A STUDY OF DIFFUSION IN MICA MINERALS

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by

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ABSTRACT

An extensive literature survey of ion exchange studies revealed that artificial weathering experiments, carried out on mica minerals, can lead to the theoretical analysis of diffusion processes. Of the various techniques which are adapted to ion exchange experiments for mica minerals, the high solution (volume) - solid (volume) ratio method is the most suitable.

Phlogopite reacts more readily than muscovite, and for three cations, the relative potassium replacing power in phlogopite is

$$Ba > Na > Sr.$$

The potassium-barium exchange reaction in phlogopite is accompanied by the uptake of water (or OH_3^+ ions, or both) into the structure, resulting in a basal expansion of 1Å at 40°C and 2.3Å at 60-80°C. Upon heating the exchanged phlogopite at 500°C for 2 hours, the expanded spacing either collapses almost completely, or the much reduced X-ray intensity peak shifts from 2.3Å to 1Å.

The K-Ba exchange rates in phlogopite do not follow the $(\text{time})^{\frac{1}{2}}$ diffusion law, in agreement

with results published in the literature. The apparent diffusion coefficients, calculated for cylindrical particles, range from 4.3×10^{-13} cm^2 sec^{-1} to 0.83×10^{-13} cm^2 sec^{-1} for temperatures between $40^{\circ}C$ and $80^{\circ}C$. Because the diffusion coefficients are time dependent, approximate apparent activation energies can be calculated from rate theory. The calculated energy is approximately 16,000 cal $mole^{-1}$.

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CHAPTER 1

INTRODUCTION

Diffusion in Geological Processes

Diffusion plays a significant role in many geological processes. During solidification, besides the usual fluid flow processes, a considerable part of the mass transport occurs by diffusion mechanisms which move the ions through the liquid phase to the crystallization sites. The solid state reactions associated with metamorphism are governed by ion exchange diffusion. The exchanging ions move through the crystal lattice with varying ease, each with a definite diffusion rate. The overall reaction rate is controlled by the mobility of the ion which has the lowest diffusion rate at the prevailing temperature of metamorphism.

At atmospheric conditions, the chemical weathering of the sheet silicates is also controlled by an ion exchange diffusion process (White, 1956, Mortland, 1958, Reed and Scott, 1962, Rausell-Colom et al., 1965). During weathering exchange occurs between the interlayer cation of the solid and the cation(s) present in the solution (rain

water) in contact with the minerals.

It is extremely difficult, or even impossible, to reproduce the conditions of solidification and metamorphism in the laboratory. Because of these difficulties, most of the diffusion investigations reported in the literature have been carried out on metals, or on simple oxides and halides of metals. In comparison, very little information is available on the ion exchange properties of the complex silicate minerals. However, weathering, which occurs in a relatively low and narrow temperature range, can be sufficiently simplified for laboratory studies.

Purpose of the Study

The limited knowledge on the ion exchange properties of silicate minerals renders the study of the diffusion processes greatly desirable. Accordingly, the present study was designed to obtain experimental information on these processes.

To a large extent, the study was exploratory in nature, for a considerable amount of time was given to the design and testing of different experiments that might be used to obtain information on diffusion in minerals up to 300°C. Because of the

experimental advantages, it was then decided to proceed with an investigation of certain ion exchange reactions involving two potassium-bearing mica minerals.

CHAPTER 2

REVIEW OF PREVIOUS WORK

Part 1. Ion Exchange Processes in Mica Minerals

One of the processes that may take place during the weathering of potassium-bearing mica minerals is the loss of interlayer potassium accompanied by a gain of other cations. To understand the atomic mechanisms associated with the ion exchange processes, a mathematical model must be defined, which has to take into consideration the effect of crystallographic anisotropy, and the particle shape.

Experiments on a biotite-vermiculite (Barshad, 1954) and on pure biotite (Mortland, 1958) indicated that the cation exchange path is parallel to the cleavage face. Visual observations of the ion exchange front were also carried out. To facilitate the measurements, muscovite, biotite and phlogopite flakes, cut to 1 x 1 mm to 25 x 25 mm sizes with estimated thicknesses of 10 μm to 0.5 mm were used. The experimental methods also varied widely. Rausell-Colom et al. (1965) sealed the flakes in glass ampules with various cation solutions. Wells and Norrish (1968) used the same minerals, but leached the flakes at a constant flow rate. A potassium

precipitation method was used by Scott et al. (1967, 1968), and Newman (1970) boiled the samples in NaCl solution for short periods of time.

The exchanged or "weathered" zones were clearly visible on biotite and phlogopite in all cases, and the exchange could be measured under the microscope. The zones were found to advance uniformly and at right angles to all four edges, independently of the directions of the cuts with respect to the natural edges. Where cracks developed on the flakes as a result of cutting, or where the surface layers were uneven, the front moved at right angles to these openings as well. Although the diffusion rate in muscovite is extremely slow, after 18 months of treatment traces of the same directional diffusion path could be observed.

Scott and Smith (1967) made a shallow pin-hole on the surface of a biotite flake. After 18 months of diffusion reaction a large, circular transformed zone developed around the hole. It is evident from these experiments that the diffusion in micas occurs in a radial direction, parallel to the cleavage faces.

From microscopic observations, it was concluded that the shape of crushed mica particles

can be regarded either as a plane sheet or as a cylinder. Because of the radial path of the diffusion however, it is clear that the mathematical model has to be an isotropic cylinder with the axis perpendicular to the basal plane.

In addition to the ion exchange, the weathering process is accompanied by the uptake of water into the structure. It was proposed by Rich and Black (1964) that the hydrated solute ions are located in wedge-shaped zones, with potassium ions at the apices. These zones form at the edges and they are also distributed unevenly within the particles. As a result, the original basal spacing of the micas expands and a new crystalline phase forms. The new phase appears as a segregated vermiculite phase, irregularly interlayered with the mica phase. As the cation exchange progresses, X-ray diffraction studies show that the intensity of the 10Å, 002 reflection decreases and the intensity of the expanded phase increases (DeMumbrum, 1959, Le Roux and Rich, 1969, Tomita and Sudo, 1971), indicating the gradual conversion of the mica into vermiculite.

The expansion is usually about 1 - 2Å, but, in special cases, it can be somewhat greater. Scott and Smith (1966) reported that the exchange reaction with sodium ion at 25°C expanded the lattice

spacing of muscovite to 12.3Å. Under the same conditions the basal spacing of biotite and phlogopite expanded to 15Å. The exchange of potassium with barium at 120°C causes the same degree of expansion in the three mica minerals (Reichenbach and Rich, 1968). An extreme case was reported by Mackintosh et al. (1971), who observed that biotite, phlogopite and muscovite expanded to 36Å after dodecylammoniumchloride ($CH_3(CH_2)_{11}NH_3Cl$) treatment at 70°C.

The phase transformation introduces an additional factor into the mathematical analysis of the diffusion process. Because of the difficulties associated with this effect, no direct diffusion coefficient calculation have been reported in the literature. The usual practice is to saturate the mica first with a cation, and to study the properties of the altered products in either self or inter-diffusion experiments (Rausell-Colom et al., 1965, Reichenbach and Rich, 1968, Brown and Newman, 1970).

Part 2. Ion Exchange Experimental Techniques

A substantial part of the present thesis was concerned with the establishment and introduction of the laboratory techniques appropriate for ion

exchange experiments up to 300°C. An extensive survey was, therefore, carried out on ion exchange methods.

2.1 Sample Preparation

It was shown by Mackenzie and Milne (1953) that the method used in sample preparation affects the cation exchange capacity, and the influence of filing and crushing in a mechanical agate mortar were investigated. In order to determine the effect of crushing time as well, samples of muscovite were taken at various time intervals, up to 24 hours. The required size fraction was separated by dry sieving.

The cation exchange capacity of muscovite was determined by exchanging the potassium with calcium. Each of the samples were treated three times with the exchanging solution and the extracted potassium was measured. The filed sample released about 6 meq K/100g mica, while grinding for only one hour increased the potassium release to almost 30 meq K/100g (Fig. 2-1).

It is of interest to note that the X-ray powder patterns did not show any difference between the filed and the first one or two ground samples. As the grinding continued however, both the relative intensities and the sharpness of the lines changed.

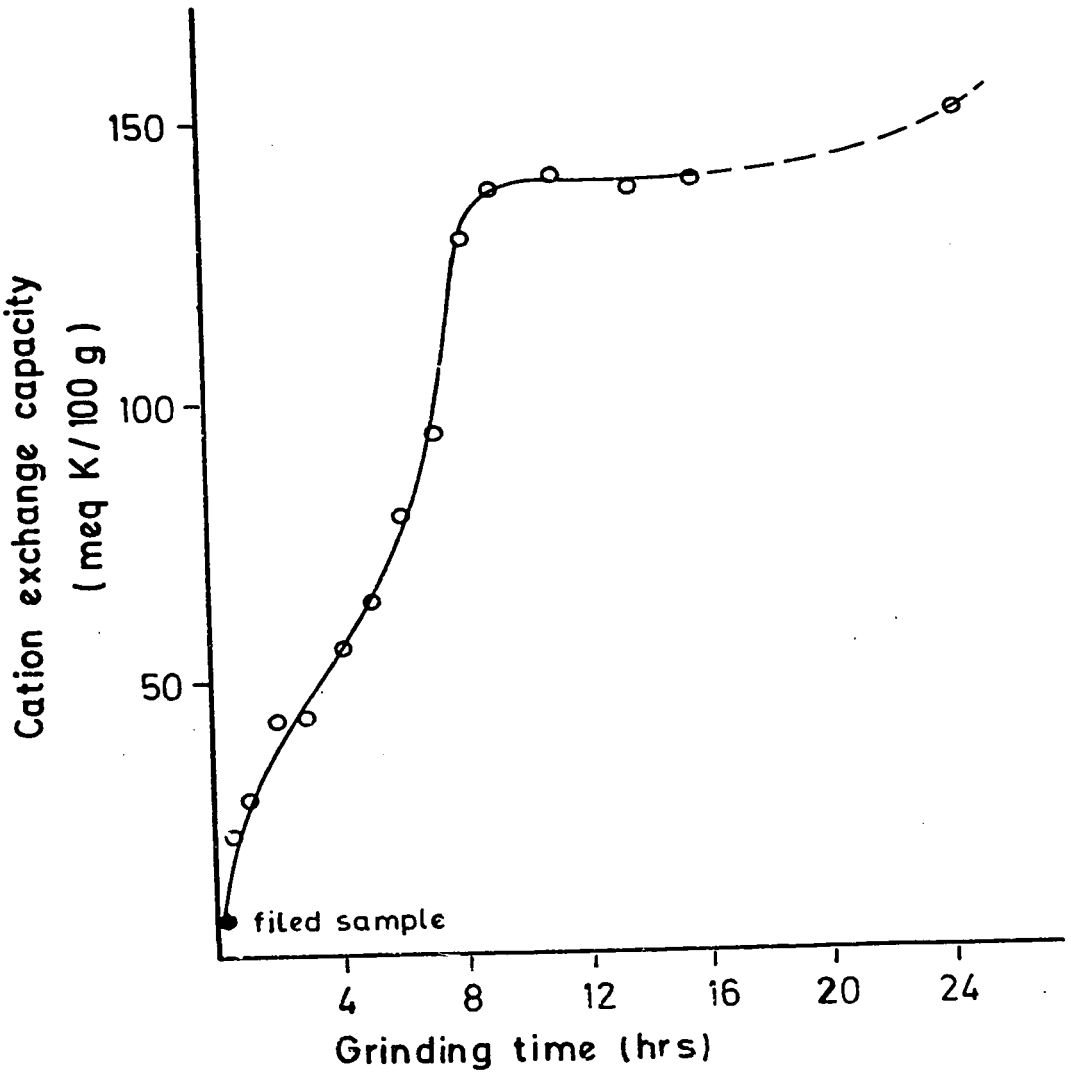


Fig. 2-1 Relationship between cation exchange capacity and grinding time for muscovite (Mackenzie and Milne, 1953).

After grinding for 8 hours, no sharp lines could be observed. On further grinding two additional lines, common in hydrous micas, appeared. At the same time the sharpness of the lines increased and the new relative intensities differed from the original intensities. In addition, the sample, prepared by crushing for 24 hours and heated to 1000°C, had an X-ray pattern identical to that of leucite. After similar heat treatment, the filed sample still retained the muscovite pattern.

It may be concluded that although the experiments were carried out on muscovite only, the sample preparation method could influence the reactivity of the other potash-mica minerals as well.

The effect of particle size on the exchangeability of potassium was studied by several investigators (Scott and Reed, 1965, Reed and Scott, 1966, Scott, 1968, Mackintosh and Lewis, 1968). In most of these investigations the samples were prepared by crushing in a hammer mill. The finer fractions were separated either by wet sieving or by sedimentation.

It was found that initially the small particles released potassium much more readily than the larger ones (Fig. 2-2). Even muscovite released

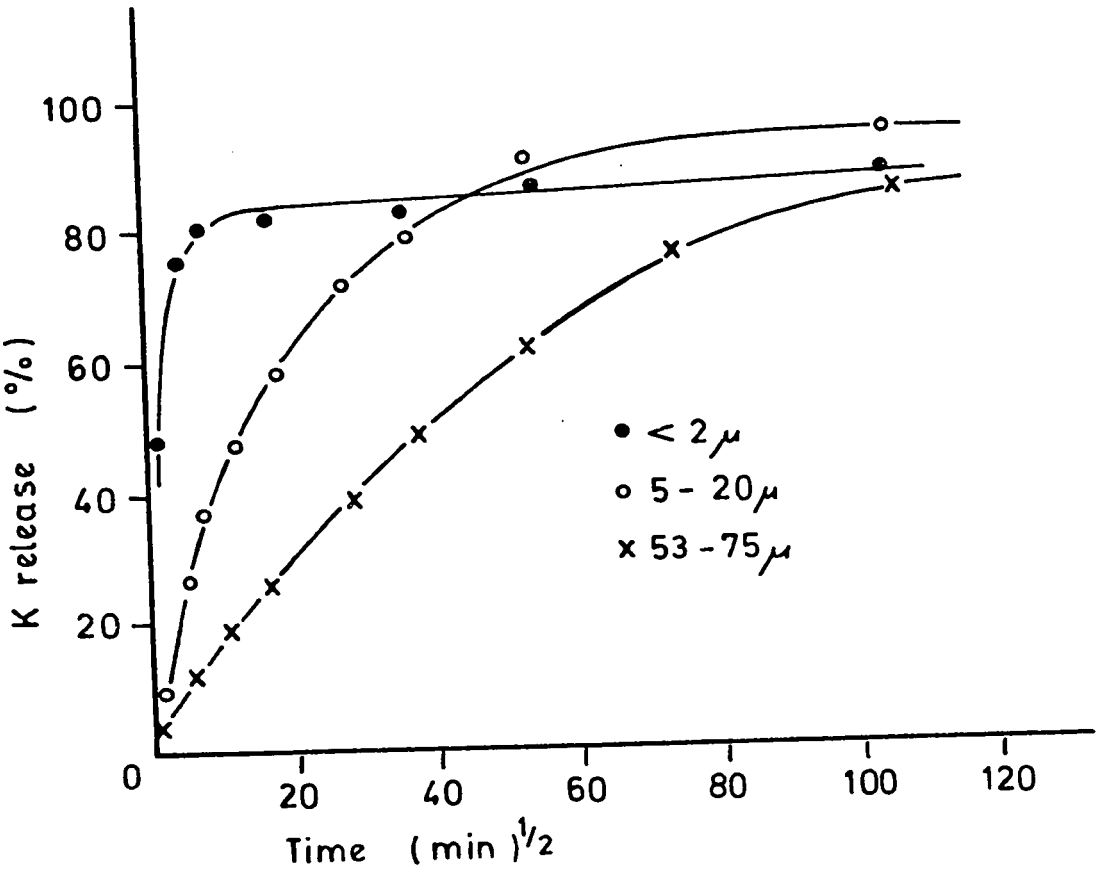


Fig. 2-2 Influence of particle size on the release of potassium from biotite at 70°C (Mackintosh and Lewis, 1968).

more than 50% of the total potassium in a few hours when the 0.2 - 0.7 μm size fraction was used. Under the same conditions particles of the 50 - 60 μm size fraction needed more than 100 days to reach the same degree of potassium depletion (Fig. 2-3). It seems that the optimum particle size is around 20 μm for the three mica minerals.

2.2 Diffusion Techniques

General Considerations. From the experimental point of view, solid state diffusion processes can be classified into two types: self diffusion and interdiffusion. In self diffusion experiments, the measurements are carried out with radioactive tracer methods. In interdiffusion or ion exchange studies, chemical analysis can also be used. In the present work, ion exchange was studied, using chemical analysis.

Very often, in ion exchange experiments, the solid is finely powdered to simplify the measurements. To facilitate the calculations of the diffusion coefficient, the particles are suspended in concentrated aqueous solution. Under this condition the exchanging cation concentration remains constant during the experiment.

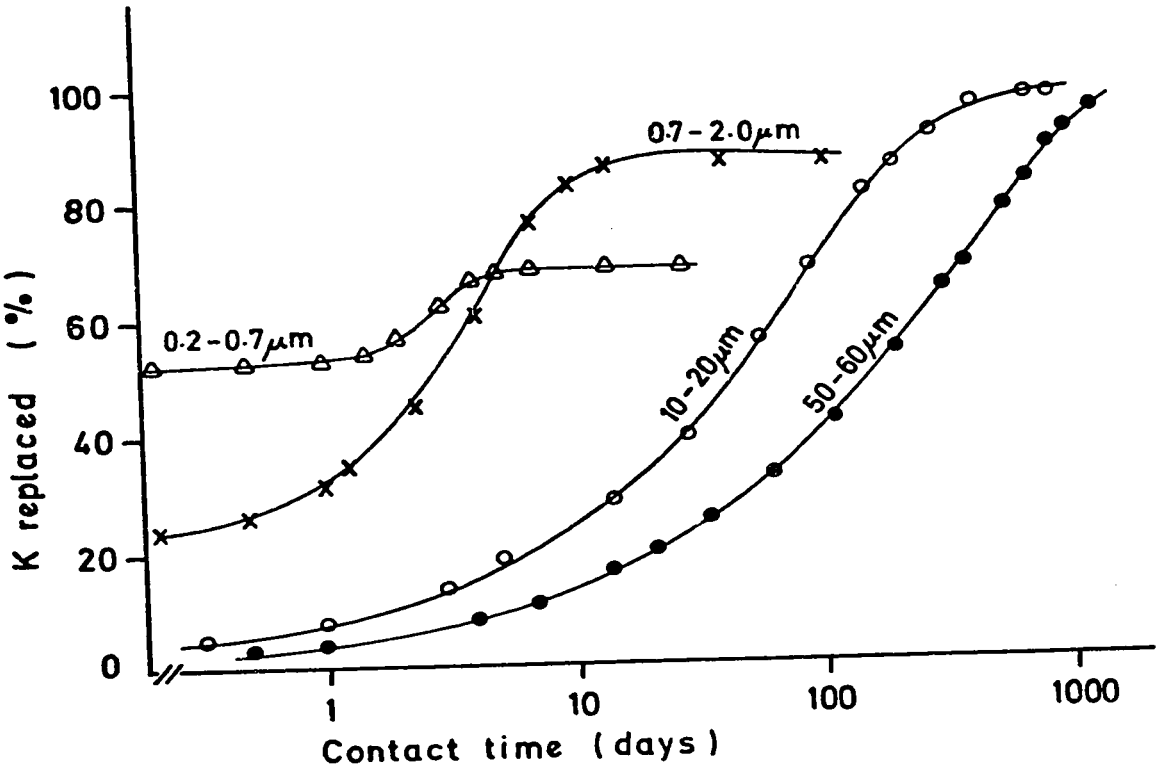


Fig. 2-3 Potassium replaced from four different size fractions of muscovite (Scott, 1968).

In experiments carried out at ambient temperature the reaction vessel can be a beaker or a flask. To ensure complete mixing, the solution is stirred and at definite time intervals, samples are withdrawn for analysis. To maintain constant concentration, the solution has to be protected from evaporation or refilled periodically.

At moderate temperatures the reaction vessels are sealed pyrex glass vials or reaction tubes. The heat source is either a bath or an oven with constant temperature control and furnished with sample holders. The mixture is agitated either by shaking or by rotating the containers at a slow speed (Barrer and Hinds, 1953, Barrer and Raitt, 1954, Barrer and Sammon, 1955). The samples are removed at regular time intervals from the heat source and quenched to stop the reaction, the two phases are separated, and both are analysed for the exchanged cation. In the solid phase the exchanger concentration is also determined.

At elevated temperatures, the high vapour pressure that builds up in a sealed container, has to be balanced. Up to about 190^{o}C pyrex glass can be used in pressurized steel bombs (Barrer and Rees, 1960). Above this temperature however, pyrex reacts

with water and fused silica glass, silver or gold tubes have to be used.

Ion Exchange Methods for Mica Minerals. It is well known that over long (geologic) time periods, the micas alter completely. The resistance of these minerals to weathering and to ion exchange reactions observed in the laboratory on the other hand indicate that the mica minerals are inert to a great extent. While the experimental methods briefly described above can be employed for a wide range of materials, the inertness of the mica minerals required the modification of these techniques (Barshad, 1954, White, 1956, Mortland, 1958, Scott et al., 1960, Smith, 1966).

To further the understanding of mica behaviour, studies were carried out in which the effects of

a) the total concentration of cations in the interlayer position (or the layer charge),
b) the fluorine content and
c) the structural variations

on the diffusion process were investigated.

a) The effect of the magnitude of the layer charge on the replaceability of K was demonstrated by Barshad (1954). The results, summarized in Table 2-1, show that the increase in layer charge reduces the amount of replaceable potassium. It is to be noticed that the layer charge increases with increasing K content.

b) Although the two trioctahedral micas react more readily than muscovite, there is a variation in behaviour within the different biotites and phlogopites. This variation may be the consequence of the differences in fluorine concentration. The substitution of the hydroxyl group with F^- decreases the activity (Rausell-Colom et al., 1965, Mackintosh et al., 1971). A comparison (Newman, 1969) between F content and an exchange parameter R^K_{Na}, calculated from the K/Na concentration ratios in the solution, showed decreasing activity with increasing fluorine concentration (Fig. 2-4). When the OH^- group was replaced by F^-, ion exchange reaction could not be induced in a synthetic fluor-phlogopite (Newman, 1970).

c) The concentration of fluorine in muscovite is usually low (Deer, Howie and Zussman, 1962). In a detailed structural study of the two mica

Table 2-1

Replaceability of K^+ with Mg^{++} from Samples of Varying Interlayer Charge and Total K

Sample	Interlayer charge meq/100g	Total K meq/100g	K replaced with Mg^{++} meq/100g	K replaced with Mg^{++} % of total K
Biotite	206	196.8	148.1	77.2
Biotite	240	234.4	36.2	16.6
Muscovite	262	255.0	19.9	7.9

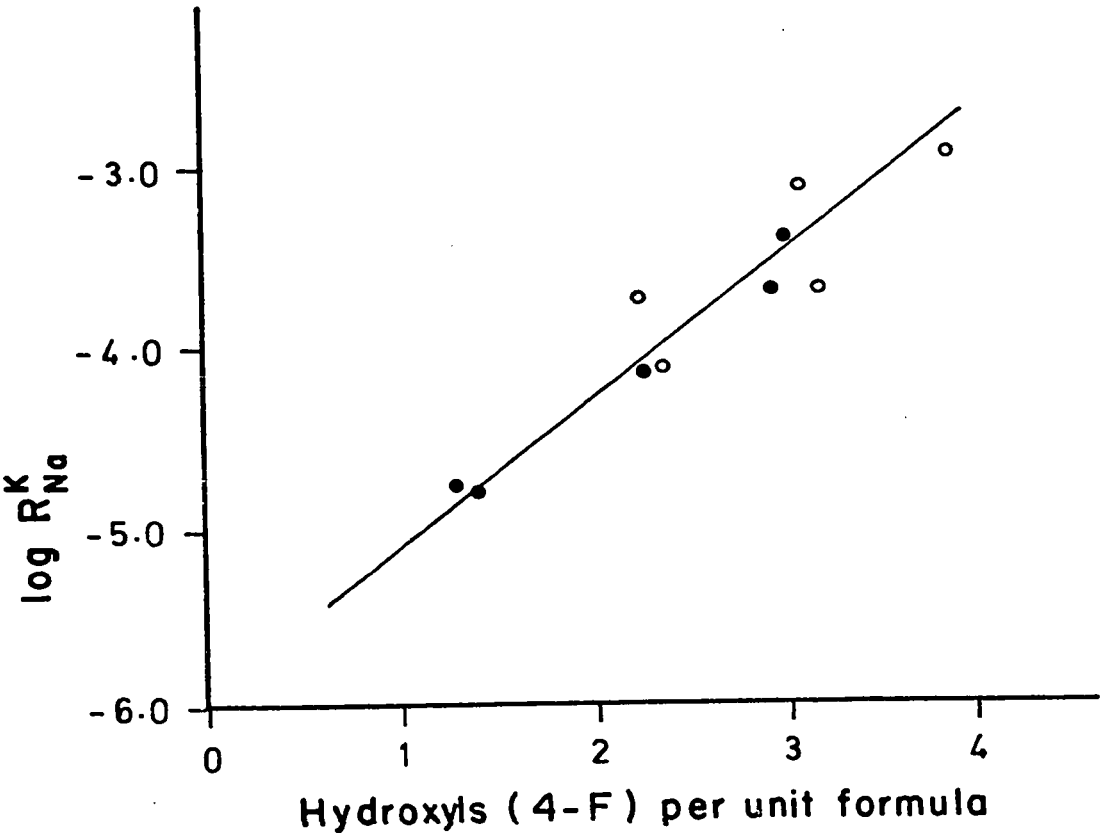


Fig. 2-4 Correlation between hydroxyl content (4-F) and R^{K}_{Na}, a measure of activity, for biotites (o) and phlogopites (●) (Newman, 1969).

types, Vedder (1964) found differences in the orientation of the hydroxyl groups. In the trioctahedral micas the dipoles are perpendicular to the cleavage plane and in muscovite the dipoles are at an angle. From these observations it was postulated (Quirk and Chute, 1968) that in the vertical position the protons are close to the interlayer cations and as a result, there is a repulsion between the positive charges. The inclined position on the other hand brings the negative ends of the dipoles closer to the cations, with a consequent increase in electrostatic interaction (Dolcater et al., 1972).

Experiments, in which the effect of K^+ concentration on diffusion rate was investigated, were also carried out (Rausell-Colom et al., 1965, Scott and Smith, 1966). It was found that even when the potassium concentration in the solution was very low, the ion exchange process stopped completely. These studies indicated that in consequence of the great affinity of potassium to mica, strong bonds develop between the mica surface and potassium. The potassium will, therefore, preferentially accumulate in the surface layer, blocking any further ion exchange.

Although these isolated observations did not provide a coherent picture, they indicate some guidelines for the development of specialized ion exchange techniques for micas. It was concluded that to enhance the reaction, the extracted potassium has to be removed from the particles to keep the surface layer concentration equal to that of the bulk of the solution.

There are several methods which effectively prevent the accumulation of potassium.

High Solution-solid Ratio Method. To establish the relationship between the exchangeability of interlayer potassium and the level of potassium in the solution, Scott and Smith (1966) equilibrated different amounts of micas in NaCl solutions. It was found that the ion exchange reaction is very sensitive to the K ion concentration. In the case of biotite, an increase from 7 ppm to 10 ppm potassium in the solution decreased the amount of exchangeable potassium from 100% to 30%. Phlogopite showed the same behaviour, but a slight shift toward higher K^+ tolerance was observed (Fig. 2-5). Muscovite exchanged only 17% of the total potassium in the presence of 0.12 ppm K^+, and the process ceased at the 4 ppm level (Fig. 2-6).

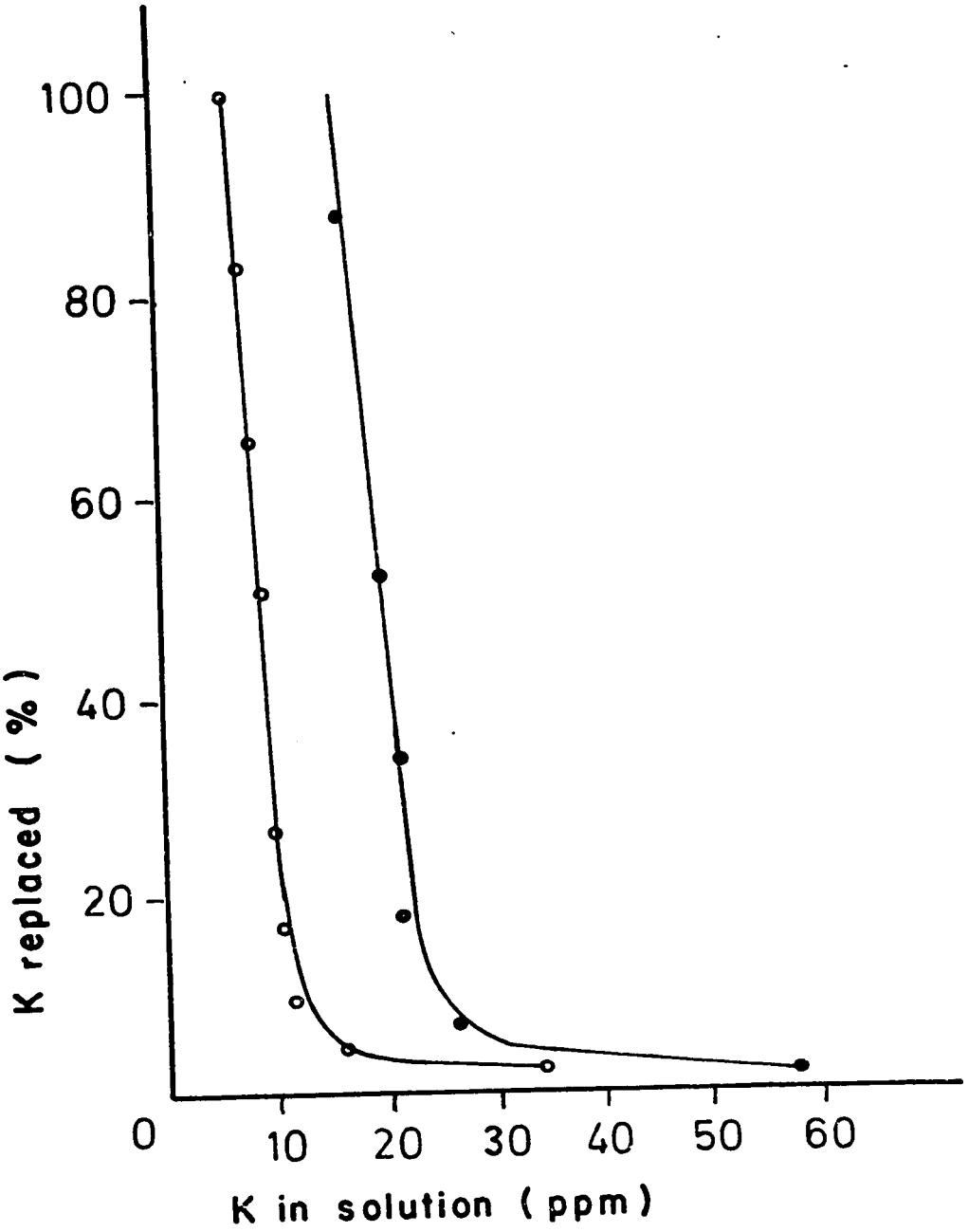


Fig. 2-5 Potassium extracted from biotite (o) and phlogopite (●) as a function of equilibrium K levels in the solution (Scott and Smith, 1966).

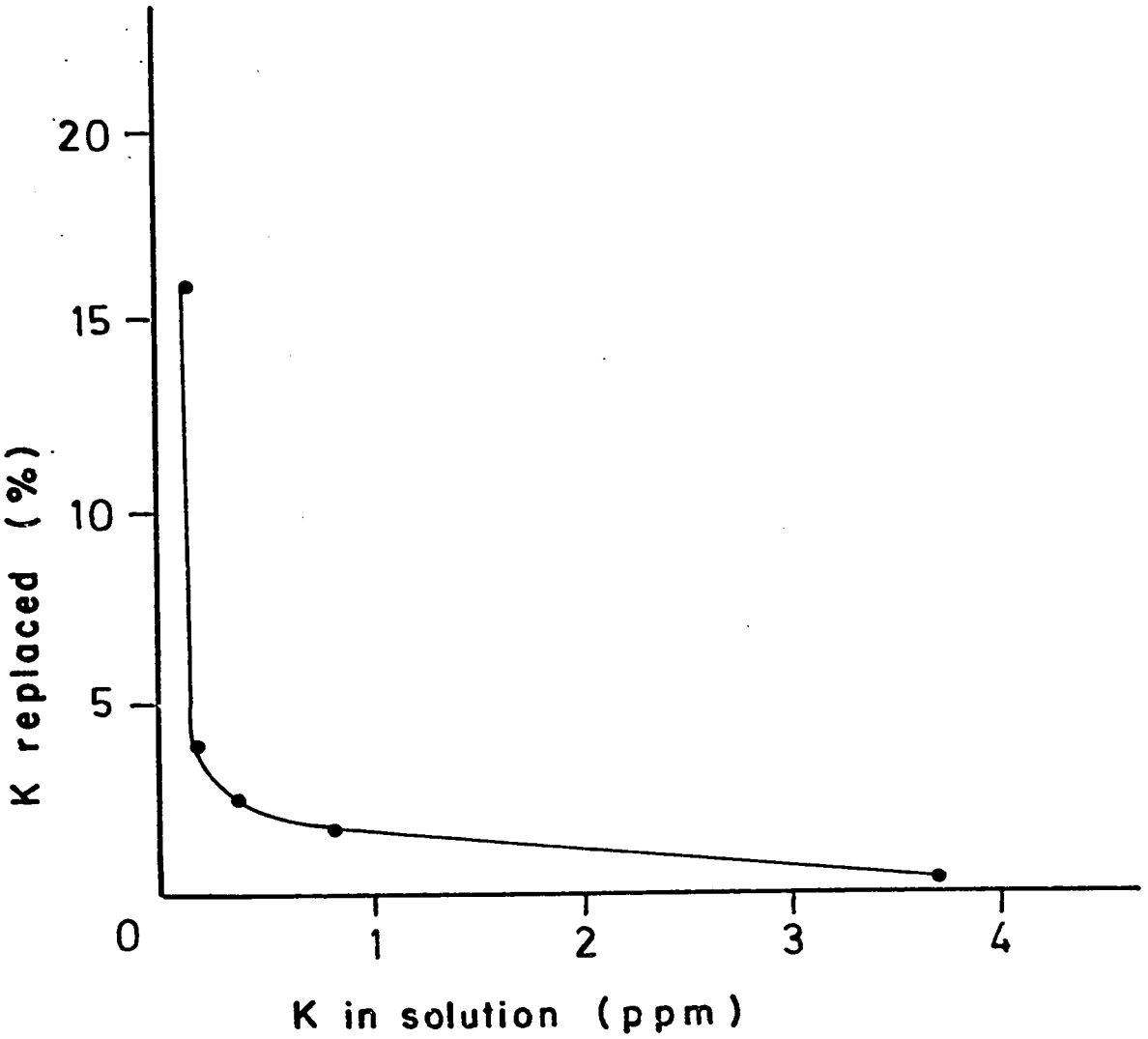


Fig. 2-6 Potassium extracted from muscovite as a function of equilibrium K levels in the solution (Scott and Smith, 1966).

The necessity to use a large volume of extracting solution was further demonstrated when it was observed that 0.1 g and 0.5 g biotite samples, each in 1 liter NaCl solution, released 95% and 35% of the total potassium respectively (Fig. 2-7). In both cases Na and K exchanged until an equilibrium distribution of the two cations was established between the mica and the solution. Equilibrium was reached at different degrees of potassium extraction because different amounts of mica, and therefore total potassium, were present in the two experiments.

Successive Extraction Method. In this method the potassium concentration is kept low by changing the solution before a predetermined tolerance level is reached. The technique is very effective and has been used successfully in the ion exchange studies of both mica types.

Using this method mica can be saturated comparatively easily with any of the alkali or alkaline earth cations. Almost complete exchange can be achieved in 21 days even in muscovite by replacing large volumes of hot solutions every 2-3 days. (Dr. Kodama, personal communication).

Potassium Precipitation Method. The removal of the extracted potassium in the form of an insoluble salt

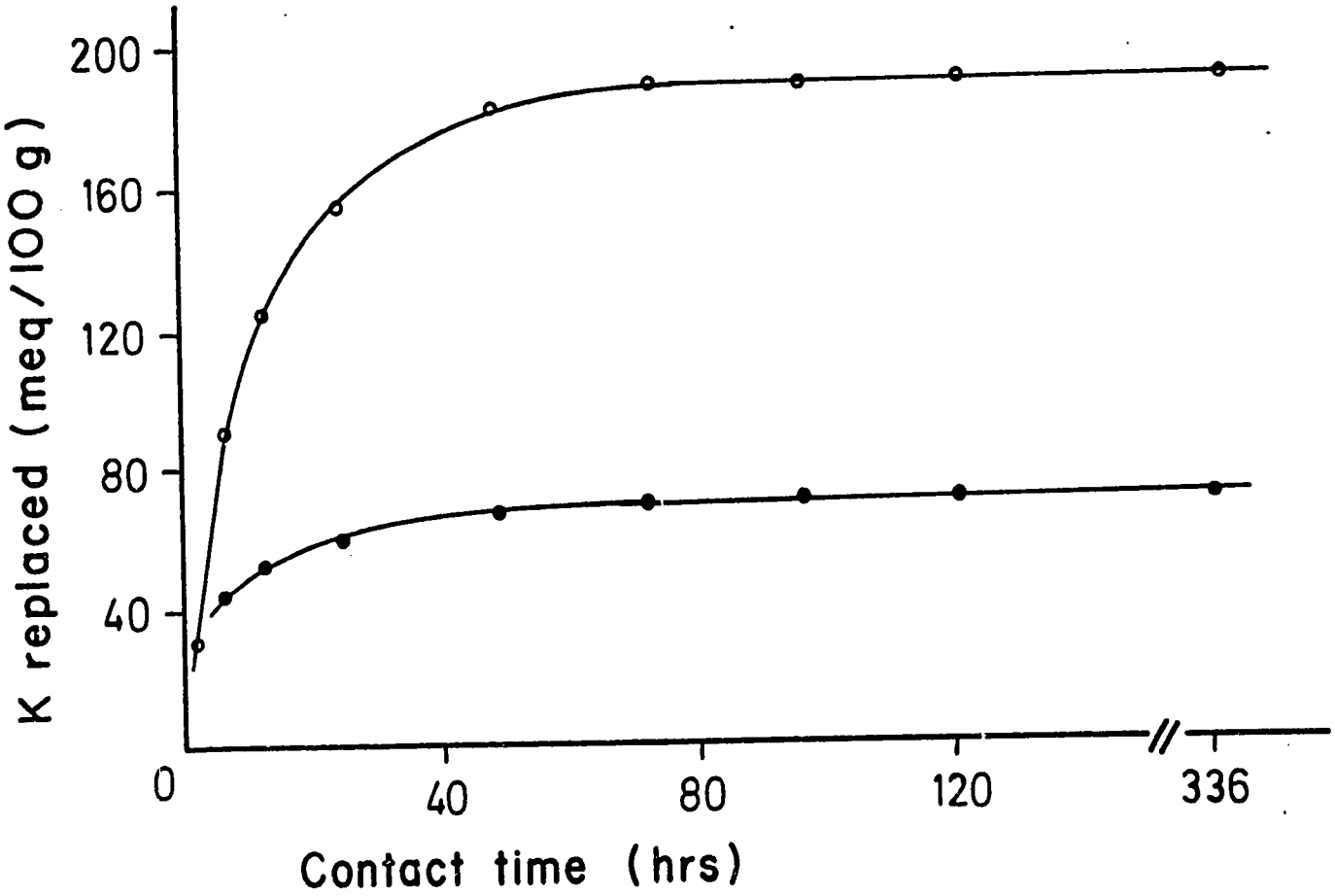


Fig. 2-7 Potassium extracted by equilibrating 0.1 g (o) and 0.5 g (●) biotite samples in 1 liter NaCl solution (Scott and Smith, 1966).

was found to enhance greatly the exchange reaction. Of the very few compounds which form insoluble salts with potassium, sodium tetraphenylboron (NaTPB) is used generally in ion exchange experiments.

The method was developed in 1960 (Scott et al., 1960) and has been applied widely since (DeMumbrum, 1959, 1963, Reed and Scott, 1962, 1966, Scott and Reed, 1962, 1965, Scott and Smith, 1966, 1967, Newman and Brown, 1966, Thompson et al., 1967, Newman, 1967, Scott, 1968, Ross and Kodama, 1970, Gast and Klobe, 1971), despite restrictions and difficulties which limit its usefulness. Because NaTPB decomposes at 80°C (Flaschka and Barnard, 1960) it can be used only up to 50°C. In the presence of mica minerals, especially muscovite, the compound becomes unstable even below 50°C. The decomposition can be arrested by adding Na_2EDTA to the solution.

Because both the precipitating and the stabilizing agents are sodium salts, in most cases only sodium can be used as the exchanging cation. The relative power of the cations to replace potassium varies with the composition of the samples. Barshad (1954) proposed that the sequence of the relative replacing power is

$$Ba > Mg > Na > Ca$$

for biotite-vermiculite. Rausell-Colom et al. (1965) found it to be

$$Na > Sr > Mg \sim Li = Ba > Ca$$

for a pure biotite sample. Consequently the mixing of two cations in the solution introduces an additional variable into the study of ion exchange processes.

For chemical analysis, the precipitated potassium can be dissolved in acetone. For X-ray diffraction analysis the separation of the two solids is not essential because the sharp 8Å peak of the potassium salt does not interfere with the mica patterns.

Extraction with Molten Salts. Basically, this method is a combination of successive extractions with high "solution" to solid ratio. The most frequently used salt is lithiumnitrate (White, 1956, 1958, Bronson et al., 1959, DeMumbrum, 1963, Tomita and Sudo, 1971), which melts at 264°C. The finely powdered sample, mixed with a large excess of salt, is kept at 300°C for up to about 24 hours. In an experiment (Bronson et al., 1959), the 7.45% potassium content of the original muscovite was reduced to 0.70% after repeating the extraction process for about 400 hours.

These methods have been reviewed because of their potential applicability for ion exchange experiments in mica minerals. It was realized that a specific study will have to be carried out to establish the adaptability of these techniques and to modify them for the present purpose.

CHAPTER 3

MATERIALS AND ANALYTICAL METHODS

Description of Materials

In the first part of the thesis work, three materials were used:

a) a pegmatitic muscovite,

b) a microcrystalline muscovite of hydrothermal (?) origin and

c) a phlogopite from a pyroxene-phlogopite skarn.

a) The pegmatite body from which the muscovite was taken is located 27 miles N.E. of Yellowknife, District of Mackenzie. The hand specimen KG-407-61-3, collected by R. Kretz, consisted of muscovite, quartz, albite, apatite and traces of garnet, potash feldspar and magnetite. Most of the muscovite occurs as tabular crystals of varying thickness with diameters up to 3 cm (Kretz, 1970). On closer inspection the mica was found to be clear, colourless, and to contain, in very minor amounts, inclusions of the other minerals.

b) The microcrystalline muscovite (M.7) was obtained from Dr. H. Kodama of the Soil Research Institute of the Department of Agriculture.

The sample originated from Miyori, Tochigi, Japan, and it is thought to be a hydrothermal product. The material was a creamy white, fine powder and contained less than 10% impurity of quartz and pyrite.

c) The source of the phlogopite is a body of skarn, of the amphibolite facies, near Otter Lake, W. Quebec. The specimen was collected by R. Kretz from a roadcut exposure at Lawless Lake, between Campbell's Bay and Otter Lake. The phlogopite occurred in blocks of 6 x 4 x 1/4 cm sizes and it was clear, dark brown and essentially free of inclusions.

Sample Preparation

a) The pegmatite hand specimen was broken up to free the mica blocks. These were cleaved and the impurities and inclusions were removed from the thin sheets under a binocular microscope. The resulting muscovite was better than 98% pure.

The sample was crushed in a Glen Creston ball mill using an alumina-ceramic grinding vial and plexiglass beads. The estimated maximum grinding time was 5 hours. The very fine particles were removed by sedimentation in distilled water and decantation. This was repeated three or four

times. The wet residue was then washed with acetone and air dried. The resulting white powder was dry sieved and the fraction that passed through a 270 mesh (53 μm) nylon monofilament sieve was used in the subsequent experiments.

b) The microcrystalline muscovite was washed repeatedly to remove the very fine powder fraction. The large aggregates and the impurities were separated from the pure material as the residue. Similarly to the crushed muscovite, the sample was dried by evaporating the acetone at room temperature. The particles are probably smaller than 20 μm (Dr. Kodama, personal communication) and are larger than 1 μm.

c) The phlogopite blocks were cut into small pieces with a diamond saw first, then crushed in the ball mill for 1 hour. The fraction between 140 and 325 mesh of the dry sieved powder was retained and used.

Analytical Methods

Duplicate samples of mica powders were dissolved by the standard hydrofluoric-perchloric acid method. The determinations of Al, total Fe, Mg, Ca, Na, K, Li, and subsequently Sr and Ba were carried out on a Techtron model AA-4 atomic absorption spectrophotometer, using the recommended

instrument settings (Angino and Billings, 1967). The reference solutions were prepared from Fisher Atomic Absorption Standard Solutions. A sample calibration curve is presented in Fig. 3-1.

The atomic absorption analysis was carried out with a tenfold dilution of the mica solutions for the determination of potassium, while iron and magnesium required a 1:20 dilution of the phlogopite sample. In order to overcome interferences, the following procedure was used:

(i) Ca^{++} and Mg^{++} determined in the presence of La^{3+}.

(ii) Al^{3+} determined in the presence of excess K^{+}.

(iii) Sr^{++} and Ba^{++} determined in the presence of La^{3+} and Na^{+}.

In addition, reagent blanks were analysed along with the samples in each case. The silica content was determined gravimetrically with the Bennett-Hawley method (Bennett and Hawley, 1965). The results of the analyses are given in Table 3-1.

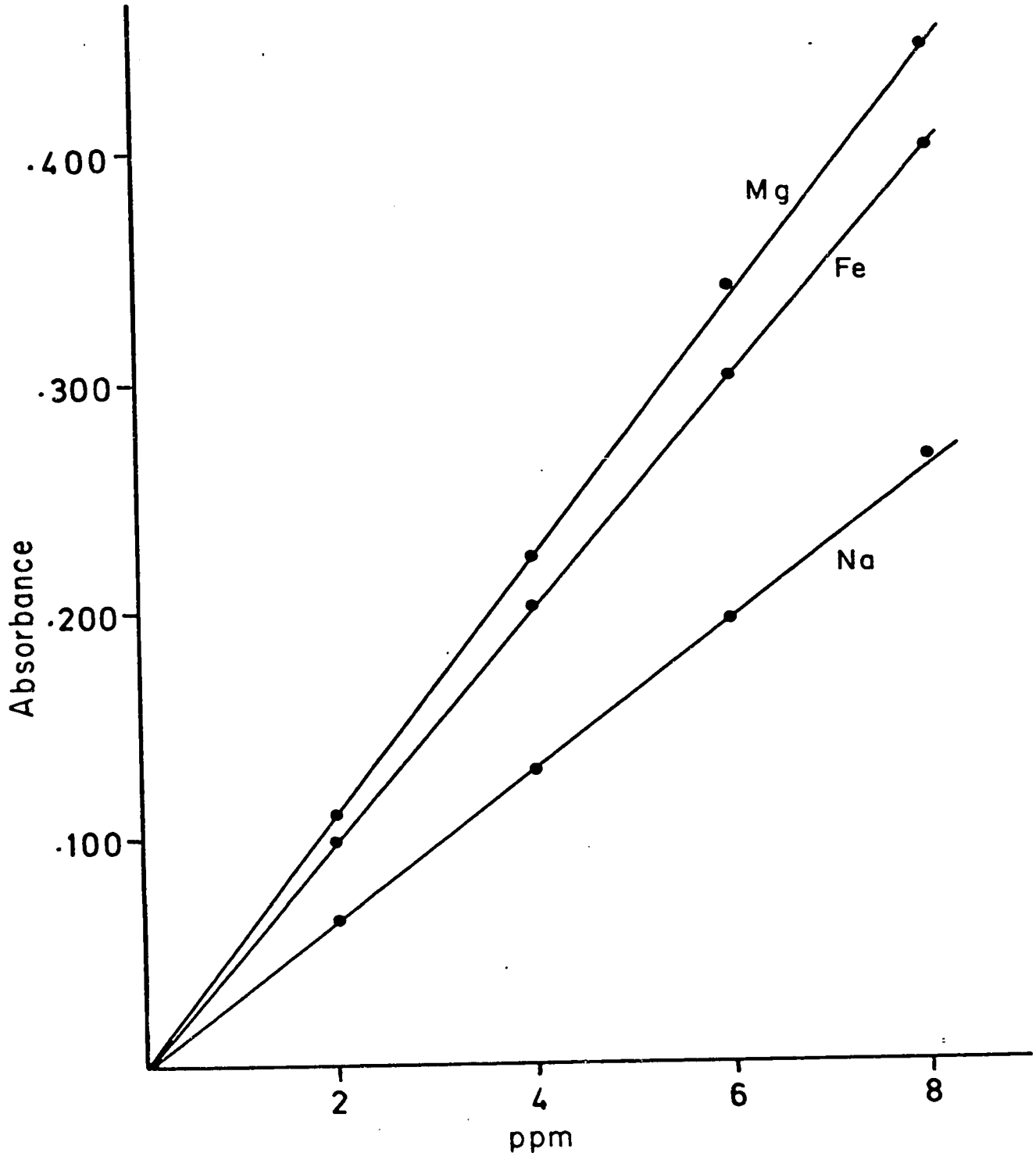


Fig. 3-1 Example of working curves relating absorbance to concentration for a routine analysis.

Table 3-1

Chemical Analysis of the Micas (wt %)

	KG-3 Muscovite	M.7 Muscovite	Phlogopite
SiO_2	45.6	47.86*	-**
Al_2O_3	34.0	35.90*	-**
Fe_2O_3	0.94@	0.43@	5.15@
MgO	0.10	0.41*	24.40
CaO	0.10	0.09*	-**
Na_2O	0.79	0.15	0.27
K_2O	10.36	9.59	10.30
Li_2O	0.034	- ≠	0.013
H_2O	5.30Δ	4.60*	2.0 ≠≠

* = given by Dr. Kodama

≠ = not detected

** = not determined

≠≠ = loss of weight at ∿700°C in air

@ = total iron expressed as Fe_2O_3

Δ = determined by Mr. S. Courville of the Geological Survey of Canada

CHAPTER 4

INVESTIGATION OF THE EXPERIMENTAL METHODS

A series of studies was carried out in which the use of different ion exchange experimental methods, suitable for two-phase systems (powdered solid-aqueous solution), were investigated. In the majority of these experiments specialized ion exchange techniques, reviewed in Chapter 2, Part 2, as suitable to diffusion rate measurements in mica minerals, were studied.

The following techniques were studied:

(i) glass tube method (pyrex glass); between 100°C and 300°C, using crushed (KG-3) muscovite,

(ii) precipitation method; at 50°C, using crushed (KG-3) muscovite,

(iii) successive extraction method; at 92°C, using $BaCl_2$ solution with uncrushed (M.7) muscovite,

(iv) extraction with molten $LiNO_3$; at 300°C, using M.7 muscovite, and

(v) high solution-solid ratio method; at 92°C, using $BaCl_2$ solution and phlogopite.

(i) Glass Tube Methods

The simplest reaction vessel which can be used is the sealed glass tube. The first type that was tested was designed by R. Kretz, and is similar to tubes originally used by Barrer (Barrer and Rees, 1960). Its application was investigated at 100°C and 135°C. The tube is made of two pieces (Fig. 4-1) to facilitate closing and opening. The upper curved half holds the powder which is mixed with the solution in the lower half when the test temperature is reached. The two halves are assembled with ground glass joints and sealed with high temperature silicon grease or with a standard taper teflon sleeve. While these seals work well at low temperatures, it was found in the present investigation that at 100°C and above silicon grease was inadequate. The teflon sleeve did provide a better seal, but at temperatures above 100°C the increasing vapour pressure limits the use of simple glass tube reaction vessels. At the 135°C test temperature the glass could not support any longer the high (~4 atm) vapour pressure.

A steel bomb was designed by the author to balance the high inside pressure and to establish whether pyrex can be used at temperatures above 190°C. The design of the bomb is shown in Fig. 4-2.

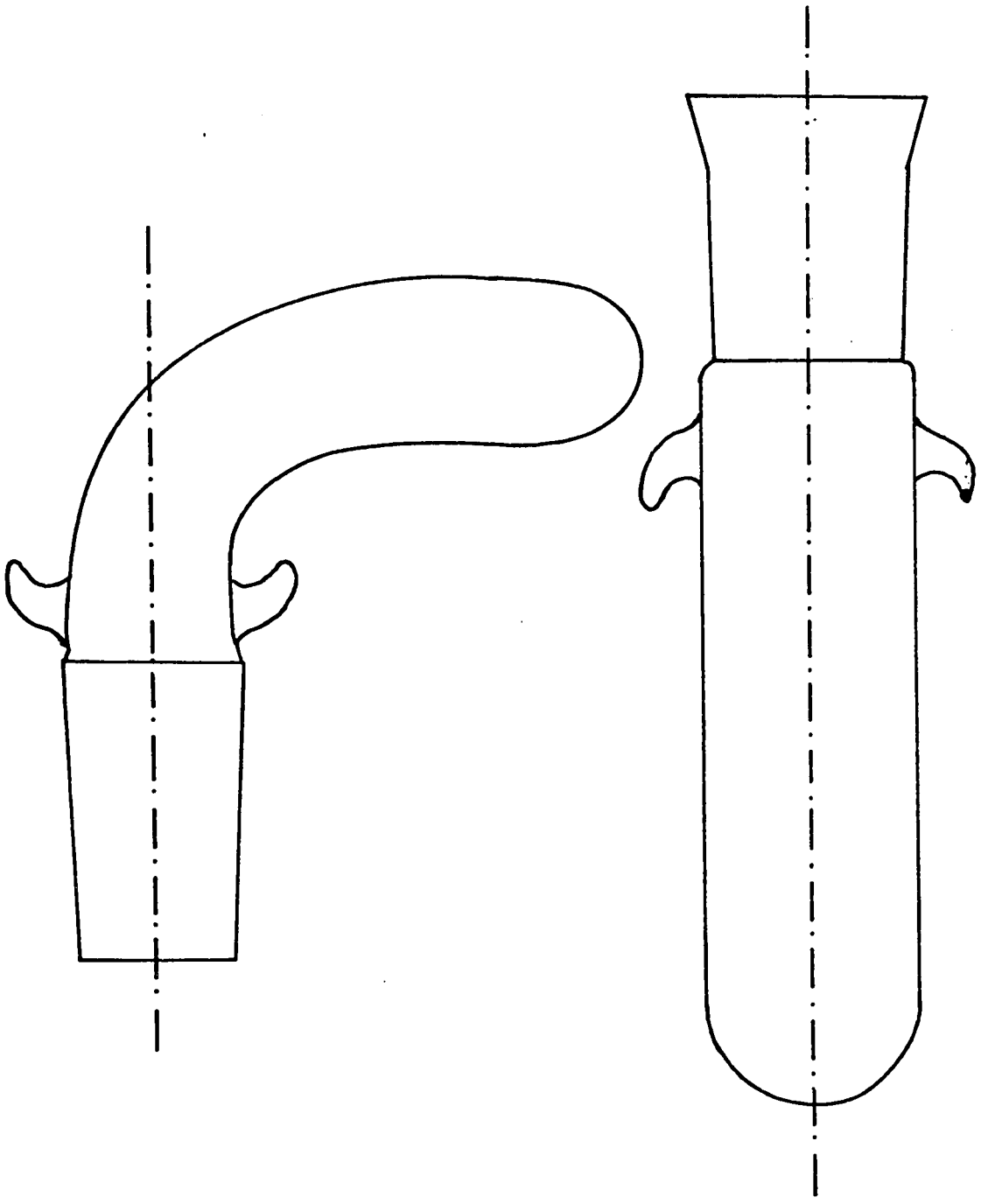


Fig. 4-1 Pyrex reaction tube with standard taper ground glass joints (Scale 1:1).

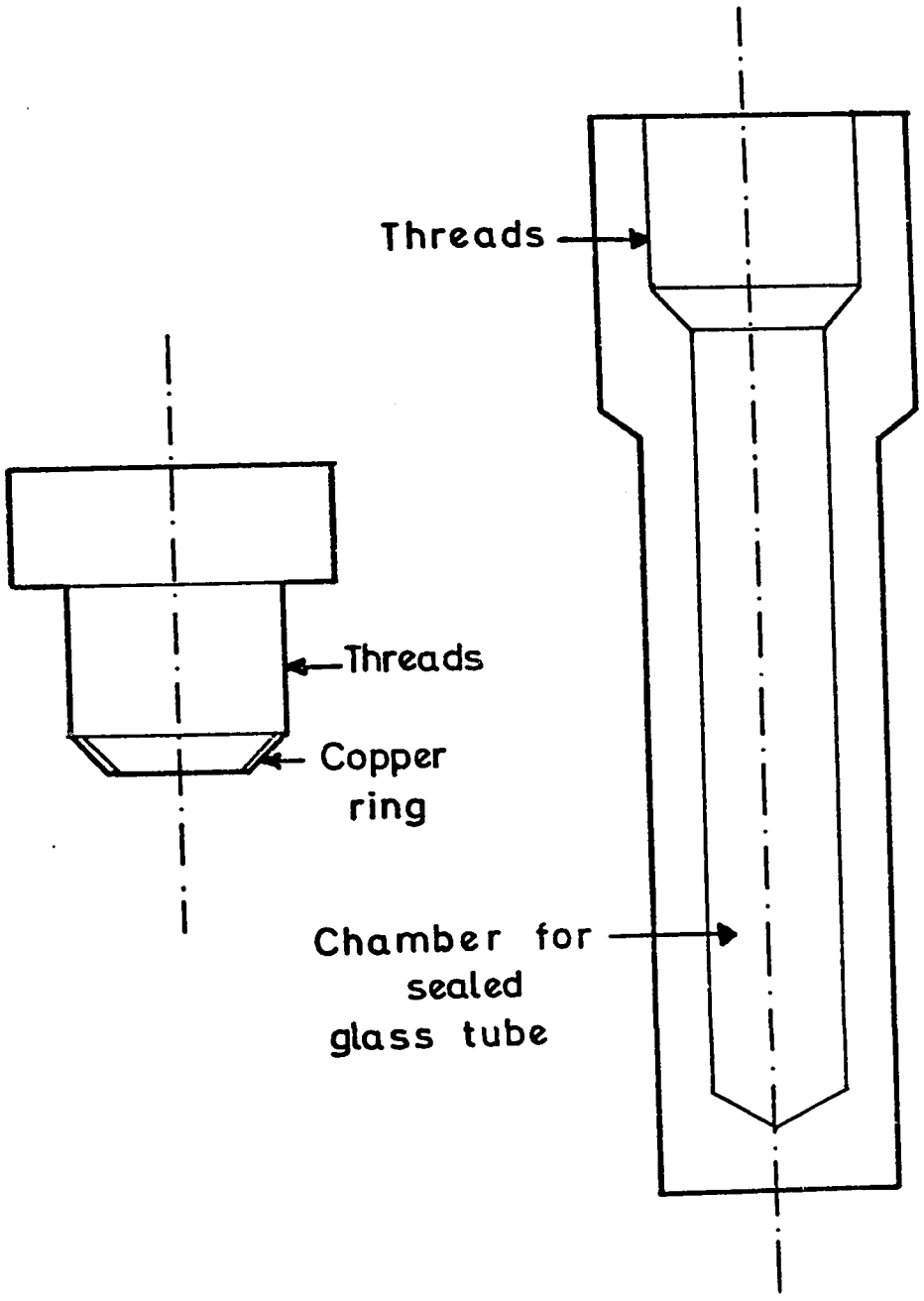


Fig. 4-2 The design of the steel bomb for high temperature experiments. The bomb can hold a 4" long fusion-sealed glass tube with 2 ml capacity (Scale 1:1).

The conical copper ring ensures the leak proof closing of the bomb. The thread had to be carefully lubricated. The best lubrication was obtained with a mixture of silicon lubricant and extra-fine, precision graphite powder. The bombs, which were tested to 300°C, reliably protected fusion-sealed glass tubes that were enclosed within them from breaking. It was found, however, that pyrex reacted with water at this high temperature. Qualitative analysis indicated the presence of a considerable amount of sodium and potassium in the distilled water after 2 days of reaction time. After 4 days of reaction at 300°C, both the inside and the outside of the pyrex tubes were coated with a white, amorphous, chalk-like material.

These investigations were carried out in a Blue M Power-O-Matic-60 constant temperature oven. The maximum attainable temperature was 325°C, $\pm$3°C. The oven was modified to hold 6 bombs or reaction tubes on a spindle. The spindle was rotated at 1.5 RPM to agitate the reaction mixture.

(ii) Potassium Precipitation Method

In order to investigate the use of the precipitation technique of Scott et al. (1960, Reed and Scott, 1966), experiments were carried out with the KG-3 muscovite. The exchange solution

contained 2N LiCl, 0.01N NaTPB and 0.01M disodium EDTA as the stabilizer of the precipitating agent. To ensure complete precipitation and to repress the solubility of KTPB, a tenfold excess of the NaTPB was used.

Five 50 mg samples were mixed with 100 mls solution in polyethylene bottles. The bottles were placed into a water bath and kept at $50^{o}C \pm 0.25^{o}C$. The samples were removed at intervals of integer multiples of $(days)^{\frac{1}{2}}$, up to 25 days and quenched, to stop the reaction. First the solution was filtered off, then the two solids were separated for chemical analysis. Because the potassium compound is soluble in acetone, and mica readsorbs the dissolved potassium readily, a 60% (v/v) acetone-water - 0.5N NH_4Cl solution was used. The potassium salt was dissolved by shaking the two solids in 200 ml solution. The muscovite was separated and washed reagent free. The muscovite samples were dissolved and analysed for K^+, Na^+ and Li^+ in the usual manner.

Because the exchanging solution contained two cations and three compounds, a parallel experiment was also carried out in which only LiCl was used. The samples obtained from these tests were also analysed for K^+, Na^+ and Li^+.

The chemical analysis showed that in the course of both experiments the sodium concentration of muscovite remained approximately constant. The results of the chemical analysis also show (Fig. 4-3) that in the presence of the precipitating agent, the lithium concentration in muscovite increased only by 0.6 meq/100g (curve a), although after 25 days, the potassium concentration decreased by about 20 meq/100g (curve b). In the parallel experiment on the other hand, the lithium exchanged with potassium readily and the exchange occurred in a 1:1 ratio (curves c and d). The stippled portions of the curves originate at the lithium and potassium concentrations of the untreated muscovite.

The location of the two sets of curves in Fig. 4-3 is unexpected. The precipitating agent in the solution was expected to promote the ion exchange to a greater degree than it could occur in the parallel experiment. This observation may indicate either that the experimental method is not fully satisfactory or that the inherent properties of the muscovite are not yet sufficiently understood. The experimental method has been fully tested within the purpose of the present work, but further refinements of the technique are needed to clarify the apparent

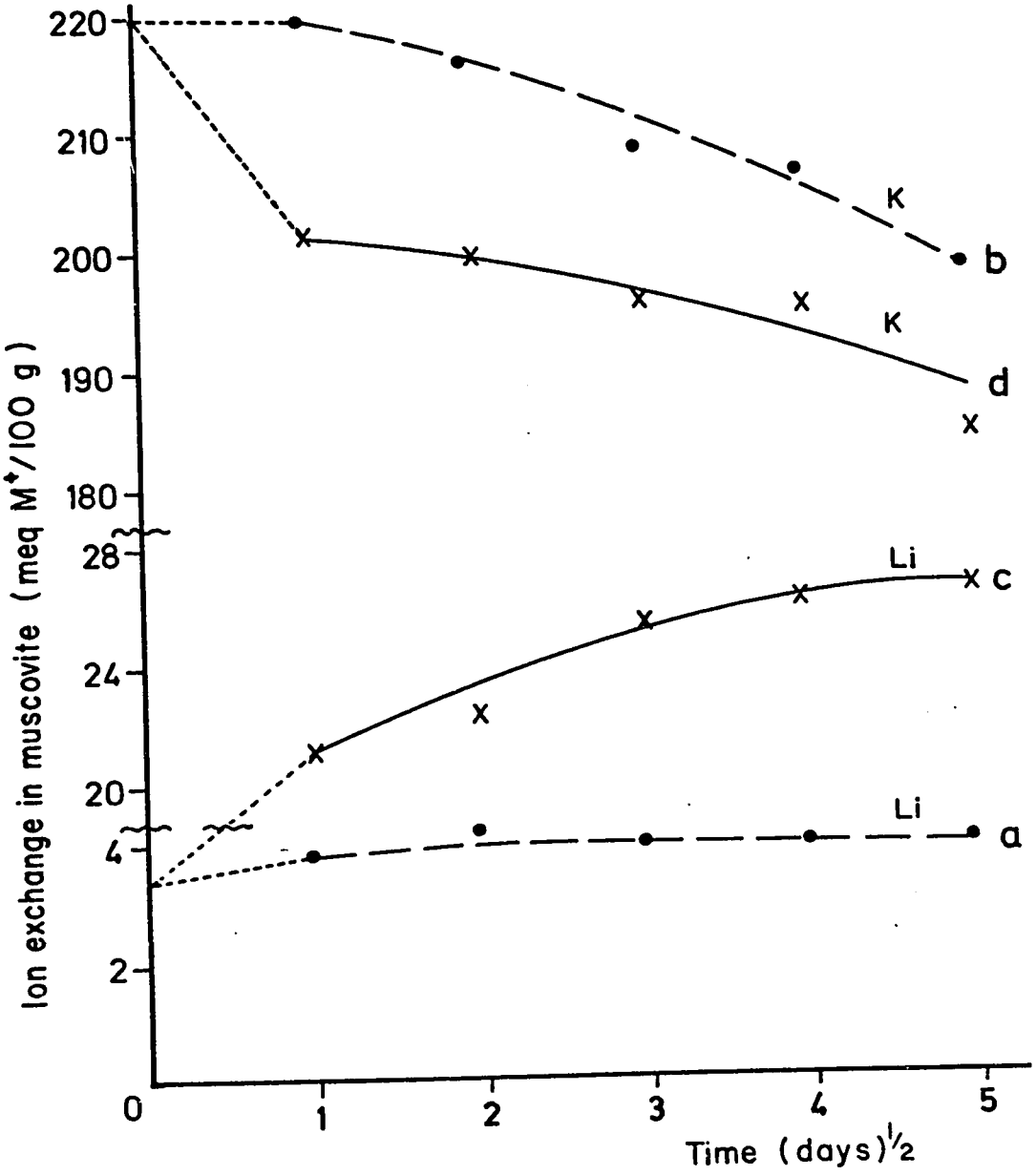


Fig. 4-3 Exchange of lithium for potassium in muscovite at 50°C. Dashed lines a and b: with NaTPB; solid lines c and d: without NaTPB.

contradiction indicated by the results.

(iii) Successive Extraction Method

In mica, barium exchanges with potassium relatively easily. Therefore, 400 ml 0.2N $BaCl_2 \cdot 2H_2O$ solutions were used with 0.5 g sample. In addition, to avoid the effects of crushing, micro-crystalline (M.7) muscovite was used. The experiment was carried out at 92°C ±1°C in an Eberbach Water Bath Shaker, model 6250. Because of the high temperature, a polypropylene bottle was used and the shaker bath was filled with distilled water.

The reaction was stopped by quenching after approximately 24 hours and the solution was separated by filtering. The filtrate was saved for later chemical analysis and the muscovite was returned into the reaction vessel which was filled with fresh barium solution. This procedure was repeated 12 times.

After each 6 runs the muscovite was prepared for X-ray diffraction analysis by dispersing about 20 mg dry powder in 1 ml distilled water. The dispersion was deposited on glass slide and dried at room temperature. In this manner uniformly oriented specimens were obtained.

The X-ray diffraction charts are shown in Fig. 4-4. Curves a and d were obtained by Fe/Mn

Kα, curve b by Cu/Ni Kα and curve c by Co/Fe Kα radiation. The charts for samples a, b and d were obtained from the X-ray laboratory of the Geology Department of the University of Ottawa, while chart c was prepared at the Soil Research Institute of the Department of Agriculture. In all cases Philips X-ray diffractometers were used.

The 002 basal spacing of the untreated muscovite (Fig. 4-4, curve a) expanded to 12.2Å in consequence of the experiment (curves b and c) indicating the formation of a new phase. The progress of the reaction can be estimated from the intensity ratios of the expanded/original peaks. It was estimated that each 6 successive extractions removed about 20-25% of the total potassium content. It is to be noted that when the sample was kept at 500°C for 2 hours, the expanded lattice collapsed almost completely (curve d).

The filtrates were analysed for potassium and the analytical results are presented in Table 4-1 and Fig. 4-5. It can be seen from column 5 of Table 4-1 that the first 6 extractions removed 28.4% of the total potassium from muscovite, and that the total depletion for all 12 extractions was 47.1%. The results of the muscovite analysis showed that the original 7.96% K concentration was reduced to 4.0%

Fig. 4-4 X-ray diffraction charts of
a) original M.7 muscovite;
b) M.7 treated 6 times with Ba^{++};
c) M.7 treated 12 times with Ba^{++};
d) as c, after heating at 500°C for 2 hours.

(Chart speed for curves a and b 10 mm/min.; for curves c and d 20 mm/min.).

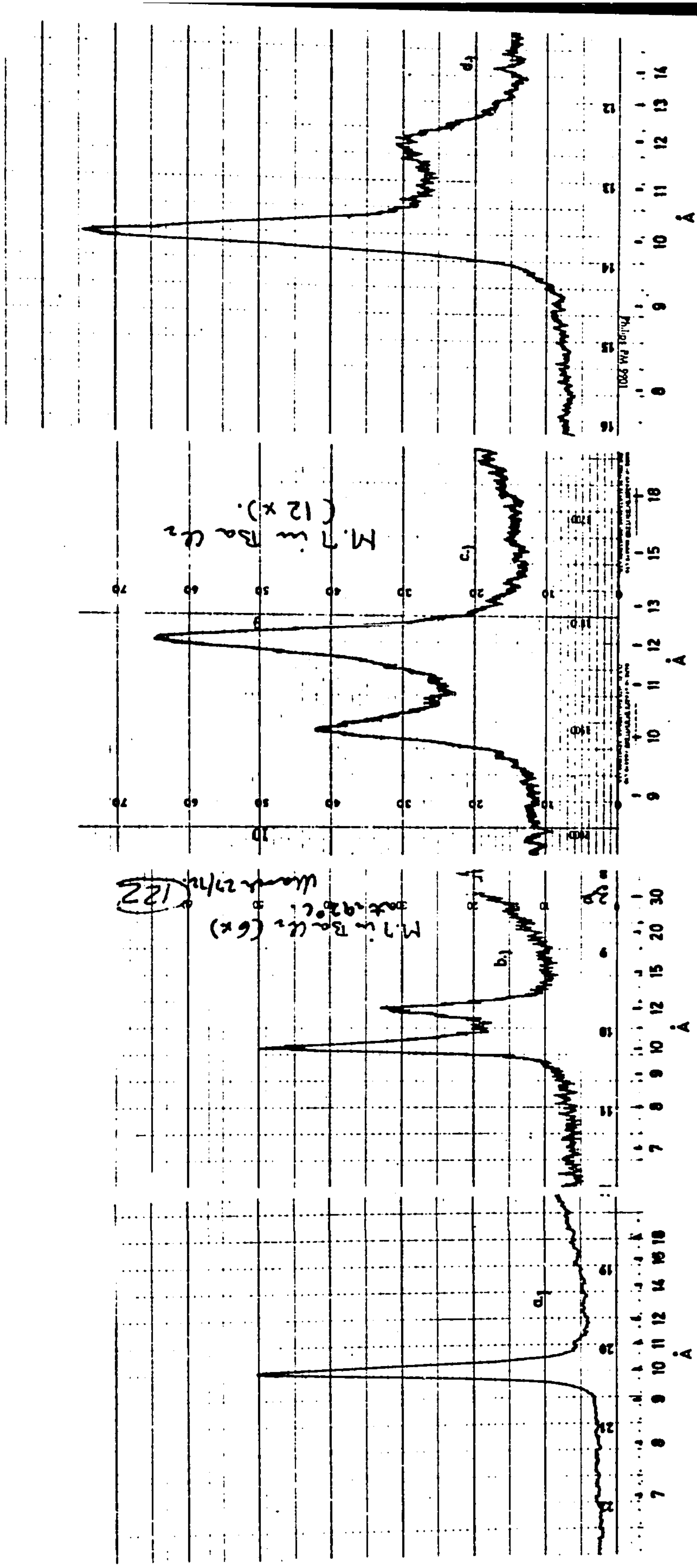


Table 4-1

Potassium Concentrations in 12 Successive Extracting Solutions

Sol'n No	K ppm found	K mg removed	K % of total	K % cumulative
1	5.45	2.18	5.5	5.5
2	5.30	2.12	5.3	10.8
3	5.00	2.00	5.0	15.8
4	4.55	1.82	4.6	20.4
5	4.15	1.66	4.2	24.6
6	3.80	1.52	3.8	28.4
7	3.65	1.46	3.7	32.1
8	3.35	1.34	3.4	35.5
9	3.35	1.34	3.4	38.9
10	2.85	1.14	2.8	41.7
11	2.70	1.08	2.7	44.4
12	2.70	1.08	2.7	47.1

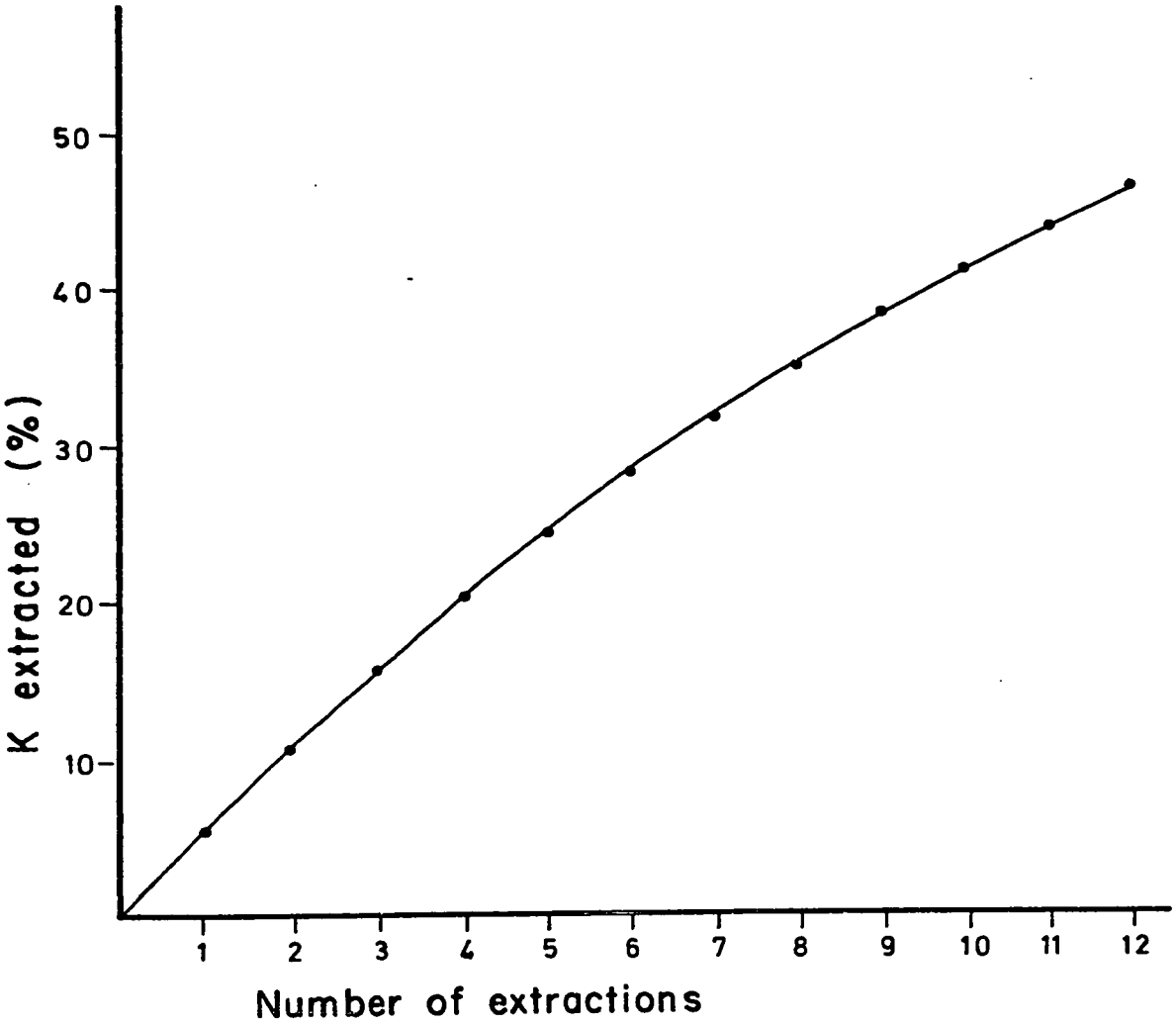


Fig. 4-5 Percent of total potassium removed from M.7 muscovite using 12 successive extracting solutions of 0.2 N $BaCl_2.2H_2O$.

The high tolerance shown by the muscovite toward potassium ion accumulation in the solution is unusual. Scott and Smith (1966) have carried out an experiment in which various amounts of muscovite samples were equilibrated in NaCl solutions. They have found that 4 ppm K^+ in the solution effectively prevented further ion exchange in muscovite (Fig. 4-6). The single point in Fig. 4-6 shows that the first extracting solution removed 5.5% potassium in the presence of 5.4 ppm K^+. The particle size of the materials used in the two experiments were probably comparable. The muscovite samples, used in the equilibrium experiment, were prepared by crushing in a hammer mill. This preparation method is expected to increase the reactivity of muscovite (Mackenzie and Milne, 1953). In the present experiment, fine-grained muscovite (M.7) was used and therefore mechanical crushing was not necessary. It has been suggested that although the particle size greatly effects the reactivity of the mica minerals, the reactivity is also a function of the layer charge of the original material. The mica used in the equilibrium experiment contained 247 meq K/100g, while the concentration of potassium in the M.7 muscovite was only 205 meq/100g. It is possible,

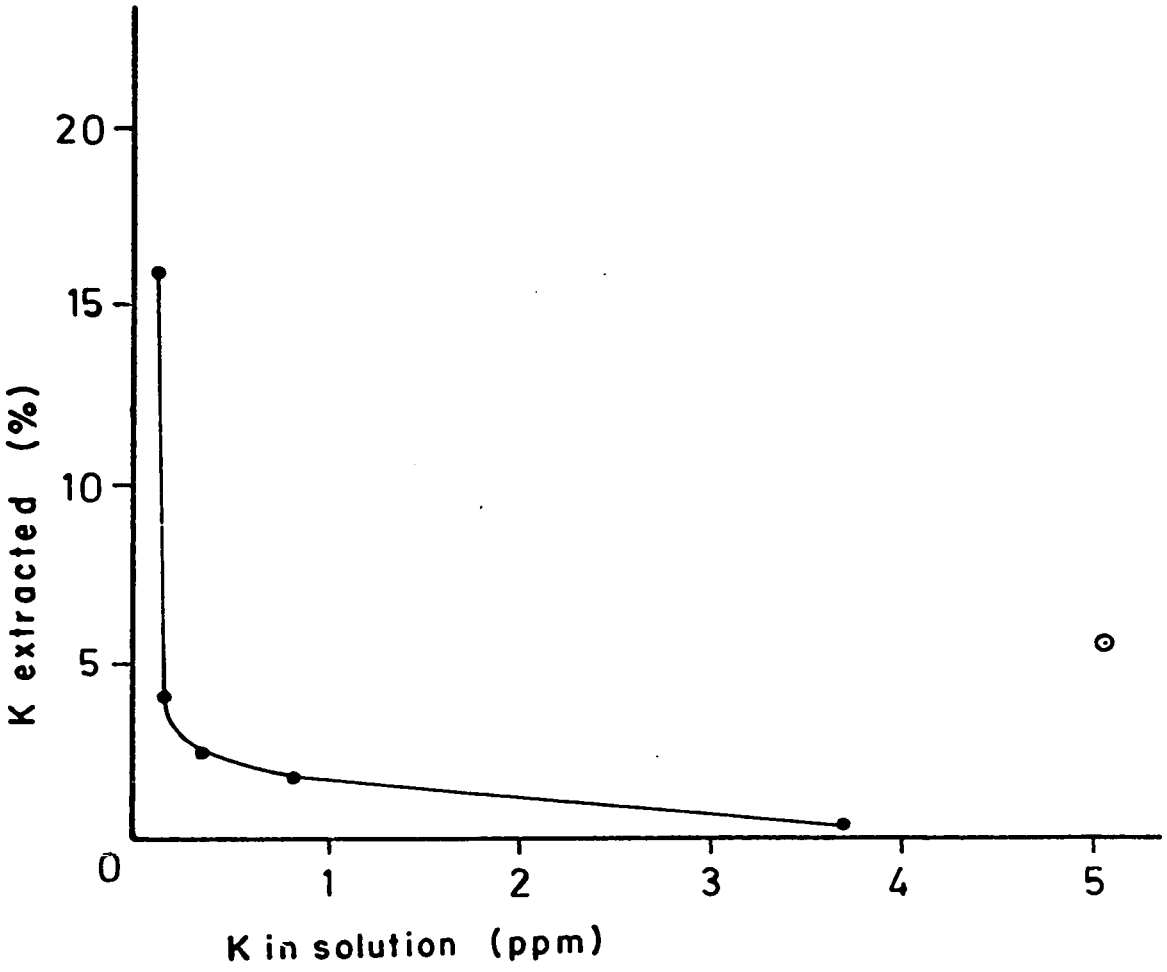


Fig. 4-6 Relationship between extracted potassium and K accumulation in the solution for 2 different muscovites. ● : equilibrium experiment with crushed muscovite (Scott and Smith, 1966); ⊙ : the first solution from the successive extraction experiment with uncrushed muscovite.

therefore, that the difference in behaviour is due to the difference in the layer charge of the two samples.

(iv) Extraction with Molten Lithium Nitrate

About 0.5 g of the M.7 muscovite was mixed with a large excess of salt in a fused silica dish. The mixture was heated to 300°C in a muffle furnace and kept at constant temperature for 20 hours. The dish was then removed from the furnace, cooled, and the $LiNO_3$ dissolved in distilled water. The solution was separated by filtering and the mica was dried before mixing with a fresh portion of the salt. Altogether, the muscovite was kept at 300°C for about 200 hours during which the reagent was renewed 4 times.

The mica was prepared for X-ray diffraction analysis after 200 hours reaction time. It was found that the first two lines had shifted from 10Å and 4.9Å to 12.4Å and 6.2Å, respectively, indicating the complete conversion of the K-muscovite to Li-vermiculite. The subsequent chemical analysis confirmed the completion of the ion exchange. The original potassium concentration of 205 meq/100g was reduced to 14 meq/100g, and the lithium content changed from nil to 210 meq Li/100g muscovite.

When the $LiNO_3$ was dissolved for the third time, it was found that the consistency of the mica became gel-like and as a consequence, filtration was not feasable any longer. The swelling effect of the high temperature was probably enhanced by the water employed to dissolve the salt. It was found by Bronson et al. (1959) that filtration became increasingly difficult even when the separations were carried out at 300°C. Although $LiNO_3$ dissolves in isopropyl alcohol, the end product does not seem to be suitable for further studies.

(v) High Solution-solid Ratio Method

It has been shown (Scott and Smith, 1966) that of the three potassium-bearing mica minerals,* phlogopite is the least sensitive toward potassium accumulation in the solution. Therefore, phlogopite was selected for the study of this method. The specimen was prepared by milling for 1 hour and the 44-105 μm size fraction was separated by dry sieving.

Two solution-solid ratios were compared. In addition, the relative replacing power of Na^+, Ba^{++} and Sr^{++} with the potassium in this mica was also compared. In one series (Set 1) 450 ml, and in the second (Set 2) 100 ml solutions with 0.1 g phlogopite were used. The experiment was carried

* (muscovite, phlogopite and biotite)

out in the shaker bath for about 80 hours, at 92°C.

The six samples were prepared for X-ray diffraction analysis as described before. The charts were obtained from the Soil Research Institute of the Department of Agriculture, using Philips X-ray diffractometer and Co/Fe Kα radiation. The X-ray patterns are shown in Fig. 4-7. The lattice spacing expanded by 2.1Å as the result of ion exchange in the large-volume sodium solution (curve a) and in both barium solutions (curves c and f). The broadening of the lines at the base to the right of the peaks also indicates ion exchange, but to a much lesser degree. The degrees of exchanges, estimated from the relative intensity ratios of the expanded/original peaks, are summarized in Table 4-2 for the 6 samples.

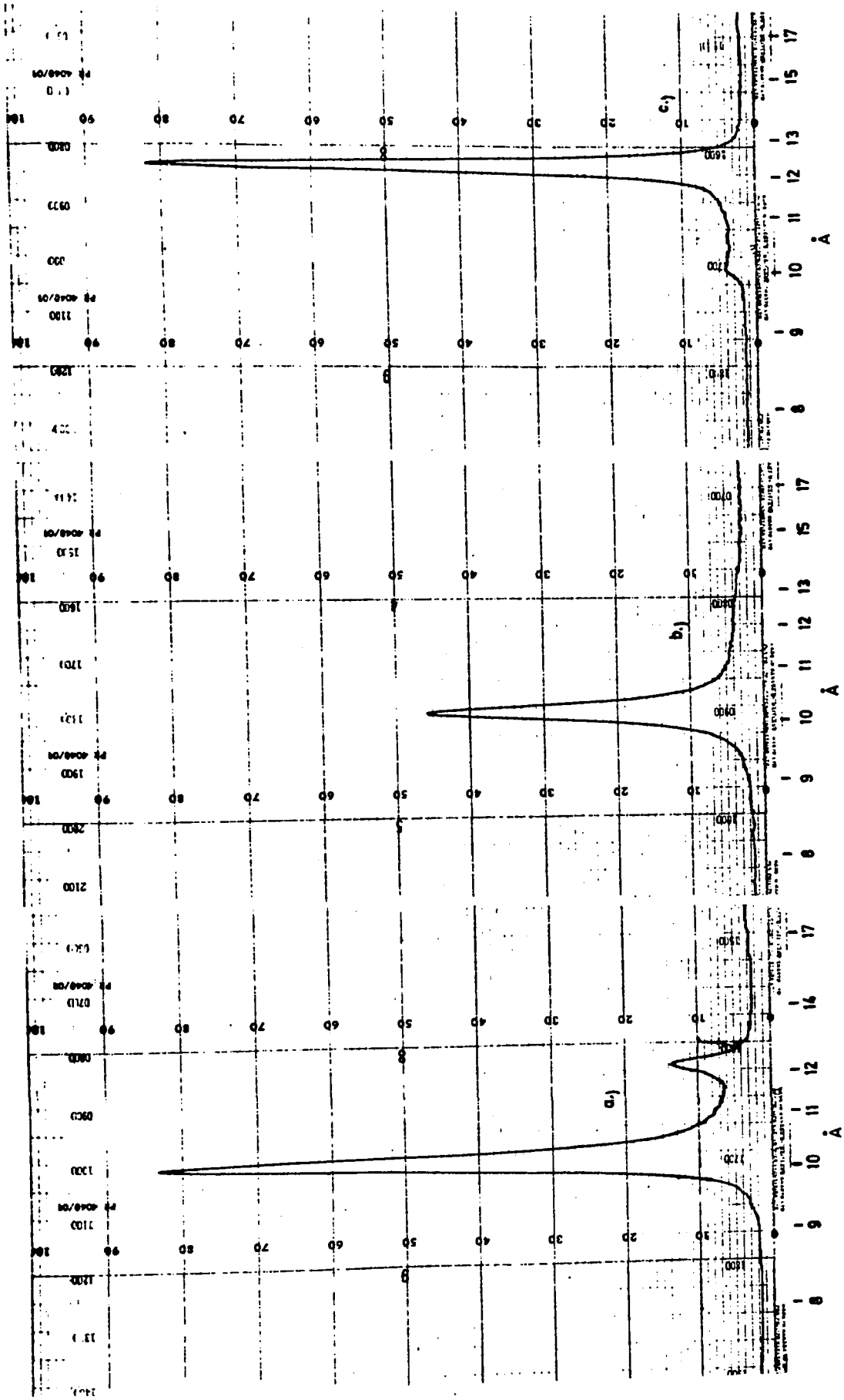
The results of the subsequent phlogopite chemical analyses are given in Table 4-3. The various cations exchanged with the potassium approximately as it was anticipated, although the exchange of barium with potassium in Set 1 is surprisingly high, considering the short reaction time.

It can be seen in Table 4-3 that potassium exchanges preferentially with barium. This effect is probably due to the relative sizes of the cations.

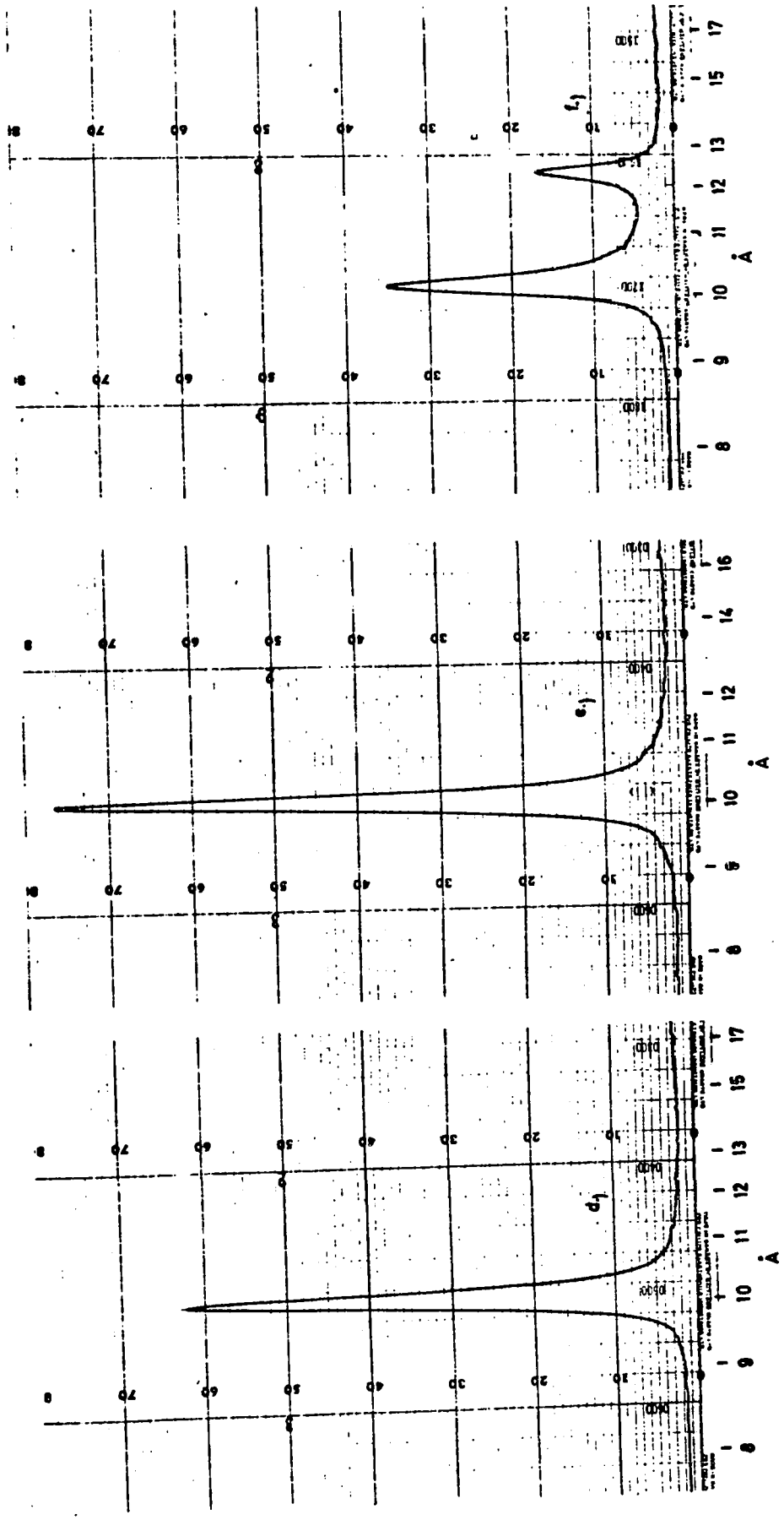
Fig. 4-7 X-ray diffraction charts of phlogopite.

A Solution volume 450 ml
a: 1.0N NaCl;
b: 1.0N $SrCl_2.6H_2O$;
c: 1.0N $BaCl_2.2H_2O$.

B Solution volume 100 ml
d: 1.0N NaCl;
e: 1.0N $SrCl_2.6H_2O$;
f: 1.0N $BaCl_2.2H_2O$.



A



B

Table 4-2

Estimated Degree of Ion Exchange in Phlogopite

Solution	Set 1 (large volume)	Set 2 (small volume)
NaCl	minor	slight
$SrCl_2$	slight	none ?
$BaCl_2$	major	minor

Table 4-3

Changes in Phlogopite Composition in Different Solutions at 92°C as a Function of Solution Volumes (meq cation/100g phlogopite)

	K	Na	Sr	Ba	K% removed
NaCl					
Set 1	171	57	-	-	21.5
Set 2	202	16	-	-	7.0
$SrCl_2$					
Set 1	192	-	33	-	12.0
Set 2	199	-	12	-	8.0
$BaCl_2$					
Set 1	53	-	-	168	76.0
Set 2	161	-	-	56	26.0
Original phlogopite	218	9	nil	nil	

Table 4-4 shows the valences and the Pauling ionic radii of the 5 cations considered in this study, as well as the hydrated radii. In general, the alkaline earth cations are hydrated to a lesser degree than the alkali cations, and, similarly to the behaviour of the Li group, the magnitude of hydration decreases with the increase of ionic size (Cotton and Wilkinson, 1962). The hydrated radii in Table 4-4 are for 6 coordination, and although the cations are in 12 coordination in the interlayer position of the mica, the trend in size change is evident. It is possible, that not only the ionic radius, but the hydrated radius of barium is also the closest to that of potassium. It may be concluded, therefore, that the size, rather than the valence of the exchanging cation is the more important factor of the ion exchange process in mica minerals.

The loss on ignition was determined before the samples were prepared for chemical analysis. The dried samples were heated over a gas flame to a dull red colour of the platinum crucible for 45 minutes, then cooled in a dessicator and weighed. Heating was repeated for periods of 30 minutes, until constant weight was obtained. The results are presented in Table 4-5.

Table 4-4

Valences and Radii of 5 Cations

	Valence number	Ionic radii Å	Hydrated radii Å
Li	1	0.60	3.40
Na	1	0.95	2.76
K	1	1.33	2.32
Sr	2	1.13	not known
Ba	2	1.35	not known

Table 4-5

Weight Loss of Phlogopite Ignited at ~700°C. (%)

	Na^+	Sr^{++}	Ba^{++}
Set 1	5.8	15.0	13.7
Set 2	2.8	4.0	1.7

CHAPTER 5

ION EXCHANGE EXPERIMENTS

The investigation of the various diffusion techniques lead to the conclusion that the high solution-solid ratio method should be used for ion exchange measurements. Mixtures of 0.1 g phlogopite powder and 210 ml, 1 normal barium solution were used. The experiment was carried out in the shaker bath at three different temperatures and the samples were removed according to the schedule shown in Table 5-1. In all cases the reaction was stopped by quenching in an ice bath. The solid was separated from the solution in a Millipore suction filtering apparatus with Duralon filter discs of 1 μm pore size. The filtrates and washings were collected for the subsequent potassium analysis.

Each sample was prepared for X-ray diffraction analysis in the usual manner. The X-ray work was carried out at the Geology Department of this University, using Fe/Mn Kα radiation. It was found that the 10Å basal spacing of the samples expanded as shown in Table 5-2. The intensities of the expanded peaks were irregular at the two lower temperatures. On the other hand, at 80°C the relative

Table 5-1

Reaction Times of the Ion Exchange Experiments at 40°C, 60°C and 80°C

T = 40°C		T = 60°C		T = 80°C	
Sample number	Reaction time (hrs)	Sample number	Reaction time (hrs)	Sample number	Reaction time (hrs)
1-40	1.5	1-60	1.5	1-80	0.5
2-40	6.25	2-60	6.25	2-80	1.5
3-40	10	3-60	16	3-80	3.25
4-40	16	4-60	49	4-80	6.25
5-40	49	5-60	100	5-80	10
6-40	100	6-60	196	6-80	16
		7-60	289	7-80	49
				8-80	100

Table 5-2

Expansion of Phlogopite

Test temperature °C	Expansion Å	Number of Samples
40	1	6
60	2.3	7
80	2.3	8

intensity ratios of the 12.3Å/10Å peaks increased with the reaction time as shown in Table 5-3. Two of these samples, 5-80 and 8-80, were then placed in a muffle furnace and kept at 500°C for 2 hours. The subsequent X-ray analysis showed that the pronounced 12.3Å expansion in sample 5-80 (Fig. 5-1, curve a) collapsed almost completely (curve b). The superlattice of sample 8-80 also collapsed, but a very small, new peak appeared at 11Å (curve d).

For the chemical analysis of the extracting solutions, the filtrates and washings were combined and reduced to the original, experimental volume. The analysis was carried out for potassium only. Because of the high density of the 1 normal Ba^{++} solution, the reference solutions were prepared in the same matrix. The results of the analysis are given in Table 5-4.

The tolerance of phlogopite toward potassium ion in the solution has been mentioned above. In Fig. 5-2, the increase of the potassium concentration in the extracting solutions is shown for the three temperatures. (Data from Table 5-4, column 2). The maximum value of 13.2 ppm K at 80°C is still well below the critical value for this mineral (Scott and Smith, 1966).

Table 5-3

Relative Intensity Ratios of the Expanded/Original Peaks

Sample No	1-80	2-80	3-80	4-80	5-80	6-80	7-80	8-80
Reaction time (hr)	0.5	1.5	3.25	6.25	10	16	49	100
12.3Å/10Å	0.1	0.2	0.4	0.5	0.5	0.9	1.3	2.0

Fig. 5-1 X-ray diffraction charts of phlogopite in 1.0N $BaCl_2.2H_2O$ solution at 80°C.
a : sample 5-80, reaction time 10 hrs;
b : sample 5-80 kept at 500°C for 2 hrs;
c : sample 8-80, reaction time 100 hrs;
d : sample 8-80 kept at 500°C for 2 hrs.

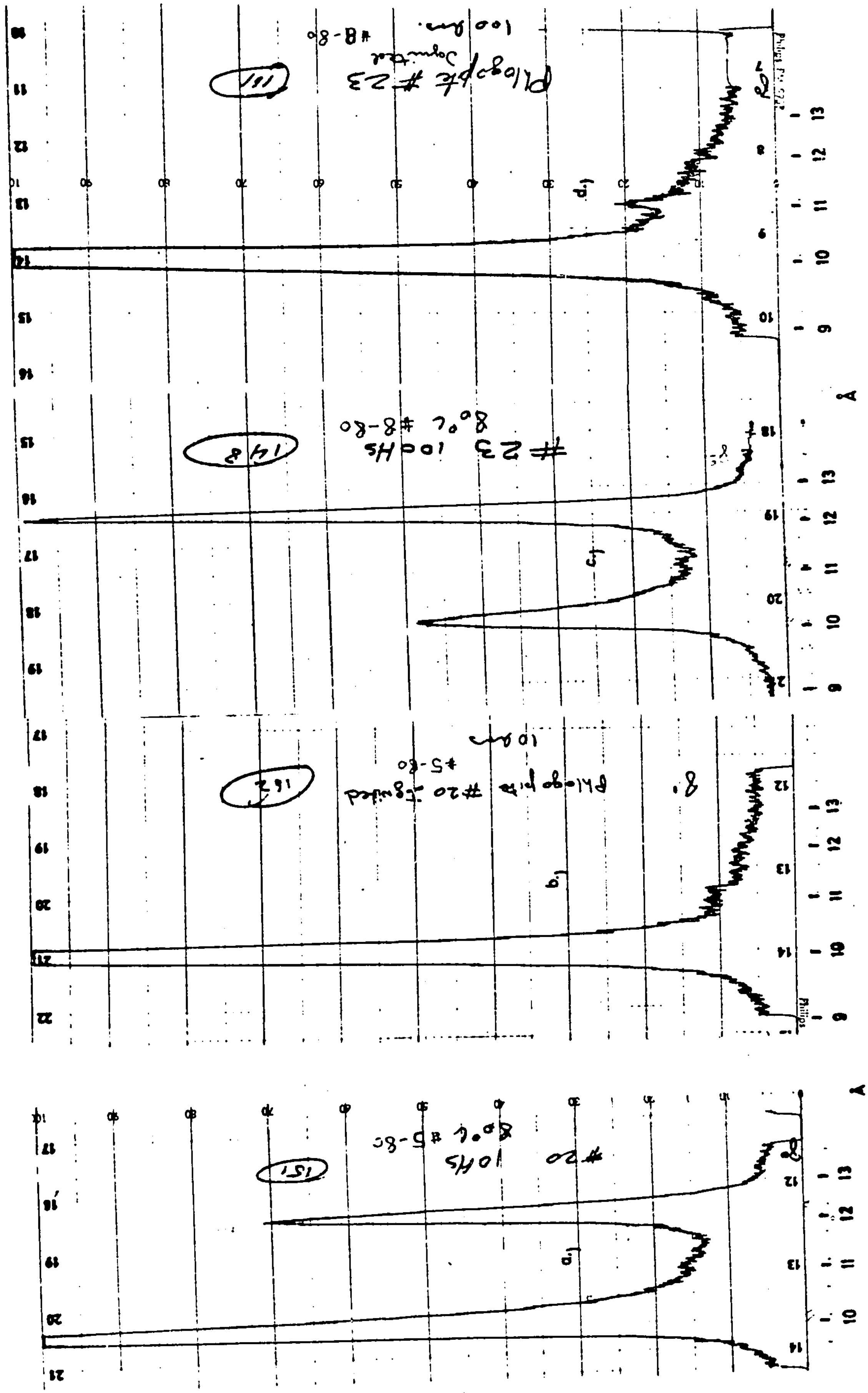

#23 100 Hs
80°C #8-80
#20 10 Hs
80°C #5-80

Table 5-4

Potassium Analysis of Extracting Solutions

Sample No	K ppm	K mg	% of total K removed	reaction time (hrs)
1-40	3.55	0.82	8.8	1.5
2-40	3.86	0.89	10.0	6.25
3-40	3.98	0.91	10.1	10
4-40	4.10	0.94	10.5	16
5-40	4.29	0.99	11.3	49
6-40	4.54	1.04	11.4	100
1-60	5.83	1.34	14.8	1.5
2-60	7.00	1.61	17.6	6.25
3-60	8.55	1.97	21.2	16
4-60	9.70	2.12	23.4	49
5-60	9.41	2.16	25.1	100
1-80	8.40	1.93	20.9	0.5
2-80	9.69	2.23	24.8	1.5
3-80	10.62	2.44	27.4	3.25
4-80	11.30	2.60	29.9	6.25
5-80	11.97	2.75	31.2	10
6-80	12.59	2.90	32.5	16
7-80	13.21	3.04	34.2	49
8-80	14.01	3.22	35.5	100

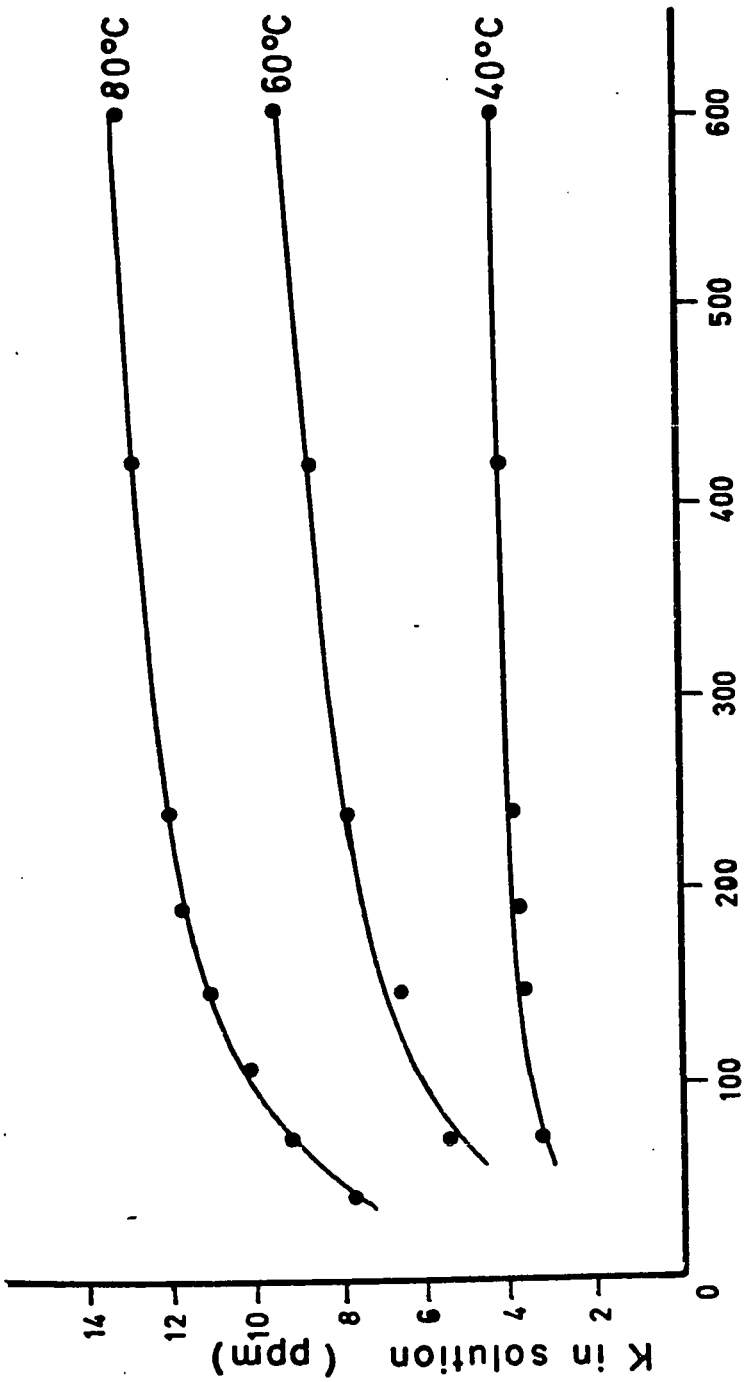


Fig. 5-2 Variation of potassium ion concentration in 1N $BaCl_2.2H_2O$ solutions as a function of reaction time, at 40°C, 60°C and 80°C.

The progress of the ion exchange is shown in Fig. 5-3. Because the potassium ions are exposed on the surfaces and edges of the particles, these ions are removed relatively easily. Therefore, the initial exchange in Fig. 5-3 is high. As the ion exchange progresses, the potassium becomes less easily accessible, and the reaction has to slow down. The effect of increasing temperature on the ion exchange process is also demonstrated in Fig. 5-3.

The usual sample preparation technique, employed for the chemical analysis of silicate minerals, was not satisfactory and had to be modified. The repeated digestion with $HF-HClO_4$ did not always produce a clear solution. It is possible that in some samples BaF_2 or $KClO_4$ precipitated. To correct this effect the samples were treated with hot concentrated HCl. After the excess acid was evaporated, a clear solution was obtained. The phlogopite samples were analysed for potassium and barium, along with the appropriate reagent blanks. The analytical results are given in Table 5-5. As shown in column 4, the layer charge remained almost unchanged. It is possible that during the experiment some of the divalent iron oxidized to the trivalent state, changing the net charge of the mica. This was

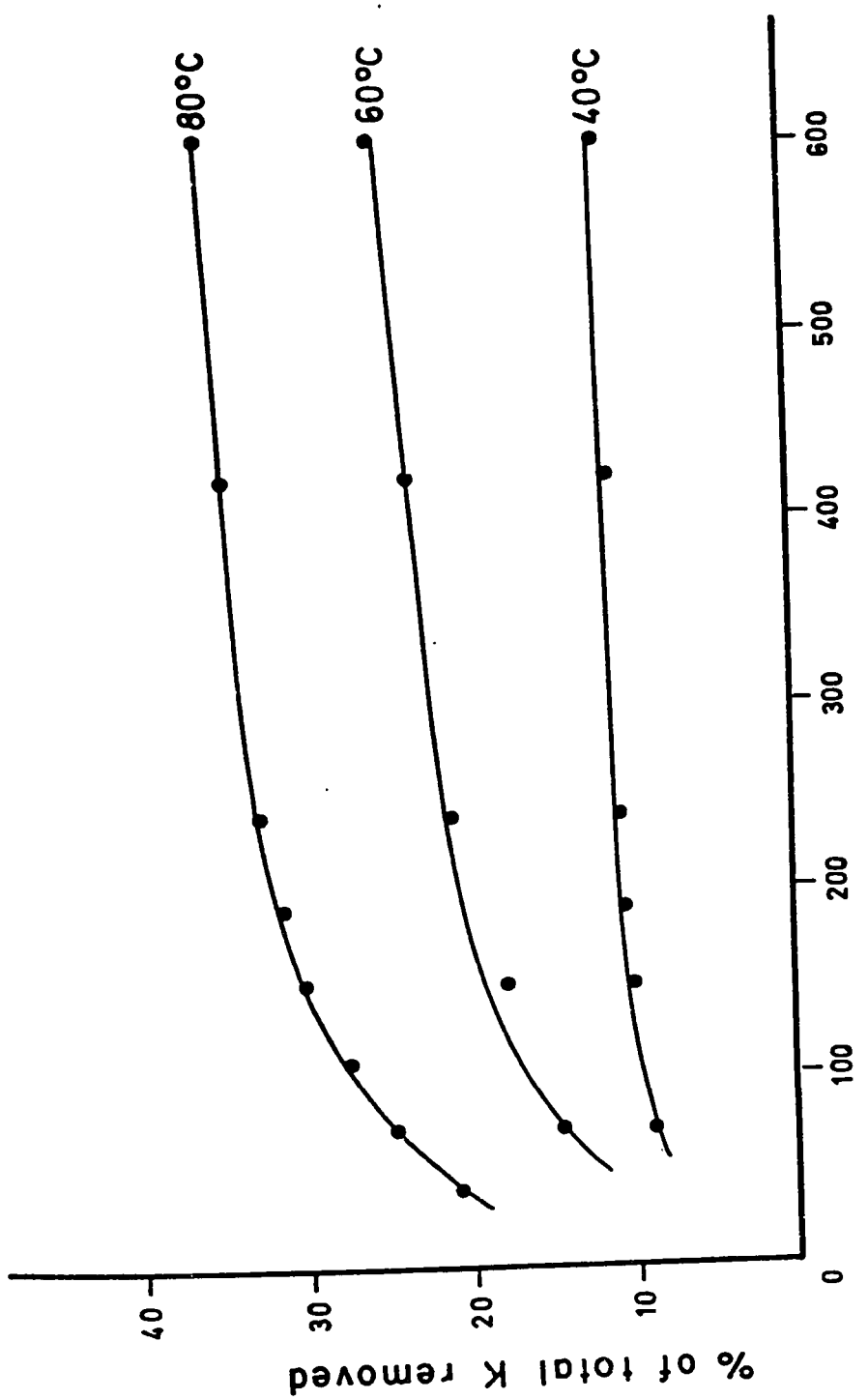


Fig. 5-3 Percent of the total potassium extracted from phlogopite in 1N $BaCl_2.2H_2O$ solutions at 40°C, 60°C and 80°C.

Table 5-5

Potassium and Barium Analysis of Exchanged Phlogopite (meq cation/100g phlogopite)

Sample No	K	Ba	K+Ba *	reaction time (hrs)
1-40	201	23.4	224	1.5
2-40	201	25.3	226	6.25
3-40	200	26.6	226	10
4-40	201	28.8	229	16
5-40	195	29.1	224	49
6-40	199	30.3	229	100
1-60	186	35.4	221	1.5
2-60	181	41.3	222	6.25
3-60	170	45.7	216	16
4-60	169	50.5	220	49
5-60	163	52.1	215	100
1-80	173	48.0	221	0.5
2-80	163	58.0	221	1.5
3-80	155	64.0	219	3.25
4-80	147	69.0	216	6.25
5-80	148	71.2	219	10
6-80	142	75.7	218	16
7-80	138	79.7	218	49
8-80	135	80.4	215	100

* 219 meq K/100g in original mica

not investigated however in the present study.

From the analytical results of the experiment, diffusion coefficients have been calculated for phlogopite. The details of the calculation and the results will be discussed in Chapter 6.

CHAPTER 6

THE THEORETICAL ANALYSIS OF THE DIFFUSION MECHANISM

During natural and induced weathering phlogopite alters to vermiculite. Because only the macroscopic changes can be measured in the experiments, to obtain information on the associated atomic processes, a theoretical analysis has to be carried out. Using diffusion theory for the analysis of the experimental results, the microscopic processes can be understood. While this is true in principle, a full study may be, and very often is, extremely complex. It is seldom that the rate controlling process is simple and consists only of a single, elementary step. In general, the direct evaluation of the experimental results provides an apparent diffusion coefficient D_a which, in case of a single mechanism, is identical to the physical, true diffusion coefficient. When the rate controlling mechanism is complex, the individual physical diffusion coefficients D_i can be evaluated from D_a only after the diffusion kinetics have been fully explored.

In phlogopite, no diffusion takes place in the direction parallel to the c axis and the diffusion process has a radial symmetry. Therefore,

the diffusion equation for phlogopite powder is (Crank, 1953):

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left(rD_a \frac{\partial C}{\partial r} \right) \quad - - - - - - - - [1]$$

where

C = solute concentration

t = time

r = radial coordinate

D_a = apparent diffusion coefficent.

Initially, inside the particle the solute concentration is zero, that is

$$\text{at} \quad t = 0 \quad \text{and} \quad 0 < r < a, \quad C^s_{Ba} = 0,$$

where a is the particle radius. During the experiments, as described in Chapter 5, the solution is well stirred and the barium concentration in the solution, C^l_{Ba} remains constant at the surface of the particle. Therefore, provided the loss of solute from the solution is negligibly small

$$\text{at} \quad t \geq 0 \qquad C^l_{Ba} = C_0.$$

Crank (1953) has shown that the solution of the differential equation (Eq. [1]) for the above conditions leads to the following measurable ratio between the amount of solute in the solid M_t at

time t, and at infinite time M_∞

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

In Eq. [2], the q_n's are the positive, non-zero roots of the Bessel function and α is the ratio of the amounts of solute in the liquid and in the solid, calculated from

$$\alpha = \frac{AC_\infty^l}{\pi a^2 C_\infty^s} \quad \text{- [3]}$$

where

A = volume of solution cylinder of unit height

πa^2 = volume of solid cylinder of unit height

C_∞^l = concentration of solute left in the liquid at infinite time

C_∞^s = concentration of solute in the solid at infinite time.

The numerical evaluation of D_a from Eq.[2] is inconvenient and therefore Crank (1953) developed a semi-graphical method. In Fig. 6-1, a family of curves is shown which define $(D_a t/a^2)^{\frac{1}{2}}$ in terms of

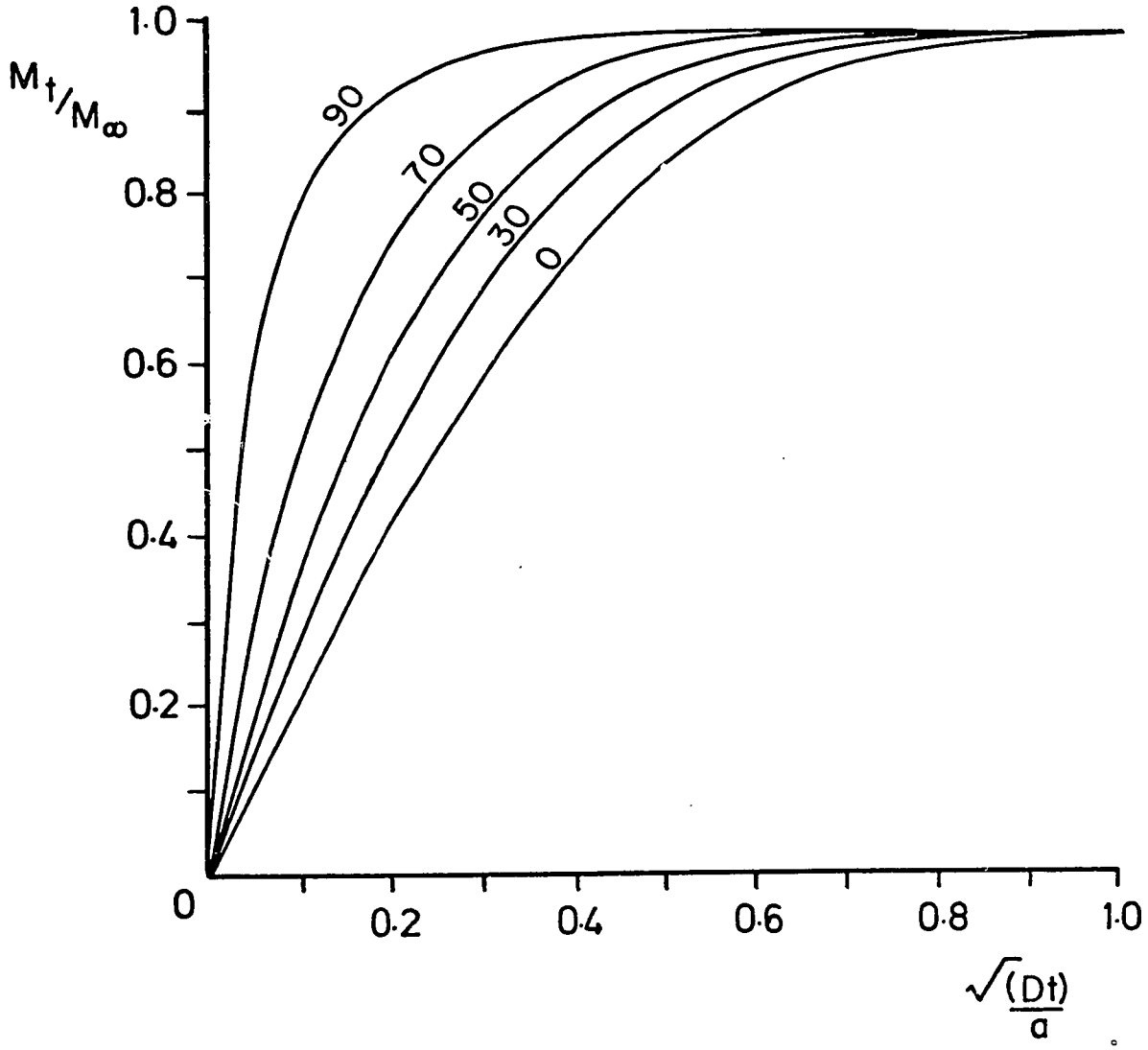


Fig. 6-1 Uptake of solute by a cylinder from a stirred solution of limited volume. Numbers on curves show percentages of total solute finally taken up by cylinder (Crank, 1953).

the experimentally determined M_t/M_∞ ratios. The curves have been calculated for five values of the final fractional solute uptake, M_∞/AC_o, where AC_o is the amount of solute in the liquid at $t = 0$. The ratios, expressed in percentages, are given at the corresponding curves. Because at the experimental conditions

$$\frac{M_\infty}{AC_o} = 0.001,$$

(Appendix I), the zero fractional uptake curve was used for the calculation of the apparent diffusion coefficient D_a. In Table 6-1, the calculated values of D_a (column 6) for the corresponding, experimental M_t/M_∞ ratios (column 3) are given. In the calculation,

$$M_\infty = 15.1 \text{ mg Ba},$$

the maximum amount of barium content in 100 mg phlogopite and

$$a = 9.7 \times 10^{-4} \text{ cm}$$

were used. The radius a is the average of 230 particle measurements.

Table 6-1 clearly demonstrates that the apparent diffusion coefficient is not constant but decreases with increasing time. When D_a is not independent of time, an approximate apparent activation energy can be calculated directly from

Table 6-1

Apparent Diffusion Coefficients of Barium in Phlogopite at 40°C, 60°C and 80°C

Sample No	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 $cm^2 sec^{-1}$
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}
6-60	3.61	0.239	0.115	840	1.77×10^{-14}
7-60	4.08	0.270	0.130	1020	1.54×10^{-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}

rate theory (Glasstone, Laidler and Eyring, 1941). The apparent diffusion coefficient is then described as

$$D_a = \beta\lambda^2 \frac{kT}{h} \frac{Q^{\neq}}{Q} \exp\left(-\frac{\Delta Ea}{RT}\right) \text{ - - - - - - - - - - - [4]}$$

where

β = a geometrical factor, usually $0.1 < \beta < 1$.

λ = distance between two successive equilibrium positions

kT/h = a frequency factor with k = Boltzmann constant, h = Planck constant and T in ^{o}K,

$Q^{\neq}/Q$ = partition function ratio $\simeq$ 1.

From Eq. [4] the approximate apparent activation energies were determined for each test temperature. The calculated values and their variations are shown in Table 6-2.

From penetration rate measurements in phlogopite and biotite flakes, Rausell-Colom et al. (1965) found that the potassium-barium exchange activation energies were in the range of 10,700-11,100 cal/mole. It was also indicated, as found in the

Table 6-2

Approximate Apparent Activation Energies at 40°C, 60°C and 80°C

D_a (cm^2 sec^{-1})	T (°K)	$\frac{\Delta E_a}{RT}$	ΔE_a (cal $mole^{-1}$)	variation (%)
6.14×10^{-14}	313	25.05	15,524 ± 1,124	7.2
8.03×10^{-14}	333	24.84	16,378 ± 1,374	8.4
8.25×10^{-13}	353	22.57	15,775 ± 1,474	9.3

present study as well, that the apparent diffusion coefficient is time dependent.

CONCLUSIONS

Metamorphism, diagenesis, hydrothermal alteration, weathering, soil formation and, to some extent, magmatic differentiation are complex chemical reactions on a large scale. Because of the complexity of these processes, the theoretical analysis of any experimental result is forbidding, if not impossible. Without the separation of the many variables which influence the reactions, the experimental results can be meaningless. In order to obtain meaningful results, the complex processes have to be simplified and reduced to a small scale which can be reproduced in the laboratory. In the experiment of this study, as described in Chapter 5, the multicomponent system present in natural weathering (or in hydrothermal alteration), was reduced to the two-component system of a single mica and a single cation (in aqueous solution) which excluded any interferences and side reactions. Even in this simple system, it was found (Table 6-1) that the rate controlling mechanism of the exchange process in phlogopite is not a single, elementary step. The X-ray diffraction analyses indicated that one of the associated mechanisms is

the diffusion of water into the phlogopite structure. The water molecules (or OH_3^+ ions, or both) interact with the diffusing cations both chemically and mechanically. It seems very possible therefore that the diffusion of water into the interlayer position has a very strong effect on the potassium-barium exchange in phlogopite. It is therefore suggested that the diffusivity of water in phlogopite and its interaction with the interlayer cations should be investigated and that the preliminary lattice expansion study, carried out in the present work (Appendix II), be further expanded.

REFERENCES

Angino, E.E. and Billings, G.K., 1967, Atomic Absorption Spectrometry in Geology. Elsevier, Amsterdam.

Barrer, R.M. and Hinds, L., 1953, Ion Exchange in Crystals of Analcite and Leucite. J. Chem. Soc. 386, pp. 1879-1888.

_____ and Raitt, J.S., 1954, Ion Exchange in Ultramarine. J. Chem. Soc. Part IV, pp. 4641-4651.

_____ and Rees, L.V.C., 1960, Self-diffusion of Alkali Metal Ions in Analcite. Trans. Farad. Soc. No. 449, Vol. 56, Part 5, pp. 709-721.

_____ and Sammon, D.C., 1955, Exchange Equilibria in Crystals of Chabazite. J. Chem. Soc. Part III, pp. 2838-2849.

Barshad, I., 1954, Cation Exchange in Micaceous Minerals: II. Replaceability of Ammonium and Potassium from Vermiculite, Biotite and Montmorillonite. Soil Sci. 78, pp. 57-76.

Bennett, H. and Hawley, W.G., 1965, Methods of Silicate Analysis. 2nd ed., Academic Press, London.

Bronson, R.D., Spain, J.M. and White, J.L., 1959, Potassium-depleted Muscovite. Part I. Preparation using Filtration Process for Treatment with Molten Lithium nitrate. Proc. 8th Natl. Conf. Clays Clay Min. pp. 39-43.

Brown, C.B., Bailey, G.W. and White, J.L., 1962, Removal of Reaction Products from Muscovite treated with Molten Lithium nitrate. Amer. Miner. 47, pp. 998-1000.

Brown, G. and Newman, A.C.D., 1970, Cation Exchange Properties of Micas III. Release of Potassium Sorbed by Potassium-depleted Micas. Clay Minerals, 8, pp. 273-278.

Cotton, F.A. and Wilkinson, G., 1962, Advanced Inorganic Chemistry. A Comprehensive Text. Interscience, New York.

Crank, J., 1956, The Mathematics of Diffusion. Clarendon Press, Oxford.

Deer, W.A., Howie, R.A. and Zussman, J., 1962, Rock Forming Minerals, Vol. 3, Sheet Silicates. Longmans, Green, London.

DeMumbrum, L.E., 1959, Exchangeable Potassium Levels in Vermiculite and K-depleted Micas, and

Implications Relative to Potassium Levels in Soils. Soil Sci. Soc. Amer. Proc. 23, pp. 192-194.

DeMumbrum, L.E., 1963, Conversion of Mica to Vermiculite by Potassium Removal. Soil Sci. 96, pp. 275-276.

Dolcater, D.L., Jackson, M.L. and Syers, J.K., 1972, Cation Exchange Selectivity in Mica and Vermiculite. Amer. Miner. 57, pp. 1823-1831.

Flaschka, H. and Barnard, A.J., 1960, Tetraphenylboron as an Analytical Reagent. Advan. Anal. Chem. Instr. (Reilley, C.N., editor), Interscience, New York, 1, pp. 1-117.

Gast, R.G. and Klobe, W.D., 1971, Sodium-Lithium Exchange Equilibria on Vermiculite at 25° and 50°C. Clays Clay Min. 19, 311-318.

Glasstone, S., Laidler, K.J. and Eyring, H., 1941, The Theory of Rate Processes. The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena. McGraw-Hill, New York.

Kretz, R., 1970, Variation in the Composition of Muscovite and Albite in a Pegmatite Dike near

Yellowknife. Can. J. of Earth Sci. 7, No. 5, pp. 1219-1235.

Le Roux, J. and Rich, C.I., 1969, Ion Selectivity of Micas as Influenced by Degree of Potassium Depletion. Soil Sci. Soc. Amer. Proc. 33, pp. 684-690.

Mackenzie, R.C. and Milne, A.A., 1953, The Effect of Grinding on Micas. I. Muscovite. Min. Mag. 30, pp. 178-185.

Mackintosh, E.E. and Lewis, D.G., 1968, Displacement of Potassium from Micas by Dodecylammonium chloride. Trans. 9th Int. Congr. Soil Sci. 2, pp. 695-703.

_____ and Greenland, D.J., 1971, Dodecylammonium-Mica Complexes-I Factors Affecting the Exchange Reaction. Clays Clay Min. 19, pp. 209-218.

Mortland, M.M., 1958, Kinetics of Potassium Release from Biotite. Soil Sci. Soc. Amer. Proc. 22, pp. 503-508.

Newman, A.C.D., 1967, Changes in Phlogopites during their Artificial Alteration. Clay Minerals, 7, pp. 215-227.

Newman, A.C.D., 1969, Cation Exchange Properties of Micas I. The Relation between Mica Composition and Potassium Exchange in Solutions of Different pH. Soil Sci. 20, pp. 357-373.

_____, 1970, The Synergetic Effect of Hydrogen Ions on the Cation Exchange of Potassium in Micas. Clay Minerals, 8, pp. 361-373.

_____ and Brown, G., 1966, Chemical Changes during the Alteration of Micas. Clay Minerals, 6, pp. 297-310.

Quirk, J.P. and Chute, J.H., 1968, Potassium Release from Mica-like Clay Minerals. Trans. 9th Int. Congr. Soil Sci. 2, pp. 671-681.

Rausell-Colom, J.A., Sweatman, T.R., Wells, C.B. and Norrish, K., 1965, Studies in the Artificial Weathering of Mica. Experimental Pedology, (Hallsworth, E.G. and Crawford, D.V., editors), Butterworths, London, pp. 40-72.

Reed, M.G. and Scott, A.D., 1962, Kinetics of Potassium Release from Biotite and Muscovite in Sodium Tetraphenylboron Solutions. Soil Sci. Soc. Amer. Proc. 26, pp. 437-440.

Reed, M.G. and Scott, A.D., 1966, Chemical Extraction of Potassium from Soils and Micaceous Minerals with Solutions Containing Sodium Tetraphenylboron: IV. Muscovite. Soil Sci. Soc. Amer. Proc. 30, pp. 185-188.

Graf von Reichenbach, H. and Rich, C.I., 1968, Preparation of Dioctahedral Vermiculites from Muscovite and Subsequent Exchange Properties. Trans. 9th Int, Congr. Soil Sci. 1, pp. 709-719.

Rich, C.I. and Black, W.R., 1964, Potassium Exchange as Affected by Cation Size, pH, and Mineral Structure. Soil Sci. 97, pp. 384-390.

Ross, G.J. and Kodama, H., 1970, Differential Release of Potassium from Interstratified Mica Clay Minerals as Related to Probable Differences in their Mica Layer Components. Clays Clay Min. 18, pp. 151-156.

Scott, A.D., 1968, Effect of Particle Size on Interlayer Potassium Exchange in Micas. Trans. 9th Int. Congr. Soil Sci. 2, pp. 649-659.

_____, Hunziker, R.R. and Hanway, J.J., 1960, Chemical Extraction of Potassium from Soils and Micaceous Minerals with Solutions Containing

Sodium Tetraphenylboron: I. Preliminary Experiments. Soil Sci. Soc. Amer. Proc. 24, pp. 191-194.

Scott, A.D. and Reed, M.G., 1961, Determination of the Precipitated Potassium in Sodium Tetraphenylboron-Micaceous Mineral Systems. Soil Sci. Soc. Amer. Proc. 24, pp. 326-327.

_____, 1962, Chemical Extraction of Potassium from Soils and Micaceous Minerals with Solutions Containing Sodium Tetraphenylboron: II. Biotite. Soil Sci. Soc. Amer. Proc. 26, pp. 41-45.

_____, 1965, Expansion of Potassium-depleted Muscovite. Proc. 13th Natl. Conf. Clays Clay Min. pp. 247-261.

Scott, A.D. and Smith, S.J., 1966, Susceptibility of Interlayer Potassium in Micas to Exchange with Sodium. Proc. 14th Natl. Conf. Clays Clay Min. pp. 69-81.

_____, 1967, Visible Changes in Macro Mica Particles that Occur with Potassium depletion. Proc. 15th Natl. Conf. Clays Clay

Min. pp. 357-373.

Scott, A.D. and Smith, S.J., 1968, Mechanism for Soil Potassium Release by Drying. Soil Sci. Soc. Amer. Proc. 32, pp. 443-444.

Thompson, T.D., Wentworth, S.A. and Brindley, G.W., 1967, Hydration States of an Expanded Phlogopite in Relation to Interlayer Cations. Clay Minerals, 7, pp. 43-49.

Tomita, Katsutoshi and Sudo, Toshio, 1971, Transformation of Sericite into an Interstratified Mineral. Clays Clay Min. 19, pp. 263-270.

Vedder, W., 1964, Correlation between Infrared Spectrum and Chemical Composition of Mica. Amer. Miner. 49, pp. 736-768.

Wells, C.B. and Norrish, K., 1968, Accelerated Rates of Release of Interlayer Potassium from Micas. Trans. 9th Int. Congr. Soil Sci. 2, pp. 683-694.

White, J.L., 1956, Reactions of Molten Salts with Layer-lattice Silicates. Proc. 4th Natl. Conf. Clays Clay Min. No. 456, pp. 133-146.

_____, 1958, Layer Charge and Interlamellar Expansion in a Muscovite. Proc. 5th Natl. Conf. Clays Clay Min. No. 566, pp. 289-294.

APPENDIX I

The Calculation of the Final Fractional Solute Uptake

According to the law of conservation of mass,

$$M_\infty + M_\infty \frac{AC_\infty^l}{\pi a^2 C_\infty^s} = AC_o \quad \text{- - - - - - - - - - - - - [I-1]}$$

where

M_∞ = amount of solute in the solid at infinite time

$M_\infty \frac{AC_\infty^l}{\pi a^2 C_\infty^s}$ = amount of solute left in the liquid at infinite time

AC_o = amount of solute in the liquid at t=0.

Recalling Eq. [3], Chapter 6

$$\frac{AC_\infty^l}{\pi a^2 C_\infty^s} = \alpha$$

and substituting α into Eq. [I-1]

$$M_\infty + M_\infty \alpha = AC_o$$

or

$$M_\infty (1+\alpha) = AC_o$$

and rearranging, we get

$$\frac{M_\infty}{AC_o} = \frac{1}{1+\alpha} \quad \text{- - - - - - - - - - - - - - - [I-2]}$$

The value of α was calculated from the experimental data in the following manner:

$\rho = 2.83 g/cm^3 \equiv$ the average density of phlogopite

$a = 9.7 \times 10^{-3}$ mm $\equiv$ average particle radius

$(a^2 = 94.0 \times 10^{-6} mm^2)$

$v = \pi a^2 h = 35.3 mm^3 \equiv$ volume of 0.100g phlogopite used

$h = v/\pi a^2 = \frac{35.3 \times 10^6}{3.14 \times 94.0} = \frac{35.3 \times 10^6}{295.2} = 1.19 \times 10^5$ mm

$\equiv$ height of particle cylinder

$V = 210 cm^3 = 2.1 \times 10^5 mm^3 \equiv$ volume of solution used

$H = h = 1.19 \times 10^5$ mm $\equiv$ height of solution cylinder

$A = V/H = \frac{2.1 \times 10^5 mm^3}{1.19 \times 10^5 mm} = 1.76 mm^2 \equiv$ area of solution cylinder of unit height

$$C_{\infty}^{l} = 0.07 \text{ mg Ba/mm}^3$$

$$C_{\infty}^{s} = 0.425 \text{ mg Ba/mm}^3.$$

Consequently,

$$\alpha = \frac{1.76 \times 0.07 \times 10^6}{3.14 \times 94.0 \times 0.425} = 980,$$

and from Eq. [I-2]

$$\frac{M_{\infty}}{AC_o} = \frac{1}{1+\alpha} = \frac{1}{981} = 0.001.$$

APPENDIX II

Preliminary Study of Lattice Expansion of Phlogopite in Distilled Water

Three phlogopite powder samples were placed in distilled water for different periods of time and at various temperatures. The reaction times and temperatures were as follows:

Sample 8-60 = 12½ days at 60°C

Sample 9-80 = 10 hours at 80°C

Sample KP = intermittently up to 4 months at ambient temperature.

The X-ray diffraction patterns of the first two samples revealed that the lattice expanded by 1Å. The expanded peaks were definite with very low intensities, which persisted in sample 9-80 even after it was kept at 500°C for 2 hours in the muffle furnace.

The first X-ray diffraction pattern of sample KP was taken after 59 days of reaction time. The sample was then heated to 500°C and kept at the temperature for 2 hours and, again for 24 hours. The X-ray analysis was repeated after each heat treatment.

The sample preparation for the X-ray analysis did not permit quantitative comparison of the peak intensities from sample to sample. It seems, however,

that the 1Å expansion observed on the first graph decreased in intensity but did not disappear entirely.

The experiment was continued with the same sample, but the "solution" was replaced with fresh distilled water about once every week. X-ray diffraction patterns were taken after 39 days and again after an additional 25 days of reaction time. The intensity of the 11Å peak appeared to increase, and did not diminish when the sample was kept at 500°C for 16 hours.

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