Clays and Clay Minerals, 1971, Vol. 19, pp. 209–218. Pergamon Press. Printed in Great Britain

DODECYLAMMONIUM–MICA COMPLEXES—I FACTORS AFFECTING THE EXCHANGE REACTION

E. E. MACKINTOSH,* D. G. LEWIS and D. J. GREENLAND
Waite Agricultural Research Institute, University of Adelaide, Glen Osmond, South Australia 5064

(*Received* 14 *January* 1970)

Abstract—Dodecylammonium chloride (DAC) is used as a reagent to displace potassium from a wide range of mica minerals. Displacement is rapid and essentially complete for trioctahedral micas even in dilute solutions (0·02N DAC) at low suspension concentrations. Increasing the suspension concentration, or the concentration of potassium in the extracting solution decreased the extent to which potassium could be displaced before equilibrium was established. Under standardized conditions of temperature and suspension concentration, the rate of potassium displacement increased as the particle size decreased although complete displacement was more difficult to achieve for the finest fraction ($< 2\mu$) than for the coarser particles.

The trioctahedral samples were shown to be more susceptible to potassium depletion by DAC than dioctahedral material. Within the range of trioctahedral samples examined the rate of reaction was found to be closely related to the fluorine content of the sample. Data obtained for the more resistant dioctahedral specimens was not sufficiently detailed to enable any similar relation to be established.

INTRODUCTION

IT HAS been established that micas react with alkylammonium cations (Weiss, 1963; Mackintosh and Lewis, 1968). Part of the reaction involves the replacement of potassium ions from the mica structure by the alkylammonium ion, and may be represented as:

$$\text{K-mica} + R^+ \rightleftharpoons R\text{-mica} + \text{K}^+.$$

However studies of the potassium replacement reaction using inorganic cations have shown that a simple representation of the reaction in this way is not entirely adequate, as changes in the structure other than potassium displacement also occur.

At present little is known of the factors which control the potassium displacement reaction, and the other changes occurring in the mica structure. The reactions of inorganic ions with the dioctahedral micas tend to be slow, and incomplete. The alkylammonium ions, particularly the *n*-dodecylammonium ions (Mackintosh and Lewis, 1968) are more effective than the inorganic ions and provide a convenient means for studying the potassium displacement reaction. In the present paper several of the factors which influence the displacement of potassium are considered, including the composition and structure of the micas. In a subsequent paper the nature of the reaction products will be discussed.

*Present address. Department of Soil Science, University of Guelph, Guelph, Ontario, Canada.

MATERIALS

Micas

General descriptions and some chemical data for the primary mica minerals used are presented in Table 1.

Reagents

The dodecylamine was obtained from Fluka A. G. Chemische Fabrik. Dodecylammonium chloride (DAC) was prepared by dissolving the amine in benzene and bubbling dry HCl gas through the solution (Ralston and Eggenberger, 1948). The product was filtered and recrystallized twice from benzene.

METHODS

Potassium displacement

For the determination of potassium displaced by DA^+, suspensions of small quantities of mica were shaken in measured volumes of DAC solution (usually 0·025 N) on an end-over-end shaker inside an oven maintained at a constant temperature of 70°C ± 1°. After selected shaking periods samples were extracted using a syringe and the suspensions filtered by forcing the liquid through a type SS MF-millipore membrane (pore size 3μ). Potassium in solution was determined by flame photometry using an EEL flame photometer with i.r. sensitive photocell for increased sensitivity to potassium. DAC concentrations of less than 0·045N did not interfere with the determination. Further pro-

https://doi.org/10.1346/CCMN.1971.0190402 Published online by Cambridge University Press

Table 1. Descriptions of samples

No.	Sample	Locality	Colour	External morphology	Total potassium (me/100 g) (dried in air at 110°C)	% Fluorine‖
1	Biotite*	Harts Range, N. T.	dark brown	sheets	215	0·76
2	Biotite†	Bancroft, Ontario	dark brown	sheets	200	3·06
3	Lepidomelane†	Faraday Township, Ontario	dark brown	sheets	200	1·46
4	Phlogopite*	Harts Range, N. T.	dark amber	sheets	215	3·67
5	Phlogopite†	Quebec	dark amber	sheets	201	6·07
6	Phlogopite†	Bedford Township, Ontario	amber	sheets	213	2·35
7	Fluorphlogopite‡	Synthetic	clear, colourless	coarse grained	248§	9·40§
8	Muscovite*	Harts Range, N. T.	colourless	sheets	220	0
9	Muscovite*	Barrier Range, N.S.W.	colourless	sheets	219	0·20
10	Muscovite†	Effingham Township, Ontario	colourless	sheets	220	0·56
11	Zinnwaldite*	Londonderry, W.A.	dark grey	radiating sheaves	222	3·71
12	Lepidolite*	Grosmont, W.A.	lilac	sheets	210	8·75
13	Lepidolite†	Karibib, South Africa	lilac	fine grained	220	6·78
14	Lepidolite*	Coolgardie, W.A.	lilac	fine grained	211	6·31

*Supplied by Specimen Minerals Ltd., Adelaide.
†Supplied by Ward's Natural Science Establishment Inc., New York.
‡Supplied by K. Norrish, Division of Soils, C.S.I.R.O.
§As determined from the structural formula ($K_2Mg_4Li_2Si_8O_{20}F_4$).
‖Analysis by K. Norrish (*X*-ray fluorescence spectography).

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cedural details are given by Mackintosh and Lewis (1968).

Particle size fractionation

Samples of each mica were ground in a Siebtechnik mill and separated into a number of fractions. Particle size fractions down to 20 μ e.s.d. were separated by wet sieving to ensure as complete as possible separation of finer particles. Sedimentation under gravity was used for separation of fractions $< 5\,\mu$ and $< 2\,\mu$ e.s.d. Even after wet sieving the fractions separated did not consist solely of particles with dimensions in the chosen range since electron micrographs of Pt/C replicas indicated that small amounts of fines ($< 0{\cdot}1\,\mu$ e.s.d.) occurred as coatings on the surfaces of larger particles. In some instances these coatings could be partially removed by ultrasonic treatment of the suspensions prior to sieving.

RESULTS

pH changes

Adsorption of DA^+ onto a surface can result in a decrease in the pH of the suspension (Cowan and White, 1958). The pH of a suspension of 20 mg of sample in 200 ml of 0·025N DAC solution decreased gradually from an initial value of $5{\cdot}8 \pm 0{\cdot}1$, but did not fall below 5·0 during the time periods normally used. At higher suspension concentrations (200 mg/200 ml) treatment for 3 months at 70°C caused the pH to fall to 3·1. When the susceptible Ontario biotite was shaken with DAC solutions at controlled pH's of 3·0 and 5·3, the rates of potassium release differed by less than 5 per cent, indicating that pH is not a significant factor influencing the replacement of K^+ by DA^+ (see Tucker, 1964; Wells and Norrish, 1968).

Particle size

The relationship between apparent particle size of the readily attacked Ontario biotite and potassium displaced by DAC (20 mg/200 ml of 0·025N DAC at 70°C) is shown in Fig. 1. These results were calculated on the basis of the determined initial potassium contents of each size fraction. For the $< 2\mu$ fraction this was 176 me/100 g, compared with 199 me/100 g for the $53–75\mu$ fraction. The loss of potassium occurred during the wet sieving. Oxidation and resultant loss of charge occurred at the same time.

For the fractions greater than 2μ e.s.d. displacement of potassium was virtually complete, and the amount released within the first minute of the reaction was directly proportional to the calculated edge area of the particles. Similar relationships were found for the other micas. For particles $< 2\mu$ e.s.d. the reaction, although initially more rapid, did not proceed beyond about 80 per cent displacement of potassium. A similar result was obtained for the Quebec phlogopite. A muscovite (Harts Range) and lepidolite (Grosmont) were also examined, but the reaction was so slow that it was not possible to determine whether the material $< 2\mu$ would release less potassium than other size fractions.

Most subsequent data were obtained using the $53–75\mu$ fraction, as this was least altered by the grinding and fractionation procedure.

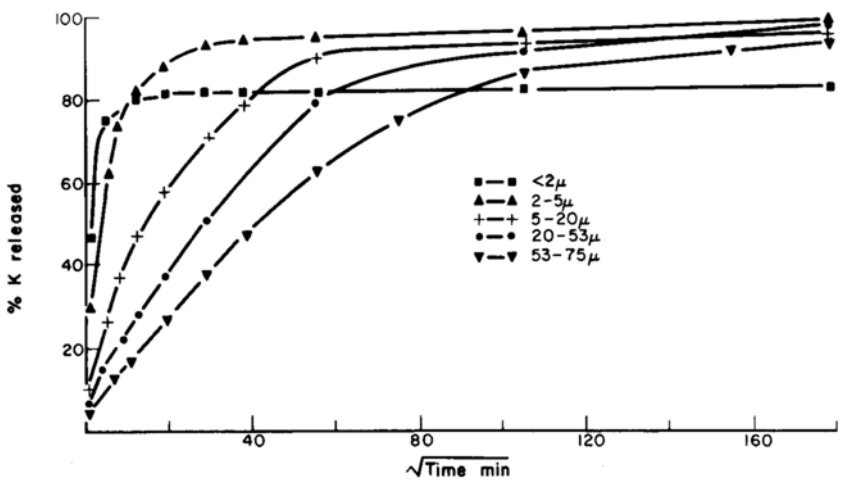


Fig. 1. Effect of particle size on the displacement of potassium from Ontario biotite. Sample size was 20 mg shaken at 70°C in 200 ml of 0·025N DAC.

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Initial DAC concentration

The rate of potassium release from the 53–75μ fraction of the Ontario biotite, in solutions of different initial DAC concentration, is shown in Fig. 2. A relatively rapid reaction occurred in solutions as dilute as 0·005N, but little increase in reaction rate occurred beyond a concentration of 0·025N. This was also true of other mica samples.

Suspension concentration

The rate of potassium release from the Harts Range biotite (53–75μ) in 0·025N DAC at 70°C at different suspension concentrations is shown in Fig. 3. The rate and extent of displacement decreased as the concentration increased. A similar decrease in the rate and extent of reaction was produced by adding potassium ions to the initial

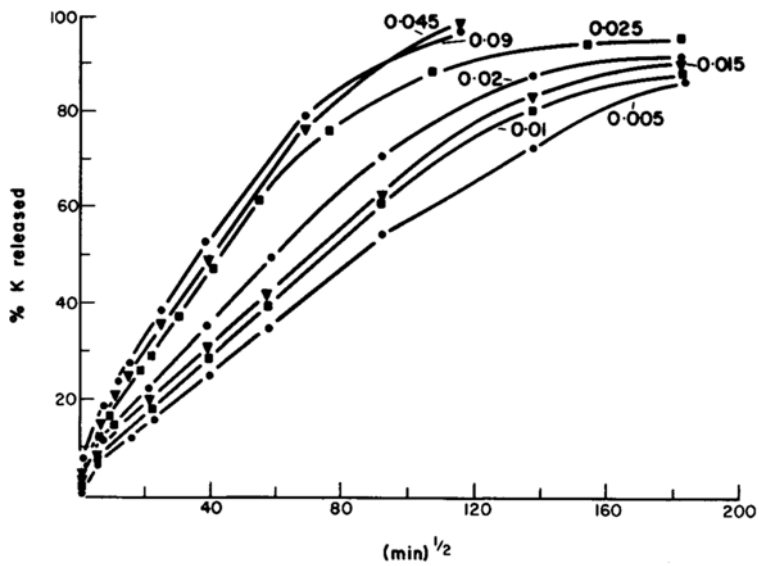


Fig. 2. Effect of DAC concentration on potassium displacement from the 53–75μ fraction of Ontario biotite. (20 mg/200 ml of xN DAC at 70°C).

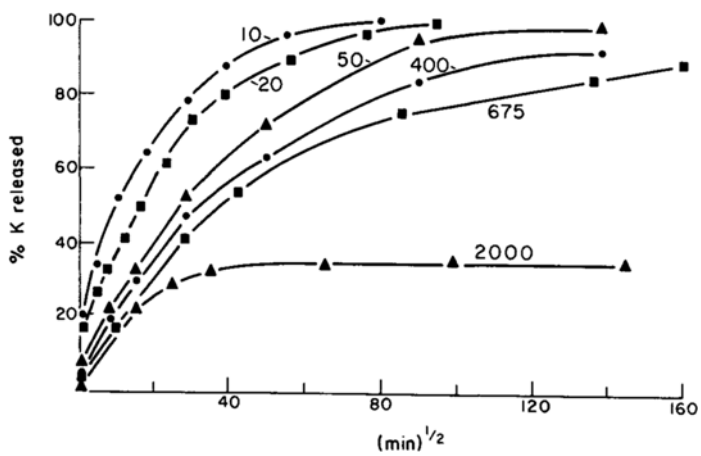


Fig. 3. Influence of suspension concentration on the rate and extent of potassium displacement from Harts Range biotite (53–75μ fraction in 200 ml 0·025N DAC at 70°C). The figures by each curve represent the sample weight (in mg) in each run.

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DAC solution. For samples of Ontario biotite in solutions containing initially 200 mg of K per 1. the reaction ceased after displacement of less than 50 per cent of the total potassium from the sample. Due to the high initial concentration it was not possible to measure accurately the extent of potassium released by analysis of the filtrate. An estimate of the depletion was gained from an examination of the altered mica by X-ray diffraction and comparison with patterns from a range of samples depleted to known extents.

Chemical constitution of the mica

Comparison of the data in Figs. 4a and b with

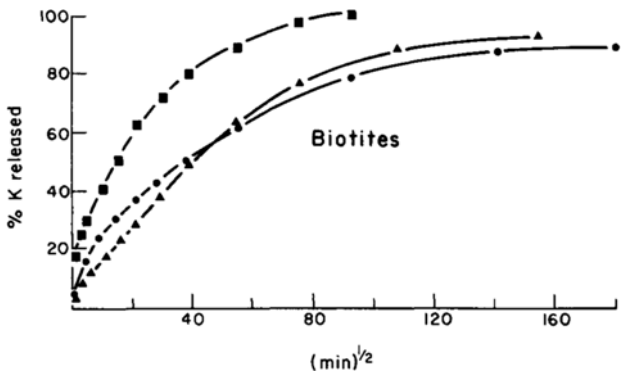


Fig. 4a. ■—■ Harts Range; ▲—▲ Ontario; ●—● Lepidomelane.

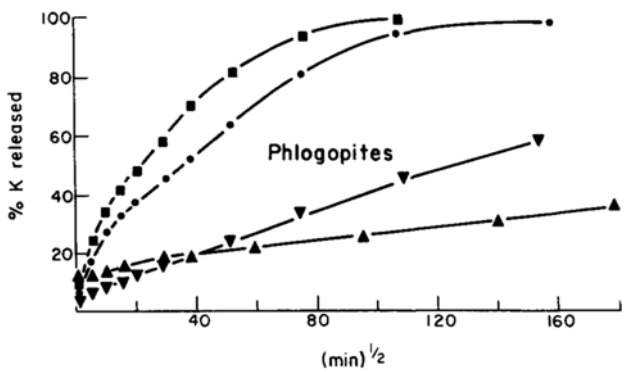


Fig. 4b. ■—■ Ontario; ●—● Harts Range; ▼—▼ Quebec; ▲—▲ Synthetic.

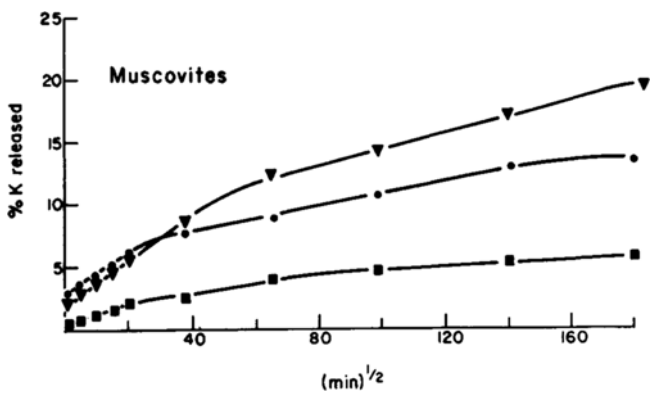


Fig. 4c. ▼—▼ Ontario; ●—● Harts Range; ■—■ Barrier Range.

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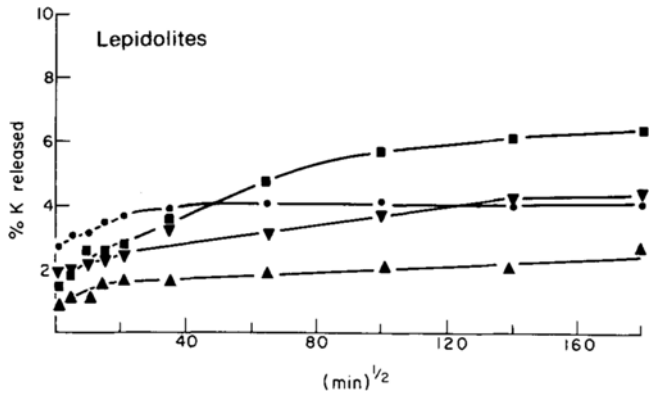


Fig. 4d. ■—■ Grosmont; ▼—▼ Coolgardie; ▲—▲ South Africa; ●—● Zinnwaldite.

Fig. 4. Displacement of potassium from micas of different chemical constitution. Samples, each 20 mg, of 53–75μ fraction shaken with 200 mls of 0·025N DAC at 70°C in all cases. Fig. 4a. Ferruginous micas. Fig. 4b. Phlogopites. Fig. 4c. Muscovites. Fig. 4d. Lithium micas.

those shown in Figs. 4c and d illustrates the much greater rate of release from trioctahedral than from the dioctahedral micas. Of the trioctahedral micas two with relatively high fluorine contents reacted more slowly than the others. Similarly the lepidolites which reacted even more slowly tend to have higher fluorine contents than the muscovites (Figs. 4c and d).

Figure 5 shows the relation between the fluorine content of the trioctahedral micas and S^2 where S is the slope of the straight line portion of Figs. 4a and b. The parameter S^2 has been used as a measure of the apparent diffusion coefficient of K^+ in the system.

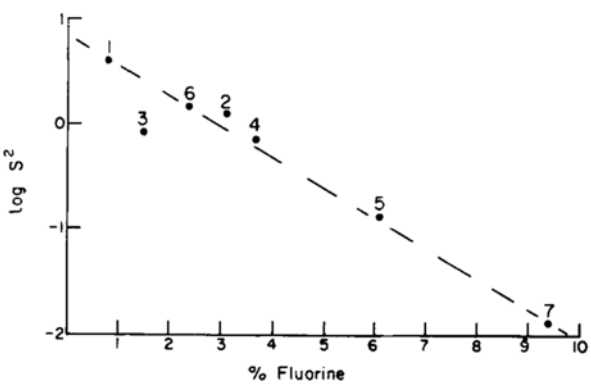


Fig. 5. Relationship between fluorine content of trioctahedral micas and log S^2. Values of S are derived from the slopes of the straight line portions of Figs. 4a and 4b. The numbers by each point identify each sample (see Table 1).

Alteration of the physical structure of the mica

When potassium is replaced within the mica structure by the larger dodecylammonium cation the basal spacing increases. In the presence of excess alkylammonium solution the micas usually expand to give an 001 spacing near 36 Å. For the trioctahedral micas the 36 Å phase was noticed after contact periods of a few minutes, the intensity of the low angle peak and 3 or 4 higher orders increasing with time as the intensity of the original 10 Å peak decreased.

Figure 6 shows the X-ray tracing of a sample of Harts Range biotite which has had approximately 40 per cent of the potassium displaced. The residual 10 Å mica peak could be detected until 90–95 per cent of the original potassium had been removed from the sample.

DISCUSSION

Potassium displacement as a function of time

By observing the inward movement of the replacement front in a single mica crystal, Rausell-Colom *et al.* (1964) showed that a linear relation existed between distance and $t^{1/2}$. From this they concluded that the rate of potassium displacement by strontium and other inorganic ions was a diffusion controlled process, the region of diffusion being between the mica sheets.

For the small particles used in the present study it was not possible to make direct observation of a single particle to assess the movement of a boundary. The results for the DA^+ system are

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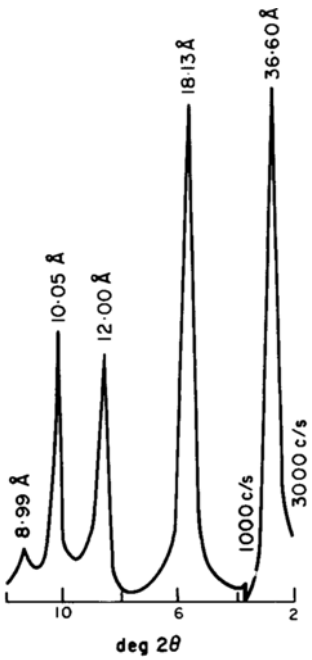


Fig. 6. X-ray diffraction tracing of a sample of biotite (Harts Range) from which 40 per cent of the potassium had been displaced by DAC.

shown as the amount of K^+ in solution in contact with known amounts of samples as a function of time, since the concentration of K^+ in solution is related to the extent to which the displacement reaction has proceeded. A generalized curve relating $t^{1/2}$ with concentration can be calculated for an idealized particle of regular shape if the following simplifying assumptions are made:

(1) a linear relationship is maintained between $t^{1/2}$ and the distance moved by the replacement front;
(2) the displacement front moves progressively inward from the periphery towards the centre of the particle with no preferred axis;
(3) all the potassium displaced from the outer altered material appears in the solution; and
(4) there is no inhibition of release by the K^+ in solution.

The resultant curve is given in Fig. 7, the absolute units of $t^{1/2}$ depending on the particle size.

Although the relation is curvilinear, a straight line can be fitted to the data up to approximately 50 per cent K displacement with an error of only a few per cent. The fact that the experimentally determined displacement of potassium by DAC conforms in shape to the general curve of Fig. 7 and is directly proportional to $t^{1/2}$ over a wide range indicates that the diffusion of potassium ions away

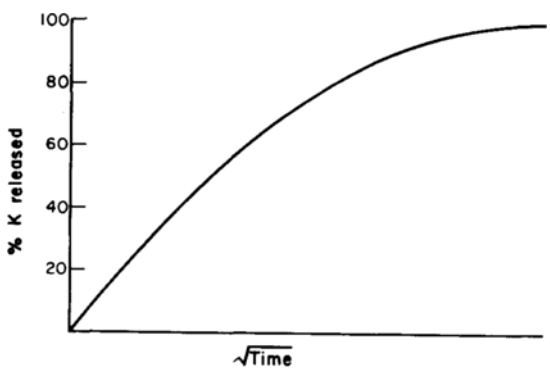


Fig. 7. Theoretical curve showing the displacement of potassium by DAC from an ideal regular particle of mica as a function of time.

from the interface between the original and expanded phases of the crystal is likely to be the rate controlling step.

The displacement mechanism

If the displacement of potassium is considered to be a simple exchange process represented by

$$\text{K-mica} + DA^+ \rightleftharpoons \text{DA-mica} + K^+$$

equilibrium may be expected at some ratio of DA^+ to K^+ in the external solution. The data of Fig. 3 tend to confirm this. For different suspension concentrations (1·0 or 0·34%) potassium displacement ceased at comparable concentrations of K^+ in solution (approximately 290 μg K/l) although the extent of depletion of the solid phase differed considerably (35% and 90% resp.). The rate of displacement was also increased by increasing the initial concentration of DA^+ (Fig. 2) although increases beyond 0·025N had little effect. This suggests that at or above this concentration, the rate controlling steps occur within the mica structure and not at the edge of the crystal.

When structural K^+ is replaced by DA^+ the 001 spacing increases to approximately 36 Å. A diagramatic representation of the possible configuration of the alkyl chains within each interlayer after the exchange process has occurred is given in Fig. 8. The concentration of "free" K^+ ions near the expanded interface is high (approaching 1·4N in Zone 4). A large concentration difference thus exists between the exchange site and the external solution and the K^+ tends to diffuse away from the exchange site and accumulate in the external solution. Since release of K^+ ceases when a "critical" level of K^+ is reached in the external solution, irrespective of the degree of depletion achieved, it is suggested that the K^+ concentration

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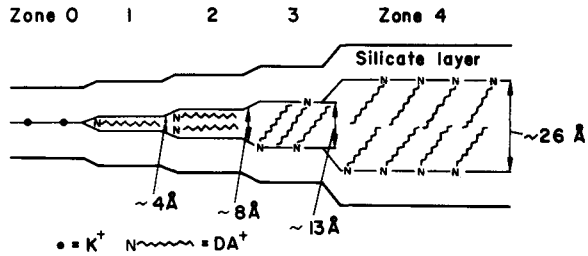


Fig. 8. Diagramatic representation of the changes which occur within each interlayer of a mica as potassium is displaced by DAC.

at or near the exchange site must be reduced to this critical level before further exchange and expansion can occur. The displacement of K^+ can then be considered as a spasmodic process, successive exchanges occurring after a time delay influenced by,

(1) the "critical" concentration to be reached and
(2) the rate of decline in concentration at the interface.

The latter condition will depend on the diffusion coefficient of the K^+ within the expanded phase. For all samples the (001) spacing of the DA^+-mica was approximately 36 Å, so it seems reasonable to suggest that the environment within the expanded phase is constant and that the diffusion coefficient of K^+ within the 26 Å channel of the expanded interlayer will also be constant for all types of mica.

Figures 4a–d show that the pattern of K^+ release as a function of time varies widely, being influenced by mineral type, i.e. reflecting differences in chemical composition. The "critical" concentration also varied widely, e.g. 290 p.p.m. for the Hart's Range biotite to less than 3 p.p.m. for the Hart's Range muscovite and even lower for the lepidolites. The data of Rausell-Colom *et al.* (1964) show differences in the critical concentration between different micas and also between different cations for the one mica sample. Newman (1969) showed that for exchange of K^+ by Na^+ in the expanded phase the exchange parameter differed widely for different micas. These data are all consistent with the idea that the "critical" concentration controls the pattern of K^+ release.

If the diffusion coefficient of K^+ within the expanded interlayer is constant for all micas then the slope of the plot of release against $t^{1/2}$ as reported here or distance against $t^{1/2}$ as reported by Rausell-Colom *et al.* (1962) must be interpreted as an "apparent" diffusion coefficient which is controlled by the "critical" concentration applicable to each sample or system.

Mathematical implications

The liberation of K^+ as a result of exchange can be regarded mathematically as an instantaneous source of K^+ deposited at the interface between the original and expanded phases. The concentration distribution away from the site of release can be calculated for any time (see for example Barrer, 1951 or Crank, 1956). The total amount of potassium released into the solution can also be calculated. However each successive exchange shifts the position of the interface, so a full mathematical solution should consider a spasmodic series of instantaneous sources coupled with a moving boundary. A rigorous solution to this problem has not yet been attempted.

Influence of chemical composition of sample

Although there is a great difference in the ease with which the dioctahedral and trioctahedral micas release their potassium, there are also differences within each of these groups.

For the trioctahedral micas used in this study, Fig. 5 gives the relation which was found between fluorine content and S^2 where S is the slope of the straight lines fitted to the data of Figs. 4a and b. The parameter S^2 is used here as a measure of the apparent diffusion coefficient D. Since the slope of the distance vs. $t^{1/2}$ plot used by Rausell-Colom *et al.* (1964) is equal to $D^{1/2}$, the slope of the graph of displacement vs. $t^{1/2}$ should also be related to D. In fitting the straight lines, the rapid reaction which occurs at small values of t was avoided since this may be influenced by rapid non-diffusive displacement of K from external surfaces or to complete displacement from the smaller particles adhering to the surface of the larger crystals. For all samples except the lepidomelane a straight line could be fitted to an appreciable portion of the data in Figs. 4a and b. For the lepidomelane the data is completely curvilinear and the average slope for the range of K depletion from 25–50 per cent was used.

Figure 5 shows that for the trioctahedral micas at least, there is a significant dependence of S^2 and hence the apparent diffusion coefficient D on the fluorine content of the sample. Rausell-Colom *et al.* (1964) established a similar logarithmic relation between fluoride content and D for

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their biotites and phlogopites. Newman (1969) also showed a relation for his trioctahedral samples between fluoride content and the Na/K exchange properties of the expanded materials.

Although some displacement of K^+ could be effected from the dioctahedral minerals, the small amounts involved did not permit reliable estimates of S and a similar relation between fluoride and D could not be established. For these minerals, other factors in addition to fluoride content must be important and a wider range of samples will need to be examined for extended time periods and correlation of K release with various chemical or mineralogical properties will be necessary before definite conclusions can be drawn.

X-ray diffraction data

The expanded phase of all the mica materials examined gave (001) spacings near 36 Å if examined immediately after removal from the reaction mixture. Other smaller spacings could be produced by drying or washing treatments prior to X-ray examination. The 36 Å phase corresponds to a double layer of alkylammonium ions oriented with the nitrogen atom near the charge site with the alkyl chain extending away from the surface at an angle of approximately 55° (Walker, 1967). The alkyl chains from adjacent mica surfaces do not interpenetrate and the interlayer space may also contain excess salt, free amine or water.

When the concentration of salt in the external solution is low, little or no free salt or amine is present in the interlayer and varying degrees of interpenetration of opposing alkyl chains can occur. Ultimately a single layer complex with (001) spacing near 23 Å can be formed (Walker, 1967). Detailed investigation of the conditions leading to the various spacings was not attempted but the results obtained are in agreement with the data reported by Walker (1967).

For the dioctahedral micas contact periods of several days or weeks were necessary before a 36 Å phase could be detected. Occasionally peaks at approximately 18 Å could be detected during the early stages of reaction. This corresponds to Zone 2 as suggested by Jordan (1949). The 18 Å phase was not observed for the more susceptible samples since a 36 Å phase appeared within a few minutes. This rapid appearance of the 36 Å phase with an integral sequence of higher order reflections combined with the persistence of the original 10 Å peak as shown in Fig. 6 suggests that potassium is displaced from the trioctahedral micas by edge weathering and not interstratification. This has been noted also by Rausell-Colom *et al.* (1964) and Scott (1968).

For the trioctahedral samples the extent of the intermediate stages between 10 Å and 36 Å as suggested in Fig. 8 must be limited and no conclusive evidence for their existence could be found by X-ray diffraction studies. From a consideration of the charge density of the mica minerals and the space available between charged sites it would seem that the single-layer "flat" orientation of the alkyl chains (Zone 1) is unlikely to persist except possibly at the interface with the original material. The double layer (Zone 2) probably exists in a limited region as an unstable intermediate since only occasionally was this 18 Å phase observed and then only in the initial stages of expansion of the dioctahedral samples. However, in the ill-defined zone which must exist between the original mica and the fully expanded material a number of orientations may co-exist. The distance over which the lattice expansion from 10 to 36 Å occurs is not known. Such expansion must require very considerable flexing of the individual lamellae, so it is unlikely that the expansion fronts within successive interlayers will be sufficiently well aligned to allow identification of the intermediate zones unless a particular zone is extensive.

REFERENCES

Barrer, R. M. (1951) *Diffusion In and Through Solids.* 464 p. Cambridge University Press, Cambridge.

Cowan, C. T. and White, D. (1958) The mechanism of exchange reactions occurring between sodium montmorillonite and various *n*-primary aliphatic amine salts: *Trans. Faraday Soc.* **54**, 691–697.

Crank, J. (1956) *The Mathematics of Diffusion.* p. 347. Oxford University Press, Oxford.

Mackintosh, E. E. and Lewis, D. G. (1968) Displacement of potassium from micas by dodecylammonium chloride: *Intern. Soc. Soil Sci. Trans., Adelaide* **2**, 695–703.

Newman, A. C. D. (1969) Cation exchange properties of micas – I. The relation between mica composition and potassium exchange in solutions of different pH: *J. Soil Sci.* **20**, 357–373.

Ralston, A. W. and Eggenberger, D. N. (1968) Conductivities of aqueous solutions of dodecylammonium chloride: *J. Am. Chem. Soc.* 436–437.

Rausell-Colom, J. A., Sweatman, T. R., Wells, C. B. and Norrish, K. (1964) Studies in the artificial weathering of mica. *Experimental Pedology* (Edited by Hallsworth, E. G. and Crawford, D. V.) pp. 40–72.

Scott, A. D. (1968) Effect of particle size on interlayer potassium exchange in micas: *Intern. Soc. Soil Sci. Trans., Adelaide* **2**, 649–660.

Tucker, B. M. (1964) The solubility of potassium from soil illites – I. The dependence of solubility on pH: *Aust. J. Soil Res.* **2**, 56–66.

Walker, G. F. (1967) Interactions of *n*-alkylammonium ions with mica-type layer lattices: *Clays and Clay Minerals* **7**, 129–143.

Weiss, A. (1963) Organic derivatives of mica-type layer-silicates: *Angew. Chem. Intern. Ed. Engl.* **2**, 134–144.

Wells, C. B. and Norrish, K. (1968) Accelerated rates of release of interlayer potassium from micas: *Intern. Soc. Soil Sci. Trans., Adelaide* **2**, 683–694.

https://doi.org/10.1346/CCMN.1971.0190402 Published online by Cambridge University Press

Résumé – Le chlorure de dodécylammonium (DAC) est utilisé pour déplacer le potassium d'un grand nombre de minéraux de la famille des micas. Le déplacement est rapide et pratiquement complet pour les micas trioctaédriques même en solution diluée (DAC 0,02 N), pour des suspensions de faible concentration. L'augmentation de la concentration de la suspension ou de la concentration en potassium de la solution d'extraction diminue la quantité de potassium qui peut etre déplacé avant que l'équilibre ne soit atteint. Dans des conditions normalisées de température et de concentration de la suspension, la vitesse de déplacement du potassium augmente quand la taille des particules diminue; toutefois, le déplacement complet est plus difficile à atteindre pour les fractions les plus fines ($< 2\mu$) que pour les particules plus grossières.

On a montré que les échantillons trioctaédriques sont plus sensibles à l'appauvissement en potassium par le DAC, que les matériaux dioctaédriques. A l'intérieur de la gamme d'échantillons trioctaédriques étudiés, on a trouvé que la vitesse de réaction est étroitement reliée à la teneur en fluor de l'échantillon. Les résultats obtenus pour les spécimens dioctaédriques les plus résistants ne sont pas suffisamment détaillés pour permettre d'établir une relation analogue.

Kurzreferat – Dodecylammoniumchlorid (DAC) wird als Reagens verwendet um Kalium aus einem weiten Bereich von Glimmermineralien zu verdränden. Die Verdrängung ist schnell und im wesentlichen vollständig für trioktaedrische Glimmer, sogar in verdünnten Lösungen (0,02 N DAC) bei niedrigen Suspensionskonzentrationen. Bei Zunahme der Suspensionskonzentration, oder der Konzentration von Kalium in der Extrahierlösung, verringerte sich das Ausmass in dem Kalium verdrängt werden konnte ehe sich Gleichgewicht einstellte. Unter Normalbedingungen von Temperatur und Suspensionskonzentration, nahm die Geschwindigkeit der Kaliumverdrängung mit abnehmender Teilchengrösse zu, obwohl vollständige Verdängung für die feinste Fraktion ($< 2\mu$) schwieriger erreichbar war als für die gröberen Teilchen.

Es wurde gezeigt, dass die trioktaedrischen Proben dem Kaliumentzug durch DAC gegenüber mehr anfällig waren als das dioktaedrische Material. Innerhalb des Bereichs der trioktaedrischen Proben wurde festgestellt, dass die Reaktionsrate in engem Zusammenhang mit dem Fluorgehalt der Probe stand. Die für die widerstandsfähigeren dioktaedrischen Proben erhaltenen Daten waren nicht detailliert genug um feststellen zu können ob eine ähnliche Beziehung besteht.

Резюме — Додециламмонийхлорид (Д.А.Х.) использовался в качестве реагента для удаления К из различных слюдоподобных минералов. Удаление К из триоктаэдрических слюд протекало быстро и почти полностью даже при применении разбавленных растворов (0,02 N Д.А.Х.) при низких концентрациях суспензии. Увеличение ее концентрации или концентрации К в экстрагирующем растворе уменьшало удаление К до достижения равновесия. При стандартных условиях температуры и концентрации суспензии скорость удаления К возрастала с уменьшением размеров частиц, хотя для наиболее тонких фракций ($<2\mu$) полное удаление К достигалосб труднее, чем для более грубых фракций.

Показано, что триоктаэдрические слюды более чувствительны к удалению К с помощью Д.А.Х., чем диоктаэдрические. Найдено, что у исследованных триоктаэдрических слюд скорость реакции тесно связана с содержанием фтора. Данные, полученные для более устойчивых диоктаэдрических слюд, недостаточны для выяснения аналогичных закономерностей.

https://doi.org/10.1346/CCMN.1971.0190402 Published online by Cambridge University Press