POTASSIUM RELEASE FROM MUSCOVITE AS INFLUENCED BY PARTICLE SIZE*

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Abstract – Completeness of exchange of K from muscovite by Ba^{2+} ions decreased with particle size below $20\,\mu$. Accompanying K exchange at 120°C, using a repeated batch technique, was a marked loss of Si and the formation of boehmite in the finer fractions. Several possible explanations for the unexpected high K retention of fine mica fractions are discussed. The formation of a diffusion-inhibiting surface "skin" is discounted, because equilibrium was obtained more rapidly with the fine fractions than with coarser fractions. The average degree of bending of unit mica layers due to peripheral expansion is probably greater in large particles. With bending, rotation of tetrahedra and shifting of adjacent layers with respect to each other may induce greater release of K and a lower selectivity for this ion. Fault planes may induce preferential expansion of individual layers and initiate interstratification and splitting of particles. Splitting of particles may reduce bending and increase K selectivity.

INTRODUCTION

SPECIFIC surface and specific weatherability are the two characteristics of minerals considered the most important factors determining the reaction rates of chemical weathering (Jackson and Sherman, 1953). There is some evidence in the literature that particle size not only affects specific surface, but also weatherability of minerals.

Mortland and Lawton (1961) observed higher rates of K-release by NaCl solutions from large biotite particles than from finer ones. This was explained in terms of concentration gradients, determined partly by the "reactive K" of the minerals. However, it can be shown by isotopic exchange in equilibrated exchange systems that interlayer cations in unexpanded micas are almost completely immobilized (DeHaan, Bolt, and Pieters, 1965; Reichenbach, 1968; Reichenbach and Rich, 1968). Hence, interlayer-K cannot be regarded as reactive. The results obtained by Mortland and Lawton need, therefore, some further consideration.

As will be discussed later, specific surface of the minerals can be eliminated as a factor determining the rate of reactions by using a repeated batch-type technique. Specific weatherability, in a restricted sense insofar as only alterations caused by exchange reactions are considered, can then be characterized by selectivity coefficients which are obtained in a relative scale.

K-exchange from muscovite is a less complicated mechanism, because the total charge of the mineral remains constant during the muscovite-vermiculite alteration; whereas, with biotites the rates of K-release might be influenced by the oxidation of Fe^{2+} in the octahedral sheet of the structure.

As has been shown in a previous paper by the authors (1968), interlayer-K can be removed almost completely from muscovite by using $BaCl_2$-solution at 120°C. In the present paper some results shall be presented concerning the K-Ba-selectivity of different size fractions of muscovite.

MATERIALS AND METHODS

A muscovite sample from Amelia, Virginia, was wet ground and separated into the particle size fractions $< 0.08\,\mu$, $0.08–0.2\,\mu$, $0.2–2\,\mu$, $2–5\,\mu$, and $5–20\,\mu$. 40 mg of each fraction was placed in 100 ml polypropylene bottles each containing 75 ml of $0.1\,N$ $BaCl_2$. The bottles were autoclaved at 120–122°C. Reaction periods of 0.5, 1, 2, 5, and 10 days were chosen. Duplicates were investigated for each particle size-reaction time combination.

After the respective reaction time was completed, the samples were centrifuged, the supernatant liquid removed by suction, and a fresh 75 ml portion of $BaCl_2$ solution was added. This procedure was repeated until up to 40 changes of the solution had been made.

K-concentrations were determined in the solutions with the Perkin-Elmer 303 atomic absorption instrument, and the amounts of exchanged K were calculated. Samples of the mineral fractions were digested with HF for total analysis before and after the experiment. K and Ba were determined by atomic absorption. Al and Si (the latter after digestion with NaOH) were determined photometrically according to the method of Shapiro and Brannock (1956). The X-ray diffraction work was conducted using a General Electric XRD-5 instrument with Ni-filtered Cu Kα radiation.

RESULTS

X-ray diagrams of the $5-20\mu$ fraction after various numbers of treatment are shown in Fig. 1. Dioctahedral Ba-vermiculite, characterized by the reflection at 12·1 Å, was produced by the exchange reaction. Intermediate reaction products were observed showing varying intensity relations of the 10 and 12·1 Å reflections. Additionally, a peak can be seen between 10 and 12·1 Å. This peak shifts from 10·6 to 11·3 Å with increasing numbers of treatment and suggests increasing proportions of expanded interlayers in interstratified segments of the particles. Results on effect of other ions and humidity are given elsewhere (Reichenbach and Rich, 1968).

Numerous investigations mainly of trioctahedral micas (Mortland, 1958; Reed and Scott, 1962; Walker, 1963; Raussell-Colom *et al.*, 1965) have shown that the minerals expand in a centripetal direction and that the exchange occurs in a shifting zone separating the expanded margin from the still contracted center of the particles. Scott and Reed (1966) observed, on the other hand, interstratification of $< 2\mu$ muscovite from which K was partially exchanged, but the $< 50\mu$ fraction did not show interstratification.

The amounts of K released after 5-day treatments are plotted in Fig. 2 against the number of BaCl$_2$ treatments for the different fractions. Relative to the $5-20\mu$ fraction, larger amounts of K were released in 25 extractions from the $2-5\mu$ fraction, but with particle size decreasing further the K release decreased strongly. The lowest equilibrium concentrations of K in the solution were found for the $< 0.08\mu$ fraction. The centripetal model cited above did not suggest these unexpected results obtained concerning the rates of K-release from the different particle size fractions.

Some indication that not only ion exchange but also dissolution must have occurred is given by the X-ray diagrams of the fractions obtained after the BaCl$_2$ treatment. The respective diagrams are shown in Fig. 3, together with the diagrams of untreated samples.
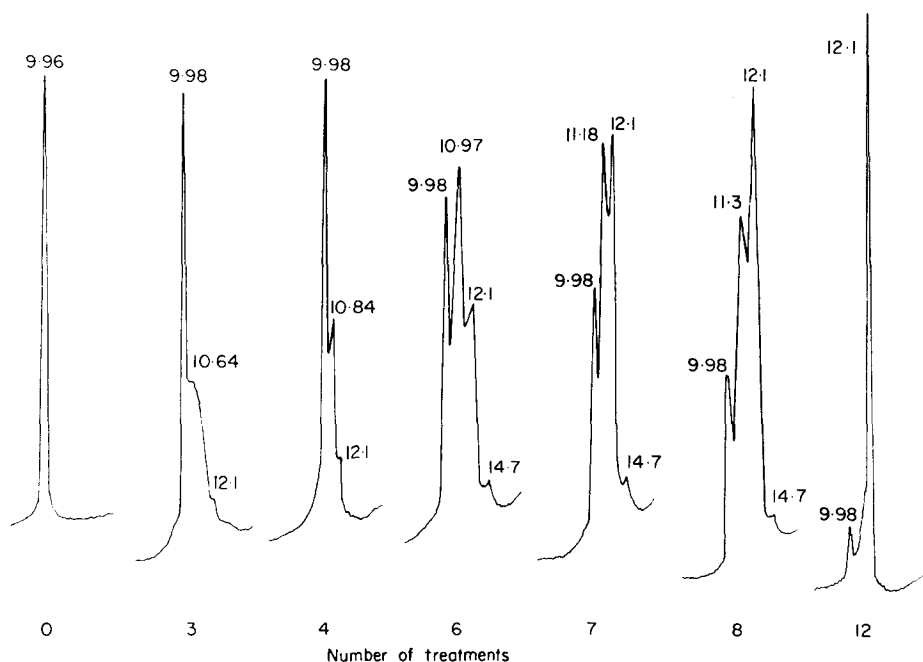

Fig. 1. Alteration of $5-20\mu$ muscovite to vermiculite by Ba–K exchange at 120°C with increasing number of 2-day treatments as indicated by X-ray diffraction patterns.
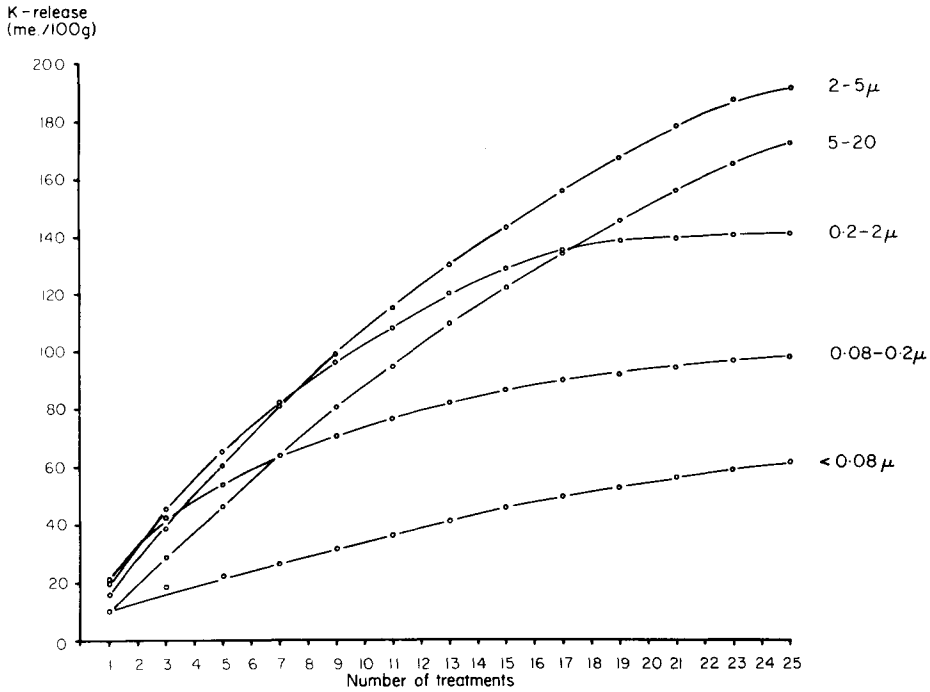
Fig. 2. Relation between accumulative K-release from different particle size fractions of muscovite and number of 5-day treatments.
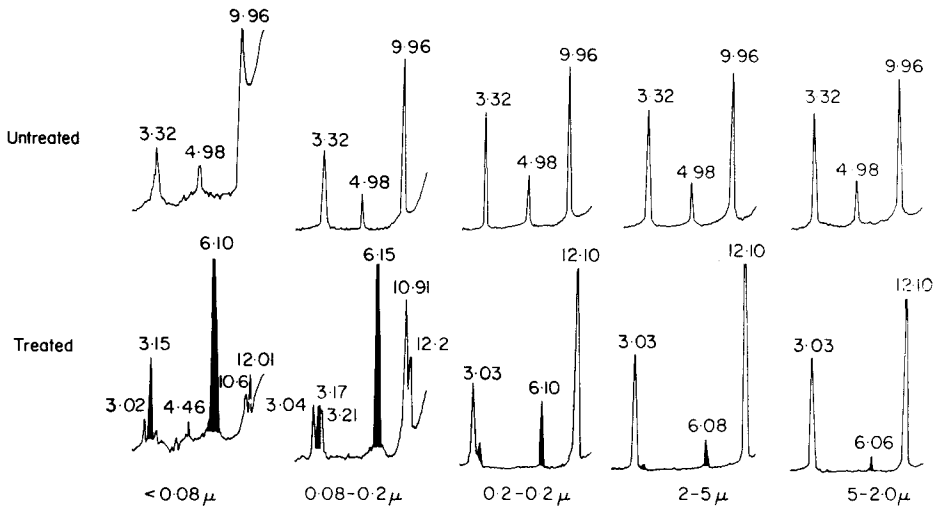

Fig. 3. X-ray diagrams of particle size fractions, untreated and after 40 treatments of 2 days each with 0·1 N BaCl$_2$-solution at 120°C. Boehmite is indicated by filled-in peaks.

It is confirmed by these diagrams that in spite of equal reaction times Ba-K-exchange is less complete in the finer than in the coarser fractions. Additionally, reflections can be seen at 6·11, 3·16, 2·35, 1·98, and 1·86 Å, the intensity of which in-creases with decreasing particle size. These reflections are attributed to boehmite. The forma-tion of boehmite implies that portions of muscovite and/or vermiculite must have dissolved. This is proven by chemical analysis of the reaction

products. The SiO_2/Al_2O_3 ratio of treated samples decreases with decreasing particle size (Table 1). This is due to decreases of the SiO_2 contents as well as to increases of Al_2O_3 contents. Hence, Si must have been transferred into solution and was removed with the exchange solutions, whereas Al remained in the residue through the formation of

DISCUSSION

In discussing the effect of particle size on K release from micas, one needs to consider the experimental conditions, particularly those of the solution phase. Two extreme cases might be distinguished:

(1) If the exchange gradient is maintained during

Table 1. Chemical composition of particle size fractions of muscovite as influenced by 40×5-day autoclave treatments with $BaCl_2$ solution

| Sample | SiO_2 | Al_2O_3 | SiO_2/Al_2O_3 | Dissolved SiO_2 | K-release |
| | | | *Untreated* | *Original amount* | |
(μ)	(%)		(%)	(%)	
<0·08	34·12	30·4	1·12	8·9	—
0·08–0·2	40·75	34·4	1·19	3·8	—
0·2–2	41·01	33·2	1·23	—	—
2–5	41·36	32·8	1·26	—	—
5–20	41·48	34·3	1·21	1·8	—
			Treated		
<0·08	13·6	56·7	0·24	80·6	78·6
0·08–0·2	27·8	43·5	0·64	48·3	56·9
0·2–2	34·0	38·1	0·89	27·5	74·3
2–5	37·3	33·7	1·11	10·1	90·3
5–20	38·6	32·4	1·19	3·4	92·3

boehmite. Assuming that no loss of Al has occurred, the Si dissolved during the $BaCl_2$ treatment can be calculated. Based on the original sample weight, the loss of Si markedly increased with decreasing particle size and amounted to 80·6% in case of the $< 0·08 \mu$ fraction.

A comparison of the losses due to dissolution and of the K released during the experiment indicates that for the $< 0·08 \mu$ fraction the total K release could be explained by dissolution of the silicate structure, whereas for the $5–20 \mu$ fraction K release was almost completely due to Ba–K exchange in the interlayers of the mineral particles, the structure of which remained intact.

The fact that for the $< 0·08 \mu$ fraction the released amounts of K correspond to the portions of minerals dissolved does not mean, however, that K release might not be equally caused by cation exchange followed by a dissolution of the K-free expanded portions of the minerals. The X-ray patterns and Ba content (58 meq/100 g) of the residue show that vermiculite layers have formed by K exchange. The large amount of dissolution and yet significant layer expansion in the $< 0·08 \mu$ fraction should be accompanied by greater K loss than found (Table 1). The formation of allophane-like material would have a lower Si/Al ratio than muscovite and could retain K ions.

the whole reaction period – for instance by percolation of fresh exchange solution through a thin layer of the exchanger or by addition of precipitating agents – then the rate of K release is determined by diffusion coefficients and by the specific surface of the particles. In this case, proportionality between specific surface and exchange rates can be expected.

This condition is fulfilled if Na-tetraphenylborate (NaTPhB) is used. Reed and Scott (1966), therefore, observed with muscovite distinctly higher exchange rates from the $< 10 \mu$ fraction than from the $< 50 \mu$ fraction. The same relation was found for K exchange from biotite varying in particle size (Scott and Reed, 1962a). On the other hand, for illite Scott and Reed (1962b) observed no difference between amounts of K released from $< 20 \mu$ and $< 2 \mu$ fractions, respectively. Hence, the conclusion can be drawn that in spite of the low solubility of KTPhB the exchange gradient cannot be maintained with illite. Consequently, factors other than specific surface become rate determining.

(2) The other case is characterized by the condition that the exchanged K remains in the solution phase of the exchange system. At a given concentration of the exchange solution and at a given mineral-solution ratio, the amount of K released per treatment depends exclusively on the K selectivity of

the minerals, this being the determining factor for the K equilibrium concentration in the solution phase. However, this is only true if reaction periods are sufficiently long in order to establish equilibrium.

In the experiment described in this paper, conditions were chosen in a way that the rates of K release were determined by the K selectivity of the muscovite samples. The exchange systems were at least very close to equilibrium after reaction periods of 5 days. This is shown by Fig. 4 in which K release is plotted against the number of treatments

in Table 1. However, this cannot be regarded as an explanation for the effect of particle size on K release. More Si was dissolved from the small particles, of course; but relative to the surface area, dissolution of Si was even higher for the coarse fractions.

Furthermore, it is assumed that a residue layer should certainly affect the K diffusion rate but should not decrease markedly the equilibrium concentration of K in the solution phase. Hence, if K release is hampered by a residue layer in the finer
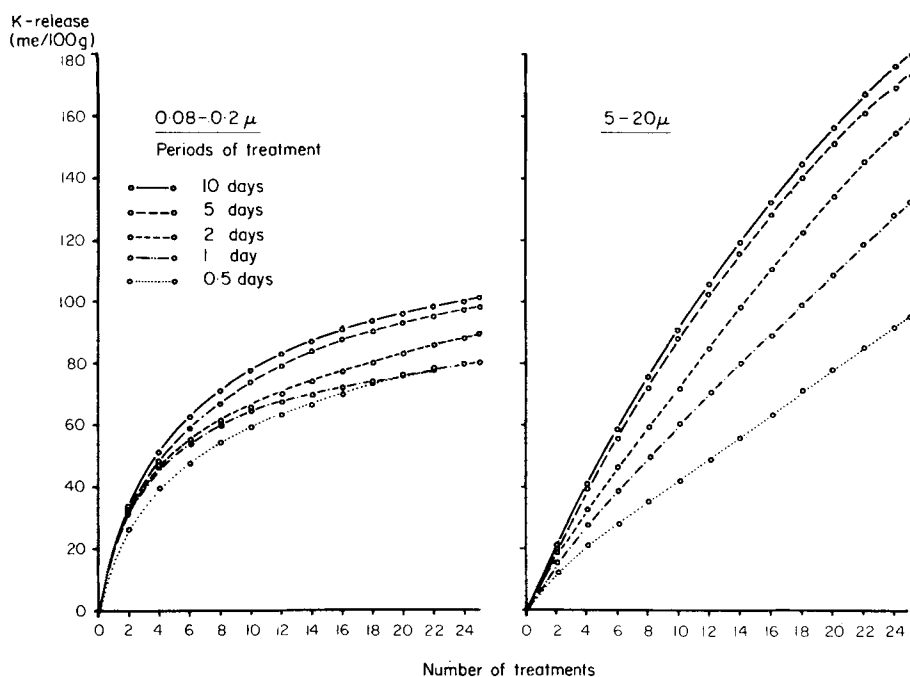

Fig. 4. Relation between K-release from $0.08-0.2\,\mu$ and $5-20\,\mu$ fractions of muscovite and number of $BaCl_2$-treatments using different treatment periods.

for the different reaction times. Only a small increase of exchange rates is obtained with 10-day treatments compared to 5-day treatments. Exchange rates depend much more on reaction time for the $5-20\,\mu$ fraction than for the $0.08-0.2\,\mu$ fraction. This is expected as a consequence of the lower specific surface of the coarser fraction. Nevertheless, even at reaction periods of 0.5 days, more K is released from the coarser fraction. Hence, the conclusion can be drawn that the coarser muscovite particles have a lower K selectivity than the finer ones.

It was reported by Correns (1961) that K release from feldspars was found to be hampered by a residue layer, formed by weathering or dissolution of Si from the lattice, as it was found from the data

fractions, a more pronounced relation between rates of K release and reaction time, compared to the coarser fractions, should be expected. Actually, the contrary was found (Fig. 4).

It is concluded, therefore, that differences in K selectivity between the particle size fractions are related to differences in the exchange mechanism or, more specifically, in the interaction of exchange and expansion of the minerals.

Within the range of the exchange front separating the expanded and the contracted portion of the minerals, deforming forces must be originated by the exchange process and by the related expansion of the interlayers. The action of these forces must result in a corresponding bend of the elementary layers. The magnitude of these forces depends, as

long as no complete cleavage of minerals occurs during the exchange, on the thickness of the particles – that is, on the number of elementary layers combined in one particle.

As shown by Radoslovich (1963), the internal stress in layer silicates can be compensated by rotation of the tetrahedra and by a corresponding transition of the ideal hexagonal to ditrigonal arrangement of O-atoms in the surface of the tetrahedral layer. In case of bending of the elementary layers, the tetrahedral layer on the concave side would be shortened by increasing angles of rotation, whereas on the convex side stretching should occur by decreasing angles of rotation. Due to these arrangements, the coordination of K ions in the interlayers must change as a consequence of either (or both) the tetrahedra rotating or (and) of shearing forces causing some shifting and misfit of adjacent layers.

It seems possible that the bonds of K ions in the zone of transition between collapsed and expanded areas of the mineral are loosened to a degree determined by the formation of elementary layers which increases with distance from the thickness of the particles. A decrease of the b-dimension of muscovite treated with $LiNO_3$ was found as a result of Li–K exchange by Burns and White (1963). The authors conclude that bonding of interlayer K should be affected by this alteration. Leonard and Weed (1967) found negative as well as positive changes in the b-dimension of dioctahedral micas when K was replaced by a variety of ions. We found no change, however, due to Ba–K exchange in the mica studied here. Radoslovich (1963) also discusses the possibility that weathering stability of muscovite could be influenced by unit cell dimensions and by rotation of the tetrahedra respectively.

If these mechanisms are effective, K selectivity should depend not only on particle thickness, but on the uniformity of the exchange front. Exchange from some layers occurring at a more rapid rate than from others results in the interstratification and a reduction in the average bonding of the layers. Thus, the release of stress imposed by expansion may possibly be effected more easily by a complete expansion of occasional single interlayers than by a uniform marginal expansion. With decreasing particle size the width of a non-uniform transition zone (exchange front) approaches the dimension of the radius of the particles, and complete expansion of individual interlayers is more likely. With a decrease in bending of the layers, exchange of K may be inhibited.

High resolution transmission electron micrographs of this muscovite (Brown and Rich, 1968, and Fig. 5) reveal planes 5 to 20 unit layers apart which apparently weather preferentially. These may be growth step planes where there is less order than in normal interlayers. Bassett (1959) proposed that K exchange from one interlayer by hydrated cations may induce stronger bonding of K in the next interlayer. Thus, interstratification may be developed in the weathering process by skipping layers in which K is strongly bound.

If K-selectivity of muscovite is related to particle size, a similar relationship should apply to other micas. The results obtained by Mortland and Lawton (1961) and Scott (1968) are in accordance with this conclusion. Furthermore, it will be shown in a later paper by the senior author that applying the method described in this article to different size fractions of biotite, the same particle size-selectivity relation is obtained as for muscovite, although the K concentrations in the equilibrium solutions are much higher in the biotite system.

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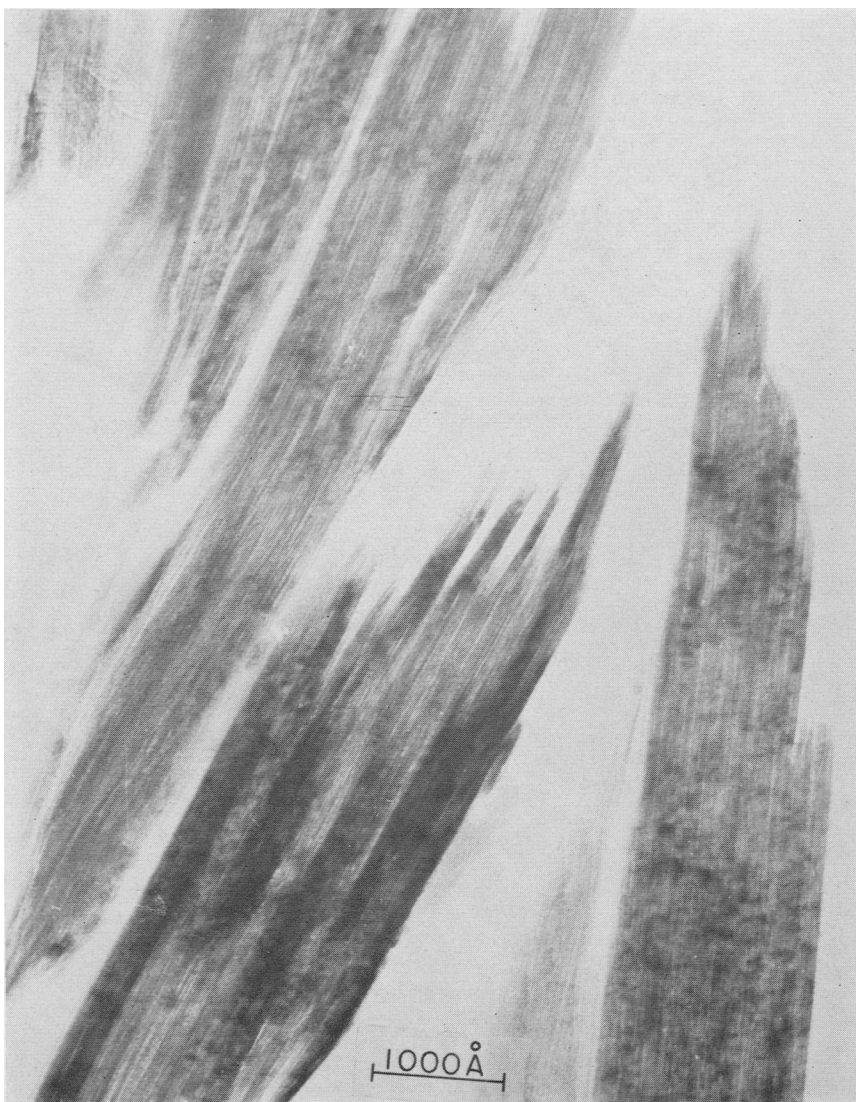
Fig. 5. Transmission electron micrograph of ultramicrotome section cut normal to (001) planes of $0 \cdot 2$–2μ muscovite after 40 2-day treatments in the autoclave. (Professor J. Brown, Georgia Institute of Technology, is thanked for this ultramicrotome and electron micrograph work.)

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Résumé – L'achèvement de l'échange du K à partir du muscovite par les ions Ba^{2+} diminuait pour des dimensions de particule inférieures à 20 μ. L'échange de K à 120°C, au moyen d'une technique de charge répétée, s'accompagnait d'une perte importante de Si ainsi que de la formation de boehmite dans les fractions les plus fines. On discute plusieurs explications possibles de la rétention anormalement élevée des fractions fines de mica. On rejette la possibilité de la formation d'une "peau" à la surface qui empêcherait la diffusion parce que l'équilibre s'obtenait plus rapidement avec les fractions fines qu'avec les fractions plus grossières. Le degré moyen de pliure des couches uniformes de mica en raison de l'expansion périphérique est probablement moins important dans le cas des grandes paricules. Avec la pliure, la rotation des tétrahèdres et le déplacement des couches adjacentes par rapport l'une à l'autre peuvent avoir pour résultat une libérati on plus importante de K et une sélectivité réduite pour cet ion. Des plans de défauts peuvent avoir pour résultat une expansion préférentielle des couches individuelles et initier l'interstratification et la fente des particules. La fente des particules est susceptible de réduire la pliure et d'augmenter la sélectivité au K.

Kurzreferat – Es wurde eine Abnahme in der Vollständigkeit des K-Austausches im Muskowit durch Ba^{2+} Ionen bei Teilchengrössen von unter 20 μ festgestellt. Bei wiederholtem Satzbetrieb war der K-Austausch bei 120°C von einem deutlichen Si Verlust und einer Bildung von Boehmit in den feineren Fraktionen begleitet. Verschiedene mögliche Erklärungen für die unerwartet hohe Festhaltung des K in feinen Glimmerfraktionen werden erörtert. Die Bildung einer diffusions verhindernden "Oberflächenhaut" kommt nicht in Frage, da sich bei den feinen Fraktionen ein Gleichgewichtszustand schneller einstellt als bei den gröberen Fraktione. Das durchschnittliche Mass der Biegung von Einzelglimmerschichten infolge einer Expansion am Aussenumfang ist vermutlich bei grösseren Teilchen mehr ausgeprägt. Die durch das Biegen bedingte Drehung der Tetraeder und Verschiebung benachbarter Schichten gegeneinander kann eine vermehrte Freigabe von K und geringere Selektivität für dieses Ion zur Folge haben. Fehlerebenen können zu besonderer Expansion einzelner Schichten führen und Zwischenlagerung sowie Abspaltung von Teilchen mit sich bringen. Die Abspaltung von Teilchen kann die Biegung vermindern und die K Selektivität erhöhen.

Резюме — Обмен K^+ мусковита на Ba^{2+} понижается при размере частиц менее 20мк. Параллельно с обменом К при 120°C происходят заметная потеря Si и образование бёмита в более мелких фракциях. Обсуждается возможность удержания К мелкими фракциями слюды. Исключается образование поверхностной «кожи», предотвращающей диффузию, так как равновесие достигается намного быстрее в мелких фракциях, чем в более грубых. Средняя степень изгиба слоев слюды вследствие периферического расширения, вероятно, больше в крупных частицах. По мере изгибания, вращение тетраэдров и относительное смещение соседних слоев могут вызвать большее выделение К и более низкую селективность для этого иона. Плоскости нарушения могут быть причиной преимущественного расширения отдельных слоев и вызывать интерстратификацию, а также расщепление частиц. Последнее может уменьшить изгиб частиц и увеличить селективность в отношении К.