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 SOXHLET-EXTRACTION APPARATUS.

 The University of Oklahoma, Ph.D., 1973
 Geology

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GRADUATE COLLEGE

EXPERIMENTAL WEATHERING OF CHLORITE USING

SOXHLET-EXTRACTION APPARATUS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

BEN D. HARE

Norman, Oklahoma

1973

EXPERIMENTAL WEATHERING OF CHLORITE USING

SOXHLET-EXTRACTION APPARATUS

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ABSTRACT

Previous investigations of weathering phenomena have suggested
that chlorite may be experimentally altered to a vermiculite-like
mineral by leaching certain cations from the brucite sheet. This study
was initiated to determine if, under experimental laboratory conditions,
chlorite could be so altered.

Four samples of well-ordered metamorphic chlorite (two ground to
74 microns and two ground to 37 microns) were leached with warm water
from 20 to 52 weeks in a soxhlet extractor. Periodic removals of both
solid and liquid phases were done to monitor structural and chemical
changes.

All four of the study samples underwent observable changes in
structure and composition. One of the 74-micron samples (leached for
52 weeks) and a 37-micron sample (leached for 44 weeks) showed the
greatest degree of change. The chemical data derived from fluorescence
analysis of these two samples no longer "fit" the 4-layer chlorite
model, nor were the samples completely altered to vermiculite. Instead
they appear to be an intermediate state between chlorite and vermicu-
lite, "fitting" a 3-layer clay model (like vermiculite) while lacking
some vermiculite properties.

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INTRODUCTION

Purpose of Investigation

The primary objectives of this study are: (1) to experimentally

weather, by leaching with warm-water solutions, a nonexpandible, well-

ordered chlorite both structurally and chemically, (2) to attempt to de-

fine a direction of weathering or an end product toward which chlorite

weathering proceeds, (3) to provide a general model for the weathering

of chlorite, and (4) to attempt to provide qualitative data on the rate

of chlorite weathering.

My interest in the alteration process of chlorite is an out-

growth of a Master's study done at The University of Oklahoma (Hare,

1969). In that study I had ample supportive evidence (rock fragments,

heavy minerals, light minerals, paleocurrent indicators, and others) to

postulate a Ouachita Mountain source for Thurman Sandstone sediments in

southeastern Oklahoma. However, many of the Ouachita Mountain forma-

tions have a high chlorite content (Wong, 1964; Weaver, 1958), whereas

only traces of chlorite are present in the Thurman sediments. In an

attempt to resolve this apparent anomaly, arguments by Weaver (1958) and

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Johnson (1964) that postulate the alteration of chlorite to magnesium-rich vermiculite under surface weathering conditions were used. The present study is a laboratory test of the hypothesis, stated not only by Weaver (1958) but also by Loughnan (1969) and others, that the mineral chlorite can be altered to vermiculite or a vermiculite-like mineral by weathering processes operating at or near the earth's surface.

Previous Investigations of Experimental Alteration

As part of the initial planning of this project, a literature search was made for previous investigations of experimental silicate alteration, especially alteration of phyllosilicates. This search was greatly facilitated by the Generalized Information Processing System (GIPSY), a data storage and retrieval system at the Merrick Computer Center of The University of Oklahoma.

It became apparent that experimental alteration studies fall into two main groups: (1) those that induced alteration by elevated temperatures, extremes of pH, and elevated pressures, thus yielding alteration conditions analogous to hydrothermal and other magmatic processes and (2) those that used warm- to hot-water solutions either as standing water or as circulating water under about 1 atmosphere (atm.) pressure, thus creating conditions analogous to surface, tropical weathering conditions.

Papers representative of the first group are those by Rausell-Colom and others (1964) and Norton (1937).

The second group is well represented by the work of Tamm (1929), Correns (1961), Pedro (1961), Parham (1969), Henin and Pedro (1964), and Borovec and Neuzil (1966). Of special interest to the current study are

the last four papers. These studies are pertinent because they used a soxhlet-extraction apparatus (fig. 1), as I have done for the alteration process.

Of the studies using soxhlet extraction, Pedro (1961) and Henin and Pedro (1964) studied the effects of leaching on polymineralic rock types. Parham (1969) used monomineralic feldspar species. For this study one mineral, chlorite, was used to reduce the number of variables involved in the leaching process so that more useful chemical information could be provided. It should be noted that none of the previous investigations involved the experimental weathering of phyllosilicates.

Pedro (1961) experimentally weathered samples of two volcanic rocks, basalt and trachyandesite. The experiment was run for 2 years and according to Pedro was halted when 1,600 liters of water had drained through the basalt and 1,450 liters through the trachyandesite. He noted the formation of a number of new minerals not present at the beginning of the experiment. These were boehmite (AlOOH), gibbsite (Al(OH)$_3$), hematite (Fe$_2$O$_3$), and stilphnosiderite (Fe$_2$O$_3$·nH$_2$O). Pedro thus concluded that under the conditions of the experiment the silica and the alkaline-earth cations were easily leached out, the iron and titanium were left intact, and the aluminum showed some mobility.

Borovec and Neuzil (1966) used soxhlet-extraction apparatus to weather plagioclase (An$_{60-64}$) and microcline experimentally. They summarized their results as follows:

1. K-feldspar, under the conditions of the experiment, was more stable than plagioclase.

2. The hydrolytic decomposition of both feldspars proceeded toward free hydroxides of Al and Si.

3. The migration ability of Al under conditions of neutral pH and $70^{\circ}C$ temperature was 15 to 20 times less than that of Si.

4. The origin of a semi-impermeable residual layer formed mostly by the colloidal phase of Al on the surface of feldspar grains is assumed, and this layer affects the rapidity and intensity of hydrolysis.

5. Mobility of the alkalies and Ca exists under the experimental conditions in the sequence Na > Ca > K.

6. No new crystalline phases were formed.

Parham (1969) artificially weathered microcline and a plagioclase (An_{70}) using soxhlet extractors. The experiment proceeded for 140 days, and approximately 7.0 liters of water flowed over the samples per day. Parham noted that the hot percolating water became progressively more translucent and milky when leaching the plagioclase but appeared to reach a limit with the microcline. Oxidation of minor amounts of iron were also noted, as was the formation of new crystalline phases, possibly halloysite and boehmite.

Method of Alteration Used

The apparatus used in this study to simulate natural weathering conditions was a soxhlet extractor (see fig. 1; also Pedro, 1961). The soxhlet extractor consists of three parts: (1) a boiling flask, containing the initial aqueous solution, (2) a soxhlet tube, where a paper thimble containing the mineral sample is placed, and (3) a condensing tube, where the vapor phase of the heated solution is condensed. In the present study approximately 300 milliliters (ml) of distilled water were placed in the boiling flask. After condensation of approximately 250 ml

of water in the soxhlet tube, the overflow level was reached, and the water flushed through the sample and back into the boiling flask. Thus the soxhlet extractor is a closed system where distilled water cycles through the sample as a leaching agent. Approximately 250 ml of water flushed through the sample every hour, or about 6.0 liters per day. The condensed water in the soxhlet tube was at a temperature of approximately $60^{o}C$. According to Pedro (1961) this is a high-humidity atmosphere, which serves to keep the CO_2 partial pressure at a fairly constant value.

According to Pedro (1961), the percolation water has the dissolved gases O_2 and CO_2 present in concentrations of 4.10 mg/l and 0.15 mg/l, respectively. This is contrasted with 9.15 mg/l and 0.58 mg/l in rainwater at $20^{o}C$; or approximately 1/2 as much O_2 and 1/4 as much CO_2 than the concentrations of rainwater. The lower CO_2 concentration serves to make the initial solution less acid than rainwater, i.e., the pH will remain closer to neutrality than if the CO_2 concentrations were high enough to generate appreciable amounts of HCO_3^-.

The reduced oxygen concentration serves to keep the Eh value lower than rainwater. However, the water is well aerated and oxidation of iron still occurs. This phenomenon is discussed in detail in later sections.

Condensing
Tower

condensation

Soxhlet
Tube

sample thimble

chemical leaching

Boiling
Flask

initial solution
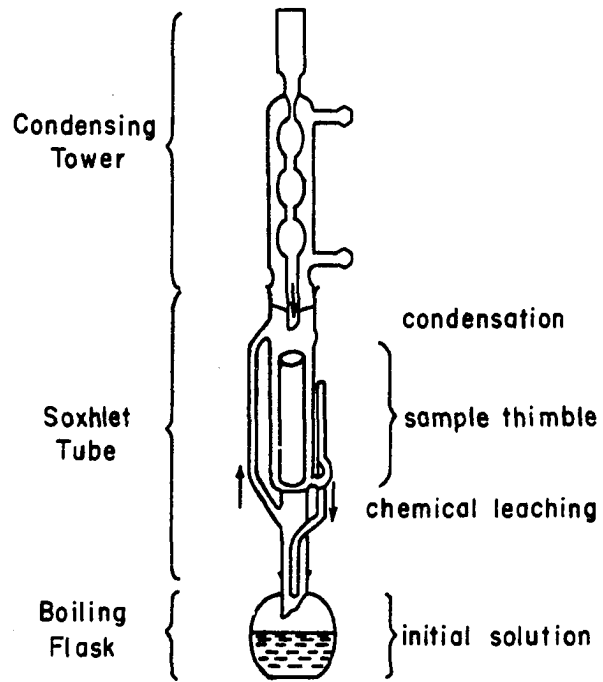
Figure I. Soxhlet Extraction Apparatus.

(After Hénin and Pedro, 1964)

METHODS OF INVESTIGATION

Several methods or techniques were used to determine the progress, if any, of the experiment. The methods were chosen to (1) demonstrate purity of the initial samples, (2) to provide chemical analyses of both initial and terminal samples, and (3) to relate structural changes of terminal samples to changes in chemical composition.

Little useful data were obtained through two of the techniques, differential thermal analysis and solution studies. The DTA analyses did indicate an absence of other mineral phases. The failure of the solution studies to yield useful data could be rectified in future experiments by imposing additional controls on the boundary conditions of the experiment. Examples are: (1) using a system that will not yield silica from the apparatus, (2) using the same amounts of starting material and not removing any of the sample for X-ray diffraction until the end of the experiment, and (3) developing more precise regulation of the temperature in the boiling flasks, thus insuring approximately similar volumes of H_2O flowing over the samples.

Further discussion of these and other methods are in the following paragraphs.

X-Ray Diffraction

X-ray diffraction patterns of the initial unweathered chlorites

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were made to closely define the structure and properties of the initial material. Of special interest were: (1) the basal (001) spacing of the unweathered material, (2) detection of other mineral phases, if any, in the samples, (3) determination of the degree of crystallinity of the initial chlorites, and (4) the presence or absence of any expandible phases. For comparison with the initial samples, material was removed weekly from the extractors and studied by X-ray diffraction. As it became apparent the weathering process proceeded slowly, this sampling interval was expanded to a period of 4 weeks. Samples thus removed were dispersed in distilled water by an ultrasonic transducer, then sedimented on a glass slide to give preferred orientation of the (001) face parallel to the slide surface. These slides were then examined on a Siemens diffracto-meter using a copper K-alpha radiation source at 35 kilovolts and 18 mill-amperes. Detection of the diffracted beam was done by scintillation counter. An initial diffractogram was produced by scanning from 3° to 45° at a rate of 1° 2θ/min. Additional patterns were produced by a slow scan rate of 0.125° 2θ/min. across the (001) and (003) peaks, that is, from 6.0° 2θ to 6.5° 2θ and 18.5° 2θ to 19.0° 2θ, respectively. This was done to expand the scale of the patterns so that more accurate d-spacings and various ratios of peak height and width could be determined.

Examination of the initial and terminal diffraction patterns showed no other mineral phases than chlorite to be present.

X-Ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy was done on the initial and ter-minal samples to determine the chemical composition of the samples in terms of the oxides of magnesium, iron, aluminum, silicon, and calcium.

A structural model for the chlorite imposing a particular distribution of the elements within the structure was assumed. By comparing models, that is, the distribution and amount of the elements in particular sites for the initial and terminal samples, it was hoped information could be provided about: (1) the ions being leached and their relative rates of removal, and (2) the relative susceptibilities of different parts of the chlorite structure to leaching. Discussions of the chlorite model and the results of this method of investigation appear in later sections.

Analytical determination of the elements was done using a Siemens fluorescence spectrometer with either a tungsten or chromium tube and either a scintillation counter or gas-flow proportional counter, depending on the element to be determined. Samples to be examined by the fluorescence method were mixed with polyvinyl alcohol corresponding to an amount 20 percent by weight and then compressed into a briquette using a hydraulic press pumped to 30 tons per square inch pressure.

For each of the elements determined, a standard calibration curve of counts per minute versus weight percent of the element was prepared using samples of known composition. The weight percent of the elements in the sample chlorites used in this study could then be determined once a count-per-minute value was established. This is a good analytical method as it is non-destructive and concentrations of a few parts per million are detectable.

In general, elements with greater atomic number are detected with greater precision than those of atomic number less than 20. Appendix 5 summarizes statistical data for the fluorescence analysis.

Differential Thermal Analysis

Differential-thermal-analysis patterns of the initial and subsequent

experimentally weathered chlorites were run on a Robert L. Stone DTA unit. The range of temperatures was from $20^{\circ}C$ to $1,100^{\circ}C$, with a heating rate of $10^{\circ}C/min$. Of interest were the low-range endotherms around $100^{\circ}C$, corresponding to loss of absorbed water and the mid-range endotherms around $600^{\circ}C$, corresponding to destruction of the brucite layer of chlorite (Mackenzie, 1957). The initial samples have a mid-range endotherm and no low-range endotherm. As the experiment progressed, it was expected that a low-range endotherm would develop and the size of the mid-range endotherm would be diminished. These predicted effects are due to destruction of the brucite layer and subsequent sorption of H_2O on the weathered mineral surfaces. No noticeable change was observed for the two endotherms over the duration of the weathering experiment.

The DTA studies were useful in that they demonstrated purity of the original samples as no mineral phases other than chlorite were detected. This method is equally sensitive to X-ray diffraction for detection of other minerals and less sensitive than the visual methods of observation, SEM and petrographic microscope.

Scanning Electron Microscopy

In order to determine if prolonged weathering induced surface morphological effects, scanning-electron microscope photographs of both unweathered and weathered samples were made. The instrument used was a Jeolco SEM housed in the X-ray laboratory of the School of Geology and Geophysics, The University of Oklahoma. This approach was also used by Parham (1969). Samples to be examined by SEM were sedimented on to a copper "button" and coated with gold.

Examination of the samples by SEM showed a rather homogeneous

distribution of particle sizes and the absence of other mineral phases.

Solution-Chemistry Studies

Chemical analysis of the solutions percolating through the samples were done to determine the ratios of various cations in solution as a function of time. I believed that such analysis in conjunction with detailed structural analysis would provide information about the structural sites of weathering and the kinetics of the weathering process. Cations analyzed in the solutions were Si^{+4}, Al^{+3}, Mg^{+2}, and Fe as Fe^{+2}. Solutions were removed from the boiling flasks and stored in polyethylene bottles. All analyses except Si^{+4} were kindly done by the U. S. Geological Survey Water Resources Division, Oklahoma City, Oklahoma. The analytical methods used are defined by Brown and others (1970). Further description of these methods was supplied by Gene A. Bednar, USGS hydrologist (1971, pers. comm.), as follows:

Sample Preparation

1. Samples were acidified with 1:1 reagent grade HNO_3 in quantities equivalent to 3.0 ml per liter of sample. No record was kept of initial volume of sample. However, I believe no sample volume exceeded 500 ml. Most were considerably less as I recall.

2. Samples were allowed to stand at least 72 hours after acidification for dissolution of any precipitated metal.

3. Samples were then filtered through a millipore filter pad with an average pore size of 0.45 microns just prior to analyses. Filtration is necessary for removal of any extraneous suspended material in samples.

Sample Analysis

1. Iron (Fe) was determined by atomic-absorption spectro-
    photometry. Analysis of a test sample using this method
    resulted in a mean value of 0.390 mg/l and a standard
    deviation of 0.026 mg/l.

2. Magnesium (Mg) was determined by atomic-absorption spec-
    trophotometry. Analysis of a test sample using this
    method resulted in a mean value of 2.1 mg/l and a stand-
    are deviation of 0.32 mg/l.

3. Aluminum (Al) was determined by the Ferron-orthophen-
    anthroline method. Analysis of a test sample using this
    method resulted in a mean value of 0.54 mg/l and a stand-
    ard deviation of 0.06 mg/l.

I did the silica analyses in the geochemistry laboratory of the
Oklahoma Geological Survey. Silica was determined spectrophotometric-
ally using the yellow molybdosilicic-acid complex described by Carlson
and Banks (1952) and DeSesa and Rogers (1954). A stock silica solution
of 4 mg/cc or 4,000 ppm was prepared by dissolving 10.1214 g of sodium
metasilicate ($Na_2SiO_3 \cdot 9H_2O$) in 250 cc of distilled H_2O. Appropriate di-
lutions ranging from 0.75 ppm to 200 ppm were then prepared from the
stock solution. Absorbance was measured at 332 mμ using a Zeiss spec-
trophotometer. According to DeSesa and Rogers (1954), Beer's law is
best followed by the "yellow" complex in the range 0.5 to 10 ppm of
silica. This was observed to be true in the present study also; that
is, standards above 10 ppm silica did not fit a straight-line calibra-
tion curve. In every case silica concentration in the solutions leached

through the chlorite samples was found to be in excess of 10 ppm, or
beyond the optimum range of the method employed.

I believe that much of the silica was derived from the Pyrex
glass of the extractors. In order to substantiate this belief, one
sample of distilled water was stored in a glass bottle for 3 weeks,
and another sample of distilled water was boiled in a Pyrex flask for
1 hour. The absorbances of these two samples were measured against
fresh distilled water from a polyethylene tank as a blank. The stored
sample of distilled water had a silica concentration in excess of 10
ppm, and the boiled sample had a silica concentration of 1.0 ppm. Be-
cause of the substantial contribution of silica from the extractors,
no silica concentrations are reported in this study. Charles J. Mankin
(1971, pers. comm.) believes that the contribution of silica from the
glassware is so great in proportion to the amount of silica released
from the chlorite that the error involved in making the silica deter-
mination, when using a silica-enriched blank, is more than the silica
contribution of the mineral. No exact precision data are available on
the spectrophotometer analysis of silica according to the USGS methods
manual (Brown and others, 1970); however, DeSesa and Rogers (1954) say
the coefficient of variation for their study was 2.01 percent. I sug-
gest that this problem of acquiring silica concentrations for experi-
mental weathering studies can be circumvented by using teflon-lined ex-
tractors.

Other alternatives to the use of teflon-lined extractors include
the use of another system or apparatus for the leaching of chlorite,
also made of nonsilicate material. However, I know of no commercially

marketed apparatus, and in attempts to describe a better apparatus,

some notable drawback is usually encountered. Most alternative sug-

gestions for a leaching system require continuous flow of H_2O across

the sample, resulting in enormous volumes of H_2O. The soxhlet extrac-

tion apparatus is free of that problem because water is recycled.

Perhaps the best alternative is to simply boil the mineral specimen

in a nonsilicate flask. However, this does not duplicate the natural

leaching process, which was one of the goals in designing this research

project.

Other problems are encountered in trying to perform chemical

analyses for silica because of the nature of silica itself. The chem-

ical removal of Si from rocks and minerals during weathering proceeds

by the reaction $SiO_2 + H_2O = H_4SiO_4$ (Garrels and Mackenzie, 1971).

Quartz has a solubility at about $25^{\circ}C$ of 6.5 ppm dissolved silica;

other forms have higher solubilities. Silica solubilities are usually

reported as SiO_2 without regard to the dissolved species (Garrels and

Mackenzie, 1971). Part of the silica in a weathering situation may not

go into solution as H_4SiO_4 but rather may separate as colloidal or amor-

phous SiO_2 (Krauskopf, 1967). If the concentration of colloidal silica

is high enough, coagulation may occur, but only the silica in colloidal

form will coagulate, the silica in true solution as H_4SiO_4 is unaffected

(Krauskopf, 1967). In doing chemical analyses for silica using a spec-

trophotometer, it is important that all the silica present form the yel-

low molybdosilicic-acid complex in order to measure the absorbance.

Absorbance of silica in forms other than the complex are not registered

at the same wavelengths as the yellow complex.

DeSesa and Rogers (1954) present several methods for making colloidal silica soluble in order to insure that all the silica will form the yellow complex. However, no coagulated colloidal silica was observed in any of the solutions of the present study.

THE CHLORITE MODEL

General

Chlorites are a group of minerals generally resembling the micas because of their layered phyllosilicate structure. They are monoclinic with unit cell measurements of a = 5.3$\overset{o}{A}$, b = 9.2$\overset{o}{A}$, and c = 14.3$\overset{o}{A}$ (Deer and others, 1966). Chemically they are hydrous silicates of aluminum, magnesium, and ferrous (sometimes ferric) iron. In addition, some chlorites may contain calcium, manganese, or chromium. Their ideal chemical formula suggested by Deer and others (1966) is $(Mg, Al, Fe)_{12} (Si, Al)_8 O_{20} OH_{16}$.

Structurally the chlorites are made of alternating talc-like and brucite layers. This structure also leads to an alternation of tetrahedral and octahedral layers (Foster, 1962). Foster suggested this leads to the general formula $X_m Y/_4 O_{10}(OH)_8$ (half unit cell) with the tetrahedral layers having the formula $X_{m/2} Y/_4 O_{10}(OH)_2$ and the octahedral layers having the formula $X_{m/2}(OH)_6$, where X and Y represent octahedral and tetrahedral cations, respectively, and m is generally less than 6. Isomorphous substitutions of trivalent cations (usually Al^{+3}) for tetravalent Si in the Y positions causes charge unbalance in the tetrahedral layers. This is compensated for by substitution of trivalent cations

for divalent cations in the octahedral layers.

Caillere and Hénin (1957) suggest the following schematic representation:

$$
\left.
\begin{array}{l}
6\ OH^- \\
4\ Mg^{2+},\ 2\ Al^{3+} \\
6\ OH^-
\end{array}
\right\}
\quad
\begin{array}{l}
\text{Brucite Layer} \\
\text{(resultant charge +2)}
\end{array}
$$

$$
\left.
\begin{array}{l}
6\ O_2^- \\
3\ Si^{4+},\ 1\ Al^{3+} \\
4\ O^{2-},\ 2\ OH^- \\
6\ Mg^{2+} \\
4\ O^{2-},\ 2\ OH^- \\
3\ Si^{4+},\ 1\ Al^{3+} \\
6\ O^{2-}
\end{array}
\right\}
\quad
\begin{array}{l}
\text{Mica Layer} \\
\text{(resultant charge -2)}
\end{array}
$$
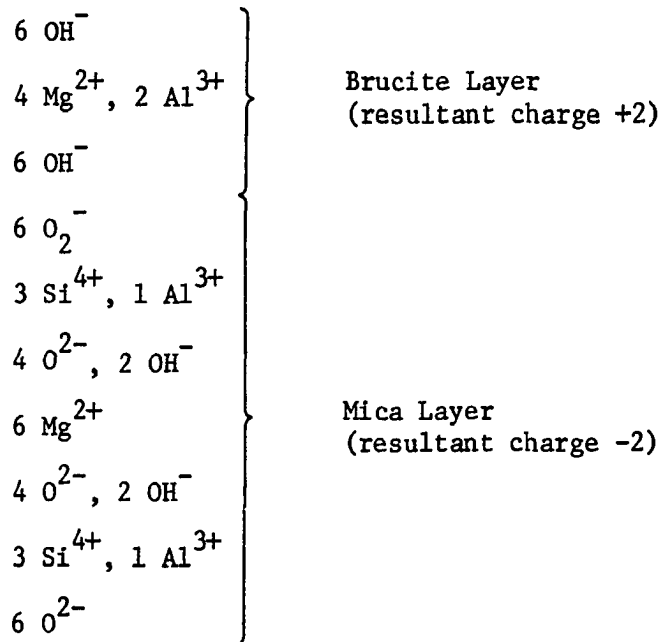
As stated by Foster (1962) substitution of Al^{3+} in the tetrahedral layers leads to Al^{3+} substitution in the brucite octahedral sheet to satisfy charges on the structure.

Structural Formulas

In this study, structural models are proposed for the initial unweathered chlorites and the terminal weathered chlorites. These models are constructed using the structural formula calculations (and their inherent assumptions) of Foster (1962) and Marshall (1949). The structural formula calculations of Foster are applied to a four-layer chlorite model (fig. 2). One of the terminal samples no longer "fit" the four-layer model and so Marshall's three-layer structural model was applied.

Both structural formula models involve (1) making chemical analyses of the sample and (2) distributing the elements detected during that

analysis within an assumed structural model that has unit cell dimensions

corresponding to those observed for the actual samples.

In the case of chlorite, the elements are distributed among two

octahedral and two tetrahedral layers with certain limitations. These

limitations are:

1. All Fe^{+2} is placed in octahedral layers.

2. All Mg^{+2} is placed in octahedral layers.

3. All Si^{+4} is placed in tetrahedral layers.

4. Enough Al^{+3} is allotted to the tetrahedral layers to give a

   total of eight cations to those layers; then the remaining

   Al^{+3} is allotted to the octahedral layers.

An advantage of the structural formula models is the integration

of observed chemical analyses with observed X-ray diffraction measurements.

Disadvantages are: (1) the assumptions do not allow Fe^{+2} substitution in

the tetrahedral layers, and (2) Al^{+3} is arbitrarily allotted to the tetra-

hedral layers first, which in certain cases could leave no Al^{+3} available

for the octahedral layers.

However, a comparison of the ionic radii of $Fe^{+2}(0.64\overset{o}{A})$, $Al^{+3}(0.50\overset{o}{A})$,

and $Si^{+4}(0.41\overset{o}{A})$ shows a greater than 15 percent difference in radius length.

Thus, substitution of Fe^{+2} for either Al^{+3} or Si^{+4} would violate the 15

percent substitution rule.

Also, because few dioctahedral chlorites (those with octahedral

layers filled with trivalent cations) are observed in nature, the arbitrary

allotment of Al^{+3} to tetrahedral layers first is a good assumption.

The purpose for using structural formula models in this study is

twofold:

Brucite Sheet

Mica Sheet

Brucite Sheet

Mica Sheet

$c \approx 14$ Å

$\otimes$ $\otimes$ $\otimes$ $\otimes$ $+ H_2O$

$c \approx 14$ Å

(a) chlorite

(b) vermiculite

octahedral layer

tetrahedral layer

$\otimes$ interlayer cation, usually Mg^{2+}
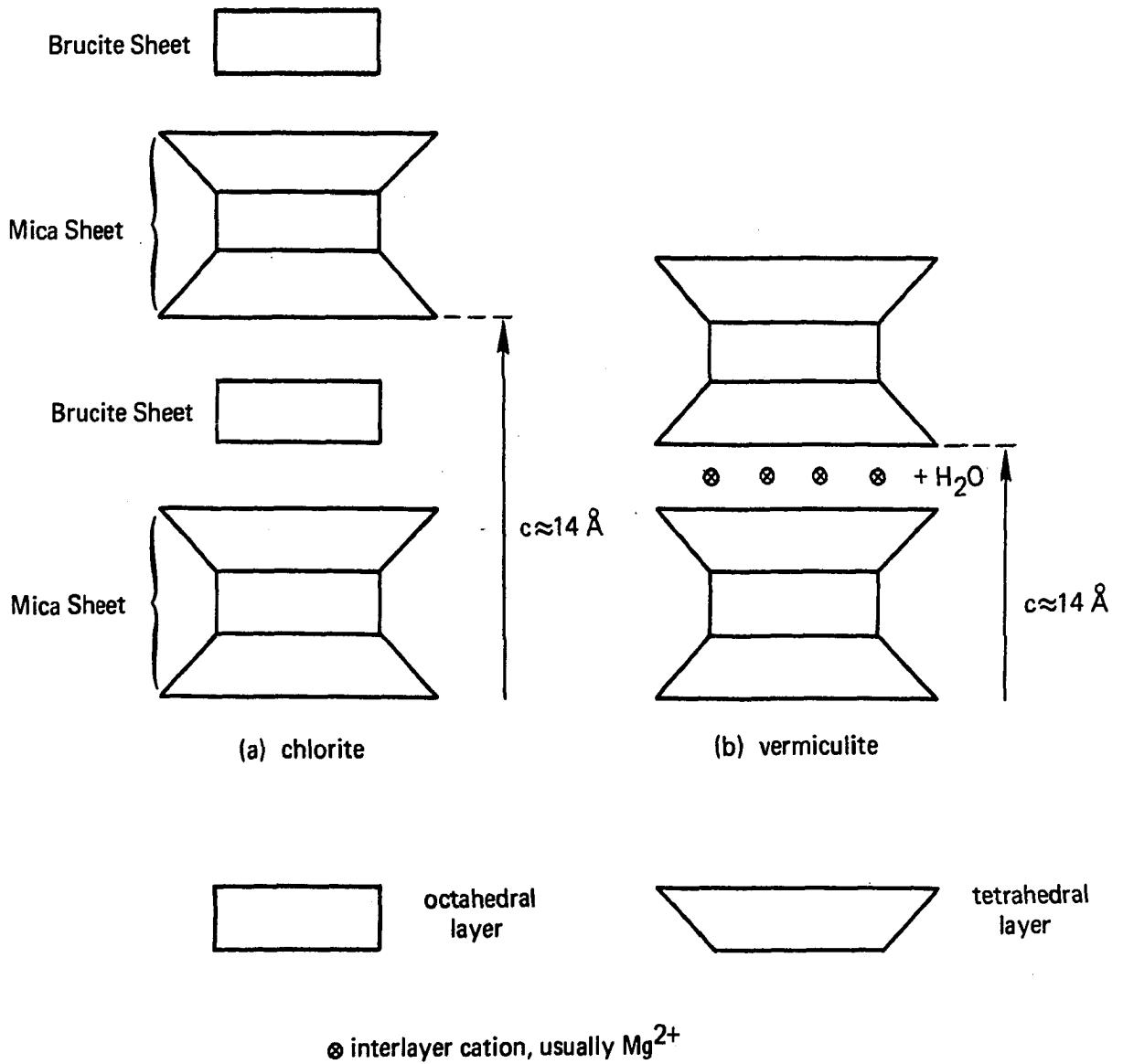
Figure 2. (a) Chlorite Structure   (b)   Vermiculite Structure

1. By having the elements restricted to certain portions of the structure, a comparison of cation loss between initial and terminal samples allows determination of the sites of weathering (octahedral vs. tetrahedral sites).

2. If the analyses of the terminal samples no longer fit the original model and another model has to be used, conclusions can be drawn about the direction in which chlorite weathering proceeds.

The structural formulas of tables 4 and 5 of this study were calculated after Foster (1962) and reflect the distribution of the various elements (from chemical analyses) within a theoretical four-layer structure with unit-cell parameters as mentioned above. A change of great enough magnitude in either the X-ray-diffraction measurements or the chemical analyses during the weathering experiment involves the possible consideration of other models; in this study a three-layer clay structure, as proposed by Marshall (1949), had to be considered for one of the terminal samples. Ultimately all structural-formula calculations for phyllosilicates are based on fitting observed chemical analyses into some combination of tetrahedral and octahedral layers that yield the observed X-ray parameters for the a, b, and c axes.

DISCUSSION AND RESULTS

General

The initial chlorite sample used in this study was supplied by Ward's Natural Science Establishment and is a well-ordered, metamorphic chlorite from Chester, Vermont (Martin, 1955). Approximately 75 grams of the initial sample were ground using a uniform-particle-size grinder, and sample splits were made to obtain four samples. Two of these, hereafter referred to as sample 1-0 and 2-0, were 200-mesh Equivalent Spherical Diameter or 74-microns ESD. Sample 1-0 was subjected to the weathering process for 52 weeks, and the terminal sample is labeled sample 1-52. Sample 2-0 was leached for 44 weeks as was sample 3-0; therefore, the terminal samples are referred to as 2-44 and 3-44, respectively. Sample 4-20 represents 20 weeks of study of sample 4-0. Samples 3-0 and 4-0 were 400-mesh ESD or 37-microns ESD. Two different particle sizes were used to study the effects of particle size on the kinetics of the weathering action.

The particular chlorite was chosen because of its documentation in the literature (Martin, 1955) and because its well ordered nature and metamorphic origin (as opposed to sedimentary origin) virtually assured no expandible phase in the initial sample. Since one of the initial goals

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was to determine if chlorite weathering proceeded toward an expandible vermiculite-like member, the absence of an expandible phase in the initial material was necessary.

Purity of the chlorite samples used can be demonstrated by four methods. These are X-ray diffraction, differential thermal analysis, scanning-electron microscopy, and petrographic microscope examination. None of the methods revealed the presence of any other mineral phases in the samples. For X-ray diffraction the limits of detectability are probably about 3.0-5.0 percent; therefore, it would be possible to unknowingly have another mineral phase present. The same limitations are also applicable on the use of DTA for detection of small amounts of other minerals in chlorite (Mackenzie, 1957). Thus, the two visual methods, petrographic and SEM examination are believed to be the best evidence against the presence of other mineral phases.

Petrographic examination of the samples was done using the Zeiss research microscope of the Amerada Hess Corporation, Tulsa, Oklahoma. The technique used was to smear about 0.1 g of the chlorite in Lakeside Cement and to examine the slide at 250x magnification. All of the samples thus examined showed uniformity of grain size and relief. No opaque or heavy minerals were noted. The small particle-size diameter of the samples made quantitative observations difficult.

SEM examination showed all of the grains to have the same particle morphology and uniform size.

Data analyses, especially of fluorescence analyses, were done to attempt to demonstrate changes from initial to terminal samples both structurally and chemically. Thus, four methods of fluorescence-data comparison

were used in this study. They are: (1) direct comparison of the oxide

analyses in tables 1 and 2 and appendix 3; (2) some component, in this

case Al, is assumed constant (Krauskopf, 1967), and relative changes in

amounts of the other elements are calculated (see table 3); (3) ratios

of certain cations are compared in both initial and terminal samples

(see table 6); and (4) using the structural-formula calculations of Foster

(1962), a particular distribution of the various cations is assumed, and

changes in the number of atoms in various positions is noted and used to

interpret structural sites of weathering (see tables 4 and 5).

Interpretations from X-ray-diffraction data are based on quanti-

tative measurements (appendix 1) and empirical observations (figs. 3, 4,

5).

As mentioned earlier, solution analyses yielded little useful in-

formation and indicate a low level of reproducibility of the experiment

as performed. The solution data are presented in figures 6, 7, 8, and 9

and in appendix 4 as examples of the type of data acquired so that others

doing similar studies might develop methods of circumventing problems en-

countered in this study.

Qualitative Observations

After about 1 week of weathering, the residual water in the boil-

ing flasks of samples 1-0 and 2-0 became cloudy and, with prolonged wea-

thering, became milky and translucent. For samples 3-0 and 4-0 in the

smaller particle size, the water became cloudy in about 3 days (Parham,

1969).

Another observed phenomenon was the formation of a red ferric

oxide coating on the surface of the samples after about 1 month of weather-

ing. When withdrawing the sample for X-ray studies, this coating could be removed by stirring the sample in the soxhlet tube and mixing the coated grains with uncoated grains, thus restoring an overall green color. However, the red coating was formed again within about 2 weeks. Terminal samples 1-52, 2-44, and 3-44 were visibly covered with the oxidized coating to such an extent that they had to be subjected to the free-iron-oxide-removal method of Mehra and Jackson (1960) prior to fluorescence analysis so that the iron percentages reported were due only to iron in the chlorite structure and not to iron on the surfaces of the mineral grains.

Chemical Analyses by X-Ray Fluorescence Spectroscopy

The chemical analyses of the initial samples are given in table 1 and those of the terminal or weathered samples in table 2 (see also appendix 2, 3). These analyses were reported with the H_2O present and also H_2O free and recalculated to 100 percent.

Samples 1 and 2 are obtained from different grindings of the same materials. Samples 3 and 4 are from the same sample split. A discussion of variations in the analyses is given in appendix 2 and 3.

According to Reiche (1943), there are three distinct ways of comparing chemical analyses in weathering studies. Reiche lists these three methods as:

1. Some component is assumed to remain constant in quantity during rock alteration. For each of the remaining components, in turn, the amount which would be present in the weathered rock, had it retained its initial relation to the "constant" constituent, is then calculated.

2. The quantities, or percentages, of the individual substances in the altered and unaltered rock are directly compared.

3. Comparison is made of the ratios between certain groups of substances in the altered rock and in the fresh rock.

TABLE 1

CHEMICAL ANALYSES OF INITIAL SAMPLES

Oxide	Sample 1-0		Sample 2-0		Sample 3-0 Sample 4-0	
	H_2O	H_2O free	H_2O	H_2O free	H_2O	H_2O free
MgO	26.52	30.91	27.42	31.16	27.19	30.82
Al_2O_3	12.16	14.17	13.15	14.94	13.34	15.17
SiO_2	32.27	37.62	32.76	37.22	32.67	37.03
FeO	14.60	17.02	14.47	16.44	14.81	16.78
CaO	00.21	00.24	00.18	00.20	00.13	00.15
H_2O	14.20		11.40		11.68	
Totals	99.96	99.96	100.00	99.96	99.87	99.95

TABLE 2

CHEMICAL ANALYSES OF TERMINAL SAMPLES

Oxide	Sample 1-52		Sample 2-44		Sample 3-44		Sample 4-20	
	H_2O	H_2O free	H_2O	H_2O free	H_2O	H_2O free	H_2O	H_2O free
Mg	33.10	39.42	28.74	32.84	32.43	37.54	30.07	34.26
Al_2O_3	13.04	15.53	12.22	13.96	15.00	17.36	13.20	15.04
SiO_2	22.53	26.83	31.73	36.25	24.70	28.59	30.84	35.14
FeO	15.16	18.05	14.69	16.78	14.16	16.39	13.49	15.37
CaO	00.10	00.12	00.09	00.10	00.11	00.10	00.13	00.14
H_2O	15.98		11.69		13.07		12.14	
Totals	99.91	99.95	99.16	99.93	99.47	99.98	99.87	99.95

In this study I have relied primarily on comparison methods "2" and "3" (see tables 2 and 4). However, a comparison of the oxide analyses by Reiche's method 2 is of interest because of the H_2O variation between the initial and terminal samples. Using this direct comparison, tables 1 and 2 show an increase of about 2 percent in the total H_2O percentage from initial to terminal samples. This increase is primarily due to an increase in the amount of adsorbed H_2O, that is H_2O driven off after heating to $300^{\circ}C$. I suggest that this increased amount of H_2O in the terminal samples is due to the coordination of H_2O molecules around Mg, as an interlayer cation, rather than Mg in octahedral coordination in the brucite layer. This is more characteristic of vermiculite than chlorite. Further evidence for this modification of the chlorite structure will be offered in a later discussion.

Table 3 gives the percent change in the oxide constituents, with weight percentage of Al_2O_3 held constant. This method was essentially described by Merrill (1906) and incorporated in Reiche's (1943) method 1.

I elected to hold the weight of Al_2O_3 constant from initial to terminal samples because this is the standard method used by numerous researchers of weathering phenomena (Loughnan, 1969; Carroll, 1970). This is based on the assumption that Al has limited mobility under the conditions of this experiment. As evidence I will present later suggests, this assumption is entirely invalid; that is, Al does show some mobility and is actively leached from the chlorite as the experiment proceeds. If the initial assumption that Al is immobile, meaning that the weight of Al in the sample is constant, is invalid, then the percentage losses of Si, Fe, and Ca shown in table 3 are too low (Merrill, 1906). By the same reason-

TABLE 3

PERCENT CHANGE IN OXIDE CONSTITUENTS[1]

| Oxide | Sample | | | |
	1-0 to 1-52	2-0 to 2-44	3-0 to 3-44	4-0 to 4-20
MgO	+16.44%	+12.77%	+ 6.37%	+12.14%
Al_2O_3	0.00	0.00	0.00	0.00
SiO_2	-34.88	+ 4.19	-32.55	- 4.23
FeO	- 3.22	+ 9.23	-14.65	- 7.53
CaO	-51.17	-51.88	-31.25	0.00

[1]Calculated as $100(A/BC) - 100\%$ where:

A = % of constituents in weathered sample

B = % of constituents in unweathered sample

$$C = \frac{\% \ Al_2O_3 \ \text{in weathered sample}}{\% \ Al_2O_3 \ \text{in unweathered sample}}$$

ing, the percentage gains of Mg are also too low. Therefore, the absolute values in table 3 are not of primary interest, but rather their magnitude and sign, indicating loss or gain.

In table 3 all four sample series show a relative gain in the amount of Mg present in the terminal samples. For example, in the series 1-0 to 1-52 the table is interpreted as showing 16.44 percent more MgO in 1-52 than in 1-0, with the understanding that no new MgO has been added.

As for the other constituents, table 3 shows relative losses of SiO_2 and FeO from samples 1-0, 3-0, and 4-0. Sample 2-0 shows small relative gains in these two constituents. Note that the factor

$$(C) = \frac{\% \ Al_2O_3 \ \text{in weathered sample}}{\% \ Al_2O_3 \ \text{in unweathered sample}}$$

is smaller for sample 2-0 than for the other three samples. This is interpreted as indicating some mobility or loss of Al during the leaching process. CaO shows relatively large losses in samples 1-0, 2-0, and 3-0 and shows no change in sample 4-0. As shown in table 1, CaO is present in trace amounts only, and even a slight variation will cause a large negative percentage. Based on observations of other chlorites (Foster, 1962), the Ca^{+2} is probably present as an interlayer cation.

Thus far I have provided information indicating relative losses or gains of certain constituents during the course of the experiment. Of more specific interest is where in the chlorite structures these various cations are removed, and whether or not specific portions of the chlorite structure are more susceptible to weathering than others. Tables 4 and 5 provide some insight into these questions.

Table 4 shows the structural formulas for the initial samples. The calculations were patterned after Foster (1962) and represent half-unit cell values. The divalent cations, Fe^{+2}, Mg^{+2}, and Ca^{+2} and the trivalent cation, Al^{+3}, shown within the first set of parentheses, occupy octahedral sites. The second set of parentheses enclosing Si^{+4} and Al^{+3} represent atoms in tetrahedral configurations.

Table 5 shows the structural formulas of the terminal samples. With the exception of sample 1-52, all are calculated after Foster (1962). Sample 1-52, as shown in table 3, had 34.88 percent less SiO_2 than sample 1-0. Therefore, this required the allocation of more Al atoms to complete

TABLE 4

STRUCTURAL FORMULAS FOR INITIAL SAMPLES

Sample[1,2]	Formula
1-0	$(Al_{.852}Fe^{+2}_{1.205}Mg_{3.900}Ca_{.021})(Si_{3.187}Al_{.812})O_{8.233}(OH)_{9.767}$
2-0	$(Al_{.760}Fe^{+2}_{1.190}Mg_{4.029}Ca_{.018})(Si_{3.240}Al_{.760})O_{10.325}(OH)_{7.675}$
3-0 4-0	$(Al_{.778}Fe^{+2}_{1.220}Mg_{3.994}Ca_{.013})(Si_{3.223}Al_{.777})O_{10.253}(OH)_{7.747}$

[1]All samples calculated after Foster (1962).

[2]Slight differences between samples 1 and 2 arise because they are different grindings of the same material.

TABLE 5

STRUCTURAL FORMULAS FOR TERMINAL SAMPLES

Sample[1]	Formula
1-52	$(Fe^{+2}_{1.07}Mg_{4.167})(Al_{1.298}Si_{1.90})O_{19.805}(OH)_{4.195}$
2-44	$(Al_{.605}Fe^{+2}_{1.225}Mg_{4.273}Ca_{.009})(Si_{3.168}Al_{.832})O_{10.715}(OH)_{7.285}$
3-44	$(Al_{.350}Fe^{+2}_{1.217}Mg_{4.970}Ca_{.012})(Si_{2.542}Al_{1.458})O_{10.064}(OH)_{7.936}$
4-20	$(Al_{.603}Fe^{+2}_{1.118}Mg_{4.444}Ca_{.013})(Si_{3.061}Al_{.939})O_{10.281}(OH)_{7.719}$

[1]Sample 1-52 calculated by method of Marshall (1949); all others calculated after Foster (1962).

the tetrahedral layer, and as a result, no Al remained to allocate to
the octahedral layer. None of the published structural formulas I have
examined for chlorite show a complete absence of octahedral Al. Thus,
sample 1-52 was recalculated on a three-layer clay model after Marshall
(1949).

Note that sample 3-44, which in table 3 had 32.55 percent less
SiO_2 than sample 3-0, has only .35 Al atoms in octahedral positions.
With a longer period of leaching, this sample would probably have lost
all its octahedral Al and would perhaps best be represented on a three-
layer clay model rather than a four-layer chlorite model. I suggest that
these two samples, 1-52 and 3-44, have been altered by this experiment
to the extent that they are no longer chlorites. However, they do not
have all of the characteristics of a vermiculite either. Therefore,
samples 1-52 and 3-44 are interpreted to represent an intermediate state
between chlorite and vermiculite.

A comparison between tables 4 and 5 shows the following relation-
ships between initial and terminal samples:

1. The percentage of tetrahedral Al increases toward the termi-
   nal sample, whereas Si decreases.

2. The increase in tetrahedral Al is accompanied by a decrease
   in the amount of octahedral Al.

3. A relative decrease of Fe^{+2} is accompanied by an increase of
   Mg^{+2} from initial to terminal samples for all four series.

Information concerning the relative rates of removal of the various
cations is also demonstrated by table 6. This table consists of two parts:
part 1 shows the variation of cation ratios derived from the structural

formulas of tables 4 and 5; part 2 shows the variation of Fe/Mg and Si/Al, and the values are derived from the chemical analyses of tables 1 and 2.

Part 1 gives greater structural information about the leaching process than does part 2, which is based on data that assumes no particular distribution of the elements. Part 1 gives the following information about the relative rates of removal of the cations and the standard sites of removal:

1. Fe^{+2}/Mg^{+2} ratio decreases from initial to terminal samples, indicating more rapid removal of Fe than Mg. Based on the assumptions of tables 4 and 5, this is leaching from an octahedral site.

2. The ratio of Si to tetrahedral Al decreases from initial to terminal samples in all four series. This indicates preferential removal of Si from the tetrahedral layers.

3. A ratio of tetrahedral Al to octahedral Al increases (going to ∞ in sample 1-52) from initial to terminal samples in all four series. This indicates more rapid removal of Al in octahedral coordination than Al in tetrahedral coordination.

Part 2 also indicates more rapid removal of Fe than Mg and more rapid removal of Si than Al.

Data presented in these sections allow the postulation of an order of apparent ease of removability of the major cations. Table 3 indicates (assuming Al to be constant) that Si is more easily removed than is Fe and that Fe is more easily removed than Mg. This is reflected also in tables 4 and 5 where no constituent is assumed constant and is further illustrated by table 6. This postulated order is summarized as, in order

TABLE 6

VARIATION OF CATION RATIOS FROM UNWEATHERED

TO WEATHERED SAMPLES

	Samples							
Ratio	1-0	1-52	2-0	2-44	3-0	3-44	4-0	4-20
Part 1[1]								
Fe^{+2}/Mg	0.30	0.25	0.29	0.28	0.30	0.24	0.30	0.25
Si/Al_{tet}	4.76	1.46	4.21	3.82	4.13	1.73	4.13	3.02
Al_{tet}/Al_{oct}	0.95	∞	1.00	1.36	1.00	4.08	1.00	1.74
Part 2[2]								
Fe/Mg	0.55	0.45	0.52	0.51	0.54	0.43	0.54	0.44
Si/Al	2.65	1.72	2.49	2.59	2.44	1.64	2.44	2.33

[1] Part 1 is from structural formulas.

[2] Part 2 is from oxide analyses (H_2O free).

of decreasing ease of removability, Si > Fe > Al > Mg.

Thus far, I have indicated that the weathering of chlorite proceeds along two lines: (1) the removal of Si from the tetrahedral layers, and (2) the removal of Fe^{+2} and Al^{+3} from one of the octahedral layers. Two octahedral layers are in the chlorite structure, one situated between the two tetrahedral layers of the mica-like unit and another constituting the brucite layer. The traditional concept of chlorite weathering is that the brucite layer is destroyed, leaving Mg as an interlayer cation (Loughnan, 1969). In order to evaluate which of the octahedral layers has been leached during this study, an examination of the X-ray diffraction characteristics is necessary.

X-Ray Diffraction

According to Petruk (1964), X-rays diffracted from evenly or-
dered basal planes of chlorite (002, 004, etc.) represent reflections
from in-phase octahedral layers, thus the diffracted X-rays reinforce
each other to produce a diffraction line or peak. As the heavy-atom
content of the octahedral layers increases, the intensity of the dif-
fracted beam increases. This is due to the increase of the atomic-
scattering factor, which is approximately equal to the atomic number of
the element being studied (Cullity, 1956).

When the X-rays are diffracted from odd-ordered basal planes
of chlorite (001, 003, etc.), the octahedral layers are out of phase and
the reflections cancel each other. If the two chlorite octahedral layers,
the brucite and mica-like octahedral layers, contain the same number of
heavy and light atoms, then the odd-ordered basal reflections are can-
celed completely. According to Petruk (1964), if the number of heavy
atoms in the mica-like octahedral layer is more than the number of heavy
atoms in the brucite octahedral layer, the intensity of 001 increases.

An examination of figures 3, 4, and 5 yields some insight into
which octahedral layer is leached. The initial diffraction patterns of
samples 1-0, 2-0, and 3-0 show the 002 diffraction peak to be about twice
as intense as the 001 peak. However, in the subsequent patterns, 1-24,
1-52; 2-24, 2-44; and 3-24, 3-44, the ratio of 002 to 001 is almost 1:1.
The presence of more heavy atoms in the mica-like octahedral layer than
in the brucite layer causes increased intensity of the 001 peak (Petruk,
1964). This suggests that the octahedrally coordinated Fe^{+2} is prefer-
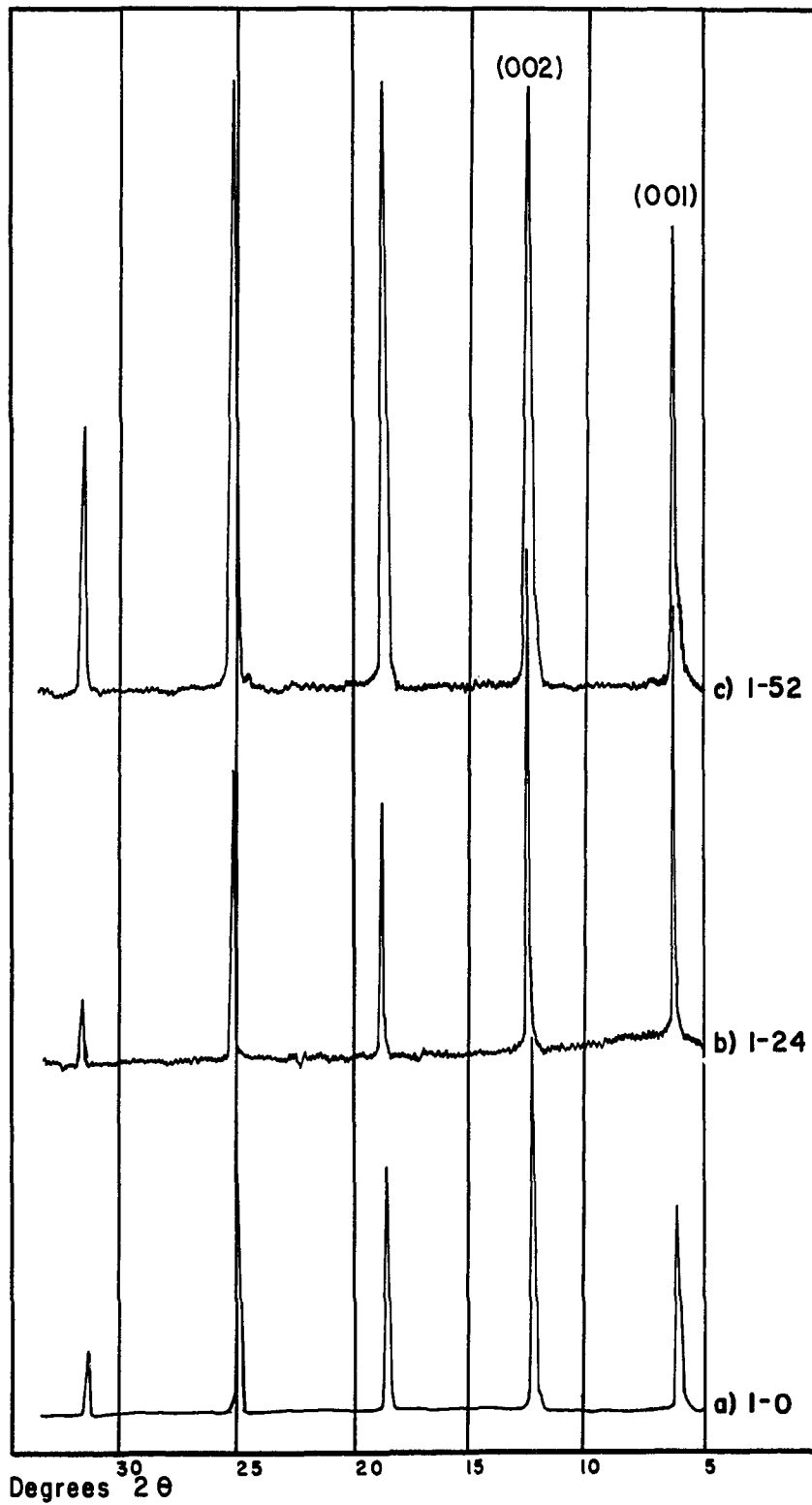entially removed from the brucite layer rather than from the mica-like

FIGURE 3. SELECTED DIFFRACTION PATTERNS,
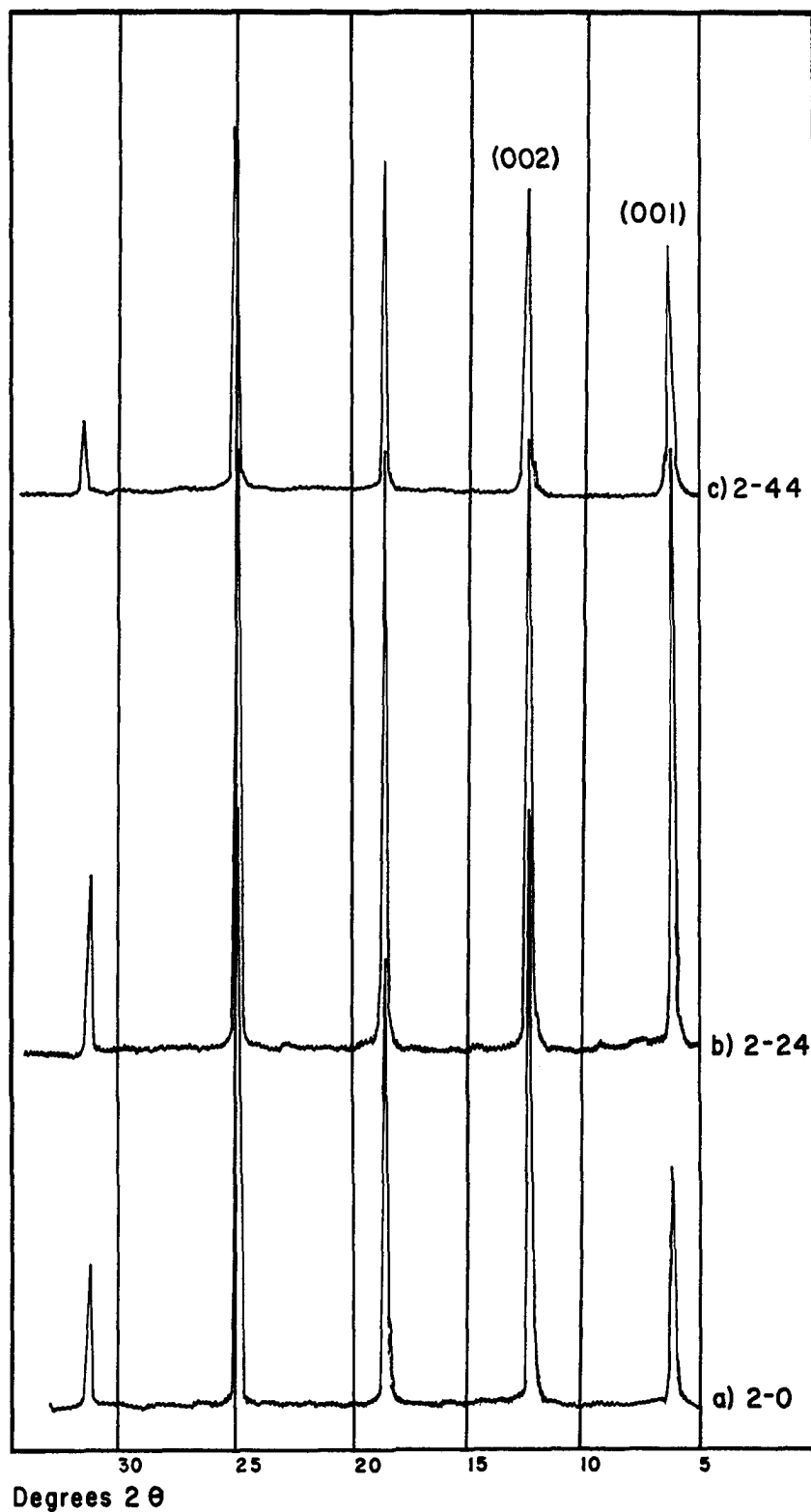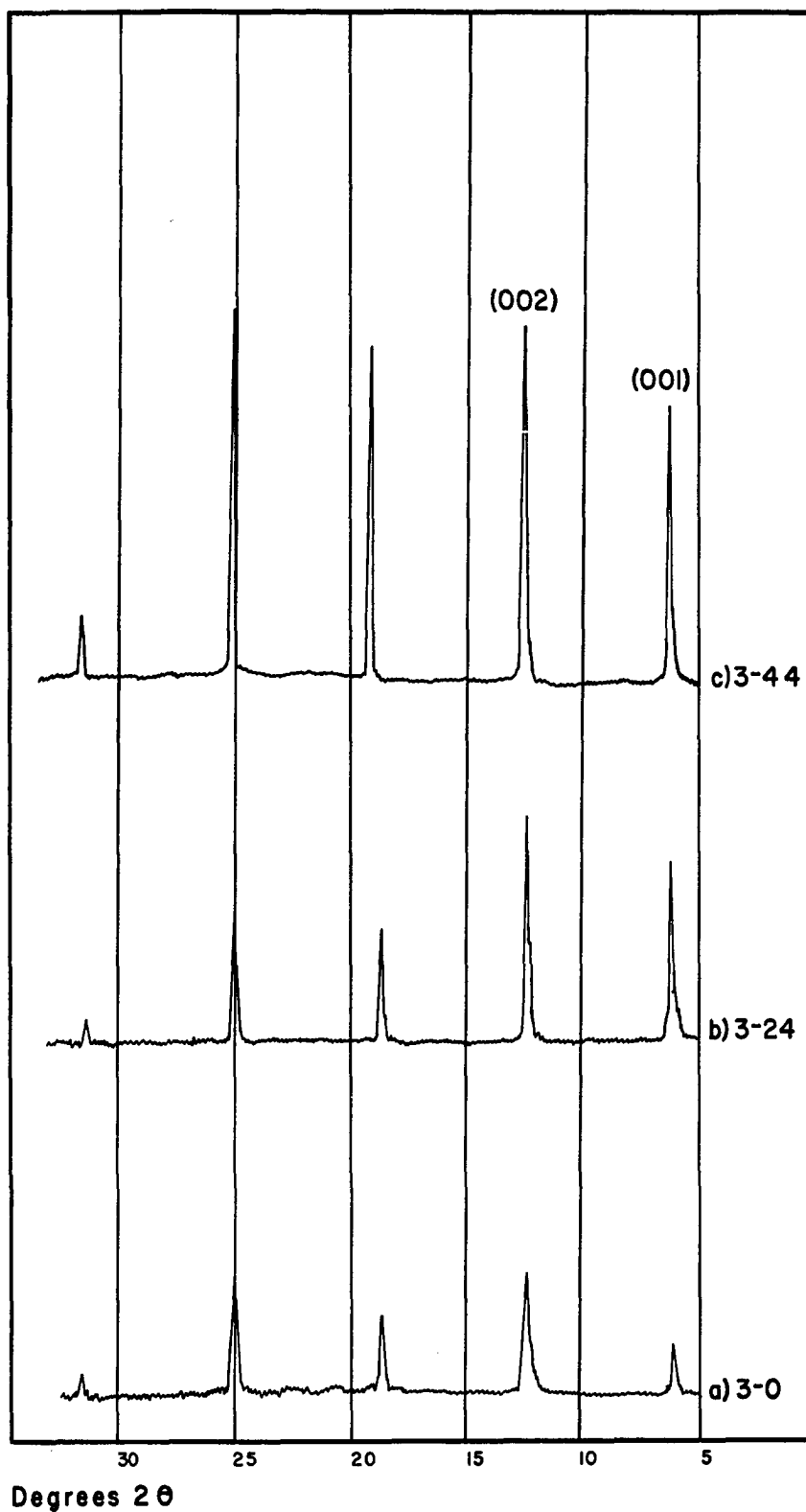SAMPLE I

Degrees 2 θ

FIGURE 4. SELECTED DIFFRACTION PATTERNS, SAMPLE 2

Degrees 2θ

FIGURE 5.   SELECTED DIFFRACTION PATTERNS
            SAMPLE 3

octahedral layer. Note the slight decrease in the intensity of 001 for

terminal samples 1-52, 2-44, and 3-44 (figs. 3, 4, 5) with respect to 002.

This may indicate that with prolonged weathering, the mica-like octahedral

layer is attacked, releasing Fe^{+2}.

Another X-ray-diffraction feature that should be mentioned is the

slight increase in the basal 001 spacing from initial to terminal samples

for all four series. This increase was approximately 0.3 to 0.4Å and pro-

bably represents the propping open of some of the layers by adsorbed H_2O

(tables 1, 2). Although the chemical analyses of some of the terminal

samples (1-52 and 3-44) best fit a three-layer clay model, the diffrac-

tion patterns are still primarily those of a chlorite.

Solution Chemistry

Until now, the discussion has been concerned primarily with the

solid material. Study of the solutions that had leached through the

solids yielded information about the relative rates of release of the

various cations.

Figures 6, 7, 8, and 9 illustrate the solution chemistry data.

Confidence limits at the 95-percent level were established by the method

presented by Simpson and others, (1960, p. 163-165). Figures 6 and 7

show data derived from the first 96 hours of weathering of sample 4-0,

which was weathered for a total of 20 weeks. Data for the remainder of

sample 4-0 and for the other samples are given in figures 8 and 9. Note

that ratios of the selected cations rather than concentration terms are

used. This is because volume losses of the solution developed from

sample to sample caused by incomplete condensation and leakage of the

vapor around the joints of the extractor. These volume losses render

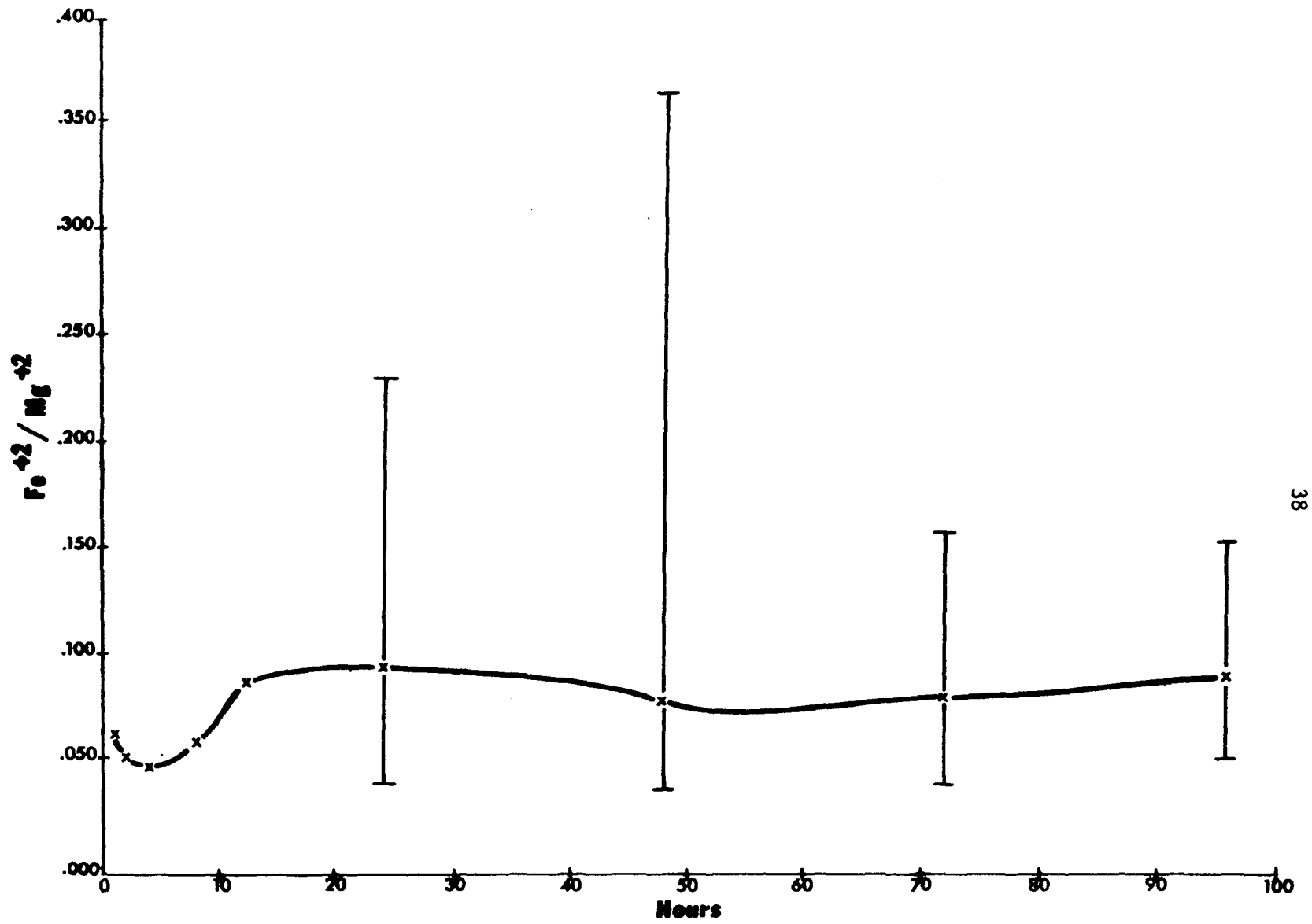**FIGURE 6.** Fe^{+2}/Mg^{+2} in solution vs. Time (Duration of Weathering), Sample 4.
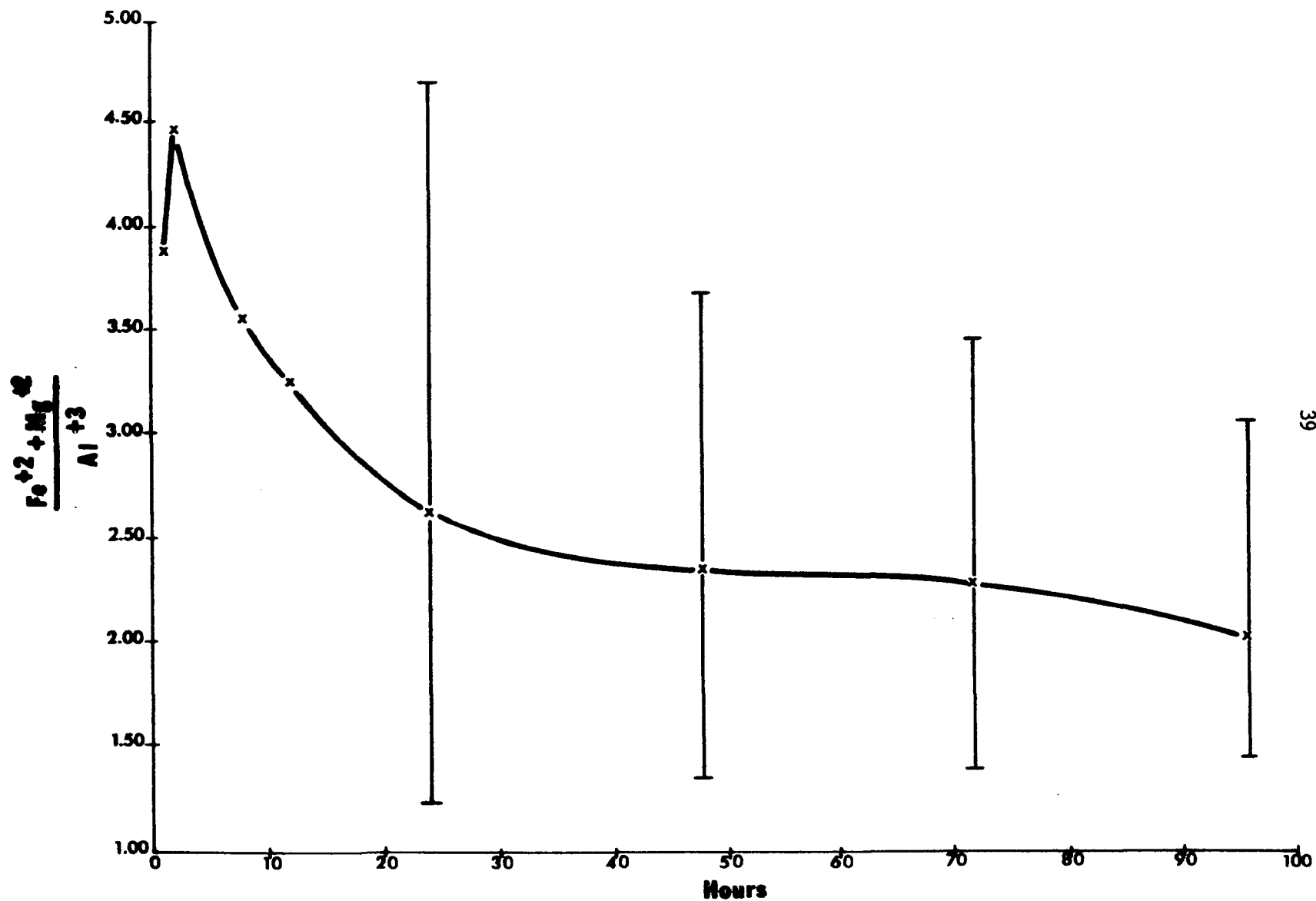
FIGURE 7. $\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$ in solution vs. Time (Duration of Weathering), Sample 4.
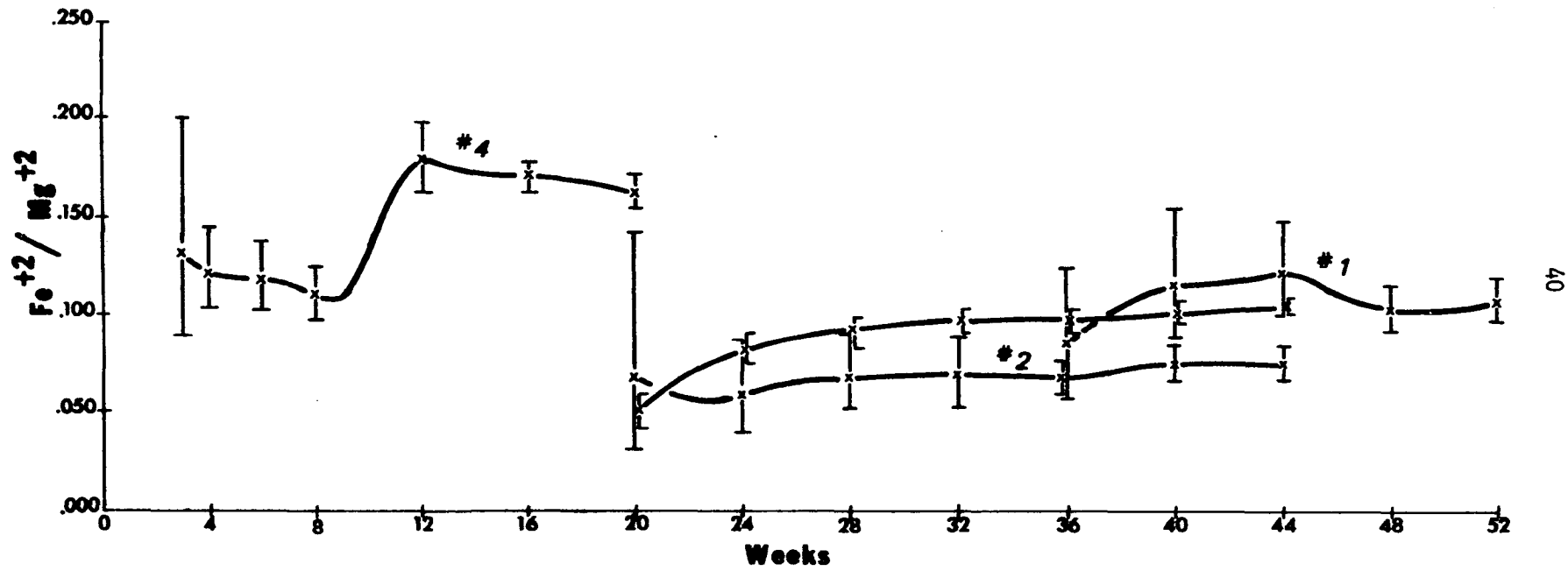
FIGURE 8. Fe^{+2} / Mg^{+2} in solution vs. Time (Duration of Weathering), Samples 1, 2, 3, 4.
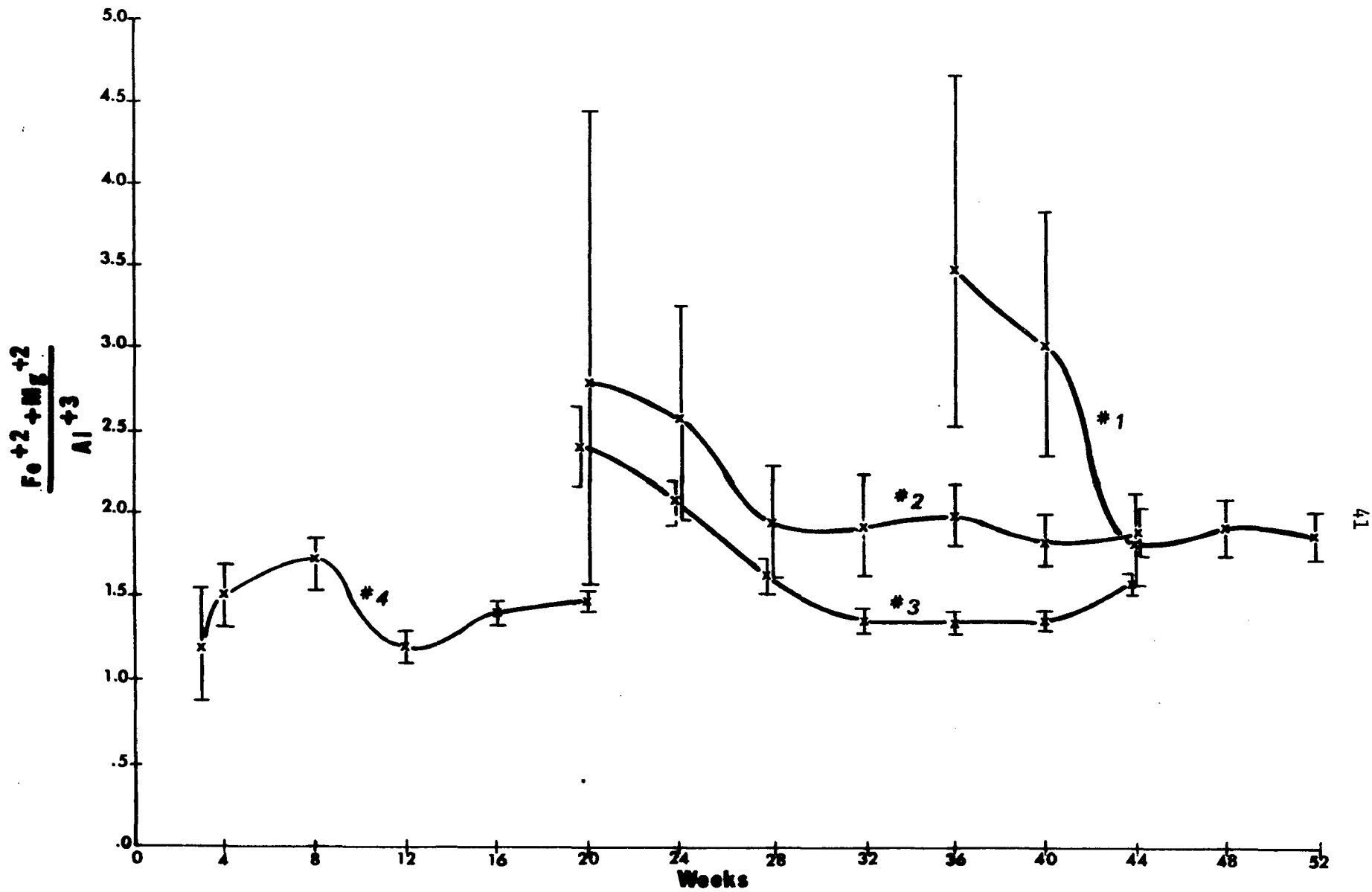
FIGURE 9. $\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$ in solution vs. Time (Duration of Weathering), Samples 1, 2, 3, 4.

comparison of concentration terms between samples meaningless.

Note that the ratios Fe^{+2}/Mg^{+2} and $\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$ remain essentially constant over the time period of the experiment. This might be taken to indicate congruent solution, that is, simple dissolution of the chlorite into water. However, the structural formulas of table 5 (compared with those of table 4) show differential removal of Fe^{+2}, Si^{+4}, and Al^{+3} from octahedral and tetrahedral layers. This is indicative of incongruent solution and is the predicted method of chlorite weathering (Loughnan, 1969, p. 107).

In spite of the essential constancy of the ratios, some variation is observed. The following interpretations of those variations are offered with the knowledge that information presented in earlier paragraphs suggest limitations on the usefulness of the solution chemistry data.

Figure 6 is a plot of the Fe^{+2}/Mg^{+2} ratios in the solution. For approximately the first 4 hours, more Mg^{+2} appeared to be leached than Fe^{+2}, which was reflected by the decrease in the Fe^{+2}/Mg^{+2} ratio. From approximately 5 hours to 13 hours the amount of Fe^{+2} being leached was much greater than Mg^{+2}, and after a leveling off up to approximately 30 hours, the amount of Fe^{+2} steadily increased.

Figure 7 is a plot of the $\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$ ratio for the first 96 hours of leaching sample 4-0. This plot was done to compare the relative rates of removal of Fe^{+2} and Mg^{+2} with Al^{+3}. For the first 2 hours of the experiment, the amount of Fe^{+2} and Mg^{+2} in solution increased several times over the amount of Al^{+3}. After that period, Al^{+3} began to be leached from the chlorite, causing a steady decrease in the $\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$

ratio. At approximately 96 hours, one atom of Al^{+3} had been removed for every atom of Fe^{+2} and Mg^{+2} removed.

The Fe^{+2}/Mg^{+2} solution data for all four samples is summarized in figure 8. On this graph the ratio was plotted against time in weeks. Except for the irregular variations shown in sample 4-0, the amount of Fe^{+2} in solution tended to increase in respect to Mg^{+2}. Note that sample 3-44, although weathered for a shorter time than 1-52, showed about the same Fe^{+2}/Mg^{+2} ratio. This is believed to be due to the smaller particle size of sample 3-44, which thus increases the surface area available for attack.

Figure 9 is a plot of $\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$ vs. time in weeks. Once again, sample 4-0 shows irregular variation; however, the shapes of the curves for samples 1-0, 2-0, and 3-0 are similar. Note that samples 1-52 and 2-44 have approximately the same value for the $\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$ ratio. The value for sample 3-44 is somewhat smaller, indicating more Al^{+3} is being leached from the smaller particle-sized sample.

Scanning Electron Microscopy

Figures 10 and 11 are provided to show the effects of the weathering process on the physical features of the chlorite. The greatest physical changes are shown for sample series 1-0 to 1-52 (fig. 10). Sample 1-0 is characteristically composed of grains devoid of surface and edge features, with no fraying of the edges or spalling of flakes from the surface noted. Sample 1-52, however, is composed of grains with irregular edges and surfaces, apparently due to breakdown of the grains along preferred planes. Samples 2-0 to 2-44 and 3-0 to 3-44 (fig. 11) exhibit the same features as samples 1-0 to 1-52, but not to the same extent.

I-0 (6,000X)

I-52 (1,000X)

2-0 (2,000X)

2-44 (2,000X)

FIGURE 10. SELECTED SEM PHOTOGRAPHS

3-0 (2,800X)

3-44 (2,800 X)

FIGURE II. SELECTED SEM PHOTOGRAPHS

Additional chemical information was provided by using the Jeolco

Scanning-Electron Microscope in conjunction with the Princeton Gamma-Tech

Non-Dispersive Analyzer at The University of Oklahoma School of Geology

and Geophysics. In samples 1-0 and 1-52, comparisons of Fe^{+2}/Mg^{+2} and

Si^{+4}/Al^{+3} ratios were made to see if the edges were preferentially leached

in relation to interiors of the grains. Comparisons were made between

the edges of weathered and unweathered grains, between the edges and in-

teriors of unweathered grains, and between the interiors of weathered and

unweathered grains. A comparison of 50 edge points on sample 1-0 with 50

edge points on sample 1-52 for Fe^{+2}/Mg^{+2} ratios indicated a significant

difference between the samples at the 95-percent-confidence level, with

the ratio being lower for 1-52. This is interpreted as meaning that more

Fe^{+2} was leached from the edges than Mg^{+2}. A comparison of Si^{+4}/Al^{+3} ratios

for both edges and interior portions indicates that this ratio remains es-

sentially constant from initial to terminal samples. Evidence presented

earlier indicated pronounced loss of Si^{+4} from the chlorite; therefore,

the only way the Si^{+4}/Al^{+3} ratio could remain constant is for Al^{+3} to be

leached also. This is substantiated by other evidence already presented.

Comparison of Results of this Study with Previous Investigations

Pedro (1961) concluded that iron and titanium were not leached

from the weathered material of his experiment. In this study Fe was

leached from the chlorite (see table 3).

Borovec and Neuzil (1966) indicated Al mobility to be 15 to 20

times less than that of Si. Table 3 of this study indicates the mobi-

lity of Al to be at maximum 35 times less than that of Si. If some

mobility of Al occurs as discussed in other sections, the Al mobility in

this study may be closer to that observed by Borovec and Neuzil.

Parham (1969) noted the presence of new mineral phases and the oxidation of iron as the result of his weathering studies. Although the formation of new mineral phases was not discovered in this study, iron was observed to be oxidized.

Johnson (1964) studied naturally weathered chlorite with resulting vermiculite interlayers. Although the 001 diffraction peak was more intense than normal chlorites, the d-spacings were in standard positions. In this study, chemical analyses and structural formulas show considerable alteration of the chlorite, but the diffraction patterns are essentially those of chlorite.

PROPOSED MODEL FOR CHEMICAL WEATHERING OF CHLORITE

Because the topic of this dissertation is the experimental wea-
thering of chlorite, I consider presentation of a possible model for
such weathering and its possible end product to be essential. This dis-
cussion will necessarily summarize and reiterate much of the material
presented under the preceding section.

Chlorite is composed of four structural layers, two of which
have cations in tetrahedral coordination and two which have cations
in octahedral coordination (fig. 2a). The tetrahedral layers are pop-
ulated by Si^{+4} and Al^{+3} cations, and the brucite layer (octahedral) is
populated by Mg^{+2}, Al^{+3}, and Fe^{+2} cations. The octahedral layer of the
mica-like unit is trioctahedral, as indicated by a 060 d-spacing of
$1.54\overset{o}{A}$ (Brindley and Gillery, 1956). This means that the mica-like octa-
hedral layer is occupied by the divalent cations Mg^{+2} and Fe^{+2}.

In this arrangement (fig. 2), the brucite layer is bonded by
simple electrostatic attraction between the negatively charged tetra-
hedral layers and the H^{+} protons of the brucite $(OH)^{-}$ groups. The
mica-like octahedral layer is shielded by the tetrahedral layers. These
inhomogeneities appear to leave the brucite and tetrahedral sheets more
susceptible to attack by leaching than the octahedral layer of the mica-
sheet.

Based on evidence previously presented in this study, chlorite weathering proceeds in the following ways.

1. Si^{+4} is removed from the tetrahedral layers, increasing the relative amount of Al^{+3} in the tetrahedral sites. This creates a net negative charge on the mica-sheet.

2. Fe^{+2} is removed from octahedral coordination in the brucite sheet, along with Al^{+3}, at a faster rate than Mg^{+2}. Removal of Al^{+3} further increases the charge unbalance on the structure.

3. With prolonged weathering, the mica-sheet octahedral layer may be leached.

4. The weathering process of this experiment also results in an increase in the amount of adsorbed H_2O on the study samples, accompanied by an increase of 0.3 to 0.4Å for the basal 001 d-spacing.

If, as suggested earlier, the mineral, chlorite, can be weathered to produce a mineral like vermiculite, then the mica-sheet should remain intact, but the brucite sheet should be altered to Mg^{+2} and perhaps some Fe^{+2} as interlayer cations.

Burns (1970) discussed sedimentary geochemistry of the transition elements and provided a basis for predicting the method of Fe^{+2} removal. Using crystal-field-theory considerations, we see that Fe^{+2} has a d^6 configuration (6 electrons in the outer d-orbital). In an octahedral field, the d_{z^2} and $d_{x^2-y^2}$ orbitals are repelled from the ligands more than are the d_{xz}, d_{xy}, and d_{yz} orbitals. This leads to a splitting of the d-orbital into two energy levels, with the d_{z^2} and $d_{x^2-y^2}$ being the highest

levels (fig. 12).

According to Burns (1970), an H_2O molecule approaches the central transition-metal ion along a vacant t_{2g} orbital and forms an activated complex, which instead of being octahedral is distorted into a pentagonal bipyramid. The H_2O molecule is the seventh ligand and is bonded by the lone-pair electrons of the oxygen atom. This pentagonal bipyramid decays spontaneously, forming an octahedral complex again with an H_2O group.
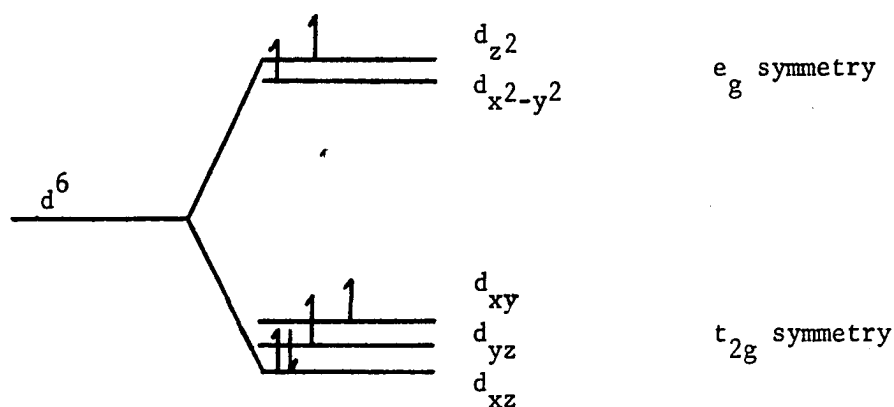
Figure 12. Splitting of d-orbital in an octahedral field (high-spin d^6 case).

Repetition of this process five times leaves the metal ion in octahedral coordination with H_2O. Burns states that the crystal-field-stabilization energies of Fe^{+2} in the low-spin state favor formation of the pentagonal bipyramid complex. However, the low-spin state leaves no t_{2g} orbitals vacant for substitution. Thus, the high-spin state illustrated above offers the best chance for substitution. These ideas are offered as a possible explanation for the removal of Fe^{+2} from the brucite layer of chlorite. The data presented in this study do not bear any relation to

the above as a possible mechanism for the weathering of chlorite, but are presented for consideration as possible mechanisms.

In comparing the terminal samples 1-52, 2-44, 3-44, and 4-20 with the vermiculite model, it does not appear that the weathering experiment produced vermiculite from the initial samples. The terminal samples are similar to vermiculite in their chemical compositions, structural configurations, and increased 001 d-spacings. They differ, however, from vermiculite because they lack the expansible properties of vermiculite, and the X-ray-diffraction patterns do not show the same intensity relationships between peaks as does vermiculite (Grim, 1968). I suggest that the terminal samples in this study are an intermediate state between chlorite and vermiculite. Of the four samples, 1-52 and 3-44 are believed to most closely approach the desired end product. Their progression toward this end product is believed to be due to the length of time allowed for leaching sample 1-52 and for the size of the sample 3-44 particles.

The complete removal of Al^{+3} from the brucite layer may be the first main threshold to cross in the formation of vermiculite. I suspect that complete or near-complete removal of Fe^{+2} from the brucite layer is also necessary, a condition not met by any of my weathered samples.

Day and Selbin (1969) provide information which might explain the apparent order of removability for the major cations of this study. That order is, in descending order of removability: Si > Fe > Al > Mg. The ranking of the Fe > Al > Mg can best be explained in terms of the electronic ground states of those elements (Day and Selbin, 1969, table 3-4). Ranked in descending order of the energy level of the ground state, we find Fe > Al > Mg. Iron has a ground-state-energy level of $^5D_4$;

aluminum, $^2P_{1/2}$; and magnesium, $^1S_0$. Examination of Day and Selbin's table shows Mg has the same ground-state-energy level as the inert gases and thus would not be expected to be easily leached.

To find why Si is more easily leached than Fe, we must examine the type of bonds formed by each and their relative strengths (Day and Selbin, 1969, table 10-6). Si^{+4}, having a coordination number of 4, forms tetrahedral compounds through sp^3 hybrid bonds. According to the Valence Bond Theory (Day and Selbin, 1969), this relative bond strength is 1.991. Fe^{+2}, having a coordination number of 6, forms octahedral compounds through d^2sp^3 hybrid orbitals, which is the most stable hybrid bond. The relative bond strength of the d^2sp^3 hybrid is 2.923. Thus, on the basis of Valence Bond Theory, Si to O bonds are predicted to be weaker than Fe to O bonds.

Geological observations may serve to substantiate this apparent order of removability. These are:

1. Si and Fe are relatively easily removed from mineral structures and show some mobility as evidenced in the case of Si by the common occurrence of quartz overgrowths, chert lenses in carbonate rocks, and bedded chert and in the case of Fe by the common occurrence of ferric-oxide-stained rocks and minerals, sometimes involving immense thicknesses of rock.

2. The less removability and relative immobility of Al are indicated by the retention of Al in laterite zones where severe leaching has removed most other metallic cations.

3. Lack of Mg mobility and removability is indicated by Mg retention in soil profiles of the minerals montmorillionite and vermiculite (see Loughnan, 1969; Droste, 1956).

CONCLUSIONS

In this section are presented the conclusions based on the evidence in the preceding sections of this paper. Most have been mentioned or listed in the sections on "Discussion and Results" and "Proposed Model for Chemical Weathering of Chlorite." All of the following conclusions should be prefaced by "under the conditions of this experiment."

1. Soxhlet extractors are effective devices for experimental weathering studies. Circulation of distilled H_2O through the chlorite leads to a cloudy appearance of the water after 3 days to 1 week. Longer periods of leaching (2-4 weeks) caused the residual water to become transluscent and milky.

2. Si^{+4}, Al^{+3}, Fe^{+2}, and Mg^{+2} are all leached from the chlorite structure. Si^{+4} is leached from the tetrahedral layers and Al^{+3}, Fe^{+2}, and Mg^{+2} are leached from the octahedrally coordinated brucite layer. The cations can be arranged, in decreasing order of removability, as $Si^{+4} > Fe^{+2} > Al^{+3} > Mg^{+2}$.

3. Although the weathering process is believed to proceed toward a vermiculite end member, the X-ray diffraction patterns of the most altered sample (1-52) were still essentially that of a chlorite. This is significant because the chemical

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analyses no longer fit the chlorite model.

4. Attempts to provide kinetic data on the rate of chlorite

weathering, primarily through solution chemistry studies,

were unsuccessful.

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APPENDIX 1

POWDER DIFFRACTION DATA

Sample	hkl	d(Å)
1	001	13.44
1	002	7.13
1	003	4.59
1	004	3.54
1	005	2.84
1	060	1.54
2	001	14.03
2	002	7.11
2	003	4.75
2	004	3.55
2	005	2.85
2	060	1.54
3,4	001	13.49
3,4	002	7.13
3,4	003	4.73
3,4	004	3.56
3,4	005	?
3,4	060	?

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Sample	hkl	d(Å)
1-52	001	13.75
1-52	002	7.08
1-52	003	4.68
1-52	004	3.55
1-52	005	2.84
1-52	060	1.54
2-44	001	14.28
2-44	002	7.13
2-44	003	4.68
2-44	004	3.55
2-44	005	2.84
2-44	060	1.54
3-44	001	13.98
3-44	002	7.13
3-44	003	4.69
3-44	004	3.55
3-44	005	2.84
3-44	060	1.54
4-20	001	13.81
4-20	002	7.16
4-20	003	4.67
4-20	004	3.56
4-20	005	?
4-20	060	1.54

APPENDIX 2

WEIGHT-LOSS DATA

(in three parts)

Part A. Adsorbed H_2O Loss

Sample	Unfired Weight (grams)	Heated to 300°C (grams)	Difference (grams)	Percent Loss
1	0.0671	0.0649	0.0022	3.278
2	1.2254	1.2209	0.0045	0.360
3,4	1.0097	1.0029	0.0077	0.760
1-52	0.0290	0.0271	0.0019	6.551
2-44	0.1724	0.1698	0.0026	1.508
3-44	0.2060	0.2023	0.0037	1.796
4-20	0.1764	0.1730	0.0034	1.927

Part B. Total H_2O Loss

Sample	Unfired Weight (grams)	Heated to 1,000°C (grams)	Difference (grams)	Percent Loss
1	0.0671	0.0571	0.0100	14.903
2	1.2254	1.0797	0.1457	11.880
3,4	1.0097	0.8842	0.1255	12.429
1-52	0.0290	0.0247	0.0043	14.827
2-44	0.1724	0.1514	0.0210	12.180
3-44	0.2060	0.1785	0.0275	13.340
4-20	0.1764	0.1526	0.0238	13.490

Part C. Summary

Sample	Percent Adsorbed H_2O	Percent "Bound" H_2O	Total H_2O
1	3.278	11.6205	14.903
2	0.360	11.520	11.880
3	0.760	11.669	12.429
4	0.760	11.669	12.429
1-52	6.551	8.276	14.827
2-44	1.508	10.672	12.180
3-44	1.796	11.554	13.340
4-20	1.927	11.563	13.490

Data for this appendix was obtained by the method of "difference," that is, the sample was weighed, heated to a temperature sufficient to remove H_2O, and reweighed. The weight loss difference is assumed to be H_2O loss.

The main source of error for this method is an error in weighing the samples. Because of the small amount of Sample 1 available, any errors could have a substantial effect on the H_2O percentage recorded. This might be the source of the obvious difference in adsorbed H_2O for Sample 1 and Sample 2, which represent different grindings of the same material.

Other sources for this difference other than weighing errors are:

(1) Smaller particle sizes possibly present in Sample 1, thus giving increased surface error for adsorption of H_2O.

(2) Re-adsorption of H_2O on to Sample 2 during the period it was being removed from the oven and weighed. This would decrease the amount of adsorbed water recorded for that sample.

APPENDIX 3

FLUORESCENCE-SPECTROSCOPY DATA

| Oxide | Sample | Sample 1, Oxide Percent by Weight | |
		H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	27.83	26.52	30.91
Al_2O_3	12.76	12.16	14.17
SiO_2	33.87	32.27	37.62
FeO	15.33	14.60	17.02
CaO	0.22	0.21	0.24
H_2O	14.90	14.20	---
Total	104.91	99.96	99.96

| Oxide | Sample | Sample 2, Oxide Percent by Weight | |
		H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	28.56	27.42	31.16
Al_2O_3	13.70	13.15	14.94
SiO_2	34.12	32.76	37.22
FeO	15.07	14.47	16.44
CaO	0.19	0.18	0.20
H_2O	11.88	11.40	---
Total	103.52	99.38	99.96

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Oxide	Sample	Sample 3, Oxide Percent by Weight	
		H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	28.93	27.19	30.82
Al_2O_3	14.24	13.39	15.17
SiO_2	34.75	32.67	37.03
FeO	15.75	14.81	16.78
CaO	0.14	0.13	0.15
H_2O	12.43	11.68	--
Total	106.24	99.87	99.95

Oxide	Sample	Sample 4, Oxide Percent by Weight	
		H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	28.93	27.19	30.82
Al_2O_3	14.24	13.39	15.17
SiO_2	34.75	32.67	37.03
FeO	15.75	14.81	16.78
CaO	0.14	0.13	0.15
H_2O	12.43	11.68	--
Total	106.24	99.87	99.95

		Sample 1-52, Oxide Percent by Weight	
Oxide	Sample	H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	30.93	33.10	39.42
Al_2O_3	12.19	13.04	15.53
SiO_2	21.06	22.53	26.83
FeO	14.17	15.16	18.05
CaO	0.09	0.10	0.12
H_2O	14.83	15.98	--
Total	93.27	99.91	99.95

		Sample 2-44, Oxide Percent by Weight	
Oxide	Sample	H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	29.94	28.74	32.84
Al_2O_3	12.73	12.22	13.96
SiO_2	33.05	31.73	36.25
FeO	15.30	14.69	16.78
CaO	0.09	0.09	0.10
H_2O	12.18	11.69	--
Total	103.29	99.16	99.93

		Sample 3-44, Oxide Percent by Weight	
Oxide	Sample	H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	33.09	32.43	37.54
Al_2O_3	15.31	15.00	17.36
SiO_2	25.20	24.70	28.59
FeO	14.45	14.16	16.39
CaO	0.11	0.11	0.10
H_2O	13.34	13.07	--
Total	101.50	99.47	99.98

		Sample 4-20, Oxide Percent by Weight	
Oxide	Sample	H_2O Present (calc. to 100%)	H_2O Free (calc. to 100%)
MgO	33.41	30.07	34.26
Al_2O_3	14.67	13.20	15.04
SiO_2	34.27	30.84	35.14
FeO	14.99	13.49	15.37
CaO	0.14	0.13	0.14
H_2O	13.49	12.14	--
Total	110.97	99.87	99.95

A discussion of fluorescence spectroscopy methods can be found in Cullity (1956), Zussman (1967), and Willard and others (1965).

Of special interest here is the slight differences in percentages of the various elements for Sample 1 and Sample 2. These samples are different grindings of the same material, therefore, only slight differences in particle size distribution could account for analytical variations among the elements. Also, in the making of the briquettes for fluorescence analyses, incomplete or improper mixing of the PVA could effect the number of counts per minute obtained from fluorescence of the sample.

APPENDIX 4

SOLUTION-CHEMISTRY DATA

Sample	Fe^{+2}/Mg^{+2}	$\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$
1-36 wks.	0.086	3.47
1-40 wks.	0.116	1.84
1-44 wks.	0.122	2.06
1-48 wks.	0.103	1.59
1-52 wks.	0.108	1.87
2-20 wks.	0.068	2.78
2-24 wks.	0.060	2.56
2-28 wks.	0.069	2.13
2-32 wks.	0.070	1.92
2-36 wks.	0.069	1.98
2-40 wks.	0.076	1.83
2-44 wks.	0.076	1.89
3-20 wks.	0.051	2.39
3-24 wks.	0.083	2.06
3-28 wks.	0.092	1.62
3-32 wks.	0.096	1.35

Sample	Fe^{+2}/Mg^{+2}	$\dfrac{Fe^{+2} + Mg^{+2}}{Al^{+3}}$
3-36 wks.	0.098	1.35
3-40 wks.	0.102	1.40
3-44 wks.	0.105	1.58
4-1 hrs.	0.063	3.90
4-2 hrs.	0.052	4.47
4-4 hrs.	0.048	4.34
4-8 hrs.	0.059	3.56
4-12 hrs.	0.088	3.26
4-24 hrs.	0.074	2.63
4-48 hrs.	0.081	2.36
4-72 hrs.	0.084	2.29
4-96 hrs.	0.095	2.19
4-3 wks.	0.132	1.19
4-6 wks.	0.122	1.40
4-8 wks.	0.106	1.59
4-12 wks.	0.226	0.97
4-16 wks.	0.193	1.30
4-20 wks.	0.176	1.40

APPENDIX 5

STANDARD DEVIATIONS OF FLUORESCENCE-SPECTROSCOPY ANALYSES[1]

Element	Percent Standard Deviation	
	Standard Samples	Experiment Samples
Fe	± 4.296	± 0.315
Mg	±21.915	± 2.086
Si	±13.557	± 4.165
Al	± 6.223	± 0.898
Ca	± 1.670	± 0.041

[1]These percent standard deviations represent standard deviations of (a) all the standard samples and (b) all the experiment samples rather than standard deviations of repetitive analyses for each sample. Therefore, these are standard deviations over a range of samples.