DIFFUSION IN FE-MG OLIVINE
AT ELEVATED TEMPERATURES

by

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ABSTRACT

In the process of deformation of a solid at low strain rates, the rate of atomic migration in the crystal lattice is a critical factor. Experiments designed to measure the diffusion coefficient of Fe in olivine were unsuccessful. It is theoretically shown that at temperatures greater than one-half of the melting temperature the diffusion coefficient of Mg in olivine silicate is an exponential function of temperature and pressure.

$$D_{T,P} = 1.27 \times 10^{-4} \exp(-38{,}000/RT) \exp(-P\ 3.0/RT)$$

The results also indicate that at $T > .5T_m$ and at nonhydrostatic stresses <500 bars the experimentally determined steady state creep of the upper mantle rocks dunite and peridotite may be governed by movement of dislocations. It is shown that the rate limiting parameter in the creep equation is probably the ionic diffusion coefficient in the olivine silicate structure.

RESEARCH OBJECTIVES

The primary objective of the present research was to determine experimentally the coefficient for chemical diffusion of Mg and Fe in olivine and its temperature and pressure dependence. Such data might then be applied to determine the diffusion mechanism and to a re-interpretation of presently known creep rates in olivine. A secondary objective was to apply existing theory to recent experimental results by other authors to determine if theories developed for monotomic and diatomic systems could be extended to the more complicated silicate structures.

Due to the length of time required for each diffusion experiment (100 to 150 hours) and the problems encountered with obtaining good samples (see Experimental Results), the experimental scope of the work was reduced to the problem of determing the diffusion coefficient of Fe into olivine and its dependence on temperature. The theoretical work met with more success and it was concluded that existing theories developed for "simple" materials could be applied to data obtained for olivine crystals.

THEORETICAL FRAMEWORK

Ionic diffusion in crystals is made possible by the presence of lattice imperfections. The abundance of these structural defects can be described by a Boltzman distribution and hence the density of defects should be, and ordinarily is, sensitive to temperature.

Diffusion occurs when an ion or vacancy traverses a free energy barrier in the crystal. The parameter of interest is the activation free energy $\Delta G'$, required to move the ion or vacancy from a "ground state" lattice site to an "excited state" between two lattice sites. It will be shown that the temperature dependence of the diffusion coefficient may be represented by $\Delta H'$, the enthalpy of activation and the pressure dependence by $\Delta V'$, the volume of activation. The necessary theoretical development of the equations used in later calculations will be given under headings of $\Delta G'$, $\Delta H'$, $\Delta V'$.

$\Delta G'$

The thermodynamic description of the motion of a defect between lattice sites was first given by Wert and Zener (1949). They showed that the rate at which a defect traverses a free-energy barrier is:

$$\frac{1}{\tau} = v \exp\left\{\frac{-\Delta G'}{RT}\right\} \qquad (1)$$

where:

v = vibration frequency (lattice) in direction of defect motion

$\Delta G'$ = free energy necessary to move from minimum energy site to the top of the barrier

From Zener's (1952) formulation for the motion of a lattice defect through a cubic crystal, the diffusion coefficient becomes:

$$D = \frac{1}{2} \Sigma_i \; \Gamma_i \; (\Delta X_i)^2 \qquad (2)$$

where:

i = index of the possible jump the defect cou. make

Γ_i = rate at which the ith jump is made

ΔX_i = co-ordinate change (spacial co-ordinates)

In an orthorhombic mineral such as olivine, the diffusion coefficient would become a second rank tensor $[D_{ij}]$ due to the difference in the energy barriers in the three crystallographic directions.

Following Zener (1952), we assume that the most probable jump dominates the diffusion process. All the Γ_i then become equal and the summation over $(\Delta X_i)^2$ reduces to a geometrical factor times the square of the lattice parameter. For diffusion of a sole atom (2) becomes:

$$D = fa^2 \tau^{-1} \qquad (3)$$

where:

a = Lattice parameter

f = geometric factor (usually between 1 and 3)

Combining eq's (1) and (3) and assuming that values for f, a, and ν are known at the relevant temperature and pressure, a calculation of $\Delta G'$ may be made.

$$\Delta G' = -RT \ln\left\{\frac{D}{fa^2\nu}\right\} \qquad (4)$$

$\Delta H'$

The temperature dependence of the diffusion coefficient has been observed experimentally to be of the form:

$$D = Do \exp\left\{- \Delta H/RT\right\} \tag{5}$$

where:

D = diffusion coefficient at absolute temp. T

R = gas constant

$\Delta H'$ = enthalpy of activition

By differentiating eqn (5) partially with respect to 1/T at constant P, we obtain:

$$\Delta H' = -R \left[\frac{\partial \ln D}{\partial (1/T)}\right]_P \tag{6}$$

Thus by measuring D as a function of T, $\Delta H'$ may be calculated.

Using the expression for $\Delta G'$ and basic thermodynamics Sears (1950), we obtain the following theoretical value

$$\Delta H' = \frac{\partial (\Delta G'/T)}{\partial (1/T)}_P \tag{7}$$

Substituting in eqn. (7)

$$\Delta H' = \frac{\partial (-RT \ln D/fa^2 D)}{\partial (1/T)}_P \tag{8}$$

$$= R \left[- \frac{\partial (\ln D)}{\partial (1/T)}_P + \frac{\partial (\ln fa^2 D)}{\partial (1/T)}\right]_P$$

Wert and Zenner (1950) state that the lattice parameter, a, and the frequency of vibration, v, are much less sensitive to changes

in temperature and pressure than is D. Thus $\Delta H'$ may be approximated by:

$$\Delta H' = -R \left[\frac{\partial (\ln D)}{\partial (1/T)} \right]_P \tag{9}$$

$\Delta V'$

The pressure dependence of the diffusion coefficient has been observed experimentally to be of the form:

$$D = Do \exp\left\{ -P \, \Delta V'/RT \right\} \tag{10}$$

where:

D = diffusion coefficient at temp. T and pressure P

R = gas constant

ΔV^1 = activation value for diffusion

By differentiating eqn. (10) partially with respect to P at constant T we obtain:

$$\Delta V' = -RT \left[\frac{\partial \ln D}{\partial P} \right]_T$$

Thus by measuring D as a function of P at constant T, $\Delta V'$ may be calculated.

Using the thermodynamic relation for $\Delta G'$, Sears (1950)

$$\Delta V' = \left[\frac{\partial \Delta G'}{\partial P} \right]_T \tag{11}$$

Substituting in eqn. (11)

$$\Delta V' = -RT \left[\frac{\partial (\ln D)}{\partial P}_T - \frac{\partial \ln (fa^2\nu)}{\partial P}_T \right]$$

If the second term on the right-hand side is assumed to be of

second order importance, (Rice and Nachtrieb, 1963), then we obtain:

$$\Delta V' = -RT\left[\frac{\partial(\ln D)}{\partial (P)}\right]_T \tag{12}$$

Another of the methods used for calculating the activation volume was proposed by Keyes (1963) using the idea of activated processes and an independent calculation of $\Delta G'$. Keyes adopts a strain-energy model in which a torque L, is applied to the two ends of an isotropic solid and the solid is maintained at a constant external temperature and pressure. The work done is then assumed to be used in creating vacancies in the crystal. Keyes (1963) concludes that a measurement of the pressure derivative of the elastic shear modulus and an independent calculation of $\Delta G'$ may be related to the activation volume:

$$\Delta V' = \Delta G' \frac{\partial(\ln \mu)}{\partial (P)}_T - \chi = \Delta G'\left\{\frac{\partial (\ln \mu)}{\partial (\ln V)}_T - 1\right\}\chi \tag{13}$$

where:

μ = elastic shear modules

χ = Isothermal compressibility

from basic thermodynamics:

$$\frac{\partial(\ln \mu)}{\partial(\ln V)}_T = (2\gamma_{th} + \frac{1}{3}) \tag{14}$$

where: γ_{th} = thermal

and thus:

$$\Delta V' = 2\,\Delta G'(\gamma_{th} - \frac{1}{3})\,\chi \tag{15}$$

Keyes (1963) has applied the formula to simple crystals, such as NaCl and KCl and the activation volume turns out to be the same order of magnitude as the atomic volume, although 2 to 5 times smaller.

Employing a hard-shere model for the crystal (perfect crystal with atomic radii equal to the nearest neighbour distance), Lazarus and Nachtrieb (1963) conclude that the activation volume for atomic diffusion in a cubic crystal should vary from .5 to 1.0 atomic volumes, for other crystal symetries they expect smaller activation volumes (<.5 atomic volume) due to the more "open" structures involved. Thus Keyes' theory seems to lie within the hard-sphere model range, although the actual mechanism of diffusion (i.e. interstitial vacancy, or ionic) is impossible to determine from this approach.

There have been other attempts to obtain a value for $\Delta V'$ through the use of theories relating diffusion and melting. Rice and Nachtrieb (1959) with their theory of corresponding states have derived the theoretical relationship:

$$\Delta V' = \frac{\Delta V_m}{\Delta H_m} \Delta H' \qquad (16)$$

where ΔV_m and ΔH_m represent the volume change and enthalpy of melting. It must be remembered that this $\Delta V'$ refers to the activation volume for self-diffusion at the melting temperature and would be of limited value when discussing other diffusion mechanisms at lower temperatures.

INFLUENCE OF GRAIN BOUNDARIES AND DISLOCATIONS

The theories referred to above have dealt with the single crystal assumption; however, the effect of grain boundaries and dislocation "barriers" must not be neglected. The process of grain boundary diffusion can be studied theoretically if use is made of work by Fisher (1951) on the relation between grain boundary and bulk diffusion. The crystalline model is shown in figure 1. Assuming that direct diffusion from A to B is of secondary importance, Fisher derives the modified diffusion equation:

$$\frac{\partial c'}{\partial t} = D' \frac{\partial^2 c'}{\partial y^2} + \frac{2D}{\omega} \frac{\partial c}{\partial x}_{x} = 0 \qquad (17)$$

where:

c' = grain boundary concentration of solute

c = grain bulk concentration of solute

D' = grain boundary diffusion coefficient

D = grain bulk diffusion coefficient

ω = grain boundary thickness

For most periods of time:

$$\frac{\partial c'}{\partial t} >> \frac{\partial c}{\partial t}_{max.}$$

allowing

$$\frac{\partial c'}{\partial t}_{t=\infty} \rightarrow 0 \quad \text{or} \quad c'_{t=\infty} \rightarrow \text{max. value}$$

In this case the approximate solution of equation (17) becomes:

$$c(x_1 y_1 t) = \exp\left\{\frac{-2y}{\omega (\Pi Dt)^{\frac{1}{2}} (D'/D)^{\frac{1}{2}}}\right\} \operatorname{erfc}\left\{\frac{x}{2\sqrt{Dt}}\right\} \qquad (18)$$

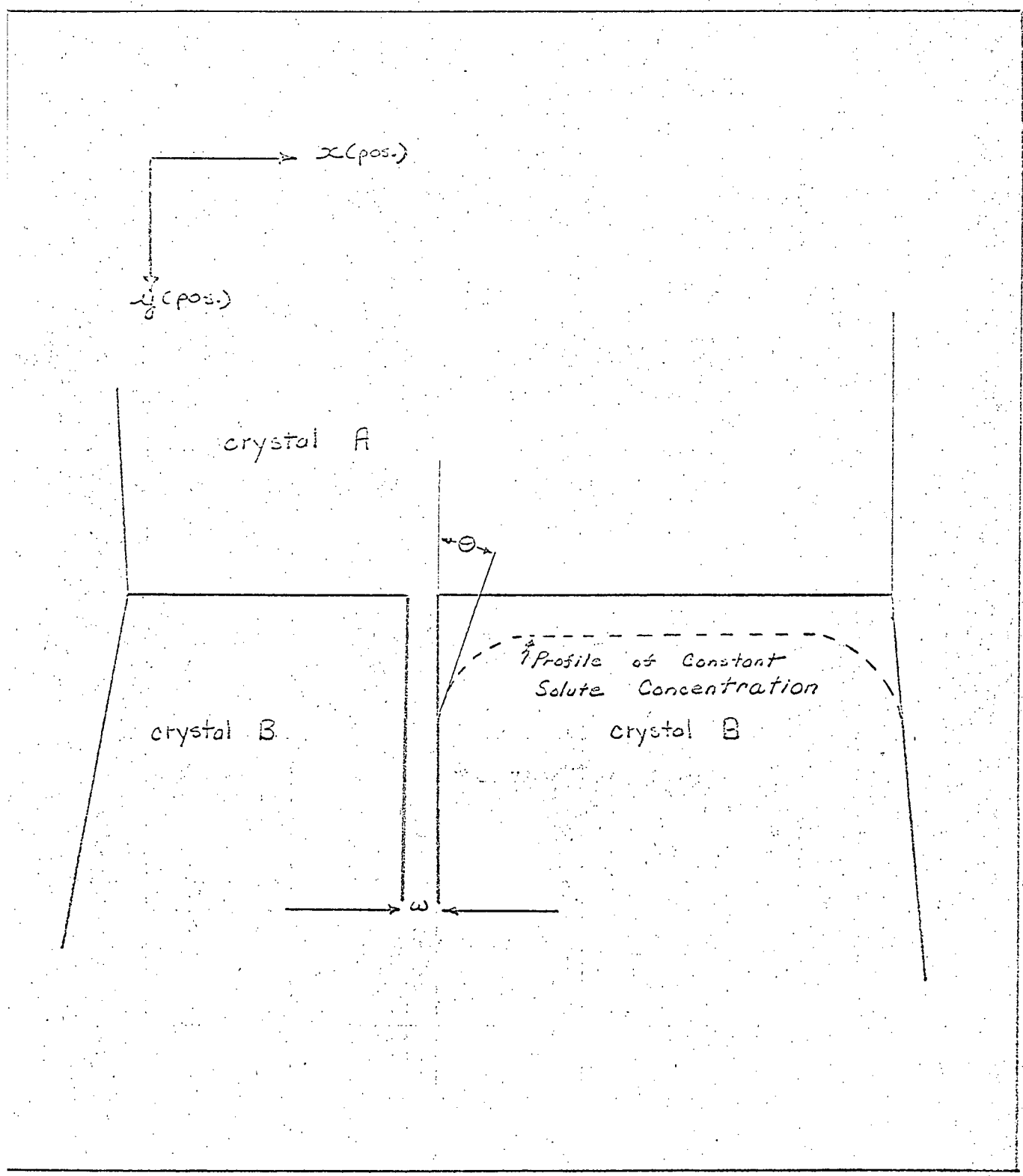


Fig 1. Fisher's Model for Grain Boundary Diffusion

The easiest way to obtain data for this equation would be to measure the amount of solute diffused into a thin slab "dy" parallel to the free surface. Thus S, the amount of solute in this slab becomes:

$$S = \int_{y}^{y+dy} \int_{-\infty}^{t\ \infty} c(x_1 y_1 t)\,dxdy \qquad (19)$$

The value of D(x,y,t) may be directly obtained from measurement of C(x,y,t) where xy (or near the middle of the grain where boundary effects are negligible).

Further work by Whipple (1954) has shown that for meaningful results appreciable solute concentrations must be obtained. In his solution of the differential equation (17) Whipple (1954) made use of a dimensionless parameter β where:

$$\beta = \left\{\frac{D'}{D} - 1\right\} \frac{\omega}{2\ \ Dt} \qquad (20)$$

Assuming different values for β, Whipple plotted solute concentrations in grain B versus β. For perceptible grain boundary diffusion effects (Θ <85°, see figure 1) he found that

$$\beta > 1.0 \qquad (21)$$

For olivine, at a temperature of approximately 1000°c, using the data of Jander and Stamm (1932)

$$D \simeq 7 \times 10^{-11}\ cm^2/sec$$
$$t = 3.6 \times 10^5\ sec$$
$$\omega = 10^{-5}\ cm$$
$$\beta = 1.0$$

$$\beta = \left\{\frac{D'}{7 \times 10^{-11}} - 1.0\right\} \frac{10^{-5}}{2(7 \times 10^{-11} \times 3.6 \times 105)^{\frac{1}{2}}}$$

$$D' \simeq 7 \times 10^{-8} \qquad (22)$$

Thus D' would have to be 1000 times larger than D to satisfy Whipple's criterion. In many cases (Adda and Philibert, 1966), $\frac{D'}{D}$ is 10^3 or 10^4; however, a value of 10^{-5} for ω is quite large (Adda and Philibert, p.718) and would have to be assumed the maximum allowable grain boundary thickness. Thus both D and D' may be calculated, using eqn's (18) and (19) bearing in mind the above limitations.

Since D' is much larger than D, grain boundary phenomena will dominate the short time, low temperature region. The high temperature, long time region will be dominated by bulk diffusion processes, with the boundaries acting as constant composition sources and sinks for the much slower bulk diffusion processes.

CREEP RATES

Diffusion coefficients once obtained may be applied to calculations of creep rates and viscosity of materials. A general equation for creep rate is (Weertman, 1970)

$$\dot{\varepsilon} = f(\sigma)\, D_{T,P} \qquad (23)$$

where $f(\sigma)$ is a function of the differential stress σ and $D_{T,P}$ is the pertinent diffusion coefficient.

The two creep mechanisms of most interest in geophysics are diffusion or Herring-Nabarro creep (low stress and High temperature) and creep resulting from the "climb" or un-pinning of dislocations (higher stress and high temperature).

In Herring-Nabarro creep (Nabarro, 1948; Herring 1950), the grain boundaries or dislocations are fixed and act only as sources or sinks for the diffusing ions and vacancies. The resulting equation is:

$$\dot{\varepsilon} = \frac{C\,D\,\Delta V'}{k\,T\,a^2}\,\sigma \qquad (24)$$

where:

$\dot{\varepsilon}$ = strain rate

D = diffusion coefficient for vacancies

$\Delta V'$ = activation volume for creep

a = mean grain radius

σ = differential shearing stress

C = numerical constant

In dislocation or Weertman creep (Weertman, 1957), the dislocations have moved as far as possible and have become fixed in position. Creep occurs when the dislocations "climb" out of their pinned positions. This movement is accomplished by the exchange of the dislocation with a vacancy; it is the vacancy diffusion which permits the creep. The resulting theoretical equation derived by Weertman (1957) is:

$$\dot{\varepsilon} = \text{constant} \cdot \frac{D}{M^{\frac{1}{2}}} \left\{\frac{\sigma}{\mu}\right\}^{4.5} \qquad (25)$$

where:

M = density of Frank - Reed sources

μ = shear modules

D = diffusion coefficient for self-diffusion

σ = differential shearing stress

Care must be taken when applying diffusion data to the calculation of creep rates. In calculations of diffusion creep, the vacancy diffusion coefficient is needed and for dislocati creep the coefficient of self diffusion is used. In minerals such as olivine the rate limiting diffusion is probably that of the cations. One might expect the O^{2-} anions to be the rate limiting ones due to their larger size and thus smaller diffusion coefficient. It has been observed however, Passmore et al, 1966) that the O^{2-} diffusion is a grain boundary phenomenum and would have little effect over long periods of time. (see eqn's (18).

Experimental work by Sherby (1962), at high temperatures ($T > .5Tm$) has resulted in an empirical equation of the following form:

$$\dot{\varepsilon} = \text{constant} \cdot D\, g^2 \left\{ \frac{\sigma}{\mu} \right\}^{5.0} \qquad (26)$$

where:

g = grain size

D = diffusion coefficient for self-diffusion

μ = modules of rigidity

σ = differential shearing stress

The "constant" and the power law (5.0) were determined empirically.

The use of cation diffusion data in the aforementioned vacancy-migration creep equations can lead to errors up to approximately 20%, the reason being that the vacancy population is a function of temperature while the base composition differences which provide the diffusion are independent of temperature.

INFLUENCE OF GRAIN BOUNDARIES ON CREEP

In a polycrystalline aggregate, the grain boundary creep is probably the dominant process (REE, Ree and Eyring, 1960). Grain boundary creep is caused by the pile up of dislocations on the boundaries and subsequent sliding of the grains along the boundaries. Ree and Eyring (1960) developed the following theoretical equation for the creep of aggregates of Al and Al-Mg alloy crystals:

$$\dot{\varepsilon} = \sin h \left\{ \frac{\sigma}{\sigma_o} \right\} \exp \left\{ -\Delta H'/RT \right\} \qquad (27)$$

The model was based on a mechanism of thermally-activated self diffusion and the activation energy for creep is assumed to be the activation energy for self-diffusion.

EXISTING EXPERIMENTAL DATA

Rheological processes in the mantle of the earth seem most likely to be controlled by creep in the crystalline state. Nabarro (1948). Specific calculations of the rheological properties require experimental data and these are outlined below.

Sherby and Burke (1967) have presented an excellent review of the experimental data on metals and alloys. The equivalence of the enthalpy of activation for creep and that of diffusion was observed and is illustrated in Figure 2.

A recent book by Askill (1970), extends the data of Sherby and Burke (1967) and also presents data on some oxides.

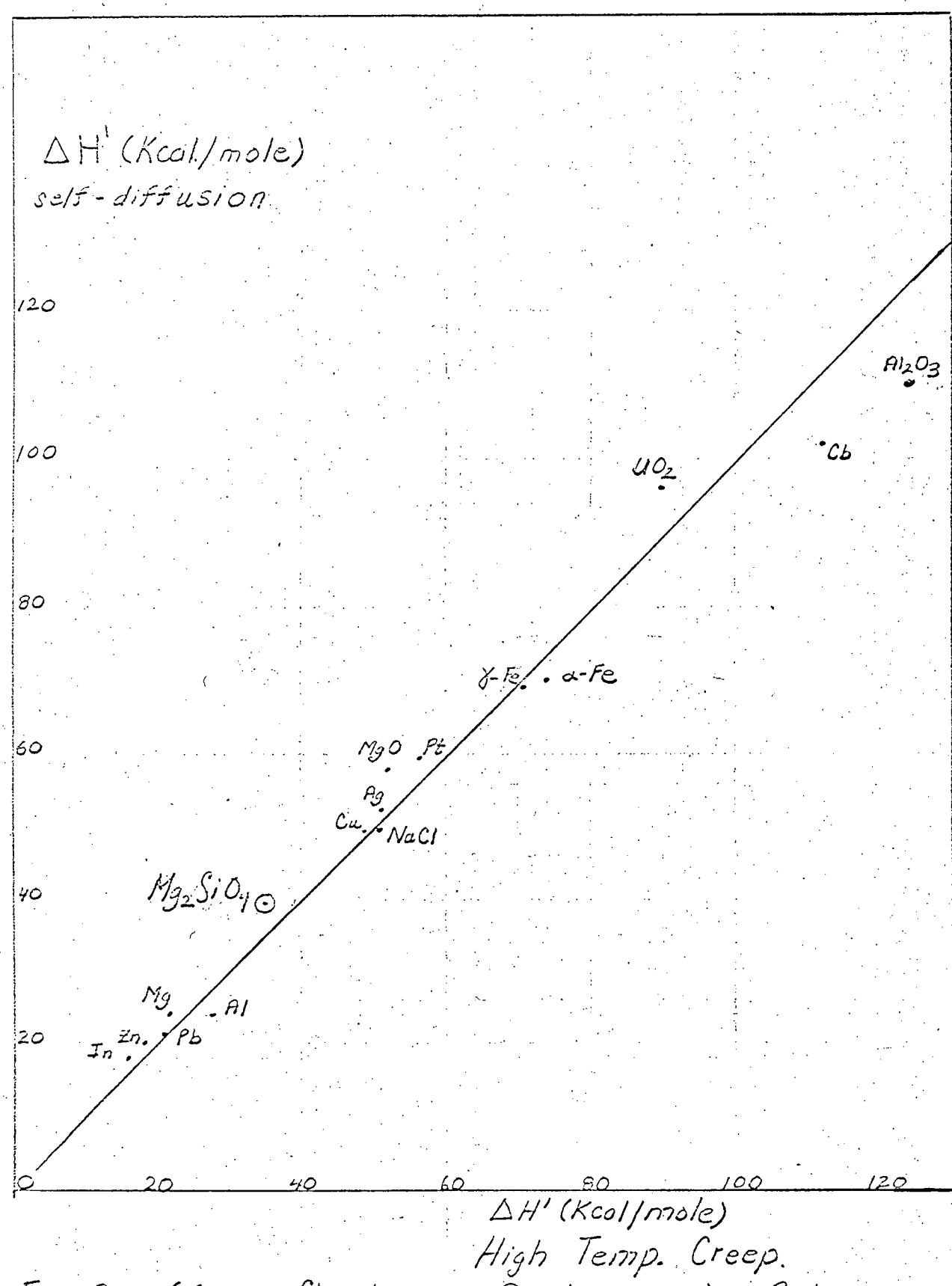


Fig. 2. (from Sherby and Burke, 1967) Relation of $\Delta H_{dif.}$ vs. ΔH_{creep}. {⊙ = point calculated for Mg_2SiO_4 this thesis}

Diffusion coefficients and enthalpies of activation are presented and where possible the experimental conditions of the measurements.

Since the advent of the nuclear reactor and the generation of radioactive "tracers", much work has been done on the rheological properties of ceramic materials used in reactor construction. MacKenzie (1968) has published a summation of this data and used the results to indicate that the region of the upper mantle probably exhibits the same creep processes as evidenced by BeO, MgO, and Al_2O_3.

Diffusion data on geological materials is scanty relative to those on metals and alloys. At present, data are available for the diffusion of various cations (K,Na, and Li) anto SiO_2 crystals at various temperatures and along the different crystallographic axis. Fyfe and Verhoogen (1958) have published a short list of diffusion coefficients of interest in petrology. They discuss the various factors (temperature, pressure and differential stress) influencing the rate of diffusion. Of special interest in this data is the early work of Jander and Stamm (1932) on the diffusion of Mg, Ni, and Ge into silicates, Mg_2SiO_4, Ni_2SiO_4 and germanates, Mg_2GeO_4.

The use of the electron micro-probe in measuring relative abundances of atomic species has become an invaluable tool in diffusion experiments.

Varshneya and Cooper (1969) have used the electron micro-probe in their analysis of diffusion in synthetic tectites. They made a simple one-dimensional diffusion couple and measured concentrations of Fe along profiles at temperatures up to 1490°C.

In the field of Metallurgy, the electron micro-probe is used extensively for diffusion studies and an excellent book has been published which outlines some of these experiments (McKinley, Heinrich, and Wittry, 1966).

Recent measurements reported by Eaton (1968) and Misra and Murrel (1965) on the high temperature creep of dunite, appear to be the only data available for comparison with olivine diffusion data. Eaton observed that up to temperatures of 950°C the strain rate versus temperature followed a modified Ree-Eyring equation and thus he was able to calculate an activation enthalpy for creep.

Misra and Murrel (1965) have made high temperature creep measurements on Norwegian peridotite up to temperatures of 750°C. They observed a linear dependence between the log. of the creep rate and the temperature. This dependence was interpreted as an activation enthalpy for creep.

APPARATUS: GENERAL DESCRIPTION

The basic experimental apparatus consisted of an externally heated, piston-cylinder device, which was placed in a two-post press frame. A one-dimensional diffusion couple was introduced between the opposed pistons and held at constant temperature and pressure for a specified length of time. Upon

completion of each experiment, the samples were cut and polished and examined on the electron micro-probe.

Figure 3 illustrates a cross-section of the pressure system as it was assembled during the experiments. A detailed description of the system may be found in Appendix A. The sample was contained in a small graphite cap-and-sleeve which had the same tolerance as the piston-to-cylinder wall. The pressure system was accurate to ± 200 pounds over the range of operation.

Heat was supplied by a Nichrome resistance furnace and the temperature was measured with standard sheathed chromel-alumel thermocouples. The temperature was controlled by a continuously proportioning bridge with one arm of platinum resistance in the furnace. The temperature was known to an accuracy of ±5°C up to 1000°C. Figure 4 illustrates the temperature controlling and recording apparatus as it was during the experiments. A more detailed schematic of the temperature controller may be found in Appendix B.

CALIBRATION

PRESSURE CALIBRATION

The pressure system was calibrated using a Baldwin Model 120 strain indicator and a Bourdon strain gauge bridge. Both instruments were supplied by the Mineral Engineering Department, U.B.C. The gauge had recently been calibrated by the Mineral Engineering Department to indicate 12.5 pounds applied load equivalent to 1.0 micro-strain units on the bridge. The bridge dial

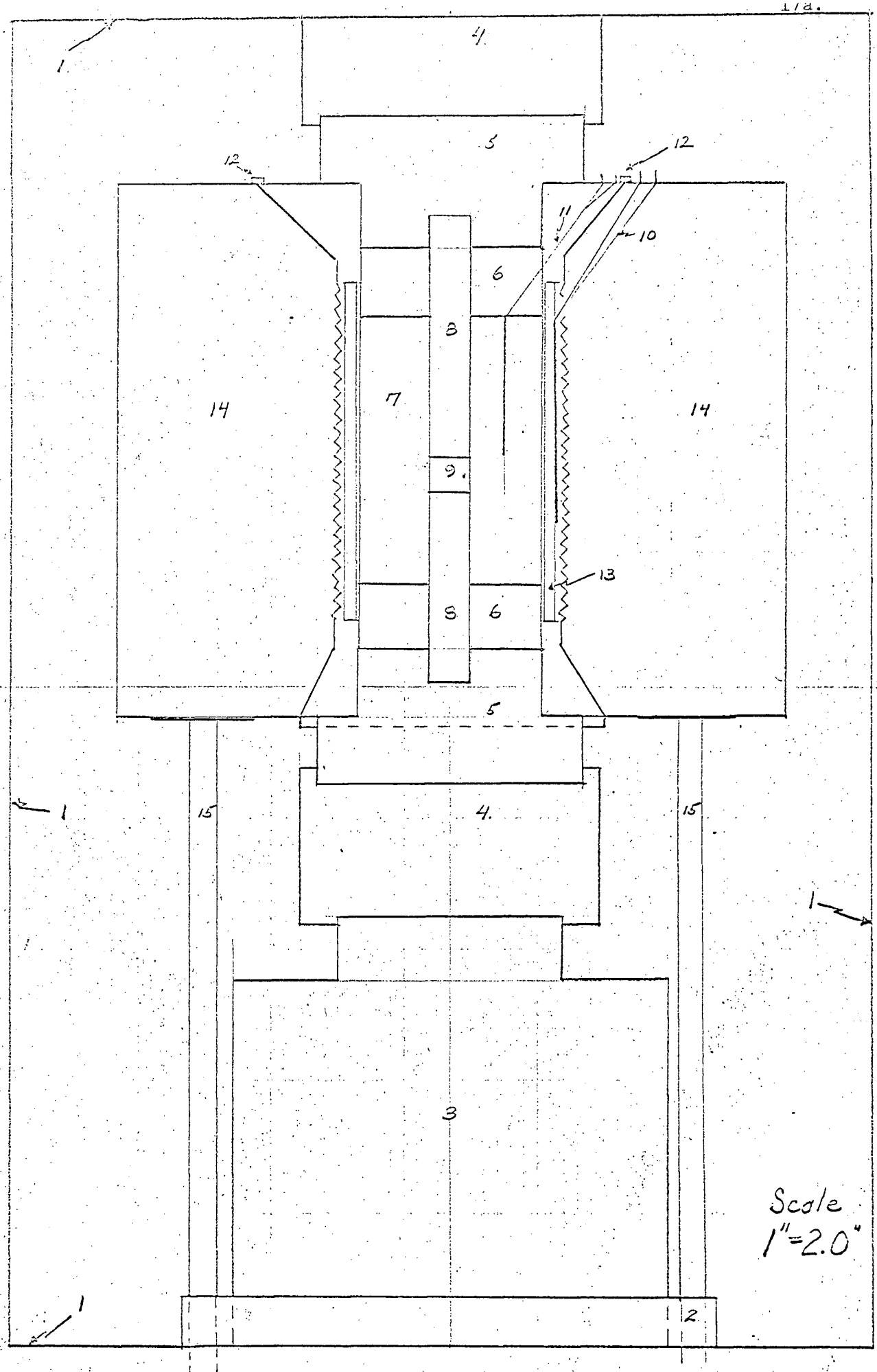


Fig 3. Assembled Pressure Intensifier and Furnace.

Fig. 3 Caption

Item	Description
1.	Press Frame (.8% hot rolled steel)
2.	Ram support ring
3.	Enerpac RLC-100, 100 ton ram
4.	Intensifier Ring (310 Stainless Steel)
5.	Intensifier Ring (Inconnel X-750)
6.	Insulating Rings (Asbestos)
7.	Bomb Cylinder (Rene R-41 Steel)
8.	Pistons (Rene R-41)
9.	Sample (See Fig. 9)
10.	Temperature Controller element (14.5 platinum)
11.	Temperature Recording Thermocouple (Chromel-Alumel)
12.	Power leads to heating element
13.	Ceramic Furnace Core
14.	Furnace (Finebrick and Asbestos Board)
15.	Furnace Support

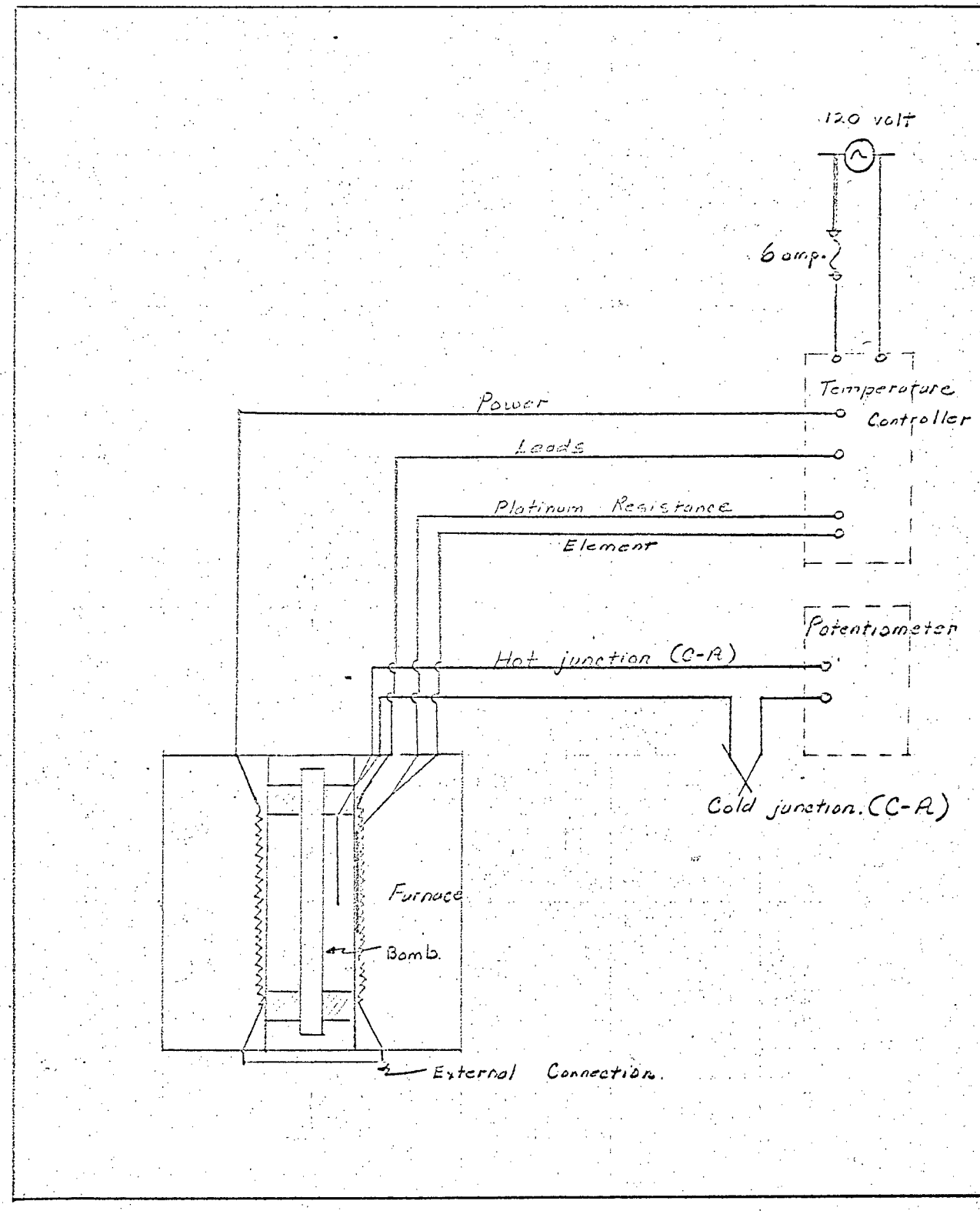


Fig 4. Arrangement of Temperature Controller and Temperature Recorder Apparatus.

was easily readable to $\pm .5$ micro-strain units. For the calibration a small cylinder of Rene R-41 steel of the same dimensions as a sample, was used in the apparatus.

The calibration curve up to 30,000 pounds is shown in Figure 5; the gauge reading refers to the oil pressure gauge on the ram and the load was obtained from the Bordon meter. The best fit line yields the equation:

$$A_1 = 540. + 19.24G \tag{28}$$

where:

A_1 = applied load in pounds

G = gauge reading in p.s.i.

The zero point error is due to the compressing of the insulating rings (see Figure 3) before the pistons take up the applied load. This factor was realized and no runs were made below a gauge setting of 200 p.s.i. The error in reading the ram gauge was $\pm$ 10 p.s.i. which would result in an error of 200 pounds on the applied load. Noting this error, it was found that the experimental calibration agrees with the curve supplied by Enerpac:

$$A_1 = 19.625G \tag{29}$$

where the constant is the surface area of the ram in square inches.

The insulating rings and the distance of the ram from the furnace maintained the ram at all times below 60°C. Thus the pressure was assumed accurate to $\pm$ 200 pounds over the range of operation.

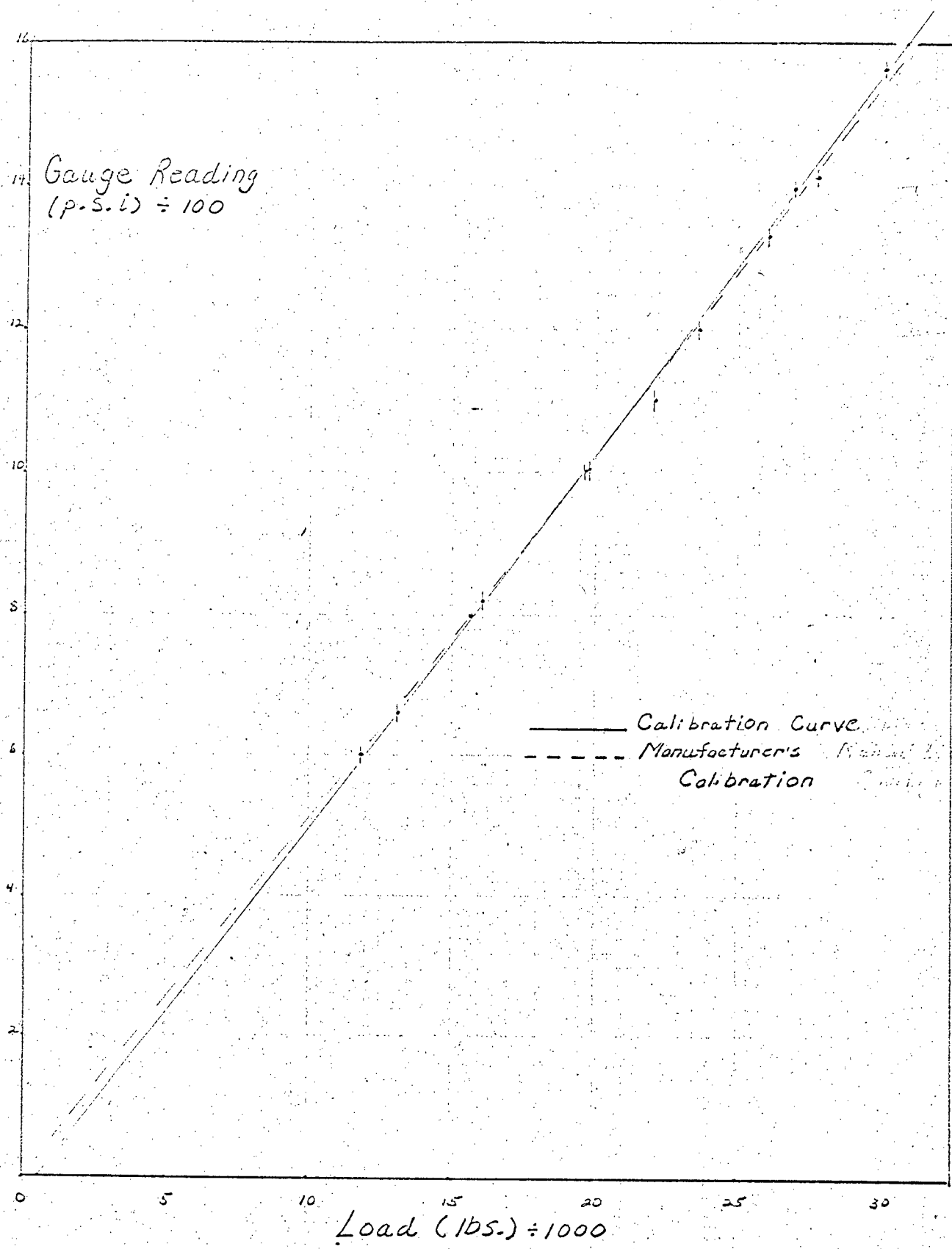


Fig 5. Pressure Calibration

TEMPERATURE CALIBRATION

Aschematic representation of the calibration of the furnace temperature is shown in Figure 6. Before the furnace was calibrated, the thermocouple to be used in the pressure vessel was calibrated against a working standard thermocouple supplied by Dr. H.J. Greenwood of the Geology Department, U.B.C. The W.S. thermocouple had itself been calibrated by Dr. T.M. Gordon of the Geology Department, U.B.C. against U.S. National Bureau of Standards melting points and the corrections to the W.S. were known. The pressure vessel thermocouple was then placed in a high temperature furnace along with the W.S. thermocouple and both temperatures were recorded when the furnace reached equilibrium. Thus the pressure vessel thermocouple was calibrated to N.B.S. melting points.

The calibration of the experimental furnace then proceeded by noting temperatures on the pressure vessel thermocouple and the W.S. thermocouple at various controller settings.

The final corrections to be applied to temperature readings are summarized in the following formula:

$$T_s = T_m - \Delta T \tag{30}$$

where:

T_s = Sample temperature (W.S. thermocouple)

T_m = Pressure Vessel Temperature (Pres. Ves. Thermocouple)

$\Delta T = -T_s + T_m$

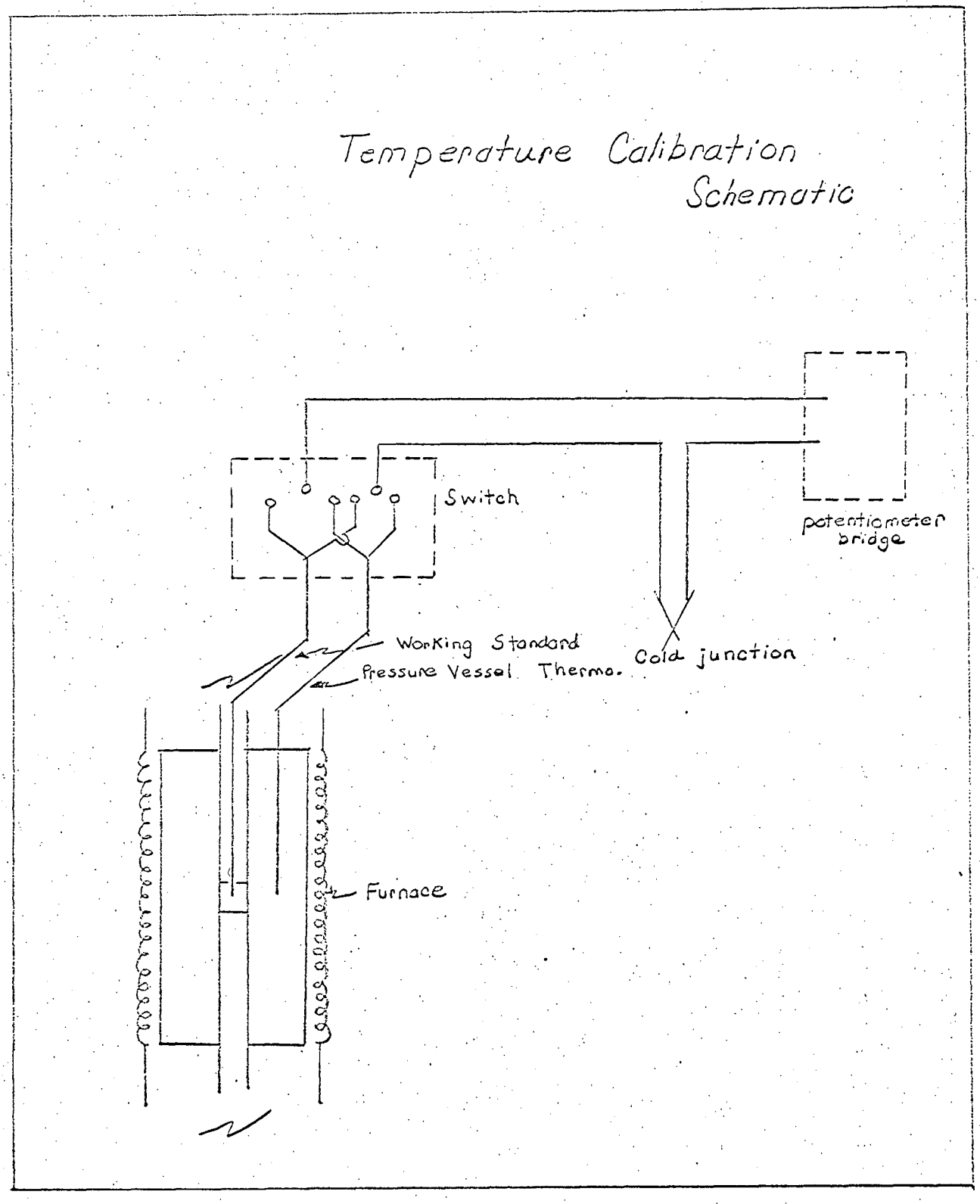


Fig 6. Experimental arrangement for Temp. Calibration

All values of T_s and T_m were corrected to N.B.S. melting points before they were used in the calibration. Errors in these corrections were a second order effect and were neglected. An error of $\pm$ .5°C was allowed for in recording the values of T_s and T_m.

The thermal gradients within the sample cavity were not measured. The point at which the calibrated temperatures were recorded in the sample cavity did not vary by more than .1 inches with respect to the location of the diffusion interface during the experimental runs. A subjective estimate of the temperature error resulting from errors in positioning of the samples was $\pm$3°C. The final accuracy of the temperature calibration was set at $\pm$5°C. The curve of T_m versus ΔT is plotted in Figure 7 and was used during the experimental runs to calculate the sample temperature.

EXPERIMENTAL RESULTS

INTRODUCTION

Three samples of olivine were prepared and "run" at various temperatures to test the feasibility of the experimental arrangement and to correlate the results with theoretical developments. All experiments were of 150 hours duration and the same procedure was followed in each experiment. Upon completion of the experiment, each sample was removed from the apparatus, imbedded in a bakelite holder and prepared for examination on the electron micro-probe.

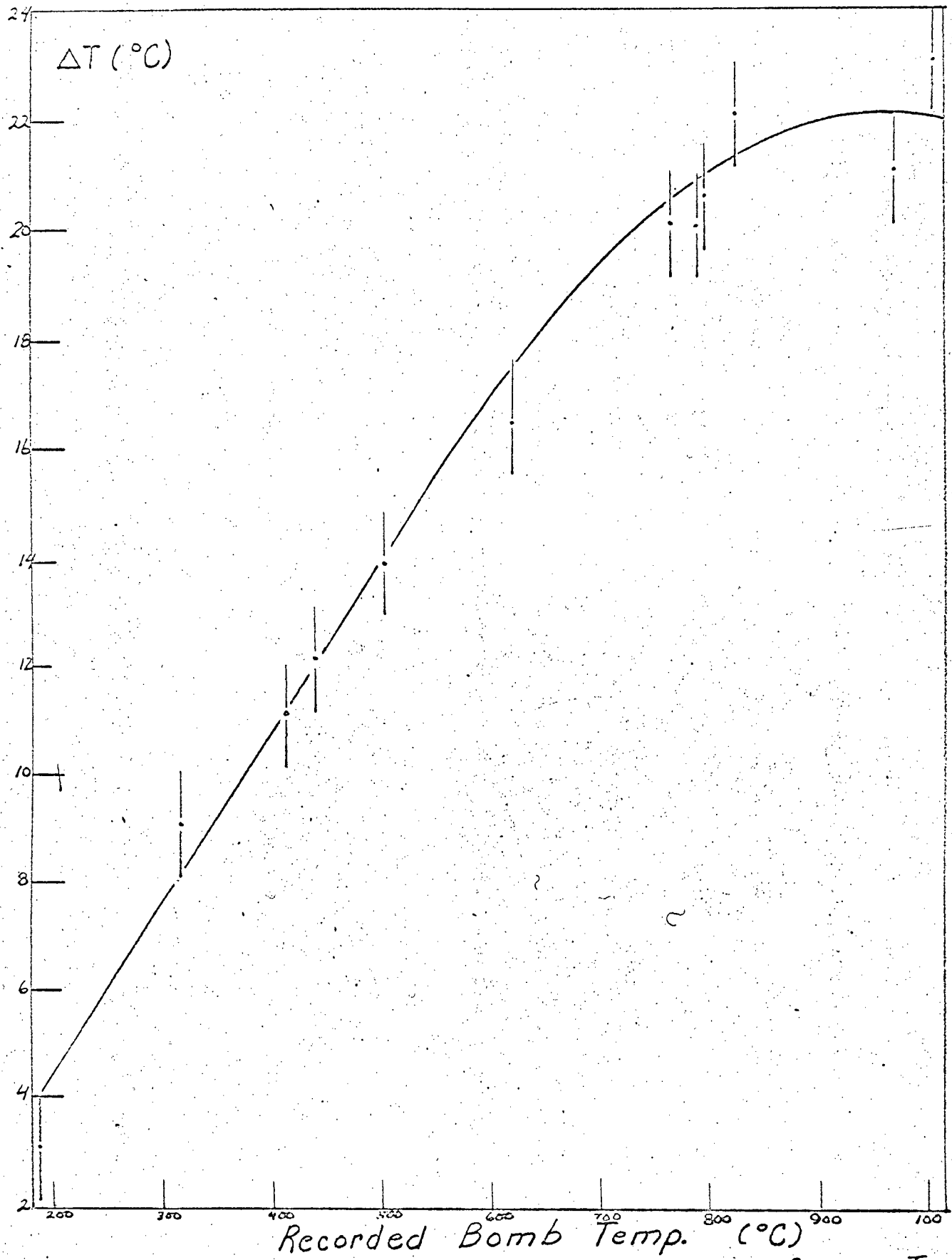


Fig 7. Temp. Difference: Bomb Temp. vs. Sample Temp.

SPECIMENS

The samples used were natural olivine crystals taken from volcanic bombs or flows. The bulk composition was determined using the x-ray diffractometer and the initial concentration of Fe was determined by making random scans over a crystal with the electron micro-probe and taking an average value. Micro-probe scans were also made along the grain boundaries of some of the crystals and it was noted that the Fe concentration did not vary by more than 5% along the edges, relative to the interior of the grains. It was decided to discard the initial 10 microns in the final diffusion profile in order to obtain a more accurate fit of the experimental data.

A small chip of each sample was powdered and to each was added a "spike" of KBr standard. X-ray diffractometer oscillations were made over the d_{130} olivine peak and the 27.03°, 2θ peak for KBr. Using the formula derived empirically be Medaris and Fisher (1969):

$$X = 15.8113\,(3.0358-d_{130})^{\frac{1}{2}} - 7.2250 \qquad (31)$$

where:

X = fraction of forsterite in the olivine

The bulk composition of each sample was calculated (see Appendix C).

Each sample was then polished into a cylindrical shape .2 inches in height and .3 inches in diameter. The contact surface was then re-polished in order to minimize the contact resistance. The other half of the diffusion couple (a mixture of

enstatite of non-constant Fe concentration) was prepared in the same way. The diffusion couple was then mounted in the holder as shown in Figure 8.

The Fe concentration on the grain boundaries in the enstatite was observed on the electron micro-probe to be a factor of from 1.5 to 2.0 greater than in the olivine crystals and thus there was essentially an infinite amount of Fe available for diffusion. The solutions for the diffusion equation in a semi-infinite slab (see Crank 1956, or Jost 1952) could then be applied to the experimental concentration profiles.

EXPERIMENTAL PROCEDURE

Each specimen was prepared as indicated in Figure 8. All the pieces of the pressure intensifier were cleaned before use and the pistons and cylinder wall were lightly rubbed with emery paper to remove any dust particles on the surfaces. The pressure system was then assembled and the furnace was placed around it. The pressure was then applied and in all cases 600 p.s.i. was used in order to obtain good surface contact at a fairly low pressure. At this load pressure the sample pressure (over 0.07 sq. in.) would be approximately 10 kilobars.

The furnace controller was then set and the furnace turned on and left to come to equilibrium; in all cases this equilibrium was reached within three hours. The pressure was then re-adjusted to 600 p.s.i. and the timing of the experiment began.

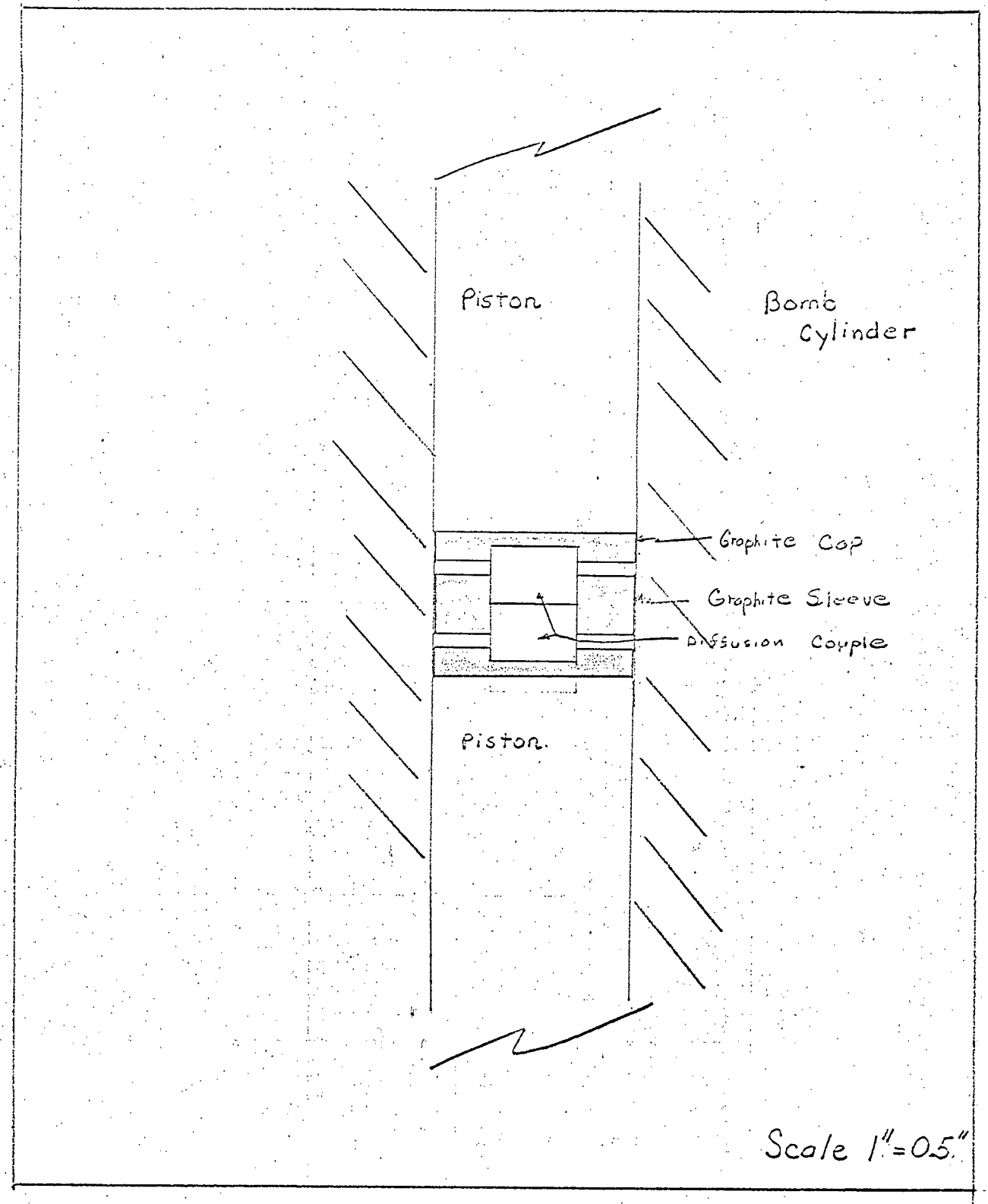


Fig. 8. Specimen Holder and Specimens; arrangement during experimental run.

Three"runs" were made: one at 625°C, one at 750°C and one at 1000°C. The temperature and pressure were recorded at regular four hour intervals and no subsequent adjustment was found to be necessary in the temperature; however, the pressure needed slight "boosts" as it would slowly decrease to 595 or 590 p.s.i. over the space of 50 hours. Thus the temperature and pressure were assumed constant to ±5% over the duration of the experiments. At the end of each "run" the pressure was relieved and then the temperature was reduced quickly; the sample and holder were removed, vacuum sealed in Epoxy and mounted in a Bakelite cylinder. This cylinder was then cut perpendicular to the diffusion surface and polished for probe examination.

After each run, the pressure apparatus was thoroughly cleaned and the pressure vessel thermocouple was checked against the Working Standard.

EXPERIMENTAL RESULTS

Electron micro-probe analysis of the samples produced negative results. At the low temperatures (625°C, 750°C) the samples underwent minor amounts of fracturing which disturbed the coupling surface. An even more serious problem was the fact that the grains became separated by as much as 5 to 10 microns and thus surface and not grain boundary diffusion became the dominant mechanism. The process of surface diffusion is much more complex and the theories presented for grain bulk and grain boundary diffusion do not apply.

At the higher temperature (1000°C) it was observed that the fracturing was still present. In addition, there was some deterioration of the graphite sleeve. The graphite caps (see Figure 8) had fractured and the sleeve was cracked the length of the sample. The sample was tested on the electron micro-probe but no detectable diffusion of Fe had occured.

THEORETICAL RESULTS

Extrapolation of existing diffusion theory and data to estimate the activation parameters of diffusion and the creep rate in olivine is presented below.

The early work of Jander and Stamm (1932) provides values for the diffusion of Mg into Mg_2SiO_4 at two temperatures:

$$D_{1070°C} = 7.14 \times 10^{-11} \quad cm^2/sec$$
$$D_{1200°C} = 1.3---2.6 \times 10^{-10} \ cm^2/sec$$

Substituting these values into equation (6) provides an estimate of $\Delta H'$. The two values of $D_{1200°C}$ result from a difference in the transference number. The value of the transference number refers to the proportion of the flow contributed by the ion in question: a transference number of 1.0 would imply that the total amount of diffusing material would be Mg. If the transference number is 1.0, the higher value of $D_{1200°C}$ is applicable and if the transference number is 0.5 the lower value applies. The following values for $\Delta H'$ were calculated:

t = 1.0	$\Delta H'$ = 38.0 Kcal/mole
t = 0.5	$\Delta H'$ = 18.0 Kcal/mole

From Anderson (1968), the necessary data on polycrystalline forsterite was obtained to allow a calculation of $\Delta G'$. The Equation used was:

$$\Delta G' = -RT \ln \left\{ \frac{D}{fa^2 \nu} \right\} \tag{4}$$

f was chosen to be 1.5; however, changing this constant by a factor of 2 either way will only change the calculation of G' by 5% (Keyes, 1963, p.74).

The value of v was calculated using the formula for the Debye frequency (Kittel, 1966, p.175)

$$\nu_D = \frac{9N}{4\,\Pi V} \left\{ \frac{2}{c_t^{\,3}} + \frac{1}{c_l^{\,3}} \right\}^{-1} \tag{32}$$

where:

N = Avogadro's number

V = Molar volume of forsterite

c_t, c_l = Transverse and Longitudinal Wave Velocities in the Crystal

The wave velocities were assumed to be approximately equal and the velocity along the "c" crystallographic axis in forsterite was used.

$\Delta G'$ was calculated at a temperature of 1343°C and the values of V and c_t were calculated at that temperature using the formulae:

$$c_{t\ (1343°K)} = c_{273°K} + \left.\frac{\partial c_T}{\partial T}\right|_P \Delta T \tag{33}$$

$$\rho_{1343°K} = \frac{\mu_{1343}}{v_{s\,1343}^{\,2}} = \frac{\mu_{273} + (\partial \mu / \partial T)_P \, \Delta T}{v_{s\,273} + (\partial v_s / \partial T)\, \Delta T^{\,2}} \tag{34}$$

where:

$$v = \frac{\text{atomic wt}}{\rho_{1343}}$$

The calculated value of $\Delta G'$ is:

$$\Delta G' \simeq 54.0 \text{ Kcal/mole}$$

This value of $\Delta G'$ may now be used in equation (4) to calculate the activation volume of diffusion. Using the thermal Gruneisen's constant (assumed independent of temperature, Anderson, 1968, p.502) and a value of v_o calculated at 1343°C; $\Delta V'$ becomes

$$\Delta V' = 2\Delta G'(\gamma_{th} - \tfrac{1}{3})\,\chi = \frac{54(2)(.85 - .33)\times 10^3 \times 4.2 \times 10^7}{8.1 \times 10^5 \times 10^6}$$

$$\simeq 3 \text{ cm}^3/\text{mole} \qquad (35)$$

The actual atomic volume to be used for comparison with eqn. (35) must be calculated from the ionic radii of Mg, as no values for $\Delta V'$ have been experimentally determined.

Since the Mg is in 6-fold ionic co-ordination in the olivine structure, the ionic radius is 0.66 Å, which yields an atomic volume of 0.7cm^3/mole. If the Mg is assumed to be in an unexited ground state during the diffusion jump (valence of 0.0) then the atomic volume becomes 13.9 cm^3/mole. Since the calculated value of $\Delta V'$ is 3.0cm^3/mole, we would expect an atomic volume of greater than 6.0 (see page 8). An explanation of the apparent discrepancy between the calculated $\Delta V'$ and actual atomic volumes may be that the calculated activation volume is really an average value calculated over the total diffusion jump distance. The Mg atom would have the ionic activation volume

near the ground state or low energy sites and during the time the Mg atom was near the top of the Free-energy barrier it would have the larger atomic activation volume. A simple average of the two values of activation volume yields a value of 7.6 cm^3/mole which when compared with the value of 3.0 calculated from the combined theories of Keyes (1963) and Zenner (1952) is within the approximate limits set out on page 8 . From these calculations it appears that this strain-energy model may be applied to the more complex diffusion systems, with the same theoretical limits.

The most important test of these calculations of $\Delta H'$ and $\Delta V'$ is to determine if they in turn are equal to the values determined for high temperature creep. Eaton (1968) determined a $\Delta H'$ for creep of dunite of 35.1 Kcal/mole using the Ree-Eyring equation. The samples were dunite consisting of approximately 85% olivine. The olivine was quoted as being 93% forsterite. Not only did the data fit the assumption of Ree-Eyring diffusion creep, as stated by Eaton, but also the calculations of $\Delta H'$ based on diffusion data presented here (38.0 Kcal/mole).

Misra and Murrell (1965) calculated a $\Delta H'$ of approximately 31.0 Kcal/mole. The samples were peridotite consisting of 80% olivine, 15% pyroxene and accesory iron oxides. Unfortunately no calculation of the composition of the olivine was made. Misra and Murrell (1965) state that their calculation of $\Delta H'$ was based on only one measurement at 700°C and may have a large error. Considering this fact and the error of 20% we have allowed in our

estimate of $\Delta H'$ for diffusion, the activation enthalpy for peridotite creep fits the value we have obtained for Mg diffusion in olivine.

Unfortunately, no estimates of $\Delta V_c'$ have been made experimentally. Both Eaton (1968) and Misra and Murrell (1965) performed their creep experiments under the conditions of no confining hydrostatic pressure and thus only the temperature and stress dependence of the creep rate could be calculated.

CONCLUSIONS

EXPERIMENTAL

From the three experiments on olivine samples, no perceptible grain bulk or grain boundary diffusion was observed. This was due to the inferior quality of the specimens and their subsequent breakdown as outlined in the section on experimental results.

After temperature and pressure calibration, the equipment designed for the experiment was found to be accurate to $\pm 5°C$ up to temperatures of 1000°C and accurate to ± 200 pounds up to a pressume of 30,000 pounds. The method of using the electron microprobe to "scan" for various atomic concentration was found to be a useable technique for diffusion distances greater than 10 microns.

THEORETICAL

It has been shown that the enthalpy of activation for diffusion of Mg into Mg_2SiO_4 was 38.0 Kcal/mole, derived from the

data of Jander and Stamm (1932). The activation volume of diffusion for Mg into Mg_2SiO_4 was calculated using eqn's (4) and (15) as being approximately 3.0 cm^3 mole. A general diffusion equation for Mg chemical diffusion in Mg_2SiO_4 may be written:

$$D = 1.27 \times 10^{-4} \exp(-38{,}000/RT) \exp(-P\ 3.0/RT) \qquad (36)$$

where:

R = gas constant (cal/g.mole deg.) or (bar cm^3/mole deg.)

T = temperature (°K)

P = pressure (bars)

D = diffusion coefficient (cm^2/sec)

The pre-exponential constant was calculated from the data of Jander and Stamm (1932).

Weertman (1970) in his calculations of the creep strength of the earth's mantle uses a diffusion coefficient based on Shewman's "rule of thumb" (Shewman, 1963). This rule was empirically derived and states that for most materials a T_m (melting temperature), D is approximately 10^{-8} and at $T_m/2.0$, D is approximately 10^{-16}. Following Weertman's reasoning, assuming the lowest point on the MgO-SiO_2 eutectic represents the melting point of dunite, rather than the melting point of pure forsterite, the melting point becomes 1550°C. A calculation of D in equation (36) using T = 1048°K gives a result of

$$D_{\substack{1048°K \\ P=1\ atm.}} = 1.4 \times 10^{-12}$$

Weertmas states that he tried to circumvent his lack of knowledge of $\Delta H'$ and $\Delta V'$ by using the aforementioned "rule of thumb". It appears from our estimate of $\Delta H'$ and $\Delta V'$ that Weertman's value for $D_{1048°K}$ of 10^{-16} is approximately four orders of magnitude too small.

CREEP RATES

If the steady state creep of mantle materials such as dunite is a diffusion dominated process, the enthalpies of activation and diffusion should be approximately equal. Assuming the chemical diffusion of Mg in Mg_2SiO_4, $\Delta H'$ was calculated to be 38.0 Kcal/mole. Within the 20% estimated error, this value agrees with Eaton's (1968) $\Delta H_c'$ of 35.1 for the steady state creep of dunite and with Misra and Murrell's (1965) H_c' of 31.0 Kcal/mole for the steady state creep of peridotite.

The author knows of no calculation, either experimental or theoretical, for the activation volume of creep. The activation volume of diffusion of 3.0 cm^3/mole calculated in this paper from the theories of Zener (1952) and Keyes (1963) agrees with the hard-sphere crystal model (see page 26) and assuming that the pressure dependence of the creep rate occurs in the diffusion coefficient (see page 11) the activation volume for creep will be assumed equal to 3.0 cm^3/mole.

Weertman (1970) has calculated theoretical creep rates based on a process of dislocation movement (see Figure g) and

has compared his results with those obtained by Eaton (1968). If a recalculation of Weertman's equation (1970, p.151, eqn.9) is made with the determination of the diffusion coefficient in eqn (36) the creep rates are seen to increase and within the error of 20% for $\Delta H'$ agree with the values determined by Eaton (1968) (see Fig.g). Thus it appears that the cationic diffusion in olivine is the dominant process in determining the temperature and pressure dependence of the high-temperature, low stree creep of dunite-peridotite rocks.

Gordon (1965) has made an estimate of the viscosity of the mantle based on a Herring-Nabarro creep model. He assumes an activation enthalpy of approximately 70 Kcal/mole and an activation volume of approximately 10 cm^3/mole from the diffusion of O ions in a periclase structure. Below depths of 400 km. the periclase structure may be the dominant one (Ringwood, 1966), however, Gordon's (1965) calculations of the creep rate above this depth seem dubious. If an olivine structure is assumed for the upper mantle then Zharkov's (1960) estimate of oxygen ion diffusion in olivine should be used. Zharkov's estimate for anion diffusion in olvine was 93.0 Kcal/mole and from the data presented in this paper this value appears to be approximately 2.5 times too large. McKenzie (1968) has stated that the anion diffusion is probably a grain boundary effect and thus would not dominate at temperatures above .5 T_m.

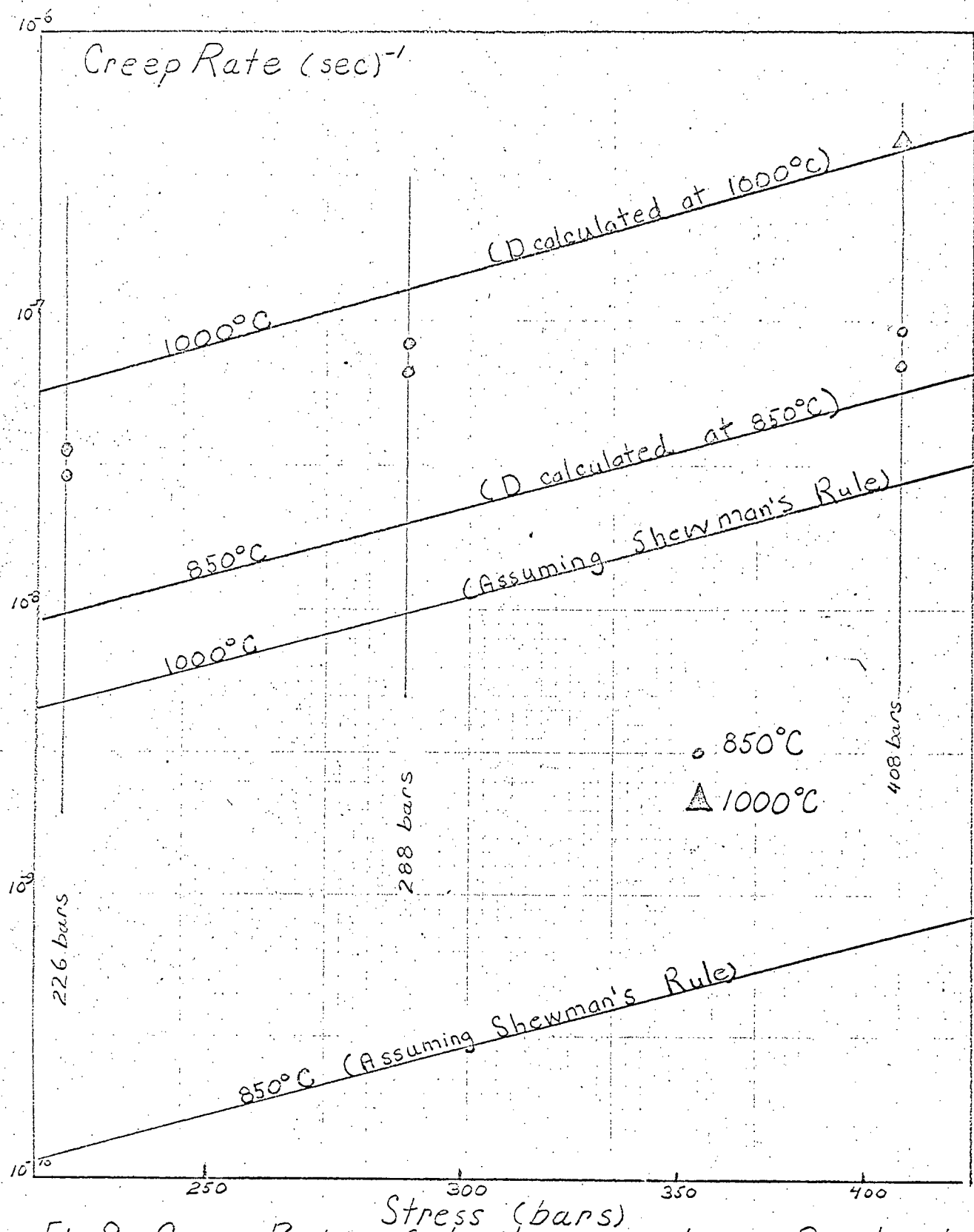


Fig 9. Creep Rate of dunite vs. stress. Dunite data from Eaton (1968). Theoretical curves from Weertman (1970)

It has been shown that the creep rate of upper mantle rocks (above 400 km.) is dependent on temperature and pressure through the cationic diffusion in the olivine silicates. The calculation of creep rates at greater depths must not be made using an extrapolation of the diffusion coefficient presented here. In the region of the mantle below 400 km., calculations of cationic diffusion in minerals having the spinel or rutile structure must be used.

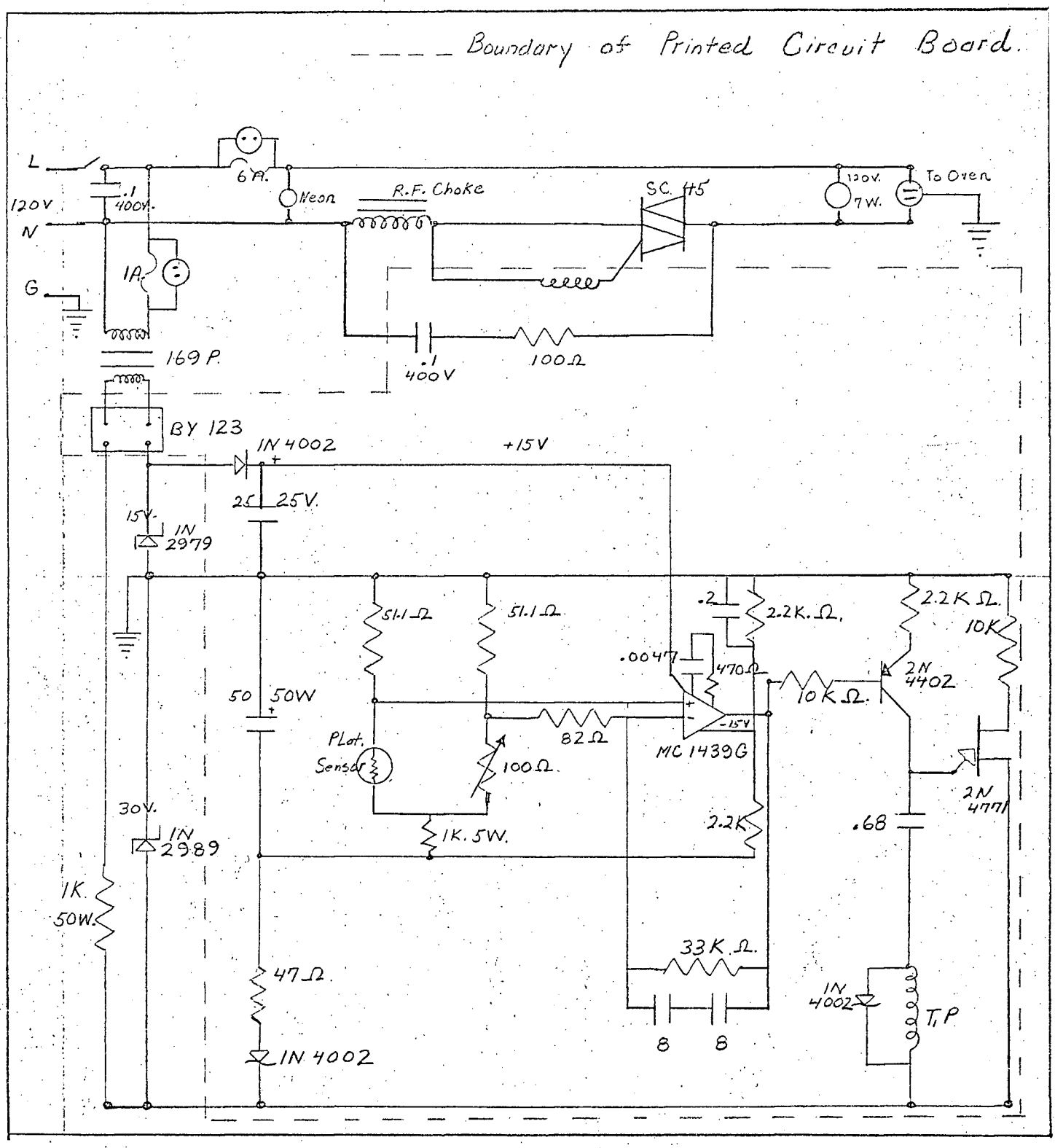
APPENDICIES

APPENDIX A

ENGINEERING SPECIFICATIONS OF APPARATUS

The frame was fabricated from 0.8% carbon, hot-rolled steel. From standard engineering calculations, the elongation of the tensile members would be .002 in. at 100 tons applied load and the deflection of the cross-members would be .003 in. at 100 tons. The yield point of the tensile members if 70,000 p.s.i. and for the deflection members is 42,000 p.s.i. The maximum operating values were 8,000 and 6,000 p.s.i. respectively. Thus, a safety factor of greater than five was obtained, even when operating at ambient furnace temperatures of 1000°C. Threaded nuts were used at the four joints; 4.5 in. nuts had a tensile strength a factor of nine over the applied load and thus assembly ease was gained at no loss of pressure stability.

The central pressure vessel and pistons were made from Rene-R-41 steel (Cobalt-nickel alloy) with a clearance of .001 in. between the pistons and cylinder walls. The pistons were backed on circles of Inconnel X-750 (nickel-steel alloy) and these in turn were backed on circles of 310 stainless Steel. The various alloys were selected for strength as well as resistance to creep at the elevated temperatures.



Appendix B. Circuit Diagram for Oven Temperature Controller

APPENDIX C

Calculation of bulk composition of olivine crystals:

Samples I and II

From diffractometer oscellations:

2θ (degrees)	d spacing (Angstroms)
32.285	2.773
32.280	2.773
32.305	2.771
32.280	2.773

$$\bar{d} = 2.7725$$

$$\bar{d} \cong 2.773$$

From Fisher and Medaris (29):

$$X \text{ Forsterite} = 15.8113 \left\{ 3.0358 - 2.7725 \right\} - 7.2250$$

$$\times \text{ For.} = .8878$$

Samples I and II are approximately 89% For.

Sample III

2θ (degrees)	$d_{(130)}$ spacing (Angstroms)
32.220	2.778
32.230	2.777
32.230	2.777
32.250	2.776

$$\bar{d} = 2.7770$$

$$\times \text{For.} = 15.8113 \left\{ 3.0358 - 2.7770 \right\} - 7.2250$$

$$\times \text{For.} = .8288$$

Sample III is approximately 83% For.

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