



OVERDUE FINES:

25¢ per day per item

RETURNING LIBRARY MATERIALS:

Place in book return to remove
charge from circulation records

SOLUBILITY OF ROCK PHOSPHATES AS INFLUENCED BY CALCIUM
ION ACTIVITY IN SOLUTION AND SURFACE AREA

by

Michael Alan Wilson

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTERS OF SCIENCE

Department of Crop and Soil Sciences

1979

ABSTRACT

SOLUBILITY OF ROCK PHOSPHATES AS INFLUENCED BY CALCIUM ION ACTIVITY IN SOLUTION AND SURFACE AREA

By

Michael Alan Wilson

A laboratory study was conducted to determine the effect of Ca ion activity on the solubility of six rock phosphates. This solubility was examined at 65°C, using neutral ammonium citrate and varying the Ca ion activity from 3.6×10^{-2} to 1.79×10^{-4} M Ca as $\text{Ca}(\text{NO}_3)_2$. A constant ionic strength of 0.15 was maintained with KNO_3 . The results of the study confirm the inverse relationship between solubility and the final Ca ion activity in solution. The theoretical function of this relationship should be: $\text{Log } [\text{P}] = -1.67 \text{ Log } (\text{Ca}) + \text{Log } k$. A plot of the $\log [\text{P}]$ vs. $\log (\text{Ca})$ revealed a straight line function as predicted by theory, but the average slope was -0.98, unlike the theoretical -1.67. No correlation with physical or chemical data could be found to account for this difference in slope.

It was also found that a wide range in solubility occurred between rock phosphates. The surface area of the -150+270 mesh fraction was measured using N_2 gas adsorption. The surface area effect correlated with the difference in solubility for all but the Tennessee rock phosphate, which had a solubility much lower than the surface area would indicate.

DEDICATION

to Dr. O. W. Bidwell

ACKNOWLEDGEMENTS

A special thanks to Dr. Boyd Ellis for his help and concern with my intellectual and personal development. His skills for scientific pursuit are given freely and without hesitation.

I would like to thank the members of my guidance committee, Drs. Max Mortland, Darryl Warncke, and Matt Zabik. Their insight into my work was both valuable and enlightening.

I also appreciate the help of Ms. Teresa Huges and the members of the Soil Chemistry staff.

Finally, I would like to thank all the friends, colleagues, and fellow students who have made Michigan State a very pleasant and developmental part of my life.

TABLE OF CONTENTS

	page
LIST OF TABLES	v
LIST OF FIGURES.	vi
INTRODUCTION	1
LITERATURE REVIEW.	4
MATERIALS AND METHODS.	14
RESULTS AND DISCUSSION	17
LIST OF REFERENCES	33
APPENDIX	36

LIST OF TABLES

Table	Page
1 ACS Solubility Index	13
2 Rock Phosphate Composition	15
3 Slope of solubility and percent change of solubility of rock phosphates between (Ca) of 8.9×10^{-3} and 1.6×10^{-2} <u>M</u>	19
4 Difference of final and initial Ca activity as measured in solution.	28
5 Equilibrium solubility concentrations of Ca and P and their Ca:P molar ratios (of whole rock and -150+270 mesh fraction)	29
 APPENDIX	
I Supplementary data for six rock phosphates	36
II Results and Experimental Data.	37

LIST OF FIGURES

Figure		Page
1	The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of India rock phosphate.	20
2	The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Central Florida rock phosphate. . .	21
3	The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of North Carolina rock phosphate . . .	22
4	The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Tennessee rock phosphate.	23
5	The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Missouri rock phosphate	24
6	The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Idaho rock phosphate.	25
7	The effect of the Ca ion activity (moles/liter) on the solubility (ppm P) of six rock phosphates	26
8	The relationship of surface area (m^2/g) on the solubility (ppm P) of six rock phosphates.	31

INTRODUCTION

Phosphorus, one of the essential nutrients for plant growth, continues to be deficient in many soils. Widespread deposits of rock phosphate are available for conversion to soluble fertilizer forms, but many countries lack the energy and/or technology with which to make use of their natural resource. In some South American and African nations, the availability and cost of importing processed fertilizer may make phosphate application impractical. Because of this, the direct application of phosphate rock may be a suitable recourse to solve this problem.

Phosphate rock is an apatite mineral that is found in deposits around the world. It can be sedimentary, metamorphic, or igneous in origin. Each deposit, being unique within itself, must be given separate evaluation as to whether it is economically feasible to mine. Amount of overburden, thickness of the deposit, %P₂O₅, and location are just part of the consideration necessary. Many of the phosphate beds have unfavorable deposition, being buried under large amounts of waste, or have a steep dip. Although in the past, some deposits have been inconceivable to mine, with new technologies becoming available, more of the deposits are physically and economically attainable.

The use of rock phosphate for direct application as a phosphate fertilizer has several advantages. Among them are the low cost and small energy requirement involved in processing, and the fact that only limited technological skills are necessary to make it ready for

application. The most widely used method for preparation of the rock phosphate is the physical method of grinding, wet screening, or hydro-separation. For a underdeveloped country, these aspects could make a form of phosphate fertilization accessible where a highly processed form may be too costly or unavailable.

Though there are vast reserves of rock phosphate in the world, each deposit differs in the type of rock phosphate; the chemical structure, physical nature, and the amount of waste (non-rock phosphate) present in the deposit. These factors affect the suitability for the use of that particular deposit.

Another aspect of rock phosphate in relation to processed phosphate fertilizers is the decreased solubility. It can be an advantage in the aspect of slow release fertilization, but also a disadvantage if there is a need for immediate uptake of P. This solubility problem is the pivotal aspect in the use of rock phosphates.

The nature of the apatite mineral is only one-half of the picture that determines the solubility. The properties of the soil: pH, ions in the soil solution, and other minerals present, will also have an influence. So, in determining the suitability for the use of a rock phosphate, aspects of the soil as well as a particular rock phosphate must be examined. This is apparent by the fact that the reactivity or solubility for a particular rock phosphate will vary between soils.

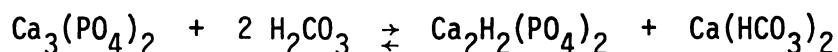
In the past, the influences of the soil that have been studied were limited to pH and how it reacted with various structural components of the apatite mineral. But it is known that the reactivity of a rock phosphate will differ even between soils with the same pH. Thus, other ions in the soil solution must present an influence on rock phosphate

solubility. A common ion present in most soils is Ca. In this study, the effect of Ca ion activity in the soil solution is examined.

LITERATURE REVIEW

Currently, rock phosphate is being examined as a phosphorus (P) fertilizer source for underdeveloped countries. For many years, apatite availability has been compared with other P fertilizer sources, especially superphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$). In making these comparisons, researchers have examined many factors that influence apatite availability. Studies have pointed out factors, such as soil conditions or type of crop, that influence the use of rock phosphate as a fertilizer source.

Truog (28) classified certain plants according to their power to feed on rock phosphate. He suggested that rock phosphate would react with carbonic acid (given off by plant roots) in the soil:



Theoretically, plants that had large uptakes of Ca would shift the reaction to the right by removing one of the products; thereby increasing the breakdown of the rock phosphate.

Cook (16) tested this idea by growing pot cultures of several crops in Ca-saturated and H-saturated exchange materials. He posulated that if a H-saturated exchange material were placed in the system, it would adsorb the soluble Ca by exchange reactions and then even plants that were weak feeders of Ca would utilize rock phosphate more effectively. The results of the experiment confirmed both his and Truog's hypotheses. Cook found that oats (a weak Ca feeder) grew more effectively on the H-saturated exchange material with rock phosphate than on the Ca-saturated

material. Buckwheat (a strong Ca feeder) grew equally well on Ca-saturated or H-saturated material.

Bartholomew (4) tested the effect of F on rock phosphate availability when he found that rock phosphate applied to a soil with a high F content stimulated Sudan grass growth less than rock phosphate applied to a soil with a low F content. His conclusions were that this inverse relationship with F could be used to predict rock phosphate availability. But, in later papers (5,6), this close correlation was not found between F content of the apatite minerals and plant yield. It was acknowledged that F had an influence on rock phosphate solubility, but no strict correlations could be made.

Up to this point (1935), little was known about what conditions would be best for the utilization of rock phosphate. It was known that there was a pH effect on the availability, but little work had been done in regards to this. Joos and Black (21) measured this effect by growing Sudan grass in pots of bentonite-sand mixture. The availability of rock phosphate was found to be fairly high at pH 4.6 and 5.6, but low at pH 6.6. They also examined particle size, finding that the -400 mesh rock phosphate particles exhibited a greater availability than the 150 to 300 mesh. They concluded that the availability of rock phosphates to plants is governed by many more factors than just pH.

Ellis, et al. (17) showed that a pH 6.0 or less was needed for satisfactory availability of P from rock phosphate and that rock phosphate should be applied at least one year prior to liming to be an effective P source. This conclusion was also confirmed by others (19,20,30). They suggested that rock phosphate reacted with soil acidity to become soluble, after which soluble P was transformed into strengite. Upon

liming, the unavailable P was converted from $\text{Fe}(\text{OH})_2\text{H}_2\text{PO}_4$ to a more available phosphate. The formation of Fe and Al phosphate was confirmed by Chu, Moschler, and Thomas (14), who reported that the amount of strengite formed was a function of pH and the soil free Fe content.

Caro and Hill (9) examined particle density, surface area, exchangeable P and chemical solubility of rock phosphates. They correlated yield with each of these factors and found the best correlation to be with citric acid solubility and bound CO_3 content of the apatite mineral. Poorest correlation was with readily exchangeable P and surface area. This result was confirmed by Bennett (5), who found no correlation between surface area of rock phosphate and availability. He concluded that chemical solubility would be a better test for availability than a direct physical measure.

Several authors examined the use of chemical solubility to determine the agronomic effectiveness of rock phosphate. Armiger and Fried (2) concluded ammonium citrate and citric acid solubility tests were "equally effective indexes." Engelstad, et al. (18) and Lehr and McCellan (22) also found ammonium citrate or citric acid solubility to be an effective measure of availability. Lehr and McCellan, in turn, related this solubility to structural substitution of CO_3^- and F^- for PO_4^{3-} .

In a 1958 paper by Armiger and Fried (1), the effect of particle size on P availability was again examined. They found, as in prior studies, that fineness of grind did affect availability, but that fine grinding did not affect all sources alike. In fact, they found that the -100 mesh was only slightly less effective than the -325 mesh size and concluded that other characteristics were more important in determining agronomic effectiveness than was particle size.

F. van der Paauw (29) examined factors controlling the efficiency of rock phosphates for potatoes and rye on humic sandy soils. The two factors found to control the availability of P were pH and fixing capacity of the soil. By comparing two rock phosphates with monocalcium phosphate, he found that a high fixing capacity of a soil depressed the availability of rock phosphates more than monocalcium phosphate. Also, pH had a significant effect on rock phosphate availability, but little or no effect on the monocalcium phosphate. His results showed that pH was inversely proportional to the amount of water-soluble P in the soil solution. In summery, van der Paauw mentions that rock phosphates are not effective when the aim is complete elimination of P deficiency. To achieve this, soil pH would need to be lower than is optimal for plant growth.

The author also mentioned the effect of microorganisms and plants on the solubility of rock phosphates. Even though van der Paauw discredits any overwhelming effect by plants, Butkevich (8), claims that the breakdown of rock phosphates is more a plant than soil effect. He states that the soil is "primarily a medium which determines the interaction of the plants with the phosphorite rather than a factor operating directly in its decomposition". Thus, he suggests that soils are important only in that they determine the capacity of plants to breakdown the rock phosphate.

From the literature, it can be seen that there are many factors which contribute to the solubility and availability of rock phosphates for plants. Soil factors, such as pH, and Ca and Fe activity, contribute as much as plant species or type of rock phosphate.

Prior to 1950, apatites were considered to be a basic Ca phosphate, present in a solid phase, but it was questioned as to whether they had

a unique mineral structure, crystalline form, and if it could be characterized by a unique solubility. In 1955, Clark (15) reported that hydroxyapatite could be described by: $pK_{sp} = 115.5 = 10pCa + 6pPO_4 + 2pOH$. But many other investigators could not varify this value "in vitro" or in aqueous solutions equilibrated with soils. In 1971, Weir, Chien, and Black (29) reported two pK values to describe the solubility. Several other workers also found two pK_{sp} values for hydroxyapatite, one close to Clark's value and another of lower value, indicating greater solubility. The results of various workers have shown that hydroxyapatites do have a solubility constant, but not all found the same solubility, even though the hydroxyapatites used have the same structural formula.

The solubility of a commercial hydroxyapatite was tested by Weir, et al. by varying the solid/solution ratio (0.1, 0.5, 1.0, and 10 g/100 ml solution). All solutions followed a constant solubility line except the 0.1 g sample which tended to diverge in the direction of lower solubility at high values of $-\log (Ca)(OH)_2$ or low pH. They formulated four hypotheses to explain this divergence:

- 1) Incomplete saturation of solutions.
- 2) Presence of small amounts of F impurity.
- 3) Development of a surface complex that controlled solubility.
- 4) Hydroxyapatite had a range of "activities" ** and that the higher "activity" dissolved preferentially.

The first three were determined to be false, and it was the fourth hypothesis that they concluded to be true. They reasoned that no divergence was found with 0.5, 1.0, and 10.0 g samples because so little of the solid dissolved that all the solutions were in equilibrium with essentially the same solid with high reactivity. They contended that at

** This use of "activity" is not in the usual physical chemistry sense, but implies physical reactivity.

high pH values, the 0.1 g sample fell on the line because, again, little of the solid was dissolved. As the pH decreased, the solutions were in equilibrium with a solid of lower physical reactivity, thus causing the divergence.

To test the hypothesis that the divergence of points represent a succession of solids with differing reactivity, they preformed an experiment using large quantities of residual solids (after treatment with 1N NH_4Cl to remove the more soluble fraction) and obtained a line with a constant slope (slope = $-\text{Ca}^{++}/\text{PO}_4^{-3}$). Thus, they concluded that hydroxyapatites had a range of reactivities and solubilities and associated them with some physical parameters such as the degree of crystallinity of the solids. This conclusion related the difference not to chemical properties, but to the physical differences of the apatite.

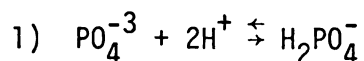
In another paper by Chien and Black, The Activity Concept of Phosphate Rock Solubility (12), this theory was also found to apply to the apatite in rock phosphate. They preformed three experiments to test the solubility hypothesis on a mineral of the formula $[\text{Ca}_{9.74} \text{Na}_{0.21} \text{Mg}_{0.05} (\text{PO}_4)_{5.19} (\text{CO}_3)_{0.81} \text{F}_{2.32}]$. These experiments varied both solid/solution ratio (1 and 10 g/100 ml solution) and the solution used to dissolve the rock phosphate (HCl and alkaline ammonium citrate). The results of all experiments varified that the "activity" concept was applicable to rock phosphate. The third experiment was the most illustrative. Both 1 and 10 g samples per 100 ml solution were extracted with HCl three times, and the six sample solutions were designated as: 7, 16, or 27% extracted (by weight) and compared with unextracted samples. Over an acid pH range, the 1 g sample showed a lower solubility than the 10 g sample; but after preliminary extraction, the percent extracted

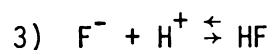
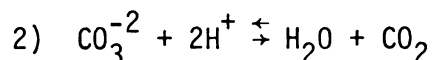
did not influence the solubility constant. Therefore, this paper verifies the conclusion that rock phosphates as well as apatites display two separate solubilities.

It should again be noted that many workers assumed that all rock phosphates were composed of the same basic mineral, and thus, differences in reactivity could be attributed to physical rather than compositional parameters. Recent research shows that most commercial rock phosphates are a CO_3 apatite in which some CO_3 and F have substituted for PO_4 . Subsequent work by McCellan and Lehr (24) and Chien and Black (12,13) have shown that "phosphate rocks are not fluorapatite admixed with other substances, but that they are a series of carbonate-substituted apatites, in which fluorapatite is an end member" (10).

In fact, many of the physical parameters can be directly related to the chemical composition. In 1972, Lehr and McCellan (22) found that the amount of CO_3 substitution was directly related to the unit cell length and the solubility. They reported that citrate soluble P of an apatite in rock phosphate increased with a decrease in CO_3 substitution.

Chien outlined the dissolution thermodynamically in a 1977 paper (10), in which he found that the free energy of dissolution, ΔG_d , equal to 163.3 kcal for a CO_3 apatite of the average formula, $\text{Ca}_{10-0.42x} \text{Na}_{0.3x} \text{Mg}_{0.12x} (\text{PO}_4)_{6-x} (\text{CO}_3)_x \text{F}_{2+0.4x}$. The positive value of dissolution means that some driving force is needed in order to stimulate dissolution. The driving force provided is the H^+ in the soil solution. In the pH range of 3.5 to 6.5, the acid soil range in which rock phosphate is most responsive, the following reactions take place with CO_3 apatites:





By the result of the reactions, the influence on reactivity for CO_3 apatite may be derived and described by the following equation:

$$\Delta G_r = -(2.5 + 14.8x)$$

with x representing the substitution of OH for F ions and ranging from 0.0 to 2.0. The results show that with increasing CO_3 and OH substitution, the ΔG_r becomes increasingly negatively and thus, more reactive.

Lehr and McCellan (22) characterized a number of rock phosphates. In this characterization, they used the solubility index based on apatite composition and did not relate the "citrate-soluble P_2O_5 as a fraction of the total P_2O_5 content (grade) of the particular rock sample." Instead, they associated the P_2O_5 solubility with the kind of apatite supplying the P_2O_5 . This statistically derived index, "Absolute Citrate Solubility" for a given rock is:

$$\text{ACS} = \frac{\text{AOAS Cit-Sol } \text{P}_2\text{O}_5 \text{ (\%)}}{\text{Theor. } \text{P}_2\text{O}_5 \text{ (\%) of Apatite}}$$

This is defined as the ratio of the citrate-soluble P_2O_5 content to the theoretical P_2O_5 of a particular rock phosphate. This basis of defining the solubility was devised to be a guide to the reactivity and effectiveness of each rock phosphate. Because of the wide range of variables that account for the solubility and potential use of each apatite mineral for direct application, this index is quite helpful to evaluate the individual rocks. By using this guide, McCellan and Lehr were able to standardize the value and potential of a wide range of rock phosphates. In the past, many false assumptions had been made by investigators concerning the value of a particular rock phosphate. Among these were

assumptions that the difference in agronomic response could be attributed solely to physical properties, such as particle size and surface area. Studies show that these are only contributing factors, and that apatite composition is one of the primary factors in determining response. The use of the "Absolute Citrate Solubility" stabilized the variability between theoretical and actual response.

With this basis of relating solubility to apatite composition, it was also found that the length of the a-axis of the apatite unit cell, a_0 , (determined by x-ray powder diffraction) is statistically related to the ACS by:

$$ACS = 421.4 (9.369 - a_0)$$

By thorough investigation, it was found that these two methods were in close agreement (Table 1).

TABLE 1. ACS Solubility Index

TVA No.	Rock Phosphate Source	a_0^s	Solubility Index (ACS)	
			x-ray	Chemical
MR-464	Central Florida (Polk County Peeble)	9.345	10.1	14.0
MR-465	Idaho Shale Phosphorite	9.356	5.48	9.37
MR-467	North Carolina clastic phosphorite	9.322	19.8	22.6
MR-468	Tennessee Brown (Columbia, Tenn)	9.358	5.06	13.7
MR-469	India (Jhamar-Kotra)	9.365	1.69	5.1
MR-505	Missouri (by-product concentrate)	9.373	1.20	1.20

a_0^s = length of a-axis of apatite unit cell.

MATERIALS AND METHODS

I. Rock Phosphates.

The rock phosphates used in this study; Central Florida, Idaho, North Carolina, Tennessee, India, and Missouri, were characterized in detail by Lehr and McCellan (22). They determined apatite composition (Table 2) and theoretical citrate solubility. The rock phosphates used in this study were selected to represent a cross-section of available, but differing forms. The Missouri rock phosphate is of an igneous origin, the India is metamorphic, and the others sedimentary. They vary in Ca content from 42.3 to 54.2% and their P_2O_5 content ranges from 29.9 to 40.1%.

II. Experimental Methods.

The solubility of the rock phosphates were tested in neutral ammonium citrate solution (pH=7) (3). The solid/solution ratio used was 1 g/100 ml, and the 250 ml flasks were shaken in a water bath at 65°C for 24 hours. Eleven different levels of Ca were added, using $Ca(NO_3)_2$, and keeping the ionic strength constant at 0.15 with KNO_3 . Also, the solubility of the rock phosphate and the -150+270 mesh fraction (wet sieved) was tested with no $Ca(NO_3)_2$ or KNO_3 added to the solutions. Two replications were made of both experiments.

In order to prepare the solutions for analysis, they were passed through a 0.45 μ m millipore filter. It was discovered that the solutions had an excessively high salt content, thus preventing color

TABLE 2. Rock Phosphate Composition[†]

Component	ROCK PHOSPHATE, %					
	India	Central Florida	North Carolina	Tennessee	Missouri	Idaho
CaO	54.2	47.5	48.6	42.3	50.1	46.8
P ₂ O ₅	40.1	32.7	29.9	30.7	34.7	32.3
F	3.6	3.6	3.5	3.2	3.4	3.2
CO ₂	0.7	3.3	5.4	1.4	2.8	2.4
Na ₂ O	0.11	0.66	0.99	0.40	0.27	0.96
K ₂ O	0.02	0.15	0.13	0.65	0.16	0.36
MgO	0.04	0.32	0.55	0.28	0.63	0.37
Al ₂ O ₃	0.30	1.20	0.46	1.40	0.34	1.10
Fe ₂ O ₃	0.40	1.45	0.68	1.20	2.60	0.44
SiO ₂	1.2	5.2	1.6	10.00	2.8	5.4
S	<0.01	0.4	1.1	0.2	0.08	0.9

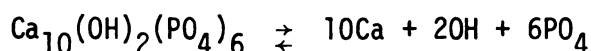
[†]From Lehr and McCellan (22).

formation during the analysis of P. To reduce this salt content in solution, a 10 ml aliquot was dried on a sand bath and ashed in a muffle furnace at 400°C (25). Extensive testing was performed in order to insure no volatilization of P. The ash was then brought back into solution with 6N HCl and P was analyzed by the use of a Technicon-Autoanalyzer II (880 nm), employing the Ascorbic Acid-Molybdate colorimetric method.

The Ca ion concentration was measured with a Perkin-Elmer 303 Atomic Adsorption Spectrophotometer. Lanthanum oxide was used to stabilize the matrix. The surface area of the -150+270 mesh fraction was measured using a Perkin-Elmer Shell Model 212B Sorptometer. The N₂ adsorption procedure was employed with the continuous flow method of Nelsen and Eggertsen (26). The results were plotted by the 3-point BET method (7).

RESULTS AND DISCUSSION

Rock phosphate solubility is influenced by chemical and physical factors. The chemical makeup of each rock phosphate has a large effect on its solubility, with the important components being CO_3 , PO_4 , Ca, and F or OH. The influence of Ca can be examined in more detail by looking at a hydroxyapatite and its breakdown upon dissolution:



with the solubility constant, K° , equal to

$$K^\circ = (\text{Ca})^{10} (\text{OH})^2 (\text{PO}_4)^6$$

The total P measured in solution is:

$$\text{Total P} = \text{H}_2\text{PO}_4^- + \text{HPO}_4^{=} + \text{PO}_4^{-3}$$

or:

$$\text{Total P} = (K^\circ)^{1/6} (\text{Ca})^{-5/3} (\text{OH})^{-1/3} \left(\frac{\text{H}^2}{K'K''} + \frac{\text{H}}{K''} + 1 \right)$$

Looking at the effect of Ca on the total P, it can be seen that P measured in solution or the solubility of rock phosphate is a function of $\text{Ca}^{-5/3}$ or $[\text{P}] = k (\text{Ca})^{-5/3+}$. By taking the log of both sides, the equation becomes $\log [\text{P}] = -5/3 \log (\text{Ca}) + \log k$. Therefore, if rock phosphate is allowed to come to equilibrium in a solution where only Ca activity is varied, a plot of $\log [\text{P}]$ vs. $\log (\text{Ca})$ should yield a straight line with a slope of -1.67. Any deviations from this should be attributed to compositional or experimental factors. For example, the effect of substitution of other ions for Ca would tend to reduce the

⁺"k" is a constant that includes K° , K' , and K'' .

slope, while any substitutions for PO_4^{-3} would increase it. Chien (11) looked at the influence of chemical substitution on the solubility and called this effect one of the key factors in determining solubility.

There are several independent variables that influence solubility. The physical factors are surface area (SA), and particle density (pd), while the chemical influences are Ca, CO_3 , and OH or F. The other factors that affect the solubility are the experimental conditions of the experiment. All of these factors were held constant, but have an effect on the dissolution. They include temperature ($T=65^\circ\text{C}$), pressure ($\text{Pr}=1 \text{ atm}$), and solid/solution ratio ($\text{S/S}=1 \text{ g/100 ml}$).

The solubility, or change in solubility of the rock phosphate (as expressed by the amount of P in solution) is a function of all the physical and chemical factors and may be represented mathematically as:

$$P = f(\text{Pr}, T, \text{S/S}, \text{pd}, \text{SA}, \text{CO}_3, \text{OH}, \text{F}, \text{Ca})$$

If these are independent variables, the total differential may be written:

$$\begin{aligned} dP = & \frac{\partial P}{\partial \text{Pr}} d\text{Pr} + \frac{\partial P}{\partial \text{S/S}} d\text{S/S} + \dots \\ & \dots + \frac{\partial P}{\partial \text{Ca}} d\text{Ca} \end{aligned}$$

(Pr, T, S/S, pd, SA, CO_3 , OH, F, Ca)

The function $\frac{\partial P}{\partial \text{Ca}} d\text{Ca}$ may be evaluated for a single rock phosphate if all other independent variables are held constant. From the solubility product, it is expected that the function $\frac{\partial P}{\partial \text{Ca}} d\text{Ca}$ should be $[P] = k (\text{Ca})^{-5/3}$. This function varies between rock phosphates because many of the factors that are held constant for a single rock are now variable. Looking at two different rocks and their solubilities, the P, T, and S/S still remain constant, while SA, pd, CO_3 , OH, and F become variable and

influence the difference of solubility at a certain level of Ca in solution.

The results confirm that there is decreasing solubility with increasing Ca ion activity in solution. Figures 1 thru 6 show the results, plotted as $\log [P]$ vs. $\log (Ca)$. The linear regressions (r^2) of 0.86, 0.91, 0.93, 0.94, 0.98, and 0.99 show a very good fit of experimental data to the theoretical function. But the average slope of -0.98 was much less than the theoretical -1.67. The solubility theory predicts that slopes will vary by substitution of Ca and PO_4 , as well as other factors, but an examination of the known chemical and physical properties of these rock phosphates showed nothing that correlated with the reduced slopes (See Appendix I).

Table 3. Slope of solubility and percent change of solubility of rock phosphates between (Ca) of 8.9×10^{-3} and 1.6×10^{-2} M.

ROCK PHOSPHATE	SLOPE	%DECREASE IN SOLUBILITY
India	-0.69	32
Central Florida	-0.70	32
North Carolina	-1.01	45
Tennessee	-1.08	47
Missouri	-1.17	49
Idaho	-1.22	49

Table 3 reveals the slopes and the associated change in solubility of the rock phosphate with varying Ca ion activity. Four of the rock phosphates were rather uniformly affected by Ca activity, but the India and Central Florida were less affected.

Figure 7 shows how each rock phosphate has its own solubility range. The North Carolina and Central Florida rock are highly soluble.

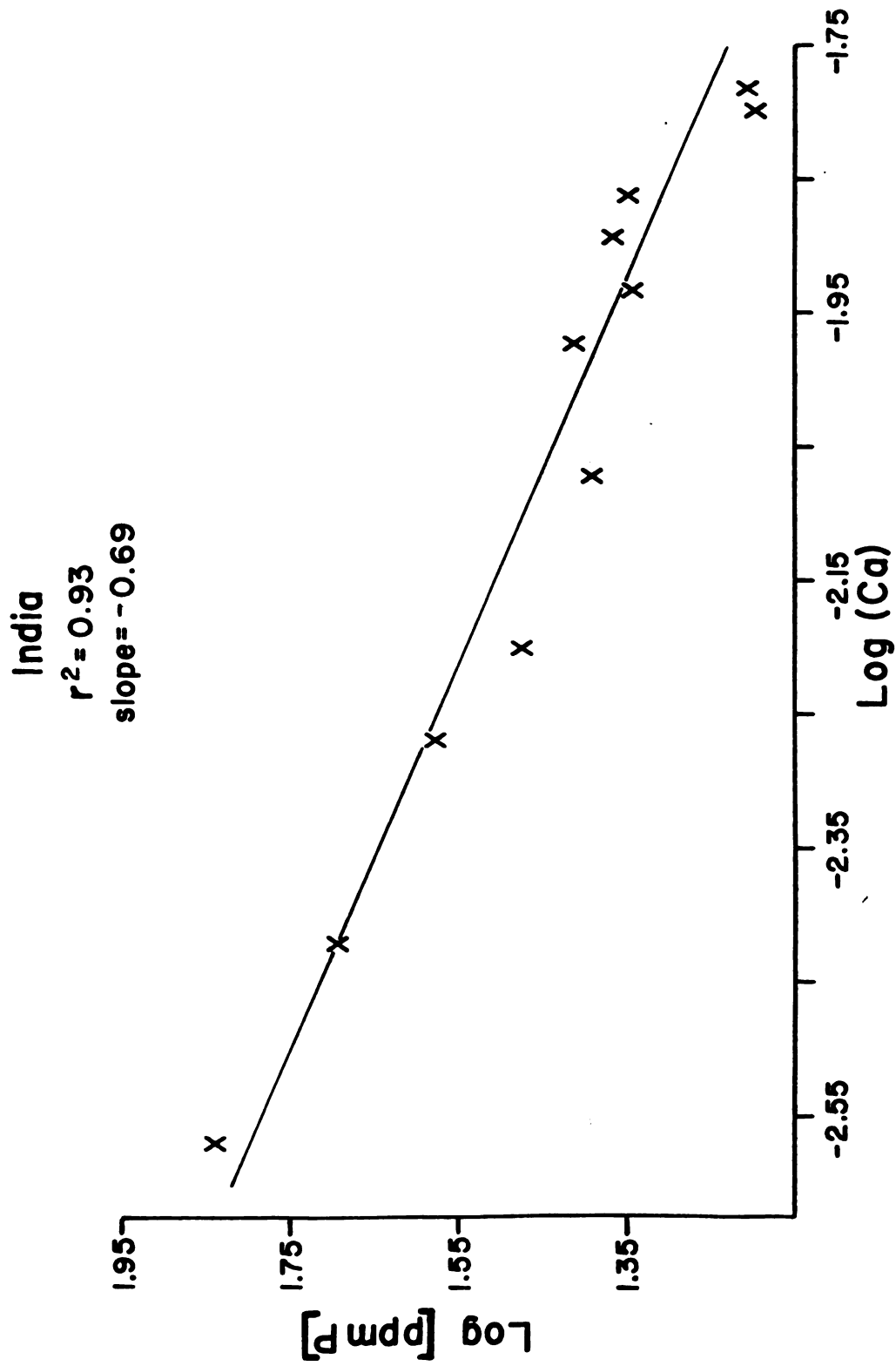


Figure 1. The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of India rock phosphate.

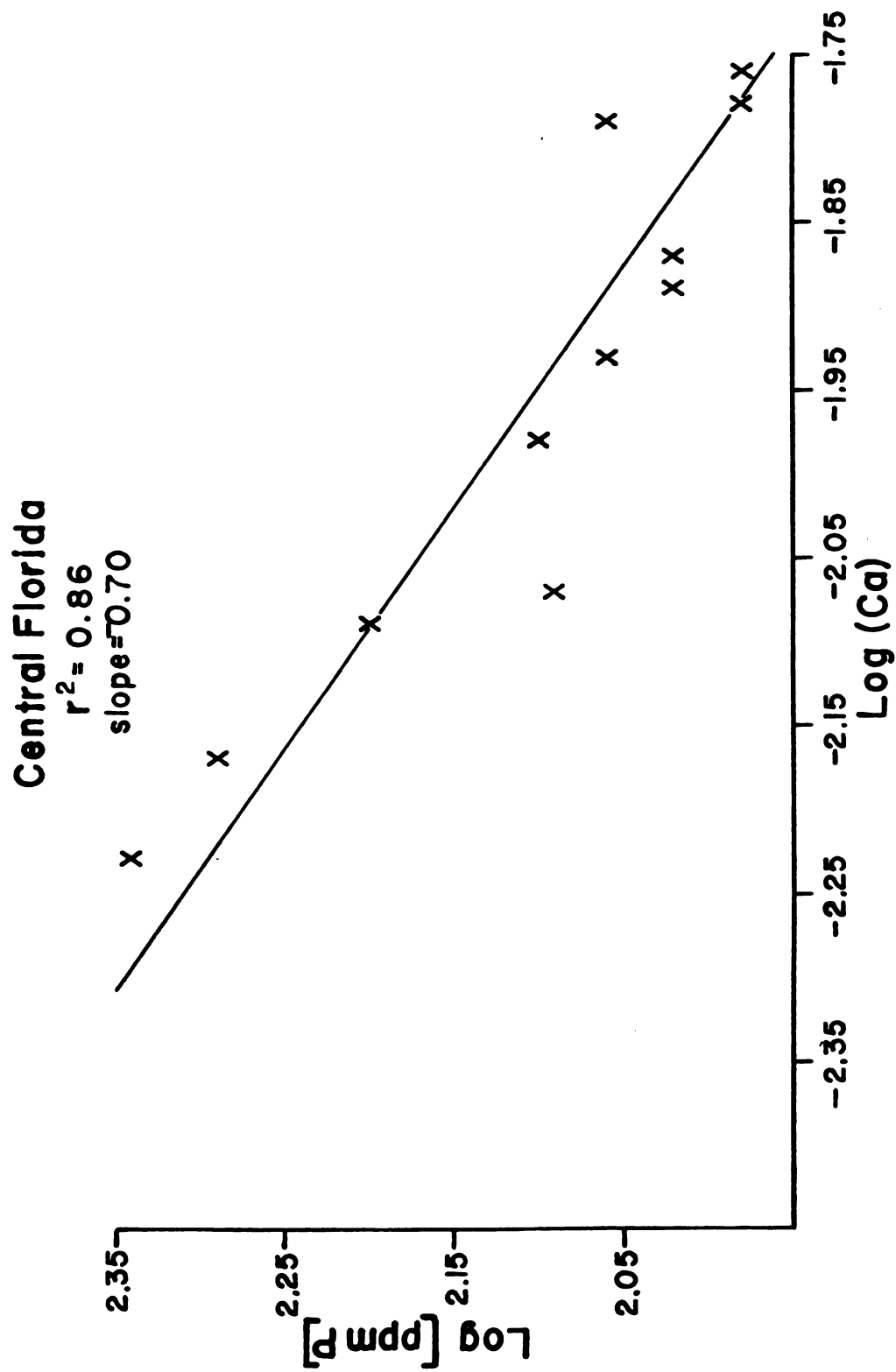


Figure 2. The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Central Florida rock phosphate.

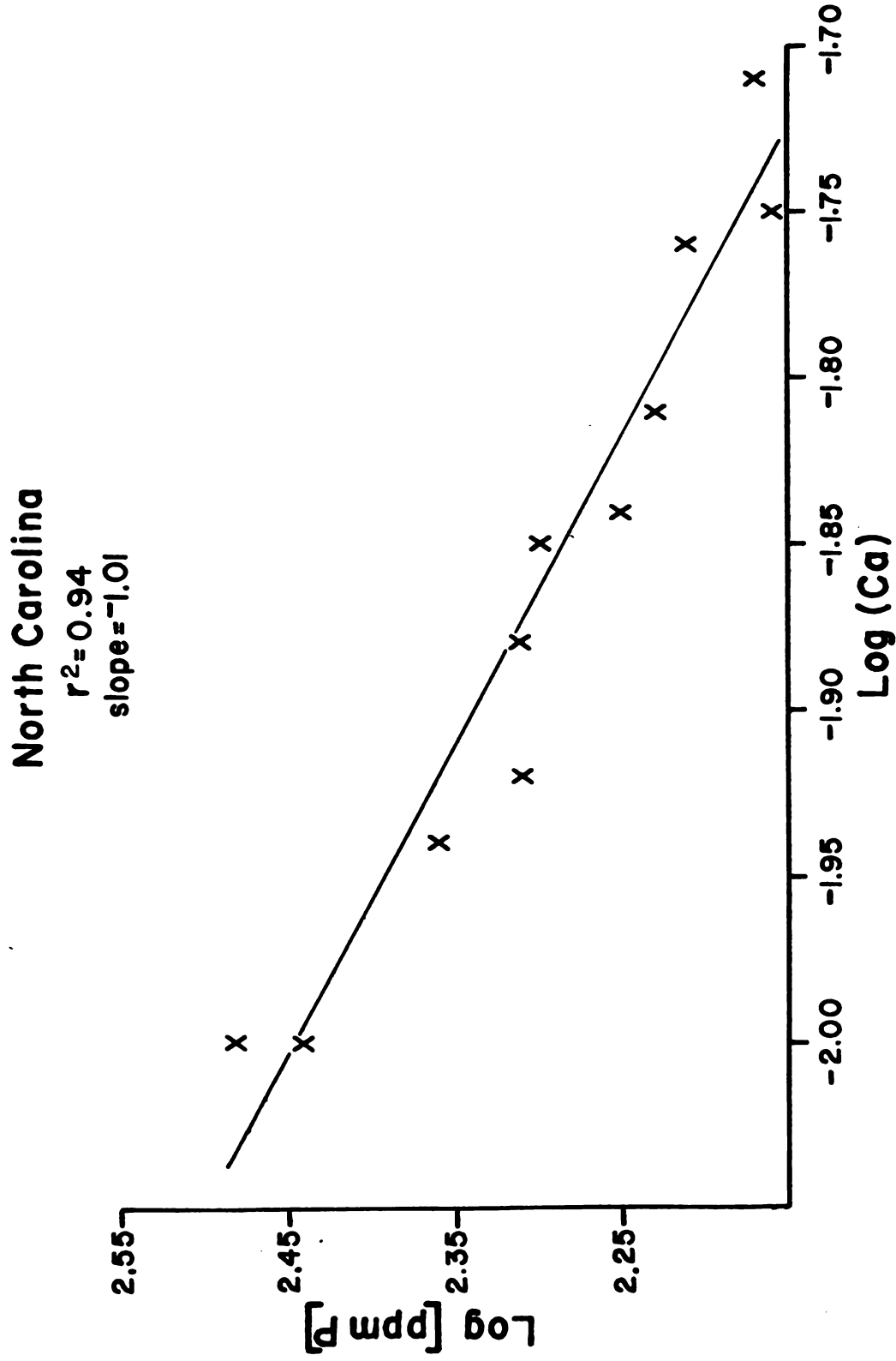


Figure 3. The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of North Carolina rock phosphate.

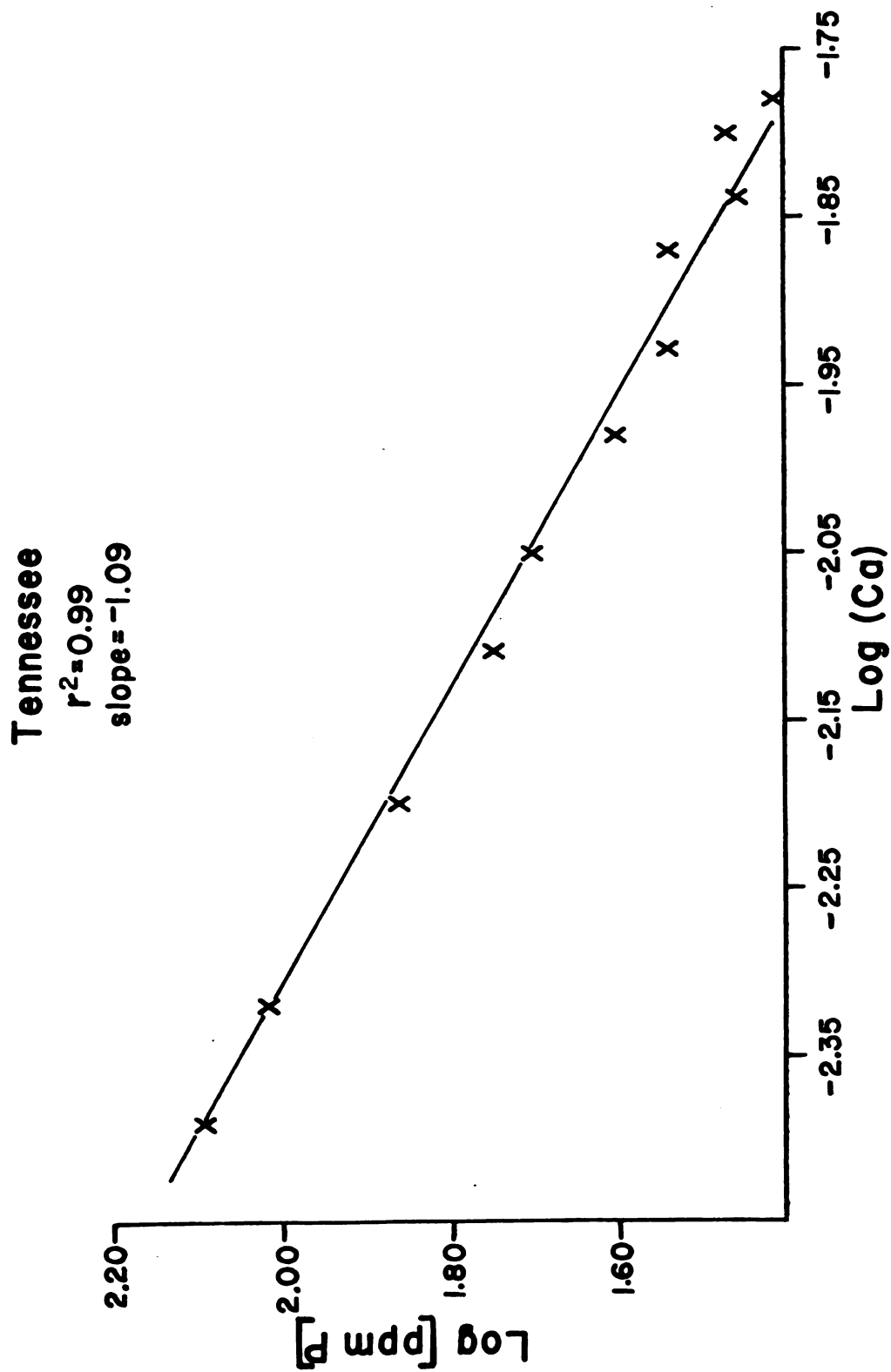


Figure 4. The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Tennessee rock phosphate.

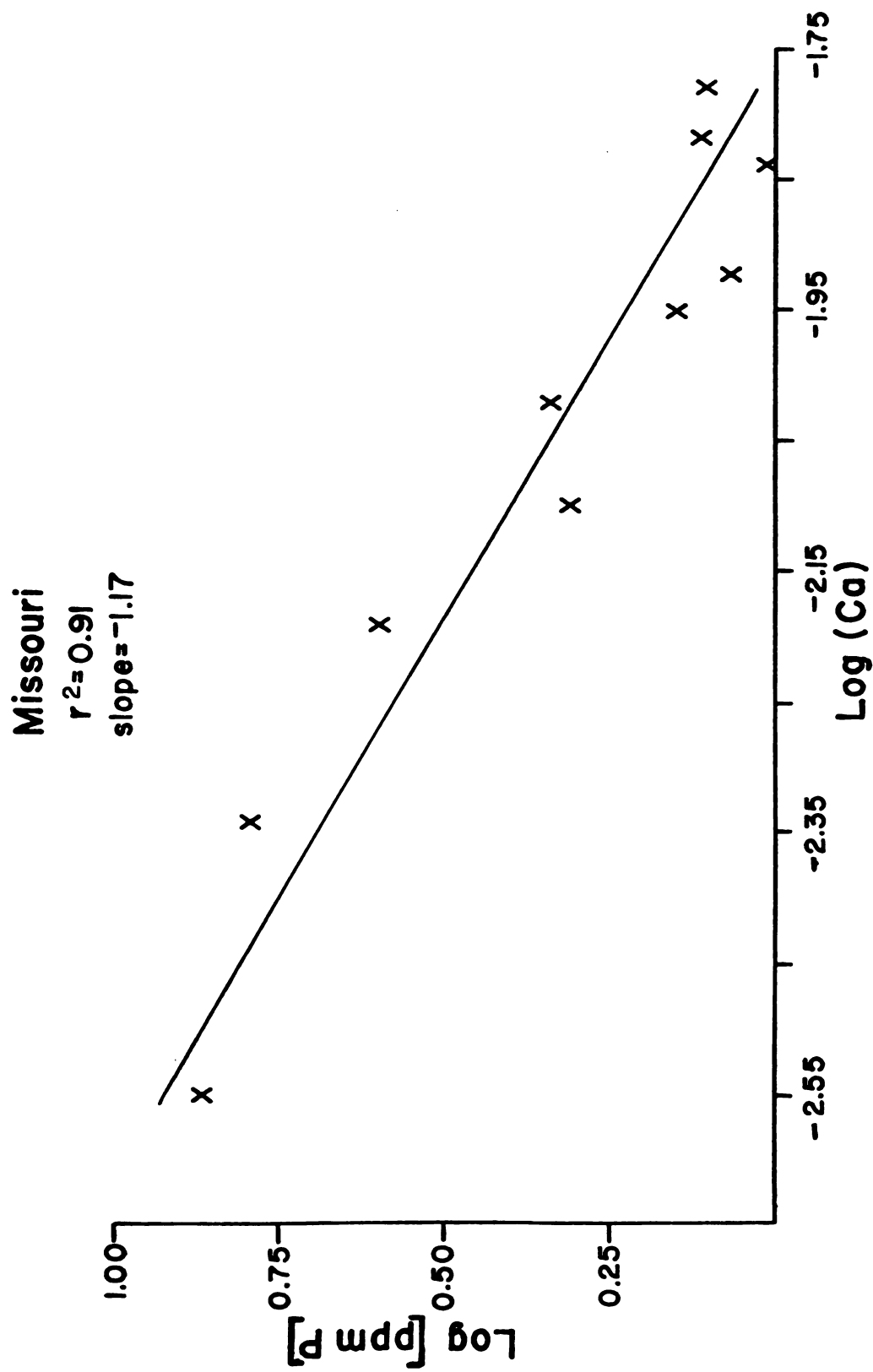


Figure 5. The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Missouri rock phosphate.

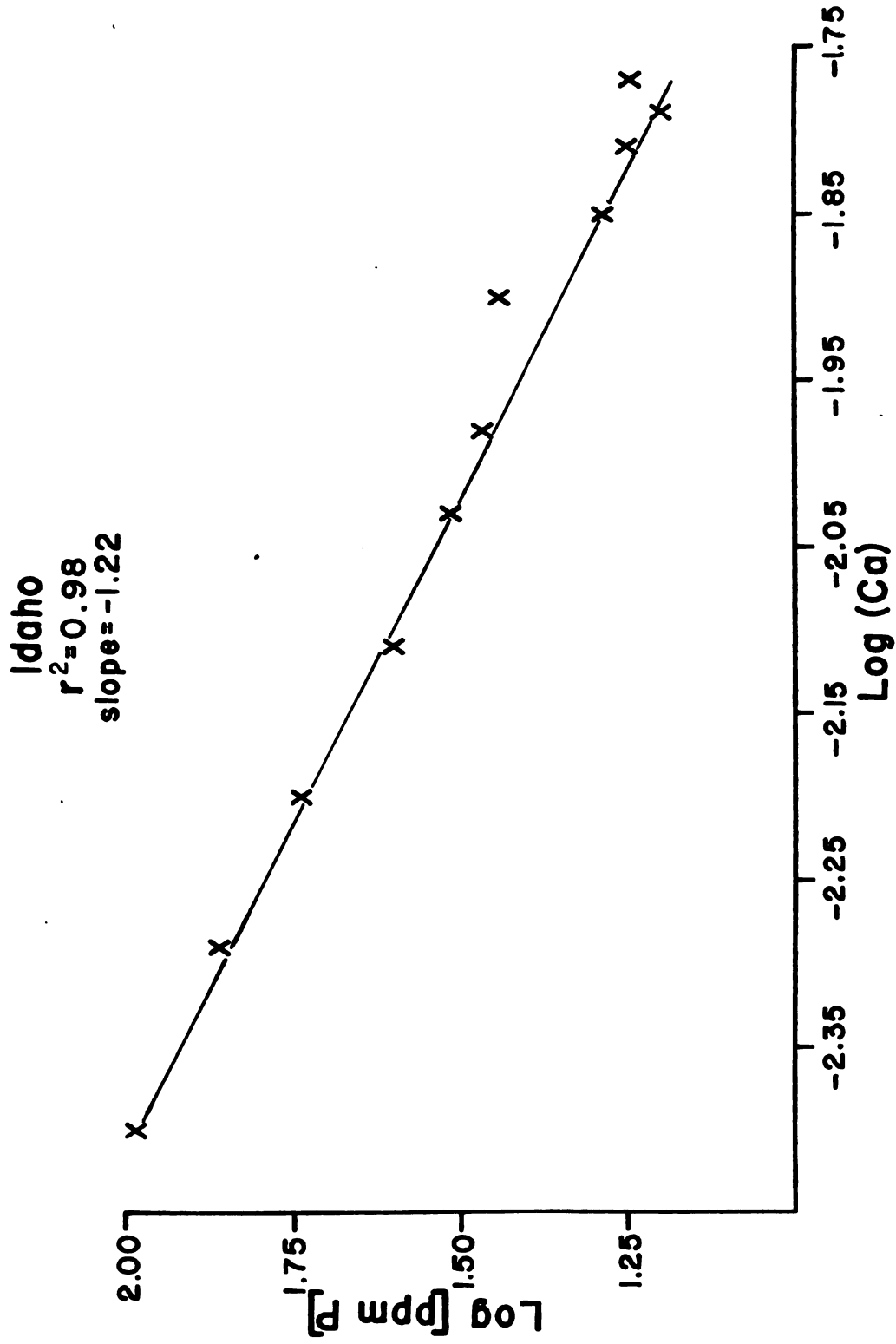


Figure 6. The effect of Ca ion activity (moles/liter) on the solubility (ppm P) of Idaho rock phosphate.

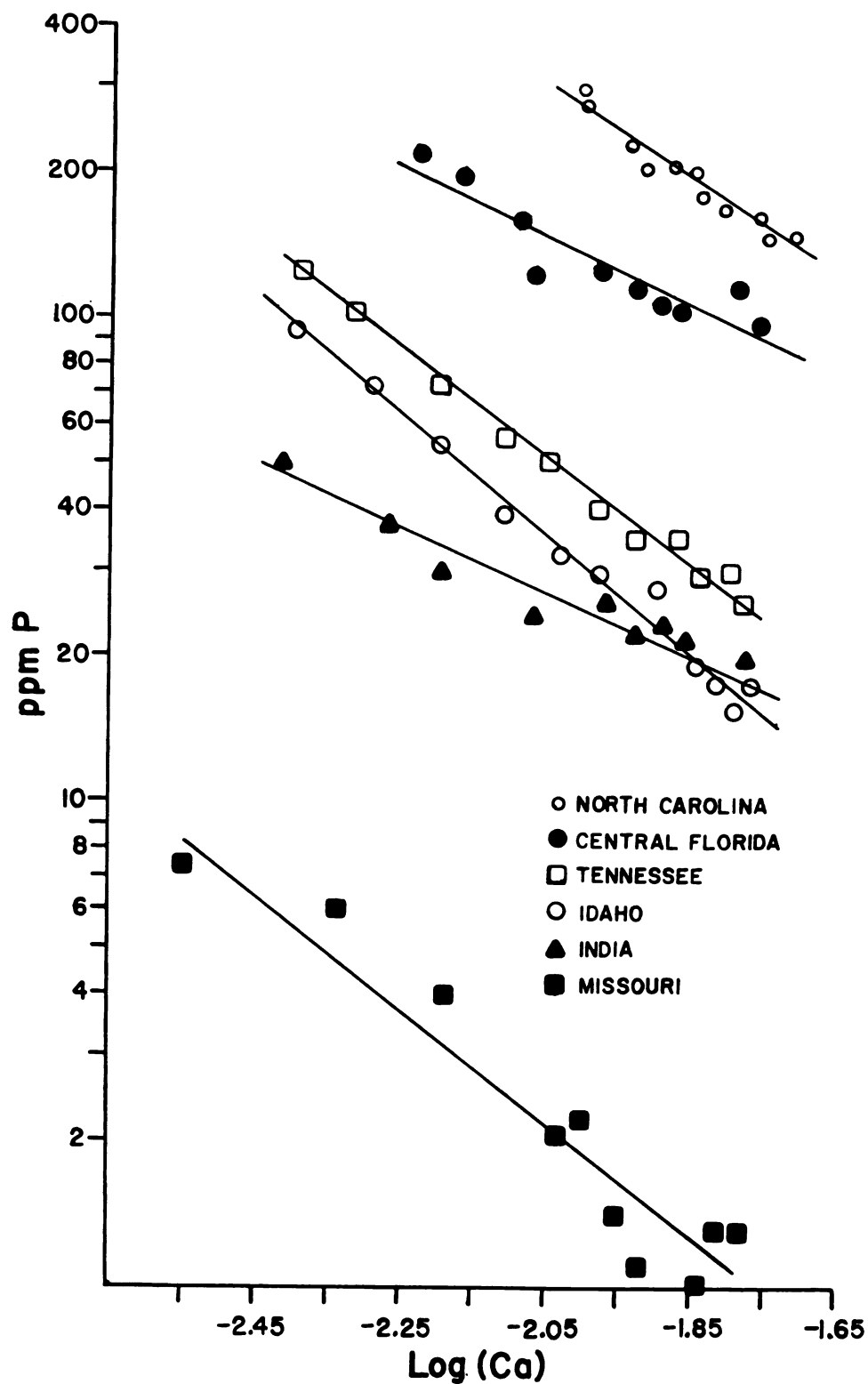


Figure 7. The effect of the Ca ion activity (moles/liter) on the solubility (ppm P) of six rock phosphates.

The Tennessee, India, and Idaho rocks are grouped together at a lower solubility, while the Missouri rock is by itself, almost insoluble.

The initial and final Ca activities were measured for the experiment. Table 4 presents the difference of these activities, which indicates the degree of dissolution of the rock phosphate. As the Ca ion activity is increased in the sequence of solutions, this difference decreases. This shows the decrease in solubility of the rock phosphate as the Ca activity increases. At the higher Ca activities, some of the solutions show a loss of Ca. These losses are very small and seemingly insignificant, but may suggest the precipitation of some Ca compound in solution (eg. CaF_2).

A series of solutions had no initial addition of $\text{Ca}(\text{NO}_3)_2$ or KNO_3 . For these solutions, the equilibrium concentration of Ca and P was measured and the Ca:P molar ratio was calculated (Table 5). Theoretically the ratio is 1.67, but the results show that for all rock phosphates, the Ca:P ratio is slightly higher. The Missouri rock is 10 times higher than the others at 20.08 for the whole rock phosphate, while the molar ratio for the -150+270 mesh fraction is 28.00. This is an indication of the impurity of the rock phosphates. One impurity is the presence of the alkaline earth carbonates. These carbonates, which contain Ca, Sr, and Ba, are easily soluble, and are very abundant in the Missouri rock.[†] This would explain the high Ca:P ratio. A small amount was also detected in the Idaho and North Carolina rock, which have slightly higher ratios than the others, but the presence of these carbonates does not seem sufficient to explain the higher than expected ratios completely. Another possibility could be the presence

[†]Chien, S. H., and C. A. Black. (13)

Table 4. Difference of final and initial Ca activity as measured in solutions.

INITIAL CA ACTIVITY ($\times 10^3$)	(Ca) _{final} - (Ca) _{initial} ($\times 10^3$)					
	INDIA	CENTRAL FLORIDA	NORTH CAROLINA	TENNESSEE	MISSOURI	IDAHO
0.36	2.3	5.6	9.5	3.7	2.4	3.6
1.80	2.0	4.9	8.2	3.0	2.4	3.4
3.60	1.7	4.5	7.9	2.7	2.8	2.8
5.40	0.9	3.1	6.7	2.3	2.6	2.4
7.10	1.4	3.5	6.2	1.9	2.5	2.2
8.90	1.7	3.0	5.3	1.6	2.3	1.5
10.70	1.2	2.3	3.7	1.2	1.2	1.9
12.50	0.5	1.1	3.0	1.1	2.0	1.8
14.30	-0.3	1.8	3.2	0.1	0.9	1.0
16.10	-0.2	0.6	1.9	-0.2	0.4	0.1
17.90	-1.3	-0.6	1.6	-1.2	-1.2	-0.8

Table 5. Equilibrium solubility concentrations of Ca and P and their Ca:P molar ratios (of whole rock and -150+270 mesh fraction).*

Source	Equilibrium solution (whole rock)			Equilibrium solution (-150+270 mesh fraction)		
	Ca	P	Ca:P ⁺	Ca	P	Ca:P
	ppm			ppm		
India	289	82	2.73	199	58	2.65
Central Florida	755	236	2.48	710	225	2.43
North Carolina	1240	355	2.70	1100	325	2.62
Tennessee	471	153	2.38	460	155	2.29
Missouri	252	9.7	20.10	278	7.8	28.00
Idaho	488	113	3.33	460	118	3.00

*These solutions had no $\text{Ca}(\text{NO}_3)_2$ or KNO_3 initially added.

⁺molar ratio

of Ca in the rock phosphate structure which is not associated with PO_4 .

Other factors which vary from rock to rock may influence P release. One of these factors, surface area, was measured in this study (Figure 8). Except for the Tennessee rock, there was a very good, curvilinear relationship between the solubility and surface area of the rock as measured by N_2 adsorption. The two relatively insoluble rocks (India and Missouri), which were not sedimentary rock phosphates, but metamorphic and igneous respectively, had surface areas less than $1 \text{ m}^2/\text{g}$. But the failure of the Tennessee rock to dissolve at a high level as indicated by the surface area of $12 \text{ m}^2/\text{g}$, shows that factors other than surface area may also affect solubility. A possibility may be the impurity of other clay minerals in the rock phosphate. An indication of this is the high SiO_2 content (10.0%) of the Tennessee rock phosphate (See Table 2).

Another factor that has an influence on solubility is crystallinity. An example of this is the Missouri rock, which is made of large crystals. Whereas, the other rock phosphates have many smaller particles that are easily soluble, the Missouri rock does not. Along the same line, the origin of the rock plays a factor. All are sedimentary except the India and Missouri, as mentioned above, and their smaller, less crystalline particles account for part of their solubility, as opposed to the more crystalline igneous and metamorphic type. This effect was measured by surface area.

The other factors which account for the differences in curve fit are most likely chemical (i.e. structural composition). This has been discussed previously and appears to be a major factor in the differences. The experimental factors also play a part in the diversity of

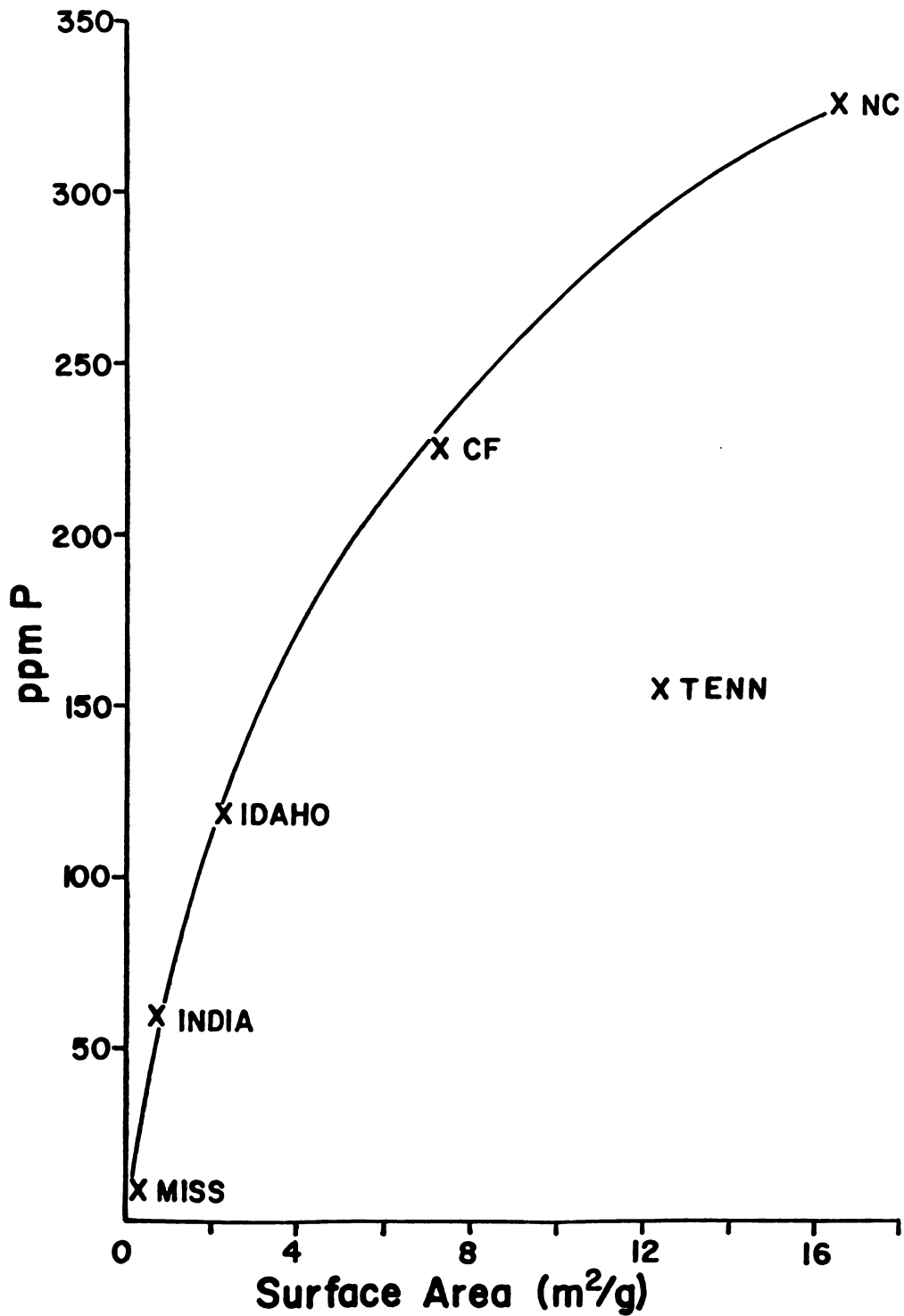


Figure 8. The relationship of the surface area (m^2/g) on the solubility (ppm P) of six rock phosphates.

the results. For example, CO_2 may have accumulated in the flasks. Since the flasks were stoppered during the experiment, the breakdown of the rock phosphate would possibly produce CO_2 by the release of CO_3 from the structure. This production could buildup and slow the reaction in certain cases.

The practical implications of the effect of Ca ion activity on solubility of rock phosphates may be seen by an example. If one assumes that a solubility level of 50 ppm P is needed for practical agronomic purposes, the level of Ca needed in solution differs depending on the type of rock phosphate. To obtain 50 ppm from India rock, it is necessary to have a Ca activity of 3.6×10^{-3} M. With the Idaho rock, 6.8×10^{-3} M is necessary, and with Tennessee, the level of Ca to permit this solubility is 9.1×10^{-3} M. On the other hand, no matter what the level of Ca, the Missouri rock will never be that soluble, while the North Carolina and Central Florida will release over 50 ppm P at any practical Ca ion activity in a soil solution.

Another factor that would need to be examined prior to application is the Ca:P molar ratio discussed previously. It was seen that the Missouri rock phosphate (with a 20:1 molar ratio), would add a large amount of Ca upon dissolution and release of P. With this release, the Ca activity will increase at a much larger rate than it would with a rock phosphate that had a 3:1 ratio; thus correspondingly decreasing solubility. Therefore, one should be aware not only of the solubility of the rock phosphate for soil application, but also the amount of Ca it will release as it becomes soluble.

LIST OF REFERENCES

13. Chien, S. H., and C. A. Black. 1976. "Free Energy of Formation of Some Carbonate Apatites in Phosphate Rocks." Soil Sci. Soc. Amer. Jour., 40:234-239.
14. Chum C. R., W. W. Moschler, and G. W. Thomas. 1962. "Rock Phosphate Transformations in Acid Soils." Soil Sci. Soc. Amer. Proc., 26:476-478.
15. Clark, J. S. 1955. "Solubility Criteria for the Existence of Hydroxyapatite." Canadian Jour. of Chem., 33:1696-1700.
16. Cook, R. L. 1935. "Divergent Influence of Degree of Base Saturation of Soils on the Availability of Native, Soluble, and Rock Phosphates." Amer. Soc. of Agron., 27:297-311.
17. Ellis, R., Jr., M. A. Quader, and E. Truog. 1955. "Rock Phosphate Availability as Influenced by Soil pH." Soil Sci. Soc. Amer. Proc., 19:484-487.
18. Engelstad, O. P., A. Jugsujinda, and S. K. DeDatta. 1974. "Response by Flooded Rice to Phosphate Rocks Varying in Citrate Solubilities." Soil Sci. Soc. Amer. Proc., 38:524-529.
19. Finn, B. J., R. L. Cook, and C. M. Harrison. 1957. "Comparison of Rock Phosphate to Superphosphate for Oats and Alfalfa on Three Podzolized Soils of Eastern Canada." Agronomy Journal, 49:465-468.
20. Jones, O. S. 1948. "Availability of Phosphorus in Rock Phosphate as Influenced by Potassium and Nitrogen Salts, Lime, and Organic Matter." Amer. Soc. Agron. Jour., 40:765-770.
21. Joos, L. L., and C. A. Black. 1950. "Availability of Phosphate Rock as Affected by Particle Size and Contact with Bentonite and Soil of Different pH Values." Soil Sci. Soc. Amer. Proc., 15:69-75.
22. Lehr, J. R., and G. H. McCellan. 1972. A Revised Laboratory Reactivity Scale for Evaluating Phosphate Rocks for Direct Application. Tennessee Valley Authority Bulletin Y-43, Muscle Shoals, AL.
23. Lindsay, W. L., and E. C. Moreno. 1960. "Phosphate Phase Equilibria in Soils." Soil Sci. Soc. Amer. Proc., 24:177-182.
24. McCellan, G. H., and J. R. Lehr. 1969. "Crystal Chemical Investigation of Natural Apatites." Amer. Mineral., 54: 1374-1391.
25. Murphy, J., and J. P. Riley. 1962. "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." Anal. Chim. Acta., 27:31-36.

26. Nelsen, F. M. and F. T. Eggertsen. 1958. "Determination of Surface Area: Adsorption Measurement by a Continuous Flow Method." Anal. Chem., 30:1387-1390.
27. Paauw, F. van der. 1965. "Factors Controlling the Efficiency of Rock Phosphates for Potatoes and Rye on Humic Sandy Soils." Plant and Soil, 22:81-98.
28. Truog, E. 1916. The Utilization of Phosphates by Agricultural Crops, Including a New Theory Regarding the Feeding Power of Plants. Wis. Agr. Exp. Sta. Res. Bul. 41.
29. Weir, D. R., S. H. Chien, and C. A. Black. 1971. "Solubility of Hydroxyapatites." Soil Science, 111:107-112.
30. Volk, Garth W. 1944. "Availability of Rock and Other Phosphate Fertilizers as Influenced by Lime and Form of Nitrogen Fertilizer." Jour. Amer. Soc. Agron., 36:46-56.

APPENDIX

APPENDIX I. Supplementary Data for Six Rock Phosphates.

Source	Solubility			Rock Phosphate Composition *						
	Slope	Surface Area m ² /g	Whole ppm P	Molar Ratio Ca:P	CaO	CO ₃	P ₂ O ₅	F	$\frac{\text{CaO}}{\text{P}_2\text{O}_5}$	$\frac{\text{CO}_3}{\text{PO}_4}$
India [†]	-0.69	0.70	82	2.73	54.2	1.0	40.1	3.6	1.35	0.028
C. Florida [†]	-0.70	7.30	236	2.48	47.5	4.5	32.7	3.6	1.47	0.164
N. Carolina ^{††}	-1.01	16.70	355	2.70	48.6	7.4	29.9	3.5	1.59	0.266
Tennessee [†]	-1.08	12.40	153	2.38	42.3	1.9	30.7	3.2	1.40	0.079
Missouri ^{§§}	-1.17	0.25	9.7	20.10	50.1	3.8	34.7	3.4	1.35	0.008
Idaho ^{††}	-1.22	2.33	113	3.33	46.8	3.3	32.3	3.2	1.43	0.089

* Data from Lehr and McCellan (22).

[§] a_o = length of a-axis of apatite unit cell.

[†] Non-detectable alkaline earth carbonates. Chien and Black (13).

^{††} Small Amount of alkaline earth carbonates. Chien and Black (13).

^{§§} Abundant alkaline earth carbonates. Chien and Black (13).

APPENDIX II. Results and Experimental Data^{*}

Source	[Ca]initial	(Ca)initial	[Ca]final	(Ca)final	P
	$\text{M/l} \times 10^3$				ppm
Idaho	1.0	0.36	11.0	3.9	95
	5.0	1.8	14.4	5.2	72
	10.0	3.6	17.8	6.4	54
	15.0	5.4	21.8	7.8	40
	20.0	7.1	25.9	9.3	32
	25.0	8.9	29.2	10.4	30
	30.0	10.7	35.4	12.6	28
	35.0	12.5	39.9	14.3	19
	40.0	14.3	42.9	15.3	18
	45.0	16.1	45.2	16.2	16
	50.0	17.9	47.8	17.1	17
Missouri	1.0	0.36	7.9	2.8	7.4
	5.0	1.8	12.8	4.6	6.0
	10.0	3.6	17.9	6.4	4.0
	15.0	5.4	22.3	8.0	2.1
	20.0	7.1	26.8	9.6	2.2
	25.0	8.9	31.4	11.2	1.4
	30.0	10.7	33.4	11.9	1.1
	35.0	12.5	40.4	14.5	1.0
	40.0	14.3	42.6	15.2	1.3
	45.0	16.1	46.1	16.5	1.3
	50.0	17.9	46.6	16.7	1.3

^{*}Average of two replications (Activity Coefficient = 0.357).

APPENDIX II. Results and Experimental Data(con't)*

Source	[Ca]initial	(Ca)initial	[Ca]final	(Ca)final	P
	$M/l \times 10^3$				ppm
Tennessee	1.0	0.36	11.3	4.1	124
	5.0	1.8	13.3	4.8	104
	10.0	3.6	17.5	6.3	73
	15.0	5.4	21.6	7.7	57
	20.0	7.1	25.2	9.0	51
	25.0	8.9	29.3	10.5	40
	30.0	10.7	33.2	11.9	35
	35.0	12.5	38.1	13.6	35
	40.0	14.3	40.1	14.4	29
	45.0	16.1	44.4	15.9	29
	50.0	17.9	46.6	16.7	26
India	1.0	0.36	7.5	2.7	69
	5.0	1.8	10.6	3.8	50
	10.0	3.6	14.9	5.3	37
	15.0	5.4	17.7	6.3	30
	20.0	7.1	23.8	8.5	24
	25.0	8.9	29.7	10.6	26
	30.0	10.7	33.1	11.9	22
	35.0	12.5	36.3	13.0	23
	40.0	14.3	39.0	14.0	23
	45.0	16.1	44.5	15.9	15
	50.0	17.9	46.3	16.6	20

* Average of two replications (Activity Coefficient = 0.357).

APPENDIX II. Results and Experimental Data(con't)*

Source	[Ca]initial	(Ca)initial	[Ca]final	(Ca)final	P
	$M/1 \times 10^3$				ppm
C. Florida	1.0	0.36	16.6	5.9	218
	5.0	1.8	18.8	6.7	196
	10.0	3.6	22.6	8.1	160
	15.0	5.4	23.9	8.5	122
	20.0	7.1	29.6	10.6	126
	25.0	8.9	33.2	11.9	116
	30.0	10.7	36.4	13.0	105
	35.0	12.5	37.9	13.6	104
	40.0	14.3	44.9	16.1	115
	45.0	16.1	46.6	16.7	95
	50.0	17.9	48.3	17.3	96
N. Carolina	1.0	0.36	27.8	9.9	299
	5.0	1.8	28.1	10.0	278
	10.0	3.6	32.2	11.5	229
	15.0	5.4	33.9	12.1	203
	20.0	7.1	37.2	13.3	206
	25.0	8.9	39.8	14.2	200
	30.0	10.7	40.4	14.4	179
	35.0	12.5	43.3	15.5	168
	40.0	14.3	49.1	17.5	161
	45.0	16.1	50.2	18.0	145
	50.0	17.9	54.6	19.5	149

* Average of two replications (Activity Coefficient = 0.357).

MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03143 2788