RELATIONSHIPS BETWEEN ALUMINUM AND SOIL ACIDITY IN SEVERAL MICHIGAN SOILS AND RELATED MINERALOGY STUDIES

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PAUL EUGENE RIEKE

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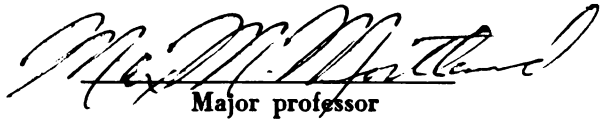

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ABSTRACT

RELATIONSHIPS BETWEEN ALUMINUM AND SOIL ACIDITY IN SEVERAL MICHIGAN SOILS AND RELATED MINERALOGY STUDIES

by Paul Eugene Rieke

Fifty-eight horizon samples from fourteen acid soil series in Michigan were surveyed for relationships between pH in water, pH in KCl solution, and extractable aluminum. Determinations of pH in a water suspension and a N KCl suspension indicated that the surface and subsurface horizon samples comprised separate populations.

In a more detailed study of nineteen horizon samples representing the Munising, Iron River, Ontonagon, Miami, and Fox soil series, relationships between exchangeable aluminum (extracted with N KCl), extractable aluminum (extracted with N NH_4OAc adjusted to pH 4.8), and various methods for exchangeable acidity were compared. Exchangeable hydrogen was found to be the predominant source of the total acidity in the surface horizons high in organic matter. In subsurface samples exchangeable aluminum contributed significantly to the total acidity, depending on pH and the horizon studied.

Exchangeable aluminum was closely correlated with extractable aluminum only when those samples which exhibited pH values below 3.9 in N KCl were omitted. The extractable aluminum fraction was suggested to include some of the polymerized forms of aluminum.

Liming the nineteen soil samples with $CaCO_3$, followed by 16 weeks moist incubation, resulted in a decrease in the exchangeable aluminum

level to essentially zero. Extractable aluminum and exchangeable acidity were decreased to a lesser extent.

Acidification and subsequent moist incubation in the laboratory resulted in considerably increased exchangeable aluminum levels in the nineteen horizon samples. The presence of organic matter reduced this effect, apparently by adsorbing the exchangeable hydrogen ions.

Most of the nineteen horizons contained clay minerals which exhibited aluminum interlayering to some degree. The effect of removal of the interlayer is shown for one horizon and discussed.

A dialysis experiment was used in an effort to develop an interlayer in pure vermiculite and bentonite-clay systems. A mixture of magnesium and aluminum chlorides with a molar ratio (Mg/Mg+Al) of 0.8 was titrated to pH 10.0 in the presence of clay minerals and dialyzed in distilled water for 20, 40, and 60 days. An interlayer was formed in both vermiculite and bentonite which exhibited greater heat stability than when pure magnesium or pure aluminum-clay systems were used. The heat stability of the interlayers formed in bentonite was greater than for interlayers found in vermiculite.

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By

Paul Eugene Rieke

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CHAPTER I

INTRODUCTION

The problem of soil acidity has been studied and restudied many times. The importance of pH and its effect on nutrient availability has, perhaps, received more attention than other aspects of soil acidity. Methods of predicting the amount of lime needed to correct soil acidity have also been reported on numerous occasions. Most of these reports were based on the assumption that the exchangeable hydrogen ion was the sole source of acidity in soils.

Recently, however, exchangeable aluminum was found to contribute to soil acidity. In fact, some acid soils have been found to be essentially aluminum-saturated, and not hydrogen-saturated, as was thought previously. In these soils, exchangeable aluminum was found to be the major source of soil acidity. In pure clay systems, it was found that hydrogen-saturated clays altered spontaneously to hydrogen, aluminum-clays. This leads to the conclusion that a study of the contribution of exchangeable aluminum to the total acidity in acid soils must also be related to the mineralogy of the soils being studied.

Clay minerals generally constitute the smallest sized fraction of the minerals in the soil. Because of their very small size, and internal surface, the specific surface of some clay minerals is very high. Weathering of soil clay minerals involves decomposition of the clay lattice with the resultant release of exchangeable aluminum as well as other ions. Because of their high specific surface, the swelling clays are particularly susceptible to weathering. As exchangeable aluminum ions are released upon weathering they are adsorbed on the remaining

exchange sites. It has been suggested that the aluminum released from one clay mineral layer may form a more or less stable structure in the space between other layers of the clay mineral under the proper conditions.

Study of the soil system leads to many difficulties because of the presence of organic and inorganic, and living and inert fractions. This results in a very complex system in which single factors can seldom be isolated. Therefore, many workers have used cation exchange resins, or pure clay mineral systems, in order to better control the variables. Still, in the soil the sum total of all the variables are operative, and studies of the soil system involve an effort to assess the various factors that affect the particular problem being investigated.

The aluminum status of Michigan soils has not been studied in detail. Therefore, the following objectives have been undertaken in this thesis:

1) To survey the pH and aluminum relationships of profile samples from several acid soils in Michigan.

2) To characterize the physical and chemical properties of these soils and to relate these properties particularly to the aluminum and acidity fractions. The effect of increasing and decreasing the pH on the aluminum status of these soils was also studied.

3) To study the relationships between aluminum and the mineralogy of these soils.

4) To contribute to the understanding of the process of interlayering of pure clay minerals.

CHAPTER II

LITERATURE REVIEW

Historical background of soil acidity

As early as 1904, Veitch observed that NaCl extractions of acid soils, low in organic matter, contained no appreciable quantities of HCl, and concluded that the acidity of the filtrate was due to solution of alumina. The soils with higher organic matter content showed low aluminum levels. Upon addition of a base to a NaCl extract from an acid soil, he observed a white precipitate which he identified as hydroxides of aluminum, iron and manganese.

Investigations by Daikuhara in Japan (1914) and Kappen in Germany (1916) supported these findings. Kappen hypothesized that the acidity developed because of hydrolysis of the aluminum and iron in the leachate.

Mirasol (1920) suggested that aluminum was largely responsible for the acid reaction of a KNO_3 extract of an acid soil. He ruled out iron and manganese as major factors in soil acidity.

More emphasis was placed on aluminum toxicity rather than its contribution to acidity (Magistad, 1925). Hartwell and Pember (1918) showed that the presence of aluminum in acid soils was the principle reason why barley and rye were affected differently in soils of a given pH. Hartwell *et al.* (1919) stressed that "the elimination of the effect of aluminum in acid soils seems likely to prove of more importance than neutralization of the acidity."

Although the presence of soluble aluminum and iron was generally recognized in acid soils, these authors did not comment on the source of the aluminum and iron found. Mattson (1926), however, did observe that even base-saturated soils eventually yielded aluminum and iron ions

upon continued electrodialysis. He, also, reported that extraction of an acid soil with a neutral salt removed aluminum and iron. If the sample was then leached with dilute HCl, it would again yield aluminum and iron to neutral salt extraction although the dilute acid leachate did not contain appreciable amounts of iron or aluminum. This was repeated several times with continued aluminum and iron removal by neutral salt extraction after the acid treatment. He attributed the ability of the neutral salt to extract more aluminum than the dilute acid to the high concentration of chloride ion, which in the presence of free acid favors formation of soluble chlorides of iron and aluminum.

Greater attention was being focused on the exchangeable hydrogen fraction of soil acidity than on the exchangeable aluminum fraction. Jenny (1961) suggested that the change of emphasis was accelerated by the application of potentiometric and conductimetric titrations, and the discovery of junction potential in pH measurements of soil suspensions. In a review as late as 1952, Mehlich and Coleman discussed soil acidity and pH with reference to exchangeable cations and titration curves of several clay systems. They did not discuss the role of exchangeable aluminum in soil acidity although reference is made to the reported presence of considerable quantities of exchangeable aluminum in base unsaturated soils (Paver and Marshall, 1934; Mukherjee et al., 1947).

Meanwhile, workers in other countries continued to report the presence of aluminum in acid clay systems. Paver and Marshall (1934) in England showed that acid clays are really saturated with hydrogen and aluminum, not hydrogen alone. The source of the aluminum ions was the crystal lattice of the clay minerals as hydrogen replaced them. They suggested that hydrogen arises in soil solution not only from direct exchange, but also from the hydrolysis of aluminum. Mukherjee et al. (1947, 1948), in India, reported large proportions of aluminum ions on exchange sites of electrodialyzed or acid-leached clays. Schofield (1946),

again in England, showed that aluminum displaced into solution from clays could be titrated, and therefore, could contribute to soil acidity. He also showed a mechanism whereby aluminum ions could polymerize and release hydrogen ions.

Still it was not until the reports of Harward and Coleman (1954) and Low (1955) were published in the literature in the United States that the aluminum concept of acid soil systems was seriously considered. Thus, 50 years after the aluminum theory was introduced by Veitch (1904), its acceptance again became widespread in the United States.

Discussion of aluminum hydrolysis

Schofield and Taylor (1954) suggested that the first stage in the hydrolysis of an aluminum salt in solution is:

$$Al(6H_2O)^{+3} + H_2O \rightleftharpoons Al(OH)(5H_2O)^{+2} + H_3O^{+1} \qquad (1)$$

Further hydrolysis yields:

$$Al(OH)(5H_2O)^{+2} + H_2O \rightleftharpoons Al(OH)_2(4H_2O)^{+1} + H_3O^{+1} \qquad (2)$$

$$Al(OH)_2(4H_2O)^{+1} + H_2O \rightleftharpoons Al(OH)_3(3H_2O) + H_3O^{+1} \qquad (3)$$

with precipitation of $Al(OH)_3$.

Low (1955) observed, in the titration of aluminum systems with NaOH, that $Al(OH)_3$ precipitated at pH 4.0 in an $AlCl_3$ solution. However, in an Al-bentonite suspension with the same aluminum concentration, the pH required for $Al(OH)_3$ formation was 4.7-5.0. He concluded that the hydrolysis of aluminum adsorbed on clays is inhibited by the electrostatic interaction between the charge on the clay and the aluminum ions.

The addition of NaCl to an Al-vermiculite suspension (Rich, 1960a) resulted in a sharp drop in pH. This was interpreted as an indication that aluminum was not replaced, so the hydrolysis of the adsorbed aluminum occurred with release of hydrogen ions.

Jackson (1960) and Barshad (1960a) proposed that as hydrolysis of aluminum occurs, the hydrogen ion released upon reduction of the charge from the trivalent aluminum monomer, $Al(6H_2O)^{+3}$, to divalent aluminum monomer, $Al(OH)(5H_2O)^{+2}$, will be adsorbed on the vacant exchange site. This hydrogen ion then will replace another aluminum from the clay lattice. The newly released aluminum ion will hydrolyze and release another hydrogen ion. This process will continue until equilibrium is attained. Rich and Thomas (1960) stated that hydrolysis of adsorbed aluminum continues only if there are adsorbents present to hold the products of the hydrolysis. Barshad (1960b) pointed out that true hydrogen saturation of clays can be maintained only under conditions which prevent aluminum ions from remaining in an adsorbed state, as in the presence of a complexing agent.

Evolution of hydrogen-clays to hydrogen, aluminum-clays

Several workers have recently studied the problems involved in attempts to prepare hydrogen-saturated clays and the related decomposition of these clays. Aldrich and Buchanan (1958) in attempting to hydrogen-saturate pure clays used a pretreatment of acidified NaCl in order to remove as much adsorbed aluminum as possible. They suggested that aluminum removed by this treatment comes largely from nonlayer lattice compounds. Their basis for this theory was the fact that the clays that showed the least amount of aluminum present after being treated by their hydrogen saturation method, also showed the strongest x-ray diffraction patterns. The opposite relationship was observed for other clays. Simultaneously, Higdon and Marshall (1958)

reported variation in resistance to decomposition and resulting aluminum saturation of two bentonites. Hectorite has been reported as being especially susceptible to decomposition (Kalovoulos, 1960).

Davis et al. (1962) studied the effect of temperature on the resulting neutralization titration curves of hydrogen-bentonite. Increased temperatures resulted in increased amounts of aluminum present as apparent from the titration curves.

The rate of evolution of hydrogen-clays to aluminum clays was found to follow a parabolic relationship (Eeckman and Laudelout, 1961). In an effort to study this evolution quantitatively, these authors calculated an interdiffusion coefficient, D, for the rate of exchange of hydrogen on the exchange sites on the face of the crystal, with aluminum on the exchange sites on the edge of the crystal. Since it has been found impossible to raise the hydrogen-saturation above a certain maximum level, the remaining part of the cation exchange capacity is satisfied by aluminum ions. These aluminum ions arise from the crystal lattice of the gibbsite layer, and are adsorbed at the crystal edges where they readily replace adsorbed hydrogen ions. The interdiffusion coefficient, D, for the aluminum ions adsorbed at the edge of the clay crystal, and the hydrogen ion adsorbed on the face of the crystal, was found to be very small, in the order of 10^{-20} cm^2 per second at room temperature.

These authors (Eeckman and Laudelout, 1961) also studied a hydrogen-montmorillonite clay suspension which was allowed to age to a hydrogen, aluminum-clay. It was then resaturated with hydrogen followed by another aging cycle. This was repeated for a total of three cycles. The cation exchange capacity decreased 16% for each aging cycle. It was assumed that the cation exchange capacity due to broken bonds at the edges of the crystals remained constant. Therefore, the reduction in cation exchange capacity resulted from a lowering of the permanent charge due to isomorphous substitution. A decrease was

observed in the parameter, D/r_0^2, where r_0 is the diffusion radius. If D is assumed to be constant, the decrease in D/r_0^2 is due to a greater diffusion radius. Also, assuming the tetrahedral layer is not affected in this acid dissolution, the increase in r_0 should be roughly proportional to the extent of the peripheral dissolution of the gibbsitic layer. This was found to be true.

McLean et al. (1959) added various symmetry amounts of sulfuric acid to several Ohio soils, and measured the increase in extractable aluminum. The total amounts of extractable aluminum developed by addition of the acid were suggested to be dependent on the initial stage of weathering of the particular soil. The less weathered soils released relatively greater amounts of extractable aluminum than the more highly weathered soils. These comparisons were made on the acid treated soils which received the proper symmetry amounts of acid to decrease the pH to 3.8. The authors state that for strongly podzolized B horizons the total amounts of extractable aluminum were more dependent on individual soil characteristics than on stage of weathering, although no data were given for these soils.

Polymerization of aluminum ions

Aluminum ions in solution are known to polymerize under the proper conditions. Ruff and Tyree (1958) used a light scattering technique to show that the molecular weight of the aluminum particles in solution increased as the OH/Al ratio increased. Aging the solution increased the size of the aluminum polymer, also. $Al_6(OH)_{15}^{+3}$ was suggested by Brosset et al. (1954) as the main product of an aged aluminum solution.

Jackson (1963a) calculated the ratios of different monomer ion species of aluminum in saturated solution [in contact with solid phase $Al(OH)_3$] as a function of solution pH. As the solution pH increases the

monomer concentration of all aluminum ion species decreases, including the monovalent aluminum monomer, $Al(OH)_2(4H_2O)^{+1}$. The concentration of this ion species is very low ($<10^{-9}$ M) at all pH values. At solution pH values much above 4.0, the concentration of the divalent aluminum monomer is also very low. Jenny (1961) pointed out that the replacement of the aluminum monomer species from clay systems by KCl follows the valence rule: $Al(OH)_2^{+1} > Al(OH)^{+2} > Al^{+3}$. Based on this ease of replacement and the fact that the concentrations of the monovalent and divalent aluminum monomer species occur in very low concentrations at normal acid soil pH levels, Jackson (1963a) predicted that the presence of these two hydroxymonomers would be limited to insignificant amounts in soils. Therefore, the trivalent monomer $Al(6H_2O)^{+3}$, and polymerized aluminum ions should be most prevalent.

Rich (1960a), Hsu and Rich (1960), and Jackson (1960) have reported that aluminum polymerizes in the presence of clay minerals as Schofield predicted (1946). The larger the aluminum polymer, the less easily it can be replaced (Jackson, 1963a). The greater the OH/Al ratio, the greater the amount of polymerization that occurs in a resin suspension (Hsu and Rich, 1960) and in clay suspensions (Rich, 1960a; Shen and Rich, 1962). The aluminum exchangeable with salts, decreased concurrently with a higher OH/Al ratio.

Extraction and measurement of acidity fractions

Various salts and buffers have been used for the extraction of aluminum. McLean, et al. (1959) extracted aluminum with a neutral salt and a cation exchange resin. They obtained greater quantities of aluminum with the salt than with the resin. Neutral salts had been used for this purpose even previous to 1904 according to Veitch. Yuan (1959) pointed out that buffered extractants may cause hydrolysis of aluminum resulting in release of hydrogen to solution while the aluminum remains

in the soil. Data from McLean, et al. (1959) substantiate this. The extraction of a Mahoning soil sample with NH_4OAc buffered to pH 4.8 gave 5.2 me. Al/100 gm.; extraction with NaCl gave 3.1 me./100 gm.; and Mehlich's $BaCl_2$-triethanolamine buffer adjusted to pH 8.1 gave only 0.3 me. Al/100 gm. soil.

McLean, et al. (1958), in suggesting the use of normal NH_4OAc adjusted to pH 4.8 for the extraction of aluminum, stated there was no evidence that aluminum extracted at this pH is released from the clay crystal. In none of the soils studied did the aluminum extracted exceed the cation exchange capacity. However, McLean, et al. (1959) reported that aluminum extracted exceeded the measured cation exchange capacity for some podzolized soils known to contain free iron and aluminum. Lin and Coleman (1960) found acidified salt solutions to extract quantities of aluminum in excess of the cation exchange capacity.

Potentiometric titration of a neutral salt leachate of an acid soil (Yuan, 1959; Coleman et al.,,1959) with a base gives a measure of exchangeable acidity including exchangeable aluminum and electrostatically bonded exchangeable hydrogen. Coleman et al.(1959) obtained a measure of the contribution of each fraction to the acidity by titration of the leachate to pH 4.0 for exchangeable hydrogen and to pH 8.3 for exchangeable aluminum. They compared this to back titration of the neutralized leachate with HCl in the presence of KF. The fluoride ion forms a neutral hexafluoride complex with aluminum which allows a measure of aluminum by the alkalinity developed on the addition of KF. Both methods agreed closely. Yuan (1959) used a similar procedure, but added NaF to complex the aluminum.

Thomas (1960), and Lin and Coleman (1960) used conductimetric titrations for measuring aluminum in soils and clays, as did Low (1955). Lin and Coleman (1960) titrated aluminum-saturated soils and clays potentiometrically to pH 6.0 in N KCl as a measure of the aluminum

present. They titrated to pH 6.0 because of the development of weak acid charges above pH 6.0. They also assumed that the acidity titrated below pH 6.0 was all attributable to exchangeable aluminum.

Coleman et al.(1958) obtained a measure of the pH dependent acidity by determining the exchangeable acidity removed by Mehlich's $BaCl_2$-triethanolamine (buffered to pH 8.1) after the soil sample had been leached with N KCl. They assumed the electrostatically bonded hydrogen and aluminum were replaced by leaching with the KCl solution.

Two buffering regions have generally been recognized (Yuan, 1959) in the potentiometric titration of hydrogen, aluminum-clay systems. However, a third buffering range has been observed recently (Schwertmann and Jackson, 1963) by titrating a hydrogen, aluminum-montmorillonite system in the presence of N KNO_3 using a continuously recording instrument. The three ranges are explained as: (1) titration of the electrostatically bonded hydronium associated with the clay, H_3O^+, which functions as a strong acid; (2) titration of aluminohexahydronium, $Al(OH_2)_6^{+3}$, which functions as a weak acid; and (3) a weaker acid group due to the titration of hydroxy-aluminum polymers that occur in the pH range 5.5-7.6. Upon aging of the H-montmorillonite system for 135 days, the H_3O^+ fraction decreased to nearly zero as aluminum ions from the clay lattice replaced the hydrogen ions. The second and third buffer ranges increased accordingly, along with a simultaneous increase in exchangeable aluminum. The authors (Schwertmann and Jackson, 1963) concluded that the proton retaining site of the third buffer range originated during aging in the slow hydrolysis and interlayer polymerization of monomeric trivalent aluminum. The resulting polymerized hydroxy-aluminum ions were not salt exchangeable. A partially neutralized 0.1 N $AlCl_3$ solution aged for 7 months also exhibited the third buffer range while an unneutralized solution did not show this effect to any appreciable extent.

This third buffer range is suggested to be very important in terms of liming acid soils because it occurs over the pH range of 5.5-6.5, and is due to the very weak acid groups of the hydroxy-aluminum polymers formed from aluminum ions liberated during natural weathering.

Increasing the OH/Al ratio in an aluminum-clay system causes the pH to increase and the exchangeable aluminum to decrease (Rich, 1960a; Shen and Rich, 1962). Some of the aluminum was fixed in a non-exchangeable form. Adding $Ca(OH)_2$ to an aluminum resin reduced the NaCl-replaceable aluminum to nearly zero (Thomas, 1960). The same result was observed for an aluminum-saturated subsoil and an aluminum-bentonite. Liming of an acid soil with an appreciable exchangeable aluminum level should have the same effect on the salt replaceable aluminum level. However, Moschler et al.(1960) in a greenhouse study observed that a small amount of lime reduced more than an equivalent amount of exchangeable aluminum. Thomas (1960) observed the same result, and suggested that the aluminum was fixed as charged intermediate hydroxy-aluminum compounds, either $Al(OH)_2^{+1}$ or $Al(OH)^{+2}$, at the expense of negative sites on the clays. Using Jackson's argument (1963a) that the amounts of the monovalent and divalent monomers should be low in soils, and since Thomas (1960) was unable to extract the aluminum lost upon liming, it is suggested that polymers were formed which were not replaceable by the neutral salt extraction.

McLean et al.(1960) used the Mehlich (1941) and Woodruff (1947) buffers, and $Ca(OH)_2$ titrations to determine lime requirement of several acid Ohio soils. These were compared to moist incubations with increasing $CaCO_3$ levels in the laboratory. The Mehlich and Woodruff buffers did not predict high enough lime requirements as determined by the $CaCO_3$ incubations for those soils with high extractable aluminum levels. The authors suggest that the Mehlich and Woodruff buffers are too strong to indicate by change of pH, the relatively weaker acidity of soils with

high extractable aluminum levels. The Shoemaker, McLean, and Pratt (SMP) buffer (1961) was recommended for lime requirement determinations, and found to correlate more closely with $CaCO_3$ incubation data for lime requirement predictions than the other buffer methods. Ross (1962) observed that the lime requirement for several Michigan soils determined by the SMP buffer method was very closely correlated with $CaCO_3$ incubations of these soils in the greenhouse.

Formation of interlayers in 2:1 expanding clay minerals

Aluminum ions released by acid weathering of clay minerals in soils tend to be adsorbed by the remaining clay minerals (Jackson, 1963a). Since most of the exchange sites of the 2:1 expanding clay minerals are on the faces of the crystals due to isomorphic substitutions, many of the aluminum ions released by weathering will be adsorbed in the interlayer areas. As the exchange sites become saturated with hydrated aluminum ions, the hydrated ion structures are subjected to steric pinching (Jackson, 1960) because the area occupied by individual exchange sites is less than the size of an aluminum hexahydroxymonomer. This is especially true for vermiculite (Jackson, 1963a) which has a high charge density. The adjacent aluminum monomers tend to polymerize by sharing hydroxyls, but the polymers retain a net positive charge. The resulting charged aluminum polymer may be very large, and thus becomes essentially unexchangeable. This results in a net reduction of the effective cation exchange capacity of the clay.

A complete, uncharged $Al(OH)_3$ interlayer would form a chlorite-like mineral which would contain a gibbsite sheet instead of the brucite sheet more commonly found in chlorite (Jackson, 1960).

Cation exchange resins have been used (Thomas, 1960; Hsu and Rich, 1960) to study the form of aluminum fixed in aluminum-saturated resins at various pH levels. The use of resins serves the advantage of

not being a source of exchangeable aluminum ions as a clay mineral would be during the course of the experiment. Dowex-50 cation exchange resin was aluminum-saturated and titrated with NaOH. By plotting the ratio of salt replaceable aluminum to $Ca(OH)_2$ titratable aluminum on the resin versus the percentage aluminum saturation, Thomas (1960) suggested that the predominant form of aluminum fixed was $Al(OH)_2^{+1}$. Hsu and Rich (1960) used essentially the same procedure with Dowex-50 cation exchange resin, but made several other measurements. As the pH of the aluminum resin was increased by addition of NaOH, both salt exchangeable aluminum and cation exchange capacity decreased linearly. The decrease in exchangeable aluminum proceeded at a much faster rate, however, indicating that aluminum was being precipitated in a form with a net charge much less than the trivalent form. Upon further titration, when exchangeable aluminum reached zero, the cation exchange capacity was found to increase, and eventually reached the original value. It was suggested that the excess OH^- completely neutralized the aluminum to $Al(OH)_3$ with concurrent release of exchange sites.

Controlling the OH/Al ratio of an aluminum-saturated resin at ratios less than 3 by adding graded amounts of $AlCl_3$ and NaOH, Hsu and Rich (1960) were able to show that aluminum was fixed at these pH levels in the form $Al(OH)_2^{+1}$. They proposed that the aluminum polymerized into a gibbsite type structure but maintained a net positive charge. The high charge density of the resin, which would tend to hinder complete hydrolysis of aluminum, and geometrical spacial limitations were suggested as reasons why aluminum did not undergo complete hydrolysis at these pH levels.

Artificial chlorites prepared from montmorillonite were formed by Caillere and Henin (1949) by the precipitation of magnesium hydroxide in a montmorillonite suspension. Longuet-Escard (1950) prepared pure $Al(OH)_3$ and $Ni(OH)_2$ interlayers in montmorillonite. Various mixtures

of aluminum and nickel also produced stable interlayers. Montmorillonite hydroxide complexes have been likewise shown for cobalt, zinc, and ferrous iron (Caillere and Henin, 1950; Youell, 1951).

Rich and Obenshain (1955) added a partial aluminum interlayer to a vermiculite clay, fractionated from a Red-Yellow Podzolic soil, by adding N $AlCl_3$ to the clay and subjecting the suspension to several wetting and drying cycles. However, adjusting the pH of the suspension to pH 7.0 was more effective in producing an aluminum interlayer. Using pure vermiculite, Rich (1960a) utilized various methods in attempting to produce an aluminum interlayer. Saturating the exchange sites with aluminum followed by an 18 day incubation period was more effective in producing an interlayer than adding NaCl to the aluminum-vermiculite suspension. Adjusting the pH of the aluminum-vermiculite-NaCl suspension to pH 4.5 gave slightly increased interlayering. However, a partially neutralized $AlCl_3$ solution (hydroxy-aluminum solution) which was aged for 2 weeks until clear of the hydroxide precipitate, was found to be the most effective in producing an interlayer. The resulting X-ray peaks were 13.6 A° when dried at 25° C., and 12.3 A° when heated to 200° C. If the clay suspension was heated at 100° C. for 15 minutes for each washing with N $AlCl_3$, while saturating the clay with aluminum, for a total of 5 cycles, the resulting interlayer was found to be nearly as stable as the hydroxy-aluminum treated clay.

Aluminum fixation in montmorillonite was produced by Shen and Rich (1962) by adding graded amounts of NaOH to an $AlCl_3$-montmorillonite system and incubating for 6 months. Increasing the OH/Al ratio resulted in interlayers in the montmorillonite giving X-ray peaks (after heating to 500° C.) ranging from 10.0 A° with no aluminum added, to 15.5 A° with an OH/Al ratio of 1.35.

Simultaneous dropwise additions of $Al(NO_3)_3$ and NaOH solutions into a dilute montmorillonite suspension agitated by a Waring blender

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(Slaughter and Milne, 1960) were found to develop a 14.7 A^{o} complex. Replacing aluminum with magnesium also gave a stable 14.7 A^{o} peak. Three sequences were studied to see which method gave the most stable interlayer. The methods were: (1) NaOH was rapidly added to a $MgCl_2$-clay suspension; (2) fresh $Mg(OH)_2$ precipitate was added to the clay suspension; and (3) $MgCl_2$ was rapidly added to a NaOH-clay suspension. The latter two methods were found to give X-ray peaks at 14.5 A^{o}, slightly less than the first method which resulted in a 14.7 A^{o} peak.

The $Mg(OH)_2$ interlayer was found to be slightly more heat stable than the $Al(OH)_3$ interlayer (Slaughter and Milne, 1960). However, the intensity of the (002) peak of the aluminum interlayer was found to be slightly less than would be expected from a fully developed gibbsite layer.

Hydrothermal treatments of montmorillonite and vermiculite in the presence of aluminum or magnesium sources resulted in some chlorite-like clays (McCaleb, 1961).

Synthetic clay minerals and clay mineral structure

Hydrothermal formation of minerals under high pressures and temperatures has been used often in the study of synthetic mineral formation. This method has been applied to synthetic clay preparation as well (Nelson and Roy, 1958; McCaleb, 1961). A minimum amount of aluminum was found to be necessary in the hydrothermal synthesis of a 14 A^{o} chlorite in addition to the magnesium and silicon sources (Nelson and Roy, 1958). This was explained by the necessity of having a small residual charge in both the octahedral and tetrahedral layers. Aluminum substitution for silicon in the tetrahedral layer would give this layer a net negative charge, while aluminum substitution for magnesium in the octahedral brucite layer would result in a net positive

charge. The increased attraction of the oppositely charged layers increases the stability of the chlorite. This structure was originally proposed by Pauling (1930) for an ideal chlorite. The aluminum in the tetrahedral layer is found in four-coordination while in the octahedral layer, it occurs in six-coordination.

As the substitution by aluminum increases simultaneously in both the silica tetrahedral layer and the magnesium octahedral layer, the (001) basal spacing was found to decrease (Gillery, 1959) for synthetic chlorites. Albee (1962) analyzed ninety natural chlorites and observed the same relationship. As the ratio of total number of aluminum ions (both in the tetrahedral and octahedral layers) per 10 cations increased from 1 to 3.7, the basal spacings decreased from 14.75 to 14.0 A^{o}, respectively, following a linear relationship. Synthetic chlorites prepared hydrothermally showed a similar relationship, but the slope of the line was less, indicating the effect of aluminum substitution was not as great for synthetic chlorites.

As the chromium content of natural chromium chlorites increased, the (007) basal spacing was found to increase, while the intensity of the (001) spacing decreased (Lapham, 1958). Substitution of chromium in the octahedral layer resulted in a higher (007) spacing than substitution in the tetrahedral layer. Since chromium has the same charge as aluminum, and its ionic size is larger, the substitution of chromium for aluminum in the tetrahedral layer would be expected to cause an increase in the basal spacing.

Henin (1956), DeKimpe and Gastuche (1960), and DeKimpe et al. (1961) synthesized clay minerals at normal temperatures and pressures. The variation in the coordination of aluminum with pH, concentration of aluminum, and ratio of silicon to aluminum were found to be important.

Pedogenic interlayering of soil clays

Since aluminum is a product of weathering of clay minerals, and the presence of exchangeable aluminum may result in precipitation of an aluminum interlayer in pure clay minerals, as has been discussed, it is not unreasonable to find aluminum interlayering in weathered soils. Jackson (1960) terms this a natural pedogenic process. The recognition of aluminum interlayers in soil clay minerals has been variously recognized and reported. Terminology suggested has included a "dioctahedral vermiculite" (Brown, 1953; Rich and Obenshain, 1955), a "chlorite-like mineral" (Klages and White, 1957), a "chlorite-like intergrade" (Weed and Nelson, 1962), an "intergradient chlorite-expansible layer silicate" (Dixon and Jackson, 1962), and a "2:1-2:2 intergrade" (Jackson, 1963a, 1963b).

The degree of stability of the interlayer when subjected to increasing heat treatments (Klages and White, 1957) gives an indication of the degree of interlayering of aluminum. A complete gibbsite interlayer in an aluminum chlorite, as shown in Figure 1, would theoretically maintain a 14 A^{o} peak upon potassium saturation and heating to 550^{o} C. A pure vermiculite (Figure 1) would collapse to 10 A^{o} after potassium-saturation and heating to 110^{o} C. The presence of positively-charged hydroxy-aluminum polymers (Figure 1) in the interlayer positions could prevent complete collapse to 10 A^{o}. As the degree of interlayering increases, the amount of collapse upon heating to 110^{o} and 550^{o} C. decreases. Dixon and Jackson (1959, 1962) measured the aluminum which was released by removing the interlayer from the coarse clay fraction of a soil. They were able to prove that larger amounts of aluminum were released from the clays which exhibited greater amounts of interlayering from X-ray patterns. A complete series from vermiculite to chlorite was suggested (Klages and White, 1957) as being theoretically possible in soils.

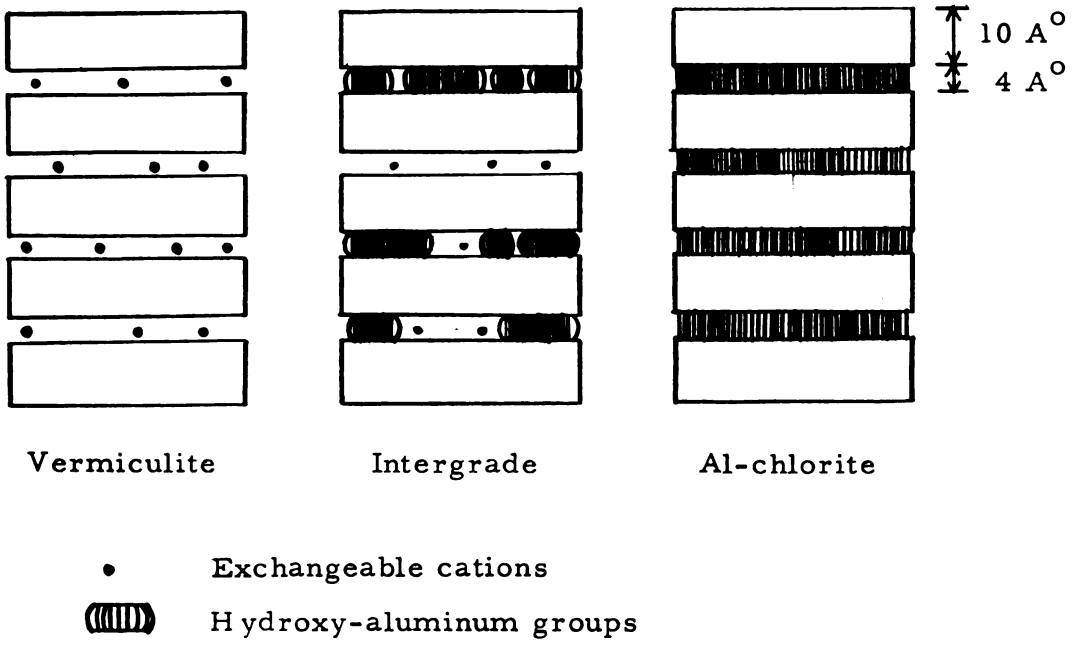

Figure 1. Diagrams of intergradient chlorite-expansible 2:1 layer silicate structure showing its relation to end-members vermiculite (left) and chlorite (right) in an edge view (Taken from Dixon and Jackson, 1962, Figure 3).

The presence of aluminum interlayering in soils has been generally observed (Jackson, 1963b). However, a few exceptions have been reported. Acid gley soils of western Kentucky (Hutcheson et al., 1959) and some grumusols (Kunze et al., 1954; Sawhney and Jackson, 1958) contained little aluminum interlayering.

Good drainage conditions apparently favor aluminum interlayering. The well-drained members of a catena were observed to contain a greater amount of interlayering than the poorly drained members (Sawhney, 1960b). Surface horizons also tend to exhibit a greater amount of interlayering according to several workers (Glenn et al., 1960; Rich, 1960b; Thiesen et al., 1959), but exceptions have been reported (Weed and Nelson, 1962).

Aluminum interlayering has been found to be most prevalent in the coarser clay fractions (Rich and Obenshain, 1955). This was explained by Dixon and Jackson (1962) by the facts that vermiculite tends to exist in larger particles in soils than montmorillonite, and that montmorillonite is more readily weathered. Also, because of the higher charge density of vermiculite, it is more readily interlayered by the positively-charged hydroxy-aluminum polymers. Jackson (1963b) reported that aluminum could be fixed on both surfaces of an expanded montmorillonite resulting in a collapse of the lattice to only 18 A^{o} upon heating at 550° C. However, he suggests that an intercalated gibbsite sheet would attach to only one face of a layer, when the layers are widely separated (20-40 A^{o}).

Iron has been found to occur with aluminum in pedogenic interlayers (Sawhney, 1960a; Dixon and Jackson, 1962), but much more aluminum than iron was released upon removal of the interlayer. Dixon and Jackson (1962) also suggested that allophanic interlayering was possible.

An increase in the cation exchange capacity of the clay fraction of soils has been reported after the interlayer has been removed (Glenn, 1960; Dixon and Jackson, 1962). This was suggested as evidence that the interlayer aluminum occurred as positively-charged hydroxy-aluminum groups.

Removal of the interlayer in soil clays

Several methods have been utilized to remove the interlayer. Boiling acid and base treatments were not found as effective as boiling the clay for 5 minutes in normal ammonium fluoride followed by boiling for 1 hour in normal potassium chloride (Rich and Obenshain, 1955). Acetic and citric acids adjusted to various pH levels were found to be rather ineffective methods by Klages and White (1957). Boiling the clay for 3 to 6 hours in sodium citrate was used by Tamura (1958). Sawhney (1960b) increased the extraction time to 6 to 9 hours boiling time with sodium citrate, but Glenn (1960) reported that this method was not as effective as a sodium fluoride extraction. The variability of the effectiveness of the several methods used are evidently a reflection on the degree and stability of the interlayers.

A heat pretreatment of 400° C. for 4 hours was proposed by Dixon and Jackson (1959). The clay was then boiled for exactly 2.5 minutes in 0.5 N NaOH in a nickel beaker. They suggested this treatment would decompose the positively-charged hydroxy-aluminum polymers in the interlayer area, but would not appreciably affect the gibbsite or brucite layers in chlorite. Later (Dixon and Jackson, 1962), the pretreatment heating time was reduced to 1 hour because destructive effects were observed on the kaolinite fraction of some soils.

Subsequent to removal of the interlayer aluminum some increased expansion to 18 A° upon magnesium-saturation and glycerol-solvation was observed (Glenn, 1960; Dixon and Jackson, 1962). This indicated that some montmorillonite contained interlayer aluminum.

Synthesis of aluminum and magnesium hydroxide minerals

Precipitation of the hydroxides of magnesium and aluminum under the proper conditions will result in crystalline forms (McCaleb, 1961;

Ne

Br

ex

pr

we

Th

ra

wa

Nelson and Roy, 1958). These forms can be examined by X-ray methods (Brown, 1961).

Mortland and Gastuche (1962) were able to crystallize a mineral, exhibiting either a 7.9 or a 7.6 A^{o} basal spacing depending on the proportions of Al and Mg. Mixtures of 0.25 M $MgCl_2$ and 0.25 M $AlCl_3$ were adjusted to pH 10.0 with NaOH and dialyzed for 30 days at 60° C. The molar ratio (Mg/Mg + Al) was varied from 0 to 1. At a molar ratio of 0.8 the 7.9 A^{o} species was found, but a basal spacing of 7.6 A^{o} was found in the mineral crystallized at the 0.1-0.7 molar ratios.

CHAPTER III

MATERIALS AND METHODS

Chemical characterization of several Michigan soils

Profile samples were collected in October, 1960, from fourteen acid soil series representative of soils in agricultural use in Michigan. In all cases attempts were made to select sites which were representative of virgin conditions. Legal descriptions for location of the profile samples are shown in Table 13 in the Appendix.

The samples were air-dried in the greenhouse, ground to pass a 4-mesh sieve, and stored in glass jars until needed for analysis or treatment.

Duplicate pH determinations were made using a 1:1 soil:solution ratio. The suspension was stirred intermittently with a glass rod for thirty minutes, followed by pH determination using a model G Beckman pH meter in conjunction with a calomel electrode and a Beckman glass electrode. pH was also determined in a N KCl suspension using a 1:2.5 soil: solution ratio, and intermittant stirring over a thirty minute equilibration period.

Aluminum was extracted with N NH_4OAc adjusted to pH 4.8 according to the method outlined by McLean et al. (1958). Ten grams of soil were weighed into a 125-ml. flask. Fifty ml. of the extraction solution were added, and the mixture was shaken for 16 hours on a rotary shaker. The sample was then filtered and another 50 ml. of the extraction solution was leached through the soil in 10 ml. increments.

The filtrate was slowly taken to dryness on a hot plate. Ten ml. of distilled water were added and taken to dryness. Two ml. of 1:1 HNO_3

were added and taken to dryness. Five ml. of 30% H_2O_2 were added, and taken to dryness. Two ml. of 1:1 HCl were added and taken to dryness on the steam bath, followed by heating 1 hour on the steam bath to dehydrate the silica. The residue was taken up with 10-ml. of 0.01 N HCl, diluted to 100 ml., and stored in a glass storage bottle.

Extractable aluminum was determined by an aluminon method modified somewhat from that described by Chenery (1955). The aluminum buffer solution was prepared as follows: 0.05% ammonium aurin tricarboxylic acid (Eastman Kodak Chemical), 2 N sodium acetate, 1.5% gum acacia, adjusted to pH 4.2 with acetic acid, and taken to volume. The pH was checked after 24 hours and adjusted as necessary. The buffer solution was stored in a brown glass acid bottle to prevent decomposition by sunlight.

The standard aluminum curve was determined with the use of an aluminum solution prepared by dissolving a carefully weighed amount of aluminum metal with concentrated HCl. The aluminum solution was then diluted to obtain a standard stock solution which was used for preparation of the standard curve. It was found that under the conditions of this method, solutions of greater than 100 μg. of aluminum in 50 ml. gave less reliable data.

An appropriate aliquot of either the standard aluminum solution or unknown solution was added to a 100 ml. beaker. Ten ml. of the aluminum buffer solution and ten ml. of a 0.2% thioglycollic acid solution was added. The thioglycollic acid was used to reduce ferric iron which interferes with the aluminon procedure (Chenery, 1955). The pH was then determined and adjusted to pH 4.2 with 2 N HCl or NaOH. The strength of the sodium acetate in the buffer solution prevented a pH change greater than 0.05 pH unit for any of the aliquots added, therefore, pH was checked only occasionally. The solution was then transferred to a 50 ml. volumetric flask, brought to volume, stoppered, and mixed.

Each solution was then heated for 10 minutes in a hot steam bath to develop the color complex. This complex was found to be very stable, but in all cases, after cooling to room temperature, percent transmission was determined between 3 and 6 hours after heating. Percent transmission was determined with a Coleman Model 14 Universal Spectrophotometer at 530 mμ wavelength using a purple filter (number 14-214). An 8-volt battery was used as a power supply for the exciter lamp because of variable AC line voltage.

Selection of soils for further study

Of the 19 profiles, 5 were chosen for further study because they apparently were representative samples and contained appreciable extractable aluminum levels. Those selected were the Munising, Ontonagon, Iron River, Miami, and Fox profiles.

The Munising series is a well to moderately well-drained, minimal to medial Podzol, with a fragipan, developed in strongly acid, reddish, sandy loam glacial till derived from red sandstone of the Lake Superior region of the Northern Lake States.

The Ontonagon series is a moderately well-drained, gray-wooded soil developed from clay to silty clay lacustrine sediments, derived from a variety of rocks, but with colors strongly influenced by the highly ferruginous formations of the Lake Superior region.

The Iron River series is a well to moderately well-drained Podzol soil of glacial uplands developed from glacial drift in the Lake Superior region.

The Miami series is a well-drained, Gray-Brown Podzolic soil developed in highly calcareous till of Wisconsin age with a loess capping up to 18 inches thick.

The Fox series is a well-drained, Gray-Brown Podzolic soil developed in silty or loamy outwash material, underlain by stratified calcareous gravel and sand at depths of from 24-42 inches.

Physical and chemical characterization of selected soils

Mechanical analyses were carried out on the nineteen horizon samples. Hydrogen peroxide was employed to destroy organic matter. The soil sample was then leached with 200 ml. N HCl on hard (No. 50 Whatman) filter paper on a Buchner funnel to destroy carbonates, and to H-saturate the clays. Chlorides were removed by washing with water. The sample was transferred to a beaker, titrated with 0.1 N NaOH to pH 9.5, and mixed for 15 minutes with the use of an electric stirrer. The sample was then shaken overnight, and the pH was adjusted to 9.5 again. The sands, separated by washing the silts and clays through a 300 mesh sieve, were placed in a beaker, dried, and weighed. The silt and clay fractions were transferred to a sedimentation cylinder, brought to volume, shaken, and allowed to settle in a constant temperature room. Twenty-five ml. samples were taken at the appropriate times, and depths by the pipette method. The percentages of sand, silt, and clay for each horizon were determined. Samples for clay fraction x-ray analyses were taken with 500 ml. of the Na-saturated clay kept in suspension and the remaining portion dried and stored.

Percentage of organic matter was determined by the Walkley-Black method as outlined by Jackson (1958, pp. 219-221).

Exchangeable bases were extracted by shaking 10 grams of soil with 100 ml of neutral normal NH_4OAc for one hour and filtering. Calcium, potassium, and sodium were determined with a Coleman flame-photometer. Magnesium was determined with a Beckman DU flame-photometer.

Exchangeable aluminum (differentiated from extractable aluminum) was extracted with N KCl using 100 ml. of solution to 10 grams of soil, shaking for one hour, and filtering. Aluminum was determined by the aluminon method as previously described. Mehlich's (1948) $BaCl_2$-triethanolamine buffered to pH 8.1 was used for exchangeable acidity determinations.

A few soils were selected for more precise characterization of the acidity fraction. These samples were leached with KCl as above, followed by extracting the weak acid portion of the exchangeable acidity fraction by Mehlich's method as suggested by Coleman et al. (1959).

These same samples were titrated with 0.1 N NaOH in the presence of N KCl. Five grams of soil and 50 ml. of N KCl were added to 125-ml. flasks. Increasing increments of base were added to individual flasks, and shaken for 48 hours. The pH of each treatment was then determined and titration curves were drawn.

Cation exchange capacity determinations were made by measuring the Na from a Na-saturated soil sample as replaced by N NH_4OAc (Jackson 1958, pp. 63-65). Sodium was determined with a Coleman flamephotometer.

The cation exchange capacity of the mineral fraction of soils 1-12 was determined by destroying organic matter with H_2O_2. The cation exchange capacity for the organic fraction was determined by difference between total cation exchange capacity and that measured for the mineral fraction.

Exchangeable (N KCl exchangeable) and extractable (extracted with N NH_4OAc adjusted to pH 4.8) iron were determined by the o-phenanthroline method outlined by Jackson (1958, p. 389). Determinations were carried out on the same leachates as were used for exchangeable and extractable aluminum determinations.

Lime requirement was determined by the Shoemaker, McLean, and Pratt (1961) method.

Moisture equivalent was determined using the centrifuge and moisture equivalent boxes. The samples were centrifuged at 2440 rpm for 30 minutes, weighed, oven-dried, and reweighed.

Incubation studies

In order to study the effect of liming on the aluminum and acidity fractions in these soils, each of the nineteen profile samples was limed and incubated in the laboratory. Lime requirement was determined by the Shoemaker, McLean, Pratt method (1961). Four hundred grams of air-dry soil were mixed with the appropriate amount of precipitated $CaCO_3$ in order to apply the required amount of lime on an acre basis (2,000,000 per acre furrow slice assumed). The limed sample was mixed in a V-shaped end-over-end mixer for at least 15 minutes, and placed in a pint glass jar. The appropriate amount of distilled water was added to bring the sample to the moisture equivalent percentage, and this was allowed to stand for at least 1 hour. Then the sample was emptied on clean brown paper, thoroughly mixed to attain uniform moisture throughout the sample, and put back into the pint jar for incubation at room temperature ($27\pm5^{\circ}$ C.). Once each week the jars were opened, and allowed to aerate for 4 hours. At the end of 2 weeks the samples were dried at 60° C. under a partial vacuum to a moisture percentage equal to one-half the moisture equivalent percentage. A 40-gram subsample was taken for chemical analyses, oven-dried, and stored in a glass bottle. The remaining portion of the sample was brought back to moisture equivalent, mixed, and incubated as outlined above. The same procedure was followed as subsamples were taken after 4, 6, 8, and 16 week incubation periods, with the exception that the samples were not dried and rewetted after the 8-week subsampling.

Other samples which received no treatment, and a 1-symmetry treatment of $\underline{N}$ H_2SO_4 were incubated, and subsampled in the same manner.

The acid treated sample was brought to the moisture equivalent by adding the volume of water added with H_2SO_4 and the necessary amount of distilled water to bring the total to the required moisture percentage.

Two of the horizons (numbers 13 and 16) showed a lowering of pH upon liming and incubation. It was suggested that this may have been a result of the release of nitrates upon decomposition of organic matter during incubation. Therefore, a 10 gram sample was shaken for 30 minutes with 50 ml. of distilled water and filtered. Another 50 ml. of water was leached through the soil in 10 ml. increments. Organic matter in the combined filtrate and leachate was destroyed with 5 ml. of 30% H_2O_2, followed by drying slowly on a hot plate. Nitrates were determined colorimetrically with the phenol disulfonic acid method (Jackson, 1958).

Soil clay mineral identification

Identification of the clay minerals present in each of the horizons was determined from basal spacing reflections indicated by X-ray diffraction. A thin clay film was deposited on a porous ceramic plate by drawing the water from a Na-saturated clay suspension (from mechanical analysis previously described) through the ceramic plate using a vacuum pump. The clay particles are oriented parallel to the surface of the ceramic plate. The clay film was then leached with several increments of a solution of 0.1 N $MgCl_2$ and 3% glycerol, followed by leaching with several increments of 10% glycerol solution. The resulting Mg-saturated, glycerol-solvated clay film was allowed to air-dry, and then X-rayed using a scanning goniometer. The X-ray source was a Norelco X-ray unit using Cu Kα radiation generated at 35 kv and 20 ma. The scanning rate of the goniometer was 1° 2θ per minute. The basal spacing reflections were recorded with a Brown recorder. The scale factor was 4 unless otherwise indicated.

The clay film was then leached with 0.1 N KCl to K-saturate the clay minerals previous to subjection to drying at 110°C. for at least 6 hours. The K-saturated, heated clay film was X-rayed, heated to 550° C. for at least 3 hours and X-rayed again.

The resulting X-ray tracings exhibited rather poor peaks for several horizons. In an effort to obtain more precise tracings the clay suspensions were treated for removal of iron by the citrate-bicarbonate-dithionite method suggested by Mehra and Jackson (1960). Since the clay suspension was already Na-saturated and dispersed, the final Na citrate washing was followed by washing with distilled water to remove the citrate ion, but was not boiled in 2% Na_2CO_3 to disperse the suspension.

Clays from several horizons which exhibited an appreciable amount of interlayering in the 2:1-2:2 expansible layer clays were treated for removal of this interlayer material as described by Dixon and Jackson (1962). Aliquots of the Na-saturated clay suspensions were treated for iron removal as mentioned above (Mehra and Jackson, 1960), H-saturated by washing three times with 0.03 N HCl, and washed free of chlorides with acetone and water. Washing with acetone then freed the clay of water. One washing with benzene prevented aggregation upon drying at 110° C. in a small Pyrex beaker. The benzene wash previous to drying was found very important as samples which were dried from water eventually resulted in very poorly oriented clay films. This was probably due to aggregation of the clay particles as the authors suggested (Dixon and Jackson, 1959). The clay was then heated at 400° C. for slightly over one hour in a muffle furnace, followed by boiling with clay in 0.5 N NaOH for exactly 2.5 minutes in a nickel beaker. Care was taken to keep a constant 1:1 ratio between mg. clay and ml. of base. The dissolved iron and aluminum were removed by centrifugation. The clay was washed once with water, and taken up in water for preparation of oriented clay films for X-raying.

Artificial interlayering of pure clay minerals

In order to study the possibility of crystallizing an interlayer of magnesium and aluminum hydroxides in 2:1 expanding lattice clay

minerals, a dialysis experiment was designed. Pure magnesium and pure aluminum chloride-clay systems were incorporated into the experiment. A mixture of magnesium and aluminum chlorides was also included to determine if the 7.9 A^{o} mineral crystallized by Mortland and Gastuche (1962) could be incorporated into the interlayer of Wyoming bentonite, which can expand to interlayer distances of over 8 A^{o}. This would allow a large enough space for the 7.9 A^{o} mineral to form in the interlayer area. The bentonite clay used was a Wyoming bentonite. X-ray diffraction patterns (Figure 26, Appendix) indicated this was a pure sample.

The vermiculite was a pulverized form supplied by the Zonolite Company. This mineral was found to be a mixture of discrete vermiculite and mica with some regularly and, perhaps, some randomly interstratified forms present according to the X-ray diffraction patterns (Figure 26, Appendix). Total potassium analysis showed this clay contained 3.9% potassium.

The clays were sodium saturated by washing five times with N NaCl and removing the supernatant by centrifugation. Chlorides were removed by washing with water, followed by washing with 95% ethyl alcohol until free of chlorides according to the silver nitrate test. The clays were dried overnight at 110° C. Two percent suspensions were prepared and stored. Solutions of 0.5 M $MgCl_2 \cdot 6H_2O$ and 0.5 M $AlCl_3 \cdot 6H_2O$ were prepared. One hundred ml. of the clay suspension and one hundred ml. of the proper chloride solution were mixed in a 250-ml. beaker. The suspension was titrated with approximately 4 N NaOH to pH 10.0, stirring constantly with a magnetic stirrer. pH readings were taken periodically.

In the mixed aluminum-magnesium systems, the chloride solutions were mixed to give the (Mg/Mg+Al) molar ratios 0.7 and 0.8. Table 1 shows the treatments used.

Table 1. Treatments studied in the dialysis experiment.

Sample No.	Molar ratio (Mg/Mg+Al)	Clay mineral present
1	0.8	None
2	0	Vermiculite
3	0.8	Vermiculite
4	1.0	Vermiculite
5	0	Bentonite
6	0.7	Bentonite
7	0.8	Bentonite
8	1.0	Bentonite

The neutralized suspensions were divided into three fractions and transferred into cellophane dialysis tubing (Central Scientific Company). The ends of the dialysis tubing were tied and, hereafter, will be called dialysis bags. The three dialysis bags for each treatment were placed in a quart jar which was filled with distilled water and stoppered. The samples were incubated in a constant temperature water bath at $60\pm3^{\circ}$ C. The distilled water was changed and the dialysis bags were shaken every 24 hours. One of the dialysis bags was removed from each treatment after 20, 40, and 60 day incubation periods. The pH of the suspension was determined immediately after removal.

Attempts to prepare oriented clay films on porous ceramic plates for X-ray analysis proved unsuccessful because the films were found to crack upon drying. Therefore, a few drops of the suspension were placed on a glass slide and allowed to dry. The clay particles should orient parallel to the surface of the slide upon drying.

A 10-ml. portion of the clay suspension was placed in a 15-ml. centrifuge tube. The clay was washed four times with normal potassium chloride followed by three washings with water to remove excess salt.

The clay was resuspended in water and a slide was prepared as described above. X-ray diffraction patterns were run on the potassium-saturated clay after air-drying, and after the following heat treatments: 110° C. for 4 hours, and 200, 300, 400, and 500° C. for 2 hours.

CHAPTER IV

RESULTS AND DISCUSSION

Survey of 58 horizon samples

Data for extractable aluminum, and pH determined in water, and N KCl suspensions, for the fifty-eight horizon samples are shown in Table 14 of the Appendix. The water pH values ranged from 4.6 to 7.6. When pH was determined in KCl suspension, a range in pH from 3.4 to 6.9 was found.

Figure 2 shows a plot of water pH versus KCl pH values. A positive linear correlation is present, as would be expected. There are two populations evident in Figure 2. The surface horizons (circled dots) generally have higher KCl pH values for a given water pH when compared to the subsurface horizons. The linear correlation coefficient for the relationship between water pH and KCl pH was 0.935^{**} for all 58 samples as shown in Table 2. When the surface samples are analyzed as a separate group, the correlation coefficient increases to 0.993^{**}. The regression lines for the surface and subsurface samples (Figure 2) show a very slight difference in slope for the two groups.

Table 2. Water pH and KCl pH relationships for 58 horizon samples.

Population	r value[a]	Linear regression equation
All horizons (58)	0.935^{**}	KCl pH=1.01 pH-1.11
Surface horizons (14)	0.993^{**}	KCl pH=1.02 pH-0.94
Subsurface horizons (44)	0.937^{**}	KCl pH=0.92 pH-0.70

a--** refers to significance at the 1% level.

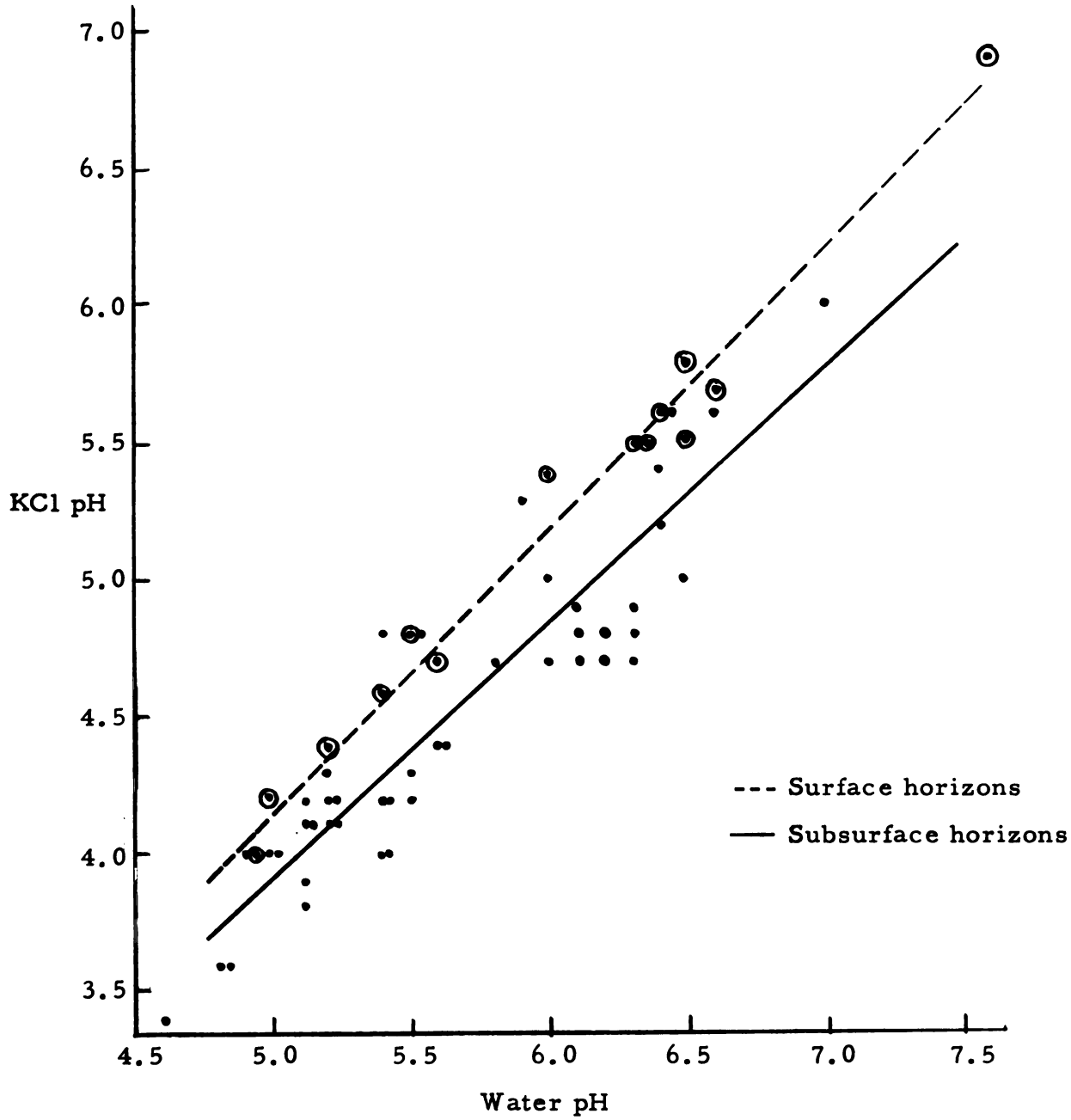

Figure 2. Water pH versus KCl pH for 58 horizon samples. Circled dots refer to surface horizons

The difference observed between surface and subsurface horizon samples apparently lies in the source of acidity in the two groups. Virgin surface soil samples contain considerable quantities of organic matter whereas the subsurface horizon samples normally contain very low amounts. The main source of acidity from the organic fraction in the pH range studied here lies in the ionization of humus carboxyl groups (Jackson, 1963a). This acidity is pH dependent, increasing as the pH increases. The source of acidity in the mineral fraction which is predominant in the subsurface samples is mainly from KCl exchangeable alumino-hydronium cations and the polyalumino-hydronium edges (OH_2) according to Jackson (1963a). It is apparent in Figure 2 from the difference in position of the linear regression equations that KCl is slightly more effective in causing ionization of the acid fraction of the mineral portion than of the organic fraction. This may be explained by relatively greater quantities of exchangeable aluminum present in the lower horizons and will be discussed in detail later. The potassium ion from KCl may cause replacement of the adsorbed aluminum ions resulting in $AlCl_3$ in solution. In determining the pH of the KCl suspension, the electrodes would be measuring the pH of $AlCl_3$ in the suspension. However, the adsorbed aluminum ions would not contribute directly to the pH reading of the water pH determination.

Extractable aluminum values ranged from 0.2 to 30.4 me./100 gm. The relationships of extractable aluminum to water pH and KCl pH are shown in Figures 3 and 4, respectively. A logarithmic relationship was apparent, therefore, extractable aluminum was plotted on a log scale. Determination of pH in water gave slightly better correlation (Table 3) with the logarithm of extractable aluminum than determination of pH in KCl solution, although the points tended to be quite scattered. The surface horizons, with an average of 1.4 milliequivalents of extractable aluminum per 100 grams of soil, gave some indication of consisting of a

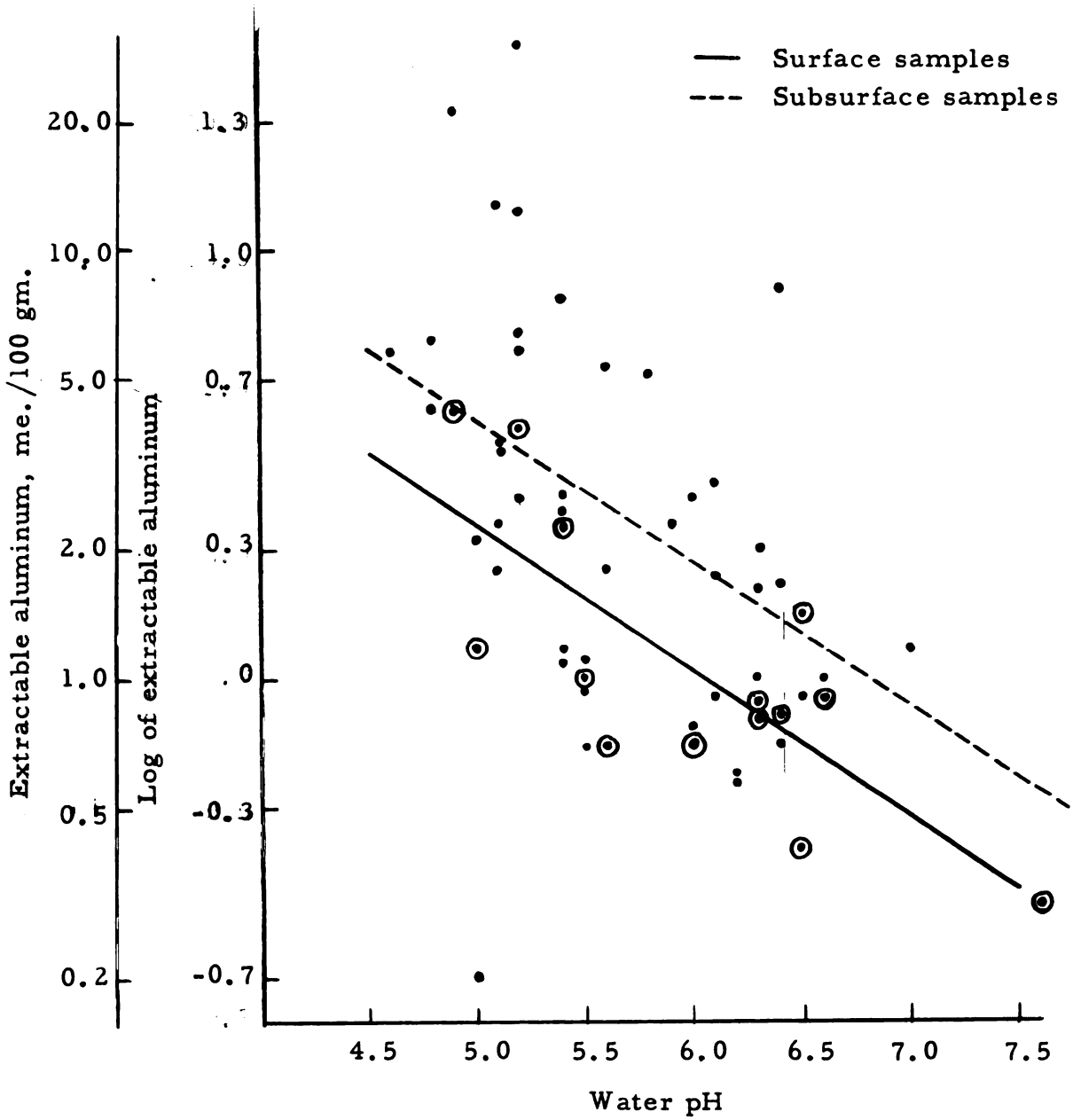

Figure 3. Linear correlation between water pH versus logarithm of extractable aluminum for fifty-eight horizon samples. Circled dots refer to surface samples, the solid line represents the linear regression equation for the surface horizons. The dotted line represents the linear regression equation for subsurface horizons.

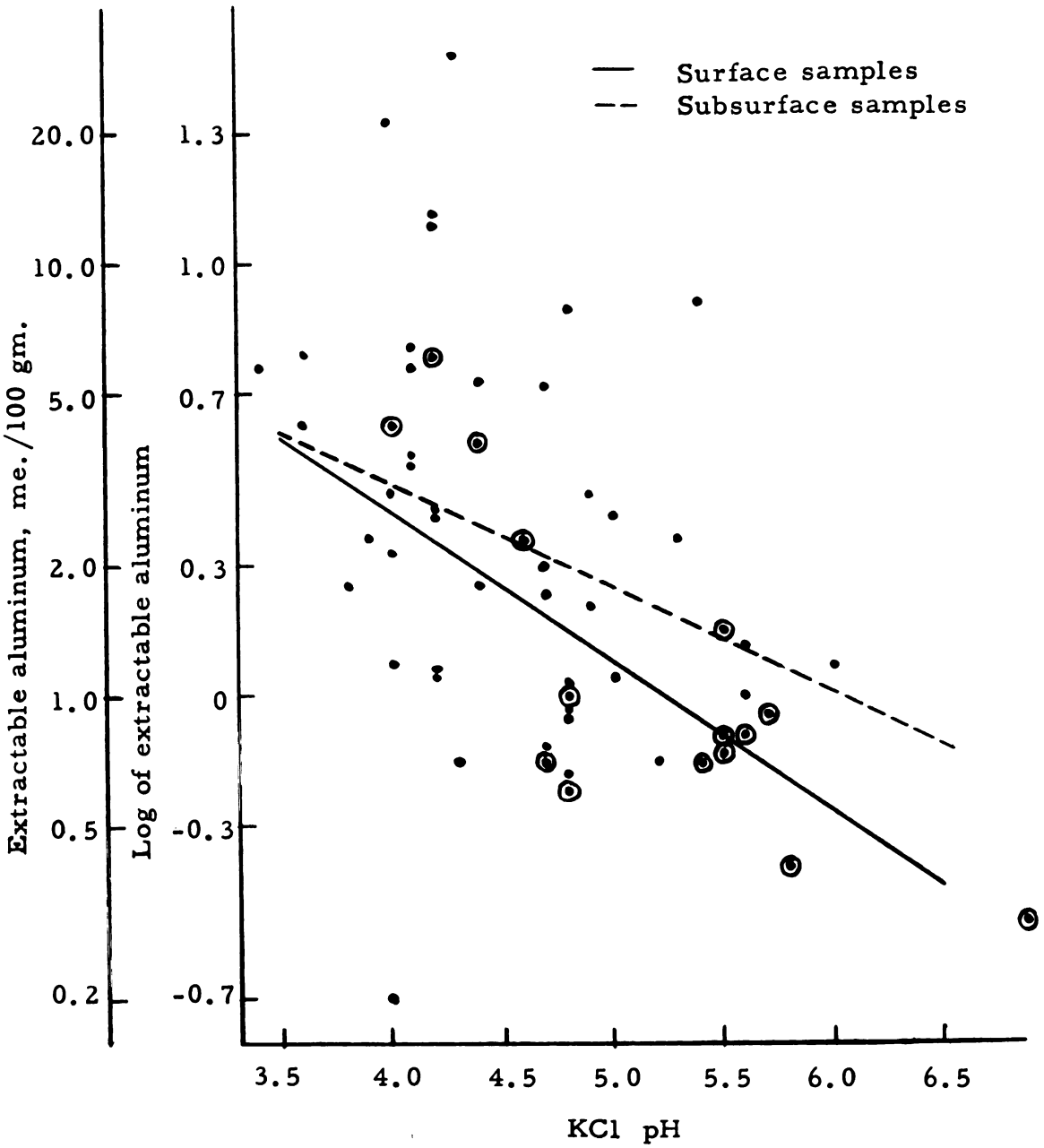

Figure 4. KCl pH versus logarithm of extractable aluminum for fifty-eight horizon samples. Circled dots refer to surface horizons. The solid line represents the linear regression equation for the surface horizons. The dotted line represents the linear regression equation for subsurface horizons.

Table 3. Correlation coefficients and regression equations for linear correlation between pH and logarithm of extractable aluminum in several horizon samples.

Population	r[a]	Linear regression equation
All samples (58)	-0.533**	
Surface samples (14)	-0.770**	log extractable Al=2.030 - 0.336 pH
Subsurface samples (44)	-0.474**	log extractable Al=2.29 - 0.341 pH
All samples (58)	-0.477**	
Surface samples (14)	-0.806**	log extractable Al=1.792 - 0.342 KCl pH
Subsurface samples (44)	-0.302*	log extractable Al=1.429 - 0.236 KCl pH

a- ** indicates significant linear correlation at the 1% level
* indicates significant linear correlation at the 5% level

population different from the subsurface samples, which averaged 4.1 me./100 grams. A difference in the slope for surface and subsurface horizons was observed when pH was determined in a KCl suspension as seen in Figure 4. However, because of the wide scatter of the points for the subsurface samples shown in Figures 3 and 4, and the poor correlation coefficients which resulted (Table 3), further interpretation of these data would be difficult and questionable.

The presence of appreciable quantities of aluminum on the exchange sites would contribute to the acidity of a KCl suspension as discussed previously. Therefore, one might predict that the difference between water pH and KCl pH would be greater for those horizons which contain more extractable aluminum. Plotting water pH minus KCl pH versus extractable aluminum indicated there is no apparent relationship in these soils. Difference in pH was found to bear a closer relationship to depth in the profile (Table 4) than to extractable aluminum level. A maximum

Table 4. Difference between water pH and KCl pH determinations, and extractable aluminum at increasing depths in the profile for fifty-eight horizon samples.

	Depth in profile to center of horizon, inches							
	0-3	4-7	8-11	12-15	16-19	20-23	24-27	28-31
No. of horizons sampled	15	8	11	8	9	5	0	2
(Water pH-KCl pH)	0.81	1.00	1.09	1.13	1.32	1.22	--	1.10
Extractable Al, me./100 gm.	1.43	1.69	5.77	7.23	2.67	3.58	--	1.65

difference between water pH and KCl pH values was observed at the 16-19 inch depth. For most profiles this would correspond to the horizon of maximum clay percentage. The depth of maximum extractable aluminum occurred higher in the profile (between 8-15 inches) for these soils than the depth for greatest average difference between water pH and KCl pH.

It should be pointed out that the data in Table 4 present only a general picture of these data. For instance, the extractable aluminum average can be greatly affected by only one horizon when so few horizons are being considered. The 8-11 and 12-15 inch depths are suggested as examples. If the extractable aluminum data for samples 3 and 4 from the B horizons of the Munising series are omitted, the average extractable aluminum values decrease to 4.2 and 4.4 me./100 gms. for the 8-11 and 12-15 inch depths, respectively. Still, the trend for extractable aluminum to be higher in the lower horizons is evident.

Characterization of 19 selected horizon samples.

Five profiles consisting of nineteen horizon samples from the Munising, Ontonogan, Iron River, Miami, and Fox series were selected

for further characterization of the acidity fraction. General characterization of these samples is reported in Tables 15, 16, and 17 of the Appendix, which give percent sand, silt, and clay, texture, percent organic matter, moisture equivalent, exchangeable bases, percent base saturation, exchangeable hydrogen, the sum of exchangeable hydrogen and aluminum, lime requirement, exchangeable iron, and cation exchange capacity measurements.

Samples numbered 1, 5, 9, 13, and 16 are the A_1 horizon samples for the Munising, Ontonagon, Iron River, Miami and Fox soil series, respectively. These will be referred to as surface horizon samples hereafter, and will appear as circled dots on all scatter diagrams. The remaining sample numbers through number 19 correspond to the subsurface horizon samples for the same soil series.

Exchangeable aluminum extracted with a solution of N KCl, is differentiated from extractable aluminum which is extracted with N NH_4OAc adjusted to pH 4.8. This nomenclature will be used throughout the remainder of this thesis. Exchangeable aluminum data for the selected soils are shown in Table 19 in the Appendix. Figure 5 indicates there is a rather poor correlation between exchangeable and extractable aluminum in these soils. The surface horizons contained very little exchangeable aluminum while the subsurface horizons contained variable amounts.

Samples 3 and 4 indicated on Figure 5, contained very high amounts of extractable aluminum. These values even exceeded the cation exchange capacity (Table 17, Appendix). This was particularly noticeable for sample 4 which had a cation exchange capacity of 14.8 me./100 gm., but contained 30.4 me./100 gm. of extractable aluminum. McLean et al. (1959) reported that extractable aluminum could exceed the cation exchange capacity in the B horizons of Podzol soils. Samples 3 and 4 are B horizons of the Munising series described

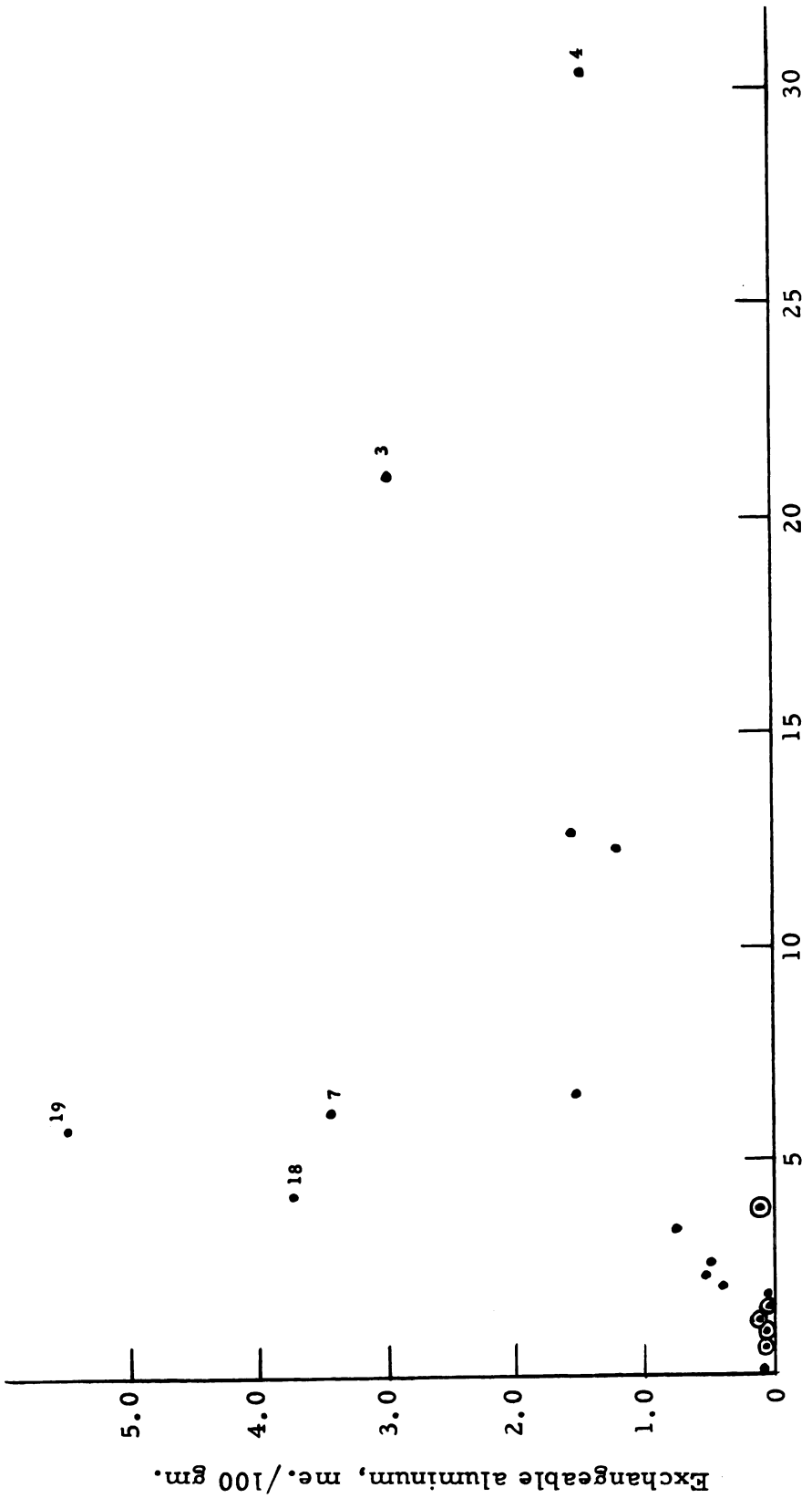

Figure 5. Plot of exchangeable aluminum versus extractable aluminum. Circled dots refer to surface horizons.

previously as a minimal to medial Podzol. Since the podzolization process in soil development results in the accumulation of free iron and aluminum oxides in the B horizon (Stobbe and Wright, 1959), high amounts of extractable aluminum would be expected in samples 3 and 4.

When the ratio of extractable aluminum to exchangeable aluminum is high, as would be the case for points in the lower right corner of Figure 5, it is suggested that the aluminum has polymerized to a large extent. Conversely, for points in the upper left part of Figure 5, as typified by samples 7, 18, and 19, the quantities extractable and exchangeable aluminum are more nearly equal. Care must be taken in interpretation of these points, however, as it was found that for samples 7, 18, and 19 the KCl pH was 3.6 or below. At this pH, it would be possible for the KCl solution to remove some easily soluble $Al(OH)_3$ or to extract some hydroxy-aluminum polymers from the interlayer positions of the 2:1 expansible clay minerals. The clay mineral fractions (to be discussed later) of horizons 7, 18, and 19 were found to contain appreciable interlayer material.

If samples 7, 18, and 19 are omitted, the correlation coefficient increases from 0.396 to 0.798**, indicating a much closer relationship between extractable and exchangeable aluminum.

Exchangeable aluminum apparently bears a logarithm relationship to pH as does extractable aluminum. The logarithm of exchangeable aluminum is plotted versus water pH and KCl pH in Figures 6 and 7, respectively. The surface horizons again appeared to consist of a population different from the subsurface horizons. Therefore, separate linear regression equations were calculated and are shown in Table 5. From the slopes of the lines plotted in Figures 6 and 7, it is apparent that exchangeable aluminum decreased more rapidly with an increase in pH for the subsurface horizons than for the surface horizons. The nature of the exchange sites in the organic fraction of the surface horizons is

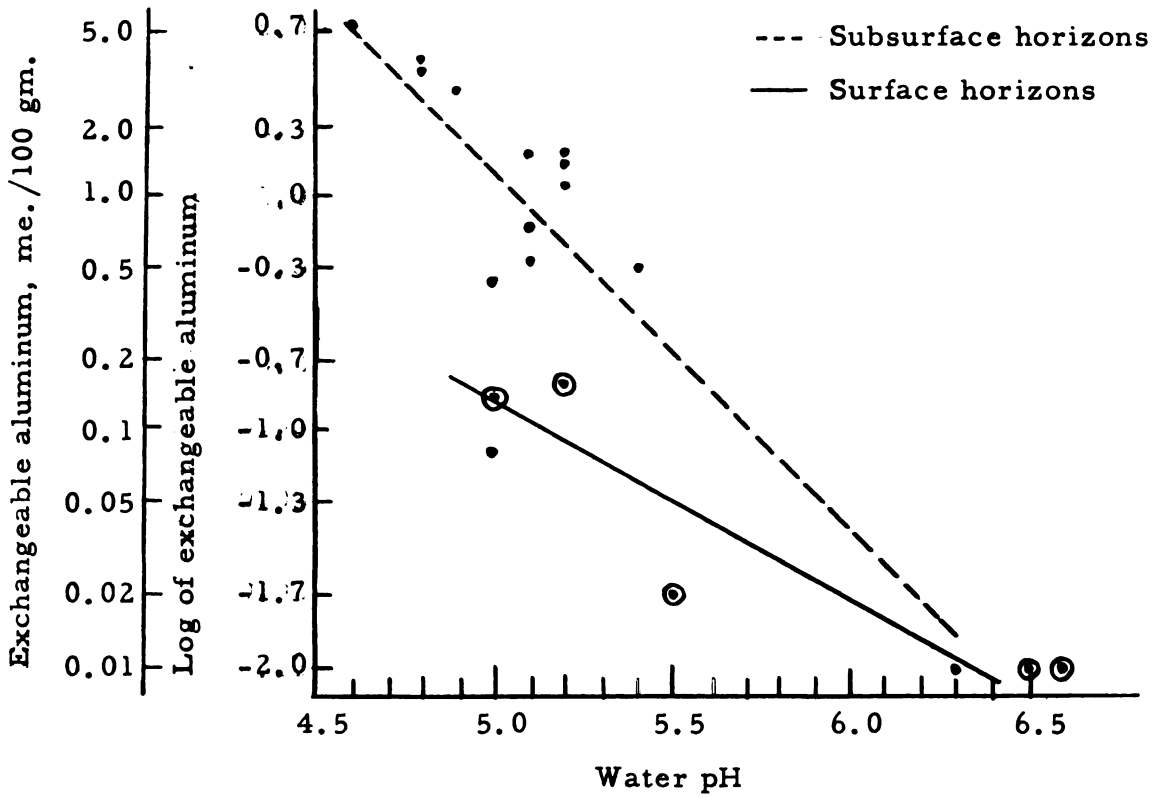

Figure 6. Linear correlation between logarithm of exchangeable aluminum and water pH for nineteen horizon samples. Circled dots refer to surface samples.

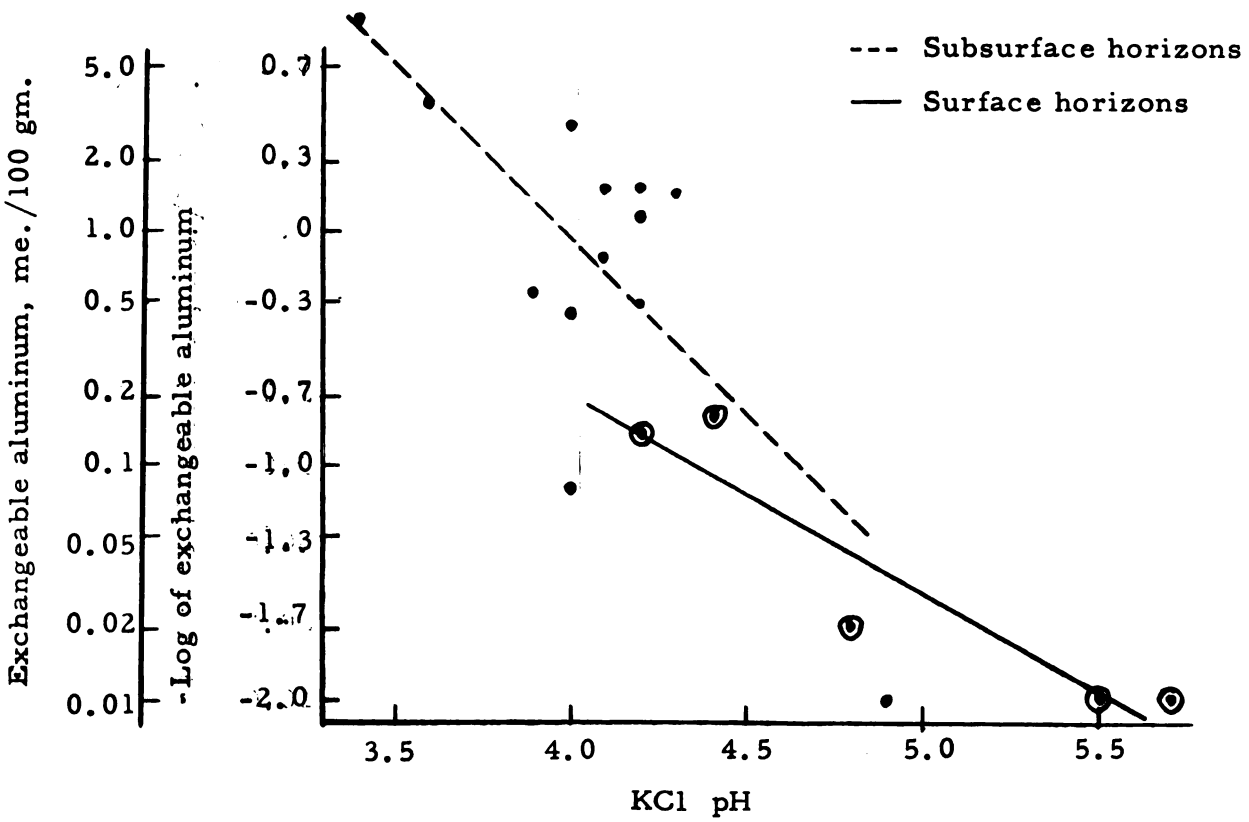

Figure 7. Linear correlation between logarithm exchangeable aluminum and KCl pH for nineteen horizon samples. Circled dots refer to surface samples.

Table 5. Correlation coefficients and regression equations for linear correlation between various measures of the acidity of raw and Mississippi mill samples

Table 5. Correlation coefficients and regression equations for linear correlation between various measures of the acidity of several Michigan soil samples.

Population	r[a]	Linear regression equation
5 surface samples--Figure 6	-0.940*	Log exchangeable Al = 2.908 - 0.760 pH
14 subsurface samples--Figure 6	-0.820**	Log exchangeable Al = 7.624 - 1.506 pH
5 surface samples--Figure 7	-0.953*	Log exchangeable Al = 2.796 - 0.867 KCl pH
14 subsurface samples--Figure 7	-0.749**	Log exchangeable Al = 5.977 - 1.501 KCl pH
19 horizon samples--Figure 8	0.814**	Lime requirement = 2.73 + 1.38 (exchangeable Al)
19 horizon samples-Figure 9	0.507*	Lime requirement = 3.48 + 0.157 (extractable Al)
19 horizon samples--Figure 10	0.807**	Lime requirement = 0.68 + 0.45 exchangeable (H+Al)
19 horizon samples--Figure 11	0.968**	Exchangeable acid = 0.95 + 1.31 exchangeable (H+Al)
19 horizon samples-Figure 12	0.782**	Lime requirement = 0.60 + 0.32 exchangeable (H+Al)
19 horizon samples--Figure 13	0.803**	Lime requirement = 1.91 + 0.116 (pH 6.8 - initial pH) x CEC
16 horizon samples--Figure 13	0.933**	Lime requirement = 0.61 + 0.22 (pH 6.8 - initial pH) x CEC
19 horizon samples	0.781**	Exchangeable (H+Al) = 3.53 + 0.225 (pH 6.8 - initial pH) x CEC
16 horizon samples (minus 5, 7, 8)	0.887**	Exchangeable (H+Al) = 1.72 + 0.360 (pH 6.8 - initial pH) x CEC
19 horizon samples	0.655**	Exchangeable acidity = 6.45 + 0.255 (pH 6.8 - initial pH) x CEC
16 horizon samples (minus 5, 7, 8)	0.840**	Exchangeable acidity = 3.40 + 0.489 (pH 6.8 - initial pH) x CEC

a- ** refers to significant linear correlation at the 1% level
* refers to significant linear correlation at the 5% level

quite different from the exchange sites on the mineral fraction of soils. The adsorption energy of aluminum evidently varies with the type of exchange site which is predominant. Table 17, in the Appendix, shows that the cation exchange capacities for the organic fraction of surface samples 1, 5, and 9 were greater than the exchange capacities for the mineral fraction.

The relationships between lime requirement determined by the Shoemaker, McLean, Pratt method (1959) and exchangeable and extractable aluminum are shown in Figures 8 and 9, respectively. Exchangeable aluminum measurements give a much better correlation with lime requirement than extractable aluminum. The surface horizons apparently represent a separate population as has been suggested previously. This is especially noticeable for the exchangeable aluminum plot in Figure 8. The correlation coefficient increases to 0.921^{**} when the subsurface horizons are considered alone. Omitting the surface horizons for the extractable aluminum correlation with lime requirement results in a lower correlation coefficient, 0.443.

Iron evidently contributed little to the acidity fraction in these soils. Table 16, in the Appendix, shows that small amounts of exchangeable (N KCl exchangeable) and extractable (N NH_4OAc, pH 4.8) iron were found. The extractable iron appeared to be related to extractable aluminum. For example, samples 3 and 4 which contained the highest amounts of extractable aluminum, also showed the highest amounts of extractable iron.

An empirical measure of the exchangeable hydrogen fraction in these soils can be obtained by subtracting the sum of exchangeable bases and exchangeable aluminum from the cation exchange capacity. These data are shown in Table 16 in the Appendix. Cation exchange capacity determinations were made by displacing sodium from a sodium-saturated soil with normal ammonium acetate adjusted to pH 7.0. The pH-dependent

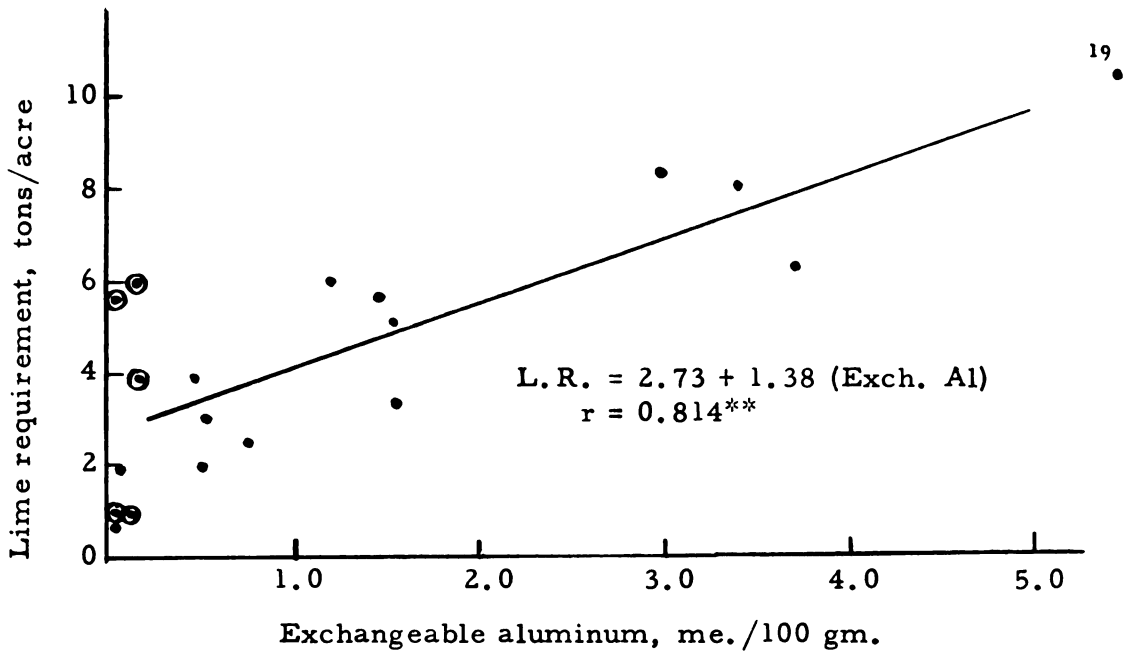

Figure 8. Linear correlation between lime requirement and exchangeable aluminum for nineteen horizon samples. Circled dots refer to surface samples.

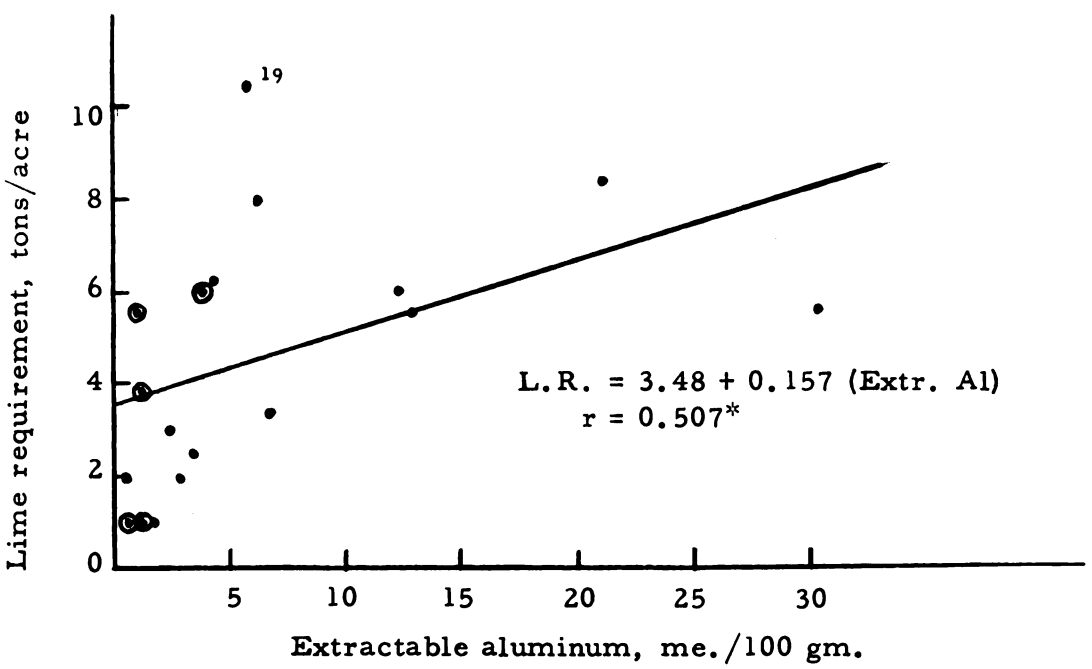

Figure 9. Linear correlation between lime requirement and extractable aluminum for nineteen horizon samples. Circled dots refer to surface samples.

acidity developed at pH 7.0 approaches that developed at pH 6.8 which is often considered by other workers as the most desirable pH in liming recommendations. Therefore, the cation exchange capacity determined at pH 7.0 should include the pH-dependent acidity that is considered important in acid soils.

When the sum of exchangeable hydrogen calculated by difference plus exchangeable aluminum (see Table 16, Appendix) is plotted versus lime requirement, a fairly good positive correlation is observed as shown in Figure 10.

Figure 11 shows the correlation between the sum of exchangeable hydrogen plus aluminum and exchangeable acidity determined by the $BaCl_2$-triethanolamine method. A very close correlation was found, although the exchangeable acidity measurements were about 1.5 times greater than the sum of exchangeable hydrogen and aluminum. This can be partially explained by the higher amount of exchangeable acidity developed by the higher pH of the exchangeable acidity method (pH 8.1) versus the pH at which the cation exchange capacity (pH 7.0) was determined.

It is interesting to note that the plot of lime requirement against exchangeable acidity in Figure 12 results in a diagram very similar to that in Figure 10. This should be expected since exchangeable acidity and the sum of exchangeable hydrogen and aluminum are closely correlated. Sample 19 deviates considerably from the calculated regression curve in both figures. This sample contained the highest amount of exchangeable aluminum (5.45 me./100 gm.) and the lowest pH (4.6) of the samples studied. The buffer (Shoemaker, McLean, Pratt, 1959) used to determine lime requirement reacts readily with exchangeable aluminum as Figure 8 would suggest by the linear relationship for subsurface soils which contain appreciable amounts of exchangeable aluminum. A lime requirement of 10.4 tons per acre was found for

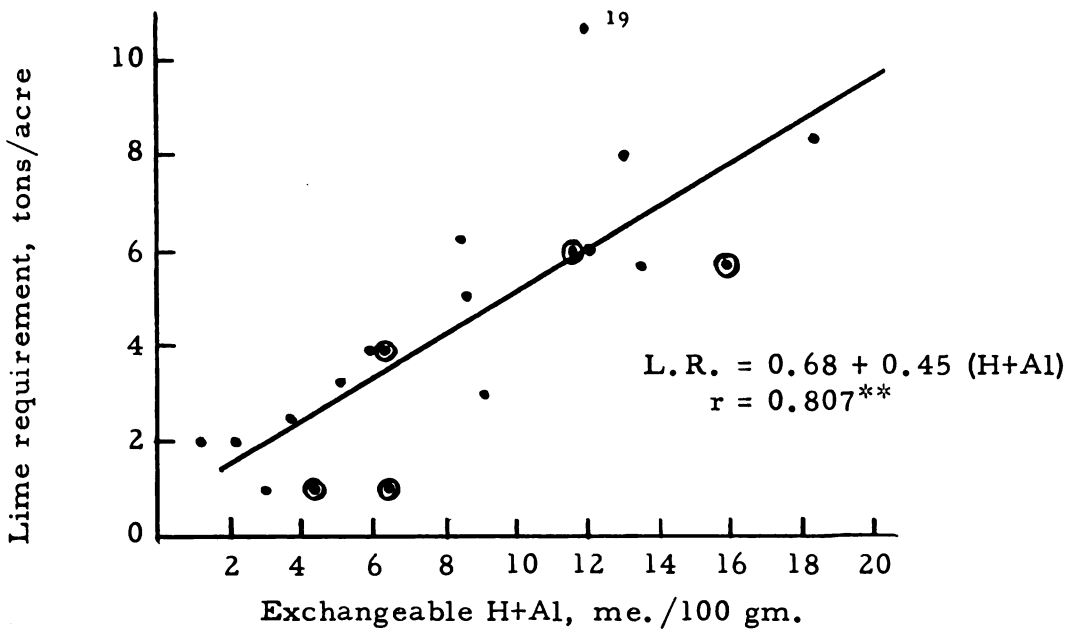

Figure 10. Linear correlation between lime requirement and the sum of exchangeable hydrogen and aluminum. Circled dots refer to surface samples.

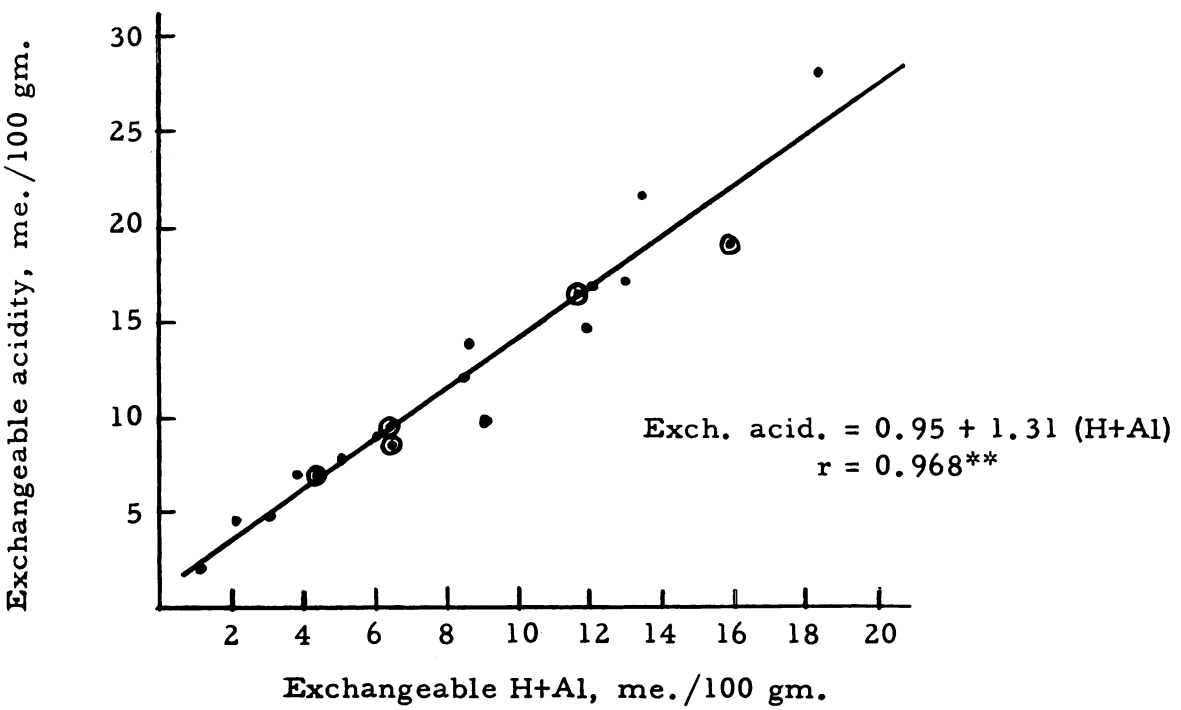

Figure 11. Linear correlation between exchangeable acidity and the sum of exchangeable hydrogen and aluminum. Circled dots refer to surface samples.

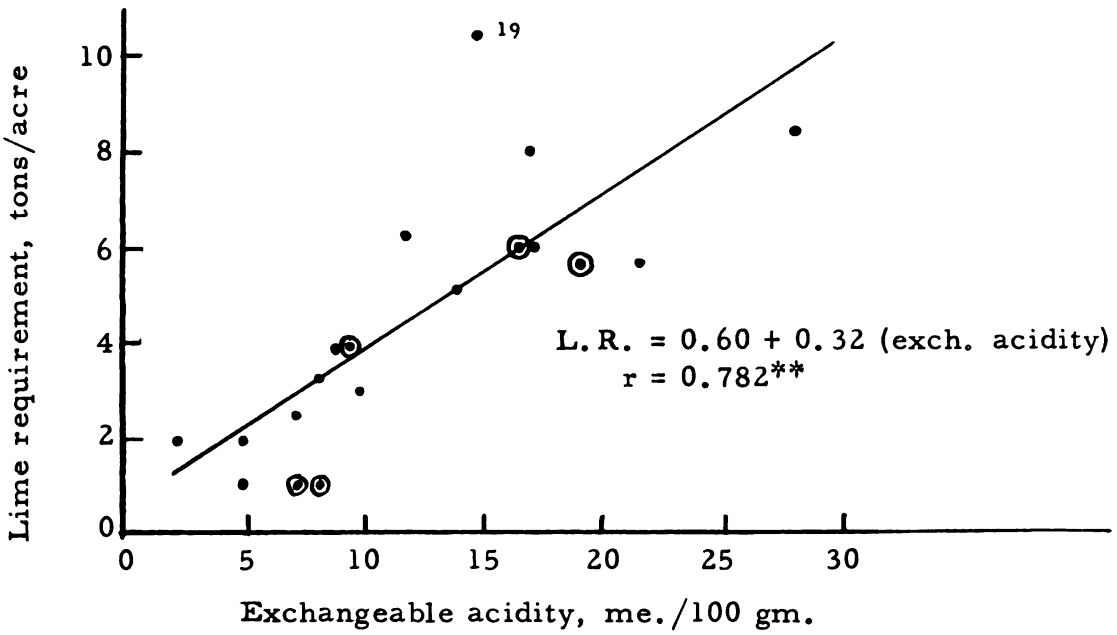

Figure 12. Linear correlation between lime requirement and exchangeable acidity. Circled dots refer to surface samples.

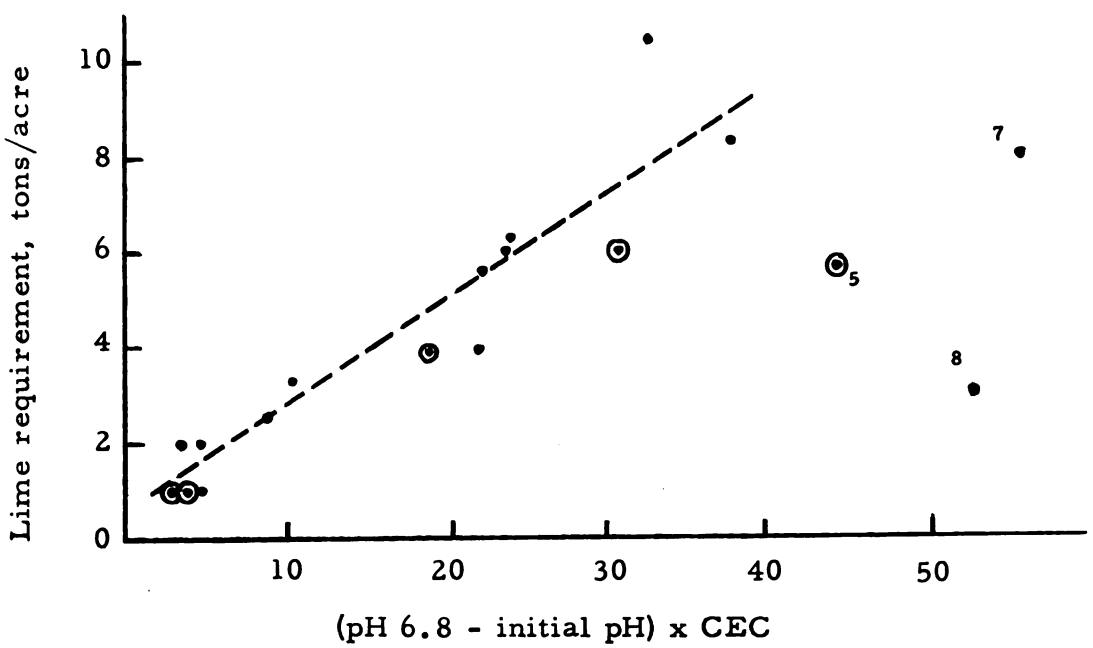

Figure 13. Linear correlation between lime requirement and (pH 6.8 - initial pH) x CEC. Circled dots refer to surface samples. The dotted line represents the linear regression plot for data omitting samples 5, 7, and 8.

sample 19 by this method. Methods for determination of total exchangeable acidity in Figures 10 and 12 indicate that the lime requirement for sample 19 is much higher than would be predicted. This will be discussed further in the liming studies section.

Another empirical method for determining a measure of the total acidity involves the use of the product of (pH 6.8-initial pH) x CEC. Figure 13 shows this relationship plotted against lime requirement. A good correlation is observed with a correlation coefficient of 0.803**. It is apparent that samples 5, 7, and 8 result in high values for the empirical relationship (pH 6.8-initial pH) x CEC. These samples represent the A_1, and B horizons of the Ontonagon series. Sample 5 contained over 40% clay and 14% organic matter while, samples 7 and 8 contained over 70% clay. The resulting cation exchange capacities (Table 17, Appendix) were very high, exceeding 28 me./100 gm. None of the other horizon samples studied had cation exchange capacities more than 20 me./100 gm. The percent base saturation (Table 16, Appendix) was also found to exceed 50% for all three horizons, although, the pH was 5.5 for sample 5 and less than 5.2 for samples 7 and 8.

If samples 5, 7, and 8 are omitted, the correlation increases to 0.933**. The dotted line in Figure 13 is the linear regression line resulting when samples 5, 7, and 8 are omitted.

When the sum of exchangeable hydrogen and aluminum is plotted against (pH 6.8-initial pH) x CEC, a diagram similar to Figure 13 results. This plot is not reproduced but Table 5 shows the linear correlation statistics. The linear correlation data for exchangeable acidity versus (pH 6.8-initial pH) x CEC are also included in Table 5. When samples 5, 7, and 8 are omitted, (pH 6.8-initial pH) x CEC gives increased correlation with other measures of acidity.

Exchangeable hydrogen can be estimated by the difference between cation exchange capacity and the summation of exchangeable bases plus

exchangeable aluminum as was pointed out previously. The sum of exchangeable hydrogen and exchangeable aluminum can be used as a measure of total acidity. Table 6 shows these data and the percent of acidity due to exchangeable hydrogen. The percent of the acidity due to exchangeable hydrogen was highest for the A_1 horizons of each soil series (numbers 1, 5, 9, 13, and 16). These samples also contained the highest percent organic matter. When the percent of acidity due to exchangeable hydrogen is plotted against pH as shown in Figure 14, two factors are seen to affect the relationship. The surface horizons (circled dots) all contained a majority of the acidity due to exchangeable hydrogen, therefore the presence of organic exchange sites would appear to be important. This may be related to the difference in adsorption energies of hydrogen and aluminum on the organic exchange sites as discussed earlier. The second factor involved is pH. At a pH above about 6.0; the acidity present would be in the form of exchangeable hydrogen. Very small amounts of exchangeable aluminum were found for any of the samples with pH above 6.0, including one subsurface sample (number 17). As pH decreased the contribution of exchangeable aluminum to the total acidity increased (Figure 14). This increase was quite marked for the subsurface samples.

As soil pH increases, percent base saturation increases. For the nineteen soil samples studied here, this relationship was observed (Table 16, Appendix), but a wide scattering of the points resulted in rather poor correlation. The correlation coefficients for percent base saturation were 0.533^{*} versus pH in water and 0.498^{*} versus pH in KCl solution. Wide variation in the physical and chemical properties of these soils is suggested as the cause for the poor correlation observed.

When the exchangeable aluminum in the KCl leachate was determined by titration with NaOH the results were consistently greater than when aluminum was determined colorimetrically. Coleman et al. (1959)

Table 6. Exchangeable hydrogen and percent of total acidity due to exchangeable hydrogen for nineteen horizon samples.

Sample number	Depth of sample (inches)	Exchangeable hydrogen (me./100 gm.)	Exchangeable hydrogen plus aluminum (me./100 gm.)	Percent of acidity due to exchangeable hydrogen
1	0-4	6.3	6.4	98.2
2	4-7	1.1	1.2	91.7
3	10-12	15.5	18.4	84.2
4	12-16	12.0	13.4	89.6
5	0-2	15.9	15.9	100.0
6	2-3	5.9	6.3	93.7
7	5-12	9.7	13.1	74.0
8	12-18	8.6	9.2	93.5
9	0-5	11.4	11.6	98.3
10	7-12	10.9	12.1	90.1
11	13-19	7.1	8.6	82.6
12	19-25	3.5	5.1	68.6
13	0-6	4.4	4.4	100.0
14	7-11	2.9	3.7	78.4
15	12-20	1.7	2.2	77.3
16	0-4	6.5	6.5	100.0
17	6-8	2.9	2.9	100.0
18	13-17	4.8	8.5	56.5
19	18-22	6.4	11.9	53.8

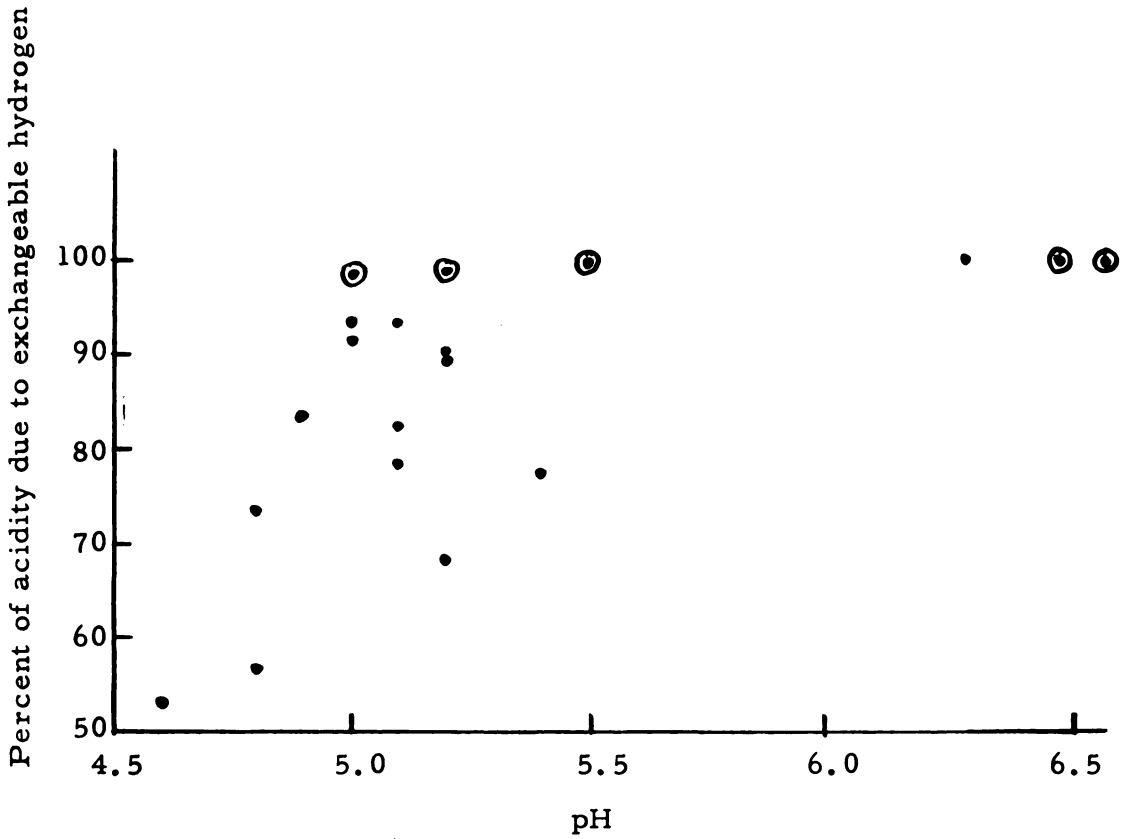

Figure 14. Graph of pH versus percent of acidity due to exchangeable hydrogen. Exchangeable hydrogen was determined by the difference between the sum of exchangeable aluminum plus exchangeable bases and the cation exchange capacity. Circled dots refer to surface horizons.

suggested titrating the KCl leachate to pH 4.0 for a measure of exchangeable hydrogen. This method resulted in very small amounts of exchangeable hydrogen measureable by titration in the KCl leachates of the soils studied here. This is shown in Table 7. The acid surface horizons with higher amounts of organic matter should contain measureable quantities of exchangeable hydrogen in the KCl leachate. Since the exchangeable aluminum levels in the surface horizons were very low, it is suggested that the difference between the aluminum determined colorimetrically and the milliequivalents of base consumed in titration of the KCl leachate is a measure of the exchangeable hydrogen replaced by KCl. This measure of exchangeable hydrogen cannot be compared with the exchangeable hydrogen data in Table 6 because the amount of pH-dependent acidity developed at the pH of the KCl leachate was considerably lower than at pH 7.0, at which the cation exchange capacity was determined. It should also be pointed out that the pH of the KCl leachate varied from 3.8 to 5.5. The amount of acidity present would vary considerably with this variation in pH. The pH of the KCl leachate apparently reached a minimum when appreciable levels of exchangeable aluminum were present. For samples 7, 18, and 19, which contained more than 3 milliequivalents of exchangeable aluminum per 100 grams, the pH was 3.8, while the pH of all other horizons was higher.

Leaching the soil sample with a N KCl solution should remove the exchangeable aluminum and hydrogen. If the sample is then extracted by the $BaCl_2$-triethanolamine method, the acidity developed is a measure of the pH dependent acidity, according to Coleman et al. (1959). Table 8 compares the initial exchangeable acidity measured by the $BaCl_2$-triethanolamine method with the pH dependent acidity developed after leaching with KCl for several samples. The acidity titrated in the KCl leachate is also shown. The total acidity in the KCl treated sample was equal to or greater than that determined in an untreated sample. If part of the acidity was removed by leaching with KCl solution, the $BaCl_2$-triethanolamine

Table 7. Exchangeable aluminum and hydrogen in nineteen Michigan horizon samples.

Sample number	Aluminum measured in KCl leachate: Colorimetrically (me./100 gm.)	Aluminum measured in KCl leachate: Titration (me./100 gm.)	pH of KCl leachate	Hydrogen in KCl leachate by titration (me./100 gm.)	Hydrogen by difference (me./100 gm.)
1	0.14	0.43	3.9	0.04	0.33
2	0.08	0.31	4.2	0	0.23
3	2.94	3.31	4.2	0	0.37
4	1.44	1.77	4.4	0	0.33
5	0.02	0.30	4.8	0	0.28
6	0.44	0.74	4.2	0	0.30
7	3.40	3.81	3.8	0.10	0.51
8	0.55	0.82	4.1	0	0.27
9	0.16	0.47	4.5	0	0.31
10	1.20	1.58	4.3	0	0.38
11	1.54	1.89	4.3	0	0.35
12	1.55	1.83	4.2	0	0.28
13	0.01	0.11	5.5	0	0.10
14	0.75	1.03	4.3	0	0.28
15	0.50	0.74	4.4	0	0.24
16	0.01	0.12	5.5	0	0.11
17	0.01	0.10	4.8	0	0.09
18	3.71	4.15	3.8	0.08	0.52
19	5.45	5.88	3.8	0.10	0.53

Table 8. Total exchangeable acidity and pH dependent acidity of several horizon samples.

Sample number	Initial exchangeable acidity (me./100 gm)	Acidity in KCl treated sample		
		pH dependent acidity (me./100 gm.)	Acidity titrated in KCl leachate (me./100 gm.)	Total (me./100 gm.)
1	9.3	8.8	0.47	9.27
2	2.1	1.9	0.31	2.21
3	28.0	24.7	3.31	28.01
4	21.5	21.2	1.77	22.99
5	19.0	20.3	0.30	20.60
6	9.2	10.9	0.74	11.64
7	17.0	14.6	3.91	18.51
8	9.7	10.9	0.82	11.72
16	8.1	10.1	0.12	10.22
17	4.9	5.7	0.10	5.70
18	11.8	9.6	4.23	13.75
19	14.9	9.5	5.98	15.38

solution may buffer the suspension to a higher pH than in the unleached soil-buffer suspension. This could result in the development of a greater amount of pH-dependent acidity.

Samples 3, 4, 7, 8, 18, and 19 were shaken in N KCl with increasing increments of NaOH added to different flasks. The pH was determined after 48 hours and titration curves plotted. Coleman et al. (1959) suggested that titration to pH 6.0 would give a measure of aluminum if the soil sample is essentially aluminum-saturated. Figure 15 shows the titration curve for sample 7 as an example. The point at which pH 6.0 was reached was found to be 4.25 ml. of 0.1475 N NaOH. This corresponds to 12.4 milliequivalents of base for 100 grams of soil. Acidity

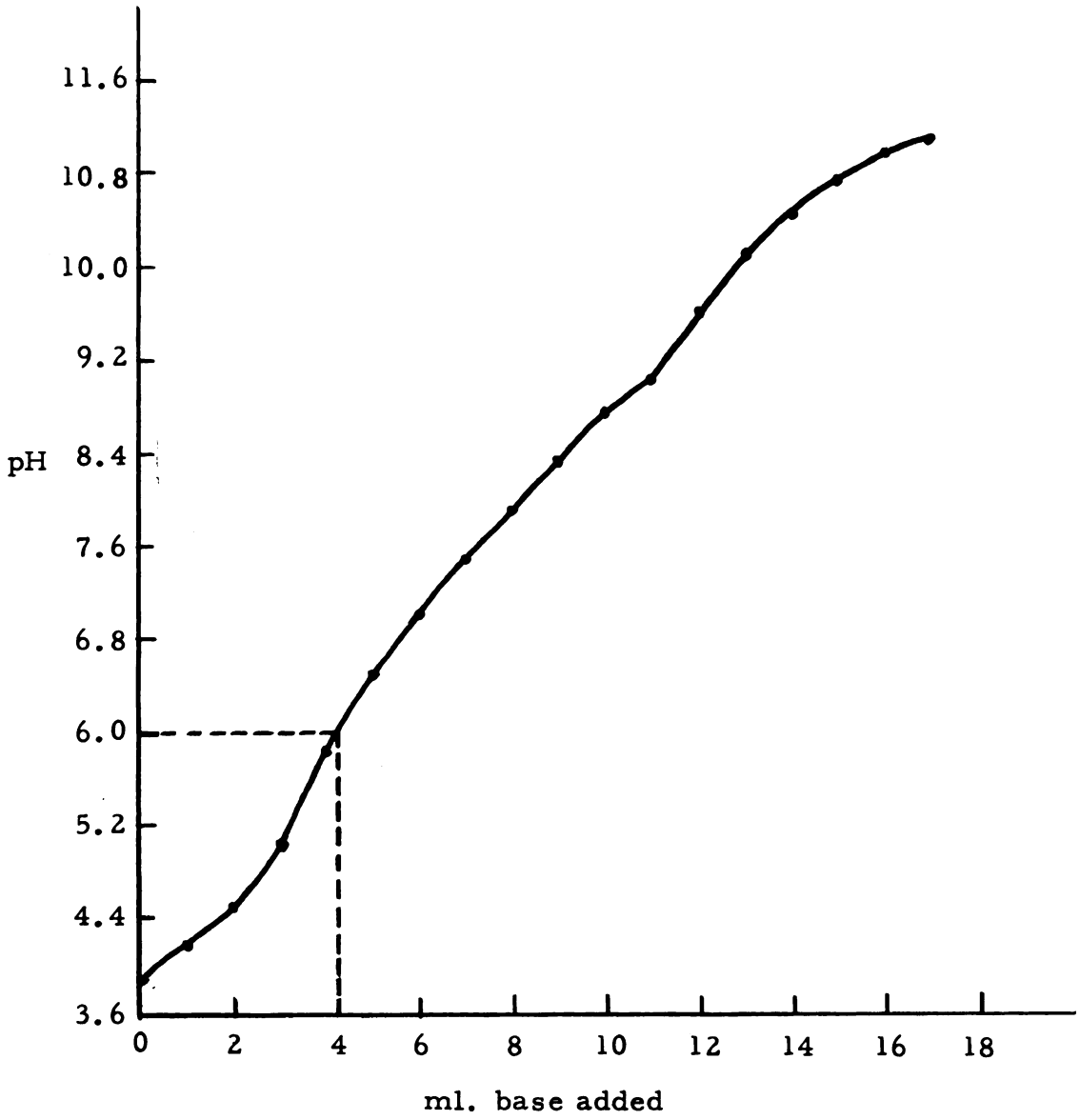

Figure 15. Titration curve for sample 7 in a 1:10 soil:N KCl suspension ratio.

titrated to pH 6.0 in N KCl is shown in Table 9 for samples 3, 4, 7, 8, 18, and 19.

The acidity measured by this method exceeds the exchangeable aluminum (Table 7) measured for all samples. Titrating to pH 6.0 probably results in neutralization of some hydroxy aluminum-polymers which are not exchangeable by N KCl in the extraction for exchangeable aluminum. Also, some pH-dependent acidity should develop below pH 6.0. However, the acidity measured by titrating to pH 6.0 in KCl suspension results in lower values than when determined by the $BaCl_2$-triethanolamine method for total exchangeable acidity (Table 8) which is buffered at pH 8.1. This may be explained by development of greater amounts of pH-dependent acidity at the higher pH, as well as further hydrolysis of hydroxy-aluminum polymers.

However, the neutralization of the hydroxy-aluminum polymers may not be complete. Schwertmann and Jackson (1963) suggest that neutralization of the hydroxy-aluminum polymers in soils occurs over the pH range 5.5 to 6.5. Samples 3 and 4 were suggested to contain high amounts of hydroxy-aluminum polymers because of very high levels of extractable aluminum, as discussed previously. Table 9 shows that the ratio of acidity titrated in a KCl suspension to the total exchangeable acidity is lower for samples 3 and 4 than for the other samples titrated. This would lend support to the argument that the hydroxy-aluminum polymers are not completely neutralized at pH 6.0. However, these data must again be considered with care. Table 9 also shows the pH determined in a N KCl suspension with a 1:2.5 soil:solution ratio. This pH was lower for all samples than for the blank titration sample with a 1:10 ratio. Part of the increase in pH for the titration procedure can be accounted for by the dilution effect of the higher soil:solution ratio. The pH increase was greatest for samples 7, 18, and 19 which also showed the highest ratio of acidity titrated to exchangeable acidity (Table 9). Because of the lower

Table 9. Acidity measured by titrating soil samples in N KCl as compared with other measures of acidity.

Sample number	pH with no base added (1:10 ratio)	KCl pH (1:2.5 ratio)	Acidity titrated (me./100 gm.)	Exchangeable acidity (me./100 gm.)	Ratio of titrated acidity(to pH 6.0): exchangeable acidity	Extractable aluminum (me./100 gm.)
3	4.1	4.0	12.0	28.0	0.43	21.1
4	4.4	4.3	11.2	21.5	0.52	30.4
7	3.85	3.6	12.4	17.0	0.73	6.2
8	4.1	3.9	5.9	9.7	0.61	2.3
18	3.9	3.6	10.0	11.8	0.85	4.2
19	3.85	3.4	13.6	14.9	0.93	5.8

pH of the KCl suspensions for these samples, some aluminum may be released from the structure of the clay minerals. This aluminum could then account for part of the increase in pH mentioned above, and could also be titrated, which may explain at least part of the increase in the ratio of titrated acidity to exchangeable acidity for samples 7, 18, and 19 in Table 9.

Effects of liming

The effect of adding precipitated calcium carbonate to the acid soil samples resulted in a very rapid increase in pH. Table 18, in the Appendix, shows that after two weeks of incubation the pH increased markedly. Subsequent sampling dates resulted in small increases or decreases.

All of the subsurface samples, except number 6, attained pH 6.8 or greater by the end of the 16 week incubation period. Sample 6 was slightly below with a pH of 6.65. However, none of the surface samples attained pH 6.8 upon liming and incubation. Samples 13 and 16 even decreased in pH. A decrease in pH upon liming with very small rates and subsequent incubation was observed by Ross (1962). The lime rate used for samples 13 and 16 was only one ton on an acre basis. Since samples 13 and 16 are high in percent organic matter, it was thought that decomposition of organic matter with release of organic acids and nitrates may have caused the decrease in pH. Table 10 shows the effect of liming and subsequent incubation on the percent organic matter and water soluble nitrates. The concentration of nitrates increased 25 fold for both samples. Percent organic matter decreased 0.5% for sample 13, and 0.2% for sample 16.

Additions of lime resulted in a rapid decrease in exchangeable aluminum simultaneously with pH increase. Table 19, in the Appendix, shows that exchangeable aluminum decreased to less than 0.1

Table 10. Effect of liming and incubation on percent organic matter and water soluble nitrates for samples 13 and 16.

Sample number	pH	Organic matter (percent)	Nitrates (ppm)
13-initial	6.5	4.30	13.5
13-limed	6.25	3.78	338.
16-initial	6.6	5.98	26.5
16-limed	6.3	5.78	650.

me./100 gm. for all samples after incubation for 2 weeks. The check samples which were incubated show some fluctuation, but no relationship to pH change was observed. Extractable aluminum also decreased upon liming, although a measurable quantity remained after 16 weeks incubation (Table 20, Appendix). The percent of extractable aluminum remaining after liming and incubation varied from 17.9 to 85% with most samples still containing 30-50% of the original amount in an extractable form. There was no relationship apparent between the percentage of extractable aluminum remaining after liming and other properties.

Table 21, in the Appendix, shows the effect of liming on the exchangeable acidity. Considerable variation in the reduction in exchangeable acidity was observed. For those samples which originally contained high amounts of exchangeable aluminum (numbers 7, 18, and 19, for example) the decrease in exchangeable acidity was greatest. Samples 13 and 16 showed the least decrease in exchangeable acidity. The increase in water-soluble nitrates found in these samples after liming and incubation could have caused this.

Effects of adding acid and incubation

The effect of adding a symmetry (equivalent to the cation exchange capacity) amount of sulfuric acid to the nineteen samples resulted in a marked decrease in pH (Table 22, Appendix) as would be expected. The pH decreased between the 2 and 4-week sampling dates indicating the samples had not reached equilibrium. No pH readings were taken for the 6 and 8-week sampling dates, but the pH after 16 weeks of incubation increased to values exceeding the readings after 2 weeks.

Table 11 shows that the drop in pH was greatest for the surface samples. The high cation exchange capacities of the surface samples (because of high quantities of organic matter) required greater amounts of acid for a one-symmetry addition. This would partially explain the greater decrease in pH for surface horizons. However, the organic matter may have adsorbed the hydrogen ions which would tend to prevent them from attacking the lattice of the clay minerals present, and cause the pH to remain low. If aluminum were released from the clay mineral by the action of hydrogen ions, the aluminum ions would become adsorbed on the exchange sites of the mineral fraction. The resulting aluminum-saturated soil would have a higher pH than a hydrogen-saturated soil.

Data from the Munising, Ontonagon, and Iron River profiles support the above explanation. The pH values of the surface samples were lower than for subsurface samples after adding acid. Percent aluminum saturation was calculated using the cation exchange capacity values. Exchangeable aluminum exceeded the cation exchange capacity for a few samples. These were rounded off at 100% aluminum saturation as shown in Table 11. Percent aluminum saturation was lowest for the surface samples and highest for the subsurface samples.

The increase in exchangeable aluminum, compared to the initial value, was found to be related to the milliequivalents of acid added (Figure 16). A correlation coefficient of 0.714^{**} was found for this relationship.

Table 11. Effects of acidification of nineteen horizon samples.

Sample number	Acid added (me./100 gm.)	pH after 16 weeks	Decrease in pH units	Exchangeable aluminum		Aluminum saturation (percent)
				16 weeks (me./100 gm.)	Increase (me./100 gm.)	
1	10.5	2.7	2.3	4.88	4.74	46.5
2	1.8	3.1	1.9	1.95	1.87	100.
3	19.9	3.5	1.4	18.88	15.84	94.9
4	13.8	3.8	1.4	10.66	9.22	77.2
5	33.9	3.2	2.3	7.10	7.08	20.9
6	12.4	3.1	1.9	7.99	7.55	64.4
7	28.0	3.5	1.3	19.54	16.14	69.8
8	31.1	3.6	1.5	15.10	14.55	48.5
9	19.3	3.3	1.9	7.99	7.83	41.4
10	14.8	3.6	1.6	11.66	10.46	78.8
11	9.6	3.8	1.3	8.88	7.34	92.5
12	6.3	3.7	1.5	7.77	6.22	100.
13	12.3	3.9	2.6	2.89	2.88	23.5
14	5.0	3.8	1.3	4.22	3.47	84.4
15	3.3	3.8	1.6	3.33	2.83	100.
16	17.4	4.5	2.1	11.32	11.31	65.1
17	6.9	4.4	1.9	1.78	1.77	25.8
18	12.0	3.5	1.3	13.10	9.39	100.
19	14.8	3.4	1.2	15.98	10.53	100.

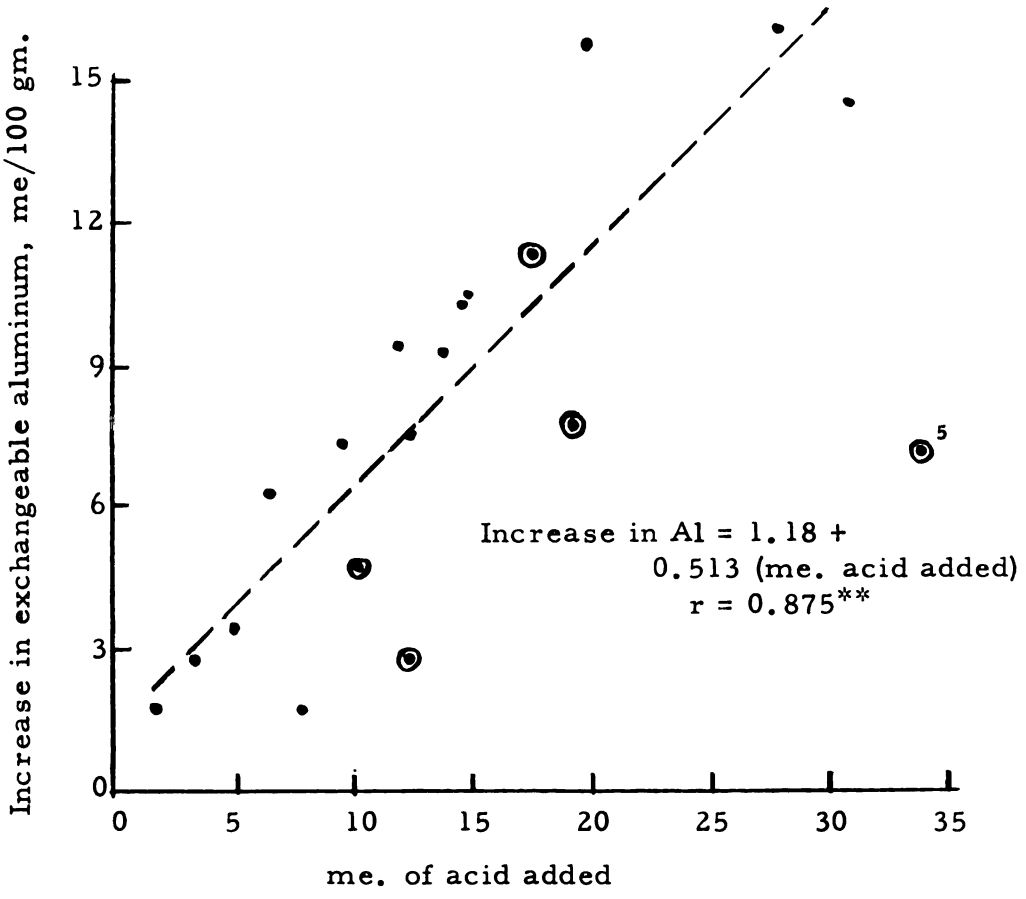

Figure 16. Linear correlation between me. of acid added and increase in exchangeable aluminum. Circled dots refer to surface horizons. The dotted line represents the linear regression equation when sample 5 is omitted. The regression equation and the correlation coefficient also represent the population when sample 5 is omitted.

Sample 5 received the greatest quantity of acid, but showed an increase of only a medium amount of exchangeable aluminum. This sample contained over 14% organic matter. Table 17, in the Appendix, shows that the exchange capacity of the organic fraction was over 20 me./100 gm. This would also suggest that the organic matter absorbed the hydrogen ions, which reduced the effectiveness of the added acid on decomposition of the clay lattice.

If sample 5 is omitted, the correlation coefficient for the linear correlation between amount of acid added and increase in exchangeable aluminum is found to increase to 0.875**.

Soil clay mineral identification

An estimation of the relative amounts of the clay minerals present in each horizon sample was made from observation of the X-ray diffraction tracings. The results are given in Table 12. A range in percent abundance of each mineral is given since a rigorous quantitative determination of the minerals present would involve other methods of study. Since a range is given, it is possible for the apparent sum of percentages for any one sample to exceed 100%.

X-ray diffraction tracings for these soils have been recorded recently by other workers (Cummings, 1959; Ross, 1962). Therefore, they will not be recorded in this thesis, although an example is shown in Figure 17 for sample 11, from the B horizon of the Iron River profile. The upper three tracings are those for the clay fraction which was treated for removal of free iron oxide. A-1 shows the tracing for the Mg-saturated, glycerol-solvated clay. Upon K-saturation and heating to 110° C., a very broad series of peaks was observed between 10 and 14 A°. Heating to 550° C. caused further collapse toward 10 A°, but a tailing off to nearly 14 A° was present. This indicated the presence of considerable quantities of interlayer aluminum in the expansible clay minerals.

Table 12. Estimation[a] of various clay minerals in the clay fraction of nineteen horizon samples.

Sample number	Type of clay mineral[b]						
	K	I	V	M	C	V-C	Al-intergrade
1	xxxx	xx	x	xxxx	x	0	x
2	xxxx	xx	x	xxxx	x	0	0
3	xxx	xx	xx	xx	xx	0	xxx
4	xxx	xx	xx	xx	xx	0	xxxx
5	xxxx	xxxx	xx	xx	xx	0	x
6	xxxx	xxxx	xx	x	xx	0	x
7	xx	xxxx	xxx	xx	xx	0	x
8	xxx	xxx	xxx	xx	x	0	xx
9	xxxx	xx	xxxx	xx	xx	0	xx
10	xxx	xx	xxx	x	xxx	0	xxx
11	xxx	x	xxxx	0	xxx	0	xxx
12	xxx	xx	xxxx	0	xxx	0	xxx
13	xxx	x	xxx	0	xx	xx	xx
14	xxx	xx	xxx	0	xx	xx	xx
15	xxx	xx	xxx	0	xx	xx	xxx
16	xxxx	x	xxx	xx	xx	0	xxx

16	xxxx	x	xxx	xx	xx	0	xxx
17	xxxx	x	xxxx	x	xx	0	xxx
18	xxxx	xx	xxx	xx	x	0	xx
19	xxxx	xx	xxx	xx	xx	0	x

[a]Quantitative estimation was made from X-ray tracings.

Legend:
- x 0-9 percent
- xx 10-19 percent
- xxx 20-29 percent
- xxxx 30-40 percent

K=kaolinite
I =illite
V=vermiculite
M=montmorillonite
C=chlorite
V-C=randomly interstratified vermiculite and chlorite
AI=intergrade=aluminum intergrade

Figure 17. X-ray diffraction tracings of oriented soil clay films on porous ceramic plates. Treatments: 1, Mg-saturated, glycerol-solvated; 2, K-saturated and heated to 110° C.; 3, K-saturated and heated to 550° C.; A, free iron removed; B, free iron and aluminum interlayers removed. The clay was fractionated from sample number 11.

Removal of the interlayer by the method of Dixon and Jackson (1959) resulted in the X-ray diffraction tracings seen for treatment B in Figure 17. The Mg-saturated, glycerol-solvated clay showed a less intense peak at 14 A^{o} than found in treatment A-1. Most of the decrease in peak intensity can be accounted for in the shoulder toward the high side of 14 A^{o} in treatment B-1. This shoulder tails off to 18 A^{o} indicating the presence of montmorillonite, perhaps randomly interstratified with a 14 A^{o} clay mineral. Treatment B-2 shows the effect of K-saturation and heating to 110° C. Incomplete collapse to 10 A^{o} was noted, but most of the interlayer aluminum was evidently removed when treatments A-2 and B-2 are compared. Heating to 550° C. verifies removal of the interlayer material as only strong 10 A^{o} and medium 14 A^{o} peaks are present.

Removal of the interlayer material did not appear to affect the chlorite fraction as the peak intensity was apparently similar in treatments A-3 and B-3 of Figure 17. However, the 7 A^{o} peaks in treatments B-1 and B-2 are decreased in intensity compared to treatments A-1 and A-2. The 4.7 and 3.55 A^{o} peaks are also decreased in intensity for treatments B-1 and B-2. These are the third and fourth order peaks, respectively, for the 14.2 A^{o} chlorite. This suggests that the decreased intensity of the 7 A^{o} peaks after removal of the interlayer is caused by the decreased intensity of the higher order peaks of chlorite.

Clays from samples 3, 7, 15, and 19 were also treated for removal of interlayer aluminum. Sample 3 appeared to contain a small amount of randomly interstratified vermiculite and chlorite which was masked by the broad shoulders on the 10 and 14 A^{o} peaks of the untreated clay. Sample 7 showed the presence of a small quantity of regularly interstratified vermiculite and chlorite. This was not evident in the untreated clay. Treatment of samples 15 and 19 led to similar interpretations to those shown in Table 12. The results of removal of the interlayer

material are not included in Table 12 since the other clay fractions were not subjected to this treatment.

When soils containing appreciable quantities of exchangeable aluminum are limed, the aluminum is changed to a nonexchangeable form as was shown by the liming studies. The exchangeable aluminum adsorbed on the exchange sites of an acid soil (Jackson, 1963a, Eeckman and Laudelout, 1961) may be precipitated as $Al(OH)_3$ in the interlayer space upon neutralization with lime. Therefore, several samples which contained more than 1.4 milliequivalents of exchangeable aluminum in 100 grams of soil were examined after liming. These were sample numbers 3, 4, 7, 11, 18, and 19. No difference in the degree of interlayering was observed. Apparently, the quantity of exchangeable aluminum present in these samples was too low to result in any observable difference in the degree of interlayering shown by X-ray diffraction tracings.

Development of artificial interlayers in pure clay minerals

Most efforts to incorporate artificial interlayers in 2:1 expansible clay minerals have involved the use of closed systems from which excess salts are not removed. It was thought that use of the dialysis method would yield further information into the interlayering of clay minerals. The results of the dialysis experiment are shown in Figures 18 through 25. The effects of potassium-saturation and increasing heat treatments are given. The figures correspond to treatments 1 through 8 shown in Table 1 in the Materials and Methods section.

Similar X-ray patterns were found for samples which had been dialyzed 20, 40, or 60 days. Increasing the length of dialysis time apparently had no effect on the heat stability of the interlayer developed nor on the heat stability of the hydroxide form of magnesium and/or aluminum found present in each system.

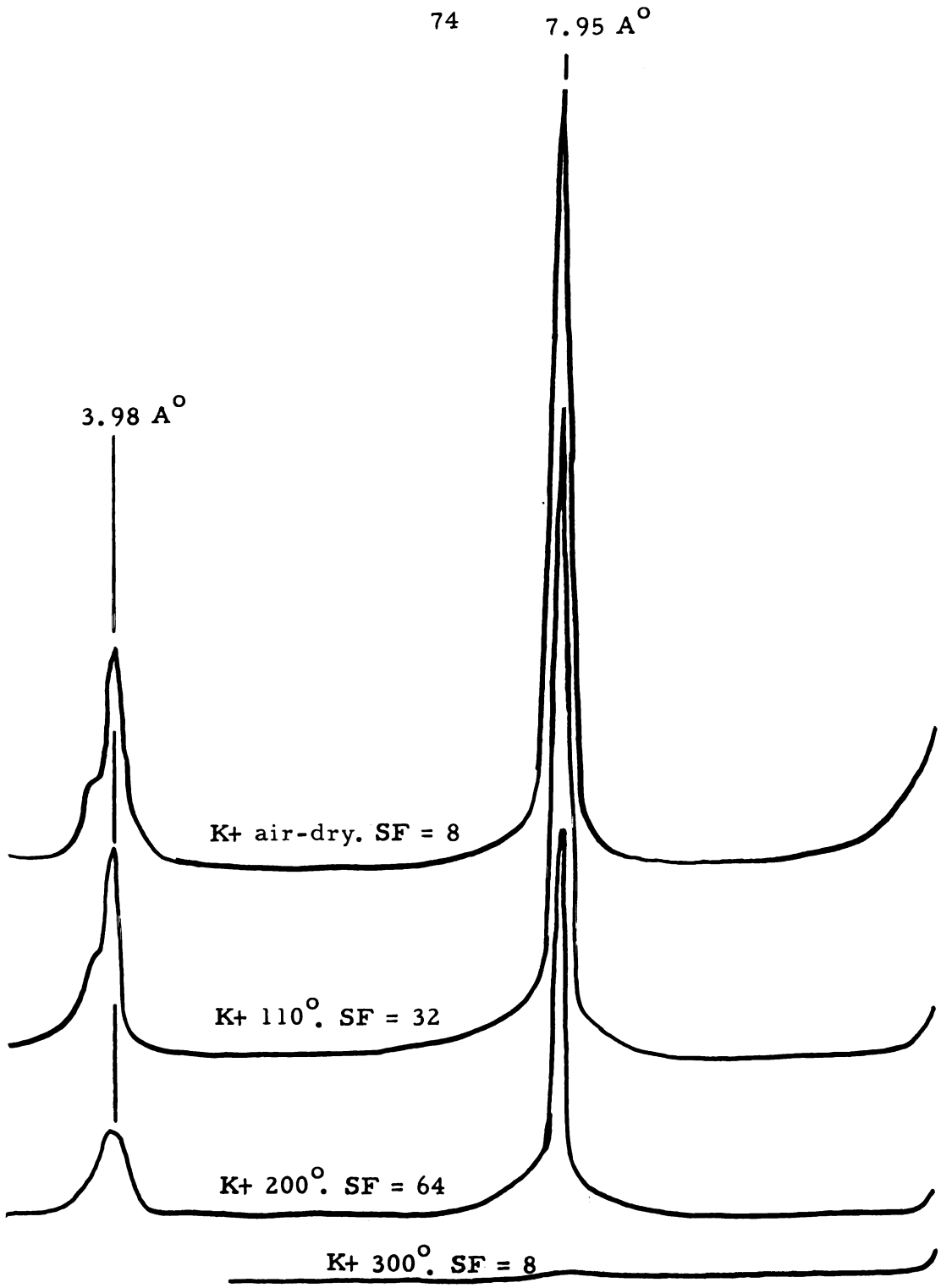

Figure 18. Effect of K-saturation and heat treatments on smoothed X-ray diffraction patterns for dialysis sample 1 (Mg/Mg + Al ratio of 0.8 and no clay present). Scale factors were used as indicated.

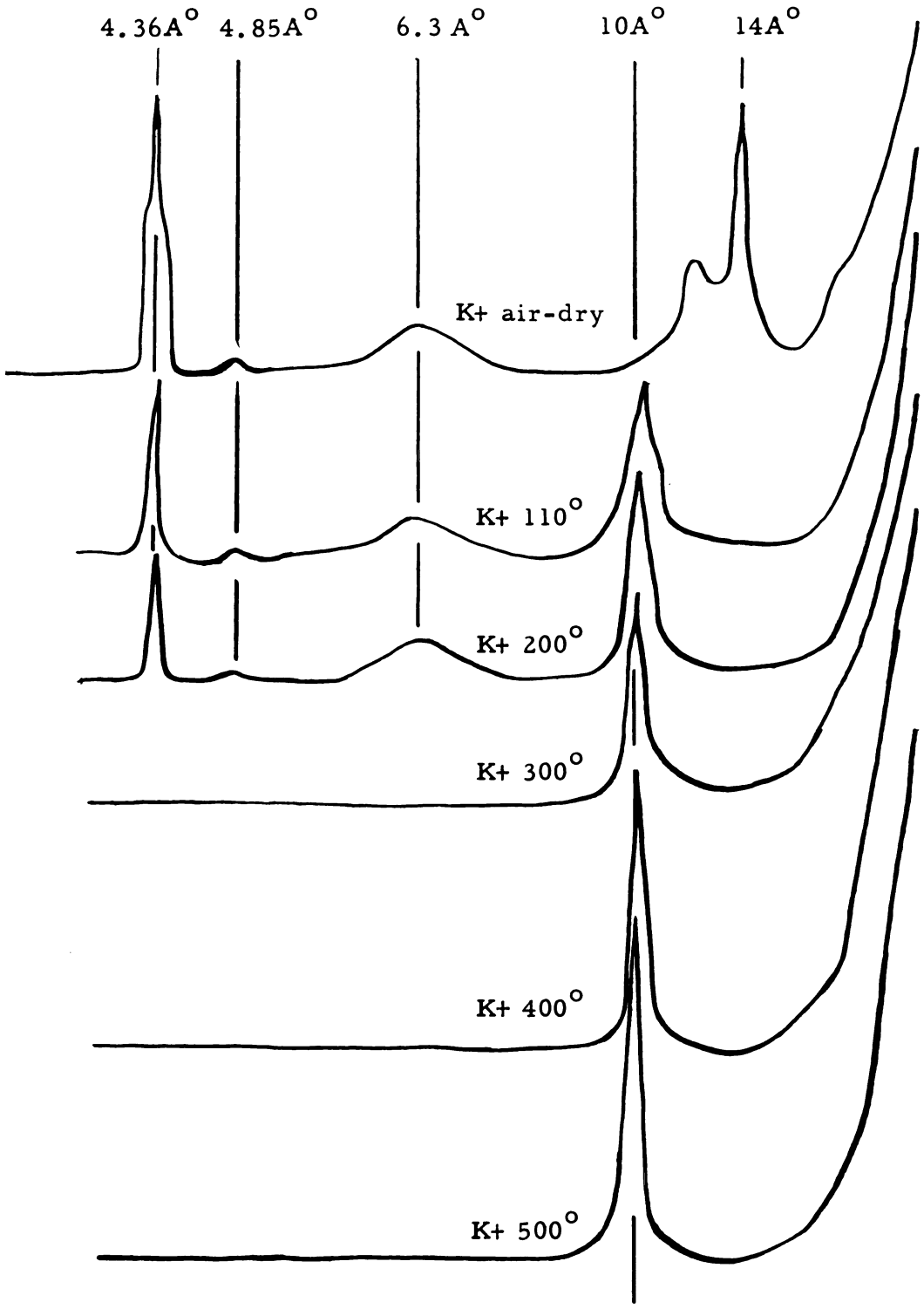

Figure 19. Effect of K-saturation and heat treatments on smoothed X-ray diffraction patterns for dialysis sample 2 (Mg/Mg + Al ratio of 0 in vermiculite). A scale factor of 8 was used.

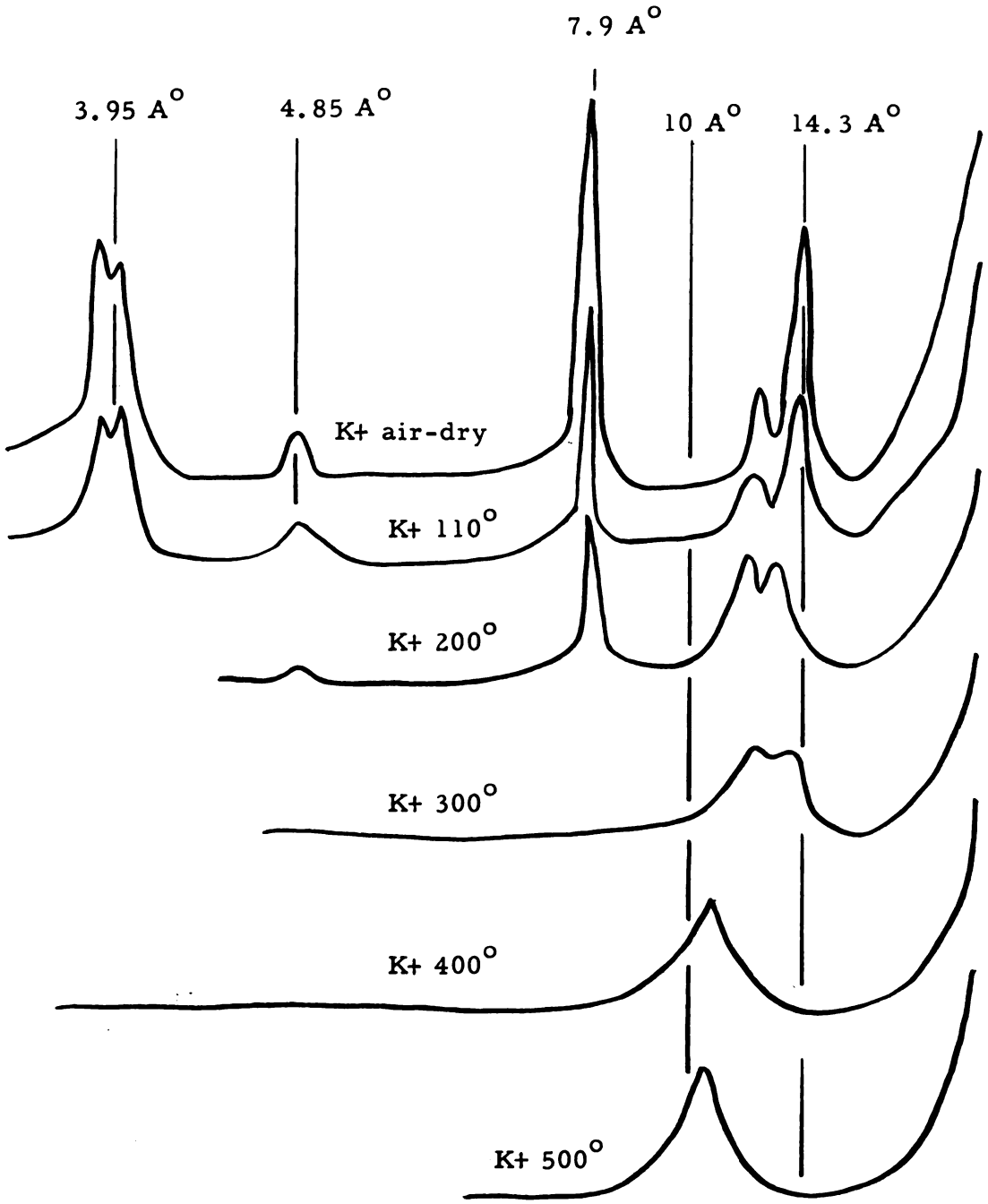

Figure 20. Effect of K-saturation and heat treatments on smoothed X-ray diffraction patterns for dialysis sample 3 (Mg/Mg + Al ratio of 0.8 in vermiculite). A scale factor of 8 was used.

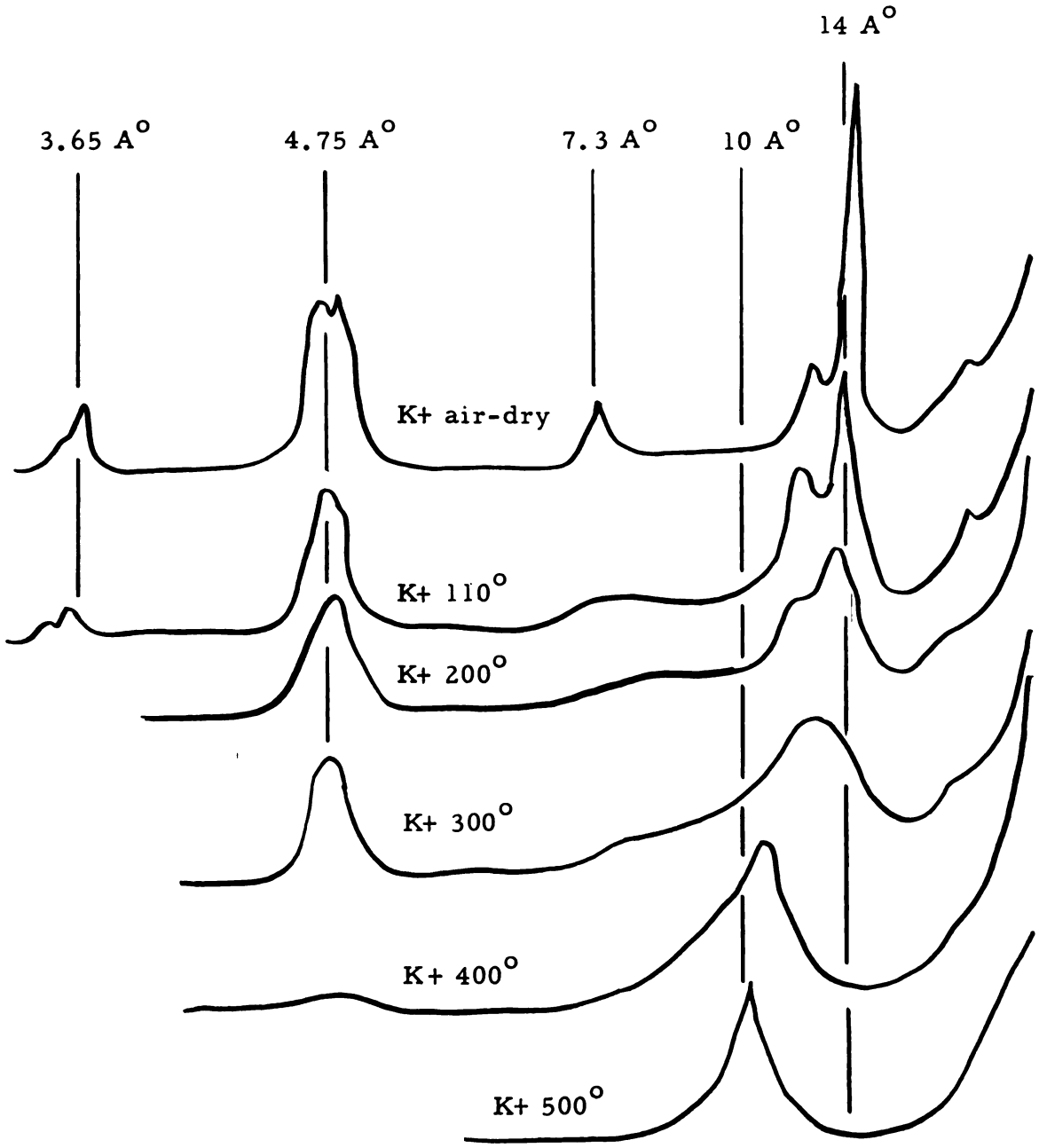

Figure 21. Effect of K-saturation and heat treatment on smoothed X-ray diffraction tracings for dialysis sample 4 (Mg/Mg + Al ratio of 1.0 in vermiculite). A scale factor of 8 was used.

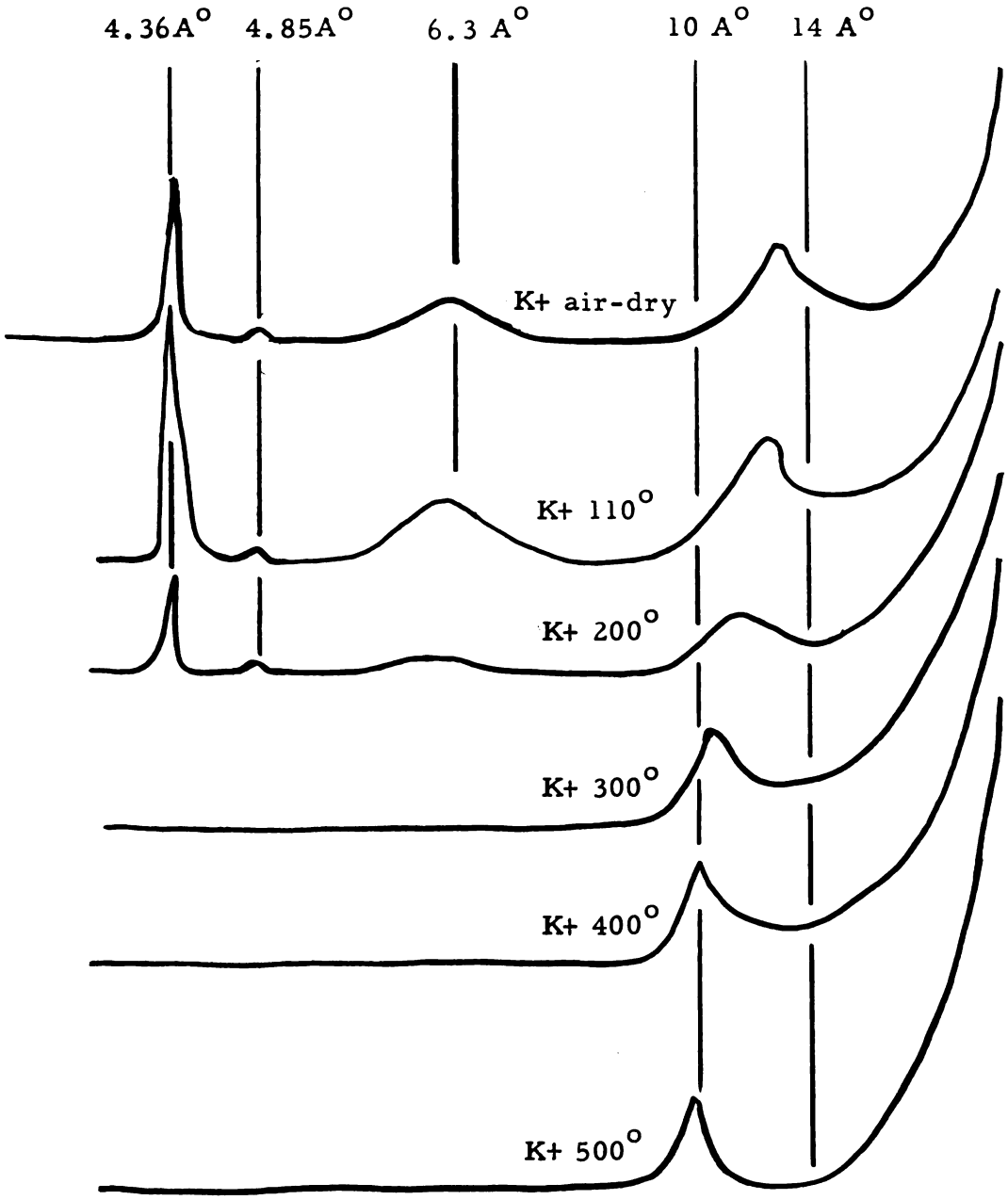

Figure 22. Effect of K-saturation and heat treatments on smoothed X-ray diffraction patterns for dialysis sample 5 (Mg/Mg + Al ratio of 0 in bentonite). A scale factor of 8 was used.

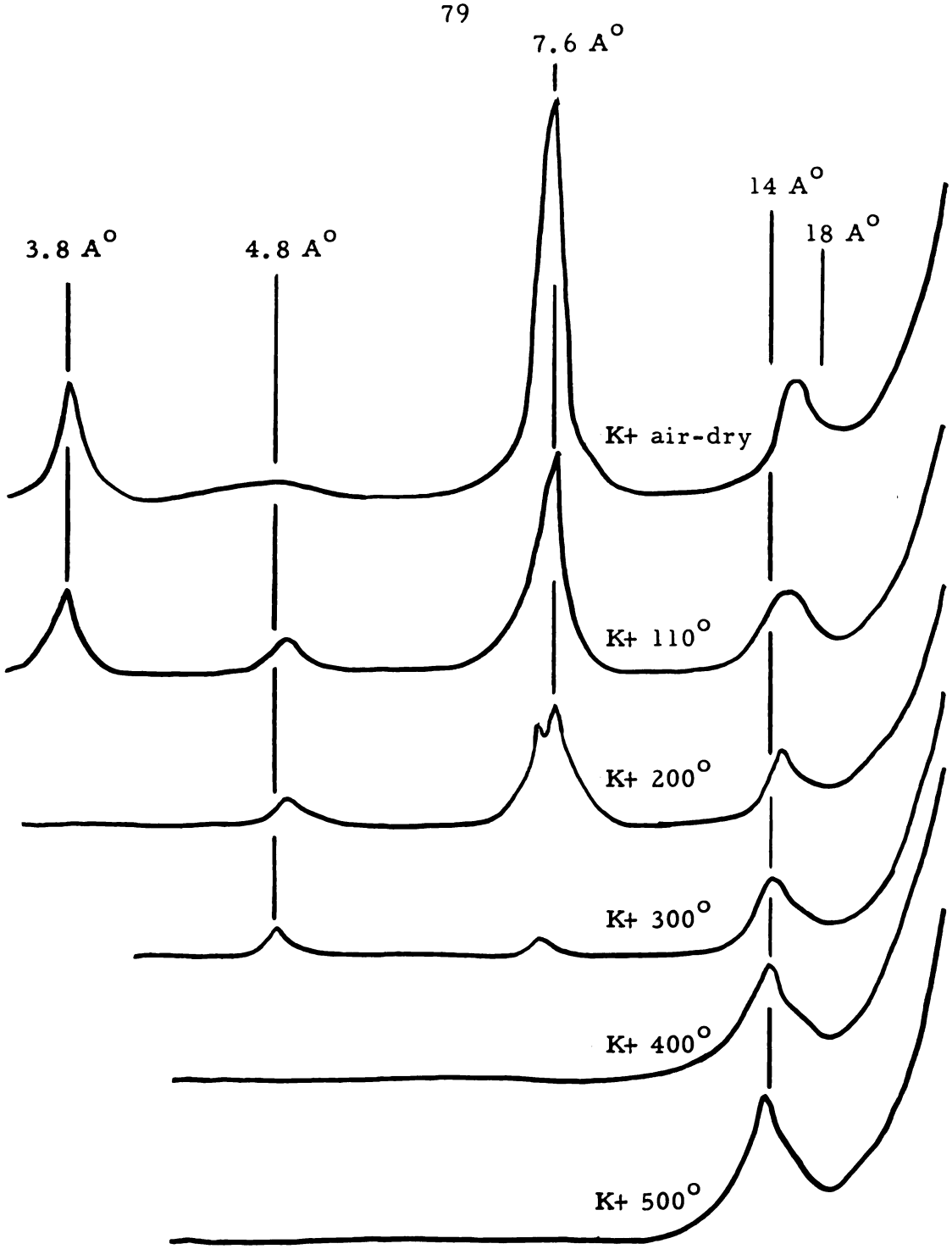

Figure 23. Effect of K-saturation and heat treatments on smoothed X-ray diffraction patterns for dialysis sample 6 (Mg/Mg + Al ratio of 0.7 in bentonite). A scale factor of 8 was used.

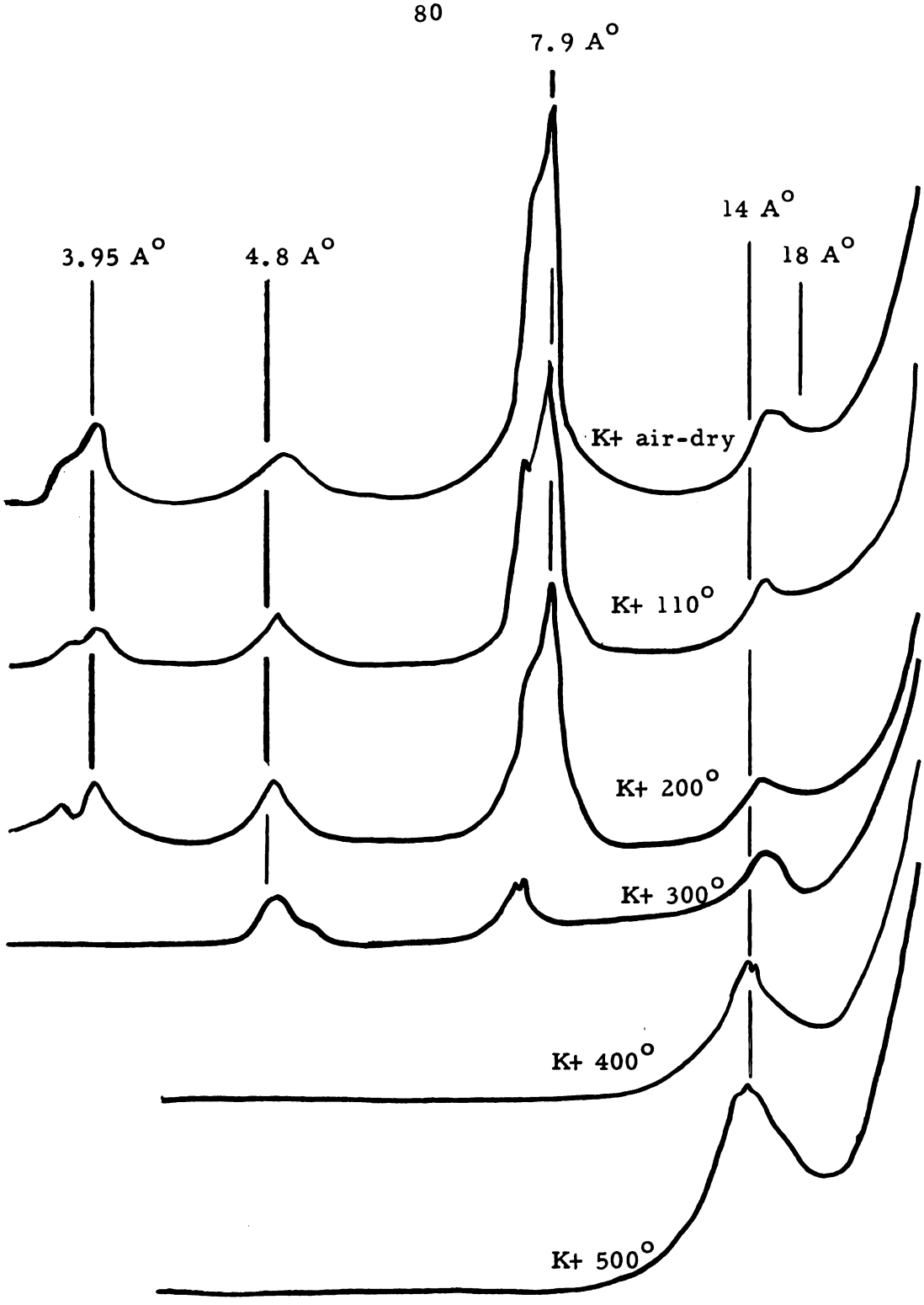

Figure 24. Effect of K-saturation and heat treatments on smoothed X-ray diffraction patterns for dialysis sample 7 (Mg/Mg + Al ratio of 0.8 in bentonite). A scale factor of 8 was used.

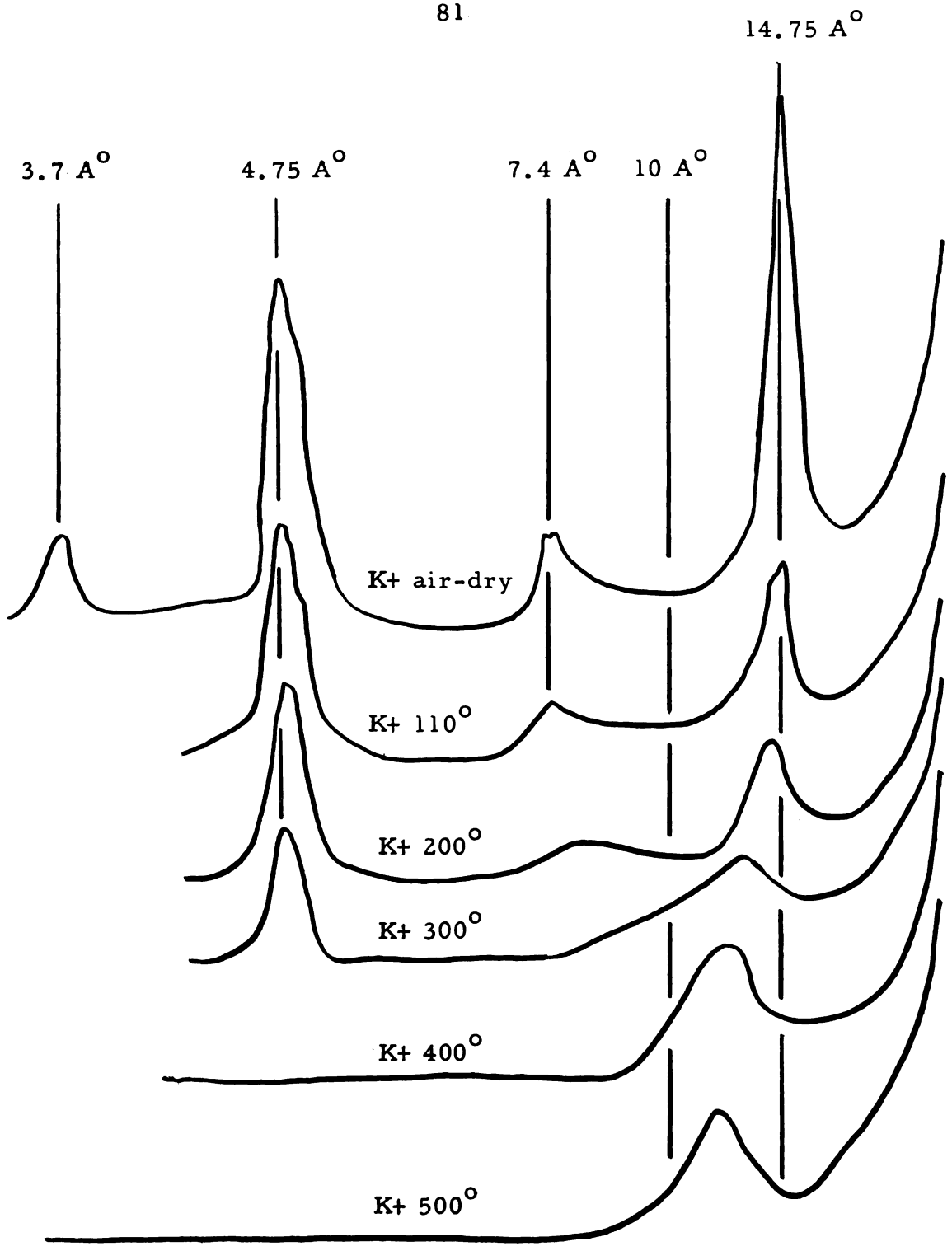

Figure 25. Effect of K-saturation and heat treatments on smoothed X-ray diffraction patterns for dialysis sample 8 (Mg/Mg + Al ratio of 1.0 in bentonite). A scale factor of 8 was used.

Figure 18 shows smoothed X-ray patterns for dialysis sample 1, the mixture of aluminum and magnesium chlorides in the absence of clay. A very sharp 7.95 A^{o} first order peak was observed as Mortland and Gastuche (1962) reported. Heating the mineral to 110° C. and 200° C. apparently improved the crystallinity of the mineral. It was found necessary to increase the scale factor of the X-ray recording unit to 32 and 64 as shown on Figure 18. Heating to 300° C. resulted in decomposition of the mineral. Mortland and Gastuche[a] reported that differential thermal analysis showed that this 7.95 A^{o} mineral gave an endothermic peak at 290° C.

A 7.9 A^{o} peak was observed for the magnesium-aluminum hydroxide mineral when it was formed in the presence of vermiculite, as shown in Figure 20, and bentonite, Figure 24. In the presence of bentonite, a shoulder on the 7.95 A^{o} peak is formed at about 7.6 A^{o}. This was not observed in the presence of vermiculite, although the peaks at about 3.95 A^{o} indicate two phases might be present. Mortland and Gastuche (1962) reported that two phases of the mineral were found. A 7.63 A^{o} mineral was formed when a (Mg/Mg+Al) molar ratio of 0.7 was used. They also observed a 3.80 A^{o} peak for the (002) reflection. This is verified in Figure 23 as well.

Figures 21 and 25 indicate that brucite formed in the magnesium-vermiculite and bentonite systems. The brucite was decomposed during the 400° C. heat treatment. McKenzie (1957) reported that brucite began to break down at 385-390°, but the endothermic peak occurred over 400° according to differential thermal analysis. Since the heat treatment used in this study was continuous for two hours, decomposition of the brucite could occur. In the aluminum-clay systems, a very broad pseudo-boehmite peak was observed at 6.3 A^{o} as shown in Figures 19 and 22.

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[a]Personal communication

Aluminum formed a very weak interlayer in vermiculite (Figure 22). Heating to 110° C. resulted in nearly complete collapse to 10 A°. Subsequent heat treatments merely resulted in a sharper 10 A° peak. However, a somewhat more complete aluminum interlayer occurred in the bentonite system (Figure 22). The peaks observed for the aluminum-bentonite system generally were quite diffuse. Heating at 110° C. and higher temperatures resulted in a gradual collapse of the clay lattice to 10 A°. It is assumed that a more complete interlayer is indicated by greater heat stability of the observed X-ray peaks. This assumption has been suggested by other workers (Rich, 1960a).

Replacing aluminum with magnesium resulted in more complete interlayers as shown in Figures 21 and 25. Again, the bentonite clay showed a more stable interlayer than was found in the vermiculite clay. Second and third order reflections were observed for the air-dry diffraction patterns. The appearance of higher order reflections is typical of a chlorite-type structure. The magnesium-vermiculite clay collapsed gradually to 10 A° upon increasing heat treatments. The magnesium-bentonite clay collapsed to slightly under 12 A° after heating to 500° C.

When a mixture of magnesium and aluminum was added to the clay systems more stable interlayers were formed than in pure magnesium or aluminum clay systems. The magnesium, aluminum-vermiculite system (Figure 20) resulted in a slightly more stable interlayer than was found for the magnesium-vermiculite system (Figure 21), but heating at 500° C. collapsed the peak to about 10.4 A°.

The molar (Mg/Mg+Al) ratios 0.7 and 0.8 gave similar results as seen in Figures 23 and 24, respectively. The K-saturated, air-dry treatment gave a rather broad peak slightly over 15 A°. Subsequent heat treatments resulted in collapse to a stable 14 A° peak. This indicates a complete interlayer was formed.

The vermiculite clay used in this study contained 3.9% potassium, indicating a mixture of mica and vermiculite. Some of the layers may have been only partially filled with potassium ions. If these layers could not expand to 14 A^{o} the hydroxides of magnesium and/or aluminum could not enter the interlayer area. This is one possible explanation for the less stable interlayers found in the vermiculite-clay than in the bentonite-clay. The clays were sodium-saturated prior to this study. Sodium-saturated bentonite is capable of expanding to hundreds of Angstrom units in aqueous suspensions. Vermiculite can expand to only 14 A^{o}; therefore, only a 4 A^{o} interlayer space is present. The greater expansion of the bentonite would result in greater accessibility to the hydroxides formed, giving another explanation for the formation of more stable interlayers in the bentonite systems.

Jackson (1960) suggested that aluminum interlayers form more readily in vermiculite than in montmorillonite during the natural soil weathering processes because of a higher charge density and steric pinching.

However, the high charge density of vermiculite may serve an opposite effect in the system studied here. The clay systems were titrated to pH 10.0. Therefore, magnesium and aluminum hydroxides would form with no positive charge. The high charge density of vermiculite may have some effect on causing an unbalance of the charge of the hydroxide in the interlayer space. This, also, could explain less complete interlayers found in the vermiculite systems.

DeKimpe et al. (1961) reported that the pH of the aluminum system was important in synthetic clay mineral preparations. As pH increases, aluminum changes from six-coordination to four-coordination. At pH 10.0, the aluminum ions apparently occurred in four-coordination as $Al(OH)_4^-$ ions. This may be the reason that the aluminum systems resulted in very little interlayering.. At pH 10.0, the magnesium system

would occur as $Mg(OH)_2$ and would tend to form a more complete interlayer as was observed.

The presence of both magnesium and aluminum in the system resulted in an interlayer which was stable at 14 A^{o} upon heating at 500^{o} C. Nelson and Roy (1958), in using hydrothermal synthesis methods, found that the presence of some aluminum resulted in a more stable chlorite than when aluminum was absent. They suggested this was a result of simultaneous isomorphous substitution of aluminum for magnesium in the brucite interlayer, and for silicon in the tetrahedral layer. The resulting charges balanced each other giving a more stable clay mineral. If it is assumed that a brucite interlayer forms in the mixed magnesium, aluminum-clay systems, it is conceivable that aluminum would replace some of the magnesium ions in the brucite layer. This would result in a net positive charge in the brucite layer which could balance part of the negative charge of the clay lattice. A more stable interlayer may result.

CHAPTER V

GENERAL DISCUSSION

Addition of KCl to an acid soil suspension results in a decrease in pH. The same effect is observed when a fertilizer containing a salt, such as potassium chloride or potassium sulfate, is added to an acid soil. The addition of the potassium ions causes a shift in the equilibrium in the soil with exchangeable acidity being displaced into the soil solution. The major portion of the exchangeable acidity can occur as exchangeable hydrogen ions, or from hydrogen ions arising from the hydrolysis of exchangeable aluminum, typical of very acid subsoils found in this study, as well as elsewhere (Yuan, 1963).

The source of the cation exchange capacity is important in consideration of the acidity fraction of a soil. Exchange sites in the organic fraction react differently than those in the inorganic fraction (Dawson et al., 1951). The exchange sites in the organic fraction have a higher affinity for hydrogen ions than for other cations, although organic matter functional groups are known to form complexes with polyvalent metal cations (Mortensen, 1963), including aluminum. The formation of aluminum-organic matter complexes may explain why little aluminum was found exchangeable to N KCl in the surface soils studied. Aluminum complexed with organic matter may be extractable. This was indicated when extractable aluminum values were found to be considerably higher than exchangeable aluminum levels in the surface horizons.

Results obtained in this study cannot be applied directly for practical application in the consideration of lime requirement and acidity because the soils studied represented virgin soil profiles. In a survey

of several soils of Poland, Dobrzanski (1960) observed that cultivated soils generally contained less extractable aluminum than virgin forest soils. He attributed this to the use of lime in the fertilization program.

Additions of lime have been found to rapidly reduce the exchangeable aluminum level of soils by Moschler et al. (1960), as well as in this study. This would indicate that a small amount of lime in a soil management program would reduce exchangeable aluminum in an acid soil to essentially zero. However, this does not necessarily imply that aluminum cannot still be important from the standpoint of soil acidity and liming. Aluminum which has polymerized is neutralized between pH 5.5 and 6.5 or 7.0 in soils. This is important since most workers suggest liming to pH 6.5 or 6.8. Therefore, studies reported here can contribute to understanding of aluminum reactions in cultivated soils in Michigan, although virgin soils were investigated. It is suggested that extraction of aluminum with N NH_4OAc adjusted to pH 4.8 results in a more meaningful measure of the aluminum which contributes to soil acidity in surface soils than does extraction with N KCl. This is based on the apparent extraction of polymer forms of aluminum by the NH_4OAc and the role of this aluminum in the pH range from 5.5 to 6.5.

Soil management practices play a vital role in the aluminum reactions in the soil. For instance, continued additions of high amounts of ammonium sulphate have been found to substantially lower the pH of a Michigan soil.[a] Howard (1919) observed a decrease in pH and an increase in exchangeable aluminum with continued use of ammonium sulphate.

In certain cases, acid subsoil samples which contain high amounts of exchangeable or extractable aluminum may be incorporated into the plow layer. This becomes especially important as deeper plowing is being

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[a] Wolcott and Foth, unpublished data.

more widely practiced. Experiments are being conducted at present on the advantages of plowing to 24 inches in certain sandy soils in Michigan. This practice is being used to incorporate clay from the B horizon into the surface soil. The result of such a practice could give unusually high lime requirements in certain soils due to the presence of high amounts of exchangeable and extractable aluminum.

The B_{hir} horizon of the Munising series occurs at a depth of from 6 to 12 inches, varying with location. Sample 3 examined in this study is an example of this horizon. This horizon is often incorporated into the plow layer which has resulted in very high lime requirements.

The source of aluminum ions which contribute to soil acidity ultimately is the mineral fraction of the soil. Weathering of soils is a natural process which results in the gradual physical and chemical destruction of the mineral fraction. Other ions, in addition to aluminum, are released during the weathering of the mineral fraction. The dynamics of potassium release and fixation have received considerable attention in the literature (Mortland et al., 1957; Cummings, 1959, for example). Release of magnesium from clay minerals in magnesium-deficient soils may be important. Barshad (1960a) has suggested the magnesium-rich clay minerals are more susceptible to weathering than those low in magnesium.

When an aluminum interlayer is formed in an expanding clay mineral, the lattice structure cannot collapse to 10 A^{o} under normal soil conditions. A practical effect of the presence of the interlayer is decreased potassium and ammonium fixation. Decreased ammonium fixation has been observed in pure vermiculite (Rich, 1960a) with an artificial aluminum interlayer incorporated, and in a naturally-occurring vermiculite, which exhibited some aluminum interlayers (Rich, 1960b).

Jackson (1963a) suggested that aluminum bonding in soils is important in other soil properties, such as anion retention and soil aggregation, in addition to those mentioned in the above discussion.

CHAPTER VI

SUMMARY AND CONCLUSIONS

In the survey of fifty-eight horizon samples from Michigan soils the surface horizons appeared to comprise a population separate from the subsurface horizons. For a given water pH (determined in a water suspension), the surface samples consistently gave higher KCl pH values than the subsurface samples. This was suggested to be caused predominantly by the presence of greater amounts of exchangeable aluminum in the subsurface samples. As pH increased, the extractable aluminum decreased following a logarithmic relationship.

In a more detailed study of nineteen horizon samples representing five soil series,the following relationships were observed between various measures of soil acidity:

1) Exchangeable aluminum decreased as water pH and KCl pH increased, following a logarithmic relationship. The surface horizons constituted a population different from the subsurface horizons.

2) Exchangeable aluminum (extractable with N KCl) and extractable aluminum (extractable with N NH_4OAc buffered at pH 4.8) were not closely correlated. Exchangeable aluminum levels were found to be highest for those soils which exhibited the lowest KCl pH. It was suggested that KCl could remove some aluminum from the lattice of the clay mineral when the KCl pH is very low. This apparently was a major cause for the poor correlation between exchangeable and extractable aluminum.

3) The NH_4OAc adjusted at pH 4.8 was believed to remove polymerized aluminum from the interlayer of expansible clay minerals.

4) Exchangeable aluminum was more closely correlated with lime requirement than was extractable aluminum when the subsurface horizons were considered separately. When the surface horizons were included, the correlation between exchangeable aluminum and lime requirement decreased, but remained nearly the same for extractable aluminum versus lime requirement.

5) Iron contributed only a very small amount to the total soil acidity in these soils.

6) Exchangeable hydrogen was the predominant source of soil acidity in the surface horizons.

7) Several chemical and empirical methods for determination of soil acidity were found closely correlated with lime requirement.

8) Leaching with N KCl removed some exchangeable hydrogen which could be titrated, but the magnitude was small for all samples.

Adding lime to the nineteen horizon samples, followed by moist incubation for 16 weeks in the laboratory, caused exchangeable aluminum to decrease essentially to zero. Extractable aluminum decreased to 30-50% of the original level. Exchangeable acidity was decreased variable amounts by liming. The effects of the original exchangeable aluminum level and the presence of high amounts of organic matter were found to be important. Two surface horizons, high in organic matter, gave a 25-fold increase in water-soluble nitrates and a slight decrease in percent organic matter upon liming and incubation.

Acidification and incubation for 16 weeks resulted in a marked increase in the exchangeable aluminum level. Presence of organic matter in the surface horizons tended to reduce the effectiveness of the acid added in increasing exchangeable aluminum.

Removal of the interlayer aluminum in several soil clay minerals resulted in better differentiation of the 10 and 14 A^{o} clay minerals. A small amount of montmorillonite became evident in one of the horizons

after this treatment, which led to different conclusions as to the clay minerals present.

Interlayers of varying stages of completion and heat stability were formed in vermiculite and bentonite dependent upon the treatment in the dialysis experiment. The following observations were made:

1) A 7.95 A^{o} mineral was crystallized during dialysis in the presence of a molar (Mg/Mg+Al) ratio of 0.8 of magnesium and aluminum chlorides titrated to pH 10.0.

2) A 7.9 A^{o} peak was observed for this mineral crystallized in the presence of an expansible clay mineral. There was some indication of a 7.6 A^{o} phase as well.

3) Pure aluminum-clay systems resulted in a very limited amount of interlayer development. The pure magnesium-clay system resulted in a somewhat more complete interlayer development, although increasing heat treatments caused collapse of the clay lattice toward 10 A^{o}.

4) A 14 A^{o} peak which was stable at 500^{o} C. resulted when a molar ratio of 0.7 or 0.8 (Mg/Mg+Al) was used in the presence of bentonite. A less stable interlayer was found in vermiculite than in bentonite.

Results of the dialysis experiment lead to the conclusion that variables which were not incorporated into this study need to be controlled. The size fraction of the clay mineral present is important. Dixon and Jackson (1959), as well as others, have reported that a greater amount of interlayer aluminum was found in the coarse clay fraction than in the finer clays. The effect of pH is also important, especially as it affects the coordination number of aluminum.

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APPENDIX

Table 13. Legal descriptions for the location of profile samples.

Munising series:
W 1/2 NW 1/4 NE 1/4 sec 36 T54N R34W
Rudy Larson farm, Chassel, Michigan
Houghton County

Ontonagon series:
NW 1/4 Sec 21 T48N R40W
Ed Warachek farm,
Ontonagon County

Iron River series:
NE 1/4 SE 1/4 Sec 11 T42N R35W
Iron River County

Miami series:
SW 1/4 NW 1/4 SW 1/4 Sec 2 T5N R2W
Clinton County

Fox series:
NE 1/4 NE 1/4 NE 1/4 NW 1/4 Sec 9 T1S R9W
MSU-Kellogg farm
Kalamazoo County

Pence series:
NW 1/4 Sec 19 T43N R32W
Iron River County

McBride series:
SE 1/4 SW 1/4 SW 1/4 Sec 31 T9N R6W
Montcalm County

Grayling series:
SW 1/4 SW 1/4 SE 1/4 NE 1/4 Sec 26 T9N R6W
Montcalm County

Nester series:
NW 1/4 NW 1/4 NE 1/4 Sec 21 T9N R6W
Montcalm County

continued

Table 13 - continued

Kawkawlin series:
SW 1/4 NW 1/4 SW 1/4 Sec 5 T9N R6W
Montcalm County

Montcalm series:
NE 1/4 NE 1/4 NE 1/4 NE 1/4 Sec 30 T9N R7W
Montcalm County

Morley series:
SW 1/4 NW 1/4 SW 1/4 Sec 3 T4S R6E
Saline, Michigan
Washtenaw County

Warsaw series:
NE 1/4 NW 1/4 SE 1/4
Kalamazoo County

Kent series:
NE 1/4 NE 1/4 SE 1/4 Sec 24 T6N R11W
Kent County

Table 14. Water pH, KCl pH, and extractable aluminum for fifty-eight horizon samples.

Sample number	Depth (inches)	Horizon	pH determined in Water	pH determined in N KCl	me./100 gm. Extractable Al
Soil series					
Munising					
1	0-4	A_1	5.0	4.2	1.2
2	4-7	A_2	5.0	4.0	0.2
3	10-12	Bhir	4.9	4.0	21.1
4	12-16	Bir	5.2	4.3	30.4
Ontonagon					
5	0-2	A_1	5.5	4.8	1.0
6	2-3	A_2	5.0	4.0	2.1
7	5-12	$B_{21}t$	4.8	3.6	6.2
8	12-18	$B_{22}t$	5.1	3.9	2.3
Iron River					
9	0-5	A_1	5.2	4.4	3.9
10	7-12	Bh	5.2	4.2	12.4
11	13-19		5.1	4.2	12.7
12	19-25		5.2	4.1	6.6
Miami					
13	0-6	A_1	6.5	5.5	1.4
14	7-11	A_2	5.1	4.1	3.4
15	12-20	B	5.4	4.2	2.7
Fox					
16	0-4	A_1	6.6	5.7	0.9
17	6-8	A_2	6.3	4.9	1.6
18	13-17	B_1	4.8	3.6	4.2
19	18-22	B_{21}	4.6	3.4	5.8
Pence					
20	0-4	A_1	4.9	4.0	4.2
21	4-6	A_2	5.1	3.8	1.8
22	6-20		5.4	4.8	7.8
23	20-27		5.8	4.7	5.1
24	27-32		6.0	5.0	2.6

continued

Table 14 - Continued

Sample number	Depth (inches)	Horizon	pH determined in Water	pH determined in N KCl	me./100 gm. Extractable Al
McBride					
25	1-4	A_1	6.0	5.4	0.7
26	4-5	A_2	5.5	4.8	1.0
27	5-8		5.1	4.1	3.5
28	9-11		5.2	4.2	2.6
29	16-22		5.4	4.2	1.1
30	26-30		5.5	4.3	0.7
Grayling					
31	2-4	A_1	5.4	4.6	2.3
32	4-5	A_2	5.9	5.3	2.3
33	9-12		6.4	5.4	8.1
34	15-19		6.1	4.9	2.9
Nester					
35	0-6	A_1	6.5	5.8	0.4
36	7-11	A_2	6.3	4.8	1.0
37	13-24		5.4	4.0	1.2
Kawkawlin					
38	0-4	A_1	6.3	5.5	0.8
39	7-11		5.2	4.1	5.8
40	13-16		5.6	4.4	5.3
41	17-22		6.3	4.7	2.0
Montcalm					
42	0-7	A_1	5.6	4.7	0.7
43	7-10	A_2	6.0	4.7	0.7
44	11-15	B_2n	6.2	4.8	0.6
45	17-19	A_2	6.2	4.7	0.6
46	21-24		6.1	4.7	1.7
Morley					
47	0-6	A_1	6.3	5.5	0.8
48	6-8		5.6	4.4	1.8
49	12-16		5.5	4.2	1.1
50	19-22		6.1	4.8	0.9

continued

Table 14 - Continued

Sample number	Depth (inches)	Horizon	pH determined in Water	pH determined in N KCl	me./100 gm. Extractable Al
Warsaw					
51	0-7	A_1	7.6	6.9	0.3
52	8-13		7.0	6.0	1.2
53	14-22		5.4	4.0	3.0
Kent					
54	0-5	A_1	6.4	5.6	0.8
55	5-8		6.4	5.6	1.3
56	9-11		6.6	5.6	1.0
57	12-14		6.4	5.2	0.7
58	15-20		6.5	5.0	1.1

Table 15. Physical properties of nineteen Michigan horizon samples.

Sample number	Composition of separates: Sand %	Silt %	Clay %	Texture	Organic matter %	Moisture equivalent %
1	75.5	21.0	3.6	loamy sand	6.33	13.2
2	81.8	16.1	2.1	loamy sand	1.01	7.0
3	68.5	16.1	15.0	sandy loam	4.04	17.2
4	72.0	20.0	8.1	sandy loam	2.39	13.8
5	19.1	39.1	41.8	clay	14.37	41.9
6	31.1	45.5	23.8	loam	3.28	21.8
7	6.2	19.2	74.6	clay	1.14	33.2
8	4.7	15.5	79.8	clay	0.85	35.2
9	16.2	72.7	11.1	silt loam	6.86	32.0
10	17.0	73.4	9.6	silt loam	2.76	23.6
11	17.1	74.9	8.0	silt loam	1.68	21.0
12	14.8	78.6	6.6	silt loam	0.78	19.0
13	58.9	32.5	8.5	sandy loam	4.30	18.6
14	62.5	29.6	7.9	sandy loam	1.10	13.9
15	66.0	28.0	6.0	sandy loam	0.52	10.8
16	36.1	52.7	11.1	silt loam	5.98	30.1
17	33.7	53.5	12.7	silt loam	1.02	18.3
18	29.8	47.5	22.7	loam	0.52	19.9
19	49.1	24.7	26.3	sandy clay loam	0.31	19.8

Table 16. Some chemical properties of nineteen Michigan horizon samples.

Sample number	Exchangeable bases					Base saturation	Exchangeable hydrogen
	Ca	K	Mg	Na	Total	(percent)	(me./100 gm.)
	--------(me./100 gm.)---------						
1	2.7	0.3	0.9	0.2	4.1	39.0	6.3
2	0.4	0.1	0.1	0.0	0.6	33.3	1.1
3	0.8	0.2	0.3	0.3	1.5	7.5	15.5
4	0.2	0.1	0.1	0.1	0.4	2.9	12.0
5	12.8	1.0	3.0	1.0	17.9	52.8	15.9
6	4.3	0.2	1.2	0.4	6.1	49.2	5.9
7	9.1	0.6	3.5	1.7	14.9	53.2	9.7
8	15.1	0.6	3.7	2.5	21.9	70.4	8.6
9	6.2	0.2	0.8	0.5	7.7	39.9	11.4
10	1.8	0.1	0.4	0.4	2.7	18.2	10.9
11	0.4	0.1	0.2	0.2	1.0	10.4	7.1
12	0.6	0.1	0.3	0.3	1.2	19.0	3.5
13	6.4	0.4	1.1	nd*	7.9	64.2	4.4
14	0.7	0.3	0.3	nd	1.3	26.0	2.9
15	0.6	0.2	0.3	nd	1.1	33.3	1.7
16	9.6	0.4	0.9	nd	10.9	63.0	6.5
17	3.2	0.2	0.6	nd	4.0	58.0	2.9
18	1.7	0.3	1.5	nd	3.5	29.4	4.8
19	1.5	0.3	1.2	nd	3.0	20.3	6.4

*nd = not determined.

Exchangeable hydrogen plus aluminum (me./100 gm.)	Lime requirement (tons/acre)	(pH 6.8-initial pH) x CEC	Iron extracted by KCl --(me./100 gm.)--	Iron extracted by NH_4OAc pH 4.8 --(me./100 gm.)--
6.4	3,9	18.9	0.01	0.01
1.2	2.0	3.2	nd	nd
18.4	8.3	37.8	0.06	1.10
13.4	5.65	22.1	0.03	0.70
15.9	5.65	44.1	nd	0.06
6.3	3.9	22.3	nd	0.25
13.1	8.0	56.0	0.02	0.38
9.2	3.0	52.9	0.01	0.32
11.6	6.0	30.9	nd	nd
12.1	6.0	23.7	nd	nd
8.6	5.1	16.3	0.01	0.25
5.1	3.3	10.1	nd	nd
4.4	1.0	3.7	0.01	nd
3.7	2.5	8.5	nd	nd
2.2	2.0	4.6	0.03	0.25
6.5	1.0	3.5	0	nd
2.9	1.0	3.5	nd	nd
8.5	6.25	24.0	0.03	0.16
11.9	10.4	32.8	0.01	0.14

Table 17. Cation exchange capacities of nineteen Michigan horizon samples. All data are given in me./100 gm.

Sample number	Whole soil	Mineral fraction[a]	Organic fraction[a]
1	10.5	2.8	7.7
2	1.8	1.1	0.7
3	19.9	6.3	13.6
4	13.8	9.1	4.7
5	33.9	13.5	20.4
6	12.4	6.6	5.8
7	28.0	26.9	1.1
8	31.1	29.3	1.8
9	19.3	8.1	11.2
10	14.8	6.7	8.1
11	9.6	4.7	4.9
12	6.3	5.4	0.9
13	12.3	nd	nd
14	5.0	nd	nd
15	3.3	nd	nd
16	17.4	nd	nd
17	6.9	nd	nd
18	12.0	nd	nd
19	14.9	nd	nd

[a] nd = not determined

Table 18. *Effect of liming on pH of nineteen Michigan horizon samples.*

Table 18. Effect of liming on pH of nineteen Michigan horizon samples.

Sample number	Initial pH	Limed samples Incubation period--weeks 2	4	6	8	16	Check (unlimed samples) Incubation period--weeks 4	8
1	5.0	6.65	6.7	6.75	6.65	6.6	5.1	5.15
2	5.0	7.5	7.6	7.6	7.5	7.5	5.3	5.4
3	4.9	6.5	6.5	6.5	6.5	6.7	4.55	4.55
4	5.2	6.7	6.8	6.8	6.75	6.9	4.8	4.8
5	5.5	5.9	5.95	5.95	5.85	5.85	5.0	4.9
6	5.0	6.5	6.5	6.55	6.5	6.65	4.8	4.8
7	4.8	6.8	6.8	6.85	6.9	7.15	4.3	4.25
8	5.1	6.6	6.65	6.65	6.7	7.0	5.05	5.0
9	5.2	6.4	6.25	6.4	6.25	6.4	4.85	4.9
10	5.2	6.85	6.95	7.05	7.05	7.2	4.9	4.85
11	5.1	6.95	7.25	7.2	7.15	7.2	4.8	4.8
12	5.2	7.1	7.4	7.45	7.4	7.4	4.75	4.75
13	6.5	6.25	6.3	6.2	6.15	6.2	5.75	5.7
14	5.1	7.0	7.0	6.8	6.75	6.8	4.9	4.85
15	5.4	7.2	7.3	7.3	7.2	7.3	5.0	4.95
16	6.6	6.35	6.4	6.4	6.3	6.3	6.05	6.25
17	6.3	6.7	6.7	6.75	6.75	6.9	5.9	5.85
18	4.8	7.25	7.45	7.45	7.4	7.45	4.2	4.15
19	4.6	7.5	7.5	7.6	7.6	7.6	4.15	4.15

Table 19. Effect of liming and incubation on exchangeable aluminum in nineteen Michigan horizon samples. All exchangeable aluminum data are given in me./100 gm.

Sample number	Initial	Limed samples (time, weeks) 2	4	8	16	Check (unlimed) 8
1	0.14	0.06	0.08	0.10	0.02	0.13
2	0.08	<0.01	<0.01	<0.01	<0.01	0.02
3	2.94	0.09	0.12	0.10	0.01	3.08
4	1.44	0.02	0.04	0.06	0.01	1.63
5	0.02	0.02	0.10	0.07	0.02	0.04
6	0.44	0.04	0.07	0.04	0.02	0.40
7	3.40	<0.01	<0.01	<0.01	<0.01	3.31
8	0.55	<0.01	<0.01	<0.01	<0.01	0.58
9	0.16	0.10	0.10	0.11	0.06	0.18
10	1.20	0.09	0.12	0.09	0.02	1.37
11	1.54	0.05	0.06	0.04	0.02	1.64
12	1.55	<0.01	<0.01	0.02	0.02	1.50
13	0.01	<0.01	<0.01	<0.01	<0.01	0.02
14	0.75	<0.01	<0.01	<0.01	<0.01	0.73
15	0.50	<0.01	<0.01	<0.01	<0.01	0.49
16	0.02	0.02	0.01	0.02	0.02	0.01
17	0.01	<0.01	<0.01	<0.01	<0.01	0.02
18	3.71	<0.01	<0.01	<0.01	<0.01	3.19
19	5.45	<0.01	<0.01	<0.01	<0.01	4.60

Table 20. Effect of liming on extractable aluminum of nineteen Michigan horizon samples. All data are given in me./100 gm.

Sample number	Initial	Limed	Percent extr. Al remaining
1	1.2	0.4	33.3
2	0.2	0.17	85.0
3	21.1	6.6	31.3
4	30.4	13.8	45.4
5	1.0	0.3	30.0
6	2.1	0.5	23.8
7	6.2	1.5	24.2
8	2.3	1.0	43.5
9	3.9	0.7	17.9
10	12.4	4.1	33.1
11	12.7	5.3	41.7
12	6.6	2.9	43.9
13	1.4	0.6	42.9
14	3.4	1.1	32.4
15	2.7	1.3	48.1
16	0.9	0.3	33.3
17	1.6	0.7	43.8
18	4.2	1.8	42.9
19	5.8	1.9	32.8

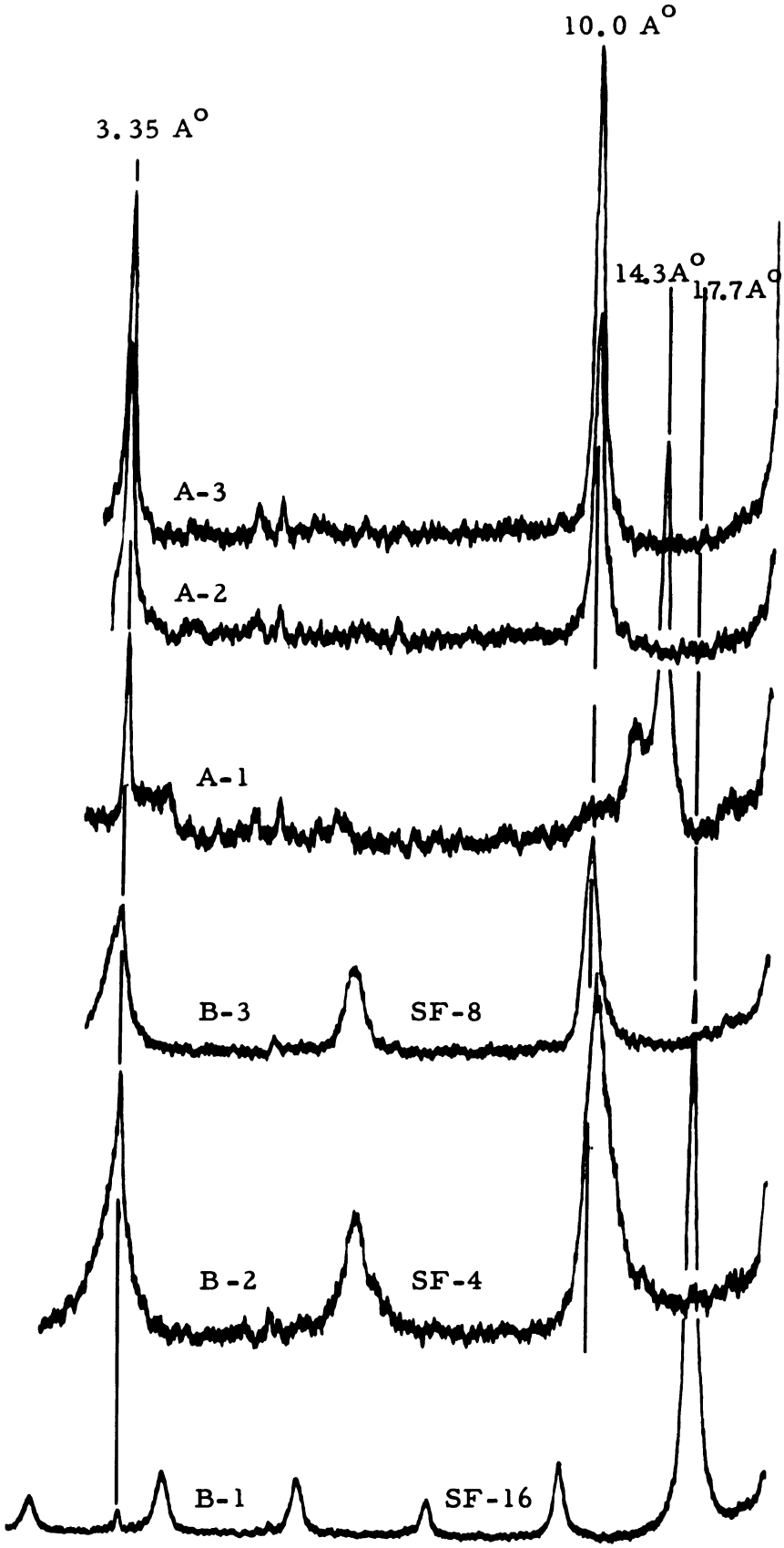
Table 21. Effect of liming on exchangeable acidity of nineteen Michigan horizon samples. All exchangeable acidity data are given in me./100 gm.

Sample number	Initial	Limed samples (time, weeks) 2	4	6	8	Percent of original exchangeable acidity remaining after 16 weeks	Check (time, weeks) 4	8
1	9.3	4.7	4.3	4.2	4.4	47.3	8.1	7.9
2	2.1	1.0	1.1	1.0	0.9	42.9	1.2	1.5
3	28.0	10.9	11.5	11.5	11.9	42.5	23.5	24.6
4	21.5	9.2	9.9	10.1	10.0	46.5	17.1	17.9
5	19.0	13.0	13.7	13.6	13.1	68.9	19.1	19.2
6	9.2	4.5	4.3	4.4	4.2	45.7	9.1	9.2
7	17.0	5.0	5.0	4.7	4.9	28.8	16.1	16.9
8	9.7	5.2	6.0	5.7	6.3	64.9	9.1	9.3
9	16.4	8.3	8.4	8.3	8.5	51.8	15.4	15.0
10	16.6	6.0	6.1	6.0	5.8	34.9	14.1	14.1
11	13.9	5.3	5.2	5.2	4.7	33.8	12.5	12.6
12	8.1	3.5	3.3	3.2	3.4	42.0	7.9	7.8
13	7.1	6.0	6.4	6.3	6.2	87.3	6.9	7.3
14	7.1	2.4	3.1	2.9	3.1	43.7	6.1	6.1
15	4.8	1.7	1.9	1.8	1.8	37.5	4.2	4.4
16	8.1	6.7	7.1	7.6	7.7	95.1	8.1	7.9
17	4.9	2.8	3.3	3.1	3.2	65.3	4.6	4.8
18	11.8	3.0	2.2	2.1	2.4	20.3	11.9	11.6
19	14.8	1.7	2.1	1.9	2.0	13.5	14.6	14.3

Table 22. The effects of acidification on pH for nineteen Michigan horizon samples.

Sample number	Initial pH	pH after incubation		
		2 weeks	4 weeks	16 weeks
1	5.0	2.55	2.4	2.7
2	5.0	2.9	2.75	3.1
3	4.9	3.4	3.2	3.45
4	5.2	3.85	3.7	3.8
5	5.5	2.9	2.75	3.2
6	5.0	2.95	2.8	3.1
7	4.8	3.15	3.05	3.5
8	5.1	3.2	3.1	3.55
9	5.2	3.1	2.9	3.3
10	5.2	3.6	3.3	3.6
11	5.1	3.75	3.5	3.8
12	5.2	3.7	3.45	3.7
13	6.5	3.65	3.45	3.9
14	5.1	3.7	3.5	3.85
15	5.4	3.8	3.6	3.8
16	6.6	4.05	3.75	4.45
17	6.3	4.0	3.8	4.35
18	4.8	3.3	3.15	3.5
19	4.6	3.2	3.1	3.4

Figure 26. X-ray diffraction tracings for vermiculite and bentonite clays. The top three tracings are those for vermiculite denoted by A. The lower three tracings, denoted B, are for bentonite. Treatment 1 refers to the magnesium-saturated, glycerol-solvated clay; 2 denotes K-saturation and heating to 110° C.; 3 denotes K-saturation and heating to 550° C. A scale factor of 4 was used unless otherwise indicated.


10.0 A°
3.35 A°
14.3A°
17.7A°
A-3
A-2
A-1
B-3
SF-8
B-2
SF-4
B-1
SF-16