Clays and Clay Minerals, 1970, Vol. 18, pp. 333–338. Pergamon Press. Printed in Great Britain

ION SELECTIVITY BY WEATHERED MICAS AS DETERMINED BY ELECTRON MICROPROBE ANALYSIS*

J. LE ROUX,† C. I. RICH and P. H. RIBBE‡
Virginia Polytechnic Institute,
Blacksburg, Va. 24061, U.S.A.

(*Received* 2 *March* 1970)

Abstract—Electron probe micro-analysis studies on individual particles (40–60 mesh) of weathered micas treated with solutions containing equivalent amounts of Rb and Sr showed partial segregation of these elements. Rb was concentrated at particle and step edges, at cracks, and, in the case of partially K-depleted biotite, at boundaries of vermiculite and mica zones ("wedge zones"). The scarcity of wedge zones in mica from which nearly all of the K had been removed reduced the overall selectivity for Rb. The restricted exchange of interlayer Mg ions from vermiculite-like zones by a mixed Rb–Sr solution was observed in earlier studies with these micas. The proposed explanation for these results was a closing down of the interlayer space at the edge of the particle due to Rb concentration in these positions. This explanation is confirmed by the present study.

INTRODUCTION

CATION selectivity studies of micas are complicated by changes in the interlayer spacing during the course of selectivity measurement (Reichenbach, 1968; le Roux and Rich, 1969). This behavior exemplifies exchange system with phase transition (Helfferich, 1962). The replacement of large hydrated cations in vermiculite by smaller cations is particularly difficult. Walker (1963) proposed that trapping of the larger ions is caused by the contraction of the interlayer space at the crystal edges by the smaller ions.

Le Roux and Rich (1969) studied muscovite and biotite samples (5–20μ) that were artificially depleted of K to varying degrees and, after Mg saturation, were repeatedly treated with a mixed Rb–Sr solution. The initial Rb–Sr treatments removed a portion of the interlayer Mg, and both Rb and Sr entered the altered mica. In subsequent treatments Rb continued to exchange Mg but the Sr concentration within the particle did not increase. It was postulated that Rb, because of its low affinity for H_2O and because of its concentration at the interlayer edges, caused an expulsion of H_2O and a closing down of the interlayer space at the particle edges. Thus, entry of the relatively large hydrated Sr ions was restricted. Rb, on the other hand, continued to diffuse into the interlayer space, replacing Mg, but at an ever-decreasing rate. In the present study this hypothetical model of ion segregation was tested with the electron microprobe.

Previous microprobe studies of cation exchange in micas have been made by Rausell-Colom *et al.* (1965), who examined the diffusion of Ca into a biotite flake. They made scans across the optical boundary which indicated the extent of the exchange process. The gradual but complete change from K to Ca in the interlayer space occurred over a distance of about 60μ perpendicular to the flake edge and about 10μ beyond the optical boundary. An inflection in the composition–distance curve for both K and Ca occurred at about 40μ; it was noted in several scans across the exchange front.

Hill and Sawhney (1969) treated small blocks of soil with Cs and studied thin sections of the treated specimens with the electron probe. Cs was found to concentrate in zones of clay accumulation and in weathered mica grains.

MATERIALS AND METHODS

Preparation of samples

Portions of hand specimens of muscovite and biotite from Amelia, Virginia, were wet-ground and screened. Particles that passed a 40 mesh, but not a 60 mesh, screen were used in the present study. Particles of this size (250–420μ) were chosen,

*Support from NSF Grant GA-1373 and the Molecular Structures Laboratory at VPI is gratefully acknowledged.

†Present address: Department of Soil Science, University of Natal, Pietermaritzburg, South Africa.

‡Research Associate in Agronomy, Professor of Agronomy, and Associate Professor of Mineralogy, respectively.

https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

rather than the 5–20μ size used in the study of le Roux and Rich (1969), in order to improve the possibility of detecting ion segregation by means of the electron probe.

Chemical treatment

Because muscovite has much greater retentivity than biotite for K, the two minerals were treated differently to exchange K. In the case of muscovite (M1) a 250 mg sample was placed in a 4-l. Nalgene bottle and 3000 ml of 0·1N $BaCl_2$ was added. The bottle was placed in an autoclave at 120°C for approximately 24 hr. After cooling the system and decanting the solution phase, the treatment was repeated 15 times. This method has been shown to be effective for exchanging most of the K from silt-size muscovite particles (Reichenbach and Rich, 1968). Following this treatment, the samples were autoclaved six times at 120°C in 0·1N $MgCl_2$ to exchange Mg for Ba ions. Analysis of the solution after the sixth treatment did not indicate the presence of Ba.

In the case of biotite (B1), a 100 mg sample was boiled in 800 ml of 0·1N $BaCl_2$ for 1 hr. A second biotite sample (B2) was given autoclave treatment similar to that given M1 except that only three $BaCl_2$ treatments were given. Both samples were washed with 0·1N $MgCl_2$ until no Ba was detected in the wash solution.

The Rb–Sr selectivity study was similar to that reported by le Roux and Rich (1969). Samples weighing 50 mg were placed in centrifuge tubes and 10 ml of a solution of 0·002N RbCl and 0·002N $SrCl_2$ was added. These tubes were shaken for 10 min and then centrifuged. The supernatant solution was removed, and the washing procedure was repeated for a total of 10 extractions. Each extract was analyzed for Rb and Sr. After washing excess salts from the samples, sub-samples were dissolved in HF–$HClO_4$ (Jackson, 1958) and analyzed for Rb, Sr, and K using a Model 303 Perkin-Elmer atomic absorption instrument.

Electron microprobe techniques

Individual grains of the treated mica samples were mounted on fused silica disks on which a thin collodion film has just been applied. The grains were then coated with carbon by vacuum deposition to make them conducting. An ARL-SM electron microprobe, operated at 15 kV and 0·25μA, was used to obtain elemental analyses along traverses across the particles. The sulfates of Ba, Rb, and Sr were used as standards for these elements, synthetic $CaMgSi_2O_6$ was used for Mg, and $(Na_{.65}K_{.35})AlSi_3O_8$ for K. X-ray scanning images of the distribution of individual elements within the particles were recorded photographically from an oscilloscope.

The high take-off angle (52·5°) of the ARL-SM microprobe helps to minimize irregular absorption effects caused by imperfect cleavage surfaces on the mica particles. Only at edges and cracks are the surface features likely to affect the X-ray intensities. The scanning profiles show that these effects were not significant.

RESULTS AND DISCUSSION

Rb and Sr uptake by K-depleted micas

Analyses of the Rb–Sr solutions used to treat the K-depleted and Mg-saturated mica samples (Fig. 1) show that more Rb than Sr was removed from the solutions by the samples. Moreover, after the fifth sequential treatment, there was no further depletion of Sr by the altered mica, whereas Rb continued to be taken up, but at a diminishing rate. These results agree with those reported by le Roux and Rich (1969) on smaller particles. Work with other altered biotite samples showed that an amount of Mg equivalent to the Rb entering

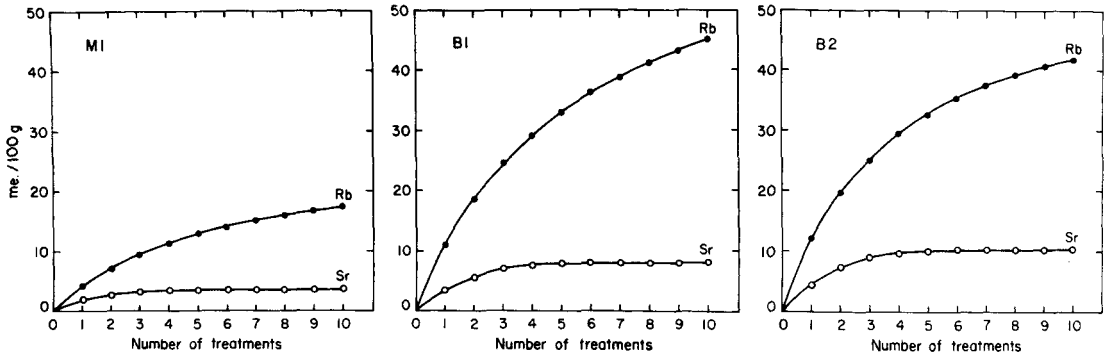


Fig. 1. Uptake of Rb and Sr by partially K depleted muscovite (M1) and biotite (B1, B2) based on Rb–Sr depletion from solution.

https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(a)

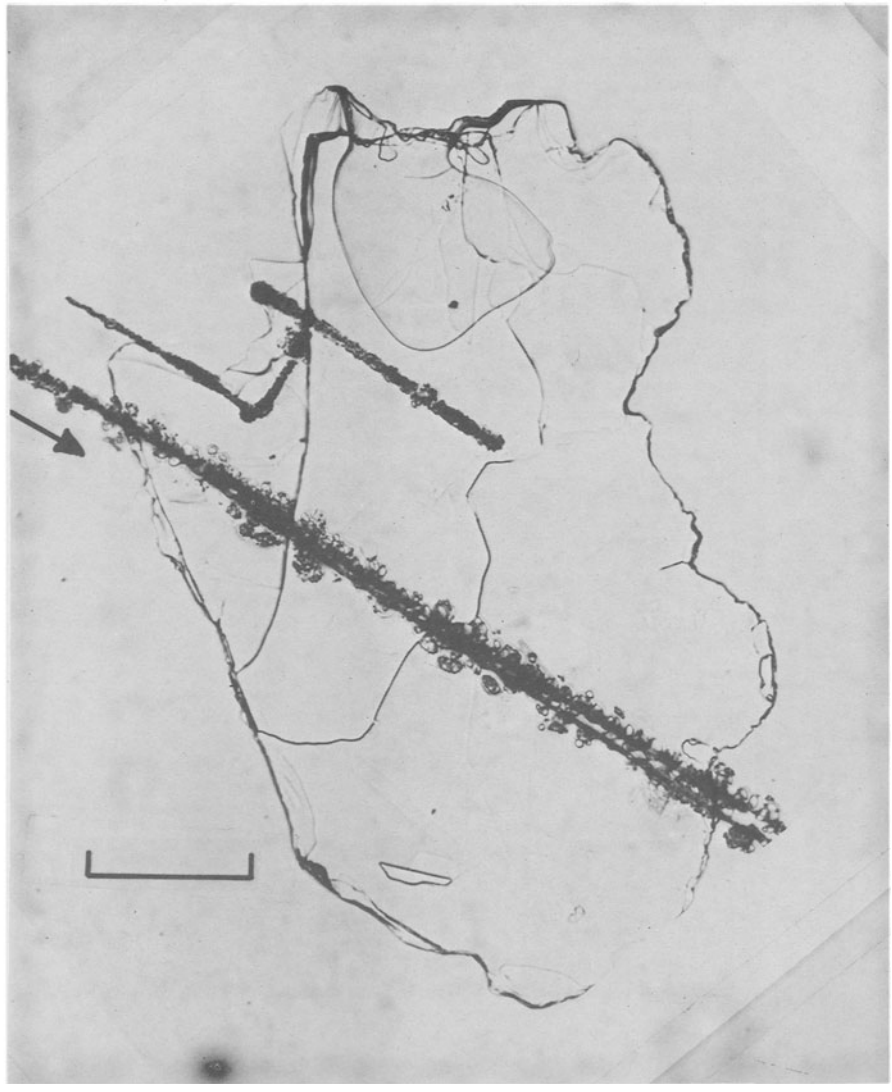
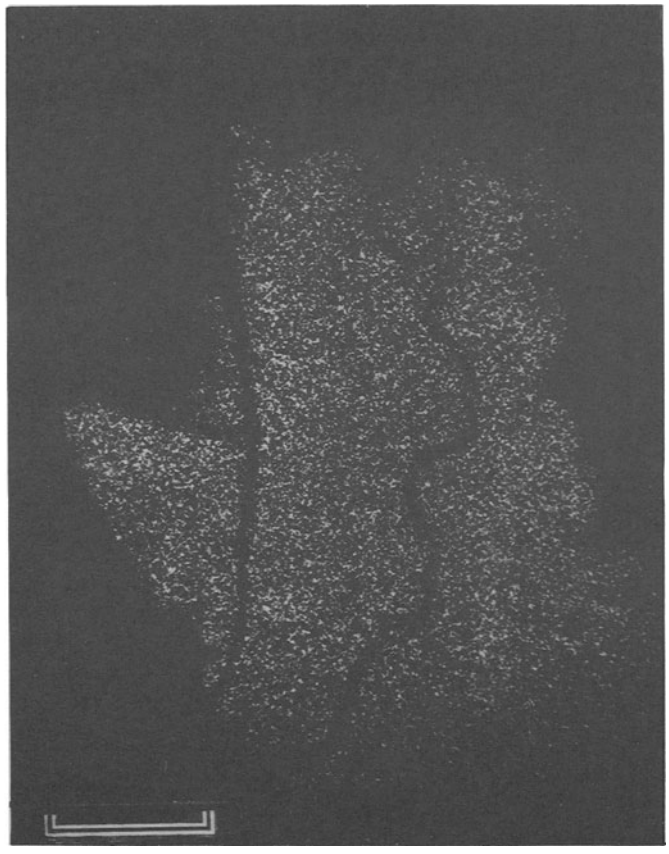


Fig. 2. A muscovite particle (M1) after partial K depletion and Rb–Sr treatment. (a)—Photomicrograph with transmitted light. The arrow indicates the traverse recorded in Fig. 3; (b) and (c)—Microprobe X-ray images of the distributions of K and Rb, respectively, in the same particle. The scale indicates 100μ.

[*Facing page* 334]

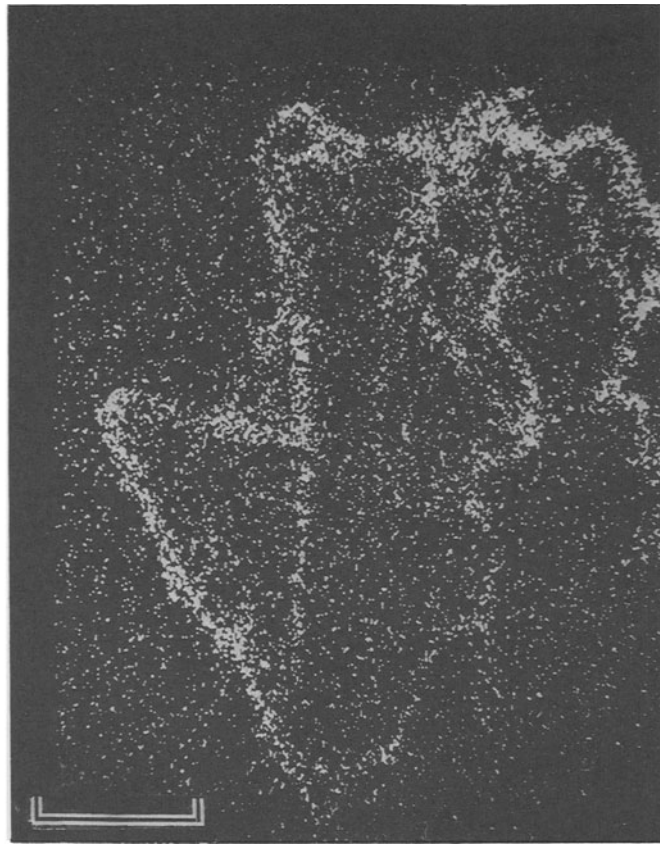
https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(b)



https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(c)



https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(a)

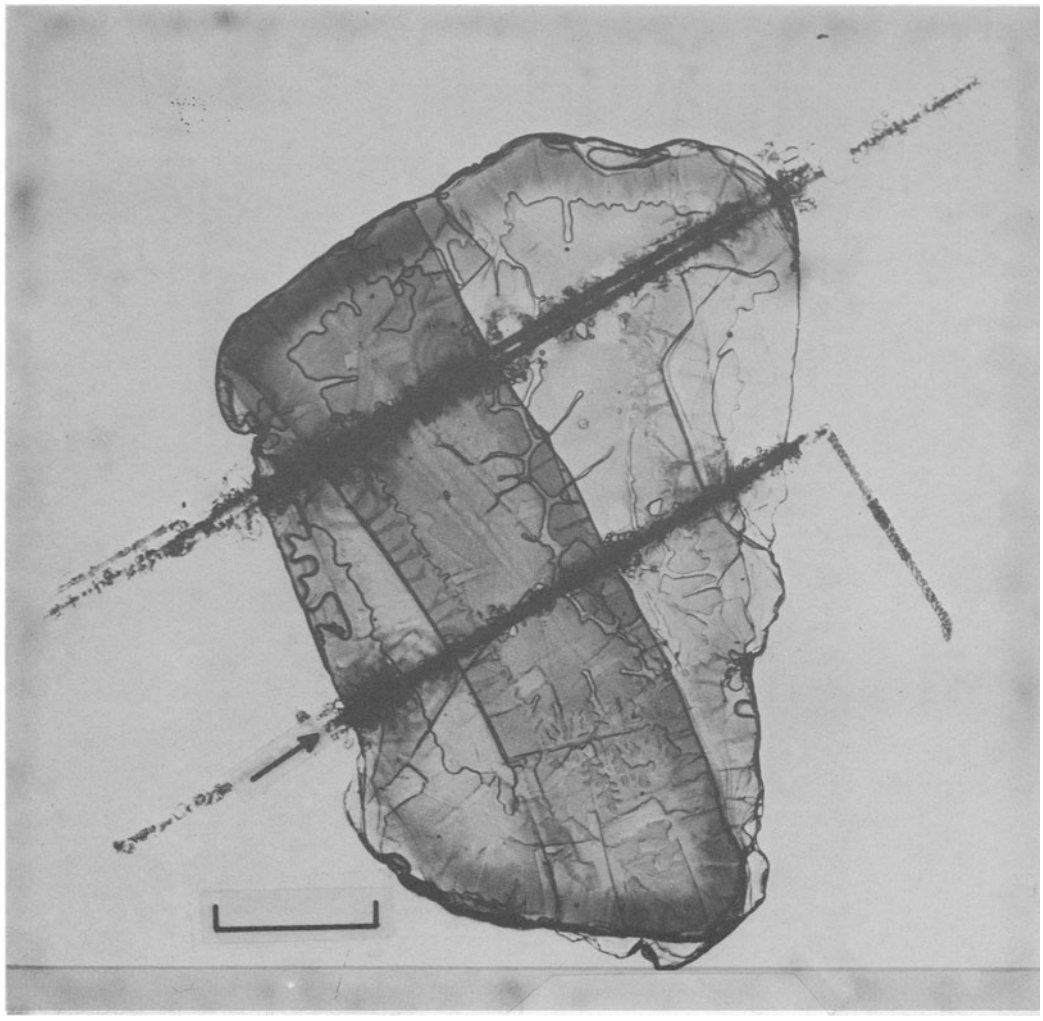


Fig. 4. **A biotite particle (B1)** after **partial K depletion and Rb–Sr treatment. (a)—Photomicrograph** with transmitted light. The arrow indicates the traverse recorded in Fig. 5; (b) and (c)—Microprobe X-ray images of the distributions of K and Rb, respectively, in the same particle. The scale indicates 100μ.

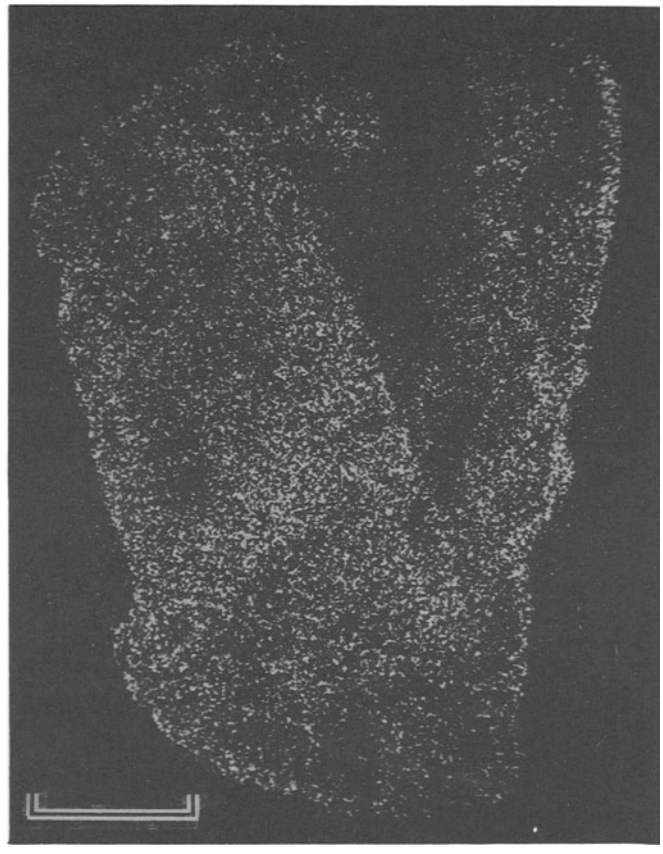
https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(b)



https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(c)



https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(a)

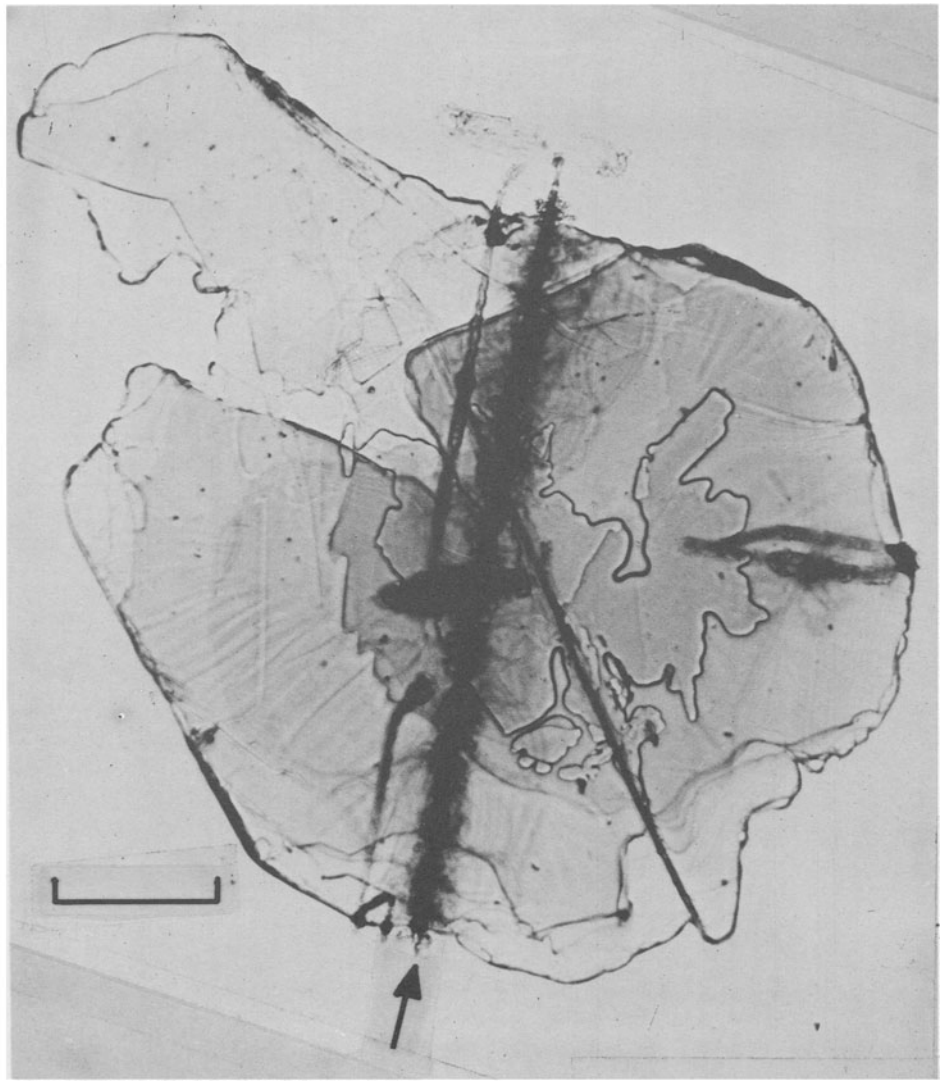
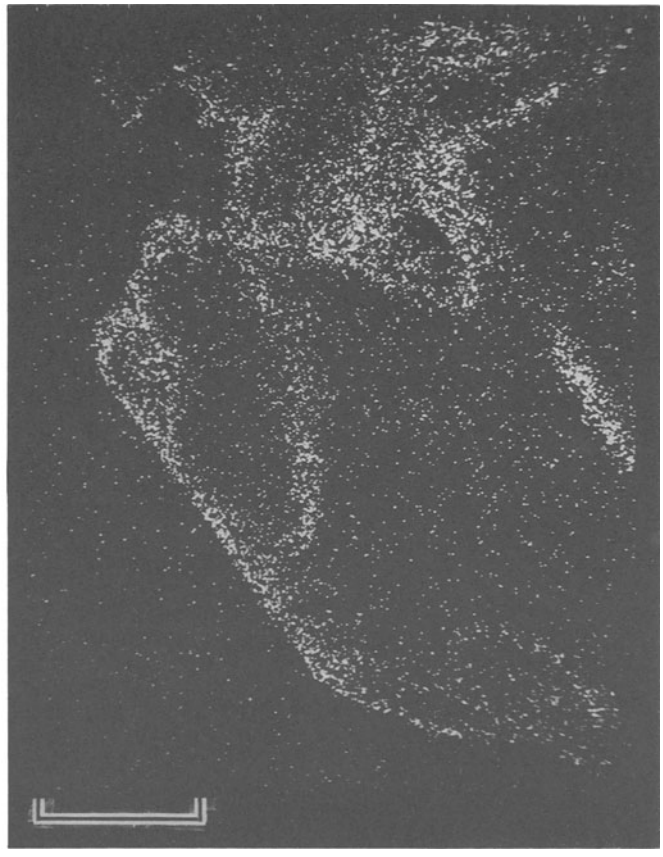


Fig. 6. A biotite particle (B2) after nearly complete K removal and treatment with Rb–Sr. (a)—Photomicrograph with transmitted light. The arrow indicates the traverse recorded in Fig. 7. (b)—Microprobe X-ray images of the distribution of Rb in the same particle. The scale indicates 100μ.

https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

(b)



https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

the particle was being removed from the sample after the Sr concentration came to equilibrium.

Atomic absorption analyses of the mica sample before K depletion (MO and BO) and after K depletion and treatment with the Rb–Sr solution (M1, B1, and B2) (Table 1) support the results of the solution analyses. The summation of K + Rb ; Sr suggests that there was imcomplete exchange of Ba or Mg from the samples by the Rb–Sr solution. This was confirmed by the electron probe analyses for Ba and Mg. Furthermore, chemical analyses of similarly altered samples from the 5–20μ fraction show that there was no loss in charge (Le Roux and Rich, 1969; Reichenbach and Rich, 1968).

Electron microprobe and optical microscope studies

A transmitted light photomicrograph of the M1 flake after electron probe analysis is presented in Fig. 2(a). The traverse marked by an arrow is one for which analyses are reported in Fig. 3. Although this particle had much more extensive treatment than the biotite samples, there is little physical evidence of alteration.

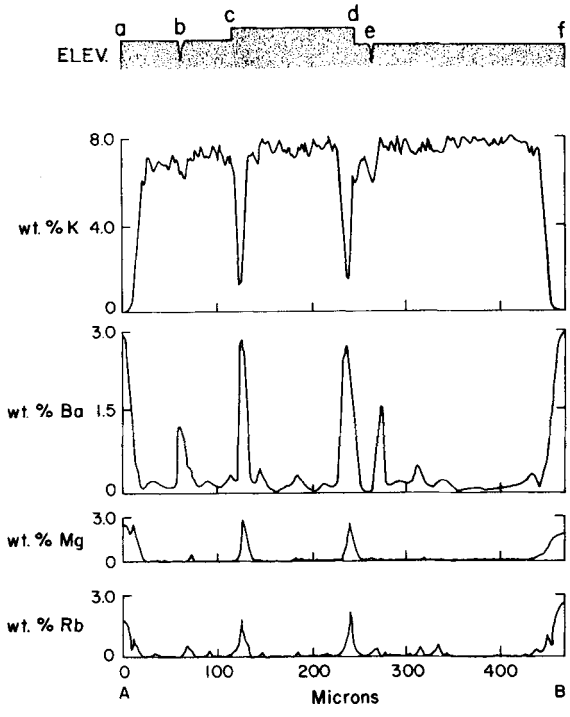


Fig. 3. Electron microprobe analyses along a traverse in muscovite (M1) and a profile of the surface topography along this traverse obtained by observing the particle with reflected light.

A sketch of the surface topography along the traverse is presented at the top of Fig. 3. The loss of K from the particle edges (*a* and *f*) and from edges at steps (*c* and *d*) and cracks (*b* and *e*) is shown by the traverse and the whole particle scan (Fig. 2(b). The distribution of Rb in the same particle is shown in Fig. 2(c). About the same level of background "noise" is indicated in the particle away from edges and steps as from the slide itself. A significant proportion of the Ba remained largely in the edges and steps of the particle, but a small amount was observed in the entire traverse. This emphasizes that analysis of extracts is not an accurate method for showing completeness of exchange of Ba in muscovite; analysis of the sample itself is required. The entry of Ba through surface imperfections is also suggested. This supports the findings of Raman and Jackson (1964) who showed that scrolls formed from surface layers. Our own electron microscopic observations of carbon–platinum replicas of surfaces of the altered micas examined in this study confirm the presence of these features. Scrolls apparently develop at abutments of individual domains of different crystallographic orientation (Sunagawa, 1964).

Diffusion of ions may have been more limited at the two cracks than at the edges, so exchange of Mg as well as Rb and Sr was restricted. Shallow cracks may expose relatively few layers to exchange, and, if only layers near the surface are exchanged, the effect is to lower the X-ray intensity for the exchange element relative to an "infinitely thick" sample.

The limited K depletion restricted major exchange to relatively narrow peripheral zones. This together with the low uptake of Sr reduced the possibility of detecting segregation of Rb and Sr within the particles.

Potassium was more easily removed from the biotite than from the muscovite particles. In the case of B1, 40·5 per cent of the original K was removed in the course of weathering by exchange. A single flake from this sample (Fig. 4(a)) has light scallop-like figures near edges that are probably wrinkles similar to those observed by Rausell-Colom *et al.* (1965) in partially altered micas. The heavier curved lines on the lower surface probably delineate the collodion-particle interface.

Continuous microprobe analyses (Fig. 5) were made along the traverse indicated in Fig. 4(a). Microprobe X-ray images of the distribution of K and Rb in the same particle are shown in Fig. 4(b and c), respectively. Potassium was removed from the particle edges (*a* and *f*) and step edges (*b*, *c*, *d*, and *e*, Fig. 5). A section, left of center and about 90μ wide, contained about 3 per cent K.

https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

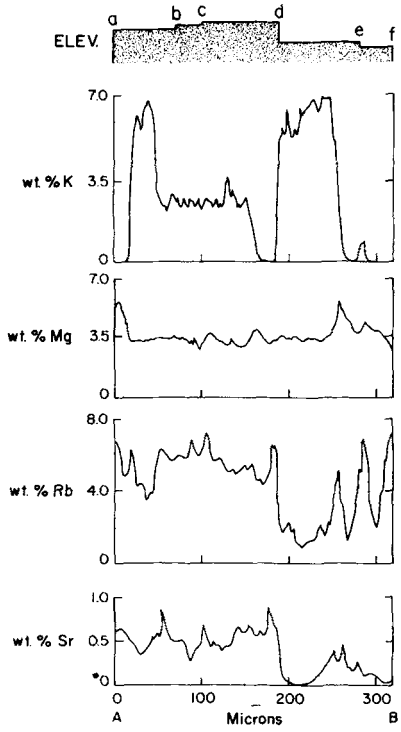


Fig. 5. Electron microprobe analyses along a traverse in biotite (B1) and a profile of the surface topography along this traverse obtained by observing the particle with reflected light.

This may represent a zone of interstratified mica and vermiculite layers or a limited number of surface layers from which all of the K had been removed.

According to the probe analysis, the biotite particle contained approximately 3·5 per cent Mg, most of which is assumed to be in octahedral positions. An elemental analysis of the untreated biotite sample by atomic absorption indicated 3·58 per cent Mg. A portion of the Mg remained in interlayer positions. The incomplete exchange is indicated by the peaks which are located some distance from edges. One would expect this distribution because interlayer Mg ions would be removed first from the edges of the particle.

The profiles of Rb and Sr are of particular interest, since they demonstrate that Rb was concentrated at edges as well as near the front where the exchange of K by Ba and Mg had last been most active. "Wedge zones" probably occur at this exchange front (Rich and Black, 1964). Examples of accumulation of Rb at wedge zones are the Rb peaks at about 20 and 250μ. Partial segregation of Rb and Sr is evident. Although Rb was concentrated at edge and wedge zones, this element was present in all portions of the surface of the particle (Figs. 4(c) and 5). Entry of cations through minute surface cracks and steps as well as through the major edges is thus indicated. Concentration of Rb ions at the edges, as postulated to explain the trapping of divalent ions within the particle, is therefore confirmed. A secondary concentration of Rb in the wedge zones is also evidence that supports the theory that wedge zones are sites for high selectivity of Rb, K, and other large monovalent ions.

The biotite particle from sample B2 that was examined is shown in Fig. 6(a). The distribution of Rb in the particle is indicated in Fig. 6(b). Although all but 6·5 of 229 m-equiv./100g of K had been removed from the biotite in preparing sample B2 (Table 1), only 48·7 m-equiv./100g of Rb and Sr

Table 1. Effect of K-depletion of muscovite and biotite on subsequent selectivity of Rb and Sr ions as determined by atomic absorption analysis after dissolution of micas in $HClO_4$–HF

Sample	K		Rb		Sr		Rb/Sr	ΣK + Rb + Sr
	m-equiv./100g	Wt.%	m-equiv./100g	Wt.%	m-equiv./100g	Wt.%		m-equiv./100g
				Muscovite				
M0	245	9·58	0·0	0·0	0·0	0·0		245·0
M1	203·4	7·9	14·8	1·3	2·3	0·1	6·4	220·5
				Biotite				
B0	229	8·96	0·0	0·0	0·0	0·0		229·0
B1	126·2	4·9	42·3	3·7	6·8	0·3	6·2	176·3
B2	6·5	0·25	39·5	3·4	9·2	0·4	4·3	55·2

*M0 and B0 are samples of the 40–60 mesh muscovite and biotite, respectively, prior to any cation exchange treatment. The structural formula for M0 is $(K_{0.99}Na_{0.01})(Al_{1.77}Fe'''_{0.10}Ti_{0.04}Mg_{0.10})(Si_{3.05}Al_{0.95})O_{10}(OH)_2$ and for B0: $(K_{0.84}Na_{0.05}Ca_{0.07})(Al_{0.42}Fe''_{1.34}Fe'''_{0.15}Mg_{0.65}Ti_{0.11})(Si_{2.85}Al_{1.15})O_{10}(OH)_2$. Treatments for M1, B1, and B2 are described in the text.

https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

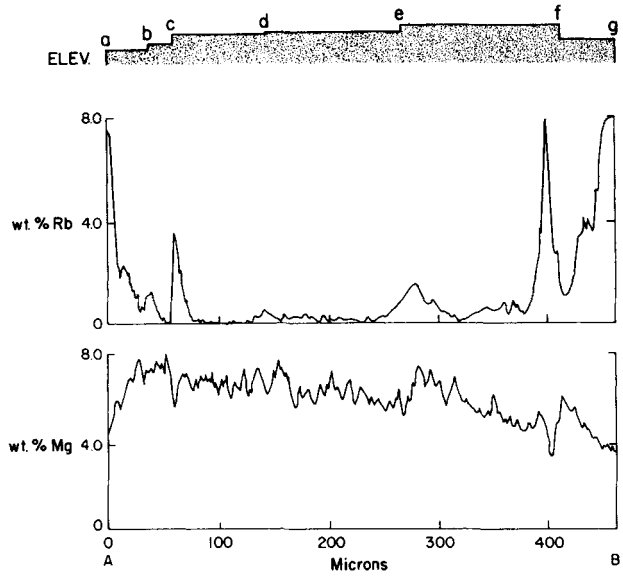


Fig. 7. Electron microprobe analyses along a traverse in biotite (B2) and a profile of the surface topography along this traverse obtained by observing the particle with reflected light.

was taken up. That considerable Mg was trapped within one of the particles from B2 is confirmed by the Mg analysis along the traverse indicated in Fig. 7. If one assumes an average of 6 per cent Mg, this is 2·5 per cent Mg (or 205 m-equiv./100g) in excess of that in the octahedral layer. Rb was concentrated at the edges of the particle (*a* and *g*) and at edges of the steps (*b*, *c*, *d*, *e*, and *f*, Fig. 7). Since no K was detected by the electron probe, the small amount of K indicated to be present (Table 1) was probably too scattered or was buried too deeply for detection. The number of wedge sites would be expected to be much less abundant than in the particle from B1. This is borne out by the Rb distribution. Rb was concentrated only at edges. Although 0·4 per cent Sr was present in the bulk sample (Table 1), it was not detected by electron probe analysis. The nearness in wavelength of a SiK_β satellite peak (see Fig. 1, Smith and Ribbe, 1966) and the small amount of Sr present made the analysis of this element difficult. The probable more even distribution of Sr within the particle compared to the one from B1 contributed to the difficulty with the analysis of this element in B2. Variation of Sr content between particles and location within individual particles also may be contributing factors.

The 8·0 per cent Rb at the maxima is equivalent to 3·8 per cent K, considerably less than the 8·96 per cent K in the original biotite. This suggests that all interlayer positions in the closed zones need not be free of divalent ions for closure to occur. The degree of interlayer expansion depends on the equilibrium of two opposing forces. The affinity of certain cations for water molecules tends to cause a separation of the silicate layers, whereas the electrostatic attraction between the interlayer cations and the negatively charged silicate layers tends to bring the layers together (Kittrick, 1966). For a given cation system, expansion of minerals within the vermiculite and smectite groups decreases with the specific negative charge. The expanded micas studied here have a very high charge and thus collapse would occur with only partial saturation of exchange sites with Rb. A small X-ray diffraction peak at 10·4Å from the Rb–Sr treated particle examined here supports the conclusion that the interlayer space at edges collapsed. No peak in this region was found in the portion of the Mg-saturated sample that had not been treated with the Rb–Sr solution. It is evident that changes in the interlayer space and other aspects of the micromorphology of weathered micas have much to do with ion selectivity by these minerals.

REFERENCES

Helfferich, F. (1962) *Ion Exchange*: McGraw-Hill, New York.

Hill, D. E. and Sawhney, B. L. (1969) Electron microprobe analysis of thin sections of soil to observe loci

https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press

of cation exchange: *Soil Sci. Soc. Am. Proc.*: **33**, 531–534.
Jackson, M. L. (1958) *Soil Chemical Analysis*: Prentice-Hall, Englewood Cliffs, New Jersey.
Kittrick, J. A. (1966) Forces involved in ion fixation by vermiculite: *Soil Sci. Soc. Am. Proc.* **30**, 801–803.
Le Roux, J. and Rich, C. I. (1969) Ion selectivity of micas as influenced by degree of potassium depletion: *Soil Sci. Soc. Am. Proc.* **33**, 684–690.
Raman, K. V. and Jackson, M. L. (1964) Vermiculite surface morphology: *Clays and Clay Minerals* **12**, 423–429.
Rausell-Colom, J. A., Sweatman, T. R., Wells, C. B. and Norrish, K. (1965) Studies on the artificial weathering of mica, pp. 40–72. In *Experimental Pedology*, (Edited by Hallsworth, E. G. and Crawford, D. V.) Butterworths, London.
Reichenbach, H. G. von (1968) Cation exchange in interlayers of expansible layer silicates: *Clay Minerals* **7**, 331–341.
Reichenbach, H. G. von and Rich, C. I. (1968) Preparation of dioctahedral vermiculite from muscovite and subsequent exchange properties: *Trans Intern. Congr. Soil Sci.*, 9th (Adelaide) **I**, 709–719.
Rich, C. I. and Black, W. R. (1964) Potassium exchange as affected by cation size, pH, and mineral structure: *Soil Sci.* **97**, 384–390.
Smith, J. V. and Ribbe, P. H. (1966) X-ray emission microanalysis of rock-forming minerals III. Alkali feldspars: *J. Geol.* **74**, 197–216.
Sunagawa, I. (1964) Growth spirals in phogopite crystals: *Am. Mineralogist* **49**, 1427–1434.
Walker, G. F. (1963) The cation exchange reaction in vermiculite: *Proc. Intern. Clay Conf.* **I**, 177–181.

Résumé – Des études d'analyses par microsonde électronique sur des particules individuelles (40–60 mesh) de micas altérés à l'air, traitées avec des solutions contenant des quantités équivalentes de Rb et Sr, ont montré une ségrégation partielle de ces éléments. Rb était concentré aux bords de la particule et de la couche, aux cassures et, dans le cas de biotite déficiente en K, aux limites de vermiculite et de mica (zones intercalaires "wedge"). La rareté des zones "wedge" dans le mica qui a presque totalement perdu K, réduit la sélectivité d'ensemble pour Rb. L'échange restreint des ions Mg entre les couches à partir des zones comme la vermiculite par une solution mixte Rb–Sr a été observé au cours d'études antérieures sur ces micas. L'explication proposée pour ces résultats était une fermeture de l'espace entre les couches au bord de la particule dû à la concentration Rb dans ces positions. Cette explication est confirmée par l'étude actuelle.

Kurzreferat – Elektronenmikroskopische Studien von Einzelteilchen (Siebfeinheit 40–60) verwitterter Glimmer, die mit äquivalente Mengen von Rb und Sr enthaltenden Lösungen behandelt wurden, zeigten eine teilweise Abscheidung dieser Elemente. Das Rb war konzentriert an Teilchen- und Stufenkanten, an Rissen, und, im Fall von teilweise an Kalium verarmtem Biotit, an den Grenzen von Vermiculit- und Glimmerzonen ("Keilzonen"). Der Mangel an Keilzonen im Glimmer aus welchem beinahe das gesamte K entfernt worden war, verminderte die Gesamtselektivität für Rb. Der beschränkte Austausch von Zwischenschicht-Mg-Ionen aus vermiculitartigen Zonen durch eine gemischte Rb–Sr Lösung wurde bereits in früheren Arbeiten mit diesen Glimmern beobachtet. Die vorgeschlagene Erklärung dieser Ergebnisse war die Schliessung des Zwischenschichtraumes an der Teilchenkante infolge einer Konzentration von Rb in diesen Stellungen. Diese Erklärung wird durch die gegenwärtige Arbeit bekräftigt.

Резюме — Изучение с помощью электронного микрозонда отдельных частиц (40–60 меш) выветрелых слюд, обработанных растворами, содержащими эквивалентные количества Rb и Sr, обнаружило частичное обособление этих элементов. Rb концентрировался на гранях частиц и ступеней роста, в трещинках, а в биотите с дефицитом калия — на границах вермикулитовых и слюдяных зон («вклиненные» зоны). Очень незначительное количество подобных зон в слюде, из которой удалены почти все ионы K, понижает общую селективность в отношении Rb. Ограниченный обмен межслоевых ионов Mg вермикулитоподобных зон при обработке смешанным Rb–Sr раствором наблюдался на ранних стадиях обработки слюд. Объяснение полученных результов заключается в том, что происходит уменьшение межслоевого промежутка на краях частиц вследствие концентрации на них Rb.

https://doi.org/10.1346/CCMN.1970.0180605 Published online by Cambridge University Press