DIFFUSION AND DIFFUSION CREEP IN OLIVINE AND ULTRABASIC ROCKS

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The applicability of Winchell’s compensation law relating the activation energy to the pre-exponential constant is examined for diffusion in orthosilicate, and the diffusion coefficients of oxygen, silicon, magnesium and iron in olivine are estimated. Effects of high solid pressure and the partial pressure of $H_2O$ on diffusion are also evaluated by means of the compensation law and Liempt’s empirical law between melting temperature and activation energy.

The rate of diffusion creep in ultrabasic rocks is evaluated. The rate-controlling process of creep changes with temperature; oxygen lattice diffusion is the rate-controlling process at high temperatures, while the oxygen grain boundary diffusion dominates at low temperatures. The strain rate by diffusion creep is so small that diffusion creep cannot be the dominant mechanism for flow at the actively deforming part in the upper mantle. The time and distance required to reach a state of chemical equilibrium between two geologic media in contact are also evaluated by using the values of the diffusion coefficients.

1. Introduction

The diffusion coefficients of O, Si, Mg and Fe in olivine are necessary for understanding geological phenomena such as the anelastic deformation in the upper mantle, ionic exchange reactions between minerals and rock masses, and so forth. Experimental data for the diffusion of major elements in olivine have not been reported except for Mg–Fe interdiffusion in olivine lattice (Miserer, 1971, and Buening and Buseck, 1973).

In this paper, Winchell’s compensation law (Winchell, 1969) relating the activation energy to the pre-exponential factor of the diffusion coefficients is applied to olivine, and the lattice and grain boundary diffusion coefficients of major elements in olivine are estimated. The role of grain boundary in diffusive mass transport in ultrabasic rocks is pointed out.

2. Lattice Diffusion Coefficients for O, Si, and Mg–Fe in Olivine

The chemical composition of natural olivine is $(Mg, Fe)_2SiO_4$, and fur-
thermore we have to consider all the ion species, Si$^{4+}$, Mg$^{2+}$, Fe$^{2+}$, and O$^{2-}$, in order to account for the dynamic properties in the upper mantle. However, the only reliable experimental data available on diffusion in olivine are those of Mg-Fe interdiffusion (MISENER, 1971, and BUENING and BUSECK, 1973). Therefore, we try to estimate the values of the diffusion coefficients for Si and O in olivine.

**Winchell** (1969) presented an empirical relation between the activation energy $E$ and the pre-exponential factor $D_o$ in the expression of the diffusion coefficient $D = D_o \exp \left(-E/RT\right)$ as follows;

$$E = A \log D_o + B \quad (1)$$

where $A$ and $B$ are constants. Equation (1) is generally applicable to all ion species, and further the correlation exhibits less scatter among materials with a similar structure (Winchell, 1969). Figure 1 shows the relation of compensation between $E$ and $\log D_o$ of the Mg-Fe interdiffusion coefficients in olivine, determined experimentally by MISENER (1971) and BUENING and BUSECK (1973). A linear relation is observed, and the Mg-Fe interdiffusion data are represented by

![Fig. 1. Compensation correlation between activation energy $E$ and logarithm of pre-exponential factor $D_o$ for the lattice diffusion coefficients in olivine. The solid line is drawn on the basis of the experimental data of Mg-Fe interdiffusion from MISENER (1971) and BUENING and BUSECK (1973). The hatched area and dotted area show the estimated domains of the lattice self-diffusion coefficients of Si and O in olivine (Fo$_{90}$) to be found. The dashed line shows the relation obtained theoretically (see text). The arrows with symbols of P-up and $P_{H_2}O$-up show the directions of the changes in $E$ and $\log D_o$ associated with increase in hydrostatic (solid) pressure and water pressure, respectively.](image-url)
where $E$ and $D_o$ are expressed in units of cal/mole and cm$^2$/sec, respectively.

The oxygen diffusion coefficient which is calculated tentatively from the experimental observation of the collapse of dislocation loops in olivine during thermal annealing (GoETZE and KOHLSTEDT, 1973) is also plotted in the same figure. The data points lie almost on the straight line (2) determined from Mg–Fe interdiffusion.

STOCKER and ASHBY (1973) presented the estimated diffusion coefficients of oxygen in olivine, based on the experimental data of oxygen diffusion in several oxide compounds and those of deformation in peridotite by CARTER and AvÉ LALLEMANT (1970). As we see in Fig. 1, both of them also lie almost on the line represented by (2).

The empirical relation (1) presented by WINCHELL (1969) can be interpreted theoretically as follows.

The pre-exponential factor $D_o$ in the diffusion coefficients in metals is expressed as

$$D_o = f_a^n v \exp(S/R)$$

where $f$, $a$, $v$, $S$ and $R$ are the dimensionless geometrical factors of the order of unity, the lattice parameter, the frequency of the lattice vibration, the activation entropy, and the gas constant, respectively (ZENER, 1950). Although metals and silicates are quite different materials, the physical context involved is common for all crystalline substances.

KUMAZAWA (1974) derived the activation energy as a function of mean atomic weight $\bar{M}$ and acoustic shear wave velocity $V_s$ as

$$E = b\bar{M}V_s^2$$

where $b$ is a constant. The derivation of $S$ from (4) by $-(\partial E/\partial T)$ gives

$$S = -(\partial \ln V_s^2/\partial T)E$$

which is equivalent to KEYES' (1963) formula

$$S = -(\partial \ln G/\partial T - \alpha)E$$

where $G$ and $\alpha$ are the shear modulus and the thermal expansion coefficient, respectively. Comparing (3) with (5), we have

$$E = c \log D_o + c \log (f_a^n v)$$

where $c = R/(\log e(\partial \ln V_s^2/\partial T))$. Since $c$ and $\log (f_a^n v)$ do not depend on the ion species, and do not change much with temperature, equation (7) has the same expression as (1) which is derived empirically.

The relation between $E$ and $D_o$ in (7) is plotted for olivine by the
dashed line in Fig. 1, using the known physical constants. It is seen that (7) gives a certain degree of approximation, and it is insufficient to use (7) for the estimation of the diffusion coefficient. This is mainly due to the fact that (4) or (6) are rough approximations. It is pointed out that (7) fits quite well with (2), if the numerical magnitude of $S$ is larger by a factor of 2 than that given by (5) or (6). This discrepancy should be resolved in the future.

As a consequence of the systematics shown in Fig. 1, it is pointed out that Winchell's relation seems to hold for the diffusion of different ions in olivine, and that the systematics represented by (2) can be used to estimate the diffusion coefficient of various ion species in olivine.

The only published data on the diffusion of Si in silicate minerals are those for Si–Ge interdiffusion in Zn$_2$SiO$_4$ (Borchardt and Schmalzried, 1972). While Zn$_2$SiO$_4$ has no olivine structure but has a phenacite structure (grouped into nesosilicate which is constructed with isolated SiO$_4^{4-}$ as olivine structure), the relation of $E$ to log $D_o$ in Zn$_2$SiO$_4$ is also represented by the same line (2) as shown in Fig. 1. This fact implies that the value of the diffusion coefficient of Si in olivine is close to that in Zn$_2$SiO$_4$.

We may estimate the value of the lattice selfdiffusion coefficient of Si in olivine (Fo$_{90}$; (Mg$_{0.9}$, Fe$_{0.1}$)$_2$SiO$_4$) as about 100 kcal/mole of the activation energy along line (2). A possible range of domain is indicated schematically by the hatched area in Fig. 1. The numerical expression of this estimation is written as

$$D^{\text{Si}}_{\text{latt}} = 5 \times 10 \exp (-1.0 \times 10^{4}/RT)$$

(8)

where $D^{\text{Si}}_{\text{latt}}$ is the lattice selfdiffusion coefficient of Si in olivine expressed in units of cm$^2$/sec.

The activation energy of lattice selfdiffusion of oxygen is expected to be 130–150 kcal/mole. A possible range of domain is indicated schematically by the dots in Fig. 1. The numerical expression is as follows.

$$D^{\text{O}}_{\text{latt}} = 1 \times 10^{6} \exp (-1.4 \times 10^{4}/RT)$$

(9)

Further, the average value of the experimental results (Buening and Buseck, 1973) of Mg–Fe interdiffusion in olivine (Fo$_{90}$) is expressed as

$$D^{\text{Mg-Fe}}_{\text{latt}} = 7 \times 10^{-2} \exp (-6.5 \times 10^{4}/RT)$$

(10)

The interdiffusion coefficient $D^{\text{Mg-Fe}}_{\text{latt}}$ is obtained from the analysis of the profiles of the Fe diffusion into olivine, and is related to the selfdiffusion coefficients $D^{\text{Mg}}_{\text{latt}}$ and $D^{\text{Fe}}_{\text{latt}}$ by the following expression.

$$D^{\text{Mg-Fe}}_{\text{latt}} = (X_{\text{Fe}} D^{\text{Mg}}_{\text{latt}} + X_{\text{Mg}} D^{\text{Fe}}_{\text{latt}})(\partial \ln a_{\text{Fe}}/\partial \ln X_{\text{Fe}})$$

where $X_{\text{Fe}}$ and $X_{\text{Mg}}$ are the mole fraction of Fe and Mg, respectively, and $a_{\text{Fe}}$ is the activity of Fe (Darken, 1948). The selfdiffusion coefficients of Si and
Fig. 2. Lattice and grain boundary diffusion coefficients in olivine estimated by the compensation law.

O, and interdiffusion coefficient of Mg–Fe in olivine expressed by (8), (9) and (10) are the most reasonable values at the present stage. They are shown in Fig. 2 by the solid lines.

### 3. Effects of High Pressure and Water Pressure on Diffusion

#### 3.1 High pressure effect

The activation energies of diffusion in metals are represented by a linear function of melting temperatures $T_m$ (LIEMPT, 1935, and SHERBY and SIMNAD, 1961) as

$$E = CT_m$$

where $C$ is a constant mainly related to the crystal structure. This relation holds well for different materials with different $E$ and $T_m$. In the case of olivine, both $T_m$ and $E$ are a function of the chemical composition and thus the relations between $T_m$ and $E$ in Mg–Fe interdiffusion (data from BUENING and BUSECK, 1973) are plotted in Fig. 3 in order to see if (11) holds or not for olivine. It is shown in this figure that relation (11) seems to be applied satisfactorily to interdiffusion in olivine. The estimated values of the activation energy of oxygen and silicon diffusion are also plotted in the same figure. The dashed lines show the expected relation (11) in oxygen and silicon diffusion.

The melting temperature of silicates increases with pressure. If a change
of melting temperatures and the associated changes in activation energies under high pressures satisfy (11), we can evaluate the effect of high pressure on the diffusion coefficients using the compensation relation (2). It is noted that the numerical parameters (A and B in (1) or c and log \((f\alpha^0)\) in (7)) are insensitive to pressures and thus the compensation law established at an ordinary pressure is safely applied to high pressures. It is known that relation (11) is compatible with experimental data on metals at high pressures Tsukahara, 1974b).

The rate of increase in melting temperature induced by pressure is about 4.5 deg/kbar for olivine; averaged value of 4 deg/kbar for MgSiO\(_4\) (Davis and England, 1964) and 5 deg/kbar for Fe\(_2\)SiO\(_4\) (Akimoto \textit{et al}., 1967). Therefore, the activation energies for all ion species of lattice diffusion in olivine as a function of pressure \(P\) (kbar) are expressed from (11) as

\[
E(P) = C(T_{m0} + (dT_m/dP)P) = (E_0/T_{m0})(T_{m0} + 4.5 \times 10^{-3}P) 
\]

where \(E_0\), \(T_{m0}\) are the activation energy and the melting temperature at 1 bar, respectively. Further, the corresponding pre-exponential factors are expressed from (2) and (12) as

\[
\log D_0(P) = \log D_{0b} + (2.2 \times 10^{-6}) \log D_{0a} + 1.5 \times 10^{-5}P 
\]

where \(D_{0b}\) is the pre-exponential factor of the lattice diffusion coefficient at 1 bar. The arrow with a symbol of \(P\)-up in Fig. 1 shows schematically the di-
rection of change in $E$ and $\log D_0$ with an increase in hydrostatic pressure.

In Fig. 3, the arrows with a symbol of $P$-up show the directions and amounts of changes in melting temperature and the corresponding activation energy in olivine ($\text{Fo}_90$) applying the hydrostatic pressure of 50 kbar. It is shown that oxygen diffusion with the largest activation energy is affected most significantly by pressure. The numerical values for each species are listed in the last section.

Not only the activation energy but also the pre-exponential factor in the diffusion coefficient is a function of pressure as expected from the compensation law. Therefore, the evaluation of the pressure effect only by changes in the activation energy as has been made (e.g., WEERTMAN, 1970, and STOCKER and ASHBY, 1973) will give an over-estimation of the pressure effect on the diffusion coefficient.

3.2 Water pressure effect

Contrary to the solid pressure, the water pressure has quite a different effect. The melting temperatures of silicates are reduced with water pressure. If the changes of melting temperatures and the associated changes in activation energies under hydrous conditions follow (11), we can evaluate the effect of water pressure on the diffusion coefficients. The decrease of melting temperature with water pressure is caused by $H_2O$ in olivine lattice. The state of olivine under water pressure is regarded as a binary system between olivine and $H_2O$. The binary system between $\text{Mg}_2\text{SiO}_4$ and $\text{Fe}_2\text{SiO}_4$ is followed by a decrease of melting temperature of olivine with the Fe content, and the different values of $E$ and $\log D_0$ in the interdiffusion of Mg-Fe lie on the line expressed by (2) in Fig. 1. Therefore, relation (11) may be assumed to be satisfied also in the case of olivine with $H_2O$. The arrow with a symbol of $P_{H_2O}$-up in Fig. 1 shows schematically the direction of change in $E$ and $\log D_0$ with increase of water pressure.

The reduction of melting temperature is about 200°C by 10 kbar of water pressure (estimated value from the phase diagram on silicate minerals such as garnet and enstatite, YODER and CHINNER, 1960, and KUSHIRO et al., 1968). However, variations in the melting point are non-linear with respect to the water pressure. Therefore, the same type of expression as (12) and (13) is impossible to express the effect of higher pressures. Now we like to demonstrate how much the diffusion coefficients are affected by the water pressure by considering a particular condition; at a water pressure of 10 kbar. The corresponding reduction of activation energies of lattice diffusion of oxygen, silicon, and magnesium and iron when the melting temperature is reduced by 200°C are shown in Fig. 3 by the arrows with a symbol of $P_{H_2O}$-up. They are expressed numerically as follows;
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\[ E^O_0(P_{H_2O}=10 \text{ kbar}) = E^0_0 - 1.5 \times 10^4 \]
\[ E^{Si}_0(P_{H_2O}=10 \text{ kbar}) = E^{Si}_0 - 1.0 \times 10^4 \]  
\[ E^{Mg-Fe}_0(P_{H_2O}=10 \text{ kbar}) = E^{Mg-Fe}_0 - 5.0 \times 10^3 \]  

where \( E^O_0, E^{Si}_0, \) and \( E^{Mg-Fe}_0 \) are the activation energies at 1 bar under dry condition expressed in units of cal/mole. Further, the associated change in \( D_o \) is given by (2) as

\[ D^O_0(P_{H_2O}=10 \text{ kbar}) \approx 6 \times 10^{-2} D^0_0 \]
\[ D^{Si}_0(P_{H_2O}=10 \text{ kbar}) \approx 2 \times 10^{-1} D^{Si}_0 \]
\[ D^{Mg-Fe}_0(P_{H_2O}=10 \text{ kbar}) \approx 4 \times 10^{-1} D^{Mg-Fe}_0 \]  

The diffusion coefficients of O, Si, and Mg–Fe are increased by factors of 20, 8, and 3 respectively, as an effect of 10 kbar of water pressure at 1000°C. It is obvious that the water pressure affects the diffusion coefficients considerably at low water pressure.

4. Rate-Controlling Process and the Strain Rate of Diffusion Creep in Ultrabasic Rocks

The strain rate of diffusion creep is controlled by the diffusion of the slowest ion species to migrate through the fastest path of the two; grain boundary and lattice. The amounts of the mass transported both through the crystal lattice and along the grain boundary in natural rocks must be evaluated in order to determine the rate-controlling process and to evaluate the strain rate.

4.1 Flow equations of lattice diffusion creep

A flow equation of the lattice diffusion creep is given theoretically by HERRING (1950);

\[ \dot{\varepsilon} = 13 D_{latt} V_0 d^2 RT \]  

where \( \dot{\varepsilon} \) is the longitudinal strain rate, \( D_{latt} \) is the lattice diffusion coefficient, \( V_0 \) is the volume of the diffusing unit in lattice, \( \sigma \) is the deviatoric stress, and \( d \) is the grain diameter. In the case of compounds, the diffusion coefficient in (16) is identified as that of the ion species whose diffusion is the slowest and rate-controlling in the creep.

When the oxygen lattice diffusion is the rate-controlling process in the diffusion creep of the olivine aggregate with the grain diameter of 0.5 cm, the flow equation is written by

\[ \dot{\varepsilon}_{latt}(P) = (8 \times 10^{-12} \times 10^{-5} \sigma / T) \exp \left( -\left( 1.4 \times 10^6 + 3.1 \times 10^{-1} P \right) / RT \right) \]  

where \( \dot{\varepsilon} \) is the strain rate in sec⁻¹, \( \sigma \) is the deviatoric stress in bar, \( P \) is the
pressure in bar. The value of $V$ is taken as 11 cm$^3$/mole (= the volume associated with the diffusion of gram atoms of oxygen = (molar volume of olivine)/4).

If the oxygen ions diffuse more rapidly along grain boundary layers, the diffusion of the other ions becomes the rate-controlling process. In this case, the silicon lattice diffusion is the rate-controlling process in the diffusion creep in the olivine aggregate, and the flow equation is written as

$$\dot{\rho}_{\text{latt}}(P) = \left(1 \times 10^{-3} + 1.8 \times 10^{-9} P \sigma / T\right) \exp \left(- (1.0 \times 10^6 + 2.2 \times 10^{-1} P) / RT\right) \quad (18)$$

where $V$ is taken as 44 cm$^3$/mole.

Further, if oxygen and silicon diffuse very fast along the grain boundary layer, the diffusion of magnesium and iron becomes the rate-controlling process in the diffusion creep of the olivine aggregate, and the flow equation is written as

$$\dot{\rho}_{\text{latt}}(P) = \left(8 \times 10^{-7} + 1.2 \times 10^{-10} P \sigma / T\right) \exp \left(- (6.5 \times 10^4 + 1.4 \times 10^{-1} P) / RT\right) \quad (19)$$

where $V$ is taken as 22 cm$^3$/mole.

The effect of the water pressure is evaluated by using (14) and (15) in the calculation of (16).

### 4.2 Grain boundary diffusion coefficients

We have no reliable data on oxides or silicates. In the case of metals, the activation energy for grain boundary diffusion is about one half of that for lattice diffusion (Shewmon, 1963). Stocker and Ashby (1973) assumed $E_{\text{gb}} / E_{\text{latt}} = 2/3$ and $D_{\text{ogb}} = D_{\text{olatt}}$. Since the compensation law is applied to non-crystalline materials such as silicate glasses (Winchell, 1969), it is expected that the compensation law holds for the diffusion along the grain boundary which is regarded as the disordered portion in the crystal lattice. Therefore, the reduction of $E$ should be associated with that of $D_{\text{gb}}$ when we try to estimate the grain boundary diffusion coefficients from the lattice diffusion coefficients.

Assuming that $E_{\text{gb}} = (1/2)E_{\text{latt}}$, and that the same compensation law holds for grain boundary diffusion, the pre-exponential term $D_{\text{gb}}$ for grain boundary diffusion is determined from (2). Further, the pressure effect is evaluated by (12) and (13) as in the case of lattice diffusion. The grain boundary diffusion coefficients are listed in the last section, and are shown in Fig. 2 by the dashed lines with the lattice diffusion coefficients. The assumption, $!E_{\text{gb}} = (1/2)E_{\text{latt}}$, is mainly based on experimental data on metals (Shewmon, 1963). Errors will be introduced by this rough application of data on metals to silicates. However, the above evaluated values of the grain boundary diffusion coefficients will be useful judging from the present technical level in experimental studies.
4.3 Flow equation of grain boundary diffusion creep

The grain boundary diffusion creep was formulated by Coble (1963) as follows;

\[ \dot{\varepsilon} = 4\pi w D_{gb} V \sigma / d^3 RT \]
\[ \dot{\varepsilon} = (4\pi w D_{gb} V \sigma / d^3 RT) \exp (-E_{gb} / RT) \]  

where \( D_{gb} \), \( d \), \( w \) are the grain boundary diffusion coefficient, the grain diameter and the width of the grain boundary layer respectively.

The grain diameter is about 0.5 cm in rocks. The width of the grain boundary layer is of the order of 10 \( \mu \)m, which has been derived from the microhardness on polycrystalline oxides with a little impurity (e.g., Jorgensen and Westerbrook, 1964). This estimated width is larger than that \( 2b \) (\( b \) = the length of Burger’s vector) which was employed by Stocker and Ashby (1973) on olivine polycrystals. Since much impurity should be concentrated at the grain boundaries in natural rocks, the thicker width of the grain boundary is more realistic. Based on the discussion above, the flow equations rate-controlled by grain boundary diffusion are evaluated by (20) in the same way as in the evaluation of (17), (18), and (19);

\[ \dot{\varepsilon}_{gb}^{Mg,P} (P) = (1 \times 10^{-5} + 6.4 \times 10^{-9} P \sigma / T) \exp (- (3.3 \times 10^{4} + 7.2 \times 10^{-3} P) / RT) \]
\[ \dot{\varepsilon}_{gb}^{Si} (P) = (6 \times 10^{-4} + 5.6 \times 10^{-9} P \sigma / T) \exp (- (5.0 \times 10^{4} + 1.1 \times 10^{-1} P) / RT) \]
\[ \dot{\varepsilon}_{gb}^{O} (P) = (8 \times 10^{-3} + 1.3 \times 10^{-9} P \sigma / T) \exp (- (7.0 \times 10^{4} + 1.5 \times 10^{-1} P) / RT) \]  

4.4 Comparison of strain rate between grain boundary diffusion creep and lattice diffusion creep

The strain rate of the grain boundary diffusion creep (21) is compared with those rate-controlled by lattice diffusion; (17), (18), and (19). The slowest ion and the fastest path are variable depending on temperature as indicated by the heavy solid line in Fig. 4.

It is noted that there is a considerable ambiguity in the numerical values of \( D_{o} \), \( E \) and the pressure effect, and thus we have to be careful in deriving any decisive conclusion. However, we can conclude the followings with regard to the flow mechanism in ultrabasic rocks: (i) Within the temperature range expected in the upper mantle of the earth, the dominant controlling mechanism of diffusion creep is the lattice diffusion of oxygen at higher temperature conditions and the grain boundary diffusion at lower temperature conditions. (ii) When the strain rate by diffusion creep is compared with that by dislocation creep given by Tsukahara (1974a);

\[ \varepsilon = 6.3 \times 10^{9} \sigma^{2.7} \exp (-1.2 \times 10^{9} / RT) \]

the strain rate by diffusion creep is so small that the dominant mechanism of
large tectonic flow in the upper mantle can never be the diffusion creep. (iii) However, the diffusion creep is dominant for the deformation in the inactive part of the mantle under low deviatoric stress.

5. Migration Depth of Ion in Minerals and Rocks

The diffusion of ion species is a major process to account for the chemical equilibration in most geologic bodies in contact. Suppose that two homogeneous media are in contact and start to approach the equilibrium state. Once we have the diffusion coefficient of an ion, then we can evaluate the depth $Z$ to which the diffusive migration of the ion takes place. This depth is a possible extent of the exchange reaction of ions (either different elements or isotopes) in mineral grains, or a possible extent of the metasomatic reaction in polycrystalline rocks.

The approximate value of $Z$ is generally given in terms of time $t$;

$$Z = \sqrt{D_{\text{eff}} t^{1/2}}$$

$$= \sqrt{D_{\text{eff}} + 3wD_{\text{gb}}/d} t^{1/2}$$

where the second term in the effective diffusion coefficient $D_{\text{eff}}$ represents the contribution from the grain boundary diffusion in polycrystalline aggregate.

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**Fig. 4.** Strain rates of diffusion creep in olivine with the grain diameter of 0.5 cm at $\sigma = 10$ bar and $P = 1$ bar as a function of the reciprocal absolute temperature. The solid lines with symbols Mg-Fe, Si, and O show the theoretical diffusion creep which are rate-controlled by the diffusion of Mg-Fe, Si and O, respectively. The heavy solid line with O shows the diffusion creep rate-controlled by the slowest ion through the fastest path. The line A indicates the strain rate by dislocation creep (Tsukahara, 1974a).
Fig. 5. Effective diffusion coefficients in olivine with grain size of 0.5 cm at 1 bar under dry condition.

Fig. 6. The relation between the annealing time and the depth of the region where diffusive exchange of various species are reached in equilibrium state when two polycrystalline olivine aggregates (grain size of 0.5 cm) are in contact.

with the grain diameter $d$ and grain boundary width $w$. The numerical values of $D_{\text{eff}}$ are shown in Fig. 5 under the condition of $d=0.5$ cm and $w=10 \mu$m. It is shown that the dominant path for diffusion is changeable with temperature. For example, it is along the grain boundary layer for all ion species at
1000°C. At 1600°C, however, the dominant path is through the lattice for Si and Mg-Fe, while it is along the grain boundary for O.

The relations of $Z$ to $t$ in (22) at 1000°C and 1500°C are illustrated as a function of temperature in Fig. 6. For example, the equilibrium state in partition of Mg-Fe between two polycrystalline olivine aggregates can be reached down to 10 cm depth from the contacting surface in $10^6$ years at 1000°C. However, it takes $3 \times 10^6$ years for oxygen isotopes under the same condition.

On the other hand, the fractionation of oxygen isotopes between two single grains (diameter = 1 cm) in contact does not attain the equilibrium within $2 \times 10^{11}$ years under dry condition at 1000°C. The equilibrium partition of Mg and Fe in the same mineral grains can be reached in $2 \times 10^7$ years.

Such a numerical evaluation of the diffusion or equilibration velocity in silicates is very useful in the interpretation of the known geological phenomena. Further, the competitive different paths will afford some clues in the analyses of the thermal history of rocks, minerals, etc.

6. Summary

The lattice diffusion coefficients are derived by empirical laws as functions of temperature and pressure as follows;

\[
D_{\text{lat}}^0(P) = 1 \times 10^{4+2.4 \times 10^{-5}P} \exp \left(-1.4 \times 10^4 + 3.1 \times 10^{-1}P/RT\right)
\]
\[
D_{\text{lat}}^0(P) = 5 \times 10^{7+1.4 \times 10^{-6}P} \exp \left(-1.0 \times 10^7 + 2.2 \times 10^{-1}P/RT\right)
\]
\[
D_{\text{lat}}^{\text{Mg-Fe}}(P) = 7 \times 10^{-2+1.1 \times 10^{-5}P} \exp \left(-6.5 \times 10^{-2} + 1.4 \times 10^{-1}P/RT\right)
\]

where the lattice diffusion coefficients are expressed in units of cm$^2$/sec, and $P$ is the pressure expressed in units of bar.

The lattice diffusion coefficients at a water pressure of 10 kbar (=total pressure) are as follows;

\[
D_{\text{lat}}^0(P_{\text{H}_2\text{O}=10 \text{kbar}}) = 6 \times 10^8 \exp \left(-1.3 \times 10^4/RT\right)
\]
\[
D_{\text{lat}}^0(P_{\text{H}_2\text{O}=10 \text{kbar}}) = 1 \times 10^7 \exp \left(-9.0 \times 10^4/RT\right)
\]
\[
D_{\text{lat}}^{\text{Mg-Fe}}(P_{\text{H}_2\text{O}=10 \text{kbar}}) = 3 \times 10^{-3} \exp \left(-6.0 \times 10^4/RT\right)
\]

The grain boundary diffusion coefficients are derived as functions of temperature and pressure as follows;

\[
D_{\text{gb}}^0(P) = 2 \times 10^{-1+1.3 \times 10^{-5}P} \exp \left(-7.0 \times 10^4 + 1.5 \times 10^{-1}P/RT\right)
\]
\[
D_{\text{gb}}^0(P) = 3 \times 10^{0+0.8 \times 10^{-6}P} \exp \left(-5.0 \times 10^4 + 1.1 \times 10^{-1}P/RT\right)
\]
\[
D_{\text{gb}}^{\text{Mg-Fe}}(P) = 1 \times 10^{-1+0.4 \times 10^{-6}P} \exp \left(-3.3 \times 10^4 + 7.2 \times 10^{-2}P/RT\right)
\]

A set of diffusion coefficients described in the above is internally con-
sistent and is expected to be most reliable at present, since it is based on a reasonable interpretation of the recently published experimental data and also on the known systematics for the diffusion process.

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