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A Revised Laboratory Reactivity Scale for Evaluating Phosphate Rocks for Direct Application

TENNESSEE VALLEY AUTHORITY

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supported in part by the

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FOREWORD

Scientists at TVA's National Fertilizer Development Center have, over the years, developed a broad base of information on the chemistry of phosphates. This has led to a much better understanding of the chemical changes that occur as phosphate rocks are processed into fertilizers, and what happens to fertilizer phosphate when it is applied to the soil Use of this accumulated knowledge has led to numerous improvements in fertilizer processes and products As a part of this work, studies were made of phosphate rocks to determine why investigators have reported such widely different results when finely ground, but otherwise untreated, phosphate rocks were used as fertilizers

This study, supported in part by the Agency for International Development, has resulted in the development of a new way of comparing phosphate rocks. Hopefully, it will contribute to more efficient use of natural and economic resources

SUMMARY 3

INTRODUCTION 5

LABORATORY EVALUATION OF PHOSPHATE ROCKS 7
Conventional Laboratory Evaluation Methods 7
Other Citrate Procedures 7
Composition and Solubility of Apatites 7
Conventional Notation of "Citrate-Soluble P_2O_5" 8
"Absolute Citrate Solubility" Basis 8

AGRONOMIC EVALUATION OF PHOSPHATE ROCKS 13
Factors Controlling Availability 13
Recent Greenhouse Evaluations 14
Recent Field Evaluation with Flooded Rice 18
Factors Affecting Direct Application Practices 19

REFERENCES 22

APPENDIX A 23

APPENDIX B 27

APPENDIX C 36

TABLES

1 Phosphorus response of flooded Nato rice to phosphate rocks of differing chemical reactivity 15
2 Statistical correlation between absolute citrate solubility of phosphate rock sources and agronomic response of Nato rice 15
3 Phosphorus response of flooded Nato rice to AID series of phosphate rocks . . . 15
4 Phosphorus response of buckwheat and alfalfa to phosphate rocks on three acid soils 17
5 Statistical correlation between citrate solubility of phosphate rock sources and response of buckwheat and alfalfa 17
6 Physical and chemical properties of phosphate rocks used in slash pine seedling experiment 17
7 Phosphorus response of flooded rice in Thailand to AID phosphate rocks 18
8 Statistical correlation between citrate solubility of phosphate rock sources and agronomic response of flooded rice in Thailand 19

FIGURES

1 Comparison of two phosphate rocks with same grade but different in the amount and composition of the apatite each contains 8
2 Comparison of absolute citrate solubilities of phosphate rocks 10
3 Absolute citrate solubilities of phosphate rocks 12
4 Correlation between agronomic response of Nato rice and absolute citrate solubilities of phosphate rocks calculated from x-ray measurements of apatite composition 16

Summary

A new laboratory reactivity index has been devised for comparing the potential value of various phosphate rocks for direct application use, based on differences in the compositions of their apatite mineral components.

In past years, both the basis for selecting rocks for direct application and the laboratory method used to evaluate "available P" have contributed to the erratic patterns of agronomic response This led to much disagreement among investigators over the relative effectiveness of certain phosphate rocks, and even raised some doubt over the use of any raw phosphate rock as a source of available P by direct application

It was generally assumed that most phosphate rocks contained the same phosphate mineral, fluorapatite, so that differences in their citrate-soluble, or "available," P_2O_5 and in their agronomic responses were attributed to differences in their physical properties, mainly particle size and surface area Gradually, the basis for distinguishing among rocks became that of geographic origin, with all rocks from the same general deposit area assumed to possess similar characteristics The adaptation of the AOAC method to phosphate rocks to differentiate them on the basis of their "citrate-soluble P_2O_5" contributed further to the confusion This introduced another false premise by relating the amount of citrate-soluble P_2O_5 as a fraction of the total P_2O_5 content (grade) of the particular rock sample This lack of effective laboratory or mineralogical guidelines has had an adverse effect on expanding the use of phosphate rocks as direct-application fertilizers.

New insight into the compositions of phosphate rocks was obtained recently from characterization studies that showed that the compositions of their apatitic phosphate minerals varied markedly. With few exceptions, the apatites were not fluorapatite, but belonged to the series of carbonate apatites in which PO_4 is replaced by CO_3 and F, and Ca is replaced by Na and Mg in the fluorapatite structure Chemical reactivity of the apatite increased as the degree of substitution increased

It has now been shown in recent solubility studies that the citrate solubility of a phosphate rock, as measured in the laboratory, is related primarily to the composition of its apatite mineral and is virtually independent of its P_2O_5 content (grade) or such physical parameters as particle size or surface area of the rock This does not mean, however, that the physical parameters have no effect on the total process of phosphorus utilization by plants when the dissolution of rocks occurs under soil conditions.

Accordingly, the citrate solubility of a phosphate rock has been redefined on an absolute basis to eliminate the fortuitous consideration of P_2O_5 grade in making comparisons among different rock sources This "Absolute Citrate Solubility" (ACS) index for any given rock is defined as the ratio of its citrate-soluble P_2O_5 to the theoretical P_2O_5 content of its particular apatite composition, or

$$\text{ACS} = \frac{\text{AOAC Cit-Sol } P_2O_5\ (\%)}{\text{Theor } P_2O_5\ (\%) \text{ of apatite}}$$

This statistically derived model that relates citrate solubility to apatite composition was obtained for a representative group of about 50 phosphate rocks It correctly associated P_2O_5 solubility with the kind of apatite supplying the P_2O_5, and not merely the amount of apatite, or P_2O_5 grade of the phosphate rock This absolute index offers a reliable basis for comparing rock reactivities on a relative scale in a laboratory evaluation, and for comparing rock sources in agronomic evaluations

Since it has been shown that citrate solubility is related primarily to apatite composition, and a statistical model already exists by which an apatite's composition can be derived from its x-ray unit-cell parameters, then the absolute citrate solubility of an apatitic rock can be predicted directly from the interrelationship by

$$\text{ACS} = 421\ 4\ (9\ 369 - a_0)$$

where a_0 is the length of the a axis of the apatite unit cell, as determined by x-ray powder diffraction The ACS values predicted by this statistical model are in close agreement with values obtained from actual solubility measurements of citrate-soluble P_2O_5

When the ACS values of a wide assortment of phosphate rocks are compared, it is obvious that phosphate rocks differ markedly in their ability to supply available phosphorus These differences occur even among phosphate rocks from the same general geographic area, but usually to a lesser extent

In several greenhouse tests using series of well-characterized phosphate rocks, a high degree of correlation was shown between the ACS indexes of the rocks and the various measures of agronomic response to their available phosphorus The conditions imposed in greenhouse tests do not fully simulate actual field conditions, however. The effectiveness of a phosphate rock in supplying available P under field conditions depends not only on its solubility, as measured in the laboratory, but also on such factors as the

pH, mineral composition, organic-matter content of the soil, and the particle size and manner of mixing of the phosphate rock in the soil Under field conditions, the particle size of the rock and its degree of mixing in the soil become important factors in the rates at which the P is released, transported, and replenished in the soil system, whereas the effects of these factors are minimized in the confined small volumes of soil used in greenhouse tests

It can be tentatively concluded that phosphate rocks with ACS values below the 50 60% range on the relative scale are too marginal for use in direct application as the sole source of P for growing crops. The commercial rocks that have been used most widely and in increasing amounts for direct application (notably Tunisian, Israeli, and some Moroccan types) were shown to rank high on the relative scale Some Eastern U S. phosphates appear to offer the same potential for use as direct application fertilizers

The newly devised reactivity scale based on the absolute citrate solubility principle offers a simple, rational basis for rating the potential value of phosphate rocks for direct application.

Introduction

Phosphate rocks have a long history of laboratory evaluation, field testing, and limited use as direct-application fertilizers, but the economic and agronomic value of using pulverized raw rock in this manner has been a subject of wide controversy

No satisfactory guidelines have existed that predict crop response accurately, or that account for the divergent results among experimenters. As a consequence, the erratic pattern of results that has been obtained by the indiscriminate choice of phosphate rocks has had a deterrent effect on their proper exploitation under agronomic conditions where a reactive phosphate rock could supply the phosphorus requirements of a particular crop

Two factors have been primarily responsible for the confusion over the selection and use of phosphate rocks for direct application Until quite recently, all phosphate rocks were generally assumed to contain the same phosphate mineral, fluorapatite, so that differences in reactivity were attributed to physical rather than compositional parameters. The results of recent research show, however, that the apatite components of phosphate rocks—particularly the sedimentary types used widely in commerce—have compositions markedly different from that of fluorapatite, and differ accordingly in their chemical reactivity Some apatites whose compositions approach that of fluorapatite are virtually insoluble or unavailable to plants under usual soil conditions, while apatites having highly modified compositions are capable of releasing available phosphorus under the same soil conditions

The second contributing factor concerns the inability of the conventional laboratory evaluation method to forecast accurately the "phosphorus availability" of a particular rock These citrate-solubility procedures provide only a crude distinction among the different apatite compositions found in various phosphate rocks, since the manner of expressing solubilities, or "available P_2O_5," as a function of total phosphorus content falsely equates the level of solubility with the amount of the apatitic calcium phosphate that is present, rather than to its compositional form. Thus, analyses of different grades of the same phosphate rock yield seemingly different measures of apatite solubility, which has been a source of disagreement among results obtained by independent investigators

Since the fundamental distinctions among types and sources of phosphate rocks thus remained obscure, a somewhat indiscriminate basis for evaluating phosphate rocks has persisted over the years Phosphate rocks of similar grade, or perhaps of similar geographical origin, often were treated as equivalent reagents More often, in comparisons of phosphorus fertilizer sources, a single "phosphate rock" was chosen arbitrarily to represent this category of phosphorus sources These bases of selection have been responsible in large measure for the erratic pattern of agronomic response data, and for the stigma attached to phosphate rocks in general on the basis of poor agronomic response of some arbitrarily chosen phosphate rock

Despite these shortcomings in the evaluation methods, satisfactory results continue to be obtained in actual field practice under certain agronomic situations Statistics show a steady growth in the use of phosphate rocks for direct-application fertilizers in recent years During the period 1953-54, domestic consumption was estimated to be about 880,000 tons of rock, supplied mainly from Florida, Tennessee, and western U S deposits Although there has been little change in domestic use in the interim period, there has been a steady increase in worldwide consumption, especially in developing countries Consumption in 1968 reached 4 million tons of rock (1 2 million tons of P_2O_5), which was a 9% increase over 1967, and a 50% increase over the period 1962-68 (1). More recent statistics for 1969-70 placed consumption at about 6 million tons of rock (2 million tons of P_2O_5) (2)

The factor most likely responsible for this increasing popularity and expanded use in foreign agriculture is that the sources of the phosphate rocks being supplied are now recognized as among the most reactive types known, which makes them suitable substitutes for prepared fertilizers in some agricultural applications This factor has also stimulated their use in developing nations where prepared fertilizers are in short supply, or too costly for wide use

The absence of a similar growth in domestic consumption of rock for direct application must be attributed to several factors The now recognized low reactivity of most domestic rocks makes them too inefficient to compete either agronomically or economically with the ample supply of low-cost, high-analysis, prepared fertilizers and the highly advanced technology for their effective use over a wide range of agricultural conditions.

The ever increasing use of phosphate rocks for direct application, as reflected by these statistics, demonstrates that the problem is not one of technical or agronomic feasibility. The use of phosphate rocks for direct application is now well established in agriculture. What is urgently

needed, therefore, is a reliable laboratory and field evaluation procedure that can determine which phosphate rocks are best suited for some specific agrononic situation

This report describes a new laboratory reactivity index, and its applications and limitations in predicting agronomic response. This index, which is based on recently developed information on composition of the apatitic components of phosphate rock, can serve as a basis for predicting their ability to supply available phosphorus. Use of this index should make it easier to realize the full potential of phosphate rocks as primary or supplemental sources of fertilizer phosphorus

Laboratory Evaluation of Phosphate Rocks

With the discovery and development of new phosphate reserves in developing countries of the world continuing at an accelerated pace in recent years, the need for fundamental characterization data became urgent. As an outgrowth of TVA's extensive investigation of the physical, chemical, and mineralogical properties of phosphate rocks, the important properties have been correlated, and rapid methods were developed to evaluate important properties (11, 12) The major finding was that the compositions of the apatite minerals in sedimentary phosphate ores varied widely, but nearly all belonged to the same series of carbonate apatites (francolites) in which CO_3 + F replaced PO_4, and Na + Mg replaced some Ca Chemical reactivity and thermal stability of the apatites were related to the degree of substitution

These new findings provided a basis for reappraising the existing laboratory methods used to evaluate the P availability of phosphate rocks for direct application. The search for an improved procedure has resulted in a classification of phosphate rock availabilities that is based on a single parameter which correlates with apatite composition, rather than making use of empirical solubility measurements. The development of this procedure is described in the following review.

CONVENTIONAL LABORATORY EVALUATION METHODS

The reexamination of conventional citrate procedures in light of the new descriptions of phosphate rock compositions identifies factors contributing to their unreliability, and suggests a modification to improve their usefulness These single-extraction methods assume that certain organic complexing agents, mainly citrates or citric acid, function as mild solvents whose solvent properties closely approximate those of soil solution with respect to water-insoluble basic calcium phosphates In principle, these solubility indexes obtained in laboratory evaluations should provide a relative measure of P availability for various rock sources.

By precedent, the official Association of Official Agricultural Chemists (AOAC) laboratory citrate procedure, which was first adopted in 1884 for determining the availability of water-insoluble calcium phosphates, has since been applied to the apatitic forms of basic calcium phosphates that are found in phosphate rocks. The official method used in the United States specifies a neutral solution of ammonium citrate as the extractant. Although this solvent is able to differentiate among the various classes of calcium phosphates because of the marked differences in their relative solubilities, it lacks the sensitivity to give more than a crude distinction among the compositional varieties of the group of highly basic (apatitic) calcium phosphates Unless the procedural steps are rigidly observed, the solubility indexes obtained by different experimenters on the same rock sources may show considerable disagreement However, despite its shortcomings, the neutral ammonium citrate procedure has survived as the most widely employed method, since it provides a crude index of rock reactivity that has been related to actual measured responses in agronomic evaluations

OTHER CITRATE PROCEDURES

In a search for improved laboratory procedures, other citrate solvents have been considered; the two most widely tested solvents are 2% citric acid solution and alkaline ammonium citrate solution (6, 9, 14)

The alkaline citrate solvents depress the solubility of the apatitic forms of basic calcium phosphates in comparison to the more acidic water-insoluble calcium phosphates. While this solvent provides a sharper distinction between these two groups of calcium phosphates than neutral ammonium citrate solution, it is too insensitive for differentiating the types of apatite compositions that are found in phosphate rocks.

On the other hand, these apatitic calcium phosphates show much higher levels of solubility in a 2% citric acid solvent, thereby providing a more sensitive laboratory method for distinguishing among the various apatite compositions on the basis of their relative solubilities or chemical reactivities The solubility index obtained using citric acid also has been correlated with P availability and agronomic response (3, 6, 14), but the concentrations of dissolved P obtained with this solvent are unrealistically high measures of "available phosphorus" under actual field conditions with less acidic soil solutions.

COMPOSITION AND SOLUBILITY OF APATITES

In principle, all citrate procedures attempt to differentiate among the compositional types of calcium phosphates

on the basis of empirical solubility measurements. This is particularly difficult, and requires the utmost precision, when dealing with the highly basic calcium phosphates of the apatite variety When these procedures are applied to the apatites in phosphate rocks, the solubility measurements can be affected by particle size, by slight shifts in pH, and by other soluble calcium sources present as associated mineral impurities (gypsum, calcite, and dolomite) These experimental difficulties tend to reduce the accuracy of solubility determinations as indicators of the apatite's composition or reactivity

From the results of rock characterization studies (11, 12), the small but significant variations in apatite compositions can be defined much more accurately and rapidly from crystallographic parameters than from empirical solubility measurements The most useful parameter is the *a*-axis dimension of the apatite unit cell, as determined by x-ray powder diffraction Neither particle size nor associated mineral matter interferes with this determination of apatite composition

When a series of apatite concentrates of known composition were analyzed according to the AOAC neutral ammonium citrate procedure, the amounts of citrate-soluble P_2O_5 were well correlated with the differences in apatite composition (appendixes A and B) The amount of P solubilized was essentially a linear function of apatite composition among the series of carbonate apatites, and virtually independent of either the grade of the phosphate rock concentrate or the particle size variations within the range of sizes in these rock samples, 150 mesh to 5 microns (appendix B).

CONVENTIONAL NOTATION OF "CITRATE-SOLUBLE P_2O_5"

The finding that the measured levels of citrate-soluble P_2O_5 obtained for a particular phosphate rock were independent of variations in grade points to a further source of error in existing solubility indexes where the conventional notation of citrate-soluble P_2O_5 is used The convention is to express the amount of solubilized P_2O_5 as a percentage of total P_2O_5 in the material analyzed This can introduce a considerable error if the phosphate rocks being compared differ in their degree of beneficiation This basis of comparison introduces an erroneous implication that grade of the rock, or more specifically the quantity of apatite present, controls the amount of citrate soluble P, whereas it has now been shown that the level of solubility is primarily a function of the apatite composition Grade becomes a limiting factor only when the amount of apatite solid phase is insufficient to saturate the citrate solvent This concept applies generally to equilibrium solubility determinations where composition, not quantity, of the saturating solid phase is the important consideration.

The error introduced in comparing the solubilities of phosphate rocks becomes less apparent when they have nearly the same P_2O_5 content but it is not eliminated entirely The reason for this is illustrated in figure 1 which shows the change in theoretical P_2O_5 content of the apatites with increasing degrees of carbonate substitution.

For some arbitrarily selected "BPL" grade (70% BPL in figure 1), two phosphate rocks with compositions represented by points A and B differ in the type and quantity of apatite each contains, despite their identical P_2O_5 grade. Phosphate rock A contains about 80% by weight of an apatite having a theoretical P_2O_5 content of 39 5%, whereas rock B contains about 92% apatite having a theoretical P_2O_5 content of about 34 8%. Obviously, therefore, the P_2O_5 grade of the phosphate rocks, even when they are the same, does not provide a common basis for comparing relative solubilities.

"ABSOLUTE CITRATE SOLUBILITY" BASIS

To avoid these problems, an absolute basis has been devised to relate the level of citrate-soluble P_2O_5 of a particular phosphate rock to the type of apatite composition it contains, thus eliminating the fortuitous effect of grade.

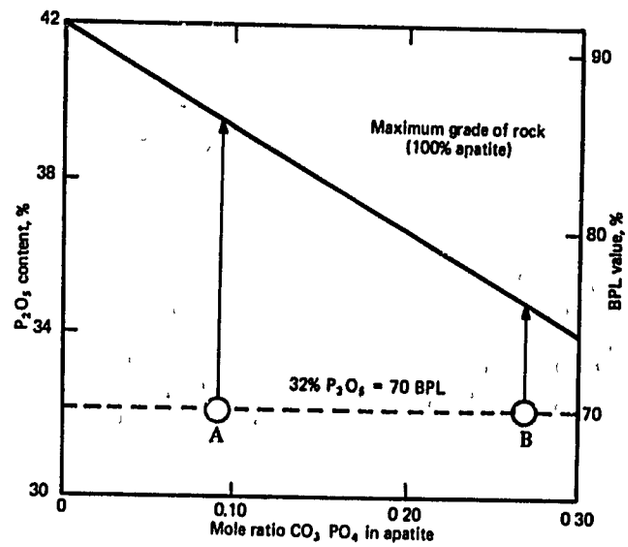

Figure 1. Comparison of two phosphate rocks with same grade but different in the amount and composition of the apatite each contains. Rock A is representative of Western U.S. ores, Rock B of North Carolina and Tunisia ores.

On this new basis, the citrate solubility of a phosphate rock is expressed as the ratio of citrate-soluble P_2O_5 (as determined by the AOAC procedure) to the theoretical P_2O_5 content of the particular apatite mineral in the rock sample, as determined from independent crystallographic parameters. This solubility relationship is defined as the absolute citrate solubility (ACS) It specifies that a fixed amount of apatite will be dissolved by the citrate treatment, depending upon the compositional form of the apatite in a rock. The nearly constant value of this amount for a particular rock has been demonstrated in TVA research by successive extraction tests in which a constant amount of apatite dissolved, even though the P_2O_5 grade was decreased progressively by each extraction It was also found that the ACS values remained relatively constant for different screen-size fractions of the same phosphate rock which extended over the particle-size range 150 mesh to 5 microns.

The effect of grade was also examined by arbitrary downward adjustments of grade of selected rock samples by dilution with an inert component(acid-washed quartz sand). The amount of apatite that dissolved and its ACS value remained constant If the conventional basis had been used to express citrate-soluble P_2O_5 in relation to total P_2O_5, or grade, then the effect of lowering the grade with a diluent would necessarily imply that the solubility of the apatite increases progressively, which is, of course, an invalid conclusion This dilution factor tends to raise the apparent "citrate-soluble P_2O_5" level of a phosphate rock in a laboratory evaluation, whereas the rock may have only marginal value as a direct application fertilizer when evaluated agronomically

Absolute Citrate Solubility Index of Phosphate Rocks

The absolute citrate solubility relationship applies, with few exceptions, to the types of apatitic calcium phosphates found in sedimentary and metamorphic phosphate rock deposits which supply the bulk of phosphatic raw materials. These apatites belong to the series of carbonate apatites known collectively as francolite, and are represented by the general empirical formula

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$$

The value for the theoretical P_2O_5 content of an apatite to be used in calculating its ACS index can be derived from previously established correlations between chemical and crystallographic properties of francolite-type apatites (12) The method of calculation is illustrated in appendix A.

The noteworthy exceptions are the phosphate rocks that contain hydroxyapatite varieties (Curacao, Sechura, Peru) and the iron-aluminum phosphate ores (Christmas Island Zone C; some Senegal ores, and Florida "leached-zone" ore).

Using a series of 50 well-characterized phosphate rocks, the ACS index of each was derived from the chemical relationship

$$ACS = \frac{\text{AOAC CS } P_2O_5\ (\%)}{\text{Theor } P_2O_5\ (\%) \text{ of apatite}}$$

The values so obtained ranged from near 0 for unreactive apatites with compositions approaching that of fluorapatite to a maximum of 23% for the most reactive apatites that had the highest degrees of carbonate substitution. The levels of solubility indicated by the ACS indexes were well correlated with apatite composition, as shown in table B-1 and figure B-3 (appendix B)

These ACS index values for the series of 50 phosphate rocks are plotted on a relative reactivity scale in figure 2 in which the most reactive rock (MR-467, from North Carolina) is taken as 100

This chart of relative solubilities demonstrates clearly the wide range of reactivities among representative types of phosphate rocks, and even among rocks from the same geographical area This solubility scale also correlates closely with the compositions of the apatites in the various rock examples

From this successful correlation of analytical data that relates citrate solubility of a phosphate rock to the form of apatite it contains, a new ACS relationship was derived to eliminate the need for a chemical determination of citrate-soluble P_2O_5 This relationship makes use of the newly established statistical correlation between apatite composition and its citrate solubility, and the previously established correlation between apatite composition and its crystallographic parameters The crystallographic parameter used here is the a-axis unit-cell dimension, where the value of a_0 ranges from about 9 320 Å for the most highly substituted apatites to about 9 370 Å for those with compositions closely approaching that of fluorapatite and having only insignificant levels of carbonate substitution (12)

The statistical model derived from these two correlations that predicts the ACS index of an apatitic phosphate rock is

$$ACS = 421\ 4\ (9\ 369 - a_0)$$

where a_0 is the a-axis length of the apatite unit cell, as measured by x-ray diffraction, and the absolute citrate solubility (ACS index) is expressed in percent. It corresponds to, but replaces, the conventional notation of citrate solubility expressed as percent of total P_2O_5 in the rock.

From this simple relationship based on a single measured physical parameter, a reliable solubility index can be predicted rapidly for most apatitic phosphate rocks, where the values can be compared directly without regard to the usual variations in grade

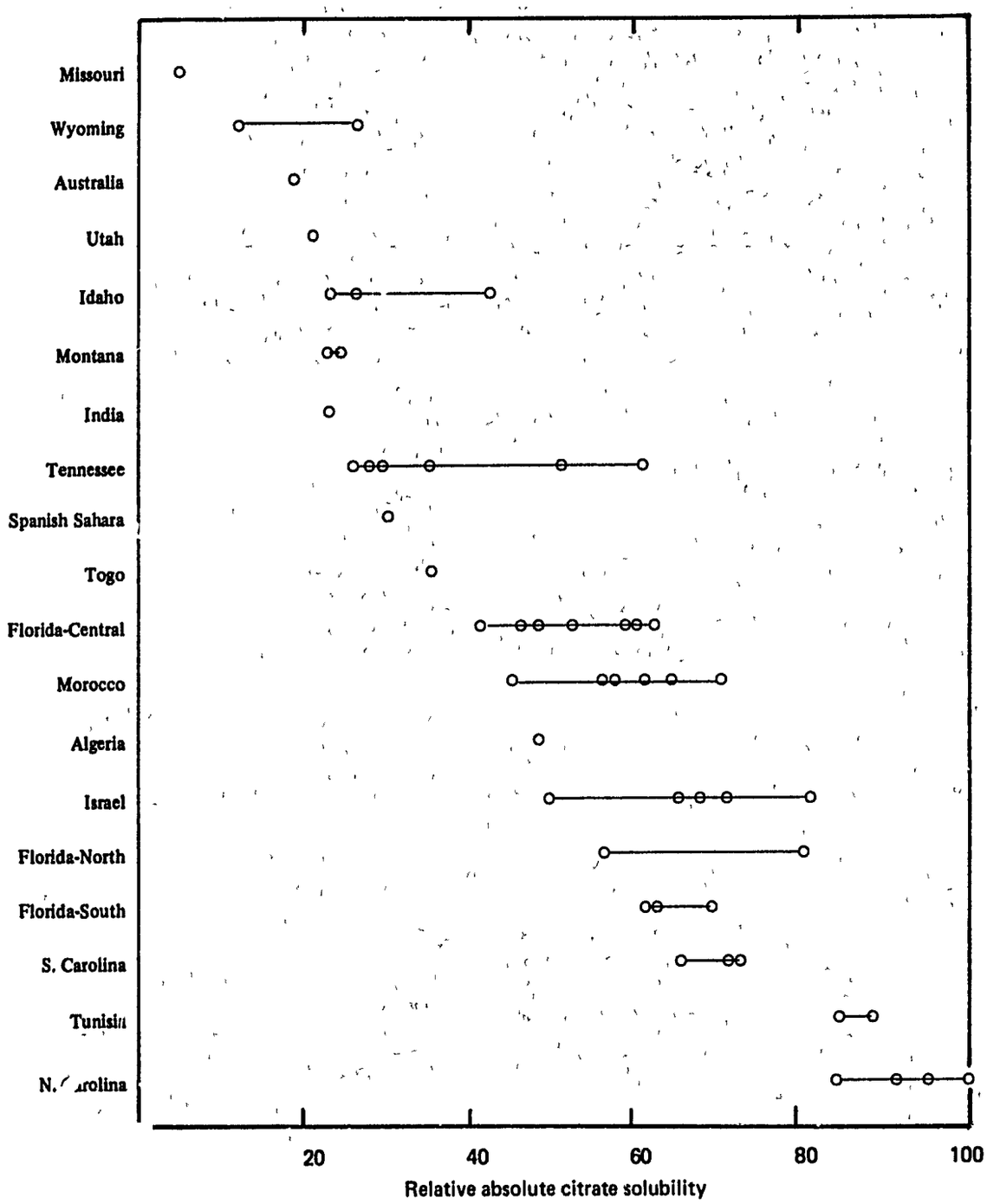

Figure 2. Comparison of absolute citrate solubilities of phosphate rocks. (ACS value of MR-467 from North Carolina taken as 100)

Application of ACS Index to Other Phosphate Rocks

A sample calculation of the ACS index for a typical rock sample is shown in appendix C, along with a comparison of the values of citrate-soluble P_2O_5 predicted from the index and actually obtained by chemical analysis in duplicate determinations

The results of similar calculations for a series of 145 phosphate rocks are summarized in figure 3. These rocks were selected to represent the important domestic and foreign commercial deposits, and are grouped in the figure according to their geographical origin so as to illustrate the range of variation that can occur among rocks from geographically related deposits The ACS values are compared in figure 3 on a relative scale, which is based on the highest ACS value (23 6%) (sample from Rebiba, Algeria) taken as 100 on the relative scale This range in properties for rocks from a particular geographical source has been responsible, no doubt, for discrepancies in agronomic response obtained by different investigators on rock samples having a common geographical origin As is illustrated in figures 2 and 3, the range in properties is considerable for many of the rock sources that have been widely tested for their agronomic response It is then apparent that no arbitrary choice of a "typical rock" can be made

This new laboratory evaluation procedure yields a rapid, reliable prediction of the citrate solubility, or P availability, of a particular phosphate rock sample without the need for chemical determinations of its P_2O_5 content or its citrate-soluble fraction The results can be compared directly on a reactivity scale with known phosphate rocks for a preliminary judgment of their potential for direct application use.

Laboratory evaluation thus serves as a valuable screening procedure, but in no way eliminates the necessity of actual agronomic evaluation, since other factors aside from rock composition must be considered These relationships between laboratory evaluation and agronomic evaluation are considered in the following section

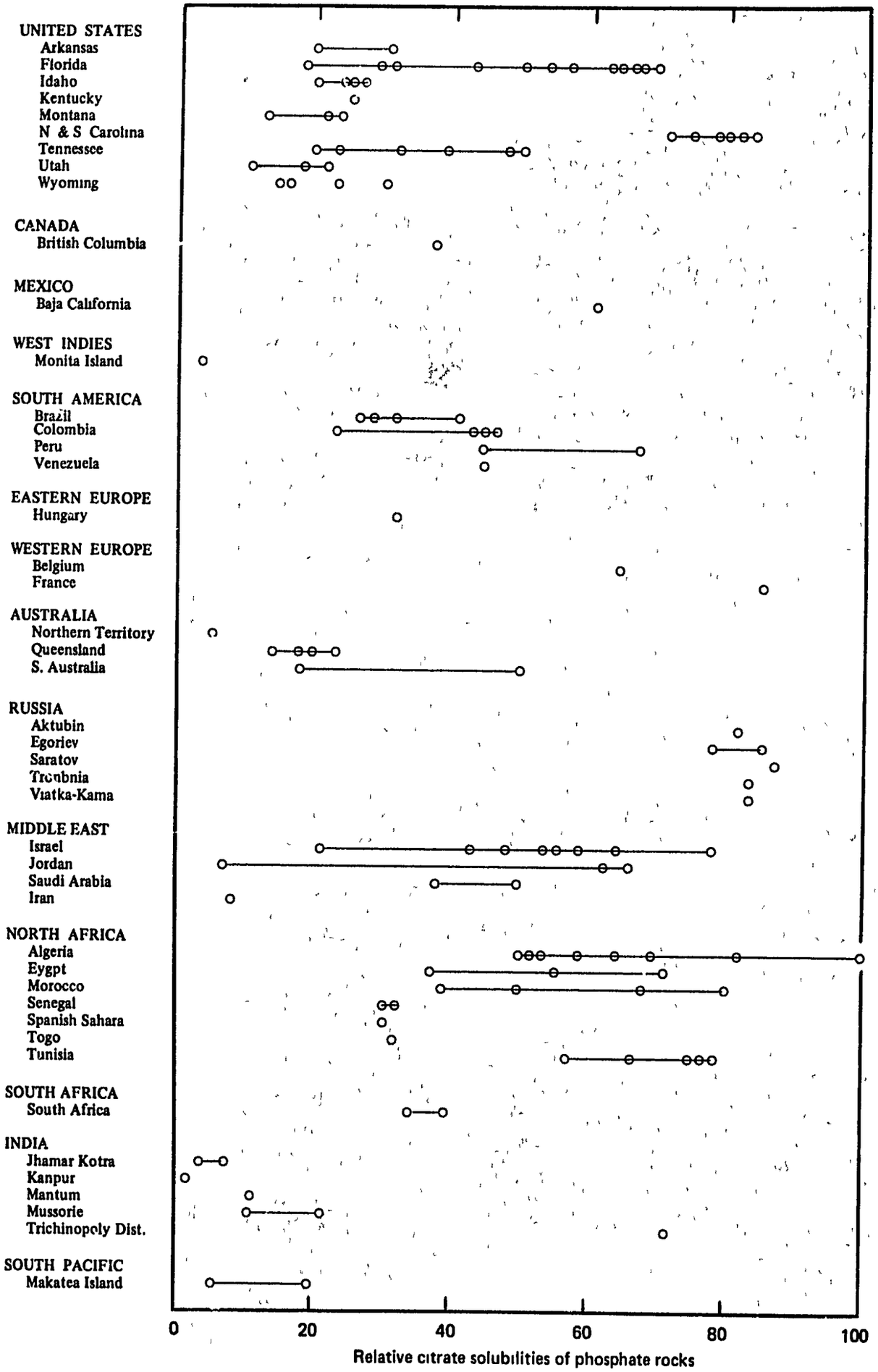

Figure 3. Absolute citrate solubilities of phosphate rocks. (Algerian rock taken as 100)

Agronomic Evaluation of Phosphate Rocks

No comprehensive agronomic evaluation of the relative reactivity scales for phosphate rocks shown in figures 2 and 3 has been made since the recent reclassification of phosphate rock compositions and their relative reactivities by McClellan and Lehr (12)

The following review of some preliminary results from greenhouse pot culture tests provides supporting evidence for the scale of relative P availabilities predicted by the laboratory evaluation In all tests, the composition of the apatite mineral appeared to be the major controlling factor. To standardize the tests and simulate usual field practice, all the phosphate rocks tested were finely ground The rocks in the AID series (appendix A) were ground commercially to 80% minus 200 mesh, all other rocks were ground to 100% minus 200 mesh. The grinding did not produce uniform particle-size distributions among the rocks, however. Hence, until more agronomic data become available, the proposed reactivity scale should be considered as a tentative guideline only

Agronomic evaluation of phosphate rocks as sources of available P requires some initial consideration of two sets of factors. One set is associated with the actual plant-culture tests in which phosphorus response can be affected by soil type, test crop, and climatic factors aside from the primary factor of rock reactivity or solubility (14). The second set of factors concerns the physical properties of the whole rock (particle size distribution, surface area, porosity) and the unit crystallite size of the apatite component. These physical parameters can have far greater influence on the dissolution of apatite in soils than on the laboratory measurements of its solubility (6)

No systematic evaluation of both sets of variables appears to have been made Unfortunately, the results of much of the past agronomic studies of phosphate rocks are difficult to evaluate, since small but significant differences in the physical and chemical properties of rocks from different sources, even from the same geographical deposit, were unrecognized or simply ignored

Consequently, widely differing opinions have arisen over the relative importance of such factors as the physical parameters of the whole rock, the composition and crystallite size of the apatite component, the soil type, the particular crop, and other growth conditions with regard to P availability of different rock sources and P uptake by growing crops. Many reports reflected the viewpoint that phosphate rock sources were mutually interchangeable, or that any rock could be rendered suitable for direct application merely by grinding it to a sufficient fineness.

Several major conclusions can be drawn from the pattern of results from these past studies Phosphate rock sources differed widely in their reactivity or release of available P Soil pH markedly influenced apatite dissolution, limiting the effectiveness of the rocks to acid soil types Their ability to supply available P to growing crops was roughly related to their degree of solubility in various citrate solvents

FACTORS CONTROLLING AVAILABILITY

The first clear recognition of the important factors that controlled the crop utilization of P from phosphate rock sources emerged from the detailed laboratory characterization study of rock sources by Caro and Hill (6), and the corroborative agronomic evaluation of this well-characterized series of rock sources by Armiger and Fried (3, 4).

Although chemical methods alone were used to determine the approximate compositions of the apatitic phosphate rocks, Caro and Hill were able to establish a highly significant statistical correlation between the "bound CO_2" in the rock's composition and its degree of solubility in various citrate solvents Physical parameters such as particle size, surface area, and porosity were shown to be relatively unimportant variables They thus concluded that the chemical composition of the apatite component of phosphate rocks was the controlling factor in laboratory indexes of rock reactivity

The corroborative agronomic evaluation of this same series of phosphate rocks under controlled greenhouse conditions also showed a high degree of correlation between "bound CO_2" content (apatite composition) and P response by both buckwheat and alfalfa Thus for the first time a close relationship was established between the apatite compositions of phosphate rocks and the results of both laboratory and agronomic evaluations of their reactivity.

As in the laboratory evaluation, physical parameters of the phosphate rocks were not related significantly to agronomic response as measured by dry-matter yields and P uptake in these particular experiments, although under field conditions the particle size of phosphate rocks and their method of distribution in soils can be very significant as discussed below.

Some soil factor other than pH was shown by Armiger and Fried (3) to influence utilization of P from phosphate rocks by crops Although an acidic soil condition is required to bring about dissolution of apatitic phosphates, other soil reactions apparently deplete the supply of available phosphorus before utilization by plants can take place In their study, six acid soils with about the same pH (5.4-5.8) were selected to create favorable conditions for release of available P from phosphate rock sources Three soils showed similar favorable responses by buckwheat and alfalfa crops to the levels of available P supplied by the phosphate rocks, but on the other three acid soils crop response was so poor that no yield comparisons were possible The soil factors responsible for this unexpected behavior were not identified Aside from pH, Waggaman and Hoffman (14) consider soil organic matter and mineral composition as factors that can influence P utilization by crops In studies of P response of pine seedling in two acid soils, Bengtson *et al* (5) found that yields in one acid soil were markedly affected by some interaction of solubilized P with an unidentified soil constituent

It would appear from the available evidence that the two major factors that control the release of available P from phosphate rock sources are soil pH and the chemical composition of the apatite component Phosphorus response by crops may differ among acid soils, however, because of the effect of other soil properties on P mobility. Plants may have to compete with chemical interactions of solubilized P with soil components This qualification places some restriction on predictions of agronomic effectiveness of phosphate rocks that rely entirely on laboratory reactivity scales

RECENT GREENHOUSE EVALUATIONS

The primary objective in the following reviews is to test the validity of the ACS reactivity scale, which is based on x-ray-derived apatite compositions, by applying it to agronomic data obtained with well-characterized series of phosphate rock sources.

The agronomic data from this group of experiments provide tests of three different series of rocks, a variety of crop types (Nato rice, buckwheat, alfalfa, and pine seedlings), and several types of responsive acid soils. Detailed descriptions of the agronomic studies are given elsewhere (3, 4, 5, 7, 13)

Nato Rice

In greenhouse pot experiments described by Terman *et al.* (13), the phosphorus response by Nato rice to a series of phosphate rocks was tested on a responsive acid soil. The rock sources were from a series that was selected on the basis of laboratory characterizations to give a range of apatite compositions Properties of the phosphate rocks, their apatite components, and agronomic measures of P-response obtained from each source are summarized in table 1 Also included in the table are comparative responses obtained from water-soluble P sources

The simple statistical correlations of the three agronomic measures of P response with the absolute citrate solubility index are shown in table 2 The high degree of correlation provides supporting evidence for the laboratory reactivity scale based on apatite compositions derived from x-ray unit-cell data The findings also agree with the earlier conclusions of Caro and Hill (6) that P availability of phosphate rocks is related primarily to apatite composition and not to physical parameters of the phosphate rock sources

In more recent experiments on Nato rice with a new series of phosphate rocks, Engelstad (7) describes similar findings of a close relationship between agronomic response to applied P and the solubility properties or compositions of this new series of phosphate rocks, according to greenhouse pot tests and in some of the cooperative field tests The rock series used in these tests is described in detail in appendix A, and a report of the joint TVA/USAID rice fertilization project will be published elsewhere (8).

A further test of the laboratory reactivity index is provided by the summarized properties of the phosphate rocks, their apatite components, and the agronomic measures of P response shown in table 3 for this second greenhouse experiment with Nato rice The same soil, crop, plant-culture procedures, and P rates were used in this second experiment as in the earlier study

The simple statistical correlations between the levels of agronomic response to P applied as phosphate rock and the ACS index derived from x-ray unit-cell data are shown in figure 4.

Thus both greenhouse experiments with rice, which were independent tests of two series of phosphate rock sources under similar experimental conditions, yielded similar results that demonstrate a close agreement between predicted reactivities of phosphate rock sources and the levels of P response by the test crop.

Buckwheat and Alfalfa

A further test of the absolute citrate solubility index was obtained by reevaluating the results of an earlier study reported jointly by Caro and Hill (6) and Armiger and Fried (3). In this study, a series of 10 chemically characterized phosphate rocks were evaluated as P sources on six acidic soils, with both buckwheat and alfalfa being used as test crops

Fortunately, the same samples of phosphate rock from the USDA collection used in this reported study were

Table 1. Phosphorus response of flooded Nato rice to phosphate rocks of differing chemical reactivity

P source	Properties of rock: P_2O_5 content, % Total	AOAC cit.-sol.	Properties of apatite: Unit-cell length, a_0, Å	Theoretical P_2O_5, %	ACS X-ray[a]	ACS Chem.[b]	Response of rice[c]: Total P uptake, mg/pot	Yield of dry matter, g/pot	No. of seed heads
Phosphate rocks									
Tunisia (Gafsa)	29.2	7.0	9.326	35.0	18.1	20.0	43.9	56.8	20
North Carolina	30.1	7.6	9.327	35.2	17.7	21.6	43.9	57.2	21
Central Florida	32.8	5.3	9.337	36.7	13 5	14 5	34.1	46.3	14
Morocco	36.9	3.9	9.347	38.2	9.3	10.2	32.4	43.9	13
Togo	36.6	3.1	9.351	38.7	7.6	8.0	32.0	42.2	12
Quebec, Canada[d]	40.5	2 0	9.381	42.2	–	4.7	30.3	38.2	12
Soluble sources									
CSP, -35 mesh	47.6	–	–	–	–	–	46.7	56.4	22
CSP, -6 +9 mesh	47.6	–	–	–	–	–	50.5	59.7	23
MAP, -6 +9 mesh	62 0	–	–	–	–	–	53 4	59.7	23

[a]Calculated from a_0 determined by x-ray, ACS = 421.4 (9.369 - a_0).
[b]Calculated from AOAC citrate-soluble P_2O_5; ACS = 100 x CS P_2O_5/P_2O_5 content of apatite determined by x-ray.
[c]Mean of straw plus grain for three rates· 50, 100, 200 mg P/pot
[d]Igneous apatite in the fluor-hydroxyapatite series for which the x-ray ACS relationship does not apply; ACS derived from chemical relationship only

Table 2. Statistical correlation between absolute citrate solubility of phosphate rock sources and agronomic response of Nato rice

Absolute citrate solubility (ACS)	Correlation factor, r, of: P uptake	Yield of dry matter	No. of seed heads
X-ray basis	0.939	0.974	0.926
Chemical basis	0 951	0.983	0 948

Table 3. Phosphorus response of flooded Nato rice to AID series of phosphate rocks

P source	Properties of rock: P_2O_5 content, % Total	AOAC cit -sol	Properties of apatite: Unit-cell length, a_0, Å	Theoretical P_2O_5, %	ACS[a]	Response of rice[b]: Total P uptake, mg/pot	Yield of dry matter, g/pot
North Carolina	29 9	7 8	9.322	34.5	19.8	76 1	74.1
North Florida	32 4	6 6	9.334	36 3	14 8	51 5	54 5
Central Florida	32 7	5.3	9 345	37.9	10.1	48.3	49.6
Idaho	32.3	3 7	9.356	39.5	5.48	46.1	47.3
Tennessee	30 7	4.5	9 357	39.6	5.06	35.7	35.0
India[c]	40 1	2 1	9 365	40 8	1.69	28.7	31.1
Missouri[d]	34.7	0.5	9 373	42 0	1.20[e]	31,8	34,5

[a]Calculated from a_0 determined by x-ray, ACS = 421.4 (9 369 - a_0)
[b]Mean for two crops at three rates 50, 100, 200 mg P/pot.
[c]Coarsely crystalline sedimentary carbonate apatite from Jhamar Kotra, Rajasthan, with physical and chemical properties closely approaching those of igneous apatites
[d]Igneous apatite of fluor-hydroxyapatite isomorphous series.
[e]Measured by AOAC procedure, ACS = 100 x CS P_2O_5/P_2O_5 content of apatite determined by x-ray.

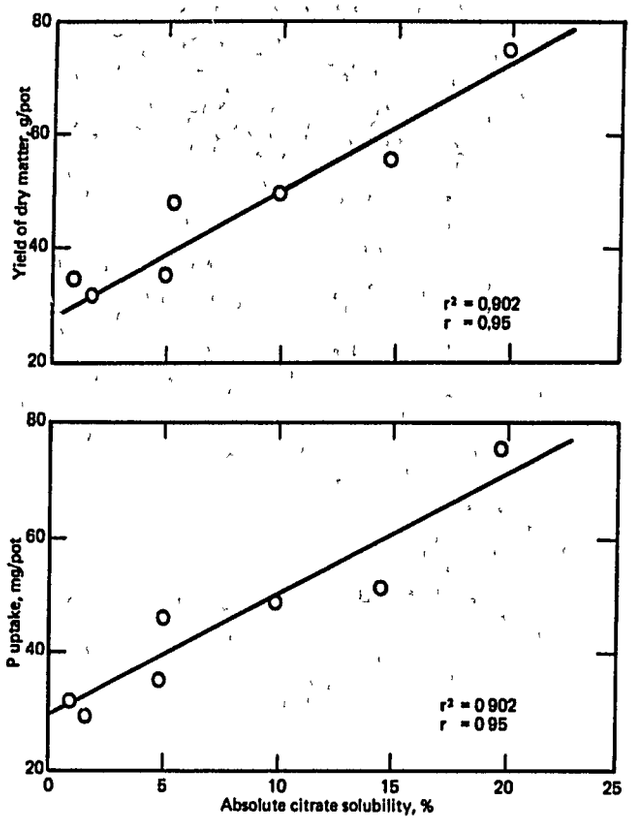

Figure 4. Correlation between agronomic response of Nato rice and absolute citrate solubilities of phosphate rocks calculated from x-ray measurements of apatite composition

subsequently made available to TVA for more extensive characterization. These new characterization data confirm and refine the scale of relative reactivities of the phosphate rocks that Caro and Hill established from chemical characterizations alone

Nine of the 10 phosphate rocks in Caro and Hill's original series (6) are described in table 4, and these form the basis for the reevaluation of the agronomic response data Included in table 4 are the pertinent properties of the apatite mineral components derived from x-ray data, and a tabulation of the measures of agronomic response reported in tables 2 and 3 and figures 1-4 of Armiger and Fried's report (3) The Curacao phosphate rock was omitted from this comparison because it is an atypical sedimentary apatite that belongs in the fluorhydroxyapatite isomorphous series for which the established relationships do not apply The other nine rocks all contain apatites belonging to the series of carbonate-substituted fluorapatites, as do the vast majority of commercial phosphate rocks

Armiger and Fried (3) found that three of the six acid soils were unresponsive to phosphate, but that the other three showed equally high response to the rock sources. All had pH values within the narrow range 5 4-5 8, which was considered to be quite favorable for apatite dissolution. The agronomic measures of P response that are reported, therefore, represent mean values for dry-matter yields and P uptake for only the three responsive soils, where no attendant soil factors due to soil-phosphorus interactions were apparent

The simple statistical correlations obtained between the absolute citrate solubility indexes derived for the rock sources and their reported agronomic data for P response by both buckwheat and alfalfa are compared in table 5. The ACS indexes show a better correlation than the conventional AOAC citrate solubility index.

This high degree of correlation obtained with the ACS index has even greater significance when one considers that the ACS values were based solely on apatite compositions derived from x-ray data This clearly demonstrates that the release of available P from phosphate rocks is controlled primarily by the chemical composition of the apatite component, rather than by some combination of physical and chemical properties of the whole rock. Recognition of this factor permits the use of the simpler, more reliable x-ray procedure to evaluate apatite compositions, rather than the empirical solubility methods based on citrate solvents.

The correlations obtained here are consistent with the conclusions reached in other greenhouse evaluations with different crops, soil types, and series of phosphate rocks. The results also confirm and refine the close relationship between rock compositions and their P availability originally postulated by Caro and Hill (6).

Slash Pine Seedlings

Further evidence of a close correlation between apatite composition and the degree of agronomic response is reported by Bengtson *et al.* (5) in a summary of unpublished greenhouse results obtained with pine seedlings (*Pinus elliottii*) grown on two acid soils and treated with the series of phosphate rocks that are characterized in table 6. Bengtson reported that "dry matter production and P uptake were closely and positively correlated with degree of substitution (of the apatite) and citrate solubility of the rock" in one soil test Smaller differences were observed among the P sources on the other acid soil because of the influence of some unidentified soil-phosphorus source interaction The correlation factors calculated on the new ACS index basis (table 6) ranged from 94 to 96% for the pine seedling test on the soil showing strong responsiveness to P "availability."

Table 4. Phosphorus response of buckwheat and alfalfa to phosphate rocks on three acid soils

P source[a]	Properties of rock: P_2O_5, %	Properties of rock: AOAC cit.-soly.[b]	Properties of apatite: Unit-cell length, a_0, Å	Properties of apatite: Theoretical P_2O_5, %	Properties of apatite: ACS X-ray[c]	Properties of apatite: ACS Chem[d]	Response of indicated crop[e]: Buckwheat[f] Total P uptake mg/pot	Buckwheat[f] Yield of dry matter, g/pot	Alfalfa Total P uptake, mg/pot[g]	Alfalfa Yield of dry matter, g/pot[h]
S. Carolina	27.1	10.0[i]	9.322	34 4	19 8	16.3	24.7	8.72	10.2	25.0
Tunisia (Gafsa)	29.9	16.4	9.324	35.0	19.0	17.2	26.1	9.11	8.4	27.6
Morocco	32 1	13.6	9.331	35.8	16.0	15.8	24.5	8.54	8.3	22.8
Florida (910)	30.9	10.4	9.334	36.2	14.7	11.6	20.3	7.95	7.8	21.8
Florida (1446)	32.8	7.6	9.337	36.7	13.5	8.2	16.0	6 34	7.2	17.5
Idaho	33 0	4.5	9.354	39.0	6.3	5.9	15.3	5.88	6.0	19.3
Tennessee	35 0	5.1	9.356	39.4	5.5	7.1	12.5	4.30	5.1	14.0
Montana	37.1	3 0	9.356	39.4	5.5	4.3	10 8	3.73	3.9	11 2
Virginia (ign.)[j]	40.3	1.5	9 380	42.2	–	2.5	4.7	2.35	1.6	6.83

[a]Samples from USDA collection (now at TVA); lot numbers are those of Armiger and Fried (3) Further descriptions given by Caro and Hill (6).
[b]100 x CS P_2O_5/P_2O_5 content of rock
[c]Calculated from a_0 determined by x-ray, ACS = 421 4 (9.369 - a_0).
[d]Calculated from AOAC solubility; ACS = 100 x CS P_2O_5/P_2O_5 content of apatite determined by x-ray.
[e]Reported in tables 2 and 3 and figures 1-4 of Armiger and Fried (3).
[f]Mean values on three soils
[g]Average of first, fourth, and seventh cuttings on three soils
[h]Mean totals of seven cuttings on three soils
[i]Reported value appears low, Caro and Hill (6) reported 17.2%, TVA found 19.8%. The higher values are more characteristic of South Carolina phosphate rocks
[j]Igneous apatite to which the x-ray relationship does not apply, ACS calculated from chemical data only

Table 5. Statistical correlation between citrate solubility of phosphate rock sources and response of buckwheat and alfalfa

	Correlation factor, r, for indicated crop: Buckwheat P uptake	Buckwheat Yield of dry matter	Alfalfa P uptake	Alfalfa Yield of dry matter
AOAC cit.-sol. P_2O_5 % of total P_2O_5	0.936	0 928	0.824	0.904
ACS, x-ray basis	0.946	0 955	0.940	0.913
ACS, chemical basis	0.971	0 942	0 907	0.927

Table 6. Physical and chemical properties of phosphate rocks used in slash pine seedling experiment

Phosphate rock	Properties of rock: P_2O_5 content, % Total	Properties of rock: AOAC cit -sol.	Properties of apatite: Unit-cell length, a_0, Å	Properties of apatite: Theoretical P_2O_5, %	Properties of apatite: ACS X-ray[a]	Properties of apatite: ACS Chem.[b]
Tunisia (Gafsa)	29.2	7.0	9 326	35 0	18.1	20.0
North Carolina (U.S.)	30.1	7.6	9 327	35.2	17.7	21.6
Central Florida (U.S.)	32.8	5.3	9.337	36 7	13.5	14.4
Morocco	36.9	3 9	9.347	38.2	9.3	10.2
Togo	36.6	3.1	9 351	38.7	7.6	8.0
Tennessee (U.S.)	35 0	3.2	9 356	39 4	5.5	8.1
Wyoming (U S.)	31.1	2.4	9.361	40.2	3.4	8.0
Canada, igneous type[c]	40.5	2.0	9 381	42 2	–	4.7

[a]Calculated from a_0 determined by x-ray, ACS = 421 4 (9.369 - a_0)
[b]Calculated from AOAC solubility; ACS = 100 x CS P_2O_5/P_2O_5 content of apatite determined by x-ray
[c]Member of the fluor-hydroxyapatite isomorphous series, to which the x-ray relationship does not apply; ACS calculated from chemical data only

RECENT FIELD EVALUATION WITH FLOODED RICE

In a recent compilation of research on rice fertilization in Thailand, Jugsujinda (10) summarizes the results of field evaluations in Central Thailand of a series of phosphate rocks on a high-yield variety of flooded rice (hybrid RD-1). The phosphate rocks that were used in this jointly sponsored TVA/USAID study were the AID series described in table 3 and appendix A Earlier studies in Central Thailand had demonstrated that some phosphate rocks appeared to be about equally effective for rice on the local acid soils as the more expensive, water-soluble manufactured phosphatic fertilizers

In this recent field study, the six phosphate rocks were compared with concentrated superphosphate as P sources for flooded rice on acid soils at two locations (Klong Luang and Bangkhen experiment stations). The phosphorus sources were applied at four rates (25, 50, 100, and 200 kg P_2O_5/ha), and three successive crops were grown (1969 wet season, 1970 dry season, 1970 wet season) to test both the initial and the residual effects of a single P application Phosphorus response was measured by yields of rough rice expressed as the mean value for the four application rates These agronomic measures of P response are summarized in table 7 along with the solubility properties of the phosphate rocks.

The data in table 7 provide a further statistical test of the laboratory reactivity index of phosphate rocks based on the composition of their apatite component The statistical correlations of the agronomic measures of P response with the different solubility indexes are shown in table 8

The high degree of correlation obtained for the initial crop grown on the acid soil of Bangkhen Station provides further support for the laboratory reactivity scale based on apatite composition. Jugsujinda concluded that although concentrated superphosphate gave the highest yield, the three most reactive rocks (North Carolina, North Florida, and Central Florida) were nearly as effective sources of P as superphosphate, but the rocks from Idaho and Tennessee were distinctly inferior, and the rock from Missouri was of little or no value as a P source

In the subsequent crop tests of residual values at Bangkhen, the poorer correlations were attributed to unexpectedly high grain yields from the control plots, which tended to obscure the effects of the P treatments, particularly in the second crop In the third crop, the ranking of all P sources (including superphosphate) on the basis of grain yields was different for each application rate Thus, a comparison of the averaged yields in table 7 shows very little difference among the rock sources, as is also reflected by the low degree of correlation in table 8 Obviously, factors other than apatite composition were controlling P availability during the growth of the third crop This poor correlation may also imply that the residual P was no longer in the apatitic form in which it was applied initially, but present as intermediate products of soil-phosphorus interactions If so, then the third crop provides no direct comparison of residual values of phosphate rock compositions *per se*

In the Klong Luang experiments, the first-crop yields of grain showed a pattern of agronomic response to the phosphate rock sources similar to that found at Bangkhen, but the actual grain yields were not as well correlated with

Table 7. Phosphorus response of flooded rice in Thailand to AID phosphate rocks

	Solubility index of apatite			Yield of rough rice, kg/ha[e]					
	ACS		AOAC	Bangkhen Station			Klong Luang Station		
P source[a]	X-ray[b]	Chem.[c]	cit -soly.[d]	Crop 1	Crop 2	Crop 3	Crop 1	Crop 2	Crop 3
Phosphate rocks									
North Carolina	19.8	22 6	26.1	5,046	4,183	4,047	5,310	2,682	2,564
North Florida	14.8	18.2	20.4	4,783	4,040	3,972	5,433	3,237	3,238
Central Florida	10.1	14.0	16.2	4,819	3,934	4,151	5,314	2,957	2,644
Idaho	5.48	9.37	11.5	4,314	4,164	4,172	5,150	2,757	2,698
Tennessee	5.06	11.4	14.9	4,159	3,889	3,963	4,511	3,084	2,755
Missouri	1.20	1.20	1.4	3,886	3,767	4,088	2,329	1,141	1,613
Control									
Concentrated superphosphate	–	–	–	5,522	4,354	4,433	5,901	3,683	3,251

[a]Rocks are described in table 3 and appendix A
[b]Calculated from a_0 determined by x-ray. ASC = 421.4 (9.369 - a_0).
[c]Calculated from AOAC citrate-soluble P_2O_5; ACS = 100 x C S P_2O_5/P_2O_5 content of apatite determined by x-ray.
[d]AOAC C S P_2O_5/P_2O_5 content of rock.
[e]Mean for four application rates of P

Table 8. Statistical correlation between citrate solubility of phosphate rock sources and agronomic response of flooded rice in Thailand

	Correlation factor, r, of grain yield					
	Bangkhen Station			Klong Luang Station		
Citrate solubility	Crop 1	Crop 2	Crop 3	Crop 1	Crop 2	Crop 3
ACS, x-ray basis	0 945	0 678	0 261	0 707	0 522	0.551
ACS, chemical basis	0 931	0 699	0 327	0 833	0.720	0 711
AOAC cit sol.	0 904	0 700	0 346	0 842	0 750	0 725

the apatite compositions of the individual rock sources The soil at Klong Luang, however, is strongly acidic (pH 4.5-4.8), which would tend to increase the rate of decomposition of all apatites, thereby minimizing the effect of small compositional differences on the dissolution process

Thus, the three most reactive rocks (North Carolina, North Florida, and Central Florida) performed equally well, and nearly as well as concentrated superphosphate, when compared on the basis of grain yield, and Jugsujinda concluded that the differences among these sources were not statistically significant Idaho rock was slightly less effective, but even its difference in grain yield was not considered statistically significant Tennessee rock was definitely inferior, and Missouri rock produced little measurable effect as a P source The performance of the rock sources at Klong Luang was better than at Bangkhen, but the poorer correlation of grain yields with apatite compositions indicate that some other factor influenced rock decomposition, most probably the more acidic nature of the soil

In the second and third crops, intended as tests of the residual values at Klong Luang, the ranking of the rock sources on the basis of grain yield differed for each application rate, indicating an even greater influence of factors other than rock composition on the release and uptake of P In this connection, it seems unlikely to assume that the reserve supply of P is present exclusively in the form of the apatitic rock as applied initially, but rather that the release of P is controlled by a mixture of residual apatite and soil-phosphorus intermediate reaction products. This condition would prevent any correlation of crop response in residual tests with the composition of the initially applied P sources

In summary, the field data from the two Thailand experiments show a reasonably good correlation between the general performance of phosphate rock sources and their respective apatite compositions, as defined by the laboratory reactivity index (ACS). The correlation between rock composition and agronomic response was better at Bangkhen (93-95%) than at Klong Luang (71-83%), where low soil pH was a complicating factor The relationship holds for first-crop response, but not for subsequent crops intended to test residual values, where alteration products of apatite may also contribute to the release of available P. The field experiments also demonstrate that phosphate rocks with the highest ACS values approached superphosphates in their effectiveness as sources of available P in this particular rice cultivation

FACTORS AFFECTING DIRECT APPLICATION PRACTICES

From the foregoing discussions, the obvious first consideration is the selection of potentially reactive rock sources to avoid needless testing of unresponsive apatitic phosphate rocks This can now be done conveniently and reliably by the laboratory evaluation method based on the absolute citrate solubility index, which avoids many of the shortcomings discussed by Waggaman and Hoffman (14) for previous single evaluation methods It must be emphasized, however, that a laboratory index merely predicts the phosphate rock's ability to supply available P, but cannot predict how efficiently the supply of available P will be utilized by crops under actual field conditions Much of the past criticism of laboratory evaluation methods stems from a failure to recognize this practical limitation The additional effects of the soil system cannot be ignored

In actual field use, other factors must be considered in addition to the primary consideration of the apatite's composition and solubility properties The importance of soil pH is widely recognized, since acidic conditions are required for dissolution of basic calcium phosphates such as apatites The mineral composition and organic matter content of an acid soil can introduce complicating factors, as was illustrated in the previous discussions of greenhouse tests in which unknown soil-phosphorus chemical interactions competed with crops for the supply of solubilized phosphorus Although the primary considerations of rock reactivity and soil pH can be readily evaluated, there is no simple or practical laboratory procedure by which these unresponsive types of acidic soils can be identified in advance of actual agronomic testing

In any experimental testing of phosphate rocks for direct application, therefore, one must draw a clear distinction between unresponsive rocks and unresponsive

acidic soils to avoid erroneous generalized conclusions. This requires a combination of both laboratory evaluation and agronomic evaluation, since neither method is reliable when used independently

The importance of particle size of the phosphate rock (or similar considerations of apatite crystallite size) has been a source of much confusion Recent TVA studies, as well as the results of the earlier studies by Caro and Hill (6) with rock samples that ranged in particle size from 100- to minus 325-mesh, have shown that particle size and related physical parameters have little influence on the levels of phosphorus solubility as measured in laboratory evaluations, but may have controlling effect on the dissolution processes as they occur under field conditions These particle-size effects are much less likely to show up in greenhouse pot tests, in which the P sources are finely ground, intimately mixed, and uniformly distributed in a confined soil volume, and the amount of soil solution is regulated closely These conditions tend to minimize or eliminate the effects of particle size and placement on the processes of dissolution and transport of available P.

These favorable circumstances are unlikely to be attained under actual field conditions Bulk samples of phosphate rock from commercial sources are not likely to be closely sized to a particular desired degree of fineness, and, furthermore, it is difficult to distribute the rock evenly and mix it uniformly in the soil The agronomic responses measured in greenhouse tests are likely, therefore, to exceed those obtained in larger scale field trials

Although the degree of grinding has no measurable effect on the citrate solubility of the apatite, a smaller particle size permits a more intimate and uniform distribution in the active soil zone, thereby both influencing a larger volume of soil and decreasing the transport distance of solute P to plant roots Because of the much lower solubility of mineral phosphates in comparison to the phosphate compounds in prepared fertilizers, a much greater dependence is placed on efficient rates of solution and transport of available P to sustain crop needs by mineral phosphates.

Particle size or surface area of the phosphate rock becomes the important variable in the rates at which P is released, transported, and replenished in the soil system, whereas these rate processes are of no concern in laboratory measurements of available P of rock sources It is then apparent that fine grinding is beneficial in the field performance of a phosphate rock, and it may be presumed that there is no lower limit beyond which further grinding would produce no beneficial effect A compromise must then be reached between the cost of fine grinding and the extent to which the finer grinding increases crop yields.

In conclusion, the prospects for more realistic evaluation of phosphate rocks for direct application may lead to their increased use under certain agronomic conditions, so as to avoid the past misuses of a valuable resource. A satisfactory laboratory evaluation method is now available, but it serves only to predict the potential of a particular rock phosphate to supply available P, thereby eliminating unresponsive rocks from further consideration It provides no indication of how efficiently the supply of available P from the phosphate rock will be utilized by crops, since factors other t' an composition of the phosphate rock influence the dissolution and transport processes under field conditions.

When the interferences caused by these other factors are minimal or absent, as in closely controlled greenhouse evaluations, then a high degree of correlation can be clearly demonstrated between the amount of available P supplied by rocks and its utilization by crops. The level of P availability of a rock is, in turn, directly related to the composition of its apatite mineral component. These interrelationships form the basis of a relative reactivity scale based exclusively on apatite compositions of various phosphate rocks It permits comparisons of phosphate rocks that are independent of either their geographical origin or their P_2O_5 grade (content of accessory minerals).

The absolute citrate solubility scales (figures 2 and 3) do not, at present, have firmly established cut-off points that indicate rocks of too marginal economic or agronomic value for direct application use

Some guidelines can be drawn, however, from actual field practices The phosphate rocks that have been used most widely and successfully in agriculture are generally those from sources now known to contain the most highly substituted apatites These apatitic rocks fall somewhere above the 60% point on the ACS scale of figure 2 On the other hand, poor responses have been reported quite consistently for those phosphate rocks that are now recognized to contain apatites with low levels of carbonate substitution, as, for example, the domestic phosphates from western United States and Tennessee, and the crystalline metamorphic or igneous apatites (Kola, U.S S R , Quebec, Canada, Phalaborwa, Africa, Missouri, U S , and others). This group of generally unresponsive apatitic phosphate rocks falls usually below about 40% on the ACS relative scale. Rocks of intermediate composition (40 60% on the ACS scale of figure 2) constitute a marginal group for use as direct application fertilizers as the primary source of P, but they may be quite satisfactory for sustaining or raising the phosphorus status of marginal soils

As shown in figure 3, phosphate rocks from a particular geographical area, for example, some of the principal commercial sources (Florida, Morocco, Israel) may range from submarginal to superior types for direct application. The laboratory ACS index provides a basis for making this crucial distinction to ensure selection of a reactive variety of phosphate rock

Finally, one important qualification must be considered when selecting phosphate rocks for direct application. The

reactivity of a phosphate rock is decreased drastically by thermal treatment such as calcination. On heating, the apatite minerals in sedimentary phosphate rocks tend to alter to fluorapatite, with an accompanying increase in crystallite size during the chemical reorganization Both of these changes progressively lower the initial reactivity of the phosphate rock to that of the generally unresponsive igneous and metamorphic apatites Hence, only natural phosphate rocks or concentrates that have not been upgraded by thermal treatment should be considered for direct application The ACS reactivity index of a phosphate rock is unaffected by physical beneficiation steps that upgrade its P_2O_5 content, except for calcination treatments which drastically lower the ACS index value.

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Appendix A

CHARACTERIZATION OF PHOSPHATE ROCK SERIES USED IN AID RICE FERTILIZATION PROJECT[1]

Background—From discussions of the Advisory Committee for Rice Fertilization with TVA on March 3-6, 1969, the committee recommended to TVA that a worldwide test of phosphate rock availability in rice culture be tested during the next crop season. Selection and characterization of a series of suitable phosphate rocks similar to the series used in previous TVA greenhouse experiments was assigned to TVA's Fundamental Research Branch

Characterization—Six domestic phosphate rocks from deposits that were expected to provide a wide range of carbonate substitution in the apatite component were recommended for procurement by the International Fertilizer Development Staff These sources are from deposits in Idaho, Tennessee, North and Central Florida, North Carolina, and Missouri, a seventh rock from the newly discovered deposit in the Jhamar-Kotra district of India was included in the series by the International Fertilizer Development Staff. A 2-ton sample of concentrate from each source was obtained for immediate distribution to cooperating rice experiment stations and for subsequent characterization, all concentrates had been uniformly sized at 70% through 200 mesh

Characterization studies to provide background information for the experimenters were made on representative samples of the phosphate rocks from the sources listed in the tabulation.

Source of concentrate	Type	TVA No
Idaho shale phosphorite	Sedimentary	MR-465
Florida (Polk County) pebble	Sedimentary	MR-464
North Florida (Occidental mine)	Sedimentary	MR-466
North Carolina clastic phosphorite	Sedimentary	MR-467
Tennessee brown, Columbia, Tenn	Sedimentary	MR-468
India (Jhamar-Kotra district, Udaipur[a])	Metamorphic	MR-469
Missouri (byproduct concentrate)	Igneous	MR-505

[a]High grade material from block-D zone, Hindustan Zinc Company.

Chemical Composition—The compositions of the phosphate rock concentrates with respect to the significant constituents are shown in table A-1, and the compositions of the apatite minerals in these rocks are shown in table A-2

Also shown in table A-2 are the calculated theoretical compositions based on previously derived correlations between unit-cell dimensions and chemical composition according to the general empirical formula of a francolite-type apatite, $(Ca_{10-a-b}Na_aMg_b)(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$ Using this approach, it is possible to confirm that the phosphate mineral is truly apatitic, and the grade of the concentrate can be determined

To calculate the theoretical composition of the apatite, the value of the mole ratio CO_3 PO_4 that corresponds to the measured *a*-axis unit-cell dimension is determined graphically (table A-3) or approximated by the relationship $a_0 = -0.204[x/(6-x)] + 9.374$, where x/(6-x) represents the mole ratio CO_3 PO_4 in the empirical formula The graphical solution yields a more accurate value since the relationship is slightly curvilinear The molar proportions of PO_4, CO_3, and F in the apatite composition are then determined from the mole ratio, sodium and magnesium are derived from the relationships in which moles Na/formula weight = a = 1.327[x/(6-x)], and moles Mg/formula weight = b = 0.515[x/(6-x)], moles of calcium required to fill the remaining cation sites in the structure = 10-a-b

Theoretical compositions of the apatite minerals in the seven phosphate rocks calculated from the single *a*-axis parameter and converted to the oxide bases are shown in table A-2 The calculated grade and chemical composition of the individual rock samples with respect to its apatite content are based on the P_2O_5 content found by chemical analysis, these calculated values are in very close agreement with the compositions obtained by chemical analysis

These results show that the important phosphate mineral in all seven phosphate rocks is apatite and that the compositions of the individual apatites provide the desired

[1]TVA Fundamental Research Branch internal progress report of June 1969.

Table A-1. Gross composition of phosphate rocks to be used in rice culture experiment

Constituent	Composition, %[a]						
	MR-464	MR-465	MR-466	MR-467	MR-468	MR-469	MR-505[b]
CaO	47 5	46.8	48 3	48 6	42 3	54.2	50.1
P_2O_5	32 7	32 3	32.4	29 9	30.7	40 1	34.7
F	3.6	3.2	3.7	3 5	3.2	3.6	3 4
CO_2	3.3	2.4	4.0	5.4	1.4	0.7	2.8
Na_2O	0.66	0.96	0 68	0.99	0.40	0.11	0.27
K_2O	0.15	0.36	0.21	0.13	0.65	0.02	0.16
MgO	0.32	0.37	0.46	0.55	0.28	0.04	0.63
Al_2O_3	1.20	1.10	0.75	0.46	1.40	0.30	0.34
Fe_2O_3	1.45	0.44	0.73	0.68	1.20	0.40	2.60
SiO_2	5.2	5.4	2.8	1.6	10.0	1.2	2.8
Total S	0 4	0 9	0.4	1.1	0.2	<0.01	0.08
Sulfide-S	0 005	0 008	0.005	0.08	0.006	nil	nil
Ign. loss (1100° C)	6.8	6 9	8.0	11.1	5.3	0.9	2.6

[a]Samples dried at 105° C to obtain compositions on a moisture-free basis
[b]TiO_2 content estimated to be about 5% (heavy mineral group)

range of carbonate substitution and citrate solubility for the agronomic field tests (table A-3) Use of this series of phosphate rocks to test previously derived correlations between crystallographic and chemical properties again demonstrates that grade and composition of a phosphate rock can be closely approximated from the single crystallographic parameter, *a*-axis unit-cell length, and from the P_2O_5 content shown by chemical analysis of the phosphate rock after removal of free carbonate minerals by the Silverman extraction procedure

Phosphorus Availability—The progressive increase in phosphate availability with increasing carbonate substitution, as measured by the neutral ammonium citrate method (AOAC), is shown in the figure The solid line shows the correlation found for the seven rocks in the present series, and the dashed line is the correlation found in a previous study of 17 rocks that represented a similar range of carbonate substitution (Proc Intern. Colloq Solid Inorg. Phos., Toulouse, France, 1967)

In previous studies, samples were ground to pass 200 mesh, the phosphate rocks in the present series had been ground for shipment in the form of 70% through 200 mesh and had to be evaluated in this condition This coarser grinding would have a greater effect on the citrate solubility of igneous and metamorphic apatites (MR-505, MR-469) because of the nonporous, coarsely crystalline nature of their individual particles In sedimentary apatites, the geometric surface contributes only a part of the specific surface, so that citrate solubility is less sensitive to small variations in particle-size distribution

Because the difference in the correlations found in the earlier studies and the present series of rocks is so small, the results of TVA Greenhouse Experiment 165-B on rice (December 1968) using the previous series of phosphate rocks should be comparable to those of the rice culture tests now in progress with the new series of seven phosphate rocks

Accessory Minerals—Except for the igneous apatite, MR-505, other phosphate minerals were not present in the accessory mineral groups of the phosphate rocks. Sample MR-505 contained about 2.5% monazite, which is a highly insoluble rare-earth phosphate Although its contribution to the P_2O_5 content is included in the analysis of the head sample (table A-1), it does not contribute to the P_2O_5 content reported in table A-2, since it is not solubilized by extraction with hot 1.3 HCl. It is highly unlikely, therefore, that this accessory phosphate mineral in MR-505 will make any contribution to the available P_2O_5 in the plant-culture experiments.

The accessory minerals in the seven rocks were primarily quartz, calcitic and dolomitic carbonates, illite clay, hydrous iron oxide, and assorted heavy minerals, the igneous apatite MR-505 contained muscovite in place of clay, ilmenite ($FeTiO_3$) in place of simple hydrous iron oxides, and fluorite (CaF_2) in addition to the quartz, calcite, and heavy minerals. Collectively, the types of accessory minerals common to these phosphate rocks should have no effect on their behavior as phosphate fertilizers.

Table A-2. Composition of apatite component in phosphate rocks used in rice experiment: comparison of compositions calculated from x-ray data with those found by analysis

Rock sample	Apatite composition, %						Sum of constituents[a]	Wt % apatite in rock sample
	CaO	P_2O_5	F	CO_2	MgO	Na_2O		
MR-464								
Theoretical[b]	55.45	37.90	4.44	3.36	0.33	0.63	100.24	
Calculated[c]	47 2	(32.3)	3.8	2.9	0.28	0.54		85.2
Found[d]	47.5	32.3	3.8	3.5	0.29	0.63		
MR-465								
Theoretical	55.57	39.58	4.19	2.04	0 20	0.35	100.17	
Calculated	46.1	(32.8)	3.5	1.7	0.17	0.29		82.9
Found	46.8	32.8	3.4	1.8	0.18	0.95[e]		
MR-466								
Theoretical	55.38	36.53	4 65	4 42	0.45	0.82	100.25	
Calculated	48.95	(32.3)	4.1	3.91	0.40	0.72		88.4
Found	48.4	32.3	3 8	3.7	0.39	0.61		
MR-467								
Theoretical	55 27	35.08	4.89	5.55	0.55	1.09	100.37	
Calculated	47 8	(30.3)	4.2	4.8	0 48	0.94		86.4
Found	48.2	30.3	3.6	5.0	0.50	1.04		
MR-468								
Theoretical	55.62	39.58	4.17	2.04	0.17	0.34	100.16	
Calculated	43.2	(30.7)	3.2	1.58	0.13	0.26		77.6
Found	43.1	30.7	3.2	1.5	0.23	0.31		
MR-469								
Theoretical	55.59	41.09	3.93	0.88	0.08	0.15	100 06	
Calculated	54.4	(40.2)	3.8	0.86	0.08	0.15		97.8
Found	54.3	40.2	3 6	0.7	0 02	0.12		
MR-505								
Theoretical	55.62	42.22	3 77	–	–	–	100.02	
Calculated	47.8	(36 3)	3.3	–	–	–		86.0
Found	49.0	36 3	3.5	0.2	0.53	0 28		

[a]Oxide basis, corrected for fluorine equivalence of oxygen in structure

[b]Theoretical apatite composition calculated from *a*-axis unit-cell parameter (x-ray), as described in text.

[c]Calculated composition and grade of concentrate based on actual P_2O_5 content from chemical analysis

[d]Actual composition of apatite phase obtained by chemical analysis, apatite mineral was extracted with warm 1 3 HCl from a weighed sample of phosphate rock that had been treated with Silverman's solution to remove free carbonate minerals, washed, and dried at 105° C

[e]The high Na_2O content is typical of western phosphoria due to exchangeable sodium on clay in addition to the sodium present in the apatite structure

Table A-3. Comparison of properties of the apatites in relation to degree of carbonate substitution

Phosphate rock[a]	Calculated unit-cell dimensions X-ray a_0 (Å)	X-ray c_0 (Å)	Infrared[b] a_0 (Å)	Mole ratio CO_3/PO_4 X-ray	Chem.	P_2O_5, % Total P_2O_5	Cit-sol P_2O_5[c]	Cit-sol., % of total
MR-505 Missouri	9.373	6.878	9.372	0.000	0.008	34.7	0.5	1.4
MR-469 India (Jham Kot)	9.365	6.884	9.363	0.035	0.028	40.1	2.1	5.2
MR-468 Tennessee	0.357	6.892	9.362	0.082	0.079	30.1	4.5	14.9
MR-465 Idaho	9.356	6.894	9.352	0.083	0.089	32.3	3.7	11.5
MR-464 Central Florida	9.345	6.890	9.344	0.142	0.164	32.7	5.3	16.2
MR-466 North Florida	9.334	6.894	9.335	0.195	0.184	32.4	6.6	20.4
MR-467 North Carolina	9.322	6.888	9.331	0.256	0.266	29.9	7.8	26.1

[a]Arranged in order of increasing carbonate substitution, and probable order of increasing availability.
[b]Estimated from relative intensities of C-O and P-O absorption bands and the established relationship between this ratio and x-ray unit-cell values
[c]Neutral ammonium citrate (AOAC) method

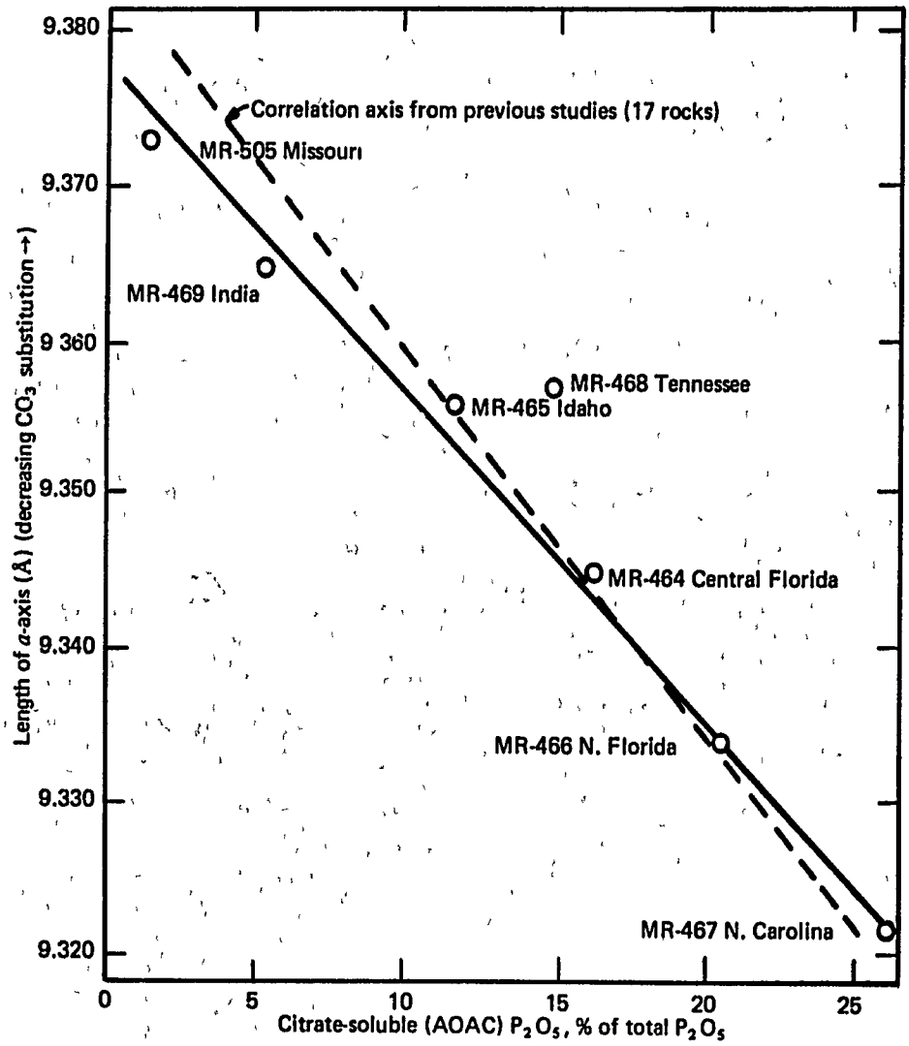

Figure A-1. Correlation of available P_2O_5 as measured by AOAC method with degree of carbonate substitution in apatites based on length of unit-cell *a*-axis

Appendix B

CORRELATIONS OF PHOSPHATE ROCK PROPERTIES WITH CITRATE SOLUBILITY[1]

In further investigations of phosphate rock properties that affect their use as direct application fertilizers, selected samples were studied to determine the effects of differences in their chemical and physical properties on their citrate-soluble phosphorus The series of samples include 42 phosphate rocks chosen from the TVA reference collection and the series of seven phosphate rocks used in the AID rice fertilization study, as described in appendix A These rocks were chosen not only to represent the wide range of substitution of CO_3 for PO_4 in the apatite compositions, but also to represent typical phosphate rocks from the major commercial sources

In table B-1, the 49 phosphate rocks are identified by source, and a description of their important chemical and physical properties is given

Previous studies of phosphate rocks for direct application use were based on chemical characterization as the principal measure of variability among phosphate rocks in attempts to correlate the differences in their degree of citrate solubility (6) The results of these earlier studies led to the conclusion that the "bound CO_2" in the apatite minerals and the solubility of the apatitic phosphate in 2% citric acid were the two best measures of availability for untreated phosphate rocks

The statistical correlations of the unit-cell dimensions of apatites with their compositions allows a more precise comparison in the present study of the relationship advanced by Caro and Hill (6). In an initial test of the proposed relationship between apatite composition and citrate solubility, the citrate solubilities and compositions of the 49 phosphate rocks were compared in figures B-1 and B-2 The compositions in figure B-1 are based on the physical unit-cell parameter derived by x-ray, while in figure B-2 the compositions are based on the chemically derived mole ratio of CO_3 PO_4 in the apatites, which corresponds to Caro's "bound CO_2" content.

A high degree of correlation is evident in both figures However, the interpretation of the correlation is complicated by the fact that as the degree of substitution increases, there is an accompanying decrease in mean crystallite size of the apatite mineral. It remains, therefore, to determine whether the change in citrate solubility is due specifically to a chemical or a physical property of the apatite component in these rocks.

Since the comparisons of rocks in table B-1 involve difference in grade, the correlation between citrate solubility and rock composition was retested, using the absolute citrate solubility basis, which eliminates grade effects As shown in figure B-3, a high degree of correlation persists between citrate solubility and composition of the apatite minerals that is independent of P_2O_5 grade of the rocks

The important implication of figure B-3 is that crystal chemical composition of the apatite, rather than the quantity of apatite in a rock, seems to determine the level of solubility of the apatite in neutral ammonium citrate solution Thus, each apatite composition in the solid solution series of carbonate apatites should have a unique solubility

As a further demonstration of this point, the rock in the series of 49 sources having the highest citrate solubility in neutral ammonium citrate solution (MR-467) was subjected to repeated extractions under conditions that conformed to the AOAC procedure The results, shown in table B-2, reveal that the citrate soluble fraction was essentially constant as the total P_2O_5 content of the rock, or its grade, decreased by about one-third Only when this constant amount of citrate-soluble P_2O_5 is expressed as the fraction of the total P_2O_5 in each extraction is it made to appear that citrate solubility increases from the initial value of 23% to a final value of 33%

The possible effect of differences in grade was reexamined in another test in which the rock sample (MR-467) was intimately mixed with varying amounts of an inert mineral, quartz This simulates a range of grades which can be analyzed by a single citrate extraction The results shown in table B-3 reveal that a fairly constant amount of citrate-soluble P_2O_5 was obtained for all mixtures that contained at least 50% phosphate rock It is likely that in the more dilute mixtures of phosphate rock, the exposed surface area and hence rate of solution become limiting factors on the levels of citrate solubility obtained in the AOAC procedure

The constant amount of P_2O_5 dissolved in each extraction seems to be a unique characteristic of apatite composition for a particular rock, and not the actual content of apatite As shown by the results in tables B-2 and B-3, the fraction of the total P_2O_5 that is solubilized would seem to increase as the grade of the sample decreases, whereas the absolute citrate solubility remained nearly constant. On this

[1]Data from TVA Fundamental Research Branch internal progress reports of October 1969 and December 1970.

Table B-1. Citrate solubility of phosphate rocks

No.	Source	P_2O_5, % Total, of Rock	P_2O_5, % Total, of Apatite[a]	C.S.[b]	Cit. soly. of P_2O_5, % Usual[c]	Cit. soly. of P_2O_5, % Absolute[d]	Length of *a* axis, Å[e]	Mole ratio $CO_3:PO_4$
113	Idaho	31.3	39.0	2.0	6.4	5.1	9.354	0.088
118B	Spanish Sahara	34.8	39.0	2.7	7.8	6.9	9.354	0.060
128A	Idaho	30.3	39.7	2.3	7.6	5.8	9.358	0.078
18	Utah	28.9	39.6	1.9	6.6	4.8	9.357	0.100
14	Togo	36.6	38.7	3.1	8.5	8.0	9.351	0.075
13	N. Carolina	30.2	34.5	6.6	21.9	19.1	9.323	0.262
101	Morocco	31.6	34.8	5.1	16.1	14.6	9.325	0.236
111	Florida	33.6	37.0	3.9	11.6	10.5	9.339	0.169
98	Tennessee	27.7	37.4	3.0	10.8	8.0	9.342	0.137
24	Tennessee	35.6	39.4	2.6	7.3	6.6	9.356	0.045
15	Gafsa, Tunisia	29.2	35.0	7.0	24.0	20.0	9.326	0.285
106	Morocco	31.4	35.8	4.5	14.3	12.6	9.331	0.22[illegible]
137	Florida (North)	32.7	35.6	4.5	13.8	12.6	9.330	0.178
22	S. Carolina	28.3	34.4	5.6	19.8	16.3	9.322	0.273
124	Morocco	32.1	35.0	4.8	15.0	13.7	9.326	0.214
122X	Israel	33.8	36.0	5.8	17.2	16.1	9.333	0.178
103	S. Carolina	26.4	35.5	5.2	19.7	14.7	9.329	0.292
20	Florida	30.8	36.2	4.9	15.9	13.5	9.334	0.197
16	Morocco	33.1	37.2	4.7	14.2	12.6	9.341	0.185
17	Morocco	36.9	38.2	3.9	10.6	10.2	9.347	0.098
23	Wyoming	31.1	40.2	2.4	7.7	6.0	9.361	0.061
202	Tunisia	27.4	34.8	6.6	24.1	18.9	9.325	0.289
69B	S. Carolina	33.0	34.8	5.5	16.7	16.1	9.325	0.211
102	Morocco	33.6	35.9	5.7	17.0	15.9	9.332	0.158
160	Florida	33.2	37.2	4.0	12.1	10.8	9.340	0.156
49	Florida	28.6	36.7	4.3	15.0	11.7	9.337	0.140
95	Wyoming	33.4	40.0	1.1	3.3	2.8	9.360	0.068
135	Florida (South)	31.3	35.8	5.0	16.0	14.0	9.331	0.222
129	Florida	33.2	36.0	4.8	14.5	13.3	9.333	0.175
97	Montana	36.9	39.4	2.1	5.7	5.3	9.356	0.056
136	Florida (South)	32.2	36.0	5.0	15.5	13.9	9.332	0.205
104	Montana	34.3	40.4	2.1	6.1	5.1	9.362	0.056
93	Tennessee	34.1	39.8	2.5	7.3	6.3	9.358	0.065
68	N. Carolina	30.5	34.8	7.2	23.6	20.7	9.324	0.264
133X	Algeria	31.2	37.2	4.0	12.8	10.8	9.340	0.212
126X	Israel	33.5	37.9	4.2	12.5	11.1	9.345	0.155
171	Tennessee	34.6	38.2	4.4	12.7	11.5	9.347	0.138
94	Tennessee	31.1	38.8	2.3	7.4	5.9	9.351	0.089
21	N. Carolina	30.1	35.2	7.6	25.2	21.6	9.327	0.259
134	Florida (South)	30.5	36.1	5.6	18.4	15.5	9.333	0.228
110	Florida	33.6	36.7	3.4	10.1	9.3	9.337	0.124
505	Missouri	34.7	42.0	0.5	1.4	1.2	9.373	0.008
469	India (J-K)	40.1	40.8	2.1	5.2	5.1	9.365	0.028
466	Florida (North)	32.4	36.3	6.6	20.4	18.2	9.334	0.184
44	Australia	39.2	41.0	1.8	4.6	4.4	9.366	0.012
465	Idaho	32.3	39.5	3.7	11.5	9.4	9.356	0.089
467	N. Carolina	29.9	34.5	7.8	26.1	22.6	9.322	0.266
464	Florida	32.7	37.9	5.3	16.2	14.0	9.345	0.120
468	Tennessee	30.7	39.6	4.5	14.9	13.7	9.358	0.061

[a] P_2O_5 content of apatite, calculated from length of *a* axis
[b] Soluble in neutral ammonium citrate solution, AOAC method.
[c] Fraction of rock P_2O_5 citrate soluble
[d] (Citrate-soluble P_2O_5)/(P_2O_5 content of apatite).
[e] Determined by x-ray

Table B-2. Successive citrate extractions of phosphate rock (MR-467, North Carolina. Each extraction made for 1 hour at 65° C with 100 ml neutral ammonium citrate solution/g solid)

Extn. No.	P_2O_5 content, %, of input solid		Cit. soly. of P_2O_5, %		Composition of residue, %	
	Total	C.S.	Conventional[a]	Absolute[b]	Acid insol.	Apatite
1	30.5	7.1	23.3	20.6	4.0	88.1
2	30.2	7.0	23.2	20.3	5.1	87.3
3	29.5	7.3	24.7	21.2	6.6	85.3
4	28.5	7.3	25.6	21.2	8.7	82.4
5	27.6	7.3	26.4	21 2	11.4	79.8
6	25.7	7.3	28.4	21.2	16.1	74.3
7	23 4	7.0	29.9	20.3	22.3	67 6
8	20.7	6.9	33.3	20.0	30.0	59.8

[a]Fraction of input P_2O_5 citrate soluble.
[b](Citrate-soluble P_2O_5)/(P_2O_5 content of apatite); apatite contained 34 5% P_2O_5.

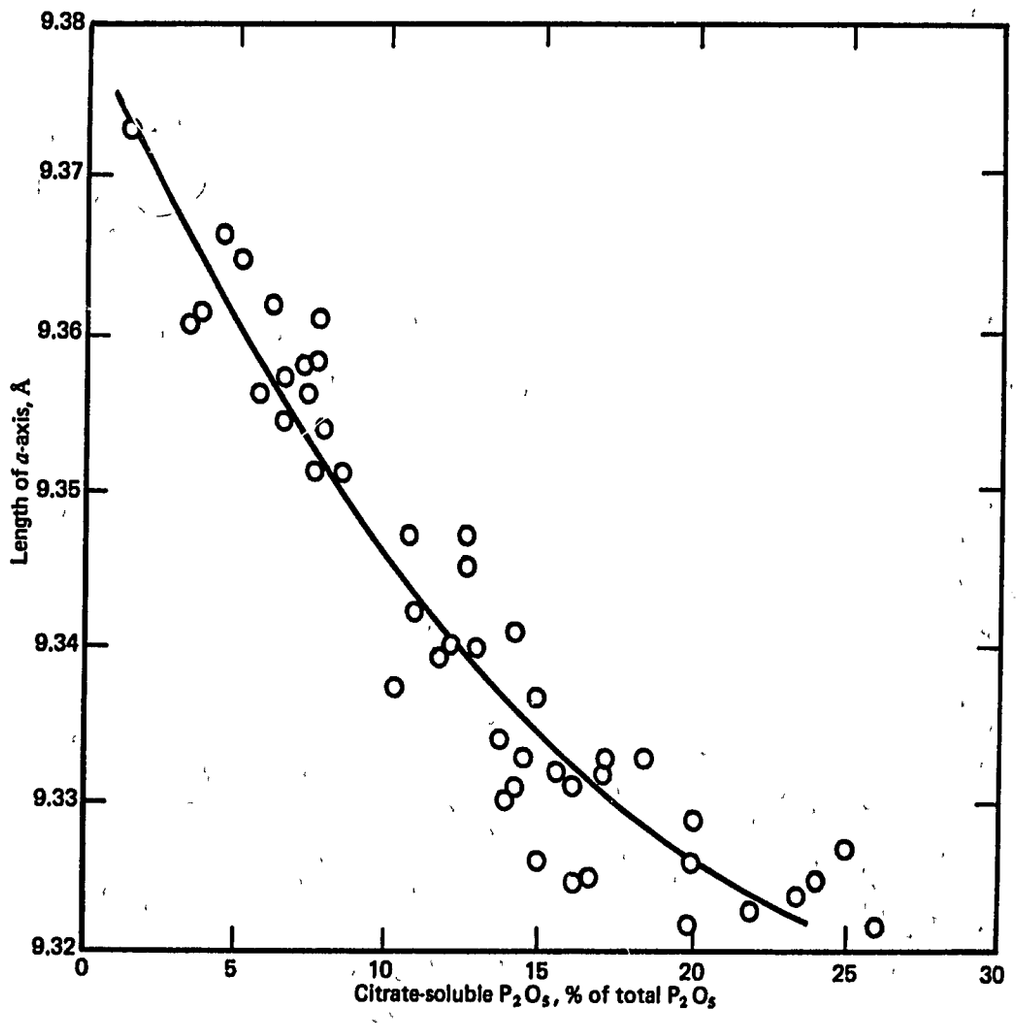

Figure B-1. Relation between citrate solubility of apatite and its composition as indicated by length of *a*-axis

Table B-3. Citrate extractions of mixtures of phosphate rock and quartz (MR-467, North Carolina. Each extraction made with 1 g of mixture by AOAC method)

Composition of mixture, g		P_2O_5 content of mixture, %		Cit. soly. of P_2O_5, %	
Phosphate rock	Quartz	Total[a]	C.S.	Conventional[b]	Absolute[c]
0 91	0 09	27 2	5 7	21.0	16.6
0 86	0 14	25.7	5 9	23.0	17.1
0.80	0.20	23.9	6.0	25.1	17.4
0 69	0.31	20.6	5.6	27.2	16.1
0.65	0.35	19 4	5.7	29.4	16.4
0.50	0.50	14.9	5.5	36.9	15.8
0.25	0.75	7.6	4.7	61.8	13.6

[a]The phosphate rock contained 29.9% P_2O_5.
[b]Fraction of input P_2O_5 citrate soluble.
[c](Citrate-soluble P_2O_5)/(P_2O_5 content of apatite); apatite contained 34.5% P_2O_5.

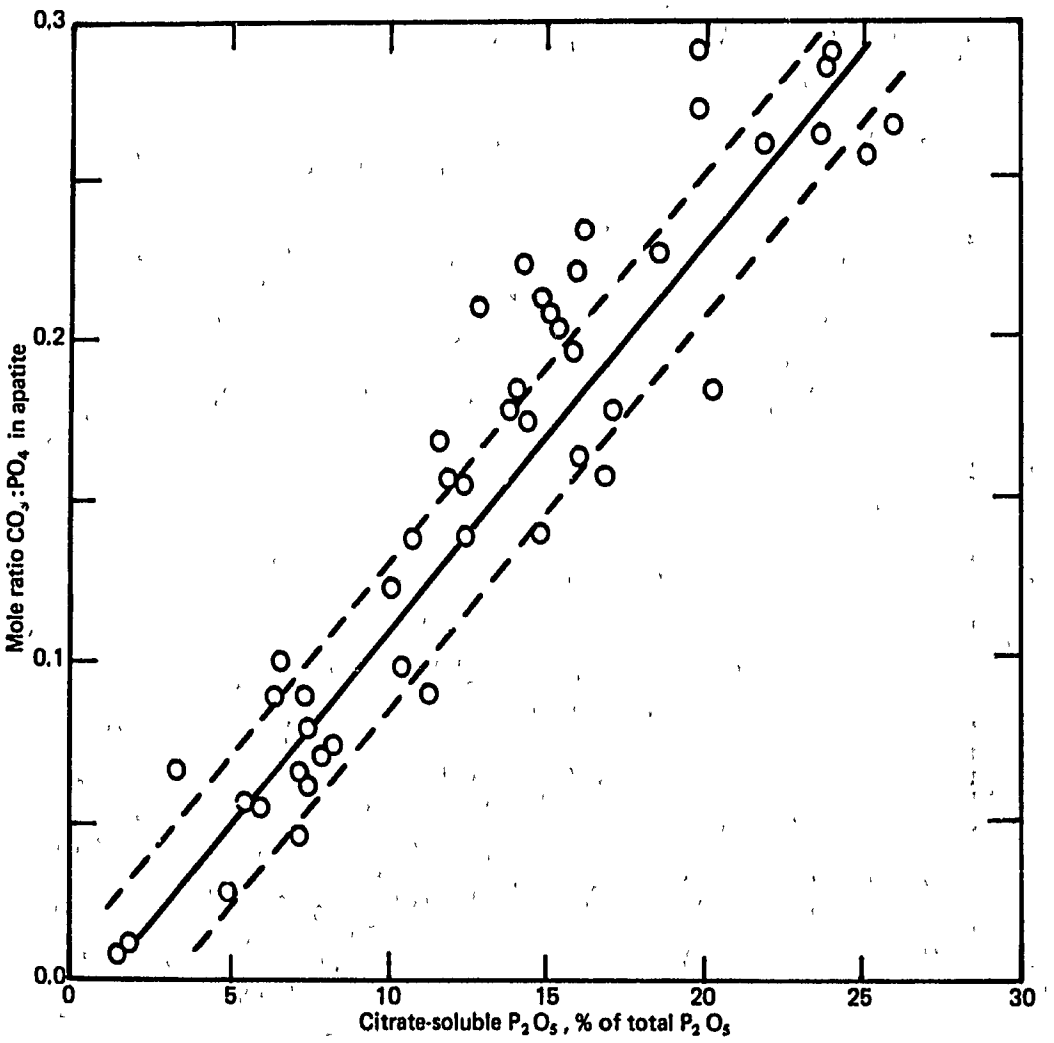

Figure B-2. Relation between citrate solubility of apatite and its composition as indicated by mole ratio CO_3:PO_4

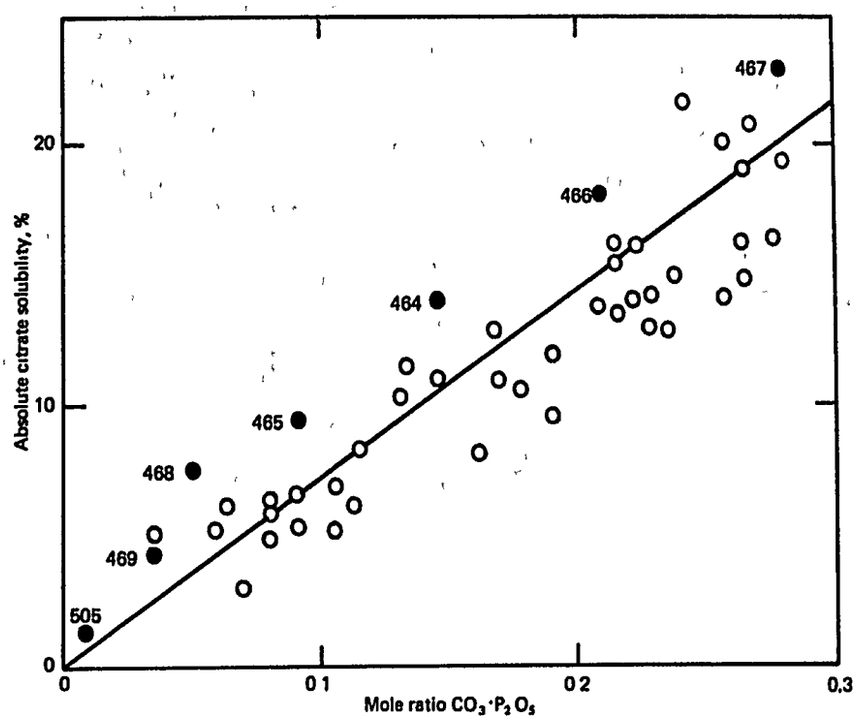

Figure B-3. Relationship between absolute citrate solubility and crystal chemical composition of apatite in phosphate rocks

new basis, the relationship between citrate solubility and apatite composition can be represented without interferences from spurious grade effects (figure B-3).

Physical Studies—The two physical parameters evaluated in this study are x-ray crystallite size of the apatites and physical screen fractions (aggregates, small crystallites) Previous studies have shown that variation in composition of the apatite is reflected in variations in physical parameters. One of these variations is a decrease in x-ray crystallite size with decrease in the value of *a* that results from increase in substitution of CO_3 for PO_4 in the apatite

In figure B-4 the increase in citrate solubility with decrease in crystallite size is shown to follow the semilogarithmic relationship

$$ACS = 71.22 - 20.80 \log XC \qquad (14)$$

where XC = x-ray crystallite size, Å

which has a correlation coefficient of 0.92. The semilogarithmic relationship is the normal response of many chemical and physical parameters to variations in crystallite size. As shown by equation 14, a tenfold increase in x-ray crystallite size results in a tenfold decrease in citrate solubility The general explanation of this decreased solubility is that the surface area of the sample is inversely proportional to the mean diameter of the apatite crystallite size. The theoretical surface areas calculated from the x-ray crystallite size, listed in table B-4, show an eightfold difference between the largest and smallest values of the surface areas

The surface areas of the seven AID rocks were measured by the acetic acid-toluene method described by Mesmer and Irani [*Anal Chem* 35 1067-69 (1963)] The screen fractions (aggregates of individual apatite crystallites) were prepared by wet screening to effect disintegration of large aggregates and removal of fines from the surfaces of particles on the larger screens The minus 5-μm fraction was removed by decantation of the fines from an aqueous suspension All the screened samples were dried for 24 hours at 205°C before measurements of surface area The cross sectional area of acetic acid was taken as 22.4 $Å^2$ The results are shown in table B-4

The surface areas measured by the toluene-acetic acid method are less than the theoretical areas because the x-ray crystallite sizes are averages that may not correspond to the actual physical size of the apatite crystallites. Electron microscope studies have shown that the x-ray data only approximate the actual size of the apatite crystallites, and the errors may be as much as several percent Furthermore, the theoretical surface area contains no correction for texture or the degree of contact between adjacent surfaces of crystallites, a highly individual property of each phosphate rock that can significantly decrease the effective

Table B-4. Surface areas of seven AID phosphate rocks

No.	Source	Surface area, m^2/g, of indicated screen fraction[a] -150 +200 mesh	-200 +325 mesh	-325 mesh +5 μm	Theoretical surface area,[b] m^2/g
464	Florida	8 2	9.0	9.7	44.0
465	Idaho	3.3	2.8	4 5	32.6
466	Florida (North)	20.0	22.0	26.0	39.5
467	N. Carolina	34.0	36.0	37.0	75.0
468	Tennessee	17.0	19.0	23 0	32.6
469	India	3.1	3.2	3.8	9.4
505[c]	Missouri	2.5	7.8	2.2	9.4

[a]Measured by the toluene-acetic acid method of Mesmer and Irani
[b]Calculated from the relation $S = 6/\rho D$, where S = surface area, m^2/g, ρ = density, 3 2 g/cc, D = equivalent spherical diameter, μm, of crystallites, taken as *a* crystallite size as determined by x-ray
[c]Sample contained residual flotation agent that may have caused erratic results

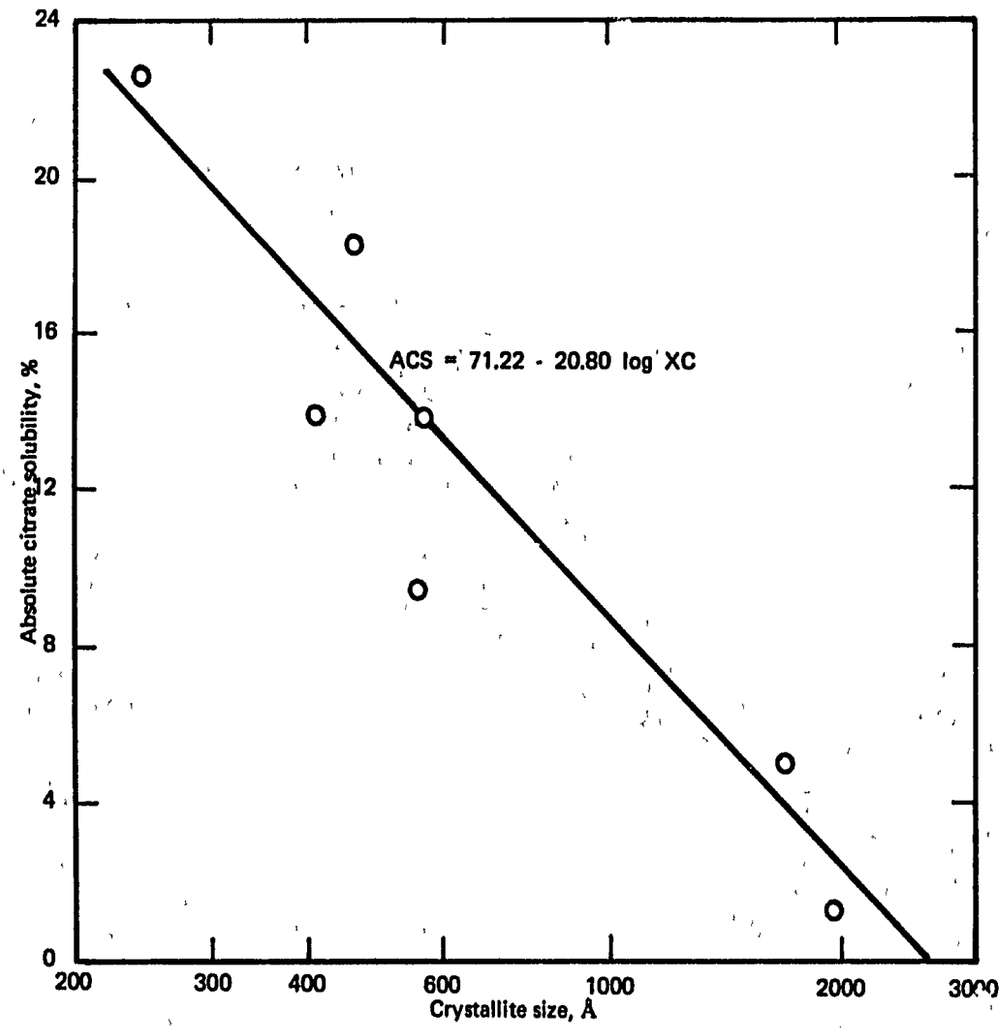

Figure B-4. Effect of crystallite size on absolute citrate solubility

surface area. In addition, the use of acetic acid restricts the surface area to that contributed by surfaces and pores accessible to the acetic acid molecule which is assumed to have a cross sectional area of 22 4 Å², whereas the theoretical surface area calculation contains no such restriction.

In spite of these discrepancies, the data show some interesting trends. The rocks with the highest citrate solubilities have the largest surface areas and, on this basis, can be placed in the same order of reactivity as that shown by solubility in neutral ammonium citrate or 2% citric acid solutions. The Tennessee phosphate rock (MR-468) is an exception, this rock contains more than 20% impurities, principally quartz and clay. The clay minerals have large surface areas and contribute a significant error in the calculation of these areas The surface area of the apatite portion of the sample should be about the same as that of the Idaho rock (MR-465) based on the similarities in composition and crystallite size shown by x-ray examinations.

It is noteworthy that decrease in particle (screen) size (aggregates of apatite crystallites) resulted in relatively small increases in surface area, which shows that the geometric surface area associated with the decrease in average physical particle size is not a significant fraction of the total surface area of these phosphate rocks The specific geometric surface area, that is, the surface area of 1 g of spheres with the mean diameter of the openings in the two screens, is 0 02 m^2 for the minus 150- plus 200-mesh fraction, 0 03 m^2 for the minus 200- plus 325-mesh fraction, and 0 08 m^2 for the minus 325-mesh plus 5-μm fraction. It is thus apparent that the geometric surface area constitutes no more than 4% of the total surface of any screen fraction measured by the toluene-acetic acid method, so that most of the total surface area is that of the individual apatite crystallites and pores The crystallite size has been shown to be a function of the composition of the apatite and it probably determines the porosity, whereas the properties of the screen fractions are controlled by the aggregates of crystallites comprising the physical particles

The x-ray crystallite sizes of the residues from the successive 1-hour extractions of the North Carolina rock (MR-467) showed approximately a 20% decrease in the size of the *a* crystallite size after eight extractions The changes in the *c* crystallite size were erratic The decrease in crystallite size on repeated extractions may indicate some influence of texture on the dissolution An increase in crystallite size because of selective dissolution of smaller crystallites would have been expected theoretically, and further work will be required to confirm these observations.

The effect of the physical particle size (aggregates of crystallites) on the citrate solubility of the P_2O_5 was investigated by wet-screening the material into minus 150- plus 200-mesh, minus 200- plus 325-mesh, and minus 325-mesh plus 5-μm fractions, and the citrate-soluble and total P_2O_5 were determined on each fraction. The results, summarized in figure B-5, show a small but consistent increase in citrate-soluble P_2O_5 with decreasing particle size, but the citrate solubility of the untreated head sample was generally higher than that of the corresponding minus 325-mesh plus 5-μm fraction. The same result was reported by Caro and Hill (6) on their dry-screened minus 325-mesh composite samples, and they attributed the difference to the effects of grinding In our data, the difference could represent a very reactive portion of the sample that was discarded with the minus 5-μm material A similar increase in solubility with decreasing screen size is shown by the citric acid solubility data in table B-5

To evaluate this effect, portions of the same head sample were ground and dry-screened into the same fractions as before, except that all the material passing the 325-mesh screen was composited for evaluation The data in table B-6 show the same small but consistent increase in solubility with decreasing particle size that was observed in the wet-screened samples, and the same difference between the untreated head sample and the minus 325-mesh composite, except for the North Carolina rock (MR-467) which equals it Thus the difference cannot be ascribed to a reactive very fine fraction alone

From these data there was calculated the total P_2O_5, citrate-soluble P_2O_5, and the fraction of the total P_2O_5 that was citrate soluble for each screen fraction. These calculations could not be made on the wet-screened fractions because weight records were not kept and some material was discarded The rock from north Florida (MR-466) is the only sample in which the minus 325-mesh composite contributed more than 20% of the total citrate-soluble P_2O_5 This means that, although there is a small but consistent increase in citrate solubility with decreasing screen size, the contribution of the minus 325-mesh material is less than 20% of the total citrate-soluble P_2O_5 and is, of course, directly proportional to the weight percent represented by that screen fraction. The apparent increase in total citrate-soluble P_2O_5 in the minus 325-mesh composite is small compared with the total sample, and is not the major source of variability observed in these series of tests

Comparisons of the data on wet- and dry-screened samples indicate that the minus 5-μm material discarded in the wet-screened samples added significantly only to the North Florida rock (MR-466) and contributed small increases to the other rocks The small differences observed in the data from the different screen fractions may represent differences in the relative efficiencies of the two methods of screening It is usually considered that wet screening is more efficient and produces more uniform samples, but that dry screening is more practical, particularly if large samples are involved

Table B-5. Citrate solubility of screen fractions of phosphate rocks
(C.S. = citric acid-soluble P_2O_5, % of sample; ACS = absolute citrate solubility, %)

Through on	150 mesh 200 mesh	200 mesh 325 mesh	325 mesh 5 μm	Average	Rank
MR-464, Florida					
C S	6 7	7.0	7.9	7.2	3
ACS	17.7	18 5	20.8	19.0	
MR-465, Idaho					
C S	6.4	6.6	7.0	6.7	4
ACS	16.0	16.5	17.5	16.7	
MR-466, Florida (North)					
C S	7.6	7.6	8.1	7.8	2
ACS	20.9	20.9	22.3	21.4	
MR-467, North Carolina					
C.S.	12.4	12.2	13.1	12.6	1
ACS	36.0	35.4	38.0	36.5	
MR-468, Tennessee					
C.S.	6.3	6.7	6.9	6.6	4
ACS	15.9	16.9	17.4	16.7	
MR-469, India					
C S	2.9	3.2	4.4	3.5	6
ACS	7.1	7.8	10.8	8.8	
MR-505, Missouri					
C.S	0.8	1.1	0.8	0.9	7
ACS	1.9	2.6	1.9	2.1	

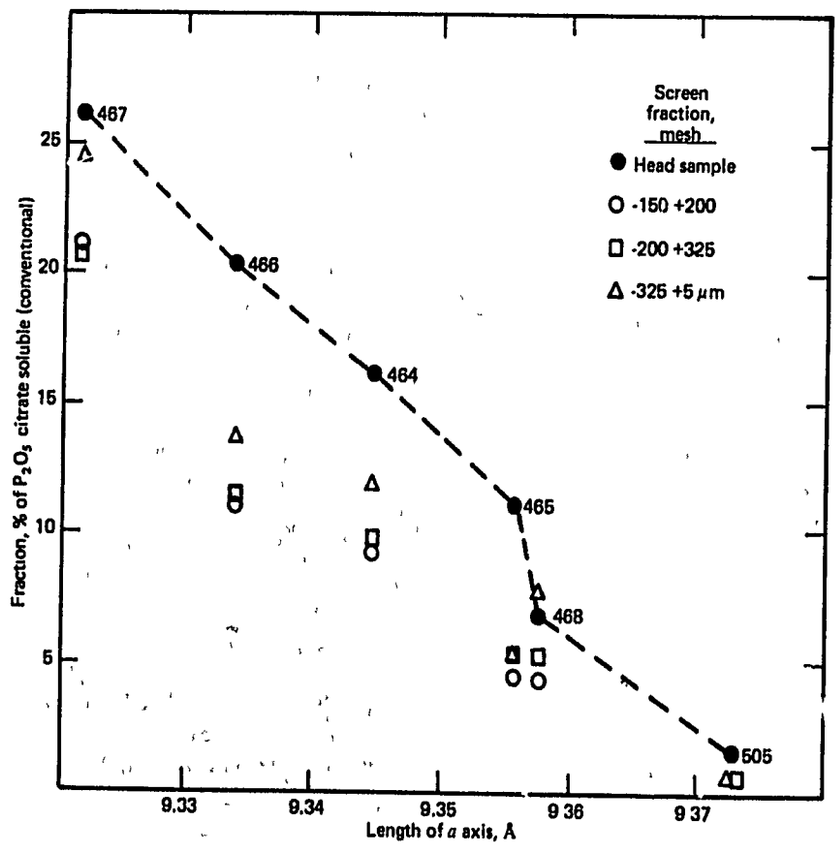

Figure B-5 Effects of crystal chemical composition of apatite and physical particle size of phosphate rock on conventional citrate solubility

Summary—The citrate solubility of phosphate rocks is a function of their chemical and physical characteristics and increases with increase in substitution of CO_3 for PO_4 in the apatite structure This substitution is accompanied by a decrease in crystallite size and a resultant increase in surface area of the apatite

The apatites in phosphate rocks have a characteristic limit of dissolution in neutral ammonium citrate that can be correlated with their crystal chemical composition. From derived statistical models it was shown that the ACS of the apatite in the sample provided a better basis for comparing phosphate rocks than the conventional fraction of the total P_2O_5 that is citrate soluble.

The increase in citrate solubility with decrease in crystallite size and increasing surface area was larger than the increase with decrease in particle (screen) size. The small but consistent increase in apparent citrate solubility with decreasing particle size decreased in significance when compared with the percent of total citrate-soluble P_2O_5 contributed by each screen fraction

In conclusion, it has been shown that both chemical and physical factors are significant in the tenfold difference in citrate solubility of the P_2O_5 of phosphate rocks observed in this study The quantitative significance of each factor is uncertain, but it is apparent that variation in crystal chemical composition and related changes in physical properties cause more variation in citrate-soluble P_2O_5 than any variation in physical particle size The combination of unavoidable errors in measurements of apatite crystal properties and in analytical results contribute to the scatter of data.

Table B-6. Citrate solubility of screen fraction of phosphate rock (rocks dry screened; no material discarded)

Rock	Screen fraction, mesh	Wt % of head sample	P_2O_5, % Total	P_2O_5, % C.S.	C.S. P_2O_5, % of total P_2O_5	Grams P_2O_5/100 g head sample Total	Grams P_2O_5/100 g head sample C.S.	C S. P_2O_5, % of total P_2O_5 in head sample	Distribution %, of total C.S. P_2O_5 in head sample
464	-150 +200	48.2	31.5	2 5	7.9	15.2	1.2	3 8	38.8
Florida	-200 +325	36.8	33.3	3.9	11.7	12.2	1 4	4 3	43 8
	-325	15.0	33.5	3.9	11.6	5.0	0 6	1.7	17.3
		100.0	32 4	3 2	9.8	32.4	3.2	9.8	99.9
465	-150 +200	57.2	32 9	1 9	5.8	18 8	1.1	3.3	51.0
Idaho	-200 +325	36.4	32 0	2.3	7.2	11.6	0.8	2.6	39.8
	-325	6.4	31 0	2.7	8.7	2.0	0.2	0.6	9.2
		100.0	32.4	2.1	6.5	32.4	2.1	6.5	100.0
466	-150 +200	39.4	32.1	3.4	10.6	12.6	1.3	4.2	30.8
Florida	-200 +325	43.2	32.9	4 7	14.3	14.2	2.0	6.2	45.6
(North)	-325	17.4	33.2	6.1	18.4	5.8	1.1	3.2	23.5
		100.0	32.6	4.4	13.6	32.6	4.4	13.6	99.9
467	-150 +200	21.1	29 8	5.5	18.4	6.3	1.2	3.9	16.9
N. Carolina	-200 +325	64.4	30 4	7.2	23 7	19.6	4.6	15.3	66.4
	-325	14.5	30 6	8.0	26.1	4.4	1.2	3.8	16.5
		100 0	30.3	7.0	23.0	30.3	7.0	23.0	99.8
468	-150 +200	59.9	32.0	1.7	5.3	19.2	1.0	3.2	52.2
Tennessee	-200 +325	30.9	28.8	2.0	6.9	8.9	0.6	2.1	34.2
	-325	9.2	26.5	2.3	8.7	2.4	0.2	0.8	13.6
		100.0	30.5	1.8	6.1	30.5	1.8	6.1	100.0
505	-150 +200	48.8	32.7	0.1	0.3	16.0	0.0	0.1	50.0
Missouri	-200 +325	37.7	35.9	0.1	0.3	13.5	0.0	0.1	50.0
	-325	13.5	32.7	0.1	0.3	4.4	0 0	0.0	0.0
		100.0	33.9	0.1	0.3	33.9	0.0	0.2	100.0

Appendix C

SAMPLE CALCULATION TO ILLUSTRATE THE EVALUATION PROCEDURE FOR DETERMINING THE RELATIVE REACTIVITY OF A PHOSPHATE ROCK FOR DIRECT APPLICATION USE

Sample Description—TVA sample No. PR-8, a prepared concentrate of a sedimentary phosphate rock (73% BPL; 33.25% P_2O_5) from an unspecified Moroccan source.

Step 1: X-Ray Evaluation

Determine unit-cell dimension a_0 $a_0 = 9\ 337$ Å

This a_0 dimension corresponds to an apatite composition with the empirical formula $Ca_{9.67}Na_{0.24}Mg_{0.09}(PO_4)_{5.08}(CO_3)_{0.92}F_{2.37}$ and a theoretical P_2O_5 content of 36 85%

Step 2: Calculation of Absolute Citrate Solubility (ACS)

From the statistically derived correlation·

$$ACS = 421\ 4\ (9.369 - a_0)$$

In PR-8: $ACS = 421.4\ (9.369 - 9.337)$

$= 13.48\%$

Step 3: Relative Citrate Solubility (RCS)

Referring to figure 2 in which sample MR-467 (North Carolina) with ACS = 22 6% is used as the base 100%,

RCS of Sample PR-8 = (13 48/22 6) (100) = 60%

The value of 60% falls in the upper range for Moroccan phosphate rocks (45-72% RCS), and compares with the most reactive rocks in the Central Florida group, for example

Predicted AOAC Citrate-Soluble P_2O_5:

From the chemical relationship: $ACS = \frac{\%\ CS\ P_2O_5}{Theor.\ P_2O_5}$

In PR-8: % CS P_2O_5 = (13.48)(36 85)/100 = 5.0%

By chemical analysis, CS P_2O_5 = 5.1, 5.0%.

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