CALCIUM DIFFUSION IN A MUGEARITE MELT

ABSTRACT

The diffusion coefficients of calcium are determined for a range of temperatures from 1230 (D= $1.07\times10^{-7}cm^2/sec$) to 1423°C (D=$3.36\times10^{-7}cm^2/sec$) in a mugearite melt at atmospheric pressure. Diffusion is induced by establishing an initial concentration difference. The diffusion gradient is measured with the electron microprobe in conjunction with a statistical technique which eliminates the need for comparisons with standards, and hence affords a considerable saving in the time required for an analysis. The measured curve is evaluated using methods assuming both composition dependent and constant diffusion coefficients. While the latter gives reasonably consistent results, the former is more appropriate as a composition dependence over the concentration range used is discernible. The activation energy obtained from the estimated coefficients, 29.5 kcal per mole, is shown to be consistent with the classification of calcium diffusion as a Ca^{++} cation controlled process.

The application of mass transfer data to the modelling of diffusion controlled crystal growth in a cooling dike is outlined.

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by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Master of Science.

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July 1970

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INTRODUCTION

General

Shaw (1963) pointed out the need for work on the kinetic properties of natural systems, including information on viscosity and diffusion, in order to better understand the mechanism of intrusion and crystallization of magmatic bodies. Since then an extensive investigation of viscosity has been effected (Shaw et al. 1968, Shaw 1969, Bottinga and Weill 1970), but diffusion coefficients for elements in natural melts have not as yet been determined, no doubt largely a result of the absence of an expedient analytical method to detect the individual concentration gradients in a multicomponent system. The availability of the electron microprobe, however, has prompted the author to examine it as a device for measuring diffusion gradients. The theory and method of analysis are presented in connection with the measurement of calcium diffusion in a mugearite melt, for a range of temperatures. The activation energy of the process is thereby determined.

Previous Work

The geological literature includes several publications concerned with diffusion which are mostly qualitative discussions of its rôle and importance in geological processes. Interest was aroused in the late nineteenth century by proponents of the Soret effect (for a summary see Wahl 1946, and Eitel 1954) but its importance remained questionable. The ensuing controversy prompted Bowen (1921) to undertake the first experimental work in geology from which he obtained estimates of the diffusion rates of the elements of diopside and plagioclase. From his experiments he concluded that diffusion caused by the Soret effect is too slow to account for any appreciable concentration gradients before complete solidification of most igneous bodies.

In 1946, Wahl suggested that differentiation by thermodiffusion (Soret effect plus convection) is important and cited several examples including Mount Johnson with its pulaskite-essexite association (see also Philpotts 1968). Barth (1952) supported his views and argued in favour of the process, although no kinetic data was available to conclusively prove or disprove its importance.

Recently, Oppenheim (1968), to test the possible effects of electrical currents within the earth, has performed experiments in which differentiation is achieved by electrolysis of a molten basalt, and some Soviet workers have revived interest in the Soret effect (Schienmann 1969) and are apparently working on diffusion, although nothing has been published to the author's knowledge.

EXPERIMENTAL PROCEDURE

Method of Diffusion

The method utilized was similar to that used by Bowen (1921), that is, diffusion vertically against gravity caused by an initial concentration gradient. The starting material or base rock was spiked by adding calcium oxide in sufficient quantity to allow detection by the electron microprobe. At the same time, the difference was kept as small as possible to minimize composition dependence of the diffusion coefficient. The diffusion couple was held in a platinum crucible with a .508 cm outside diameter and .0381 cm walls, formed by crimping one end of a tube shut and welding it. The crucible was about 2.3 cm long, thus allowing each part of the diffusion couple to occupy at least 1 cm of constant diameter cross-section. The wall thickness was greater than that absolutely necessary but served to help equalize any temperature gradients along the sample length. The calcium oxide spiked material, being denser than the base material, was placed at the bottom of the crucible to prevent convection.

Sample Preparation

The starting material was a fine-grained dike rock which was crushed and fused in a 50 ml alumina crucible in air for three hours at 1350°C to allow for the degassing of water and other volatiles. Preliminary investigation revealed minor contamination and reaction with the crucible over a distance of much less than 0.1 cm. This contaminated material was discarded and the remainder crushed to 100 mesh and ground in a mechanical agate mortar for forty minutes. Half of this material was weighed into convenient 1.6 gm lots to which 0.046 gm of calcium oxide was added, and these portions were then ground for an additional forty minutes. The other half was retained as the base material. Both spiked and base samples were then fused in platinum for four more hours at 1420°C. The former was reground for another forty minutes and the latter crushed to 50 mesh or less.

A small quantity of spiked powder was added to the crucible and fused long enough to allow bubbles to escape (about 10 minutes). The process was repeated many times until the crucible was half filled. This procedure was necessary to prevent the formation of large bubbles stretching right across the crucible as they would never rise to the surface. The filling was done at 1420°C as the melt was sufficiently inviscid at this temperature to allow rapid degassing. The charge was then left for about twenty hours to allow homogenization after which it was quickly withdrawn from the furnace. A tool steel rod was then forced down the crucible to flatten the meniscus. Material which had coated the upper half of the crucible was then removed by reaming with a flat ended drill rod and a fine silica carbide abrasive. This also formed a flat interface on the glass surface.

The unspiked material had to be added quickly to prevent unwanted diffusion. At the same time, bubble formation had to be avoided. This was achieved by filling the remainder of the crucible with the relatively coarse base material (except at the interface where a fine dusting of powder was used to form a flat surface) and fusing for 15-20 seconds at 1420°C. Because of compaction upon melting, this had to be repeated two or three times, but the aggregate loading time formed an insignificant portion of the total run times and the correction required was insignificant.

Analysis of the Starting Material

The rock was collected from a dike on the eastern side of Mount Royal, Quebec, Canada and the fused material has the bulk and normative compositions given in Table I. These correspond closely to the mugearites described by Muir and Tilley (1961). The analysis recalculated to one hundred percent is used as the base rock analysis and the composition of the spiked rock is also shown. The rock is texturally similar to photomicrograph B in Muir and Tilley (1961) and consists of about 60 percent feldspar (.1mm), 25 percent green altered pyroxene or amphibole (.1mm) sometimes preserved as aligned oxide minerals, 10 percent calcite occuring as small patches throughout the matrix, and 5 percent oxides. Scattered phenocrysts of plagioclase (.5mm) with replaced cores of muscovite and minor scapolite are also present.

To check for iron loss to the crucible, and alkali loss which might occur during prolonged heating, small samples of the base rock were heated for various lengths of time in open platinum crucibles at 1420°C. The results (Table II) indicate insignificant loss compared with the analytical variation of the analyses. The oxidation state of iron was not controlled and the

FeO content was found to have changed from 5.44 to 1.97 percent in a sample fused for 20 hours at 1420°C.

TABLE I

ANALYSES OF THE FUSED MUGEARITE, BASE, AND SPIKED MATERIAL

	Mugearite (fused)	Base rock	Spiked rock
SiO_2	52.87	53.00	51.52
TiO_2	2.00	2.01	1.95
Al_2O_3	18.19	18.24	17.73
Fe_2O_3	2.77	2.78	2.70
FeO	5.44	5.45	5.30
MnO	.19	.19	.19
MgO	3.48	3.49	3.39
CaO	7.43	7.45	10.04
Na_2O	4.60	4.61	4.48
K_2O	2.17	2.18	2.12
P_2O_5	.60	.60	.58
	99.74	100.00	100.00

C.I.P.W. norm	
Q	-
Or	12.81
Ne	-
Ab	38.88
An	22.55
Di	5.71
He	2.70
En	2.44
Fs	1.33
Fo	2.49
Fa	1.50
Mt	4.03
Il	3.80
Ap	1.42
	99.64

TABLE II

IRON AND ALKALI ANALYSES OF BASE ROCK FUSED FOR VARIOUS LENGTHS OF TIME AT 1420°C

Time in minutes	Weight percent		
	FeO*	Na_2O	K_2O
15	7.52	4.60	2.30
60	7.65	4.60	2.11
90	8.15	4.75	2.23
240	7.95	4.60	2.26
1200	7.90	4.73	2.00

* Total iron expressed as FeO

Apparatus

A vertical Pt60-Rh40-wound furnace was used with an internal alumina tube slightly wider than the crucible so that a Pt and Pt87-Rh13 thermocouple could be placed at the midsection of the charge.

The temperature gradient was determined before each run at the run temperature and was always less than 1.5°C over the length of the sample. The temperature was monitored continuously using a digital voltmeter and was kept at ± 2.0°C for the duration of the experiment by adjusting a variac which controlled the external power supply. The run temperature was attained within about two minutes of lowering the crucible into position by preheating the furnace 20 or 30°C above the run temperature.

THEORY

Diffusion Equations

Given an n-component system in which each species, i, is diffusing because of n concentration gradients, dc_i/dx, a general set of equations describing the flux, J_i, of each species is

$$[1] \qquad J_i = D_{i1}\,dc_1/dx + \ldots + D_{in}\,dc_n/dx \qquad i=1,n$$

where the fluxes are considered linear functions of the concentration gradients (Onsager 1945-46). The units of c_i can be expressed in many ways (Bird et al. 1960, pp. 496) and for convenience x-ray counts per cm^3 are used. The number of counts was verified in these experiments to be a linear function of the weight percent calcium oxide, and making the common assumption of negligible volume change on mixing, this unit can thus be considered proportional to grams calcium oxide per unit volume. The D_{ii} (cm^2 per sec) are the main diffusion coefficients of each species i and the $D_{ij}, i \neq j$, are the cross-diffusion coefficients accounting for the effect of concentration gradient j on the flux J_i. These equations have been dealt with for n-component systems where the coefficients are not composition dependent (Fujita and Gostings 1956, Baldwin et al, 1955), but formulation for $n > 3$ in a manner which permits them to be applied to experimental data is difficult and requires extreme precision in measurement. In this work the composition differences, apart from calcium, were so small (see Table I) that no other gradients could be detected. For most practical purposes it is sufficient to determine the diagonal coefficients, Dii, separately and this is the procedure used here. The equations describing the process (i.e. the change in concentration at any time at any position) assume a simple form analagous to those describing heat conduction (Carslaw and Jaeger 1959)

[2] $$\partial c(x,t)/\partial t=\partial^2 DC(x,t)/\partial x^2$$

where c(x,t) is the concentration at position, x, at time, t, and D is assumed dependent on concentration and hence on x. If D is not concentration dependent then [2] becomes

[3] $$\partial c(x,t)/\partial t=D\partial^2 c(x,t)/\partial x^2$$

Equation [3] gives a satisfactory description of the system if the concentration difference between the couples is kept small. Should any dependence exist then an averaged value of D is obtained for the specified composition range.

Evaluation of the Diffusion Gradient

The solution to [3] for some time, $t=T$, assuming an initial concentration difference, C_o, is (Carslaw and Jaeger 1959)

$$[4] \qquad c(x,T)=(C_o/2)(1-\mathrm{erf}(x/2\sqrt{DT}))$$

which can be rewritten

$$[5] \qquad -(2c(x,T)/C_o)+1=\mathrm{erf}(x/2\sqrt{DT})$$

$$=2/\sqrt{\pi}\int_o^{x/2\sqrt{DT}} e^{-\lambda^2}d\lambda$$

$$=2/\sqrt{\pi}\int_o^{x} e^{-\lambda^2/4DT}d\lambda$$

Thus by plotting observed values of the left side of [5] on normal probability paper (Bennet and Franklin 1954) one can obtain an estimate of the second moment about the mean, s, and noting that

$$[6] \qquad s=2DT$$

calculate D, since the run time T is known.

Equation [2] can be utilized to analyse a given concentration gradient employing Boltzmann's integration technique (Jost 1960). Defining a variable, b, such that

[7] , $b=x/\sqrt{t}$

then

[7] $dx=\sqrt{t}db$

and

[7] $dx=b/2\sqrt{t}dt$.

Substituting the above into [2] gives

[8] $bdc/2=d(Ddc/db)$

which can be integrated and rearranged into

[9] $$1/2\int_{0}^{c} bdc=Ddc/db$$

and

[10] $$D=(1/2)(db/dc)\int_{0}^{c} bdc$$

respectively. At the end of a run of duration T [7] becomes $b=x/\sqrt{T}$, so [10] is now

[11] $$D=(1/2T)(dx/dc)\int_{0}^{c(x)} xdc$$

By determining dx/dc graphically at the concentration c(x) of interest, as well as the integral on the right, D can be evaluated at that concentration. The plane x=0 is not necessarily the original interface but is determined such that

[12] $$\int_{0}^{c(x=0)} x\,dc = \int_{c(x=0)}^{C_o} -x\,dc$$

since conservation of mass requires

[13] $$\int_{0}^{C_o} x\,dc = 0$$

The above two methods of evaluation assume that diffusion has taken place in an infinitely extended system. Practically speaking there should be no significant change at the ends of the sample. This was ensured by comparison with standards of the same composition difference, and by verifying that the curve had leveled out a few mm before the endpoints. The composition extremes were then fixed quite accurately by averaging the points in the level parts of the curve.

Measurement of the Diffusion Gradient

The sample was ground along its length to half its thickness and polished to a degree suitable for microprobe analysis. Ten-second counts were taken on a central line along the length of the sample at 0.05 cm, and in some cases 0.025 cm, intervals.

To evaluate the curve, one is interested in obtaining the composition of points relative to each other. If the microprobe was completely stable (no drift, etc.) one could simply analyse each position in turn, with as many ten-second counts as required to gain the desired statistical precision. This is not the case, however, and so the following procedure, utilizing a blocking and randomization scheme (Cochran and Cox 1957), was used to obtain the required internal consistency. A block was taken to be composed of one ten-second count at each of the positions along the length of the sample. The order of the positions analysed was then randomized within each block, and as many blocks as desired were completed. The analysis of each block was performed as quickly as possible. Thus any drift components are incorporated in the variance of the estimate of each position, the precision of the analysis then being

[14]

$$\bar{c}(x) \pm t_{.025,p-1}\hat{\sigma}/\sqrt{p}$$

(95% confidence interval)

where $\bar{c}(x)$ is the mean of the readings at position x, $\hat{s}$ is an estimate of the standard deviation and p is the number of readings (blocks). Up to 32 readings were taken at each position but 12–14 were ultimately found to be sufficient. In general, the precision required and hence the value selected for p would depend on the overall difference in counts between the spiked sample and the base material. In these experiments the range was about 300 counts and the precision obtained with p set at 14 was plus or minus about 20 counts for 95 percent confidence limits, that is, plus or minus 6.7 percent of the total range. A curve obtained using 14 analyses per position is shown in Fig. 1.

The validity of using the absolute number of counts as a measure of the concentration is explained as follows. It was determined for calcium that

$$[15]\quad \begin{matrix}\text{Composition of sample}\\ \text{in weight percent CaO}\end{matrix} = \left[\frac{\text{Counts on sample-background 1}}{\text{Counts on standard-background 2}}\right] \times \left[\begin{matrix}\text{Composition of standard}\\ \text{in weight percent CaO}\end{matrix}\right]$$

which can be rewritten

$$[15]\quad \text{Counts on sample} = \text{Composition of sample} \times \left[\frac{\text{Counts on standard-background 2}}{\text{Composition of standard}}\right] + \text{background 1}$$

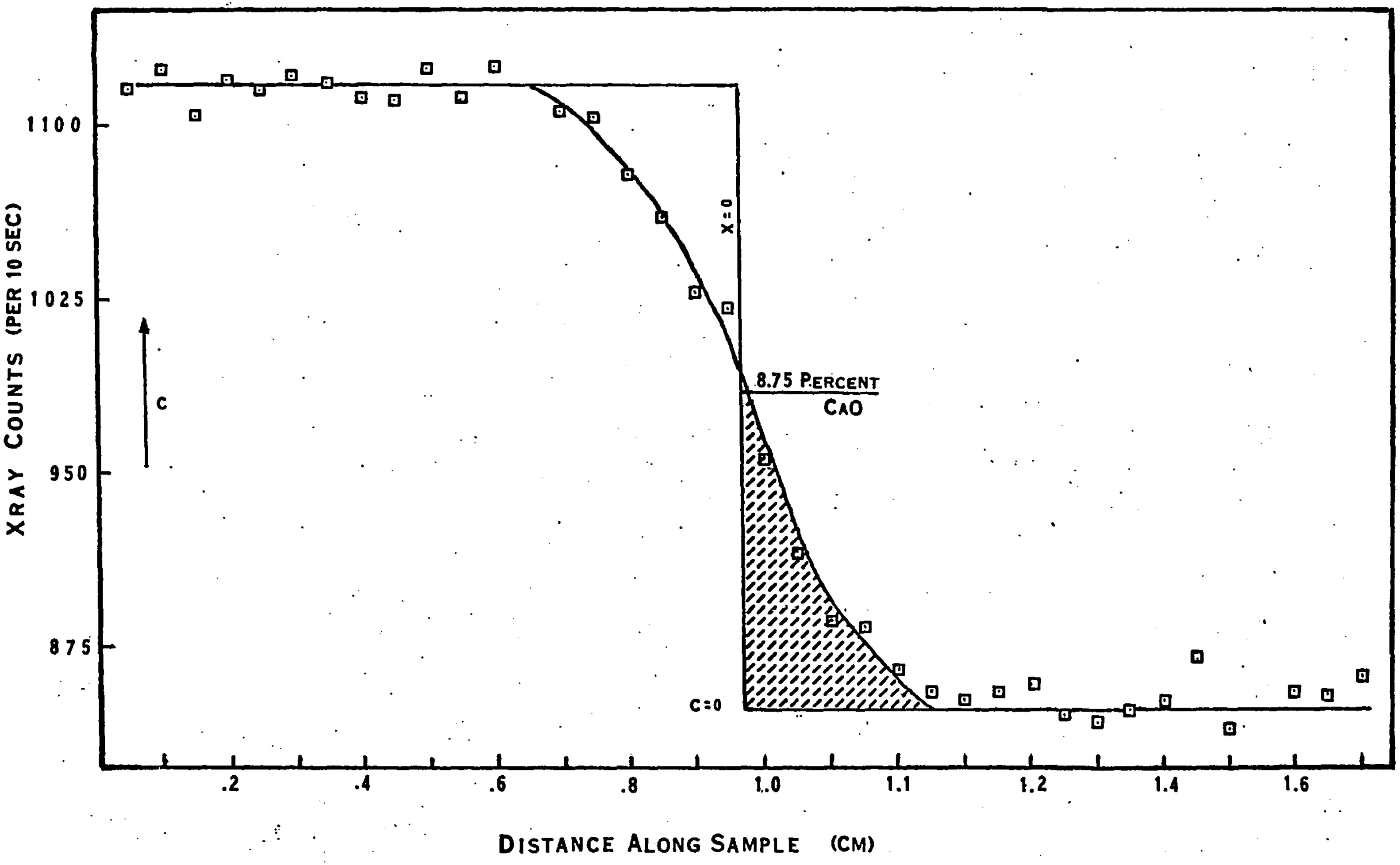
Thus, all other things remaining constant, the number of counts is directly proportional to the composition of the sample.

It is evident from [15] that if a significant average change in "Counts on standard" occurs between blocks (because, say, of a change in the operating characteristics with time) it is not correct to compute the mean of the readings of the same position in the different blocks as each would obviously contribute a disprpportionate weight, and [14] would no longer be valid. Such a change is reflected in a variation of the mean from one block to the next and can readily be corrected by discarding blocks which are significantly different from the others or by multiplying each reading in these blocks by a suitable correction factor.

The procedure outlined above eliminates the need for constant comparisons with a standard to obtain the composition of each position. Assuming that an equal number of measurements would have to be made on both standard and sample to gain a desired precision, this method saves half the time required for the analysis.

Figure 1 An example of the curve obtained from the run at 1344°C of duration 43200 seconds. The line $x=0$ is obtained according to equation [12] and serves as the abcissa for the integration in equation [11]. The shaded portion is the area integrated.

FIGURE 1


XRAY COUNTS (PER 10 SEC)
1100
1025
950
875
C
X=0
8.75 PERCENT
CAO
C=0
.2
.4
.6
.8
1.0
1.1
1.2
1.4
1.6
DISTANCE ALONG SAMPLE (CM)

CALCULATIONS AND RESULTS

Example of Calculation

Concentrations (counts per cm^3) taken from the curve of Fig.1. are plotted on normal probability paper (Fig.2a) according to the method involving equations [3,5]. The run time is T=43200 seconds. The value of x is .137 cm, and using [6]

$$\text{since} \quad s = x^2$$

$$\text{one has } D = s/2T = 2.18\times10^{-7}\,cm^2/sec$$

It can be seen that the points depart from a straight line, which should not occur if D is constant throughout the concentration range. This corresponds to a skewed bell curve when values of dc/dx taken from the graph are plotted against x (Fig.2b), whereas it can be verified that the same differential of [4] is symmetrical.

The analysis of the same run as above using equations [2,11] is for a composition midway between the spiked and base rock composition. Here (see Fig.1)

$$\int_{0}^{c=8.75\%CaO} x\,dc = 14.3 \text{ count-cm}$$

$$dx/dc = 0.00135 \quad cm/count$$

$$1/2T = 1/86400 \quad /sec$$

and so by this method

$$D_{c=8.75\%CaO} = 2.24X10^{-7} \quad cm^2/sec \ .$$

Figure 2 a-An example of the evaluation of the diffusion coefficient using equation 5. The departure of the points from the straight line expected under the assumptions of the model is evident.

b-The departure in 2a is mirrored as a skewed bell curve when dc/dx is plotted against x.

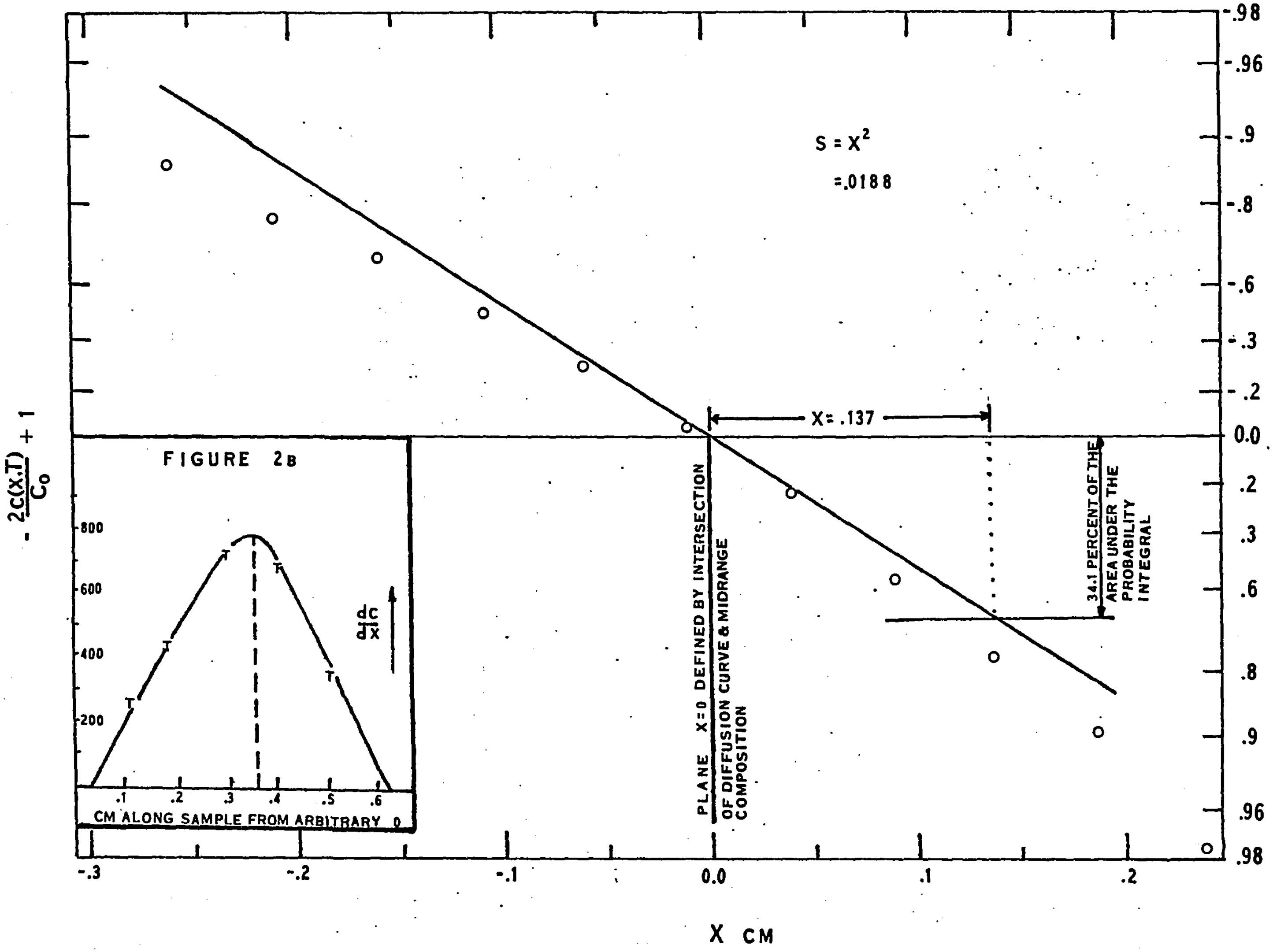

$-\frac{2c(x,T)}{C_o}+1$
.98
.96
.9
.8
.6
.3
.2
0.0
.2
.3
.6
.8
.9
.96
.98
S = X^2
=.0188
X= .137
PLANE X=0 DEFINED BY INTERSECTION OF DIFFUSION CURVE & MIDRANGE COMPOSITION
34.1 PERCENT OF THE AREA UNDER THE PROBABILITY INTEGRAL
FIGURE 2B
800
600
400
200
$\frac{dc}{dx}$
.1
.2
.3
.4
.5
.6
CM ALONG SAMPLE FROM ARBITRARY 0
-.3
-.2
-.1
0.0
.1
.2
X CM

FIGURE 2 A&B

Computed Diffusion Coefficients and Activation Energy

The results using the two methods of evaluation, determinations using [11] made at 8.75 percent CaO, are presented in Table 3. The variation of the diffusion coefficient with temperature, Tm^{o} absolute, can be expressed as an activated process

[16]
$$D=Ae^{-Q/RTm}$$

where Q is the activation energy of diffusion, R the gas constant, and A a pre-exponential constant. Hence changing [16] to

[16]
$$\text{Log}_{10}D=-Q/(2.303RTm)+\text{Log}_{10}A$$

one can estimate Q from the slope of the line of a $\text{Log}_{10}D$ versus 1/Tm plot (Fig.3). The value of Q obtained by least squares is 29.5 kcal per mole and the pre-exponential A is $2.04\text{X}10^{-3}\text{cm}^{2}$/sec.

The errors involved in using the method of equation [11] are extensively discussed by Rhines and Mehl (1938). The chief source of error in these experiments is that a statistical variation in the points requires a subjective fit to be made to obtain the diffusion curve. Thus interpretational differences, especially near the endpoints, cause some variation in the integrated areas. The slope dx/dc, on the other hand, can be estimated quite accurately especially at the midrange compositions. In view of the above, the calculated diffusion coefficients are considered to be accurate to plus or minus 15 percent. From Table III, the estimates using the constant coefficient method [5] are scattered on both sides of the other estimates, and except for one case, are within the limits of error given for the latter. One would expect equation [5] to give results consistently near the midrange composition values when the composition dependence is not too severe, as is the case in these experiments. These estimates, however, are considered to be less reliable than the others because of the extension of the probability paper near the edges (Fig.2a). This gives undue weight to the ends of the diffusion curve - precisely the parts which are most difficult to estimate. The exact slope of the fitted line is hence extremely hard to evaluate. Thus the method using equation [11] is preferred. In the limiting case of no composition dependence, equal results would be obtained at all positions (all concentrations) on the curve.

Because of discrepancies in preparation, the CaO content in some spiked samples was found to be .1 or .2 percent lower than quoted in Table I. This was readily compensated for using [11], and was judged to have no significant effect on estimates utilizing [5].

TABLE III

CALCULATED DIFFUSION COEFFICIENTS

- cm^2/sec -

Temperature °C	Composition Dependent D Method	Constant D Method
1230	1.07	1.93
1265.5	1.49	1.56
1300	1.63	1.47
1344	2.24	2.18
1389.5	2.87	2.93
1423	3.36	2.95
	$X10^{-7}$	$X10^{-7}$

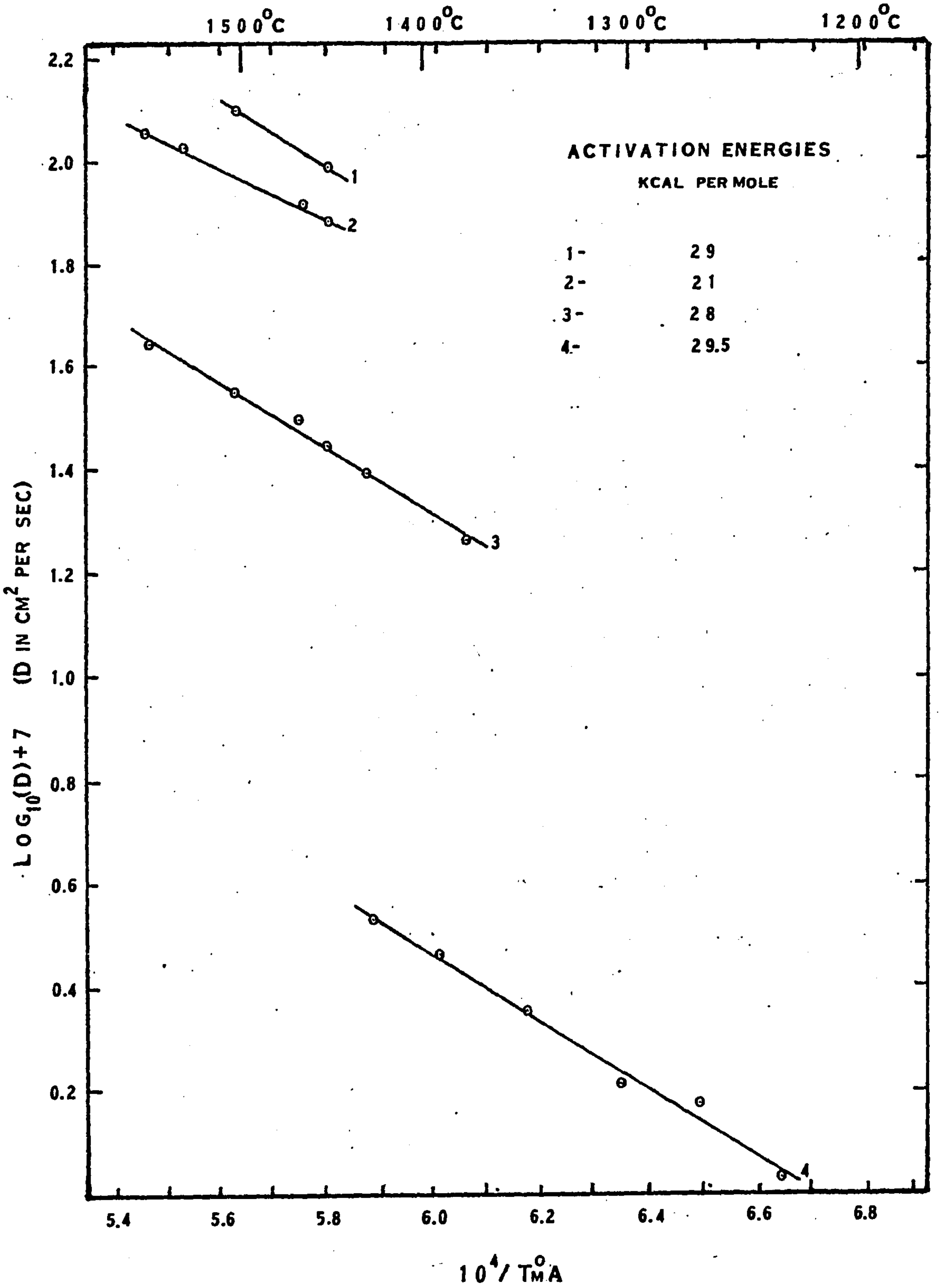
Based on column 1:

Activation Energy $Q=29.5$ kcal/mole

Pre-exponential $A=2.04X10^{-3}cm^2/sec$

Figure 3 Diffusion coefficients obtained by McCallum and Barrett(1952) for slags containing 37.5, 32.5, and 27.5 percent CaO are given by lines 1, 2, and 3 respectively. Each contained 10 percent Al_2O_3, the rest being SiO_2. Line 4 is derived from the mugearite in this investigation, evaluated at 8.75 percent CaO.

FIGURE 3



1500°C
1400°C
1300°C
1200°C
ACTIVATION ENERGIES
KCAL PER MOLE
1- 29
2- 21
3- 28
4- 29.5
1
2
3
4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
LOG$_{10}$(D)+7 (D IN CM^2 PER SEC)
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
10^4/ T°$_M$A

DISCUSSION

Calcium diffusion in $CaO-Al_2O_3-SiO_2$ systems of various proportions was followed by McCallum and Barrett (1952), and their results are plotted in Fig.3. The activation energy at 27.5 percent CaO was determined to be 28 kcal per mole which is remarkably close to that in the present work, although their coefficients are about one order of magnitude higher. A decrease in the diffusion rates is evident for decreasing CaO content, but this observation may be fortuitous as the mugearite melt is compositionally quite different from the slags. Towers et al. (1953) using radioactive calcium determined its coefficients in a slag of 40 percent CaO, 20 percent Al_2O_3, and 40 percent SiO_2. The data showed considerable spread and gave estimates of $3.3X10^{-7}$ and $1.3X10^{-6}cm^2/sec$ at 1350 and 1450°C. The activation energy was calculated to be 70 kcal per mole plus or minus 20 kcal per mole.

To maintain electrical neutrality, either cations plus anions must migrate together (anion controlled diffusion), or the cations must migrate separately (cation controlled diffusion) with some other sort of charge compensating mechanism being operative. In the former case, the activation energy might be expected to be closer to that required for viscous flow, which is an anion controlled process. This activation energy was determined by McCallum and Barrett to be about 46 kcal and hence they proposed that the rate determining step was the jump of a cation from one equilibrium position to another. Their explanation of the charge compensation is not clear and they, themselves, point out that the mechanism is hard to visualize. The results of this work are consistent with this division into anion and cation controlled processes. Euler and Winkler (1957) demonstrated that melts with (Si+Al)/O* ratios between .40 and .47 consistently display viscosity activation energies of 50 to 60 kcal per mole, and hence one would expect this rock, (Si+Al)/O=.430, to have a value somewhere in that range. Consequently the 29.5 kcal per mole estimate obtained here would tend to support a Ca^{++} cation controlled process.

The variation in concentration of the other elements due to the calcium diffusion was unfortunately impossible to record. Presumably it is through cross-diffusion, because of <u>activity</u> gradients of all the species, that the <u>chemical potential</u> of each component in the melt is equalized, and electrical neutrality preserved. As far as the present analytical procedure is concerned, one can only hope to evaluate the diffusion rates of all the elements separately. This approach should,

*in atomic percent

nevertheless, provide a useful phenomenological description of the system at hand, and provide sufficient information, in conjunction with thermal and momentum transport properties, to attempt quantitative modelling of cooling magmas. Bird et al. (1960) give various examples of mass transfer models utilized in engineering analysis, often using simplified approximations where the mathematics becomes intractable. As an illustration, the following description of the growth of a crystal in a cooling dike, using the activated process description of D as a function of temperature, equation [16] , is presented. For simplicity consider an idealized plane crystal of unit area which grows by accretion on each face. Suppose, further, that the growth process is diffusion controlled and the crystal nucleates at time t_o and grows from t_o to t_f, during which time the melt is supersaturated with respect to the crystal by an amount Δc_o; where Δc_o is conveniently expressed in terms of the rate controlling element. Then the change in Δc_o away from the face a distance x after an elapsed time is described by

$$\partial c/\partial t=D(t)\partial^2 c/\partial x^2 \qquad [17]$$

If the substitution

$$dz=D(t)dt \qquad [18]$$

is made in [17] then an analytical solution can be obtained (Carslaw and Jaeger 1959), that is,

[19] $$c(x,z)=2\Delta c_o \operatorname{erf}(x/2\sqrt{z})$$

(for x positive)

assuming growth on two faces, and that the crystals do not compete for material. The mass of the crystal, M, (expressed in terms of the rate controlling element) is obtained by integration of $2\Delta c_o$ less [19]

[20] $$M=2\int_0^{\infty}(\Delta c_o-c(x,z))\,dx \;.$$

The above may be evaluated if z can be procured. Integrating [18] over the time of interest, one has

[21] $$z=\int_{t_o}^{t_f}D(t)\,dt$$

and since it has been shown that

[16] $$D(t)=Ae^{-Q/RTm(t,y)}$$

(where Tm is now a function of time and a specified position, y, in the dike) [21] can be numerically evaluated if a suitable temperature history is available. In this case, ignoring latent heat, one has for a dike of width 2a (Carslaw and Jaeger 1959)

$$\text{[22]}\quad Tm(y,t)=(Tm^{o}/2)\left\{\mathrm{erf}\left[(a-y)/2\sqrt{\kappa t}\right]-\mathrm{erf}\left[(a+y)/2\sqrt{\kappa t}\right]\right\}$$

where κ is the thermal diffusivity and Tm^{o} is the initial temperature. Thus the size of the crystal is ultimately given by equation [20]. To have such a model duplicate the textural variation in a dike would obviously require the incorporation of a suitable nucleation model and much refinement, and it is included merely to outline how phenomenological measurements of diffusion could be employed. For simplicity, only equations for which analytical solutions are available were used, but the sophistication of the model can be increased many-fold by utilizing appropriate numerical techniques.

ACKNOWLEDGEMENTS

The author would like to thank Dr. A.R. Philpotts for guidance during the course of this work. Thanks are also extended to Dr. W.H. MacLean for assistance and discussion regarding the use of the electron microprobe, and to Mr. W. Doig for technical advice.

Funds were made available by Dr. A.R. Philpotts through National Research Council grant No. A-2668.

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