

Antarct. Meteorite Res., **15**, 143–151, 2002

## Comparison of Fe-Mg interdiffusion coefficients in olivine

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**Abstract:** We have compared Fe-Mg interdiffusion coefficients in olivine reported in several literatures by analyzing experimentally produced diffusion profiles. 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. For our experimental results, the Fe-Mg interdiffusion coefficient in olivine reported by D.J. Misener (Carnegie Inst. Washington Publ., **634**, 117, 1974) with oxygen fugacity dependence gives the best fit to the observed profile. The Fe-concentration dependence of the Fe-Mg interdiffusion coefficient in olivine is important when the Fe content varies widely.

### 1. Introduction

Since chemical zoning in minerals provides information on their thermal history, it is often applied to calculating the cooling rate or burial depth by solving the diffusion equation on the assumption that chemical zoning is produced by diffusional modification except for primary igneous zoning (*e.g.*, Miyamoto *et al.*, 1986). For the calculation, the atomic diffusion coefficient in minerals is one of the most important factors to have influence on the result. Although several literatures report the diffusion coefficient of an atom in a mineral, there is often much difference among the reported values of the diffusion coefficient.

Miyamoto and Mikouchi (1998) evaluated the atomic diffusion coefficients of Fe-Mg and Ca in olivine reported in several literatures on the basis of their diffusion experiments. Because Chakraborty (1997) reported the Fe-Mg interdiffusion coefficient in olivine after the paper by Miyamoto and Mikouchi (1998), we, in this paper, compared his result with the previously reported values on the basis of the same experimental result as that employed in Miyamoto and Mikouchi (1998).

In addition, we also compared the Fe-Mg interdiffusion coefficients previously reported among several literatures under the same conditions (*e.g.*, the Fe concentration in olivine and oxygen fugacity), because almost all literatures compare the diffusion coefficients that are expressed in different conditions.

### 2. Experiments

Diffusion experiments were conducted in a one-atmosphere, gas-mixing furnace. Aliquots of approximately 125 mg of powdered synthetic starting-glass of an angrite melt

composition were pressed into pellets and placed onto a Pt wire loop. We selected the angritic glass for heating experiments, because the Fe-rich composition of the angritic glass is expected to produce strong zoning profiles in Mg-rich San Carlos olivine. A few small plates (1 mm in size) of a single crystal of San Carlos olivine (Fo<sub>91</sub>) were put on the pellet. The plates were prepared by cutting a single crystal of olivine perpendicular to the *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<sub>2</sub> of two log units above the iron-wüstite (IW) buffer. The olivine plates were not preannealed (Chakraborty, 1997).

Chemical zoning of olivine in run products was measured along profiles parallel to the *c* direction selected on the basis of back-scattered electron images, by making spot analyses every 2 μm from core to rim. The details of experimental procedures are given in Miyamoto and Mikouchi (1998).

### 3. Diffusion coefficients

Table 1 summarizes Fe-Mg interdiffusion coefficients reported in the representative literatures. We employed the Fe-Mg interdiffusion coefficient along the *c* axis, because it is the largest among three crystallographic axes (*e.g.*, Buening and Buseck, 1973). We compared the Fe-Mg interdiffusion coefficients of olivine in the *c* direction (*D*<sub>Fe</sub>) reported by Buening and Buseck (1973) (B&B), Misener (1974) (MI), Nakamura and Schmalzried (1984) (N&S), Jurewicz and Watson (1988) (J&W) and Chakraborty (1997) (CH).

The *D*<sub>Fe</sub> reported by Buening and Buseck (1973) is determined as a function of temperature, oxygen fugacity and the Fe concentration of olivine:

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

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

where *f*O<sub>2</sub>, *C*<sub>Fe</sub>, *R* and *T* are oxygen fugacity in atm, the Fe component (=100 × Fe/(Mg+Fe)) in mol%, the gas constant in kcal mol<sup>-1</sup> K<sup>-1</sup> and temperature in K, respectively.

The *D*<sub>Fe</sub> reported by Misener (1974) is

$$D_{\text{Fe}}=(0.41+0.0112 C_{\text{Fe}}) \times 10^{-2} \exp[(-58.88+0.0905 C_{\text{Fe}})/RT].$$

Table 1. The Fe-Mg interdiffusion coefficient in olivine.

Reference	Axis	Oxygen fugacity	Fe-concentration dependence	Temperature range	Method and samples
Buening and Buseck (1973)	a, b, c	10 <sup>-12</sup> atm	Yes	1200-1000	San Carlos olivine surrounded by powdered synthetic fayalite
Misener (1974)	a, b, c	FMQ	Yes	1100- 900	Diffusion couples; Synthetic forsterite St. John's Island olivine, Rockport fayalite
Nakamura and Schmalzried (1984)	-	10 <sup>-8-12</sup> bar	Yes	1280-1050	Synthetic (polycrystalline) olivine
Jurewicz and Watson (1988)	a, b, c	10 <sup>-8</sup> atm	No	1350-1220	St. John's Island olivine immersed in olivine-saturated, basaltic melt
Chakraborty (1997)	c	10 <sup>-12</sup> bar	No	1300- 980	Diffusion couples; Synthetic forsterite green San Carlos olivine, greenish-brown San Carlos olivine, St. Peters Dome fayalite

Although the  $D_{Fe}$  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):

$$D_{Fe} = \exp[\ln(0.0041 + 0.000112 C_{Fe}) - 3.4538] (fO_2)^{1/6} \exp[(-39.27 + 0.0905 C_{Fe})/RT] \\ = 0.03163 \times 10^{-2} (fO_2)^{1/6} (0.41 + 0.0112 C_{Fe}) \exp[(-39.27 + 0.0905 C_{Fe})/RT].$$

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.

Nakamura and Schmalzried (1984) did not report difference in  $D_{Fe}$  due to difference in the crystal axis of olivine.

The  $D_{Fe}$  reported by Jurewicz and Watson (1988) is

$$D_{Fe} = 1.0 \times 10^{-4} \exp(-50.3/RT),$$

at oxygen fugacity of  $10^{-8}$  atm. Although Jurewicz and Watson (1988) reported the oxygen-fugacity dependence, we extrapolated the  $D_{Fe}$  value of J&W by using an equation for variation with oxygen fugacity similar to that of B&B:

$$D_{Fe} = 2.15 \times 10^{-3} (fO_2)^{1/6} \exp(-50.3/RT).$$

They do not report the Fe-concentration dependence of  $D_{Fe}$ .

The  $D_{Fe}$  reported by Chakraborty (1997) is

$$D_{Fe} = 5.38 \times 10^{-5} \exp(-54.0/RT),$$

at oxygen fugacity of  $10^{-12}$  bar for the Fa component of 14. He did not report the Fe-concentration dependence of  $D_{Fe}$ . We also extrapolated the  $D_{Fe}$  value of CH by using an equation for variation with oxygen fugacity similar to that of B&B:

$$D_{Fe} = 5.38 \times 10^{-3} \times (fO_2)^{1/6} \exp(-54.0/RT).$$

We calculated the temperature dependence of the oxygen fugacity (2 log unit above the IW buffer) using the  $fO_2$ -temperature relation of the IW buffer reported by Eugster and Wones (1962).

$$\log(fO_2) = 8.57 - 27215/T.$$

#### 4. Calculations

It was assumed here that compositional gradients of the Fa component observed for olivine in the run product were controlled by atomic diffusion. Namely, the initial uniform profile of San Carlos olivine was modified by Fe-Mg diffusion from the angritic Fe-rich melt. 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 elongated in a direction or is approximately spherical.

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, 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:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} (r^2 D \frac{\partial C}{\partial r}) \right\}.$$

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. For radial flow in a sphere, similar boundary conditions were employed.

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 the Fa component because San Carlos olivine is compositionally uniform.

A diffusion profile was calculated by numerically solving the diffusion equation under the conditions 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. For the boundary conditions ( $C_B$ ) of diffusion calculations, we used the Fa component of 28 on the basis of the concentrations at the extreme rim of olivine. This value is broadly consistent with that estimated from the glass composition by using partition coefficients, that is, Fa of about 30 (*e.g.*, Stolper, 1977).

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

## 5. Results and discussion

Figure 1 compares the Fe-Mg interdiffusion coefficients along the  $c$  axis under the conditions that the Fa component is 14 and oxygen fugacity is  $10^{-12}$  atm. We chose this value of Fa, because Chakraborty (1997) reports the Fe-Mg interdiffusion coefficient at the Fa component of 14 and he does not report the Fe-concentration dependence. The  $D_{Fe}$  values shown by solid lines and triangles in Fig. 1 are all under the same conditions except for the value by Jurewicz and Watson (1988), because they do not report the Fe-concentration dependence of  $D_{Fe}$ . The  $D_{Fe}$  by B&B is the largest and that by CH is the smallest. There are about two orders of magnitude difference in  $D_{Fe}$  at 1250°C between

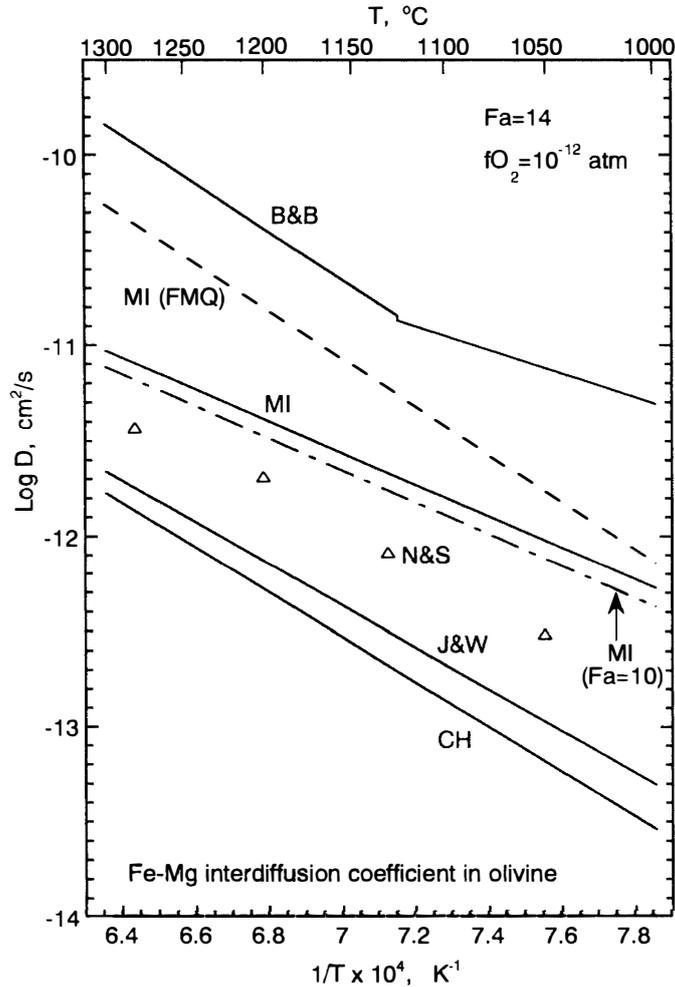


Fig. 1.  $\log D$  ( $\text{cm}^2/\text{s}$ ) vs.  $1/T$  ( $\text{K}^{-1}$ ) plot of the Fe-Mg interdiffusion coefficients along the  $c$  axis in olivine. Solid lines except for J&W and triangles show the Fe-Mg interdiffusion coefficients computed for the Fa component of 14 and the oxygen fugacity of  $10^{-12}$  atm. The values for J&W are at the oxygen fugacity of  $10^{-12}$  atm, but they do not report the Fe-concentration dependence of the diffusion coefficient. B&B: Buening and Buseck (1973); MI (FMQ): Misener (1974); MI and MI (Fa=10): Misener (1974) with the oxygen fugacity dependence; N&S (triangles): Nakamura and Schmalzried (1984); J&W: Jurewicz and Watson (1988); CH: Chakraborty (1997). MI (FMQ) (dashed line) shows the Fe-Mg interdiffusion coefficient reported by Misener (1974) for the Fa component of 14 and the oxygen fugacity along the FMQ (fayalite-magnetite-quartz) buffer. The dashed-dotted line shows the Fe-Mg interdiffusion coefficient reported by Misener (1974) for the Fa component of 10 and the oxygen fugacity of  $10^{-12}$  atm, which are the same conditions as those of J&W.

them (Fig. 1).

Figure 1 also shows the values of the  $D_{\text{Fe}}$  by Misener (1974) under three different conditions. The dashed line indicates the values at the Fa component of 14 along the FMQ buffer condition that are a function of the same expression reported by Misener (1974). The solid line labeled MI indicates the values at the Fa component of 14 and

oxygen fugacity of  $10^{-12}$  atm computed using the expression we deduced. The former value is several times larger than the latter one (Fig. 1). There is a large difference in the activation energy (the slope of the line in Fig. 1) between them. The dashed-dotted line labeled MI (Fa=10) shows the values at the Fa component of 10 and oxygen fugacity of  $10^{-12}$  atm computed using the expression we deduced. Although the conditions employed for the dashed-dotted line are the same as those of J&W, there is a salient difference between MI (Fa=10) and J&W. The difference between the dashed-dotted line labeled MI (Fa=10) and solid line labeled MI is caused by the difference in the Fa component of olivine, that is, the larger the Fa component is, the larger the diffusion coefficient is.

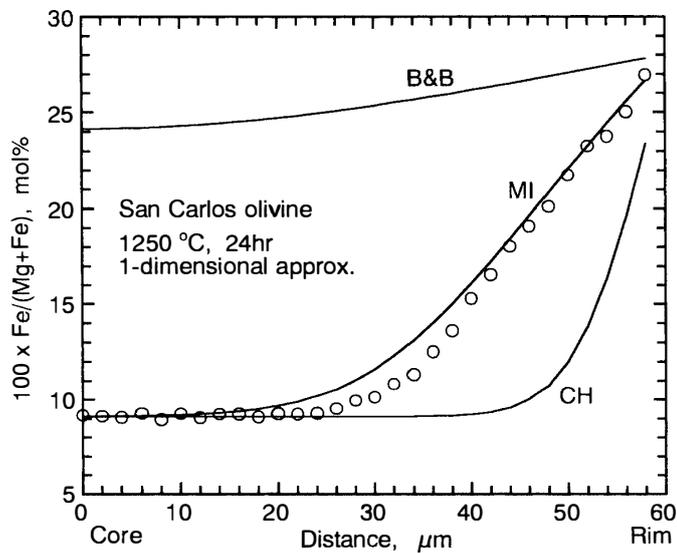


Fig. 2. Comparison of zoning profiles of the Fa ( $=100 \times \text{Fe}/(\text{Mg}+\text{Fe})$ , mol%) component calculated by using the diffusion coefficients reported by Buening and Buseck (1973) (B&B), Misener (1974) (MI) and Chakraborty (1997) (CH). Open circles show the profile observed for San Carlos olivine experimentally heated at  $1250^\circ\text{C}$  for 24 hrs in an angritic Fe-rich composition glass. Curves show profiles calculated for 24 hrs at  $1250^\circ\text{C}$  and oxygen fugacity of two log units above the IW (iron-wüstite) buffer by using one-dimensional approximation.

Open circles in Fig. 2 show that the Fa component of olivine in the run product drastically increases within a few tens of micrometers of the rim probably due to atomic diffusion from the surrounding Fe-rich angritic melt. The validity of this experimental method depends on the fact that diffusion in the melt adjacent to olivine crystal is much more rapid than in the crystal itself. Theoretical diffusion profiles calculated using the  $D_{\text{Fe}}$  in olivine reported by Buening and Buseck (1973), Misener (1974) and Chakraborty (1988) are compared with the profile observed in the experimental olivine in Fig. 2. The  $D_{\text{Fe}}$  in olivine reported by B&B is about one order of magnitude larger than that by MI at  $1250^\circ\text{C}$  (Fig. 1) and the calculated profile shows correspondingly more extensive diffusion. The  $D_{\text{Fe}}$  in olivine reported by CH is several times smaller than that by MI at

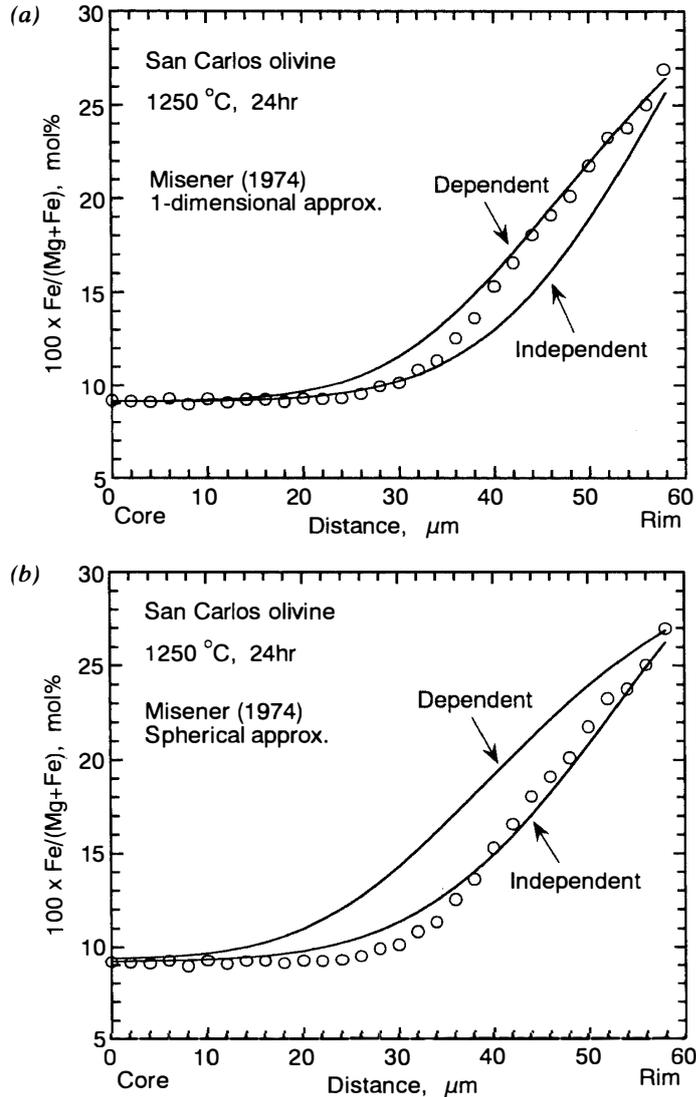


Fig. 3. Comparison of zoning profiles of the Fa component calculated by using the diffusion coefficients reported by Misener (1974) between the Fe-concentration dependent and Fe-concentration independent diffusion coefficients. Open circles show the profile observed for San Carlos olivine that is the same as shown in Fig. 2. Curves show profiles calculated for 24 hrs at 1250°C and oxygen fugacity of two log units above the IW buffer by using (a) the one-dimensional approximation and (b) the spherical approximation.

1250°C (Fig. 1) and the calculated profile shows correspondingly less extensive diffusion.

It is obvious from Fig. 2 that the  $D_{Fe}$  of MI gives a better fit than those of B&B and CH, that is, the value of B&B is too large and that of CH is too small for our experiment.

Figure 3 shows the difference in the profiles calculated by using between the Fe-concentration dependent and Fe-concentration independent diffusion coefficients by Misener (1974). Figures 3a and b show the results of one-dimensional and spherical approximations, respectively. The profile for the Fe-concentration independent diffusion-

coefficient by MI is calculated by fixing the  $C_{Fe}$  value of the expression that reported by MI to the initial (uniform) value of the Fa component (=9). The curvature of the profiles around a high Fe-concentration gradient is different each other, suggesting that the Fe-concentration dependence of the Fe-Mg interdiffusion coefficient in olivine is important when the Fa component varies widely like our experiment. The difference in the curvature between the two profiles is mainly due to the fact that the diffusion coefficient for a high Fe-concentration is larger than that for a low Fe-concentration, that is, the higher the Fe-concentration is, the larger the diffusion coefficient is.

Figure 3 also compares differences between the one-dimensional and spherical approximations. For the same diffusion time, the profile calculated by spherical approximation gives a profile in which atomic diffusion is much more extensive (Fig. 3). 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.

This evaluation of the diffusion coefficients is based on the experimental product performed under the restricted condition. Experimental products under different conditions (*e.g.*, temperature, chemical composition of olivine, oxygen fugacity) may give different results.

## 6. Conclusions

The conclusions reached in the present study are the following:

(1) The Fe-Mg interdiffusion coefficients in olivine reported should be compared under the same conditions (*e.g.*, Fe concentration and oxygen fugacity), because experimental conditions are different among the literatures.

(2) There are about two orders of magnitude difference in the Fe-Mg interdiffusion coefficients at 1250°C reported by Buening and Buseck (1973) and Chakraborty (1997). Other reported values fall between these extremes.

(3) For our experiment, the profile calculated by using the Fe-Mg interdiffusion coefficient reported by Misener (1974) with oxygen fugacity dependence gives the best fit to the observed profile.

(4) The Fe-concentration dependence of the Fe-Mg interdiffusion coefficient in olivine is important when the Fa component varies widely.

## Acknowledgments

Helpful suggestions and review by Dr. G. A. McKay greatly improved the manuscript. We thank Prof. M. Kimura for a constructive review.

## References

- Buening, D.K. and Buseck, P.R. (1973): Fe-Mg lattice diffusion in olivine. *J. Geophys. Res.*, **78**, 6852–6862.  
Carslaw, H.S. and Jaeger, J.C. (1959): *Conduction of Heat in Solids*, 2nd ed. Oxford, Clarendon Press, 510 p.  
Chakraborty, S. (1997): Rates and mechanisms of Fe-Mg interdiffusion in olivine at 980°C–1300°C. *J. Geophys. Res.*, **102**, 12317–12331.  
Crank, J. (1975): *The Mathematics of Diffusion*, 2nd ed. Oxford, Clarendon Press, 414 p.

- Eugster, H.P. and Wones, D.R. (1962): Stability relations of the ferruginous biotite, annite. *J. Petrol.*, **3**, 82–125.
- Jurewicz, A.J.G. and Watson, E.B. (1988): Cations in olivine, Part 2: Diffusion in olivine xenocrysts, with applications to petrology and mineral physics. *Contrib. Mineral. Petrol.*, **99**, 186–201.
- Misener, D.J. (1974): Cationic diffusion in olivine to 1400°C and 35 kbar. *Carnegie Inst. Washington Publ.*, **634**, 117–129.
- Miyamoto, M. and Mikouchi, T. (1998): Evaluation of diffusion coefficients of Fe-Mg and Ca in olivine. *Mineral. J.*, **60**, 2917–2920.
- Miyamoto, M., McKay, D.S., McKay, G.A. and Duke, M.B. (1986): Chemical zoning and homogenization of olivines in ordinary chondrites and implications for thermal histories of chondrules. *J. Geophys. Res.*, **91**, 12804–12816.
- Nakamura, A. and Schmalzried, H. (1984): On the Fe<sup>2+</sup>-Mg<sup>2+</sup>-interdiffusion in olivine (II). *Phys. Chem.*, **88**, 140–145.
- Stolper, E. (1977): Experimental petrology of eucrite meteorites. *Geochim. Cosmochim. Acta*, **41**, 587–611.

*(Received October 29, 2001; Revised manuscript accepted January 11, 2002)*