

Variable initial zoning profiles and Fe-Mg diffusion coefficients for olivine: Effects on cooling rates calculated by diffusion modeling in a pallasite

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Abstract: Because chemical zoning of minerals contains information about the thermal history of the parent body, the cooling rate or burial depth can be calculated by solving the diffusion equation. Several factors influence the results of these calculations. We evaluated the cooling rate (and burial depth) calculated by using different initial (starting) zoning profiles and different diffusion coefficients on the basis of the Fe-Mg chemical zoning profile observed for pallasite (Esquel) olivine. Uncertainties in initial compositional profile and Fe-Mg diffusion coefficient in olivine both lead to error in model cooling rates. Discrepancies between different experimentally determined diffusion coefficients lead to uncertainties in model cooling rate that exceed those due to initial zoning profiles by one order of magnitude. These results highlight the need for accurate determination of diffusion coefficients in olivine.

key words: diffusion, pallasite, olivine, cooling rate, chemical zoning

1. Introduction

Because chemical zoning in minerals provides information on their thermal history of the parent rock, compositional profiles are often used to calculate the cooling rate or burial depth by solving the diffusion equation assuming that chemical zoning, except for primary igneous zoning is produced by diffusional modification (*e.g.*, Miyamoto *et al.*, 1986). There are several factors that influence the results of these calculations. For example, although the atomic diffusion coefficient in minerals is one of the most important factors, there is often a great deal of variation among the reported values of the diffusion coefficient of an element in a mineral.

Another factor that affects these calculations is the initial zoning profile that is assumed (initial condition). It is sometimes difficult to determine this initial zoning profile, because chemical zoning has been affected by diffusional modification. In this case, we need to estimate an appropriate initial profile. Because the estimated initial profile may not be completely correct, it is necessary to examine the effect of different initial profiles on model cooling rates obtained by diffusion calculations.

In this paper, we calculate cooling rates (and burial depths) on the basis of the Fe-Mg chemical zoning profile previously observed for olivine in the Esquel pallasite (Miyamoto, 1997), and compare the effect of uncertainty in initial zoning profile with the effect of uncertainty in diffusion coefficient. In our previous paper, we used an unzoned crystal for the initial condition and the Fe-Mg diffusion coefficient of olivine reported by Buening and Buseck (1973) for solving the diffusion equation to calculate the cooling rate and burial depth of pallasite olivine. Olivine diffusion coefficients have also been determined experimentally by Misener (1974) and Chakraborty (1997).

2. Method

2.1. Calculation procedures

It was assumed that atomic diffusion controls compositional gradients of the Fa [=Fe/(Mg+Fe)] (mol%) component in pallasite olivine. A calculated diffusion profile was fitted to the observed zoning to obtain the cooling rate or burial depth (e.g., Miyamoto *et al.*, 1986, 2002). Calculations were made assuming several different initial profiles and an unzoned initial profile. For a specific linear cooling rate (or burial depth) from an initial temperature (T_1), a diffusion profile was calculated by numerically solving the diffusion equation. The cooling rate (or burial depth) that generated a compositional profile most similar to the observed zoning profile was determined by the non-linear least-squares method (Simplex method). Although the initial temperature (T_1) was estimated to be 1100°C by Miyamoto (1997), the cooling rate and burial depth were calculated for various initial temperatures for comparison.

For the burial depth calculation, it was assumed that the sample was buried in a hot slab at a uniform initial temperature of T_1 and that the ambient temperature at its surface was 200 K. A thermal diffusivity of 0.1 cm²/s for the slab was estimated from diffusivities of iron metal and olivine that are the major constituents of pallasite (Miyamoto, 1997). For a specific burial depth, the change in temperature as a function of time was calculated by using the analytical expression of the solution of the heat diffusion equation from Carslaw and Jaeger (1959, p. 235). Using the temperature-time relation for a specific burial depth, a compositional profile resulting from diffusion of chemical zoning was calculated by numerically solving the diffusion equation. The burial depth for which the calculated zoning profile best fit the observed zoning profile was determined by the non-linear least-squares method.

The Fa component at the rim of the olivine grain (boundary condition) as well as the cooling rate (or burial depth) were simultaneously determined by using the non-linear least-squares method (Simplex method). It must be noted that a one-dimensional approximation was used in all of these calculations of zoning profiles (see Miyamoto *et al.*, 2002). The details of calculation procedures are similar to those described in Miyamoto *et al.* (1986, 2002).

2.2. Initial profile

Because different initial zoning profiles result in different cooling rates, we calculate the cooling rate (or burial depth) by using different initial zoning profiles to evaluate the sensitivity of these calculations to the assumed initial conditions. Several initial profiles

were calculated by using the Rayleigh equation for closed-system fractional crystallization and the difference in the cooling rate (or burial depth) was calculated for the different initial profiles. The equation is

$$\frac{C_L}{C_0} = f_{O_2},$$

where C_0 and C_L are the initial concentration in the bulk liquid and the concentration in the observed liquid, respectively. K_D is the distribution coefficient, and F is the fraction of liquid remaining. We used the distribution coefficient for Fe/Mg of 0.30 (e.g., Stolper, 1977).

2.3. Diffusion coefficient

The cooling rate obtained by modeling the Fe-Mg zoning profile on the basis of atomic diffusion is strongly dependent on the Fe-Mg interdiffusion coefficient (D_{Fe}). Although several investigators report the D_{Fe} for olivine, there are approximately two orders of magnitude variation among these values (See Fig. 1 in Miyamoto *et al.*, 2002). The largest value is reported by Buening and Buseck (1973) and the smallest one is by Chakraborty (1997).

Miyamoto *et al.* (2002) evaluated the Fe-Mg diffusion coefficients of olivine by employing the experimentally produced chemical zoning pattern and concluded that the profile calculated by the Fe-Mg diffusion coefficient reported by Misener (1974) with oxygen-fugacity variation gives the best fit to the zoning profile. Miyamoto and Mikouchi (1998) and Miyamoto *et al.* (2002) also extrapolated the D_{Fe} reported by Misener (1974) by using an equation for variation with oxygen fugacity similar to that of Buening and Buseck (1973), because the D_{Fe} reported by Misener (1974) is determined under the FMQ (fayalite-magnetite-quartz) buffer of oxygen fugacity. This extrapolation enabled us to employ the Fe-Mg diffusion coefficient of Misener (1974) under any oxygen-fugacity condition. The expression for the D_{Fe} proposed by Miyamoto *et al.* (2002) is

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

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. The oxygen fugacity of a pallasite measured by Brett and Sato (1984) was employed.

We recalculated the cooling rate and burial depth of Esquel olivine by using the D_{Fe} reported by Misener (1974) with oxygen-fugacity variation and compared them with those reported by Buening and Buseck (1973) and Chakraborty (1997).

3. Results and discussion

Figure 1 shows initial zoning profiles calculated using the closed-system fractional crystallization model. The initial profile changes as a function of the fraction of liquid remaining (F). In order to evaluate the difference in the cooling rate, we used the initial zoning profile for an extreme case (e.g., F of 1%). The observed zoning profile (open circles in Fig. 1) was measured by an electron probe and is the same as that used

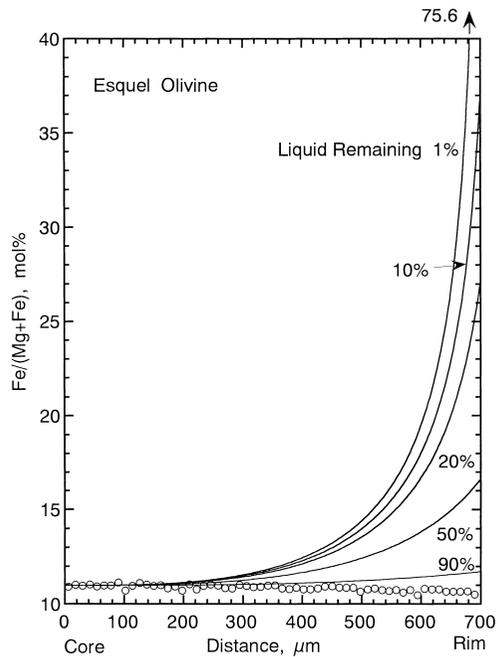


Fig. 1. Initial zoning profiles (solid curves) for starting the diffusion calculation. The profiles were calculated by using the Rayleigh equation for closed-system fractional crystallization. Numbers on curves show the fraction of liquid remaining. Open circles show the observed Fe-Mg zoning profile for Esquel pallasite olivine (Miyamoto, 1997). A calculated Fe-Mg diffusion profile starting with the initial profile (solid curve) was fitted to the observed zoning profile (open circles) to obtain the best-fit cooling rate (or depth).

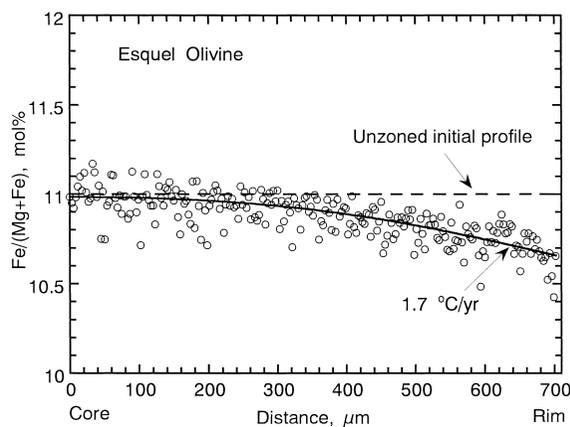


Fig. 2. An example (solid curve) of the best-fit results calculated by using an initial unzoned compositional profile (dotted line) and the Fe-Mg diffusion coefficient reported by Misener (1974) with oxygen-fugacity variation (Miyamoto et al., 2002).

in our previous study (Miyamoto, 1997). A calculated Fe-Mg diffusion profile starting with the initial profile (one of the solid curves in Fig. 1) was fitted to the observed zoning profile (open circles) to obtain the best-fit cooling rate. Figure 2 shows an example (solid curve) of the best-fit results calculated by using an unzoned initial profile (dotted line) and the D_{Fe} reported by Misener (1974) with oxygen-fugacity variation (Miyamoto *et al.*, 2002).

Figure 3a shows the cooling rates obtained using the different initial profiles expressed as a function of the fraction of liquid remaining, and the diffusion coefficient by Misener (1974) with oxygen fugacity variation. There is less than one order of magnitude difference in the cooling rate. The slowest cooling rate is obtained for the initial profile for F of 1%, and the fastest cooling rate is for the unzoned initial profile. Given the great difference in the shape of the initial profile (Fig. 1), the effect of this variable on the cooling rate is not substantial. Figure 3b shows the effect of the initial profile on the calculated burial depth.

Figure 4a compares the results of the cooling rates obtained for the D_{Fe} reported by Buening and Buseck (1973), Misener (1974) with the oxygen-fugacity variation (Miyamoto *et al.*, 2002), and Chakraborty (1997) as a function of initial temperatures of cooling. Unzoned initial zoning profile was used. The fastest cooling rate is obtained using the data of Buening and Buseck (1973), and the slowest using those of Chakraborty (1997) for the same initial temperature. Because we used a linear cooling rate, the difference in the cooling rate of approximately two orders of magnitude is the same as those for the diffusion coefficient (See Fig. 1 in Miyamoto *et al.*, 2002). In fact, linear cooling rates are generally proportional to the diffusion coefficients.

Figure 4b compares the results of the burial depth, showing the difference is approximately one order of magnitude. In general, while linear cooling rates are proportional to the diffusion coefficients, the burial depth is inversely proportional to the square root of the diffusion coefficient.

In conclusion, the difference in the diffusion coefficient has more influence on the

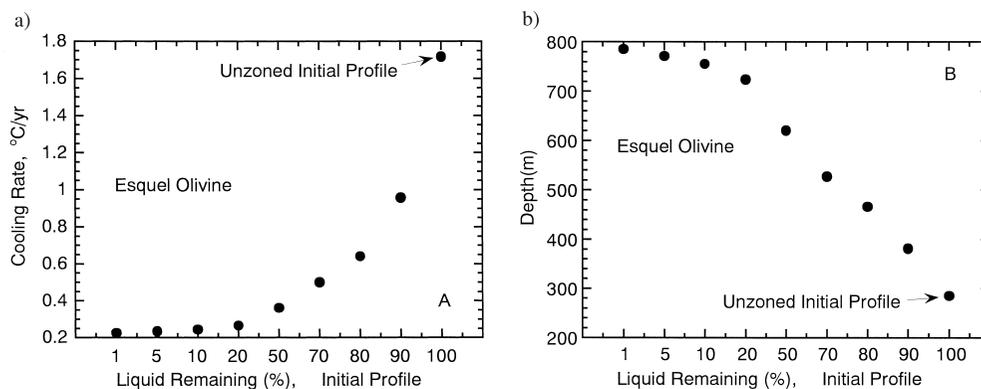


Fig. 3. The difference in the cooling rate (a) and burial depth (b) due to the difference in the initial profile for diffusion calculation. The initial profile is shown as a function of the fraction of liquid remaining for closed-system fractional crystallization. Cooling is from 1100°C.

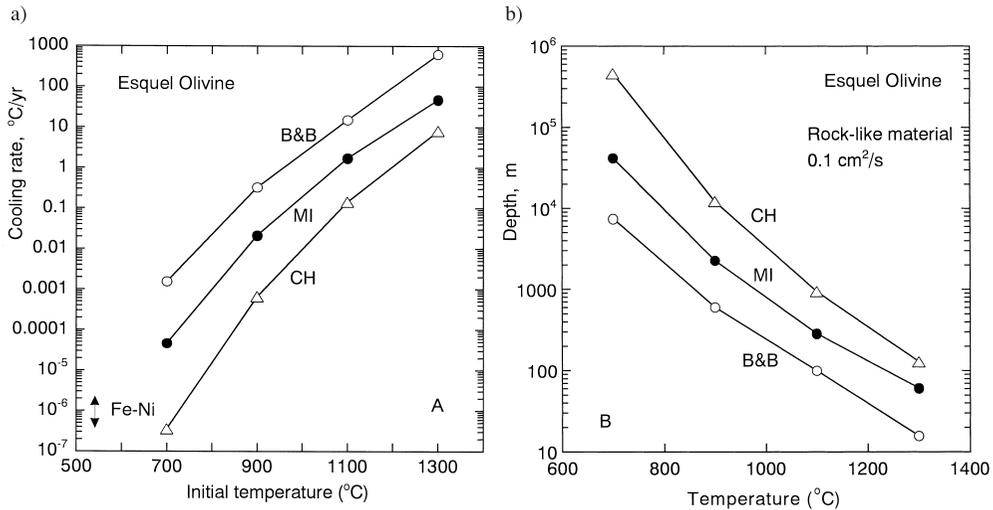


Fig. 4. Comparison of the cooling rate (a) and burial depth (b) calculated by the Fe-Mg diffusion coefficients of Buening and Buseck (B&B) (1973) (open circles), Misener (MI) (1974) with oxygen-fugacity variation (Miyamoto et al., 2002) (solid circles) and Chakraborty (CH) (1997) (open triangles). The cooling rate is shown as a function of initial temperature of cooling. Unzoned initial profile was used. Fe-Ni (arrows) show the range of the cooling rate of pallasites obtained by Fe-Ni data (e.g., Wood, 1979).

cooling rate (or burial depth) than that of the initial zoning profile. Establishing the Fe-Mg diffusion coefficient within an uncertainty of one order of magnitude would reduce the error in the cooling rate calculations to a level comparable to the error due to variable initial profiles.

4. Conclusions

This study evaluated model cooling rates and burial depths for pallasite based on Fe-Mg zoning in olivine, and compared uncertainties due to initial zoning profiles with uncertainties due to different experimental calibrations for the diffusion coefficient. The conclusions of the present study are the following:

(1) The difference in the model cooling rate due to the difference in the initial profile is less than one order of magnitude. This corresponds to a few times difference in the model burial depth.

(2) The differences in the model cooling rates due to the differences in the previously reported Fe-Mg interdiffusion coefficients are approximately two orders of magnitude. The difference in the model burial depth is approximately one order of magnitude.

(3) The differences in the previously reported Fe-Mg interdiffusion coefficients have more influence on the cooling rate (or burial depth) than that of the initial zoning profile.

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References

- Brett, R. and Sato, M (1984): Intrinsic oxygen fugacity measurements on seven chondrites, a pallasite, and a tektite and the redox state of meteorite parent bodies. *Geochim. Cosmochim. Acta*, **48**, 111–120.
- 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°–1300°C. *J. Geophys. Res.*, **102**, 12317–12331.
- Misener, D.J. (1974): Cationic diffusion in olivine to 1400°C and 35 kbar. *Geochemical Transport and Kinetics*, ed. by A.W. Hofmann *et al.* Washington, D.C., Carnegie Inst., 117–129 (Carnegie Inst. Washington, Publ., **634**).
- Miyamoto, M. (1997): Chemical zoning of olivine in several pallasites. *J. Geophys. Res.* **102**, 21613–21618.
- 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.
- Miyamoto, M., Mikouchi, T. and Arai, T. (2002): Comparison of Fe-Mg interdiffusion coefficients in olivine. *Antarct. Meteorite Res.*, **15**, 143–151.
- Stolper, E. (1977): Experimental petrology of eucrite meteorites. *Geochim. Cosmochim. Acta*, **41**, 587–611.
- Wood, J.A. (1979): Review of the metallographic cooling rates of meteorites and a new model for the planetesimals in which they formed. *Asteroids*, ed. by T. Gehrels. Tucson, University of Arizona Press, 849–891.