

# EXTRACTION OF INTERLAYER K FROM PHLOGOPITE SPECIFIC EFFECTS OF CATIONS ROLE OF Na AND H CONCENTRATIONS IN EXTRACTION SOLUTIONS

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**Abstract**—The accurate optical observation of alteration fringes developing in phlogopite flakes, shows that the morphology of the fringes is specific for some cations, such as Na, Mg and Ca, replacing K.

A careful chemical study of the exchange kinetics of interlayer K shows that, beside the classical effect of blocking the exchange reaction with cations such as K, Rb, Cs,  $\text{NH}_4$ , it is possible to induce an increase of the rate of K exchange when adding to a concentrated solution of one cation, a very small amount of other cation such as Na or H. The effects of mixtures such as Ca-Na and Ca-H are reported here in detail. Attention is drawn to the decisive part played by the impurities which may be contained in the reagents used.

## INTRODUCTION

THE OPTICAL observations of the progress of the diffusion boundary on the mica flakes, and the kinetic studies of the removal of interlayer K, which have been reported in various work, give some information on the exchange process of K.

The amounts of extracted K and the distance of boundary may generally be linearly related to the square root of time of treatment, and suggests that this exchange is a diffusion-controlled process (Reed and Scott, 1962; Raussell-Colom *et al.* 1965; Rousseau, 1966; Quirk and Chute, 1967; Barbaro, 1968), although, as shown by Wells and Norrish (1968) the exponent attributed to time in the relations between the distance of penetration of the alteration fringe and time, may differ from 0.5.

The release of K may produce a decrease of the layer charge (Raussell-Colom 1965; Robert 1968) or not (Scott and Reed 1966; Reichenbach and Rich, 1968) according to the composition of the mica and the nature of the reagents used. Cations such as K, Cs, Rb,  $\text{NH}_4$  present in small amounts in the treatment solutions may have a blocking effect on K replacement (Raussell-Colom, 1965; Scott and Smith, 1966; Wells and Norrish, 1968).

The effect of pH has led to conclusions which are sometimes contradictory. Indeed, for some authors (Marshall and Dowell, 1965; Hossner, 1966; Smith and Scott, 1966; Chute and Quirk, 1967) the pH, over a large range, produces no observable change in the release of potassium by salt solutions. For others (Rich, 1964; Tucker (I), 1964) the potassium replacement is affected by pH variations. Lastly recent work by Newman (1969) shows that the effect of pH is more or less

effective according to the nature of the mica samples.

In this paper an accurate optical method is reported and new information concerning the special part played by certain cations added in small amounts to concentrated salt solutions, clear up some details of K depletion.

## MATERIALS AND METHODS

**Materials.** Three specimens of phlogopite were used in the present work. Chemical analyses of these micas are given in Table 1.

**Optical study.** Simultaneously to the replacement of K by another cation, hydration of the mineral occurs. This effect is followed by the formation of an alteration fringe on the mica flakes, originating in natural or artificial defects.

Table 1. Chemical analyses of phlogopites

	A	B	C
SiO <sub>2</sub>	39.80	39.08	39.80
Al <sub>2</sub> O <sub>3</sub>	20.00	24.90	23.00
TiO <sub>2</sub>	0.84	1.10	0.70
FeO	3.60	4.50	2.80
MgO	21.05	20.50	22.00
K <sub>2</sub> O	9.30	9.00	9.00
Na <sub>2</sub> O	0.50	0.30	0.50
F	0.66	0.70	2.14
Ignition loss	3.67	3.50	1.96

A—Phlogopite, Madagascar.

B—Phlogopite from Boubée, Paris.

C—Phlogopite, Madagascar.

Thin mica flakes of about  $10 \times 10$  mm and approximately 0.2 mm thick were used. Sharp and straight but not very deep cuts were drawn on the flakes with razor blades. Each of these samples was treated, at determined temperature, with 400 ml of concentrated salt solutions (2 N). In such conditions, since the contact times between samples and salt solutions were relatively short, there were no K blocking effects. The formation and movement of the alteration fringe were observed in optical microscopy. The use of phase contrast and coloured light (generally green), resulted in a very contrasting image, on which the alteration fringes, and in particular the edges, were well defined. As a result the distance measurements were accurate, the morphological observations easy, and the photographs distinct. We will see later that specific effects of cations can be detected by this method.

*Chemical study.* In order to achieve a more complete study, optical experiments were followed by the chemical determination of the exchange kinetics of interlayer K.

The phlogopite samples were crushed to pass through a 0.2 mm sieve. Samples of 40 or 50 mg of mica were shaken in 400 ml of nitrate or chloride solutions, at temperatures between 40–98°C. In order to prevent any contamination of the solutions by impurities, such as Na or K, each piece of the alteration set which was in contact with the solutions in containers was made of polyethylene.

The reagents were obtained from high purity salts. At determined intervals of time, samples of 10 ml were pipetted from the solution and renewed by an equal amount of the original solution. A quantitative determination of K, by using a flame photometer, and of Mg, by using atomic absorption, was then carried out.

## RESULTS AND DISCUSSION

### *Optical observations*

*Specificity of cations.* Variations of the movement rate of the diffusion boundary, according to the nature of cations (Raussell-Colom *et al.*, 1965) and of anions (Rousseau, 1966; Wells and Norrish, 1968) have already been shown by different authors.

Owing to the optical method used we were able to find that the alteration fringes shows a morphological aspect specific to the cation which replaces the interlayer K, but unaffected by the anion used in the related experiments.

These specific effects were observed in an identical way on the three phlogopite samples studied. They were completely reproducible. The distinctive features pointed out for these fringes were

particularly clear in the initial phase, but they were also easily seen for fringes of about  $50 \mu$  in width. They were difficult to observe when the whole flake was altered.

We selected here as examples the cases of Na, Mg and Ca. The photographs presented were obtained with the A sample.

*K–Na exchange.* The diffusion boundary develops continuously along the cut-edges. It moves parallelly to the cut with a great regularity as a function of time (Fig. 1).

*K–Mg exchange.* The formation of a continuous boundary, parallel to the initial cut can also be observed. Moreover some cracks, perpendicular to the boundary appear, and constitute, in their turn, the starting of other areas of the diffusion process (Fig. 2). These cracks appeared in a systematic way along the diffusion front. They are highly characteristic of the K–Mg exchange since they had never been observed in the two other cases presented.

*K–Ca exchange.* In this case the straight diffusion boundary does not appear and the exchange process develops as it would start from discrete points along the cut. This fact gives rise to the development of nearly circular alteration areas, which partially overlap (Fig. 3).

### *Effects of "impurity" cations in the extraction solutions*

In the reagents used, one of the cations had a constant and high concentration (2 N) to which was added a second cation at a lower concentration varying from  $10^{-4}$  N to 0.2 N.

It is well known that small amounts of cations such as K, Cs,  $\text{NH}_4$  often inhibit the release of interlayer K. However we now show that it is possible, in an opposite way, to increase the progression rate of the diffusion boundary when adding to concentrated salt solutions, very small amounts of other cations such as Na or H.

The effects of adding Na to Ca, Mg and Li solutions, and H to Ca, Na, Li solutions were determined. Only the results for the two contrasting Ca–Na and Ca–H systems are reported, since the addition of Na to Mg and Li solutions and of H to Na and Li solutions yielded comparable results. Considering the special part played by protons, the behaviours of the two groups were different. As a matter of fact, protons, when too concentrated, dissolved the mica.

Addition of Ca to concentrated solutions of Na and Mg were also studied, but an increase in the progression rate of the alteration fringe was not observed.

*Ca–Na pair.* The progression rate of the diffusion boundary increased significantly when small

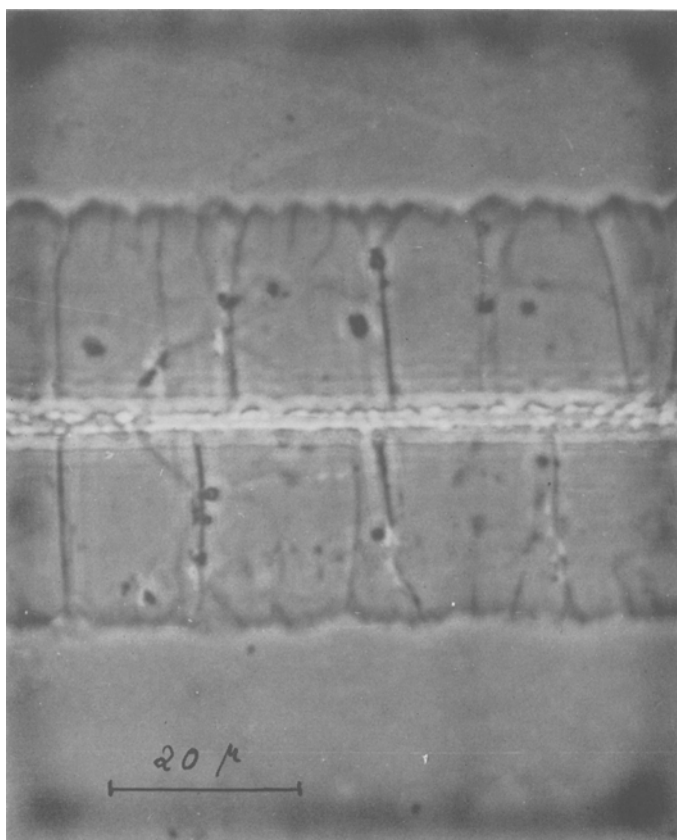


Fig. 1. Fringe of diffusion from the cut edges of a phlogopite flake.  
Treatment: 2 N  $\text{NaNO}_3$ , for 6 hr at  $70^\circ\text{C}$ .

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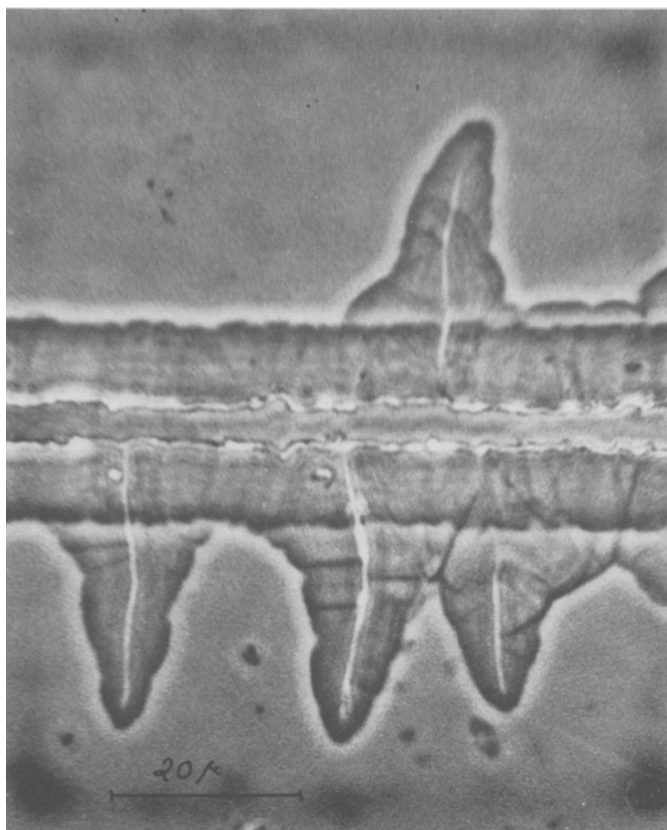


Fig. 2. Fringe of diffusion from the cut edges of a phlogopite flake.  
Treatment: 2 N  $\text{Mg}(\text{NO}_3)_2$ , for 6 hr at 70°C.

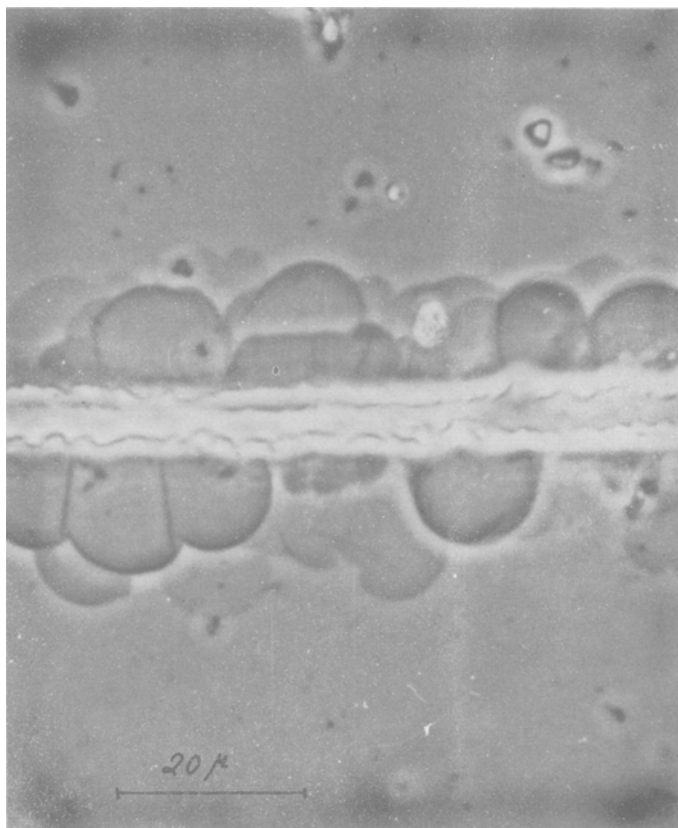


Fig. 3. Fringe of diffusion from the cut edges of a phlogopite flake.  
Treatment: 2 N  $\text{Ca}(\text{NO}_3)_2$ , for 8 hr at 70°C.

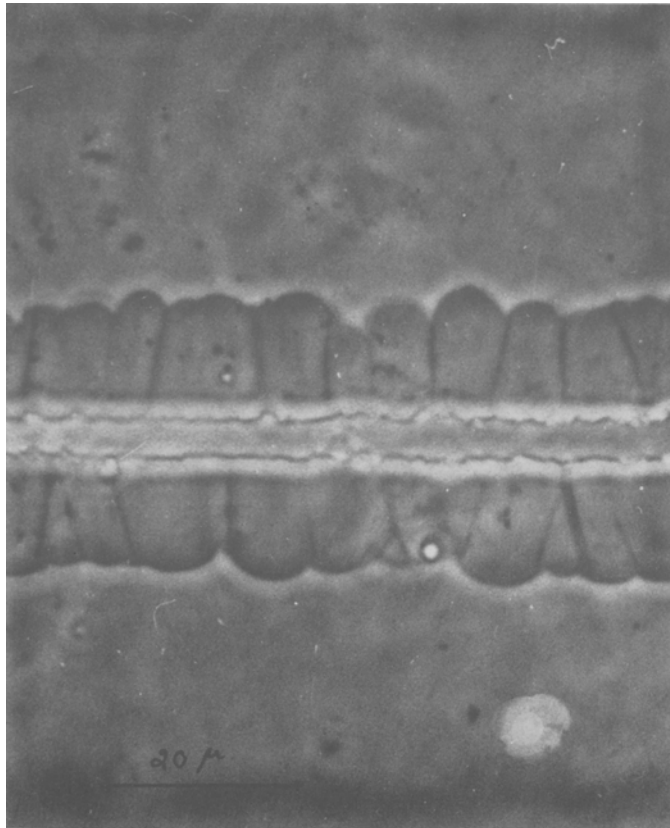
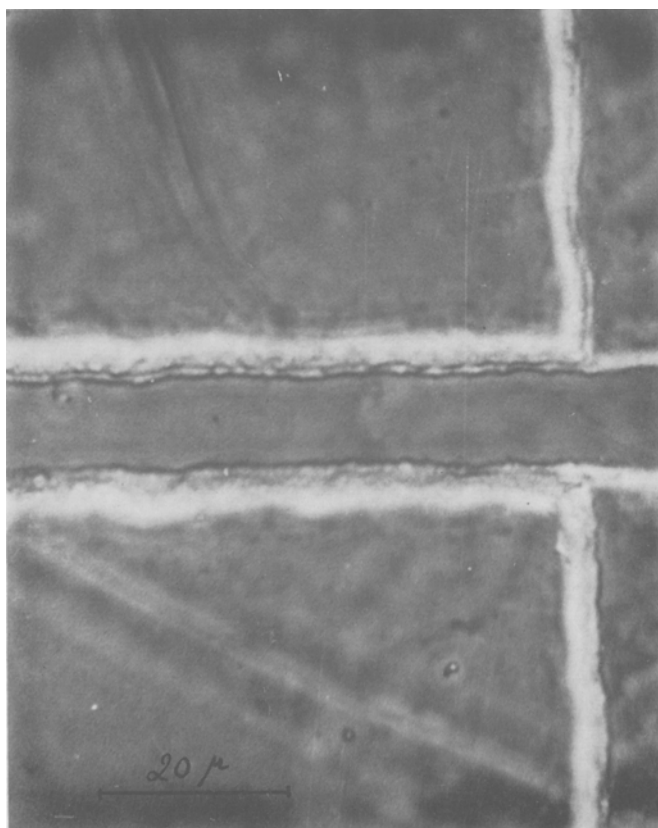


Fig. 4. Fringe of diffusion from the cut edges of a phlogopite flake.  
Treatment: 2 N  $\text{Ca}(\text{NO}_3)_2$  + 0.02 N  $\text{NaNO}_3$  mixture, for 6 hr at 70°C.



**Fig. 5.** Broadening of the initial cut by a dissolution band. Treatment: 0.05 N  $\text{HNO}_3$ , for 2 hr at  $70^\circ\text{C}$ .

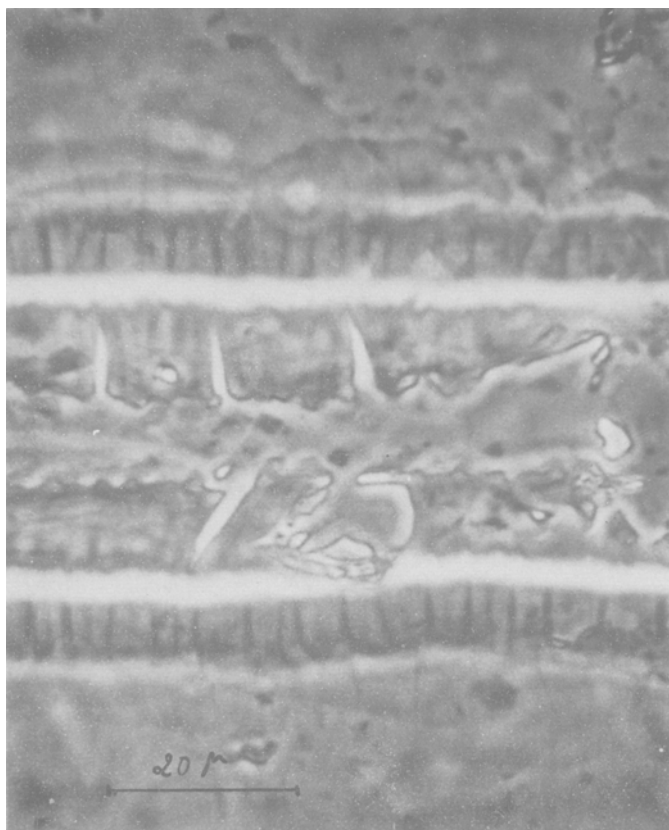


Fig. 6. Narrow fringe of diffusion in front of the dissolution band. Treatment: 2 N  $\text{Ca}(\text{NO}_3)_2$  + 0.05 N  $\text{HNO}_3$  mixture, for 2 hr at 70°C.



amounts of Na, about  $10^{-3}$  N, were added to a 2 N  $\text{Ca}(\text{NO}_3)_2$  solution. The alteration fringe kept the specific morphological aspect of the K-Ca exchange, but developed more regularly than in the case of a pure calcium nitrate solution (Fig. 4).

**Ca-H pair.** With the experimental procedure used, the phlogopite samples treated with a pure nitric acid solution of about  $10^{-4}$  N, did not show any evidence of alteration. But the same acid concentration in a 2 N  $\text{Ca}(\text{NO}_3)_2$  solution caused, as observed with Na, an increase in the progression rate of the boundary line.

When the nitric acid concentration reaches 0.005 N in a pure solution, the mica was attacked. Optically a broadening of the initial cut was observed, without any formation of an alteration fringe (Fig. 5). The same acid concentration in a 2 N  $\text{Ca}(\text{NO}_3)_2$  solution strongly increased the dissolution of the mica and a narrow alteration fringe could be observed near the edges of the boundary line (Fig. 6).

**Discussion.** Three conclusions are drawn from the results reported here:

(1) The differences which appears in the progression rate and the morphology of the diffusion boundaries, according to the nature of the cations studied here, should express the features of exchange.

The progress of the diffusion boundary is related to the diffusion process of the ions in the interlayer space, and therefore, to the interaction between the layer charge and the charge of the cation which replaces K. The cations in the interlayer space tend to rehydrate, and as a result, the hydration processes which take place in this exchange and vary with the nature of the cation, are likely to be responsible for the stress exerted on the crystalline layers. This stress produces wrinkles and splits giving a characteristic aspect to the alteration fringe and controls the stability of the altered phase.

(2) As far as the release of K by means of biionic solutions is concerned, the role of Na and H ions at very low concentration, is to initiate the exchange reaction either through an increase of the number of reaction places where the substitution of K-Ca becomes effective, or through a catalytic effect, or even by improving the hydration process of the mineral. The two latter cases would in fact express a lowering of the potential barriers which the Ca ions must necessarily pass to replace K. This suggests, as it will be seen in the final discussion, a two-step process in which for instance a Ca-Na exchange follows a prior Na-K exchange.

When the H concentration increases, exchange and dissolution of the lattice occur simultaneously. These observations confirm the statements of

Wells and Norrish (1968), who attribute two roles to the protons.

On the one hand, they have an effect similar to that of other cations which are likely to replace K. On the other hand, they may dissolve mica.

(3) Considering the fact that, for instance, an addition of Ca to a concentrated Na solution did not increase the rate progression of the diffusion boundary, the observed features are characteristic of the added ions, and should not be, in fact, attributed to the biionic nature of the solution. These features were only effective when the "impurity" cations were more efficient in the K extraction than the major cations of the solutions.

#### *Chemical study of the role of Na and H concentrations in extraction solutions*

The chemical study confirms the role of Na and H ions in the exchange of interlayer K, as shown by optical observations. The results presented here are those obtained with the A phlogopite sample.

**Ca-Na pair.** The amounts of extracted K have been determined in two cases (Fig. 7). Firstly, the phlogopite samples were treated with salt solutions of 2 N  $\text{Ca}(\text{NO}_3)_2$  to which amounts of  $\text{NaNO}_3$  were added in order to obtain Na normality from  $10^{-2}$  to 0.2. Secondly, the samples were treated with pure salt solution of  $\text{NaNO}_3$  with the same normalities as in the latter mixtures.

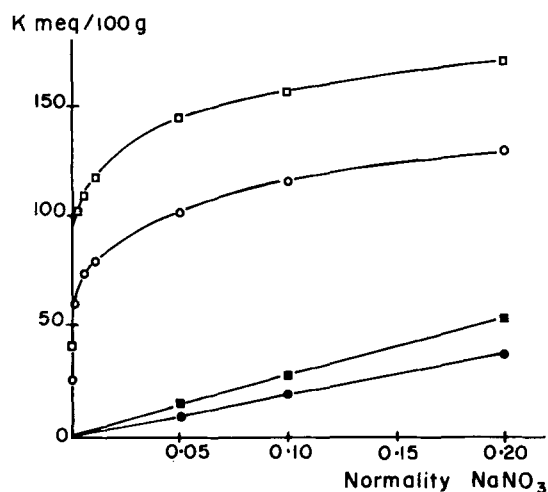


Fig. 7. Amounts of K released from < 0.2 mm phlogopite treated with  $\text{NaNO}_3$  solutions of various normalities. In pure solutions, after 2 hr ●; and after 6 hr ■ at  $70^\circ\text{C}$ . In mixtures with 2 N  $\text{Ca}(\text{NO}_3)_2$ , after 2 hr ○; and after 6 hr □ at  $70^\circ\text{C}$ .

Table 2 shows the results obtained at two temperatures with various normalities of  $\text{NaNO}_3$ , in pure solution and in  $2\text{N Ca(NO}_3)_2$  solution. The amounts of extracted K have been obtained after shaking the samples for a period of 2 hr in the solution.

It can be seen from Table 2 that a  $10^{-3}$  normality in Na, which is equivalent to a percentage of about 0.01 in the Ca salt used, may strongly increase the amount of extracted K, as compared to the pure  $\text{Ca(NO}_3)_2$  solution. The lower the temperature, the higher the effect. On the other hand, the pure  $10^{-3}\text{N NaNO}_3$  solution causes no extraction of the interlayer K.

**Ca-H pair.** The procedure was the same as with Ca-Na pair, but, as already mentioned, the H ion may have two roles according to the concentration. In order to clarify this process, the extracted amounts of interlayer K and of octahedral cations, that is Mg in the case of phlogopite, were simultaneously determined. This determination was performed for the Ca-H mixture and for the pure nitric acid solution with the same normalities as in the mixtures.

**Release of structural Mg.** Figure 8 shows that in the case of normality below 0.0025 N, the structure is only very slightly attacked. Above this value, the amounts of extracted Mg increase quickly. Moreover it can be seen that the lattice is more strongly attacked in the case of the mixture than in the pure nitric acid solution, the H concentrations being the same.

**Release of interlayer K.** As has been optically

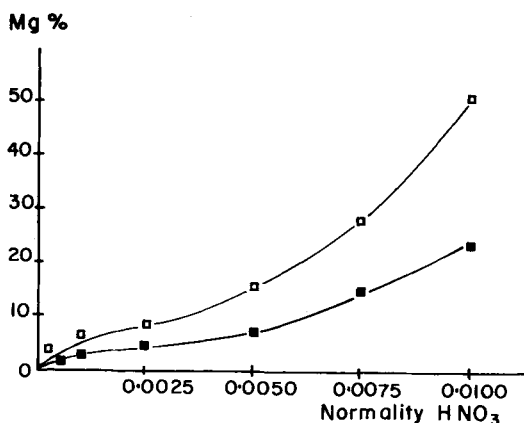


Fig. 8. Percentage of lattice Mg of  $<0.2\text{ mm}$  phlogopite extracted with  $\text{HNO}_3$  solutions of various normalities. In pure solutions, after 6 hr at  $70^\circ\text{C}$  ■. In mixtures with  $2\text{N Ca(NO}_3)_2$  after 6 hr at  $70^\circ\text{C}$  □

observed, an H normality of  $2 \cdot 10^{-4}\text{ N}$ , for instance does not dissolve the phlogopite lattice, but strongly increases the replacement rate of K by Ca. Thus a difference of about 45 m-equiv. appears after 2 hr of treatment at  $70^\circ\text{C}$ , and a difference of about 65 m-equiv. after 6 hr at the same temperature, as compared to the pure  $\text{Ca(NO}_3)_2$  solution (Fig. 9). The effect reported here is strictly equivalent to that observed with Na since the  $2 \cdot 10^{-4}\text{ N HNO}_3$  pure solution does not involve any K extraction under the same conditions.

With acid normality above 0.0025 N, the process

Table 2. Amounts of K extracted with mixtures of  $2\text{N Ca(NO}_3)_2$  solution to which various amounts of  $\text{NaNO}_3$  are added

	Na normality contained in the $2\text{N Ca(NO}_3)_2$ solution								
	0	$10^{-3}$	$5 \cdot 10^{-3}$	$10^{-2}$	$0.5 \cdot 10^{-1}$	$10^{-1}$	$2 \cdot 10^{-1}$		
$\text{K}_{\text{Ca} + \text{Na}}$ in	meq/100 g	70°C	25	61	72	78	103	115	129
		90°C	128	140	150	167	195	198	198
$\text{K}_{\text{Ca} + \text{Na}} - \text{K}_{\text{Ca}}$	in meq/100 g	70°C		36	47	53	78	90	104
		90°C		12	22	39	67	70	70
$\text{K}_{\text{Na}}$ in	meq/100 g	70°C				2	9	19	38
		90°C				4	12	25	45

$\text{K}_{\text{Ca} + \text{Na}}$  = amounts of K extracted with the Ca-Na mixtures.

$\text{K}_{\text{Ca} + \text{Na}} - \text{K}_{\text{Ca}}$  = difference between the amounts of K extracted with the mixture, and the amounts extracted with the pure solution of  $2\text{N Ca(NO}_3)_2$ .

$\text{K}_{\text{Na}}$  = amounts of K extracted by the pure solutions of  $\text{NaNO}_3$ .

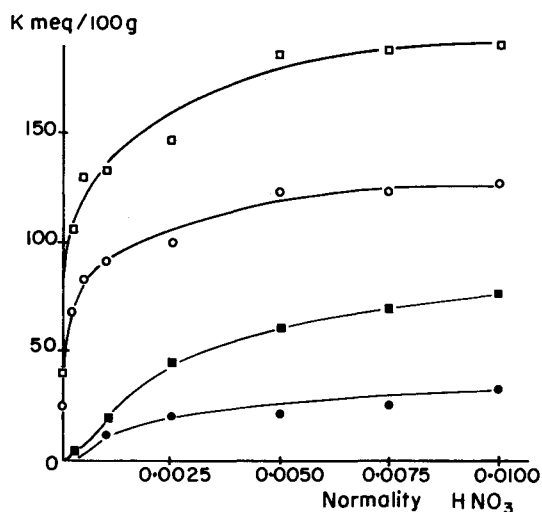


Fig. 9. Amounts of K released from < 0.2 mm phlogopite treated with HNO<sub>3</sub> solutions of various normalities. In pure solutions, after 2 hr ●; and after 6 hr ■, at 70°C. In mixtures with 2 N Ca(NO<sub>3</sub>)<sub>2</sub>, after 2 hr ○; and after 6 hr □ at 70°C.

is more complicated because of the dissolution of the lattice, but the K depletion develops regularly.

**Discussion.** The results reported here show that one of the cations present at a very low concentration in a biionic solution, may increase the replacement rate of K in a mica such as phlogopite. As it can be seen from Figs. 7 and 9 and Table 2, it is not merely an additive effect, in which the role of one cation would be summed up with that of the other. Such increasing of K exchange has also been observed by Rich (1964) in soil samples treated with Mg-NH<sub>4</sub> mixtures.

As the incorporation of a second cation of low normality does not notably disturb the chemical properties of a concentrated solution of a given cation, a special reaction process participating in K replacement must take place. The optical observations show that the replacement of K by Na does not involve any special exchange area. As a matter of fact, the exchange occurs continuously along the replacement front in contact with the solution. In the case of Ca, on the contrary, the exchange starts only in limited areas. The replacement may therefore be performed in two stages. At a first stage the more active of the two cations would replace preferentially the interlayer K. At a second stage this cation would in his turn be replaced easily by the less active cation, because of the changes in the physical and chemical properties of the solid phase following the first replacement. The more active cation would then be

able to participate in a new cycle. After the samples have been treated with Ca-Na and Ca-H mixtures, it can be established indeed, that K of the phlogopite sample is completely replaced by Ca.

In view of the cationic charges, the exchange of the interlayer K makes necessary the replacement of two K in the case of one Ca, but of one K in the case of one Na. The required energy by cation is then logically lower in the second case. Consequently, the Na-K exchange which requires this lower energy occurs first. On the other hand the K replacement is accompanied by an hydration which produces an increase of the interlayer distance. This increase corresponds to the formation of a double water layer hydrate, which is easily detected by X-ray diffraction. But in the case of layer silicates the hydration states are more stable with divalent cations, such as Mg or Ca, than with monovalent cation such as Na (Thompson *et al.* 1967, Chaussidon, 1969). In consequence the Ca-Na exchange which follows the prior K-Na exchange corresponds to an increasing stability of the hydrated state. This fact suggests that the Na should be liberated and may then participate in a new exchange cycle. The observed features may therefore be closely linked to the water layers structures.

We have also shown that with normalities below 0.0025 N, the H ions could replace the interlayer K, just as Na would have done, and in this case the increase of K extraction was not due to the attack of the structure. This mechanism is in agreement with that proposed by Tucker (1964 and 1967) for the K-Ca exchange in soil illites, suggesting that the displacement of K by Ca was subject to a prior replacement by hydrogen ions. With higher normality H dissolves the octahedral layer of the lattice, and this attack is enhanced by the release of K. The incorporation in the acid treatment solution of a highly-concentrated cation likely to replace K, increases therefore the dissolution of the mica. Since protons favour this replacement, they really play a double role. The dissolution of the structure may produce some modifications of the exchange kinetics of K as it can be seen by a comparison of curves 7 and 9.

There is a very regular distribution of the points along curve 7, relative to Ca-Na mixtures, contrary to curve 9, relative to Ca-H mixtures, where the points corresponding to 0.0025 N HNO<sub>3</sub> are significantly under the curve; this is precisely the normality about which the attack of the structure began. Some points here will need further study, but they may account for the difficulties which have been met with in explaining the effect of pH on the interlayer K replacement.

## CONCLUSION

The results reported here draw attention to the difficulties which arise in interpreting the exchange kinetics of the interlayer K of layer silicates, owing to the decisive part played by the impurities contained in the reagents used. However the present study is also meant to clarify the role of the protonic concentration of the treatment solutions, and to show some specific aspects of the role of cations such as Na, Mg and Ca in the removal of interlayer K from phlogopite.

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**Résumé**—L'observation optique précise des franges d'altération se développant dans les paillettes de phlogopite démontre que la morphologie de ces franges est spécifique pour quelques cations, tels que Na, Mg et Ca remplaçant K.

Une minutieuse étude chimique de la cinétique d'échange de K en inter-couche montre que, à part l'effet classique de blocage de la réaction d'échange avec des cations comme K, Rb, Cs, NH<sub>4</sub>, il est possible d'induire une accélération de la vitesse d'échange de K en ajoutant à une solution concentrée d'un cation une très faible quantité d'un autre cation, par exemple Na ou H. Les effets de mélanges comme Ca–Na ou Ca–H sont reportés ici en détail. L'attention est attirée sur la part décisive jouée par les impuretés que peuvent contenir les réactifs utilisés.

**Kurzreferat**—Die genaue optische Beobachtung von Randveränderungen in Phlogopitschuppen erweist, dass die Morphologie der Ränder für manche Kationen, wie etwa Na, Mg und Ca, die das K ersetzen, kennzeichnend ist.

Eine sorgfältige chemische Untersuchung der Austauschkinetik des Zwischenschichtenkaliums zeigt, dass es möglich ist, neben der klassischen Wirkung einer Blockierung der Austauschreaktion mit Kationen wie K, Rb, Cs, NH<sub>4</sub>, durch Zugabe einer sehr kleinen Menge anderer Kationen wie Na oder H zu einer konzentrierten Lösung eines Kations eine Zunahme in der Geschwindigkeit des K Austausches herbeizuführen. Die Wirkungen von Mischungen wie Ca–Na und Ca–H werden in Detail beschrieben. Es wird auf die entscheidende Rolle aufmerksam gemacht, die durch möglicherweise in den zur Verwendung gelangenden Reagenzien anwesende Verunreinigungen gespielt wird.

**Резюме** — Прецизионное оптическое изучение каемок изменения на флогопитовых чешуйках показывает, что морфология этих каемок специфична для некоторых катионов, таких как Na, Mg и Ca, замещающих K. Тщательно выполненное химическое изучение кинетики обмена межслоевого K свидетельствует о том, что наряду с классическим эффектом блокирования обменных реакций с катионами (например, K, Rb, Cs, NH<sub>4</sub>), возможно вызвать увеличение скорости обмена K добавлением к концентрированному раствору одного катиона очень небольших количеств другого катиона (Na или H). Детально рассмотрен эффект действия смесей (Ca–Na, Ca–H). Обращено внимание на решающую роль примесей, которые могут содержаться в используемых реактивах.