EFFECT OF PARTICLE SIZE ON POTASSIUM SORPTION BY POTASSIUM-DEPLETED PHLOGOPITE*

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Abstract—Sorption of K from mixed KCl and CaCl₂ solutions by K-depleted, Ca-saturated phlogopite was studied to determine the effect of particle size. The experiments were done at room temperature with 25 mg of K-depleted phlogopite samples in 50 ml solutions which were 0.002 N with respect to KCl and 0.02 N with respect to CaCl₂.

Sorption of K increased sharply with increase in particle size. The 54-75 μm fraction sorbed nearly all, whereas the 0.2-2 μm fraction sorbed less than half, of its depleted K. The 5-20 μm fraction sorbed an intermediate amount. This relationship is explained by the same hypothesis which accounts for the increase of K release with increase in particle size. That is, bending of unit mica layers due to peripheral expansion is greater in large and thick particles than in small and thin ones. This increased bending induces the greater K release from large particles. Similarly, bending due to peripheral collapse of hydrated layers is greater in large particles than in small ones. Thus, more energy is needed to initiate layer collapse and restrict further K uptake in the large particles which results in their greater K sorption capacity.

These results imply that in natural conditions, as in soils, the coarse vermiculite and weathered mica fractions may be more effective in sorbing K from solution than their fine counterparts.

INTRODUCTION

Studies in the artificial weathering of micas have shown that the amount of K which can be replaced by a hydrated cation increases with an increase in particle size (e.g., Reichenbach and Rich, 1969; Scott, 1968). To explain this effect, Reichenbach and Rich (1969) postulated that because of the direct relationship between particle size and thickness, bending of unit mica layers due to peripheral expansion is greater in large and thick particles than in small and thin ones. Increased bending, in conjunction with rotation of tetrahedra and shifting of adjacent layers with respect to each other, induces greater K release. Evidence supporting this hypothesis has recently been obtained by Ross and Rich (1973).

Similarly, it may be postulated than bending due to peripheral collapse of hydrated layers is greater in large particles than in small ones. Hence, it would be expected that after K depletion large particles would sorb more K from solution than would small particles, since more energy is needed to initiate collapse in the large particles. This hypothesis was tested by comparing the rate and extent of K sorption by large and small particles of K-depleted phlogopite.

MATERIALS AND METHODS

A portion of a sheet of phlogopite from Loughborough Country, Ontario was wet-ground and screened to separate 54-75 μm particles. Particle size fractions of 0.2-2 μm and 5-20 μm were obtained by combined sedimentation and centrifugation methods. To obtain K-depleted, Ca-saturated samples, the mineral fractions were extracted with CaCl₂ using a batch technique (Ross and Rich, 1973). By this procedure about 99 per cent of the total K was extracted from the 54-75 μm and 5-20 μm fractions and about 96 per cent of the 0.2-2 μm fraction. Samples of the 54-75 μm and 0.2-2 μm fractions were also depleted to half the initial amount of K by means of the same technique. Samples of 25 mg were placed in 100 ml polyethylene bottles each containing a solution of 50 ml consisting of 0.002 N KCl and 0.02 N CaCl₂. The

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‡The structural formula of this phlogopite is (K₀.₇₋Nₐ₀.₉Ca₀.₄Na₀.₄) (Al₂₋₆Fe₃₊₆⁹Fe⁹₀₇Mg₂.₇₇) (Si₆₀Al₄₀)O₁₅₋OH₂ (Ross and Rich, 1973).
bottles were shaken at room temperature for 2 hr after which the solution was filtered through a Millipore filter under suction. After washing with H₂O₂, the mineral was washed from the filter into the bottle with a fresh 50 ml solution of KCl and CaCl₂ and shaken for 2 days after which the filtering procedure was repeated. Subsequent reaction periods were increased to 3 days or longer.

The sorption of K by the minerals was measured by determining the concentration of K in solution after each extraction period and by determining the total interlayer K and Ca after the experiment by HF/HClO₄ dissolution of the mineral fractions. K and Ca were determined with a Perkin-Elmer 303 atomic absorption instrument.

Portions of the mineral fractions were analyzed before and after the experiment by X-ray diffraction. The samples were sedimented on glass slides and irradiated with Cu Kα radiation using a General Electric XRD instrument.

To measure particle thickness, some of the K-depleted particles were deposited from suspension on copper grids coated with 0.25 per cent Formvar. The specimens were then shadow-casted at a 45° angle with platinum–iridium in an Edwards Hi Vacuum shadow-caster coating unit. The length of the shadows, indicating the particle thickness, was measured on electron micrographs which were obtained using a Siemens Elmiskop electron microscope.

RESULTS

Elemental analyses of the K-depleted samples prior to K sorption gave total layer charges of 220, 225 and 221 m equiv per 100 g for the 54–75, 5–20 and 0.2–2 μm fractions, respectively. After K sorption the respective layer charges were 223, 225 and 217 m equiv per 100 g and the K contents of the samples agreed with the amounts indicated by the curves in Figs. 1 and 3.

Figure 1 shows that the completely K-depleted size fractions sorbed K rapidly during the first 2 hr and then more slowly. After 8 days no more K was taken up. The 54–75 μm fraction regained nearly all of its interlayer K, whereas the 0.2–2 μm fraction sorbed less than half of its interlayer K. The 5–20 μm fraction acquired an intermediate amount.

Figure 2 compares the X-ray diffraction patterns

Fig. 1. Potassium sorption at room temperature by 25 mg samples of K-depleted, Ca-saturated phlogopite from 50 ml solutions consisting of 0.002 N KCl and 0.02 N CaCl₂. Solutions were renewed after each K determination.

Fig. 2. X-ray diffraction patterns of oriented aggregates of the 54–75 μm fraction of phlogopite before (a) and after (b) K depletion with 0.2 N CaCl₂. (c) is sample (b) after K resorption (d) is the initially K-depleted 0.2–2 μm fraction after K resorption. Counting rate for (a), (b) and (c) is 5000 cps and for (d) 1000 cps.
of basally oriental specimens before (curve a) and after (curve b) K depletion and after K sorption. The K-depleted, Ca-saturated sample shows an integral sequence of sharp reflections with basal spacings typical of Ca-saturated vermiculite. Compared with the original phlogopite, the K-treated 54–75 μm fraction (curve c), which contained about 10 per cent hydrated layers, gives broader reflections and a larger first-order basal spacing. In addition, the basal reflections show significant deviations from an integral series. The K-treated 0.2–2 μm fraction (curve d) which contained about 50 per cent hydrated layers shows a relatively strong 14 Å peak; the remaining reflections closely match those for the K-treated 54–75 μm fraction.

The results in Fig. 3 were obtained to determine whether partially K-depleted phlogopite resorbed more of its depleted K than did completely K-depleted phlogopite. A comparison with Fig. 1 shows that this is the case for the 54–75 μm fraction. However, the half-depleted 0.2–2 μm fraction resorbed considerably less of its depleted K than did its completely K-depleted counterpart.

The electron micrographs showed that most particles had an irregular shape and were often elongated which precluded determinations of a definite diameter to thickness ratio. The 0.2–2 μm particles examined were between 1–2 μm in size and were less than 0.1 μm thick; their average thickness was 0.06 μm. The 54–75 μm particles examined ranged from 40 to 80 μm in size and their average thickness was 2.5 μm.

Fig. 3. Potassium sorption at room temperature by 25 mg samples of partially K-depleted, Ca-saturated phlogopite from 50 ml solutions consisting of 0.002 N KCl and 0.02 N CaCl₂. Solutions were renewed after each K determination.

**DISCUSSION**

The 54–75 μm particles were about 40 times as thick as the 0.2–2 μm particles. Assuming that particle thickness rather than particle size was the primary controlling factor, the large increase of K sorption by K-depleted phlogopite with an increase in particle size may be explained by the same hypothesis that accounts for the increase of K release of mica with an increase in particle size (Reichenbach and Rich, 1969; Ross and Rich, 1973). They postulated that, during K release, bending of unit mica layers due to peripheral expansion is greater in large and thick particles than in small and thin ones. Increased bending in conjunction with rotation of tetrahedra and shifting of adjacent layers would induce greater K release. Similarly, bending of elementary layers due to peripheral collapse is greater in large particles than in small ones. Thus, more energy is required to initiate collapse in large particles and consequently more K can be sorbed before interlayer collapse blocks further uptake.

The X-ray pattern for the fine fraction, which shows a strong 14 Å reflection, confirms the presence of a relatively large hydrated component in this fraction. The broad, non-integral basal reflections and relatively large basal spacings of the reconstituted mica component in both the coarse and the fine fraction indicate structural irregularities which may be caused by trapped hydrated Ca-ions. These data also suggest that the original mica is not reconstituted when K is sorbed by altered micas (cf. Brown and Newman, 1970; Kodama and Ross, 1972).

The comparison of K sorption by partially and completely K-depleted phlogopite suggests that the type of weathering, or more specifically the mechanism of K release, of the large particles is different from that of the small ones. If K release progressed uniformly from the periphery to the center in all layers, it might be expected that, because of the shorter diffusion path, the partially K-depleted particles would resorb more of their depleted K than the completely K-depleted particles. This situation is obtained for the large particles but not for the small ones. This difference in behavior suggests that, in contrast with the large particles, the small particles released K more rapidly from some layers than from others, a process which would leave a structure with part of the layers completely expanded while the remaining part remained more or less non-expanded (cf. Scott, 1968). In such particles there would be fewer expanded layers per unit thickness than in the completely K-depleted particles. This mixed assemblage of expanded and unexpanded layers would require less bending of elementary layers for peripheral collapse and would result in the observed smaller uptake of depleted K by the partially K-depleted small particles as compared with those which had been completely K-depleted.

In previous experiments on K release from micas it was found that the concentration of K at which such release was stopped was lower for small particles than for larger ones, and it was concluded
that the smaller particles had a higher K selectivity
(Reichenbach and Rich, 1969; Ross and Rich, 1973). The present experiments on K resorption
by K-depleted mica show that more K was sorbed
from solution by large particles than by small ones.
Therefore, it is reasonable to conclude that the
large particles had a higher K selectivity. This
apparent contradiction is resolved by the pro-
posed mechanism of K release and resorption.
However, these results show that in cases where
ion selectivity is affected by a phase transition of the
structural change and of the approach to equilibri-
um should be specified when comparing selectivity.

In conclusion, the hypothesis in which bending
of elementary layers is considered a major factor
affecting K exchange explains both the greater
K release from original mica and the greater
K resorption by K-depleted mica with an increase in
particle size. The data also suggest that in large
particles K exchange progresses from the periphery
to the center more or less uniformly in all layers
whereas in small particles K is released rapidly
from some layers and more slowly from the
remaining ones. The results imply that in natural
conditions, as in soils, the coarse vermiculite and
coarse weathered mica fractions may be more effec-
tive in sorbing K from solution than their fine
counterparts.

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Résumé — La fixation de K à partir de solutions mixtes KCl et CaCl₂ par une phlogopite ouverte dont
on avait extrait le potassium et saturé par Ca, a été étudiée afin de déterminer le rôle de la taille des
particules. Les expériences ont été conduites à température ambiante avec des échantillons de 25 mg
de phlogopite ouverte dans 50 ml de solutions de concentration 0,002 N en KCI et 0,02 N en CaCl₂.

La fixation de K augmente brutalement quand la taille des particules augmente. La fraction 54–75
µm fixe pratiquement tout le potassium retiré, alors que la fraction 0, 2–2 µm en fixe moins de la
moitié. La fraction 5–20 µm en fixe une quantité intermédiaire. Cette relation est expliquée par la
même hypothèse que celle qui rend compte de l’augmentation de la libération de K quand la taille des
particules augmente. Selon cette hypothèse, la courbure des feuilles de mica due à l’expansion
périphérique est plus grande dans les particules grandes que dans les particules petites
et minces. Cette courbure accrue induit la libération plus élevée de K à partir des grandes particules.

D’une façon similaire, la courbure due à la fermeture périphérique des feuilles hydratées est plus
importante avec les grandes particules qu’avec les petites. Ainsi, une énergie plus élevée est requise
pour initier la fermeture des feuilles et pour restreindre une fixation ultérieure de K dans les grandes
particules, ce qui entraîne leur capacité de fixation pour K plus élevée.

Ces résultats impliquent que dans les conditions naturelles, comme dans les sols, les fractions
grossières de vermiculite et de mica altérés soient plus efficaces pour la fixation de K à partir d’une
solution, que leurs équivalents fins.

Kurzreferat — Um den Einfluß der Teilchengrößen zu bestimmen, wurde die Sorption von K aus KCl-
und CaCl₂-Mischlösungen (0,002 n KCl, 0,02 n CaCl₂) durch K-verarmten, Ca-gesättigten Phlogopit
untersucht. Die Versuche wurden bei Raumtemperatur mit 25 mg-Proben K-verarmten Phlogopits in
50 ml Lösung ausgeführt.

Mit Zunahme der Teilchengrößen steigt die K-Aufnahme stärker an. Die 54–75 µm-Fraktion sor-
briert fast die gesamte, die 0,2–2 µm-Fraktion weniger als die Hälfte der vorher freigesetzten K-
Menge. Die 5–20 µm-Fraktion sorbiert eine mittlere Menge. Diese Verhältnisse werden mit der
gleichen Hypothese erklärt, auf die auch der Anstieg der K-Freisetzung mit zunehmender Teilchen-
größe zurückgeführt wird: Die Verbindung der einzelnen Glämerschichten durch randliche Auf-
weitung ist in großen und dicken Teilchen größer als in kleinen und dünnen. Diese verstärkte Verbie-
gung bewirkt größere K-Freisetzung aus großen Teilchen. In ähnlicher Weise ist die Verbindung durch
randliche Kontraktion hydratisierter Schichten in großen Teilchen größer als in kleineren. Infolge-
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dessen ist mehr Energie erforderlich, um in großen Teilen die Schichtkontraktion und eine Einschränkung der weiteren K-Aufnahme auszulösen, was eine größere Sorptionskapazität für K zur Folge hat.


Резюме — Для определения влияния размера частиц на сорбцию изучалась сорбция К флогопитом, обедненным К и насыщенным Ca, из смешанного раствора KCl и CaCl₂. Исследования проводились при комнатной температуре с 25 мг образцами флогопита обеденного К в 50 мл растворе, являвшемся 0,002N относительно KCl и 0,02N относительно CaCl₂.

С увеличением размера частиц сорбция К значительно повышалась. Фракция 54–75 μм сорбировала почти весь истощенный К, в то время как фракция 0,2–2 μм сорбировала меньше половины потерянного ею К. Фракция 5–20 μм сорбировала среднее количество. Эта зависимость сорбции объясняется той же гипотезой согласно которой выделение К повышается при увеличении размера частицы. Таким образом, перегиб агрегата слоев вследствие периферийного расширения сильнее в крупных толстых частицах, чем в небольших тонких. Этот увеличенный перегиб вызывает повышенное выделение К из крупных частиц. Таким же образом, перегиб вследствие периферийного оседания гидратированных слоев бывает более высоким в крупных частицах, чем в небольших. Поэтому для порождения оседания слоя и ограничения дальнейшего восприятия К крупной частицей, в результате чего сорбируется большее количество К, требуется большие энергии.

Из результатов вытекает, что в таких естественных условиях как земля крупные частицы вермикулита и фракции выветрелой слюды, очевидно, более эффективно сорбируют К из растворов, чем мелкие.