Canadian Mineralogist
Vol. 12, pp. 394-398 (1974)

POTASSIUM-BARIUM EXCHANGE IN PHLOGOPITE

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ABSTRACT

The potassium of a phlogopite was partly replaced with barium. The ion exchange experiment was carried out at 40°, 60° and 80°C for a maximum of 100 hours reaction time. The apparent diffusion coefficients for the K-Ba exchange were found to be time-dependent. The apparent activation energy is 16,000 ± 1,700 cal mole^{-1}.

INTRODUCTION

It is well known from observations and experiments that during weathering, the potassium mica minerals undergo both chemical and structural transformations. The interlayer potassium of the mica is replaced by a hydrated cation and the structure of the original mineral changes to that of a vermiculite-like mineral. The ion exchange reaction is evidently a diffusion process which occurs between the mica mineral and the aqueous solution of the exchanging cation. Experiments have shown, however, that these minerals release only a small portion of their potassium, presumably because equilibrium is established between solution and mica potassium while the K^+ concentration in the solution is still very low. The equilibrium proportion of $K^{sol'n}/K^{mica}$ is the lowest for muscovite and somewhat higher for biotite and phlogopite. The ion exchange rate is also higher in biotite and phlogopite than in muscovite, as determined by Scott *et al.* (1960), Reed & Scott (1962), Thompson *et al.* (1967) and Wells & Norrish (1968).

Experiments have been carried out by a number of investigators, in which the interlayer potassium was replaced by an alkali or alkaline-earth cation. In the experiments of Barshad (1954), White (1956), DeMumbrum (1959), Newman & Brown (1966), Thompson *et al.* (1967), Reichenbach & Rich (1968) and Le Roux & Rich (1969), the mica was first saturated with a cation, and then the properties of the potassium-depleted products were studied. Raussell-Colom *et al.* (1965) on the other hand followed the progress of the ion exchange optically and measured the distance of potassium depletion on large mica flakes, using the data obtained to calculate diffusion coefficients and activation energies.

The purpose of the present study is to investigate K-Ba exchange in mica by a direct method, somewhat different from that employed by Raussell-Colom *et al.* (1965), and to provide further information on the exchange capacity of rock-forming minerals. Experiments were carried out in which the potassium of a powdered phlogopite was partly replaced with barium in aqueous solution. From the data obtained, diffusion coefficients and activation energies were calculated and analysed by the use of diffusion and rate theory.

MATERIAL AND METHODS

Material

The phlogopite was obtained from a pyroxene-phlogopite skarn of the amphibolite facies, located near Otter Lake, Western Quebec. The mineral occurred in clear, dark brown flakes, essentially free of inclusions. These flakes were treated in a ball mill for one hour. The 140-325 mesh fraction of the dry sieved powder was retained and used in the subsequent experiments.

Experimental method

Several methods may be used to exchange the interlayer potassium of phlogopite with alkali or alkaline-earth cations. To study the kinetics of the ion exchange reaction however, the boundary conditions must be clearly specified. Accordingly, the experiment was set up to have a small volume of phlogopite powder reacting with a large volume of well-stirred, concentrated (1*N*) $BaCl_2 \cdot 2H_2O$ solution. The maximum reaction time was 100 hours. The large solution volume and the relatively short reaction time ensured that the potassium concentration in the aqueous solution remained at a low level. The experiments were carried out at 40, 60 and 80°C. At regular time intervals samples were removed from the constant-temperature water bath, quenched, and separated for the subsequent *x*-ray and chemical analysis.

Analytical methods

The untreated phlogopite was analysed for total iron, magnesium, potassium and sodium, and the reaction products were analysed for potassium and barium. The samples were decomposed by the HF-$HClO_4$ method, and analysed by the standard atomic absorption technique. The analyses for the untreated phlogopite are: total iron expressed as FeO, 4.63; MgO, 24.40; K_2O 10.30 and Na_2O 0.27 wt. %

X-ray diffraction analyses of the treated and untreated phologopite were also obtained. Samples were prepared by dispersing about 20 mg of powder in 1 ml of distilled water. The dispersion was deposited on a glass slide and dried in air at room temperature. The diffraction charts were obtained by Fe/Mn $K\alpha$ radiation.

RESULTS AND DISCUSSION

The *x*-ray diffraction analysis showed that during the ion exchange process the 10 Å basal spacing of the untreated phlogopite partly expanded. At 40°C the basal spacing increased by 1Å and at 60 and 80°C by 2.3Å. This result is in close agreement with the values reported for micas by Bronson *et al.* (1959), Scott & Reed (1965), Reed & Scott (1966), Newman (1967) and Scott & Smith (1968).

The intensity of the peaks for the expanded phase was initially low, but increased as the reaction progressed. Two of the samples that were treated at 80°C, one for 10 and the other for 100 hours, were heated to 500°C in air for two hours. The *x*-ray diffraction analysis showed only a partial collapse of the expanded phase (Fig. 1).

In order to investigate the effect of the diffusion of water into the phlogopite structure, supplementary experiments were carried out using only distilled water. Sample A was treated at 80°C for 10 hours and sample B at ambient temperature for about 4 months. In both samples the basal spacing expanded by 1Å, but in sample A it was of very low intensity. In sample B the intensity increased with increasing reaction time. Next, both samples were heated to 500°C, sample A for 2 hours and sample B for periods of 2, 18 and 42 hours. In none of these samples did the structure collapse to its original position; indeed, the intensity of the peaks remained practically unchanged.

The analytical results of the ion exchange experiments are presented in Figure 2. From the chemical analysis the diffusion coefficients for the three temperatures can be calculated.

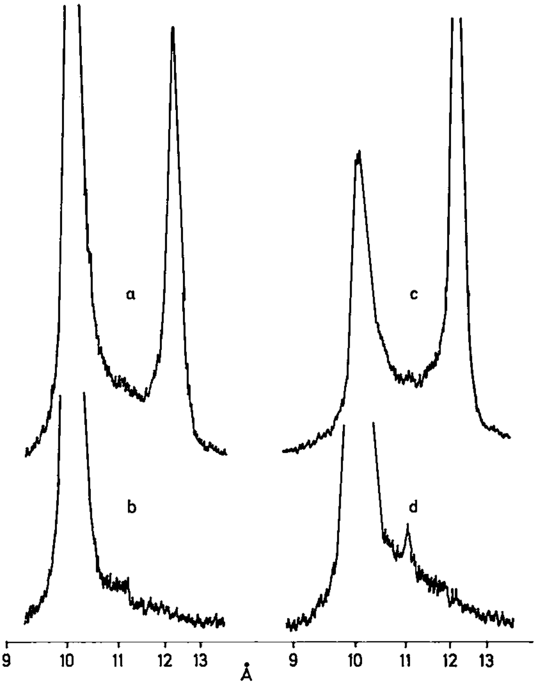

FIG. 1. *X*-ray diffraction charts of phlogopite that was treated in 1*N* $BaCl_2 \cdot 2H_2O$ solution at 80°C.
a: sample 5-80, reaction time 10 hrs;
b: " 5-80, kept at 500°C for 2 hrs;
c: " 8-80, reaction time 100 hrs;
d: " 8-80, kept at 500°C for 2 hrs.

Usually, however, in ion exchange experiments only macroscopic changes can be measured. To obtain information on the associated atomic processes, a theoretical analysis must be carried out. While this is true in principle, a full study may be, and very often is, extremely complex. Seldom does the rate-controlling mechanism consist of a single, elementary step. In general, the initial evaluation of the experimental results provides only an apparent diffusion coefficient,D_a, which is identical with the true, individual diffusion coefficient D_i only when the process is controlled by a single energy barrier.

During natural and induced weathering of the mica minerals, the interlayer potassium exchanges with a cation, and the exchange is always accompanied by the diffusion of water into the crystal structure. The water expands the basal spacing of the mica, which is a primary indication of the complex nature of the ion exchange process. Consequently, the diffusion coefficient evaluated directly from the experimental result is an apparent diffusion coefficient.

To evaluate D_a, an appropriate model must be considered. Because in phlogopite little or

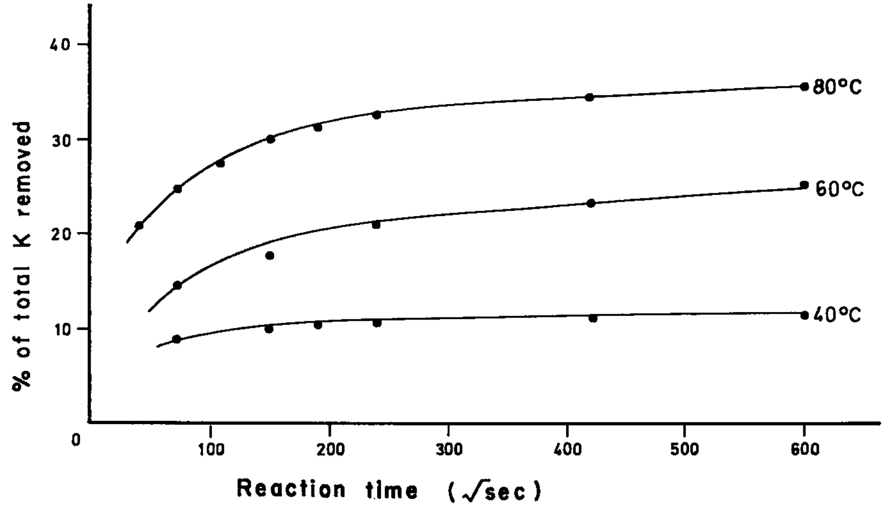

FIG. 2. Per cent of the total potassium extracted from phlogopite in 1N $BaCl_2 \cdot 2H_2O$ solutions at 40°, 60° and 80°C.

no diffusion takes place in the direction parallel to the c axis, the diffusion process is radially symmetrical (Mortland 1958, Reed & Scott 1962), and the appropriate diffusion equation is and the appropriate diffusion equation is (Crank 1956):

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r D \frac{\partial C}{\partial r}\right) \qquad (1)$$

Where $C =$ Ba concentration in the crystal, $t =$ time, and $r =$ radial coordinate. Initially the particles are free of solute, that is,

at $t = 0$ and $0 < r < a$ $C = 0$,

where a is the average particle radius. Since the initial solute concentration was high and the solution was well-stirred, the barium concentration at the surface of the particles remained constant.

Because concentration distribution in the individual mica particles cannot be measured, macroscopic or average concentraton changes were determined. The solution of Eq. (1) was then expressed as the ratio of the total amount of solute in the solid (M_t) at time t and at infinite time (M_∞). Accordingly, (Crank 1956):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2 q_n^2} \exp\left(-\frac{D_a q_n^2 t}{a^2}\right) \qquad (2)$$

where α is the ratio of the amount of solute in the liquid and in the solid at infinite time and the q_n's are the positive, non-zero roots of the Bessel function. Eq. (2) was derived for processes in which diffusion is controlled by a single energy barrier and the activation energy is independent of the concentration. Under these conditions D_a is independent of time.

The theoretical time dependence of M_t, expressed by Eq. (2), was compared to the experimental results. In Table 1, the calculated apparent diffusion coefficients are given. The analysis showed that D_a is not constant but decreases with increasing time at each test temperature. This effect is possibly due either to the increase of water concentration, or to the Ba - K concentration change, or both.

When D_a is not independent of time, an approximate apparent activation energy, E_a, can

TABLE 1. APPARENT DIFFUSION COEFFICIENTS OF BARIUM IN PHLOGOPITE AT 40°C, 60°C AND 80°C

Sample Number	M_t Ba, mg	M_t/M_∞	$\left(\frac{D_a t}{a^2}\right)^{\frac{1}{2}}$	$t^{\frac{1}{2}}$ $(sec)^{\frac{1}{2}}$	D_a cm^2sec^{-1}
1-40	1.61	0.106	0.050	74	42.90×10^{-14}
2-40	1.74	0.115	0.055	150	12.60×10^{-14}
3-40	1.83	0.121	0.058	190	8.76×10^{-14}
4-40	1.98	0.131	0.062	240	6.25×10^{-14}
5-40	2.00	0.132	0.064	420	2.19×10^{-14}
6-40	2.08	0.138	0.066	600	1.14×10^{-14}
1-60	2.43	0.161	0.076	74	99.20×10^{-14}
2-60	2.84	0.188	0.088	150	32.37×10^{-14}
3-60	3.14	0.208	0.098	240	15.68×10^{-14}
4-60	3.47	0.230	0.110	420	6.45×10^{-14}
5-60	3.58	0.237	0.113	600	3.35×10^{-14}
1-80	3.29	0.218	0.103	42	56.60×10^{-13}
2-80	3.96	0.262	0.125	74	26.83×10^{-13}
3-80	4.38	0.290	0.140	108	15.80×10^{-13}
4-80	4.74	0.314	0.152	150	9.66×10^{-13}
5-80	4.89	0.324	0.156	190	6.34×10^{-13}
6-80	4.86	0.322	0.155	240	3.92×10^{-13}
7-80	5.13	0.340	0.165	420	1.45×10^{-13}
8-80	5.52	0.365	0.178	600	0.83×10^{-13}

be calculated directly from rate theory (Glasstone *et al.* 1941):

$$D_a = \beta\lambda^2 \frac{kT}{h} \frac{Q^{\ddagger}}{Q} \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (3)$$

where β = a geommetrical factor, usually $0.1 < \beta < 1$.
λ = distance between two equilibrium positions.
kT/h = a frequency factor with k = Boltzmann constant, h = Planck constant and T in °K.
$Q^{\ddagger}/Q$ = partition function ratio $\simeq 1$.

From the diffusion coefficients, an average apparent activation energy was calculated, using Eq. (3). The value of ΔE_a was found to be ~16,000 cal mole^{-1} with a scatter of ~1,700 cal mole^{-1}. Raussell-Colom *et al.* (1965) found ΔE_a to be about 11.0 kcal mole^{-1} for the K-Ba exchange in phlogopite and biotite, somewhat less than the value reported here.

These activation energies may be compared with others for the diffusion of various ions in various minerals. For example, the diffusion of argon in phlogopite gave $\Delta E_a = 28.0$ kcal mole^{-1} (Evernden *et* al. 1960). Beattie & Dyer (1957) calculated 16.3 kcal mole^{-1} from diffusion experiments of sodium in analcime. In ultramarine, the apparent activation energy ranges from 16.1 to 27.0 kcal mole^{-1}, depending on the cation exchange pairs (Barrer & Raitt 1954). The self-diffusion of water in zeolites gave ΔE_a between 8.1 and 11.0 kcal mole^{-1} (Barrer & Fender 1961).

CONCLUSION

The diffusion of ions and molecules in minerals is evidently an important part of many mineral-forming reactions that take place within rocks (*e.g.* exsolution, homogenization of zoned crystals, hydrothermal alteration), and it plays an important role in rock weathering and the formation of soils as well. More data are needed on the capacity various minerals have for exchanging different ions in different structural sites, at various temperatures, for these data would contribute to a better understanding of the chemical reactions that take place in earth materials.

ACKNOWLEDGEMENTS

The author wishes to thank Drs. H. Kodama, Soil Research Institute of the Department of Agriculture, and R. Kretz, D. D. Hogarth and D. Cronan of the University of Ottawa for their advice and helpful suggestions. This work was supported by the National Research Council of Canada, through a Grant awarded to R. Kretz.

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Manuscript received May 1974.