoride levels significantly greater than those found in seawater were needed. From this observation he concluded that apatites were metastable with respect to normal ocean water.

Chemical factors which affect the formation kinetics of apatite are, as expected, close to those which alter apatite equilibria. The link between kinetics and equilibria is, however, an uncertain one. It should be kept in mind, too, that the factors affecting apatite formation are closely linked. For example an increase in pH favors apatite formation, but the effect of fluoride is greatest at lower pH's (Leckie, 1969). What then is the optimum combination of  $F^-$  and pH, given oceanic conditions, for apatite formation?

#### Oceanographic conditions relating to phosphorite formation

Most often noted in the literature is the association of areas of oceanic upwelling with phosphorite deposits. Some authors have explained this association using modifications of the Kazakov hypothesis presented earlier. Mansfield (1940) focused on the effect of increased volcanic activity in increasing the  $F^-$  of seawater, thus decreasing apatite solubility. It has been shown, however, that direct precipitation from a supersaturated water column is ruled out

by kinetic factors. There must be other factors associated with upwelling areas which play an important role in phosphate deposition.

Upwelling areas are regions of extremely high primary productivity. This is a direct consequence of the input of high nutrient waters to the photic zone. The continual supply of phosphate is used by organisms in photosynthesis. The oxidation and decay of the organisms occurs to some extent in the water column but a considerable portion of the oxidation occurs after the dead organisms settle to the bottom either directly or in fecal pellets. Bottom regeneration of nutrients has been reported off the Oregon coast (Atlas, 1973; Gordon, 1973) and off the coast of Southwest Africa (Calvert and Price, 1971). It may be typical for other upwelling areas as well, such as in the Peru-Chile region. Such regeneration would serve to further reduce the oxygen content of the waters which bathe the sediments in the upwelling area. Even in the absence of local bottom regeneration, the waters covering the sediments are usually quite low in dissolved oxygen ( $\leq 1-2 \text{ ml O}_2/\text{l}$ ). This feature makes upwelling areas similar to stagnant basins, which have been proposed as major areas for phosphate deposition by some authors (Blackwelder, 1916; Brooks, Presley and Kaplan, 1968). Sholkovitz (1973) suggests that the dissolved oxygen content of the water overlying sediments plays a significant role in determining early sediment diagenesis and interstitial waters where apatite must be forming.

The shallow depths associated with coastal upwelling areas can result in significant warming of the water, which would tend to promote apatite formation. In addition, shallow areas of the modern ocean would undergo significant temperature fluctuations due to the many changes in sea level over geologic history. Gulbrandsen (1969) discusses the temperature effect, and Bushinskii (1964, 1966) presents geological evidence for sea level changes associated with phosphorite formation. Burnett (1974) also correlates warming periods with periods of phosphate deposition.

There is a notable lack of data on the interstitial water chemistry in areas of phosphorite formation. Relevant studies are those of Brooks et al. (1968), Sholkovitz (1973), Baturin (1972), Baturin and Shishkina (1973), and Shishkina, Baturin, and Bykova (1972). A feature in common to all of these studies was the dramatic increase in dissolved phosphate in the interstitial fluids. Concentrations ranged as high as several hundred  $\mu\text{M PO}_4/\text{l}$ , compared to  $\sim 3 \mu\text{M}$  in the water column. Fluorine also was found to be significantly enriched in the interstitial waters of upwelling areas. Shishkina et al. found interstitial  $\text{F}^-$  concentrations of up to  $580 \mu\text{M}$ . This is near or above saturation with respect to  $\text{CaF}_2$ . Normal sea water contains  $\sim 80 \mu\text{M/l}$  of  $\text{F}^-$ . Depletions of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  were observed in the interstitial waters of the Santa Barbara Basin. The pH's in the interstitial waters generally ranged from 7.2-8.0. Approximate calculations



show the interstitial waters in that area to be supersaturated with respect to apatite (see Figure 4.3). Overall, one can see in the areas of coastal upwelling many of the necessary ingredients for phosphorite formation.

Generally the sediments showed some  $\text{SO}_4$  reduction. In addition to the effect of  $\text{SO}_4$  reduction mentioned earlier, the formation of  $\text{S}^{-2}$  will cause the precipitation of metal sulfides. This will free the  $\text{PO}_4$  which may have been adsorbed onto the metal (hydroxide) before it precipitated as a sulfide (Brooks et al., 1968).

Some have suggested that the formation of apatite occurs in estuarine, rather than in open ocean, waters or sediments (Martens and Harris, 1970; Bushinskii, 1964; Pevear, 1966, 1967). I tend to favor the upwelling area for several reasons. There is a great deal of similarity between the circulation and nutrient behavior in an upwelling area compared to an estuary (Sverdrup, Johnson, and Fleming, 1942). Also, it has been observed that direct precipitation of apatite can occur in interstitial waters of marine sediments (Burnett, 1974). Finally, the phosphate levels in current estuarine sediments are found to be controlled generally by Fe or Al-phosphates, rather than Ca-phosphates (Bray, Bricker and Troup, 1973).

The phosphorites found in upwelling areas have been described in the works of Dietz, Emery and Shepard (1942), Bushinskii (1964, 1966), Baturin (1966), Burnett (1974) and others. Most of the basic

structures were listed in Table 4.1. In an interesting study, Baturin and Dubinchuk (1974) examined an Aghulas Bank phosphorite by electron microscopy. Even within the same phosphorite, they found evidence of different stages of phosphate growth. Baturin and Dubinchuk concluded that phosphatization depends on the diagenetic environment of various macro- and micro-environments in the sediment.

The precipitation of phosphates in certain microenvironments in the sediments has also been mentioned by others (e.g. Burnett, 1974). The physico-chemical conditions inside a foraminiferal test, for example, may be quite different from the surrounding sediment. Possibly the pH at the surface of a mineral grain would be raised sufficiently to promote apatite precipitation. Wollast (1971) shows that heterogeneous precipitation may occur in small cracks at reactant concentrations less than saturation because of surface energy effects. Persistence of the apatite in the long-run, though, requires that the sediment be at or above apatite equilibrium. Even though a sediment is, on the average, saturated or supersaturated with respect to apatite, it may be that the required energy barriers are overcome only at surfaces, in cavities, or in other special micro-environments in the sediment. In any event, the type of phosphorite found will be a function of the sediment type in which it formed. Where there is considerable limy mud or limestone, the phosphorite will likely appear as a replaced limestone. In the diatomaceous sediments off the coast

of Chile and Peru, apatite is found mainly as a chemical precipitate on the surface of diatoms or mineral grains (Burnett, 1974).

Synthesis: apatite formation in the ocean

The most recent discussion of apatite formation, pertaining especially to the Peru-Chile shelf, is that of Burnett (1974). He considers many of the factors which were discussed above in his model for authigenic apatite formation. Much of the discussion to follow will incorporate his observations and conclusions, as well as those of Tooms et al. (1969), Bushinskii (1964, 1966), and Gulbrandsen (1969).

Upwelling areas are favored regions for modern apatite formation. They receive a continual source of nutrients from deeper waters which is assimilated by phytoplankton during photosynthesis. The phytoplankton eventually settle to the sediment floor either directly or in the fecal material of grazing organisms. Their decay on the relatively shallow shelf area is determined by the temperature and oxygen content of the waters which cover the sediment. The low oxygen water bathing the sediments is also high in phosphate. The low  $O_2$  and high  $PO_4$  causes much of the phosphate release to occur in the sediments while producing a slight barrier to back diffusion of phosphate out of the sediment. The continual supply of phosphate to the sediments is necessary to maintain the high level of dissolved phosphate. Without the fairly steady supply of organic phosphorous

to the sediments, much of the phosphate would diffuse back into the water column. In addition, since apatite formation is very slow, a steady supply of phosphate must be provided. Apatite formation, per se, occurs in the sediments by direct precipitation or by replacement of existing sediment. Precipitation in normal seawater is prohibited by kinetic barriers.

The upwelling area should provide a sediment of high biogenic content relative to terrigenous, clayey material for optimum apatite formation. Not only will clays dilute the sediment, preventing high concentrations of dissolved phosphate, but clays can also adsorb significant quantities of dissolved phosphate.

Apatite formation will depend on a number of factors as outlined in the first sections of this chapter. The data in Table 4.2 and Figure 4.3 show that sediments in an upwelling area should be highly supersaturated with respect to an ideal apatite, even considering temperature and pH changes. Even the measured (non-ideal) solubility of an actual apatite taken from an upwelling area (see Chapter III) is only  $\sim 3\text{-}5 \mu\text{M PO}_4$  at  $\text{pH} \sim 7.4$  and  $10^\circ\text{C}$ . Though the effect of solution composition on the solubility is unknown, I estimate that the apatite solubility (as  $\text{TPO}_4$ ) in a  $\text{Ca}^{+2}$  depleted,  $\text{F}^-$  enriched sediment would increase by possibly a factor of 3-5. This would still make most sediments in upwelling areas supersaturated with respect to apatite. More data on the exact nature of the equilibrating phase and

of the pore water composition is required before quantitative estimates can be made.

The kinetic factors discussed above indicate that apatite crystallization is most likely to occur on surfaces of other mineral grains (or on detrital fish-bone apatite), in micro-cracks, or along grain boundaries. I feel that the most likely combination of chemical factors to accelerate nucleation and crystallization are a lowered Mg/Ca arising from diagenetic reactions and sulfate reduction, increased F/Ca (near fluorite saturation) at moderate pH's (7.2-7.8), and increased dissolved phosphate. High  $F^-$  levels are required, according to the data of Simpson (1969), to form apatites of normal  $F^-$  content. Temperature will also play a decisive role in the kinetics of apatite formation. The critical Mg/Ca ratio for apatite formation (1:4.2) proposed by Martens and Harris is a kinetic barrier which will be altered under interstitial water conditions (high  $F^-$ , heteronucleation). The range of solution compositions which define the metastable amorphous calcium phosphate region and the field of apatite crystallization remains to be determined. The definition of such a field at various temperatures in terms of Ca-Mg-F- $PO_4$ -pH- $CO_3$  under conditions of homogeneous and heterogeneous nucleation would be most enlightening (not to mention time-consuming) in unraveling the principal factors controlling apatite formation.

Phosphorite formation has apparently occurred at only certain

times in the earth's history (Burnett, 1974; Tooms et al., 1969).

The discussions of Burnett and Tooms et al. suggest that temperature may be the key factor in promoting apatite precipitation. Burnett correlates maximum of sea level (interglacial, warm periods) with the most active phosphorite formation, suggesting that the decrease in solubility accompanying the warming would be sufficient to induce precipitation. Cook (1970) stresses pH in addition to temperature in apatite formation and transformations. At periods of low sea level, the phosphorite would be concentrated by winnowing (Bushinskii, 1964). In fact, evidence of periodic winnowing is common to many phosphate deposits (Cook, 1967; Bushinskii, 1964). Estimates have been made (J. Thiede, personal communication) that the sea surface temperature off Northwest Africa has increased by about 6°C since the last glacial maximum. If this change is assumed to also represent the change in bottom and interstitial water temperature, then a decrease in apatite solubility of 15-25% since the last glacial would be predicted. Although the change in temperature may be enough to shift the balance in favor of apatite precipitation, I suspect that there are factors relating to the circulation and biology of the oceans which will more strongly influence phosphate formation. The commonly noted association of phosphorites with high surface organic productivity and the suspected influence (on phosphate formation) of the dissolved oxygen content of the waters intersecting the sediments

(Sholkovitz, 1973) leads to this conclusion. Global and local reduction of primary production during glacial periods and the consequent rise in  $O_2$  (also increased solubility in glacial periods) would tend to inhibit apatite formation. The theme of biological interaction of N, P, and  $O_2$  was considered by Piper and Codispoti (1975) in their discussion of the association of phosphorite deposits and black shale. They focused on the possible effects of altered denitrification rates on the precipitation of apatite in the oceans. I agree with their emphasis on the broad interrelationships between biological activity and the chemistry of the oceans, especially in relation to phosphorite formation.

Thus far the possible role of organic catalysis in apatite formation has not been mentioned. McConnell (1965) emphasizes the effect which enzymes may have in accelerating apatite precipitation. Too little is known about the nature of the organic matter in the sediments of upwelling areas, however, to assess the importance of such mechanisms. They remain a possibility, though.

I have summarized the above discussion on apatite formation in the modern ocean as a schematic diagram shown in Figure 4.6. It does not necessarily represent the exact conditions of deposition for all phosphorite formations. For example, the shelf area may be considerably wider for some phosphate deposits. Circulation patterns may also be altered in the case of deposition in an epicontinental sea

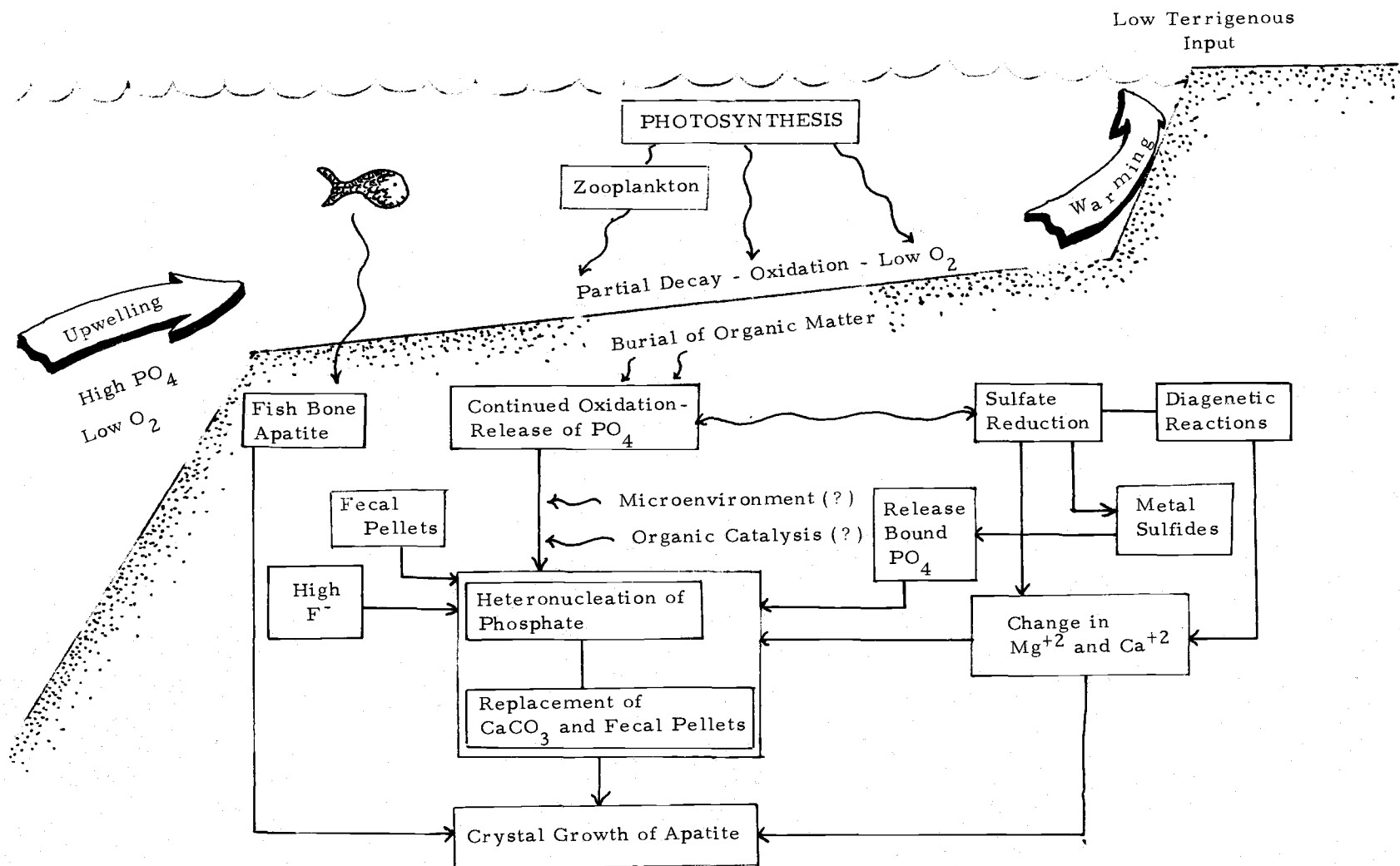


Figure 4.6. Model of phosphorite genesis in upwelling areas.



or as in Australia as suggested by deKeyser and Cook (1972). The model does attempt to correspond to current conditions in the ocean. The model incorporates many of the ideas of others who have studied phosphorite formation as well as my own. It is likely that at one time or another scientists have suggested all possible mechanisms and relationships concerning phosphorite formation.

The main feature of the model is that apatite formation occurs in the sediments, rather than in the water column or at the sediment water interface. In the sediments of upwelling areas one finds the necessary phosphate supply and also a highly elevated  $F^-$  level. The source of the high  $F^-$  may be volcanic but is uncertain at this time; only its presence is verified. A quantitative estimate of the changes in  $Ca^{+2}$ ,  $Mg^{+2}$ , and  $SO_4^{-2}$  required to initiate apatite precipitation cannot yet be made. Only qualitative data are available to indicate, for example, that lower levels of  $Mg^{+2}$  not only increase the rate of phosphate precipitation and crystallization, but also will reduce the equilibrium solubility of apatite. Other factors, as indicated in the discussion above, will moderate the rate of apatite formation as well as its equilibrium solubility in the sediments. Both rate and equilibrium factors need to be considered in studying apatite formation. With time, diagenetic reactions will bring the interstitial waters to a certain condition of supersaturation, a condition which is defined by a combination of factors, rather than any single factor. The factors

will include  $\text{Ca}^{+2}$ ,  $\text{F}^-$ ,  $\text{TPO}_4$ , pH,  $\text{Mg}^{+2}$ ,  $\text{SO}_4^{-2}$ , and temperature. Particular combinations of these factors will allow apatite precipitation to occur at a reasonable rate. Other combinations will inhibit the formation of apatite. Again, quantitative estimates of the conditions of formation cannot yet be made. A study of the interstitial water composition in regions of apatite formation would be most valuable in determining the chemical factors necessary for phosphorite formation. I feel that in addition to chemical (equilibrium and kinetic) factors, physical and biological factors need to be considered in studying the phosphorite problem. This study could include the global cycling of nitrogen and phosphorous down to the microchemistry of the interstitial environment.

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## APPENDICES

## APPENDIX I

Thermodynamic estimates of phosphate stability on seawater

Thermodynamic solubility products and estimates of activity coefficients can be used to calculate the solubility of calcium phosphates in seawater. If the solid is represented by  $X_l Y_m Z_n$  then the thermodynamic reaction quotient for its dissolution is:

$$K^o = a_X^l a_Y^m a_Z^n / a_{XYZ} \quad A-1$$

where:

$a_i^J$  = the activity of the  $i$ th ion raised to the  $J$ th power

$a_{XYZ}$  = the activity of the solid phase

This quantity can be related to an apparent (stoichiometric) solubility product,  $K'_{SP}$  by

$$\begin{aligned} K'_{SP} &= [X]^l [Y]^m [Z]^n \\ &= K^o_{SP} / f_X^l f_Y^m f_Z^n \end{aligned} \quad A-2$$

where:

$[I]$  = total concentration of ion  $I$

$K^o_{SP} = K^o a_{XYZ}$  = thermodynamic solubility product

$f_i^J$  = total activity coefficient of  $i$ th ion raised to  $j$ th power

Alternately, the solubility product can be expressed as  $-\log K'_{SP}$  ( $= pK'_{SP}$ ), so that

$$pK'_{SP} = 1 \cdot p[X] + m \cdot p[Y] + n \cdot p[Z] \quad A-3$$

and

$$pK^O_{SP} = 1 \cdot pa_X + m \cdot pa_Y + n \cdot pa_Z - pa_{XYZ} \quad A-4$$

The solubilities of the following pure phases in seawater at 33.3‰ and 25° will be calculated: fluorapatite, hydroxyapatite, octacalcium phosphate, brushite, monetite, and a postulated hydroxyapatite "surface complex" (Rootare et al., 1962). The solubility products are given in Table A1.1. The  $(PO_4^{-3})$  and  $(HPO_4^{-2})$  concentrations are functions of pH (at constant temperature and salinity) and can be calculated from the following relations:

$$(PO_4^{-3}) = TPO_4 / (1 + \frac{X^3}{K'_3 K'_2 K'_1} + \frac{X^2}{K'_2 K'_3} + \frac{X}{K'_3}) \quad A-5$$

$$(HPO_4^{-2}) = TPO_4 / (1 + K'_3/X + X/K'_2 + X^2/K'_1 K'_2) \quad A-6$$

where  $TPO_4 = (H_3PO_4) + (H_2PO_4^-) + (HPO_4^{-2}) + (PO_4^{-3})$

$X$  = the operational hydrogen ion activity ( $X = 10^{-pH}$ )

$K'_i$  = the  $i$ th apparent dissociation constant of  $H_3PO_4$  (Kester

Table A1.1. Thermodynamic solubility product of calcium phosphates.

		$K_{SP}^0$ (25°)	Ref.
Fluorapatite	$Ca_5(PO_4)_3F$	$1.2 \times 10^{-60.5}$	1
Hydroxyapatite	$Ca_5(PO_4)_3OH$	$6.3 \times 10^{-59}$	2
Octacalcium phosphate	$Ca_4(PO_4)_3(H)$	$1.25 \times 10^{-47}$	3
Monetite	$CaHPO_4$	$1.26 \times 10^{-7}$	4
Brushite	$CaHPO_4 \cdot 2H_2O$	$2.56 \times 10^{-7}$	5
Hydroxyapatite surface complex	$Ca_2(HPO_4)(OH)_2$	$5.24 \times 10^{-28}$	6

- 1 Farr and Elmore (1962)
- 2 Avnimelech et al. (1973)
- 3 Moreno, Brown, and Osborn (1960)
- 4 McDowell et al. (1971)
- 5 Gregory, Moreno, and Brown (1970)
- 6 Rootare, Dietz, and Carpenter (1962)

and Pytkowicz, 1967)

Estimates of the total activity coefficients for the various species

can be made using the relation (Pytkowicz et al., 1966):

$$a_I = \gamma_F^I \cdot f_T^I$$

A-7

where  $a_I$  = activity of ion I

$\gamma_F$  = free activity coefficient of I

$f_T$  = total activity coefficient of I

$I_T$  = total (free + ion-paired) concentration of I

$I_F$  = free concentration of I

Total concentrations of  $\text{Ca}^{+2}$  and  $\text{F}^-$  can be estimated from the salinity using chlorinity ratios (Pytkowicz and Kester, 1971). Free concentrations have been calculated by Pytkowicz and Hawley (1974) and estimates for the free-ion activity coefficients can be made using the mean-salt method. Use of the mean-salt method for anions, such as  $\text{F}^-$ , involves the calculation

$$(\gamma_F) = \frac{\gamma_{\pm \text{KF}}}{\gamma_{\pm \text{KCl}}} \quad \text{A-8}$$

One assumes in this calculation that KF solutions are completely dissociated.  $a_H$  is simply  $10^{-\text{pH}}$  (pH is measured on the NBS scale) and  $a_{\text{OH}}$  can be calculated from

$$a_{\text{OH}} = a_w K_w^0 / a_H \quad \text{A-9}$$

where  $K_w^0$  = thermodynamic ion product of water

$a_w$  = activity of water

Finally,  $f_{\text{PO}_4}$  and  $f_{\text{HPO}_4}$  can be obtained from

$$f_{\text{PO}_4} = \frac{K_1^0 K_2^0 K_3^0}{K_1' K_2' K_3'} \gamma_{\text{H}_3\text{PO}_4} \quad \text{A-10}$$

$$f_{\text{HPO}_4} = \frac{K_1^{\circ} K_2^{\circ}}{K_1 K_2} \gamma_{\text{H}_3\text{PO}_4} \quad \text{A-11}$$

and we take  $\gamma_{\text{H}_3\text{PO}_4} = 1$ , although this is uncertain and may be higher (C. Culberson, private communication). Equations A-5 to A-11 above can be combined to give the expressions shown in Table A1.2 for the total phosphate in equilibrium with each of the phases mentioned. The values of the constants used in the calculations are also given in the table.

The results of these calculations are shown in Figure A1.1. According to these calculations, which do not account for pressure effects, the bulk of seawater is supersaturated with respect to a pure hydroxyapatite and a pure fluorapatite, and it is highly undersaturated with respect to non-apatitic phosphates. Kramer (1964) made a similar calculation for pure hydroxyapatite and reached the same conclusion. He used a  $K_{\text{SP}}^{\circ}$  calculated from free energy data and obtained a value of  $1.0 \times 10^{-57}$  for the solubility product of hydroxyapatite.

One can see from Figure A1.1 that pure fluorapatite should be the most stable phase in seawater. According to our calculations, hydroxyapatite is more stable than fluorapatite only at pH's greater than about 11.5, though this pH will vary according to the solubility products used in the calculation.

The solubility relationships described above apply to seawater

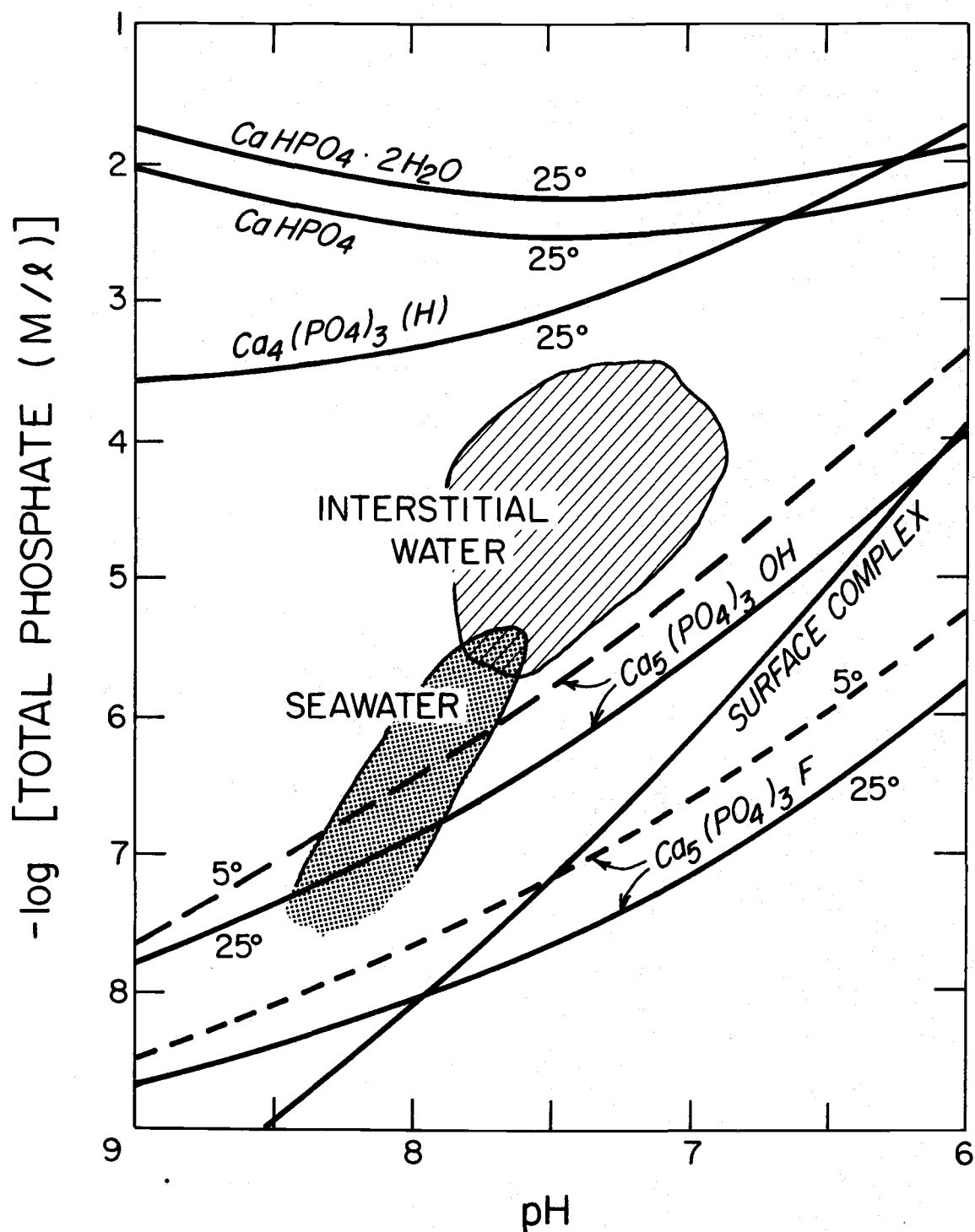


Figure A1.1. Estimates of the solubility of pure mineral phases in seawater at 25°C. Calculations are based on thermodynamic solubility products and estimated activity coefficients.



Table A1.2. Equations and constants used in the estimation of total phosphate in equilibrium with various calcium phosphates.

<u>Compound</u>	<u>Equilibrium Total Phosphate</u>
$\text{Ca}_5(\text{PO}_4)_3\text{F}$	$(K_{\text{SP}}^{\text{O}}(\text{FAP})/f_{\text{Ca}}^5 f_{\text{F}} [\text{Ca}^{+2}]_{\text{T}}^5 [\text{F}^-])^{1/3} \times A$
$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	$(K_{\text{SP}}^{\text{O}}(\text{HAP}) \times a_{\text{H}}/f_{\text{Ca}}^5 [\text{Ca}^{+2}]_{\text{T}}^5 a_{\text{w}} K_{\text{w}})^{1/3} \times A$
$\text{Ca}_4(\text{PO}_4)_3\text{H}$	$(K_{\text{SP}}^{\text{O}}(\text{OCP})/f_{\text{Ca}}^4 [\text{Ca}^{+2}]_{\text{T}}^4 a_{\text{H}})^{1/3} \times A$
$\text{CaHPO}_4$	$(K_{\text{SP}}^{\text{O}}(\text{MON or BRU})/f_{\text{Ca}} [\text{Ca}^{+2}]_{\text{T}}) \times B$
SFC complex	$(K_{\text{SP}}^{\text{O}}(\text{Complex}) \times a_{\text{H}}^2/f_{\text{Ca}}^2 [\text{Ca}^{+2}]_{\text{T}}^2 a_{\text{w}}^2 K_{\text{w}}^2) \times B$

and

$$A = \frac{K_1' K_2' K_3'}{\gamma_{\text{H}_3\text{PO}_4} K_1^{\text{O}} K_2^{\text{O}} K_3^{\text{O}}} \left( 1 + \frac{a_{\text{H}}}{K_3'} + \frac{a_{\text{H}}^2}{K_2' K_3'} + \frac{a_{\text{H}}^3}{K_1' K_2' K_3'} \right)$$

$$B = \frac{K_1' K_2'}{\gamma_{\text{H}_3\text{PO}_4} K_1^{\text{O}} K_2^{\text{O}}} \left( 1 + \frac{K_3'}{a_{\text{H}}} + \frac{a_{\text{H}}}{K_2'} + \frac{a_{\text{H}}^2}{K_1' K_2'} \right)$$

Table A1.2. Continued.

<u>Dissociation Constants</u>			<u>Concentration Constants</u>	
	<u>5°C</u>	<u>25°C</u>		
$K_1^0$	$8.48 \times 10^{-3}$	$6.92 \times 10^{-3}$	$[Ca]_T = .01003$	$f_{Ca} = .23$
$K_1'$	$2.7 \times 10^{-2}$	$2.7 \times 10^{-2}$	$[F]_T = 66.7 \times 10^{-6}$	$f_F = .35$
$K_2^0$	$5.24 \times 10^{-8}$	$6.17 \times 10^{-8}$	$a_w = .982$	
$K_2'$	$6.2 \times 10^{-7}$	$7.91 \times 10^{-7}$		
$K_3^0$	$2.26 \times 10^{-13}$	$4.78 \times 10^{-13}$	assumed for 25° and 5° C	
$K_3'$	$0.46 \times 10^{-9}$	$2.50 \times 10^{-9}$		
$K_w$	$0.185 \times 10^{-14}$	$1.008 \times 10^{-14}$		

estimated  $\Delta pK$  (5°-25°) = 0.95 pK units (more soluble)

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of normal composition. A change in the major cation composition of seawater, such as can occur in interstitial waters, will alter the relative saturation state of seawater with respect to the apatites. A discussion of these effects can be found in Chapter IV.

Furthermore, the above calculations are valid for only pure mineral phases. Such phases are rarely, if ever, found in nature and are quite difficult to produce even in the laboratory. Marine apatites generally contain structural ions other than Ca,  $PO_4$ , F, and OH (Gulbrandsen, 1966; McConnell, 1973). It is usually impossible, though, to assign an exact chemical formulation to the apatitic phase

of a marine phosphorite because of the complicating presence of undetermined amounts of other, non-apatitic, phases. Still, substitution in the apatite lattice is known to occur to some extent, and it is useful to consider how compositional variation will affect the solubility of apatite. The compositional variation in apatites can, perhaps, be likened to that in magnesian calcites,  $\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3$ . Magnesian calcites are organically precipitated in the marine environment but they are unstable and eventually convert to calcite (Land, 1967). Magnesian calcites are more soluble than pure calcite, but they don't have a true reversible, equilibrium solubility (Chave et al., 1962). Bricker and Garrels (1967) discuss the effect of solid solution and other factors affecting the solid phase on mineral equilibria in natural environments. If the analogy between Mg-calcites and substituted apatites holds, then one would expect an enhanced solubility of substituted apatites over the pure mineral phase. A higher solubility for substituted apatites is often mentioned in the literature on apatite, but only recently have data become available to substantiate this observation (Chien, 1972).

Finally, to illustrate a consequence of using apparent constants in describing the solubility of apatite I will consider the effect on the apparent solubility product of a pure fluorapatite for a change in temperature from 5°C to 25°C at pH = 8.0. One can calculate the  $[\text{PO}_4^{-3}]$  concentration from  $\text{TPO}_4$  and the pH according to Eq. A-5,

using the values listed in Table A1.2. If an equilibrium  $\text{TPO}_4$  of 1.0  $\mu\text{M}$  is measured at  $5^\circ$  and 0.5  $\mu\text{M}$   $\text{TPO}_4$  at  $25^\circ$  one finds that at  $5^\circ$   $-\log(\text{PO}_4^{-3}) = 7.36$  and  $-\log(\text{PO}_4^{-3}) = 7.00$  at  $25^\circ$ . So the apparent solubility product at these two temperatures is (expressed as  $\text{pK}'_{\text{SP}}$ ):

$$\text{at } 5^\circ, \text{ pK}'_{\text{SP}} = 5 \text{ pCa} + 3 \text{ pPO}_4 + \text{pF} = 36.26$$

$$\text{at } 25^\circ, \text{ pK}'_{\text{SP}} = 5 \text{ pCa} + 3 \text{ pPO}_4 + \text{pF} = 35.18$$

One normally expects that the lower solubility product (higher  $\text{pK}'_{\text{SP}}$ ) will have the lower solubility. It is seen that this is not necessarily the case when one uses apparent constants, as the apatite was more soluble at lower temperatures but showed a smaller solubility product. Therefore, to determine the solubility, in terms of total dissolved phosphate, one must use the apparent dissociation constants of phosphoric acid for conversion of  $\text{PO}_4^{-3}$  to  $\text{TPO}_4$ . One cannot assume, in comparing  $\text{K}'_{\text{SP}}$ 's at different temperatures and salinities, that a lower  $\text{PO}_4^{-3}$  implies a lower total phosphate.

## APPENDIX II

Methods and procedures for apatite solubility experiments

Solubility experiments on natural apatites were performed using several different methods. One method involved sealing small amounts (0.1 - 1.0 g) of apatite in 100 ml Pyrex ampoules filled with seawater. These ampoules were either heat sealed or sealed with a rubber septum. They were then placed in a water bath (at  $10.0 \pm 0.1^\circ\text{C}$ ) unless otherwise indicated and either rotated continuously on their sides at about 12 rpm, or rotated end over end daily.

The second method used employed a continuous pumping apparatus. This method was used to collect most of the data. Eight glass columns (30 cm x 0.7 cm) were each packed with ~15 g of apatite and glass wool was inserted in both ends of the tube. Each glass column was connected by tygon tubing to a 75 ml water reservoir on one end and a peristaltic pump on the other end. The pump pulled the water from the reservoir, through the apatite column, and then returned the water to the reservoir. The pumping rate was 1.0 ml/min. A rubber stopper was mounted on each reservoir and had holes for ingoing and outgoing liquid as well as holes for a gas bubbling tube and a larger hole for the pH probe and for drawing samples from the reservoir. The reservoirs and apatite columns were immersed in the water bath, but the pump was not.

Water-saturated air with a constant  $p\text{CO}_2$  was bubbled through reservoirs during the course of each experiment. This was done to adjust and maintain the pH at a constant value. This procedure was only effective when the alkalinity remained nearly constant. Several methods of gas mixing were tried. The one used with the most success is illustrated in Figure 3.1 which also shows the pumping arrangement for the samples.

During early experiments only pH and total inorganic dissolved phosphate were measured. Later experiments included measurement of fluoride, alkalinity, and occasionally calcium. The pH was measured with a Corning Model 476050 micro-combination pH electrode and a Corning Model 112 Digital pH meter. Dissolved inorganic phosphate was measured with a Technicon AutoAnalyzer using the method described in Atlas et al. (1971). The alizarin-blue method of Greenhalgh and Riley (1961) was used to determine the fluoride concentrations. Alkalinity was measured by titration of a 10-15 ml sample with HCl using a Gran extrapolation to determine the endpoint. A Sargent Model S30072-15 combination electrode was used to determine the pH during the alkalinity titrations. Calcium was measured on a diluted sample with a Jarrell-Ash Model 810 atomic absorption spectrophotometer. The seawater was 33.3‰, and was filtered through a  $0.45\ \mu$  filter before use. The seawater was preserved with  $\sim 15$  drops/l of  $\text{HgCl}_2$  (saturated).

Before the beginning of each experiment, the columns were washed with the seawater to be used in the experiment. Sometimes this wash was preceded by a wash with .01 N HCl, followed by a distilled water wash. Occasionally, only a distilled water wash preceded the seawater wash. The sample pretreatment was found to affect the final results, so the wash sequence used will be given in the description of each experiment. The reservoirs were then filled with the seawater and pumping was begun. In some experiments samples were withdrawn periodically for measurement of phosphate. In other experiments, the pumping was stopped after a specified time interval and pH, phosphate, fluoride, and alkalinity were measured.

## APPENDIX III

Description of samples used in apatite solubility study.  
Microprobe analysis of apatite sample.

A total of nine different apatites were used in this solubility study. Most were examined in thin section and all were x-rayed to confirm the presence of apatite and to try to detect the presence of other phases. Chemical analyses were performed on all the apatites. Data on the apatites is given in Tables A3.1-A3.3. In addition, BET surface areas were determined for 20-30 mesh samples of COW, 4-28 and FAP (Stump, 1963). They were found to be about  $15 \text{ m}^2/\text{g}$ ,  $0.5 \text{ m}^2/\text{g}$  and  $0 \text{ m}^2/\text{g}$ , respectively.

Of the apatites used in this study, none conform to the ideal stoichiometry as described earlier. Since there are other phases present, I thought it would be useful to examine the relationship of the bulk composition to the composition of the apatite on a microscopic scale. This could be accomplished by the use of an electron microprobe. Burnett (1974) used the microprobe to analyze the apatitic component of the sediments off the coast of Chile and Peru. He showed that calcium, for example, was not confined solely to the apatite phase. He also indicated compositional variation between light and dark sections of phosphorite ovules.

A section of 4-28 was used for microprobe analysis, and the results were rather surprising. The sample consisted of closely



Table A3.1. Samples used in apatite solubility study.

<u>Sample Identification</u>	<u>Comment</u>
1. FAP	Crystalline fluorapatite from Durango, Mexico. Obtained from Wards Scientific.
2. COW	Fossilized manatee rib from Bone Valley Formation, Florida.
3. 4-28	From Meade Peak Member of the Phosphoria Formation at Gros Ventre Slide near Jackson, Wyoming. Pelletal phosphorite. Detrital quartz main impurity.
4. T7-61	From the ore zone in the Retort Member of the Phosphoria Formation near Elliston, Montana. Oolitic. Very fine grained. $\sim 1 \mu$ equidimensional crystals. Small amounts of quartz and feldspars. Trace of clay.
5. PD-18-30	From off Chile coast from about 400 m depth. Small quartz and feldspar shards. Clay. Recent formation. See Burnett (1974).
6. PD-15-17	From same general area as PD-18-30. See Burnett (1974) for further details.
7. AUS-1	Pelletal phosphorite from the Ardmore outlier. Australia. Marine origin (Cook, personal communication).
8. AUS-2	From Australia. Duchess outlier. Pelletal phosphorite.
9. SC-2	From off Southern California. Depth unknown. Fecal pellets in sample.

Table A3.2. Sample composition of apatites used in this study.

<u>Sample ID</u>	<u>FAP</u>	<u>COW</u>	<u>4-28</u>	<u>PD-15-17</u>	<u>PD-18-30</u>	<u>AUS-1</u>	<u>AUS-2</u>	<u>T7-61</u>	<u>SC-2</u>
Constituent in %									
P	17.47	15.94	15.78	7.45	7.06	15.39	15.32	16.12	12.78
Ca	39.88	37.45	36.88	19.87	18.30	34.88	35.73	36.45	32.59
F	3.05	3.15	2.70	(2.45)	(1.70)	3.28	3.02	2.50	3.30
CO <sub>2</sub>	0.55	3.75	1.92	3.36	2.67	1.35	1.26	1.46	4.36
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.21	0.15	4.00	2.20	1.53	0.22	0.08	1.64
Al <sub>2</sub> O <sub>3</sub>	0.12	0.97	0.57	3.20	3.84	1.51	0.72	0.77	0.57
MgO	0.05	0.17	0.14	1.68	1.36	0.27	0.12	0.18	0.85
Na <sub>2</sub> O	0.40	0.80	1.02	1.41	1.57	0.33	0.46	0.21	1.41
K <sub>2</sub> O	0.002	0.011	0.212	0.416	0.540	0.077	0.778	0.328	0.324

Table A3.3. X-ray data for apatites used in this work.

hKl	<u>002</u>			<u>102</u>		<u>210</u>	<u>211</u>	<u>112</u>	<u>300</u>	<u>202</u>	<u>301</u>		<u>212</u>	<u>310</u>
Sample ( )	d spacing													
	I/I°													
PD-15-17	3.44	3.33	(3.20)	3.17	3.13	3.04	2.78		2.69	2.62			2.28	2.24
	35	62	14	22	(10)	14	100		54	30	--	--	11	25
PD-18-30	3.43	3.33	3.21	(3.14)		3.05	2.78		2.69	2.62			2.28	2.24
	45	38	34	(22)		17	100	--	54	30	--	--	11	24
AUS-1	3.44	3.34		3.17		3.06	2.80	2.78	2.70	2.62	2.51	2.46	2.28	2.24
	39	16	--	12		17	100	(61)	55	28	5	2	7	23
T7-61	3.44	3.34		3.17		3.06	2.80	2.78	2.70	2.62	2.51	2.45	2.29	2.24
	39	13	--	14		16	100	(60)	57	26	3	2	7	21
4-28	3.44	3.34		3.17		3.05	2.79		2.70	2.62	2.51		2.29	2.24
	42	10	--	11		15	100	--	57	28	5	--	7	23
COW	3.44			3.17		3.05	2.79		2.69	2.62	2.51		2.28	2.24
	36	--	--	13		16	100	--	55	25	3	--	7	20
SC-2	3.44	3.33		3.17		3.05	2.79		2.69	2.62	2.51	2.45	2.29	2.24
	39	9	--	17		17	100	--	53	29	6	3	9	21
AUS-2	3.44	3.35		3.17		3.06	2.79	2.77	2.70	2.62	2.51	2.45	2.28	2.24
	40	45	--	14		27	100	(60)	58	28	5	4	9	24
FAP (this work)	3.44			3.17		3.07	2.80	2.77	2.71	2.62	2.52		2.29	2.25
	52	--	--	17		18	100	56	55	36	6	--	7	23
FAP (Young et al.,1969)	3.44			3.17		3.07	2.81	2.77	2.71	2.63	2.52		2.29	2.26
	46	--	--	18		16	100	34	39	23	5	--	5	15
Synthetic FAP	3.44			3.17		3.07	2.80	2.77	2.70	2.62	2.52		2.29	2.25
	42	--	--	13		17	100	54	62	29	6	--	7	22

packed pellets with detrital material (mostly quartz) distributed throughout the sample. Step scans were made across these grain boundaries and into each grain looking for possible compositional changes from the edge to the center of each grain. The step size was  $6\mu$  and a  $1\mu$  beam was used. The Ca, P, and F contents of the material were simultaneously monitored. The results are illustrated in Figure A3.1. Sharp gradients were found in all three elements. The gradients were most often, but not necessarily, associated with grain boundaries. The surprising effect was the inverse relationship between Ca and P changes to those of F. While Ca and P contents fell, the F content generally rose. A triangular plot of the relationship between Ca, P, and F is given in Figure A3.2. The scales were modified to expand the  $F^-$  variation. The Ca:P ratio is constant at about 10:5.15, and shows varying proportions of F. In fact, the F content of the apatite varies by almost a factor of 2. The average Ca:F ratio is close to that of a pure fluorapatite, but excursions in the Ca:F ratio take the ratio to well beyond that encountered in a pure fluorapatite. Dilution of the apatite by a non-calcic, non-phosphatic material high in fluoride would account for the observed distribution. No such material was observed in the x-ray pattern, but it might go undetected because of relatively low concentration. The data do not fall on a mixing line between  $CaF_2$  and a hydroxy- or fluorapatite. Rather it appears that there is  $F^-$  substitution in an

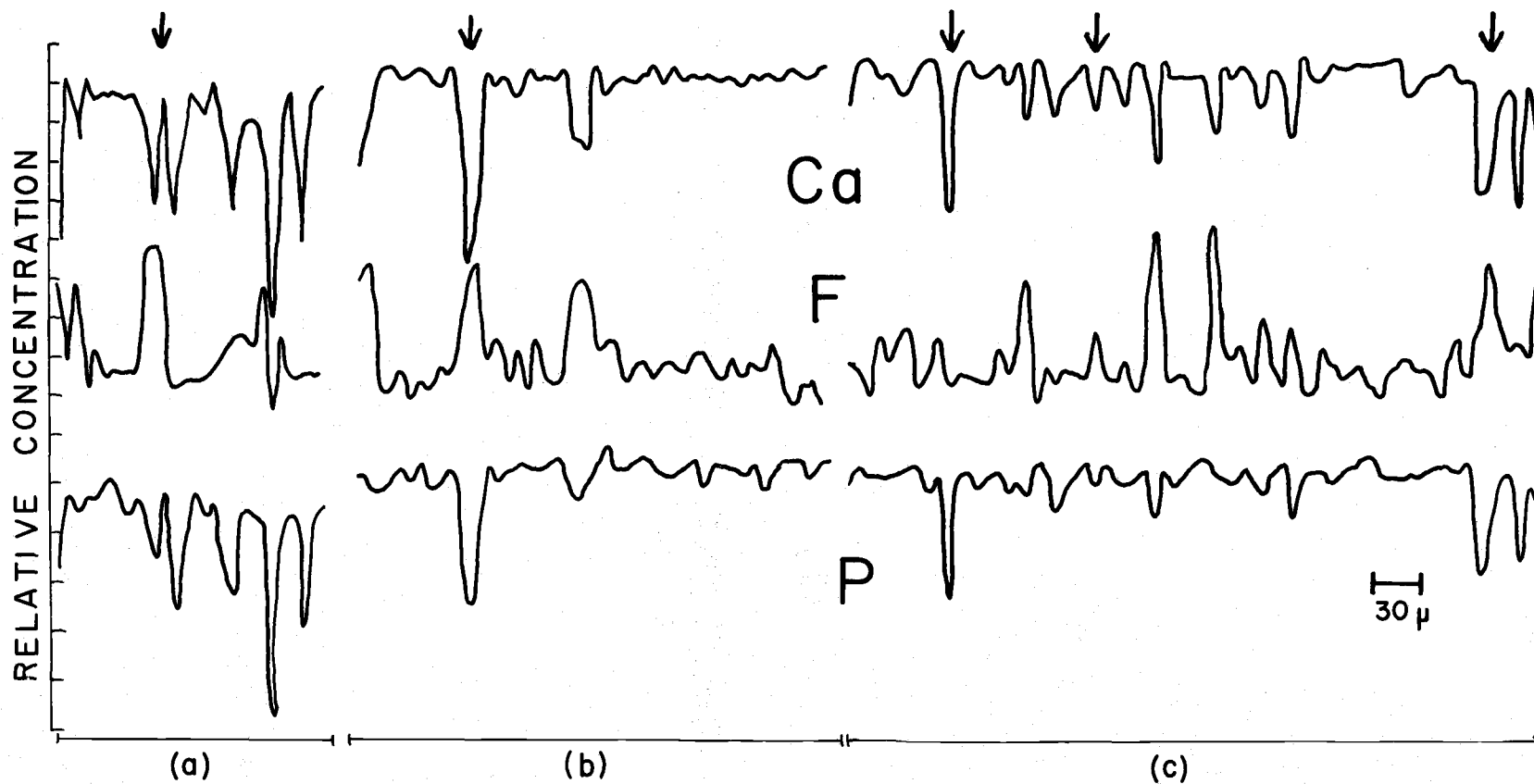


Figure A3.1. Variation in concentrations of Ca, P, and F along section of sample 4-28. Step size was 5  $\mu$ . F varies by nearly a factor of 2. a, b, and c are separate locations of same sample. Arrows indicate grain boundaries.

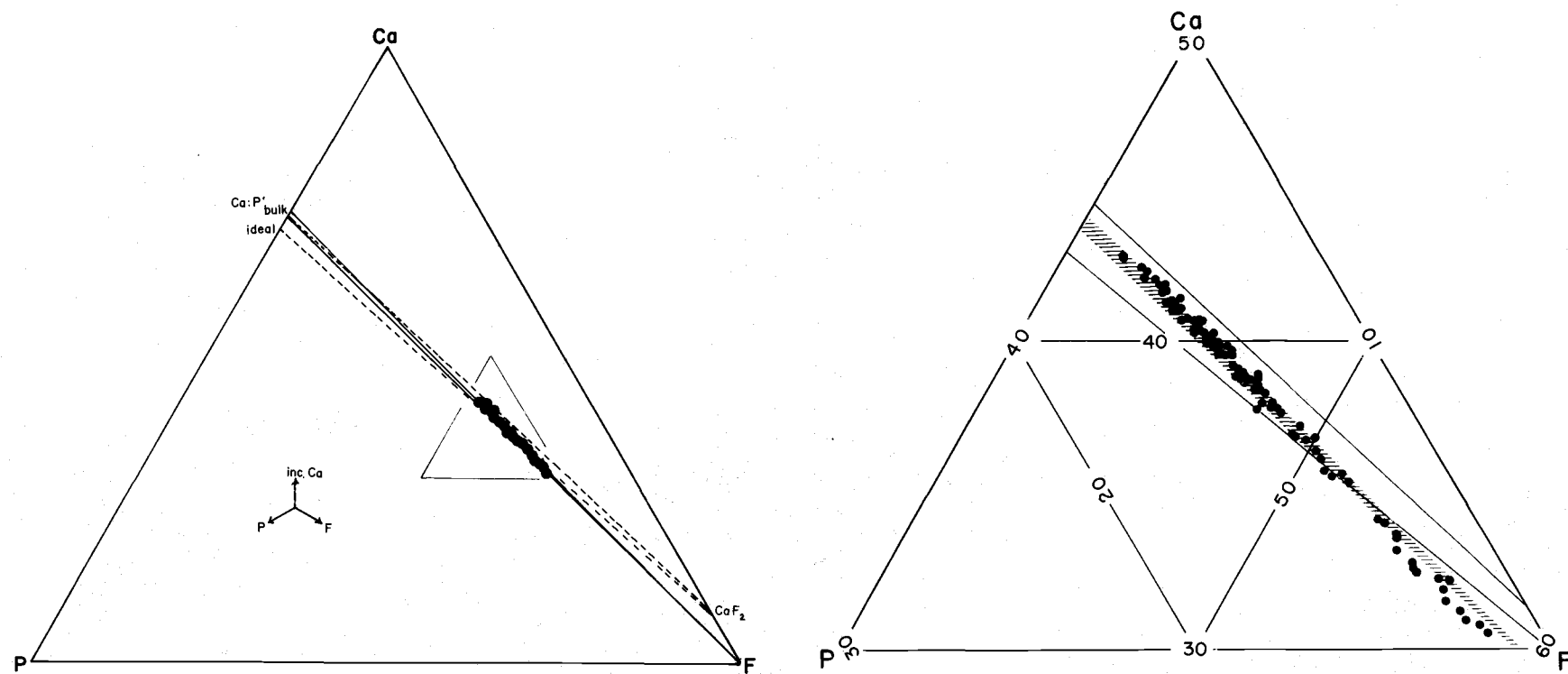


Figure A3.2. Triangle plots of data in Figure A3.1. Scales have been adjusted to clearly show large variation in  $F^-$  at constant Ca:P ratio. Plot on right is expanded scale of portion of other diagram. Slope of data points indicates that  $F^-$  variation is not the result of mixing with  $CaF_2$ .

apatitic phosphate with a Ca:P ratio of  $\sim 2:1$ . Ideal apatite has a Ca:P ratio of 1.67:1, though it is higher when  $\text{CO}_3^{-2}$  substitutes for  $\text{PO}_4^{-3}$  in the apatite lattice. This behavior is similar to that proposed by Borneman-Starinkevitch and Belov (1953) for carbonate apatite as a solid solution of  $x \cdot \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + y \cdot \text{Ca}_{10}(\text{PO}_4)_5\text{CO}_3\text{F}_3$ .

In summary, the samples we studied are all apatitic but have different compositions. An exact stoichiometry cannot be assigned definitely for each apatite because of two reasons: undetermined amounts of non-apatitic phases; and micro-compositional variation in the apatitic phase.

## APPENDIX IV

Data for apatite solubility studies

Table A4.1. Data for experiment of changing surface solution ratio. \*\* (Sfc. area of COW  $\sim 15 \pm 0.5 \text{ m}^2/\text{g}$ ). Initial  $\text{pH} \approx 8.20$ ,  $\text{TPO}_4 = .07 \text{ } \mu\text{M}$ . Temp =  $10^\circ\text{C}$ , S = 33.3‰.

<u>WT COW</u> <u>(gms)</u>	<u>Time</u> <u>(days)</u>	<u>pH</u>	<u>TPO<sub>4</sub></u>	<u>F<sup>-</sup></u>	<u>pHPO<sub>4</sub></u>	<u>pPO<sub>4</sub></u>
.1	6	7.977	1.95	66.0	5.741	6.978
.25	6	7.835	4.30	64.2	5.393	6.773
.5	6	7.615	7.56	62.2	5.147	6.747
1.0	6	7.071	13.3	57.0	4.929	7.074
.25	25	7.355	5.30	66.2	5.308	7.168
.5	25	6.687	10.0	59.6	5.114	7.647
BLK	50	8.174	.07	67.2	7.193	8.237
.01	50	8.110	.49	68.5	6.346	7.455
.05	50	7.918	1.50	70.4	5.845	7.149
.1	50	7.648	2.65	71.2	5.588	7.169
.25	50	6.851	6.42	66.4	5.194	7.638
.50	50	6.270	10.44	59.1	4.982	8.176
1.0	50	5.964	17.0	49.9	4.770	8.431
0.1*	50	7.864	2.98	82.6	5.545	6.904

\* Initial alk  $\approx 2.2 \text{ meq/l}$ , final alk not measured

\*\* Sample pretreatment - brief ( $\sim 1 \text{ min}$ ) .01 N HCl wash; followed by DDW wash and seawater wash.



Table A4.2. Final data at each pH for beaker experiments.\* (10°C)  
 (Initial  $F^-$  = 67.5  $\mu$ M,  $TPO_4$  = .01  $\mu$ M, alk = 2.30 meq/l)

Sample	pH	$TPO_4$ ( $\mu$ M) <sup>4</sup>	Alk (meq/l)	$F^-$ ( $\mu$ M)	$pHPO_4$	$pPO_4$	Time (hrs)
<u>Experiment #1</u> - initial equilibration							
COW	7.963	4.64	1.26	106	5.364	6.615	290
FAP	8.212	(1.48)	2.33	69.5	5.874	6.877	290
4-28	8.203	.83	2.33	72.5	6.125	7.137	290
<u>Experiment #2</u> - undersaturation - high to low pH							
COW	8.112	4.16	2.03	99.3	5.418	6.521	250
FAP	8.157	1.97	2.29	67.5	5.746	6.804	250
4-28	8.161	1.34	2.30	68.1	5.914	6.967	250
COW	7.507	5.19	(2.25)	86.0	5.312	7.020	200
FAP	7.512	2.44	2.34	71.7	5.640	7.342	200
4-28	7.520	1.61	(2.31)	69.4	5.820	7.515	200
COW	6.810	7.41	2.75	58.1	5.220	7.624	100
FAP	6.770	3.61	2.47	69.7	5.539	7.984	100
4-28	6.760	2.75	2.39	66.4	5.659	8.114	100
<u>Experiment #3</u> - start undersaturated, then low to high pH							
COW	6.717	6.35	2.59	58.3	5.305	7.803	400
FAP	6.721	26.1	2.58	73.6	4.690	7.184	400
4-28	6.683	1.52	2.42	68.7	5.933	8.465	400
COW	8.024	3.25	1.67	98.6	5.521	6.712	440
FAP	8.224	20.8	2.55	74.3	4.728	5.718	440
4-28	8.172	.69	2.28	69.0	6.203	7.246	440

\* Sample pretreatment: Soak in deionized distilled water for 24 hours after crushing, sieving, and ultrasonifying to remove fines. No acid wash. Rinse with seawater prior to experiment. Only seawater washes between experiments 1, 2, and 3.

Table A4.3. Data for repeated 48 hr column equilibrations\* at pH  $\approx$  8.2. Initial values pH = 8.2,  $\text{TPO}_4 = .05 \mu\text{M}$ ,  $\text{F}^- = 67.5 \mu\text{M}$ , alkalinity = 2.30 meq/l

Equilibration #		1	2	3	4	5	6	7	8
PD- 15-17	pH	7.745	7.929	8.025	8.071	8.116	8.143	8.165	8.169
	$\text{TPO}_4$	3.58	2.92	2.59	2.46	2.34	2.25	2.16	2.18
	$\text{F}^-$	51.8	61.5	67.4	69.6	70.8	71.3	72.1	70.3
	Alk	0.80	1.15	1.44	1.66	1.81	1.90	1.99	2.08
COW	pH	7.779	7.940	8.010	8.042	8.069	8.105	8.122	8.130
	$\text{TPO}_4$	9.96	9.94	9.88	9.77	9.53	9.40	9.16	9.17
	$\text{F}^-$	127	132	131	131	130	129	128	124
	Alk	0.91	1.20	1.42	1.62	1.73	1.82	1.88	1.98
4-28	pH	8.154	8.201	8.208	8.193	8.193	8.210	8.215	8.198
	$\text{TPO}_4$	(.20)	--	.18	.09	.10	.09	.08	.09
	$\text{F}^-$	77.3	--	71.4	69.7	69.2	68.9	68.5	67.9
	Alk	2.12	--	2.26	2.27	2.29	2.28	2.29	2.30
SC-2	pH	8.095	8.179	8.193	8.172	8.181	8.193	8.200	8.193
	$\text{TPO}_4$	2.41	1.84	1.58	1.45	1.31	1.20	1.10	1.08
	$\text{F}^-$	74.9	76.7	75.5	73.1	71.8	72.5	71.2	69.7
	Alk	1.87	2.12	2.18	2.21	2.23	2.24	2.26	2.28
PD- 18-30	pH	7.949	8.113	8.157	8.156	8.170	8.190	8.194	8.193
	$\text{TPO}_4$	3.75	3.13	2.84	2.68	2.50	2.37	2.24	2.22
	$\text{F}^-$	54.9	60.9	64.2	64.2	64.7	65.6	66.1	64.9
	Alk	1.31	1.80	2.01	2.13	2.18	2.20	2.23	2.27
AUS-2	pH	8.010	8.161	8.188	8.177	8.186	8.206	8.208	8.205
	$\text{TPO}_4$	.65	.33	.26	.22	.21	.20	.17	.18
	$\text{F}^-$	39.5	52.9	58.6	61.5	62.0	64.2	64.2	63.5
	Alk	1.51	1.98	2.14	2.20	2.23	2.24	2.27	2.30

\* Sample pretreatment: distilled water wash only.

Table A4.4. Data for repeated column equilibrations at pH  $\approx$  7.4.\*  
 Initial values:  $\text{TPO}_4 = .05 \mu\text{M}$ ,  $\text{F}^- = 67.5 \mu\text{M}$ ,  
 alkalinity = 2.30 meq/l.

Equilibration #		1	2	3	4**	5	6
PD- 15-17	pH	7.574	7.483	7.445	(7.40)	7.411	7.400
	$\text{TPO}_4$	4.58	4.87	5.06	4.92	5.27	5.28
	$\text{F}^-$	53.8	50.9	50.2	53.7	52.6	54.8
	Alk	3.37	2.79	2.55	2.41	2.46	2.38
COW	pH	7.560	7.497	7.447	(7.43)	7.418	7.409
	$\text{TPO}_4$	13.5	12.3	11.5	11.0	11.1	10.8
	$\text{F}^-$	97.4	87.2	81.9	80.2	77.2	76.2
	Alk	3.63	3.00	2.71	2.49	2.54	2.45
4-28	pH	7.436	7.402	7.399	(7.39)	7.386	7.393
	$\text{TPO}_4$	.46	.43	.43	.30	.37	.39
	$\text{F}^-$	57.1	62.2	64.2	95.1	66.2	67.3
	Alk	2.51	2.37	2.36	2.35	2.34	2.35
SC-2	pH	7.479	7.420	7.395	(7.40)	7.398	7.396
	$\text{TPO}_4$	3.92	4.05	3.92	3.30	3.68	3.18
	$\text{F}^-$	54.4	56.3	58.2	73.1	62.7	64.4
	Alk	2.76	2.50	2.43	2.39	2.39	2.35
PD- 18-30	pH	7.521	7.431	7.395	(7.39)	7.395	7.396
	$\text{TPO}_4$	4.75	4.92	4.87	4.42	4.60	4.45
	$\text{F}^-$	48.0	49.2	51.2	57.0	57.2	57.9
	Alk	3.03	2.55	2.42	2.36	2.38	2.36
AUS-2	pH	7.495	7.408	7.399	(7.39)	7.389	7.389
	$\text{TPO}_4$	.98	1.12	1.12	.93	1.06	1.05
	$\text{F}^-$	46.1	49.4	53.2	68.6	66.3	64.9
	Alk	2.79	2.42	2.36	2.33	2.36	2.36

\* Sample pretreatment - seawater wash only

\*\* Initial  $\text{F}^- = 99.9 \mu\text{M}$ ; pH estimated from alkalinity and  $\text{P}_{\text{CO}_2}$

Table A4.5. Data for repeated column equilibrations near pH = 7. \*  
Initial values:  $\text{TPO}_4 = .38 \mu\text{M}$ ,  $\text{F}^- = 67.5 \mu\text{M}$ , alkalinity = 2.30 meq/l.<sup>4</sup>

Equilibration #		1	2	3	4	1a**	2a**
PD-15-17	pH	7.111	6.988	7.012	6.990	6.973	6.799
	$\text{TPO}_4$	8.28	9.42	9.37	9.99	6.81	8.50
	$\text{F}^-$	48.0	46.7	48.2	48.2	67.0	62.4
	Alk	3.05	2.80	2.53	2.57	2.05	2.54
COW	pH	7.134	6.997	7.012	6.990	6.937	6.790
	$\text{TPO}_4$	12.7	12.2	11.5	11.4	9.42	10.6
	$\text{F}^-$	60.5	54.9	54.7	53.7	86.7	81.8
	Alk	3.23	2.94	2.60	2.63	1.91	2.57
4-28	pH	7.008	6.912	6.978	6.946	7.033	6.789
	$\text{TPO}_4$	.96	1.09	.94	.98	.51	.82
	$\text{F}^-$	60.9	61.6	63.4	64.2	75.9	66.8
	Alk	2.49	2.39	2.38	2.41	2.35	2.41
SC-2	pH	7.038	6.930	6.980	6.954	7.038	6.714
	$\text{TPO}_4$	6.98	7.92	6.99	7.15	3.72	5.19
	$\text{F}^-$	60.0	60.0	60.2	60.6	76.9	69.1
	Alk	2.69	2.53	2.47	2.52	2.42	2.61
PD-18-30	pH	7.058	6.938	6.976	6.952	6.999	6.786
	$\text{TPO}_4$	6.95	7.69	7.31	7.47	5.19	6.49
	$\text{F}^-$	51.6	50.7	53.6	55.2	72.3	64.0
	Alk	2.74	2.56	2.42	2.49	2.19	2.48
AUS-2	pH	7.017	6.920	6.976	(6.933)	7.012	6.752
	$\text{TPO}_4$	2.50	2.99	2.65	2.79	1.27	2.01
	$\text{F}^-$	57.7	58.2	58.4	60.1	73.7	63.4
	Alk	2.57	2.45	2.38	2.43	2.27	2.46

\* Sample pretreatment - seawater wash only

\*\* Run at 25°C

Table A4.6. pH and  $p\text{PO}_4$  for samples measured at 25°C.

	<u>pH</u>	<u><math>p\text{PO}_4</math></u>	<u><math>\Delta p\text{PO}_4^*</math></u>	<u>pH</u>	<u><math>p\text{PO}_4</math></u>	<u><math>\Delta p\text{PO}_4^*</math></u>
PD-15-17	6.973	6.852	.456	6.799	6.951	.437
COW	6.937	6.711	.546	6.790	6.866	.528
4-28	7.033	7.915	.412	6.789	7.978	.391
SC-2	7.038	7.044	.387	6.714	7.265	(.342)
PD-18-30	6.999	6.942	.471	6.786	7.083	.454
T7-61	7.017	7.712	.429	6.784	7.764	.482
AUS-1	7.023	7.422	.485	6.779	7.542	.482
AUS-2	7.012	7.539	.324	6.752	7.632	.243
Avg. = .429 $\pm$ .157 (2 $\sigma$ )						

\*  $\Delta p\text{PO}_4$  is calculated from  $p\text{PO}_4(10^\circ) - p\text{PO}_4(25^\circ)$  at each pH

Table A4.7. Data for column equilibrations run from supersaturation ( $\text{TPO}_4$ ).  $10^\circ\text{C}$ .  $\text{F}^-$  initial =  $67\ \mu\text{M}$ .

	Initial* $\text{TPO}_4$ $\mu\text{M/l}$	Final $\text{TPO}_4$ $\mu\text{M/l}$	pH	$\text{F}^-$ $\mu\text{M/l}$	Alk meq/l	$\text{pPO}_4$	$\text{pHPO}_4$
PD-							
15-17	5.78	2.88	8.072	70.8	1.77	6.718	5.576
COW	16.6	7.27	7.966	107	1.39	6.418	5.169
4-28	1.13	.08	8.173	59.7	2.34	8.203	7.161
SC-2	5.78	1.17	8.146	63.6	2.19	7.040	5.972
PD-							
18-30	5.78	2.59	8.162	55.4	2.28	6.680	5.628
T7-61	1.13	.19	8.165	59.7	2.28	7.812	6.762
AUS-1	1.13	.42	8.180	60.0	2.33	7.459	6.424
AUS-2	1.13	.10	8.173	55.1	2.33	8.097	7.055
PD-							
15-17	17.0**	8.97	7.157	45.2	3.28	7.150	5.092
COW	17.0	12.7	7.206	63.1	3.72	6.946	4.938
4-28	5.85	1.35	7.038	53.3	2.51	8.103	5.926
SC-2	17.0	7.40	7.072	47.4	2.77	7.327	5.184
PD-							
18-30	17.0	7.69	7.117	43.1	3.05	7.260	5.163
T7-61	5.85	2.19	7.041	53.3	2.50	7.890	5.716
AUS-1	5.85	3.02	7.043	48.6	2.52	7.748	5.576
AUS-2	5.85	1.97	7.079	37.6	2.67	7.894	5.758

\* Preceded by 45-minute soak in 0.01 N NaOH and seawater rinse then a 22-hour pre-equilibration with low- $\text{PO}_4$  seawater.

\*\* Preceded by a ~ 24 hour pre-equilibration from undersaturation at pH  $\approx 7.2$ .

Table A4-8. Data for column experiments run from undersaturation, comparing results in seawater of zero and regular initial alkalinity.

Sample	pH	Initial		pH	Final		Length of run (hours)
		TPO <sub>4</sub> μM/l	Alk meq/l		TPO <sub>4</sub> μM/l	Alk meq/l	
with alkalinity							
COW A	6.382	.06	2.19	6.007	26.2	0.95	64
COW B				6.025	30.9	1.00	
4-28A				6.337	6.29	2.01	
4-28B				6.346	3.46	2.05	
FAP A				6.377	.44	2.18	
FAP B				6.371	.41	2.16	
COW A	6.944	.05	2.20	6.343	36.2	0.54	89
COW B				6.390	39.9	0.64	
4-28A				6.866	2.08	1.82	
4-28B				6.855	1.32	1.83	
FAP A				6.917	.37	2.04	
FAP B				6.909	.29	2.09	
COW A	7.556	.06	2.20	6.733	26.4	.31	66
COW B				6.738	33.4	.31	
4-28A				7.479	.66	1.66	
4-28B				7.495	.42	1.80	
FAP A				7.553	.33	2.02	
FAP B				7.540	.27	1.97	
COW A	8.217	.02	2.19	7.098	18.7	.18	94
COW B				7.134	22.7	.20	
4-28A				8.136	.21	1.80	
4-28B				8.152	.11	1.90	
FAP A				8.226	.22	2.19	
FAP B				8.238	.12	2.26	
without alkalinity						TCO <sub>2</sub> <sup>a</sup> (μM)	116
COW A	7.598	.87	---	5.258	116	n.m.	
COW B				5.397	112	n.m.	
4-28A				6.228	5.60	0	
4-28B				6.389	3.30	0	

Table A4-8. Continued

<u>Sample</u>	<u>pH</u>	<u>Initial</u>		<u>pH</u>	<u>Final</u>		<u>Length of run (hours)</u>
		<u>TPO<sub>4</sub></u> <u>μM/l</u>	<u>Alk</u> <u>meq/l</u>		<u>TPO<sub>4</sub></u> <u>μM/l</u>	<u>TCO<sub>2</sub><sup>a</sup></u> <u>(μM)</u>	
FAP A				7.617	.45	7	
FAP B				7.876	.58	15	
COW A	5.735	.08	---	5.115	141	---	74
COW B				5.226	150		
4-28A				6.249	7.82		
4-28B				5.919	9.27		
FAP A				6.678	.67		
FAP B				6.876	.36		
COW A	7.539	.08	---	5.321	110	---	114
COW B				5.524	105		
4-28A				6.371	4.95		
4-28B				6.707	1.88		
FAP A				7.792	.21		
FAP B				8.029	.16		
COW A	8.039	3.33	---	5.664	52.2		96
COW B				5.748	56.2		96
4-28A*				6.945	2.02		72
4-28B*				7.224	1.11		72
FAP A*				8.013	1.59		96
FAP B*				8.055	2.17		96

Sample treatment: The samples were initially soaked in HCl ~ 1/2 hr, followed by a rinse with distilled deionized water (DDW), then a soak for about 1 hr in DDW. This was followed by a second seawater rinse, soak cycles of ~ 1 hr each. The columns were then rinsed a third time with seawater, and finally filled for the experimental run.

<sup>a</sup> by gas chromatograph - approximate values (μM)

\* Supersaturation with respect to phosphate