SUSCEPTIBILITY OF INTERLAYER POTASSIUM IN MICAS TO EXCHANGE WITH SODIUM*

by

A. D. Scott and S. J. Smith

Department of Agronomy
Iowa State University, Ames, Iowa

ABSTRACT

Interlayer K in muscovite, biotite, phlogopite, illite and vermiculite-hydrobiotite samples was replaced by cation exchange with Na. The rate and amount of exchange varied with the mineral and the level of K in solution.

Essentially, all the K in muscovite, biotite, phlogopite and vermiculite was exchangeable when the mass-action effect of the replaced K was reduced by maintaining a very low level of K in solution. The time required for this exchange varied from $<$ 10 hr with vermiculite to $>$ 45 weeks with muscovite. Only 66% of the K in the illite was exchangeable under these conditions. When the replaced K was allowed to accumulate in the solution, the amount of exchange was determined by the level of K in solution required for equilibrium. These levels decreased with the degree of K-depletion and with the selectivity of the mica for K. The order of selectivity was muscovite $>$ illite $>$ biotite $>$ phlogopite $>$ vermiculite. Decreasing the K in solution from 10 to 7 ppm increased the exchangeable K in biotite from 30 to 100%. A K level of only 0.1 ppm restricted the exchange of K in muscovite to 17%.

A decrease in layer charge was not required for K exchange, but a decrease did occur in K-depleted biotite and vermiculite. Muscovite with the highest layer charge (247 meq/100 g), least expansion with Na (12.3 Å), and least sensitivity to solution pH had the highest selectivity for K and the slowest rate of exchange. The K in vermiculite was the most readily exchangeable.

INTRODUCTION

The replacement of interlayer K in micas by other cations occurs with an expansion of the mineral lattice and, together, these changes constitute a major aspect in mica weathering. Therefore, reference can be made to reviews of mineral weathering (Arnold, 1960; Jackson and Sherman, 1953) for a general discussion of interlayer K replacement. Various chemical methods that have been used in the laboratory to extract interlayer K from micas have been discussed by Scott and Reed (1965).

In a study of cation exchange in micaceous minerals, Barshad (1954) extracted K from vermiculite, biotite and muscovite by leaching or boiling with neutral salt solutions. With these methods, much of the native K was

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not replaceable. Nevertheless, he showed that the replaceability of interlayer K is 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. These factors are still considered of major importance. However, it is now known that the great selectivity of K-depleted micas for K must also be considered. It has been established that very small amounts of fixable cations in the extracting solution interfere with the replacement of interlayer K or NH_4 from contracted layer silicates (Hanway, Scott, and Stanford, 1957; Scott, Hunziker, and Hanway, 1960). As a result, solutions that contain sodium tetraphenylboron (NaTPB) have been used to extract large amounts of K from micas (Scott and Reed, 1962; Reed and Scott, 1966; Smith and Scott, 1966). However, the relationship between the levels of K in solution and the exchangeability of interlayer K in various micas has not been established. This relationship and the effect of various mineral characteristics on their selectivity for K are considered in this paper.

MATERIALS

Muscovite, biotite, and phlogopite samples from Ontario, Canada, were obtained from Ward's Natural Science Establishment. These micas and a South Carolina vermiculite–hydrobiotite (trioctahedral vermiculite with 1:1 regularly interstratified 10:14 Å component) supplied by the Zonolite Company were ground in a Christy and Norris hammer mill and dry screened to separate the $< 50\,\mu$ material. Grundite illite from the Illinois Clay Products Company was dispersed in water without pretreatment, and the $< 2\,\mu$ fraction was separated by sedimentation.

Exchangeable K determinations were made by shaking 0.5 g portions of the mineral samples in 10 ml 1 N NH_4OAc (pH 7.0) or NaCl (pH 6.2) for 30 min, filtering and leaching with another 40 ml of the extractant. The amounts of K extracted in this manner and the total K values determined with these samples are given in Table 1.

TABLE 1.—TOTAL AND EXCHANGEABLE K CHARACTERISTICS OF MINERAL SAMPLES

Mineral sample	meq K per 100 g		
	Total	Exchangeable	
		NH_4OAc	NaCl
$< 50\,\mu$ muscovite	222	3.8	4.7
$< 50\,\mu$ biotite	199	3.1	5.4
$< 50\,\mu$ phlogopite	195	3.9	6.9
$< 50\,\mu$ vermiculite	56	1.2	4.5
$< 2\,\mu$ illite	123	4.8	4.8

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RESULTS AND DISCUSSION

Equilibrated Systems

The NH_4-exchangeable K values in Table 1 were obtained by leaching 0.5 g samples of the minerals with 50 ml NH_4OAc. Leaching with additional amounts of NH_4OAc did not remove more K. Thus, it may be concluded that the interlayer K in these minerals was generally inaccessible to exchange with NH_4 and that these amounts of K were on the external surfaces of the particles. The data in Table 1 also show more K was replaced by Na than by NH_4 when the same extraction procedure was used. In the case of vermiculite, part of this difference can be attributed to K between the layers of the expanded

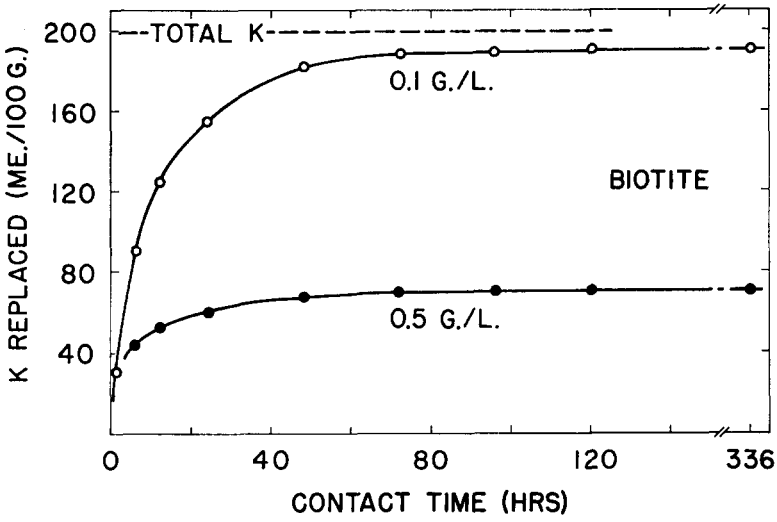


FIG. 1.—K extracted by equilibrating 0.1 and 0.5 g samples of 10–20 μ biotite in 1 liter 1 N NaCl.

portion of the sample. This K would be accessible to replacement by Na but not NH_4 because the lattice would be contracted by adsorbed NH_4. In general, however, the greater replacement of K by Na means that Na replaced some of the interlayer K from the contracted layer silicates. The extent to which this exchange can occur and the limiting conditions involved were therefore determined by equilibrating small mica samples with large volumes of NaCl.

Figure 1 shows the results obtained when 0.1 g and 0.5 g samples of biotite were placed in 1 liter of 1 N NaCl. These mixtures were shaken continuously to hasten equilibration. The amounts of K replaced were calculated by taking aliquots of the solutions periodically and determining the amounts of dissolved K. Both solutions had a pH of about 6.6 throughout the experiment. The

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biotite used in this experiment was a 10–20 μ sample that was separated from the < 50 μ material by sedimentation.

When 0.5 g biotite was placed in 1 liter of 1 N NaCl, the Na ions continued to replace K until 35% of the total K was replaced. On the other hand, with only 0.1 g biotite in this volume of solution, equilibrium was not attained until 95% of the K was replaced. In each case, an exchange of Na for K occurred until an equilibrium distribution of these cations between the mica and solution was established. To attain this equilibrium K level, however, different degrees of K depletion had to occur in the two mica samples because different amounts of mica and therefore total K were present.

These results show that much more than 5 meq K/100 g biotite (Table 1) is readily exchangeable with Na. Actually, all the K in biotite appears to be exchangeable if the accumulation of replaced K in the extracting solution is limited. Otherwise, Na will replace K to a degree that is determined by the level of K-accumulation that can occur in the particular extraction method employed. This effect of fixable cations in the extracting solution and the replacement of interlayer cations in contracted layer silicates has been emphasized before. This experiment, however, has shown that it should be possible to determine the critical levels of K in solution for various degrees of K-depletion by varying the mica/solution ratio.

The results in Fig. 1 show that an appreciable amount of time is required for exchange reactions involving the interlayer K in micas. This has been observed in non-equilibrium extraction experiments and attributed to the time required for Na and K diffusion within the particle (Reed and Scott, 1962). In the present experiment with biotite, equilibration was attained in 5 days. Therefore, in subsequent determinations of the critical levels of K in solution for different degrees of K exchange by Na, ample time was allowed for equilibration.

Samples of 10–20 μ biotite, phlogopite and vermiculite were placed in 1 N NaCl (pH 6.2). Samples of 10–20 μ muscovite and < 2 μ illite were placed in 1 N NaCl–0.01 M disodium dihydrogen EDTA (pH 4.6). The amount of mica and volume of solution were varied widely. Each mixture was shaken intermittently by hand and the amount of K in solution was determined periodically until no change was detected. The mixtures were then allowed to stand for an additional period of time before the final equilibrium levels of K in solution were determined. The total equilibration time allowed for biotite, phlogopite and vermiculite was 4 months; for muscovite and illite, it was 18 months.

The data in Figs. 2 and 3 show the extent to which the interlayer K in the various micas can be exchanged by Na when the replaced K is allowed to accumulate to different levels in the solution. In the case of biotite, only 2.2% of the total K was exchangeable with 35 ppm K in solution. When the level of K in solution was reduced to 10 ppm the Na-exchangeable K increased to 30%. A further reduction of only 3 ppm in the K level (from 10 to 7 ppm) resulted in all the interlayer K being exchangeable with Na.

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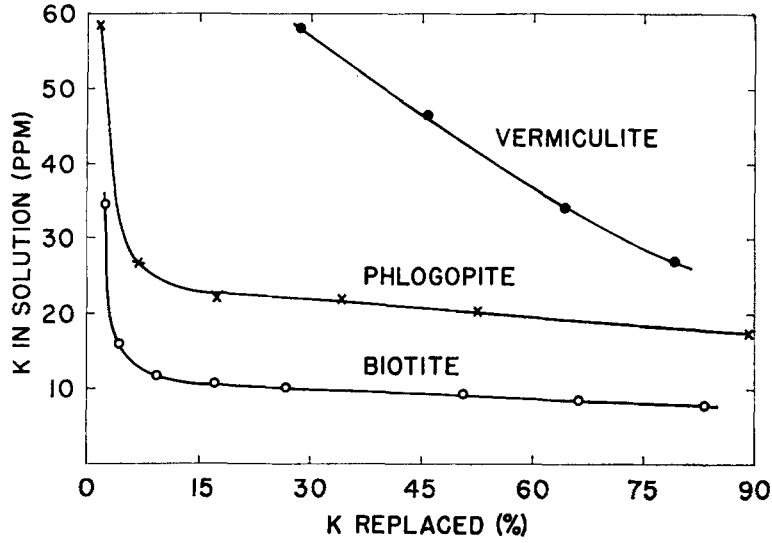


FIG. 2.—Relationship between the equilibrium levels of K in 1 N NaCl solutions and the amounts of K extracted from 10–20 μ samples of biotite, phlogopite and vermiculite.

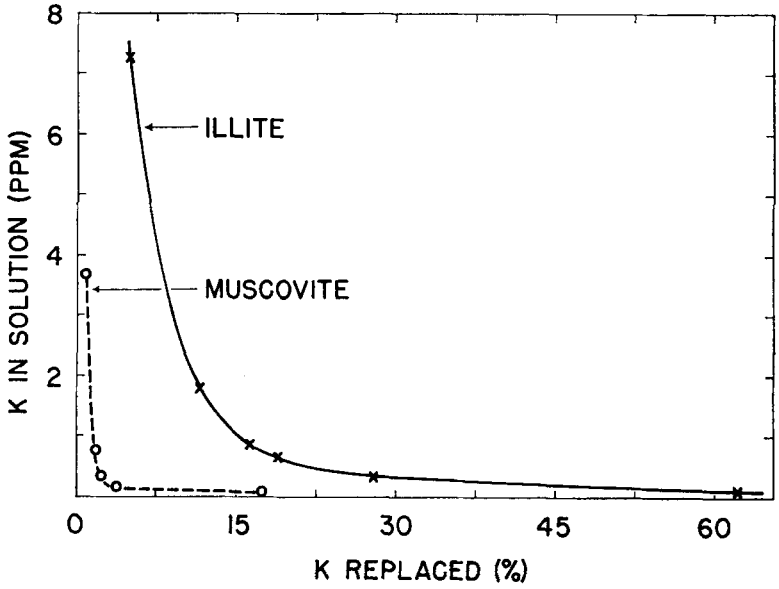


FIG. 3.—Relationship between the equilibrium levels of K in 1 N NaCl–0.01 M EDTA solutions and the amounts of K extracted from < 2 μ illite and 10–20 μ muscovite samples.

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This relationship between the equilibrium concentration of K in solution and the K content of the biotite differs from that obtained by Mortland and Lawton (1961) with 0.1 N NaCl and previously K-depleted biotite. Lower levels of K in solution would be anticipated with a more dilute NaCl solution. Otherwise, the differences must be associated with the effect of their prior treatment of the biotite and/or K impurities in the NaCl.

The micaceous minerals differed markedly in regard to the levels of K in solution required for the same degree of interlayer K exchange by Na. Phlogopite tolerated higher levels of dissolved K than biotite. Vermiculite was even less sensitive to the K in solution. On the other hand, much lower concentrations of K in solution interfered with the exchange of interlayer K in muscovite and illite. The 7 ppm K level that permitted all the K in biotite to be exchanged did not allow any of the interlayer K in muscovite or illite to be exchanged. Also, the accumulation of only 0.1 ppm replaced K in the 1 N NaCl–0.01 M EDTA solution limited the exchange of K to 62% and 17% in illite and muscovite, respectively. This difference between the dioctahedral and trioctahedral minerals would have been even greater if acidic or neutral NaCl solutions had been used in both cases. This conclusion is based on the observation that fixable cations in an extracting solution have less effect on the exchange of interlayer cations when the pH of the solution is decreased (Hanway, Scott, and Stanford, 1957).

In all cases, the same NaCl solution was used for the equilibration and the standards for the K determinations by flame emission. Consequently, the experimentally determined values for the K in solution (Figs. 2 and 3) are actually a measure of replaced K. Reagent grade NaCl with a K analysis of $< 0.0005\%$ K was selected for these experiments. Thus, there could have been as much as 0.3 ppm K in the 1 N NaCl solutions due to impurities in the salt. This amount of dissolved K from impurities was unimportant in the biotite, phlogopite and vermiculite experiments. In the case of muscovite and illite, however, the tremendous effect of an additional 0.1 ppm K indicates that the background level of K from impurities could be involved in the limited exchange observed. Also, it is now evident from the muscovite and illite data why NaCl, which frequently contains 0.005% K (3 ppm K in a 1 N NaCl solution), can be ineffective in replacing K from these minerals.

The micaceous minerals exhibited a strong preference for K over Na when they were equilibrated with NaCl solutions. This preference for K can be expressed in terms of a selectivity coefficient. Following the notation of Helfferich (1962, p. 153), the selectivity coefficients $\left(k \frac{K}{Na} \right)$ for these ion exchange equilibria were greater than 1. The magnitude of these coefficients, however, varied with the degree of K-depletion in the mineral. Therefore, to compare the minerals, values of $k \frac{K}{Na}$ were calculated for each mineral at 15% K-depletion. These values ranged in order of magnitude from 10^3 for ver-

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miculite to 10^6 for muscovite. These values are quite different from those reported for the exchange of K (by Na or Ca) from external surfaces and possibly interlayer positions at the periphery of mica particles (Bolt, Sumner, and Kamphorst, 1963; Rich and Black, 1964; Marshall and McDowell, 1965).

Non-equilibrium Extractions

It was concluded from the equilibrium experiments that differences between the micas in regard to the exchangeability of their interlayer K may be observed because of K in the solution. Therefore, this effect of dissolved K must be reduced to a minimum before the micas can be compared further. This can be done by precipitating the replaced K with sodium tetraphenylboron (NaTPB) in the extracting solution.

Methods of extracting the interlayer K from various micas with NaCl–NaTPB solutions have been developed (Scott and Reed, 1962; Reed and Scott, 1966; Smith and Scott, 1966). These methods were used to determine the exchangeability of the interlayer K in the 5 micas. The vermiculite, biotite and phlogopite experiments were carried out with 0.5 g samples of $< 50\ \mu$ material in 10 ml of 1 N NaCl–0.2 N NaTPB–0.01 M EDTA, whereas comparable samples of $< 50\ \mu$ muscovite and $< 2\ \mu$ illite were placed in 10 ml 1.7 N NaCl–0.3 N NaTPB–0.01 M EDTA. The pH of these solutions increased from 5.7 to 6.8 during the first 7 days of contact and was constant thereafter. The amounts of K replaced by Na in different periods of time are shown in Fig. 4.

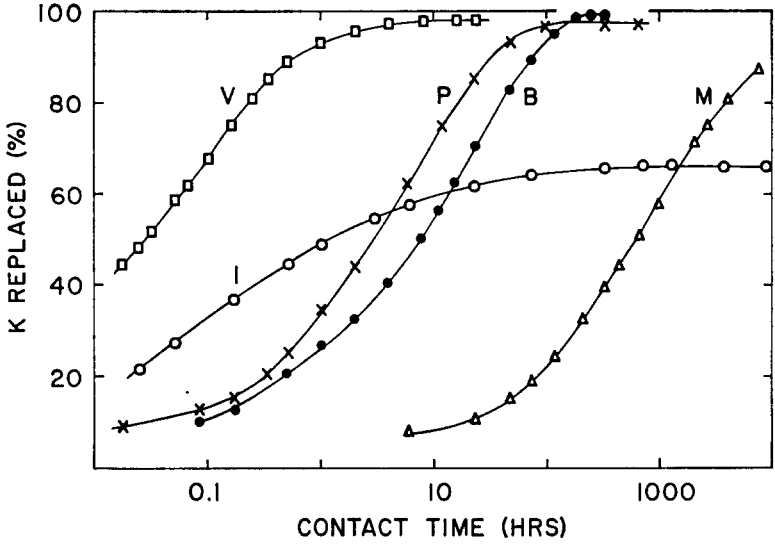


FIG. 4. K extracted from $< 2\ \mu$ illite and $< 50\ \mu$ vermiculite, phlogopite, biotite and muscovite samples in NaCl–NaTPB solutions.

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The solubility of KTPB in water is known to be 18×10^{-5} moles per liter (Flaschka and Barnard, 1960, p. 10), but the concentration of K in the extracting solutions used in this experiment 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 solution. Despite this very low K level, differences between the minerals in regard to the rate and amount of K replaced by Na are evident in Fig. 4. This means the interlayer K in the various minerals is not equally exchangeable when the interfering effects of K in solution are eliminated. In the case of vermiculite, only 1 min was required for the exchange of 42% of the K and 0.5 hr for more than 90%. With phlogopite, biotite and muscovite, 90% of the K was replaced in 1.5, 3 and 315 days, respectively. Because $< 50\ \mu$ samples with similar particle size distribution were used in each case, these differences must be associated with inherent characteristics of the minerals.

The results obtained with illite were quite different. There was a rapid exchange of part of the interlayer K despite the strong selectivity for K exhibited by this mineral (Fig. 3). This difference can be attributed to the smaller particle size ($< 2\ \mu$) of the illite. A major difference between the illite and other minerals, however, is the fact that only 66% of the K is exchangeable. The reason for the rest of the K not being exchangeable has not been fully explained, but it cannot be attributed to the presence of high charge density muscovite-like layers. Instead, there are indications that other interlayer materials make the rest of the K inaccessible to exchange (Smith and Scott, 1966).

Basal Spacing and Layer Charge

The basal spacing and the layer charge of the various micaceous minerals were determined before and after K-depletion with NaCl–NaTPB solutions. The basal spacings were determined with oriented aggregates of wet Na-saturated samples on porous plates. The degraded samples were diluted with NaCl–NaTPB solution and deposited on the porous plate without removing the KTPB. The readsorption of K and associated lattice changes are avoided by this procedure (Scott and Reed, 1965). The layer charge of the minerals was calculated by summing the total K and Na values determined with Na-saturated samples. The degraded samples were analyzed after the KTPB was removed by leaching the mineral with a 0.5 N NaCl–60% acetone–water solution.

When the interlayer K in muscovite was replaced by Na, the lattice expanded to 12.3 Å (Table 2). Under the same conditions the trioctahedral micas expanded to 15.0 Å. This difference can be attributed to the higher layer charge of the muscovite. As a result, however, there was much less interlayer space available for ion diffusion in the particles during the degradation period, and a much slower rate of K-depletion was observed. Part of the illite expanded to 12.3 Å, part to 15.0 Å. Thus, this sample must contain layers with

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a high charge like muscovite and others with a low enough charge to permit more expansion with Na. There was no evidence of a 10 Å spacing in the Na-degraded illite, even though 34% of the K was still present. Therefore, the remaining K must have been in 10 Å layers with random location, or in expanded layers with other interlayer materials that block its accessibility to exchange.

TABLE 2.—EFFECT OF MAXIMUM K-DEPLETION ON THE BASAL SPACING AND LAYER CHARGE OF MICAS

Mineral sample	Maximum basal spacing (Å)	Layer charge (meq/100 g)*	
		Original	Degraded
$< 50\ \mu$ muscovite	12.3	247	246
$< 50\ \mu$ biotite	15.0	224	184
$< 50\ \mu$ phlogopite	15.0	211	208
$< 50\ \mu$ vermiculite	15.0	194	163
$< 2\ \mu$ illite	12.3/15.0	156	156

*110°C oven-dry basis.

The layer charge of muscovite, phlogopite and illite did not change with K-depletion. Therefore, it may be concluded that a decrease in layer charge is not required for the exchange of interlayer K by Na, even when the charge is as high as 247 meq/100 g. However, a comparison of the results obtained with phlogopite and muscovite suggests that a lower charge does contribute to greater expansion and more rapid K replacement.

A decrease in layer charge occurred when biotite and vermiculite were K-depleted. In the case of vermiculite, the changes in K content and layer charge occurred so rapidly it was not possible to determine their relationship. With biotite, however, it has been found that the change in layer charge occurs after the mineral is K-depleted. Therefore, the K release behavior of biotite should be determined by the original layer charge of the mineral. As a result, biotite exhibits a slightly greater selectivity for K and a slower rate of K release than phlogopite. The lower layer charge of vermiculite, and possibly the very rapid decrease in charge that occurs with K-depletion is responsible for the faster release of interlayer K from this mineral.

The layer charge values for degraded micas in Table 2 are the minimum values observed with these minerals. Na-degraded muscovite with < 10 meq K/100 g has retained a charge of 247 meq/100 g for a period of 6 years in a neutral NaCl–NaTPB solution. Also, after an initial decrease to 184 meq/100 g during the first 14 days, the layer charge of biotite has been constant for 5 years.

pH Effect

The data in Fig. 4, showing the exchangeability of the interlayer K in micas, were determined with NaCl–NaTPB solutions that increased in pH

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from 5.7 to 6.8 during the degradation period. These results have been attributed to the exchange of Na for K, even though the solution was slighty acidic during the initial stages of K-depletion. However, Tucker (1964) has concluded that the displacement of interlayer K from soil illite even in neutral solutions involves the combined action of H and the replacing cation. Therefore, the effect of H ions on the exchange of interlayer K in micas by Na was determined. To do so, 0.5 g samples of the micas were placed in 10 ml of 2 N Na–0.3 N NaTPB–0.01 M EDTA solutions that were buffered at pH 4.6, 7.2, and 9.2 by adding the Na as 1.9 N NaCl–0.1 N NaOAc, 1.7 N NaCl–0.3 N NaH_2PO_4 and 1.9 N NaCl–0.05 N $Na_2B_4O_7$, respectively. The amounts of K extracted by these solutions in selected periods are shown in Table 3.

TABLE 3.—K EXTRACTED FROM MICAS IN 2 Na-0.3N NaTPB-0.01M EDTA SOLUTIONS BUFFERED AT DIFFERENT pH LEVELS

Mineral sample	Contact time (hr)	K replaced (%)		
		pH 4.6	pH 7.2	pH 9.2
< 50 μ muscovite	24	11.5	9.6	9.0
< 50 μ biotite	3	55.3	29.7	21.8
< 50 μ phlogopite	3	63.1	45.0	38.3
< 50 μ vermiculite	0.1	58.1	49.2	44.6
< 2 μ illite	0.5	44.9	43.6	41.8

The contact periods for this experiment were generally selected to cover a period of rapid change in the K content of the minerals. In the case of muscovite, however, the contact period was limited to 24 hr because the pH of the NaOAc solution had increased to 5.0. This increase in the pH of acidic NaTPB solutions is related to the instability of TPB in an acid medium and possibly a reaction between TPB and H ions (Flaschka and Barnard, 1960). The rate of pH increase varies, but it occurs whether mica is present or not. Therefore, the increase observed with NaOAc solutions and probably the increase from 5.7 to 6.8 in the pH of the usual NaCl–NaTPB extractant should not be interpreted as a result of H exchange for K. It has not been possible to maintain the pH of NaTPB solutions near 4.6 for longer periods by adding more buffer. Therefore, longer extraction periods with acidic NaTPB solutions do not appear feasible. On the other hand, the pH of the solutions buffered at 7 and 9 did not change for several months.

There was an appreciable effect of the solution pH on the amount of K extracted from the trioctahedral minerals. By comparison, the effect on the dioctahedral minerals was small. However, these data show that the effect of the H ions even in neutral extracting solutions must be considered. The results obtained at pH 9.2 suggest that H ions are not essential for the replacement of interlayer K by Na.

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The reason for this effect of the solution pH is not evident from the results of this experiment. However, the results do show that the effect is greater in the micas with the most octahedral Mg. Since this octahedral Mg is more susceptible to dissolution than Al and the reactions involving the release of octahedral cations are pH dependent (Marshall, 1964, p. 77), it is possible that the differences observed in Table 3 are due to a differential destruction of the micas. On the other hand, Tucker (1964) has suggested that the replacement of some K by H makes the rest of the interlayer K more accessible to exchange by other cations. This effect was attributed to a change in lattice charge distribution that occurs when H_3O ions replace the K. In the present experiment, there was no evidence of a decrease in the layer charge of phlogopite at any of the pH levels used. Also, in the equilibration experiments with mica samples in unbuffered NaCl solutions, the solution pH did not increase (from 6.6) as would be expected if an exchange of H for K occurred.

CONCLUSIONS

More than 90% of the K in muscovite, biotite and phlogopite is exchangeable with Na. This should also be the case with many of the mixed layer micaceous minerals. The exchange of all the K in vermiculite–hydrobiotite bears this out. However, the exchange of only 66% of the K in illite shows that some of the K in less well-crystallized micas can be inaccessible to exchange.

The observation that interlayer K in micas is easily exchanged by Na emphasizes the need for careful selection and description of the method used in exchangeable K determinations. NH_4 can be used to replace the K held on external surfaces of contracted mica particles, but interlayer K in an expanded component of the sample may be trapped and not replaced by the NH_4 ions. On the other hand, if Na is used, variable amounts of interlayer K in the contracted mica may be removed along with that in the expanded mineral. The extent to which this occurs will depend upon the level of K in the solution from impurities or replaced K and the extraction time involved in the method. Consequently, the portion of the total K extracted by Na can vary greatly.

The rate of exchange of interlayer K in micas is much slower than that usually encountered in exchange reactions. Also, the differences between the minerals in regard to rate can be very large as shown by the 0.5-hr and 45-week periods required for 90% exchange in $< 50\ \mu$ vermiculite and muscovite, respectively. These rate differences are probably due to differences in the mineral selectivity for K, maximum basal spacing, layer charge, etc.

There is a considerable difference in the micas in regard to the levels of K in solution that limit K release. On the basis of these levels, the resistance of these minerals to weathering by K-depletion should follow the sequence: muscovite > illite > biotite > phlogopite > vermiculite (hydrobiotite). Also, the very low levels of dissolved K required for K release by muscovite and

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illite show why most of the K in these minerals is relatively unavailable to plants.

The selectivity of the micas for K increased with the degree of K depletion. This increase was particularly evident as the exchange progressed from the K on the outer surfaces to the interlayer K at the periphery of the particles. However, the continuous nature of this relationship does not lead to a distinction of discrete fractions of K that are held with different specificity. The designation of specific fractions of the K in these minerals as being more or less easily exchanged is therefore more a result of the method.

Even in the absence of interferences from K in solution the Na–K exchange characteristics of the various micas are quite different. These differences can be related to their layer charge, the occurrence and rate of charge changes, maximum expansion with K-depletion and even their response to changes in solution pH. However, why muscovite has the greatest specificity for K, least expansion, least response to H ions and the slowest rate of K-exchange is still uncertain. The effect of empty cation positions suggested by Barshad (1954) may be involved. Also, the distinct difference between the dioctahedral and trioctahedral minerals in their specificity for K is consistent with Bassett's (1960) suggestion that differences in hydroxyl orientation are a major factor. Nevertheless, in this investigation, the initial layer charge was a good index of the ease with which the K in these micas can be exchanged.

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