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The work since October 1968 was primarily focussed upon tektites and was presented in the form of a paper entitled "Micro Inhomogeneities and Diffusion in Tektites" at the Third International Tektite Symposium in April 1969 in Corning, N.Y.

The paper dealt with three aspects of tektite research:

- i. Homogeneity of a Thailand tektite;
- ii. Measurement of the effective binary diffusion coefficient of iron in a laboratory simulated tektite; and,
- iii. Calculation of the homogenization times of a hypothetical rock containing lamina of fluctuating iron content.

This paper has been submitted for publication, and a copy is included here as the major part of this report.

The examination of homogeneity is a follow-up of the first Semiannual Report (October 1967). The data presented there made it necessary to give a more critical examination to the inhomogeneities on at least a semi-quantitative basis.

A new experimental design, called the Matrix Method, was therefore developed. The scheme permitted accumulation

of microprobe X-ray counts over long periods without introducing the errors due to electronic drift. The net standard error was therefore considerably reduced.

With this scheme of analysis, it has been shown in the paper that away from isolated inhomogeneities the Thailand tektite is perhaps the most homogeneous of all glasses examined.

The second topic of the paper concerns the measurement of the effective binary diffusion coefficient of iron. This represents a continuation of the work presented in the third semiannual report (October, 1968). It provides information on the kinetics of iron diffusion in a tektite glass and hence made possible a calculation such as of homogenization times of a laminated structure.

This calculation is interesting in that the ultimate results do not seriously depend upon the geometrical shapes involved, i. e., a cylindrical symmetry or spherical symmetry do not significantly alter the results of this one-dimensional calculation.

It has been shown that if the homogenization of iron alone were considered, the production of a tektite from a specimen of subgreywacke would require temperatures exceeding 1800°C for times greater than 32 seconds.

To pin down the requirements of minimum thermal history for homogenization, it has become obvious that investigations are necessary on the diffusion kinetics of species with a lower mobility such as silicon. Our intention is to measure the effective binary diffusion coefficient of silicon in laboratory simulated tektites in the near future.

INHOMOGENEITIES AND IRON DIFFUSION
IN A THAILAND TEKTITE*

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ABSTRACT

Sections of a Thailand Tektite were examined under an Electron Microprobe for composition fluctuations. A comparison is made with similar data from a laboratory synthesized tektite of duplicate composition.

To estimate the kinetics of the diffusive mixing of local composition fluctuations, effective binary diffusion coefficients were measured at various temperatures above 1000°C. Data for Fe, in particular, is used to calculate the homogenization times of a hypothetical tektite source with a periodic variation of iron. This in turn is used to suggest limits for the thermal history of tektite glasses.

*Presented at the Third International Tektite Symposium, Corning, New York, 1969.

INHOMOGENEITIES AND IRON DIFFUSION
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A. K. Varshneya and A. R. Cooper

Introduction

The glassy nature of tektites has long been recognized.⁽¹⁾ Many hypotheses concerning their origin have been suggested and are 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⁾

A crystalline material can be made to vitrify in two ways following an impact. High pressures associated with a shock wave without a significant amount of heat energy produce the so-called diaplectic glasses⁽⁵⁾ (also termed the theto-morphic glasses by Chao⁽⁶⁾). 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.

Petrographic study reveals the absence of grain boundaries in most tektites. Pronounced flow structure consisting of schlieren of glasses of slightly different composition accompanied by strain birefringence are often observed.⁽⁷⁾ This suggests that formation of tektite material took place by an actual melting with a finite amount of long distance diffusion.

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⁽⁸⁾ suggests that they might have been glassy to some extent even before the impact.⁽⁹⁾

No large bodies of natural glass approximating the tektite composition are found in the vicinity of the recovery areas of the tektites. Even an individual terrestrial mineral matching the chemical composition of tektites exactly is not found. Closest, perhaps, are the subgreywackes from Henbury, Australia⁽¹⁰⁾, but these deposits are physical mixtures of minerals including quartz grains of 0.2 - 0.5 mm sizes.

It is evident that a necessary requirement for a tektite originating on the earth is a thermal history following the impact which is of sufficient temperature and sufficient duration to permit melting and homogenizing of the mineral mixture. This requirement of an extensive thermal history

although sufficient, is not a necessary one for a tektite produced on the moon in view of the possibility that some fraction of the lunar crust may be glassy.

An impact on a glassy mineral on the moon giving rise to moderate temperatures could not only be compatible with the observed ultimate homogeneity of tektites but could also be consistent with the diaplectic nature of the Muong-Nong tektites.

The present investigation attempted to estimate the possible thermal histories of a Thailand tektite which would be consistent with its observed homogeneity.

The approach thus far included the following:

- i. A study of the homogeneity of a Thailand tektite relative to two laboratory synthesized melts.
- ii. A measurement of the effective binary diffusion coefficient of iron in the synthetic composition as a function of temperature.
- iii. The use of diffusion coefficients obtained from (ii) to calculate the homogenization times of a hypothetical rock with laminations of fluctuating iron content.

Glass Compositions

Table I shows the composition of four tektites used in this study. The first one is a Thailand tektite 2172.⁽¹¹⁾ The second composition is an attempted duplication. It was prepared by melting 500 g. of thoroughly mixed analytical grade chemicals in air in a globar electric resistance furnace at 1550°C for 24 hours. The glass had bubbles. The third composition, TA, is a simplified representation of the tektite system. It eliminates all the minor constituents. A globar melt obtained at 1550°C was broken to pieces and later heated in a zirconia crucible in a gas fired kiln for 4 hours at 1800°C to yield a bubble-free glass.

The fourth composition, TB, has no iron - the missing iron is compensated by a proportionate increase in the rest of the constituents. A 1550°C globar melt was later fired at 1800°C. Two such repeated meltings could not rid the glass of bubbles (up to 1/4 mm size) and hence it was employed as such.

Homogeneity Determinations

A section of the Thailand tektite containing a radial plane and pieces of the two synthetic compositions, JC3 and TA, were examined under the electron microprobe for contained chemical inhomogeneities.

TABLE I

Chemical Composition (wt. %) of Glasses Used

	Thailand Tektite 2172	Synthetic Tektite			Synthetic Tektite	
		JC3	TA	TB	TA	TB
SiO ₂	73.0	72.0	72.0	76.2		
Al ₂ O ₃	12.83	13.0	13.0	13.75		
Fe ₂ O ₃	0.64	} 5.7	} 5.5			
FeO	4.37					
MgO	2.48	2.7				
CaO	1.91	2.0	5.5	5.8		
Na ₂ O	1.45	1.62				
K ₂ O	2.40	2.31	4.0	4.25		
TiO ₂	0.73	0.72				
MnO	0.09	0.1				

In order to separate small concentration variations from the time dependent drift of the electron microprobe, the following technique was used. The electron beam was stepped 10 μ in a forward direction 100 times and then stepped backwards on the same trace (Fig. 1). A matrix was generated where a column represents a particular position on the trace and a row represents a particular time interval while following the trace.

Consider the situation where 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 defocussing of the electron beam at any stage during the analysis. Slight imperfections in the specimen stage which can cause significant defocussing over the 1 mm traverse are thus removed. At the same time, it is easy to show⁽¹²⁾ that the column means will be influenced by the inhomogeneities in A and B only, whereas the row means 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.⁽¹³⁾

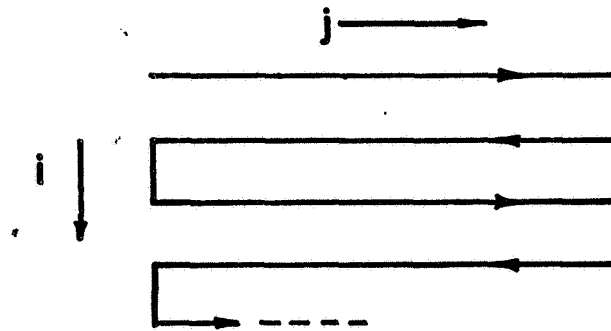
Microanalyses were performed in this manner for two pairs; Fe-Si and Al-Ca in the three glasses. Fig. 2 and Fig. 3 show a plot of the column means of the Si/Fe ratio

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

THE SEQUENCE OF DATA COLLECTION IS :



and the Ca/Al ratio for the three glasses against the distance from an arbitrary point. The dashed lines represent the 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 of iron oxide content of 5.0 wt. %, a fluctuation of 0.05 wt. % can be detected.

While 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 could be identified to be corresponding to about 5.25 wt. % iron oxide. This may well be due to remnants from a meteoritic inclusion. An additional scan on the same sample 200 μ away revealed no iron rich peak.

Table II 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, then it can be stated with 95% confidence that a significant inhomogeneity (or drift) exists.

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

FIG. 2: PLOT OF COLUMN MEANS OF THE Si/Fe RATIO MATRIX

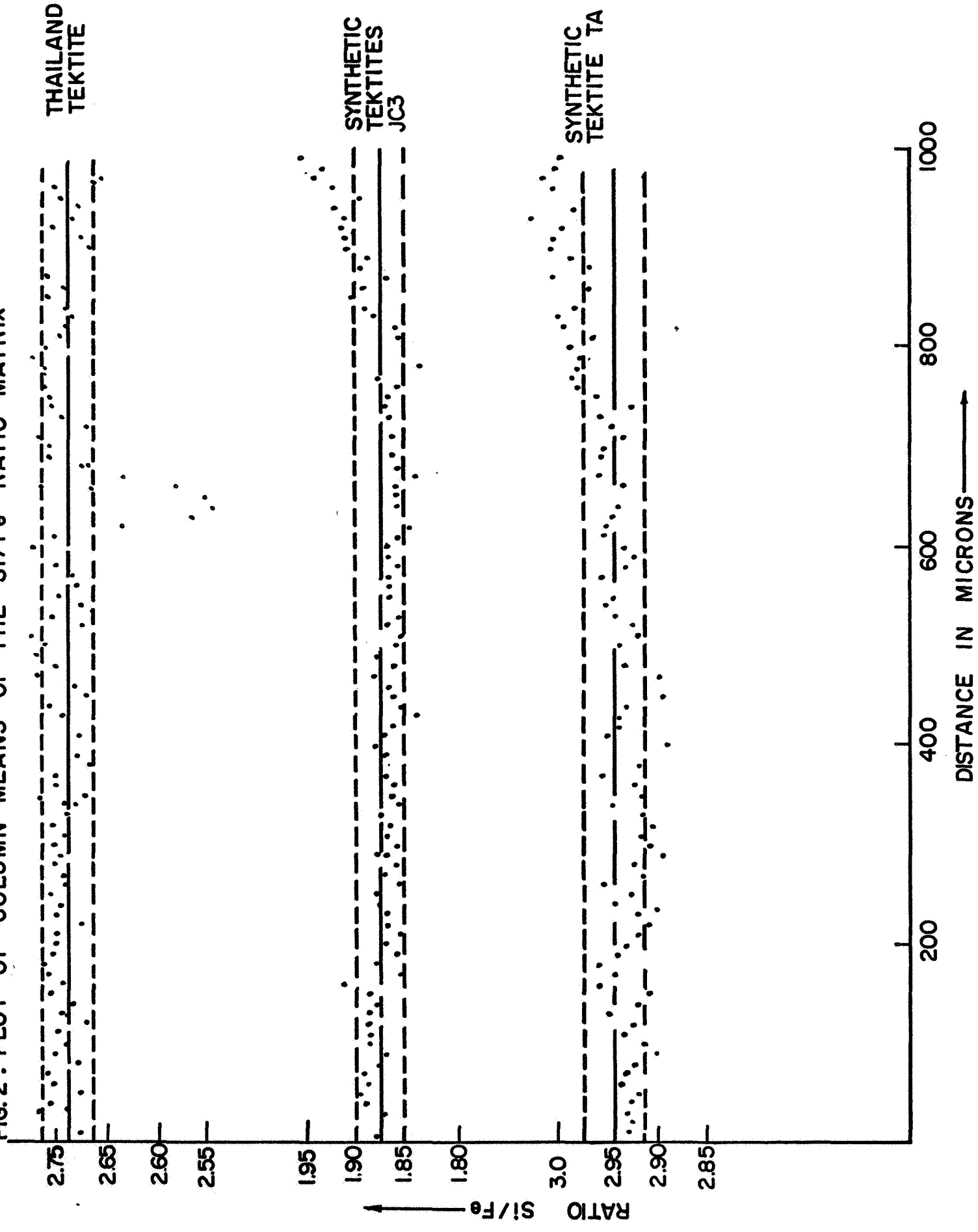


FIG. 3: PLOT OF COLUMN MEANS OF C_a/AI RATIO MATRIX

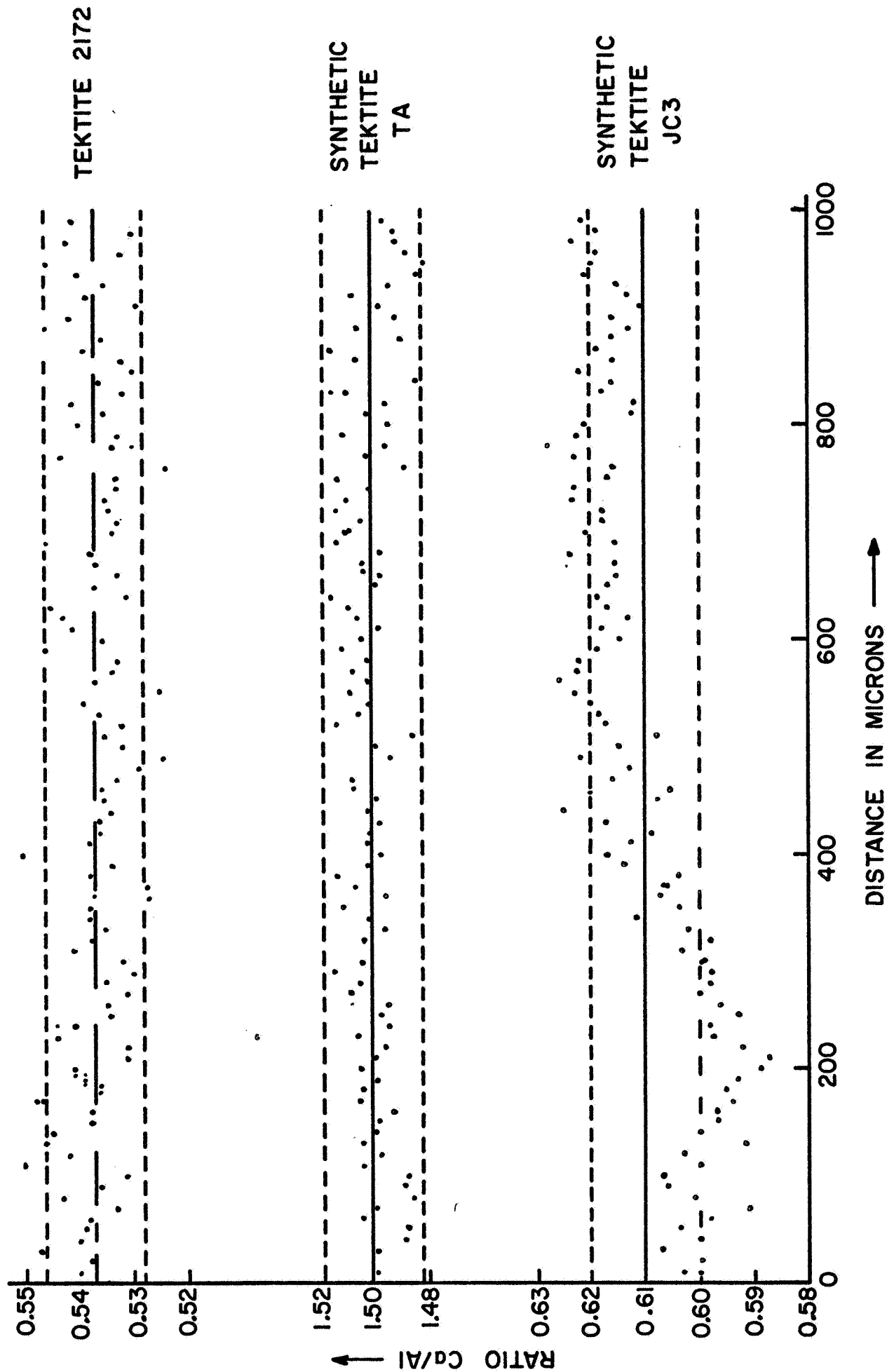


TABLE II

F Values for the Distribution of Si/Fe and Ca/Al Ratios

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

Effective Binary Diffusion Coefficient (EBDC) of Iron

The definition of the effective binary diffusion coefficient,⁽¹⁴⁾ D_{iM} , in a multicomponent system follows Fick's first law as

$$J_i = - D_{iM} \nabla C_i \quad (1)$$

where J_i is the mass flux and C_i is the mass concentration of species i . Equation (1) treats the diffusion of i as if it were moving in a matrix of all other species put together as species M . In a multicomponent system, when diffusion is limited to a specific "direction" in the composition space, the EBDC is a meaningful coefficient to describe the mixing behavior of a species⁽¹⁵⁾ as is its inter-diffusion coefficients matrix⁽¹⁶⁾ which is tedious to obtain⁽¹⁷⁾ and use when the number of components exceeds 3. Since we will be concerned onwards with the EBDC only, we will henceforth use the simpler notation, D , instead of D_{iM} .

To assure the proper directionality of diffusion of Fe, the diffusion was carried out in synthetic glasses TA and TB whose compositions have already been given in Table I. On a pseudo-ternary composition space, the line joining TA and TB points towards pure Fe_3O_4 (Fig. 4).

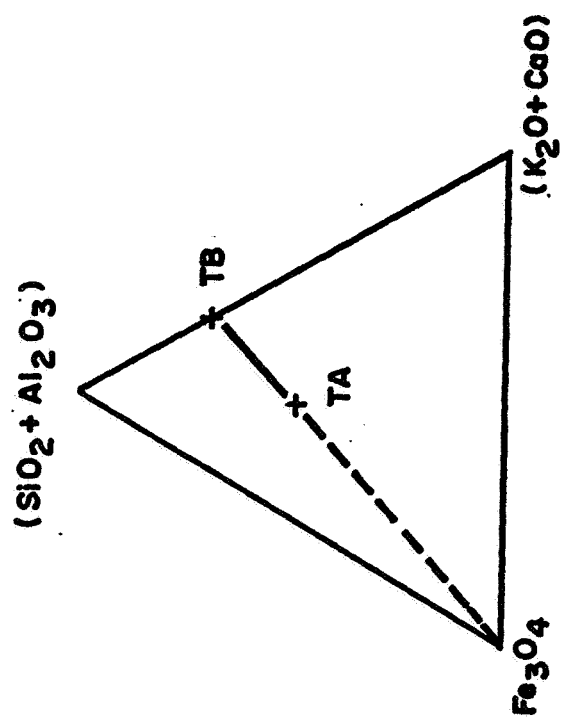


Fig. 4: Location of glasses TA and TB on a pseudo-ternary composition space

Fig. 5 shows the diffusion assembly. The specimens are 8 mm in diameter and about 3 1/2 mm thick discs with polished faces in contact. The housing is made out of slip cast pulverized fused SiO_2 . Diffusion was carried out inside a globar furnace in air with a temperature control of $\pm 10^\circ\text{C}$.

Samples were cut parallel to the cylindrical axis, and later microanalyzed. A typical plot of X-ray counts of Fe on the ordinate against distance in microns from the interface is shown in Fig. 6. For a constant EBDC, the concentration, C_i , as a function of distance, x , from the original interface at time, t , in a unidirectional semi-infinite couple is given by⁽¹⁸⁾

$$C_i = 1/2 C_{i0} [1 - \text{erf } x/2 \sqrt{Dt}] \quad (2)$$

where

$$C_{i0} = C_i \text{ at } t = 0 \text{ for } x < 0$$

Equation (2) enables a calculation of D from the experimental profiles. The results seem to be unaffected by the presence of bubbles in glass TB because constant values of the EBDC were obtained from experiments conducted at the same temperature for various lengths of time. Table III lists the various experiments performed.

A plot of the logarithm of EBDC of Fe against the reciprocal of absolute temp is shown in Fig. 7. A straight line.

FIG. 5 : THE DIFFUSION ASSEMBLY

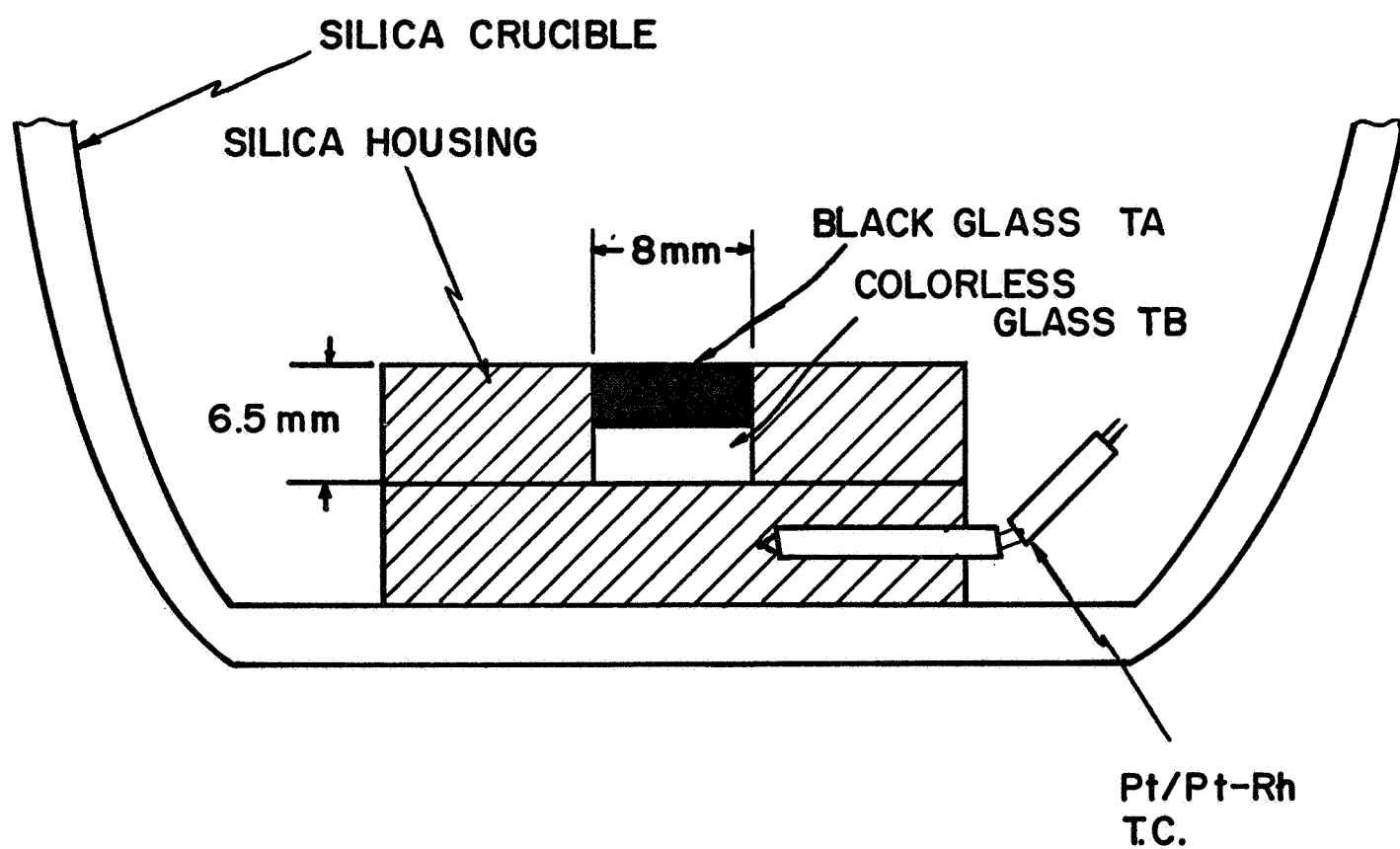


FIG. 6: DISTRIBUTION OF Fe AFTER DIFFUSION AT 1490°C FOR 3 HRS.

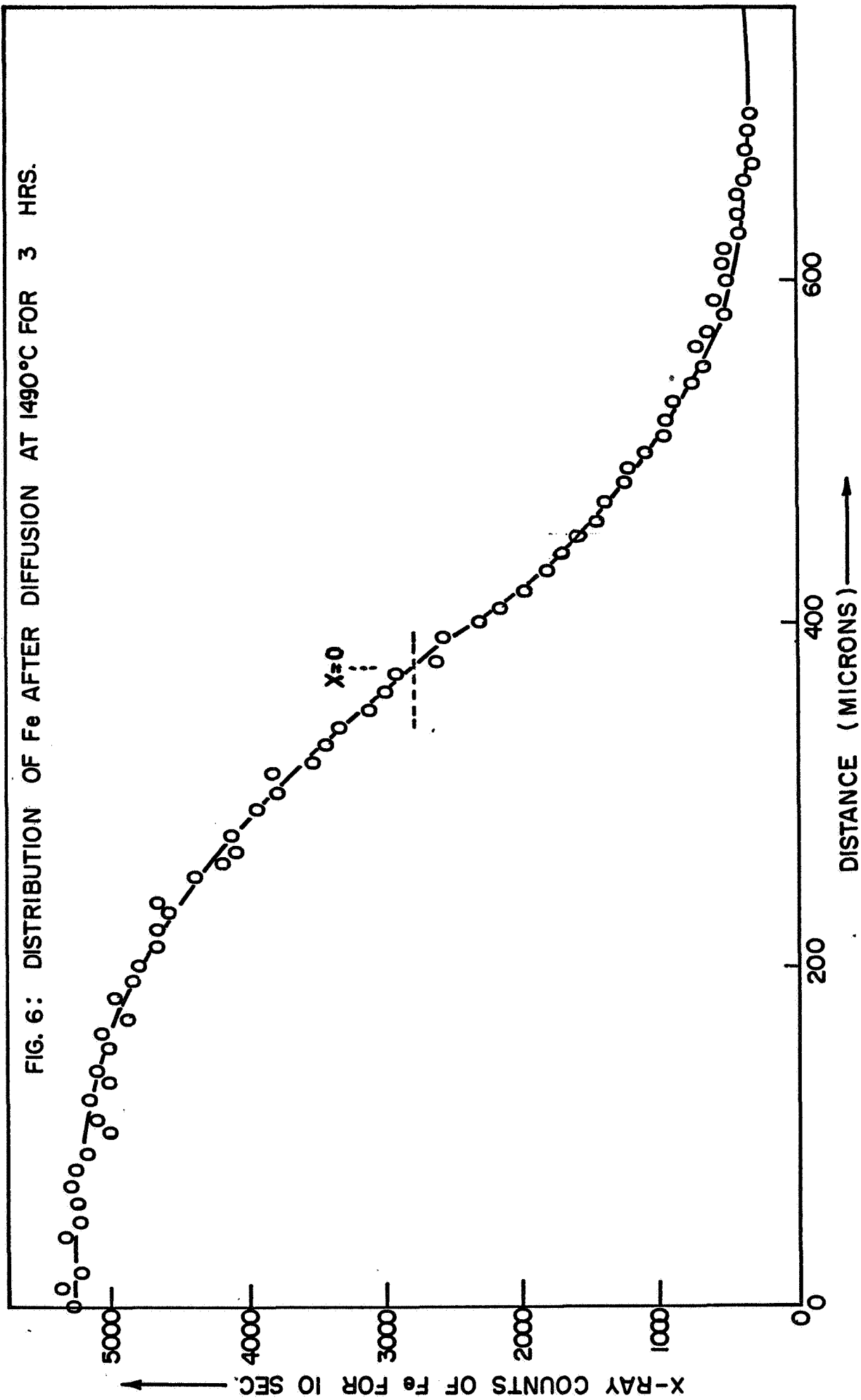


TABLE III

Experiments Conducted to Measure EBDC of Fe

Experiment	T°C	Diffusion Time	D cm ² /sec
(1)	1160°C	6.15 hrs.	1 x 10 ⁻¹⁰
(2)	1160°C	20 hrs.	0.75 x 10 ⁻¹⁰
(3)	1160°C	67.5 hrs.	1.4 x 10 ⁻¹⁰
(4)	1260°C	5 hrs.	6.5 x 10 ⁻¹⁰
(5)	1260°C	19.5 hrs.	5.1 x 10 ⁻¹⁰
(6)	1370°C	4.5 hrs.	1.2 x 10 ⁻⁹
(7)	1370°C	9.5 hrs.	1.23 x 10 ⁻⁹
(8)	1490°C	3 hrs.	7.5 x 10 ⁻⁹
(9)	1490°C	3.5 hrs.	8.0 x 10 ⁻⁹

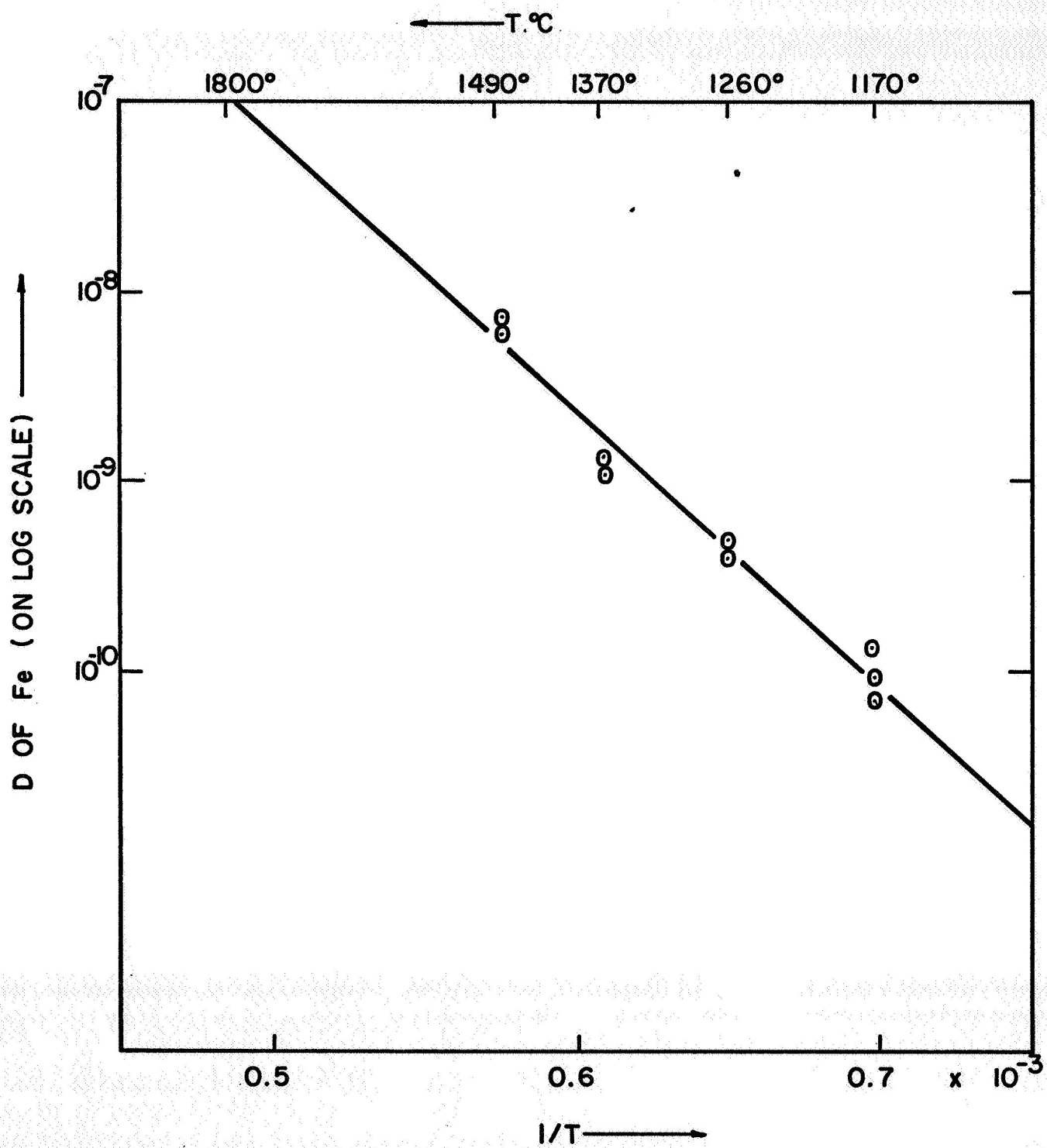


FIG. 7: PLOT OF D Vs. $1/T$

corresponding to the Arrhenius rate type equation

$$D_{(T)} = D_0 \exp (-\Delta H_D/RT) \quad (3)$$

can be drawn through this data to yield an activation energy ΔH_D for the EBDC of iron to be ~ 64 Kcal/mol.

Homogenization of a Laminated Structure with Fluctuating Iron Content

Simple models to calculate the time dependent temperature distribution in certain geological phenomena have been used by Lovering. (19)

The model of a laminated structure with fluctuating concentration has been used by Cooper⁽²⁰⁾ to estimate the homogenization times of striations by diffusive mixing in a glass tank.

Consider the case of a laminated structure of iron inhomogeneity shown in Fig. 8. Each iron rich lamina is of thickness $2\delta_1$, and the iron 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 iron in all the iron rich lamina is C_{i0} and in all the iron depleted lamina is zero at time $t = 0$. The concentration, C_i , at $x = 0$ and $t \geq 0$ is given by⁽²¹⁾

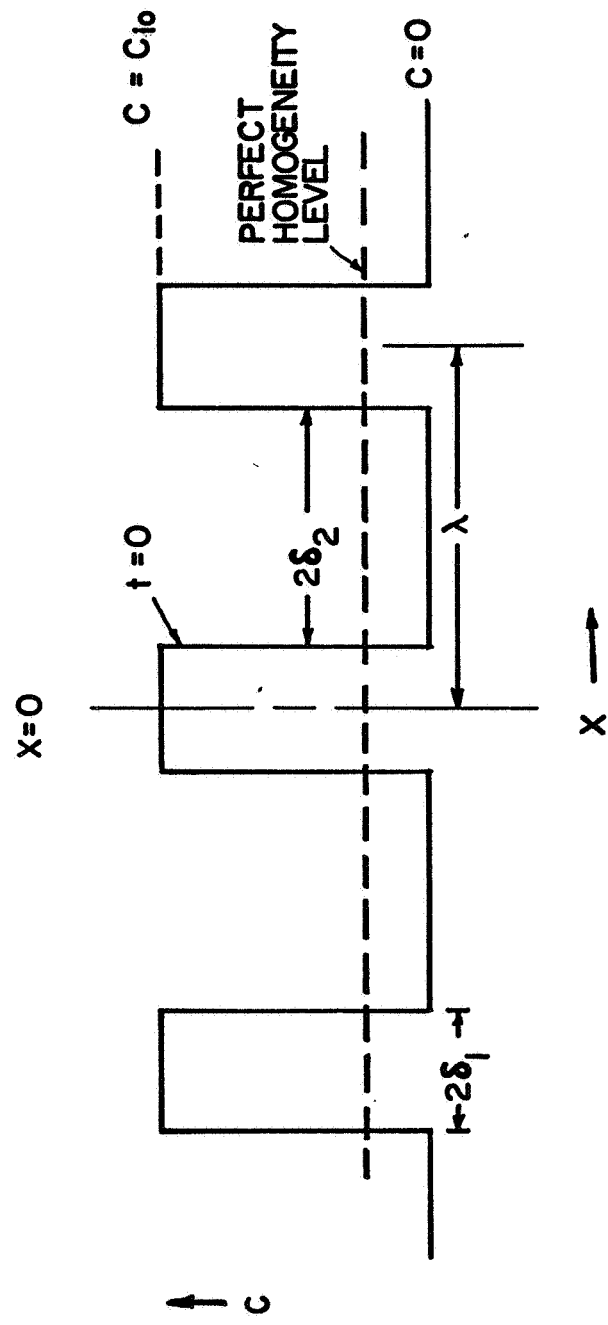


FIG. 8: A HYPOTHETICAL MINERAL COMPOSITE

$$C_i = \frac{1}{2} C_{i0} \sum_{n=-\infty}^{\infty} [\operatorname{erf}\{(\delta_1 + 2n(\delta_1 + \delta_2))/2\sqrt{(Dt)_{\text{eff}}}\} + \operatorname{erf}\{(\delta_1 - 2n(\delta_1 + \delta_2))/2\sqrt{(Dt)_{\text{eff}}}\}] \quad (4)$$

where

$$\begin{aligned} (Dt)_{\text{eff}} &= \text{EBDC} - \text{time product for iron} \\ &= \int D_{(T)} \left(\frac{dt}{dT}\right) dT \text{ for iron} \\ &\quad \text{thermal cycle} \end{aligned} \quad (5)$$

Equation (4) can be solved for various ratios of δ_1/δ_2 . It can be seen 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.

When $\delta_1 = \delta_2$, a more convenient form⁽²²⁾ of equation (4) for long times is

$$\frac{C_i - 0.5}{C_{i0} - 0.5} \approx \frac{4}{\pi} \exp [-4\pi^2 (Dt)_{\text{eff}}/\lambda^2] \quad (6)$$

The left hand side of equation (6) is just the fractional change in concentration at $x = 0$ above the mean. No significant iron inhomogeneity is detected by the microprobe when $(C_i - 0.5)/(C_{i0} - 0.5) \approx 0.01$. This corresponds to $(Dt)_{\text{eff}}/\lambda^2 \approx 0.12$. If $(C_i - 0.5)/(C_{i0} - 0.5)$ were 0.0005, $(Dt)_{\text{eff}}/\lambda^2 \approx 0.2$.

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

Fig. 9 shows a sketch of an arbitrarily chosen thermal history which would homogenize an iron fluctuation wavelength of 40μ . Significant diffusion occurs only within the shaded area. A variety of thermal histories could be substituted for that shown in Fig. 9. Higher temperatures would permit shorter times while longer times naturally allow lower maximum temperatures.

Table IV is presented to permit additional insight into the thermal history necessary to homogenize 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 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 due to the parabolic relationship between $(Dt)_{\text{eff}}$ and λ .

The above calculation is based upon two main assumptions, namely:

- i. All the iron comes from the mineral itself and not from the meteorite.
- ii. The EBDC follows the Arrhenious relation up to at least 1800°C .

FIG. 9: A POSSIBLE THERMAL HISTORY FOR HOMOGENIZATION
OF A MINERAL COMPOSITE WITH $\lambda = 40\mu$

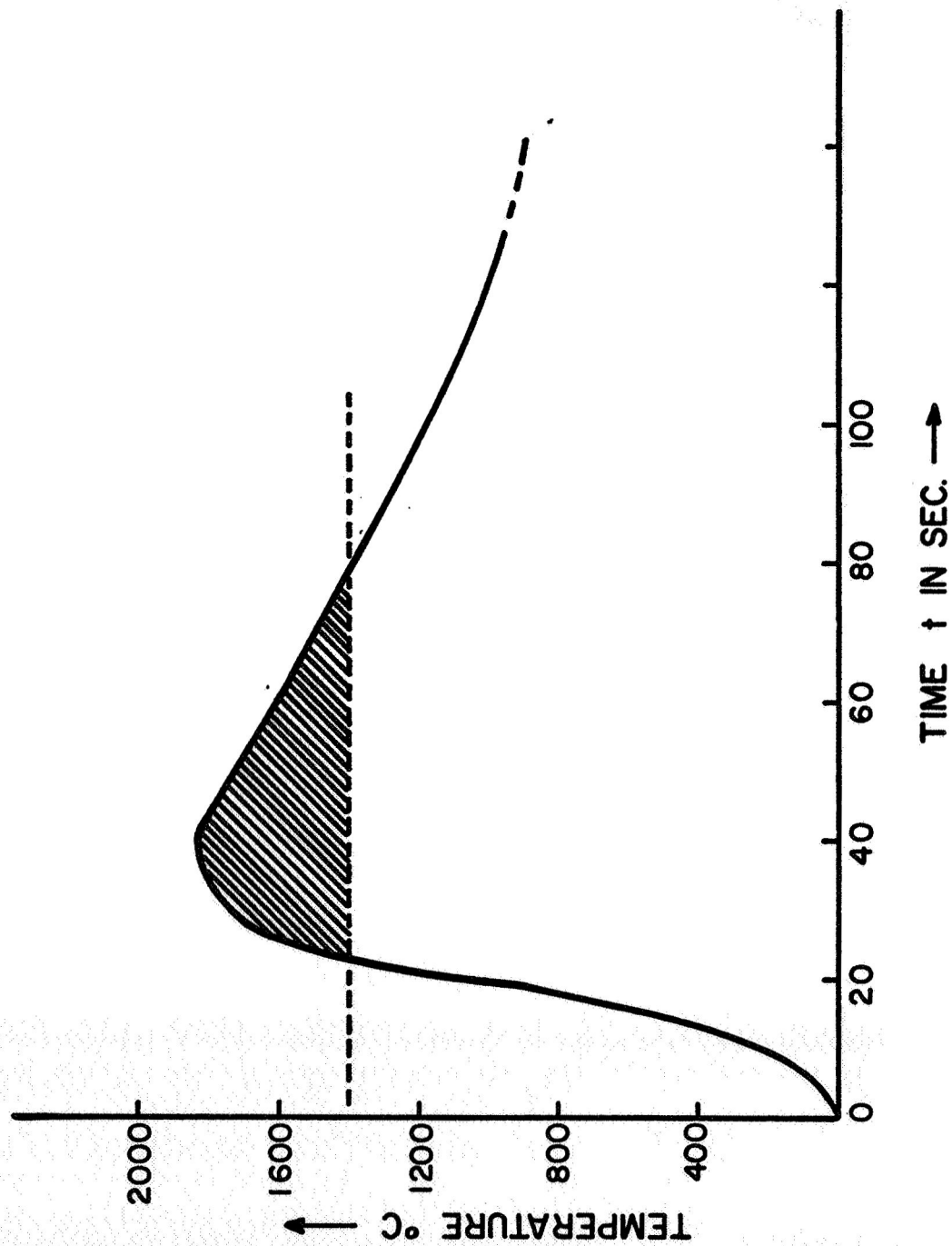


TABLE IV

Homogenization Times at 1550°C and 1800°C for Various Particle Sizes ($\lambda/2$)

λ	$(Dt)_{\text{eff}}$	$t_{1550^\circ\text{C}}$	$t_{1800^\circ\text{C}}$
40 μ	$3.2 \times 10^{-6} \text{ cm}^2$	320 sec	32 sec.
100 μ	$0.2 \times 10^{-4} \text{ cm}^2$	~33 mins.	3.3 mins.
400 μ	$3.2 \times 10^{-4} \text{ cm}^2$	9 hrs.	0.9 hrs.

The first of these assumptions seems likely because the transport of iron through the distances of the order of centimeters for the case of 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 meteorite are very slim.

The second assumption seems plausible and although there is no theoretical basis for expecting Arrhenius behavior of the EBDC, the results shown in Fig. seem to suggest that the Arrhenius rate equation gives a reasonable description of the temperature dependence.

Conclusions

So far the estimates of the thermal history of a Thailand tektite 2172 have been made through considerations of the diffusion behavior of iron alone. It is likely that other rate considerations such as the removal of bubbles and the homogenization of the less mobile species such as silicon would require more extensive thermal histories than the ones calculated here. Even with the data presented here, it is difficult to conceive of obtaining 2172 tektite from Henbury subgreywacke containing 1/2 mm quartz grains unless the temperatures exceeded 1800°C for long times.

Acknowledgments

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