ABSTRACT

COMPARISON OF LOW-TEMPERATURE WITH HIGH-TEMPERATURE DIFFUSION OF SODIUM IN ALBITE

By

Alan Bailey

These experiments were carried out in part, to test the defect model for diffusion at lower temperatures. More specifically, this study was designed to compare low-temperature with high-temperature diffusion to determine if these high-diffusivity paths are present in albite.

Diffusion coefficients and activation energies were determined for sodium in albite at low temperatures by means of exchange experiments and at high temperatures by means of the sectioning technique.

From the exchange experiments, the following apparent diffusion coefficients were determined:

25°C	$6.18 \times 10^{-24} \text{cm}^2/\text{sec}$
45	8.05
75	12.1

The activation energy for the process was less than 5000 cal/mole Na.

From the sectioning experiments, a lattice diffusion coefficient of about $8 \times 10^{-13} cm^2/sec$ was determined at 595°C. Using this and diffusion coefficients determined by other workers at higher temperatures, an activation energy of about 45 kcal/mole Na was determined for lattice diffusion. Using the lattice diffusion coefficient determined in the study and the activation energy for lattice diffusion, diffusion coefficients were calculated for lattice diffusion at the temperatures of the exchange experiments:

25°C	$6 \times 10^{-35} cm^2/sec$
45	8×10^{-33}
75	4×10^{-30}

From these results and the behavior of the sectioning curves, it was concluded that low-temperature release of Na is controlled by diffusion along high-diffusivity paths in the solid. Strained incipient cleavages, dislocations and twin planes are possible high-diffusivity paths existing in the solid. The results of the study indicate that these high-diffusivity paths become significant at lower temperatures and should be incorporated in models for alteration in weathering and low-rank metamorphism.

COMPARISON OF LOW-TEMPERATURE WITH HIGH-TEMPERATURE DIFFUSION OF SODIUM IN ALBITE

By

Alan Bailey

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Geology

1970

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to:

Dr. T. A. Vogel for assistance in all areas throughout the course of the study and constant examination of the problem.

Dr. M. M. Mortland for indispensable advice on the theoretical aspects of the study.

Dr. B. G. Ellis for advice on the theoretical aspects of the study and the use of counters in the Soil Science Department.

Dr. H. B. Stonehouse for advice and evaluation of the study.

Dr. C. Spooner for reading the manuscript and suggestions offered.

Dr. B. W. Wilkinson, Michigan State University Reactor Laboratory, for advice and use of facilities.

TABLE OF CONTENTS

Chapter Page

APPENDICES

Appendix

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Statement of the Problem

This study is designed to determine how feldspars alter in hydrous environments at temperatures of weathering and low-grade metamorphism. A rate law and an activation energy are determined for the exchange process in a simplified laboratory system consisting of an activated albite in a salt solution. Diffusion in feldspar is also examined at higher temperatures by the sectioning technique and diffusion coefficients and activation energies determined. The results of both parts of the study are combined to produce a model for alteration in weathering and metamorphism.

At high temperatures, work by Sippel and others indicates that diffusion in feldspars at these temperatures is primarily lattice diffusion. Work by physicists (Lidiard and Tharmlingham, 1959) and chemists (Harrison, 1961) indicate that, at lower temperatures, high-diffusivity paths may become important in ionic solids.

Models developed for natural weathering include the incongruent dissolution model of Correns, the model of

DeVore involving ionic groups and straight ionic exchange models such as that suggested by Fredrickson. These models do not incorporate the mechanical heterogeneity present in real crystals. In light of the defect model suggested by physicists and chemists for low-temperature diffusion, it might be said that this study is designed to examine the defect model as applied to feldspars.

Studies of the time and temperature dependence of geologic reactions are needed to explain nonequilibrium assemblages such as those found in weathering (feldspar→ kaolinite halloysite or sericite). More important is the determination of how an assemblage, equilibrium or non-equilibrium, formed. For an equilibrium assemblage, it is implied that a certain temperature must have been attained (perhaps greater than that predicted by equilibrium thermodynamics--see Fyfe and Verhoogen, 1958) and, probably that water or other volatiles must have been present to catalyze the reaction. Obviously, equilibrium thermodynamics will give us little information on catalysts. It may not predict correct temperatures and will say nothing about the time-dependence of the reaction or the manner in which it proceeds. A study of the exchange reactions involves diffusion and rates and activation energies are fundamental data needed for any understanding of diffusion in feldspars. Although only albite was studied, this work should serve as an indication of rates and energies needed for most feldspars.

Method of Solving

Much work has been done on equilibrium thermodynamics but little on the reactions involved in the systems studied. For this study the laboratory approach seemed most advisable because of the complexity of the heterogeneous reactions involved and lack of previous investigation. If any fundamental information is to be gained, simplified laboratory systems (such as feldspar-solution systems) must be examined first.

A large number of such systems, however, could be chosen for the study. The reaction chosen for this study was that between albite and 0.1N NaCl solution in the low-temperature range. This system was chosen because it represents a simplified analog of a situation found in nature. The low-temperature range was chosen because it is experimentally easier to work with and because time can be expected to play a more important part at low temperature. Further, this exchange system provides a convenient way of determining diffusion coefficients at low temperatures.

In addition to the feldspar-NaCl solution system, dry diffusion in albite was studied. This was done because earlier similar work by metallurgists (Gulbrasen, 1943), chemists (Delmon, 1961) and geochemists (Correns, 1961) indicated that solid diffusion might play a major role. There are, however, many ways in which material may move through solids. The sectioning technique provides a convenient way of studying diffusion at higher temperatures.

The exchange study involved exchange of non-radioactive sodium for radioactive sodium (Na^{24}) and, in addition, the sectioning experiments also made use of radioactive sodium Na^{22} so that self diffusion could be examined. The driving force in such monoelement reactions is thermal and is not complicated by chemical interaction. (Data from such systems is more fundamental and can be interpreted more definitely.)

Summary

In summary, an understanding of the way in which minerals alter requires information on the time and temperature variation of the reactions. The role of diffusion in such heterogeneous reactions necessitates a knowledge of solid diffusion and its variation with time and temperature. Any reaction, whether low- or high-temperature, must involve diffusion and, therefore, rates and activation energies play a major role. Because of the complexity of heterogeneous reactions and lack of data at this stage, simplified laboratory studies offer the best possibility for gaining fundamental information on such systems.

CHAPTER II

PREVIOUS WORK

Introduction

A large number of studies have been done on the alteration of feldspars in the laboratory. Quantitative studies of the time and temperature variation of the alteration process are much less numerous. Included below are laboratory studies on the alteration of feldspar and biotite which were directed toward time and temperature variations and the mechanism of alteration (e.g., kinetics). Biotite is also included because there have been a number of quantitative rate studies done with this mineral. The same general principles apply to both k-feldspar and biotite; however, there are basic differences in the specific mechanisms by which the two mineral groups alter.

Few studies on diffusion in feldspars have been published and summaries of all are included below. One study on diffusion in clays is also included, and finally, included are two summaries of articles which develop theoretical models for the alteration of feldspar. The summaries in each section are arranged chronologically.

Mineral Dissolution Studies

Feldspar Studies

Correns and Engelhardt (1938) studied the release of Al_2O_3, SiO_2 and K_2O from adularia in open systems. The grain size was generally less than 1 micron and both dialysis and ultrafiltration were used to separate the solid from the solution. Temperature and pH were varied. Using a variation of Fick's 1st law, a diffusion coefficient for K through the residual layer was determined which was of the order of magnitude of $10^{-19}cm^2/sec$.

Fredrickson and Cox (1954) examined the breakdown of albite crystals suspended in a bomb for 100 hours. Pure water and temperatures of 200 to 350°C were used. They found that the crystal broke into small fragments and gel and zeolites were formed. The mechanism suggested is a weakening and expansion of the structure followed by breakdown to fragments, ions and gel. This study represents an extreme in the studies given here in the sense that there was complete breakdown of the mineral.

Nash and Marshall (1956) studied the surface chemistry of a K-feldspar and plagioclases in closed systems. They found that the surface properties varied with the mineral. They say that this is incompatible with theories that postulate the formation of a completely amorphous product layer. The release of Na from albite by HCl was studied as a function of time and an initially rapid release of Na determined was followed by a decreasing rate of release. The time span was about 80 hours but only 3 points were used for each curve. Another interesting result of Nash and Marshall's study, which will be given here for later use, is a set of curves giving the Na released from albite as a function of the concentration of various salts. Above a concentration of about .01 meq/ml the amount of Na released was fairly independent of the salt concentration.

Correns (1961) summarizes the work done in his laboratory on the experimental weathering of silicates. In general, open systems were used. The effects of variation in flow-rate, pH and temperature are discussed and some consideration is given to the composition of the solution used to alter the minerals. The general process arrived at is as follows: metals are first released preferentially from the mineral leaving an amorphous layer of Al_2O_3 and SiO_2 which also dissolves, but at a slower rate. The further removal of metals is hindered by this residual layer more and more as it increases in thickness. Eventually, a state is arrived at in which the Al_2O_3-SiO2 removal rate becomes fixed relative to the rate of release of metals. The residual layer then maintains a constant thickness. In addition to the above, Correns also compares his work (dilute solutions, 20°C) with that of Morey and Chen (100-200°C, more concentrated solutions) and concludes that more extreme conditions and closed systems result in the formation of pseudomorphs rather than only dissolution. He also argues against weathering by exchange of alkalis by hydrogen or the hydronium ion and postulates that the aluminum carries the residual charge. Part of the evidence cited for this is the migration of particles of solid in electrodialysis. It is argued that exchange does not really take place since the framework is decomposed in the process.

Correns (1962) studied the release of materials from adularia in a dialysis apparatus with a still attached to provide a continuous supply of distilled water. Release of material from albite powder was also studied. Results are similar to those obtained in the above studies by Correns and co-workers.

Wollast (1965) studied the release of Si and Al from orthoclase over periods of 150-300 hours under varying pH. The release of Al was also studied over shorter periods of time. The author reaches the conclusion that, initially, release of Si and Al is consistent with diffusion from an altered layer. In a closed system, the Al reaches the equilibrium value for $Al(OH)_3$ under the given conditions. The Si is then said to reach a value which is determined by diffusion into solution and reaction with $Al(OH)_3$ to form a dehydrated Al-silicate. No work was done with the release of K or Na. Presumably, the work was done at room temperature.

Manus (1968) studied the long-term (300 days) release of constituents from 200-300 mesh perthitic feldspars in columns at 40°C. Release of alkalis was retarded by a residual layer. Phyllosilicates were identified in the products by x-ray diffraction.

Parham (1969) leached potassium feldspars and plagioclase in an apparatus that recycled the water. The study was done at 78°C over a period of about 140 days. By means of the electron microscope he observed material with the morphology of halloysite forming on the potassium feldspar and possible plates of boehmite on the plagioclase. The distribution of the product seemed to be controlled by crystallographic features.

Biotite Studies

Mortland (1958) studied the release of K from biotite in the presence of NaCl solutions. Work was done using both open and closed systems and rates examined as a function of a leaching rate, concentration of NaCl, temperature and time. It is concluded that the release rate is essentially independent of the amount of K left in the biotite for a large percentage of the removal because the rate depended on the concentration of K at reactive sites. The concentration at reactive sites is maintained at a constant level over a large part of the removal.

Mortland and Ellis (1959) studied the release of fixed K from biotite that had been artificially weathered to various degrees using 0.1N NaCl and then treated with KCl to reintroduce the K. The rate of release of K was found to be dependent on the amount of weathering. Loss of charge, resulting in a possible change of diffusion geometry, is suggested as the cause for this dependence.

Ellis and Mortland (1959) studied the release of fixed K from vermiculite using 0.1N NaCl in an open system. They found the process to be controlled by film diffusion with an activation energy of 3550 cal/mole.

Mortland and Lawton (1961) studied the relationship between K release from biotite using 0.1N NaCl and the size of the grains. Initially, the small particles lost a larger percentage of their K. After 50% of the K was removed, however, the larger particles lost as much as the fine. The Fe^2/Fe^3 ratios varied with the size and the alteration.

Diffusion Studies

Rosenquist (1949) measured diffusion coefficients for Pb and Ra in albite and microperthite. The tracer method was used with a thin layer of radioactive material in the form of a glass being deposited on the surfaces of several fragments. The samples were held at a fixed temperature for a measured length of time. The glass was then removed with a chisel and the activity of the surface measured. Activation energies and diffusion coefficients were determined for three directions in the albite for Ra and one direction for Pb. For Ra at 823°C the following results are given:

$$\perp(001),\ D = 2.53 \times 10^{-10} \mathrm{cm}^2/\mathrm{sec}$$

$$\perp(010),\ D = 1.33$$

$$\neq[100],\ D = 6.35$$

Activation energies are 24.3, 24.0 and 29.2 kcal/mole, respectively. For Pb at 873°C and $\perp(001)$, $D = 4.68 \times 10^{-11}$ $\mathrm{cm}^2/\mathrm{sec}$ and the activation energy was found to be 43.2 kcal/mole. From the data for Ra, it can be seen that, while some anisotropy is indicated, it is within an order of magnitude.

Jensen (1952) measured diffusion coefficients of $10^{-12}\mathrm{cm}^2/\mathrm{sec}$ and $10^{-11}\mathrm{cm}^2/\mathrm{sec}$ at 550°C for Na^{22} in microcline perthite. The thin-layer method was used with a slip coating of Na_2CO_3 with Na^{22} used as the initial layer. No direction is specified and results are complicated to some extent by the perthitic nature of the material used.

Sippel (1963) measured diffusion coefficients and activation energies for the self-diffusion of Na^{22} in a number of Na-bearing minerals. Again, the thin-layer was used. In this case, however, the thin-layer was produced by deuteron bombardment and was about 20μ thick. The material was annealed for 15-40 hours at fairly high temperatures and then sectioned by grinding off layers with silicon carbide paper. Most of these sectioning plots of concentration vs x^2 displayed curvature. Sippel attributes this curvature to a combination of diffusion along internal surface and lattice diffusion. From previous work, Sippel (1959), using an extremely high resolution proton scattering technique, concluded that the initial slope of the sectioning plots gives an estimate of the lattice diffusion coefficient even though the plots may show curvature. This assumption was tested by measuring the initial slope of the c vs x^2 plot for polycrystalline NaCl and fairly good agreement was found with that determined for single crystals. Using these methods, Sippel obtained diffusion coefficients of $8.0 \times 10^{-11} cm^2/sec$ at 850°C and $2.8 \times 10^{-10} cm^2/sec$ at 940°C for polycrystalline samples of albite. The last value was determined above an inversion point.

Jensen (1964) summarizes work done by metallurgists and physicists in a discussion of the role of diffusion in geologic situations and the factors affecting it. The effects of structural transformations with temperature, chemical potential and pressure are emphasized. He also considers the theoretical derivation of the diffusion coefficient from an atomic model and mechanisms for diffusion. He arrives at the conclusion that the primary mechanism for lattice diffusion in the silicates is interstitial network diffusion. In nature, material is said to move long distances by movement into crystals along flaws and breaks. Ultimately, however, the process is controlled by lattice diffusion.

Lai and Mortland (1968) studied the diffusion of Na and Cs in plugs of Na-vermiculite and plugs of K-vermiculite. The thin-layer initial condition and sectioning technique were used to determine diffusion coefficients. It was found that heterogeneous diffusion occurred in the Na-vermiculite (which contains internal surfaces). The heterogeneous nature of the diffusion is indicated by the curvature of the sectioning plots and the time variation of the diffusion coefficients. In the K-vermiculite, which contains little internal surface, homogeneous diffusion was observed. The results from the Na-vermiculite are compared with theoretical models for heterogeneous diffusion.

Studies in Which Theoretical Models Are Derived

Fredrickson (1951) derives a model for the weathering of albite in which a layer of crystalline water is said to form on the surface of the feldspar. This is followed by interdiffusion of H and Na resulting in the breakdown of the mineral. The formation of structured water adsorbed to the surface has been questioned by a number of workers.

DeVore (1957) considers the surface crystallography of the feldspars and arrives at a theoretical alteration scheme in which chains of tetrahedra are released from the (100) and (010) surfaces. These chains then polymerize to sheets which are used to construct the various phyllosilicates.

Summary

The essential features of these studies described above are listed in Table 1. In the portion of the table involving reactions between solid and liquid, the arrangement is approximately according to the amount of disruption produced in the mineral. In the work of Fredrickson and Cox the crystals were partially destroyed and new minerals with completely different structures produced. In the work of Nash and Marshall, only the surficial material was effected. With respect to this scale, the present study lies approximately between Parham's study and Mortland's study. The process is exchange as in the biotite studies. The exchange, however, is a different type because of the difference in crystal structure. With respect to the dry diffusion portion, the dry diffusion experiments carried out in this study are most similar to those of Sippel, but conducted at much lower temperatures where different mechanisms may become important.

TABLE 1.--Summary of previous work.

Investigator(s)	Type of Study	Mineral(s)	System	Physical State of Solid	Temperature	Method
Fredrickson and Cox (1954)	dissolution	albite	closed	single crystals	200-350°C	reaction with water
Correns and Engelhardt (1938)	dissolution	k-feldspar	open	finely ground powder	20°C	reaction with salt solutions
Correns (1961)	dissolution	representatives from most classes of silicates	open	finely ground powder	20-42°C	reaction with salt solutions
Correns (1962)	dissolution	adularia and albite	recycled	finely ground powder	20-40°C	reaction with re-cycled water
Wollast (1965)	dissolution	k-feldspar	closed	finely ground powder	20°C ?	reaction with buffered water
Manus (1968)	dissolution	perthitic k-feldspar and plagioclase with some k-feldspar	open	200-230 mesh material	40°C	reaction with water with adjusted pH
Parham (1969)	dissolution	k-feldspar and plagioclase	recycled	fragments with 1/2-3/4 in diameter	78°C	reaction with re-cycled water
Mortland (1958)	exchange	biotite	open and closed	< 60 mesh material	20-60°C	reaction with salt solutions
Mortland and Ellis (1959)	exchange	biotite and altered biotite	open	35-60 mesh material and variable size	5-40°C	reaction with salt solutions
Ellis and Mortland (1959)	exchange	k-vermiculite	open	< 60 mesh	25°C	reaction with salt solutions
Mortland and Lawton (1961)	exchange	biotite	open and closed	variable size $\left(\begin{array}{l}<250\mu \\ \longrightarrow <2\mu\end{array}\right)$	25°C ?	reaction with salt solutions
Nash and Marshall (1956)	surficial exchange	k-feldspar and full range of plagioclases	closed	finely ground powder	25°C	reaction with salt solutions
Rosenquist (1949)	dry diffusion	albite and microperthite	-----	selected crystal fragments	823 and 873°C	solid exchange technique
Jensen (1952)	dry diffusion	microcline perthite	-----	selected crystal fragments	550°C	sectioning technique
Sippel (1963)	dry diffusion	albite and a range of Na-bearing silicates	-----	(albite) polycrystalline aggregate	850 and 940°C	sectioning technique
Lai and Mortland (1968)	dry diffusion	Na-vermiculite and k-vermiculite	-----	pressed pellets of oriented platelets	25°C	sectioning technique

CHAPTER III

THEORY

General Statement

This section includes an outline of the theory for the two sets of experiments, a discussion of heterogeneous diffusion, consideration of a simplified atomic model for diffusion and a discussion of the major variables effecting the diffusion coefficient.

Theory for Exchange Experiments

Exchange between a solid (feldspar) and a liquid (salt solution) falls in the province of heterogeneous kinetics which are notoriously complex. One of the reasons for this complexity is that, generally, the actual reaction in the heterogeneous case can occur only at the surface of contact. The displacement of this surface governs the rate of reaction and the concept of order used so often in homogeneous kinetics has little use here. In the solid-liquid $\Longrightarrow$ solid-liquid reaction the extent of reaction is indicated by a quantity, α, which is the fraction of the original volume of the reacting solid destroyed. The fundamental rate of reaction is the rate of advance of the interface. Since the gross rate observed depends on the area of the reaction interface, the change in the geometry of the interface with time is important. An approximation used in this study is that the area of the "reaction interface" does not change significantly during the period of time over which the exchange is examined. The linear displacement of the interface may be governed by the rate of nucleation of new solid or it may be governed by the rate of transfer of matter to or from the interface. The exact case depends on how thoroughly the solid product covers the wolid reactant (Pannetier and Souchy, 1967). Initially, when little product is present, nucleation can be expected to govern in any reaction. In a situation such as that arranged in these exchange experiments (isotopic exchange), nucleation cannot be expected to play a strong limiting role since the nuclei are physically and chemically the same as the reactant and do not require any addition of energy or attainment of critical size to grow. The product, however, in this experiment effectively covers the reactant.

Harrison (in Bamford and Tipper, 1969, pp. 404-413) has obtained an equation suited for the present exchange studies by solving Fick's law for one-dimensional self-diffusion into our out of a semi-infinite solid into a well-stirred fluid phase. The initial conditional applied in the solution of Fick's second law is $C = C_o$, $x > 0$, $t = 0$. The boundary condition is $C = C_1$, $x = 0$, $t \geq 0$.

If the experimental conditions are such that diffusion is examined for a short period of time and the concentration of diffusing species is effectively constant, then the semi-infinite model can be used with the above boundary and initial conditions. The solution to Fick's 2nd law (Crank, 1956, pp. 18-19, 30; outline given in Appendix A) is:

$$\frac{(C - C_1)}{(C_o - C_1)} = \text{erf}\left[\frac{x}{2(Dt)^{\frac{1}{2}}}\right]$$

where C = concentration diffusing species at distance x, time t.

C_1 = concentration diffusing species in the solution.

C_o = concentration diffusing species in the solid.

The mass of material passing through a surface of unit area is given by the integral of the flux with respect to time. By Fick's 1st law, the flux at x = 0 is given by

$$J = -D\left(\frac{\partial C}{\partial x}\right)_{x = 0}$$

Letting the concentration in the solution in the initial portion of the reaction be small, $\left(\frac{\partial C}{\partial x}\right)_{x = 0}$ can be determined. The formula given for the total amount of material per unit surface area diffused into or out of the solid by time t is then given by

$$M_t = \int_o^t D\left(\frac{\partial C}{\partial x}\right)_{x = 0} dt = 2C_o\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

where M_t = total amount of material released per unit area.

C_o = initial concentration diffusing species in solid.

t = time.

If the diffusion control does not begin at time $t = 0$, then the integration should not be carried out over the whole interval. The indefinite integral gives

$$M_t = 2\,\frac{C_o\sqrt{D}\sqrt{t}}{\sqrt{\pi}} + C$$

For the total amount of material diffused out of a solid both sides are multiplied by the surface area of the solid.

$$M_{t,\text{total}} = 2\,\frac{C_o S\sqrt{D}\sqrt{t}}{\sqrt{\pi}} + C$$

If the volume into which the diffusion takes place is constant, then the above equation can be put in terms of concentration changes:

$$C_t = 2\,C_o\,\frac{S\sqrt{D}\sqrt{t}}{V\,\sqrt{\pi}} + C$$

This indicates that, if the concentration is plotted against the square root of time, then the slope will equal

$$2\,\frac{C_o S\sqrt{D}}{V\,\sqrt{\pi}}$$

Theory for the Sectioning Experiments

One method of determining for material independently of the above dissolution experiment is by means of the sectioning method. This method involves the solution of Fick's 2nd law, $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} D\left(\frac{\partial C}{\partial x}\right)$ (Shewmon, 1963, pp. 6-11), for certain conditions. These conditions are as follows: $|x| > 0$, $C \to 0$ as $t \to 0$, for $x = 0$, $C \to \infty$ as $t \to 0$. The mathematical steps in the solution and application of the boundary conditions are given in Appendix II of Wahl and Bonner (1951). Experimentally, these conditions can be realized by placing an extremely thin layer of the material to be diffused on a slab of the material in which diffusion is to take place. For these boundary conditions, the solution to Fick's 2nd law is given by

$$\frac{C}{C_o} = - \frac{1}{2\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}}$$

where C = concentration diffusing species at distance x after time t.

C_o = concentration at interface at time $t = 0$.

D = diffusion coefficient.

t = time.

x = distance into solid.

Taking the log of both sides and combining constants gives

$$\log C = \left(\frac{-0.1086}{Dt}\right) x^2 + \text{constant} .$$

This shows that for a plot of log C vs x^2 the slope will be $\frac{-.1086}{Dt}$, and t will therefore determine D from such a plot. The technique is particularly easy if one uses a radioactive tracer. Since the concentration of tracer is proportional to the activity, one can determine the diffusion coefficient by diffusing tracer into the solid and measuring the activity of layers after known amounts have been ground off the surface. Diffusion coefficients at several temperatures enable determination of activation energies.

In the method used in this study the concentration (activity) of a slice at depth x was not determined. Instead, the activity of the mineral fragment after a layer of known thickness was ground off was determined. The equation given above must be modified to suit this method. Essentially, the modification involves allowance for contribution to the measured activity by active atoms below the surface of the mineral (Wahl and Bonner, p. 74). Using the exponential absorption law, a layer dx thick and x below the surface will contribute $k\,dA = C\ e^{-\mu x}\,dx$ to the activity measured at the surface. k is the proportionality constant between the activity and concentration and μ is the linear absorption coefficient for γ-radiation in albite. Putting the original expression for concentration into this and integrating from the surface to infinite depth in the mineral gives

$$\text{I.}\quad A = \frac{A_o}{2\sqrt{\pi Dt}} \int_o^\infty e^{-\left(\frac{x^2}{4Dt} + \mu x\right)} dx$$

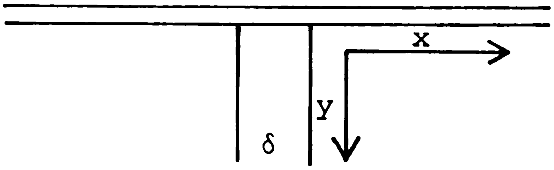
as the expression for the activity at the surface after diffusion has occurred. If a layer x units thick is ground off, the activity is given by

$$\text{II.}\quad A_x = \frac{A_o}{2\sqrt{\pi Dt}} \int_x^\infty e^{-\left(\frac{x^2}{4Dt} + \mu x\right)}$$

If we let $y = \frac{x}{2\sqrt{Dt}} + \mu\sqrt{Dt}$, I becomes $A = \frac{A_o}{\sqrt{\pi}} e^{\mu^2 Dt} \int_{y_o}^\infty e^{-y^2} dy$ $= \frac{A_o}{2} e^{\mu^2 Dt}(1 - \text{erf } y_o)$ [where $y_o = \frac{0}{2\sqrt{Dt}} + \mu\sqrt{Dt} = \mu\sqrt{Dt}$]. In the same fashion II becomes $A_x = \frac{A_o}{2} e^{\mu^2 Dt}(1 - \text{erf } y)$. Taking the ratio of I and II, $\frac{A_x}{A} = \frac{1 - \text{erf } y}{1 - \text{erf } y_o}$. Since $\frac{A_x}{A} \approx \frac{A_x}{A_o}$ well below the surface and since erf $y_o \approx 0$, $\text{erf} = 1 - \frac{A_x}{A_o}$. This says that y can be determined by measuring A_o and A_x. Going back to the defining equation for y $\left(y = \frac{x}{2\sqrt{Dt}} + \mu\sqrt{Dt}\right)$, it can be seen that the slope of a plot of y vs x equals $\frac{1}{2\sqrt{Dt}}$ with an intercept $\mu\sqrt{Dt}$. This holds for large x. At smaller x there will be a slight deviation.

Heterogeneous Diffusion

The thin-film solution to Fick's 2nd law given above assumes homogeneous diffusion. In practice, many solids may have high-diffusivity paths along grain boundaries, fractures and "free" surface. Metallurgists have found that diffusion under such conditions tend to occur by movement along the high-diffusivity paths followed by diffusion into the lattice from the paths. Fisher (1951) has developed a simplified model for such a process. Consider a high-diffusivity slab of thickness δ imbedded in a low-diffusivity medium (see diagram).



The z-dimension will be unity through this treatment. The high-diffusivity coefficient is designated by D_b (b for boundary) and the low-diffusivity coefficient by D_l (l for lattice). At time t equals 0 a thin layer of tracer is placed on a surface which is perpendicular to the high-diffusivity slab. The y-coordinate is taken as parallel the high-diffusivity slab and the x-coordinate as parallel to the surface. If one takes an element dy of the slab, how will the concentration change in it with time? The change in concentration in the volume element with time will be given by the flux of material entering the element (times the area through which it enters) minus the flux of material leaving the element (times the area through which it leaves) all divided by the volume of the element. In the form of an equation: change of concentration/unit time = 1/volume [area end of element (flux into element-- flux out other end) - area side of element (2 × flux out side of element)]. In symbols

$$\frac{\partial C}{\partial t} = \frac{1}{1 dy \delta}\left[1\delta\left[Jy - \left(Jy + \frac{\partial Jy}{\partial y}\,dy\right)\right] - 2dyJx\right]$$

$$= -\frac{\partial Jy}{\partial y} - \frac{2}{\delta}J_x.$$

J_x and J_y are given by Fick's 1st law as

$$J_x = -D_1\left(\frac{\partial C}{\partial x}\right) \qquad \text{and} \qquad J_y = -D_b\left(\frac{\partial C'}{\partial x}\right)$$

Putting these in the above equation we get

$$\text{III.} \quad \frac{\partial C'}{\partial t} = D_b\,\frac{\partial^2 C'}{\partial y^2} + \frac{2\,D_1}{\delta}\left(\frac{\partial C}{\partial x}\right)_{x = 0}$$

In the above C' is the concentration in the slab and C the concentration in the lattice. In Fisher's treatment, he assumes that the tracer in the lattice is primarily from the nearby grain boundary. Numerical analysis of the above equation indicated that the concentration in the slab rises at a quickly decreasing rate and spends most of its time at its current value. This leads to the approximate condition that $\frac{\partial C'}{\partial t} = 0$. Using this approximation one can simplify the problem to diffusion into slices at right angles to the high-diffusivity slab containing a constant concentration at a given y (C' not a function of time). Under these conditions the concentration in each slice is given by

$$\text{IV.} \quad C = M(y)\ \text{erfc}\left(\frac{x}{2\sqrt{D_1 t}}\right) \qquad \text{(Shewmon, p. 14)}$$

where M(y) = C'. The problem becomes one of finding M(y). Placing $\frac{\partial M(y)}{\partial t} = 0$ and $C = M(y)\ \text{erfc}\left(\frac{x}{2\sqrt{D_1 t}}\right)$ in III gives

$$0 = D_b \frac{\partial^2 M(y)}{\partial y^2} + \frac{2\ D_1}{\delta}\left[\frac{\partial M(y)\,\text{erfc}}{\partial x}\left(\frac{x}{2\sqrt{D_1 t}}\right)\right]_{x=0}$$

where

$$\left[\frac{\partial M(y)\,\text{erfc}}{\partial x}\left(\frac{x}{2\sqrt{D_1 t}}\right)\right]_{x\,=\,0} = \left[\frac{M(y)}{\sqrt{D_1 \pi t}}\left[e^{-\frac{x^2}{2\sqrt{D_1 t}}}\right]_x^{\infty}\right]_{x\,=\,0}$$

$$= -\frac{M(y)}{\sqrt{\pi D t}}$$

III becomes $0 = D_b \dfrac{\partial^2 M(y)}{\partial y^2} + \dfrac{2D_1 M(y)}{\delta\sqrt{\pi D_1 t}} = \dfrac{\partial^2 M(y)}{\partial y^2} + \dfrac{2D_1}{D_b \delta \sqrt{\pi D_1 t}} M(y)$

A solution to this differential equation is

$$M(y) = \exp\left(-\sqrt{\frac{2D_1}{D_b \delta \sqrt{\pi D_1 t}}}\, y\right)$$

Putting this expression for M(y) back into IV

$$C = \exp\left(-\sqrt{\frac{2D_1}{D_b \delta \sqrt{\pi D_1 t}}}\, y\right) \operatorname{erfc}\left(\frac{x}{2\ D_1 t}\right)$$

This gives the concentration as a function of x, y and t. In order to find the concentration of tracer, x, y and t must be determined. In order to find the quantity of tracer in an infinitely wide layer dy high and 1 unit thick, the above function is integrated over the volume giving

$$dQ(y,t) = \exp\left(-\sqrt{\frac{2D_1}{D_b \delta \sqrt{\pi D_1 t}}}\, y\right) dy \int_{-\infty}^{+\infty} \operatorname{erf}\left(\frac{x}{2\sqrt{D_1 t}}\right) dx$$

Taking the log of both sides gives

$$\text{V.} \quad \ln Q(y,t) = -\sqrt{\frac{2D_1}{D_b \delta \sqrt{\pi D_1 t}}}\, y + \text{constant}$$

This equation indicates that if the logarithm of the quantity of tracer is plotted against the diffusion coordinate, a straight line with slope $-\sqrt{\dfrac{2D_1}{D_b \delta \sqrt{\pi D_1 t}}}$

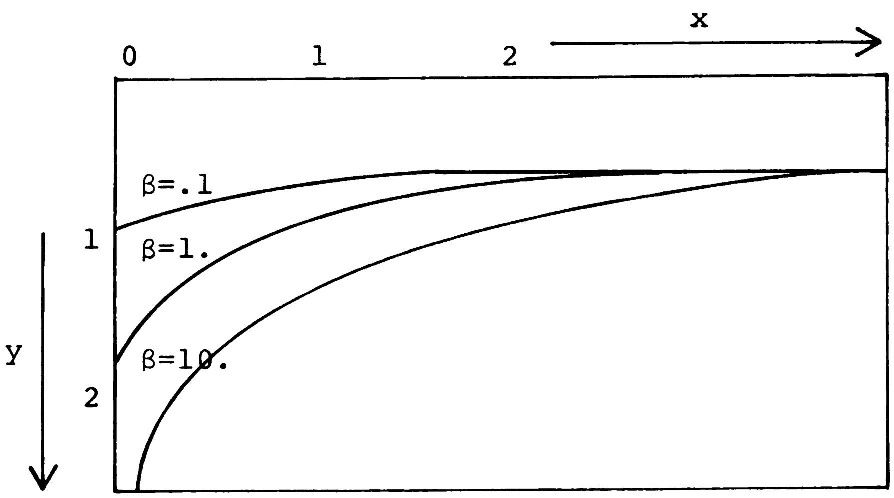
results when dealing with heterogeneous diffusion as described above. Among other conditions, this solution will only be good in regions where there is no contribution from the original surface. A more detailed treatment has been carried out by Whipple (1954) with less restrictive assumptions which allow for the contribution from the surface through the lattice to a point x,y. In addition to being more correct, it shows the time dependence of the overall distribution of the diffusing species better. Whipple's solution for the concentration as a function of x, y and t is

$$C = \operatorname{erfc} \eta + \frac{\eta}{\sqrt{\pi}} \int_{o}^{\pi} \exp\left(\frac{-\eta^2 \tau^2}{4}\right) \operatorname{erfc} \; \frac{1}{2}\left(\frac{1}{\tau^2 \beta} - \frac{1}{\beta \zeta}\right) d\tau$$

where

$$\zeta = \frac{x - \frac{1}{2\delta}}{\sqrt{D_1 t}} , \qquad \eta = \frac{y}{\sqrt{D_1 t}} , \qquad \beta = \left(\frac{D_b}{D_1} - 1\right) \frac{\delta}{2\sqrt{D_1 t}} .$$

It is difficult to get a physical feeling for this unwieldy solution. A better physical interpretation can be achieved by use of a method in which the shape of contours of the ratio c/c_o in a grain and in the vicinity of a grain boundary is examined. In particular, the tangent of the angle at which a particular contour intersects the grain boundary can be taken as a measure of the influence of the grain boundary. On the next page is a diagram taken from Whipple.



From this diagram one can see that, for smaller β (larger times), the concentration contours are less distorted.

The diffusion coefficients from sectioning and exchange experiments in heterogeneous substances can be confusing without clear definition of what is being measured. Harrison (1961) has subdivided heterogeneous diffusion into three types. Type A is for long times and corresponds to small thetas in Whipple's diagram. The effect is that of homogeneous diffusion, but the bulk diffusion coefficient will be a weighted average of D_l and D_b. If D_c is the macroscopic, measured coefficient, then the relationship between D_c and D_l and D_b is given by

$$D_c = fD_b + (1 - f)D_l$$

where f is the fraction of volume that can be assigned to high-diffusivity paths.

Type B corresponds to intermediate times and is best visualized by means of Whipple's contours.

Type C is for very short times in which the diffusion distance in the lattice is very small. Here the diffusion into the bulk solid is primarily along high-diffusivity paths. The macroscopic diffusion picture is similar to that in homogeneous diffusion with the exception that diffusion occurs only through a fraction, f, of the cross-sectional area. If diffusion coefficients are calculated by means of an exchange experiment using the relationship $M_t = 2C_o\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$ the D calculated will be an apparent coefficient (D_a). The relationship between D_a and D_b is given by $D_a = f^2D_b$.

Diffusion Coefficient

The above discussion has been concerned with macroscopic diffusion only. However, more complete understanding of the factors involved in diffusion, Fick's 1st law must be considered from an atomic aspect.

As an initial point, consider an interstitial atom vibrating with frequency ν in a crystal lattice (Girifalco, 1964, pp. 38-47). In order to move from one interstitial position to the next, the atom will have to squeeze between several neighboring atoms of the lattice. In doing so, it will have to overcome an energy barrier. The number of times an atom will do this is given by the probability an atom receives sufficient thermal energy (this depends on the height of the energy barrier and the temperature through the Boltzmann equation $e^{-E/RT}$ times the number of attempts it makes (the vibrational frequency). The jump frequency, then, is given by $\Gamma = \nu e^{-E/RT}$.

Such random jumps, however, will give no net movement of matter. For net movement a concentration gradient must be present. To see this, consider the movement of matter across a plane midway between two interstitial planes. The flux of matter from right to left will be given by $J_{R\rightarrow L} = \alpha\Gamma N(R)$ α = geometric factor, Γ = jump frequency, $N(R)$ = number. In the same way, the flux from left to right is given by $J_{L\rightarrow R} = \alpha\Gamma N(L)$. The net flux of matter across the plane will be given by $J = \alpha\Gamma[N(L) - N(R)]$. This indicates that, if there are no atoms on the left and a certain number on the right, then there will be a net movement from right to left until the concentration gradient is eliminated. This can be accomplished merely by thermal agitation without any chemical driving force. If λ is the spacing between the interstitial planes and we are concerned with the movement through 1cm^2, the above formula can be put in terms of concentrations

$$J = \alpha\Gamma\lambda[C(L) - C(R)]$$

$$\frac{\Delta C}{\lambda} = \frac{\partial C}{\partial x} \text{ on a megascopic scale}$$

$$J = \alpha\Gamma\lambda^2 \frac{\partial C}{\partial x}$$

By comparison with Fick's 1st law ($J = D \frac{\partial C}{\partial x}$) we find that $D = \alpha\Gamma\lambda^2$. Since $\Gamma = \nu e^{-E/RT}$, $D = \alpha\lambda^2 e^{-E/RT} = D_o e^{-E/RT}$.

Effect of Variables on Diffusion

Diffusion-controlled reactions, homogeneous diffusion and heterogeneous diffusion, and the diffusion coefficient have been examined. The study involves the effect of temperature. In general, an increase in temperature gives an exponential increase in the diffusion coefficient. At low temperatures only a few atoms have the thermal energy to squeeze between adjacent ions into a nearby hole, however at higher temperatures, more atoms have the required thermal energy and a greater amount of material diffuses. In certain cases, with lattice diffusion, the quantity E also contains factors allowing for the readjustment of the structure after the ions have moved. With heterogeneous diffusion, then the effects of diffusion become more complex. Generally, activation energies are lower for grain boundary diffusion than for lattice diffusion, and this means that an increase in temperature will increase the lattice diffusion coefficient more than the grain boundary coefficient. The activation energies for grain boundary diffusion in metals are about half that for the lattice diffusion (Shewmon, 1963, p. 171). However, no activation energies could be found for diffusion along high-diffusivity paths in silicates. Depending on the type of disruption, the activation energy could vary all the way down to that for surface diffusion. Consider the following equation

$$\frac{D_b}{D_l} = \frac{D_{b,o}}{D_{l,o}} e^{(E_l - E_b)/RT}$$

where $E_l - E_b > 0$. When T increases $e^{(E_l - E_b)/RT}$ becomes smaller and D_l becomes larger relative to D_b. At a high enough temperature, lattice diffusion will become as important as grain boundary diffusion. Above this temperature only the effects of lattice diffusion will be seen because, though both types of diffusion are occurring, the lattice makes up a much larger volume of the solid than the grain boundaries. The presence of grain boundaries will no longer effect the diffusion coefficient. This effect has been demonstrated with diffusion in single crystals and polycrystalline samples of silver (LeClaire, 1953). Above 700°C the diffusion coefficients for both the single crystals and the polycrystalline samples were found to be the same.

Among the major variables not considered in this study are pressure, impurities and chemical potential of all species in a system. The interested reader should consult Shewmon.

CHAPTER IV

SUMMARY OF PROCEDURE

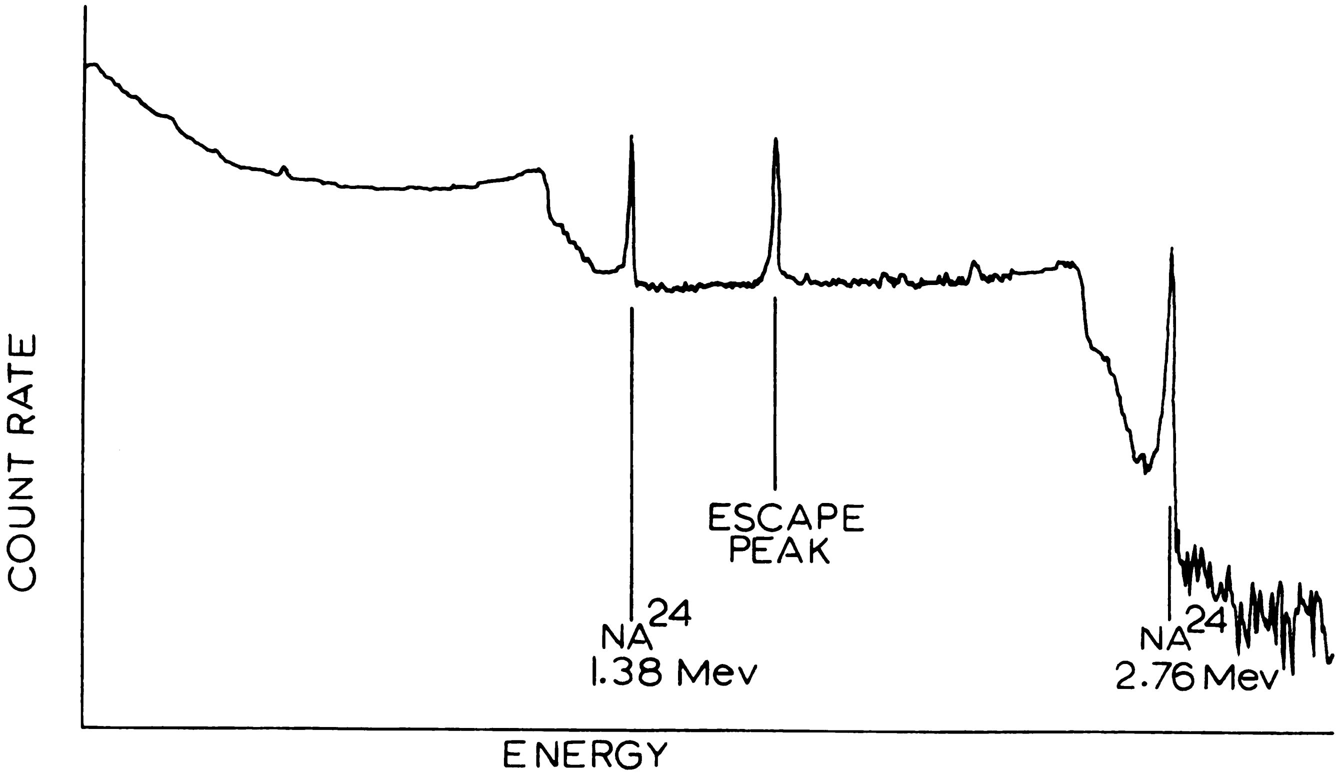
Introduction

The study involved two parts: in one part the exchange of activated sodium in albite for nonactivated sodium from .1N NaCl solution was studied, and in the second part, self-diffusion was examined in albite and a self-diffusion coefficient determined by means of the sectioning technique. A more detailed description of the procedure used in both parts is given in the Appendix. The procedure for the exchange part will be summarized first below.

Exchange Study

Thirty-five grams of almost pure albite from Amelia County, Virginia were ground to a fine powder with a specific surface area of 1.4 M^2/gm and 5 gram portions irradiated in the MSU reactor for 10 minutes at a flux of 10^{12} neutrons/cm^2 sec. Standard 10 ppm Na solutions were irradiated at the same time. After 24 hours only Na^{24} remained active (see Figure 1). The 5 grams were then placed in a semipermeable membrane (along with some NaCl

Figure 1



GAMMA-RAY SPECTRUM OF
IRRADIATED ALBITE
(TAKEN 24 HOURS AFTER
IRRADIATION)

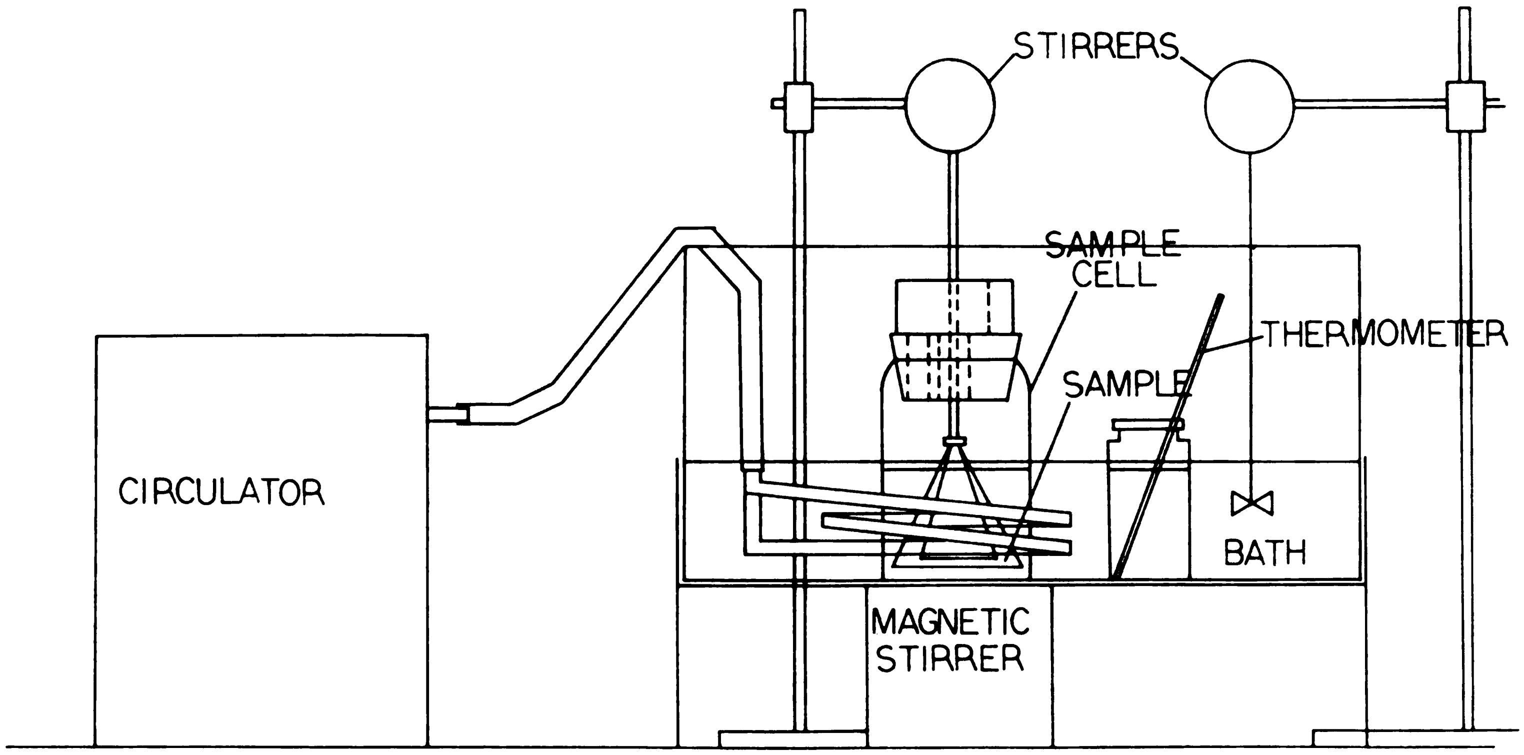
solution) and the membrane suspended in a reaction cell containing more solution. In all runs, 5 grams of solid were used per 500 ml of solution and the reaction cell was placed in a controlled-temperature bath (see Figure 2). A stirring bar agitated the solution inside the cell while rotation of the membrane agitated the sample. To make the runs, 2 ml of solution were collected from the cell outside the membrane, at approximately 1 hour time intervals and the exact time recorded. Two ml of 0.1N NaCl solution were used to replace that withdrawn. The samples and standards were then counted on a γ-spectrometer and the concentration of the sodium released calculated to give release of sodium as a function of time. Three runs were made at 25, 45, and 75°C and runs with and without the membrane were made at 65°C. The solid was centrifuged out when no membrane was used (a much slower and less complete procedure). Similar curves were obtained with and without the membrane, indicating it had little effect on the movement of sodium.

Sectioning Study

For solid diffusion studies, the sectioning method was used with the thin-layer initial condition. Cleavage fragments of the same albite as used for the dissolution experiments were selected and ground (using a wet diamond lap) on a side opposite a major cleavage until that side was parallel to the cleavage. The cleavage face was then

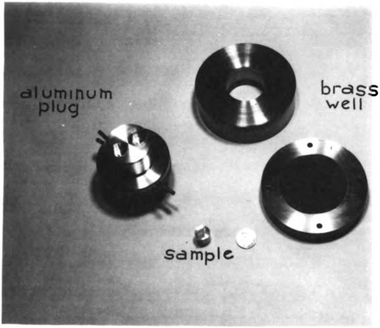
Figure 2

SCHEMATIC OF EQUIPMENT USED DURING DISSOLUTION EXPERIMENTS



ground slightly so that it was exactly parallel to the back side (as indicated by measurement in several places with a micrometer). The surface was abraded slightly with dry carborundum paper. A layer of Na^{22} was produced on the prepared surface by clamping it against a very slightly dampened Millipore filter that had been saturated with a Na^{22} Cl solution until an activity of about 700,000 cpm was obtained and then dryed. After about 1 hour, contact produced an activity on the surface of 10-20,000 cpm. The fragment was placed in an oven, the temperature raised immediately to 300°C and, at a rate of 25°/30 min., from there to the diffusion temperature. The sample was kept at the required temperature for a recorded length of time and removed after decreasing the temperature in the same way it was increased. The sample was mounted on a brass plug (for later grinding), the thickness of the sample plus plug measured with a micrometer, and the activity determined in a controlled-geometry counter with a NaI detector. The counts taken before diffusion were taken with the same counting geometry throughout. After counting, the sample (mounted on the plug) was placed in a grinder which was constructed so as to grind off small amounts of material in layers parallel to the surface of the fragment (see Figure 3 and the section on grinding in the Appendix). A layer approximately .1 mil (.0001") was ground off, the sample cleaned, the thickness of the sample plus plug measured with a micrometer, and the activity measured in

Figure 3



GRINDER UNASSEMBLED

GRINDER ASSEMBLED

the controlled-geometry counter. Since Na^{22} has a half life of 2.6 years, no correction was made for radioactive decay in the solid diffusion studies. The counting-grinding operation was repeated 4 to 8 times for each sample and the data used to construct plots of y vs x. Four diffusion runs were made: one run at 300°C with a time of 24 hours, two runs at 500°C with times of 69 and 154 hours and one run at 595°C with a time of 107 hours. In each run three fragments, cut parallel the major cleavages (010, 001 and 110), were used. The designation of the cleavages was verified by optical examination of thin sections of fragments on a universal stage. In the 500° runs the 001 fragments were lost through breakage. At 595° the 110 fragment was lost.

CHAPTER V

RESULTS

Treatment of Exchange Data

Concentration-Time Plots

From the exchange experiments, curves of concentration of radioactive sodium in the solution vs elapsed time were obtained at 25, 45 and 75°C. These are shown in Figure 4. The general features include a rapid rise during the first two or so hours to about 7, 10 and 13 ppm. This is followed by a decreasing rate of increase over the remaining 20 or so hours to concentrations of 10, 14 and 18 ppm.

Plots of Concentration vs $\sqrt{t}$

In order to test the results against the exchange equation given in the theory section, the concentrations were plotted against the square root of time. Plots for 25, 45 and 75°C are shown in Figure 5. The curves are fairly linear after the initial portion. Slopes determined by the least-squares method using values of $\sqrt{t}$ from 17 to about 40 are given in Table 2.

Figure 4

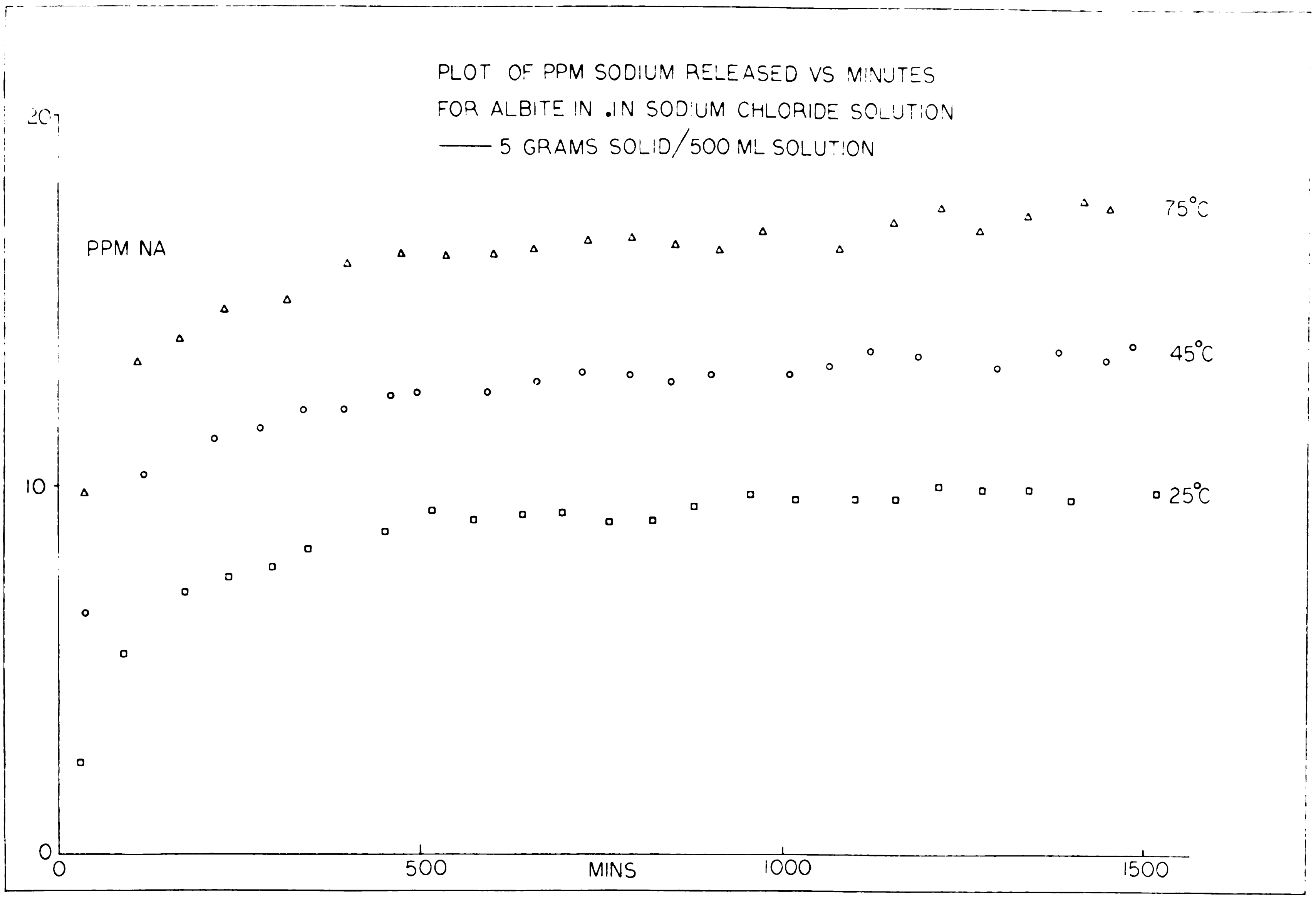

PLOT OF PPM SODIUM RELEASED VS MINUTES
FOR ALBITE IN .1N SODIUM CHLORIDE SOLUTION
—— 5 GRAMS SOLID/500 ML SOLUTION
PPM NA
20
10
0
0
500
MINS
1000
1500
75°C
45°C
25°C

Figure 5

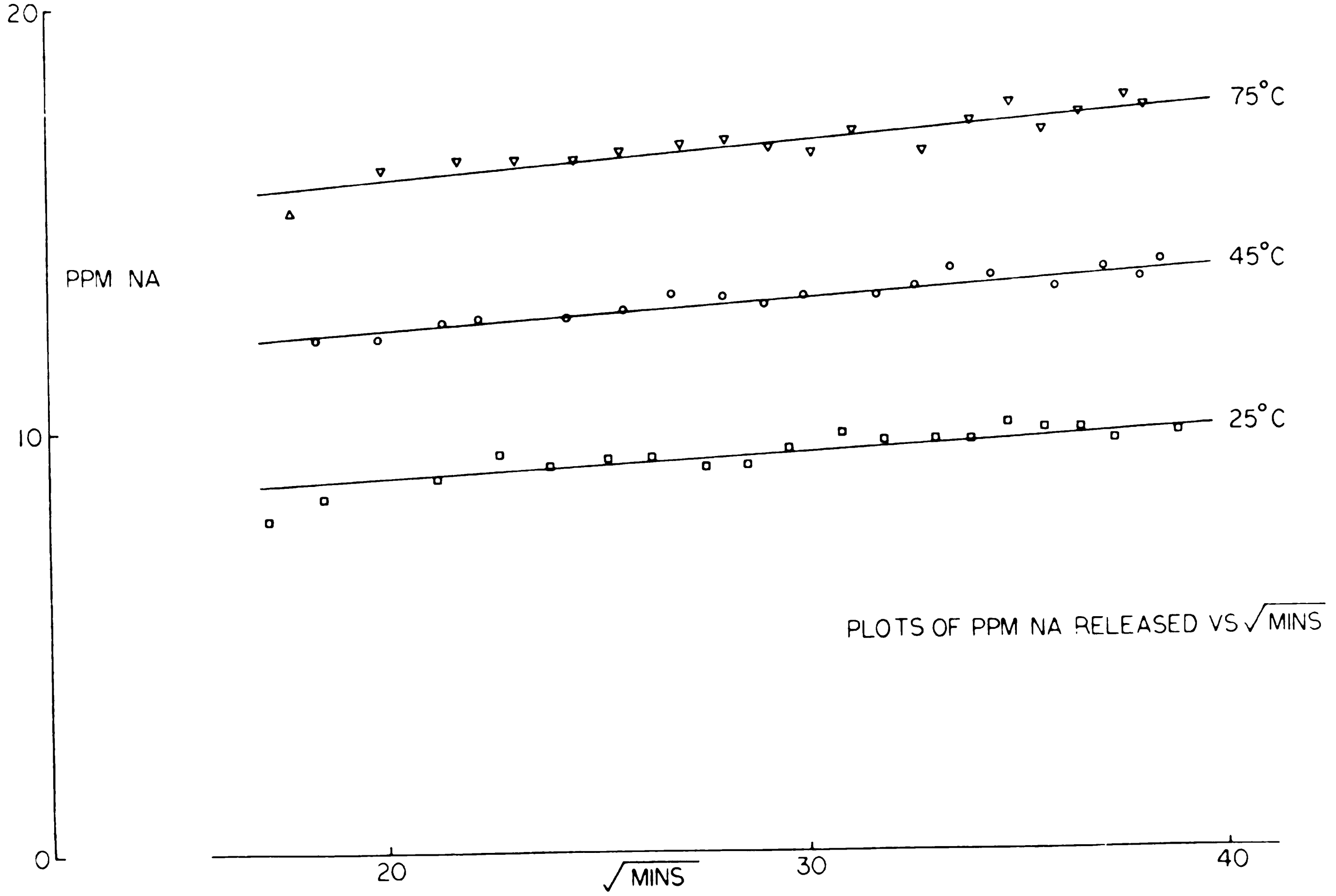

PPM NA
20
10
0
75°C
45°C
25°C
PLOTS OF PPM NA RELEASED VS $\sqrt{\text{MINS}}$
20
30
40
$\sqrt{\text{MINS}}$

TABLE 2.--Temperature slope data from exchange experiments.

Temperature	Slope
25°C	6.78×10^{-8} ppm/$\sqrt{\text{min}}$
45	7.74
75	9.48

It can be seen that the slopes increase with temperature.

Plot of Log Slope vs $\frac{1}{T}$

From the theory section, the slopes of the plots described in the last section are equal to

$$2\,\frac{C_o\, S\sqrt{D}}{V\sqrt{\pi}}$$

The primary temperature dependence of this term comes from D. D varies with temperature according to the equation

$$D = D_o\, e^{-\frac{E}{RT}}$$

where D_o is fairly independent of temperature, E is the activation energy, R the gas constant and T the temperature in degrees kelvin. The slope can then be written

$$2\,\frac{C_o\, S\sqrt{D_o}}{V\sqrt{\pi}}\, e^{-\frac{E}{2RT}}$$

A plot of the common logarithm of the slope vs $\frac{1}{T}$ will therefore equal

$$-\frac{E}{4.6R}.$$

Such a plot is given in Figure 6. From this an activation energy of about 2730 cal/mole Na was determined. It must be emphasized that the exact value obtained for the activation energy depends upon the model used to derive the formula for the slope. By looking at the concentration-time curves, however, it can be seen that the temperature dependence is not strong.

Diffusion Coefficients from Exchange Process

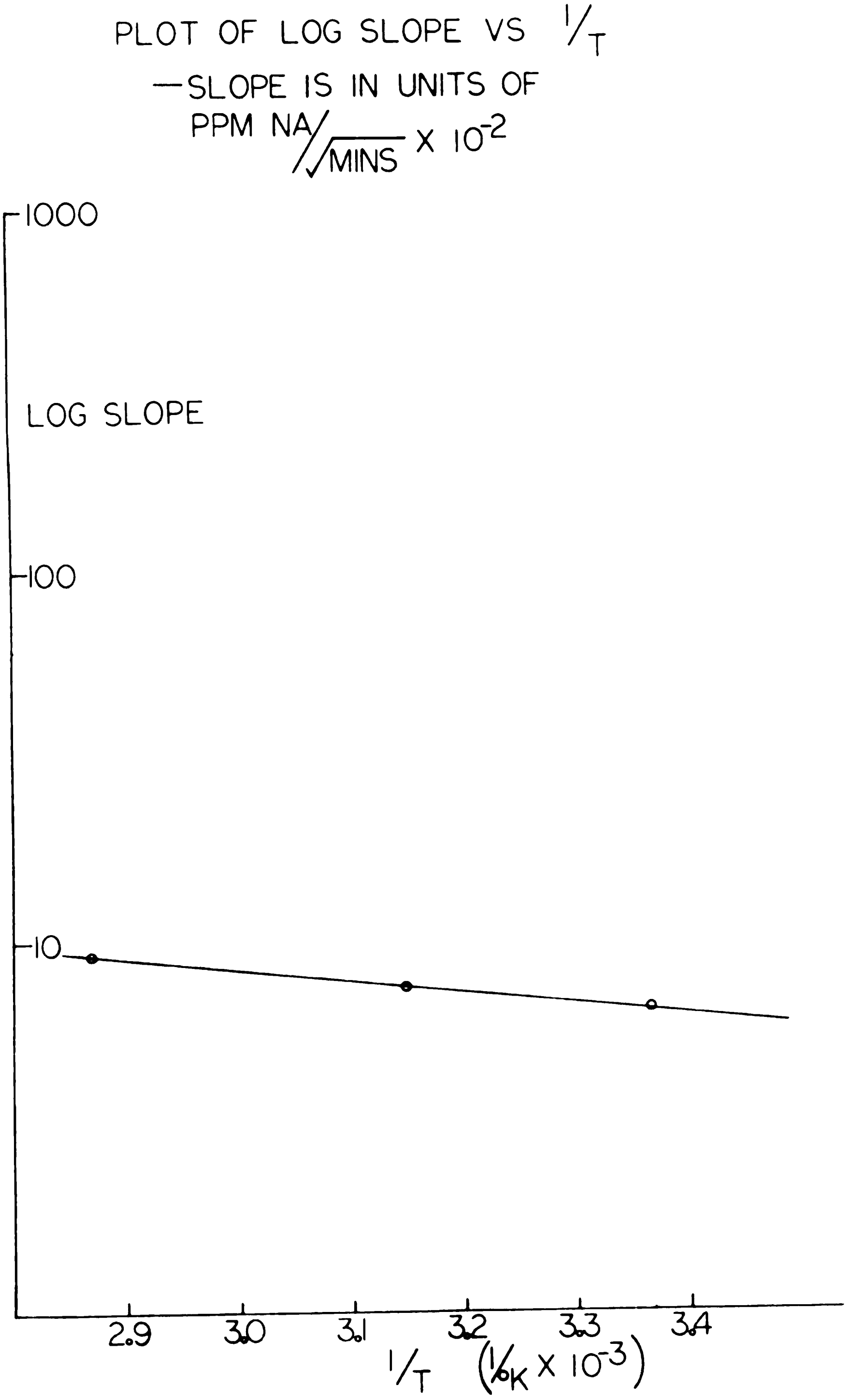
In addition to activation energies, the diffusion-control equation given in the theory section and the slopes enable calculation of diffusion coefficients.

From the theory section, the slope of concentration vs the square root of time is equal to

$$2\,\frac{C_o\ S\sqrt{D}}{V\sqrt{\pi}}$$

As an example of the calculation of D, consider the case at 25°C:

Figure 6


PLOT OF LOG SLOPE VS $1/T$
—SLOPE IS IN UNITS OF
PPM NA/$\sqrt{MINS}$ X 10^{-2}
1000
LOG SLOPE
100
10
2.9
3.0
3.1
3.2
3.3
3.4
$1/T$ ($1/°K$ X 10^{-3})

$$2\,\frac{C_o\,S}{V} = \frac{2 \times .223\,\frac{\text{gm}}{\text{cm}^3} \times 7 \times 10^4\text{cm}^2}{500\ \text{cm}^3}$$

$$= 6.24 \times 10^3\,\frac{\text{gm}}{\text{cm}^4}$$

$$6.78 \times 10^{-3}\,\frac{\frac{\text{gm}}{\text{cm}^3}}{\sqrt{\text{min}}} = 6.24 \times 10^3\,\frac{\text{gm}}{\text{cm}^4}\,\sqrt{\frac{D}{\pi}}$$

$$1.085 \times 10^{-11}\,\frac{\text{cm}}{\sqrt{\text{min}}} = \sqrt{\frac{D}{\pi}}$$

$$1.18 \times 10^{-22}\,\frac{\text{cm}^2}{\text{min}} = \frac{D}{\pi}$$

$$6.18 \times 10^{-24}\,\frac{\text{cm}^2}{\text{sec}} = D$$

In like manner, the apparent diffusion coefficients were calculated for 45 and 75°C. The coefficients are given in the table below.

TABLE 3.--Diffusion coefficients from exchange experiments.

Temperature	Coefficient
25°C	6.18×10^{-24}cm^2/sec
45	8.05
75	12.1

Errors in Exchange Experiments

With respect to errors in the dissolution part of the experiments, there are several possible sources within each concentration-time curve (neglecting errors due to original weighing and volume determinations). The errors occur in concentration determination and time determination. The time error is within a few minutes and is not felt to be significant. The concentration determination involves both volume determination and activity determination. Since the total counts ranged from about 100,000 initially to about 40,000 after 24 hours, the errors in activity can be expected to be in the neighborhood of 1%. Again, this is not significant for the purposes of this experiment. The major source of errors is felt to be the volume determinations. Even though equal volumes of sample and standard were collected at the same temperature and the pipet rinsed after each sample, it is difficult to measure 2 ml of 0.1 N NaCl solution. This is particularly true at 75°C. The volume determinations are therefore felt to be the major source of error.

Treatment of Sectioning Data

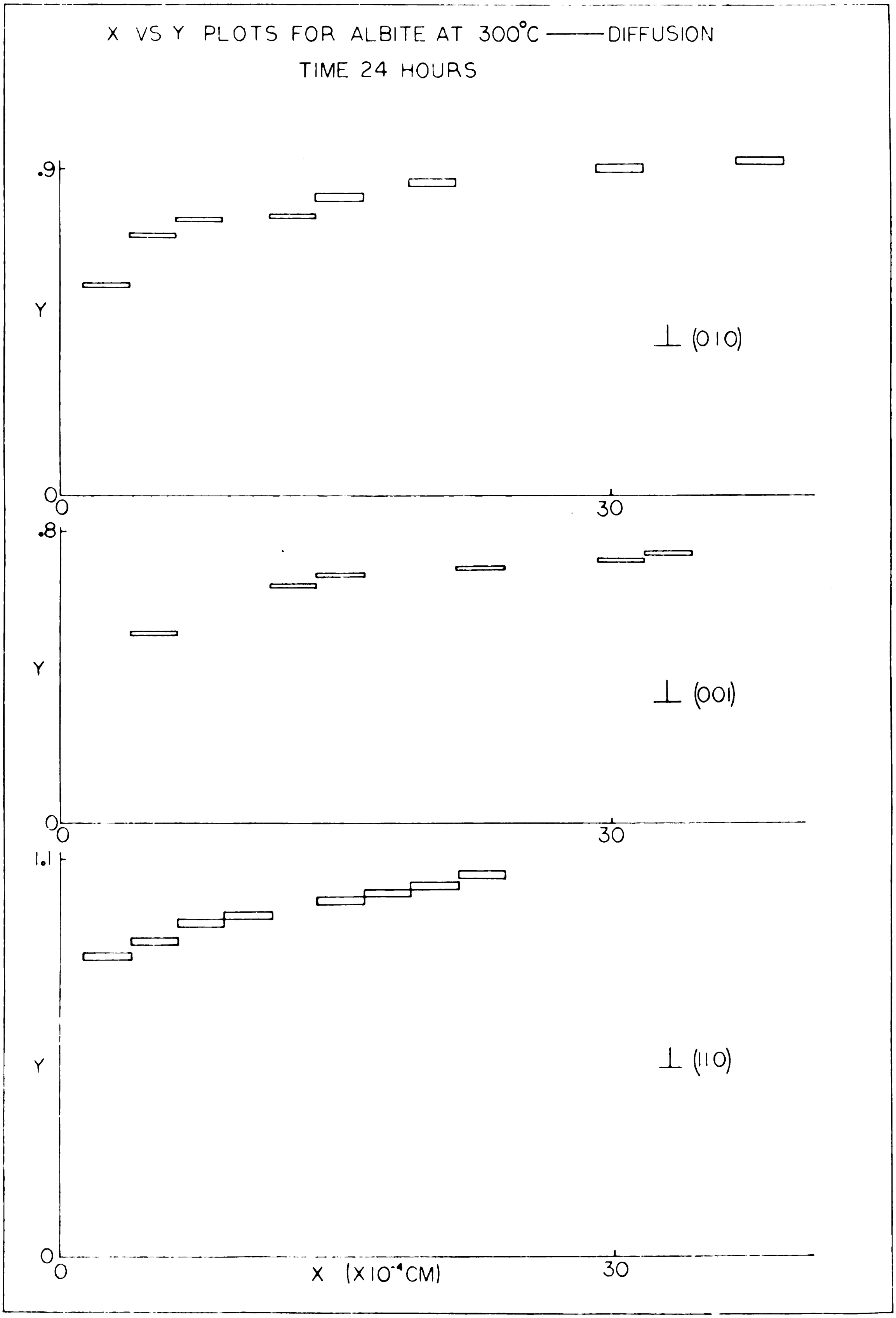
y vs x Plots for Sectioning

For the examination of diffusion in solid individual fragments y was plotted against x for several directions in the lattice and several different temperatures. Some runs were also made in which time was varied. The effects of direction were found to be unimportant at the level of accuracy reached in this part of the study and the curves in the three directions (001, 010 and 110) are treated as if they are equivalent. Justification for this approximation can be found in the work of Rosenquist. In working in the range of 800-1000°C, Rosenquist found diffusion coefficients that varied in different directions. The variation, however, was within an order of magnitude. As indicated in the section on the discussion of errors, the diffusion coefficients determined at lower temperature (595°C) by the sectioning method are felt to be good only to a little less than an order of magnitude. Therefore the differences due to direction are ignored.

Sectioning Results for 300°C

The differences that occur when the temperature is changed, however, are marked and felt to be significant. At 300°C (see Figure 7) the plots consist of slightly curved lines with shallow slopes and y-intercepts of .5-.8. According to the theory outlined for homogeneous diffusion, such plots of y vs x should give straight lines with intercepts of $\mu\sqrt{Dt}$ where μ is the linear absorption coefficient for Na^{24} γ-radiation (1.3 Mev) in albite, D is the diffusion coefficient and t is time. μ can be calculated from mass absorption coefficients for the elements for 1.3 Mev radiation (Chappel, 1956) and the formula for

Figure 7


X VS Y PLOTS FOR ALBITE AT 300°C ——— DIFFUSION
TIME 24 HOURS
.9
Y
0
0
30
⊥ (010)
.8
Y
0
0
30
⊥ (001)
1.1
Y
0
0
30
⊥ (110)
X (X10⁻⁴CM)

albite. When this is done it is found that $\mu \approx .145/\text{cm}$. Assuming a diffusion coefficient of $10^{-11}\text{cm}^2/\text{sec}$ (probably much too large) and a time of 10^5 seconds we get

$$Yo = \frac{.145}{\text{cm}} \sqrt{10^{-11} \times 10^5 \frac{\text{cm}^2}{\text{sec}} \text{sec}}$$

$$= .145 \sqrt{10^{-6}}$$

$$= .145 \times 10^{-3}$$

This is essentially 0. The initial slope of the 300°C curves must be quite steep for the curves to pass through the point 0,0. But the theory for homogeneous diffusion predicts straight lines. From these considerations it was deduced that, at 300°C, the curves must represent the heterogeneous diffusion. Material is moving through the solid along high-diffusivity paths faster than through the lattice of the crystal.

Sectioning Results for Higher Temperatures

Runs were made at 500 and 595°C. Looking at Figures 8 and 9 we see that, at 500°C, there is still a marked curvature. The curves, however, have a definite slope toward the origin, even though strongly curved. Curves from longer runs at 500°C seem to flatten out even more (Figures 8 and 9). At 595°C (Figure 10) there are fairly straight lines which pass through the origin. These represent fairly homogeneous diffusion. According to Sippel (1963), estimates of the crystal diffusion

Figure 8

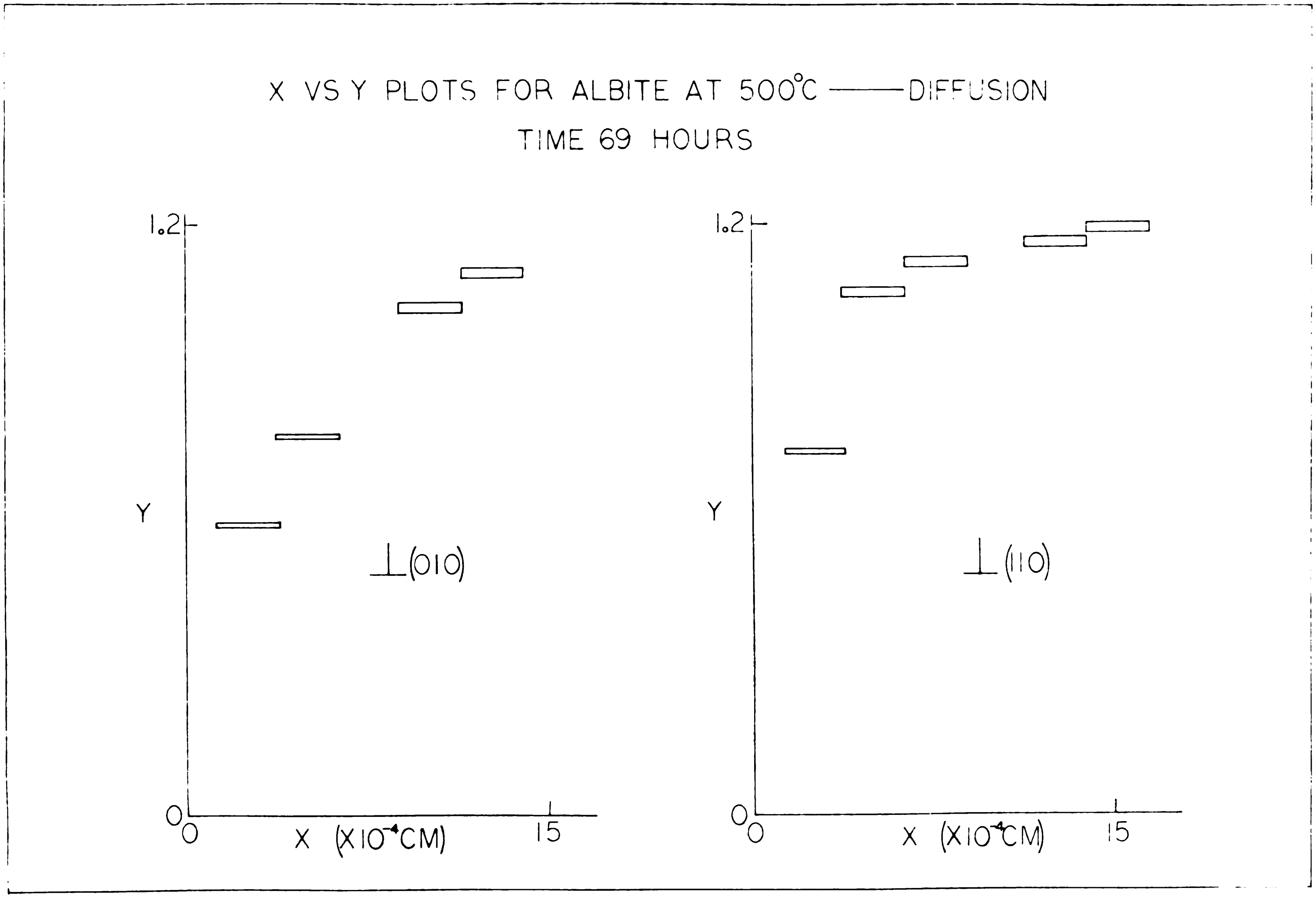

X VS Y PLOTS FOR ALBITE AT 500°C —— DIFFUSION
TIME 69 HOURS
1.2
Y
0
0
X (X10⁻⁴CM)
15
⊥(010)
1.2
Y
0
0
X (X10⁻⁴CM)
15
⊥(110)

Figure 9

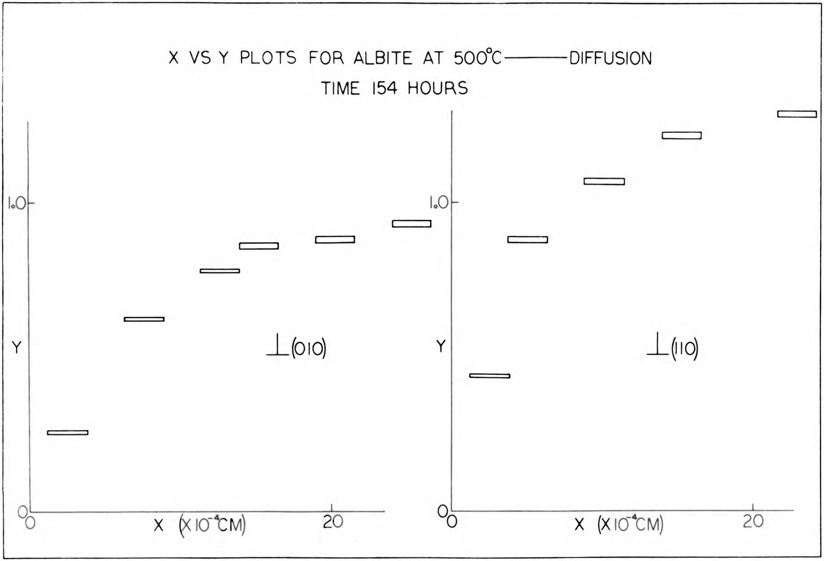
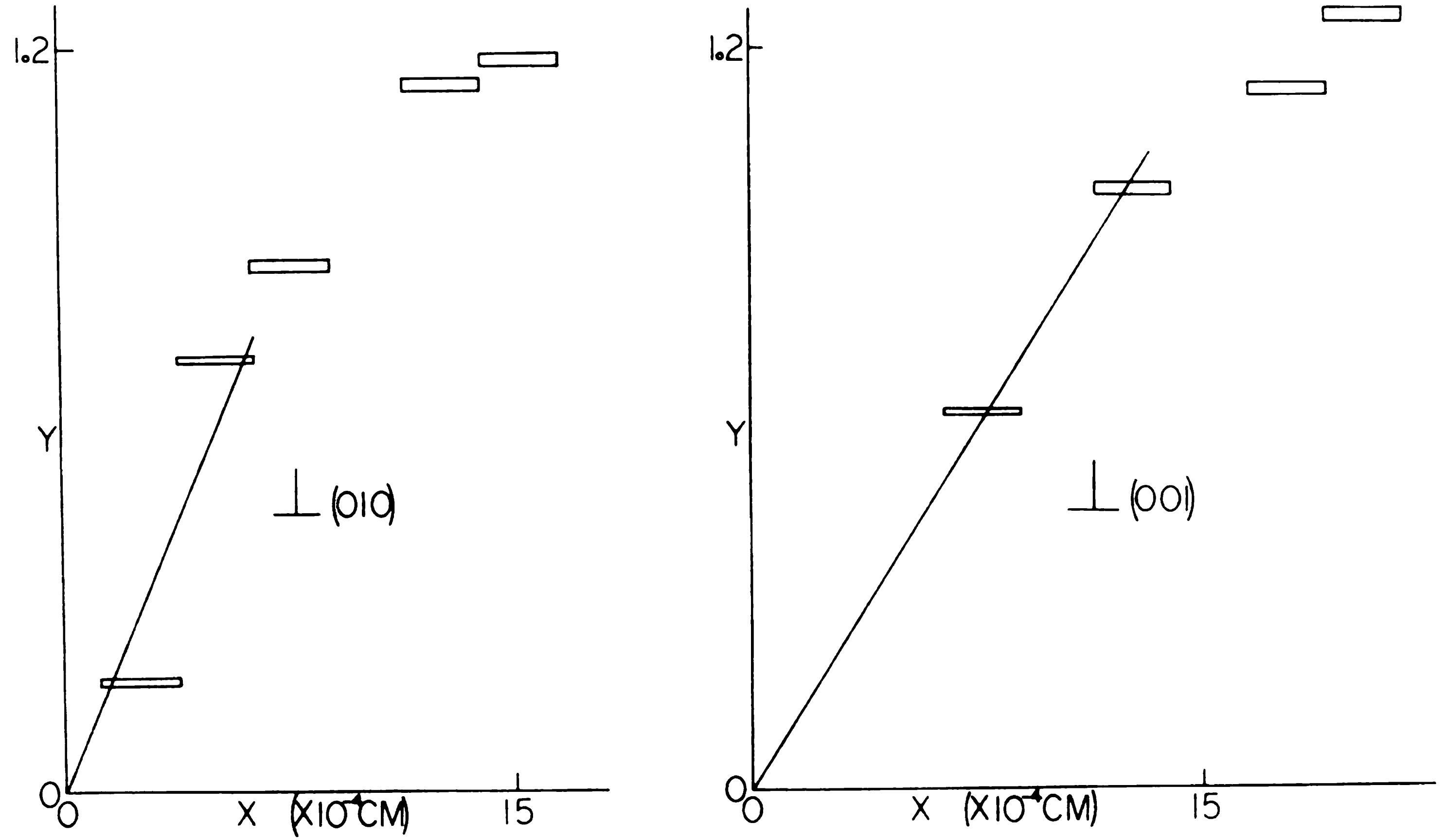

X VS Y PLOTS FOR ALBITE AT 500°C——DIFFUSION
TIME 154 HOURS
Y
1.0
0
0
X (X10⁻⁴CM)
20
⊥(010)
Y
1.0
0
0
X (X10⁻⁴CM)
20
⊥(110)

Figure 10



X VS Y PLOTS FOR ALBITE AT 595°C —— DIFFUSION

TIME 107 HOURS

coefficient can be obtained from initial slopes of such plots as the ones obtained at 595°C. From such initial slopes (lines through 0,0 and the first two points) values of $D = 5 \times 10^{-13} cm^2/sec$ for the direction (010) and $D = 1 \times 10^{-12} cm^2/sec$ for the direction (001) were obtained. These were calculated to slide rule accuracy, but are probably only good to half an order of magnitude. An average of the two values was taken as the value for the diffusion coefficient at 595°C and was found to be equal to about $8 \times 10^{-13} cm^2/sec$.

Errors in Sectioning Experiment

The errors in the solid diffusion curves result from two sources. These are counting errors and errors due to the measurement of thickness. The counting errors are on the order of a percent. Errors in thickness (determination of x) are fairly large. Thickness was estimated to 0.1 mil using a Lufkin micrometer. While curves can be found in which measurements were made to 0.1 mil (.0001 inches) (Turnbull and Hoffman, 1954) this is an estimate which is felt to be good only to about ±.05 mil ($\pm 1.27 \times 10^{-4}$cm). Even with such errors, however, the average diffusion coefficient is felt to be good under an order of magnitude, as indicated by its compatibility with Sippel's data. This is, however, working at the limit of the sectioning method under these conditions.

Activation Energy for Lattice Diffusion

Sippel (1963) has determined diffusion coefficient of $8.00 \times 10^{-11} cm^2/sec$ at 850°C and $2.8 \times 10^{-10} cm^2/sec$ at 940°C for Na in albite at higher temperatures. The value at 940°C is said by Sippel to occur above an inversion point. This inversion, however, is from triclinic to monclinic albite and, since the triclinic albite is almost monoclinic, one cannot expect the inversion to alter the diffusion coefficient much. The logs of the three values of the diffusion coefficient were plotted against the reciprocal of temperature (absolute) (Figure 11). From the slope of this plot an activation energy of about 45.8 k cal/mole Na was calculated. This is similar to other values obtained for the diffusion of more mobile constituents in the lattice of silicates.

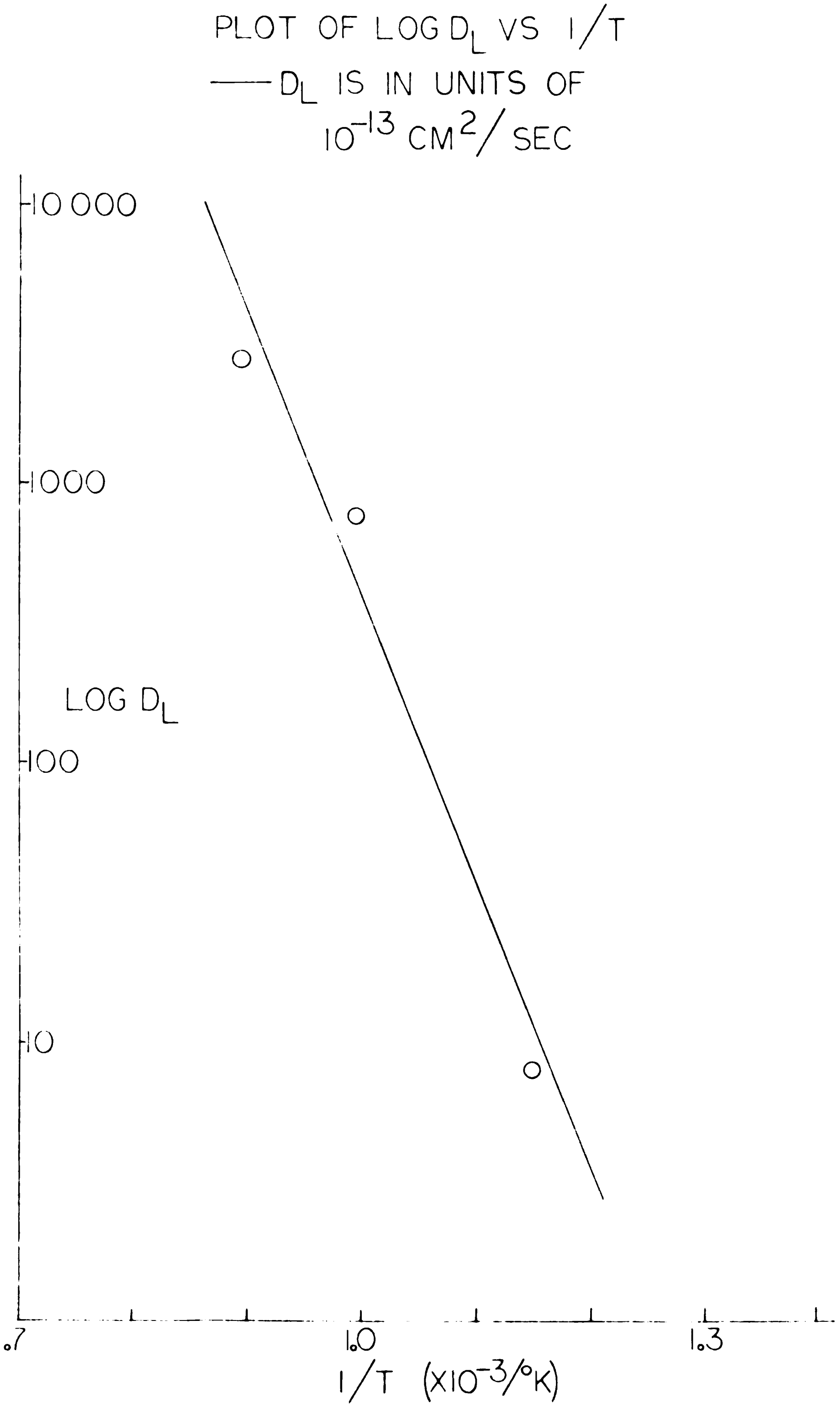
Lattice Diffusion Coefficients at Lower Temperatures

Using the activation energy and diffusion coefficient determined in this study at 595°C, lattice diffusion coefficients were calculated at 25, 45 and 75°C. As a sample of the calculations consider the case at 25°C:

$$\frac{D_{1,595}}{D_{1,25}} = \frac{D_o\, e^{-E/RT_{595}}}{D_o\, e^{-E/RT_{25}}} = e^{E/R(3.36 - 1.15) \times 10^3}$$

$$= e\, \frac{45.8 \times 10^3 \times 2.2 \times 10^{-3}}{1.99} = e^{50.9}$$

Figure 11


PLOT OF LOG D_L VS 1/T
—— D_L IS IN UNITS OF 10^{-13} CM^2/SEC
10 000
1000
100
10
LOG D_L
.7
1.0
1.3
1/T (X10^{-3}/°K)

$$D_{1,25} = \frac{D_{1,595}}{e^{50.9}} = \frac{7.94 \times 10^{-13}}{1.26 \times 10^{22}} = 6.3 \times 10^{-35}\ \frac{\text{cm}^2}{\text{sec}}\ .$$

Below is a table giving crystal diffusion coefficients at 25, 45 and 75°C.

TABLE 4.--Lattice diffusion coefficients at lower temperatures.

Temperature	Coefficient
25°C	6.30×10^{-35} cm^2/sec
45	7.94×10^{-33}
75	3.97×10^{-30}

CHAPTER VI

CONCLUSIONS

Model Suggested by the Study

The results of the study are compatible with a model for low-temperature alteration in which release of alkalis is controlled by movement along high-diffusivity paths not accessible to liquids in the normal sense. The evidence for this comes from both the exchange data and the diffusion studies.

Exchange Evidence

Considering the exchange data first, beyond the very initial portion, the data for the low-temperature release of sodium fit a model in which the rate of release is controlled by diffusion. This is indicated by the parabolic rate law (predicted by diffusion-control theory) and the low activation energy obtained for the process (if the process were controlled by chemical reaction, a much stronger temperature dependence would be expected).

Sectioning Evidence

When the high-temperature data for solid lattice diffusion are considered, however, a high activation energy (reasonable for lattice diffusion in most silicates) is obtained. This stronger temperature dependence means that, when the Arrhenius equation is used to extrapolate to the temperatures of the dissolution experiments, diffusion coefficients are calculated which are much smaller (10 orders of magnitude) than the diffusion coefficients obtained from the dissolution data. The large difference between the diffusion coefficients and the activation energies determined by the exchange experiments and those lattice coefficients determined by the sectioning method means that, though exchange is controlled by diffusion, it is not controlled by lattice diffusion. Control by diffusion through an adsorbed film of solution is ruled out by the small values of the coefficients.

Evidence for Heterogeneous Diffusion

There are, however, several ways material may move through a solid. The series of solid diffusion curves offers evidence as to the processes involved. At 300 and 500°C plots of y vs x gave curved lines, whereas the theory for homogeneous diffusion predicts straight lines passing through the origin. These curved lines indicate heterogeneous diffusion and that high-diffusivity paths must be important in addition to lattice diffusion. This is verified by the fairly straight curves passing through the origin obtained at 595°C. Since the higher activation energy for lattice diffusion causes it to be more effected by a temperature increase than diffusion along high-diffusivity paths, a point is reached at which lattice diffusion and movement along high-diffusivity paths occur with equal ease. Since the volume of the lattice is much greater than the volume in high diffusivity paths, the diffusion becomes homogeneous above this temperature.

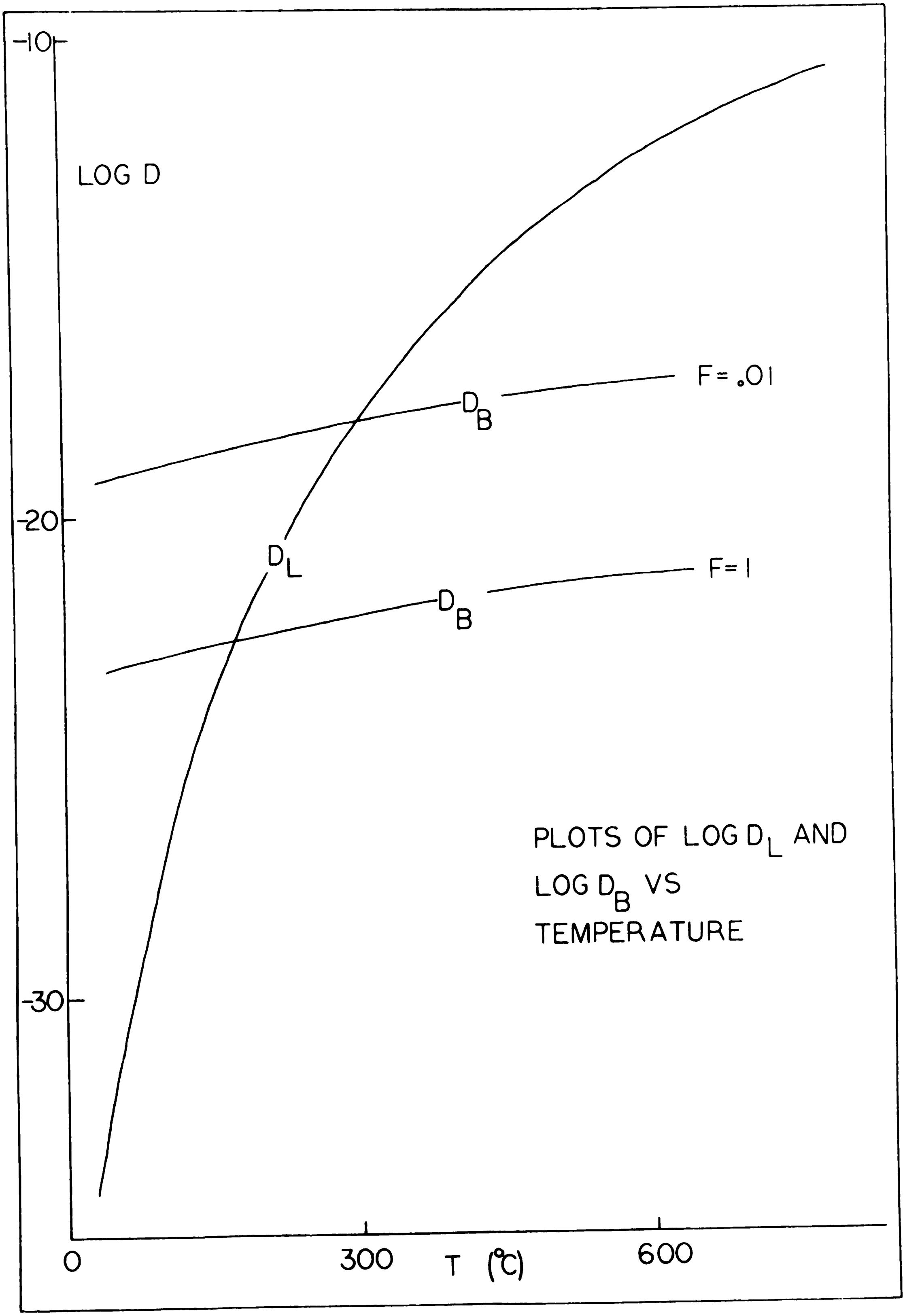
Temperature Variation of the Process

The dissolution diffusion coefficients are interpreted to be diffusion coefficients where high-diffusivity paths are dominant and the coefficients obtained at 595°C to be diffusion coefficients for lattice diffusion. In Figure 12, the logs of the lattice diffusion coefficients and coefficients for high-diffusivity paths are plotted as functions of temperature. To construct the curves, the activation energies and diffusion coefficients determined in this study were used with an equation of the type

$$D_{T_x} = D_T e^{\frac{E}{R}\left(\frac{1}{T} - \frac{1}{Tx}\right)}$$

At this point it is stated again that the coefficients from the exchange coefficients are apparent coefficients. If high-diffusivity paths are operative, then the apparent coefficients must be modified.

Figure 12


-10
-20
-30
LOG D
D_L
D_B
F=.01
D_B
F=1
0
300
600
T (°C)
PLOTS OF LOG D_L AND
LOG D_B VS
TEMPERATURE

The real high-diffusivity coefficients must be calculated using the equation

$$D_a = f^2 D_b$$

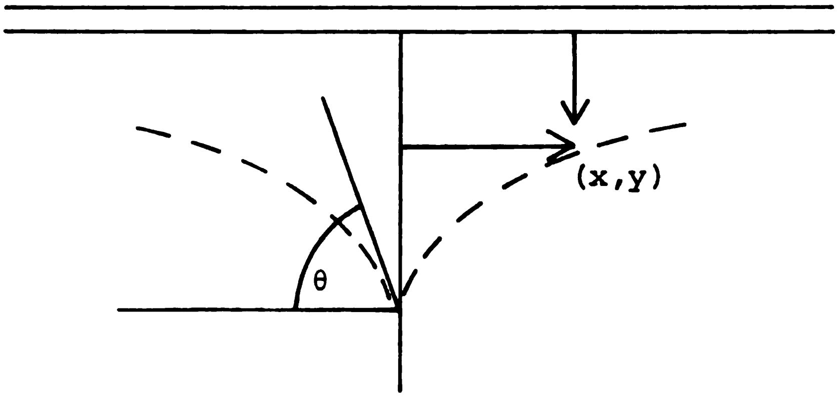
or

$$\frac{D_a}{f^2} = D_b$$

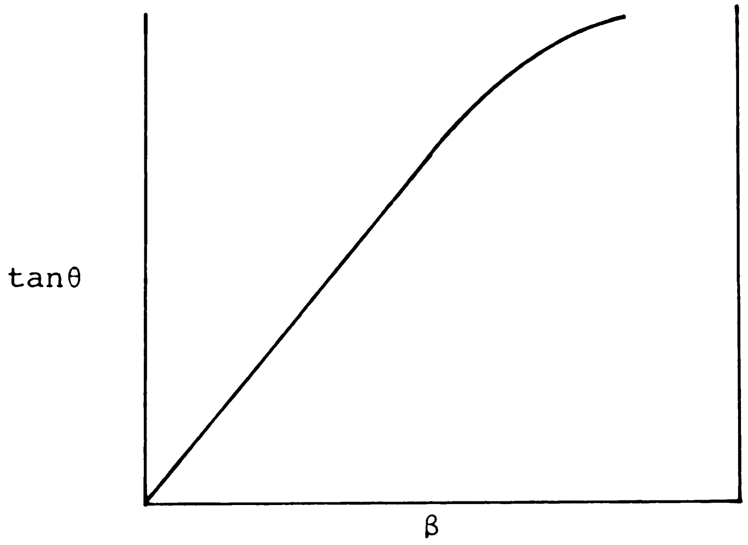
where f is the fraction of the crystal perpendicular to the diffusion direction which is taken up by the high-diffusivity paths. If f is, say .01, then D_b will be increased by four orders of magnitude. The line representing D_b therefore represents a minimum.

Time Variation of the Process

The absolute values of the diffusion coefficients, however, are not sufficient alone to obtain a good picture of the process. The overall distribution of diffusing species in the solid can be visualized by examining contours of the quantity c/c_o in a cross-section of the solid.



This type of distribution (not predicted by Fisher's treatment) comes about because material will move through the lattice to a point (x,y) from the surface in addition to moving from the grain boundary. The angle theta is a measure of the relative importance of movement along the high-diffusivity path. The shape of a particular contour varies with time as well as the ratio D_l/D_b and this variation is indicated by a diagram, taken from Whipple's paper, in which the tangent of theta is plotted as a function of $\beta = \left(\frac{D_b}{D_l} - 1\right)\frac{\delta}{2\sqrt{D_l t}}$



(after Whipple, 1954).

Since tanθ is inversely proportional to $\sqrt{t}$ longer times will produce smaller thetas. The contours will not be as distorted by the high-diffusivity path. tanθ, however, is directly proportional to $\left(\frac{D_b}{D_l} - 1\right)\frac{1}{\sqrt{D_l}}$. For very small D_l and relatively large D_b, there will be large thetas and the concentration contours will be greatly distorted.

Looking at the plots of D_l and D_b vs temperature, the hypothesis can be made that, as lower and lower temperatures are approached, it will take more and more time to overcome the increasing difference between the diffusion coefficients.

Nature of the High-Diffusivity Paths

The low-temperature diffusion control, heterogeneous nature of the diffusion and its dependence on temperature and time have been discussed. What can be said about the nature of the high-diffusivity paths? The most obvious high-diffusivity paths are incipient cleavages (010, 001 and 110). Even without any disruption, these directions would have higher diffusivity for alkali ions due to the higher densities of these ions on these planes. Examination of thin sections of the material, however, shows the presence of many incipient cleavages. Some disruption is therefore present. It seems reasonable that this type of disruption is also present in the grains of the ground sample used for the dissolution experiments. Along these partially disrupted cleavage planes activation energies would be lowered by separation of the neighboring ions and general disruption. Dislocations and twin planes are other possible high-diffusivity paths. Strain, which would be localized along these defects may also play a role. These factors may be enhanced in the exchange experiments by the grinding.

Application to Natural Processes

The results of the study indicate that relatively rapid movement of ions along high-diffusivity paths (not accessible to solutions in the normal sense) is possible. With this model the extensive reaction of inert silicates in diffusion-controlled situations can be explained.

In this study, the situation has been one of pure exchange in a short period of time with the mineral maintaining its structural integrity. In nature, diffusion and chemical attack, such as that described by Correns, may occur. Even in this situation, diffusion-controlled reactions occur. Diffusion may occur before much distruction of the lattice occurs and the completely open system of Correns is not correct because residual material in the alteration of a feldspar may form an inert product (kaolinite, gibbsite, illite, feldspar) which may cover the reacting material. These situations give a diffusion-controlled situation similar to that in this study. If the product is another silicate similar to albite (another feldspar), then the situation will be very similar to the one in this study. Diffusion controlled reactions can also be envisioned in the formation of oriented products seen scattered throughout grains in thin sections of rocks. Part of this orientation is due to the location of favorable nucleation sites, but a diffusion problem still exists.

In conclusion, natural application can be found for the principles demonstrated by this study. They clarify the reaction and the effects of temperature and time on such situations. They help explain extensive alteration of inert silicates under mild conditions and are of use in considering diagenesis in sediments and the formation of metamorphic rocks.

CHAPTER VII

RECOMMENDATIONS FOR FUTURE STUDIES

Several areas for further study are indicated by the present work. One is a more detailed examination of imperfections in silicates (dislocations, grain boundaries, microscopic and submicroscopic cleavages). Autoradiography, electron microscopy and etching are possible techniques that could be used.

Another is the quantitative examination of strain induced by grinding in the exchange process. This might be studied by examining exchange rates after annealing to remove the strains or by examining rates of release as a function of grinding time. Determination of the specific surface would be necessary to remove the effect of increased surface area in the second method.

The quantitative examination of interdiffusion is a more complex extension of the present study. This could be carried out by changing the composition of the solution in the exchange experiments. Exchange in .1 N KCl is an example.

A study of the rate of redistribution of radioactive tracer between two solids in aqueous solution is still more complex, but closer to the natural situation.

REFERENCES CITED

REFERENCES CITED

Chappell, D. G. (1956). Gamma ray attenuation. Nucleonic, vol. 14, pp. 40-41.

Correns, C. W. and W. Engelhardt. (1938). Neue Untersuchungen über die Verwitterung des Kalifeldspates. Chemie der Grde. Bd 12, pp. 1-22.

Correns, C. W. (1963). Experiments on the decomposition of silicates and discussion of chemical weathering. Clays and Clay Minerals, Tenth Conf. pp. 443-459.

Correns, C. W. (1962). Über die Chemische Verwitterung von Feldspäten. Norsk Geol. Tidsskr. Bd 42 (part 2), pp. 272-282.

Crank, J. (1956). Mathematics of Diffusion. Oxford University Press.

Delmon, B. (1961). L'Étude des réactions limitées par les processus d'interface. Revue de L'Institut Francais du Pétrole. Vol. 16, pp. 1-57.

DeVore, G. W. (1951). Surface chemistry of feldspars as an influence on their decomposition products. Clays and Clay Minerals. Vol. 6, pp. 26-41.

Ellis, B. G. and M. M. Mortland. (1959). Rate of potassium release from fixed and native forms. Soil Sci. Soc. Amer. Proc. Vol. 23, pp. 451-453.

Fisher, J. C. (1951). Calculation of diffusion penetration curves for surface and grain boundary diffusion. Journal of Applied Physics. Vol. 22, pp. 74-77.

Fredrickson, A. F. (1951). Mechanism of Weathering. Bull. GSA. Vol. 62, pp. 221-232.

Fredrickson, A. F. and J. E. Cox. (1954). "Solubility" of albite in hydrothermal solutions. Am. Miner. Vol. 35, pp. 738-749.

Fyfe, W. S., F. J. Turner and J. Verhoogen. (1958). Metamorphic reactions and metamorphic facies. Geol. Soc. America Memoir 73, pp. 1-259.

Girifalco, L. A. (1964). Atomic Migration in Crystals. Blaisdell Publishing Company.

Harrison, L. G. (1961). Influence of dislocations on diffusion kinetics in solids with particular reference to the alkali halides. Trans. Faraday Society. Vol. 57 (part 2), pp. 1191-1199.

Harrison, L. G. (1969). The theory of solid phase kinetics. In Comprehensive Chemical Kinetics, edited by C. H. Bamford and C. F. H. Tipper, Vol. 2, pp. 377-462, Elsevier Publishing Co.

Hoffman, R. E. and D. J. Turnbull. (1951). Lattice and grain boundary self-diffusion in silver. Journal of Applied Physics. Vol. 22, pp. 634-639.

Jensen, M. L. (1952). Solid diffusion of radioactive sodium in perthite. Am. J. Sci. Vol. 250, pp. 808-821.

Jensen, M. L. (1964). The rational and geological aspects of solid diffusion. Canadian Mineralogist. Vol. 8, pp. 271-290.

Lai, T. M. and M. M. Mortland. (1968). Cationic diffusion in clay minerals: I. Soil Sci. Soc. Amer. Proc. Vol. 32, pp. 56-61.

Lidiard, A. B. and K. Tharmalingam. (1959). Diffusion processes at low temperatures. Disc. Faraday Soc. No. 28, pp. 64-86.

Manus, R. (1968). Experimental chemical weathering of two alkali feldspars. Ph.D., University of Cincinnati. pp. 1-100.

Mortland, M. M. (1958). Kinetics of potassium release from biotite. Soil Sci. Soc. Amer. Proc. Vol. 22, pp. 503-508.

Mortland, M. M. (1959). Release of fixed potassium as a diffusion controlled process. Soil Sci. Soc. Amer. Proc. Vol. 23, pp. 363-364.

Mortland, M. M. and K. Lawton. (1961). Relationships between particle size and potassium release from biotite and its analogues. Soil Sci. Soc. Amer. Proc. Vol. 25, pp. 473-476.

Nash, V. E. and C. E. Marshall. (1956). The surface reactions of silicate minerals, Part I. The reaction of feldspar surfaces with acidic solutions. Univ. Missouri Coll. Agr. Res. Bull. 613, pp. 1-36.

Nash, V. E. and C. E. Marshall. (1956). The surface reactions of silicate minerals, Part II. Reactions of feldspar surfaces with salt solutions. Univ. Missouri Coll. Agr. Res. Bull. 614, pp. 1-36.

Pannetier, G. and P. Souchay. (1967). Chemical Kinetics. Elsevier Publishing Co.

Parham, W. (1969). Formation of halloysite from feldspar: low temperature artificial weathering versus natural weathering. Clays and Clay Minerals. Vol. 17, pp. 13-22.

Rosenquist, I. T. (1949). Some investigations in the crystal chemistry of silicates. I. Diffusion of Pb and Ra in feldspars. Acta Chemica Scandinavica. Vol. 3, pp. 569-583.

Shewmon, P. G. (1963). Diffusion in Solids. McGraw-Hill Book Company.

Sippel, R. F. (1959). Diffusion measurements in the system Cu-Au by elastic scattering. Phys. Rev. Vol. 115, pp. 1441-1445.

Sippel, R. F. (1963). Sodium self diffusion in natural minerals. Geochim. Cosmochim. Acta. Vol. 27, pp. 107-120.

Wahl, A. C. and N. A. Bonner. (1951). Radioactivity Applied to Chemistry. John Wiley and Sons.

Wang, J. H. (1951). Radioactivity applied to self-diffusion studies. In Radioactivity Applied to Chemistry, edited by Wahl and Bonner, pp. 62-81, John Wiley and Sons.

Whipple, R. T. P. (1954). Concentration contours in grain boundary diffusion. Philosophical Magazine. Vol. 45, pp. 1225-1236.

Wollast, R. (1967). Kinetics of the alteration of k-feldspar in buffered solutions at low temperature. Geochim. Cosmochim. Acta. Vol. 31, pp. 635-648.

APPENDICES

APPENDIX A

DERIVATION OF DIFFUSION EQUATION FOR EXCHANGE

APPENDIX A

DERIVATION OF DIFFUSION EQUATION FOR EXCHANGE

Consider Fick's 2nd law for the case described in the text and the following initial and boundary conditions:

$$C = C_o, \qquad x > 0, \qquad t = 0$$

$$C = C_1, \qquad x = 0, \qquad t \geq 0$$

Using the Laplace transform $\left[f(p) = \int_o^\infty e^{-pt} f_{(t)dt} \right]$ on both sides of Fick's 2nd law gives

$$\text{I.} \quad \int_o^\infty e^{-pt} \frac{\partial^2 C}{\partial x^2} \, dt - \frac{1}{D} \int_o^\infty e^{-pt} \frac{\partial C}{\partial t} \, dt = 0$$

Since the order of differentiation and integration can be interchanged, the first integral becomes

$$\text{II.} \quad \frac{\partial^2}{\partial x^2} \int_o^\infty C_e{}^{-pt} \, dt = \frac{\partial^2 \overline{C}}{\partial x^2}$$

Integrating by parts, the second integral becomes

$$\text{III.} \int_0^\infty e^{-pt} \frac{C}{t}\, dt = \left[Ce^{-pt}\right]_0^\infty + p\int_0^\infty Ce^{-pt}\, dt$$

$$= - C_o + p\overline{C}$$

Putting II and III in I gives

$$\frac{\partial^2\overline{C}}{\partial x^2} - \frac{p\overline{C}}{D} + \frac{C_o}{D} = 0$$

A general solution to this equation is

$$k_1 e^{\sqrt{\frac{P}{D}}\, x} + k_2 e^{-\sqrt{\frac{P}{D}}\, x} + \frac{C_o}{p} = \overline{C}$$

$$k_1 = 0 \text{ since } \overline{C} \not\rightarrow \infty \text{ as } x \rightarrow \infty$$

$$k_2 = \frac{C_1 - C_o}{p} \text{ since } \overline{C} = \frac{C_1}{p} \text{ at } x = 0$$

$$\text{then } \overline{C} = \left(\frac{C_1 - C_o}{p}\right) e^{-\sqrt{\frac{P}{D}}\, x} + \frac{C_o}{p}$$

this corresponds to

$$C = (C_1 - C_o) \left(\text{erf C} \frac{x}{2\sqrt{Dt}}\right) + C_o$$

in a table of Laplace transforms and can be rearranged to

$$\frac{C - C_1}{C_o - C_1} = \text{erf} \frac{x}{2\sqrt{Dt}} \, .$$

APPENDIX B

DETAILED DESCRIPTION OF PROCEDURE

APPENDIX B

DETAILED DESCRIPTION OF PROCEDURE

Exchange Diffusion Study

Sample Preparation

Approximately 35 grams of unaltered albite from Amelia County, Virginia were found in a tungsten carbide mortor in portions of a few grams. The resulting powder was placed in a plastic jar and shaken with a tungsten carbide ball until thoroughly mixed. The specific surface area of a portion was then determined by nitrogen adsorption and use of the BET equation and found to be about 1.4 M^2/gram. The composition of this albite was essentially that of pure albite ($NaAlSi_3O_8$) with about .25% K_2O and .20% CaO as determined by x-ray fluorescence.

Solution Preparation

Approximately 6 liters of 0.1N NaCl were prepared by placing 5.8448 grams NaCl in a 1 liter volumetric flask and bringing to volume with distilled, deionized water. This operation was repeated six times to give six liters which were all placed in a five-gallon polyethylene bottle.

The pH as measured using a Photovolt Digicord pH meter with a D 3204 glass electrode was 5.57 at 23°C.

Apparatus

The sample cell consisted of a 1 liter polyethylene bottle with the upper portion cut off at the shoulder and plugged with a number 14 rubber stopper in which two large holes were drilled. During the runs the bottle was placed in a water bath, the temperature of which was controlled by a Lauda/Brinkmann model K-2/R circulator. A teflon-coated stirring bar was placed inside the cell and a thermometer in a water-filled bottle set in the bath to determine the temperature. The sample itself was contained (with some solution) in a cellophane semipermeable membrane which was suspended through one of the holes from a stirrer. The sack was used to keep the solid particles out of the solution collected. One run was made without the membrane, indicating it had little effect on the movement of Na. When no membrane was used the solid was centrifuged out, as indicated in a later description of the experimental runs. The material inside the membrane was agitated by rotation of the membrane, while the stirring bar agitated the solution outside the membrane. Samples of the solution were collected by inserting a 2 ml pipet through the other hole in the stopper. A diagram of the apparatus is shown in Figure 2.

Experimental Runs

Five grams of albite and several 7 ml portions of 10 ppm NaCl solution were placed in polyvials and irradiated for 10 minutes in the MSU reactor at a flux of 10^{12} neutrons/cm^2sec. Previous examination of the spectrum of the irradiated albite using a high-resolution [Ge(Li)] detector indicated that, while Si and Al were activated, only sodium remained activated 24 hours after the irradiation (Figure 2). About 24 hours after the irradiation the solid and approximately 200 ml of 0.1N NaCl solution were placed in a presoaked cellophane membrane and the membrane suspended in the reaction cell containing about 400 ml of the 0.1N NaCl solution. In all runs 5 grams of albite were used per 500 ml of NaCl solution. The magnetic stirrer and stirrer from which the sample was suspended were then started. The polyvials containing the irradiated NaCl solution were all emptied into a 100 ml volumetric flask and the flask suspended in the water bath. A 100 ml flask of unirradiated NaCl solution was also placed in the bath. To collect a sample of the solution, both stirrers were stopped and 2 ml of the solution withdrawn from the cell, outside the membrane, using a 2 ml transfer pipet inserted through the hole in the stopper. The sample was placed in a labeled plastic counting tube, the tube capped and the time recorded. Two ml of unirradiated solution were used to replace the solution withdrawn. The position of the surface of the solution in the bottle with respect to a reference line drawn on the side of the bottle was noted to detect loss due to evaporation. If any decrease was noted, deionized water was added to maintain the volume. Two ml of the irradiated 10 ppm NaCl solution were also placed in the counting tubes. After 10 or so samples had been collected, the samples, standards and background were counted on a Packard automatic γ-ray spectrometer. Each sample was counted for 10 minutes using a voltage of 8.1, a gain of 9.5% and the counter windows open (since only the activated sodium was present). The counting sequence was: empty tube--sample--standard--empty tube. The concentration of released Na was calculated using the following formula:

$$\begin{matrix}\text{concentrated}\\ \text{sample}\end{matrix} = \frac{(\text{activity sample--background})}{(\text{activity standard--background})} \times \begin{matrix}\text{concentration}\\ \text{standard}\end{matrix}$$

Runs were made at 25, 45 and 75°C.

As mentioned above, one run was made without the membrane in order to ascertain possible effects of the membrane. This was carried out at 65°C using a centrifuge to remove the solids. The same experimental setup except that 5 grams of albite was placed loose in 5000 ml of solution in the cell. The suspension was agitated with both a magnetic stirring bar and with a stirrer with a paddle. To collect a sample, both stirrers were stopped, the time recorded and 5 ml of the suspension withdrawn. The stirrers were then started again and the 5 ml centrifuged in a bench centrifuge at about 1275 rpm for 10 minutes. The centrifuge tube was then carefully removed and the top 2 ml of solution pipeted off. The 2 ml was clear and no turbidity could be seen. The 2 ml samples and standards were then counted as described above. The remaining liquid in the centrifuge tube was poured off the solid in the bottom and 5 ml of fresh 0.1N NaCl solution at the bath temperature added. The solid was brought back into suspension using a teflon-coated stirring rod and the suspension poured back into the sample cell to restore the lost solid and solution.

With the membrane, samples were collected every hour for 24 hours. Without the membrane, samples were collected every two hours for 24 hours. The time-concentration and temperature-rate relationships were then examined.

Sectioning Diffusion Study

The procedure used in the study of diffusion in the solid will be described here. To determine diffusion coefficients for the albite, the method outlined in the theory section for homogeneous diffusion was attempted.

Sample Preparation

Small fragments with the largest cleavage surface parallel one of the major cleavages (010, 001, and 110) were selected so as to be as free of fractures as possible. The fragments were prepared by first grinding the side opposite the cleavage on a diamond lap in water until it was approximately parallel the cleavage surface on the front side. Since the cleavage surfaces were not perfect, it was necessary to grind a small portion off the cleavage and as parallel to it as possible. The thickness of the resulting fragment was then measured in several places with a micrometer (±.0001 inches) to make sure the back side was parallel the front side. The front side was then abraded slightly with 400 mesh carborundum paper dry and wiped with a Kimwipe to remove the dust. The resulting fragments had flat surfaces about 5×10 mm^2 and about parallel the major cleavages. At this stage the sample was ready for a layer of tracer to be placed on it. The transfer of a layer of Na^{22} was made in the following way. Rectangles (10×20 mm^2) of 5μ Millipore filter paper were cut and taped to standard petrographic slides. The filter paper was then saturated repeatedly with a weak solution of $NaCl^{22}$. Ten drops were placed on each slide over a period of 24 hours. The final activity of the slide was about 700,000 counts/minute. The slides were allowed to dry completely. The transfer was then made by clamping the mineral fragment between the doped filter paper on the slide and another petrographic slide in a small c-clamp. This was done in such a way that the dryly abraded surface was pressed firmly against the active Millipore filter. The Na^{22} in the filter was then exchanged with the Na^{23} in the surficial layer of the albite. It was found that little transfer could be made when the filter was completely dry. The transfer was attempted again after dampening the paper by spraying a fine mist of distilled water in the air over the paper using a plastic atomizer. The paper still had a dry appearance, but the transfer was as efficient as when the paper was moistened by placing a small drop of the $Na^{22}Cl$ solution on the paper with a dropper. The transfer time was an hour to two hours and the activity of the mineral surface resulting from such a treatment was in the range of 10-20,000 counts/minute (background was about 1200 counts/minute). The best transfer seemed to occur when the mineral was clamped most squarely against the filter paper as indicated by the indentation in the paper after removal. By grinding off several layers of the mineral before much diffusion had occurred (right after doping and mounting) it was found that the activity was primarily in the top several microns of the mineral. After transfer and before measuring the activity, the surface of the mineral was cleaned with a dry Kimwipe to remove any NaCl crystals. Measurement of the activity before and after such cleaning indicated little decrease in activity.

Experimental Runs and Apparatus

After the above preparation, the sample was placed in an oven and the temperature increased slowly to the temperature at which diffusion was to be examined. It was found that the temperature of the oven could be increased rapidly to 300°C. Above this temperature, however, rapid increase of the temperature caused the fragments to break. A rate of increase of 25°C per 30 minutes was found to be a reasonable compromise between a slow rate of temperature increase and a short period of variable temperature relative to the period under which diffusion in the mineral was to be examined. Fragments parallel the 001 cleavage still broke at 500°C however.

After diffusion for a given period of time, the temperature was reduced to 300°C at a rate equal to the rate it was increased at and the sample was removed from the oven. As mentioned in the section on homogeneous diffusion, one needs activity as a function of depth in the mineral. In order to do this, layers of the mineral had to be ground off parallel the doped surface. A device was machined from brass and aluminum to attain this end. In general, it consisted of a brass well which contained a disc of 400 mesh carborundum paper mounted in the bottom and an aluminum plug which fitted in the well. The bottom of the well could be removed to change the carborundum paper. A hole was machined in the end of the aluminum plug (offset from the axis of the plug) in which a small brass with mounted sample could be placed. A picture of the device is given in Figure 3.

The mineral fragment was mounted on the brass plug using epoxy and the epoxy cured in a low-temperature oven at 60°C for 45 minutes. After mounting, the activity was measured using a Nuclear-Chicago Model 8725 Analyzer/Scaler with a standard NaI scintillation crystal. The sample on the plug was placed under the crystal in a plastic stand in such a way to maintain the same geometry with respect to the crystal each time. The stand was located in a lead "house" to lower the background. The activities measured before diffusion were measured in exactly this way with the exception that the fragments were not epoxied to the brass plug, but merely set on it. New brass plugs had to be machined whenever a fragment was epoxied to the plug.

After measuring the activity, a layer was ground off in the device described above by placing the brass plug in the aluminum plug and then placing the aluminum plug in the well. The face of the mineral fragment then rested against the carborundum paper. When the plug was turned, material was ground off the mineral fragment. All grinding was done with methanol in the well to prevent radioactive dust from being thrown into the air. One or two turns were generally sufficient to remove .0001-.0002 inches of material. This was determined by measuring the change in thickness of the sample and plug with a micrometer after grinding. The thickness could be estimated to .0001 inches and, by taking several measurements, the parallel nature of the surface could be verified. Before measuring the activity and after grinding, the fragment was cleaned carefully with a Kimwipe and methanol to remove dust. All tissues and abrasive were carefully discarded in radioactive waste containers while wet so as to not allow radioactive dust into the air.

After the above grinding, the activity and background were measured again. From such activity-thickness measurements, plots of x vs y were obtained as outlined in the section on homogeneous diffusion. The first three runs were made using 010, 001 and 110 fragments at 300°C for 24 hours. Runs were then made with 010, 001 and 110 fragments at 500°C for about three days and at 500°C for about six days. During these runs the 001 fragments broke. Four fragments were sectioned (two after three days, two after six days) and plots made of x vs y. Runs were then made at 595°C using 010, 001 and 110 fragments. These runs were about five days in length and the 110 fragment broke. Again, the fragments were sectioned and plots made of x vs y.