RELEASE OF MAGNESIUM BY LEACHING FROM VERMICULITE, MICA AND PROCHLORITE

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This is to certify that the

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ABSTRACT

RELEASE OF MAGNESIUM BY LEACHING FROM VERMICULITE, MICA AND PROCHLORITE

by Lloyd R. Hossner

Four gram samples of vermiculite, mica and prochlorite were leached at a constant rate of 4 milliliters per minute for 8640 minutes at 30° C. Leaching solutions were 0.05 N $CaCl_2$ at pH 6.8, 0.05 N $CaCl_2$ adjusted to pH 5.0, and 0.05 N $CaCl_2$ adjusted to pH 3.0. The < 2 μ fraction of vermiculite and the < 110 μ, 44-53 μ and 0.2-2.0 μ fractions of mica and prochlorite were used. The rate of release of magnesium, potassium, iron and aluminum was measured as a function of time.

Release of magnesium was affected by pH and particle size. The logarithm nonlinear rate of release plotted against time decreased linearly after an initial rapid decline for about 3000 minutes. The lone exception was prochlorite at pH 6.8 which decreased nonlinearly for the entire leaching period. As pH or particle size decreased the rate of magnesium release increased.

Potassium release was not particularly affected by either pH or particle size. When the logarithm of the rate of release of potassium was plotted against time linear rate of release curves were obtained after an initial nonlinear decrease.

Iron and aluminum were detected in the leachate in large quantities at pH 3.0. Aluminum was present in small amounts at pH 5.0.

Alteration of mica to vermiculite was accomplished quite readily with any of the treatments used. The amount altered was dependent more on particle size than on pH.

Preferential release of magnesium from the brucite layer of prochlorite was not detected by chemical or X-ray analysis. This is contrary to previously published results.

As leaching proceeds a residue layer is formed on the outer surface of the particles whose composition depends on the pH of the leaching solution. As the pH decreases the layer contains increasingly more iron and less aluminum. The formation of this residue layer is probably similar to those cited previously in the literature. Magnesium released from the octahedral layer must pass through this residue layer. It is proposed that this is the rate limiting step in the release of magnesium from these minerals.

RELEASE OF MAGNESIUM BY LEACHING FROM VERMICULITE, MICA AND PROCHLORITE

By

Lloyd R. Hossner

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TO YVONNE

This thesis is affectionately dedicated to my wife

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INTRODUCTION

Magnesium ranks seventh in abundance in the scale of elemental occurrence in the earth's crust. Consequently, most soils contain adequate magnesium for optimum plant growth. With the use of higher rates of high analysis fertilizer and the resulting higher crop yields, greater amounts of magnesium are being removed from the soil. Some soils which originally contained adequate levels are now subject to magnesium deficiency.

Magnesium in primary and secondary minerals in the soil may be released to a soluble form where it may be utilized by plants, leached from the profile, or become an exchangeable cation. On the other hand, soluble or exchangeable magnesium may be subject to fixation by the silicate minerals of the soil.

A large portion of the magnesium in the soil is found occupying the octahedral sites within the mineral lattice; it may constitute up to 25 per cent or more of the total mineral. The mechanism of magnesium release from these minerals has not been completely characterized.

It has been postulated that lattice magnesium can be displaced by protons to an exchangeable position with comparative ease. Theoretically the reaction can occur until all of the lattice magnesium is depleted if a supply of protons is readily available.

In view of the apparent lack of basic magnesium research it appears that a study of the release of magnesium from some of the common soil minerals is in order.

The objectives of this study are:

1. To measure the rate and magnitude of magnesium release from three common soil minerals; vermiculite, prochlorite and mica.

2. To compare the release of magnesium to that of other lattice constituents; namely, potassium, iron and aluminum.
3. To study the chemical and physical changes of the minerals as they are affected by the intensity of chemical weathering and removal of lattice ions.

REVIEW OF LITERATURE

Importance of Magnesium in Plants

Magnesium is an essential element for the growth of plants. It is the only metallic element in the chlorophyll molecule and occupies a position in plants analogous to the iron of hemoglobin of the blood. Magnesium is a necessary cofactor in many of the enzyme reactions in the metabolism of all plants. In this capacity it aids in the translocation of starch and is believed to be essential for the formation of oils and fats, and in the translocation and absorption of phosphorus. The highest concentrations of magnesium are in those parts of the plant concerned with the vital processes such as the seeds and leaves with relatively lower concentrations being found in the stems and roots (Cooper et al., 1947).

Availability of Soil Magnesium

Magnesium occurs in the soil in water soluble, exchangeable, and fixed forms as well as being present within the crystal lattice of primary and secondary minerals. The supply of the total magnesium that is available to plants is dependent upon the presence and nature of the magnesium bearing minerals, operation of magnesium fixation phenomena, the soil weathering processes, and the balance between exchangeable ions (Bear, 1951).

The displacing power of the divalent cations places them in the normal lyotrophic order, magnesium < calcium < barium, but the ease

with which these cations are displaced when once in combination with the complex is magnesium < calcium < barium (Weigner and Jenny, 1927). Jenny (1936) was of the opinion that the explanation lay in the solubility of the hydroxides where $Mg(OH)_2 < Ca(OH)_2 < Ba(OH)_2$. Mattson (1933) concluded that Jenny's explanation was inadequate since sequioxides combine with bases only above the isoelectric point. He felt that the stability was due to the stability of the silicate group. Kardos and Joffe (1938) showed that the affinity of Mg^{++} for the $SiO_3^{=}$ ion is greater than for Ca^{++} and that the stability of magnesium in its compounds is irrevocably related to the oxygen ion, with the degree and magnitude of the attraction being modified by the atom to which the oxygen is attached (such as H, Si, C, P and S). With electrodialysis studies Mattson (1933) and Prince and Toth (1937) found that the per cent of exchangeable magnesium released was relatively low in comparison to the other exchangeable cations. Magnesium, under these conditions, reacted in the same manner as iron and aluminum which is indicative of a high degree of stability of the Mg-silicate structure.

Prince et al. (1947) reported that magnesium fixation occurred in about one-half of the soils with which they worked. Other investigators (Gorski and Glebowski, 1961; Mattson, 1933; Prince, 1951) have observed similar fixation of magnesium by soil materials. MacIntire et al. (1934) were of the opinion that in the soil system two types of acid complexes are operative. One reacts with magnesic materials to form exchangeable complexes. The other reacts much more extensively with excessive incorporation of magnesium over an extended period of time to form absorption complexes not measurable by conventional methods, although measured by successive agitated extractions with 0.02 N nitric acid. Prince et al. (1947) in their work with New Jersey soils have described an "ideal soil" as one in which the exchange complex is occupied by 20 per cent hydrogen, 65 per cent calcium, 10 per cent

magnesium and 5 per cent potassium on an equivalent basis. However, in only six of the twenty soils studied was the magnesium present to the extent of 10 per cent of the exchange complex.

Mineral Sources of Magnesium

Many primary minerals commonly found in soils contain appreciable quantities of magnesium within their crystal structure. For example; biotite 2-20 per cent, horneblende 2-26 per cent, talc 10-20 per cent, olivine 27-51 per cent, augite 6-20 per cent and magnesite 25-28 per cent. The secondary minerals of soils also contain substantial amounts of magnesium; vermiculite 22-24 per cent, illite 1-4 per cent, chlorite 20-38 per cent and montmorillonite 0-25 per cent.[1] No consistent correlation between the total magnesium in soils and their crop producing power were noted by Prince et al. (1947).

Release of Nonexchangeable Magnesium to Plants

Weathering of primary minerals either found in or added to the soil may release substantial amounts of plants nutrients to readily available forms. Vageler (1933) has stated that "under equal conditions of trading and transport tropical soils are worthless unless their content of primary minerals is considerable." Van Der Marel (1947) found that primary minerals were the source of nearly all of the calcium, magnesium and potassium absorbed by plants from Indonesian soils. The colloidal weathered fractions supplied practically none of the cations. He has shown that although the mineral andesine weathers quite slowly,

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[1]All values expressed as per cent MgO.

even when treated with hydrochloric acid, it was able to supply most crops with the necessary potassium when present in large amounts. Liberation of magnesium from finely ground olivine was sufficient to meet the needs of plants when combined with sandy soil at the rate of 0.2 gram of olivine to 500 grams of soil (Semb and Oien, 1961). Release of magnesium was influenced by the degree of fineness of the material and directly proportional to the degree of acidity. Graham (1941) demonstrated that the sand and silt fraction of certain soils deliver enough nutrients to produce nearly normal plants. Longstaff and Graham (1951) employed horneblende, olivine, talc, magnesite and dolomite as magnesium sources for soybeans in sand and colloidal clay mixtures. Plants supplied with magnesite and dolomite were able to utilize 45 and 66.5 per cent, respectively, of the total magnesium present. Olivine also supplied sufficient magnesium to produce near normal plants. Horneblende and talc released meager amounts of magnesium. Albrecht et al. (1938) have reported possible breakdown of colloidal inorganic clay, resulting in a portion of the lattice magnesium becoming available for plant consumption.

In determining the weathering or decomposition of a slightly soluble mineral by means of plants it appears that the nature of the mineral (the crystal lattice and condition of the surface), the surface area, stage of weathering, acidity, temperature and species of plant are among the determinative factors (Steenbjerg, 1964).

Release of Lattice Magnesium by Chemical Weathering

The preponderance of magnesium in common primary and secondary minerals in soils is octohedrally coordinated and has been thought to be released too slowly to meet the requirements of rapidly growing plants.

Release of non-exchangeable magnesium has commonly been measured by attack of the crystal lattice with acid solutions. Correns and his co-workers (1961), have made extensive studies of the course of decomposition of various minerals (potassium feldspar, albite, leucite, muscovite, tremolite, olivine and volcanic glass). They found that the decomposition rate of these minerals was dependent upon water flow rate, grain size, temperature and pH of the solutions. Jackson et al. (1948) state that weathering rates are controlled by intensity and capacity factors operating as a function of time. They list as intensity factors temperature, rate of water movement, acidity of solutions (proton intensity, H^+), biotic activity and the degree of oxidation (electron intensity) and its fluctuation (oxidation reduction, Δe^-). Capacity factors listed were specific surface of the particles and the nature of the minerals being weathered.

Several examples of acid dissolution methods have appeared recently in the literature. Stahlberg (1961) found a greater percentage of their magnesium than of their calcium was released from augite and horneblende when boiled in normal hydrochloric acid; these two minerals were more stable than phlogopite and particularly biotite. Release of non-exchangeable calcium and magnesium varied greatly among 131 cultivated topsoils. Acid treatment of finely crushed olivine with boiling normal nitric and hydrochloric acid released 44-67 per cent of its magnesium content. The solubility of the olivine was directly proportional to the degree of acidity (Semb and Oien, 1961). Complete removal of the octohedral cations of biotite and glauconite in relatively short periods of time (8 hours) was accomplished by Gastuche and Fripiat (1962) using 2 N hydrochloric acid in saturated silica solutions at elevated temperatures (74-100° C). Their work demonstrated that the octohedral cations were much more mobile and susceptible to acid dissolution than were those in the tetrahedral layer.

The acidity of naturally occurring soils and artificially acidified clays and soils is due mainly to the presence of exchangeable aluminum (Coleman, 1953; Low, 1953). It has been postulated that after the exchange of basic ions with H ion, the H ions disappear from the exchange positions and are replaced by aluminum ions which are either a part of the interior of the crystal lattice (tetrahedral or octohedral positions) or part of free $Al(OH)_3$ and Al_2O_3 which are present in the soil or clay as impurities. Magnesium ions and possibly Fe^{++} or Fe^{+++} can be replaced to the surface in a similar way. If the H ion is replaced on the surface by Mg ions, the Mg ions can again be replaced by other hydrogen ions and this process can be repeated until all of the magnesium is exhausted. Barshad (1960) has demonstrated that the relative proportions of Mg^{++} and Al^{+++} displaced was dependent on the total MgO and Al_2O_3 contents of the crystal structure of the acidified minerals, the nature of the acidifying solution and technique of acidification. From a consideration of the geometry of the crystal structure of the clay mineral he has postulated that the H ions enter the interior of the crystal lattice as a bare proton rather than as a hydronium ion (H_3O). Droste (1960) envisions the weathering of the brucite layer of chlorites as a buildup of a hydration envelope at the weathered edges of the lattice due to the attack of externally opposed hydroxyl groups by hydrogen ions. As each hydroxyl is changed to water, half a divalent charge and one-third of a trivalent charge would no longer be needed to balance the negative charge of the hydroxyl with a resultant excess positive charge building up. As hydroxyls change to water, a certain amount of the octohedral cations go into solution and leave the structure. Only those cations necessary to balance the charge of the mica layers persist in the lattice. Murray and Leininger (1956) proposed that the mechanism for weathering chlorite and illite seems to include oxidation of the iron in the lattice with subsequent

release of magnesium and potassium. Correns (1961) concluded that the often-reported hypothesis that an exchange of alkali ions by hydrogen or hydronium ions occurs in the weathering of feldspars and mica is not correct. Any excess positive charge would be carried by the residual aluminum. He does not, however, account for hydrogen or hydronium ions in the decomposition products. Nash and Marshall (1956) on the other hand, are of the opinion that the first reaction of decomposition is one of cation exchange with hydrogen replacing the cation of the mineral. Garrel and Howard (1957) working with potassium feldspars reached a similar conclusion. They report "The first result of reaction is a surface layer that grades from an outer portion that is structurally disrupted to an inner portion that retains the original silicate structure but with hydrogen substituted for potassium." The above workers are in complete accord as to the presence and general nature of the "structurally disrupted" portion of the lattice. Correns (1961) refers to this as the "residue layer" and has estimated its thickness and chemical composition. The thickness of the residue layer in his experiments varied with pH and treatment but generally was between 0.01 and 0.2 μ thick.

Release of Lattice Ions as a Rate Controlled Process

Release of magnesium from the mineral lattice by acid attack has been characterized as a first-order reaction. The rate of magnesium release from H-saturated hectorite has been measured by Kerr et al. (1956). Two consecutive first order reactions were occurring; (1) strong acid was undergoing a rapid, spontaneous reaction to weak acid, and (2) the resulting weak acid was undergoing a slow spontaneous reaction to yield neutral clay. For each milliequivalent of strong-acid hydrogen undergoing reaction, one milliequivalent of Mg ion was

released from the crystal lattice. In addition, for each milliequivalent of weak-acid hydrogen ion undergoing reaction, one millimole of silica was released from the lattice. Their proposal consisted of a two step reaction. The rate determining step in the first reaction series consisted of a proton attacking the monohydroxylated Mg at the crystal edge resulting in formation of water. The Mg ion would then be instantly released from the lattice and a second proton would quickly become attached to the highly nucleophilic Si-O system. The resulting dihydroxylated silicon was assumed to be a monobasic weak acid. This acid could then undergo a relatively slow first order hydrolysis, or depolymerization, to be released from the edge of the lattice as a low molecular weight silicate or silicic acid. Upon release of magnesium and silica, the freshly exposed crystal edge would be identical with the crystal before attack and the same sequence of reactions could be repeated. Osthaus (1955) measured the release of magnesium using acid dissolution techniques. He concluded that release of iron, aluminum and magnesium were first order reaction with respect to acid concentration, temperature and concentration of undissolved ion in the lattice.

Preferential removal of lattice ions in solutions which do not drastically affect the basic structure of the mineral have also been reported. Removal of potassium from vermiculite and biotite by leaching with 0.1 N NaCl was found to be a first-order reaction (Mortland and Ellis, 1959; Ellis and Mortland, 1959; Mortland, 1958). The rate limiting step in the sequence of reactions was proposed to be film diffusion. Diffusion of ions through solution films is a first-order reaction and can be written in logarithmic form as:

$$\ln \frac{dC}{dt} = \ln B - \frac{qD}{vl} t$$

where C is the amount of ion remaining in the mineral at time t, B is a constant, q is the cross-sectional area of the diffusion film, V is the

volume of the diffusion chamber, l the thickness of the diffusion film and D the diffusion coefficient.

Other possible rate limiting reactions listed by Mortland and Ellis (1959) for potassium release were the amount of ion remaining in the mineral and diffusion of the ion from the mineral particle. Each can be expressed as an equation for a straight line.

Meller (1958) has shown that for the former process:

$$\ln \frac{dC}{dt} = \ln A - kt$$

where C is the amount of ion remaining in the mineral at time t, A is a constant and k is the first order rate constant.

Solution of Fick's diffusion equation, as given by Jost (1952), simplifies to a logarithmic form for diffusion of ions out of a slab.

$$\ln \frac{\bar{C} - C_f}{C_i - C_f} = \ln \frac{8}{\pi^2} - \ln At \qquad A = \frac{\pi^2 D}{h^2}$$

where $\bar{C}$ is the average concentration diffusing out of the particle, C_i and C_f are the initial and final concentration of ion within the particle, t is the time, h is the width of the particles and D is the diffusion coefficient.

METHODS AND MATERIALS

Three minerals were used in the study; a mica, a prochlorite and a vermiculite.

The mica and prochlorite samples were obtained from Wards Natural Science Establishment. These two minerals were passed through a 140 mesh sieve using a file and agate mortar to grind the samples down to the proper size. This constituted the < 110 μ fraction. Two additional fractions were obtained for use in the experiment. One was the fraction which passed through a 270 mesh sieve but remained on a 325 mesh sieve (44-53 μ) after shaking mechanically for 12 hours. The other fraction was obtained by grinding samples in an automatic mortar and pestle under acetone to approximately 2 μ, and then separating the 0.2-2.0 μ fraction by sedimentation and centrifugation. This treatment was apparently quite harsh and resulted in the loss of soluble cations from the lattice.

The vermiculite sample was obtained from the Zonolite Company and the < 2 μ fraction obtained by sedimentation. The sample was found by X-ray diffraction to contain vermiculite plus some mica interstratified with vermiculite.

The < 2.0 μ fraction of vermiculite and the 0.2-2.0 μ fraction of the mica and prochlorite were calcium saturated with 0.1 $\underline{N}$ $CaCl_2$, washed free of chloride with distilled water, dried at 100° C and ground in an agate mortar to pass a 140 mesh sieve.

Analysis of the < 110 μ fraction of prochloride and mica and the < 2 μ fraction of vermiculite for magnesium, potassium, iron and aluminum is given in Table 1.

Table 1. Chemical analysis, location and source of minerals used in the leaching studies.

Mineral	Per cent				Location and Source
	Mg	K	Fe	Al	
Vermiculite	12.41	3.26	5.47	6.82	- Zonolite Co.
Mica	13.82	7.80	3.40	5.87	Cotopaxi, Colo. Ward's
Prochlorite	18.63	0.07	5.52	7.81	Chester, Vt. Ward's

Four gram mineral samples were leached in a constant temperature chamber maintained at 30 ± 0.5^{o} centigrade. Leaching solutions used were 0.05 N $CaCl_2$, 0.05 N $CaCl_2$ adjusted to pH 5.0, and 0.05 N $CaCl_2$ adjusted to pH 3.0. The pH of the 0.05 N $CaCl_2$ solution was determined to be 6.8. The solution acidity was adjusted with HCl. A constant ionic strength of 0.075 was maintained in each of the different leaching solutions by removing an amount of $CaCl_2$ corresponding to the amount of HCl added.

Each sample was leached at a constant rate of 4 milliliters per minute for a total of 8640 minutes. The constant leaching rate was maintained using a carefully controlled hydraulic head.

Samples were prepared for leaching in the apparatus shown in Figure 1 in the following manner:

A number 50 Whatman filter paper was placed in the bottom of a 9 centimeter Buchner funnel. The rubber gasket was set on the filter paper and the sample to be leached was evenly spread on the filter paper inside the gasket. Another filter paper was then placed over the sample and the plastic inset was inserted within the Buchner funnel and bolted into place. The four corner bolts were tightened by hand using wing nuts to provide a watertight seal. When the sample was prepared for leaching in this manner, a sample approximately 1 millimeter thick was contained between the two filter papers.

Samples of the leachate were taken at timed intervals during the leaching period and analyzed for potassium, magnesium, iron and aluminum. The pH of the leachate at each sampling time was recorded.

Magnesium was determined on a Perkin Elmer model 303 atomic absorption unit. Two thousand parts per million lanthanum was added to the sample prior to determination to prevent any possible interference from aluminum and silicon. Potassium was determined on the Coleman flame photometer. Iron was determined colorimetrically using a

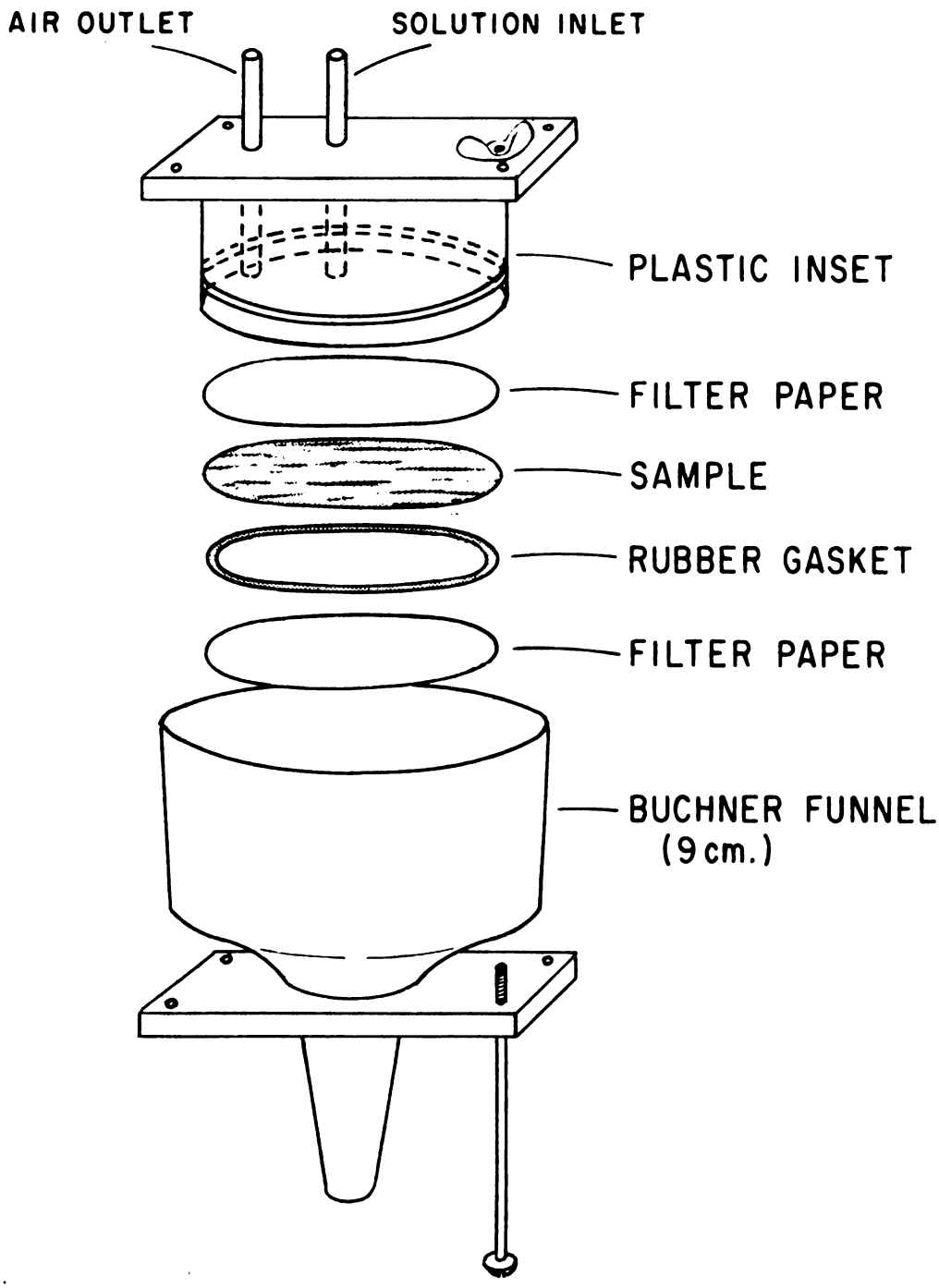

Figure 1. Diagram of apparatus used to leach mineral samples.

12 milliliter sample by the o-phenanthroline method as described by Jackson (1958). Aluminum was also determined colorimetrically using the aluminon procedure of Cheney (1955). The pH was determined on a model G Beckman pH meter.

After leaching, the sample was washed free of chlorides with distilled water and part of the sample was taken for X-ray analysis. The remaining portion was divided for differential analysis and for analysis of total potassium, magnesium and iron.

The calcium-saturated, leached fraction taken for differential thermal analysis was dried in the air and passed through a 140 mesh sieve. Prior to analysis it was placed in a constant humidity room for at least four days. Unleached samples were calcium saturated and prepared in the same manner. Thermograms were prepared using an instrument manufactured by the Robert L. Stone Company, Austin, Texas. Heating rate of the furnace was 13° C per minute. A resistance of 150 ohms was used for the mica and vermiculite and 200 ohms for the chlorite.

The second portion of the leached sample, as well as unleached samples, were sodium saturated using 0.1 N NaCl and washed free of excess salt with methanol using a Buchner funnel under suction. The sample was air dried and ground finely in an agate mortar after which it was dried for 2 hours at 100° C and duplicate 0.1 gram samples taken for analysis. Magnesium, potassium and iron were determined as described previously on HF digests by the method of Jackson (1958).

Oriented specimens were prepared for X-ray diffraction by depositing 30 milligrams of material on ceramic plates. Samples requiring dispersion treatment were boiled for 5 minutes in 2 per cent Na_2CO_3, transfered to a 100 milliliter plastic centrifuge tube and centrifuged at a speed sufficient to throw down the solid material.

The supernatant solution was completely decanted and the mineral sample dispersed in 100 milliliters of distilled water. This treatment was only necessary for the vermiculite samples and the 0.2-2.0 μ fraction of the prochlorite and mica. Tracings were made with the Phillips-Norelco X-ray unit using a copper source and a nickel filter. Specimens were glycerol solvated, magnesium saturated and dried over calcium chloride. When heat treatments were desired the specimens were potassium saturated using 0.1 N KCl and washed free of chlorides prior to heating.

RESULTS AND DISCUSSION

Release of Magnesium, Potassium, Iron and Aluminum from Mineral Sources

In all of the leaching experiments, the logarithm of the rate of potassium or magnesium release plotted against time decreased linearly after approximately 3000 minutes. Prior to this time the rate of release decreased rapidly with time. This relationship was consistent regardless of particle size, pH, or mineral with the exception of prochlorite when leached at a pH of 6.8. The plot was either a continuous linear function of decreasing rate to termination of the experiment (apparent first order kinetics) or an initial linear plot which approached a constant rate (apparent zero order kinetics) during the latter stages of leaching. The kinetics of potassium release appear to be essentially the same as those reported by Mortland (1958), Ellis and Mortland (1959), and Mortland and Ellis (1959). They concluded that the rate-limiting step in potassium release from biotite and vermiculite was probably film diffusion.

Iron and aluminum were not detected in the leachate solution at pH 6.8. Aluminum was found in the leachate at pH 5.0 but only in small amounts and during the initial minutes of leaching. There was no measurable release of iron at pH 5.0. Rate of release curves for iron and aluminum at pH 3.0 were quite different from those of potassium and magnesium. Initially, little or no aluminum or iron was detected in the leachate. A rapid increase to a peak rate of release occurred between 360 and 720 minutes after initiation of leaching. This peak rate was followed by a slow decrease in release rate to the termination of the leaching time.

Vermiculite

Only the < 2.0 μ fraction of vermiculite was used in the study, therefore no data were obtained for the influence of particle size on the release of the different elements from this mineral.

The rate of release of magnesium and potassium with respect to the three acidity levels used is shown in Figure 2. The logarithmic rate of release for both potassium and magnesium yielded linear functions at each pH after leaching for 3000 minutes. The possible exception was for potassium at pH 3.0 where potassium release went to zero at 7200 minutes of leaching. In any event the plot was linear over the range from 1500 to 6300 minutes before dropping abruptly to zero.

Magnesium release increased with decreasing pH with the rate of release being in the ratio of approximately 1:1.2:5.6 over the linear range with leaching solutions of pH 6.8, 5.0 and 3.0 respectively.

Analysis of the leachate for iron and aluminum revealed that neither were present in measurable quantities at pH 6.8. Small amounts of aluminum were detected at pH 5.0 but were present only in the early stages of leaching (prior to 2100 minutes). Iron was not detected in the leachate at pH 5.0. At pH 3.0 appreciable amounts of both iron and aluminum were present in the leachate. During the early stages of leaching the rates of iron and aluminum release actually exceeded that of magnesium (Figure 3). At the 2160 minute sampling time the ratio of Mg:Al:Fe was about 1:1:1 but at the end of leaching the ratio was approximately 3.3:2.5:1.

Initially the ratio of Mg:Al:Fe in the vermiculite, as computed from Table 1, was 2.3:1.2:1. During the final minutes of leaching the ratio of release of these elements into solution was 3.3:2.5:1. The preferential retention of iron in the mineral is evidently taking place. Furthermore, the ratio of Mg:Al in the mineral was 1.8:1 but at the

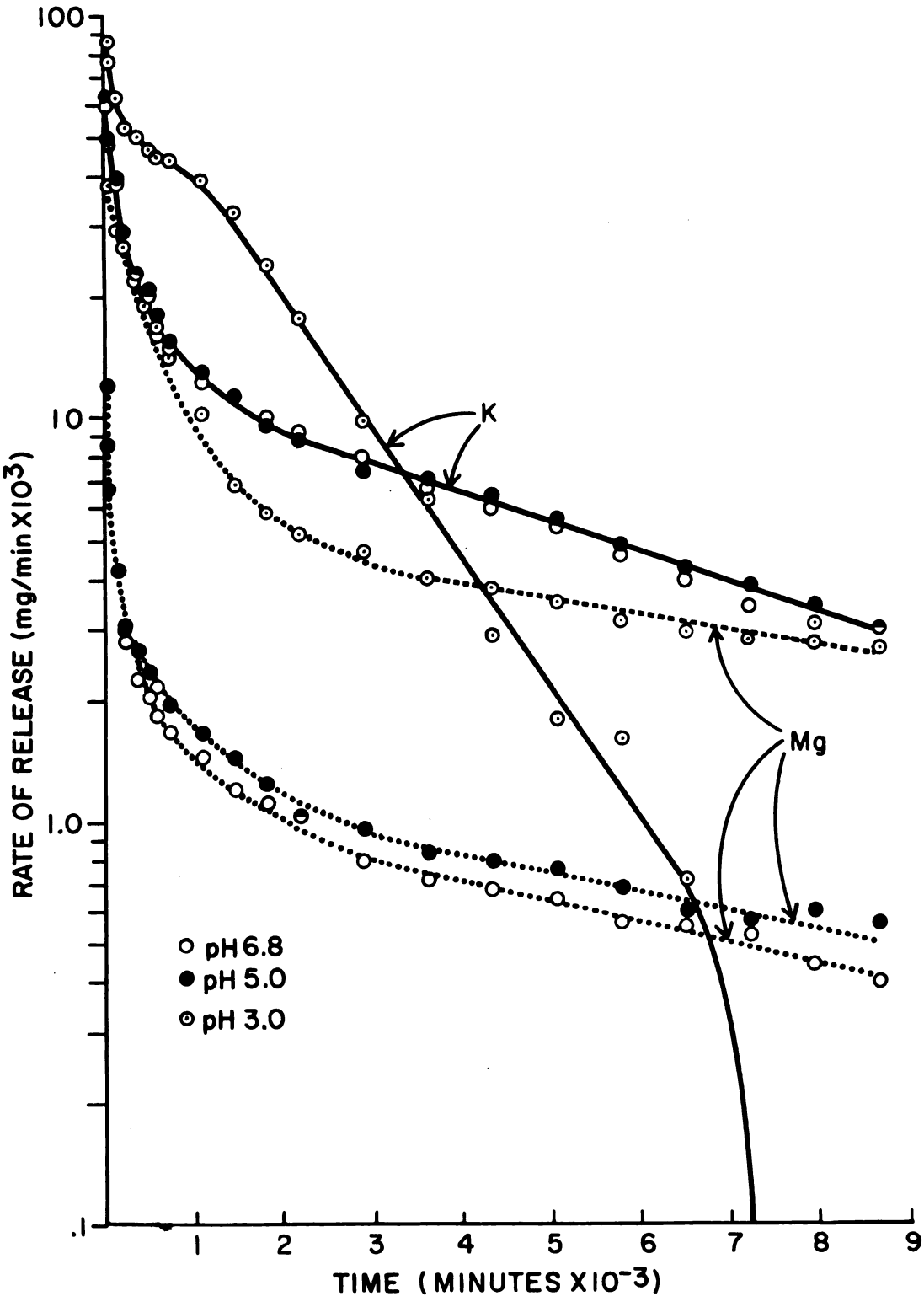

Figure 2. Rate of release of Mg and K from the $< 2\ \mu$ fraction of vermiculite leached with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

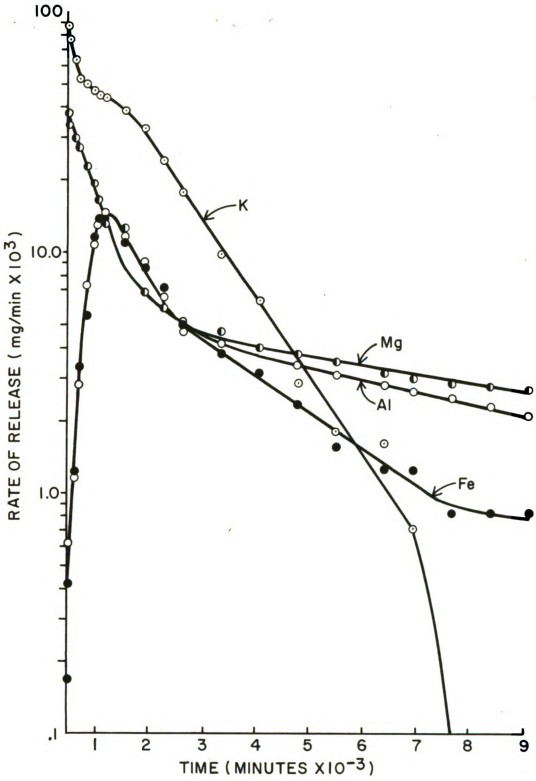

Figure 3. Rate of release of Mg, K, Fe and Al from the $<2\ \mu$ fraction of vermiculite leached with 0.05 N $CaCl_2$ at pH 3.0.

termination of leaching the ratio was 1.3:1. Obviously aluminum is being released at a higher rate than magnesium at this particular point in relation to its content in the mineral. An examination of Figure 3 indicates that this is probably only a temporary relationship since the two curves are slowly diverging. In due time it could be expected that the relationship will be reversed or a better assumption would be that a point will be reached when the ratio of release will correspond to their relative proportions in the mineral.

Potassium release did not vary at the two higher acidity levels and the final total analyses (Table 2) indicates there was little difference in the final concentration of potassium following either treatment. At pH 3.0, however, the release of potassium was markedly different over the entire time period and no potassium could be detected in the leachate following the 6480 minute sampling. The total amount of potassium remaining in the vermiculite after leaching was still 0.79 per cent, however, indicating that 24 per cent of the total K still remained in the mineral in a very resistant state.

The total analysis of the leached and unleached vermiculite indicate an increase in the per cent composition of iron and magnesium and a large decrease in potassium. Since all analysis are based on a dry weight basis it appears that the large loss of potassium and probably silicon in comparison to the lower losses of magnesium, aluminum and iron has resulted in a net increase in per cent composition of magnesium and iron. This is to be expected if the release of magnesium, aluminum and iron is essentially occurring at the surface of the particle, and potassium and silicon are being removed somewhat preferentially. Correns (1961) reported the data of Bohmeke (1946) who has worked with the decomposition of muscovite. For the $< 1\ \mu$ size fraction at pH 5.8 and 22° C the ratio of K:Al:Si release was about 16:1:14. At pH 3.0 the ratio was 4.5:1:3.5. Since iron does not appear in the leachate at

Table 2. Per cent Mg, K and Fe prior to and after leaching the < 2 μ fraction of vermiculite with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

Treatment	Per cent		
	Mg	K	Fe
Unleached	12.53	3.26	5.47
pH 6.8	12.53	1.37	5.47
pH 5.0	12.62	1.25	5.47
pH 3.0	12.82	0.79	5.79

pH 6.8 and 5.0 it would seem that an increase in per cent iron should be noted in the respective total analysis, but this is not the case.

The only detectable change revealed by X-ray analysis (Figure 4) was the disappearance of the interstratified mica-vermiculite fraction of the sample with apparent alteration to vermiculite. The loss of the interstratified material increased with decreasing pH.

Differential thermograms are shown in Figure 5 for leached and unleached calcium saturated samples. No differences in the low temperature endothermic peaks is evident with treatment. The high temperature endotherms, however, are more pronounced with all of the leached samples. The two endotherms observed at 880° and 960° C have been categorized as resulting from a two stage loss of hydroxyl water (Mackenzie, 1957) and are observed to vary with leaching treatment. Both the intensity of the high temperature endothermic peaks and their positions have been altered by the leaching treatments. The exotherm between 300° and 400° C is from the loss of methanol which was used to wash the clays following the leaching treatment.

Mica

Rate release curves for potassium and magnesium from mica at the three pH levels are shown in Figure 6. The most interesting aspect of the plot is the apparent non-dependence of potassium release on pH for this material once the linear portion of the curve is established. This could be interpreted as supporting the proposal of Mortland and Ellis (1959) that the rate limiting step for K release is film diffusion. With the exception of the 0.2-2.0 μ size fraction where the potassium was already 55 per cent depleted before initiation of the leaching, the intensity of potassium release was essentially the same regardless of pH or particle size.

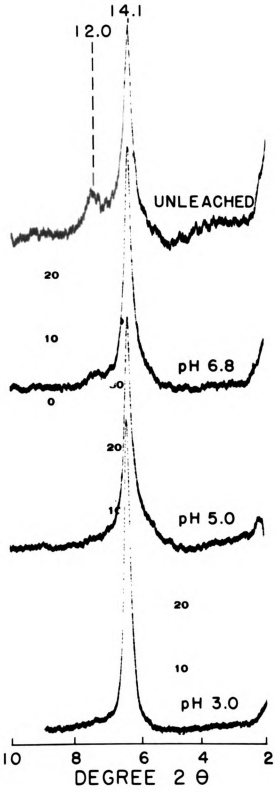

Figure 4. X-ray diffraction patterns for the < 2 μ fraction of vermiculite prior to and after leaching with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

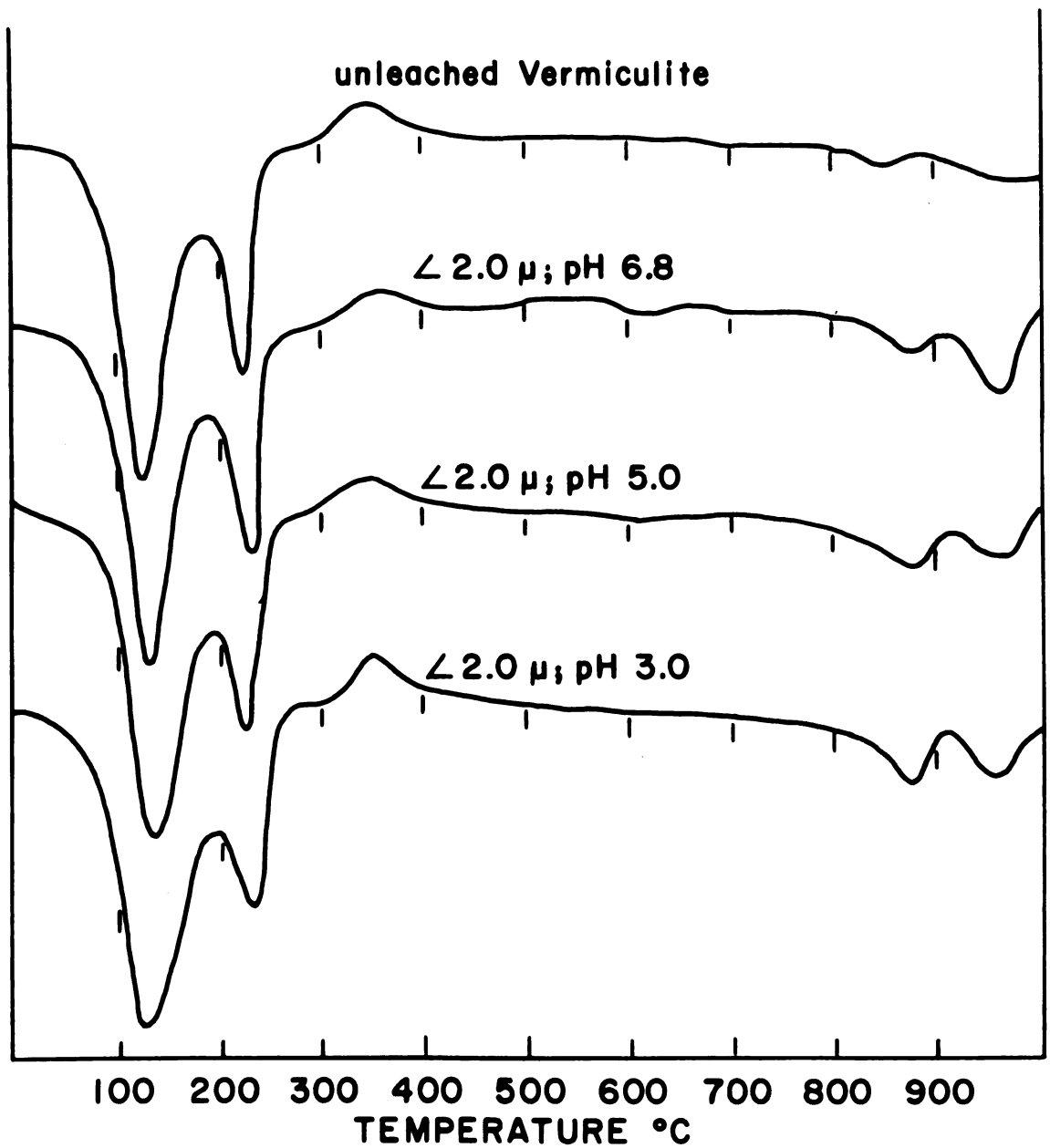

Figure 5. Differential thermal analysis curves for the < 2 μ fraction of vermiculite prior to and after leaching with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

Magnesium release was affected considerably by acidity, expecially at pH 3.0 as compared to pH 6.8 and 5.0 (Figure 6). Release rates at the two higher pH values varied in the early stages of leaching but as leaching time increased the difference between the release rates decreased. The release of magnesium at pH 3.0 was about seven times greater than that at pH 5.0 and 6.8 at the termination of leaching. This was evidently due to the decomposition of the lattice structure of the mica. At pH 3.0 the release of aluminum at all sampling times after 360 minutes was greater than and essentially paralleled that of magnesium (Figure 8). At the two higher pH levels magnesium release gave two straight line components after a rapid initial drop. At pH 6.8, the last 2880 minutes of leaching were characterized by apparent zero order kinetics. A change in the rate of magnesium release at pH 5.0 is observed at 5100 minutes, but a linear decrease is still noted.

Size is an important factor in the release of magnesium as indicated by Figure 7. Release of magnesium increased with increasing surface area. The effect of size on magnesium release seems to be more pronounced than is the effect of pH. The amount of magnesium released from the 0.2-2.0 μ fraction approaches the rate release of magnesium from < 110 μ fraction leached at pH 3.0. At pH 3.0 however the entire lattice is being decomposed.

Release of K was not as affected by size as was the release of magnesium. The 0.2-2.0 μ fraction as mentioned earlier was "weathered" considerably in the process of grinding and separation and is not a legitimate comparison with the "unweathered" fractions. A change in the rate of potassium release is observed with the 44-53 μ size fraction at about 4800 minutes. Ellis and Mortland (1959) reported a similar change in rate when leaching biotite with 0.1 N NaCl. At pH 3.0 potassium release is characterized by a change in slope at about 2160 minutes followed by a linear decrease with the ratio of potassium,

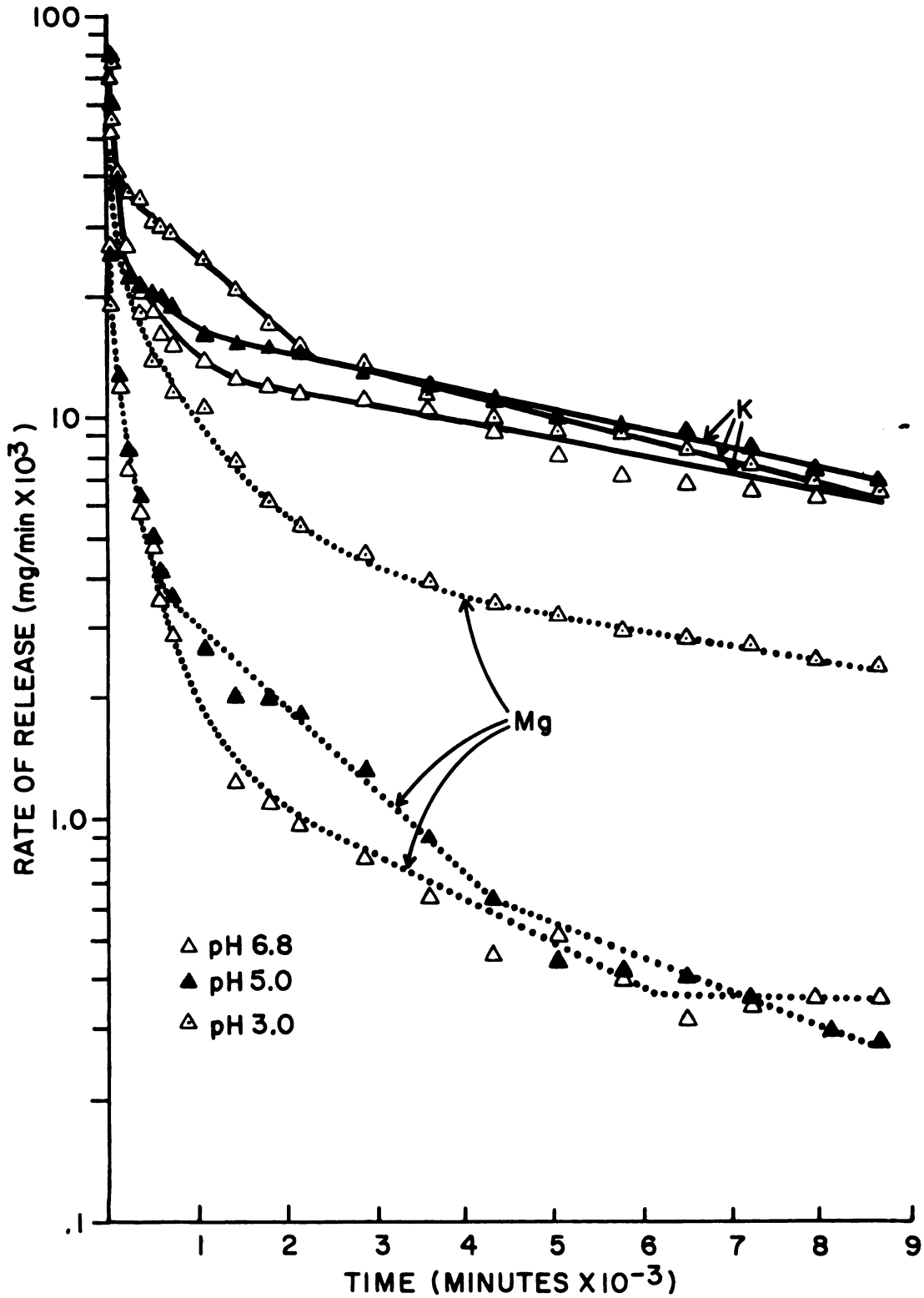

Figure 6. Rate of release of Mg and K from the < 110 μ fraction of mica leached with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

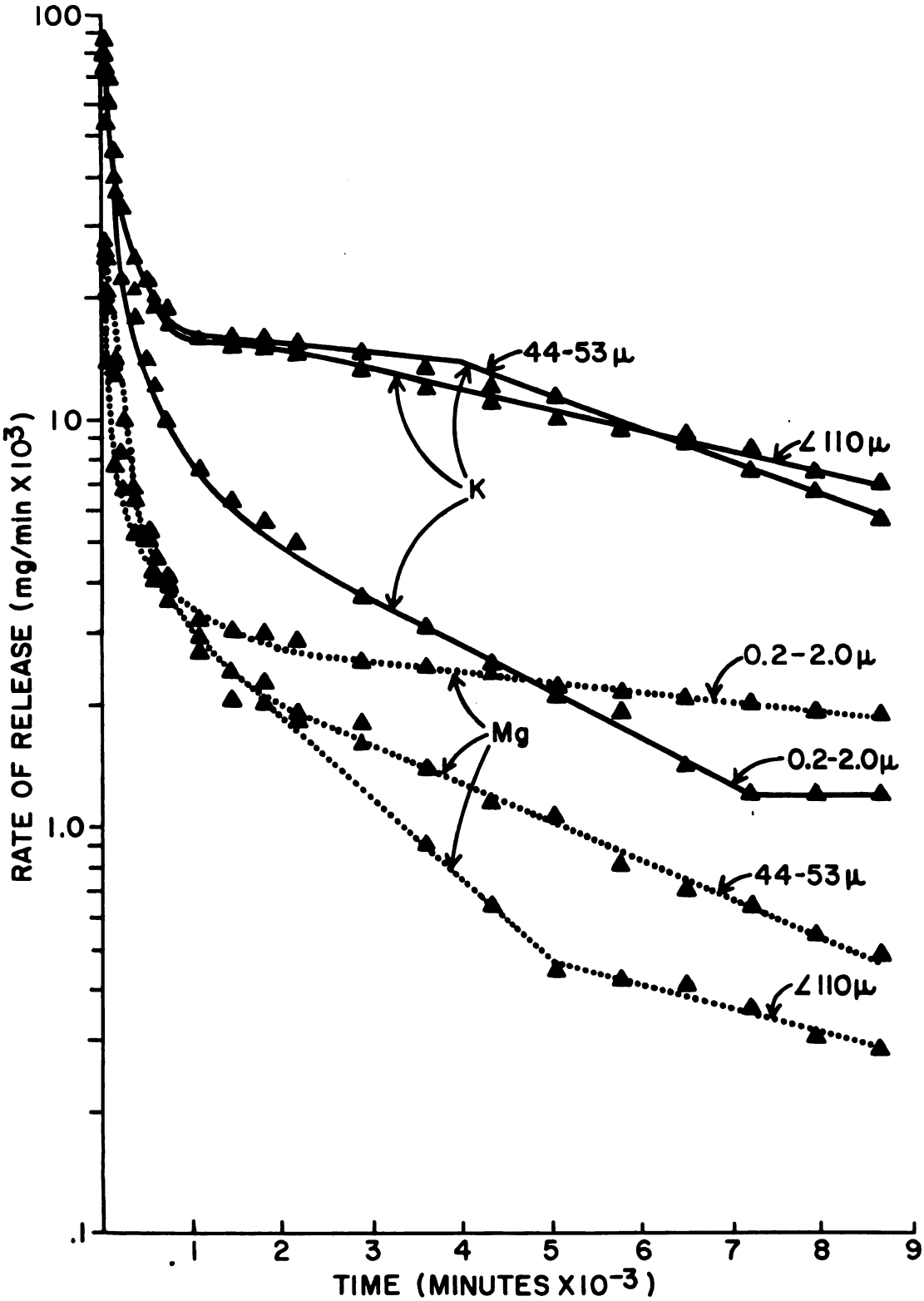

Figure 7. Rate of release of Mg and K from the < 110 μ, 44-53 μ, and 0.2-2.0 μ fractions of mica leached with 0.05 N $CaCl_2$ at pH 5.0.

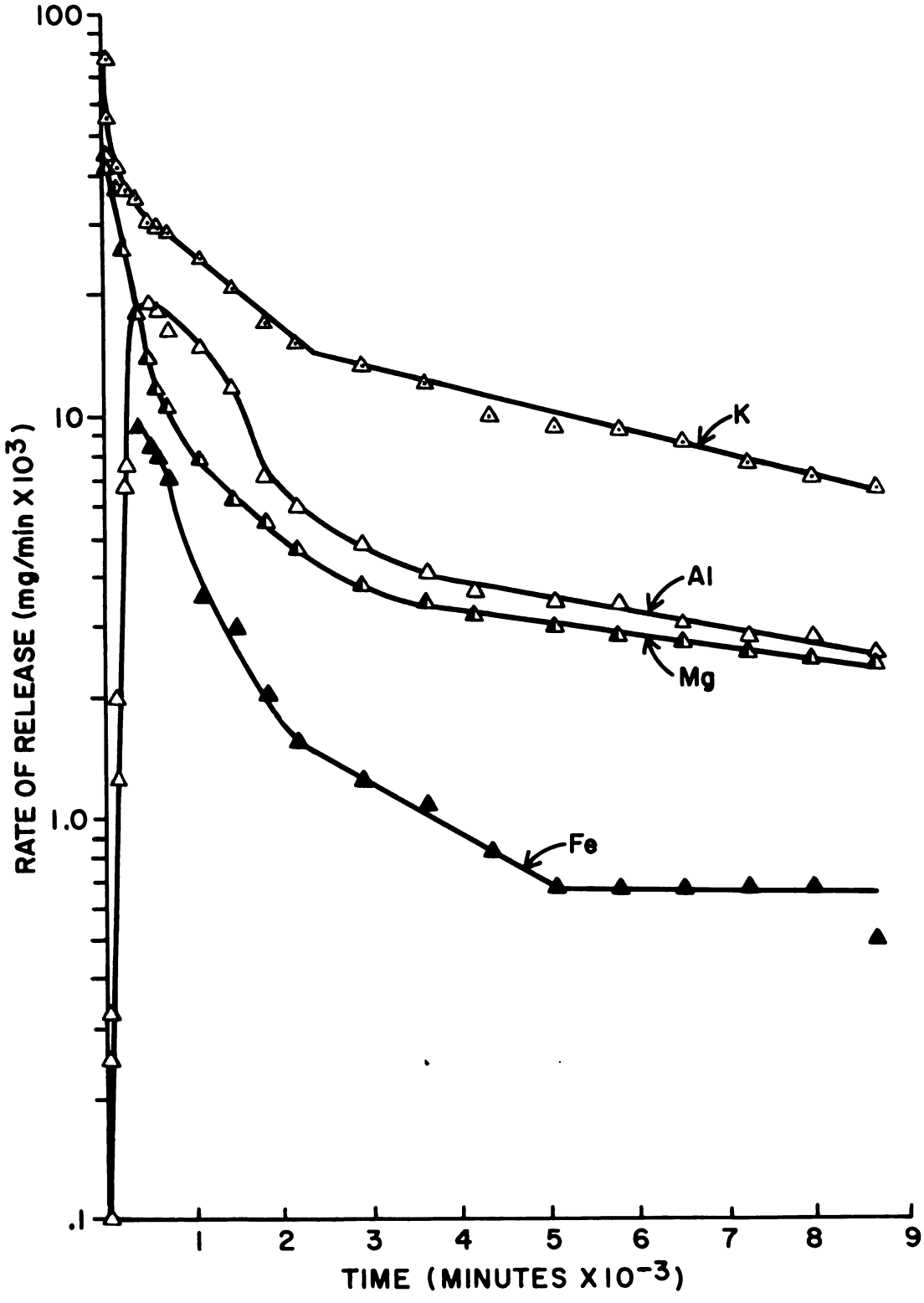

Figure 8. Rate of release of Mg, K, Fe and Al from the $< 110\ \mu$ fraction of mica leached with 0.05 N $CaCl_2$ at pH 3.0.

magnesium, iron and aluminum remaining roughly the same for the duration of the leaching treatment. The change in the slope of the K curve is at the same point where the aluminum and iron release curves change slopes. A re-examination of the data for the 44-53 μ fraction leached at pH 5.0 showed that the change of slope noted for the potassium release occurred at the identical point where aluminum was last detected in the leachate solution. This indicates that the release of aluminum and possibly iron in some way is related to the release of potassium from the mica at the lower pH treatments. Cook and Rich (1963) have demonstrated that expansion of muscovite does not occur when treated with acid solution (10 per cent HCl) and the mineral merely decomposes.

As with the vermiculite, there is a preferential retention of iron within the mica. The formation of a residue layer is evidently occurring and the release of magnesium is probably being controlled by diffusion through this layer. An increase in the total iron content of the material is apparent with each treatment from the total analysis shown in Table 3.

The X-ray diffraction patterns for glycerol-solvated specimens of leached mica (Figure 9) indicate that it is quite readily weathered to vermiculite regardless of treatment. The percentage undergoing weathering did not increase appreciably with decreasing pH for the < 110 μ size fraction. As particle size decreased, however, a higher proportion of vermiculite was formed as indicated by the relative intensities of the 10 and 14 Å peaks.

Differential thermograms of the leached and unleached mica (Figure 10) showed the effect of the leaching treatment on the physical and chemical structure of the mica. The tracing of the original mica gave a shallow endotherm between 0° and 350° C and a small exotherm at about 870° C. With any subsequent treatment the two endotherms at 130° and 230° C, indicating release of the absorbed interlayer water,

Table 3. Per cent Mg, K, and Fe prior to and after leaching various size fractions of mica with 0.05 $\underline{N}CaCl_2$ at 6.8, 5.0 and 3.0.

Treatment	Per cent		
	Mg	K	Fe
< 110 μ, unleached	13.82	7.80	3.40
0.2-2.0 μ, unleached	11.50	3.62	4.00
< 110 μ, pH 6.8	13.62	5.08	3.48
< 110 μ, pH 5.0	13.72	4.63	3.45
< 110 μ, pH 3.0	13.82	4.50	3.50
44-53 μ, pH 5.0	13.81	4.40	3.59
0.2-2.0 μ, pH 5.0	11.35	2.95	4.23

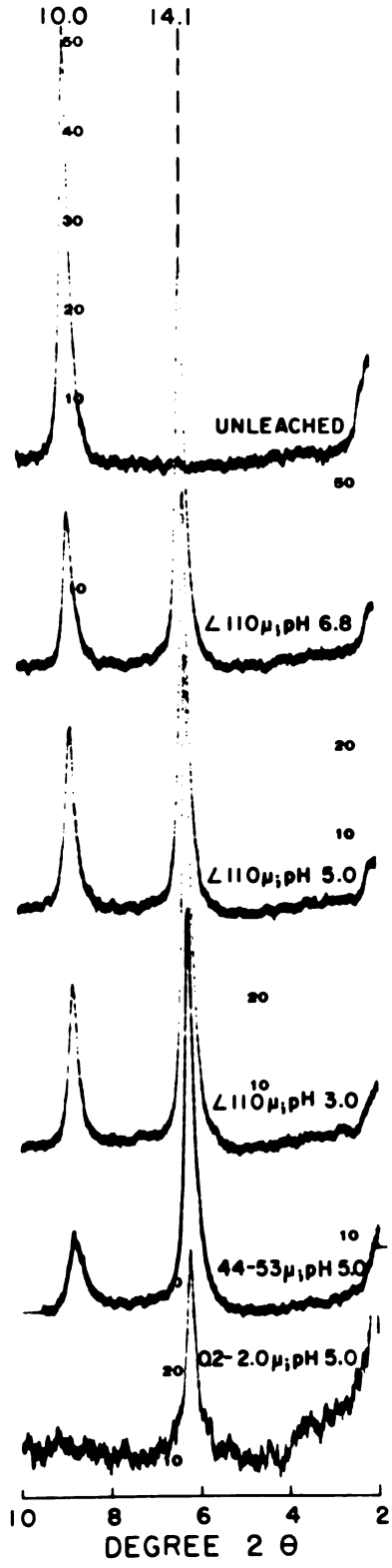

Figure 9. X-ray diffraction patterns for the < 110 μ, 44-53 μ, and 0.2-2.0 μ fractions of mica prior to and after leaching with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

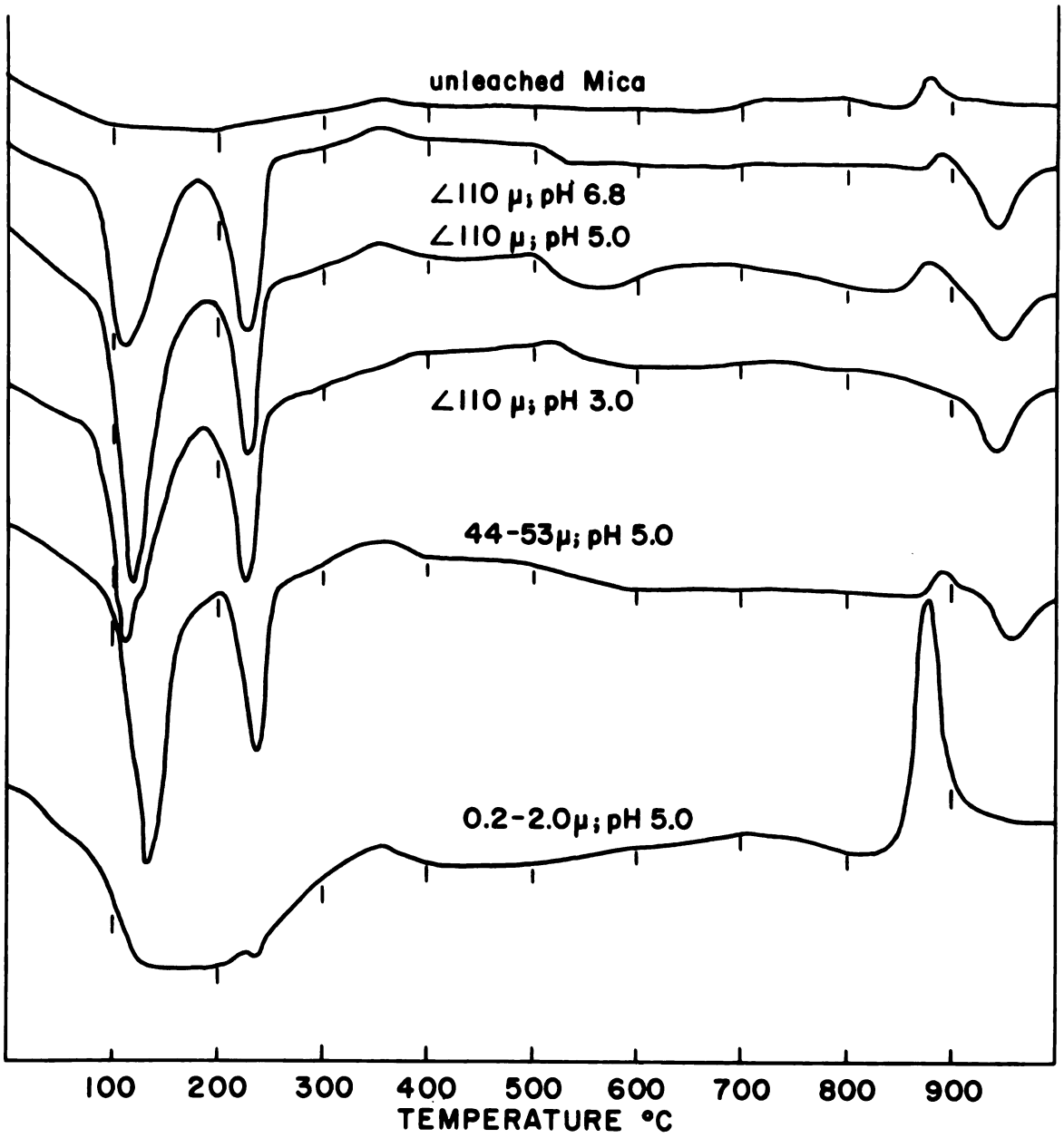

Figure 10. Differential thermal analysis curves for the < 110 μ, 44-53 μ and 0.2-2.0 μ fractions of mica prior to and after leaching with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

were the most conspicuous peaks. The low temperature endotherm of the 0.2-2.0 μ fraction was not separated into two distinct endotherms but rather a single, broad endotherm. At a pH of 6.8 and 5.0 the exotherm at 870° is still noticeable and the appearance of a small endotherm at about 950° is evident. At pH 3.0 the exotherm disappears altogether and a rather broad endotherm at 950° is the only high temperature peak.

Leached samples of 44-53 μ material at pH 5.0 gave thermograms identical to the < 110 μ material at that pH. The leached 0.2-2.0 μ fraction, however, was very much different from the other leached samples in that it exhibited no noticeable high temperature endotherm. The exotherm at 870° was about 8 times more intense with this treatment. The exotherm at 870° C can be attributed to decomposition of the octohedral layer and formation of a spinel type mineral. The endotherm at 950° is probably associated with the breakdown of the anhydrous structure. The order of the exotherm-endotherm inversion is usually reverse of that noticed here with the endotherm appearing before the exotherm. The position of the endotherm may be associated with the formation of an amorphous glassy phase at about 950°. This phase is formed between the alkali and silica in the structure. It has been suggested that the width of the endothermic peak may indicate the amount of potassium in the mineral (Kerr, Kulp and Hamilton, 1949). When most of the potassium was removed following the leaching of the 0.2-2.0 μ fraction the endotherm at 950° also disappeared.

Prochlorite

Prochlorite is classified as an aluminum rich chlorite consisting of alternating mica and brucite sheets. The mica sheet is thought to be negatively charged with excess substitution of aluminum for silicon in the tetrahedral layer and Al^{+++}, Fe^{+++}, Fe^{++} and Mg^{++} occupying the

octohedral sites. The brucite sheet is a layer of magnesium hydroxide with varying amounts of Fe^{+++} and Al^{+++} resulting as a residual positive charge. These sheets are held to one another primarily by electrical attraction and by hydrogen bonds between the hydrogens of the hydroxyls of the brucite sheet and the oxygens of the mica sheets.

The magnesium in both the brucite and mica sheets is octohedrally coordinated. The prochlorite differs from the vermiculite and the mica used in the leaching experiments in that the magnesium is available from either the mica or brucite layer and is thought to be held with less energy in the brucite layer. Total magnesium in the prochlorite was about 50 per cent greater than that found in either the mica or the vermiculite.

Linear plots of the logarithmic rate of release against time were obtained for magnesium at pH 3.0 and pH 5.0, but a non-linear plot was obtained for release at pH 6.8. Therefore, the rate of release with respect to magnesium is a first order reaction at the two lower pH levels but not at pH 6.8 (Figure 11).

Rate of magnesium release from the < 110 μ and the 44-53 μ fractions, was identical for the first 5400 minutes (Figure 12). At this time an increase in the release rate was noted for the 44-53 μ fraction relative to the release of magnesium from the <110 μ material which continued to decrease logarithmically. Magnesium release from the 0.2-2.0 μ fraction dropped rapidly from an initial high rate to the linear portion of the curve. The high initial rate is probably due to the large number of exposed magnesium ions at the broken edges.

Several workers have written of the apparent ease of dissolution of the brucite layer (Bayliss, 1964; Droste, 1962; Weaver, 1950; Jackson, 1957; Klages and White, 1957). The magnesium from this layer is supposedly much more mobile than that of the mica layer. Once the magnesium is removed preferentially an expanding lattice

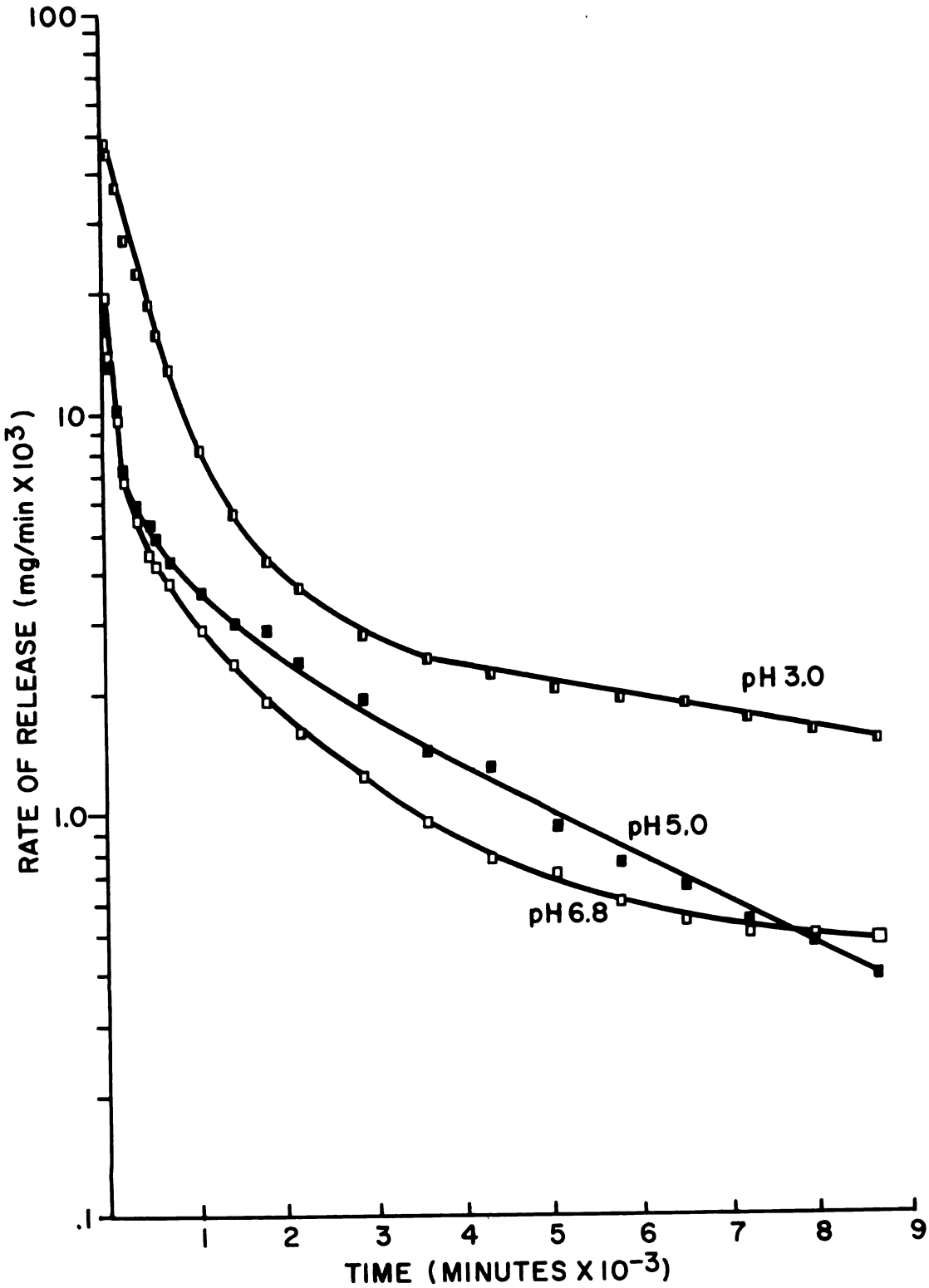

Figure 11. Rate of release of Mg from the < 110 μ fraction of prochlorite leached with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

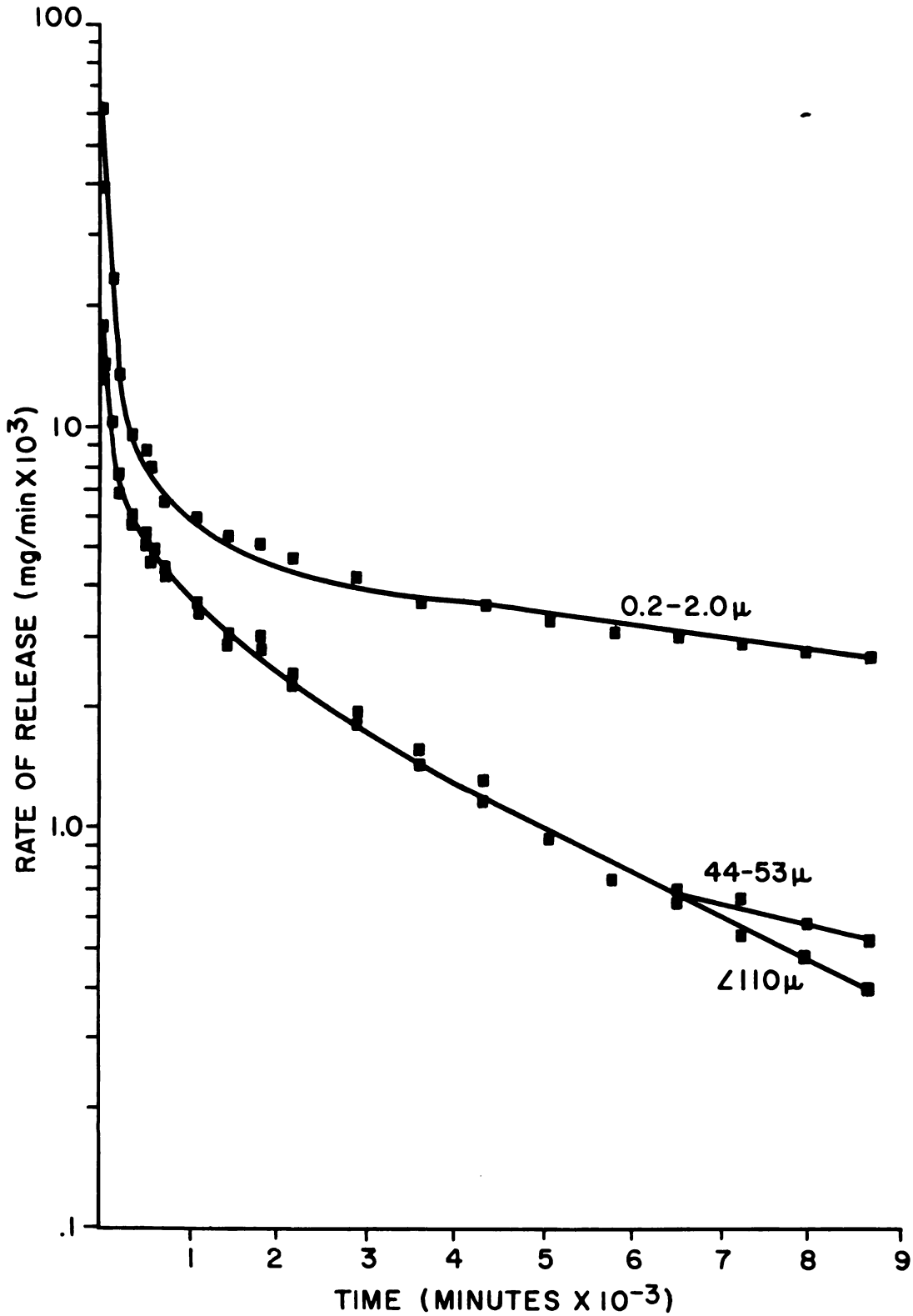

Figure 12. Rate of release of Mg from the <110 μ, 44-53 μ and 0.2-2.0 μ fractions of prochlorite leached with 0.05 N $CaCl_2$ at pH 5.0.

mineral should be formed. However, a comparison of the release of magnesium from the mica and the prochlorite does not indicate a difference in magnesium release as great as would be expected if this were the case. The magnitude of their release is more in the order of the initial amount of magnesium present than for preferential release from the brucite layer.

X-ray tracings of glycerol-solvated specimens of the leached chlorite samples indicate that there was no expansion of the lattice structure following any of the treatments (Figure 14). Also, potassium saturation of the specimen followed by heating to 450° C indicated no contraction of the lattice. Either the loss of magnesium was not sufficient to allow a freely expanding lattice because the treatments were not rigorous enough, or there was not sufficient differential release and the lattice was simply dissolving at the surface. To test whether the treatments used were severe enough to effect alteration, three 0.5 gram samples of the 44-53 μ fraction prochlorite were placed in quart containers and solutions of 0.01 N HCl, 0.1 N HCl and 1.0 N HCl in 0.05 N $CaCl_2$ were added. The containers were placed in an oven regulated at 60° C and allowed to remain for 10 days. The supernatant solution was decanted twice during the incubation period and replaced with new solution. At the termination of the experiment it was visually evident that there was a large loss of total material, especially in the 1.0 N HCl. Neither glycerol solvation nor potassium saturation and heating to 450° C gave any indication of lattice expansion or collapse following the acid treatments. Since a series of acidified salt solutions ranging from 1.0 N HCl to near neutrality had not caused collapse or expansion it is concluded that under the conditions of this experiment, the release of magnesium from the prochlorite was essentially a surface reaction. Further evidence that magnesium is not released preferentially from the brucite layer is that the ratio of Mg:Al:Fe being released at pH

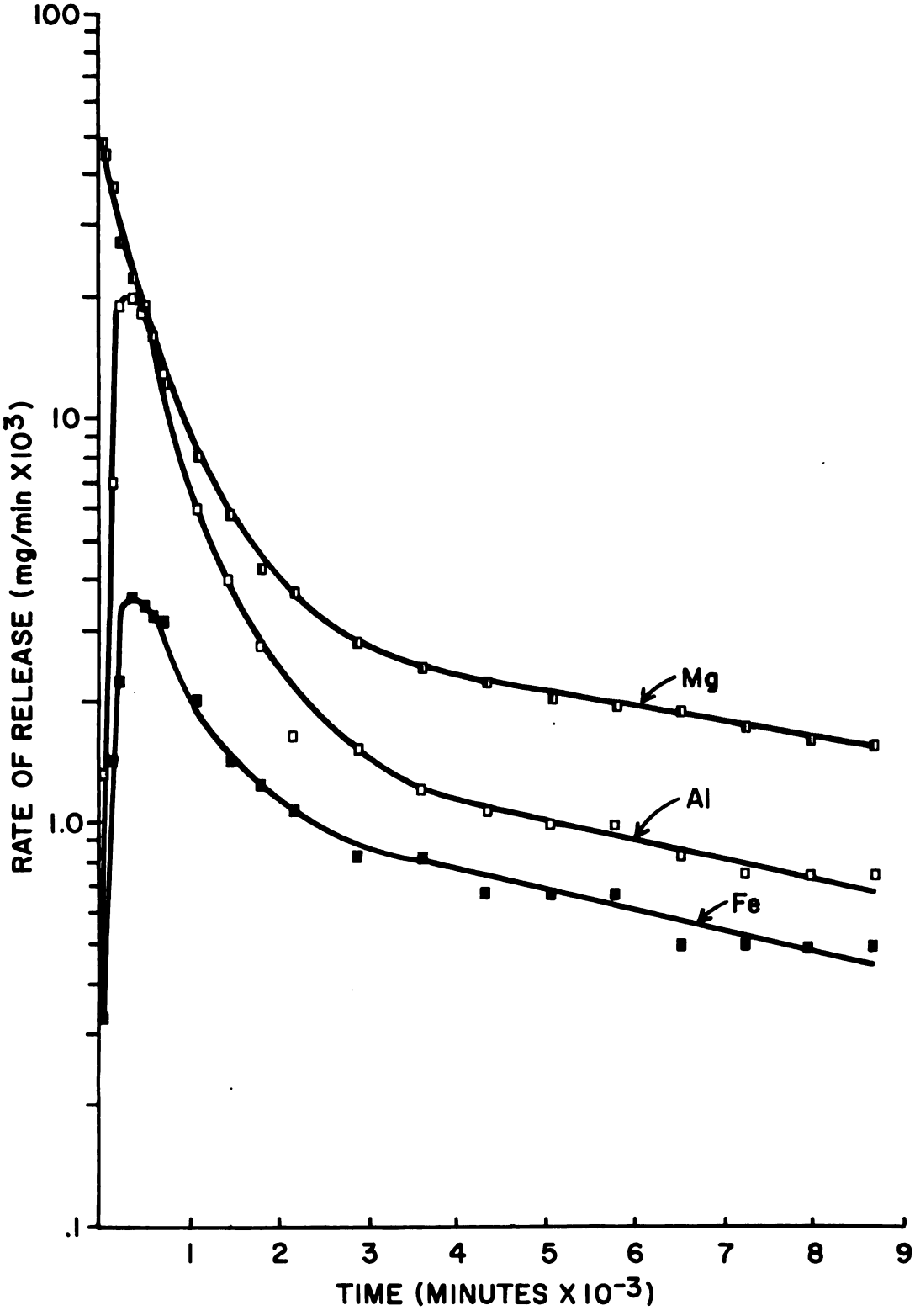

Figure 13. Rate of release of Mg, Fe and Al from the < 110 μ fraction of prochlorite leached with 0.05 N $CaCl_2$ at pH 3.0.

3.0 (Figure 13) is 3.1:1.5:1. The ratio in the mineral is 3.4:1.4:1. The equilibrium release of the constituents is nearly identical to the mineral composition.

The total analysis of leached and unleached samples of prochlorite are given in Table 4. Increases in total iron are not evident at pH 6.8, 5.0 and 3.0 for the < 110 μ size fraction. Leaching the 0.2-2.0 μ material at pH 5.0 resulted in a 10 per cent increase in the total iron content of the sample. Magnesium increased when leaching < 110 μ samples at pH 6.8 and 5.0 and when the 44-53 μ fraction was leached at pH 5.0. All other treatments resulted in slight decreases in total magnesium.

Thermograms for the unleached and leached prochlorite samples are shown in Figure 15. With decreasing particle size and leaching the endotherm between 0° and 350° C became more pronounced. The major endotherm located at 670° C for the original sample tended to move to a lower temperature with decreasing particle size. The size of the endotherm also decreased markedly with the 0.2-2.0 μ fraction. Martin (1955) noted the same tendency with chlorite samples and attributed the smaller amplitude as being due to the energy required to remove the hydroxyl water from the brucite layer. The third endotherm located at 850° C is attributed to dehydration of the mica sheet and almost disappears with the 0.2-2.0 μ material. The major exothermic peak is observed at 870° C. The amplitude of the exotherm increased with decreasing particle size and leaching. This peak is due to the recrystallization of the chlorite to form olivine. A small exothermic peak is noted for the < 110 μ unleached material. Martin (1955) has concluded that the reason for a smaller exothermic reaction is due to steric hinderance and simultaneous reaction. The large particles prevent the rapid expulsion of OH water and the gradual elimination of water takes place at the same time that the recrystallization reaction occurs.

Table 4. Per cent Mg, K, and Fe prior to and after leaching various size fractions of prochlorite with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

Treatment	Per cent		
	Mg	K	Fe
< 110 μ, unleached	18.63	0.07	5.52
0.2-2.0 μ, unleached	16.60	0.03	5.30
< 110 μ, pH 6.8	19.43	0.12	5.52
< 110 μ, pH 5.0	18.67	0.11	5.37
< 110 μ, pH 3.0	18.08	0.07	5.17
44-53 μ, pH 5.0	18.86	0.04	5.10
0.2-2.0 μ, pH 5.0	16.40	0.03	5.85

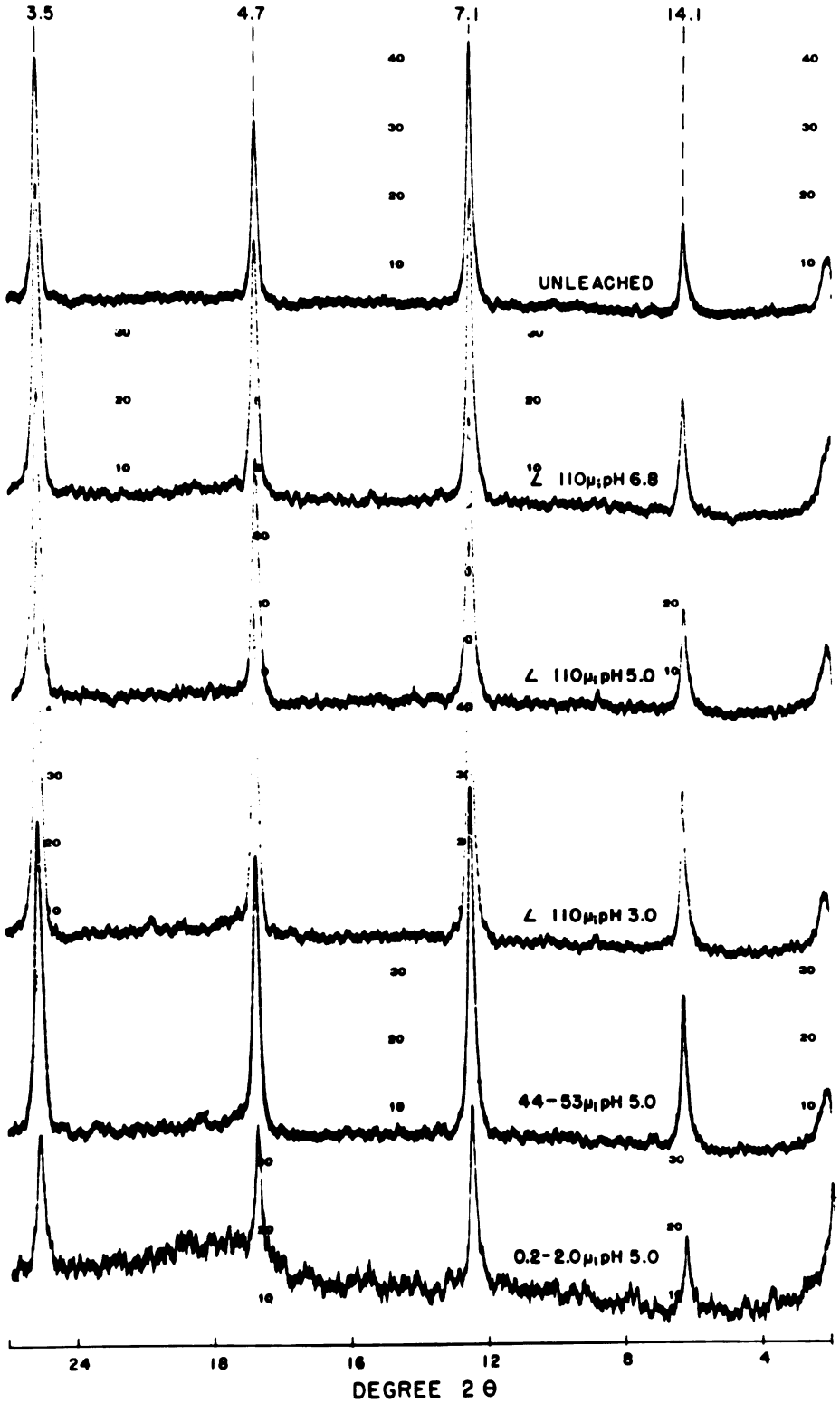

Figure 14. X-ray diffraction patterns for the < 110 μ, 44-53 μ and 0.2-2.0 μ fractions of prochlorite prior to and after leaching with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

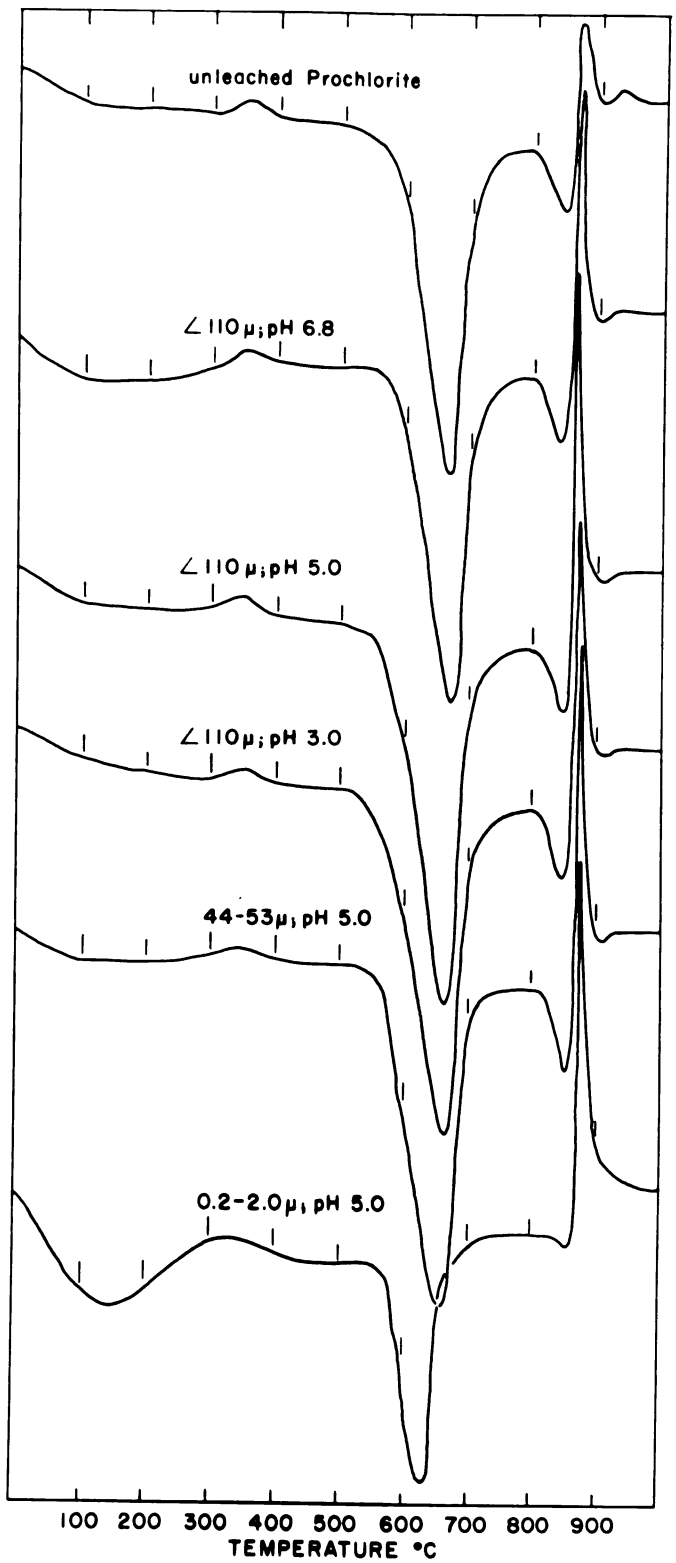

Figure 15. Differential thermal analysis curves for the < 110 μ, 44-53 μ and 0.2-2.0 μ fractions of prochlorite prior to and after leaching with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0.

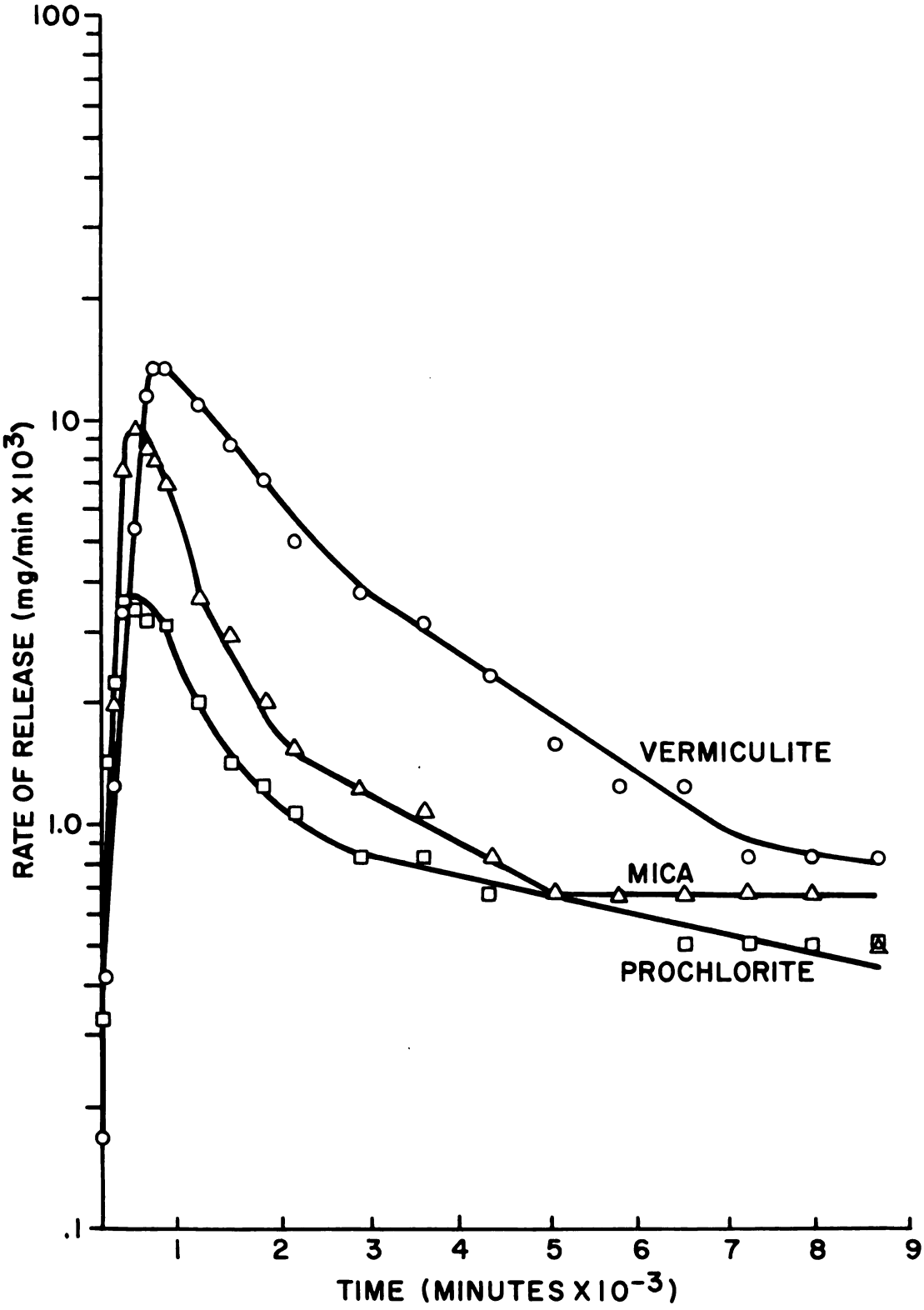

Figure 16. Rate of release of Fe from the $< 2\ \mu$ fraction of vermiculite and the $< 110\ \mu$ fraction of mica and prochlorite leached with 0.05 N $CaCl_2$ at pH 3.0.

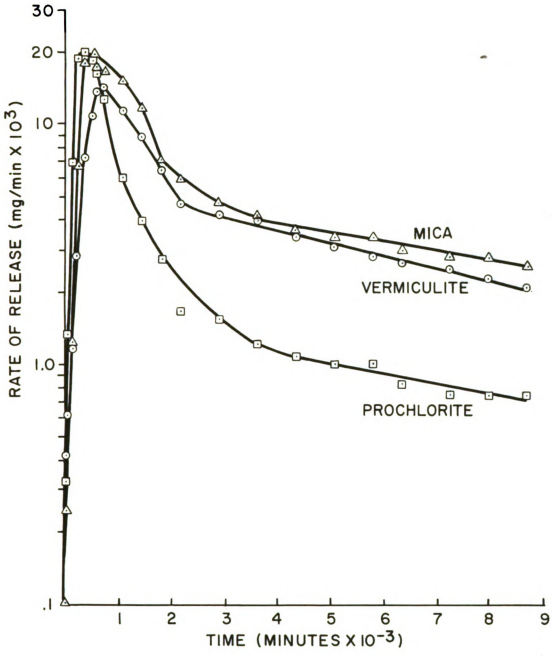

Figure 17. Rate of release of Al from the $< 2\ \mu$ fraction of vermiculite and the $< 110\ \mu$ fraction of mica and prochlorite leached with 0.05 N $CaCl_2$ at pH 3.0.

The rate of release of iron and aluminum decreased in a generally linear fashion after the initial peak release rate.

Changes in the Acidity of the Leachate Solutions

The pH of the leachate solution for prochlorite, mica and vermiculite leached with 0.05 N $CaCl_2$ at pH 6.8, 5.0 and 3.0 are given in Table 5. The pH of the leachate was initially quite high and never decreased to the initial pH of 6.8 or 5.0 when leaching the minerals with solutions adjusted to these levels. The leachate solution approached pH 3.0 very closely in all instances for this treatment, but only in the final stages of leaching.

The pH of leachate solutions for the various size fractions of mica and prochlorite leached at pH 5.0 are shown in Table 6. Decreasing particle size was associated with a corresponding increase in the final pH of the leachate solutions after 6840 minutes of leaching.

A noticeable relationship exists between minerals being leached and the pH of the leachate. This is not surprising since Stevens (1946) has proposed using the abrasive pH of a mineral as a diagnostic tool in mineral identification.

Changes in the pH of acid-mineral systems have been used as an index to weathering (Graham, 1941) but the variability encountered here would exclude using them in a purely quantitative manner. Qualitatively, however, it can be stated that a loss of hydrogen from the system coupled with a high loss of basic cations from the minerals accounts for the high initial pH of the leachate solutions. As the quantity of basic cations available for release is reduced, more hydrogen ions pass through the sample resulting in a drop in the leachate pH.

Table 5. Leachate solution pH for prochlorite, mica and vermiculite leached with 0.05 N $CaCl_2$ solutions at pH 6.8, 5.0 and 3.0. The size fraction for vermiculite is < 2.0 μ and for prochlorite and mica < 110 μ.

Time, Minutes	Prochlorite pH			Mica pH			Vermiculite pH		
	6.8	5.0	3.0	6.8	5.0	3.0	6.8	5.0	3.0
30	7.60	7.40	6.60	7.60	7.90	6.90	7.25	7.25	6.50
60	7.70	7.35	5.70	7.71	8.10	6.88	7.18	7.30	6.10
120	7.43	7.20	4.70	7.67	7.60	5.90	7.32	7.20	5.15
240	7.10	7.10	4.90	7.48	7.60	4.65	7.15	7.25	4.30
360	7.22	7.40	4.10	7.40	7.65	3.92	7.25	7.35	3.90
480	7.49	7.70	3.61	7.30	7.65	3.70	7.24	7.25	3.69
600	7.20	7.20	3.50	7.50	7.40	3.52	7.25	7.20	3.55
720	7.55	6.65	3.35	7.48	7.50	3.45	7.25	7.15	3.47
1080	7.40	7.25	3.25	7.20	7.60	3.20	7.29	6.95	3.28
1440	7.55	7.05	3.20	7.30	7.50	3.18	7.18	6.98	3.18
1800	7.40	7.38	3.12	7.35	7.20	3.11	7.08	6.95	3.14
2160	7.10	7.25	3.08	7.20	7.20	3.10	7.05	7.00	3.08
2880	7.05	7.20	3.10	7.10	7.35	3.05	7.02	7.00	3.06
3600	7.32	7.05	3.03	7.00	6.95	3.05	7.05	7.00	3.04
4320	7.15	7.05	3.05	7.08	6.85	3.03	7.15	7.10	3.02
5040	7.05	7.05	3.03	7.20	6.85	3.03	7.10	7.02	3.02
5760	7.02	6.50	3.03	6.99	6.75	3.03	7.08	6.99	3.02
6480	7.00	5.70	3.03	6.98	6.60	3.03	6.90	6.90	3.02
7200	6.90	5.60	3.03	7.00	6.70	3.03	6.90	6.82	3.01
7920	7.00	5.60	3.01	7.01	6.40	3.01	6.98	6.70	3.01
8640	7.00	5.50	3.01	7.01	6.60	3.01	6.95	6.50	3.01

Table 6. Leachate solution pH of prochlorite and mica leached with 0.05 N $CaCl_2$ adjusted to pH 5.0.

Time Minutes	Prochlorite size, μ			Mica size, μ		
	110	44-53	0.2-2.0	110	44-53	0.2-2.0
30	7.40	7.38	7.20	7.90	7.45	6.90
60	7.35	7.30	7.10	8.10	7.40	7.05
120	7.20	7.27	7.25	7.60	7.35	7.40
240	7.10	7.19	6.96	7.60	7.30	6.95
360	7.40	7.15	6.96	7.65	7.25	6.93
480	7.70	7.05	6.96	7.65	7.20	6.91
600	7.20	7.00	6.92	7.40	7.15	6.90
720	6.65	7.00	6.88	7.50	7.15	6.88
1080	7.25	6.85	6.82	7.60	7.05	6.86
1440	7.05	6.80	6.82	7.50	7.00	6.82
1800	7.38	6.75	6.80	7.20	6.98	6.80
2160	7.25	6.71	6.80	7.20	6.88	6.75
2880	7.20	6.55	6.80	7.35	6.79	6.70
3600	7.05	6.38	6.80	6.95	6.70	6.70
4320	7.05	6.25	6.78	6.85	6.60	6.70
5040	7.05	5.90	6.72	6.85	6.50	6.70
5760	6.50	5.82	6.62	6.75	6.33	6.62
6480	5.70	6.15	6.71	6.60	6.20	6.59
7200	6.60	5.79	6.71	6.70	5.90	6.59
7920	5.60	5.59	6.70	6.40	6.00	6.59
8640	5.50	5.42	6.60	6.60	6.00	6.58

SUMMARY AND CONCLUSIONS

Curves obtained by plotting the logarithmic rate of release of magnesium from mica, prochlorite and vermiculite samples against time gave straight lines except for prochlorite leached at a pH of 6.8 This indicates that the rate of release of magnesium from these minerals is an apparent first order reaction. In this respect the results given here are in agreement with those of Kerr et al. (1956) and Osthaus (1955).

The rate of magnesium release increased with decreasing particle size and pH. Consistent relationships between particle size, pH and mineral composition were not too apparent. This is especially true at pH 5.0 and 6.8 where the rate of magnesium release was quite low and changes in the slope of the release curves were observed.

Leaching of the mineral samples resulted in a general increase in the per cent composition of magnesium although it is apparent from the analysis of the leachate solution that considerable magnesium was lost from the lattice. The loss of magnesium when calculated on a total weight basis is apparently being "camouflaged" by the release of large amounts of potassium and probably silicon from the vermiculite and mica samples.

Release of octahedral magnesium is not accompanied by release of proportionate quantities of iron and aluminum contained in the lattice when leached at pH 6.8 and 5.0. At pH 3.0 there is preferential retention of iron within the mineral. Iron and aluminum remaining in the mineral must constitute a residue layer which is being formed on the surface of the particle. This residue layer is probably similar to

those reported by Correns (1961), Garrel and Howard (1959) and Nash and Marshall (1956). All indications are that the residue layer continues to increase in thickness with increasing time for the duration of the experiments.

Release of magnesium from the mineral systems at pH levels comparable to those found in soils is very small even when a strong gradient for movement of the ions such as that found in the leaching column is present. For example, the mica and vermiculite samples contained about one-half and one-fourth as much potassium as they did magnesium but the rate of release of potassium was about seventeen and six times greater, respectively, at the termination of the leaching period at pH 6.8. The total amount of magnesium released from the minerals was probably not greater than 4-5 per cent with any of the leaching treatments and was substantially less for the larger particle sizes and higher pH values. Using as an average release rate that found at 3000 minutes after initiation of leaching for the 0.2-2.0 μ fraction of mica and prochlorite and the < 2 μ fraction of vermiculite leached at pH 5.0, it could be estimated that about 5, 5 and 1.5 per cent of the total magnesium, respectively, was removed from the leached sample.

Alteration of the mica sample was quite readily accomplished with a vermiculite-like structure being formed. Solvation with glycerol resulted in expansion of the lattice from 10 to 14 Å. The proportion of < 110 μ mica which did not expand to 14 Å following leaching and treatment with glycerol was not lowered by decreasing the pH of the leaching solution. As particle size decreased, however, a greater proportion of the mica was converted to vermiculite.

Preferential weathering of the brucite layer from prochlorite was apparently not occurring during leaching of this mineral. This was confirmed by chemical and X-ray analysis. This observation is contrary

to previously published data on the weathering of chlorites. Numerous reports are contained in the literature which deal with the apparent ease of removal of the brucite layer.

The interstratified mica-vermiculite portion of the vermiculite sample was readily weathered to vermiculite as evidenced by the disappearance of this fraction from the X-ray tracing.

Iron was the most resistant of the elements to be removed by leaching from the lattice. Aluminum was detected in the leachate solution at pH 5.0 and 3.0 but iron was present only when leaching at pH 3.0. Aluminum was removed in preference to iron at pH 3.0.

A possible explanation for the magnesium release curves obtained is as follows:

1. The initial rapid rate of magnesium release is due to the exchange of magnesium by H and Ca ions at the broken edges of the particles. This is evidenced by the large initial withdrawal of H ions from solution and resultant high pH of the leachate solution in the initial minutes of leaching.

2. As release of magnesium continues the weathering front moves farther into the particle leaving a structurally disarranged residue layer rich in aluminum and iron and partially devoid of magnesium. As the pH of the system is decreased, the layer consists of less aluminum and more iron.

3. Magnesium ions located in the octohedral layer are released from these sites by H ions which, because of their size, can easily traverse the residue layer. As the leaching time increases the thickness of the residue layer increases accordingly and also the distance which the magnesium ions have to move to reach the solution phase. This results in a decrease in the rate of magnesium release with advancing time. All indications

are that the residue layer continues to increase in thickness with increasing time. Alteration in size or complexity could account for the sudden changes in rate of magnesium release which are observed at pH 6.8 and 5.0.

4. As the pH of the leaching solution is lowered there is a resulting increase in proton activity and an increased solubility of iron and aluminum. The weathering front proceeds as before but the outer edges of the residue layer are also going into solution. This results in a slower increase in the thickness of the residue layer and a resulting higher rate of release.

5. The rate limiting step in the process is probably the diffusion of magnesium through the residue layer to the bulk solution. This is especially evident at the high pH levels where the acidity apparently has little effect on the final rate of release.

LITERATURE CITED

Albrecht, W. A., Graham, E. R., and Ferguson, Carl E. Plant growth and the breakdown of inorganic soil colloids. Soil Sci. 47:455-458. 1939.

Barshad, I. Significance of the presence of exchangeable magnesium ions in acidified clays. 131:988-990. 1960.

Bayliss, P., and Loughnan, F. C. Minerological transformations accompanying the chemical weathering of clay-slates from New South Wales. Clay Min. Bull. 5:353-359. 1964.

Bear, F. E., Prince, A. L., Toth, S. J., and Purvis, E. R. Magnesium in plants and soils. N. J. Agri. Exp. Sta. Bull. 760. 1951.

Bohmeke, A. Untersuchungen uber die verwitterung des muscovit: Dissertation, Gottingen. 1946: as cited by Correns, C. W. Experiments on the decomposition of silicates and discussion of chemical weathering: in Clays and Clay Minerals, 10th Conf., Permagon Press, New York. Pp. 443-459. 1961.

Cheney, E. M. A preliminary study of aluminum and the tea bush. Plant and Soil. 6:174-200. 1955.

Coleman, N. T., and Harward, M. E. The heats of neutralization of acid clays and cation-exchange resins. J. Am. Chem. Soc. 75:6045-6046. 1953.

Cook, M. G., and Rich, C. I. Negative charge of dioctohedral micas as related to weathering: in Clays and Clay Minerals, 11th Conf., Pergamon Press, New York. Pp. 443-459. 1963.

Cooper, H. P., Paden, W. R., and Garman, W. H. Some factors influencing the availability of magnesium in soil and the magnesium content of certain crops. Soil Sci. 63:27-41. 1947.

Correns, Carl W. Experiments on the decomposition of silicates and discussion of chemical weathering: in Clays and Clay Minerals, 10th Conf., Pergamon Press, New York. Pp. 443-459. 1961.

Droste, John B. Clay mineral alteration in some Indiana soils: in Clay and Clay Minerals, 9th Conf., Pergamon Press. Pp. 329-342. 1960.

Ellis, B. G., and Mortland, M. M. Rate of potassium release from fixed and native forms. Soil Sci. Soc. Amer. Proc. 23:451-453. 1959.

Garrell, R. M., and Howard, Peter. Reactions of feldspar and mica with water at low temperature and pressure: in Clays and Clay Minerals, 6th Conf., Pergamon Press, New York. Pp. 68-88. 1957.

Gastuche, M. C., and Fripiat, J. J. Acid dissolution techniques applied to clay structure determinations and controlled by physical methods. Science of Ceramics. G. Stewart, ed. 1:121-138. 1962.

Goldich, S. S. A study in rock weathering. Jour. Geol. 46:17-58. 1938.

Gorski, M., and Glebowski, H. Fertilization with magnesium. Chem. Abst. 55:9754g. 1961.

Graham, E. R. Acid Clay--An agent in chemical weathering. Jour. Geol. 49:392-401. 1941.

Graham, E. R. Soil development and plant nutrition: I. Nutritient delivery to plants by the sand and silt separates. Soil Sci. Soc. Amer. Proc. 6:259-262. 1941.

Jackson, M. L. Frequency distribution of clay minerals in major great soil groups as related to factors of soil formation: in Clays and Clay Minerals, 6th Conf., Pergamon Press, New York. Pp. 133-143. 1957.

Jackson, M. L. Soil Chemical Analysis. Prentice-Hall, Inc., Englewood Cliffs, N. J. 1958.

Jackson, M. L., Tyler, S. A., Willis, A. L., Bourbeau, G. A., and Pennington, R. P. Weathering sequence of clay-size minerals in soils and sediments: I. Fundamental generalizations. J. Phys. and Colloid Chem. 52:1237-1260. 1948.

Jenny, H. Simple kinetic theory of ionic exchange. Jour. Phys. Chem. 40:501-517. 1936.

Jost, W. Diffusion. Academic Press, Inc., New York. 1952.

Kardos, L. T., and Joffe, J. S. Preparation, composition and chemical behavior of the complex silicates of Mg, Ca, Sr, and Ba. Soil Sci. 45:293-307. 1938.

Kerr, G. T., Zimmerman, R. H., Fox, H. A., Jr., and Wells, F. H. Degredation of hectorite by hydrogen ion: in Clays and Clay Minerals. Natl. Acad. Sci.-Natl. Res. Council Pub. 456. Pp. 340-347. 1956.

Kerr, P. F., Kulp, J. L., and Hamilton, P. K. Differential thermal analysis of reference clay mineral specimens. Prelim. Rep. No. 3 of "Reference Clay Minerals, A. P. I. Research Project 49." American Petroleum Institute, New York. 1949.

Klages, M. G., and White, J. L. A chlorite-like mineral in Indiana soils. Soil Sci. Soc. Amer. Proc. 21:16-20. 1957.

Longstaff, W. M., and Graham, E. R. Release of mineral magnesium and its effect on growth and composition of soybeans. Soil Sci. 71:167-174. 1951.

Low, P. F. The role of aluminum in the titration of bentonite. Soil Sci. Soc. Amer. Proc. 19:135-139. 1955.

Mattson, S. Laws of colloidal behavior: XI. Electrodialysis in relation to soil processes. Soil Sci. 36:149-163. 1933.

MacIntire, W. H., Shaw, W. M., and Robinson, B. The distinction between magnesium absorbed and that exchangeable four years after lysimeter incorporation of oxides and carbonates. Soil Sci. 37:289-303. 1934.

MacKenzie, Robert C. The Differential Thermal Investigation of Clays. Mineralogical Society, London. 1957.

Marel, Van Der, H. W. Tropical soils in relation to plant nutrition. Soil Sci. 65:495-501. 1947.

Martin, R. T. Reference chlorite characterization for chlorite identification in soil clays: in Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Res. Council, pub. 395. Pp. 117-145. 1955.

Meller, Alexander, and Bright, John E. The rate of reactions as a function of time. J. Phys. Chem. 62:495-497. 1958.

Mortland, M. M. Knetics of potassium release from biotite. Soil Sci. Soc. Amer. Proc. 22:503-508. 1958.

Mortland, M. M., and Ellis, Boyd. Release of fixed potassium as a diffusion controlled process. Soil Sci. Soc. Amer. Proc. 23:363-364. 1959.

Murray, H. H., and Leininger, R. K. Effect of weathering on clay minerals: in Clays and Clay Minerals. Natl. Acad. Sci.-Natl. Res. Council, pub. 456. Pp. 340-347. 1956.

Nash, V. E., and Marshall, C. E. The surface reactions of silicate minerals: Part I. The reactions of feldspar surfaces with acidic solutions. Univ. Missouri Coll. Agr. Res. Bull. 613. 1956.

Nash, V. E., and Marshall, C. E. The surface reactions of silicate minerals: Part II. Reactions of feldspar surfaces with salt solutions. Univ. Missouri Coll. Agr. Res. Bull. 614. 1956.

Osthaus, Bernard. Kinetic studies on montmorillonites and nontronite by the acid-dissolution technique: in Clays and Clay Minerals, Natl. Acad. Sci.-Natl. Res. Council, pub. 456. 1955.

Prince, A. L. Magnesium economy in the coastal plain soils of New Jersey. Soil Sci. 71:91-98. 1951.

Prince, A. L., and Toth, S. J. Electrodialysis and cation exchange studies on soils of varying organic matter content. Soil Sci. 43:205-217. 1937.

Prince, A. L., Zimmerman, Miryam, and Bear, F. E. Magnesium supplying powers of twenty N. J. soils. Soil Sci. 62:69-78. 1947.

Stahlberg, S. Studies on the release of bases from minerals and soils. IV. The release of calcium and magnesium by boiling normal hydrochloric acid. Soils and Fert. 24:37. 1961.

Steenbjerg, F. Weathering of minerals as indicated by plants. Jour. Soil Sci. 5:205-213. 1954.

Stevens, R. E., and Carron, M. K. Simple field test for distinguishing minerals by abrasive pH. Am. Min. 33:31-50. 1948.

Semb, G., and Oien, A. Preliminary investigations on the liberation of magnesium from olivine. Soils and Fert. 24:3282. 1961.

Vageler, P. An Introduction to Tropical Soils. (Translated by H. Greene.) The Macmillan Co., New York. 1933.

Weaver, Charles E. A discussion on the origin of clay minerals in sedimentary rocks: in Clays and Clay Minerals, Natl. Acad. Sci. -Natl. Res. Council, pub. 566. Pp. 159-173. 1958.

Weigner, G., and Jenny, H. On base exchange. 1st Internat'l Cong. Soil Science. Pp. 46-51. 1927.