PHOSPHORUS FRACTIONATION OF SOME CALCAREOUS SOILS OF AFGHANISTAN AND OKLAHOMA

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CHAPTER I

INTRODUCTION

Phosphorus is a major nutrient occurring in most plants in quantities that are much smaller than those of nitrogen and potassium. Only a small percentage of fertilizer phosphate will be used by plants while a major portion soon becomes "fixed" in the soil.

Availability of phosphorus in the soil is dependent on stage of soil weathering, pH, organic matter content, soil texture, percentage of calcium carbonate and percentage of hydrated iron and aluminum oxides. Under acidic conditions where the exchange complex contains ionized aluminum and iron, these ions combine with phosphate to form insoluble compounds of aluminum and iron. The large amount of soluble and exchangeable iron and aluminum in acid soils means high "fixation" of phosphorus. "Phosphate fixation" in alkaline and calcareous soil is usually due to the formation of calcium phosphate. The phosphate ion may form a clay-calcium-phosphate complex. It has also been suggested that phosphorus may form carbonate-phosphate complexes rather than simple tricalcium phosphate.

Soil phosphorus may be broadly classified into organic and inorganic forms. The inorganic forms are more related to plant availability and they may be grouped into the chemical forms of aluminum phosphate, iron phosphate, calcium phosphate and reductant soluble phosphate (25). Phosphate fertilizer added to the soil is changed into all of the four forms of phosphate not only in acid soils but also in neutral soils. According to the principle of the solubility product, calcium phosphate is more soluble than the other forms of phosphate; therefore, it is more easily removed by crops or is easily shifted to the less soluble forms.

Total phosphorus supply in most soils appears to be adequate to supply crop needs for many years, but the major portion of the phosphorus compounds in soil are not available for the crop plant.

Many soils of the world are calcareous and the phosphorus chemistry of these soils has not been as intensively investigated as the noncalcareous acid soils. Most of the important agricultural soils of Afghanistan are calcareous and for this reason it was decided that a study of calcareous soils to learn more about their phosphorus chemistry would be remunerative.

The objectives of this study are as follows:

1. To study the extent and rate of conversion of ammonium phosphate into various phosphorus compounds both in the greenhouse and under a constant temperature condition.
2. To relate the amount of soil phosphorus extracted by several procedures to yield, aluminum phosphate, easily soluble phosphate, calcium phosphate and available phosphate.
3. To study the mineralogical composition of these calcareous soils.

It was hypothesized that applied phosphorus fertilizers will greatly decrease in solubility after 24 hours of contact with the soil and will be converted to aluminum phosphate but after 10 and 30 days calcium phosphate content will begin to increase and aluminum phosphate concentration will decrease. It was also hypothesized that the availability of fertilizer phosphorus to plants after one, 10 and 30 days of incubation will not be significantly different from each other.

CHAPTER II

REVIEW OF LITERATURE

Total supply of phosphorus in many soils might be adequate to take care of crop needs for many years but a large portion of phosphorus in the soil may not be available. Different forms of phosphorus are different in their availability to plants.

Fractionation of Soil Phosphorus

Fractionation of inroganic phosphorus in the soil has recently received extensive study in soil fertility and soil genesis. The only important difference between the different methods of fractionation lies in the type and concentration of extraction solutions.

Dean (34) was one of the first investigators to attempt a complete systematic fractionation of soil phosphorus. He found that many soils contained a large amount of insoluble phosphorus. He divided the soil phosphorus compounds into three fractions:

1. Organic phosphorus soluble in sodium hydroxide.
2. Inorganic phosphorus dissolved by extraction with sodium hydroxide followed by an acid extraction.
3. Insoluble phosphorus compounds.

His initial extraction solution was 0.25 N sodium hydroxide with which soluble or exchangeable calcium and magnesium interferred in the extraction of phosphorus from alkaline soils. To overcome this Ghani

(47) modified the procedure of Dean by extracting first with 0.2 N acetic acid until the phosphorus extract was very low or nil in basic ions and finally with 2 N sulfuric acid. Ghani separated phosphates into the following fractions:

1. Mono-, di- and tricalcium phosphate soluble in acetic acid.
2. Iron and aluminum phosphate soluble in alkalies.
3. Total organic phosphate (nucleic acid, phytin, licithin, etc.) also soluble in alkalies.
4. Phosphates of apatite nature, soluble in sulfuric acid.
5. Insoluble phsophate.

Iron and aluminum fractions included adsorbed and surface precipitated phosphorus. Ghani (48) further modified his procedure by adding 8-hydroxyquinoline to the acetic acid.

Fisher and Thomas (41) developed a rapid extraction method to estimate the phosphorus present in the following three groups of materials:

1. Amorphous and finely divided cyrstalline phosphates of calcium, magnesium and manganese.
2. Amorphous phosphates of aluminum and iron.
3. Phosphorus adsorbed upon hydroxides and present in the form of apatite.

They used two extracting solutions, 0.002 N sulfuric acid and 0.3 per cent solution of potassium acid sulfate.

Ghani and Islam (49) have shown that the addition of either one per cent of hydroxyquinoline or 0.5 per cent of selenious acid to acetic acid almost inhibited the adsorption of phosphorus by iron and aluminum hydroxide films. Williams (145) modified the procedure of Ghani

(48) by extraction with 2.5 per cent acetic acid and one per cent hydroxyquinoline and 0.1 N sodium hydroxide. These procedures mentioned so far did not differentiate aluminum phosphate from iron phosphate. Both Ghani (48) and Williams (145) used an acid extraction before alkali extraction. Therefore, they may not have obtained a complete separation of calcium phosphate from the iron and aluminum phosphates.

Bhangoo and Smith (11) fractionized phosphorus into:

1. Calcium phosphate soluble in 0.1 N hydrochloric acid.
2. Adsorbed phosphorus, soluble in cold alkali.
3. Phosphorus soluble in hot alkali after the removal of 1 and 2 and this extraction included iron and aluminum phosphates.
4. Organic phosphorus.

According to Chang and Jackson (24) inorganic phosphorus in the soil can be divided into four main groups: calcium phosphate, aluminum phosphate, iron phosphate and reductant soluble phosphate extracted after the removal of the first three forms. Calcium phosphate exists mainly as apatite, but dicalcium, monocalcium and octacalcium phosphates also exist in small amounts as transitional forms.

The methods presently receiving the widest use for fractionation of inorganic phosphorus are those of Chang and Jackson or a modification of their procedure. Chang (25) after reviewing the criticisms of other investigators made the following modifications:

1. Extraction of aluminum phosphate with 0.5 N ammonium fluoride at a pH of 7 for one hour for paddy soils and extraction at a pH of 8.2 for one hour for upland soils.
2. Extraction of iron phosphate with 0.1 N sodium hydroxide for nine to 12 hours.

3. Extraction of calcium phosphate with 0.5 N sulfuric acid for one hour after the extraction of occluded phosphate.

This modification differs from that of Chang and Jackson only in the order of the different forms and the pH of the ammonium fluoride solution used to extract aluminum phosphate.

Glenn, et *al*. (51) studied the selectivity of different extraction solutions used by Chang and Jackson (25) for fractionation of discrete compounds in the soil by using natural soil samples, and synthetic and natural phosphate minerals. In the modifed flow-sheet proposed, aluminum-bound phosphate is extracted from soils with a minimum extraction of iron phosphate by use of 0.5 N ammonium fluoride of pH 8 to 8.5 instead of pH 7. Iron phosphate is extracted with 0.1 N sodium hydroxide after extraction of aluminum phosphate and the extraction was found to be complete during a nine-hour or longer extraction period. The reductant-soluble iron phosphate and occluded aluminum phosphate are extracted after sodium hydroxide extraction of iron phosphate and before extraction of calcium phosphate with 0.5 N sulfuric acid. (This reagent was otherwise found to extract appreciable amounts of occluded iron and aluminum phosphates.) Dithionite-citrate and 0.5 N ammonium fluoride at pH 8 to 8.5 extracted negligible amounts of calcium phosphate from natural soil containing much calcium phosphate, indicating a very large particle size for the latter.

Petersen and Corey (103) described a modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. They stated that the use of constant suction pipettes, two molybdophosphoric reductants with different sensitivities, and isobutyl alcohol extraction for the determination of reductant-soluble phosphates greatly increased the speed of phosphate determinations.

Williams, et al. (146) fractionated inorganic phosphorus in the soil by using a modified Chang and Jackson procedure (25). Their second acid treatment increased the amount of extracted calcium phosphate. Further modification simplified the colorimetric determinations of inorganic phosphate in several of the extracts. Their final procedure is outlined in Table I. They stated that phosphate sorbed during the fluoride extraction was usually completely recovered in the succeeding sodium hydroxide extraction. This enabled mutually compensating corrections to be applied to the ammonium fluoride phosphorus and the first sodium hydroxide phosphorus values.

Mehta, et al. (92) developed a procedure for determining organic phosphorus in soils which consisted of successive extraction with concentrated hydrochloric acid and 0.5 N sodium hydroxide at room temperature, and 0.5 N sodium hydroxide at 90 C. The difference in content of inorganic and total phosphorus in the combined extract was taken as the total organic phosphorus in the soil.

Russell (114) stated that various chemical methods have been used for determining the properties of the principal inorganic phosphates present in the soil and these are based on the following assumptions:

1. Dilute acid dissolves all calcium phosphates present except the apatites.
2. Concentrated solution of acids dissolve apatite.
3. Fluorides displace phosphate from the surface of hydrated aluminum oxide and subsequent treatment with alkali displaces it from the surface of hydrated ferric oxides.

TABLE I

PROCEDURE AND NOMENCLATURE USED FOR THE FRACTIONATION OF SOIL INORGANIC PHOSPHATE

Stage No.	Treatment	Name of fraction
1	0.5 N NH_4Cl for 30 minutes.	Easily soluble P
2	0.5 N NH_4F pH 8.2 for 24 hours with correction for resorption of phosphate from solution during extraction.	NH_4F-P
3	0.1 N NaOH and 1 M NaCl for 17 hours.	First NaOH-P
4	Extraction with dithionite-citrate-bicarbonate.	Reductant soluble P
5	1 M NaOH for 17 hours.	Second NaOH-P
6	0.5 N HCl for one hour followed by 1 N HCl for four hours if first HCl-P $>$20 ppm.	First HCl-P Second HCl-P Sum = acid extractable Ca-P
I	Ignition at 550 C for one hour followed by 1 N HCl for 16 hours.	Residual organic P
7	Na_2CO_3 fusion.	Residual inorganic P

4. Reducing solutions containing an iron chelating agent will remove phosphate present below the surface of iron oxide films and in the particular phosphate present in nodules of hydrated oxides.

Distribution of Phosphorus

Total and available phosphorus have been extensively studied. Little work has been done on the distribution of the various discrete chemical forms of inorganic phosphate. The distribution of various forms of inorganic phosphorus in soils is affected by the activities of different ions in the soil, pH, age, drainage, fertilizer practices and mineralogical nature.

Hamilton and Lessard (53) concluded that subsurface samples were more highly saturated with bases than the surface soil samples. The contribution of calcium phosphate to total phosphates increased from 41.1 per cent in the surface layer to 88.4 per cent in the 18 to 24 inch layer. Aluminum phosphate was higher in the 0 to 6 inch layer and accounted for five per cent or less of the phosphorus in the subsurface layers. Iron phosphate concentration was negligible for all layers. Residual phosphates formed as a substantial percentage of the total phosphorus in the surface soil. Organic phosphorus decreased with depth into the soil profile.

Chang and Jackson (24) stated that the relative amounts of the four inorganic phosphate fractions in various layers of two soil profiles studied were, in increasing order of abundance; aluminum phosphate, calcium phosphate, iron phosphate and reductant-soluble iron phosphate, but the third layer of Kirwin profile was an exception and in that horizon the amount of calcium phosphate was higher than both iron phosphate and reductant-soluble iron phosphate. All of these four forms of inorganic phosphate were in general higher in the subsoil than in the surface soil.

Williams and Walker (147) fractionated 62 horizons from 16 New Zealand basaltic soil profiles varying widely in degree of weathering and leaching. They concluded that as the degree of weathering of the profile increased acid extractable calcium phosphate declined rapidly to zero, ammonium fluoride phosphate increased to maximum values and then declined.

Weir (139) stated that occluded iron phosphate accounted for 46 to 75 per cent of the total fractionated phosphorus in 12 soils representative of the major agricultural soils of Trinidad. The 0.002 N sulfuric acid extractable phosphate test was well correlated with calcium phosphate but not with the iron or aluminum phosphate content.

Ghobdian (50) found that about 60 to 90 per cent of inorganic phosphorus in the soil occurred as calcium phosphate while iron phosphate made up four to 45 per cent, and up to 10 per cent of these were occluded phosphate.

McGeorge (89) concluded that sandy soils were lower in electrodialyzable phosphate than loamy or clay loams. Non-calcareous and acid soils were usually lower in electrodialyzable phosphate than calcareous soils. He believed this was due to the fact that acid soils have been largely depleted of their phosphate because phosphates are more soluble at acid reactions.

Shaimukhy (121) showed that in the upper humus horizon 45 to 75 per cent of the total phosphorus was organic phosphorus. Aluminum, iron and calcium phosphate was not higher than 25 per cent of the total phosphorus. The concentration of total phosphorus decreased with soil depth and calcium phosphate increased with depth.

Aldrich and Buchanan (1) and Walker and Adams (136) found that the total phosphorus content of the soil was closely related to the phosphorus content of the parent materials.

Bates and Baker (6) determined the distribution of total, total organic, total inorganic and extractable phosphorus for samples from a Nigerian forest profile. For the sand fraction and aggregated fraction of the fine earth, they concluded that soil phosphorus was accumulated in the surface soil. Below two inches there was a marked reduction in the content of total phosphorus reflecting a large decrease in the amount of organic phosphorus. Thereafter the total phosphorus was fairly constant down the depth of the profile. Only the surface soil contained an appreciable amount of phosphorus soluble in acetic acid.

Williams and Saunders (145) stated that total soil phosphorus decreased downward and then increased in the lowest horizon in the soils they studied. They concluded that in general, poor drainage was reflected in:

1. Much lower total organic phosphorus, lower total phosphorus, but rather higher inorganic phosphorus.
2. A very abrupt fall in the organic phosphorus with depth.
3. Higher phosphorus content for sands, but much lower contents in clays.
4. Higher amount and proportions of the soil inorganic phosphorus was present as sand correspondingly lower amounts and proportion as clays.

5. Higher acid-soluble inorganic phosphorus in the soil reflecting both the higher amounts and higher solubility of the phosphorus in the sands.
6. Lower content of hydrosulfite-extractable iron in the upper horizons but higher contents in the gleyed subsoils.

Nye and Bertheux (98) stated that in thoroughly leached soils the acid-soluble phosphate decreased sharply with depth and the alkali-soluble phosphorus decreased rather more slowly with depth.

Patel and Mehta (101) stated that in six typical soil profiles of Gujarat the top soil layers were richer than the subsoil in total and available phosphorus.

Bauwin and Tyner (7) studied the distribution of non-extractable (insoluble) phosphorus in the soil horizons of four Illinois soil type sequences developed on Peorian loess. The relative portion of the total soil phosphorus occurring in non-extractable form in the various horizons was $B > A > C$. No relation was found between the degree of soil maturity and level of non-extractable phosphorus for the A horizons, but a very significant increase in the non-extractable phosphorus of the B horizons was found to occur with increasing soil maturity. This was particularly true from the early through the medial stages of soil development. They also concluded that the accumulation of non-extractable phosphorus was associated with the soil development process.

Available Phosphorus in the Soil

Methods of determination of plant available phosphorus have been discussed in the literature for more than a century. Initially, the soil chemists looked for a chemical that would extract the same amount of phosphorus from the soil as the plant roots, but they did not consider the difference between different plants to extract phosphorus from the soil. A soil may contain a large amount of total phosphorus but a very small amount of available phosphorus. The form of phosphorus in the soil is an important factor in availability of phosphorus for plant growth.

In the methods of determining available phosphorus in the soils not only the extraction is important by itself but it should be accompanied by an accurate reading of phosphate in the extract. Tisdale and Nelson (130) defined available phosphorus as the sum of water-soluble and citrate-soluble phosphorus in the soil.

Petter and Averitt (104), Staddart (126) and Frap (42) developed a 0.5 N nitric acid method for extraction of available phosphorus. Truog (132) later suggested 0.002 N sulfuric acid buffered with ammonium sulfate at a pH of 3 and a ratio of extraction of 200 ml of solvent to one gram of soil. Morgan (94) used a 10 per cent sodium acetate solution to extract available phosphorus from the soil.

McGeorge (88) suggested a carbonic acid extraction for alkaline Arizona soils, because this acid was weak and was similar to the mechanism he believed was operative at plant root surfaces. Bray (14) developed a test for extraction of available phosphorus for Illinois soils. Bray (15) also developed rapid tests for measuring and differentiation between adsorbed and acid-soluble forms of phosphorus. Finally, Bray and Kurtz (16) introduced their #1 and #2 methods. The extracting solution in the #1 method was made up of 0.03 N ammonium fluoride and 0.02 N hydrochloric acid while in the #2 method the concentration of ammonium fluoride remained the same as #1 but the concentration of hydrochloric acid was increased to 0.1 N. They also stated that their methods will need to be modified if appreciable amounts of arsenic or quantities of iron much over 15 ppm are extracted.

Olsen, et _al_. (100) developed a method in which the extraction solution was 0.5 N sodium bicarbonate and applicable for most calcareous or alkaline soils. Watanabe and Olsen (137) finally recommended the Murphy and Riley (96) procedure which used a single reagent for determining phosphorus. They also reported that this method was accurate for determining phosphorus in the soil extract. The method is based on the reduction of the ammonium molybdi-phosphate complex by ascorbic acid in the presence of antimony. The color produced is stable for 24 hours and it is less subject to interfering substances than are other methods involving reduction of stannous chloride. A disadvantage of ascorbic acid as the reductant has been that certain phosphorus compounds through the hydrolysis reaction may produce inorganic orthophosphate during the long period required for development of the molybdenum blue color. This tends to give higher values in solutions enriched with the dissolved organic phosphate. The use of the Murphy and Riley (96) method on the sodium bicarbonate extract eliminated the use of carbon black in the determination of soluble phosphorus by the sodium bicarbonate procedure.

Saunder (117) introduced a method in which the extracting solution was hot 0.1 N sodium hydroxide for extracting available phosphorus from tropical soils, particularly red soils, where phosphorus was present in strongly sorbed forms. Watanabe and Olsen (137) slightly modified the procedure of Truog and Meyer (133), and Dickman and Bray (35), however, this did not change the procedure of Pons and Guthrie (108) whc concluded that phosphorus determination in water extracts of soil may be inaccurate due to the interference from dissolved organic matter or some material sorbed by carbon black. Watanabe and Olsen (137) also stated that for studies which involve large soil water ratios or low concentrations of phosphorus the isobutyl alcohol method of concentration by Pons and Guthrie (108) is recommended. They also stated that the isobutyl alcohol method is suitable but undesirable for routine procedure. Stannous chloride has not been entirely satisfactory for reducing the molybdi-phosphate complex because organic matter in the soil extract causes instability of the blue color, but ascorbic acid as a reducing agent appears to overcome these objections.

Ohiari (99) and Pratt and Garber (109) were not able to find a significant correlation between calcium phosphate and the Bray and Kurtz #1 method in relation to available phosphate. They also stated that calcium phosphate as measured by the Chang and Jackson (25) method was not related to available phosphorus as indicated by the Bray and Olsen tests. However, Ohiari (99) found a significant correlation between aluminum phosphate and the Bray and Kurtz #1 test, but no significant correlation with iron and organic phosphate in Oklahoma soils. Benavides (9) on the other hand, found a significant correlation between the Bray and Kurtz #1 available phosphorus and calcium phosphate, iron phosphate and organic phosphate but no significant correlation with aluminum phosphate.

Weir (140) concluded that the 0.002 N sulfuric acid extractable phosphorus test was well correlated with the calcium phosphate content but not with the iron phosphate or aluminum phosphate contents, Caldwell (17) used the Murphy and Riley method on sodium bicarbonate extracts with a favorable result in estimating the phosphorus requirement of wheat soils. Experimental results (33) suggested that phosphorus fractions associated with aluminum in acid pasture soils under clover were more available than those associated with iron and organic phosphorus.

Plessis and Burger (107) extracted soil samples with eight reagents for available phosphorus. They found a relationship between plant phosphorus and aluminum phosphate, iron phosphate and calcium phosphate. Weir (140) on the other hand, placed procedures in the order of decreasing precision of estimating the available phosphorus in the soil as follows: first, 0.002 N sulfuric acid method by Truog; second, 0.1 N hydrochloric acid method of Bray; third, 0.5 N sodium bicarbonate method by Olsen, et al.; fourth, 10 per cent sodium acetate method of Morgan; and fifth, the 0.1 N sodium hydroxide method of Saunder.

Dean (34) found that occluded phosphorus in the soil was not changed by long continued use of phosphorus fertilizers. He stated that calcium, iron and aluminum phosphate fractions were related to available phosphorus. Thomas (129) found that plant uptake of residual phosphorus in calcareous soil was significantly correlated to the phosphorus extracted in sodium bicarbonate and dilute acid ammonium fluoride.

Khanna (70) stated that soil test values obtained with the Bray and Kurtz method #2 had a significant positive relationship with calcium phosphate fraction while the Olsen, et al. (100) method had a correlation with "saloid-bound" phosphorus, and the aluminum and iron phosphate fractions. Significant negative relationships indicated that calcium phosphate increased or decreased at the expense of aluminum phosphate or iron phosphate by fertilization and cropping.

Jackson, et *al*. (64) extracted available soil phosphorus with 0.025 N hydrochloric acid and 0.03 N ammonium fluoride (modified Olsen procedure). The extracted phosphorus was correlated with the phosphorus uptake by oats and clovers in the greenhouse and with the phosphorus uptake and yield of lucerne in the field. They concluded that no method was found to be significantly superior to any other in predicting the phosphorus status of the soil. However, the Olsen method was the least affected by soil pH and generally yielded the highest correlation coefficient. Kaila (67) compared the Bray #1 test and the Olsen test with acetic acid extraction in 346 mineral soils. He determined the inorganic phosphorus fraction extracted by ammonium chloride, ammonium fluoride, sodium hydroxide and sulfuric acid and concluded that the Bray #1 test gave higher average significant correlation values in sandy soils than in the clays; the acetic acid test did the reverse. The Bray #1 and Olsen tests on the average extracted equal amounts of phosphorus and were closely correlated with each other and least closely with acetic acid values. Chang (20) reported that in eight paddy soils representing the main types of Taiwan soils the availability of aluminum phosphate, iron phosphate and organic phosphorus decreased while that of calcium phosphate tend to be increased with decreasing pH. Occluded phosphorus was unavailable in these soils. Availability of soil aluminum phosphate to rice was higher than that of added aluminum phosphate and the availability of soil calcium phosphate was lower than tricaclium phosphate. Availability of organic phosphorus was low in acid soils but higher in neutral soils.

Islam and Rahman (62) suggested that for tropical soils or red earths with high phosphate adsorption capacity the availability of soil phosphorus to the plant was controlled by the degree of phosphate saturation of the soil. Determination of the degree of phosphate saturation would give a better measure of soil phosphate status than other methods.

Stroehlein, et al. (128) compared ammonium polyphosphate to ammonium orthophosphate with successive crops grown on four calcareous soils in the greenhouse and found that ammonium polyphosphate was a suitable phosphorus source for barley and tomatoes growing in calcareous soils. Dutil and Duman (37) applied basic slag, superphosphate and ground rock phosphate to calcareous soils in pot experiments. They kept the pots free from vegetation for one year and then extracted phosphorus with 0.5 N sodium bicarbonate, 0.005 N sulfuric acid, and 0.5 N ammonium oxalate. They found that extractable phosphorus decreased very rapidly with superphosphate and basic slag for the first four months and then very slowly with little difference noted between the two fertilizer forms at the end of the experiment. They also stated that in a standard biological test the uptake of phosphorus by wheat was slightly better from basic slag than from the superphosphate treatment, and with rock phosphate phosphorus uptake was similar to that from untreated soils. High rates of rock phosphate reduced both yield and phosphorus uptake.

Ensminger (39) stated that applied phosphorus accumulated in the soil and the extent of accumulation was in proportion to the amount applied. The yield of cotton, vetch and ladino clover showed the effect of residual fertilizer phosphorus and was directly related to the fertilization history.

Rogers (113) found that the eroded soil material from corn fields was richer in nitrogen and phosphorus than the total soil. Bar, et al. (5) concluded that the rate of decreasing availability of phosphorus on addition of calcium carbonate was higher in soils of low phosphorus content than those richer in phosphorus, and soil treatment with calcium sulfate enhanced the decrease in phosphate solubility.

Hinkle (57) found by chemical analysis that calcareous soils are well supplied with total phosphorus, but the amount available to crops during the growing season is often very small. McGeorge (89) also stated that at alkaline reactions the soil requires more soluble phosphate to supply the needs of the crop than do neutral or slightly acid soils. In acid soils available phosphorus is present in a large part as the H_2PO_4 ion while in alkaline soils HPO_4 is the important phosphate ion.

Midgley (93) stated that the lack of phosphorus availability in alkaline calcareous soils seems to be due to a carbonate phosphate complex rather than simple tricalcium phosphate. He also stated that the silicate ion is capable of replacing phosphorus. Weir and Sopur (141) stated that the phosphate activity in calcareous soil was governed only by such compounds as dicalcium phosphate and octacalcium phosphate which dissolve or precipitate fast enough to affect the phosphate solution concentration, because hydroxyapatite attains solution equilibrium so slowly that changes imposed on a soil which would necessitate either dissolution or precipitation of this phosphate compound will require a considerable period of time for any new equilibrium to be established. Thus solubility measurements of phosphate reactions in calcareous soil very often do not correspond to any known solubility product.

Gracio and Lima (52) applied P^{32} alone or in combination with oxalic acid, EDTA, starch, starch-carbonate, calcium carbonate or soluble glass. They grew a test crop for 37 days in pots. They concluded that with the exception of starch all treatments tended to increase the uptake from the soil phosphorus supply but the increase was significant only with EDTA, calcium carbonate and soluble glass. Only soluble glass was effective in promoting phosphorus uptake from fertilizer phosphorus. Increasing the rate of added organic substance decreased the plant dry weight and phosphorus uptake. They also stated that dry weight of plants from silicate-treated pots compared favorably with that of plants from pots pretreated with large amount of unlabelled superphosphate.

Lewis, et al. (79) concluded that in general the salts of calcium which have a common ion with phosphate fertilizer compounds caused the greatest fixation of both fertilizer and soil phosphate. Sodium salts on the other hand increased the availability of both fertilizer and soil phosphate. Magnesium salts were intermediate between calcium and sodium in their release of soil phosphate and fixation of fertilizer phosphate. In general, increasing the rate of salt application decreased the availability of fertilizer and soil phosphate. Increasing the rate of sodium carbonate, however, increased both available soil and fertilizer phosphate.

Lutz and Rich (84) measured the effect of 13 salts and urea on availability of phosphorus in monocalcium phosphate tagged with P^{32}, on the yield of oats in the greenhouse. They measured the yield and percentage fertilizer phosphorus in the plant and then calculated the amount of phosphorus removed. They concluded that the salts did not increase the percentage of water-soluble phosphorus in the soil but in general the salts increased the amount of phosphorus removed from the soil by the Bray and Kurtz #1 method. Where lime was applied, with a few exceptions, salts increased the availability of phosphorus applied to the plants in the greenhouse and field experiments.

Phosphorus Fixation and Mechanism

Only a small portion of the phosphorus applied to soil will be removed in the harvested portion of the crops or lost by leaching and volatilization. The major part of the added phosphorus fertilizer soon becomes "fixed". The clay fraction of the soil is responsible for this fixation but the exact mechanism by which clay is able to fix phosphorus is not known. Tisdale and Nelson (130) defined fixation of phosphorus as a reduction in the solubility of phosphorus added. Phosphorus fixation in the soil is dependent on pH value, content of clay and nature and amount of exchangeable cations present in the exchange complex (131).

Bear (8) indicated that the retention of phosphorus may be due to the result of a reaction between free oxides of iron and aluminum or formation of insoluble salts of iron and aluminum or calcium as well as fixation by clay minerals. Harter (54) showed that the sediments of a eutrophic lake were capable of adsorbing a large amount of phosphorus from water.

Coleman, et _al._ (30) found a significant correlation between adsorbed phosphorus and the exchangeable aluminum content of the soil. They also stated that the removal of exchangeable aluminum reduced phosphate sorption. Cho and Caldwell (28) found more of the total soil phosphorus in the aluminum and iron fractions in acid soils and more of the total soil phosphorus in the calcium fraction of calcareous soils. Chandler (18) showed that phosphate fixation in acid soils was due to iron and aluminum, but in calcareous soils calcium was responsible for phosphate fixation. Stoddart (126) found a higher ratio of iron and aluminum to calcium for acid soils than non-acid soils.

Kittrick and Jackson (73) stated that phosphate compounds of aluminum, iron and calcium gave higher phosphate concentrations in solution when suspended in pure water than the phosphate concentration known to exist in the soil solution. They also stated that the common ion effect indicated that an excess of the common ions, aluminum, iron or calcium supplied by non-phosphate soil minerals should indeed maintain phosphorus at very low levels of concentration.

Hsu and Rennie (60) stated that sorption and precipitation are the results of chemical union between aluminum and phosphate. They reported that the factor governing the availability of phosphorus is not its form but the total activity of ions that can fix phosphate, i.e., aluminum in the system. They also found that exchangeable aluminum on resin precipitated phosphate from solution and an exchange reaction likely occurred between the Al^{3+} in the soil and other cations in the solution. Precipitated phosphate may be adsorbed by the resin through aluminum bridges. In this case the decrease of phosphate in solution is controlled by the solubility product of aluminum phosphate and the data should be expected to follow the adsorption isotherm.

Lindsay, et al. (80) stated that the K_{sp} value of highly purified synthetic varisite, $Al(OH)_2H_2PO_4$, was found to be 30.5 at 25 C and the equilibrium between varisite and its constituent ions in solution was attained only very slowly. The solubility criteria indicated that the immediate reaction products of phosphate applied to acid soils are much more soluble than varisites, but upon aging these intermediate reaction products are slowly transformed into varisite which may exist with gibbsite as a stable solid phosphate.

Kittrick and Jackson (74) found that at pH 4 the predominant aluminum and phosphate ions in solution were Al^{3+} and $H_2PO_4^-$. Rennie, et al. (111) on the other hand, concluded that the calcium ion will not precipitate phosphate from solution if the pH is sufficiently low. They obtained no significant precipitation of calcium phosphate until the pH approached 5.5 and maximum precipitation did not occur until the pH approached 7.6. The precipitation of iron and aluminum phosphates were negligible at pH 5.

Lagos (77) analyzed seven soils for four phosphate fractions and reported that in two soils of pH >7.5 a larger portion of the fertilizer occurred as the tricalcium phosphate fraction while in soils of pH<7.5 the phosphate fertilizer was more pronounced in iron and aluminum phosphate fractions. An average of 25 per cent of the added phosphorus was retained in the soluble and loosely bound fraction. Phosphate fixation capacity of the soils ranged from 48 to 64 per cent and averaged 58.7 per cent. The phosphate content of each fraction as a percentage of the inorganic phosphorus was used as a criterion for determining the degree of chemical weathering of the soil.

McGeorge and Breazeale (90) believed that phosphate fixation in calcareous soils is due in many cases to formation of a compound more basic than tricalcium phosphate and additional calcium as calcium carbonate is a definite part of the calcium phosphate molecule. Midgley (93) also believed that phosphate in calcareous soils seems to be fixed as a carbonate-phosphate complex rather than simple tricalcium phosphate. McGeorge (88) stated that Arizona soils have a strong fixing power for soluble phosphate because of the large amount of solid-phase calcium carbonate and high pH.

Perkins (102) studied the effect of various mixtures of cations with phosphate on phosphate precipitation through a range of pH values from 2.5 to 9.5 and concluded that increasing cationic concentrations increased phosphate precipitation whether single or mixed cations were used. As the pH increased from 2.5 to 9.5 phosphate fixation by calcium steadily increased. At acid reactions calcium phosphate precipitated slightly more phosphate than magnesium, but at basic reaction, much more. In general the more complex the cationic solution with total cation concentration remaining constant the lower the phosphate precipitation.

Joos and Black (65) pointed out that the availability of phosphate rock was relatively high at pH 4.6 and 5.6, but was reduced at pH 6.6. They also reported a reaction between phosphate rock and bentonite at pH 4.6 and 5.6. Stelly and Pierre (125) found that the amount of phosphate dissolved from apatite and phosphate rock increased as the pH of the solution was lowered.

Mack and Barber (85) concluded that soil incubated at -20.5 C for nine months released more phosphate when leached with water than the soil incubated at 2.7 C. At a leaching temperature of 32 C more phosphate was released than at 16 C. They also found a direct relationship between released phosphorus and a decrease in acid-soluble phosphorus and an increase in alkali-soluble phosphorus.

Neller and Comar (97) stated that phosphorus fixation varies directly with soil clay content and to a lesser degree with the silt and organic matter content. Rennie and Mackercher (111) on the other hand, believed that organic matter is equally as important as inorganic colloids in sorption of phosphorus. However, Kardus (68) stated that the over-all effect of the organic phase in soil is a reduction in phosphorus fixation.

Stout (127) found that ground samples of kaolinite and halloysite fixed three to four millimoles of phosphate per 100 grams of oven dried clay but he did not find a significant phosphate fixation with bentonite clay. Murphy (95) also stated that grinding of kaolinite increased phosphorus fixation bv kaolinite. He believed that this intense grinding exposes a considerable number of hydroxyl ions which become active in fixation of phosphate by an anion exchange reaction between the phosphate ion and the hydroxyl ion of the clay.

Kittrick and Jackson (74) found that greenalite and kaolinite react with phosphate by a mechanism of chemical precipitation to form a separate phase phosphate crystal at room temperature as well as at 90 C. Berger and Thomas (10) reported anion sorption in soils high in kaolinite clay and aluminum and iron oxides. Mehlich (91) also stated that soils high in kaolinite, iron oxide and gibbsite have a high affinity for anions. Schofield and Samson (118) stated that the mechanism of proton adsorption at low pH values could account for anion sorption by kaolinite. Wada (135) showed that at pH 4.0 ammonium phosphate reacts rather rapidly with allophane and halloysite to form an insoluble phosphate "ammonium-substituted taranakite". He also reported that the reaction was retarded at pH 7.0. He noticed that a 10.1 A spacing of halloysite changed to 13.2 A due to phosphate fixation. Kelly and Midgley (69) showed that phosphate fixation increased the pH of the kaolinite-phosphate mixture. He also observed that ferric hydroxide increased the pH more than kaolinite.

Wild (143) measured the retention of phosphorus in kaolinite, montmorillonite and Rothamsted subsoil clay. He believed that the exchangeable cations determine the extent of formation of basic aluminum phosphate. Allaway and Rhoades (2) found that phosphorus accumulated in the soil as surface sorbed phosphate, or as a combination of iron and aluminum phosphate or both.

Ramulu, et al. (110) noticed a significant correlation between phosphorus fixation and dithionite extractable iron. They also reported that pure kaolinite fixed more phosphorus than a mixture of kaolinite and vermiculite. Kittrick and Jackson (74) stated that the addition of goethite to an iron phosphate suspension diminished the soluttion phosphate concentration from 10 ppm to one ppm and a similar result was obtained by the addition of kaolinite to an aluminum phosphate suspension.

Coleman (31) studied the amount of phosphate fixed by the coarse and fine fractions of kaolinite and montmorillonite clays both before and after their free iron and aluminum oxides had been removed. He found that all of the phosphorus held by coarse clay and most of the phosphate held by fine clay was fixed by free iron and aluminum oxides. Kaolinite and montmorillonite in fine clay fixed rather large amounts of phosphorus but the kaolinite, montmorillonite, quartz and mica in the coarse clay mineral were unable to fix phosphorus. He also stated that phosphorus fixation by both coarse and fine clay was influenced by reaction and exchangeable cations only as long as the free iron and aluminum oxides were present which shows that the activity of these free oxides determines the amount of phosphorus fixed by clay and fixation was not influenced so much by the type of clay material but by the amount and activity of free iron and aluminum oxides. Coleman (31) also reported that the fixation of phosphate by montmorillonite and kaolinite clay was due to both the free iron and aluminum oxides and the clay mineral, but the amount of phosphate fixed by either clay was largely dependent on the activity of the free iron and aluminum rather than by the type of clay.

Ensminger (40) indicated that a crystalline compound was formed on phosphating kaolinite and Cecil colloid. He concluded that fixation by these clays was due to the precipitation of aluminum phosphate rather than by hydroxyl replacement in the crystal lattice of aluminosilicate minerals.

Hemwall (56) hypotehsized that phosphate is "fixed" by clay minerals by reacting with soluble aluminum which originated from the exchangeable sites or from lattice dissociation of the clay minerals to form a highly insoluble aluminum phosphate compound. The problem was approached in general by showing (a) that clays support an appreciable aluminum concentration in solution and (b) that there is a solubility product relationship between the aluminum and phosphate concentration in a clay-phosphate suspension. On the basis of experimental evidence the hypothesis was correct. He also stated that the insoluble aluminum phosphate formed was varisite ($AlPO_4 \cdot 2H_2O$) and the rate of fixation was found to be dependent upon the rate at which the clay replenishes the

the soil solution with soluble aluminum. Low and Black (82) also tested the hypothesis which stated that kaolinite dissociated into aluminum ions, thereby disturbing the equilibrium and causing the clay to be dissolved in accordance with solubility-product principles. The digestion of kaolinite in phosphate solutions resulted in a release of silica which was proportional to the phosphate fixed. Low and Black (83) also concluded that one of the mechanisms of phosphate fixation by kaolinite was the phosphate-induced decomposition of the clay with the released aluminum being precipitated as aluminum phosphate. They presented evidence that kaolinite ionizes into a hydroxyaluminum complex as a cation and a silicate radical as an anion.

Black (12) conducted a phosphate fixation study and concluded that ground kaolinite had a maximum fixation at pH 3 to 4 regardless of the concentration of phosphate or the time of contact. The importance of kaolinite in fixing phosphate in an unavailable form in the soil was considered to be the greatest at the high phosphate concentration in immediate vicinity of the source of soluble phosphate.

Coleman (32) was the first investigator who really postulated that phosphate fixation by clay minerals was due to the aluminum content of the clay. He suggested at least two different kinds of phosphate fixation mechanisms. One which operates above pH 5 and "fixes" phosphate more slowly. He also reported that at the pH range of most soils (pH 5 to 7), montmorillonitic and kaolinitic clays fixed almost as much phosphate in 24 hours as in one month, but the more acidic reaction (below pH 5) both clays fix considerably more phosphate in one month than in 24 hours. He also stated that little or no phosphate was fixed by clay minerals, montmorillonite and kaolinite, but that all of the phosphate was fixed by the free iron and aluminum oxides on the clays. There was evidence to indicate that phosphate ions replaced hydroxyl ions from the free iron and aluminum hydroxides rather than the clay mineral.

Kelly and Midgley (69) stated that phosphate fixation is a physicochemical exchange of phosphate ion for the exposed hydroxyl ions. Though it seems to be an equilibrium reaction, in soil it is greatly shifted toward phosphate fixation, because of the very low concentration of hydroxyl ion in the soil solution and the high hydroxyl concentration of hydrated ferric oxides on the surfaces of the soil particles. When they heated ferric hydroxide which lost its hydroxyl ions as water, its phosphate fixing capacity decreased from 100 to zero. After heating it resembled anhydrous ferric oxide which fixed no phosphate at any time. They also reported that if a soil contained a large amount of hydrated iron oxide heating at a high temperature will decrease its fixation capacity, but if it contains a large amount of hydrated aluminum oxides heating may actually increase its fixing capacity for phosphate.

McAuliffe, et *al*. (87) measured the extent of hydroxylic surfaces for kaolinite, halloysite, diaspore and gibbsite. In the case of kaolinite and halloysite the hydroxylic surfaces were about two-thirds of the total. They also studied the kinetics of the exchange between phosphate on the surface of soil minerals with phosphate in solution by use of phosphate solution containing P^{32}. They reported two reactions, the first of which corresponds to rapid exchange between phosphate in solution and phosphate on soil surfaces. Phosphate after sorption on the surface undergoes a further reaction, the nature of which remains to be determined.

Cole, et al. (29) stated that when a soluble phosphate fertilizer is added to calcareous soils, the reaction with calcium carbonate consists of a rapid monolayer sorption of phosphate on the calcium carbonate surface and at high phosphate concentrations in the vicinity of fertilizer particles, the precipitation of dicalcium phosphate or a similar compound may be substantial. The initial products of these reactions are characterized by very high specific surfaces and greater phosphate solubility than the stable hydroxyapatite or fluoroapatite. They also added that a sodium carbonate solution readily removes sorbed phosphorus from calcium carbonate surfaces by the combined effect of the reduction of the calcium concentration in solution and precipitation of carbonate and an exchange between the bicarbonate ion and the phosphate ion for a position on the calcium carbonate surface.

Low and Black (83) applied the solubility-product principle to clays by reactions with strong acid or base. When they treated kaolinite with strong acid, the silicate ions from the clays reacted with the hydrogen ion of the acid to form a weak silicic acid, the ionization of which was repressed by the presence of an excessive acid concentration. In this manner the activity of the silicate ion is decreased and clay dissolved. If, on the other hand, kaolinite was treated with a strong base, the activity of the aluminum ion would be decreased by the formation of a stable aluminate and would cause dissociation of the clay mineral. According to their hypothesis any ion that is capable of reducing the activity of either ion of the clay should, if present in sufficient amount, cause the clay to dissociate. Ions such as phosphate and arsenate in large excess should effect the "breakdown" of the clay by precipitating the aluminum. They also found that the addition of both phosphate and 8-hydroxyquinoline to kaolinite produced considerable increase in the concentration of silica in the solution.

Weiser (142) studied the penetration and fixation of phosphates in both field and greenhouse experiments. He concluded that the soil penetration of superphosphate may be enhanced by certain materials such as sulfate and nitrate salts of sodium, potassium, ammonium and magnesium. Sodium, ammonium and certain organic phosphates penetrated more quickly in soil than did superphosphate. He also stated that exposure of phosphate to relatively large amounts of soil, a situation observed in cases of deep penetration resulted in enhanced fixation.

Hsu and Jackson (59) stated that when a strongly acidic highly weathered soil undergoes an increase in pH by calcium carbonate addition, a slow back-transformation to calcium phosphate occurred but considerable aluminum and iron phosphate persisted. The rapid fall in calcium phosphate as the pH dropped from 6.5 to 4.5 together with the phenomena noted above, gives evidence that transformation of phosphate in soils is mainly controlled by pH, but the rates of transformation are controlled by the slow rate of diffusion of an ion along moisture film joining adjacent soil particles. Iron coatings further slow down the rate of back-transformation. Reducing conditions promoted the formation of aluminum phosphate instead of iron phosphate.

Samie, et al. (116) used tagged monocalcium phosphate on 16 Egyptian soils of various calcium contents and found that exchangeable calcium, but not water-soluble calcium or calcium carbonate, increased phosphate fixation.

Haseman, et *al*. (55) stated that the rate of phosphate fixation by montmorillonite, illite and kaolinite clays increased with rise in temperature, increasing concentration of phosphate and lowering in pH. The rate of fixation by hydrous oxides, gibbsite and goethite increased with rise in temperature, but was affected little by variation in pH in the 0.1 M phosphate solution. The decreasing order in which the soil minerals fixed phosphate was: gibbsite, goethite, kaolinite and montmorillonite.

Log and Dev (81) stated that clay fractions ($>2\mu$) having montmorillonite as the dominant clay mineral fixed more phosphate than predominantly kaolinitic clay. A sample rich in illite fixed more phosphate in the absence of ferric oxide at pH 4 while other samples showed high fixation when free ferric oxide was not removed.

Weller (138) reported that the chelating ability of iron and aluminum found in the vicinity of phosphorus fertilizer granules was effective in reducing phosphate fixation. Plessis and Burger (107) stated that phosphate fixation took place in two steps: a rapid initial fixation which obeyed the Langmuir adsorption isotherm followed by a slow continuous process. Fixation in these soils which contained predominantly illite, montmorillonite and kaolinite clays besides 1.5 per cent free iron oxide was affected by time, pH, and amount of potassium dihydrogen phosphate applied in the laboratory study, but was little affected by moisture and liming to pH 7.0.

Hsu (58) calculated the amount of phosphate fixed from the decrease in phosphate concentration in the solution and indicated that the relationship between the phosphate fixed and the concentration in the solution followed the Langmuir adsorption isotherm. Adherence to the Langmuir adsorption isotherm was considered for an adsorption reaction under his experimental conditions (pH 7, absence of exchangeable aluminum in the soil and a short period of shaking) although its application to phosphate fixation should be subjected to some limitations in interpretation.

Hsu and Rennie (60) studied the reaction of "aluminum hydroxide" with phosphate in order to elucidate the role of this compound in the fixation of phosphate in the soil. They also studied the application of the Langmuir adsorption isotherm as an indicator of sorption. They concluded that the initial fixation of phosphate by X-ray amorphous "aluminum hydroxide" at pH values of 7, 6, 5 and 3.8 and at initial phosphate concentration ranging from 2 to 100 ppm of phosphorus and in certain instances upt to molar concentrations was shown to be primarily a result of a sorption reaction which occurred very rapidly and was practically completed within a half hour, but was followed by a slow decomposition-precipitation process. The sorption mechanism was suggested to be basically the same as the decomposition-precipitation reaction, except that the latter requires the release of the aluminum ion into solution. The solution Al^{3+} activity was limited by the solubility of aluminum hydroxide and thus became negligible at pH 5 and above, but this limitation did not affect the surface aluminum activity. They stated further that in the derivation of the Langmuir adsorption isotherm, it was implicitly assumed that the gas particles moved in the free space and no force other than the attraction of the solid interferred with their kinetic movement. The kinetic movement of phosphate ions in an aqueous solution, however, was affected by other ions in solution. The ions which attract phosphate will enhance the forces of sorption. Langmuir sorption isotherm can only hold where the interference froces due to the interaction of ions is negligible or when it is constant throughout the experiment. In this phosphate-aluminum-hydroxide system Al^{3+} ion can be released to the solution by aluminum hydroxide through dissolution. The aluminum ion in the solution can compete with the aluminum hydroxide surface for phosphate and shift the position of the sorption equilibrium. Kurtz, et al. (76) on the other hand, concluded that the amount of phosphate sorbed was a function of concentration of phosphate in solution and they recognized that the Freundlich equation may hold in a limited range but that it is not applicable to all sorption reactions. In equilibrium studies both with phosphate and with cations, sorption may follow Freundlich's equation and this is typical for polar sorptions of which exchange sorption is an important type. With the base exchange reaction other cations are released in amounts equivalent to those sorbed.

According to Kolthoff (75) theoretically the Freundlich equation can represent exchange reactions when applied to ions and he believed that the sorption was an exchange reaction. However, his curve began to level off when as little as 0.13 gram of phosphorus was sorbed per gram of clay. It seemed that this sorption and the sorption that displaced silica are not the same.

Low and Black (82) plotted the amount of phosphate fixed by kaolinite against the final concentration in the solution and produced a typical sorption curve which could be represented by the Freundlich adsorption equation having the form:

$$\frac{x}{m} = Kc^{1/n}$$

where $\frac{x}{m}$ = the amount of phosphate adsorbed per given weight of adsorbent,

x = the amount of the solute absorbed,

m = the weight of the adsorbent,

K = the proportionality constant,

c = the concentration of the solutes in the equilibrium solution, and

n = a constant.

Obedience to this equation is an indication that a sorption equilibrium had been reached within the relatively short period of 3/2 hours. They also noticed that the degree of sorption was increased by increasing the temperature. The exchange of phosphate ions for hydroxyl ions of a crystal lattice is a type of chemical sorption.

Fried and Shapiro (44) had earlier shown that the constant calculated from the Langmuir isotherm had a sound theoretical approach to some of the problems of phosphate retention in soils. The Langmuir adsorption equation (78) may be written in the form:

$\frac{x}{m} = \frac{Kbc}{1+Kc}$ and in linear form this equation becomes

$$\frac{c}{x/m} = \frac{1}{Kb} + \frac{c}{b}$$

where c = the final solution concentration (equilibrium concentration) in ug P/ml,

$\frac{x}{m}$ = ug P adsorbed per gram of soil,

b = the adsorption maximum, and

K = a constant related to the bonding energy of the solid colloids for the phosphorus.

A straight line plot of $\frac{c}{x/m}$ against c can be assumed to be indicative of a sorption reaction. In such a case the sorption maximum and the energy of sorption can readily be calculated and it can be assumed that the conditions are such that a unimolecular sorbed layer is present on the surface of colloids.

Rennie and Mackercher (112) plotted the sorption data according to the Langmuir equation and concluded that the data showed satisfactory agreement with the Langmuir isotherm when the phosphorus solution concentration was less than 20 ug P/ml as a straight line relationship existed for the four soils. The isotherm for all soils breaks in the vicinity of a final solution concentration of 20 ug P/ml.

Fried and Shapiro (44) measured both the intensity of phosphate supply and the capacity of a soil to continue to supply phosphorus. They found that the pattern of phosphate supply for four low phosphate fixing soils could be predicted by assuming the phosphate released was a desorption phenomenon as described by the Langmuir adsorption isotherm. Langmuir (78) stated that the sorbed molecules are held to the surface by valence forces of the same type as occurs between the bound atoms in a molecule.

The Fate of Soluble Phosphate Applied to Soils

Generally, soluble phosphate added to the soil is largely converted into iron and aluminum phosphates in acid soils and into calcium phosphates in calcareous soils. Chang and Jackson (25) and their modified procedures in the fractionation of phosphate make it possible to trace the transformations of phosphorus applied to the soil. Juo and Ellis (66) noticed a rapid precipitation of phosphorus applied to soils to form colloidal aluminum and iron phosphates and these products then crystallized into hydrated compounds which were less available for plants.

Sharif and Ulrich (122) used neutral loam soils in a pot experiment and found that monocalcium phosphate was completely converted and superphosphate partially converted into aluminum and iron phosphates. They also stated that calcium phosphate was highly available to wheat and beans and showed a high isotopic exchange associated with a large surface area.

Robertson, et al. (112) applied concentrated superphosphate and rock phosphate to soils at rates up to 349 lb/A. In lateritic soils phosphorus applied as superphosphate was largely converted to aluminum and iron phosphates after two years. Conversion of phosphorus from rock phosphate occurred at a much slower rate than concentrated superphosphate. They also reported that there was a conversion of phosphorus from superphosphate to occluded phosphorus other than aluminum and iron phosphates. Most of the phosphorus applied after 8, 11 and 13 years had been converted to occluded phosphorus.

Maning and Solomon (86) studied the form of phosphorus after more than 65 years of phosphate fertilization. They concluded that superphosphate treatments resulted in a major portion of the phosphate reverting to aluminum and iron phosphate and calcium phosphate was found to a lesser degree. Rock phosphate treatment, on the other hand, showed an increase in the calcium phosphate fraction. Organic and occluded phosphate fractions were not greatly affected by various treatments.

Shelton and Coleman (123) stated that phosphate applied to many red clay soils was rapidly fixed as iron and aluminum phosphate thereby reducing the solubility and availability of phosphorus fertilizers. They further stated that applied phosphorus was rapidly converted (within six months) to aluminum and iron phosphates. The initial increase in aluminum phosphate was greater than iron phosphate at all rates, but with increasing elapsed time after application there was a decrease in aluminum phosphate and an increase in iron phosphate. They believed that aluminum phosphate comes into solution and can be used by plants before it changes to the less soluble iron phosphate.

Chang and Jackson (24) reported that the application of soluble phosphate fertilizer greatly increased the amount of aluminum and iron phosphate at all three lime levels but increased the calcium phosphate only slightly at the highest lime level. They stated that at the initial stage of weathering and also right after application of phosphate fertilizer, calcium phosphate and aluminum phosphate are more likely to be formed than iron phosphate. This is due to higher activities in the soil of calcium and aluminum ions than iron ions which are controlled by the activities of the respective cations of calcium carbonate and aluminum silicate and gibbsite and iron oxides. As time elapsed the calcium and aluminum phosphate decreased in concentration and iron phosphate gradually increased which is the least soluble compound among them.

Chang and Chu (23) studied the fate of added soluble phosphate in six Taiwan soils, with pH ranging from 5.3 to 7.5. After three days they found that the added phosphate was mainly fixed in decreasing order of aluminum, iron, and calcium phosphate. After 100 days the amount of aluminum and calcium phosphate decreased while iron phosphate was increasing. Chang (22) also concluded that phosphate added to the soil was fixed at early stages mostly as aluminum phosphate in the acid soils and was stabilized as long as waterlogged conditions were maintained. He also found that the availability of iron phosphate increased due to the reducing conditions in the soil produced by addition of organic matter to waterlogged soils.

Lewis, et al. (79) found a reduction in availability of applied phosphorus within 24 hours. Khan and Chowdhury (7) also stated that 88 per cent of the phosphate added as superphosphate was retained by the soil in insoluble forms three days after application. Most of the superphosphate was converted into sesquioxide-bound phosphate and sorbed. Yuan, et al. (148) found that over 80 per cent of the applied phosphate was retained by the soil as aluminum and iron phosphates. Less than 10 per cent was in the water soluble and calcium phosphate forms.

Chang (22) studied soils with pH 7.6, 5.5, 4.5 and 4.15 by applying phosphorus alone and/or with organic matter in flooded containers and then fractionated the soil for forms of phosphorus. He concluded that in acidic soils fixation of added phosphorus was generally completed after five to nine days. Thereafter soluble phosphate increased slightly. In alkaline soils phosphorus fixation was generally completed after 13 days. Gerth (46) stated that decalcification leads to the formation of iron and aluminum phosphates, while slow weathering in the presence of calcium carbonate promoted the formation of apatite and tricalcium and octacalcium phosphates. High levels of exchangeable calcium resulted in increase in total and lactate-soluble phosphates. Hsu (58) treated a slightly acid soil (pH 6.4) with dilute sodium dihydrogen phosphate solution at pH 7 and stated that there was rapid fixation of phosphorus due to surface sorption on amorphous aluminum hydroxides and iron oxides present in the soil. Sen Gupta and Cornfield (119) stated that the water soluble phosphate added to soil containing 16.5 per cent calcium carbonate was fixed largely in easily replaceable and non-apatite calcium phosphate forms; fixation in soils with 0.15 per cent calcium carbonate content occurred as aluminum and iron phosphate. Fixation of added phosphorus increased with time and usually decreased with rates. Sen Gupta and Cornfield (120) also reported that aluminum-bound phosphate expressed as a percentage of the total soil phosphorus was negatively correlated with calcium carbonate percentage. The proportion of other phosphate fractions was not significantly correlated with calcium carbonate content. Inert phosphorus and apatite fractions accounted for a greater proportion of the phosphorus in calcareous soils than in non-calcareous soils.

Fried and Black (43) found that a surface coating of iron or aluminum compounds on exchange materials was found to retain a large portion of added phosphorus. The amount of this retention increased as the concentration of phosphate in solution increased. They added that retention was a function of both the concentration of phosphorus in solution and the length of time allowed for equilibrium.

Dinca and Serbannescu (36) studied the nature and content of phosphorus formed by contact between phosphorus fertilizers and the soil. In high calcium carbonate chestnut and chernozem soils mainly calcium phosphate was formed; in podzolic brown soils easily and difficultly available iron and aluminum phosphates appeared. Ryzhove and Saakyant (116) applied high rates of phosphorus to calcareous soils low in humus and cropped with a rotation of cotton and lucerne. They stated that phosphorus accumulated in the surface and subsurface layers and was soluble in hydrocarbonic acid and 0.5 N citrate. Bapt and Bedeker (4) stated that in soils high in calcium carbonate most of the retained phosphorus was bound to calcium but in the soils low in calcium carbonate phosphate was bound to aluminum and iron. Arrambarri (3) applied phosphorus to calcareous soils and found that the total phosphorus content and specific surface of soil are the most important factors affecting the fertility of calcareous soil in relation to phosphorus. Soils with high absorbing surfaces contained higher amount of exchangeable phosphorus and the ratio of exchangeable phosphorus to total phosphorus provided a measure of phosphorus availability. Fuller and McGeorge (45) stated that a certain amount of phosphorus added to calcareous soils becomes unavailable to plants and is referred to as "fixed". They also stated that soluble phosphorus may be fixed in organic as well as inorganic forms.

CHAPTER III

MATERIALS AND METHODS

The calcareous soils studied in this investigation were collected from fields in Afghanistan and Okalhoma, USA, where crop plants had responded to phosphorus fertilization. A modified version of the Chang and Jackson (26) phosphate fractionation procedure was made of the soils studied before and after incubation with ammonium phosphate and after a period of plant growth in the greenhouse.

The soils studied in this investigation were collected from Bolan, Darulaman, Pos-i-shan, Shishem Bagh, Kokoran, Mazar, Shamalan and Boghra experiment stations in Afghanistan and from Marshall, Harper and Texas counties in Oklahoma, USA.

Soil Properties

Physical Properties

<u>Mechanical analysis</u>. The particle size distribution was determined by the use of the soil hydrometer (13) while carbonate and organic matter were removed by using 1 N sodium acetate buffered at pH 5 and hydrogen peroxide, respectively (72).

Chemical Properties

Data for chemical properties of the soils studied in this investigation are reported in Table II.

TABLE II

CHEMICAL CHARACTERISTICS OF THE BOLAN CLAY LOAM, SAN SABA CLAY LOAM, WOODWARD LOAM AND RICHFIELD LOAM SOILS

Sample No.	Soil type	Depth (in.)	pH (1:1 KCl)	Per cent organic matter	Per cent $CaCO_3$	Total phosphorus (ppm)	Organic phosphorus (ppm)
1	Bolan clay loam	0-9	8.3	1.25	19.12	918	293
2		9-16	8.4	0.75	20.58	888	288
3		16-24	8.4	0.43	20.71	791	231
4		24-32	8.4	0.25	20.55	667	147
5		32-39	8.4	0.15	21.73	650	140
6		39-47	8.4	0.13	21.00	650	138
7		47-55	8.4	0.12	23.00	617	138
8		55-63	8.7	0.10	23.41	600	127
9		63-71	8.4	0.08	23.53	528	48
10		71-79	8.6	0.06	23.54	518	33
11	San Saba clay loam	0-9	7.2	2.90	3.81	450	210
12		9-24	7.3	1.30	13.47	383	80
13		>24	7.6	0.88	10.26	347	22
14	Woodward loam	0-6	8.0	1.33	5.29	591	256
15		6-13	7.9	0.95	4.25	445	220
16		13-25	7.9	0.50	6.75	400	90
17		25-36	7.9	0.25	20.26	385	50
18	Richfield loam	0-12	7.6	1.22	2.15	560	238
19		12-18	7.9	1.15	15.65	667	117
20		18-28	8.0	0.60	12.95	638	68
21		>28	8.0	0.50	8.20	576	55

Soil pH. Soil pH was determined by using a Beckman Zeromatic pH meter with glass electrode in a soil suspension of 1 N KCl-soil ratio of 1:1 after one hour.

Organic matter and calcium carbonate. Determination of organic matter and calcium carbonate was done by the methods outlined in Handbook 60 of the US Department of Agriculture (134).

Phosphorus: 1. Available phosphorus. Available phosphorus was determined by the #1 method of Bray and Kurtz 1:50 soil:extracting solution ratio (16) and by the Dickman and Bray modified procedure (35) and in the 0.5 M sodium bicarbonate extract of Olsen, et al. (100).

2. Total and organic phosphorus. Analysis of total and organic phosphorus was made by the procedure of Mehta, et al. (92).

3. Inorganic phosphorus fractionations. Fractionation of inorganic phosphorus was accomplished by a modified Chang and Jackson (25) procedure as outlined by Petersen and Corey (103). The modifications are as follows: Calcium phosphate was extracted twice with 0.5 N sulfuric acid instead of once (26, 103). The soil was also washed twice with 25 ml portions of saturated sodium chloride after "saloid-bound" phosphate extraction. There was no washing with saturated sodium chloride in the procedure of Chang and Jackson or Petersen and Corey at this point (26, 103). This was done only in incubation study where there was a significant amount of bound phosphate.

Mineralogical Properties

Preparation of soil for X-ray diffraction was done by the procedure outlined by Kittrick and Hope (72).

Analysis of Applied Water-Soluble Phosphate

A 10 ml aliquot of 1000 ppm phosphorus standardized solution of monobasic ammonium phosphate ($NH_4H_2PO_4$) was added to a 50 gram soil sample in a 250 ml beaker to give 200 ug of phosphorus per gram of soil. The soil was kept at approximately field capacity by periodic watering from a wash bottle and allowed to stand for one, 10, and 30 days in a constant temperature room. Then the samples were immediately placed in an oven at 110 C for 24 hours. The oven-dried soil samples were analyzed for "saloid-bound" phosphate, aluminum phosphate, iron phosphate, reductant soluble phosphate, calcium phosphate and available phosphorus. The phosphorus fixed was taken as the difference between the concentration of phosphorus added to the soil and the phosphorus recovered by the modified Chang and Jackson (25) procedure after one, 10, and 30 days.

Greenhouse Study

Four levels of ammonium phosphate were added to each of the three soils collected from Marshall County (San Saba clay loam), Harper County (Woodward loam) and Texas County (Richfield loam) of Oklahoma and the treatments were replicated three times. No phosphorus was added to 80 soil samples from Afghanistan for the first crop. Nitrogen was applied as ammonium nitrate at a rate of 200 ppm to all of these soils. Ammonium phosphate was applied in solution at rates to give 0, 200, 400, and 600 ppm of added phosphorus.

Sorghum-Sudangrass hybrid, sorghum (_Sorghum_ _vulgare_ Pers.) x Sudangrass /_Sorghum_ _vulgare_, var. _sudanensis_ (Piper) Staph._7, was planted on June 30, 1970 for the first crop. Enough distilled water was added to bring the soil to approximately field capacity as previously determined. The plants were thinned to four plants per pot after they had become established.

The first crop was harvested on July 21, 1970 approximately three weeks after planting. They were oven-dried in a forced air oven and the individual weight of all four plants in each pot was recorded.

The second planting was done on July 24, 1970. All Afghan soils received 200 ppm of phosphorus and 200 ppm of nitrogen while soils from Oklahoma received only 200 ppm of nitrogen. The second crop was harvested on August 14, 1970. Total phosphorus of both crops were determined by published procedures (27, 63, 105).

In both croppings the pots were arranged in a randomized complete block design. Statistical analyses of the desired variables were done according to the procedures of Steel and Torrie (124).

CHAPTER IV

RESULTS AND DISCUSSION

Chemical Properties

The chemical properties of the soils studied in this investigation are shown in Table II. The pH of these soils ranged from 7.2 to 8.7. The pH of Afghan soils, due to their high carbonate content, was higher than the Oklahoma soils. The Afghan soils were high in free carbonates compared with the Oklahoma calcareous soils. Bolan clay loam, at a depth of 71 to 79 inches had 23.54 per cent calcium carbonate. Generally the Afghan soils increased in carbonate content with depth. Woodward loam at the depth of 25 to 36 inches had 20.26 per cent calcium carbonate, which was the highest for the Oklahoma soils, while Richfield loam at a depth of 0 to 12 inches had the lowest calcium carbonate content of the soils reported here.

The organic matter content of these soils ranged from 0.06 per cent for Bolan clay loam to 2.9 per cent for San Saba clay loam.

Total phosphorus was the highest in Bolan clay loam and was the lowest in San Saba clay loam. Total phosphorus in Bolan clay loam, Woodward loam and San Saba clay loam decreased with depth while the Richfield loam total phosphorus first increased with depth and then decreased. Organic phosphorus in the surface soil samples was high in Bolan clay loam, while the Oklahoma surface soils had more or less similar organic phosphorus content. Inspite of their low organic matter these calcareous soils contain significant amounts of organic phosphorus. The lowest organic phosphorus of the soils studied is present in Bolan clay loam at a depth of 71 to 79 inches, while the surface sample of the same soil has the highest organic phosphorus of the soils studied. Organic phosphorus in all of these soils is less than 50 per of the total phosphorus. Organic phosphorus in all the soils studied in this investigation decreased with depth.

Fate of Applied Water-Soluble Phosphorus

Soluble phosphorus applied as ammonium phosphate was predominantly converted to calcium phosphate, followed by aluminum phosphate. Reductant soluble and iron phosphates were negligible before and after the incubation period.

Calcium Phosphate

Calcium phosphate contents as affected by applied soluble phosphate are shown in Figues 1 to 3 and Tables III and IV. In Bolan clay loam calcium phosphate increases with time of incubation at all depths, and generally decreases with depth as shown in Figure 1. In San Saba clay loam (Figure 2) calcium phosphate content increases with time of incubation at all depths. Calcium phosphate in all of the incubation periods and in all of the soils studied increases with depth. Before incubation the surface soils had the lowest calcium phosphate content of the entire soil profile, while at a depth of more than 24 inches calcium phosphate was the dominant phosphate compound. Thirty days after the beginning of the incubation period 45 to 52 per cent of the soluble phosphate applied to San Saba clay loam was converted to calcium

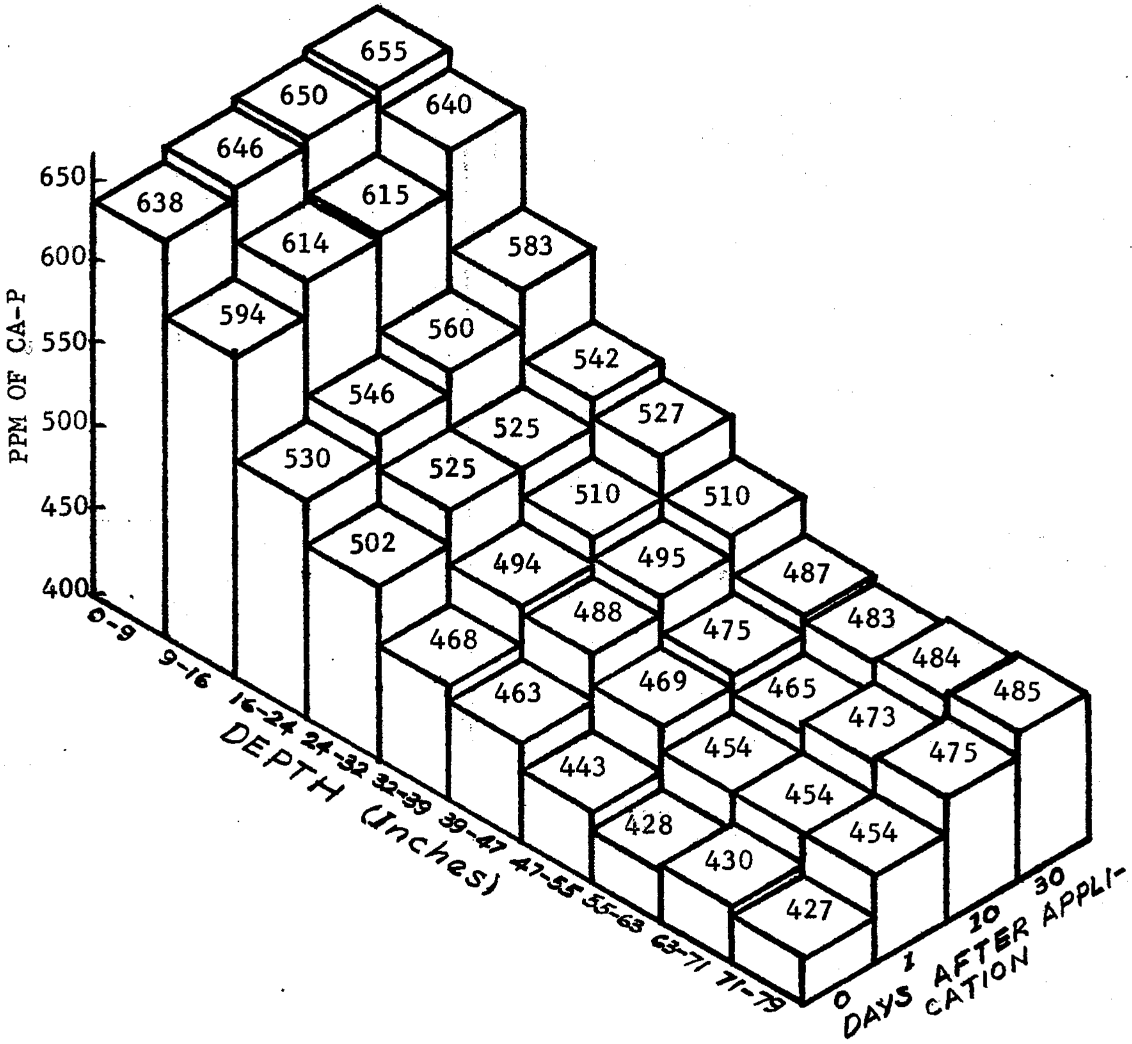

Figure 1. Calcium Phosphate Extracted from Bolan Clay Loam by 0.5 N H_2SO_4 after Treatment with 200 ppm of P as $NH_4H_2PO_4$

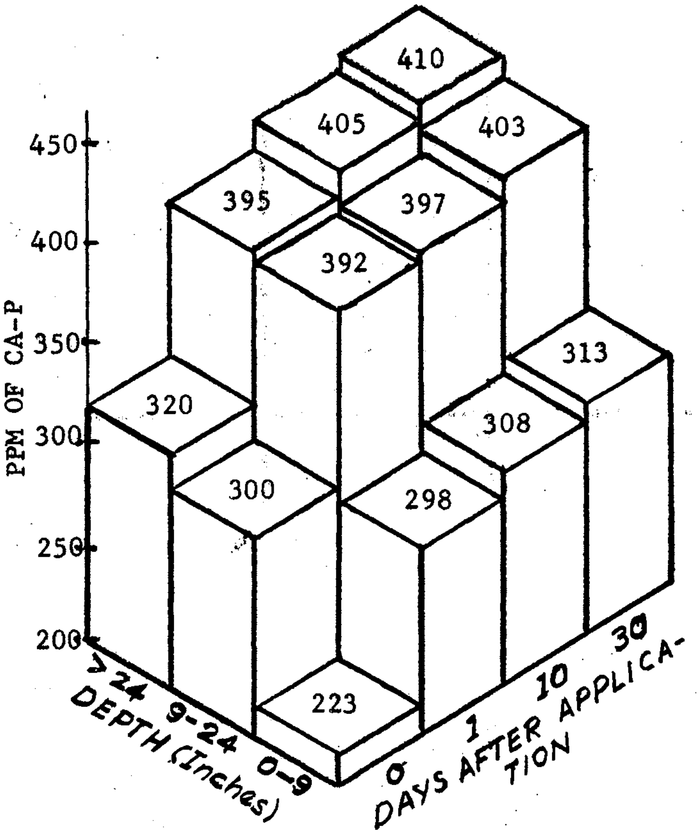

Figure 2. Calcium Phosphate Extracted from San Saba Clay Loam by 0.5 N H_2SO_4 after Treatment with 200 ppm of P as $NH_4H_2PO_4$

phosphate. More than 35 per cent of the phosphorus applied to the San Saba soil was converted to calcium phosphate one day after the beginning of the incubation period.

The conversion of soluble phosphate to calcium phosphate in Richfield loam soil is shown in Figure 3. The rate of conversion of soluble phosphate to calcium phosphate increases with incubation time at all depths. The amount of calcium phosphate in the untreated soil increases with depth to a maximum and then decreases again. Conversion of soluble phosphate to calcium phosphate was lower in the surface one foot than in the deeper layers 30 days after the beginning of the incubation period.

The data on the conversion of soluble phosphate to calcium phosphate in Woodward loam indicate that calcium phosphate increased with time of incubation as shown in Table III. Calcium phosphate content is the lowest in the 6 to 13 inch sample and then increases in the deeper samples. Calcium phosphate content in this profile is the highest at a depth of 25 to 36 inches.

Aluminum Phosphate

Aluminum phosphate content of these soils is reported in Tables III through VI.

Bolan clay loam did not show any significant amount of aluminum phosphate before incubation. Soluble phosphate applied to this soil was converted to aluminum phosphate largely during one day of incubation and then the rate of conversion decreased with time. The conversion of soluble phosphate to aluminum phosphate was highest in the 0 to 24 inch sample.

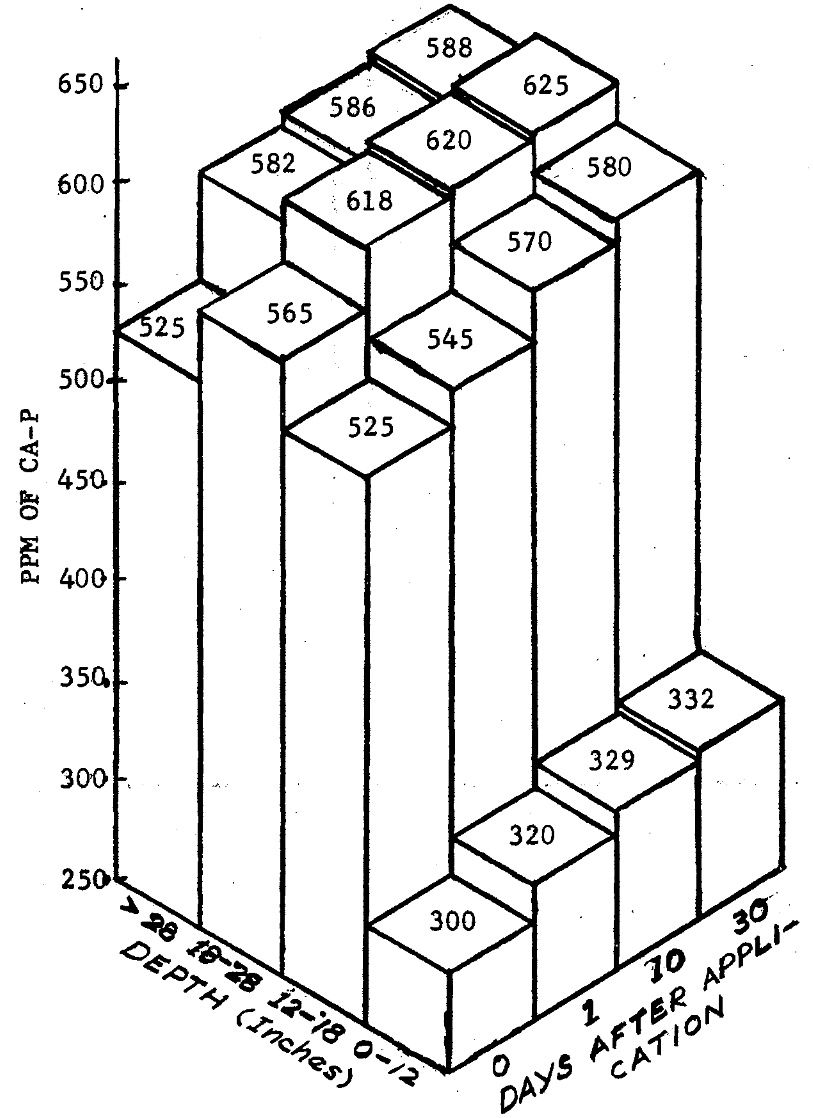

Figure 3. Calcium Phosphate Extracted from Richfield Loam by 0.5 N H_2SO_4 after Treatment with 200 ppm of P as $NH_4H_2PO_4$

TABLE III

DISTRIBUTION OF FORMS OF PHOSPHORUS IN WOODWARD LOAM

Form of phosphorus	Incubation time (days)	Depth (inches) 0-6	6-13	13-25	25-36
		ppm			
Total inorganic P	0	335	225	310	335
Aluminum P	0	11.7	1.7	6.7	0
	1	102.0	130.2	88.1	4.4
	10	115.1	138.1	92.2	4.7
	30	120.3	174.0	94.3	6.7
Calcium P	0	325	215	280	330
	1	364	218	315	425
	10	375	225	317	440
	30	377	226	319	450
Easily soluble P	0	0	0	0	0
	1	115	70	83	93
	10	108	60	80	88
	30	105	53	76	80
Total added	0	337	217	287	330

San Saba clay loam at a depth of 0 to 9 inches had 33.4 ppm of aluminum phosphate before incubation which is the highest amount of aluminum phosphate in the soils studied in this investigation, while Bolan clay was the lowest. The largest conversion of soluble phosphate to aluminum phosphate took place in this soil during one day of incubation as shown in Table IV. At a depth of 0 to 9 inches 44.35 per cent of the soluble phosphate was converted to aluminum phosphate after 24 hours incubation, while the rate of conversion was very slow in the next 29 days. At a depth of 9 to 24 inches 26.65 per cent of the soluble phosphate was converted to aluminum phosphate after one day of incubation. Thirty days after the beginning of incubation period 38.9 per cent of the applied phosphate was present as aluminum phosphate. In samples taken at a depth greater than 24 inches 39.65 per cent of the phosphorus applied was converted to aluminum phosphate after 24 hours of incubation while after 30 days 52.2 per cent of the phosphorus applied was aluminum phosphate. In general, however, aluminum phosphate content increased with time of incubation in all of the samples of the whole profile.

Woodward loam followed more or less the same trend as San Saba clay loam as shown in Table III. The amount of aluminum phosphate increased with the time of incubation. The largest conversion of soluble phosphate to aluminum phosphate took place one day after the beginning of incubation period. In samples taken at a depth of 0 to 6 inches 45.15 per cent of the phosphate applied was converted to aluminum phosphate, while at a depth of 25 to 36 inches, only 2.2 per cent of the phosphate applied was converted to aluminum phosphate after 24 hours of incubation. Conversion was the highest at a depth of 6 to 13 inches in

TABLE IV

DISTRIBUTION OF FORMS OF PHOSPHORUS IN SAN SABA CLAY LOAM

Form of phosphorus	Incubation time (days)	Depth (inches)		
		0-9	9-24	>24
		ppm		
Total inorganic P	0	240	303	325
Aluminum P	0	33.4	0	0
	1	122.1	53.3	79.3
	10	133.6	54.8	85.0
	30	135.0	77.8	104.4
Calcium P	0	223	300	320
	1	298	392	395
	10	308	397	405
	30	313	403	410
Easily soluble P	0	0	0	0
	1	30	27	25
	10	25	25	7
	30	13	15	5
Total added	0	256	300	320

TABLE V

DISTRIBUTION OF FORMS OF PHOSPHORUS IN BOLAN CLAY LOAM

Form of P	Incubation time (days)	Depth (inches)									
		0-9	9-16	16-24	24-32	32-39	39-47	47-55	55-63	63-71	71-79
		ppm									
Total inorganic P	0	625	600	560	520	510	512	479	473	480	485
Aluminum P	0	0	0	0	0	0	0	0	0	0	0
	1	7.2	8.2	7.6	3.1	3.0	2.2	2.1	2.0	2.0	2.2
	10	2.5	2.6	1.6	1.5	1.3	1.2	0.8	0.75	0.75	0.70
	30	2.2	2.1	1.5	1.0	1.1	1.0	0.4	0.3	0.15	0.15
Calcium P	0	638	594	530	502	468	463	443	428	430	427
	1	646	614	546	525	494	488	469	454	454	454
	10	650	615	560	525	510	495	475	465	473	475
	30	655	640	583	542	527	510	487	483	484	485
Easily soluble P	0	0	0	0	0	0	0	0	0	0	0
	1	190	180	183	176	173	173	173	174	171	170
	10	186	180	183	173	170	173	170	173	170	170
	30	174	156	158	155	153	155	148	153	149	149
Total added		638	594	530	502	468	463	443	428	430	427

this profile and after 30 days of incubation 86.15 per cent of the phosphate applied was converted to aluminum phosphate.

Richfield loam followed more or less the same trend as San Saba clay loam and Woodward loam in which the highest rate of conversion was obtained after one day of incubation as shown in Table VI. The rate of conversion was also higher in the surface horizons than in the subsoil where 34.55 per cent of the phosphorus applied was converted to aluminum phosphate after one day of incubation. The rate of conversion was the lowest in the 12 to 18 inch sample and then increased with depth.

Easily Soluble or "Saloid-Bound" Phosphate

The easily soluble or "saloid-bound" phosphate is reported in Tables III to VI. "Saloid-bound" phosphate content was negligible before incubation in all of the soils studied in this investigation.

One day after the beginning of incubation period in Bolan clay loam in the 0 to 9 inch sample, 95 per cent of the soluble phosphate applied was still present as "saloid-bound" phosphorus and then decreased with depth as shown in Table V. However, in the sample taken at a depth of 71 to 79 inches 85.0 per cent of the phosphorus applied was still present as "saloid-bound" phosphate. The amount of "saloid-bound" phosphate decreased with time of incubation in samples from all soil depths.

The data on "saloid-bound" phosphate for San Saba clay loam are reported in Table IV which shows that at a depth of 0 to 9 inches 85 per cent of the soluble phosphate applied was converted to forms other than "saloid-bound" phosphate and only 15 per cent of the phosphorus was present in this form. The rate of conversion to forms other than

TABLE VI

DISTRIBUTION OF FORMS OF PHOSPHORUS IN RICHFIELD LOAM

Form of phosphorus	Incubation time (days)	Depth (inches)			
		0-12	12-18	18-28	>28
		ppm			
Total inorganic P	0	322	550	570	521
Aluminum P	0	19.2	0	0.8	0.24
	1	88.3	26.7	37.6	68.00
	10	94.0	28.0	39.0	76.00
	30	96.0	30.1	60.1	82.00
Calcium P	0	300	525	565	525
	1	320	545	618	582
	10	329	570	620	586
	30	332	580	625	588
Easily soluble P	0	0	0	0	0
	1	145	105	110	128
	10	130	93	100	113
	30	123	83	83	105
Total added	0	319	525	566	525

"saloid-bound" phosphate increased with depth of sampling. The amount of "saloid-bound" phosphate decreased with time of incubation at all depths. At a depth of greater than 24 inches only 2.5 per cent of the phosphorus applied was present in this form 30 days after the beginning of the incubation period.

The data for "saloid-bound" phosphorus in Woodward loam are reported in Table III. One day after the beginning of incubation of 0 to 6 inch sample, 57.5 per cent of the phosphorus applied was present as "saloid-bound" phosphorus while at the same time at a depth of 6 to 13 inches only 35 per cent of the phosphorus applied was present in the form of "saloid-bound" phosphate. The amount of "saloid-bound" phosphate decreased with the incubation period. Thirty days after the beginning of the incubation period in the 6 to 13 inch sample only 26.5 per cent of the soluble phosphate applied was present in this form.

The data for Richfield loam are reported in Table VI. One day after the beginning of incubation period the 0 to 12 inch sample showed 72.5 per cent of the phosphorus applied to be present in this form. Thirty days after the beginning of incubation period at the same depth, 61.5 per cent of the phosphorus applied was still present in this form. This profile followed more or less the same trend as Bolan clay loam, in which a large portion of the phosphorus applied was still present in this form 30 days after the beginning of incubation period. The amount of "saloid-bound" phosphate decreased with the time of incubation in samples at all depths.

The total inorganic phosphorus before incubation agrees very closely with the total inorganic phosphorus added in all of the soils studied in this investigation as shown in Tables III to VI. In Bolan clay loam, at lower depths, in spite of two extractions of calcium phosphate with 0.5 N sulfuric acid, the values obtained by the fractionation procedure was still lower than that obtained by the procedure of Mehta, et al. (92) which indicates that the fractionation procedure did not extract all of the inorganic phosphorus. In some cases, even a third extraction of calcium phosphate gave some phosphate yield. Three washings with 25 ml portions of saturated sodium chloride seems to be better than two washings.

The first hypothesis which indicates that phosphorus applied to soil will greatly decrease in solubility in 24 hours cannot be rejected because the rate of conversion of soluble phosphate to other fractions was the highest one day after the beginning of incubation period in all of the soils studied in this investigation. However, the second part of the hypothesis which says that a major fraction of the soluble phosphate will be converted to aluminum phosphate one day after the beginning of incubation period cannot be rejected in San Saba clay loam. The same thing is true with the samples from the surface horizons of Woodward loam and Richfield loam, but the second part of the same hypothesis cannot be accepted for Bolan clay loam where the amount of conversion of soluble phosphate to aluminum phosphate was very small. The third part of the same hypothesis which says that 10 days after the beginning of the incubation period the amount of aluminum phosphate will start to decrease while the amount of calcium phosphate will still be increasing cannot be accepted for San Saba clay loam, Woodward loam and Richfield loam. But it cannot be rejected for Bolan clay loam.

Available Phosphorus

The data for available phosphorus of the soils studied in this investigation are reported in Figures 4 to 11.

Bray #1 (16). Bolan clay loam before incubation had the lowest available phosphorus content compared to the other soils studied in this investigation. The data for Bolan clay loam are reported in Figure 4. The amount of available phosphorus extracted by this procedure generally increased with the incubation period in all samples at all soil depths. The amount of available phosphorus present is higher in the surface horizons while at the lower depths the amount of available phosphorus after 1, 10 and 30 days incubation is not significantly different from each other.

The data for San Saba clay loam are reported in Figure 5 which shows that the amount of available phosphorus increases with the incubation period in all samples taken at all depths. One day after the beginning of incubation period the 0 to 9 inch sample showed 60 per cent of the phosphorus applied as available phosphorus, while at a depth of 9 to 24 inches only 37.5 per cent of the phosphorus applied was still available. Thirty days after the beginning of incubation period at a depth of 0 to 9 inches, 62.5 per cent of the phosphorus applied was still available, while at the same time, the amount of available phosphorus at lower depths was smaller than the amount of the available phosphorus in the 0 to 9 inch sample.

The data for Woodward loam are reported in Figure 6. The amount of available phosphorus extracted by the Bray #1 procedure (16) from Woodward loam is higher than all of the other soils studied in this

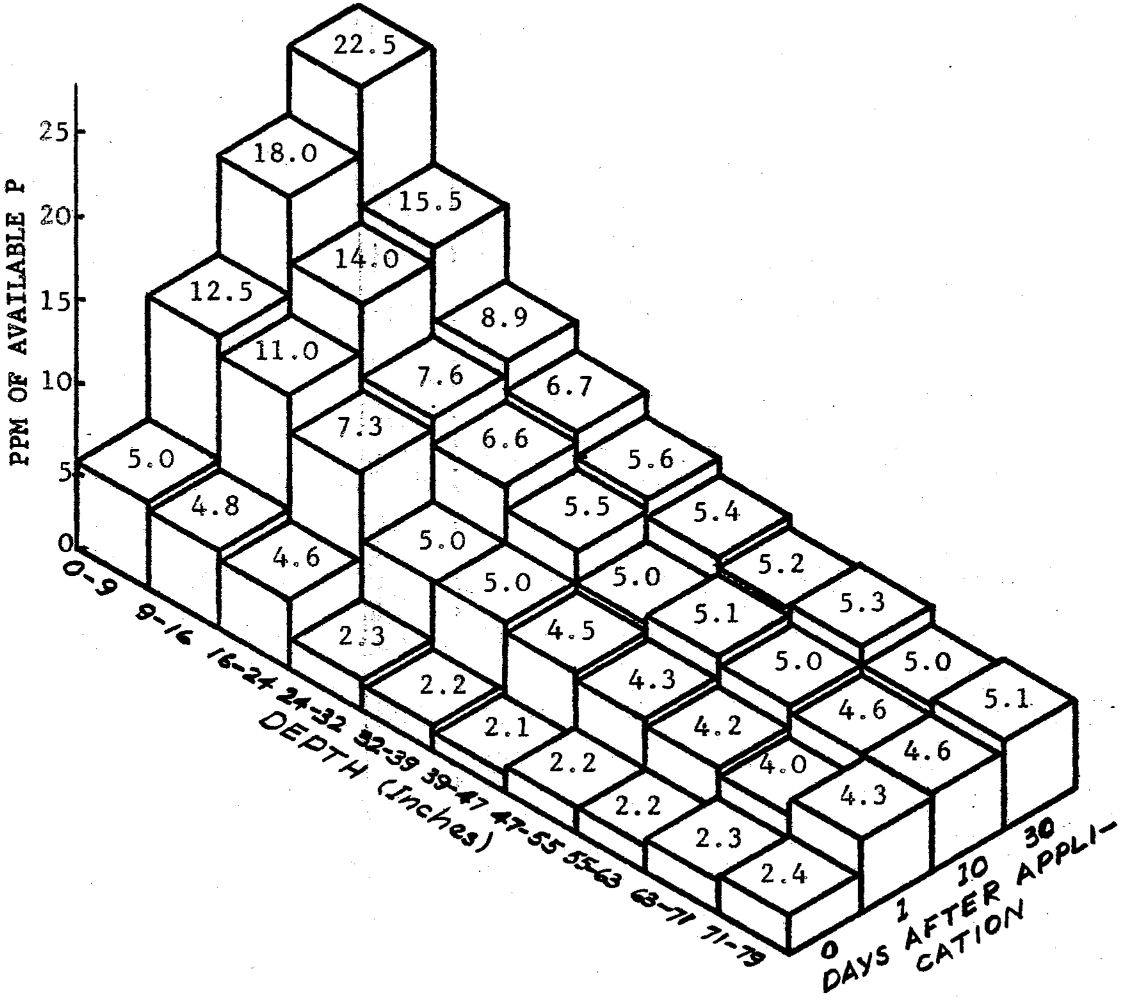

Figure 4. Phosphorus Extracted from Bolan Clay Loam by Bray #1 (1:50) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

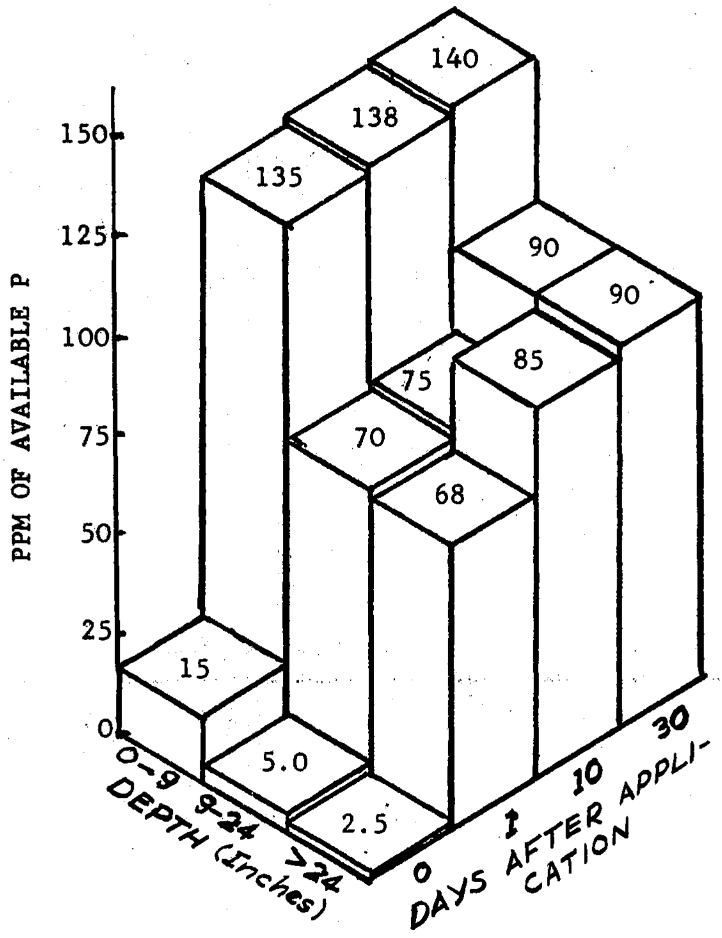

Figure 5. Phosphorus Extracted from San Saba Clay Loam by Bray #1 (1:50) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

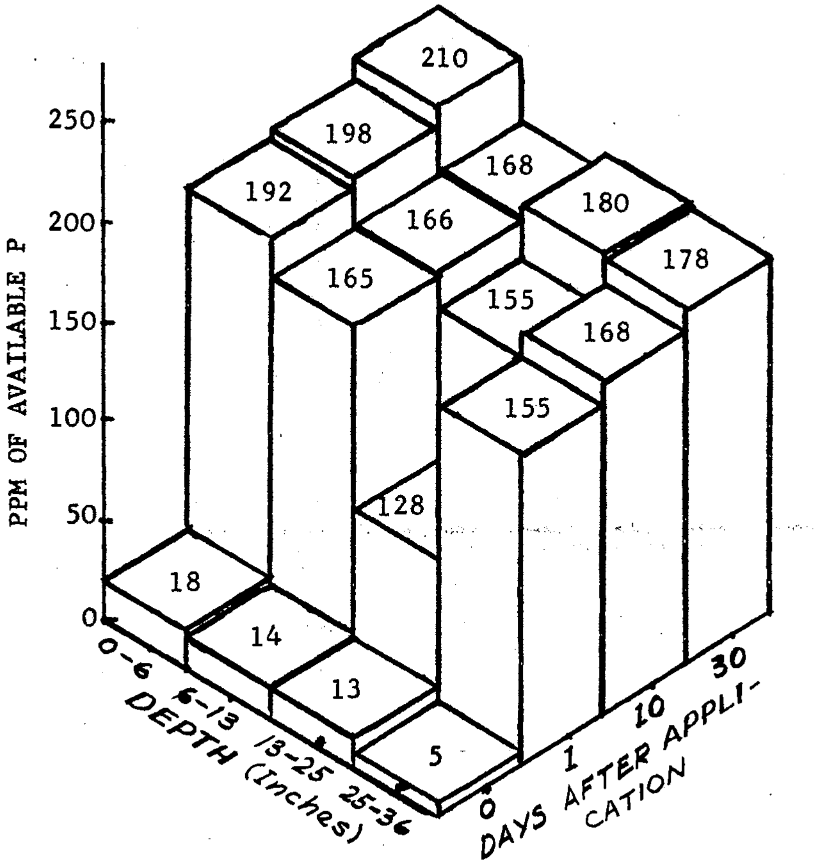

Figure 6. Phosphorus Extracted from Woodward Loam by Bray #1 (1:50) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

investigation. The amount of available phosphorus increases with the incubation period in samples taken at all depths. At a depth of 0 to 6 inches after one day of incubation 87 per cent of the phosphorus applied was still available, while 30 days of incubation in the same sample, 96 per cent of the applied phosphorus was in the available form. The amount of avilable phosphorus in this profile increased with the time of incubation. The amount of available phosphorus was the highest at a depth of 0 to 6 inches. Even at a depth of 25 to 36 inches 86.5 per cent of the soluble phosphorus applied was available after 30 days of incubation. The amount of available phosphorus in Woodward loam was higher than the amount of available phosphorus present in Bolan clay loam and San Saba clay loam.

Available phosphorus extracted by the procedure of Bray #1 (16) from Richfield loam is shown in Figure 7. The data in this figure follow more or less the same trend as that for the Woodward loam soil. One day after the beginning of incubation period of the 0 to 12 inch sample, 84 per cent of the soluble phosphate applied was present in the available form, while 30 days after incubation at the same depth, 94 per cent of the soluble phosphate applied was still available. The amount of available phosphorus at the lower depths was much smaller than the amount of available phosphorus at a depth of 0 to 12 inches. The amount of available phosphorus in Richfield loam increased with the time of incubation. The amount of available phosphorus in this profile was the lowest after one day of incubation and then increased with the time of incubation. Thirty days of incubation of samples taken at a depth of greater than 28 inches only 4.3 per cent of the soluble phosphorus applied was present in the available form. The second hypothesis

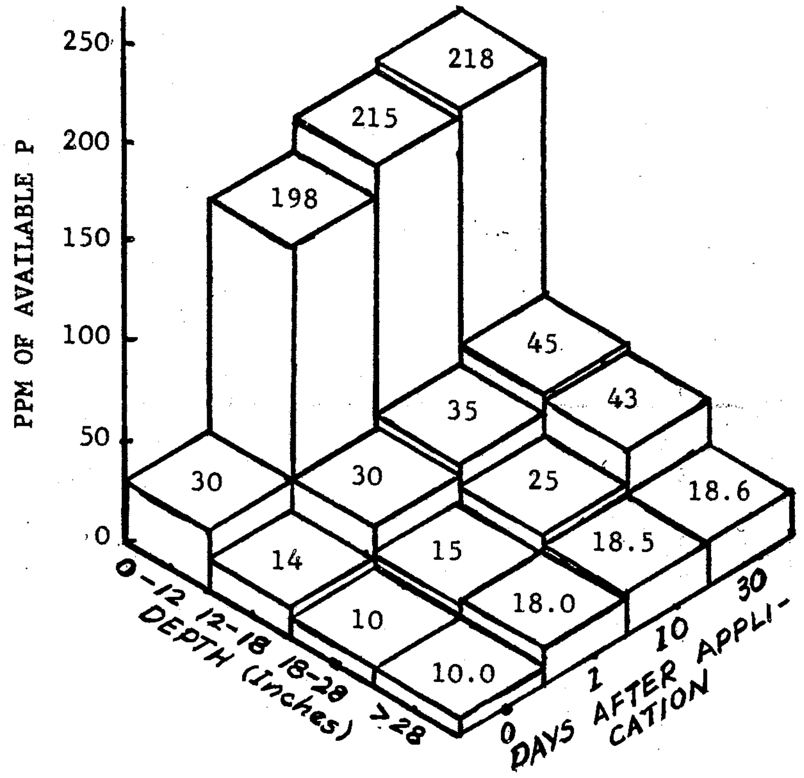

Figure 7. Phosphorus Extracted from Richfield Loam by Bray #1 (1:50) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

says that the availability of phosphorus to plants after 1, 10 and 30 days of incubatior will not be significantly different from each other. The amount of available phosphorus extracted by the procedure of Bray #1 (16) was the lowest after one day of incubation in all of the soils studied in this investigation, although the amount of available phosphorus after one day of incubation was increasing slightly which resulted in the highest available phosphorus after 30 days of incubation in all of the soils studied. Still, there was no significant difference between 1, 10 and 30 days. Therefore, the hypothesis cannot be rejected.

Bicarbonate procedure (34, 100). The data for the bicarbonate method are shown in Figures 8 to 11. In Bolan clay loam the amount of available phosphorus extracted by this procedure was higher than all of the other soils studied in this investigation (Figure 8). One day after the beginning of incubation period at the 0 to 9 inch sample 74.25 per cent of the soluble phosphorus applied was still available, while 30 days after the beginning of incubation period at the same depth 68.25 per cent of the soluble phosphorus applied was present in this form. The amount of available phosphorus present in the soil samples after each incubation period was not significantly different from one depth to another in this profile. Before incubation the amount of available phosphorus was the highest at a depth of 0 to 9 inches.

San Saba clay loam did not follow the same trend as Bolan clay loam as shown in Figure 9. The amount of available phosphorus in San Saba clay loam increased with the incubation period at all depths. The same thing was true with the trend of available phosphorus of this profile as it was extracted with Bray #1 (16). The amount of available phosphorus before incubation was the highest in the 0 to 9 inch sample

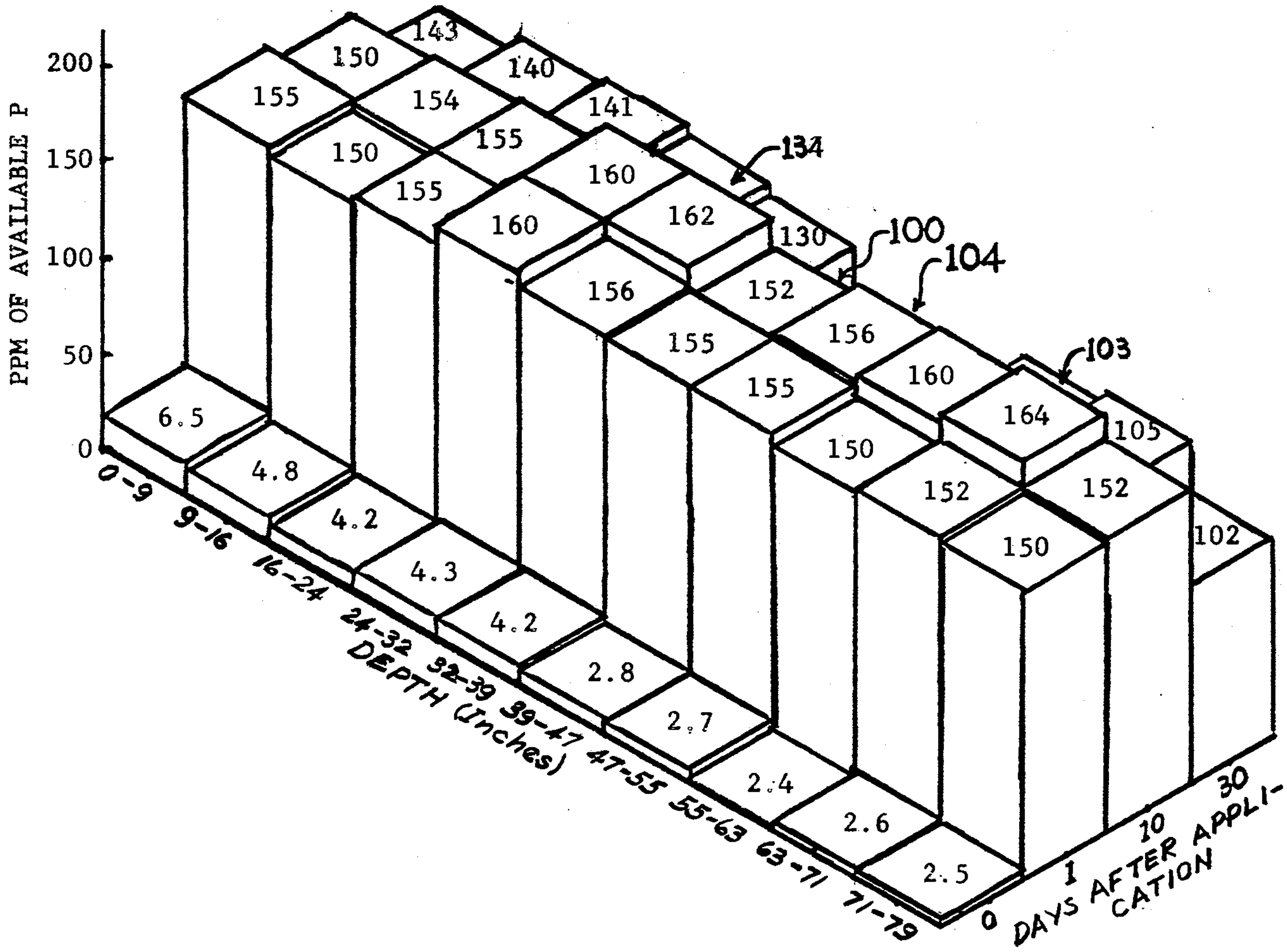

Figure 8. Phosphorus Extracted from Bolan Clay Loam by Bicarbonate (Olsen, Dickman and Bray) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

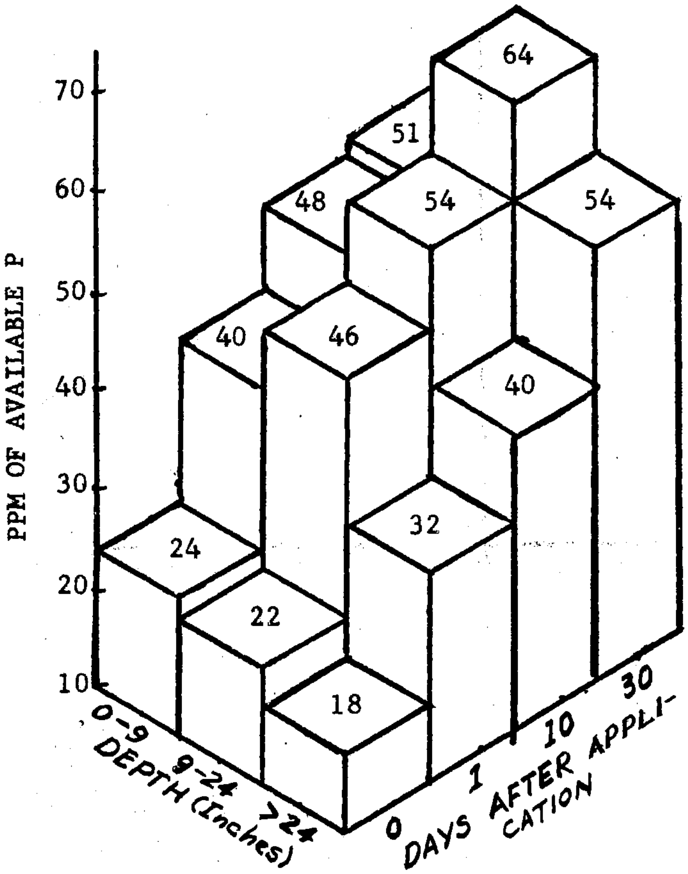

Figure 9. Phosphorus Extracted from San Saba Clay Loam by Bicarbonate (Olsen, Dickman and Bray) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

and then it decreased with depth. The amount of available phosphorus was the highest 30 days after the beginning of incubation period of samples from all three depths of this profile. One day after the beginning of incubation perioa of the 0 to 9 inch sample 8 per cent of the phosphorus applied was still available, while 30 days after incubation at the same depth 13.5 per cent of the soluble phosphorus applied was available. Thirty days after the beginning of incubation period the 9 to 24 inch sample had 21 per cent of the soluble phosphate applied still in the available form and this amount is the highest in the whole profile.

The amount of available phosphorus extracted by the bicarbonate method from Woodward loam is given in Figure 10. The amount of available phosphorus extracted by this method increased with the incubation period at all soil depths except the 13 to 25 inch sample. Other depths were similar to San Saba clay loam and at this depth the amount of available phosphorus after 1, 10 and 30 days was very close to each other. One day after incubation the 0 to 6 inch sample showed that 40 per cent of soluble phosphate applied was available. Thirty days after the beginning of incubation period of the 13 to 25 inch sample bicarbonate phosphorus was the lowest in this profile, while samples taken at depths greater than 25 inches had 54 per cent of the soluble phosphorus applied still available and this was the highest amount for this period of incubation in this profile. The amount of available phosphorus was the lowest at all depths one day after incubation, compared to 30 days.

Available phosphorus from Richfield loam is shown in Figure 11. This profile followed more or less the same trend as San Saba clay loam, in which the amount of available phosphorus increased with the

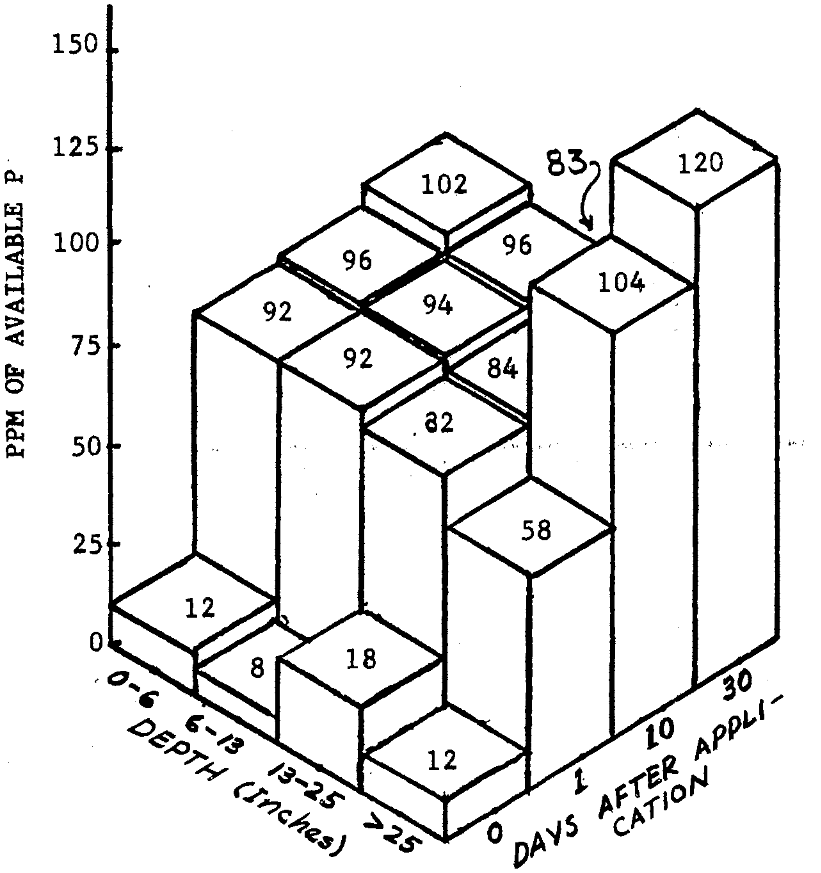

Figure 10. Phosphorus Extracted from Woodward Loam by Bicarbonate (Olsen, Dickman and Bray) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

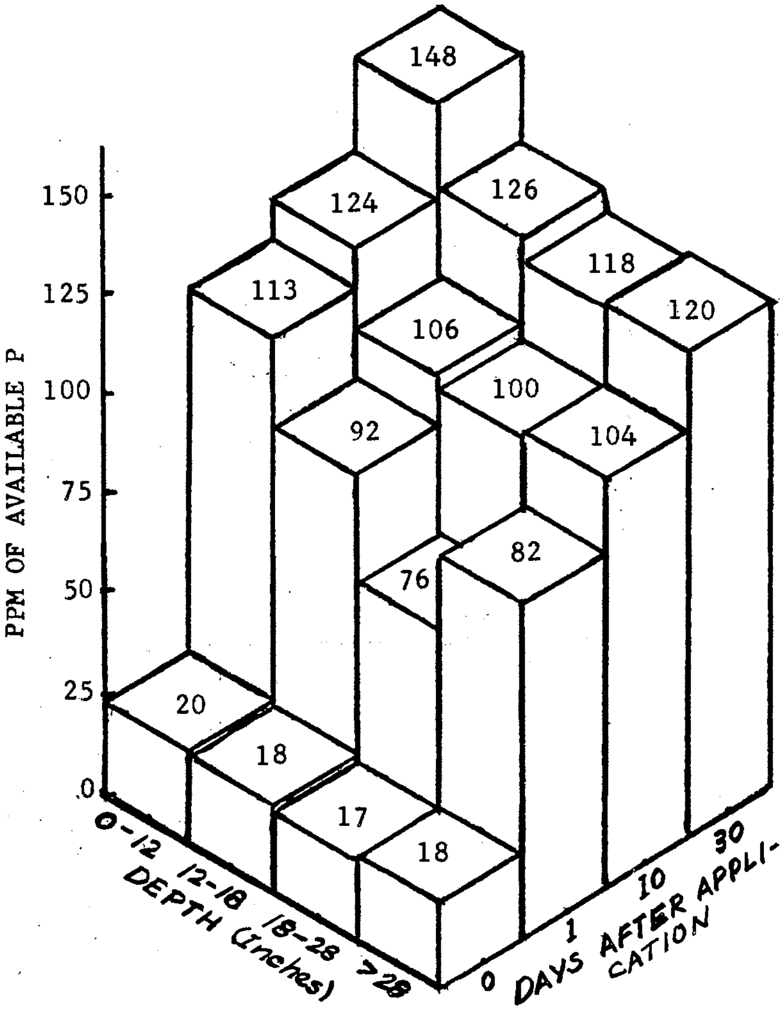

Figure 11. Phosphorus Extracted from Richfield Loam by Bicarbonate (Olsen, Dickman and Bray) after Treatment with 200 ppm of P as $NH_4H_2PO_4$

incubation period. One day after the beginning of incubation period the 0 to 12 inch sample showed 46.5 per cent of the soluble phosphorus applied was still available, while in the same sample 30 days after the beginning of incubation period, 64 per cent of the soluble phosphorus applied was present in this form. The amount of available phosphorus before incubation was the highest in the 0 to 12 inch sample. One day after the beginning of incubation period these soils were significantly lower in available phosphorus than after 10 and 30 days of incubation.

The second hypothesis which says that the availability of phosphorus to plants after 1, 10 and 30 days of incubation will not be significantly different from each other cannot be rejected, based on the data obtained by the bicarbonate method for Bolan clay loam, San Saba clay loam and Woodward loam but the same hypothesis cannot be accepted based on the data obtained from the Richfield loam.

Generally, as the result of the soluble phosphate applied, the pH of the soils studied in this investigation decreased which might be due to the conversion of ammonium ion in the fertilizer applied to nitrate through microbial activities which will finally make nitric acid (Table VII). At the same time phosphoric acid can also be formed.

Dry Matter Production of Sorghum Plants (Sorghum x Sudangrass Hybrid)

The dry matter obtained from the greenhouse experiment is reported in Tables VIII and IX and the analysis of variance for the forage yield on San Saba clay loam, Woodward loam and Richfield loam is shown in Table X. Phosphate fertilization of all of the soils studied in this investigation increased the yield over their control treatments.

TABLE VII

EFFECTS OF AMMONIUM PHOSPHATE APPLICATION ON THE pH

Type of soil	Depth (in.)	Incubation period (days) 0	1	10	30
Bolan clay loam	0-9	8.3	8.1	8.0	8.0
	9-16	8.4	8.2	8.0	8.0
	16-24	8.4	7.9	8.0	8.0
	24-32	8.4	8.0	7.9	8.0
	32-39	8.4	8.2	8.1	8.1
	39-47	8.4	8.0	8.0	8.0
	47-55	8.4	8.4	8.2	8.3
	55-63	8.7	8.7	8.5	8.4
	63-71	8.4	8.3	8.3	8.1
	71-79	8.6	8.4	8.3	8.3
San Saba clay loam	0-9	7.2	6.8	7.0	6.9
	9-24	7.3	7.2	7.2	7.1
	>24	7.6	7.2	7.2	7.1
Woodward loam	0-6	8.0	7.3	7.3	7.3
	6-13	7.9	7.5	7.6	7.8
	13-25	7.9	7.6	7.8	7.8
	25-36	7.9	7.6	7.6	7.7
Richfield loam	0-12	7.6	7.5	7.5	7.5
	12-18	7.9	7.8	7.9	7.8
	18-28	8.0	7.7	8.0	7.9
	>28	8.0	7.9	7.9	7.8

TABLE VIII

DRY MATTER PRODUCTION OF SORGHUM-SUDANGRASS HYBRID AS INFLUENCED BY THE RATE OF PHOSPHATE FERTILIZER IN THREE OKLAHOMA SOILS*

Location	Rate of P (ppm)	1st crop, ave. wt. (g/pot)	2nd crop, ave. wt. (g/pot)
San Saba clay loam	0	0.073	0.395
	200	1.025	0.066
	400	1.278	0.058
	600	1.244	0.114
Woodward loam	0	0.264	0.300
	200	1.112	0.153
	400	0.959	0.272
	600	0.815	0.431
Richfield loam	0	0.003	0.766
	200	0.587	0.578
	400	0.883	0.449
	600	0.654	0.841

*The mean values of dry matter not joined by a common line are significantly different at 5% level.

TABLE IX

DRY MATTER PRODUCTION OF SORGHUM-SUDANGRASS HYBRID IN GRAMS PER POT AS INFLUENCED BY PHOSPHATE APPLICATION ON BOLAN CLAY LOAM

Sample No.	Soil No. III		Soil No. IV		Soil No. V		Soil No. VI	
	0 P	200 ppm P	0 P	200 ppm P	0 P	200 ppm P	0 P	200 ppm P
1	0.260	1.858	0.219	1.518	0.214	1.138	0.326	0.500
2	0.191	1.410	0.148	1.425	0.219	0.873	0.150	1.611
3	0.105	0.833	1.478	1.079	0.220	1.000	0.332	2.713
4	0.101	1.648	0.200	1.332	0.221	2.404	1.006	1.441
5	0.770	1.002	0.221	1.616	1.024	1.190	1.000	1.437
6	0.332	1.939	0.423	2.671	0.433	1.276	1.000	0.978
7	0.237	1.804	0.172	1.552	0.128	1.138	0.428	0.456
8	0.211	1.721	0.108	1.048	0.200	0.920	0.120	1.609
9	0.491	3.184	0.573	3.793	0.227	0.905	0.223	1.780
10	0.185	1.769	0.224	1.620	0.180	1.736	0.162	1.421
11	0.195	1.130	0.179	1.187	0.114	0.462	0.199	0.358
12	0.257	1.868	1.184	7.958	0.279	0.892	0.249	0.630
13	0.894	6.936	0.120	0.908	0.744	1.325	0.247	1.913
14	1.007	7.035	0.182	1.921	0.265	0.550	0.122	1.720
15	0.262	2.626	0.182	1.280	0.170	1.471	0.315	1.029
16	0.212	1.289	0.352	2.502	0.283	0.668	0.283	1.620
17	0.732	4.703	0.310	2.258	0.853	0.565	0.247	1.414
18	0.179	1.133	0.179	1.181	0.237	1.306	0.199	0.753
19	0.202	1.476	0.205	1.521	0.201	1.361	0.813	1.098
20	0.302	2.099	0.425	2.355	0.438	0.573	0.156	1.571

TABLE X

ANALYSIS OF VARIANCE OF DRY MATTER PRODUCTION OF SORGHUM-SUDANGRASS HYBRID AS INFLUENCED BY RATE OF PHOSPHATE, NUMBER OF CROPS AND LOCATIONS

SV	df	MS
Blocks	2	0.010
Locations (L)	2	0.002
Crops (C)	1	2.049**
P levels (P)	3	0.371**
L x P	6	0.024
L x C	2	1.049**
P x C	3	1.439**
L x P x C	6	0.137*
Error	46	0.056

*Significant at 5% level.
**Significant at 1% level.

Analysis of variance was also conducted for forage yields of individual soils and the results indicated that there was no significant difference in the yields between 200, 400 and 600 ppm of phosphorus. Control treatments in all of these soils significantly yielded lower than the fertilized treatments. The first harvest was fertilized with both nitrogen and phosphorus, while the second crop in all of the Oklahoma soils was fertilized only with nitrogen. In Bolan clay loam the first crop was not fertilized with phosphorus but the second crop was fertilized with phosphorus. Two hundred ppm of phosphorus is more economical than 400 and 600 ppm of phosphorus, but in a long-term experiment the higher rates might work better as far as soil phosphate fixing capacity is concerned. Under similar conditions even 100 ppm of phosphorus might be more economical for the first crop.

There was no significant difference between the soil sampling locations, but there was a significant difference between the rates of phosphorus as shown in Table X. However, Duncan's multiple range test did not show any significant difference between 200, 400 and 600 ppm treatments, while all of these fertilized treatments were significantly different from their control treatments. There was no significant difference in the yield of the second crop and in some cases the control treatment for the second crop was higher than the fertilized treatments. This might be explained by the removal of plant nutrients other than phosphorus by the first crop where the yields of fertilized treatments were much higher than the control treatments. All of the soils studied in this investigation gave high yields for the first crop. There was no significant increase in yield of the second crop due to residual effects of phosphorus from the first crop. There was an interaction between locations and phosphorus levels and this interaction was largely due to phosphate levels because the soil sample locations were not significantly different from each other. There was also interaction between croppings and phosphate levels and this is due to both croppings and phosphate levels because both of them were significantly different. There was also interaction between locations, phosphate levels and croppings. The significant interaction between croppings and locations is mainly due to croppings because the locations were not significantly different from each other.

Phosphate Uptake by Sorghum-Sudangrass Hybrid

Both crops were analyzed for total phosphorus and the results indicate that the higher the rate of phosphorus applied the greater the uptake. The amount of phosphorus in the plant tissues was significantly different from each other between 0, 200, 400 and 600 ppm of phosphorus. The amount of phosphorus removed from the soil by both crops is reported in Table XI. The amount of phosphorus removed by the first crop is significantly higher than the amount removed by the second crop.

TABLE XI

REMOVAL OF PHOSPHORUS FROM THE SOIL BY SORGHUM-SUDANGRASS HYBRID AS INFLUENCED BY THE RATE OF PHOSPHORUS FERTILIZATION IN THREE CALCAREOUS OKLAHOMA SOILS

Type of soil	P level (ppm)	Average amount of P (mg/pot) 1st crop	2nd crop
San Saba clay loam	0	0.33	0.621
	200	3.23	3.000
	400	5.55	2.420
	600	5.47	2.330
Woodward loam	0	0.59	1.110
	200	3.88	0.466
	400	4.30	0.816
	600	5.22	1.800
Richfield loam	0	0.19	0.962
	200	4.29	0.260
	400	9.17	0.350
	600	9.96	0.760

Analysis of variance was conducted for both crops on soils from all of the three locations and the results are shown in Table XII. Phosphate uptake by sorghum plants from soils taken from three locations was significantly different from each other. Differences in the

TABLE XII

ANALYSIS OF VARIANCE OF PHOSPHATE REMOVAL IN MG/POT BY SORGHUM PLANTS AS INFLUENCED BY THE RATE OF PHOSPHATE FERTILIZATION

SV	df	MS
Blocks	2	0.004
Locations (L)	2	5.946**
P levels (P)	3	47.336**
Croppings (C)	1	173.527**
L x P	6	3.034**
L x C	2	17.153**
P x C	3	33.104**
L x P x C	6	7.363**
Error	46	.014

**Significant at 1% level.

uptake due to differences in the levels of phosphorus were significantly different from each other. There were also significant differences between the two crops in all of the soils studied in this investigation. There were significant interactions between locations and phosphorus levels. This interaction was due to both phosphorus levels and locations. There was also significant interaction between locations and crops. This interaction was due to cropping and locations, because there were significant differences in phosphorus yields between locations and crops. The significant interaction between cropping, locations and phosphorus levels resulted from all of these three factors.

A correlation study was conducted to compare dry matter production with phosphate uptake and the results are reported in Table XIII. In San Saba clay loam there was a highly significant correlation between the yield of the second crop with phosphate uptake and was significant at the 5% level of probability and was lower than the correlation obtained for the first crop. Correlation of phosphorus uptake versus yield of both crops together was also significant at the 5% level of probability. Correlation between yield and phosphate uptake for Woodward loam for both crops is only significant at the 5% level of probability, while the correlation for both crops together was significant at both 1% and 5% levels of probability.

Correlation between yield and phosphate uptake for Richfield loam was highly significant for the first crop while the correlation for the second crop was not significant. Correlation between yield and phosphate uptake for both crops was significant only at the 5% level of probability.

The correlation coefficient between yield and phosphorus uptake for both crops in the three soils studied was significant at both the 1% and 5% levels of probability. In general there was a significant correlation between the dry matter production and the phosphate uptake. In Richfield loam soil the non-significant correlation might be due to a herbicide which was spread on that soil before the soil samples were taken. In the first crop the yield of the control treatment was very low because the herbicide might have interferred with growth. However, at the 200, 400 and 600 ppm of phosphorus treatments the effect of the herbicide on plant growth was not as great as on the control because more phosphorus was absorbed by the plants.

TABLE XIII

CORRELATION COEFFICIENT VALUES (r) COMPARING THE DRY MATTER PRODUCTION WITH PHOSPHATE UPTAKE OF SORGHUM-SUDANGRASS HYBRID FROM THREE CALCAREOUS OKLAHOMA SOILS

Type of soil	Treatment	r
San Saba clay loam	First crop	0.8654**
	Second crop	0.5857*
	Both crops	0.6321*
Woodward loam	First crop	0.6658*
	Second crop	0.6021*
	Both crops	0.7944**
Richfield loam	First crop	0.8617**
	Second crop	-0.2481
	Both crops	0.4309*
All three soils	Both crops	0.7694**

*Significant at 5% level of probability.
**Significant at 1% level of probability.

A correlation study was also conducted to compare dry matter production with the form of phosphorus and the results are given in Table XIV. There was a highly significant correlation for San Saba clay loam between dry matter production and aluminum phosphate, calcium phosphate and available phosphorus (both bicarbonate and Bray #1) in the first harvest. However, the correlation coefficient between dry matter production and any of the phosphate forms was not significant for the second crop. Although the second crop was not fertilized with phosphorus the uptake of phosphorus was higher on those treatments which had the

TABLE XIV

CORRELATION COEFFICIENT VALUES (r) COMPARING THE DRY MATTER PRODUCTION AND SOIL FRACTIONS OF PHOSPHORUS

Soil type	Phosphorus fraction	r
San Saba clay loam (First crop)	Al-P	0.9920**
	Ca-P	0.9785**
	Bicarbonate (available P)	0.9682**
	Bray #1 (available P)	0.9737**
San Saba clay loam (Second crop)	Al-P	-0.2509
	Ca-P	-0.2510
	Bicarbonate (available P)	-0.1094
	Bray #1 (available P)	-0.1304
Woodward loam (First crop)	Al-P	0.8651**
	Ca-P	0.8854**
	Bicarbonate (available P)	0.8033**
	Bray #1 (available P)	0.9716**
Woodward loam (Second crop)	Al-P	0.5978*
	Ca-P	0.6094*
	Bicarbonate (available P)	0.6804*
	Bray #1 (available P)	0.4141
Richfield loam (First crop)	Al-P	0.8700**
	Ca-P	0.9085**
	Bicarbonate (available P)	0.8904**
	Bray #1 (available P)	0.9458**
Richfield loam (Second crop)	Al-P	0.6123*
	Ca-P	0.4481
	Bicarbonate (available P)	0.5904*
	Bray #1 (available P)	0.5731*

*Significant at 5% level of probability.
**Significant at 1% level of probability.

high rate of phosphate fertilization applied for the first crop. The yield of the second crop might have been affected by factors other than phosphorus. San Saba clay loam produced a high yield for the first crop which might have removed some other plant nutrients from the soil. However, the yield of the control treatment was not as high to affect the level of other nutrients.

For Woodward loam available phosphorus by Bray #1 (16) is highly correlated with the yield of the first crop. This was the highest correlation between the yield and phosphate fraction of any of the soils studied in this investigation. There was also a highly significant correlation between the yield and the phosphate forms (Al-P, Ca-P, and available P by the bicarbonate method) for the first crop. For the second crop the Bray #1 was not significantly correlated with yield, while all other forms were significantly correlated with the yield. For the second crop the phosphate uptake was high but may not have been high enough to increase the yield or the yield might have been limited by factors other than phosphorus. The first fertilized crop yielded very high compared to the control treatments. This high yield might have removed some other plant nutrients which might have been the limiting factors for yield.

Iron deficiency of the sorghum-sudangrass hybrid plants was noticed on the first crop grown on Woodward loam and this deficiency was more severe on the second crop. For the second crop the forage yield was highly correlated with available phosphorus extracted by the bicarbonate procedure of Olsen, et _al_. (100). This was the highest correlation in the second crop for any of the soils studied.

For Richfield loam the highest correlation of dry matter with phosphate form was obtained with Bray #1 (16) in the first crop as was the case for Woodward loam. Dry matter was also significantly correlated with Al-P, Ca-P and available phosphorus extracted by the procedure of Olsen, et al. (100). For the second crop only Ca-P was not significantly correlated with the yield, while all other forms of phosphorus were significantly correlated with the yield.

Mineralogical Study

The third objective of this investigation was to study the mineralogy of these soils. Type of clay minerals is probably very important in phosphorus fixation. Percentage sand, silt, fine clay and coarse clay in these soils is reported in Table XV. Type of clay mineral is shown in Table XVI and Figures 13 to 34 show the results of an X-ray diffraction study of the soils investigated. Only one representative sample of fine and corase clay from each profile is shown. The schematic diagram of the diffracted X-ray beam according to Bragg's law is represented in Figure 12.

Bolan clays as shown in Tables XVI and XVII and Figures 13 and 14 had a diffraction spacing of approximately 10 A. After potassium saturation, however, in some horizons this spacing was very weak. Bolan clays also had a diffraction spacing of 14.72 A. This spacing was not affected significantly by any of the treatments. This indicates that Bolan clays contain chlorite. Before heating Bolan clay had two spacings of approximately 7.16 and 3.56 A, but after heating both of these spacings disappeared. This indicates that these spacings were due to kaolinite. The 3.56 A is second order maximum for kaolinite. Bolan

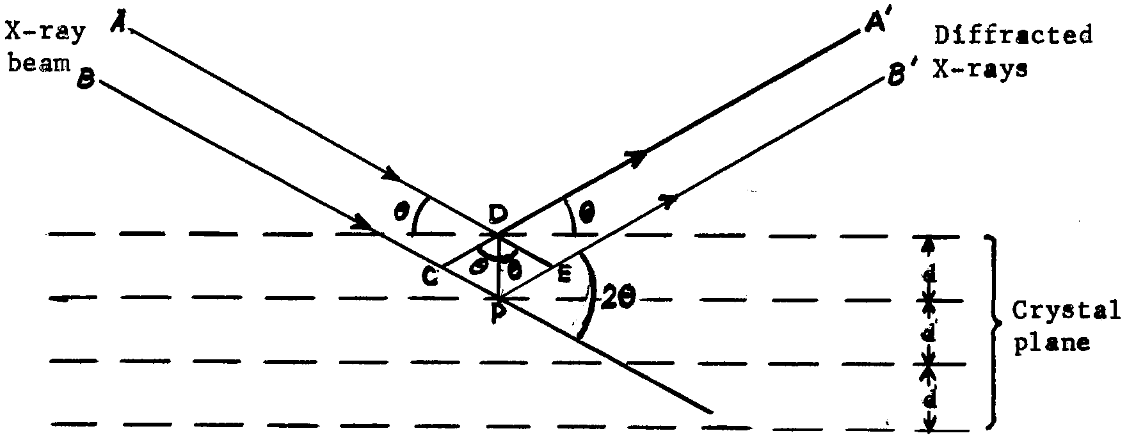

Figure 12. Diffraction from Crystal Planes According to Bragg's Law, $n\lambda = 2d\sin\theta$

clays also contained quartz and plagioclase feldspar.

San Saba clays had a diffraction spacing of approximately 15.8 A after the clay was saturated with magnesium chloride as shown in Tables XVIII and XIX and Figures 15 to 16. Upon glycerol solvation this spacing expanded to approximately 18.4 A. Clay from the 0 to 9 inch depth when saturated with potassium chloride collapsed to 12.99 A, while clays from the lower depths of this profile upon potassium saturation collapsed and there was not an intense diffraction spacing at 12.99 A. This indicates that the San Saba clays have montmorillonite in both the fine and coarse fractions. San Saba fine clay at a depth of 9 to 24 inches before potassium saturation had a diffraction spacing of approximately 10 A. This spacing also collapsed upon potassium saturation. This spacing is due to the presence of illite. San Saba coarse clays from the 0 to 24 inch depth also had a diffraction spacing of approximately 7.2 A before the soil was heated at 500 C for four hours and upon heating this spacing disappeared. This spacing is believed to be due to the presence of metahalloysite, San Saba clays also have

TABLE XV

PARTICLE SIZE DISTRIBUTION OF DIFFERENT SOILS AT VARIOUS DEPTHS

		Per cent			
Location	Depth (in.)	Sand	Silt	Fine clay	Coarse clay
Bolan clay loam (Bost, Afghanistan)	0-9	25.10	35.86	24.60	14.39
	9-16	28.47	27.57	23.50	20.42
	16-24	26.27	29.73	22.85	20.88
	24-32	29.52	26.35	20.00	23.96
	32-39	29.20	30.35	19.35	21.05
	39-47	29.15	30.30	20.05	20.32
	47-55	30.55	30.60	20.07	18.64
	55-63	28.75	40.25	20.10	10.84
	63-71	28.35	40.40	19.10	6.14
	71-79	17.95	41.75	32.25	7.82
San Saba clay loam (Oklahoma)	0-9	11.26	21.98	21.98	44.70
	9-24	11.28	17.48	17.48	53.60
	>24	15.40	16.32	16.46	51.80
Woodward loam (Oklahoma)	0-6	33.32	28.60	28.60	9.46
	6-13	37.00	22.48	22.48	18.13
	13-25	40.34	18.40	18.38	22.84
	25-36	31.30	19.86	19.86	29.93
Richfield loam (Oklahoma)	0-12	35.00	28.78	28.78	7.36
	12-18	19.00	31.46	31.42	18.12
	18-28	11.00	30.30	30.28	28.38
	>28	12.02	36.30	36.24	15.39
Dorulaman clay loam (University farm, Kabul, Afghanistan)	0-8	10.35	48.90	10.10	30.20
Dorulaman clay loam (Ministry of Ag. farm, Kabul, Afghanistan)	0-8	11.75	49.00	9.00	29.60

Continued next page

TABLE XV, Continued

Location	Depth (in.)	Per cent Sand	Silt	Fine clay	Coarse clay
Shishem Bagh sandy loam (Ningerhar, Afghanistan)	0-8	54.50	24.22	6.80	13.20
Pos-i-shan silty clay (Baghlan, Afghanistan)	0-8	4.88	48.34	19.20	26.00
Mazar silty clay (Mazari Shariff, Afghanistan)	0-8	3.89	45.37	23.80	26.50
Kokoran clay loam (Kandahar, Afghanistan)	0-8	25.50	48.90	4.20	22.90
Shamalon clay (Bost, Afghanistan)	0-8	20.75	36.50	15.30	23.30
Baghra sandy clay (Bost, Afghanistan)	0-8	47.00	5.50	22.30	19.75

TABLE XVI

X-RAY DIFFRACTION AND d-SPACINGS IN ANGSTROMS OF THE 00l FOR BOLAN FINE CLAY (LESS THAN 0.2μ)

Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
0-9	10.643, 3.3482	10.643; 4.307; 4.1106	10.643; 4.287; 3.3606; 3.184	10.155; 4.13; 3.95; 3.26; 3.184	Illite, quartz, potassium feldspar
0-16	10.643, 3.348	10.643; 4.307; 3.348	10.04; 3.49; 3.348; 3.167	10.04; 3.348; 3.107	Illite, quartz, plagioclase feldspar
16-24	10.643, 3.348	10.643; 4.307; 3.348	3.15, 10.04	10.155; 3.348; 3.184	Chlorite, illite, quartz, plagioclase feldspar
24-32	9.927; 7.2; 4.092; 3.39; 3.36	10.643; 7.132; 6.505; 3.559; 3.348	10.04; 3.49; 3.569; 3.14	10.155; 3.348; 3.184	Chlorite, illite, quartz, kaolinite, plagioclase feldspar
32-39	14.717; 10.773; 7.189; 6.56; 3.559; 3.348; 3.118	14.717; 10.040; 7.13; 3.558; 3.348	14.72; 10.643; 7.189; 3.568; 3.348; 3.1617	14.717; 10.643; 7.36; 5.006; 3.56; 3.3482; 3.1617	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
39-47	14.717; 10.773; 7.189; 6.56; 3.558; 3.348; 3.118	14.717; 10.517; 7.13; 6.56; 5.03; 4.76; 3.558; 3.348	14.72; 10.04; 7.13; 3.561; 3.15	14.717; 10.69; 9.36; 5.006; 3.56; 3.348; 31617	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
47-55	14.717; 10.64; 7.189; 6.56; 4.766; 3.348	14.717; 10.517; 7.13; 6.56; 5.03; 4.76; 3.558; 3.348	14.72; 10.04; 7.2; 3.36; 3.15	14.72; 10.04; 3.56; 3.348; 3.15	Chlorite, illite, quartz, plagioclase feldspar

Continued next page

TABLE XVI, Continued

Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
55-63	10.64; 7.189; 6.56; 4.766; 3.348	10.517; 7.13; 6.56; 5.03; 4.75; 3.558; 3.348	14.72; 10.04; 7.2; 3.36; 3.15	14.72; 10.04; 3.56; 3.348 3.15	Chlorite, illite, quartz, plagioclase feldspar
63-71	10.64; 7.189; 6.56; 4.766; 3.348	10.517; 7.13; 6.56; 5.03; 4.75; 3.558; 3.348	14.72; 10.04; 7.2; 3.36; 3.15	10.04; 3.348; 3.15; 5.03	Chlorite, illite, quartz, plagioclase feldspar
71-79	10.64; 4.3079; 4.11; 3.37	10.52; 4.37; 4.07; 3.348	10.04; 3.558; 3.36; 3.15	10.04; 4.308; 4.11; 3.348; 3.1617	Calcite, illite, quartz, plagioclase feldspar

TABLE XVII

X-RAY DIFFRACTION AND d-SPACINGS IN ANGSTROMS OF THE 00l FOR BOLAN COARSE CLAY (0.2 to 2.0μ)

Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
0-9	14.476; 10.155; 7.1897	14.717; 10.04; 7.1897; 5.00; 4.76; 3.5587; 3.1187	14.243; 10.04; 7.132; 5.006; 4.766; 3.558; 3.348; 3.15	14.717; 10.15; 5.0065; 4.073; 3.348; 3.15	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
9-16	14.476; 10.04; 3.348	14.717; 10.04; 7.189; 4.3079; 4.11; 3.5587; 3.348	14.243; 10.04; 7.132; 6.32; 5.0; 4.76; 4.26; 3.56; 3.35	14.717; 10.155; 4.269; 4.07; 3.56; 3.348; 3.15	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
16-24	14.476; 4.282; 4.09; 3.36	14.717; 10.04; 7.189; 4.98; 4.716; 3.348; 3.118	14.717; 10.04; 4.26; 4.073; 3.558; 3.139	14.717; 10.155; 4.269; 4.07; 3.348; 3.15	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
24-32	14.717; 10.04; 7.1897; 5.035; 4.038; 4.1106; 3.558; 3.36	14.717; 10.04; 7.189; 4.98; 4.716; 3.348; 3.118	14.717; 10.04; 4.26; 4.073; 3.558; 3.139	14.717; 10.155; 4.269; 4.07; 3.348; 3.15	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
32-39	14.717; 10.04; 7.189; 5.035; 4.766; 3.5587; 3.348	14.717; 10.04; 7.189; 4.98; 4.716; 3.348; 3.118	14.717; 10.04; 4.269; 4.073; 3.56; 3.14	14.717; 10.15; 4.269; 4.073; 3.1399; 3.348	Chlorite, illite, kaolinite, quartz, plagioclase feldspar

Continued next page

TABLE XVII, Continued

Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
39-47	14.717; 10.04; 7.189; 5.035; 4.766; 3.5587; 3.348	14.717; 10.04; 7.189; 4.98; 4.716; 3.348; 3.118	14.717; 10.04; 3.568; 3.348; 3.15	14.717; 10.15; 5.0065; 3.37; 3.16	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
47-55	14.717; 10.04; 7.189; 5.035; 4.766; 3.5587; 3.348	14.717; 10.04; 7.189; 5.034; 3.5587; 3.3482	14.717; 10.04; 3.56; 3.2522; 3.3482; 3.15	14.717; 10.15; 3.3482; 3.15	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
55-63	14.717; 10.04; 7.189; 5.035; 4.766; 3.5587; 3.348	14.717; 10.04; 7.189; 5.034; 3.5587; 3.3482	14.717; 10.04; 3.56; 3.15	14.717; 10.155; 5.03; 4.26; 3.3482; 3.15	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
63-71	14.717; 10.04; 7.189; 5.035; 4.766; 3.5587 3.348	14.717; 10.04; 7.189; 5.034; 3.5587; 3.3482	14.717; 10.04 7.189; 5.00; 3.568; 3.3482	14.717; 10.155; 5.034; 3.3482	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
71-79	14.717; 10.04; 7.189; 5.035; 4.766; 3.5587; 3.348	14.717; 10.04; 7.189; 5.034; 3.5587; 3.3482	14.717; 10.04; 7.189; 5.00; 3.568; 3.3482	14.717; 10.155; 5.034; 4.28; 3.3482	Chlorite, illite, kaolinite, quartz, plagioclase feldspar

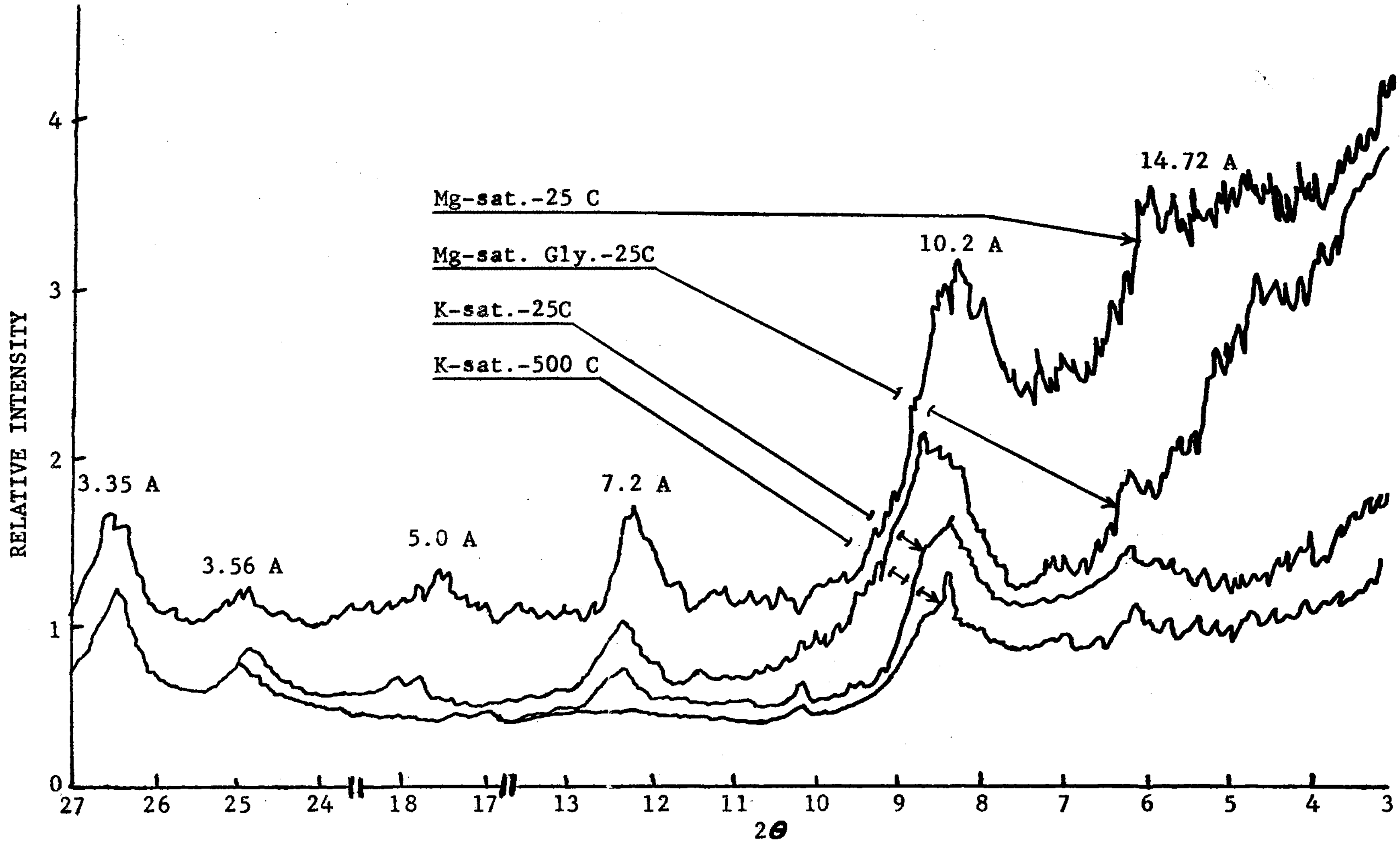

Figure 13. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of the Bolan Clay Loam Soil Taken at a Depth of 39 to 47 Inches

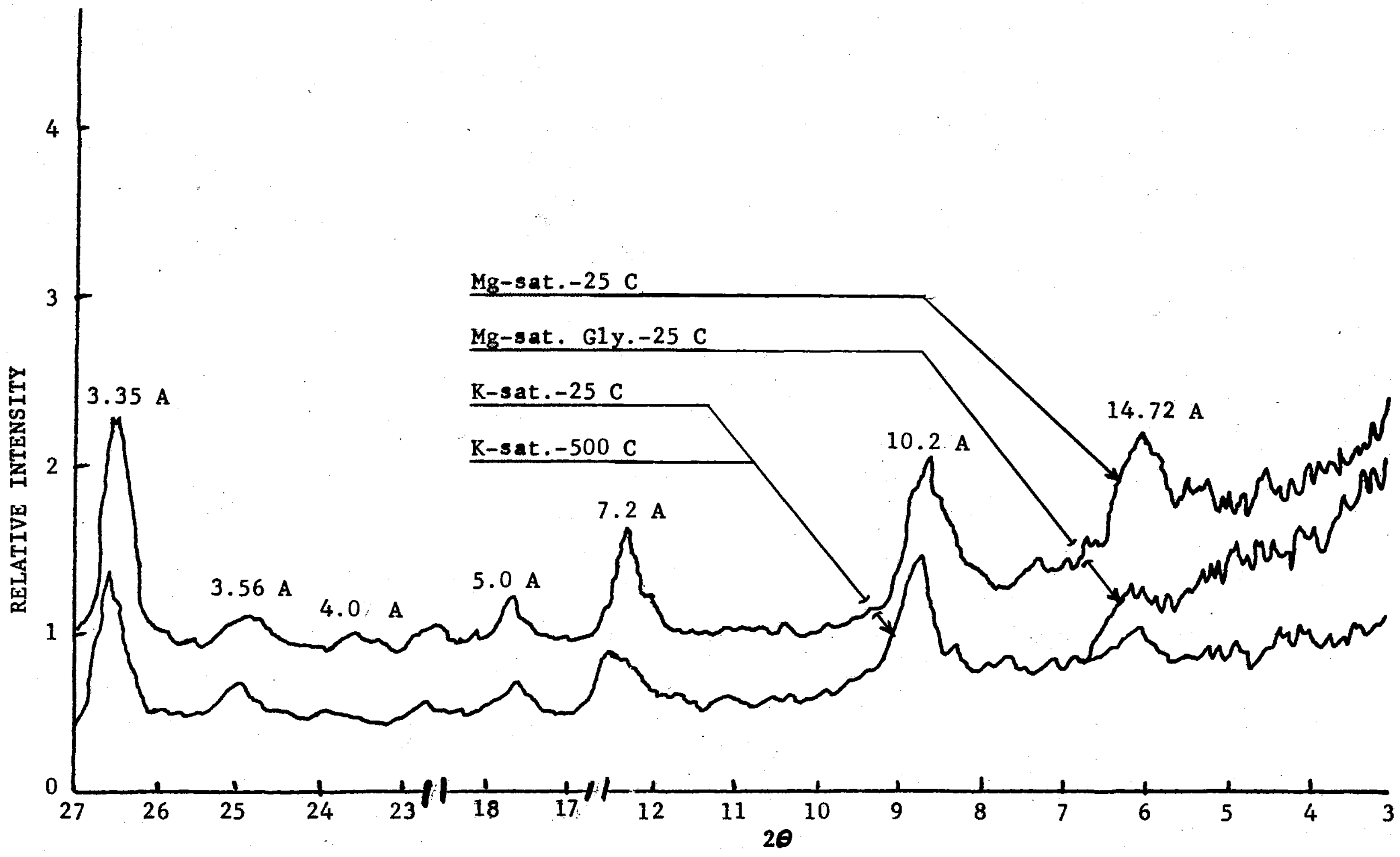

Figure 14. X-ray Diffraction Pattern and d-spacing in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of the Bolan Clay Loam Soil Taken at a Depth of 9 to 16 Inches

TABLE XVIII

X-RAY DIFFRACTION PATTERN AND d-SPACINGS IN ANGSTROMS OF THE 00l OF THE THREE OKLAHOMA FINE CLAYS (LESS THAN 0.2μ)

Location	Depth (in.)	Mg-sat.-25 C	Mg-sat. Bly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
San Saba clay loam	0-9	15.77; 7.25; 3.56; 3.35	17.4; 7.25; 3.56; 3.35	12.5; 3.56; 3.35	3.35	Montmorillonite, quartz
	9-24	17.6; 10.04; 3.35	10.04; 4.35; 4.13	3.35, 3.18	3.18	Illite, quartz, plagioclase feldspar
	>24	14.28, 3.56	17.65, 3.56	3.16	3.16	Montmorillonite, plagioclase feldspar
Woodward loam	0-6	16.0; 4.29; 3.35	22.07; 10.27; 4.27; 4.11; 3.35	3.35, 3.16	3.35, 3.16	Montmorillonite, illite, quartz, plagioclase feldspar
	6-13	16.35; 10.04; 3.35	22.07; 10.27; 3.35	3.35	3.35	Montmorillonite, illite, quartz
	13-25	14.7; 10.73; 3.35	22.07; 10.27; 3.35	3.35	3.35	Montmorillonite, illite, quartz
	25-36	14.7; 10.27; 3.35	22.07; 10.27; 3.35	3.56, 3.35	3.35	Montmorillonite, illite, quartz

Continued next page

TABLE XVIII, Continued

Location	Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
Richfield loam	0-12	17.66; 4.27; 3.35	22.07; 10.04; 4.27; 3.35	3.35, 3.16	3.35, 3.16	Montmorillonite, illite, quartz, plagioclase feldspar
	12-18	16.98; 10.04	22.07; 10.04; 3.56	3.35, 3.16	3.35, 3.16	Montmorillonite, illite, quartz, plagiocalse feldspar
	18-28	15.77; 10.04; 3.35	18.4; 10.04; 7.24	3.35, 3.16	3.35, 3.16	Montmorillonite, illite, quartz, plagioclase feldspar
	>28	15.77; 7.189; 4.27	22.07; 4.13; 3.35	3.35, 3.16	3.35, 3.16	Montmorillonite, illite, quartz, plagioclase feldspar

TABLE XIX

X-RAY DIFFRACTION PATTERN AND d-SPACINGS IN AGNSTROMS OF THE 00l OF THE THREE OKLAHOMA COARSE CLAYS (0.2 to 2μ)

Location	Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
San Saba clay loam	0-9	15.5; 7.19; 3.56; 3.35	18.4, 7.19	12.99; 7.13; 3.56; 3.35	3.35, 3.16	Montmorillonite, metahalloysite, quartz, plagioclase feldspar
	9-24	14.72; 7.25; 3.56; 3.35	17.65; 7.189; 3.56	7.19; 3.36; 3.16	3.35	Montmorillonite, metahalloysite, quartz, plagioclase feldspar
	>24	15.22; 7.25; 3.56; 3.35	17.75; 17.19; 5.0; 3.56; 3.35	3.15	3.35	Montmorillonite, quartz
Woodward loam	0-6	10.04, 3.35	3.56, 3.16	3.16	3.35, 3.16	Illite, quartz, plagioclase feldspar
	6-13	14.72; 10.04; 7.19; 3.56; 3.35	17.65; 10.04; 7.19; 4.27; 3.56	10.04; 7.19; 3.35	10.04; 3.35; 3.16	Montmorillonite, metahalloysite, illite, quartz, plagioclase feldspar
	13-25	14.72; 10.04; 7.13	10.04; 7.13; 3.35	7.13; 3.35; 3.16	10.04; 3.35; 3.16	Illite, kaolinite, quartz, plagioclase feldspar

Continued next page

TABLE XIX, Continued

Location	Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
Woodward loam	25-36	14.72; 10.04; 4.98; 3.56	3.35	3.16	3.35, 3.16	Illite, quartz, plagioclase feldspar
Richfield loam	0-12	15.77; 10.04; 7.13; 3.56; 3.35	19.2; 10.04; 7.2; 3.35	3.35, 3.16	3.35, 3.16	Montmorillonite, illite, quartz, plagioclase feldspar
	12-18	15.77; 10.04; 7.13	18.4; 10.04; 7.13	7.13; 3.35; 3.16	3.35, 3.16	Montmorillonite, illite, kaolinite, quartz, plagioclase feldspar
	18-28	15.77; 10.04; 7.13	18.4; 10.04; 7.13	3.35, 3.16	3.35, 3.16	Montmorillonite, vermiculite, illite, quartz, plagioclase fledspar
	>28	15.22; 10.04; 7.13	18.4; 10.04; 7.13	3.35, 3.16	3.35, 3.16	Montmorillonite, vermiculite, illite, quartz, plagioclase feldspar

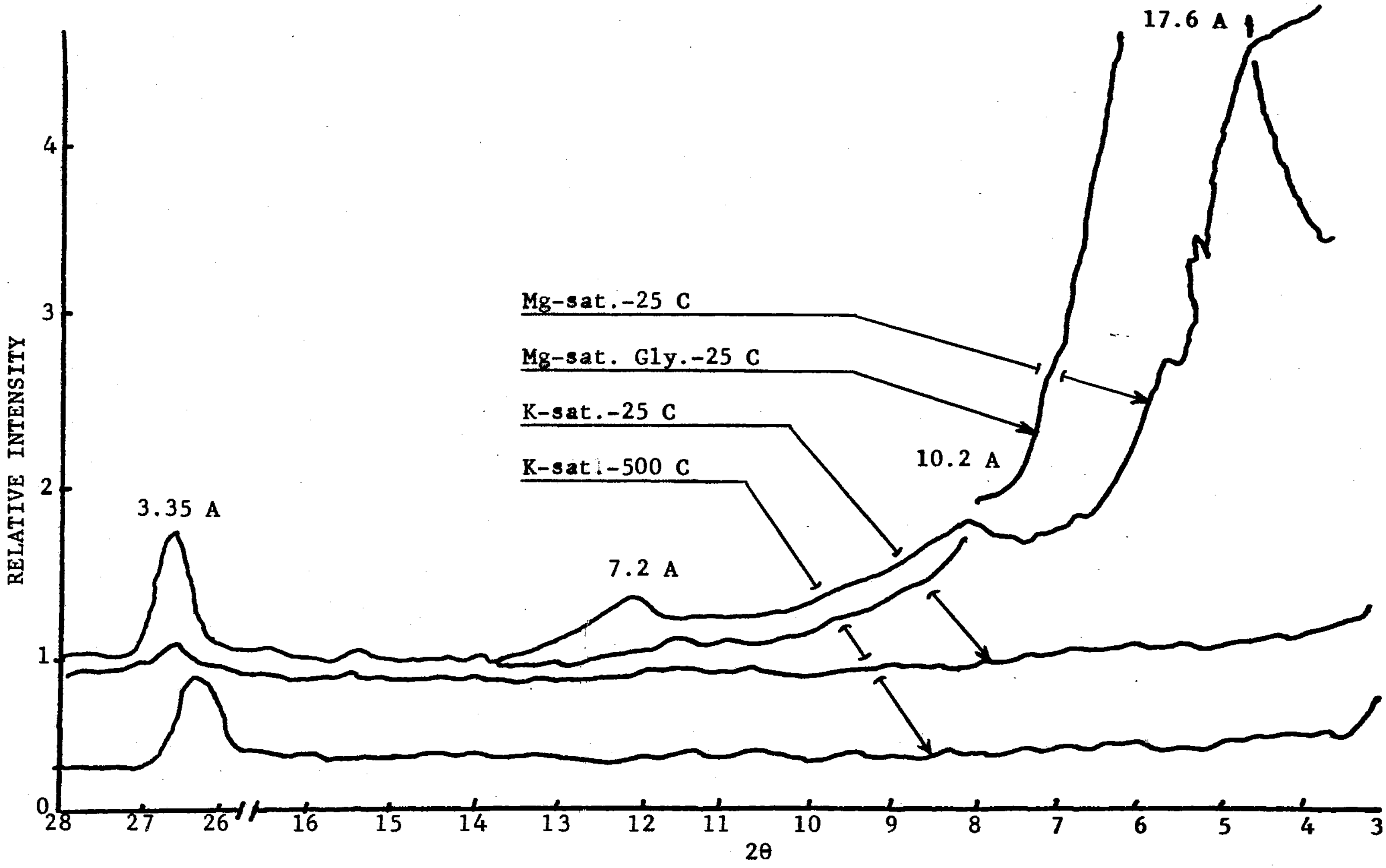

Figure 15. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of San Saba Clay Loam Soil Taken at a Depth of 9 to 24 Inches

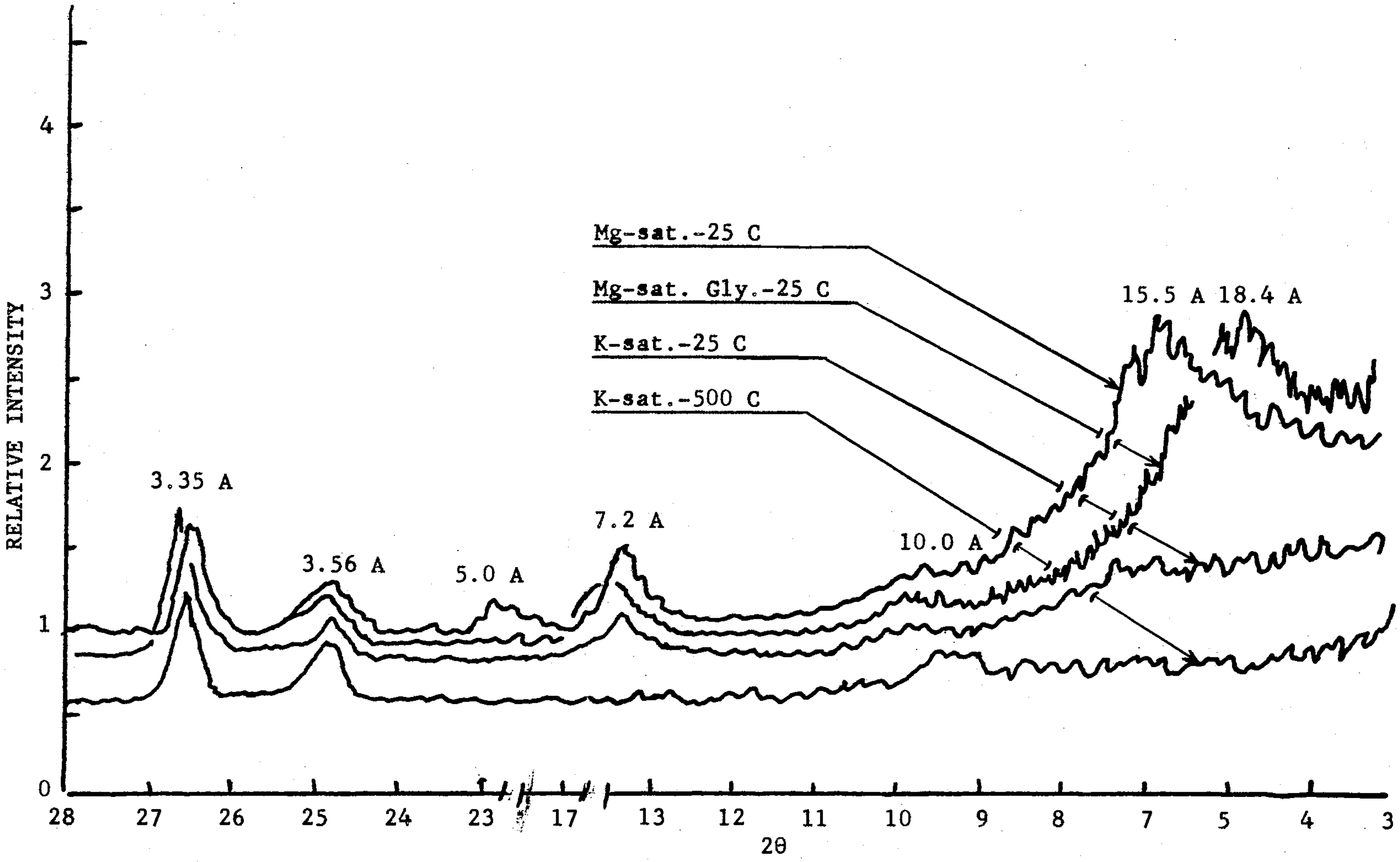

Figure 16. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of San Saba Clay Loam Soil Taken at a Depth of 0 to 9 Inches

plagioclase feldspar and quartz in the clay fraction.

The diffraction spacings for Woodward clays are shown in Tables XVIII and XIX and Figures 17 and 18. Fine clay extracted from the 0 to 6 inch sample had a diffraction spacing of 16 A after the clay was saturated with magnesium chloride. When this fine clay was solvated with glycerol the 16 A spacing expanded to 22.0 A and upon potassium saturation collapsed. This spacing (22.0 A) was due to the presence of montmorillonite. Coarse clay extracted from the same sample did not show a spacing for montmorillonite. Coarse clay extracted from the 6 to 13 inch sample had a spacing of approximately 7.2 A before the clay was heated, but upon heating the spacing was destroyed. This is an indication of the presence of halloysite or kaolinite. Coarse clay extracted from the 13 to 25 inch sample before heating had a diffraction spacing of approximately 7.13 A. When the clay was heated the spacing was destroyed. This indicates that the coarse clay was kaolinite. The clays from the Woodward soil also had a spacing of approximately 10 A. In some cases the 10 A spacing upon potassium saturation disappeared but in some other cases this spacing was not affected by potassium saturation. This indicates that Woodward loam probably contains illite. Quartz and plagioclase feldspar were also present in the coarse clay fraction of this profile.

X-ray diffraction spacings for the Richfield soil clays are reported in Tables XVIII and XIX and Figures 19 and 20. Richfield clay after magnesium saturation had a diffraction spacing of approximately 16 A. When the clay was solvated with glycerol the spacing expanded and upon potassium saturation the spacing was destroyed. This indicates that the Richfield soil contains montmorillonite. At a depth of

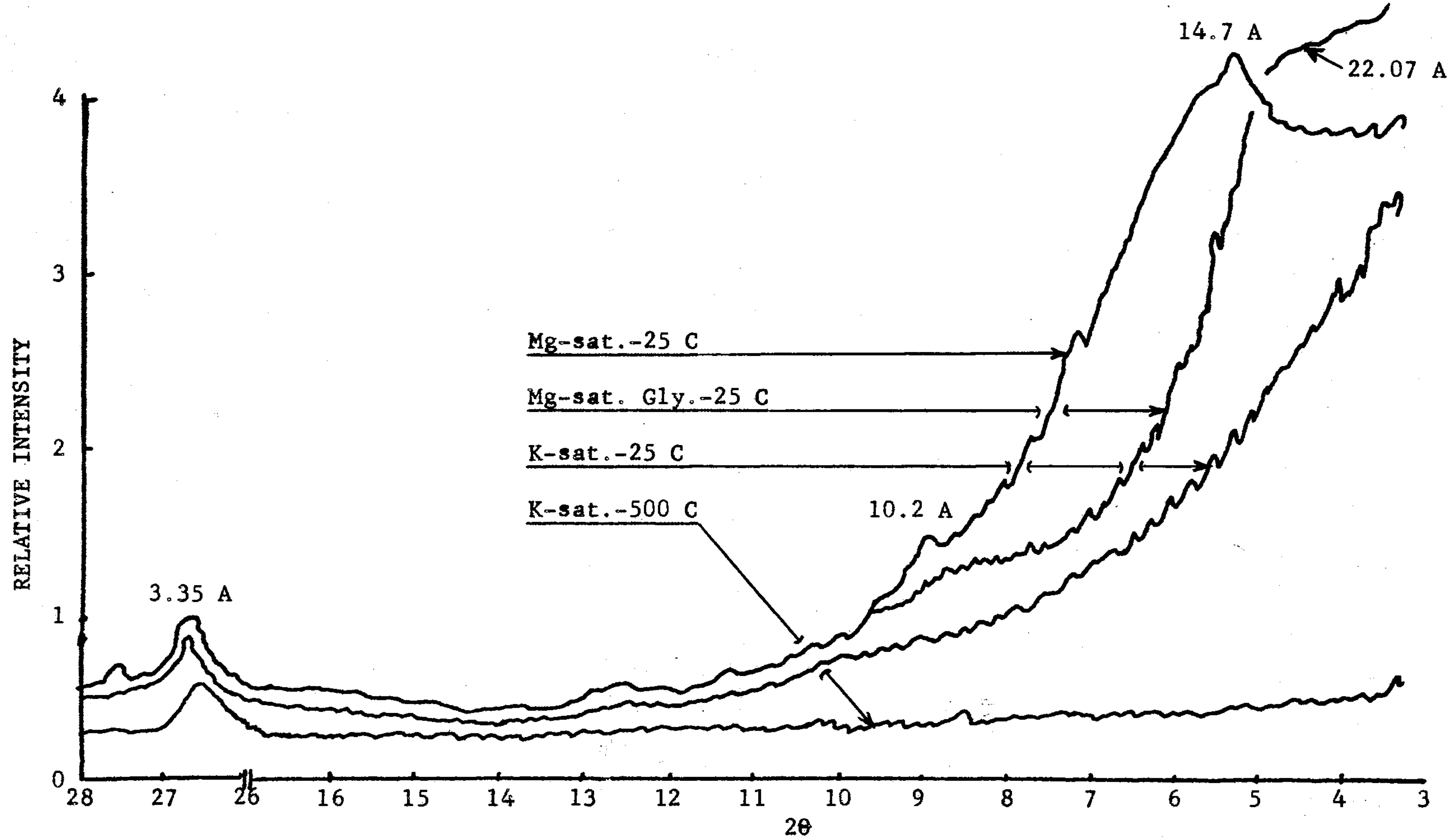

Figure 17. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Woodward Loam Soil Taken at a Depth of 6 to 13 Inches

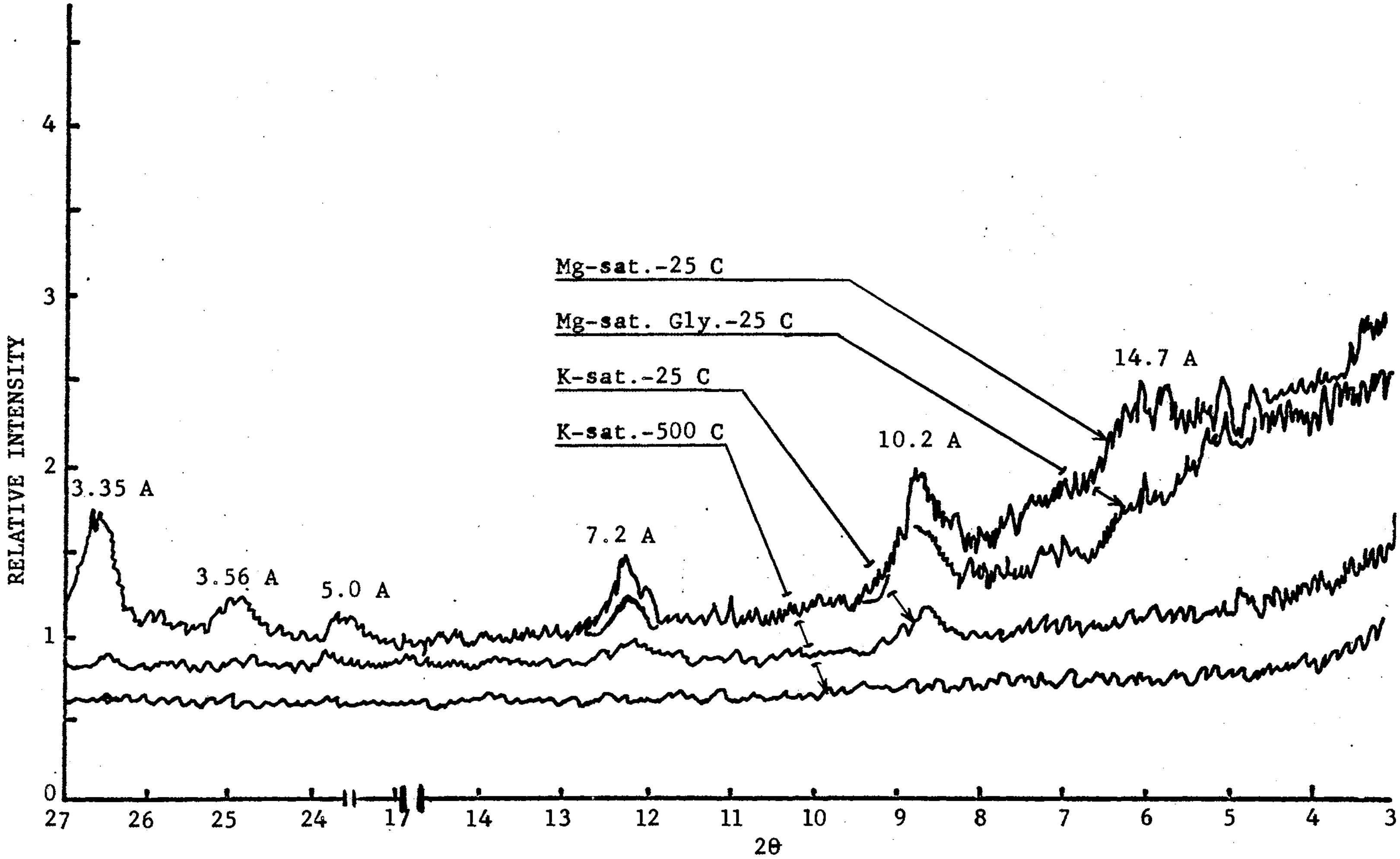

Figure 18. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of Woodward Loam Soil Taken at a Depth of 13 to 25 Inches

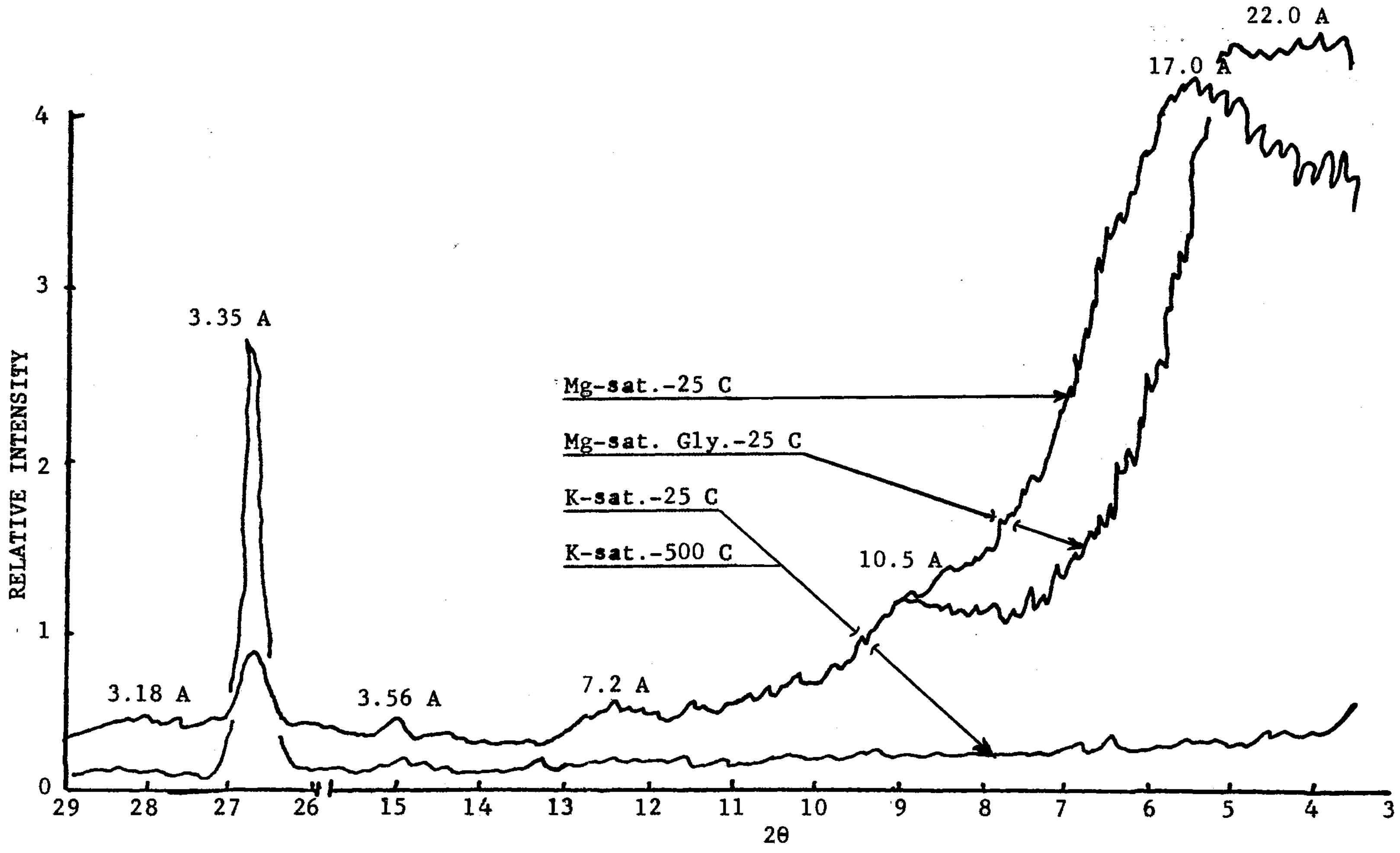

Figure 19. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Richfield Loam Soil Taken at a Depth of 0 to 12 Inches

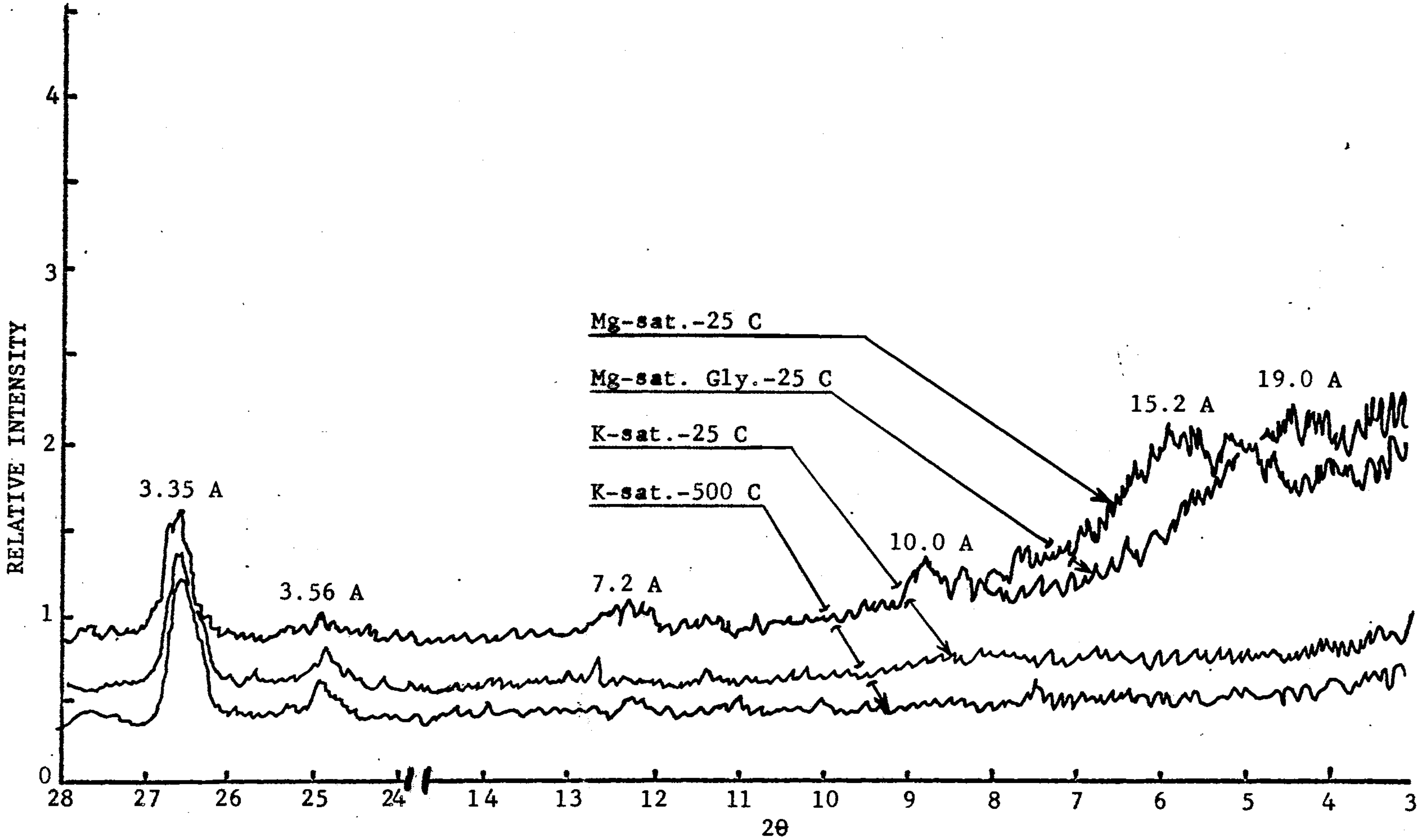

Figure 20. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of Richfield Loam Soil Taken at a Depth of 0 to 12 Inches

12 to 18 inches the coarse clay in this profile had a spacing of approximately 7.13 A after the clay was saturated with magnesium. Glycerol solvation did not change this spacing. This spacing was not significantly affected by potassium saturation but was destroyed by heating. This indicates the coarse clay contained kaolinite. In clay extracted from the samples taken below 18 inches the 7.13 A spacing was destroyed when the soil was saturated with potassium. This spacing might be a second-order vermiculite, because it was not affected by glycerol solvation. Richfield clays also had a spacing of approximately 10 A after the soil was saturated with magnesium. This spacing was not affected by glycerol solvation but was collapsed after the clay was sautrated with potassium. This indicates that Richfield clays contain illite. Richfield clays also had a spacing for quartz and plagioclase feldspar. Montmorillonite was present in the entire soil profile in both coarse and fine fractions and at all depths.

Dorulaman clays have a spacing of approximately 14.72 A after the coarse clay was treated with magnesium as shown in Figures 21 and 22 and Tables XX and XXI. The spacing did not change significantly when the coarse clay was solvated with glycerol. However, the spacing was collapsed when the clay was saturated with potassium chloride. This indicates that the coarse clay contains vermiculite. The coarse clay also had a second-order spacing for vermiculite which followed the same trend as the 14.72 A spacing. This spacing was also collapsed by potassium saturation. Dorulaman clays had a 10 A spacing before the clays were treated with potassium chloride, but upon potassium saturation this spacing collapsed which indicates that these clays also contain illite. Dorulaman coarse clay also had diffraction spacings for

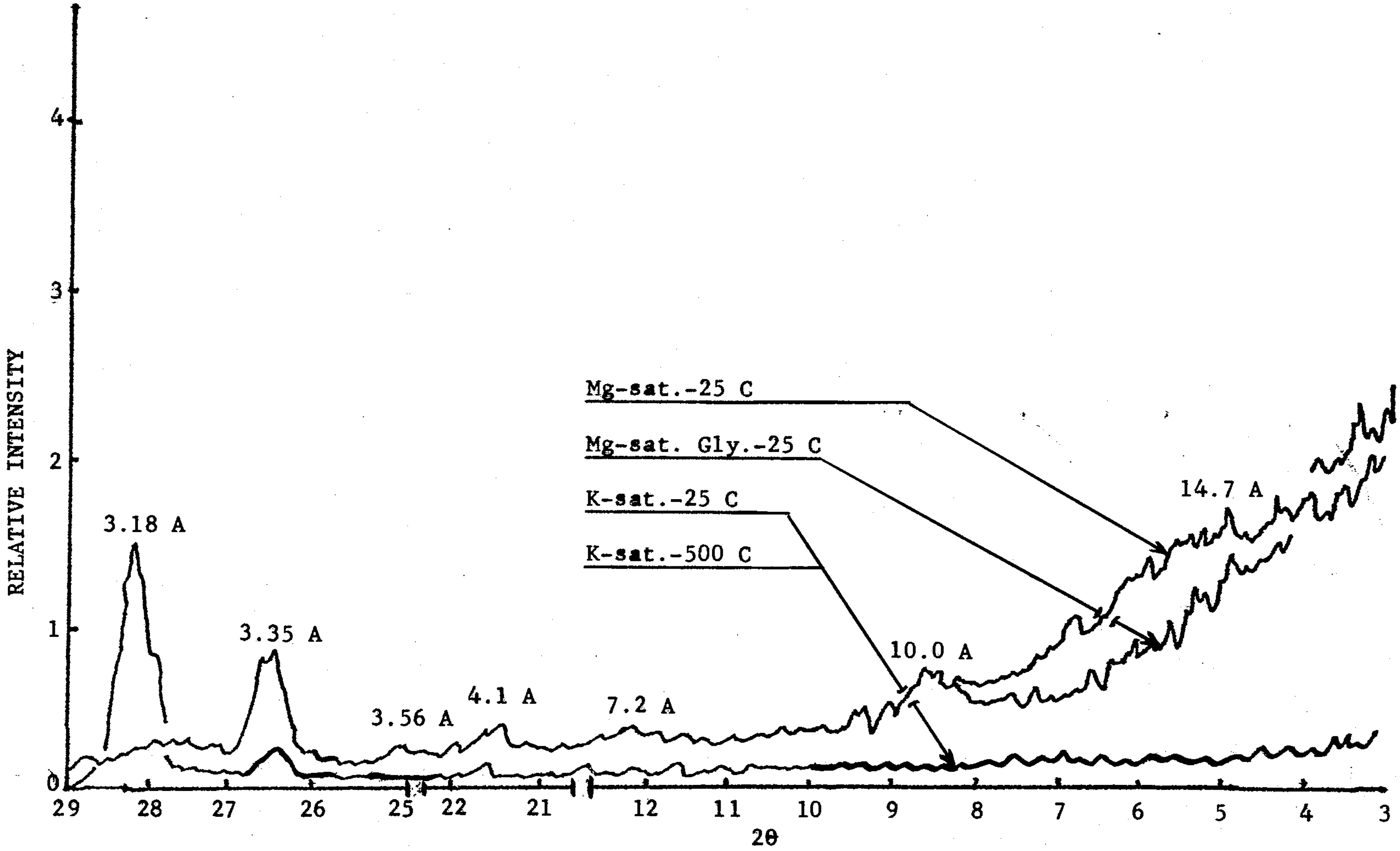

Figure 21. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Dorulaman Clay Loam Soil Taken at a Depth of 0 to 8 Inches

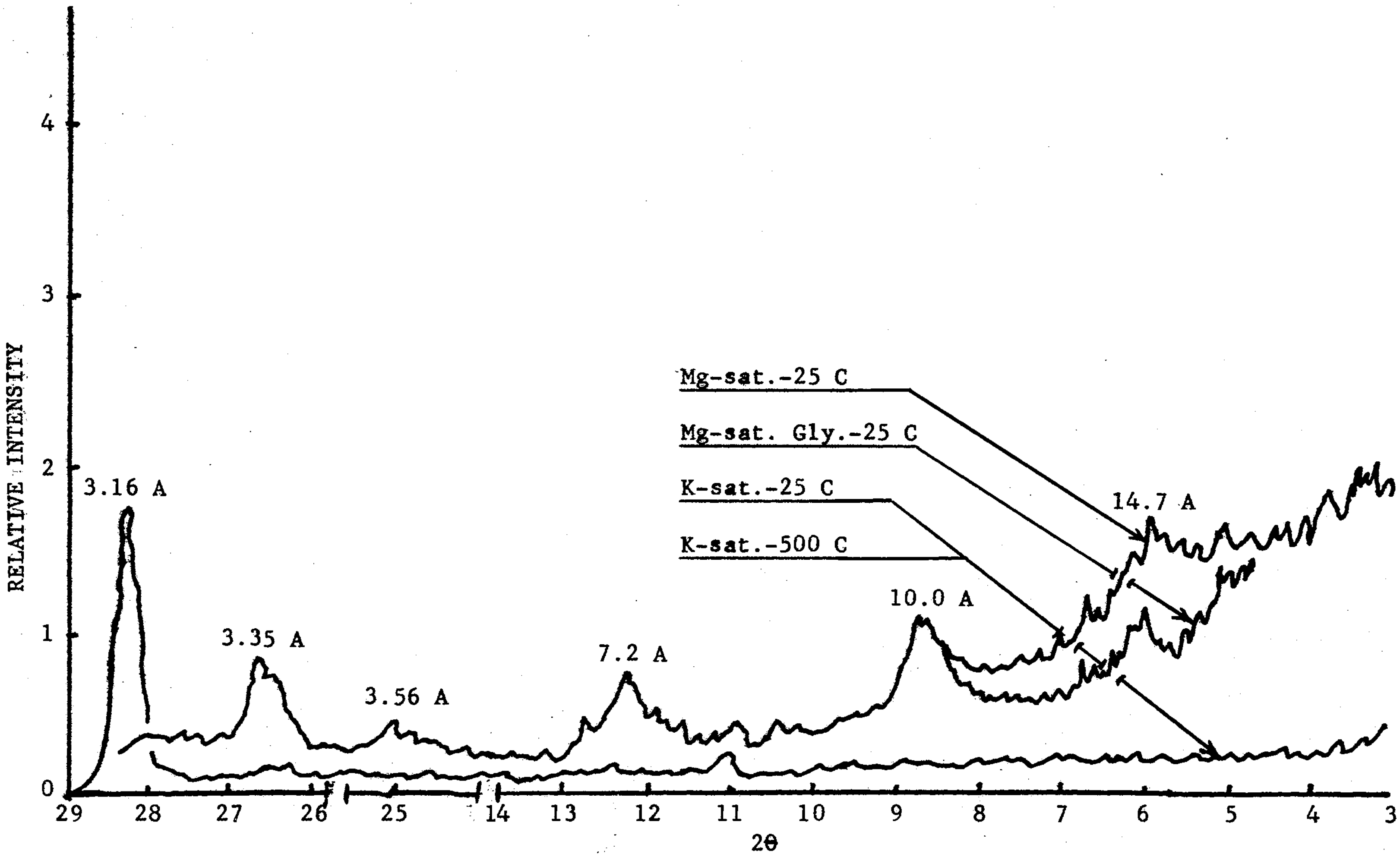

Figure 22. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of Dorulaman Clay Loam Soil Taken at a Depth of 0 to 8 Inches

TABLE XX

X-RAY DIFFRACTION PATTERN AND d-SPACINGS IN ANGSTROMS OF THE 00l OF SOME AFGHAN FINE CLAYS (LESS THAN 0.2μ)

Location	Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
Dorulaman c. l. (Univ. Farm, Kabul, Afgan.)	0-8	10.155; 7.25; 5.0; 4.1; 3.56; 3.35; 3.18	10.04; 7.18; 5.0; 4.1; 3.56; 3.35; 3.18	10.04; 3.35; 3.18	10.04; 3.35; 3.18	Vermiculite, illite, quartz, plagioclase feldspar
Dorulaman c. l. (Roy. Afg. Min. of Ag., Kabul, Afghan.)	0-8	18.30; 12.9; 10.2; 4.07; 3.56; 3.18	18.3; 13.4; 10.2; 4.07; 3.56; 3.18	3.35, 3.18	10.04; 3.35; 3.18	Vermiculite, illite, quartz, plagioclase feldspar
ShishemBagh s. l. (Ningerhar, Afg.)	0-8	15.77; 10.4; 3.35; 3.18	20.53; 10.04; 3.35; 3.18	3.35, 3.16	10.63; 3.35; 3.18	Montmorillonite, illite, quartz, plagioclase feldspar
Pos-i-shan si. c. (Baghlan, Afg.)	0-8	14.72; 10.643; 7.19; 5.03; 3.35	17.72; 10.04; 7.19; 5.03; 3.35	7.25; 3.56; 3.35; 3.18	10.4, 3.37	Montmorillonite, illite, metahalloysite, quartz
Mazar si. c. (MazariShariff, Afg.)	0-8	15.77; 7.2; 5.03; 3.35	17.2; 10.04; 7.2; 5.03; 3.35	3.56; 3.35; 3.16	10.27; 3.35; 3.16	Montmorillonite, illite, vermiculite, kaolinite, quartz, plagioclase feldspar

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TABLE XX, Continued

Location	Depth (in.)	Mg-sat. 25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
Kokoran c. l. (Kandahar, Afg.)	0-8	14.72; 10.27; 7.13; 5.03; 4.07; 3.56; 3.35	14.72; 10.273; 7.3; 5.03; 4.07; 3.56; 3.35	3.56, 3.19	3.35, 3.18	Vermiculite, illite, kaolinite, quartz, plagioclase feldspar
Shamalon c. (Alkaline, fr. Bost, Afg.)	0-8	14.72; 10.64; 7.19; 5.0; 4.76; 3.56; 3.35	15.22; 10.04; 7.2; 4.11	3.56; 3.37; 3.18	10.52; 3.35; 3.18	Vermiculite, illite, kaolinite, quartz
Shamalon c. (Non-alk., fr. Bost, Afg.)	0-8	14.72; 10.64; 7.19; 5.0; 4.76; 3.56; 3.35	14.72; 10.04; 7.2; 5.0; 4.74; 3.56; 3.35	14.72; 7.13; 3.56; 3.35	14.72; 3.35; 3.16	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
Boghra s. c. (Bost, Afghanistan)	0-8	12.02; 10.5; 7.13; 4.26; 4.07; 3.35	12.26; 10.52; 7.13; 4.26; 4.07; 3.35	12.26; 7.13; 3.35	3.35, 3.16	Interstratified mica-chlorite, kaolinite, illite, quartz, plagioclase feldspar

TABLE XXI

X-RAY DIFFRACTION PATTERN AND d-SPACINGS IN ANGSTROMS OF THE 00l OF SOME AFGHAN COARSE CLAYS (0.2 to 2.0μ)

Location	Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
Dorulaman c. 1. (Univ. Farm, Kabul, Afghan.)	0-8	15.23; 10.04; 7.13; 4.32; 4.13; 3.35	15.22; 10.04; 7.3; 4.30; 4.13; 3.35	10.04, 3.16	10.04, 3.36	Vermiculite, illite, quartz
Dorulaman c. 1. (Roy. Afg. Min. of Ag. Kabul, Afg.)	0-8	17.65; 15.23; 10.04; 7.13; 4.3; 4.13; 3.35	15.22; 10.04; 7.3; 4.30; 4.13; 3.35	10.04, 3.16	10.04, 3.36	Vermiculite, illite, quartz
Shishem Bagh s. 1. Ningerhar, Afghan.)	0-8	15.2; 10.04; 7.19; 3.35	15.2; 14.72; 10.04; 7.19; 3.56; 3.35	14.72; 9.8; 3.35; 3.16	14.72; 10.27; 3.37; 3.18	Chlorite, illite, vermiculite, quartz
Pos-i-shan si. c. (Baghlan, Afghan.)	0-8	14.727; 10.04; 7.19; 5.0; 4.31; 3.56; 3.35; 3.19	14.72; 10.04; 7.25; 5.03; 4.31; 4.73; 3.56; 3.35	10.04; 3.56; 3.13	14.72; 10.04; 3.37	Chlorite, illite, vermiculite, kaolinite, quartz, plagioclase feldspar
Mazar si. c. (MazariShariff, Afghan.)	0-8	14.72; 10.04; 7.13; 5.03; 3.56; 3.35	14.32; 10.04; 7.13; 4.93; 4.71; 3.56; 3.35	3.56; 3.35 3.16	10.27; 3.35; 3.16	Vermiculite, illite, kaolinite, quartz, plagioclase feldspar

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TABLE XXI, Continued

Location	Depth (in.)	Mg-sat.-25 C	Mg-sat. Gly.-25 C	K-sat.-25 C	K-sat.-500 C	Type of major mineral
Kokoran c. l. (Kandahar, Afg.)	0-8	14.72; 10.04; 7.13; 5.03; 4.76; 3.56; 3.35	17.72; 14.72; 7.13; 4.9; 4.71; 3.56; 3.35	7.13; 3.58; 3.35	3.35, 3.18	Vermiculite, kaolinite, quartz, plagioclase feldspar
Shamalon c. (Alkali, fr. Bost, Afg.)	0-8	14.72; 10.04; 7.13; 5.03; 4.76; 3.56; 3.35	18.39; 17.72; 10.04; 7.13; 4.97; 4.77; 3.56; 3.35	14.72; 3.56; 3.35; 3.16	14.72, 10.27	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
Shamalon c. (Non-alk., fr. Bost, Afg.)	0-8	14.72; 10.04; 7.13; 5.03; 4.76; 3.56; 3.35	14.2; 10.04; 7.13; 5.03; 4.74; 4.27; 4.07; 3.56; 3.35	14.72; 10.04; 7.13; 3.56; 3.35	14.72; 10.04; 3.35; 3.18	Chlorite, illite, kaolinite, quartz, plagioclase feldspar
Boghra s. c. (Bost, Afghanistan)	0-8	12.00; 10.52; 7.13; 4.26; 4.07; 3.35	12.26; 10.512; 7.13; 3.35	12.26; 7.13; 3.35; 3.18	12.26; 10.27; 3.35; 3.16	Interstratified mica-chlorite, illite, kaolinite, quartz, plagioclase feldspar

quartz and plagioclase feldspar. Dorulaman fine clay did not contain vermiculite but illite was present.

There was no significant difference in the mineralogy of the secondary minerals of clays from the University farm in Dorulaman and the Royal Afghan Ministry of Agriculture farm in Dorulaman.

Shishem Bagh soil coarse clay fraction had a diffraction spacing of approximately 10 A as shown in Tables XX and XXI and Figures 23 and 24. This indicates these coarse clays contain illite. Shishem Bagh coarse clays also had a diffraction spacing of approximately 15.2 A after the soil was saturated with magnesium. This spacing was not destroyed by potassium saturation and was not affected by glycerol solvation either. Heating at 500 C for four hours also did not cause this spacing to collapse. This indicates that the Shishem Bagh coarse clays contain chlorite. Shishem Bagh fine clays on the other hand, had a diffraction spacing of approximately 15.8 A after the clay was saturated with magnesium and upon glycerol solvation this spacing expanded to 20 A. However, potassium saturation destroyed this spacing. This is an indication that Shishem Bagh soil fine clay fraction contains montmorillonite.

Shishem Bagh soil coarse clay also had a diffraction spacing of 7.2 A after the clay was saturated with magnesium. Upon glycerol solvation this spacing was not affected, but when the clay was saturated with potassium the spacing disappeared. This indicates that these clays have a second-order spacing for vermiculite. Quartz and plagioclase fledspars were also present in the Shishem Bagh soil clays.

Pos-i-Shan soil clays have a diffraction spacing of approximately 10 A before the clay was saturated with potassium as shown in Tables XX

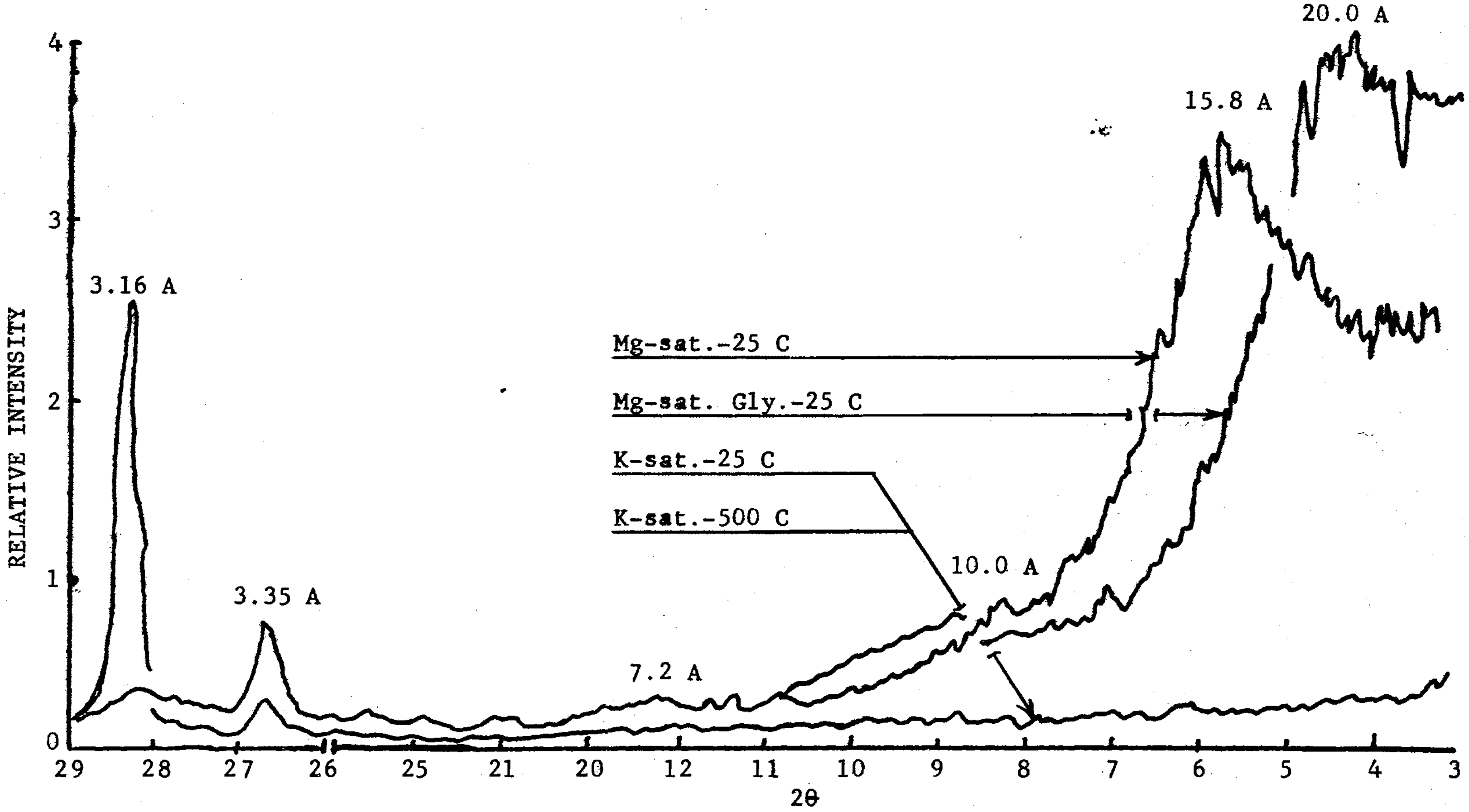

Figure 23. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Shishem Bagh Sandy Loam Soil Taken at a Depth of 0 to 8 Inches

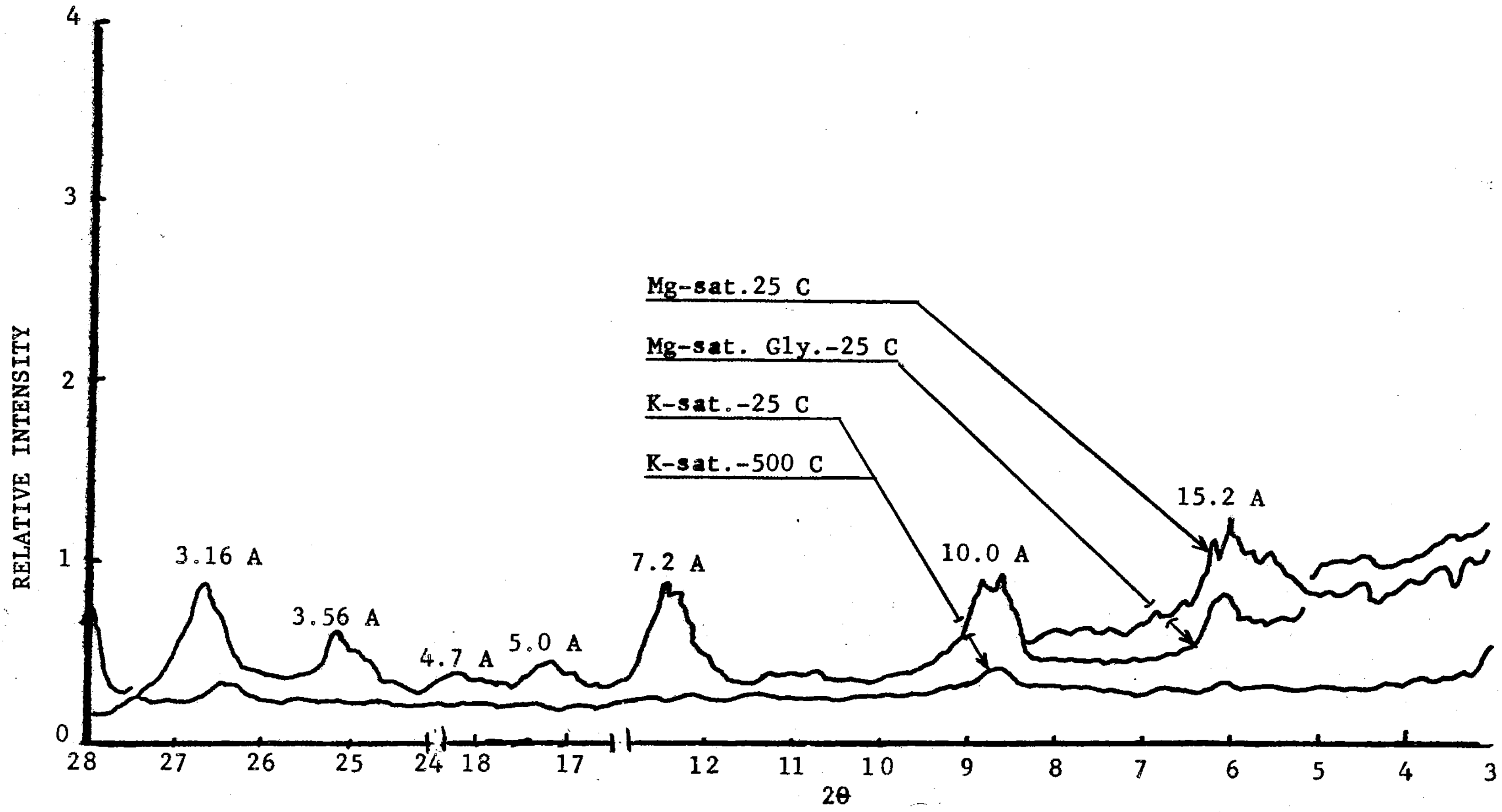

Figure 24. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0 μ) Fraction of Shishem Bagh Sandy Loam Soil Taken at a Depth of 0 to 8 Inches

and XXI and Figures 25 and 26. Upon potassium saturation this spacing disappeared in the fine clay, but was still present in the coarse clay. This indicates that both fine and coarse clays contain illite. Pos-i-Shan coarse clay also had a spacing of 14.72 A after the soil was saturated with magnesium. This spacing did not disappear due to any of the treatments. This indicates that Pos-i-Shan coarse clays contain chlorite. Pos-i-Shan coarse clay had a diffraction spacing of 7.2 A and which was not affected by glycerol solvation and potassium saturation, but was destroyed by heating at 500 C for four hours. This indicates that Pos-i-Shan coarse clay contains halloysite and/or kaolinite. Pos-i-Shan coarse clay also had a diffraction spacing of approximately 3.56 A before the clay was heated, but upon heating this spacing was also destroyed, which further confirms the presence of kaolinite. Quartz and plagioclase feldspar were also present in Pos-i-Shan clays.

X-ray diffraction pattern d-spacing for Mazar clays are reported in Tables XX and XXI and Figures 27 and 28. Mazar coarse clay had a diffraction spacing of approximately 14.72 A after the clay was saturated with magnesium. Upon glycerol solvation this spacing was not significantly changed but when the clay was saturated with potassium this spacing disappeared. This indicates that Mazar coarse clay contains vermiculite. Mazar coarse clay also had a diffraction spacing of approximately 7.3 A which followed the same trend as the 14.72 A spacing. This spacing is probably vermiculite second-order because it did not change with glycerol solvation, but was destroyed upon potassium saturation. Mazar coarse clay also had a diffraction spacing of approximately 3.56 A. This spacing was not affected by glycerol solvation or potassium saturation, but was destroyed by heating. This spacing is

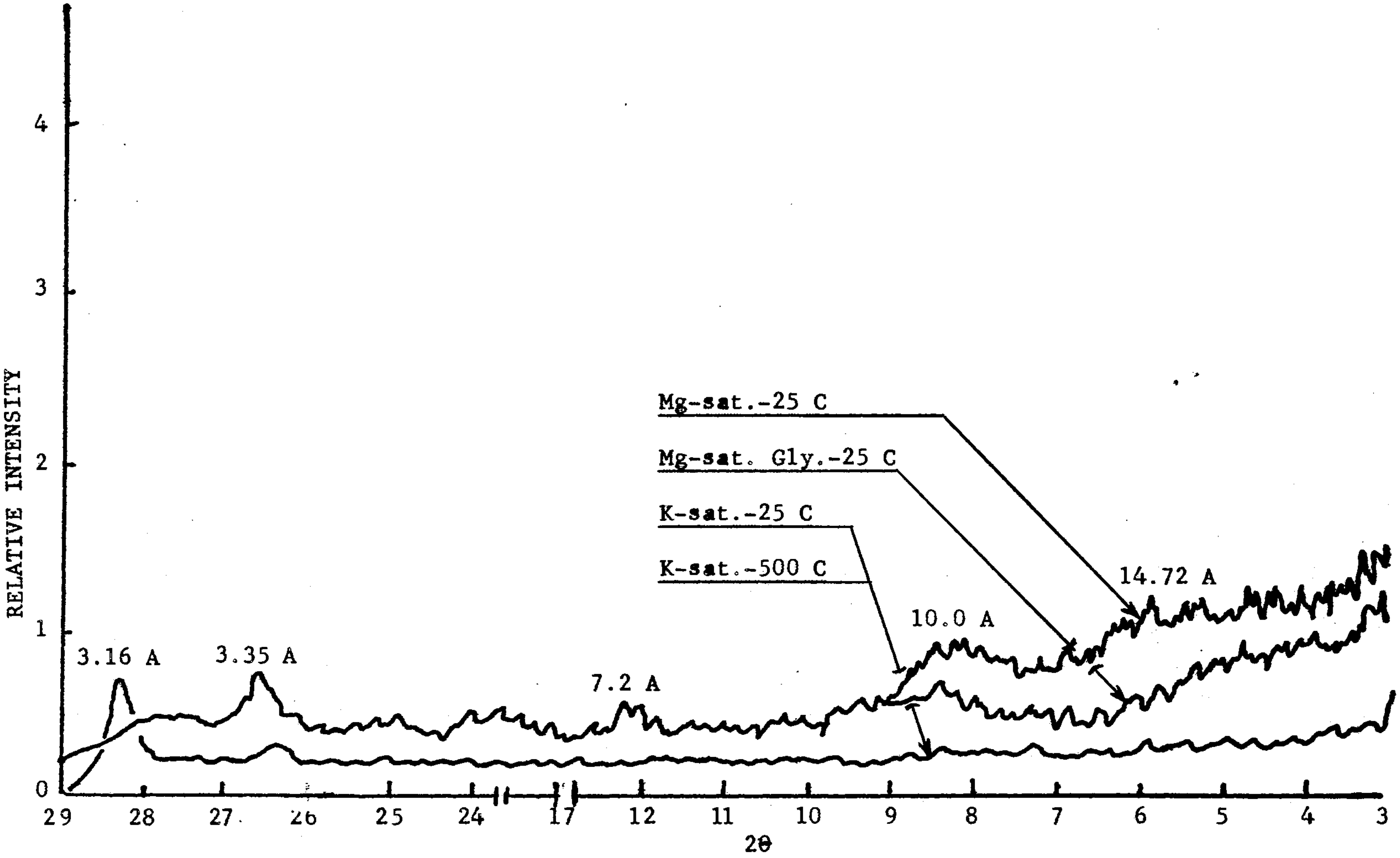

Figure 25. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Pos-i-Shan Silty Clay Soil Taken at a Depth of 0 to 8 Inches

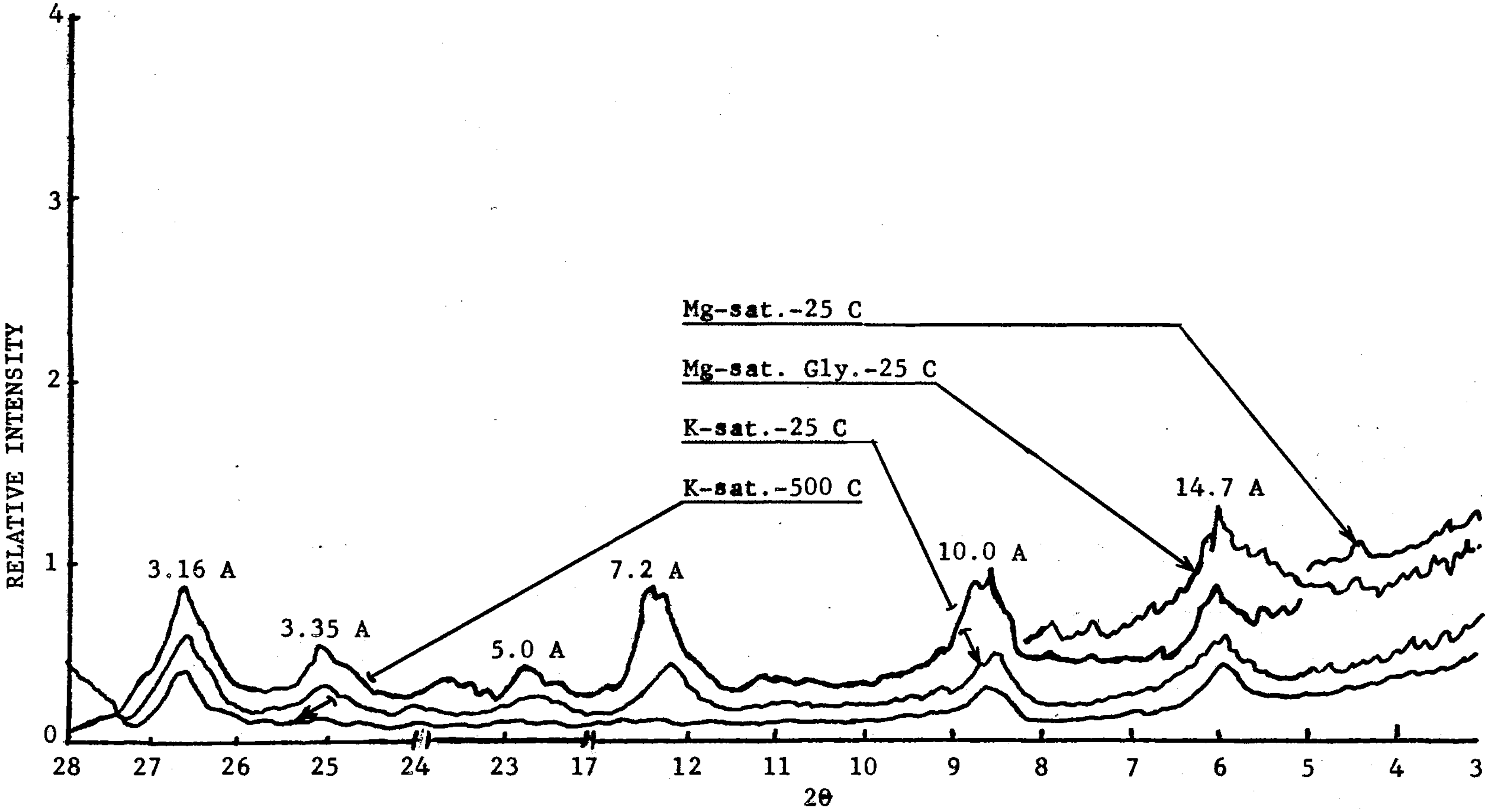

Figure 26. X-ray Diffraction Patter and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0µ) Fraction of Pos-i-Shan Silty Clay Soil Taken at a Depth of 0 to 8 Inches

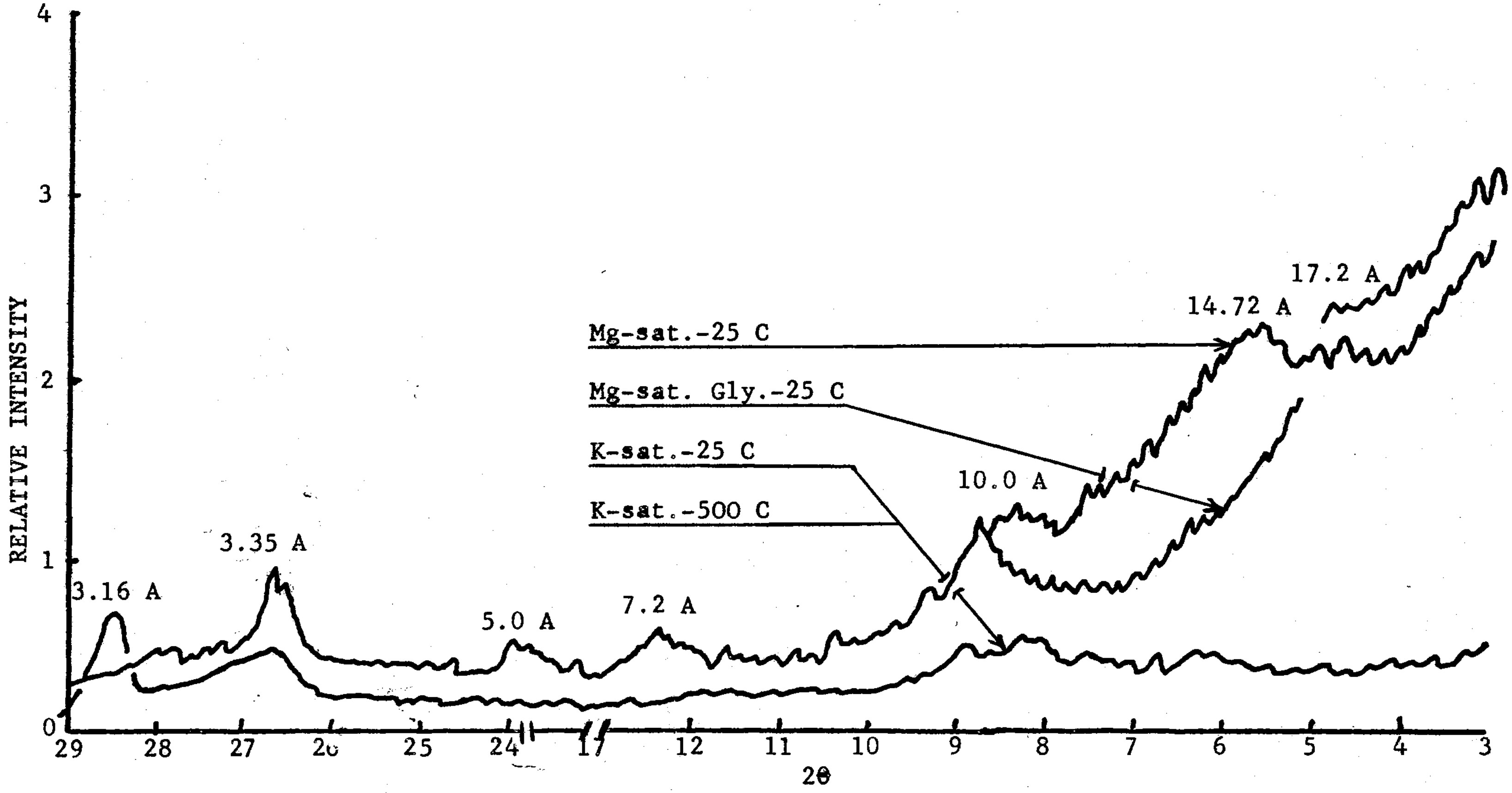

Figure 27. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Mazar Silty Clay Soil Taken at a Depth of 0 to 8 Inches

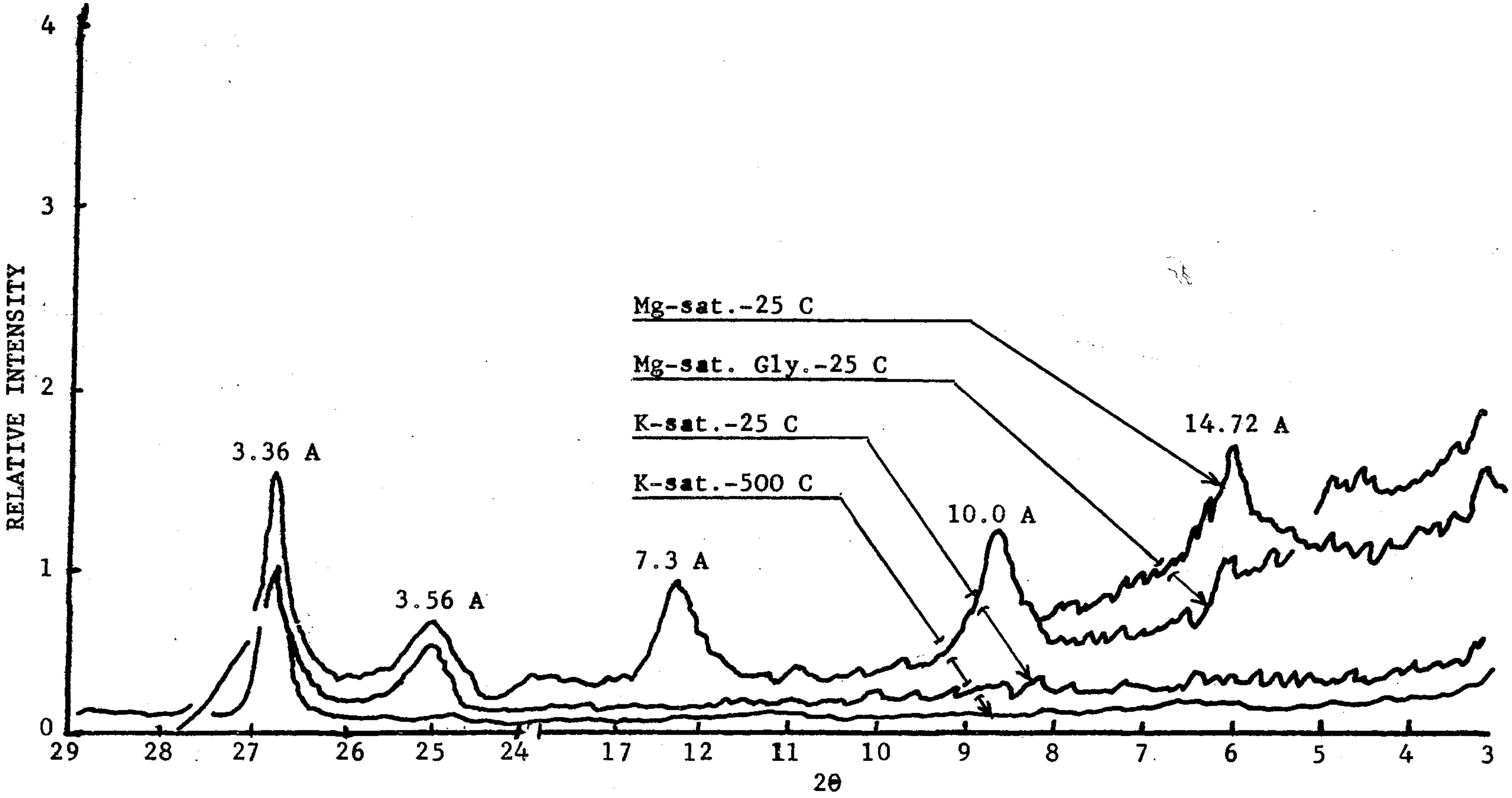

Figure 28. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of Mazar Silty Clay Soil Taken at a Depth of 0 to 8 Inches

probably due to the presence of kaolinite and is known as a kaolinite second-order spacing. Mazar coarse clay had a diffraction spacing of approximately 10 A before the soil was treated with potassium. Potassium saturation caused this spacing to collapse which indicates the presence of illite.

Mazar soil coarse and fine clays also contain quartz and plagioclase feldspar. Mazar soil fine clay had a diffraction spacing of approximately 14.72 A after the clay was saturated with magnesium. When the fine clay was solvated with glycerol the spacing was expanded to 17.2 A and upon potassium saturation this spacing was destroyed. Mazar fine clay also contained illite and second-order vermiculite. Mazar fine clay also had a diffraction spacing of 7.13 A after the clay was saturated with magnesium. Upon glycerol solvation this spacing was not affected but was destroyed by potassium saturation. This indicates the second-order of vermiculite.

X-ray diffraction and d-spacings of Kokoran soil clays are reported in Tables XX and XXI and Figures 29 and 30. Both coarse and fine clays had diffraction spacings of 14.7 A after the clays were saturated with magnesium. Upon glycerol solvation the spacings were not affected significantly, but when they were saturated with potassium these spacings disappeared. This indicates that these spacings were due to the presence of vermiculite. Kokoran soil coarse clay also had a diffraction spacing of 7.13 A. This spacing was also destroyed by potassium saturation. This is a second-order indication of vermiculite, because this spacing was not affected by glycerol solvation. Kokoran soil coarse clay also had a spacing of approximately 3.56 A and this spacing was not affected by potassium saturation or glycerol solvation but was

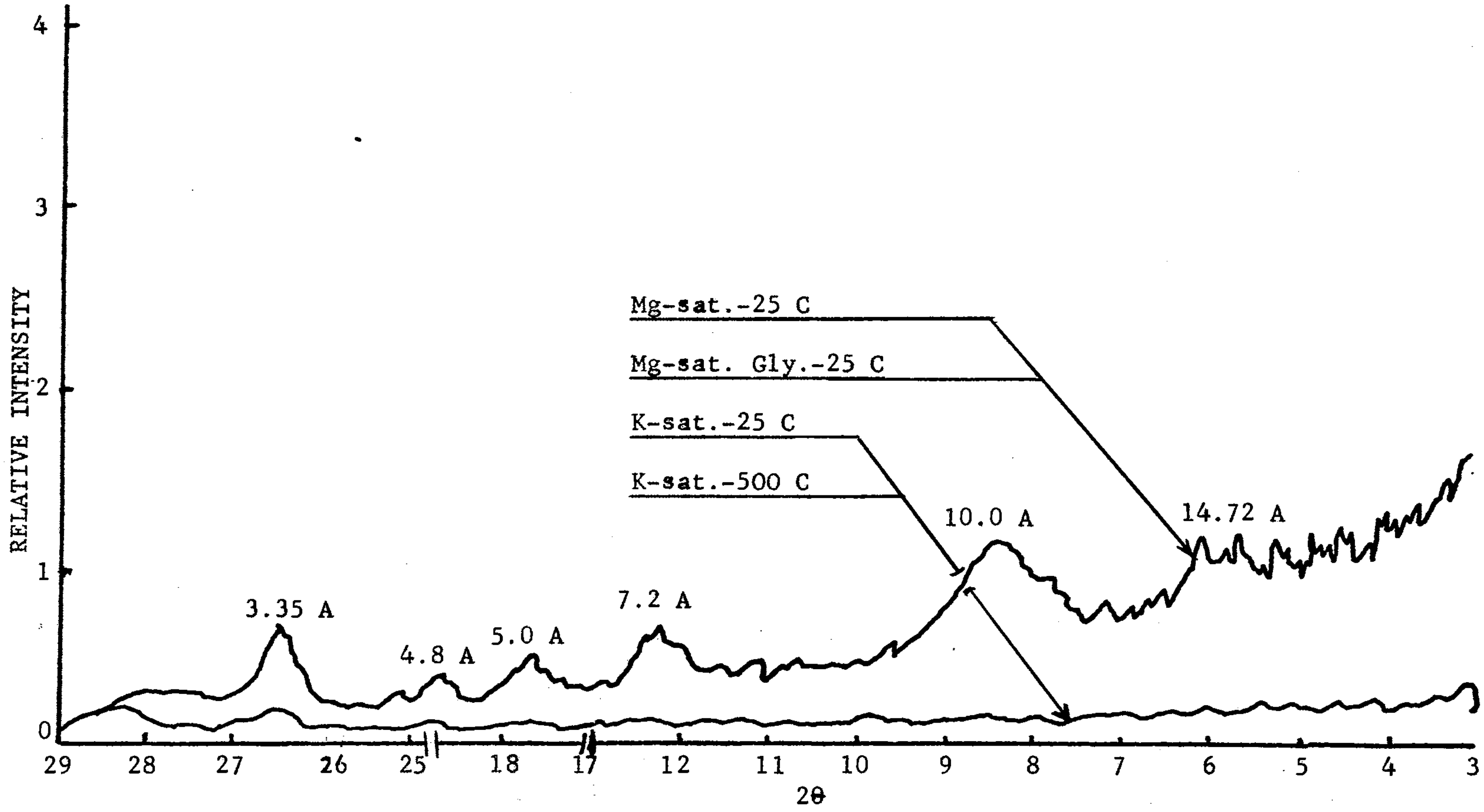

Figure 29. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Kokoran Clay Loam Soil Taken at a Depth of 0 to 8 Inches

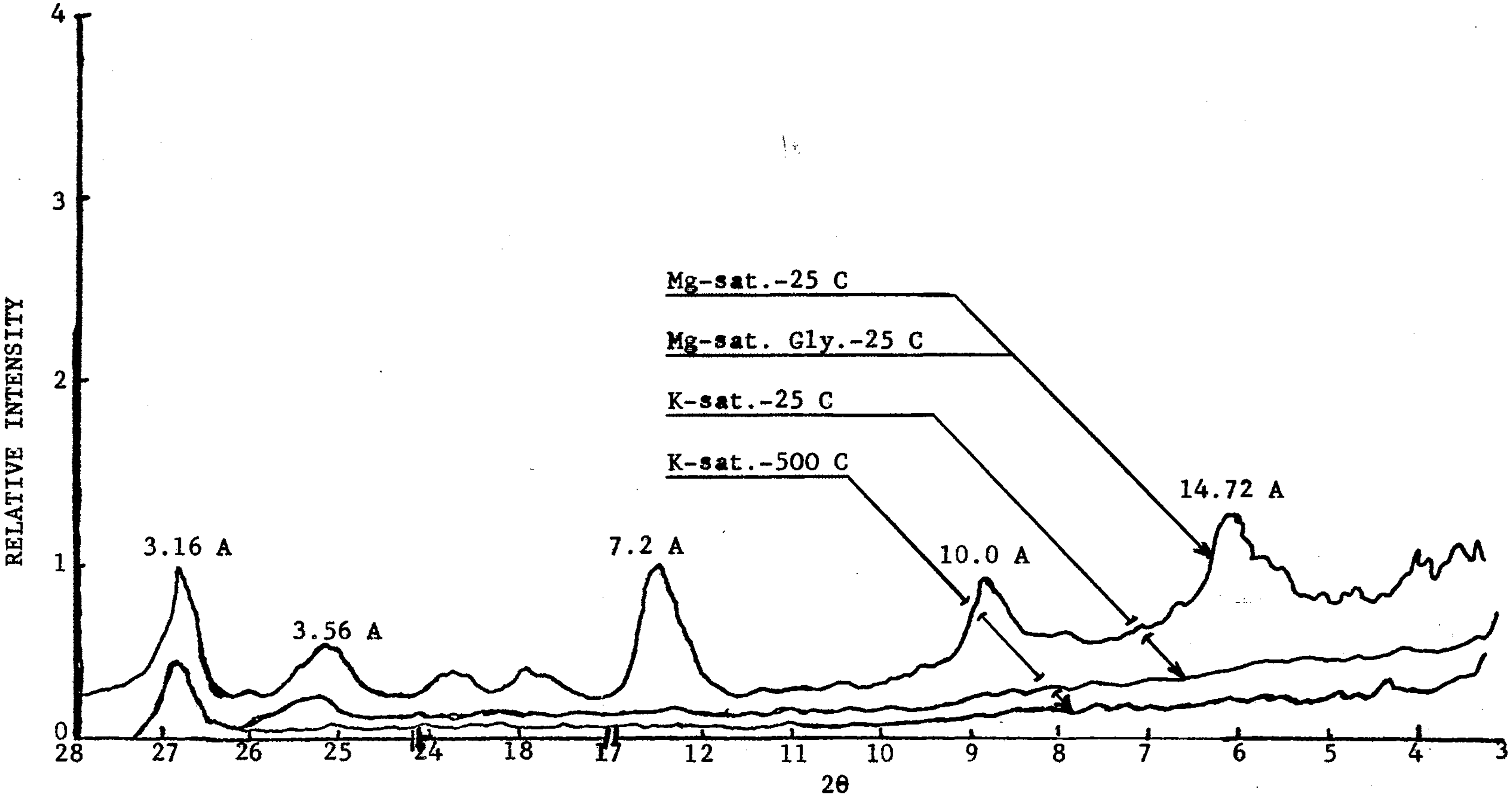

Figure 30. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of Kokoran Clay Loam Soil Taken at a Depth of 0 to 8 Inches

destroyed by heating at 500 C for four hours. This indicates the presence of kaolinite in the Kokoran soil coarse clay as indicated by second-order diffraction. Kokoran soil clays also have a 10 A spacing which was not affected by glycerol solvation but was collapsed by potassium saturation. This spacing was probably due to the presence of illite. Kokoran clays also contain quartz and plagioclase feldspar.

X-ray diffraction and d-spacings of Shamalan soil clays are reported in Tables XX and XXI and Figures 31 and 32. Shamalan fine clay (alkali or sodic soil area) had a diffraction spacing of approximately 14.72 A after the clay was saturated with magnesium. This spacing was not affected significantly upon glycerol solvation but was destroyed when the clay was saturated with potassium. This indicates that Shamalan alkali soil fine clay contains vermiculite. Another sample from the Shamalan area (non-alkali) had a diffraction spacing of 14.72 A and was not significantly affected by any of the treatments. Therefore, Shamalan non-alkali fine clay probably contains chlorite instead of vermiculite. Both fine soil clays had a diffraction spacing of approximately 3.56 A and this spacing was not affected by glycerol solvation or potassium saturation, but was destroyed by heating at 500 C for four hours. This spacing was probably second-order kaolinite. Fine clay samples from both soils contained quartz, illite, and plagioclase feldspar.

Boghra soil clays had a diffraction spacing of 12.3 A after the clays had been saturated with magnesium as shown in Tables XX and XXI and Figures 33 and 34. This spacing was not affected by potassium saturation or heating. This spacing is believed to be interstratified mica-chlorite. Both Boghra soil coarse and fine clays have a

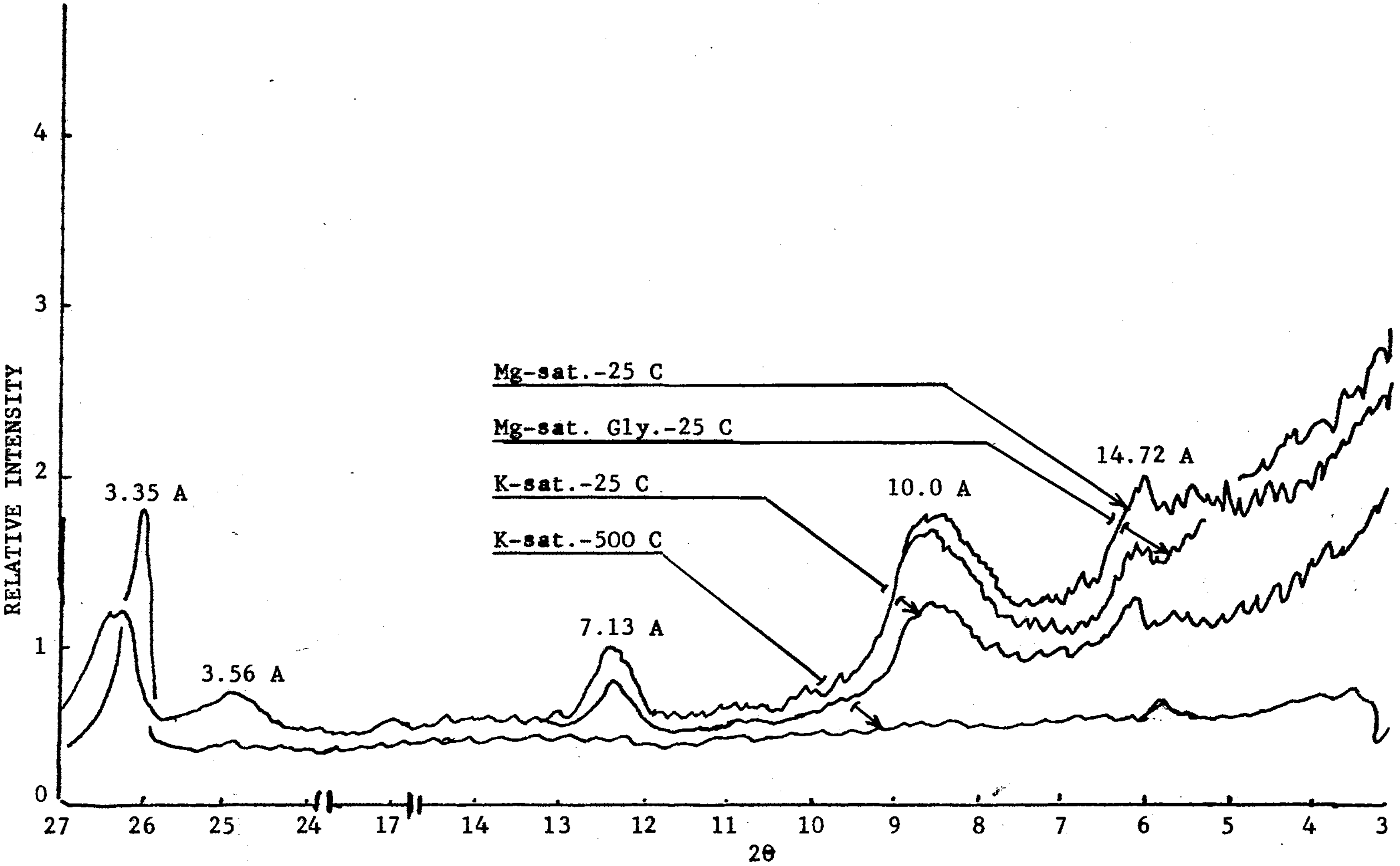

Figure 31. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Shamalan Clay Soil Taken at a Depth of 0 to 8 Inches

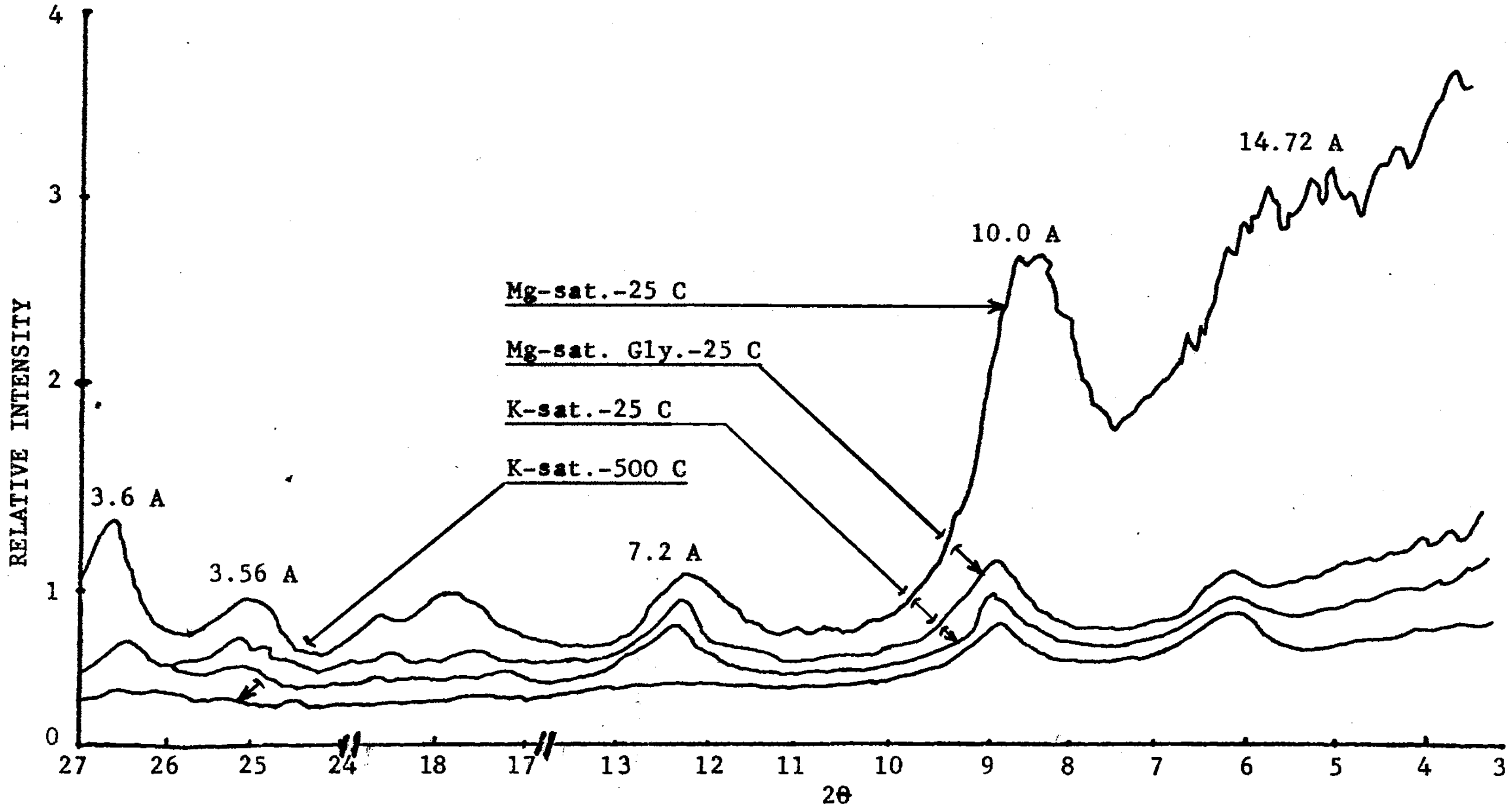

Figure 32. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of Shamalan Clay Soil Taken at a Depth of 0 to 8 Inches

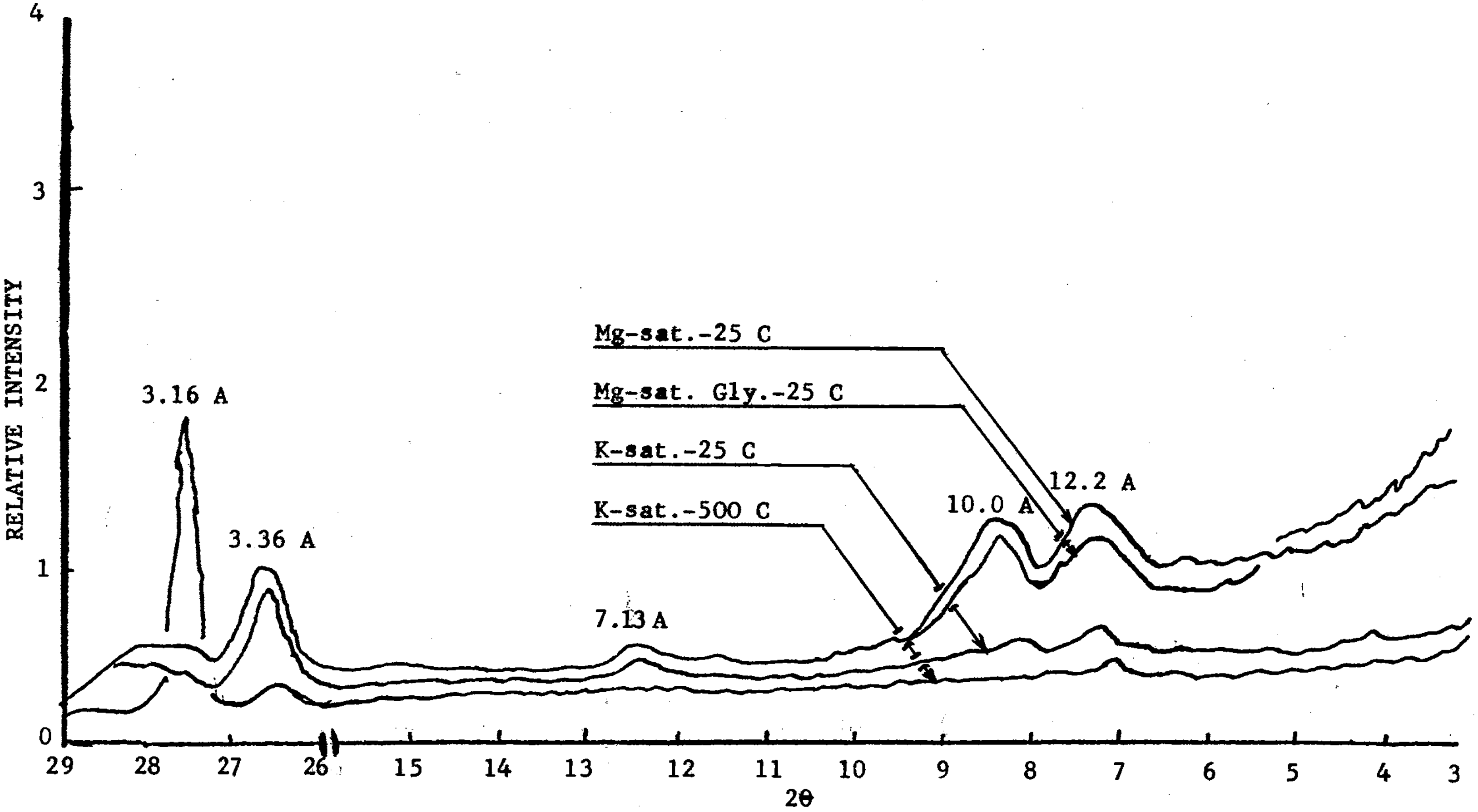

Figure 33. X-ray Diffraction Pattern and d-spacings in Angstroms of the Fine Clay (Less than 0.2μ) Fraction of Boghra Sandy Clay Soil Taken at a Depth of 0 to 8 Inches

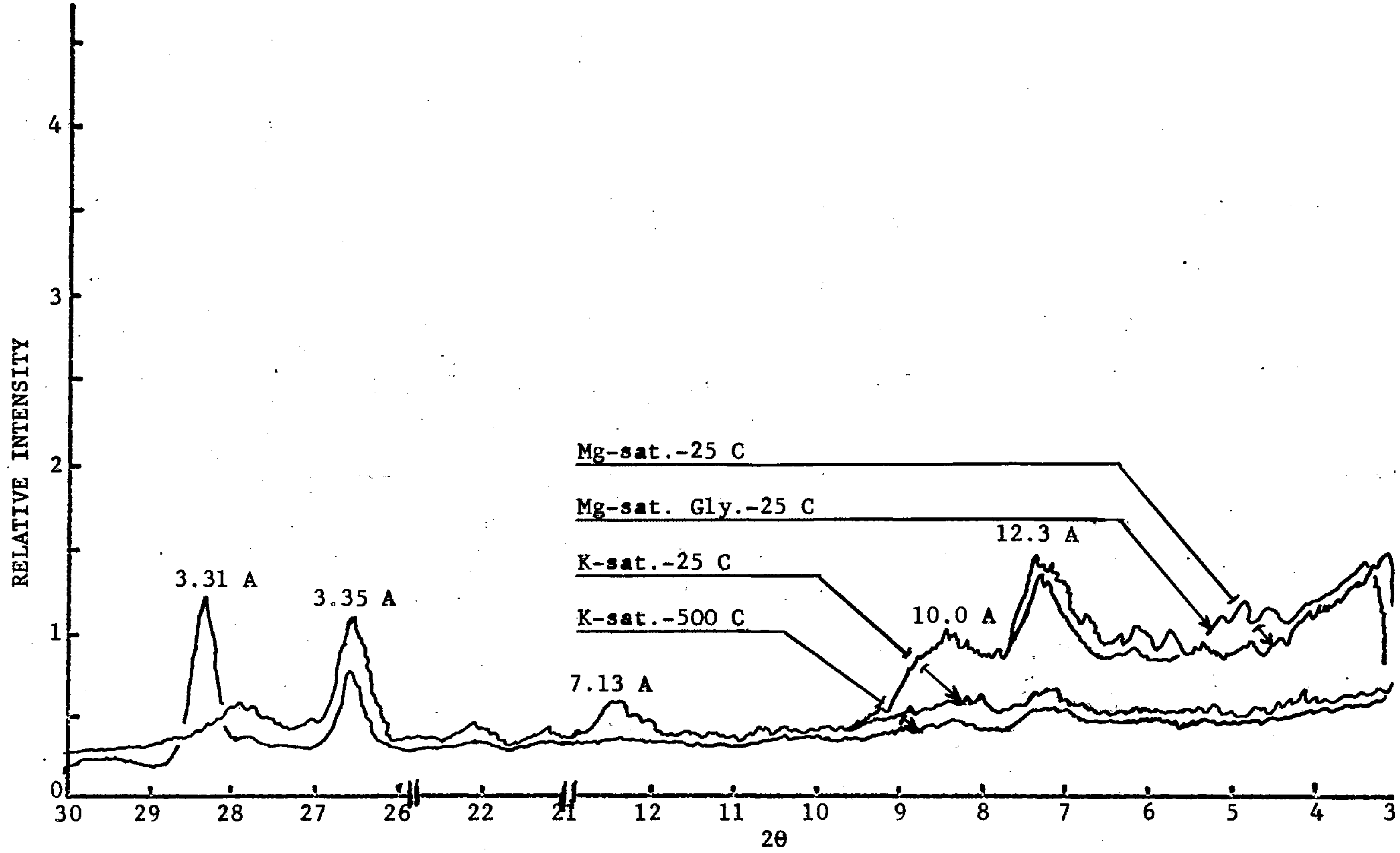

Figure 34. X-ray Diffraction Pattern and d-spacings in Angstroms of the Coarse Clay (0.2 to 2.0μ) Fraction of Boghra Sandy Clay Soil Taken at a Depth of 0 to 8 Inches

diffraction spacing of approximately 10 A. This spacing was collapsed by potassium saturation. This shows that Boghra clays also contain montmorillonite-illite. Boghra soil coarse clay als had a diffraction spacing of approximately 7.13 A before the clay was heated. After the clay was heated at 500 C for four hours this spacing disappeared. This indicates that Boghra soil coarse clay contains kaolinite. Both coarse and fine clays contained quartz and plagioclase feldspar.

CHAPTER V

SUMMARY AND CONCLUSIONS

Soluble ammonium phosphate added to the calcareous soils studied in this investigation was converted predominantly to calcium phosphate followed by aluminum phosphate. The rate of conversion was strongly influenced by the amount of calcium carbonate present. Afghan soils were very high in calcium carbonate compared to the three Oklahoma soils studied in this investigation. Aluminum phosphate content generally increased with time of incubation in the three Oklahoma soils but in Bolan clay loam the amount of aluminum phosphate formed one day after incubation was higher than after 30 days of incubation.

Iron and reductant soluble phosphate content were negligible in these soils before incubation and did not change after incubation. Generally the availability of phosphorus according to soil test was the lowest one day after incubation in the three Oklahoma soils. There was a slight increase in the amount of available phosphorus with time of incubation. This increase was not significant in most cases. Available phosphorus extracted by the procedure of Bray #1 (16) from Bolan clay loam followed the same trend with respect to the incubation period as these Oklahoma soils. However, the available phosphorus extracted by the procedure of Olsen, et al. (100) was the lowest 30 days after the incubation compared to one day after incubation. The largest conversion of soluble phosphorus to the other forms took place during the first day of incubation. Application of soluble ammonium phosphate slightly decreased the pH of all the soils studied in this investigation.

Two extractions with sulfuric acid was better than one extraction for all of these calcareous soils. Three washings between each fractionation procedure with 25 ml portions of saturated sodium chloride was better than two washings.

With the exception of Richfield loam the total phosphorus in all other soils studied in this investigation decreased with depth. However, the Richfield loam soil showed the total phosphorus to increase with depth in the upper horizons and then decrease in the lower horizons. Organic phosphorus in all of these soils decreased with depth.

All phosphate fertilizer treatments yielded significantly higher than the control treatment but there was no significant difference in the yields between 200, 400 and 600 ppm of phosphorus treatments. The first crop harvested which was fertilized with phosphorus, yielded significantly higher than the second non-fertilized crop. The amount of phosphorus in the plant tissue was closely correlated with the amount of soluble ammonium phosphate applied. Yield of the second crop in some cases was slightly depressed by the residual phosphorus applied to the soil for the first crop. This might be due to inadequate supply of other nutrients in relation to phosphorus. High rates of phosphorus generally require high rates of nitrogen for proper physiological balance in plants.

Chlorite and illite are the dominant clay minerals in Afghan soils while montmorillonite is the dominant clay mineral in the Oklahoma soils. Both Afghan and Oklahoma soils contained quartz and plagioclase feldspar. Kaolinite and vermiculite were also present in some of these soils.

Suggestions for Future Research

1. Phosphate fractionation of calcareous soils for calcium phosphate needs at least two extractions with 0.5 N sulfuric acid.

2. Three washings with 25 ml portions of saturated sodium chloride between each fractionation procedure is better than two washings.

3. Phosphate fertilizer should be applied to each crop grown on calcareous soil.

4. Large phosphate applications are not economical at least on a short-term basis. However, large phosphate applications need to be studied further in an attempt to determine the fixation capacity of these soils and to ascertain if the yields due to residual phosphate will continue or if these soils must be fertilized with phosphate each year.

5. A study of long-time phosphate response on these calcareous soils should be conducted under field conditions.

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