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EFFECT OF PARTICLE THICKNESS ON POTASSIUM EXCHANGE FROM PHLOGOPITE*

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Abstract—Rates of exchange of K with Ca for fine (0·2–2 μm) and coarse (54–75 μm) and for thin and thick (37–45 μm) phlogopite particles were determined using a repeated batch technique, which gave a measure of K selectivity.

Potassium selectivity of the fine fraction was higher than that of the coarse one throughout the exchange process in which 93 per cent of the total K was exchanged from the fine fraction and 100 per cent from the coarse one. Potassium selectivity of the thin 37–45 μm particles was higher initially than that of the thick 37–45 μm particles but the difference disappeared subsequently and practically 100 per cent of the total K was exchanged from both the thin and thick particles.

The results are interpreted as tentatively confirming the hypothesis that bending and deformation of elementary layers during K exchange increase with particle thickness, which in turn increase K exchange and decrease K selectivity.

The K exchange curves for the fine and coarse phlogopite fractions suggest that in natural conditions, as in soils, where K is not continuously removed from solution, vermiculization of coarse mica particles may be not only more complete but also more rapid than vermiculization of fine mica particles.

INTRODUCTION

SEVERAL hypotheses have been proposed to account for the decrease in completeness of K exchange from micas with decrease in particle size. Mortland and Lawton (1961), studying K release from biotite in NaCl solutions explained this observation by assuming a higher concentration of "reactive K" in the larger particles. However, de Haan *et al.* (1965); Reichenbach (1968) and Reichenbach and Rich (1969) using isotope exchange techniques showed that interlayer cations in unexpanded micas are about completely immobilized. Correns (1961) reported that K release from feldspars was hampered by an Al–O residue layer formed by dissolution of other components from the structure. That a residue layer inhibited the diffusion of K from micas was discounted by Reichenbach and Rich (1969) because equilibrium was obtained more rapidly with the fine fractions than with the coarser ones. Scott (1968) explained his results by two release mechanisms, "edge" and "layer" weathering. Edge weathering would be dominant in larger particles where K exchange would proceed uniformly in all layers from the periphery to the center. Layer weathering would be more important in small particles where K would be exchanged only in some layers resulting in a stronger bonding of K in adjacent non-expanded layers (Bassett, 1959). Consequently, layer weathering would render part of the interlayer K non-exchangeable in the smaller particles. Reichenbach and Rich (1969) proposed that, because of the greater thickness of larger particles, bending of unit mica layers due to peripheral expansion would be greater in larger particles. Bending would cause rotation of tetrahedra and shifting of adjacent layers with respect to each other, which would induce greater release of K. There is evidence that weathering in mica along certain planes with more disorder may be more rapid than along other planes (Brown and Rich, 1968). Because of the shorter distance in smaller particles, the more rapidly weathering interlayers would open more readily all the way through. Thus, splitting would be more frequent per unit thickness in small particles, which would further reduce bending and, consequently, K release.

This investigation was designed to test the latter hypothesis; namely, that particle thickness is a primary factor controlling K release in micas. For this purpose, K release was compared from equal-size thin and thick phlogopite particles, which were obtained by wet-sieving and gravity sedimentation.

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MATERIALS AND METHODS

A phlogopite sample from Loughborough County, Ontario*, obtained from Ward's National Science Establishment was wet ground and separated into 25–37 μm, 37–45 μm, and 54–75 μm size fractions by wet-sieving and into 0·2–2 μm by means of gravity and a centrifuge. Because thin particles settle more slowly than thick particles of the same size and composition, thin and thick particles of the sieved fractions were separated by gravity. The suspension containing a sieved size fraction was transferred to a glass tube 60 cm long 3 cm in dia., which was closed at the bottom by a clamped rubber tube. After 10 min, or longer, the clamp was opened and the settled thick particles were drawn off separately from the thinner particles remaining in suspension. Separation according to this procedure was repeated several times with the suspensions containing the thicker particles and with the with the suspensions containing the thinner particles to obtain the thickest and thinnest particles present in the original suspensions. The thin and thick particles obtained in this way were wet-sieved again through the appropriate sieves to eliminate particles smaller than those in the original suspensions.

The thickness of thin and thick 37–45 μm particles separated by the above method was measured on scanning electron micrographs obtained by using a Cambridge Stereoscan Mark II A. The specimen stubs were covered with glue which had been dissolved from Sellotape with chloroform. Dry particles were sprinkled on the stubs and were coated with gold in an Edwards coating unit. Good particle-edge views were obtained under the scanning electron microscope by tilting the specimen stubs up to 90 degrees.

Potassium was exchanged with Ca by treating 20 mg of sample with 100 ml 0·2 N$CaCl_2$ in polypropylene bottles at 80°C in an incubator. In some cases the mineral to solution ratio was 40 mg to 200 ml. After two days reaction, the solution was separated by filtering under suction through a Millipore filter. The mineral was washed from the filter into the bottle with a fresh 100 ml portion of $CaCl_2$ solution. This procedure was repeated every two days until no more K could be detected in solution.

Concentrations of K in the solutions were determined with a Perkin–Elmer 303 atomic absorption instrument. Samples of the mineral fractions were dissolved with HF and $HClO_4$ for elemental analysis before and after the experiment. K, Na, Ca, Mg and Fe were determined by atomic absorption analysis. Silica and Fe^{2+} were determined by methods of Shapiro and Brannock (1956) and Al by the method of Hsu (1963).

*The structural formula for this phlogopite is

$(K_{0\cdot97}Na_{0\cdot06}Ca_{0\cdot04})(Al_{0\cdot16}Fe''_{0\cdot04}Fe'''_{0\cdot07}Mg^{2\cdot77})(Si_{2\cdot60}Al_{1\cdot40})O_{10}(OH)_2$.

RESULTS

The K exchange curves for a fine and coarse size fraction are shown in Fig. 1. These curves serve as comparison for the K exchange curves for the thin and thick particles. It is apparent that the rates of K exchange in this experiment were determined by the K selectivity of the phlogopite samples since the exchange systems were at, or very close to, equilibrium after reaction periods of two days. This nearness to equilibrium was confirmed by the fact that no additional K was exchanged by prolonging the reaction periods. The curves in Fig. 1 for the accumulation of K in solution during the first reaction period show the rates at which the fine and coarse fractions reached their respective equilibrium concentrations. Initially, K exchange from the fine fraction was faster but its equilibrium concentration was markedly lower than that of the coarse fraction. After eight reaction periods, practically all the K was exchanged from the coarse fraction whereas the fine fraction had retained about 7 per cent of its total K. Elemental analysis of the extracted samples gave K contents which agreed with the amounts indicated by the curves.

Five scanning electron micrographs were taken from the thin and 5 from the thick particles of the 37–45 μm fraction. The photographs were taken from different viewing areas at about 2300 times magnification and edges from up to 13 particles per photograph could be measured. The average thickness of measurable edges of 52 particles in the thin particle fraction was 0·20 μm; the average thickness of 36 particles in the thick particle fraction was 1·54 μm. The thin particles ranged from 0·045 to 0·50 μm in thickness and the thick particles from 0·43 to

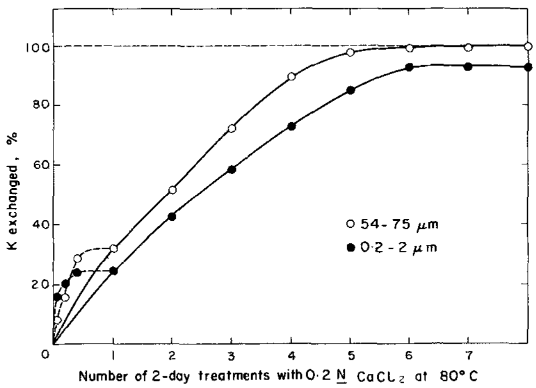

Fig. 1. Rates of exchange of K with Ca for a fine and coarse particle size fraction of phlogopite. Exchange during the first two days is indicated by dashed lines.

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3·55 μm. Thus the thick particles had an average thickness 7·7 times that of the thin particles. The longest diameters of the thin and thick particles, most of which were irregular in shape, ranged from about 30–60 μm.

The exchange of K from thin and thick particles is plotted in Fig. 2. Because the thin and thick particles were separated by gravity, the diameters of a disproportionately large number of thin particles in the 37–45 μm fraction may have been near 37 μm, which could have influenced K exchange. To recognize this possible size effect, K exchange from the thick particles in the 25–37 μm fraction was included in this comparison. However, the rates of K exchange from the thick particles in both the 25–37 μm and the 37–45 μm fractions were practically the same. As shown, much less K was exchanged from the thin particles than from the thick ones in the first reaction period. Subsequently, K exchange from the thin particles was slightly larger than that from the thick particles so that after several reaction periods, the amount of K exchanged from the thin particles approached the amount (100 per cent) exchanged from the thick ones.

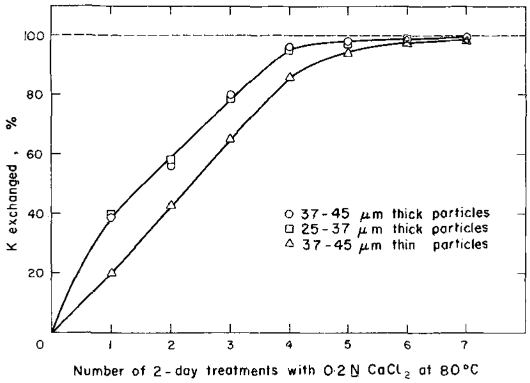

Fig. 2. Rates of exchange of K with Ca for thin and thick phlogopite particles.

DISCUSSION

The K selectivity of the fine phlogopite fraction was greater than that of the coarse fraction throughout the duration of the exchange reaction. Reichenbach and Rich (1969) obtained similar results for muscovite under comparable experimental conditions and explained the results by the hypothesis tested in this study.

The K selectivity of the thin phlogopite particles as compared with the thick ones was higher during the initial stage of exchange. However, the difference disappeared subsequently and is explained as follows:

As particles were comminuted by wet-grinding, splitting occurred at the weakest planes, e.g. planes at growth steps (Brown and Rich, 1968). Consequently, thin particles, which were produced by splitting thicker ones, had exposed fewer easily accessible exchange sites than did thick particles. Therefore, for the thin particles there was less bending of elementary layers and higher K selectivity in the first half of the exchange reaction. Splitting of particles during K exchange may also occur as a result of structural expansion (Scott and Smith, 1967). Such splitting was probably more frequent in the thick particles so that their relatively low K selectivity was not maintained in the last half of the exchange reaction.

Splitting during K exchange may be enhanced by a decrease in particles size as well (Scott, 1961). This process may have contributed to the greater increase in K selectivity of the 0·2–2 μm particles as compared with the 37–45 μm thin particles as K exchange proceeded. Because of the shorter distances in small particles, the more rapidly weathering interlayers open more readily all the way through the particle and result in more frequent splitting per unit thickness. Thus, in small particles bending is reduced by splitting and K selectivity increases with K exchange, whereas in large particles bending increases and K selectivity may be reduced.

In conclusion, the results for K exchange from thin and thick particles are interpreted as tentatively confirming the hypothesis that the bending and deformation of elementary layers, which occur during K exchange, increase with particle thickness, and in turn increase K exchange and decrease K selectivity. The validity of this hypothesis requires further testing. Because of the direct relationship between particle size and thickness, the relatively large thin particles were probably not thin enough to establish conclusively the difference in K selectivity of thin and thick particles. A fruitful approach might be to compare K exchange and selectivity of equal-size, thin and thick fine-silt or clay particles. The experimental difficulties in obtaining such particles, however, are rather formidable. The K exchange curves for the fine and coarse phlogopite fraction suggest that in natural conditions, as in soils, where K is not continuously removed from solution, vermiculization of coarse mica particles may be not only more complete but also more rapid than vermiculization of fine mica particles.

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Résumé – Les taux d'échange de K contre Ca pour des particules de phlogopite fines (0, 2–2 μm) ou grossières (54–75 μm) et minces ou épaisses (37–45 μm) ont été déterminés au moyen d'une technique d'échange en milieu fermé avec contacts répétés, ce qui a donné une mesure de la sélectivité pour K.

La sélectivité pour le potassium de la fraction fine est plus élevée que celle de la fraction grossière, sur la totalité d'un processus d'échange dans lequel 93% seulement du potassium total ont été échangés avec la fraction fine, pour 100%, avec la fraction grossière. La sélectivité pour le potassium des particules 37–45 μm minces est initialement plus élevée que celle des particules 37–45 μm épaisses, mais, par la suite, la différence disparaît, et pratiquement 100% du *K* total sont échangés aussi bien avec les particules minces qu'avec les particules épaisses.

On interprète ces résultats en considérant qu'ils confirment, au moins temporairement l'hypothèse selon laquelle la courbure et la déformation des feuillets élémentaires pendant l'échange de *K* augmentent avec l'épaisseur des particules, ce qui augmente ensuite l'échange de *K* et diminue la sélectivité du minéral pour cet ion.

Les courbes d'échange de K pour les fractions fines et grossières de la phlogopite suggèrent que dans les conditions naturelles, comme dans les sols, là ou *K* ne disparait pas de la solution d'une façon continue, la vermiculitisation des particules grossières du mica peut être non seulement plus complète mais aussi plus rapide que la vermiculitisation des particules fines du même mica.

Kurzreferat – Die Austauschraten von K durch Ca wurden an feinkörnigen (0,2–2 μm) und groben (54–75 μm) sowie an dicken und dünnen (37–45 μm) Phlogopit-Teilchen bestimmt. Es wurde ein Austauschverfahren gewählt, das durch aufeinanderfolgende Gleichgewichtseinstellungen ein Maß für die K-Selektivität ergab.

Die K-Selektivität der feinen Fraktion war während des gesamten Austauschvorganges, in dessen Verlauf 93% des Gesamtkaliums aus der feinen und 100% aus der groben Fraktion ausgetauscht wurden, größer als die der groben Fraktion. Die K-Selektivität der dünnen 37–45 μm-Teilchen war anfangs größer als die der dicken 37–45 μm-Teilchen, jedoch verschwand der Unterschied nach und es wurden praktisch 100% des Gesamtkaliums sowohl aus den dünnen als auch aus den dicken Teilchen ausgetauscht.

Die Ergebnisse wurden als vorläufige Bestätigung der Hypothese gedeutet, daß Verbiegung und Verformung der Elementarschichten während des K-Austausches mit der Teilchendicke zunehmen, wodurch wiederum der K-Austausch erhöht und die K-Selektivität erniedrigt wird.

Die K-Austauschkurven der feinen und der groben Phlogopit-Fraktionen läßt vermuten, daß unter natürlichen Bedingungen – wie in Böden –, wo K nicht ständig aus der Lösung entfernt wird, die Vermiculitisierung der groben Glimmerteilchen nicht nur vollständiger, sondern auch schneller verläuft als die Vermiculitisierung der feinen Glimmerteilchen.

Резюме — Посредством повторного порционного метода определяли скорость обмена K с Ca в мелких (0,2–2 μm) и крупных (54–75 μm), также в тонких и толстых (37–45 μm) частицах флогопита, давшего некоторую селективность по отношению к K.

Селективность мелких частиц по отношению к калию была выше, чем крупных в течение всего процесса обмена во время которого общий обмен K в мелких фракциях = 93% а в крупных 100%. Селективность тонких 37–45 μm частиц по отношению к калию первоначально была выше, чем толстых частиц 37–45 μm, но позднее разница эта исчезла и произошел почти что 100% обмен K как в тонких так и в толстых частицах.

Результаты ориентировочно подтверждают гипотезу, что изгиб и деформация элементарных слоев во время обмена K повышается если частицы толстые, что в свою очередь ускоряет обмен K и понижает селективность по отношению к K.

Кривая обмена К в мелких и крупных частицах флогопита ведет на мысль, что в естественных условиях таких как в почве, где непрерывно из раствора не удаляется К, вермикулизация крупных частиц слюды может быть не только более полная, но также и более быстрая, чем вермикулизация мелких частиц.

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