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**The chemistry and mineralogy of phosphorus in excessively
fertilized soils**

Pierzynski, Gary Michael, Ph.D.

The Ohio State University, 1989

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THE CHEMISTRY AND MINERALOGY OF PHOSPHORUS IN EXCESSIVELY
FERTILIZED SOILS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By

Gary Michael Pierzynski, B.S., M.S

* * * * *

The Ohio State University

1989

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A handwritten signature in dark ink, appearing to read "Terry J. Logan", is written over a horizontal line. The signature is fluid and cursive.

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- Pierzynski, G.M., S.R. Crouch, and L.W. Jacobs. 1986. Use of direct-current plasma spectrophotometry for the determination of molybdenum in plant tissue digests and soil extracts. *Commun. Soil Sci. Plant Anal.* 17: 419-428.
- Pierzynski, G.M., and L.W. Jacobs. 1986. Molybdenum accumulation by corn and soybeans from a molybdenum-rich sewage sludge. *J. Environ. Qual.* 15: 394-398.
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FIELDS OF STUDY

Major Field: Soil and Environmental Chemistry

Studies in Phosphorus Soil Chemistry. Professor
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Chapter I

INTRODUCTION

1.1 Introduction

It is necessary at the beginning of this dissertation to define excessively fertilized soils. For our purposes the term applies to soils that have received quantities of phosphorus (P) from fertilizers, manures, or sewage sludges that exceed amounts required for normal crop growth. The onset of high-input agriculture coinciding with the introduction of high-yielding crop varieties, when farmers were encouraged to build soil P levels, has produced a generation of farmers who continue to apply P even after soil tests no longer indicate a need, a practice sometimes referred to as "recipe" farming (Cope, 1981). High percentages of soils in Ohio and Michigan were shown to have Bray-P1 extractable levels in excess of 100 kg P/ha (Logan, 1978). Crops grown on soils with available P levels greater than 40-80 kg P/ha would show little or no response to P additions (Johnson, 1988).

These high levels of soil P have become an issue for two major reasons: 1) Despite the success of the Clean Water Act and its amendments in removing point source discharges of P into our surface waters, eutrophication

remains a persistent problem in many areas such as the lower Great Lakes and Chesapeake Bay. The major source of the P is diffuse (non-point source) and represents runoff from agricultural land of P originally applied as inorganic fertilizers as well as native soil P; and, 2) with the current economic problems of American farmers, the question of utilizing the soil P "reserve" for crop growth becomes important in the effort to reduce production costs.

It was recognized early in the history of P fertility research that the primary mechanisms for P removal from soil were crop removal and erosion and that these losses were usually minor. The fact that P inputs frequently exceeded outputs, and that P accumulation was occurring in manured soils was noted some 50 years ago (Pierre, 1938). The scenario that develops is that, as P accumulates in a soil, eventually all of the adsorption sites are occupied and secondary P solids may precipitate (Larsen, 1967; Sample et al., 1980). The use of the word "solids" is preferred over the term "minerals" since "minerals" are defined as having specific crystalline structures which cannot be assured.

The formation of secondary P solids as a result of P additions requires study since the extent to which excessive applications of P are ultimately precipitated as thermodynamically stable, low activity solids, is not

known. Metastable minerals such as dicalcium phosphate dihydrate (DCPD) can readily dissolve if ortho-phosphate (o-phosphate) activities decrease with cropping, but less soluble minerals such as the apatites or variscite are thermodynamically favored and would not dissolve as readily (Lindsay, 1979). If a significant portion of applied P ends up as thermodynamically stable solids with low solubility, then there is little economic advantage to building up or maintaining high levels of soil P.

The approaches used in studying secondary P minerals can be broadly categorized into two types: 1) the indirect approach utilizing equilibrium experiments in which the soil solid phases are assumed to be in equilibrium (i.e., ions in solution are in equilibrium with a solid that is thermodynamically favored in that system) or steady state (i.e., meta-stable condition in which the indicators of equilibrium are time invariant within the experiment but ion activities may not be controlled by the thermodynamically favored solid) with an aqueous phase and, through ion activity calculations, the presence of a specific secondary P mineral is inferred; and, 2) a number of direct approaches dependent upon the interaction of secondary phosphate solids with energy sources such as x-rays, electron beams, infrared radiation or visible light.

The underlying objective in most research on high P soils is to determine the availability of the P as a plant nutrient or as a pollutant. This objective may not be clear when considering the intricacies of identifying a P solid in soils (indirectly or directly) but is more apparent when reviewing the voluminous literature on soil extractants, P pollution of surface waters, residual P availability, etc. This objective also underlies the research to be described in this dissertation and shall be approached by obtaining as much information as possible on the secondary P solids and combining that information with empirical estimates of P availability. We can now consider the literature in more detail.

Chapter II

LITERATURE REVIEW

2.1 Forms of P in the Soil and the Associated Nomenclature

The role of P in agricultural systems has been studied extensively. One result of effort this has been an over abundance of descriptive terminology for the various forms of P in soil. It then becomes necessary for the author to define the terminology that will be used in this dissertation.

The processes involving the inorganic solid-phase P fractions and their interactions with solution P can be expressed as:

Solution P $\xrightleftharpoons{k_1}$ Labile P $\xrightleftharpoons{k_2}$ Nonlabile P $\xrightleftharpoons{k_3}$ Residual P
where k denotes the rate constant in the direction of solution P. We would then have $k_1 \gg k_2 \gg k_3$. The organic P fractions, composed of the biomass, organic P, and stable organic P, also affect solution P levels.

Soil solution P can be estimated by soil solution displacement, or extraction with water or weak salts. This is probably the most environmentally active form because it is readily available for leaching and runoff as

well as use by biota and for conversion to various inorganic forms.

Labile P, or perhaps better termed rapidly equilibrating P, represents P that can readily replenish solution P if solution P is depleted. Using terms such as "rapid" implies a time frame and, although arbitrary, 24 to 48 h is frequently used for laboratory purposes (Barber, 1984). This concept arises from the resolution of the isotope exchange reaction of soil P into a fast reaction, essentially complete in 24 h, and a slow one that may continue for times in excess of seven d (Jose and Krishnamoorthy, 1972). Forms of P contributing to labile P include P weakly adsorbed to Al and Fe oxides and to the edges of clay minerals, as well as highly-soluble secondary P solids (Murrmann and Peech, 1969). Labile P is estimated with either resin extraction (Amer et al., 1955) or as isotopically exchangeable P (Olsen and Sommers, 1982). The combination of solution and labile P is generally thought to represent the majority of plant-available P.

Non-labile P, or slowly equilibrating P, are forms that can replenish solution P and labile P when they are depleted, but on a much longer time scale. Phosphorus strongly adsorbed to Fe and Al oxides and clay minerals, as well as sparingly soluble primary and secondary P solids, comprise the majority of this classification.

Residual inorganic P includes P that does not contribute to the equilibria of the other more reactive P forms. It includes occluded P, physically encapsulated P in minerals structurally devoid of P, and P present within the lattices of silicate minerals. A study of New Zealand soils revealed that apatite present as inclusions with primary minerals contributed to major portion of residual inorganic P (Syers et al., 1969).

Finally, P present in organic forms exists within living organisms (biomass), decomposing organisms (organic P) or relatively stable organic materials present in humic and fulvic acids (stable organic P). Organic P occurs primarily as ester linkages on inositols as well as phospholipids and nucleic acids (Cosgrove, 1977).

The reader should bear in mind that these classifications of P are arbitrary and not mutually exclusive. Due to the ubiquitous presence of P in soil, however, they aid in understanding this very complicated system.

Another classification scheme that has been used extensively is selective chemical dissolution. This method, originally employed by Chang and Jackson (1957), is based on the premise that, in soils in which the P cycle is in dynamic equilibrium, inorganic P can be fractionated into gross categories such as Ca, Fe, or Al bound. The method implies that the chemistry of a

particular fraction is sufficiently distinct from the remaining fractions that one fraction can be selectively extracted. The usefulness of this procedure with soils amended with P can be questioned, most importantly because the criteria for dynamic equilibrium cannot be ensured.

2.2 Phosphate Solubility Equilibria

From a theoretical standpoint, the study of secondary P solids with the solubility equilibria approach seems quite appropriate. In a soil of average total P content of approximately 600 mg P/kg at 10% moisture, the concentration of P in the soil solution is $10^{-0.71}$ M P if all of the P in the soil is in solution. Since water-soluble P concentrations are generally $< 10^{-3.5}$ M, the balance of the P must be associated with solid phase (Lindsay, 1979). If a number of solids appear to be possible (e.g., calcium phosphates), the theory predicts that the solid phase controlling the activity of the ion in question will be the solid that maintains the lowest solution activity of that ion. Since the chemical potential of the ion will be the lowest wherever the activity is lowest, then that solid represents the most stable environment for that ion (Sposito, 1981).

It is important to summarize what thermodynamics can and cannot tell us. For the general precipitation-dissolution reaction

where v = stoichiometric coefficients and m and n refer to ionic valences, we can calculate the equilibrium constant (K) as

$$K = (C^{m+})^{v1}(A^{n-})^{v2} / (C_{v1}A_{v2}(s)) \quad (2.2)$$

and from this, the ion activity product (IAP), where $IAP = (C^{m+})^{v1}(A^{n-})^{v2}$ (Sposito, 1981). If a solution in question has an IAP that is equal to that expected for a particular solid, then indirect evidence that the solution is in equilibrium with that solid, in its standard state, has been obtained. If the IAP is not equal to that expected for a particular solid, then a number of possibilities exist: 1) the system may not have reached equilibrium (i.e. kinetics of precipitation-dissolution are a limiting factor); 2) the system may be in equilibrium with a different solid; and 3) the system may be in equilibrium with the solid but the solid may not be in its standard state (Sposito, 1981).

Implicit in this discussion is that ion activities can be accurately determined. The development of computer models such as GEOCHEM (Sposito and Mattigod, 1980), which attempt to account for all of the possible forms of an ion in solution, including ion pairs and soluble complexes,

have made this task much easier. One major research topic remaining in ion speciation is the role of soluble organics, primarily fulvic acids, and their effects on ion activities. Several models, run with GEOCHEM, have been presented as attempts to model the influence of fulvic acids on ion activities. The mixture model assumes that the influence of the fulvic acids on ion activities can be estimated by the influence of a mixture of simple organic acids, with known metal complexation constants, on ion activities. The mixture of organic acids was chosen because they gave pH titration curves similar to the soluble organics extracted from a sludge amended soil (Sposito et al., 1982). The fulvate model, developed from the same sludge-soil system as the mixture model, contains experimentally determined complexation constants for four metals for which ion specific electrodes exist (Cd^{2+} , Cu^{2+} , Ca^{2+} , and Pb^{2+}). The common logarithms of these constants were then correlated with the metals' Misono softness parameter. This allowed the prediction of complexation constants for metals for which ion specific electrodes do not exist (Mn^{2+} , Mg^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+}) (Sposito et al., 1981).

Blaser and Sposito (1987) studied a water-soluble, chestnut-leaf-litter extract and, using fluorescence spectroscopy, determined that the dominant Al complexing species with the organic ligands were the quasiparticle

species Al^{3+} and $\text{Al}(\text{OH})^+$ with conditional stability constants of $10^{8.55}$ and $10^{-1.8}$, respectively. These constants could be used in a chemical speciation model to estimate the degree of complexation of Al by naturally occurring organic ligands.

To date no studies have been carried out in which the relative merits of the models used to take into account the effects of fulvic acids on ion activities have been considered.

Applications of the solubility equilibria approach, in various forms, have been in use for some time. Early work made distinctions between iron (Fe) and aluminum (Al) phosphates in acid soils as opposed to calcium (Ca) phosphates in high pH soils (Whitson and Stoddard, 1907). Much of the early work in P fertility dealt with increasing the availability of P through liming. This presumably converted Fe or Al phosphates to more soluble Ca phosphates (Pierre, 1938). More recent studies of high P soils using this approach can also conveniently be categorized into those dealing with high or low pH soils.

2.1.1 High pH Soils

O'Connor et al. (1986) noted that the addition of sewage sludge increased P availability, relative to comparable fertilizer P additions, on calcareous soils. They hypothesized the the sludge additions caused a change

from a less soluble to a more soluble P solid phase controlling P solubility. Equilibrium experiments indicated similar P solubilities, however, with both fertilizer or sludge amended systems being in apparent equilibrium with either octacalcium phosphate (OCP) or beta-tricalcium phosphate (TCP). The difference in P availability was attributed to a slight pH reduction that accompanied sludge additions.

A study of 28 near-neutral and alkaline Colorado soils indicated that, after greenhouse cropping, OCP was an important fertilizer residue in only one heavily manured soil (Fixen and Ludwick, 1982). Tricalcium phosphate, or a mineral similar in composition, may have accounted for at least a portion of the residues. Additions of P to calcareous soils were found to induce formation of OCP or DCPD (Moreno et al., 1960; Withee and Ellis, 1965).

A statement common to many studies of high pH soils is that the apatite minerals do not seem to control P solubilities despite being the thermodynamically favored reaction product (e.g. Withee and Ellis, 1965; Harrison and Adams, 1987). Exceptions to this include a study of limed soils that had not received P for at least 5 years which were shown to be in equilibrium with fluoroapatite (Murrmann and Peech, 1968). An apparent flaw in this work is that Ca concentrations were not actually measured but

were assumed to be equal to the Ca concentration in the background electrolyte. Harrison and Adams (1987) used a novel approach in some high P and pH ultisols in which initial solution data indicated supersaturation with respect to hydroxyapatite but after several extractions with 0.01 M MgCl_2 , which exchanged Mg^{+2} for Ca^{+2} and dissolved soil P, an apparent equilibrium with hydroxyapatite was obtained. The hypothesis was put forth that hydroxyapatite does form in soils but it is coated with more soluble Ca phosphates.

An additional common factor of the studies of high pH soils is that many of the data points do not indicate equilibrium with any one Ca phosphate mineral but fall between lines on stability diagrams. Naturally, any of the factors highlighted at the beginning of this section could be probable causes for this observation. Other possibilities discussed in the literature include the influence of soluble organic matter on obtaining equilibrium (Moreno et al., 1960; Arambarri and Talibudeen, 1959), that labile P determines the concentration of P in solution (Murrmann and Peech, 1969), the wide variety of reaction products due to P additions (Bell and Black, 1970b), and Ca phosphate coatings of unknown solubility on precipitated secondary P solid particles (Harrison and Adams, 1987; Rootare et al., 1962).

2.2.2 Low pH Soils

When one considers low pH soils, the number of solids considered is reduced and basically includes only variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), amorphous Al phosphate ($\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$). Obviously, many other Fe and Al phosphate solids exist but their presence has not been suggested in soils. Variscite is the thermodynamically stable Al phosphate in soil systems and equilibrium studies have indicated that it may control P solubility in acid soils that had not been amended with P for at least five years (Wright and Peech, 1960). A subsequent study, in which crystalline variscite and strengite were added to limed soils, showed that these minerals increased labile P by only small amounts and, therefore, were not in equilibrium with the labile P pool (Murrmann and Peech, 1969). Other authors have questioned whether crystalline variscite can form in soils (Hsu, 1965; Larsen, 1967; Webber, 1978).

Receiving increasing attention in the last 20 years has been the amorphous analog of variscite ($\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$). First noted explicitly as a reaction product of exchangeable Al and o-phosphate ions (Coleman et al., 1960), it has since been implied as a reaction product between o-phosphate ions and montmorillonite (Webber, 1971), aluminosilicates, aluminum hydrous oxides, aluminum oxides and allophanic soils (Veith and Sposito, 1977), an

Al saturated peat (Bloom, 1981), and an acidic montmorillonitic soil separate (Traina et al., 1986). The values of pK_{SO} , where $pK_{SO} = pa_{Al^{3+}} + 2pa_{OH^-} + pa_{H_2PO_4^-}$, given in the literature vary somewhat with reviews suggesting a range of 27-29 (Traina et al., 1986; Veith and Sposito, 1977).

Strengite is not often implied as a controlling solid phase for P solubility. Under some soil conditions, namely acidic with low Al^{3+} and high Fe^{3+} activities, strengite may be thermodynamically favored over variscite (Lindsay, 1979). A solid solution exists between variscite and strengite and the formation of a pure Fe or Al phosphate in soils is not likely (Hsu, 1965).

An additional P solid which has been considered recently in the literature is $MnPO_4 \cdot 1.5H_2O$ which is believed to control P solubility in high Mn soils with $pH < 7.2$ and $pe + pH$ below 16 (Boyle and Lindsay, 1986).

2.3 Direct Methodologies for Studying P Solids in Soils

The greatest obstacle in the study of phosphate minerals in soils with direct methodologies is the fact that the average P concentration in soils is only about 600 mg P/kg, some of which is present as organic P, and that the analytical techniques used are simply not sensitive enough at this concentration (Lindsay and Vlek, 1977). Attempts to concentrate P would seem warranted,

but other than observations that P tends to be concentrated in the clay-sized fraction (Lindsay and Vlek, 1977; Norrish, 1968; Hanley and Murphy, 1970), there has been no work in this area. Density separations of soils or soil separates may be successful since the densities of P minerals such as variscite or apatite are sufficiently distinct from that of the bulk of the mass in a clay-sized fraction (Jaynes and Bigham, 1986). A unique aspect of the research to be described in this dissertation is the attempt to obtain soils with total P concentrations much higher than average and this, in combination with P concentrating techniques, may produce soil separates with total P concentration high enough to warrant the use of direct methodologies.

The sensitivity problem has been circumvented in studies in which soils or soil constituents are reacted with saturated solutions of P fertilizers. In these cases solutions with high P concentrations are produced and there is little difficulty in identifying precipitates with techniques such as x-ray diffraction or optical mineralogy. The classical study is one in which three soils and eight soil constituents were reacted with five different P fertilizers and some 30 crystalline and several colloidal phosphate solids were identified after the filtrates were aged (Lindsay et al., 1962). Of particular interest is that monocalcium phosphate (MCP)

produces a solution pH of 1.48 when dissolved in water, and even when reacted with a soil with a high water pH (Webster silty clay loam, pH 8.3) the filtrate pH was <2.39. The product from MCP additions to two of the soils was colloidal $(\text{Fe, Al, X})\text{PO}_4 \cdot n\text{H}_2\text{O}$, where X indicates cations other than Fe or Al. The reaction of the remaining fertilizers (mono or di-ammonium phosphate and mono or di-potassium phosphate) with whole soils produced filtrate pH values >3.74 and did not have colloidal $(\text{Fe, Al, X})\text{PO}_4 \cdot n\text{H}_2\text{O}$ as a product. The persistence of any of the reaction products in soil environments is not known.

Optical examination of soil thin sections was found to be superior to x-ray diffraction for the identification of fertilizer reaction products in soils (Bell and Black, 1970a). With these methods, DCPD was found to be the most prevalent reaction product in soils that had been in contact with solid phosphate fertilizers. It was noted that despite pH values as low as 2.8 near the fertilizers no evidence of formation of Fe or Al phosphates was found although they may have been present in quantities insufficient to detect (Bell and Black, 1970b).

Norrish (1968) used the fact that minerals of the plumbogummite group $(\text{XAl}_3(\text{PO}_4)_2\text{OH} \cdot \text{H}_2\text{O})$ where X = Pb, Ca, Sr or Ba) are more resistant than kaolinite to attack by hydrofluoric acid (HF) to concentrate P in the kaolinitic clay fractions of some Australian soils. Untreated clay

fractions contained four to five times more P than the whole soils while HF-treated clay fractions contained up to 230 times more P than whole soils. Plumbogummite minerals were identified by x-ray diffraction in some of the soils. Norrish (1968) thought that these minerals were pedogenic and may be the result of P fertilization.

Sawhney (1973) utilized thin sections and an electron microprobe to find distinct P-rich particles in the sand and silt fractions of some Connecticut soils and sediments. Representative particles contained P in association with Al, Fe, and Si, and he felt that P was not present as a coating but rather occurred throughout the particles since thin sections were being analyzed. A number of Ca phosphate particles were also identified and assumed to be detrital apatite. The association of P with Al, Fe, Si and Ca has been noted in similar studies (Quershi et al., 1969).

Webber (1971) noted that the reaction of o-phosphate with montmorillonite (Wyoming bentonite) produces amorphous Al phosphate. This product appears to form in the interlayer positions of this clay, as evidenced by x-ray diffraction lines at 2.3 and 1.15 nm, and does not appear to crystallize with aging at 25°C. Heating to 300°C causes the 2.3 nm spacing to collapse to 1.67 nm. This spacing is believed to represent the sum of the d_{001}

spacing of the clay (0.97 nm) and the edge spacing of orthorhombic AlPO_4 (0.7 nm) (Kodama and Webber, 1975).

2.4 Assessing P Availability of Excessively Fertilized Soils

2.4.1 Availability Indices

Plant available P has long been estimated through the use of one of several dilute chemical extractants (Bray and Kurtz, 1945; Olsen et al., 1954). These extractants, developed using correlations between P uptake and extractable P, focused primarily on identifying P deficient soils through the removal of part of the solution and labile P pools. The usefulness of these extractants as excessively high P levels is not well understood since the extractants can dissolve variable amounts of precipitated P compounds and it is not clear to what extent P extracted from precipitated forms correlates with P uptake.

Cox et al. (1981) found that extractable P (Olsens (0.5 M NaHCO_3) or double acid (0.05 M HCl + 0.0025 M H_2SO_4)) could be successfully modelled in cropped soils that were receiving annual applications of P fertilizers as well as in soils that were not receiving any additional P. The empirical relationships $\text{dX/dT} = -k(\text{X} - \text{X}_{\text{eq}})$, where X = extractable P, kg/ha; T = time, years; k = loss constant, year^{-1} ; and X_{eq} = equilibrium level of X, kg/ha,

were developed to estimate the decline in extractable P with time after P fertilization and subsequent cropping. The loss constant, k , was found to be the greatest in calcareous soils and in soils with a high P fixing capacity. Information such as this can potentially be used to estimate the minimum annual P addition required to maintain some critical soil test value and, therefore, to prevent the development of high P soils.

Anion exchange resin has also been used to study available P in both high and low P soils. The resin acts primarily as a sink for P and offers the advantage over chemical extractants in that it should only remove P that can readily respond to such a sink. The analogy can be drawn to that of a growing root. The common procedure is to use a chloride saturated resin at a 1:1 resin-to-soil ratio in 10 to 100 mL of water or dilute electrolyte for 16 to 24 h (Olsen and Sommers, 1982; Amer et al., 1955). Studies of varying factors such as the saturating anion, shaking time, resin-to-soil ratio or solution-to-soil ratio have been performed. The major findings were: 1) P extracted is dependent on the saturating anion although the only real advantage in using one anion over another would be a reduction in pH changes when using HCO_3^- , 2) the rate-determining step in the exchange of P from the soil to the resin is P desorption from the soil to the water phase, 3) P extracted increases up to a resin-to-

soil ratio of approximately two, and 4) at a constant solution-to-resin ratio, P extracted decreases as the amount of soil increases, due to increases in the salt concentration of the solution phase and subsequent increased competition for resin exchange sites by other anions (Amer et al., 1955; Sibbessen, 1978).

Barrow and Shaw (1977) offer a more pessimistic view on the use of anion exchange resins. For a simple Cl-resin-dilute phosphate solution system in equilibrium, they develop the equation

$$[P]_S = k_1 P_r^2 / [RV(Cl_i - P_r/R)] \quad (2.3)$$

where $[P]_S$ = phosphate concentration in solution, k_1 is the selectivity coefficient for the resin (4.02 for Dowex-2 resin), P_r = P sorbed by the resin, R = weight of the resin, V = volume of solution, and Cl_i = the exchange capacity of the resin. The rate of approach to equilibrium was decreased by enclosing the resin in mesh bags, increasing the volume of solution, and decreasing the vigor of shaking. When considering resin-soil systems, the concentration of P in solution was important in determining the amount of P extracted from the soil and even when concentrations of P in solution had reached low levels, considerable P remained on the soil in equilibrium with the solution P. This implied that the resin was not acting as an infinite sink for P at low resin-soil ratios, as many authors had assumed. This study suggests that a

good deal of caution is warranted when considering the results of resin experiments. Clearly the results from two soils of widely differing properties are not directly comparable, as no single value exists for resin extractable P, and both the phosphate concentration in solution and the resin-extractable P should be taken into account when interpreting results to ensure that the proper relationship between resin, soil, and solution P is identified.

Chien and Clayton (1980) found that the desorption data presented by Amer et al. (1955) could be described by a simple modified Elovich equation in the form

$$q = (1/b)\ln(ab) + (1/b)\ln t \quad (2.4)$$

where q is the amount adsorbed by the resin at time t and a and b are empirical constants. This provided a single equation to be used for a system, rather than a series of first-order equations representing successive periods of time, that previous authors had used. This allowed for a single comparison of a and b values between soils to determine relative rates of dissolution of soil P.

2.4.2 Excessively Fertilized Soils

Few studies have been conducted that deal specifically with excessively fertilized soils. Barber (1979) studied a Raub silt loam soil amended for 25 years with varying amounts of P and having Bray P₁ extractable P levels up to 71 mg P/kg. At the highest application rate

(54 kg P/ha/yr), total P increased from 400 to 632 mg P/kg but only 12% of the total P was in the estimated available form (resin extractable). Bray P1 extractable P increased 1 mg/kg for every 17 kg net P/ha added while total P increased 1 mg/kg (approximately 2 kg P/ha) for every 4.5 kg net P/ha added, indicating that some P was lost due to erosion or leaching. When P additions were stopped and cropping was continued for up to eight years, resin and Bray P1 levels decreased, with the rate of decrease highest where the P level was highest at the time P application ceased. The process of increasing soil P levels by fertilization and decreasing soil P levels by cropping appeared to be reversible.

In a study of five acidic high P soils from the southeastern U.S., Novias and Kamprath (1978) noted that available P extracts correlated well with total cumulative P uptake under greenhouse conditions. Through selective chemical dissolution they also noted that most residual P came from the estimated Al-bound fraction (NH_4F extractable). Without implying the presence of any P solid phase they indicated that this agrees with a broad interpretation of the unified P activity diagram. A similar study with high P neutral and calcareous soils under greenhouse conditions found that Olsen P (0.5 M NaHCO_3 , shaken for 0.5 h), Colwell P (0.5 M NaHCO_3 , shaken

for 16 h), resin P, and isotopically exchangeable P all correlated well with total P uptake (Bowman et al., 1978).

2.4.3 Potential Environmental Activity of Soil Applied P

The fate of applied P needs to be discussed in the context of its availability as a pollutant. Soluble P, labile P and nonlabile P (the latter two as particulate matter) can all be transported away from the point of application through surface runoff of water or sediments, interflow, or as tile drainage. Johnson et al. (1976) studied the Fall Creek watershed in central New York and found that approximately 20% of the dissolved P lost from the watershed was from diffuse sources associated with farming.

The amount of P leaving the point of application through subsurface drainage would appear to be minimal. Loss of P with subsurface drainage water was insignificant when compared to losses associated with surface runoff (Baker et al., 1975). In a study of two management levels under high and low fertility levels, o-phosphate levels in the tile drainage were not influenced by either management regime or P level, and concentrations never exceeded 0.01 mg P/L (Zwerman et al., 1972). On an annual basis, total P losses through tile drainage never exceeded 1.27 kg P/ha over a three year period on a variety of soils in Iowa, Minnesota and Ohio (Logan et al., 1980).

So the majority of agricultural P entering surface waters originates as surface runoff of soluble P and sediments. This quantity of P is influenced by such variables as surface texture, land uses and season. The percent clay in the surface soil and the proportion of drainage area in row crops was found to account for 85% of the variability in total P unit area loads in the Southern Ontario Great Lakes Basin (Miller et al., 1982). Hubbard et al. (1982) found that 90-98 % of the P in a Michigan watershed was carried in sediments except during winter months when 33% of the P was in solution. The greatest total P loss by all mechanisms came from soils cropped to corn or prepared as conventional seedbeds due to greater sediment losses when compared to areas under forest or other crops such as oats or alfalfa (Wendt and Corey, 1980).

Once the P has left the point of application it is thought that potentially bioavailable P generally does not exceed 60% of the total P (Sonzogni et al., 1982). DePinto et al. (1981) found that an average of 21.8% of the total particulate P was ultimately available to algae (Selenastrum capricornutum) in a bioassay procedure using sediments from lower Great Lakes tributaries. An estimate of algal-available P can be obtained through the use of 0.1 M NaOH solution using a wide soil-to-solution ratio (Dorich et al., 1980).

One useful application of the research described in this dissertation would be an argument in favor of reducing P inputs to agricultural soils. The question that arises is what benefits would come about relative to P loadings to surface waters in light of reduced P inputs to soils. Since P sorption to soils has been shown to undergo a fast reaction followed by a longer slow reaction, one would expect the potentially soluble P in a soil to decline with time after P additions. Water extractable P was shown to decrease from 100 to 57 mg P/kg in a Bernow fine sandy loam after 15 days following an addition of 190 mg P/kg soil (Sharpley, 1982).

Soluble or extractable P will decline with successive runoff events or extractions. On a Bernow fine sandy loam and a Woodward loam, soluble P levels declined during each runoff event, presumably due to decline in soluble P in the surface layer (Sharpley, 1980). Desorbed P from a Hoytville soil declined from 14 to 2 mg P/kg after 10 sequential 480 minute extractions (Oloya and Logan, 1980). Sharpley et al. (1977) reported that the mean dissolved inorganic P concentration in surface runoff from pasture decreased to approximately 0.5 mg P/L within four months from approximately 3.2 mg P/L immediately after fertilization. It would appear that P loadings to surface waters would decline within one year of reduced P applications.

2.5 Objectives and Hypothesis

One point that becomes evident as the literature is reviewed is the need to preserve soil conditions found in the field throughout any procedures used in the laboratory if one wishes to best extrapolate laboratory results to conditions that existed in the field. As an example consider the use of solubility equilibria and the fact that only P bearing solids that are in contact with the soil solution will participate in reactions controlling P solubility. Hence, grinding the soil sample would not be appropriate. Likewise, if amorphous fertilizer reaction products do form, then excessive drying of the soil samples, which could influence the crystallinity of such solids, would not be appropriate. To this end, all soil samples used in the research described in this dissertation were minimally disturbed. The analogous situation also exists with regard to laboratory procedures and their potential to create undesirable artifacts. Examples of procedures that were avoided are the removal of organic matter and carbonates, which utilize harsh extractants, prior to dispersion and examination with electron microscopy, and even aqueous particle size separation, which utilizes large volumes of water, and might dissolve more soluble phosphate solids.

The complete picture of P chemistry in high P soils and its effects on P release characteristics will most

likely be elucidated only by application of several or more of the discussed experimental approaches and this was the approach taken in pursuing the following objectives:

1. To determine the effects of large accumulations of P from various sources on the chemistry of P solid phases in soil.

2. To determine the effects of large P accumulations on the solubility and availability of P in soil.

The overall experimental approach proceeds from the general hypothesis: That large accumulations of P result in precipitation of secondary P solids and that this change in solid phase mineralogy is reflected in the solubility and bioavailability of soil P.

Chapter III

PHOSPHATE CHEMISTRY IN EXCESSIVELY FERTILIZED MIDWESTERN

SOILS: MINERALOGY

3.1 Introduction

A long standing theory on the fate of P in excessively fertilized soils is that P precipitates as some secondary phosphate solid and that this solid ultimately controls the solubility of P in that system regardless of any additional P loadings (Mattingly and Talibudeen, 1967). The solubility equilibria approach has been used extensively to identify such solids (Lindsay, 1979), but there has been little success in identifying these solids with direct methodologies. The greatest obstacle in the study of phosphate solids with direct methodologies is that the average P concentration in soils is only about 600 mg P/kg, some of which is present as organic P, and the techniques used are simply not sensitive enough at this concentration (Lindsay and Vlek, 1977). Attempts to concentrate P have been tried, but other than observations that P tends to be concentrated in the clay-sized fraction (Lindsay and Vlek, 1977; Norrish, 1968; Hanley and Murphy, 1970), there has been no work in this area. Density separations of soils or soil separates

may be successful since the densities of P minerals such as variscite or apatite are sufficiently distinct from that of the bulk of the mass in a clay-sized fraction (Jaynes and Bigham, 1986).

Norrish (1968) used the fact that phosphate minerals of the plumbogummite group ($XAl(PO_4)_2OHH_2O$, where X= Pb, Ca, Sr, or Ba) were more resistant than kaolinite to attack by hydrofluoric acid (HF) to concentrate P in the kaolinitic clay fractions of some Australian soils. Untreated clay fractions contained four to five times more P than whole soils, while HF-treated clay fractions contained up to 230 times more P than whole soils. In some soils the concentration of P was sufficient for identification of the plumbogummite minerals with x-ray diffraction (XRD).

Lindsay et al. (1962) circumvented the sensitivity problem by reacting soils or soil constituents with concentrated solutions of P fertilizers. In these cases solutions with high P concentrations were produced and there was little difficulty in identifying precipitates with techniques such as XRD or optical mineralogy. Three soils and eight soil constituents were reacted with five different P fertilizers and some 30 crystalline and several colloidal phosphate solids were identified after the filtrates were aged.

Sawhney (1973) utilized thin sections and an electron microprobe and found distinct P-rich particles in the sand and silt fractions of some Connecticut soils and sediments. Representative particles contained P in association with Al, Fe and Si, and P was not present as a coating but rather throughout the particles since thin sections were being analyzed. A number of Ca phosphate particles were also identified and assumed to be detrital apatite. The association of P with Al, Fe, Si and Ca has also been noted in similar studies (Quershi et al., 1969).

The purpose of this experiment was to attempt to concentrate P in excessively fertilized soils through particle size and density separations to facilitate the study of secondary P solids with a number of direct methodologies.

3.2 Materials and Methods

Given the review of the literature and an appreciation of typical properties of Midwestern soils I located soils which had Bray-P1 extractable P levels in excess of 150 mg P/kg, which represented a variety of P sources, that had developed the high P condition under field conditions over as long a period of time as possible, and which had a comparable low P sample available as a control. Samples from the surface horizons of soils mapped as Plainfield loamy sands, Metea sandy loams, McBride/Montcalm associations (hereafter referred

to as McBride), Blount silt loams, and Howard loams as well as a sludge-amended mine spoil material were collected in the fall of 1986. After sampling, the soils were sieved through a 2mm sieve and stored at field moisture at 277°K. Sample descriptions are given in Table 1.

The Metea, Blount, and mine spoil samples were taken directly from established field plot experiments while the remaining samples were taken from fields under commercial crop production. An accurate cropping and P fertilization history is not available for each sample. All sites had been under crop production for more than 20 y and total and Bray P1 P levels will have to serve as the primary indicators of P status. Anecdotal evidence for the Plainfield high P sample indicated that this site had been under potato and other vegetable crop production for approximately 50 y. Anecdotal evidence for the Howard sample indicated that this site had received dairy manure periodically for over 75 y. Field experiments conducted on the mine spoil, Blount sludge P, and the Blount fertilizer P samples have been described previously (Hinesley et al., 1984). These samples have received approximately 27000, 24000, and 1900 kg P/ha, respectively, over 14 y period. The pH values were obtained from a 1:1 soil-to-water extract and Bray P1 and

Table 1. Soil sample characteristics.

Soil	P source	location	soil family
Plainfield			
low P	fertilizer	Waushara Co., WI	mixed, mesic typic udipsamments
medium P	fertilizer	Waushara Co., WI	mixed, mesic typic udipsamments
high P	fertilizer	Portage Co., WI	mixed, mesic typic udipsamments
Metea			
fert. P	fertilizer	Ingham Co., MI	loamy, mixed, mesic arenic hapludalfs
sludge P	sewage sludge	Ingham Co., MI	loamy, mixed, mesic arenic hapludalfs
McBride			
low P	fertilizer	Montcalm Co., MI	coarse-loamy or sandy, mixed, frigid alfic fragiorthods
high P	fertilizer	Montcalm Co., MI	coarse-loamy or sandy, mixed, frigid alfic fragiorthods
Blount			
fert. P	fertilizer	Will Co., IL	fine, illitic, mesic aeric ochraqualfs
sludge P	sewage sludge	Will Co., IL	fine, illitic, mesic aeric ochraqualfs
Mine Spoil			
sludge P	sewage sludge	Fulton Co., IL	unknown classification
Howard			
manure P	dairy manure	Cortland Co., NY	loamy-skeletal, mixed, mesic glossoboric hapludalfs

Table 1. (continued)

Soil	Bray Pl P	Total P	pH	Sand	Silt	Clay	Clay Mineralogy#
	- (mg/kg) -			-----	%	-----	
Plainfield							
low P	29	210	6.6	93.1	6.0	0.9	k, q, s, Al-i, ch(tr)
med. P	129	410	6.6	89.1	8.7	2.2	k, q, s, Al-i, ch(tr)
high P	218	540	5.6	91.5	6.2	2.3	k, q, Al-i, s(tr), ch(tr)
Metea							
fertilizer P	137	680	7.4	64.5	27.8	7.7	k, q, Al-i, cm, v, ch, s(tr)
sludge P	348	3020	7.0	63.0	30.1	6.9	k, q, cm, Al-i, ch, s(tr)
McBride							
low P	52	400	5.7	73.3	22.8	3.9	k, q, Al-i, cm, ch(tr)
high P	255	560	5.4	73.5	22.5	4.0	k, q, Al-i, ch
Blount							
fertilizer P	246	1700	7.0	9.3	69.9	20.8	k, q, cm, s, v, Al-i
sludge P	613	5440	5.7	8.8	72.6	18.6	k, q, cm, Al-i, v, s
Mine Spoil							
sludge P	641	8340	5.6	6.5	70.3	23.2	k, q, cm, v, s, Al-i(tr)
Howard							
manure P	185	1860	6.4	36.1	46.2	17.7	k, q, cm, Al-i

#k=kaolinite, q=quartz, s=smectite, Al-i=Al interlayered 2:1 clays, ch=chlorite, cm=clay mica, v=vermiculite, (tr)=trace quantities

total P were determined according to Olsen and Sommers (1982).

To estimate mineralogical composition, the samples were treated to remove organic matter (H_2O_2 at 373°K) and carbonates (1 M sodium acetate buffer, pH 5.0), ultrasonically dispersed, and the resulting suspension passed through a 50 micron sieve where the sand sized particles were retained. The clay sized fraction was separated from the remaining suspension via an automated procedure utilizing sedimentation (Rutledge et al., 1967). Magnesium saturated, K-saturated and glycerated subsamples as suspensions of the clay separates were ultrasonically dispersed and allowed to air-dry on 27 - by - 46 mm glass slides creating parallel-oriented specimens. The Mg-saturated and glycerated specimens were subsequently x-rayed while the K-saturated specimens were x-rayed after air-drying, after heating at 623°K for 2 h, and again after heating at 773°K for 2 h. All x-ray diffraction analyses were conducted with a Phillips x-ray diffractometer using Cu K-alpha radiation at 35 kV and 20 mA. Particle size separates were analyzed for total P according to Olsen and Sommers (1982).

A separate particle size separation procedure was used for samples whose clay sized fractions were to be subjected to density separations and examination with electron microscopy. Nine of the eleven samples were

fractionated into particle size fractions utilizing non-aqueous liquids according to Essington (1985). Non-aqueous liquids were used to ensure the integrity of the solids. The procedure involved ultrasonically dispersing whole soil samples that had not been pretreated for removal of organic matter or carbonates and that had been soaked in ethanol containing 10% polyvinylpyrrolidone (PVP) by weight for 48 h. Sand sized particles were removed with a 50 micron sieve and a manual sedimentation procedure was used to separate out the clay sized particles (< 2 microns) from the remaining suspension. The clay sized fraction obtained from this procedure was further separated by particle density.

Density separations were made utilizing 30 mL density gradients contained in 50-mL Oak-Ridge-type teflon centrifuge tubes. The gradients were constructed with varying proportions of ethanol containing 20% PVP by weight and tetrabromoethane, giving a density range of 1.8 to 2.95 g/cm^3 , and then split into 3 - 10 mL portions giving the density separates of <2.2 , $2.2-2.5$, and $>2.5 \text{ g/cm}^3$. Six tubes containing not more than 0.5 g of clay each were prepared for each sample. The tubes were centrifuged at 8000 rpm for 24 h at which point the six 10 mL portions representing each density range were combined, diluted with pure ethanol, and centrifuged to concentrate the solids and to wash out excess PVP. The density

separates were analyzed for total P according to Olsen and Sommers (1982).

All density separates were examined with a JEOL 200CX scanning transmission electron microscope (STEM, JEOL (USA) Inc., Peabody, Mass) operated with an accelerating voltage of 200 kV and equipped with a Tracor Northern (Tracor Northern Inc., Middleton, WI.) energy dispersive x-ray analyzer. Density separates were ultrasonically dispersed in a small volume of water before being mounted on polyvinylformal coated, 300 mesh, Cu-transmission electron microscope (TEM) grids. The Particle Recognition and Characterization (PRC) program from Tracor Northern was used to collect energy dispersive x-ray spectra (EDS) from approximately 300 particles in each density separate. The PRC program controls a 6.5 nm diameter electron beam as it rasters across a low magnification (5000X) field of view. A particle is recognized by the difference in contrast relative to the polyvinylformal background. The particle is characterized by collecting EDS data from the approximate geometric center of the particle. A succession of fields of view can be examined with the PRC program until the desired number of particles have been characterized. The electron beam diameter during EDS acquisition was also 6.5 nm. The regions of interest monitored with each EDS collected were the K-alpha lines for Al from 1.30 to 1.60 keV, Si from 1.60 to 1.92 keV, P

from 1.92 to 2.16 keV, K from 3.16 to 3.52 keV, Ca from 3.54 to 3.86 keV, Mn from 5.74 to 6.14 keV, and Fe from 6.20 to 6.64 keV. Particles were classified as P-rich if they gave 100 x-ray counts per minute (cpm) or more from the P region of interest. A count rate of 100 cpm for P represents an approximate P concentration of 0.5 % by weight (Joy et al., 1986).

Selected density separates were x-rayed utilizing a Phillips x-ray diffractometer using Cu K-alpha radiation at 35 kV and 20 mA. All XRD analyses were performed using back-filled randomly oriented mounts. Selected density separates were also examined utilizing a Mattson Polaris Fourier transformed infrared (FTIR) spectrophotometer (Mattson Instruments, Madison, WI) coupled to an MS-DOS computer. Diffuse reflectance spectra were collected from ground mineral samples diluted with a powdered matrix of spectroscopic-grade KBr.

3.3 Results and Discussion

3.3.1 Sample Chemical and Mineralogical Characterization

Chemical and mineralogical characterization data are presented in Table 1. With the finer textured soils, it was difficult to locate low P samples. The coarser textured soils (Plainfield and McBride) have lower total P as compared to the remaining soils despite their history of heavy P fertilization. However, the proportion of this total P present as Bray P1 extractable P, for the high P

from 1.92 to 2.16 keV, K from 3.16 to 3.52 keV, Ca from 3.54 to 3.86 keV, Mn from 5.74 to 6.14 keV, and Fe from 6.20 to 6.64 keV. Particles were classified as P-rich if they gave 100 x-ray counts per minute (cpm) or more from the P region of interest. A count rate of 100 cpm for P represents an approximate P concentration of 0.5 % by weight (Joy et al., 1986).

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soils, is much greater as compared to the remaining samples.

One common concern when sampling soils based solely on soil mapping units is the variability that can occur within a mapping unit that could lead to samples with widely variable properties. The Plainfield and McBride soils would fall into this category; however, similar particle size analysis and mineralogical make-up of the clay fractions would indicate that this was not a problem. The clay fractions of all samples would be classified as being of mixed mineralogy.

3.3.2 Total P in Particle Size and Density Separates

The highest total P concentrations were in the clay sized fractions (Table 2) which is in agreement with previous work (Norrish, 1968; Hanley and Murphy, 1970). The only exception to this was the Blount fertilizer P sample which had the highest total P concentration in the sand sized fraction. This implies the presence of a detrital P-bearing mineral in this soil, such as apatite, but XRD analysis of the sand and silt sized fractions from both Blount samples did not confirm the presence of apatite (data not shown). The sand and silt fractions were also examined with the electron optical technique described in detail in the next section. The presence of pure Ca phosphate particles was not confirmed with this technique.

Table 2. Total P in particle size fractions.

Sample	sand	silt	clay
	----- (mg P/kg) -----		
Plainfield low P	10	125	1995
Plainfield med. P	25	188	3010
Plainfield high P	65	250	5430
Metea fert. P	205	425	1955
Metea sludge P	775	3500	16265
McBride low P	55	100	3200
McBride high P	70	200	2490
Blount fert. P	3400	350	2325
Blount sludge P	5500	1325	18045
Mine spoil	10850	3525	16025
Howard manure P	525	400	5165

Considering only the clay sized fraction, an enrichment factor (EF) defined as $EF = (\text{total P concentration in clay}) / (\text{total P in whole soil})$ can be calculated to obtain EF values ranging from 1.4 to 10.1 for the Blount fertilizer P and Plainfield high P samples, respectively. Therefore, particle size separation was an effective means of concentrating P relative to the whole soil samples.

Without exception, the highest total P concentrations occurred in the lowest density separate with decreasing total P concentrations as density increased (Table 3). Within the clay fraction density separation effectively concentrated the P in one density separate relative to the remaining two. The densities of the well crystallized secondary P minerals frequently discussed in the literature (e.g., variscite or apatite) are all $> 2.5 \text{ g/cm}^3$. Therefore the majority of the P in these samples is not likely present as well crystallized P minerals since the highest total P concentrations occurred in the $< 2.2 \text{ g/cm}^3$ density separate.

3.3.3 Electron Microscopy

Figures 1 and 2 are representative EDS from a non-P-rich and a P-rich particle, respectively, from the $>2.5 \text{ g/cm}^3$ density separate of the Plainfield high P soil. The P K-alpha peaks represent 50 cpm (integrated area) in Figure 1 and 288 cpm in Figure 2. The Cu peaks are from

Table 3. Total P in density separates of the clay fractions.

Sample	----- density -----		
	<2.2 g/cm ³	2.2-2.5 g/cm ³	>2.5 g/cm ³
	----- (mg P/kg) -----		
Plainfield low P	3310	1580	920
Plainfield high P	6280	4970	1495
Metea fert. P	3025	950	510
Metea sludge P	12090	3640	2285
McBride low P	2940	1270	1110
McBride high P	5680	3940	2260
Blount fert. P	2470	1290	370
Blount sludge P	6830	2390	485
Howard manure P	6165	4375	770

Figure 1. Example x-ray spectrum from a particle that was not classified at P-rich.

Figure 2. Example x-ray spectrum from a P-rich particle.

the TEM grid. Note the complex elemental make-up of the P-rich particle with readily detectable concentrations of Al, Si, Ca and Fe associated with P. Such varied elemental composition of P-bearing particles had been noted previously (Sawhney, 1973).

We define: Percent P-rich Particles (PPP) = $(n_p/n)100$, where n_p = number of P-rich particles in a density separate and n = total number of particles counted in that density separate. The standard deviation for such grain counts is given by $sd = (y_i(100 - y_i)/n)^{0.5}$, where y_i = PPP and n is as before (Brewer, 1976). Table 4 gives the PPP values for the five soils considered.

The density separations effectively concentrated P-bearing particles in one density separate relative to the remaining two when considering PPP values, with significant differences occurring in the Plainfield high P, Metea sludge P, McBride low P and Blount sludge P samples. It is statistically inappropriate to compare PPP values across samples; however, the data illustrates a trend of higher PPP values for the sample with the highest total P concentration within a pair of related samples. This point permits the conclusion that P tends to reside in discrete P-rich particles rather than being relatively uniformly distributed across particles in a particular sample.

Table 4. PPP values, plus or minus one standard deviation, for all soils. PPP=(n_p/n)100, where n_p = number of P-rich particles in a density separate and n= total number of particles counted in that density separate (approximately 300 for each density separate).

<u>Density</u> (gm/cm ³)	PLAINFIELD		METEA		HOWARD
	<u>Low P</u>	<u>High P</u>	<u>Low P</u>	<u>High P</u>	<u>Manure P</u>
<2.2	0.6 ± 0.6a ^e	15.3 ± 2.0a	3.0 ± 1.0a	11.8 ± 1.8a	3.0 ± 1.0a
2.2-2.5	0a	3.0 ± 1.0b	0.7 ± 0.5a	4.8 ± 1.2b	1.3 ± 0.7a
>2.5	1.3 ± 0.7a	10.0 ± 1.7a	0.7 ± 0.5a	2.0 ± 0.8b	3.0 ± 1.0a
	MCBRIDE		BLOUNT		
	<u>Low P</u>	<u>High P</u>	<u>Low P</u>	<u>High P</u>	
<2.2	2.7 ± 1.3a	6.0 ± 1.4a	0.3 ± 0.3a	4.5 ± 1.2a	
2.2-2.5	0b	5.0 ± 1.3a	0.3 ± 0.3a	3.0 ± 1.0ab	
>2.5	2.0 ± 1.1ab	3.3 ± 1.0a	0.3 ± 0.3a	1.0 ± 0.5b	

^eMeans within a sample followed by the same letter are not significantly different at the 5% level.

Relative concentrations of detectable elements in a particle can be determined from the EDS data with the equation:

$$C_1/C_2 = k (I_1/I_2) \quad (3.1)$$

where C = concentration, I = intensity (cpm) and k is a unitless theoretical constant incorporating factors influencing x-ray generation and detection for a particular electron microscope-x-ray detector configuration (Romig, 1982). A typical application of equation 3.1 would be the determination of metal concentration ratios in alloys. In this ideal situation standards could be prepared with varying metal concentration ratios allowing for the empirical determination of k values and subsequent determination of metal concentration ratios in unknowns. Values of k can be calculated from theoretical considerations, however, and for K-alpha x-ray lines the theoretical values show good agreement with experimentally determined values (Romig, 1982). The values of k used in this experiment were $k_{AlSi}=1.465$, $k_{AlP}=1.749$, $k_{AlK}=2.211$, $k_{AlCa}=2.296$, $k_{AlMn}=1.935$, and $k_{AlFe}=1.912$.

The proper use of equation 3.1 is dependent upon two criteria. The first criterion is the assumption that the sum of the masses of the elements determined represents all of the cations present in a particle. My verification of this was simply the observation that K-alpha peaks for

other elements (e.g. Mg, S, Ti, Cl) were rarely encountered and these elements are likely present at levels below the detection limit of this technique. From this assumption relative concentrations can be expressed as weight or atom percents. The second criterion is that the particles are thin enough to warrant ignoring secondary absorption of x-rays (thin-film assumption). To verify this, synthetic apatite particles with particle sizes ranging up to approximately 4 microns were mounted on TEM grids and treated in a fashion identical to that of the samples. The observation that Ca:P concentration ratios were invariant as particle size increased (data not shown) was confirmation that secondary x-ray absorption was not a problem in the particle size range used (< 2 microns). Meeting the second criterion is a direct result of the use of a high gun potential (200kV) in the electron microscope.

To illustrate the use of equation 3.1 consider the energy dispersive x-ray data from a single synthetic apatite particle. This particle produced 2222 and 5576 x-ray cpm for the P and Ca regions of interest, respectively. From the theoretical k values listed previously we can determine that $k_{P/Ca} = 1.313$. Therefore, the P-to-Ca concentration ratio (C_P/C_{Ca} , as weight percent) is 0.523 which leads to a P concentration of 40.4 atom%. This differs from the actual value of 37.5 atom%

by only 2.9 atom%. The difference is most likely due to the use of a theoretical rather than an empirically determined value of k_{PCa} .

Figures 3 to 9 are P concentration frequency distribution diagrams for selected density separates from the Plainfield high P, Metea sludge P, and McBride high P samples. Phosphorus concentrations were generally <35 atom%. The exception to this was the $>2.5 \text{ g/cm}^3$ density separate from the Plainfield high P sample (Figure 4). In addition, the highest frequency generally occurred at a P concentration of <20 atom%. This indicated that ortho-phosphate species could not be the only anionic component balancing the positive charge from the cations if the particles had a homogeneous elemental composition. This comes from the fact that the lowest possible P concentration would be 25 atom% for a monovalent cation (e.g. K_3PO_4) if all the positive charge were balanced by ortho-phosphate species. If the P-rich particles did not have a homogeneous elemental composition and had, for example, a P-rich coating on a P-poor particle, then any P concentration less than the anticipated maximum of 50 atom% (e.g. variscite, dicalcium phosphate) would be possible since x-rays would be collected from both a P-rich and a P-poor region within the particle.

The characteristics of the P-concentration frequency distribution change with density for the Plainfield high P

Figure 3. Phosphorus₃ concentration frequency distribution diagram for P-rich particles in the <2.2 g/cm³ density separate of the Plainfield high P sample. Element symbols denote the element predominantly associated with P in a particular P concentration range. For example, if there were 20 P-rich particles within a concentration range and 15 of those particles had one of the six elements determined present at a higher atom% relative to the remaining five elements, then that element is noted in this diagram.

Figure 4. Phosphorus₃ concentration frequency distribution diagram for P-rich particles in the >2.5 g/cm³ density separate of the Plainfield high P sample. Element symbols denote the element predonminantly associated with P in a particular P concentration range. For example, if there were 20 P-rich particles within a concentration range and 15 of those particles had one of the six elements determined present at a higher atom% relative to the remaïning five elements, then that element is noted in this diagram.

Figure 5. Phosphorus concentration frequency distribution diagram for P-rich particles in the $<2.2 \text{ g/cm}^3$ density separate of the Metea sludge P sample. Element symbols denote the element predominantly associated with P in a particular P concentration range. For example, if there were 20 P-rich particles within a concentration range and 15 of those particles had one of the six elements determined present at a higher atom% relative to the remaining five elements, then that element was noted in this diagram. An asterisk denotes an association between P and Al, Fe, or Ca.

Figure 6. Phosphorus concentration frequency distribution diagram for P-rich particles in the 2.2-2.5 g/cm³ density separate of the Metea sludge P sample. Element symbols denote the element predominantly associated with P in a particular P concentration range. For example, if there were 20 P-rich particles within a concentration range and 15 of those particles had one of the six elements determined present at a higher atom% relative to the remaining five elements, then that element was noted in this diagram. An asterisk denotes an association between P and Si, Al, or Fe.

Figure 7. Phosphorus concentration frequency distribution diagram for P-rich particles in the $< 2.2 \text{ g/cm}^3$ density separate of the McBride high P sample. Element symbols denote the element predominantly associated with P in a particular P concentration range. For example, if there were 20 P-rich particles within a concentration range and 15 of those particles had one of the six elements determined present at a higher atom% relative to the remaining five elements, then that element was noted in this diagram.

Figure 8. Phosphorus concentration frequency distribution diagram for P-rich particles in the 2.2-2.5 g/cm³ density separate of the McBride high P sample. Element symbols denote the element predominantly associated with P in a particular P concentration range. For example, if there were 20 P-rich particles within a concentration range and 15 of those particles had one of the six elements determined present at a higher atom% relative to the remaining five elements, then that element was noted in this diagram.

Figure 9. Phosphorus concentration frequency distribution diagram for P-rich particles in the $>2.5 \text{ g/cm}^3$ density separate of the McBride high P sample. Element symbols denote the element predominantly associated with P in a particular P concentration range. For example, if there were 20 P-rich particles within a concentration range and 15 of those particles had one of the six elements determined present at a higher atom% relative to the remaining five elements, then that element was noted on this diagram. An asterisk denotes an association between P and Si or Ca.

sample (Figures 3 and 4). At the lower density ($<2.2 \text{ g/cm}^3$) the highest frequency occurred at the 0-5% concentration range with the predominant element associated with the P being Si. At the higher density ($>2.5 \text{ g/cm}^3$) the highest frequency occurred at the >50% concentration range with the predominant element associated with P being Ca. This density separate was unique from the standpoint of having high P concentrations and having the P associated with Ca (these are not simple Ca phosphates, however; see Table 5).

The characteristics of the P concentration frequency distribution do not change with density for the Metea sludge P (Figures 5 and 6) or the McBride high P (Figures 7 to 9) samples. The primary point to be taken from these diagrams is that P concentrations can vary considerably with the Metea sludge sample having the highest frequencies at P concentrations $>10 \text{ atom\%}$ as compared to the McBride high P sample with the highest frequencies at P concentrations $<10 \text{ atom\%}$.

Phosphorus-rich particles can be categorized further based on the predominant cation associated with P. Such categories are presented in Table 5 with the general format Y-X (Z), where Y represents the element present in the highest concentration in that category, X represents the element or elements that are present at the second highest concentration in the category, and Z is equal to

Table 5. Phosphorus elemental associations in the format Y-X(Z) where Y represents the cation present in the highest concentration in the category, X represents the cation or cations present in the second highest concentration, and Z= the percentage of the P-rich particles within a density separate that fall into the category. Y-X.

PLAINFIELD		
<u>Density</u> (gm/cm ³)	<u>Low P</u>	<u>High P</u>
<2.2	Si-Al(100)	Al-X(45.9) X=Si, Ca, Fe Si-Al(45.8) Fe-Al(6.3) Ca-Al(2.1)
2.2-2.5	-	Si-Al(100)
>2.5	Ca-X(100) X=Mn, Si	Ca-X(45.4) X=Al, K, Fe Si-X(36.6) X=Al, K Fe-X(10.0) X=Al, Si Al-Si(3.3) Ca (3.3)
METEA		
	<u>Fertilizer P</u>	<u>Sludge P</u>
<2.2	Fe-X(33.3) X=Si, Al Ca-X(22.2) X=Al, Fe Si-Al(33.3) Al-Fe(11.1)	Al-X(39.0) X=Si, Ca, Fe Fe-X(38.9) X=Al, Ca, Fe Si-X(16.7) X=Al, Fe Ca-Fe(5.6)
2.2-2.5	Fe-K(50.0) Al-Si(50.0)	Al-X(53.4) X=Si, Ca, Fe Fe-X(26.7) X=Al, Si, Ca Si-X(20.0) X=Al, Fe
>2.5	Fe-Al(50.0) Si-Al(50.0)	Al-X(50.0) X=Ca, Fe Fe-Al(33.3) Si-Al(16.7)

Table 5. (continued)

MCBRIDE

	<u>Low P</u>	<u>High P</u>
<2.2	Al-X(50.0) X=Si, Ca Fe-Al(50.0)	Al-X(88.8) X=Si, Ca, Fe Si-Al(5.5) Fe-Al(5.5)
2.2-2.5	-	Al-X(60.0) X=Si, Fe Fe-Al(26.7) Si-Al(13.3)
>2.5	Si-Al(33.3) Ca-Fe(33.3) Al-Si(33.3)	Al-X(40.0) X=Si, Fe Si-Al(40.0) Fe-Al(10.0) Ca-Si(10.0)

BLOUNT

	<u>Fertilizer P</u>	<u>Sludge P</u>
<2.2	Fe-Al(100)	Fe-X(50.0) X=Al, Ca Al-X(42.8) X=Fe, Si Si-Fe(7.1)
2.2-2.5	Al-Si(100)	Al-X(66.6) X=Fe, Si Si-Al(22.2) Ca-Fe(11.1)
>2.5	Ca-Fe(100)	Si-Al(50.0) Ca-Al(50.0)

Table 5. (continued)

HOWARD	
<u>Manure P</u>	
<2.2	Al-X(66.6) X=Si, K, Ca Fe-Al(22.2) Si-Al(11.1)
2.2-2.5	Fe-Al(75.0) Al-Si(25.0)
>2.5	Al-X(33.3) X=Si, Fe Fe-Al(33.3) Al-Si(11.1) Ca-Si(11.1)

the percentage of the P-rich particles within a density separate that fall into the category Y-X.

Numerous categories exist within a sample and within a density separate (Table 5). None of the samples appear to contain a single uniform P-rich solid and, furthermore, the $>2.5 \text{ g/cm}^3$ density separates do not contain particles whose elemental make-up suggests that well crystallized secondary phosphate minerals had been separated from the bulk of the mass of the clay fraction. The concept of simple Al, Fe, Ca or Mn phosphate solids existing in these soils is not supported by this work. In addition, the high pH samples (Metea soils, Blount fertilizer P soil, Howard soil) do not have categories suggesting the existence of predominantly Ca phosphate solids. These observations bring into question the use of solubility equilibria for predicting solid phase control of P solubility. While it cannot be shown for certain that the solids found with this method are participating in the equilibrium with solution P, it is clear that relating equilibrium solution results to a particular P solid phase must be done with caution. There is general agreement between solubility equilibria results and the electron microscope results for the Plainfield high P, the McBride soils and the Blount sludge P sample in that the presence of the amorphous analog of variscite was suggested by the equilibrium solution data (Chapter 4) and we see that the

categories for these samples generally have Al as a member.

The frequency with which Si occurs in the categories raises questions about the nature of these P-rich particles. Three possibilities can explain the occurrence of the Si: 1) Si is an integral part of the particle itself and the particle has a relatively homogeneous elemental composition, 2) Si is present as part of a separate mineral phase within the particle, i.e. a phosphate coating on an aluminosilicate nucleus, a possibility suggested by the frequency with which Al occurs in the categories and previous equilibrium studies (Chapter 4), and 3) the P-rich particles are clusters of small particles held together by some cementing agent and that Si may be present in a non-P-rich particle within a cluster.

Elemental ratios calculated from the relative concentration data (expressed as atomic percents) have the potential for providing some insight into the nature of these P-rich particles. As a first attempt we can deal with Al/Si ratios in individual particles within each density separate. The mineralogical data for the clay fractions (Table 1) suggest that non-P-rich aluminosilicate and silicate mineral particles would have Al/Si ratios ranging from 0 (e.g. quartz) to approximately 1.0 (e.g. kaolinite). Twenty-nine randomly selected

particles from the $<2.2 \text{ g/cm}^3$ density separate of the Blount sludge P sample support this, having Al/Si ratios ranging from 0 to 1.18. I propose that an Al/Si ratio greater than 2.0 represents an atypical particle relative to the expected ratios for silicate and aluminosilicate minerals present in these samples. Table 6 gives the abundance of the P-rich particles with Al/Si ratios greater than 2.0 within each density separate. The data in this table indicate that as much as 100 % of the P-rich particles in a density separate have atypical Al/Si ratios. This is an alternate expression of the Al enrichment of P-rich particles illustrated in Table 5.

A degree of complexity can be added by assuming that this Al enrichment is in fact an Al phosphate coating on an aluminosilicate mineral particle. For the amorphous analog of variscite (Veith and Sposito, 1977) with the formula $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$, Al and P are present in a one-to-one ratio. For particles in the category Al-X we can calculate the ratio $(\text{Al} - \text{P})/\text{Si}$ which is in effect an approximate Al/Si ratio in a particle after the Al phosphate coating is removed. Table 7 gives the abundance of Al-associated P-rich particles with $(\text{Al} - \text{P})/\text{Si}$ greater than 2.0 within each density separate. The data in this table indicate that as much as 100 % of the Al-associated P-rich particles have ratios inconsistent with the existence of an aluminosilicate phase within the P-rich

Table 6. Percent of P-rich particles with Al/Si > 2.0 where Al and Si are concentrations expressed as atom%.

Sample	----- density -----		
	<2.2 g/cm ³	2.2-2.5 g/cm ³	>2.5 g/cm ³
Plainfield low P	0	-#	0
Plainfield high P	29.2	0	0
Metea fert. P	25.0	0	0
Metea sludge P	22.2	37.5	66.7
McBride low P	50.0	-	100.0
McBride high P	55.6	53.3	20.0
Blount fert. P	0	100.0	0
Blount sludge P	28.6	33.3	0
Howard manure P	11.1	50.0	44.4

#not applicable

Table 7. Percent of P-rich particles that have Al as the predominant cation associated with P and that have $(Al - P)/Si > 2.0$ where Al, Si, and P are concentrations expressed as atom%.

Sample	----- density -----		
	<2.2 g/cm ³	2.2-2.5 g/cm ³	>2.5 g/cm ³
Plainfield low P	-#	-	-
Plainfield high P	59.1	-	0
Metea fert. P	100.0	0	-
Metea sludge P	57.1	25.0	0
McBride low P	50.0	-	0
McBride high P	62.5	55.6	50.0
Blount fert. P	-	100.0	-
Blount sludge P	16.7	50.0	-
Howard manure P	50.0	0	66.7

#not applicable

particle. This conclusion is in agreement with observations by Sawhney (1973) that P was relatively uniformly distributed throughout P-rich particles mounted as thin sections, and concluded that the P was not present as a particle coating.

To summarize briefly, elemental ratios indicate some Al enrichment in the P-rich particles but are not entirely consistent with the concept of Al phosphate coatings on aluminosilicate mineral phases. Elemental ratios cannot be used to examine the possibilities of homogeneous P-rich particles or of P-rich particles as clusters since we have no anticipated values for the ratios.

In the absence of strong evidence for a separate aluminosilicate mineral phase within the P-rich particles, two other sources for the Al and Si can be discussed. The emphasis is placed on the high pH soils (e.g. Blount fertilizer P, Metea samples) which, by traditional interpretation of phosphate chemistry, should not contain Al dominated P-rich particles. These Al dominated P-rich particles may have actually formed under low pH conditions and the observed high pH values are only the result of liming without subsequent dissolution of the P-rich solids. In particular, published reports of the field experiments with the Blount fertilizer P sample indicate that this soil was limed (Hinesley et al., 1984). The second possibility is ortho-phosphate induced weathering

of aluminosilicate minerals (Veith and Sposito, 1977; Karathanasis et al., 1983) which would supply both Al and Si under the pH ranges seen in the samples studied in this experiment.

Electron micrographs of individual P-rich particles can also provide some insight into the nature of these particles. Plates I to IV represent two particles each from the $<2.2 \text{ g/cm}^3$ density separates from the Plainfield high P and Blount sludge P samples, respectively. It should be noted that there was little difficulty encountered in locating and isolating P-rich particles and that the limited number of individual particle descriptions given reflects my limited access to the analytical electron microscope.

The particle shown in Plate I has a morphology suggestive of a separate coating of a substance on another particle. The EDS data supports this observation with Figure 10 showing an x-ray spectrum taken from across the entire particle with readily detectable concentrations of Al, Si, P and Ca. The characteristics of the x-ray spectrum change when taken from the center of the particle with the dominant peaks coming from Ca and P (Figure 11). Finally, when x-rays are gathered from the particle coating only (taken from the far right side of the particle where the coating has separated from the main particle, Figure 12), the Ca peak is absent. These EDS

Plate I. Photomicrograph of a P-rich particle₃ found in the Plainfield high P sample, <2.2 g/cm³.

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Figure 10. Average x-ray spectrum from particle shown in Plate I.

Figure 11. X-ray spectrum from the center of the particle shown in Plate I.

Figure 12. X-ray spectrum from the particle coating on the particle shown in Plate I.

data are suggestive of a particle coating containing Al, Si and P surrounding a particle containing Ca. The entire particle has approximate dimensions of 2.3 microns long by 1.3 microns wide.

Plate II shows a second particle from the same density separate and from the same soil as the particle in Plate I. This is a rather large particle having an approximate width of 2.5 microns and a length that cannot be determined from this photomicrograph. The particle morphology is nondescript; however, the EDS data suggests a variable elemental make-up. Figures 13 to 15 are x-ray spectra taken along a transect from left to right at the top of the particle (as shown in Plate II). Figures 13 and 14 would indicate a P-rich particle with Al as the predominant cation while Figure 15 gives a spectrum that would not be classified as P-rich.

Plates III and IV show particles taken from the Blount sludge P sample and have similar morphologies. Both particles have the approximate dimensions of 1 micron wide by 2 microns long and have the appearance of a loosely organized collection of smaller particles. Figure 16 is the x-ray spectrum collected from the left half of the particle shown in Plate III and is representative of the entire particle. This spectrum would be classified as Al dominant, as would the spectrum representing the entire particle shown in Plate IV (Figure 17). The unique

Plate II. Photomicrograph of a P-rich particle found in the Plainfield high P sample, $<2.2 \text{ g/cm}^3$.

Figure 13. X-ray spectrum from the top left region of the particle shown in Plate II.

Figure 14. X-ray spectrum from the top center region of the particle shown in Plate II.

Figure 15. X-ray spectrum from the top right region of the particle shown in Plate II.

Plate III. Photomicrograph of a P-rich particle found in the Blount sludge P sample, $<2.2 \text{ g/cm}^3$.

Figure 16. X-ray spectrum from the left half of the particle shown in Plate III.

Plate IV. Photomicrograph of a P-rich particle found in the Blount sludge P sample, $<2.2 \text{ g/cm}^3$.

Figure 17. Average x-ray spectrum from the particle shown in Plate IV.

feature of the x-ray spectrum in Figure 17 is the occurrence of the Ti peak. Closer examination of the P-rich particle revealed a Ti-rich area (seen as the slightly darker region at the very top of the particle in Plate IV) at the top of the particle (Figure 18) with the remainder of the particle being low in Ti (e.g. Figure 19, taken from the center of the particle). These final two x-ray spectra would suggest that a rutile-like particle (TiO_2) was surrounded by the P-rich material.

For all of the P-rich particles described, electron diffraction indicated that the particles were amorphous. Plate V is the electron diffraction pattern taken from the lower region (away from the rutile particle) of the particle shown in Plate IV and is representative of all four P-rich particles described.

3.3.4 X-ray Diffraction and Infrared Spectroscopy

The $<2.2 \text{ g/cm}^3$ density separates from the Plainfield high P, Metea sludge P and Blount sludge P samples, and the $2.2\text{--}2.5 \text{ g/cm}^3$ density separates from the Plainfield high P and Blount sludge P samples were x-rayed. The resulting diffraction patterns were examined for the presence of crandallite, gorceixite (both plumbogummite group minerals), various apatites, brushite, variscite, strengite and tricalcium phosphate (Joint Committee on Powder Diffraction Standards, 1974) with negative results. In addition, the Blount sludge P sample ($<2.2 \text{ g/cm}^3$) was

Figure 18. X-ray spectrum from the uppermost region of the particle shown in Plate IV.

Figure 19. X-ray spectrum from the center region of the particle shown in Plate IV.

Plate V. Electron diffraction pattern from the particle shown in Plate IV.

heated to 573°K for 12 h in an attempt to induce crystallization of variscite from its amorphous analog (Kodama and Webber, 1975) which also yielded negative results.

The $<2.2 \text{ g/cm}^3$ density separates from the Plainfield low and high P samples and the Blount samples were examined with FTIR. Figures 20 and 21 are the FTIR transmittance spectra from the Plainfield and Blount soils, respectively. The primary feature to note in these spectra is that within a soils series changes in total P concentration (Plainfield and Blount samples) or changes in pH conditions (Blount samples) do not induce discernable changes in the FTIR spectra and, therefore, little can be concluded when using this technique on these samples. Absorption bands unique to phosphate solids might include the P-O stretching within the approximate range of 900 to 1200 cm^{-1} , the O-P-O bending from approximately 420 to 600 cm^{-1} or modes for the metal-O bond in the approximate region of 550 to 870 cm^{-1} (Ross, 1974). Adsorption bands in these spectra in the range 504 to 1104 cm^{-1} can readily be assigned to quartz, illite or kaolinite (van der Marel and Beutelspacher, 1976).

3.4 Conclusions

Particle size and density separations were effective means of concentrating P in these soils. Phosphorus does exist within discrete P-rich particles whose abundances

Figure 20. FTIR spectra for the Metea fertilizer P_3 (top) and Metea sludge P (bottom) $< 2.2 \text{ g/cm}^3$ density separates.

Figure 21. FTIR spectra for the Blount fertilizer P_3 (top) and Blount sludge P (bottom) $< 2.2 \text{ g/cm}^3$ density separates.

are positively associated with total P concentrations in the soils. The P in the P-rich particles is generally associated with Al and Si along with various combinations of Ca or Fe within each particle. High pH soils do not contain predominantly Ca phosphate particles.

Model calculations using elemental ratios suggest an Al enrichment associated with the P and that the Si present in the particles is not likely associated with aluminosilicate minerals expected in these soils.

Individual particle descriptions indicate two types of particles. The first type is an Al-dominated P-rich coating on a separate particle, and the second type is an Al-dominated P-rich solid existing as a loose cluster of what appear to be smaller particles. Both types of particle were amorphous by electron diffraction.

The suggestion that P exists as some amorphous Al enriched solid is in agreement with results from solubility equilibria experiments (Chapter 4) on some of these samples as well as with Lindsay et al. (1962) who found a colloidal Fe and Al phosphate solid as a reaction product of monocalcium phosphate and several different soils. That such P-rich particles exist under high pH conditions (e.g. the Metea soils) further suggests that they are kinetically stable in most soil environments.

Chapter IV
PHOSPHATE SOLUBILITY EQUILIBRIA IN EXCESSIVELY FERTILIZED
MIDWESTERN SOILS

4.1 Introduction

Solubility equilibrium experiments have long been a popular approach in studying solid phase control of P solubility in soils. These experiments are based on the assumption that the soil solids have come to either equilibrium (ions in solution are in equilibrium with a solid that is thermodynamically favored in that system) or to a steady-state (a meta-stable condition in which the indicators of equilibrium are time invariant within the experiment but ion activities may not be controlled by the thermodynamically favored solid) with an aqueous phase and, through ion activity calculations, the presence of a P bearing solid can be inferred.

Typical presentations of data from equilibrium experiments categorize soils as high pH, in which P solubility is thought to be controlled by Ca phosphates, and low pH, in which P solubility is thought to be controlled by either Fe or Al phosphates (Lindsay, 1979). O'Connor et al. (1986) found P solubility in fertilized and sludge-amended calcareous soils to be controlled by

either octacalcium phosphate (OCP) or beta-tricalcium phosphate (TCP), and that the difference in P availability from the two P sources could not be attributed to changes in P solid mineralogy. Fixen and Ludwick (1982) studied 28 near-neutral and alkaline Colorado soils and found that OCP was an important fertilizer residue in only one heavily manured soil, and that TCP or a mineral similar in composition may have been an important fertilizer residue in some of the remaining soils. Variscite is the thermodynamically favored Al phosphate in acid soil systems and equilibrium studies have indicated it may have controlled P solubility in acid soils that had not been amended with P for at least five years (Wright and Peech, 1960). Other authors dispute that crystalline variscite can form in soils (Hsu, 1965; Larsen, 1967; Webber, 1978).

Implicit in this discussion is that ion activities can be accurately determined. The development of computer models such as GEOCHEM (Sposito and Mattigod, 1980), which attempt to account for all of the possible forms of an ion in solution, including ion pairs and soluble complexes, have made this task much easier. One major research topic remaining in ion speciation is the role of soluble organics, primarily fulvic acids, and their effects on ion activities. Several models, run with GEOCHEM, have attempted to account for the influence of fulvic acids on ion activities. The mixture model assumes that the

influence of fulvic acids on ion activities can be estimated by the influence of a mixture of simple organic acids, with known metal complexation constants, on ion activities. The mixture of organic acids was chosen because they gave pH titration curves similar to the soluble organics extracted from a sludge amended soil (Sposito et al., 1982). The fulvate model, developed from the same sludge-soil system as the mixture model, contains experimentally determined complexation constants for metals for which ion specific electrodes exist (Cd^{2+} , Cu^{2+} , Ca^{2+} , and Pb^{2+}). The common logarithms of these constants were then correlated with the metals' Misono softness parameter. This allowed the prediction of complexation constants for metals for which ion specific electrodes do not exist (Mn^{2+} , Mg^{2+} , Fe^{2+} , Ni^{2+} , and Zn^{2+}) (Sposito et al., 1982).

Blaser and Sposito (1987) studied a water-soluble, chestnut-leaf-litter extract and, using fluorescence spectroscopy, determined that the dominant Al complexing species with the organic ligands were the quasiparticle species Al^{3+} and $\text{Al}(\text{OH})^+$, with conditional stability constants of $10^{8.55}$ and $10^{-1.8}$, respectively. These constants can be used in a chemical speciation model to estimate the degree of complexation of Al by naturally occurring organic ligands.

Despite the large number of studies that have been conducted utilizing this indirect approach, I felt that some discrepancies and deficiencies existed in this body of literature. Factors such as the assumption of steady-state at sampling, the rigor of speciation, working with "artificial" high P conditions or the lack of information on acidic soils needed to be taken into account. The purpose of this experiment was to rigorously apply the indirect equilibrium approach to a variety of Midwestern soils that were amended with excessive quantities of P from fertilizers, sewage sludge, or manure sources over long periods of time under field conditions.

4.2 Materials and Methods

Complete sample descriptions were given in the previous chapter. All of the samples that were collected were used in this experiment.

The equivalent of 25 g of dry soil and 50 mL of deionized water was added to a 125-mL dark polyethylene bottle. The bottles were stored at 298 ± 0.5 °K and shaken once per day. The head space of each bottle was replaced daily with room air to prevent the development of anoxic conditions. Preliminary experiments demonstrated that with daily aeration dissolved O_2 concentrations remained at 80-85% of that expected in pure water in equilibrium with atmospheric O_2 . Duplicate samples were sacrificed at

t= 21, 42, 105, and 118 d and triplicate samples were sacrificed at t= 124 and 130 d. The equilibrium solutions were transferred to 30-mL centrifuge tubes and centrifuged at 12000 rpm for 30 min. The supernatant solutions were analyzed for pH and inorganic C before filtering through a 0.2 micron polycarbonate filter. These solutions were stored at 277°K while awaiting further analysis.

Complete analysis of the solutions involved measurement of Ca, Mg and Mn (t= 130 d only for Mn) by atomic adsorption, K and Na by flame emission, inorganic and organic C with a Dohrmann Xertex Carbon Analyzer, P colorimetrically by the molybdenum blue procedure (Olsen and Sommers, 1982), Al colorimetrically by the ferron procedure (Barnhisel and Bertsch, 1982), Fe colorimetrically with the o-phenanthroline procedure (Olson and Ellis, 1982), and F, Cl, NO₃ and SO₄ by ion chromatography. Solution speciation was performed with GEOCHEM (Sposito and Mattigod, 1980). For purposes of comparison, the soluble organic fraction was accounted for with the mixture model (Sposito et al., 1982) and the fulvate model (Sposito et al., 1981) with the Al complexation constants of Blaser and Sposito (1987) incorporated. For t= 21, 42, 105, 118, and 124 d replicated data were averaged prior to entering them into GEOCHEM. To assess variability in the data, individual replicates were entered into GEOCHEM for t= 130 d.

4.3 Results and Discussion

4.3.1 Influence of Time on Selected Solution Parameters

Due to the large amount of data it is not possible to present or discuss all of the information in detail. Tables 8 to 10 present a complete listing of measured solution parameters for all samples at $t = 21$ and 130 d. Data from $t = 42$, 105, 118, and 124 d are given in the appendix. In all cases, supernatant pH values were higher at $t = 42$ d or 105 d when compared to $t = 21$ d (data not shown). With three exceptions, supernatant pH values remained higher than those at $t = 21$ d for the remainder of the experiment (Tables 8 to 10). The exceptions were the McBride soils and the mine spoil material where, after an initial pH rise, supernatant pH values declined to levels below those of $t = 21$ d (Tables 9 and 10). In all cases total pH changes were ≤ 1.0 over the course of the experiment.

Organic C concentrations showed the greatest relative changes over time. The Plainfield low and medium P samples had no changes in organic C concentration over time (Table 8), while all remaining samples had higher organic C concentrations at $t = 130$ d when compared to $t = 21$ d (Table 8 to 10). Organic C concentrations rose steadily over the course of the experiment (data not shown).

Table 8. Measured solution parameters for the Plainfield soils.

Parameter	Low P		Medium P		High P	
	-----		time(d) -----		-----	
	21	130	21	130	21	130
pH	6.3	6.8	6.5	7.2	6.1	6.3
organic C						
(mg/L)	6.8	6.8	6.2	6.1	16.7	26.5
inorganic C [#]	2.99	3.40	3.02	3.19	3.43	3.61
Ca	3.60	3.38	3.34	3.33	4.14	3.79
Mg	3.52	3.44	3.52	3.38	4.11	4.04
K	4.68	4.61	3.89	3.82	3.25	3.23
Na	3.89	3.98	4.07	4.54	4.13	4.40
Fe	6.45	6.02	nd ^e	6.38	6.09	5.12
Al	nd	5.65	5.48	5.79	4.93	4.90
Mn	na ^{&}	nd	na	nd	na	nd
PO ₄	3.98	5.24	4.46	4.45	4.02	4.46
SO ₄	4.61	4.22	4.62	4.32	4.17	3.86
Cl	3.97	4.28	nd	4.65	3.50	3.88
F	nd	nd	4.71	4.53	5.13	4.57

[#]concentrations for inorganic C and all subsequent table entries
are expressed as the negative logarithm of the molar concentration.

^enot detectable

[&]not available

Table 9. Measured solution parameters for the Metea and McBride soils.

Parameter	Metea				time(d)	McBride			
	Fertilizer		Sludge			Low P		High P	
	P		P						
	21	130	21	130		21	130	21	130
pH	6.9	7.6	6.9	7.5		6.7	6.4	6.4	5.8
organic C (mg/L)	13.8	19.5	28.1	39.9		44.8	56.6	13.9	18.3
inorganic C [#]	2.74	2.76	2.60	2.67		2.95	3.32	3.64	3.82
Ca	3.02	2.93	2.65	2.59		3.60	3.54	3.83	3.64
Mg	3.42	3.40	3.71	3.68		3.82	3.90	4.02	3.98
K	4.11	4.08	3.97	4.00		3.94	3.87	3.53	3.51
Na	4.15	4.12	3.60	3.67		4.14	4.47	4.31	4.57
Fe	6.57	5.88	6.20	4.95		5.39	5.46	5.67	5.78
Al	5.28	5.33	5.06	4.90		4.50	4.60	4.86	4.99
Mn	na ^{&}	5.87	na	4.31		na	6.52	na	nd [@]
PO4	4.24	4.47	4.66	4.54		5.68	6.13	4.13	4.29
SO4	3.77	3.54	3.14	3.11		4.24	4.23	4.34	4.01
Cl	nd	4.72	4.04	4.04		nd	4.13	nd	4.65
F	4.49	4.38	4.54	4.46		nd	nd	4.73	4.53

[#]concentrations for inorganic C and all subsequent table entries are expressed as the negative logarithm of the molar concentration.

[@]not detectable

[&]not available

Table 10. Measured solution parameters for the Blount, mine spoil, and Howard samples.

Parameter	Blount				time(d)	Mine Spoil		Howard	
	Fertilizer		Sludge			21	130	21	130
	P		P						
	21	130	21	130					
pH	7.0	7.5	6.2	6.4		6.2	5.8	6.9	7.4
organic C (mg/L)	21.1	31.0	49.2	80.4		73.4	129.0	30.2	78.9
inorganic C [#]	2.60	2.68	3.13	3.47		3.01	3.68	2.47	2.46
Ca	3.09	2.96	3.10	3.12		2.93	3.02	3.08	2.87
Mg	3.27	3.17	3.20	3.26		3.02	3.09	3.28	2.98
K	3.71	3.74	3.53	3.61		3.54	3.63	3.29	3.21
Na	4.08	4.19	3.79	3.91		3.62	3.55	4.03	4.21
Fe	6.35	5.78	5.54	5.39		6.01	5.03	6.05	5.53
Al	5.00	5.06	4.72	4.57		4.69	4.41	4.79	4.57
Mn	na ^{&}	nd ^e	na	4.74		na	4.75	na	4.14
PO4	4.19	3.93	3.82	3.73		3.89	3.66	4.85	5.79
SO4	3.70	3.49	3.26	3.19		3.17	3.11	3.98	4.62
Cl	nd	4.38	5.11	4.21		4.10	3.84	4.56	4.11
F	4.34	4.25	4.50	4.35		4.40	4.33	4.65	4.38

[#]concentrations for inorganic C and all subsequent table entries are expressed as the negative logarithm of the molar concentration.

^enot detectable

[&]not available

Figures 22 to 27 present selected solution parameter data over time for the Plainfield medium P and mine spoil samples. Both samples show an initial rise in supernatant pH with the mine spoil sample then showing a decline in supernatant pH to a value less than that at $t = 21$ d (Figures 22 and 24). Calcium and H_2PO_4^- activities remained relatively constant with time for both samples (Figure 22 and 24) with the Plainfield medium P sample also having relatively constant solution Carbon concentrations (Figure 23). The mine spoil material is representative of samples having variable organic and inorganic Carbon concentrations with time (Figure 25 and 26). Both samples exhibit considerable variability in Al^{+3} activities over time (Figure 27).

The fact that a single ion has constant activity over time is not in itself a sufficient criterion to determine whether or not a system is in steady-state. For a system to be in equilibrium with a solid it must maintain a constant ion activity product (IAP) for that solid over time. This requires that either all of the ion activities used in calculating that IAP be time invariant or, that if the ion activities are not time invariant, they must change in such a way as to maintain a constant IAP (Sposito, 1981). These criteria will be discussed in more detail as we consider each class of P solids.

Figure 22. Calcium, H_2PO_4^- , and H^+ activities (negative logarithm) for the Plainfield medium P sample over time.

Figure 23. Inorganic C concentrations (pCO_3 , minus log molar) and organic C concentrations (mg C/L) for the Plainfield medium P sample over time.

Figure 24. Calcium, H_2PO_4^- , and H^+ activities (negative logarithm) for the mine spoil material over time.

Figure 25. Inorganic C concentrations (minus log molar) for the mine spoil material over time.

Figure 26. Organic C concentrations for the mine spoil material over time.

Figure 27. Aluminum activities over time for the Plainfield medium P and mine spoil samples.

4.3.2 Calcium Phosphates

In the unified phosphate activity diagram presented by Lindsay (1979), the pH at which the control of P solubility switches from Al phosphates to Ca phosphates is approximately 5.8. This pH will vary somewhat as the assumptions used in this diagram are modified and, therefore, it is necessary to consider Ca phosphates for all of the supernatant solutions analyzed in this experiment. Double function plots were employed for the Ca phosphates and in Figures 28 to 32 the lines, taken from the right side and from the bottom up, represent equilibrium with hydroxyapatite (HA, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$), beta-tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$), octacalcium phosphate (OCP, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 2.5 \text{H}_2\text{O}$), anhydrous dicalcium phosphate (DCP, CaHPO_4), and dicalcium phosphate dihydrate (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). A line for fluoroapatite (FA, $\text{Ca}_5(\text{PO}_4)_3\text{F}$), which would fall below HA, was not drawn because doing so would require unnecessary assumptions regarding F^- activity. Since F^- activities were determined, FA was considered using solubility product constants with the reference value of $\log \text{IAP} = -0.21$ representing equilibrium. Thermodynamic data were taken from Lindsay (1979). Error bars represent two times the standard deviation for the x and y variables at $t = 130 \text{ d}$.

All of the data points for the Plainfield low P sample fall at or below the HA line, with the HA line

Figure 28. Calcium double function plot for the Plainfield samples. The lines, taken from the right side and from the bottom up, represent hydroxyapatite, beta-tricalcium phosphate, octacalcium phosphate, anhydrous dicalcium phosphate, and dicalcium phosphate dihydrate. Numbers represent the order of sampling over time for each sample with 1, 2, 3, 4, and 5 representing $t = 21, 42, 105, 118,$ and 124 d, respectively. Error bars denote the 95% confidence limits at $t = 130$ d.

Figure 29. Calcium phosphate double function plot for the Metea samples. The lines, taken from the right side and from the bottom up, represent hydroxyapatite, beta-tricalcium phosphate, octacalcium phosphate, anhydrous dicalcium phosphate, and dicalcium phosphate dihydrate. Numbers represent the order of sampling over time for each sample with 1,2,3,4, and 5 representing $t = 21, 42, 105, 118,$ and 124 d, respectively. Error bars denote the 95% confidence limits at $t = 130$ d.

Figure 30. Calcium phosphate double function plot for the McBride samples. The lines, taken from the right side and from the bottom up, represent hydroxyapatite, beta-tricalcium phosphate, octacalcium phosphate, anhydrous dicalcium phosphate, and dicalcium phosphate dihydrate. Numbers represent the order of sampling over time for each sample with 1,2,3,4, and 5 representing $t = 21, 42, 105, 118,$ and 124 d, respectively. Error bars denote the 95% confidence limits at $t = 130$ d.

Figure 31. Calcium phosphate double function plot for the Blount samples. The lines, taken from the right side and from the bottom up, represent hydroxyapatite, beta-tricalcium phosphate, octacalcium phosphate, anhydrous dicalcium phosphate, and dicalcium phosphate dihydrate. Numbers represent the order of sampling over time for each sample with 1,2,3,4, and 5 representing $t = 21, 42, 105, 118,$ and 124 d, respectively. Error bars denote the 95% confidence limits at $t = 130$ d.

Figure 32. Calcium phosphate double function plot for the Howard manure P and mine spoil samples. The lines, taken from the right side and from the bottom up, represent hydroxyapatite, beta-tricalcium phosphate, octacalcium phosphate, anhydrous dicalcium phosphate, and dicalcium phosphate dihydrate. The numbers represent the order of sampling over time for each sample with 1,2,3,4, and 5 representing $t = 21, 42, 105, 118,$ and 124 d, respectively. Error bars denote the 95% confidence limits at $t = 130$ d.

falling within the 95% confidence limits (CL) at $t = 130$ d (Figure 28). The Plainfield medium P sample indicates a slightly higher P solubility by plotting above the HA line in a region of "intermediate" solubility, that is, above HA and below OCP without any apparent equilibrium with a solid phase. The Plainfield high P sample plots entirely below the HA line indicating that this soil is either in equilibrium with a less soluble Ca phosphate solid or not in equilibrium with any Ca phosphate. The latter possibility is likely given that the pH of the supernatant at $t = 130$ d was much lower than that of the other two Plainfield samples (Table 8) and this would suggest that Al phosphates might control P solubility. Fluoride concentrations were not detectable in the Plainfield low P samples and the Plainfield medium P sample was supersaturated with respect to FA having a log IAP value of 6.7 at $t = 130$ d. The Plainfield high P sample had a log IAP for FA of 0.47 ± 0.77 at $t = 130$ d, which would put the reference value within the 95% CL and indicating that equilibrium with FA may have existed for this sample. Each of the data points from $t = 130$ d plots down and to the right of the corresponding data point for $t = 21$ d for all of the Plainfield samples. This change in position was most likely due to the increase in supernatant pH over the same time period (Table 8).

Results for the McBride soils (Figure 30) were similar to those obtained for the Plainfield low and high P samples with the exception that the McBride low P soil did not indicate possible equilibrium with HA. The log IAP for FA for the McBride high P sample was -0.91 ± 0.76 at $t = 130$ d. Data points for the McBride high P sample generally plotted upward and to the left at the later sampling times as compared to the first two sampling times. This change in position corresponded to reductions in supernatant pH over time for this sample (Table 9). The position on the double function plot for low pH samples is also suggestive of control of P solubility by Al phosphates and will be discussed further in the following section.

The Metea soil data fall into a region of "intermediate" solubility between OCP and TCP (Figure 29). These results are similar to those obtained by O'Connor et al. (1986) in two respects: 1) the P solubilities shown here are typical for soils with a $\text{pH} > 7.0$, and 2) there was no readily apparent difference in solubility between P sources. The Blount fertilizer P sample (Figure 31) and the Howard sample (Figure 32) fell into this same pH category and gave similar results. The final four data points for the Blount fertilizer P sample (Figure 31) plot on the OCP line indicating an apparent equilibrium with this mineral.

The remaining two samples, the Blount sludge P soil and the mine spoil material, both received Chicago sewage sludge. The samples had similar 1:1 soil-to-water pH values with the mine spoil material ending up with a slightly more acidic supernatant pH (Table 10). The mine spoil material plotted slightly below the HA line (Figure 32) with the line falling within the 95% CL while the Blount sludge P sample plotted slightly above the same line (Figure 31). Both of these samples were supersaturated with respect to FA, having log IAP values at $t = 130$ d of 6.5 and 3.8 for the Blount and mine spoil samples, respectively. The time variation for the data points for the mine spoil sample followed a trend similar to the McBride high P sample.

That data points fall into regions of "intermediate" solubility and the additional factor of apatite minerals not controlling P solubility despite being the thermodynamically favored reaction product are common results for solubility equilibria experiments with high pH systems (e.g. Withee and Ellis, 1965; O'Connor et al., 1986; Harrison and Adams, 1987). Possible causes discussed in the literature include the effect of soluble organic matter on obtaining equilibrium (Moreno et al., 1960; Arambarri and Talibudeen, 1959), that labile P (adsorbed P) determines the concentration of P in solution (Murrmann and Peech, 1969), the wide variety of reaction

products due to P additions (Bell and Black, 1970b), and that Ca phosphates of unknown solubility may coat precipitated secondary P particles (Harrison and Adams, 1987). With the exception of the three samples which indicate possible equilibrium with HA or FA, the results from this study do not contradict the observations regarding intermediate solubilities and apatites controlling P solubility and, unfortunately, do not provide any evidence as to the possible cause.

Since some of the samples indicated a probable equilibrium with a particular P solid, we can examine the influence of time on attainment of a constant IAP for that solid. The classic example of this would have a solid beginning to dissolve at the onset of a similar experiment with the rate of dissolution > rate of precipitation and an IAP indicating undersaturation with respect to that solid. As dissolution progresses, the rate of dissolution eventually equals the rate of precipitation and a constant IAP results (Sposito, 1981). This is evident in the Blount fertilizer P sample which has OCP log IAP values of 8.9, 10.0, 11.2, 11.5, 11.3, and 11.5 at $t = 21, 42, 105, 118, 124,$ and 130 d, respectively, indicating that a steady-state condition relative to OCP (reference log IAP = 11.8) occurred between 42 and 105 d. This condition could have also existed in the Plainfield low and high P samples which indicated an apparent equilibrium with their

respective solids at $t = 21$ d (e.g. Plainfield low P, log IAP = 13.8, 10.3, 14.7, 13.4, 16.0, and 14.1 for HA at their respective times, reference log IAP = 14.5). Quite the opposite was true with the McBride high P and mine spoil samples which approached equilibrium with their respective solids from supersaturation (e.g. mine spoil, log IAP = 16.3, 18.6, 16.1, 14.9, 14.2, and 14.0 for HA at the respective times). These results suggest that attainment of a steady-state condition is a sample-dependent phenomenon and that the equilibration times frequently reported in the literature (e.g. O'Connor et al., 1986, 24 h; Harrison and Adams, 1987, 14 d) may not be adequate.

4.3.3 Aluminum Phosphates

The first question that needed to be addressed when considering Al phosphate solubility is which of the models best represents Al complexation by soluble organics. One problem that became immediately apparent was that the mixture model produced unacceptable variability in predicted Al^{3+} activities when replicate data from $t = 130$ d were used with GEOCHEM. As an example, consider the mine spoil material with total Al concentrations (log M) of -4.45, -4.30, and -4.49 for the three replicates and the resultant estimates of Al^{3+} activities (log(activity)) of -21.05, -8.77, and -23.08. This variability problem was apparent in 10 of the 11 samples considered. The

cause of this variability was traced to the Al-citric acid complex. Citric acid is one of the simple organic acids used in the mixture model and it has a relatively high affinity for Al. If the Al: citric acid concentration ratio was one or less, then extremely low Al^{3+} activities were predicted and, conversely, if the Al: citric acid ratio was greater than one then much higher Al^{3+} activities were predicted. For this reason alone, the mixture model was discarded and all results are based on the use of the fulvate model with the independent Al complexation constants of Blaser and Sposito (1987) incorporated into it.

The solids initially considered for the Al phosphates were K-taranakite ($\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$, $\log K_{\text{SO}} = -22.5$), variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, $\log K_{\text{SO}} = -30.5$) and the amorphous analog of variscite ($\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$). The thermodynamic data for K-taranakite and variscite are taken from Lindsay (1979). The values of $\log K_{\text{SO}}$, where $\log K_{\text{SO}} = \log(a_{\text{Al}}) + 2\log(a_{\text{OH}}) + \log(a_{\text{H}_2\text{PO}_4})$, for the amorphous analog of variscite vary somewhat in the literature with reviews suggesting a range of -27 to -29 (Traina et al., 1986; Sposito and Veith, 1977). The value of $\log K_{\text{SO}}$ for variscite, where we also have $\log K_{\text{SO}} = \log(a_{\text{Al}}) + 2\log(a_{\text{OH}}) + \log(a_{\text{H}_2\text{PO}_4})$, includes the hydrolysis of water and was chosen so that a single log IAP value could be calculated for each sample.

All samples were undersaturated with respect to K-taranakite (data not shown).

Calculated values for log IAP for all samples at $t = 130$ d are given in Table 11. That the log IAP values for the Metea soils, the Howard soil, and the Plainfield low P soil indicated undersaturation with respect to variscite was an anticipated result based on the pH of the supernatant solutions (Tables 8 to 10; Lindsay, 1979). The unexpected result is that the log IAP values for the Plainfield medium P and Blount fertilizer P samples indicated an apparent equilibrium with variscite despite relatively high supernatant pH values (Tables 8 and 10) and previous conclusions regarding Ca phosphate solids. In light of these contradictory results and the fact that the greatest degree of uncertainty lies in the estimates of Al^{3+} activities, it would appear that Al^{3+} activities are overestimated in these two samples.

The remaining samples indicate an apparent equilibrium with $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$. This solid was first noted explicitly as a reaction product of exchangeable Al and ortho-phosphate ions (Coleman et al., 1960), and has since been implied as a reaction product between ortho-phosphate ions and montmorillonite (Webber, 1971), aluminosilicates, aluminum hydrous oxides, aluminum oxides and allophanic soils (Veith and Sposito, 1977), an Al saturated peat (Bloom, 1981), and an acidic montmorillonitic soil

Table 11. Values of log IAP and its standard deviation for variscite and $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$ for all samples at $t=130$ d.

Sample	log IAP
Plainfied	
low P	-30.9 ± 0.1
med. P	-30.7 ± 0.7
high P	-28.7 ± 0.4
Metea	
fert. P	-31.5 ± 0.4
sludge P	-31.1 ± 0.2
McBride	
low P	-29.5 ± 0.1
high P	-28.6 ± 0.1
Blount	
fert. P	-30.8 ± 0.4
sludge P	-27.5 ± 0.1
Mine spoil	
sludge P	-26.9 ± 0.3
Howard	
manure P	-31.7 ± 0.2
Variscite	-30.5
$\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$	-27 to -29

separate (Traina et al., 1986). Lindsay et al. (1962) noted a similar compound (colloidal $(\text{Fe}, \text{Al}, \text{X})\text{PO}_4 \cdot n\text{H}_2\text{O}$, where X indicates cations other than Fe or Al) as a reaction product of a saturated solution of monocalcium phosphate and soil. Further evidence for the existence of an amorphous Al phosphate solid comes from the electron microscope observations of density separates from the Plainfield high P soils, both McBride soils and the Blount sludge P soil samples (Chapter 3). Discrete P-rich particles were found in these density separates that had Al as the principal cation associated with the P. In addition, electron diffraction of selected P-rich particles indicated that they were amorphous.

The log IAP values for the samples that appeared to be in equilibrium with $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$ indicated this condition at all of the sampling times (e.g. Blount sludge P with log IAP= -27.5, -28.5, -27.2, -28.2, -27.4, and -27.5 at the respective sampling times). Samples that appeared to be at equilibrium or undersaturated with respect to variscite had decreasing log IAP values over the course of the experiment (e.g. Howard soil exhibited the maximum change with log IAP= -29.6, -29.6, -31.3, -32.5, -31.6, and -31.7 at the respective times). The Blount fertilizer P sample did not exhibit its apparent equilibrium with OCP until between 42 and 105 d and, likewise, it did not exhibit its apparent equilibrium with

variscite until the same time, with log IAP of -29.8 and -30.8 at $t = 42$ and 105 d, respectively. In agreement with results from the Ca phosphates, the attainment of a steady-state condition is a sample dependent phenomenon.

4.3.4 Iron and Manganese Phosphates

Two Fe phosphate minerals were considered for data from $t = 130$ d, strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, $\log K_{\text{SO}} = -6.85$) and vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, $\log K_{\text{SO}} = 3.11$), with thermodynamic data taken from Lindsay (1979). Without redox measurements it is impossible to speciate Fe_T concentrations into Fe(III) and Fe(II) forms; however, the Fe_T concentrations can be entered into GEOCHEM as all Fe^{2+} or Fe^{3+} and any calculations that indicate that a solution is undersaturated with respect to strengite or vivianite can be assumed to be correct since true Fe^{2+} or Fe^{3+} activities will be no greater than those predicted with this method.

Calculations for strengite indicated that in fact seven of the eleven samples were undersaturated with respect to this mineral. However, the Plainfield high P, McBride high P, Blount sludge P and the mine spoil material were all supersaturated with respect to strengite, having log IAP values of -4.6, -4.8, -4.8, and -4.4, respectively. Therefore, I cannot rule out the possibility that these four samples were in equilibrium with strengite. Calculations for vivianite indicated that

the Metea sludge P and Blount fertilizer P samples were at equilibrium or slightly undersaturated with respect to vivianite having log IAP values of -3.1 and -2.1, respectively. All other samples were undersaturated with respect to this mineral. Once again I cannot rule out the possibility that these two samples were in equilibrium with vivianite.

A recent series of papers has examined the possibility that Mn phosphates control P solubility in some soils (e.g. Boyle and Lindsay, 1986) including the divalent Mn minerals $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ and the trivalent Mn mineral $\text{MnPO}_4 \cdot 1.5\text{H}_2\text{O}$. Six samples had detectable Mn concentrations at the $t = 130$ d sampling (Tables 8 to 10). Direct calculation of the log IAP was possible for the divalent Mn minerals and all of the samples were undersaturated with respect to any of the divalent Mn phosphates. Calculated log IAP values were no closer than 2.0 units from any of the reference values (data not shown).

Consideration of the trivalent Mn mineral required an estimate of the redox conditions in the samples. Redox measurements were not made during the course of the experiment; however, an estimate of redox could be obtained from dissolved O_2 measurements taken in preliminary work. These measurements indicated that,

under the experimental conditions, dissolved O_2 concentrations remained at approximately 80-85 % of those expected in pure water in equilibrium with atmospheric O_2 . Using this approximation, calculated log IAP values indicated that all the samples were supersaturated with respect to $MnPO_4 \cdot 1.5H_2O$ with the closest log IAP value being 3.5 units greater than the reference value. Since the greatest source of error in these calculations was likely the assumption regarding redox conditions, and decreasing the log IAP by 3.5 units would require unreasonably low dissolved O_2 concentrations, it is unlikely that these samples were in equilibrium with this trivalent Mn phosphate.

4.4 Conclusions

Three samples provided results suggestive of an equilibrium condition with a single P solid phase. They were the Plainfield low P soil with HA and the McBride low P and Blount sludge P soils with $Al(OH)_2H_2PO_4$. Four additional samples, the Plainfield and McBride high P soils, the Blount fertilizer P and the mine spoil material, yielded contradictory results because the solution data were consistent with the existence of both an Al and a Ca phosphate solid. It is possible that this may have been a fortuitous result for the Plainfield, McBride and mine spoil samples given the variability in the data and the fact that the supernatant pH values for

these samples were near the pH at which control of P solubility changes from Al to Ca. The remaining four samples did not yield results suggestive of equilibrium with any of the Ca or Al phosphate solids considered. Results for Fe phosphates were largely inconclusive in the absence of redox measurements. However, I cannot rule out the possibility that strengite or vivianite controls P solubility in some of the samples. Results for Mn phosphates were more conclusive despite the lack of redox measurements and it is unlikely that Mn phosphates control P solubility in any of the samples considered. No generalizations can be made with regard to the influence of the P source on the P solubility characteristics of any sample.

Samples with a high supernatant pH (>6.8) frequently exhibited "intermediate" solubility relationships (more soluble than HA and less soluble than OCP, e.g. Figure 29). This, in combination with the time required for some samples to reach a steady-state condition, makes it difficult to draw definite conclusions from such samples. The Blount fertilizer P sample would appear to be the exception rather than the rule. Samples having a low supernatant pH provide consistent evidence for the existence of the amorphous analog of variscite throughout the experiment. This work represents the first instance in which the existence of a secondary P mineral was

indicated through both a direct (Chapter 3) and an indirect method.

Chapter V

UTILIZATION OF AN ANION EXCHANGE RESIN EXTRACTION TO ASSESS RESIDUAL AVAILABLE PHOSPHORUS

5.1 Introduction

In Chapter 3 it was concluded that P exists as discrete P-rich particles in the soils considered. The particles were amorphous, generally contained two or more cations in association with the P, and have undetermined solubility characteristics. Empirical extraction techniques must be used to assess the availability of the P for plant growth and as a pollutant in the absence of any a priori knowledge regarding the solubility characteristics of the P-bearing solids. Plant available P has long been estimated through the use of several dilute chemical extractants (Bray and Kurtz, 1945; Olsen et al., 1954). These extractants, developed using correlations between P uptake and extractable P, focuses primarily on identifying P deficient soils through the removal of part of the labile P pool. The usefulness of these extractants at excessively high P levels is not well understood since the extractants can dissolve variable amounts of precipitated P compounds and it is not clear to

what extent P extracted from precipitated forms correlates with P uptake.

Anion exchange resin has also been used to study available P in both high and low P soils. The resin acts primarily as a sink for P and offers the advantage over chemical extractants in that it should only remove P that can most readily respond to such a sink. Each P fraction will, in fact, respond to the resin although each will respond to a different extant. The analogy can be drawn to that of a growing root. The common procedure is to use a chloride saturated resin at a 1:1 resin-to-soil ratio (R/S) in 10 to 100 mL of water or dilute electrolyte for 16 to 24 h (Olsen and Sommers, 1982; Amer et al., 1955). Studies of varying factors such as the saturating anion, shaking time, resin-to-soil ratio or solution-to-soil ratio have been performed. The major findings were: 1) P extracted is dependent on the saturating anion although the only real advantage in using one anion over another would be a reduction in pH changes when using HCO_3^- (a secondary equilibrium between H^+ and HCO_3^- counters the tendency of the resin to lower pH), 2) the rate-determining step in the exchange of P from the soil to the resin is P desorption from the soil to the water phase, 3) P extracted increases as R/S increase to approximately two, and 4) at a constant solution-to-resin ratio, P extracted decreases as the amount of soil increases, due

to increases in the salt concentration of the solution phase and subsequent increased competition for resin exchange sites by other anions (Amer et al., 1955; Sibbessen, 1978).

Vaidyanathan and Talibudeen (1970) concluded that the rate limiting step in the transfer of P from the soil to the resin was the diffusion of P into the resin. They also demonstrated that at low R/S values (approximately 1.0) less than 30% of the labile P pool is removed after anion exchange resins were in contact with soils for as long as 12 d. Barrow and Shaw (1977) note that at low values of R/S resins do not act as infinite sinks for P. Phosphate concentrations in solution and resin extractable P should both be measured when conducting a resin extraction experiment to ensure that the proper relationship between resin, soil and solution P is identified.

Anion exchange resin was chosen for this experiment because the mass of the resin in contact with the soil could be varied and the soil could therefore be exposed to increasingly larger P sinks. If the kinetics of dissolution for the P-bearing solids are relatively fast (within the time frame of the experiment) then increasing the size of the P sink should induce dissolution of the P-bearing solid and this would be seen as an increase in resin extractable P values as R/S increased. An analogous

experiment was performed by van der Zee et al. (1987) who used Fe oxide-coated filter paper strips as an infinite sink to determine reversibly adsorbed P in soils. The P adsorbed by a single strip of paper plateaued at 15 h and a 20 h contact time (4 strips) was considered to be reasonable to assess the amount of reversibly adsorbed P. First-order kinetics under the conditions of an infinite P-sink suggested that the amount of P adsorbed would continue to decrease with time. For this experiment, large increases in resin extractable P as R/S increased would suggest high P availability and, conversely, slight or no increases in resin extractable P as R/S increased would suggest low P availability. The purpose of this experiment was to investigate the influence of varying R/S values on resin extractable P from excessively fertilized soils as an attempt to assess the availability of residual P.

5.2 Materials and Methods

All resin extractable P values were obtained from duplicate analyses utilizing the equivalent of 0.5 g of air-dry soil, 20 mL of 0.05 M NaCl, and varying amounts of Cl-saturated Dowex 2x8 anion exchange resin (20-50 mesh). The anion exchange resin was contained in nylon mesh bags to facilitate the separation of the soil from the resin as well as to eliminate the need to grind the samples. Barrow and Shaw (1977) noted that enclosing the resin in

mesh bags decreased resin extractable P values and increased variability as compared to using unconfined resin. Sibbessen (1977) found that enclosing the resin in mesh bags actually increased resin extractable P as compared to using unconfined resin. The soil, 0.05 M NaCl, and resin bags were all contained in 50 mL centrifuge tubes placed on an end-over-end shaker until sampling. The Plainfield, Metea and McBride soils were used in an initial experiment which had R/S values of 0, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 with sampling times of 1, 4, 8, and 9 d for R/S=20 and t= 9 d for the remaining ratios. A second set of samples was run with the Plainfield, Metea, and McBride soils at R/S=40 and the Blount, Mine spoil and Howard soils with R/S= 0, 1.0, 2.0, 5.0, 10.0, 20.0, and 40.0. The second set of samples was sampled at t= 9 d only. At R/S=40 the resin had the capacity to adsorb from approximately 470 (mine spoil) to 18600 (Plainfield low P) times the mass of P in the samples.

At sampling the resin bags were removed, cut open, and the resin placed on a 60-mesh stainless steel sieve where it was washed free of soil particles with deionized water. The resin was then transferred to a 125 mL erlenmeyer flask where it was exposed to 2-20 mL aliquots of 0.5 M HCl for 20 min each. The HCl from each washing was combined in a volumetric flask after filtering through

Whatman #42 filter paper. The flasks were brought to volume with deionized water and saved for P analysis. The supernatant solutions were analyzed for pH before filtering through Whatman #42 filter paper and storage for later P analysis. All P analysis were done colorimetrically by the molybdenum blue procedure (Olsen and Sommers, 1982).

5.3 Results and Discussion

Resin extractable P levels remained steady or declined at R/S= 20 from 1 to 9 d (Table 12). The original premise of this experiment was that P solids may or may not dissolve in response to the P-sink resulting in steady or increasing resin extractable P with time. Studies by Barrow and Shaw (1977) and Sibbessen (1978) demonstrated the increase in resin extractable P with time and results from the Metea soils also support this. Declining resin extractable P levels for the Plainfield and McBride soils was an unexpected result. A plausible explanation for this would be a slowly dissolving solid in the resin-soil-solution system that was releasing an anion that would compete for P for resin exchange sites. Supernatant P concentrations, expressed as mg P/kg soil (Table 13), would argue against this however, as they are also declining with time. The combination of declining resin extractable P levels and declining supernatant P concentrations suggest a readsorption of P by the soil or

Table 12. Resin extractable P values over time at R/S= 20.

Sample	time(d)			
	1	4	8	9
	(mg P/kg)			
Plainfield				
low P	33.1	22.5	12.0	2.9
medium P	47.6	41.2	35.6	12.9
high P	58.1	58.7	39.3	19.4
Metea				
fertilizer P	89.5	75.6	123.0	93.8
sludge P	245.3	250.7	289.2	293.0
McBride				
low P	24.6	39.2	14.7	7.6
high P	79.8	78.4	60.3	51.5

Table 13. Supernatant P concentrations (expressed as mg P/kg soil) over time at R/S=20.

Sample	time(d)			
	1	4	8	9
	(mg P/kg)			
Plainfield				
low P	16.6	10.8	2.0	nd [#]
medium P	15.8	9.2	2.4	nd
high P	12.6	9.6	2.4	nd
Metea				
fertilizer P	17.2	14.8	11.2	nd
sludge P	20.6	32.4	17.4	18.4
McBride				
low P	5.4	8.0	nd	nd
high P	10.0	12.4	4.8	6.2

[#]not detectable

a soil constituent or possibly a precipitation mechanism removing P from solution. The common factor for the Plainfield and McBride soils as compared to the Metea soils are the extremely low supernatant pH values (Table 14 to 16) induced by the exchange resin. Similar reductions in pH have been shown to increase phosphate adsorption by kaolinite and alumina (Chen et al., 1973), goethite (Hingston et al., 1967) and acid soils (Obihara and Russel, 1972). While the exact reason for the reduction in resin extractable P over time cannot be determined with the data from this experiment, this phenomenon must be noted as a potential limitation of this procedure when supernatant pH values fall below approximately 4.3.

Tables 14 to 18 present supernatant pH values and supernatant P concentrations for each R/S value for each soil. The first point to note from these tables is the decline in pH that occurs as R/S increases with the maximum change in pH being 2.9 units for the Plainfield low and medium P samples. Sibbessen (1978) noted reductions in suspension pH by as much as 0.5 units when R/S increased from approximately 0.5 to 2.0 and results from these soils in the same range of R/S are in complete agreement.

Large changes in supernatant pH induce complications in light of the changes in the solubility of P solids due

Table 14. Supernatant P concentrations (expressed as mg P/kg soil) and pH for the Plainfield soils.

R/S	<u>Low P</u>		<u>Medium P</u>		<u>High P</u>	
	P	pH	P	pH	P	pH
	(mg P/kg)		(mg P/kg)		(mg P/kg)	
0		6.4		6.6		6.4
0.5	nd [#]	6.0	5.4	6.5	4.6	6.0
1.0	nd	5.9	4.9	6.2	3.2	5.9
2.0	nd	5.7	3.8	6.2	4.0	5.7
5.0	nd	5.1	nd	5.8	nd	5.1
10.0	nd	4.4	nd	5.0	nd	4.4
20.0	nd	3.7	nd	4.4	nd	3.7
40.0	nd	3.5	nd	3.7	nd	3.7

[#]not detectable

Table 15. Supernatant P concentrations (expressed as mg P/kg soil) and pH for the Metea soils.

R/S	<u>Fertilizer P</u>		<u>Sludge P</u>	
	P	pH	P	pH
	(mg P/kg)		(mg P/kg)	
0		7.6		7.3
0.5	19.8	7.1	39.7	6.8
1.0	6.6	7.0	18.4	6.7
2.0	6.3	7.0	13.6	6.7
5.0	4.8	6.7	18.5	6.5
10.0	nd [#]	6.6	12.2	6.4
20.0	nd	6.1	18.4	5.9
40.0	nd	5.1	2.2	6.1

[#]not detectable

Table 16. Supernatant P concentrations (expressed as (mg P/kg soil) and pH for the McBride soils.

R/S	<u>Low P</u>		<u>High P</u>	
	P	pH	P	pH
	(mg P/kg)		(mg P/kg)	
0		5.6		5.5
0.5	nd [#]	5.6	28.5	5.3
1.0	nd	5.5	10.7	5.3
2.0	nd	5.4	12.0	5.2
5.0	nd	5.1	6.9	4.8
10.0	nd	4.8	6.3	4.3
20.0	nd	4.3	6.2	4.0
40.0	nd	3.7	nd	3.8

[#]not detectable

Table 17. Supernatant P concentrations (expressed as mg P/kg soil) and pH for the Blount soils.

R/S	<u>Fertilizer P</u>		<u>Sludge P</u>	
	P	pH	P	pH
	(mg P/kg)		(mg P/kg)	
0		7.1		6.2
1.0	20.5	6.9	48.0	6.1
2.0	12.0	6.9	37.8	6.1
5.0	10.5	6.7	28.5	6.0
10.0	9.1	6.6	20.1	5.7
20.0	nd [#]	6.3	17.3	5.5
40.0	nd	6.5	10.7	5.1

[#]not detectable

Table 18. Supernatant P concentrations (expressed as mg P/kg soil) and pH for the Mine spoil and Howard samples.

R/S	<u>Mine Spoil</u>		<u>Howard</u>	
	P	pH	P	pH
	(mg P/kg)		(mg P/kg)	
0		6.1		6.4
1.0	54.1	6.1	10.1	6.5
2.0	42.4	6.0	9.7	6.2
5.0	29.6	6.0	4.3	6.1
10.0	19.2	6.0	nd [#]	6.0
20.0	17.8	5.7	nd	5.5
40.0	7.6	5.6	nd	4.9

[#]not detectable

to changes in pH. Lindsay (1979) notes the maximum change in H_2PO_4^- activity due to a pH change for Al phosphates would be a reduction of H_2PO_4^- activity by one log unit for each one unit reduction in pH. This suggests that as R/S increases (and supernatant pH decreases) two sinks would be competing for solution P; the possible reprecipitation of Al phosphate solids and the resin itself. Conversely, if a Ca phosphate was controlling P solubility in a soil, decreases in supernatant pH would increase H_2PO_4^- activities and could contribute to increases in resin extractable P as R/S increased. The large changes in supernatant pH values, as seen with the Plainfield soils, would therefore have to be noted as a potential limitation of this method.

The second point to note from Tables 14 to 18 is the consistent reduction in supernatant P concentration as R/S increases. With the exception of the Metea and Blount sludge P samples and the mine spoil material, all of the samples have supernatant P concentrations below the detection limit (approximately 2.0 mg P/kg for supernatant concentrations) of this procedure at the higher R/S values. The fact that all of the samples that have detectable supernatant P concentrations at R/S= 40 had been amended with large amounts of sludge suggests a competitive affect from other anions in these soil-resin-solution systems. Alternatively, the fact that these

three samples have the highest resin extractable P levels suggest the resin may not be capable of reducing supernatant P concentrations to low levels under high P conditions. The maximum possible reduction in supernatant P concentrations is desirable if the resin is to be considered an infinite sink (Barrow and Shaw, 1977).

The remaining discussion shall deal with all of the samples at all values of R/S at $t = 9$ d. Figures 33 through 38 present the influence of R/S on resin extractable P for all soils with error bars denoting the 95% confidence limits. The variability problem associated with enclosing the resin in mesh bags noted by Barrow and Shaw (1977) is also evident in this experiment. The alternative to enclosing the resin in mesh bags would have been to grind the soil to a particle size less than that of the resin so that the resin could be retained on a sieve and could be separated from the soil. In keeping with our stated objective regarding minimally disturbing the samples, this alternative was deemed unacceptable.

The Plainfield high P sample exhibits the behavior anticipated in the development of this technique by having significant increases in resin extractable P as R/S increases from 10 to 40 (Figure 33). These increases in resin extractable P come about despite strong evidence for the existence of Al phosphates (Chapters 3 and 4) and the reduction in supernatant pH with increasing R/S (Table 14)

Figure 33. Resin extractable P versus R/S for the Plainfield soils.

Figure 34. Resin extractable P versus R/S for the McBride soils.

Figure 35. Resin extractable P versus R/S for the Metea soils.

Figure 36. Resin extractable P versus R/S for the Blount soils.

Figure 37. Resin extractable P versus R/S for the Mine spoil material.

Figure 38. Resin extractable P versus R/S for the Howard soil.

which could create a competitive sink for P in this soil. The Plainfield medium P sample follows a similar, yet nonsignificant, trend. At corresponding R/S values from 0 to 20 the Plainfield medium and high P samples have significantly higher resin extractable P values as compared to the Plainfield low P sample. A situation analogous to the relationship between the Plainfield medium and low P samples exists for the McBride samples (Figure 34).

The Plainfield medium and high P samples have declining resin extractable P levels when comparing $R/S=0$ to $R/S=0.5$ to 10 (Figure 33). A similar trend is seen with the McBride high P sample (Figure 34) and the Blount sludge P sample (Figure 36). This suggests that the resin is not capable of adsorbing all of the P in solution when the smaller masses of resin are used. The cause of this does not appear to be related to the capacity of the resin for P since samples with much higher resin extractable P levels (e.g. Figure 37) do not exhibit this behavior. A competitive anion which is preferentially adsorbed by the resin relative to P may explain this phenomenon.

The Metea samples exhibit a second type of curve as compared to the Plainfield medium and high P samples by reaching a plateau in resin extractable P at $R/S=10$ (Figure 35). The shape of the curves would suggest that either a finite source of P had been exhausted by the

resin or that dissolution kinetics prevented the release of additional P to the resin within the time frame of the experiment. The fertilizer P sample appears to fit the latter possibility given the relatively steady resin extractable P levels over time while the sludge P sample appears to fit the former possibility given the slight increases in resin extractable P over time (Table 12). A previous experiment (Chapter 4) presented evidence for the existence of Ca phosphates of unknown solubility characteristics in both Metea soils. A separate experiment (Chapter 3) indicated that P existed in P-rich predominantly Al containing particles. Data from this experiment would also argue against the bulk of the P in these samples existing as Ca phosphate solids since a pH reduction of 2.5 units for the fertilizer P sample would have likely produced large increases in resin extractable P if Ca phosphates were present (Lindsay, 1979). By the same arguments, the data from this experiment do not support the existence of octacalcium phosphate in the Blount fertilizer P sample (Chapter 4; Figure 36). It could also be argued that the reductions in supernatant pH did, in fact, dissolve Ca phosphates in the Metea fertilizer P sample and that the P subsequently precipitated as an Al phosphate. Once again, the relatively steady resin extractable P levels over time (Table 12) would argue against this possibility.

Results for the Blount sludge P sample are somewhat inconclusive in light of the extreme variability at R/S= 10 and 40 (Figure 36). The behavior of this sample would be expected to be similar to that of the mine spoil material since both samples have similar supernatant pH ranges (Tables 17 and 18) and both received large additions of Chicago sludge. Visual inspection of the data in Figure 37 suggests that resin extractable P increased as R/S increased although the increases are not statistically significant.

The best evidence for the existence of a pool of P able to respond to the resin is presented by the Howard soil (Figure 38). This sample has significant increases in resin extractable P as R/S increases from 5 to 40 along with a corresponding tripling of resin extractable P over the same R/S range. Equilibrium experiments (Chapter 4) suggested that this sample was in equilibrium with a Ca phosphate solid yet supernatant pH values (Table 18) do not place this sample in a category (Ca phosphates implied by equilibrium experiments and high supernatant pH in this experiment) with the Metea soils or the Blount fertilizer P sample.

A wide range of maximum resin extractable P levels (maximum resin extractable P value at any R/S value within sample) exists in these samples. Values ranging from 18.5 (Plainfield low P) to 369 mg P/kg (mine spoil) were found

yet in all cases the maximum resin extractable P level from any sample represented no more than 14% of the total P concentration in that sample (Table 19). This would suggest that, at best, 14% of the residual P in these samples would become available under the influence of a large capacity sink. This result is in agreement with those of Barber (1979) who found resin P to represent no more than 12% of the total P in a Raub silt loam soil amended with varying amounts of P over a long period of time.

The percent of the total P available by resin extraction generally increased as R/S increased (Table 19). No relationship exists between the source of P or the soil pH and available P by this method. These relatively low percentages are supportive of conclusions by Vaidyanathan and Talibudeen (1970) that anion exchange resin removes P primarily from the labile P pool only, even at the high R/S values used in this experiment.

An estimate of the availability of residual P for crop growth can be made by examining the maximum increase in resin extractable P as R/S increased from 1.0 (the lowest nonzero ratio common to all samples) to the R/S value at which the maximum resin extractable P occurred. The minimum increase of 15.7 mg P/kg was with the Plainfield medium P sample while the maximum increase of 260 mg P/kg was with the mine spoil material. Barber

Table 19. Resin extractable P as a percent of total P at each value of R/S.

Sample	R/S							
	0.0	0.5	1.0	2.0	5.0	10.0	20.0	40.0
	%							
Plainfield								
low P	0.4	0.4	0.4	0.4	0.6	1.1	1.4	8.8
medium P	3.2	1.1	1.5	2.0	2.1	4.2	3.1	5.6
high P	2.7	0.7	1.2	1.4	2.3	2.4	3.6	4.6
Metea								
fertilizer P	3.9	3.7	5.8	7.6	9.2	13.0	13.8	8.3
sludge P	1.2	1.1	1.7	2.9	3.0	8.0	9.7	5.9
McBride								
low P	0.5	0.4	0.5	0.3	0.7	1.5	1.9	5.3
high P	3.6	0.9	1.2	1.6	3.3	7.2	9.2	9.5
Blount								
fertilizer P	na [#]	3.2	3.1	4.2	5.4	6.4	4.0	4.1
sludge P	na	1.3	1.2	1.6	2.3	3.3	4.0	3.8
Mine spoil								
sludge P	na	1.0	1.3	1.6	1.9	3.0	3.5	4.4
Howard								
manure P	na	2.0	2.0	2.4	2.7	4.1	5.4	7.6

[#]not applicable

(1979) determined that a corn-soybean-wheat-hay crop rotation removed as much as 22 kg P/ha annually over a 25 y period. This rate represents approximately 10 mg P/kg soil annually and means that the available P in these soils could supply the P for such a crop rotation for approximately 1 to 26 y. Despite the relatively low degree of availability, the high P samples could possibly supply P crop needs for long periods of time.

5.4 Conclusions

The greatest drawback to the proposed resin procedure are the large changes in supernatant pH that the resin can induce. Exceedingly low supernatant pH values may be a contributing factor in the decline in resin extractable P values that occurred with some samples. Despite these drawbacks the resin procedure produced the anticipated response in resin extractable P as R/S increased in some samples, which indicated that the P in these samples could respond to a large capacity sink. The proportion of total P available was quite low, however, with less than 14% of the total P being available as shown by this procedure. Additional verification of this with field or greenhouse experiments would seem warranted.

An additional benefit of this procedure and the reduction in supernatant pH values was additional evidence arguing against the existence of Ca phosphate solids in high pH samples. It is important to note this benefit in

the context of the experimentation presented here since future refinements of the resin technique would have to involve attempts to minimize pH changes, and this benefit would be lost. The results from this experiment and the experiment in Chapter 3 are suggestive of Al dominated P solids existing even under high pH conditions. A Ca phosphate solid may be thermodynamically favored under high pH conditions but the conversion of Al phosphates to Ca phosphates must occur at a slow rate.

Chapter VI

THE CHEMISTRY AND MINERALOGY OF PHOSPHORUS IN EXCESSIVELY FERTILIZED SOILS: SUMMARY AND CONCLUSIONS

6.1 Summary

The hypothesis presented in Chapter 2 stated, in essence, that large additions of P to soils would induce precipitation of secondary P solids. The sum of the research presented in this dissertation could be described as a number of approaches pursuant with the objectives corresponding to the hypothesis. The unique aspect of this research is that a number of approaches were taken, as opposed to a single approach described in most of the literature on this same topic.

The single approach that I have eluded to is the solubility equilibria approach. For the sake of comparison, this approach was also taken with the soils considered here with a traditional interpretation of the results presented. The experimental method involved the addition of water to the samples, incubation in a constant temperature (298°K) environment, and periodic sacrificing of samples. In consideration of information presented in the literature, the major conclusion from the equilibrium work is the implication of the existence of the amorphous

analog of variscite in the acid soils. This solid had not been shown to exist in similar soils prior to this work. Results for the high pH soils were largely consistent with similar research with similar soils reported in the literature in that data would fall in a region of "intermediate" solubility (more soluble than hydroxyapatite and less soluble than octacalcium phosphate) on a double function plot with little evidence for the existence of one solid. The exception to this was the Blount fertilizer P sample which had results consistent with the existence of octacalcium phosphate. A secondary conclusion from this experiment dealt with the length of time required for samples to reach a steady-state condition. Some samples had not reached a steady-state condition after 130 d, while times reported in the literature are generally 14 d or less.

The second approach to demonstrating that P solids existed and then characterizing them as much as possible was a direct approach. An attempt was made to concentrate the P in the samples by particle size fractionation. The total P concentration was generally highest in the clay sized fraction and this separate was further separated by density. Density gradients were constructed with varying proportions of ethanol and tetrabromoethane and sampled to give density separates of <2.2 , $2.2-2.5$, and >2.5 g/cm³. Total P concentrations were highest in the <2.2 g/cm³

density separate. A scanning transmission electron microscope was employed to collect energy dispersive x-ray spectra from numerous individual particles in the density separates. Regions of interests for the K-alpha x-ray energies from Al, Si, P, K, Ca, Mn and Fe were monitored.

The primary technique used in this direct approach was, in effect, an automated grain count with particles classified as P-rich or not. The primary conclusion being that P does exist as discrete P-rich particles within the soils studied and the abundances of such particles is positively associated with total P concentration.

Concentrating the P via density separations, which in itself was very successful, may not have been necessary to actually find the P-rich particles, but made the process much easier and provided additional useful information as well. Data on the elemental make-up of the P-rich particles revealed that each particle likely contained several cations in association with P and the predominant cation association was Al regardless of soil pH. Calcium phosphate represented, at best, a minor component of the P-rich particles within any sample.

The final experiment was an attempt to assess the availability of the P in these samples as a plant nutrient or as a pollutant. The samples were exposed to increasingly larger masses of an anion exchange resin at a constant soil-to-solution ratio. Increasing resin-to-soil

ratios indicated that some samples had a pool of P that was able to respond to a large capacity sink. Reductions in supernatant pH induced by the resin introduced a complicating factor, although this phenomenon provided additional evidence that the bulk of the P does not exist as Ca phosphate solids in the high pH samples.

6.2 Conclusions

The greatest contribution to the P literature from the research described in this dissertation is the opportunity to compare results from both indirect and direct approaches to the stated hypothesis. For low pH samples ($\text{pH} < 7.0$) the existence of an amorphous, primarily Al phosphate solid is supported by equilibrium experiments as well as by direct observation of P-rich particles. For high pH samples ($\text{pH} > 7.0$) the existence of Ca phosphate solids of undetermined solubility characteristics is suggested by equilibrium experiments but is not supported by direct observation of P-rich particles. Results from the direct method do not vary with soil pH. It can be suggested that Ca phosphates do, in fact, exist in the high pH samples but are not being detected by the direct method. However, results from the resin extraction experiment argue strongly against this possibility since reductions in supernatant pH did not produce the anticipated increases in resin extractable P had Ca phosphates been present.

A second important contribution to the P literature is with regard to the existence of P-rich particles. Relatively few studies have been able to show that such particles exist and they are very limited in scope. Prudent use of electron microscope automation has greatly expanded this knowledge base.

This research would advise against the use of solubility equilibria to study secondary P solids. No direct evidence was found for the existence of the "traditional" secondary P minerals (e.g. octacalcium phosphate, hydroxyapatite) or even simple Al or Ca phosphate solids. Furthermore, the solids that were found are uncharacterized at this time. These points illustrate that the most logical extension of this research is to further characterize the P-rich solids. A refinement of the P concentrating techniques to the point where analytical methods such as FTIR or a surface spectroscopic method could successfully be applied would seem warranted.

The agronomic justification for this research dealt with the economic advantage, if any, to building or maintaining high levels of soil P. Results from the resin extraction experiment indicated that less than 14% of the total P, or of the added P when comparing related samples, was available. This implies that the P-rich particles represent a relatively unavailable source of plant available P and the adage that "added soil P being as good

as money in the bank" is not likely to be true. Even at this relatively low degree of availability, some samples would likely meet crop P needs for as long as 26 y without further P additions.

Management recommendations for such extremely high P soils would have to be for little or no P to be added until soil P tests indicate P fertility slightly above sufficiency. The environmental ramifications from the proposed management recommendations would be favorable since reductions in P applications to agricultural soils would ultimately lead to reductions of P inputs to surface waters. In soils that currently have high total P concentrations and in which P additions have been stopped, inputs of P to surface waters would be associated with runoff events that generate significant erosional losses. Such soils are likely to be a source of "particulate-P" for long periods of time. The stability of the P-rich particles in a sedimentary environment is not known. Supernatant P concentrations seen in the equilibrium experiment would imply that algae, an efficient P user, would not be P limited in water in contact with the high P soils.

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APPENDIX

Table 20. Measured solution parameters for the Plainfield soils.

Parameter	Low P				time(d)	Medium P			
	42	105	118	124		42	105	118	124
pH	6.5	6.8	6.9	6.9		6.6	7.0	7.2	7.2
organic C (mg/L)	5.2	5.3	5.9	5.7		12.0	5.2	5.5	5.5
inorganic C [#]	3.14	3.25	3.29	3.40		3.06	3.07	3.03	3.21
Ca	3.56	3.36	3.48	3.45		3.48	3.38	3.36	3.37
Mg	3.54	3.44	3.53	3.44		3.48	3.41	3.38	3.39
K	3.48	4.63	4.54	4.58		3.82	3.82	3.80	3.83
Na	3.78	3.53	3.90	4.01		4.02	3.98	4.20	4.40
Fe	6.45	6.35	6.57	6.38		6.57	6.20	nd ^e	6.53
Al	nd	5.83	5.54	5.77		nd	5.65	5.54	5.95
PO ₄	5.47	4.92	5.47	4.68		4.43	4.43	4.44	4.44
SO ₄	4.26	4.38	4.38	4.33		4.54	4.35	4.34	4.35
Cl	3.49	3.63	4.31	4.26		nd	nd	nd	4.81
F	nd	nd	nd	nd		4.65	4.68	4.56	4.59

Table 20 (continued)

Parameter	High P time(d)			
	42	105	118	124
pH	6.5	5.6	6.4	6.4
organic C (mg/L)	18.7	19.8	18.2	25.2
inorganic C#	3.57	3.46	3.59	3.64
Ca	4.09	3.83	3.53	3.96
Mg	4.22	4.08	3.73	3.70
K	3.99	3.28	3.14	3.25
Na	4.18	3.66	4.21	4.21
Fe	6.14	5.60	5.84	5.26
Al	4.76	4.85	5.62	4.89
PO ₄	4.42	4.26	4.44	4.41
SO ₄	4.09	3.97	3.38	3.87
Cl	4.13	3.56	3.91	3.87
F	4.74	4.70	nd	4.63

#concentrations for inorganic C and all subsequent table entries are expressed as the negative logarithm of the molar concentration.

nd not detectable

Table 21. Measured solution parameters for the Metea soils.

Parameter	Fertilizer P				time(d)	Sludge P			
	42	105	118	124		42	105	118	124
pH	7.0	7.5	7.7	7.5		7.1	7.5	7.7	7.5
organic C (mg/L)	12.9	14.9	18.3	17.5		27.2	29.9	36.0	36.3
inorganic C [#]	2.77	2.66	2.66	2.75		2.64	2.57	2.56	2.67
Ca	2.98	2.94	2.93	2.97		2.64	2.64	2.60	2.62
Mg	3.39	3.38	3.41	3.41		3.71	3.71	3.72	3.70
K	4.14	4.08	4.05	4.09		3.95	4.01	3.97	4.01
Na	4.16	4.00	3.91	4.26		3.60	3.48	3.58	3.68
Fe	6.45	6.09	6.01	5.97		6.05	5.82	5.79	5.79
Al	5.65	5.33	5.49	5.24		5.06	5.06	5.31	5.01
PO ₄	4.58	4.51	4.47	4.47		4.59	4.58	4.43	4.56
SO ₄	3.74	3.64	3.59	3.59		3.12	3.11	3.10	3.11
Cl	nd ^e	nd	nd	5.00		4.26	3.73	4.06	4.07
F	4.46	4.48	4.39	4.41		4.49	4.54	4.48	4.49

[#]concentrations for inorganic C and all subsequent table entries are expressed as the negative logarithm of the molar concentration.

^enot detectable

Table 22. Measured solution parameters for the McBride soils.

Parameter	Low P				time(d)	High P			
	42	105	118	124		42	105	118	124
pH	6.6	6.8	6.7	6.7		6.5	5.9	5.9	5.7
organic C (mg/L)	44.2	50.8	56.0	54.4		13.2	13.2	15.3	15.9
inorganic C [#]	2.92	3.08	3.29	3.28		3.77	3.82	3.81	3.91
Ca	3.49	3.53	3.61	3.58		3.85	3.65	3.76	3.73
Mg	3.75	3.86	3.93	3.88		4.13	4.01	4.03	4.01
K	3.45	3.81	3.88	3.90		3.47	3.50	3.48	3.49
Na	4.19	3.61	4.06	4.28		4.22	3.93	4.01	4.36
Fe	5.85	5.39	5.56	5.54		5.47	5.75	6.05	5.78
Al	4.45	4.48	4.83	4.51		4.85	4.91	5.24	5.04
PO ₄	5.89	5.19	5.71	5.65		4.22	4.22	4.27	4.28
SO ₄	4.16	4.90	4.75	5.04		4.20	4.09	4.06	4.04
Cl	3.62	3.67	4.13	4.17		4.10	4.63	4.46	4.77
F	nd ^e	nd	nd	nd		4.60	4.71	4.58	4.65

[#] concentrations for inorganic C and all subsequent table entries are expressed as the negative logarithm of the molar concentration.

^e not detectable

Table 23. Measured solution parameters for the Blount soils.

Parameter	Fertilizer P				time(d)	Sludge P			
	42	105	118	124		42	105	118	124
pH	7.1	7.6	7.6	7.5		6.8	6.6	6.6	6.4
organic C (mg/L)	18.7	23.9	27.8	28.2		46.4	55.0	72.1	74.3
inorganic C [#]	2.55	2.56	2.64	2.66		3.06	3.39	3.47	3.53
Ca	3.00	2.99	2.97	2.98		3.21	3.15	3.15	3.16
Mg	3.15	3.19	3.11	3.17		3.32	3.30	3.30	3.27
K	3.68	3.69	3.71	3.72		3.59	3.61	3.59	3.61
Na	4.09	4.02	3.97	4.10		3.84	3.74	3.76	3.87
Fe	6.27	5.90	5.79	5.81		5.90	5.50	5.35	5.45
Al	5.14	5.02	5.20	4.37		4.70	4.59	4.92	4.52
PO ₄	3.96	3.96	3.95	3.91		3.86	3.72	3.71	3.75
SO ₄	3.66	3.54	3.52	3.50		3.25	3.20	3.19	3.20
Cl	4.86	4.67	4.67	4.44		4.71	4.15	4.36	4.26
F	4.31	4.30	4.27	4.29		4.36	4.40	4.35	4.38

[#]concentrations for inorganic C and all subsequent table entries are expressed as the negative logarithm of the molar concentration.

Table 24. Measured solution parameters for the mine spoil and Howard samples.

Parameter	Mine Spoil				time(d)	Howard			
	42	105	118	124		42	105	118	124
pH	6.8	6.1	6.0	5.9		6.9	7.4	7.6	7.4
organic C (mg/L)	78.1	104.3	118.7	125.5		38.9	52.8	62.3	66.8
inorganic C [#]	2.93	3.37	3.65	3.61		2.35	2.42	2.41	2.48
Ca	3.11	3.04	3.05	3.04		2.95	2.96	2.85	2.92
Mg	3.21	3.11	2.59	3.12		3.15	3.18	3.04	3.15
K	3.61	3.55	3.64	3.59		3.92	3.21	3.19	3.20
Na	3.69	3.61	3.56	3.66		3.99	3.82	4.01	4.06
Fe	5.79	5.48	5.18	5.42		5.97	5.75	5.60	5.60
Al	4.71	4.41	4.85	4.40		4.54	4.59	4.95	4.58
PO ₄	3.98	3.54	3.58	3.65		5.10	5.41	5.59	5.65
SO ₄	3.16	3.11	3.11	3.11		4.16	4.24	5.92	4.47
Cl	4.10	4.03	3.93	3.87		4.55	4.00	4.29	4.19
F	4.30	4.35	4.32	4.34		4.55	4.48	4.36	4.48

[#]concentrations for inorganic C and all subsequent table entries are expressed as the negative logarithm of the molar concentration.

Table 25. X-ray count data (counts/30-s) for P-rich particles.

Sample	Al (13)	Si (14)	P (15)	V (16)	Ca (20)	Mn (25)	Fe (26)
1 A #	314	538	57	0	31	64	519
2 A	0	0	154	0	500	70	23
3 A	0	14	106	0	257	12	16
1 C	346	65	59	0	115	20	120
1 C	646	963	70	25	94	24	475
1 C	105	173	74	15	12	86	264
1 C	159	87	103	36	30	14	126
1 C	728	103	107	49	194	41	259
1 C	470	1040	99	25	10	9	753
1 C	231	385	53	34	20	0	143
1 C	850	288	346	40	86	24	131
1 C	398	117	62	13	253	54	138
1 C	632	655	100	40	43	390	686
1 C	205	195	52	12	23	16	475
1 C	527	983	66	33	41	15	376
1 C	222	327	81	38	36	0	425
1 C	427	695	77	28	14	1	431
1 C	982	1546	52	72	5	10	293
1 C	894	992	168	59	9	512	4896
1 C	447	857	52	52	86	30	626
1 C	445	825	59	58	1	0	542
1 C	501	1160	70	16	20	6	419
1 C	548	1119	78	74	19	31	410
1 C	783	1468	83	94	65	0	1015
1 C	321	86	70	14	75	22	117
1 C	510	958	57	39	6	0	441
1 C	960	1086	52	64	31	32	768
1 C	362	256	51	0	119	46	366
1 C	620	1505	82	180	40	43	917
1 C	218	87	70	47	156	38	108
1 C	386	251	131	18	0	0	2701
1 C	657	1148	70	66	37	0	500
1 C	152	160	111	16	26	0	168
1 C	473	796	69	85	46	0	553
1 C	169	111	73	5	21	35	1341
1 C	668	1035	113	6	1	12	412
1 C	12	15	282	0	885	26	33
1 C	406	862	97	10	78	9	337
1 C	406	2332	61	67	0	6	260
1 C	140	167	50	16	9	166	371
1 C	196	0	263	24	24	0	42
1 C	132	66	61	9	74	0	47
1 C	812	461	137	109	191	14	219
1 C	535	978	61	25	2	0	712
1 C	678	1880	112	31	27	16	2754
1 C	373	584	124	20	23	14	451
1 C	309	130	71	10	72	30	171
1 C	311	362	166	42	53	0	419
1 C	274	77	71	0	26	0	956
1 C	716	1482	69	51	4	40	290
1 C	328	0	56	44	39	0	65
2 C	346	735	59	44	108	28	159
2 C	172	314	56	50	59	22	736

Table 25 (continued)

2 0	257	1403	53	19	19	14	310
2 0	744	1170	66	52	192	276	940
2 0	445	897	56	5	34	29	665
2 0	457	838	51	30	70	15	365
2 0	668	1377	53	35	58	0	474
2 0	742	1363	55	37	100	12	345
2 0	74	257	51	13	93	0	31
3 0	98	153	62	47	12	15	1
3 0	0	0	198	12	108	0	0
3 0	40	63	60	0	74	5	0
3 0	0	49	137	3	115	0	28
3 0	0	0	131	7	39	0	5
3 0	140	158	67	45	42	0	1138
3 0	84	224	57	51	52	0	67
3 0	505	959	78	79	53	174	765
3 0	166	328	69	0	255	182	353
3 0	170	296	59	61	68	21	580
3 0	154	348	106	77	222	0	8250
3 0	153	217	55	2	31	0	602
3 0	101	308	53	19	202	18	37
3 0	0	0	284	13	66	0	18
3 0	199	466	79	154	554	34	258
3 0	115	1092	63	18	56	0	97
3 0	0	0	79	5	57	0	0
3 0	212	310	52	31	82	14	2503
3 0	0	111	61	37	71	4	35
3 0	5	0	93	0	88	0	18
3 0	0	0	129	29	208	0	11
3 0	0	0	108	0	42	0	0
3 0	985	2017	57	36	119	0	1389
3 0	0	0	181	23	42	12	0
3 0	0	0	307	6	36	0	2
3 0	17	86	68	0	96	0	12
3 0	3	0	93	0	139	0	13
3 0	0	14	58	0	152	0	10
3 0	0	0	217	28	130	0	7
3 0	0	0	302	41	49	7	0
1 D	273	134	56	9	33	15	2214
1 D	267	686	90	0	107	0	8706
1 D	434	770	162	69	177	0	655
1 D	327	739	59	28	59	12	685
1 D	40	0	76	0	415	1	23
1 D	49	0	344	0	1053	0	290
1 D	76	346	128	14	0	0	68
1 D	341	5	141	11	56	0	242
1 D	220	207	71	14	95	117	2676
1 D	101	35	66	30	36	0	131
1 D	10	0	444	86	48	0	2043
1 D	199	332	76	51	101	0	374
1 D	155	166	57	19	33	0	956
1 E	0	50	69	7	37	0	104
1 E	41	0	71	2	38	24	187
1 E	61	25	150	0	41	56	699
1 E	184	130	135	71	25	30	799

Table 25 (continued)

1 E	104	127	37	34	75	7	122
1 E	143	0	145	0	155	20	132
1 E	152	203	155	44	115	0	159
1 E	141	500	416	4	365	2	569
1 E	161	193	56	11	41	1	203
1 E	17	7	77	31	217	0	2157
1 E	67	0	65	0	86	0	51
1 E	114	154	67	0	46	0	79
1 E	65	70	67	5	50	10	122
1 E	133	128	108	0	203	0	96
1 E	34	90	91	1	32	14	661
1 E	70	74	54	17	101	0	284
1 E	0	18	69	10	23	13	217
1 E	128	111	61	24	129	14	619
1 E	151	296	150	1	160	53	203
1 E	60	0	77	0	168	8	136
1 E	423	0	939	0	1194	0	827
1 E	218	236	82	32	143	0	219
1 E	102	79	91	5	29	0	413
1 E	70	32	72	27	108	0	153
1 E	126	150	68	0	116	0	60
1 E	20	0	104	12	130	4	136
1 E	50	23	106	34	75	16	278
1 E	67	67	106	0	66	60	484
1 E	65	39	78	0	69	26	98
1 E	90	0	92	0	89	0	48
1 E	83	26	77	24	82	28	242
1 E	113	0	120	14	105	9	32
1 E	14	0	107	0	16	1	675
1 E	113	0	128	17	128	6	57
1 E	122	44	215	13	187	0	252
1 E	379	1	200	0	39	0	164
2 E	131	266	112	0	156	14	301
2 E	50	25	125	1	122	50	165
2 E	59	55	77	0	155	11	128
2 E	140	40	95	8	147	0	158
2 E	46	0	291	0	102	0	1333
2 E	178	50	98	15	149	0	58
2 E	19	0	134	14	172	0	1827
2 E	92	116	54	16	92	1	183
2 E	101	0	151	0	130	87	148
2 E	221	570	106	87	202	22	427
2 E	165	42	293	9	204	121	214
2 E	175	121	93	0	287	17	124
2 E	46	87	110	41	120	3	227
2 E	151	253	52	44	18	1	245
2 E	56	0	312	0	187	13	1460
2 E	250	94	143	31	97	55	2074
2 E	123	45	214	50	382	54	238
2 E	312	124	286	64	339	0	334
2 E	178	182	80	3	36	0	633
2 E	389	459	129	53	192	0	589
2 E	188	57	316	0	392	35	438
1 F	391	30	242		48		2413
1 F	261		112		30		1275

Table 25 (continued)

1 F	373	471	63		74		512
1 F	211	5	128	0	105	19	39
3 F	136	713	67	176	94	21	99
3 F	0	0	674	0	38	0	44
3 F	365	257	279		30		233
1 G	687	178	131	0	37	0	1452
1 G	447	4	94	12	0	0	2349
1 G	394	68	147	0	71	18	1536
1 G	294	56	53	25	99	0	74
1 G	631	632	75	40	33	63	538
1 G	494	435	109	150	50	20	160
1 G	1297	662	72	70	55	61	263
1 G	356	0	104	27	274	67	38
1 G	487	6	63	21	19	249	372
1 G	1129	1128	102	212	60	20	1049
1 G	694	305	58	39	44	19	789
1 G	301	187	62	22	10	0	317
1 G	564	552	51	64	21	0	361
1 G	137	63	52	0	0	20	119
1 G	89	1392	1197	59	51	93	44
1 G	479	30	61	11	3	0	576
1 G	681	946	57	201	29	0	660
1 G	876	1069	62	81	18	7	490
2 G	494	415	54	92	13	0	339
2 G	232	0	63	11	29	0	528
2 G	268	124	84	40	16	4	542
2 G	611	499	63	50	0	24	426
2 G	197	101	64	0	0	0	865
2 G	439	77	128	39	4	11	2019
2 G	474	634	67	41	21	3	113
2 G	346	81	192	9	14	37	155
2 G	315	176	131	48	30	6	39
2 G	387	38	170	2	34	0	2857
2 G	567	693	80	21	46	176	519
2 G	447	773	51	38	18	19	477
2 G	422	295	68	10	8	55	299
2 G	236	157	55	92	10	0	1258
2 G	718	1134	77	89	26	17	797
3 G	330	770	72	33	69	2	977
3 G	386	758	60	0	63	10	404
3 G	0	105	89	5	502	119	14
3 G	102	148	50	13	51	98	343
3 G	149	315	51	22	93	0	193
3 G	371	231	103	34	516	0	161
3 G	232	46	58	11	73	230	491
3 G	62	189	58	8	179	50	2
3 G	531	728	245	115	192	0	529
3 G	75	56	51	26	21	25	498
1 H	23	0	97	16	99	22	132
2 H	301	121	110	16	90	0	0
3 H	0	0	659	0	2292	0	19
1 I	214	182	144	9	98	9	359
1 I	8	17	51	11	49	5	27

Table 25 (continued)

1 I	35	52	222		89		303
1 I	73	0	213	15	143	0	303
1 I	107	125	91	5	70	0	219
1 I	183	40	155	21	102	10	235
1 I	39	37	171		75		241
1 I	91	118	62		22		50
1 I	63	30	112		56		24
1 I	0	2	130	26	123	0	3178
1 I	104	0	360		114		458
1 I	505	1136	82	81	51	0	2131
1 I	46	9	135		30		52
1 I	41	9	250	0	155	0	1049
2 I	69	26	170	16	81	0	228
2 I	3503	5806	53	2325	139	0	425
2 I	430	633	83	10	15	0	405
2 I	516	1244	51	86	2	17	205
2 I	368	239	79	21	7	63	310
2 I	1036	4	167	35	32	0	236
2 I	42	41	69	0	18	8	131
2 I	733	0	368	75	34	0	412
2 I	1	0	157	0	71	9	19
3 I	20	0	170	15	116	8	0
3 I	1	0	157	0	71	9	19
3 I	412	768	89	123	94	3	344
1 K	408	69	217	31	34	0	66
1 K	236	378	50	68	93	0	907
1 K	360	706	88	55	53	118	907
1 K	142	139	55	28	45	0	244
1 K	56	0	141	0	46	6	44
1 K	120	97	78	2	57	1	381
1 K	189	178	53	26	0	0	452
1 K	69	0	78	24	16	27	687
1 K	91	175	0	93	20	5	11
2 K	247	167	79	24	223	146	1281
2 K	130	0	60	35	116	133	990
2 K	95	36	51	0	113	28	435
2 K	251	303	65	67	84	35	395
3 K	252	77	169	10	4	224	524
3 K	362	730	53	127	0	0	511
3 K	70	8	59	1	10	26	1382
3 K	66	135	174	12	562	73	26
3 K	224	91	80	0	7	256	551
3 K	137	138	131	34	79	2	192
3 K	234	0	107	12	13	0	970
3 K	301	527	66	40	18	29	325
3 K	365	82	101	32	26	0	3422
1 P	422	214	125	21	90	14	212
2 P	553	47	237	6	87	4	400

#Numbers indicate the density with 1,2, and 3 denoting 2.2, 2.2-2.5, and 2.5 g/cm³, respectively. Letters indicate the sample with A,C,D,E,F,G,H,I, and K denoting the Plainfield low P, Plainfield high P, Metea fertilizer P, Metea sludge P, McBride low P, McBride high P, Blount fertilizer P, Blount sludge P, and Howard manure P, respectively.

Table 26. Summary of x-ray diffraction data for the $<2.2 \text{ g/cm}^3$ density separate from the Metea sludge P sample.

X-RAY DIFFRACTION STEP SCAN DATA

biel.xrd metea 07:50:41 02-08-1989 , gmp
INITIAL $2\theta = 2^\circ$ $\Delta 2\theta = .1^\circ$ # DATA POINTS = 681 $\Delta T = 10 \text{ SECONDS}$ FINAL $2\theta = 70^\circ$

COUNTS	2θ	d(I)	COUNTS	2θ	d(I)	COUNTS	2θ	d(I)	COUNTS	2θ	d(I)	COUNTS	2θ	d(I)
153	2.000	44.13	39	7.000	12.62	35	12.000	7.37	33	17.000	5.21	55	22.000	4.04
150	2.100	42.03	39	7.100	12.44	37	12.100	7.31	35	17.100	5.18	64	22.100	4.02
132	2.200	40.12	40	7.200	12.27	40	12.200	7.25	38	17.200	5.15	63	22.200	4.00
131	2.300	38.38	42	7.300	12.10	42	12.300	7.19	38	17.300	5.12	67	22.300	3.98
110	2.400	36.78	39	7.400	11.94	45	12.400	7.13	38	17.400	5.09	66	22.400	3.97
112	2.500	35.31	37	7.500	11.78	33	12.500	7.08	37	17.500	5.06	66	22.500	3.95
104	2.600	33.95	36	7.600	11.62	29	12.600	7.02	40	17.600	5.03	61	22.600	3.93
93	2.700	32.69	37	7.700	11.47	29	12.700	6.96	38	17.700	5.01	68	22.700	3.91
85	2.800	31.53	37	7.800	11.32	29	12.800	6.91	39	17.800	4.98	63	22.800	3.90
79	2.900	30.44	38	7.900	11.18	30	12.900	6.86	40	17.900	4.95	66	22.900	3.88
78	3.000	29.42	36	8.000	11.04	30	13.000	6.80	39	18.000	4.92	66	23.000	3.86
68	3.100	28.48	38	8.100	10.91	30	13.100	6.75	43	18.100	4.90	61	23.100	3.85
67	3.200	27.59	37	8.200	10.77	31	13.200	6.70	43	18.200	4.87	66	23.200	3.83
63	3.300	26.75	34	8.300	10.64	31	13.300	6.65	39	18.300	4.84	64	23.300	3.81
62	3.400	25.96	36	8.400	10.52	31	13.400	6.60	43	18.400	4.82	69	23.400	3.80
57	3.500	25.22	28	8.500	10.39	29	13.500	6.55	42	18.500	4.79	65	23.500	3.78
60	3.600	24.52	40	8.600	10.27	29	13.600	6.51	45	18.600	4.77	62	23.600	3.77
53	3.700	23.86	38	8.700	10.16	31	13.700	6.46	46	18.700	4.74	68	23.700	3.75
55	3.800	23.23	38	8.800	10.04	29	13.800	6.41	42	18.800	4.72	65	23.800	3.74
53	3.900	22.64	35	8.900	9.93	27	13.900	6.37	45	18.900	4.69	64	23.900	3.72
55	4.000	22.07	36	9.000	9.82	32	14.000	6.32	45	19.000	4.67	64	24.000	3.70
49	4.100	21.53	33	9.100	9.71	28	14.100	6.28	46	19.100	4.64	64	24.100	3.69
52	4.200	21.02	33	9.200	9.60	31	14.200	6.23	53	19.200	4.62	61	24.200	3.67
45	4.300	20.53	31	9.300	9.50	28	14.300	6.19	53	19.300	4.59	64	24.300	3.66
47	4.400	20.07	34	9.400	9.40	30	14.400	6.15	58	19.400	4.57	66	24.400	3.64
48	4.500	19.62	35	9.500	9.30	29	14.500	6.10	73	19.500	4.55	68	24.500	3.63
47	4.600	19.19	31	9.600	9.21	30	14.600	6.06	104	19.600	4.53	66	24.600	3.62
46	4.700	18.78	33	9.700	9.11	30	14.700	6.02	112	19.700	4.50	69	24.700	3.60
49	4.800	18.39	27	9.800	9.02	31	14.800	5.98	103	19.800	4.48	76	24.800	3.59
48	4.900	18.02	33	9.900	8.93	30	14.900	5.94	87	19.900	4.46	78	24.900	3.57
45	5.000	17.66	29	10.000	8.84	32	15.000	5.90	86	20.000	4.44	84	25.000	3.56
45	5.100	17.31	30	10.100	8.75	30	15.100	5.86	74	20.100	4.41	82	25.100	3.54
46	5.200	16.98	31	10.200	8.66	29	15.200	5.82	73	20.200	4.39	87	25.200	3.53
43	5.300	16.66	33	10.300	8.58	31	15.300	5.79	75	20.300	4.37	82	25.300	3.52
40	5.400	16.35	30	10.400	8.50	34	15.400	5.75	77	20.400	4.35	79	25.400	3.50
45	5.500	16.05	30	10.500	8.42	30	15.500	5.71	76	20.500	4.33	81	25.500	3.49
45	5.600	15.77	34	10.600	8.34	31	15.600	5.68	89	20.600	4.31	77	25.600	3.48
46	5.700	15.49	33	10.700	8.26	31	15.700	5.64	140	20.700	4.29	73	25.700	3.46
47	5.800	15.22	34	10.800	8.18	27	15.800	5.60	131	20.800	4.27	54	25.800	3.45
47	5.900	14.97	30	10.900	8.11	29	15.900	5.57	82	20.900	4.25	71	25.900	3.44
46	6.000	14.72	30	11.000	8.04	33	16.000	5.53	70	21.000	4.23	71	26.000	3.42
59	6.100	14.48	30	11.100	7.96	29	16.100	5.50	72	21.100	4.21	82	26.100	3.41
51	6.200	14.24	32	11.200	7.89	30	16.200	5.47	68	21.200	4.19	103	26.200	3.40
50	6.300	14.02	31	11.300	7.82	31	16.300	5.43	71	21.300	4.17	130	26.300	3.39
47	6.400	13.80	33	11.400	7.76	34	16.400	5.40	56	21.400	4.15	253	26.400	3.37
49	6.500	13.59	30	11.500	7.69	32	16.500	5.37	66	21.500	4.13	618	26.500	3.36
46	6.600	13.38	32	11.600	7.62	32	16.600	5.34	70	21.600	4.11	343	26.600	3.35
43	6.700	13.18	32	11.700	7.56	34	16.700	5.30	57	21.700	4.09	117	26.700	3.34
44	6.800	12.99	32	11.800	7.49	36	16.800	5.27	70	21.800	4.07	94	26.800	3.32
39	6.900	12.80	29	11.900	7.43	32	16.900	5.24	73	21.900	4.05	91	26.900	3.31

Table 26 (continued)

X-RAY DIFFRACTION STEP SCAN DATA														
hrel.xrd mte 07:50:41 02-08-1989 .5cm														
INITIAL 2 θ = 2° 62 θ = 11° * DATA POINTS = 681 6T = 10 SECONDS FINAL 2 θ = 70°														
COUNTS	*2 θ	d(1)	COUNTS	*2 θ	d(1)	COUNTS	*2 θ	d(1)	COUNTS	*2 θ	d(1)	COUNTS	*2 θ	d(1)
89	27.000	3.30	59	32.000	2.79	81	37.000	2.43	69	42.000	2.15	49	47.000	1.93
74	27.100	3.29	56	32.100	2.79	80	37.100	2.42	68	42.100	2.14	51	47.100	1.93
78	27.200	3.28	60	32.200	2.78	79	37.200	2.41	74	42.200	2.14	46	47.200	1.92
36	27.300	3.26	57	32.300	2.77	79	37.300	2.41	96	42.300	2.13	52	47.300	1.92
93	27.400	3.25	54	32.400	2.76	75	37.400	2.40	78	42.400	2.13	52	47.400	1.92
79	27.500	3.24	52	32.500	2.75	81	37.500	2.40	64	42.500	2.13	52	47.500	1.91
82	27.600	3.23	51	32.600	2.74	88	37.600	2.39	58	42.600	2.12	47	47.600	1.91
80	27.700	3.22	53	32.700	2.74	83	37.700	2.38	56	42.700	2.12	43	47.700	1.90
84	27.800	3.21	54	32.800	2.73	74	37.800	2.38	54	42.800	2.11	48	47.800	1.90
72	27.900	3.20	56	32.900	2.72	71	37.900	2.37	56	42.900	2.11	52	47.900	1.90
65	28.000	3.18	59	33.000	2.71	75	38.000	2.37	56	43.000	2.10	51	48.000	1.89
63	28.100	3.17	56	33.100	2.70	72	38.100	2.36	51	43.100	2.10	46	48.100	1.89
62	28.200	3.16	59	33.200	2.70	86	38.200	2.35	51	43.200	2.09	49	48.200	1.89
59	28.300	3.15	53	33.300	2.69	85	38.300	2.35	52	43.300	2.09	47	48.300	1.88
59	28.400	3.14	52	33.400	2.68	83	38.400	2.34	53	43.400	2.08	50	48.400	1.88
60	28.500	3.13	53	33.500	2.67	76	38.500	2.34	57	43.500	2.08	49	48.500	1.88
59	28.600	3.12	52	33.600	2.66	73	38.600	2.33	54	43.600	2.07	48	48.600	1.87
62	28.700	3.11	56	33.700	2.66	62	38.700	2.32	53	43.700	2.07	47	48.700	1.87
63	28.800	3.10	60	33.800	2.65	56	38.800	2.32	54	43.800	2.07	46	48.800	1.86
59	28.900	3.09	62	33.900	2.64	58	38.900	2.31	54	43.900	2.06	54	48.900	1.86
59	29.000	3.08	63	34.000	2.63	58	39.000	2.31	53	44.000	2.06	50	49.000	1.86
61	29.100	3.07	66	34.100	2.63	64	39.100	2.30	57	44.100	2.05	48	49.100	1.85
67	29.200	3.06	76	34.200	2.62	73	39.200	2.30	53	44.200	2.05	49	49.200	1.85
75	29.300	3.05	87	34.300	2.61	102	39.300	2.29	58	44.300	2.04	44	49.300	1.85
66	29.400	3.04	102	34.400	2.60	85	39.400	2.28	57	44.400	2.04	48	49.400	1.84
66	29.500	3.03	103	34.500	2.60	67	39.500	2.28	69	44.500	2.03	52	49.500	1.84
68	29.600	3.02	116	34.600	2.59	59	39.600	2.27	64	44.600	2.03	49	49.600	1.84
75	29.700	3.01	123	34.700	2.58	63	39.700	2.27	63	44.700	2.03	53	49.700	1.83
70	29.800	3.00	127	34.800	2.58	61	39.800	2.26	63	44.800	2.02	66	49.800	1.83
65	29.900	2.99	119	34.900	2.57	67	39.900	2.26	64	44.900	2.02	94	49.900	1.83
62	30.000	2.98	112	35.000	2.56	68	40.000	2.25	65	45.000	2.01	141	50.000	1.82
64	30.100	2.97	93	35.100	2.55	77	40.100	2.25	69	45.100	2.01	99	50.100	1.82
59	30.200	2.96	98	35.200	2.55	77	40.200	2.24	66	45.200	2.00	66	50.200	1.82
61	30.300	2.95	87	35.300	2.54	69	40.300	2.24	66	45.300	2.00	53	50.300	1.81
64	30.400	2.94	96	35.400	2.53	62	40.400	2.23	65	45.400	2.00	55	50.400	1.81
61	30.500	2.93	94	35.500	2.53	62	40.500	2.23	63	45.500	1.99	57	50.500	1.81
67	30.600	2.92	90	35.600	2.52	63	40.600	2.22	82	45.600	1.99	56	50.600	1.80
71	30.700	2.91	85	35.700	2.51	62	40.700	2.21	77	45.700	1.98	57	50.700	1.80
72	30.800	2.90	84	35.800	2.51	66	40.800	2.21	70	45.800	1.98	54	50.800	1.80
60	30.900	2.89	87	35.900	2.50	64	40.900	2.20	62	45.900	1.98	53	50.900	1.79
62	31.000	2.88	82	36.000	2.49	61	41.000	2.20	57	46.000	1.97	52	51.000	1.79
68	31.100	2.87	78	36.100	2.49	53	41.100	2.19	53	46.100	1.97	47	51.100	1.79
66	31.200	2.86	82	36.200	2.48	63	41.200	2.19	50	46.200	1.96	47	51.200	1.78
63	31.300	2.86	92	36.300	2.47	62	41.300	2.18	54	46.300	1.96	46	51.300	1.78
62	31.400	2.85	122	36.400	2.47	59	41.400	2.18	56	46.400	1.96	45	51.400	1.78
58	31.500	2.84	107	36.500	2.46	63	41.500	2.17	51	46.500	1.95	48	51.500	1.77
59	31.600	2.83	94	36.600	2.45	62	41.600	2.17	49	46.600	1.95	47	51.600	1.77
60	31.700	2.82	91	36.700	2.45	63	41.700	2.16	51	46.700	1.94	43	51.700	1.77
64	31.800	2.81	82	36.800	2.44	63	41.800	2.16	52	46.800	1.94	46	51.800	1.76
62	31.900	2.80	75	36.900	2.43	66	41.900	2.15	49	46.900	1.94	46	51.900	1.76

Table 26 (continued)

X-RAY DIFFRACTION STEP SCAN DATA

b:el.xrd mtea 07:50:41 02-08-1989 .jmb

INITIAL 2 θ = 2° 2 θ = .1° # DATA POINTS = 681 ST = 10 SECONDS FINAL 2 θ = 70°

COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)
44	52.000	1.76	58	57.000	1.61	84	62.000	1.50	51	67.000	1.40	0	72.000	1.31
47	52.100	1.75	56	57.100	1.61	78	62.100	1.49	48	67.100	1.39	0	72.100	1.31
44	52.200	1.75	54	57.200	1.61	72	62.200	1.49	53	67.200	1.39	0	72.200	1.31
51	52.300	1.75	56	57.300	1.61	69	62.300	1.49	52	67.300	1.39	0	72.300	1.31
50	52.400	1.74	52	57.400	1.60	63	62.400	1.49	56	67.400	1.39	0	72.400	1.30
48	52.500	1.74	56	57.500	1.60	68	62.500	1.48	73	67.500	1.39	0	72.500	1.30
50	52.600	1.74	56	57.600	1.60	59	62.600	1.48	91	67.600	1.38	0	72.600	1.30
48	52.700	1.74	52	57.700	1.60	60	62.700	1.48	75	67.700	1.38	0	72.700	1.30
53	52.800	1.73	60	57.800	1.59	60	62.800	1.48	77	67.800	1.38	0	72.800	1.30
52	52.900	1.73	54	57.900	1.59	56	62.900	1.48	87	67.900	1.38	0	72.900	1.30
56	53.000	1.73	51	58.000	1.59	53	63.000	1.47	110	68.000	1.38	0	73.000	1.29
57	53.100	1.72	52	58.100	1.59	54	63.100	1.47	96	68.100	1.38	0	73.100	1.29
56	53.200	1.72	55	58.200	1.58	54	63.200	1.47	94	68.200	1.37	0	73.200	1.29
58	53.300	1.72	50	58.300	1.58	51	63.300	1.47	70	68.300	1.37	0	73.300	1.29
63	53.400	1.71	55	58.400	1.58	56	63.400	1.47	59	68.400	1.37	0	73.400	1.29
61	53.500	1.71	52	58.500	1.58	53	63.500	1.46	48	68.500	1.37	0	73.500	1.29
63	53.600	1.71	54	58.600	1.57	53	63.600	1.46	48	68.600	1.37	0	73.600	1.29
73	53.700	1.71	54	58.700	1.57	62	63.700	1.46	52	68.700	1.37	0	73.700	1.28
69	53.800	1.70	58	58.800	1.57	68	63.800	1.46	56	68.800	1.36	0	73.800	1.28
70	53.900	1.70	54	58.900	1.57	69	63.900	1.46	47	68.900	1.36	0	73.900	1.28
69	54.000	1.70	56	59.000	1.56	62	64.000	1.45	52	69.000	1.36	0	74.000	1.28
74	54.100	1.69	60	59.100	1.56	58	64.100	1.45	51	69.100	1.36	0	74.100	1.28
70	54.200	1.69	56	59.200	1.56	53	64.200	1.45	48	69.200	1.36	0	74.200	1.28
72	54.300	1.69	61	59.300	1.56	50	64.300	1.45	51	69.300	1.35	0	74.300	1.28
66	54.400	1.69	61	59.400	1.55	49	64.400	1.45	47	69.400	1.35	0	74.400	1.27
68	54.500	1.68	68	59.500	1.55	53	64.500	1.44	48	69.500	1.35	0	74.500	1.27
75	54.600	1.68	74	59.600	1.55	53	64.600	1.44	45	69.600	1.35	0	74.600	1.27
93	54.700	1.68	94	59.700	1.55	53	64.700	1.44	45	69.700	1.35	0	74.700	1.27
86	54.800	1.67	124	59.800	1.55	52	64.800	1.44	51	69.800	1.35	0	74.800	1.27
82	54.900	1.67	90	59.900	1.54	53	64.900	1.44	49	69.900	1.34	0	74.900	1.27
81	55.000	1.67	92	60.000	1.54	54	65.000	1.43	44	70.000	1.34	0	75.000	1.27
82	55.100	1.67	72	60.100	1.54	54	65.100	1.43	0	70.100	1.34	0	75.100	1.26
85	55.200	1.66	67	60.200	1.54	50	65.200	1.43	0	70.200	1.34	0	75.200	1.26
73	55.300	1.66	71	60.300	1.53	53	65.300	1.43	0	70.300	1.34	0	75.300	1.26
72	55.400	1.66	62	60.400	1.53	51	65.400	1.43	0	70.400	1.34	0	75.400	1.26
73	55.500	1.65	65	60.500	1.53	51	65.500	1.42	0	70.500	1.33	0	75.500	1.26
69	55.600	1.65	60	60.600	1.53	52	65.600	1.42	0	70.600	1.33	0	75.600	1.26
71	55.700	1.65	57	60.700	1.52	50	65.700	1.42	0	70.700	1.33	0	75.700	1.26
67	55.800	1.65	64	60.800	1.52	52	65.800	1.42	0	70.800	1.33	0	75.800	1.25
66	55.900	1.64	58	60.900	1.52	43	65.900	1.42	0	70.900	1.33	0	75.900	1.25
66	56.000	1.64	63	61.000	1.52	50	66.000	1.41	0	71.000	1.33	0	76.000	1.25
60	56.100	1.64	67	61.100	1.52	49	66.100	1.41	0	71.100	1.32	0	76.100	1.25
64	56.200	1.64	71	61.200	1.51	47	66.200	1.41	0	71.200	1.32	0	76.200	1.25
60	56.300	1.63	83	61.300	1.51	51	66.300	1.41	0	71.300	1.32	0	76.300	1.25
60	56.400	1.63	95	61.400	1.51	49	66.400	1.41	0	71.400	1.32	0	76.400	1.25
63	56.500	1.63	107	61.500	1.51	48	66.500	1.40	0	71.500	1.32	0	76.500	1.24
57	56.600	1.62	106	61.600	1.50	47	66.600	1.40	0	71.600	1.32	0	76.600	1.24
57	56.700	1.62	108	61.700	1.50	44	66.700	1.40	0	71.700	1.32	0	76.700	1.24
58	56.800	1.62	102	61.800	1.50	49	66.800	1.40	0	71.800	1.31	0	76.800	1.24
57	56.900	1.62	91	61.900	1.50	49	66.900	1.40	0	71.900	1.31	0	76.900	1.24

Table 27. Summary of x-ray diffraction data for the 2.2-2.5 g/cm³ density separate from the Metea sludge P sample.

X-RAY DIFFRACTION STEP SCAN DATA

b:\#2.xrd blount 06:04:00 02-09-1999 , gap
INITIAL 2 θ = 5° 2 θ = .1° # DATA POINTS = 601 ST = 10 SECONDS FINAL 2 θ = 65°

COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)
36	5.000	17.55	22	10.000	9.94	24	15.000	5.90	56	20.000	4.44	54	25.000	3.53
34	5.100	17.31	24	10.100	8.75	21	15.100	5.86	51	20.100	4.41	51	25.100	3.54
40	5.200	16.98	22	10.200	9.66	22	15.200	5.82	53	20.200	4.39	70	25.200	3.53
41	5.300	16.66	23	10.300	9.53	19	15.300	5.79	52	20.300	4.37	74	25.300	3.52
37	5.400	16.35	24	10.400	9.50	19	15.400	5.75	55	20.400	4.35	91	25.400	3.50
35	5.500	16.05	22	10.500	9.42	20	15.500	5.71	79	20.500	4.33	80	25.500	3.49
36	5.600	15.77	22	10.600	9.34	20	15.600	5.68	123	20.600	4.31	90	25.600	3.48
35	5.700	15.49	25	10.700	9.26	18	15.700	5.64	294	20.700	4.29	71	25.700	3.46
36	5.800	15.22	24	10.800	9.18	20	15.800	5.60	355	20.800	4.27	52	25.800	3.45
34	5.900	14.97	24	10.900	9.11	17	15.900	5.57	114	20.900	4.25	58	25.900	3.44
35	6.000	14.72	24	11.000	9.04	20	16.000	5.53	67	21.000	4.23	63	26.000	3.42
36	6.100	14.48	24	11.100	7.96	17	16.100	5.50	53	21.100	4.21	87	26.100	3.41
40	6.200	14.24	20	11.200	7.89	20	16.200	5.47	51	21.200	4.19	139	26.200	3.40
35	6.300	14.02	21	11.300	7.82	18	16.300	5.43	49	21.300	4.17	245	26.300	3.39
31	6.400	13.80	25	11.400	7.76	22	16.400	5.40	51	21.400	4.15	652	26.400	3.37
34	6.500	13.59	21	11.500	7.69	20	16.500	5.37	51	21.500	4.13	1960	26.500	3.36
33	6.600	13.39	22	11.600	7.62	20	16.600	5.34	47	21.600	4.11	1307	26.600	3.35
33	6.700	13.19	22	11.700	7.56	19	16.700	5.30	47	21.700	4.09	278	26.700	3.34
31	6.800	12.99	21	11.800	7.49	23	16.800	5.27	55	21.800	4.07	154	26.800	3.32
32	6.900	12.80	24	11.900	7.43	20	16.900	5.24	76	21.900	4.05	125	26.900	3.31
30	7.000	12.62	21	12.000	7.37	22	17.000	5.21	50	22.000	4.04	123	27.000	3.30
31	7.100	12.44	24	12.100	7.31	22	17.100	5.18	44	22.100	4.02	96	27.100	3.29
35	7.200	12.27	34	12.200	7.25	20	17.200	5.15	42	22.200	4.00	97	27.200	3.29
29	7.300	12.10	37	12.300	7.19	22	17.300	5.12	51	22.300	3.98	127	27.300	3.26
31	7.400	11.94	29	12.400	7.13	22	17.400	5.09	51	22.400	3.97	136	27.400	3.25
30	7.500	11.78	24	12.500	7.08	25	17.500	5.06	47	22.500	3.95	120	27.500	3.24
30	7.600	11.62	22	12.600	7.02	27	17.600	5.03	46	22.600	3.93	121	27.600	3.23
31	7.700	11.47	20	12.700	6.96	29	17.700	5.01	51	22.700	3.91	110	27.700	3.22
31	7.800	11.32	19	12.800	6.91	25	17.800	4.98	53	22.800	3.90	127	27.800	3.21
30	7.900	11.18	21	12.900	6.86	22	17.900	4.95	54	22.900	3.88	99	27.900	3.20
29	8.000	11.04	19	13.000	6.80	24	18.000	4.92	51	23.000	3.86	67	28.000	3.19
29	8.100	10.91	22	13.100	6.75	22	18.100	4.90	48	23.100	3.85	55	28.100	3.17
22	8.200	10.77	21	13.200	6.70	21	18.200	4.87	52	23.200	3.83	46	28.200	3.16
29	8.300	10.64	21	13.300	6.65	23	18.300	4.84	49	23.300	3.81	41	28.300	3.15
26	8.400	10.52	21	13.400	6.60	21	18.400	4.82	94	23.400	3.80	42	28.400	3.14
22	8.500	10.39	25	13.500	6.55	22	18.500	4.79	92	23.500	3.78	78	28.500	3.13
29	8.600	10.27	25	13.600	6.51	22	18.600	4.77	50	23.600	3.77	77	28.600	3.12
40	8.700	10.16	27	13.700	6.46	25	18.700	4.74	53	23.700	3.75	74	28.700	3.11
29	8.800	10.04	22	13.800	6.41	24	18.800	4.72	47	23.800	3.74	76	28.800	3.10
27	8.900	9.93	19	13.900	6.37	25	18.900	4.69	50	23.900	3.72	72	28.900	3.09
25	9.000	9.82	19	14.000	6.32	25	19.000	4.67	48	24.000	3.70	75	29.000	3.08
25	9.100	9.71	22	14.100	6.28	21	19.100	4.64	55	24.100	3.69	73	29.100	3.07
25	9.200	9.60	20	14.200	6.23	27	19.200	4.62	52	24.200	3.67	74	29.200	3.06
22	9.300	9.50	17	14.300	6.19	27	19.300	4.59	45	24.300	3.66	40	29.300	3.05
26	9.400	9.40	20	14.400	6.15	41	19.400	4.57	59	24.400	3.64	46	29.400	3.04
22	9.500	9.30	20	14.500	6.10	55	19.500	4.55	51	24.500	3.63	49	29.500	3.03
24	9.600	9.21	20	14.600	6.06	32	19.600	4.53	49	24.600	3.62	48	29.600	3.02
24	9.700	9.11	19	14.700	6.02	104	19.700	4.50	74	24.700	3.60	91	29.700	3.01
22	9.800	9.02	23	14.800	5.98	100	19.800	4.48	57	24.800	3.59	31	29.800	3.00
22	9.900	8.93	22	14.900	5.94	59	19.900	4.46	57	24.900	3.57	52	29.900	2.99

Table 27 (continued)

X-RAY DIFFRACTION STEP SCAN DATA

b:2,ard blount 04:04:00 02-09-1999 .380

INITIAL 2 θ = 5 $^{\circ}$ 2 θ = .1 $^{\circ}$ # DATA POINTS = 601 IT = 10 SECONDS FINAL 2 θ = 45 $^{\circ}$

COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)
54	30.000	2.98	112	35.000	2.56	68	40.000	2.25	49	45.000	2.01	403	50.000	1.92
52	30.100	2.97	95	35.100	2.55	103	40.100	2.25	55	45.100	2.01	239	50.100	1.92
47	30.200	2.96	76	35.200	2.55	115	40.200	2.24	62	45.200	2.00	125	50.200	1.92
50	30.300	2.95	64	35.300	2.54	77	40.300	2.24	58	45.300	2.00	61	50.300	1.91
54	30.400	2.94	63	35.400	2.53	45	40.400	2.23	59	45.400	2.00	60	50.400	1.91
52	30.500	2.93	65	35.500	2.53	41	40.500	2.23	71	45.500	1.99	74	50.500	1.91
57	30.600	2.92	61	35.600	2.52	39	40.600	2.22	115	45.600	1.99	66	50.600	1.90
65	30.700	2.91	56	35.700	2.51	44	40.700	2.21	126	45.700	1.98	61	50.700	1.90
53	30.800	2.90	56	35.800	2.51	45	40.800	2.21	88	45.800	1.98	52	50.800	1.90
47	30.900	2.89	52	35.900	2.50	46	40.900	2.20	59	45.900	1.98	46	50.900	1.79
44	31.000	2.88	58	36.000	2.49	47	41.000	2.20	46	46.000	1.97	45	51.000	1.79
46	31.100	2.87	61	36.100	2.49	43	41.100	2.19	39	46.100	1.97	39	51.100	1.79
49	31.200	2.86	75	36.200	2.48	46	41.200	2.19	39	46.200	1.96	35	51.200	1.78
45	31.300	2.86	119	36.300	2.47	44	41.300	2.18	39	46.300	1.96	30	51.300	1.78
38	31.400	2.85	223	36.400	2.47	49	41.400	2.18	36	46.400	1.95	30	51.400	1.79
33	31.500	2.84	172	36.500	2.46	58	41.500	2.17	35	46.500	1.95	29	51.500	1.77
33	31.600	2.83	93	36.600	2.45	50	41.600	2.17	38	46.600	1.95	25	51.600	1.77
33	31.700	2.82	69	36.700	2.45	58	41.700	2.16	37	46.700	1.94	29	51.700	1.77
40	31.900	2.81	59	36.800	2.44	53	41.900	2.16	40	46.800	1.94	29	51.900	1.76
42	31.900	2.80	59	36.900	2.43	52	41.900	2.15	37	46.900	1.94	20	51.900	1.76
40	32.000	2.79	55	37.000	2.43	57	42.000	2.15	39	47.000	1.93	33	52.000	1.76
41	32.100	2.79	51	37.100	2.42	67	42.100	2.14	37	47.100	1.93	34	52.100	1.75
49	32.200	2.78	56	37.200	2.41	108	42.200	2.14	34	47.200	1.92	33	52.200	1.75
42	32.300	2.77	59	37.300	2.41	189	42.300	2.13	33	47.300	1.92	36	52.300	1.75
33	32.400	2.76	69	37.400	2.40	143	42.400	2.13	33	47.400	1.92	38	52.400	1.74
29	32.500	2.75	73	37.500	2.40	81	42.500	2.13	32	47.500	1.91	36	52.500	1.74
31	32.600	2.74	70	37.600	2.39	47	42.600	2.12	35	47.600	1.91	41	52.600	1.74
27	32.700	2.74	67	37.700	2.38	39	42.700	2.12	35	47.700	1.90	39	52.700	1.74
27	32.800	2.73	55	37.800	2.38	38	42.800	2.11	36	47.800	1.90	35	52.800	1.73
30	32.900	2.72	49	37.900	2.37	34	42.900	2.11	38	47.900	1.90	40	52.900	1.73
30	33.000	2.71	46	38.000	2.37	34	43.000	2.10	39	48.000	1.89	37	53.000	1.72
26	33.100	2.70	43	38.100	2.36	37	43.100	2.10	36	48.100	1.89	35	53.100	1.72
27	33.200	2.70	48	38.200	2.35	33	43.200	2.09	39	48.200	1.89	38	53.200	1.72
31	33.300	2.69	48	38.300	2.35	36	43.300	2.09	31	48.300	1.88	39	53.300	1.72
26	33.400	2.68	45	38.400	2.34	38	43.400	2.08	32	48.400	1.88	42	53.400	1.71
27	33.500	2.67	49	38.500	2.34	36	43.500	2.08	32	48.500	1.88	43	53.500	1.71
30	33.600	2.66	46	38.600	2.33	35	43.600	2.07	33	48.600	1.87	42	53.600	1.71
29	33.700	2.66	47	38.700	2.32	31	43.700	2.07	35	48.700	1.87	40	53.700	1.71
40	33.800	2.65	42	38.800	2.32	39	43.800	2.07	32	48.800	1.86	49	53.800	1.70
36	33.900	2.64	43	38.900	2.31	40	43.900	2.06	38	48.900	1.86	47	53.900	1.70
39	34.000	2.63	47	39.000	2.31	40	44.000	2.06	43	49.000	1.86	49	54.000	1.70
52	34.100	2.63	56	39.100	2.30	34	44.100	2.05	40	49.100	1.85	54	54.100	1.69
63	34.200	2.62	39	39.200	2.30	32	44.200	2.05	40	49.200	1.85	55	54.200	1.69
90	34.300	2.61	197	39.300	2.29	32	44.300	2.04	39	49.300	1.85	59	54.300	1.69
99	34.400	2.60	164	39.400	2.28	34	44.400	2.04	39	49.400	1.84	59	54.400	1.69
109	34.500	2.60	79	39.500	2.29	33	44.500	2.03	42	49.500	1.84	62	54.500	1.68
119	34.600	2.59	48	39.600	2.27	37	44.600	2.03	48	49.600	1.84	74	54.600	1.68
129	34.700	2.58	47	39.700	2.27	42	44.700	2.03	55	49.700	1.83	151	54.700	1.68
144	34.800	2.58	52	39.800	2.26	46	44.800	2.02	98	49.800	1.83	125	54.800	1.67
129	34.900	2.57	55	39.900	2.25	49	44.900	2.02	206	49.900	1.83	112	54.900	1.67

Table 27 (continued)

X-RAY DIFFRACTION STEP SCAN DATA

5:02.770 51count 09:04:00 02-09-1989 . 290

INITIAL 2 θ = 5° 2 θ = 1.1° # DATA POINTS = 501 IT = 10 SECONDS FINAL 2 θ = 45°

COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)
80	55.000	1.67	161	60.000	1.54	44	65.000	1.43	0	70.000	1.34	0	75.000	1.27
90	55.100	1.67	82	60.100	1.54	0	65.100	1.43	0	70.100	1.34	0	75.100	1.26
101	55.200	1.66	63	60.200	1.54	0	65.200	1.43	0	70.200	1.34	0	75.200	1.26
85	55.300	1.66	56	60.300	1.53	0	65.300	1.43	0	70.300	1.34	0	75.300	1.26
73	55.400	1.66	52	60.400	1.53	0	65.400	1.43	0	70.400	1.34	0	75.400	1.26
63	55.500	1.65	57	60.500	1.53	0	65.500	1.42	0	70.500	1.33	0	75.500	1.26
69	55.600	1.65	53	60.600	1.53	0	65.600	1.42	0	70.600	1.33	0	75.600	1.26
65	55.700	1.65	55	60.700	1.52	0	65.700	1.42	0	70.700	1.33	0	75.700	1.26
59	55.800	1.65	51	60.800	1.52	0	65.800	1.42	0	70.800	1.33	0	75.800	1.25
51	55.900	1.64	56	60.900	1.52	0	65.900	1.42	0	70.900	1.33	0	75.900	1.25
52	56.000	1.64	59	61.000	1.52	0	66.000	1.41	0	71.000	1.33	0	76.000	1.25
55	56.100	1.64	59	61.100	1.52	0	66.100	1.41	0	71.100	1.32	0	76.100	1.25
52	56.200	1.64	65	61.200	1.51	0	66.200	1.41	0	71.200	1.32	0	76.200	1.25
51	56.300	1.63	79	61.300	1.51	0	66.300	1.41	0	71.300	1.32	0	76.300	1.25
53	56.400	1.63	72	61.400	1.51	0	66.400	1.41	0	71.400	1.32	0	76.400	1.25
50	56.500	1.63	96	61.500	1.51	0	66.500	1.40	0	71.500	1.32	0	76.500	1.24
47	56.600	1.62	107	61.600	1.50	0	66.600	1.40	0	71.600	1.32	0	76.600	1.24
49	56.700	1.62	96	61.700	1.50	0	66.700	1.40	0	71.700	1.32	0	76.700	1.24
47	56.800	1.62	95	61.800	1.50	0	66.800	1.40	0	71.800	1.31	0	76.800	1.24
45	56.900	1.62	26	61.900	1.50	0	66.900	1.40	0	71.900	1.31	0	76.900	1.24
45	57.000	1.61	48	62.000	1.50	0	67.000	1.40	0	72.000	1.31	0	77.000	1.24
48	57.100	1.61	53	62.100	1.49	0	67.100	1.39	0	72.100	1.31	0	77.100	1.24
48	57.200	1.61	50	62.200	1.49	0	67.200	1.39	0	72.200	1.31	0	77.200	1.23
45	57.300	1.61	58	62.300	1.49	0	67.300	1.39	0	72.300	1.31	0	77.300	1.23
43	57.400	1.60	56	62.400	1.49	0	67.400	1.39	0	72.400	1.30	0	77.400	1.23
42	57.500	1.60	52	62.500	1.48	0	67.500	1.39	0	72.500	1.30	0	77.500	1.23
45	57.600	1.60	48	62.600	1.48	0	67.600	1.39	0	72.600	1.30	0	77.600	1.23
40	57.700	1.60	44	62.700	1.48	0	67.700	1.39	0	72.700	1.30	0	77.700	1.23
39	57.800	1.59	41	62.800	1.48	0	67.800	1.38	0	72.800	1.30	0	77.800	1.23
43	57.900	1.59	40	62.900	1.48	0	67.900	1.39	0	72.900	1.30	0	77.900	1.23
36	58.000	1.59	40	63.000	1.47	0	68.000	1.38	0	73.000	1.29	0	78.000	1.22
35	58.100	1.59	40	63.100	1.47	0	68.100	1.38	0	73.100	1.29	0	78.100	1.22
39	58.200	1.59	42	63.200	1.47	0	68.200	1.37	0	73.200	1.29	0	78.200	1.22
37	58.300	1.58	39	63.300	1.47	0	68.300	1.37	0	73.300	1.29	0	78.300	1.22
42	58.400	1.59	39	63.400	1.47	0	68.400	1.37	0	73.400	1.29	0	78.400	1.22
48	58.500	1.59	49	63.500	1.46	0	68.500	1.37	0	73.500	1.29	0	78.500	1.22
43	58.600	1.57	52	63.600	1.46	0	68.600	1.37	0	73.600	1.29	0	78.600	1.22
41	58.700	1.57	50	63.700	1.46	0	68.700	1.37	0	73.700	1.29	0	78.700	1.21
44	58.800	1.57	30	63.800	1.46	0	68.800	1.36	0	73.800	1.29	0	78.800	1.21
44	58.900	1.57	27	63.900	1.46	0	68.900	1.36	0	73.900	1.29	0	78.900	1.21
42	59.000	1.56	70	64.000	1.45	0	69.000	1.36	0	74.000	1.29	0	79.000	1.21
46	59.100	1.56	67	64.100	1.45	0	69.100	1.36	0	74.100	1.29	0	79.100	1.21
48	59.200	1.56	48	64.200	1.45	0	69.200	1.36	0	74.200	1.29	0	79.200	1.21
46	59.300	1.56	42	64.300	1.45	0	69.300	1.36	0	74.300	1.29	0	79.300	1.21
52	59.400	1.55	39	64.400	1.45	0	69.400	1.35	0	74.400	1.27	0	79.400	1.21
63	59.500	1.55	45	64.500	1.44	0	69.500	1.35	0	74.500	1.27	0	79.500	1.20
95	59.600	1.55	45	64.600	1.44	0	69.600	1.35	0	74.600	1.27	0	79.600	1.20
174	59.700	1.55	42	64.700	1.44	0	69.700	1.35	0	74.700	1.27	0	79.700	1.20
200	59.800	1.55	46	64.800	1.44	0	69.800	1.35	0	74.800	1.27	0	79.800	1.20
195	59.900	1.54	48	64.900	1.44	0	69.900	1.34	0	74.900	1.27	0	79.900	1.20

Table 28. Summary of x-ray diffraction data from the sand sized separate from the Blount fertilizer P sample.

X-RAY DIFFRACTION STEP SCAN DATA

BISANI.XRD SANI 07143151 01-06-1989 , GMP
INITIAL 2 θ = 10° 420 = .1° 9 DATA POINTS = 551 17 = 40 SECONDS FINAL 2 θ = 63°

COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)
74	10.000	8.84	80	15.000	5.90	111	20.000	4.44	116	25.000	3.56	170	30.000	2.98
73	10.100	8.75	70	15.100	5.86	105	20.100	4.41	115	25.100	3.54	189	30.100	2.97
73	10.200	8.66	68	15.200	5.82	102	20.200	4.39	131	25.200	3.53	187	30.200	2.96
74	10.300	8.58	69	15.300	5.79	108	20.300	4.37	141	25.300	3.52	176	30.300	2.95
77	10.400	8.50	68	15.400	5.75	130	20.400	4.35	176	25.400	3.50	201	30.400	2.94
81	10.500	8.42	68	15.500	5.71	166	20.500	4.33	209	25.500	3.49	165	30.500	2.93
70	10.600	8.34	63	15.600	5.68	273	20.600	4.31	249	25.600	3.48	170	30.600	2.92
71	10.700	8.26	70	15.700	5.64	647	20.700	4.29	188	25.700	3.46	223	30.700	2.91
68	10.800	8.18	73	15.800	5.60	2096	20.800	4.27	147	25.800	3.45	263	30.800	2.90
68	10.900	8.11	68	15.900	5.57	936	20.900	4.25	150	25.900	3.44	269	30.900	2.89
73	11.000	8.04	65	16.000	5.53	302	21.000	4.23	184	26.000	3.42	192	31.000	2.88
73	11.100	7.96	59	16.100	5.50	162	21.100	4.21	233	26.100	3.41	147	31.100	2.87
69	11.200	7.89	65	16.200	5.47	124	21.200	4.19	381	26.200	3.40	147	31.200	2.86
69	11.300	7.82	63	16.300	5.43	115	21.300	4.17	634	26.300	3.39	132	31.300	2.86
69	11.400	7.76	73	16.400	5.40	104	21.400	4.15	1365	26.400	3.37	134	31.400	2.85
71	11.500	7.69	70	16.500	5.37	104	21.500	4.13	5110	26.500	3.36	116	31.500	2.84
68	11.600	7.62	65	16.600	5.34	109	21.600	4.11	4278	26.600	3.35	117	31.600	2.83
70	11.700	7.56	64	16.700	5.30	113	21.700	4.09	4143	26.700	3.34	112	31.700	2.82
70	11.800	7.49	59	16.800	5.27	131	21.800	4.07	748	26.800	3.32	118	31.800	2.81
69	11.900	7.43	65	16.900	5.24	187	21.900	4.05	436	26.900	3.31	112	31.900	2.80
67	12.000	7.37	67	17.000	5.21	246	22.000	4.04	421	27.000	3.30	121	32.000	2.79
69	12.100	7.31	68	17.100	5.18	136	22.100	4.02	319	27.100	3.29	129	32.100	2.79
71	12.200	7.25	71	17.200	5.15	123	22.200	4.00	262	27.200	3.28	145	32.200	2.78
69	12.300	7.19	71	17.300	5.12	128	22.300	3.98	327	27.300	3.26	152	32.300	2.77
74	12.400	7.13	72	17.400	5.09	118	22.400	3.97	503	27.400	3.25	138	32.400	2.76
69	12.500	7.08	72	17.500	5.06	118	22.500	3.95	435	27.500	3.24	126	32.500	2.75
68	12.600	7.02	75	17.600	5.03	110	22.600	3.93	314	27.600	3.23	109	32.600	2.74
66	12.700	6.96	76	17.700	5.01	105	22.700	3.91	395	27.700	3.22	110	32.700	2.74
63	12.800	6.91	68	17.800	4.98	113	22.800	3.90	406	27.800	3.21	112	32.800	2.73
65	12.900	6.86	71	17.900	4.95	120	22.900	3.88	518	27.900	3.20	127	32.900	2.72
71	13.000	6.80	73	18.000	4.92	139	23.000	3.86	317	28.000	3.18	126	33.000	2.71
72	13.100	6.75	73	18.100	4.90	140	23.100	3.85	221	28.100	3.17	128	33.100	2.70
69	13.200	6.70	74	18.200	4.87	145	23.200	3.83	194	28.200	3.16	120	33.200	2.70
66	13.300	6.65	75	18.300	4.84	150	23.300	3.81	185	28.300	3.15	128	33.300	2.69
69	13.400	6.60	70	18.400	4.82	163	23.400	3.80	126	28.400	3.14	122	33.400	2.68
78	13.500	6.55	72	18.500	4.79	225	23.500	3.78	112	28.500	3.13	125	33.500	2.67
90	13.600	6.51	76	18.600	4.77	190	23.600	3.77	103	28.600	3.12	119	33.600	2.66
80	13.700	6.46	75	18.700	4.74	142	23.700	3.75	103	28.700	3.11	123	33.700	2.66
88	13.800	6.41	74	18.800	4.72	138	23.800	3.74	101	28.800	3.10	148	33.800	2.65
82	13.900	6.37	81	18.900	4.69	166	23.900	3.72	100	28.900	3.09	141	33.900	2.64
76	14.000	6.32	77	19.000	4.67	168	24.000	3.70	96	29.000	3.08	134	34.000	2.63
70	14.100	6.28	76	19.100	4.64	166	24.100	3.69	105	29.100	3.07	159	34.100	2.63
70	14.200	6.23	80	19.200	4.62	195	24.200	3.67	104	29.200	3.06	167	34.200	2.62
68	14.300	6.19	85	19.300	4.59	187	24.300	3.66	125	29.300	3.05	176	34.300	2.61
66	14.400	6.15	86	19.400	4.57	125	24.400	3.64	140	29.400	3.04	180	34.400	2.60
71	14.500	6.10	88	19.500	4.55	115	24.500	3.63	131	29.500	3.03	178	34.500	2.60
66	14.600	6.06	103	19.600	4.53	119	24.600	3.62	133	29.600	3.02	195	34.600	2.59
64	14.700	6.02	116	19.700	4.50	111	24.700	3.60	170	29.700	3.01	197	34.700	2.58
70	14.800	5.98	122	19.800	4.48	107	24.800	3.59	191	29.800	3.00	210	34.800	2.58
79	14.900	5.94	115	19.900	4.46	116	24.900	3.57	173	29.900	2.99	215	34.900	2.57

Table 28 (continued)

X-RAY DIFFRACTION STEP SCAN DATA											
9:5AM1.XRD SAN1 07:43:51 01-06-1989 , GMD											
INITIAL 2 θ = 10 $^{\circ}$ 62 θ = .1 $^{\circ}$ * DATA POINTS = 531 AT = 40 SECONDS FINAL 2 θ = 65 $^{\circ}$											
COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)
225	35.000	2.56	160	40.000	2.25	143	45.000	2.01	1583	50.000	1.82
223	35.100	2.55	259	40.100	2.25	132	45.100	2.01	2012	50.100	1.82
221	35.200	2.55	615	40.200	2.24	131	45.200	2.00	1304	50.200	1.82
216	35.300	2.54	448	40.300	2.24	124	45.300	2.00	350	50.300	1.81
205	35.400	2.53	217	40.400	2.23	140	45.400	2.00	292	50.400	1.81
208	35.500	2.53	141	40.500	2.23	170	45.500	1.99	323	50.500	1.81
185	35.600	2.52	132	40.600	2.22	277	45.600	1.99	287	50.600	1.80
177	35.700	2.51	130	40.700	2.21	696	45.700	1.98	229	50.700	1.80
168	35.800	2.51	137	40.800	2.21	468	45.800	1.98	194	50.800	1.80
172	35.900	2.50	141	40.900	2.20	259	45.900	1.98	175	50.900	1.79
175	36.000	2.49	153	41.000	2.20	143	46.000	1.97	173	51.000	1.79
195	36.100	2.49	163	41.100	2.19	122	46.100	1.97	180	51.100	1.79
209	36.200	2.48	154	41.200	2.19	113	46.200	1.96	160	51.200	1.78
259	36.300	2.47	142	41.300	2.18	104	46.300	1.96	147	51.300	1.78
625	36.400	2.47	135	41.400	2.18	100	46.400	1.96	125	51.400	1.78
1331	36.500	2.46	138	41.500	2.17	104	46.500	1.95	117	51.500	1.77
688	36.600	2.45	171	41.600	2.17	101	46.600	1.95	108	51.600	1.77
248	36.700	2.45	204	41.700	2.16	100	46.700	1.94	113	51.700	1.77
192	36.800	2.44	190	41.800	2.16	110	46.800	1.94	111	51.800	1.76
179	36.900	2.43	144	41.900	2.15	119	46.900	1.94	111	51.900	1.76
181	37.000	2.43	137	42.000	2.15	127	47.000	1.93	116	52.000	1.76
161	37.100	2.42	154	42.100	2.14	126	47.100	1.93	122	52.100	1.75
151	37.200	2.41	220	42.200	2.14	116	47.200	1.92	125	52.200	1.75
163	37.300	2.41	318	42.300	2.13	109	47.300	1.92	127	52.300	1.75
165	37.400	2.40	1008	42.400	2.13	115	47.400	1.92	125	52.400	1.74
153	37.500	2.40	578	42.500	2.13	113	47.500	1.91	125	52.500	1.74
144	37.600	2.39	209	42.600	2.12	108	47.600	1.91	130	52.600	1.74
137	37.700	2.38	164	42.700	2.12	95	47.700	1.90	132	52.700	1.74
124	37.800	2.38	140	42.800	2.11	104	47.800	1.90	125	52.800	1.73
117	37.900	2.37	127	42.900	2.11	105	47.900	1.90	132	52.900	1.73
110	38.000	2.37	119	43.000	2.10	111	48.000	1.89	138	53.000	1.73
106	38.100	2.36	121	43.100	2.10	119	48.100	1.89	142	53.100	1.72
110	38.200	2.35	114	43.200	2.09	114	48.200	1.89	145	53.200	1.72
114	38.300	2.35	103	43.300	2.09	109	48.300	1.88	153	53.300	1.72
119	38.400	2.34	112	43.400	2.08	100	48.400	1.88	143	53.400	1.71
133	38.500	2.34	117	43.500	2.08	101	48.500	1.88	134	53.500	1.71
126	38.600	2.33	119	43.600	2.07	111	48.600	1.87	132	53.600	1.71
124	38.700	2.32	116	43.700	2.07	110	48.700	1.87	136	53.700	1.71
123	38.800	2.32	118	43.800	2.07	118	48.800	1.86	141	53.800	1.70
124	38.900	2.31	116	43.900	2.06	125	48.900	1.86	152	53.900	1.70
133	39.000	2.31	122	44.000	2.06	139	49.000	1.86	148	54.000	1.70
154	39.100	2.30	122	44.100	2.05	155	49.100	1.85	137	54.100	1.69
203	39.200	2.30	124	44.200	2.05	144	49.200	1.85	150	54.200	1.69
459	39.300	2.29	123	44.300	2.04	142	49.300	1.85	149	54.300	1.69
1251	39.400	2.28	124	44.400	2.04	135	49.400	1.84	156	54.400	1.69
710	39.500	2.28	133	44.500	2.03	138	49.500	1.84	181	54.500	1.68
218	39.600	2.27	132	44.600	2.03	155	49.600	1.84	215	54.600	1.68
145	39.700	2.27	129	44.700	2.03	201	49.700	1.83	428	54.700	1.68
138	39.800	2.26	141	44.800	2.02	288	49.800	1.83	831	54.800	1.67
141	39.900	2.26	150	44.900	2.02	500	49.900	1.83	493	54.900	1.67
									1592	59.900	1.54

Table 28 (continued)

X-RAY DIFFRACTION STEP SCAN DATA											
B:SAWI,XRD SAWI 07:43:51 01-06-1989 , 5ND											
INITIAL 2θ = 10° 52θ = .1° * DATA POINTS = 551 ΔT = 40 SECONDS FINAL 2θ = 65°											
COUNTS	*2θ d(1)	COUNTS	*2θ d(1)	COUNTS	*2θ d(1)	COUNTS	*2θ d(1)	COUNTS	*2θ d(1)	COUNTS	*2θ d(1)
988	60.000 1.54	159	65.000 1.43	0	70.000 1.34	0	75.000 1.27	0	80.000 1.20		
550	60.100 1.54	0	65.100 1.43	0	70.100 1.34	0	75.100 1.26	0	80.100 1.20		
225	60.200 1.54	0	65.200 1.43	0	70.200 1.34	0	75.200 1.26	0	80.200 1.20		
173	60.300 1.53	0	65.300 1.43	0	70.300 1.34	0	75.300 1.26	0	80.300 1.19		
155	60.400 1.53	0	65.400 1.43	0	70.400 1.34	0	75.400 1.26	0	80.400 1.19		
147	60.500 1.53	0	65.500 1.42	0	70.500 1.33	0	75.500 1.26	0	80.500 1.19		
153	60.600 1.53	0	65.600 1.42	0	70.600 1.33	0	75.600 1.26	0	80.600 1.19		
140	60.700 1.52	0	65.700 1.42	0	70.700 1.33	0	75.700 1.26	0	80.700 1.19		
139	60.800 1.52	0	65.800 1.42	0	70.800 1.33	0	75.800 1.25	0	80.800 1.19		
148	60.900 1.52	0	65.900 1.42	0	70.900 1.33	0	75.900 1.25	0	80.900 1.19		
151	61.000 1.52	0	66.000 1.41	0	71.000 1.33	0	76.000 1.25	0	81.000 1.19		
155	61.100 1.52	0	66.100 1.41	0	71.100 1.32	0	76.100 1.25	0	81.100 1.18		
162	61.200 1.51	0	66.200 1.41	0	71.200 1.32	0	76.200 1.25	0	81.200 1.18		
150	61.300 1.51	0	66.300 1.41	0	71.300 1.32	0	76.300 1.25	0	81.300 1.18		
163	61.400 1.51	0	66.400 1.41	0	71.400 1.32	0	76.400 1.25	0	81.400 1.18		
170	61.500 1.51	0	66.500 1.40	0	71.500 1.32	0	76.500 1.24	0	81.500 1.18		
171	61.600 1.50	0	66.600 1.40	0	71.600 1.32	0	76.600 1.24	0	81.600 1.18		
174	61.700 1.50	0	66.700 1.40	0	71.700 1.32	0	76.700 1.24	0	81.700 1.18		
161	61.800 1.50	0	66.800 1.40	0	71.800 1.31	0	76.800 1.24	0	81.800 1.18		
156	61.900 1.50	0	66.900 1.40	0	71.900 1.31	0	76.900 1.24	0	81.900 1.18		
144	62.000 1.50	0	67.000 1.40	0	72.000 1.31	0	77.000 1.24	0	82.000 1.17		
153	62.100 1.49	0	67.100 1.39	0	72.100 1.31	0	77.100 1.24	0	82.100 1.17		
139	62.200 1.49	0	67.200 1.39	0	72.200 1.31	0	77.200 1.23	0	82.200 1.17		
146	62.300 1.49	0	67.300 1.39	0	72.300 1.31	0	77.300 1.23	0	82.300 1.17		
144	62.400 1.49	0	67.400 1.39	0	72.400 1.30	0	77.400 1.23	0	82.400 1.17		
144	62.500 1.48	0	67.500 1.39	0	72.500 1.30	0	77.500 1.23	0	82.500 1.17		
141	62.600 1.48	0	67.600 1.38	0	72.600 1.30	0	77.600 1.23	0	82.600 1.17		
137	62.700 1.48	0	67.700 1.38	0	72.700 1.30	0	77.700 1.23	0	82.700 1.17		
151	62.800 1.48	0	67.800 1.38	0	72.800 1.30	0	77.800 1.23	0	82.800 1.16		
147	62.900 1.48	0	67.900 1.38	0	72.900 1.30	0	77.900 1.23	0	82.900 1.16		
146	63.000 1.47	0	68.000 1.38	0	73.000 1.29	0	78.000 1.22	0	83.000 1.16		
144	63.100 1.47	0	68.100 1.38	0	73.100 1.29	0	78.100 1.22	0	83.100 1.16		
150	63.200 1.47	0	68.200 1.37	0	73.200 1.29	0	78.200 1.22	0	83.200 1.16		
153	63.300 1.47	0	68.300 1.37	0	73.300 1.29	0	78.300 1.22	0	83.300 1.16		
158	63.400 1.47	0	68.400 1.37	0	73.400 1.29	0	78.400 1.22	0	83.400 1.16		
169	63.500 1.46	0	68.500 1.37	0	73.500 1.29	0	78.500 1.22	0	83.500 1.16		
175	63.600 1.46	0	68.600 1.37	0	73.600 1.29	0	78.600 1.22	0	83.600 1.16		
206	63.700 1.46	0	68.700 1.37	0	73.700 1.28	0	78.700 1.21	0	83.700 1.15		
245	63.800 1.46	0	68.800 1.36	0	73.800 1.28	0	78.800 1.21	0	83.800 1.15		
416	63.900 1.46	0	68.900 1.36	0	73.900 1.28	0	78.900 1.21	0	83.900 1.15		
353	64.000 1.45	0	69.000 1.36	0	74.000 1.28	0	79.000 1.21	0	84.000 1.15		
305	64.100 1.45	0	69.100 1.36	0	74.100 1.28	0	79.100 1.21	0	84.100 1.15		
206	64.200 1.45	0	69.200 1.36	0	74.200 1.28	0	79.200 1.21	0	84.200 1.15		
159	64.300 1.45	0	69.300 1.35	0	74.300 1.28	0	79.300 1.21	0	84.300 1.15		
152	64.400 1.45	0	69.400 1.35	0	74.400 1.27	0	79.400 1.21	0	84.400 1.15		
152	64.500 1.44	0	69.500 1.35	0	74.500 1.27	0	79.500 1.20	0	84.500 1.15		
154	64.600 1.44	0	69.600 1.35	0	74.600 1.27	0	79.600 1.20	0	84.600 1.14		
156	64.700 1.44	0	69.700 1.35	0	74.700 1.27	0	79.700 1.20	0	84.700 1.14		
150	64.800 1.44	0	69.800 1.35	0	74.800 1.27	0	79.800 1.20	0	84.800 1.14		
158	64.900 1.44	0	69.900 1.34	0	74.900 1.27	0	79.900 1.20	0	84.900 1.14		

Table 29. Summary of x-ray diffraction data from the silt sized
separate from the Blount fertilizer P sample.

X-RAY DIFFRACTION STEP SCAN DATA

B:\SILT.XRD SILT 07:36:51 01-03-1989 , GMP

INITIAL 2 θ = 2° 620 = .1° 8 DATA POINTS = 631 6T = 40 SECONDS FINAL 2 θ = 65°

COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)
328	2.000	44.13	86	7.000	12.62	67	12.000	7.37	62	17.000	5.21	129	22.000	4.04
315	2.100	42.03	81	7.100	12.44	72	12.100	7.31	64	17.100	5.18	120	22.100	4.02
297	2.200	40.12	84	7.200	12.27	79	12.200	7.25	69	17.200	5.15	118	22.200	4.00
284	2.300	38.38	77	7.300	12.10	82	12.300	7.19	66	17.300	5.12	118	22.300	3.98
256	2.400	36.78	79	7.400	11.94	83	12.400	7.13	69	17.400	5.09	123	22.400	3.97
228	2.500	35.31	80	7.500	11.78	65	12.500	7.08	78	17.500	5.06	106	22.500	3.95
223	2.600	33.95	83	7.600	11.62	66	12.600	7.02	85	17.600	5.03	107	22.600	3.93
190	2.700	32.69	81	7.700	11.47	68	12.700	6.96	78	17.700	5.01	184	22.700	3.91
180	2.800	31.53	75	7.800	11.32	71	12.800	6.91	67	17.800	4.98	158	22.800	3.90
157	2.900	30.44	71	7.900	11.18	76	12.900	6.86	71	17.900	4.95	172	22.900	3.88
150	3.000	29.42	74	8.000	11.04	76	13.000	6.80	75	18.000	4.92	137	23.000	3.86
130	3.100	28.48	74	8.100	10.91	69	13.100	6.73	73	18.100	4.90	129	23.100	3.85
123	3.200	27.59	78	8.200	10.77	73	13.200	6.70	66	18.200	4.87	169	23.200	3.83
119	3.300	26.75	80	8.300	10.64	73	13.300	6.63	73	18.300	4.84	264	23.300	3.81
117	3.400	25.96	80	8.400	10.52	84	13.400	6.60	80	18.400	4.82	326	23.400	3.80
111	3.500	25.22	82	8.500	10.39	111	13.500	6.53	74	18.500	4.79	214	23.500	3.78
115	3.600	24.52	82	8.600	10.27	81	13.600	6.51	74	18.600	4.77	152	23.600	3.77
110	3.700	23.86	86	8.700	10.16	112	13.700	6.46	75	18.700	4.74	136	23.700	3.75
98	3.800	23.23	90	8.800	10.04	80	13.800	6.41	79	18.800	4.72	189	23.800	3.74
103	3.900	22.64	80	8.900	9.93	77	13.900	6.37	73	18.900	4.69	165	23.900	3.72
103	4.000	22.07	72	9.000	9.82	66	14.000	6.32	79	19.000	4.67	228	24.000	3.70
102	4.100	21.53	75	9.100	9.71	69	14.100	6.28	87	19.100	4.64	280	24.100	3.63
100	4.200	21.02	72	9.200	9.60	63	14.200	6.23	82	19.200	4.62	193	24.200	3.67
98	4.300	20.53	75	9.300	9.50	61	14.300	6.19	78	19.300	4.59	119	24.300	3.66
100	4.400	20.07	71	9.400	9.40	64	14.400	6.15	93	19.400	4.57	127	24.400	3.64
94	4.500	19.62	75	9.500	9.30	64	14.500	6.10	104	19.500	4.53	122	24.500	3.63
95	4.600	19.19	66	9.600	9.21	72	14.600	6.06	134	19.600	4.53	104	24.600	3.62
98	4.700	18.78	71	9.700	9.11	70	14.700	6.02	134	19.700	4.50	113	24.700	3.60
90	4.800	18.39	67	9.800	9.02	80	14.800	5.98	115	19.800	4.48	115	24.800	3.59
96	4.900	18.02	73	9.900	8.93	81	14.900	5.94	95	19.900	4.46	121	24.900	3.57
92	5.000	17.66	68	10.000	8.84	77	15.000	5.90	99	20.000	4.44	133	25.000	3.56
91	5.100	17.31	72	10.100	8.75	65	15.100	5.86	102	20.100	4.41	163	25.100	3.54
91	5.200	16.98	70	10.200	8.66	64	15.200	5.82	108	20.200	4.39	194	25.200	3.53
96	5.300	16.66	76	10.300	8.58	63	15.300	5.79	140	20.300	4.37	201	25.300	3.52
88	5.400	16.35	71	10.400	8.50	66	15.400	5.75	194	20.400	4.35	246	25.400	3.50
90	5.500	16.05	72	10.500	8.42	67	15.500	5.71	357	20.500	4.33	266	25.500	3.49
88	5.600	15.77	69	10.600	8.34	64	15.600	5.68	1075	20.600	4.31	181	25.600	3.48
89	5.700	15.49	69	10.700	8.26	67	15.700	5.64	3687	20.700	4.29	144	25.700	3.46
90	5.800	15.22	68	10.800	8.18	62	15.800	5.60	761	20.800	4.27	146	25.800	3.45
89	5.900	14.97	70	10.900	8.11	63	15.900	5.57	304	20.900	4.25	175	25.900	3.44
93	6.000	14.72	67	11.000	8.04	64	16.000	5.53	152	21.000	4.23	258	26.000	3.42
92	6.100	14.48	69	11.100	7.96	64	16.100	5.50	110	21.100	4.21	454	26.100	3.41
89	6.200	14.24	68	11.200	7.89	69	16.200	5.47	108	21.200	4.19	861	26.200	3.40
85	6.300	14.02	67	11.300	7.82	67	16.300	5.43	106	21.300	4.17	2051	26.300	3.39
84	6.400	13.80	66	11.400	7.76	63	16.400	5.40	103	21.400	4.15	9124	26.400	3.37
86	6.500	13.59	65	11.500	7.69	64	16.500	5.37	113	21.500	4.13	8217	26.500	3.36
90	6.600	13.38	68	11.600	7.62	61	16.600	5.34	112	21.600	4.11	2732	26.600	3.35
75	6.700	13.18	67	11.700	7.56	66	16.700	5.30	143	21.700	4.09	890	26.700	3.34
79	6.800	12.99	60	11.800	7.49	60	16.800	5.27	238	21.800	4.07	506	26.800	3.32
81	6.900	12.80	72	11.900	7.43	66	16.900	5.24	377	21.900	4.05	645	26.900	3.31

Table 29 (continued)

X-RAY DIFFRACTION STEP SCAN DATA											
B:SILT.XRD SILT 07:36:51 01-05-1989 , 3ND											
INITIAL 2θ = 2° 2φ = .1° # DATA POINTS = 631 DT = 40 SECONDS FINAL 2θ = 55°											
COUNTS	2θ	d(1)	COUNTS	2θ	d(1)	COUNTS	2θ	d(1)	COUNTS	2θ	d(1)
371	27.000	3.30	125	32.000	2.79	127	37.000	2.43	172	42.000	2.15
303	27.100	3.29	120	32.100	2.79	124	37.100	2.42	273	42.100	2.14
458	27.200	3.28	126	32.200	2.78	149	37.200	2.41	873	42.200	2.14
734	27.300	3.26	115	32.300	2.77	168	37.300	2.41	1289	42.300	2.13
658	27.400	3.25	91	32.400	2.76	169	37.400	2.40	748	42.400	2.13
474	27.500	3.24	85	32.500	2.75	166	37.500	2.40	237	42.500	2.13
544	27.600	3.23	74	32.600	2.74	148	37.600	2.39	199	42.600	2.12
687	27.700	3.22	77	32.700	2.74	113	37.700	2.38	161	42.700	2.12
849	27.800	3.21	79	32.800	2.73	97	37.800	2.38	116	42.800	2.11
434	27.900	3.20	78	32.900	2.72	91	37.900	2.37	102	42.900	2.11
294	28.000	3.18	85	33.000	2.71	89	38.000	2.37	102	43.000	2.10
246	28.100	3.17	84	33.100	2.70	86	38.100	2.36	104	43.100	2.10
170	28.200	3.16	80	33.200	2.70	93	38.200	2.35	102	43.200	2.09
117	28.300	3.15	84	33.300	2.69	139	38.300	2.35	129	43.300	2.09
113	28.400	3.14	82	33.400	2.68	149	38.400	2.34	128	43.400	2.08
99	28.500	3.13	82	33.500	2.67	140	38.500	2.34	126	43.500	2.08
96	28.600	3.12	100	33.600	2.66	163	38.600	2.33	117	43.600	2.07
89	28.700	3.11	105	33.700	2.65	149	38.700	2.32	105	43.700	2.07
82	28.800	3.10	103	33.800	2.65	114	38.800	2.32	103	43.800	2.07
78	28.900	3.09	105	33.900	2.64	135	38.900	2.31	122	43.900	2.06
87	29.000	3.08	124	34.000	2.63	156	39.000	2.31	107	44.000	2.06
91	29.100	3.07	144	34.100	2.63	223	39.100	2.30	103	44.100	2.05
104	29.200	3.06	161	34.200	2.62	693	39.200	2.30	98	44.200	2.05
127	29.300	3.05	175	34.300	2.61	1713	39.300	2.29	94	44.300	2.04
120	29.400	3.04	174	34.400	2.60	904	39.400	2.28	103	44.400	2.04
152	29.500	3.03	198	34.500	2.60	200	39.500	2.28	105	44.500	2.03
228	29.600	3.02	201	34.600	2.59	132	39.600	2.27	104	44.600	2.03
254	29.700	3.01	235	34.700	2.58	114	39.700	2.27	120	44.700	2.03
189	29.800	3.00	249	34.800	2.58	132	39.800	2.26	134	44.800	2.02
190	29.900	2.99	235	34.900	2.57	164	39.900	2.26	125	44.900	2.02
198	30.000	2.98	192	35.000	2.56	309	40.000	2.25	133	45.000	2.01
181	30.100	2.97	164	35.100	2.55	1012	40.100	2.25	136	45.100	2.01
185	30.200	2.96	152	35.200	2.55	603	40.200	2.24	162	45.200	2.00
249	30.300	2.95	164	35.300	2.54	180	40.300	2.24	180	45.300	2.00
187	30.400	2.94	165	35.400	2.53	114	40.400	2.23	205	45.400	2.00
175	30.500	2.93	142	35.500	2.53	103	40.500	2.23	387	45.500	1.99
262	30.600	2.92	121	35.600	2.52	105	40.600	2.22	1092	45.600	1.99
223	30.700	2.91	124	35.700	2.51	102	40.700	2.21	662	45.700	1.98
150	30.800	2.90	134	35.800	2.51	109	40.800	2.21	277	45.800	1.98
106	30.900	2.89	133	35.900	2.50	111	40.900	2.20	147	45.900	1.98
121	31.000	2.88	153	36.000	2.49	141	41.000	2.20	130	46.000	1.97
139	31.100	2.87	179	36.100	2.49	132	41.100	2.19	115	46.100	1.97
139	31.200	2.86	267	36.200	2.48	107	41.200	2.19	103	46.200	1.96
110	31.300	2.86	1053	36.300	2.47	117	41.300	2.18	93	46.300	1.96
93	31.400	2.85	1671	36.400	2.47	133	41.400	2.18	97	46.400	1.96
104	31.500	2.84	709	36.500	2.46	176	41.500	2.17	97	46.500	1.95
99	31.600	2.83	216	36.600	2.45	214	41.600	2.17	97	46.600	1.95
90	31.700	2.82	160	36.700	2.45	183	41.700	2.16	114	46.700	1.94
99	31.800	2.81	158	36.800	2.44	150	41.800	2.16	122	46.800	1.94
129	31.900	2.80	151	36.900	2.43	142	41.900	2.15	149	46.900	1.94

Table 29 (continued)

(X-RAY DIFFRACTION STEP SCAN DATA)

9:SILT.XRD SILT 07:36:31 01-05-1989 3rd

INITIAL 2 θ = 2° Δ 2 θ = .1° # DATA POINTS = 631 Δ T = 40 SECONDS FINAL 2 θ = 55°

COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)	COUNTS	2 θ	d(1)
125	52.000	1.76	171	57.000	1.61	160	62.000	1.50	0	67.000	1.40	0	72.000	1.31
134	52.100	1.75	154	57.100	1.61	146	62.100	1.49	0	67.100	1.39	0	72.100	1.31
122	52.200	1.75	151	57.200	1.61	146	62.200	1.49	0	67.200	1.39	0	72.200	1.31
125	52.300	1.75	135	57.300	1.61	134	62.300	1.49	0	67.300	1.39	0	72.300	1.31
127	52.400	1.74	132	57.400	1.60	136	62.400	1.49	0	67.400	1.39	0	72.400	1.30
126	52.500	1.74	142	57.500	1.60	147	62.500	1.48	0	67.500	1.39	0	72.500	1.30
121	52.600	1.74	137	57.600	1.60	144	62.600	1.48	0	67.600	1.38	0	72.600	1.30
133	52.700	1.74	138	57.700	1.60	158	62.700	1.48	0	67.700	1.38	0	72.700	1.30
144	52.800	1.73	125	57.800	1.59	141	62.800	1.48	0	67.800	1.38	0	72.800	1.30
143	52.900	1.73	138	57.900	1.59	147	62.900	1.48	0	67.900	1.38	0	72.900	1.30
165	53.000	1.73	123	58.000	1.59	146	63.000	1.47	0	68.000	1.38	0	73.000	1.29
158	53.100	1.72	119	58.100	1.59	133	63.100	1.47	0	68.100	1.38	0	73.100	1.29
133	53.200	1.72	115	58.200	1.58	151	63.200	1.47	0	68.200	1.37	0	73.200	1.29
119	53.300	1.72	132	58.300	1.58	167	63.300	1.47	0	68.300	1.37	0	73.300	1.29
115	53.400	1.71	147	58.400	1.58	180	63.400	1.47	0	68.400	1.37	0	73.400	1.29
111	53.500	1.71	153	58.500	1.58	197	63.500	1.46	0	68.500	1.37	0	73.500	1.29
126	53.600	1.71	154	58.600	1.57	234	63.600	1.46	0	68.600	1.37	0	73.600	1.29
126	53.700	1.71	141	58.700	1.57	301	63.700	1.46	0	68.700	1.37	0	73.700	1.28
136	53.800	1.70	136	58.800	1.57	670	63.800	1.46	0	68.800	1.36	0	73.800	1.28
134	53.900	1.70	129	58.900	1.57	469	63.900	1.46	0	68.900	1.36	0	73.900	1.28
154	54.000	1.70	137	59.000	1.56	485	64.000	1.45	0	69.000	1.36	0	74.000	1.28
167	54.100	1.69	139	59.100	1.56	217	64.100	1.45	0	69.100	1.36	0	74.100	1.28
166	54.200	1.69	142	59.200	1.56	157	64.200	1.45	0	69.200	1.36	0	74.200	1.28
167	54.300	1.69	169	59.300	1.56	139	64.300	1.45	0	69.300	1.35	0	74.300	1.28
178	54.400	1.69	208	59.400	1.55	143	64.400	1.45	0	69.400	1.35	0	74.400	1.27
229	54.500	1.68	283	59.500	1.55	160	64.500	1.44	0	69.500	1.35	0	74.500	1.27
620	54.600	1.68	521	59.600	1.55	153	64.600	1.44	0	69.600	1.35	0	74.600	1.27
1169	54.700	1.68	1802	59.700	1.55	157	64.700	1.44	0	69.700	1.35	0	74.700	1.27
718	54.800	1.67	2193	59.800	1.55	171	64.800	1.44	0	69.800	1.35	0	74.800	1.27
358	54.900	1.67	1537	59.900	1.54	179	64.900	1.44	0	69.900	1.34	0	74.900	1.27
261	55.000	1.67	650	60.000	1.54	191	65.000	1.43	0	70.000	1.34	0	75.000	1.27
545	55.100	1.67	261	60.100	1.54	0	65.100	1.43	0	70.100	1.34	0	75.100	1.26
364	55.200	1.66	188	60.200	1.54	0	65.200	1.43	0	70.200	1.34	0	75.200	1.26
361	55.300	1.66	157	60.300	1.53	0	65.300	1.43	0	70.300	1.34	0	75.300	1.26
198	55.400	1.66	160	60.400	1.53	0	65.400	1.43	0	70.400	1.34	0	75.400	1.26
153	55.500	1.65	154	60.500	1.53	0	65.500	1.42	0	70.500	1.33	0	75.500	1.25
152	55.600	1.65	153	60.600	1.53	0	65.600	1.42	0	70.600	1.33	0	75.600	1.25
136	55.700	1.65	146	60.700	1.52	0	65.700	1.42	0	70.700	1.33	0	75.700	1.25
133	55.800	1.65	148	60.800	1.52	0	65.800	1.42	0	70.800	1.33	0	75.800	1.25
131	55.900	1.64	159	60.900	1.52	0	65.900	1.42	0	70.900	1.33	0	75.900	1.25
130	56.000	1.64	174	61.000	1.52	0	66.000	1.41	0	71.000	1.33	0	76.000	1.25
130	56.100	1.64	171	61.100	1.52	0	66.100	1.41	0	71.100	1.32	0	76.100	1.25
135	56.200	1.64	173	61.200	1.51	0	66.200	1.41	0	71.200	1.32	0	76.200	1.25
135	56.300	1.63	289	61.300	1.51	0	66.300	1.41	0	71.300	1.32	0	76.300	1.25
135	56.400	1.63	188	61.400	1.51	0	66.400	1.41	0	71.400	1.32	0	76.400	1.25
135	56.500	1.63	220	61.500	1.51	0	66.500	1.40	0	71.500	1.32	0	76.500	1.24
130	56.600	1.62	214	61.600	1.50	0	66.600	1.40	0	71.600	1.32	0	76.600	1.24
130	56.700	1.62	203	61.700	1.50	0	66.700	1.40	0	71.700	1.32	0	76.700	1.24
125	56.800	1.62	194	61.800	1.50	0	66.800	1.40	0	71.800	1.31	0	76.800	1.24
127	56.900	1.62	165	61.900	1.50	0	66.900	1.40	0	71.900	1.31	0	76.900	1.24

Table 30. Summary of x-ray diffraction data for the <2.2 g/cm³ density separate from the Blount sludge P sample. 174

X-RAY DIFFRACTION STEP SCAN DATA

B:11.XRD 11 07:48:51 02-01-1989 , SMP
INITIAL 2θ = 10° 2θ = .1° # DATA POINTS = 551 ΔT = 10 SECONDS FINAL 2θ = 65°

COUNTS	2θ d(Å)	COUNTS	2θ d(Å)	COUNTS	2θ d(Å)	COUNTS	2θ d(Å)	COUNTS	2θ d(Å)
35	10.000 8.94	32	15.000 5.90	92	20.000 4.44	91	25.000 3.55	55	30.000 2.99
38	10.100 8.75	28	15.100 5.86	96	20.100 4.41	98	25.100 3.54	67	30.100 2.97
33	10.200 8.56	31	15.200 5.82	93	20.200 4.39	89	25.200 3.53	56	30.200 2.95
35	10.300 8.53	32	15.300 5.79	98	20.300 4.37	86	25.300 3.52	61	30.300 2.95
32	10.400 8.50	35	15.400 5.75	94	20.400 4.35	83	25.400 3.50	59	30.400 2.94
34	10.500 8.42	32	15.500 5.71	108	20.500 4.33	89	25.500 3.49	64	30.500 2.93
29	10.600 8.34	29	15.600 5.68	147	20.600 4.31	78	25.600 3.48	64	30.600 2.92
31	10.700 8.26	29	15.700 5.64	146	20.700 4.29	76	25.700 3.46	62	30.700 2.91
31	10.800 8.18	31	15.800 5.60	92	20.800 4.27	81	25.800 3.45	64	30.800 2.90
29	10.900 8.11	31	15.900 5.57	79	20.900 4.25	82	25.900 3.44	59	30.900 2.89
31	11.000 8.04	32	16.000 5.53	81	21.000 4.23	86	26.000 3.42	63	31.000 2.88
29	11.100 7.96	31	16.100 5.50	76	21.100 4.21	107	26.100 3.41	60	31.100 2.87
32	11.200 7.89	32	16.200 5.47	77	21.200 4.19	150	26.200 3.40	55	31.200 2.86
31	11.300 7.82	30	16.300 5.43	73	21.300 4.17	207	26.300 3.39	55	31.300 2.86
30	11.400 7.76	31	16.400 5.40	73	21.400 4.15	608	26.400 3.37	48	31.400 2.85
31	11.500 7.69	31	16.500 5.37	67	21.500 4.13	254	26.500 3.36	49	31.500 2.84
33	11.600 7.62	31	16.600 5.34	75	21.600 4.11	150	26.600 3.35	55	31.600 2.83
32	11.700 7.56	33	16.700 5.30	84	21.700 4.09	111	26.700 3.34	57	31.700 2.82
34	11.800 7.49	32	16.800 5.27	74	21.800 4.07	94	26.800 3.32	61	31.800 2.81
33	11.900 7.43	34	16.900 5.24	70	21.900 4.05	39	26.900 3.31	57	31.900 2.80
36	12.000 7.37	35	17.000 5.21	66	22.000 4.04	91	27.000 3.30	52	32.000 2.79
41	12.100 7.31	34	17.100 5.18	69	22.100 4.02	32	27.100 3.29	53	32.100 2.79
43	12.200 7.25	36	17.200 5.15	71	22.200 4.00	101	27.200 3.29	53	32.200 2.78
37	12.300 7.19	33	17.300 5.12	72	22.300 3.98	91	27.300 3.26	46	32.300 2.77
34	12.400 7.13	38	17.400 5.09	73	22.400 3.97	97	27.400 3.25	51	32.400 2.76
32	12.500 7.08	40	17.500 5.06	72	22.500 3.95	88	27.500 3.24	50	32.500 2.75
29	12.600 7.02	41	17.600 5.03	70	22.600 3.93	83	27.600 3.23	49	32.600 2.74
28	12.700 6.96	37	17.700 5.01	72	22.700 3.91	96	27.700 3.22	49	32.700 2.74
25	12.800 6.91	37	17.800 4.98	67	22.800 3.90	71	27.800 3.21	51	32.800 2.73
28	12.900 6.86	36	17.900 4.95	72	22.900 3.88	68	27.900 3.20	50	32.900 2.72
27	13.000 6.80	37	18.000 4.92	68	23.000 3.86	67	28.000 3.18	52	33.000 2.71
26	13.100 6.75	35	18.100 4.90	68	23.100 3.85	64	28.100 3.17	47	33.100 2.70
32	13.200 6.70	40	18.200 4.87	77	23.200 3.83	59	28.200 3.16	48	33.200 2.70
29	13.300 6.65	35	18.300 4.84	75	23.300 3.81	64	28.300 3.15	49	33.300 2.69
29	13.400 6.60	41	18.400 4.82	77	23.400 3.80	56	28.400 3.14	47	33.400 2.68
27	13.500 6.55	37	18.500 4.79	71	23.500 3.78	63	28.500 3.13	52	33.500 2.67
28	13.600 6.51	39	18.600 4.77	73	23.600 3.77	59	28.600 3.12	51	33.600 2.66
30	13.700 6.46	40	18.700 4.74	69	23.700 3.75	62	28.700 3.11	53	33.700 2.66
26	13.800 6.41	40	18.800 4.72	65	23.800 3.74	55	28.800 3.10	50	33.800 2.65
32	13.900 6.37	45	18.900 4.69	69	23.900 3.72	58	28.900 3.09	63	33.900 2.64
29	14.000 6.32	48	19.000 4.67	71	24.000 3.70	59	29.000 3.09	70	34.000 2.63
26	14.100 6.29	50	19.100 4.64	69	24.100 3.69	59	29.100 3.07	79	34.100 2.63
25	14.200 6.27	55	19.200 4.62	67	24.200 3.67	59	29.200 3.06	75	34.200 2.62
27	14.300 6.19	74	19.300 4.59	70	24.300 3.66	55	29.300 3.05	114	34.300 2.61
28	14.400 6.15	39	19.400 4.57	70	24.400 3.64	57	29.400 3.04	125	34.400 2.60
24	14.500 6.10	119	19.500 4.55	75	24.500 3.63	74	29.500 3.03	124	34.500 2.60
27	14.600 6.06	147	19.600 4.53	92	24.600 3.62	90	29.600 3.02	151	34.600 2.59
25	14.700 6.02	140	19.700 4.50	89	24.700 3.60	67	29.700 3.01	159	34.700 2.58
31	14.800 5.98	117	19.800 4.48	80	24.800 3.59	69	29.800 3.00	142	34.800 2.58
29	14.900 5.94	101	19.900 4.46	79	24.900 3.57	62	29.900 2.99	107	34.900 2.57

Table 30 (continued)

X-RAY DIFFRACTION STEP SCAN DATA

Si:11.XRD II 07:49:51 02-01-1989 .EXP

INITIAL 2 θ = 10° 2 θ = 11° * DATA POINTS = 551 IT = 10 SECONDS FINAL 2 θ = 65°

COUNTS	*2 θ	d(Å)	COUNTS	*2 θ	d(Å)	COUNTS	*2 θ	d(Å)	COUNTS	*2 θ	d(Å)	COUNTS	*2 θ	d(Å)
102	35.000	2.55	89	40.000	2.25	66	45.000	2.01	87	50.000	1.82	85	55.000	1.67
98	35.100	2.55	79	40.100	2.25	48	45.100	2.01	60	50.100	1.82	29	55.100	1.67
93	35.200	2.55	51	40.200	2.24	48	45.200	2.00	50	50.200	1.82	79	55.200	1.66
93	35.300	2.54	63	40.300	2.24	67	45.300	2.00	49	50.300	1.81	79	55.300	1.66
90	35.400	2.53	59	40.400	2.23	71	45.400	2.00	47	50.400	1.81	75	55.400	1.66
89	35.500	2.53	61	40.500	2.23	83	45.500	1.99	47	50.500	1.81	79	55.500	1.65
86	35.600	2.52	62	40.600	2.22	73	45.600	1.99	49	50.600	1.80	74	55.600	1.65
91	35.700	2.51	62	40.700	2.21	67	45.700	1.98	46	50.700	1.80	72	55.700	1.65
87	35.800	2.51	67	40.800	2.21	55	45.800	1.98	44	50.800	1.80	59	55.800	1.65
84	35.900	2.50	65	40.900	2.20	53	45.900	1.98	37	50.900	1.79	72	55.900	1.64
85	36.000	2.49	59	41.000	2.20	51	46.000	1.97	41	51.000	1.79	65	56.000	1.64
90	36.100	2.49	66	41.100	2.19	56	46.100	1.97	45	51.100	1.79	64	56.100	1.64
104	36.200	2.48	63	41.200	2.19	55	46.200	1.96	40	51.200	1.78	60	56.200	1.64
130	36.300	2.47	67	41.300	2.18	52	46.300	1.96	40	51.300	1.78	62	56.300	1.63
108	36.400	2.47	64	41.400	2.18	49	46.400	1.96	37	51.400	1.78	67	56.400	1.63
92	36.500	2.46	65	41.500	2.17	48	46.500	1.95	41	51.500	1.77	60	56.500	1.63
84	36.600	2.45	64	41.600	2.17	49	46.600	1.95	40	51.600	1.77	60	56.600	1.62
83	36.700	2.45	65	41.700	2.16	46	46.700	1.94	42	51.700	1.77	59	56.700	1.62
79	36.800	2.44	65	41.800	2.15	49	46.800	1.94	44	51.800	1.76	57	56.800	1.62
83	36.900	2.43	66	41.900	2.15	47	46.900	1.94	45	51.900	1.76	55	56.900	1.62
73	37.000	2.43	75	42.000	2.15	49	47.000	1.93	45	52.000	1.75	57	57.000	1.61
79	37.100	2.42	85	42.100	2.14	46	47.100	1.93	44	52.100	1.75	54	57.100	1.61
80	37.200	2.41	99	42.200	2.14	46	47.200	1.92	49	52.200	1.75	59	57.200	1.61
86	37.300	2.41	78	42.300	2.13	47	47.300	1.92	46	52.300	1.75	46	57.300	1.61
94	37.400	2.40	66	42.400	2.13	44	47.400	1.92	47	52.400	1.74	54	57.400	1.60
91	37.500	2.40	61	42.500	2.13	45	47.500	1.91	48	52.500	1.74	55	57.500	1.60
87	37.600	2.39	55	42.600	2.12	49	47.600	1.91	45	52.600	1.74	51	57.600	1.60
80	37.700	2.38	53	42.700	2.12	49	47.700	1.90	46	52.700	1.74	52	57.700	1.60
77	37.800	2.38	51	42.800	2.11	55	47.800	1.90	52	52.800	1.73	49	57.800	1.59
69	37.900	2.37	54	42.900	2.11	53	47.900	1.90	54	52.900	1.73	52	57.900	1.59
73	38.000	2.37	48	43.000	2.10	47	48.000	1.89	54	53.000	1.73	49	58.000	1.59
73	38.100	2.36	55	43.100	2.10	42	48.100	1.89	54	53.100	1.72	47	58.100	1.59
83	38.200	2.35	50	43.200	2.09	48	48.200	1.89	56	53.200	1.72	49	58.200	1.59
80	38.300	2.35	55	43.300	2.09	45	48.300	1.88	62	53.300	1.72	47	58.300	1.59
74	38.400	2.34	51	43.400	2.08	45	48.400	1.88	65	53.400	1.71	53	58.400	1.59
64	38.500	2.34	50	43.500	2.08	44	48.500	1.88	65	53.500	1.71	49	58.500	1.59
64	38.600	2.33	53	43.600	2.07	46	48.600	1.87	72	53.600	1.71	51	58.600	1.57
61	38.700	2.32	54	43.700	2.07	44	48.700	1.87	71	53.700	1.71	46	58.700	1.57
57	38.800	2.32	50	43.800	2.07	46	48.800	1.86	71	53.800	1.70	52	58.800	1.57
61	38.900	2.31	52	43.900	2.06	42	48.900	1.86	74	53.900	1.70	49	58.900	1.57
66	39.000	2.31	55	44.000	2.06	44	49.000	1.86	75	54.000	1.70	55	59.000	1.56
75	39.100	2.30	52	44.100	2.05	46	49.100	1.85	77	54.100	1.69	52	59.100	1.56
98	39.200	2.30	50	44.200	2.05	47	49.200	1.85	71	54.200	1.69	53	59.200	1.56
92	39.300	2.29	54	44.300	2.04	45	49.300	1.85	73	54.300	1.69	55	59.300	1.56
86	39.400	2.29	57	44.400	2.04	44	49.400	1.84	75	54.400	1.69	55	59.400	1.55
58	39.500	2.29	62	44.500	2.03	47	49.500	1.84	83	54.500	1.68	50	59.500	1.55
61	39.600	2.27	66	44.600	2.03	52	49.600	1.84	95	54.600	1.68	123	59.600	1.55
69	39.700	2.27	65	44.700	2.03	69	49.700	1.83	38	54.700	1.68	112	59.700	1.55
71	39.800	2.26	62	44.800	2.02	105	49.800	1.83	92	54.800	1.67	25	59.800	1.55
74	39.900	2.26	70	44.900	2.02	114	49.900	1.83	92	54.900	1.67	30	59.900	1.54

Table 30 (continued)

X-RAY DIFFRACTION STEP SCAN DATA

P:11.190 11 07:19:51 02-01-1999 . CWP
 INITIAL $2\theta = 10^\circ$ $\Delta 2\theta = 1^\circ$ # DATA POINTS = 551 $\Delta T = 10$ SECONDS FINAL $2\theta = 45^\circ$

COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$
69	60.000	1.54	45	65.200	1.43	0	70.000	1.34	0	75.000	1.27	0	80.000	1.20
66	60.100	1.54	0	65.100	1.43	0	70.100	1.34	0	75.100	1.26	0	80.100	1.20
62	60.200	1.54	0	65.200	1.43	0	70.200	1.34	0	75.200	1.26	0	80.200	1.20
64	60.300	1.53	0	65.300	1.43	0	70.300	1.34	0	75.300	1.26	0	80.300	1.19
63	60.400	1.53	0	65.400	1.43	0	70.400	1.34	0	75.400	1.26	0	80.400	1.19
62	60.500	1.53	0	65.500	1.42	0	70.500	1.33	0	75.500	1.26	0	80.500	1.19
61	60.600	1.53	0	65.600	1.42	0	70.600	1.33	0	75.600	1.26	0	80.600	1.19
69	60.700	1.52	0	65.700	1.42	0	70.700	1.33	0	75.700	1.26	0	80.700	1.19
72	60.800	1.52	0	65.800	1.42	0	70.800	1.33	0	75.800	1.25	0	80.800	1.19
73	60.900	1.52	0	65.900	1.42	0	70.900	1.33	0	75.900	1.25	0	80.900	1.19
80	61.000	1.52	0	66.000	1.41	0	71.000	1.33	0	76.000	1.25	0	81.000	1.19
83	61.100	1.52	0	66.100	1.41	0	71.100	1.32	0	76.100	1.25	0	81.100	1.18
94	61.200	1.51	0	66.200	1.41	0	71.200	1.32	0	76.200	1.25	0	81.200	1.18
109	61.300	1.51	0	66.300	1.41	0	71.300	1.32	0	76.300	1.25	0	81.300	1.18
117	61.400	1.51	0	66.400	1.41	0	71.400	1.32	0	76.400	1.25	0	81.400	1.18
118	61.500	1.51	0	66.500	1.40	0	71.500	1.32	0	76.500	1.24	0	81.500	1.18
113	61.600	1.50	0	66.600	1.40	0	71.600	1.32	0	76.600	1.24	0	81.600	1.18
103	61.700	1.50	0	66.700	1.40	0	71.700	1.32	0	76.700	1.24	0	81.700	1.18
93	61.800	1.50	0	66.800	1.40	0	71.800	1.31	0	76.800	1.24	0	81.800	1.18
91	61.900	1.50	0	66.900	1.40	0	71.900	1.31	0	76.900	1.24	0	81.900	1.18
91	62.000	1.50	0	67.000	1.40	0	72.000	1.31	0	77.000	1.24	0	82.000	1.17
81	62.100	1.49	0	67.100	1.39	0	72.100	1.31	0	77.100	1.24	0	82.100	1.17
92	62.200	1.49	0	67.200	1.39	0	72.200	1.31	0	77.200	1.23	0	82.200	1.17
63	62.300	1.49	0	67.300	1.39	0	72.300	1.31	0	77.300	1.23	0	82.300	1.17
65	62.400	1.49	0	67.400	1.39	0	72.400	1.30	0	77.400	1.23	0	82.400	1.17
60	62.500	1.48	0	67.500	1.39	0	72.500	1.30	0	77.500	1.23	0	82.500	1.17
62	62.600	1.48	0	67.600	1.38	0	72.600	1.30	0	77.600	1.23	0	82.600	1.17
52	62.700	1.48	0	67.700	1.38	0	72.700	1.30	0	77.700	1.23	0	82.700	1.17
52	62.800	1.48	0	67.800	1.38	0	72.800	1.30	0	77.800	1.23	0	82.800	1.16
51	62.900	1.48	0	67.900	1.38	0	72.900	1.30	0	77.900	1.23	0	82.900	1.16
52	63.000	1.47	0	68.000	1.38	0	73.000	1.29	0	78.000	1.22	0	83.000	1.16
49	63.100	1.47	0	68.100	1.38	0	73.100	1.29	0	78.100	1.22	0	83.100	1.16
52	63.200	1.47	0	68.200	1.37	0	73.200	1.29	0	78.200	1.22	0	83.200	1.16
50	63.300	1.47	0	68.300	1.37	0	73.300	1.29	0	78.300	1.22	0	83.300	1.16
50	63.400	1.47	0	68.400	1.37	0	73.400	1.29	0	78.400	1.22	0	83.400	1.16
54	63.500	1.46	0	68.500	1.37	0	73.500	1.29	0	78.500	1.22	0	83.500	1.16
57	63.600	1.46	0	68.600	1.37	0	73.600	1.29	0	78.600	1.22	0	83.600	1.16
61	63.700	1.46	0	68.700	1.37	0	73.700	1.29	0	78.700	1.21	0	83.700	1.16
65	63.800	1.46	0	68.800	1.36	0	73.800	1.29	0	78.800	1.21	0	83.800	1.16
59	63.900	1.46	0	68.900	1.36	0	73.900	1.29	0	78.900	1.21	0	83.900	1.15
55	64.000	1.45	0	69.000	1.36	0	74.000	1.28	0	79.000	1.21	0	84.000	1.15
48	64.100	1.45	0	69.100	1.36	0	74.100	1.28	0	79.100	1.21	0	84.100	1.15
47	64.200	1.45	0	69.200	1.36	0	74.200	1.28	0	79.200	1.21	0	84.200	1.15
46	64.300	1.45	0	69.300	1.35	0	74.300	1.28	0	79.300	1.21	0	84.300	1.15
45	64.400	1.45	0	69.400	1.35	0	74.400	1.27	0	79.400	1.21	0	84.400	1.15
49	64.500	1.44	0	69.500	1.35	0	74.500	1.27	0	79.500	1.20	0	84.500	1.15
47	64.600	1.44	0	69.600	1.35	0	74.600	1.27	0	79.600	1.20	0	84.600	1.14
47	64.700	1.44	0	69.700	1.35	0	74.700	1.27	0	79.700	1.20	0	84.700	1.14
48	64.800	1.44	0	69.800	1.35	0	74.800	1.27	0	79.800	1.20	0	84.800	1.14
50	64.900	1.44	0	69.900	1.34	0	74.900	1.27	0	79.900	1.20	0	84.900	1.14

Table 31. Summary of x-ray diffraction data for the $\text{Ca}_2\text{g/cm}^3$ density separate from the Blount sludge P sample after heating at 573 K for 12 h.

X-RAY DIFFRACTION STEP SCAN DATA

3:1130.XRD 300C 06:21:54 04-07-1999 , EMP
INITIAL 2 θ = 5° 2 θ = 11° # DATA POINTS = 601 4T = 10 SECONDS FINAL 2 θ = 65°

COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)
41	5.000	17.66	23	10.000	9.84	21	15.300	5.90	92	20.000	4.44	71	25.000	3.55
41	5.100	17.31	29	10.100	9.75	21	15.100	5.86	79	20.100	4.41	73	25.100	3.54
43	5.200	16.98	24	10.200	9.66	22	15.200	5.82	77	20.200	4.39	91	25.200	3.53
42	5.300	16.66	26	10.300	9.59	20	15.300	5.79	72	20.300	4.37	75	25.300	3.52
39	5.400	16.35	25	10.400	9.50	24	15.400	5.75	69	20.400	4.35	72	25.400	3.50
41	5.500	16.05	22	10.500	9.42	23	15.500	5.71	77	20.500	4.33	70	25.500	3.49
40	5.600	15.77	25	10.600	9.34	23	15.600	5.68	98	20.600	4.31	65	25.600	3.48
40	5.700	15.49	28	10.700	9.26	23	15.700	5.64	125	20.700	4.29	64	25.700	3.46
40	5.800	15.22	25	10.800	9.18	20	15.800	5.60	110	20.800	4.27	67	25.800	3.45
38	5.900	14.97	24	10.900	9.11	18	15.900	5.57	70	20.900	4.25	68	25.900	3.44
44	6.000	14.72	23	11.000	9.04	22	16.000	5.53	60	21.000	4.23	73	26.000	3.42
39	6.100	14.48	24	11.100	8.96	21	16.100	5.50	58	21.100	4.21	80	26.100	3.41
38	6.200	14.24	23	11.200	8.89	21	16.200	5.47	54	21.200	4.19	106	26.200	3.40
41	6.300	14.02	24	11.300	8.82	23	16.300	5.43	56	21.300	4.17	172	26.300	3.39
39	6.400	13.80	22	11.400	8.76	22	16.400	5.40	56	21.400	4.15	352	26.400	3.37
39	6.500	13.59	26	11.500	8.69	22	16.500	5.37	57	21.500	4.13	515	26.500	3.36
40	6.600	13.38	23	11.600	8.62	23	16.600	5.34	56	21.600	4.11	299	26.600	3.35
42	6.700	13.18	24	11.700	8.56	18	16.700	5.30	53	21.700	4.09	131	26.700	3.34
41	6.800	12.99	29	11.800	8.49	26	16.800	5.27	56	21.800	4.07	95	26.800	3.32
44	6.900	12.80	25	11.900	8.43	21	16.900	5.24	55	21.900	4.05	87	26.900	3.31
40	7.000	12.62	29	12.000	8.37	23	17.000	5.21	47	22.000	4.04	85	27.000	3.30
43	7.100	12.44	29	12.100	8.31	25	17.100	5.18	46	22.100	4.02	75	27.100	3.29
41	7.200	12.27	38	12.200	8.25	23	17.200	5.15	50	22.200	4.00	74	27.200	3.29
37	7.300	12.10	31	12.300	8.19	27	17.300	5.12	52	22.300	3.98	88	27.300	3.28
39	7.400	11.94	29	12.400	8.13	26	17.400	5.09	55	22.400	3.97	96	27.400	3.25
36	7.500	11.78	27	12.500	8.08	28	17.500	5.06	50	22.500	3.95	77	27.500	3.24
39	7.600	11.62	25	12.600	8.02	29	17.600	5.03	57	22.600	3.93	76	27.600	3.23
37	7.700	11.47	22	12.700	7.96	30	17.700	5.01	57	22.700	3.91	76	27.700	3.22
37	7.800	11.32	24	12.800	7.91	28	17.800	4.98	57	22.800	3.90	78	27.800	3.21
39	7.900	11.18	24	12.900	7.86	27	17.900	4.95	54	22.900	3.88	57	27.900	3.20
41	8.000	11.04	22	13.000	7.80	28	18.000	4.92	53	23.000	3.86	59	28.000	3.18
39	8.100	10.91	22	13.100	7.75	29	18.100	4.90	49	23.100	3.85	52	28.100	3.17
35	8.200	10.77	22	13.200	7.70	25	18.200	4.87	51	23.200	3.83	53	28.200	3.16
41	8.300	10.64	22	13.300	7.65	27	18.300	4.84	59	23.300	3.81	53	28.300	3.15
41	8.400	10.52	22	13.400	7.60	27	18.400	4.82	60	23.400	3.80	54	28.400	3.14
44	8.500	10.39	25	13.500	7.55	30	18.500	4.79	57	23.500	3.78	52	28.500	3.13
44	8.600	10.27	23	13.600	7.51	28	18.600	4.77	56	23.600	3.77	49	28.600	3.12
44	8.700	10.16	21	13.700	7.46	29	18.700	4.74	53	23.700	3.75	54	28.700	3.11
39	8.800	10.04	21	13.800	7.41	29	18.800	4.72	54	23.800	3.74	52	28.800	3.10
35	8.900	9.93	23	13.900	7.37	30	18.900	4.69	53	23.900	3.72	46	28.900	3.09
33	9.000	9.82	19	14.000	7.32	33	19.000	4.67	49	24.000	3.70	47	29.000	3.08
29	9.100	9.71	22	14.100	7.28	39	19.100	4.64	58	24.100	3.69	46	29.100	3.07
30	9.200	9.60	20	14.200	7.23	45	19.200	4.62	52	24.200	3.67	46	29.200	3.06
31	9.300	9.50	22	14.300	7.19	51	19.300	4.59	55	24.300	3.66	47	29.300	3.05
32	9.400	9.40	21	14.400	7.15	43	19.400	4.57	53	24.400	3.64	55	29.400	3.04
27	9.500	9.30	22	14.500	7.10	94	19.500	4.55	53	24.500	3.63	59	29.500	3.03
28	9.600	9.21	22	14.600	7.06	121	19.600	4.53	54	24.600	3.62	59	29.600	3.02
29	9.700	9.11	20	14.700	7.02	134	19.700	4.50	70	24.700	3.60	54	29.700	3.01
29	9.800	9.02	19	14.800	6.98	117	19.800	4.48	69	24.800	3.59	55	29.800	3.00
24	9.900	8.93	21	14.900	6.94	94	19.900	4.46	52	24.900	3.57	52	29.900	2.99

Table 31 (continued)

I-RAY DIFFRACTION STEP SCAN DATA

8:11:20.19D 200C 06:21:54 04-07-1999 , 5MB

INITIAL 2 θ = 5° S2 θ = .1° # DATA POINTS = 501 IT = 10 SECONDS FINAL 2 θ = 45°

COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)	COUNTS	2 θ	d(A)
52	30.000	2.98	105	35.000	2.56	63	40.000	2.25	59	45.000	2.01	100	50.000	1.82
48	30.100	2.97	89	35.100	2.55	68	40.100	2.25	55	45.100	2.01	71	50.100	1.82
47	30.200	2.96	84	35.200	2.55	60	40.200	2.24	57	45.200	2.00	49	50.200	1.82
48	30.300	2.95	78	35.300	2.54	50	40.300	2.24	56	45.300	2.00	41	50.300	1.81
50	30.400	2.94	82	35.400	2.53	48	40.400	2.23	58	45.400	2.00	40	50.400	1.81
49	30.500	2.93	81	35.500	2.53	50	40.500	2.23	62	45.500	1.99	39	50.500	1.81
52	30.600	2.92	75	35.600	2.52	50	40.600	2.22	68	45.600	1.99	42	50.600	1.80
53	30.700	2.91	81	35.700	2.51	54	40.700	2.21	66	45.700	1.98	38	50.700	1.80
48	30.800	2.90	76	35.800	2.51	55	40.800	2.21	49	45.800	1.98	37	50.800	1.80
47	30.900	2.89	79	35.900	2.50	54	40.900	2.20	49	45.900	1.98	34	50.900	1.79
53	31.000	2.88	69	36.000	2.49	55	41.000	2.20	46	46.000	1.97	36	51.000	1.79
51	31.100	2.87	72	36.100	2.49	48	41.100	2.19	43	46.100	1.97	31	51.100	1.79
52	31.200	2.86	82	36.200	2.48	50	41.200	2.19	45	46.200	1.96	35	51.200	1.78
43	31.300	2.86	98	36.300	2.47	48	41.300	2.18	45	46.300	1.96	31	51.300	1.78
43	31.400	2.85	105	36.400	2.47	47	41.400	2.18	42	46.400	1.96	28	51.400	1.78
44	31.500	2.84	87	36.500	2.46	49	41.500	2.17	39	46.500	1.95	34	51.500	1.77
45	31.600	2.83	73	36.600	2.45	52	41.600	2.17	43	46.600	1.95	32	51.600	1.77
45	31.700	2.82	74	36.700	2.45	48	41.700	2.16	44	46.700	1.94	33	51.700	1.77
46	31.800	2.81	65	36.800	2.44	53	41.800	2.16	39	46.800	1.94	36	51.800	1.76
46	31.900	2.80	67	36.900	2.43	52	41.900	2.15	39	46.900	1.94	33	51.900	1.76
40	32.000	2.79	68	37.000	2.43	58	42.000	2.15	39	47.000	1.93	37	52.000	1.76
38	32.100	2.79	66	37.100	2.42	67	42.100	2.14	37	47.100	1.93	36	52.100	1.75
45	32.200	2.78	67	37.200	2.41	80	42.200	2.14	35	47.200	1.92	36	52.200	1.75
38	32.300	2.77	70	37.300	2.41	82	42.300	2.13	36	47.300	1.92	38	52.300	1.75
35	32.400	2.76	76	37.400	2.40	65	42.400	2.13	34	47.400	1.92	40	52.400	1.74
40	32.500	2.75	83	37.500	2.40	53	42.500	2.13	36	47.500	1.91	34	52.500	1.74
36	32.600	2.74	78	37.600	2.39	44	42.600	2.12	36	47.600	1.91	39	52.600	1.74
39	32.700	2.74	68	37.700	2.38	43	42.700	2.12	39	47.700	1.90	38	52.700	1.74
38	32.800	2.73	63	37.800	2.38	41	42.800	2.11	44	47.800	1.90	43	52.800	1.73
41	32.900	2.72	59	37.900	2.37	39	42.900	2.11	42	47.900	1.90	41	52.900	1.73
41	33.000	2.71	58	38.000	2.37	40	43.000	2.10	42	48.000	1.89	40	53.000	1.73
38	33.100	2.70	60	38.100	2.36	43	43.100	2.10	36	48.100	1.89	43	53.100	1.72
38	33.200	2.70	60	38.200	2.35	42	43.200	2.09	39	48.200	1.89	46	53.200	1.72
36	33.300	2.69	62	38.300	2.35	38	43.300	2.09	37	48.300	1.88	46	53.300	1.72
37	33.400	2.68	60	38.400	2.34	39	43.400	2.08	37	48.400	1.88	50	53.400	1.71
41	33.500	2.67	53	38.500	2.34	41	43.500	2.08	35	48.500	1.88	51	53.500	1.71
40	33.600	2.66	51	38.600	2.33	41	43.600	2.07	37	48.600	1.87	59	53.600	1.71
38	33.700	2.66	51	38.700	2.32	42	43.700	2.07	36	48.700	1.87	84	53.700	1.71
46	33.800	2.65	47	38.800	2.32	39	43.800	2.07	38	48.800	1.86	55	53.800	1.70
49	33.900	2.64	51	38.900	2.31	39	43.900	2.06	36	48.900	1.86	72	53.900	1.70
49	34.000	2.63	51	39.000	2.31	44	44.000	2.06	37	49.000	1.86	67	54.000	1.70
61	34.100	2.63	59	39.100	2.30	44	44.100	2.05	39	49.100	1.85	62	54.100	1.69
73	34.200	2.62	58	39.200	2.30	39	44.200	2.05	36	49.200	1.85	65	54.200	1.69
93	34.300	2.61	81	39.300	2.29	41	44.300	2.04	35	49.300	1.85	66	54.300	1.69
100	34.400	2.60	66	39.400	2.29	39	44.400	2.04	40	49.400	1.84	70	54.400	1.69
112	34.500	2.60	53	39.500	2.29	44	44.500	2.03	41	49.500	1.84	73	54.500	1.68
121	34.600	2.59	48	39.600	2.27	46	44.600	2.03	43	49.600	1.84	81	54.600	1.68
132	34.700	2.58	48	39.700	2.27	46	44.700	2.03	48	49.700	1.83	85	54.700	1.68
136	34.800	2.58	56	39.800	2.26	48	44.800	2.02	69	49.800	1.83	85	54.800	1.67
126	34.900	2.57	55	39.900	2.26	50	44.900	2.02	96	49.900	1.83	79	54.900	1.67

Table 31 (continued)

1- θ Y DIFFRACTION STEP SCAN DATA

B:1130.TRD 300C 06:21:54 04-07-1999 SMP

INITIAL $2\theta = 5^\circ$ $\delta 2\theta = .1^\circ$ # DATA POINTS = 601 $ST = 10$ SECONDS FINAL $2\theta = 45^\circ$

COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$	COUNTS	2θ	$d(\text{\AA})$
76	55.000	1.67	73	60.000	1.54	45	65.000	1.43	0	70.000	1.34	0	75.000	1.27
78	55.100	1.67	61	60.100	1.54	0	65.100	1.43	0	70.100	1.34	0	75.100	1.26
81	55.200	1.66	58	60.200	1.54	0	65.200	1.43	0	70.200	1.34	0	75.200	1.26
70	55.300	1.66	62	60.300	1.53	0	65.300	1.43	0	70.300	1.34	0	75.300	1.26
63	55.400	1.66	58	60.400	1.53	0	65.400	1.43	0	70.400	1.34	0	75.400	1.26
70	55.500	1.65	59	60.500	1.53	0	65.500	1.42	0	70.500	1.33	0	75.500	1.26
64	55.600	1.65	60	60.600	1.53	0	65.600	1.42	0	70.600	1.33	0	75.600	1.26
63	55.700	1.65	59	60.700	1.52	0	65.700	1.42	0	70.700	1.33	0	75.700	1.26
60	55.800	1.65	61	60.800	1.52	0	65.800	1.42	0	70.800	1.33	0	75.800	1.25
57	55.900	1.64	64	60.900	1.52	0	65.900	1.42	0	70.900	1.33	0	75.900	1.25
54	56.000	1.64	69	61.000	1.52	0	66.000	1.41	0	71.000	1.33	0	76.000	1.25
54	56.100	1.64	70	61.100	1.52	0	66.100	1.41	0	71.100	1.32	0	76.100	1.25
61	56.200	1.64	82	61.200	1.51	0	66.200	1.41	0	71.200	1.32	0	76.200	1.25
53	56.300	1.63	97	61.300	1.51	0	66.300	1.41	0	71.300	1.32	0	76.300	1.25
57	56.400	1.63	102	61.400	1.51	0	66.400	1.41	0	71.400	1.32	0	76.400	1.25
53	56.500	1.63	104	61.500	1.51	0	66.500	1.40	0	71.500	1.32	0	76.500	1.24
55	56.600	1.62	106	61.600	1.50	0	66.600	1.40	0	71.600	1.32	0	76.600	1.24
54	56.700	1.62	97	61.700	1.50	0	66.700	1.40	0	71.700	1.32	0	76.700	1.24
52	56.800	1.62	94	61.800	1.50	0	66.800	1.40	0	71.800	1.31	0	76.800	1.24
50	56.900	1.62	83	61.900	1.50	0	66.900	1.40	0	71.900	1.31	0	76.900	1.24
47	57.000	1.61	85	62.000	1.50	0	67.000	1.40	0	72.000	1.31	0	77.000	1.24
46	57.100	1.61	81	62.100	1.49	0	67.100	1.39	0	72.100	1.31	0	77.100	1.24
48	57.200	1.61	74	62.200	1.49	0	67.200	1.39	0	72.200	1.31	0	77.200	1.23
48	57.300	1.61	70	62.300	1.49	0	67.300	1.39	0	72.300	1.31	0	77.300	1.23
47	57.400	1.60	66	62.400	1.49	0	67.400	1.39	0	72.400	1.30	0	77.400	1.23
47	57.500	1.60	61	62.500	1.48	0	67.500	1.39	0	72.500	1.30	0	77.500	1.23
47	57.600	1.60	54	62.600	1.48	0	67.600	1.38	0	72.600	1.30	0	77.600	1.23
44	57.700	1.60	51	62.700	1.48	0	67.700	1.38	0	72.700	1.30	0	77.700	1.23
41	57.800	1.59	53	62.800	1.48	0	67.800	1.38	0	72.800	1.30	0	77.800	1.23
46	57.900	1.59	50	62.900	1.48	0	67.900	1.38	0	72.900	1.30	0	77.900	1.23
41	58.000	1.59	46	63.000	1.47	0	68.000	1.38	0	73.000	1.29	0	78.000	1.22
42	58.100	1.59	48	63.100	1.47	0	68.100	1.38	0	73.100	1.29	0	78.100	1.22
43	58.200	1.58	44	63.200	1.47	0	68.200	1.37	0	73.200	1.29	0	78.200	1.22
43	58.300	1.58	47	63.300	1.47	0	68.300	1.37	0	73.300	1.29	0	78.300	1.22
40	58.400	1.58	49	63.400	1.47	0	68.400	1.37	0	73.400	1.29	0	78.400	1.22
41	58.500	1.58	47	63.500	1.46	0	68.500	1.37	0	73.500	1.29	0	78.500	1.22
37	58.600	1.57	47	63.600	1.46	0	68.600	1.37	0	73.600	1.29	0	78.600	1.22
46	58.700	1.57	54	63.700	1.46	0	68.700	1.37	0	73.700	1.28	0	78.700	1.21
44	58.800	1.57	60	63.800	1.46	0	68.800	1.36	0	73.800	1.28	0	78.800	1.21
47	58.900	1.57	58	63.900	1.46	0	68.900	1.36	0	73.900	1.28	0	78.900	1.21
48	59.000	1.56	51	64.000	1.45	0	69.000	1.36	0	74.000	1.28	0	79.000	1.21
38	59.100	1.56	46	64.100	1.45	0	69.100	1.36	0	74.100	1.28	0	79.100	1.21
42	59.200	1.56	45	64.200	1.45	0	69.200	1.36	0	74.200	1.28	0	79.200	1.21
48	59.300	1.56	44	64.300	1.45	0	69.300	1.35	0	74.300	1.28	0	79.300	1.21
54	59.400	1.55	44	64.400	1.45	0	69.400	1.35	0	74.400	1.27	0	79.400	1.21
57	59.500	1.55	40	64.500	1.44	0	69.500	1.35	0	74.500	1.27	0	79.500	1.20
68	59.600	1.55	45	64.600	1.44	0	69.600	1.35	0	74.600	1.27	0	79.600	1.20
99	59.700	1.55	44	64.700	1.44	0	69.700	1.35	0	74.700	1.27	0	79.700	1.20
99	59.800	1.55	43	64.800	1.44	0	69.800	1.35	0	74.800	1.27	0	79.800	1.20
89	59.900	1.54	47	64.900	1.44	0	69.900	1.34	0	74.900	1.27	0	79.900	1.20