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Susceptibility of interlayer potassium in illites to exchange

Samuel Joseph Smith
Iowa State University

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SUSCEPTIBILITY OF INTERLAYER POTASSIUM
IN ILLITES TO EXCHANGE

by

Samuel Joseph Smith

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

Major Subject: Soil Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa
1967
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INTRODUCTION

The exchange of interlayer K in contracted micaceous minerals by hydrated cations is one of the main processes by which micas weather to reactive clay minerals in soils. Also, the release and fixation of cations associated with this exchange can have an appreciable effect on the availability of plant nutrients in soils. Thus, detailed information about this exchange process is considered basic to an understanding of many chemical and mineralogical characteristics of soils.

Essentially all of the K in muscovite, biotite, phlogopite and vermiculite-hydrobiotite has been replaced by cation exchange in laboratory experiments. In the case of Grundite illite, however, only 66 percent of the K has been exchanged. It is now necessary to determine if this limited exchange of interlayer K is characteristic of all illites and why part of the K in this type of mineral is not exchangeable. This information is considered particularly pertinent because illite is a major constituent of many soil clays.

The term illite is used here as a general name for naturally occurring micaceous clay materials that contain a 10 Å component in a mixed-layer configuration with different amounts of expanding type silicate layers. Seven of these materials were selected for this investigation. These illites differ in regard to crystallinity and amount of mixed-layering but they all have an appreciable amount of K between the layers of the 10 Å component. The primary objective of this study was
to determine the susceptibility of this interlayer K to ex-
change by other cations.
LITERATURE REVIEW

Characteristics of Illite

The name illite was proposed by Grim, Bray and Bradley (1937) for the clay mineral constituent of argillaceous sediments belonging to the mica group. This material was named illite, in honor of the state of Illinois, a pioneer state in clay research. For general information about illite, reference can be made to articles by American Petroleum Institute (1951), Bradley and Grim (1961), Geiseking (1949), Grim (1953), Jackson (1964), Keller (1964), Marshall (1964) and Pask (1957).

While Grim, Bray and Bradley (1937) used the name illite as a general term for the mica-type clay minerals, not as a specific mineral name, confusion has developed in recent years in regard to the usage of this term and the characteristics of the material referred to. Barshad (1954) presented evidence that illite is a mixture of potash-mica and vermiculite. Berry and Mason (1959) refer to illite as clay mica. Jackson (1964) refers to extensive evidence that illite is mica with intermixed expanding layers. He presents additional evidence that this is the case in a recent paper (Raman and Jackson, 1966). Keller (1964) regards illite as a rock term. Yoder (1959) also regards illite as a rock term for a randomly interstratified material with mica and montmorillonite layers. It is evident from these papers that the term illite is frequently used in the literature in reference to the entire mixed-layer.
assemblage of 10 Å and open lattice silicates in the clay-size material. The properties of this illite are then often related to the micas in terms of the differences imposed by the presence of the expanded layers. On the other hand, some investigators like Gaudette, Eades and Grim (1965) contend that the term illite should be used as a group name for only the 10 Å nonexpanding portion of the clay material in argillaceous sediments, and that mixed-layer assemblages of this 10 Å material with expanded layer silicates be described as illite-montmorillonite, illite-vermiculite etc. The nomenclature committee to the International Mineralogical Association currently includes the term illite only in a footnote until further research shows if illite constitutes a valid group apart from the micas, or should be included along with interstratified minerals (Brindley, 1966).

The materials that are generally referred to as illites in the literature are phyllosilicates containing 2 Si tetrahedral layers with an Al octahedral layer sandwiched between. Generally, two-thirds of the octahedral positions are occupied, giving the mineral a dioctahedral structure. Some substitution of Al by Fe and Mg may occur. Illites have about one-sixth of the Si in the tetrahedral layer replaced by Al, compared to one-fourth in the well-crystallized micas. This isomorphous substitution often gives rise to a charge deficiency (layer charge) of 130-160 me./100 g. The layer charge is primarily balanced by K ions that electrostatically bind the
silicate layers together. However, part of the layer charge can be balanced by other cations, frequently Na, H, Mg and Ca. The substitution of these cations for K may result in expanded layers.

The size of the naturally occurring illite particles is small, usually < 2 μ. While the layer charge may be 160 me./100 g., the cation exchange capacity (CEC) is frequently 10-40 me./100 g. These typical CEC values are determined with NH₄ as the replacing cation and, therefore, constitute a measure of only the exchange sites on external surfaces and all surfaces of the expanded (hydrated) layers.

X-ray diffraction data shows part of the illite has a 10 Å basal spacing. However, the 10 Å peak in the diffraction pattern is a band which tails toward the higher spacings, due to the presence of expanded layers randomly mixed with the 10 Å material. In general, the broader the band, the greater the mixed-layering. The 10 Å material does not expand on treatment with glycerol or glycol, but this treatment can alter the spacing of the expanding portion of the mineral. Thus, there is often a greater distinction between the components of illite when x-ray patterns are obtained with glycerol or glycol saturated samples.

Glaucnites are illites that have considerable replacement of Al by Fe and Mg in the octahedral layer (Grim, 1953). A distinguishing feature of glauconites is that they are formed at times of slow sedimentation, in relatively shallow water,
during marine diagenesis. Bacterial action is thought necessary for glauconite formation.

Metabentonite is a term applied to the potassium bearing Ordovician clays formed by the alteration of volcanic ash (American Petroleum Institute, 1951). This material appears to be composed of varying amounts of illite and montmorillonite (Hower and Mowatt, 1966), but in general terms metabentonite can be regarded as simply another illite.

Factors Affecting Interlayer K Exchange

When mica particles are placed in an extracting solution like NaCl, an exchange of interlayer K by Na occurs. If the replaced K accumulates in the extracting solution, the exchange will be limited by the mass action effect of this K in solution. In fact, Hanway, Scott and Stanford (1957) and Scott, Hunziker and Hanway (1960) have shown that very small amounts of fixable cations (K, NH₄, Cs and Rb) interfere with the replacement of interlayer K from contracted layer silicates. This occurs because all of the fixable cations tend to contract the mineral lattice. Scott, Hunziker and Hanway (1960) showed that a K/Na solution ratio of 0.0005 was enough to block further exchange of interlayer K from vermiculite. The extent to which interlayer K in various micas can be exchanged in 1 N NaCl solution when the replaced K is allowed to accumulate to different levels in solution was recently determined (Scott and Smith, 1966). With 15 percent K replacement, the levels of K
in solution for phlogopite, biotite, Grundite illite, and muscovite were 23, 10, 1, and 0.1 ppm, respectively.

The release of interlayer K from micas involves the diffusion of the K ion from within the particle to the extracting solution, and vice versa for the replacing cation. Mortland and Ellis (1959) concluded diffusion of Na and K ions through a solution film at the particle edge was the rate limiting process in the release of fixed K from vermiculite by NaCl leaching. Reed and Scott (1962) derived a mathematical expression, based on Fick's law, that accurately described interlayer K release from narrow size ranges of mica particles in NaTPB solution. The rate limiting process was the diffusion of K and Na ions within the interlayer space of the mica. The expression of Reed and Scott was applicable to wide ranges in particle size when a variable diffusion coefficient was used (Sorensen, 1964).

Barshad (1954) in a study of cation exchange in micaceous minerals removed K from vermiculite, biotite and muscovite with neutral salt solutions. Under these conditions much of the K was not replaced. However, he showed the exchange of interlayer K was affected by the magnitude of the layer charge, particle size, presence of difficultly exchangeable H, nature of the replacing cation, and the fixed or native character of the K. He concluded the crystal lattice of a micaceous mineral would be contracted if the interlayer charge was greater than 150 me./100 g.
For the exchange of interlayer K, an expansion of the lattice must occur. This lattice expansion associated with K depletion of micaceous minerals has been studied extensively (Barshad, 1948; Bailly, 1963; Caillerè, Hénin and Guennelson, 1949; Cook and Rich, 1963; Demumbrum, 1963; Mortland, 1958; Scott and Reed, 1962a, 1962b, 1965; Scott and Smith, 1966; White, 1950). White (1950) removed 10.8 percent of the K from Fithian illite using sodium cobaltinitrite and observed a lattice spacing of 17.9 Å when the degraded mineral was glycerol solvated. Demumbrum (1963) degraded Fithian illite to an unspecified degree with NaTPB solution. He observed only expansion to 14 Å upon glycerol solvation. Bailly (1963) removed 61 percent of the K from Morris illite and observed 14 and 18 Å lattice spacings upon glycerol solvation.

Scott and Smith (1966) determined the basal spacing of various micaceous minerals after maximum K depletion with NaTPB solution. Muscovite expanded to 12.3 Å. Under the same conditions biotite, vermiculite and phlogopite expanded to 15.0 Å. This difference was attributed to the higher layer charge of muscovite. Grundite illite expanded to 12.3 and 15.0 Å. It was concluded the illite contained some layers with a high charge like muscovite, and others with a lower charge which permitted more expansion.

Raman and Jackson (1966), Rich and Black (1964) and Tucker (1964a, 1964b) have stressed the role of H ions in replacing interlayer K from illites. Tucker (1964b) has concluded the
displacement of interlayer K from soil illite even in neutral solution involves the combined action of H and the replacing cation. Scott and Smith (1966) found an appreciable effect of solution pH on K replacement from trioctahedral micas but little effect on dioctahedral micas.

There is little data on the effect of other cations on the replacement of interlayer K. Williams and Jenny (1952) studied the replacement of non-exchangeable soil K by various metallic cations. They found Na to be the most effective cation. Smith and Scott (1966) found NaCl was the most effective salt to use with NaTPB solution for the extraction of interlayer K from Grundite illite.

**K Extraction by Leaching and Equilibration**

Leaching and equilibration methods have been used extensively to remove interlayer K from trioctahedral micas (Barshad 1948, 1954; Caillère, Hénin and Guennelson, 1949; Ellis and Mortland, 1959; Mortland, 1958; Scott and Smith, 1966). Mortland (1958) removed more than 75 percent of the interlayer K from <250 μ biotite by leaching with 0.1 N NaCl. Scott and Smith (1966) removed 95 percent of the interlayer K from 10-20 μ biotite by equilibrating 0.1 g. in 1 liter of 1 N NaCl. However, even with trioctahedral micas, interlayer K release by leaching and equilibration methods can be slow and often only a small part of the interlayer K is released. For instance, when Mortland (1958) equilibrated 20 g. of <250 μ
biotite in 1 liter of 0.1 N NaCl, equilibration had not been reached 14 days later, and less than 5 percent of the K had been replaced.

Leaching and equilibration methods are generally less effective with dioctahedral micas than trioctahedral micas. Rausell-Colom, Sweatman, Wells and Norrish (1965) found interlayer K from trioctahedral micas was readily exchanged in aqueous salt solutions, but could detect no K exchange with dioctahedral micas. This difference is due to the effect of the K in the extracting solution. Scott and Smith (1966) found a 7 ppm solution K level that allowed all the K in 10-20 μm biotite to be exchanged in 1 N NaCl did not allow any of the interlayer K in 10-20 μm muscovite to be exchanged. Obviously, dioctahedral micas are more sensitive than trioctahedral micas in regard to the blocking effect of solution K on interlayer K release.

With illites, leaching and equilibrium methods frequently result in an exchange of K from only the external surfaces and possibly interlayer positions at the periphery of the particles (Bolt, Sumner and Kamphorst, 1963; Rich and Black, 1964; Tucker, 1964a). For example, less than 2 percent of the K was exchanged in a 1.2 g. sample of soil illite equilibrated in 200 ml. of M/300 CaCl₂ (Tucker, 1964a).

Interlayer K replacement can be obtained by equilibrating dioctahedral micas in salt solutions if the concentration of K in the solution is low. Scott and Smith (1966) recently
removed 17 and 61 percent of the K from muscovite and Grundite illite, respectively, by equilibrating 0.075 g. samples in 15 liters of 1 N NaCl. However, such experiments are not practical on a routine basis because extremely large volumes of solution and small amounts of mineral must be used to keep the K in the solution at a low enough level.

K Extraction with Solutions Containing a K Precipitant

The accumulation of replaced K in the solution can be avoided by using a K precipitant in the extracting solution. Methods for the extraction of interlayer K from micas by using K precipitants have been discussed in some detail by Reed (1963) and Scott and Reed (1965). With these procedures essentially all the K in biotite, muscovite, phlogopite and vermiculite-hydrobiotite has been extracted. However, variable results have been obtained with illite.

White (1950) extracted 10.8 percent of the K from Fithian illite using sodium cobaltinitrite to precipitate solution K. Hanway (1954) introduced the use of sodium tetraphenylboron (NaTPB) in the extraction of interlayer K from Grundite illite. Today, NaTPB solutions are used extensively because all fixable cations (K, NH₄, Cs and Rb) that block interlayer K release are precipitated. Scott, Hunziker and Hanway (1960) extracted 47 percent of the K from Grundite illite using successive NaTPB extractions. Later, Scott and Reed (1962b) were able to extract 68 percent of the K from Grundite illite in a single,
63-day, NaTPB extraction. Bailly (1963) extracted 61 percent of the K from Morris illite in 28 days using NaTPB solution. Smith and Scott (1963) heated Grundite illite at 450°C. for 24 hours and subsequently extracted 93 percent of the K using NaTPB solution. Data of Raman and Jackson (1966) indicate 33, 34, and 44 percent of the K in Beavers Bend, Marble Head, and Fithian illite, respectively, was removed by NaTPB solution.

Smith and Scott (1966) have found that only 66 percent of the K in naturally occurring Grundite illite is extractable by exchange with Na even when the replaced K is precipitated with TPB. This amount was extracted in 1 week. Contact times with NaTPB solution longer than a year did not remove more K. Subjecting the illite to ultrasonic vibration in NaTPB solution for 72 hours, however, resulted in essentially complete K replacement. There was no evidence from the x-ray diffraction patterns or layer charge determinations that these results were due to a destruction of the mineral by ultrasonics.
MATERIALS

The following illite samples were used in this study.
1. Beavers Bend - Clay from the Blaylock formation in Beavers Bend State Park, Oklahoma.
2. Marble Head - Clay from pockets in Silurian dolomite near Marble Head, Wisconsin.
3. Rock Island - Clay from pockets in Ordovician limestone in Rock Island County, Illinois.
4. Fithian - Pennsylvanian underclay from an area near Fithian, Illinois.
5. Morris - Pennsylvanian underclay from an area near Morris, Illinois.
7. Glauconite - Greensand from Monmouth County, New Jersey.

Beavers Bend was obtained from W. Bellis, University of Oklahoma, Norman, Oklahoma; Marble Head and Rock Island were obtained from H. Gaudette, University of New Hampshire, Durham, New Hampshire. Fithian (A.P.I. No. 35), Morris (A.P.I. No. 36), Metabentonite (A.P.I. No. 41) and Glauconite were obtained from Ward's Natural Science Establishment, Rochester, New York.

Beavers Bend is considered to be an exceptionally pure, well-crystallized illite. The material is described in detail by Gaudette, Eades and Grim (1965) and Mankin and Dodd (1963). It is fine-grained and has a light-olive color. Beavers Bend has a predominantly dioctahedral structure and very few, if
any, expanded layers. Mankin and Dodd (1963) have proposed Beavers Bend as a reference clay mineral due to its relative purity. However, chlorite has been reported present as a mechanical mixture in some samples. Recently, Raman and Jackson (1966) found 29 percent chlorite in a Beavers Bend sample.

Marble Head is also a well-crystallized illite. It is a laminated gray clay. In recent years, Marble Head has been used as a reference clay sample in the Clay Mineralogy Laboratory at the University of Illinois. Detailed analysis of Marble Head (Gaudette, 1965) showed a noticeable lack of quartz, chlorite, and other contaminants. Gaudette, Eades and Grim (1965) found Marble Head had a dioctahedral structure, and approximately 5 percent expanded layers present.

Rock Island is a light-gray, well-crystallized illite. Detailed analysis by Gaudette, Eades and Grim (1965) showed this material has a dioctahedral structure and approximately 5 percent expanded layers. A mechanical mixture of chlorite has been reported in some samples.

Fithian was first described by Grim, Bray and Bradley (1937) and was one of the original samples assigned the name illite. It is a greenish-gray underclay with a dioctahedral structure. Gaudette, Eades and Grim (1965) found 10-15 percent expanded layers present.

Morris is a grayish-green underclay from the area near Morris, Illinois, where the commercially available Grundite Bond Clay is mined. It has a dioctahedral structure and more
expanded layers than Fithian.

The Metabentonite occurs in association with the Martinsburg shale in southwestern Virginia. The sample has a pink color. Hower and Mowatt (1966) have recently reported detailed chemical and structural characteristics of a metabentonite sample from this Martinsburg formation. Their material had a dioctahedral structure and 23 percent expanded layers.

The New Jersey greensand is a glauconite which is generally considered to be a mechanical mixture of contracted and mixed-layer silicates. It occurs as green argillaceous pellets. Burst (1958) has reported detailed chemical and structural properties of the material. By segregation of pellets, he was able to distinguish a well-crystallized component with a dioctahedral structure. Toler and Hower (1959) segregated greensand particles and found the more crystalline particles still contained 10 percent expanded layers.

The illite samples were put through a 60 mesh screen, mixed thoroughly and air-dried. In some cases, a minimum amount of crushing by hand or a ceramic mill was employed to pass all the sample through the screen. Rock Island was all <200 mesh when received. None of the samples received further pretreatment.

Several chemical characteristics of the illite samples are given in Table 1. The total K values are slightly lower than some that have been reported in the literature. This can be attributed to the fact that these K values apply to the whole
Table 1. Chemical characteristics of illites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total analysis</th>
<th>Layer charge</th>
<th>Exchangeable K</th>
<th>CEC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pH&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>K (me./100 g.)</td>
<td>Na (ppm)</td>
<td></td>
<td>NH₄&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Na (me./100 g.)</td>
</tr>
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<td>Beavers Bend</td>
<td>122</td>
<td>4.8</td>
<td>0.27</td>
<td>826</td>
<td>138</td>
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<tr>
<td>Marble Head</td>
<td>184</td>
<td>3.7</td>
<td>0.94</td>
<td>392</td>
<td>209</td>
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<tr>
<td>Rock Island</td>
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<td>6.5</td>
<td>0.06</td>
<td>700</td>
<td>100</td>
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<tr>
<td>Fithian</td>
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<td>1.10</td>
<td>1180</td>
<td>132</td>
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<td>Morris</td>
<td>103</td>
<td>8.4</td>
<td>0.77</td>
<td>784</td>
<td>126</td>
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<td>Metabentonite</td>
<td>135</td>
<td>12.8</td>
<td>0.92</td>
<td>784</td>
<td>162</td>
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<tr>
<td>Glauconite</td>
<td>174</td>
<td>21.8</td>
<td>0.11</td>
<td>126</td>
<td>196</td>
</tr>
</tbody>
</table>

<sup>a</sup>Na saturated illite leached with NH₄ or Ca salt

<sup>b</sup>pH with 0.5 g. illite in 10 ml 1 N NaCl
sample, whereas others have used fractions of the natural material. X-ray diffraction analyses showed there was 10 Å material in all the samples. This 10 Å material did not expand when the samples were Mg saturated and glycerol solvated. Therefore, it was concluded from the chemical and x-ray data that these particular samples were suitable illitic materials for this study.

In a few experiments, other K-bearing minerals were included for comparative purposes. Grundite from the Illinois Clay Products Company was dispersed in water without pretreatment and the < 2 μ fraction was separated by sedimentation. This fraction contained 123 me. K/100 g. Grundite is the trade name for Pennsylvanian underclay mined by the Illinois Clay Products Company at Morris, Illinois. Muscovite from Ontario, Canada, and orthoclase from Climax, Colorado, were obtained from Ward's Natural Science Establishment. Both of these minerals were ground and dry screened to separate the < 50 μ material. These muscovite and orthoclase fractions contained 220 and 244 me. K/100 g., respectively.
METHODS

Total K and Na were determined by HF-HClO₄ digestion as described by Jackson (1958). Exchangeable K was determined by leaching 0.5 g. air-dry samples (110°C. basis) with 50 ml. neutral normal NH₄OAc or NaCl. Carbon was determined by a dry combustion method as described by Black (1957). Nitrogen was determined by the semi-micro Kjeldahl method described by Bremner (1965). The analyses of K and Na in the various solutions were made with a Baird Atomic Model KY-2 flame photometer using Li as an internal standard.

Portions of the original illites were leached with neutral normal NaOAc solution, a small amount of normal NaCl solution, and finally with 95 percent ethanol to prepare chloride-free, Na saturated samples. Samples of degraded illite were Na saturated by leaching with 0.5 N NaCl - 60 percent acetone-water to remove the KTPB, with 90 percent acetone-water to remove the excess salts, and with a small amount of water to remove the acetone. Cation exchange capacity (CEC) was determined by leaching 0.5 g. air-dry samples (110°C. basis) of the original Na saturated illites with 50 ml. neutral normal NH₄OAc or Ca(OAc)₂. Layer charges were determined by summing the total K and Na contents of the Na saturated samples.

The general procedure of extracting K with a NaTPB (sodium tetraphenylboron) solution and determining the precipitated K is described by Smith and Scott (1966). In this method, 0.5 g. (110°C. basis) of air-dry illite was placed in erlenmeyers that
contained 1.03 g. NaTPB and 10 ml. 1.7 N NaCl-0.01 M disodium dihydrogen EDTA. The illite-extracting solution mixtures were swirled gently and stored at 25°C. for specific periods. The mixtures were then placed in approximately 700 ml. of distilled water that contained 500 me. NH₄Cl. Six mmol. HgCl₂ were added and the systems were boiled 20 minutes, cooled and filtered. The filtrates were diluted to 1 liter with distilled water and K was determined.

X-ray diffraction analyses were made with a General Electric XRD-6 diffractometer. A scintillation counter and Ni-filtered Cu radiation were used in each case.
RESULTS AND DISCUSSION

Equilibrated Systems

The NH$_4^+$-exchangeable K values in Table 1 are the maximum amounts of K that were replaceable with NH$_4^+$. Obviously, Na replaced more of the K in these minerals. This difference is due to the fact that the mica layers remained contracted and the interlayer K remained inaccessible to exchange when NH$_4^+$ was present, whereas Na expanded the lattice and replaced K to a degree determined by the level of K that accumulated in solution (Scott and Smith, 1966). The extent to which K can be replaced from a mineral with different levels of K in solution can be determined by placing various amounts of the mineral in different volumes of extracting solution and allowing the systems to equilibrate. Such an experiment was carried out with samples of 4 of the 7 illites in a 1 N Na solution.

Samples of Beaver Bend, Marble Head, Fithian, and Morris were placed in a 0.785 N NaCl-0.1 M Na$_2$HPO$_4$-0.015 M NaH$_2$PO$_4$ solution that was buffered at pH 7.2. The amount of the sample and the volume of solution were varied widely. The mixtures were shaken frequently while they were stored for 1 year in a constant temperature room at 25°C. At the end of this period, the amounts of K in the extracting solutions were determined. It was assumed from previous observations with Grundite, that 1 year would be adequate time for equilibrium (Scott and Smith, 1966). The pH of each system was determined and was found to
Figure 1. The relationship between the equilibrium levels of K in a 1 N Na solution and the percent K replaced from illites.
remain at pH 7.2 throughout this period.

The data in Figure 1 show the extent to which the interlayer K in the illites was exchanged by Na when the replaced K accumulated to different levels in the solution. Obviously, the accumulation of replaced K in the extracting solution limited the amount of interlayer K that was extracted from all the illites. In each case, however, more of the K in the illites was replaced as the K in solution decreased. A decrease of only a few ppm K in solution resulted in a large increase in the amount of K replaced. For example, with 2 ppm K in solution, 10 percent of the K was replaced from Morris, whereas nearly 40 percent of the K was replaced when there was only 0.5 ppm K in solution. Differences between illites with regard to the effect of K in solution are particularly evident when there was more than 1 ppm K in solution. The K in Morris was the most susceptible to exchange by Na, whereas the K in Marble Head was the most resistant. These differences between the illites decreased as the degree of K replacement increased. Furthermore, the data in Figure 1 suggest that all the K in these illites may be replaceable if a low enough level of K is maintained in the solution. This means the K in solution must be kept below this level to determine the effects of other factors on the exchange of the interlayer K in these illites. Otherwise, differences observed between illites could be due to the blocking effect of K in solution.

The standard solutions for the K analyses were prepared
with the same Na solution as was used in the equilibrium experiment. Consequently, the experimentally determined values for the K in solution are a measure of the K replaced from the illites. The actual level of K in solution for each degree of K replacement may have been higher than that shown in Figure 1 because of K impurities in the Na salts. To minimize this error, however, reagent grade NaCl with < 0.0005 percent K analysis (< 0.3 ppm K in 1 N NaCl) was selected for these experiments. No K content was listed in the lot analysis of the reagent grade Na phosphate compounds, but the small amounts of these salts in the solution would not be expected to increase the K level of the solution appreciably.

The results of the equilibrium experiment emphasize the importance of using salt solutions that are free of K impurities to study the exchange of interlayer K in illites. Reagent grade NaCl commonly contains 0.005 percent K (3 ppm K in 1 N NaCl). Solutions prepared from this salt could easily contain enough K impurities to limit the exchange of interlayer K in illites. For instance, Figure 1 shows that less than 10 percent of the interlayer K would be replaced from the 4 illites with a 1 N NaCl solution that contained this 3 ppm K. This effect of K impurities accounts for the limited amount of K that various investigators have been able to extract from illites by extensive leaching with NaCl solution.

The strong preference these 4 illites exhibited for K over Na can be expressed in terms of selectivity coefficients.
Following the notation of Helfferich (1962), selectivity coefficients \( K^k_{Na} \) were calculated for these ion exchange equilibria and found to be greater than 1. The magnitude of these coefficients, however, varied with the degree of K depletion. Thus, to compare the illites, selectivity coefficients were determined at the same degree of K depletion. At 15 percent K depletion, selectivity coefficients ranged in the order of magnitude from \( 1 \times 10^5 \) for Morris to \( 3 \times 10^5 \) for Marble Head. In a similar equilibration experiment with \( 1 \text{ N NaCl} \), Scott and Smith (1966) found selectivity coefficients of vermiculite, phlogopite, biotite, Grundite and muscovite at 15 percent K depletion to be \( 1 \times 10^3 \), \( 5.4 \times 10^4 \), \( 1.3 \times 10^4 \), \( 1.3 \times 10^5 \) and \( 1 \times 10^6 \), respectively. Thus, the selectivity coefficients that were determined for the 4 illites in this study are comparable to the coefficient obtained previously with Grundite. Also, these data show the illites vary less than micas in regard to their selectivity for K. Since all the illites have similar K-selectivity coefficients relative to the micas, the weathering sequence for micaceous minerals (Scott and Smith, 1966), based on the levels of K in solution that limit K exchange, can now be addended. On the basis of these levels, the resistance of micaceous minerals to weathering by K depletion should follow the sequence: muscovite > illites > biotite > phlogopite > vermiculite.

The selectivity coefficients that were calculated here for illites with 15 percent K depletion are higher than those
reported for the exchange of K (by Na or Ca) from external surfaces and possibly interlayer positions at the periphery of illite particles (Bolt, Sumner and Kamphorst, 1963; Rich and Black, 1964). This difference reflects the greater resistance of the interlayer K to exchange and the increase in this resistance as more of the interlayer K is replaced.

Non-equilibrium Extractions

It was concluded from the equilibrium experiments that differences between the illites in regard to interlayer K exchange exist when the extracting solution contains K. Therefore, the effect of the dissolved K had to be reduced to a minimum before the illites could be compared further. This was done by precipitating the replaced K with NaTPB in the extracting solution.

A method of using NaTPB solutions to extract interlayer K from illites has been developed with Grundite (Smith and Scott, 1966). This method was used to determine the exchangeability of the interlayer K in the 7 illites. The solubility of KTPB in water is $18 \times 10^{-5}$ moles per liter (Flaschka and Barnard, 1960) but the level of K in the extracting solution used here can only be estimated because TPB decomposes and NaCl affects the solubility of NaTPB. According to this estimate, there was < 0.005 ppm K in the extracting solution. This level of K in solution should have been low enough to cause no blocking effect on interlayer K exchange.
Figure 2. K extracted from Beavers Bend in NaTPB solution for different periods.
Figure 3. K extracted from Marble Head in NaTPB solution for different periods
Figure 4. K extracted from Rock Island in NaTPB solution for different periods.
Figure 5. K extracted from Fithian in NaTPB solution for different periods.
Figure 6. K extracted from Morris in NaTPB solution for different periods
Figure 7. K extracted from Metabentonite in NaTPB solution for different periods
Figure 8. K extracted from Glauconite in NaTPB solution for different periods
The amounts of K in the illites that were replaced by Na in different periods of time with NaTPB solution are shown in Figures 2-8. It is obvious from these data that the interlayer K in the various illites is not equally exchangeable even when the interfering effects of K in solution are eliminated. Differences between illites are apparent with regard to the amount and to the rate of K exchange.

This method of extracting K from illites removed 94, 44, 83, 70, 67, 83, and 77 percent of the K from Beavers Bend, Marble Head, Rock Island, Fithian, Morris, Metabentonite, and Glauconite, respectively. Thus, all the K was not replaced from any of the illites. Furthermore, the amount of K replaced did not depend on the total K content. In fact, the sample with the highest K content, Marble Head, had the least K replaced.

In general, the replaceable K in the 7 illites was extracted within a week. Longer extraction periods (up to a year) failed to remove more of the K. A similar limitation to the amount of K that can be extracted with NaTPB solutions has been observed previously with Grundite, but not with vermiculite, phlogopite, biotite, or muscovite (Scott and Smith, 1966; Smith and Scott, 1966). In a previous study with Grundite, Smith and Scott (1966) showed the method of replacing, separating and determining the K is adequate, but that some of the K in Grundite is not accessible to exchange by Na in the absence of ultrasonic vibrations. The limited K exchange
observed with the illites in this study is probably not due to the method either. Instead, it appears that only a portion of the K in most illites is accessible to exchange by Na, and that the limited exchange is due to some inherent characteristic of illite material. This limited K exchange constitutes a major difference between illites and micas.

There is no consistent relationship between the total or the extractable K in these illites and the rate of K release. Consequently, neither of these mineral parameters can account for the differences that exist between the illites in regard to rate of K release. These differences between the illites are evident in Figure 9, which shows the relative rate with which the extractable K in the 7 illites was removed. The smooth curves in Figure 9 were obtained from data in Figures 2-8. The results of Morris and Fithian are quite different from the other illites. There was a rapid exchange of part of the interlayer K in these 2 samples. This rapid exchange of K was attributed at first to a smaller particle size. If this were the case it would be expected that the exchangeable K and CEC values for these samples would also be higher than those for the other illites. From Table 1 it can be seen that an appreciable difference in these values did not exist. Therefore, the rapid exchange of interlayer K from Morris and Fithian is not considered to be due to particle size. Instead, it is considered more likely that these 2 samples contained some silicate layers of lower layer charge that were easily expanded
Figure 9. Comparison of the relative rates with which the extractable K in the various illites was removed with NaTPB solution.
in the NaTPB solution to release K by complete layers.

There was no relationship (Figure 9) between the initial rate of K release and time required for complete release of extractable K. Metabentonite, with one of the slowest initial rates, had all of the extractable K released in the shortest time, approximately 3 days. Glauconite, on the other hand, released more than 80 percent of its extractable K in 1 week, yet, extractable K continued to be released for 8 weeks.

Comparison of the curves in Figure 9 with the curves that have been obtained with other micaceous minerals in NaTPB solutions (Scott and Smith, 1966) shows that the curves of Morris and Fithian are similar in shape to that of Grundite, whereas the curves of the other illites are similar in shape to those of the micas. Differences in the Grundite and mica curves have been considered in a theoretical study by Sorensen (1964)*. A similar kinetic study of the rates with which the illites in this study released K to NaTPB solution was made to further characterize these illites.

Kinetics of K Release

Reed and Scott (1962) described K release from muscovite and biotite particles of a narrow size-range in NaTPB solution. Their treatment, based on Fick's law, involved the solution of a two-dimensional radial diffusion problem in which K diffuses from a receding weathering front to the particle periphery. The mica particles were assumed to be flat circular plates.
Sorensen (1964) generalized the equation of Reed and Scott (1962) to account for a wide variation in particle size. Sorensen's treatment characterized the mineral in terms of one effective particle size and incorporated a variable diffusion coefficient to reflect the behavior of all the particles. His general equation can be expressed, in simplified form, as

\[ u^{-x} \ln u \, du = k \, dt \]  

(1)

where \( u \) is the fraction of interlayer K remaining in the mineral at time \( t \), and \( x \) and \( k \) are constants containing properties of the variable diffusion coefficient and the mineral, respectively. Integration of equation 1 gives

\[ u^m (1 - m \ln u) = 1 - k m^2 t \]  

(2)

where \( m = 1 - x \). The value of \( m \) that is appropriate for a certain mineral sample cannot be computed directly, thus, Sorensen determined the applicability of this equation to the K release data of several micaceous minerals in NaTPB solution by assigning different values to \( m \). For the case of < 50 \( \mu \) biotite and muscovite, Sorensen showed the applicable \( m \) value was zero. With < 2 \( \mu \) Grunidite and various size fractions of vermiculite the applicable \( m \) value was -1.

The \( m \) values used in this investigation were 1, 0, -1 and -2. When \( m = 0 \), Equation 2 cannot be used. However, substitution of \( x = 1 \) (\( m=0 \)) into general Equation 1 gives an equation which can be integrated. When \( m = 1 \), Equation 2 reduces to the original equation of Reed and Scott (1962). Thus, for the
various values of \( m \) the following equations were obtained:

\[
\begin{align*}
 m &= 1, \quad 1 - u (1 - \ln u) = k t \\
 m &= 0, \quad \ln^2 u = 2 kt \\
 m &= -1, \quad 1 - \left(\frac{1 + \ln u}{u}\right) = k t \\
 m &= -2, \quad 1 - \left(\frac{1 + 2 \ln u}{u^2}\right) = 4 kt
\end{align*}
\]

A plot of the terms on the left side of these equations against time should give a straight line if the equations are applicable. More information can be obtained, however, by plotting the log of the left terms against \( \log t \) because greater emphasis is thereby given to that part of the extraction period when a major portion of the \( K \) is released. In addition to being linear, the curve for this log-log plot must have a slope of unity for the equation to be applicable. Only the interlayer \( K \) that is extractable will be considered in this kinetic study because only the release of the extractable \( K \) can be characterized in regard to rate. Thus, \( u \) becomes the fraction of the extractable \( K \) that remains in the mineral at any particular time.

Equation 3 (\( m = 1 \)) described \( K \) release from narrow size fractions of biotite and muscovite in NaTPB solutions (Reed and Scott, 1962). Therefore, this equation was used first with the Beavers Bend data because this mineral is considered to be the most highly crystalline and "mica-like" of the illites. The results in Figure 10 show that this equation is not applicable for Beavers Bend. When Equations 4 and 5 (\( m = 0 \) and -1,
Figure 10. Plot of the K extraction data for Beavers Bend obtained with Equation 3 (m = 1)
respectively) were used (Figure 11), straight line relationships for major portions of the release of K from Beavers Bend were obtained, but the slopes were greater than unity.

Figures 12-17 show the curves obtained with Equations 4 and 5 (m = 0 and -1, respectively) and the K release data for the other 6 illites. Straight line relationships for major portions of K release were obtained with all samples, depending on the value of m, but in no case was a slope of unity obtained. Figures 18 and 19 show the applicability of Equation 6 (m = -2) to the K release data for Fithian and Morris, respectively. Again, the curves are linear, but the decrease in m from 0 to -1 and now to -2 has increased the slope of the curves. Table 2 indicates the extent to which the incorporation of a variable diffusion coefficient described K release from the 7 illites. The percent extracted K giving a straight line relationship varies from 66 percent (Fithian and Rock Island) to 99 percent (Morris). The slopes range from 0.82 (Rock Island) to 1.61 (Metabentonite).

By using equation 1 and suitable values of m it was possible to obtain linear relationships for most of the K release data for these illites. However, the slopes of the curves varied slightly from unity. Sorensen (1964) obtained slopes ranging from 0.98 to 1.10 in his study with micaceous minerals, and he noted that an inaccurate estimate of the total extractable K would affect the value of u and may cause the slope of the resulting plot to differ from unity. When values ± 5
Figure 11. Plots of the K extraction data for Beavers Bend obtained with Equation 4 (m = 0) and Equation 5 (m = -1)
Figure 12. Plots of the K extraction data for Marble Head obtained with Equation 4 (m = 0) and Equation 5 (m = -1)
Figure 13. Plots of the K extraction data for Rock Island obtained with Equation 4 (m = 0) and Equation 5 (m = -1)
Figure 14. Plots of the K extraction data for Fithian obtained with Equation 4 \((m = 0)\) and Equation 5 \((m = -1)\).
Figure 15. Plots of the K extraction data for Morris obtained with Equation 4 ($m = 0$) and Equation 5 ($m = -1$)
Figure 16. Plots of the K extraction data for Metabentonite obtained with Equation 4 (m = 0) and Equation 5 (m = -1)
Figure 17. Plots of the K extraction data for Glauconite obtained with Equation 4 \((m = 0)\) and Equation 5 \((m = -1)\)
Figure 18. Plot of the K extraction data for Fithian obtained with Equation 6 (m = -2)
Figure 19. Plot of the K extraction data for Morris obtained with Equation 6 (m = -2)
Table 2. Summary of the extent to which the various equations describe the release of K by illites in NaTPB solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>m</th>
<th>Percent extractable K giving straight line relationship</th>
<th>Slope of line$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beavers Bend</td>
<td>0</td>
<td>87</td>
<td>1.34</td>
</tr>
<tr>
<td>Marble Head</td>
<td>-1</td>
<td>88</td>
<td>1.25</td>
</tr>
<tr>
<td>Rock Island</td>
<td>0</td>
<td>97</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>66</td>
<td>0.89</td>
</tr>
<tr>
<td>Fithian</td>
<td>-1</td>
<td>66</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>-2</td>
<td>97</td>
<td>1.27</td>
</tr>
<tr>
<td>Morris</td>
<td>-2</td>
<td>99</td>
<td>0.92</td>
</tr>
<tr>
<td>Metabentonite</td>
<td>-1</td>
<td>92</td>
<td>1.61</td>
</tr>
<tr>
<td>Glauconite</td>
<td>-1</td>
<td>93</td>
<td>1.21</td>
</tr>
</tbody>
</table>

$^a$Theoretical slope is 1.00.

percent of the total extractable K value used for Beavers Bend were substituted into Equation 4 ($m = 0$) the slopes of the resulting plots were not appreciably changed. Furthermore, the total extractable K values for these 7 illites were well established by degrading samples for very long periods. Thus, inaccurate determination of the total extractable K values can not be the reason the slopes differ from unity in this study.

Other reasons for these deviations in the slopes of the curves were not investigated because the size of the particles in these < 60 mesh samples was not well enough defined for a
detailed theoretical treatment. However, it is obvious that a theoretical model for the release of interlayer K from illite particles must differ slightly from the model used for the micas. Some factor that is now assumed to be constant is probably influencing the release of K and causing the exponential relationship between the K release and time terms in Equation 1 that gives the curves a slope other than unity.

Nevertheless, the applicability of the various equations to the K extraction data of the illites does emphasize similarities and differences in the K release behavior of these minerals that were not evident previously. Since Equation 4 describes the release of K from < 50 μ micas (Sorensen 1964) and from Beavers Bend it may be concluded that Beavers Bend behaves like the micas. On the other hand, Marble Head, Meta-bentonite and Glauconite behave more like < 2 μ Grundite and vermiculite (Sorensen, 1964) in that Equation 5 describes their K release. The behavior of Rock Island suggests this mineral has characteristics that are similar to both Beavers Bend and the group that includes Marble Head. Fithian and Morris differ from all the other illites and from the micas, vermiculite and Grundite samples employed in previous kinetic studies (Reed and Scott, 1962; Sorensen, 1964).

It is obvious from this study that the release of K from illites is not easily described on a theoretical basis. While one equation may describe the release of K from micas or vermiculites, this study shows several different equations are
needed for illites. This complex behavior of the illites with regard to K release is probably due to variations in the mixed-layering in these minerals and a variable effect from the expanded portion of the lattice.

Basal Spacing and Layer Charge

Differences in the behavior of micaceous minerals in regard to interlayer K exchange have been related to the charge and the expanding characteristics of the mineral lattice (Barshad, 1954; Scott and Smith, 1966). The changes in basal spacing and layer charge associated with maximum K depletion were therefore determined for the 7 illites.

The basal spacings of the K depleted illites were determined with oriented aggregates of wet, Na saturated samples. The degraded samples were diluted with NaTPB solution and deposited on porous ceramic plates with suction and without removing the KTPB. This procedure prevents the readdsorption of K and associated lattice changes (Scott and Reed, 1965). After x-ray diffraction patterns were obtained with the moist oriented aggregates, 10 percent glycerol-water solution was added and the samples were allowed to dry overnight in air. They were then re-saturated with the same glycerol solution, oriented with suction, and x-rayed. The layer charges in these illites were calculated by summing total K and Na values that were determined with Na saturated samples.

When the interlayer K in the illites was replaced by Na,
the lattices expanded to 12.3 and/or approximately 15 Å (Table 3). Beavers Bend, Rock Island and Metabentonite expanded to only 12.3 Å, whereas Glauconite expanded to only 15.2 Å. The other illites exhibited varying amounts of expansion to 12.3 and approximately 15 Å. The glycerol treatment did not affect the basal spacing of the K depleted illites. The wider spacings of montmorillonite, that have been reported by Bailly (1963) and White (1950) with K depleted illites, were not observed with these 7 illites. Instead, these basal spacings of the K depleted illites are comparable to those observed with Na-degraded micas (Scott and Smith, 1966).

The interlayer space available for ion diffusion does not appear to be the factor that limits the amount of interlayer K that can be extracted. Beavers Bend and Metabentonite released 94 and 83 percent of their total K, respectively, yet both of these illites expanded to only 12.3 Å. Furthermore, the fact that Metabentonite released its K faster than other illites with wider spacings suggests the basal spacing did not have a major effect on the rate of K release either.

The data in Table 3 show a decrease in layer charge was not required for large amounts of K exchange. This is consistent with previous observations of Scott and Smith (1966) with micas. Actually, with Fithian and Morris, an increase in layer charge was observed with degradation. This is considered to be a result of the manner in which layer charge was measured rather than a real increase. Apparently, the original samples
Table 3. Effect of maximum K depletion on the basal spacing and layer charge of illites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum extracted K (percent total K)</th>
<th>Maximum basal spacing (Å)</th>
<th>Layer charge (me./100 g.)</th>
<th>Original</th>
<th>Degraded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beavers Bend</td>
<td>94</td>
<td>12.3</td>
<td>138</td>
<td>138</td>
<td>138</td>
</tr>
<tr>
<td>Marble Head</td>
<td>44</td>
<td>12.3/15.0</td>
<td>209</td>
<td>209</td>
<td>209</td>
</tr>
<tr>
<td>Rock Island</td>
<td>83</td>
<td>12.3</td>
<td>100</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Fithian</td>
<td>70</td>
<td>12.3/15.0</td>
<td>132</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>Morris</td>
<td>67</td>
<td>12.3/15.2</td>
<td>126</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>Metabentonite</td>
<td>83</td>
<td>12.3</td>
<td>162</td>
<td>162</td>
<td></td>
</tr>
<tr>
<td>Glauconite</td>
<td>77</td>
<td>15.2</td>
<td>196</td>
<td>172</td>
<td></td>
</tr>
</tbody>
</table>
contained interlayer cations other than K and Na that were not removed when the mineral was leached with NaCl. These exchange sites were not included in the original layer charge determinations, but they were exposed by the NaTPB treatment and included in the layer charge values for the degraded samples.

A decrease (22 me./100 g.) in layer charge was determined with Glauconite. Similarly, Raman and Jackson (1966) observed a 13 me./100 g. charge decrease when 50 me. K/100 g. was removed from a glauconite with a NaTPB solution. Since Glauconite is a hydrous iron silicate, this decrease in charge is probably due to oxidation of Fe$^{2+}$ to Fe$^{3+}$.

Scott and Smith (1966) found the initial layer charge to be a good index of the ease with which K in micas can be replaced. There was no consistent relation between the layer charge and K release data for these illites. Marble Head, with the highest layer charge, did have the least (44%) replaceable K. Also, it is always possible that some of the K in the other illites resisted exchange because it was located in isolated regions of high charge. However, the fact that essentially all (> 95%) the K in muscovite with a charge of 247 me./100 g. can be removed (Scott and Smith, 1966) makes this unlikely. Consequently, some other factor must be responsible for the limited K release observed with these illites.
Nitrogen and Carbon Content

All the illite samples contained N and C (Table 1). Therefore, the possibility that nitrogenous organic materials interfere with the exchange of part of the K in these illites was considered. It was thought that this interference would be due to particle coatings, or a blocking of the interlayer diffusion pathways inside the particles. Therefore, this investigation proceeded along two rather distinct lines. In one case, samples were treated with an alkaline hypobromite solution to remove exterior nitrogenous organic materials. In the other, samples were heated at 450°C for 24 hours to remove nitrogenous organic materials from the interior as well as the exterior of the particles.

Hypobromite oxidation

Alkaline hypobromite solutions can be used to oxidize soil organic matter and disperse soil (Bremner, 1965; Jackson, 1956). As pointed out by Bremner (1965), the alkaline hypobromite method has an advantage over acidic methods of oxidation because the ammonium formed during oxidation is converted to N₂ and evolved instead of being retained by the soil. This reaction can be expressed by the equation (using NaOBr):

\[ 2\text{NH}_3 + 3 \text{NaOBr} \rightarrow \text{N}_2 + 3 \text{NaBr} + 3 \text{H}_2\text{O} \]

In this study, bulk samples of Beavers Bend, Marble Head, Fithian, and Morris were treated with alkaline sodium hypobromite (NaOBr- NaOH) solution, washed with dilute NaCl
solution, and air-dried. The procedure was the same as that of Bremner (1965) except Na reagents were substituted for K reagents. The total K, N, C, and 14-day, NaTPB-extractable K values determined with original and NaOBr treated samples are given in Table 4.

There were appreciable amounts of N in Beavers Bend, Fithian and Morris after the pretreatment but nearly all of the C was gone. Consequently, most of the remaining N was probably in the form of interlayer ammonium. Infra-red analysis has indicated that this is the case for NaOBr treated Grundite. If so, it is significant that so much of the original N in these illites is in this form. On the other hand, much of the N in Marble Head must be present as inaccessible interlayer nitrogenous organic materials because appreciable amounts of both N and C were present after the NaOBr treatment. The NaOBr treatment removed a small amount of K from the illites. This was expected because some of the K is accessible to exchange with even NH$_4$ (Table 1). However, these data show the NaOBr treatment did not result in more of the K in these illites being extractable by NaTPB. Since the treated samples were placed in NaTPB solutions for only 14 days, it was considered possible that the extracted K values simply reflected a decrease in the rate of K release and that more K might have been

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Table 4. Characteristics of illites before and after NaOBr treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>K (me./100 g.)</th>
<th>N (ppm)</th>
<th>C (%)</th>
<th>14-day, NaTPB-extractable K (% total K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>Treated</td>
<td>Original</td>
<td>Treated</td>
</tr>
<tr>
<td>Beavers Bend</td>
<td>122</td>
<td>114</td>
<td>826</td>
<td>742</td>
</tr>
<tr>
<td>Marble Head</td>
<td>184</td>
<td>180</td>
<td>392</td>
<td>252</td>
</tr>
<tr>
<td>Fithian</td>
<td>101</td>
<td>98.6</td>
<td>1180</td>
<td>784</td>
</tr>
<tr>
<td>Morris</td>
<td>103</td>
<td>100</td>
<td>784</td>
<td>574</td>
</tr>
</tbody>
</table>
Figure 20. K extracted from original and NaOBr treated Marble Head by different contact periods in NaTPB solution.
extracted if longer extraction periods had been used. Therefore, the effect of different extraction periods on the amounts of K replaced from NaOBr treated samples were determined with Marble Head. It is apparent from the curves in Figure 20 that the NaOBr treatment did not enhance the amount of K extracted in any extraction period. Thus, it was concluded that nitrogenous organic coatings on the mineral particles are not responsible for the limited extraction of K from these illites.

The data in Table 4 and Figure 20 show the NaOBr treatment actually decreased the amount of K extracted by NaTPB. This decrease can be attributed to the fact that the NaOBr treatment saturated the illites with Na. Previous work with Grundite has shown that Na saturated samples always release less K than the original samples.

Preheat at 450°C

In a thermal study of ammonium fixation and release by clay minerals, Scott, Hanway and Stanford (1956) observed a large, ill-defined, exothermic peak at approximately 400°C. in the DTA curve of Grundite which they attributed to the oxidation of organic material. Consequently, Edwards (1960) heated Grundite at 450°C. for 24 hours to remove this material

---

and was successful in removing essentially all the N and C in the samples. Earlier experiments, by Grim and Bradley (1940) with optical and thermal techniques, have shown no structural changes occur in illite that is heated at temperatures below 800°C. Berger (1965) found no structural derangement occurred with Marble Head and Fithian samples at temperatures below approximately 930°C. Therefore, it was anticipated that illite samples could be heated at 450°C. to remove N and C compounds from the interior as well as the exterior of the particles without serious alterations in the mineral itself.

Smith and Scott (1963) heated Grundite at 450°C. and found nearly all the K in the treated Grundite was extractable by NaTPB. That is, heating the mineral at 450°C. increased the amount of interlayer K that could be replaced by exchange with Na from 66 to 93 percent of the total. Since the heat treatments also reduced the N and C content it was thought the increase in extractable K was due to the removal of interfering nitrogenous organic material. Therefore, a similar study was conducted with the 7 illites.

Individual illite samples (0.5 g.) were placed in pyrex erlenmeyers and heated in a muffle furnace at 450°C. on a raised platform for 24 hours. A few samples were placed in platinum crucibles and heated for 24 hours in a muffle furnace at 500 or at 550°C. for 24 hours. The samples were then allowed to cool to room temperature and the changes in various mineral characteristics were determined. Total K analyses
showed the K contents of the illites were not altered by these heat treatments. The data in Table 5 show, however, that other changes did occur.

Heating reduced the N content of all the illites. This decrease varied from 56 to 100 percent of the N in the original sample but only one of the minerals, Glauconite, had all the N removed by heating at 450°C. Traces of N remained in some samples even after heating at a temperature as high as 550°C. Therefore, heat can not be relied upon to remove all the N compounds from layer silicates and thereby provide conclusive evidence that the exchange of K is limited by the presence of such compounds between the silicate layers.

It was anticipated that the removal of N by heating would make the illite samples acidic. However, there was no consistent effect of heating on the pH values of the illites. Also, except for Morris, the heat treatment did not alter the layer charge of the illites enough to anticipate any related effect on K release.

Heating increased the amount of exchangeable K in all the samples. Furthermore, by heating, the differences between Na and NH₄ as replacing cations for exchangeable K were eliminated. Thus, a change in the accessibility of the K in these minerals to exchange was induced by the heat treatment. This is also evident in the increase in NaTPB extractable K that occurred when the illites were heated. However, most of the heated illites still contained an appreciable amount of K that
Table 5. Characteristics of illites before and after heating samples for 24 hours

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Beavers Bend</th>
<th>Marble Head</th>
<th>Rock Island</th>
<th>Fithian</th>
<th>Morris</th>
<th>Metabentonite</th>
<th>Glaucnnte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (ppm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>826</td>
<td>392</td>
<td>700</td>
<td>1180</td>
<td>784</td>
<td>784</td>
<td>126</td>
</tr>
<tr>
<td>450°C</td>
<td>364</td>
<td>112</td>
<td>168</td>
<td>112</td>
<td>84</td>
<td>168</td>
<td>0</td>
</tr>
<tr>
<td>500°C</td>
<td>140</td>
<td>14</td>
<td>-</td>
<td>56</td>
<td>14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>550°C</td>
<td>14</td>
<td>0</td>
<td>-</td>
<td>28</td>
<td>14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH (0.5 g./10 ml. 1 N NaCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>6.0</td>
<td>7.8</td>
<td>6.8</td>
<td>3.7</td>
<td>2.6</td>
<td>8.0</td>
<td>6.4</td>
</tr>
<tr>
<td>450°C</td>
<td>5.9</td>
<td>9.5</td>
<td>5.3</td>
<td>4.0</td>
<td>2.9</td>
<td>7.7</td>
<td>5.8</td>
</tr>
<tr>
<td>Layer charge (me./100 g.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>138</td>
<td>209</td>
<td>100</td>
<td>132</td>
<td>126</td>
<td>162</td>
<td>196</td>
</tr>
<tr>
<td>450°C</td>
<td>136</td>
<td>207</td>
<td>101</td>
<td>130</td>
<td>105</td>
<td>156</td>
<td>192</td>
</tr>
<tr>
<td>Exchangeable K (me./100 g.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl None</td>
<td>1.6</td>
<td>1.9</td>
<td>1.9</td>
<td>1.5</td>
<td>2.5</td>
<td>1.3</td>
<td>3.6</td>
</tr>
<tr>
<td>450°C</td>
<td>3.6</td>
<td>9.2</td>
<td>5.9</td>
<td>12.0</td>
<td>30.2</td>
<td>9.8</td>
<td>13.0</td>
</tr>
<tr>
<td>NH4OAc None</td>
<td>0.7</td>
<td>1.0</td>
<td>0.7</td>
<td>0.7</td>
<td>0.9</td>
<td>0.5</td>
<td>3.2</td>
</tr>
<tr>
<td>450°C</td>
<td>3.0</td>
<td>10.6</td>
<td>3.4</td>
<td>11.8</td>
<td>29.1</td>
<td>9.0</td>
<td>15.3</td>
</tr>
<tr>
<td>NaTPB-Extractable K (% of total K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>94</td>
<td>44</td>
<td>83</td>
<td>70</td>
<td>67</td>
<td>83</td>
<td>77</td>
</tr>
<tr>
<td>450°C</td>
<td>98</td>
<td>63</td>
<td>89</td>
<td>90</td>
<td>87</td>
<td>96</td>
<td>72</td>
</tr>
</tbody>
</table>
was not replaceable. Except for the Glauconite data, the values shown in Table 5 are the maximum amounts of K that could be extracted with NaTPB solution after heating. Therefore, there is little chance that this heat pretreatment can be used as a means of obtaining K-free illites. The heated Glauconite was still releasing K when this experiment was terminated (at 16 weeks) but the decreasing rate of K release exhibited by this mineral in the latter stages of the experiment indicated that complete K removal from this illite was also very improbable.

The amounts of K extracted from preheated samples of Beavers Bend, Marble Head, Fithian, Morris and Glauconite in NaTPB solution for different periods are shown in Figures 21, 22, 23, 24 and 25, respectively. For comparison, curves indicating the amounts of K extracted from unheated samples of these illites are also given. These results show the heat treatment affected the subsequent extraction of K from the illites in different ways. With all the illites there is an increase in the K extracted initially. Thereafter, K was extracted from heated and unheated Marble Head at about the same rate. Heating Beavers Bend resulted in much larger portions of the K being extracted during the shorter contact periods. On the other hand, heating delayed the extraction of K from Glauconite. With Morris and Fithian there was no consistent effect of the heat treatment on the rate with which the different segments of interlayer K were extracted.
Figure 21. K extracted from preheated Beavers Bend in NaTPB solution for different periods
Figure 22. $K$ extracted from preheated Marble Head in NaTPB solution for different periods.
Figure 23. K extracted from preheated Fithian in NaTPB solution for different periods.
Figure 24. K extracted from preheated Morris in NaTPB solution for different periods
Figure 25. K extracted from preheated Glauconite in NaTPB solution for different periods.
The susceptibility of the K in Glauconite to exchange was not increased appreciably by a heat treatment that removed all the N in the sample. Also, there is no relationship between the amounts of residual N and non-extractable K after heating. Furthermore, Beavers Bend released essentially all its K before and after the heat treatment despite the presence of appreciable amounts of N in both samples. Thus, the limited extraction of K from illite does not appear to be due to steric blocking by nitrogen compounds.

The heat treatment was more effective than the NaOBr treatment (Table 4) in removing N from the illites. In both cases, part of the nitrogen may have resisted removal because it was located in inaccessible positions between the layers. The low carbon content of the NaOBr treated illites and of heated Grundite (Edwards, 1960) indicates this residual N may be largely in the form of NH$_4$. If so, this residual N should have offered no interference in the exchange of K because NH$_4$ ions are also precipitated by NaTPB.

It is obvious from the data in Table 5 and Figures 21-25 that heating affects the subsequent release of K from illites in different ways. Thus, the enhanced K exchange observed after heating probably involved alterations in the various mineral structures. If these alterations occur at temperatures as low as 450°C, they are not evident from x-ray diffraction data. X-ray patterns only showed the 10 Å peaks were considerably sharpened by heating. However, these mineral alterations
could have still occurred and not have been detected by routine x-ray diffraction methods. Bassett (1960) has suggested differences in lattice hydroxyl orientation can affect K release from micas. Brown (1965) has recently suggested differences in lattice K-O bond lengths as a possible reason that K release from micas can vary. Changes in these properties by the heat treatment may be responsible for the changes in K release observed with the 7 illites. However, a determination of these lattice parameters would require more refined x-ray techniques, and more homogenous materials than those used in this study.

Modifications in Extraction Procedure

A general method of extracting interlayer K from illites with NaTPB solutions was adopted for this study on the basis of the results Smith and Scott (1966) obtained with Grundite and different methods. Since this method did not extract all the K in the illites (Figures 2-8), various modifications were made in the method to determine if more of the K could be extracted and to ascertain the reason for the incomplete replacement of the interlayer K in these minerals.

Clay/solution ratio

The reactions involved in the extraction of K from illite in NaTPB solution can be expressed by

\[
\text{K-illite} + \text{Na} + \text{TPB} \rightarrow \text{KTPB} + \text{Na-illite}
\]

\[
\text{K} + \text{TPB} \rightarrow \text{KTPB}
\]
As K replacement from the mineral proceeds, the solution TPB level decreases and the solution K level increases, since the K_{sp} of KTPB remains constant. Consequently, the solution K level could accumulate to a point where further K exchange from the mineral ceased. If, however, less illite was used in the same amount of NaTPB solution, the solution TPB would remain at a higher level and the solution K at a corresponding lower level. In this event, there would be less chance of solution K interfering with K exchange and thus a larger portion of mineral K could be exchanged. Therefore, 0.1 g. instead of 0.5 g. samples of Beavers Bend, Marble Head, Fithian and Morris were degraded for 14 days in the usual amount of NaTPB solution and replaced K determined. The results in Table 6, show that slightly more of the K was extracted when the sample size was decreased, but the differences are not considered significant.

Complexing reagents

Chemical analyses of illites nearly always show quantities of Ca present (Grim, 1953). According to Gaudette, Eades and Grim (1965) this Ca can be between the layers of Beavers Bend, Marble Head, Rock Island and Fithian. Therefore, the possibility existed that Ca, which has a relatively high bonding energy, interfered with K exchange. This interference should have been reduced by the EDTA in the NaTPB solution because Ca is strongly complexed with EDTA (log of the stability constant of this complex is 10.7, Vogel, 1961). Nevertheless, additional amounts of EDTA were added to Beavers Bend, Marble Head,
Table 6. Effect of modifications in the usual NaTPB extraction procedure on the amount of extractable K in illites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total K (me./100 g.)</th>
<th>K extracted (me./100 g.)</th>
<th>Usual method</th>
<th>0.1 g. sample</th>
<th>0.1M EDTA</th>
<th>1.7N NaF</th>
<th>Ultrasonic vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beavers Bend</td>
<td>122</td>
<td>115</td>
<td>116</td>
<td>116</td>
<td>114</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>Marble Head</td>
<td>184</td>
<td>80.5</td>
<td>82.5</td>
<td>80.8</td>
<td>82.0</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>Fithian</td>
<td>101</td>
<td>70.8</td>
<td>74.4</td>
<td>72.8</td>
<td>73.8</td>
<td>91.7</td>
<td></td>
</tr>
<tr>
<td>Morris</td>
<td>103</td>
<td>68.6</td>
<td>70.9</td>
<td>71.0</td>
<td>71.6</td>
<td>93.4</td>
<td></td>
</tr>
</tbody>
</table>
Fithian and Morris samples that had been degraded in the usual NaTPB solution for 4 months. These systems with an EDTA concentration of 0.1 M were then allowed to stand 7 days and replaced K was determined. The results (Table 6) indicate that there was no effect of this EDTA addition on K replacement.

Stanford (1947) concluded that interlayer Al in Fithian illite prevents or greatly inhibits the fixation of added K. Therefore, he added NaF to his systems to complex the Al and thereby eliminate this effect. Similarly, in some of the K extraction experiments with illites, NaF was used instead of NaCl in the NaTPB extracting solution. Beavers Bend, Marble Head, Fithian and Morris were degraded for 14 days in this NaF-NaTPB solution and replaced K was determined. The results (Table 6) show, however, that the maximum amount of K replaced was not increased by the NaF.

According to Rich and Black (1964) K exchange in micaceous minerals may be hindered by the presence of hydroxy-Al (or Fe) "islands" in interlayer positions. If this was the factor limiting K release from illites in this study there should have been some effect of the fluoride and/or the EDTA extractions on K release. Furthermore, when Grundite was dispersed by treatments with hydrogen peroxide, sodium dithionite and bicarbonate (Jackson, 1956) which should have removed iron impurities, no increase in K replacement was observed1.

Therefore, the effects of other treatments of this nature were not investigated further.

**Ultrasonics**

Smith and Scott (1966) have shown that essentially all the K in < 2μ Grundite can be replaced by a 72-hour contact period with a NaTPB solution if the mixture is exposed to ultrasonic vibrations (Measuring and Scientific Equipment ultrasonic oscillator, 20 kc., 60 watt). There was no evidence from x-ray diffraction data or layer charge determinations that the mineral was destroyed by this treatment. Also, the shape of the K-extraction curve did not suggest that ultrasonics increased the extractable K by causing lateral fractures in the particles.

To determine if ultrasonics has a similar effect on K release from illites in general, Beavers Bend, Marble Head, Fithian and Morris were placed in NaTPB solution and subjected to ultrasonic vibration for 72 hours. The procedure was the same as described by Smith and Scott (1966). The ultrasonic treatment increased K release in all cases, as seen in Table 6. Marble Head, which offered the most resistance to K depletion had 141 me. K/100 g. (77% of the total K) extracted. The other samples had more than 90 percent of their total K extracted. Thus, ultrasonics in conjunction with NaTPB solution was very effective in enhancing K release from illites. It is anticipated that total K removal would have resulted if longer ultrasonic times had been used.

Since the ultrasonic vibrations enhanced the susceptibility
of the K in all the illites to exchange, additional experiments were carried out to determine why this should be. Samples (0.5 g.) of < 2 μ Grundite, < 50 μ muscovite and <50 μ orthoclase were placed in 1 N NaCl solution (10 ml.) and subjected to ultrasonic vibrations for different periods. The amounts of K released to the NaCl solution were determined in each case. Also, the Grundite residues from this treatment with NaCl and ultrasonic vibrations were subsequently placed in NaTPB solution for 14 days. The amounts of K replaced by Na under these conditions are reported in Table 7. The total K-extracted values for Grundite in this table were obtained by combining the amounts of K removed by the NaCl-ultrasonic treatment with those removed in the subsequent 14-day contact period with NaTPB.

Relatively little K was extracted by placing these minerals in the NaCl solution. This was expected with orthoclase because the 3-dimensional silicate structure of this mineral precludes physical access by the Na ions to the K sites in the lattice. In the case of Grundite and Muscovite, the replacement of K by Na is limited by the mass action effect of the K in solution. Despite these differences in the cause of the limited K replacement by Na, however, all the minerals released more K when the mixtures were subjected to ultrasonic vibrations. Furthermore, the replacement of K by Na continued to occur as long as the ultrasonic treatment was continued. Thus, the ultrasonic vibrations must have caused some grinding of
Table 7. K extracted from K-bearing minerals in 1 N NaCl solution during ultrasonic vibration periods

<table>
<thead>
<tr>
<th>Ultrasonic vibration period (hours)</th>
<th>K extracted (me./100 g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grundite</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
</tr>
<tr>
<td>0</td>
<td>4.7</td>
</tr>
<tr>
<td>4</td>
<td>8.3</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>14.4</td>
</tr>
<tr>
<td>48</td>
<td>-</td>
</tr>
<tr>
<td>72</td>
<td>19.3</td>
</tr>
</tbody>
</table>

*K extracted by 14-day contact period with NaTPB solutions after ultrasonic vibration treatments in NaCl solutions.*

On the other hand, it is evident from the Grundite data (Table 7) that the pretreatment with ultrasonic vibrations did not increase the total amount of Na-exchangeable K in the mineral. Any grinding of the particles that occurred during the pretreatment apparently did not expose to exchange any K that was not already accessible to extraction. Therefore, the benefits of using ultrasonic vibrations during the extraction of K with NaTPB should not be attributed entirely to a grinding effect. Instead, it is suggested that the ultrasonic treatment provides additional energy for the exchange process, either
through a relaxation of the forces holding the mica layers together or an enhancement of the replacing power of the Na ions.

**K-mineral impurities**

The entire sample of each illite was used in this investigation. Thus, the question arises as to whether other K-minerals are present as impurities and are causing the limited extraction of K. There was no evidence in the x-ray diffraction patterns of these illites that such materials were present. Also, a separation of only the <2 μ fraction as was done with Grundite would reduce the amount of these impurities yet only 66% of the K in the <2 μ Grundite is exchangeable (Smith and Scott, 1966). Thus, a similar fractionation of the 7 illites employed here was not considered necessary.

**Replacing cation**

To determine whether cations other than Na could be used to extract more of the K in illites, samples of Beavers Bend, Marble Head, Fithian, and Morris were degraded in NaTPB solutions that were 1.7 N with respect to various chloride salts. In this experiment, the salts were LiCl, NaCl, MgCl₂, CaCl₂, SrCl₂, and BaCl₂. Ten ml. of 1.7 N salt solution was added to erlenmeyers containing 1.03 g. NaTPB, 0.037 g. EDTA, and 0.5 g. illite, and the systems degraded for 1 hour, 1, 28 and 56 days. The extracted K values are given in Figures 26-29.

There was some Na in all the extracting solutions (due to
Figure 26. K extracted from Beavers Bend by different periods in NaTPB solutions containing different replacing cations
Figure 27. K extracted from Marble Head by different periods in NaTPB solutions containing different replacing cations.
Figure 28. K extracted from Fithian by different periods in NaTPB solutions containing different replacing cations.
Figure 29. K extracted from Morris by different periods in NaTPB solutions containing different replacing cations
the NaTPB and the disodium dihydrogen EDTA in the solution), so these results do not give an exact measure of the effectiveness with which each cation replaces interlayer K. However, these results show that there was no advantage in using another salt, in place of NaCl, in the NaTPB extracting solution. Also, in general, the relative replacing power of the various cations for K appears to have followed the lyotrophic series initially.

**Extracting solution pH**

In this investigation, the interlayer K in the illites was usually extracted with an unbuffered NaTPB solution even though it has been observed with micas that the pH of NaTPB solution can change during the degradation period (Reed and Scott, 1966). Thus, a determination of the changes in the pH of these unbuffered systems was needed for a proper interpretation of the K extraction results in terms of an exchange of Na for K. Furthermore, Tucker (1964b) has concluded that the displacement of interlayer K from soil illites in even neutral solutions involves some action by H ions while Scott and Smith (1966) and Smith and Scott (1966) concluded the extraction of interlayer K from Grundite is not affected by differences in the pH of the extracting solution. Therefore, it was also necessary to determine the effect of the solution pH on the exchangeability of the K in the 7 illites employed here.

First, attention was given to the stability of the pH of the unbuffered NaCl-NaTPB solution during the degradation of 4
illites. A buffered but acidic NaTPB solution was also used in this experiment because it has been reported that a reaction between TPB and H ions can quickly change the pH of acidic solutions (Flaschka and Barnard, 1960; Scott and Smith, 1966). Several 0.5 g. samples of Beavers Bend, Marble Head, Fithian and Morris were placed in 10 ml. of the usual 1.7 N NaCl - 0.01 M EDTA solution and in 10 ml. of 1.9 N NaCl - 0.1 N NaOAc - 0.01 M EDTA solution that was buffered at pH 4.6, and 1.03 g. of NaTPB was added to each system. The pH of these illite-solution mixtures was determined periodically and the results are reported in Tables 8 and 9.

The usual NaTPB solution was slightly acidic when no illite was present. The pH of this solution was further reduced by the addition of the illites even though the Beavers Bend and Marble Head materials were fairly neutral (Table 1). Thus, there was an opportunity for H replacement of K to occur in the initial stages of the usual K-degradation experiments. The data in Table 8 shows the pH did not remain constant when the usual NaTPB solution was used. Since the pH of the solution increased when there was no illite present, much of the increase can be attributed to the reaction of TPB with H. However, the higher pH values observed with the illite-solution mixtures indicate that some H also reacted with the clay. Thus, it can be concluded that the K extraction results obtained with the usual NaTPB solution cannot be attributed to an exchange of K by Na alone.
Table 8. pH of usual NaTPB extracting solution after different periods of illite degradation

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 minute</th>
<th>1 hour</th>
<th>1 day</th>
<th>7 day</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>5.1</td>
<td>-</td>
<td>5.7</td>
<td>6.1</td>
</tr>
<tr>
<td>Beavers Bend</td>
<td>4.6</td>
<td>4.9</td>
<td>6.0</td>
<td>7.8</td>
</tr>
<tr>
<td>Marble Head</td>
<td>4.2</td>
<td>4.6</td>
<td>7.0</td>
<td>8.2</td>
</tr>
<tr>
<td>Fithian</td>
<td>3.9</td>
<td>4.3</td>
<td>6.2</td>
<td>7.1</td>
</tr>
<tr>
<td>Morris</td>
<td>2.7</td>
<td>4.8</td>
<td>6.3</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Table 9. pH of acidic, buffered NaTPB extracting solution after different periods of illite degradation

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 minute</th>
<th>1 hour</th>
<th>1 day</th>
<th>7 day</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>4.6</td>
<td>4.6</td>
<td>4.8</td>
<td>7.2</td>
</tr>
<tr>
<td>Beavers Bend</td>
<td>4.6</td>
<td>4.6</td>
<td>4.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Marble Head</td>
<td>4.6</td>
<td>4.6</td>
<td>4.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Fithian</td>
<td>4.6</td>
<td>4.6</td>
<td>4.8</td>
<td>7.3</td>
</tr>
<tr>
<td>Morris</td>
<td>4.6</td>
<td>4.6</td>
<td>5.0</td>
<td>7.2</td>
</tr>
</tbody>
</table>
When the NaTPB solution was buffered at pH 4.6 with NaOAc, the illite additions did not alter the initial pH of the solution or the changes in pH that occurred during the degradation period. More important, however, is the observation that the pH of all the systems increased despite the presence of the buffer. A repeat of this experiment with additional amounts of buffer also failed to keep the solution acidic for 7 days. However, the data in Table 9 shows the pH of the acidic solution was fairly constant for a day. Thus, experiments designed to evaluate the effect of acidic solutions on the amount of K extracted with NaTPB should be confined to short degradation periods.

Since the pH of the usual NaTPB solution and the NaTPB solution buffered at pH 4.6 changed during the degradation period, a similar experiment was carried out with NaTPB solutions buffered at pH 7.2 and at pH 9.2. For these experiments the buffer solutions were added as 1.7 N NaCl-0.1 M Na₂HPO₄-0.1 M NaH₂PO₄-0.01 M EDTA and as 1.9 N NaCl-0.05 M Na₂B₄O₇-0.01 M EDTA, respectively. The pH of these solutions did not change over a period of 1 week when the NaTPB and/or illites were present. Thus, the problem of controlling the pH of NaTPB solutions appears to be limited to acidic conditions.

To determine the effect of the extracting solution pH on the exchangeability of the K in the 7 illites, a 2 hour contact period was selected. This period is long enough to include a period of rapid K exchange in the illites, and yet short enough
that the pH 4.6 buffer remains at a constant pH. Samples (0.5 g.) of the 7 illites with 1.03 g. NaTPB were therefore placed in 10 ml. of the usual unbuffered solution and in 10 ml. of the solutions buffered at pH 4.6, pH 7.2, and pH 9.2, and allowed to degrade 2 hours. The amounts of K extracted by these solutions are given in Table 10.

There was an appreciable effect of solution pH on the amounts of K extracted from Beavers Bend, Metabentonite and Glauconite, in that more K was extracted as the pH decreased. Scott and Smith (1966) observed a comparable effect with trioctahedral micas but not with dioctahedral micas. Therefore, these 3 illites may have more trioctahedral character than originally considered. There was no consistent relationship

Table 10. K extracted in 2 hours from illites in NaTPB solutions at different pH levels

<table>
<thead>
<tr>
<th>Sample</th>
<th>K extracted (% total K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unbuffered</td>
</tr>
<tr>
<td>Beavers Bend</td>
<td>15.7</td>
</tr>
<tr>
<td>Marble Head</td>
<td>20.9</td>
</tr>
<tr>
<td>Rock Island</td>
<td>28.6</td>
</tr>
<tr>
<td>Fithian</td>
<td>51.7</td>
</tr>
<tr>
<td>Morris</td>
<td>53.7</td>
</tr>
<tr>
<td>Metabentonite</td>
<td>40.8</td>
</tr>
<tr>
<td>Glauconite</td>
<td>14.6</td>
</tr>
</tbody>
</table>
between the amount of K extracted from the other illites and a decrease in the pH of the extracting solution.

The extracted K values obtained with the usual unbuffered solution and the solution buffered at pH 4.6 are quite comparable. This is to be expected since the pH values of these systems were comparable for short degradation periods (Tables 8 and 9). Further, it is seen that there was no advantage, with regard to K extracted, to using any of the buffered extracting solutions instead of the usual unbuffered NaTPB solution.

The results obtained at pH 9.2 suggest that H ions are not essential for the replacement of interlayer K by Na. Tucker (1964b) has suggested that the replacement of some interlayer K in soil illites by H makes the rest of the interlayer K more accessible to exchange by other cations, and he attributed this effect to a change in lattice charge distribution that occurs when H$_3$O ions replace the K. In this study, layer charge determinations of Beavers Bend, Marble Head, Fithian and Morris degraded in the acidic buffer solution were determined and found to be the same as the original Na saturated values. Also, in equilibration experiments with micaeous minerals in unbuffered NaCl solution it has been found that the solution pH did not increase (from pH 6.6) as would be expected if an exchange of H for K was necessary (Scott and Smith, 1966). Thus, it is concluded that H ions are not essential for the replacement of interlayer K in illites, but their presence can enhance the
replacement of K from some illites.

Changes in Basal Spacing During Degradation

The changes in x-ray diffraction patterns that occur when increasing amounts of interlayer K in muscovite are replaced by Na have been determined by Scott and Reed (1965). It was concluded from these changes that < 50 μ particles were K depleted essentially by edge weathering, whereas < 2 μ particles were K depleted by layers, and that the latter mode of K depletion gave rise to various mixed-layer structures during the degradation period. Consequently, a similar study was conducted to determine if the 7 illites differ in regard to the occurrence of edge weathering and mixed-layering when they are K depleted.

A small Na saturated sample of each illite was sedimented with suction on a separate porous ceramic plate and x-rayed while wet. The ceramic plates with the sedimented samples were then placed in individual petri dishes and enough NaTPB solution was added to nearly cover the ceramic plates. At various times the ceramic plates were removed, and the excess solution in the sedimented samples was removed by suction. The wet oriented aggregates were then x-rayed in a moist atmosphere. The ceramic plates were subsequently returned to the petri dishes to continue the degradation process. The NaTPB solution was changed periodically, as the KTPB precipitate accumulated in the solution. The experiment was continued until the x-ray patterns for each illite exhibited little change over long
Figure 30. Smoothed x-ray diffractometer tracings of Beavers Bend after different periods of degradation in NaTPB solution
Figure 31. Smoothed x-ray diffractometer tracings of Marble Head after different periods of degradation in NaTPB solution.
Figure 32. Smoothed x-ray diffractometer tracings of Rock Island after different periods of degradation in NaTPB solution.
Figure 33. Smoothed x-ray diffractometer tracings of Fithian after different periods of degradation in NaTPB solution.
Figure 34. Smoothed x-ray diffractometer tracings of Morris after different periods of degradation in NaTPB solution.
Figure 35. Smoothed x-ray diffractometer tracings of Metabentonite after different periods of degradation in NaTPB solution
Figure 36. Smoothed x-ray diffractometer tracings of Glauconite after different periods of degradation in NaTPB solution.
periods of degradation. The same machine settings were used for all the x-ray diffraction patterns. Consequently, higher intensity diffraction peaks were obtained with the more crystalline illites. Smoothed tracings of the x-ray diffraction patterns for the illites are given in Figures 30-36. The last tracing in each figure was obtained with samples that were degraded in NaTPB solution until the maximum amount of K had been replaced.

The 8.0 Å peak in many of the tracings is due to the lattice spacing of the KTPB precipitate (Norment, Henderson and South, 1960). The intensity of this peak increased as K depletion progressed, but this peak did not interfere with the observation of changes in the basal spacing of the illites.

The peaks at 7.1 and 14.3 Å in the x-ray pattern for the original Beavers Bend (Figure 30) show there was a mechanical mixture of chlorite in this sample (Gaudette, Eades and Grim, 1965; Raman and Jackson, 1966). However, this contamination did not interfere with the observation of basal spacing changes that occurred when K was replaced by Na. As degradation proceeded in Beavers Bend, the mineral lattice expanded from 10 to 12.3 Å and a gradual change in the relative heights of the 10 and 12.3 Å peaks in the tracings was observed. These 10 and 12.3 Å peaks are quite distinct and there is little evidence in the tracings that mixed-layering occurred in the degraded samples. This means the illite particles were K depleted and expanded at the edges while the inner core of the particles
retained a 10 Å spacing. The weathering front must have been quite sharp, to have not produced some evidence of intermediate spacings. Also, the stress from the outer expanded fringe did not cause many layers to expand across the particles or there would have been mixed-layering. Thus, it was concluded that K depletion from Beavers Bend was essentially by edge weathering.

Optical evidence that this mode of weathering occurs in micas has been obtained by Mehmel (1938), Mortland (1958), Rausell-Colom, Sweatman, Wells and Norrish (1965), and Weiss, Mehler and Hoffman (1956). More recently, direct visible evidence for this mode of weathering in macro mica particles has been obtained by Scott and Smith (1967). Therefore, these x-ray diffraction data support the conclusion in the kinetics section of this thesis that Beavers Bend behaves like the micas in regard to K release.

When the interlayer K in Marble Head (Figure 31) was replaced by Na the basal spacing of most of the mineral expanded to 12.3 Å. The skewing of the 10 Å peak toward lower values of 2θ and the fact that the decreasing 10 Å peak and the increasing 12.3 Å peak tend to smear together in the tracings for the intermediate weathering stages, however, shows this expansion occurred in random layers. That is, the K in some layers was replaced faster than in others. This replacement produced a random mixture of expanded and contracted layers in the mineral since no distinct intermediate peaks are evident between the 10 and 12.3 Å peaks. Thus, it was concluded that K depletion of
Marble Head occurs more by complete layers than by edge weathering.

A small amount of expansion to 15.0 Å occurred in Marble Head during K depletion. Consequently, some regions of the mineral must have a relatively low layer charge, even though the layer charge for the whole mineral is 209 me./100 g. The smearing together of the 15.0 and 12.3 Å peaks, seen in Figure 31, can also be attributed to the mixed-layering.

The x-ray diffraction tracings of Fithian (Figure 33), Morris (Figure 34), Metabentonite (Figure 35) and Glauconite (Figure 36) show that mixed-layer structures developed in these minerals as degradation occurred. Therefore, these illites behaved like Marble Head in that they released their K more by layers than by edge weathering. With the loss of interlayer K, Metabentonite expanded to only 12.3 Å whereas Glauconite expanded to only 15.2 Å. Portions of Fithian and Morris expanded to 12.3 Å, others to approximately 15 Å.

Rock Island (Figure 32) was K depleted by layers during the initial stages of degradation, but the sharp 12.3 Å peak and the persistence of a sharp 10 Å peak in the latter stages shows there was an appreciable amount of K depletion by edge weathering. This interpretation is consistent with the previous conclusion in the kinetics section that Rock Island has K release characteristics similar to both the micas and the illites with a more mixed-layer type of structure.

Part of the K depleted Rock Island may have expanded from
10 Å to more than 12.3 Å. However, the 14.3 Å peak in the tracings due to chlorite (Gaudette, Eades and Grim, 1965) interfered with the observation of such an expansion. Nevertheless, it is obvious from the final tracing that the degraded Rock Island was nearly all 12.3 Å material.

The intensity of the peaks due to the illites is greater in the final tracings than in the original tracings. This is attributed primarily to better orientation of the degraded samples, although some increase in intensity would be expected at a lower diffraction angle (Mortland, 1958).

The final tracings in Figures 30-36 show no evidence of a 10 Å basal spacing. This appears odd since most of the samples still contained appreciable amounts of K. For example, the final Marble Head tracing had no 10 Å peak even though there was still 103 me. K/100 g. in the mineral. Apparently, the contracted layers containing this K were too randomly distributed to diffract the x-rays.

The results of this section show that Beavers Bend, the only sample to have nearly all its K replaced, is the only sample that is K depleted by edge weathering. On the other hand, the other illites, which have varying amounts of replaceable K, release K by layers. Marble Head, which appears to have formed the most mixed-layer structures, has the least amount of K replaceable. Consequently, it is concluded that the limited K exchange in illites is related to the formation of mixed-layer structures.
SUMMARY AND CONCLUSIONS

Samples of Beavers Bend, Marble Head, Rock Island, Fithian, Morris, Metabentonite and Glauconite were used to determine the susceptibility of the interlayer K in illites to exchange by other cations.

Various amounts of Beavers Bend, Marble Head, Fithian, and Morris were placed in different volumes of a 1 N Na solution (0.785 N NaCl-0.1 M Na₂HPO₄-0.015 M NaH₂PO₄) buffered at pH 7.2. The exchange of the interlayer K in these illites by Na was controlled by the level of K that accumulated in solution. For any particular level of K in solution, the susceptibility of the interlayer K to exchange decreased in the following order Morris > Beavers Bend > Fithian > Marble Head.

The selectivity of the illites for K in this equilibrium experiment increased with the degree of K depletion. At 15 percent K depletion, the selectivity coefficients calculated for these illites ranged from $1 \times 10^5$ to $3 \times 10^5$. A comparison of these values with the data obtained with micas (Scott and Smith, 1966) shows the illites vary much less in regard to selectivity for K. However, like the micas, the illites have a selectivity coefficient of sufficient magnitude to make it necessary to maintain the K in solution at a very low level to evaluate the effect of other factors on K exchange.

A very low level of K was maintained in the extracting solution during degradation experiments with the illites by
adding NaTPB to precipitate the replaced K. In these experiments, 0.5 g. illites and 1.03 g. NaTPB were placed in 10 ml. 1.7 N NaCl-0.01 M EDTA solution, and 94, 44, 83, 70, 67, 83, and 77 percent of the K in Beavers Bend, Marble Head, Rock Island, Fithian, Morris, Metabentonite and Glauconite, respectively was replaced. These amounts were generally extracted in 1 week. Longer extraction periods failed to extract more K. This limited exchange of interlayer K constitutes a major difference between illites and micas.

A kinetic study of the rates with which the illites released K to NaTPB solution was made using a moving boundary diffusion equation with a variable diffusion coefficient. This equation has previously described K release from other micaceous minerals and has accounted for differences in their K release (Sorensen, 1964). For the equation to describe K release, a linear relationship with a slope of unity was required between the K release term and time. Linear relationships were obtained with major segments of replaced K for all illites but the slopes varied slightly from unity. Nevertheless, this kinetic treatment emphasized differences and similarities in the K release behavior of the illites not evident previously. Beavers Bend behaves like the micas, whereas Marble Head, Metabentonite, and Glauconite behave like Grundite and vermiculite. Rock Island has characteristics similar to both Beavers Bend and the group including Marble Head. The K release behavior of Fithian and Morris was different from all the
other illites.

When the interlayer K in the illites was replaced by Na, the lattices expanded to 12.3 and/or approximately 15 Å. These basal spacings are comparable to those obtained previously with K depleted micas (Scott and Smith, 1966). There was no evidence that any of these illites expanded to give wider spacings characteristic of the lower charge clay mineral montmorillonite. Glycerol additions had no effect on the expansion of the K depleted illites.

There was no relation between the maximum amount of K replaced and the layer charge of the illites. A decrease in layer charge was not required for K exchange, but a slight decrease did occur in K depleted Glauconite.

All illites contained quantities of N and C. Therefore, it was considered that nitrogenous organic substances could be responsible for the limited K exchange observed with the samples. It was thought such substances could be interfering with exchange of K by coating the particle, or by steric blocking within interlayer areas. When samples of Beavers Bend, Marble Head, Fithian and Morris were treated with alkaline sodium hypobromite solution to remove such coatings, however, the replacement of interlayer K was not enhanced.

Nitrogenous organic materials were removed from exterior and interior portions of the illites by heating the mineral at 450°C. This treatment enhanced the replacement of interlayer K, but it did not necessarily remove all of the N. There was
no relation between the residual N and the non-extractable K. Also, it was found with Glauconite that heating could actually decrease the amount of extractable K, even though all the N was removed. Further, it was apparent from the shape of the K extraction curves that the various illites were affected differently by heating. Thus, it was concluded that the effect of heating on K extraction was due to a mineral alteration, rather than the removal of nitrogenous organic substances.

The effects of various modifications in the extraction procedure was determined with Beavers Bend, Marble Head, Fithian and Morris. Varying the sample/solution ratio, and using complexing reagents like NaF and EDTA in the extracting solution had no appreciable effect on the amounts of K replaced. By using ultrasonic vibrations during a 72-hour degradation period with the usual NaTPB solution, however, it was possible to increase the amount of extractable K in Beavers Bend from 94 to 98 percent, in Marble Head from 44 to 77 percent, in Fithian from 70 to 91 percent and in Morris from 67 to 91 percent. A subsequent experiment showed that enhanced K extraction occurred only when the ultrasonic vibrations were used in the NaTPB solution. It was suggested that ultrasonics causes a relaxation of the forces binding the silicate layers together and/or increases the energy of the replacing cation.

When the K was replaced from the illites in NaTPB solution buffered at pH 4.6, 7.2, and 9.2, the amounts extracted from Beavers Bend, Metabentonite and Glauconite increased as the pH
decreased. No such relationship was observed with the other illites. The usual unbuffered NaTPB solution was as effective as any of the buffered solutions in extracting K.

To determine the effect of different cations on the exchangeability of the interlayer K in illites, samples of Beavers Bend, Marble Head, Fithian and Morris were placed in NATPB solutions containing LiCl, NaCl, MgCl₂, CaCl₂, SrCl₂ and BaCl₂, and degraded for various periods. The relative replacing power of the cations appeared to follow the lyotropic series initially, but in all cases a limited amount of exchange occurred. The usual NaTPB solution containing NaCl was as effective as any of these other solutions in extracting the K.

Experiments by Scott and Reed (1965) indicated that K could be removed from layer silicates by edge weathering or by random layers. An x-ray diffraction study of the changes in basal spacing that occur in the 7 illites upon K depletion showed that Beavers Bend was K depleted by edge weathering, whereas the other illites weathered more by layers. Beavers Bend is also the only illite that has essentially all of its K replaceable. The illites which formed mixed-layer structures had varying amounts of interlayer K replaceable.

It has been concluded that much of the K in illites is susceptible to exchange by other cations. The amount of this exchange varies from one illite to another, but the extent to which exchange occurs depends upon the level of K in solution and the extraction time involved in the method. This exchange
involves a simple replacement of the interlayer K by other cations and an associated expansion of the lattice. If Na is the replacing cation, the expansion of the illite lattice is limited to 12.3 and/or approximately 15 Å. A decrease in layer charge or the presence of H ions is not essential for this exchange of interlayer K.

A portion of the interlayer K in most illites is not susceptible to exchange regardless of the level of K in solution or the extraction time used. This portion can be reduced considerably if the samples are heated at 450°C, or subjected to ultrasonic vibrations in the presence of TPB. The limited exchange of K is not due to coatings on the particles or steric blocking by extraneous substances within the interlayer space. Neither can it be attributed to the method used to replace, separate and determine the K, since the preheat and ultrasonic data show the method is adequate. Consequently, one is left with the basic mineral to explain why limited exchange of K occurs in illites, but not micas.

It is difficult to understand why a portion of the K in an illite, with its lower layer charge and smaller particle size, would be less susceptible to exchange than the K in a mica. However, the x-ray data show the illites weather more by a loss of K from complete layers, whereas the micas weather essentially by uniform edge weathering. Thus, it has been concluded that the limited exchange of K in illites is due to the formation of mixed-layer structures.


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