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REDISTRIBUTION OF POTASSIUM IN SYNTHETIC Micas
ANALOGOUS TO ILLITE

by

Keith Francis Thompson
B. Sc., University of Manchester, England (1955)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
June, 1966

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Submitted to the Department of Geology and Geophysics on May 24, 1966, in partial fulfillment of the requirement for the degree of Ph.D.

ABSTRACT

Several one-layer, monoclinic disordered micas were synthesized bearing an enrichment of beta-active potassium, $^{40}$K. The latter served to trace exchange of potassium upon treatment of the micas with aqueous solutions of potassium and sodium salts. The data allowed calculation of values of $D/a^2$ sec$^{-1}$, where $D$ equals the diffusion coefficient, and $a$ the radius of diffusion. The values were between $(1.41 \pm 0.45) \times 10^{-10}$ sec$^{-1}$ for one specimen at 100°C and $(9.44 \pm 1.37) \times 10^{-9}$ sec$^{-1}$ for a second at 450°C.

In a group of 13 such micas, X-ray diffraction study evidenced mixed-layering and b-axis disorder to varying degrees. A correlation between the degree of development of mixed-layering and the disorder was observed. A two-layer monoclinic illite, of natural occurrence, is suggested to exhibit both phenomena likewise.
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INTRODUCTION

An examination of the possibility of observing exchange of the interlayer potassium of synthetic illitic micas when treated in aqueous solutions of sodium or potassium chloride at moderately elevated temperatures was undertaken. Information was also sought upon the nature of potential mineralogical modifications of the micas.

The system studied pertains to one of the most abundant, and enduring sedimentary mineral groups, and the principal alkalis of sediments. Although behaviour in potassium solutions was principally considered, it will be indicated that the presence of relatively small quantities of potassium ion are capable of dominating the effects occurring in more complex solutions. There is an experimental analogy to processes of diagenesis. Conversely, by employing solutions of pure sodium salts, effects identical to those observed during the weathering of illites were produced (Cook and Rich, 1963), and the kinetics examined.

There is little published data concerning the diffusion or self diffusion of potassium in silicate minerals or synthetic products. In a glass, Ehrmann, de Billy, and Zarzycki (1961) obtained a value of $1.13 \times 10^{-13}$ cm$^2$ sec$^{-1}$ at 325°C - 375°C for potassium. Sendt (1964) measured values between 1.3 and $2.1 \times 10^{-9}$ cm$^2$ sec$^{-1}$ at 626°C in glasses of differing compositions. Barrer and Rees (1960) determined coefficients of self diffusion of alkali cations in a synthetic analcite at 25°C to 114°C. The values for potassium were $1.96 \times 10^{-17}$ at 25°C and $3.03 \times 10^{-15}$ cm$^2$ sec$^{-1}$ at 88°C. Verhoogen (1952) obtained $2.0 \times 10^{-10}$ cm$^2$ sec$^{-1}$ at 500°C for potassium diffusion in quartz, parallel to the c axis.
As far as the above writers provide data, the relevant values of D at temperatures of 100°C and 350°C employed in this work, have been calculated where necessary. They are presented in Table 2, Volume 3. Synthetic micas were utilized for numerous reasons. It is not possible to separate an illite fraction of uniform properties, completely free of potentially potassium-bearing contaminants, from natural materials by presently available methods. Had this been achieved, it would have required the use of tracer $^{40}K$, the nuclide employed because of the duration of the experiments, in the aqueous phase. This was deemed undesirable. Synthesis provides the advantages of purity of phase, economy in utilization of $^{40}K$, and knowledge of its structural site. The methods of synthesis and findings of Warshaw (1960) were employed.

A single composition of starting material was used, which, expressed as a hypothetical mica, was $K_{0.5}(Al_{1.9}Mg_{0.1})(Si_{3.6}Al_{0.4})_{10}(OH)_2$, or as oxides: $SiO_2$ 57.05%, $Al_2O_3$ 30.93%, MgO 1.06%, K$_2$O 6.21% and H$_2$O 4.75%.

EXPERIMENTAL METHODS

Standard hydrothermal techniques were employed in synthesis. The reagent grade materials used were $Al(NO_3)_3\cdot 9H_2O$, $Mg(NO_3)_2\cdot 6H_2O$ and KCl. The source of $SiO_2$ was a technical grade sol, "Ludox," prepared by E. I. du Pont de Nemours and Company, containing approximately 4 mg of sodium per g of $SiO_2$. Weights of these reagents, calculated from the formulation above, were combined in a dilute fluid.
bearing colloidal silica, dissolved ions, and nitric acid. Owing to the difficulty of drying the hydrated nitrates reproducibly, they were employed directly. The $\text{SiO}_2$ content of "Ludox" was evaluated by evaporation, followed by ignition at $900^\circ\text{C}$ for several hours. The composition $0.3050 \, g \, \text{SiO}_2$ per $g$ "Ludox" was determined.

For synthesis, a sufficient quantity of the initial preparation to yield 200 mg of oxides was evaporated to dryness in a teflon bowl to avoid loss by adhesion. Three such mixtures, employed in exchange experiments, bore in addition an enrichment in $^{40}\text{K}$, obtained as 303µg in 1 mg of KCl from the Atomic Energy Commission, Oak Ridge National Laboratory.

The dry solids were transferred to a platinum crucible and intermittently brought to approximately $600^\circ\text{C}$ over a Fisher burner to convert the nitrates to oxides. Several additions of nitric acid were made to further the evolution of HCl derived from potassium chloride. Heating was carried out for 30 minutes in all. The material was ground in an agate mortar.

X-ray diffraction examination of the product, an amorphous oxide mixture, revealed only a broad band with a $3.8\AA$ maximum, similar to that of common glass ($3.9\AA$) but distinct from that of pure silica glasses (approximately $4.1\AA$). The ignited oxides were sealed in platinum or gold tubes, 5/32 inch in diameter, 2 inches in length and 0.002 to 0.005 inch wall thickness, with 0.1 to 0.2 ml of demineralized water, by welding with gold in an oxyacetylene flame.

Sealed, weighed tubes were placed in a Morey bomb with that volume of water calculated to produce the desired pressure at the
temperature of synthesis, as determined from the tables of Kennedy (1950). The bomb was sealed with a stainless steel cone. Pressure control by this means was estimated to yield deviations from the mean of less than $\pm 10\%$. The bomb was heated within a cylindrical electric furnace and a temperature gradient of $6^\circ C$ was measured over its length during an average run. Temperature control was provided by a variable voltage transformer which was pre-set. Stability relied upon consistency of line voltage and the high heat capacity of the furnace. At equilibrium, constancy of temperature, with excursions of less than $2^\circ C$ was commonplace. Temperatures were determined with chromel-alumel thermocouples and a Leeds-Northrup potentiometer. The combination was calibrated in boiling demineralized water and in crystallizing potassium nitrate at $33^4^\circ C$.

(2) Potassium Exchange

Procedures employed fall into two categories, those relevant to $100^\circ C$ and those relevant to elevated temperatures and pressure. In the first case, where potassium chloride was employed, approximately 77 mg of $\beta$-active illitic mica was placed in a $500$ ml flask with $125$ ml of $0.5$ molar potassium chloride. The flask was suspended within a water bath at $100^\circ C$. Both vessels were fitted with reflux condensers.

At elevated temperatures recourse was made to procedures closely similar to those employed in synthesis. Solution and active illitic mica were sealed in a welded, noble metal tube of capacity slightly less than $1$ ml. The requirements were that a sufficient quantity of synthetic material be employed to provide an adequate $\beta^-$ counting rate, preferably over 50 counts per minute, secondly that the solution con-
tain a much greater mass of potassium than the solid, and thirdly,
that the concentration of the solution should not exceed feasible
natural molarities in chloride ion. In practice, weights of synthetic
materials were between 24.2 and 44.0 mg. Weights of KCl ranged from
80.8 to 90.9 mg in 0.3 ml of demineralized water. Concentrations
were therefore between 3.61 and 4.06 molar. The excess of KCl was
employed to dilute, as far as practicable, the \(^{40}\)K released from the
solid phases.

Temperature control was maintained as during syntheses. Applied
pressures were controlled by a pump and valves, and measured on a
Bourdon tube gauge which was calibrated against a standardized gauge.

After treatments the solids were washed twice with fresh 0.5
molar KCl and then maintained in the solution for over five hours.
It was sought to thus be certain of having exchanged even the "slower"
surface potassium sites (Bolt and Sumner, 1962). A similar procedure
was followed after synthesis and prior to the initial \(\beta\)-counting.
Thus, changes in specific activity were attributed to changes in
the structural, not including surface, potassium.

Several auxiliary experiments, employing solutions of sodium
salts, were carried out in covered beakers in a thermostat-controlled
oven, or gently boiling over a heater.

(3) X-Ray Diffraction Technique

A North American Philips geiger counter spectrometer was used
as the principal means of characterizing the synthetic products.

Copper K \(\alpha_1, \alpha_2\) radiation was employed, produced at 40 kilovolts
potential and 30 milliamperes filament current. Instrumental components
and settings were maintained thus: nickel filtration, $1^\circ$ and 0.006 inch slits, scale factor 8, yielding 400 c.p.s. for full-scale deflection, and a time constant of $\frac{1}{4}$ seconds. Charts from which data were obtained were prepared at $1/4^\circ$ 20 per minute scan.

The instrument was aligned at the outset of the investigation to obtain spacing errors of less than 0.001A for a pressed powder standard of silicon. The precision of location of a peak at $8.85^\circ$ 20, involving seven replicate runs of four sample preparations, was represented by a sample standard deviation of $\pm 0.02^\circ$ 20. Values of $\sigma$ given by Chayes and MacKenzie (1957) for similar replication of the much sharper peaks of quartz, range from $\pm 0.0116$ to $\pm 0.0169^\circ$ 20.

Samples were generally prepared by wet smearing of some 20 mg of material on glass. Smooth, coherent films were obtained which were placed against the goniometer mounting surface to minimize sample surface displacement from the axis of rotation. Such displacement leads to serious error (Parish and Lovitzsch, 1959). All modes of sample preparation resulted in powder patterns of randomly oriented grains, owing to the aggregation of particles which develops during synthesis.

(4) Beta Counting

Counting was carried out on a "widebeta", manufactured by Sharp Laboratories Incorporated. The instrument possesses numerous features of value in low activity-level counting. A gas-flow sample detector employing methane operates in the proportional region. High efficiency of particle detection is promoted by the
use of a 2-1/4 inch diameter, thin window (500 µg per cm²), and a
two sample-to-window distance of 0.005 inch. This close approach was
facilitated by the mechanical loading, from below upwards, of carefully
machined powder-holding planchette assemblies. Solid state circuit
components allow continuous operation and exhibit excellent stability
of the high voltage supply to the detector. A pre-set potential of
3.07 kv was maintained. The counter provides automatic sample recycling
as well as loading, and a print-out of data. Measured background
activity values were between 1.10 and 7.17 s⁻¹ counts per minute,
reduced by a cosmic radiation detector operated in anticoincidence with
the sample detector immediately below it, and by heavy shielding.

Counting precision and the expectable accuracy of a single
evaluation of beta activity depended upon determinations of the follow-
ing variables:

1) Relative efficiency of the counting system
2) Stability of the system during counting period
3) Sample weight and geometry
4) Background activity
5) Sample counting rate

Relative efficiency was determined by accumulating counts from a
137Cs standard, generally to a total greater than one million, giving
a coefficient of variation of approximately 0.1%. Such counts were
determined by summing over 10.00 minute intervals separated by counts
of the samples. After a period of counting, maximally some 30 hr,
subsets of the standard counts were examined for evidence of variation
in counter performance over the period of use. None was found on any
occasions.

Samples, in equilibrium with the moisture content of the air-conditioned laboratory air, were weighed to 0.1 mg on a Mettler balance, adjacent to the counter. Geometry was maintained constant for each series of measurements. This was controlled by lucite planchette inserts, 1-1/4 in. in diameter, bearing a wide, right-cylindrical recess of 0.014 in. depth. Within this, a uniformly thin layer of sample was spread, also 0.014 in. thick. Separate experiments demonstrated the absence of self-absorption in such layers, and a linear relationship between activity and weight counted (Figure 2, Volume 3). This relationship provided the means of standardizing observed activities. Exchange experiments in Series C (Volume 3) were carried out progressively on a single sample, initially of 77.1 mg, of synthetic mica. Minor losses attending transfers etc. necessitated correction of observed activities for weight decreases.

Observed counting rates, modally of the order of 50 counts per minute, were corrected for background, counter performance variation and weight counted. Standard deviations attached were computed for fluctuation of background during its determination and during sample counting, and for sample rate fluctuation. Coefficients of variation of 1% were sought and values between 0.4% and 1.75% obtained. These values represent counting precision. The remaining variables listed above involve further possible random errors. Therefore six sets of fully independently replicated data, each of two or three standardized sample counting rates, were obtained. The overall coefficients of variation for the sets were 0.84%, 1.42%, 1.06%, 1.58% and 8.11%.
It will be noted that overall precision is generally not inferior to counting precision. Rates quoted below bear counting standard deviations.
RESULTS AND DISCUSSION

(1) Potassium Exchange Experiments

Results and principle details are presented in Table 6, volume 3. Three synthetic micas were employed, each the 1Md polytype, a determination principally based upon the data of Yoder and Engster (1955). The micas varied significantly in degree of disorder and extent of mixed-layering. X-ray diffraction data for synthesis numbers 10 and 20, which were employed in exchanges against aqueous potassium chloride, are given in Table 10, Volume 3, for the untreated states. Synthesis number 18, exchanged against molar solutions of sodium salts, is illustrated in initial and final states in Figure 4. Similarly, syntheses 10 and 20 are illustrated in Figure 3, Volume 3.

(a) Exchange Series C

After each treatment, examination of the material by X-ray diffraction, at 1/4° 2θ per minute scanning rate, did not reveal evidence of modification.

Peak height ratios, positions of maxima, and their forms were examined, but revealed only random variations. Within the limits of sensitivity of the measurements, the illitic mica behaved inertly. However, after C4, at 468.3 hours, approximately 18 days, two new peaks of such low intensity that they were occasionally obscured by electronic "noise", appeared in the record. These, at 3.26° and 3.22°, compare well with spacings for potassium feldspar, although several expectably more intense maxima were not observable. The record is shown in Figure 3, labeled "100°C". This phase is further discussed below.
(b) Exchanges E, F, and G.

Three treatments of synthesis 20, at 250°C, 350°C, and 450°C respectively, are described. There were minor progressive changes in the diffraction features of the mica. These are observable in Figure 3, Volume 3, where the original state and that after exchanges F and G are shown. They are:

1) Reduction in the width at half-height of 001, produced by a reduction in diffracted intensity on the low-angle side of the maximum.

2) Progressive reduction in the asymmetry of 002 on the high-angle side.

3) Reduction of background in the region of 28°20, equivalent to the reduction of the tail of 003 on the high-angle side.

These changes are interpreted as representing the progressive elimination of expanded, intercalated, hydrated layers in the mixed structures, involving replacement by potassium. It is a notably slow process, apparently diffusion controlled. The changes are of the nature of those occurring during the diagenetic alteration of illites (Weaver, 1959; Burst, 1959; Flawn et al., 1960). The cause of hindrance to the entry of potassium was not specifically investigated.

After exchanges F and G there were observable once again extremely low peaks in positions compatible with the occurrence of potassium feldspar. If indeed an aluminosilicate crystallized, it is pointed out that the source of the components need not be the micaceous phase. Synthesis 10 contained accessory boehmite, and synthesis 20, cristobalite. Traces of isotropic material, possibly unconverted glass, were
observed by microscope examination of other syntheses.

(c) Exchanges I, J and K

Synthesis 18 was employed to examine the effect of a more strongly hydrated cation, sodium, and the relative effects of two anions, chloride and citrate. The latter is known to complex aluminum. A particular objective was to examine the possibility of occurrence of an aluminous boundary layer about the mica crystallites, such as is described for weathering aluminosilicates by Correns (1963), or the occurrence of interlayer hydroxy-aluminum complexes, possibly polymerized, as postulated for natural materials by Jackson (1963) and others. The citrate extractant, however, after conversion to sodium chloride, did not prove to bear significantly more aluminum than a blank, upon spectrographic examination.

The experiments demonstrated that sodium ion is capable of replacing potassium in structures of the layer charge of these particular micas. This is either montmorillonitic (up to approximately 0.55 e⁻ per unit of O₁₀(OH)₂) or vermiculitic with anomalous expandability (approximately 0.6 e⁻ to 0.8 e⁻ per unit of O₁₀(OH)₂). The rate of replacement is a great deal more rapid than in the case of potassium exchange, probably enhanced by the entry of water concomitantly with sodium, accompanied by layer separation. The significant difference between the effects of chloride and citrate possibly lies in the occurrence of steric hindrance due to large citrate complexes in the edge zones. It is not ascribed to a lower sodium acitivity in view of the findings of Walker (1963): the external concentration of
an exchanging ion did not effect the rate of exchange in vermiculite.

In Exchange K, a solution simultaneously 1 molar in sodium citrate and 0.5 molar in potassium chloride was employed. Beta counting revealed an anomalous increase in activity following 4 hours treatment, which must be interpreted as zero change in the mica activity. As illustrated in Figure 4, E, there was no development of a $17\text{A}^0$ peak upon magnesium saturation and ethylene glycol solvation, as was the case following extraction of potassium with sodium citrate and chloride. The difference is attributed to the presence of potassium in the citrate solution, apparently inhibiting lattice expansion by being strongly preferentially adsorbed at the edge-interlayers. Such an effect has been reported previously by Rich and Cook (1962) who state that as little as 10 ppm dissolved K$^+$ is sufficient to block exchange. The phenomenon is probably operative and of great importance in nature.
(2) Interpretation of Data in Terms of a Diffusion Parameter, \( D/a^2 \)

A diffusion equation is adopted on the basis of a model involving several assumptions. Principally, the latter concern the boundary conditions, the most appropriate geometrical approximation, and the constancy of the constancy of the coefficient of diffusion, \( D \).

It is demonstrated below that observed decreases of activity in Series C are proportional to the square root of the duration of treatment and may therefore be interpreted as representing a diffusion controlled process. The only evidence of other chemical reaction lies in the low, possibly feldspar, peaks observed after exchanges C3, F1, and G1. It is suggested that the intensity of these is proportional to the quantity of produce in each case, matrixes being closely similar. The intensities are sub-equal in all cases and thus bear no relationship to observed decreases in activity which differ markedly. It is considered that the reaction did not significantly affect the micaceous phase.

Frick's second law of diffusion, derived on the assumption that \( D \) is constant, independent of concentration, is:

\[
\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}
\]

As in the present case the concentration of diffusing substance, potassium, is fixed by the layer charge, there is no question of variation of \( D \).

The above equation relates to uniaxial diffusion, for example normal to the surface of a slab. The anisotropy of micas recommends a solution in terms of only radial diffusion in a cylinder. A solu-
tion of the equation in terms of a series of error functions is given by Jost (1960). For values of a quantity \( a/\sqrt{Dt} \) greater than 2.24 the series converges very rapidly and three terms yield a good approximation. The final result is

\[
\frac{\bar{c}}{c_0} = 1 - \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{Dt}}{a}
\]

for uniaxial diffusion out of a slab. Herein \( \frac{\bar{c}}{c_0} \) equals the fraction of diffusing material remaining after time \( t \) seconds, \( D \) equals the diffusion coefficient in \( \text{cm}^2 \text{sec}^{-1} \), and \( a \) equals the half thickness.

The analogous solution for a cylinder allowing radial diffusion alone, in planes normal to the axis, is

\[
\frac{\bar{c}}{c_0} = 1 - \frac{h}{\sqrt{\pi}} \cdot \frac{\sqrt{Dt}}{a}
\]

The fraction lost, \( F \), equals \( 1 - \frac{\bar{c}}{c_0} \),

\[
\therefore F = \frac{h}{\sqrt{\pi}} \cdot \frac{\sqrt{Dt}}{a}
\]

This is applied to the data obtained.

The relevant initial conditions for a cylinder of radius \( a \) are

\( c = c_0 \) for \( 0 < r < a \) at \( t = 0 \).

Concerning this, the enrichment in \(^{40}\text{K}\) in synthesis 10 was by a factor of 31, and in 20, by 18. The external concentration of \(^{40}\text{K}\) in ordinary potassium chloride is approximated as zero, being in fact \( 1.18 \times 10^{-9} \) atoms of \(^{40}\text{K}\) per atom of potassium (Smith, 1964). In the case of the maximum observed exchange, a decrease of activity of \( 12.87 \pm 0.58\% \),
the calculated observable counts per minute due to the ordinary potassium which replaced the original are 0.29. The decrease in counting rate (after exchange Gl) was 5.06 ± 0.23 c.p.m. The effect of the uptake of ordinary potassium is obscured by counting fluctuations.

A second, similar effect, potentially more significant, is the possible re-entry into the structure of $^{40}$K released from it. This was minimized by employing much greater masses of potassium outside the solid phase than within it, minimally by a factor of 25.

A further implication of the boundary condition is the postulate that the rate of migration of vacancies in the interlayer regions, that is of potassium, is not affected by the concentration of potassium chloride in the fluid phase. Walker (1963) observing the diffusion of hydrated Sr$^{++}$ into a vermiculite crystal bearing hydrated Mg$^{++}$, found the rate to be independent of the concentration of Sr$^{++}$ in solution between 0.4N and 4N, outside which limits other diffusion processes become rate-limiting.

The measurements made to evaluate $F$ were of $c_0$, the initial activity per unit weight, and the activity after exchange, $c$.

(3) Values of $D/a^2$

The data are presented in Table 7, and Figures 5 to 7, Volume 3. Details of the beta counting involved are given in Table 20.

A test of the relevancy of the equation to the data may be carried out for Series C. In the equation $F = (4/\sqrt{t}) \cdot (\sqrt{Dt}/a)$, $F$ is proportional to $\sqrt{t}$ for constant $D$ and $a$, and a linear relationship
should be found. The data are plotted in Figure 6. An excellent approach to linearity is evidenced by the first three data points, the fourth being suggestive of curvature. Statistically, however, curvature cannot be demonstrated. A value of $D/a^2$ for the self diffusion of potassium in the illitic synthetic mica number 10 is taken as the mean of the consistent intermediate values of $D/a^2$ from each of the data points. The intermediate values are weighted according to their standard deviations (Worthing and Geffner, 1943). The mean, for 100°C is thus

$$D/a^2 = (1.41 \pm 0.45) \times 10^{-10} \text{ sec}^{-1}.$$  

The consistency of values for exchanges El, Fl and Gl may be tested on an Arrheius plot, $\log_{10} D/a^2$ versus $1000 T^{-1}$ °K, where

$$\log_{10} D/a^2 = \log_{10} D_0/a^2 - \frac{Q}{2.303RT},$$  

$D_0$ is a constant for the system, $Q$ represents the activation energy for migration, $R$ the gas constant, and $T'$, temperature in degrees Kelvin. In Figure 7, apparent compatibility of the data is observed for synthesis 20, while synthesis 10 evidently exchanges at a greater rate.

A value of $Q$ of 11,600 calories per g ion is determinable from a linear extrapolation of the data. However, the value of $D_0/a^2$ obtained, $10^{-4.5}$ sec$^{-1}$, is inordinately low for a reasonable estimate of $a$, which might be suggested to be of the order of magnitude of one micron. Unfortunately $a$ is not accessible to measurement. It is less than or equal to an indeterminate mean planar dimension of the crystallites.

Owing to the impossibility of achieving more than slight disaggregation
of the synthetics by the only means considered acceptable, ultrasonic vibration, estimates of crystallite size were incomplete. Four hours of intense vibration yielded the following data for a synthesis bearing 3T (?) as well as 1Md mica: > 10μ equivalent spherical diameter, 48.3 weight percent, entirely aggregated; 1 - 10μ esd, 31.4%, aggregated; 0.3 - 1μ esd, 16.4%, largely disaggregated; <0.3μ esd, 3.9%, single crystals. Estimation of degree of aggregation was by means of X-ray diffraction study of preparations carefully sedimented to obtain maximum preferred orientation.

Estimates of values of D are therefore, at best, to an order of magnitude. Small degrees of exchange lead to large uncertainties in F, the difference of two large numbers, though each be of high precision. Based upon initial decreases of activity to a large extent, values of D/a^2 are possibly high. This possibility would be partially compensated by known factors which tend to cause underestimation of F: the finite activity of potassium postulated to enter the mica in replacement, and also of that concluded to cause collapse of a small proportion of the expanded layers in cases E, F and G.
DISORDER IN SYNTHETIC 1Md MICAS AND A REPRESENTATIVE ILLITE OF 2M POLYTPISM.

INTRODUCTION

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INTRODUCTION

The term illite was proposed as a mineral group name for the approximately \(10^6\) layer silicates of soils and sediments, originally by Grim, Bray, and Bradley, (1937). "No account is taken of whether a given polytype is or can be specified" (Bradley and Grim, 1961). The occurrence of \(1M_d\) polytypes in illitic accumulations was demonstrated by Levinson (1955) and Yoder and Eugster (1955). The nature of \(2M\) micas of like occurrence is less clear. Levinson (1955) states that "... at least three polymorphs exist among micas called illites ... and therefore all minerals of this type may not be considered a defect or poorly crystallized \(2M\) muscovite structure as many workers have erroneously concluded from the work of Grim et al. (1937)." Yoder and Eugster (1955) examined \(2M\) polymorphs in several sediments, including the Fithian illite. It would appear that the characteristic illitic asymmetry of the basal diffraction maxima was always attributed to "mixed-layer \(1M_d +\) montmorillonite."

In contrast to the error mentioned by Levinson, it appears that an oppositely extreme view has recently been adopted by some workers. For example, Velde and Kower determine the proportions of micaceous components of some 60 Palaeozoic shales in terms of the two minerals employed in their working curves" \(2M\) (muscovite) and \(1M_d\) (illite)" (p. 1248).

On the other hand Weaver (1965) reports on numerous "two-layer monoclinic illites" from Palaeozoic shales, showing X-ray diffraction patterns which exhibit the characteristic asymmetry of the approximately \(10^6\) basal maximum.
In the course of work by the writer in investigating potassium exchange kinetics, a group of synthetic micas was prepared. Thirteen of these were of the 1M polytypic form, of which eight exhibited varying degrees of disorder and would be termed 1Md by the criteria of Yoder and Eugster (1955). It was the intention in the synthetic work to simulate as closely as possible the properties of illites. Comparison of the features of the 1Md forms was made with published data as well as with a 0.3\(\mu\) to 3\(\mu\) esd fraction of illite from Marblehead, Wisconsin. The latter, described by Dr. H. E. Gaudette (1965) and kindly supplied by him, is a 2M polytypic form which has been used as a reference clay sample in the Clay Mineralogy Laboratory at the University of Illinois for several years. It appears to be a typical and representative material. The departures in X-ray diffraction characteristics of the 2M illite from those of 2M muscovite were closely paralleled by those of the 1Md synthetic micas from 1M muscovite. In fact, despite the differences in polytypism, there are close quantitative similarities between the 2M illite and the 1Md materials.

In the syntheses, four compositions were investigated, of which only one yielded substantially disordered products, that employed by Warshaw (1960) in preparing "synthetic illites". This was of the composition of her "gel number 12," which yielded, at 400\(^\circ\)C, a product sufficiently disordered to exhibit no evidence of polytypic affinities, yet which compared closely in number and position of diffraction maxima to a less than 0.2\(\mu\) fraction of Fithian illite. The compositions were as follows, on the basis of their formulation
as hypothetical layer silicates:

(1) $K\,Al_2(AlSi_3)\,O_{10}(OH)_2$, ideal muscovite. Employed in syntheses numbered 6, 7, and 14 below.

(2) $K_{0.5}(Al_{1.9}Mg_{0.1})(Al_{0.4}Si_{3.6})O_{10}(OH)_2$, Warshav's "gel No. 12." Employed in syntheses 2, 5, 9, 10, 18, 20, and 21.

(3) $K_{0.97}(Al_{1.98}Mg_{0.02})(Al_{0.95}Si_{3.05})O_{10}(OH)_2$, representing a composition on the muscovite-potassium montmorillonite join at 95% muscovite. Employed in syntheses 3 and 4.

(4) $K_{0.83}(Al_{1.92}Mg_{0.08})(Si_{3.25}Al_{0.75})O_{10}(OH)_2$, a composition analogous to (3) but at 75% muscovite. The montmorillonite is idealized: $K_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$. Employed in synthesis 16.

The initial preparations, having cation ratios in accordance with the above formulae, yielded products which were single phase to X-ray diffraction in cases (1), (3) and (4). As far as can be determined therefore, these formulae are realistic. Composition (2) yielded accessory cristobalite in five runs, but accessory boehmite in two, 9 and 10. The cause was not determined but the difference substantiates the X-ray diffraction evidence that the products in all of the seven syntheses differed significantly. As the accessories formed metastably, reaction kinetics could likewise have played a significant role in determining the nature of the micas. Such could depend upon unsuspected and uncontrolled variables.
EXPERIMENTAL METHODS

(a) Synthesis

The starting materials employed in the initial preparations comprised aluminum nitrate, \(\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}\), magnesium nitrate, \(\text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\), potassium chloride, \(\text{KCl}\), aluminum metal, and "Ludox", a silica sol bearing approximately 4 mg of sodium per g SiO\(_2\). The preparations, as dilute acidic sols bearing dissolved salts, were evaporated to dryness, ground, and several additions of concentrated nitric acid made with intermittent heating prior to ignition to an oxide mixture of glass-like properties. Portions of the mixtures, frequently 200 mg, were sealed by welding into gold or platinum tubes with 0.1 to 0.2 ml of demineralized water. They were maintained at the requisite temperatures and pressures in a Morey bomb.

(b) X-Ray Diffraction

A North American Philips geiger counter spectrometer was employed, using Cu K\(\alpha_1\) radiation (40 kv, 30 ma). A nickel filter removed K\(_\beta\) radiation. Instrumental components were 1° divergence and anti-scatter slits, and a 0.006" receiving slit. A scale factor of 8 was employed giving 400 counts per second full scale deflection, and a time constant of 4 seconds. Runs from which data were obtained were carried out at 1/4° 20 per minute scanning rate, and a 1/2 in. per minute chart speed, over the interval 2° to 63° 20.

The illite sample was prepared as a randomly oriented powder in an aluminum holder by surface leveling with a razor edge. Synthetic products, because of their natural state of aggregation, produced randomly oriented preparations by any means. Wet smearing on planar
Glass was commonly employed.

The low, broad peaks of 1Md materials were subject to minor random displacement by electronic noise. The precision of location of a peak at 8.85° 20 involving seven replicate runs for four sample preparations was ± 0.02° 20. Values of the standard deviation given by Chayes and MacKenzie (1957) for similar replication of the relatively sharp peaks of quartz range from ± 0.0118° to ± 0.0169° 20.

RESULTS AND DISCUSSION

Details of the syntheses and products are given in Table 8. X-ray diffraction patterns of representative materials are shown in Figure 8. In Table 9, X-ray diffraction data for 1M muscovite syntheses 7 and 14 are compared with similar data published by Yoder and Eugster (1955). The principal differences between 1M and 1Md diffraction patterns, according to the authors quoted, concern the form of 001 and the relative intensities of the hkl's. They state (p. 244) "In some runs all of the hkl's were absent, and this was interpreted as evidence of complete disorder of the layers. ... As greater order of the layers is obtained, the hkl's appear, and the intensity of these may be used as a measure of the amount of remaining disorder. In particular the 112 and 112 reflections are useful for this purpose."

These phenomena are observed in the present work, also displacements of maxima which are most prominent in the cases of basal peaks where such displacements are attributable to mixed-layering. A survey of the observations made on the X-ray patterns of the micas is made in terms of three diffraction effects in the 1Md group. Comparison with
the illite is made for each effect. These effects are (1) the asymmetry of the basal maxima, particularly 001 (and equivalent 002 in the illite), (2) displacements of the basal maxima, and (3) suppressions of maxima hkl.

(a) Asymmetry of the Approximately 10Å Basal Maxima.

The asymmetry the basal maxima in micas is attributed to mixed-layering, the introduction of expanded, hydrated interlayers into the 10Å sequence (Yoder and Eugster, 1955; Bradley, 1954; Harrison and Murray, 1959, and others). It may be noted in Figure 8, where maxima 001, 002, 003 and 005, in the vicinity of 9°, 18°, 27° and 45° 2θ respectively, show it varying degrees. In the case of 001 it is in the direction of lower angles (herein termed -ve asymmetry), in the remainder towards higher angles (+ve). These are also the directions of peak displacement.

The asymmetry is measured by the means adopted by Nelson (1956): the peak median at one quarter of the height above the base line joining adjacent minima is located. The separation in degrees 2θ between this position and that of the apex is termed φ, the asymmetry. In 001 peaks of the muscovite formulations it ranges between -0.02° 2θ (No. 3) and -0.05° 2θ (No. 14); φ is -0.06° 2θ in 16 (K+ = 0.83), and in the low-potassium micas between -0.06° 2θ (No. 21) and -0.34° 2θ (No. 9). Nelson observed a range from -0.07° 2θ to -0.36° 2θ in Palaeozoic shale illites. The value observed in Marblehead illite is -0.22° 2θ.
(b) Displacements of Basal Maxima

The small displacements from 1M peak positions do not result in impressive departures from an integral sequence of basal spacings. The sequences for three 1M syntheses and three 1Md products are shown in Table 11. Therefore a more sensitive measure was adopted, the separation in degrees 2θ of basal maxima 001 and 002, termed Δ21, and of 001 and 003, termed Δ31. These values are given in Table 12 which demonstrates a significant displacement for the 1Md preparations, further evidencing mixed-layering.

Data for Marblehead illite is shown in Table 16, where displacements of each basal peak from the ideal 2M muscovite position (data of Yoder and Eugster, 1955), and the associated asymmetries are given. Comparison is made with synthesis 10, chosen on the basis of a similar value of a, the peak displacements of which are compared with 1M muscovite (data of Yoder and Eugster, 1955). The agreements are remarkable, as they must depend upon the percentage, spacing, and distribution of expanded layers. The introduction of the latter may be termed a "c-axis disorder" by analogy with the term "b-axis disorder" which is widely employed.

(c) b-Axis Disorder

The suppression of peaks hkl referred to by Yoder and Eugster, particularly 112 and 112, is characteristic of b-axis disorder, with the following provision. Suppression is not uniform, but affects preferentially those maxima where k is not equal to 3n (n = 0, 1, 2...). The accepted explanation in other clay mineral groups, the kaolinites,
vermiculites, and chlorites, wherein the effect is also observed, involves random translations of entire layers parallel to the \( b \) axis by units of \( nb/3 \). The discontinuity originates in the interlayer region, the locus of the interlayer cations in chlorites and vermiculites. By virtue of the coordination of these cations by hydroxyls and water molecules in the respective minerals, and the association between basal oxygen ions and the \( \text{OH}^- \) or \( H_2O \) groups, potential cation sites repeat at intervals of \( b/3 \). In micas, the explanation of \( b \)-axis disorder advanced by Smith and Yoder (1956, read in 1954) and invoked by Yoder and Eugster (1955) involves rotational "stacking errors" between mica layers, stated to yield the same results.

In the 1Md micas, if the effect occurs, there would be expected a suppression of the maxima \( hkl \), \( k \neq 3n \), with little effect upon maxima \( hkl \), \( k = 0 \) or \( 3 \). Therefore, in Table 10, the \( hkl \) peak heights of two representative syntheses are normalized on the basis of the ratio of the 020 intensity in 1M muscovite (Yoder and Eugster, 1955) to that in the synthetic mica. Suppression of all maxima is evident, except 132, but the significant fact is that suppressions of the expected type are greater. That of 112 and 112, maxima unique among mica polytypes to the 1M form, is most marked. This is also evident in Figure 9.

(d) Certain Parametric Relationships Among a Group of 1M and 1Md Synthetic Micas.

As a measure of \( b \)-axis disorder in the synthetic micas, the ratio of peak heights 131/112 is adopted. The maximum 131 would be expectably
less suppressed than 112, and the ratio should increase with increasing disorder. The relationship between three parameters, $\alpha$, the asymmetry of 001, $\Delta 2\theta$, a measure of intercalation of expanded layers, and the ratio 131/112, a measure of b-axis disorder, is examined in Figures 12 and 13. The plots evidence significant correlation between the three parameters. A correlation between $\alpha$ and $\Delta 2\theta$ is perhaps expectable, but there is no theoretical basis for a relationship between the degree of mixed-layering and the degree of b-axis disorder, as there appears to be. The theory is proposed that loci of translation exist at the hydrated, expanded interlayers. Hydration of the interlayer cations, or the possible occurrence of planar alumino-hydroxy complex ions, could lead to potential cation sites at intervals of $b/3$, as in vermiculites and chlorites, allowing nb/3 translations. The repeat distance of potassium ions, parallel to b in a 10A layer, is equal to $b$.

By the above theory, the effects in the 1Md micas become analogous to those in related mineral groups. It is of interest to examine the 2M illite for evidence of b-axis disorder.

(e) Evidence of b-Axis Disorder in a 2M Illite

Random-orientation powder patterns of Marblehead illite and a pegmatite muscovite, (ground to pass a 325 mesh screen of approximately 40u aperture) were compared. Illite peaks were normalized in intensity to compare with those of the muscovite. The results are shown in Table 18. It is terminated as the higher $\theta 2\theta$ region is approached by a "multiplicity of index" problem. The possible indexes
of an observed reflection become numerous. Only one anomaly is
evident; the agreement with expectation on the basis of a postulate
of b-axis disorder in the illite is excellent.

As the maximum employed for standardization (131, 202) is
subject to enhancement by other layer silicates, further examination
is required. This is particularly so as a highly disordered 1Md,
exhibiting no unique maxima, but only reflections virtually coincident
with those of 2M, could be present, yet remain undetected. For
this reason it is necessary to examine the intensity ratio of two
maxima which are unique to the 2M polymorph, and not subject to
interference from undetectable contaminants (as could be the case if
a chosen peak of 2M were coincident with the maximum intensity of a
contaminant which, because of dilution, produced intensity in that
region only). Of the two 2M peaks, one must of the type h31, and
the other, hkl, k ≠ 3. The best approximation available is a com-
posite peak 135 + 043 and the maximum 023, both resolvable from other
mica polymorph maxima, and not subject to undetectable interference.
The first occurs at 2.132Å (Yoder) and is given as 135 + 206 at
2.13Å, 2.14Å, a doublet, by Bradley and Grim (1961).

Considering therefore the intensity ratio 135/023, it was
found to be 0.77 in the muscovite employed. Yoder and Eugster's
published 2M data yield a ratio of 0.71. The Marblehead illite
provided a ratio of 2.0. There is then, internal evidence compatible
with the occurrence of b-axis disorder.

In view of the similarities of the disorder phenomena in the
synthetics and the illite, in which the maxima 114 and 115, charac-
teristic of 2M polytypes, are evident it is suggested that the illite, by analogy, be termed 2Md.

Synthetic procedures have not produced such disorder in 2M polytypes, nor is it evident in metamorphic or igneous muscovites. The possibility remains that the hydrated interlayers are introduced during weathering (Harrison & Murray, 1959). If strain is required for the displacements they could perhaps be produced during burial.
SECTION I, INTRODUCTION

(a) The System Investigated

The work was undertaken to examine features of mineralogical change and redistribution of the initial population of potassium in synthetic micas analogous to illite when treated in aqueous solutions at moderately elevated temperatures and pressures. There is thus an experimental analogy to processes of diagenesis. A particular objective was the determination of rates of exchange of potassium between the solid and fluid phases, ideally values of the coefficient of self diffusion of potassium in the solid, $D$, as relevant to the particular system, or values of $D/a^2$ where $a$ represents the radius of diffusion.

Further, information was sought upon the behaviour of the solid during treatment, whether recrystallization would occur, or whether other modifications of the structure would result. Numerous reported values of $D$ relate to high temperature, dry system investigations. Extrapolation of this data to lower temperatures is of no value, if, in natural aqueous choride solutions, chemical reaction ensues at rates greater than those of internal migration.

The system studied represents the most abundant and one of the most enduring sedimentary mineral groups, and the principal alkali of sediments. The choice represents in part a reflection of the above consideration.
(b) Survey of Published Data Concerning the Diffusion of Large Alkali Cations in Silicate Structures

Attention is largely confined to examinations of systems wherein the diffusing ions move in structures of low water content, in the sense that they do not contain a continuum of molecules of water. Thus, for example, the considerable body of data concerning diffusion in zeolites is not considered, (refer to Ames, 1965), nor is that concerning inter-crystalline, ionic diffusion in clay-water systems.

Relevant data is scant. Values for synthetic glasses were recently determined at single temperatures by Ehrmann, de Billy, and Zarzycki (1961) and by Sendt (1964). The former obtained values of $D$ at 325 - 375°C in a sodium-calcium silicate glass equal to $1.6 \times 10^{-10}$ for sodium, $1.13 \times 10^{-13}$ for potassium, $0.47 \times 10^{-15}$ for rubidium and $0.67 \times 10^{-13}$ cm$^2$ sec$^{-1}$ for hydronium ion. Sendt, employing six mixed-alkali silicate glasses of varying potassium content at 626°C, obtained a range of $D$ values for potassium between $1.3$ and $2.1 \times 10^{-9}$ cm$^2$ sec$^{-1}$ and between $3.2 \times 10^{-9}$ to $6.3 \times 10^{-8}$ cm$^2$ sec$^{-1}$ for sodium. For an obsidian, Sippel (1963) determined $4.9 \times 10^{-10}$ cm$^2$ sec$^{-1}$ for sodium at 357°C. Extrapolation of his data yields a value of approximately $10^{-15}$ cm$^2$ sec$^{-1}$ at 100°C. The stated activation energy is 22,900 calories per g ion.

Both Barré and Rees (1960) and Sippel studied the diffusion of sodium in the feldspathoid analcite. Their respective values of $D$ at 357°C are $2.3 \times 10^{-9}$ and $1.31 \times 10^{-9}$ cm$^2$ sec. Further deter-
minations by the former investigators relate to self-diffusion of
the listed cations in synthetic analcites of the type \( \text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \)
where \( \text{M} \) represents the alkali. The following data are given.

Table 1. Coefficients of Self-Diffusion for Alkali Cations in
Synthetic Analcite. (Barrer and Rees, 1960).

| Cation | \( T^\circ\text{C} \) | \( D \text{ cm}^2 \text{ sec}^{-1} \) | Activation Energy,
Q cals per \( \sigma \) ion |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>25.32</td>
<td>( 1.14 \times 10^{-13} )</td>
<td>11,500</td>
</tr>
<tr>
<td>K</td>
<td>25.0</td>
<td>( 1.96 \times 10^{-17} )</td>
<td>16,400</td>
</tr>
<tr>
<td>K</td>
<td>88.0</td>
<td>( 3.03 \times 10^{-15} )</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>109</td>
<td>( 1.11 \times 10^{-18} )</td>
<td>20,100</td>
</tr>
<tr>
<td>Cs</td>
<td>114</td>
<td>( 4.68 \times 10^{-20} )</td>
<td>26,000</td>
</tr>
</tbody>
</table>

The authors state that in the case of K and Rb analcites the struc-
tural channels do not contain water. The value of \( D_0 \) for potassium
is given as \( 2.57 \times 10^{-15} \), whereby \( D_K^+ \) at 350\( ^\circ \text{C} \) may be calculated as
\( 6.09 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1} \).

Verhoogen (1952) determined the diffusivity of alkali cations
in quartz parallel to the \( c \) axis by application of an electrical
potential gradient across a thin slab. His values are quoted for
500\( ^\circ \text{C} \):
\[
\begin{align*}
\text{Li}^+ & \quad 1.1 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1} \\
\text{Na}^+ & \quad 5.8 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1} \\
\text{K}^+ & \quad 2.0 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}
\end{align*}
\]

For potassium the Arrhenius relationship was given:

\[D = 0.18 \times \exp \left( \frac{-31,700}{RT} \right)\].

Calculated values of \(D\) for potassium may be obtained:

\[
\begin{align*}
350^\circ C, \ \text{K}^+ & \quad D = 1.33 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1} \\
100^\circ C, \ \text{K}^+ & \quad D = 4.66 \times 10^{-20} \text{ cm}^2 \text{ sec}^{-1}.
\end{align*}
\]

Sippel's data is for the self diffusion of sodium only and was obtained employing natural minerals. Its reliability is suggested by its close agreement in the case of analcite with the determination of Barrer and Rees (1960), despite problems concerning grain boundary, fracture, etc. diffusion. In the absence of data for potassium self diffusion (or diffusion) in common rock-forming minerals it is necessary to draw inferences from the data for sodium. Sippel found the mobility of sodium to progressively decrease in the following minerals and obsidian in the order of listing: analcite, obsidian, albite, orthoclase, acmite, determined by the temperature, \(T_D\), required to raise \(D\) to \(10^{-10} \text{ cm}^2 \text{ sec}^{-1}\). A parameter was determined
which correlated the nature of the structure with a function of the temperature measured experimentally. Sippel found that the "number of anion valence electrons per cm$^3$" plotted against the temperature function $T_D/T_F$ yielded a diagram of low scatter to which a straight line could be fitted. $T_F$ represents the temperature of fusion. On this basis a factor $F$ was determined, equal to $10^{-3} \times T_F \times$ (valence electron density), suggested to place minerals in order of values of $D$ at any temperature. These wholly empirical factors suggest that interlayer ionic mobility in biotite ($F = 24.5$) is intermediate between the rate for the same ion in alkali feldspars ($F$ between 21 and 22) and in "pyroxene" ($F = 26.7$, augite). Measured values for $D$ for sodium self diffusion in albite and acmite were $2.8 \times 10^{-10}$ at $940^\circ C$ for the former, and less than $10^{-11}$ cm$^2$ sec$^{-1}$ at $940^\circ C$ for the latter. A further value of $8.0 \times 10^{-11}$ cm$^2$ sec$^{-1}$ for albite at $850^\circ C$ allows graphical extrapolation to approximately $10^{-17.6}$ at $350^\circ C$ and $10^{-26}$ at $100^\circ C$. The method of Sippel's derivation of the valence electron density is not detailed, but it may be observed that ratios of the values for mineral pairs are often close to density ratios, therefore ionic coordination is not considered. Statements concerning $T_F$ do not mention incongruent melting; details of structure are omitted from consideration. With numerous reservations it might be tentatively accepted that rates of self diffusion of sodium in biotite lie in the indicated region. Although values of $D$ for potassium are generally less than the analogous values for sodium, this is possibly not the case in micas, where bond energy significantly increases upon substitution of the smaller sodium ion,
allowing contact of the basal oxygen layers. The latter are maintained at a separation of approximately 0.7A in muscovite (Radoslovich, 1960, 1962). As the effects of difference in ionic radius, distribution of charge between octahedral and tetrahedral layers, and possible variation in degree of defectiveness (frequency of interlayer vacant sites particularly) are largely unknown, it would be merely speculative to attempt to estimate values of D for potassium self diffusion in muscovitic or illitic structures.

A summary tabulation of the quoted values of the diffusion coefficients of potassium may be made, as in Table 2.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Glass</th>
<th>Analcite</th>
<th>Quartz</th>
<th>D_{Na^+} in Albite</th>
</tr>
</thead>
<tbody>
<tr>
<td>350° C</td>
<td>1.13 x 10^{-13}</td>
<td>6.09 x 10^{-11}</td>
<td>1.33 x 10^{-12}</td>
<td>2.5 x 10^{-18}</td>
</tr>
<tr>
<td>100° C</td>
<td>\sim 3 x 10^{-15}</td>
<td>4.6 x 10^{-15}</td>
<td>\sim 10^{-20}</td>
<td>10^{-26}</td>
</tr>
</tbody>
</table>

The significance of the values of D may be illustrated by employing a relationship quoted widely (for example Jost, 1960) between D and the mean square displacement of a diffusing particle, \( \Delta x^2 \) :

\[
\Delta x^2 = 2Dt
\]

where t equals time in seconds, and uniaxial diffusion in a slab of isotropic material is under consideration. An average reference
particle undergoing consecutive displacements \( d \) will exhibit a mean
displacement of zero after \( n \) consecutive displacements, as these,
in the \( +x \) and \( -x \) directions, are of equal probability, completely
independent and at random. The mean square displacement will have
a non-zero value however:

\[
\Delta x^2 = nd^2
\]

of which square roots may be taken yielding the root mean square
displacement. The actual total displacement, \( x \), of a particular
particle after \( n \) displacements \( d \) may have any value between 0 and \( \pm nd \).

The value \( \sqrt{\Delta x^2} \) is thus closely related to some measure of
the displacement of a boundary, the migration of which is rate-
limited by the diffusion of a particular species of particle.
Comparison may be made between the equation \( \Delta x^2 = 2Dt \) and the
often-observed relationship of Tammann (1923):

\[
x^2 = 2kt
\]

Herein \( x \) equals the thickness of a boundary layer, \( t \) equals time
from the initiation of formation of the layer, and the constant
\( k \) is proportional to the diffusion coefficient. The particular
application of the equation has been to cases of tarnishing reactions
on metals.

The significance of values of \( D \) may be illustrated by evalua-
tions of the time required for the attainment of several chosen
values of root mean square displacements according to the first
equation.

Table 3. Values of the Interval t Required to Attain Illustrative Root Mean Square Displacements at Certain Values of D (cm\(^2\) sec\(^{-1}\))

<table>
<thead>
<tr>
<th>(\sqrt{\Delta x^2})</th>
<th>D = 10(^{-10})</th>
<th>D = 10(^{-15})</th>
<th>D = 10(^{-20})</th>
<th>D = 10(^{-25})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 micron</td>
<td>0.5 sec</td>
<td>0.58d</td>
<td>158 y</td>
<td>15.8 my</td>
</tr>
<tr>
<td>1.0 &quot;</td>
<td>50 &quot;</td>
<td>58d</td>
<td>15,844 yr</td>
<td>1.58 \times 10^9 y</td>
</tr>
<tr>
<td>10 &quot;</td>
<td>1.39 hr</td>
<td>15.84 y</td>
<td>1.58 my</td>
<td></td>
</tr>
<tr>
<td>100 &quot;</td>
<td>5.79 d</td>
<td>1.58 \times 10^3 y</td>
<td>158 my</td>
<td></td>
</tr>
<tr>
<td>0.1 cm</td>
<td>1.58 y</td>
<td>1.58 \times 10^5 y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 cm</td>
<td>158 y</td>
<td>15.8 my</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is evident that migration of potassium at rates determined by coefficients of diffusion in the range of Table 3 cannot produce large scale geological effects. This statement applies whether the diffusion coefficient relates to migration in grain boundary zones, fractures, regions of near-perfect crystallization or wheresoever. Net effects are determined by a rate-limiting step. Thus one must concur with Verhoogen (1952): large scale metasomatic processes, for example, are not rate-limited by coefficients of diffusion in the above range. The latter are considered to span a considerable portion of the spectrum of values for monovalent cations within silicate minerals. Rates for divalent cations are markedly lower. It is probable that diffusion of Si\(^{4+}\) in silicates is negligible.
On the other hand, intracrystalline diffusion is capable of producing significant small scale changes. As examples there may be quoted alkali ion ordering in feldspars to produce perthites, and exsolution phenomena such as the development of rutile in quartz, and lamellae of orthopyroxene or pigeonite(calcium-poor) in the augites of numerous basic plutonic rocks. Such diverse phenomena as the serpentinization of olivine, the pseudomorphous oxidation of pyrites, the montmorillonitization of glass shards, and the kaolininitization of feldspar are possibly rate-limited by complex diffusion processes of reactant transfer across the product layer. Analogy to metal oxidation may be drawn.

Modification by diffusive transfer in phases crystallized in equilibrium is probably negligiblein a closed system, as the chemical potentials of all components are initially equal. A great contrast to this situation exists in sedimentary rocks where values of \( u \) probably vary markedly for any component from phase to phase. Chemical modifications in both solids and fluids in response to diffusive transfer may be of greater significance than is presently envisaged. This could be of importance to bulk particle or crystallite composition because feasible root mean square displacements at low values of \( D \) are comparable with particle sizes. Modification of clay mineral interlayer cation populations could be involved for instance.
(c) Relative Merits of Synthetic and Natural Materials for the Purpose of the Experiments.

Ideally, natural minerals would be employed. However, in the present case their principal disadvantage lies in the impossibility of obtaining complete and certain separation of illites from the usually associated minerals. The latter generally include quartz, potassium feldspar, chlorite and other clay minerals. Although of significantly different physical properties, separations based upon these differences are largely precluded by the importance of phenomena due to surface properties relative to bulk properties in silt and clay grades, and the overlap of particle size ranges for each species. Several techniques for separation utilizing differences in surface charge appear promising but have not resulted in practical clay separatory techniques. These include the electrophoretic method of Beavers and Larson (1953), whereby clay particle mobilities of 1.98 to 2.8 microns sec$^{-1}$ volt$^{-1}$ cm$^{-1}$ were observed for "illite" and Wyoming bentonite respectively. A process of paper electrochromatography was reported on by McNeal and Young (1963) with similar low mobilities. The latter could possibly be improved by substituting a less polar curtain material whereupon clay particles are not adsorbed.

Assuming that an illitic fraction of specific properties (particularly with regard to degree of mixed layering) could be segregated, then examination of the kinetics of potassium redistribution would require placing tracer potassium in an external phase.
This would entail the costly use of considerable quantities of \(^{40}\text{K}\).

If segregation were incomplete, ambiguity could occur in the data obtained for lack of knowledge of the precise structural sites of the tracer transferred.

Synthesis entails the disadvantage of the required demonstration of the similarity of the product to the natural material, but the advantages of purity of phase, the known presence of only one potassium-bearing phase (within the limits of detection by X-ray diffraction), economy in utilization of \(^{40}\text{K}\), and knowledge of its structural site, obtain.

(d) Survey of Reported Syntheses of Disordered Dioctahedral Micas

Yoder and Eugster (1955), in examining the stability field of muscovite, encountered poorly crystallized synthetic phases based upon the structure of the 1M mica polytype, yet evidencing considerable layer stacking disorder, which they termed 1Md muscovite. Examination of numerous natural micas formed at moderate temperatures led them to conclude that the 1Md heteropolytype or mixed-layer phase is of relatively common occurrence. Their syntheses employed starting materials of the composition of ideal anhydrous muscovite. Sources of the required cations varied however, and from their tabulation of results it may be noted for instance that their mixtures (a) and (b), maintained at 350°C and 15,000 p.s.i. for 1460 hours, yielded 1M muscovite alone, while glass (c), maintained at 350°C and 15,000 p.s.i. for 1460 hours in two identical runs, yielded 1Md
alone. The appearance of ld thus seemed to result, in part, from variations of unknown nature in the starting materials.

Warshaw (1960) synthesized phases similar to natural illites by employing starting mixtures which differed significantly from the ideal muscovite formulation in bearing more SiO₂, less A₃O₃ and K₂O. The products were reproducibly disordered, but based upon the 3T polytype structure. One such, sufficiently disordered to exhibit no evidence of polytypic affinities, compared closely in number and position of diffraction maximato a less than 0.2μ fraction of the Fithian "type specimen" illite. Warshaw suggests reference to this as merely "mica D", of unspecifiable polytypism. Concerning her work, Roy (1961) stated "By proper control of the composition, i.e. partial internal charge compensation for lack of potassium, Warshaw was able to prepare phases which behave essentially identically with illite."

Velde (1965) has prepared ld micas from kaolinite and potassium hydroxide. His principal concern was the stability relationships. Minimal information is given concerning the nature of the disordered products.

The techniques and compositions reported by Warshaw were employed in this work.

(e) Compositions of Preparations for Hydrothermal Treatment

The compositions investigated were within the systems K₂O-Al₂O₃-SiO₂-H₂O and K₂O-MgO-Al₂O₃-SiO₂-H₂O. Only five com-
positions were chosen. On the basis of their formulation as hypothetical layer silicates they were the following:

(A) \( K_2Al_2(AlSi_3)O_{10}(OH)_2 \): equivalent to ideal muscovite. Prepared with the possibility in view of employing it in exchange experiments, also as a standard with which to compare the disordered, but analogous, layer silicates.

(B) \( K_0.5Al_2(Al_{0.5}Si_{3.5})O_{10}(OH)_2 \): equivalent to the composition of 50\% muscovite, 50\% pyrophyllite. It was investigated by Warshaw (1960), and exhibits, chemically, several of the features of the analyses of illite: lower potassium oxide and higher silica than muscovite. It was prepared to compare the features of the actual crystallization with those of illites. Represented by synthesis 15.

(C) \( K_{0.5}(Al_{1.9}Mg_{0.1})(Si_{3.6}Al_{0.4})O_{10}(OH)_2 \): lies close to the muscovite-pyrophyllite join but Mg is introduced, leading to a slight redistribution of charge deficiency between the octahedral and tetrahedral layers. Investigated by Warshaw and inferred by her to yield the product closest in nature to illite of those she obtained. It was therefore adopted for use in obtaining illite-like micas for the potassium exchange studies of this work.

(D) \( K_{0.97}(Al_{1.98}Mg_{0.02})(Al_{0.95}Si_{3.05})O_{10}(OH)_2 \): represents a composition on the muscovite-potassium montmorillonite join at 95\% muscovite. The montmorillonite represented is idealized, being
\( K_{0.33} (Al_{1.67}Mg_{0.33})Si_{4}O_{10}(OH)_{2} \). Employed in preparation number 3 for syntheses 3 and 4.

(E) \( K_{0.83} (Al_{1.92}Mg_{0.08}) (Al_{0.75}Si_{3.25})O_{10}(OH)_{2} \): a composition similar to (D) but made up of 75% muscovite and 25% idealized K-montmorillonite. Employed in preparation number 7 and synthesis 16.

Formulas of the above hypothetical layer silicates in terms of oxides are set out below.

<table>
<thead>
<tr>
<th>Compositions in Terms of Oxides</th>
<th>%SiO₂</th>
<th>%Al₂O₃</th>
<th>%MgO</th>
<th>%K₂O</th>
<th>%H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>45.25</td>
<td>38.40</td>
<td>nil</td>
<td>11.83</td>
<td>4.52</td>
</tr>
<tr>
<td>B</td>
<td>55.44</td>
<td>33.60</td>
<td>nil</td>
<td>6.21</td>
<td>4.75</td>
</tr>
<tr>
<td>C</td>
<td>57.05</td>
<td>30.93</td>
<td>1.06</td>
<td>6.21</td>
<td>4.75</td>
</tr>
<tr>
<td>D</td>
<td>46.16</td>
<td>37.66</td>
<td>0.17</td>
<td>11.47</td>
<td>4.54</td>
</tr>
<tr>
<td>E</td>
<td>49.83</td>
<td>34.69</td>
<td>0.86</td>
<td>10.02</td>
<td>4.60</td>
</tr>
</tbody>
</table>

It appears that compositions D and E have not previously been investigated. They were chosen for the reason that, at \( 463^\circ\)C and 650 bars, composition C (preparation 2, synthesis 2) yielded an excess of SiO₂. This was suggestive of a required reduction in the amount of the most siliceous end-member adjacent to the composition, namely pyrophyllite. Desiring to retain magnesium, the join muscovite-montmorillonite was chosen, and two compositions
lower in SiO₂ than C were examined. It is notable that D and E both crystallized as single phases in terms of major diffraction effects, but at 400°C were higher in structural order than the products of C, tending towards the muscovite condition.

Had further time for synthesis been available, investigation of similar compositions would have been continued and the products probably used for the exchanges. In practice composition (C) was spiked with ⁴⁰K and employed. It should be noted that the products from this material varied in their degree of disorder and two runs exhibited a different accessory phase from the remainder. Therefore the layer silicates probably were chemically variable also.
SECTION II, EXPERIMENTAL METHODS

(1) MEANS OF SYNTHESIS

The methods employed were, in general, based upon those described by Luth and Ingamells (1965), Warshaw (1960), and by Roy and Tuttle (1956). The work of Warshaw in particular was drawn upon heavily, for her study determined certain compositions of oxide mixtures which yielded phases analogous to illite upon hydrothermal treatment.

(a) Materials Employed

The starting materials were, with two exceptions, reagent grade chemicals. They comprised the hydrated nitrates of aluminum and magnesium, aluminum and magnesium metal, the carbonate, nitrate and chloride of potassium, and two sources of silica. The most important was "Ludox", a technical grade silica sol prepared by E. I. du Pont de Nemours and Company which contains approximately 4 mg. of sodium per g of SiO₂. A silica glass of exceptional spectrographic purity was employed once, and a glass of natural composition was used in synthesis 1 only. The latter was prepared by heating to 1100°C a Silurian illite* from Marblehead, Wisconsin. Its analysis is given on page 190. [H. F. Gaudette, (1965)]

* Provided by courtesy of Dr. Gaudette.
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Twenty-one syntheses were carried out from ten initial preparations which represented six compositions. The preparations were made up from combinations of the materials listed above. In all except three cases, which were regarded merely as auxiliary experiments (syntheses 8, 11, and 12), the preparations were initially aqueous fluids containing colloidal silica, salts in solution, and nitric acid. The materials incorporated in each case are detailed in Table 4 below.

Table 4. Summary of Starting Materials Employed.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Preparation Number</th>
<th>Components of Initial Preparations (for conversion to oxide mixtures)</th>
<th>Employed in Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4</td>
<td>KCl, Al metal, &quot;Ludox&quot;</td>
<td>6 and 7</td>
</tr>
<tr>
<td>A</td>
<td>5</td>
<td>$K^+$ and Al$^{3+}$ as standardized nitrate solutions; &quot;Ludox&quot;</td>
<td>14, 17, and 19</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>$K_2CO_3$, Al$^{3+}$ solution, silica glass (&lt;5 μ).</td>
<td>8</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>KCl, Al$^{3+}$ solution, &quot;Ludox&quot;</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>6</td>
<td>$K^+$ &amp; Al$^{3+}$ solutions, &quot;Ludox&quot;</td>
<td>15</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>KCl, Al(NO$_3$)$_3$.9H$_2$O, &quot;Ludox&quot;, Mg(NO$_3$)$_2$.6H$_2$O</td>
<td>2, 5, 9, 10, 13, 18, 20 &amp; 21</td>
</tr>
<tr>
<td>D</td>
<td>3</td>
<td>As preparation 2.</td>
<td>3 and 4</td>
</tr>
<tr>
<td>E</td>
<td>7</td>
<td>As preparation 5 with the addition of Mg$^{3+}$ solution as nitrate</td>
<td>16</td>
</tr>
</tbody>
</table>
(b) Standardization of Reagents

As specific cation ratios were required in the initial preparations, knowledge of the purity and water content of the reagents was essential.

Of the seven liquid preparations, the first four employed crystalline Al(NO$_3$)$_3$.9H$_2$O, Mg(NO$_3$)$_2$.6H$_2$O and KCl. The latter could be dried before weighing but this proved to be impracticable for the hydrated salts as they exhibited variable weight losses, dependent upon the drying technique. They were therefore employed directly.

Preparations 5 to 7 employed stock solutions of the metals and of diluted "Ludox", dispensed by volume. The solutions were standardized as follows.

Aluminum Nitrate Solution.

10.9692 g. of stock solution at pH1 was weighed in a pre-ignited platinum crucible. The solution was evaporated to dryness, ignited at 1125°C for 2 hours, cooled to 110°C, and placed in a dessicator. While in the latter, the crucible was transferred to a gas-tight weighing bottle. The yield of alumina was 0.1758 g., the density of the solution 1.0558 g/ml, giving an aluminum concentration of 9.0 mg Al$^{+++}$ per ml. of solution at 25°C.
Magnesium Nitrate Solution.

0.5224 g of reagent grade magnesium turnings, of greater than 99.81% purity, were dissolved in one liter of 0.1N nitric acid. Considering the possible range of impurity levels, the concentration was taken as 0.52 ± 0.00 mg per ml.

Potassium Nitrate Solution.

In a pre-ignited platinum crucible, approximately 1.39 g of finely divided, reagent grade, anhydrous potassium carbonate was placed. A negligible weight loss occurred between drying the carbonate at 110°C and 435°C. A dry weight of 1.3923 g was dissolved in one liter of 0.25 N nitric acid, yielding a concentration of 768.16 µg K⁺ per ml. The value was confirmed by a precise flame-photometer analysis. 65 ml of the solution was diluted to 500 ml with demineralized water and 20 ml of solution bearing 1600 µg/ml of lithium were added. It was thus at 98.52 µg K⁺/ml. Solutions of primary standard grade potassium phthalate bearing the same lithium concentration and 108.48 and 86.78 µg K⁺/ml were used as standards. In the analysis, four runs of six showed no instrument drift over the period of measurement and these indicated that the "unknown" contained 97.91, 97.97, 99.18 and 99.52 µg K⁺/ml, or a mean of 98.64 ± 0.72*. The accuracy of the preparation of the potassium solution was therefore considered adequate.

* 0.72 is the sample standard deviation determined from the range, (Bauer, 1960).
Silica Sol, "Ludox".

The weight of dry, ignited, solids was computed as SiO$_2$. A quantity of "Ludox" was pipetted into a weighed, ignited, platinum crucible and quickly provided with an air-tight cover. The weight of "Ludox" was determined, the liquid evaporated to dryness and ignited at 900°C for several hours. After cooling in a dessicator it was sealed while within the latter and reweighed. The results of two determinations were as follows.

<table>
<thead>
<tr>
<th>Wt. of &quot;Ludox&quot;</th>
<th>Wt. of SiO$_2$</th>
<th>g. SiO$_2$ per g &quot;Ludox&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.752 g</td>
<td>1.449 g</td>
<td>0.304(9) g</td>
</tr>
<tr>
<td>4.9126 g</td>
<td>1.4984 g</td>
<td>0.3050 g</td>
</tr>
</tbody>
</table>

Ten months later, prior to a second set of syntheses, 50 ml of "Ludox" was diluted to 500 ml. The density was found to be 1.018 g. per ml. and the sol yielded 0.0361 g SiO$_2$ per g of dilute "Ludox". The effective concentration was therefore 0.0368 g SiO$_2$ per ml.

Solution Enriched in $^{40}$K.

1 mg of potassium bearing 30.3% of $^{40}$K was obtained from the Atomic Energy Commission's Oak Ridge National Laboratory. This concentration may be compared to the natural abundance of $1.21 \times 10^{-2}$ g $^{40}$K per 100 g of ordinary potassium (Smith, 1964). The material, as 1.9 mg of KCl, was dissolved in 10 ml of 6N nitric
acid, diluted to 15 ml with pipette - measured washings, and stored in a polyethylene bottle, adequately sealed.

The concentration of $^{40}$K in the solution was therefore 20.2 μg/ml. The total calculated $\beta^-$-activity was 4242 decays per minute, based upon the "best experimental values" quoted by Smith.

Five milliliters of the solution were employed in synthesis 7, and 2 ml in each of syntheses 10, 17, 18 and 19. The remaining volume of approximately 1.25 ml was used in synthesis 20.

(c) Combination of Reagents and Treatment of Initial Preparations

For purposes of systematization, the composition of an initial preparation was determined upon the assumption, seldom realized, that the reactants would crystallize as a single micaceous phase having the cation ratios of the preparation. The compositions were represented as hypothetical micas. To make up each preparation, the weights in gram atoms of the cations represented in each of the mica formulas were summed, and the weight percentages obtained. A suitable amount of the required preparation was chosen, often 1/100 of a gram "molecule", and maintaining the required weight ratios, the weights of the necessary cations were determined. The weights or volumes of the reagents were calculated therefrom.

Crystalline nitrates were dissolved in water and made acid
with nitric acid to prevent the precipitation of aluminum hydroxide by the basic "Ludox" sol. The standardized solutions were dispensed by volume. In preparations 1 to 4, "Ludox" was weighed-out in a closed weighing bottle bearing a dropper.

A sufficient quantity of a preparation to yield, modally, 200 mg of oxides was pipetted into a "Teflon" evaporating bowl. The quantity was carefully determined in the cases where an enrichment of $^{40}$K was to be added. If KCl was present, concentrated nitric acid was added to further the reaction:

$$KCl + HNO_3 \xrightarrow{H^+} KNO_3 + HCl^+$$

Evaporation to dryness at 70$^\circ$C was followed by transfer of the material to a platinum crucible. Ignition of the nitrates was carried out, usually for 30 minutes. No nitrous oxide was observably released after the initial rise in temperature. In the first thirteen syntheses the reduction to oxides was carried out over a Fisher burner at approximately 600$^\circ$C, in the remaining cases on an electric heater at less than 500$^\circ$C. The oxides were ground in an agate mortar.

The ignited oxides of preparation number 2 were examined by X-ray diffraction. They would be termed X-ray amorphous but order is not absent, for an exceptionally broad band occurs with its maximum at 3.6Å. Common soda glass shows a similar pattern, with a maximum at 3.9Å. However, two pure, commercial silica glasses were found to exhibit their peak maxima at a spacing of
4.09\AA, significantly closer to the cristobalite spacing of 4.04\AA.
The "oxide mixture" therefore exhibits a feature common to glasses, particularly those departing from a pure SiO_2 composition. It is possible that even at this stage of the syntheses the components are other than an intimate mechanical mixture.

(d) High Pressure and Reaction Vessels Employed

The ignited oxides were sealed in noble metal tubes with 0.10 to 0.21 ml of demineralized water. The tubing was generally of platinum, 0.002 in. to 0.004 in. thick, 5/32 in. internal diameter and 1-1/2 in. to 3 in. in length. It was fabricated in the laboratory from sheet metal by welding an interlocking, flanged seam with gold. Syntheses 16 to 18, and 21 employed commercial gold tubing, 5/32 in. internal diameter, and 0.005 in. wall thickness.

Sealing was carried out by welding with gold, employing an oxyacetylene flame. The procedure required cooling of the lower end of the tube. The use of liquid nitrogen for this purpose was eventually successfully superseded by the use of cold water. A few instances of loss of vapour during welding were noted. In the case of the gold tubes the tightly compressed upper portion was heated until a continuous seam of molten metal appeared in place of the slit-like orifice. Seals were examined under a binocular microscope and frequently were tested by heating the tube in water to 80-90° C.
Copper tubing, of 1/4 in. outside diameter, was employed in syntheses 1 and 2 and sealed with silver solder. The mica produced in synthesis 2 was typical in its diffraction features when compared with certain runs of the same composition carried out in gold or platinum.

It was of interest to determine whether or not leakage of the bomb fluid into the sample tube occurred during synthesis. A significant weight gain, greater than 2 mg, was considered to indicate failure of the seal. In all, such behaviour occurred six times, entirely in the cases of platinum tubes, especially the thinner-walled examples which tended to fail upon flexure due to compression.

The pressure vessels used were two, a Tuttle and a Morey type. The former was an elongate, "cold-seal", "test-tube" type and the latter similar but of one-half the internal capacity. Both could be used in either of two fashions, connected to a pressure pump by capillary tubing, or sealed with a solid, stainless steel cone.

(e) Procedures of Hydrothermal Treatment; Temperature and Pressure Control

The required temperatures were obtained with the use of an electric furnace consisting of a resistance-wound ceramic tube, 2-1/2 in. in diameter and 24 in. in length, heavily insulated. Temperature control during treatment relied only upon the voltage
stability of the mains, smoothed by a constant-voltage transformer and the high heat capacity of the furnace. The furnace current was altered by means of a variable-voltage transformer. The system showed remarkable stability as determined by frequent observations of temperature and often by the continuous operation of a recording potentiometer. After reaching thermal equilibrium, constancy of temperature with excursions of less than 2°C was commonplace. Drifts of up to 5°C occurred occasionally. This stability was obtained only after the use of the Tuttle-type vessel, run with its seal outside the furnace, was discontinued following synthesis 4. It had shown such temperature gradients as the following:

Base of bomb, thermocouple well: 465°C
17.8 cm above base, outer surface: 417°C
6.2 cm below top: 370°C

The Morey bomb was suspended entirely within the furnace, the ends of which were closed, with its base below furnace center. The following temperatures were then measured at equilibrium:

Thermocouple well near base: 505°C
20 cm above base at seal: 511°C

An aluminum oxide preparation ("Loktite") was employed to prevent welding of the threads of the bomb seal.

Temperature measurements were made with a frequently renewed
chromel-alumel thermocouple and a portable Leeds-Northrup potentiometer. The accuracy of the combination was determined at 100°C in boiling, demineralized water, and at 334°C in crystallizing potassium nitrate. The observed potential at 100°C was 3.1 mV, the room temperature 25°C, giving an effective total potential of 4.10 mV, the expected value. The first deflections were observed at 3.05 and 3.15 mV, indicating a precision of ± 0.1°C at 100°C. Despite maintaining a heated enclosure, the potassium nitrate crystallized rapidly. At 50% crystal-coverage of the melt surface an effective total potential of 13.62 mV was developed, equivalent to 334°C. However, at 90% coverage a potential of 13.57 mV was developed, possibly indicative of super-cooling. It was concluded that no error could be demonstrated with certainty.

Required pressures were obtained without the use of a pump, except in the case of synthesis 1 and the potassium-exchange experiments. A volume of water, calculated to produce the chosen pressure at the temperature of synthesis was sealed in the bomb. This volume was determined by reference to the pressure-volume-temperature relationships determined for water by G. C. Kennedy (1950). His corrections published in 1957 did not apply to the region of interest.

Pressures determined in this manner are subject to two principal inaccuracies. The large temperature gradient in bomb in syntheses 2 to 4 required the estimation of an average for the calcu-
lation of pressure. Secondly, in all cases, the volume of water recovered from the bomb was less than was introduced. Therefore mean specific volumes (cubic centimeters per gram) and mean pressures were determined. Except in two cases of significant leakage, numbers 2 and 4, the average loss was 0.35 ml. In the eighteen runs above 400°C the maximum loss was 0.5 ml in synthesis 8. Considering temperature variation also, the maximum possible range of pressure was from 810 to 980 bars, that is, 170 bars and 19% of the mean. Therefore pressures are considered to have been well within approximately ± 10% of the means quoted in Table 8, page 126, for the higher temperature syntheses.

At the conclusions of runs the bomb were quenched in water, opened, the contained tube weighed, and its contents washed into demineralized water for partial disaggregation by ultrasonic vibration.
(2) PROCEDURES EMPLOYED FOR POTASSIUM-EXCHANGE EXPERIMENTS

The experiments fall into two groups differing widely in technique, those at 100°C and atmospheric pressure, and those at temperatures greater than 100°C and at elevated pressures.

The exchanges at 100°C were carried out in a 500 ml flask containing 125 ml of 0.5 molar potassium chloride solution and up to 77 mg of a synthetic illitic phase. The flask was suspended within a water bath maintained at 100°C. Both vessels were closed, and fitted with individual reflux condensers. The potassium chloride solution was thereby maintained extremely close to its original concentration.

The exchanges at temperatures between 250°C and 450°C required the re-use of systems similar to those employed for synthesis. The active micaceous material was sealed in a gold tube with a solution of potassium chloride. The tube was placed in a Morey-type vessel, the required water pressure applied by means of a pump and measured on a Bourdon-tube gauge. A limitation was placed upon the proportions and amounts of reactants by the small volumes of the gold tubes employed, generally 0.8 to 1 ml. The requirements were that a sufficient quantity of active material for an adequate β-counting rate, preferably over 50 counts per minute, be used, secondly that the solution contain a much greater mass of potassium than the solid, and that the concentration of the solution should
not be excessive when formed from the limited volume of water that could be added. In practice the weights of synthetic material employed were between 24.2 and 44.0 mg. Weights of KCl employed ranged from 80.8 to 90.9 mg. in 0.3 ml. of demineralized water. Solution concentrations therefore ranged from 3.61 to 4.06 molar. The weight of potassium in solution was in all cases minimally twenty-five times greater than the weight in the solid phase which contained 5.16 per cent potassium by weight. The large difference was employed to dilute as far as practicable the \(^{40}\text{K}\) released from the illitic phases.

Temperature control of the bomb was carried out in the same manner as during the syntheses. Fluctuations during an experiment were less than \(\pm 3^\circ\text{C}\), rarely \(\pm 5^\circ\text{C}\). Periods of heating-up were reduced to approximately two hours. Pressure control was by means of a high pressure water pump and a system of valves. The pressure gauge was calibrated against a standardized, temperature-compensated Heise Gauge.

At the conclusion of the treatments the solids were washed with fresh 0.5 molar KCl for a sufficient period to repopulate certain slowly exchangeable potassium sites first recognized in illites by Sumner and Bolt (1962). It was intended that any internally-released \(^{40}\text{K}\) should be removed from surface adsorption sites so that any change in specific activity could be attributed to the structural, not the surface, potassium population.
Exchanges of sodium for potassium, employing molar sodium chloride and sodium citrate were carried out in covered beakers in a thermostat-controlled oven or gently boiling over a heater.

(3) X-RAY DIFFRACTION TECHNIQUE

(a) Instrumental Features

A North American Philips geiger counter spectrometer was used as the sole means of characterizing the synthetic products, although some microscopic examinations were made.

Copper Kα, 02 radiation was employed, produced at 40 kilo-volts potential and 30 milliamperes filament current. A nickel filter removed Kβ radiation. Instrumental components were kept unchanged, a 1° divergence slit, a 0.006 inch receiving slit and a 1° anti-scatter slit. Resolution was sacrificed to obtain intensity for the recognition of minor phases. A scale factor of 8 was employed giving 400 counts per second for full-scale deflection. Intensities are recorded in later sections as peak heights above background and are equal to percentages of the value 400 c.p.s. A time constant of 4 seconds was maintained.

Scanning speeds were 1/4° 2θ per minute for charts from which data were measured, and 1° 2θ per minute for others. The chart speed was 1/2 inch per minute. Slow scanning was adopted to resolve low intensity peaks from spurious peak-like noises. The range covered was 2° to 63° 2θ.
The alignment of the instrument was checked at the outset of the work and found reasonably satisfactory. However, the goniometer zero angle was relocated with an aligning bar and the axis rotated to bring the sample mounting surface parallel to the beam in the zero goniometer position. Alignment was checked employing a silicon standard at 1/8° per minute scanning rate with the results tabulated below.

(b) Accuracy of Data

The attainable accuracy is limited by the alignment of the goniometer and was estimated as illustrated in the table.

Table 5. Observed Deviations of Silicon Diffraction Peaks

<table>
<thead>
<tr>
<th>Index of Silicon Spacing</th>
<th>True Peak Position, ( \theta_{2\theta} ), CuK(_{\alpha 1})</th>
<th>( \theta_{2\theta} ), Obsvd. (means of 4)</th>
<th>( \Delta \theta_{2\theta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>28.442</td>
<td>28.442</td>
<td>0.000</td>
</tr>
<tr>
<td>220</td>
<td>47.302</td>
<td>47.304</td>
<td>+0.002</td>
</tr>
<tr>
<td>311</td>
<td>56.122</td>
<td>56.122</td>
<td>0.000</td>
</tr>
<tr>
<td>422</td>
<td>88.030</td>
<td>88.024</td>
<td>-0.006</td>
</tr>
</tbody>
</table>

The errors in \( d \) values related to the observed deviations in angular position are both less than 0.0007Å, that is, negligible.

The potential accuracy of a determination of a value of \( d \) was therefore adequate for the purpose of phase characterization.
Values of $\Delta \theta$ for silicon peaks were checked periodically and not observed to be greater than $+0.005^\circ$ on 111 at the end of the investigation. Variations are probably attributable to minor accidental movements. Accuracy in the low $2\theta$ region was expectably high, the basis of the above data. However, a cholesterol standard, polished on a surface grinder, consistently showed a negative deviation of $-0.025^\circ$ to $-0.032^\circ$ $2\theta$ for its 33.6 $\AA$ spacing peak. The inconsistency may be in part due to axial divergence of the beam between the Soller slits. The effect is maximal at low angles, produces peak asymmetry on the low angle side and shift of the profile in the same direction. Such asymmetry was observed.

(c) Precision of Data

The principal causes of imprecision are considered to be twofold. Firstly, the majority of synthetic products exhibit low, broad peaks which are subject to displacement by instrumental noise. The modal intensities of maxima above the background are of the order of 40 c.p.s., the background fluctuating by some 6 c.p.s. Such fluctuations are capable of shifting the maximum of a broadened peak from its true position. Secondly, specimen surface displacements from the goniometer axis of rotation lead, if variable, to lack of precision between runs. For example, a displacement as small as 0.001 in. produces an error of $0.017^\circ 2\theta$ at $10^\circ 2\theta$ (Parish and Lowitzsch, 1959).
The precision of location of a peak at $8.85^\circ 2\theta$ involving seven replicate runs for four sample preparations was represented by a sample standard deviation of $\pm 0.02^\circ 2\theta$. Values of $\sigma$ given by Chayes and MacKenzie (1957) for similar replication of the relatively sharp peaks of quartz range from $\pm 0.0118$ to $\pm 0.0169^\circ 2\theta$.

(d) Sample Preparation

Diffraction patterns of the synthetics invariably exhibited random orientation, evidently due to particle cementation into aggregates. Samples could therefore be prepared variously with the same results. Sedimentation onto common and silica glasses, steel, and porous ceramic tile were employed. All except the first proved undesirable as their diffraction effects were detrimental to the record. The tile bore quartz and potassium feldspar. The objective of the trials was to obtain a substrate suitable at once for diffraction and $\beta^-$ counting. Wet smearing of some 20 mg. on glass was commonly adopted. Samples were placed with the powder film in contact with the goniometer mounting surface to minimize displacement error. Because of the fine grain sizes they were smooth and coherent.
(4) BETA COUNTING

Counting was carried out on a "Widebeta", manufactured by Sharp Laboratories Incorporated. The instrument possesses numerous features of value in low activity-level counting. A gas-flow sample detector employing methane operates in the proportional region. High efficiency of particle detection is promoted by the use of a 2-1/4 inch diameter, thin window (500 µg per cm²), and a sample-to-window distance of 0.005 inch. This close approach was facilitated by the mechanical loading, from below upwards, of carefully machined powder-holding planchette assemblies. Solid state circuit components allow continuous operation and exhibit excellent stability of the high voltage supply to the detector. A pre-set potential of 3.07 kv was maintained, a level near the upper inflexion of a plateau suitable for the beta particle energies employed by various users. The counter provides automatic sample recycling as well as loading, and a print-out of data. Measured background activity values were between 1.10 and 7.17 β⁻ counts per minute, reduced by a cosmic radiation detector operated in anticoincidence with the sample detector immediately below it, and by heavy shielding.
(a) Accuracy

The principal objective of the counting procedure was to determine relative changes of activity. Accuracy was sought chiefly to enhance reproducibility and relevant considerations are discussed in part (6). Factors related to accuracy alone are losses of counts by coincidence and proper functioning of the counter. Coincidence loss was wholly negligible at the rates employed, generally less than 100 counts per minute. Counter functioning was tested to determine whether or not random data was obtained from the truly random input of a radioactive source. The data was found to conform to the required Poisson distribution by means of a chi square test. Details are given in Appendix 3.

(b) Precision

Overall precision and the expectable accuracy of a single standardized counting rate depended upon determinations of the following variables.

1) Relative efficiency of the counting system
2) Stability of the system during a period of counting
3) Sample weight and geometry
4) Background activity
5) Sample counting rate

Values of standard deviations of means were determined individually for quantities (4) and (5) only. These precision indexes
are not necessarily estimators of overall precision as accidental error attends processes (1) to (3) also. (See Part (C) below).
The above variables will be discussed in turn.

(1) Relative Efficiency

The observed counting rate of a reference or standard sample may vary, dependent upon instrumental factors, particularly the detector high voltage. An estimate of the relative efficiency of the counting system was made during each period of operation by means of a standard sample of $^{137}\text{Cs}$. This was counted for 10.00 minutes, the invariant pre-set counting interval, after each replication of the set of samples. Over several months of intermittent use, repeated series of counts of the standard for totals of 300 to 500 minutes yielded mean activity values close to 4,600 counts per minute. This rate was arbitrarily adopted as one with which to standardize the relative efficiency. An observed counting rate for the standard was divided into 4,600 and the ratio employed as a correction factor. Values of the ratio varied from 1.0059 to 0.9628 over the ten month period of use, a range of 4.4% of the mean, and indicative of excellent long term stability.

No allowance for decay of the standard, of a half-life of 30 years, was made during the period of use.

(2) Stability During a Period of Counting

Maximally three samples and the standard were counted during a single period of operation. The maximum total counting time was approximately 30 hours. The stability of counter performance was
estimated by considering subsets of the observed standard counts. Means and standard deviations of sub-sets of five to ten, e.g., the first ten, the second, etc., were compared. Deviations beyond 2σ from the grand mean were never encountered. Ranges of means of sub-sets were small, to the remarkable extent that two means differing by less than one count per minute, yet measured 26 hours apart, were once observed. The counter was considered adequately stable over the required periods.

(3) Sample Preparation

Control of the sample mass and geometry was of importance. Weighings of the dry powder sample directly onto the planchette were carried out on a Mettler balance adjacent to the counter. Weights up to 80 mg. were commonly employed, and were determined to the nearest 0.1 mg. Control of the level of adsorbed moisture, other than by air-equilibrium, was not maintained. Sample geometry was determined by the planchettes: lucite discs with a central cavity 1-1/4 inches in diameter and 0.010 or 0.014 inches deep were used. Some series of counts were made with other holders bearing thin inserted discs of silica glass or stainless steel. The insert surfaces were, in these planchettes, similar distances below the lucite rim. Thus powder layers of reproducible thickness and only slightly variable area were formed and were covered with a thin plastic film. The sample surface was 0.005 inches below the rim of the planchette holder which contacted the counter window support. The effect of self absorption in this geometry
was negligible as is shown below (Figure 2).

(4) Background Activity

This value was determined for individual planchette and holders before or after each run. Variations were due to trace activities contaminating the counter after other usages. Total counts per planchette-assembly were accumulated to values between 249 and 3,225, giving coefficients of variation between 6.32% and 1.75%. The higher percentage values increase the coefficient of variation for the sample count extremely little.

(5) Sample Counting Rates

These rates were modally of the order of 50 counts per minute. Total counts accumulated were in general greater than 10,000, as values of the coefficient of variation close to 1% were sought. The values actually achieved ranged from 0.40 to 1.75%.

Three of the factors described above were employed to correct and standardize counting rates of samples. Background was subtracted, multiplication by the relative efficiency factor carried out, and further, to compare a decreased weight of samples after treatment with an original weight and condition, a weight correction was applied. The correction factor was determined on the basis of Figure 2 which demonstrates a linear relationship between sample weight and count rate for weights up to approximately 80 mg. Therefore the rate was multiplied by the ratio of the weight originally counted to that employed. Linearity demonstrates the
insignificance of self-absorption in the thin samples.

(C) Overall Precision

Standardized counting rates were calculated by the method of Evans (1955), which is detailed in Appendix 3. Allowance was made for statistical fluctuations while counting the background, the sample plus the background, as well as for background fluctuation during the second procedure. The values of the standard deviations of the means are those determined by the counting statistics only, and need not be representative of the precision of all the procedures involved. The errors of the entire determination of a standardized rate include also those of sample weight and geometry control, standardization and stability of the counter, and extrapolation to standard weights.

The overall precision was estimated by obtaining six sets of fully independently replicated data. The resulting grand means comprise 23% of the rates determined and should provide a reliable estimate of overall precision. The sets of individual means are tabulated below.

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.38 ± 0.81 c.p.m.</td>
<td>95.24 ± 0.78 c.p.m.</td>
<td>99.32 ± 0.41 c.p.m.</td>
</tr>
<tr>
<td>98.35 ± 0.80 c.p.m.</td>
<td>94.29 ± 0.42 c.p.m.</td>
<td>96.70 ± 0.54 c.p.m.</td>
</tr>
<tr>
<td>99.02 ± 0.81 c.p.m.</td>
<td>(Synthesis 7, treated)</td>
<td>97.11 ± 0.39 c.p.m.</td>
</tr>
<tr>
<td>(Synthesis 7)</td>
<td></td>
<td>(Synthesis 10)</td>
</tr>
</tbody>
</table>
IV
95.78 ± 1.24 c.p.m.
94.04 ± 1.36 c.p.m.
94.06 ± 1.55 c.p.m.
(Synthesis 10, treated)

V
26.20 ± 0.32 c.p.m.
26.80 ± 0.32 c.p.m.

VI
45.49 ± 0.40 c.p.m.
40.55 ± 0.36 c.p.m.
(Synthesis 10, treated)

The considerations which arise in estimating means of the sets, the standard deviations of the means, and the resulting coefficients of variation are discussed in Appendix 3. A justification of the method used is given therein. It employed the following statistics:

\[
\bar{Y} = \text{the grand mean of a set, taken as the arithmetic mean c.p.m.}
\]

\[
s^n = n \sqrt{\frac{\sum (Y_i - \bar{Y})^2}{(n-1)}} \text{ c.p.m.}
\]

\[
\omega = \text{the coefficient of variation of a set}
\]

\[
\omega = \frac{100 \, \frac{s^n}{\bar{Y}}} \%
\]

where \(Y_i\) equals the value of a mean in a given set, and \(n\) equals the number of means in the set. Results are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Set I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average, (\bar{Y})</td>
<td>98.25 c.p.m.</td>
<td>94.77</td>
<td>97.71</td>
<td>94.63</td>
<td>26.50</td>
<td>43.02</td>
</tr>
<tr>
<td>S.D., (s^n)</td>
<td>± 0.83 c.p.m.</td>
<td>± 0.67</td>
<td>± 1.39</td>
<td>± 1.00</td>
<td>± 0.42</td>
<td>± 3.49</td>
</tr>
<tr>
<td>Coeff. Var., (\omega)</td>
<td>0.84%</td>
<td>0.72%</td>
<td>1.42%</td>
<td>1.06%</td>
<td>1.58%</td>
<td>8.11%</td>
</tr>
</tbody>
</table>
The mean overall precision, \( \bar{\omega} \), is indicated to be 2.29\%, the arithmetic mean of the values \( \omega \).

The anomalously high value 8.11\% in set VI includes a mean which was suspected of being erroneous at the time of determination.

The means \( \bar{\bar{y}} \) are determined and utilized once only, for the specific purpose of determining the maximum probable values of the coefficients of variation. A valid objection exists to the use of the arithmetic mean of the values of sets I, II, IV, and V for any other purpose. Therefore it will be noted that in these cases the data is employed elsewhere to determine \( \bar{x} \), the grand mean of consistent means, those drawn from a single population.

\[
\bar{x} = \frac{\sum (X_i / \sigma_{X_i}^2)}{\sum 1 / \sigma_{X_i}^2} \approx \bar{\bar{y}}
\]

The subject is discussed further in Appendix 3.

(d) Counting of Beta Activity Due to \( ^{40}K \) in Synthetic Silicates and Minerals.

At the outset of this investigation no information was available upon the absorptive capacity of silicates, either as aggregates or single crystals, for the \( \beta^- \) radiation of \( ^{40}K \) of maximum energy 1.32 MeV. Such information, in conjunction with the value of the counting yield, \( \epsilon \), of the beta counter to be employed, was essential to assess the required enrichment of \( ^{40}K \) in the synthetic phases.
Accordingly, thin tablets of Marblehead illite (Gaudette, 1965) each of 4 cm$^2$ area and of various weights were prepared by centrifugation of a suspension upon a porous ceramic tile. The tablets were removed after drying. Counting of the slabs singly and in pairs yielded, after background correction, the data plotted in Figure 1. The fitted curve suggests that self-absorption is not evident below 50 mg cm$^{-2}$ of illite (200 mg sample) at which mass the counting rate is 10.2 $\beta^-$ counts per minute.

A further test for self-absorption, and linearity of the relationship between weight counted and beta count observed, is shown in Figure 2, page 83. This employed thin layers of synthetic mica powders, in standard geometry, the data being that obtained after exchange C3 prior to its correction for weight counted. There is no significant departure in the data from a straight line through the origin. On this basis a multiplier $W$ equal to the ratio of weights counted upon different occasions could be legitimately applied to yield fully standardized counting rates.

Employing the constants given in Appendix 1, particularly the specific activity of $^{40}\text{K}$, 14.03 $\beta^-$ decays per minute per microgram, and the experimentally determined counting yield (efficiency) of 49.33% for KCl, it is possible to determine the K$_2$O content of the illite using 10.2 c.p.m. per 200 mg. 6.07 wt. % K is calculated, equivalent to 7.35% K$_2$O. This may be compared with the published value 7.98% K$_2$O (Gaudette, 1965). The reasonable agreement, considering the lack of refinement in obtaining the data, indicates that
Figure 1. Self-Absorption of Beta Radiation of Normal $^{40}$K Content of Marblehead Illite.
Figure 2. Absence of Self-Absorption of $^{40}$K Beta Radiation in Thin Layers of Synthetic Illitic Micas.
highly accurate and precise potassium determinations could be carried out on the $\beta^-$ counter used if further work were done. The efficiency for silicates is probably greater than 49.33%. Correction for actinide element $\beta^-$ emission could be made by alpha counting on the same instrument.
SECTION III. RESULTS AND DISCUSSION

PART 1. POTASSIUM EXCHANGE EXPERIMENTS: DATA AND MODIFICATIONS OF SYNTHETIC MATERIALS.

The principal details of the experiments are given in Table 6. The X-ray diffraction patterns of important regions are shown for the initial and final states of syntheses 10 and 20 in Figure 3. These exchanges were against aqueous potassium chloride. Figure 4 shows the initial and final states of synthesis 18 employed in Exchanges K, I and J against molar solutions of sodium chloride and sodium citrate.

Before the principal experiments at temperatures above 100°C were carried out, two tests of the stability of illitic micas under the conditions to be employed were made. A 0.3 to 0.8u fraction of the Marblehead illite, described by H. E. Gaudette (1965) and employed as a reference clay sample at the University of Illinois, was maintained in 0.05 molar KCl at 350°C, 200 bars, for 10 hours. A reduction in the width at half height of the 002 basal maximum was found to occur. This may be explained in terms of the entry of potassium into hydrated interlayers with their reduction in separation to approximately 10Å. No new phases were observed to develop. A second test utilized 16 mg of synthesis 6, 1M muscovite bearing accessory potassium feldspar. The sample was maintained at 317°C ± 5°C and 600 bars in 2.0 molar KCl. No change was evidently produced, in particular there was no formation of kalsilite as had been produced in experiment B1 described below.

* Duration of experiment, 96.5 hr
Table 6
Details of Exchange Experiments

<table>
<thead>
<tr>
<th>Exchange Series &amp; Number</th>
<th>Weight Counted</th>
<th>Number of counts Averaged</th>
<th>Standard'dz Counting Rate: *+</th>
<th>Duration of Exch. Treatment</th>
<th>Cumulative Duration</th>
<th>Temp.</th>
<th>Pressure</th>
<th>Exchange Solution</th>
<th>Cumulative Change in Act' %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A syn.VII</td>
<td>52.4mg</td>
<td>3</td>
<td>98.26±0.47 c.p.m.</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>52.4mg &amp;38.9mg</td>
<td>2</td>
<td>94.50±0.37 c.p.m.</td>
<td>9 hr</td>
<td>9 hr</td>
<td>100°C</td>
<td>1.01 bars</td>
<td>KCl 0.5molar</td>
<td>-3.74%</td>
</tr>
<tr>
<td>A2</td>
<td>38.9mg</td>
<td>1</td>
<td>93.90±0.67 c.p.m.</td>
<td>45 hr</td>
<td>54 hr</td>
<td>100°C</td>
<td>1.01 bars</td>
<td>KCl 0.5 molar</td>
<td>-4.47%</td>
</tr>
<tr>
<td>B syn.VII</td>
<td>52.4mg</td>
<td>3</td>
<td>98.26±0.47</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B1</td>
<td>4.2mg</td>
<td>1</td>
<td>11.03±1.60 (per 52.4mg)</td>
<td>93 hr</td>
<td>93 hr</td>
<td>302±6°C</td>
<td>100 bars</td>
<td>K₂CO₃ 20 molar</td>
<td>-88.9%</td>
</tr>
<tr>
<td>C Syn. X 1Mδ</td>
<td>77.1mg</td>
<td>3</td>
<td>97.71±1.39</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>77.1mg</td>
<td>1</td>
<td>96.23±0.68 c.p.m.</td>
<td>45 hr</td>
<td>45 hr</td>
<td>100°C</td>
<td>1.01 bars</td>
<td>KCl 0.5 molar</td>
<td>-1.51 ±1.57%</td>
</tr>
<tr>
<td>C2</td>
<td>77.1mg</td>
<td>1</td>
<td>95.30±0.47</td>
<td>97.5</td>
<td>142.5</td>
<td>100°C</td>
<td>1.01 bars</td>
<td>KCl 0.5 molar</td>
<td>-2.47 ±1.50%</td>
</tr>
<tr>
<td>C3</td>
<td>73.3mg 64.5 56.3</td>
<td>3</td>
<td>94.75±0.79 c.p.m.</td>
<td>136.27hr</td>
<td>277.8 hr</td>
<td>100°C</td>
<td>1.01 bars</td>
<td>KCl 0.5 molar</td>
<td>-3.03 ±1.63%</td>
</tr>
<tr>
<td>C4</td>
<td>51.3mg</td>
<td>1</td>
<td>94.68±0.56</td>
<td>189.5</td>
<td>468.3</td>
<td>100°C</td>
<td>1.01 bars</td>
<td>KCl 0.5 molar</td>
<td>-3.10 ±1.53%</td>
</tr>
<tr>
<td>D syn X 10 1Mδ</td>
<td>24.7mg</td>
<td>1</td>
<td>43.62±0.32 c.p.m.</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D1</td>
<td>15.75mg 24.7mg</td>
<td>2</td>
<td>43.02±3.49 c.p.m.</td>
<td>94 hr</td>
<td>94 hr</td>
<td>Approx. 250° Variable</td>
<td>236 bars</td>
<td>KCl 4 molar</td>
<td>(-1.37%</td>
</tr>
</tbody>
</table>

* + Standardized Counting rate: corrected for weight counted, background & its variation, and for counter performance. Counts per minute.
<table>
<thead>
<tr>
<th>D2</th>
<th>22.35mg</th>
<th>1</th>
<th>43.78±0.33</th>
<th>114.5hr</th>
<th>208.5hr</th>
<th>250±2°C</th>
<th>276 bars</th>
<th>KCl, 4 molar</th>
<th>(+0.37)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E Syn.XX 1Md</td>
<td>52.85mg</td>
<td>1</td>
<td>39.31±0.32 c.p.min.</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-2.93 +1.21%</td>
</tr>
<tr>
<td>El</td>
<td>37.5mg</td>
<td>1</td>
<td>38.16 ±0.35</td>
<td>114.5hr</td>
<td>114.5hr</td>
<td>250±2°C</td>
<td>276 bars</td>
<td>KCl, 4 molar</td>
<td>-</td>
</tr>
<tr>
<td>F Syn.XX 1Md</td>
<td>52.85mg</td>
<td>1</td>
<td>39.31±0.32 c.p.min.</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fl</td>
<td>39.5mg</td>
<td>1</td>
<td>36.44±0.38</td>
<td>108 hr</td>
<td>108 hr</td>
<td>-</td>
<td>350±5°C Initial 6 hrs-300 to 390°C</td>
<td>276 bars</td>
<td>KCl, 4 molar</td>
</tr>
<tr>
<td>Gl Syn.20 1Md</td>
<td>38.1mg</td>
<td>1</td>
<td>34.25 cpm +0.66</td>
<td>96 hr</td>
<td>96 hr</td>
<td>-</td>
<td>452±3°C</td>
<td>500 bars</td>
<td>KCl, 4 molar</td>
</tr>
<tr>
<td>H1 Syn. 10 recovered from C4</td>
<td>32.7mg</td>
<td>1</td>
<td>86.26 cpm +0.80 cpm</td>
<td>4 hr</td>
<td>4 hr</td>
<td>-</td>
<td>100°C</td>
<td>1.01 bars</td>
<td>Sodium citrate 1 molar</td>
</tr>
<tr>
<td>Syn.18 Untreated</td>
<td>80.2mg</td>
<td>1</td>
<td>123.43±0.8</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>I l Syn.18</td>
<td>26.8mg</td>
<td>1</td>
<td>99.92±1.29</td>
<td>4 hr</td>
<td>4 hr</td>
<td>95±5°C</td>
<td>1.01 bars</td>
<td>Molar NaCl</td>
<td>-19.05 +1.27%</td>
</tr>
<tr>
<td>J l Syn.18</td>
<td>24.6mg</td>
<td>1</td>
<td>111.66±1.4</td>
<td>4 hr</td>
<td>4 hr</td>
<td>95±5°C</td>
<td>1.01 bars</td>
<td>Molar Na citrate</td>
<td>-9.54%</td>
</tr>
<tr>
<td>K l Syn.18</td>
<td>24.9mg</td>
<td>1</td>
<td>129.61±1.5</td>
<td>4 hr</td>
<td>4 hr</td>
<td>95±5°C</td>
<td>1.01 bars</td>
<td>Molar in Na citrate 0.5molar in KCl</td>
<td>(+5.0%)</td>
</tr>
</tbody>
</table>
Figure 3.

Effects Upon X-ray Diffraction Patterns of 1Md Micas of Treatments With Potassium Chloride Solutions.

A: Synthesis 10: Original condition. Silicon internal standard present, 111, CuKα true position 28.466° ± 20°
"100°C": Synthesis 10 after 468 hr in 0.5 molar KCl at 100°C. Incipient development of potassium feldspar.

"450°C": Synthesis 20 after 96 hours in 4 molar KCl, 452 ± 3°C, 500 bars. Trace of potassium feldspar.

1M: Ordered muscovite, synthesis 7, for comparison.
Figure 4. Replacement of Potassium by Sodium in a Synthetic 1Md Mica.

A  Synthesis 18 1Md + cristobalite. Original condition

B  Synthesis 18. Treated for 4 hours, 95 ± 5°, molar NaCl. Potassium loss 19.05% Na⁺ saturated.

C  Sample as in "B". Mg²⁺ saturated, glycolated. Note loss of asymmetry of 001.

D  Synthesis 18, treated for 4 hrs., 95 ± 5° C, molar sodium citrate solution. Potassium loss 9.54%. Mg²⁺ saturated, glycolated.

E  Synthesis 18. Treated for 4 hrs., 95 ± 5° C, solution molar in sodium citrate and 0.5 molar in potassium chloride. Potassium loss zero. Mg²⁺ saturated, glycolated. Loss of asymmetry of 001.
(a) Exchange Series A and B

These were preliminary experiments carried out on synthesis 7, a 1M muscovite bearing considerable potash feldspar. The presence of two potassium-bearing phases allows no specific conclusions regarding exchange to be drawn. In series A at 100°C the decrease in activity in 54 hours, -4.47%, was much higher than that found for a 1Md mica in exchange Cl, -1.51%. It is doubtful that this is an effect of the potash feldspar as, by analogy with Na⁺ in albite, the values of D for K⁺ in potassium feldspar are extremely low. Traces of contaminants in the micaeous phase were observed and removed by flotation after exchange Al, possibly incompletely. Thereafter the solids were exposed to the atmosphere for minimal periods and, as previously, were manipulated in carefully cleaned containers.

Exchange B1 is of interest in that it represents the only case of extensive recrystallization. This initial experiment at elevated temperature employed concentrated K₂CO₃ solution at 302 ± 6°C. Extensive homogenization of ⁴₀K resulted, accompanying the crystallization of kalsilite, KAlSiO₄. No evidence of K-feldspar remained, but a single broad peak at 26.20° 2θ, readily distinguishable from the sharp maxima of kalsilite, is suggestive of a mica residual. The position and form are comparable to the peak of transitory existence at 26.04° to 26.40° 2θ seen in 1Md synthetics immediately after preparation. Therein it is migratory, disappears upon drying, and is considered to represent mixed-layering between 10° layers and an unstable hydrate of greater spacing. The latter phenomenon is discussed and illustrated on pages 167 and 154.
The recrystallization demonstrates the importance of the properties of the anion in similar systems. Hydrolysis of \( \text{CO}_3^{2-} \), leading to high pH levels, appears to have brought about the degradation of silicates which remain unchanged at even higher temperatures in the presence of \( \text{Cl}^- \), although metastable with respect to kalsilite. It is allowed that the several cases of persistence involved lower anion concentration and higher pressures.

(b) Exchange Series C

Series A had indicated the possibility of observing measurable exchange at 100°C. The objective of Series C was to obtain information upon the exchange of potassium bearing no water of hydration, occupying interlayer structural sites fully analogous to those of muscovites. It is therefore valuable to have information upon the variation in possible potassium sites in illitic micas. Bolt, Sumner, and Kamphorst (1963) examined the exchange of potassium in an illitic soil. They determined that the total layer charge of the material was 1200 meq per g (that of muscovite is approximately 2500 meq per g) and that it could be satisfied by three categories of potassium, 500 μg/g comprises surface potassium; 95% to 96% of this was attributed to planar surfaces, while 4% to 6% of it was ascribed to edge-interlayer sites. The remaining 700 μg/g was not found to be exchangeable, and was ascribed to interlayer sites. Sumner and Bolt (1962) had previously noted that approximately four hours was required to complete the repopulation of the exchangeable potassium sites of illite.
It is therefore expected that the result of washing the illitic materials used by the writer with fresh, ordinary KCl after each treatment, followed by allowing them to stand in further fresh solution (0.5N) for over 4 hours, effectively exchanged surface $K^+$. Thus changes in activity are ascribed to changes in the lattice $K^+$ population if no mineralogical change can be demonstrated. The behaviour of the potassium-bearing phase as an inert substrate is a further pre-requisite if decreases in activity are to be employed for evaluation of coefficients of diffusion.

Examination of synthesis 10 by X-ray diffraction after treatments C1 to C4 revealed no progressive changes in peak height ratios, peak positions or forms. Within the limits of sensitivity of the measurements, the illitic material behaved inertly. However, after C4, at 468.3 hours, approximately 18 days, two new peaks appeared in the record, at 3.26Å and 3.22Å. These values compare well with those of Donnay (1952) for two peaks of synthetic $KAlSi_{3}O_8$, a feldspar, at 3.258Å and 3.223Å. The record is shown in Figure 3, labeled "100° C". The origin of the Si and Al of the feldspar is not determinable. Accessory boehmite is present and possibly a silica source, as cristobalite formed in other syntheses from the same initial preparation (number 2) as well as traces of hydralsite.

(c) Exchanges D

The first was interrupted by an extensive power failure resulting in indeterminable temperature variations. The results were disregarded.
(d) Exchanges E, F and G

Three treatments of synthesis 20 at 250°, 350° and 450° C respectively are described. There were minor progressive changes in the diffraction features of the illitic phase. These are recognisable in Fig. 3 where the original state and that after F and G are shown. They are:

1) Reduction in the width at half height of 001, produced by a decrease in the diffracted intensity in the tail on the low angle side.

2) Progressive reduction in the asymmetry of 002 on the high angle side.

3) Reduction of the background in the region of 28° 2θ, equivalent to reduction of the tail of 003 on the high angle side.

The original nature of basal peaks, particularly their asymmetries and displacements from the positions of the same maxima for well crystallized 1M muscovite is attributed to mixed-layering or heteropolytypism in the 1Md structures. This is discussed in the section concerning the synthetic products. The observed changes are compatible with the progressive elimination of mixed-layering, i.e. an elimination of the expanded interlayers bearing hydrated cations. It is a notably slow process, probably diffusion controlled. The changes are of the nature of those occurring during the diagenetic alteration of "mixed-layer illite-montmorillonite." (Weaver, 1959; Burst, 1959). The identity of the replaced cations is uncertain, in both the natural and synthetic cases. (Weaver, 1965).
At temperatures of 350° and 450° C potassium feldspar appears in minor quantity. It is not certain that this represents recrystallization of the mica. The considerations noted above (Series C) apply.

(e) Exchanges I, J, and K.

These were carried out to determine the relative effects of an anion which would complex aluminum (citrate ion) and one which would not (chloride), in the case of replacement of potassium by hydrated sodium. The hypothesis to be tested was that an aluminous boundary layer or interlayer Al\(_n\)(OH)\(_{2n}\)\(^+\) type complexes could be present and lead to reduced exchange rates. In a period of four hours, molar sodium chloride replaced twice as much interlayer potassium as did molar sodium citrate. Conversion of the citrate employed to sodium chloride, and subsequent spectrographic examination, revealed, by comparison with a blank, no significant increase in aluminum. It was therefore concluded that the hypothesis could be rejected in the case of synthesis 18, the material tested. 18 is similar to 20, and other 1Md products of preparation 2 which crystallized with cristobalite. However, syntheses 9 and 10, also derived from the same batch of preparation 2, crystallized as 1Md micas of greater degree of disorder, with accessory boehmite, Al\(_2\)(OH)_3. It is not concluded that interlayer complexes of the type Al\(_n\)(OH)\(_{2n}\)\(^+\) are necessarily absent in these cases. Observations compatible with their presence were made after heat treatment of synthesis 9 (detailed on p.152) but the case could not be proven.

The phenomena related to potassium displacement are of interest
by their analogy to the weathering illites. (Compare Cook and Rich, 1963). The exchange involved replacement of an unhydrated cation by a hydrated one, evidenced by X-ray diffraction. After extraction, the material was left sodium-saturated and allowed to equilibrate with laboratory air. The pattern is shown in Figure 4B. There is a slight reduction in intensity of the basal reflections which broaden, increase in asymmetry, and change in spacing from 10.09Å to 10.14Å. Exchange of sodium for magnesium followed by glycolation revealed the presence of a now sufficiently high percentage of expandable interlayers to produce a discrete 17Å peak. Intercalayering is indicated by the absence prior to Mg\(^{++}\) plus-glycol treatment, of a discrete 12.4Å peak characteristic of sodium montmorillonite bearing one layer of water.

The exchange versus sodium citrate was possibly reduced in rate over that versus the chloride by the steric effect of the large citrate ion which could have blocked interlayer edges. A lesser activity of sodium, unless extremely low, is discounted as the cause on the basis of the observations of Walker (1963): exchange rates were not affected by external concentration over wide limits.

Exchange J demonstrated a significant effect. Employing a solution 1 molar in sodium citrate and 0.5 molar in potassium chloride prevented any measurable exchange. The effect of sodium was completely inhibited. This is evidenced in Table 6 and Fig. 4, E. After treatment, the originally present expansible layers still took up ethylene
glycol however. This is shown by the development of symmetry and
to position change of 001 towards an apparently smaller spacing, as is
to be expected (see page 157).

This effect of potassium is considered to be of extreme impor-
tance in nature. It has been observed by other investigators (White,
1958; Rich and Cook, 1962). The tendency of high concentrations of
potentially lattice-expanding, strongly hydrated cations (all except
K⁺, Rb⁺, Cs⁺, of those which are not highly complexed in connate
fluids) would be to displace potassium from clay micas. Preservation
of observed states appears to depend upon the maintenance of certain
levels of K⁺ concentration in the associated fluids. Other factors,
temperature, pressure and mica layer charge are no doubt also
operative. Time did not permit an evaluation of minimum potassium
activities required to prevent the initiation of expansion. The
subject is considered to be one of interest with regard to possible
future work.
PART 2. POTASSIUM EXCHANGE EXPERIMENTS: INTERPRETATION OF DATA IN TERMS OF A DIFFUSION PARAMETER, $D/a^2$

(a) Choice of Model and Diffusion Equation.

Several assumptions are necessary in the formulation of a diffusion model. These concern the boundary conditions, the most appropriate geometrical approximation, and the constancy of the coefficient of diffusion, $D$.

The probable rate-limiting diffusion should be considered. In the system employed, exchange between two major phases is involved, the fluid and the mica-like crystals. Values of $D$ at room temperature for liquids lie in the range $10^{-5}$ to $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. Values relevant for large monovalent ions in dense silicate structures lie with a high probability below $4.9 \times 10^{-10}$ measured for sodium diffusion in obsidian (Sippel, 1963). Values in more ordered structures are much lower and could be further depressed in the case of potassium by analogy with the data for analcite (Barrer and Rees, 1960). The two ranges are separated by many orders of magnitude and the rate-limiting process would be expected to occur in the micaeous structure.

A further consideration is the possible effect of a boundary layer such as is described for marginally hydrolyzed silicate crystals by Corrrens (1963) and Nash and Marshal (1956). A lesser degree of crystalline perfection is to be expected therein and such lesser ordering would be expected to lead to higher values of $D$.

A second type of boundary layer which is present with certainty is composed of adsorbed hydrated ions adjacent to the mica.
surfaces. As the layers represent a fluid component it is most probable that, at moderately elevated temperatures, diffusion of potassium across such adsorbed layers would not be rate-limiting. It is therefore considered probable that the values of D calculated herein relate to potassium migration within illitic micaceous structures.

Fick's second law of diffusion, derived on the assumption that D is constant, is:

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

D in numerous systems is known to be a function of the concentration of the diffusing substance in the host material, due in part to such possible effects as variation produced in the degree of defectiveness of the host, and lattice strain. However, in the present case the lattice concentration of potassium is determined by the charge of the alumino-silicate sheets which is assumed to be constant for the potassium-saturated, approximately 10Å layers of a single mica.

The above expression involves uniaxial diffusion, normal to the major surface of a slab. Solutions of the equation for this and other geometries are available, particularly for axial symmetry, where radial diffusion in one or many circular sections of a right cylinder is involved, and for spherical symmetry where diffusion is directed along all radii. The solutions relate to particular initial and boundary conditions of concentration.

Solutions have been obtained in two ultimate forms, relating
a fractional change in measured concentration to either an exponential series or a series of error functions (Jost, 1960; Barrer, 1951). They may be discussed in terms of the solutions for a slab.

For a slab of thickness 2a cm, of initial uniform concentration of diffusing material equal to \( c_0 \), and of mean concentration \( \bar{c} \) after a period of \( t \) sec of diffusion, there holds for a finite system the equation

\[
\frac{\bar{c}}{c_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- \frac{(2n+1)^2 \pi^2}{2a} D t \right]
\]

for diffusion out of the slab into a medium of zero concentration of the diffusing material. Analogous solutions exist for the cylindrical and spherical cases. For the same initial and boundary conditions, the solution for a cylinder is

\[
\frac{\bar{c}}{c_0} = \sum_{l=0}^{\infty} \frac{1}{\xi_l^2} \exp \left[- \frac{\xi_l^2 D t}{a^2} \right]
\]

where \( a \) is now the cylinder radius and the \( \xi_l \) are the roots of the equation \( J_0(x) = 0 \) where \( J_0(x) \) is the Bessel-function of zero order. Furthermore,

\[
\xi_l = 2.405, 5.520, 8.654, 11.792, \ldots
\]

In the case of the sphere:

\[
\frac{\bar{c}}{c_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[- \frac{n^2 \pi^2 D t}{a^2} \right]
\]
where \( a \) is the radius of the sphere.

For \( t \) sufficiently large and \( \bar{c}/c_o \) sufficiently small, the first term in each case provides a good approximation.

The solution as a series of error functions for a slab with the same initial and boundary conditions, namely,

\[
c = c_o \text{ for } 0 < x < 2a \text{ at } t = 0
\]

and \( c = 0 \) for \( x = 0 \) and \( x = 2a \) at \( t > 0 \),

is as follows:

\[
\frac{\bar{c}}{c_o} = \frac{1}{2} \int_0^\infty \left\{ \left[ \text{erf} \left( \frac{(2n+1)2a - x}{2\sqrt{Dt}} \right) - \text{erf} \left( \frac{4na - x}{2\sqrt{Dt}} \right) \right] \right.
\]

\[
- \left[ \text{erf} \left( \frac{4na - x}{2\sqrt{Dt}} \right) - \text{erf} \left( \frac{(2n-1)2a - x}{2\sqrt{Dt}} \right) \right] \right\}
\]

The series converges very rapidly for values of \( 2a/2\sqrt{Dt} \) greater than 2.24. Employing the terms \( n = 0 \) and \( n = \pm 1 \), the solution finally obtained is

\[
\frac{\bar{c}}{c_o} = 1 - \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{Dt}}{a} \quad \text{(Jost, 1960)}.
\]

\( \bar{c}/c_o \) equals the fraction remaining. The fraction lost, \( F \), equals \( 1 - \bar{c}/c_o \).

\[
\therefore \quad F = \frac{2}{\sqrt{\pi}} \cdot \frac{\sqrt{Dt}}{a}
\]
The values of $F$ compatible with rapid convergence are therefore less than $\sim 0.5$, employing the condition quoted above. In this range the values of $F$ yielded for given values of $D$, $t$, and $a$, agree with those obtained from the exponential series solution to the fourth decimal place. (Jost, 1960, p. 42).

The analogous solution for a cylinder is

$$F = \frac{4}{\sqrt{\pi}} \cdot \frac{\sqrt{Dt}}{a} \quad \text{(Hart, 1960)},$$

and for a sphere

$$F = \frac{6}{\sqrt{\pi}} \cdot \frac{\sqrt{Dt}}{a},$$

as may be derived from the equations of, for example, Barrer and Falconer (1956) and Reichenberg (1953).

The cylindrical model is chosen to provide an appropriate equation for use in this work. The basal planes of micas represent the locus of the weakest ionic bonds in the structure. Furthermore, the analysis of the muscovite structure by Radoslovich, (1960, 1962) demonstrated that the oxygen surfaces of adjacent layer units are not in contact, with a separation of some $0.7^\circ$. As a similar separation is expectable in the micas employed here, diffusion of potassium in these particularly "open" zones is expected to be much more rapid than through the structure. Calculations for other models are readily carried out for comparison.

The initial and boundary conditions which are considered to apply with only a small approximation are those quoted above. For a cylinder of radius $a$ they are, firstly,

$$c = c_0 \text{ for } 0 < r < a \text{ at } t = 0,$$
that is, a uniform initial concentration, particularly of the tracer \(^{40}\text{K}\) (a condition met by synthesis), and secondly,
\[ c = 0 \text{ for } r = a \text{ and } t > 0, \]
the boundary condition for the solution and solid phase.

The systems investigated comprised a synthetic illitic mica enriched in \(^{40}\text{K}\) and aqueous solutions of KCl. The apparent contradiction is considered to be resolvable in these terms: \(c = 0\) is taken as the constant marginal concentration of \(^{40}\text{K}\) for the immediate mica-edge potassium sites and for the adjacent solution. This is part of the approximation, for the true \(^{40}\text{K}\) level in ordinary potassium is \(1.18 \times 10^{-4}\) atoms \(^{40}\text{K}\) per atom of potassium. It is considered allowable as even in the case of the maximum decrease in activity measured, \(12.87 \pm 0.58\%\), the calculated counts observable due to ordinary potassium presumed to enter the structure are 0.29 per minute. The decrease in counting rate (before and after exchange G1) was \(5.06 \pm 0.23\) c.p.m. The effect of \(^{40}\text{K}\) uptake is obscured by the imprecision. A second, similar effect, potentially more significant, is the possible re-entry into the structure of \(^{40}\text{K}\) released from it. This was minimized by maintaining in the closed systems a mass of potassium in the solution at least 25 times greater than that in the mica. The mica enrichment in \(^{40}\text{K}\) was 18 to 31 times ordinary.

The adopted boundary condition \(c = 0\) pre-supposes that the effect of an environment of aqueous KCl has no effect upon the rate of migration of vacancies, and therefore of potassium, in the structure. This is supported by the analogous experiments of G. F. Walker (1963) wherein the diffusion coefficients governing the entry of hydrated
Sr$^{++}$ into a vermiculite crystal bearing hydrated Mg$^{++}$ were determined. At constant temperature, the rate was independent of the concentration of the external Sr$^{++}$ solution between 0.4 and 4N. The limits exist, according to Walker, only because other diffusive processes become rate limiting outside of them.

Adoption of the same boundary conditions was made by Ames (1965) who measured the diffusion of alkali tracer ions into zeolites. The tracer was added to an external solution already 0.2N in the ordinary ion and its diffusion into the zeolite, pre-equilibrated with the ordinary solution, was followed. Neither the original lattice concentration of alkali, nor the concentration of the external solution, enter into the calculation of D. Identical means are employed by Barrer (Barrer and Rees, 1960). In the experiments of the present writer, two relative concentrations of $^{40}\text{K}$ were measured, $c_0$, the original activity, and $\bar{c}$, the activity after a period of exchange. The fractional loss, $F = (c_0 - \bar{c})/c_0$, was determined. Calculations are carried out according to the equation

$$F = \frac{4}{\sqrt{\pi t}} \cdot \frac{\sqrt{Dt}}{a}$$

$$\therefore \frac{D}{a^2} = \frac{F^2 \pi}{16t}$$

The values of D/a$^2$ determined herein relate to the diffusion of $^{40}\text{K}$, octahedrally coordinated by oxygen ions which are largely charge-satisfied. The rates would be expected to apply to all potassium in 10$^2$ layers in the same structure and possibly be similar in magnitude to rates in micaceous minerals of like layer-charge.
(b) Diffusion Data and Values of $D/a^2$

The data are presented in Table 7, and in Figures 5 to 7. Details of the beta counting involved are given in Table 20, Appendix 3.

All experiments yielding relevant data have been employed in obtaining values of $D/a^2$ with the exception of two, Exchange Series D, numbers 1 and 2 and Series J. The experiment D1 at 250°C was interrupted by an extensive power failure, and for 16 hours the temperature varied. It is therefore excluded. Series J yielded data from which $D/a^2$ could be calculated. It refers however to a somewhat artificial system wherein molar sodium citrate was employed to extract potassium. The results are discussed in other sections. Exchange H did not fulfill the initial conditions of the equation.

(c) Discussion of Data and Values of $D/a^2$

In three experiments (C4, F1 and G1) low X-ray diffraction feldspar peaks compatible with the presence of potassium appeared, as is evident in Figure 3. It cannot be claimed with certainty that this represents reaction of the micaceous phase as accessory phases were initially present, potential reactants and sources of silicon and aluminum. However, it is necessary to test the data to obtain evidence that the changes in activity represent a process of diffusion.

In the equation $F = (\ln \sqrt{t})/(\sqrt{t}/a)$, $F$ is directly proportional to $\sqrt{t}$, for constant D and a. Therefore $F$ versus $\sqrt{t}$ should yield a linear relationship. The data of Series C allows this test, as shown in Figure 6. The points C1 to C3 are suggestive of a linear
<table>
<thead>
<tr>
<th>Synthesis and Exchange</th>
<th>Cumulative Fractional Exchange F</th>
<th>Standard Deviation of F</th>
<th>Cumulative Duration of Exchange (Seconds)</th>
<th>Temperature of Exchange °C</th>
<th>( \frac{1000}{T^\circ K} )</th>
<th>( D/a^2 \pm \sigma D/a^2 \ sec^{-1} ) (Cylindrical Model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10, C1</td>
<td>0.0151</td>
<td>0.0157</td>
<td>( 1.62 \times 10^5 )</td>
<td>100</td>
<td>2.68</td>
<td>(2.76 ± 2.87) ( \times 10^{-10} )</td>
</tr>
<tr>
<td>10, C2</td>
<td>0.0247</td>
<td>0.0150</td>
<td>( 5.13 \times 10^5 )</td>
<td>100</td>
<td>2.68</td>
<td>(2.33 ± 1.41) ( \times 10^{-10} )</td>
</tr>
<tr>
<td>10, C3</td>
<td>0.0303</td>
<td>0.0163</td>
<td>( 1.00 \times 10^6 )</td>
<td>100</td>
<td>2.68</td>
<td>(1.77 ± 0.97) ( \times 10^{-10} )</td>
</tr>
<tr>
<td>10, C6</td>
<td>0.0310</td>
<td>0.0153</td>
<td>( 1.69 \times 10^6 )</td>
<td>100</td>
<td>2.68</td>
<td>(1.11 ± 0.55) ( \times 10^{-10} )</td>
</tr>
<tr>
<td>20, E1</td>
<td>0.0293</td>
<td>0.0121</td>
<td>( 4.12 \times 10^5 )</td>
<td>250 ± 2</td>
<td>1.91</td>
<td>(4.01 ± 1.68) ( \times 10^{-10} )</td>
</tr>
<tr>
<td>20, F1</td>
<td>0.0730</td>
<td>0.0126</td>
<td>( 3.89 \times 10^5 )</td>
<td>350 ± 5</td>
<td>1.61</td>
<td>(2.69 ± 0.46) ( \times 10^{-9} )</td>
</tr>
<tr>
<td>20, G1</td>
<td>0.1287</td>
<td>0.0187</td>
<td>( 3.46 \times 10^5 )</td>
<td>452 ± 3</td>
<td>1.38</td>
<td>(9.49 ± 1.37) ( \times 10^{-9} )</td>
</tr>
<tr>
<td>18, I1</td>
<td>0.1905</td>
<td>0.0127</td>
<td>( 1.44 \times 10^4 )</td>
<td>95 ± 5</td>
<td>2.72</td>
<td>(4.92 ± 0.33) ( \times 10^{-7} )</td>
</tr>
</tbody>
</table>

Table 7. Values of \( D/a^2 \pm \sigma D/a^2 \ sec^{-1} \) for the Self Diffusion of \( ^{40}K \) in Synthetic Illitic Micas.

† Values result in a weighted mean of \( (1.41 ± 0.45) \times 10^{-10} \ sec^{-1} \) for Series C.
Figure 5. Fractional Decrease of Beta Activity of Micas versus Time.
Figure 6. Fractional Decrease of Beta Activity of Synthesis 10 versus the Square Root of Time.
relationship; an indication of curvature is likewise apparent, and tends to be confirmed by the data point C4. However, the wide precision limits preclude the possibility of certain decision. On the basis of the locations of points C1 to C4 (their approach to linearity) and the marked change of curvature between C3 and C4, suggesting that the latter is possibly anomalous, it is concluded that the data allows interpretation in terms of the decrease of F controlled by a diffusion process, presumed to be lattice migration of potassium. A process of dilution of the activity by neoformation of a phase of lesser or zero activity from the mica is considered less likely: the intensity of the new peaks is not proportional to the observed activity changes, and the probability of a linear reaction rate seems high, while both reactants remain effectively at the same activity. Considering these factors, and the compatibility of the data and the model, values of $D/a^2$ are calculated from the equation above.

It is clear that there was insufficient diffusive loss of $^{40}K$ to allow highly precise estimates of $D/a^2$. The determination of $F$ involves the subtraction of two large numbers, almost equal, $(c_0 - \bar{c})$. Values of $c_0$ and $\bar{c}$ employed bear coefficients of variation for counting alone (probably the major source of imprecision) less than 1.43%, excepting a single case at 1.93%. Nevertheless, the coefficient for $F$ rises markedly and equals that for $D/a^2$ in each case, thus:
<table>
<thead>
<tr>
<th>Exchange Number</th>
<th>Coeff. Var. of D/a^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>103%</td>
</tr>
<tr>
<td>C2</td>
<td>60.5%</td>
</tr>
<tr>
<td>C3</td>
<td>54.8%</td>
</tr>
<tr>
<td>C4</td>
<td>49.6%</td>
</tr>
<tr>
<td>E1</td>
<td>41.9%</td>
</tr>
<tr>
<td>F1</td>
<td>17.1%</td>
</tr>
<tr>
<td>G1</td>
<td>14.5%</td>
</tr>
<tr>
<td>I1</td>
<td>6.7%</td>
</tr>
</tbody>
</table>

Counting employed the micaceous phase and the KCl utilized. The situation is not alleviated by counting KCl, owing to its significant beta activity. 61.2 mg reagent grade KCl had an activity of 26.50 ± 0.42 c.p.m. (Efficiency of counter therefore 49.33%.) An incremental addition of $^{40}$K required once again the subtraction of two large numbers for its determination, as well as a greater counting period to attain equal precision. The results of counting "used KCl" were poor. In two cases a spurious decrease in activity was determined. Dilution by inseparable solids (< 0.1μm equivalent settling diameter) may have been involved.

Considering further the dissolution of phase; the solubility of aluminosilicates and alumina is virtually negligible. Dissolution followed by reaction is not prominent by the X-ray evidence. Dissolution at elevated temperature followed by precipitation could have occurred. The dissolution of micas is incongruent, involving the initial loss of interlayer material, then the octahedral cations,
finally the tetrahedral cations, (Barbara S. Neumann, 1963; The latter processes may occur simultaneously, though at much lower rates than the first. The reactant required however is $H_3O^+$, initially to retain charge balance as it replaces interlayer cations. In the experiments, however, although a pH of 5 existed in the aqueous KCl initially, the concentration of $K^+$ was greater by minimally more than four orders of magnitude. The effect of interlayer displacement of $K^+$ by $H_3O^+$ was therefore negligible after a possible initial reaction (Garrels and Howard, 1958). The effect of layer-edge attack by $H_3O$, therefore, would also be slight; in addition the products of incipient reaction, forming a disordered layer, tend to remain bound.

$D/a^2$ From Series C

A mean, weighted according to the standard deviations of the intermediate means, was determined by the method for consistent means, (Appendix 3) as

$$D/a^2 = (1.41 \pm 0.45) \times 10^{-10} \text{ sec}^{-1}.$$  

This best estimate applies to the system investigated alone. The slab model yields a value greater by a factor of 4, the spherical model a value lesser by a factor of 0.4. The limitations of the data are realized.

Theoretical reasoning suggests, and in the opinion of the writer compellingly, that the values of $D/a^2$ tend towards the maximal possible for the materials. It is not to be expected that all potassium which is not exchangeable at room temperature occupies
sites of equal exchangeability or equally high activation energy. The calculations are based upon small percentage exchanges, the initial portion of a curve, which will overestimate the exchangeability of the bulk of the potassium.

Several subsidiary factors suggest the possibility of a slight underestimation of $F$, namely

1) Re-entry into the structure of the $^{40}\text{K}$ released

2) The expanded hydrated layers possibly bear for example $\text{Na}^+$ and $\text{Mg}^{++}$. The displacement of these by potassium could occur. The effect was not demonstrable in Series C but probably occurred in $F$ and $G$.

$D/a^2$ From Exchanges El, Fl, and Gl.

The compatibility of these results may be tested upon a plot of $\log_{10} D/a^2$ against $1000/T^{\circ}\text{K}$. These parameters are derived from the Arrhenius equation for the temperature dependence of a rate constant:

$$D/a^2 = D_0/a^2 \exp[-Q/RT']$$

where $Q$ is the activation energy for inter-site migration, $R$ is the gas constant, 1.9869 calories per degree per mole, and $T'$ represents degrees Kelvin. $D_0$ is a constant for the system. Alternatively stated:

$$\log_{10} D/a^2 = \log_{10} D_0/a^2 - \frac{Q}{2.303R.T'}$$

and $\log_{10} D/a^2$ is linearly related to $\frac{1}{T}$, as $Q$ has a negligible dependence upon $T$ over a small range.

In Fig. 7 apparent compatibility of the data for El, Fl and
Figure 7. Arrhenius Plot of Data of Exchanges E, F, and G.
Cl is observed for synthesis 20, while synthesis 10 appears to exchange at a greater rate. This is in keeping with the possible effect of the lesser degree of structural order observed in synthesis 10 by X-ray diffraction.
(d) Estimation of the Diffusion Radius, $a$.

Estimation is hindered by lack of knowledge concerning the difference between crystallite size and diffusion radius. Estimation of crystallite size is prevented by aggregation of synthetic particles grown in close proximity, observed for micas by Yoder and Eugster (1955) as well as by the writer. Acceptable means of disaggregation were considered limited to one, ultrasonic vibration. Chemical means displace potassium or contaminate particle edges (e.g. complex phosphate ion adsorption), grinding induces structural disorder.

Initial attempts with ultrasound produced minor effect. Later in the work a stronger source was found to be available. With it, in the case of synthesis 17, which bears considerable 3T in addition to 1Md mica, 4 hours of intense vibration yielded the following distribution of particle sizes: $> 10\mu$, 48.3% weight percent; $1 - 10\mu$, 31.4%; $0.3$ to $1\mu$, 16.4%; and $< 0.3\mu$, 3.9%, estimated as equivalent spherical diameters according to the centrifuge data of Jackson (1956). Careful sedimentation in water of preparations for X-ray diffraction led to maximum preferred grain orientation in portions from each size range. Patterns indicated the absence of aggregation in the $< 0.3\mu$ range, a trace in the $0.3$ to $1\mu$ range, and its persistence above $1\mu$. It may only be concluded that the modal e.s.d. of individual crystallites is $> 0.3\mu$, possibly $> 0.3$ and $< 1\mu$, or possibly $> 1\mu$.

Yoder and Eugster (1955) report maximal crystal diameters of approximately 20\mu for synthetic micas (electron micrographs).

There is little information concerning the relationship between equivalent spherical diameters and true grain sizes for illites.
two hydrated cations. The data of Walker (1963) relates to the latter case for a vermiculite. The values compare as follows.

| $K^+$ Self-Diffusion (Series C) | Entry of $Na^+(H_2O)x$ Exchange I 1 | $Sr^{++}(H_2O)y$ Substituting $Mg^{++}(H_2O)z$ *
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$D/a^2$ sec$^{-1}$ (100°C)</td>
<td>$1.41 \times 10^{-10}$</td>
<td>$4.92 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$28$ (estimated)$^+$</td>
</tr>
</tbody>
</table>

---

* Walker (1963); Sr phase 15$^o$, Mg phase 14.4$^o$.

$^+$ Approximation employing $a^2 = 10^{-8}$ cm. to the given $D$ value, $2.8 \times 10^{-7}$ cm$^2$ sec$^{-1}$ at 62°C.
The value of $D_0/a^2$ obtained for the synthesis 20 data is $10^{-4.5}$. The value of $a$, the diffusion radius, is not determinable but is less than or equal to the effective average grain radius, insofar as the basal planes can be approximated as circular in form. If indeed it is as large as one micron, $10^{-4}$ cm, as discussed below, the value of $D_0$ becomes $10^{-12.5}$ sec$^{-1}$. This appears to be an inordinately low value. The lowest value of $D_0$ observed in the literature by the writer is $10^{-6.39}$ for the diffusion of rubidium in synthetic analcite (Barrer and Hees, 1960).

The activation energy, determined employing $10^{-4.5}$, is 11,600 calories per g ion, quoted for the sake of completeness, the data being suspect. It is noteworthy that the difference of the logarithms $D/a^2$ at $T^0K$ and $D_0/a^2$ provides a small multiplier of a large number, $2.303RT'$. A corrected value of the energy of activation would not differ greatly from that determined.

$D/a^2$ From Il

Lattice release of potassium possibly provided hindrance to sodium entry, for a closed system with regard to these ions was employed.

The exchange of a hydrated cation for one unhydrated produces a discontinuity of basal spacing, or layer separation, across the migrating boundary, in this case from $14^0\text{A}$ or $15^0\text{A}$ on the sodium-rich side to approximately $10^0\text{A}$ on the other. The associated value of $D/a^2$ would be expected to be intermediate between that for potassium self-diffusion ($10^0\text{A}$ maintained) and that for the exchange of
Kahn (1959) provides the following information for fractions of the Fithian illite. For equivalent spherical diameters of 0.14μ and 0.05μ, (determined by ultracentrifugation) the mean "largest dimension" of ten randomly chosen grains in electronmicrographs of the same fractions was 0.24μ and 0.05μ respectively. It is possible therefore that the writer's values are not unreasonable estimates. Though crystals of e.s.d. greater than 1μ are almost certainly present in the syntheses, this value is adopted as representing an average crystal dimension in the basal plane, and consequently a maximum diffusion radius, but only for the purpose of drawing inferences and suggesting possibilities.

(e) Estimate of Layer Charge of 1Md Micas Employed.

The data of Walker (1963) confirms the expectation that rates of cation exchange in layer silicates are proportional to layer charge density. His data also conform to a model involving diffusion control within the hydrated interlayers of the structure. Measurements on three vermiculites of layer charge 0.65e−, 0.7e− and 0.8e− per unit of [0₁₀(OH)₂] demonstrated that the required times for the migration of the phase boundary over 100μ were approximately 1.4 hours, 2.3 hours and 9 hours respectively. Employing the relationship

\[ \Delta x^2 = 2Dt \]  

(Jost, 1960)

where \( \Delta x^2 \) equals the square of the mean displacement of a diffusing particle, the ratios of values of D are as 1: 0.58: 0.15. Thus a relatively small increase in layer charge in the hydrated system de-
creases D by almost an order of magnitude. The effect is probably more pronounced in anhydrous layer structures, where increase in charge tends to decrease the number of vacancies which facilitate diffusion.

Thus an estimate of layer charge is required for the synthetics. This cannot be achieved by analysis, or consideration of the composition of the starting materials, as they did not crystallize as one phase. Cation exchange capacity would not estimate the 10Å layer charge.

The following observations were therefore employed:

1) Immediately after formation, syntheses 9 and 10 were observed to exhibit d"001" values of approximately 10.17Å and d"003" of 3.41Å. The latter peak migrated to 3.34Å as the material dried. The collapse was irreversible upon rehydration. Such irreversible dehydrational collapse is a feature of highly charged vermiculites bearing hydrated potassium which are allowed to air dry. A typical vermiculite possesses a layer charge of some 0.6 to 0.8 units of electron charge, e⁻, per [0_10(OH)_2] unit.

(2) With or without pre-treatment, the 1Må products of preparation 2 adsorb ethylene glycol between a small percentage of layers. This occurs in the case of montmorillonitic layer charge, between approximately 0.3 e⁻ and 0.55 e⁻, and also with fine grained vermiculite (Walker, 1958).

(3) Sodium citrate extraction of potassium allows the development of a 17Å peak upon glycolation, and of an approximately 17.7Å.
peak employing glycerol following Mg$^{++}$ saturation. These are montmorillonitic expansions. However, Cook and Rich (1963) describe a "specimen-type" muscovite of anomalously low layer charge, 187 meq/100g, but still approximately equivalent to a highly charged vermiculite, which expanded to 18.4 Å after potassium extraction, Mg$^{++}$ saturation, and glycerol treatment. This behaviour is anomalous for the layer charge and is expectable only with montmorillonite. Effects probably vary with charge site, as well as particle size.

The evidence is conflicting but the first observation, if correctly interpreted in terms of potassium dehydration, seems to allow only one conclusion: . high vermiculitic layer charge, at least in part.

The allowable conclusions concerning layer charge therefore appear to be:

1. Entirely high vermiculitic, of the order of 0.8 e$^-$ per $[\text{O}_1\text{O}(\text{OH})_2]$ unit, exhibiting anomalous behaviour upon treatment with organic liquids (cf. Cook and Rich).
2. Entirely montmorillonitic, the spontaneous dehydration being due to an unsuspected cause.
3. Of heterogeneous layer charge, vermiculitic and montmorillonitic.
PART 3, DETAILED RESULTS OF SYNTHESSES

(a) Tabulation of Data

Table 8 presents information concerning the conditions and duration of synthesis and lists the products obtained. X-ray diffraction patterns of representative materials are shown in Figure 8 in an untreated or "original" condition. Further examples are presented in Figures 3, 4, 10, and 11. General and particular features of the micas are discussed below. It might be noted here that the syntheses were undertaken for the purpose of studies utilizing them, not primarily as an investigation of part of the system $K_2O-MgO-Al_2O_3-SiO_2-H_2O$.

(b) Principal Products and Their Features

These were three polytypic variants of micas fundamentally related to muscovite (as is evidenced by their $d_{hkl}$ values), namely the 1M, 1Md, and 3T polytypes. It is suspected that, as was found by Warshaw (1960), the 3T variant also exhibits disorder and should properly be termed 3Td. However, as it occurred with 1Md, this was not proven.

(1) 1M Muscovite

1M muscovite was obtained in syntheses 6, 7, and 14. The products of 3 and 4 were closely similar. $d$ values are given in Table 9. All tabulated values were measured from charts prepared at $1/4^\circ 2\theta$ per minute scanning rate. Data is uncorrected for synthesis 7, the instrument alignment having been excellent. At
the time of measurement of synthesis $^{14}$, minor alignment error yielded the following deviations in $^\circ28$ for a silicon standard: 111 maximum, + 0.003$^\circ$; 311 maximum, zero error; 331 maximum, -0.001$^\circ$. The relationship between error and peak position is linear. A silicon powder internal standard in synthesis $^{14}$ yielded, on 111, 28.43$^\circ$ 28, an error of -0.01$^\circ$ 28. The applied corrections are evident in the tabulation.
Figure 8. X-ray Diffraction Patterns of Representative Synthetic Micas

Synthesis 14. 1M muscovite; 1°20' min⁻¹, Scale Factor 8,
Time Constant 4 sec.; CuKα radiation, 30 Kv, 40 ma.
Slits 1°, 0.006", 1°; Other patterns under identical conditions except 2 and 20.
Synthesis 16, 1Md muscovite, closely approaching 1M state.
No other phases detected. Composition inferred \( K_{0.833} (Al_{1.916} Mg_{0.083}) (Si_{3.25} Al_{0.75})_{10} (OH)_{2} \)

Synthesis 2. 1Md + cristobalite. Time constant 2 sec.
From preparation 2, K

\[ 0.5(Al_{1.9} Mg_{0.1}) (Si_{3.6} Al_{0.4})_{11} + H_2O. \]


Synthesis 9. 1Md + boehmite. Mica in initially expanded, hydrated state, evidenced by maximum
at 26.05° 2θ, 3.42A. Preparation 2.

Synthesis 15. 1Md + boehmite. Identical to 9 but in equilibrium state. Preparation 2.
<table>
<thead>
<tr>
<th>Synthesis No.</th>
<th>Reaction Vessel</th>
<th>Cation Ratio</th>
<th>T°C</th>
<th>P(bars)</th>
<th>Duration(hrs)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu</td>
<td>K_{1.0}Al_{2.3}Mg_{0.1}Si_{5.58}</td>
<td>390±5</td>
<td>276</td>
<td>168</td>
<td>Kalsilite, Alk. feldspar, Kaolinite, trace micas</td>
</tr>
<tr>
<td>2</td>
<td>Cu open</td>
<td>K_{0.5}(Al_{1.9}Mg_{0.1})<em>{(Si</em>{3.6}Al_{0.4})}Prep. 2</td>
<td>463±3</td>
<td>650</td>
<td>192</td>
<td>1Md mica + cristobalite</td>
</tr>
<tr>
<td>3</td>
<td>Pt, open</td>
<td>K_{0.966}(Al_{1.983}Mg_{0.017})<em>{(Si</em>{3.05}Al_{0.95})}Prep. 3</td>
<td>470±5</td>
<td>1200</td>
<td>120</td>
<td>1M mica</td>
</tr>
<tr>
<td>4</td>
<td>Pt</td>
<td>Prep. 3</td>
<td>890±5</td>
<td>300 to 600</td>
<td>72</td>
<td>1M Mica</td>
</tr>
<tr>
<td>5</td>
<td>Stellite</td>
<td>Prep. 2</td>
<td>495±10</td>
<td>1050</td>
<td>52</td>
<td>1Md + cristobalite Trace 3T</td>
</tr>
<tr>
<td>6</td>
<td>Pt open</td>
<td>K_{1.0}Al_{2}(AlSi_{3})</td>
<td>465±5</td>
<td>600</td>
<td>96</td>
<td>1M muscovite + minor K-feldspar</td>
</tr>
<tr>
<td>7*</td>
<td>Pt</td>
<td>Prep. 4</td>
<td>500±5</td>
<td>900</td>
<td>96</td>
<td>1M muscovite + K-feldspar</td>
</tr>
<tr>
<td>8</td>
<td>Pt, open</td>
<td>K_{1.0}Al_{2}(AlSi_{3})</td>
<td>495±5</td>
<td>900</td>
<td>90</td>
<td>1Md + 3T(d) + cristobalite + hydralsite</td>
</tr>
<tr>
<td>9</td>
<td>Pt</td>
<td>Prep. 2</td>
<td>465±3</td>
<td>900</td>
<td>92.5</td>
<td>1Md + boehmite Trace 3T, occasionally not resolved</td>
</tr>
<tr>
<td>10*</td>
<td>Pt</td>
<td>Prep. 2</td>
<td>463±2</td>
<td>950</td>
<td>93</td>
<td>1Md + boehmite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Glass prepared from illite, Marblehead, Wisconsin</td>
<td>463±2</td>
<td>950</td>
<td>93</td>
<td>( ^4 \text{Muscovite + feldspar + cristobalite} )</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>12</td>
<td>Pt</td>
<td>( K_{1.0}Al_{2}(AlSi_3) )</td>
<td>317±5</td>
<td>600</td>
<td>96.5</td>
<td>1Md + 3T(?)d</td>
</tr>
<tr>
<td>13</td>
<td>Pt open</td>
<td>Prep. 2</td>
<td>317±5</td>
<td>600</td>
<td>96.5</td>
<td>3Td + ?kaolinite</td>
</tr>
<tr>
<td>14</td>
<td>Pt open</td>
<td>( K_{1.0}Al_{2}(AlSi_3) ) Prep. 5</td>
<td>402±2</td>
<td>1200</td>
<td>93</td>
<td>1M muscovite</td>
</tr>
<tr>
<td>15</td>
<td>Pt open</td>
<td>( K_{0.5}Al_{2.0}(Si_{3.5}Al_{0.5}) ) Prep. 6</td>
<td>402±2</td>
<td>1200</td>
<td>93</td>
<td>3T (?)d + 1Md</td>
</tr>
<tr>
<td>16</td>
<td>Au</td>
<td>( K_{0.83}(Al_{1.916}Mg_{0.083}) ) (Si_{3.25}Al_{0.75}) Prep. 7</td>
<td>402±2</td>
<td>1200</td>
<td>93</td>
<td>1Md, approaching 1M state</td>
</tr>
<tr>
<td>17*</td>
<td>Au</td>
<td>Prep. 5</td>
<td>475±5</td>
<td>800</td>
<td>96</td>
<td>1Md + 3Td; minor hydralsite</td>
</tr>
<tr>
<td>18*</td>
<td>Au</td>
<td>Prep. 2</td>
<td>475±5</td>
<td>800</td>
<td>96</td>
<td>1Md + cristobalite Trace 3T</td>
</tr>
<tr>
<td>19*</td>
<td>Au</td>
<td>Prep. 5</td>
<td>460±2</td>
<td>900</td>
<td>98</td>
<td>1Md + hydralsite 3T (?)d</td>
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<tr>
<td>20*</td>
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<td>Prep. 2</td>
<td>460±2</td>
<td>900</td>
<td>98</td>
<td>1Md + cristobalite, trace 3T</td>
</tr>
<tr>
<td>21</td>
<td>Au</td>
<td>Prep. 2</td>
<td>505±1</td>
<td>1100</td>
<td>31</td>
<td>1Md + cristobalite, trace hydralsite</td>
</tr>
</tbody>
</table>

* Syntheses bearing an enrichment of \( ^4 \)K.
Table 9. Comparison of X-Ray Data for 1M Muscovites 7 and 14 With That of Yoder and Eugster (1955) For a Synthetic 1M Muscovite.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Yoder &amp; E.gster</th>
<th>14</th>
<th>7</th>
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<tr>
<td></td>
<td>$\theta_0$</td>
<td>$d_A$</td>
<td>I</td>
</tr>
<tr>
<td>001</td>
<td>8.775</td>
<td>10.077</td>
<td>&gt;100</td>
</tr>
<tr>
<td>002</td>
<td>17.610</td>
<td>5.036</td>
<td>37</td>
</tr>
<tr>
<td>020</td>
<td>19.780</td>
<td>4.488</td>
<td>90</td>
</tr>
<tr>
<td>111</td>
<td>20.420</td>
<td>4.349</td>
<td>27</td>
</tr>
<tr>
<td>112</td>
<td>24.315</td>
<td>3.660</td>
<td>60</td>
</tr>
<tr>
<td>112</td>
<td>29.055</td>
<td>3.073</td>
<td>50</td>
</tr>
<tr>
<td>113</td>
<td>30.515</td>
<td>2.929</td>
<td>6</td>
</tr>
<tr>
<td>023</td>
<td>33.310</td>
<td>2.689</td>
<td>16</td>
</tr>
<tr>
<td>130</td>
<td>34.745</td>
<td>2.582</td>
<td>50</td>
</tr>
<tr>
<td>131</td>
<td>34.980</td>
<td>2.565</td>
<td>90</td>
</tr>
<tr>
<td>200</td>
<td>35.200</td>
<td>2.550</td>
<td>22</td>
</tr>
<tr>
<td>131</td>
<td>36.680</td>
<td>2.450</td>
<td>11</td>
</tr>
<tr>
<td>132</td>
<td>37.385</td>
<td>2.405</td>
<td>4</td>
</tr>
<tr>
<td>114</td>
<td>37.800</td>
<td>2.380</td>
<td>12</td>
</tr>
<tr>
<td>040</td>
<td>40.155(b)</td>
<td>2.246</td>
<td>8</td>
</tr>
<tr>
<td>220</td>
<td>40.650(b)</td>
<td>2.219</td>
<td>7</td>
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<tr>
<td>041</td>
<td>41.200?</td>
<td>2.191</td>
<td>4</td>
</tr>
<tr>
<td>133</td>
<td>41.900(b)</td>
<td>2.156</td>
<td>20</td>
</tr>
<tr>
<td>202</td>
<td>42.870</td>
<td>2.109</td>
<td>6</td>
</tr>
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<td>005</td>
<td>45.035</td>
<td>2.013</td>
<td>32</td>
</tr>
<tr>
<td>133</td>
<td>46.400(b)</td>
<td>1.957</td>
<td>7</td>
</tr>
<tr>
<td>134</td>
<td>47.860(b)</td>
<td>1.900</td>
<td>4</td>
</tr>
<tr>
<td>116</td>
<td>55.045</td>
<td>1.668</td>
<td>18</td>
</tr>
<tr>
<td>151</td>
<td>55.590(b)</td>
<td>1.653</td>
<td>12</td>
</tr>
<tr>
<td>204</td>
<td>56.250(b)</td>
<td>1.635</td>
<td>12</td>
</tr>
<tr>
<td>135</td>
<td>61.210?</td>
<td>1.514</td>
<td>4</td>
</tr>
<tr>
<td>060</td>
<td>61.885</td>
<td>1.499</td>
<td>33</td>
</tr>
</tbody>
</table>
(2) \(1M_d\) Micas

\(1M_d\) micas obtained showed significant variations in X-ray diffraction patterns, principally in the following features:

1. the asymmetry of the basal diffraction maxima, 001 and 002 in particular,
2. the positions of these maxima or the values of \(d_{001}\),
3. their intensities relative to, for example, 020, and
4. the intensities of peaks hkl relative to the 2.57\(\AA\) maximum (indexed 13\(\bar{1}\) by Yoder and Eugster (1955), and 200 + 13\(\bar{1}\) by Bradley and Grim, 1961).

These features are discussed below and parameters based upon them in Part (f) of this section. The differences occur not only between \(1M_d\) phases prepared from different initial preparations, (those with the ideal muscovite formulation and those lower in potassium alike), but between products of the same preparation synthesized under only slightly differing conditions (cf 10 and 20, Table 10 and Figures 12 and 13).

(3) \(b\)-Axis Disorder in \(1M_d\) Phases

The principal differences between \(1M\) and \(1M_d\) diffraction patterns as discussed by Yoder and Eugster (1955) concern the form of 001 and the relative intensities of the hkl's. They state (p. 244), "In some runs all of the hkl's were absent, and this was interpreted as evidence of complete disorder of the layers. ... As greater order of the layers is obtained, the hkl's appear, and the intensity of these may be used as a measure of the amount of remaining disorder. In particular the 11\(\bar{2}\) and 112 reflections are useful for this purpose." The latter maxima at 24.315° 2θ, 3.660°, and 29.055° 2θ,
3.073 Å according to their data, are unique to the 1M and 1Md polytypes, as far as the latter retains them, and serve to distinguish 1M from 2M and 3T. No mention is made of peak displacement in the 1Md form though it must exist. It is determinable only with difficulty in other than basal maxima due to imprecision in locating broad, low, noisy peaks and the smallness of the displacements.

Table 10 gives diffraction data for synthesis 10, representing an extreme of disorder observed in the 1Md polytypes, and synthesis 20 of intermediate degree. Both were employed in exchange experiments. Listed intensities, I, represent peak heights above background (the only measure employed in this work). Values I', given for all except the basal peaks, represent a normalization on the basis of a comparison of the intensity of 020 in Yoder and Eugster's 1M muscovite with 020 in the 1Md phases.

\[
I'_{hkl} = \left( \frac{I(020, \text{Yoder & Eugster's 1M})}{I(020, \text{synthetic 1Md})} \right) I_{hkl}
\]

On the basis of the values of I', and not considering 020, it is evident that all peaks, with the apparent exception of 132, are reduced in intensity in the 1Md phases, to the extent that numerous of them are absent. The significant point, however, is that reductions are not uniform but preferential, being greater in cases where k of the index hkl is other than 3 or 0. Maxima 331 are much less diminished. This is more readily seen in Figure 9, where I' is represented
Table 10. X-ray data for syntheses 10 and 20 with observed and normalized peak heights.

<table>
<thead>
<tr>
<th>Synthetic 1M, Yoder &amp; Engster</th>
<th>Synthesis 20</th>
<th>1Md</th>
<th>Synthesis 10</th>
<th>1Md</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl (Bradley)</td>
<td>hkl (Yoder)</td>
<td>d(Å)</td>
<td>I</td>
<td>d(Å)</td>
</tr>
<tr>
<td>001</td>
<td>001</td>
<td>10.077</td>
<td>100</td>
<td>10.08</td>
</tr>
<tr>
<td>002</td>
<td>002</td>
<td>5.036</td>
<td>37</td>
<td>5.02</td>
</tr>
<tr>
<td>020,110</td>
<td>020</td>
<td>4.488</td>
<td>90</td>
<td>4.50</td>
</tr>
<tr>
<td>111</td>
<td>111</td>
<td>4.349</td>
<td>27</td>
<td>4.35</td>
</tr>
<tr>
<td>021</td>
<td>021</td>
<td>4.115</td>
<td>16</td>
<td>3.66</td>
</tr>
<tr>
<td>112</td>
<td>112</td>
<td>3.660</td>
<td>60</td>
<td>3.34</td>
</tr>
<tr>
<td>022; 003</td>
<td>003; 022</td>
<td>3.356</td>
<td>100</td>
<td>3.34</td>
</tr>
<tr>
<td>112</td>
<td>112</td>
<td>3.073</td>
<td>50</td>
<td>3.07</td>
</tr>
<tr>
<td>113</td>
<td>113</td>
<td>2.929</td>
<td>6</td>
<td>2.68</td>
</tr>
<tr>
<td>023</td>
<td>023</td>
<td>2.689</td>
<td>16</td>
<td>2.58</td>
</tr>
<tr>
<td>130</td>
<td>130</td>
<td>2.582</td>
<td>50</td>
<td>2.56</td>
</tr>
<tr>
<td>131, 200</td>
<td>131</td>
<td>2.565</td>
<td>90</td>
<td>2.44</td>
</tr>
<tr>
<td>131, 205</td>
<td>131</td>
<td>2.550</td>
<td>22</td>
<td>2.40</td>
</tr>
<tr>
<td>132, 201</td>
<td>132</td>
<td>2.405</td>
<td>4</td>
<td>2.40</td>
</tr>
<tr>
<td>130</td>
<td>130</td>
<td>2.380</td>
<td>12</td>
<td>2.191</td>
</tr>
<tr>
<td>040</td>
<td>040</td>
<td>2.246</td>
<td>8</td>
<td>2.219</td>
</tr>
<tr>
<td>041</td>
<td>041</td>
<td>2.219</td>
<td>7</td>
<td>2.191</td>
</tr>
<tr>
<td>133, 202</td>
<td>133</td>
<td>2.156</td>
<td>20</td>
<td>2.15</td>
</tr>
<tr>
<td>202</td>
<td>202</td>
<td>2.109</td>
<td>6</td>
<td>2.00</td>
</tr>
<tr>
<td>005</td>
<td>005</td>
<td>2.013</td>
<td>32</td>
<td>1.95</td>
</tr>
<tr>
<td>133, 204</td>
<td>133</td>
<td>1.957</td>
<td>7</td>
<td>1.90</td>
</tr>
<tr>
<td>134</td>
<td>134</td>
<td>1.900</td>
<td>4</td>
<td>1.668</td>
</tr>
<tr>
<td>151</td>
<td>151</td>
<td>1.653</td>
<td>12</td>
<td>1.635</td>
</tr>
<tr>
<td>060; 331</td>
<td>060</td>
<td>1.499</td>
<td>33</td>
<td>1.496</td>
</tr>
</tbody>
</table>

* I' = I x 90/35 = 2.57I  † I' = 2.31I
Figure 9. Suppression of Diffraction Maxima in 1Md Micas.
on a $^{0.20}$ scale. The most apparent relative suppressions are of 112, 112, and of the peaks in the higher $^{0.20}$ region. The assigned indexes beyond approximately 2.56$^{0}$ must be accepted with slight reservation, as in the higher 20 region the multiplicity of indexes assignable to an observed maximum increases. This is suggested by the minor variations in indexes given by Yoder and Eugster compared with those of Bradley and Grim, although observed spacings also differ slightly.

The observation of suppression of hkl peaks where $k \neq 3n$ is common to the clay mineral groups comprising the kaolinites, vermiculites, and chlorites. In these it is attributed to varying degrees of randomness in the relationship between adjacent sheets extending in the ab plane, the alumino-silicate layers. (Brindley and Robinson, 1946; Hendricks and Jefferson, 1938; Robinson and Brindley, 1948.) The disorder involves random translations of varying numbers of sheets in the ab plane parallel to b by units of nb/3, where n = 0, 1, 2 ... Brindley (1961) provides the following concise explanation of the suppression of maxima: "Layer displacements of b/3 cause phase changes of k x 120$^{0}$, so that if k is not a multiple of 3, phase changes of 0$^{0}$, 120$^{0}$, and 240$^{0}$ occur randomly and the corresponding hkl reflections are cut out. When k is a multiple of 3, the phase changes are multiples of 360$^{0}$ and the corresponding hkl reflections are unaffected". The ion-layers producing maxima hkl in the ordered form progressively lose their periodicity in the direction C*, normal to ab, upon the increase of b-axis disorder. Thus hkl bands may occur, of reduced or indetectable intensity and
characteristically broadened. The periodicity of ion-layers parallel to the basal planes is not disturbed by the process.

Translations of nb/3 in kaolinites appear to be readily possible at the oxygen layer-hydroxyl layer (inter-aluminosilicate layer) contacts. The inter-hydroxyl spacing in the basal "plane" is b/3 in the idealized structure and even in the distorted actual structure appears to allow re-formation of O-OH hydroxyl bonds upon displacement. An analogous situation is possible in chlorites and vermiculites where the opposing oxygen surfaces at the interlayer discontinuity are separated by cations coordinated either by OH⁻ or H₂O.

b-axis disorder has been observed in micas by several investigators and expalantions of it proposed by Hendricks and Jefferson (1939) and Smith and Yoder (1956). To attribute the nb/3 displacements to a potassium-saturated interlayer region encounters the difficulty that the K⁺ ion separation in the relevant direction is equal to the b-axis dimension. Therefore the former writers attribute the translation to the octahedral layer level, while the latter invoke "a change in the interlayer stacking angle of 120°", that is, an equivalent rotation. Smith and Yoder explain the occurrence of the mica polymorphs or polytypes on the basis of regularly repeated "rotations" of entire sheets at the interlayer level. The degree of rotation may be specified with reference to the inter-potassium

* "rotation" is actually a growth phenomenon
or interlayer vector, joining the potassium ion below a layer to that nearest and above the layer. The vector is parallel to the sheet a axis in the 1M polytype and ascends obliquely through the structure in the ac plane due to the approximately a/3 displacement at the octahedral layer level. In projection on ab, the plane of the sheets, the vectors show repeated 0° rotations in the 1M polytype, alternating 120° and 240° rotations in 2M, and repeated 120° rotations in the 3T polytype. The numeral designates the number of layers in the repeat distance normal to ab, and the letter the symmetry, monoclinic or trigonal. The listed examples are the observed muscovite polytypes. Six are possible on the basis of hexagonal layer symmetry, as shown by Smith and Yoder. The ditrigonal symmetry of basal oxygen layers, accompanying other distortions, described by Radoslovich (1960), satisfactorily accounts for the absence of three polytypes based upon rotations which are odd multiples of 60°.

Smith and Yoder state that "Frequent random stacking faults result in disordered crystals", a "stacking fault" meaning that the orderly sequence of inter-vector angles is interrupted erroneously, e.g. in 1M: 0°, 0°, 120°, 0°, 0°, .... Such errors produce the effects of b-axis disorder. Concerning the latter as it occurred in their synthetic 1Md micas, Yoder and Engster (1955) state: "The nature of the disorder has been described by Hendricks and Jefferson (1939) and amplified by Smith and Yoder (1955)" (sic).
A further observation concerning the origin of b-axis disorder in the 1Md micas of this work is made in Part 3, (f).

As a measure of the degree of b-axis disorder in the synthetics, the ratio of peak heights of the maxima at or close to 34.98° and 29.055° 2θ was determined. The positions are Yoder and Eugster's for 1M muscovite, representing spacings of 2.565Å and 3.073Å, indexed 131 and 112 by them, also indexed 131+ 200 and 112 by Bradley and Grim (1961). Thus the ratio I(131)/I(112) would expectably increase as 112 is suppressed by b-axis disorder. The ratio for Yoder and Eugster's 1M muscovite is 1.80, for synthesis 7, 0.78 (minimum observed), for synthesis 10, 3.28. Care must be employed in applying the ratio. Almost all layer silicates produce diffracted intensity in the region of 35° 2θ, while the peak at 29.055° 2θ is unique to 1M structures.

(4) Heteropolytypism of 1Md Phases

Further observations concerning the 1Md micas pertain to the positions and natures of the basal reflections. The maxima 001 are invariably asymmetrical, skewed towards the low-angle region (Figures 3 and 8). Following Nelson (1956) the asymmetry was measured at one quarter of the peak height above the base line joining adjacent minima (see Figure 11, curves A). The position of the peak median at 1/4 height was determined, and the difference in degrees 2θ between this position and that of the maximum was termed the asymmetry, α° 2θ. Observed values of α ranged from 0.02° 2θ in synthesis 3 (1M mica) to 0.43° in synthesis 15 (3T, probably 3Td, + minor 1Md). Smaller angles may be entirely instrumental
(Klug and Alexander, 1954; Parish, 1960). Yoder and Eugster (1955) state that the asymmetry of 001 is due to "a larger proportion of 1M muscovite, yet with a continuum of randomly interstratified mica and montmorillonite in decreasing proportions from mica to montmorilllonite." Again, on p. 253 is stated: "The characteristics of the '10 Å diffraction line' which Grim describes, are those of a complex mixed-layered structure. ...This conclusion has apparently been reached by Kerr et al (1950, p. 13) and Jackson (1952, p. 5), as well as by others." Evidence for mixed-layering or heteropolytypism was therefore sought in the 1Md micas.

The theory of diffraction effects due to mixed layering, in the present instance the occurrence in single crystallites of potassium-saturated 1M layers, presumably of d001 equal to 10.077Å, and of layers expanded to a non-measurable spacing by hydrated interlayer cations, is well developed.

Diffracted intensity is a continuous function of the Bragg angle θ and is given by

\[ I = \Theta \cdot |F_\parallel|^2 \cdot \phi \]  

(MacEwan, Ruiz Amil, and Brown, 1961).

\( \Theta \) is an angle dependent factor; the layer structure factor \( F_\parallel \) depends upon the nature and Z coordinates of the ions; the mixing function \( \phi \) depends upon the most important variables in the present case, the two spacings involved, \( d_1 \) and \( d_2 \), the probability of occurrence of each, \( p_{d_1} \), and the mode of their intermixing, given
by \( p_d d_2 \), the probability of \( d_2 \) following \( d_1 \). \( \Phi \) is a function of \( \theta \) and crystal size also.

Calculated values of \( \Phi \) plotted against a function of \( \theta \) (i.e., \( r^* \), given by \( 2 \sin \theta / \lambda \), the reciprocal spacing) show that observed basal maxima of a mixed structure are intermediate in position between the peaks which would be exhibited by the components \( d_1 \) and \( d_2 \) alone. Thus such structures give a non-integral series of basal reflections; i.e., the spacings of the maxima are not all sub-multiples of a fundamental repeat distance \( d(001) \).

This criterion is applied to syntheses 3, 7, and 14 where mixing should be virtually absent, and to 5, 21 and 10, 1Md forms:

Table 11. Non-Integral Basal Spacing Sequences in Three 1Md Synthetic Micas

<table>
<thead>
<tr>
<th></th>
<th>1Md</th>
<th>1Md</th>
<th>1Md</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>( d(001) )</td>
<td>10.05(^\circ)</td>
<td>10.07(^\circ)</td>
<td>10.08(^\circ)</td>
</tr>
<tr>
<td>2( \times d(002) )</td>
<td>10.06</td>
<td>10.08</td>
<td>10.10</td>
</tr>
<tr>
<td>3( \times d(003) )</td>
<td>10.05</td>
<td>10.08</td>
<td>10.08</td>
</tr>
<tr>
<td>5( \times d(005) )</td>
<td>10.05</td>
<td>10.06</td>
<td>10.08</td>
</tr>
</tbody>
</table>

For comparison, Yoder and Eugster's type 1M muscovite yields 10.07\(^\circ\), 10.072, 10.068, and 10.065\(^\circ\). A "typical air-dry illite" is illustrated by Bradley and Grim (1961), p. 223, giving the approximate sequence 10.05\(^\circ\), 9.96, 9.99, 9.96, 9.95\(^\circ\). They conclude that "the reciprocal spacings stand in essentially integral sequence." The 1Md forms in Table 11 are shown below to have displaced basal maxima.
The features of the sequences are similar to Bradley and Grim's. The writer would therefore disagree with their conclusion and considers that the test is subjective.

A further test was made by comparing separations in degrees 2θ of the positions of 001 and 002, also of 001 and 003, termed Δ21 and Δ31 respectively. Sensitivity and elimination of possible sample position error on the goniometer are gained. Regardless of whether or not other criteria can effect subdivision, two groups can be compared: the ordered, high potassium syntheses, and the disordered, low potassium examples, as in the table.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean Δ21</th>
<th>Mean Δ31</th>
<th>Ranges of Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M (Y. &amp; E 1955)</td>
<td>17.785°</td>
<td>8.835°</td>
<td>-</td>
</tr>
<tr>
<td>High potassium, ordered Syntheses 3, 4, 6, 7, 14</td>
<td>17.77°</td>
<td>8.83°</td>
<td>17.75° to 17.79°</td>
</tr>
<tr>
<td>Low potassium, 1Md 2, 5, 9, 10, 18, 20, 21</td>
<td>17.90°</td>
<td>8.93°</td>
<td>17.87° to 17.97°</td>
</tr>
</tbody>
</table>

These differences are highly significant and are compatible with the occurrence of mixed-layering in the 1Md syntheses.

The direction of the peak shifts is consistent in all of the 1Md syntheses bearing little or no 3T or 3Td, i.e., 001 towards
smaller angles, though this is difficult to detect, and 002, 003, 005 towards larger angles, as shown in Table 13 below.

Table 13. Displacements of Basal Maxima in 1Md Micas Due to Mixed-Layering

<table>
<thead>
<tr>
<th></th>
<th>Position in Degrees 2θ</th>
<th>001</th>
<th>002</th>
<th>003</th>
<th>004</th>
<th>Asymmetry</th>
<th>α, (001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7(1M)</td>
<td>8.78</td>
<td>17.61</td>
<td>26.55</td>
<td>45.06</td>
<td></td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>14(1M)</td>
<td>8.77</td>
<td>17.57</td>
<td>26.51</td>
<td>44.93</td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>21(1Md)</td>
<td>8.76</td>
<td>17.64</td>
<td>26.63</td>
<td>45.27</td>
<td></td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>20 &quot;</td>
<td>8.77</td>
<td>17.64</td>
<td>26.66</td>
<td>45.27</td>
<td></td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>5 &quot;</td>
<td>8.78</td>
<td>17.72</td>
<td>26.66</td>
<td>45.26</td>
<td></td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>2 &quot;</td>
<td>8.84</td>
<td>17.74</td>
<td>26.74</td>
<td>45.38</td>
<td></td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>18 &quot;</td>
<td>8.78</td>
<td>17.74</td>
<td>26.74</td>
<td>45.38</td>
<td></td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>10 &quot;</td>
<td>8.75</td>
<td>17.73</td>
<td>26.69</td>
<td>45.24</td>
<td></td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>9 &quot;</td>
<td>8.75</td>
<td>17.65</td>
<td>26.62</td>
<td>45.25</td>
<td></td>
<td>0.34</td>
<td></td>
</tr>
</tbody>
</table>

Despite the presence of random errors (standard deviation on 001 ≈ ±0.02° and coefficient of variation for α up to 60%) the trends are reasonably well defined. As the 1Md basals are thus composite maxima, they are not properly indexed as 003 etc., but as 003/001, i.e., with the associated reflection.

(5) 3T Micas

Synthesis 15, prepared from the formulation of $K_{0.5}Al_{2}(Si_{3.5}Al_{0.5})O_{11}$ (preparation 6) yielded 3T and 1M micas, one or both disordered. The sealed platinum tube gained 7 mg during the run, probably evi-
dancing a system "open" to the bomb fluid. The product evidenced
the maximum observed asymmetry of 001, 0.43° a, and maximum quantity of 3T
mica.

The 3T maxima distinguishable from those of 1M are tabulated
below and compared with the d values of the natural 3T muscovite
described by Axelrod and Grimaldi (1949).

Table 14. Comparison of Certain Spacings of a 3T Muscovite (Axelrod
and Grimaldi) With Those of Synthesis 15.

<table>
<thead>
<tr>
<th>3T Muscovite</th>
<th>Synthesis 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>dA</td>
<td>I</td>
</tr>
<tr>
<td>3.873</td>
<td>10</td>
</tr>
<tr>
<td>3.596</td>
<td>8</td>
</tr>
<tr>
<td>3.110</td>
<td>10</td>
</tr>
<tr>
<td>2.884</td>
<td>16</td>
</tr>
<tr>
<td>2.457</td>
<td>7</td>
</tr>
<tr>
<td>2.136</td>
<td>12</td>
</tr>
</tbody>
</table>

Ideally located at 19.765° 2θ, the 3T peak 1010 interferes with
020, 1M, ideally at 19.780° 2θ, while 1014, often the strongest 3T peak
observed, is unique. Therefore, the ratio of peak heights
(020 + 1010) / 1014
was adopted as a semi-quantitative measure of the
amount of 3T present. In 15 the value is 0.13. A "significant"
quantity is therefore present in syntheses 8 (0.15), 12 (0.12),
17 (0.28) and 19 (0.14). In 18 where 3T is occasionally not resolvable,
the ratio equals 0.09. 3T is also minor in 5 (0.08), 9 (once resolved,
and 20 (0.09). It is not detectable in other normal syntheses.
3T is, however, the micaceous phase resulting from the reconstitution
of an illite glass (synthesis (11), in which instance it was well
ordered.

Synthesis 13 is of interest in that, as it was run concurrently
with 12, much greater disorder developed in the low-potassium
product (13, preparation 2) at 317° ± 5° C. In the latter a typical
hk band, tailing over some 15° 2θ from 19.92° 2θ is present.

(c) Subsidiary Products and Variations

Of the syntheses employed in the exchanges with potassium
chloride solutions, number 10 bore no determinable potassium-bearing
contaminants, while in 20 minor cristobalite was present. By analogy
with other cristobalites, a low potassium content was probably present.
No account could be taken of this and it may be noted that the pro-
bable rate of change of activity in synthesis 20 at 100° C is less
than that observed in 10. Synthesis 10 was associated with minor
boehmite. Observed spacings for the two materials were as follows:
<table>
<thead>
<tr>
<th>γ AlO(OH)*, Boehmite (10)</th>
<th>SiO₂, Cristobalite (20)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Observed</strong></td>
<td><strong>Expected</strong></td>
</tr>
<tr>
<td>dÅ</td>
<td>I</td>
</tr>
<tr>
<td>6.11</td>
<td>4</td>
</tr>
<tr>
<td>3.16</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Both syntheses are hydrothermal products of the same preparation, number 2, run under similar conditions. The variable leading to different paths of crystallization was not determined. The apparent anomaly of excess alumina in one case and excess silica in the other possibly involves one or more of following factors: (a) failure of silica to crystallize; (b) in the cases where excess silica remained in runs of preparation 2 (six out of eight) it is possible that alumina was represented by rarely detectable hydralsite. This was observed in one case, 21. (c) Utilization of SiO₂ in the micas of syntheses 9 and 10. The latter differ significantly from all others derived from preparation 2 in their greater degree of disorder. This is illustrated by the plots of Part 3, (f).

Hydralsite, a sheet silicate of the approximate composition 2Al₂O₃·2SiO₂·H₂O was described by Roy and Osborn (1954) who quote the spacings compared in Table 15 with those observed here.

* American symbol α; γ recommended in Brown (1961)
Table 15. Occurences and d Values of Hydralsite

<table>
<thead>
<tr>
<th>Hydralsite Roy and Osborn, 1954</th>
<th>8</th>
<th>17</th>
<th>19</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>dA</td>
<td>I</td>
<td>dA</td>
<td>I</td>
<td>dA</td>
</tr>
<tr>
<td>8.91 80</td>
<td>8.98 38</td>
<td>8.96 3</td>
<td>8.91 80</td>
<td>8.93 0.2</td>
</tr>
<tr>
<td>4.448 60</td>
<td>3.42 25</td>
<td>3.41 6</td>
<td>3.41 23</td>
<td></td>
</tr>
<tr>
<td>3.414 100</td>
<td>2.44 14</td>
<td>2.44 6</td>
<td>2.44 8</td>
<td></td>
</tr>
<tr>
<td>2.430 50</td>
<td>2.08 5</td>
<td>2.08 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.362 40</td>
<td>1.85 4</td>
<td>1.81 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.074 20</td>
<td>1.77 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.044 10</td>
<td>1.471 5</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1.845 20</td>
<td>1.450 10</td>
<td>1.81 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.810 10</td>
<td>1.768 20</td>
<td>1.81 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.768 20</td>
<td>1.471 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.471 5</td>
<td>1.450 10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A further cause of product variation is possibly to be inferred from a comparison of syntheses 14, 17 and 19, all from preparation 5. The first proved the mixture to be capable of yielding a pure LHM muscovite, yet the others produced a disordered mica, probably lower in potassium content, and hydralsite, potassium-free. Occasional procedures of sealing the noble metal tubes by means of an oxy-acetylene flame resulted in an observable vapour loss from the tube. Such runs were abandoned. It is possible that an unnoticed loss
occurred in sealing 17 and 19, the rapidly evolving steam transporting potassium. By extension, it is possible that variation in the micas of preparation 2, which is readily explained by variation in potassium content, arose in like manner.

It may be noted here that many of the results do not represent the attainment of equilibrium. Cristobalite is metastable relative to keatite and quartz, in addition boehmite is metastable with respect to diasporie (Roy and Osborn, 1954) under the conditions of synthesis. The stability of the disordered micas was not investigated in long syntheses. In adequate periods, however, Yoder and Fugster (1955) found that ideal muscovite compositions yielded in turn 1M and 2M phases at temperatures as low as 350°C and that 1Md was an initial metastable product. The products of the syntheses carried out here are, in significant part at least, determined by reaction kinetics.

(d) Characteristics of Natural Illites

If it is to be maintained that the 1Md micas of this study are analogous to illites, it is necessary to detail the features of the latter for comparison.

Definitions of illite are frequently broad and non-specific. The term was proposed by Grim, Bray, and Bradley, (1937) as a mineral group name for the approximately 10Å layer silicates of soils and sediments. In 1962 Grim made the following statements (p. 20):

"Illite clay minerals appear to differ from the well crystallized
micas in having relatively less replacement of aluminum for silicon, less potassium, and some randomness in stacking of the silicate layers"; "some interlayer water may occur." He also states that "interlayering of montmorillonite between the mica layers... may prevail."

The important features are stated, but two semantic questions remain. Firstly, authors vary in their concepts of the allowable degree of mixed-layering when the unmodified term "illite" is to be applied. Yoder and Eugster (1955) state (p. 254) that "Proof has yet to be obtained that the materials now called illite are not all mixed-layered structures."

Weaver (1959) states that he adopts a limit of 10%. Clays with a greater quantity are termed "mixed-layered illite - montmorillonite." Warshaw (1960) employs limits of 25%. Bradley and Grim (1961) merely employ the term "a small proportion," and this is retained in a recent classification of layer silicates (Warshaw and Roy, 1961).

The second question of usage and meaning concerns the statement that the mixing is with "montmorillonite" layers. This would appear to imply that, within a crystallite, there occur layers of lower charge which are expansible upon ethylene glycol treatment, in a sequence of those of higher charge, the "illitic" potassium-bearing layers. This is advocated by Weaver (1965), for example. It would be equally possible to observe the effects of mixed-layering in a structure of virtually uniform layer charge, for instance in a hypothetical vermiculite of high layer charge, having 85% of its interlayers saturated with potassium (of 10Å spacing) and 15% randomly
intercalated bearing hydrated sodium at 12.6\(^{0}\). The effects in this case depend only upon differences in interlayer ion population.

The synthetic products are mixed-layered. However, the departures from muscovite spacings are small and it is considered that they may be termed "illitic" in the usage of most writers. The degree of mixed-layering is not estimated closely because of two difficulties which also exist in the case of natural materials: (1) the mode of introduction of layers greater than some 10A in thickness is not known, i.e. the degree of randomness, and (2) the uncertainty that all thickened layers will vary further upon the laboratory treatment used to estimate their percentage.

Concerning statement (1) above, unless a Fourier analysis is carried out, it is uncertain that the mixing is purely random. Published curves (for example MacEwan, Ruiz Amil, and Brown, 1961) for the estimation of degree of mixed-layering, assume random distribution. Statement (2) concerns the possible presence of alumino-hydroxy complexes in interlayer sites. Such would produce an expanded interlayer which is not mutable in thickness upon glycolation, and is itself not exchangeable. Their presence is difficult to detect. They are suspected of occurring in heat-treated syntheses 9 and 10, as well as in the Marblehead illite.

(e) Comparison of Features of Natural Illites and the Synthetic 1Md Micas.

Comparison is based upon published data and the writer's observations on the illite described by H. E. Gaudette (1965) from the
Silurian Burnt Bluff Group, Marblehead, Wisconsin. Features are compared under the following headings:

(1) Asymmetries and Displacements of Basal Maxima
(2) Effect of Heat Treatment
(3) Behaviour Upon Ethylene Glycol Solvation
(4) Layer Charge
(5) b-Axis Disorder

Firstly, although in the definition of illite, "no account is taken of whether a given polytype is or can be specified" (Bradley and Grim, 1961, p. 222), the synthetic materials are based on the 1M structure and the place of such illites in nature should be discussed. On the same page the above authors state that: "In shales, representing the accumulated detritus from coarser rocks, the determinable grains are generally the characteristic two-layer muscovite. Other equally micaceous but finer grained accumulations, presumed to have originated as bentonite, indicate that the determinable fraction is of the single-layer structure." Again, Levinson (1955), published spacings for a certain fine-grained fraction of Fithian illite, a type material forming a Pennsylvanian underclay. The maximum 3.07Å, very weak, is recorded in a table of values headed "1Md Illite."
The spacing is unique among micaceous minerals to 1M and 1Md and is not liable to interference from peaks of quartz, carbonates, feldspars, nor any clay mineral except possibly certain kaolinite-group members which could be distinguished by other more intense maxima. Weaver (1959, p. 164) states: "All the mixed-layer illite-montmorillonites (which in most instances formed from volcanic ash) appear to
have a 1M or 1Md structure." This is indicative of common occurrence.

It is the belief of the writer that natural illites which exhibit significant asymmetry of the basal maxima are mixed-layered crystallizations based upon either the 1M, 2M or 3T polytypic forms. This is in partial accord with the statement of Levinson (1955):

"... at least three polymorphs exist among micas called illites or hydrous micas (all dioctahedral) and therefore all minerals of this type may not be considered a defect or poorly crystallized 2M muscovite structure as many workers have erroneously concluded from the work of Grim et al. (1937)." It might be suggested further that it appears to be implicit in the writing of Yoder and Eugster (1955) that they do not concede the possibility of mixed-layering (a c-axis disorder) nor extensive b-axis disorder occurring in 2M micas. Concerning Grim's inference that illites are less well crystallized than 2M muscovite, Yoder and Eugster state: "It is not clear whether he means the peaks on the X-ray pattern are broad owing to fine grain size, or that some peaks tail-off to higher angles owing to disorder. The writers have not observed a 2M muscovite which exhibits either of these diffraction phenomena." They did however examine 2M polymorphs in several sediments, including the Fithian illite. It would appear that asymmetry in the basal maxima was always attributed to "mixed-layer 1Md + montmorillonite."

In contrast to the error mentioned by Levinson,
It is possible that the pendulum has now swung fully. For example, Velde and Hower (1963) determine the proportions of micaceous components of some 60 Palaeozoic shales in terms of the two minerals employed in their working curves "2M (muscovite) and 1Md (illite)."

On the basis of the writer's belief expressed above, and the inference of Gaudette that the Marblehead illite is a representative sample, comparisons are made in the following paragraphs between 1Md synthetics and the 2M Marblehead, as well as other illites of unspecified polytypism described in the literature.

1) Asymmetries and Displacements of Basal Maxima

As may be noted in Figure 8 for the 1Md syntheses, the basal maxima 001, 002, 003, and 005, in the vicinity of 9° 29, 18° 28, 27° 26 and 45° 26, show varying degrees of asymmetry. In the case of 001 it is in the direction of lower angles, in the remainder, in the direction of higher angles. These directions are also the directions of displacement from the ideal 1M positions. The effect is attributed to mixed-layering and confirmed by the fact that treatments known to modify hydrated expanded layers alter the asymmetries and peak positions.

The following statements refer to natural illites: Bradley (1954, p. 329), "The modifications of mica(basal) diffraction maxima imposed by the presence of a few thicker layers, either chloritic or expandable, are on the low angle side of the first mica node and on the high angle side of the third." He states further: "Diagrams of illites modified by small proportions of oversize layers within (the)
packets exhibit real asymmetry” (as opposed to diffracted intensity
on the low angle side of the 10° maximum which is no longer apparent
after correction for different diffraction efficiencies over the
angular spread of the broad maximum). Harrison and Murray (1959) made
similar observations upon shale illites weathering to grossly mixed-
layered clays in soil profiles. The effects progressively increase
as expandable layers are introduced.

The asymmetries and displacements observable in Marblehead illite
relative to 2M muscovite are compared in Table 16 with those for syn-
thesis 10 relative to 1M. Directions towards higher angles are
henceforth termed +ve and towards lower angles, -ve.

Table 16. Asymmetries and Peak Displacements of Basal Maxima Compared
for Marblehead Illite and Synthesis 10.

<table>
<thead>
<tr>
<th>Displacements from Ideal, °2θ</th>
<th>Peak Asymmetries, 1/4 height, °2θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marblehead 2M Illite</td>
<td>Synthesis 10</td>
</tr>
<tr>
<td>-0.02°, 002</td>
<td>-0.03°, 001</td>
</tr>
<tr>
<td>+0.15°, 004</td>
<td>+0.12°, 002</td>
</tr>
<tr>
<td>+0.20°, 006</td>
<td>+0.13°, 003</td>
</tr>
<tr>
<td>+0.50°, 0010</td>
<td>+0.20°, 005</td>
</tr>
<tr>
<td>Marblehead 2M Illite</td>
<td>Synthesis 10</td>
</tr>
<tr>
<td>-0.22° = α</td>
<td>-0.29° = α</td>
</tr>
<tr>
<td>-0.06°</td>
<td>0.00°</td>
</tr>
<tr>
<td>+0.08°</td>
<td>+0.04°</td>
</tr>
<tr>
<td>+0.05°</td>
<td>+0.08°</td>
</tr>
</tbody>
</table>

Synthesis 10 was chosen for comparison on the basis of its similar value
of α. All factors considered, the agreement is remarkable. The
anomaly in the peaks adjacent to 18°2θ is unexplained, except pos-
sibly in terms of layer structure factor variation, or the presence of two discrete spacings, both greater than approximately 10\(\text{Å}\).

The range in values of \(\alpha\) in the 1M disordered synthetics is from \(-0.06^\circ\) to \(-0.34^\circ\) 2\(\theta\). Nelson (1956) observed a range between \(-0.07^\circ\) and \(-0.36^\circ\) in illites from shales.

Further published measurements of 001 (or analogous 002 maxima) asymmetries include those of Flawn et al (1960) who observed that diagenesis, continuing into low grade metamorphism, in the illites of the Ouachita System induced changes in the "sharpness ratio." The ratio of the height of the basal maximum at the peak, to the height above the baseline of a point on the low angle flank at the arbitrarily chosen position of 8.425\(^\circ\) 2\(\theta\) (10.5\(\text{Å}\)), was measured. It defines the "sharpness ratio." In "unmetamorphosed" illites the ratio is 1.8 to 2.3. In those having been subjected to "low grade metamorphism" the ratio is approximately 12. In synthesis 9, 1M\(d\), it is approximately 2.5; in 7, 1M muscovite, it is 13.7. In synthesis 20, in its original state, it is 1.87. After 108 hrs at 350\(^\circ\) C in 4 molar KCl it increases to 2.98. Anomalously however, after 96 hours at 452\(^\circ\) C, it did not increase, although the expected concomitant change in 002, is marked (depicted in Figure 3). As stated in a previous section, the observed changes are in keeping with those observed due to diagenesis.

(2) Effect of Heat Treatment

Figure 11 shows the effect of oven heating in air upon Marblehead illite (lower left) and upon two synthetic products, 9 and 15, shown as parts B and C respectively. A temperature of 120\(^\circ\) C was maintained
Figure 10

Initial Changes in Synthetic 1Md Micas

Discussion on pages 167 and 169

A1
Synthesis 10, immediately after synthesis, never having dried

A2
Synthesis 10, specimen of A1 placed over CaCl₂ for 10 minutes

A3
Synthesis 10, same specimen, dried 15 minutes

B
Synthesis 9, after 2 days in laboratory air

C
Synthesis 3, after several weeks in laboratory air

D1
Synthesis 9, initial state followed by 10 minutes over CaCl₂

D2
Synthesis 9, a further fraction dried 30 minutes

Figure 11

Comparison of Effects of Heating and Glycol Solvation on the 10Å peaks of an Illite and 1Md Synthetic Micas

"Illite": 0.3 - 3μ fraction, Marblehead illite; peak median at 1/4 height is shown in this and other cases, defining asymmetry, a.

A
Synthesis 21 1Md + cristobalite. Reversal of asymmetry upon glycol solvation.

B
Synthesis 9. Heated in air to 120ºC and 500ºC.

C
Synthesis 15, 3T and 1Md. Original condition; heated to 500ºC.
Figure 10.

Figure 11.
for 18 hours, 350°C for approximately 5 hours, and 500°C for 24 hours. As a precaution against rehydration in laboratory air (approximately 40% relative humidity) the samples were transferred from the oven to a CaCl₂ dessicator previously oven-dried, thence rapidly to a mylar-sealed diffractometer chamber containing a silica-gel tray. The first test of this type, of synthesis 15, also employed a dry helium atmosphere. All samples were sodium saturated before heating.

Examination of sodium-saturated Clay Spur montmorillonite revealed metastable persistence of the dehydrated spacing in laboratory air, therefore in the remaining heating tests only the desiccants were employed.

Only extreme mica types were examined, those of maximal and near minimal asymmetry of 001. Table 17 indicates the results.

Table 17. Effects of Heating in Air: Marblehead Illite and Syntheses 9, 10, 14 and 15.

<table>
<thead>
<tr>
<th></th>
<th>Illite</th>
<th>9, 1Md</th>
<th>10, 1Md</th>
<th>15,3T(d?)+1Md</th>
<th>14, 1M</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₀₀₂ Å</td>
<td>α</td>
<td>d₀₀₁ Å</td>
<td>α</td>
<td>d₀₀₁ Å</td>
<td>α</td>
</tr>
<tr>
<td>Original</td>
<td>10.04 -0.22&lt;sup&gt;+&lt;/sup&gt;</td>
<td>10.11 -0.34</td>
<td>10.11 -0.30</td>
<td>10.19 -0.37</td>
<td>10.12 -0.05</td>
</tr>
<tr>
<td>120°C</td>
<td></td>
<td>10.11 -0.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>350°C</td>
<td>10.06 -0.14</td>
<td></td>
<td></td>
<td>10.09 -0.05</td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td>10.02 -0.13</td>
<td>10.11 -0.09</td>
<td>10.11 -0.07</td>
<td>10.00 -0.05</td>
<td>10.11 -0.10</td>
</tr>
</tbody>
</table>

<sup>+</sup> -ve sign indicates skew to low angle region. α = 0 in a symmetrical peak.
It will be noticed that the 1Md synthetics, 9 and 10, exhibited partial collapse only: $a$ decreased, but without measurable change in $d_{001}$. Water of hydration was therefore removed. If rehydration was successfully avoided, and this can involve extreme precautions in cases of high layer-charge, then it might be suggested that interlayer components of considerable size remain. Such could be $\text{Al(OH)}_2^+$ complexes of the type postulated by Jackson (1963) or inferred to be present in certain "dioctahedral vermiculites" by Hathaway (1955). The latter found that the interlayer material of the originally 14Å layers did not fully dehydroxylate with contraction to 10Å at 500°C. The Marblehead behaved similarly to 9 and 10. Synthesis 15 shows major collapse. The greater part of the peak displacement was apparently due to water of hydration, but $a = -0.05$ evidences a real reaminging asymmetry, also evident in 003. Synthesis 14 shows no significant change of spacing. This was measured more accurately in earlier runs. The increase in asymmetry results from decrease in peak height without much change in the originally slightly skewed basal region.

Partial reversibility of the dehydration of synthesis 15 after treatment at 350°C was shown by heating in an atmosphere of 100% humidity at 60°C for 30 minutes. A spacing of only 10.14Å was regained, however, and an asymmetry of -0.13°. This is sufficient nevertheless to conclusively demonstrate the role of water in peak displacement and asymmetry.

In no case did spontaneous rehydration, if such occurred, obscure the effects of heating, though it conceivably decreased them. The objectives of the tests, a comparison, was met, and similarity demon-
(3) Behavior Upon Ethylene Glycol Solvation

Treatment of the synthetic 1Md micas with ethylene glycol vapour at 60°C yielded the same result in several tested cases. The result is shown in Figure 11, A, for synthesis 21. A reversal of asymmetry, from the low angle flank to the high angle flank takes place, and a significant peak shift. The following are mean values of five replications of the diffractometer measurements: Prior to treatment, \( d_{001} = 10.09^\circ, 8.76 \pm 0.016^\circ 2\theta; \alpha = -0.06 \). Post-treatment, \( d_{001} = 10.06^\circ, 8.79 \pm 0.016, \alpha = +0.08 \).

The observed differences are explicable in the following manner: the original "001" represents 001 (\( 10^\circ \)/001\( x^\circ \)), a composite maximum, where \( x \) equals the spacing of the expanded layers. This might be suggested to be approximately 12.4\( ^\circ \), representative of sodium or potassium montmorillonite in low charge layers for the reason given below. Furthermore, on the evidence of the heat treatments, it is probable that chloritic (Al or Mg) hydroxyl complexes may also be present. Thus \( x \) would include an approximately 14\( ^\circ \) component. It is known however that such complexes do not glycolate (Hathaway, 1955; Slaughter and Milne, 1960). Glycol complexes, interlayered in montmorillonoids, exhibit a 17\( ^\circ \) spacing with a wide range of originally hydrated interlayer cations and may do so also with potassium. As a 17\( ^\circ \) spacing could be developed upon extraction of potassium with sodium citrate, an explanation on the basis of expansion of a small percentage of the layers to 17\( ^\circ \) is proposed. Thus the potentially observable maxima are 001 (10\( ^\circ \)/001(17\( ^\circ \)) and 00l (10\( ^\circ \)/002(8.5\( ^\circ \)), the first at a
higher, the second at a lower spacing than the original. Theory indicates, for the closely similar case 10/17.5°, (MacEwan, Ruiz Amil, and Brown, 1961) that the greater spacing maximum is suppressed until the percentage of expanded layers exceeds approximately 30%, and that the lesser spacing, the observed maximum, is not displaced unless more than some 10% of expanded layers occur. It is concluded that a similarly low percentage of expandable layers is present in synthesis 21. The development of a high-angle-side skew is attributed to the diffraction effects of the second order reflection of the expanded layers.

Marblehead illite, 0.3 to 3.0μ, gave the following results for five replications of each state: untreated, d₀₀₂ 10.03 8° 6, 8.84 ± 0.01 2θ; a - 0.22° 2θ; treated, d₀₀₂ 10.00 8° 1, 8.84 ± 0.02° 2θ; a - 0.16. A test of the significance of the difference of two means, based on the ranges of the intermediate means (Bauer, 1960) revealed that a significantly decreased at a 95% confidence level. Thus the synthetic materials behave as does a reference sample of illite, though differing in degree of response. It is possible that the illite contains a greater number of non-glycolable, expanded layers than do the synthetics. Such would be the property of any layers bearing aluminum hydroxide complexes.

It is to be noted that peak displacements depend not upon the quantity of expanded layers alone, but upon their arrangement. For example, random intercalation of 50% 14.0° layers in a 10° mineral results in a doublet, 10.3° and 13.2°. Reduction of the percentage of 14° layers would tend to suppress the 13.2° subsidiary maximum and decrease the displacement of the originally 10.3° subsidiary maximum.
It is expectable that an asymmetrical peak close to 10Å could develop. Such segregation could be operative in illites. Harrison and Murray (1959) discuss asymmetries identical to those described herein for untreated materials and conclude: "This type of mixed-layer structure has been termed segregated mixed-layer to distinguish it from regular or random mixed-layer structures."

(4) Layer Charge

Treatment of Marblehead illite with molar sodium citrate solution for four days at 70°C, followed by saturation with Mg++ ion and ethylene glycol treatment, produced no detectable change. This is possibly attributable to high layer charge. Both syntheses 9 and 18, treated with molar sodium citrate for 4 hours at 100°C, showed expansion to 17.4Å and 17.0Å respectively upon glycol treatment. X-ray patterns for synthesis 18 are shown in Figure 4. Glycerol treatment of 18 yielded a 17.7Å spacing. All of these features are compatible with a low layer charge, less than ~0.55 e⁻ per unit of 0.10(OH)₂. Anomalously, however, Cook and Rich (1963) obtained an 18.4Å "montmorillonitic" spacing after removal of 4/5ths of the potassium of a muscovite and treatment with Mg++ and glycerol. The layer charge of 187 meq./100g is that of a high vermiculite, but such minerals remain at 14.3Å after Mg++ plus glycerol treatment. On the other hand, after potassium removal from illites of layer charge 153 and 186 meq./100g, they observed typically vermiculitic behaviour.

As stated in a previous section, the evidence is conflicting. It would appear that the synthetic materials could be equal to, or lower than certain natural illites in layer charge, or be of heter-
ogeneous charge distribution.

(5) b-Axis Disorder

Evidence of b-axis disorder in the 1Md micas is presented above. The writer is not aware of a demonstration of the phenomenon in a 2M mica. There is at first some difficulty in visualizing how it could arise. 2M muscovite in nature crystallizes under conditions which appear to preclude disorder in it as well as in the 1M form. For example, metamorphic rocks bear 1M, 2M and 3T polytypes, and igneous muscovites are generally 2M. Synthetic 2M muscovite is invariably ordered. It is suggested that weathering, by developing hydrated interlayers, initiates disordering which could be furthered mechanically during, for example, burial. The elimination of expanded layers during diagenesis is remarkably slow.

Table 19 (page ), presents observed spacings and intensities for Marble head illite. Careful examination at a 1/4° 2θ scanning rate revealed no intensity in the regions of occurrence of the principal diagnostic peaks of 1M micas, 112 and 112. The analogous maxima of 2M are 114 and 114, also unique to their polytype. If b axis disorder is present, these and other hkl maxima where k ≠ 0 or 3 would be expected to be suppressed.

To test the theory, randomly oriented powder mounts of 0.3 to 3μ e.s.d. Marblehead illite and < 325 mesh muscovite diffraction patterns were prepared. The latter material was prepared from a coarsely crystalline pegmatite muscovite. In Table 18 observed hkl intensities are listed and indexes assigned by reference to the data of Brown (1961), and of Yoder and Eugster (1955). The Marblehead
data is normalized by multiplication by the peak height ratio \([131, 20\overline{2} \text{ (muscovite)}/131, 20\overline{2} \text{ (illite)}]\), equal to 0.74(3).

Table 18. Suppressions of Diffraction Maxima hkl, \(k \neq 3n\), in Marblehead Illite Relative to a 2M Muscovite.

<table>
<thead>
<tr>
<th>Illite</th>
<th>Muscovite</th>
<th>Indexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_{\text{obs}})</td>
<td>(I'_{\text{stand.}})</td>
<td>(I_{\text{obs.}})</td>
</tr>
<tr>
<td>49</td>
<td>36.4</td>
<td>25</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>2.2</td>
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</tr>
<tr>
<td>2</td>
<td>1.5</td>
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<td>14</td>
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</tr>
<tr>
<td>11</td>
<td>8.2</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>13</td>
</tr>
<tr>
<td>30</td>
<td>22.3</td>
<td>13</td>
</tr>
<tr>
<td>35</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>3.7</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>8.2</td>
<td>5</td>
</tr>
</tbody>
</table>

The list is terminated by the "multiplicity of index" problem. Discrepancies in index become significant in the higher angle region.
Of the maxima listed, suppression would not be expected in only the last four. The group contains only one anomaly. Of the remainder, suppression would be expected in all. This is found except in the case of 111. Agreement with the expected result is good, based on the postulate of b-axis disorder in the illite. The marked anomaly in the case of 111 concerns the intensity in the region 19.92°2θ. In this region, 020 intensity is indexed by Levinson (1955) from a single-crystal Weissenberg photograph of a 2M hydrous mica. It is worthy of note that the 020 intensity is not markedly reduced by b-axis disorder in 1Md forms, nor is 022 reduced by it in disordered kaolinites. By similarity of structure these peaks occur at 19.78°2θ and 19.80°2θ respectively.

It may be argued that the foregoing is an inadequate demonstration for the reason that diffracted intensity from other layer-silicates might spuriously increase the peak height in the 35°2θ region of the illite, where the peak 131, 202, used for comparison, occurs.

In this respect it is noted that a trace of chlorite is present in the sample. If a 1Md mica were present, so disordered that its maxima 112 and 115 were absent, it would contribute to the 35°2θ maximum and remain undetectable. Its unsuppressed peaks are almost coincident with certain of those of the 2M polytype.

It is therefore necessary, if possible, to demonstrate disorder in the 2M by reference to maxima which are unique to that structure and not interfered with by possible contaminants, one of the type h3l and one khl, k ≠ 3. The best approximation to this condition is the peak at 2.13°, indexed 135 by Brown, and 135, 043 by Yoder, and the
peak at 3.74 Å given as 023 by both. The possible interferences from other minerals are negligible, excepting a minor quartz peak at 2.128 Å. Its presence would be determinable and its effect correctable. It is absent in the present instance.

The peak height ratio I(135, 043)/I (023) in Yoder and Eugster’s published tabulation for a randomly oriented 2M muscovite is 0.71. In the muscovite employed here it is 0.77. Disorder, by decreasing I(023) preferentially, will increase the value. In the illite it was determined as 2.0. It thus appears that, on this basis also, b-axis disorder may be postulated for the 2M illite. It could therefore be designated 2Md. This is proposed for the Marblehead illite. Time did not permit evaluation of other natural illites exhibiting uniquely 2M diffraction maxima but such an investigation should be undertaken. However, the Marblehead has been employed as a typical reference standard at the University of Illinois.
(f) Relationship Between Parameters Which Estimate Degree of Disorder in Synthetic 1Md Micas.

It is attempted to demonstrate that several of the characteristic features of the 1Md micas, which resemble closely a representative 2M disordered illite, can be related to a single phenomenon, the introduction of hydrated, expanded interlayers into an otherwise potassium-bearing 10Å mica.

The correlations between three parameters are shown in Figures 12 and 13. The parameters are (1), α, the asymmetry of 001, which is towards the low angle region for the untreated state; (2) ∆21 the separation in degrees 2θ of 001 and 002; (3) the ratio 131/112 for 1Md micas, which estimates the degree of b-axis disorder.

A relationship between (1) and (2) is expectable. There need be none between either of these and (3), as, for example, a sharp symmetrical 001 peak may be observed in certain hydrated halloysites which exhibit disorder (Sudo and Takahasi, 1956). As the presence of 3T mica increases 131 without contributing to 112, and also affects the intensity and form of 001 in an unknown manner when 1Md is present, syntheses bearing 3T mica are omitted from the figures.

Figures 12 and 13 are strongly suggestive of correlation between
Figure 12. Plot of 001 Asymmetry, $\alpha$, versus the Separation of Basal Diffraction Maxima for Synthetic Micas, $\Delta 2\theta$. 
Figure 13. Plot of 001 Asymmetry versus a Function of b-Axis Disorder.
all of the parameters. This leads to the conclusion that the locus of the b-axis disordering operation is largely the site of introduction of the units or groups of expanded interlayers. It does not preclude stacking faults as postulated by Smith and Yoder, but they are, at least, fewer.

(9) Initial Changes in \(1\text{Md Micas}\)

In Figure 10, *parts A1, A2, A3, D1 and D2 show diffraction patterns for \(1\text{Md syntheses 10, and 9, respectively, while still moist after removal from the platinum tube. Progressive migration of the exceptionally intense maximum at } 26.04^\circ \text{ 28, 3.42}\AA, \text{can be traced to } 26.4^\circ \text{ 28, 3.38}\AA \text{ in part A3. The change was brought about by drying for 15 minutes over CaCl}_2. \text{ Part D1 represents 10 minutes drying of synthesis 9; a doublet is already evident, } 26.62^\circ \text{ 28, 3.35}\AA, \text{and approximately } 26.08^\circ \text{ 28, 3.42}\AA. \text{ The larger spacing is eliminated after 30 minutes over CaCl}_2. \text{ Parts B and C were untreated, dried in the laboratory air; B, number 9, represents a 2 day stage, and C, synthesis 3 (1Md approaching 1M) a stage after several weeks. The dehydration is irreversible.}

The full pattern of synthesis 9 while partially originally hydrated is shown in Figure 8. This and Figure 10 demonstrate the relatively small displacement of 001 (to \(8.70^\circ \text{ 28, 10.16}\AA \text{ in the latter while moist}).

The observations are compatible with the explanation that a large hydrated interlayer spacing, with a high order reflection on the low angle side of 003, is unstable in dry air and spontaneously dehydrates allowing partial collapse of the structure. Such an impressive

* Figure 10, p. 154.
change would be expected to involve a major interlayer component, namely potassium. Comparative details are unknown to the writer, but published information states that potassium vermiculites formed in aqueous solution exhibit spontaneous collapse to 10.4Å upon air drying. Montmorillonites remain at 12.4Å.

If dehydration of potassium were the case, the anomaly exists of vermiculitic behaviour here, and montmorillonitic behaviour after potassium removal.
SECTION IV. SUGGESTIONS FOR FURTHER WORK

Further evaluations of $D/a^2$ might, with some advantage, be attempted in a system wherein, after synthesis, less change from "equilibrium" potassium concentration of the fluid was entailed in attempting to assess exchange. This might be possible if the mica were grown in dilute solution, this solution analyzed for potassium, then fully replaced by a solution of very high specific activity due to potassium (conceivably $^{42}$K) but of identical potassium concentration. With no significant activity in the solid phase initially, the uptake from the solution could be monitored. The rate constant would be a composite one if a mixed layered mica were employed, for potassium appears to enter the expanded interlayers also. Marginal collapse might occur, and the two rates prove almost equal. This would be of interest in relation to mixed-layer clay diagenesis. The growth of 1Md mica in 8 ml of dilute potassium solution was found feasible in synthesis 5.

Although probably the case, it would be of interest to demonstrate the reconstructive nature of the change 1M + 2M muscovite using a spiked 1M and external K. The change is relatively rapid at 700° C and 3k bars.

The level of potassium required to stabilize micas against rapid expansion by highly hydrated cations, e.g. Na+, Mg++, and Ca++, (important in connate fluids and much greater in concentration than potassium) would be of interest. As little as 10 ppm is suggested by Cook and Rich (1963). The values no doubt depend upon many
variables.

If any of the numerous, small-scale, "reaction rim" phenomena common in many types of rock could be reproduced in the laboratory, and boundary migration rate constants determined, some interesting studies in "geochronometry" could be performed. This applies to weathering of dense rocks and single crystals also. As far as such rates depend upon diffusion in a solid layer, a temperature dependence similar to that for diffusion could be expected, i.e.

\[ k \approx \exp(-Q/RT) \].
## APPENDIX 1

### Table of Physical & Chemical Constants

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avogadro's number</td>
<td>$N$</td>
<td>$(6.02257 \pm 0.00009) \times 10^{23}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(g \text{ mole})^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>Number of seconds per year</td>
<td></td>
<td>$3.1558 \times 10^7$</td>
<td></td>
</tr>
<tr>
<td>Normal atmospheric pressure</td>
<td></td>
<td>760 mm Hg</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= 1.0325 \text{ bars}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= 14.696 \text{ pounds per sq. in.}$</td>
<td>(2)</td>
</tr>
<tr>
<td>Bar</td>
<td></td>
<td>$10 \text{ dynes per sq. cm.}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= 14.504 \text{ pounds per sq. in.}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$^{40}$K per atom of ordinary K</td>
<td>$f$</td>
<td>$1.18 \times 10^{-4}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Mass of $^{40}$K per g of ordinary K</td>
<td></td>
<td>$1.21 \times 10^{-4}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Specific activity of K for $\beta^-$ decay $\gamma$ emission</td>
<td></td>
<td>$28.3 \beta^-$ decays sec$^{-1}$ K$^{-1}$ + 0.6 (1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3.40 \gamma$-emissions sec$^{-1}$ K$^{-1}$ + 0.01(1)</td>
<td></td>
</tr>
<tr>
<td>Specific activity of $^{40}$K (relative to constants above)</td>
<td></td>
<td>$14.03 \beta^-$ decays $^{-1}$ $^{-1}$ $^{-1}$ $^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\mu g \text{ min}$</td>
<td></td>
</tr>
<tr>
<td>$\beta^-$ decay constant, $^{40}$K (data above)</td>
<td>$\lambda_{\beta}$</td>
<td>$4.914 \times 10^{-10}$ yr$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Gas Constant, R</td>
<td></td>
<td>cal(g mole)$^{-1}$ deg$^{-1}$</td>
<td>(2)</td>
</tr>
</tbody>
</table>
APPENDIX 1 (continued)

Sources


APPENDIX 2

The Radioactive Decay of \( ^{40}\text{K} \)

The significance in this work of the value of the specific activity of \( ^{40}\text{K} \) lies in its use to estimate the activity of synthetic phases due to known additions of \( ^{40}\text{K} \)-enriched "spike," and to determine the counter efficiency, \( \varepsilon \) which relates the observed counting rate, \( N \), and the disintegration rate: \( \varepsilon = 100N/N_0\% \). The value of \( \varepsilon \), determined by duplicate runs of KCl, was 49.33%.

Natural potassium comprises the three nuclides \( ^{39}\text{K} \), \( ^{40}\text{K} \), and \( ^{41}\text{K} \), subscripts and superscripts representing atomic numbers and mass numbers respectively. Relative abundances, according to Smith (1964), and also Friedlander, Kennedy, and Miller (1965) are \( ^{39}\text{K} 93.10 \), \( ^{40}\text{K} 0.0118 \), and \( ^{41}\text{K} 6.88 \) in units of atoms per 100 atoms of ordinary potassium.

The decay scheme of the single radioactive nuclide of natural occurrence, \( ^{40}\text{K} \), is shown in figure 1. The principal modes of decay are negatron (\( \beta^- \)) emission and electron capture.

\[
\begin{align*}
\text{figure 1.} \\
	ext{Decay scheme of } ^{40}\text{K}.
\end{align*}
\]
The former yields electrons of maximum energy 1.32 MeV though generally much less due to energy-sharing with the simultaneously created antineutrino:
\[
\text{neutron} + \text{proton} + \beta^- + \bar{\nu}
\]

Electron capture (E.C.) describes the interaction of an electron of the K orbital of potassium with a proton resulting in the formation of a neutron which is retained by the nucleus and the emission of a neutrino. The daughter nuclide $^{40}_{18}\text{Ar}$ undergoes de-excitation by emission of a 1.46 MeV $\gamma$ radiation. Extremely rare positron ($\beta^+$) decay, by the process
\[
\text{proton} + \text{neutron} + \beta^+ + \nu
\]
competes with electron capture in the formation of $^{40}_{18}\text{Ar}$.

The decay of any radioactive nuclide is expressed by the equation
\[
dn/dt = -\lambda n,
\]
where $n$ represents the number of atoms present at time $t$ and $\lambda$ equals the fraction decaying per unit time. In the case of $^{40}_{18}\text{K}$ the several decay modes permit evaluation of several decay constants:
\[
\lambda_\beta = \text{decay constant for electron producing events}
\]
\[
\lambda_e = \text{decay constant for E.C. resulting in } \gamma \text{ emission}
\]
\[
\lambda_{^{40}_{18}\text{K}} = \lambda_{\text{total}} = \lambda_\beta + \lambda_e
\]
A survey of the literature concerning the determination of these constants is presented by Smith (1964). His conclusions are presented here. Prior to the development of modern $\beta$ and $\gamma$ counting techniques,
\( \lambda_e \) was as accurately determined by the methods of geochronology as by the former means. Smith, contributing to the symposium "The Phanerozoic Time Scale" notes the adoption by the symposium of \( \lambda_\beta = 4.72 \times 10^{-10} \text{ yr}^{-1} \) and the value \( f = (1.19 \pm 0.01) \times 10^{-4} \) atoms of \(^{40}\text{K}\) per atom of ordinary K (Nier, 1950). He points out however that recent, precise, experimental values differ. The specific \( \beta \) and \( \gamma \) activities of potassium are determined. The means of those with errors less than 4% are

\[
\frac{dn_\beta}{dt} = 28.3 \pm 0.6 \text{ \( \beta \) decays sec}^{-1} \text{ g}^{-1} \text{ K}
\]

and

\[
\frac{dn_\gamma}{dt} = 3.40 \pm 0.01 \text{ \( \gamma \) emissions sec}^{-1} \text{ g}^{-1} \text{ K}
\]

From these values are obtained

\[
\lambda_\beta = \left( \frac{dn_\beta}{dt} \right) \frac{A}{N_f}
\]

\[
\lambda_e = \left( \frac{dn_\gamma}{dt} \right) \frac{A}{N_f}
\]

where \( A \) equals the atomic weight of potassium and \( N \) equals Avogadros Number. Employing the mean of four recent determinations of \( f \), \( 1.18 \times 10^{-4} \) atoms \(^{40}\text{K}\), equivalent to \( 1.21 \times 10^{-4} \) g \(^{40}\text{K}\) g\(^{-1}\) ordinary K, and the constants of Appendix I,

\[
\lambda_\beta = 4.91 \times 10^{-10} \text{ yr}^{-1}
\]

and

\[
\lambda_{\text{total}} = (5.50 \pm 0.11) 10^{-10} \text{ yr}^{-1}
\]

also,

\[
t_{1/2} = (1.26 \pm 0.025) \times 10^9 \text{ yr}.
\]
APPENDIX 3

Beta Counting Data, Computations, Precision Indexes and Chi Square Tests.

(a) Counting Data

Detailed counting data is set forth in Table 20, pages 178 to 180.

(b) Computations

To indicate the mode of treatment of the data the following survey is presented.

In the hypothetical case of a counter having zero background, data can be accumulated in either of two fashions, as in case (a) or (b):

(a) The total source counts, \( Z \), in a period \( t \) can be recorded.

(b) Counts \( x_1, x_2, \ldots x_n \) accumulated in \( n \) contiguous and equal intervals which sum to the period \( t \) may be recorded.

In case (a) the result is reported as a rate of

\[ Z + \sqrt{Z} \text{ counts per interval } t \]  

where \( \sqrt{Z} = \sigma \) is the standard deviation (S.D.) of the single observation. The coefficient of variation is:

\[ w = \frac{100\sigma}{Z} = \frac{100}{\sqrt{Z}} \% \]  

In case (b), the mean, \( \bar{x} \), is determined:

\[ x_1 + x_2 + x_3 \ldots + x_n = \sum_{i=1}^{n} x_i = Z \]  

\[ \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \]
<table>
<thead>
<tr>
<th>Sample (Synthesis Number) and condition</th>
<th>Background Rate, B c.p.m.</th>
<th>(\frac{(s + b)t_s}{t_s}) c.p.m.</th>
<th>Observed Rate, S c.p.m.</th>
<th>Observed Rate 137 Cs c.p.m.</th>
<th>Rate Factor R</th>
<th>Weight Factor W</th>
<th>Standardized Rate S x R x W</th>
<th>Grand Means of Replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis 7, Original Condition</td>
<td>3.50 ± 0.59</td>
<td>30265</td>
<td>97.38 ±0.81</td>
<td>4278.391</td>
<td>1.0000</td>
<td>1.00</td>
<td>97.38 ±0.81</td>
<td>Set I, 98.26 ±0.47</td>
</tr>
<tr>
<td>Synthesis 7, Original Condition</td>
<td>3.20 ± 0.57</td>
<td>32506</td>
<td>98.38 ±0.80</td>
<td>1729.633</td>
<td>0.9997</td>
<td>1.00</td>
<td>98.35 ±0.80</td>
<td>(consistent)</td>
</tr>
<tr>
<td>Synthesis 7, Original Condition</td>
<td>3.20 ± 0.57</td>
<td>31867</td>
<td>99.60 ±0.81</td>
<td>4755.950</td>
<td>0.9942</td>
<td>1.00</td>
<td>99.02 ±0.81</td>
<td></td>
</tr>
<tr>
<td>After Exchange A1 7</td>
<td>1.72 ± 0.19</td>
<td>34909</td>
<td>95.25 ±0.78</td>
<td>90 Sr Standard</td>
<td>0.9999 Equiv.</td>
<td>1.00</td>
<td>95.24 ±0.78</td>
<td>Set II 94.50 ±0.37</td>
</tr>
<tr>
<td>After Exchange A1 7</td>
<td>1.82 ± 0.10</td>
<td>52579</td>
<td>69.96 ±0.31</td>
<td>&quot;</td>
<td>1.0006 Equiv.</td>
<td>1.347</td>
<td>94.29 ±0.42</td>
<td>(consistent)</td>
</tr>
<tr>
<td>After Exchange, A2 7</td>
<td>1.82 ± 0.10</td>
<td>21384</td>
<td>69.46 ±0.50</td>
<td>&quot;</td>
<td>1.0036 Equiv.</td>
<td>1.347</td>
<td>93.90 ±0.67</td>
<td></td>
</tr>
<tr>
<td>After Exchange B1 7</td>
<td>1.82 ± 0.10</td>
<td>2164</td>
<td>0.89 ±0.13</td>
<td>&quot;</td>
<td>0.9935 Equiv.</td>
<td>12.48</td>
<td>11.03 ±4.16</td>
<td></td>
</tr>
</tbody>
</table>

| Synthesis 10 Original Condition        | 2.13 ± 0.12              | 66546                           | 101.85 ±0.42            | 47172.30 c.p. 10 m.             | 0.9752        | 1.00           | 99.32 ±0.41                  | Set III 97.71 ±1.39       |
| Original 10 Condition                  | 2.13 ± 0.12              | 33709                           | 100.02 ±0.56            | 47578.0 c.p. 10 m.              | 0.9668        | 1.00           | 96.70 ±0.54                  | (inconsistent)            |
| Original 10 Condition                  | 2.13 ± 0.12              | 64882                           | 100.86 ±0.41            | 47778.0 c.p. 10 m.              | 0.9628        | 1.00           | 97.11 ±0.39                  |                           |
| Synthesis 10  | 2.13±0.12 | 31480  | 99.42±0.70 | 47527.06 | 0.9679 | 1.00 | 96.23±0.68 |
| After Exchange C1 |  | 310   |  | c.p.m. 10 m. |  |  |  |
| Synthesis 10  | 7.17±0.13 | 38597  | 97.15±0.48 | 46892.6  | 0.9810 | 1.00 | 95.30±0.47 |
| After Exchange C2 |  | 370   |  | c.p.m. 10 m. |  |  |  |
| 10          | 2.53±1.03 | 37221  | 90.52±1.17 | 45729.85 | 1.0059 | 1.05 (73.3mg) | 95.78±1.24 |
| After Exchange C3 |  | 400   |  | (consistent means) |  |  |  |
| 10          | 2.53±1.03 | 32812  | 79.50±1.15 | 46470.01 | 0.9899 | 1.20 (64.5mg) | 94.04±1.36 |
| After Exchange C3 |  | 400   |  | (consistent means) |  |  |  |
| 10          | 2.53±1.03 | 28703  | 69.23±1.14 | 46344.98 | 0.9926 | 1.37 (56.3mg) | 94.06±1.55 |
| After Exchange C3 |  | 400   |  | (consistent means) |  |  |  |
| 10          | 2.13±0.08 | 32646  | 63.16±0.37 | 46030.02 | 0.9933 | 1.50 (51.3mg) | 94.68±0.56 |
| After Exchange C4 |  | 500   |  | (consistent means) |  |  |  |
| Syn. 10, 10 Original Condition | 1.10±0.06 | 20764  | 44.04±0.32 | 46446.30 | 0.9904 | 1.00 (24.7mg) | 43.62±0.32 |
| 10, 10 After Exchange D1 | 1.23±0.06 | 14461  | 28.90±0.26 | 45822.70 | 1.0039 | 1.57 (15.8mg) | 45.49±0.40 |
| 10, 10 After Exchange D1 | 2.77±0.18 | 18604  | 40.50±0.36 | 45942.46 | 1.0013 | 1.00 (21.6mg) | 40.55±0.36 |
| 10 10 After Exchange D2 | 2.49±0.07 | 21560  | 39.78±0.30 | 46183.60 | 0.9960 | 1.11 (23.3mg) | 43.78±0.33 |
| Synthesis 20 original condition | 1.19±0.05 | 16689  | 40.54±0.33 | 4743593 | 0.9679 | 1.00 (52.9mg) | 39.31±0.32 |
| 20 After Exchange E1 | 2.05±0.06 | 14618  | 27.19±0.25 | 4618336 | 0.9960 | 1.41 (37.5mg) | 38.16±0.35 |

**Sample (Synthesis Number) and Condition**
- Background Rate, B c.p.m. = \( \frac{(s+b)ts}{t_s} \) c.p.m.
- Observed Rate, S c.p.m.
- Rate Factor R = \( \frac{Observed\ Rate}{1376s} \)
- Weight Factor W
- Standardized Rate S x R x W

**Grand Means of Replicates**
<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis 20</td>
<td>After Exchange F1</td>
<td>2.74±0.10</td>
<td>12856</td>
<td>430</td>
<td>27.20±0.28</td>
<td>45925.74</td>
<td>1.0016</td>
</tr>
<tr>
<td>Synthesis 20</td>
<td>After Exchange G1</td>
<td>3.14±0.15</td>
<td>4894</td>
<td>180</td>
<td>24.05±0.42</td>
<td>44801.11</td>
<td>1.0268</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>Reagent Grade</td>
<td>1.44±0.08</td>
<td>8307</td>
<td>300</td>
<td>26.25±0.32</td>
<td>46109.53</td>
<td>0.9976</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>Reagent Grade</td>
<td>1.44±0.08</td>
<td>8213</td>
<td>290</td>
<td>26.88±0.32</td>
<td>46131.79</td>
<td>0.9971</td>
</tr>
<tr>
<td>KCl Employed in</td>
<td>Exchange D1</td>
<td>1.44±0.08</td>
<td>13731</td>
<td>470</td>
<td>27.77±0.27</td>
<td>46233.85</td>
<td>0.9949</td>
</tr>
<tr>
<td>KCl Employed in</td>
<td>Exchange E1</td>
<td>2.13±0.08</td>
<td>20380</td>
<td>590</td>
<td>32.41±0.25</td>
<td>46124.62</td>
<td>0.9973</td>
</tr>
<tr>
<td>KCl Employed in</td>
<td>Exchange F1</td>
<td>2.44±0.09</td>
<td>14040</td>
<td>430</td>
<td>30.21±0.96</td>
<td>45925.74</td>
<td>1.0016</td>
</tr>
<tr>
<td>KCl Employed in</td>
<td>Exchange G1</td>
<td>2.69±0.14</td>
<td>6606</td>
<td>180</td>
<td>34.01±0.47</td>
<td>44801.11</td>
<td>1.0268</td>
</tr>
<tr>
<td>Syn. 10 (from Ex. C4)</td>
<td>After Exchange H1</td>
<td>1.92±0.08</td>
<td>16527</td>
<td>430</td>
<td>36.52±0.31</td>
<td>45925.74</td>
<td>1.0016</td>
</tr>
<tr>
<td>Synthesis 18</td>
<td>Original Condition</td>
<td>4.18±0.17</td>
<td>21.146</td>
<td>170</td>
<td>120.21±0.87</td>
<td>44801.11</td>
<td>1.0268</td>
</tr>
<tr>
<td>Synthesis 18</td>
<td>After Exchange I1</td>
<td>2.86±0.15</td>
<td>8327</td>
<td>240</td>
<td>31.83±0.41</td>
<td>43860.33</td>
<td>1.0488</td>
</tr>
<tr>
<td>Synthesis 18</td>
<td>After Exchange J1</td>
<td>2.67±0.14</td>
<td>8479</td>
<td>240</td>
<td>32.66±0.41</td>
<td>43860.33</td>
<td>1.0488</td>
</tr>
<tr>
<td>Synthesis 18</td>
<td>After Exchange K1</td>
<td>2.85±0.15</td>
<td>9071</td>
<td>220</td>
<td>38.38±0.46</td>
<td>43860.33</td>
<td>1.0488</td>
</tr>
</tbody>
</table>

Set V
26.50
±0.23 c.p.m.
(consistent means)
The required standard deviation of the mean, \( \sigma_{\bar{x}} \), can be found from that of a single observation, \( \sigma \):

\[
\sigma = \sqrt{m} = \sqrt{x}
\]

or, \( \sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}} = \frac{1}{n} \sqrt{\sum_{i=1}^{n} x_i} \) \hspace{1cm} (5)

where \( m \) equals the true mean of the population whence the \( x_i \) were drawn.

The result in case (b) is reported as:

\[
\bar{x} \pm \sigma_{\bar{x}} = \frac{1}{n} \left( \sum_{i=1}^{n} x_i \pm \sqrt{\sum_{i=1}^{n} x_i} \right)
\]

counts per interval \( \frac{t}{n} \) \hspace{1cm} (6)

The coefficient of variation, \( \frac{100\sigma_{\bar{x}}}{\bar{x}} \% \) proves to be, by employing equations (3) and (4), equal to \( \frac{100}{\sqrt{Z}} \) as in case (a). It is noteworthy that no one method rather than another can reduce the percentage uncertainty in truly random data.

In this work, samples were counted for repeated intervals of 10.00 minutes for three purposes:

1) To allow periodic counting of the \(^{137}\)Cs standard.
2) To provide alternation in sample counting.
3) To provide a means of examining the randomness of the data.

The counter, as any other, required a determination of the
background. The following measurements were made.

\[ t_b: \text{ interval in minutes employed in counting background} \]

\[ b.t_b: \text{ background counts recorded} \]

\[ t_s: \text{ interval in minutes employed in counting background plus sample} \]

\[ (s+b).t_s: \text{ sample + background counts recorded}. \]

The following required values were calculated:

\[ B: \text{ average background rate in counts per minute.} \]

\[ S: \text{ true average source rate in counts per minute.} \]

\[ B = \frac{1}{t_b} (b.t_b \pm \sqrt{b.t_b}), \text{ analogous to equation (6) above.} \]

\[ \therefore B = b + \sqrt{\frac{b}{t_b}} \text{ counts per minute (c.p.m.)} \] (7)

\[ S + B = \frac{1}{t_s} [(s + b)t_s + \sqrt{(s + b)t_s}] \text{ c.p.m.} \] (8)

\[ \therefore S + B = s + b + \sqrt{\frac{s}{t_s} + \frac{b}{t_s}} \text{ c.p.m.} \] (9)

Subtracting (7) from (9) with the appropriate propagation of error:

\[ S = s + \sqrt{\frac{s}{t_s} + \frac{b}{t_s} + \frac{b}{t_b}} \text{ c.p.m.} \] (10)

where \[ s = \frac{(s+b)t_s}{t_s} - b \text{ c.p.m.} \] (11)

Concerning equation (10) it is noted that fluctuations in backgrounds are allowed for twice, during the determination of \( bt_b \) and of \( (s+b)t_s \), as is necessary; furthermore, the S.D. obtained is that of a mean because of the analogy between the right hand sides of
equations (8) and (6). Although \((s+b)t_s\) is effectively a value of 
\(Z\) obtained as in equation (3), the factor \(1/\tau_\theta\) in equation (8) 
yields a mean rate accompanied by the S.D. of a mean. Similarly, 
expression (1) containing \(\sigma\), yields the right hand side of equation 
(6), containing \(\sigma_x\), upon substitution and multiplication by \(1/n\).
(c) Precision Indexes

(1) Examination of the Data of Replicate Activity Determinations: Consistent and Inconsistent Means.

Six sets of replicates of determinations of standardized counting rates were obtained. As each mean activity bears a standard deviation the question arises of how the grand means should be computed. It hinges upon the matter of whether the means of a set are drawn from a single population, and are thus to be termed consistent means, or whether they are drawn from several populations and are to be termed inconsistent means.

The test of consistency applied, described by Worthing and Geffner (1943) is one of the less arbitrary of several applicable. The statistic $hx$ is determined, where

$$hx = \frac{x_2 - x_1}{2(\sigma_{x_1}^2 + \sigma_{x_2}^2)}$$

The $\bar{x}_i$ are two means of a set, the $\sigma_{x_i}$ their S.D.'s of the mean; $x$ is a deviation in, and $h$ the modulus of precision of, a normal distribution. As $h$ equals $1/\sigma \cdot \sqrt{2}$, the test compares as a ratio the difference between two means and the standard deviation of that difference, $\sigma(\bar{x}_2 - \bar{x}_o)$.

$$\sigma(x_2 - x_1) = \sigma_{x_1}^2 + \sigma_{x_2}^2$$

The test may be conducted at the 99% confidence level. Thus if the
probability of occurrence of a difference as great as $\bar{x}_2 - \bar{x}_1$ on
the basis of the computed $\sigma_{(x_2 - x_1)}$ is found to be less than 0.01
the means may be declared inconsistent. This criterion corresponds
to a critical value of hx of 1.83, determined from a tabulation. If
the computed hx equals or exceeds 1.83 the means are declared inco-
sistent.

On this basis the value 99.32 ± 0.41 c.p.m. is inconsistent
with the others of set III, and the two values of set VI are inconsis-
tent. Thus twelve remaining means, or 80% of the total, bear standard
deviations which contain further significant information, as they
probably estimate the total error in the determination, not merely
that in counting. An error in standardization affects the count rate
much more than the standard deviation, and would tend to render means
inconsistent. The range of coefficients of variation of the twelve
means is from 0.40% to 1.65%. Values in this range are general for
the single determinations of standardized counting rates and may be
taken as an initial estimate of overall precision.

Information concerning the two categories of means is presented
in the following table.

<table>
<thead>
<tr>
<th>Consistent Means</th>
<th>Inconsistent Means</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drawn from a single population of means.</td>
<td>Drawn from more than one population.</td>
</tr>
<tr>
<td>In the case at hand consistency demonstrates that the error in counting is probably greater than that in the auxiliary procedures.</td>
<td>Suggestive of the converse.</td>
</tr>
</tbody>
</table>
### Consistent Means (continued)

<table>
<thead>
<tr>
<th>Grand Mean: $\bar{x}$</th>
<th>Grand Mean, designated $\bar{Y}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{x} = \frac{\sum_{i=1}^{n} (x_i / \sigma^2_{x_i})}{\frac{1}{n} \sum_{i=1}^{n} \frac{1}{\sigma^2_{x_i}}}$</td>
<td>$\bar{Y} = \frac{\sum_{i=1}^{n} Y_i}{n}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard deviation of grand mean: $\sigma_{\bar{x}}$</th>
<th>Sample standard deviation of grand mean: $s_{\bar{y}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\bar{x}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \frac{1}{\sigma^2_{x_i}}}$</td>
<td>$s_{\bar{y}} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \bar{y})^2}{n-1}}$</td>
</tr>
</tbody>
</table>

| $\sigma_{\bar{x}} < \sigma_{x_i}$ | $s_{\bar{y}} > \sigma_{x_i}$ |

The last tabulated observation is of significance in estimating coefficients $\omega_i$ for the methods relating to consistent means will yield the lowest values.

Replicate sets I, II, IV and V comprise consistent means. The best estimate of the grand means can only be made with the relevant statistics. The values 98.26, 94.50, 94.75, and 26.50 c.p.m. respectively, were so derived and are used in all quotations except for the estimation of overall precision.
(2) Overall Precision

The somewhat arbitrary procedure of computing means of the sets without regard to the standard deviations, that is, employing \( \bar{Y} \) and \( s_\bar{Y} \), is adopted. The reasons are three-fold:

1) The presence of inconsistent means necessitates it in two cases, sets III and VI.

2) Values of \( \omega \) from \( \sigma_\bar{X} / \bar{X} \) estimate the precision of the replication, and do not give information on the range of values in a set. To lend confidence to single determinations the latter is required.

3) \( \bar{\omega} \) from \( s_\bar{Y} / \bar{Y} \) is maximal.

For comparison with values of \( \bar{X} \), the values of \( \bar{Y} \) for sets I, II, IV and V are 98.25, 94.77, 94.63, and 26.50 respectively.

The overall coefficient of variation thus assessed is

\[
\bar{\omega} = \frac{\sum_{i=1}^{6} \omega_i}{6} = 2.29\%
\]

(3) Summary

The standard error of a single determination of a standardized counting rate probably requires no extension in better than 80% of the cases, as 12 out of 15 of the replicates appeared to be limited in error to that of counting alone. The values of \( \omega_{(counting)} \) for single determinations are less than 1.75%. If greater confidence is sought, precision limits may be extended using \( \bar{\omega} \).
Chi Square Test

Several tests of samples of data were carried out to demonstrate the absence of spurious counts or malfunctions which could lead to non-random data.

For i determinations of a counting rate,

\[ \chi^2 = \sum (\bar{N} - N_i)^2 / \bar{N} \]

where \( \bar{N} \) equals the mean counting rate. Employing the value of \( \chi^2 \) and the relevant degrees of freedom, \((i - 1)\), a probability \( P \) is determined from a tabulation. Values of \( P \) indicative of satisfactory operation are \( 0.1 < P < 0.9 \).

Two such tests yielded values of \( P \) equal to 0.35 and 0.6.

Frequent preparation of histograms of data also evidenced satisfactory approaches to Poisson distributions.
APPENDIX 4

Illite from Marblehead, Wisconsin

This material, which was employed as a standard for comparison of the properties of the synthetic micaceous phases, was kindly supplied by Dr. H. E. Gaudette. It was also fully described by him (Gaudette, 1965). The rock occurs as a friable gray mudstone forming large "pockets" in carbonates of the Silurian Burnt Bluff Group. The samples described by Gaudette are stated by him to be "exclusively mono-mineralic," although intercalations higher in the section bear "variable amounts of quartz and chlorite." The sample available to the writer was found to exhibit, in the ground, bulk sample, reflections in addition to those of muscovite, due to quartz, potassium feldspar, and chlorite.

A size fraction between 0.3 and 3μ e.s.d. was obtained by centrifugation, the only prior treatment having been dispersion in di-ionized water accompanied by ultrasonic vibration. A portion was dried at 60°C, lightly ground in a mortar and prepared as a randomly oriented powder mount for X-ray diffraction. Portions were also employed for studies of the effects of heating in air and of exposure to ethylene glycol vapour at 60°C.

The analysis quoted by Gaudette for the less than 2 micron fraction is given below.
<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2$</td>
<td>52.87</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>24.90</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>0.78</td>
</tr>
<tr>
<td>$\text{FeO}$</td>
<td>1.19</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>3.60</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>0.69</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>0.22</td>
</tr>
<tr>
<td>$\text{K}_2\text{O}$</td>
<td>7.98</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}^-$</td>
<td>2.56</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}^+$</td>
<td>6.73</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>1.02</td>
</tr>
</tbody>
</table>

X-ray diffraction data are given in Table 19 overleaf.
Table 20. X-ray Diffraction Data for 0.3 to 3 Micron Marblehead Illite and Synthetic 2M Muscovite (Yoder and Engster, 1955).

<table>
<thead>
<tr>
<th>Illite Marblehead</th>
<th>Synthetic 2M Muscovite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I</strong></td>
<td><strong>d(Å)</strong></td>
</tr>
<tr>
<td>24</td>
<td>10.13</td>
</tr>
<tr>
<td>25</td>
<td>10.04</td>
</tr>
<tr>
<td>19</td>
<td>4.98</td>
</tr>
<tr>
<td>27</td>
<td>4.48</td>
</tr>
<tr>
<td>6</td>
<td>4.36</td>
</tr>
<tr>
<td>12</td>
<td>3.973</td>
</tr>
<tr>
<td>14</td>
<td>4.109</td>
</tr>
<tr>
<td>100</td>
<td>3.889</td>
</tr>
<tr>
<td>32</td>
<td>3.735</td>
</tr>
<tr>
<td>3</td>
<td>3.87</td>
</tr>
<tr>
<td>5</td>
<td>3.49</td>
</tr>
<tr>
<td>29</td>
<td>3.33</td>
</tr>
<tr>
<td>32</td>
<td>3.32</td>
</tr>
<tr>
<td>7</td>
<td>3.20</td>
</tr>
<tr>
<td>4</td>
<td>2.98</td>
</tr>
<tr>
<td>4</td>
<td>2.86</td>
</tr>
<tr>
<td>22</td>
<td>2.82</td>
</tr>
<tr>
<td>16</td>
<td>2.58</td>
</tr>
<tr>
<td>45</td>
<td>2.580</td>
</tr>
<tr>
<td>21</td>
<td>2.57</td>
</tr>
<tr>
<td>3</td>
<td>2.50</td>
</tr>
<tr>
<td>3</td>
<td>2.47</td>
</tr>
<tr>
<td>12</td>
<td>2.446</td>
</tr>
<tr>
<td>7</td>
<td>2.39</td>
</tr>
<tr>
<td>9</td>
<td>2.38</td>
</tr>
<tr>
<td>4</td>
<td>2.25</td>
</tr>
<tr>
<td>5</td>
<td>2.236</td>
</tr>
<tr>
<td>7</td>
<td>2.184</td>
</tr>
<tr>
<td>10</td>
<td>2.149</td>
</tr>
<tr>
<td>6</td>
<td>2.14</td>
</tr>
<tr>
<td>6</td>
<td>2.051</td>
</tr>
<tr>
<td>12</td>
<td>1.99</td>
</tr>
<tr>
<td>14</td>
<td>1.975</td>
</tr>
<tr>
<td>6</td>
<td>1.736</td>
</tr>
<tr>
<td>6</td>
<td>1.699</td>
</tr>
<tr>
<td>12</td>
<td>1.670</td>
</tr>
<tr>
<td>5</td>
<td>1.65</td>
</tr>
<tr>
<td>7</td>
<td>1.602</td>
</tr>
<tr>
<td>9</td>
<td>1.501</td>
</tr>
</tbody>
</table>

A single chlorite peak, 004, the most intense, is present:

9 3.52
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ACKNOWLEDGEMENTS

The writer gratefully acknowledges financial support for this work by the Office of Naval Research and the Atomic Energy Commission through the good offices of Professor R. R. Shrock and Professor P. M. Hurley. Thanks are expressed to Professor J. W. Winchester for the provision of beta counting facilities. The writer is grateful for the advice and assistance of members of his thesis committee. He also asserts his appreciation of the patient endurance by his wife, Carol, of periods of grass-widowhood, and of her continued help and encouragement.
BIOGRAPHY

The writer was born in Romford, England, on March 16th, 1933. His primary education was completed there and in Windsor, Ontario. In 1949 he matriculated, while attending St. Bonaventure's Grammar School, London. Obtaining an Advanced Level School Certificate in 1952, he entered the University of Manchester. He obtained the degree of B.Sc. with Honours in Geology in 1955 and thereafter was employed by the Iraq Petroleum Company as a field and petroleum exploration geologist. In 1960 he came to the United States, entering the Massachusetts Institute of Technology in 1961.

The writer married in 1962. He and his wife, Carol, are the parents of three children, Kathryn, Gregory, and Rebecca.