Oxygen self-diffusion along high diffusivity paths in forsterite

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Diffusion profiles of ¹⁸O tracer in single crystals of forsterite following anneals at 1100° and 1200°C have been determined by a depth profiling technique using secondary ion mass spectrometry. The diffusion penetration profiles showed error function forms with developed tails. The profiles were analyzed in terms of diffusion in the forsterite lattice together with a contribution from dislocation. The present results of lattice diffusion lie in the range of the extrapolation of lines on Arrhenius plots reported previously for intracrystalline diffusion in forsterite. The dislocation diffusion coefficients are about 10⁴ times faster than the lattice diffusion at the same temperature. Diffusion along the dislocations takes place within a pipe with radius of about 0.1 nm surrounding the dislocation line. Based on the above results, O diffusion along high diffusivity paths, such as dislocations and grain boundaries, play an important role on the diffusional creep in olivine under laboratory condition.

INTRODUCTION

Rheology of olivine is of particular importance in the dynamics of the earth's interior since olivine is the predominant phase in the upper mantle. Recently, Karato *et al.* (1986) found a diffusional creep regime for polycrystalline olivine in laboratory. Ozawa (1989) presented the first evidence that spinel in upper-mantle rock deformed by a diffusional creep mechanism. Karato *et al.* (1986) has argued that the diffusional creep mechanism may also control the rheology of olivine at low stress and small grain size which correspond to the conditions in the earth.

The self-diffusion of ionic species in minerals controls the diffusional creep, *i.e.*, diffusional creep rate is controlled by the slowest moving ionic species diffusing over its fastest path (e.g. Gordon, 1985). Since forsterite is the Mg end-member of mantle olivine which contains about 10% fayalite component, analysis of diffusion in forsterite is one of the most basic key to unders-

tand the physical properties of rheology in mantle. In this aspect, many studies have been made to determine lattice diffusion of O or Mg in forsterite (Söckel *et al.*, 1980; Reddy *et al.*, 1980; Jaoul *et al.*, 1980; Morioka, 1981; Jaoul *et al.*, 1981).

In the case of MgO and Al₂O₃, it has been shown that diffusion along high diffusivity paths plays an important role in the diffusional creep phenomena (see Gordon, 1985). For fast diffusion in olivine, Watson (1986) has made a pioneer work to determine O grain boundary diffusion coefficients using natural samples. However, the grain boundary diffusion is not self-diffusion but chemical diffusion because the experiments have been done under chemical activity gradients.

We have investigated diffusion mechanism in minerals using several techniques and discussed implications for geo-scientific events (Morioka, 1980, 1981, 1983; Nagasawa, 1983; Morioka *et al.*, 1985; Yurimoto and Nagasawa, 1989; Yurimoto *et al.*, 1989). This paper outlines results of oxygen diffusion along high diffusivity

paths in forsterite single crystals. To our knowledge, this paper presents, for the first time, a direct measurement of O self diffusion rate in olivine along high diffusivity paths; although preliminary studies have been presented by Yurimoto *et al.* (1990 a,b). In this respect, we report a new set of diffusion data for forsterite, particularly for the purpose of demonstrating the application of the data to a high temperature creep mechanism of olivine.

SAMPLE PREPARATION AND DIFFUSION ANNEALING

Forsterite single crystals were synthesized by the Czochralski (CZ) method. The starting reagents, MgO and SiO₂, supplied by Wako Pure Chemical Co. of quality better than 3N, were weighed in the correct stoichiometric proportions for Mg₂SiO₄, mixed and pre-heated at 1250°C for several hours in air, and then loaded into an Ir crucible. A continuous gas flow of nitrogen at a rate of 200–300 ml min⁻¹ was introduced during the crystal growth. Good quality forsterite crystal free from visible internal imperfections such as cracks, gas bubbles and any other inclusions were pulled along the [100] direction at a rate of 3 mm hour⁻¹ and rotation rate of 10 rpm. In this way, crystals were obtained up to 30 mm in diameter and 100 mm in length. The conditions for synthesis were similar to those employed by Morioka (1983).

The crystals were oriented by the back-reflec-

tion Laue-photograph method and cut using a low-speed diamond saw into rectangular prisms with (001) surfaces of 5 × 5 mm and a height of 2 mm along the crystallographic *c*-axis. One surface was polished to 0.1 µm diamond paste. After polishing, the crystals were pre-annealed at 1200°C in air for 10 hours in order to keep the dislocation conditions of the crystal surface constant during diffusion annealing.

Forsterite crystals enveloped in a Pt plate (1 mm thickness) were annealed with focused infrared lamps in an ¹⁸O-enriched CO₂ atmosphere (99% ¹⁸O enrichment and 6.4 kPa) at temperatures of 1100 and 1200°C. The temperature was measured on the crystal surface by a Pt-Pt-Rh thermocouple, and regulated by PID control system. The temperature fluctuations were within ±3°C of the set temperature. Although temperature gradient between the thermocouple and the center of the sample could not be measured directly, the distance between them is only 1 mm and the diffusion in this study occurred only in the region near the surface. Thus the systematic error from the true anneal temperature is believed to be within ±5°C. That present results of lattice diffusion (Table 1) lie in the range of the previous reports (Söckel *et al.*, 1980; Reddy *et al.*, 1980; Jaoul *et al.*, 1980; Jaoul *et al.*, 1981) also supports the estimation of temperature systematic error. The durations of the annealing ranged from 1 hour to 4 hours.

Table 1. Oxygen self-diffusion coefficients on forsterite along *c*-axis

Temperature °C	Anneal time sec.	D^l m ² sec ⁻¹	δD^b m ³ sec ⁻¹	D^d m ² sec ⁻¹
1100	3960	$3.20 \pm 1.54 \times 10^{-21}$	$2.1 \pm 1.1 \times 10^{-28}$	$1.7 \pm 1.3 \times 10^{-17}$
1100	15060	$2.81 \pm 0.51 \times 10^{-21}$	$2.1 \pm 2.0 \times 10^{-28}$	$3.0 \pm 2.9 \times 10^{-17}$
1100	14400	$2.28 \pm 0.66 \times 10^{-21}$	$4.1 \pm 2.2 \times 10^{-28}$	$5.6 \pm 3.7 \times 10^{-17}$
1200	8208	$6.67 \pm 1.26 \times 10^{-21}$	$1.6 \pm 0.5 \times 10^{-28}$	$2.0 \pm 0.8 \times 10^{-17}$
1200	3654	$1.38 \pm 0.40 \times 10^{-20}$	$2.7 \pm 1.2 \times 10^{-27}$	$3.9 \pm 1.9 \times 10^{-16}$
1200	9000	$3.97 \pm 1.50 \times 10^{-21}$	$7.5 \pm 4.6 \times 10^{-28}$	$9.9 \pm 7.2 \times 10^{-17}$

D^l : lattice diffusion coefficient, D^b : grain boundary diffusion coefficient, D^d : dislocation diffusion coefficient, and δ : grain boundary width.

The errors in the diffusion coefficients represent the standard deviation of several SIMS analyses.

A dislocation pipe radius $a=0.1$ nm has been used to calculate D^d .

MEASUREMENT OF CONCENTRATION GRADIENTS

The distribution of oxygen isotopes in the annealed specimens was determined by a depth-profiling analysis with a Cameca IMS-3F ion microprobe. The basic conditions for measurement are described elsewhere in detail (Yurimoto *et al.*, 1989).

The primary beam was mass filtered $^{16}\text{O}^-$ accelerated to 5.5 or 8 keV and adjusted for a beam current of 20 to 50 nA and a spot size of about 50 μm in diameter. The primary beam was rastered over a $350 \times 350 \mu\text{m}$ area during irradiation in order to bore holes with flat bottoms into the forsterite. Secondary ions from the sputtering process were collected from the central area of 60 μm in diameter using a mechanical aperture. A multibeam interferometer was used to measure the final crater depth. The sputter rate was constant as shown in Yurimoto *et al.* (1989).

The intensities of the negative secondary ions $^{16}\text{O}^-$, $^{17}\text{O}^-$, $^{18}\text{O}^-$ and $^{28}\text{Si}^-$ were measured. Molecular ion interferences were absent on the masses 16, 18 and 28. There was $^{16}\text{O}^{17}\text{O}^-$ interference for mass 17. Since the interference was sensitive to residual gases in the sample chamber of the SIMS, the chamber vacuum was maintained below 0.5 μPa during the measurement. Moreover, in order to reduce the interference, energy filtering was achieved by offsetting the sample accelerating voltage (+100 ~ +150 V) and the energy band-pass was set at ± 5 eV. In spite of these setting, a few amount of $^{16}\text{O}^{17}\text{O}^-$ interference was still remaining as shown in Fig. 1. The interference produced no problems to determine O diffusion coefficients in this study because we used ^{18}O isotope as self diffusion tracer.

The possible problems caused by electrostatic charging under ion beam bombardment were eliminated by depositing ~20 nm of gold on the sample surface and by feedback of the shift of the maximum voltage of the ion kinetic energy distribution of mass 28.

Since the secondary ion signal for $^{16}\text{O}^-$ was diluted with the primary beam (Yurimoto *et al.*, 1989), the intensity ratio $^{18}\text{O}^- / ^{28}\text{Si}^-$ was used to

Fig. 1. (a) Diagram showing secondary ion intensity ratio against ^{28}Si vs. depth from surface for forsterite along the c-axis. The background level of ^{18}O which is the initial ^{18}O concentration in the forsterite is shown by arrow. (b) ^{18}O penetration profile in forsterite along the c-axis showing contributions from diffusion in the lattice, and along dislocations. The background signal corresponding to natural ^{18}O has been subtracted.

obtain the penetration plot of $^{18}\text{O}^-$ in forsterite. The absence of chemical gradients near or under the crystal surface was confirmed by the signals for $^{28}\text{Si}^-$. Therefore, the intensity ratio is directly proportional to the isotopic concentration of $^{18}\text{O}^-$.

RESULTS

For a semi-infinite medium and for a con-

Fig. 2. Plot of the logarithm of the lattice and the dislocation diffusion coefficients for ^{18}O along the c -axis in single crystal forsterite as a function of reciprocal temperature, with previously reported results for the self-diffusion of O and Mg. The error bars represent the standard deviation. SHS denotes Sockel *et al.* (1980); ROMC, Reddy *et al.* (1980); JFDM, Jaoul *et al.* (1980); M, Morioka (1981); JHA, Jaoul *et al.* (1983); and D^e was determined by Karato *et al.* (1986).

stant concentration source with a surface concentration C_0 , the lattice diffusion coefficient D^l is written as (Crank, 1975):

$$\frac{C - C_0}{C_1 - C_0} = \text{erf} \frac{y}{\sqrt{D^l t}} \quad (1)$$

where C is the isotopic concentration at depth y from the surface, C_1 is the initial isotopic concentration in the crystal and t is the annealing time. A typical penetration plot in forsterite is presented in Fig. 1. The penetration profile can be clearly resolved into an error function region, which satisfies the relation in eq. (1), plus a tail region. The error function and the tail regions can be ascribed to the result of lattice diffusion and the fast diffusion of ^{18}O along high diffusivity paths, such as dislocations at the crystal surface, respectively (Le Claire and Rabinovitch,

1984). By the same reasons as Yurimoto *et al.* (1989) and Sakaguchi *et al.* (1992) we recognized that the tail can be ascribed to the fast diffusion of ^{18}O along dislocations introduced into the surface region of the crystal by mechanical treatment. By analyzing the shapes of the tail, we determined diffusion rates of O along the dislocations and along the low angle tilt boundaries¹ according to the method developed by Yurimoto and Nagasawa (1989) and Le Claire (1963), respectively. The substance of the method is described in Appendix.

Table 1 summarizes the average lattice and dislocation diffusion coefficients, D^l and D^d , and the product of grain boundary width δ and grain boundary diffusion coefficient D^b along the c -axis for forsterite determined in the present work, along with the conditions under which these values were obtained. A plot of the logarithm of the diffusion coefficient as a function of reciprocal temperature is presented in Fig. 2.

The present results of lattice diffusion lie in the range of the extrapolation of lines reported previously (Sockel *et al.*, 1980; Reddy *et al.*, 1980; Jaoul *et al.*, 1980; Jaoul *et al.*, 1983). The dislocation diffusion coefficient is about 10^4 times faster than the lattice diffusion at the same temperature. The diffusivity along dislocations is nearly equal to the self-diffusion coefficients for Mg in forsterite. The radius a of the diffusion pipes along the c -axis, which correspond to the high diffusivity paths, was calculated to be 0.1 ± 0.05 nm.

DISCUSSION

Recently experimental results have indicated that olivine rheology is controlled by a diffusional creep mechanism at low stresses and small grain sizes (Karato *et al.*, 1986). In the diffusional creep regime, strain accommodation occurs by diffusion of the ionic species which constitute the rock. In general the diffusional creep

¹Since low angle tilt boundaries belong to a part of category of grain boundaries, we use the term of "grain boundary" instead of low angle tilt boundary in the following section.

of solids follows the following relation:

$$\dot{\epsilon} = A \frac{\Omega \sigma}{b^2 RT} D^e \quad (2)$$

where $\dot{\epsilon}$ is the strain rate, A a numerical constant dependent on the geometry of flow ($A=14$ for small strain diffusion creep) (see Raj and Ashby, 1971; Ashby *et al.*, 1978; Spingarn and Nix, 1978), Ω the molar volume, σ the stress deviator, b the grain size, R the gas constant, T the absolute temperature and D^e the effective diffusion coefficient. D^e is given by

$$D^e = 1 / \sum (v_i / D_i^e) \quad (3)$$

(Gordon, 1975, 1985), where v_i and D_i^e are the stoichiometric coefficient of the i th species in the material and its effective diffusion coefficient, respectively.

Since effective diffusion of an ion comprises the diffusion through lattice and through high diffusivity paths, effective diffusion rates change with the length of anneal time. Harrison (1961) classified the form of effective diffusion as type-A, -B and -C. Type-A diffusion is observed when $(D_i^l t)^{1/2} \geq 300L$, where D_i^l is D^l of the i th species, and L is the average distance between dislocations. When this condition is satisfied, D_i^e can be described by the relation of Hart (1957):

$$D_i^e = f D_i^d + (1-f) D_i^l \quad (4)$$

where f is the volume fraction of the material in the dislocation, and D_i^d is D^d of the i th species. Type-C diffusion is observed only when the anneal time is so short that $(D_i^l t)^{1/2} \ll a$. In this case, diffusion from the dislocation pipe into the surrounding lattice can be neglected and D_i^e is characterized by D_i^d . When the condition for neither type-A nor type-C is satisfied, the diffusion is Type-B and the diffusion coefficient is complicated because the effective diffusion both along the dislocation and into the surrounding lattice must be considered. The experimental conditions of the present study correspond to type-B diffusion.

Since components of forsterite are Mg, Si, and O, D^e is determined by D_i^e of these elements as shown in eq. (3). Values for D^l of O and Mg

in forsterite have been measured by several works (Söckel *et al.*, 1980; Reddy *et al.*, 1980; Jaoul *et al.*, 1980; Morioka, 1981; Jaoul *et al.*, 1983). Despite the differences in sample characteristics, annealing condition and analytical method, the results are fairly consistent (cf. Fig. 2). Values for D^l of Si in forsterite in published works, on the other hand, show large discrepancies (Söckel *et al.* 1980; Jaoul *et al.* 1981). Although the most recent work of Si diffusion in natural olivine confirms that Si is the slowest lattice diffusing species (Houlier *et al.*, 1990), no investigations have been made for the Si diffusion along high-diffusivity paths. Therefore, in this paper we will mainly discuss only the effect of diffusivities of O and Mg. Further work on Si, especially for enhancement along high-diffusivity paths, is necessary for a strict quantitative test.

Since most of the creep experiments were performed within the range of several hours (e.g. Mackwell *et al.*, 1985; Karato *et al.*, 1986), $(D^l t)^{1/2}$ of O in the forsterite lattice is at most several tens of nanometers at 1300°C, which is two orders of magnitude larger than the diffusion pipe radius determined in this study, and three orders of magnitude smaller than the grain size in the diffusional creep regime for olivine as reported by Karato *et al.* (1986). Moreover, since deformation of olivine continued in steady strain rate during the run duration, the effective time of diffusion for the deformation may be much shorter than the total run time. Therefore, the D_0^d in the laboratory creep experiments is classified as Types-B to -C, and with a value nearly equal to D_0^d .

The $(D^l t)^{1/2}$ for Mg in the forsterite lattice is several micrometers at 1300°C, one hour, which is much greater than the typical spacing (calculated from average dislocation density reported by Karato *et al.*, (1986)) between dislocations and is comparable to the grain radius in the diffusional creep regime. The D_{Mg}^d is classified as nearly Type-A, and can be described by eq. (4). Since Karato *et al.*, (1986) reported that the dislocation density in the diffusional creep regime is about $5 \times 10^{11} \text{ m}^{-2}$, it can be con-

cluded from eq. (4) that D_{Mg}^{e} will be significantly influenced by diffusion along dislocations or along grain boundaries when $D^{\text{d}}/D^{\text{l}}$ is greater than 2×10^8 . To the best of the authors' knowledge, no observations have been made for diffusion coefficients of cations along high diffusivity paths in forsterite. However, since $D^{\text{d}}/D^{\text{l}}$ for cation is $\sim 10^5$ for MgO (Sakaguchi *et al.* 1989) and $\sim 10^4$ for NiO (Atkinson and Taylor, 1979), it is unlikely that such high diffusion coefficient of Mg along dislocations achieved in forsterite. Therefore, D_{Mg}^{e} would not be much enhanced by dislocations or grain boundaries under the creep experimental condition, i.e. $D_{\text{Mg}}^{\text{d}} \gg D_{\text{Mg}}^{\text{e}} \geq D_{\text{Mg}}^{\text{l}} \approx D_{\text{O}}^{\text{d}} = D_{\text{O}}^{\text{e}}$.

Since diffusional creep rate will be controlled by the slowest moving ionic species diffusing over its fastest path (Gordon, 1985), it is conceivable that effective diffusion of O controls the diffusional creep rather than that of Mg. In fact, effective diffusion coefficient for diffusional creep for mantle olivine determined by Karato *et al.* (1986) lies in the range of the extrapolation for O dislocation diffusion in forsterite (Fig. 2).

The creep experiments in laboratories were performed at higher stress and higher strain rate than in the earth. When laboratory results are extrapolated to the lower stress levels in the earth, it is necessary to take it into consideration that D_{O}^{e} decreases according to Harrison's treatment, which shows that the effective diffusion coefficient is strongly dependent on grain size, sub grain size, dislocation density, dislocation distribution and strain rate. Therefore, if the diffusional creep mechanism dominates the rheology of olivine in the upper-mantle, the rheological properties must be mainly controlled by the lattice diffusion of the slowest species.

SUMMARY AND CONCLUSIONS

Oxygen diffusion penetrations along the c -axis from the surface into forsterite single crystal have been analyzed by SIMS after treatment at the temperatures of 1100°C and 1200°C. The present results for O lattice diffusion lie in the range of the extrapolation of lines reported previously.

The dislocation diffusion coefficients for O are about 10^4 faster than the lattice diffusion coefficient at the same temperature. The O diffusivity along dislocations is nearly equal to the self-diffusion coefficients for Mg in forsterite. The fast diffusivity region of a dislocation can be pictured as a pipe with 0.1 nm radius.

The diffusional creep of olivine previously observed in laboratories could be controlled by the O diffusion along high diffusivity paths, such as dislocations. When laboratory results are extrapolated to lower stress levels in the earth, it is necessary to correct for the fact that D_{O}^{e} decreases according to the Harrison's treatment.

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APPENDIX

The analysis of dislocation pipe radius for diffusion and mathematical procedure for dislocation diffusion coefficient have been fully described by Yurimoto and Nagasawa (1989). We describe the substance of the procedure below.

The analysis of the high-diffusivity paths was

generally based on the grain-boundary model and the dislocation pipe model. Le Claire (1963) has developed the equation of the grain boundary contribution (δD^b) as

$$\delta D^b = 0.66 \left(\frac{d \ln \langle c \rangle}{d y^{6/5}} \right)^{-5/3} \left(\frac{4 D^l}{t} \right)^{1/2} \quad (5)$$

where $\langle c \rangle$ is the total average concentration at depth y . Le Claire and Rabinovitch (1984) indicate that the dislocation array contribution appears as

$$a^2 D^d = \left[\frac{A(\alpha)}{\left(\frac{\partial \ln \langle c \rangle}{\partial y} \right)} \right]^2 D^l \quad (6)$$

where $A(\alpha)$ is an α -dependent factor describing tail slopes, $\alpha = a/(D^l t)^{1/2}$, and the parameter of a is dislocation pipe radius. Low-angle grain boundaries can be described geometrically as planar arrays of individual dislocations. According to Turnbull and Hoffman (1954), the diffusion in the direction of the dislocation pipes is written as

$$\delta D^b = D^d \frac{\pi a^2}{L} \quad (7)$$

where L is the space of dislocation pipes. The grain size (b), which means the space between grain boundaries, appears as

$$b = \frac{2(D^l t)^{1/2} (4.1 D^l (D^l t)^{1/2} / \delta D^b + 1.56)}{\langle c \rangle_{\text{Int}}^b / c_0} \quad (8)$$

where $\langle c \rangle_{\text{Int}}^b$ is the intersection value of an extrapolation of the tail back to the surface ($y=0$) and the ordinate, and c_0 is the surface concentration. The dislocation pipe radius appears as

$$a = \left(\frac{b L \frac{\langle c \rangle_{\text{Int}}^d}{c_0}}{2\pi (D^l t)^{0.92}} \right)^{6.25} \quad (9)$$

where $\langle c \rangle_{\text{Int}}^d$ is the intersection value of an extrapolation of the tail back to the surface ($y=0$) and the ordinate. Therefore, D^d and a are obtained using an iteration procedure with the help of eqs. (6), (7) and (9).