

**Fe<sup>2+</sup>-Mg INTERDIFFUSION IN ORTHOPYROXENE: CONSTRAINTS FROM CATION ORDERING AND STRUCTURAL DATA AND IMPLICATIONS FOR COOLING RATES OF METEORITES:** J. Ganguly, Dept. of Geosciences, University of Arizona, Tucson, AZ 85721, and V. Tazzoli, Centro di Studio per la Cristallografia Strutturale, Università di Pavia, Via Bassi, 4, I-27100 Pavia, Italy

Orthopyroxene crystals in a number of meteorites exhibit compositional zoning of Fe and Mg, which provide important constraint on their cooling rates. However, attempts to model cooling rate of these crystals from Fe-Mg zoning profiles [1] suffer from the lack of any measured or theoretically well constrained Fe-Mg interdiffusion data in OPx. It has been assumed that Fe-Mg interdiffusion in OPx is only slightly slower than that in olivine [1]. The purpose of this paper is to (a) calculate the Fe-Mg interdiffusion coefficient ( $D(\text{Fe-Mg})$ ) in OPx from the available data on the kinetics and thermodynamics of intracrystalline Fe-Mg fractionation and (2) provide analytical formulation relating cooling rate to the length of the diffusion zone across the interface of the overgrowth of a mineral on itself with application to Mg diffusion profile across OPx overgrowth on OPx in certain mesosiderites.

Besancon [2] and Saxena et al [3] have studied the kinetics of Fe-Mg disordering and their equilibrium distributions between the non-equivalent octahedral sites, M1 and M2, at 1 bar, 600 - 800°C. Since the Fe-Mg order-disorder in OPx involves diffusion of Fe and Mg, these data permit an approximation of  $D(\text{Fe-Mg})$ , within the framework of the Absolute Reaction Rate theory [4], according to which

$$D = \lambda^2 K \quad (1)$$

in an ideal solution, where  $\lambda$  is the distance between successive equilibrium positions of the diffusing species, and  $K$  is the specific rate constant governing the diffusion process. Analysis of the crystal structure of OPx suggests that the diffusion of divalent cation must be fastest parallel to c-axis and slowest parallel to a-axis. Macroscopic diffusion of Fe and Mg in OPx (in response to a compositional gradient) involves both ordering and disordering process (i.e. transfer of Fe from M1 to M2 site and the reverse). Thus, in order to calculate  $D$  from  $K$  according to eqn. (1), we have taken the average of the disordering and ordering rate constants; the latter is derived from the measured values of  $K(\text{disord})$  and  $K_{\text{d}}$ , using the relation  $K_{\text{d}} = K(\text{disord})/K(\text{ord})$  [5,6], where  $K_{\text{d}}$  is the intracrystalline distribution coefficient ( $= (\text{Fe/Mg})_{\text{M1}}/(\text{Fe/Mg})_{\text{M2}}$ ). In order-disorder process in OPx, the observed effect is the result of (anisotropic) diffusive exchange of Fe and Mg along different directions, but structural considerations suggest that it should be dominated by Fe-Mg exchange parallel to the c- and b-axes. The average distance ( $\lambda$ ) between the octahedral sites along these directions is  $\sim 3.744 \text{ \AA}$ . We, thus, obtain from eqn. (1) and the intracrystalline exchange data of [2] and [3],

$$D \approx 3.7(10^{-6})\exp(-27961/T) \text{ cm}^2/\text{s}; \quad (Q = 55.6 \text{ kcal}) \quad (2a)$$

and

$$D \approx 7.6(10^{-4})\exp(-32,159/T) \text{ cm}^2/\text{s}; \quad (Q = 63.9 \text{ kcal}) \quad (2b)$$

respectively ( $Q$ : activation energy), as average of Fe-Mg interdiffusion coefficient in OPx ( $\text{Mg}/(\text{Mg}+\text{Fe}) \sim 0.5$ ) along c- and b-axes at  $f\text{O}_2$  defined by WI buffer (Fig.1). Theoretical considerations suggest that the change of  $f\text{O}_2$  should affect  $D$  according to the relation  $D \propto f\text{O}_2^{1/6}$  [7,8]. Also the available experimental data on the compositional dependence of  $K$  [2] suggest that  $D$  should decrease with increasing Mg concentration, and would be about an order of magnitude slower at  $X_{\text{Mg}} \sim 0.15$ . Eqn (2) yields Fe-Mg interdiffusion coefficients of OPx, which are of the same order as those in garnet between 600°C and 1000°C [8,9], but are at least 3 orders of magnitude slower than those in olivine [10]. The similarity of Fe-Mg interdiffusion in OPx and garnet is also supported by observational data [11,12].

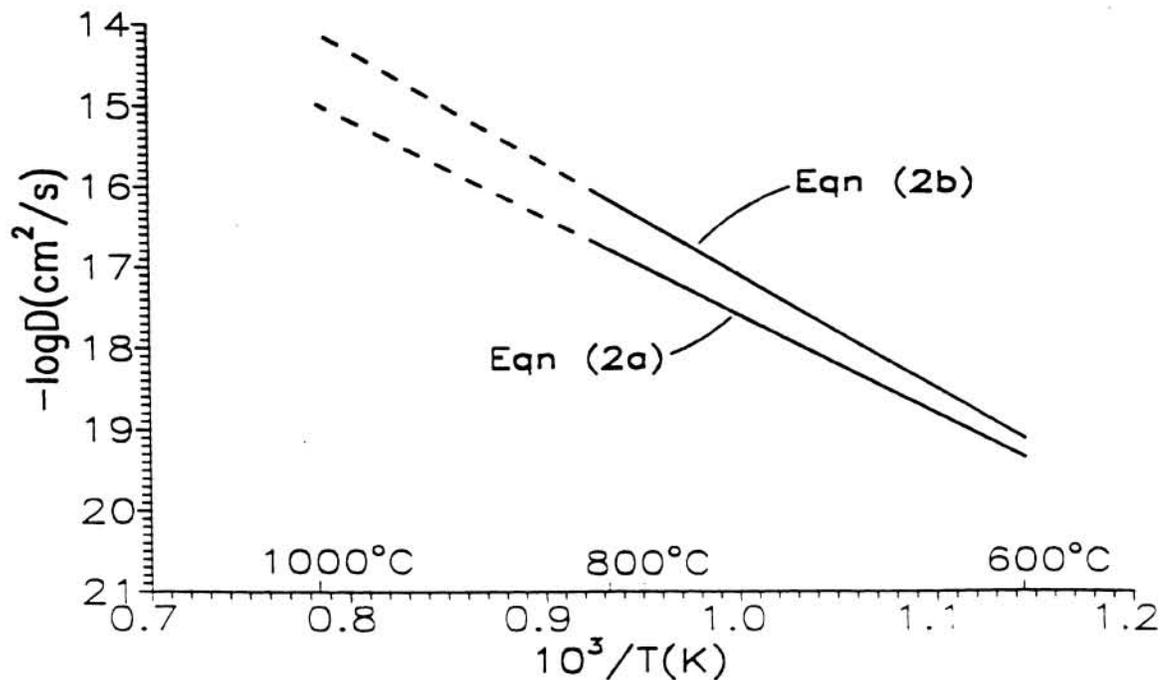
Assuming that the cooling rate followed an asymptotic relation  $1/T = 1/T^{\circ} + \eta t$ , where  $\eta$  is

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a cooling time constant ( $K^{-1}t^{-1}$ ) and  $T^{\circ}$  is the initial temperature, we have derived the following relation relating  $\eta$  to the length of the diffusion zone ( $X$ ) measured normal to the interface of an overgrowth of a mineral on itself when the core and overgrowth have different but initially homogeneous compositions, and are large compared to the length of the diffusion zone.

$$\eta = 64D(T^{\circ})R/QX^2 \quad (3),$$

where  $D(T^{\circ})$  is the diffusion coefficient at the initial temperature  $T^{\circ}$ . In order to use eqn. (3), one needs to correct the measured diffusion profile for the convolution or spatial averaging effect of the microprobe beam as discussed by Ganguly et al. [13]. However, as shown by these workers, the correction is negligible for  $X \geq 15 \mu\text{m}$  if the profile was measured by a finely focussed beam in a modern electron-microprobe. We have applied eqns. (2) and (3) to calculate the high temperature cooling rate of two mesosiderites, **Lowicz** and **Clover Springs**, on the basis of published Mg zoning profile in OPx/OPx couples and temperature of formation of the overgrowths [1]. The results yield cooling rate ( $dT/dt = -nT^2$ ) of 1-30 K/100 year for Lowicz, and about a factor of ten less for Clover Springs between 600 -1100°C. However, the difference in the length of diffusion zoning between the two samples may be due to different crystallographic orientations of the direction of measurement of concentration profiles. These cooling rates are geologically rapid, but are 3-4 orders of magnitude slower than those estimated earlier [1].



- [1] Delaney J. et al. (1981) *Proc. LPS*, 12B, 1315; [2] Besancon J. R. (1981) *Amer Min* 66, 965; [3] Saxena S. K. et al. (1987) *Phys Chem Min* 15, 140; [4] Glasstone S. K. et al. (1941) *The theory of rate processes*. McGraw; [5] Mueller R. F. (1967) *Phys Chem Solids* 28, 2239; [6] Ganguly J. (1982) *Adv Phys Geochem* 2, 58; [7] Buening D. K. and Buseck P. R. (1973) *JGR* 78, 6852; [8] Chakraborty S. and Ganguly J. (1991) in Ganguly J. ed. *Adv Phys Geochem* 8, 120; [9] Chakraborty S. and Ganguly J. (1992) *CMP* 111, 74; [10] Misener D. J. (1974) in Hoffman A. et al. ed. *Geochem Transport & Kinetics*, 117; [11] Smith D. and Barron B. R. (1991) *Amer Min* 76, 1950; [12] Anovitz L. (1987) *Ph.D. Diss., U. Mich*; [13] Ganguly J. et al. (1988) *Amer Min* 73, 901.