Evaluation of diffusion coefficients of Fe-Mg and Ca in olivine

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Abstract

We evaluated the diffusion coefficients of Fe-Mg and Ca in olivine reported in several literatures by analyzing the diffusion profiles experimentally produced. Both the Fe and Ca contents of olivine in run products drastically increase toward the rim within a few tens of micrometers probably due to atomic diffusion from the surrounding Fe- and Ca-rich melt. The chemical zoning profiles of olivine measured with an electron microprobe were compared with those calculated by numerically solving the diffusion equation by using different diffusion coefficients. The diffusion coefficient of Fe-Mg in olivine reported by Misener (1974) gives a better fit than that by Buening and Buseck (1973), that is, the latter is too large. The diffusion coefficient of CaO in olivine reported by Jurewicz and Watson (1988b) gives a better fit than that by Morioka (1981), that is, the latter is too small. Our calculations for analyzing chemical zoning on the basis of atomic diffusion successfully reproduce the curvature of a profile experimentally made by diffusional modification of initial uniform profile of olivine.

Introduction

Chemical zoning in minerals provides information on thermal history such as cooling, reheating and annealing of terrestrial rocks or extraterrestrial materials (meteorites and lunar rocks etc.). Chemical zoning caused by diffusional modification except for primary igneous zoning is used to calculate the cooling rate or burial depth by solving the diffusion equation (e.g., Miyamoto *et al.*, 1986).

Each element has its own rate of diffusion, or diffusion coefficient, in a mineral. Different values of the diffusion coefficient can derive information on different values of the cooling rate and burial depth. This means that we can determine the cooling rates (or burial depths) over a wide range by using chemical zoning of different elements in various minerals, because the diffusion coefficients of different elements in various minerals cover a wide range (e.g., Freer, 1981). Thus, it is important to obtain accurate values of the atomic diffusion coefficients in minerals for calculations, because results of the cooling rate and burial depth are strongly dependent on the diffusion coefficient employed for the analysis of chemical zoning profiles.

We have studied the cooling rate and burial depth of many meteorites and lunar samples

FIG. 1. Log D (cm^2/s) vs. $1/T$ (K^{-1}) plot of diffusion coefficients of Fe-Mg and Ca in olivine. Solid lines show Fe-Mg diffusion coefficients for the Fa component of 9.6 and the oxygen fugacity of two log units above the iron-wüstite (IW) buffer. B&B: Buening and Buseck (1973); MI: Misener (1974). Dotted lines show Ca diffusion coefficients. J&W: Jurewicz and Watson (1988b) for a St. John's olivine (approximately 90% forsterite); MO: Morioka (1981) for a synthetic forsterite.

by analyzing chemical zoning of olivine and pyroxene (e.g., Miyamoto *et al.*, 1986). One problem with these calculations is, for example, that there are large differences between the diffusion coefficients of Fe-Mg and Ca in olivine reported by different investigators (Fig. 1).

The differences in reported diffusion coefficients may be due to differences in the nature of olivine used for experiments to determine the diffusion coefficients. For example, Morioka (1981) used a synthetic forsterite, while Jurewicz and Watson (1988b) used a natural olivine.

We have, therefore, evaluated the diffusion coefficients of Fe-Mg and Ca in olivine reported by several workers, as well as our method for calculating diffusional modification of chemical zoning, by analyzing experimentally produced diffusion profiles. Although these experiments were designed for a different purpose, chemical zoning profiles in the run products are favorable for experimental confirmation of the diffusion coefficients in olivine and of the method for calculating diffusional modification.

Experiments

A diffusion experiment was conducted in a one-atmosphere, gas-mixing furnace in generally the same manner as Miyamoto and Mikouchi (1996). The temperature was measured with a type R thermocouple (Pt₈₇Rh₁₃-Pt) calibrated against the melting point of Au (1064°C) and was believed accurate to $\pm 1^\circ\text{C}$. The oxygen fugacity (f_{O_2}) was measured using a solid ceramic (stabilized zirconia) oxygen electrode and controlled by mixing appropriate ratio of H₂ and CO₂, with an approximate error less than ± 0.2 log unit. Synthetic starting glass of an angrite melt composition based on the bulk composition of the Asuka 881371 angrite meteorite (Yanai 1994; Table 1) was prepared from reagent grade chemicals. Aliquots of approximately 125 mg of powdered starting material were pressed into pellets and placed onto a Pt wire loop. A few small plates (1 mm in size) of a single crystal of San Carlos olivine (Fo₉₀, Table 1) were put on the pellet. The plates were prepared by cutting a single crystal of olivine perpendicular to *b* axis after its crystallographic orientation was measured by using single-crystal X-ray diffraction (precession method). The starting material with olivine plates was then heated in a furnace at 1250°C for 24 hr under the f_{O_2} of 2 log units above the iron-wüstite (IW) buffer. The flowing rates of the gases were 130 cc/min for H₂ and 480 cc/min for CO₂. The samples were quenched in air by extracting the rod from the furnace.

We selected the angritic glass and San Carlos olivine for heating experiments to evaluate the diffusion coefficients of Fe-Mg and Ca in olivine, because the Fe- and Ca-rich composition of the angritic glass is expected to produce strong zoning profiles in this Mg-rich olivine. We performed the experiment at 1250°C so as to reduce the effect of olivine overgrowth on zoning profiles, because this temperature was determined to be a little below the olivine liquidus temperature of this starting glass.

Electron probe microanalysis was performed with the JEOL JXA-733 microprobe at the Ocean Research Institute, University of Tokyo. Chemical zoning of olivine in run products was measured along profiles parallel to the *c* axis selected on the basis of back-scattered electron images, by making spot analyses every 2 μm from core to rim. The accelerating voltage was 15 kV and the beam current was 12 nA on a Faraday cage. Thirteen major elements were analyzed (Si, Mg, Fe, Ca, Na, K, Mn, Al, Ti, Cr, V, Ni and P). Counting times at peak wavelengths were 30 s. The background intensity of each element was counted on both sides of the peak wavelength. The convolution effect in the measurement of diffusion profiles due to spatial averaging in microprobe analysis is negligible, because the spot analyses were performed at 2 μm intervals (Ganguly *et al.*, 1988).

Calculations

It was assumed here that compositional gradients of the Fa ($=100 \times \text{Fe}/(\text{Mg}+\text{Fe})$, mol%) and CaO contents observed for olivine in the run product were controlled by atomic diffusion. Namely, the initial uniform profile of San Carlos olivine was modified by atomic diffusion. We have independently calculated Fe-Mg inter diffusion and Ca diffusion because the Ca content in olivine is very low. The diffusion equation for linear flow in one-dimension is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right)$$

where C , x and t are the Fa component or CaO content (wt%), position and time, respectively. For radial flow in a sphere, position is noted by the one dimensional variable r by putting $u = Cr$, where r is radial distance (e.g., Carslaw and Jaeger, 1956; Crank, 1972) in spherical coordinates.

Boundary conditions are

$$\frac{\partial C(0, t)}{\partial x} = 0$$

$$C(X, t) = C_B$$

where position X is at the interface between olivine and the adjacent matrix. C_B is the concentration at the grain boundary with matrix.

Initial condition is

$$C(x, 0) = C_I$$

where C_I is an initial concentration profile. Diffusion calculations were started by using a uniform initial profile for each element because San Carlos olivine is compositionally uniform.

A diffusion profile was calculated by numerically solving the diffusion equation under the condition of constant temperature of 1250°C and 24 hr and was compared with that of olivine in the run product experimentally heated at 1250°C for 24 hr. The constant concentration (C_B) was fixed to the concentration at the extreme rim of olivine during diffusion calculations.

We calculated the zoning profile produced by atomic diffusion from the initial uniform profile by using different reported diffusion coefficients. The calculated results were compared with the observed profiles to evaluate the diffusion coefficients reported by different workers.

We employed the inter diffusion coefficients of Fe-Mg (D_{Fe}) of olivine in the c direction reported by Buening and Buseck (1973) (B&B) and Misener (1974) (MI). The D_{Fe} of B&B is determined as a function of temperature, oxygen fugacity and the Fe concentration of olivine:

$$D_{\text{Fe}} = 10^2 (f_{\text{O}_2})^{1/6} \exp(-0.045C_{\text{Fe}} - 3.47) \exp[(-61.06 + 0.2214C_{\text{Fe}})/RT] \quad T \geq 1125^\circ\text{C}$$

$$D_{\text{Fe}} = 10^2 (f_{\text{O}_2})^{1/6} \exp(-0.0501C_{\text{Fe}} - 14.03) \exp[(-31.66 + 0.2191C_{\text{Fe}})/RT] \quad T < 1125^\circ\text{C}$$

where f_{O_2} , C_{Fe} , R and T are oxygen fugacity in atm, the Fa component in mol%, the gas constant in kcal mol⁻¹ K⁻¹ and temperature in K, respectively.

Although D_{Fe} of MI is determined as a function of temperature and Fe concentration, but under the FMQ buffer (fayalite-magnetite-quartz), we extrapolated the D_{Fe} value of MI by using an equation for variation with oxygen fugacity similar to that of B & B (Miyamoto *et al.*, 1986):

$$D_{Fe} = \exp[\ln(0.0041+0.000112C_{Fe})-3.4538] (f_{O_2})^{1/6} \exp[(-39.27+0.0905C_{Fe})/RT] \\ = 0.03163 \times 10^{-2} (f_{O_2})^{1/6} (0.41+0.0112C_{Fe}) \exp[(-39.27+0.0905C_{Fe})/RT]$$

This expression is different from the one published by Miyamoto *et al.* (1986) in that the term “3.4538” was inadvertently omitted from the original publication. The D_{Fe} reported by Jurewicz and Watson (1988b) is similar to that by MI, and will not be considered separately. Likewise, the D_{Fe} reported by Nakamura and Schmalzried (1984) is similar to that by MI, although they do not report difference in D_{Fe} due to difference in the crystal axis of olivine, and we will not consider the values of Nakamura and Schmalzried (1984) separately. We calculate the temperature dependence of the oxygen fugacity (2 log unit above the IW buffer) using the f_{O_2} -temperature relation of the IW buffer reported by Eugster and Wones (1962).

$$\log(f_{O_2}) = 8.57-27215/T$$

The atomic diffusion coefficients of Ca (D_{Ca}) in olivine were taken from Morioka (1981) (MO) and Jurewicz and Watson (1988b) (J & W).

$$D_{Ca} = 71.5 \exp(-99.3/RT) \quad (\text{Morioka, 1981}) \\ D_{Ca} = 7.0 \times 10^{-6} \exp(-42.7/RT) \quad (\text{Jurewicz and Watson, 1988b})$$

Morioka (1981) used a synthetic forsterite and Jurewicz and Watson (1988a,b) used a natural olivine from St. John's Island, Egypt (Fa is about 10).

For the boundary conditions (C_B) of diffusion calculations, we used Fa of 28 and CaO of 1.0 which are estimated on the basis of the concentrations at the extreme rim of olivine. These values are broadly consistent with those estimated from the glass composition by using partition coefficients, that is, Fa of about 30 (e.g., Stolper, 1977) and about 0.8 of CaO (Jurewicz and Watson, 1988a).

Results and Discussion

Diffusion coefficients

Both the Ca and Fe contents of olivine in run products drastically increase within a few tens of micrometers of the rim probably due to atomic diffusion from the surrounding Ca- and Fe-rich angritic melt (Figs. 2 and 3; Table 1).

Theoretical diffusion profiles calculated using D_{Fe} in olivine reported by B&B and by MI are compared with the profile observed in the experimental olivine in Fig. 2. The D_{Fe} in

FIG. 2. Comparison of zoning profiles of the Fa ($=100 \times \text{Fe}/(\text{Mg} + \text{Fe}), \text{ mol\%}$) component calculated by using the diffusion coefficients reported by Buening and Buseck (1973) (B& B) and Misener (1974) (MI). Open circles show a profile every $2 \mu\text{m}$ interval observed for San Carlos olivine experimentally heated at 1250°C for 24 hr in an angritic Fe- and Ca-rich composition glass. Curves show diffusion profiles calculated under the condition of 1250°C and 24 hr by using (a) spherical approximation and (b) one-dimensional approximation.

FIG. 3. Comparison of zoning profiles of the CaO content calculated by using the diffusion coefficients reported by Jurewicz and Watson (1988b) (J & W) and Morioka (1981) (MO). Open circles show a profile every 2 μm interval observed for San Carlos olivine that is the same as shown in Fig. 2. Curves show diffusion profiles calculated under the condition of 1250°C and 24 hr by using (a) spherical approximation and (b) one-dimensional approximation.

TABLE 1. Chemical compositions of angritic glass and San Carlos olivine.

	Angritic glass	San Carlos olivine*
SiO ₂	38.6	40.0
Al ₂ O ₃	10.73	0.02
TiO ₂	1.01	0.0
FeO	23.37	9.39
MnO	0.22	0.14
MgO	10.64	49.6
CaO	14.57	0.09
NiO	0.0	0.37
Cr ₂ O ₃	0.18	0.02
Total	99.30	99.63
mg#**	44.8	90.4

* From Miyamoto et al. (1983)

** $100 \times \text{Mg} / (\text{Mg} + \text{Fe})$, atomic %

olivine reported by B&B is about one order of magnitude larger than that by MI at 1250°C (Fig. 1) and the calculated profile shows correspondingly more extensive diffusion. It is obvious from Fig. 2 that the D_{Fe} of MI gives a better fit than that of B & B, that is, the value of B & B is too large.

Results for Ca are shown in Fig. 3. The D_{Ca} in olivine reported by J & W is about one order of magnitude larger than that by MO at 1250°C (Fig. 1). Our analysis shows that the value of J & W gives a much better fit than that of MO, that is, the value of MO is too small (Fig. 3). The zoning profile calculated by D_{Ca}

of J & W agrees well with that of the observed one (Fig. 3).

Method of calculation

For analysis of a line profile of chemical zoning, one-dimensional or spherical approximation is usually applied to calculation of a zoning profile (e.g., Carslaw and Jaeger, 1959). This is dependent on the shape of olivine, that is, the shape of olivine is approximately spherical or is elongated in a direction. To evaluate differences between these approximations, we calculated theoretical profiles over a range of diffusion times, and compared them with the observed profile. For the Fe-Mg diffusion coefficient of MI, the time that gave the best fit for the spherical approximation was 14 hr, and for the one-dimensional approximation 19 hr. For the Ca diffusion coefficient of J & W, the best fit times are 23 and 29 hr, respectively. Fig. 4 compares the best-fit profiles between spherical approximation and one-dimensional approximation. There is no salient difference in the curvature of the profiles calculated by using two different approximations (Fig. 4). However, for the same diffusion time the profile calculated by spherical approximation gives a profile in which atomic diffusion is much more extensive (Fig. 2). In other words, the profile calculated by the spherical approximation apparently corresponds to that calculated by using a larger diffusion coefficient for the one-dimensional approximation.

Our calculations for analyzing chemical zoning on the basis of atomic diffusion successfully reproduce the curvature of an experimental profile produced by diffusional modification of initial uniform profile. This implies that analysis of chemical zoning is valid for deducing thermal history (e.g., cooling rate or burial depth), as long as the zoning profile is dominated by atomic diffusion and the diffusion coefficient used for calculation is correct.

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FIG. 4. Comparison of zoning profiles calculated by using spherical approximation (solid curve) and one-dimensional approximation (dotted curve). Open circles show a profile every 2 μm interval observed for San Carlos olivine that is the same as shown in Fig. 2. (a) The Fa component by using the diffusion coefficient reported by Misener (1974). (b) The CaO content by using the diffusion coefficient reported by Jurewicz and Watson (1988b). The curve shows the best-fit profile for each case.

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