Kinetics of potassium release from biotite in solutions containing sodium tetraphenylboron

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REED, Marion Guy, 1931—
KINETICS OF POTASSIUM RELEASE FROM BIOTITE IN SOLUTIONS CONTAINING SODIUM TETRAPHENYLBORON.

Iowa State University of Science and Technology Ph.D., 1963
Agriculture, general
University Microfilms, Inc., Ann Arbor, Michigan
KINETICS OF POTASSIUM RELEASE FROM BIOTITE
IN SOLUTIONS CONTAINING SODIUM TETRAPHENYLBORON

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Soil Fertility

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Of Science and Technology
Ames, Iowa
1963
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INTRODUCTION

The K in micas occurs primarily in the interlayer positions and is relatively difficult to replace with other cations. When mica particles are placed in an extracting solution, K is released to the solution until an apparent equilibrium is established. It has been shown that the amount of K in solution necessary to stop K release is relatively small. Only if the released K is removed, from the solution, will the process of K release continue. The kinetics of the process by which K is released under these conditions, however, has not been fully resolved.

There is considerable interest in the processes involved in K release from micas since the K in micas is one of the ultimate sources of K for plant nutrition. As plants remove the water-soluble and exchangeable K, interlayer K is released to the plant-available forms. The ability of a soil to continue to supply K to plants is dependent on this process of release.

K release is also an important process in the weathering of micas. It is generally believed that K removal is the first stage of weathering of the K micas to their respective weathering products. The natural leaching of soils containing K micas tends to keep the concentration of K in solution low and hence K is released to the solution.
To study the processes of K release by micas it is necessary to keep the concentration of K in the extracting solutions very low. A common method for achieving this is by leaching the mica with a salt solution. However, with the leaching method, it is difficult to keep the K concentration in the solution constant and also very high leaching rates are necessary to maintain a relatively low concentration in solution. On the other hand, NaTPB can be used to keep the concentration of K in solution constant and at a low level. With NaTPB in the solution the K level in solution is governed by the solubility product constant of KTPB which is precipitated. Also, the effect of the concentration of K in solution on K release can be easily studied with NaTPB extracting solutions by merely adjusting the concentration of NaTPB.

A theoretical equation for the release of K from mica has been derived assuming that the rate limiting process involves the diffusion of K radially from a receding weathering front to the edge of the particle. The equation accurately describes K release from biotite in extracting solutions containing NaTPB. However, the equation contains a group of parameters which are constant with time but vary with the extracting solution and biotite characteristics.

The primary objective of this thesis was to evaluate the significance of some of the parameters in the
theoretical equation. Attention was focused mainly on the parameters affected by the characteristics of the extracting solution.
LITERATURE REVIEW

Nature of Potassium in Mica

Pauling (1930) was first to formulate the structure of micas. Micas are contracted 2:1 layer silicates made up of stacked layers each consisting of an octahedral sheet sandwiched between two tetrahedral sheets. In well-crystallized mica, one-fourth of the Si is replaced by Al in the tetrahedral sheets. The resulting charge deficit is balanced by interlayer cations. In biotite and muscovite, the balancing cations are K which occupy the cavities formed by the hexagonal rings of oxygens on the bases of the linked tetrahedra of opposite lattice layers (Pauling, 1930; Jackson and West, 1930; Bragg, 1937; Page and Baver, 1939; and Barshad, 1952).

Jackson and West (1930) give the distance from the center of interlayer K ions to the seat of a charge in the tetrahedral sheet as 2.19 Å whereas the distance to a charge in the octahedral sheet is 4.99 Å. Wear and White (1951) concluded that since the distance between the center of the K ion and the seat of the charge is approximately twice as far in the case of the octahedral sheet as in the tetrahedral sheet, the force of attraction between the layers should be approximately four times greater where the charge is in the
tetrahedral sheet. Since the charge deficit in micas is primarily in the tetrahedral sheet, this at least partly explains the relatively great tenacity with which potassium micas are held in the contracted state.

Page and Baver (1939) stated that since the interlayer surface consists of a layer of oxygen atoms arranged hexagonally, the space in the center of the hexagon is the size of an oxygen atom which is 2.8 Å. The diameter of the K ion is 2.66 Å so it should fit nicely in this space. The K ion should bind the two layers together tightly because the K ion is very close to the negative charges distributed in the tetrahedral sheet. Barshad (1950) gave the calculated value for the radius of the spherical cavity within the network of oxygen atoms as 1.35 Å.

In explaining the unique behavior of K, NH₄, Rb and Cs as balancing cations in micas, Barshad (1952) suggests that because of their size, these ions are in the middle of the cavity formed by the hexagonal oxygen rings and consequently are attached equally to the two sheets resulting in a strongly contracted mica. On the other hand, small ions tend to "bury" themselves in one layer in the relatively large holes and the binding force is reduced.
Barshad (1948) removed considerable K from a sample of 1-μ biotite by leaching with 1 N MgCl₂ for three months. Part of the K-depleted biotite was resaturated with K while the rest remained Mg saturated. Water loss on heating between 20 and 150°C was 0.34 per cent for the K-saturated biotite and 12.77 per cent for the Mg-saturated material. By x-ray diffraction analysis, basal spacings of 10.29 Å and 14.47 Å were shown for the K-saturated biotite and the Mg-saturated material, respectively. He concluded that he had converted biotite to vermiculite by removing the interlayer K.

Barshad (1954) attempted to relate removal of native and fixed K from vermiculite and biotite to the interlayer charge by leaching samples of different charge with 1 N MgCl₂. He found that native K is replaced much more readily from vermiculite and biotite samples with interlayer charges ranging from 194 to 215 me./100 g. than from those with 240 to 262 me./100 g. Similarly fixed K was replaced much more readily from samples with a charge of 159 me./100 g. than those with a charge ranging from 216 to 219 me./100 g. It should be noted that the fixed-K data were from samples of K-saturated vermiculite only and the native-K data were from samples of biotite or vermiculite. Without specifying the
cation, Barshad (1954) concluded that a crystal lattice with an interlayer charge greater than 150 me./100 g. would be contracted.

Caillére et al. (1949) altered a sample of phlogopite by boiling it in 40 per cent MgCl₂ for 135 hours. The resulting material had basal spacings of 10, 12 and 14 Å. They concluded from the x-ray and D.T.A. data that the phlogopite was converted to vermiculite.

Mortland (1958) studied the rate of K release from samples of < 250-μm biotite by leaching with 0.1 N NaCl at a constant rate. The release rate was constant until approximately half of the K was removed after which the rate decreased logarithmically with time. There were approximately 6 ppm. K in the leachate during the period of constant K release when a leaching rate of 4 ml. per minute and 20 g. of biotite were used. When the leaching rate was increased to 9 ml. per minute and 10 g. of biotite were used, the leachate contained approximately 4.4 ppm. K during the period of constant K release. The increased leaching rate resulted in a 3-fold increase in the rate of K release during the period of constant K release.

X-ray diffraction patterns of the biotite degraded to different degrees showed either a 10 Å or 14 Å spacing or both indicating that there was no significant interlayering of expanded and nonexpanded material. Photomicrographs of
partially weathered biotite showed a band of expanded material on the outside edges and biotite in the centers of the particles.

In the same study, Mortland (1958) studied the rate of K release from biotite where 20 g. of < 250 μ biotite were allowed to equilibrate in a liter of 0.1 N NaCl. After the exchangeable K was removed, the K in solution increased linearly with the logarithm of time. When the sample was placed in the equilibrium system, 5.4 me. K/100 g. were released from the mineral immediately. Apparently this was exchangeable K. After 7 days, 58 ppm. K were in solution and 7.67 me. of K/100 g. were removed from the biotite. Only 2.3 me./100 g. of interlayer nonexchangeable K were released by the biotite. This probably represented the fringe between exchangeable K and nonexchangeable interlayer K. Therefore, it is doubtful that the results of this experiment give the rate of release of interlayer K to equilibrium solutions.

Mortland and Ellis (1959) studied the release of fixed K from 35 to 60 mesh vermiculite by leaching with 0.1 N NaCl. A mathematical expression describing diffusion from a slab did not fit the experimental data whereas an expression describing diffusion through a film of constant dimension fit the data closely. They concluded that the rate-limiting process in the experiment was the diffusion of Na and K ions through a solution film to and from the particles rather than
diffusion within the interlayer space.

It should be pointed out that both the equation describing film diffusion and the one describing particle diffusion do not consider the moving weathering front that Mortland (1958) has shown exists when K is removed from biotite. That is, the equations consider that none of the interlayer K ions are physically trapped by the contracted lattice and all of the K ions are free to move on a concentration gradient. If the K in the vermiculite is fixed K, it is reasonable that the lattice is in a collapsed state which means that the K ions are immobile until the lattice is expanded around the K ion.

The rates of K release from fixed and native forms were compared by Ellis and Mortland (1959) by leaching weathered biotite that contained fixed K and unweathered biotite with 0.1 N NaCl. There was little difference between x-ray patterns of weathered biotite containing fixed K and unweathered biotite. There was much difference, however, between the K release rates of the two materials. The native biotite released K at nearly a constant rate initially; then the rate decreased logarithmically with time whereas the fixed K release rate decreased with time. The ease of release of fixed K appeared to be directly related to the extent of the previous K removal. This could be the result of a reduction in charge density during the first K extraction. In one case,
where the total K was reduced to 38 me./100 g., the total charge decreased from 202 to 179 me./100 g.

Mortland and Lawton (1961) studied the relationships of particle size of biotite to K release, oxidation state of iron, cation-exchange capacity and total charge of the mineral. A large sample of < 250 μ biotite was leached with 0.1 N NaCl and at different stages of K removal, samples were removed and fractionated into different size fractions. In the early stages of K removal, the smaller particles released K much faster than the larger particles. By the last stage, when 50 per cent of the total K was removed, the larger particles had lost about as much K as the smaller particles. The FeII/FeIII ratios were lower in smaller particles and with higher degrees of K removal.

Release of Interlayer Potassium to Precipitants

White (1950) was the first to use K precipitants to remove large amounts of K from micaceous minerals. He treated illite with sodium cobaltinitrite which precipitated the K as it was released by the illite. X-ray diffraction patterns of glycerol solvated samples showed the formation of an expanded basal spacing of 17.9 Å at the expense of the 9.92 Å spacing when K was removed.

Hanway (1954) in a study of NH₄ fixation and release in
soils and micaceous minerals, introduced sodium tetraphenylboron (NaTPB) as a precipitant for K released by minerals. Illite treated with NaTPB and then NH₄ saturated contained considerably more fixed NH₄ than the untreated NH₄-saturated illite. Apparently this increase in NH₄ fixing capacity was due to K being removed from the illite during the NaTPB treatment.

De Mumbrum (1959) employed NaTPB to remove large amounts of K from biotite, muscovite and vermiculite to study the exchangeable K levels of K-depleted materials. Mica samples were mixed with equal weights of NaTPB, moistened and dried at 110°C. They were washed with pure acetone to remove the excess NaTPB and the KTPB precipitate. Possibly, much of the K once precipitated was readsorbed by the mica since KTPB is ionized when dissolved in acetic solution. However, by this method, 67 per cent of the K was removed from biotite and 25 per cent from muscovite. X-ray diffraction patterns showed the formation of expanded material at the expense of the collapsed mica as K is removed. The K-depleted biotite expanded to 12.6 to 13.0 Å when Mg saturated and glycerol solvated whereas the K-depleted muscovite expanded to 14 Å.

Different quantities of K were added to the K-depleted biotite and dried at 110°C. When exchangeable K was plotted against total K after the K additions, the exchangeable K was constant at 0.4 me./100 g. until the total K increased to
75 me./100 g.; above this the exchangeable K increased sharply. In the K release experiments a constant exchangeable K level of 0.4 me./100 g. was maintained even though the total K contents exceeded 75 me./100 g. Apparently, during readsorption the lattice collapsed and physically inhibited further readsorption of K.

Scott et al. (1960) extracted K from soils and micaceous minerals with NaTPB-NaCl solutions to determine the ease with which nonexchangeable K can be removed when the blocking effect of fixable cations is reduced. Essentially all of the K in vermiculite, 12 per cent of the K in muscovite and as much as 47 per cent of the K in illite was removed by the NaTPB-NaCl solutions. It was shown however that some of the released K was probably readsorbed by the degraded mineral when acetone was added to dissolve and remove the precipitated KTPB. Thus, to reduce this effect and to enhance the amount of K extracted, Scott and Reed (1962a) treated < 50 µ biotite samples with NaCl-NaTPB solutions and evaluated various methods of separating the precipitated K from the resulting mixture. Boiling the degradation system in 0.5 N NH₄Cl gave the least readsorption of K by the mineral and consequently the highest amount of K removed. It was observed that TPB solutions decompose with time, especially when in contact with finely divided minerals. A small amount of EDTA in the extracting solution stabilizes
the TPB against decomposition.

Most of the K in biotite was easily extracted by placing the biotite in 1 N NaCl - 0.067 N NaTPB solutions that also contained a small amount of EDTA. The rate of K removal from biotite varied inversely with particle size. The rate of K release in each size fraction was relatively rapid initially then the rate decreased with time. There was no period of constant rate as was shown by Mortland using NaCl leaching.

Na-saturated biotite that contained only 3.9 me. K/100 g. after extraction with NaTPB, had an expanded lattice with a 15 Å basal spacing with or without glycerol. On air-drying the sample with glycerol, 13.7 and 14.2 Å spacings were shown but the sample without glycerol lost one layer of water and gave a 12.3 Å spacing. The loss of this interlayer water resulted in an endothermic peak at 135°C in the differential thermal curve.

In similar work with illite, Scott and Reed (1962b) determined the rate of K removal and the effect of the K extraction on the mineral properties. Only the first 30 me. K/100 g. were removed from illite at a rate comparable to the rate from < 50 μ biotite. The rest of the K was removed at a progressively slower rate but it was possible to remove 74 me./100 g. (68 per cent of the total) by extracting the illite for 63 days. During this time, the amount of K removed was linearly related to the logarithm
of time.

The amount of \( \text{NH}_4^- \) adsorbed and fixed by moist \( \text{NH}_4^- \)-saturated \(< 2 \mu \) illite was increased by 62.4 me. and 35.2 me./100 g., respectively, when 69.1 me. K/100 g. were removed. There was no evidence of a change in charge density of the illite when this much K was removed, but the lattice of the Na-degraded illite was largely expanded to the 14 Å by glycerol.

Reed and Scott (1962), in a study of the mechanism of K release from micas, extracted K from different size fractions of biotite and muscovite using NaTPB solutions. K was released from biotite much faster than from muscovite, even though, in each case, the K concentration in solution was the same. There was an inverse relationship between particle size and rate of K release from biotite and muscovite. K release by each size fraction was very rapid initially then decreased with time.

Release of Interlayer Potassium to Molten Salts

White (1954) treated muscovite with molten lithium nitrate (LiNO₃) to remove the interlayer K. The untreated muscovite contained 223 me. K and 15 me. Li/100 g. whereas the treated muscovite contained 63 me. K and 94 me. Li/100 g. The treated muscovite had a basal spacing of 17.8 Å with
glycerol.

By treating a < 5-μ muscovite sample with molten LiNO₃, White (1956) removed a large portion of the interlayer K from mica and Li was fixed in a nonexchangeable position. When the degraded sample was Ba saturated and glycerol solvated, x-ray diffraction showed a basal spacing of 17.8 Å.

White (1956) suggested that Li ions migrate to the empty octahedral positions and thus reduce the layer charge. The 006 x-ray diffraction peak is widely used to differentiate between dioctahedral and trioctahedral minerals. An 006 spacing of 1.50 Å is associated with the dioctahedral micas while a 1.53 Å spacing is associated with the trioctahedral micas. The 006 spacing was not changed from 1.50 to 1.53 Å by the molten LiNO₃ treatment as one might expect if the Li migrated to the octahedral sheet. The charge density was reduced from 238 me./100 g. to 155 me./100 g. after treating the muscovite with molten LiNO₃ at 300°C for 18 hours.

In another study, White (1958) studied the expansion properties of muscovite treated with molten LiNO₃ to reduce the layer charge to different levels. No significant lattice expansion took place until the layer charge was reduced to 163 me./100 g. whereupon it expanded to 11.8 Å with a relatively broad peak. It was concluded that no expansion would take place in muscovite until the surface charge density was reduced to $6.7 \times 10^4$ esu/cm².
Bronson et al. (1959) removed 90 per cent of the K from muscovite with molten LiNO$_3$. Different quantities of K were added back to the degraded muscovite and the 001/002 ratios were inversely related to the total K content. The 001/002 ratios could be used to indicate in a relative manner the extent of weathering.

The swelling characteristics of muscovite treated with molten LiNO$_3$ for different periods of time were studied by Bailey (1961). The basal spacing of the expanded material was 12.26 Å regardless of the charge density when Na saturated. However, when it was Ca saturated the expanded spacing started at 14.97 Å and increased to 15.77 Å as the charge density was reduced. Mg-saturated samples started at 12.27 Å and increased to 14.02 Å as the charge density was reduced. When the samples were glycerol solvated all of the Na-, Ca- and Mg-saturated samples expanded to 18 Å.

White et al. (1961) showed by infrared spectroscopy that Li ions migrate into the vacant octahedral sites of muscovite and montmorillonite when treated with molten LiNO$_3$ at 300°C. The Al-OH flexion frequency (915 m$^{-1}$) was eliminated by the molten LiNO$_3$ treatment indicating that the bonding in the octahedral sheet is altered by the presence of the Li ion.
Mechanism of Potassium Release

Walker (1949), in a study of the natural decomposition of biotite in the soil, postulated that

Initially, the process of weathering appears to lie in the replacement of the most accessable K ions by water molecules which are of similar size. . . . As this replacement continues toward the interior of the flakes, the binding between the layers loosens and the spacing increases slightly.

It was postulated that oxidation of ferrous iron, substitution of OH for O and loss of Mg take place in order to balance the lattice charges when K ions are replaced by water molecules.

X-ray diffraction of a number of samples with different amounts of total K showed that in biotite samples of low total K the intensity of the 14 Å peak was high and the intensity of the 10 Å peak was low whereas it was just the opposite in samples with high total K. It was concluded that as K is removed from biotite, expanded material is formed at the expense of contracted biotite.

Jackson et al. (1952) studied the sequence of weathering of layer silicates by observing minerals weathered to different degrees naturally. It was postulated that some or all of the following chemical weathering reactions take place when layer silicates are weathered: 1) depotassification,
2) hydroxylation of the apical oxygen, 3) dealumination of substituted tetrahedral sheets and 4) oxidation of octahedral Fe.

Norrish (1954) explained the swelling of expanding minerals on the basis of the swelling index, $U\varepsilon/v\sigma$, where $U$ is the total hydration energy for the interlayer cations, $\varepsilon$ is the dielectric constant of the solvating liquid, $v$ is the valence of the interlayer cation and $\sigma$ is the surface charge density. This indicates that if everything else is held constant, the ease of lattice expansion is inversely related to charge density. Bailey (1961) placed cations in the order of decreasing swelling index as follows: Al > Mg > Ca > Li > Na > K. Bailey showed that when muscovite weathered by LiNO₃ treatment was saturated with the different cations the basal spacings fit the order of Norrish's (1954) swelling index.

Arnold (1960) suggested that the weathering of biotite involved 1) K removal and adsorption of hydronium ions, 2) oxidation of Fe, 3) hydroxylation of oxygen and 4) interlayer hydration layer by layer. Dealumination was suggested as a possible mechanism of charge reduction in dioctahedral micas.

The replacement of Mg with Sr in vermiculite is somewhat analogous to replacement of K by a non-fixable cation in micas in that as Mg replaces Sr, the lattice expands (14.4 Å to 15.0 Å). Walker (1959) showed by x-ray diffraction that
the increase in intensity of the 15.0 Å peak occurred at the expense of the intensity of the 14.4 Å peak as Mg was replaced by Sr in vermiculite. Photomicrographs showed that when a vermiculite flake was immersed in 2 M SrCl₂ a boundary between expanded material and contracted material moved inward from the edge of the flake. The rate of movement of the boundary was proportional to the square root of time indicating particle diffusion is the rate controlling process. The activation energy for the process was 12 kcal./g. ion which is greater than energies involved in diffusion of ions in solution.

Mortland and Ellis (1959) concluded that the rate controlling process in removing fixed K from vermiculite by leaching with 0.1 N NaCl is diffusion of Na and K ions through a solution film at the edge of the particle. Mortland and co-workers (Ellis and Mortland, 1959; Mortland, 1960; Mortland and Lawton, 1961) have suggested the film diffusion process is also the rate limiting process in K removal from biotite during 0.1 N NaCl leaching. They apply the equation \( r = B(C' - C) \), where \( r \) is the rate of K release, \( B \) is the film diffusion velocity constant, \( C' \) is the concentration of "reactive" K and \( C \) is the concentration of K in the bulk solution. Using the leaching method of extracting K, it is difficult to evaluate the validity of the equation and the theory on which it is based. First of all, \( C \) is not
constant with time nor is it an independent variable since in the leaching method C is an unknown function of the rate of K release. Also C' is an undefined variable. That is, the point at which it manifests itself and the factors that regulate it are unknown. In addition, not all particles see the same environment in the leaching procedure. That is, the uppermost particles in the sample are receiving fresh solution containing no K while the lower particles are being leached with solution containing variable amounts of K released by the upper particles. This is a fact regardless of the leaching rate but increasing the leaching rate would tend to reduce the effect. It is possible that the particles in the upper part of the sample released K rapidly enough to "saturate" the leaching solution to the point that it could not extract much K from the lower part of the sample. This would give a leachate of constant K concentration until the particles could not release K fast enough to "saturate" the leaching solution; then the K concentration in the leachate would decline.

Reed and Scott (1962) derived a mathematical expression that describes the release of interlayer K from mica particles in NaCl-NaTPB solutions. The NaTPB precipitates the K as it is released by the mica keeping the K concentration in solution very low and constant with time. The rate determining process was assumed to be the simultaneous diffusion
of the replacing ions and K ions within the interlayer space of the particle. Also, it was assumed that the K diffused from a receding weathering front to the edge of the particle. Within the front, the K concentration is constant and equal to that in the original mineral. Between the weathering front and the edge of the particle is the weathered portion of the mica and the zone of K diffusion. Under these assumptions, a given K ion remains physically trapped by the collapsed mineral until it is intercepted by the receding weathering front; then it diffuses within the expanded weathered region to the edge of the particle.

The validity of these assumptions and the resulting mathematical expression was evaluated with experimental data. The results obtained for each size fraction were accurately described by the equation. K release rates determined on samples having a wide range of particle sizes deviated from the theory during the latter stages of K removal. This is expected since it was assumed in the derivation that all particles in the sample are equal in diameter. To corroborate this, the K release rate was determined on a biotite sample having a narrow range in particle size (50 to 62 μ). The experimental data for the 50 to 62 μ sample showed no tendency to deviate from the theory in the latter stages of K removal even though 90 per cent of the K was removed after 113 hours.
The problem of determining the mechanism of K release from micas is simplified considerably by using a K precipitant such as NaTPB because in this system, each particle is in the same environment and the concentration of K in solution remains constant with time.

Sodium Tetraphenylboron in Soils and Micaceous Mineral Studies

The literature on NaTPB and its uses as a precipitant for K is quite extensive. The most comprehensive bibliographies have been written by Barnard (1955, 1956), Barnard and Büeuchl (1957) and Flaschka and Barnard (1960). Only recently has NaTPB been employed extensively in soil and mineral studies.

Scott and co-workers (Scott et al., 1960; Scott and Reed, 1960, 1962a, 1962b; Reed and Scott, 1961, 1962) have done much to develop techniques, elucidate properties of NaTPB and define experimental conditions for the use of sodium tetraphenylboron in extraction of K from micaceous minerals. Scott et al. (1960) extracted up to 100, 12 and 47 per cent of the K from vermiculite, muscovite and illite samples, respectively. Acetone-water solutions were used to separate the KTPB from the K-depleted mineral. Successive extractions were made to maximize K removal. Scott and
Reed (1960) reported a method of determining the amount of K precipitated as KTPB without allowing readsorption of the K by the mineral. The extracting solution was diluted with 0.5 N NH₄Cl and boiled until the TPB ion was thermally decomposed. The K was then determined in the filtered solution.

Three flame photometric methods of determining K precipitated as KTPB in micaceous mineral systems were developed by Reed and Scott (1961). The first method involved the direct flame photometric determination of K (KTPB) dissolved in acetone-water solutions. In the second method, samples containing KTPB precipitate were heated to 350°C in a muffle furnace for 20 minutes. They were then dissolved in dilute acid and the K determined flame photometrically. The third and most preferred method for general use with micaceous mineral systems involved diluting the system with 0.5 N NH₄Cl, adding HgCl₂ and boiling for 20 minutes. The K was determined in the filtered solution. The HgCl₂ reacts with the TPB ion to form phenyl mercury.

Scott and Reed (1962a) employed NaTPB to study the extraction of K from biotite. Most of the K in biotite was easily extracted by placing the biotite in 1 N NaCl - 0.067 N NaTPB solutions that also contained EDTA. The EDTA stabilized the TPB against decomposition. In a similar study, Scott and Reed (1962b) extracted K from illite using 1 N NaCl - 0.067 N NaTPB solutions. Illite released K rapidly
in the early stages but after about 50 per cent of the K was removed, extraction was very slow. Only 68 per cent of the K was removed in 63 days. There was no evidence of a change in charge density after K removal. Reed and Scott (1962) studied the kinetics of K release by biotite and muscovite by extracting different size fractions in 0.2 N NaTPB - 1 N NaCl - 0.1 M EDTA. As much as 90 per cent of the K was removed from < 50 μ biotite in a period of 113 hours, however only 60 per cent of the K was removed from muscovite in 840 hours. A mathematical expression was derived on the assumption that diffusion of K and Na within the particle was the rate limiting process in K release from micas. The expression accurately described the results obtained with each particle size.

Bailey (1961), in a study of the swelling characteristics of an artificially weathered muscovite, used NaTPB to remove K from muscovite after the charge density had been reduced by a molten LiNO₃ treatment. Brown (1961) and White (1962) also removed K from muscovite previously weathered with molten LiNO₃; they studied the 001/002 ratio as an indicator of the degree of weathering. Both Bailey (1961) and Brown (1961) heated the NaTPB-muscovite system to 300°C to enhance K extraction. It is quite likely that the TPB ion was decomposed after a short time at 300°C.

De Mumbrum (1959) extracted K from biotite, muscovite
and phlogopite with NaTPB. Samples of each were mixed with an equal quantity of NaTPB, moistened and dried at 110°C. The samples were washed TPB free with acetone. As much as 67 per cent of the K was removed from biotite whereas only 25 per cent of the K was removed from muscovite even after a large number of treatments. Mortland and Lawton (1961) employed NaTPB to remove K from biotite in a study of the relationship between total K in biotite and the K concentration in an equilibrium 0.1 N NaCl solution. They dried moistened mineral-NaTPB mixture at 110°C then removed the TPB with acetone.
MATERIALS AND METHODS

Biotite samples from Wards Natural Science Establishment were ground in a Cristy and Norris laboratory hammer mill with a 1/16-inch screen and dry screened to obtain samples of < 50, 50 to 250 and 250 to 1000 μ material. A 10 to 20 μ size fraction was separated from the < 50 μ sample by sedimentation. Samples of 50 to 62 μ and 250 to 297 μ biotite were obtained from the 50 to 250 μ and the 250 to 1000 μ size fractions, respectively, by a wet sieving process.

To determine the rate of K release, 0.5-g. samples of biotite were placed in 10 ml. of 1 N NaCl - 0.2 N NaTPB - 0.01 N disodium dihydrogen EDTA and stored in a constant temperature room at 25°C for different periods of time. At the end of each extraction period, samples were transferred to approximately 800 ml. of 0.5 N NH₄Cl containing 4 mmol. of HgCl₂ and boiled for 20 minutes. The systems were then cooled, filtered and the K in the filtrate was determined with a Perkin-Elmer model 52C flame photometer. This method of determining K that has been precipitated as KTPB in aqueous NaTPB-micaceous mineral systems has been described by Reed and Scott (1961) and by Scott and Reed (1960).

Exchangeable K values were determined by leaching with neutral normal NH₄OAc. Total K, Na and Fe were determined as described by Jackson (1958, pp. 278-294). Ferrous iron
was also determined as described by Jackson (1958, pp. 320-321). Total N determinations were made by Kjeldahl analysis using a Hoskins Steam distillation apparatus (Bremner, 1960).

Specimens were prepared for x-ray diffraction studies by placing about 5 to 10 mg. of mineral in 3 ml. of either water or the extracting solution and filtering the system through a ceramic plate. This procedure left a thin well-oriented specimen on the face of the plate. Moist specimens were kept moist by saturating the ceramic plate with either water or the extracting solution and passing water saturated air over the specimen during the analysis. The x-ray diffraction studies were made on a General Electric x-ray diffractometer model XRD-5 equipped with a scintillation counter. All x-ray analyses were made with Cr Kα radiation and a V filter.
THEORETICAL ASPECTS OF POTASSIUM RELEASE

The process by which K is released from mica particles to solutions containing NaTPB should involve only the simultaneous diffusion of the replacing ions and K within the particle, the exchange between the replacing ions and K at the adsorption site, and the precipitation of the released K as KTPB. Presuming the exchange and precipitation reaction rates to be relatively rapid, it may be assumed that the rate determining process in this extraction is the diffusion of the cations within the interlayer space of the particle. With these basic premises in mind, Reed and Scott (1962) derived a mathematical expression to describe the release of interlayer K from micas.

The mica particles can be regarded as being flat circular discs with radius $r_b$ as shown in Figure 1. In this diagram $\tau$ is the interlayer space through which the interlayer K diffuses from the interior to the particle periphery and $\delta$ is the original basal spacing of the mineral. The weathering front within the particle from which the K diffuses is denoted by a cylinder with radius $r_a$. In the region, $r < r_a$, the K concentration is constant and equal to that of the original particle. The region $r_a < r < r_b$ is the weathered portion of the particle and the zone of K diffusion. That is, the K diffuses radially from $r_a$ to $r_b$. 
Figure 1. Schematic diagram of biotite particle
As K is released by the particle, the weathering front recedes and \( r_a \) decreases. Thus, a two-dimensional radial diffusion problem with a moving boundary is involved in the release of K from these particles.

Considering a unit mass of mica particles, it can be stated from Fick's law that

\[
\frac{dQ}{dt} = D \left( \frac{\partial C}{\partial r} \right)_b A_b
\]

where \( Q \) is the mass of K in the mica, \( D \) is the diffusion coefficient, \( (\partial C/\partial r)_b \) is the concentration gradient of K in the interlayer space \( \tau \) at \( r = r_b \), and \( A_b \) is the area at the particle periphery through which K diffuses. For a quasi-steady state, the K concentration \( C \) in the interlayer space of the weathered region of the particles can be described by the expression from Crank (1956, p. 117)

\[
C = \frac{C_a \ln (r_b/r) + C_b \ln (r/r_a)}{\ln (r_b/r_a)}
\]

where \( C_a \) and \( C_b \) are the K concentrations at the limits of the diffusion path. The application of this expression assumes that the diffusion space is uniform, that is, \( \tau \) and the mineral charge density must be constant in the region \( r_a < r < r_b \). If this equation is differentiated with respect to \( r \) the expression
is obtained for the K concentration gradient at \( r_b \).

The peripheral area across which the K diffuses from each interlayer space is \( 2 \pi r_b \tau \). Assuming all particles have equal radii, the number of interlayer spaces in a unit mass of mica is \( \frac{1}{\pi r_b^2 \rho \delta} \) where \( \rho \) is the original density of the mica. Therefore, the total area at the periphery of the particles through which K diffuses is given by

\[
A_b = \frac{2\tau}{r_b \rho \delta}
\]  

and by combining Equations 1, 3 and 4

\[
\frac{dQ}{dt} = - \frac{2\tau D (C_a - C_b)}{\rho \delta r_b^2 \ln (r_b/r_a)}
\]  

If \( r_a \) is expressed in terms of variable \( Q \), Equation 5 can be integrated easily. Since \( Q \), the mass of K in a unit mass of mica at time \( t \), is proportional to the volume of unweathered mica, the relationship

\[
\frac{Q}{Q_o} = \frac{r_a^2}{r_b^2}
\]  

can be obtained. \( Q_o \) is the mass of K in the mica initially.
Differential Equation 5 then becomes

\[ \ln \frac{Q_0}{Q} \, dQ = - \frac{4\pi D (C_a - C_b)}{\rho \delta r_b^2} \, dt \]  \[7\]

Integration of Equation 7 between the limits of 0 and t on variable t, and \( Q_0 \) and Q on variable Q gives the transcendental function

\[ Q (1 - \ln \frac{Q}{Q_0}) = Q_0 - \frac{4\pi D (C_a - C_b) t}{\rho \delta r_b^2} \]  \[8\]

which can be simplified for computation purposes by dividing by \( Q_0 \) to obtain

\[ \frac{Q}{Q_0} (1 - \ln \frac{Q}{Q_0}) = 1 - \frac{4\pi D (C_a - C_b) t}{Q_0 \rho \delta r_b^2} \]  \[9\]

where \( Q/Q_0 \) is the fraction of the initial K content of the particles that is still present at time t.

Equation 9 states that a plot of the term on the left, that is \( (Q/Q_0) [1 - \ln (Q/Q_0)] \), against t for a mica sample with one particle size should give a straight line if the term

\[ \frac{4\pi D (C_a - C_b)}{Q_0 \rho \delta} \]

is a constant.
The validity of assumptions involved in the derivation of rate Equation 9 and the applicability of this mathematical equation was evaluated by Reed and Scott (1962) with experimentally determined K release data. The data were obtained by placing different size fractions of biotite and muscovite in NaCl-NaTPB solutions for different periods of time. A plot of the experimental values of the left term, \((Q/Q_0) [1 - \ln (Q/Q_0)]\), against time gave straight lines for each particle size fraction. Therefore, the expression accurately described the experimental K release data for each size fraction. The expression did not describe the difference due to particle size.

The objective of this study was to evaluate the significance of some of the parameters in Equation 9. Attention is focused mainly on the parameters affected by the characteristics of the extracting solution rather than inherent characteristics of the mica.
POTASSIUM RELEASE WITH DIFFERENT LEVELS
OF POTASSIUM IN THE EXTRACTING SOLUTION

The theoretical equation

\[ \frac{Q}{Q_0} (1 - \ln \frac{Q}{Q_0}) = 1 - \frac{4\pi D (C_a - C_b) t}{Q_0 \rho \delta r_b^2} \]

that was derived by Reed and Scott (1962) for the rate of K release by mica particles, contains the term \( C_b \) which is the concentration of K in the extracting solution. Therefore, it is to be expected that the concentration of K in the extracting solution will be one of the factors determining the rate of K release observed in any particular extraction experiment. For instance, Mortland (1958) observed an increase in the rate of K release by biotite when his rate of leaching the biotite with 0.1 N NaCl was increased. This increase in rate of release was probably due to the decrease in K concentration in solution that also occurred when the faster rate of leaching was used. More quantitative information about the effect of \( C_b \) on the rate of K release is needed, however.

To obtain this information, samples of 10 to 20 \( \mu \) biotite were placed in 1 N NaCl - 0.001 M EDTA solutions that contained NaTPB and different concentrations of K. After different periods of contact, aliquots of the system containing
approximately 0.1 g. of biotite were taken from the system and filtered. The biotite samples were washed TPB free with 100 ml. of 0.5 N NH₄Cl in 60 per cent acetone-water, washed chloride free with 70 per cent acetone, dried at 110°C for 48 hours and analyzed for total K.

In this experiment, the extracting solution had to contain the desired level of K before the biotite was added. Otherwise, some of the K in the biotite would have been released under a condition of increasing K concentration in the extracting solution. That is, with an extracting solution that initially contained no K there would have been a gradual increase in dissolved K due to the K released by the biotite. This change in K concentration would have continued until the level determined by the TPB concentration was attained. Furthermore, in the preparation of the extracting solution with the desired level of dissolved K, it was necessary to consider the possibility of supersaturating the solution with KTPB. In preliminary experiments, where the K was added to the NaTPB solution by release from biotite particles, supersaturation did occur. Therefore, in addition to containing the desired level of K, the extracting solution was always equilibrated with KTPB precipitate.

At first, the extracting solution was prepared by adding excess KTPB as a powder but it required a very long time to equilibrate. Thus, it was necessary to precipitate the KTPB
from the extracting solution and allow the system to equilibrate. This was done by adding an excess of NaTPB to the solution then precipitating the excess with an equivalent amount of KCl. The extracting solution-KTPB systems were allowed to equilibrate until the dissolved K concentration by analysis was constant. This generally required about three days.

The extracting solutions for this study were prepared to contain final NaTPB concentrations of approximately 0.0003, 0.001 and 0.01 N. The K concentrations in these solutions were determined to be 3.5, 1.0 and 0.35 ppm, respectively. To maintain these concentrations of K in solution throughout the extraction period fluctuations in TPB concentrations had to be kept at a minimum. Thus, large volumes of extracting solutions were used in each case. Nine liters of extracting solution per gram of biotite were used with the 3.5 and 1.0 ppm. K systems and four liters per gram were used in the case of the 0.35 ppm. K system. In the case of the two solutions with the lower TPB concentrations, it was also necessary to add NaTPB periodically during the extraction to replace NaTPB removed by the precipitation of released K. The concentration of K in solution was determined periodically and if there was an increase in K concentration, NaTPB was added to the solution. The amount of NaTPB added to reduce the K to the desired concentration was computed from the solubility
product constant, $2.25 \times 10^{-8}$, which was determined in preliminary experiments with KTPB in 1 N NaCl - 0.0001 M EDTA solution at 25°C. It may be noted that solubility product values of $2.25 \times 10^{-8}$ and $3.16 \times 10^{-8}$ have been reported for KTPB in water at 20° and 25°C, respectively (Flaschka and Barnard, 1960).

The quantity of K remaining in the biotite as a function of time with different concentrations of K in the extracting solution is shown in Figure 2. With these dissolved K levels, it was possible to remove essentially all of the K from the biotite. Also, it is obvious from Figure 2 that the K was released more rapidly when the concentration of K in the extracting solution was lowest. These differences in the rate of K release can be seen more readily in Figure 3 where the rate for the 3.5 and 0.35 ppm. K system has been plotted on a logarithmic scale against extraction time. It is obvious from this graph that the difference in rate of release is really quite large. This means that to remove K from biotite rapidly, one should use extracting solutions containing as little K as possible. In the 3.5 ppm. K extracting solution, K was released from the biotite at a constant rate during the early part of the extraction period. In the case of the 0.35 ppm. K and the 1.0 ppm. K systems, this period of K release at a constant rate was not observed. Mortland (1958), on the other hand, observed this constant rate with 6 ppm. K
in solution which was higher than any K concentration used in this study. The significance of this constant rate will be discussed later.

The experimental values of the left term, \( \frac{Q}{Q_0} \left[ 1 - \ln \left( \frac{Q}{Q_0} \right) \right] \), in the theoretical equation were calculated from the release data of this experiment. These values are plotted against time in Figure 4. Theoretically, the curves should be straight lines if the term \( \frac{4\pi D (C_a - C_b)}{Q_0 \rho \beta r_b^2} \) is constant with time. This appears to be the case for a large part of the contact time. However, each curve shows deviation from linearity in the early stages of K removal and again in the latter stages.

The deviation from a straight line in the latter stages of K removal can be attributed to the broad range in particle size (10 to 20 \( \mu \)). The equation was derived assuming that all particles in the sample have equal radii. Also, in a sample with particles of different size, the small particles would be K depleted first. The average size of the particles still releasing K, \( r_b \) of the equation, would then increase and the observed rate of release would decrease. In this experiment the smallest particles were 10 \( \mu \) in size. When they were K depleted, the rate of K release decreased as shown in Figure 4.

In early stages of K removal, the release rate is slower in each case than is predicted by the theoretical equation.
Figure 2. K remaining in 10 to 20 μm biotite after different periods of contact time with 1 N NaCl - 0.001 M EDTA solution containing NaTPB and three concentrations of K.
Figure 3. Rate of K release from 10 to 20 μ biotite after different periods of contact time with 1 N NaCl - 0.0001 M EDTA solution containing NaTPB and two concentrations of K
Figure 4. The relationship between experimentally determined values of the term \((Q/Q_0) [1 - \ln (Q/Q_0)]\) in the theoretical equation and the contact period in the extraction of K from 10 to 20 \(\mu\) biotite with 1 N NaCl - 0.0001 M EDTA solutions, two solution/mineral ratios and three concentrations of dissolved K.
3.5 ppm K, 9000 ml./g.
1.0 ppm K, 9000 ml./g.
1.0 ppm K, 4000 ml./g.
0.35 ppm K, 4000 ml./g.

10 μ PARTICLE
K DEPLETED

3.5ppm K

CONTAC T TIME (hrs.)

0.35 ppm K  1.0 ppm K
In the derivation of the equation, no consideration was made for describing the K release during the formation of the weathering front. Obviously, a certain amount of K must be released before a uniform diffusion medium of constant dimension, \( \tau \), is established. The first increment of K removed from the biotite allows a small amount of expansion at the edge of the particle as shown in Figure 5a. K ions tend to keep the lattice contracted whereas the Na ions that replace the K ions tend to hydrate and expand the lattice. X-ray diffraction patterns of the original and K-depleted biotite show the basal spacing increases from 10 to 15 \( \AA \) (two layers of water) when the K is replaced by Na (Figure 7). Thus, until the lattice has expanded to 15 \( \AA \) at the edge (Figure 5b), the weathering front has not completely formed and the release of K will not be described by the theoretical equation. Thereafter, the release of K from biotite is accurately described by the equation as the diffusion zone of constant interlayer spacing increases (Figure 5c).

By comparing the curves for the 3.5 ppm. K system in Figures 3 and 4, it may be observed that K was released at a constant rate during the same period that the initial part of the curve in Figure 4 deviated from linearity. Apparently, K was released at a constant rate while the weathering front was being established. Furthermore, when the concentration of K in solution was reduced in this experiment, less time
Figure 5. Schematic diagrams of interlayer space in biotite at different stages of K removal and different concentrations of K in solution; (a) lattice beginning to expand at the edge, (b) edge fully expanded with low concentration of K in solution, (c) diffusion zone of constant interlayer spacing established, (d) edge fully expanded with high concentration of K in solution
was involved in establishing the weathering front and the period of constant release was less. In fact, as shown in Figure 3, there was no obvious period of constant K release rate when there was only 0.35 ppm. K in solution. It may be noted that Mortland (1958) also observed a shorter constant rate period when he used a more rapid NaCl-leaching rate and the concentration of K in solution was decreased.

To explain this relationship between the concentration of K in the extracting solution and the time involved in establishing the weathering front it is necessary to consider the process of K replacement. The interlayer K ions at the periphery of the particle are replaced by Na which tends to expand the lattice. The amount of expansion that occurs, however, will be determined by the relative expansion and contraction forces due to the Na and K, respectively, in the interlayer weathered region and the contraction force transmitted from the central contracted portion of the particle through the rigidity of the particle layers themselves. Consequently, it will be the K/Na ratio in this weathered region that will determine the degree of expansion. This ratio, of course, will be affected by the concentration of K in solution. If the K concentration in the extracting solution is increased, the concentration gradient for the K within the weathered region will be reduced. As a result, the distance from the contracted portion of the particle to that point in
the weathered region where the K/Na ratio is at or below the critical level for expansion will be greater. That is, K depletion will occur for a longer period of time and a deeper weathered region will be established, as illustrated by comparing Figures 5d and 5b, before the lattice will be expanded to 15 Å at the edge.

The linear portions of the curves (Figure 3) for the different K concentrations in the extracting solution have different slopes which means that different rates of K release were obtained. The rate of release is inversely related to the concentration of K in the extracting solution. This is to be expected from the theoretical equation because the rate of release is given by the term 
\[ \frac{4\pi D (C_a - C_b)}{Q_0 \rho b r_b^2} \] which contains \( C_b \). In fact it has been determined mathematically with the theoretical equation that the difference in rate with which K was released in the 3.5 ppm. K and 1.0 ppm. K systems was entirely due to the difference in \( C_b \). This was not true for the 0.35 ppm. K system.

The system containing 0.35 ppm. K had a solution/mineral ratio of 4000 ml./g. whereas the other two systems had a ratio of 9000 ml./g. It was thought possible that this difference in solution/mineral ratio could have been responsible for the different behavior of the 0.35 ppm. K system in regard to the release rate. Therefore, duplicate samples of
10 to 20 μ biotite were degraded in the 1.0 ppm. K extracting solution using a solution/mineral ratio of 4000 ml./g. The results obtained with two periods of contact are plotted in Figure 4. It is evident that the solution/mineral ratio had no effect on the release of K by biotite.
CRITICAL CONCENTRATIONS OF K IN SOLUTION FOR K RELEASE

When biotite particles are placed in an extracting solution and the released K is allowed to accumulate in the solution, the concentration of dissolved K will increase until it reaches a critical level which prevents further release. On the other hand, large amounts of K can be extracted from biotite by maintaining a low K concentration in the extracting solution. Thus, to study the kinetics of K release from biotite, more information about the magnitude of the critical level and its significance is needed.

Mortland and Lawton (1961) presented data that indicated that the K concentrations in 0.1 N NaCl solutions in equilibrium with biotite containing different total K contents were directly and linearly related to the total K in the biotite. Their data suggest that if biotite were degraded in a solution that contained 3.5 ppm K, it would be impossible to remove more than about 80 per cent of the K. However, as shown in Figure 2, the extracting solution containing 3.5 ppm K removed more than 95 per cent of the K from the biotite in 169 hours.

An experiment was set up to determine the relationship between the critical K concentration in solution and the amount of K remaining in degraded biotite. Samples of 10 to 20 μ biotite were placed in different quantities of
1 N NaCl - 0.001 M EDTA solution. Based on preliminary experiments, 0.5, 0.1, 0.325 and 0.325-g. samples of biotite were placed in 100, 200, 2000 and 3000 ml. of 1 N NaCl - 0.0001 M EDTA, respectively, to attain different critical K levels at equilibrium. The EDTA was added to make the solution comparable to the solutions employed in other experiments with NaTPB in this study. The samples were equilibrated in a constant temperature room at 23°C. The K concentration in solution was determined periodically to determine when the K concentration had reached a constant level.

The critical K concentration in solutions that have been equilibrated with biotite containing different amounts of remaining K are shown in Figure 6. If small amounts of K are remaining in the biotite the critical concentration of K in the solution is about 7.5 ppm. K. With higher amounts of K remaining in the biotite, the critical K concentration in solution is higher; however, it is not markedly higher unless the amount of K remaining in the biotite is greater than 175 me./100 g. Above 175 me./100 g. total K, the critical concentration of the equilibrium solution increases sharply with higher amounts of total K in the biotite.

Apparently, if the K concentration in this extracting solution is maintained below about 7.5 ppm. K, nearly all of the K in the biotite can be removed but if the solution contains more than 7.5 ppm. K, only part of the original total K
Figure 6. Concentration of K in 1 N NaCl - 0.0001 M EDTA solutions in equilibrium with 10 to 20 μm biotite containing different amounts of total K
can be removed regardless of the extraction time. K concentrations in solution between 7.5 ppm. and 11 ppm.
have a large effect on the amount of K that can be removed from biotite. For example, an extracting solution with the concentration of K maintained at 10 ppm. K will decrease the K content of biotite from 197 me./100 g. to about 150 me./100 g. whereas an extracting solution containing 8 ppm. K will deplete the K content to about 35 me./100 g. Extracting solutions containing more than about 11 ppm. K will not remove much K from biotite regardless of the extraction time.

Portions of the biotite samples, that contained 168, 148 and 67 me. K/100 g. total K after equilibrium was established, were sedimented on ceramic plates for x-ray diffraction studies. The ceramic plates were saturated with the equilibrium solution to keep the oriented biotite samples moist during the analyses. The diffraction patterns are shown in Figure 7. An x-ray pattern for a biotite sample in a 0.2 N NaTPB - 1.0 N NaCl - 0.01 M EDTA solution, pattern A, is also shown in Figure 7 for comparative purposes. Each of the NaCl equilibrium patterns shows a relatively sharp 15 Å even though the K concentration in solution is high enough to stop K release completely. Apparently, K release is not stopped because of a general collapse of the lattice as the K concentration in solution approaches the critical
Figure 7. Tracings of x-ray diffraction patterns of oriented 10 to 20 μ biotite samples containing different amounts of total K after equilibration in 1 N NaCl - 0.0001 M EDTA solutions and a sample containing 159 me./100 g. after K extracted in 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solution.
A. 159 me. K/100g (NaTPB)

B. 178 me. K/100g

C. 148 me. K/100g

D. 67 me. K/100g
level. There is some indication, however, that a larger part of the lattice near the weathering front is in a partially contracted state when equilibrium is established. The 10-Å peak for the biotite samples containing larger amounts of total K are relatively broad and skewed toward the low angle side when the biotite is in equilibrium with a NaCl solution (Figures 7B and 7C). On the other hand, the 10-Å peak remains narrow and sharp when the biotite is in a NaTPB solution and the K is continuing to be released (Figure 7A). Apparently, the increase in K concentration in the extracting solution as equilibrium is approached results in a deeper zone of partially contracted lattice near the weathering front.
EFFECT OF POTASSIUM REMOVAL ON BIOTITE CHARACTERISTICS

Mortland and Lawton (1961) showed that after K was removed from biotite by leaching with 0.1 N NaCl, the total charge density of the biotite had decreased. There was also an accompanying oxidation of ferrous iron to ferric iron but there was no stoichiometric relationship between decrease in charge and Fe oxidation. The decrease in charge density was observed in all size fractions. Brown (1961) suggested that K is not removed from muscovite until the layer charge has been decreased; after which the K ions are free to move from the mineral. Scott and Reed (1962b) showed that large quantities of K can be removed from illite without any decrease in total charge. In view of these results, an experiment was set up to relate the amount of K removed from biotite with change in charge density, oxidation state of Fe, particle size and expansion properties of the K-depleted biotite.

Five-gram samples of three particle size fractions of biotite (10 to 20 μ, 50 to 62 μ and 250 to 297 μ) were placed in 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solutions for different periods of time to prepare samples of each size fraction with five different levels of total K. In each case, the extraction period was adjusted so the total K levels attained with each particle size fraction was about the same.
The necessary extraction periods were calculated using the theoretical release equation as modified by Reed and Scott (1962) to describe K release from different particle size fractions. After the extraction time had elapsed, the systems were filtered and the residues were placed in 1000 ml. of 0.5 N NH₄Cl in 60 per cent acetone-water for one hour to dissolve the KTPB and NH₄ saturate the biotite. The samples were then filtered and leached with an additional 200 ml. of 0.5 N NH₄Cl in 60 per cent acetone-water. They were washed chloride free with 70 per cent acetone and the acetone was washed out with 20 ml. of water. Ferrous iron and total amounts of K, Na, NH₄ and Fe were determined on each sample as described under Materials and Methods. The results are given in Table 1.

No significant change in charge density took place when K was removed from the 10 to 20 μ biotite. There was a decrease in charge during the latter stages of K removal from the 50 to 62 μ fraction. The charge was decreased in the 250 to 297 μ fraction even though only 35 per cent of the K was removed. The charge density decrease appears to be more closely related to extraction time than the amount of K removed from the biotite. No significant oxidation of Fe occurred when K was removed from the 10 to 20 μ biotite. Oxidation of ferrous iron to ferric iron occurred whenever there was a change in charge density. However, there was
Table 1. Change in charge density and oxidation state of Fe in biotite as affected by particle size and amount of K extracted with 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solutions.

<table>
<thead>
<tr>
<th>Particle size fraction</th>
<th>Contact time (hrs.)</th>
<th>Total analysis (me./100 g.)</th>
<th>Change\textsuperscript{a} in total charge (K+Na\textsubscript{+}\textsuperscript{+} +NH\textsubscript{4}\textsuperscript{+})</th>
<th>Fe\textsubscript{II}</th>
<th>Fe oxidized\textsuperscript{b} (mmol./100 g.)</th>
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<td>I (10-20μ)</td>
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<tr>
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</tr>
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<td>180</td>
<td>126</td>
<td>69.7</td>
<td>22.0</td>
<td>217.7</td>
<td>- 5</td>
</tr>
<tr>
<td>480</td>
<td>88.8</td>
<td>80.0</td>
<td>46.7</td>
<td>215.5</td>
<td>- 7</td>
</tr>
<tr>
<td>1339</td>
<td>42.0</td>
<td>114</td>
<td>55.4</td>
<td>211.4</td>
<td>-12</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Based on 223 me./100 g. total charge in original biotite.

\textsuperscript{b} 261 mmol./100 g. total Fe in all samples.
no stoichiometric relationship between Fe oxidation and decrease in charge. In each case, more Fe was oxidized than can be explained by the decrease in charge.

No significant decrease in charge density or oxidation of Fe took place in the samples that were exposed to the extracting solution for less than 100 hours. But, in all samples in contact with the extracting solution longer than 100 hours, some decrease in charge and some oxidation of Fe took place. The larger particles tended to lose charge when lesser amounts of K were removed but this was not necessarily a direct particle size effect since the extraction time was much longer with the larger particles than the smaller ones to obtain a similar K content. Thus, it is quite possible that a decrease in charge is a result of the expanded weathered biotite being in contact with the extracting solution for an extended period of time. In support of this, it can be shown that the K release data shown in Table 1 for the 250 to 297 μ size fraction are described by the theoretical equation. Thus the rate of K release was not affected by the charge decrease that occurred during the extraction period. The decrease in charge that is sometimes observed when K is extracted from biotite is probably an indirect result of the K removal and has nothing to do with the process by which the K is released.

The expansion properties of the samples containing
different amounts K were studied by x-ray diffraction. Portions of the different size fractions of biotite from the extraction system were sedimented on porous ceramic plates and kept moist by saturating the plate with the extracting solution in order that the diffraction patterns would indicate the basal spacings of the biotite during K extraction. Also, portions of the NH$_4$-saturated samples were sedimented on ceramic plates from water suspensions and were kept moist during the analysis by saturating the plate with water. For simplicity, the 10 to 20, 50 to 62 and 250 to 297 μ biotite fractions hereafter will be denoted as I, II and III, respectively.

The patterns for the Na-saturated I samples (Na-I) with different amounts of total K are shown in Figure 8. With increasing amounts of K removed from the sample, the intensity of the 15-Å peak increases and the intensity of the 10-Å peak decreases. The 10- and 15-Å peaks are the only peaks shown indicating that the interlayering of expanded and contracted material was not prevalent. The intensity of the 15-Å peak is greater than the intensity of the 10-Å peak, in each case, relative to the amounts of the corresponding material in the sample. For example, in Figure 8B, the two peaks have nearly equal intensities even though only 20 percent of the K has been removed from the biotite. Also, in Figure 8E, no 10-Å peak is observed although nearly 13 per
Figure 8. Tracings of x-ray diffraction patterns of oriented Na-saturated 10 to 20 µm biotite samples containing different amounts of total K after treatment with 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solutions for different periods of time.
C. 124 me. K/100 g
B. 159 me. K/100 g
A. 199 me. K/100 g

E. 26.6 me. K/100 g.
D. 108 me. K/100 g.
cent of the K was still in the biotite. Similar observations were made by Mortland (1958). The 8-Å peak shown in the patterns for Na-saturated samples represents a lattice spacing for the KTPB present with the biotite (Norment et al., 1960). Patterns for Na-II and Na-III were similar to those shown in Figure 8 for Na-I.

Diffraction patterns for the NH$_4$-III samples are shown in Figure 9. By comparing the relative intensities of the 15- and 10-Å peaks in these patterns with those for the Na-I samples (Figure 8) with similar amounts of total K, it is shown that on NH$_4$ saturating the degraded biotite, the relative intensities on the 15-Å peaks are reduced and the intensities of the 10-Å peaks are increased. But in each case, a 15-Å peak remains after NH$_4$ saturation. An explanation for this is that when the samples were placed in the solution containing NH$_4$, the lattice collapsed at the edge preventing further exchange of NH$_4$ for Na. The only peaks shown are 10 and 15 Å, therefore, the biotite contained only fully expanded material with two layers of water and fully contracted material. The effect of replacing Na with NH$_4$ in a biotite sample containing only 42 me./100 g. is clearly shown in Figure 10. The pattern for Na-III (Figure 10A) shows a high-intensity peak at 15 Å and only a 10-Å peak with low intensity, whereas the pattern for NH$_4$-III (Figure 10C) shows a higher 10-Å peak with a reduction in the intensity of the
Figure 9. Tracings of x-ray diffraction patterns of oriented NH₄-saturated, 250 to 297 μ biotite samples containing different amounts of total K after treatment for different periods of time with 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solutions
Figure 10. Tracings of x-ray diffraction patterns of oriented 250 to 297 μ biotite samples containing 42.0 me. K/100 g. after treatment with 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solutions

A. Na-saturated, moist with NaTPB solution
B. NH₄-saturated, moist
C. NH₄-saturated, airdry
A 42.0 me. K/100g.

B 42.0 me. K/100g.

C 42.0 me. K/100g.
15-Å peak. The specimen for the NH₄-III sample was air-dried over CaCl₂ for four weeks, after which the basal spacings were determined again. A comparison of Figures 10B and 10C shows that drying the specimen over CaCl₂ did not affect the position or the relative intensity of the peaks. The water associated with the expanded region of the particles was apparently trapped by the contracted edges when the degraded biotite was NH₄ saturated.

With two samples, NH₄-I that contained 26.6 me. K/100 g. and NH₄-II that contained 86.8 me. K/100 g., considerably more Na was replaced by NH₄ than in the other samples. The NH₄-I sample contained 170 me. NH₄/100 g. and the NH₄-II sample contained 109 me. NH₄/100 g. The amount of Na replacement by NH₄ appears to be difficult to control even though each sample was NH₄ saturated in a similar manner. The Na- and NH₄-saturated samples of biotite I and II were analyzed by x-ray diffraction and the resulting patterns are shown in Figure 11. The patterns (Figures 11A and 11C) for the Na-saturated samples show peaks for 15-Å basal spacings only. The pattern (Figure 11B) for the II fraction which contained 109 me. NH₄/100 g. after NH₄ saturation shows a relatively sharp 10-Å peak with only a small 15-Å peak. This indicates that the NH₄ replaced the Na and the lattice collapsed to a relatively uniform 10-Å spacing. On the other hand, the pattern (Figure 11D) for the NH₄-II sample which contained
Figure 11. Tracings of x-ray diffraction patterns of oriented biotite samples after treatment with 0.2 M NaTPB - 1 M NaCl - 0.01 M EDTA solution

A. Na-saturated, 50 to 62 \( \mu \)
B. \( \text{NH}_4 \)-saturated, 50 to 62 \( \mu \)
C. Na-saturated, 10 to 20 \( \mu \)
D. \( \text{NH}_4 \)-saturated, 10 to 20 \( \mu \)
170 me. NH₄/100 g. shows a broad 10-Å peak which is skewed toward the low angle side. Apparently, the contracted material was poorly crystalline; that is, the basal spacing was not a uniform 10-Å spacing.
EFFECT OF pH ON POTASSIUM RELEASE

The diffusion coefficient, D, in the theoretical equation is a function of the mobility of the diffusing ions. Since the K ion that is released must be replaced by another charged ion, the process involves the simultaneous diffusion of the K ions and the replacing ions. In a case such as this, where the diffusing ions are coupled, there is only a single diffusion coefficient. If the replacing ion were intrinsically more mobile than the K ion, a diffusion potential would be established which would tend to slow the replacing ion and accelerate the K ion. Thus, the mean effective diffusion coefficient would be increased. The mobility of H ions in water at 25°C is about seven times greater than Na ions. This difference is expected to be as large in the interlayer space. Therefore, if the H ion concentration in the Na extracting solution is increased, that is, the pH is decreased, the rate of K release should also increase.

To determine the effect of the pH of the extracting solution on the rate of K release from biotite, 6-g. samples of 10 to 20 µ biotite were degraded for 24 hours in 120 ml. of 0.2 N NaTPB - 1 N Na - 0.01 EDTA solutions. The pH of these solutions was adjusted to pH 5, 7 and 9 by using NaOAc - HOAc, NaH₂PO₄ - NaOH and NaOH - H₃BO₃, respectively.
At the end of the extraction time, each sample was placed in 500 ml. of 0.5 N NH₄Cl in 60 per cent acetone-water, swirled and let stand for 30 minutes. They were then filtered, washed with an additional 200 ml. of 0.5 N NH₄Cl in 60 per cent acetone-water, washed chloride free with 70 per cent acetone and washed free of acetone with 20 ml. of water. Duplicate samples of each were taken for determination of ferrous iron and total amounts of K, Na, NH₄ and Fe. The results are given in Table 2.

It is shown in Table 2 that K extraction for 24 hours in solutions with pH 7 and 9 resulted in small decreases in charge density (4.3 and 6.8 me./100 g.) but K removal in solutions with pH 5 resulted in a charge decrease of 17.8 me./100 g. The amount of Fe oxidized is in the same order of magnitude as the decrease in charge for samples extracted in solutions with pH 5 and 7 but at pH 9, 26 mmol./100 g. of Fe were oxidized and the decrease in charge was only 6.8 me./100 g. It is logical that more Fe was oxidized in alkaline solutions since the oxidation potential for Fe II = Fe III + e⁻ is positive in alkaline solutions and negative in acid solutions. Since there was more Fe oxidized than there was decrease in charge, apparently some other process tended to increase the charge. No attempt was made to determine this process.

In this experiment more K was removed from the biotite
Table 2. K content, change in charge density and oxidation state of Fe in 10 to 20 μm biotite as affected by the pH of extracting solutions containing NaTPB

<table>
<thead>
<tr>
<th>Biotite sample</th>
<th>K (me./100g.)</th>
<th>Na (me./100g.)</th>
<th>NH₄ (me./100g.)</th>
<th>Total charge K+Na+NH₄ (me./100g.)</th>
<th>Change in total charge (mmol./100g.)</th>
<th>Fe II oxidized (mmol./100g.)</th>
<th>Fe oxidizeda</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄-degraded at pH 5</td>
<td>41.4</td>
<td>50.6</td>
<td>114</td>
<td>206.0</td>
<td>-17.8</td>
<td>209</td>
<td>15</td>
</tr>
<tr>
<td>NH₄-degraded at pH 7</td>
<td>41.6</td>
<td>25.9</td>
<td>152</td>
<td>219.5</td>
<td>-4.3</td>
<td>222</td>
<td>2</td>
</tr>
<tr>
<td>NH₄-degraded at pH 9</td>
<td>82.8</td>
<td>67.7</td>
<td>66.5</td>
<td>217.0</td>
<td>-6.8</td>
<td>198</td>
<td>26</td>
</tr>
<tr>
<td>NH₄-undegraded</td>
<td>199</td>
<td>23.4</td>
<td>1.4</td>
<td>223.8</td>
<td>-</td>
<td>224</td>
<td>-</td>
</tr>
</tbody>
</table>

a261 mmol./100 g. total Fe in all samples.
when the pH of the extracting solution was reduced from pH 9 to 7. A further reduction in pH to 5, however, had no additional effect. In other experiments (see Figure 12), it has been observed that the K content of < 50 μ biotite can be reduced to 41 me. K/100 g. in less than 5.5 hours with a solution at pH 5. Thus, the fact that more K was not removed in 24 hours at pH 5 in this experiment, indicates that other factors will have to be considered before the effect of pH alone can be determined. In this regard it may be noted that 6 gm. samples were extracted in 120 ml. solution in this experiment as compared to the usual method of using 0.5 g. in 10 ml.

Considering that the H ion is a very effective replacing ion, it was expected that some adsorption of H ions by the degraded biotite would take place in solutions with pH 5. To determine the amount of H adsorbed during K removal from biotite, a 0.5-g. sample of < 50 μ biotite was placed in 10 ml. of a weakly buffered solution of 0.2 N NaTPB - 0.1 N NaOAc - 0.9 N NaCl - 0.01 M EDTA adjusted to pH 5.0 with HOAc. The pH of the system was determined frequently with a pH meter and when the system deviated from pH 5.0, it was titrated back to pH 5.0 with 0.5 N HCl. The accumulative amounts of HCl added to maintain the extracting solution at pH 5 were used as a measure of the adsorption of H ions by the degrading biotite after different periods of time.
Figure 12. K release and H adsorption by < 50 μ biotite after different periods of time in 0.2 N NaTPB - 0.9 N NaCl - 0.1 N NaOAc - HOAc - 0.01 M EDTA solutions at pH 5
To relate the adsorption of H ions to K release in biotite, it was necessary to determine the release of K from the biotite under similar conditions. Therefore, separate samples of the 10 to 20 μ biotite were degraded in comparable systems. In this case, the pH of the solution was not determined but the extracting solutions were maintained at pH 5 by adding HCl periodically. The quantity of acid added to the systems was based on the results of the H adsorption experiment. Little error was introduced by this method since a determination of the pH of the solution after more than 95 per cent of the K was removed showed the pH was 5.0. The curves for K release and H adsorption as a function of contact time are shown in Figure 12.

As K ions were released by the biotite, H ions from the extracting solutions were adsorbed. The ratio of H adsorbed/K released as shown in Figure 13 was constant at 0.47 during the removal of the last half of the K. It is logical that a small amount of H would be adsorbed on the newly formed interlayer surfaces in preference to Na but it is not expected that it would occupy 47 per cent of the exchange sites in a normal Na solution. An explanation for this is that the H ions may have had some role in the process of K release and once they became adsorbed, they were difficult to replace with Na. In view of the relative mobilities of the H ions and the Na ions, it is possible that the H ions could have been the principal
Figure 13. Ratio of H adsorbed/K released by < 50 μm biotite after different periods of time in 0.2 N NaTPB < 0.9 N NaCl - 0.1 N NaOAc - HOAc - 0.01 M EDTA solution at pH 5
replacing ions when K was released. More work certainly needs to be done in this area before more positive statements can be made about the mechanisms involved.
Ellis and Mortland (1959) showed that there was a large difference in the rates of K release from native biotite and degraded biotite containing fixed K when the two materials were leached with 0.1 N NaCl solutions. The degraded biotite containing fixed K was prepared by leaching biotite with 0.1 N NaCl to remove K to different degrees then the degraded material was resaturated with K by drying it in the presence of KCl. X-ray diffraction patterns for the two materials were very similar but the K release rates were directly related to the extent of K removal which the biotite had undergone before it was resaturated with K. A loss in charge resulted when the biotite was K depleted and it was concluded that the difference in K release from the native biotite and the degraded biotite containing fixed K may be the result of the difference in charge density of the two materials.

In light of Ellis and Mortland's (1959) results, an experiment was set up to determine if similar results would be obtained with extracting solutions containing NaTPB. A sample of < 50 μ biotite that was K depleted with a 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solution was allowed to stand in the extracting solution for about 18 months after which it was resaturated with K by boiling for eight hours in 0.5 N KCl. A part of the resulting K-saturated degraded
Table 3. K content and total charge in < 50 μ biotite samples that have been degraded in solutions containing NaTPB

<table>
<thead>
<tr>
<th>Biotite sample</th>
<th>Total analysis (me./100 g.)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Na</td>
<td>Total charge</td>
<td>Change in total charge</td>
</tr>
<tr>
<td>Na-undegraded</td>
<td>199</td>
<td>26.5</td>
<td>225.5</td>
<td>-</td>
</tr>
<tr>
<td>NH₄-degraded</td>
<td>4.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-degraded</td>
<td>164.</td>
<td>16.6</td>
<td>180.6</td>
<td>-44.9</td>
</tr>
</tbody>
</table>

*Not determined for Na.*

Biotite (K-degraded) was oven-dried at 110°C for 48 hours and another part was airdried over CaCl₂ for 48 hours. Total K and Na were determined on the oven-dried K-degraded biotite and a Na saturated sample of undegraded < 50 μ biotite. Also, total K was determined on a sample of the degraded biotite which had been NH₄ saturated by boiling a portion of the degraded biotite in 0.5 N NH₄Cl for 20 minutes. The results are shown in Table 3.

The total K content of the undegraded biotite was 199 me./100 g. and after the long period of contact with the solution containing NaTPB, the total K content was decreased to 4.14 me./100 g. After the degraded biotite was
resaturated with K, the total K content had increased to 164 me./100 g. The undegraded biotite had a total charge of 225.5 me./100 g, but the total charge on the K-degraded biotite was only 180.6 me./100 g. As suggested in a previous chapter, the decrease in charge of the biotite probably took place while the expanded biotite was in the extracting solution for about 18 months.

Rates of fixed K release were determined on airdried and ovendried samples of the degraded biotite described in Table 3. Samples of the undegraded biotite were included in this experiment to determine the rate of native K release under the same condition. The method used to determine the rate of K release is described under Materials and Methods.

As shown in Figure 14, the fixed K release rates from the airdried and ovendried samples of the K-degraded biotite were similar but they were much higher than the rate of native K release from the undegraded biotite. An explanation for this difference in release rates for the fixed and native forms of K is that the charge density was lower in the degraded sample and the charge density affected the tenacity with which the layers were bound together. It was stated in a previous chapter that a decrease in charge density during K removal probably had nothing to do with the process of K removal. In this experiment, however, it was the difference in the initial charge density of the biotite that affected
Figure 14. Release of K from air dried and oven dried K-degraded < 50 μm biotite and also air dried undegraded < 50 μm biotite after different periods of time in 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solutions.
the release rate.

To determine the applicability of the theoretical equation for describing the release of fixed K, a plot of the left term, \((Q/Q_0) [1 - \ln (Q/Q_0)]\), against time is shown in Figure 15. A straight line is shown for the undegraded biotite indicating that the equation accurately describes the release of K from the sample. However, the experimentally determined values for the degraded biotite containing fixed K form a curve. Thus, the equation does not accurately describe the release of fixed K from the previously degraded biotite. The fact the equation does not describe the data is possibly due to the fact that the initial charge density of the previously degraded material may not be uniform in the biotite particle. If the decrease in charge takes place only in the expanded region of the particle over a period of time as postulated in a previous chapter, it would be expected that the region near the edge of the particle would have a lower charge density than the region nearer the center since the region near the edge would have been in contact with the extracting solution for a longer period of time. If the charge density is lowest near the edge and if rate of K release is inversely related to the initial charge density, the rate of K release would be higher in the early stages of K removal than the equation would predict. Thereafter, the rate would decrease as the K is released from the regions of
Figure 15. A plot of the experimental values of the left term of the theoretical equation, \((Q/Q_0) [1 - \ln (Q/Q_0)]\), against time for airdried and ovendried K-degraded < 50 \(\mu\) biotite and also airdried undegraded < 50 \(\mu\) biotite in 0.2 N NaTPB - 1 N NaCl - 0.01 M EDTA solutions.
higher charge farther from the edge. This explanation agrees with the experimental results shown in Figure 15.

Portions of the undegraded and degraded biotite samples were sedimented on ceramic plates for x-ray diffraction analysis. The Na-undegraded and K-degraded samples were sedimented on the plates from water suspensions but the Na-degraded sample was sedimented on the plate from the extracting solution in order that the diffraction patterns would indicate the basal spacing of the biotite with no readsorbed K. The patterns are shown in Figure 16. The pattern for the undegraded biotite (Figure 16A) shows only a sharp 10-Å peak and the pattern for the Na-degraded sample containing 4.14 me. K/100 g. (Figure 16B) shows only an equally sharp 15-Å peak. On removing nearly all of the K from biotite, a completely expanded material resulted which by the sharpness of the peak, shows a high degree of crystalinity. When the degraded biotite was resaturated with K, the 15-Å material was contracted to 10-Å; but the 10-Å peak, as shown in Figure 16C, is not as sharp as the 10-Å peak for the undegraded biotite and it tends to be slightly skewed toward the low angle side. Diffraction patterns for the K-degraded sample after airdrying, ovendrying at 110 °C and ovendrying at 250 °C were all similar to the pattern for the sample in the moist state. This indicates that the lack of sharpness of the 10-Å peak is probably not due to trapped
Figure 16. Tracing of x-ray diffraction patterns of moist oriented < 50 μ biotite samples before and after treatment with 0.2 N NaTPB - 0.01 M EDTA solutions and also after re-saturation with K

A. Na-undegraded
B. Na-degraded
C. K-degraded
water in the interlayer space. It is possible that the lower charge of the degraded material results in poorer crystallinity and consequently a broader 10-Å peak in the diffraction pattern.
SUMMARY AND CONCLUSIONS

The theoretical equation,

\[
\frac{Q}{Q_0} \left( 1 - \ln \frac{Q}{Q_0} \right) = 1 - \frac{4\pi D (C_a - C_b) t}{Q_0 \rho \delta r_b^2}
\]

was derived by Reed and Scott (1962) to describe the release of K from mica particles in solutions containing NaTPB. In the equation, \( \frac{Q}{Q_0} \) is the fraction of the initial K content of the particles that is present at time \( t \), \( D \) is the mean effective diffusion coefficient, \( \tau \) is the interlayer space, \( C_a \) and \( C_b \) are the K concentrations at the limits of the diffusion path, \( Q_0 \) is the mass of K in the mica initially, \( \rho \) is the original density of the mica, \( \delta \) is the original 001 spacing of the mica and \( r_b \) is the radius of the particle. The equation was derived on the basis that the rate determining process is the diffusion of the K and the replacing ions within the interlayer space of the particle from a receding weathering front to the edge of the particle.

Values of the left term, \( \left( \frac{Q}{Q_0} \right) \left[ 1 - \ln \left( \frac{Q}{Q_0} \right) \right] \), in the equation were calculated from experimental K release data and plotted against contact time. A straight line was obtained which indicated that the equation accurately described the experimental K release results. The slope of the line gave the value of the term
which was constant with time. Parameters for characteristics of the extracting solution and the biotite are contained in this constant term. The objective of this thesis was to evaluate the significance of some of these parameters. Since the term contains parameter \( C_b \), the concentration of K in the extracting solution, the rate of K release was studied in solutions containing different concentrations of K. When extracting solutions containing 3.5, 1.0 and 0.35 ppm. K were employed, the rate of K release from biotite was inversely related to the K concentration of the solutions. In the 3.5 ppm. K extracting solution, K was released from the biotite at a constant rate during the early part of the extraction time. This was not observed in the other solutions. When the experimental values of the left term, 
\[
\frac{4\pi D (C_a - C_b)}{Q_o \rho \delta r_b^2}
\]
were calculated from the release data of the experiment and plotted against time, it was found that the curves deviated from linearity in the early stages and latter stages of K release. The deviation from linearity in the latter stages was attributed to the fact that a broad range in particle size was used in the experiment whereas the equation was derived on the basis that all particles in the sample were equal in radii.
In the early stages of K release, the rate of release was slower in each case than was predicted by the equation. In the derivation of the equation, no consideration was made for the release of K during the formation of the weathering front. A certain amount of K had to be removed before the weathering front of constant dimension required by the equation was established. Despite these deviations, however, the theoretical equation described the release of most of the K in the biotite.

It was shown for the case of the 3.5 ppm. K system that the period of time that the experimental results deviated from the theoretical equation while the weathering front was being established coincided with the period of time that K was released at a constant rate. With lower K concentrations in solution it took less time to establish the weathering front and less K was removed before the weathering front was fully established. Mortland (1958) also observed periods of constant K release rates when biotite was leached with 0.1 N NaCl solutions in which the filtrate contained about 6 ppm. K. Apparently, the occurrence of a period of constant K release rate is associated with K release in solutions with high dissolved K levels.

The slopes of the linear portion of the curves were used with the theoretical equation to show that the difference in the rate with which K was released in the 3.5 and 1.0 ppm. K
systems was entirely due to the difference in $C_b$. This was not true for the 0.35 ppm. K system.

When biotite particles are placed in an extracting solution and the released K is allowed to accumulate in the solution, the concentration of dissolved K will increase until it reaches a critical level which prevents further release. It was shown that the critical K concentration in solution decreases sharply as K is removed from the biotite until about 25 me. K/100 g. are removed, after which, the critical concentration decreases more slowly until it is about 7.5 ppm. K at very low total K contents. It was concluded that if the K concentration in the extracting solution employed in this study is maintained below about 7.5 ppm., nearly all of the K will be removed from the biotite. If it is maintained at a higher level, lesser amounts will be removed regardless of the extraction time.

X-ray diffraction patterns for the biotite in equilibrium with the extracting solution showed that a sharp 15 $\AA$ spacing existed. This indicates that the K release did not stop at equilibrium because of a general collapse of the lattice. There was some indication, however, that there may have been a partially contracted region near the weathering front. The 15-$\AA$ spacing was the only expanded spacing observed regardless of the concentration of K in the extracting solution, therefore, parameter $\tau$ in the theoretical
equation is a constant for different $C_b$ values.

When K was removed from biotite, a reduction in charge density was sometimes observed. This decrease in charge appeared to be related to the amount of time the expanded region of the lattice was exposed to the extracting solutions. In addition, the theoretical equation accurately described the K release as a function of time even though the charge density of the biotite was decreasing during the extraction period. Thus, it is concluded that the decrease in charge is probably an indirect result of K removal and has nothing to do with the process by which K is released. Each sample that showed a decrease in charge also showed some oxidation of ferrous iron to ferric iron. However, there was no stoichiometric relationship between Fe oxidation and decrease in charge.

During K release, the only basal spacings observed were either 15-Å or 10-Å spacings which indicates that there was no significant amount of interlayering of 15- and 10-Å material. As K was removed, the 10-Å peak decreased and the intensity of the 15-Å peak increased. The intensity of the 15-Å peak was greater than the 10-Å peak relative to the amount of K remaining in the biotite. This agrees with results reported by Mortland (1958) for a similar study using 0.1 N NaCl leaching to remove the K from biotite.

When the degraded biotite was NH$_4$ saturated, some samples
showed nearly total collapse of the lattice to 10 Å while others showed very little collapse. The magnitude of retention of the 15-Å spacing was closely related to the amount of Na and its accompanying water that was trapped when the biotite was NH$_4$ saturated. Airdrying the samples did not change the diffraction patterns. Apparently, the water associated with the expanded region of the particles was trapped by lattice contraction at the edges when the samples were NH$_4$ saturated.

The diffusion of K and replacing ions in the interlayer space involves a mean effective diffusion coefficient. Since this mean effective diffusion coefficient is a function of the mobilities of the diffusing ions involved and the mobility of the H ion is about seven times that of Na, it was expected that the K release rate would be higher in extracting solutions with low pH. Experimental data showed that the solutions with pH 5 and 7 extracted the same amount of K but the solutions with pH 9 extracted considerably less K in the same amount of time. K extraction in solutions with pH 7 and 9 for 24 hours resulted in small decreases in charge density but K removal in solutions with pH 5 resulted in a charge decrease of 17.8 me./100 g. The amount of Fe oxidized was in the same order of magnitude as the decrease in charge for samples extracted in solutions with pH 5 and 7 but at pH 9, 26 mmol./100 g. were oxidized and the decrease in charge was
only 6.8 me./100 g. When K was extracted from biotite at pH 5, H ions from the extracting solutions were adsorbed by the biotite. During the extraction of the last half of the K from the sample, 47 per cent of the K removed was replaced by H ions even though the solution contained 120 thousand Na ions per H ion. The H ions may have had some role in the process of K release and once they were adsorbed, they were difficult to replace with Na. The probable role of the H ion is as a replacing ion for K. The high mobility of the H ion would tend to increase the mean effective diffusion coefficient D.

Ellis and Mortland (1959) showed that K release from degraded biotite containing fixed K was much more rapid than the release from undegraded biotite. In this study, a sample of highly degraded biotite which had been resaturated with K released K much more rapidly than did a sample of native biotite. The tenacity with which the layers are bound is directly related to the charge density, therefore, it was expected that K would be released faster from samples with low charge. The total charge of the K-degraded biotite was 181 me./100 g. whereas the total charge of the native biotite was 225 me./100 g. It was concluded that the difference in rate of K release was due to the lower charge density in the K-degraded biotite. The diffraction pattern for the K-degraded biotite showed a 10-Å peak only but the peak was
relatively broad and slightly skewed toward the low angle side which indicated the sample was poorly crystalline relative to the native biotite. The release of the fixed K was not described by the theoretical equation. It is quite possible that the charge density was lower near the edges than near the center. This would account for the higher initial rate than was predicted by the equation.


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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. A. D. Scott for his advice and assistance during the course of these studies and in the preparation of this manuscript.