EXPANSION OF POTASSIUM-DEPLETED MUSCOVITE*

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ABSTRACT

MUSCOVITE samples were K-depleted with NaCl-NaTPB solutions. By varying the extraction period, samples that varied in total K from 219 to 15 meq per 100 g. were prepared. This treatment did not change the layer charge in the mineral, but it did increase the basal spacing of the mineral from 10 to 12.3 Å.

The changes in basal spacing that occurred when increasing amounts of interlayer K were replaced by Na and the effects of subsequent treatments for the removal of KTPB were determined with two size fractions. In each case, the interlayer K at the periphery of the muscovite particles was replaced by Na, and a fringe of K-depleted mineral with a basal spacing of 12.3 Å developed. In a $<50\mu$ sample the particles retained an inner core of 10 Å mineral as the weathered fringe increased. There was no evidence of inter-stratification. With this sample there was considerable Na trapping when the KTPB was removed with NH_4Cl-acetone-water solutions. On the other hand, with a $<2\mu$ sample, mixed-layer structures developed as K was removed, and less Na trapping occurred. Na trapping was reduced by removing the KTPB with boiling NH_4Cl.

Undried Na-degraded muscovite with only 15 meq K per 100 g did not expand beyond 12.3 Å. The NH_4-degraded muscovite samples had a basal spacing of 10.4 Å.

INTRODUCTION

MICA weathering in soils has been attributed for several years (Denison, Fry and Gile, 1929) to a loss of K and a gain in water. Consequently, a great deal of attention has been directed to the development of an understanding of how the K is lost, the effect it has on the mineral, and the general concept that micas weather to expanded layer silicates (Arnold, 1960; Jackson and Sherman, 1953). In many cases, the investigations have involved a study of mica alterations that have occurred in various natural deposits. However, much of our detailed information regarding the processes by which interlayer K is released and the associated changes in mica that occur with chemical weathering has been obtained with artificial weathering experiments in the laboratory.

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Various chemical methods of extracting interlayer K from mica in the laboratory have been used. In some cases the minerals have been leached or equilibrated with aqueous salt solutions (Barshad, 1948; 1954; Caillère, Hénin and Guennelson, 1949; Cook and Rich, 1963; Ellis and Mortland, 1959; Mortland, 1958). These methods have been most useful with trioctahedral micas, but even with these minerals the extraction of interlayer K has been slow and often only a small portion of the total K has been extracted. With dioctahedral micaceous minerals these methods are usually quite ineffective. On the other hand, a large part of the interlayer K in muscovite has been extracted by treating the mineral with molten $LiNO_3$ at 300°C (Bronson, Spain and White, 1960; Cook and Rich, 1963; White, 1956; 1958). With this method, however, the layer charge in the mineral is also reduced.

Interlamellar expansion of micaceous minerals is determined by the layer charge, interlayer cations, adsorbed liquid and particle size (Jonas and Roberson, 1960). The effect of layer charge in mica weathering has been given particular attention. White (1958), for instance, has stated that the layer charge of muscovite must be reduced to about 160 meq per 100 g for expansion to occur. On the other hand, the fact that interlayer K release is blocked by fixable cations in the extracting solution has been emphasized by Hanway, Scott and Stanford (1957) and Scott, Hunziker and Hanway (1960). The interlayer K in mica cannot be extracted with solutions of NH_4 or other fixable cation salts. Also, the effectiveness with which other aqueous salt solutions extract this K is impaired by the accumulation of replaced K and/or K impurities in the salt. This problem can be alleviated by using extracting solutions that contain reagents that will precipitate K. Solutions that contain sodium *tetraphenylboron* (NaTPB) are particularly effective in this regard because this reagent precipitates all the fixable cations and the solubility of KTPB is very low (Flaschka and Barnard, 1960). The application of NaTPB to the extraction of interlayer K from micaceous minerals was initiated by Hanway (1956) with illite. It has now been used with various micaceous minerals (DeMumbrum, 1959; 1963; Mortland and Lawton, 1961; Scott, Hunziker and Hanway, 1960; Scott and Reed, 1962a and b).

White (1951) extracted 10.8 per cent of the K in Fithian illite when he used sodium cobaltinitrite to precipitate the K. Today, with NaCl–NaTPB solutions, 68 per cent of the K in illite and more than 90 per cent of the K in vermiculite, biotite and muscovite can be extracted (Reed and Scott, 1965; Scott and Reed, 1962a and b). For this, effective methods of using NaTPB extracting solutions had to be developed. These methods of extracting interlayer K with NaTPB solutions are not so effective with dioctahedral minerals as they are with trioctahedral minerals. In particular, the K in muscovite is difficult to remove by ion exchange because the release of K is slow, and the NaTPB tends to decompose in the presence of muscovite. Nevertheless, Reed and Scott (1965) have succeeded in replacing most of the K in muscovite with Na. The swelling properties and the layer charge of muscovite samples that were K-depleted in this manner are reported here.

MATERIALS AND METHODS

Muscovite from Effingham Township, Ontario, was obtained from Wards Natural Science Establishment, Inc., and ground in a Christy and Norris laboratory hammer mill with a 1/16-in. screen. The ground material was dry screened to obtain a $<50\mu$ sample. A portion of the $<50\mu$ sample was subjected to sonic vibrations in water, and $<2\mu$ particles were removed periodically by sedimentation. The $<2\mu$ material was dried and crushed to pass a 60-mesh screen. This method of preparation increased the exchangeable K level in the $<50\mu$ and $<2\mu$ samples to 3 meq and 19 meq per 100 g respectively. NH_4-saturated samples of the $<50\mu$ and $<2\mu$ muscovite contained 219 meq and 188 meq total K per 100 g respectively. Portions of the $<2\mu$ and $<50\mu$ muscovite were placed in 2 N NaCl–0.2 N NaTPB–0.01 M disodium dihydrogen EDTA and stored in a constant temperature room at 25°C. At the end of different extraction periods, samples of the K-depleted muscovite were taken for X-ray analyses and total K determinations. These samples were obtained by shaking the mineral-solution mixture and removing an aliquot. These aliquots contained KTPB as well as the mineral and extracting solution; therefore, the effects of this KTPB and of various treatments for its removal were determined. The specific methods employed are described with the experiments.

The various degraded muscovite samples have been numbered to distinguish between the different levels of K depletion; that is, all samples taken at the same stage of K removal have the same number. Further distinctions between the samples with the same number have been made by specifying the size fraction, the major exchangeable cation and the method of removing the KTPB.

The X-ray analyses were made with a General Electric XRD-5 diffractometer through co-operation with the Soils Research Laboratory of the Iowa Engineering Experiment Station. Ni-filtered Cu $K\alpha$ radiation was used in all but one experiment, which will be noted in the results.

RESULTS AND DISCUSSION

K Depletion and Layer Charge

The muscovite-extracting solution mixtures were sampled periodically, and the degree to which the mineral had been K-depleted was established by determining the total K in the degraded mineral. Generally this was done by placing an aliquot of the mineral-extracting solution mixture in a 1 : 1 acetone-water solution that was also 0.5 N in respect to NH_4Cl. The KTPB was dissolved by this acetone solution and removed by filtering and leaching with more of the same solution. In a few cases, however, the aliquot was placed in an aqueous 0.5 N NH_4Cl solution and the KTPB was decomposed by boiling. The solution was cooled, and the mineral was separated by filtering and leached with NH_4Cl. The application of these methods to muscovite

samples has been discussed elsewhere (Reed and Scott, 1965). However, the usual addition of $HgCl_2$ to the boiling solution was not made in these experiments because the K in the mineral was determined rather than the K extracted. NH_4Cl solutions were used with both methods because the NH_4 ion blocks the re-adsorption of K by the degraded mineral (Scott and Reed, 1961). Also, portions of the original $<50\mu$ and $<2\mu$ muscovite were NH_4 saturated by leaching with 0.5 N NH_4Cl.

The NH_4Cl-treated samples of original and degraded muscovite were leached free of chloride and acetone with a few increments of water. The mineral sample was then mixed and stored in a moist state. All these samples were analyzed for total K. Some were also analyzed for total Na and NH_4 to determine the change in layer charge and to account for differences in the X-ray diffraction patterns. Total K and Na determinations were made by HF digestion and flame photometry. The semimicro-Kjeldahl method described by Bremner (1965) was used to determine the total NH_4 values.

TABLE 1.—LAYER CHARGE AND ADSORBED CATIONS IN DEGRADED MUSCOVITE AS AFFECTED BY K DEPLETION AND SUBSEQUENT TREATMENTS FOR KTPB REMOVAL

Mineral sample	KTPB removal*	Total analysis, meq/100 g			
		K	Na	NH_4	Layer charge $\Sigma(K, Na, NH_4)$
$<50\mu$ muscovite					
NH_4–original	—	219	25.5	2.9	247
NH_4–degraded I	acetone	174	38.8	31.7	244
NH_4–degraded II	acetone	72.0	136	42.6	251
NH_4–degraded II	boiled	74.6	32.2	141	248
NH_4–degraded III	acetone	65.4	143	40.7	249
NH_4–degraded IV	acetone	29.4	175	40.2	245
NH_4–degraded V	acetone	15.0	201	30.4	246
$<2\mu$ muscovite					
NH_4–original	—	188	19.8	23.7	231
NH_4–degraded V	acetone	37.8	43.6	147	228
NH_4–degraded V	boiled	39.9	33.0	153	226

* KTPB dissolved in 1 : 1 acetone-water or destroyed by boiling, in both cases, with 0.5 N NH_4Cl.

The results of these analyses for a few selected samples of K-depleted muscovite are given in Table 1. The K content of the $<50\mu$ and $<2\mu$ materials was reduced from 219 meq to 15 meq K per 100 g and from 188 meq to 38 meq K per 100 g respectively. In each case, the K was replaced by an equivalent amount of Na and/or NH_4. There was no evidence of a change in the layer charge as measured by the sum of the three cations.

The interlayer K in the muscovite samples was replaced by Na during the extraction period with NaTPB solutions. Part of the Na was subsequently

replaced by NH_4 during the treatment for the removal of KTPB. It is evident from the data in Table 1, however, that the size of the particles and the nature of the NH_4 treatment (for KTPB removal) had a tremendous effect on the amount of NH_4 adsorbed. When $<50\mu$ degraded particles were placed in acetone-water solutions of NH_4Cl, the amount of NH_4 adsorbed was relatively small and independent of the degree of K depletion. Apparently, the edges of these particles were contracted by this small amount of adsorbed NH_4. As a result, further exchange of NH_4 for Na was precluded and the remaining interlayer Na was trapped. With smaller particles and/or boiling NH_4Cl solutions there was much less Na trapping. Similar differences can be anticipated when K is added to the degraded muscovite. Thus, these results are pertinent to an understanding of K fixation by weathered mica.

The $<2\mu$ NH_4 original muscovite contained 188 meq K per 100 g, whereas the comparable $<50\mu$ sample contained 219 meq per 100 g. Part of this difference (16 meq per 100 g) can be accounted for by the different amounts of exchangeable K that were removed when these samples were NH_4-saturated. However, it is evident that the layer charge of the $<2\mu$ sample was lower. The total K and layer-charge values for the $<50\mu$ sample were comparable to those determined with $>50\mu$ muscovite particles. Thus, the behavior of the $<50\mu$ sample is considered typical of muscovite. Since Mackenzie and Milne (1953) have shown that muscovite is sensitive to dry grinding, the $<2\mu$ sample was prepared by grinding mica in water with sonic vibrations. The exchangeable K and cation exchange-capacity values of 19 meq and 23.7 meq per 100 g do not appear excessive for this state of subdivision. Also, it will be noted later that there was no effect of this grinding on the X-ray diffraction pattern. Nevertheless, the decrease in layer charge indicates that some change occurred in the mineral; thus, the results obtained with the $<2\mu$ sample must be interpreted in terms of this change as well as of an effect of particle size.

KTPB and Glycerol Effects

The samples of Na-degraded muscovite that were available for X-ray analysis also contained KTPB. Therefore, the effect of this KTPB and different treatments for its removal were investigated with respect to the preparation of oriented aggregates and the observation of changes in the basal spacing of the mineral. It was not possible to add NH_4 to block the re-adsorption of K during the removal of the KTPB because the NH_4 would alter the basal spacing. Also, the K-depleted portion of the mineral was already saturated with Na, which should maximize the expansion of the lattice. Thus, methods of removing KTPB that would also maintain this condition of Na saturation were evaluated.

Samples of $<50\mu$ Na-degraded muscovite II, which contained 72 meq total K per 100 g, were used in this study. The X-ray diffraction tracings obtained with undried oriented aggregates on porous ceramic plates are shown in Fig. 1. Curve A was obtained with a sample that was freed of KTPB by the

foam-flotation and boiling-NaCl method that was used with biotite (Scott and Reed, 1962a). A comparison with curve D shows that the X-ray diffraction pattern was affected by the re-adsorption of K during this treatment. This
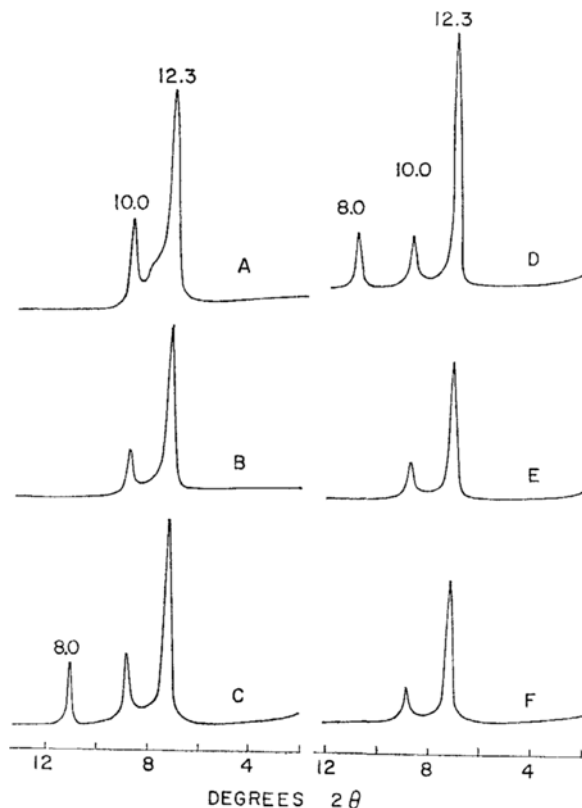

FIG. 1. KTPB and glycerol effects on smoothed X-ray diffractometer tracings of $<50\,\mu$ Na-degraded muscovite II.

A. KTPB removed by foam flotation and boiling NaCl.
B. KTPB removed with solution of NaCl–acetone–water.
C. Diluted with water.
D. Diluted with NaCl–NaTPB solution.
E. Oriented aggregate leached with NaCl–NaTPB solution.
F. Same as E plus 10% glycerol–water additions.

change in pattern did not occur when the sample was placed in a 1 : 1 acetone-water solution of NaCl to dissolve the KTPB (curve B). However, previous chemical studies have shown that K is re-adsorbed under these conditions (Reed and Scott, 1965). The absence of a change in the X-ray diffraction pattern when

K was adsorbed in the presence of acetone is consistent with the results that were obtained with this sample and NH_4Cl-acetone additions. The patterns of less degraded muscovite are affected by the adsorption of small amounts of NH_4 or K from acetone solutions.

The samples for curves C and D were not freed of KTPB but they were diluted with water and with 1 N NaCl–0.2 N NaTPB respectively, before they were deposited on the ceramic plates. There was little obvious effect from adding water but there was less tendency for KTPB to be dissolved by the dilution if NaTPB were also added. Also, the rate of K release by muscovite was slow enough that the relationship between K content and basal spacings determined with duplicate samples was not appreciably affected by the added NaTPB. Thus, it was concluded that the method used in obtaining curve D would provide the best measure of the changes in basal spacing associated with K removal.

Curves E and F were obtained with oriented aggregates that were prepared in this manner. However, the mineral was subsequently leached with a 1 N NaCl solution in 1 : 1 acetone-water to remove the KTPB. The oriented aggregate for curve F was also leached with successive increments of a 10 per cent glycerol–water solution. There was no change in the basal spacing of the Na-degraded muscovite when glycerol was added. Other treatments with glycerol, including the preparation of a paste by mixing the Na-degraded mineral with pure glycerol with or without removing the KTPB gave similar results. Consequently the oriented aggregates that were subsequently prepared to study the effect of K-depletion were not treated with glycerol.

According to Arnott and Abrahams (1958), KTPB should give a reflection at 7.91 $\pm$ 0.02 Å. In this study, KTPB in the oriented aggregates gave rise to peaks at 8.0 Å in the diffractometer tracings. These peaks did not interfere with the study, but, if they must be removed, curve E would indicate that the KTPB can be removed by leaching the degraded mineral with acetone after it is deposited on the ceramic plate. Under suction the acetone solution moves through the thin mineral layer very quickly, allowing a minimum opportunity for the re-adsorption of K by the mineral. This treatment may reduce the degree of orientation of the mineral and thus the intensity of the peaks. However, the preferred orientation can be improved by adding a final increment of water without suction to raise the sample slightly and by then applying suction to reform the film.

Undried Na-Degraded Muscovite

Smoothed X-ray diffractometer tracings that were obtained with Na-degraded samples of $<50\mu$ and $<2\mu$ muscovite are shown in Fig. 2. These tracings were obtained with undried oriented aggregates on porous ceramic plates. To prepare the oriented aggregates, aliquots of the mineral-extracting solution mixture were diluted with 2 N NaCl–0.2 N NaTPB solution and spread over the surface of the ceramic plates under suction. The KTPB in the sample was not removed; thus each tracing has an 8.0 Å peak.

The tracings in Fig. 2 show the changes in basal spacing that occurred when the interlayer K in these muscovite samples was replaced by Na. It is obvious that this exchange of cations resulted in an expansion of the mineral from
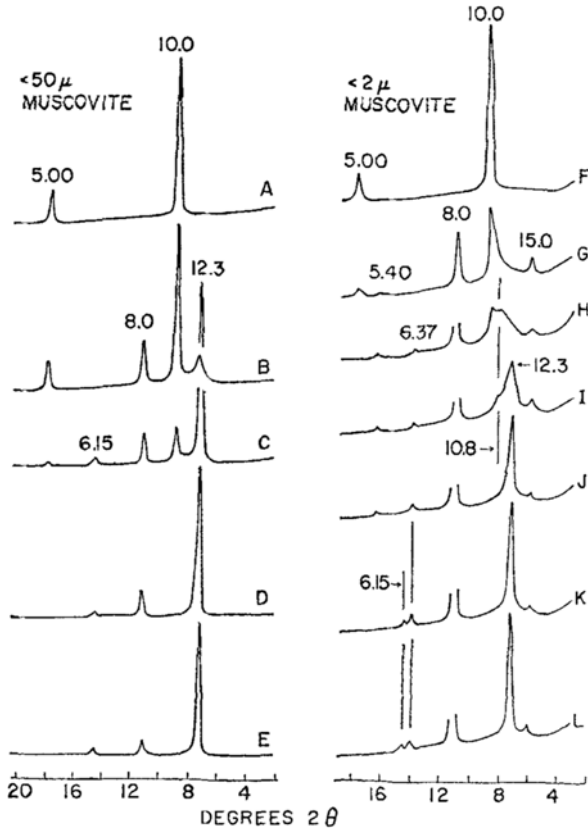

FIG. 2. Effect of K depletion on smoothed X-ray diffractometer tracings of Na-degraded muscovite.

$<50\mu$ muscovite with 219, 174, 72.0, 29.4 and 15.0 meq K per 100 g shown by curves A, B, C, D and E respectively. $<2\mu$ muscovite with 188, 158, 117, 76.0, 50.1, 37.8 and 28.0 meq K per 100g shown by curves F, G, H, I, J, K and L respectively.

10 Å to 12.3 Å. Furthermore, it should be emphasized that this expansion occurred without a loss of layer charge (see Table 1). Curve E, for instance, was obtained with a degraded muscovite sample that had a layer charge of 246 meq per 100 g. and a K content of only 15 meq per 100 g. Thus, the conclusion of White (1958) that the layer charge of muscovite must be reduced for expansion to occur is not applicable to these weathering conditions.

Instead, the release of K and expansion of muscovite was controlled by the level of fixable cations in the solution as anticipated (Scott, Hunziker and Hanway, 1960).

The progressive change in the X-ray diffraction pattern of the mineral that occurred with increasing amounts of K replacement by Na was not the same with the two sized fractions. In the case of $<50\mu$ muscovite there was no indication of interstratified expanded and contracted layers—simply a decrease in the 10 Å reflection and an increase in the 12.3 Å reflection. On the other hand, various mixed-layer structures developed as the $<2\mu$ material expanded. Also, with this sample, a small 15 Å peak appeared in the tracing as soon as the K depletion was initiated. This 15 Å peak did not increase with the degree of K depletion; hence, it may be attributed to the presence of a small amount of lower charge density material. Since this 15 Å spacing was not observed with the $<50\mu$ sample, the grinding treatment was probably responsible for its presence. Also, it will account for the lower layer charge values for $<2\mu$ muscovite in Table 1.

The X-ray results for the $<50\mu$ muscovite are consistent with the model that has been found applicable in a kinetic study of K release from muscovite particles in NaTPB solutions (Reed and Scott, 1962). In this model the particles were regarded as being flat circular discs with an expanded weathered zone surrounding an inner core that had the same basal spacing and K content as the original particle. The boundary between the weathered zone and the inner core was considered to be a weathering front that receded within the particle as K was released. Thus, K release was treated as a two-dimensional radial diffusion problem in which K diffused from a receding weathering front to the periphery of the particle. The validity of this model has been verified by the applicability of the moving boundary diffusion equation to experimentally determined K release data. The X-ray diffraction tracings now show that the weathered portion of the muscovite particles has expanded to 12.3 Å, while the inner core has remained at 10 Å. As the weathering front moved toward the center of the particle, the change in the relative amounts of 10 Å and 12.3 Å material was reflected in the height of the peaks. The weathering front was apparently sharp and not a large enough part of the overall sample to produce other peaks in the diffractometer tracings.

Optical evidence for this mode of mica weathering has been obtained by Mortland (1958) with NaCl-leached biotite. Also, Walker (1959) has shown that the replacement of Mg in vermiculite by Sr occurs in this manner. Even earlier, Bray (1937) suggested that mica particles with beidellite (expanded layers) at the edge develop through a loss of K by chemical weathering. Now, a combination of K release (Reed and Scott, 1962) and X-ray data show that much of the K in $<50\mu$ muscovite particles can be replaced in this manner. Furthermore, these data show that the inner 10 Å core persists until more than 65 per cent of the interlayer cation sites are occupied by hydrated Na ions; that is, the entire layer did not expand from the stress imposed by the outer expanded fringe.

When the interlayer K in the $<2\mu$ muscovite particles was replaced by Na, the basal spacing of the mineral increased from 10 Å to 12.3 Å but various mixed-layer structures existed at different intermediate stages of K depletion. Many of the spacings indicated by the tracings must have resulted from random interstratification of successive 10 Å and 12.3 Å spacings. However, there was a distinct reflection at 10.8 Å that was probably associated with a regular sequence of two 10.0 Å and one 12.3 Å spacings. The small peak at 6.37 Å suggests that another regular interstratified structure involving the 15.0 Å spacing also exists. If so, it was still present when there was only 38 meq K per 100 g in the muscovite (curve L).

The presence of a 5.40 Å peak (second-order reflection for the 10:10:12.3 Å structure) and a 15.0 Å peak in curve G indicates that the initial release of K by the $<2\mu$ particles involved a replacement of all the K in regularly spaced (00l) planes. Thereafter, K release and expansion proceeded from the edge as in $<50\mu$ particles. The partially K-depleted $<2\mu$ particles are, therefore, more comparable to the interstratified weathered mica particles that are frequently observed in soils (Jackson and Sherman, 1953). The difference in the behavior of the $<2\mu$ and $<50\mu$ samples can be attributed to the effect of particle size on expansion (Jonas and Roberson, 1960). However, Mortland (1958) observed only edge weathering with $<2\mu$ biotite particles. Thus, the intensity and rate of weathering must also be a factor. In the present work 30 meq K per 100 g was extracted from the $<2\mu$ muscovite particles in the first 6 hr (curves F and G). At this rate of K replacement, the strain on the particle was apparently enough to cause a few layers to expand to the center of the particle, even though the interlayer cation sites were still occupied by K.

A small amount of material in the $<2\mu$ sample expanded to 15.0 Å. Otherwise, the maximum basal spacing observed with undried Na-degraded muscovite was 12.3 Å. These results are particularly significant because the mineral contained large amounts of Na, which tends to hydrate, and there was no effect of decreasing the particle size. The $<50\mu$ Na-degraded V sample, for instance, contained about 230 meq Na per 100 g. Also, this maximum spacing was not increased by treating the various degraded muscovite samples with glycerol (Fig. 1, curve F). With similar NaTPB treatments biotite and illite expanded to 14 Å (Scott and Reed, 1962a; 1962b). In fact, most of the K-depleted micaceous minerals that have been prepared in the laboratory by various chemical methods have had basal spacings that exceed 12.3 Å (Barshad, 1948; Caillère, Hénin and Guennelson, 1949; Cook and Rich, 1963; De Mumbrum, 1959; 1963; Mortland, 1958; White, 1956). The limited expansion observed here with Na-degraded muscovite is probably associated with the very high layer charge in the mineral.

Undried NH₄-Degraded Muscovite

Undried portions of the NH_4-degraded muscovite samples that were prepared for the total K and layer-charge determinations were suspended in water and deposited on porous ceramic plates to prepare oriented aggregates.

The excess water was removed by suction, but the sample was kept moist before and during the X-ray study.

Smooth diffractometer tracings that were obtained with the NH_4Cl-acetone treated $<50\mu$ samples are shown in Fig. 3. These tracings must be considered in relation to the tracings in Fig. 2 and the data in Table 1 that were obtained
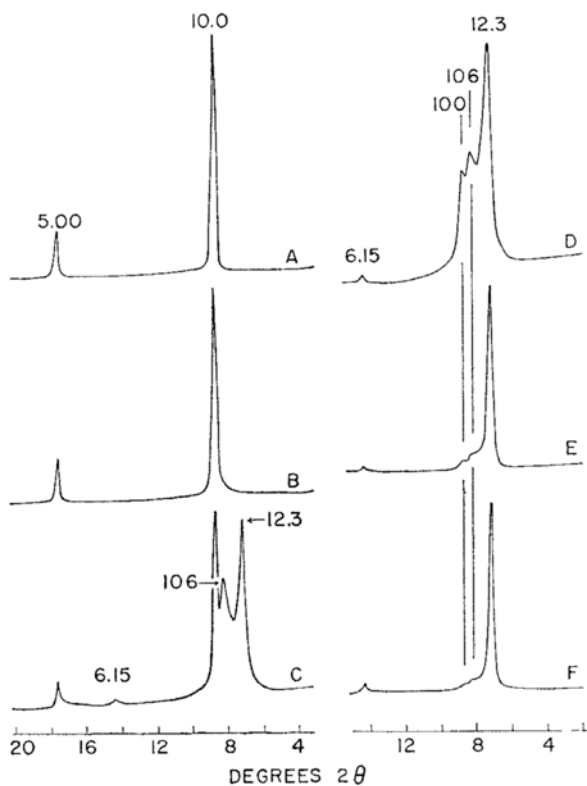

FIG. 3. Smoothed X-ray diffractometer tracings of NH_4Cl–acetone–water treated samples of $<50\mu$ degraded muscovite.

A. Original. B. Degraded I. C. Degraded II. D. Degraded III. E. Degraded IV. F. Degraded V. (K contents shown in table 1.)

with portions of the same degraded samples. Thus, a comparison of curve A in the two figures shows the original $<50\mu$ material was not affected by the NH_4Cl-acetone treatment. On the other hand, there was an effect of this treatment on the degraded muscovite samples. Also, the magnitude of this effect varied with the degree to which the mineral samples were K-depleted.

The amount of NH_4 adsorbed by the different degraded samples was

essentially constant, whereas the amount of trapped Na increased as the K content of the muscovite decreased. As a result, the relative effect of the adsorbed NH_4 decreased as the degree of K depletion increased. The NH_4-degraded V sample contained 30 meq NH_4 per 100 g; yet there was little evidence of the contracted portion of the lattice in curve F. On the other
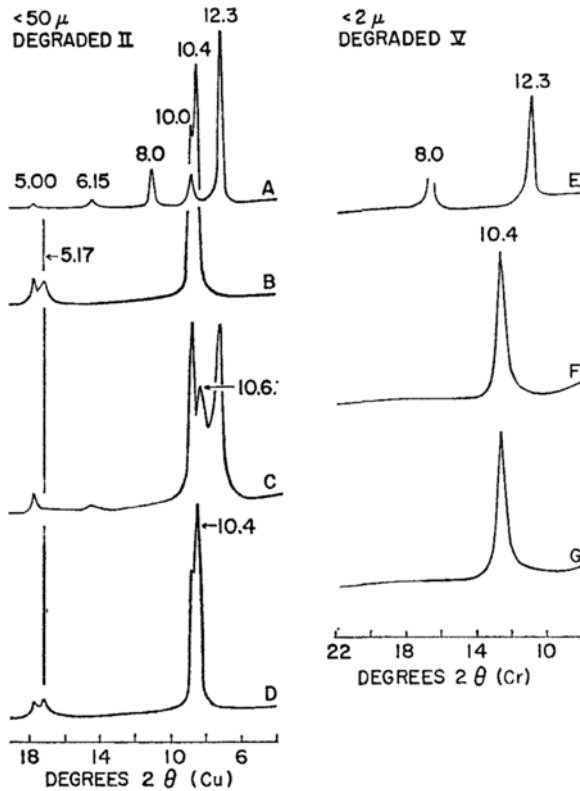

FIG. 4. Effect of NH_4Cl treatments for KTPB removal on smoothed X-ray diffractometer tracings of $<50\mu$ NH_4-degraded II and $<2\mu$ NH_4-degraded V samples.

A and E. No treatment.
B and F. Boiling NH_4Cl.
C and G. NH_4Cl–acetone–water solution.
D. Boiling NH_4Cl after NH_4Cl–acetone–water treatment.

hand, an equal amount of adsorbed NH_4 in the NH_4-degraded I sample eliminated the 12.3 Å peak from the tracing. In the latter case, there was probably not enough trapped Na to prevent the 12.3 Å spacing from being reduced throughout the particle.

When the different Na-degraded muscovite samples were placed in NH_4Cl-acetone-water solutions, part of the Na was replaced by NH_4. This exchange of NH_4 for Na was limited because the basal spacing at the outer edge of the particles was reduced from 12.3 Å to 10.6 Å by the adsorbed NH_4. The remaining Na ions in the particles were trapped, in that they were physically inaccessible for further exchange. The Na portion of the particles retained a basal spacing of 12.3 Å. Consequently, basal reflections at 10.0, 10.6 and 12.3 Å were observed with the degraded samples that were treated with NH_4Cl-acetone solutions.

Samples of $<50\mu$ NH_4-degraded II and $<2\mu$ NH_4-degraded V muscovite were prepared by the boiling NH_4Cl and the NH_4Cl-acetone methods. The effects of these methods on the basal spacing of the mineral are compared in Fig. 4. There was relatively little Na trapping in the $<2\mu$ samples when either method was used (Table 1). Thus, the Na portion of the particles was contracted to 10.4 Å along with the NH_4 portion, and there was no difference in the diffractometer tracings for the two samples (curves F and G). On the other hand, the $<50\mu$ NH_4-degraded samples prepared by the two methods were quite different. There was more NH_4 and less Na trapping in the boiling NH_4Cl-treated sample. Thus, the particles in this sample were also contracted to 10.4 Å (curve B), whereas the NH_4Cl-acetone treated sample retained a 12.3 Å spacing in the Na portion of the particles. These results are consistent with the anticipated effect of particle size on trapping. Curve D, however, shows that the effect of trapped Na on the basal spacing can be eliminated by boiling. The Na and NH_4 content of this sample was not determined but it is thought that the Na ions were dehydrated rather than replaced by NH_4.

CONCLUSIONS

Muscovite, with a layer charge of 247 meq per 100 g, can be expanded from 10.0 Å to 12.3 Å by replacing the interlayer K with Na. A decrease in layer charge is not required for this expansion and K loss. Instead, a simple exchange of Na for K occurs when the blocking effects of fixable cations in the extracting solution are reduced with NaTPB. In the absence of NaTPB and fixable cations like NH_4, this exchange of Na for K is limited by a selectivity coefficient (k_{Na}^{K}) that is very much less than one. Thus, an expansion of muscovite will occur only when the released K is maintained at a very low level by precipitation, leaching or other means. If the layer charge in muscovite is reduced, the selectivity of the mineral for K will decrease and the replacement of interlayer K will occur in the presence of higher levels of K in solution. A decrease in layer charge, therefore, is not required but it will enhance mica weathering.

The K content of muscovite can be reduced to at least 15 meq per 100 g without destroying the mineral. By following the changes in basal spacings associated with the K depletion, it is evident that mica weathering can give rise to mixed-layer structures or mica particles that have only the edges

expanded. Other changes that occur in this mineral before and after the inter-layer K is removed can now be determined. Also, an expanded, dioctahedral-layered silicate with a very high charge density is now available for various investigations involving cation fixation, trapping or freshly exposed silicate surfaces.

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