



SOLID STATE DIFFUSION IN THE FELDSPAR SYSTEM

by

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### ABSTRACT

The diffusion coefficients for the migration of sodium in single crystals of transparent oligoclase have been determined for the temperature range 700-1050° C. The diffusion coefficients for migration perpendicular to (001) for two different specimens of oligoclase are given by the following expressions:

$$D_{\text{Na}} = 7.1 \times 10^{-4} \exp \left( - \frac{32,900}{RT} \right) \text{ cm}^2 / \text{ sec.}$$

$$D_{\text{Na}} = 1.4 \times 10^{-3} \exp \left( - \frac{34,300}{RT} \right) \text{ cm}^2 / \text{ sec.}$$

The diffusion coefficient for migration perpendicular to (010) is given by:

$$D_{\text{Na}} = 2.0 \times 10^{-4} \exp \left( - \frac{29,600}{RT} \right) \text{ cm}^2 / \text{ sec.}$$

The diffusion coefficients reported have been obtained using radioactive tracer methods developed for this investigation. The sectioning technique used was based on the successive removal of thin layers of material by grinding. The concentration-penetration data was obtained by measuring the total gamma activity of the sample after the removal of each layer.

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## Table of Contents

Abstract		
Acknowledgements		
List of Tables		
List of Figures		
I.	Introduction.....	1
	A. Statement of Problem.....	1
	B. Purpose of Present Work.....	2
II.	Review of Previous Work.....	3
	A. Diffusion in the Solid State.....	3
	B. Metasomatism in Rock Formation.....	9
	C. The Feldspar System.....	12
	D. Diffusion Studies at M. I. T.....	13
III.	Experimental Techniques and Equipment.....	14
	A. Selection of Material for Diffusion Studies.....	14
	1. Criteria Followed in Selecting Material.....	14
	2. Chemical and Spectrographic Analysis of Samples.....	15
	3. Mineralogical Analysis of Samples.....	15
	4. Orientation of Material.....	15
	B. Preparation of Diffusion Couples.....	17
	1. Mechanical Preparation of Samples.....	17

a).	Source of Radiotracers Used.....	21
b).	Deposition of Radioactive Film.....	22
3.	Sealing of Diffusion Couple in Inert Atmosphere.....	28
C.	Diffusion Anneal.....	29
1.	Design of Furnace.....	29
2.	Introduction and Removal of Samples from Furnace.....	29
3.	Temperature Measurement.....	31
D.	Measurement of Radiotracer Distribution.....	32
1.	Nuclear Properties of Radio- nuclides Used.....	32
2.	Use of Scintillation Counter.....	34
a).	Design of Scintillation Counter.....	34
b).	Determination of Concentration- Penetration Data.....	35
c).	Evaluation of Data.....	38
3.	Use of Beta-ray Autoradiography.....	39
a).	Preparation of Beta-ray Autoradiographs	39
b).	Study of Microdistribution of Radiotracer.....	45
c).	Study of Grain Boundary Diffusion.....	46
E.	Methods of Evaluating Data.....	47
IV.	Experimental Results.....	52
A.	Presentation of Results.....	52
B.	Discussion of Results.....	77

V. Summary and Conclusion.....	79
Literature Cited.....	81
Biographic Note.....	93

## List of Figures

Figure Number		Page Number
1.	Grinding Machine.....	19
2.	Grinding Machine Detail.....	20
3.	Detail of Vacuum System.....	23
4.	Diagram of Shield and Specimen Holder.....	24
5.	Photograph of Evaporation Unit.....	26
6.	Diagram of Evaporation Unit Electrode Assembly.....	27
7.	Furnace Arrangement.....	30
8.	Radionuclide Decay Schemes.....	33
9.	Gamma-Ray Scintillation Counter Schematic.....	36
10.	Photograph Scintillation Counter Equipment.....	37
11.	Nuclear Emulsion Sensitivity Curve.....	41
12.	Diagram of Mounting Fixture.....	43
13.	Self-Diffusion of Sodium in Oligoclase Perpendicular to (001).....	54
14.	Diffusion Coefficient Graphs.....	55
15.	Self-Diffusion of Sodium in Oligoclase Perpendicular to (001).....	62
16.	Diffusion Coefficient Graphs.....	63
17.	Self-Diffusion of Sodium in Oligoclase Perpendicular to (010).....	69
18.	Diffusion Coefficient Graphs.....	70

## List of Tables

Table Number		Page Number
1.	Nuclear Properties of Radionuclides Used.....	32
2.	Temperature Dependence for Diffusion Na <sup>22</sup> in Oligoclase.....	53
3.	Diffusion Coefficient at 705° C.....	56
4.	Diffusion Coefficient at 800° C.....	57
5.	Diffusion Coefficient at 902° C.....	58
6.	Diffusion Coefficient at 1000° C.....	59
7.	Diffusion Coefficient at 1050° C.....	60
8.	Temperature Dependence for Diffusion Na <sup>22</sup> in Oligoclase Perpendicular (001).....	61
9.	Diffusion Coefficient at 705° C.....	64
10.	Diffusion Coefficient at 800° C.....	65
11.	Diffusion Coefficient at 1000° C.....	66
12.	Diffusion Coefficient at 1058° C.....	67
13.	Temperature Dependence for Diffusion Na <sup>22</sup> in Oligoclase Perpendicular (010).....	68
14.	Diffusion Coefficient at 1040° C.....	71
15.	Diffusion Coefficient at 1005° C.....	72
16.	Diffusion Coefficient at 900° C.....	73
17.	Diffusion Coefficient at 810° C.....	74
18.	Diffusion Coefficient at 705° C.....	75
19.	Diffusion Coefficient at 596° C.....	76



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## I. INTRODUCTION

Several geologists<sup>(163)</sup> have attempted to explain certain perplexing geological phenomena on the basis of the transport of matter over long distances through or around the grains in crystalline rocks. On the other hand many geologists<sup>(16,105)</sup> have opposed the effectiveness of solid state diffusion as a geological process, in cases of a large scale nature. However, developments in recent years have convinced most geologists of the feasibility of solid state diffusion as a geological process operative in many cases. Where 20 years ago few would have accredited in any part the origin of granite and quartzofeldspathic rocks to metasomatic replacement, today most are willing to accept a polygenetic origin of these rocks<sup>(113)</sup>.

It is paradoxical that the exponents of the extreme views have based their arguments in general on the same meagre experimental evidence. It appears in many cases that prejudice toward pre-determined theories, rather than objective evaluation of the scant experimental information available has been the rule<sup>(16, 113)</sup>.

In order to attack successfully such fundamental problems as the origin of granite and quartzo-feldspathic rocks, all pertinent available data must be objectively evaluated. As many students of the problem have previously noted, the problem should be examined as a whole, taking evidence equally from both the field and the laboratory. This has proven to be rather difficult since few people have been fully

qualified to examine evidence judicially from such varying fields of endeavor, and at the same time logically synthesize this information into a satisfactory working hypothesis. Noting the general lack of basic information, it should prove more fruitful to expend our efforts by further fundamental investigations than along lines which have appeared to be in many cases the defenses of preferred theories.

The aim of this work has been to contribute to the controversial problem of the genesis of granitic rocks, some new experimental information on the transport of sodium and potassium through feldspar in the solid state. Since experimental techniques for the accurate determination of solid state diffusion in the feldspar system have not been available, a considerable part of the work recorded here has necessarily been concerned with methodology.

## II. REVIEW OF PREVIOUS WORK

### A. Diffusion in the Solid State

The first study on mass transport in the solid state under a concentration gradient, or solid state diffusion, was reported in a paper on the diffusion of metals by Roberts-Austen (118) in 1896. Previously Parrot, Graham, Loschmidt and others had investigated gaseous diffusion phenomena. Fick (44) in 1855 published a phenomenological theory of diffusion which is still used as the theoretical basis of diffusion studies. Experimental and theoretical work on diffusion has progressed steadily since Roberts-Austen's exploratory investigation. Rapid developments in recent years have been brought about by the increasing interest in the physics and chemistry of the solid state and the development of new experimental techniques due to the ready availability of radiotracers.

Although solid state diffusion has been formally treated in general on an operational basis, a considerable effort has been made recently in the development of kinetic and statistical-mechanical theories of diffusion in order to describe the atomistic mechanism involved. In this work the subject is treated on a phenomenological basis and the concept of solid state diffusion is restricted to the movement of atoms or groups of atoms whether bearing charge or not under a concentration

gradient in solids of macro size. The atomistic mechanisms considered are (1) mass movement interstitially, (2) movement resulting from the exchange of the occupant of one structural position with that of another, or from the exchange of groups of occupants, (3) movement resulting from transfer through structural vacancies. Transport phenomena discussed here are considered as taking place in only one of the three following ways: (1) diffusion through an ordered or crystalline matrix, volume diffusion, (2) diffusion through a disordered or glass matrix, grain boundary diffusion, and (3) diffusion on free surfaces, surface diffusion. Thus, the work considered here, being restricted to the solid state, is not concerned with mass transport through the facilities of other media such as fluids or under other driving forces such as temperature.

The theoretical and experimental aspects of solid state diffusion have been the subject of an increasing number of publications recently, especially in the field of metallurgy. Barrer (8) and Jost (83) have published monographs on the subject both of which include detailed bibliographies covering work published up to 1952. Several recent books (155-162), based on the results of recent symposia on diffusion and related subjects review the voluminous work reported in the metallurgy field.

A critical review of all work on diffusion in metallurgy up to 1936 has been published by Mehl (101) and more recent work

by Birchendall (157). The present state of diffusion theory has been described in detail by LeClair (158), Seitz (129), and Zener (154). The significance of the chemical potential as the true driving force in diffusion has been discussed by Darken (35-36). Smoluchowski (1, 45, 138) and Chalmers (2, 27) reported on grain boundary diffusion, both on an experimental and theoretical basis. Read and Shokley (114) have considered the application of dislocation theory to grain boundary diffusion. The atomistic mechanisms of diffusion have been treated by Bardeen and Herring (6), Huntington (69-71), Kirkendall (86-87), Seitz (129), and Zener (153).

Work of geological interest was initiated by Van Ostrand (144) at the U. S. Geological Survey in 1915, following the earlier work of Becker (10), who considered the problem of diffusion as a mechanism in rock differentiation. Bowen (14) investigated diffusion in silicate melts and concluded from his experimental results, as did Becker earlier, diffusion through long distances was of no geological importance. Tiselius (141-142) and Hey (67) studied the diffusion rates of various materials, especially water and ammonia in solid zeolites. Recently, Rosenqvist (119-122) has initiated the first work of quantitative geological significance with his study of diffusion rates of lead and radium in feldspars. Verhoogen and Vogel (145) have recently reported on the diffusion of various ions in quartz, and Jensen

(75-76) has reported on the diffusion of sodium in perthite and copper in chalcocite at temperatures less than 500 degrees Centigrade.

In the field of ceramics Blau and Johnson (77-78) among others have contributed considerably both with regard to data and techniques on the diffusion of some alkali metals in various silicate glasses. Recent developments in semi-conductor studies have made available diffusion data of great interest, because of the uniquely high diffusion coefficients. Fuller and Struthers (48) have reported the diffusion coefficient of copper in germanium as being  $10^{-5}$  cm<sup>2</sup> per second at 700 degrees Centigrade. These results have been substantiated beyond question. Wagner (167) has recently discussed a special case of diffusion in semiconductors exhibiting an extremely low activation energy resulting in diffusion coefficients greater than those normally found in gases. Ross (124) and Wagner (146) have discussed the relationship between diffusion and reaction rates in the solid state for several sulfide compounds.

Solid state diffusion as described earlier is considered to include all the processes which tend to reduce spontaneously concentration gradients under isothermal and isobaric conditions, and not in general the atomistic processes involved as atoms move among structural positions. Volume diffusion refers to that contribution which occurs within a single grain. In considering the types of grains encountered in nature, and even in general those

Prepared in the laboratory, it is important to note how they differ from the idealized structural array of atoms. In general deviations from ideality can be classified as either reversible or irreversible. With regard to reversible deviations Wagner (147) and others have shown that the most stable state of a system does not necessarily demand that all structural positions be filled but indeed requires, in many cases, because of entropy considerations an equilibrium concentration of vacancies. It has also been found that the omnipresent impurity content greatly influences the equilibrium vacancy concentration. Buerger (23) has discussed the importance of lineage structure and others (161-162) have described in detail the problems of substructure. It should be noted that, in general, and especially in regard to the vacancy mechanism of diffusion, mass transport would be impossible in a truly perfect crystal. With regard to irreversible deviations Smith (133), among others, has described the large internal surfaces usually found in crystals of a natural origin. The importance of microsegregation phenomena and other conditions of non-equilibrium have been considered with regard to their effects on diffusion.

The recent work of Achter and Smoluchowski (1), Flanagan and Smoluchowski (45), and Smoluchowski (138) clearly indicate that at least in metals the effects of equilibrium imperfections in nearly perfect crystals such as lineage structure and other substructure phenomena have negligible effect on diffusion coefficients. They



showed that in the isometric system studied grain boundary diffusion rates were a function of the angle between the cube directions of the two grains surrounding the grain boundary. They concluded that at small angles the grain boundary consists of individual dislocations and that volume diffusion is the predominant process. As the angle increases the grain boundary diffusion rates increase and reach a maximum at  $45^{\circ}$ . No information is available for members of the more general crystallographical systems, however, Smoluchowski's work indicates that volume diffusion predominates except in areas of high lattice distortion.

Chemical techniques and the analysis of diffusion data have been reviewed by Wells (157). The use of radiotracers in diffusion measurements has been reviewed by Hofman (157). In general the techniques are available in the literature that has been surveyed by Barrer (155) and Jost (156).

## B. Metasomatism in Rock Formation

The origin of large masses of plutonic rocks is a perplexing problem. Over 95% of these plutonic masses that reach batholithic dimensions have approximately the same mineralogical composition. The most notable exceptions are the large monomineralic masses of anorthosite. Although the work of Bowen (15), Niggli (105) and others on magmatic differentiation has found general acceptance as the operational basis for explaining many igneous rocks, sufficient evidence is available to question the applicability of magmatic differentiation to the larger masses of igneous-looking rocks.

Keilhau in 1836 proposed a metasomatic origin for granite which has been continually developed, especially by a group of French and Scandinavian petrologists. The advocates of a metasomatic origin have submitted a number of field observations as the basis for their arguments. Read (113) has reviewed these observations and especially emphasized the space problem. Reynolds (115) has described in detail the sequence of geochemical changes involved and Lapadu-Hargues (90-91) has carried on a detailed statistical study of the mineralogical and chemical composition of a large number of rocks varying in type from unaltered sediments to granite. Misch (104) has studied in detail the structural and textural gradations and country rock. Gruner (62) has described the occurrence of feldspar crystals in shales and silts. A summary of the main petrological points in favor of meta-

somatism has been made by Read (113). Fairbanks (43) and recently Sullivan (136) and Goodspeed (58) have described the relationship between mineralization and granitization.

Of the several mechanisms of metasomatism considered, at the present time the diffusion process has become of increasing interest. The early work of Judd (84) on the growth of crystals in solid rock and Liesegang's (93) book on geological diffusion laid a basis for the following work. McCallien (94) in 1934 summarized the earlier concepts on metasomatic differentiation stressing the work of himself, Stillwell, and Eskola. Garrels (50) has recently reviewed the effectiveness of fluid transport while Bain (4), Duffell (39) and Brown (20) have discussed the application of the diffusion process to the formation of ore deposits. Ramberg (112) has reviewed the entire subject in a recent monograph on the origin of metamorphic and metasomatic rocks.

In interpreting the evidence available, many geologists are essentially in agreement on a metasomatic origin. However, they differ greatly on the actual mechanism involved. The original postulates of Wegman on a transformation mechanism without fusion by means of diffusion in intergranular films have been developed by Bugge (26), Perrin and Roubault (109) and Ramberg (112). Concerning the more extreme viewpoint Perrin and Roubault have proposed that diffusion through crystal lattices is the predominant mechanism of mass transport, while Ramberg has emphasized the relative importance of grain

boundary diffusion as compared to lattice diffusion. In both cases a large scale selective transport of matter in the solid state driven by chemical potential gradients has been postulated as the metasomatic agent over the long distances involved. Little experimental evidence is available both on the diffusion coefficients and the chemical potential gradients that are operating under the physical conditions involved in the metasomatic process.

C. The Feldspar System

With regard to the most prominent mineral system involved in granitization, there is a large amount of information available. Since the early work of Bailey (3) on the albitization of plagioclase feldspar a considerable amount of research has been carried out. Bowen (13) studied the phase relationships at elevated temperatures. Bowen and Tuttle (17, 143) have reported on high temperature modifications of feldspar and modifications in contiguous feldspars. Chao and Taylor (28) have carried on x-ray structural studies. Laves (92) has discussed the structure of potash feldspars in detail, and Kohler (88) has reviewed the recent results. Gates (51) has described the physical and chemical properties of natural feldspar material. A recent monograph edited by Emmons (165) discusses in great detail the plagioclase members of the feldspar system, and especially their petrogenic relationships. The work described is summed up by Emmons (42). Rosenqvist (121) has recently studied the orientation of perthite lamellae in feldspars on the basis of his experimental work on diffusion coefficients in the feldspar system.

D. Diffusion Studies at M. I. T.

The work reported here has been benefited by the author's association with the various people carrying on diffusion studies at M. I. T. Gaudin and Vincent (53) have studied self diffusion in several minerals, particularly copper sulfide in the Richards Mineral Engineering Laboratory. A group directed by Professor M. Cohen has been studying diffusion phenomena in metals. Buffington (24) has studied self diffusion in iron, Bakalar (5) has studied diffusion in iron-titanium alloys, Gatos (52) and Kurtz (89) have studied diffusion in gold-nickel alloys, and Griffiths is studying self diffusion in iron. Professor C. Wagner has been very kind in discussing many aspects of the diffusion work. In the Geology Department, Jensen (75) has reported on diffusion of copper in chalcocite and sodium in perthite.

### III. EXPERIMENTAL TECHNIQUES AND EQUIPMENT

#### A. Selection of Material for Diffusion Studies

##### 1. Criteria followed in selecting material

In order to evaluate the relative importance of the three basic mechanisms of mass transport in the solid state it is important that definite criteria be followed in choosing materials for study. The criteria depend on the mechanism under investigation, but in all cases the aim is to evaluate the variables and reduce their number to a minimum. For volume diffusion studies the most desirable material would be a perfect single crystal, while for surface diffusion studies an imperfect single crystal would be preferred. Polycrystalline material in which each grain approximates a single perfect crystal is satisfactory for grain boundary diffusion.

In general synthetic crystals are more desirable than natural crystals, both from the chemical and physical point of view. However, it has not been possible to grow satisfactory feldspar crystals of sufficient size for diffusion studies. Therefore, it has been necessary to obtain the most suitable natural crystals available. Although the feldspars are commonly found in well crystallized form, it is very difficult, if not impossible, to obtain material of the desired properties.

Following an investigation of available material, certain specimens of transparent oligoclase available in sufficient size and quantity for diffusion studies were chosen for the experimental work described here. Professor Clifford Frondel, Harvard University, was kind enough to supply

several samples of this material. Transparent crystals of labradorite and orthoclase are also available in small quantities. Professor Frondel also kindly supplied samples of these materials. These transparent specimens are the most suitable feldspar crystals for diffusion studies known to the author.

## 2. Chemical and spectrographic analysis of samples

The samples were chemically analyzed by standard flame photometer techniques with a Perkin-Elmer Flame Photometer, for sodium, potassium, and calcium. Aluminum and silicon were determined by members of the Chemical Analysis Laboratory, Metallurgy Department, Massachusetts Institute of Technology. A semiquantitative spectrographic trace element examination of the samples was carried out in the Spectrographic Laboratory, Geology Department, Massachusetts Institute of Technology. Standard techniques developed in the Spectrographic Laboratory were used ( ). The assistance of Dr. William Pinson in the spectrographic analysis is greatly appreciated.

## 3. Mineralogical analysis of samples

The microstructure of all samples was studied optically in order to determine the presence of inclusions and other grain boundary phenomena. Powder x-ray analysis of the samples was carried out using a standard North American X-ray Spectrometer. The recordings were compared with those obtained with National Bureau of Standards Feldspar Standards.

## 4. Orientation of material

The diffusion coefficients determined in the samples investigated are those perpendicular to the two prominent cleavage directions in plagioclase,



the cleavage being perfect parallel to the base (001) and good parallel to the brachypinacoid (010). The samples were oriented in a vise after the cleavage direction was checked optically.

All the work described in this part was carried out on material that had been exposed to conditions similar to those used in the actual diffusion experiments. The results of the analysis carried out on the samples used in the diffusion experiments as described above are reported in Section IV:A.

B. Preparation of Diffusion Couples

1. Mechanical preparation of samples

a). Preparation of sample cylinders

Cylinders of 0.271 inch outside diameter and of various lengths were prepared using a Felkner diamond core drill from material oriented in a wise. The equipment necessary for this work was made available by Professor H. W. Fairbairn, Geology Department, Massachusetts Institute of Technology. Sufficient care was taken in core drilling to insure true cylinders.

b). Facing cylinders and design of special grinding machine

Plane faces were ground perpendicular to the axis of the cylinder using a specially designed grinding machine which is described below. Silicon carbide cup wheels were used for grinding the cylinder faces. The wheels used were supplied by the Norton Company, Worcester, Massachusetts. A set of wheels of grit sizes 90, 220, 320, and 600 were used. The general specification was 1-3/8 X 1", Shape A31, 37C220-MB. The cylinders were stored in distilled water until ready for use.

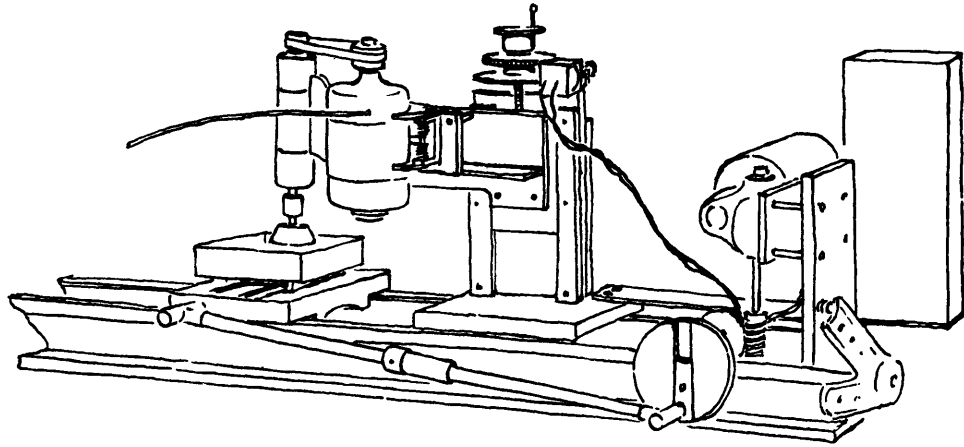
Because of the many difficulties and hazards involved in grinding radioactive samples, it was found necessary to devise some means of carrying this out automatically in a hood or other protected area. The facing of the cylinders, the sectioning of the samples for concentration penetration data, and the preparation of radioactive thin sections for autoradiographic studies were all carried out with this machine with the use of various jigs. Since portable grinding machines capable of high precision and tolerance were not available commercially it was necessary to construct the

desired machine in the Geology Department Instrument Shop, Massachusetts Institute of Technology. Mr. John Solo designed and built the machine.

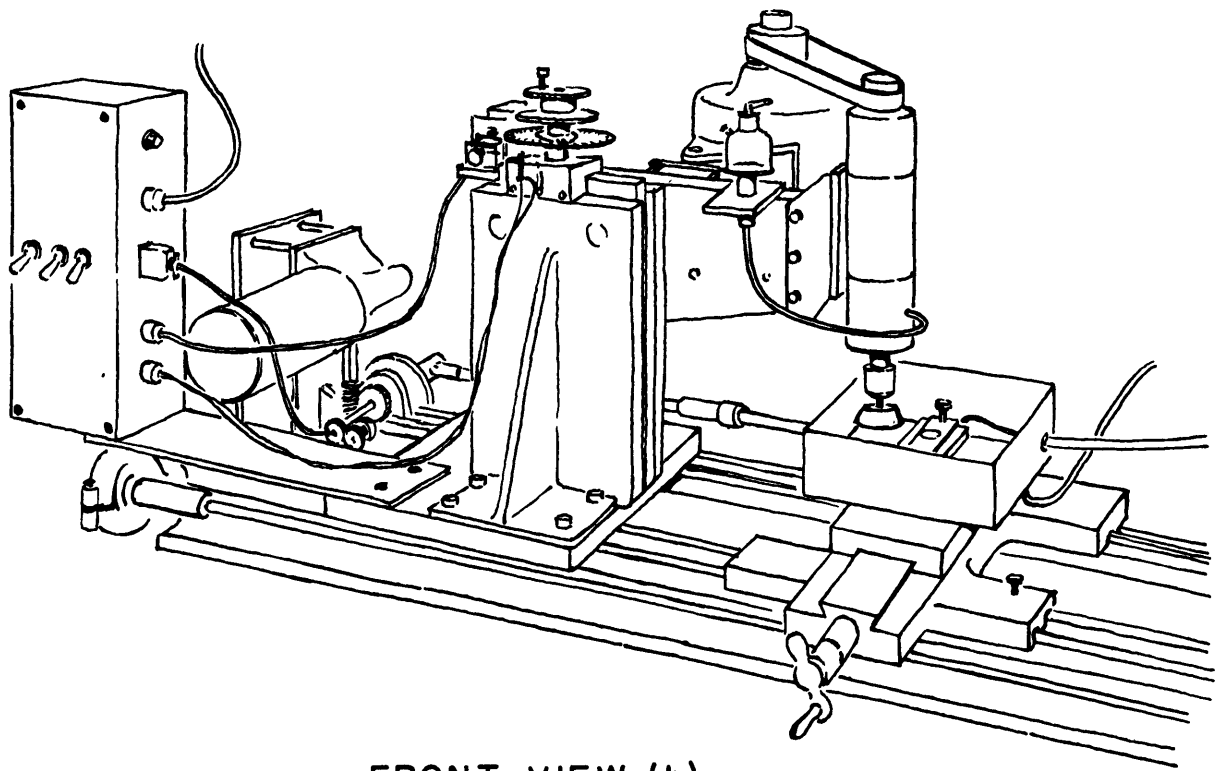
Figure 1. shows both a front and a rear view of the machine. The whole assembly can be placed in a two-by-four hood. The machine consists basically of a moving table driven reciprocally on a lathe bed under a grinder. The lathe bed was contributed by Professor Louis Ahrens, Geology Department, Massachusetts Institute of Technology. Figure 2.c depicts the jigs used to mount the materials for the various grinding operations. Figure 2.b is an exploded view of the jig used in mounting the sample cylinder for sectioning. The sample cylinder is mounted in Part m and held in place by a lock screw which is not shown in the drawing. Part n is so designed that the sample is easily and accurately oriented with regard to the spindle shaft. This is very important since the cylinder holder is removed after each sectioning in order to measure the residual radioactivity in the sample cylinder. The cylinder must be repositioned with great accuracy. When the machine is used to grind thin sections, the cylinder mounting jig, which is fastened to the table with two bolts, is removed. During grinding, water is continuously fed to the work through a nozzle. Different nozzles are used depending on the operation in progress. During operation the jig box is covered with a plastic plate to contain the water spray.

The samples are centered under the grinder spindle using the micrometer feed on the table. The table is driven by a Dumore Type KVA motor coupled to the reciprocating drive through a worm gear. The traverse distance

# FIGURE I GRINDING MACHINE

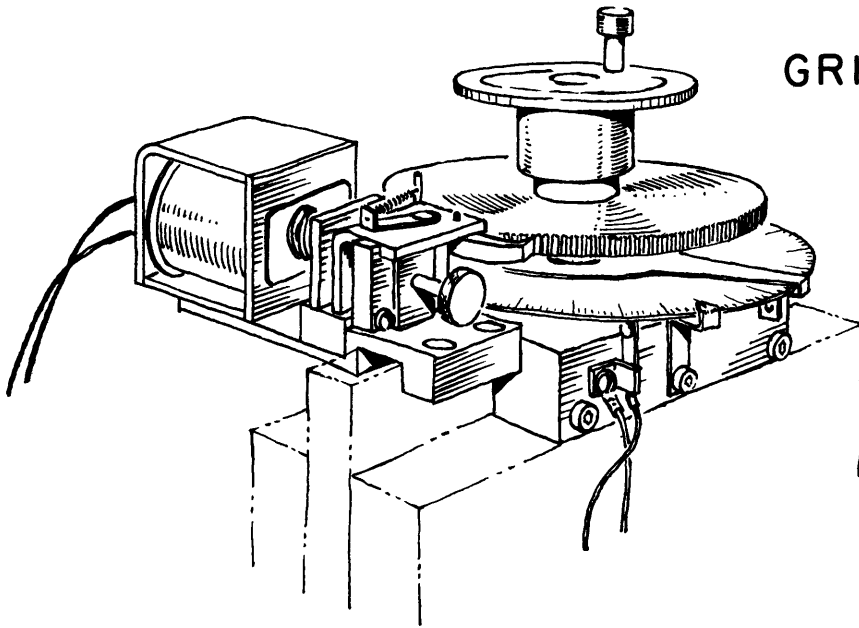


REAR VIEW (a)

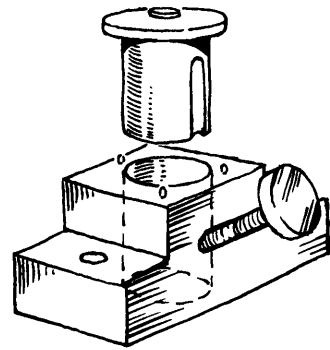


FRONT VIEW (b)

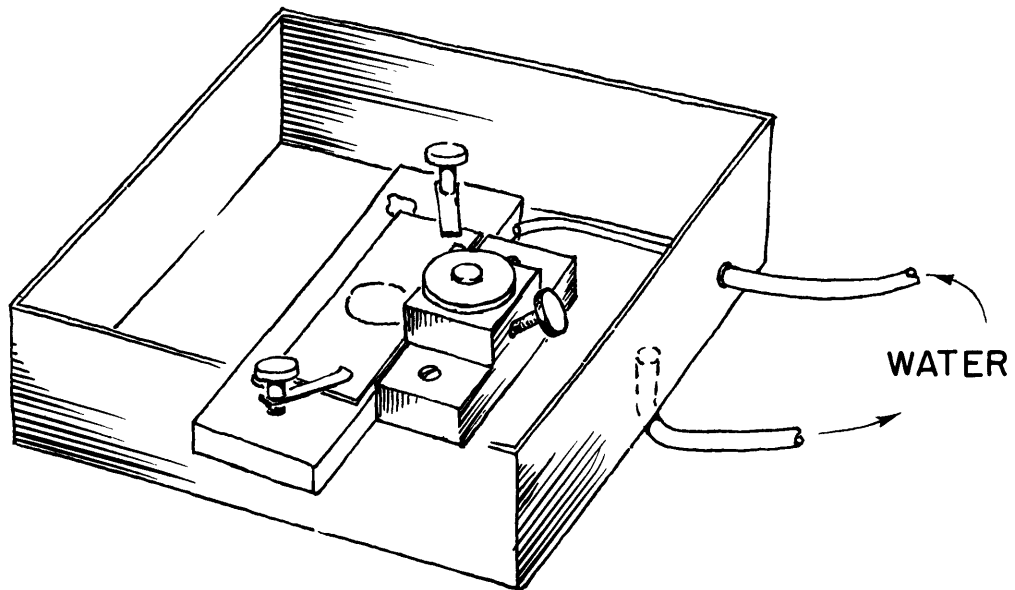
FIGURE 2  
GRINDING MACHINE  
DETAIL



DOWNFEED MECHANISM (a)



CYLINDER MOUNTING JIG (b)



MOUNTING JIG AND BOX (c)

and relative positioning of the table can be controlled through adjustment of the arm length and eccentricity of the arm bar. The table speed is well controlled through the use of a Variac allowing careful positioning of the table under the grinder.

The grinder spindle is mounted on a travel plate, which is enclosed by gibbs and driven by a fine thread. The grinder is automatically downfed in steps of 4 microns or more by a solenoid controlled pawl engaging a ratchet which drives the feed screw. Figure 2.a shows the downfeed mechanism. The rate of downfeed and positioning is controlled through a gear train and cam arrangement which allows flexibility in the downfeed cycle timing.

The machine has proven very satisfactory for most grinding operations, however, difficulties are encountered in the preparation of the thin sections necessary for autoradiographic studies.

## 2. Introduction of radioactive film on samples

### a). Source of radiotracers used

The radionuclides used in this work were  $^{22}\text{Na}$ ,  $^{24}\text{Na}$ , and  $^{42}\text{K}$ . All three radionuclides were prepared at the Massachusetts Institute of Technology Cyclotron by the following reactions:  $\text{Mg}^{22}(\text{d},2\text{n})\text{Na}^{22}$ ,  $\text{Na}^{23}(\text{d},\text{p})\text{Na}^{24}$ ,  $\text{K}^{41}(\text{d},\text{p})\text{K}^{42}$ . Mrs. Elizabeth Backofen isolated the carrier free  $\text{Na}^{22}$  used in this work by methods previously described (73). Sodium carbonate and potassium carbonate were irradiated using the outside probe and then converted to the chlorides. Mr. Earl White of the Cyclotron Laboratory was responsible for all the bombardments and his helpful cooperation made possible much of the work carried out.

b). Deposition of radioactive film

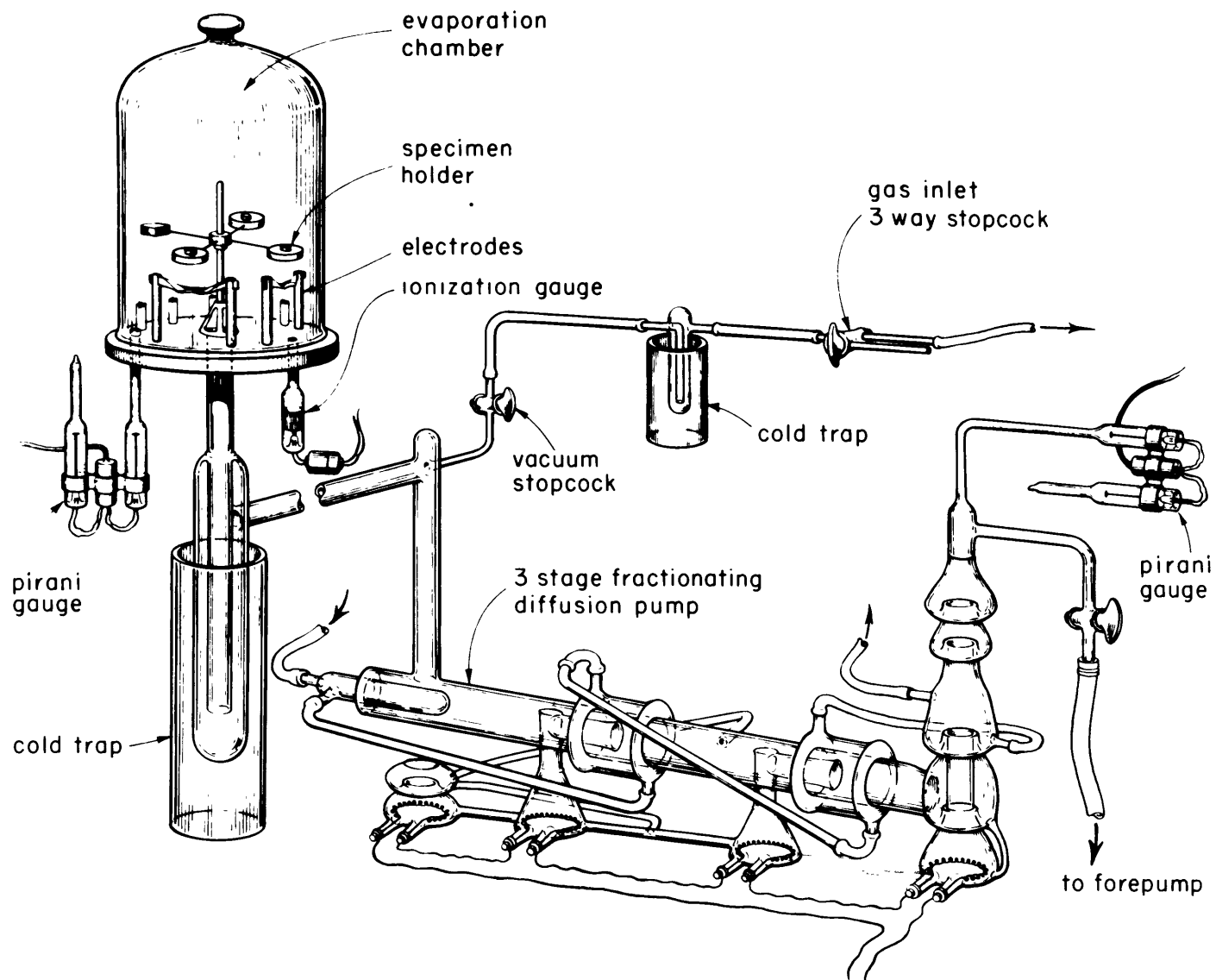
In order to study the effect of interface phenomena on the determined diffusion coefficients, three different methods of introducing the concentration gradient were used. The methods were: (1) vapor deposition followed by glazing, (2) evaporation of slips followed by glazing, and (3) in situ formation by deuteron irradiation.

(1) vapor deposition and design of equipment

The vapor depositions were made either in the unit constructed by Harvey (64) or in the unit constructed by Griffiths (89). Dr. W. Harvey and Professor H. Uhlig kindly made available their unit as did V. Griffiths and A. Kurtz, all of the Metallurgy Department, Massachusetts Institute of Technology. The basic unit is described in detail by Harvey (64).

The vacuum system consists of a three stage oil diffusion pump backed by a high capacity-high vacuum mechanical fore pump. Both the pressure in the evaporation chamber and the fore pressure were measured with a Pirani gauge. Figure 3. shows the details of the vacuum system.

The sample cylinders were mounted in the specimen holder shown in Figure 4. A layer of the radioactive salt was formed in the tantalum holder by evaporating a solution containing the desired amount of solids. In order to direct the maximum amount of radioactive material to the sample face it



DETAIL OF VACUUM SYSTEM

FIGURE 3.



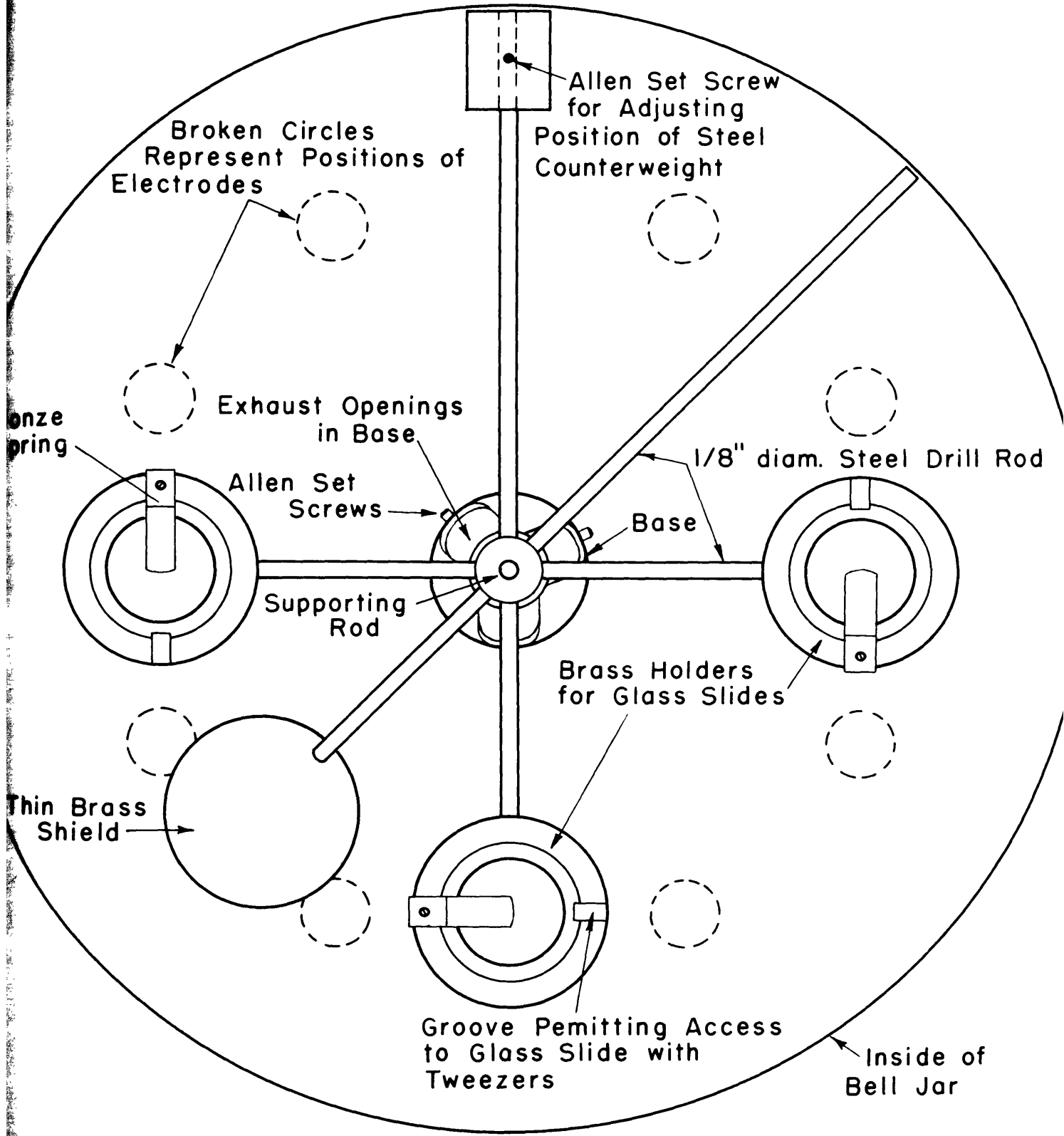


DIAGRAM OF SHIELD AND SPECIMEN HOLDER

FIGURE 4.

is necessary to control carefully the shape of the tantalum holder. Films up to one micron in thickness were deposited on the various samples. The thickness of the deposit was controlled through the voltage applied to the electrodes and through the use of a shield, as pictured in Figure 4. A satisfactory glaze was formed from the deposited radioactive film by firing at  $800^{\circ}$  C. for five minutes. Figure 5. is a photograph of the evaporation unit. Figure 6. pictures the electrode assembly used in the evaporation unit.

(2) evaporation of slips followed by glazing

The use of slips and related techniques for glazing are described in the ceramic literature (107). Blau (78), Rosenqvist (120), and Jensen (76) have applied various modifications of the method to their diffusion studies on ceramic materials. The techniques used in this work are similar to those described by Jensen (75).

Slips of the same composition as the sample were used for the work above  $900^{\circ}$  C. while sodium chloride was used for the remaining work. The slip formed by suspending finely powdered material in water was applied to a clean sample face with an eye dropper. The amount of material deposited was controlled both by the solid content of the suspension and the size of the drop. After removing water at  $110^{\circ}$  C. the glaze was formed by firing at a temperature and for a time interval necessary to obtain a well defined interface.

(3) in situ formation by deuteron irradiation

The in situ formation of a radioactive concentration gradient by deuteron irradiation has been used for diffusion studies on gold. Blau (78)



FIGURE 5.

AUTORADIOGRAPHS

FIGURE 6

(In Preparation)

has referred to the attempted use of deuteron irradiation in the diffusion studies on some glass systems by Fitzgerald. The sample cylinders used in this work were irradiated with deuterons at the M. I. T. Cyclotron. In order to reduce the probability of nuclear reactions other than the desired Oppenheimer--Phillips Reaction (d,p), a gold absorber was used to lower the energy of the deuteron beam to approximately four Mev. Although a high atomic number element was used to attenuate the beam energy, a relatively high background activity was found in all samples. Since all samples were covered with cadmium except for the face exposed to the deuteron beam in order to eliminate thermal neutron reactions, the background activity is probably due to fast neutron reactions. The range of four Mev. deuterons in feldspar is approximately 25 microns. However, no definite interface is formed due to straggling effects.

### 3. Sealing of diffusion couple in inert atmosphere

In order to control radioactive material lost through evaporation, the diffusion couples were sealed in vycor or quartz tubes and filled with argon. The tubes were evacuated using a high capacity--high vacuum mechanical pump and then filled with argon to a pressure sufficient to prevent collapse of the tubes at the elevated temperatures. The tubes were sealed using an oxy-hydrogen flame by collapsing the neck of the tube and then slowly pulling the tube with a twisting action.

## C. Diffusion Anneal

### 1. Design of furnace

The greater part of the work reported here was carried out in a vertical furnace made available by Professor R. Schuhmann, Metallurgy Department, Massachusetts Institute of Technology. The furnace and controller unit used are described in detail by Gordon (59). The equipment was constructed by Dempsey and Payton and modified by G. Powell (110) and W. Leavitt. The assistance of Payton with regard to the use of this equipment is greatly appreciated.

The furnace consists of a three inch bore R.A. 98 alundum tube wound with platinum. The tube was 24 inches long and had a  $\frac{3}{8}$  inch wall. An air spacer and  $3\frac{1}{2}$  inches of powdered magnesia were used as insulation. The furnace is shown in detail in Figure (7). The electronic controller based on the original design of Roberts (59) makes use of the platinum furnace winding as one leg of a Wheatstone bridge. A standard thyrotron phase control system is used to balance the bridge and thereby maintain constant temperature.

### 2. Introduction and Removal of Samples from Furnace

The tubes containing the diffusion couples were placed in an alundum crucible containing powdered silica. After the furnace had reached equilibrium at the desired temperature, the crucible containing the samples was quickly lowered into the calibrated area of the furnace. Platinum wire and a plastic pulley were used for raising and lowering the crucible. Figure (7) shows a cross section of the furnace containing crucible and samples.

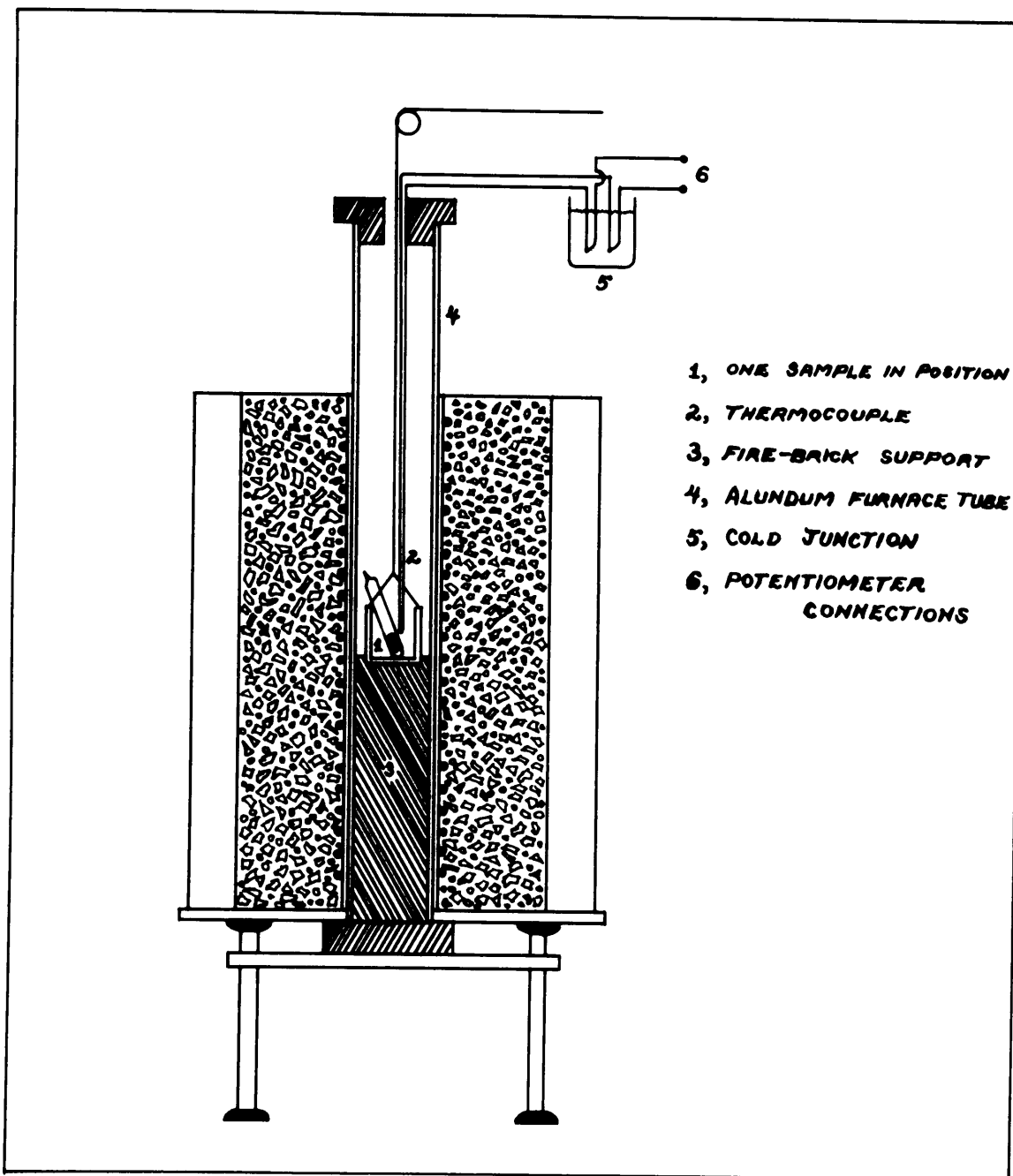


FIGURE VII FURNACE ARRANGEMENT (NOT TO SCALE).

With the furnace operating under proper control, the samples reached equilibrium conditions within five minutes. The samples were maintained at temperature for a sufficient period in order to obtain the necessary penetration of radiotracer. The samples were then quickly quenched in air by raising the crucible out of the furnace. All the samples reported here were unaffected by thermal shock as shown by visual examination.

### 3. Temperature Measurement

All temperature measurements were made with a platinum--platinum (10%) rhodium thermocouple, using an ice water bath as the reference cold junction. The measuring thermocouple was checked periodically against a standard calibrated platinum--platinum (10%) rhodium thermocouple. A sensitive Rubicon potentiometer with a sensitivity of 0.005 millivolts was used in conjunction with the thermocouple. The measuring thermocouple was placed in close proximity to the tubes containing the sample cylinders as shown in Figure (7). It was found that within the control range of the electronic controller the temperature of the measuring thermocouple was maintained to within plus or minus 2 degrees Centigrade. It was also found that the horizontal variation of furnace temperature in the calibrated zone was within plus or minus two degrees. These control ranges are in agreement with those found by the previous users of the furnace.



D. Measurement of Radiotracer Distribution

1. Nuclear Properties of Radionuclides Used

The nuclear properties of the radio nuclides used in this work are listed in Table (1). The decay schemes are shown in Figure (8).

TABLE 1.

1	2	3	4	5	6	7	8	9
Symbol	Z	T	k	Reaction		A <sub>s</sub>	A <sub>s</sub>	Yields
Na <sup>22</sup>	11	3.04	78.98	d,	---	---	---	0.065
Na <sup>24</sup>	11	14.8h	100. 100.	n, d,p	0.5	13.	1.7x10 <sup>2</sup>	---
K <sup>42</sup>	19	12.4h	6.7 6.7	n, d,p	1.0	0.98	1.5x10	---
					---	---	---	8.3

- Column
1. Radionuclide Symbol
  2. Atomic Number
  3. Half-life of Radionuclide Formed
  4. Relative Abundance of the Isotope from which Radionuclide is formed
  5. Nuclear Reaction
  6. Activation Cross Section for Thermal Neutrons in cm<sup>2</sup>
  7. Specific Saturation Activity in Rutherfords (130)
  8. Neutron Activation Susceptibility in Microrutherfords per second per gram (130)
  9. Yields in Rutherfords per Microampere hour (72)

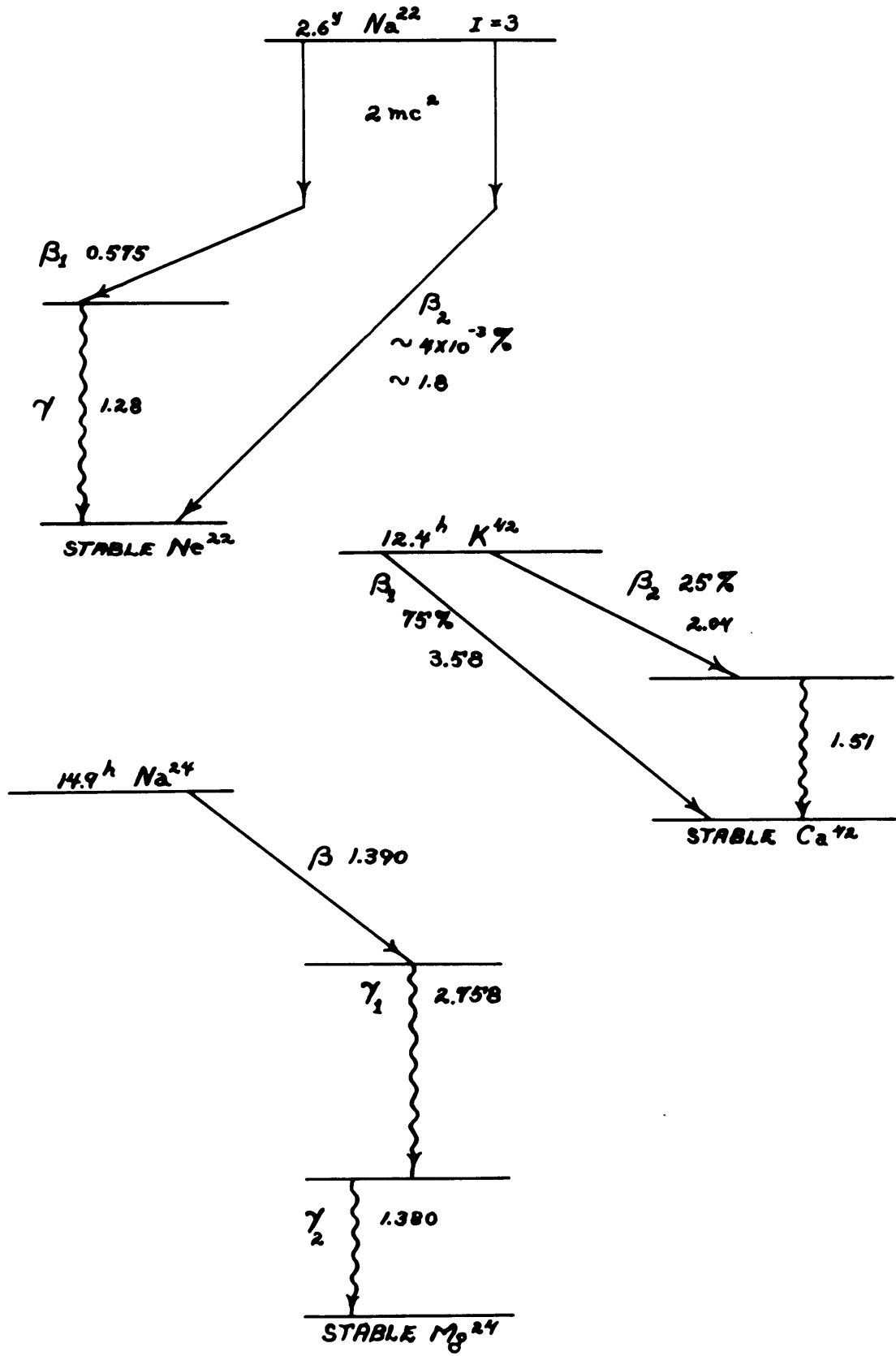


FIGURE VIII. RADIONUCLIDE DECAY SCHEMES.

## 2. Use of Scintillation Counter

### a). Design of scintillation counter

Rutherford and others developed the fundamentals of scintillation counting and applied them to studies involving alpha particle radiation. Kallman revived the techniques by introducing crystals that fluoresce upon irradiation with beta or gamma rays. Crystals designed for various uses are described in the literature. Sodium iodide crystals activated with thallium iodide were found satisfactory for gamma ray detection. The work reported here was carried out with a crystal on loan from Oak Ridge National Laboratory. This crystal was made available through the assistance of Mr. Bixby of Atomic Instrument Company, Boston, Massachusetts. A R.C.A. 5819 photomultiplier tube that had been carefully selected was used to detect the fluorescent light pulses emitted by the crystal. Optical contact was maintained between the tube and the crystal through the use of optical lucite fitted to the photomultiplier tube's face. Nujol was used to make optical contact between the components of the system.

The related electronic equipment consisted of the following units: Atomic Instrument Company scaler model 101-A, Tracer Lab. autoscaler, Atomic Instrument Company linear amplifier model 204-A, Atomic Instrument Company high voltage supply model 305, Tracerlab automatic time register, Production Instrument Company mechanical register, Standard Electric Time Clock timer, and a specially built light-tight lead shield. The lead shield had a movable platform for the accurate positioning of the

sample with respect to the crystal. Professor W. Whitehead kindly made available the Tracerlab autoscaler and Dr. L. Foster, of the Watertown Arsenal loaned the automatic time recorder. Figure (9) pictures schematically the counting equipment components. Figure (10) is a photograph of the equipment.

b). Determination of concentration-penetration data

Samples prepared as described in Section III:B were mounted in the cylinder mounting jig pictured in Figure 2b after the surfaces had been monitored by autoradiography. The alignment of the samples was checked with an Ames dial indicator sensitive to 0.000025 inches. It was found necessary to re-mount the samples several times in order to obtain a satisfactory alignment with a maximum surface variation of plus or minus 0.000025 of an inch.

The gamma activity of the samples was measured both before and after the diffusion anneal in order to determine losses of radiotracer. If necessary corrections were made to the initial value of the radioactive material due to losses in the heating process. The samples were sectioned using the techniques described in Section III:B:b. The amount of material removed after each sectioning was determined using the dial indicator. The sample jig was removed from the grinding machine and mounted in the special lead shield. The remaining gamma radiation after each cut was determined by scintillation counting. When necessary because of a relatively large removal of material, the distance between the sample and crystal was fixed in order to maintain satisfactory geometry.

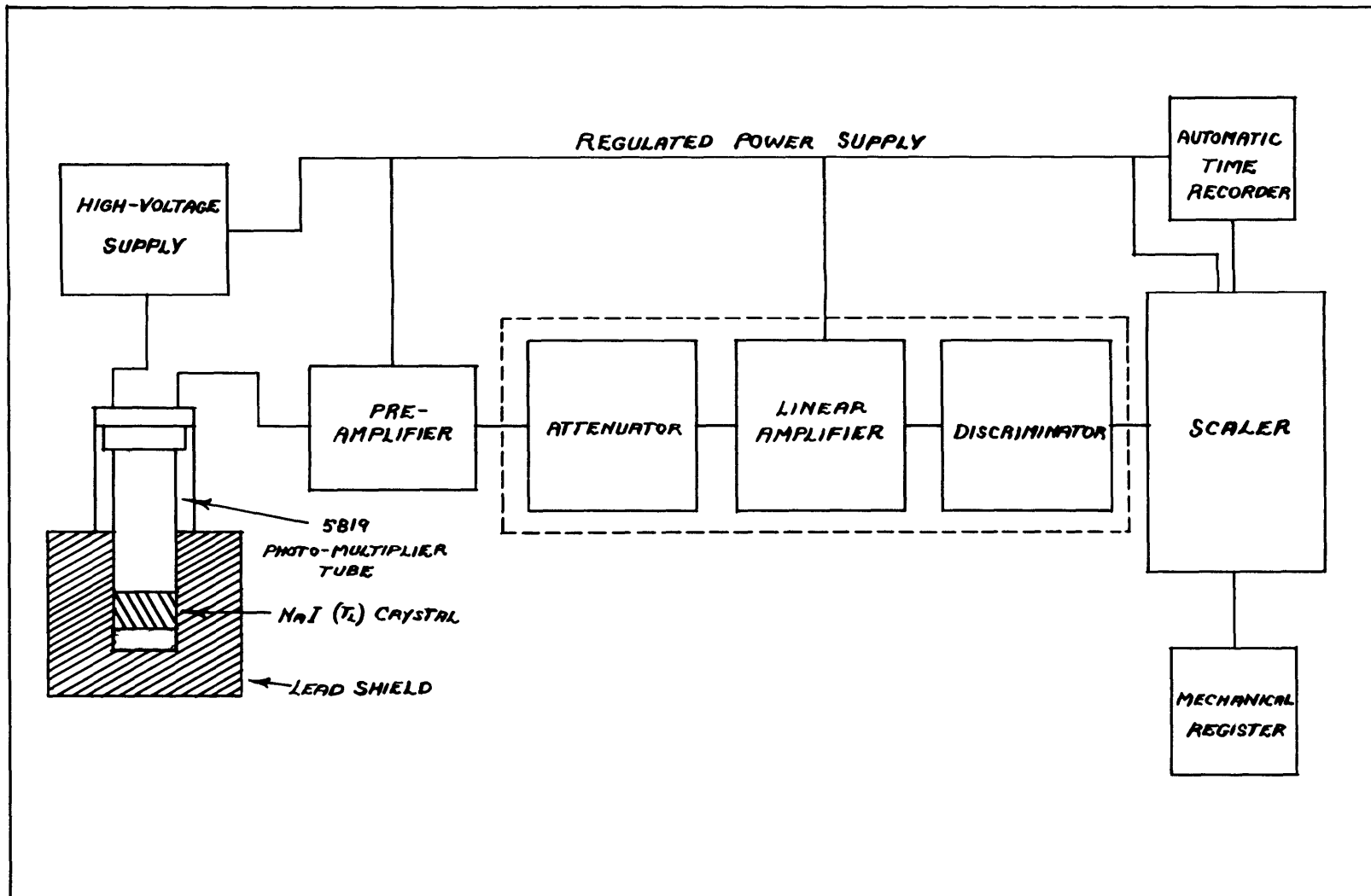


FIG. 9. GAMMA-RAY SCINTILLATION COUNTER (SCHEMATIC DRAWING)



- 37 -

P152-1



### 3. Use of beta-ray autoradiography

The usefulness of autoradiography for the solution of many problems involving microstructure is gradually being established, ( ) but several factors have retarded the development of this technique. For most microstructural investigations work on a sufficiently small scale was not possible in the past because adequate resolution could not be obtained. The difficulties of preparing the required thin sections and of applying thin photographic emulsions to such sections also tended to delay this application. Finally, autoradiography depended on the ready availability of radionuclides for preparing synthetic materials or on the possibility of rendering constituents of naturally occurring minerals radioactive by nuclear bombardment.

Boyd (18) and Herz (66) were the first to report the successful use of high resolution autoradiographs. Goodman (56), Coppens (33), Stieff (139), and Robinson ( ) have described the application of autoradiography to problems of geological interest. Hoffman and Turnbull (157) and Achter (1) have reported the use of autoradiography in the study of grain boundary diffusion. Gross (60) has reviewed the entire subject in detail and a monograph (152) radioactive measurements with nuclear emulsions is available. Doniach (38) has analyzed the problems involved in obtaining high resolution. It has been shown from the above work that successful use of the microautoradiographic technique depends on the following requirements: (1) the preparation of thin sections no more than 10 microns in thickness, (2) the use of a very sensitive fine grained nuclear emulsion



which should be as thin as possible for the maximum resolution, (3) intimate contact between the emulsion and thin section during exposure.

Stieff and Stern (139) have developed techniques for the autoradiographic study of radioactive minerals. Their method consists basically of preparing a thin section on a glass slide using standard techniques and then coating the thin section and slide with gelatin. N. T. B. stripping film is separated from its base and bonded to the thin section by the gelatin. However, in our work we were neither able to prepare thin sections of highly radioactive materials by standard techniques nor consistently successful in obtaining a satisfactory gelatin bond. Thin sections between 10 and 20 microns thick were prepared automatically using the grinding machine and techniques described in Section III:B. The sample was cemented with glycol phthalate to a cylinder of polystyrene. It was necessary to select polystyrene that was free of optical anisotropy.

Eastman Kodak N. T. B. Stripping Film was chosen for this work after an investigation of several other nuclear emulsions. This film was found satisfactory with regard to resolution and sensitivity and also possessed a low inherent background. The manufacturer (150) describes this emulsion as containing 81% by weight of silver halide, having an average diameter of 0.2 - 0.3 micron. The density of the emulsion is approximately 3.54 grams per cubic centimeter. This film is most sensitive to electrons in the energy range of 60 to 70 Kev. The sensitivity curve shown in Figure 11. flattens out fairly rapidly to a steady value at energies above 400 Kev.

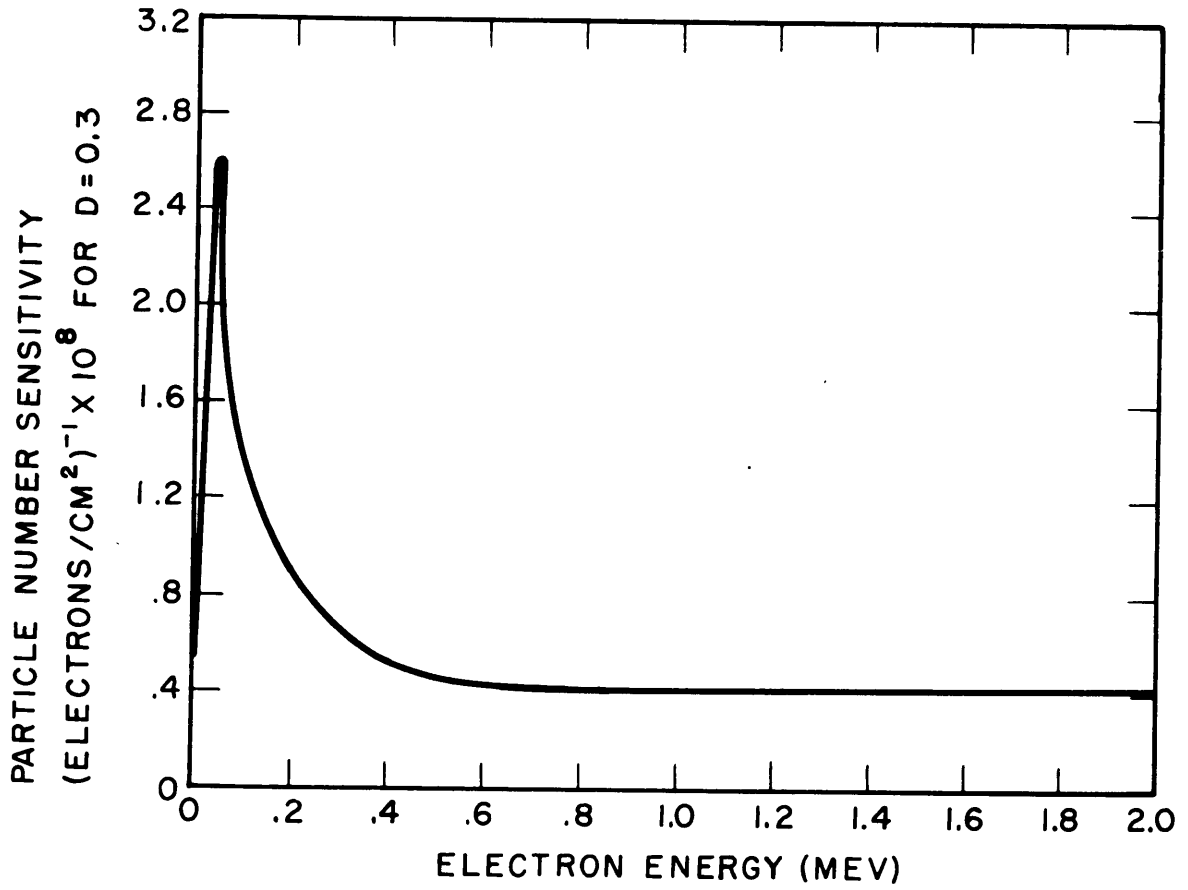


FIGURE 11.

The film consists of the emulsion, a permanent support, and a temporary support. The emulsion, 10 microns thick, is permanently attached to a 10-micron layer of cellulose nitrate. The composite of these two layers will be referred to as the "backed emulsion". The cellulose nitrate layer is attached to a layer of cellulose butyrate, which is 0.15 mm thick and serves as the temporary support. This support is removed when the film is ready for use.

The following technique was developed in conjunction with Michael (103) and has been found satisfactory in this work. The backed emulsion is stripped from its supporting layer and mounted on the specimen using the fixture shown in Figure (12). This fixture consists of a base plate, a guide, a spacer, and a cutter. For use, a square piece of double-sided Scotch Tape, having a hole in the center, is placed over the hole in the base plate so that the two holes are in register. A piece of film two inches square is cut and the backed emulsion is then loosened along one edge with a razor blade from the supporting cellulose. The piece is attached to the double-sided Scotch Tape with the emulsion side down, the support is stripped off completely by attaching a small piece of ordinary Scotch Tape and lifting gently. The operation must be carried out quite slowly to minimize fogging.

The locating pins in the guide are then inserted in the holes in the base. A ring of double-sided Scotch Tape is placed in a 0.009-in. groove previously machined in the plastic specimen mount. The surface of the sample and mount is coated with Kodak Film Lacquer.

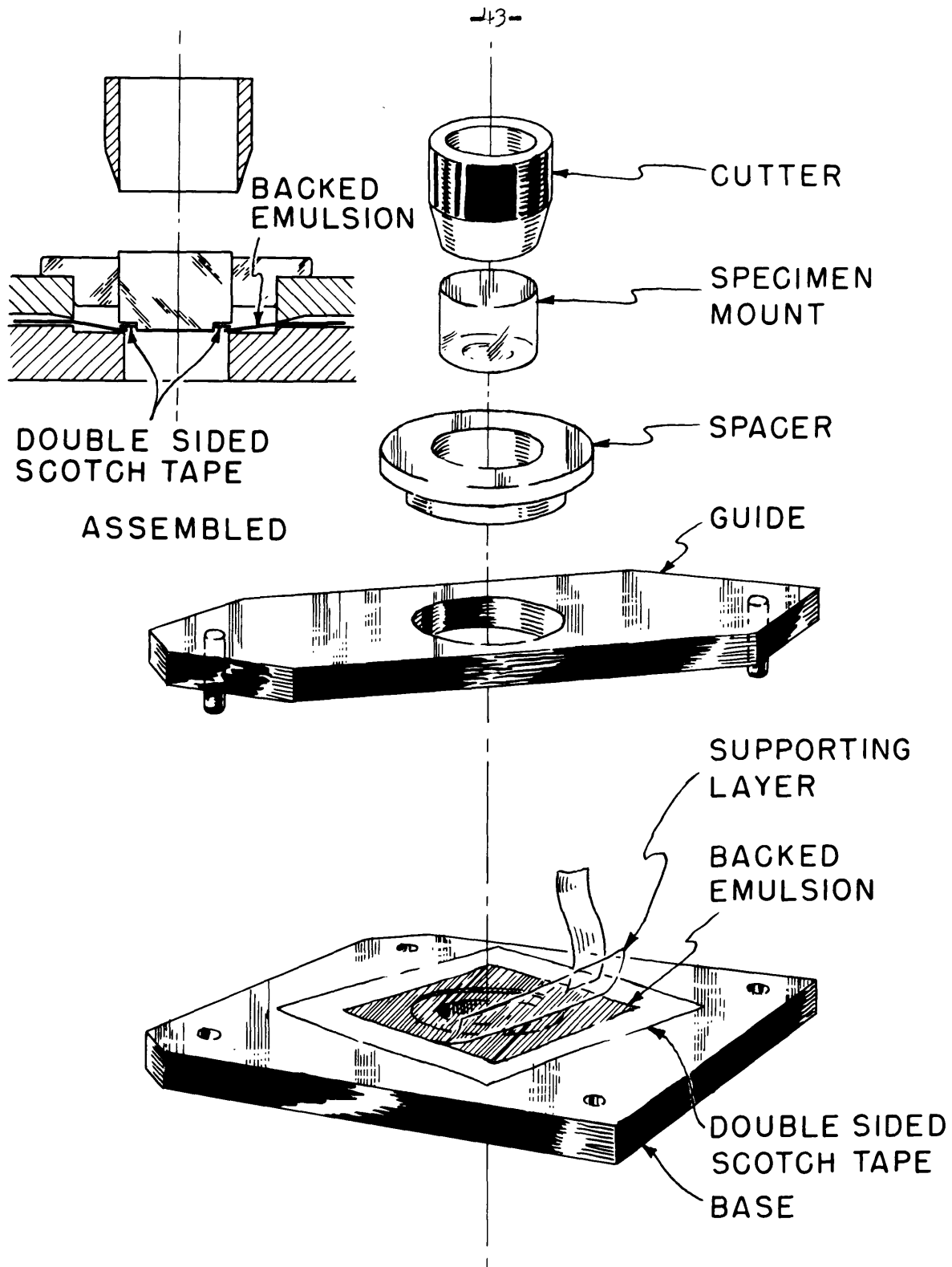


FIGURE 12.

The mount is placed inside the spacer and pressed down firmly to contact the stripped film before the lacquer dries. The ring of Scotch Tape provides an immediate bond and fixes the emulsion on the specimen before the lacquer can be effective as a cementing agent. The cross section in the upper left of Figure (12) shows the assembly at this stage of the operation. The spacer is then removed and the circular cutter is brought down to cut the film at the edge of the mount. The mount-film interface is waterproofed along this edge with Cenco Label Varnish to prevent the photographic processing solutions from penetrating between the emulsion backing and the sample mount.

The specimen is placed in a desiccator containing phosphorus pentoxide in a light-tight box for the chosen exposure time which may vary from less than one hour to several days. All manipulations are carried out in a darkroom with No. 2 Wratten Safe-light illumination. The exposed emulsion is processed in accordance with the recommendations of the manufacturer (150). It should be noted that the technique results in fixing the emulsion in place on the specimen.

The processed emulsion was examined under the microscope at magnifications of 50 to 1500 diameters with transmitted light. Because of the small grain size of the emulsion, individual grains cannot be readily observed at magnifications of less than approximately 1000 diameters. The number of silver halide grains rendered developable is determined by the radioactivity of the sample, the time of exposure of the emulsion and the

energy of the beta-particles emitted by the sample. For a given sample the exposure time may be so chosen that the developed grains corresponding to an underlying active area can be resolved only at magnifications of 1000 diameters or more. If the grain yield, that is the number of the photographic silver halide grains developable per incident beta-particle is known, a count of the developed grains will give an estimate of the activity of the sample in the neighborhood of this area of the film. Longer exposure times are used to examine areas of high grain density at lower magnifications.

The techniques described above produced autoradiographs which remain superimposed upon the samples; under favorable conditions the autoradiograph can be compared directly with the specimen by re-focusing.

b). study of microdistribution of radiotracer

Autoradiographic studies were made in order to ascertain the surface uniformity of the radiotracer films deposited on the sample cylinders. The sample faces were held in contact with Kodak no-screen x-ray film under slight pressure for a period sufficient to expose the film to approximately  $10^7$  electrons per square centimeter. The films were developed using standard techniques and were examined with a microphotometer. In several cases a recording microphotometer made available by Jarrell-Ash Company was used. In all the cylinders used in the diffusion studies there was no significant evidence of microsegregation in the deposited film.

Several samples, both before and after diffusion anneals, were examined by taking autoradiographs of sections cut parallel to the cylinder

axis. The autoradiograph showed that well defined interfaces were formed in the glazing process.

c). study of grain boundary diffusion

The use of autoradiography for evaluating the relative effects of grain boundary and volume diffusion have been reported in the literature (13). The object in using autoradiography is to be able to detect any appreciable difference in the diffusion rates by their integrated effect on the film. Standard diffusion anneals were carried out with sample cylinders of microperthite and granite using the same methods described for the diffusion study. On completion of the diffusion anneals several sections were made parallel to the face of the cylinder. Autoradiographs were made of these sections using the techniques described previously.

E. Methods of Evaluating Data

The phenomenological basis for the diffusion studies on non-steady state unidirectional flow reported here is given by Fick's second Law (44).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad D \neq D(C)$$

(1)

where C concentration of radiotracer  
D diffusion coefficient  
t time  
x directional coordinate

The solution of (1) under the experimental boundary conditions

(80)(134)

$$t=0 \quad \begin{cases} C(x^+) = 0 \\ C(0) = A_0 \end{cases}$$

$$t>0 \quad \begin{cases} C(x^+) = C(x, T) \\ C(x^-) = 0 \end{cases}$$

gives the concentration of radiotracer between x and x plus dx from the surface

$$(2) \quad C = \frac{A_0}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

where  $A_0$  is the total activity of the sample before diffusion occurred.



The total gamma activity,  $A_x$ , measured at the surface after a layer of thickness  $x$  had been removed by grinding, is given by

$$(3) \quad A_x = \int_x^{\infty} c dx$$

or substituting from equation (2)

$$(4) \quad A_x = \frac{A_0}{\sqrt{\pi D t}} \int_x^{\infty} \exp\left(-\frac{x^2}{4Dt}\right) dx$$

If  $y$  is defined as

$$y = \frac{x}{\sqrt{2Dt}}$$

equation (4) can be written

$$(5) \quad A_x = \frac{2A_0}{\sqrt{2\pi}} \int_{x=x}^{x=\infty} \exp\left(-\frac{y^2}{2}\right) dy$$

Since values of the error function are tabulated, we substitute

$$\int_0^{\infty} \exp\left(-\frac{y^2}{2}\right) dy - \int_0^x \exp\left(-\frac{y^2}{2}\right) dy = \int_x^{\infty} \exp\left(-\frac{y^2}{2}\right) dy$$

giving

$$(6) \quad A_x = 2A_0 \left(\frac{1}{2} - \text{erf}\left(\frac{x}{\sqrt{2Dt}}\right)\right)$$

or

$$(7) \quad \frac{1}{2} - \frac{A_x}{2A_0} = \text{erf}(y)$$

Values of  $y$  are obtained from tables of the error function

$$\text{erf}(y) = \frac{1}{\sqrt{2\pi}} \int_0^y \exp\left(-\frac{t^2}{2}\right) dt$$

the diffusion coefficient is obtained from the slope of the straight line

$$y = \frac{x}{\sqrt{2Dt}}$$

thus,

$$(8) \quad D = \frac{l}{(\text{slope})^2 \cdot 2t}$$

where slope =  $\frac{y}{x}$

Example: Evaluation of diffusion coefficient for Sample S 33

$$\text{Slope} = \frac{1.6}{120} = 1.33 \times 10^{-2}$$

$$D = \frac{l}{(\text{slope})^2 \cdot 2t}$$

$$= \frac{1}{(1.33 \times 10^{-2})^2 \cdot 2 \cdot 1.8 \times 10^5}$$

$$= 1.57 \times 10^{-10}$$

Evaluation of temperature dependence of the diffusion coefficient

Empirically it has been found that the temperature dependence of the diffusion coefficient is given by simple reaction rate theory (54)

$$(9) \quad D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

where  $D_0$  = Frequency factor  
 $Q$  = Energy of Activation  
 $T$  = Absolute temperature  
 $R$  = Gas constant = 2

The energy of activation is evaluated from the slope of the straight line

$$(10) \quad \log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T}\right)$$

where slope =  $-\frac{Q}{4.6}$

Example: Evaluation of activation energy and frequency factor from Figure (13).

$$\log D = \log D_0 - \frac{Q}{2.3R} \left(\frac{1}{T}\right)$$

$$Q = -4.6 \cdot \text{slope}$$

$$\text{SLOPE} = \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$D_1 = 3.2 \times 10^{-9} \text{ cm}^2/\text{SEC.}$$

$$\log D_1 = -8.4949$$

$$D_2 = 5.0 \times 10^{-11} \text{ cm}^2/\text{SEC.}$$

$$\log D_2 = -10.301$$

$$\frac{1}{T_1} = 7.5 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$$

$$\frac{1}{T_2} = 10.0 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$$

$$\text{SLOPE} = \frac{-8.4949 - (-10.301)}{(7.5 - 10) \times 10^{-4}}$$

$$= -2.22 \times 10^3$$

$$Q = -4.6 (-2.22 \times 10^3)$$

$$Q = 32,200 \text{ CAL.}$$

#### IV. EXPERIMENTAL RESULTS

##### A. Presentation of Results

The diffusion coefficients for sodium in oligoclase perpendicular (001) in the range 700-1050° C are reported in Tables 2 and 8. The diffusion coefficients for sodium in oligoclase perpendicular (010) in the range 600-1050° C are reported in Table 13. The temperature dependence for the self-diffusion of sodium in oligoclase is presented graphically in Figures 13, 15, and 17. The experimental data are reported in Tables 3 to 7, 9-12, and 14 to 19. Plots of  $\frac{x}{\sqrt{2Dt}}$  vs.  $x$  from which the diffusion coefficients were evaluated are shown in Figures 14, 16, and 18.

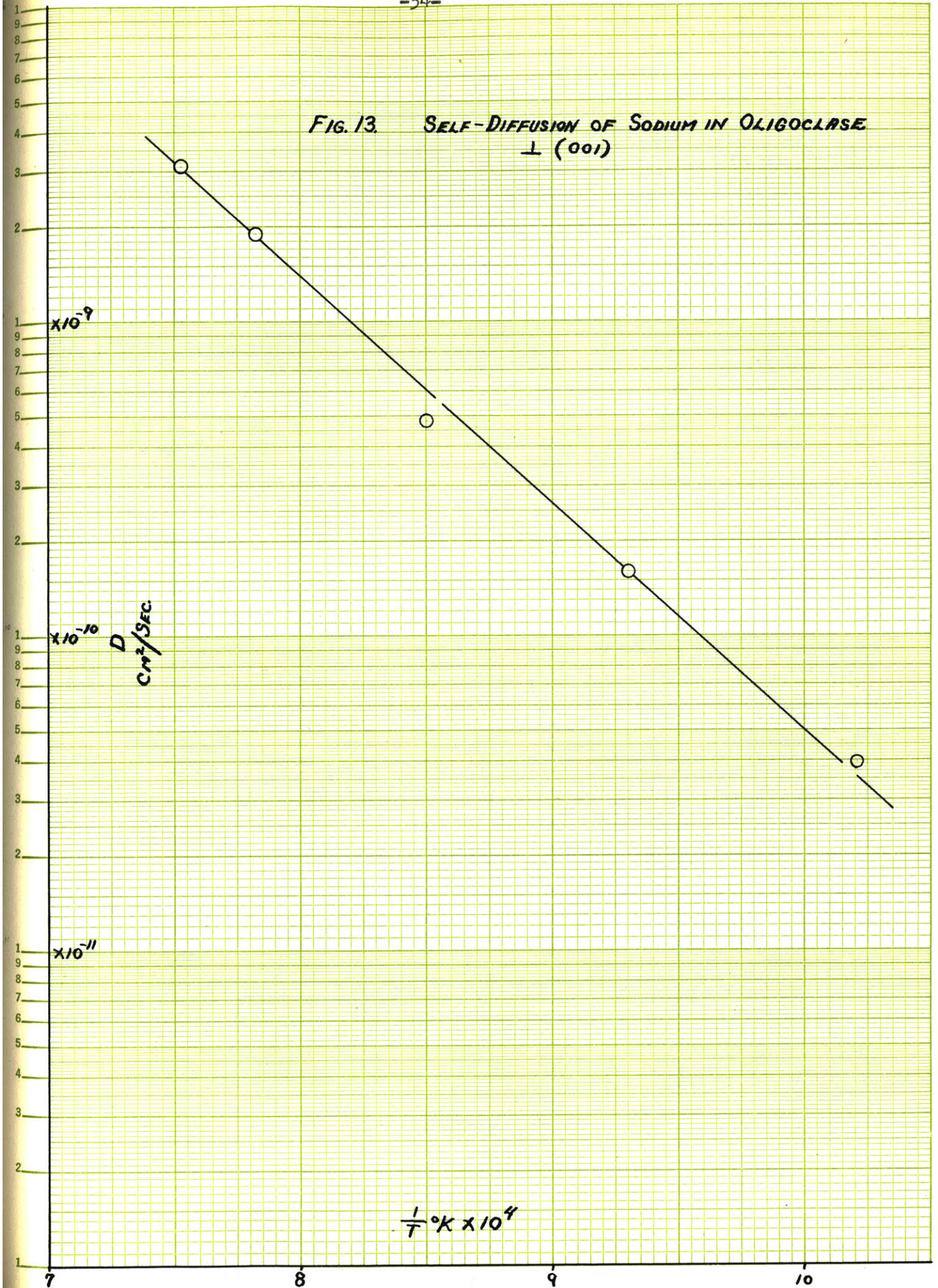
Material Oligoclase  
 Radiotracer Na<sup>22</sup>  
 Diffusion Direction Perpendicular (001)  
 Graph Figure 13

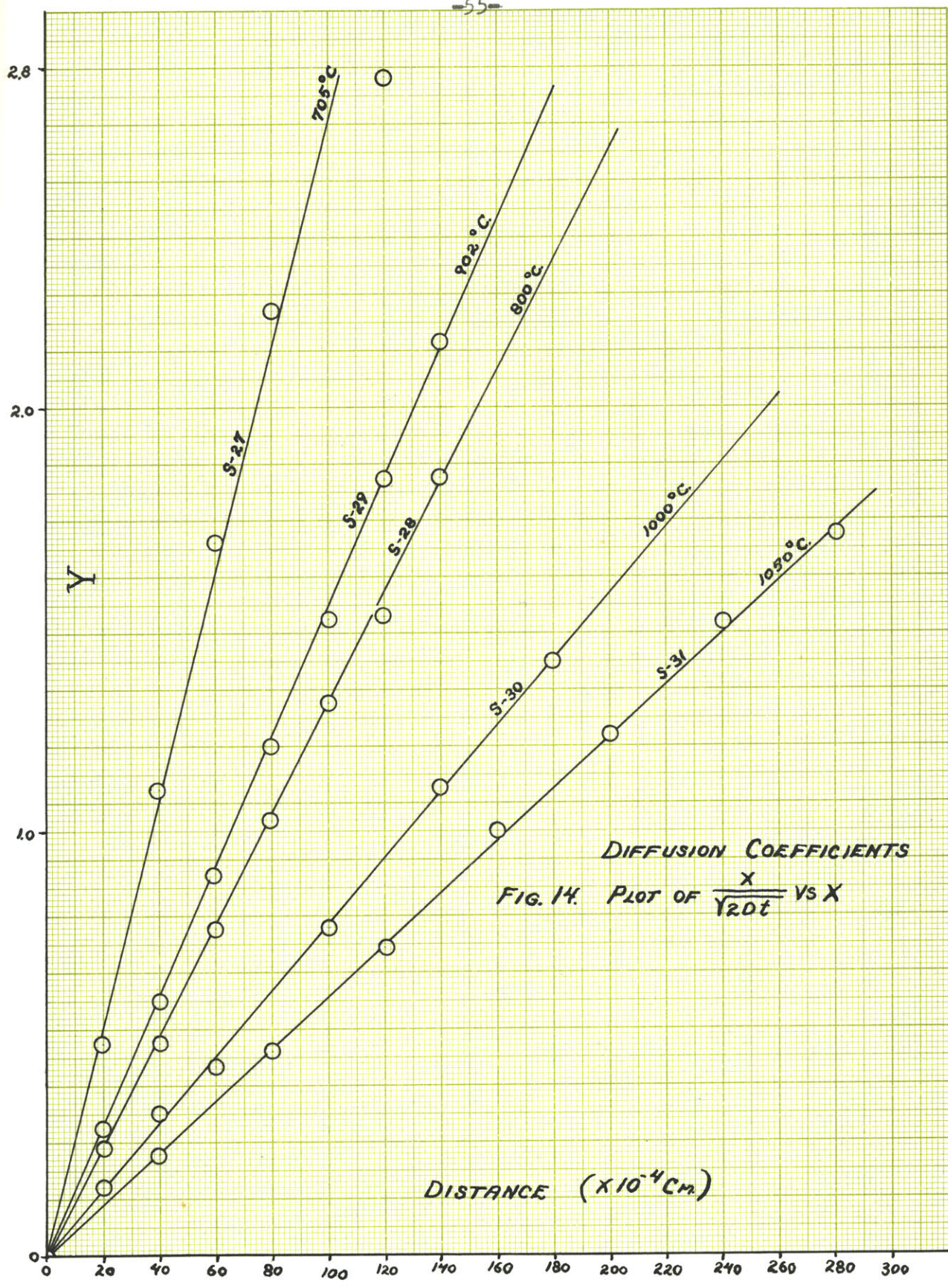
Sample	Time in Hours	T° C	T° K	$\frac{1}{T^{\circ} K} \cdot 10^4$	D cm <sup>2</sup> / sec.
S 27	50	705	978	10.2	3.9 X 10 <sup>-11</sup>
S 28	50	800	1073	9.32	1.62 X 10 <sup>-10</sup>
S 29	12	902	1175	8.51	4.88 X 10 <sup>-10</sup>
S 30	12	1000	1273	7.86	1.90 X 10 <sup>-9</sup>
S 31	12	1050	1323	7.56	3.06 X 10 <sup>-9</sup>

Activation Energy Q: 32,900 cal.  
 Frequency Factor D<sub>0</sub>: 7.1 X 10<sup>-4</sup>  
 Temperature Dependence D: 7.08 X 10<sup>-4</sup> exp ( -  $\frac{32,900}{RT}$  )

TABLE 2.

FIG. 13. SELF-DIFFUSION OF SODIUM IN OLIGOCLASE  
⊥ (001)





DIFFUSION COEFFICIENTS  
FIG. 14. PLOT OF  $\frac{X}{\sqrt{2Dt}}$  VS X

DISTANCE (X 10<sup>-4</sup> CM)



Sample S27  
 Radiotracer  $\text{Na}^{22}$   
 Temperature  $705^{\circ} \text{C}$   
 Time  $1.85 \times 10^5 \text{ sec.}$   
 Diffusion Coefficient  $3.7 \times 10^{-11}$

No.	Distance	Time	Total Count	Counting Rate	$A/A_0$	Erf(y)	y
1	0	49.0	40,960	834	-----	---	---
2	20.5	82.5	40,960	494	0.296	0.204	0.54
3	40.5	182.5	40,960	222	0.133	0.367	1.11
4	60.0	511.5	40,960	78.0	0.047	0.453	1.68
5	80.25	177.25	4,096	21.8	0.013	0.487	2.23
6	120.0	660.5	4,096	4.2	0.003	0.497	2.75

TABLE 3.

Sample S28  
 Radiotracer  $\text{Na}^{22}$   
 Temperature  $800^{\circ} \text{C}$   
 Time  $1.85 \times 10^5 \text{ sec.}$   
 Diffusion Coefficient  $1.6 \times 10^{-10}$

No.	Distance	Time	Total Count	Counting Rate	$A/A_0$	Erf(y)	y
1	0	69.5	40,960	587	0.000	-----	-----
2	20.5	87.75	40,960	465	0.396	0.104	0.265
3	40.0	116.0	40,960	351	0.299	0.201	0.528
4	59.75	158.0	40,960	257	0.219	0.281	0.78
5	80.75	225.0	40,960	180	0.153	0.347	1.02
6	100.25	359.0	40,960	112	0.095	0.405	1.32
7	120.25	577.75	40,960	68.9	0.0584	0.442	1.57
8	139.50	1037.0	40,960	37.5	0.032	0.468	1.85

TABLE 4.

Sample S29  
 Radiotracer Na<sup>22</sup>  
 Temperature 902° C  
 Time 4.32 X 10<sup>4</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf(y)	y
1	0	127.5	40,960	319	-----	-----	-----
2	21.0	169.25	40,960	240	0.376	0.124	0.318
3	40.25	232.75	40,960	174	0.273	0.227	0.605
4	60.25	347.0	40,960	116	0.182	0.318	0.911
5	80.0	545.5	40,960	73.1	0.115	0.385	1.20
6	100.5	952.5	40,960	41.0	0.0643	0.436	1.53
7	120.0	172.0	4,096	21.8	0.034	0.446	1.83
8	140.25	353.0	4,096	9.6	0.015	0.485	2.17

TABLE 5.

Sample S30  
 Radiotracer Na<sup>22</sup>  
 Temperature 1000° C  
 Time 4.32 X 10<sup>4</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/ A <sub>0</sub>	Erf(y)	y
1	0	69.75	40,960	585	-----	-----	-----
2	20.0	79.5	40,960	513	0.439	0.061	0.455
3	40.5	93.1	40,960	438	0.375	0.125	0.323
4	60.0	108.5	40,960	376	0.322	0.178	0.464
5	100.6	159.0	40,960	256	0.220	0.280	0.772
6	140.1	262.5	40,960	154	0.133	0.367	1.11
7	180.5	431.25	40,960	93.0	0.081	0.419	1.40

TABLE 6.

Sample S31  
 Radiotracer Na<sup>22</sup>  
 Temperature 1050°  
 Time 4.32 X 10<sup>4</sup>

Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf (y)	y
1	0	148.5	40,960	274	0.000	0.000	0.000
2	40.25	183.5	40,960	221	0.403	0.097	0.248
3	80.0	236.75	40,960	171	0.312	0.188	0.491
4	119.75	317.8	40,960	127	0.232	0.268	0.733
5	160.00	477.5	40,960	83.5	0.152	0.348	1.03
6	200.5	668.0	40,960	61.0	0.111	0.389	1.22
7	240.75	1010.0	40,960	38.2	0.687	0.430	1.48
8	280.25	1685.0	40,960	22.0	0.0414	0.459	1.74

TABLE 7.

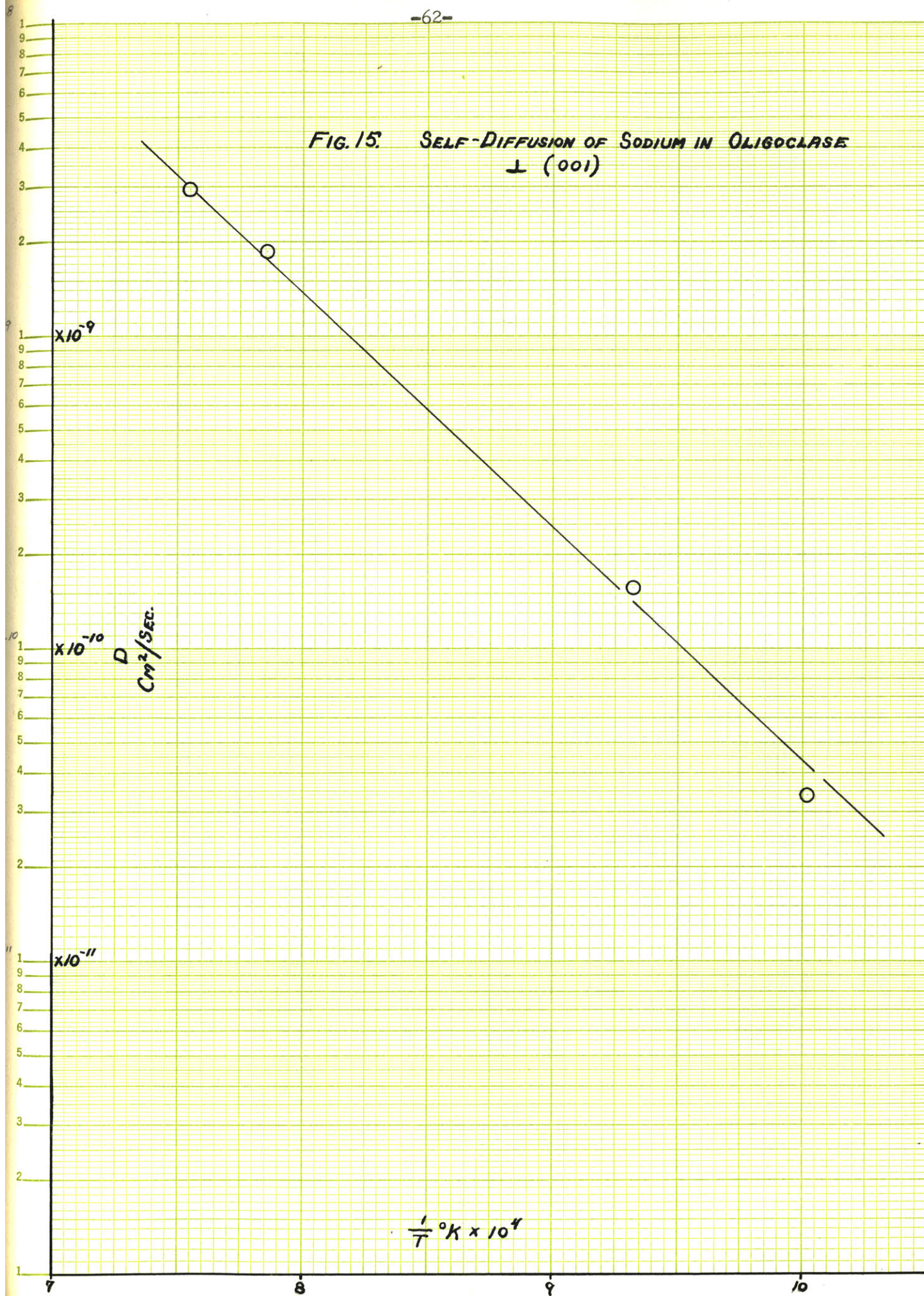
Material                      Oligoclase  
 Radiotracer                  Na<sup>22</sup>  
 Diffusion Direction        Perpendicular (001)  
 Graph                         Figure 15

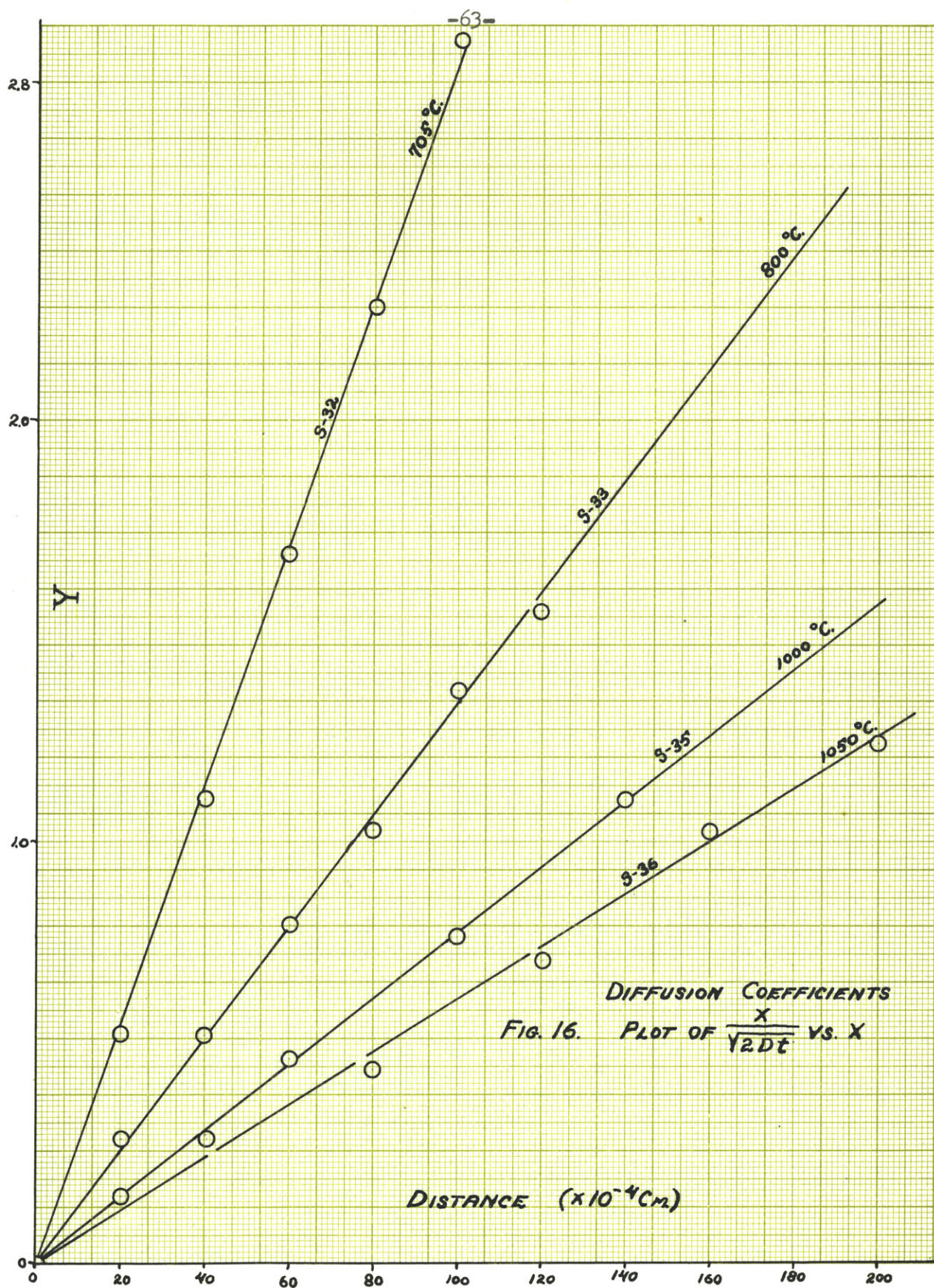
Sample	Time in Hours	T° C	T° K	$\frac{1}{T^{\circ} K} \cdot 10^4$	D cm <sup>2</sup> / sec.
S 32	50	705	978	1.02	3.41 X 10 <sup>-11</sup>
S 33	50	800	1073	0.932	1.57 X 10 <sup>-10</sup>
S 35	12	1000	1273	0.786	1.88 X 10 <sup>-9</sup>
S 36	12	1050	1323	0.756	2.96 X 10 <sup>-9</sup>

Activation Energy            Q:    34,300  
 Frequency Factor            D<sub>0</sub>:    1.44 X 10<sup>-3</sup>  
 Temperature Dependence    D:    1.4 X 10<sup>-3</sup> exp( -  $\frac{34,300}{RT}$  )

TABLE 8.

FIG. 15. SELF-DIFFUSION OF SODIUM IN OLIGOCLASE  
⊥ (001)







Sample S32  
 Radiotracer Na<sup>22</sup>  
 Temperature 705° C  
 Time 1.8 x 10<sup>5</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf(y)	y
1	0	78.75	40,960	517	0.000	0.000	0.000
2	20.0	133.75	40,960	304	0.294	0.206	0.543
3	40.0	289.0	40,960	140	0.135	0.365	1.10
4	60.5	816.5	40,960	48.2	0.0476	0.453	1.68
5	80.0	282.0	4,096	12.5	0.0128	0.487	2.23
6	100.0	1060.0	4,096	1.7	0.0016	0.498	2.88

TABLE 9.

64

Sample S33  
 Radiotracer  $\text{Na}^{22}$   
 Temperature  $800^{\circ}\text{C}$   
 Time  $1.8 \times 10^5$   
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	$A/A_0$	$\text{Erf}(y)$	$y$
1	0	60.0	40,960	680	0.000	0.000	0.000
2	20.0	78.0	40,960	523	0.385	0.115	0.292
3	40.5	101.0	40,960	404	0.297	0.203	0.537
4	60.5	141.5	40,960	287	0.211	0.289	0.803
5	80.25	192.0	40,960	211	0.155	0.345	1.02
6	100.00	332.75	40,960	121	0.089	0.411	1.35
7	119.75	509.25	40,960	78.4	0.058	0.442	1.57

TABLE 10.

Sample S35  
 Radiotracer  $\text{Na}^{22}$   
 Temperature  $1000^{\circ} \text{C}$   
 Time  $4.32 \times 10^4$   
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	$A/A_0$	Erf(y)	y
1	0	108.25	40,960	376	0.000	0.000	0.000
2	20.0	121.75	40,960	334	0.444	0.056	0.140
3	40.25	143.25	40,960	284	0.378	0.122	0.310
4	60.25	173.5	40,960	234	0.311	0.189	0.493
5	100.5	246.5	40,960	164	0.218	0.282	0.78
6	140.5	402.0	40,960	100	0.133	0.367	1.11

TABLE 11.

Sample S 36  
 Radiotracer Na<sup>22</sup>  
 Temperature 1058° C  
 Time 4.32 X 10<sup>4</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf(y)	y
1	0	73.75	40,960	553	0.000	0.000	0.000
2	40.75	98.0	40,960	416	0.376	0.124	0.318
3	81.25	115.0	40,960	354	0.320	0.180	0.470
4	119.75	154.5	40,960	363	0.238	0.262	0.712
5	160.25	242.25	40,960	167	0.151	0.349	1.03
6	200.25	331.5	40,960	122	0.110	0.390	1.23

TABLE 12.

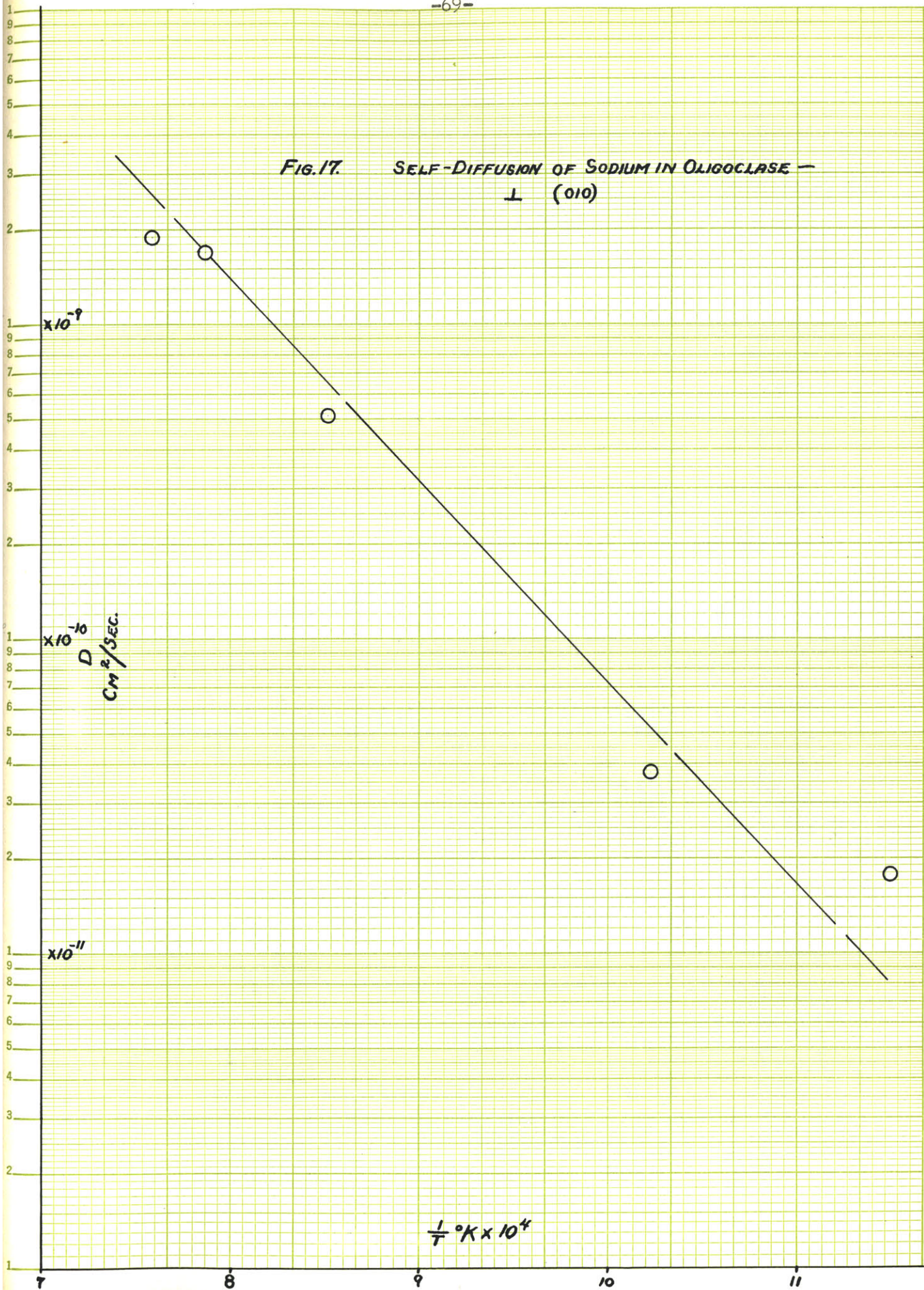
Material Oligoclase  
 Radiotracer Na<sup>22</sup>  
 Diffusion Direction Ferpendicular (010)  
 Graph Figure 17

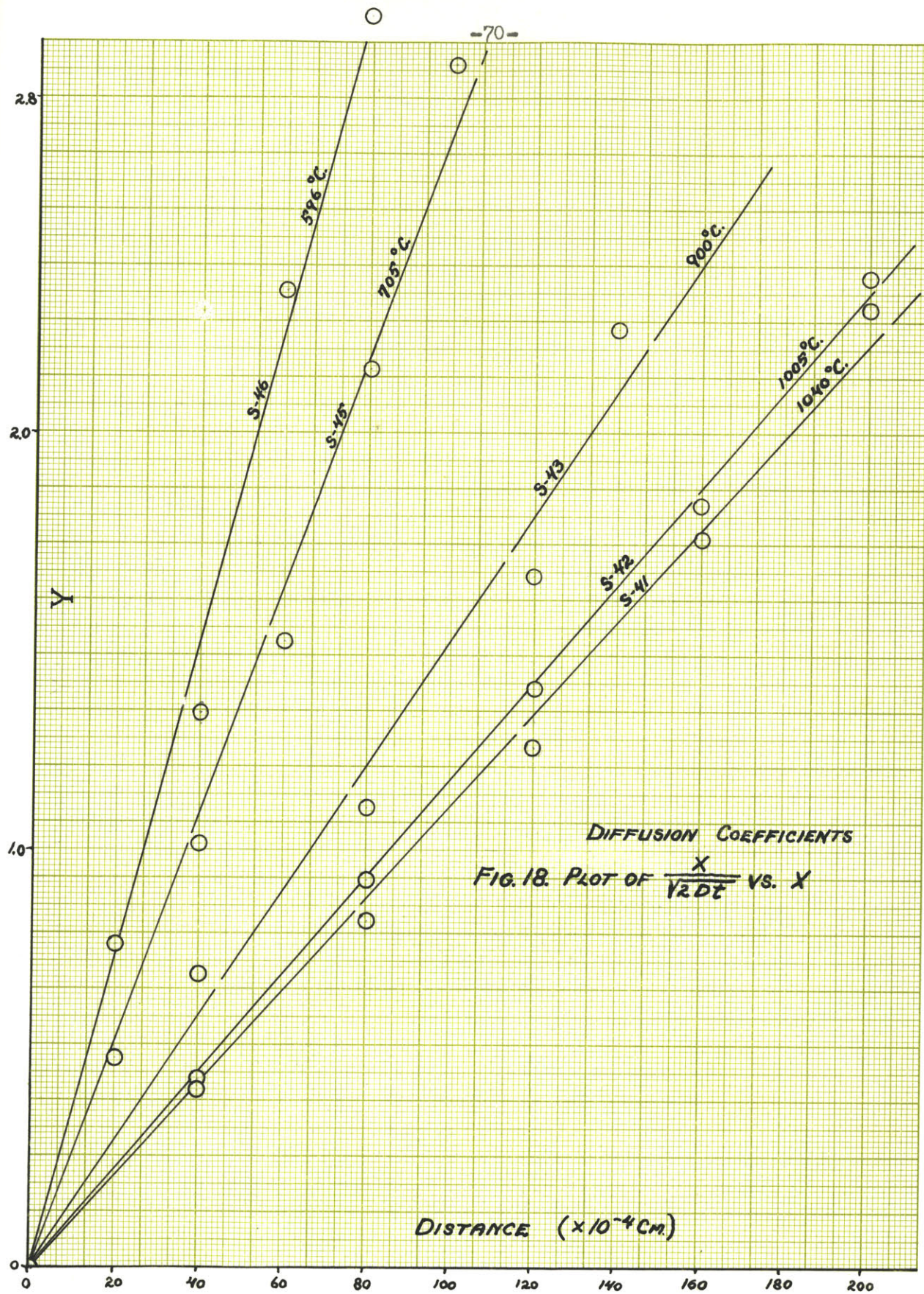
Sample	Time in Hours	T° C	T° K	$\frac{1}{T^{\circ} K} \cdot 10^4$	D cm <sup>2</sup> / sec.
S 41	6	1040	1313	7.62	1.9 X 10 <sup>-9</sup>
S 42	6	1005	1278	7.82	1.7 X 10 <sup>-9</sup>
S 43	12	900	1173	8.52	5.12 X 10 <sup>-10</sup>
S 44	24	810	1083	9.23	Missing
S 45	50	705	978	1.02	3.74 X 10 <sup>-11</sup>
S 46	50	596	869	1.15	1.76 X 10 <sup>-11</sup>

Activation Energy Q: 29,600  
 Frequency Factor D<sub>0</sub>: 1.96 X 10<sup>-4</sup>  
 Temperature Dependence D: 2.0 X 10<sup>-4</sup> exp ( -  $\frac{29,600}{RT}$  )

TABLE 13.

FIG. 17. SELF-DIFFUSION OF SODIUM IN OLIGOGLASE —  
⊥ (010)





Sample S 41  
 Radiotracer Na<sup>22</sup>  
 Temperature 1040° C  
 Time 2.16 X 10<sup>4</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf(y)	y
1	0	43.0	4,096	93.0	0.000	0.000	0.000
2	40	63.0	4,096	62.7	0.337	0.163	0.42
3	80	102.5	4,096	37.7	0.203	0.297	0.831
4	120	187.0	4,096	19.6	0.105	0.395	1.25
5	160	409.5	4,096	7.7	0.041	0.459	1.74
6	200	931.0	4,096	2.1	0.011	0.489	2.29

TABLE 14.



Sample S 42  
 Radiotracer Na<sup>22</sup>  
 Temperature 1005° C  
 Time 2.16 X 10<sup>4</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf(y)	y
1	0	102.5	40,960	398	0.000	0.000	0.000
2	40	154.0	40,960	264	0.331	0.169	0.438
3	80	284.5	40,960	142	0.178	0.322	0.922
4	120	607.5	40,960	65.6	0.082	0.418	1.39
5	160.5	142.25	4,096	27.5	0.035	0.465	1.82
6	200	426.5	4,096	7.3	0.009	0.491	2.37

TABLE 15.

Sample S 43  
 Radiotracer Na<sup>22</sup>  
 Temperature 900° C  
 Time 4.32 X 10<sup>4</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf(y)	y
1	0	89.75	40,960	454	0.000	0.000	0.000
2	40	187.0	40,960	217	0.239	0.261	0.71
3	80	330.0	40,960	122	0.134	0.366	1.11
4	120	890.5	40,960	43.7	0.048	0.452	1.67
5	140	315.5	4,096	10.7	0.0118	0.488	2.26
6	200	2000.0	4,096	00.0	0.0000	0.000	0.00

TABLE 16.

Sample S 44  
 Radiotracer Na<sup>22</sup>  
 Temperature 810° C  
 Time 8.64 X 10<sup>4</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/A <sub>0</sub>	Erf(y)	y
1	0	120.0	40,960	339	0.000	0.000	0.00
2	40	436.5	4,096	7.3	0.011	0.489	2.29
3	60	000.0	0,000	0.0	0.000	0.000	0.00

TABLE 17.

Sample S 45  
 Radiotracer Na<sup>22</sup>  
 Temperature 705° C  
 Time 1.8 X 10<sup>5</sup>  
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	A/ A <sub>0</sub>	Erf(y)	y
1	0	146.0	40,960	279	0.000	0.000	0.000
2	20	235.5	40,960	172	0.308	0.192	0.505
3	40	457.5	40,960	87.2	0.156	0.344	1.01
4	60	110.0	40,960	34.9	0.063	0.437	1.53
5	80	362.5	4,096	9.0	0.016	0.484	2.15
6	100	1202.	4,096	1.1	0.002	0.498	2.88

TABLE 18.

Sample S 46  
 Radiotracer  $\text{Na}^{22}$   
 Temperature  $596^{\circ} \text{C}$   
 Time  $1.8 \times 10^5$   
 Diffusion Coefficient

No.	Distance	Time	Total Count	Counting Rate	$A/A_0$	$\text{Erf}(y)$	$y$
1	0	48.0	40,960	853	0.000	0.000	0.000
2	20	109.25	40,960	375	0.220	0.280	0.772
3	40	258.75	40,960	158	0.093	0.407	1.32
4	61	239.5	4,096	17.1	0.010	0.490	2.33
5	80	2026.0	4,096	2.0	0.001	0.499	3.09
6	100	0000.0	0,000	0.0	0.000	0.000	0.00

TABLE 19.

## B. Discussion of Results

In general a total count of 40,960 was used for the gamma activity determinations with a resulting counting error of 0.5%. In several cases low counting rates necessitated the use of a total count of 4,096 with a resulting counting error of 4%. Figures 14, 16, and 18 clearly demonstrate that the experimental data well fits a straight line. Only in the case of S 43 is there evidence of deviations larger than to be expected from the counting errors.

Although the measured data for any diffusion coefficient can be well represented by a straight line, the resulting diffusion coefficient is not necessarily accurate. Appreciable errors can be introduced by the sectioning process and by chemical and physical variations in samples from the same specimen. It has been found that the experimental data obtained in a great variety of diffusion studies can be expressed in terms of simple reaction kinetics. The most useful test of the accuracy of the evaluated diffusion coefficients has been found to be their deviations from the line of best fit predicted by reaction kinetic theory.

The diffusion coefficients of sodium perpendicular to (001) in two different samples of oligoclase are shown in Figure 13 and Figure 15. Both samples were diffusion annealed at the same time. The sample reported in Figure 13 was obtained from Professor C. Frondel of Harvard University. The sample reported in Figure 15 was obtained from Ward's Natural Science Establishment.

Both samples probably originated from the same vicinity in North Carolina. Diffusion studies in the same crystallographic direction were carried out in samples from the two different specimens in order to compare variations in activation energy obtained between different specimens and between different crystallographic directions in the same specimen. A 4% variation in the activation energy was found between specimens and a 10 to 15% variation between crystallographic directions. The activation energy perpendicular to (010) was lower than that perpendicular to (001). Rosenqvist has also noted an anisotropy for the diffusion of radium and lead in albite. Insufficient evidence is available on the mechanism of diffusion in the feldspars to discuss this phenomena.

The diffusion coefficients perpendicular to two main crystallographic directions have been determined. There is little evidence available to indicate that the diffusion coefficient along any other direction will be very different from those already reported.

## V. SUMMARY AND CONCLUSION

The aim of this work as stated earlier has been to contribute to the controversial problem of the genesis of granitic rocks some new and accurate experimental information on the transport of sodium and potassium through feldspar in the solid state, and to apply this information to the evaluation of the role of solid state diffusion as a geological process. However, the experimental techniques used for the accurate determination of the diffusion coefficients have greatly restricted the number of diffusion coefficients that could be determined. This has been mainly due to (1) the unavailability of a sufficient source of useful single crystals of feldspar, and (2) the excessive time consumed in the sectioning process. Although preliminary work had been done in the developmental stage on the diffusion rates of potassium in oligoclase and sodium in other feldspars, it was necessary to restrict the main part of the work to the accurate determination of the diffusion coefficient of radioactive sodium<sup>22</sup> in oligoclase. Sodium<sup>22</sup> was found to be the most suitable radio-nuclide because of its long half-life, high specific activity, and satisfactory gamma emission.



The diffusion coefficients for the migration of sodium in single crystals of transparent oligoclase have been determined for the temperature range 700-1050° C. The diffusion coefficients for migration perpendicular (001) for two different specimens of oligoclase are given by the following expressions:

$$D_{\text{Na}} = 7.1 \times 10^{-4} \exp \left( - \frac{32,900}{RT} \right) \text{ cm}^2 / \text{ sec.}$$

$$D_{\text{Na}} = 1.4 \times 10^{-3} \exp \left( - \frac{34,300}{RT} \right) \text{ cm}^2 / \text{ sec.}$$

The diffusion coefficient for migration perpendicular (010) is given by:

$$D_{\text{Na}} = 2.0 \times 10^{-4} \exp \left( - \frac{29,600}{RT} \right) \text{ cm}^2 / \text{ sec.}$$

The geological implications that can be obtained from the above results indicate the same order of distance traveled for diffusing sodium ions in solid rock as that obtained by Jagitsch (74) and Jensen (76). There is no evidence that sodium can diffuse a distance greater than several meters through mineral lattices. Thus, there is no experimental confirmation of the hypotheses of Perrin and Roubault (109) or Bugge (26).

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