The role of structural iron oxidation in the weathering of trioctahedral micas by aqueous solutions

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The role of structural iron oxidation in the weathering of trioctahedral micas by aqueous solutions

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CHAPTER I. GENERAL INTRODUCTION

Micas are among the common rock-forming minerals and, consequently, are part of the parent material in which many soils form. Their importance in soils is both agronomic and mineralogic. Agronomically, micas serve as a major source of potassium (K) and several other elements that are essential to plant nutrition. Mineralogically, micas are of importance because they weather to produce several secondary layer silicates including illite, vermiculite, smectite and kaolinite. The physical and chemical properties of these secondary clay-size minerals determine to a large extent the reactions that may occur in soil systems.

The rate at which micas weather and the products that are formed as they weather depend on numerous factors including the composition of the mica, the nature of the weathering solution, and the intensity of the weathering regime. What distinguishes mica weathering from that of other soil minerals (e.g., feldspars, quartz), however, is that it often proceeds anisotropically because of the layer type of structure. For example, the interlayer cations (predominantly K)\(^a\) may be solubilized by exchange with more strongly hydrated ions (Na, Mg, Ca)\(^a\) leading to an expandable layer type structure. As a result, mica weathering can

\(^a\)Throughout this dissertation, the elemental symbol will also be used to represent the stable aquo ion or species having the same oxidation state as this ion [i.e., K also represents K(I) and K\(^+\), Al represents Al(III) species, F represents F(-I) and F\(^-\) species, etc.].
involve both the internal and external surfaces of the expanded mica and can be profoundly influenced by the unique chemical environment of the interlayer region.

Another complicating factor in the chemistry of mica weathering is the presence of redox-sensitive elements (Fe, Mn) in the mica structure. A change in the redox status of these elements, such as the oxidation of structural Fe(II), must be accompanied by a charge-balancing reaction to maintain electrical neutrality in the mica structure. Examples of charge-balancing reactions include the loss or gain of interlayer cations, the ejection of cations from the octahedral sites, and the reversible deprotonation of hydroxyl groups in the structure.

As discussed in a recent review by Scott and Amonette (1988), much of the research into the chemistry of mica weathering has focussed on either the oxidation of structural Fe or the exchange of interlayer K by other ions. The interplay between these two processes has also received attention, but some questions remain unresolved. In particular, although Fe oxidation occurs readily when the interlayer region is expanded by interlayer K exchange (Newman and Brown, 1966; Robert and Pedro, 1969; Farmer et al., 1971; Ross and Rich, 1974; Scott and Youssef, 1979), it is uncertain whether Fe oxidation can occur prior to expansion of the interlayer region and to what extent subsequent K exchange might be affected. In theory, if Fe oxidation did occur and were balanced solely by deprotonation of structural hydroxyls, the selectivity of the mica for K would be enhanced and the rate of weathering diminished. On the other hand, if Fe oxidation were balanced
by the loss of interlayer cations (i.e., the negative charge of the mica layers was decreased by the oxidation of structural Fe), a subsequent expansion of the mica should occur more readily and the rate of weathering should increase. The ejection of octahedral cations to balance oxidation may enhance the susceptibility of micas to weathering by causing some opening of the interlayer region, but could have the opposite effect if the K selectivity is enhanced by a rotation of the structural hydroxyl dipoles towards the vacant sites.

Laboratory attempts to oxidize structural Fe in biotite without expanding the interlayer region by K exchange have involved treatments with strong oxidants in solutions having high K concentrations. The most effective oxidants seem to be \( \text{H}_2\text{O}_2 \) and \( \text{Br}_2 \), although each suffers from certain limitations (Amonette et al., 1985). The results of these attempts have been mixed and are somewhat obscured by side-effects associated with the oxidants and the fact that only two micas have been studied.

Juo and White (1969) obtained "only partial oxidation" in a ground Gold Coast biotite sample (< 5-\( \mu \)m size-fraction) treated for short time periods with 30% \( \text{H}_2\text{O}_2 \)-0.2 M KCl solutions. These results may have been affected by the rapid decomposition of \( \text{H}_2\text{O}_2 \) at 80°C as well as the short treatment periods. By maintaining \( \text{H}_2\text{O}_2 \) at adequate levels with a continuous-flow system and by treating for longer time periods in 1 M KOAc at 80°C, Amonette (1983) was able to oxidize more than 50% of the structural Fe in ground Faraday biotite samples (10- to 20-\( \mu \)m) in 24 days. Identical experiments with large macroflakes of the biotite,
however, resulted in extensive exfoliation of the mica by the $\text{H}_2\text{O}_2$ treatment (Scott and Amonette, 1988). These results suggested that the oxidation observed in both instances could be due to a proportional increase in the surface area exposed to the oxidizing solution. Significant oxidation of the same biotite (5- to 10-µm size-fraction and macroflakes) has also been achieved using Br$_2$-saturated KCl solutions (Kozak, 1976), but much longer treatments are required and the results are confounded by the potential for interlayer K-HgO$^+$ exchange that exists in acidic solutions (Newman, 1970).

Amonette (1983) also studied the kinetics of the oxidative weathering process in the Faraday biotite. In his experiments with flowing 30% $\text{H}_2\text{O}_2$-1 M K solutions, he noted that after an initial period of rapid oxidation the rate of oxidation slowed until it was essentially the same as the corresponding rate of dissolution. He proposed a simple core-rind type of weathering model in which mica particles were assumed to be homogeneous two-dimensional disks consisting of an unaltered core and an oxidized rind. According to the model, the width of the oxidized rind zone expanded until the radial rate of electron diffusion (which is inversely proportional to the diffusion distance) from the core-rind boundary in the interior of the mica to the bulk solution had slowed to equal the radial rate of dissolution at the exterior of the particle. From this stage, the width of the oxidized rind zone remained constant until the core was completely oxidized. One difficulty with this model, however, is that it assumes no dissolution or oxidation occurs at the basal surfaces of the mica particles. Thus, the mica is predicted to
weather at the same rate regardless of the degree of expansion or
exfoliation of the mica. Unfortunately, no direct measurements of the
extent of exfoliation, or of the relative dissolution rates of
exfoliated and unaltered samples, were made in the study, so the
validity of the model could not be verified.

Clearly, none of these laboratory weathering studies has
demonstrated conclusively that structural Fe can or cannot be oxidized
in a contracted mica by an aqueous solution. This result is at least
partly due to the limited number of micas examined in these weathering
studies and the uncertainties regarding the extent of exfoliation and
expansion of the mica layers during treatment. The central problem of
this dissertation, therefore, was to resolve the controversy regarding
the aqueous oxidation of structural Fe in contracted micas.

A solution to the problem was approached by developing and applying
a variety of experimental techniques to study the laboratory weathering
of trioctahedral micas. Three micas were chosen for this study and they
encompassed a wide range in Fe(II) content so that the role of Fe
oxidation could be segregated from other features of mica weathering.
Solutions of \( \text{H}_2\text{O}_2 \) buffered at pH 4.7 were used to oxidize the micas
because earlier work (Amonette, 1983; Amonette et al., 1985) had shown
these solutions offered the best combination of a strong oxidant with
minimal side effects. To isolate the effects of dissolution during
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pretreatments (e.g., K-depletion, deuteration, oxidation) were also applied to the micas before they received the weathering treatments. A special flow-through apparatus, constructed entirely of inert plastic and attached to a peristaltic pump, was designed to allow simultaneous treatment of several mica samples at 80°C while maintaining essentially constant levels of the oxidant and other reactants in solution. The effluent collected from these treatments after various periods was analyzed for mica constituents and the results interpreted with the aid of a kinetic model for heterogeneous dissolution adapted from earlier work of Delmon (1961a, 1961b, 1961c). These kinetic data, together with data from a K-Rb tracer study were used to establish the existence and to estimate the extent of the exfoliation and expansion reactions thought to occur during the weathering treatments.

Resolution of the problem also required the development and application of several analytical techniques. Thus, a precise and reliable method for the assay of Fe(II) in micas was developed by making several modifications to the procedures of Wilson (1955) and Peters (1968). Another method for estimating the cation occupancy of the octahedral and tetrahedral sites in micas by x-ray diffraction was developed to allow the monitoring of cation ejection reactions during weathering. And, routine use was made of Mössbauer and infrared spectroscopies to follow changes in the oxidation state of Fe and in the coordination environment of structural hydroxyls, respectively, during the weathering treatments.

In the chapters that follow, the Fe(II) and cation occupancy
techniques are discussed thoroughly and then applied, in combination with the experimental techniques that were outlined, to achieve a better understanding of the role of iron oxidation in the aqueous weathering of micas.
CHAPTER II. AN IMPROVED SEMI-MICRO METHOD FOR THE DETERMINATION OF FERROUS IRON IN NON-REFRACTORY SILICATE MINERALS

Introduction

Survey of existing methods

Procedures for the determination of the redox status of Fe in silicate minerals can generally be distinguished on the basis of method of sample decomposition and method of Fe(II) assay (Schafer, 1966; Johnson and Maxwell, 1981; Loveland, 1988). According to the first criterion, two broad groups of methods exist—those achieving sample decomposition by an alkali-salt fusion followed by dissolution of the fusion cake in an acid solution and those in which the sample is dissolved directly in a strong acid mixture (usually HF-H₂SO₄).

Both of these decomposition techniques face the considerable challenge of maintaining the original Fe(II)/Fe(III) equilibrium while preparing the sample for assay. The fusion methods seem to be more at risk in this regard than the acid decomposition methods because of the higher temperatures involved (Donaldson, 1969), although they do have the advantage of completely dissolving otherwise refractory samples. The acid decomposition methods, on the other hand, have found wide usage (in part because of their relative simplicity, high sample throughput and accessibility to most wet chemistry laboratories), but face problems
associated with the formation of insoluble fluorides and recalcitrant fluoride complexes. They generally yield higher precision than the fusion methods, however, and are probably the more accurate methods for non-refractory samples.

The second major criterion by which Fe(II) methods can be distinguished is the manner in which the Fe(II) content is assayed once the sample has been dissolved. Again, two broad categories are found--oxidimetric methods, in which the Fe(II) is determined by reaction with a known quantity of oxidant (direct titration or back-titration), and spectrophotometric techniques, which involve the chelation of Fe(II) by a chromogenic compound [e.g., 1,10-phenanthroline (phen)] and determination of the amount present by colorimetry. In both types of methods, the oxidant or chromogen can be added after the sample has been dissolved or, preferably, added at the same time as the dissolving acid so that reaction with Fe(II) occurs immediately upon dissolution of the sample and oxidation by aqueous O₂ is minimized. In the latter instance, care must be taken to ensure that the oxidant or chromogen is stable under the conditions encountered during the decomposition procedure.

Several factors can interfere with the accurate assay of the Fe(II) in the sample. The first and most obvious factor is an incomplete solubilization of the sample. This is more often a problem in the acid decomposition procedures and is usually due to the formation of insoluble fluorides after the original sample has dissolved. The addition of fluoride complexing agents such as H₃BO₃, BeCl₂ or AlCl₃ to
the HF digest can help to dissolve fluoride precipitates, although success with this approach is not completely assured. Alternatively, refractory samples may be dissolved by the use of a fusion technique. A second interfering factor is the oxidation or reduction of Fe in solution by other components originally present in the sample [e.g., sulfides, organic matter, Ti(III), Mn(IV), Cu(I), V(III), V(V)]. Short of removing the interfering component from the sample, which in itself may be a formidable task, this problem seems intractable. The accuracy of all sample-destructive methods for Fe(II) suffers to some extent from this source of error, but, in most non-sulfidic and non-carbonaceous samples, the magnitude of the error is probably small and of little significance. A third potential interfering factor is the oxidation of Fe(II) in solution by dissolved O_2. The problem is well-known and is discussed in some detail by Clemency and Hagner (1961), Schafer (1966), and Johnson and Maxwell (1981). The possibility of O_2 interference can be eliminated by conducting the entire procedure under an inert atmosphere or, more easily, by decomposing the sample in the presence of an oxidant or chromogen that is more resistant to oxidation by O_2.

Other problems arise from the presence of ions that interfere in the Fe(II) assay. For oxidimetric methods, ion couples that have formal redox potentials between those of the oxidant and Fe couples may cause errors. In large part, these errors can be eliminated by the judicious choice of the oxidizing couple. For example, Mn(II) and Cr(III) may contribute to the Fe(II) titre when the strong oxidants MnO_4^- or Ce(IV) are used in acidic solutions--use of the milder oxidants IO_3^- or VO_3^-
avoids this problem. The oxidimetric methods can also suffer from indistinct endpoints, a problem that is often solved by the addition of phosphate or fluoride ions to form colorless Fe(III) complexes and to poise the Fe(II)/Fe(III) system at a slightly lower redox potential. These additions, although yielding considerable improvements in precision, may have an impact on accuracy if blank and sample matrices are not well-matched.

With spectrophotometric techniques, various transition metal ions can give high Fe(II) assays by forming their own chromogen complexes whose absorbance maxima overlap those of Fe(II). Lower assays by these techniques may be obtained in strongly acidic solutions or when other complexing anions such as cyanide, phosphate, pyrophosphate and dichromate are present (Schilt, 1967, p. 58). Relatively high concentrations of fluoride ions can also interfere in the formation of the chromogen chelate (Stucki and Anderson, 1981; Kiss, 1974) and white light can catalyze the reduction of Fe(III)-phen to the Fe(II)-phen species (Stucki, 1981). These problems seem to be at a minimum when 1) a strongly-complexing chromogen such as phen \((\log K = 21.5)\) is used in place of the more strongly-absorbing but weakly-complexing chromogens such as ferrozine \([\log K = 15.9 \text{ (Thompson and Mottola, 1984)}]\), 2) the samples are kept under red light after addition of the chromogen (Stucki, 1981), 3) a cation-masking agent (e.g., citrate) is used, and 4) the pH of the solution is near the \(pK_a\) of the chromogen at the time absorbance is measured (Schilt, 1967). The method of Stucki (1981) seems to offer the best precision and accuracy of the spectrophotometric
Fe(II) methods for silicate minerals and has the bonus that determinations of total Fe and Fe(III) (by difference) can also be made on the same digest. A recent modification, involving the use of a mercury vapor lamp, has shortened the photoreduction step in the total Fe assay to less than 1 hour (J. W. Stucki, Department of Agronomy, University of Illinois, Urbana, IL, 1987, personal communication), thus greatly enhancing the utility of the method.

As an alternative to the sample-destructive techniques described so far, Mössbauer spectroscopy may be used to assay the Fe(II)/Fe(III) ratio of the intact sample. This technique can reveal valuable information about the structural environment of the Fe in the sample (Goodman, 1980; Heller-Kallai and Rozenson, 1981) but is not very practical for routine Fe(II) determinations because of the slow and relatively imprecise nature of the method. In addition, a sample-destructive determination of total Fe must be made if the redox values are to be reported on a mass basis. For samples high in sulfides or organic matter, however, Mössbauer spectroscopy may be the only appropriate method.

**Choice of method**

As noted by Schafer (1966) and by Loveland (1988), no single best method for the determination of Fe(II) in silicates exists. The choice of method should depend on the characteristics of the samples, the number of samples expected, the precision and accuracy required, and the availability of reagents, equipment and facilities. A good match is
obtained when the sample is decomposed completely and the assay is performed with minimal interferences and maximal accuracy, precision and speed. In general, the best results for nonrefractory samples seem to be obtained when acid-decomposition is employed and the Fe(II) assayed by the simultaneous reduction of a mild oxidant or by the method of Stucki (1981).

For the biotite weathering experiments in Chapters IV and VI, a very precise and relatively fast method was needed that could handle the large batches of homologous mica samples that were produced. Because a high resolution spectrophotometer was not readily available, several mild oxidimetric methods were examined to see if any matched these criteria.

Methods incorporating Cr(VI) (Reichen and Fahey, 1962), I(I) (Banerjee, 1974), I(V) (Van Loon, 1965), and V(V) (Wilson, 1955; Wilson, 1960; Peters, 1968) as mild oxidants were examined. In the method of Reichen and Fahey (1962), the well-known instability of Cr$_2$O$_7^{2-}$ in hot HF solutions (Sarver, 1927; Hey, 1941; Peters, 1968) is countered by the presence or addition of Fe(III) to these solutions. Nevertheless, the precision of the method (Peters, 1968; Reichen and Fahey, 1962) was not suitable. The I$^+$Cl$^-$ method of Banerjee (1974) relies on the retention of I$_2$ by a separate CCl$_4$ phase during the decomposition, and requires digestion at room temperature overnight and vigorous shaking of the sample during the final titration. The method is very precise (Banerjee, 1974), but it is not fast and seemed a bit cumbersome during the titration step. The VO$_3^-$ and IO$_3^-$ methods also seem to give very
precise results. The VO$_3^-$ methods, however, recommend overnight
digestions. The IO$_3^-$ method, although decomposing the sample rapidly,
involves boiling in open Erlenmeyer flasks and thus may be inconvenient
for large batches of samples. In short, none of the mild oxidimetric
methods that were examined fully satisfied the criteria for speed,
precision and batch analysis. The VO$_3^-$ method of Peters (1968),
however, is very precise and well-suited for batch analysis, and seemed
to offer the best opportunity for modification.

In this chapter, then, laboratory investigations of Peters' VO$_3^-$
method for Fe(II) (1968), some improvements in the precision and
rapidity of the method, and one possible source of error that may apply
to other oxidimetric methods when HF is used to decompose the sample are
reported.

Experimental

Reagents

All reagents used in this study were of A.C.S. reagent grade
quality or better.

**Acid matrix reagents** Hydrofluoric acid (48%) was used
directly from the bottle. Stock solutions of 1:3 H$_2$SO$_4$ (4.5 M) and 1:3
H$_3$PO$_4$ (3.7 M) were prepared by dilution of the concentrated acids with
deionized H$_2$O and subsequent cooling to room temperature prior to use.
A H$_3$BO$_3$-saturated solution was prepared by adding 110 g of H$_3$BO$_3$ to 2
liters of H$_2$O, heating until the H$_3$BO$_3$ had completely dissolved, and
then allowing the solution to cool overnight. The saturated supernatant solution was transferred to a manual dispensing bottle and diluted slightly with deionized H$_2$O to prevent recrystallization.

**Oxidimetric reagents**  A 0.030 M V(V) solution was prepared by weighing 7.00 g of NH$_4$VO$_3$ into a 2-liter volumetric flask and dissolving and diluting to volume with stock 1:3 H$_2$SO$_4$ solution. A 0.031 M Fe(II) solution was prepared similarly from 24.0 g of Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O. The V(V) was standardized by titrating a known amount of primary-standard grade ferrous ethylenediammonium sulfate (FES).

**Endpoint indicator**  An approximately 0.006 N solution of p-diphenylaminesulfonate was prepared by dissolving 0.1 g of the Ba salt in 100 ml of H$_2$O. Eight drops of this solution, or the Na solution (prepared by treating the Ba solution with a slight excess of Na$_2$SO$_4$ and filtering off the BaSO$_4$ precipitate), were added as an indicator during the titrations. When in the reduced state, the indicator was colorless turning to pale green near the endpoint whereas, when oxidized (E > +0.84 V), an intense purple color could be observed.

**Apparatus**

The digestions were performed in 100-ml polypropylene beakers with lids (Peters, 1968) or in 125-ml polypropylene bottles with screw caps. During the sample decomposition process, the digestion vessels were partly immersed in a water bath and kept upright by a plexiglass cover with holes drilled to the diameter of the vessels. Acid matrix reagents (HF, H$_3$PO$_4$, and H$_3$BO$_3$) were added using various types of manual
dispensers. The oxidimetric reagents [V(V) and Fe(II)] were added either by Class A volumetric pipet or by manual dispenser. In the latter instance, the amount added was determined gravimetrically using a top-loading balance with 1-mg precision. For all titrations with V(V), a 10-ml microburet with 0.02-ml graduations was used and readings were estimated to the nearest 0.01 ml.

**Mineral samples**

Five mica samples and samples of basalt, granite and peridotite were analyzed in the course of testing and developing the method. Three of the mica samples were in-house samples prepared by dry-grinding in a Waring blender and separating the different size-fractions by sedimentation in H₂O. These in-house samples were a muscovite from Effingham Township, Ontario, Canada (Musc 3A, < 50 μm), a biotite from Bancroft, Ontario, Canada (Biot 1A, < 50 μm), and a ferroan biotite originally described as a "lepidomelane" from Faraday Township, Ontario, Canada (L'ane 3B, 10-20 μm). The remaining five samples were geochemical reference specimens. These include two micas (MICA Fe and MICA Mg) from the CRPG reference collection (supplied by Geostandards, Vandoeuvre-Nancy, France) and the basalt (BCR-1, split 57), granite (G-2, split 89) and peridotite (PCC-1, split 23) from the USGS reference collection.
Methods

For reference, the Fe(II) method of Peters (1968) is summarized in the next paragraph. The results of the investigation of this method and the modifications that were made to it are described in the section that follows.

Peters' method (1968) involves placing weighed samples containing 15-20 mg FeO into 100-ml plastic beakers and then adding 20.00 ml of 0.03 M NH₄VO₃ (in 0.5 M H₂SO₄) by volumetric pipet, 20 ml of 1:3 H₂SO₄ and 5 ml of 48% HF. The beakers are covered and partly immersed in a water bath at 85°C for 1.5 hours. After stirring the contents of the beakers with a teflon rod, the thermostat of the water bath is lowered to 65°C and the beakers left to digest overnight. The next day, the beakers are removed from the water bath and allowed to cool to room temperature before quantitatively transferring their contents to 300-ml Erlenmeyer flasks containing 10 ml of 1:3 H₃PO₄. The digestates are diluted to about 150 ml with H₂O and, after adding a few drops of a 0.06 M diphenylamine-conc. H₂SO₄ indicator solution, are titrated with a 0.031 M Fe(NH₄)₂(SO₄)₂ solution (prepared in H₂O) until an apple green endpoint is observed. The digestates are then backtitrated with 0.03 M NH₄VO₃ until a permanent purple color is observed.

Results and Discussion

Preliminary investigations of Peters' method and a review of the literature associated with V(V) methods in general led to three minor
changes in the procedure. First, 125-ml polypropylene bottles were substituted for the 100-ml beakers used by Peters. The advantages to this are a larger capacity that allows digestion and titration in the same vessel, and a tight seal that minimizes silica volatilization and aids the decomposition process by maintaining a higher pressure in the vessel. Second, the 0.03 M NH$_4$VO$_3$ solution was prepared in 4.5 M (1:3) H$_2$SO$_4$ and 20 ml of this combined V(V)-H$_2$SO$_4$ solution was added to the digestion vessel rather than separate 20-ml additions of each reagent as suggested by Peters. Besides decreasing the volume of the digest and eliminating a step in the procedure, this modification has the advantage of slowing the oxidation of V(IV) by O$_2$ because of the higher acid concentration maintained in the digest (Whipple, 1974). The third modification made was the substitution of a p-diphenylaminesulfonate indicator solution for the diphenyl amine solution recommended by Peters. The sulfonate indicator was used by Wilson (1955; 1960) and, as noted by Sarver and Kolthoff (1931), develops color almost instantaneously in acidic V(V) solutions and gives a bright, sharp and reversible endpoint. In contrast, diphenyl amine is much less soluble, gives a less distinct endpoint, is slow to react with oxidants and has a tendency to precipitate when oxidized (Sarver and Kolthoff, 1931; Diehl, 1974).

**Standardization of reagents**

For any titrimetric method, the analytical conditions under which the reagents are used should approximate as closely as possible the conditions under which they are standardized. An examination,
therefore, of the precision with which standardization can be achieved under a variety of conditions should indicate the best conditions to strive for when the reagents are used to assay Fe(II) in unknown samples.

In this portion of the investigation, the effects of different amounts of $H_2SO_4$, $H_3PO_4$, and HF on the standardization of $NH_4VO_3$ (prepared in $0.5 \text{ M } H_2SO_4$) against primary-standard grade FES were examined. Initially, a $2.0 \text{ M } H_2SO_4-1.2 \text{ M } H_3PO_4$ stock solution was prepared for use as a titration matrix [a mixture suggested by Vogel (1961, p. 282) for standardization of KMnO₄ against FES]. After accurately weighing between 0.0900 and 0.1000 g of FES into 125-ml Erlenmeyer flasks, a titration matrix solution containing 10, 20, 30, 40, 50 or 60 ml of the $H_2SO_4-H_3PO_4$ stock solution diluted with $H_2O$ to 60 ml was added and the solution was stirred until the FES had dissolved. Immediately after dissolution of the FES, 8 drops of Na diphenylaminesulfonate indicator solution were added and the solution was titrated with $0.03 \text{ M } NH_4VO_3$ until a blue-purple endpoint was reached. Three FES samples were titrated for each level of acid in the titration matrix. From the equivalent weight of the FES, the apparent normality of the V(V) titrant was calculated. A series of blanks that contained no FES were also run in duplicate at each level of acid and were used to calculate corrected values of the V(V) normality. The means of these determinations are shown in Figure II-1.

When the data were not corrected for blanks, a linear increase in the apparent normality of the V(V) solution was observed in response to
FIGURE II-1. Apparent normality of a V(V) solution when standardized against FES in 60-ml solutions containing different amounts of a 2 M H$_2$SO$_4$-1.2 M H$_3$PO$_4$ mixture
\[ \text{CORRECTED FOR BLANK} \]
\[ \text{UNCORRECTED} \]
larger amounts of acid in the titration matrix. In contrast, a decrease in apparent V(V) normality was observed when the data were corrected for blank solutions. More importantly, a constant value for the normality of the V(V) solution was not obtained in either instance unless at least 40 ml, and preferably 50 ml of the acid mixture were present in the titration matrix. Clearly, the pH or ionic strength of the solution has an effect on the location of the endpoint. These results suggest that the most precise data are obtained in titration matrices that are similar in composition and concentration to the undiluted stock acid solution and that even higher concentrations of this acid mixture would pose little problem.

Next, the effects of HF addition on the location and clarity of the endpoint were examined. For this and the remaining studies, a titration matrix consisting of 40 ml 1:3 H₂SO₄ (4.5 M) and 20 ml 1:3 H₃PO₄ (3.7 M) was used because these concentrations corresponded to the amounts added in Peters' method and gave the same results as 60 ml of the stock acid solution shown in Figure II-1. Amounts of HF ranging from none to 5 ml were added to this titration matrix, and then, as before, duplicate 0.1000-g samples of FES were dissolved in the matrix and titrated with V(V) solution. The apparent normality of the V(V) solution decreased slightly as the amount of HF added increased. The clarity and stability of the endpoint, which was excellent when less than 3 ml of HF was added, decreased considerably when 5 ml of HF were present.

It seemed, therefore, that the precision of the method was greatest when less than 3 ml of unreacted HF (approximately 1.3 M HF) were
present in the titration matrix. One way of meeting this goal would be to limit the original amount of HF added during the digestion stage. This choice, however, might slow the dissolution of the mineral and thus lengthen the time required for the method, so it was not pursued. A second option would be to dilute the HF, as Peters did, but this would require transfer of the digest to a larger flask for titration and the addition of very large quantities of $\text{H}_2\text{SO}_4$ and $\text{H}_3\text{PO}_4$ if the benefits of high acid concentrations were to be realized. A third option would be to complex some of the free F(-I) ions remaining after the digestion step by the addition of $\text{H}_3\text{BO}_3$, $\text{BeCl}_2$ or $\text{AlCl}_3$, so that a concentration of approximately 1.3 M HF would be present during the titration step.

The third option was pursued in the hopes that the dilution caused by the addition of the fluoride-complexing reagent would be small enough that further additions of $\text{H}_2\text{SO}_4$ and $\text{H}_3\text{PO}_4$ would not be necessary. An experiment was conducted in which 0, 10, 20 and 30 ml of $\text{H}_3\text{BO}_3$-saturated solution were added to a titration matrix solution that contained 40 ml of 1:3 $\text{H}_2\text{SO}_4$, 20 ml of 1:3 $\text{H}_3\text{PO}_4$ and 5 ml of HF. These levels of $\text{H}_3\text{BO}_3$ corresponded to free F(-I) levels in the undiluted titration matrix solution of 5, 3.3, 1.9 and 0.9 ml HF, respectively, assuming quantitative reaction and 0.9 M $\text{H}_3\text{BO}_3$. As before, this solution was used to dissolve duplicate samples of 0.1000 g FES and these were titrated with the V(V) solution.

The titrations in which 0, 10 and 20 ml of $\text{H}_3\text{BO}_3$ were added yielded a constant value for the apparent normality of the V(V) solution and showed an increase in the clarity of the endpoint as the $\text{H}_3\text{BO}_3$ levels
increased. At the 30-ml level of H$_3$BO$_3$, however, the V(V) titer was somewhat higher (0.3%) and the endpoint was not as clear as at 20 ml. The optimal value thus seems to be at approximately 20 ml of H$_3$BO$_3$ added, when 5 ml of HF are used to decompose the sample and 60 ml of the H$_2$SO$_4$-H$_3$PO$_4$ solution are present.

Given the clarifying effects of a low concentration of free F(-I) ions on the titration endpoint, a check was made to see whether the addition of the H$_3$PO$_4$ was necessary when the F(-I) ions were also present. A titration of FES in the H$_2$SO$_4$-HF-H$_3$BO$_3$ matrix, with and without 20-ml of H$_3$PO$_4$ added, showed that the H$_3$PO$_4$ was still required to achieve a clear endpoint.

For careful work, an initial calibration of the FES primary standard may be necessary. This potential problem was noticed when two different batches of FES, each stating 99.9% purity, gave V(V) titers that differed by about 0.3%. Further investigation by the method of standard additions showed the purity of one batch to be 99.6% and the other only 99.3%. Aside from the purity problems, FES has the other prerequisites for an excellent primary standard, namely stability, high equivalent weight and stoichiometric reaction, and is probably superior to ferrous ammonium sulfate hexahydrate as a Fe(II) standard. The recommended method of calibration involves careful preparation of a K$_2$Cr$_2$O$_7$ primary standard solution and a 0.001 M (0.002 N) solution of the sodium diphenylaminesulfonate indicator. The FES (0.1000 g) is dissolved in the usual titration matrix and titrated with the Cr(VI) solution after 0.3, 0.6, 0.9 or 1.2 ml of indicator solution is added.
Correction of the results for the nominal normality of the indicator solution (i.e., an extrapolation to 0 ml of indicator solution added) should yield a consistent value for the equivalent weight of the FES. In the author's experience, triplicate determinations at each level of indicator solution have yielded an overall mean value for the FES equivalent weight with a relative error of about 0.1%.

The conclusions drawn from these reagent standardization studies are that the purity of the primary standard and the composition of the titration matrix have important effects on the titration results, and that the same titration matrix should be used for standardizing the V(V) solution as for assaying the Fe(II). The optimal matrix solution for titration of digests containing 5 ml of HF seems to be one containing 40 ml of 1:3 H$_2$SO$_4$, 20 ml of 1:3 H$_3$PO$_4$ and 20 ml of 0.9 M (saturated) H$_3$BO$_3$. Fortunately, this quantity of solution is small enough that the digestion and titration can be performed in the same 125-ml container, an advantage that improves precision and saves time.

**Modifications to the assay procedure**

Several aspects of Peters' procedure were investigated to see if improvements could be made in speed and precision. One aspect meriting consideration was the manner of measuring and delivering known amounts of reagents. Because much of the experimental error, time and, certainly, tedium in Peters' method is associated with the volumetric additions of V(V) and Fe(II), gravimetry was investigated as another way of quantifying these stoichiometric reagents. The procedure involved
weighing 0.1000-g samples into 125-ml polypropylene bottles, taring the bottles on a top-loading balance (to 1 mg precision), adding 20 ml of V(V) (0.0300 M NH₄VO₃ in 4.5 M H₂SO₄), and reweighing the bottles immediately before adding 5 ml of HF. The tightly-capped bottles were incubated in a water bath at 60°C for 4 hours (24 hours for PCC-1 samples), removed and allowed to stand in a shallow tray of cold water until they had cooled to room temperature. The caps were removed, any condensate on them rinsed into the bottles with H₂O, and then 20 ml each of H₃BO₃-saturated solution and of 1:3 H₃PO₄ were added to the bottles. The bottles were then individually tared on the balance, 20 ml of Fe(II) solution [0.0310 M Fe(NH₄)₂(SO₄)₂ in 4.5 M H₂SO₄] were added and the bottles reweighed. Immediately after adding eight drops of the p-diphenylaminesulfonate indicator solution, the contents were titrated with the same V(V) solution to a definite purple endpoint using a 10-ml microburet. The analyses were performed on six reference samples and were replicated five times. During this experiment, the additions of V(V) and Fe(II) solutions were made to tared bottles using a 20-ml volumetric pipet, after which the bottles were weighed again. Thus, the amount of each reagent added was quantified by both a volumetric and a gravimetric method. To compare the precision of the volumetric and gravimetric methods, two sets of calculations were made for each sample—one using the 20.00-ml value for the volumetric additions, and a second one using the gravimetric values. In order to convert gravimetric values to volumetric units, the densities of the V(V) and Fe(II) solutions were determined by weighing 100 ml in a tared
volumetric flask. The precision associated with each manner of addition is shown in Table II-1.

As shown by the lower means obtained for the standard and relative errors, the precision of the gravimetric method was slightly better than that of the volumetric method. For the PCC-1 samples, however, the two methods had essentially identical precision, and for the lepidomelane samples better precision was obtained with the volumetric method. A statistical comparison (paired t-test) of the precision of the two methods, however, showed no significant differences at the 0.05 level. Thus, with precision as the sole criterion, the volumetric and gravimetric methods are very similar. The two methods, however, are clearly distinguished in terms of the time required and the tedium involved. The gravimetric method is preferred because it allows the rapid addition of the reagent by a manual dispenser and thus avoids the tedious and time-consuming pipetting of the volumetric method while providing equal or slightly better precision.

Another aspect of Peters' method investigated was the digestion procedure. Earlier reports (Sieverts and Müller, 1928; Schulek et al., 1961) demonstrated the instability of the V(V)/V(IV) couple in boiling H₂SO₄ (43 to 98%) solutions. The author's experience with Peters' method suggested that the V(V)/V(IV) couple was not completely stable even in the relatively dilute HF-H₂SO₄ matrix in the 65-85°C temperature range. On the other hand, Wilson (1955, 1960) reported excellent stability of the V(V) solutions in 40% HF at room temperature. To verify the conditions under which a stable V(V) titre could be obtained,
TABLE II-1. A comparison of the precision obtained in Fe(II) determinations of six reference samples when the amounts of the redox reagents added were estimated by a volumetric or a gravimetric method

<table>
<thead>
<tr>
<th>Mineral</th>
<th>n</th>
<th>Volumetric</th>
<th>Gravimetric</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% FeO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biot 1A&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4 (5)</td>
<td>0.126 (0.315)</td>
<td>0.079 (0.273)</td>
<td>0.73 (1.84) 0.45 (1.59)</td>
</tr>
<tr>
<td>L'ane 3B&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3 (5)</td>
<td>0.032 (0.949)</td>
<td>0.061 (0.962)</td>
<td>0.15 (5.15) 0.27 (5.23)</td>
</tr>
<tr>
<td>BCR-1</td>
<td>5</td>
<td>0.087</td>
<td>0.062</td>
<td>0.97           0.66</td>
</tr>
<tr>
<td>Musc 3A</td>
<td>5</td>
<td>0.028</td>
<td>0.012</td>
<td>1.79           0.76</td>
</tr>
<tr>
<td>G-2</td>
<td>5</td>
<td>0.022</td>
<td>0.016</td>
<td>1.34           1.17</td>
</tr>
<tr>
<td>PCC-1</td>
<td>5</td>
<td>0.022</td>
<td>0.022</td>
<td>0.40           0.42</td>
</tr>
<tr>
<td>Mean</td>
<td>--</td>
<td>0.053</td>
<td>0.040</td>
<td>0.90           0.62</td>
</tr>
</tbody>
</table>

<sup>a</sup>Data with outliers are shown in parentheses.
duplicate samples of lepidomelane were digested at temperatures of 25, 40, 60 and 85°C for time periods as long as 48 hours before titrating for Fe(II). A similar experiment with samples of FES digested at one temperature (60°C) was also conducted. Duplicate samples were analyzed in each instance, except for the lepidomelane at 60°C, where four replications were run. For all determinations, the modified method involving gravimetric measurements of reagents (described in the first paragraph of this subsection) was used.

The results of this series of determinations are shown in Figure II-2 and are presented on a relative scale because of the slightly different equivalent weights of lepidomelane and FES (383.3 and 384.85 g eq⁻¹, respectively). The initial Fe(II) values for the readily soluble lepidomelane were taken from determinations of 0.5-hour digests at 60°C, whereas for FES the initial value was calculated from the calibrated equivalent weight of the standard.

The digestions at 85°C clearly resulted in low Fe(II) values, even when limited to periods of 1 hour. At 60°C, the lepidomelane samples showed a slight loss of titer in the first 24 hours, whereas the FES samples were essentially unchanged. After 24 hours, however, both samples showed a marked decline in the Fe(II) measured, similar to the 85°C treatment. The values obtained at 25 and 40°C were essentially constant and suggest that the stability of V(V) under these conditions is excellent. The relative errors associated with these data also showed a similar trend with digestion temperature. For example, the mean of the relative errors associated with the 1- and 6-hour periods
FIGURE II-2. Fe(II) values, expressed as a percentage of "initial values", that were obtained by the modified gravimetric method when lepidomelane and FES samples were digested at various temperatures and for various time periods.
for the 25°C samples was 0.11%, whereas at 40, 60 and 85°C, the comparable values were 0.15, 0.14 and 0.28%, respectively. The conclusions drawn here are 1) lower digestion temperatures improve stability of the V(V) titer, 2) digestions at 85°C are unsuitable regardless of how short the time period, and 3) the most practical digestion temperature is near 60°C where sample decomposition occurs more rapidly than at the lower temperatures and with minimal loss of precision or accuracy during the first 24 hours.

Interferences and Corrections

Although the data in Figure II-2 identify the maximum acceptable time periods for digestions at different temperatures, they also suggest that the digestion time should be minimized whenever possible. In a similar experiment with 1.2-g samples of muscovite, however, nearly opposite results were obtained. The highest Fe(II) values were obtained at 85°C after 48 hours and there was no common plateau among the various temperature treatments to indicate the "true" Fe(II) content of the sample. These data suggested that complete dissolution of the muscovite was not occurring, possibly as a result of the large sample size [1.2-g samples being needed to provide about the same amount of Fe(II) for analysis as the 0.1-g samples of lepidomelane]. To check the effect of sample size, the experiment was repeated with 0.2-g muscovite samples at 60°C. The results of the time studies at 60°C for the 0.2- and 1.2-g muscovite samples and the 0.1-g lepidomelane samples are plotted on a relative scale in Figure II-3. As in Figure II-2, the reference value
FIGURE II-3. Fe(II) values, expressed as a percentage of the "best values", that were obtained by the modified gravimetric method when lepidomelane and muscovite samples were digested at 60°C for various time periods.
for the lepidomelane samples was that obtained after 0.5 hours of digestion. The 1.2-g muscovite samples showed no evidence of a plateau region, but the 0.2-g samples yielded the same result at 12 and 24 hours. Consequently, this value was chosen as the best reference value for both sets of muscovite data in Figure II-3.

In contrast to the lepidomelane samples, both sets of muscovite samples show the effects expected from slow dissolution. The 0.2-g samples, however, seemed to be completely dissolved after 12 hours, whereas the 1.2-g samples although they seemed to have dissolved after 24 hours (visual inspection), did not yield a constant value. With longer time periods, the 1.2-g samples gave considerably higher Fe(II) values than the 0.2-g samples. After 24 hours, the 0.2-g sample data also displayed the trend towards higher Fe(II) values that was shown by the 1.2-g sample data. The data for the 0.2-g samples provide some indication that two different mechanisms may be controlling the Fe(II) values. One of these mechanisms was, obviously, the slow dissolution of muscovite (verified by visual observation). The second mechanism could involve a slow release of Fe(II) from a soluble component of the digest (e.g., a recalcitrant complex), or the slow complexation or reduction of V(V) by the digest to give an apparent increase in the Fe(II) values. Inasmuch as the muscovite and lepidomelane samples differ chiefly in the amounts of Al present in their structure relative to Fe, it seems that Al may be causing problems by complexing with Fe(II) or V(V) or by reducing V(V).

To verify the role of Al in this procedure, 0.1-g samples of
lepidomelane and 0.2-g samples of muscovite were analyzed for Fe(II) in the presence of from 0 to 37 mmol Al, which was added as 25% AlCl₃ immediately after the digestion period and before the addition of H₃BO₃ and H₃PO₄. In a separate experiment, 0.1-g samples of FES were analyzed for Fe(II) in the presence of from 0 to 5 mmol Al added as Al(OH)₃ at the same time as the FES. The effect of AlCl₃ on Fe(II) values was nil in the first experiment. The results of the second experiment are shown in Figure 11-4.

Clearly, the addition of Al in the hydroxide form greatly depressed the Fe(II) values obtained. The effect was even more pronounced when the Al hydroxide had not completely dissolved (as determined by visual inspection). This observation, combined with the absence of any effect when soluble Al was added, implies that a surface-related phenomenon is involved. Examples of such a phenomenon would be adsorption of vanadate or complex ferrous fluoride anions by a positively charged oxide surface.

The propensity of Fe and Al to form strong fluoride complexes suggests that fluoride might be a factor in the Al hydroxide effect. If so, then Mg and other oxide-forming elements with similar reactivities to fluoride might also show this effect. On the other hand, elements such as Si that form volatile fluorides would be expected to have the opposite effect on Fe(II) values. To check on these possibilities, 0.1-g samples of FES were mixed with various amounts of Al(OH)₃, MgO or SiO₂·0.7H₂O and analyzed for Fe(II) after digestion at 60°C for 24 hours (Figure II-5). As before, Al hydroxide strongly depressed the
FIGURE II-4. Fe(II) values obtained by the modified gravimetric method when FES samples were digested at 60°C for various time periods in the presence of 0 to 5 mmol of Al(OH)₃.
INCOMPLETE DISSOLUTION OF Al(OH)$_3$

Fe(II) MEASURED (cmol kg$^{-1}$)

- ○ NO Al
- □ 0.2 mmol Al
- △ 1 mmol Al
- ▼ 5 mmol Al

TIME (h)

0 3 6 24 48 72
FIGURE II-5. Fe(II) values obtained by the modified gravimetric method when FES samples were digested at 60°C for 24 hours in the presence of various quantities of Al(OH)$_3$, MgO and SiO$_2$·0.7H$_2$O.
$y = 0.48x + 259.5$

$y = -0.82x + 259.5$

$y = -2.02x^2 + 13.40x + 259.5$

- ○ Al
- □ Si
- △ Mg

Fe(II) MEASURED (cmol kg$^{-1}$)

AMOUNT PRESENT (mmol)
values obtained for Fe(II). The addition of Mg oxide also lowered Fe(II) values, but to a lesser extent than Al hydroxide. The hydrous Si oxide, however, increased the Fe(II) values slightly, presumably by the volatilization of SiF₄. These data support the premise that F⁻ ions are also involved in the mechanism that limits the Fe(II) values.

Other factors that could affect the Fe(II) data include the auxiliary acid (H₂SO₄), the oxidant itself [V(V)], and insufficient H₃BO₃ to complex the F⁻. To check on these possibilities several experiments involving the analysis of Fe(II) in FES were run with 0-1.5 mmol of Al hydroxide present. In the first, analyses of FES-Al hydroxide samples were made following the same procedures as earlier except that 6 M HCl was substituted for the H₂SO₄ in the Fe(II) and V(V) solutions. In the second experiment, 0.03 N K₂Cr₂O₇ was substituted for the V(V) oxidant and the analysis of the FES-Al hydroxide mixtures made after a 24-hour digestion. Unfortunately, the Cr(VI) completely decomposed during the digestion period so another attempt was made in which the samples were titrated directly with Cr(VI) after a 25-minute digestion and addition of H₃BO₃ and H₃PO₄. A third set of experimental analyses was conducted in which 60 to 150 ml of H₃BO₃-saturated solution or 3 g of solid H₃BO₃ were added to the FES-Al hydroxide solutions after the digestion period. These experiments involving the addition of large amounts of H₃BO₃ were performed with Cr(VI) as the oxidant, except for the 60-ml addition, which was performed with the modified gravimetric V(V) procedure. The results of these HCl, Cr(VI) and H₃BO₃ experiments were essentially the same as those obtained with the modified V(V)
method. In every instance, Fe(II) values were depressed drastically by the addition of Al hydroxide.

The exact nature of the Al hydroxide-fluoride effect is not clear from these data. The sorption phenomenon observed during the dissolution of Al hydroxide (Figure II-4) could suggest the formation of stable colloidal particles rather than complete ionic dissolution or it could merely presage the formation of redox-stable Fe(II) or V(V) oxy-fluoride complexes once dissolution is complete. The adsorbed/complexed species could be AlVO$_2$F$_4$ or MgVO$_2$F$_3$ (Sharpe, 1954), but the observation that simple titration with Cr(VI) after the digestion period yields the same results as when V(V) is present during the digestion period suggests that complexation of the oxidant may not be involved at all. Fluorochromates also form in HF solutions (Haszeldine and Sharpe, 1951), but the kinetics of complex formation, in this instance, must be very fast for the effect to be observed.

The evidence against complexation of the oxidant by these solutions, thus, suggests that a sorption/complexation reaction involving Al hydroxide, Fe(II) and F, and yielding AlFeF$_6^-$ or a complex colloidal Al-Fe hydroxyfluoride occurs. The propensity of Al to form fluoride and hydroxy-fluoride complexes in solution is well-documented (Ryss, 1956, p. 580-617) and several complex aluminofluorate precipitates have been observed when aluminosilicate minerals are dissolved in HF solutions (Langmyhr and Kringstad, 1966; Croudace, 1980). It is likely, therefore, that a stable colloidal complex resembling the mineral ralstonite (Pabst, 1939; Pauly, 1965; Croudace,
(K,Na)\(_x\)\(\text{Mg,Fe(II)}\)\(_x\)\(\text{Al,Fe(III)}\)\(_{(2-x)}\)(F,OH)\(_6\)\(\cdot H_2O\)
is responsible for the phenomenon.

Assuming that the Al coordinated to oxygen in aluminosilicate minerals behaves in a fashion similar to the Al hydroxide added in these experiments, an accurate determination of Fe(II) would require an elimination of the Al hydroxide-fluoride effect. An empirical approach to the situation is to correct the final Fe(II) results by various factors that compensate for the amounts of Al, Mg and Si in the sample. The regression equations in Figure II-5 for the data obtained in the pure FES-Al hydroxide-Mg oxide-silica system under the conditions described above provide a means for doing so. Obviously, the difficulty in applying these corrections is that analytical data for the amounts of Al, Mg and Si in the digest are needed, and one must assume that the same corrections apply to all mineral samples analyzed.

Another approach to the Al hydroxide-fluoride problem is to prevent the formation of the Fe(II)-oxyfluoride complex. This may be done by the addition of an alternative Fe(II) complexing agent, such as phen, but also requires raising the pH to 3 or above for the alternative complex to form. An attempt to eliminate the Al-hydroxide interference in this manner failed due to the simultaneous decrease in the V(V) oxidation potential as the pH was raised. It seems, however, that the Fe(II) complex formed with phen is strong enough to eliminate the Al hydroxide effect. Unpublished data (J. W. Stucki, Department of Agronomy, University of Illinois, Urbana, IL, 1986, personal communication) show
that additions of the same Al hydroxide sample used in this work, as well as an Fe-free kaolinite sample, to ferrous ammonium sulfate standards had no effect on the Fe(II) values obtained when the 1,10-phenanthroline method of Stucki (1981) was used. Thus, use of a spectrophotometric technique may be well-advised when interferences due to Al are expected.

**Recommended method**

The following method is recommended for the determination of Fe(II) in non-refractory silicate minerals, based on the author's experience and the results of the investigations reported above.

With an analytical balance carefully weigh samples containing no more than about 40 mg FeO (usually 0.1-0.2 g of sample) and transfer them into narrow-mouth 125-ml polypropylene bottles. Tare the bottles on a top-loading balance (1-mg precision), add 20 ml of a standardized solution of 0.0300 M NH₄VO₃ in 1:3 H₂SO₄ from a manual dispensing device and reweigh. When all bottles have been prepared, move them to a fume hood and add 5 ml of 48% HF to each with an all-plastic syringe pipet. Cap the bottles tightly and float them in a 60°C water bath with the aid of a support to keep them upright. After a suitable digestion period (0.5 to 4 hours for most samples, not to exceed 24 hours) remove the bottles from the water bath and let them cool in a shallow pan of water placed in the air flow of the fume hood until they reach room temperature (5-10 minutes). Remove the caps and carefully rinse the insides of the caps into the bottles with a couple ml of H₂O. With the
aid of manual dispensers add 20 ml of saturated H₃BO₃ solution and 20 ml of 1:3 H₃PO₄ to each bottle. Tare the bottles on the top-loading balance, add 20 ml of a solution of 0.0310 M Fe(NH₄)₂(SO₄)₂ in 1:3 H₂SO₄ and reweigh. Immediately before titrating the samples with the standardized NH₄VO₃ solution, add 8 drops of Na p-diphenylaminesulfonate indicator solution and a teflon-coated stirbar. Titrate, while stirring, to a permanent deep blue-purple endpoint with a 10-ml microburet. With some practice and washing of the buret tip with H₂O, additions of as little as 0.01 ml of titrant can be made, thus improving the precision of the method.

For optimum results, two sets of blanks need to be included in the analysis. The first set is to correct for slight decomposition of the V(V) during the digestion (especially important with long digestion periods). These blanks include all the reagents that are in the sample digests and follow the same procedure, but contain no sample. The second set of blanks is for standardizing the Fe(II) solution (which oxidizes slowly during storage) and should not be carried through the digestion step. These blanks include all reagents except the V(V), for which 20 ml of 1:3 H₂SO₄ is substituted, contain no sample, and can be prepared while the regular samples and blanks are digesting and cooling. Similarly, to avoid errors due to evaporation and fluctuations in room temperature, the densities of the Fe(II) and V(V) solutions should be determined by weighing in a tared 100-ml volumetric flask.

This modified method, based on earlier procedures described by Wilson (1955, 1960) and Peters (1968), was used to assay the Fe(II)
contents of five geochemical reference samples and three in-house mica reference samples. Two blocks of 5 subsamples from each reference sample were analyzed on separate days for a total of 10 replicates. Subsamples from most of the reference samples were analyzed in the same 2 batches. The MICA Fe and MICA Mg subsamples, however, were analysed in a separate two days of runs. The Q test at the 0.90 level was used to reject any outlying data. The results of these analyses (with and without outliers), adjustments for the Al, Mg and Si contents of the minerals, and recommended values from the literature are reported in Table II-2.

The Fe(II) values obtained for the five geochemical reference samples compare well with recommended values in the literature (Abbey, 1980). The overall precision of the method was also very good. The highest relative errors (after rejection of outliers) were obtained for the muscovite (0.88%), peridotite (0.80%), and granite (0.55%) samples, but these samples also had the lowest Fe(II) contents. The trioctahedral mica and basalt samples, on the other hand, yielded relative errors of less than 0.30%.

Adjustments to the sample means to compensate for the Al, Mg and Si content of the samples increased the Fe(II) values by 1-4% for most samples. However, adjustments to the means of the muscovite and granite samples (which had the highest Al:Fe ratios) resulted in Fe(II) values that were 74 and 30% higher, respectively, than the unadjusted values. The validity of these adjusted values, however, is questionable. In fact, analysis of the muscovite samples by the spectrophotometric method
TABLE II-2. Results for Fe(II) determinations of several micas and reference samples with the recommended analytical method, Fe(II) values adjusted for Al, Mg and Si in the samples, the relative changes from these adjustments, and recommended values from the literature.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Digest Time</th>
<th>n</th>
<th>Mean (SD)</th>
<th>Relative Error</th>
<th>Original Data</th>
<th>Adjusted Data</th>
<th>Literature&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>h</td>
<td></td>
<td>% FeO</td>
<td>%</td>
<td>% FeO</td>
<td>% FeO</td>
<td>% FeO</td>
</tr>
<tr>
<td>Biot 1A</td>
<td>4</td>
<td>10</td>
<td>16.95 (0.04)</td>
<td>0.20</td>
<td>17.13</td>
<td>+1.1</td>
<td>--</td>
</tr>
<tr>
<td>L'ane 3B</td>
<td>4</td>
<td>10</td>
<td>18.65 (0.03)</td>
<td>0.16</td>
<td>18.97</td>
<td>+1.7</td>
<td>--</td>
</tr>
<tr>
<td>BCR-1</td>
<td>4</td>
<td>10</td>
<td>8.85 (0.03)</td>
<td>0.28</td>
<td>9.20</td>
<td>+3.9</td>
<td>8.96</td>
</tr>
<tr>
<td>Musc 3A</td>
<td>4</td>
<td>9</td>
<td>1.40 (0.01)</td>
<td>0.88</td>
<td>2.44</td>
<td>+74.2</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10)</td>
<td>1.40 (0.02)</td>
<td>(1.62)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-2</td>
<td>4</td>
<td>9</td>
<td>1.53 (0.01)</td>
<td>0.55</td>
<td>1.98</td>
<td>+29.5</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10)</td>
<td>1.54 (0.03)</td>
<td>(1.96)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCC-1</td>
<td>24</td>
<td>9</td>
<td>5.45 (0.04)</td>
<td>0.80</td>
<td>5.53</td>
<td>+1.5</td>
<td>5.17?</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10)</td>
<td>5.46 (0.06)</td>
<td>(1.07)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MICA Fe</td>
<td>4</td>
<td>10</td>
<td>18.85 (0.04)</td>
<td>0.20</td>
<td>19.19</td>
<td>+1.8</td>
<td>18.91</td>
</tr>
<tr>
<td>MICA Mg</td>
<td>4</td>
<td>9</td>
<td>6.78 (0.02)</td>
<td>0.29</td>
<td>7.06</td>
<td>+4.2</td>
<td>6.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10)</td>
<td>6.80 (0.04)</td>
<td>(0.56)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Abbey (1980).
of Stucki (1981) gave Fe(II) values that were 26% lower than the unadjusted values reported here (J. W. Stucki, Department of Agronomy, University of Illinois, Urbana, IL, 1986, personal communication). Clearly, these spectrophotometric data, and the absence of an observable Al effect with Stucki's method, would suggest that the values obtained with V(V) and Cr(VI) methods are due to interactions of Al and F with the oxidants rather than some sort of reaction with Fe(II). Whether this is indeed the case requires investigation beyond the scope of the present study.

Conclusions

The oxidimetric NH$_4$VO$_3$ method of Peters (1968) has been modified to include sample dissolution at 60°C for 4 hours rather than overnight, gravimetric measurements of redox reagents following rapid additions by manual dispensers, a sharper titration endpoint, and the use of the same container throughout the entire process. The results obtained with the method are very precise (standard errors of 0.01-0.04% FeO for all samples) and agree well with recommended values. Interferences due to the presence of F, Al, Mg and Si were observed, however, and were attributed to the formation of a ralstonite-like complex with Fe(II) or, possibly, the formation of oxyfluoride complexes with V(V). Similar results were observed when Cr(VI) was the oxidant, HCl the matrix acid or when excess H$_3$BO$_3$ was present. These interferences are of minor concern except for samples like muscovite and granite that contain
relatively large amounts of Al relative to Fe(II). Highly reproducible results are obtained for trioctahedral micas, some of which dissolve in less than 30 minutes. Thus, the main goal of this study, which was the development of a rapid and precise batch technique for the determination of Fe(II) in non-refractory samples, and trioctahedral micas in particular, has been met.
CHAPTER III. THE ESTIMATION OF OCTAHEDRAL AND TETRAHEDRAL CATION SHEET OCCUPANCIES IN TRIOCTAHEDRAL MICAS
BY AN X-RAY DIFFRACTION TECHNIQUE

Introduction

When a monochromatic beam of x-rays is focussed on a well-ordered crystalline phase, a series of reflections is observed for each set of parallel atom planes in the crystal. The 2-theta angles at which the fundamental and higher order reflections occur are determined by the distances between the atom planes and the wavelength of the radiation involved. The relative intensities of the reflections in a given series, however, are determined not only by the spacings between atom planes, but also by the electron densities of the atoms that make up each plane. Thus, examination of the relative intensities of higher-order reflections from a set of planes may yield information regarding the kinds of atoms that make up each plane (based on their electron densities). This approach is most useful for distinguishing members of a solid solution in which isomorphous substitution of electron-rich (e.g., Fe, Mn and Ti) for electron-poor (e.g., Al, Mg and Si) atoms occurs.

X-ray diffraction methods have long been used to identify and quantify crystalline mineral phases in soils and other geological materials. The crystallinity of these minerals varies and often few, if
any, higher order reflections are observed. A notable exception to this pattern is found in the mica group, members of which give a strong series of reflections from the atom planes that lie parallel to the basal surfaces [i.e., the 00\(n\) reflections from the (001) planes]. Because the octahedral and interlayer cation sites also form planes of symmetry in the mica structure, the 00\(n\) reflections are very sensitive to the types of atoms occupying these sites.

Nagelschmidt (1937) was the first to use the relative intensities of 00\(n\) reflections to distinguish between the dioctahedral muscovite micas and the trioctahedral phlogopite-biotite micas. Brown (1951, 1955) presented calculations of intensities and structure factors for the 00\(n\) reflections of micas and suggested a method for distinguishing the Mg-rich (phlogopite) and Fe-rich (biotite) trioctahedral micas based on the relative intensities of the 003 and 005 reflections. More recently, the same set of calculations was repeated using updated atomic scattering factors and structural refinements (Brown and Brindley, 1980).

The first direct application of the techniques based on 00\(n\) reflections was by Gower (1957) who reported 004/005 intensity and structure factor ratios for random powder samples of six trioctahedral micas. He expressed his results in terms of total Fe content as a fraction of total Fe+Mg+Al content and thus did not attempt to quantify the distribution of Fe and Al between the octahedral and tetrahedral sheets. Rimsaite (1967a) reported 004/005 intensity ratios for a large number of basally oriented powder samples as part of her lengthy
investigation of the properties of rock-forming micas. In a separate work comparing fresh and weathered biotite flakes (Rimsaite, 1967b), she noted a decrease in the 004/005 intensity ratios as a result of weathering but did not directly relate it to changes in the octahedral or tetrahedral cation occupancy of the micas.

These workers, therefore, established the feasibility of x-ray diffraction intensity and structure factor analysis as a way of distinguishing among micas and monitoring the progress of weathering in micas. The method, however, has not been applied by other investigators even though considerable research has focussed on the weathering of micas (Scott and Amonette, 1988). Reasons for this may include the relatively large quantities of sample required for the random or oriented powder mounts, the relatively poor precision obtained when camera methods (which require minimal amounts of sample) are used to quantify intensities, and the high cost and limited availability of single-crystal diffractometers with step-scanning capabilities.

The intent of this chapter, then, is to report 1) calculations showing the effects of different octahedral and tetrahedral occupancies and of fluoride substitution for structural hydroxyls on the 004/005 structure factor ratios of trioctahedral micas, 2) a modified powder diffraction technique that requires very little sample and can take advantage of the precision and convenience of a powder diffractometer equipped with step-scanning capabilities, 3) chemical analyses and 004/005 structure factor ratio measurements on a suite of six micas whose compositions cover the trioctahedral mica range, and 4) a
comparison of the cation site occupancies predicted by the technique with those obtained when conventional assignments are used to calculate structural formulas. An application of this technique to monitor the changes in cation occupancy of trioctahedral micas during laboratory weathering experiments is reported in Chapter V.

Theoretical Aspects

For a powder diffractometer, the integrated intensity of an x-ray reflection (I) can be calculated by

$$ I = KVAI_0|F|^2LPT\psi p(e^{-2m}) $$  \[III-1\]

where K is a constant that includes various physical constants and instrumental factors (e.g., slit array, x-ray tube voltage and current, monochromator and detector efficiencies), V is the volume of the sample unit cell, A the absorption by the sample, I_0 is the incident beam intensity, F is the structure factor (described in more detail below), L and P are the Lorentz and polarization factors which correct for angular-dependent variability of the reflection intensity, T is a factor to correct for samples too thin to completely attenuate the x-radiation, \( \psi \) is the powder ring factor to correct for random orientation of the crystals in the sample, p is the multiplicity factor to allow for reflections at the same angle from different sets of planes, and \( e^{-2m} \) is the temperature factor to correct for loss of intensity due to thermal vibration of atoms and electrons in the sample. The expression is simplified when samples are mounted with preferred orientation, the
reflections of interest are from the same set of atom planes (e.g., 004 and 005), and the temperature factor is assumed to be negligible. The latter assumption is made purely on a practical basis as the temperature factor calculations for a monoclinic crystal as complex as a mica are difficult if not impossible. Under these circumstances, \( \psi \), \( p \) and \( e^{-2\pi m} \) become equal to 1 and the expression for reflected intensity can be reduced to

\[
I = K\nu A_0|F|^2(LP)T. \quad \text{[III-2]}
\]

A value of \( K \) for a particular set of instrumental operating conditions may be obtained by calibration with a known standard (e.g., corundum or permaquartz) when the other parameters have been measured. \( \nu \) may be calculated from the unit cell dimensions. \( A \), which is constant for flat-mounted samples, may be calculated from the average mass absorption coefficient of the sample. When intensity ratios of higher orders of the same fundamental reflection are calculated, however, the \( K \), \( \nu \), \( A \) and \( I_0 \) terms cancel and their determination becomes unnecessary.

The combined Lorentz-polarization factor for a particular reflection when a crystal monochromator is used is calculated by

\[
(LP) = \frac{1 + \cos^2(2\phi)\cos^2(2\alpha)}{\sin^2(2\phi)[1 + \cos^2(2\alpha)]} \quad \text{[III-3]}
\]

in which \( 2\phi \) is the diffraction angle of the sample and \( 2\alpha \) is the diffraction angle of the crystal in the monochromator.

And, when samples are finitely thick to x-rays (i.e., addition of more sample causes an increase in the reflected intensity), a
correction factor \((T)\), which is the effective x-ray thickness of the sample, can be calculated from the expression

\[
T = 1 - \exp\left(\frac{-2\mu^* g}{\sin \theta}\right) \tag{III-4}
\]

and included in Eq. III-2. Here, \(\mu^*\) is the average mass absorption coefficient of the sample and \(g\) is the mass of the sample per unit area. For best results, \((\mu^* g)\) should be determined empirically for each sample (Reynolds, 1985).

The structure factor for a given reflection contains the most valuable information about the sample. It may be calculated if the unit cell coordinates of each atomic structural site are known and a reasonable estimate of the number and kinds of atoms occupying the site can be made. One form of the equation that yields the theoretical structure factor \(|F_{\text{theo}}|\) is

\[
|F_{\text{theo}}|^2 = \sum_{s=1}^{N} \left(\sum_{a} n_a (f_a \cos[2\pi(hu + kv + \omega w)])^2 + \sum_{s=1}^{N} \left(\sum_{a} n_a (f_a \sin[2\pi(hu + kv + \omega w)])\right)^2 \right) \tag{III-5}
\]

where \(n_a\) is the number of atoms of type "a" occupying site type "s" in the unit cell, \(N\) is the total number of site types in the unit cell, \(f_a\) is the atomic scattering factor for atoms of type "a" (related to the electron density of the atom and obtained from published tables), \(h, k, \)
and \( h \) are the Miller indices of a particular reflection, and \( u, v, \) and \( w \) are the fractional coordinates of the atom site. For the 00\( h \) reflections of micas, Eq. [III-5] reduces to

\[
|F|^2_{\text{theo}} = \frac{N}{\sum_{s=1}^{N} (n_s)(f_a)\cos(2\pi hw)]^2. \tag{III-6}
\]

An empirical estimate of the structure factor can also be obtained by measuring the intensity of the reflection and solving Eq. [III-2] for \(|F|^2 \). This observed structure factor \((|F|_{\text{obs}})\) is, therefore, given by the equation

\[
|F|^2_{\text{obs}} = \frac{I}{KVAI_{0}(LP)T}. \tag{III-7}
\]

Inasmuch as the theoretical structure factor is calculated from certain assumptions about the locations of atoms in the sample structure, a comparison of the observed and theoretical structure factors can serve to check the validity of the assumptions that were made. In practice, these estimates of atom locations are adjusted (in conjunction with other knowledge about the structure) until the theoretical structure factor agrees with the observed structure factor. That is, a range of theoretical structure factors may be calculated from different combinations of site occupancies, but, in general, only one of these values will coincide with the observed structure factor. It is by this comparative process, therefore, that assignments of atoms among various sites in a structure may be made.
If more than one reflection from a set of parallel planes is observed, it is convenient to use two of them (x and y) in conjunction with Eq. III-7 to obtain a structure factor ratio ($|F|_{x/y}$) because the values for $K, V, A,$ and $I_0$ cancel, and the expression is reduced to

$$|F|_{x/y}^2 = \frac{(I_x)((LP)_{y,T})}{(I_y)((LP)_{x,T})}.$$  \[\text{III-8}\]

which is based solely on the parameters $I, L, P,$ and $T$. Theoretical structure factor ratios [$|F|_{x/y}^{\text{theo}}$] may also be calculated and, thus, assignments of atoms to structural sites can be made by the comparative procedure described before.

**Experimental**

**Mica samples**

Samples of six different trioctahedral micas were obtained from various sources. These samples included a phlogopite from Wakefield, Ontario, Canada and a siderophyllite from the Little Patsy Mine, near Pine, Jefferson Co., Colorado (Continental Minerals, Tucson, AZ); a phlogopite from North Burgess, Ontario, Canada and a magnesian biotite from Bancroft, Ontario, Canada (Ward's Scientific Establishment, Rochester, NY); and, a lepidomelane from Brevik, Norway (NMNH # R7117) and an annite from Massachusetts (NMNH # 45954) (National Museum of Natural History, Smithsonian Institution, Washington, D.C.). Aqueous suspensions of the siderophyllite, North Burgess phlogopite and biotite
samples were ground in a Waring blender to pass through a 50-μm sieve and then the 10- to 20-μm size-fractions were recovered by sedimentation. After drying, the micas were suspended in acetone and subjected to a brief sonification treatment to remove any ultrafine particles that may have remained. Because very small quantities of the Wakefield phlogopite, lepidomelane and annite were available, the sedimentation and sonification steps were omitted and the < 50-μm size-fraction of these micas was used in the analyses.

After a qualitative determination of the major elements present in the micas by energy-dispersive x-ray fluorescence spectroscopy (XRF), quantitative determinations of these elements were made by inductively-coupled argon plasma atomic emission spectroscopy (ICP-AES). For the ICP-AES analyses, the biotite, siderophyllite, lepidomelane and annite samples were digested in HF-H₂SO₄ and the excess fluoride complexed by addition of H₃BO₃ prior to analysis, whereas the two phlogopite samples were analyzed directly as 0.1 % aqueous suspensions. The quantities of K, Rb and Fe in all samples were determined by atomic absorption spectroscopy of HF digests. Fe(II) in these samples was analyzed by the recommended V(V) method described in Chapter II. These data were used to calculate structural formulas for each mica on the basis of 44 positive and negative charges for each unit layer.

**Diffractometers**

Two x-ray diffractometers were used, a General Electric XRD-6 and a Picker 3488K. The GE unit was equipped with a Cu source, a 1°
incident-beam Soller slit, a medium resolution diffracted-beam Soller slit, a 0.2° detector slit, a diffracted-beam flat-crystal graphite monochromator and a scintillation tube detector, and was used to measure the effective x-ray thickness of the samples. The Picker unit was equipped with 1° incident- and diffracted-beam Soller slits, and a similar monochromator and detector arrangement, but had a Mo source and a 0.005° detector slit. Pulse-height analysis was obtained with a single-channel analyzer set at 0.40 V base and 4.49 V pulse height. In addition, the Picker unit was connected to a VAX minicomputer system which allowed automated step-scanning and the collection and analysis of digitized data. Because of these latter capabilities, the Picker diffractometer was used to collect the intensity data for the mica samples.

**Effective x-ray thickness**

The calculation of $T$ in Eq. [III-4] requires a value for the product of $\mu^*$ (average mass absorption coefficient) and $g$ (areal density). The method for empirically measuring this product was basically a modification of that described by Reynolds (1985). The GE XRD-6 unit was allowed to stabilize with the Cu tube on (35 KVP, 45 mA) for a minimum of 30 minutes before starting the measurements. After blocking the incident x-ray beam, a sample of Permaquartz was placed in the sample holder. The beam was unblocked and the goniometer moved to the angle at which the maximum in the 0.334-nm quartz peak was observed (near 26.7°2-theta with Cu$_{K\alpha}$ radiation). Using the scaler to record the
counts, successive 100-s counts of this quartz reflection were measured in the sequence U-U-B-B-B-U-U-M-M-M-U-U, where U refers to the unblocked beam, and B and M to the insertion of a sample blank and a mica sample, respectively, in the diffracted beam. The sample blank (B) was comprised of a 2.5x4.0-cm rectangle of thin acetate (cut from an acetate page protector) covered on one side with two parallel strips of double stick tape (1.25x4.0 cm) and was placed between the diffracted-beam Soller slit and the detector slit with the plane of the rectangle perpendicular to the diffracted x-ray beam. The mica sample (M) consisted of the sample blank that was altered by saturating the double stick tape with the ground mica sample. The intensities observed for the blank (B) and for the mica (M) samples were averaged separately, corrected for fluctuations in the incident intensity as measured by the U data, and then used to calculate a value for \( \mu^*g \) by

\[
\mu^*g = \ln(I_B) - \ln(I_M) \tag{III-9}
\]

where \( I_B \) and \( I_M \) are the average corrected intensities for the blank and mica samples, respectively. These values for \( \mu^*g \) were valid for \( CuK\alpha \) radiation. In order to obtain values of \( \mu^*g \) for use with \( MoK\alpha \) radiation, the observed \( \mu^*g_{Cu} \) values were multiplied by a factor (0.115) which corresponded to the ratio of \( \mu_{Mo}^* \) to \( \mu_{Cu}^* \) calculated for a typical mica. An exact factor could have been calculated for each mica from the elemental analysis, but the samples were so thin that use of these exact factors would have had negligible effects on the final values of \( T \) and \( |F| \).
Observed structure factors

After determination of the effective x-ray thickness \((T)\) of the mica samples, the double stick tape impregnated with mica on one side was carefully separated from the acetate backing and transferred to a glass slide (2.5x7.7 cm) for analysis of the intensities of the 004 and 005 reflections by the Picker diffractometer. For these analyses, Mo\(K\alpha\) radiation was used (49 KVP, 17 mA) and the goniometer was advanced in steps of 0.01°2\(\theta\) in the range from 14.00 to 22.50°2\(\theta\). The diffracted beam intensity was measured for 5 s at each step, digitized, and stored sequentially in a computer file. Three replicate samples were prepared for the North Burgess phlogopite, biotite and siderophyllite micas, but the number of slides was reduced to two for the remaining micas because of the high precision obtained. Each slide was analyzed three times in succession. The intensity data from these triplicate analyses were summed at each goniometer step to create one data file for each slide. An enhanced background subtraction program was used on this data file to correct the observed intensities for background, to locate the peak maxima, and to calculate the integrated intensities, and the Lorentz, polarization and thickness factors. From these parameters, the observed structure factor ratios of the 004 and 005 reflections, \(\frac{|F_{004}|}{|F_{005}|_{\text{obs}}}\), were calculated by Eq. [III-8].

Theoretical structure factors

Once the observed structure factors had been determined, a set of structure factors for each mica was calculated using [III-6]. These
calculations relied on the elemental analyses, the recommended atomic scattering factors (Int. Union Crystallogr., 1962), and assumptions about the distribution of cations among the various sites and the fractional coordinates of those sites.

In order to make the results of these calculations easier to understand, the x-ray electron densities of the octahedral cation suite were presented as if only Fe or Mg occupied the sites and there were no vacancies. This was accomplished by multiplying the stoichiometric coefficient of each octahedral cation (obtained from the structural formula) by the ratio of the atomic scattering factor of the cation to that of either Fe(II) or Mg [e.g., \( f_{\text{cation}} / f_{\text{Fe(II)}} \)]. These values were then summed to arrive at a value for "effective" Fe(II) and "effective" Mg octahedral occupancies in the mica. For example, the heavy atoms [Fe(III), Mn, Ti, Zn] were converted to the number of Fe(II) atoms that would give the same x-ray electron density by

\[
\text{"Fe(II)"} = [\text{Fe(II)}] + 1.04[\text{Fe(III)}] + 0.83(\text{Ti})
+ 0.99(\text{Mn}) + 1.25(\text{Zn})
\]

[III-10]

where the stoichiometric coefficient of each cation is in parentheses and is multiplied by a value for the ratio \( f_{\text{cation}} / f_{\text{Fe(II)}} \). The number of "Mg" atoms was arrived at in a similar fashion by summing the Mg, Al and Li x-ray electron densities. At this stage, vacancies were accounted for by increasing the "Mg" value and decreasing the "Fe(II)" value until the same total x-ray electron density was achieved and the two values summed to six (the number of octahedral sites in the unit cell). Thus, the x-ray electron density of the octahedral cation sites
is represented by a binary system with 100% Mg occupancy at one extreme and 100% Fe(II) occupancy at the other.

**Structural formulas**

A total of four structural formulas were calculated for each mica. Three were based solely on the elemental analysis and used different cation site assignment schemes, whereas the fourth formula included the site assignments that were predicted by the observed $I_0^{004}/I_0^{005}$ ratio as well.

The first of these structural formulas was derived in the conventional manner by assuming that the tetrahedral sheet contained no vacancies and that tetrahedral sites were filled first with Si, then Al, and finally Fe(III) and Ti, if insufficient Al were present. Thus, vacancies were confined to the octahedral sites and the levels of Fe and Ti in the tetrahedral sites were at a minimum. The site assignment scheme for this structural formula is referred to as "Minimum (IV) Fe".

The second structural formula was derived by reversing the conventional priorities of assigning Al and Fe(III)+Ti the tetrahedral sheet. Vacancies were still confined to the octahedral sites and the electron density of the tetrahedral atom plane was at a maximum. The site assignment scheme for this formula is referred to as "Maximum (IV) Density".

For the third structural formula, the octahedral sites were filled entirely, first with the heavy [e.g., Fe(II), Fe(III), Ti, Mn, Zn] and then with the light (e.g., Mg, Li, Al) cations. Al was given the lowest
priority in filling the octahedral sites and, consequently, the excess Al and any vacancies were assigned to the tetrahedral sites. With these assignments, the electron density of the octahedral atom plane was at a maximum. The site assignment scheme for this formula is referred to as "Maximum (VI) Density".

The fourth structural formula was derived to show the cation site occupancies that would be predicted when the observed \(|F_{004/005}|\) ratio was compared to the range of theoretical \(|F_{004/005}|\) ratios. This was done by starting with the conventionally derived formula [Minimum (IV) Fe] and shifting the assigned electron densities of the tetrahedral and octahedral atom planes until the theoretical \(|F|\) ratio equaled the observed \(|F|\) ratio. To increase the theoretical \(|F|\) ratio, some of the Al assigned to the tetrahedral sheet was shifted to fill vacancies in the octahedral sheet. This shift, of course, resulted in an equal shift in the number of assigned vacancies from the octahedral sheet to the tetrahedral sheet. Decreases in the theoretical \(|F|\) ratio were achieved by exchanging the assignments of tetrahedral Al with those of octahedral Fe(III). The site assignment scheme for this formula, therefore, is referred to as "Predicted (XRD Data)".

Results and Discussion

**Fractional coordinates**

A major assumption was made in obtaining values of the fractional coordinates to be used in theoretical structure factor calculations.
Rather than performing a one-dimensional Fourier synthesis on each mica (which would have consumed much time), or choosing a set of coordinates for each mica from the literature (which may or may not have had any relation to the mica in question), it was decided instead to choose a single set of coordinates based on structural refinements in the literature and apply it to all six micas. Bailey (1980) tabulated structural refinement data for a number of micas from which calculations of the fractional coordinates could be made. Franzini and Schiaffino (1963) performed structural refinements on six biotites and reported fractional coordinates for each as well as the means of the six sets of coordinates. Several sets of fractional coordinates that were calculated from data tabulated by Bailey (1980) and the mean coordinates reported by Franzini and Schiaffino (1963) are given in Table III-1.

The agreement among the different sets of fractional coordinates is very good. In no instance does a pair of coordinates for the same atom plane differ by more than 0.5% of the unit cell c-dimension. Thus, for comparisons of the relative effects of different cation site occupancies on theoretical |F| ratios of a mica, the use of any of these sets of coordinates would yield essentially the same results as if a Fourier synthesis for the mica had been performed. The difficulty arises, however, when comparing the range of theoretical structure factors to an observed structure factor, inasmuch as the latter is an absolute quantity.

The mean coordinates reported by Franzini and Schiaffino (1963) were selected for the theoretical structure factor calculations because
TABLE III-1. Fractional coordinates along the c-axis (w) for the 00A atom planes in several trioctahedral mica specimens (calculated from structural refinement data)

<table>
<thead>
<tr>
<th>Atom Plane</th>
<th>Phlog\textsuperscript{a}</th>
<th>Annite\textsuperscript{a}</th>
<th>Mg\textsuperscript{a} Biotite</th>
<th>Fluor\textsuperscript{a} Phlog</th>
<th>Fluor\textsuperscript{a} Biotite</th>
<th>Fe\textsuperscript{a} Biotite</th>
<th>Avg\textsuperscript{b} Biotite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer Cation</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Basal Oxygen</td>
<td>0.16948</td>
<td>0.16746</td>
<td>0.16647</td>
<td>0.16682</td>
<td>0.16763</td>
<td>0.16698</td>
<td></td>
</tr>
<tr>
<td>Tetrahedral Cation</td>
<td>0.23007</td>
<td>0.22622</td>
<td>0.22758</td>
<td>0.22966</td>
<td>0.22833</td>
<td>0.22601</td>
<td></td>
</tr>
<tr>
<td>Apical O,F</td>
<td>0.39459</td>
<td>0.39061</td>
<td>0.39325</td>
<td>0.39502</td>
<td>0.39501</td>
<td>0.39400</td>
<td></td>
</tr>
<tr>
<td>Octahedral Cation</td>
<td>0.50000</td>
<td>0.50000</td>
<td>0.50000</td>
<td>0.50000</td>
<td>0.50000</td>
<td>0.50000</td>
<td></td>
</tr>
<tr>
<td>Apical O,F</td>
<td>0.60541</td>
<td>0.60939</td>
<td>0.60675</td>
<td>0.60498</td>
<td>0.60499</td>
<td>0.60600</td>
<td></td>
</tr>
<tr>
<td>Tetrahedral Cation</td>
<td>0.76993</td>
<td>0.77378</td>
<td>0.77242</td>
<td>0.77034</td>
<td>0.77167</td>
<td>0.77399</td>
<td></td>
</tr>
<tr>
<td>Basal Oxygen</td>
<td>0.83052</td>
<td>0.83254</td>
<td>0.83353</td>
<td>0.83318</td>
<td>0.83237</td>
<td>0.83302</td>
<td></td>
</tr>
<tr>
<td>Interlayer Cation</td>
<td>1.00000</td>
<td>1.00000</td>
<td>1.00000</td>
<td>1.00000</td>
<td>1.00000</td>
<td>1.00000</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}From structural data tabulated by Bailey (1980). Original references are as follows: Phlogopite (Rayner, 1974), Annite (Hazen and Burnham, 1973), Mg-biotite (Takeda and Ross, 1975), Synthetic Fluorphlogopite (Takeda and Morosin, 1975), Fe-biotite (Tepikin, Drits and Alexandrova, 1969).

\textsuperscript{b}Data are mean values for six biotites (Franzini and Schiaffino, 1963).
they represented data collected under the same conditions for a wide range of biotites. These coordinates yielded theoretical structure factor ratios that compared well with the observed structure factor ratios, especially for the phlogopites where only a narrow range of theoretical structure factors could be calculated. Differences in the theoretical structure factor ratios arising from the use of the average coordinate set of Franzini and Schiaffino (1963) rather than the single coordinate set that seemed most appropriate for a particular mica [e.g., Phlog (Rayner, 1974) for phlogopite, Annite (Hazen and Burnham, 1973) for annite] varied from about 0.01 for the annite to 0.03-0.04 for the biotite and siderophyllite and 0.10 for the phlogopite. As will be seen, possible errors of this size would not have a great effect on the general conclusions drawn regarding cation site occupancy, except in the instance of the Wakefield and North Burgess phlogopites where Rayner's (1974) coordinates do not seem to be appropriate.

Sensitivity of 00l reflections

As shown by Eq. [III-6], $|F|^2$ for a given reflection is a summation of the contributions of the various parallel atom planes that are oriented at the Bragg angle. The contribution of each plane is the product of two components. One represents the x-ray electron density of the atoms that make up the plane ($n_\alpha f_\alpha$). The other component [$\cos(2\pi l_\alpha w)$] represents the location of that plane in the structure and determines whether constructive or destructive interference will occur between the reflections from that plane and reflections from other planes in the
structure. In short, the x-ray electron density of the atoms in a plane determines the amplitude of the structure factor contribution from that plane, whereas the location of the plane in the structure determines the phase. It is helpful, therefore, to calculate the contributions from each atom plane in the structure to the $|F|$ for each reflection in a series. In this way the reflections that are most sensitive to the plane of interest may be identified. An example of this type of calculation is given in Table III-2 for a hypothetical mica having the formula $\text{KX}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ where X is either Mg or Fe.

One of the first things to note is that the phase of the interlayer cation contribution is always positive, whereas that of the octahedral cation contribution alternates between positive and negative for the even and odd reflections, respectively. This behavior is expected because these planes form planes of symmetry in the mica structure. Another aspect of this symmetry is that the size of the phase contribution, $|\cos(2\pi \alpha w)|$, is always at a maximum of 1 because the product $2\pi \alpha w$ is always an integral multiple of $\pi$. Consequently, the 00$\alpha$ reflections of the micas are consistently most sensitive to the electron density of the atoms that make up the interlayer and octahedral atom planes.

Comparisons of the theoretical $|F|^2$ values in Table III-2 show that all reflections except the 005 yield higher $|F|^2$ values when the denser atoms (Fe) fill the octahedral sites. The anomalous behavior of the 005 reflection is due to the negative contribution of the octahedral
TABLE III-2. Contributions of different atom planes to theoretical structure factors (|F|) calculated for basal reflections of trioctahedral micas with Mg or Fe as sole octahedral cations and assuming average atom plane spacings of Franzini and Schiaffino (1963)

<table>
<thead>
<tr>
<th>Atom Plane&lt;sup&gt;a&lt;/sup&gt;</th>
<th>001</th>
<th>002</th>
<th>003</th>
<th>004</th>
<th>005</th>
<th>006</th>
<th>(nf\cos Z&lt;sup&gt;b&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (+1)</td>
<td>17.34</td>
<td>16.68</td>
<td>15.22</td>
<td>13.76</td>
<td>12.36</td>
<td>10.97</td>
<td></td>
</tr>
<tr>
<td>Basal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (-1)</td>
<td>25.17</td>
<td>-23.68</td>
<td>-40.80</td>
<td>-17.04</td>
<td>14.98</td>
<td>24.42</td>
<td></td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (+2)</td>
<td>6.90</td>
<td>-41.94</td>
<td>-17.93</td>
<td>31.43</td>
<td>24.42</td>
<td>-20.47</td>
<td></td>
</tr>
<tr>
<td>Apical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (-1)</td>
<td>-39.72</td>
<td>11.12</td>
<td>16.91</td>
<td>-30.69</td>
<td>28.94</td>
<td>-16.03</td>
<td></td>
</tr>
<tr>
<td>Octahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg (+1)</td>
<td>-63.24</td>
<td>60.48</td>
<td>-56.52</td>
<td>52.50</td>
<td>-48.72</td>
<td>44.94</td>
<td></td>
</tr>
<tr>
<td>Fe (+1)</td>
<td>-145.92</td>
<td>141.78</td>
<td>-132.24</td>
<td>122.70</td>
<td>-112.08</td>
<td>101.52</td>
<td></td>
</tr>
<tr>
<td>Apical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (-1)</td>
<td>-39.72</td>
<td>11.12</td>
<td>16.91</td>
<td>-30.69</td>
<td>28.94</td>
<td>-16.03</td>
<td></td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (+2)</td>
<td>6.90</td>
<td>-41.94</td>
<td>-17.93</td>
<td>31.43</td>
<td>24.42</td>
<td>-20.47</td>
<td></td>
</tr>
<tr>
<td>Basal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (-1)</td>
<td>25.17</td>
<td>-23.68</td>
<td>-40.80</td>
<td>-17.04</td>
<td>14.98</td>
<td>24.42</td>
<td></td>
</tr>
<tr>
<td>Interlayer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (+1)</td>
<td>17.34</td>
<td>16.68</td>
<td>15.22</td>
<td>13.76</td>
<td>12.36</td>
<td>10.97</td>
<td></td>
</tr>
</tbody>
</table>

\(|F|^2 (\text{Mg/Fe})\)

\(|F|^2 (\text{Mg})\) 1923 229 12041 2247 12695 1823
\(|F|^2 (\text{Fe})\) 16011 4376 34392 13831 2431 9857
\(|F|^2 (\text{Mg/Fe})\) 0.12 0.05 0.35 0.16 5.22 0.18
\(|F| (\text{Mg/Fe})\) 0.35 0.23 0.59 0.40 2.29 0.43

<sup>a</sup> Valences shown assume 50% covalent bonding, except for interlayer atoms which are assumed to have 100% ionic bonding.

<sup>b</sup> Z=2π\(\delta w\), where \(\delta\) is the Miller index for given reflection (hk\(\ell\)) and \(w\) is the fractional coordinate of the atom plane.
plane to \(|F|^2\) when all the other atom planes have positive contributions. It can be seen, therefore, that great sensitivity to octahedral cation site occupancy would be obtained by calculating a ratio of the \(|F|^2\) for the 005 and any other 00\(\lambda\) reflection. As shown by the ratios of the \(|F|^2\) values that were calculated by assuming Mg versus Fe(II) occupancy, the reflection that gives the most sensitive response to octahedral cations is the 002. In theory, then, the 002/005 structure factor ratio would be a good choice. In practice, however, it is better to use ratios based on peaks that are as close together as possible and in the mid- to high-angle range to minimize corrections for instrumental geometry, polarization and sample thickness. As a result, the 004/005 structure factor ratio was deemed preferable and used to estimate octahedral cation site occupancies.

An examination of the contributions of other planes to the 004 and 005 \(|F|^2\) values reveals that the apical anions (O, OH and F) have strong contributions that oppose the octahedral contributions (Table III-2). Thus, even though the electron densities of O and F are similar, the substitution of F for OH would be expected to have a noticeable effect on the \(|F|^2\) values obtained. The tetrahedral cations also have fairly strong positive contributions to the 004 and 005 reflections so that substitution of Fe(III) for Al would have an effect on the \(|F|^2\) values. Practically speaking, analysis of the samples for F, and perhaps even Cl and Br, would eliminate any uncertainties regarding the apical anion contribution. Resolution of the contributions of the tetrahedral cations (barring the use of Mössbauer or NMR spectroscopy) must rely on
comparisons of observed and calculated $|F|^2$ and is subject to the assumptions and possible errors that result therefrom.

The sensitivity of the 004/005 structure factor ratio to octahedral cation site occupancy is very high. For the example in Table III-2, a 30-fold difference in $|F|^2_{004/005\text{(theo)}}$ ratios is seen between the Mg and Fe micas. Even when the square root of this ratio is taken, as is commonly done for graphical purposes, the 5-fold difference is quite adequate for discerning octahedral cation site occupancy.

**Observed data**

X-ray diffractograms of the 004 and 005 reflections for five of the six micas are shown in Figure III-1. Because the two phlogopites gave essentially identical intensities only the North Burgess pattern is included.

Several observations can be made about these x-ray patterns. First, the micas are highly crystalline as shown by partial resolution of the $K_{\alpha 1} - K_{\alpha 2}$ doublets in each reflection. Second, in going from the phlogopite to the annite mica the intensities of the 004 reflections (near 16.2°2θ) increase, whereas the intensities of the 005 reflections (near 20.3°2θ) decrease. These trends are as expected and relate directly to the influence of octahedral Fe content on the structure factor. Clearly, the relative intensities of these two reflections can be used to distinguish the various trioctahedral micas. Third, the locations of the peaks for the annite and lepidomelane micas are shifted to slightly lower 2θ values (larger d-spacings) than the other three
FIGURE III-1. X-ray diffraction patterns showing the 004 and 005 reflections of five trioctahedral micas (Mo$_K$ radiation)
micas. These shifts do not seem to be related to changes in octahedral Fe content inasmuch as the shift is greater for the lepidomelane than for the annite and is very small in the other micas. Instead, the larger d-spacings may be attributed to the substitution of the larger Fe(III) for Al and Si in the tetrahedral cation sites. Support for this explanation is provided later by the structural formulas for the micas, which show more tetrahedral Fe in the lepidomelane than in the annite and no tetrahedral Fe in the other micas.

The observed structure factor ratios [\(|F|_{004}/|F|_{005}(\text{obs})\)] for the six micas, expressed as a function of octahedral site electron density, are shown in Figure III-2. Theoretical limiting values for these ratios, which were calculated for a representative trioctahedral mica

\[
\{\text{Si}_3\text{Al}[\text{Mg,Fe(II)}]_3\text{O}_10(\text{OH})_2\}
\]

assuming the substitution of Fe(III) for Al in the tetrahedral sites and F for OH in the apical anion sites, are also shown. Clearly, the theoretical limiting values bracket the observed data, thus supporting the assumptions and procedures used to obtain both sets of data. The effect of F substitution for OH is one of lowering the ratio somewhat. The substitution of Fe(III) in the tetrahedral sites increases the |F| ratio when the effective octahedral Fe(II) occupancy is less than 4, but decreases it at higher octahedral densities. In fact, for high-Fe micas (e.g., lepidomelane and annite) any substitution of F or tetrahedral Fe(III) tends to decrease the |F| ratios.
FIGURE III-2. Relationship between the observed $\frac{\text{F}^1_{004}}{\text{O}05}$ ratios for six trioctahedral micas and the effective Fe(II) occupancy of the octahedral sheet, and the limits to this relationship that were calculated for a representative mica assuming the complete substitution of F for structural OH and of Fe(III) for tetrahedral Al.
OBSERVED

THEORETICAL

- UPPER \((\text{Si}_3\text{Fe}^{3+})\text{O}_{10}(\text{OH})_2\)
- LOWER \((\text{Si}_3\text{Fe}^{3+})\text{O}_{10}\text{F}_2\)
- UPPER \((\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2\)
- LOWER \((\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2\)

EFFECTIVE OCTAHEDRAL Fe(II) OCCUPANCY
Cation site occupancies

For each mica, three structural formulas, based on different assumptions about cation site occupancies, were derived from the elemental analysis data. The stoichiometric coefficients from these formulas were then used to calculate theoretical $|F|_{004/005}$ ratios for a comparison with the observed $|F|$ ratios. Lastly, the observed $|F|_{004/005}$ ratio was used in conjunction with the elemental analysis data to derive a fourth structural formula. Because it is based on two independent sets of data and fewer a priori assumptions, this formula may provide the best estimate of the cation site occupancy of the mica.

These site occupancy estimates, however, are subject to three possible sources of error. The first source of error may be in the chemical analyses used to calculate the structural formulas. The standard deviations for theoretical $|F|_{004/005}$ ratios calculated with replicate chemical data (rather than average chemical data) run in the range of 0.01-0.02. Thus, in relative terms, this source of random error affects the phlogopites more than the high-Fe micas.

A second source of error stems from the use of an average set of fractional coordinates to calculate the theoretical $|F|_{004/005}$ ratios. This possible error becomes less as the electron density of the octahedral atom plane increases because the atoms are located on a plane of symmetry whose coordinates (along with those of the interlayer cations) are fixed. As the contribution to the structure factor from the octahedral plane increases, the relative contribution of the basal anion, apical anion and tetrahedral cation planes (whose coordinates may
differ from mica to mica) becomes less. Thus, for the phlogopites, errors of as much as 0.10 in the theoretical $|F|_{004/005}$ ratios could occur whereas for the biotite and siderophyllite errors of 0.03-0.04 are possible. The high-Fe micas (lepidomelane and annite) seem to have very small error ranges associated with fractional coordinates—on the order of 0.01 in the $|F|_{004/005}$ ratio.

A third possible source of error in the site occupancy estimates is the random error introduced during the measurement of the reflected intensities. This error, fortunately, was rather small. The standard deviations of the $|F|_{004/005}$ ratios for the phlogopites, biotite and siderophyllite ranged between 0.004 and 0.006. The standard deviations for the high-Fe micas were somewhat higher at 0.019. Expressed differently, the relative error for the $|F|_{004/005}$ ratios of the six micas ranged between 0.4 and 1.4%, which is excellent for an x-ray diffraction technique.

The results of the structural formula, effective octahedral Fe(II) and Mg occupancy, and $|F|_{004/005}$ ratio calculations for the Wakefield phlogopite are given in Table III-3. This mica is characterized by having almost complete octahedral and tetrahedral site occupancy and very low quantities of heavy cations. Consequently, only minor differences in structural formulas and $|F|$ ratios can be seen. A comparison of the observed $|F|$ ratio to the theoretical $|F|$ ratios suggests that the few vacancies that do exist occur in the tetrahedral sheet. The possible error in the theoretical ratios arising from the use of average fractional coordinates is large enough, however, that a
TABLE III-3. Structural ion site occupancies and theoretical $|F|$ ratios (004/005) obtained with three different assumptions, and the predicted site occupancies derived from the observed $|F|$ ratio (004/005) for a Wakefield phlogopite

<table>
<thead>
<tr>
<th>Assigned Site Occupancies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom(Valence)$^b$</td>
</tr>
<tr>
<td>Interlayer</td>
</tr>
<tr>
<td>K (+1)</td>
</tr>
<tr>
<td>Na (+1)</td>
</tr>
<tr>
<td>Rb (+1)</td>
</tr>
<tr>
<td>Ca (+2)</td>
</tr>
<tr>
<td>Basal Anion</td>
</tr>
<tr>
<td>O (-1)</td>
</tr>
<tr>
<td>Tetrahedral</td>
</tr>
<tr>
<td>Si (+2)</td>
</tr>
<tr>
<td>Al (+1.5)</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
</tr>
<tr>
<td>Ti (+2)</td>
</tr>
<tr>
<td>Apical Anion</td>
</tr>
<tr>
<td>O (-1)</td>
</tr>
<tr>
<td>OH (-1)</td>
</tr>
<tr>
<td>F (-0.5)</td>
</tr>
<tr>
<td>Octahedral</td>
</tr>
<tr>
<td>Ti (+2)</td>
</tr>
<tr>
<td>Al (+1.5)</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
</tr>
<tr>
<td>Mg (+1)</td>
</tr>
<tr>
<td>Fe (+1)</td>
</tr>
<tr>
<td>Mn (+1)</td>
</tr>
<tr>
<td>Zn (+1)</td>
</tr>
<tr>
<td>Li (+0.5)$^b$</td>
</tr>
<tr>
<td>Binary (VI)$^c$</td>
</tr>
<tr>
<td>&quot;Mg&quot; (+1)</td>
</tr>
<tr>
<td>&quot;Fe&quot; (+1)</td>
</tr>
</tbody>
</table>

$|F|$ Ratio 0.387 0.384 0.396 0.396

---

$^a$Site occupancies assigned by the conventional method.

$^b$Valences shown assume 50% covalent bonding, except for interlayer atoms which are assumed to have 100% ionic bonding.

$^c$Binary site occupancies refer to a hypothetical octahedral cation sheet containing only Mg and Fe but having the same effective electron density as the actual octahedral sheet (see text for details).
definite statement about tetrahedral vacancies can not be made.

The North Burgess phlogopite, like the Wakefield, shows only minor differences among the structural formulas and theoretical $|F|$ ratios (Table III-4). The observed $|F|$ ratio, however, is not bracketed by the theoretical $|F|$ ratios so no predictions of site occupancy could be made. The lack of agreement between the theoretical and observed $|F|$ ratios could be the result of two factors: 1) an incomplete structural formula may have been used in the calculations and 2) slight differences may have existed between the actual fractional coordinates of the atom planes and the average values that were used. Evidence for the first factor is that the x-ray fluorescence analysis showed small amounts of Pb to be present in the sample. At the time, these amounts were considered negligible and further analysis for Pb was not made. The x-ray density of Pb, however, is roughly 3.5 times that of Fe(II) and nearly 8 times that of Mg or Al. Consequently, the presence of a relatively small quantity of Pb in the mica could result in a higher observed $|F|$ ratio than would be calculated if no Pb were assumed to be present. Evidence for a slightly different set of fractional coordinates rests mainly on the observation that about 12% of the layer charge of the North Burgess phlogopite is balanced by interlayer Ca. The substitution of divalent Ca for the monovalent alkali cations would be expected to cause more distortion in the mica structure and, as a consequence, a slight shift in the coordinates of the atom planes.

Structural formulas calculated for the Bancroft biotite (Table III-5) show that it contains 5-10% more Si, more cation-site vacancies
TABLE III-4. Structural ion site occupancies and theoretical $|F|$ ratios (004/005) obtained with three different assumptions, and the predicted site occupancies derived from the observed $|F|$ ratio (004/005) for a North Burgess phlogopite

<table>
<thead>
<tr>
<th>Atom(Valence)</th>
<th>Assigned Site Occupancies</th>
<th>Minimum $^a$ (IV) Fe</th>
<th>Maximum (IV) Density</th>
<th>Maximum (VI) Density</th>
<th>Predicted (XRD Data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (+1)</td>
<td></td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
<td>--</td>
</tr>
<tr>
<td>Na (+1)</td>
<td></td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>--</td>
</tr>
<tr>
<td>Rb (+1)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ca (+2)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Basal Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td></td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>--</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (+2)</td>
<td></td>
<td>5.91</td>
<td>5.91</td>
<td>5.91</td>
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</tr>
<tr>
<td>Al (+1.5)</td>
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<td>2.09</td>
<td>1.94</td>
<td>1.95</td>
<td>--</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ti (+2)</td>
<td>--</td>
<td>0.15</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Apical Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td></td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>--</td>
</tr>
<tr>
<td>OH (-1)</td>
<td></td>
<td>2.15</td>
<td>2.15</td>
<td>2.15</td>
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</tr>
<tr>
<td>F (-0.5)</td>
<td></td>
<td>1.85</td>
<td>1.85</td>
<td>1.85</td>
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<tr>
<td>Octahedral</td>
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</tr>
<tr>
<td>Ti (+2)</td>
<td></td>
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<td>--</td>
<td>0.15</td>
<td>--</td>
</tr>
<tr>
<td>Al (+1.5)</td>
<td></td>
<td>0.26</td>
<td>0.41</td>
<td>0.40</td>
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</tr>
<tr>
<td>Fe (+1.5)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Mg (+1)</td>
<td></td>
<td>5.13</td>
<td>5.13</td>
<td>5.13</td>
<td>--</td>
</tr>
<tr>
<td>Fe (+1)</td>
<td></td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>--</td>
</tr>
<tr>
<td>Mn (+1)</td>
<td></td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>--</td>
</tr>
<tr>
<td>Zn (+1)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Li (+0.5)</td>
<td></td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>--</td>
</tr>
<tr>
<td>Binary (VI)</td>
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<td></td>
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<tr>
<td>&quot;Mg&quot; (+1)</td>
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<td>5.77</td>
<td>5.85</td>
<td>5.64</td>
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<tr>
<td>&quot;Fe&quot; (+1)</td>
<td>0.23</td>
<td>0.15</td>
<td>0.36</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$ Site occupancies assigned by the conventional method.

$^b$ Valences shown assume 50% covalent bonding, except for interlayer atoms which are assumed to have 100% ionic bonding.

$^c$ Binary site occupancies refer to a hypothetical octahedral cation sheet containing only Mg and Fe but having the same effective electron density as the actual octahedral sheet (see text for details).

| $|F|$ Ratio | Theoretical | Observed |
|-----------|-------------|----------|
| 0.402     | 0.395       | 0.413    | 0.437    |
TABLE III-5. Structural ion site occupancies and theoretical |F| ratios (004/005) obtained with three different assumptions, and the predicted site occupancies derived from the observed |F| ratio (004/005) for a Bancroft biotite

<table>
<thead>
<tr>
<th>Atom(Valence)</th>
<th>Minimum (IV) Fe</th>
<th>Minimum (IV) Density</th>
<th>Maximum (VI) Density</th>
<th>Predicted (XRD Data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (+1)</td>
<td>1.83</td>
<td>1.83</td>
<td>1.83</td>
<td>1.83</td>
</tr>
<tr>
<td>Na (+1)</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Rb (+1)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca (+2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basal Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (+2)</td>
<td>6.34</td>
<td>6.34</td>
<td>6.34</td>
<td>6.34</td>
</tr>
<tr>
<td>Al (+1.5)</td>
<td>1.66</td>
<td>1.24</td>
<td>1.13</td>
<td>1.34</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
<td>--</td>
<td>0.13</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ti (+2)</td>
<td>--</td>
<td>0.29</td>
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<td>--</td>
</tr>
<tr>
<td>Apical Anion</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>O (-1)</td>
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<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
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<tr>
<td>OH (-1)</td>
<td>1.69</td>
<td>1.69</td>
<td>1.69</td>
<td>1.69</td>
</tr>
<tr>
<td>F (-0.5)</td>
<td>2.31</td>
<td>2.31</td>
<td>2.31</td>
<td>2.31</td>
</tr>
<tr>
<td>Octahedral</td>
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</tr>
<tr>
<td>Ti (+2)</td>
<td>0.29</td>
<td>--</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>Al (+1.5)</td>
<td>0.13</td>
<td>0.55</td>
<td>0.66</td>
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<td>Fe (+1.5)</td>
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<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>Mg (+1)</td>
<td>2.78</td>
<td>2.78</td>
<td>2.78</td>
<td>2.78</td>
</tr>
<tr>
<td>Fe (+1)</td>
<td>1.91</td>
<td>1.91</td>
<td>1.91</td>
<td>1.91</td>
</tr>
<tr>
<td>Mn (+1)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn (+1)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Li (+0.5)</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Binary (VI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;Mg&quot; (+1)</td>
<td>4.17</td>
<td>4.49</td>
<td>3.67</td>
<td>3.91</td>
</tr>
<tr>
<td>&quot;Fe&quot; (+1)</td>
<td>1.83</td>
<td>1.51</td>
<td>2.33</td>
<td>2.09</td>
</tr>
</tbody>
</table>

--- Theoretical ---  --- Observed ---

| | | | | |
|---|---|---|---|
| | 0.687 | 0.640 | 0.775 | 0.738 |

---

*aSite occupancies assigned by the conventional method.

*bValences shown assume 50% covalent bonding, except for interlayer atoms which are assumed to have 100% ionic bonding.

*cBinary site occupancies refer to a hypothetical octahedral cation sheet containing only Mg and Fe but having the same effective electron density as the actual octahedral sheet (see text for details).
and a higher layer charge than the other micas. The conventional cation site assignments \[\text{minimum (IV) Fe}\] suggest that about a third of the layer charge arises from vacancies in the octahedral sheet. A shift of all of these vacancies to the tetrahedral sheet \[\text{maximum (VI) density}\] results in a net positive charge on the octahedral sheet equal to nearly half the layer charge of the mica. Both of these situations seem extreme. It seems likely, therefore, that some vacancies occur in both the tetrahedral and octahedral sheets. Fortunately, the theoretical $|F|$ ratios provide a wide enough range to distinguish between these two extremes and the observed $|F|$ ratio supports the presence of vacancies in both octahedral and tetrahedral sites. The uncertainty associated with the vacancy distribution in the predicted structural formula is rather high, however, if an allowance of 0.04 is made in the theoretical $|F|$ ratios for possible errors in the fractional coordinates.

Tetrahedral vacancies are still predicted, but the exact quantity is subject to some question. The ease with which this mica exchanges interlayer K (Chapter VI) suggests that at least some of the layer charge originates in the octahedral sheet and, therefore, the number of tetrahedral vacancies may be less than that predicted by comparison of the theoretical and observed $|F|$ ratios.

The Little Patsy siderophyllite (Table III-6) also contains a fair number of cation-site vacancies, but has more trivalent cations and less Si than the biotite. As a consequence, all of the layer charge originates in the tetrahedral sheet and a small amount of positive charge resides in the octahedral sheet. This distribution of charge is
TABLE III-6. Structural ion site occupancies and theoretical $|F|$ ratios (004/005) obtained with three different assumptions, and the predicted site occupancies derived from the observed $|F|$ ratio (004/005) for a Little Patsy siderophyllite

<table>
<thead>
<tr>
<th>Assigned Site Occupancies</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Maximum</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom(Valence)</td>
<td>(IV) Fe</td>
<td>(IV) Density</td>
<td>(VI) Density</td>
<td>(XRD Data)</td>
</tr>
<tr>
<td>Interlayer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (+1)</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
<td>1.78</td>
</tr>
<tr>
<td>Na (+1)</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Rb (+1)</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Ca (+2)</td>
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<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Basal Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (+2)</td>
<td>5.74</td>
<td>5.74</td>
<td>5.74</td>
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</tr>
<tr>
<td>Al (+1.5)</td>
<td>2.26</td>
<td>2.17</td>
<td>1.84</td>
<td>2.12</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
<td>--</td>
<td>0.05</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ti (+2)</td>
<td>--</td>
<td>0.04</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Apical Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
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<td>0.86</td>
<td>0.86</td>
<td>0.86</td>
</tr>
<tr>
<td>F (-0.5)</td>
<td>3.14</td>
<td>3.14</td>
<td>3.14</td>
<td>3.14</td>
</tr>
<tr>
<td>Octahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti (+2)</td>
<td>0.04</td>
<td>--</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Al (+1.5)</td>
<td>1.56</td>
<td>1.65</td>
<td>1.98</td>
<td>1.70</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
<td>0.05</td>
<td>--</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg (+1)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe (+1)</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
</tr>
<tr>
<td>Mn (+1)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn (+1)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Li (+0.5)</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>Binary (VI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;Mg&quot; (+1)</td>
<td>3.18</td>
<td>3.27</td>
<td>2.79</td>
<td>3.05</td>
</tr>
<tr>
<td>&quot;Fe&quot; (+1)</td>
<td>2.82</td>
<td>2.73</td>
<td>3.21</td>
<td>2.95</td>
</tr>
</tbody>
</table>

| IFI Ratio | 0.892 | 0.873 | 0.984 | 0.921 |

---

*Site occupancies assigned by the conventional method.

**Valences shown assume 50% covalent bonding, except for interlayer atoms which are assumed to have 100% ionic bonding.

**Binary site occupancies refer to a hypothetical octahedral cation sheet containing only Mg and Fe but having the same effective electron density as the actual octahedral sheet (see text for details).
typical of micas in general and serves to underscore the unusual situation observed for the Bancroft biotite. The range in theoretical $|F|$ ratios for the siderophyllite is similar to that for the biotite, and a comparison of the observed to the theoretical $|F|$ ratios suggests that some tetrahedral vacancies may be present. This prediction is tempered again by the uncertainty in the fractional coordinates and it is possible that no tetrahedral vacancies occur.

The Brevik lepidomelane (Table III-7) contains considerable amounts of the heavier elements [notably Fe(II) and Fe(III), Ti and Mn] and about the same number of vacancies as the biotite. One result of the combination of heavy atoms and numerous vacancies is that the range in the theoretical $|F|$ ratios is large (1.10 to 1.88) and, thus, the sensitivity to cation site occupancy is high. The Fe(III) content is high enough that tetrahedral Fe(III) is present in the conventional [minimum (IV) Fe] as well as the maximum (IV) density formulas. The observed $|F|$ ratio, however, is so far below the theoretical ratio calculated for the conventional site occupancies that the predicted tetrahedral Fe content is almost twice that of the conventional formula. This prediction is reasonably well-founded because the possible error from fractional coordinates is smaller than the standard deviation of the observed $|F|$ ratio (0.02).

The Massachusetts annite (Table III-8) bears many similarities to the lepidomelane, but contains only half as much Fe(III), nearly 50% more Fe(II) and fewer vacancies. Because of the vacancies the range in theoretical $|F|$ ratios is narrower (1.43-2.06) but still quite sensitive
TABLE III-7. Structural ion site occupancies and theoretical |F| ratios (004/005) obtained with three different assumptions, and the predicted site occupancies derived from the observed |F| ratio (004/005) for a Brevik lepidomelane

<table>
<thead>
<tr>
<th>Atom(Valence)</th>
<th>Assigned Site Occupancies</th>
<th>Minimum&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Maximum&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Maximum&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Predicted&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(IV) Fe</td>
<td>(IV) Density</td>
<td>(VI) Density</td>
<td>(XRD Data)</td>
</tr>
<tr>
<td>Interlayer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (+1)</td>
<td></td>
<td>1.63</td>
<td>1.63</td>
<td>1.63</td>
<td>1.63</td>
</tr>
<tr>
<td>Na (+1)</td>
<td></td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Rb (+1)</td>
<td></td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca (+2)</td>
<td></td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Basal Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td></td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (+2)</td>
<td></td>
<td>5.62</td>
<td>5.62</td>
<td>5.62</td>
<td>5.62</td>
</tr>
<tr>
<td>Al (+1.5)</td>
<td></td>
<td>2.05</td>
<td>0.81</td>
<td>1.91</td>
<td>1.80</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
<td></td>
<td>0.33</td>
<td>1.10</td>
<td>--</td>
<td>0.58</td>
</tr>
<tr>
<td>Ti (+2)</td>
<td></td>
<td>--</td>
<td>0.47</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Apical Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td></td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>OH (-1)</td>
<td></td>
<td>3.72</td>
<td>3.72</td>
<td>3.72</td>
<td>3.72</td>
</tr>
<tr>
<td>F (-0.5)</td>
<td></td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>Octahedral</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti (+2)</td>
<td></td>
<td>0.47</td>
<td>--</td>
<td>0.47</td>
<td>0.47</td>
</tr>
<tr>
<td>Al (+1.5)</td>
<td></td>
<td>--</td>
<td>1.24</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
<td></td>
<td>0.77</td>
<td>--</td>
<td>1.10</td>
<td>0.52</td>
</tr>
<tr>
<td>Mg (+1)</td>
<td></td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe (+1)</td>
<td></td>
<td>3.42</td>
<td>3.42</td>
<td>3.42</td>
<td>3.42</td>
</tr>
<tr>
<td>Mn (+1)</td>
<td></td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Zn (+1)</td>
<td></td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Li (+0.5)</td>
<td></td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Binary (VI)&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;Mg&quot; (+1)</td>
<td></td>
<td>1.69</td>
<td>2.78</td>
<td>0.90</td>
<td>1.96</td>
</tr>
<tr>
<td>&quot;Fe&quot; (+1)</td>
<td></td>
<td>4.31</td>
<td>3.22</td>
<td>5.10</td>
<td>4.04</td>
</tr>
</tbody>
</table>

| | Theoretical | -- | Observed | |
| | ------------ | ---- | --------- | |
| | 1.461       | 1.101 | 1.884    | 1.361 |

<sup>a</sup>Site occupancies assigned by the conventional method.
<sup>b</sup>Valences shown assume 50% covalent bonding, except for interlayer atoms which are assumed to have 100% ionic bonding.
<sup>c</sup>Binary site occupancies refer to a hypothetical octahedral cation sheet containing only Mg and Fe but having the same effective electron density as the actual octahedral sheet (see text for details).
TABLE III-8. Structural ion site occupancies and theoretical |F| ratios (004/005) obtained with three different assumptions, and the predicted site occupancies derived from the observed |F| ratio (004/005) for a Massachusetts annite

<table>
<thead>
<tr>
<th>Atom(Valence)</th>
<th>Assigned Site Occupancies</th>
<th>Minimum(^a) (IV) Fe</th>
<th>Maximum(^a) (IV) Density</th>
<th>Maximum(^b) (VI) Density</th>
<th>Predicted (XRD Data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (+1)</td>
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<td>1.77</td>
<td>1.77</td>
<td>1.77</td>
<td>1.77</td>
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<tr>
<td>Na (+1)</td>
<td></td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Rb (+1)</td>
<td></td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Ca (+2)</td>
<td></td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Basal Anion</td>
<td></td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
</tr>
<tr>
<td>O (-1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrahedral</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si (+2)</td>
<td></td>
<td>5.74</td>
<td>5.74</td>
<td>5.74</td>
<td>5.74</td>
</tr>
<tr>
<td>Al (+1.5)</td>
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<td>2.07</td>
<td>1.28</td>
<td>1.91</td>
<td>1.96</td>
</tr>
<tr>
<td>Fe (+1.5)</td>
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<td>0.19</td>
<td>0.49</td>
<td>--</td>
<td>0.30</td>
</tr>
<tr>
<td>Ti (+2)</td>
<td></td>
<td>--</td>
<td>0.49</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Apical Anion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (-1)</td>
<td></td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>OH (-1)</td>
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<td>3.69</td>
<td>3.69</td>
<td>3.69</td>
<td>3.69</td>
</tr>
<tr>
<td>F (-0.5)</td>
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<td>0.31</td>
<td>0.31</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>Octahedral</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Ti (+2)</td>
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<td>--</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>Al (+1.5)</td>
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<td>0.79</td>
<td>0.16</td>
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</tr>
<tr>
<td>Fe (+1.5)</td>
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<td>0.30</td>
<td>--</td>
<td>0.49</td>
<td>0.19</td>
</tr>
<tr>
<td>Mg (+1)</td>
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<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Fe (+1)</td>
<td></td>
<td>4.52</td>
<td>4.52</td>
<td>4.52</td>
<td>4.52</td>
</tr>
<tr>
<td>Mn (+1)</td>
<td></td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Zn (+1)</td>
<td></td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Li (+0.5)</td>
<td></td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Binary (VI)(^c)</td>
<td></td>
<td>1.09</td>
<td>1.71</td>
<td>0.57</td>
<td>1.23</td>
</tr>
<tr>
<td>&quot;Mg&quot; (+1)</td>
<td></td>
<td>4.91</td>
<td>4.29</td>
<td>5.43</td>
<td>4.77</td>
</tr>
<tr>
<td>&quot;Fe&quot; (+1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| |F| Ratio | 1.725 | 1.420 | 2.056 | 1.664 |

\(^a\)Site occupancies assigned by the conventional method.

\(^b\)Valences shown assume 50% covalent bonding, except for interlayer atoms which are assumed to have 100% ionic bonding.

\(^c\)Binary site occupancies refer to a hypothetical octahedral cation sheet containing only Mg and Fe but having the same effective electron density as the actual octahedral sheet (see text for details).
to cation site occupancy. The observed $|F|$ ratio is less than the conventionally calculated theoretical ratio and predicts about 50% more tetrahedral Fe than the conventional formula. Again, the error in this prediction is probably confined to the standard deviation of the observed $|F|$ ratio (0.02).

The data presented in Tables III-3 through III-8 are summarized in Figure III-3. In this figure, the theoretical and observed $|F|_{004/005}$ ratios are plotted as a function of the effective Fe(II) occupancy, which describes the x-ray electron density of the octahedral atom plane. The range of theoretical $|F|$ ratios is shown by the open symbols (connected by dotted lines) whereas the observed $|F|$ ratio is represented by a solid horizontal line. The intersection of the solid and dotted lines corresponds to the predicted electron density of the octahedral plane, from which the site occupancies for the tetrahedral and octahedral sheets were calculated in Tables III-3 to III-8. In general, as the effective octahedral Fe(II) occupancy increases, the value of the $|F|_{004/005}$ ratio and the sensitivity of the ratio to site occupancy (as shown by the theoretical range) also increase. Thus, this method seems most applicable to the mid- and high-Fe micas, when an absolute estimate of cation site occupancy is desired. The use of individually determined fractional coordinates for the micas (instead of relying on mean values) would eliminate much of the uncertainty in the estimates for low-Fe micas, but at the expense of more time and effort.

The problems encountered here with fractional coordinates should be much less when subsamples of the same mica are analyzed after various
FIGURE III-3. The observed $\delta_{004/005}$ ratios for six trioctahedral micas and the range of theoretical $\delta_{004/005}$ ratios that were calculated for each mica assuming various octahedral and tetrahedral cation site occupancies, expressed in terms of the effective Fe(II) occupancy of the octahedral sheet [the Fe(II) occupancy associated with the conventional cation site assignment and that predicted by the observed $\delta_{004/005}$ ratio are shown by the solid symbols]
treatments. In this event, the fractional coordinates would remain relatively constant even if the site occupancies changed (e.g., ejection of cations that occurs as a result of oxidative weathering). Thus, application of this method to studies of a single mica at various stages of weathering may yield sensitive information regarding the extent of cation ejection relative to other reactions that may occur.

Summary and Conclusions

A relatively simple and precise method for the estimation of cation site occupancies in trioctahedral micas by x-ray diffraction has been developed. The method relies on comparisons of theoretical and observed structure factor ratios for the 004 and 005 reflections and thus requires the determination of chemical composition and fractional coordinates of the atom planes parallel to the basal surfaces, when absolute numbers are desired. Estimates of the fractional coordinates from the literature may be used, but they increase the uncertainty of the site occupancy estimates, especially in the phlogopite micas. The results that were obtained for six representative trioctahedral micas suggest that the conventional assignments of cations to octahedral and tetrahedral sites probably need some modifications. For example, the data support the presence of vacancies in tetrahedral sites of a magnesian biotite and the presence of as much as twice the amount of tetrahedral Fe(III) in a lepidomelane and annite than would be predicted by the conventional site assignments. The observed structure factor
ratios may be used, without reference to the theoretical ratios, for relative estimates of cation site occupancy in treated subsamples of the same mica, or even for rough classification of unknown micas. When accurate structural formulas are desired or when changes in cation occupancies during weathering need to be monitored, this method should prove valuable.
CHAPTER IV. OXIDATIVE WEATHERING OF TRIOCTAHEDRAL MICAS
BY BUFFERED H$_2$O$_2$ SOLUTIONS—1. OXIDATION AND
THE KINETICS OF DISSOLUTION

Introduction

A full understanding of the role of structural Fe oxidation in mica weathering requires knowledge of the conditions under which it can, and cannot, occur. It is generally recognized that structural Fe oxidation occurs readily in micas that have been expanded by a replacement of interlayer K with hydrated cations. What is not so clear, however, is the extent to which such oxidation may occur in micas that retain their interlayer K and thus remain contracted. Juo and White (1969), for example, reported only "partial oxidation" of a biotite they treated with a 30% H$_2$O$_2$-0.2 M KCl solution. Robert (1971) concluded, after his attempts with H$_2$O$_2$ solutions yielded oxidation of 7% of the Fe(II) present, that only the Fe(II) directly in contact with the oxidizing solution could be oxidized. On the other hand, Gilkes et al. (1972a) reported oxidation of as much as 85% of the structural Fe(II) in Bancroft biotite samples "without change in structure" after treatments by Br$_2$-saturated solutions and suggested "that expansion need not occur during natural weathering." In a later publication, however, Gilkes et al. (1972b) tacitly acknowledged that they did not know whether or not expansion had occurred during the Br$_2$ treatments, only that the final
product was contracted and thus "indistinguishable from naturally occurring specimens." Kozak (1976) conducted extensive biotite oxidation experiments with \( \text{Br}_2 \) solutions containing various amounts of KCl to inhibit expansion. He found that with high levels of K in solution, less oxidation was obtained than with lower levels, but he was unable to completely stop the oxidation process even when the solutions were saturated with KCl. Amonette (1983) treated 10- to 20-\( \mu \text{m} \) biotite samples with \( \text{H}_2\text{O}_2 \) solutions containing 1 M K to inhibit expansion and obtained oxidation of as much as 54% of the structural Fe(II). He concluded that "oxidation of structural Fe in contracted biotites is possible" and that deprotonation of structural hydroxyls was probably the charge-balancing reaction for this process. Treatments of large flakes of biotite by the same \( \text{H}_2\text{O}_2-1 \text{ M K} \) solutions, however, resulted in oxidation and extensive exfoliation of the flakes (Scott and Amonette, 1988), thus suggesting that maintenance of contracted micas in the oxidation experiments of Amonette (1983) may not have occurred.

In this chapter, then, the question of whether Fe oxidation can occur when the mica layers remain contracted is examined once more by treating three micas having a range of Fe contents in buffered \( \text{H}_2\text{O}_2-1 \text{ M K} \) solutions for various periods and monitoring the redox status of the micas, the chemical composition of the effluent and the extent of exfoliation that occurs during treatment. Inasmuch as an estimate of the latter quantity can be obtained from the relative dissolution rates of treated and untreated samples in a non-exfoliating "matrix" solution, a quantitative kinetic approach to the dissolution process is developed.
In subsequent chapters, the structural changes accompanying oxidative weathering of these micas and the effects of K-depletion on the oxidative weathering processes will also be examined.

Experimental

Micas

Samples of three trioctahedral micas were obtained from Ward's Scientific Establishment, Rochester, NY (phlogopite, biotite) and from Continental Minerals, Tucson, AZ (siderophyllite). These were a phlogopite from North Burgess, Ontario, Canada; a magnesian biotite from Bancroft, Ontario, Canada; and a siderophyllite from the Little Patsy Mine, near Pine, Jefferson Co., Colorado. Aqueous suspensions of the micas were ground in a Waring blender to pass through a 50-μm sieve and then the 10- to 20-μm size-fractions were recovered by sedimentation. After drying, the micas were resuspended in acetone and subjected to a brief sonification treatment to remove any ultrafine particles that may have remained.

After a qualitative determination of the major elements present in the micas by energy-dispersive x-ray fluorescence spectroscopy, quantitative determinations of these elements were made by inductively-coupled argon plasma atomic emission spectroscopy (ICP-AES). For the ICP-AES analyses, the biotite and siderophyllite were digested in HF-H₂SO₄ and the excess F complexed by addition of H₃BO₃ prior to analysis, whereas the phlogopite sample was analyzed directly as a 0.1%
aqueous suspension. The quantities of K, Rb, and Fe in all samples were determined by atomic absorption spectroscopy of HF digests. Fe(II) in these samples was analyzed by the V(V) method described in chapter II, Fe(III) by difference from total Fe. These data were used to calculate structural formulas for each mica on the basis of 44 positive and negative charges for each unit layer. Aluminum occupancies of the octahedral and tetrahedral sheets were assigned based on x-ray diffraction evidence using the method described in chapter III, rather than by assuming all vacancies occurred in the octahedral sheet as is conventionally done. The distribution of atoms and charges among the various sites in the structure of each mica is shown in Table IV-1.

Weathering solutions

Two weathering solutions, termed the "H₂O₂" and the "matrix" solutions, were used to treat the mica samples. The "H₂O₂" solution consisted of a 25% H₂O₂-1 M KOAc(pH 4.7)-0.1 M K₂EDTA mixture and was used for oxidative weathering treatments. The "matrix" solution had the same salt content as the "H₂O₂" solution but did not include the oxidant.

The solutions were prepared by carefully neutralizing the appropriate quantities of KOH and K₂EDTA with glacial acetic acid in a wide-mouth plastic flask partly submerged in a cold water bath. When all the solid had dissolved, sufficient cold (ca. 5°C) 30% H₂O₂ or H₂O was added to cool the solution. This mixture was then passed through a 1- to 2-μm porosity Teflon filter membrane by vacuum filtration, made to
TABLE IV-1. Distribution of atoms and charges among the structural sites of micas based on analyses of ground, sedimeted samples (10- to 20-µm diameter size-fraction) and assuming 44 positive and negative charges per unit cell

<table>
<thead>
<tr>
<th>Atom</th>
<th>Phlogopite</th>
<th>Biotite</th>
<th>Siderophyllite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Interlayer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.50</td>
<td>1.83</td>
<td>1.78</td>
</tr>
<tr>
<td>Na</td>
<td>0.09</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>Rb</td>
<td>0.00</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>Ca</td>
<td>0.11</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Occupancy</td>
<td>1.70</td>
<td>1.98</td>
<td>1.93</td>
</tr>
<tr>
<td>Charge</td>
<td>+1.81</td>
<td>+1.98</td>
<td>+1.93</td>
</tr>
<tr>
<td><strong>Octahedral</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.15</td>
<td>0.29</td>
<td>0.04</td>
</tr>
<tr>
<td>Al</td>
<td>0.27</td>
<td>0.41(0.13)</td>
<td>1.70(1.56)</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>0.00</td>
<td>0.13</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>0.27</td>
<td>1.91</td>
<td>3.24</td>
</tr>
<tr>
<td>Mg</td>
<td>5.13</td>
<td>2.78</td>
<td>0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>0.01</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Li</td>
<td>0.04</td>
<td>0.10</td>
<td>0.52</td>
</tr>
<tr>
<td>Occupancy</td>
<td>5.88</td>
<td>5.75</td>
<td>5.72</td>
</tr>
<tr>
<td>Charge</td>
<td>+12.29</td>
<td>+12.53</td>
<td>+12.75</td>
</tr>
<tr>
<td><strong>Tetrahedral</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>5.92</td>
<td>6.34</td>
<td>5.74</td>
</tr>
<tr>
<td>Al</td>
<td>2.08</td>
<td>1.38(1.66)</td>
<td>2.12(2.26)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>8.00</td>
<td>7.72</td>
<td>7.86</td>
</tr>
<tr>
<td>Charge</td>
<td>+29.92</td>
<td>+29.50</td>
<td>+29.32</td>
</tr>
<tr>
<td><strong>Anions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>F</td>
<td>1.85</td>
<td>2.31</td>
<td>3.14</td>
</tr>
<tr>
<td>OH</td>
<td>2.15</td>
<td>1.69</td>
<td>0.86</td>
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<tr>
<td>Occupancy</td>
<td>24.00</td>
<td>24.00</td>
<td>24.00</td>
</tr>
<tr>
<td>Charge</td>
<td>-44.00</td>
<td>-44.00</td>
<td>-44.00</td>
</tr>
<tr>
<td>Net Charge (VI)</td>
<td>+0.29</td>
<td>+0.53</td>
<td>+0.75</td>
</tr>
<tr>
<td>Net Charge (IV)</td>
<td>-2.08</td>
<td>-2.50</td>
<td>-2.68</td>
</tr>
<tr>
<td>Layer Charge</td>
<td>-1.80</td>
<td>-1.97</td>
<td>-1.93</td>
</tr>
</tbody>
</table>

<sup>a</sup>Al distribution between octahedral and tetrahedral sheets was adjusted to fit x-ray diffraction data (numbers in parentheses refer to conventional site assignments that allow no tetrahedral vacancies).
volume in a glass volumetric flask with $H_2O_2$ or 30% $H_2O_2$, and stored in a clean plastic container at 5°C until used. When the $H_2O_2$ solution was prepared in this manner, $H_2O_2$ levels between 25 and 30% were usually obtained. These solutions were adjusted to 25% $H_2O_2$ immediately before use by diluting with an appropriate amount of the matrix solution. During use the $H_2O_2$ solution was kept at room temperature in an aluminum foil-covered plastic container away from direct sunlight. Reagent grade chemicals were used in all instances, and the $H_2O_2$ contained small amounts (4 μg/ml) of NaNO$_3$ and Na$_3$SnO$_3$·3$H_2O$ that were added by the manufacturer to minimize autodecomposition.

**Apparatus**

The apparatus consisted of 10 reaction vessels mounted in a rack and submerged in an 80°C water bath. The reaction vessels were connected by small-bore Teflon and Tygon tubing to a 20-channel peristaltic pump that metered fresh weathering solution from a common feed bottle into the vessels at a constant rate (4 ml hr$^{-1}$) and also transferred "spent" weathering solution (i.e., effluent) from the vessels into individual sampling bottles. The reaction vessels (Figure IV-1), which were adapted from 47-mm Teflon in-line filter holders (Savillex Corp., Minnetonka, MN), were vented to the atmosphere to avoid a pressure build-up that might result from the decomposition of $H_2O_2$. The mica samples settled in a very thin layer on the bottom of the reaction vessels and were in constant contact with the weathering solution. A relatively constant volume (ca. 10 ml) of weathering
FIGURE IV-1. Schematic of a reaction vessel used to weather micas by the continuous-flow method
solution was maintained in the reaction vessels by suspending a Teflon immersion filter fitted with a 1- to 2-μm porosity Teflon membrane from the top of each vessel. All effluent collected into the sampling bottles was drawn through the immersion filters by the peristaltic pump to eliminate any mica particles (2-μm or greater) that may have been in suspension. At no point in the apparatus did the weathering solutions come into contact with glass or metallic surfaces that could have been sources of contamination.

**Experimental design**

Two experiments, which will be referred to as the "main" and the "reference state" experiments, were performed in this study. For both experiments, the temperature of the water bath was maintained at 80°C and the flow rate of weathering solution through the reactor vessels was 4 ml hr⁻¹.

The "main" experiment involved the treatment of 1300-mg mica samples for periods of 2, 4, 6, 12, 24 or 36 days with the H₂O₂ solution or for 36 days with the matrix solution. Three reaction vessels were assigned to each mica. Two of these were used to obtain the H₂O₂ weathering data, the third for the matrix weathering data. At any stage in the experiment, samples from each of the three micas were receiving the same combination of treatment period and weathering solution. Thus, the 12-day H₂O₂-treated samples for all three micas were run simultaneously and with the same batch of weathering solution. For each mica sample, effluent samples were taken after 2, 4, and 6 days and
every 3 days thereafter until the sample was terminated. At the time of sampling, the volume of effluent was measured with a plastic graduated cylinder, an aliquot was taken for immediate determination of the \( \text{H}_2\text{O}_2 \) concentration, and 60-125 ml of the effluent were stored in an acid-leached plastic bottle for later analysis of Al, Mg and Fe content.

At the end of a treatment period, the mica samples were terminated by the following procedure. The reaction vessels were disconnected from the peristaltic pump and the rack removed from the water bath. A syringe was used to add 10 ml of 1.3 M KCl to the reaction vessel being terminated. The vessel was removed from the rack, opened, and the contents transferred quantitatively using a 0.5 M KCl-60% acetone solution into a 300-ml Millipore filter holder fitted with a pre-wetted 0.2-um porosity Teflon filter membrane. Vacuum was applied to the filter apparatus and the sample washed several times with 0.5 M KCl-60% acetone, several times with 60% acetone to remove the excess salts, and then finally several times with 100% acetone. A cover glass was placed on top of the filter apparatus and the vacuum was left on for a couple hours until the sample was completely dry. When dry, the sample was quantitatively transferred to a tared glassine weighing paper, weighed and then transferred to a tared glass vial for storage.

Fe(II) analyses, by the method developed in Chapter II, were performed on subsamples taken from the storage vials. The Fe(III) content of the samples was calculated as the difference between the total Fe measured in the untreated mica and the Fe(II) measured in the \( \text{H}_2\text{O}_2 \)-treated mica. The absolute accuracy of the Fe(III) data,
therefore, is limited by the assumption that no change occurred in the total Fe content as a result of treatment.

Duplicate runs were made of the main experiment and means of the two sets of data are reported. The effluent concentration data reported for the H$_2$O$_2$-treated samples, however, are means of the samples treated for the 24- and 36-day periods in both runs and, thus, include 4 observations rather than 2.

The "reference state" experiment involved the treatment of 150-mg mica samples for 12 days by the matrix weathering solution at 80°C. For each mica, three samples that differed according to the pretreatment they had received were run. Two of the samples had been weathered for 36 days, one by the H$_2$O$_2$ solution and one by the matrix solution. The third sample had received no pretreatment. As in the main experiment, effluent samples were collected after 2, 4, 6, 9 and 12 days of treatment, stored and later analyzed for Al, Mg and Fe content. The mica samples were terminated as described for the main experiment, but, because of the limited quantities involved, no further chemical analyses were made. Only one replication of this experiment was performed.

**Effluent analyses**

The H$_2$O$_2$ concentrations in the effluent samples were determined by the following procedure. Immediately after sampling, a 0.2-ml aliquot of effluent was transferred to a flask containing 3 ml of 4.5 M H$_2$SO$_4$ and about 50 ml of H$_2$O. This solution was titrated to the first permanent pink endpoint with 0.1 M KMnO$_4$ that had been standardized with
primary standard grade ferrous ethylenediammonium sulfate
$[\text{FeC}_2\text{H}_4(\text{NH}_3)_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$. 

To determine the Al, Mg and Fe concentrations, the effluent samples were first diluted 1:10 with H$_2$O and placed in random order. Then duplicate subsamples (0.5 ml) were analyzed by flow injection into a Sciex Elan Model 250 inductively coupled argon plasma mass spectrometer fitted with a pneumatic nebulizer. Because some instrumental drift occurred, standard solutions were analyzed after every 5 effluent samples. A standard curve was calculated for each effluent sample from its position between the actual standards analyzed and assuming a linear drift with time. This linearly-interpolated, time-dependent standard curve was then used to calculate the concentrations of Al, Mg and Fe in the sample from the counts registered by the instrument.

**Kinetic model**

To quantify the rates of dissolution observed and thus aid in the comparisons between the effects of the matrix and H$_2$O$_2$ treatments, a kinetic model was developed that allowed the calculation of an empirical rate constant for each set of data. The model is based on the outline of heterogeneous kinetic theory presented in a series of papers by Delmon (1961a, 1961b, 1961c) and incorporates the effects of particle size and shape to arrive at an expression for the cumulative fraction of the sample dissolved as a function of time. A formal derivation is presented in the Appendix.

In brief, the model assumes that dissolution proceeds at a uniform
rate along all three axes of the mica particles and that the surface free energy of all cation dissolution sites is the same. The mica particles are assumed to be right cylinders of uniform size and to be of homogeneous composition and density. Because the mica particles were expected to cleave more readily along the a-b plane during the grinding process, an initial diameter to height ratio of 2:1 was chosen. The untreated particles were also assumed to have the same mass as a 20-μm diameter spherical particle. On this basis, the initial diameter and height of the cylindrical particles was calculated to be 22 and 11 μm, respectively. Lastly, the volume of a cation dissolution site was assumed to be that of a cube whose sides were roughly one-third of the average of the b and c unit cell dimensions in length, or about 0.32 nm.

Following these assumptions, the fractional amount ($\alpha$) of Al, Mg, or Fe that dissolved from the mica in time $t$ is given by

$$\alpha = 1 - \frac{a_0 - k_{app}zt}{a_0} \cdot \left[\frac{a_0 - k_{app}zt}{a_0} + \frac{a_0 - k_{app}zt}{a_0} + \frac{a_0 - k_{app}zt}{a_0}\right]^{2\lambda} + \frac{a_0 - k_{app}zt}{a_0}^{2\lambda}$$  \[IV-1\]

where $a_0$ is the starting half-height of the particle, $k_{app}$ the apparent rate constant, $z$ the depth of a cation site on the surface of the particle, and $\lambda$ a factor for the aspect ratio of the particle. The
apparent rate constant for a given set of data, $k_{\text{app}}$, was obtained by successive approximations once the other parameters had been set.

Results and Discussion

**Oxidation**

The mean oxidant concentrations in the effluent from the 24- and 36-day $H_2O_2$-treated samples are shown in Figure IV-2. Overall, it is clear that high levels of $H_2O_2$ were maintained in all treatments. The $H_2O_2$ concentrations in the phlogopite and siderophyllite effluents were similar and averaged 20-22% during the course of the experiment. The biotite treatments showed a more complicated pattern, however. During the first few days of treatment, successively lower $H_2O_2$ concentrations were measured until a minimum concentration of 14.7% was reached in the 4-day samples. For the next week or so, the $H_2O_2$ concentration rose steadily to about the 19% level. Thereafter, a much slower increase in $H_2O_2$ levels occurred until the final concentrations measured were in the 20-21% range, just below those of the other micas.

A certain amount of $H_2O_2$ decomposition would be expected to occur simply by heating the weathering solution at 80°C. Thus, the decrease in $H_2O_2$ concentration to the steady level observed in the phlogopite treatment is expected. The different effluent $H_2O_2$ concentrations for the micas, however, reflect variations in the ability of the mica samples to catalyze the decomposition of $H_2O_2$ rather than variations in the susceptibility of the micas to structural Fe oxidation, inasmuch as
FIGURE IV-2. Concentrations of H_2O_2 measured in the effluent during treatments of 1300-mg mica samples by 25% H_2O_2-1 M KOAc-0.1 M K_2EDTA solutions at 80°C
the amount of H₂O₂ required to oxidize all the Fe in any of the mica samples is negligible relative to the losses in H₂O₂ titer observed. Because Fe is a well-known catalyst for H₂O₂ decomposition (Schumb et al., 1955), the micas with high Fe content (siderophyllite) would be expected to cause more H₂O₂ decomposition and result in lower effluent H₂O₂ concentrations than micas with less structural Fe (biotite, phlogopite). Indeed, a comparison of the siderophyllite and phlogopite data supports this contention. The H₂O₂ levels for the biotite treatment, however, are much lower than those for the siderophyllite even though the siderophyllite has about 50% more structural Fe than the biotite. Obviously, a second factor must be involved.

Rates of heterogeneous catalysis are usually correlated with the total surface area of the catalytic agent. One possible explanation of the H₂O₂ data, therefore, is that a large increase in the surface area of the biotite sample occurred during treatment by H₂O₂. Evidence in support of this explanation comes from other studies of biotite weathering with continuously flowing 30% H₂O₂-0.1 M KOAc-0.1 M K₂EDTA solutions (nearly identical to the H₂O₂ solution used in the present study). Amonette (1983) observed a pattern in the effluent H₂O₂ concentrations like that seen in the present study when 10- to 20-μm Faraday biotite samples were treated with the weathering solution at 80°C. Furthermore, when macroflakes of the Faraday biotite were treated under the same conditions, there was visible evidence of extensive exfoliation (Scott and Amonette, 1988). Thus, by assuming, first, that macroflakes and 10- to 20-μm diameter mica flakes respond similarly to
H$_2$O$_2$ treatment and, second, that analogous patterns in H$_2$O$_2$ concentration data for the 10- to 20-μm micas are caused by a common factor, it is reasonable to conclude that exfoliation was responsible for the distinct pattern of the biotite H$_2$O$_2$ concentration data in the present study.

No oxidation of structural Fe(II) occurred in any of the micas as a result of treatments by the matrix solution (data not shown), but oxidation did occur during the H$_2$O$_2$ treatments (Figure IV-3). The biotite, which exhibited a roughly 7-fold increase in Fe(III) content, was clearly the mica that was most susceptible to oxidation by the H$_2$O$_2$ treatment. The siderophyllite showed a relatively small increase in Fe(III) content as a result of treatment and the phlogopite remained unchanged.

These results were surprising because the siderophyllite, which had more Fe(II) than the biotite, would be expected to show more oxidation. The small extent of oxidation in the siderophyllite, however, may be related to the fact that it showed little evidence of exfoliation during the H$_2$O$_2$ treatment. In contrast, the biotite showed evidence for substantial exfoliation during the first week of treatment, which is also when the majority of the oxidation occurred. It would seem, therefore, that the processes of oxidation and exfoliation are related, although the exact nature of the relationship cannot be discerned from these data alone.
FIGURE IV-3. Content of Fe(III) in 1300-mg mica samples after treatment for various periods by 25% $\text{H}_2\text{O}_2$-1 M KOAc-0.1 M $\text{K}_2\text{EDTA}$ solutions at 80°C.
Dissolution

The dissolution of the micas during the main experiment was monitored by measuring the concentrations of Al, Mg and Fe in the effluent samples. The cumulative dissolution data for the matrix and H\textsubscript{2}O\textsubscript{2} treatments are given in Figures IV-4, IV-5 and IV-6. Because the siderophyllite contained very small amounts of Mg (Table IV-1), Mg effluent data for this mica were at the detection limit and, therefore, are not included in Figure IV-5.

Looking first at dissolution by the matrix weathering solution, it can be seen that, in general, straight-line plots with only a slight degree of curvilinearity were obtained. A non-linear curve was obtained for the phlogopite Fe data in Figure IV-6, but this probably stems from analytical difficulties associated with the low Fe content of the mica. The precision, as shown by the range bars for the 21-day data, was very good. The micas varied in solubility with the biotite and phlogopite being the most easily dissolved and the siderophyllite much less soluble. And, for each mica, the cumulative fractions of Al, Mg and Fe dissolved after 21 days were identical, which suggests that the dissolution was homogeneous (i.e., no selective dissolution occurred). Thus, at the end of 21 days of treatment, 11% of the biotite, 9% of the phlogopite and 4% of the siderophyllite had dissolved.

The dissolution experiments with the H\textsubscript{2}O\textsubscript{2} weathering solution yielded a more complicated set of data (Figures IV-4, IV-5 and IV-6). During the first 9 days of treatment, plots having varying degrees of curvilinearity were obtained. Thereafter, essentially straight-line
FIGURE IV-4. Cumulative amounts of Al measured in the effluent during treatments of 1300-mg mica samples by the matrix (1 M KOAc-0.1 M K$_2$EDTA) and H$_2$O$_2$ (25% H$_2$O$_2$ + matrix) solutions at 80°C
SOLUBLE AI (CUMULATIVE % OF ORIGINAL IN MICA)

TIME (days)

H_2O_2

PHLOGOPITE

BIOTITE

SIDEROPHYLLITE

MATRIX
FIGURE IV-5. Cumulative amounts of Mg measured in the effluent during treatments of 1300-mg mica samples by the matrix (1 M KOAc-0.1 M K₂EDTA) and H₂O₂ (25% H₂O₂ + matrix) solutions at 80°C
SOLUBLE Mg (CUMULATIVE % OF ORIGINAL IN MICA)

TIME (days)

0 5 10 15 20

0 5 10 15 20

H₂O₂

PHLOGOPITE

BIOTITE

MATRIX
FIGURE IV-6. Cumulative amounts of Fe measured in the effluent during treatments of 1300-mg mica samples by the matrix (1 M KOAc-0.1 M K₂EDTA) and H₂O₂ (25% H₂O₂ + matrix) solutions at 80°C.
plots were obtained, although the precision of the data was poorer than in the matrix treatments. The biotite was much more susceptible to dissolution by the \( H_2O_2 \) solution than the other two micas, probably as a result of the extensive exfoliation and oxidation that occurred during the first week of treatment.

A comparison of the Al, Mg and Fe data for the \( H_2O_2 \)-treated biotite also shows that equivalent fractions of Fe and Al were recovered in the effluent (17% after 21 days), but that a substantially lower fraction of Mg was recovered (12%) during the same time period. Most of this difference occurred during the first 9 days of treatment when the rates of oxidation and exfoliation were highest. In fact, as will be shown in the next section, the rates of Al, Mg and Fe dissolution after the first 9 days were essentially identical. Thus, the preferential dissolution of the trivalent cations seems to be linked directly to the exfoliation and oxidation processes. One aspect of the oxidation process that could account for the Al and Fe dissolution results involves the ejection of octahedral cations from the mica structure to balance the excess charge created by the oxidation of structural Fe(II). The preferential ejection of trivalent Al and Fe may occur because of their small ionic radii (51 and 64 pm, respectively) and high charge relative to Mg (divalent, 66 pm ionic radius). It is probable, therefore, that the higher Al and Fe levels in the effluent are really a manifestation of this charge-balancing process rather than a solvation process per se.

Lastly, a comparison of the amounts of dissolution occurring in the matrix and the \( H_2O_2 \) solutions yields some interesting results. The
biotite seemed to be more soluble in the $\text{H}_2\text{O}_2$ solution, although once account is made for the effects of cation ejection (by extrapolation of the 9- to 21-day dissolution curve to time 0), the amounts of dissolution are roughly comparable. The other two micas, however, were nearly twice as soluble in the matrix solution as in the $\text{H}_2\text{O}_2$ solution. Recalling that dissolution is a surface-controlled process, two features of the $\text{H}_2\text{O}_2$ solutions may have been responsible for the lower dissolution observed. First, the $\text{H}_2\text{O}_2$ molecule, because of its strongly dipolar nature, would be expected to form stronger hydrogen bonds with the oxygens on the mica surface than H$_2$O. As a result, the accessibility of the surface of the mica to other molecules (OAc$^-$, EDTA$^{2-}$) that were actively involved in complexing and dissolving structural cations was less, and the overall amount of mica dissolved less. Second, the decomposition of $\text{H}_2\text{O}_2$, which was catalyzed at least partly by the mica surfaces, resulted in the production of $\text{O}_2$. Because of its non-polar hydrophobic nature, the $\text{O}_2$ may have become physically adsorbed to the mica surface or formed bubbles that floated their way to the top of the solution and escaped into the atmosphere (both of these phenomena were easily seen when examining the contents of the reaction vessels during the $\text{H}_2\text{O}_2$ treatments). The physical adsorption of $\text{O}_2$, therefore, like the bonding of $\text{H}_2\text{O}_2$, may have decreased the effective surface area available for dissolution by the $\text{H}_2\text{O}_2$ weathering solution and, as a consequence, caused less mica to be dissolved.
**Kinetics of dissolution**

The apparent rate constants \( k_{\text{app}} \) calculated with Eq. [IV-1] for the dissolution of the matrix- and \( \text{H}_2\text{O}_2 \)-treated mica samples in the main experiment are summarized in Table IV-2. Because of the exfoliation that seemed to have occurred in the biotite during the first few days of treatment by \( \text{H}_2\text{O}_2 \) solutions, the rate constants were calculated for the 9- to 21-day period when the reactions seemed to have stabilized (Figures IV-4, IV-5, and IV-6). In the matrix treatment, the mean \( k_{\text{app}} \) values ranged from 1.6 to 4.9 \( \times 10^{-4} \) s\(^{-1} \), depending on the mica. With treatment by \( \text{H}_2\text{O}_2 \), similar \( k_{\text{app}} \) values were obtained for the biotite, whereas those for the phlogopite and siderophyllite were about 60% lower than in the matrix treatment. For a given mica, the \( k_{\text{app}} \) values were consistent for Al, Mg, and Fe dissolution, thus confirming the occurrence of congruent dissolution after the first 9 days of treatment. In general, then, the trends suggested by the \( k_{\text{app}} \) values for the main experiment mirror those of the raw effluent data presented in Figures IV-4, IV-5, and IV-6.

By differentiating Eq. [IV-1] with respect to time and setting \( t = 0 \), an expression for the initial dissolution rate,

\[
\frac{d\alpha}{dt} \bigg|_{t=0} = \frac{(k_{\text{app}})(z)(\lambda^2 + 4\lambda + 3)}{a_0(\lambda^2 + 2\lambda + 1)}. \quad [\text{IV-2}]
\]

is obtained. It can also be shown that
TABLE IV-2. Apparent rate constants ($k_{app}$) for the dissolution of Al, Mg and Fe from 1300-mg mica samples treated with matrix (1.0 M KOAc-0.1 M K$_2$EDTA) or H$_2$O$_2$ (25% H$_2$O$_2$ + matrix) solutions during a 9- to 21-day period in a flow-through reactor at 80°C

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Sample</th>
<th>Matrix</th>
<th>H$_2$O$_2$</th>
<th>$10^{-4}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phlogopite</td>
<td>Al</td>
<td>3.9</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>4.2</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>4.0</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td>Al</td>
<td>5.1</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>4.9</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>4.6</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>4.9</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>Siderophyllite</td>
<td>Al</td>
<td>1.7</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>1.5</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>1.6</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>
where \( z \) is the depth of a cation dissolution site and \( S_{\text{eff}} \) and \( V_{\text{total}} \) are the "effective" surface area and total volume of the sample, respectively.

The concept of "effective" surface area is analogous to that of the activity of an aqueous species. Just as the activity of an aqueous species changes at different ionic strengths (even though the concentration remains constant), the "effective" surface area of a particle can change with the extent of competitive adsorption by the relatively inert components (e.g., \( \text{H}_2\text{O} \), \( \text{O}_2 \), \( \text{H}_2\text{O}_2 \)) of the weathering solution, even though the total surface area remains constant. Thus,

\[
S_{\text{eff}} = (\gamma_s)(S_{\text{total}}) \tag{IV-4}
\]

where \( \gamma_s \) is the fraction of the total surface area (\( S_{\text{total}} \)) that is complexed by the strong complexing agents in the weathering solution (i.e., the fraction that is "actively" dissolving). For convenience, the \( S_{\text{eff}} \) of a mica immersed in the matrix solution at 80°C is chosen as a reference state and \( \gamma_s \), under these conditions, is equal to 1.

Substitution of Eq. [IV-4] in Eq. [IV-3] yields

\[
\frac{d\alpha}{dt}_{t=0} = \frac{(k_{\text{app}})(z)(S_{\text{eff}})}{V_{\text{total}}} \tag{IV-5}
\]
It can be seen from Eq. [IV-5], therefore, that a comparison of initial dissolution rates for mica samples having identical volumes, cation site dimensions, and effective surface areas can be made directly from the $k_{\text{app}}$ values. The situation is complicated, however, when the effective surface areas of the mica samples are different. Exfoliation of the mica samples during treatment, for example, results in an increase in $S_{\text{total}}$. A change in the degree of competitive adsorption by the relatively inert components of a weathering solution (e.g. $H_2O$, $O_2$, and $H_2O_2$) from that of the matrix solution would cause a change in $\gamma_s$. The model used to calculate $k_{\text{app}}$, however, assumes that $\gamma_s$ is always 1, and it does not allow for any change in $S_{\text{total}}$ during treatment other than by dissolution. Clearly, then, the effects of exfoliation and competitive adsorption are included in the $k_{\text{app}}$ values shown in Table IV-2. Because identical concentrations of $OAc^-$ and $EDTA^2-$ (the compounds responsible for nearly all of the dissolution) were present in the matrix and $H_2O_2$ weathering solutions, it is likely that the different $k_{\text{app}}$ values obtained for a mica treated by these solutions are not the result of a change in the fundamental dissolution mechanism, but rather are due to differences in the effective surface area (i.e., $\gamma_s$ and $S_{\text{total}}$) of the mica particles. To separate the changes in effective surface area caused by exfoliation from those caused by competitive adsorption, a second experiment was conducted.

This experiment, termed the "reference state" experiment, involved the measurement of the $k_{\text{app}}$ values in the matrix solution at 80°C for untreated mica samples and for mica samples that had already received 36
days of treatment by the matrix or H$_2$O$_2$ solutions in the "main" experiment. The 150-mg samples were treated with the matrix solution under the same conditions as in the main experiment. Effluent data were collected for the 2-, 4-, 6-, 9-, and 12-day time periods and, after correcting the $a_0$ and $\lambda$ values in Eq. [IV-1] for the dissolution that occurred during the "main" experiment, $k_{app}$ values were calculated. Values of the apparent rate constant, $k_{app}$, were not calculated for the Fe effluent data, however, because of Fe contamination in the weathering solution that was used in this experiment. As a check on the effects of sample size, k$_{app}$ values for the first 12-days of dissolution of 1300-mg samples by the matrix solution in the main experiment were also calculated.

The $k_{app}$ values that were obtained for Al and Mg dissolution of previously weathered and unweathered mica samples by the matrix solution are summarized in Table IV-3. Because all of these $k_{app}$ values were obtained in the "reference state," $\gamma_s = 1$, and any difference in the rate constants can be interpreted purely in terms of differences in $S_{total}$.

The matrix and H$_2$O$_2$ pretreatments had little, if any, effect on the rate constant for phlogopite dissolution. These rate constant data, thus, corroborate previous evidence showing that no exfoliation of the phlogopite occurred during the H$_2$O$_2$ treatment. Some very large differences in $k_{app}$ values were observed for the biotite, however. The matrix pretreatment resulted in a slightly lower rate constant than in the untreated sample. This probably was a result of an elimination of
TABLE IV-3. Apparent rate constants ($k_{app}$) for the dissolution of Al and Mg from 150-mg and 1300-mg mica samples treated with the matrix solution (1.0 M KOAc-0.1 M K$_2$EDTA) for 12 days in a flow-through reactor cell at 80°C [micas had received no pretreatment or had been treated for 36 days under similar conditions with either the matrix or the H$_2$O$_2$ (25% H$_2$O$_2$ + matrix) solutions before these dissolution data were obtained.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>$10^{-4}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>None$^a$</td>
</tr>
<tr>
<td>Phlogopite</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>4.6</td>
</tr>
<tr>
<td>Mg</td>
<td>5.3</td>
</tr>
<tr>
<td>Mean</td>
<td>4.9</td>
</tr>
<tr>
<td>Biotite</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>7.7</td>
</tr>
<tr>
<td>Mg</td>
<td>7.2</td>
</tr>
<tr>
<td>Mean</td>
<td>7.4</td>
</tr>
<tr>
<td>Siderophyllite</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>2.8</td>
</tr>
</tbody>
</table>

$^a$150-mg samples from "reference state" experiment.

$^b$1300-mg samples from "main" experiment.
sharp edges and ultrafine particles during the 36-day matrix
pretreatment. The H₂O₂-pretreated sample, on the other hand yielded a
much larger rate constant than either the untreated or the
matrix-pretreated samples. Interpreting these differences purely in
terms of total surface area, it is clear that the H₂O₂-pretreated sample
had several times the total surface area of the untreated and
matrix-pretreated samples. The siderophyllite rate constant data showed
the same trends with regard to pretreatments as the biotite data, but
the differences were much smaller and suggestive of a more moderate
increase in surface area as a result of H₂O₂ treatment.

A comparison of the k_{app} values for the 150-mg and 1300-mg
untreated samples shows some effect of sample size (Table IV-3). The
lower k_{app} values in the 1300-mg samples could be a result of unequal
access to the mica particles by the dissolving solution. If so, the
situation could be avoided by using a fluidized-bed reactor similar to
that described by Wollast and Chou (1985). Alternatively, the different
rate constants may show that the flow rate was too slow to maintain the
same concentration of active dissolving agent (i.e., free EDTA⁻² and
OAc⁻) in the two studies. In either event, the k_{app} differences
observed for the untreated samples are small enough (considering the
8-fold difference in sample size) to be of little concern.

Comparisons of the k_{app} values obtained in the "reference state"
experiment and the "main" experiment allow estimates of S_{total} and γ_s
to be made for the micas treated by the H₂O₂ solution relative to the
micas treated by the matrix solution. Since γ_s = 1 for the "reference
state" data, the total surface area for the $\text{H}_2\text{O}_2$-pretreated micas $[S_{\text{total}}(H)]$ relative to that for the matrix-pretreated micas $[S_{\text{total}}(M)]$ is simply the ratio of the $k_{\text{app}}$ values obtained for these micas in the "reference state" experiment. The effective surface areas of the micas in the $\text{H}_2\text{O}_2$ solution $[S_{\text{eff}}(H)]$ relative to the matrix solution $[S_{\text{eff}}(M)]$ are given by the ratio of the $k_{\text{app}}$ values for these two solutions that were obtained in the "main" experiment. Lastly, estimates of $\gamma_s$ for samples treated by the $\text{H}_2\text{O}_2$ solutions can be made from the ratio of the $S_{\text{eff}}(H)$ values to the $S_{\text{total}}(H)$ values. That is,

$$\gamma_{s(H)} = \frac{[S_{\text{eff}}(H)]/[S_{\text{eff}}(M)]}{[S_{\text{total}}(H)]/[S_{\text{total}}(M)]} \quad [IV-6]$$

These estimates of $S_{\text{total}}$, $S_{\text{eff}}$, and $\gamma_s$ for the Al and Mg dissolution of the $\text{H}_2\text{O}_2$-treated micas relative to the matrix-treated micas are shown in Table IV-4.

Looking at the surface parameter estimates for the phlogopite, it is clear that no exfoliation occurred during $\text{H}_2\text{O}_2$ treatment since the ratio of total surface area of the mica in the $\text{H}_2\text{O}_2$ solution to that in the matrix solution is 1.0 (Table IV-4). Treatment with $\text{H}_2\text{O}_2$, however, did result in a blockage of roughly 60% of the surface sites by the competitive adsorption of $\text{O}_2$ or $\text{H}_2\text{O}_2$, thus leaving only 40% of the original surface area available for dissolution.

In contrast, the surface parameter estimates for the biotite suggest that the total surface area of the biotite after 36 days of $\text{H}_2\text{O}_2$
TABLE IV-4. Estimates of the total surface area ($S_{total}$), the total surface area complexed by strong complexers ($S_{eff}$), and the fraction of the total surface area complexed by strong complexers ($\gamma_s$) for mica samples treated with the $H_2O_2$ (25% $H_2O_2$ + matrix) solution expressed relative to samples treated with the matrix (1.0 M KOAc-0.1 M K$_2$EDTA) solution, where the subscripts H and M refer to the $H_2O_2$ and matrix treatments, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{total}(H)$</th>
<th>$S_{eff}(H)$</th>
<th>$S_{eff}(M)$</th>
<th>$\gamma_s(H)$</th>
<th>$\gamma_s(M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phlogopite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.9</td>
<td>0.4</td>
<td></td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1.0</td>
<td>0.3</td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.0</td>
<td>0.4</td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>5.7</td>
<td>1.1</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>6.6</td>
<td>1.0</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>6.1</td>
<td>1.0</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Siderophyllite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.3</td>
<td>0.5</td>
<td></td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>
treatment was more than 6 times that in the matrix treatment (Table IV-4). This difference is presumably due to large-scale exfoliation by the H$_2$O$_2$ treatment. The actively-dissolving fraction [$\gamma_S(H)$] was only about 20% of the surface available, which is much lower than for the phlogopite. This result may have been caused by the higher rate of H$_2$O$_2$ decomposition that occurred in the biotite treatment relative to the other two micas (Figure IV-2) and, consequently, produced more O$_2$ to compete with the strong complexing agents for adsorption to the mica surface sites. The net effect of these two processes (exfoliation and competitive adsorption by H$_2$O$_2$ and O$_2$) was to cancel each other out and yield essentially identical dissolution rates in the matrix and H$_2$O$_2$ treatments for the biotite.

The siderophyllite sample also showed some evidence for exfoliation in the H$_2$O$_2$ treatment, but on a much smaller scale than for the biotite (Table IV-4). The actively-dissolving fraction [$\gamma_S(H)$] was about the same as that for the phlogopite (40%), a result also supported by the similarities in their H$_2$O$_2$ effluent concentration data (Figure IV-2).

The kinetic analysis of the dissolution data, therefore, seems to provide clear evidence for considerable exfoliation in the biotite and minor amounts of exfoliation in the siderophyllite samples and confirms that no exfoliation occurred in the phlogopite sample. It also provides strong evidence for a screening effect of the H$_2$O$_2$ solutions at the surfaces of the mica that results in lower rates of dissolution. This screening is probably caused by the competition of H$_2$O$_2$ and O$_2$ with OAc$^-$ and EDTA$^{2-}$ for adsorption sites at the mica surface.
The kinetic data also show a good correlation between the extent of exfoliation and the extent of Fe oxidation by the \( \text{H}_2\text{O}_2 \) treatments. In the biotite, for example, a 7-fold increase in Fe(III) content as a result of \( \text{H}_2\text{O}_2 \) treatment is accompanied by a 6-fold increase in total surface area, whereas the phlogopite exhibited no exfoliation or oxidation. Because the phlogopite contained very little Fe(II), little or no oxidation was expected. And since the K-selectivity of the phlogopite and biotite are similar (Chapter VI), their tendency to exfoliate would also be similar. The absence of exfoliation in the phlogopite, therefore, suggests that oxidation of structural Fe is required before exfoliation can occur in 1 M K solutions.

On the other hand, the failure of the siderophyllite to oxidize (or exfoliate) to any great extent requires a different explanation. One possible explanation involves the higher K-selectivity of this mica relative to the biotite and phlogopite (Chapter VI). For Fe oxidation to occur, a charge-balancing reaction must also occur. With the possible exception of deprotonation of structural hydroxyls, the charge-balancing reactions involve an expansion of the interlayer region to allow ejection of interlayer or octahedral cations to the bulk solution. Micas with a high selectivity for K would be less prone to to expansion and, therefore, would participate less readily in the charge-balancing reactions that involve cation ejection. The net result of a high K selectivity would be to limit the occurrence of charge-balancing reactions and thereby raise the effective redox potential for the oxidation of structural Fe. Thus, differences in the
K-selectivity of the siderophyllite and biotite micas could well be responsible for the different oxidation, exfoliation, and dissolution behavior that they exhibited in this study.

Conclusions

The degree of oxidation of structural Fe in trioctahedral micas by aqueous 25% \( \text{H}_2\text{O}_2 \)-1 M K solutions is only slightly greater than the degree of exfoliation exhibited by these micas. This result implies that extensive oxidation via internal electron and proton transfer mechanisms is absent. Oxidation does seem to be required for exfoliation to occur under the conditions studied, and thus must precede exfoliation to some extent. During the oxidation process, the excess charge created is balanced in the mica structure by the ejection of octahedral cations. Of these, the trivalent cations (Fe and Al) are ejected preferentially to the divalent cations (Mg). Because of the interdependence of oxidation and exfoliation, the K-selectivity of the mica is believed to play a role in determining the extent to which both occur.

The rate at which a mica dissolves is controlled by the inherent stability of the mica, by the amount of exfoliation that occurs, and by the fraction of the total surface area that is accessible to the dissolving agents. The oxidation of structural Fe by \( \text{H}_2\text{O}_2 \) solutions, therefore, increases the rate of mica dissolution by causing exfoliation, but this increase may be tempered by the adsorption of \( \text{H}_2\text{O}_2 \).
and $O_2$ molecules at the mica surface thereby decreasing the amount of mica surface that is accessible to the dissolving agents in the solution.
CHAPTER V. OXIDATIVE WEATHERING OF TRIOCTAHEDRAL MICAS
BY BUFFERED $\text{H}_2\text{O}_2$ SOLUTIONS—2. STRUCTURAL ALTERATIONS

Introduction

When micas weather, structural alterations occur along with the changes in redox state and composition that were described in Chapter IV. The nature of these structural changes may be revealed by direct measurements of the locations and the electronic energy levels of the various atoms in the mica and its weathering products. For example, the nature of the bond energies and types of structural units present in the sample can be observed with infrared spectroscopic techniques. The locations of atoms in the mica structure and evidence for the formation of weathering products can be obtained by x-ray diffraction techniques. And, specific information about the oxidation state, coordination, and electronic environment of Fe atoms can be obtained by Mössbauer spectroscopy. Each of these techniques and their applications to the study of mica weathering processes are discussed in the paragraphs that follow.

The $^{57}\text{Fe}$ Mössbauer effect, which is essentially the recoil-free absorption of gamma rays by the $^{57}\text{Fe}$ nucleus, has been used by many investigators to follow changes in the oxidation state and bonding environment of structural Fe when micas are exposed to various weathering regimes. Two parameters, the isomer shift and the quadrupole
splitting, describe the Mössbauer spectra obtained at room temperature (the magnetic ordering temperature for micas is well below 298 K so no magnetic hyperfine splittings are observed). The isomer shift, which is proportional to the charge density of electrons at the $^{57}$Fe nucleus, provides information about the Fe oxidation state, the coordination number, and the ionic character of the Fe-ligand bonds. It is possible, therefore, to distinguish high-spin Fe from low-spin Fe, Fe in the octahedral sheet from that in the tetrahedral sheet, and Fe(II) from Fe(III) in the mica by determining the isomer shift. As a result of an asymmetric charge distribution around the $^{57}$Fe nucleus when it is in the excited state, the energy levels for this state are split and absorption of gamma rays at two different energies is allowed. The Mössbauer spectrum, therefore, consists of two peaks (a symmetric doublet) for each isomer shift. The difference in energy between the two peaks is termed the quadrupole splitting and its size depends on the amount of distortion from ideal symmetry that is present in the d-orbital arrangement at the $^{57}$Fe nucleus. Thus, for a given electron spin configuration [e.g., high-spin Fe(II)], the quadrupole splitting values contain information about the anion cage coordinating the Fe and the charge distribution in the adjacent cation sites because the charges on these atoms affect the electric field at the Fe nucleus. Both isomer shift and quadrupole splitting are measures of electronic energy levels and are reported in units of mm s$^{-1}$ (1 mm s$^{-1}$ = 4.80 x 10$^{-8}$ eV), the Doppler scanning velocity at which they are observed. More introductory information about the Mössbauer effect is provided by Greenwood and Gibb

A survey of the Mössbauer parameters reported for unweathered natural micas shows that the isomer shift values for octahedrally-coordinated Fe in di- and tri-octahedral micas are remarkably constant (Table V-1). The quadrupole splittings for Fe(II), however, display a trend towards higher values in going from the biotites to the lithionites and muscovites. Evidently, this trend is a result of an increase in the asymmetry of the electric field at the $^{57}$Fe nucleus when Li or vacancies are present in neighboring sites. One would expect to see a similar trend, but opposite in direction, for the Fe(III) quadrupole splitting. The poor precision of the Fe(III) data, however, obscures this trend, if it exists at all.

Attempts have been made to assign Fe atoms between the cis and trans sites in the octahedral sheet, with some apparent success (Annersten, 1974; Goodman and Wilson, 1973), and to follow the site occupancies as the mica weathers to see if oxidation of Fe occurs preferentially at one site or the other (Goodman and Wilson, 1973). Theoretical calculations of the electric field gradients arising from various anionic and cationic site occupancies (Goodman, 1976, 1980; Mineeva, 1978), however, show that several structural arrangements can produce the broad non-Lorentzian peaks that were the original impetus for site assignment work. Indeed, Mineeva (1978) suggested that a large
TABLE V-1. Statistical summary of Mössbauer spectral parameters (298 K) reported for octahedral Fe in natural biotites, lithionites, and muscovites

<table>
<thead>
<tr>
<th>Mica Group</th>
<th>Fe(II)</th>
<th>Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isomer Shift</td>
<td>Quadrupole Splitting</td>
</tr>
<tr>
<td>Biotite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.09</td>
<td>2.44</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>(0.03)</td>
<td>(0.06)</td>
</tr>
<tr>
<td>Range</td>
<td>1.04-1.15</td>
<td>2.31-2.54</td>
</tr>
<tr>
<td>Number of Spectra</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>Lithionite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.13</td>
<td>2.60</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>(0.03)</td>
<td>(0.08)</td>
</tr>
<tr>
<td>Range</td>
<td>1.08-1.16</td>
<td>2.45-2.72</td>
</tr>
<tr>
<td>Number of Spectra</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Muscovite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.13</td>
<td>2.86</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>(0.02)</td>
<td>(0.02)</td>
</tr>
<tr>
<td>Range</td>
<td>1.09-1.15</td>
<td>2.83-2.89</td>
</tr>
<tr>
<td>Number of Spectra</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>


b Data from studies in which two overlapping doublets were fit to an oxidation state (e.g., M1 and M2 site occupancy data) were converted to data for one equivalent doublet by calculating the centroid for each pair of overlapping peaks in the spectrum.

c Relative to metallic Fe (Preston et al., 1962).
number of slightly different charge symmetries probably exists at cation
sites in biotites and gives rise to a distribution of closely
superimposed Lorentzian doublets. If true, such a situation would make
futile any attempt to determine the precise occupancies of cis and
trans sites.

Most of the Mössbauer studies of mica weathering have involved the
oxidation of micas by thermal treatments (Pollak et al., 1962; Hogg and
Meads, 1975; Tricker and Winterbottom, 1976; Ouseph and Groskreutz,
1977; Gendler et al., 1978; Tripathi et al., 1978; Chandra and
Lokanathan, 1982; Ferrow and Annersten, 1984), and have shown drastic
changes in the values for isomer shifts and quadrupole splittings with
Fe oxidation. These changes are associated with charge-balancing
reactions such as deprotonation and dehydroxylation that may not occur
in aqueous systems. Several studies have looked at the aqueous
weathering (Rice and Williams, 1969; Yassoglou et al., 1972; Goodman and
Wilson, 1973) and K-depletion (Bowen et al., 1969) of micas at ambient
temperatures. In contrast to the thermal studies, however, little
change in either isomer shift or quadrupole splitting has been observed
when biotites weather in aqueous solution.

The Mössbauer data in the literature, thus, suggest that no major
changes in the structural environment of Fe in the mica occur as a
result of aqueous weathering, other than the obvious oxidation of Fe(II)
to Fe(III). Cation ejection is one major change associated with aqueous
weathering, but is difficult to identify by Mössbauer spectroscopy
because it seems to occur simultaneously with Fe oxidation and cannot be
isolated. The Mössbauer method seems best suited, therefore, to distinguishing between octahedrally and tetrahedrally-coordinated Fe, to monitoring the Fe(II)/Fe(III) ratios in the octahedral sheet and to providing qualitative evidence for the presence or absence of other phases (e.g., various Fe oxides) that might form as a result of oxidative weathering by aqueous solutions. In the absence of corollary data, more detailed interpretations seem speculative.

Previous x-ray diffraction studies of fresh and weathered micas have shown little, if any, change in the 00\(\alpha\) d-spacings as a result of weathering (Walker, 1949; Rimsaite, 1967a) so long as extensive K exchange does not occur. The relative intensities of the 004 and 005 reflections, however, are sensitive to the cation occupancy of the octahedral and tetrahedral sheets (Brown, 1955; Franzini and Schiaffino, 1963; Gower, 1957; Rimsaite, 1967b; Chapter III, this work), and thus can be used to measure the extent of cation ejection during weathering. In the only known application of this technique to mica weathering, Rimsaite (1967a) presented data for two pairs of biotite flakes (each pair consisting of one fresh and one naturally weathered flake from the same location) that showed a decrease of about 40% in the 004/005 intensity ratio with oxidative weathering. The octahedral cation occupancy can also be estimated from the OkO d-spacings (Rimsaite, 1967a; Farmer et al., 1971; Gilkes et al., 1972b; Ross and Rich, 1974; Sayin et al., 1979). The sensitivity of this commonly used method, however, seems to be much less than for the 004/005 intensity ratio method. Indeed, for the same two pairs of micas discussed above,
Rimsaite (1967a) observed only a 0.3% decrease in the 010 d-spacing as a result of weathering.

Infrared spectroscopy has been used by several investigators of mica weathering (Juo and White, 1969; Farmer et al., 1971; Gilkes et al., 1972b) chiefly because of the information it can provide about the octahedral cations that are coordinated to hydroxyl groups in the mica structure. A suite of absorption bands in the hydroxyl stretching region has been identified and the individual bands assigned to various combinations of cations and vacancies in the octahedral sheet (Vedder and Wilkins, 1969; Farmer et al., 1967, 1971). For example, it is possible to distinguish between hydroxyls coordinated by 2 trivalent cations and a vacancy (dioctahedral configuration) and those coordinated by 3 divalent cations (trioctahedral configuration). Highly resolved spectra can also distinguish among the various types of cations involved [e.g., 3 Mg ions, 2 Mg and 1 Fe(II), 1 Mg and 2 Fe(II), and 3 Fe(II)] in a given configuration. The changes in the absorption intensities of the hydroxyl stretching bands as a result of weathering, therefore, can provide evidence for Fe oxidation, for cation ejection (i.e., the creation of vacancies in the octahedral sheet), and for deprotonation of structural hydroxyls. Several studies, in which biotites or vermiculitized biotites have been oxidized by aqueous solutions (Farmer et al., 1971; Gilkes et al., 1972b; Juo and White, 1969), have shown an increase in the intensity of the dioctahedral hydroxyl stretching bands at the expense of the trioctahedral bands. This change is consistent with the creation of vacancies in the octahedral sheet from octahedral
cation ejection. On the other hand, conclusive evidence for the deprotonation of structural hydroxyls has not been presented, except for micas oxidized by thermal treatments at temperatures above 400°C (Scott and Amonette, 1987).

In this chapter, then, the nature of the structural alterations that occurred during the weathering of three micas by the matrix and H₂O₂ solutions described in Chapter IV is investigated by these Mössbauer, x-ray diffraction, and infrared techniques.

Experimental

Micas

Fresh and weathered samples of a phlogopite, biotite and siderophyllite were analyzed. The sources, preliminary treatments, and structural formulas of the fresh micas are described in Chapter IV. The weathered micas were samples of fresh mica that had been treated for periods of up to 36 days by flowing solutions of 1 M KOAc-0.1 M K₂EDTA (matrix) or 25% H₂O₂-1 M KOAc-0.1 M K₂EDTA (H₂O₂) at 80°C. The apparatus and procedure used to prepare these weathered samples were those of the "main" experiment described in Chapter IV.

Mössbauer analyses

Mössbauer spectra were collected with a Ranger Scientific MS-700 constant-acceleration spectrometer operating in sawtooth mode and were stored by a 1024-channel analyzer attached to an Apple IIe.
microcomputer. A $^{57}$Co/Pd source (about 2 mCi strength) was used and the gamma radiation that was transmitted through the sample measured by a scintillation detector. The velocity of the source was calibrated using the data of Preston et al. (1962) for a metallic Fe absorber at room temperature.

The absorbers contained 5-10 mg Fe cm$^{-2}$, and were prepared by diluting the appropriate quantity of mica in finely powdered sucrose. Sample holders consisted of a brass washer (18-mm inside diameter, 2.25 mm thick) with a 0.002-mil Mylar window glued on one face. After the absorber mixture was put in the sample holder, a larger piece of Mylar was placed over the open face and held by another brass washer that slipped around the circumference of the sample holder.

The spectra were fit to doublets having Lorentzian line shapes using a least squares code (MOSFIT4) obtained from P. R. Lear and J. W. Stucki of the University of Illinois at Urbana. Goodness of fit was measured by calculating a normalized $\chi^2$ value (for 1000 degrees of freedom at the 95% confidence level the normalized $\chi^2$ is 1.08).

Spectra were collected with the absorber at room temperature (298 K) or, in some instances, at nominal liquid nitrogen temperature (77 K). In the latter instance, the sample holder was mounted on a "cold finger" extending from a reservoir of liquid nitrogen into an evacuated cylinder equipped with Kapton windows. Room temperature spectra were collected for the fresh biotite and for biotite that had been treated by the $\text{H}_2\text{O}_2$ solution for 1, 2, 4, 6, or 12 days. Spectra at 77 K were collected for the fresh biotite and siderophyllite micas and for the same micas after
36 days of $H_2O_2$ treatment. The Fe content of the phlogopite mica was found to be too low for an adequate spectrum to be obtained.

**X-ray diffraction analyses**

The ratio of the observed structure factors for the 004 and 005 reflections of the fresh and weathered micas was measured by the technique described in Chapter III. This analysis was performed in triplicate on the fresh micas, and in duplicate on micas that had been treated for 36 days by either the matrix or $H_2O_2$ solutions. In addition, a single analysis was performed on the biotite samples that had been weathered for 1, 2, 4, 6, or 12 days by the $H_2O_2$ solution.

**Infrared spectroscopic analyses**

Infrared spectra for the hydroxyl stretching bands (4000-3200 cm$^{-1}$) and for the librational bands (1200-250 cm$^{-1}$) were collected using a Beckman IR-20A dispersive spectrophotometer equipped with a Nernst glower source and a thermocouple detector. To minimize the Christiansen filter effect of the 10- to 20-um diameter mica particles (Price and Tetlow, 1948), the hydroxyl stretching spectra were obtained in single-beam mode by attenuated total reflectance (ATR) of a mica-Nujol mull on a trapezoidal KRS-5 crystal. The longer wavelength spectra were obtained in ordinary double-beam transmission mode using double stick tape to present the mica to the infrared beam. A scanning rate of 60 cm$^{-1}$ min$^{-1}$ was used in most instances. Samples of fresh mica and mica that had been treated for 36 days with the $H_2O_2$ solution were analyzed.
For the siderophyllite, a sample treated for 36 days in the matrix solution was also analyzed.

Results and Discussion

Mössbauer spectra

The Mössbauer spectra (77 K) for fresh biotite and for biotite that had been treated for 36-days by the $\text{H}_2\text{O}_2$ weathering solution are shown in Figure V-1 and the parameters for the fit to the observed data are given in Table V-2. The spectrum for the untreated biotite consists of an asymmetric Fe(II) doublet centered at about 1.22 mm s$^{-1}$ (isomer shift) and with peaks about 2.48 mm s$^{-1}$ apart (quadrupole splitting). As would be expected from second-order Doppler shift and zero-point motion effects (Greenwood and Gibb, 1971, p. 50-53), these Mössbauer parameters at 77 K are somewhat higher than the mean values reported for Fe(II) in biotites at room temperature (Table V-1). The anisotropy in the peak intensities is probably a result of non-random orientation of mica particles in the absorber (Högström et al., 1969a; Annersten, 1974).

The spectrum for the $\text{H}_2\text{O}_2$-treated biotite shows the Fe(II) doublet, the emergence of an Fe(III) peak at about 0.93 mm s$^{-1}$, and a second peak overlapping the Fe(II) peak near 0 mm s$^{-1}$. Thus, two doublets were fit to this spectrum. The Fe(III) doublet had an isomer shift of 0.56 mm s$^{-1}$ and a quadrupole splitting of 0.85 mm s$^{-1}$, whereas the parameters for Fe(II) were 1.17 and 2.58 mm s$^{-1}$, respectively. The ratio of the
FIGURE V-1. Mössbauer spectra recorded at nominal liquid nitrogen temperature (77 K) for samples of untreated biotite or biotite that was treated with the H$_2$O$_2$ weathering solution for 36 days.
TABLE V-2. Parameters for Mössbauer spectra of biotite and siderophyllite samples recorded at nominal liquid nitrogen temperature (77 K) before and after treatment with H₂O₂ solutions for 36 days

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isomer Shift</th>
<th>Quadrupole Splitting</th>
<th>Peak Width</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mm s⁻¹</td>
<td>mm s⁻¹</td>
<td>mm s⁻¹</td>
<td>mm s⁻¹</td>
</tr>
<tr>
<td><strong>Fe(II)ᵃ</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Biotite (77 K)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>1.22 (0.00)</td>
<td>2.48 (0.00)</td>
<td>0.27 (0.00)</td>
<td>1.73 (0.00)</td>
</tr>
<tr>
<td></td>
<td>0.32 (0.00)</td>
<td></td>
<td>(0.00)</td>
<td>(0.00)</td>
</tr>
<tr>
<td>36 Days</td>
<td>1.17 (0.02)</td>
<td>2.58 (0.01)</td>
<td>0.24 (0.00)</td>
<td>0.72 (0.03)</td>
</tr>
<tr>
<td></td>
<td>0.27 (0.01)</td>
<td></td>
<td>(0.03)</td>
<td>(0.03)</td>
</tr>
<tr>
<td><strong>Siderophyllite (77 K)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>1.24 (0.00)</td>
<td>2.55 (0.00)</td>
<td>0.24 (0.00)</td>
<td>1.72 (0.00)</td>
</tr>
<tr>
<td></td>
<td>0.29 (0.00)</td>
<td></td>
<td>(0.00)</td>
<td>(0.00)</td>
</tr>
<tr>
<td>36 Days</td>
<td>1.22 (0.00)</td>
<td>2.43 (0.00)</td>
<td>0.24 (0.00)</td>
<td>2.02 (0.00)</td>
</tr>
<tr>
<td></td>
<td>0.29 (0.00)</td>
<td></td>
<td>(0.00)</td>
<td>(0.00)</td>
</tr>
</tbody>
</table>

ᵃStandard deviation for each parameter is enclosed in parentheses.
ᵇTotal absorption area in counts x 10⁷.
<table>
<thead>
<tr>
<th>Isomer Shift</th>
<th>Quadrupole Splitting</th>
<th>Peak Width</th>
<th>Peak Area</th>
<th>$\chi^2$</th>
<th>Fe(III)/Fe(TOT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(nij) s $^{-1}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>3.52</td>
<td>--</td>
</tr>
<tr>
<td>0.56 (0.03)</td>
<td>0.85 (0.02)</td>
<td>0.33 (0.01)</td>
<td>0.64 (0.04)</td>
<td>1.90</td>
<td>47.1 (2.5)</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.69</td>
<td>--</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.46</td>
<td>--</td>
</tr>
</tbody>
</table>
areas of the Fe(II) and Fe(III) doublets suggests that 47.1% of the Fe in the biotite is Fe(III) which compares favorably to the 49.0% measured by the method of Chapter II.

The spectra for the siderophyllite mica before and after H$_2$O$_2$ treatment are shown in Figure V-2. As expected from the very low Fe(III) content of this mica originally (< 2%) and from the lack of substantial oxidation during treatment, the spectra consist of an asymmetric Fe(II) doublet and appear to be identical. Slight decreases in the quadrupole splitting (2.55 to 2.43 mm s$^{-1}$) and in the isomer shift (1.24 to 1.22 mm s$^{-1}$) were observed with the H$_2$O$_2$ treatment, but these may reflect the small error caused by including the Fe(III) data in the Fe(II) peaks during the fitting procedure (Table V-2).

The absence of magnetic hyperfine splittings in the biotite and siderophyllite spectra at 77 K suggests that no Fe oxide phases (with the possible exception of lepidocrocite and ferrihydrite) were present in the untreated micas and that none formed during the H$_2$O$_2$ treatment. As discussed by Murad (1988), however, the lack of a magnetic hyperfine field may also be due to poor crystallinity or to the substitution of Al for Fe in the Fe oxide structure. If non-magnetically ordered oxide phases were present, they would be expected to show isomer shifts and quadrupole splittings in the same region as mica structural Fe(III). The net result would be some line broadening and an increase in the uncertainty associated with the Fe(III) Mössbauer parameters for the mica [indeed, oxide impurities could explain the large variability in Fe(III) quadrupole splittings reported for biotites in Table V-1]. The
FIGURE V-2. Mössbauer spectra recorded at nominal liquid nitrogen temperature (77 K) for samples of untreated siderophyllite or siderophyllite that was treated with the $\text{H}_2\text{O}_2$ weathering solution for 36 days.
conclusion to be drawn, therefore, is that no definitive evidence for
the presence or absence of Fe oxide minerals exists in these Mössbauer
spectra.

Several Mössbauer spectra were collected at room temperature
for the untreated biotite and for the biotite after treatment with H₂O₂
for periods of up to 12 days. The raw spectra are shown in Figure V-3,
and the Mössbauer parameters from the fitted spectra are given in Table
V-3. In general, the raw spectra show the expected development of the
Fe(III) doublet centered near 0.5 mm s⁻¹ as the length of treatment
increases. The values of the Fe(II) isomer shift and quadrupole
splitting for the untreated biotite are at the extremes of the ranges
given in Table V-1, but with H₂O₂ treatment [and increasing Fe(III)
content] these values come very close to the means of the published
values for the biotite group. This trend, however, may be an artifact
of the fitting procedure, since only a Fe(II) doublet could be fit to
the untreated and 1-day spectra. Another indication that the fit may be
in error for the untreated, 1- and 2-day spectra is the higher x² values
obtained for these spectra as compared to the 4-, 6-, and 12-day
spectra. The fraction of Fe as Fe(III) predicted from the spectra
compares fairly well with the chemically determined Fe(III) data
reported in Chapter IV (10.1, 23.2, 41.9, 45.4, and 46.4% for the 1-,
2-, 4-, 6-, and 12-day treatments, respectively), but the precision is
considerably less. At low Fe(III) levels, however, the sensitivity of
the Mössbauer spectra to Fe(III) is very poor and the chemical results
are clearly better.
FIGURE V-3. Mössbauer spectra recorded at room temperature (298 K) for samples of untreated biotite or biotite that was treated for 1, 2, 4, 6, or 12 days with the H$_2$O$_2$ weathering solution.
TABLE V-3. Parameters for Mössbauer spectra of biotite samples recorded at room temperature (298 K) before and after treatment with H$_2$O$_2$ solutions for various periods

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isomer Shift</th>
<th>Quadrupole Split</th>
<th>Peak Width</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe(II)$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biotite (RT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>0.90 (0.00)</td>
<td>2.14 (0.00)</td>
<td>0.24 (0.00)</td>
<td>1.79 (0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.29 (0.00)</td>
<td></td>
</tr>
<tr>
<td>1 Day</td>
<td>0.91 (0.00)</td>
<td>2.15 (0.00)</td>
<td>0.24 (0.00)</td>
<td>1.86 (0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.29 (0.00)</td>
<td></td>
</tr>
<tr>
<td>2 Days</td>
<td>0.88 (0.01)</td>
<td>2.18 (0.01)</td>
<td>0.23 (0.00)</td>
<td>1.79 (0.03)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.25 (0.00)</td>
<td></td>
</tr>
<tr>
<td>4 Days</td>
<td>0.85 (0.01)</td>
<td>2.23 (0.01)</td>
<td>0.22 (0.00)</td>
<td>1.26 (0.05)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.24 (0.01)</td>
<td></td>
</tr>
<tr>
<td>6 Days</td>
<td>0.84 (0.01)</td>
<td>2.25 (0.01)</td>
<td>0.21 (0.00)</td>
<td>0.84 (0.04)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.21 (0.01)</td>
<td></td>
</tr>
<tr>
<td>12 Days</td>
<td>0.84 (0.02)</td>
<td>2.26 (0.02)</td>
<td>0.22 (0.00)</td>
<td>1.02 (0.06)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.23 (0.01)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Standard deviation for each parameter is enclosed in parentheses.

$^b$Total absorption area in counts x 10$^7$. 
<table>
<thead>
<tr>
<th>Isomer Shift</th>
<th>Quadrupole Split</th>
<th>Peak Width</th>
<th>Peak Area</th>
<th>$\chi^2$</th>
<th>Fe(III)/Fe(TOT)</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.69</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>3.89</td>
<td>--</td>
</tr>
<tr>
<td>0.39</td>
<td>0.63</td>
<td>0.22</td>
<td>0.35</td>
<td>3.59</td>
<td>16.4 (1.7)</td>
</tr>
<tr>
<td>0.34</td>
<td>0.72</td>
<td>0.29</td>
<td>0.95</td>
<td>2.77</td>
<td>43.0 (2.6)</td>
</tr>
<tr>
<td>0.32</td>
<td>0.73</td>
<td>0.28</td>
<td>0.74</td>
<td>2.29</td>
<td>46.8 (2.6)</td>
</tr>
<tr>
<td>0.31</td>
<td>0.75</td>
<td>0.28</td>
<td>0.92</td>
<td>2.45</td>
<td>47.4 (3.3)</td>
</tr>
</tbody>
</table>
X-ray diffraction analyses

X-ray diffractograms for the 004 and 005 reflections of the untreated micas, and of the micas after treatment for 36 days by the matrix and \( \text{H}_2\text{O}_2 \) solutions are shown in Figures V-4, V-5, and V-6. The x-ray patterns for the phlogopite are characterized by the rather small intensity of the 004 reflection relative to that for the 005 reflection and are essentially identical for the treated and untreated samples (Figure V-4). The high degree of crystallinity of these samples is shown by the well-resolved \( K_a^1 - K_a^2 \) doublets at each reflection and the maintenance of this high resolution in the treated samples suggests that no major structural changes occur as a result of treatment. This finding is consistent with the conclusions drawn from the chemical and kinetic data presented in Chapter IV.

The diffraction traces for the biotite are shown in Figure V-5 and include traces for samples treated for 2, 4, and 6 days with the \( \text{H}_2\text{O}_2 \) solution in addition to the untreated and 36-day treated samples. In contrast to the phlogopite patterns, the 004 and 005 peak heights for the biotite are roughly equal. For the untreated and matrix treated samples, the 004 peak height is slightly greater than the 005 and the \( K_a^1 - K_a^2 \) doublet is well resolved. For the \( \text{H}_2\text{O}_2 \)-treated samples, however, the resolution of the \( K_a^1 - K_a^2 \) doublet becomes blurred and the intensity of the 005 peak increases relative to that of the 004 as treatment progresses. The loss of the \( K_a \) doublet resolution (i.e., peak broadening) with \( \text{H}_2\text{O}_2 \) treatment is evidence for thinner crystallites and
FIGURE V-4. X-ray diffractograms ($\text{Mo}_{\text{K}\alpha}$ radiation) of untreated phlogopite (U), and of phlogopite that was treated for 36 days with the matrix (M36) or $\text{H}_2\text{O}_2$ (H36) weathering solutions.
FIGURE V-5. X-ray diffractograms (Mo$_{K\alpha}$ radiation) of untreated biotite (U), of biotite that was treated for 36 days with the matrix weathering solution (M36), and of biotite that was treated for 2, 4, 6, or 36 days with the H$_2$O$_2$ weathering solution (H2, H4, H6, H36)
BIOTITE

U
M36
H2
H4
H6
H36

DEGREES TWO-THETA
FIGURE V-6. X-ray diffractograms (Mo$_{K\alpha}$ radiation) of untreated siderophyllite (U), and of siderophyllite that was treated for 36 days with the matrix (M36) or H$_2$O$_2$ (H36) weathering solutions.
a more disordered sample. Exfoliation of the mica during the \( \text{H}_2\text{O}_2 \) treatment, which would decrease the thickness of the crystallites, could be a cause of the peak broadening. The increase in the 005 peak height relative to the 004 is evidence for a decrease in the electron density of the octahedral sheet (Chapter III). This change in the diffraction pattern, therefore, suggests that a loss of octahedral cations occurred during the \( \text{H}_2\text{O}_2 \) treatment, probably to balance the charge created by oxidation. In fact, the cation ejection could be responsible for the exfoliation as well, since an expansion of the interlayer region would be required to eject the cations from the structure. Thus, cation ejection could contribute indirectly to the peak broadening that is observed. The diffraction data for the biotite, then, support the conclusions drawn from the chemical and kinetic data of Chapter IV, namely, that exfoliation and cation ejection occurred during the \( \text{H}_2\text{O}_2 \) treatment.

In Figure V-6, the diffraction traces for the siderophyllite samples are shown. As for the untreated phlogopite and biotite samples, the trace for the untreated siderophyllite sample shows a clearly resolved \( K_{α1}-K_{α2} \) doublet. And, because of the high Fe content of the siderophyllite (i.e., high electron density in the octahedral sheet), the intensity of the 004 reflection is much higher than for the 005 reflection. With the matrix treatment, the resolution of the \( K_{α1}-K_{α2} \) doublet seems to improve slightly. Otherwise, the matrix and \( \text{H}_2\text{O}_2 \) treatments produced little, if any, change in the diffraction pattern for the siderophyllite. These results are also consistent with the
conclusions reached in Chapter IV.

Using the method of Chapter III, the ratios of the observed structure factors for the 004 and 005 reflections were calculated (Table V-4). As expected from the results in Chapter III, the structure factor ratios in the untreated micas varied with the Fe content of the mica. A slight decrease in the phlogopite structure factor ratio was observed as a result of the matrix treatment, whereas increases in this ratio were observed when the biotite and siderophyllite received this treatment. These differences, although minor, probably reflect a leaching of tetrahedral cations from the basal surfaces of the micas by the matrix solution (Figure III-2), and serve to point out the sensitivity of the method to structural features near the mica surface.

With treatment by the H₂O₂ solution, all three micas yielded a sizeable decrease in the observed structure factor ratio (Table V-4). Since a decrease generally reflects a loss of electron density from the octahedral sheet, these data are good evidence for the ejection of octahedral cations to balance the charge from oxidation of structural Fe(II). This interpretation is supported by the fact that the greatest decrease in the structure factor ratio occurred in the biotite samples, which also exhibited the most oxidation. The extent of the structure factor ratio decrease for the biotite, however, seemed to slightly precede that of oxidation. That is, 20% of the decrease in the ratio occurred during the first day of treatment, whereas only 8% of the eventual increase in bulk Fe(III) occurred during that period. This observation is quite likely a result of the greater sensitivity of the
TABLE V-4. Observed x-ray diffraction structure factor ratios ($|F_{004}/005|$) for mica samples before and after treatment with matrix and $H_2O_2$ solutions for various time periods

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Phlogopite</th>
<th>Biotite</th>
<th>Siderophyllite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.436</td>
<td>0.736</td>
<td>0.919</td>
</tr>
<tr>
<td>Matrix</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36 days</td>
<td>0.426</td>
<td>0.746</td>
<td>0.960</td>
</tr>
<tr>
<td>$H_2O_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 day</td>
<td>--</td>
<td>0.709</td>
<td>--</td>
</tr>
<tr>
<td>2 days</td>
<td>--</td>
<td>0.650</td>
<td>--</td>
</tr>
<tr>
<td>4 days</td>
<td>--</td>
<td>0.625</td>
<td>--</td>
</tr>
<tr>
<td>6 days</td>
<td>--</td>
<td>0.601</td>
<td>--</td>
</tr>
<tr>
<td>12 days</td>
<td>--</td>
<td>0.600</td>
<td>--</td>
</tr>
<tr>
<td>36 days</td>
<td>0.404</td>
<td>0.600</td>
<td>0.875</td>
</tr>
</tbody>
</table>
x-ray diffraction method to changes near the mica surface than to changes in the bulk sample. The decrease in the structure factor ratio that was observed for the H$_2$O$_2$-treated phlogopite (where essentially no oxidation could be measured in the bulk sample) could also have been a result of this surface sensitivity.

The two-theta range scanned for the mica samples included angles where strong peaks for goethite, lepidocrocite, ferrihydrite and feroxyhite, and a moderate peak for hematite would be expected (Eggleton, 1988). None of the x-ray diffraction patterns, however, showed evidence for the presence of these crystalline Fe oxide phases. The existence of amorphous oxide phases on the external surfaces of the treated mica particles seems remote given the chemical environment to which the micas were subjected. Indeed, one of the selective dissolution techniques used to characterize the Fe oxide component of soils involves treatment with EDTA solutions (Borggaard, 1976; 1981). The paucity of evidence for these oxides leads to the conclusion that they are not present in any significant quantity.

**Infrared spectra**

The infrared spectra collected for the fresh micas and for micas after 36 days of weathering by the H$_2$O$_2$ solutions are shown in Figures V-7, V-8, and V-9. Spectra for the siderophyllite after treatment by the matrix solution for 36 days are also shown in Figure V-9 (similar spectra for the matrix-treated biotite and phlogopite samples were not collected). A reflectance technique was used to obtain the spectra for
FIGURE V-7. Infrared spectra of untreated phlogopite (U), and of phlogopite that was treated for 36 days with the H$_2$O$_2$ weathering solution (H36)
FIGURE V-8. Infrared spectra of untreated biotite (U), and of biotite that was treated for 36 days with the $\text{H}_2\text{O}_2$ weathering solution (H36)
FIGURE V-9. Infrared spectra of untreated siderophyllite (U), and of siderophyllite that was treated for 36 days with the matrix (M36) or \( \text{H}_2\text{O}_2 \) (H36) weathering solutions.
the hydroxyl stretching region (4000-3200 cm\(^{-1}\)). These spectra, therefore, are expected to be more sensitive to the features near the mica surface than spectra for the librational bands (1200-250 cm\(^{-1}\)), which were obtained by conventional transmission spectroscopy. Two scans, at medium- and high-gain settings on the spectrophotometer, were made of the hydroxyl stretching region for the fresh and \(\text{H}_2\text{O}_2\)-treated phlogopite samples. Only high-gain scans were made, however, of the hydroxyl stretching region for the biotite and siderophyllite samples. The width of the trace in the high-gain spectra is indicative of the random noise levels recorded when the spectra were collected. The band assignments are based on those reported by Vedder and Wilkins (1969), Farmer and Russell (1964), and Farmer et al. (1967, 1971).

The phlogopite samples exhibited strong hydroxyl stretching bands at 3705 cm\(^{-1}\) and 3660 cm\(^{-1}\) (Figure V-7). These bands are usually assigned to hydroxyls coordinated by three octahedral cations [Mg-Mg-Mg and Mg-Mg-R, respectively, where R is Fe(II), Al, or Ti] and thus are "trioctahedral" bands. There is some evidence for separate bands (i.e., shoulders on the 3660 cm\(^{-1}\) band) for each possible R cation, but the bands overlap to give the broad band and are weak relative to the 3705 cm\(^{-1}\) band. Treatment with the \(\text{H}_2\text{O}_2\) solution caused the development of two new bands in the phlogopite spectrum, a weak band at about 3550 cm\(^{-1}\) and another moderately strong band at 3450 cm\(^{-1}\). The first band is in the "dioctahedral" hydroxyl stretching region, meaning that one of the three octahedral cation sites associated with the hydroxyl is vacant. This band is also barely evident in the high-gain spectrum for the
untreated phlogopite, but seems to be more pronounced after H$_2$O$_2$ treatment. Thus, the H$_2$O$_2$ treatment seemed to have increased the dioctahedral character of the phlogopite very slightly. The band at 3450 cm$^{-1}$ is possibly the result of protonation of a basal oxygen to balance the charge loss from leaching of tetrahedral Al by the weathering solution. Further evidence for this assignment will be presented in spectra for the other micas.

The librational bands for phlogopite (Figure V-7) show strong vibrations associated with Si-0 at 1000 and 450 cm$^{-1}$, Al-0 at about 940, 770, 725 and 655 cm$^{-1}$, and Mg-0 at 815 and 590 cm$^{-1}$. There is some evidence for a shoulder at 710 cm$^{-1}$ that weakens with H$_2$O$_2$ treatment. Resolution of the Al-0 band at 940 cm$^{-1}$ with this treatment is clearly evident and may indicate distortion of the tetrahedral sheet as a result of octahedral and tetrahedral cation ejection. In general, however, the librational spectrum of the phlogopite is not changed by the H$_2$O$_2$ treatment and the structural alterations resulting from weathering seem to be minor.

The hydroxyl stretching spectrum for the untreated biotite (Figure V-8) includes a strong band at 3680 cm$^{-1}$ with some evidence for much weaker bands at 3695, 3660, and 3630 cm$^{-1}$. These four bands are in the "trioctahedral" region and can be assigned to hydroxyls associated with the Mg-Fe(II)-Fe(II), Mg-Mg-Fe(II), Fe(II)-Fe(II)-Fe(II), and Fe(II)-Fe(II)-R(III) octahedral cation groupings, respectively. In addition, two smaller bands at about 3540 cm$^{-1}$ and 3440 cm$^{-1}$ can be seen. The former of these is clearly the dioctahedral hydroxyl
stretching band associated with R(III)-R(III)-Vacancy in the octahedral sheet. The latter band is the same band that was observed in the phlogopite after \( \text{H}_2\text{O}_2 \) treatment and is believed to be associated with the protonation of basal oxygens after the loss of tetrahedral Al. The occurrence of this band in the unweathered biotite, therefore, suggests that some tetrahedral vacancies are already present in the biotite before contact with any weathering solution. A similar conclusion was drawn from the biotite x-ray diffraction data of Chapter III. Taken together, these two observations seem to provide strong evidence for tetrahedral vacancies in the unweathered biotite.

The hydroxyl stretching spectrum of the biotite changed drastically when the mica was treated by \( \text{H}_2\text{O}_2 \) (Figure V-8). The trioctahedral bands decreased in intensity, whereas the dioctahedral bands near 3525 cm\(^{-1}\) increased in width and intensity. This shift in the intensity of the trioctahedral bands to the dioctahedral bands is unmistakable evidence for the occurrence of octahedral cation ejection during the oxidation process. The adsorbed \( \text{H}_2\text{O} \) content of the biotite also seemed to increase substantially as shown by the broad band from 3200 cm\(^{-1}\) to about 3400 cm\(^{-1}\). This broad band can be taken as indirect evidence that an increase in external surface area was induced by exfoliation during the \( \text{H}_2\text{O}_2 \) treatment. The hydroxyl band at 3440 cm\(^{-1}\), which was associated with tetrahedral vacancies in the untreated mica, was also evident in the spectrum for the \( \text{H}_2\text{O}_2 \)-treated biotite, although it seemed to be obscured somewhat by the dioctahedral hydroxyl stretching bands and the adsorbed \( \text{H}_2\text{O} \) bands. The hydroxyl stretching spectra for the
biotite, therefore, support the conclusions made from the results of other, independent techniques regarding the presence of tetrahedral vacancies in the untreated mica and the occurrence of exfoliation and cation ejection during the H₂O₂ weathering treatments.

The librational spectra for the biotite were similar to those for the phlogopite with two exceptions: the Mg-O band at 815 cm⁻¹ in the phlogopite spectra was absent in the biotite spectra and the band at 590 cm⁻¹ was much less intense. These changes can be expected from the lower Mg content of the biotite relative to the phlogopite. The 940-cm⁻¹ Al-O band that is resolved in the spectra for H₂O₂-treated samples of biotite and phlogopite probably reflects a distortion of the tetrahedral sheet brought on by an increase in the dioctahedral character of the mica. White et al. (1961) were able to eliminate a similar band at 915 cm⁻¹ in muscovite (a dioctahedral mica) by treating the expanded mica with molten LiNO₃, a well-known treatment for injecting Li ions into the octahedral vacancies of layer silicates. Thus, emergence of the band at 940 cm⁻¹ with H₂O₂ treatment may be another piece of evidence for octahedral cation ejection.

In addition to spectra for untreated and H₂O₂-treated samples, spectra for the matrix-treated sample of siderophyllite are shown in Figure V-9. In the hydroxyl stretching frequencies of the spectrum for the untreated sample, two major bands are observed at 3650 cm⁻¹ and at about 3570 cm⁻¹. The strong band at 3650 cm⁻¹ is assigned to the Fe(II)-Fe(II)-Al octahedral cation grouping. The smaller band seems to be made up of three bands (3590, 3575 and 3550 cm⁻¹) and these are
probably associated with Fe(II)-Al-Li, Al-Li-Li, and Fe(II)-Al-Vac respectively (Jorgensen, 1965). With treatment by either the matrix or the H$_2$O$_2$ solutions, the hydroxyl stretching spectrum is essentially unchanged, except for the development of a band at 3440 cm$^{-1}$. This band is absent in the untreated mica and, as suggested by the x-ray diffraction data (Table V-V) and previous discussion for the other micas, is probably due to the protonation of basal oxygens following the leaching/ejection of Al from tetrahedral cation sites.

In general, the librational spectra for the siderophyllite (Figure V-9) exhibited the same features as the other two micas. No bands associated with Mg-O were expected (or found), however, and the Al-O librational bands were broader and less distinct than in the other micas. This latter observation may reflect the much higher Li and Fe contents of the mica or the presence of large quantities of Al in both the tetrahedral and octahedral sheets. The Al-O band near 950 cm$^{-1}$ was scarcely visible in the spectrum for the matrix-treated sample, but emerged more definitively with the H$_2$O$_2$ treatment, perhaps in response to an ejection of octahedral cations during oxidation. Several bands were observed in the 200-350 cm$^{-1}$ range, most notably in the matrix-treated sample. These are difficult to assign, but could be bending librations of Fe-O and Al-O. In short, except for the development of tetrahedral vacancies, the hydroxyl and librational spectra for the siderophyllite samples showed little evidence of alterations in the mica structure as a result of the weathering treatments.
Summary and Conclusions

Mössbauer spectroscopy, x-ray diffraction, and infrared spectroscopy were used to examine the structural changes that occur when micas are weathered by the matrix and H₂O₂ solutions. The Mössbauer spectra showed little evidence for change in the mica structure with H₂O₂ treatment other than the oxidation of Fe(II) to Fe(III) in the biotite and showed no evidence for the formation of magnetically ordered Fe oxide phases. Evidence for exfoliation and cation ejection (peak broadening) was seen in the x-ray diffraction patterns for the biotite treated with H₂O₂, however. Even stronger evidence for octahedral cation ejection during biotite oxidation came from a substantial decrease in the 004/005 observed structure factor ratio, and from changes in the relative intensities of the dioctahedral and trioctahedral hydroxyl stretching bands in the infrared spectrum. Small changes in the structure factor ratios and the development of a new hydroxyl band at 3440 cm⁻¹ in the infrared spectra suggest that some leaching by the matrix solution of tetrahedral cations from the exposed basal surfaces of all three micas occurred. The observance of the "new" hydroxyl band in the infrared spectrum for the untreated biotite corroborates the x-ray diffraction evidence for tetrahedral vacancies that was presented in Chapter III.

In general, therefore, the structural information presented here supports the conclusions drawn from the chemical and kinetic data in
Chapter IV. The aqueous oxidation of structural Fe in mica occurs in concert with exfoliation and octahedral cation ejection. In the absence of this oxidation, only minor structural changes are induced by the weathering solutions. None of the analyses demonstrated the existence or formation of Fe oxide phases in the treated micas, nor was conclusive evidence for the occurrence of deprotonation provided. Even if deprotonation did occur it was not the only charge-balancing reaction, and was evidently secondary to cation ejection in importance. Studies with deuterated micas should help to further define the role of deprotonation in oxidative weathering by aqueous solutions.
CHAPTER VI. OXIDATIVE WEATHERING OF TRIOCTAHEDRAL MICAS
BY BUFFERED H$_2$O$_2$ SOLUTIONS—3. K-DEPLETED
AND DEUTERATED SAMPLES

Introduction

The weathering of micas by aqueous solutions is a complex phenomenon involving the interrelated processes of dissolution, K exchange/interlayer expansion, and oxidation of structural Fe. In general, dissolution and K exchange do not require other modifications to the mica structure before they will occur. Iron oxidation, however, involves an increase in the amount of positive charge in the mica structure, and therefore must be coupled to a charge-balancing reaction in order to maintain electrical neutrality in the mica. Several charge-balancing reactions have been suggested (the ejection of interlayer cations, octahedral cations, or hydroxyl protons), all of which involve the loss of an equivalent amount of positive charge from some other site in the mica. Two of these reactions, the loss of interlayer cations and ejection of octahedral cations, have been shown to occur in an aqueous weathering environment (Newman and Brown, 1966; Veith and Jackson, 1974, Farmer et al., 1971; Ross and Rich, 1974; Scott and Youssef, 1979; Gilkes et al., 1972b; Chapter III, this work). The other reaction, deprotonation of structural hydroxyls, is known to occur when micas are oxidized by thermal treatments (Vedder and Wilkins, 1969;
Robert and Pedro, 1969), but only scant evidence for deprotonation in aqueous systems has been offered (Farmer et al., 1971). Indeed, the interpretation of the infrared spectra published by Farmer et al. (1971) was recently questioned by Scott and Amonette (1988).

The oxidative weathering experiments of Amonette (1983) and those in the previous two chapters were conducted with 1 M K solutions in an attempt to minimize the expansion of the interlayer region and, thereby, the possibility of loss or exchange of the interlayer cations by the weathering solution. The maintenance of a collapsed interlayer region would also be expected to inhibit the ejection of octahedral cations. Theoretically, then, bulk oxidation could occur in high-K solutions only when associated with deprotonation of structural hydroxyls, and thus would require that an internal proton and electron hopping mechanism similar to that suggested for thermal oxidation of Fe in hydroxylated silicates (Addison and Sharp, 1963; White and Sharp, 1971) be operative. In fact, as the results of the aqueous oxidation experiments show, oxidation does occur in high-K solutions, but only when exfoliation and octahedral cation ejection also occur. The conclusion most easily drawn, therefore, is that deprotonation, if it occurs at all in aqueous solutions, requires an opening of the mica layers by exfoliation or K exchange.

A verification of the occurrence of the deprotonation of structural hydroxyls when expanded micas are oxidized in aqueous solutions is difficult because the broad infrared bands associated with interlayer H₂O overlap, and thus may obscure, the hydroxyl stretching bands of the
mica. This problem might be avoided, however, if the structural hydroxyls were deuterated before oxidizing the mica because the deuteroxyl stretching region (2800-2500 cm⁻¹) is completely free of interferences by H₂O vibrations. Any loss of intensity in the deuteroxyl stretching bands, therefore, could be taken as evidence for a deprotonation reaction, or at least for an exchange reaction involving structural deuterons and protons from the oxidizing solution. The absence of such a loss in intensity, of course, would be equally strong evidence against the existence of a deprotonation mechanism.

Two other aspects of the role of Fe oxidation in mica weathering need clarification, as well. First, because the experiments in 1 M K solutions were assumed to have largely negated the possibility for layer charge loss as a charge-balancing reaction, this reaction has been considered of minimal importance compared to ejection of octahedral cations. The question arises, then, whether layer charge loss or cation ejection would be more favored in an environment where the weathering solution were allowed access to the interlayer region by the substitution of a hydrated cation for interlayer K. Second, because no direct measurements of particle size distribution or specific surface area have been made, the evidence for and against exfoliation of the mica during the weathering treatments has been largely of an indirect nature. As with the deprotonation mechanism, some sort of a tracer having nearly identical properties to K needs to be used in order to distinguish native interlayer K from that which may have entered the interlayer region by exchange during treatment. Rubidium (Rb), which
has a slightly stronger affinity for the interlayer region of micas than K but otherwise behaves similarly (Scott and Smith, 1987), is a reasonable and inexpensive substitute for K. An analysis of the mica solids after treatment by weathering solutions spiked with Rb, thus, should provide incontrovertible evidence that the contracted condition of the mica layers was, or was not maintained during the oxidation treatment.

The experiments in this chapter, therefore, serve to clarify some of the questions about oxidative weathering of micas that were left unanswered by Chapters IV and V. In particular, definitive proof for the presence or absence of deprotonation and exfoliation reactions during the oxidation treatments is sought. And, the changes in layer charge that occur when the interlayer region is accessible to the oxidizing solution are examined. Lastly, these results are compared with those for weathering treatments in which no strong oxidant is present in order to distinguish the changes associated with oxidation from those changes associated with other weathering reactions such as dissolution.

Experimental

Micas and apparatus

Three trioctahedral micas, a phlogopite, a biotite, and a siderophyllite were included in this study. The sources, preliminary treatments, and structural formulas of these micas, as well as the
weathering apparatus and general operating procedures for continuous-flow weathering experiments are described in Chapter IV.

**K-depletion and deuteration**

To study the oxidative weathering of micas having expanded interlayer regions, and to monitor the possible occurrence of deprotonation mechanisms during weathering, the micas were K-depleted and deuterated prior to receiving the weathering treatments. K-depletion was accomplished in sodium tetraphenylborate (NaBPh₄) solutions under conditions that would minimize the oxidation of structural Fe (Scott and Youssef, 1979). The method involved treating six 0.5-g samples of each mica with 10 ml of 1 M NaCl-0.2 M NaBPh₄-0.01 M Na₂EDTA for 8 hours at 65°C. The suspensions were centrifuged, the supernatant saved, and then the six 0.5-g samples were combined on a filter paper in a large Buchner funnel. The 3-g combined sample was washed thoroughly with a solution of 0.5 M NaCl in 60% acetone to dissolve and remove the KBPh₄ precipitate, washed with H₂O to remove the acetone, and then transferred to a 250-ml flask. To remove K reabsorbed by the mica during the washing procedure, the sample was retreated at 25°C with the supernatant solution that had been saved. After several hours, the supernatant was removed and saved, and the mica washed as before with the 0.5 M NaCl-60% acetone solution. This retreatment and washing procedure was repeated for a total of 4 times during a 72-hour period to obtain Na-saturated mica samples that had low levels of original or readsorbed K. After the last 0.5 M NaCl-60% acetone
washing, the mica was washed in 100% acetone to remove any excess salt, allowed to air-dry for several hours, and then stored in a glass vial.

Subsamples of the Na-saturated micas were deuterated at elevated temperatures in a high pressure Parr bomb. To do this, 0.5 g of Na-saturated mica were placed in a 10-mm diameter Teflon cylinder that was capped with a 0.2-um porosity Teflon filter membrane on one end. The cylinder containing the mica was placed inside the Parr bomb, to which 0.3 g of finely ground Ni(m) (a redox buffer) and 0.5 ml of D$_2$O had already been added. The bomb was sealed and then heated in a muffle furnace at 275°C. After 2 hours, the bomb was removed from the furnace and allowed to cool, the cylinder removed, and the mica recovered by rinsing with 100% acetone, filtering and air-drying. When two 0.5-g samples of each mica had been prepared, they were combined and treated for a second time in the Parr bomb under the same conditions as in the initial treatment. This procedure yielded 1-g deuterated samples of the three Na-saturated micas (hereafter referred to as Na-deuterated micas).

**Weathering treatments**

Four separate weathering treatments were applied to the Na-deuterated mica samples. Two of these treatments involved weathering with 1 M NaOAc(pH 4.7)-0.1 M Na$_2$EDTA (termed the Na-matrix solution) or 25% H$_2$O$_2$-1 M NaOAc(pH 4.7)-0.1 M Na$_2$EDTA (termed the Na-H$_2$O$_2$ solution) and were applied to the mica samples for a total of 6 hours at 80°C. The third and fourth weathering treatments involved solutions that were identical to the Na-matrix and Na-H$_2$O$_2$ solutions except that K was
substituted in place of Na and they contained 0.05 M RbCl (added as a tracer). The latter two solutions were termed the K,Rb-matrix and K,Rb-H₂O₂ solutions, respectively. Prior to treating the micas with the K,Rb solutions, however, the Na-deuterated micas were treated with a 1 M KOAc-0.1 M K₂EDTA solution that contained no Rb (referred to as the K-matrix solution) for 28 hours at 80°C. This pretreatment resaturated the interlayer region with K and caused a collapse of the mica layers, thus ensuring that a reopening of the layers during the ensuing K,Rb treatments could be detected by an increase in the Rb content of the micas. After the K-matrix pretreatment, the deuterated mica samples were treated with the K,Rb-matrix or the K,Rb-H₂O₂ solutions for six days. Duplicate 80-mg samples of mica were weathered by each of the four treatments and the apparatus and experimental conditions (e.g., temperature, flow rate) were identical to those of the "main" experiment described in Chapter IV. The effluents from the Na-saturated treatments were collected at the end of the 6-hour treatment period and analyzed for Al, Mg and Fe by the procedures of Chapter IV. The sample termination procedures were also essentially those of Chapter IV, but NaCl was substituted for KCl in the washing solutions for samples from the Na-matrix and Na-H₂O₂ treatments.

**Analytical techniques**

After the weathering treatments, less than 80 mg of each replicate mica sample remained for chemical and structural characterization. Forty mg of each replicate were dissolved and analyzed for Fe(II) using
the recommended method of Chapter II. When the titration step of this procedure was finished, the contents of the titration vessel were then diluted to 200 ml with H₂O. Subsamples of these solutions were further diluted to the appropriate levels, and analyzed for K, Na and Rb by atomic absorption spectroscopy. All dilutions were performed in plastic containers to avoid contamination from the attack of HF on glassware. The standard solutions used to calibrate the results were prepared to have the same acid matrix as the contents of the titration vessels. Duplicate samples of the unweathered Na-deuterated micas were also included in these analyses.

Most of the remaining 25-40 mg of each weathered sample was used to characterize the structural changes that might have occurred during the weathering treatment. Infrared spectra of the micas were obtained using the same reflectance and transmission techniques described in Chapter V. X-ray diffraction analyses (CuKα radiation) of the 001 reflections were performed on preferentially oriented samples that were mounted on glass slides with double stick tape. These samples had been washed with acetone and allowed to air-dry before x-ray or infrared analyses were performed.

Results and Discussion

Chemical analyses

The Fe(II) and interlayer cation contents of the untreated micas, and of the Na-deuterated micas before and after treatment by the
weathering solutions, are shown in Table VI-1. The layer charge of each mica, calculated as the sum of the interlayer cation values, is also shown. In general, more than 90% of the layer charge in the untreated micas was satisfied by K ions. After the Na-deuteration pretreatments, all of the layer charge in the phlogopite and biotite and 96% of that in the siderophyllite was satisfied by Na ions. In each Na-deuterated mica, however, associated decreases in the total layer charge and in the Fe(II) content were observed. Thus, the biotite lost 43% of its Fe(II) and 17% of its layer charge during the K-depletion procedure whereas the siderophyllite lost 27% and 10%, and the phlogopite 5% and 5%, respectively. Analyses of the Na-saturated siderophyllite before and after deuteration showed no effect of the procedure on the Fe(II) content of this mica and, presumably, the other two micas as well. The decreases in Fe(II) content, therefore, must have occurred during the K-depletion procedure.

In absolute terms, the losses of layer charge in the biotite and siderophyllite were large enough to balance no more than one-third of the increases in positive charge attributable to oxidation. Clearly, other charge-balancing reactions must have also occurred in these micas. As shown by the phlogopite, however, where the absolute layer charge loss was several times the amount of Fe(II) oxidized, some of the layer charge "loss" has to be attributed to other processes like an adsorption of hydronium ions or protonation of basal oxygens from the contact of the freshly exposed basal surfaces with the aqueous solvent. If these reactions also occurred in the biotite and siderophyllite, then the
TABLE VI-1. Interlayer cation, layer charge and Fe(II) contents of untreated mica samples and of Na-deuterated mica samples before and after treatment with Na-matrix, Na-H$_2$O$_2$, K,Rb-matrix or K,Rb-H$_2$O$_2$ solutions

<table>
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<th>Mica Sample</th>
<th>Interlayer Cation</th>
<th>Layer Charge</th>
<th>Fe(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Na</td>
<td>Rb</td>
</tr>
<tr>
<td>Phlogopite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
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<td>14$^b$</td>
<td>0</td>
</tr>
<tr>
<td>Na-deuterated</td>
<td>0</td>
<td>233</td>
<td>0</td>
</tr>
<tr>
<td>Na-matrix</td>
<td>--</td>
<td>233</td>
<td>--</td>
</tr>
<tr>
<td>Na-H$_2$O$_2$</td>
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<td>--</td>
</tr>
<tr>
<td>K,Rb-matrix</td>
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</tr>
<tr>
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<td>41</td>
<td>1</td>
</tr>
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</tr>
<tr>
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<td>16$^b$</td>
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<tr>
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<td>184</td>
<td>0</td>
</tr>
<tr>
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<td>--</td>
</tr>
<tr>
<td>Na-H$_2$O$_2$</td>
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</tr>
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<td>Untreated</td>
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<td>10$^b$</td>
<td>9</td>
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<tr>
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<td>8</td>
<td>186</td>
<td>1</td>
</tr>
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<tr>
<td>Na-H$_2$O$_2$</td>
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<tr>
<td>K,Rb-H$_2$O$_2$</td>
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<td>120</td>
<td>21</td>
</tr>
</tbody>
</table>

\[a\] Data adjusted for interlayer cation occupancy and H$_2$O content to be consistent with those for untreated mica.

\[b\] Datum estimated from structural formula (ICP-AES).
contribution of layer charge loss to balance the charge created by oxidation must be even smaller than the data in Table VI-1 suggest.

Treatment of the Na-deuterated micas by the weathering solutions produced widely differing amounts of Fe(II) oxidation (Table VI-1). For the phlogopite, very little oxidation was observed in any of the weathering treatments. For the biotite and siderophyllite samples, however, the treatment effects were large. No oxidation occurred during the K,Rb-matrix treatments, but during the Na-matrix treatments roughly 10% of the Fe(II) initially present in the Na-deuterated samples was oxidized. Treatment with Na- or K,Rb-H₂O₂ solutions caused much of the remaining Fe(II) to be oxidized. More Fe(II) was oxidized in the Na-H₂O₂ treated micas than in the K,Rb-H₂O₂ treated micas even though the treatment period for the latter micas was 24 times longer. The differences in the extent of oxidation can be attributed to the stronger tendency for the mica layers to contract in the K,Rb-solutions than in the Na solutions, and by so doing, to inhibit the transfer of electrons, protons and cations between the interlayer region of the mica and the bulk solution.

Changes in layer charge during the weathering treatments were surprisingly small considering the large quantities of Fe(II) that were oxidized in some of the treatments. Data for the Na solutions were not obtained, but, for the K,Rb solutions, little or no change in layer charge was observed in the biotite and siderophyllite samples. On the other hand, losses of as much as 17 cmol kg⁻¹ (7%) of the layer charge were observed in the phlogopite samples even though oxidation was only
about 1 cmol kg\(^{-1}\) (4%). Thus, the association between oxidation and layer charge decrease that existed during the Na-deuteration pretreatments was not repeated during the weathering treatments.

Although the changes in total layer charge were small, the composition of the cations in the interlayer changed substantially during treatment by the weathering solutions (Table VI-1). In the biotite, for example, nearly 80% of the interlayer Na was replaced by K as a result of treatments by the K-matrix and K,Rb-matrix solutions. In contrast, less than 10% of the Na was replaced by K in the siderophyllite during the same treatments. As suggested by the failure to remove all of the K from the siderophyllite during the Na-deuteration pretreatments, this difference between the two micas was the result of a higher propensity for contraction (i.e., a higher anionic field strength in the interlayer region) in the siderophyllite. Thus, only a small percentage of K needed to be present in the siderophyllite before the layers collapsed and prevented the exchange of the remaining Na. In both micas, however, no additional Rb was incorporated into the interlayer region as a result of the K,Rb-matrix treatments. This implies that all of the K that was incorporated came from the 24-hour treatment with the K-matrix solution (before the 6-day K,Rb-matrix treatment was started) and that an opening of the interlayer region did not occur during the 6-day K,Rb-matrix treatment.

The \(\text{H}_2\text{O}_2\) treatments for both micas produced even greater replacement of Na and showed substantial incorporation of Rb and K into the interlayer region (Table VI-1). It seems clear that an opening of
the interlayer region of the siderophyllite and biotite micas occurred during the K,Rb-H₂O₂ treatments and that this process was coupled to the occurrence of substantial Fe(II) oxidation. In contrast, the phlogopite mica showed essentially no incorporation of Rb or oxidation of Fe(II) during the matrix or H₂O₂ treatments. If the two processes of exposure of the interlayer region and Fe(II) oxidation were independent, the phlogopite, with an anionic field strength roughly equal to that of the biotite, would have been expected to show Rb incorporation during the K,Rb-H₂O₂ treatment. The fact that neither oxidation nor interlayer expansion has been observed independently suggests that they are indeed linked.

The implications of this linkage are clear. For oxidation of Fe(II) to occur in aqueous solutions, the interlayer region must expand or exfoliate so that the appropriate charge-balancing reaction can also occur. Conversely, if the anionic field strength is so high that expansion of the interlayer region is inhibited, no oxidation will occur because there is no way to balance the excess charge that would be created. Furthermore, this strong evidence for linkage of the oxidation and the expansion/exfoliation processes suggests that the coupling of oxidation and deprotonation via an electron and proton hopping mechanism in the mica interior (Addison and Sharp, 1963; White and Sharp, 1971) does not occur to any great extent, under the conditions imposed by aqueous solutions. Deprotonation, if it occurs at all, seems analogous to octahedral cation ejection in that it is very localized and requires an expansion of the interlayer region.
Lastly, it should be noted that the extent of oxidation achieved during the weathering of the Na-deuterated micas by the K,Rb-H$_2$O$_2$ solutions was much greater after 6 days of treatment than in the original micas after 36 days. This result stems from the irreversible alteration of the mica structure that occurs once the native K is replaced by hydrated cations. Changes in the tilting and rotation of the tetrahedra in the K-depleted mica structure alter the anionic field acting on the interlayer cations. The net result is a decrease in the anionic field strength of the mica, and thereby an increase in the propensity for expansion or exfoliation in the mineral and, hence, oxidation of structural Fe(II).

**Infrared spectra**

Selected portions of the infrared spectra for the Na-deuterated samples before and after treatment by the weathering solutions are shown in Figures VI-1, VI-2, and VI-3. The spectra are arranged to show 4 major groups of absorption bands: the OH stretching bands (3800-3100 cm$^{-1}$), the OD stretching bands (2800-2400 cm$^{-1}$), the OH bending bands (1700-1500 cm$^{-1}$) and the librational bands (1200-250 cm$^{-1}$). Because the first 3 groups of spectra were obtained by reflectance spectroscopy, they are relatively more surface sensitive than the librational spectra, which were obtained by conventional transmission spectroscopy.

In the spectrum for the Na-deuterated phlogopite before weathering ("Na" in Figure VI-1), a broad absorption band between 3600 and 3000 cm$^{-1}$ was obtained and can be attributed to interlayer H$_2$O. Further
FIGURE VI-1. Infrared spectra of Na-deuterated phlogopite samples before and after treatment with Na-matrix, Na-H$_2$O$_2$, K,Rb-matrix or K,Rb-H$_2$O$_2$ solutions.
TRANSMITTANCE

Na
H₂O₂

K
Matrix

K
H₂O₂

FREQUENCY (100 cm⁻¹)
FIGURE VI-2. Infrared spectra of Na-deuterated biotite samples before and after treatment with Na-matrix, Na-\( \text{H}_2\text{O}_2 \), K,Rb-matrix or K,Rb-\( \text{H}_2\text{O}_2 \) solutions
TRANSMITTANCE

H₂O

Na

Matrix

DN

BIOTITE
FIGURE VI-3. Infrared spectra of Na-deuterated siderophyllite samples before and after treatment with Na-matrix, Na-H$_2$O$_2$, K,Rb-matrix or K,Rb-H$_2$O$_2$ solutions
evidence for this interlayer H₂O is shown by the OH bending vibration at 1630 cm⁻¹. A hydroxyl stretching band at 3700 cm⁻¹ that was present in the spectrum for the untreated mica (Figure V-7) was obscured (or was altogether absent) in this spectrum, but a strong peak at the corresponding OD stretching frequency of 2710 cm⁻¹ was observed. It would seem, therefore, that some, if not all of the hydroxyl groups were replaced by deuter oxyls during the deuteration treatment. The librational frequencies showed Si-O vibrations at 1000 and 450 cm⁻¹, Al-O vibrations at about 930 cm⁻¹ and smaller bands corresponding to various octahedral cations in the range from 815 to 570 cm⁻¹. These latter bands are difficult to assign with any certainty in these expanded micas, as comparisons among the spectra for the 3 micas will show.

The spectra for the weathered phlogopite samples (Figure VI-1) showed considerable variability in the OH stretching and bending bands with treatment, but little or no change in the OD bands. The Na-matrix spectrum was essentially unchanged from the unweathered spectrum, but with treatment by the Na-H₂O₂ solution a strong band developed at 3250 cm⁻¹, lesser bands at 3450 cm⁻¹ and 3510 cm⁻¹, and a shoulder at about 3570 cm⁻¹. The latter two bands are probably associated with dioctahedral structural hydroxyl groups and their presence suggests that some exchange of OH for OD occurred during the H₂O₂ treatment. The band at 3450 cm⁻¹ is probably associated with protonation of basal oxygens (Chapter V) and may have been easily observed because of a replacement of interlayer H₂O by interlayer H₂O₂. The very strong band at 3250 cm⁻¹
is a previously unobserved peak and, as will be shown below, is associated with H$_2$O$_2$ treatments and the degree of expansion of the mica layers. In general, the hydroxyl stretching spectra for the K,Rb-matrix and K,Rb-H$_2$O$_2$ treated samples were similar to the corresponding Na-solution spectra. The overall intensities of the bands associated with interlayer H$_2$O and H$_2$O$_2$ (3000-3700 cm$^{-1}$ and 3250 cm$^{-1}$, respectively) were smaller, however. Lower intensities of the OH bending peaks near 1630 cm$^{-1}$ were also observed. These differences are probably related to lesser amounts of interlayer H$_2$O and H$_2$O$_2$ and would be expected from contraction of the interlayer region in the K,Rb-treated samples. Lastly, the frequency of the OD peak shifted from 2700 cm$^{-1}$ in the Na-deuterated and Na-matrix spectra to 2725 cm$^{-1}$ in the H$_2$O$_2$-treated and K,Rb-matrix spectra. X-ray diffraction data (shown in the next section) suggests that this shift was also related to a contraction of the mica layers.

The hydroxyl stretching band spectra for the biotite samples (Figure VI-2) shared many of the same features seen in the phlogopite spectra. A broad band was observed from 3700 to 3000 cm$^{-1}$ in spectra of the Na-deuterated and Na-matrix samples. The intensity of this band decreased successively in the Na-H$_2$O$_2$, K,Rb-matrix, and K,Rb-H$_2$O$_2$ treated samples. A similar decrease in intensity was observed for the OH bending bands at 1630 cm$^{-1}$, which suggests that the broad hydroxyl stretching band is associated with hydrogen bonding of interlayer water. Some minor bands were also evident in all of the hydroxyl stretching spectra except for the Na-matrix treatment. In particular, a small band
at 3450 cm$^{-1}$ was seen in these spectra and is probably due to protonation of basal oxygens associated with tetrahedral vacancies. The hydroxyl stretching bands for the di- and tri-octahedral hydroxyl sites (3700 to 3520 cm$^{-1}$) were also evident in the Na-H$_2$O$_2$ and K,Rb-solution spectra, although they were not well-defined. A strong band was present at 3240 cm$^{-1}$ in the Na-H$_2$O$_2$ and, to a much lesser extent, in the K,Rb-H$_2$O$_2$ spectra. A similar band was observed in the phlogopite spectra and is probably associated with interlayer H$_2$O$_2$ trapped by a contraction of the mica layers.

Changes in the OD stretching region (2500 to 2700 cm$^{-1}$) of the biotite spectrum (Figure VI-2) were also seen with the various treatments. A moderately intense trioctahedral band was present in the Na-deuterated spectrum at 2680 cm$^{-1}$, with some minor dioctahedral bands in the 2600-2500 cm$^{-1}$ region. These bands were also seen in the Na- and K,Rb-matrix spectra, although, as for the phlogopite, the entire OD stretching band was shifted by 25-30 cm$^{-1}$ to a higher frequency in the K,Rb-matrix spectrum and was somewhat broader. The most important change, however, occurred as a result of the H$_2$O$_2$ treatments. The OD bands were essentially eliminated by the Na-H$_2$O$_2$ treatment and considerably diminished by the K,Rb-H$_2$O$_2$ treatment. This is unmistakable evidence that an exchange of OH for OD or a complete loss of the positive charge associated with the structural hydroxyl site (i.e., "deprotonation") was induced by the oxidation treatment. The extent to which this loss of OD was related to the oxidation of structural Fe(II) is difficult to determine, although it is clear that
the greatest loss occurred in the sample that was oxidized the most.

The infrared spectra for the siderophyllite (Figure VI-3) were different in several respects from those of the other two micas. First of all, there was much less water in the interlayer region as shown by the minor bands in the OH bending spectra (1700 to 1500 cm$^{-1}$) and the smaller intensities of the broad OH stretching bands (3700 to 3000 cm$^{-1}$). Secondly, the OD stretching bands did not shift frequencies as a result of the different treatments. Thirdly, even though substantial oxidation occurred in the $\text{H}_2\text{O}_2$ treated samples, the intensities of the OD stretching bands (2800 to 2400 cm$^{-1}$) were diminished to a lesser degree than in the biotite. Thus, deprotonation or OD exchange for OH seemed to occur with treatment by the $\text{H}_2\text{O}_2$ solutions, but was not as prevalent as in the biotite.

The similarities of the siderophyllite spectra with those for the other micas included the minor band near 3450 cm$^{-1}$ that may indicate hydroxyls at tetrahedral vacancies, and the strong band at 3270 cm$^{-1}$ in the Na-$\text{H}_2\text{O}_2$ spectrum that is probably related to trapped interlayer $\text{H}_2\text{O}_2$. A dioctahedral OH stretching band at 3590 to 3570 cm$^{-1}$ was seen in most of the siderophyllite spectra, but there was little or no evidence for the trioctahedral band at 3650 cm$^{-1}$. In fact, the trioctahedral bands were obscured in almost all of the spectra obtained from the deuterated micas. This observation can be explained either by the occurrence of cation ejection to balance the oxidation during the Na-deuteration pretreatment or by the distortion of the spectra from the Christiansen effect (Price and Tetlow, 1948). In many of these spectra,
the Christiansen effect was clearly visible as the large peak preceding the hydroxyl stretching band, but that does not rule out a possible contribution of cation ejection (i.e., the transformation of trioctahedral sites to dioctahedral sites).

Treatment-induced changes in the librational spectra of the siderophyllite, and the other two micas as well, were relatively minor and, with one exception, did not lead to any consistent interpretations (Figures VI-1, VI-2, and VI-3). The exception concerns the resolution of the Si-0 and Al-0 vibrations at approximately 1000 and 930 cm^{-1}, respectively. In the untreated micas (Figures V-7, V-8, and V-9), the two vibrations were scarcely separable. After K-depletion and deuteration, however, the two peaks were clearly defined (Figures VI-1, VI-2, and VI-3). The definition was lost somewhat during the Na-matrix treatment, but was very strong in the spectra for the Na-H_{2}O_{2} and K,Rb-matrix treated samples. Then, curiously, the separation of these two vibrations nearly disappeared as a result of the K,Rb-H_{2}O_{2} treatment. The separation of the Al-0 and Si-0 vibrations may be related to the amount of distortion in the tetrahedral sheet caused by the degree of expansion and nature of the species occupying the interlayer region. Further evidence for this explanation, however, must come from measurements of the d-spacings by x-ray diffraction.

**X-ray diffraction data**

The 001 d-spacings of the air-dry Na-deuterated samples, measured before and after treatment by the weathering solutions, are summarized
in Table VI-2. In general, 3 different d-spacings were observed. These corresponded to expanded (1 layer of H₂O), intermediate, and completely contracted phases. For reference, the 001 d-spacings of the untreated K-micas were 0.98, 0.98, and 0.97 nm for the phlogopite, biotite, and siderophyllite, respectively.

The phlogopite and biotite micas had nearly identical d-spacings after each of the various treatments. The Na-deuterated samples were mostly expanded to 1.22 nm, but some completely contracted layers (0.96 nm) were also present [the 001 d-spacings of these contracted Na-saturated layers are less than those for the untreated K-micas because of the smaller ionic radii of the Na ions (0.097 nm) relative to the K ions (0.133 nm)]. Exposure of these samples to the Na-matrix solution resulted in a complete expansion of the mica layers. Treatment by the Na-H₂O₂ solution, however, caused most of the expanded layers to collapse to an intermediate d-spacing of 1.04-1.05 nm. This collapse was probably a result of the higher dipole moment of H₂O₂ relative to H₂O, and, as a consequence, the formation of stronger hydrogen bonds to link the mica layers. Treatment with the K,Rb-solutions (including the pretreatment with the K-matrix solution) also caused the phlogopite and biotite layers to collapse, but, for the K,Rb-matrix treatments the degree of contraction was not complete. Thus, rather than returning to the original 0.98-nm d-spacing, the micas only collapsed to 1.00-1.01 nm. Apparently, the anionic field strength was not high enough to completely eliminate the H₂O and H₂O₂ molecules that were caught between the layers. The extent of collapse differed, however, for the K,Rb-H₂O₂
TABLE VI-2. Values for 001 d-spacings and relative peak heights of expanded, intermediate and contracted layers in Na-deuterated mica samples before and after treatment with Na-matrix, Na-H₂O₂, K,Rb-matrix or K,Rb-H₂O₂ solutions

<table>
<thead>
<tr>
<th>Mica sample</th>
<th>Expanded</th>
<th>Intermediate</th>
<th>Contracted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d-spacing</td>
<td>Relative&lt;sup&gt;a&lt;/sup&gt;</td>
<td>d-spacing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Phlogopite</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-deuterated</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-matrix</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-H₂O₂</td>
<td>1.21&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.05</td>
</tr>
<tr>
<td>K,Rb-matrix</td>
<td>1.04</td>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td>K,Rb-H₂O₂</td>
<td>1.01</td>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td>Biotite</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-deuterated</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-matrix</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-H₂O₂</td>
<td>1.23</td>
<td>&lt;5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.04</td>
</tr>
<tr>
<td>K,Rb-matrix</td>
<td>1.00</td>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td>K,Rb-H₂O₂</td>
<td>1.00</td>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td>Siderophyllite</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-deuterated</td>
<td>1.22</td>
<td>100</td>
<td>0.96</td>
</tr>
<tr>
<td>Na-matrix</td>
<td>1.22</td>
<td>34</td>
<td>1.02</td>
</tr>
<tr>
<td>Na-H₂O₂</td>
<td>0.96&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.00</td>
</tr>
<tr>
<td>K,Rb-matrix</td>
<td>0.96</td>
<td>100</td>
<td>0.99</td>
</tr>
<tr>
<td>K,Rb-H₂O₂</td>
<td>0.99</td>
<td>100</td>
<td>0.99</td>
</tr>
</tbody>
</table>

<sup>a</sup>Peak heights are relative to the largest peak in a given mica diffractogram (peak heights for different samples cannot be compared).

<sup>b</sup>Peak is shoulder on larger peak.
treated samples. In the phlogopite, some interlayer H₂O remained and the same intermediate d-spacing was observed as for the K,Rb-matrix treated sample. The biotite, in contrast, collapsed completely to 1.00 nm. In this instance, a 1.00-nm d-spacing was considered complete collapse because of the presence of interlayer Rb ions, whose radii (0.147 nm) are sufficiently larger than those of K ions (0.133 nm) to add about 0.02 nm to the d-spacing.

The siderophyllite, as shown by the higher proportion of contracted layers in Table VI-2, seemed to have a much larger anionic field strength than the other micas. The initial Na-deuteration treatment resulted in a completely contracted sample (0.96-nm d-spacing), and roughly one-fourth of the layers were still contracted after treatment with the Na-matrix solution. Treatment with the Na-H₂O₂ solution resulted in a mixture of 3 different d-spacings: approximately 25% of the layers were expanded, 70% were at 1.02 nm, and 5% were completely contracted. As with the other micas, pretreatment by the K-matrix solution and treatment by the K,Rb-solutions also resulted in contracted mica layers. For the siderophyllite, however, the degree of contraction was complete in both the K,Rb-matrix and K,Rb-H₂O₂ treated samples after accounting for the ionic radius of the interlayer Rb ions that were present in the latter samples.

The occurrence of expanded layers in the Na-treated micas was expected from the relative hydration energies of K and Na ions. What was surprising, perhaps, was that a d-spacing of 1.22 nm was observed rather than the 1.49-nm spacing normally expected for hydrated
vermiculites. The analysis of air-dried samples was probably responsible for this anomaly. To verify this explanation, two of the weathered biotite samples (Na-matrix and Na-H$_2$O$_2$) were wet-mounted by suction onto porous quartz tiles. The diffractograms obtained by this mounting procedure were identical to those obtained for the air-dried samples, except that all of the layers that were at 1.22-1.23 nm in the air-dried sample yielded a 1.49-nm d-spacing.

X-ray diffractograms of the mica samples that were taken after K-depletion and before the deuteration treatment showed that all the layers were expanded. The presence of completely contracted layers in the Na-deuterated samples, therefore, was probably a consequence of the high pressure in the Parr bomb during the deuteration treatment. All of the contracted layers in the phlogopite and biotite samples were expanded by the Na-solution treatments. The siderophyllite samples, however, still retained some contracted layers after these treatments. Other considerations, such as dioctahedral character and a high F content, may have contributed to the higher anionic field strength of the Na-deuterated siderophyllite and thus prevented complete expansion of this mica by the Na-solution treatments.

Perhaps the most curious d-spacings observed were the 1.02- to 1.05-nm spacings for the Na-H$_2$O$_2$ treated samples. These same samples also exhibited strong hydroxyl stretching bands at 3270-3240 cm$^{-1}$ in the infrared spectra. The association between H$_2$O$_2$ treatment and these two observations suggests that well-ordered H$_2$O$_2$ may be present in the interlayer region of these micas. Conceivably, the oxygen atoms in the
$H_2O_2$ molecule could be situated in adjacent interlayer-cation sites and linked by hydrogen bonds to basal oxygens (or to oxygens in the octahedral sheet if deprotonation of structural hydroxyls had occurred). The strength of these hydrogen bonds apparently is sufficient to cause a partial contraction of the mica layers, but complete contraction may be prevented by repulsion between the structural oxygens and $H_2O_2$ oxygens. Another explanation for the intermediate d-spacings in the Na-$H_2O_2$ treated samples could be the intercalation of acetate or EDTA anions from the matrix solution. This does not seem likely, however, because of the negatively-charged environment between the mica sheets and because no evidence for the intermediate spacings was seen in the Na-matrix treated samples. Yet a third possible explanation for these spacings is that offered by Farmer et al. (1971), who observed d-spacings of 1.11 and 1.14 nm in the expanded biotites they oxidized with $H_2O_2$ solutions. These authors suggested that ejected ferric ions formed hydroxides in the interlayer regions of the mica and, thus, prevented a complete return of the layers to the original spacing. This explanation does not apply to the present study, however, because the d-spacings observed (1.02-1.05 nm) were much closer to the original spacings (0.97-0.98 nm) and because they also occurred in the phlogopite, which had almost no structural Fe.

The occurrence of the intermediate d-spacings also seems to be associated with the degree to which the Si-O and Al-O infrared vibrations (at 1000 cm$^{-1}$ and 930 cm$^{-1}$, respectively) are resolved (Figures VI-1, VI-2, and VI-3). If the resolution of the two infrared
vibrations is caused by distortion in the tetrahedral sheet, the greatest resolution would be expected in those samples containing trapped H₂O or strongly-bound H₂O₂. Conversely, the least resolution would be expected in completely collapsed micas in which no foreign molecules were trapped, and in the completely expanded micas where the forces holding the layers together would be much weaker than in the H₂O₂-intercalated micas. This scheme explains the observed data fairly well except for the K,Rb-matrix treated siderophyllite where complete collapse of the layers still results in some separation of the Si-O and Al-O vibrations. Perhaps interlayer Rb ions, by keeping the layers of the mica further apart than interlayer K ions, decrease the strain on the tetrahedral sheet from that when K is the sole interlayer cation. If so, then the low levels of Rb in the K,Rb-matrix treated mica relative to the K,Rb-H₂O₂ treated mica could explain the differences in resolution of their Si-O and Al-O vibrations seen in Figure VI-3.

Effluent analyses

The fractions of Al, Mg, and Fe that were measured in the effluent for the mica samples treated by the Na-matrix and Na-H₂O₂ solutions are shown in Table VI-3. The Na-matrix treatment caused the release of small and roughly equivalent fractions from the micas. These data would be expected for a uniform bulk dissolution process. With treatment by H₂O₂, however, larger fractions of the structural cations (particularly Al and Fe) were measured in the effluent. Part of this increase could have been related to an increase in the external surface area of the
TABLE VI-3. Fractions of Al, Mg, and Fe recovered in the effluent from Na-deuterated mica samples during treatment by Na-matrix or Na-H$_2$O$_2$ solutions for a 6-hour period$^a$

<table>
<thead>
<tr>
<th>Mica Sample</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phlogopite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-matrix</td>
<td>0.03 (0.00)</td>
<td>0.04 (0.00)</td>
<td>B.D.$^b$</td>
</tr>
<tr>
<td>Na-H$_2$O$_2$</td>
<td>0.11 (0.01)</td>
<td>0.09 (0.01)</td>
<td>1.18$^c$</td>
</tr>
<tr>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-matrix</td>
<td>0.03 (0.02)</td>
<td>0.04 (0.00)</td>
<td>0.06 (0.03)</td>
</tr>
<tr>
<td>Na-H$_2$O$_2$</td>
<td>1.22 (0.39)</td>
<td>0.28 (0.10)</td>
<td>0.70 (0.17)</td>
</tr>
<tr>
<td>Siderophyllite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-matrix</td>
<td>0.02 (0.01)</td>
<td>B.D.$^b$</td>
<td>0.06 (0.06)</td>
</tr>
<tr>
<td>Na-H$_2$O$_2$</td>
<td>1.50 (0.59)</td>
<td>B.D.$^b$</td>
<td>1.83 (0.57)</td>
</tr>
</tbody>
</table>

$^a$Expressed as a percent of amount in original K mica (standard deviation is given in parentheses).

$^b$Levels measured were at or below the detection limit.

$^c$One replication only.
micas caused by exfoliation of the mica layers. It is likely, however, that most of the increase was due to the ejection of octahedral cations to balance the charge created by Fe(II) oxidation. The large fractions of Al and Fe that were released during the Na-H$_2$O$_2$ treatments suggests that these trivalent cations are ejected preferentially to Mg during the charge-balancing process. Similar results were obtained for the K-H$_2$O$_2$ treated biotite in Chapter IV. The phlogopite, however, did not show preferential ejection of Al. This result could be related to the fact that only 11% of the Al in the phlogopite occurred in the octahedral sheet, compared with 23 and 45% in the biotite and siderophyllite, respectively (Table IV-1). The very small fraction of Fe(II) that was oxidized in the phlogopite may have been Fe that occurred in specific domains in the octahedral sheet that contained very little Al. The phlogopite, then, balanced the charge from Fe(II) oxidation mainly by the ejection of Fe(III).

Rough calculations of the fraction of the charge created by Fe(II) oxidation that was balanced by octahedral cation ejection were made by assuming that the amounts of Al, Mg, and Fe measured in the effluents for the Na-H$_2$O$_2$ treatments were entirely due to ejection of these cations. The calculations, thus, assumed that no bulk dissolution of the micas occurred during the treatment. The results of these calculations showed that the phlogopite ejected more cations than were needed to balance the charge from oxidation of structural Fe(II). The biotite and siderophyllite, however, ejected enough octahedral cations to balance only 14 and 23%, respectively, of the charge created by
Fe(II) oxidation. Since the 24-ml effluent solutions did not include the 10-ml portion that was still in the reaction flask at the time the samples were terminated, an increase of about 42% in these values (to 20 and 32% for the biotite and siderophyllite, respectively) can be made. Even with this compensation, however, the amounts of charge balanced by cation ejection are still less than one-third of the total charge created. For these two micas, then, either deprotonation or a decrease in layer charge must have occurred to balance the remaining charge. Inasmuch as a large decrease in layer charge seems unlikely from the results of the K,Rb-H$_2$O$_2$ treatments, deprotonation must have been a major factor in the oxidation mechanisms for these two Na-micas. This is clearly evident by the elimination of the OD stretching bands in the infrared spectrum for the Na-H$_2$O$_2$ treated biotite samples (Figure VI-2), and in the diminished intensity of these bands in the Na-H$_2$O$_2$ treated siderophyllite spectrum relative to the Na-deuterated spectrum (Figure VI-3). The effluent data, thus, suggest that the loss of OD shown in the infrared spectra for the H$_2$O$_2$-treated micas was due to deprotonation rather than to an exchange of protons for deuterons.

Summary and Conclusions

The results of these weathering studies with expanded and deuterated micas confirm that several charge-balancing reactions occur when micas are K-depleted and oxidized in aqueous solutions. During K-depletion, the mica layer charge decreases slightly in proportion to,
but not in equivalence with, the fraction of Fe(II) that is oxidized. Subsequent oxidation of the structural Fe(II) by $\text{H}_2\text{O}_2$ solutions containing K and Rb, however, seems to have little effect on the layer charge. Thus, the bulk of the charge created by Fe(II) oxidation in the contracted micas (and, presumably, in the expanded micas) is balanced by mechanisms other than layer charge loss.

Both octahedral cation ejection and a loss or exchange of structural hydroxyls occur in micas treated with $\text{H}_2\text{O}_2$ solutions. Although it is uncertain whether the loss of protons is permanent or if a proton exchange reaction is involved, charge balance calculations based on analyses of the effluents suggest that some permanent deprotonation must occur. When deprotonation does occur, it seems to be localized at the edges and exposed surfaces of the mica and, consequently, does not allow a means for oxidation of contracted mica layers. Indeed, the evidence from this study confirms the conclusion reached in Chapters IV and V that very little oxidation occurs without an opening of the mica layers. Furthermore, just as an expansion of the interlayer region can induce oxidation in a reducing environment (Scott and Youssef, 1979), this study has shown that the presence of a strong oxidant can induce an opening of the interlayer region in a high-K solution if there is sufficient Fe(II) in the mica.

Finally, this study has produced chemical and infrared spectroscopic evidence for the protonation of basal oxygens during K-depletion in aqueous solutions, and has demonstrated the sensitivity of the interlayer region to intercalation with $\text{H}_2\text{O}_2$. The contraction
of the Na-H\textsubscript{2}O\textsubscript{2} treated samples can most easily be explained by the enhanced hydrogen bonding provided by interlayer H\textsubscript{2}O\textsubscript{2} and is an interesting phenomenon worthy of further study.
The primary aim of this work was to examine the occurrence of structural Fe oxidation in micas weathered by aqueous solutions, and in particular, to resolve the question of whether these solutions can oxidize structural Fe in micas whose layers remain contracted. Inasmuch as the oxidation of structural Fe must be coupled to a charge-balancing reaction, considerable emphasis was placed on identifying and characterizing the possible charge-balancing reactions that can occur. To this end, several analytical and experimental techniques were developed, and weathering experiments were performed on three trioctahedral micas encompassing a wide range in Fe(II) content.

A method for the assay of Fe(II) in micas was developed after a survey of the existing methods found none that completely satisfied the multiple criteria of precision, speed, and ability to analyze large numbers of samples at the same time. The procedure that was developed involves the digestion of the sample in a HF-H₂SO₄ acid matrix that also contains a known quantity of the mild oxidant, V(V). The digestion is carried out in a plastic bottle at 60°C for 0.5 to 4 hours, after which the digestate is cooled and H₃BO₃ and H₃PO₄ are added to complex the excess fluoride and sharpen the endpoint. Then, a known excess of Fe(II) is added and the solution titrated to a purple endpoint using Na p-diphenylaminesulfonate as the indicator. Salient features of the method include gravimetric measurements of the quantities of redox
reagents added, rapid addition of all reagents by manual dispensers, a very sharp endpoint, and use of the same container throughout the procedure. Interferences from F and Al, and from Mg and Si to a lesser extent, were observed, however, and attributed to the formation of an insoluble Fe(II)-oxyfluoride compound similar to ralstonite during the digestion procedure. These interferences are believed to be common to all titrimetric Fe(II) procedures that employ HF to dissolve the sample and can be corrected for if high levels of Al are present in the sample. The results obtained by the method were very precise and agreed well with recommended values published for several standard minerals. The method, therefore, was considered quite suitable for the analysis of trioctahedral micas with low or moderate levels of structural Al.

An x-ray diffraction method for estimating the occupancy of the octahedral and tetrahedral cation sites in trioctahedral micas was also developed. This method involves calculations of a range of structure factors for the 004 and 005 reflections of the mica based on a thorough chemical analysis, values for the fractional coordinates of the planes parallel to the basal surfaces, and a series of assumptions about the distribution of the cations between the tetrahedral and octahedral sites. The calculated structure factors are then compared with the observed structure factors for the same reflections to obtain information regarding the actual cation distribution in the mica. The method can also be used to monitor relative changes in the cation site occupancies, by simply comparing the observed structure factors for samples of the same mica after various weathering treatments. Six
trioctahedral micas were analyzed by this method, which proved to be quite precise. The results showed evidence for tetrahedral vacancies in the biotite used in the weathering experiments and higher levels of tetrahedral Fe in an annite and lepidomelane than were predicted by conventional cation distribution assumptions.

An apparatus for the continuous treatment of mica samples by fresh weathering solutions was designed and constructed of inert plastic. This flow-through apparatus was used to weather mica samples at 80°C for periods as long as 36 days. Three trioctahedral micas, a phlogopite, a magnesian biotite, and a siderophyllite, were chosen to receive these weathering treatments. The 10- to 20-μm size-fraction (equivalent spherical diameter) of these micas was prepared and used in all weathering experiments and analyses.

In the first weathering experiment, samples of the micas were treated for various periods with 1 M K solutions (to inhibit the expansion of the interlayer region) that did or did not contain H₂O₂ as a strong oxidant. Samples of the effluent solution were collected at regular intervals and analyzed for their H₂O₂, Al, Mg, and Fe content. The mica samples were assayed for Fe(II) and cation site occupancy, and analyzed by Mössbauer and infrared spectroscopy, before and after treatment by the weathering solutions.

The results of this experiment showed substantial oxidation of the Fe(II) in the biotite and very slight oxidation of that in the siderophyllite after 36 days of treatment by the H₂O₂-containing solution. No oxidation of structural Fe(II) was observed in the
phlogopite or in any of the mica samples that were treated with solutions that did not contain \( \text{H}_2\text{O}_2 \). X-ray diffraction and infrared spectroscopic analyses showed that a leaching of tetrahedral cations during treatment by the non-oxidizing solutions occurred, and that an ejection of octahedral cations occurred in response to the oxidizing treatments. No Mössbauer spectroscopic evidence for the formation of magnetically ordered Fe oxide phases was found nor was there any clear infrared evidence for the permanent deprotonation of structural hydroxyls as a result of oxidation.

To compare the dissolution rates of the micas during the oxidizing and non-oxidizing weathering treatments, the cumulative amounts of Al, Mg, and Fe measured in the effluent after various periods were fit to a heterogeneous kinetic rate law. The rate constants obtained from these fits showed lower dissolution rates in the \( \text{H}_2\text{O}_2 \) solutions than in the non-oxidizing solutions for the phlogopite and siderophyllite, whereas approximately the same rates of dissolution were observed for the biotite in both solutions. The lower rates were attributed to smaller effective surface areas of the mica samples in these treatments as a result of the adsorption of \( \text{H}_2\text{O}_2 \) (or of \( \text{O}_2 \) produced by the decomposition of \( \text{H}_2\text{O}_2 \)). Thus, the equivalence of dissolution rates that were obtained with the biotite in the two weathering solutions was taken as evidence for a substantial increase in the surface area of the biotite by exfoliation during the \( \text{H}_2\text{O}_2 \) treatment. Corollary evidence for this exfoliation was also seen in the broadening of the x-ray diffraction peaks of the treated biotite samples and in the higher rate of \( \text{H}_2\text{O}_2 \).
decomposition measured during treatments of this mica.

To verify the occurrence of exfoliation during the \( \text{H}_2\text{O}_2 \) treatments, a second weathering experiment was conducted. In this experiment, untreated mica samples, and samples of the micas that had been weathered for 36 days by the 1 M K solutions with or without \( \text{H}_2\text{O}_2 \), were treated for 12 days in a non-oxidizing 1 M K solution. The dissolution rates of the phlogopite samples were the same and thus showed no effect of the previous weathering treatments. In contrast, the \( \text{H}_2\text{O}_2 \)-treated biotite samples dissolved nearly 7 times faster than the biotite samples that had been weathered only by the non-oxidizing solution. A small increase in the dissolution rate of the oxidized siderophyllite was also observed. Because the dissolution rate depends on surface area, these data provided strong evidence for the occurrence of exfoliation in those micas where oxidation also occurred, and its absence where no oxidation occurred.

To study changes in layer charge and in the status of the structural hydroxyl groups during weathering, and to verify the effects of interlayer expansion on oxidation, a third weathering experiment was performed. The micas weathered in this experiment, however, were pre-treated to replace interlayer K with Na, and to replace structural OH groups with OD groups so that any exchange of structural "protons" with the protons in solution could be detected by infrared spectroscopy. After deuteration, half of the mica samples were resaturated with K to contract the layers. These expanded and contracted micas were then treated by weathering solutions that did or did not contain \( \text{H}_2\text{O}_2 \) and
that either enhanced or inhibited the expansion of the mineral. Thus, a total of four treatment solutions were involved: 1 M Na, 1 M Na + H₂O₂, 1 M K, and 1 M K + H₂O₂. Rubidium (Rb), because of its chemical similarity to K was added to the K weathering solutions as a tracer so that a distinction between the original K present in the mica and that derived from the solution could be made if expansion of the interlayer region occurred. As in the other experiments, the effluents were collected and analyzed for the amounts of Al, Mg and Fe released by the mica samples during treatment. The micas were assayed for Fe(II) and analyzed by infrared spectroscopy before and after treatment. The layer charge relationships of the micas weathered by the K solutions were also monitored by analysis of the K, Na, and Rb in the mica before and after treatment.

The results of this experiment showed that nearly a third of the Fe(II) in the biotite and siderophyllite was oxidized during the preliminary K-depletion process. A small decrease in layer charge accompanied this oxidation. Subsequent treatment of the contracted micas by the K weathering solutions, however, caused very little change in the layer charge of the biotite and siderophyllite micas, and only a small decrease in the phlogopite. As in the previous experiments, little or no oxidation was observed in the phlogopite as a result of either the pretreatment or the weathering treatments. Substantial oxidation of Fe(II) in the biotite and siderophyllite samples occurred in both Na solutions, although more oxidation was observed from the solutions that contained H₂O₂. Oxidation and sharp increases in Rb
content were seen in the micas treated by the K solutions that contained
H\textsubscript{2}O\textsubscript{2}. In contrast, the K solutions that did not contain any H\textsubscript{2}O\textsubscript{2} caused
no oxidation of Fe(II) or change in the Rb content of the mica samples. These results provide more evidence that oxidation occurs only when an
expansion or exfoliation of the interlayer region also occurs, and suggest that layer charge is not a major charge-balancing reaction
during the later stages of weathering.

The infrared spectra for these micas showed that deuteration of the
structural hydroxyls during the preliminary treatments was successful. No infrared evidence for hydroxyl exchange or deprotonation was seen in
the phlogopite spectra as a result of weathering, but the siderophyllite
and biotite spectra showed slight and extensive losses in the
intensities of the OD stretching bands, respectively, as a result of the
H\textsubscript{2}O\textsubscript{2} treatments. The biotite and siderophyllite spectra, therefore,
showed that deprotonation or proton exchange, occurred when these micas
were oxidized in aqueous solutions.

Analyses of the effluent solutions that were collected in the third
experiment showed low and roughly comparable rates of release of the Al,
Mg, and Fe fractions from the micas treated by the Na-matrix solution.
With treatment by the Na-H\textsubscript{2}O\textsubscript{2} solution, however, the total amounts of
these cations released were much higher, and larger fractions of the Al
and Fe in the micas were released than of Mg. The higher levels of
release by the Na-H\textsubscript{2}O\textsubscript{2} treated micas were attributed to the ejection of
cations (trivalent preferentially to divalent) to balance charge created
by oxidation of structural Fe(II). Charge balance calculations,
however, showed that less than one-third of the total charge created by Fe(II) oxidation in the biotite and siderophyllite was compensated for by cation ejection. The effluent data, thus, suggest that the losses of OD observed in the infrared spectra were the result of "deprotonation" reactions to balance charge rather than proton-deuteron exchange reactions.

Three major conclusions can be drawn from this work. First, the oxidation of structural Fe(II) in trioctahedral micas by aqueous solutions does not occur unless access of the octahedral sheet to the bulk solution is allowed by an expansion or exfoliation of the mica interlayer region. Second, several reactions occur to balance the charge created by structural Fe(II) oxidation. A small portion of the charge is balanced by a loss of interlayer cations, although some of this loss is also due to replacement of the cations by hydronium ions or protonation of the basal surfaces of the mica. Most of the charge created by oxidation, however, is balanced by octahedral cation ejection and by deprotonation of structural hydroxyls. The relative contributions of these two reactions to the overall charge-balancing process are probably related to the trivalent cation and hydroxyl contents of the the mica that is oxidized. Thus, the siderophyllite ejected a larger portion of its octahedral cations and showed less evidence for deprotonation than the biotite because of its higher octahedral Al content and lower hydroxyl content. The majority of the charge created by oxidation in both micas, however, was balanced by deprotonation. Third, because structural Fe(II) oxidation does not seem
to occur without expansion or exfoliation of the mica layers, the K-selectivity of the mica plays a role in determining the extent of oxidation that can occur. Micas that have a strong tendency to remain contracted, such as the siderophyllite, resist oxidation by limiting the access of the oxidant and the egress of the protons and octahedral cation. In essence, then, the propensity for oxidation is controlled by the stronger of two competing chemical potentials: the potential for oxidation and expansion imposed by the bulk solution around the mica particles and the anionic field strength or "contraction" potential that is innate to the mica structure.
I wish to express my appreciation to the following individuals who assisted in this endeavor: J. H. Espenson and B. C. Gerstein (Ames Laboratory, US-DOE), and R. Horton and M. L. Thompson (Agronomy Department, Iowa State University) served on my graduate committee; J. E. Benson and R. O. Jacobson (Ames Laboratory-DOE) provided access to the Picker x-ray diffractometer and VAX computer used for the cation site occupancy determinations; E. DeKalb (Ames Laboratory-DOE) performed the ICP-AES and XRF analyses on the untreated mica samples; C. E. Jacobson (Earth Sciences Department, Iowa State University), S. Sorensen (Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution) and the Curator of Minerals, National Museum of Natural History, Smithsonian Institution assisted in the acquisition of specimens of the lepidomelane and annite micas; R. S. Houk and J. J. Thompson (Ames Laboratory, US-DOE) provided training and access to the ICP-MS equipment that was used to analyze the effluent samples; R. G. Barnes and D. R. Torgeson (Ames Laboratory, US-DOE) provided a spectrometer, laboratory space, and computer time for the collection and interpretation of the Mössbauer spectra; and R. G. Riley, J. S. Fruchter and Dhanpat Rai (Battelle, Pacific Northwest Laboratories, Geochemistry Section) provided financial assistance and encouragement during the writing of the dissertation.

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The following general assumptions are incorporated into this model:

1) the particles to be dissolved are of a known, mathematically describable shape and size;
2) all the particles in a sample are identical;
3) the particles are homogeneous in composition and density;
4) dissolution proceeds at a uniform rate along all three geometric axes of the particles;
5) the total surface area of the particles that is exposed to a dissolving solution decreases with dissolution or remains constant with no dissolution.

The model is based on a series of papers presented by Delmon (1961a, 1961b, 1961c). Following his approach, the dimensions of the particles are described in terms of "half-dimensions", that is, the distance from the center of each particle along each of the three primary axes to the particle surface. In this derivation, the half-dimensions are represented by a, b, and c, with a < b and a < c.

By assuming a uniform rate of dissolution along all three axes, we assume that the shortest axis will approach extinction first and therefore be diagnostic for the dissolution of the particle as a whole. Measurements of the extent of dissolution, however, are made on a mass
basis. The first step in development of the model, therefore, is to relate the extent of dissolution on a mass basis to the shape and size of the particles expressed in terms of the shortest half-dimension.

To do this, we express the longer half-dimensions \((b_0, c_0)\) in terms of the shortest \((a_0)\):

\[
b_0 = a_0 + \lambda a_0, \quad [A-1]
\]

where \(\lambda = (b_0 - a_0)/a_0\), and

\[
c_0 = a_0 + \mu a_0, \quad [A-2]
\]

where \(\mu = (c_0 - a_0)/a_0\) and the subscript "0" indicates the half-dimension at time \(t = 0\). Because the rate of dissolution is assumed equivalent along all three axes, we can write,

\[
b = a + \lambda a_0 \quad [A-3]
\]

and

\[
c = a + \mu a_0, \quad [A-4]
\]

where \(a, b,\) and \(c\) are the half-dimensions at some time \(t > 0\).

The initial mass of the particles is given by
\[ m_0 = NRV_0 \]  

and similarly, at time \( t \) by

\[ m = NRV, \]  

where \( N \) is the number of particles present in the sample, \( R \) the density of the particles (g cm\(^{-3}\)), and \( V_0 \) and \( V \) the volume of each particle (cm\(^3\)) initially, and at time \( t \), respectively.

Because we know the geometry of the particles (assumption 1), we can write

\[ V_0 = \phi_{a_0 b_0 c_0} \]  

and

\[ V = \phi_{abc}, \]  

where \( \phi \) is a "form factor".

From Eqs. [A-5] and [A-7] we can write

\[ m_0 = NR\phi_{a_0 b_0 c_0}. \]  

Similarly, from Eqs. [A-6] and [A-8] we obtain
If we represent the mass dissolved from the particles at time $t$ by $m_d$, we can write

\[
m = m_0 - m_d
\]

for the mass remaining at time $t$. Written as a fraction of the original mass present, Eq. [A-11] becomes

\[
\frac{m}{m_0} = 1 - \alpha,
\]

where $\alpha = m_d/m_0$, the fraction of the original mass that has dissolved at time $t$.

Substituting Eqs. [A-9] and [A-10] into Eq. [A-12], we obtain

\[
1 - \alpha = \frac{NR*abc}{NR*abc_0b_0c_0}, \quad [A-13]
\]

From Eqs. [A-1], [A-2], [A-3], [A-4], and [A-13] we can write

\[
1 - \alpha = \frac{a(a + \lambda a_0)(a + \mu a_0)}{a_0(a_0 + \lambda a_0)(a_0 + \mu a_0)}.
\]

\[
[A-14]
\]
By multiplying out the terms,

$$1 - \alpha = \frac{a^3 + a^2a_0(\lambda + \mu) + aa_0^2(\lambda\mu)}{a_0^3[1 + (\lambda + \mu) + (\lambda\mu)]}.$$  [A-15]

Dividing through by $a_0^3$ we obtain

$$1 - \alpha = \frac{(a/a_0)^3 + (a/a_0)^2(\lambda + \mu) + (a/a_0)(\lambda\mu)}{1 + (\lambda + \mu) + (\lambda\mu)},$$  [A-16]

or alternatively,

$$\alpha = 1 - \frac{(a/a_0)^3 + (a/a_0)^2(\lambda + \mu) + (a/a_0)(\lambda\mu)}{1 + (\lambda + \mu) + (\lambda\mu)}.$$  [A-17]

In Eqs. [A-16] and [A-17], therefore, we have expressions that relate the fraction of the original mass that has dissolved to the shape and size of the particles as represented by the shortest half-dimension, $a$. What is needed now is an expression for the half-dimension "$a" as a function of time.

To do this, the specific reaction mechanism and the rate-limiting step of the mechanism need to be identified. In the present study, the surfaces of the mica particles are assumed to consist of cation sites, in which a metal cation is coordinated by structural oxygens and, under the conditions of the "main" experiment in Chapter IV, by an aqueous
species. As a first approximation we can divide the possible aqueous coordinating species into two groups, a strongly-complexing group (e.g., EDTA$^{-2}$, Acet$^{-2}$) and a weakly-complexing group (e.g., H$_2$O, O$_2$, CO$_2$, H$_2$O$_2$, MeEDTA$^0$, MeAcet$^0$). We assume, furthermore, that it is the strong complexers that are responsible for dissolving the mica particles and that the weak complexers have an insignificant effect on the dissolution process. On the basis of these assumptions, we can propose the following dissolution reaction mechanism in which $Y$ represents the strong complexers, $W$ the weak complexers, $M$ the metal species of interest, and $S_{YM}$ and $S_{WM}$ represent the surface sites containing the metal cations (M) that are coordinated by either strong ($Y$) or weak ($W$) complexers, respectively:

\begin{align*}
Y_{bulk} & \xrightarrow{k_1} Y_{ddl} \quad \text{[Step I]} \\
W_{bulk} & \xrightarrow{k_2} W_{ddl} \quad \text{[Step II]} \\
Y_{ddl} + S_{WM} & \xrightarrow{k_3} S_{YM} + W_{ddl} \quad \text{[Step III]} \\
S_{YM} & \xrightarrow{k_4} Y_{YM} \quad \text{[Step IV]}
\end{align*}
Steps [I], [II] and [V] represent equilibria between the bulk solution (bulk) and the diffuse double layer (ddl) region extending from the surfaces of the mica particles. They incorporate the effects of diffusion and bulk solution flow rate through the reactor vessel, but are not expected to be rate-limiting at the flow rates maintained in this study.

Step [III] represents the relative tendency of the two types of aqueous species to form surface complexes with the exposed metal ions at the mica surface. Step [IV] is the actual dissolution step, in which a surface complex becomes detached from a mica particle. This step is proposed as the rate-limiting step.

Because we are dealing with a flow-through system, $Y_{bulk}$ and $W_{bulk}$ are continually being replenished, and $Y_{bulk}$ continually depleted. Furthermore, if we assume that rates of diffusion for species between the diffuse double layer region and the bulk solution are high relative to the dissolution rate (i.e., steps [I], [II], and [V] have very rapid kinetics relative to [IV]), we can substitute the bulk concentrations for the diffuse double layer concentrations. Our mechanism is then reduced to two steps:
Now consider the following. A given cation site at the surface of a mica has a finite depth, \( z \). Dissolution of the site results in a change in the shortest dimension of the mica particle \( da = -z \). The probability that this site will dissolve during a period of time, \( dt \), is related to whether the site is complexed by \( W \) or \( Y \) species. Indeed five types of reactions are possible during the time period, \( dt \):

\[
\begin{align*}
S_{WM} & \Rightarrow S_{YM} & da = 0 & \text{[Reaction A]} \\
S_{WM} & \Rightarrow S_{WM} & da = 0 & \text{[Reaction B]} \\
S_{YM} & \Rightarrow S_{WM} & da = 0 & \text{[Reaction C]} \\
S_{YM} & \Rightarrow S_{YM} & da = 0 & \text{[Reaction D]} \\
S_{YM} & \Rightarrow Y_{bulk} & da = -z & \text{[Reaction E]}
\end{align*}
\]

Only Reaction [E], however, results in dissolution and a change in the value of \( a \). If we assume that at a given site the probability of
Reaction [E] occurring \( (P_E) \) during any particular time period \( (dt) \) is constant, we can write

\[
\frac{P_E}{dt} = k_{app}
\]

\[
dt < k_{app}^{-1},
\]

where \( k_{app} \) is the apparent rate constant. The assumption of constant \( P_E \) is true so long as the equilibria for Steps [I], [II], and [V] are reached very rapidly relative to Step [IV], and the ratio \([W_{bulk}]/[Y_{bulk}]\) remains constant. Obviously, a different ratio of weak to strong complexers in the dissolving solution would result in different values for \( P_E \) and \( k_{app} \).

By extension of Eq. [A-18], the average change in the "a" dimension of a given particle during time period \( dt \) as a result of Reaction [E] is simply

\[
\frac{da}{dt} = \frac{(P_E)(-z)}{dt}.
\]

But \( P_E = k_{app}(dt) \) and \( da = a - a_0 \), so we can write

\[
a = a_0 - k_{app}(z)(dt)
\]

or, when \( t_0 = 0 \),
\[ a = a_0 - k_{\text{app}}(z)(t). \]  \[ \text{[A-21]} \]

In Eq. [A-21], we now have an expression for \( a \), the value of the shortest half-dimension, in terms of \( t \). From this expression, we can extract an apparent rate constant once an assumption about \( z \), the site depth has been made.

If we substitute Eq. [A-21] into Eq. [A-17], we obtain an expression that relates the fraction of the mica particle dissolved to the contact time between the mica and the dissolving solution:

\[ a = 1 - \left( \frac{a_0 - k_{\text{app}}zt}{a_0} \right)^3 + \left( \frac{a_0 - k_{\text{app}}zt}{a_0} \right)^2(\lambda + \mu) + \left( \frac{a_0 - k_{\text{app}}zt}{a_0} \right)(\lambda \mu) \]

\[ \frac{1 + (\lambda + \mu) + (\lambda \mu)}{[\frac{a_0}{a_0}]} \].  \[ \text{[A-22]} \]

We can apply Eq. [A-22] to describe the dissolution of any number of particles by assuming that all the mica particles have the same dimensions (i.e., a single particle size and shape). Generally, if the particles in a sample are not of uniform size, a particle-size distribution function must be included in the expression for \( a \) (Delmon, 1961c). In the present study, particle sizes ranged from 10- to 20-\( \mu \)m (equivalent spherical diameter). Sensitivity analyses showed, however, that inclusion of a particle-size distribution function in the
dissolution model for these samples had a negligible effect on the rate constants obtained. Thus, a particle-size distribution function was omitted from the model and this derivation.

In summary, an expression relating the cumulative amount of metal ion dissolved from the mica to the time of contact with the dissolving solution has been derived. To obtain the apparent rate constant, $k_{\text{app}}$, estimates of $a_0$ and $z$ are made from knowledge of the particle size-fraction used and the mica structure. These estimates are entered into Eq. [A-22] along with the cumulative fractions of the total metal ions dissolved ($\alpha$) at various times. Values of $k_{\text{app}}$ are then substituted successively into the equation until the best fit of the observed and calculated $\alpha$ values is obtained using a weighted least squares procedure.