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**MULTICOMPONENT DIFFUSION IN GLASSES - THEORY
AND APPLICATION TO TEKTITES**

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by

Arun Kumar Varshneya

CASE WESTERN RESERVE UNIVERSITY

September, 1970

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MULTICOMPONENT DIFFUSION IN GLASSES - THEORY
AND APPLICATION TO TEKTITES

by

ARUN KUMAR VARSHNEYA

Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

Division of Metallurgy and Materials Science

CASE WESTERN RESERVE UNIVERSITY

September, 1970

TO
MY PARENTS
SHAKUNTALA AND NATHI LAL
FOR
SAVING MY LIFE AT THE AGE OF FOUR
AND FOR
ALL THE LOVE AND GUIDANCE

"यदायदाहि धर्मस्य ग्लानिर्भवति भारत
अभ्युत्थानमधर्मस्य तदात्मानम् सृजाम्यहम्

O ARJUNA , WHENEVER THE TRUTH IS INSULTED
AND THE EVIL RISES, I REINCARNATE."

- LORD KRISHNA
in the GITA

MULTICOMPONENT DIFFUSION IN GLASSES - THEORY
AND APPLICATION TO TEKTITES

Abstract

by

ARUN KUMAR VARSHNEYA

Unidirectional, semi-infinite diffusion couples were made at temperatures between 650°C and 800°C, along four directions on the K_2O - SrO - SiO_2 composition space near the 20,20,60 wt. % composition. It was found that Onsager's extension of Fick's law provides an adequate description to the kinetics of multicomponent diffusion process through the use of an interdiffusion coefficients matrix. It is also shown that an eigenvector - eigen value concept is particularly helpful in visualizing the kinetics of diffusion.

The relation between the interdiffusion coefficients and the self-diffusion coefficient in this system was quantitatively examined using the atomic mobility model. The model was found to predict the results well. Calculations of the electrostatic fields and the accumulation of space charge within the system support the assumption that the system preserves stoichiometry during diffusive mixing.

The concept of an effective binary diffusion coefficient (EBDC) in a multicomponent system was applied to the problem of origin of tektites. Sections of a Thailand tektite were analyzed under an electron microprobe for composition fluctuations. A comparison is made with similar data from laboratory-synthesized tektite glasses and other natural glasses including lunar specimens from the Apollo XII site. To estimate the kinetics of diffusive mixing of local composition fluctuations, the EBDC of iron and silicon were measured as a function of temperature above 1150°C in the laboratory-synthesized tektite glasses. Limits for minimum thermal history of 2172 Thailand tektite are suggested by calculating the times required to convert a hypothetical tektite source into a specimen with comparable homogeneity.

A WORD OF THANKS . . .

At times it was frustrating. Occasionally the author resented being driven as a 'slave'. Despite these minor perturbations, the advisorship of Alfred R. Cooper, Jr., has been invaluable in this research.

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GLOSSARY

Unless locally defined, the various terms and symbols used in this thesis are meant to carry the meanings given below. Notations based upon international convention have been used freely.

Subscripts

$i, j, k, m,$	Species Variables
l	Observation Number Variable
A, l, K	Potassium
$B, 2, Sr$	Strontium
$C, 3, Si$	Silicon
O	Oxygen
u, v	Eigen Values

Superscripts

r	r th species eliminated
P, Q	End Composition Variables
a, b, c, d, e	Constants
a_{io}	Thermodynamic Activity of Oxide "io."
D	Diffusion Coefficient
D_i	Self Diffusion Coefficient ($i \neq u, v$)
D_u, D_v	Eigen Values, $D_u > D_v$
D_{ij}	Interdiffusion Coefficients

f	Function Symbol
f'_{ij}	Thermodynamic Activity Coefficient
G	$[(D_{11} - D_{22})^2 + 4D_{12} D_{21}]^{1/2}$; also used as the name of a glass.
H	Name of a Glass
ΔH	Activation Energy for Diffusion
I	Name of a Glass
J	Flux of a Species, also used as a name of a glass.
K	in general, Potassium; also used as a name of a glass.
L	Name of a Glass
L_{ij}	Conductance Matrix
M_{ij}	Intrinsic Diffusion Coefficients
n	Total Number of Species
n_y	Particle Density at Position y
q	Electro-Static Charge Density at a Position
S, Sr	in general, Strontium
T	Absolute Temperature
TA,TB,TF	Synthetic Tektite Compositions
t	Time
U_r	Relaxation Velocity
$\vec{u}$	Fast Eigen Vector
$\vec{v}$	Slow Eigen Vector
$\bar{V}$	Partial Mass Volume
W_i	Integrated X-ray Intensity of i
X_i	Concentration of i

x_{io}	Concentration of the Oxide of i
y	Distance Variable
z_i, Z_i	Charge (and Valence) of the Ion i
β	Atomic Mobility
$\hat{y}_i$	Composition Basis Vector
δ_1, δ_2	Striation Thickness (Part II and Appendix 5)
δ_{ij}	Kronecker Delta
∇	$\partial/\partial y$
λ	$y/\sqrt{t}$ (Part I); and Fluctuation Wavelength (Part II)
μ	Microns, Chemical Potential
ν	Degrees of Freedom
ρ	Density
σ	Standard Deviation
χ^2	Total Chi-Square
χ^2_ν	Total Chi-Square/Degrees of Freedom
ψ	Electrostatic Potential

CHAPTER 1

INTRODUCTION

"It is easy to tell a lie. But it is hard to tell only one lie."

-- Quoted in Ennis, Texas, News

Tektites (Greek 'tektos' = melted) are primarily high silica alumina containing glass bodies found on various parts of the earth, both on land and under the ocean beds. Their size ranges from a fraction of a millimeter to several centimeters. The majority of tektites recovered from ocean beds are smaller than a millimeter (and hence named microtektites) whereas the land samples are usually bigger. The color of these bodies varies from almost colorless to dark greyish green and they occur in shapes of dumb-bells, teardrops, buttons and other various forms. They are named according to their recovery areas, e.g., australites, indochinites and moldavites.

The glassy nature of tektites was identified as early as 1788 by J. Mayer⁽¹⁾. But not until recently has the question concerning their origin been seriously debated. Hypotheses to explain the origin of tektites have been reviewed by O'Keefe⁽²⁾. The more recognized ones associate the tektite formation with an impact of

a celestial body with the earth⁽³⁾ or the moon⁽⁴⁾.

The former, viz. the terrestrial origin hypothesis is based essentially upon the argument that the chemistry and the isotopic constitution of tektites is similar to terrestrial rocks. However, the resemblance to most other impact ejecta is little and, in some cases, impact craters associated with a tektite-strewn field have not been identified.

Ablation marks on tektites are consistent with a single entry at a grazing angle through the upper atmosphere^(3d). This naturally leads to suggest an extraterrestrial origin for tektites. Absence of ^{26}Al in tektites⁽⁵⁾ suggests that this extraterrestrial body is most likely the moon and that the tektites did not stay as satellites in the earth-moon system for more than a few years⁽⁶⁾.

Based upon a large number of computer calculations, Chapman⁽⁷⁾ showed that lunar ejecta along the principal rays emanating from the crater Tycho would be compatible with the geographical distribution of Australasian tektites. Chapman⁽⁸⁾ also succeeded in making dumbbell, button and other shapes of tektites by subjecting synthetic glasses through a wind tunnel under various conditions.

Arguments of lunar origin are naturally based upon the assumption that the chemistry of lunar surface is similar to that

of the earth. Since the average density of the moon is 3.3 g/cc and that of tektites is only 2.4 g/cc, a lunar origin requires that part of the lunar crust which acted as the source of tektites, must have undergone differentiation by volcanic activity or metamorphism.

A crystalline lattice can be made to lose its long range order in two ways following an impact. Shear associated with a shock wave without a significant amount of heat energy produce the so-called diaplectic glasses⁽⁹⁾, sometimes also termed the thetomorphic glasses⁽¹⁰⁾. The original grain boundaries of the crystalline material are preserved in these shock produced glasses. This is expected because significant homogenization between adjacent grains does not occur due to the lack of long distance diffusion which is a high temperature process.

The second way of producing a glass following an impact is by actual melting of the crystalline material.

Sufficient evidence in favor of the latter in case of most of the tektites is provided by petrographic studies⁽¹¹⁾. A primary exception, where the grain boundaries do exist is the Muong-Nong tektites. Whereas the Muong-Nong tektites can be regarded as diaplectic, the presence of a relatively high degree of homogeneity within the grains⁽¹²⁾ suggests that they might have been glassy even before the impact.

No large bodies of natural glass approximating the tektite

composition are found in the vicinity of the recovery areas of the tektites. An individual terrestrial mineral matching the chemical composition of tektites exactly is not found. Closest, perhaps, are the subgreywackes from Henbury, Australia^(3d,13) but these deposits are physical mixtures of minerals including quartz grains of 0.2 - 0.5 mm sizes. A tektite originating on the earth, therefore, requires a thermal history following the impact which is of sufficient temperature and duration to permit melting and homogenizing of the mineral mixture.

If, however, some fraction of the lunar crust were glassy, then it would be possible to explain the ultimate homogeneity of tektites in terms of, even, a moderate rise in temperature only of a glassy mineral following an impact. The diaplectic nature of Muong-Nong tektites could also be easily accounted for.

This relative ease in explaining led to the origin of the hypothesis that "the moon is glassy".

On July 20, 1969, the spaceship, Eagle, landed in Mare Tranquillitatis on the surface of the moon. Millions of TV viewers heard Commander Neil Armstrong indicate that some rocks were lined with vesicular material.

Soon after the return of Apollo XI with lunar samples, it was discovered that indeed as much as 50% or even more of the lunar soil was glassy. Glass beads less than a mm in size, which

were rather similar in appearance to the ocean bed tektites (the so-called microtektites) were abundant.

This did not end the tektites story in favor of a lunar origin because shortly afterwards, it was discovered that the chemical composition and the age estimates of Mare Tranquillitatis do not appear to have any relationship to those of tektites.

The success of the Apollo XII mission brought a new discovery. It was found that the materials from Oceanus Procellarum (Sea of Storms) is less glassy, with a chemical composition having some resemblance to that of tektites. The preliminary age estimates were still nearly the same as those of Mare Tranquillitatis.

The chemical heterogeneity of the lunar crust, thus, kept the lunar origin hypothesis of tektites alive. Since the possibility exists that glass with matching composition may be found, the question of adequate thermal history is an important one. Is it possible to make tektites out of terrestrial rock in a single melting event, perhaps following a meteor impact, and if not, what initial homogeneity of the source material is required to be consistent with the as-recovered state of tektites, are some of the questions we wish to seek answers for.

As indicated earlier, homogenization of glass is a typical diffusion process. The magnitude of diffusion coefficients of

the various constituting species determines the degree of homogenization achieved by the specimen following a thermal treatment.

Terrestrial origin of tektites is doubtful if the diffusion coefficients of the species are much too low to be compatible to achieving the observed degree of homogeneity in as-recovered tektites.

These arguments reduce the problem to a question of measuring the homogeneity in as-recovered tektites, measuring the various diffusion coefficients in the system and then speculating on possible thermal histories which would give rise to the as-observed homogeneity.

One right away faces a problem in theoretical concepts; what are these 'various diffusion coefficients' in a multicomponent system such as a tektite?

Equations of diffusion in multicomponent systems have often been written in terms of Onsager's extension of Fick's first law⁽¹⁴⁾. This phenomenological approach defines an $(n-1) \times (n-1)$ matrix of diffusion coefficients for an n component system. Calculation of this matrix becomes tedious as soon as n exceeds 3.

Some diffusion data existing in literature has been analyzed with this phenomenological approach to obtain the diffusion coefficients matrix. It has not been demonstrated, however, that a diffusion matrix is necessary and sufficient in accurately

describing diffusion behavior in a given diffusion couple. Verification of Onsager's hypothesis, thus, still remains open.

The effective binary diffusion coefficient approach^(15,16) defines only one coefficient per species in a particular diffusion couple and hence avoids the tedium involved in a matrix calculation. For this reason, it is ideally suited for a system such as that of a tektite where the number of major constituents alone exceeds 6.

While some data has been successfully interpreted⁽¹⁶⁾ in terms of an effective binary diffusion coefficient and the use of this approach has been indicated⁽¹⁷⁾ in condensed systems, the most serious drawback with this approach is that this type of coefficient is strongly dependent upon the direction of the diffusion path in the composition space.

Another fundamental property controlling the diffusion of a species is its self-diffusion coefficient. The self-diffusion coefficient of a species is directly related to its mobility and, a semiquantitative estimate through theoretical arguments⁽¹⁸⁾ or extrapolation from available literature on similar systems⁽¹⁹⁾ can be made.

Whereas some models⁽²⁰⁾ have been suggested to relate these self-diffusion coefficients to the diffusion coefficients matrix in a multicomponent system, none of these models has yet been established even on semiquantitative basis.

This project aimed at performing the following tasks:

- (i) to show experimentally that a diffusion matrix as postulated by Onsager's hypothesis is necessary and sufficient in describing multi-component diffusion in a general direction on composition space.
- (ii) to investigate the relation of mobility of individual species to the diffusion coefficients matrix in a multicomponent system.
- (iii) to apply the effective binary diffusion coefficient approach to estimate the possible thermal history consistent with the homogeneity of an as-recovered Thailand tektite.

For (i) and (ii), the system $K_2O-SrO-SiO_2$ was chosen, primarily because of its simplicity and because a considerable amount of related diffusion work has already been performed on it by the author.

This thesis is, therefore, divided into two main parts;

- (i) Diffusion in the $K_2O-SrO-SiO_2$ System, and (ii) Diffusion in Tektites.

PART I

DIFFUSION IN K_2O - SrO - SiO_2 SYSTEM

"I seem to have been only like a boy playing on the seashore and diverting myself in now and then finding a smoother pebble or a prettier shell than the ordinary whilst the great ocean of truth lay all undiscovered before me."

-- Isaac Newton

CHAPTER 2

LITERATURE SURVEY: Multicomponent Diffusion Theory and Experiments

"A lot of today's frustration is caused by a surplus of simple answers, coupled with a tremendous shortage of simple problems."

--Paul Sweeney in The Quarterly

§2.1 THE PHENOMENOLOGY OF MULTICOMPONENT DIFFUSION

In an isothermal, isobaric system in mechanical equilibrium, the introduction of a chemical concentration gradient of species i results in a diffusive flux of i so as to reduce the concentration gradient. The relation between the flux and the force is given by Fick's first law which is mathematically stated as

$$-\vec{J}_i = D_i \vec{\nabla} X_i \quad (1)$$

where $\vec{J}_i$ = flux density of i (mass units/cm².sec)

X_i = concentration of i (mass units/cm³)

and D_i = diffusion coefficient of i (cm²/sec)

If the system is isotropic, then both $\vec{J}_i$ and $\vec{\nabla} X_i$ are in the same

direction, y , in the real space of the system. And, thus, for the case of unidirectional diffusion along y , equation (1) can be rewritten as

$$-J_i = D_i (\partial X_i / \partial y) \quad (2)$$

The symbol ∇ , now onwards, will be used to stand for ' $\frac{\partial}{\partial y}$ '.

Equation (2) is true when the only independent concentration gradient present is that of species i . In a multicomponent system where the variation of i is compensated by concentration gradients of other species, equation (2) becomes inadequate.

In 1945, Onsager⁽¹⁴⁾ extended Fick's first law to describe diffusion in a multicomponent system. The flux of each species could be written as a linear combination of all the forces present. Thus

$$-J_i = \sum_j^n D_{ij} \nabla X_j \quad (3)$$

($i, j = 1, 2, \dots, n$)

Not all the concentration gradients and the fluxes are independent. Depending upon the choice of the reference frame, equation of conservation of species can be written such that one of the fluxes and one of the gradients can be eliminated from equation (3). For example, in the volume fixed reference frame (diffusion relative to the local center - of - volume), the mass fluxes,

J_i , must follow

$$\sum_{i=1}^n \bar{V}_i J_i = 0 \quad (4)$$

and the mass concentrations

$$\sum_{i=1}^n \bar{V}_i X_i = 1 \quad (5)$$

where $\bar{V}_i$ = partial mass volume*.

Equations of the type (4) and (5) reduce equation (3) to

$$-J_i = \sum_j^{n-1} D_{ij}^r \nabla X_j \quad (6)$$

$$i, j = 1, 2, \dots, (n-1)$$

where the superscript, r , on D_{ij} is used to indicate that the concentration gradient and the flux of the r th species have been eliminated.

* $\bar{V}_i$ is defined as

$$\bar{V}_i = (\partial V / \partial N_i)_{T, P, n_j, \dots}$$

It is the change in volume of the system due to addition of dn_i mass units of i provided the addition does not significantly change the overall composition of the system.

Thus, Onsager's hypothesis describes multicomponent diffusion by an equation of the form (6) involving an $(n-1)$ square matrix of diffusion coefficients. The coefficients D_{ij}^r , where $i \neq j$ are called the cross or the off-diagonal coefficients and D_{ii}^r are called the direct or diagonal coefficients.

Originally, Onsager⁽²⁴⁾ formulated equation (3) in terms of chemical potential gradients rather than the concentration gradients because it is the chemical potential gradient which is more fundamental driving force. Written mathematically

$$-J = \sum_{j=1}^{n-1} L_{ij} \nabla \mu_j \quad (7)$$

$i, j = 1, 2, \dots, (n-1)$

The matrix L_{ij} is called the fundamental coefficients or the phenomenological coefficients or the conductance matrix. Invoked by the principle of microscopic reversibility, Onsager suggested that if in equation (7) the fluxes and forces were defined such that their linear combination generates the local entropy production then the matrix of phenomenological coefficients is symmetrical, i.e.,

$$L_{ij} = L_{ji} \text{ for } i \neq j \quad (8)$$

Equation (8) is termed the "Onsager Reciprocal Relations" or

simply the ORR.

Coleman and Truesdell⁽²²⁾ have pointed out that requiring the fluxes and forces to generate entropy production is not a sufficient condition for the ORR to satisfy. The coefficients will obey ORR only when the linear equations written in a given reference frame involve a suitable choice of independent fluxes and forces. In the mass fixed frame, for example, the ORR apply only when the fluxes are mass fluxes and the forces are chemical potential gradient differences $\nabla(\mu_i - \mu_r)$, the chemical potential being expressed as the free energy per unit mass of the species.

It is not the intention here to discuss the different types of reference frames, the available choices of fluxes and forces and the conversion of one set of coefficients to another. Readers are referred to citations (23,24) for more details on the subject.

It suffices here to state that the phenomenological coefficients matrix is of no additional advantage over the practical diffusion coefficients matrix already defined by equation (3). If the ORR apply, the number of independent coefficients in an n-component system is $n \cdot (n-1)/2$.

Another frequently used set of diffusion coefficients is the intrinsic diffusion coefficients matrix proposed by Kirkaldy⁽²⁵⁾ and Guy and Smith^(20a). This matrix M_{ij} is defined

by

$$-J_i = \sum_{j=1}^{n-1} M_{ij} \nabla X_j - v X_i \quad (9)$$

$i, j = 1, 2, \dots, (n-1)$

where v is the marker's velocity. Equation (10) is an extension of Darken's relation⁽²⁶⁾ for binary systems. In fact, it can be shown⁽²⁷⁾ that M_{ij} are the dilute solutions approximations of the practical diffusion coefficients D_{ij} - a result which is consistent with Darken's use of intrinsic coefficients for binary systems. It is worthy of note that Guy and Smith's proposal requires n ($n-1$) independent coefficients.

Manning^(20c) has developed a model to describe diffusion kinetics in a multicomponent system where diffusion occurs by a vacancy mechanism. The flux of each species is written as a sum of contributions through its own mobility and through a vacancy wind effect. In an ideal system, the former determines the diagonal coefficient whereas the latter gives rise to the cross coefficients. All the coefficients can be related to the n independent tracer diffusion coefficients.

However, the concept of a vacancy wind in glassy systems is not so clear. Manning's model, therefore, will not be discussed any further and instead, we proceed to describe the atomic mobility model originally proposed by Oishi⁽²⁸⁾, Ziebold and Cooper⁽²⁹⁾, later extended to glassy systems by Cooper^(20b).

§2.2 THE MOBILITY MODEL AND ITS EXTENSION ^(20b) TO IONIC SYSTEMS

The underlying concept of this model is that relative to a fixed lattice, all the species move with their intrinsic flux densities. In addition, the lattice itself moves with a relaxation velocity, U_r , relative to the local center of volume. This velocity, U_r , locally has such values so as to satisfy

$$\sum_i^n \bar{V}_i J_i = 0 \quad (11)$$

which means that there is no overall pressure build-up.

Processes such as viscous flow in glassy systems can be imagined to give rise to this bulk relaxation. Ionic systems incorporate an additional restriction; the system acts to prevent a build-up of space charge. The electric fields are caused by the difference in mobilities of individual ions. If a particular ion, e.g. a cation, is more mobile than an anion, then the motion of cation will set up an electric field which will tend to retard its own flux and that of other cations and will increase the flux of anions in the same direction.

If $\nabla\psi$ is the intensity of local electric field and z_i are the charges on the ions, then the net flux of i is given by

$$-J_i = X_i \beta_i (\nabla \mu_i + z_i \nabla \Psi) - U_r X_i \quad (12)$$

$$i = 1, 2, \dots, n$$

Where β is the atomic mobility - the steady state velocity per unit driving force. The chemical potential, μ , is measured as free energy per particle.

The condition of nearly no build-up of space charge gives

$$\sum_{i=1}^n z_i J_i \cong 0 \quad (13)$$

In silicate structures, the volume is largely controlled by the oxygen spacing, the cations fit into the interstices. Thus

$$\bar{V}_{\text{cations}} \cong 0 \quad (14)$$

and so from (11)

$$\bar{V}_O J_O = 0 \quad (15)$$

where the subscript O stands for oxygen.

The molecular chemical potential, μ_{AO} , of a compound $A|z_O| O|z_A|$ is given by⁽³⁰⁾

$$\mu_{AO} = |z_A| \mu_O + |z_O| \mu_A \quad (16)$$

It is convenient to adopt the conventions for single anion systems that

$$\nabla \mu_O = 0 \quad (17)$$

i.e., the anion is in chemical equilibrium everywhere and migrates only when required to preserve electrical neutrality. For oxide glasses, this appears a reasonable premise since the oxygen density is nearly constant over a wide range of compositions⁽³¹⁾.

Atomic mobility, β_i , can be written in terms of the self-diffusion coefficient, D_i , as

$$\beta_i = D_i/kT \quad (18)$$

where k = Boltzmann constant

We can eliminate $\nabla \psi$ and U_r , now, to obtain for a system containing A, B, C and O ions

$$\begin{aligned} -J_A = & \frac{1}{kT} [X_{AO} (1 + X_{AO} Z_A) D_A] \nabla \mu_{AO} \\ & + \frac{1}{kT} [X_{AO} X_{BO} Z_B \Phi_{AO} D_B] \nabla \mu_{BO} \\ & + \frac{1}{kT} [X_{AO} X_{CO} Z_C \Phi_{AO} D_C] \nabla \mu_{CO} \end{aligned} \quad (19)$$

with corresponding equations for $-J_B$ and $-J_C$

where

$$\phi_{AO} = \frac{-(D_A z_A - D_O z_O)}{3} \quad (20)$$

$$\sum_{i=1}^{\infty} (D_i z_i - D_O z_O) z_i X_{iO}$$

and i sums over the cations only.

It is possible to show that for ideal solutions when equation (28) is converted to the form of (7), the ORR are obeyed which is in accordance with the suggestions of Kirkwood, et al. (24)

Requirements of stoichiometry and the reference frame enable us to rewrite equation (18) in the form

$$-J_{AO} = D_{AA} \nabla X_{AO} + D_{AB} \nabla X_{BO} \quad (21)$$

$$-J_{BO} = D_{BA} \nabla X_{AO} + D_{BB} \nabla X_{BO}$$

with

$$D_{AA} = D_A f'_{AA} + \phi_{AO} (X_{AO} z_A D_A f'_{AA} + X_{BO} z_B f'_{BA} D_B$$

$$+ X_{CO} z_C D_C f'_{CA})$$

$$D_{AB} = \frac{X_{AO}}{X_{BO}} D_A f'_{AB} + \phi_{AO} \left[\frac{X_{AO}^2}{X_{BO}} Z_A D_A f'_{AB} + \right. \\ \left. X_{AO} D_B Z_B f'_{BB} + \frac{X_{AO} X_{CO}}{X_{BO}} Z_C D_C f'_{CB} \right]$$

$$D_{BB} = D_B f'_{BB} + \phi_{BO} [X_{BO} Z_B D_B f'_{BB} + \\ X_{AO} Z_A D_A f'_{AB} + X_{CO} Z_C D_C f'_{CB}]$$

$$D_{BA} = \frac{X_{BO}}{X_{AO}} D_B f'_{BA} + \phi_{BO} \left[\frac{X_{BO}^2}{X_{AO}} Z_B D_B f'_{BA} + \right. \\ \left. X_{BO} Z_A D_A f'_{AA} + \frac{X_{BO} X_{CO}}{X_{AO}} Z_C D_C f'_{CA} \right] \quad (21)$$

where

$$f'_{ij} = \left(\frac{\partial \ln a_{iO}}{\partial \ln X_{jO}} \right)_{X_{kO}; k \neq j}$$

The model permits the interdiffusion coefficients to be written in terms of the self-diffusion coefficients of the cations and the anion. The number of independent coefficients for an n component oxide system is thus (n + 1) where one of the coefficients is that of oxygen.

§2.3 SOLUTION TO THE DIFFERENTIAL EQUATION OF DIFFUSION

For a system with n components, the flux of i is given by

$$-J_i = \sum_j D_{ij}^n \nabla x_j \quad (23)$$

where i, j = 1, 2 . . . (n-1)

Application of conservation of i yields

$$\frac{\partial x_i}{\partial t} = \nabla \sum_j D_{ij}^n \nabla x_j \quad (24)$$

which, for constant D_{ij}^n yields

$$\frac{\partial x_i}{\partial t} = \sum_j D_{ij}^n \nabla^2 x_j \quad (25)$$

The treatment onwards will involve the coefficients D_{ij}^n , i.e., where the dependent variables (that of species n) have been eliminated. Henceforth, the superscript "n" will be dropped, i.e., $D_{ij}^n \equiv D_{ij}$.

The solution to equation (25) given below follows Toor⁽³²⁾ and Fujita and Gosting⁽³³⁾.

Multiply by a constant s_i and sum over all i .

$$\frac{\partial \sum_i s_i X_i}{\partial t} = v^2 \sum_{ij} D_{ij} s_i X_j \quad (26)$$

If this equation were to be reduced to a binary form, then s_i must be chosen such that

$$\begin{aligned} \sum_{ij} D_{ij} s_i X_j &\equiv D \sum_i s_i X_i \\ &= D \sum_j s_j X_j \end{aligned} \quad (27)$$

Equating the coefficients of X_j on both sides, we obtain

$$\sum_i D_{ij} s_i = D s_j \quad (28)$$

This equation represents a system of $(n-1)$ linear homogeneous equations. A solution exists only if

$$| D_{ij} - D \delta_{ij} | = 0 \quad (29)$$

Equation (29) can be solved for D which are the eigen values of the D_{ij} matrix, represented by D_k where k has $(n-1)$ values.

For a ternary system, solution of equation (29) gives

$$D_k = \frac{(D_{11} + D_{22}) \pm \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}}}{2} \quad (30)$$

The two eigen values will be denoted by D_u and D_v with the convention that $D_u > D_v$.

The constants s_i can be calculated from equation (28) for the two eigen values. Also, equation (26) is reduced to

$$\frac{\partial \theta_k}{\partial t} = D_k \nabla^2 \theta_k \quad (31)$$

for the k^{th} eigen value where

$$\theta_k = \sum_i s_{ik} X_i$$

For a semi-infinite couple, the solutions of (32) are of the form

$$\theta_k = a_k \operatorname{erf} \left\{ \frac{\lambda}{2} \sqrt{D_k} \right\} + b_k \quad (32)$$

$$\begin{aligned} \text{where } \lambda &= \frac{\text{distance from the interface}}{\text{square root diffusion time}} \\ &= y/\sqrt{t} \end{aligned} \quad (33)$$

For boundary conditions at $t > 0$

$$\lambda = +\infty \quad \Rightarrow \quad \begin{aligned} x_1 &= x_1^Q \\ x_2 &= x_2^Q \end{aligned}$$

$$\text{and } \lambda = -\infty \quad \Rightarrow \quad \begin{aligned} x_1 &= x_1^P \\ x_2 &= x_2^P \end{aligned} \quad (34)$$

equation (32) can be unfolded to give

$$x_1 - \frac{(x_1^Q + x_1^P)}{2} = a \operatorname{erf}(\lambda/2\sqrt{D_u}) + b \operatorname{erf}(\lambda/2\sqrt{D_u}) \quad (35a)$$

$$x_2 - \frac{(x_2^Q + x_2^P)}{2} = c \operatorname{erf}(\lambda/2\sqrt{D_u}) + d \operatorname{erf}(\lambda/2\sqrt{D_u}) \quad (35b)$$

where

$$a = (1/2G) [\{(D_{11} + G - D_{22})(x_1^Q - x_1^P)/2\} + D_{12}(x_2^Q - x_2^P)]$$

$$b = [(x_1^Q - x_1^P)/2] - a$$

$$c = (1/2G) [\{(D_{22} + G - D_{11})(x_2^Q - x_2^P)/2\} + D_{21}(x_1^Q - x_1^P)]$$

$$d = [(x_2^Q - x_2^P)/2] - c$$

$$\text{and } G = [(D_{11} - D_{22})^2 + 4 D_{12} D_{21}]^{1/2} \quad (36)$$

This technique of obtaining solutions of equation (25) is not restricted to three components only. In fact, Kirkaldy⁽³⁴⁾ has shown that if a solution exists for a one-component system under

given initial and boundary conditions, then the solutions for an n-component system are linear sums of individual solutions.

§2.4 THERMODYNAMIC RESTRICTIONS ON THE D MATRIX

For the entropy production to be positive, it can be shown^(34,35) that the eigen values of the D matrix be all positive and definite.

Hence, from equation (30),

$$\begin{aligned} D_{11} + D_{22} &\geq 0 \\ (D_{11} + D_{22})^2 &\geq 4 (D_{11} D_{22} - D_{12} D_{21}) \\ \text{and } D_{11} D_{22} &\geq D_{12} D_{21} \end{aligned} \tag{37}$$

are the restrictions on the D matrix. It is worthy of note that the individual diagonal coefficients do not have to be positive; only the sum must be positive.

§2.5 DIFFUSION PATH

The continuous collection of compositions with varying values of y in a diffusion couple generates a curve on the composition space. This curve is termed the diffusion path.

The conventional method of displaying the composition space for a ternary system is an equilateral triangle. But, since

one of the components is a dependent variable, a space spanned by orthogonal $\hat{\gamma}_1$ - $\hat{\gamma}_2$ composition basis vectors represents the system equally well. At the same time, it allows concepts of linear algebra to be directly used to display various aspects of diffusion on the composition space.

In matrix notation, the flux density $\vec{J}$ can be written as

$$\vec{J} = [D_{ij}] \cdot \nabla \vec{X} \quad (38)$$

where $\vec{J} = J_1 \hat{\gamma}_1 + J_2 \hat{\gamma}_2$, $\nabla \vec{X} = \nabla X_1 \hat{\gamma}_1 + \nabla X_2 \hat{\gamma}_2$ and are written as column vectors and $[D_{ij}]$ is a 2 x 2 matrix. Note that ' ∇ ' symbol is still being used to denote scalar $\partial/\partial y$. The characteristic equation is, therefore,

$$[D_{ij} - DI] \cdot \nabla \vec{X} = 0$$

where D represents the eigen values and I the identity matrix.

Since there are two eigen values (equation 30), the two corresponding eigen vectors are given by

$$(\nabla X_2 / \nabla X_1)_u = D_{21} / (D_u - D_{22}) = (D_u - D_{11}) / D_{12} \quad (39a)$$

$$\text{and } (\nabla X_2 / \nabla X_1)_v = (D_v - D_{11}) / D_{12} = D_{21} / (D_v - D_{22}) \quad (39b)$$

With the convention $D_u > D_v$, the first direction is the direction of

"fast eigen vector" or $\vec{u}$ and the second one that of the "slow eigen vector" or $\vec{v}$.

Figure 1 shows the location of termini composition P and Q, in a hypothetical couple on the orthogonal $\hat{y}_1 - \hat{y}_2$ space. The location of P, for example is such that

$$\vec{X}(P) = X_1 \hat{y}_1 + X_2 \hat{y}_2$$

and this composition vector is limited by the restraints $X_1 > 0$, $X_2 > 0$ and $X_1 + X_2 = \rho$, the density of the system. The directions of the two eigen vectors have been drawn from each point.

The following theorems apply ⁽³⁵⁾ for the case of semi-infinite unidirectional couples:

- i. For constant D_{ij} , the diffusion path must pass through the midpoint R.
- ii. The path must be totally enclosed within the parallelogram formed by the eigen vector directions from P and Q.
- iii. At the extremities, the diffusion path must be parallel to the fast eigen vector.
- iv. Diffusion path is a straight line only if $D_u = D_v$ or the line PQ is an eigen vector.
- v. As a consequence, the extreme diffusion path between P and Q is PMRNQ where MN is parallel to the slow eigen vector.

ASSUMED

$$[D] = \begin{bmatrix} 5 & -1 \\ -4 & 2 \end{bmatrix} \text{ cm}^2/\text{sec}$$

$$D_u = 6, D_v = 1$$

$$P = (0.7, 0.1, 0.2)$$

$$Q = (0.1, 0.4, 0.5)$$

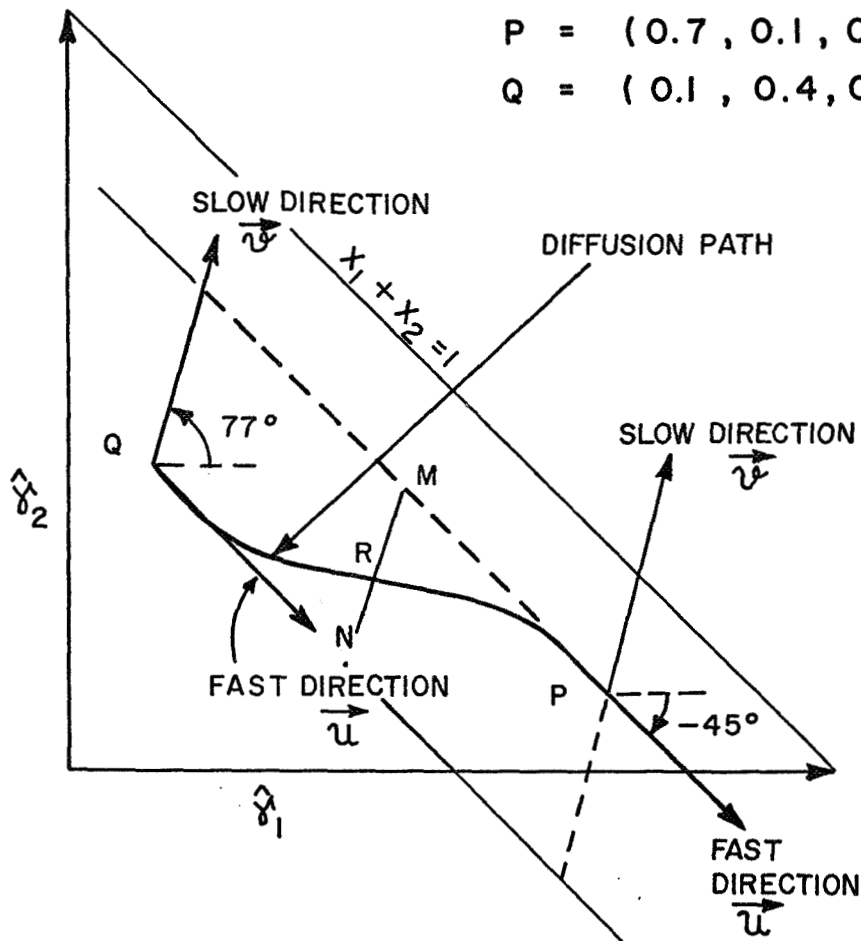


FIG. 1 : THE ORTHOGONAL $\hat{x}_1$ - $\hat{x}_2$ SPACE.

vi. At the boundaries of the composition space, the eigen vectors must rotate and, hence, $[D_{ij}]$ cannot stay concentration-independent at the boundaries.

§2.6 UPHILL DIFFUSION

When a species moves "up" its own concentration gradient, the resultant concentration distribution of the species displays extremum points (maxima and minima). This phenomenon is termed "uphill diffusion". A mathematical statement which precisely defines the occurrence of uphill diffusion is

$$J_i \frac{\partial x_i}{\partial y} > 0 \quad (40)$$

In multicomponent systems, the occurrence of uphill diffusion is not uncommon and is well recognized^(24,26).

The presence of the extremum points in concentration distributions can be neatly displayed with the help of the orthogonal $\hat{\gamma}_1 - \hat{\gamma}_2$ space.

Figures 2 and 3 show that whenever the diffusion path goes out of the shaded rectangles (formed by equi-concentration lines drawn from the mean composition point M and one of the termini), the concentration distribution displays uphill diffusion.

Accordingly, two types of concentration "hills" occur. One

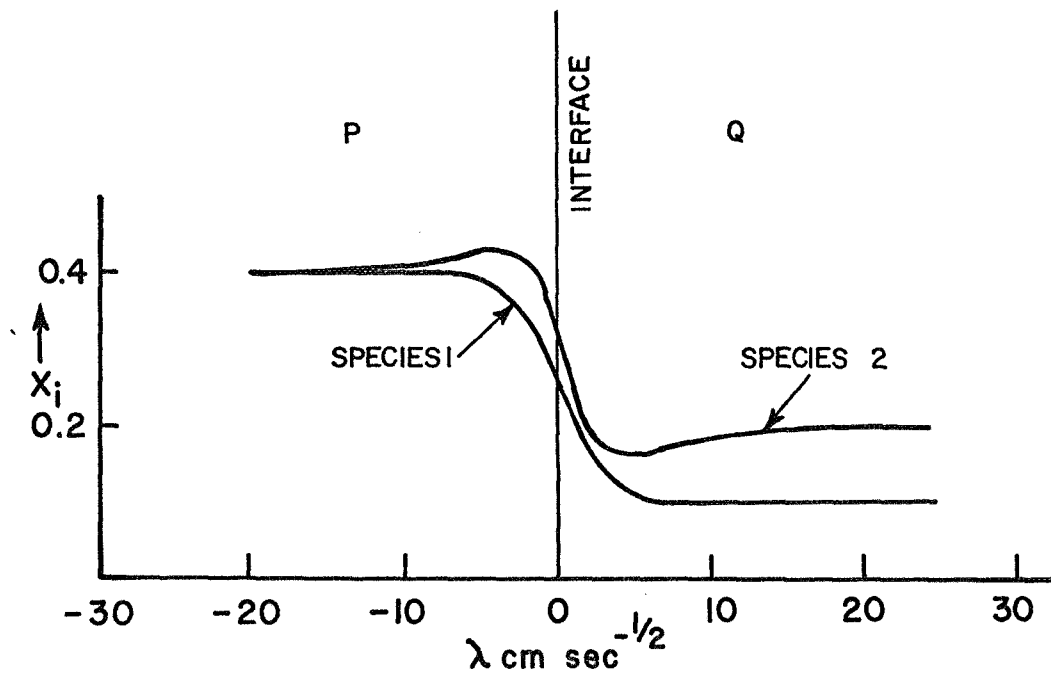
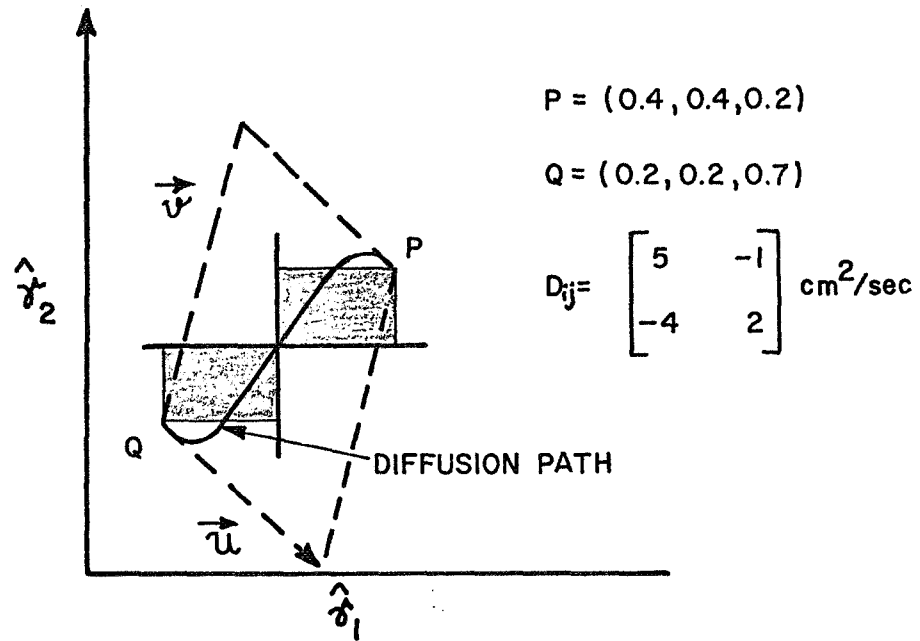
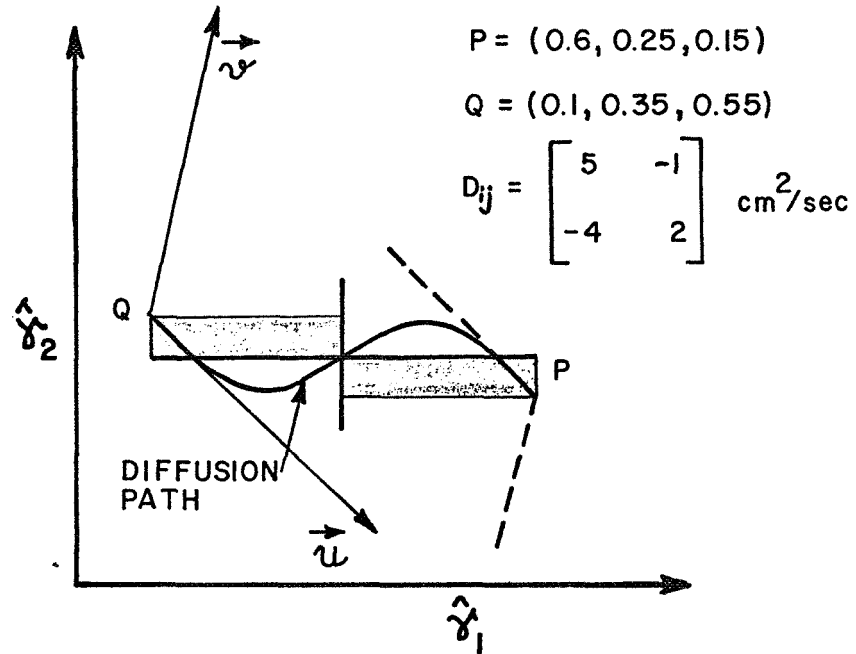


FIG. 2 : UPHILL DIFFUSION, TYPE I.



type occurs at the extremities (as in Figure 2) and the other in the vicinity of $\lambda = 0$ region (as in Figure 3). It is obvious that in a ternary system, given a set of eigen vectors, it is always possible to find a diffusion couple which will have extremum points of one type or the other in only one, two or all three distributions of its constituting species with the condition that all extremum points do not occur at the same position on the λ scale.

§2.7 DEPENDENCE OF DIFFUSION COEFFICIENT UPON CONCENTRATION GRADIENT AND TIME

Fick's Law, as stated by equation (1) for a single species, or the Onsager's extension (equation (3)) for multicomponent systems are essentially linear laws. The concentration distribution of a species after diffusion can be expressed by an equation of the form

$$X_i = f[y/h(t)] \quad (41)$$

i.e., when concentration profiles corresponding to various diffusion times are plotted on $y/h(t)$ scale, they all merge. The inapplicability of equation (41) implies "non-Fickian" diffusion.

Dependence of diffusion coefficient upon concentration gradient can be expressed by a non-linear equation for flux such as

$$-J_i = D' \nabla X_i + D''' (\nabla X_i)^3 + D'''' (\nabla X_i)^5 + \dots \quad (42)$$

Such an equation will not follow equation (41) and, therefore, gives rise to non-Fickian diffusion.

It is possible to show⁽³⁶⁾ that when the diffusion coefficients have different time dependence, then a linear equation involving higher degree terms in ∇X_i , such as

$$-J_i = D(t_1) \nabla X_i + D(t_3) \nabla^3 X_i + D(t_5) \nabla^5 X_i + \dots \quad (43)$$

will also display non-Fickian diffusion.

When equation (41) is obeyed and that $h(t) = \sqrt{t}$, the diffusion coefficient is independent of both concentration gradient and time. This condition is met by a diffusion coefficient which is either a constant or a function of concentration alone.

§2.8 THE EFFECTIVE BINARY DIFFUSION COEFFICIENT

The effective binary diffusion coefficient of a species i in a multicomponent system is defined as⁽¹⁵⁾

$$-J_i = D_{iM} \nabla X_i \quad (44)$$

This definition describes the diffusion as a binary exchange of species i with all other species put together as species M .

Comparison of equation (44) with equation (3) yields

$$D_{iM} = \sum_{j=1}^{n-1} D_{ij} \nabla X_j / \nabla X_i \quad (45)$$

For a Fickian diffusion process,

$$\begin{aligned}
 \frac{\nabla X_j}{\nabla X_i} &= f'_j \left[\frac{Y}{h(t)} \right] \cdot \frac{\partial h(t)}{\partial t} / f'_i \left[\frac{Y}{h(t)} \right] \cdot \frac{\partial h(t)}{\partial t} \\
 &= f'_j \left[\frac{Y}{h(t)} \right] / f'_i \left[\frac{Y}{h(t)} \right] = F \left[\frac{Y}{h(t)} \right] \\
 &= F [f^{-1}(X_i)]
 \end{aligned} \tag{46}$$

Hence, we notice that if D_{ij} are Fickian coefficients then D_{iM} , although concentration dependent, is also Fickian. A more proper statement concerning the concentration dependence of D_{iM} is that it is dependent upon $\partial X_j / \partial X_i$ which is the "direction" of diffusion on the composition space. An extensive treatment of the EBDC approach has been given by Cooper⁽¹⁷⁾ and Cooper and Varshneya⁽¹⁶⁾.

§2.9 PREDICTIONS OF THE ATOMIC MOBILITY MODEL

In this section, we make use of the fact that the self-diffusion coefficients of cations in the $K_2O-SrO-SiO_2$ system over the temperature range of 550°C to 800°C are known⁽³⁸⁾.

To summarize

$$D_K = 36.5 \exp (-40800/RT)$$

$$D_{Sr} = 0.17 \exp (-42700/RT)$$

$$\text{and } D_{Si} < D_{Sr} \text{ at } 750^\circ\text{C} \tag{47}$$

Although no data on the self-diffusion coefficient of oxygen in this glass is available, we assume that

$$D_K \gg D_O \quad (48)$$

The assumption is based upon the premise that alkalis are the sole charge carriers for electrical conductivity through a glass of an alkali-alkaline earth-silica system^(39,40). Data of mobility of oxygen in other systems also substantiates the validity of this assumption.

Equation (20) can be rewritten as

$$\begin{aligned} \phi_{AO} = & - \frac{1}{Z_A X_{AO}} \left[1 + \left(\frac{D_B Z_B - D_O D_O}{D_A Z_A - D_O Z_O} \right) \left(\frac{Z_B X_{BO}}{Z_A X_{AO}} \right) + \right. \\ & \left. \left(\frac{D_C Z_C - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \left(\frac{Z_C X_{CO}}{Z_A X_{AO}} \right) \right]^{-1} \\ \approx & - \frac{1}{Z_A X_{AO}} \left[1 - \left(\frac{D_B Z_B - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \left(\frac{Z_B X_{BO}}{Z_A X_{AO}} \right) - \right. \\ & \left. \left(\frac{D_C Z_C - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \left(\frac{Z_C X_{CO}}{Z_A X_{AO}} \right) \right] \quad (49) \end{aligned}$$

where A, B, C and O stand for potassium, strontium, silicon and oxygen, respectively. Hence, for D_{AA} from (22), we get

$$D_{AA} \approx D_A f'_{AA} \left[\sum_{j=B,C} \left(\frac{D_j Z_j - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \left(\frac{Z_j X_{jO}}{Z_A X_{AO}} \right) \right]$$

$$= \left[\sum_{j=B,C} D_j f'_{jA} \left(\frac{Z_j X_{jO}}{Z_A X_{AO}} \right) \right] \left[1 - \sum_{j=B,C} \left(\frac{D_j Z_j - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \left(\frac{Z_j X_{jO}}{Z_A X_{AO}} \right) \right] \quad (50)$$

If the system were thermodynamically ideal, then $f'_{ij} = \delta_{ij}$.

However, if slight non-ideality in our system exists, then $f'_{ii} \approx 1$, $f'_{ij} < 1$ when $i \neq j$. It is evident that the main contribution to D_{AA} comes from the first expression on the right hand side of equation (50). Also, since $D_A Z_A \gg D_O |Z_O|$

$$D_{AA} \approx \sum_{j=B,C} \left(\frac{D_j Z_j - D_O Z_O}{Z_A} \right) \left(\frac{Z_j X_{jO}}{Z_A X_{AO}} \right) \quad (51)$$

The result is interesting in the sense that the direct coefficient of potassium has little to do with the self-diffusion coefficient of potassium.

Also, if potassium were the only moving species in the system, the direct coefficient of potassium would be zero. This is physically meaningful and understandable. Movement of potassium ion alone would cause a space charge build-up which would soon bring the diffusion of potassium ion to a stop.

Let us consider the direct coefficient of strontium.

$$\phi_{BO} \approx - \left(\frac{1}{Z_A X_{AO}} \right) \left(\frac{D_B Z_B - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \quad (52)$$

and so

$$D_{BB} \approx D_B f'_{BB} - \left(\frac{1}{Z_A X_{AO}} \right) \left(\frac{D_B Z_B - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \left(\sum_{j=A,B,C} X_{jO} Z_j D_j f'_{jB} \right) \quad (53)$$

If the expression within the brackets were small positive, then we conclude that

$$D_{BB} < D_B \quad (54)$$

However, the actual magnitude and the sign of the expression within the brackets cannot be estimated owing to the lack of knowledge about f'_{AB} and D_O . As such, a negative value of D_{BB} is not excluded as a possibility. It is interesting to note that such a possibility is also not excluded by the thermodynamic restrictions on the $[D_{ij}]$ matrix stated in section 2.4. The cross coefficient, D_{AB} , is given by

$$D_{AB} \approx D_B f'_{BB} \left(\frac{Z_B}{Z_A} \right) \left[-1 + \sum_{j=B,C} \left(\frac{D_j Z_j - D_O Z_O}{D_A Z_A - D_O Z_O} \right) \left(\frac{Z_j X_{jO}}{Z_A X_{AO}} \right) \right] \quad (55)$$

Again, a great deal depends upon the coefficients D_O and f'_{AB} .

For D_{BA} we have,

$$D_{BA} \approx - \left(\frac{X_{BO}}{X_{AO}} \right) \left(\frac{D_B Z_B - D_O Z_O}{Z_A} \right)$$

Comparing with equation (51) we get

$$D_{BA} \approx -D_{AA} \quad (56)$$

This result is also understandable in terms of intuitive reasoning: since strontium is relatively less mobile species compared to potassium, its flux is caused primarily to prevent pressure and charge build-up resulting from the motion of potassium.

Some remarks can be made here about an apparent activation energy of the interdiffusion coefficients. In general, the different contributions of the individual self-diffusion coefficients will not give rise to an Arrhenius' rate type dependence, i.e., an equation of the sort

$$(D_{ij})_T = (D_{ij})_0 \exp - [\Delta H/RT] \quad (57)$$

for the temperature dependence of D_{ij} .

However, it is evident that if one of the self-diffusion coefficients dominates in the magnitude of D_{ij} , then the temperature dependence of D_{ij} is the temperature dependence of that particular self-diffusion coefficient. As such, if we consider D_{AA} from equation (51), we conclude that the apparent activation energy of D_{AA} should be nearly that of D_B , the self-diffusion coefficient of strontium, i.e., nearly 43 K cal/mol.

An important corollary of these calculations is that, in

an ionic system, in spite of large differences between the magnitudes of self-diffusion coefficients, the interdiffusion coefficients tend to cluster around each other. Thus, if ∇X_i is the primary gradient in the system, it is evident that the effective binary diffusion coefficient, D_{iM} , approaches the direct coefficient, D_{ii} .

This is the case of an inhomogeneity decaying into a matrix. The primary gradient of i is compensated by accumulation of small magnitudes of ∇X_j . The decay of inhomogeneity of i is, although only approximately, yet adequately described by the single coefficient, D_{iM} . Conversely, with no prior knowledge of the interdiffusion coefficients matrix, measurement of D_{AM} along the direction shown in Figure 4 has the best chances of being meaningful in describing the decay of inhomogeneity of B in the system A-B-C.

§2.10 LITERATURE SURVEY FOR MULTICOMPONENT DIFFUSION EXPERIMENTS

The system $K_2O-SrO-SiO_2$ can be regarded as a supercooled liquid over the temperature range covered in this research. The diffusion experiments, however, were carried out in a manner so as to reduce the effects of gravity, viscous flow and surface tension—essentially treating the system as a solid. For this reason, no serious attempt has been made to review literature on diffusion in liquids. Readers are referred to Tyrrell⁽⁴¹⁾ which is a good starting point.

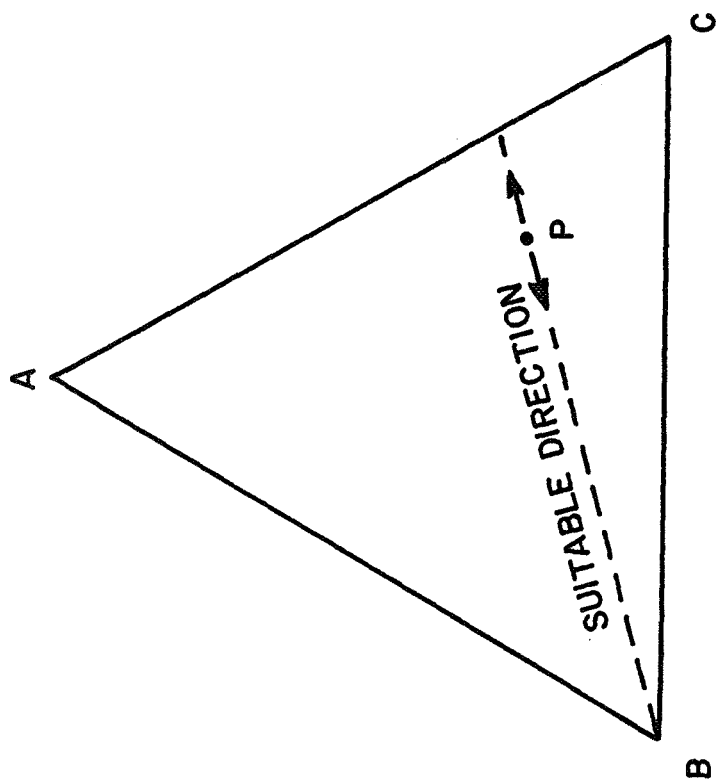


FIG. 4 : SUITABLE DIRECTION FOR THE MEASUREMENT OF
EBDC OF SPECIES B IN COMPOSITION P.

Several studies of solid state diffusion in multicomponents systems are available in literature. However, their analytical treatment as a multicomponent system is rare. In most cases, a quasi-binary treatment of the system has been made. A summary of such studies has been given by Guy and Smith^(20a).

Of the metallic systems studied, one of the earliest is Darken's experiment for diffusion in Fe-C-Si system⁽²⁴⁾. In this experiment, the concentration distribution of carbon clearly demonstrated the phenomenon of uphill diffusion. The data was later analyzed by Kirkaldy⁽⁴²⁾, Kirkaldy and Brown⁽⁴³⁾ to show that the four interdiffusion coefficients obtained were in agreement with the requirements summarized by Kirkaldy, Zia-Ul-Haq and Brown⁽⁴⁴⁾.

Chandok, Hirth and Dulis⁽⁴⁵⁾ carried out similar measurements in the Fe-C-Co and Fe-C-Co-W systems but did not analyze the data for cross coefficients.

Studies of diffusion path in ternary, multiphase systems have been carried out by Clark and Rhines⁽⁴⁶⁾ for Al-Mg-Zn, by Kirkaldy and Fedak⁽⁴⁷⁾ for Fe-Ni-Cr and Cu-Zn-Sn and by Castleman and Siegle⁽⁴⁸⁾ for Cu-Zn-Ni.

The assumption that there is a negative interaction between the interstitial and the substitutional components of an alloy leads to the relation $D_{12}^3/D_{11}^3 = kn_1$, where 3 stands for the solvent matrix, 1 for the interstitial component and n_1 is the atom

fraction of the interstitial component and k is a constant. This relation has been verified in the ternary austenite alloys Fe-C-Si, Fe-C-Mn, Fe-C-Cr, Fe-C-Ni and Fe-C-Co by Kirkaldy and his school (49,50,51). No explicit determination of the interdiffusion coefficients matrix was made in any of these systems. An attempt in this direction was made by them for two substitutional systems Cu-Al-Mn and Cu-Al-Zn, with the assumption that one of the cross coefficients is zero.

A complete calculation of interdiffusion coefficients matrix has been carried out for a few alloy systems: Ni-Co-Cr by Guy and his co-workers (52,53,54), Cu-Zn-Mn and Cu-Zn-Sn by Dayananda and his co-workers (55,56,57), Co-Ni-Fe by Sabatier and Vignes (58,59), Cu-Ag-Au by Ziebold and Ogilvie (35), Fe-Cr-C and Fe-Ni-C by Kornev and Shaidurov (60).

For the Cu-Ag-Au system, in particular, the interdiffusion coefficients matrix was found to obey thermodynamic requirements stated in section 2.4. A calculation of the phenomenological coefficients matrix in this case supported Onsager's reciprocal relations.

A good review of literature in multicomponent systems has been given by Kirkaldy (61).

Borom and his co-workers (62) have studied diffusion in the $\text{Fe}_x\text{O}-\text{Na}_2\text{O}-\text{SiO}_2$ system, but they have treated their results as

if diffusion proceeded in a constant SiO_2 matrix. Similarly, Sucov and Gorman⁽⁶³⁾ analyzed their interdiffusion data in Na_2O - CaO - SiO_2 system as if the system were quasi-binary.

The presence of an S-shaped diffusion path and the occurrence of critical points in a three-component ceramic system were, perhaps, first shown in an earlier publication by the present author⁽¹⁶⁾ on K_2O - SrO - SiO_2 glass system. The data, however, was analyzed in terms of an effective binary diffusion coefficient approach. Whereas the concentration distributions of K_2O and SrO could be described by an effective binary diffusion coefficient for each; it was stated that these effective binary diffusion coefficients would be very sensitive to "direction" of the diffusion path on the ternary composition space.

CHAPTER 3

DECONVOLUTION OF EXPERIMENTAL DATA

"To err is human; to really foul things up requires a computer."

-- Bill Vaughan in Kansas City Star

Typically, the experiments consist of measuring the chemical distribution of one or more species across a diffusion zone after a known diffusion anneal. For solid state diffusion experiments, a commonly used instrument to measure the chemical concentration of an element is the electron microprobe analyzer. A plot of X-ray counts vs. distance is obtained. Conversion from counts to chemical concentration, X , is often achieved with the help of calibrating standards (as has been done in this work) or less frequently by theoretical means⁽⁶⁴⁾.

The position $y = 0$, i.e., the original interface is located by

- (i) marks or original interfacial defects where no significant movement of markers⁽⁶⁵⁾ during diffusion is expected,

or for unidirectional semi-infinite couple by

- (ii) the use of Matano analysis⁽⁶⁶⁾

- (iii) locating the position corresponding to concentration change = 0.5 where the diffusion coefficients do not depend upon concentration.

All the experiments carried out in this research involved diffusion couples prepared from a narrow range of compositions. Thus, the D_{ij} matrix was assumed to be essentially constant in a single couple and the original interface was located primarily by (iii).

The unfolding of the experimental data to reveal the $[D_{ij}]$ matrix can be done by two methods:

- (i) Graphical technique suggested by Lindemer and Guy⁽⁶⁷⁾.
- (ii) Fitting the data to Fujita and Gosting's solution [equation 35].

§3.1 THE GRAPHICAL TECHNIQUE

For a ternary system, substitution of $\lambda=y/\sqrt{t}$ to equation (24) when diffusion is confined to one direction only, yields

$$-\lambda \frac{dx_i}{d\lambda} = \frac{d}{d\lambda} \sum_{j=1}^2 D_{ij} \frac{dx_j}{d\lambda} \quad (58)$$

Analogous to Boltzmann's technique⁽⁶⁶⁾ for diffusion of single species, the first integration of the above equation gives

$$-1/2 \int_{(x_i)_\infty}^{x_i} \lambda dx_i = \sum_{j=1}^2 D_{ij} \frac{dx_j}{d\lambda} \Big|_{\text{At } x_i = x_i} \quad (59)$$

The second integration of this equation over λ yields

$$- 1/2 \int_{\lambda_L}^{\lambda_k} \int_{(X_i)_\infty}^{X_i} \lambda dx_i d\lambda = \sum_{j=1}^2 \frac{(X_j)_k}{(X_j)_L} D_{ij} dx_j \quad (60)$$

where the limits are so chosen that at

$$\lambda = \lambda_L, \quad X_j = (X_j)_L$$

$$\text{and at } \lambda = \lambda_k, \quad X_j = (X_j)_k$$

The re-substitution of $y/\sqrt{t}$ for λ gives

$$- (1/2t) \int_{y_L}^{y_k} \int_{(X_i)_\infty}^{X_i} y dx_i dy = \sum_{j=1}^2 \frac{(X_j)_k}{(X_j)_L} D_{ij} dx_j \quad (61)$$

The left hand side of equation (61) represents a "double integration area" which is area under a plot of Matano area vs. distance and can be computed graphically.

The right hand side is further simplified if the diffusion coefficients are assumed constant, for then

$$- (1/2t) \int_{y_L}^{y_k} \int_{(X_i)_\infty}^{X_i} y dx_i dy = \sum_{j=1}^2 [(X_j)_k - (X_j)_L] D_{ij} \quad (62)$$

For a diffusion couple belonging to a ternary system, both

$i, j = 1, 2$ and, therefore one obtains two equations of the type (62) with 4 unknown D_{ij} .

It is obvious that a complete solution of the $[D_{ij}]$ requires one more set of simultaneous equations. Whereas this can be accomplished by choosing different sets of y_k and y_L in equation (62), a more effective technique is to choose a second diffusion couple whose diffusion path intersects the first one. At the point of intersection, the values of $[D_{ij}]$ for the second couple are identical to the first one - if Onsager's description of multicomponent diffusion in the form of equation (3) is correct.

§3.2 THE ANALYTICAL APPROACH

A computer fit of equation (35a) to experimental data can be conveniently achieved by statistical techniques such as chi-square.

Let $X = f(Y)$ be a continuous function. If y_ℓ is an ℓ th measurement of Y and is assumed error-free, then chi-square χ^2 is defined as

$$\chi^2 = \sum_{\ell} \frac{1}{2\sigma_\ell^2} [x_\ell - f(y_\ell)]^2 \quad (63)$$

where x_ℓ is the measurement of X at ℓ , σ_ℓ^2 is the variance of x_ℓ , and n the total number of observations.

The chi fit involves minimizing χ^2 with respect to all the unknown parameters.

A convenient method to carry out minimization of χ^2 to obtain the best estimates of the parameters and their standard deviations is the linearization technique described by various authors (68,69).

Equation (35a) is

$$x_1 - \bar{x}_1 = \Delta x_1 = a \operatorname{erf} (\lambda/2\sqrt{D_u}) + b \operatorname{erf} (\lambda/2\sqrt{D_v})$$

where $\bar{x}_1 = (x_1^P + x_1^Q)/2$

and $b = ((x_1^Q - x_1^P)/2) - a$

Taylor expansion of x_1 is

$$\Delta x_1 = (\Delta x_1)_o + \sum_{i,j} \left(\frac{\partial F}{\partial D_{ij}} \right)_o \Delta D_{ij} + \dots \quad (64)$$

where

$$F = a \operatorname{erf} (\lambda/2\sqrt{D_u}) + b \operatorname{erf} (\lambda/2\sqrt{D_v})$$

and

$$(\Delta x_1)_o = (F)_{D_{ij} = (D_{ij})_o}; (D_{ij})_o \text{ being estimates of } D_{ij}.$$

D_{ij} .

Neglecting higher order terms and defining $\Delta x_1 - (\Delta x_1)_o = \Delta x'_1$,

we get for χ^2

$$\chi^2 = \sum_{\ell} \frac{1}{\sigma_{\ell}^2} [(\Delta X'_1)_{\ell} - \sum_{i,j} \left(\frac{\partial F_{\ell}}{\partial \Delta D_{ij}} \right)_0 \Delta D_{ij}]^2 \quad (65)$$

Denoting $\left(\frac{\partial F_{\ell}}{\partial \Delta D_{ij}} \right)_0 = F'_{ij\ell}$ and for minimum χ^2 with respect to each ΔD_{ij} , we get

$$\Gamma = [\alpha]_0 \Delta D \quad (66)$$

where Γ and ΔD are written as column vectors of 4 components each, and $[\alpha]$ is a 4 x 4 matrix.

The general terms are given by

$$\Gamma_k = \sum_{\ell} \{ (\Delta X'_1)_{\ell} F'_{k\ell} / \sigma_{\ell}^2 \}$$

$$\alpha_{km} = \sum_{\ell} (F'_{k\ell} F'_{m\ell} / \sigma_{\ell}^2)$$

k and m = ij

Above equations represent a set of non-homogeneous equations in ΔD_{ij} . Evaluation of ΔD_{ij} can be conveniently achieved by using Cramer's rule or Gauss' elimination method.

These ΔD_{ij} are then applied as corrections to the original estimates. The machine could then be made to iterate until the minimum of χ^2 is found.

The variances on D_{ij} can be shown to be given by⁽⁷⁰⁾

$$\sigma_{D_{ij}}^2 = [\alpha^{-1}]_{ij} \quad (67)$$

where $[\alpha^{-1}]$ is the inverse matrix of α .

The α matrix is directly included in the set of non-homogeneous equations and, hence, presents no need for further calculations.

It is important to note that the equation $\Gamma = [\alpha]\Delta D$ cannot be solved with the help of data from distribution of a single species only. This is because the distribution of a particular species is described completely by three parameters, namely, a , D_u and D_v . Not all four parameters $[D_{ij}]$ need be independent to obtain a particular set of a , D_u and D_v . This dependence causes the $[\alpha]$ to become singular. The singularity disappears only when a second distribution of the form $X_2 - \bar{X}_2 = c \operatorname{erf} (\lambda/2\sqrt{D_u}) + d \operatorname{erf} (\lambda/2\sqrt{D_v})$ is used.

It is possible that an absolute minimum in χ^2 does not exist for all the data from a single couple. For example, if the diffusion direction is the "u" direction, then since D_v no longer takes any part in diffusion, a complete calculation of all the four D_{ij} 's is not possible. It is advisable, therefore, to minimize χ^2 simultaneously for as many directions as possible.

Whereas the linearization technique is a rapid method to converge towards the extremum points of the χ^2 surface, a satisfactory outcome is based on the premise that the curvature of the χ^2 surface, at the starting points, i.e. at the estimates $(D_{ij})_0$, is positive. Whenever the curvature becomes -ve, the linearization results in convergence towards a maximum rather than a minimum. It is also possible that some physically insignificant local minima might exist for the data⁽⁷¹⁾. The starting estimates $(D_{ij})_0$, therefore, must be so chosen that the linearization procedure iterates to converge towards the physically meaningful absolute minimum. In this research, the convergence towards the minimum has been best assured by using the set of $[D_{ij}]$ calculated by the graphical technique as the starting point. The graphical technique itself was applied to data of diffusion couples along two intersective directions. A simultaneous chi-fit to all four concentration distributions from these couples also assured the location of an absolute minimum of χ^2 surface.

§3.3 THE WEIGHTING SCHEME

Calculation of χ^2 from equation (63) or (65) requires an estimation of $(1/\sigma_\rho^2)$ which is the weight associated with the ρ th data point. If we ignore the mathematical function which describes the data, then the weight factors are the reciprocals of the

variance of each data point. This variance for an electron microprobe measurement of intensity comprises of (i) the poisson variation of the intensity and (ii) the random instrument noise level.

Whereas a measurement of the variance could be made by taking a large number of consecutive intensity measurements, W_{li} , at a given l , i.e., at a given spot, such a technique is not applicable for glasses due to ionic migration⁽⁷²⁾.

Measurement of variance, in this research, has been made by taking a number of readings, W_{oi} , at various positions on a homogeneous area of the glass, e.g., the ends of a diffusion couple. The variance, σ_o^2 , of this data includes some scatter due to local concentration inhomogeneities, but they were estimated to be negligible.

To take account of the varying values of σ_l^2 with l , it was assumed that the coefficient of variation, σ_l/W_l , remains constant with l . This provided a scheme for the calculation of $(1/\sigma_l^2)$ at each value of W for the computation of χ^2 .

§3.4 TESTING GOODNESS OF FIT

If the value of χ_v^2 (= total χ^2 /degrees of freedom) computed is less than 1.5 then it can be stated that the attempted mathematical function reasonably describes the observed data⁽⁷³⁾.

This is important since the criterion provides an easy

means to verify Onsager's hypothesis (equation 3) in our system.

For Onsager's hypothesis to be true, the values of D_{ij} calculated from two couples should adequately describe diffusion along other directions of the composition space, i.e., χ_v^2 should be less than 1.5 along all directions.

CHAPTER 4

EXPERIMENTAL PROCEDURE

"काल्ह करै सो आज कर , आज करै सो अब्ब "

"Things you wanted to do tomorrow, do today; and today's --
do them now!"

-- Mahatma Kabir

Seven glasses in the $K_2O-SrO-SiO_2$ system were chosen such that their chemical composition lay within a few wt. % for each species. This was intended for the following reasons:

- (i) Dependence of the phenomenological diffusion coefficient upon concentration would be minimized.
- (ii) Any deviation from the linear dependence of the electron microprobe X-ray counts on concentration of an element could be ignored.

The chemical composition of these glasses as calculated from batch and by wet chemical analysis are listed in Table 1. Appendix 1 briefs with the procedure followed for wet chemical analyses.

TABLE 1

CHEMICAL COMPOSITION OF GLASSES (wt.%)

Glass	K ₂ O	SrO	SiO ₂	Total
H	22.8	15.6	61.3	99.7
K	19.8	20.0	60.5	100.3
I	21.6	18.4	60.0	100.0
J	21.35	15.9	62.6	99.85
G	20.1	17.0	63.1	100.2
F	23.0	18.4	58.5	99.9
L	18.15	18.0	64.1	100.25

§4.1 GLASS MELTING

Batch corresponding to 400 g. of glass was prepared from analytical grade reagents. It was thoroughly mixed and melted in a 500 cc capacity Pt-20% Rh crucible inside a globalar electric resistance heating furnace at 1500°C. When melting was completed, glass was stirred three times over a period of an hour, with a platinum finger, after which it was left for 6 - 8 hours at 1400°C. The crucible was then taken out and cooled slowly inside a muffle furnace initially standing at 550°C.

The block of glass taken out of the crucible after cooling was free of bubbles and no cords were visible when it was viewed perpendicular to the direction of an intense light beam.

All blocks were reannealed by heating them to 550°C, holding the temperature for one hour and then cooling down to room temperature very slowly.

§4.2 SAMPLE PREPARATION

Cylinders (approximately 1/2 in. in diameter) of each of the glasses were core-drilled from the blocks. Each cylinder was ground flat perpendicular to its axis to obtain a disk about 1/2 in. thick. After the flat faces of these disks were polished, using diamond, a diffusion couple was made by placing the faces of two dissimilar glass disks in contact.

§4.3 ASSEMBLY FOR DIFFUSION

Figure 5 shows the different parts constituting the diffusion assembly. Each assembly holds two diffusion couples. The couples are surrounded by nickel foil and close fitting halves of steel blocks. Together with the couples, the steel blocks rest on a graphite plate which, in turn, rests on a steel table. An 1/8" thick steel plate serves as a covering lid. The remainder of the cavity within the steel block above the diffusion couple is occupied by a fitting piece of graphite rod to prevent curvature of the top surface of glass specimen during diffusion anneal. The exposed parts of graphite plate are prevented from oxidation by covering them with a steel foil. The housing is fastened securely to the steel table with the help of nichrome wires.

A Pt-Rh thermocouple is inserted through a hole in the middle of the cover plate to measure the temperature in the proximity of the diffusion interfaces of both the couples.

§4.4 THE DIFFUSION ANNEAL

The diffusion assembly was inserted inside a furnace which was already holding a desired temperature. After the diffusion anneal had been carried out for a specified period, the assembly was pulled out and air-cooled.

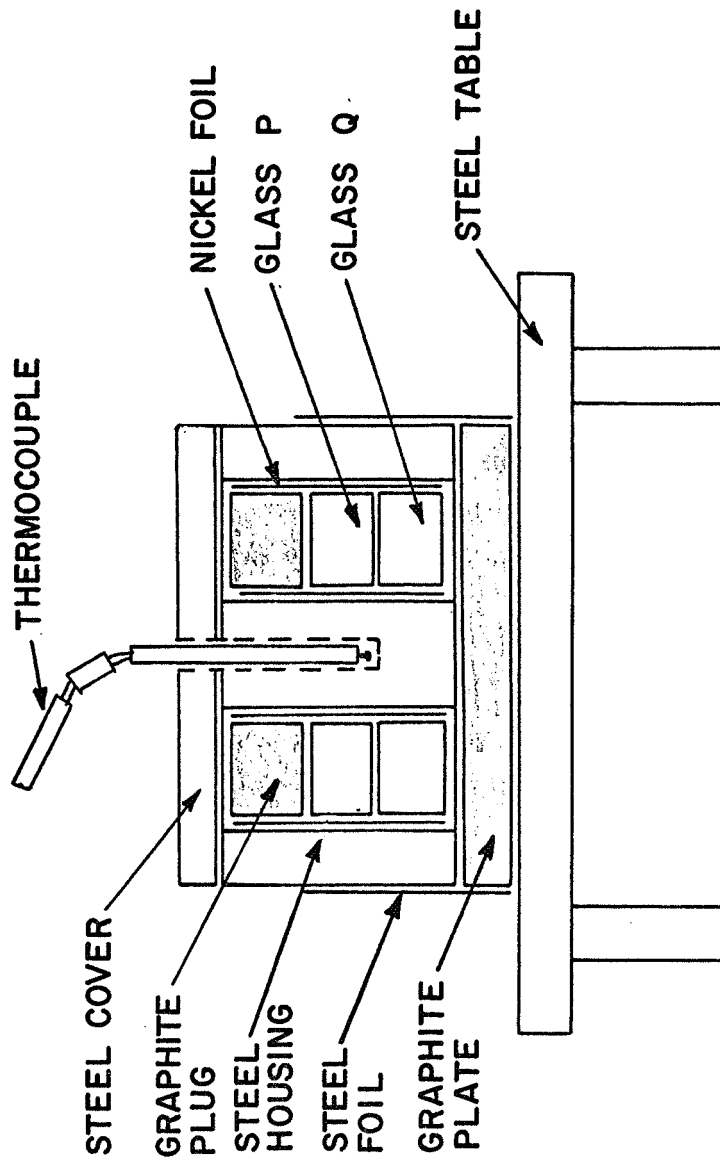


FIG. 5 : THE DIFFUSION ASSEMBLY (NOT TO SCALE).

After cooling, the samples were examined for any imperfect sealing or visible foreign inclusions on the diffusion interface. After passing this stage, the samples were reannealed at 550°C for 15 minutes.

§4.5 SAMPLES FOR MICROPROBE ANALYSIS

The diffusion couples were cut so as to expose a surface parallel to the diffusion direction. They were mounted in a 1" diameter "quick mount" cold mounting media with the flat surfaces exposed. Each mount was ground with SiC wet abrasive and polished using 3 μ diamond.

Microhardness indentations were placed on the diffusion interface to aid easy location of diffusion zone in the microprobe. The samples were then shadowed with about 300 Å thick Al film.

§4.6 MICROPROBE ANALYSIS

An "MAC 400" model microprobe was used to perform the microanalyses. It was equipped with two spectrometers so that a simultaneous analysis of two elements could be carried out. An automatic relay system connected the output of the X-ray counting system to a typewriter, an automatic specimen stepper-translator and a digital specimen current meter.

Thus, a counting cycle consisted of: count X-ray output from the two spectrometers for a preset time, while the

electron beam stayed at a particular position on the specimen, type out the two X-ray counts and the specimen current at the end of counting period, advance the specimen by a preset distance and repeat the cycle.

For all the analyses on $K_2O-SrO-SiO_2$ glass, the electron beam impinged upon the surface of the specimen in the form of a stationary line probe approximately 100μ long x 2μ wide. This mode of analysis minimized losses in X-ray intensity during the course of analysis due to ionic migration⁽⁷²⁾.

All analyses utilized a 20 Kv gun voltage, $0.03\mu a$ specimen current, a counting time of 100 seconds and a specimen stepping distance of 5μ or 10μ .

The specimen was oriented such that the diffusion interface (identified by the microhardness indentations) was parallel to the line probe. Analyses were carried out in the manner described above until the specimen traversed from one end of the diffusion zone to the other under the stationary electron line probe.

Care was particularly taken that

- (i) no position was repeatedly analyzed to avoid confusion arising from ionic migration,
- (ii) there was no significant defocussing of the electron beam due to slight imperfections of the stage while traveling from one end of the

analysis to the other, and

- (iii) there was no significant drift of the electron gun and the electronics during the microanalysis.

To ensure this the machine was allowed to stand for three hours in a 'ready-for-analysis' mode.

Conversion of X-ray counts to chemical concentration was obtained by using the assumption of linearity and the known composition of the end members.

To show the validity of the linearity assumption within the small range of chemical compositions analyzed, a composite sample of all the glasses was made. This composite sample consisted of ~200 μ thick wafer of each glass mounted such that the thickness was exposed. Analysis of K, Sr and Si in each glass was carried out in the standard manner on this composite. The results are shown in Appendix 1.

CHAPTER 5

RESULTS

"Originality is the art of concealing your source"

-- Franklin P. Jones in Quote

Figure 6 shows the location of seven glasses and the investigated "directions" of diffusion on the ternary composition space

The method of chi-squares was used to test basic criteria of Fickian diffusion in ionic systems. These criteria are

- (i) There is no significant build-up of space charge
- and (ii) The interdiffusion coefficients are not a function of concentration gradients.

Figure 7 shows the distribution of K_2O , SrO and SiO_2 in an H/L couple. The microprobe X-ray intensity for an element (after background correction) was converted to concentration of the element using the linearity assumption (Appendix 2). The conversion from concentration of the element to concentration of the oxide was accomplished on the premise that the composition of the ends of the diffusion zone are unaffected, and the same conversion factor applies over the entire diffusion zone. Deviations

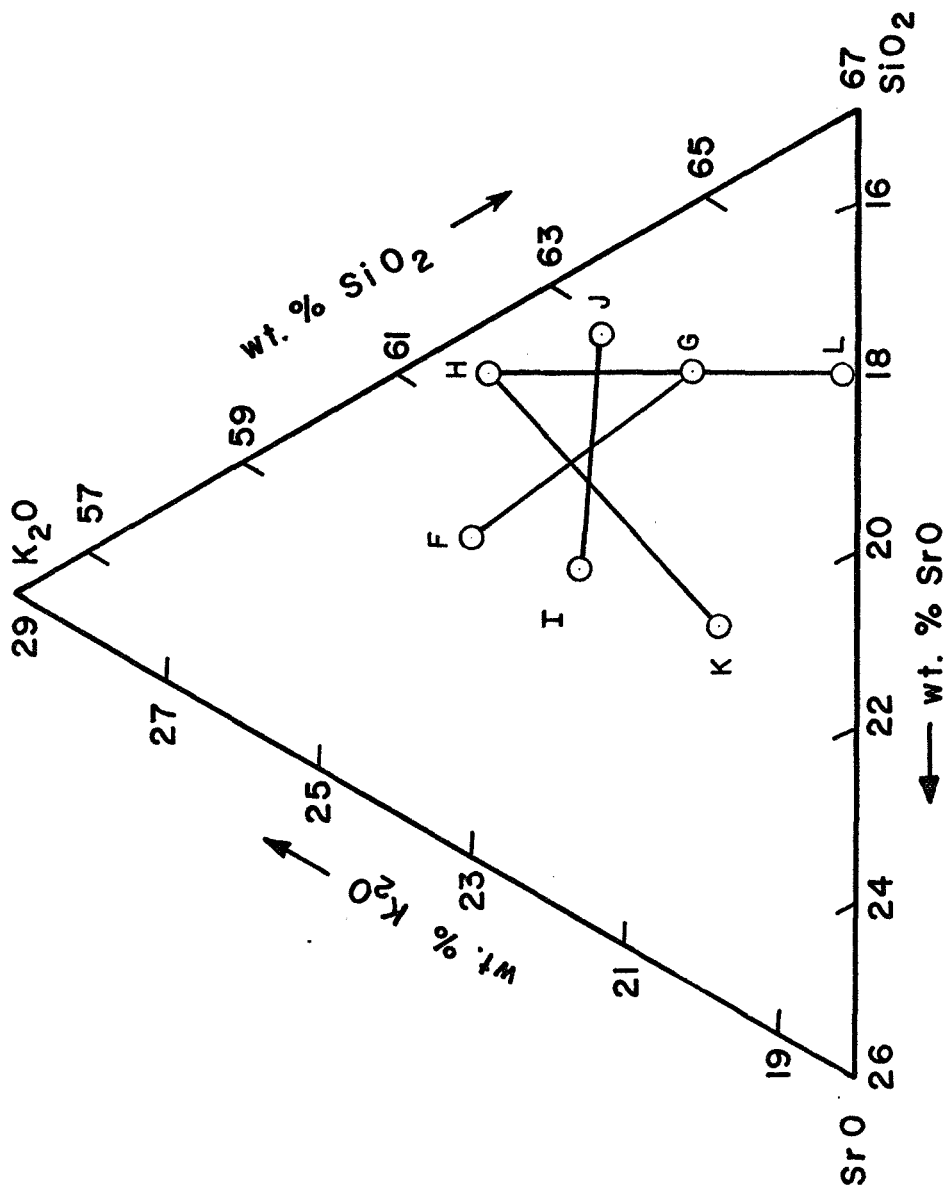


FIG. 6 : LOCATION OF GLASSES ON COMPOSITION SPACE.

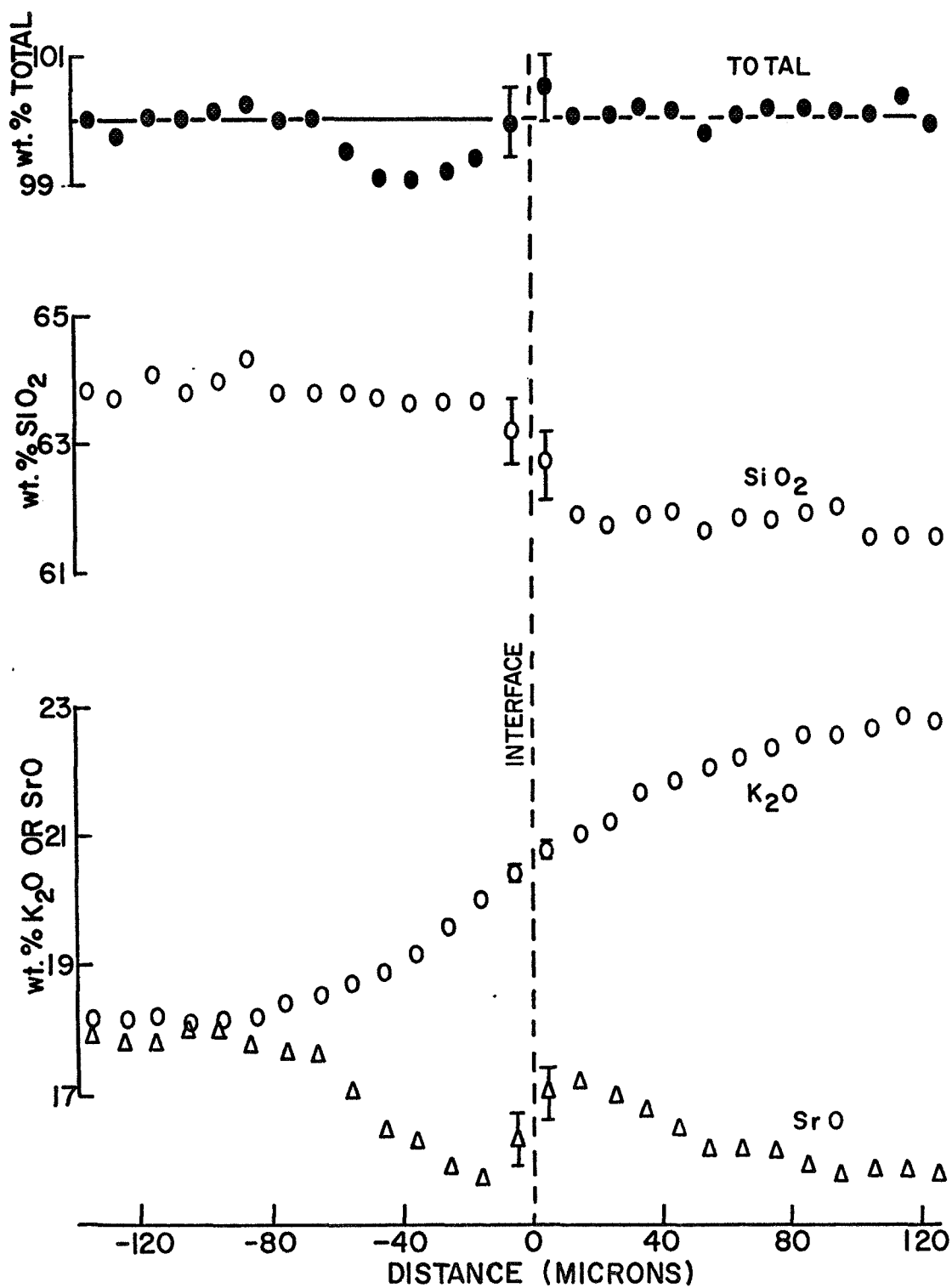


FIG. 7 : TEST OF STOICHIOMETRY ON MD 19 H/L.

from the latter, in particular, are caused by nonstoichiometry.

Confidence limits of points in the vicinity of the interface are shown by the " $\pm 2\sigma$ " vertical bars. The standard deviation of concentration was such that the standard deviation of X-ray counts was (Appendix 3)

- (i) 0.32% of the counts for K
- (ii) 1.0% for Sr
- and (iii) 0.4% for Si.

Shown on the same figure is the point-by-point sum of oxides. The null hypothesis H_0 : sum = 100%, was tested using the method of chi-squares. The weight associated with each point was the reciprocal of added variances of each oxide. $\chi^2_{\nu}(1)$ was found to be 1.6 indicating that the null hypothesis is true at the 0.1% level of confidence.

Figure 8 shows a plot of concentration of K_2O and SrO against $y/\sqrt{t}$ scale for two H/K couples where the diffusion was carried out at 713°C for

- (i) 5.45 hours
- and (ii) 72.0 hours

To demonstrate the merger of both couples for each element, a chi-square test was applied. For this,

$$\chi^2(K) \equiv \sum_{\ell=1}^n \{1/\sigma_{\ell}^2(K)\} \{x_{K1\ell} - x_{K2\ell}\}^2$$

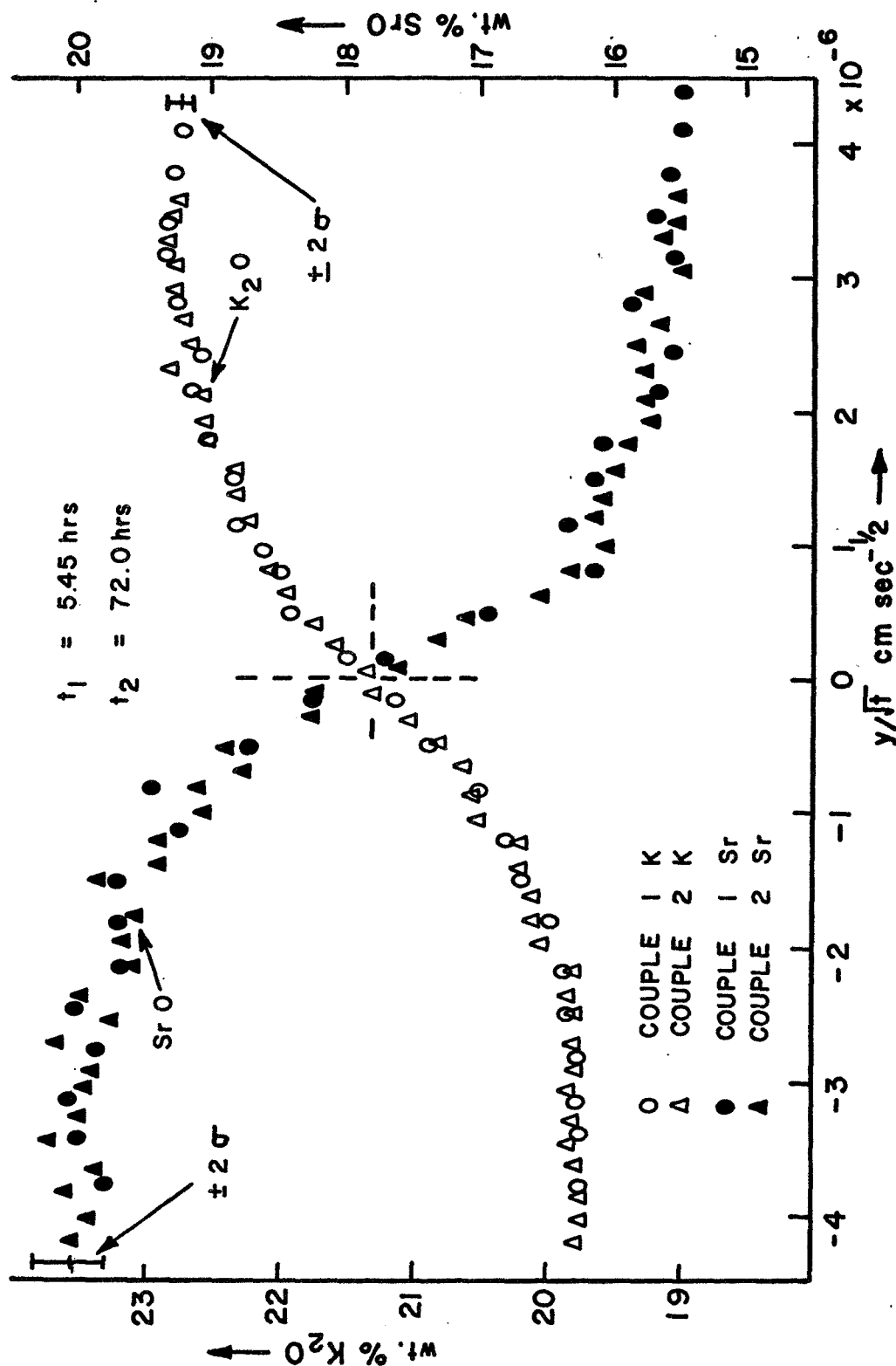


FIG. 8 : CONCENTRATION VS $y/\sqrt{t}$ PLOT FOR TWO H/K COUPLES AT 713°C.

$$\text{and } \chi^2(S) \equiv \sum_{\ell=1} \{1/\sigma_{\ell}^2(S)\} \{x_{S1\ell} - x_{S2\ell}\}^2 \quad (68)$$

where $x_{K1\ell}$, for example, is the concentration of K_2O in couple 1 at the ℓ th position, S stands for strontium, $\sigma_{\ell}^2(K)$ and $\sigma_{\ell}^2(S)$ are the variances of $(x_{K1\ell} - x_{K2\ell})$ and $(x_{S1\ell} - x_{S2\ell})$ respectively.

For a given position ℓ on couple 1, the corresponding position on the $y/\sqrt{t}$ scale of couple 2 was found by interpolation and the variances were calculated by the principle of propagation of errors⁽⁷⁴⁾.

It was found that

$$\chi_{\nu}^2(K) = 1.26$$

$$\text{and } \chi_{\nu}^2(S) = 0.9$$

indicating that the hypothesis

$$x_{K1\ell} - x_{K2\ell} = 0$$

$$\text{and } x_{S1\ell} - x_{S2\ell} = 0$$

are true, i.e. both the K_2O and SrO profiles of the two couples merge on $y/\sqrt{t}$ scale.

Table 2 lists the various experiments involving couples H/K and I/J to measure the interdiffusion coefficients. Figures 9 and 10 represent typical concentration distributions of the oxides in these couples. Figure 10, in particular, has been left as X-ray counts vs. distance from the interface, y , in order to enable a better graphical resolution for potassium. The first set of coefficients listed in Table 2 was determined by the graphical

TABLE 2
DIFFUSION EXPERIMENTS WITH H/K & I/J COUPLES

Note: All diffusion coefficients are in the units of $10^{-10} \text{ cm}^2/\text{sec}$.

Couple Name	Time Hrs.	Temp. C	Graphical calculation						Chi-fitting				$\chi^2(2)$
			$D_{11}^{+-\sigma}$	$D_{12}^{+-\sigma}$	$D_{21}^{+-\sigma}$	$D_{22}^{+-\sigma}$	$D_{11}^{+-\sigma}$	$D_{12}^{+-\sigma}$	$D_{21}^{+-\sigma}$	$D_{22}^{+-\sigma}$			
MD8 H/K & I/J	7.0	654	0.186 +0.017 -0.017	0.016 +0.017 -0.017	0.163 +0.018 -0.018	0.040 +0.021 -0.021	0.169 +0.027 -0.027	0.0218 +0.009 -0.009	0.146 +0.042 -0.042	0.003 +0.009 -0.009		1.307	
MD9 H/K & I/J	6.4	704	1.0 +0.05 -0.05	0	-0.66 +0.17 -0.17	0.07 +0.03 -0.03	0.95 +0.1 -0.1	0.054 +0.04 -0.04	1.13 +0.13 -0.13	0.008 +0.045 -0.045		1.11	
MD10 H/K & I/J	3.7	737	2.53 +0.25 -0.25	-0.014 +0.27 -0.27	-2.03 +0.5 -0.5	0.174 +0.6 -0.6	2.81 +0.225 -0.225	0.27 +0.085 -0.085	-3.0 +0.27 -0.27	-0.244 +0.078 -0.078		0.94	
MD12 H/K & I/J	5.75	760	3.22	0	-3.93	0.1	4.63 +0.28 -0.28	0.17 +0.11 -0.11	-5.33 +0.41 -0.41	-0.144 +0.125 -0.125		1.03	
MD20 H/K & I/J	6.66	806	7.6 +0.4 -0.4	0 +0.5 -0.5	11.75 +0.9 -0.9	1.0 +1.1 -1.1	9.25 +0.39 -0.39	0.172 +0.1 -0.1	10.5 +0.63 -0.63	0.001 +0.11 -0.11		1.37	

$2\sigma'$ is an estimate of difference between the maximum and minimum values. For chi-fitting, σ is the standard deviation.

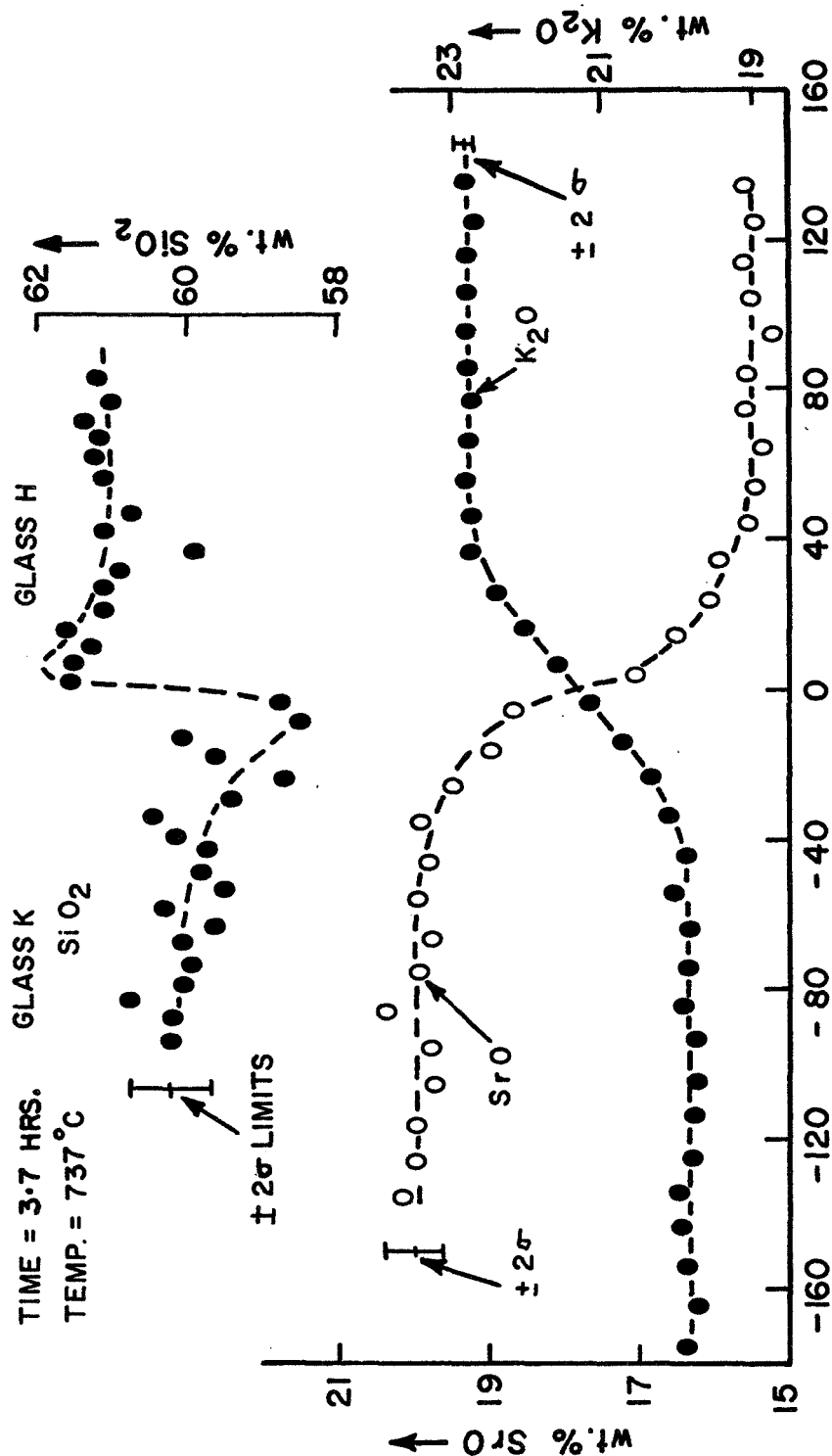


FIG. 9 : CONCENTRATION (wt.%) VS. y PLOT FOR MD10 H/K.

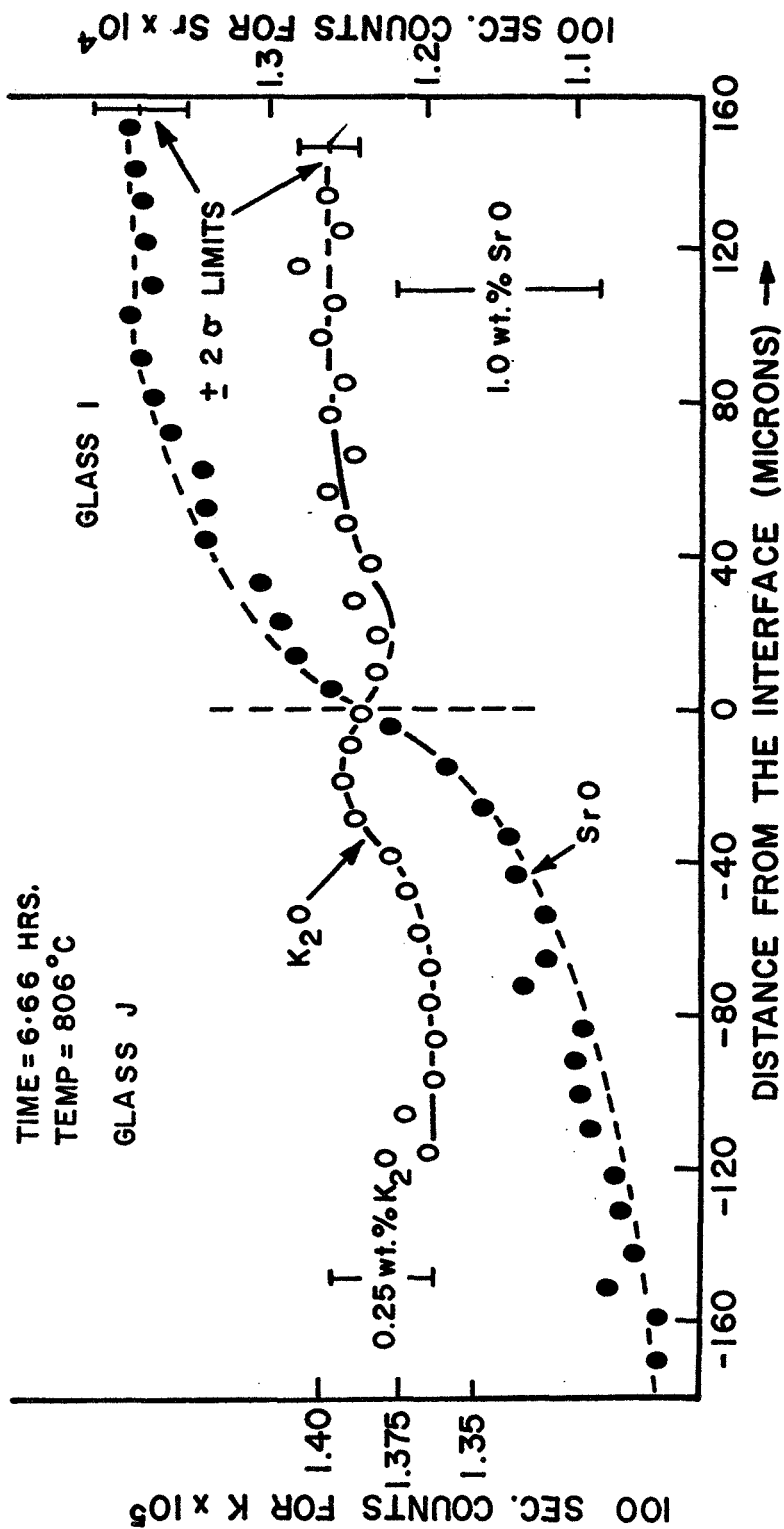


FIG. 10 : COUNTS, W, VS. DISTANCE, y, PLOT FOR MD 20 I/J.

technique. In Appendix 3 is shown a typical calculation of $[D_{ij}]$ by this method.

These coefficients were then used to apply a simultaneous chi-fit to determine the best estimates of $[D_{ij}]$ and the corresponding variances. Chi-fitting was carried out with the assumption that the end compositions and the position of the diffusion interface were known.

The last column on Table 2 is the value of χ_v^2 (chi-square over degrees of freedom) obtained in each case (denoted by $\chi_v^2(2)$) to show the goodness-of-fit. The dotted lines on Figures 9 and 10 represent the corresponding chi-fit distributions.

Figure 11 is a semilog plot of D_{11} and $|D_{21}|$ on the ordinate against the $1/T$, the reciprocal of absolute temperature. For comparison, the self-diffusion data of K^+ , and Sr^{++} and Si^{4+} in this system (around the same composition) is also shown. This data has been extracted from author's M.S. thesis⁽³⁸⁾.

Both D_{11} and $|D_{21}|$ appear to have an apparent activation energy of 48 Kcal/mol.

Owing to large errors in $|D_{12}|$ and $|D_{22}|$, no attempt to draw a similar plot has been made for these two coefficients.

Table 3 lists the experiments conducted with couples G/F and H/L. Typical examples of concentration distributions in these couples are shown in Figures 12 and 13.

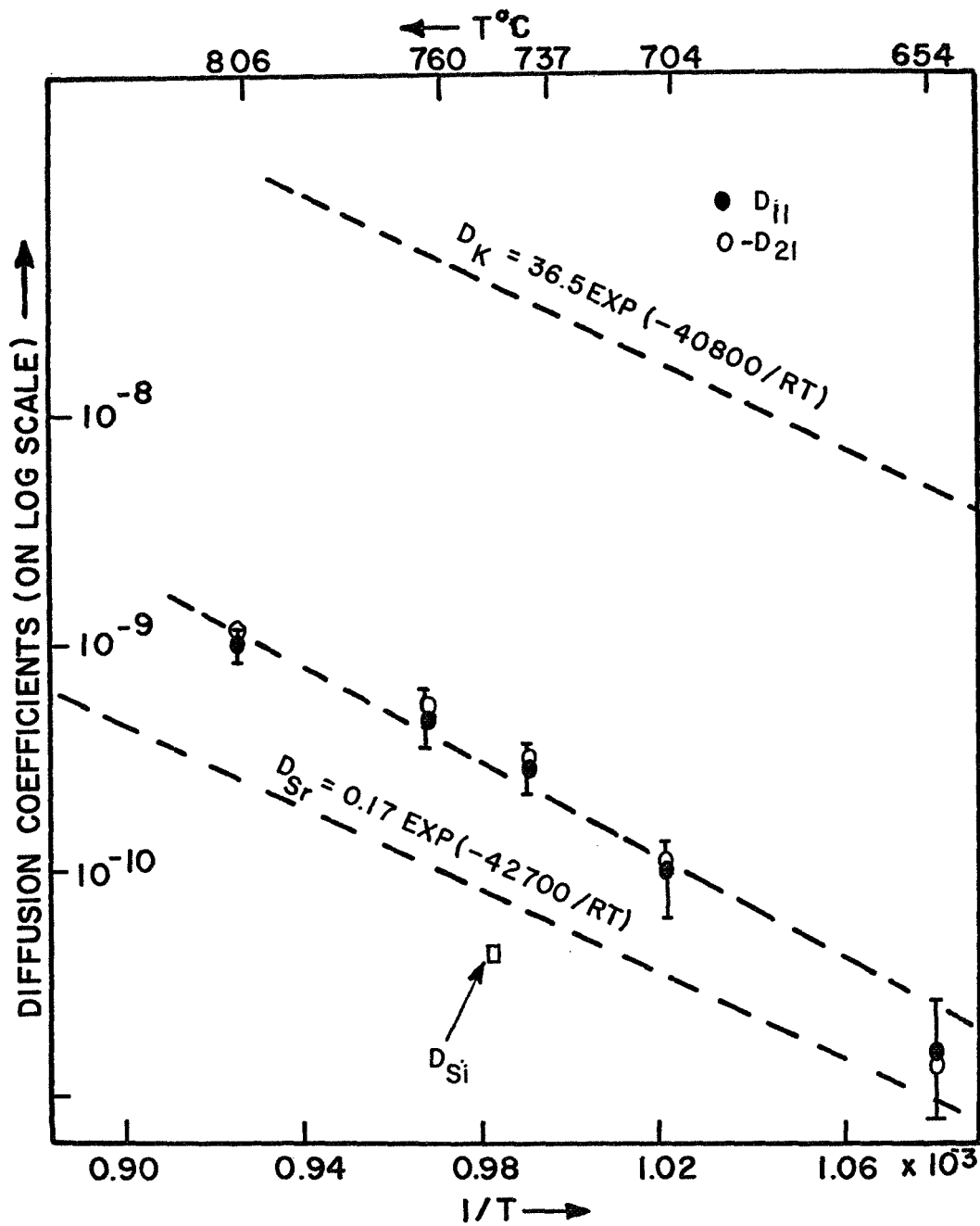


FIG. II: SEMILOG PLOT OF D_{II} & D_{2I} VS 1/T FOR H/K & I/J.

TABLE 3

DIFFUSION EXPERIMENTS WITH G/F & H/L COUPLES

Note: Diffusion coefficients are in the units of $10^{-10} \text{ cm}^2/\text{sec.}$

Couple Name	Time Hrs.	Temp. C	chi-fitting				χ^2_v
			$D_{11} \pm \sigma$	$D_{12} \pm \sigma$	$D_{21} \pm \sigma$	$D_{22} \pm \sigma$	
MD1 G/F	7.0	727	1.65 ± 0.13	0.068 ± 0.046	-2.45 ± 0.24	0.013 ± 0.09	2.03
MD2 G/F	10.45	685	0.34 ± 0.04	0.027 ± 0.016	-0.50 ± 0.074	0.008 ± 0.02	2.01
MD3 G/F	8.00	708	1.20 ± 0.1	0.02 ± 0.03	-1.50 ± 0.17	0.013 ± 0.042	3.06
MD4 G/F	7.41	770	2.82 ± 0.24	0.26 ± 0.12	-2.6 ± 0.28	-0.09 ± 0.1	1.82
MD5 G/F	7.25	793	6.16 ± 0.48	-0.29 ± 0.24	-6.70 ± 0.59	0.86 ± 0.27	2.63
MD13 H/L	7.66	713	0.62 ± 0.033	-0.092 ± 0.045	-0.76 ± 0.04	0.14 ± 0.06	2.62
MD15 H/L	12.33	670	0.125 ± 0.009	-0.021 ± 0.012	-0.162 ± 0.013	0.053 ± 0.019	2.63
MD16 H/L	19.75	632	0.054 ± 0.005	0.004 ± 0.01	-0.02 ± 0.005	-0.0001 ± 0.01	1.34
MD17 H/L	6.30	750	2.91 ± 0.11	-0.13 ± 0.13	-3.35 ± 0.18	0.29 ± 0.16	2.56
MD18 H/L	4.50	798	6.96 ± 0.24	0.17 ± 0.24	-8.31 ± 0.35	0.086 ± 0.29	2.81
MD19 H/L	6.50	774	5.47 ± 0.18	0.067 ± 0.2	-6.53 ± 0.26	0.19 ± 0.24	2.06

Note: chi square values for G/F are termed $\chi^2_v(3)$ and for H/L $\chi^2_v(4)$.

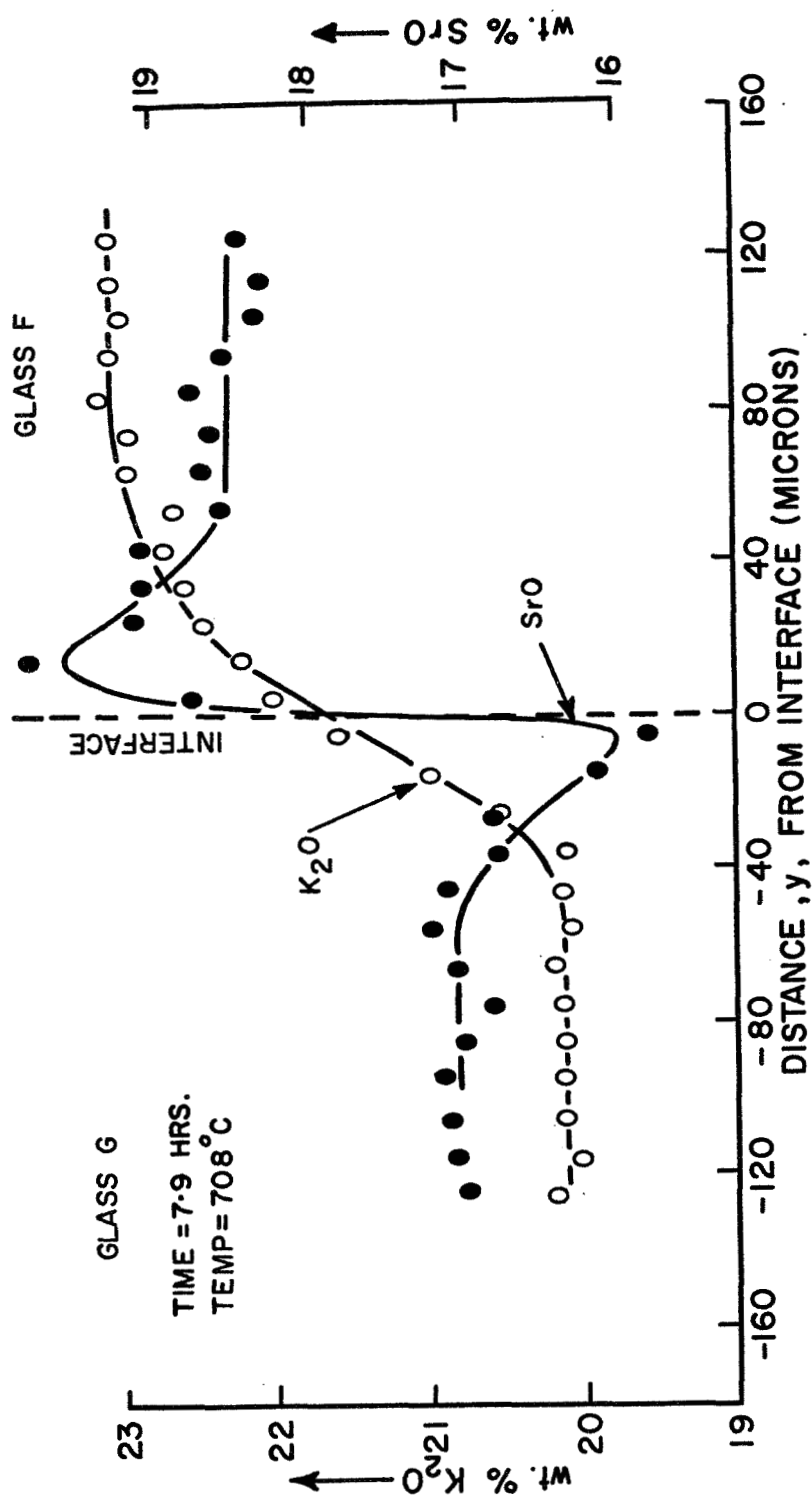


FIG. 12: DISTRIBUTIONS OF K_2O AND SrO IN MD 3 G/F.

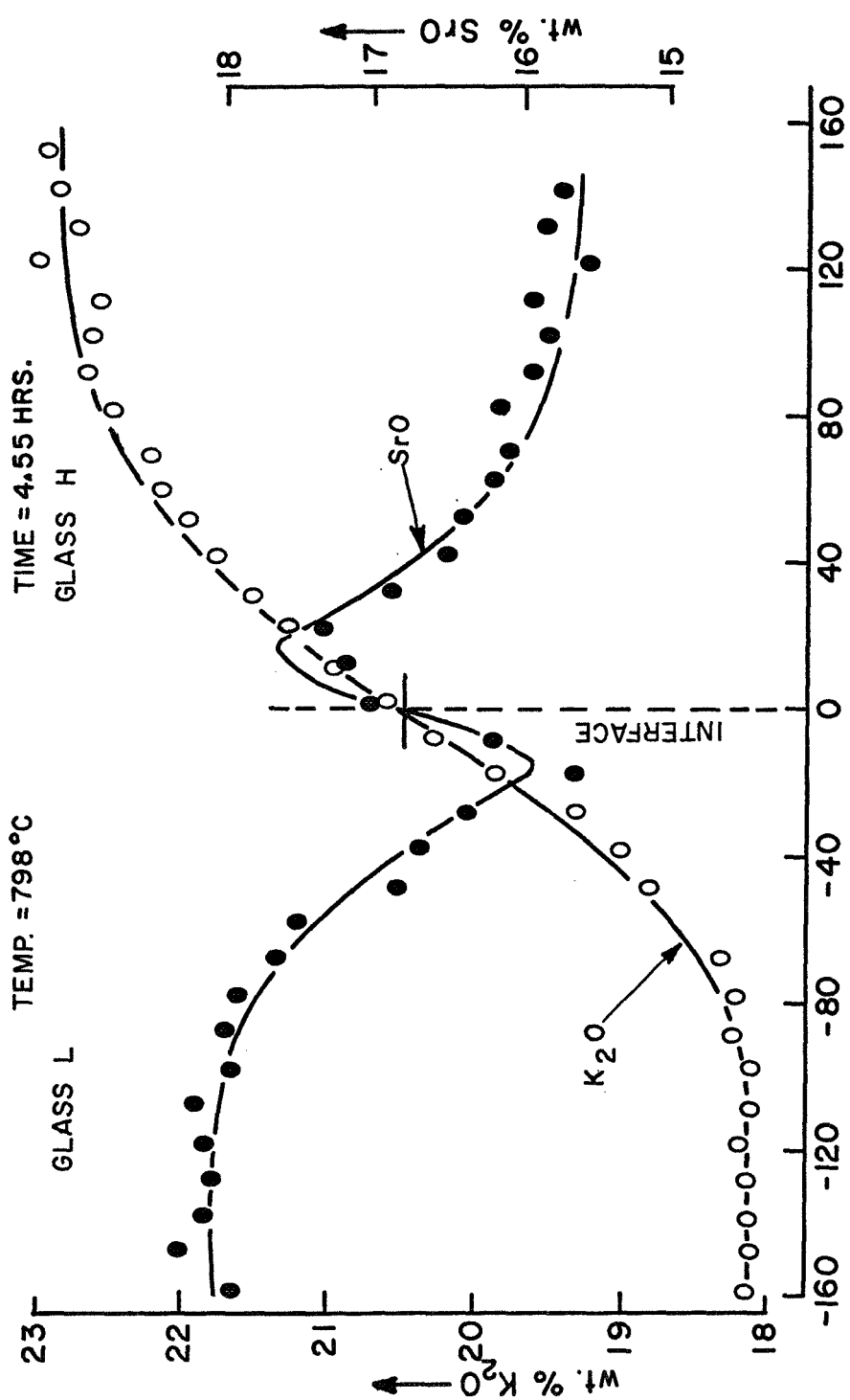


FIG. 13 : DISTRIBUTION OF K_2O AND SrO IN MD18 H/L.

For each experiment, values of $[D_{ij}]$ were interpolated from Figure 11 and Table 2. A simple goodness-of-fit test performed on couple MD1(G/F) with the interpolated parameters yielded χ^2_v of about 3.0 for each of the potassium and strontium distributions. Since this value was considered rather high, the linearization technique was then employed to obtain best fitting $[D_{ij}]$ starting with the interpolated parameters for each couple. The best fit values of $[D_{ij}]$, their variances and the corresponding χ^2_v (denoted by $\chi^2_v(3)$ and $\chi^2_v(4)$) for each couple are also listed in Table 3. Also shown on Figures 12 and 13 are the calculated distributions.

The data of D_{11} and $|D_{21}|$ determined for G/F and H/L are plotted in Figure 14 on semilog scale against $1/T$ along with previously obtained values (for H/K and I/J) in an attempt to detect any trends in the "direction" dependence of $[D_{ij}]$.

Calculation of eigen values and eigen vectors was also performed for all the diffusion experiments. The eigen values are listed in Table 4 and the eigen vectors together with the diffusion paths corresponding to Figures 9,10,12 and 13 are shown in Figures 15 through 18 on the orthogonal $\hat{\gamma}_1 - \hat{\gamma}_2$ space.

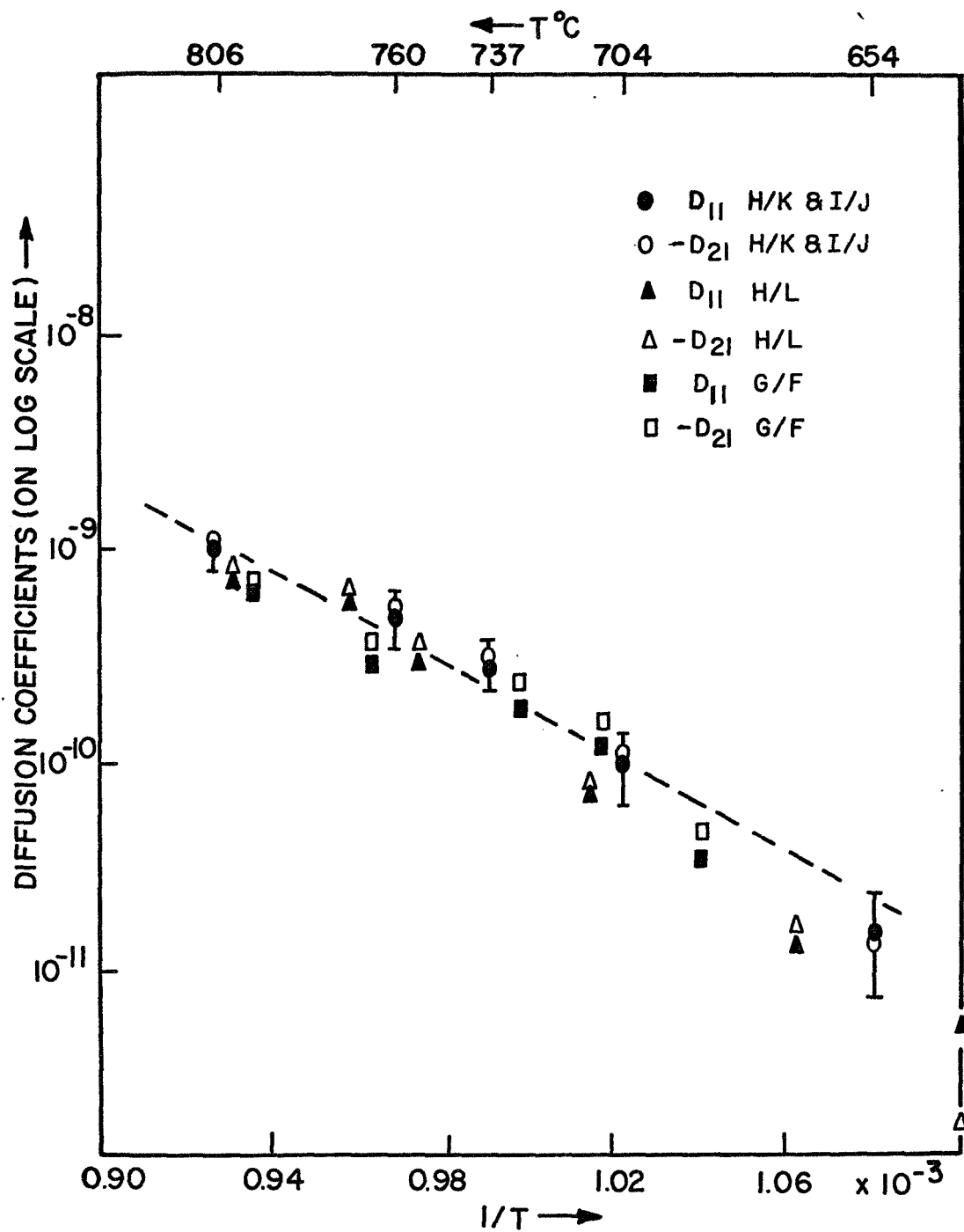


FIG. 14: SEMILOG PLOT OF D_{11} & $-D_{21}$ VS. $1/T$ FOR H/K, I/J, G/F & H/L COUPLES.

TABLE 4

EIGENVALUES OF $[D_{ij}]$

Note: all values are in 10^{-10} cm²/sec.

Couple Name	Temp C	D _u	D _v
MD 8 H/K & I/J	654	0.147	0.025
MD 9 H/K & I/J	704	0.088	0.067
MD 10 H/K & I/J	737	2.518	0.048
MD 12 H/K & I/J	760	4.43	0.057
MD 20 H/K & I/J	806	9.05	0.20
MD 1 G/F	727	1.540	0.123
MD 2 G/F	685	0.291	0.056
MD 3 G/F	708	1.174	0.038
MD 4 G/F	770	2.567	0.163
MD 5 G/F	793	6.503	0.512
MD 13 H/L	713	0.735	0.021
MD 15 H/L	670	0.158	0.020
MD 16 H/L	632	0.053	0.001
MD 17 H/L	750	3.068	0.130
MD 18 H/L	798	6.748	0.298
MD 90 H/L	774	5.386	0.273

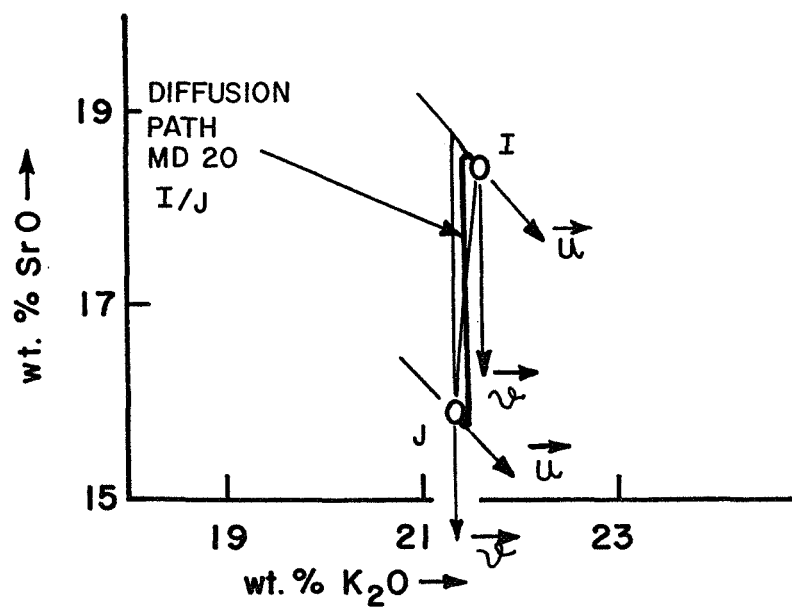
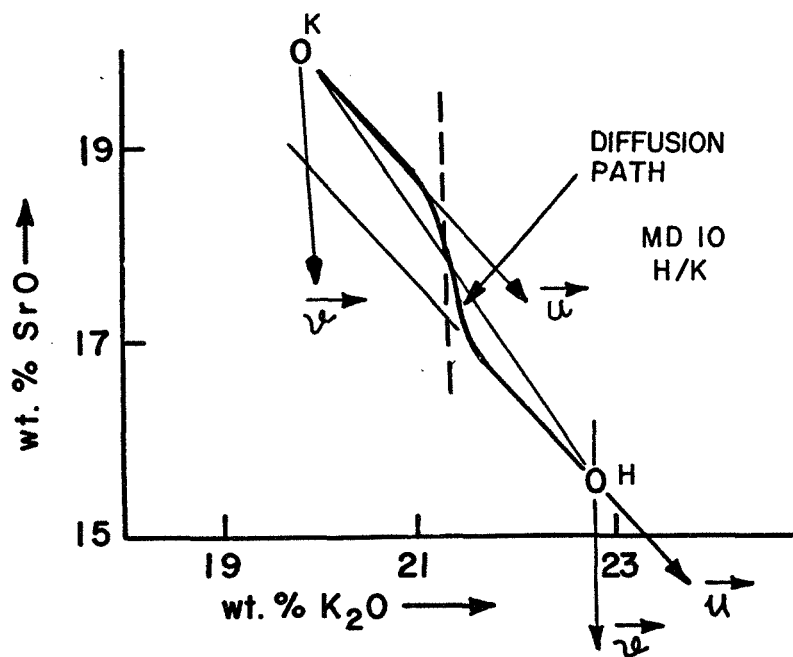


FIG.15 &16 : DIFFUSION PATHS OF H/K AND I/J COUPLES.

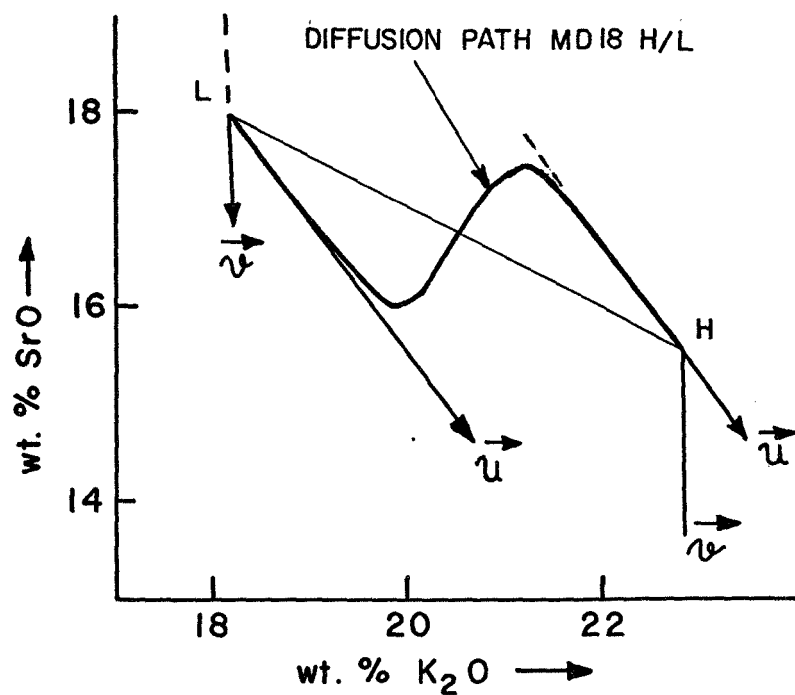
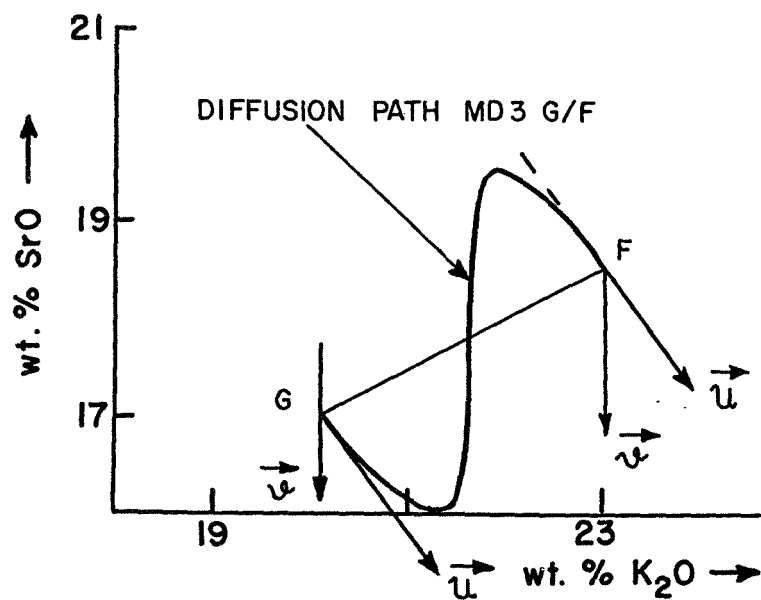


FIG. 17&18: DIFFUSION PATHS OF G/F AND H/L COUPLES.

CHAPTER 6

DISCUSSION

"Iron rusts from disuse, stagnant water loses its purity, and in cold weather becomes frozen; even so, inaction saps the vigors of the mind."

-- Leonardo da Vinci

When ions with different valence and mobility move in a multicomponent system, the net motion is such that deviations from stoichiometry are not detected. This has been experimentally demonstrated in Figure 7. At each position throughout the entire diffusion zone, the concentrations of elemental K^+ , Sr^{++} , Si^{4+} are such that the corresponding amounts of the oxides sum up to 100%. The excess contribution over 1.0 in the value of $\chi_v^2(1)$ comes primarily from the zone where Sr^{++} has a minimum. Two significant sources of error may be responsible. The first one is the finite beam diameter effect⁽⁷⁵⁾ due to which an x-ray intensity measurement along steep concentration gradients (in our case, those of Si^{4+} and Sr^{++}) requires correction. The second one is the conversion of counts to concentration of the element itself. The linearity assumption (Appendix 1) is only approximate and has been shown to be a good assumption over a limited range of composition only.

One does not expect, however, that perfect local charge neutrality would be maintained at all times owing to the varying mobilities of the ions. The electric field which is set up in the system is a measure of local accumulation of charges i.e. extent of non-stoichiometry.

Let us attempt to calculate the extent of non-stoichiometry using the mobility model.

With the aid of equations (11-17) the intensity of electric field, $\nabla\Psi$ can be shown to be

$$\nabla\Psi = \partial\Psi/\partial y = \frac{\frac{1}{|Z_o|}}{\frac{1}{kT}} \frac{\sum_i X_i D_i Z_i (\partial X_{io}/\partial y)/X_{io}}{\sum_i X_i Z_i (Z_o D_o - Z_i D_i)} \quad (69)$$

$i = A, B, C$

Since $Z_o < 0 < Z_i$, and the summation is over all the cations, the denominator never approaches zero. Thus, the electric field after time $t > 0$ never equals infinity. It is also easy to see from equation (69) that $\nabla\Psi$ is opposite to ∇X_{io} which is consistent with our notions.

When $D_i \nabla X_{io} \gg D_j \nabla X_{jo}$, which at $t > 0$ is most likely to be true for our diffusion couples with i being potassium (except at extremum points in the distribution of potassium), equation (69) simplifies to

$$\nabla\Psi = -kT \nabla X_{io} / |Z_o| Z_i X_{io} \quad (70)$$

If kT is measured in ergs, Z_i in e.s.u. of charge, then $\nabla\psi$ is in stat volts/cm.

For the couple MD18 H/L, the distribution of K_2O is given by

$$x_{K_2O} - \bar{x}_{K_2O} = 2.37 \operatorname{erf} (\lambda/2\sqrt{6.75 \times 10^{-10}}) - 0.045 \operatorname{erf} (\lambda/2\sqrt{3 \times 10^{-11}}) \quad (71)$$

With the use of this equation, the spatial distribution of $d\psi/d\lambda$ can be shown to be given by Figure 19. The electric field $d\psi/dy$ at a particular position, λ , decreases with $t^{1/2}$, and at $t = 1$ second, the maximum field is nearly 0.36 stat volts/cm.

If q_y is the charge density e.s.u. per cm^3 at y , then by Gauss' theorem⁽⁷⁶⁾

$$4 \pi q_y / \epsilon = \frac{d^2}{dy^2} \psi_y \quad (72)$$

where $\epsilon =$ dielectric constant

Figure 20 shows a plot of tq_λ against λ (with $\epsilon = 7$). The maximum value of tq_λ is nearly 3×10^3 e.s.u. sec. per cc. If n_y is the number of K^+ ions per cc at y then

$$n_y e = q_y \quad (73)$$

where e is the electronic charge (e.s.u.).

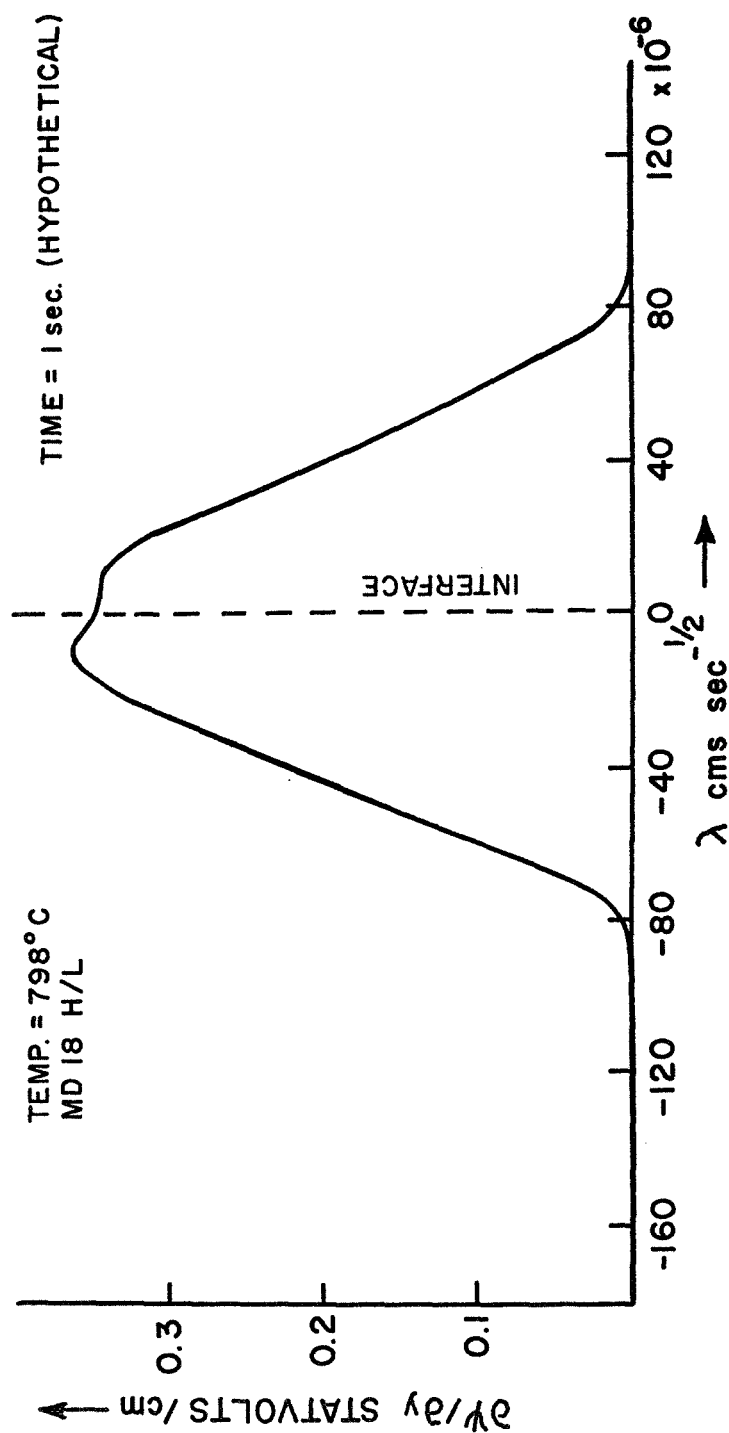


FIG.19: VARIATION OF ELECTRIC FIELD, $\partial \psi / \partial y$, WITH λ IN AN H/L COUPLE.

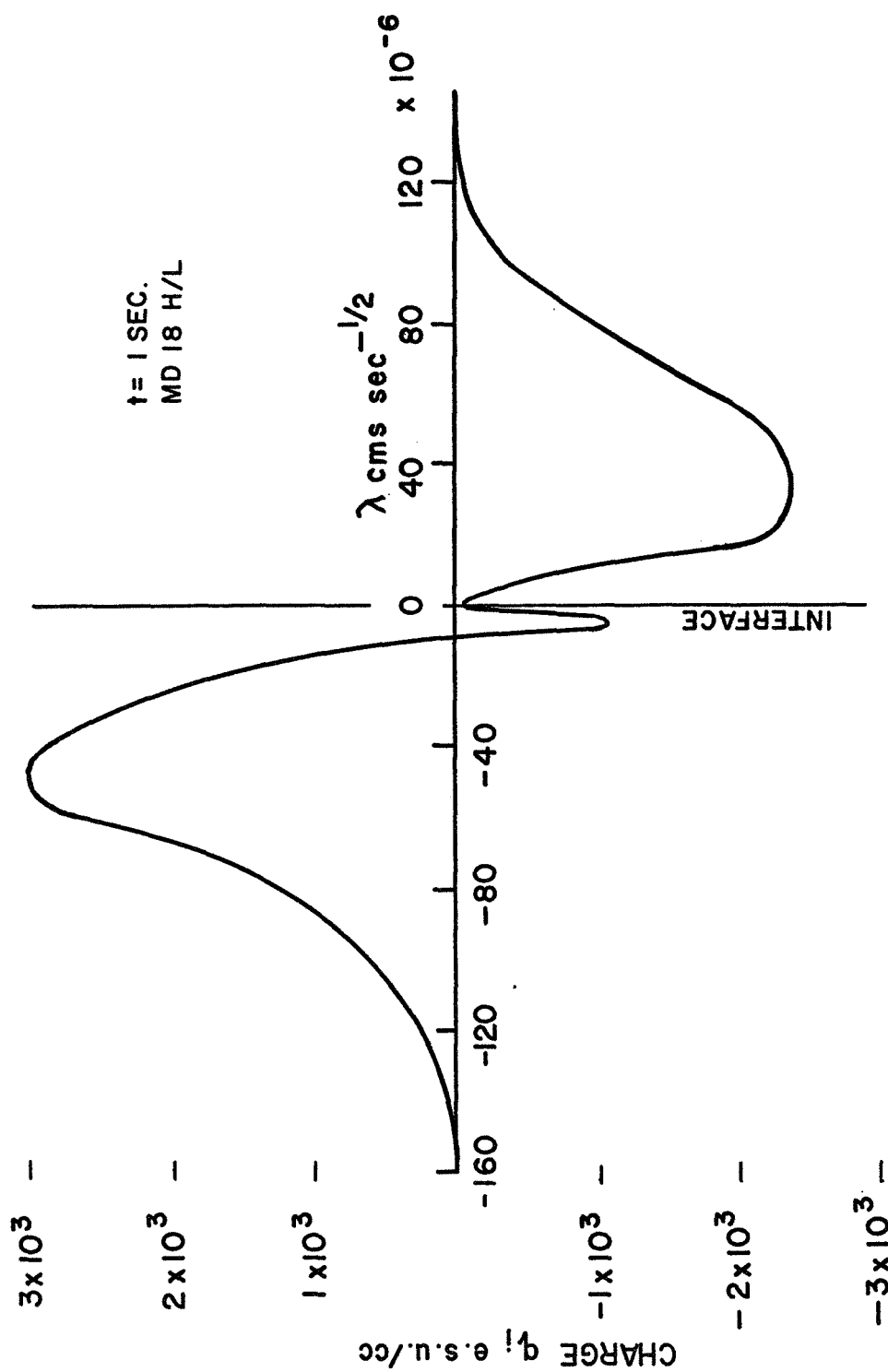


FIG.20: VARIATION OF CHARGE DENSITY.

This gives a maximum concentration of excess K^+ ions as $6.6 \times 10^{12}/t$ per cc.

For a 20% K_2O containing glass, the concentration of total potassium atoms is nearly 7×10^{21} per cc. Hence, at $t = 1$ seconds, the number of free K^+ ions corresponds to ~ 0.2 parts per billion at a maximum.

We, thus, arrive at the conclusion that except at very short times ($t < 10^{-6}$ sec.), the extent of non-stoichiometry is negligible everywhere.

It is also possible to calculate the deviation from the charge neutrality equation $\sum_i Z_i J_i = 0$ where i sums over all ions passing a particular plane.

Since

$$-J_{K_2O} = D_{11} \partial x_{K_2O} / \partial y + D_{12} \partial x_{SrO} / \partial y$$

and

$$x_{SrO} - \bar{x}_{SrO} = -3.06 \operatorname{erf} (\lambda/2\sqrt{6.75 \times 10^{-10}}) + 1.86 \operatorname{erf} (\lambda/\sqrt{3 \times 10^{-11}}) \quad (74)$$

Hence, at $y = 0$, $t^{1/2} J_{K_2O} = -4.4 \times 10^{17}$ ions of potassium $\text{cm}^{-2} \text{sec}^{-1/2}$.

If $J_{\oplus y}$ is the flux of free K^+ at y , then application of conservation principle yields

$$dJ_{\oplus y} / dy = -dq_y / dt \quad (75)$$

Using Boltzmann substitution⁽⁶⁶⁾ $\lambda = y/\sqrt{t}$ in the above equation we get

$$dJ_{\oplus y}/d\lambda = (\lambda/2t^{1/2}) (dq_y/d\lambda) \quad (76)$$

Multiply both sides by $d\lambda$ and integrate between the limits $\lambda = -\infty$ to λ

$$\int_{J_{\oplus} \text{ at } \lambda = -\infty}^{J_{\oplus} \text{ at } \lambda} dJ_{\oplus} = (2t^{1/2})^{-1} \int_{q \text{ at } \lambda = -\infty}^{q \text{ at } \lambda} \lambda dq \quad (77)$$

Since $J_{\oplus}$ at $\lambda = -\infty$ is zero, above equation yields

$$J_{\oplus \lambda} = (2t^{1/2})^{-1} \int_{q \text{ at } \lambda = -\infty}^{q \text{ at } \lambda} \lambda dq \quad (78)$$

The integral expression in equation (78) is a sort of Matano area under the plot of q against λ . This flux is a maximum at the position where the charge density is a maximum and at $t = 1$ sec. the value is ~ 0.13 e.s.u. of charge /cm²/sec.

This is equivalent to $\sim 2.4 \times 10^8$ ions of K^+ per cm² per sec. and compared to the total flux of potassium atoms (at $\lambda = 0$), it is negligible. This proves that though charge neutrality is not exact, deviations from it are very small.

The establishment of an electric field results in a net potential difference (p.d.) across the couple. The p.d. can be

found by integrating equation (70) with respect to y .

$$\begin{aligned}\psi &= (kT/|z_o| z_i) \int (\partial \ln x_{io}/\partial y) dy \\ &= (kT/|z_o| z_i) \ln x_{io} + V\end{aligned}\quad (79)$$

where V is a constant

If for convention, we write

$$\psi = 0 \text{ at } \lambda = 0; x_{io} = \bar{x}_{io}$$

then

$$\psi = (kT/|z_o| z_i) \ln (x_{io}/\bar{x}_{io}) \quad (80)$$

Since

$$x_{io}^Q/\bar{x}_{io} \approx 1.1 \quad (\text{for } K_2O)$$

where x_{io}^Q is the concentration at one end of the couple,

we obtain

$$\psi \approx 15.5 \times 10^{-6} \text{ stat volts}$$

$$\approx 0.05 \text{ } \mu \text{ volts}$$

This is the electrostatic potential difference between the position $\lambda = 0$ and $\lambda = +\infty$. The net p.d. between $\lambda = -\infty$ to $\lambda = +\infty$ is, therefore, nearly $0.1 \text{ } \mu \text{ volt}$ and is independent of time so long as the boundary conditions of semi-infinite couple are maintained.

At a given temperature, say at 750°C, the self-diffusion coefficient of K^+ in this glass ⁽³⁸⁾ is $8 \times 10^{-8} \text{ cm}^2/\text{sec}$. The direct coefficient D_{11} of potassium, however, is only $3.5 \times 10^{-10} \text{ cm}^2/\text{sec}$. from Figure 14. If the self-diffusion also occurs by ionic motion, it is an important question to ask why there is apparently no influence of any electric field on the motion of the radio tracer.

One of the possible explanations to the above is that a self-diffusion experiment in an ionic system proceeds through exchanges of $i_1 \leftrightarrow i_2$ type only where both i_1 and i_2 have the same charge. Exchanges of the type $i \leftrightarrow j$ where i and j have different valence are extremely rare owing to the charge imbalance and the elastic strain involved. The result is that there is no electric field produced in the system. The introduction of a force due to chemical concentration gradient in an interdiffusion experiment off-sets the charge neutrality condition because an ion-exchange process is no longer a necessary requirement, i.e., exchanges of the type $i \leftrightarrow \square$ can occur where $\square$ is a neutral vacant site.

The criterion that the system nearly preserves local stoichiometry enables us to write all the diffusion equations in terms of neutral molecules of K_2O , SrO and SiO_2 instead of ions themselves. This is consistent with the atomic mobility model.

Before proceeding to discuss the magnitudes of other diffusion coefficients, it is worth recognizing that all treatment of

the data assumed a complete miscibility within the system. Simple glasses, such as $\text{Li}_2\text{O-SiO}_2$ ^(77a), $\text{Na}_2\text{O-SiO}_2$ ^(77b), $\text{Na}_2\text{O-CaO-SiO}_2$ ^(77d,e), $\text{K}_2\text{O-SiO}_2$ ^(77a) are known to undergo varying extents of phase separation when heat-treated to prolonged periods in the vicinity of $\sim 750^\circ\text{C}$. Available evidence suggests ^(77c) that the lower the field strength of the ion (=charge/radius), the lesser the tendency to phase separate. The relative effects of addition of an alkaline earth oxide have not been studied in detail. From thermodynamics, it may be suggested that the contribution of configurational entropy term on the introduction of another element would favor the tendency towards mixing ^(77c). It appears, therefore, that the assumption of simple solution behavior in $\text{K}_2\text{O-SrO-SiO}_2$ over the range 650°C - 800°C is a reasonable one to make.

The negative sign of D_{21} and its large magnitude are a natural result of the coupling and the build-up of space charge restraint. The motion of Sr^{++} is primarily controlled by gradient of K^+ and is in opposite direction to the flow of K^+ .

In Table 2,3 it is shown that though in each case the magnitudes of D_{11} and D_{21} are same within the accuracy, D_{21} is more frequently larger in magnitude. One question as to why the net influence of gradient of potassium is larger on the flux of strontium than on its own flux. Perhaps, an explanation simply lies in the argument that the description of diffusion eliminated the inclusion

of the gradient of SiO_2 , i.e., measurements of D_{ij}^3 were made

$$D_{ij}^3 = D_{ij}^0 - D_{i3}^0$$

If one accepted that $D_{11}^0 \approx D_{21}^0$ for reasons of no net charge build-up, then slightly positive values of D_{13}^0 and D_{23}^0 , which are probable, would be compatible with our results.

The predictions of mobility model are very well substantiated. Figure 14 shows that both D_{11} and D_{21} in magnitude are nearly the same as D_{Sr} as expected from equations (51) and (56). The relation (57) is also established.

If the system were thermodynamically ideal, D_{12} from equation (55) would be negative and D_{22} from equation (54) would be positive.

The introduction of non-ideality in these equations led to the suggestion that both these quantities would be small with doubtful sign.

Calculations arrived at in Tables 2 and 3 are also unable to pinpoint the sign except in one case. The $\pm 3\sigma$ confidence limits for each of the D_{12} and D_{22} cover zero. Bad as they are, the mutual agreement between the predicted values and the calculated values from experimental data is remarkable.

The data of D_{11} and $|D_{21}|$ follows an Arrhenius' rate type equation with an apparent activation energy of about 48 Kcal/mol.

This also supports the prediction well. Both the coefficients are dominated by D_{Sr} which has an activation energy of 42.8 Kcal/mol.

The creation of electric fields and its effect on ionic migration appears to be rather analogous to the electro-migration phenomenon⁽⁷⁸⁾ in metals. Since most of the charge carriers are electrons, so the magnitudes of electrostatic fields that can be set up is very small. However, even these small fields have strong influence on the motion of ions in metals.

The discussion so far indicates how only small magnitudes of charge accumulation bring a great change in the kinetics of ionic motion. Perhaps, a clue lies in the argument that coulomb forces represent long range interaction.

In an earlier publication⁽¹⁶⁾ by the author, distribution of SiO_2 in approximately H/K couple could not be obtained directly owing to large scatter in the microprobe analysis for Si. Instead, the distribution of SiO_2 was obtained by adding the K_2O and SrO distributions point by point and subtracting out of 100%. It was shown statistically that this calculated profile of SiO_2 displayed at least one extremum point in the vicinity of $X = \frac{1}{2} \pm \infty$ with 94% confidence.

The scatter for the measurement of Si in this work has been reduced to a level of 0.4% of the counts. This enables us

to observe the extremum points directly as is shown in Figure 9.

It is shown that not only extremum points in the vicinity of $\lambda = \frac{1}{2} \infty$ occur, but extremum points in the vicinity of $\lambda = 0$ (called "type 2 extremum points") also occur (Figure 13).

The experimental observation of both types of extremum points supports the idea that occurrence of uphill diffusion in multicomponent systems is not uncommon. Rather, it is a natural result of difference in mobilities of individual species and coupling in between them. The net motion is co-operative in such a way that the species are conserved, that there is no net pressure build-up and that in case of charge flow, the system resists a space charge build-up.

If the termini compositions are the same and the diffusion temperature is identical in diffusion couples prepared for various times, then the concentration distributions of a particular species merge on a $y/\sqrt{t}$ scale (Figure 8). This not only means that the diffusion process in this system is Fickian, but the diffusion coefficients are independent of time as well. On composition space, the diffusion path does not vary with time.

It is seen in Table 2 that Onsager's hypothesis (equation 3) is a good representation of diffusion behavior along both H/K and I/J directions. Values of χ_v^2 (2) obtained are less than 1.5 in all cases.

Whereas directions G/F and H/L give $\chi_v^2(3)$ and $\chi_v^2(4)$ values as high as 3, the inadequacy in fitting appears primarily due to the assumption that diffusion coefficients are independent of concentration. Concentration profiles are not perfectly symmetric about $\lambda = 0$ as is seen typically in Figure 13. It must, however, be recognized that this asymmetry is in the correct direction. Compositions which are higher in their K_2O content are expected to have higher diffusion coefficients at a given temperature⁽⁷⁹⁾, resulting in flatter distributions.

With this consideration in mind, it may be said that the chi-fitting is very good along all directions and that the values of interdiffusion coefficients agree reasonably well within experimental accuracy.

It can also be seen that all calculated $[D_{ij}]$ obey the restrictions (section 2.4) imposed by thermodynamics.

However, we are not in a position to make a positive statement if we consider the error matrix associated with the $[D_{ij}]$. Whereas the standard deviation associated with D_{11} and D_{21} are generally of the order of 10%, the values D_{12} and D_{22} suffer much larger errors, even to the extent that the sign of these coefficients is questionable.

This ambiguity seriously affects the smaller eigen value, D_v . A negative eigen value gives rise to a spinodal

decomposition process. It has been shown that even an imaginary eigen value can give rise to real solutions of the diffusion equation⁽⁸⁰⁾. Concentration distributions in the latter case have a wave-like distribution near the extremities.

However, for a thermodynamically stable solution of the transport equation, the interdiffusion coefficients matrix must be positive definite⁽³⁷⁾ since this matrix is the product of two positive definite symmetric matrices, the "conductance" matrix (page13) and the thermodynamic activity coefficients matrix.

As such, no attempts to chi-fitting for a negative or imaginary eigen value were made. The computer programs were compensated to steer away during the course of χ^2 minimization to take alternative routes, should such a situation arise. In such cases (two in all), the absolute χ^2 minimum was located ultimately in the positive eigen values region.

The coupling between the various fluxes and forces as included in Onsager's hypothesis can be conveniently unfolded using the concept of eigen vectors and eigen values.

Intuition here is readily derived through a glance at equations (35). Instead of a single error function distribution for the binary system, the concentration distribution of each species is a sum of error functions whose arguments involve the eigen values as the diffusion coefficients.

Particularly convenient is the use of composition space with $\hat{\gamma}_i$ orthogonal basis vectors. If the eigen vectors and the eigen values are worked out, then it is a trivial matter to draw a fairly accurate diffusion path. The basic rules to do so have been indicated briefly in section 2.5.

To conclude, it has been shown that Onsager's hypothesis is a good description of multicomponent diffusion phenomena in the $K_2O-SrO-SiO_2$ system. The kinetics can be conveniently unraveled through the use of the eigen vector - eigen value concept. It has also been shown that the atomic mobility model satisfactorily describes the relation between the interdiffusion coefficients and the self-diffusion coefficients in this system.

PART II

DIFFUSION IN TEKTITES

"The only thing that keeps a man going is energy.
And what is energy but liking life?"

-- Louis Auchincloss in
A World of Spirit

CHAPTER 7

THE APPROACH

"Only he who attempts the ridiculous can achieve the impossible"

-- Will Henry, Chicago Tribune-
N.Y. News Syndicate

Concentration fluctuations of a species i in a body decay by a diffusion process. In section 2.9, we have seen that under appropriate conditions this diffusion process can be described adequately by the effective binary diffusion coefficient (EBDC) of i .

Estimation of thermal history of tektites has been attempted by the following procedure:

- (i) A measurement of inhomogeneities of Fe, Si, Al and Ca in tektites.
- (ii) A measurement of the EBDC of Fe and Si in laboratory synthesized tektite system.
- (iii) Calculation of homogenization times of a hypothetical mineral composite with periodic laminar concentration fluctuations of (a) Fe and (b) Si.

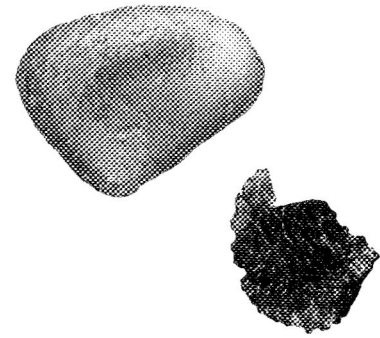
Primary focus for the measurement of inhomogeneities was Thailand tektite 2172*. Among the various tektite types, the 2172 tektite does not show any visible crystalline inclusion⁽⁸¹⁾.

Plate 1 is a photograph of some of the specimens used in this research. Whereas the external mosaic structure does not appear to be different from each other, a cut away section of 2172^{*} tektite does not show the abundance of inclusions or bubbles as does the Muong Nong. Thus, starting from parent minerals, the 2172 tektite is expected to have undergone one of the most severe thermal histories among all other tektite types.

An estimation of the most severe thermal history, naturally, demands a narrowing on the choice of chain of events, discussed in "Introduction" in the beginning of this thesis, which might have led to the formation of tektites.

The measurement of inhomogeneity in tektites also included a comparison with similar data in two laboratory synthesized tektite compositions, Muong Nong tektites, Moldavites, Aouelluol glass, obsidian, glass obtained from nuclear explosion, microtektites and glassy fragments of lunar dust from Apollo 12 site.

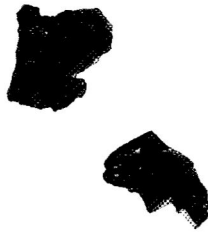
* Smithsonian Institute, Washington, D. C., code number.



MOLDAVITE



MUONG NONG TEKTITE



AQUELLOUL CRATER GLASS



NUCLEAR EXPLOSION GLASS



THAILAND TEKTITE 2172



ICELAND OBSIDIAN

CHAPTER 8

LITERATURE SURVEY

" जिन खोजा तिन पाइयाँ , गहरे पानी पैठ "

"Those who searched deep into the water, (ultimately) found Him."

-- Mahatma Kabir

Inhomogeneities in Tektites

Muong Nong tektites appear to be most inhomogeneous. The most abundant inclusions have been identified by Barnes⁽⁸²⁾ to be those of lechatelierite, a glassy phase of SiO_2 , on the basis of index of refraction. The size of these lechatelierite inclusions is usually up to 1 mm. In spite of the fact that quartz is known to melt metastably at about 1450°C , and above 900°C in presence of water⁽⁸³⁾, Barnes has emphasized that the presence of lechatelierite indicates that the source material must have reached at least 1710°C , which is the melting point of cristobalite.

The discovery of coesite, a high pressure form of silica, in Muong Nong tektites by Walter⁽⁸⁴⁾ indicated that these tektites must have suffered high pressure such as the ones resulting from an impact sometimes during their history. At the same time, if they reached 1700°C , then the temperature could not have lasted for more than 175 seconds for a 5 mm size tektite to have some coesite

unconverted to cristobalite. Walter found that these coesite grains of about 1μ diameter were present to about <100 ppm in a Muong Nong tektite.

Recently, inclusions of chromite and zircon have been found by Glass⁽⁸⁵⁾ in a Muong Nong type which also seems to suggest similar limitations upon the extent of thermal history for the Muong Nong type.

The discovery of baddeleyite + silica inclusion in Martha's Vineyard tektite by Clarke and Wosinski⁽⁸⁶⁾ and in Georgia tektites by Clarke and Henderson⁽⁸⁷⁾ and El Goresy⁽⁸⁸⁾ suggested that contrary to the Muong Nong type, these tektites might have reached temperatures above 1700°C for significant duration of time. Baddeleyite and silica are formed by the decomposition of zircon around 1775°C ⁽⁸⁸⁾.

Some "finger" type inclusions of siliceous glass have also been described by Barnes⁽⁸⁹⁾ and Chao⁽¹¹⁾. Inclusion of this type were interpreted to be the result of a highly fluid siliceous glass "plunging" into the tektite matrix⁽¹¹⁾.

Bubbles or vesicles occur in all the tektites. Their size is usually less than 500μ , and occasionally as much as 1 cm ⁽¹¹⁾. They vary in shape and abundance. The Muong Nong types display alternating, highly vesicular bands. Most australites, bediasites, moldavites and some types of thailandites are, however, relatively

free of bubbles.

These vesicles are reported to be of good vacuum⁽⁹⁰⁾. Whereas Barnes⁽⁸²⁾ has suggested that they are shrinkage bubbles, Cooper⁽⁹¹⁾ has suggested that some of them might have grown at favorable sites as a result of internal tensile stresses.

The presence of Fe-Ni spherules⁽⁹²⁾ and magnetite spherules⁽⁹³⁾ provides a strong evidence of the association of tektite formation event with a meteoritic impact. There is some possibility that some of the magnetite spherules or pure iron globules appear as a result of a spinodal decomposition process⁽⁹³⁾.

Diffusion in Tektite Glass

There is no known data on ionic diffusion in tektites in the existing literature other than the author's publication⁽⁹⁴⁾. This paper itself forms a significant part of the thesis and, hence, will not be discussed anymore in this section.

Some diffusion data of rare gasses in tektites have been reported. Measurements on argon diffusion were made by Fechtig, et al^(95a) in connection with the validity of K-Ar age determination of tektites. These authors observed that the major fraction of argon was released above 1000°C and whatever radiogenic argon formed subsequently, remained within the structure. Diffusion coefficient of Ar at room temperature was too low to cause any significant loss of radiogenic argon.

Similar conclusions were reached by Reynolds^(95b) concerning the diffusion of He and Ne in his search for cosmogenic nuclei in tektites.

Some semiquantitative studies regarding the disappearance of inhomogeneities in tektites have been made. Barnes⁽⁹⁶⁾ found that inclusions of lechatelierite almost disappeared if tektite was heated at $\sim 1500^{\circ}\text{C}$ for $\sim 1/2$ hour. In another study, the Ne-Fe spherules stayed without diffusing out into the matrix glass if the specimen was heated above 2000°C for ~ 2 min.⁽⁹⁷⁾

Calculation of Homogenization Times

A mathematical calculation of times to homogenize a system has been attempted in several systems other than the tektite glass itself. Most of these calculations use the system in the form of a simplified model to which equations of diffusion can be applied. Some examples are: calculation of homogenization times in a glass tank by Cooper⁽⁹⁸⁾, mixing in thermoplastic materials by Mohr⁽⁹⁹⁾, losses of plasticizers from polyvinyl chloride plastics by Liebhafsky⁽¹⁰⁰⁾, and in the field of geology, calculation of temperature distribution in rocks by Lovering⁽¹⁰¹⁾ and retained argon correction for K-Ar age determinations⁽¹⁰²⁾.

CHAPTER 9

MEASUREMENTS OF INHOMOGENEITY

"Faults are often disagreeable and it is to our interest not to emphasize the disagreeable."

-- Bernard de Fontenelle

Concentration distributions of selected elements were measured along an arbitrarily chosen straight line on section of specimens using an electron microprobe.

Preliminary experiments⁽¹⁰³⁾ indicated that glasses duplicating the tektite composition could be prepared with comparable levels of homogeneity within the laboratory. Therefore, whereas most specimens were compared qualitatively for their level of homogeneity, a quantitative comparison was attempted between 2172 tektite and two laboratory synthesized compositions.

The description below will, therefore, be divided into two main sets of experiments:

- (a) a quantitative comparison of 2172 tektite with laboratory synthesized glasses,
- and (b) a qualitative examination of inhomogeneities in other geological specimens.

§9.1 THE THAILAND TEKTITE 2172 VERSUS LABORATORY SYNTHESIZED TEKTITES

9.1.1 The Glasses:

Table 5 gives the nominal chemical composition of the 2172 tektite and two other glasses JC3 and TA. Glass JC3 is an attempted duplication of the tektite composition. It was prepared* by melting 500 g of thoroughly mixed analytical grade chemicals in air in a globar electric furnace at 1550°C for 24 hours. The glass had bubbles.

Glass TA is a simplified representation of the tektite system. It eliminates all the minor constituent. A globar melt obtained at 1550°C was broken to pieces and later heated in a calcia-stabilized zirconia crucible in a gas-fired kiln for a soak-time of 4 hours at 1800°C to yield a bubble-free glass. This glass has also been used for the diffusion studies which will be described in Chapter 10.

9.1.2 Electron Probe Analyses

A section of the 2172 tektite and pieces of JC3 and TA were mounted in a 1" diameter "quick mount" cold mounting media. The mount was ground flat, polished with 3 μ diamond paste, and,

* Glass melting was carried out by Mr. Jeffrey L. Cramer under directions of the author as part of an NSF summer studentship at Case Western Reserve University.

TABLE 5

CHEMICAL COMPOSITION (Wt. %) OF
TEKTITE AND SYNTHETIC GLASSES

	Thailand Tektite 2172	Synthetic Tektite JC3	Synthetic Tektite TA	Raw Materials Used
SiO ₂	73.0	72.0	72.0	SiO ₂
Al ₂ O ₃	12.83	13.0	13.0	Al ₂ O ₃
Fe ₂ O ₃	0.64	} 5.7	5.5	Fe ₃ O ₄
FeO	4.37			
MgO	2.48	2.7		MgO
CaO	1.91	2.0	5.5	CaCO ₃
Na ₂ O	1.45	1.62		Na ₂ CO ₃
K ₂ O	2.40	2.31	4.0	K ₂ CO ₃
TiO ₂	0.73	0.72		TiO ₂
MnO	0.09	0.1		MnO ₂

subsequently, shadowed with about 300 Å^o thick carbon film. The specimen was then placed in the microprobe and analyzed for desired elements with a 1.5μ diameter probe at 25 kv using the Matrix Method.

9.1.3 The Matrix Method

A frequent problem arising in electron probe analysis is the time dependent "drift" of the instrument. The gradual bending of the gun filament as the gun assembly warms up, the change in the electro-magnetic character of the lenses as they warm up, are some of the causes which contribute towards "drift."

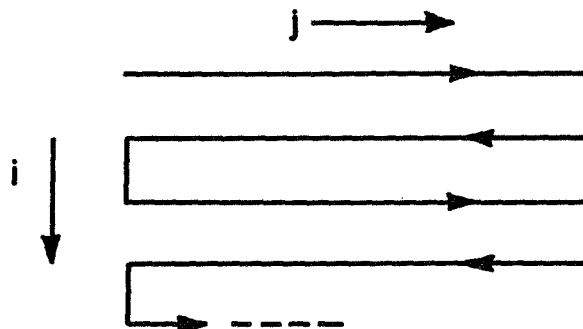
The result is a gradual change in X-ray intensity during the course of microanalyses. This can often be confused with real concentration variations within the specimen. "The Matrix Method" was developed to separate small concentration variations from the time dependent drift of the microprobe. This scheme of analysis consisted of stepping the specimen, under a stationary electron beam, 10μ in a forward direction 100 times and then stepping backward on the same trace. This is shown in Figure 21. The sequence of stepping in this manner generates a matrix of data where a column represents a particular position on the straight line trace and a row represents a particular set of consecutive readings along the trace.

FIG.21 : THE MATRIX METHOD.

No. OF COLUMNS = No. OF POSITIONS = K
 No. OF ROWS = No. OF REPETITIONS AT THE SAME POSITION = n

X_{11}	X_{12}	X_{13}	—	—	—	—	X_{1K}	MEAN $\bar{X}_{1j}$
X_{21}	X_{22}	X_{23}	—	—	—	—	X_{2K}	$\bar{X}_{2j}$
X_{31}	X_{32}	X_{33}	—	—	—	—	X_{3K}	$\bar{X}_{3j}$
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—
X_{n1}	X_{n2}	X_{n3}	—	—	—	—	X_{nK}	$\bar{X}_{nj}$
MEAN $\bar{X}_{i1}$ $\bar{X}_{i2}$ $\bar{X}_{i3}$ — — — — $\bar{X}_{iK}$								$\bar{X}_{ij}$

THE SEQUENCE OF DATA COLLECTION IS



If the microprobe simultaneously analyzes two elements, A and B, which are either independently distributed or which display a negative correlation, a matrix of the ratio of counts of A to B will be free of any effects due to defocusing of the electron beam at any stage during the analysis. Slight imperfections in the specimen stage which can cause significant defocusing over the 1 mm traverse are thus removed. At the same time, it is shown in Appendix 4 that the column means will be influenced by the inhomogeneities in A and B only, whereas the row means will be influenced by the drift of the instrument alone.

The analysis of the data to separate the contributions due to inhomogeneities and drift then becomes a simple two variables of classification, Analysis of Variance technique employing the standard F tests⁽¹⁰⁴⁾.

9.1.4. Results

Microanalyses were performed using the Matrix Method for two pairs, Fe-Si and Al-Ca, in the three glasses. Figures 22 and 23 show plots of the column means of the Si/Fe ratio and the Ca/Al ratio for the three glasses versus the distance from an arbitrary point. The dashed lines represent limits of 95% level of confidence that no inhomogeneity exists. These limits are defined by the variance of the inherent scatter in counting. For a mean value

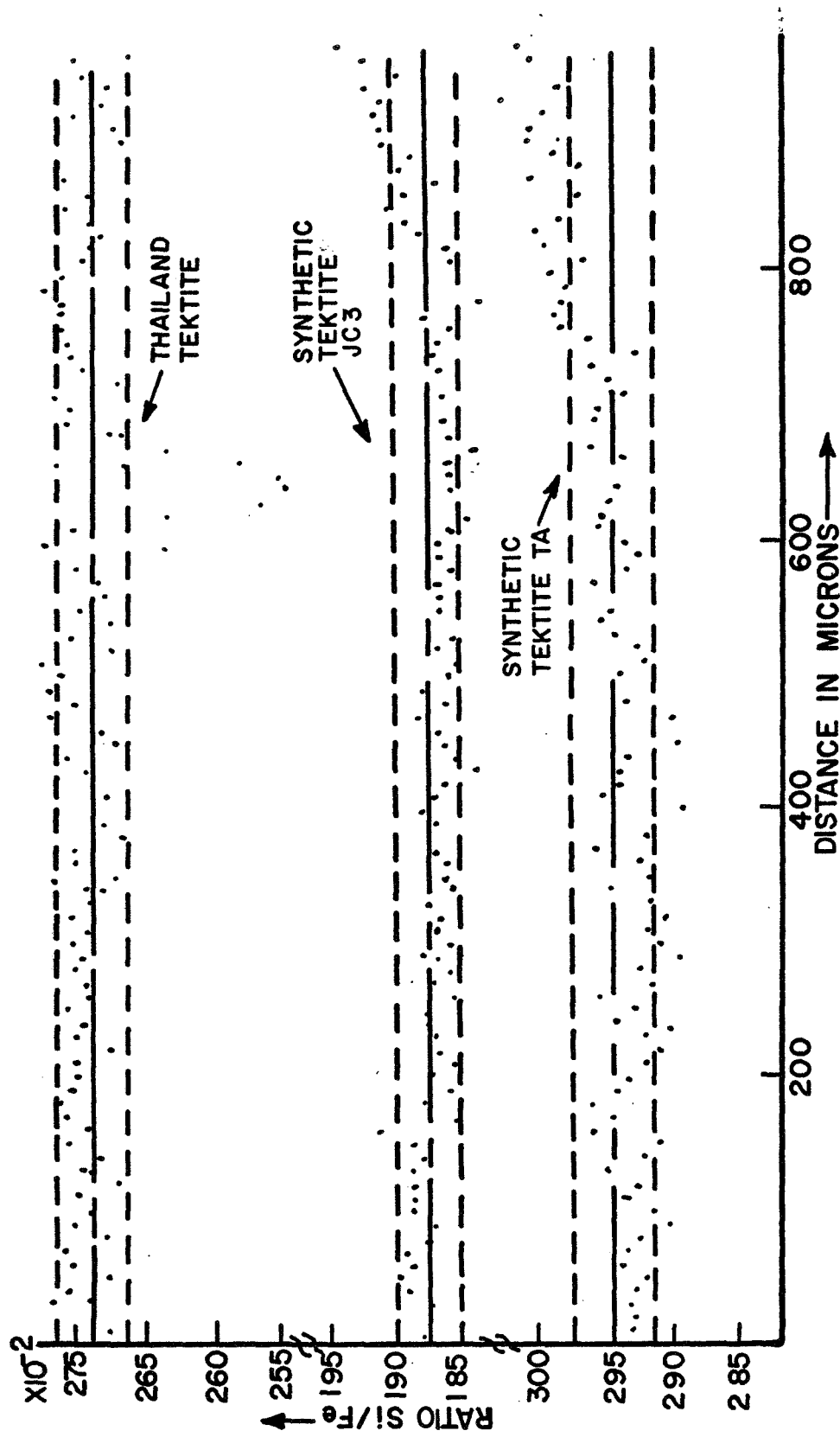


FIG. 22 : PLOT OF COLUMN MEANS OF THE Si/Fe RATIO MATRIX.

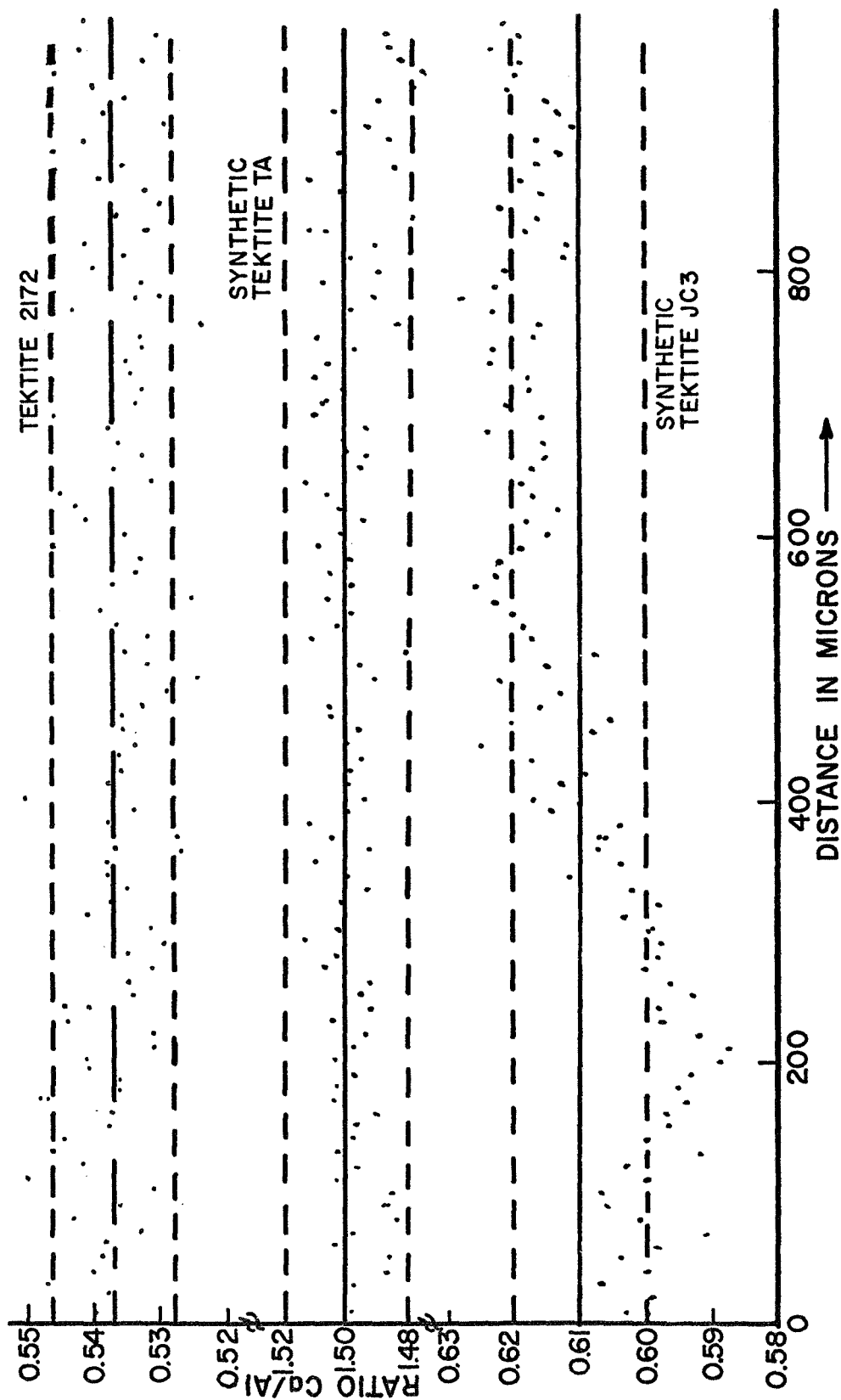


FIG. 23: PLOT OF COLUMN MEANS OF Ca/Al RATIO MATRIX.

of iron oxide content of 5.0 wt. %, a fluctuation of 0.05 wt. % can be detected.

Although there appears to be a long wavelength fluctuation in both the synthetic glasses, the tektite is relatively homogeneous except for a single iron-rich peak which corresponds to about 5.25 wt. % iron oxide. This may well be remnants of a meteoritic or a magnetite inclusion.

An additional scan on the sample 200 μ away revealed no iron-rich peak.

Table 6 shows the F values for the Si/Fe ratio and the Ca/Al ratio in the three glasses. If a measured value of F exceeds the value given in the last column, it can be stated with 95% confidence that a significant inhomogeneity (or drift) exists.

Despite large drift effects, the homogeneity of three glasses is not too different. If we ignore the 60 μ wide iron rich inclusion in the Thailand tektite, its F value of Si/Fe inhomogeneity effect drops to 1.14, indicating that, away from the inclusion, the 2172 tektite is the most homogeneous glass of all.

TABLE 6

F VALUES FOR THE DISTRIBUTION OF Si/Fe AND Ca/Al RATIOS

		Thailand Tektite 2172	Synthetic Tektite JC3	Synthetic Tektite TA	Level of 95% Confidence
Si/Fe	Inhomogeneity effect	4.5	3.9	3.4	1.30
	Drift effect	14.6	314	131	2.11
Ca/Al	Inhomogeneity effect	1.57	3.7	0.8	1.30
	Drift effect	9.3	73	7.4	2.11

§9.2 OTHER NATURAL GLASSES

9.2.1 Experiments

Cut-away sections of moldavite, Muong Nong tektite, nuclear explosion glass (from Alamogordo, New Mexico), obsidian, microtektites, auelluol crater glass, laboratory synthesized spheres corresponding to Apollo XI glass composition and lunar glass fragments from Apollo XII site were mounted in separate 1" diameter "quick mount" cold mounting media. These mounts were ground flat, polished with 3 μ diamond paste and shadowed with ~300 μ thick aluminum film.

The specimens were placed inside the microprobe and analyzed for Si, Fe and Ca distribution along arbitrarily chosen straight line paths under standard conditions of point probe, gun voltage of 25 kv, 0.03 μ a specimen current, a stepping distance of 10 μ , and a counting time of 50 seconds.

The lunar glass fragments were analyzed for Ti, and Al as well. (This mount was shadowed with 300 μ thick carbon film.)

9.2.2 Results

Table 7 lists the reported chemical analyses of specimens examined. Figure 24 through 34 are plots of x-ray intensity measurements against distance along a straight line

TABLE 7

AVERAGE CHEMICAL COMPOSITION (wt. %) OF NATURAL GLASSES

	Thailand Tektite 2172	Muong Nong Tektite	Moldavite	Aouelloul Crater Glass	Iceland Obsidian	Lunar fines XII #12033
SiO ₂	73.0	72.64	80.07	86.51	75.01	41
Al O ₃	12.83	13.40	10.56	5.76	12.27	16.0
Fe ₂ O ₃	0.64	0.58	0.15	1.31	0.80	—
Fe O	4.37	4.21	2.29	1.59	2.78	16.0
Mg O	2.48	2.25	1.46	0.91	0.08	11.0
Ca O	1.91	2.03	1.87	0.73	1.87	11.5
Na ₂ O	1.45	1.54	0.51	0.14	3.36	0.54
K ₂ O	2.40	2.50	2.95	2.05	2.80	0.39
Ti O ₂	0.73	0.76	0.80	0.55	0.33	2.6
Mn O	0.09	0.09	0.11	0.04	0.06	0.23
Cl					0.13	
SO ₃					0.07	
H ₂ O	60 p.p.m.		4 p.p.m.	0.35	0.2	

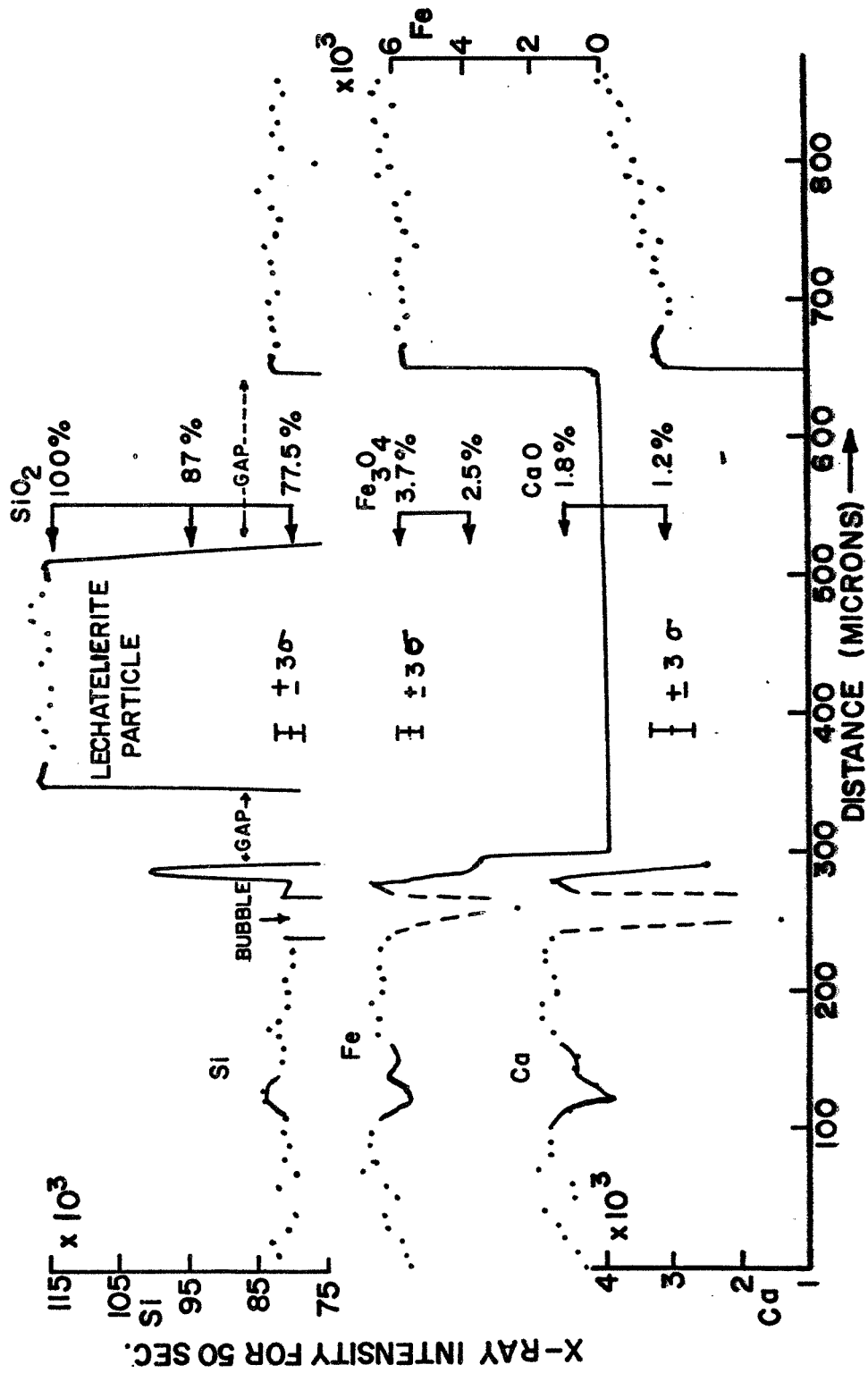
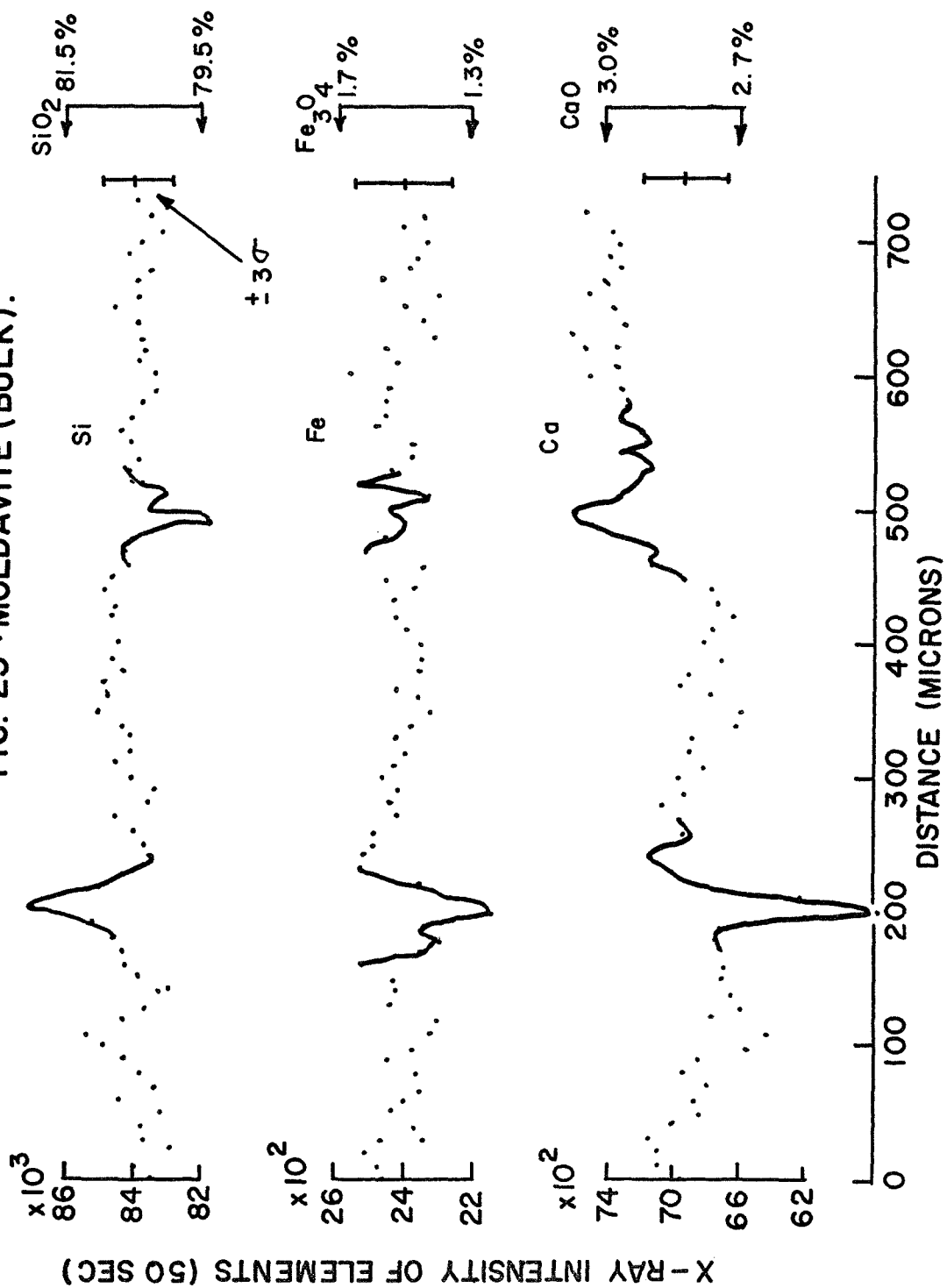


FIG.24: MUONG NONG TEKTITE.

FIG. 25 : MOLDAVITE (BULK).



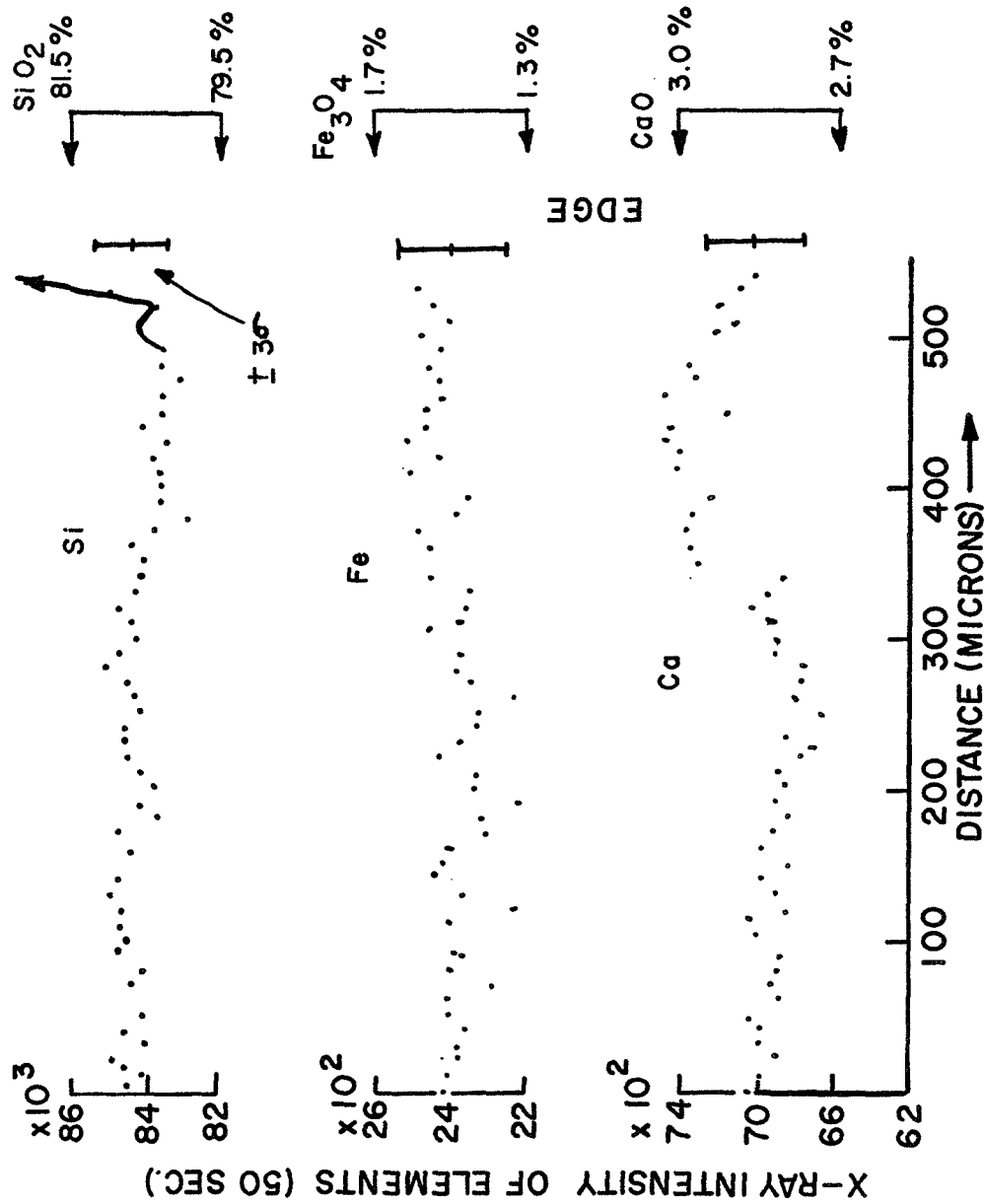


FIG. 26: MOLDAVITE (NEAR THE EDGE).

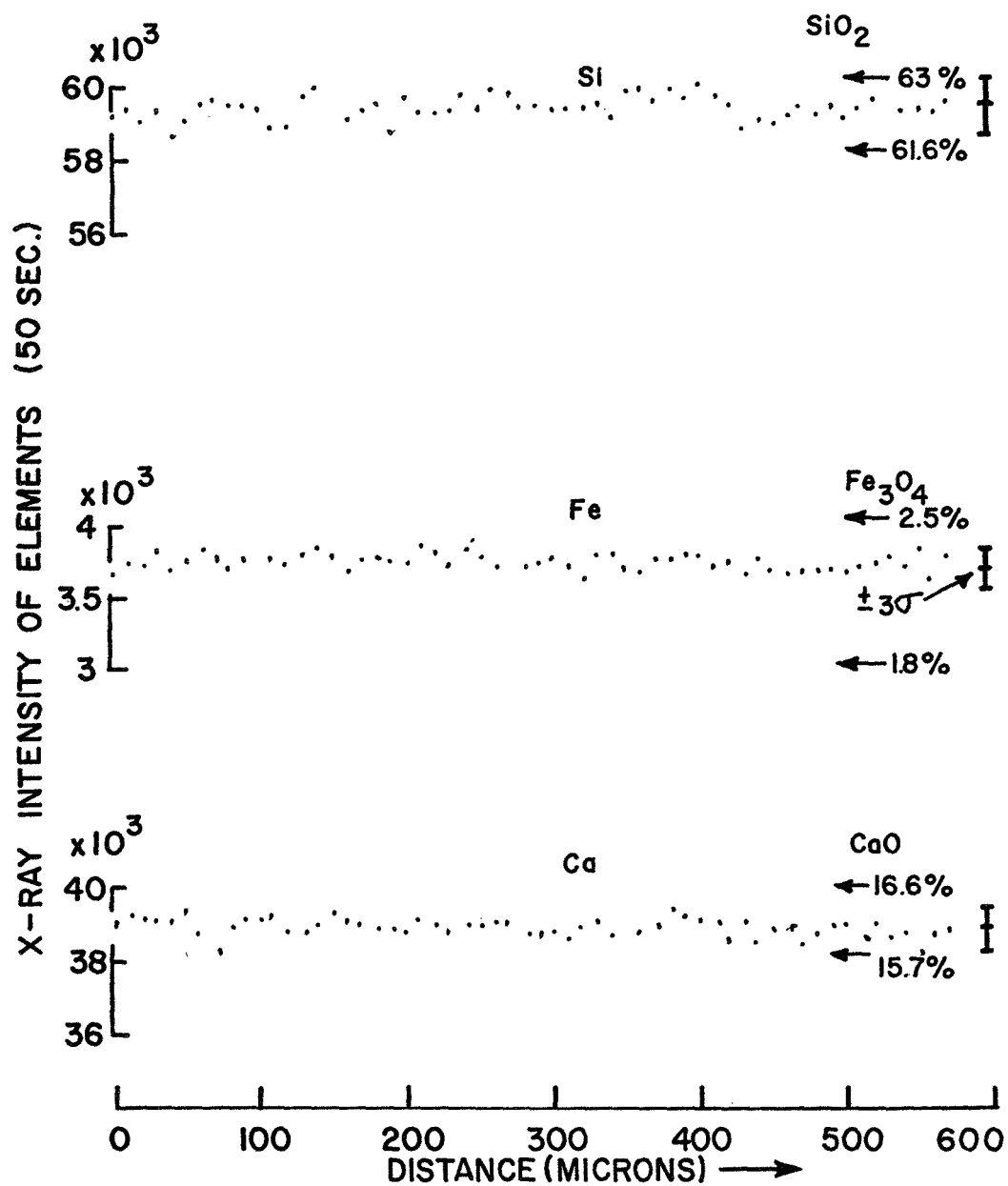


FIG.27: NUCLEAR EXPLOSION GLASS (BULK).

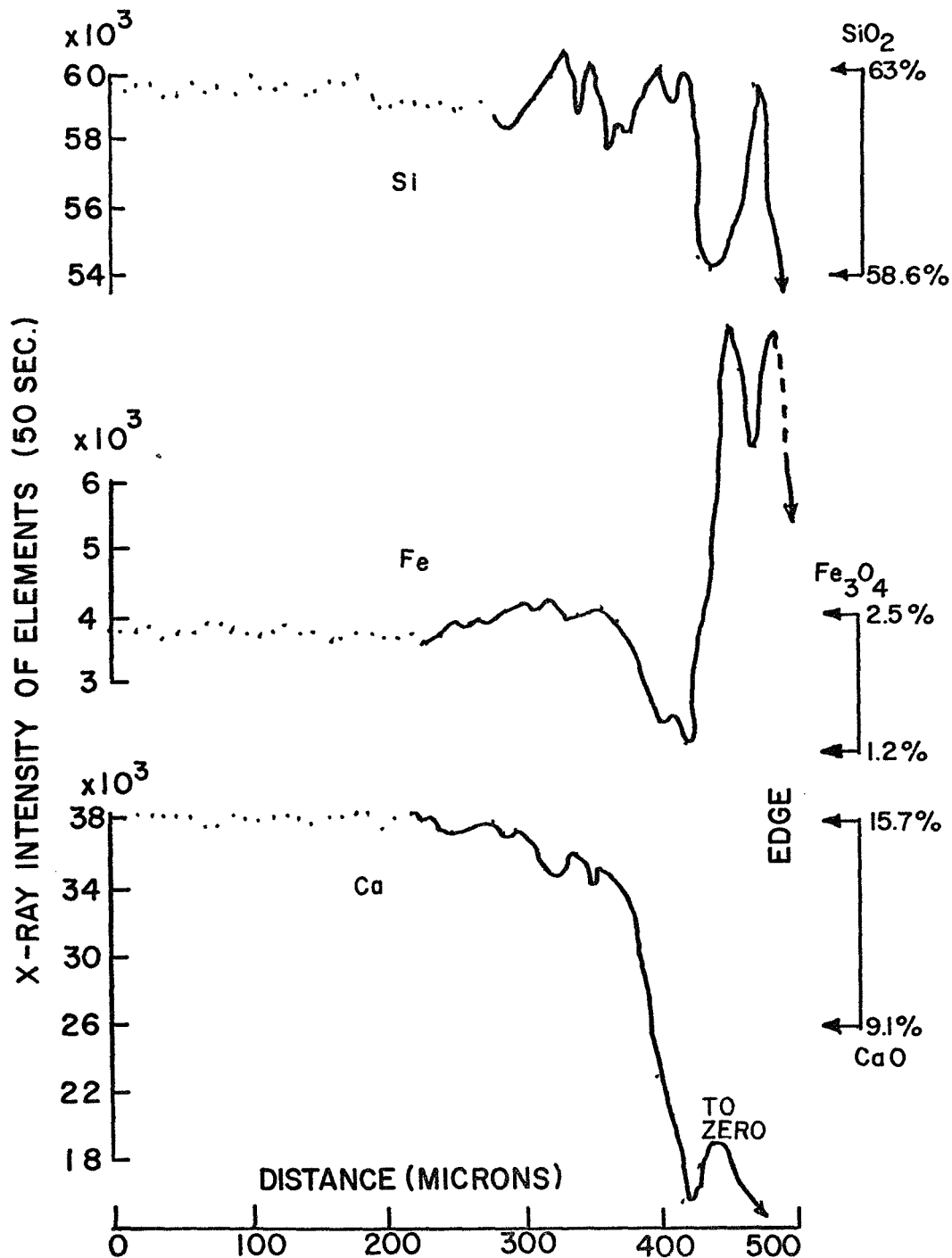


FIG. 28: NUCLEAR EXPLOSION GLASS (NEAR THE EDGE)
NOTE: COUNTING STATISTICS ARE SAME AS
IN FIG. 27.

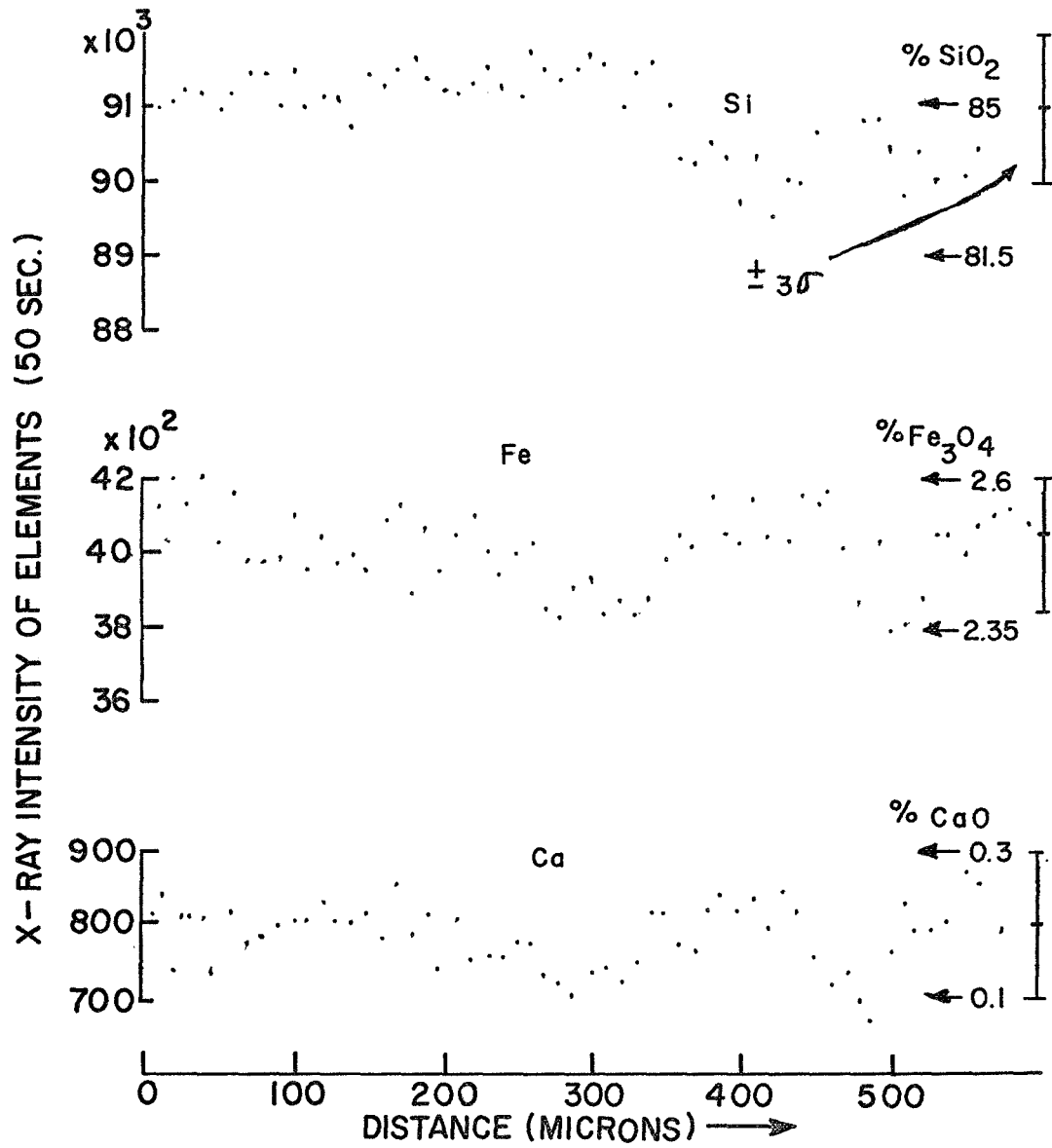
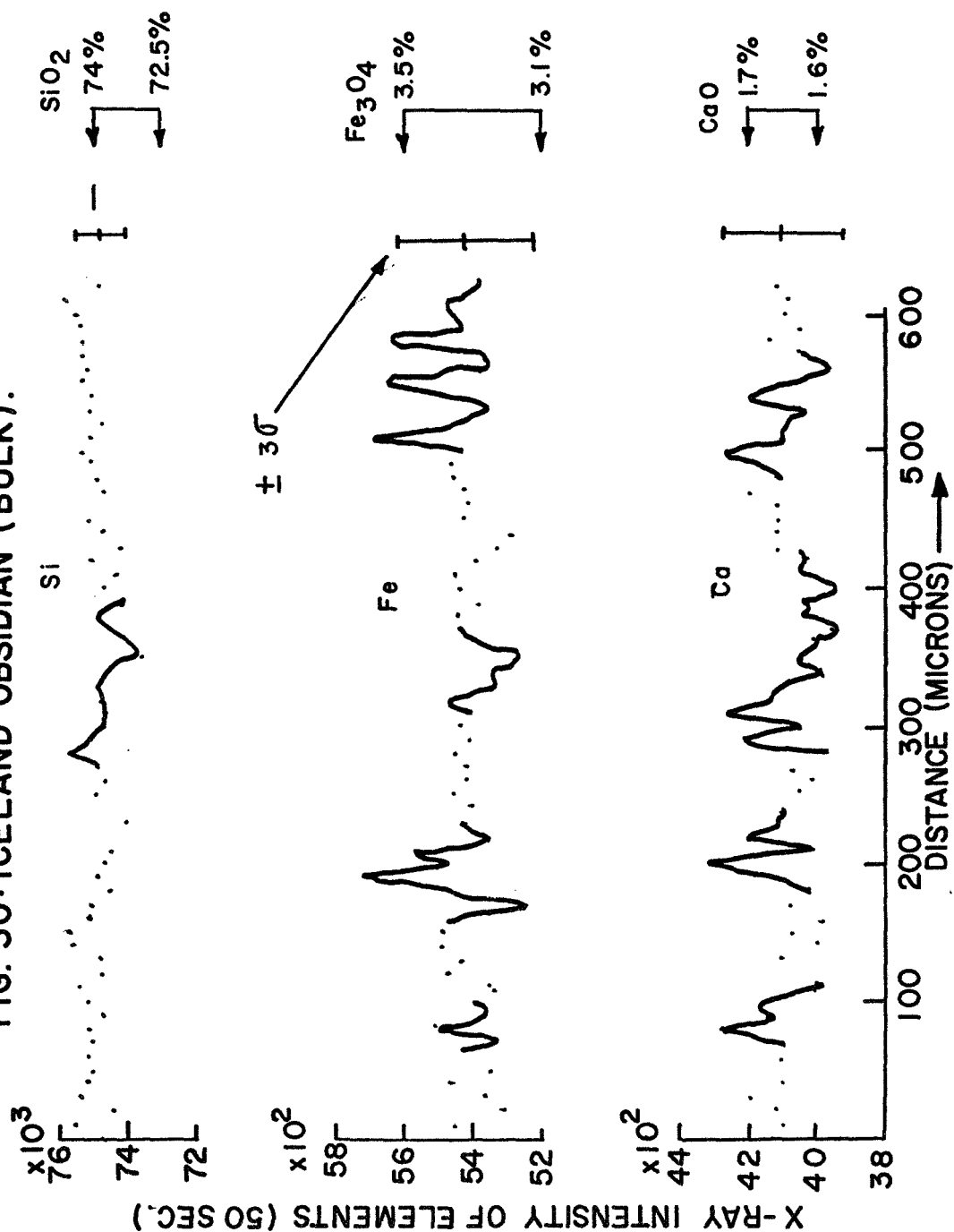


FIG. 29: AOUELLOUL GLASS (BULK).

FIG. 30: ICELAND OBSIDIAN (BULK).



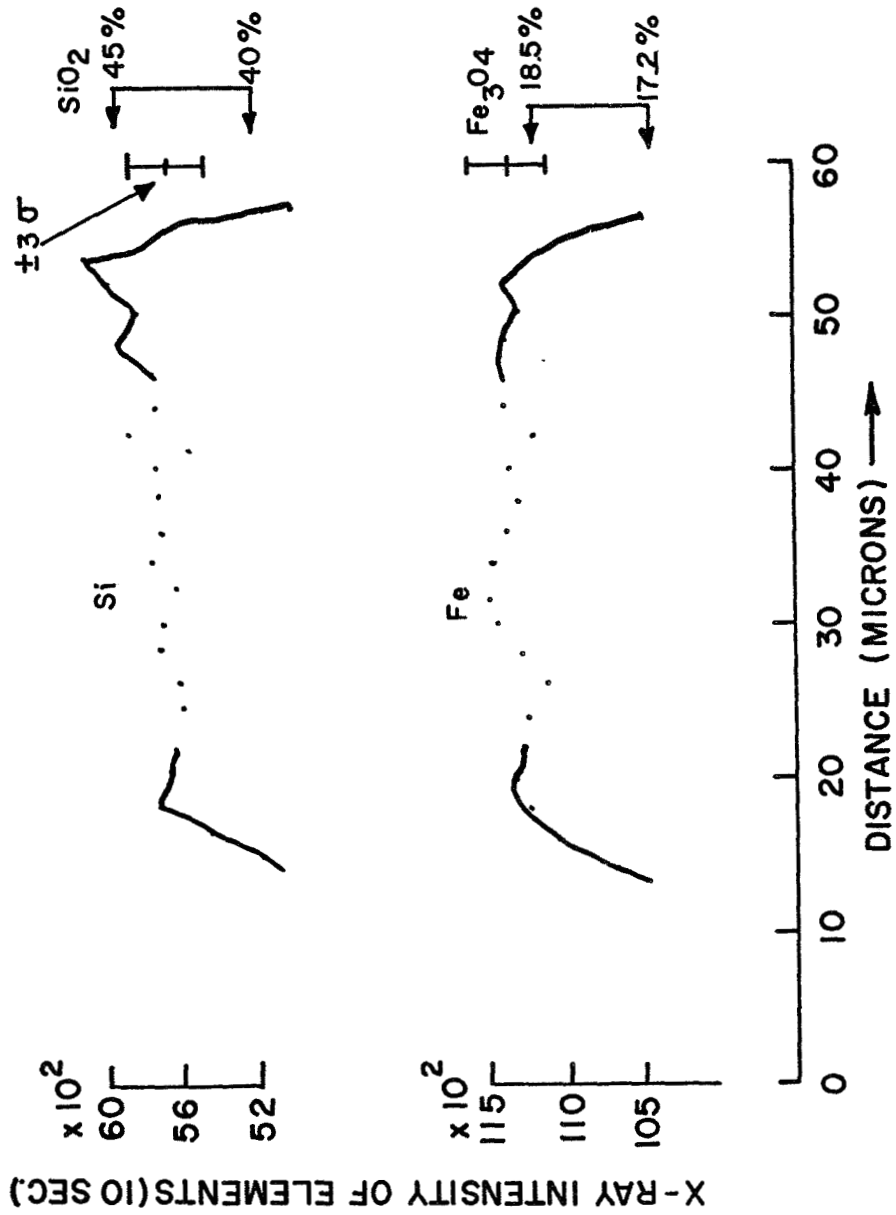


FIG. 31 : Si & Fe IN A SYNTHETIC LUNAR GLASS SPHERE (ACROSS A DIAMETER).

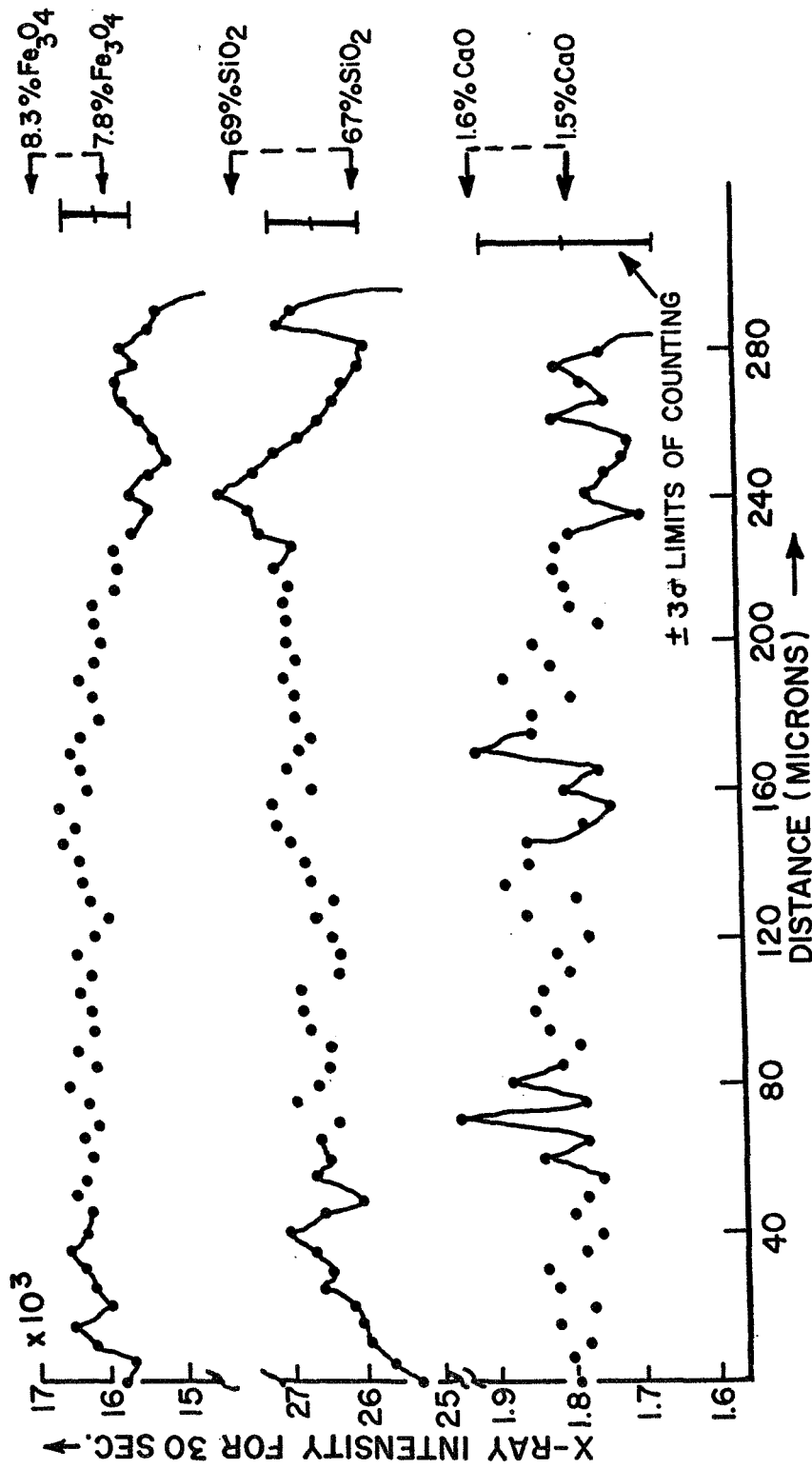


FIG. 32: DISTRIBUTION OF Fe, Si AND Ca IN A 275 μ DIAMETER IVORY COAST MICROTEKTITE SPHERULE (TRACE ACROSS A DIAMETER).

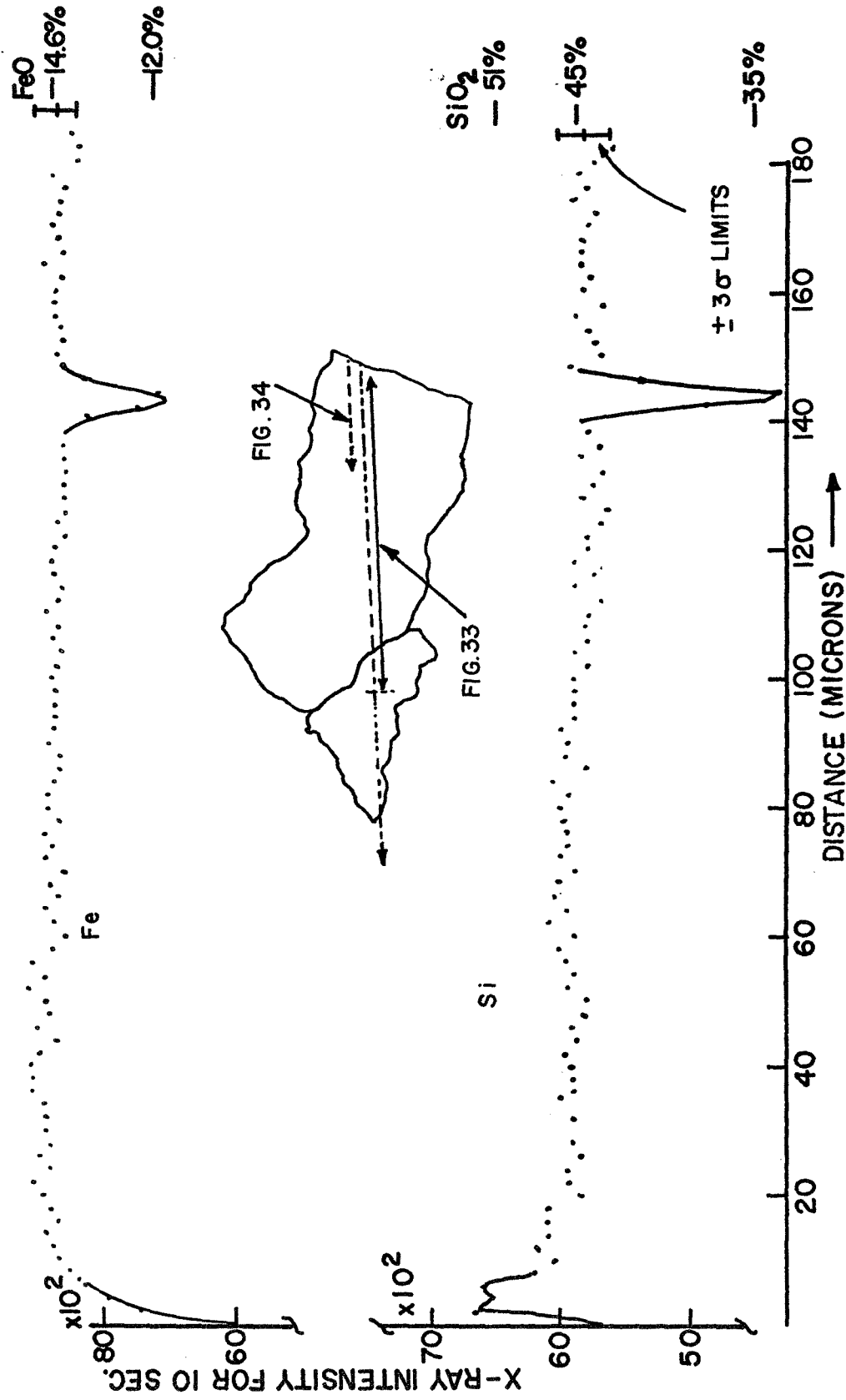


FIG. 33: APOLLO XII GLASS FRAGMENT #2.

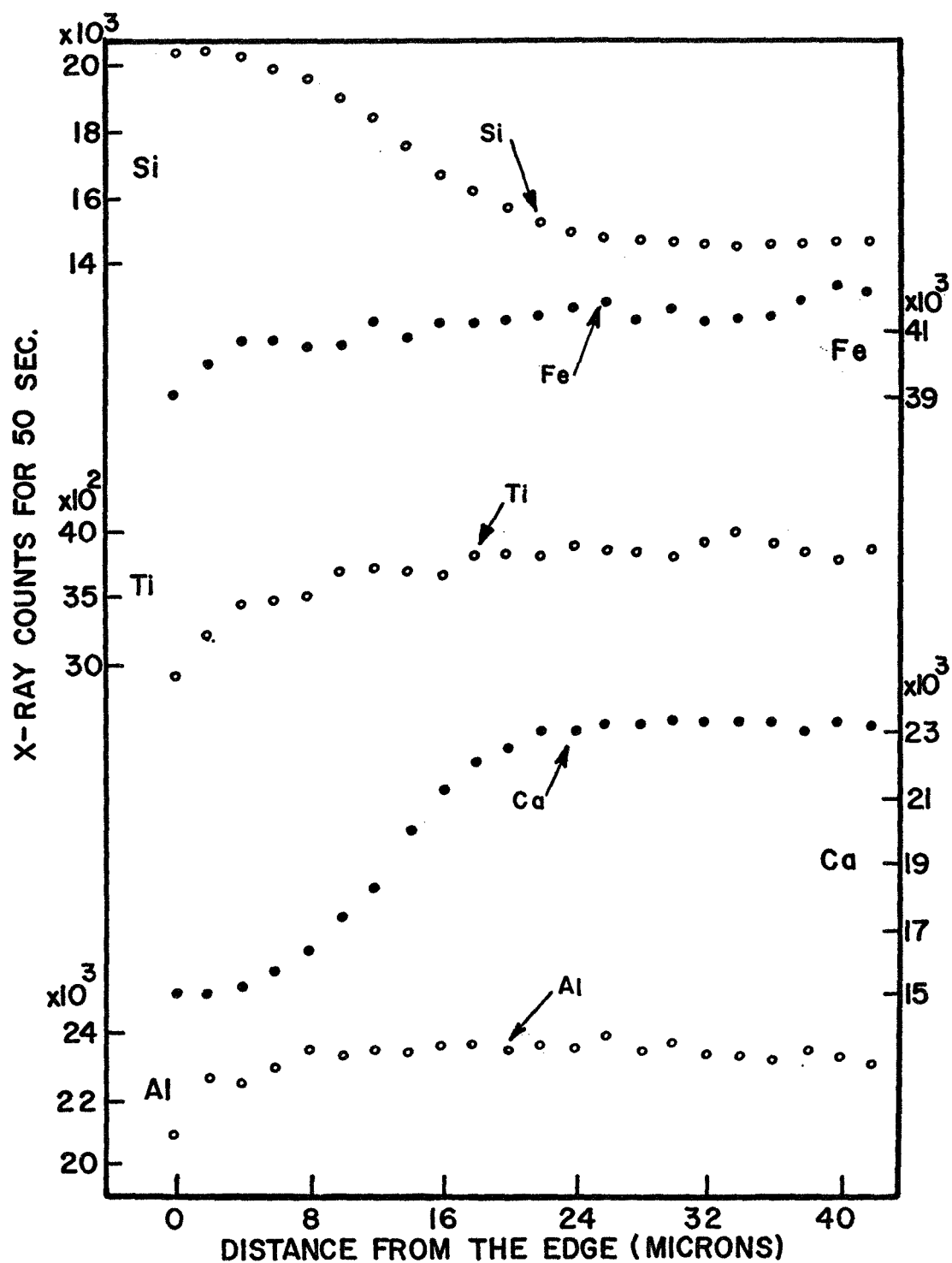


FIG. 34: VARIATION OF Si, Fe, Ti, Ca & Al IN
FRAGMENT #2 FROM THE SEA OF STORMS.

from an arbitrary origin. Calibration of counts to concentration was made against TA and TF glasses. These scales are also shown on each plot. The $\pm 3\sigma$ limits of counting statistics are also shown.

Both traces in moldavite (pale green, ~2 cm diameter disc, 4 mm thick) show significant fluctuations in all three elements. The edge (shown on Figure 26) appears to be nearly pure SiO_2 . This may be due to differential weathering which left a silica rich matrix⁽¹⁰⁵⁾.

The Muong Nong tektite (a 4mm thick x 2" long x 1" wide section, greyish-black color) appears to be the most inhomogeneous sample. The specimen shows presence of bubbles and lechatelierite particles. The latter are as big as 200 μ (or even bigger) and are virtually 100% SiO_2 .

The nuclear explosion glass (an ellipsoid, major axis ~4 mm and minor axis ~2mm) contains the least amount of SiO_2 and as high as 13% CaO. Such a glass has characteristics of a soft glass⁽¹⁰⁶⁾ and; hence, may be expected to homogenize more rapidly compared to a tektite composition. The traverse in the bulk of the specimen shows little variation of elements. However, the second trace near the edge (Figure 28) shows large magnitude fluctuations in all the three elements.

The specimen of auelluol glass (dirty brown, 1 cm size chunk) has the highest SiO_2 content (~86%). The specimen contains visible inclusions, presumably of lechatelierite⁽¹⁰⁷⁾. The present trace, however,

shows small magnitude inhomogeneities.

The iceland obsidian (a piece cut out from a 2" size chunk, dark greyish black) was analyzed with a line probe since a stationary probe revealed some indications of concentration changes⁽⁷²⁾. The specimen shows some correlated variations but the magnitude is within the $\pm 3\sigma$ limits.

Analysis of a 275 μ diameter, light brown ivory coast microtektite indicates the presence of Fe and Si inhomogeneities near the surface. The synthesized sphere (60 μ diameter, flame spray spherulized) corresponding to lunar glass composition from Apollo XI site shows small scale fluctuations only.

Lunar glass specimens appear to have varying homogeneity. One of the chips (200 μ longest dimension) appeared to have a good level of homogeneity within the bulk (Figure 33). However, the specimen had large concentration variations at one edge (Figure 34). Particularly noticeable are the negative correlation between Si and Ca and the positive correlation between Ti and Fe.

CHAPTER 10

MEASUREMENT OF EFFECTIVE BINARY DIFFUSION COEFFICIENTS OF IRON AND SILICON

"It is well to treasure the memories of past misfortunes; they constitute our bank of fortitude."

-- Eric Hoffer

§10.1 THE GLASSES:

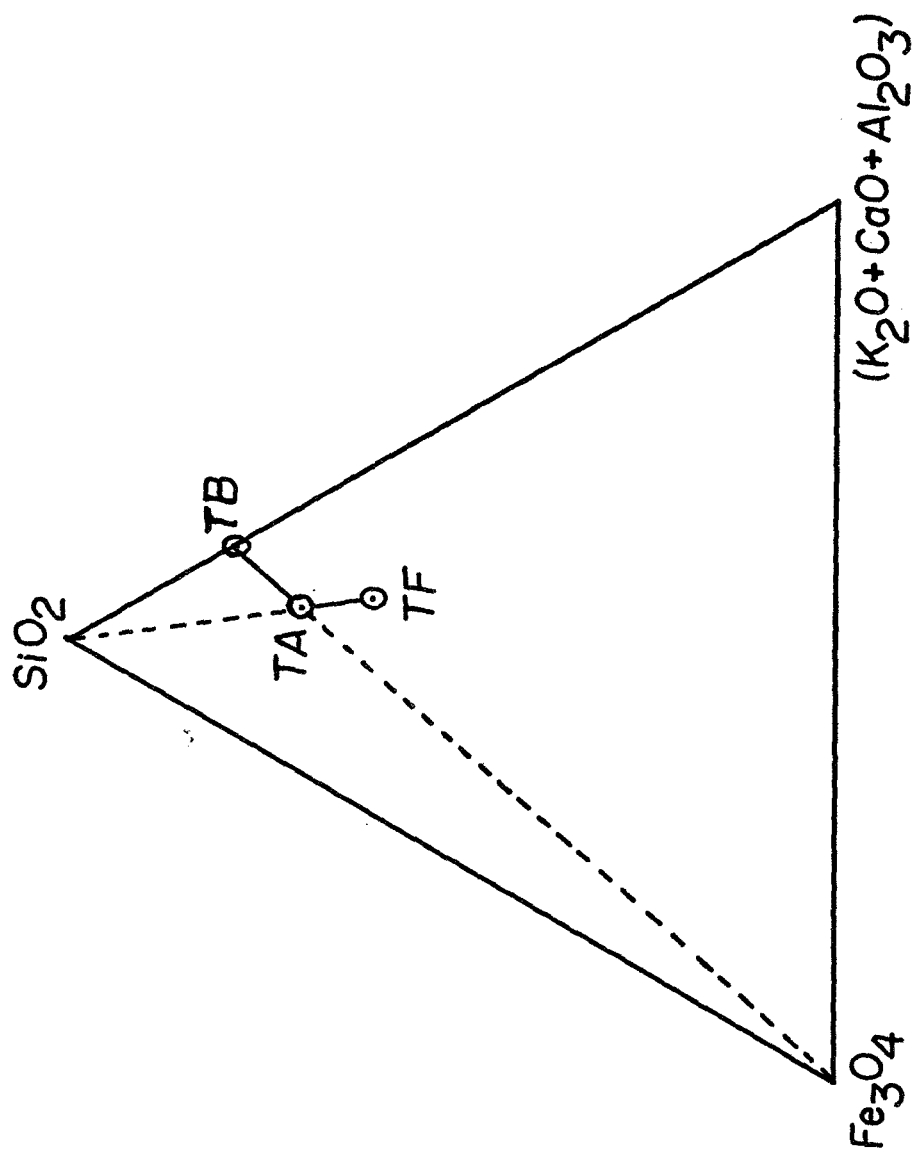
Shown in Table 8 are the compositions of glasses TA, TB and TF as calculated from the batch composition. Glass TA, which has already been mentioned in Chapter 9, is the simplified representation of the Thailand tektite eliminating all minor constituents. Glass TB is depleted in Fe and this depletion is made up proportionately by the rest of the constituents. Glass TF has some of its silicon replaced by others. On a pseudo-ternary space, shown in Figure 35, the locations of TA, TB, TF are such that the line TB-TA points towards pure Fe_3O_4 and TF-TA towards pure SiO_2 . The reasons for this have already been explained in Part I, Section 2.9.

Batches, each weighing 600 g made from analytical reagents, corresponding to each composition were thoroughly mixed and melted at 1550°C in air in a fused silica crucible inside a globar furnace for at least 60 hours.

TABLE 8: CHEMICAL COMPOSITION OF SYNTHETIC
TEKTITES FOR DIFFUSION STUDIES
(Wt. %)

	<u>TA</u>	<u>TB</u>	<u>TF</u>
SiO ₂	72.0	76.2	67.0
Al ₂ O ₃	13.0	13.75	15.32
Fe ₃ O ₄	5.5	---	6.48
K ₂ O	4.0	4.25	4.72
Ca O	5.5	5.80	6.48

FIG. 35: PSEUDO - TERNARY COMPOSITION SPACE FOR TEKTITES.



After this melting, glass TF had bubbles smaller than 1/4 mm to the extent of about 10 bubbles per cm^3 in the bulk and, hence, was accepted. Contamination from the crucible material was estimated to be negligible into the bulk, since significant attack of the crucible walls was not observed.

The separation between the crucible wall and glasses TA and TB was even sharper. However, both these glasses contained many bubbles. Broken pieces of each glass were then placed inside a calcia-stabilized-zirconia crucible and fired in a gas fired kiln with a soak time of ~4 hours at 1800°C.*

At the end of this melting, glass TA was completely bubble-free. Some attack on the crucible was observed. And, hence, glass pieces from the bulk of the melt only were accepted.

Glass TB still had bubbles and, yet, another melting at 1800°C could not rid it of bubbles completely. The abundance of these bubbles (up to 1/4 mm size) was about 25 per cm^3 in the bulk.

It was used as such.

§10.2 DIFFUSION EXPERIMENTS

Cylinders (0.8 cm in diameter) were core-drilled from

* The author is thankful to Mr. Alan King of Zirconium Corporation of America for carrying out these meltings.

each of the glasses. Each cylinder was ground flat perpendicular to its axis to obtain disks of about 3-1/2 mm thickness. After the flat faces of these disks were polished using 3 μ diamond paste, a diffusion couple was made by placing two dissimilar disks in contact.

Figure 36 shows the diffusion assembly. The housing is made out of slip-cast pulverized fused silica. It is held together by platinum wires. A Pt/Pt-Rh thermocouple is inserted in the housing.

Diffusion anneals were carried out by placing the assembly in air inside a globar furnace. Temperature was controlled to within $\pm 10^\circ\text{C}$.

§10.3 ELECTRON PROBE ANALYSES

Samples were cut along the cylindrical axes. They were mounted in "quick mount" cold mounting media such that the flat surface was exposed. These mounted samples were polished with 3 μ diamond paste.

After most diffusion anneals at high temperatures, the interface which was visible either due to color or due to a reflection contrast, was not very straight. Microhardness indentations were placed at the interface, wherever it was straight within 5 μ over a 100 μ length.

The samples were shadowed with 300 $\text{\AA}$ aluminum film and

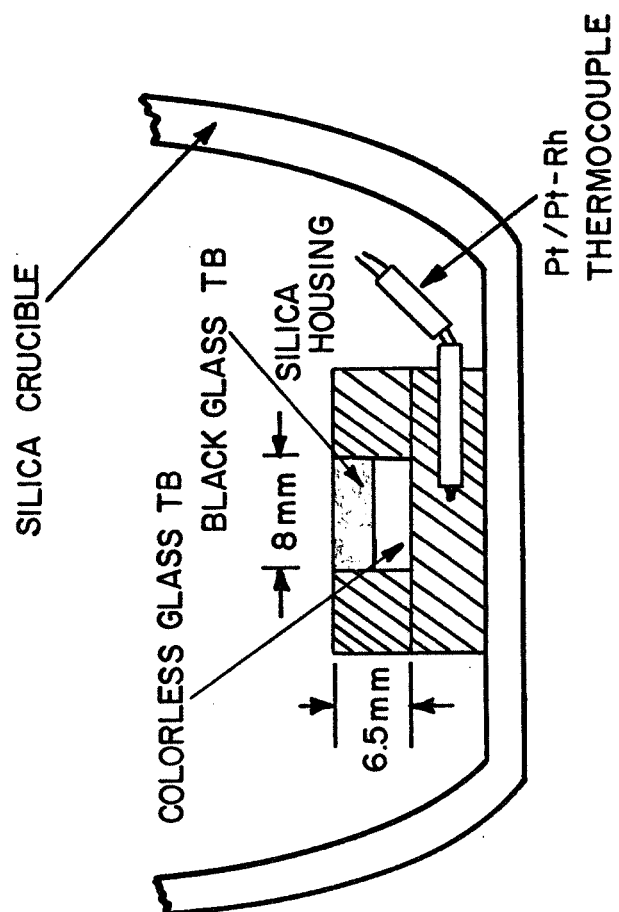


FIG.36: TEKTITES DIFFUSION ASSEMBLY.

placed in the microprobe. Analysis of Fe and Si were carried out simultaneously in each sample (regardless of whether it was a TF-TA couple or TA-TB couple), using a point probe (2 μ diameter) at 25 kv. The instrument was used in an automatic mode described in section 4.6 with steps of 5 μ or 10 μ normal to the interface.

No attempt to convert the counts to concentration was made since the calculations of EBDC described below do not require this conversion.

§10.4 CALCULATIONS AND RESULTS

A typical plot of X-ray counts of Fe versus distant y in microns from the interface is shown in Figure 37.

For a unidirectional semi-infinite couple, with the initial conditions

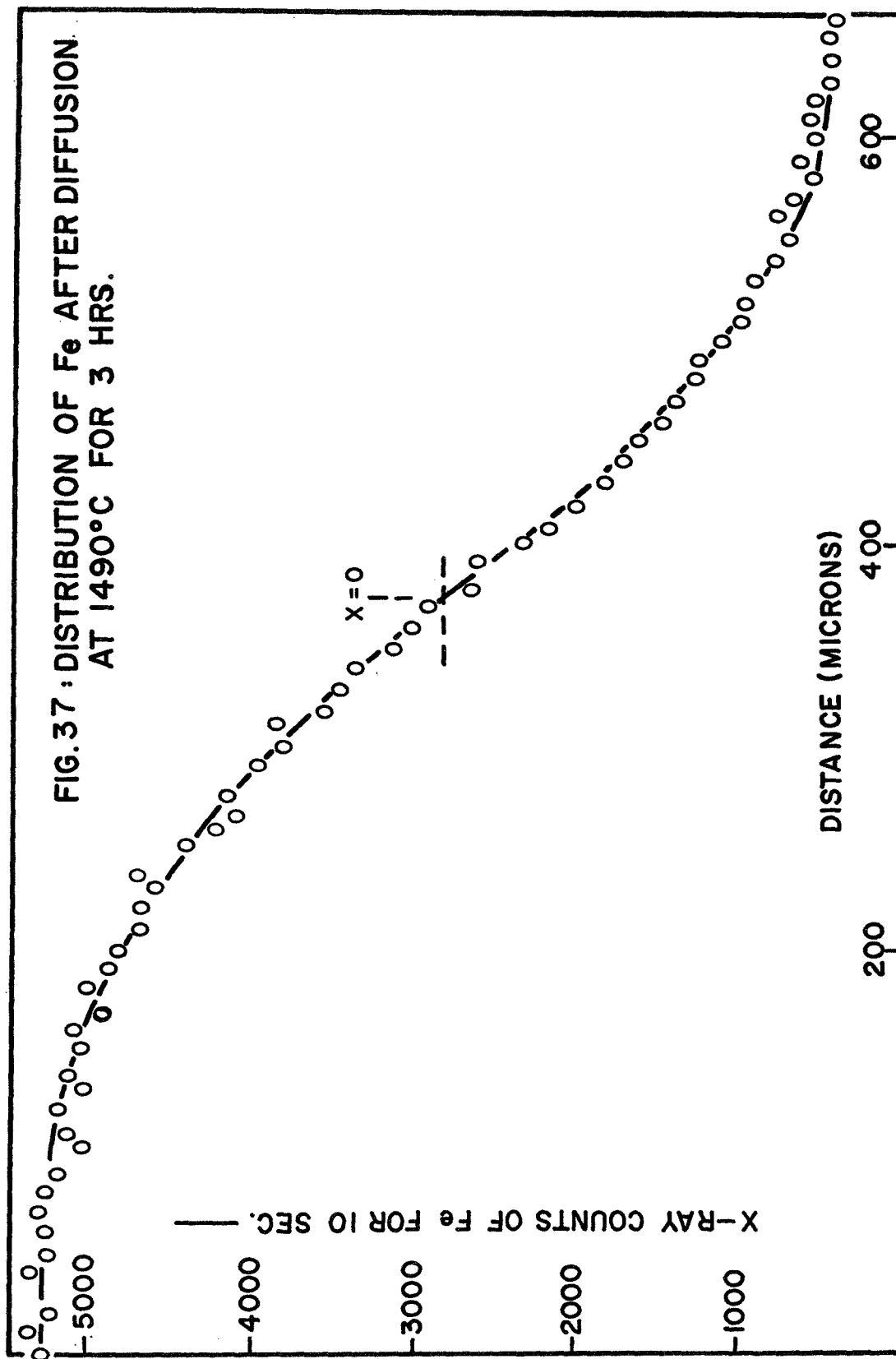
$$\left. \begin{aligned} W_i &= W_i^P \quad \text{for } y < 0 \\ &= W_i^Q \quad \text{for } y > 0 \end{aligned} \right\} \quad t = 0$$

and the boundary conditions

$$\left. \begin{aligned} W_i &= W_i^P \quad \text{for } y = -\infty \\ &= W_i^Q \quad \text{for } y = +\infty \end{aligned} \right\} \quad t > 0$$

where W_i is the intensity of the characteristic radiation of the element i , the non-steady state solution of the diffusion equation (equation 44, part 1) is

$$W_i - \left(\frac{W_i^P + W_i^Q}{2} \right) = \left(\frac{W_i^Q - W_i^P}{2} \right) [1 + \operatorname{erf} (y/2 \sqrt{(D_{iM}t)})] \quad (81)$$



where D_{iM} is the EBDC of i and is assumed constant.

The above equation enables us to calculate D_{FeM} and D_{SiM} from the various experiments. Table 9 lists the various experiments performed. The results for D_{FeM} appear to be unaffected by the presence of bubbles in the glass TB because constant values of the EBDC were obtained from the experiments conducted at the same temperature for various lengths of time. This condition of Fickian diffusion has already been discussed in part 1, section 2.7.

A plot of the logarithm of D_{FeM} and D_{SiM} against the reciprocal of absolute temperature is shown in Figure 38. Although there is no reason to expect an Arrhenius behavior for any of the D_{iM} (part 1, section 2.9), all data of D_{FeM} and D_{SiM} appear to fall on straight lines with an apparent activation energy of 64 kcal/mol. The absolute magnitude of D_{FeM} is no more than three times the magnitude of D_{SiM} .

TABLE 9

EXPERIMENTS CONDUCTED TO MEASURE EBDC OF Fe
(TA/TB COUPLES) AND Si (TA/TF COUPLES)

Experiment	Temperature °C	Diffusion Time (Hours)	D_{iM} $10^{-10} \text{ cm}^2/\text{sec.}$
TA/TB	1160	6.15	1
TA/TB	1160	20.0	0.75
TA/TB	1160	67.5	1.4
TA/TB	1260	5.0	6.5
TA/TB	1260	19.5	5.1
TA/TB	1370	4.5	12.0
TA/TB	1370	9.5	12.3
TA/TB	1490	3.0	75
TA/TB	1490	3.0	80
TA/TF	1290	6.5	3.4
TA/TF	1300	11.75	3.0
TA/TF	1320	4.3	3.3
TA/TF	1375	19.2	4
TA/TF	1385	9.4	4
TA/TF	1385	9.4	6.9
TA/TF	1435	3.0	20.6
TA/TF	1435	7.2	11.5

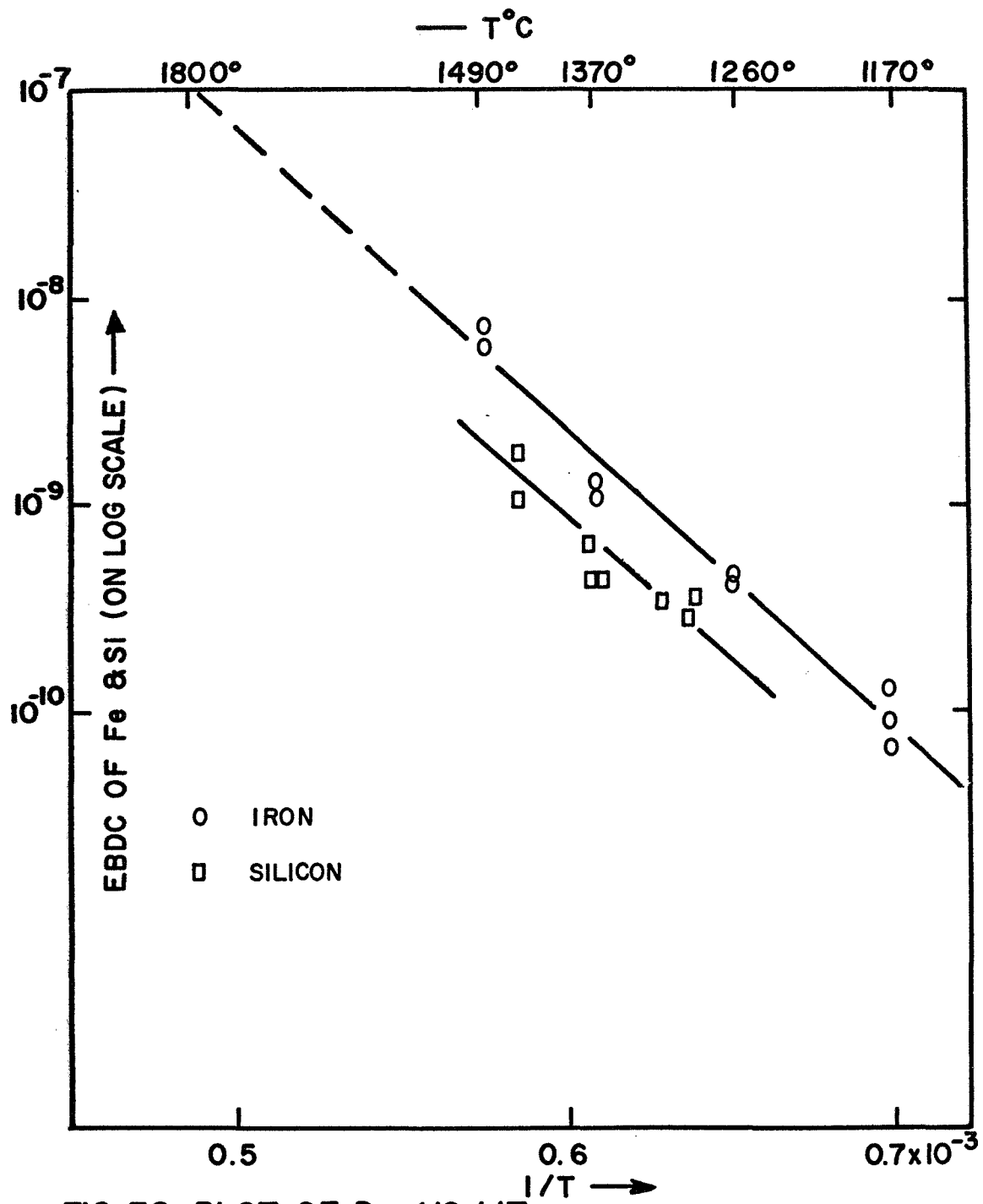


FIG. 38: PLOT OF D_{im} VS $1/T$.

CHAPTER 11

KINETICS OF HOMOGENIZATION OF A HYPOTHETICAL ROCK

"E pur si muove . . . (Nevertheless it does move . . .)"

-- Galileo Galilei

We consider below a simple hypothetical model of a rock assumed to be the parent mineral aggregate source of tektites. We will use mathematical diffusion theory to study the homogenization of this rock after a thermal treatment is applied to it.

The model rock is a unidirectional laminated structure with a periodic variation of an element, M.

Consider the laminated structure of inhomogeneity of the element, M, shown in Figure 39. Each M-rich lamina is of thickness $2\delta_1$, and the M-depleted lamina is of thickness $2\delta_2$. The wavelength of fluctuation is $\lambda = 2(\delta_1 + \delta_2)$. Assume that the concentration level of M in all the M-rich lamina is X_{MO} and in all the M-depleted lamina is zero at time, $t = 0$.

The concentration, X_M at $y = 0$ and $t > 0$ is given by the equation below⁽¹⁰⁸⁾

$$X_M = (1/2)X_{MO} \sum_{n=-\infty}^{\infty} [\text{erf} \{(\delta_1 + 2n(\delta_1 + \delta_2))/2(Dt)_{\text{eff}}^{1/2}\} + \text{erf} \{(\delta_1 - 2n(\delta_1 + \delta_2))/2(Dt)_{\text{eff}}^{1/2}\}]$$

(82)

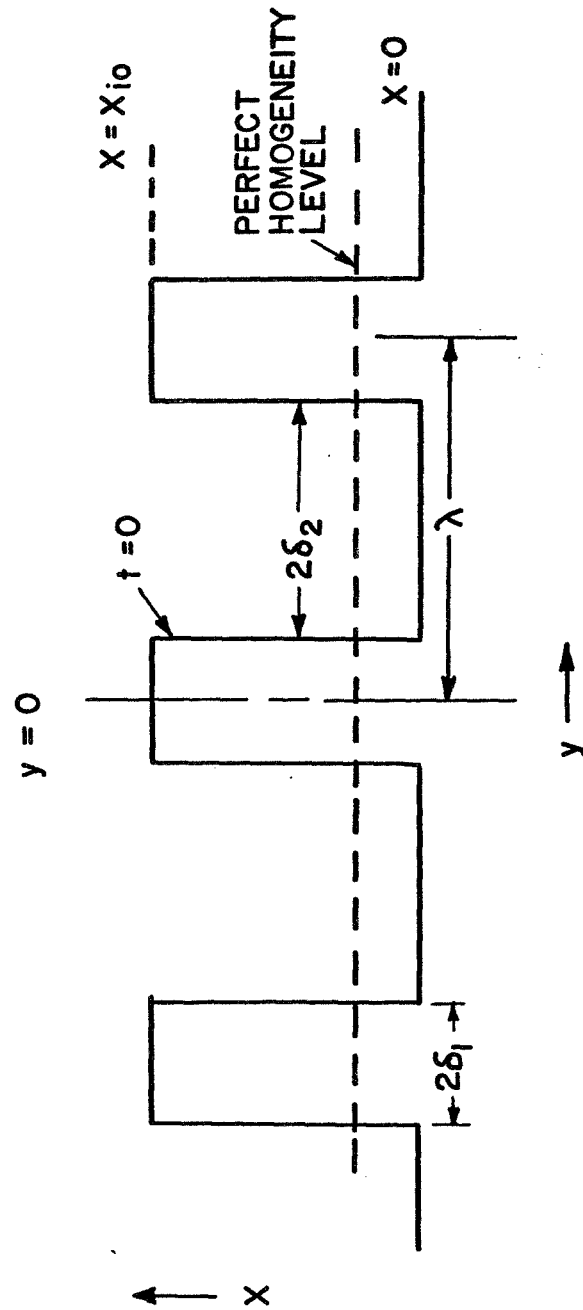


FIG.39 : A HYPOTHETICAL MINERAL COMPOSITE.

where

$$\begin{aligned} (Dt)_{\text{eff}} &= \text{EBDC} - \text{time product of } M \\ &= \int D_{(T)} (dt/dT) dT \text{ for } M \text{ thermal cycle} \end{aligned} \quad (83)$$

$D_{(T)}$ being the EBDC of M at temperature, T .

Equation (82) can be solved for various ratios of δ_1/δ_2 . It is possible to show that for large times, i.e., when $(Dt)_{\text{eff}}/\lambda^2$ exceeds 0.1, the solution behaves as if all the lamina were of equal thickness ($=\lambda/2$).

When $\delta_1 = \delta_2$, a more convenient form of equation (82) for long times is⁽¹⁰⁹⁾

$$\frac{X_M - \bar{X}_M}{X_{MO} - \bar{X}_M} \approx \frac{4}{\pi} \exp [-4 \pi^2 (Dt)_{\text{eff}}/\lambda^2] \quad (84)$$

The left hand side of equation (84) is just the fractional change in concentration at $y=0$ above the mean.

No significant inhomogeneity of M is detected by the electron microprobe when

$$\frac{X_M - \bar{X}_M}{X_{MO} - \bar{X}_M} \approx 0.01 \quad (85)$$

The figure 0.01 corresponds to the 95% level of confidence limit, expressed as a fraction of the mean, arrived at in section 9.1.4.

Equation (84) corresponds to

$$(Dt)_{\text{eff}}/\lambda^2 \approx 0.12$$

If $(X_M - \bar{X}_M)/(X_{MO} - \bar{X}_M)$ were 0.0005, we get $(Dt)_{\text{eff}}/\lambda^2 \approx 0.2$.

It is evident that when $(Dt)_{\text{eff}}/\lambda^2$ exceeds 0.2, we can no longer detect the occurrence of any further homogenization using the electron microprobe.

The above calculation assumed that the wavelength of M-inhomogeneity in the parent rock is a constant value. Rocks in reality are rarely as periodic as of Figure 39. Introduction of a second wavelength which is longer requires more time for homogenization. One such calculation is shown in Appendix 5. Also shown in this appendix is a calculation of homogenization of a 3-dimensional hexagonal structure with spherical particles rich in element M, embedded in M-depleted matrix. It is shown that the introduction of 3-dimensional diffusion does not greatly affect the results of homogenization times obtained for the unidirectional laminated structure. The error, perhaps, is no more than 20% at large times.

CHAPTER 12

DISCUSSION

"I think that in the discussion of natural problems we ought to begin not with the Scriptures, but with experiments and demonstrations."

-- Galileo Galilei

It has been demonstrated in section 9.1.4 and 9.2.2 that the 2172 tektite is one of the more homogeneous glasses examined. It does not have any features arising from shock induced lattice distortion which, otherwise, seem to be present in the lunar fragments in the form of correlated distribution of elements. Except for a single 60 μ wide peak with slight enrichment of iron, there are no signs of any crystalline inclusions or bubbles as are to a large degree in the Muong Nong tektite and to a lesser extent, in aouelloul glass.

If the age data on Thailand tektites is correct, then the lack of large scale weathering indicates that these tektite glasses have a high chemical durability. The resistance to attack was also noted while melting batches of duplicate composition (page 106). The high chemical resistivity is generally associated with hard glasses and the ones which are difficult to melt. While the microtektites,

which have been preserved under ocean beds for ~ 0.7 m.y. as well, appear more resistant, the 2172 tektite seems better in homogeneity.

Although the 2172 tektite is more homogeneous than the nuclear explosion glass which is a soft glass, it is not justifiable to directly compare the heats associated with the formation events of the two glasses since the exact recovery area of the nuclear explosion glass is not known. Certainly a volcanic event is capable of producing large chunks of relatively homogeneous glass such as the Iceland obsidian. Keeping in mind that aouelloul glass has much higher silica content, we can admit a meteoritic impact as another possibility which might have led to the formation of tektites.

To estimate the thermal history associated with the tektite formation, we use the premise (section 9.1.4) that though submillimeter wavelength composition fluctuations might exist, the 2172 tektite can be considered essentially homogeneous on a micron scale. The essential condition that the occurrence of any further homogeneity is not detected, is

$$(Dt)_{\text{eff}}/\lambda^2 > 0.2$$

The above equation gives us the values of minimum $(Dt)_{\text{eff}}$ required to homogenize rocks with various particle sizes. Since measurements of the D_{im} for Fe and Si as a function of temperature have been made (Chapter 10), it is possible to sketch arbitrary

thermal histories which would correspond to a given minimum value of $(Dt)_{\text{eff}}$. And as an example, Figure 40 is such a sketch.

After the heat producing event at $t = 0$, the temperature quickly rises to about 1800°C and then cools down. Significant diffusion occurs only within the shaded area. The $\int D_{\text{eff}} \left(\frac{dt}{dT}\right) dT$ of the shaded area is $\sim 3.2 \times 10^{-6} \text{ cm}^2$ which is sufficient to homogenize iron fluctuation wavelength of 40μ .

Table 10 is presented to permit additional insight into the thermal history necessary to homogenize iron fluctuations of various wavelengths. The last two columns give the minimum times for homogenizations at 1550°C and 1800°C if the glass were heated to that temperature instantaneously and quenched after homogenization.

For a fine particle size initially, the homogenization times are of the order of seconds, but quickly turn into minutes as the particle size is increased. It should also be recognized that homogenization of silicon fluctuations of same wavelengths would require three times longer soaking.

The above calculation for iron homogenization is based upon two main assumptions:

- (i) All the iron comes from the mineral itself and not from the meteorite, if the meteoritic impact was the cause of tektite formation.
- (ii) EBDC follows Arrhenius relation up to at least 1800°C .

The first of these assumptions seems likely because the

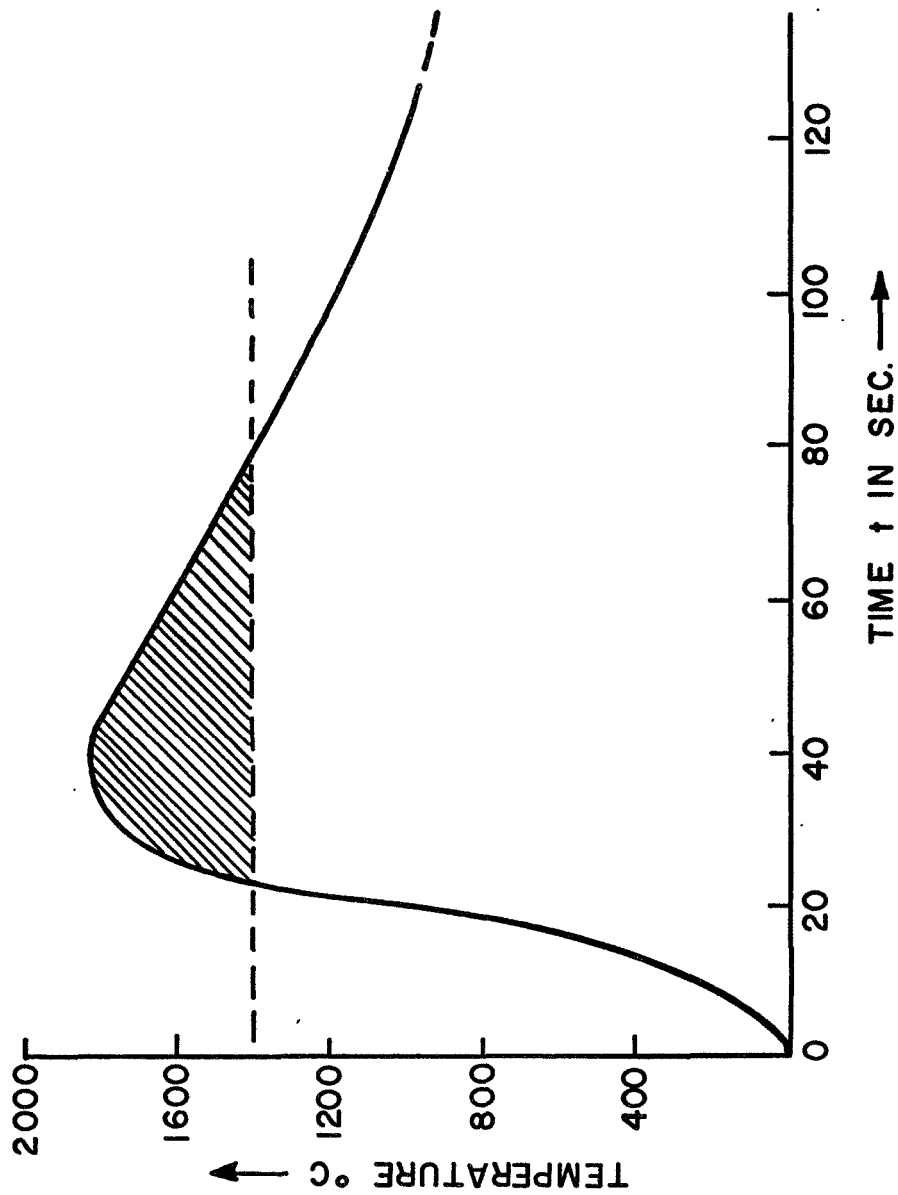


FIG. 40: A POSSIBLE THERMAL HISTORY FOR HOMOGENIZATION OF
A MINERAL COMPOSITE WITH $\lambda = 40\mu$.

TABLE 10

HOMOGENIZATION TIMES AT 1550°C and 1800°C

FOR VARIOUS PARTICLE SIZES ($\lambda/2$)

λ , microns	$(Dt)_{\text{eff}}$, cm^2	$t_{1550^\circ\text{C}}$	$t_{1800^\circ\text{C}}$
40	3.2×10^{-6}	320 sec.	32 sec.
100	0.2×10^{-4}	33 min.	3.3 min.
400	3.2×10^{-4}	9 hr.	0.9 hr.

transport of iron through the distances of the order of centimeters for large tektites is very unlikely at conceivable temperatures. Another reason is the occurrence of low Ni content in tektites. Nickel ought to diffuse as fast as iron and the chances of all the tektites being produced by no nickel containing meteorites are very slim.

Theoretical basis for expecting Arrhenius behavior of EBDC follows arguments given for the temperature dependence of the interdiffusion coefficients in §2.9. The results shown in Figure 38 seem to suggest that the Arrhenius rate equation gives a reasonable description of the temperature dependence of EBDC.

A simple calculation using the same Arrhenius equation shows that the extent of diffusive mixing over 0.7 million years under normal atmospheric temperatures on land corresponds to a thermal history of $\sim 3 \times 10^{-32} \text{ cm}^2$. Thus, for all practical purposes, the homogeneity of the Thailand tektite must be associated with the melting event or events.

If Henbury subgreywackes were to be the parent source, then the 1/4 mm quartz particles will require a thermal history of $\sim 1.2 \times 10^{-4} \text{ cm}^2$, i.e., an equivalent of 4 hours soak time at 1800°C. Such a thermal treatment is difficult to imagine unless the glass was produced inside the chest of a volcano where it stayed for a long time or it cooled exceedingly slowly because the surrounding atmosphere

was equally hot.

The moon is a favorable site, but more sampling needs be done to find a source with a matching composition.

CHAPTER 13

SUGGESTIONS FOR FUTURE WORK

"Genius is one per cent inspiration and ninety-nine per cent perspiration."

-- Thomas Alva Edison

Many of the conclusions arrived at in Part I could be given more support if the data on oxygen self diffusion coefficient and the thermodynamic activity coefficients in the $K_2O-SrO-SiO_2$ system were available.

The electric field intensity and other related effects calculated in Chapter 6 need experimental support. For example, an experiment could be carried out to show that there is a finite electrostatic potential difference across the diffusion couple during the process of diffusion which is time independent.

On quenching the couples the charges are "frozen." The magnitudes of charge accumulation are, perhaps, sufficient to cause some changes in the vibration spectra which could be detected.

It is clear that Part II has attempted to solve two variables: the parent source, and the thermal history, out of one piece of information, viz., the homogeneity in the as observed state.

An explicit calculation of either of the two variables, therefore, is impossible unless some other approach is used in conjunction with the present one.

Two types of experiments appear promising:

- (i) the oxidation state of iron or the dependence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio upon thermal history
- and (ii) nucleation and crystallization kinetics of iron silicate phases in tektites.

The first topic is important because it is not easy to duplicate the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in laboratory synthesized tektites and second one because crystallization readily occurs in tektites when exposed to atmosphere at temperatures in excess of $1200^{\circ}\text{C}^{(110)}$.

APPENDIX 1

THE ANALYSIS OF GLASSES

Analysis of glasses was carried out in two ways:

- (i) flame photometric determination of potassium content
- (ii) electron probe analysis of K, Sr and Si

Flame Photometric Determination of Potassium

Approximately 0.1 g. glass was accurately weighed out in a 25 ml. platinum crucible. It was moistened with 5 drops of water and then 5 mls. of 49% HF + 5 drops of conc. HCl were added to it. The crucible after gentle swirling, was placed on a hot plate. When the solution nearly evaporated a second aliquot of HF/HCl was added. Finally, the evaporation to dryness was concluded after addition of 2 drops of conc. H_2SO_4 .

The dried mass was brought into 250 mls. of solution (with water and 2.5 mls. conc. HCl).

For flame photometry, a dilution to bring the concentration level of potassium to ~ 20 ppm was found necessary.

The flame photometry was carried out by a Coleman flame photometer which was calibrated to read concentration of potassium with the help of 0, 10, 20 ppm K_2O standard solutions.

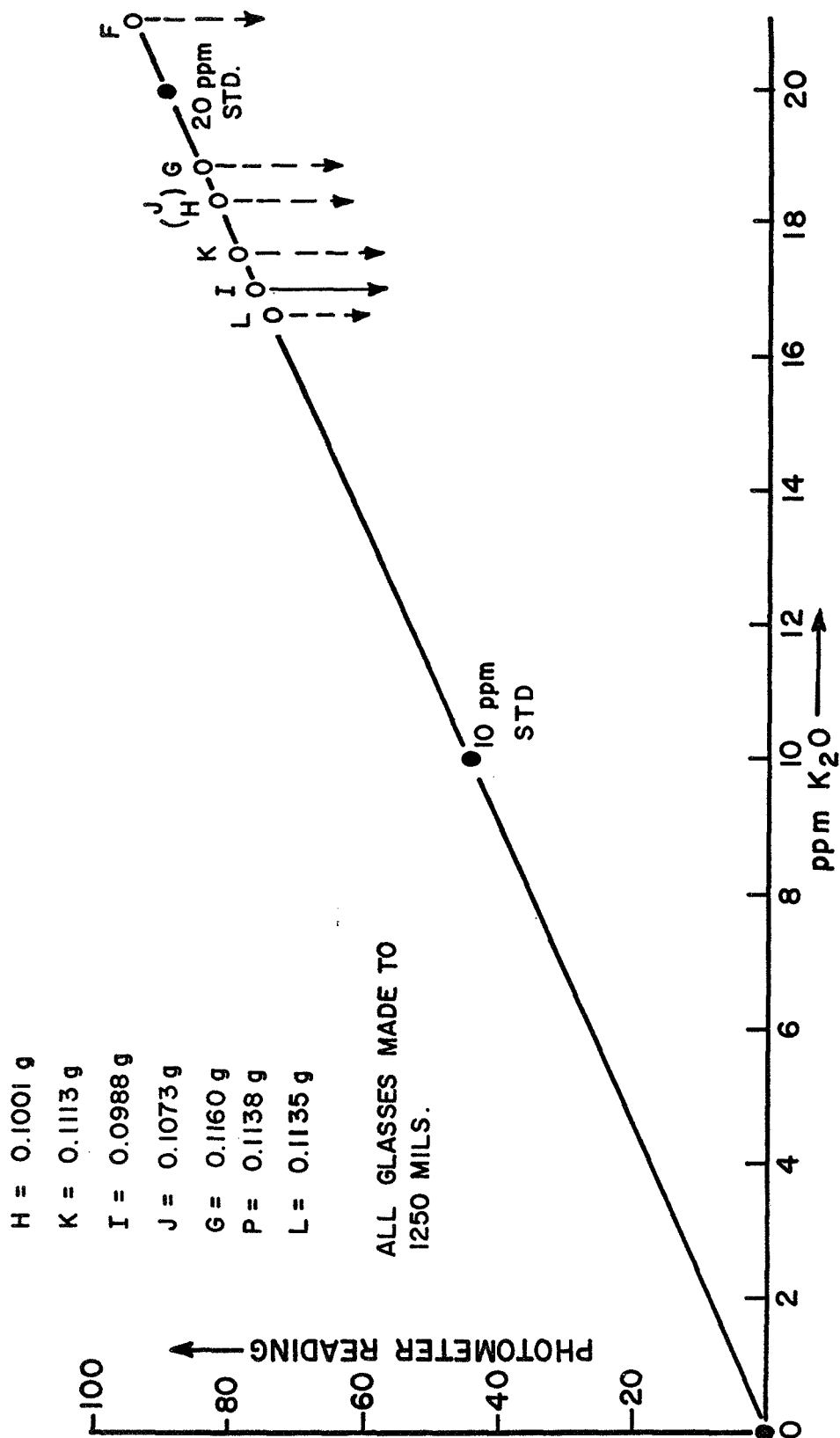


FIG. 41 : FLAME PHOTOMETER MEASUREMENTS OF K_2O IN GLASSES.

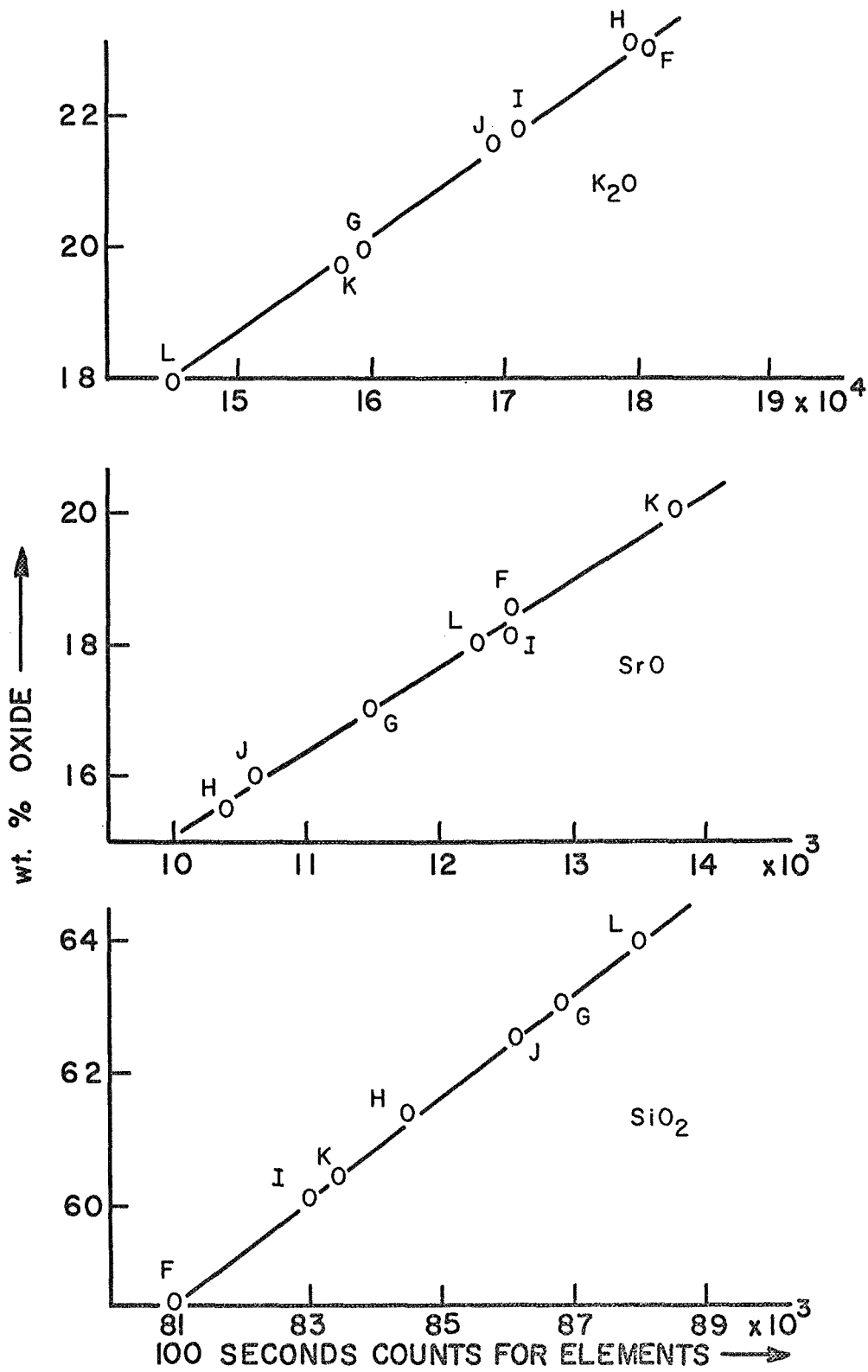


FIG.42 :ELECTRON PROBE ANALYSIS OF GLASSES.

The standard solutions and the unknown solutions were sprayed into flame individually and their corresponding characteristic emissions were noted. Figure 41 is a plot of the flame readings against chemical concentration of K_2O .

Electron Microprobe Analysis of Glasses

All glasses were ground to obtain $\sim 200\mu$ thick wafers, These wafers were cemented to each other with a heat-cement, and then sandwiched between small pieces of 125μ thick microscope cover glasses. This sandwich was then mounted in a 1" diameter mold in "quick mount" medium such that the thickness of the sandwich was exposed. The mount was ground flat, polished with 3μ diamond, shadowed with $\sim 300 \text{ \AA}$ thick aluminum film and placed in the microprobe. Analysis was carried out in the standard mode (§ 4.6) with a line probe and 100 sec. counts.

In Figure 42 is shown a plot of counts for each oxide against the chemical composition as determined by the batch formula.

It is shown that the data for each oxide falls on straight lines. This justifies the assumption that for each oxide, the x-ray counts are linearly related to the chemical concentration within the range of compositions investigated.

Coupled with the flame photometric determination of potassium, the chemical composition of glasses is estimated to be what is shown in table below.

TABLE 11

CHEMICAL COMPOSITION OF GLASSES (wt. %) *

Glass	K ₂ O	SrO	SiO ₂	Total
H	22.8 (23.1)	15.6 (15.5)	61.3 (61.4)	99.7
K	19.8 (19.7)	20.0 (20.0)	60.5 (60.3)	100.3
I	21.6 (21.8)	18.4 (18.2)	60.0 (60.0)	100.0
J	21.35 (21.5)	15.9 (16.0)	62.6 (62.5)	99.95
G	20.1 (20.0)	17.0 (17.0)	63.1 (63.0)	100.2
F	23.0 (23.0)	18.4 (18.5)	58.5 (58.5)	99.9
L	18.15 (18.0)	18.0 (18.0)	64.1 (64.0)	100.25

* Figures in parentheses represent calculated compositions of the batch.

APPENDIX 2

GRAPHICAL CALCULATION OF $[D_{ij}]$

The assumption of linearity between x-ray intensity, W_i , and the concentration X_i , i.e., the equation $X_i = a_i W_i + b_i$ where a_i and b_i are constants, enables us to rewrite equation (62) as

$$-(1/2t) \int_{Y_K}^{Y_L} \int_{(W_i)_\infty}^{W_i} A_i y dW_i dy = \sum_{j=1}^2 [(W_j)_K - (W_j)_L] D_{ij} a_j \quad (A2-1)$$

The above equation now employs the raw data directly and, hence, represents considerable simplification.

Fig. 43 is a plot of counts vs. distance from an arbitrary origin for MD20 H/K couple. The raw data for MD20 I/J has already been plotted in fig. 10.

For H/K couple,

$$\begin{aligned} a_1 &= 1.462 \times 10^{-4}, & b_1 &= -0.4 \\ a_2 &= 1.375 \times 10^{-3}, & b_2 &= 1.0 \end{aligned}$$

where the subscript "1" refers to K_2O and "2" to SrO .

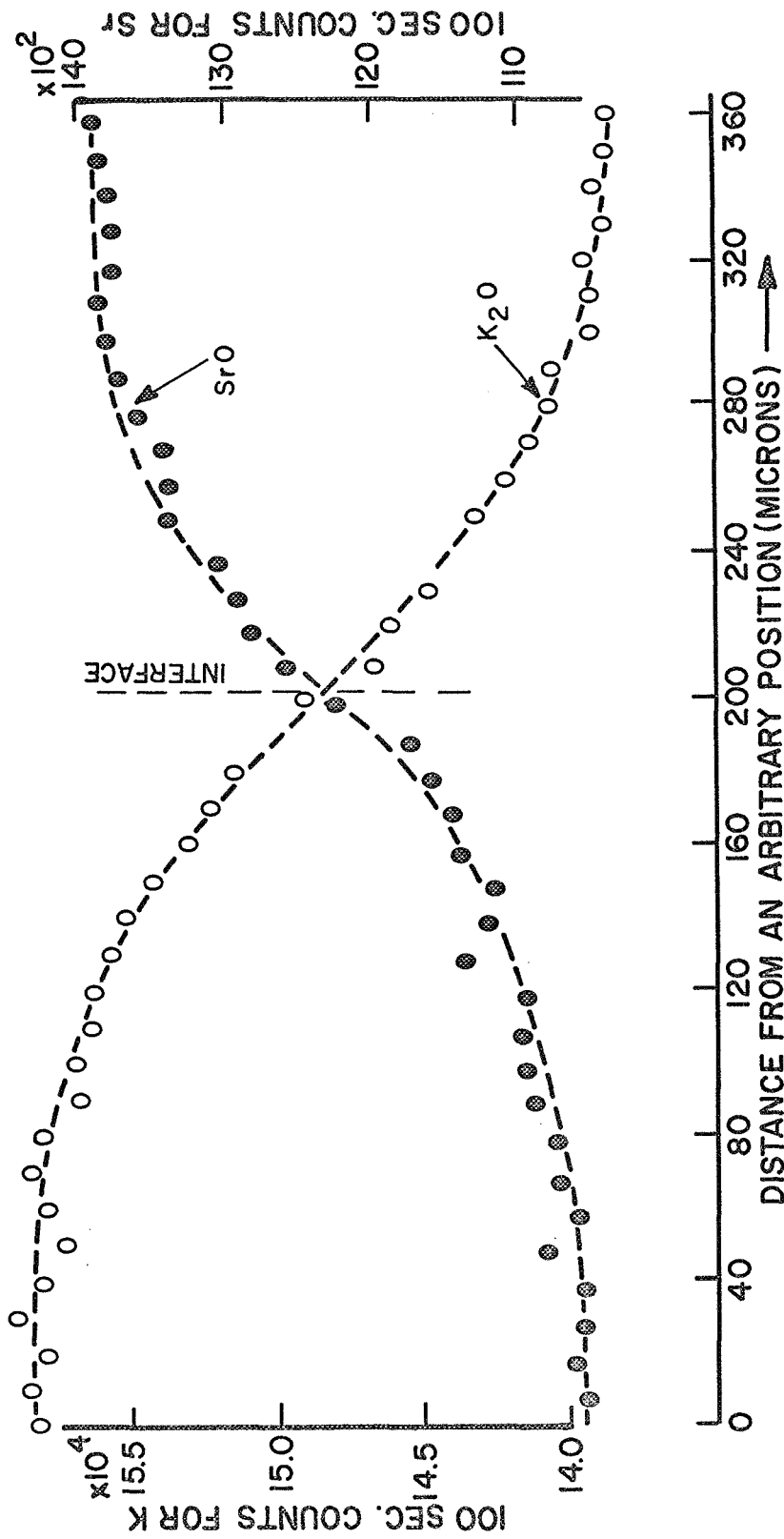


FIG.43: COUNTS VS. DISTANCE PLOT FOR MD 20 H/K.

Matano area for K_2O (from $-\infty$ to the interface)

$-\infty$ to 40μ (on arbitrary scale) = 0

$$\text{to } 70\mu = 0.05 \times 10^4 \frac{(162 + 132)}{2} = 7.42 \times 10^4$$

$$\text{to } 104\mu = 7.42 \times 10^4 + 0.1 \times 10^4 \frac{(132 + 98)}{2} = 18.92 \times 10^4$$

$$\text{to } 140\mu = 18.92 \times 10^4 + 0.175 \times 10^4 \frac{(98 + 62)}{2} = 32.02 \times 10^4$$

$$\text{to } 170\mu = 32.02 \times 10^4 + 0.3 \times 10^4 \frac{(62 + 32)}{2} = 46.12 \times 10^4$$

$$\text{to } 202\mu = 46.12 \times 10^4 + 0.4 \times 10^4 \frac{(32)}{2} = 52.52 \times 10^4$$

Double integral area by trapezoidal rule

$$\int (7.42 \times 10^4 \times \frac{30}{2} + \frac{(7.42 + 18.92)}{2} 34 \times 10^4 + \frac{(18.92 + 32.02)}{2} \times$$

$$36 \times 10^4 + \frac{(32.02 + 46.12)}{2} 30 \times 10^4 + \frac{(46.12 + 52.52)}{2} \times 32 \times$$

$$10^4] = 10^4 [111.2 + 448 + 917 + 1172 + 1478]$$

$$= 4126 \times 10^4 \text{ counts} \times \text{microns}^2$$

Matano area for MD20 H/K SrO (from $-\infty$ to interface)

$$-\infty \text{ to } 40\mu = 0$$

$$\text{to } 70\mu = 1 \times 10^2 \times \frac{(162 + 132)}{2} = 14.7 \times 10^3$$

$$\text{to } 120\mu = 14.7 \times 10^3 + 3 \times 10^2 \times \frac{(132 + 82)}{2} = 46.8 \times 10^3$$

$$\text{to } 160\mu = 46.8 \times 10^3 + 4 \times 10^2 \times \frac{(82 + 42)}{2} = 71.6 \times 10^3$$

$$\text{to } 180\mu = 71.6 \times 10^3 + 3 \times 10^2 \times \frac{(42 + 22)}{2} = 81.2 \times 10^3$$

$$\text{to } 202\mu = 81.2 \times 10^3 + 5 \times 10^2 \times \frac{(22)}{2} = 86.7 \times 10^3$$

Double integral area =

$$\begin{aligned} & \left[71.6 \times 10^3 \times \frac{120}{2} + \frac{(81.2 + 71.6)}{2} \times 10^3 \times 20 + \frac{(81.2 + 86.7)}{2} \times \right. \\ & \quad \left. 22 \times 10^3 \right] \\ & = (4280 + 1528 + 1850) \times 10^3 = 7658 \times 10^3 \text{ counts} \times \text{microns}^2 \end{aligned}$$

For MD20 I/J

$$a'_1 = 1 \times 10^{-4}, \quad b'_1 = 7.65$$

$$a'_2 = 0.96 \times 10^{-3}, \quad b'_2 = 5.4$$

Matano area for MD20 I/J K_2O ($-\infty$ to 0)

$$-\infty \text{ to } -84\mu = 0$$

$$\text{to } -64\mu = 0.05 \times 10^4 \frac{(84 + 64)}{2} = 3.7 \times 10^4$$

$$\text{to } -42\mu = 3.7 \times 10^4 + 0.1 \times 10^4 \frac{(64 + 42)}{2} = 9.0 \times 10^4$$

$$\text{to } -32\mu = 9.0 \times 10^4 + 0.1 \times 10^4 \frac{(42 + 32)}{2} = 12.7 \times 10^4$$

$$\text{to } -22\mu = 12.7 \times 10^4 + 0.025 \times 10^4 \frac{(32 + 22)}{2} = 13.37 \times 10^4$$

$$\text{to } -12\mu = 13.37 \times 10^4 - 0.025 \times 10^4 \frac{(22 + 12)}{2}$$

$$= 12.95 \times 10^4$$

$$\text{to } 0\mu = 12.95 \times 10^4 - 0.05 \times 10^4 \times \frac{12}{2} = 12.65 \times 10^4$$

Double integral area

$$3.7 \times 10^4 + \frac{20}{2} + \frac{(3.7 + 9.0)}{2} 10^4 \times 22 + \frac{(9.0 + 12.7)}{2} 10^4 \times 10$$

$$+ (12.7 + 13.37) \frac{10^4 \times 10}{2} + \frac{(13.37 + 12.95)}{2} 10^4 \times 10 +$$

$$\begin{aligned}
 & (12.9 + 12.65) \frac{10^4 \times 12}{2} \\
 & = 10^4 (37 + 139.7 + 108.5 + 130.3 + 131.0 + 153.5) \\
 & = 700 \times 10^4 \text{ counts } \mu^2
 \end{aligned}$$

For MD20 I/J SrO, the Matano area between $-\infty$ to 0μ

$$-\infty \text{ to } -25 = 0$$

$$-15\mu = 1 \times 10^2 \frac{(25 + 15)}{2} = 2.0 \times 10^3$$

$$\text{to } -5\mu = 2.0 \times 10^3 + 5.5 \times 10^2 \frac{(15 + 5)}{2} = 7.5 \times 10^3$$

$$\text{to } 0\mu = 7.5 \times 10^3 + 6 \times 10^2 \frac{(5)}{2} = 9.0 \times 10^3$$

Double integral area =

$$\begin{aligned}
 & 10^3 \left[2.0 \times \frac{10}{2} + \frac{(2.0 + 7.5)}{2} 10 + \frac{(7.5 + 9.0)}{2} 5 \right] \\
 & = 10^3 (10 + 42.5 + 41.3) = +93.8 \times 10^3 \text{ counts } \mu^2
 \end{aligned}$$

The above area calculations represent maximum values.

If we draw curves in such a way that areas are a minimum, we find that whereas for H/K couple only about 5% change occurs, for I/J couple,

double integral area for $K_2O = 566 \times 10^6$ counts² μ

double integral area for $SrO = -189 \times 10^3$ counts² μ

So that the corresponding mean values are,

for MD20 I/J $K_2O = (630 \pm 70) 10^4$ counts² μ

MD20 I/J $SrO = (-50 \pm 140) 10^3$ counts² μ

MD20 H/K $K_2O = (4126 \pm 200) 10^4$ counts² μ

MD20 H/K $SrO = (7658 \pm 400) 10^4$ counts² μ

Diffusion time for MD20 couples = 6.66 hours

The distance scale requires a correction of $\cos 15^\circ$ which is the direction of translation of specimen stage to the direction of diffusion.

Correction for the double integral area is, therefore, equal to $\cos^2 15^\circ$ or 0.907.

Substituting the concentration differentials between $-\infty$ to interface and the double integral areas with appropriate signs in eqn. (A2-1), we get

$$\begin{aligned} 1.5 D_{11} - 2.2 D_{12} &= \frac{(1.462 \times 10^{-4}) (4126 \pm 200) 10^4 \times 0.907}{2 \times 6.66 \times 60 \times 60} \\ &= (11.4 \pm 0.5) 10^{-10} \text{ cm}^2/\text{sec} \end{aligned}$$

$$\begin{aligned} 1.5 D_{21} - 2.2 D_{22} &= \frac{(1.375 \times 10^{-3}) (-7658 \pm 400) 10^3 \times 0.907}{2 \times 6.66 \times 60 \times 60} \\ &= - (19.9 \pm 1) 10^{-10} \text{ cm}^2/\text{sec} \end{aligned}$$

$$\begin{aligned} 0.125 D_{11} + 1.25 D_{12} &= \frac{(0.77 \times 10^{-4}) (630 \pm 70) 10^4 \times 0.907}{2 \times 6.66 \times 60 \times 60} \\ &= (0.915 \pm 0.093) 10^{-10} \text{ cm}^2/\text{sec} \end{aligned}$$

$$\begin{aligned} \text{and } 0.125 D_{21} + 1.25 D_{22} &= \frac{(1.02 \times 10^{-3}) (-50 \pm 140) 10^3 \times 0.907}{2 \times 6.66 \times 60 \times 60} \\ &= - (0.0965 \pm 0.27) 10^{-10} \text{ cm}^2/\text{sec} \\ &\quad (\text{A2-2}) \end{aligned}$$

From above

$$D_{11} \cong (7.6 \pm 0.4) 10^{-10} \text{ cm}^2/\text{sec}$$

$$D_{12} \cong (0 \pm 0.5) \times 10^{-10} \text{ cm}^2/\text{sec}$$

$$D_{21} = -(11.75 \pm 0.9) 10^{-10} \text{ cm}^2/\text{sec}$$

$$D_{22} = (1 \pm 1.1) 10^{-10} \text{ cm}^2/\text{sec}$$

(A2-3)

APPENDIX 3

VARIANCE OF X-RAY COUNTS

Calculated below are the variances of x-ray intensity for Sr, K and Si. Although the sample size in each case is rather small, calculations are judged to be unbiased between sample to sample.

The counting time for each observation was 100 sec.

For Sr

Sample counts W_i = 12493, 12572, 12736, 12648, 12589, 12683,
12647, 12646, 12299

$$\bar{W} = 12590.333, \quad \Sigma W_i^2 = 1426782569$$

$$\sigma^2 = 1/8 [1426782569 - 9(12590.333)^2]$$
$$= 16770$$

$$\text{So, } \sigma = 129.5$$

$$\text{and } (\sigma/\bar{W})_{\text{Sr}} \cong 1.0\%$$

For K

Sample counts W_i are

(17466, 17550, 17551, 17571, 17552, 17540, 17675, 17620,
17619, 17551, 17570, 17587, 17665) $\times 10$

$$\bar{W} = 1757.82 \times 10^2$$

$$\Sigma W_i^2 = 40169620.83 \times 10^4$$

$$\sigma^2 = 1/12 [40169620.83 - 13(1757.82)^2]$$

$$= 312680$$

or $\sigma = 559$

and $(\sigma/\bar{W})_K = 0.318\%$

For Si

Sample counts W_i are

(13551, 13727, 13707, 13732, 13697, 13778, 13679, 13709,
13750, 13738, 13623, 13691, 13638, 13644, 13598, 13658,
13674) $\times 10$

$$\bar{W} = 1368.2 \times 10^2, \quad \Sigma W_i^2 = 31824059.96 \times 10^4$$

$$\sigma^2 = 1/16 [31824059.96 - 17(1368.2)^2] \times 10^4$$

$$= 343050$$

or $\sigma = 585.7$

and $(\sigma/\bar{W})_{Si} = 0.42\%$

To convert σ_W (i.e. standard deviation of counts) to σ_X (standard deviation of concentration), we make use of the linearity assumption

$$X = a W + b \quad (A3-1)$$

or $\sigma_X^2 = a^2 \sigma_W^2$

or $(\sigma_X)_\ell = a (\sigma_W/W)_\ell \cdot W_\ell$

With the assumption that for the ℓ th observation $(\sigma_W/W)_\ell$

does not change, we can write

$$(\sigma_x) = a \cdot (\text{coefficient of variation}) \cdot W_\ell$$

(A3-2)

Equation (A3-2) provides the weighting scheme for every X_ℓ .

APPENDIX 4

THE MATRIX METHOD

Consider Fig.21

The manner in which the data is collected is
time t increasing

$$X_{11}, X_{12}, \dots, X_{1k}, X_{2k}, \dots, X_{22}, X_{21}, X_{31}, \dots, X_{nk}$$

n is the total number of rows, k is the total number of columns. Let n be an even number and time spent at each position (element) be p seconds.

The rth column comprises of n counts which were taken at times $pr, (pr + 2(k-r)p), (pr + 2kp), (pr + 2kp + 2(k-r)p), \dots$ after the starting point (i.e. beginning of X_{11}).

Let the background intensity g drift linearly with time. Thus

$$g = mt + g_0 \quad (A4-1)$$

where g_0 is a constant, m is the slope of the drift.

For all odd row numbers, the net background is given by

$$\begin{aligned} (\Sigma g)_{\text{odd}} &= \frac{n}{2} g_0 + m [pr + (pr + 2kp) + (pr + 4kp) + \dots \\ &\quad \text{to } \frac{n}{2} \text{ terms}] \\ &= \frac{n}{2} g_0 + \frac{mn}{2} pr + m \frac{n(n-2)}{4} kp \end{aligned} \quad (A4-2)$$

For all even row numbers, the net background is given by

$$\begin{aligned}
 (\Sigma g)_{\text{even}} &= \frac{n}{2} g_o + m[(pr + 2(k-r)p) + (pr + 2(k-r)p + \\
 &\quad + 2kp) + (pr + 2(k-r)p + 4kp) + \dots \text{to } \frac{n}{2} \text{ terms}] \\
 &= \frac{n}{2} g_o + \frac{nm}{2}(pr + 2(k-r)p) + \frac{mn(n-2)kp}{4}
 \end{aligned}
 \tag{A4-3}$$

The total background is a sum of (A4-2) and (A4-3)

$$\begin{aligned}
 (\Sigma g)_{\text{total}} &= ng_o + mnpr + mn(k-r)p + \frac{mn(n-2)kp}{2} \\
 &= ng_o + (mn^2kp/2)
 \end{aligned}
 \tag{A4-4}$$

Equation (A4-4) shows that the total background at a particular position, r , is a constant and does not depend upon r . Hence, the column means are free of all drift effects.

By intuitive reasoning, it can be said that the row means are free of inhomogeneities.

APPENDIX 5

HOMOGENIZATION OF OTHER MODEL ROCKS

(1) UNIDIRECTIONAL LAMINATED STRUCTURE WITH TWO WAVE LENGTHS:

Fig. 44 shows a laminar structure which is a sum of two functions,

$f_1(\bar{y}^*)$ and $f_2(\bar{y}^*)$ where

$$\begin{aligned} f_1(\bar{y}^*) &= X_{MO} \text{ for } 0 < \bar{y}^* < \pi/6 \\ &= 0 \text{ for } \pi/6 < \bar{y}^* < \pi/3 \end{aligned}$$

$$f_1(\bar{y}^* + \pi/3) = f_1(\bar{y}^*)$$

$$\begin{aligned} f_2(\bar{y}^*) &= 0 \text{ for } 0 < \bar{y}^* < 9\pi/6 \\ &= X_{MO} \text{ for } 9\pi/6 < \bar{y}^* < 10\pi/6 \\ &= -X_{MO} \text{ for } 10\pi/6 < \bar{y}^* < 11\pi/6 \\ &= 0 \text{ for } 11\pi/6 < \bar{y}^* < 2\pi \end{aligned}$$

$$f_2(\bar{y}^* + 2\pi) = f_2(\bar{y}^*)$$

Let $\bar{y}^* = (2\pi/6a)y$

so that the primary short wave length in the system is $\lambda_1 = a$. The long wave length λ_2 corresponds to $f_2(\bar{y}^*)$ and is $6a$. The average concentration of total function is $X_{MO}/2$.

Fourier components of $f_1(\bar{y}^*)$ are given by

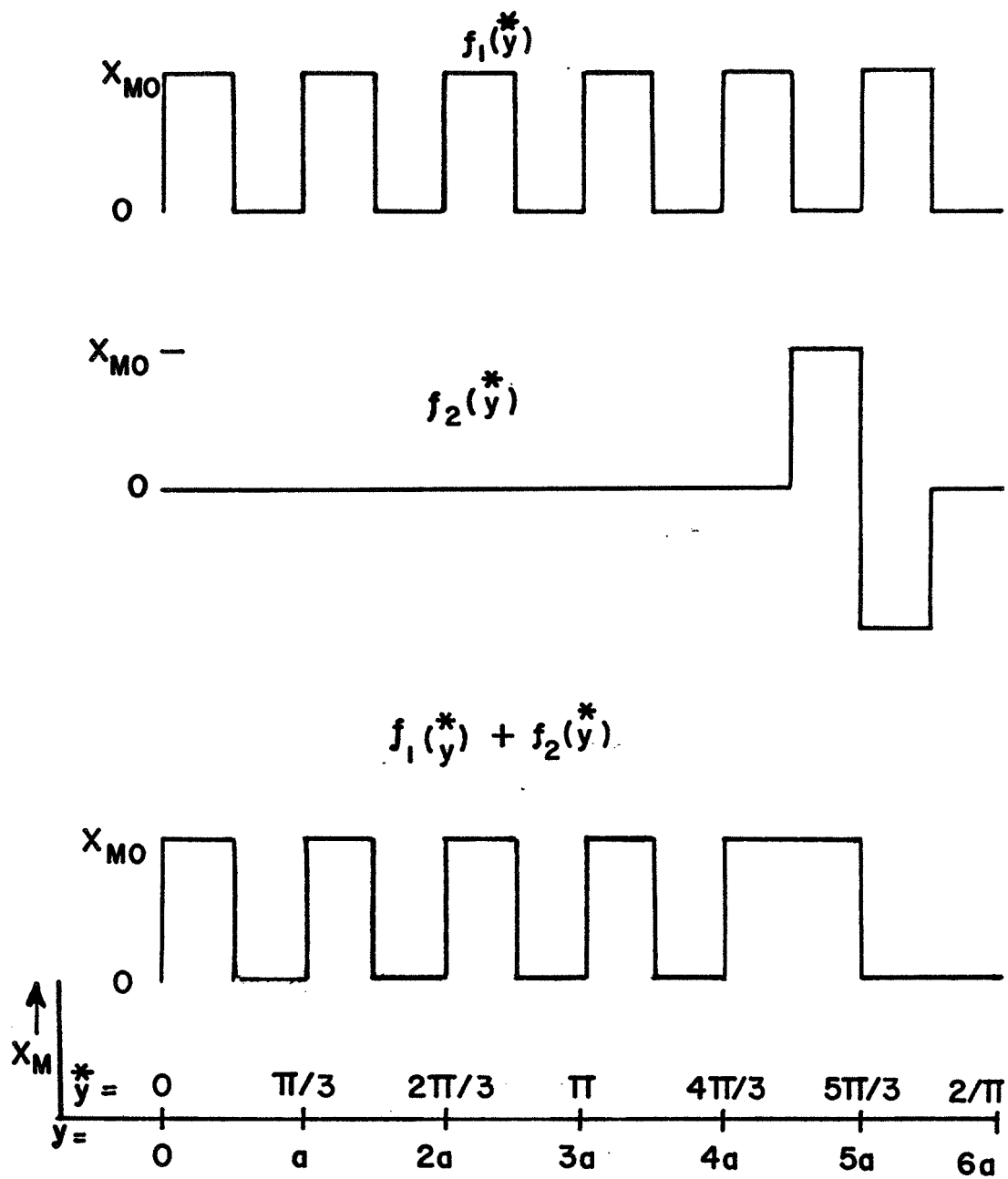


FIG. 44 : A HYPOTHETICAL LAMINAR STRUCTURE WITH TWO WAVELENGTHS.

$$f_1(y^*) = \frac{X_{MO}}{2} + \frac{2X_{MO}}{\pi} \sin 6 y^* + \frac{2X_{MO}}{3\pi} \sin 18 y^* \\ + \frac{2X_{MO}}{5} \sin 30 y^* + \frac{2X_{MO}}{7\pi} \sin 42 y^* \dots$$

(A5-1)

The amplitude of λ_1 , therefore, is $2X_{MO}/\pi$.

Also, for $f_2(y^*)$

$$f_2(y^*) = -0.232 \frac{X_{MO}}{\pi} \cos y^* - 0.433 \frac{X_{MO}}{\pi} \cos 2 y^* \\ + 0.65 \frac{X_{MO}}{\pi} \cos 4 y^* + 0.65 \frac{X_{MO}}{\pi} \cos 5 y^* \\ + 0 (\cos 6 y^*) + \dots \\ -1.33 \frac{X_{MO}}{\pi} \sin y^* - 0.25 \frac{X_{MO}}{\pi} \sin 2 y^* \\ +1.33 \frac{X_{MO}}{\pi} \sin 3 y^* + 0.375 \frac{X_{MO}}{\pi} \sin 4 y^* \\ -0.375 \frac{X_{MO}}{\pi} \sin 5 y^* - 0.66 \frac{X_{MO}}{\pi} \sin 6 y^* \\ + \dots$$

(A5-2)

For the total function,

$$\text{the amplitude of } \lambda_1 = (2 - 0.66) X_{MO}/\pi \\ = 1.33 X_{MO}/\pi$$

$$\text{and the amplitude of } \lambda_2 = 0.232 X_{MO}/\pi$$

Consider the decay of λ_2 in the total function compared to λ_1 in $f_1^*(y)$. If for $f_1^*(y)$, limit of detection of inhomogeneity is ~ 0.01 , i.e.

$$\frac{(X_M - \bar{X}_M)}{(\bar{X}_{MO} - \bar{X}_M)} \sim 0.01$$

then for the total function, the decay factor which can be tolerated is

$$\begin{aligned} &\approx 0.01 [(2X_{MO}/\pi)/(0.232 X_{MO}/\pi)] \\ &\approx 0.086 \end{aligned}$$

$$\text{So } (Dt)_{\text{eff}}/\lambda^2 \approx 0.068$$

Hence, homogenization of the total function is related to that of $f_1^*(y)$ by

$$\begin{aligned} \frac{(Dt)_{\text{eff of } (f_1 + f_2)}}{(Dt)_{\text{eff of } f_1}} &\approx \frac{0.068}{0.12} \cdot \frac{\lambda_2^2}{\lambda_1^2} \\ &\approx 20 \quad (\text{A5-3}) \end{aligned}$$

Thus, the thermal history is 20 times more than for the case discussed in Chapter 11.

(2) HOMOGENIZATION OF THE 3-DIMENSIONAL HEXAGONAL STRUCTURE
WITH SPHERICAL PARTICLES RICH IN ELEMENT M, EMBEDDED
IN M-DEPLETED MATRIX

Let us make two simplifying assumptions:

(a) all M-rich particles are of radius p , and are distributed in hexagonal packing with nearest neighbor distance = $2a$

(b) surface of the sphere $r = a$ is impermeable.

These assumptions reduce our problem to the case of diffusion of a single sphere into a concentric finite sphere.

The initial concentration is given by

$$\begin{aligned} f(r) &= X_0 \quad \text{for } 0 < r < p \\ &= 0 \quad \text{for } p < r < a \end{aligned}$$

At $t > 0$, $X_{(r)}$ is given by⁽¹¹¹⁾

$$X_{(r)} = \frac{3}{a^3} \int_0^a r^2 f(r) dr + \frac{2}{ar} \sum_{n=1}^{\infty} \exp(-D\alpha_n^2 t).$$

$$\frac{\sin \alpha_n r}{\sin^2 \alpha_n a} \int_0^a r' f(r') \sin \alpha_n r' dr'$$

(A5-4)

where α_n are the positive roots of

$$a\alpha_n \cot a\alpha_n = 1 \quad (A5-5)$$

The first term on the right hand side of (A5-4) is the mean $\bar{X} =$

$(X_0 p^3/a^3)$ in the composite. The second term which can be rewritten as

$$\frac{2X_0}{ar} \sum_{n=1}^{\infty} \exp [-(Dt/a^2) (\alpha_n a)^2] \cdot \frac{\sin r \alpha_n}{\sin a \alpha_n} \left[\frac{\sin \alpha_n p}{\alpha_n^2} - p \frac{\cos \alpha_n p}{\alpha_n} \right] \quad (A5-6)$$

represents the corrective term above the mean.

If $p = a/2$, then at $r = p$, the corrective terms up to $n = 3$ can be expressed as

$$\Delta X/X_0 = -0.102 \exp (-20.25 Dt/a^2) + 0.16 \exp (-59.7 Dt/a^2) \quad (A5-7)$$

At large times, when

$$Dt/a^2 > 0.2$$

$$|\Delta X/X_0| < 0.00176$$

Which is a negligible correction.

In the limit $r \rightarrow 0$

$$(\sin r \alpha_n)/r \rightarrow \alpha_n$$

$$\text{And so } |(\Delta X/X_0)_{r=0}| = 0.007$$

Thus, the times to achieve the limit of no further occurrence of detectable homogenization do not differ significantly from the case of unidirectional lamina discussed in Chapter 11.

ABOUT THE AUTHOR

The author was born in Agra, India, on May 25, 1944. His childhood was not a pleasant one. A malfunctioning liver confined him to bed at the age of 2 1/2. The illness nearly took his life.

After recovery, at the age of 6, he started his preliminary education.

As a student of St. John's College, Agra, he received various academic honors. He passed the U. P. State Intermediate examination with 2nd position in order of merit, in 1960, and the B.Sc. examination (Physics, Chemistry, Mathematics and General English) of Agra University (1962) with first position.

In September, 1962, he joined the Department of Glass Technology, University of Sheffield (England), from where he secured a B.Sc. Tech. Honors degree, in 1965.

Following this, he joined Professor Alfred R. Cooper to start research activities in Ceramics and Glass, at Case Western Reserve University (then, Case Institute of Technology), where he was awarded an M. S. degree, in 1968. His thesis title was "Diffusion in $K_2O-SrO-SiO_2$ Glass System."

He is a person with a true Gemini spirit. Despite being blamed for being egotistic, he is always aiming for the betterment of life within him and around him.

And . . . he is still a bachelor!

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