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Fe^{2+}-Mg interdiffusion in orthopyroxene: Retrieval from the data on intracrystalline exchange reaction

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ABSTRACT

Crystal structural data of orthopyroxene suggest that Fe-Mg interdiffusion should be fastest along the **c** axis and slowest along the **a** axis and that the overall kinetics of the Fe^{2+}-Mg fractionation, or order-disorder, between the M1 and M2 sites should be dominated by exchange along the **c** and **b** directions. Using these crystallographic constraints and a formulation of the diffusion process according to absolute reaction rate theory, we have developed an expression of the average Fe^{2+}-Mg interdiffusion coefficient along the **c** and **b** directions of orthopyroxene, $D(\text{Fe-Mg})_{\text{c-b}}$, in terms of the rate constant of the disordering process [Fe^{2+} (M2) + Mg (M1) → Fe^{2+} (M1) + Mg (M2)], the equilibrium intracrystalline distribution of Fe^{2+} and Mg, and the average distance between the neighboring M1 and M2 sites along **c** and **b**. $D(\text{Fe-Mg})_{\text{c-b}}$ has been evaluated from the available experimental data on the order-disorder process as a function of temperature and composition and is defined as follows:

$$\log D(\text{Fe-Mg})_{\text{c-b}} = -5.54 + 2.6X_{\text{Fe}} - \frac{12530}{T}.$$

This expression is valid at $T \approx 500$–800 °C, $f_{O_2} \approx$ WI to 0.8 log units above the WI buffer, and $X_{\text{Fe}} \approx 0.10$–0.50 and yields values of $D(\text{Fe-Mg})_{\text{c-b}}$ in orthopyroxene that are at least two orders of magnitude smaller than $D(\text{Fe-Mg})_{\text{c}}$ in olivine and about one order of magnitude larger than the isotropic D(Fe-Mg) in garnet at the same X_{Fe} and f_{O_2} conditions. However, because of diffusion anisotropy in orthopyroxene, the apparent difference between D(Fe-Mg) in orthopyroxene and garnet could seem smaller in terms of compositional zoning in random thin sections of natural rocks. Comparison of the value of the tracer diffusion coefficient of Mg, D^{*}_{Mg}, at $X_{\text{Fe}} = 1$, derived from the above interdiffusion data with that determined by Cygan et al. (1994) at $X_{\text{Fe}} = 0.1$ suggests that D^{*}_{Mg} increases with increasing Fe/Mg ratio.

INTRODUCTION

Knowledge of the Fe-Mg interdiffusion property in orthopyroxene, D(Fe-Mg), is important to the interpretation of the closure temperature of Fe-Mg exchange geothermometers that involve orthopyroxene and to the retrieval of cooling history of the host rocks from the retrograde compositional zoning in orthopyroxene crystals in terrestrial rocks (e.g., Lasaga, 1983; Ganguly and Chakraborty, 1991; Smith and Barron, 1991; Pattison and Bégin, 1994) and in meteorites (Ganguly et al., 1994). However, in the absence of any direct experimental data, several workers have tried to constrain Fe-Mg interdiffusion in orthopyroxene relative to that in garnet on the basis of Fe-Mg zoning profiles in coexisting orthopyroxene and garnet crystals in granulite facies rocks (Pattison and Bégin, 1994) and in mantle-derived xenoliths (Smith and Barron, 1991). The general consensus of these studies is that Fe-Mg interdiffusion in orthopyroxene is similar to that in garnet, but perhaps somewhat faster, at the conditions through which diffusion was effective in these rocks. On the other hand, Delaney et al. (1981) have argued that D(Fe-Mg) in orthopyroxene should be similar to that in olivine, which is several orders of magnitude larger than that in garnet.

In orthopyroxene, Fe and Mg fractionate between two nonequivalent octahedral sites, M1 and M2. The rate of this fractionation process has been measured experimentally by several workers (Besancon, 1981; Anovitz et al., 1988; Saxena et al., 1987; Skogby, 1992; and Sykes-Nord and Molin, 1993). Inasmuch as intracrystalline fractionation or order-disorder is a diffusion-controlled phenomenon, it should be possible to retrieve the Fe-Mg interdiffusion coefficient in orthopyroxene from these experimental data. The purpose of this paper is (1) to develop a theoretical relation between diffusion and order-disorder properties of Fe and Mg in orthopyroxene

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and (2) to predict D(Fe-Mg) in orthopyroxene from the available experimental data on the order-disorder properties. Preliminary reports of this work were presented by Ganguly and Chakraborty (1990) and Ganguly and Tazzoli (1992).

KINETICS OF INTRACRYSTALLINE Fe^{2+}-Mg FRACTIONATION

The thermodynamics and kinetics of Fe^{2+}-Mg order-disorder in ferromagnesian silicates have been reviewed extensively by Ganguly (1982). Thus, only a brief outline of the theory is given below. Following the work of Dienes (1955) on metallic alloys, Mueller (1967, 1969) treated the Fe^{2+}-Mg fractionation between the M1 and M2 sites of orthopyroxene in terms of a homogeneous chemical exchange reaction:

$$Fe^{2+}\ (M2) + Mg\ (M1) \rightleftharpoons Fe^{2+}\ (M1) + Mg\ (M2). \quad (1)$$

It was assumed by Mueller, and subsequently shown by experimental studies (e.g., Besancon, 1981; Saxena et al., 1987; Anovitz et al., 1988), that the kinetics of this exchange reaction follows a second-order rate law, which can be expressed as

$$-\frac{\partial X_{Fe(M2)}}{\partial t} = qC_0[K^+ X_{Fe(M2)}X_{Mg(M1)} - K^- X_{Fe(M1)}X_{Mg(M2)}] \quad (2)$$

where K^+ and K^- are the specific rate constants for the forward (disordering) and backward (ordering) reactions, respectively, $X_{i(j)}$ is the atomic fraction of the cation i in the site j, C_0 is the total number of M1 and M2 sites in a unit volume of the crystal, which is assumed to remain constant through an order-disorder process, and $q = C_{M2}/C_0$, where C_{M2} is the number of M2 sites in a unit volume of the crystal. Other symbols are defined in Appendix 1. For brevity, we will henceforth refer to Fe^{2+} simply as Fe.

The forward and backward rate constants are related to the equilibrium intracrystalline distribution coefficient, K_D, according to (Mueller, 1967; Ganguly, 1982),

$$K_D = \frac{Fe\ (M1)\, Mg\ (M2)}{Mg\ (M1)\, Fe\ (M2)} = \frac{K^+}{K^-} \quad (3)$$

where $i(j)$ can be either the atomic fraction or the number of atoms of i in the j site. The quantity C_0K^+, which has the dimension of t^{-1}, has been retrieved directly by modeling the experimental kinetic data (Besancon, 1981; Saxena et al., 1987; Anovitz et al., 1988; Skogby, 1992; Sykes-Nord and Molin, 1993) according to an integrated form of Equation 2, which was derived originally by Mueller (1967) and in which the ordering rate constant, K^-, was eliminated by using relation 3.

RELATIONSHIP BETWEEN Fe-Mg INTERDIFFUSION AND ORDER-DISORDER KINETICS

Formalism based on absolute reaction rate theory

According to the absolute reaction rate theory (Glasstone et al., 1941), the diffusion coefficient of a component in an ideal solution can be expressed as

$$D = \lambda^2\kappa \quad (4)$$

where λ is the average jump distance between the successive equilibrium positions of the diffusing species, and κ is the specific rate constant for diffusion. Inasmuch as the mixing property of Fe and Mg in orthopyroxene does not seem to deviate significantly from ideality at conditions of geological interest (see Ganguly and Saxena, 1987, for a review), Equation 4 should be applicable to orthopyroxene in natural rocks to a very good approximation.

The relationship between the rate constants for diffusion and order-disorder can be understood in the following way: the rate constant for the diffusion of Fe from M2 to an adjacent M1 site is, on the average, simply the forward (or disordering) rate constant for the exchange reaction and vice versa. The structural configuration of orthopyroxene (Fig. 1) suggests that the easiest diffusion path of Fe and Mg along any crystallographic direction should be through the transfer of these atoms between M2 and M1 sites. Thus, we expect that the rate constant for the interdiffusion of Fe and Mg along any crystallographic direction should be an average of the rate constants for disordering and ordering along that direction. For example, we expect that

$$\kappa(\text{Fe-Mg})_c = \tfrac{1}{2}(k_c^+ + k_c^-) \quad (5)$$

where κ(Fe-Mg)$_c$ is the rate constant for Fe-Mg interdiffusion along the **c** axis and k_c^+ and k_c^- represent, respectively, the disordering and ordering rate constants along the same direction. However, the rate constants for order-disorder are determined by measuring the change of the average site occupancies (as a function of temperature and time) of a single crystal by X-ray diffraction study (Saxena et al., 1987; Sykes-Nord and Molin, 1993) or of a collection of crystals of essentially the same composition by Mössbauer spectroscopy (Besancon, 1981; Anovitz et al., 1988; Skogby, 1992). Thus, an experimentally determined or overall rate constant represents the weighted average of the microscopic rate constants, i.e., $K^+ \approx \Sigma w_i k_i^+$, and similarly for K^-, where i stands for an axial direction (**a**, **b**, or **c**) and w_i is a weighting factor for k^+ along the same direction.

Crystallographic constraints and diffusion anisotropy

To understand how the microscopic rate constants relate to an overall rate constant, let us consider the spatial relations of the octahedral sites in the structure of orthopyroxene, which is schematically illustrated in Figure 1. The distances between the nearest-neighbor M1 and M2 sites along **a**, **b**, and **c** axes are summarized in Table 1. It is evident that these sites are most closely spaced along **c**, being linked together in a zigzag pattern. Thus, we expect that the Fe-Mg exchange along **c** should be easier than along the other crystallographic directions. On the other hand, Fe-Mg exchange along **a** should be relatively

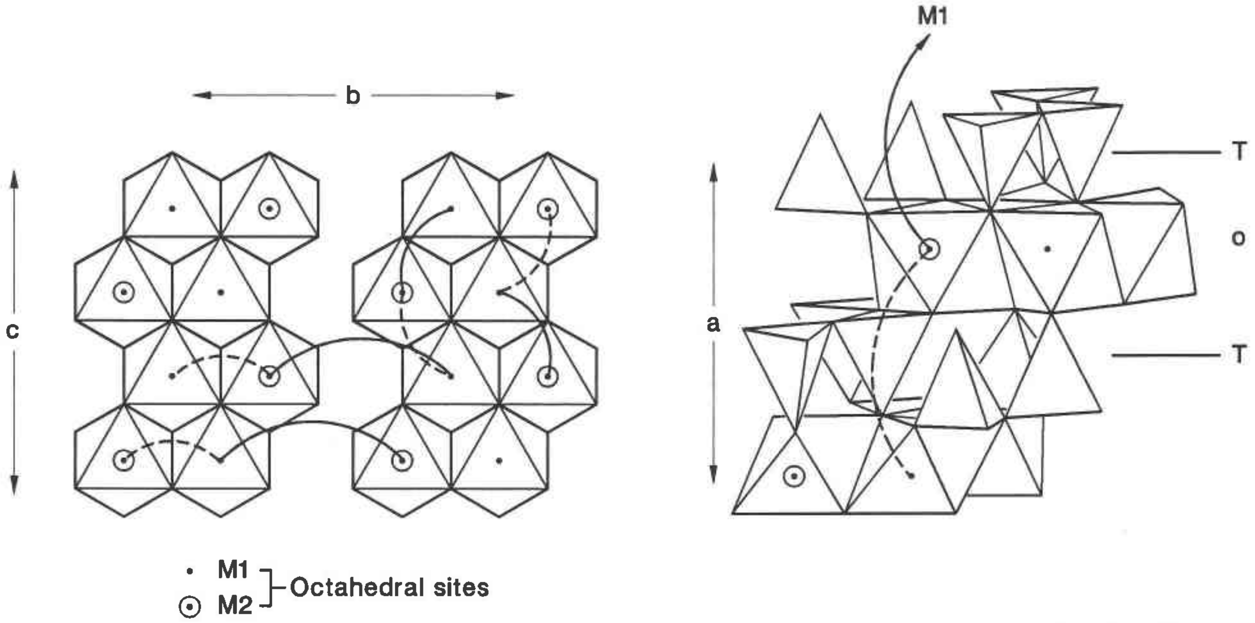

Fig. 1. Schematic illustration of the stereochemical arrangement of the octahedral sites in orthopyroxene along the **a**, **b**, and **c** directions. The solid and dashed lines indicate the jump distances summarized in Table 1. Along **a**, there is a tetrahedral (T) layer between two successive octahedral (O) layers.

difficult because there is an intervening tetrahedral layer between two successive octahedral layers. The kinetics of Fe-Mg exchange along **b** is likely to be intermediate between that along **c** and **a**. Crystallographic considerations, thus, suggest that the rate constant for the overall Fe-Mg exchange process in orthopyroxene should represent a weighted average of the microscopic rate constants along the three crystallographic directions, with relatively little contribution from $k_{\mathbf{a}}$. We also conclude from the crystal-structural data that the Fe-Mg interdiffusion in orthopyroxene should be anisotropic according to the following order: $D_{\mathbf{c}}$(Fe-Mg) $\geq$ $D_{\mathbf{b}}$(Fe-Mg) $>$ $D_{\mathbf{a}}$(Fe-Mg) and that the interdiffusion coefficient retrieved from the macroscopic order-disorder rate constants should be closer to those along **c** and **b** relative to that along the **a** axis.

Use of the experimentally determined rate constants

From the above discussion, it follows that the substitution of the experimentally determined or overall rate constants of the order-disorder process, K^+ and K^-, in place of the corresponding microscopic rate constants in Equation 5, would yield an average diffusion rate constant that is weighted relatively heavily toward the diffusion rate constants along **c** and **b**. Thus,

$$D(\text{Fe-Mg})_{\text{c-b}} = \lambda^2 \kappa_{\text{c-b}} \approx \lambda^2\left(\frac{K^+ + K^-}{2}\right). \tag{6}$$

When K^- is expressed in terms of K^+ according to Equation 3, the above relation reduces to

$$D(\text{Fe-Mg})_{\text{c-b}} \approx \frac{\lambda^2 K^+}{2}\left(1 + \frac{1}{K_{\text{D}}}\right). \tag{7}$$

When site occupancies are used instead of K_{D}, Equation 7 transforms to

$$D(\text{Fe-Mg})_{\text{c-b}} \approx \frac{\lambda^2 K^+}{2}\left[\frac{(1 - x)y + x(1 - y)}{(1 - y)x}\right] \tag{8}$$

where x = Fe (M1) and y = Fe (M2). The value of λ (i.e., the jump distance between successive equilibrium sites) should be equated to the average distance between the centers of successive M1 and M2 sites along the **c** and **b** axes.

Fe-Mg INTERDIFFUSION COEFFICIENT IN ORTHOPYROXENE

Evaluation of the disordering rate constant

Besancon (1981), Anovitz et al. (1988), and Saxena et al. (1987) have determined K_{D} and K^+ as functions of temperature for natural orthopyroxene crystals with compositions very close to the binary Fe-Mg join. Their kinetic data, along with the compositions of the orthopyroxene crystals, are illustrated in an Arrhenius plot in Figure 2. We have ignored the data on Fe-rich orthopyroxene, PX4-TM2 (81 mol% Fe) of Anovitz et al. (1988), because of the experimental problems discussed in their paper. Also, as they noted, orthopyroxene of the composition of PX4-TM2 is unstable relative to olivine + quartz at the conditions of their experiment. Thus, although they did not detect any breakdown product by X-ray diffraction, the presence of a small amount of olivine below the detection limit of X-ray diffraction cannot be ruled out (also see below).

Besancon (1981) and Anovitz et al. (1988) determined the site occupancies by Mössbauer spectroscopy, whereas Saxena et al. (1987) employed single-crystal X-ray refinement technique. The experimental temperature range was within 500–800 °C in all studies. The f_{O_2} in Besancon's experiments was controlled by a mixture of H_2 and CO_2 and was ~0.8 log f_{O_2} units above that defined by the wüstite + iron (WI) buffer when compared with the calibration of the buffer by O'Neill (1988). Anovitz et al. (1988) controlled f_{O_2} at, and ~0.5 log units above, that defined by the WI buffer, depending on the duration of their experiments. Saxena et al. (1987), on the other hand, did not buffer the f_{O_2} but instead carried out the experiments by sealing the orthopyroxene crystals in evacuated silica tubes to maintain a low but undefined f_{O_2} condition. Since the rate constants depend on f_{O_2} (see below), the lack of knowledge of f_{O_2} limits the usefulness of the data of Saxena et al. in the present work. The work of Skogby (1992) also suffers from the same problem. Further, Skogby has determined K^+ only at 650 °C, which adds to the problem of using his data for any independent and unambiguous constraint in this work.

As is evident from Figure 2, the data of Besancon (1981), Saxena et al. (1987), and Anovitz et al. (1988) agree quite well insofar as the activation energy (Q) of the disordering process is concerned. It ranges between 60701 and 66503 cal/mol, with an average of 62767 (± 2223) cal/mol. Here and elsewhere, the error represents 1 σ statistical uncertainty, arising solely from the scatter of the data but without incorporating the uncertainty of each measurement. The kinetic data do not reveal any systematic dependence of Q on the composition for the range of composition considered above ($X_{Fe} = 0.13–0.49$). From analyses of the available kinetic data from orthopyroxene crystals spanning the range of composition $X_{Fe} \approx 0.13–0.85$, Sykes-Nord and Molin (1993) have shown that Q drops sharply to ~45 kcal/mol at $X_{Fe} = 0.50–0.60$. However, they noted evidence of structural instability in the two Fe-rich crystals that they investigated ($X_{Fe} = 0.61$ and 0.85). They concluded from the crystal structural data that a small amount of Fe^{2+} had sublimated during heating, thereby introducing vacancies, and cautioned about this problem in future experimental studies and when using previously published kinetic data on orthopyroxene in the compositional range $X_{Fe} = 0.60–0.95$. In view of these problems and the others discussed by Anovitz et al. (1988), we ignored the available kinetic data on Fe-rich orthopyroxene crystals, and restricted our predictive model to $X_{Fe} \leq 0.5$, using only those Arrhenian relations that are constrained by experimental determinations at more than two different temperatures.

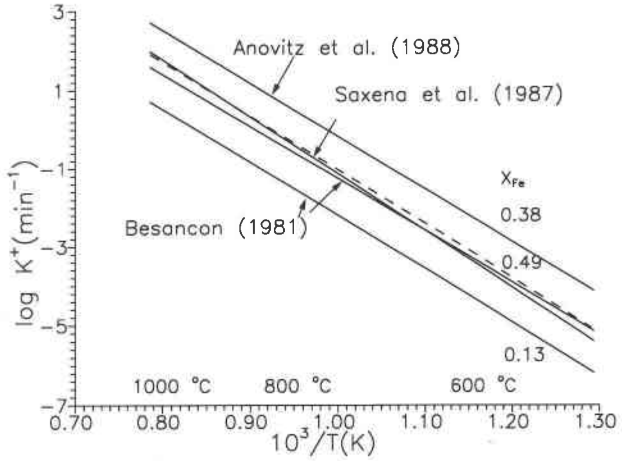

Fig. 2. An Arrhenius plot of the Fe^{2+}-Mg disordering rate constant (K^+) for orthopyroxene with $X_{Fe} < 0.5$ The experimental data (solid lines) are from Besancon (1981), Saxena et al. (1987), and Anovitz et al. (1988). The data for orthopyroxene with $X_{Fe} > 0.50$ and also for which the Arrhenian relation is poorly constrained, have been neglected (see text for discussion). The numbers on the lines indicate X_{Fe}. The f_{O_2} conditions are as follows: Besancon (1981): ~0.8 log units above the WI buffer; Anovitz et al. (1988): at the WI buffer and ~0.5 log units above the WI buffer; Saxena et al. (1987): undefined (evacuated silica tube). D is expected to vary approximately as $(f_{O_2})^{1/6}$. The dashed line represents the result of calculation according to Eq. 10 for orthopyroxene with $X_{Fe} = 0.49$.

Whereas the activation energy for Fe-Mg disordering was found to remain essentially independent of composition in the range $X_{Fe} \approx 0.10–0.50$, the kinetic data of Besancon (1981) show that log K^+ increases by approximately one order of magnitude with the increase of X_{Fe} from 0.13 to 0.49. Since the kinetic processes for both compositions were investigated by the same technique (and the same investigator), the kinetic data should be considered reliable at least in a relative sense. Also, the nature of the dependence of the rate constant on composition is in qualitative agreement with that of the Fe-Mg interdiffusion coefficient on composition in olivine (see, for example, Morioka and Nagasawa, 1991). However, the log K^+ vs. $1/T$ relation determined by Anovitz et al. (1988) for orthopyroxene with $X_{Fe} = 0.38$ lies significantly above what one would predict from the data of Besancon (1981). The difference in the f_{O_2} conditions between the two sets of experiments is too small to explain this discrepancy.

By analogy with the log D(Fe-Mg) vs. X_{Fe} relation in olivine (Morioka and Nagasawa, 1991), we assumed that log K^+ changes linearly with X_{Fe}. However, since Q has been found to be independent of composition at $X_{Fe} \approx 0.10–0.50$, the dependence of K^+ on composition has to be absorbed in the preexponential factor of the Arrhenius relation, $K^+ = K_0^+\exp(-Q/RT)$. The best fit to the data of Besancon (1981) and Anovitz et al. (1988) suggests

$$\ln K_0^+ = 26.2 + 6.0X_{Fe}\ (\pm 1.82)\ \mathrm{min}^{-1}. \qquad (9)$$

(Although the Arrhenius relation for the disordering rate constant determined by Saxena et al., 1987, for orthopyroxene with $X_{Fe} = 0.49$ agrees very well with that of Besancon, 1981, for crystals of very similar composition, we have ignored their data in the derivation of Eq. 9 because of the lack of information about the f_{O_2} condi-

Table 1. Jump distances (Å) of octahedral cations along the crystallographic axes of orthopyroxene

	a axis		b axis		c axis	
Path (Fig. 1)	Dashed	Solid	Dashed	Solid	Dashed	Solid
Enstatite	4.766	4.817	3.165	5.648	2.945	3.011
Hypersthene ($Mg_{0.51}Fe_{0.49}$)	4.804	4.849	3.228	5.705	2.989	3.049
Ferrosilite	4.839	4.884	3.270	5.807	2.996	3.068

tions in their experiments.) Thus, incorporating the average activation of energy of 66767 (± 2223) cal/mol, we obtained the following Arrhenius relation for the disordering rate constant K^+:

$$\ln K^+ = \ln K_0^+ - \frac{Q}{RT}$$

$$= (26.2 + 6.0X_{Fe}) - \frac{31589}{T}\ \mathrm{min}^{-1}. \quad (10)$$

The standard deviation of $\ln K^+$ is given by $[(1.82)^2 + (1119/T)^2]^{1/2}$.

Evaluation of the distribution coefficient

In the Mössbauer studies of Besancon (1981) and Anovitz et al. (1988), the site occupancy of Mg was treated as $(1 - X_{Fe})$ in that particular site. This is not exactly correct, since there are nonnegligible concentrations of other components in the M1 and M2 sites. Thus, their site occupancy data do not yield K_D as defined by Equation 3, which has been used to eliminate K^- in Equation 7. Further, Besancon did not constrain the equilibrium site occupancies by reversal experiments, that is, by approaching from both relatively ordered and relatively disordered initial distributions. Although Saxena et al. (1987) determined site occupancies of both Fe and Mg by single-crystal X-ray analysis within the framework of some reasonable assumptions about the distribution of other cations, they also did not constrain the equilibrium site occupancies by reversal experiments.

A better data set of K_D values as a function of temperature is provided by Molin et al. (1991), as follows:

$$\ln K_D = 0.854\ (\pm 0.013) - \frac{3027(\pm 39)}{T(K)}. \quad (11)$$

They have reversed very tightly the equilibrium site occupancies of an orthopyroxene crystal with $X_{Fe} = 0.23$ at five different temperatures between 600 and 1000 °C. Further, the site occupancies of all cations were determined by single-crystal X-ray studies, constrained by the bulk composition of the investigated crystal and the electron density of the individual sites. The calibration has recently been revised by Molin (personal communication) using more accurate microprobe data on the bulk crystal composition and with the assumption, in accordance with the results of Hawthorne and Ito (1978), that Fe^{2+} and Mn fractionate similarly between M1 and M2 sites. However, these refinements did not significantly affect the calibration.

Molin et al. (1991) carried out their experiments in evacuated silica tubes. It should be noted that K_D does not depend on f_{O_2} as long as the concentration of Fe^{2+} remains essentially unaffected. In other words, the K_D value of an orthopyroxene crystal is essentially the same at a fixed temperature (and pressure) as long as the variation of f_{O_2} does not exceed its stability limits bounded by oxidation and reduction equilibria. However, the variation of f_{O_2} can significantly affect the defect concentration, and hence the diffusion and order-disorder kinetics, by changing the Fe^{2+}-Fe^{3+} ratio (through homogeneous reaction), which is too small to be measured by microprobe analysis or to affect the K_D value. Thus, there is no internal inconsistency in our rejecting the kinetic data of Saxena et al. (1987) and acceptance of the intracrystalline equilibrium partitioning data of Molin et al. (1991), both of which have been obtained by annealing orthopyroxene single crystals in sealed and evacuated silica tubes.

Calculation of interdiffusion coefficient

Using the above data on the disordering rate constant and the equilibrium distribution coefficient (Eqs. 10 and 11, respectively) and the average distance between the centers of successive M1 and M2 sites along **c** and **b** axes, we have calculated $D(\text{Fe-Mg})_{c\text{-}b}$ in orthopyroxene according to Equation 7. Since K_D is a function of X_{Fe} due to nonideal mixing in the M1 and M2 sites and Equation 11 applies to orthopyroxene with $X_{Fe} = 0.23$, the calculation of D(Fe-Mg) should be restricted within a compositional range over which the K_D values do not change significantly relative to that defined by this equation. Even though the mixing properties of Fe and Mg in the M1 and M2 sites are not sufficiently well constrained, the available data (Ganguly, 1982; Anovitz et al., 1988) suggest that the K_D values are unlikely to be significantly different from those obtained from Equation 11 within the compositional range $X_{Fe} = 0.10$–0.50. Thus, the calculation of D(Fe-Mg) was restricted to within this compositional range. The value of λ was varied linearly as a function of composition by interpolating between the data for hypersthene ($X_{Mg} = 0.49$, $X_{Fe} = 0.51$) and enstatite (Table 1), for which λ was calculated to be 3.758 and 3.692 Å, respectively.

The predicted values of $D(\text{Fe-Mg})_{c\text{-}b}$ in orthopyroxene with $X_{Fe} = 0.10$, 0.30, and 0.50 are illustrated in Figure 3. The analytical expression of $D(\text{Fe-Mg})_{c\text{-}b}$ is as follows:

$$\log D(\text{Fe-Mg})_{c\text{-}b} = -5.54 + 2.6X_{Fe} - \frac{12530}{T}$$

$$(Q = 57338 \pm 2000\ \text{cal/mol}). \quad (12)$$

The standard error in the estimated value of D according to this expression is approximately one order of magnitude. It should be noted that Equation 12 yields an interdiffusion coefficient at $X_{Fe} \approx 0.10$–0.50 and at f_{O_2} defined between the WI buffer and 0.8 log units above that buffer, since the disordering rate constants were determined at these conditions. By analogy with the results in olivine (Buening and Buseck, 1973) and garnet (Chakraborty and Ganguly, 1991), we speculate that D(Fe-Mg) on orthopyroxene varies approximately as $(f_{O_2})^{1/6}$.

Comparison and discussion

Recently Cygan et al. (personal communication, and 1994) determined the ^{27}Mg tracer diffusion coefficient (D^*_{Mg}) at 1 bar, 800–900 °C, and f_{O_2} defined by the WI buffer in an orthopyroxene crystal with $X_{Fe} = 0.10$. The diffusion along the **c** and **b** directions has been found to be very similar, with an activation of energy of 60.71 ± 4.54 kcal/mol (Fig. 3), which is in very good agreement with that predicted above (Eq. 12). However, the values of tracer (D^*_i) and interdiffusion [$D(i - j)$] coefficients are not directly comparable. When isotopic correlation effects are ignored, the relationship between these two kinds of diffusion coefficient in a binary solution is given by

$$D(i - j) = \frac{D^*_i D^*_j}{X_i D^*_i + X_j D^*_j}(D_{\text{Thermo}}) \tag{13}$$

where D_{Thermo} reflects the nonideal mixing effect and is unity as $X_i \rightarrow 1$ (e.g., Manning, 1968; Brady, 1975; Lasaga, 1979). In principle, the tracer diffusion coefficients are also functions of composition.

It follows from Equation 13 that, as $X_{Fe} \rightarrow 1$, $D(\text{Fe-Mg}) = D^*_{Mg}(X_{Fe} = 1)$. Even though the compositional dependence of D(Fe-Mg) is not known for compositions more Fe-rich than $X_{Fe} \approx 0.50$, we extrapolate log D(Fe-Mg) linearly, for the purpose of comparison with the data of Cygan et al. (1994), to $X_{Fe} = 1$. This yields $D^*_{Mg}(X_{Fe} = 1)$, which is ~2.5 log units larger than the D^*_{Mg} determined by Cygan et al. (1994) at $X_{Fe} = 0.1$. This suggests that D^*_{Mg} in orthopyroxene increases with increasing Fe-Mg ratio. A similar conclusion was reached by Ganguly and Chakraborty (1991) about the compositional dependence of D^*_{Mg} and D^*_{Fe} in olivine, which has recently been confirmed experimentally by Chakraborty et al. (personal communication). Equation 12 can also be used to predict approximately D^*_{Fe} in pure forsterite by extrapolation to $X_{Fe} = 0$.

Ganguly et al. (1994) have compared $D(\text{Fe-Mg})_{c\text{-}b}$ in orthopyroxene derived above with the Fe-Mg interdiffusion data in garnet (Chakraborty and Ganguly, 1992) and with that along the **c** axis of olivine (Buening and Buseck, 1973; Misener, 1974) after normalizing all data to $X_{Fe} = 0.5$ and f_{O_2} conditions defined by the WI buffer. These data show that $D(\text{Fe-Mg})_{c\text{-}b}$ in orthopyroxene is at least two orders of magnitude smaller than $D(\text{Fe-Mg})_c$ in olivine and one order of magnitude larger than the isotropic D(Fe-Mg) in garnet at $T \leq 1000$ °C. Owing to the possible diffusion anisotropy in orthopyroxene discussed above, the effect of this difference of interdiffusion coefficients on the relative diffusion-induced (retrograde) zoning profiles of coexisting orthopyroxene and garnet in thin sections of natural assemblages may be considerably minimized if the plane of the section is significantly inclined to the **b** and **c** axes. Thus, analysis of Fe-Mg zoning profiles of coexisting garnet and orthopyroxene in thin sections of random orientation of rocks should indicate that D(Fe-Mg) in garnet is similar to or slower than that in orthopyroxene. Indeed, this is the conclusion from detailed study of the compositional zoning of coexisting orthopyroxene and garnet in mantle-derived xenoliths (Smith and Barron, 1991) and in a granulite facies assemblage from northern Quebec (Pattison and Bégin, 1994).

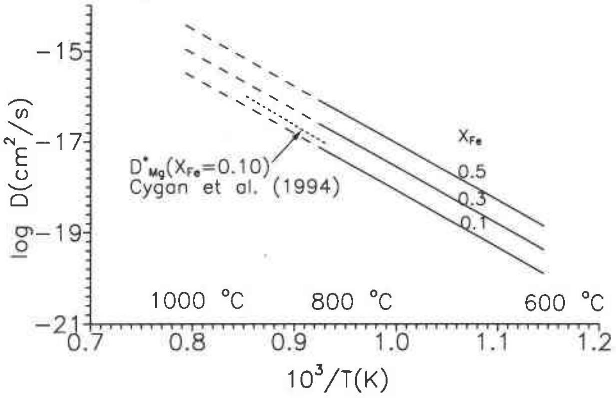

Fig. 3. An Arrhenius plot of the predicted average interdiffusion coefficient of Fe^{2+} and Mg along the **c** and **b** axes [$D(\text{Fe-Mg})_{c\text{-}b}$] of orthopyroxene. The numbers on the lines indicate orthopyroxene compositions; f_{O_2}: between the WI buffer and 0.8 log units above the WI buffer. The short-dashed line is the average of D^*_{Mg} determined by Cygan et al. (1994, and personal communication) along **b** and **c** of an orthopyroxene with $X_{Fe} = 0.1$.

Akamatsu and Kumazawa (1993) have derived a relationship between Fe-Mg interdiffusion coefficients and microscopic specific rate constants for order-disorder along the **b** axis of olivine. Noting that the term b/4 in their treatment is simply the elementary jump distance along the **b** axis, Equation 17 of Akamatsu and Kumazawa, which was derived without any appeal to the formalism of absolute reaction rate theory, can be stated as follows:

$$D_b = \frac{\lambda_b^2 k^+}{2}\left[\frac{y(1 - x)}{(1 - x)x + (1 - y)y}\right]. \tag{14}$$

There is a formal resemblance between this expression and Equation 8, the two differing with respect to the compositional terms within the brackets. (Note from Eq. 2 that Akamatsu and Kumazawa, 1993, absorbed the factor q, which equals ½ in the case of orthopyroxene, in their rate constants.) In both cases, however, the term inside the brackets is less than unity. Trial calculations of $D(\text{Fe-Mg})_{c\text{-}b}$ for various orthopyroxene compositions from Equation 14 by replacing k^+ with K^+, and consequently λ_b with $\lambda_{c\text{-}b}$, yielded values that were either almost equal to or within a factor of 4 lower than those derived from Equations 7 and 8. This is an encouraging agreement between the results from two independent formulations. However, it should be noted that the derivation of Equation 14 is based on the assumption that (1) the adjacent M1 and M2 sites within the crystal are in equilibrium with respect to the distribution of Fe and Mg throughout the process of Fe-Mg interdiffusion and (2) this local distribution is the same as macroscopic distribution. We find both these assumptions to be somewhat unsatisfactory in that the first assumption is incompatible with the diffusion along a concentration gradient (because no net transfer should take place if the adjacent M1 and M2 sites are in equilibrium), and the second assumption implies equivalence of the states of short- and long-range ordering.

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APPENDIX 1. SYMBOLS

C_0	no. of the sublattice sites M1 + M2 in a unit volume of orthopyroxene
$C_{i(j)}$	concentration of the cation i in a unit volume of the sublattice site j
$D(i\text{-}j)$	interdiffusion coefficient of i and j (cm^2/s)
D_i^*	tracer diffusion coefficient of i
f_{O_2}	oxygen fugacity (bars)
K_D	equilibrium intracrystalline distribution coefficient of Fe^{2+} and Mg (Eq. 3)
K^+, K^-	overall disordering and ordering rate constants, respectively, for intracrystalline exchange reaction of Fe^{2+} and Mg in orthopyroxene (min^{-1})
K_0^+	preexponential factor in the Arrhenius expression of K^+ (min^{-1})

$(k^+)_i$, $(k^-)_i$	disordering and ordering rate contants, respectively, for Fe^{2+}-Mg exchange along a specific crystallographic direction i (min^{-1})
Q	activation energy (cal/mol)
WI	wüstite + iron buffer
X_{Fe}, $X_{Fe(M2)}$	$Fe^{2+}/(Fe^{2+} + Mg)$ in the bulk crystal and in the M2 sublattice, respectively
x, y	$X_{Fe(M1)}$ and $X_{Fe(M2)}$, respectively
λ	av. jump distance for diffusion between two successive equilibrium positions
κ	rate constant for diffusion (cm^2/s)