

Rates and mechanisms of Fe-Mg interdiffusion in olivine at 980°-1300°C

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Abstract. Fe-Mg interdiffusion rates have been measured in olivine solid solutions using the diffusion couple technique. Measured diffusion rates along [001] at $f_{O_2} = 10^{-12}$ bars and between 980°C and 1300°C are found to be slower by about 2 orders of magnitude, compared to previous studies with the exception of some isolated data points of *Misener* [1974]. There is no change in temperature dependence within this temperature interval for any composition studied. The temperature dependence at a composition of For_{86} is described by an activation energy of 226 ± 18 kJ/mol and a preexponential factor of $(5.38 \pm 0.89) \times 10^{-9}$ m²/s. The data are consistent internally as well as with well-established theoretical models relating tracer and chemical diffusivities. It is shown that diffusion coefficients are a unique function of pressure, temperature, major element composition and oxygen fugacity for olivines and are not dependent on trace element contents of starting crystals. It is argued that a twofold classification of diffusion mechanisms into intrinsic and extrinsic is inadequate for Fe-bearing silicates, and at least three categories need to be defined. Consideration of the data in combination with the point defect chemistry indicates that the observed diffusion in olivines occurs within a "transition-metal extrinsic" regime. For low temperature extrapolations, significant changes in temperature dependence of diffusion rates are not anticipated, although the oxygen fugacity dependence may change. For calculations in natural systems the present data would yield higher closure temperatures, longer timescales, slower cooling rates, and shorter length scales of diffusion compared to those obtained using earlier diffusion data.

Introduction

Olivine is one of the most widespread silicate minerals and is a major constituent of rocks ranging from the shallowest volcanics on continents and oceans to the deepest accessible samples of the mantle. It is also an important component of most extraterrestrial silicate samples originating in the moon, Mars, or the asteroidal belt. This widespread occurrence is a consequence of the wide range of thermodynamic stability, simple chemistry, and structure of olivines. These factors make it relatively easy to find or synthesize in the laboratory olivine crystals of various compositions. The availability of samples combined with the importance in Earth and planetary sciences has meant that olivine is one of the most intensively investigated minerals. In fact, it has also been investigated by solid state chemists as a prototypical silicate and by material scientists interested in its refractory characteristics. Thus a large body of data exists on the physical and chemical properties of olivine.

Diffusion data for cations in olivine are no exception to this rule and are summarized by *Morioka and Nagasawa* [1991] and *Hermeling and Schmalzried* [1984] with later additions by *Chakraborty et al.* [1994] and *Jaoul et al.* [1995], who cite more recent literature on the topic. Of particular interest in this regard is the Fe-Mg interdiffusion

rate in olivines which is important because of its role in determining the closure temperatures of various ion exchange geothermometers, in the calculation of cooling rates and other details of thermal history from compositional zoning profiles, and in understanding the point defect chemistry of olivines. The Fe-Mg interdiffusion rates have also been used to interpret data on other transport properties of olivine such as creep rates and electrical conductivity. Indeed, Fe-Mg interdiffusion in olivine has been considered to be one of the most well known transport properties in minerals and is used as an example in introductory text books [e.g., *Putnis*, 1992]. In spite of this work, however, significant unresolved questions remain about the interdiffusion rates.

Ever since the first classical measurements by *Buening and Buseck* [1973] and *Misener* [1974] on olivine single crystals, it has remained an open question as to why *Buening and Buseck* [1973] observed a sudden change in the temperature dependence of diffusion rates (kink in an Arrhenius plot) at around 1100°C, whereas *Misener* [1974] did not. The kink has been widely interpreted as the only observed example of a transition from intrinsic to extrinsic diffusion mechanism in a mineralogical system [e.g., *Putnis*, 1992], although *Buening and Buseck* [1973] themselves suggested this as only one possible explanation of their results, and the other suggested alternatives have not been ruled out subsequently. This example has deeply influenced thought, debate, and discussion in the geochemical community and has affected the study of diffusion in silicate

minerals in general. In practically every single application of diffusion data of olivine to understand thermal history, the major uncertainty has been in the choice of diffusion data (e.g., see Miyamoto *et al.* [1986], Jones and Rubie [1991], Weinbruch *et al.* [1994], and Nakamura, [1995] for some recent examples). Accordingly, considerable effort is expended in these papers in trying to justify and rationalize the choice of a particular data set. Although diffusion rates of Fe-Mg have been measured subsequently [Nakamura and Schmalzried, 1984; Jurewicz and Watson, 1988; Jaoul *et al.*, 1995], none of these studies span the critical temperature range of interest, that is, across 1100°C, either because of limitations in the experimental techniques used or because of a different focus of the study.

Two other recent developments provided the final impetus to carry out a redetermination of Fe-Mg diffusion rates in olivines. First, during the course of a detailed study of Mg tracer diffusion rates [Chakraborty *et al.*, 1994] it was found that well-established relationships between chemical and tracer diffusion rates were apparently not valid for the olivine solid solution series, when either of the available chemical diffusion data sets was used. This had the major implication that either there were problems with the chemical and/or tracer diffusion data or our understanding of the nature of diffusion in olivine and hence probably other silicates as well. Second, to explain inconsistencies in thermal histories retrieved from zoning profiles in olivines and that expected from other independent evidence, the issue has frequently been raised (e.g. Weinbruch *et al.*, 1994) whether diffusion rates in minerals with different impurity levels (trace element contents) are the same; in particular whether diffusion rates in synthetic and natural crystals may be expected to be the same. This question has been repeatedly considered in the geochemical literature since the suggestion was made in the pioneering study of Sneeringer *et al.* [1984]. It is an objective of this study to (1) characterize the temperature dependence of Fe-Mg diffusion in olivine with the specific objective of resolving the question of a kink in the Arrhenius plot, (2) use the data to address the question of intrinsic/extrinsic diffusion in olivine in particular and by implication the nature of diffusion in Fe-bearing silicates, and (3) consider the role of trace elements and impurities in affecting diffusion rates in this system. The last two points have significant implications for the important question of extrapolation of diffusion data to temperatures and compositions outside the range of measurement, a very common geochemical dilemma. To achieve these objectives, diffusion coefficients were measured in different starting materials and over a wider range of temperature (980°–1300°C) than in any of the previous studies. Last, it was found that none of the previous studies measured diffusion coefficients directly at a typical mantle olivine composition of about Fo₉₀. It is an objective of this study to remove this shortcoming.

Experimental Method

Starting Material

This study was performed on oriented single crystals using the diffusion couple technique, with some preliminary experiments using polycrystalline material for comparison with the data set of Buening and Buseck [1973]. Four

different compositions were used for the experiments: synthetic forsterite (Fo₁₀₀), green San Carlos olivine (SC1, Fo₉₁₋₉₂), greenish-brown San Carlos olivine (SC2, Fo₈₂₋₈₄), and brown fayalite (~Fa₉₀) from St. Peters Dome, El Paso county, Colorado. The forsterite crystals were grown using the Czochralski method by H. Takei at Tohoku University and the San Carlos olivine crystals (SC1) were obtained from the Smithsonian Museum (number 136718); these are the same material used and described in detail by Chakraborty *et al.* [1994]. Crystals of SC2 were obtained from D.L. Kohlstedt (University of Minnesota), and a representative chemical analysis is given in Table 1. All of the SC2 material used in this study came from two pieces of single crystals, which were individually homogeneous, as verified by electron microprobe analyses at a number of points. There was some variation in composition (Fo₈₂–Fo₈₄) between the two crystals. The crystal of Colorado fayalite was obtained from the Harvard Mineral Museum (number 101839) and an analysis is provided in Table 1. The polycrystalline material used in the preliminary study was obtained by grinding pieces of the fayalite crystal in an agate mortar under acetone. This material was then sintered at run conditions (temperature and f_{O2}) to obtain a pellet for diffusion experiments.

All crystals used in this work were oriented using Laue X-ray diffraction patterns. The oriented crystals were ground flat (perpendicular to [001] for most runs), polished using diamond compounds (to 0.25 μm), and prepared for a diffusion anneal by cutting into pieces ~2 mm on a side. Further details are given by Chakraborty *et al.* [1994]. Etching of the surface with HF or preannealing the crystals at run conditions was found to have no significant effect on the relatively long (~tens of microns) concentration profiles typically obtained in this study. From known rates of vacancy diffusion [Nakamura and Schmalzried, 1983; Mackwell *et al.*, 1988] in olivine it is expected that the crystals used should attain point defect equilibrium with the atmosphere in a short time compared to the duration of a diffusion anneal. This was verified by the fact that for the sample dimensions and run durations of this study there was no perceptible time (run duration) or spatial (profiles measured at different parts of a sample) dependence of diffusion coefficients (see below). Because heating and cooling during preannealing sometimes resulted in the formation of microcracks in the crystals, generally the crystals were not preannealed.

Apart from the preliminary runs using polycrystalline material, two kinds of diffusion couples were used: (1) Fo+Fo₈₂(SC2) and (2) Fo₉₁(SC1)+Fa. This choice had the following advantages: (1) The compositional difference between the end-members of couple 1 is small enough that the concentration profiles are approximately symmetric (see below). Therefore diffusion coefficients at the average composition may be retrieved from these couples using a simple error function solution with constant diffusion coefficients, and these coefficients provide an independent check of the Boltzmann-Matano analysis. (2) At compositions between Fo₈₄ and Fo₉₀ we obtain data from two completely different diffusion couples (Figure 1a). This allows a test of whether diffusion rates depend on the choice of crystals (i.e., impurity contents, etc.). (3) Couple 2 is exactly the kind of setup used in the experiments of Misener [1974] and similar to that of Buening and Buseck [1973],

Table 1. Composition of Starting Crystals

	SC2	Fa
Major oxide, wt %		
FeO	15.65	61.12
MgO	44.45	3.91
MnO	-	3.96
SiO ₂	40.35	30.14
Total	100.45	99.13
Trace Elements, ppm		
Na	77	<5
K	<5	16
Sc	4.5	123
Ti	<500	-
Cr	41	135
Co	178	2.9
Ni	2839	-
Cu	<10	-
Zn	95	3000
As	<0.05	0.116
La	0.53	0.11
Sm	-	0.22
Eu	<0.015	0.017
Ho	<0.02	3.2
Er	-	21
Yb	-	123
Lu	-	27
Ta	-	0.04
In	0.45	2.3

Dash, not determined

which allows a direct comparison to be made with these studies.

Diffusion Anneal

Two olivine crystals were placed with their polished faces in contact in an alumina sample holder and were pressed

against each other by a spring-loaded alumina rod. The sample container had openings on the sides such that all sides of the olivine crystals were exposed to the furnace atmosphere (Figure 1b). With this arrangement the [001] directions of the two crystals were aligned, but the crystallographic directions were random within (001) with respect to each other. The diffusion anneals were performed in a vertical gas-mixing furnace equipped with a ZrO₂ sensor and B-type thermocouples. Oxygen fugacity during the runs was maintained at 10⁻¹² bars by a flowing gas mix of CO-CO₂, which was continuously monitored using the sensors and controlled to ±0.1 log units. Temperature was monitored to remain within ±2°C by thermocouples, whose junctions were adjacent to the interface between olivines. The thermocouples were calibrated against the melting points of pure metals (e.g., Au and Ni). Samples were introduced after the furnace had equilibrated to nominal run conditions (temperature T and f_{O₂}) and were slowly heated to ~300°C by gradually changing the height of the sample. Following this, they were introduced rapidly to the hot spot, where they attained run temperatures within 5 min. For quenching, samples were simply pulled to the cold end of the furnace

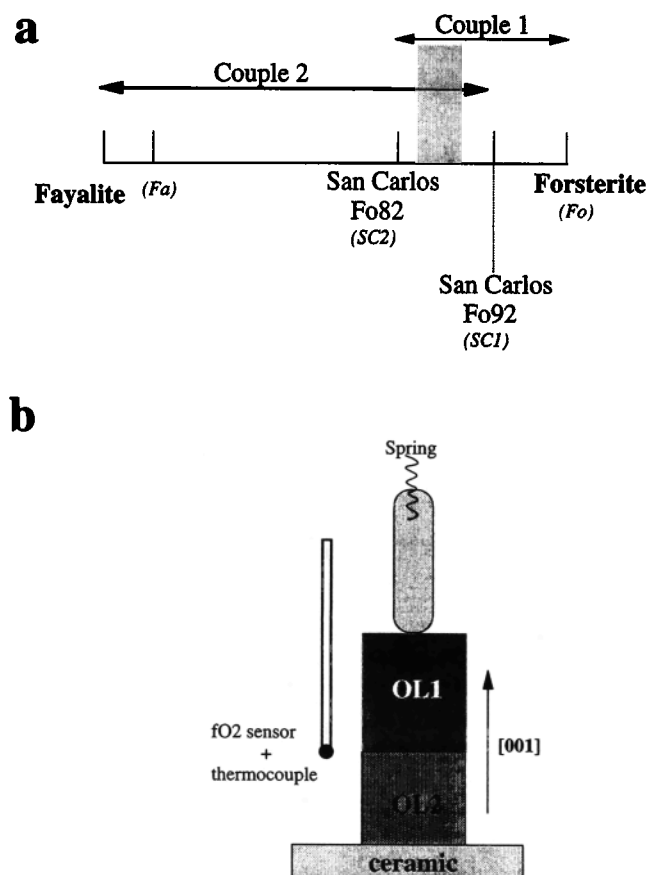


Figure 1. (a) Composition ranges of different diffusion couples used in this study. The sample names, as used in the text, are indicated in *italics*. The shaded region highlights the compositional domain where diffusion data could be obtained from both couples.

(b) Schematic experimental setup showing two oriented olivine crystals (denoted as OL1 and OL2), held together in a spring loaded ceramic holder. The position of thermocouples and oxygen fugacity sensor is also indicated.

Table 2. Experimental Details

Run	T, °C	Time, hours	Log f_{O_2}	Diffusion Couple
OLID-3	1100	164	-11.80	SC1+Fa
OLID-5	1000	208	-11.98	SC1+Fa
OLID-6	1000	215	-11.98	SC1+Fa powder
OLID-7	1000	120	-11.98	SC1+Fa powder
OLID-8	1100	164	-12.02	SC2+Fo
OLID-9	1200	117	-11.98	SC2+Fo
OLID-10	1000	360	-11.97	SC2+Fo
OLID-11	1100	426.5	-11.98	SC2+Fo
OLID-202	1300	51.5	-12.04	SC2+Fo
OLID-203	1250	88.75	-12.01	SC2+Fo
OLID-204	1200	254.15	-11.95	SC2+Fo
OLID-205	1050	331.25	-12.09	SC2+Fo
OLID-206	1150	338.50	-11.97	SC2+Fo
OLID-207	980	336.50	-11.96	SC2+Fo

and allowed to cool in a reducing atmosphere whereby the temperature dropped to $\sim 300^\circ\text{C}$ within 5 min. Run durations varied between 46–460 hours. Quenching experiments have shown that the interface welded together within the first 30 min of a diffusion anneal. Details of annealing conditions are provided in Table 2.

The experimental setup described here fixes pressure P , T and f_{O_2} . To completely define the state of a homogeneous (Fe,Mg)-olivine crystal, it is theoretically necessary to fix an additional intensive thermodynamic variable, usually taken to be a_{SiO_2} (silica activity). Variation of a_{SiO_2} over the entire permissible range of zero to one is expected to affect diffusion rates of octahedral cations by less than a factor of 2 from considerations of point defect chemistry [Stocker and Smyth, 1978], and no resolvable influence of a_{SiO_2} on Mg tracer diffusion rates has been found [Chakraborty *et al.*, 1994]. Further, external imposition of a constant a_{SiO_2} on an interdiffusion couple where Fe/Mg is constantly changing would set up a continuous flux of minority point defects (i.e., those not responsible for the charge neutrality condition), which may even lead to a morphological instability of the diffusion zone. Under these circumstances, no attempts were made to control a_{SiO_2} externally in these experiments. Measured diffusion rates in this study were independent of run duration and location in the sample, and there was agreement between diffusion rates obtained using different diffusion couples (see later). These provide a posteriori justification of the approach and indicate that the controlling variables were adequately defined in the present experimental setup, at least to the extent that differences can be resolved.

Diffusion Profiles and Calculation of Diffusion Coefficients

After the diffusion anneal the samples were mounted in epoxy and sectioned perpendicular to the interface. Typically, more than one section was prepared for analysis. Concentration profiles were measured using a Cameca SX-50 electron microprobe at the Bayerisches Geoinstitut with an accelerating voltage of 15 kV and a beam current of 20 nA on the Faraday cage. A well-focussed beam with a nominal diameter of $\sim 1\ \mu\text{m}$, as measured by fluorescence on SnO_2 , was used. Complete chemical analyses were carried out at intervals of $1\ \mu\text{m}$, stepped using the automated stage movement setup of Cameca. The accuracy of the stepping mechanism was tested using calibration samples. Standards used for the analyses were synthetic fayalite or pure metal for Fe, forsterite for Mg, MnTiO_3 for Mn, and andradite for Si. Counting times at the peak were 30 s. Analyses with weight percent oxide totals lying outside 99–101 were considered unacceptable and rejected. Typically, more than one concentration profile was measured on a given run product, and sometimes as many as eight have been measured on different sections and along parallel traverses on the same section. These profiles could always be superposed on each other in a normalized concentration (range: 0–1, normalization is to the total number of octahedral cations) plot, and diffusion coefficients obtained from different profiles in a single run were indistinguishable within error in most cases. Figure 2 shows two examples of concentration profiles measured in this study. In addition to chemical analyses the run products were studied by optical

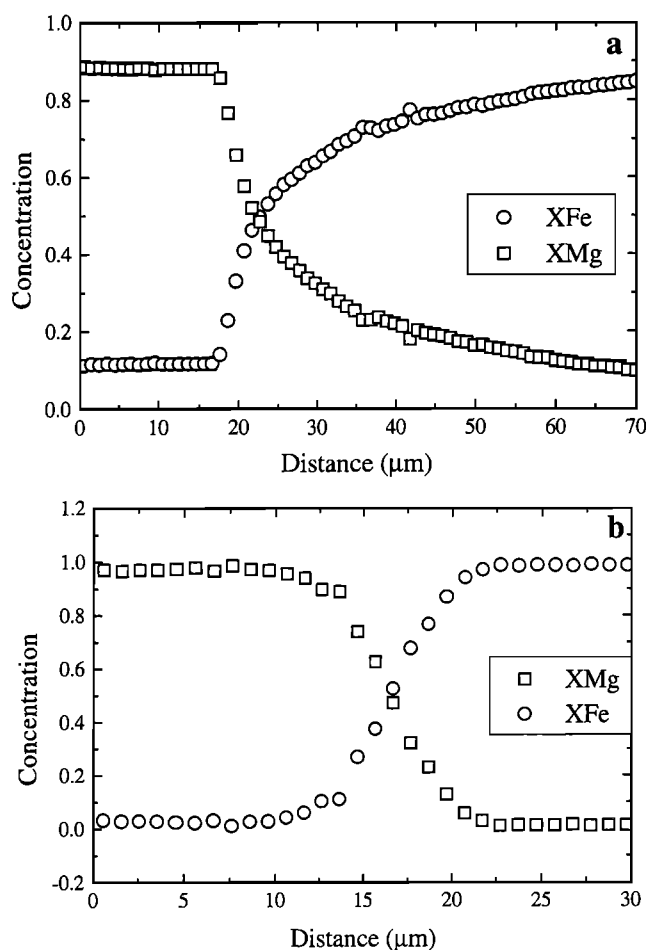


Figure 2. Typical compositional profiles from (a) sample OLID-5 run at 1000°C for 208 hours using couple 2 and (b) sample OLID-10 run at 1000°C for 360 hours using couple 1. Note the difference in penetration lengths between the two samples; couple 1, annealed for a longer time, shows a much shorter profile because of the compositional dependence of diffusion rates. Also, note that for the conditions of (Figure 2b), the profile lengths are approaching the resolution of an electron microprobe as discussed in the text.

microscopy and high-resolution backscattered- and secondary- electron imaging to identify potential disturbing artifacts. Elemental mapping using fluorescent Xrays of the diffusion zone in selected samples showed regular, parallel diffusion fronts and no irregularities. Some of the sections from this study are the subject of an intensive transmission electron microscopy (TEM) study [Meissner *et al.*, 1995; E. Meissner, manuscript in preparation]. Detailed results will be presented elsewhere, but we note here that (1) the interfaces appeared well annealed in TEM images, (2) no extraneous phases were found, and (3) excepting a zone of a few hundred nanometers around the interface, where dislocation densities are high to accommodate the lattice mismatch between the two sides of the couple, the region where profiles are measured is free from any major structural disruptions.

Measured concentration profiles were treated using standard Boltzman-Matano analyses [e.g. Buening and

Buseck, 1973] to obtain diffusion coefficients as a function of composition. The formula for the determination of diffusivity as a function of composition, $D(C^*)$ at some particular composition C^* is

$$D(C^*) = -\frac{1}{2t} \left(\frac{dX}{dC} \right)_{C^*} \int_{C_1}^{C^*} X dC \quad (1)$$

where t is the duration of the diffusion anneal, X is the distance coordinate, and C_1 is the composition of one starting end-member. As may be seen from Figure 2, it was not necessary to smooth the profiles to calculate slopes and areas required for the Boltzmann-Matano analyses. Diffusion coefficients can be obtained at any composition along the profile. Retrieved diffusion coefficients at some selected compositions are reported in Table-3, where the reported errors are obtained by propagating the analytical uncertainty only [e.g., see Chakraborty *et al.*, 1993]. A measure of the true uncertainties combining errors from all possible sources may be obtained by comparing data from different runs at the same conditions; this uncertainty is variable (7-98%), depending largely on the position in the profile (central part or extremity) at which the diffusion coefficients were calculated.

Results

The most apparent feature of the diffusion profiles is the strong compositional dependence of Fe-Mg interdiffusion rates in the olivine solid solution series. Diffusion rates increase with increasing Fe content of olivine, as has been found in all other previous studies. This behavior is apparent from the strong asymmetry of concentration profiles when couple 2, spanning a larger compositional range, is used (Figure 2a). A comparison of diffusion penetration lengths from couple 2 (more Fe-rich average composition) and couple 1 for experiments run at the same temperature (Figures 2a and b) also illustrates this aspect very clearly; although couple 1 was annealed for a longer time at the same temperature and f_{O_2} , the profile length is shorter. There is no significant variation in diffusion coefficients obtained from different profiles measured on the same sample at different positions (Figure 3a) and from runs at the same conditions for different durations (Figure 3b).

The compositional range $Fe_{85}-Fe_{90}$ is spanned by both couples 1 and 2. This allows a comparison of interdiffusion coefficients obtained using different couples at the same composition. Such a comparison can be carried out for data from all temperatures. Two examples are shown in Figure 4, which shows that data obtained from the two couples are perfectly compatible with each other; there is excellent agreement in the trend of compositional dependence as well as the absolute values of diffusivity obtained in the overlapping compositional range using the different couples. This compositional dependence is the same as that found in earlier studies [Buening and Buseck, 1973; Misener, 1974; Nakamura and Schmalzried, 1984]; with increasing Fe-content, diffusivities increase almost exponentially by about 2 orders of magnitude across the olivine solid solution series. Other details, such as an increase in the compositional dependence of diffusion rates with increasing temperature, also agree with earlier studies [e.g., Nakamura

Table 3. Diffusion Coefficients

Run	Composition, mole % Fo	Diffusivity*, m ² /s
OLID-3	25	1.0x10 ⁻¹⁵ , [8]
	29	1.0x10 ⁻¹⁵ , [10]
	40	6.6x10 ⁻¹⁶ , [8]
	49	2.7x10 ⁻¹⁶ , [7]
	52	2.7x10 ⁻¹⁶ , [7]
	73	8.2x10 ⁻¹⁷ , [10]
	80	5.7x10 ⁻¹⁷ , [33]
	84	2.9x10 ⁻¹⁷ , [35]
	87	1.0x10 ⁻¹⁷ , [98]
OLID-5	26	2.0x10 ⁻¹⁶ , [9]
	33	1.6x10 ⁻¹⁶ , [10]
	42	1.1x10 ⁻¹⁶ , [12]
	45	7.4x10 ⁻¹⁷ , [8]
	54	4.6x10 ⁻¹⁷ , [12]
	67	1.5x10 ⁻¹⁷ , [15]
	86	4.6x10 ⁻¹⁸ , [80]
OLID-8	85	1.1x10 ⁻¹⁷ , [16]
	88	9.7x10 ⁻¹⁸ , [5]
	93	5.5x10 ⁻¹⁸ , [4]
OLID-9	85	1.2x10 ⁻¹⁶ , [11]
	86	7.0x10 ⁻¹⁷ , [10]
	88	6.5x10 ⁻¹⁷ , [9]
	92	5.8x10 ⁻¹⁷ , [9]
	93	6.5x10 ⁻¹⁷ , [9]
OLID-10	85	4.0x10 ⁻¹⁸ , [51]
	88	3.9x10 ⁻¹⁸ , [37]
	90	4.5x10 ⁻¹⁸ , [45]
	93	2.8x10 ⁻¹⁸ , [17]
OLID-11	85	7.1x10 ⁻¹⁸ , [17]
	88	8.6x10 ⁻¹⁸ , [9]
	91	6.8x10 ⁻¹⁸ , [8]

Table 3. (continued)

Run	Composition, mole % Fo	Diffusivity*, m ² /s
OLID-202	92	5.5x10 ⁻¹⁸ , [8]
	95	5.8x10 ⁻¹⁸ , [8]
	86	4.1x10 ⁻¹⁶ , [10]
	89	2.1x10 ⁻¹⁶ , [10]
	93	2.0x10 ⁻¹⁶ , [10]
	97	1.7x10 ⁻¹⁶ , [10]
OLID-203	85	6.2x10 ⁻¹⁷ , [10]
	86	5.8x10 ⁻¹⁷ , [10]
	89	3.4x10 ⁻¹⁷ , [10]
	92	3.4x10 ⁻¹⁷ , [10]
OLID-204	86	6.0x10 ⁻¹⁷ , [10]
	88	3.8x10 ⁻¹⁷ , [10]
	90	2.3x10 ⁻¹⁷ , [10]
	92	1.8x10 ⁻¹⁷ , [10]
OLID-205	85	1.2x10 ⁻¹⁷ , [10]
	87	9.4x10 ⁻¹⁸ , [10]
	90	6.5x10 ⁻¹⁸ , [10]
OLID-206	92	3.1x10 ⁻¹⁸ , [10]
	86	2.7x10 ⁻¹⁷ , [10]
	88	2.1x10 ⁻¹⁷ , [10]
OLID-207	91	1.9x10 ⁻¹⁷ , [10]
	85	1.6x10 ⁻¹⁸ , [25]
	87	2.0x10 ⁻¹⁸ , [20]
	95	2.1x10 ⁻¹⁸ , [45]

* Values in brackets are percent error.

and Schmalzried, 1984]. The agreement in data obtained from the two couples is important for a number of reasons: (1) It is an internal check on the experimental method. (2) It shows that diffusivities are uniquely defined for a given P, T, X (major element composition), and f_{O₂}. (3) There is no influence of initial defect (point, as well as higher dimensional) characteristics or trace element concentrations on diffusion rates, once the thermodynamic parameters

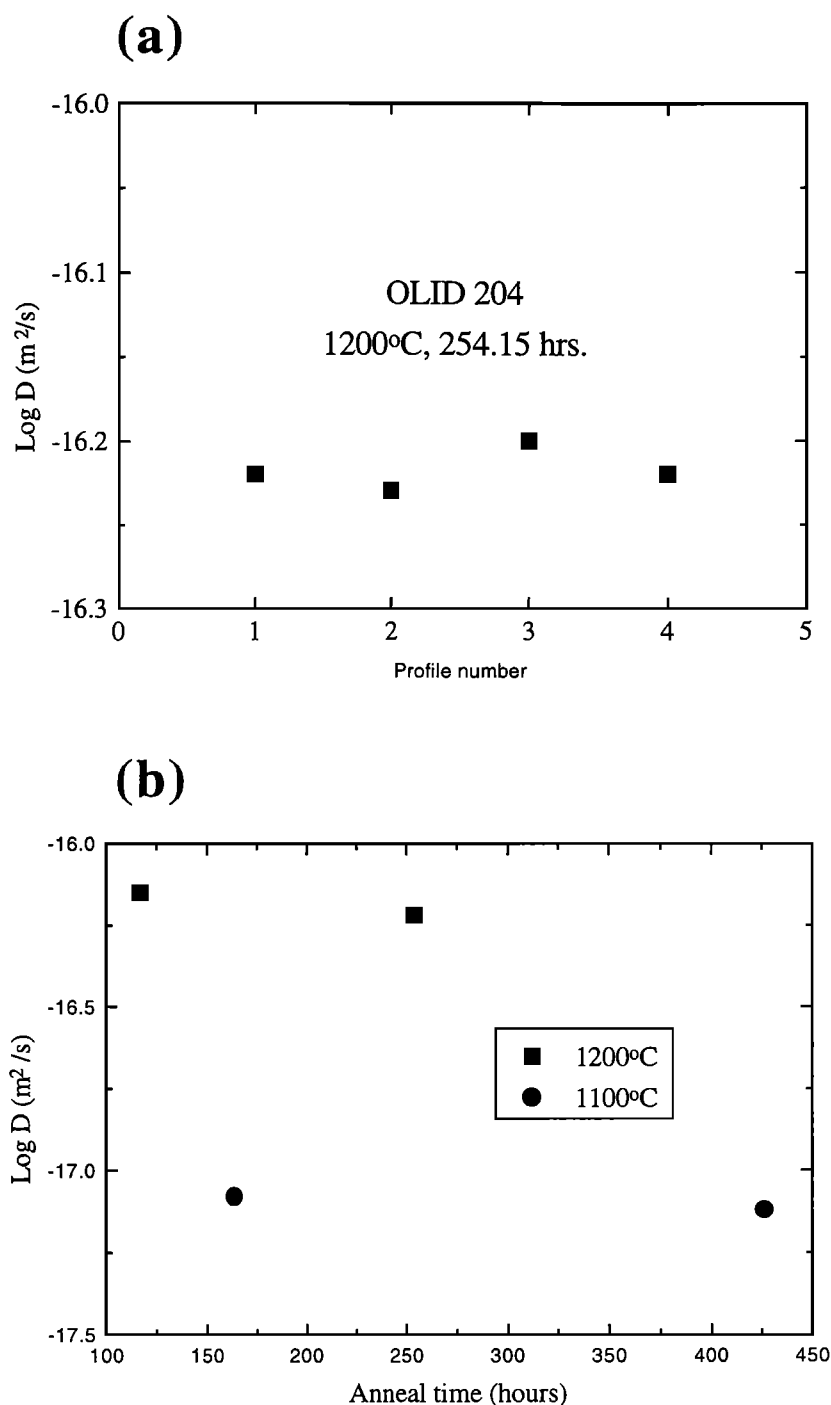


Figure 3. (a) Diffusion coefficients obtained from different profiles measured at different positions on the same sample, OLID-204. (b) Diffusion coefficients obtained for olivine of composition Fo86 from samples annealed for different durations at two different temperatures.

mentioned in point 2 are fixed. We can draw this last conclusion because the defect and trace element concentrations of the initial material (synthetic forsterite, San Carlos olivines and fayalite) in the two diffusion couples are very different (see Table 1). (4) The data from the two couples converge at compositions around Fo_{90} from two directions, constituting a sort of "reversal" of diffusion data. Additionally, the compositional range Fo_{90-93} , which is typical of most mantle olivines, falls almost exactly in the middle of the compositional range spanned by couple 1

(Fo_{100-82}). This means that concentration gradients at the intermediate compositions are very well defined (middle of the diffusion profiles), and diffusion coefficients are directly determined at these compositions. This is in contrast to most previous studies which typically used standard mantle olivine ($\sim\text{Fo}_{90}$) as the Mg-rich end-member of a diffusion couple. As a result, the most Mg-rich compositions at which diffusion coefficients were directly determined were $\sim\text{Fo}_{80}$, and even these were from slopes determined near the extremities of the diffusion profiles where uncertainties are

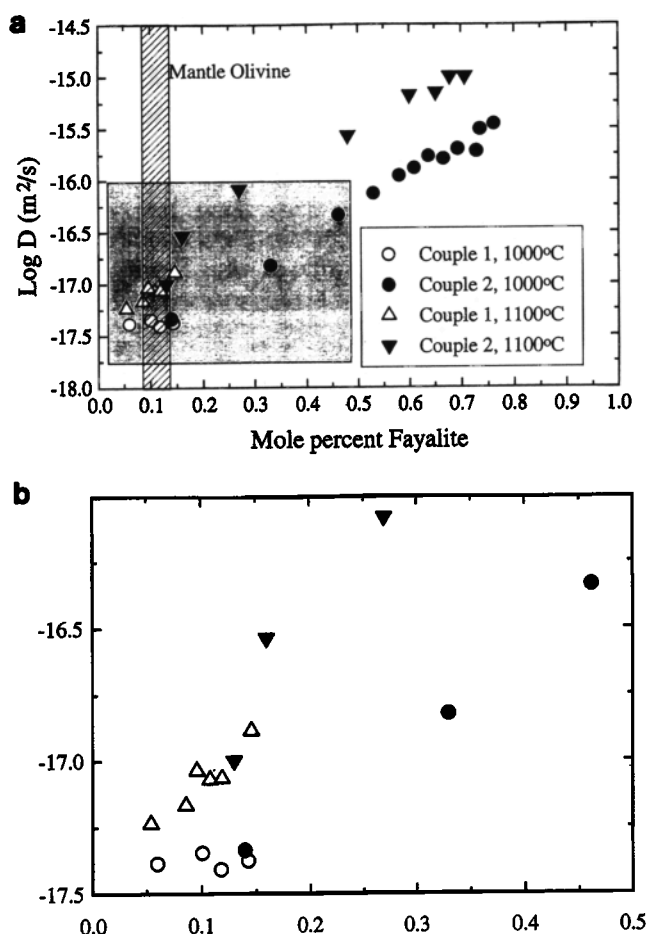


Figure 4. (a) Compositional dependence of diffusion rates obtained from two different temperatures. Data obtained using different diffusion couples (couple 1: open symbols and couple 2: solid symbols) are found to be compatible with each other and are highlighted in the (b) enlargement of the shaded region in Figure 4a. Approximate composition range of common mantle olivines is marked by the hatched region. Also, note the high density of points obtained using different couples in this region.

inherently higher (see, for example, Table 3). Following this, diffusion coefficients at $\sim\text{Fo}_{90}$ were obtained by extrapolation assuming a linear relationship between log D and composition to be valid even at terminal segments of the solid solution series. The result is not trivial, considering the widespread use of diffusion coefficients for mantle olivine compositions and the fact that at the extremities of solid solution series transport properties are expected to show strong nonlinear (in log space) changes in compositional dependence. This expectation is based on both macroscopic phenomenological and point defect thermodynamic considerations [e.g., *Schwieger et al.*, 1973; *Yurek and Schmalzried*, 1974]. While much of the work has been done on oxide systems, *Schwieger et al.* [1973] demonstrate that such strong nonlinear changes occur near the forsterite-rich ends of the (Co,Mg)-olivine system. The weak dependence of diffusion rates and activation energies (see below) on composition (e.g., Figure 4) for typical mantle compositions simplifies modeling calculations involving compositional variation in olivines.

The temperature range of 980° - 1300°C covered in this work is the largest covered in any single study (same diffusion couple and experimental technique) on olivines so far. In most earlier studies it was not possible to measure diffusion coefficients at temperatures above 1200°C, the melting point of fayalite, because fayalite was used as one end-member of a diffusion couple. This problem was overcome by the use of couple 1 ($\text{Fo}_{100}\text{-Fo}_{82}$) in this study. It was not possible to extend the temperature range below 980°C because the length of the compositional profiles obtained ($\sim 8 \mu\text{m}$) for reasonable run durations was too small to be accurately measured using an electron microprobe for the Mg-rich compositions of the diffusion couples used in this study. In principle, it is possible to make corrections for the convolution effect due to beam spreading and measure even shorter profiles [e.g., *Ganguly et al.*, 1988; *Chakraborty and Ganguly*, 1992]. However, for asymmetric profiles resulting from compositionally dependent diffusion rates this procedure may introduce additional uncertainties in the determination of slopes at various points. This was considered unnecessary for the objectives of the present study. Determination of low-temperature diffusion kinetics in olivines using another method is currently underway, and results from this study will be reported elsewhere.

Temperature dependence of diffusion coefficients at any given composition for constant $f_{\text{O}_2} = 10^{-12}$ bars shows a linear behavior on an Arrhenius plot (log D vs. $1/T$) within the temperature range of 980° - 1300°C (Figure 5). There is no hint of a change of mechanism of diffusion in any composition studied here. Best fits of the data to the Arrhenius equation $D(T) = D_0 \exp(-Q/RT)$ at the most well-constrained composition of Fo_{86} yield an activation energy

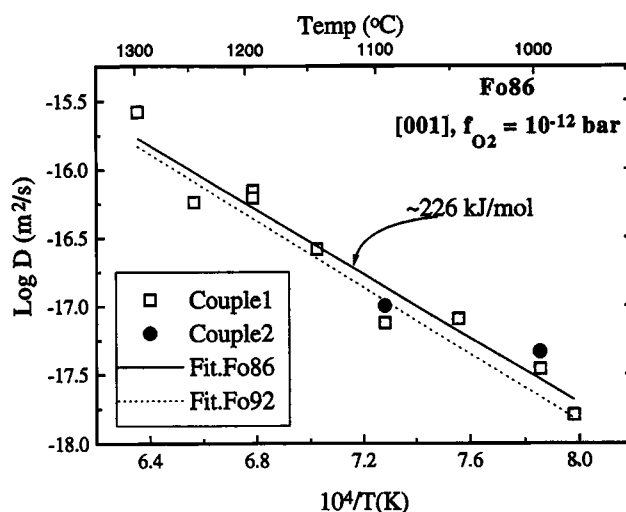


Figure 5. Arrhenius plot showing data obtained using different diffusion couples (open symbols: couple 1 and solid symbols: couple 2) at the most well-constrained composition of Fo_{86} . The solid line is a combined fit to data from both couples. Each plotted point is the mean of at least four different determinations on a sample. A similar fit to data at another composition (Fo_{92}) is shown as a dotted line where individual data points have been omitted for clarity. This comparison of diffusion data highlights the relatively weak influence of composition on diffusion rates in Mg-rich olivines commonly found in mantle samples.

of 226 ± 18.5 kJ/mol (54 ± 4.4 kcal/mol) and a preexponential factor D_0 of $(5.38 \pm 0.89) \times 10^{-9}$ m²/s for diffusion parallel to [001] at an $f_{O_2} = 10^{-12}$ bars. Each point used to obtain these parameters is the mean from at least four profiles on a sample, and data from different couples as well as replicate runs are included. Figure 5 also shows best fits to the data at different compositions (spanning much of the range commonly seen for mantle olivines), which illustrate the extent to which D_0 and Q depend on composition (e.g., for Fo_{92} we obtain $D_0 = 6.59 \times 10^{-9}$ m²/s and $Q = 229 \pm 18$ kJ/mol). As noted above, the variation over this compositional range is not large. It is to be emphasized that these fits are for constant f_{O_2} conditions, and for modeling most nonisothermal natural processes, appropriate corrections for the variation of diffusivity with f_{O_2} during heating/cooling are necessary. This topic is discussed in detail with illustrations by *Chakraborty and Rubie* [1996].

Although it was not the objective of this study to explore the dependence of diffusion rates on crystallographic orientation or oxygen fugacity, some test experiments showed that the observed dependencies were consistent with results from earlier studies [*Buening and Buseck*, 1973; *Misener*, 1974; *Nakamura and Schmalzried*, 1984; *Jurewicz and Watson*, 1988; *Chakraborty et al.*, 1994], and these were not pursued further.

Comparison With Previous Studies

The most significant observation of this work is that the measured diffusion rates are significantly slower than those reported in most previous studies at the same conditions

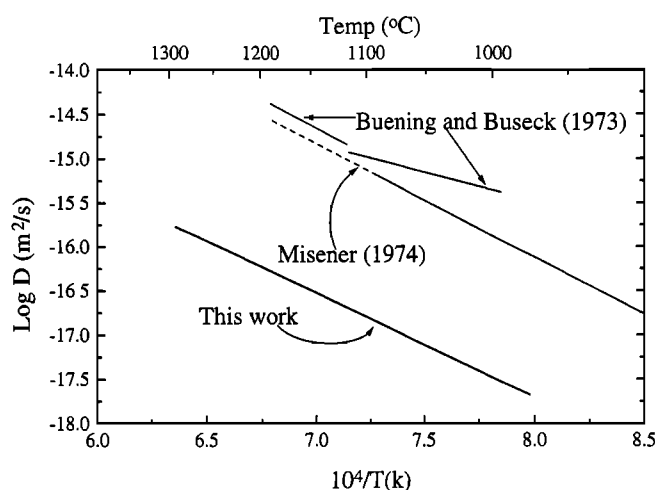


Figure 6. Comparison of Fe-Mg interdiffusion rates measured in this work with previous results. The line from this study is the best fit to experimental data shown in Figure 5 whereas those for *Buening and Buseck* [1973] and *Misener* [1974] are calculations for diffusion parallel to [001] in Fo_{86} using the Arrhenius expressions provided by them. The data from this study as well as the calculations for *Buening and Buseck* [1973] are for an $f_{O_2} = 10^{-12}$ bars. Diffusion rates found in this work are about 2 orders of magnitude slower than that obtained using equations from earlier studies. However, it is not appropriate to calculate diffusivity at Fo_{86} using the Arrhenius expression from *Misener* [1974]; see text for details.

(Figure 6). Over the temperature range of measurements, Fe-Mg interdiffusion rates are on the average about 2 orders of magnitude slower than those obtained using equations given by either *Buening and Buseck* [1973] or *Misener* [1974]. There is no obvious explanation for the discrepancy with *Buening and Buseck* [1973], while part of the discrepancy with *Misener* [1974] may only be apparent, as shown below. Before discussing these works further, we reiterate that detailed examination (including TEM observations) of experimental samples from this study failed to show any artifacts and the results show excellent internal consistency, as discussed further in the section on the relationship between chemical and tracer diffusion coefficients.

We can speculate about possible reasons for the observation of enhanced diffusion rates in the earlier studies. The study of *Misener* [1974] has often been criticized for being done without an explicit f_{O_2} control. It is now well established that oxygen fugacity controls the point defect chemistry and hence transport rates (diffusion, creep and electrical conduction) in Fe-bearing olivines; even in nominally Fe-free olivines it has been shown to have some effect [*Chakraborty et al.*, 1994]. As the study of *Misener* was carried out with samples enclosed in silica glass tubes and fayalite was one end-member of the diffusion couple, it has often been argued that oxygen fugacity in those runs should have been close to that determined by the equilibria between quartz-fayalite-magnetite (QFM), that is, $\sim 10^{-7}$ bar at 1300°C to $\sim 10^{-11}$ bar at 1000°C. However, this is by no means a demonstrated fact; rather, in view of the vacuum prevailing within the silica glass capsules, it is quite possible that the oxygen fugacity was not controlled at all during the runs, particularly at the lower temperatures of the study. Second, there was widespread use of Pt in those experiments (Pt capsules, Pt wires used to wrap samples, and Pt wound furnace), which might have caused some destabilization of Fe-rich olivine or at least affected the point defect chemistry in some uncontrolled manner. In any case, assuming that the oxygen fugacity of the runs in the study of *Misener* [1974] varied along the QFM buffer and that $D \sim kf_{O_2}^{1/6}$, where k is a constant, does not remove all of the discrepancy between his data and those obtained in this work for the more Fe-rich ($<Fo_{80}$) compositions.

The situation is different for Mg-rich olivines. The Arrhenius equation provided by *Misener* [1974] and usually used to calculate diffusivities in olivine [*Misener*, 1974, equation (4)] is stated to be valid in the range of composition $0.1 \leq X_{Mg} \leq 0.8$ only, that is, not for usual mantle olivine compositions with $X_{Mg} \approx 0.9$. In spite of this, all applications and discussion of his diffusion data (e.g., see the various references cited in this work) have used this equation to calculate diffusivity for relatively Mg-rich olivines. It can be seen from Figure 10 of his work, however, that diffusivities which he obtained in more Mg-rich olivines (e.g., $X_{Mg} > 0.9$) using Fo_{90} -MgO pellet couples are not well reproduced by his (4) and are considerably slower. Reading off the data from his figure 10 and correcting these for a possible effect of f_{O_2} on diffusion, assuming that these high temperature runs were close to QFM, we find that his data and those from this study agree within half an order of magnitude. Even if the oxygen fugacity was not that defined by the QFM buffer, as discussed above, it is reasonable to expect that conditions in an evacuated silica-glass tube were relatively more oxidizing

compared to those of this study ($f_{O_2} = 10^{-12}$ bar). Most notably, *Misener* [1974] presents results of two experiments carried out using a synthetic forsterite- $\text{Fe}_{0.3}\text{Fa}_{0.7}$ diffusion couple in the same Figure 10. The data from these runs should be similar to those using couple 1 ($\text{Fo}-\text{Fe}_{0.82}$) of this study. Indeed, we find that on using an f_{O_2} correction as above, these data agree exactly with those found in this study. For example, at 1300°C for an olivine of composition $\text{Fe}_{0.3}$ we obtain $D = 3 \times 10^{-16} \text{ m}^2/\text{s}$ from the plot of *Misener* [1974] whereas D found in this work is $2 \times 10^{-16} \text{ m}^2/\text{s}$ (see data for run OLID-202 in Table 3). This remarkable agreement for Mg-rich compositions suggests that probably the data from the Fe-rich compositions were somehow affected by the poor f_{O_2} control in the study of *Misener* [1974].

The study of *Buening and Buseck* [1973] does not suffer from any of the above ambiguities regarding f_{O_2} control. However, the diffusion couples used in that study consisted of oriented single crystals on one side and polycrystalline pellets on the other side. The authors themselves recognized the potential problems of this setup and were very clear in stating this in at least two different contexts: (1) In the data reduction section they stated that their approach assumed that diffusion rates in the polycrystalline material were so fast compared to that in the single crystal that no concentration gradients developed in this part of the couple and (2) the observed kink in the Arrhenius plot could be due to a change from intrinsic to extrinsic diffusion mechanism or due to a transition from lattice-controlled to grain boundary-controlled diffusion.

It is difficult to judge the nature of the polycrystalline material used in their study in terms of grain size, degree of compaction, size of the pellet, etc. However, as mentioned in the section on experimental setup, we tried to carry out some diffusion couple experiments with single crystals of San Carlos olivine (SC1) and pellets prepared by powdering single crystals of fayalite (same material as in experiments using couple 2). With the sample preparation techniques available more than 20 years ago, *Buening and Buseck* could not analyze the powdered pellet part of their diffusion couples and had to assume that there was no gradient in this part. We would like to point out that the concentration profiles illustrated in their work [e.g. *Buening and Buseck*, 1973, Figure 1] were obtained only from the single crystal part of the diffusion couple. Observation of the powdered pellet part of our couples using the improved sample preparation and analytical technology available now show that the pellet did not act as an infinite reservoir, and there were concentration gradients in this part of the couple as well. This is consistent with current notions about the efficiency of grain boundary diffusion rates (e.g., only 2 orders of magnitude faster than volume diffusion rates, as measured in forsterite aggregates [*Farver et al.*, 1994]). Consequently, the diffusion penetration distance in the single crystal depended on the nature of the adjacent pellet (grain size, degree of compaction, etc.) and could be quite variable for similar run conditions. It is possible that with extremely fine-grained pellets the condition of infinite reservoir may be achieved; since it is not possible to exactly reconstruct the experiments of *Buening and Buseck* [1973], further discussion of this question is unlikely to resolve the issue, and we have to leave this as a possible explanation of the discrepancy between their results and ours. We note that

Buening and Buseck [1973] themselves stated quite clearly that if the assumption of the polycrystalline part of their diffusion couple acting as an infinite reservoir is not valid, then the equations used by them to retrieve diffusion rates (e.g., their (9)) would also be invalid, and, accordingly, retrieved diffusion coefficients may be in error.

Another factor which may affect both these earlier studies [*Buening and Buseck*, 1973; *Misener*, 1974] may have to do with the spatial resolution of electron microprobes. Although profiles of the order of tens of microns are typically unaffected by the spreading of excitation volume within the sample for crystalline silicates under normal operating conditions in modern microprobes, this may not have been the case in older machines. The low takeoff angle of Xrays in older machines might have considerably enhanced this effect, and, indeed, reanalysis of some profiles (same samples or similar samples produced in the laboratory) measured in the 1960s and early 1970s have led us to believe that this effect may not be trivial [e.g., see *Ganguly et al.*, 1996]. It is also worth noting that even for the longest run durations (336 hours) in the study of *Buening and Buseck* [1973], we find that the profile lengths of the lowest-temperature experiments in our study are within the limits where convolution effects begin to affect profile lengths even in modern microprobes. In any case, as already noted in the results section, it is difficult to obtain accurate diffusion data using Boltzman-Matano analysis on short, steep concentration profiles.

The study of *Nakamura and Schmalzried* [1984] used only polycrystalline samples, and therefore it is difficult to compare their results with this study and some discrepancy may be expected. However, they observed that their results were in better agreement with those of *Misener* [1974], which is similar to the findings of this study. *Jurewicz and Watson* [1988] present different diffusion rates for Fe and Mg, so that it is not clear which one of these should be compared to our Fe-Mg interdiffusion rates; the difference in the diffusivities of Fe and Mg makes one suspect that they might have measured tracer diffusion rates which are then not comparable to our data for chemical diffusion. *Jaoul et al.* [1995] studied diffusion at high pressures, at different temperatures, and for a different crystallographic orientation (along [010]), so that their results are not directly comparable to ours.

Relationship Between Chemical and Tracer Diffusion Coefficients

It can be shown that for diffusion in ionic systems or in a crystal with more than one sublattice the self- or tracer-diffusion coefficients and chemical or interdiffusion coefficient are related to each other through

$$D(\text{Fe-Mg}) = \frac{D_{\text{Fe}}^* D_{\text{Mg}}^*}{X_{\text{Fe}} D_{\text{Fe}}^* + X_{\text{Mg}} D_{\text{Mg}}^*} \left(\frac{d \ln a_{\text{Fe}_2\text{SiO}_4}}{d \ln X_{\text{Fe}_2\text{SiO}_4}} \right) \quad (2)$$

where the equation has been written explicitly for Fe-Mg olivines and $D(\text{Fe-Mg})$ is the interdiffusion coefficient at a given composition, as determined in this work. D_i^* is the self-diffusion coefficient of element i , X_i is the mole fraction of i , and a_i is the thermodynamic activity of component i , all at the same composition at which $D(\text{Fe-Mg})$ is to be calculated. The term within brackets is the so-called

thermodynamic factor and may be denoted by ϕ . This relationship may be derived in a number of ways, the derivation for ionic solutions going back to Nernst and Planck and that based on balancing lattice sites to Manning [1968] or Brady [1975]. This equation has been shown to be valid for all ionic solutions and semiconductors, both crystalline and molten, where enough data were available. In the above a small correction due to the correlation factor f has been neglected.

It is apparent that $D(\text{Fe-Mg})$, D_{Fe}^* , and D_{Mg}^* are not all independent of each other; given any two, the third can be determined for any given composition. More interestingly, even any two of these quantities are not independent; because unless they obey the relationship $D_{\text{Fe}}^* \phi > D(1-2)X_{\text{Fe}}$, the remaining quantity D_{Mg}^* becomes negative if (2) is to be satisfied, which is impossible for a diffusion coefficient in a stable system. Thus, for olivine solid solutions one can write that

$$D_{\text{Mg}}^* \phi > D(\text{Fe-Mg}) X_{\text{Fe}} \quad (3)$$

needs to be fulfilled. The value of ϕ has been determined quite accurately for binary Fe-Mg olivine solid solutions [e.g., Seckendorff and O'Neill, 1993]. Using alternative activity models [e.g., Sack and Ghiorso, 1989] to calculate ϕ does not make any difference to the arguments presented below. If Mg-tracer diffusion data measured at different compositions for the same crystallographic orientation, temperature, and oxygen fugacity by Chakraborty *et al.* [1994] are used, (3) is not fulfilled for any of the previous interdiffusion data sets (Buening and Buseck, [1973] or Misener, [1974] when the Arrhenius equation of the latter is used) at any temperature. However, all diffusion coefficients found in this work at different temperatures and compositions satisfy (3), giving us added confidence that the diffusion data are internally consistent (Figure 7) and there is no reason to doubt (2). As the determination of diffusion coefficients given by Chakraborty *et al.* [1994] and this study involved completely different experimental setups, analytical determination, and data reduction procedures, we believe that this compliance with (3) is an added indication that our results may be more reliable than those from previous studies. It should be noted that (3) provides an excellent means of constraining the slower tracer diffusion coefficient in a binary system if the interdiffusion coefficient and thermodynamic mixing properties are known; for compositions depleted in the slower diffusing component (i.e., as $X_{\text{Fe}} \rightarrow 1$), the relationship practically provides a method for the determination of D_{Fe}^* , where i is the slower diffusing element.

Diffusion Mechanisms

General Discussion and Definition of Terminology

Much of the application of Fe-Mg interdiffusion data in olivines is in the study of meteorites that have experienced thermal events at around 600°C [e.g., Jones and Rubie, 1991; Weinbruch *et al.*, 1994], and so the reliability of extrapolation of diffusion data to lower temperatures is of great concern. If there is a change of slope on an Arrhenius plot related to a change of mechanism of diffusion, for example, from intrinsic to extrinsic, extrapolations to low temperatures will be incorrect. Such a change of mechanism was postulated by Buening and Buseck [1973] as one of the

possible explanations for the kink observed in their study. The ambiguity in the definition of intrinsic and extrinsic mechanisms for silicate solid solutions has already been discussed by Chakraborty *et al.* [1994], and Jaoul *et al.* [1995] have mentioned that in principle one can distinguish three different cases. In the following we attempt to delineate the three possible scenarios that may arise during diffusion in a Fe-bearing silicate and discuss the observed results in terms of these. Following up on the discussion by Chakraborty *et al.* [1994], one can define the following:

Intrinsic diffusion. This is diffusion controlled by thermally activated point defect concentrations. In this case, at a fixed composition, the point defect concentrations and hence diffusion rates are a function of P and T only and not of any chemical potential [see Schmalzried, 1983]. As temperature increases from any given state, the concentration of point defects increases, and diffusion of a particle becomes easier because of the enhanced thermal motion as well as the increased availability of sites into which the particle can jump. The activation energy of diffusion is accordingly relatively large, consisting of a sum of two terms: an energy of formation of point defects and an energy of migration. It was shown by Chakraborty *et al.* [1994] that intrinsic diffusion may be expected in silicates in only very rare cases where extremely high temperatures and purity of crystals are attained.

Pure extrinsic diffusion (PED). This is diffusion controlled by point defect concentrations determined by the

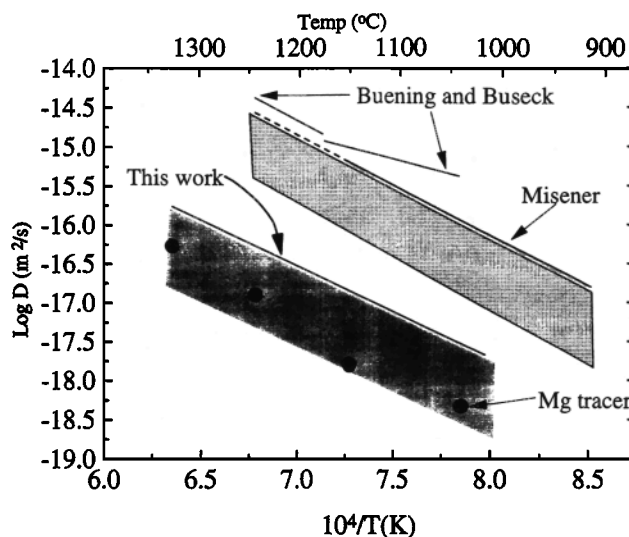


Figure 7. Relationship between Fe-Mg interdiffusion and Mg tracer diffusion rates in olivines of the same composition (Fo_{92} , in this case). Solid lines indicate best fits to an Arrhenius equation from various interdiffusion studies (as indicated by the labels). Solid circles indicate Mg tracer diffusion data in San Carlos olivine (Fo_{92}) from Chakraborty *et al.*, [1994]. Dashed line indicates best fit to Arrhenius equation for tracer diffusion data. The stippled region indicates the approximate permissible range of values for Mg tracer diffusivity allowed by the Fe-Mg interdiffusion data of Buening and Buseck [1973] and Misener [1974] if equations (2) and (3) (see text) are to be valid. The gray shaded region shows the corresponding permissible range for the interdiffusion data obtained in this work. The measured tracer diffusion data (solid circles) fall well within this limit at all conditions where measurements have been done.

presence of an impurity. It is the definition of this "impurity" that introduces the ambiguity in the definition of extrinsic diffusion in silicates; this has been discussed at length by *Chakraborty et al.* [1994]. Thermodynamically, it may be defined as the situation when at a fixed P , T , and major element composition, the defect concentrations and hence diffusion rates are controlled by some chemical potential (which determines the amount of impurities and hence point defect concentrations in the crystal). In this case, as temperature is increased from a given state (at a fixed chemical potential), the concentration of point defects remain fixed, and diffusion becomes easier only because of enhanced thermal motion. The activation energy of diffusion is relatively small, consisting of only the energy of migration term. This is the reason one observes a kink in an Arrhenius plot when transition from intrinsic to extrinsic diffusion occurs; the slopes in such a plot are proportional to the activation energy of diffusion (Figure 8).

Transition metal-extrinsic diffusion (TaMED). This is in some ways a mixed behavior between intrinsic diffusion and PED and is a unique feature of materials with more than one sublattice. It is similar to PED in that the defect concentrations and diffusion rates are controlled by the presence of an "impurity" (a nonstoichiometric component, as defined above) and hence a chemical potential at a fixed P , T , and major element composition. However, unlike PED, as a crystal is heated from a given initial state, the concentration of point defects change with temperature, even at a constant chemical potential; this behavior is analogous to intrinsic diffusion. The most common example of this is the redox reaction of Fe where at constant f_{O_2} if a crystal with a given Fe content is heated, the Fe^{2+}/Fe^{3+} ratio changes. If the point defect concentrations are related to the presence of Fe^{3+} in the crystal (an impurity), then these change as well. As a consequence the activation energy in

these cases is once again a sum of two terms (as described in the subsection on intrinsic diffusion): a formation energy and a migration energy. Unlike intrinsic diffusion however, the formation energy may be positive or negative in this case, so that the slope in this region may be higher or lower than that in the pure extrinsic region (PED) in an Arrhenius plot (Figure 8). This provides for the possibility of a second kink in an Arrhenius plot, the transition from pure extrinsic (PED) to transition metal-extrinsic (TaMED); we discuss the likely magnitude of this effect for the olivine system in more detail below. We have used the terms "pure extrinsic" (PED) and "transition metal-extrinsic" (TaMED) in the absence of any established nomenclature to describe and distinguish between the two scenarios described here. Although TaMED has been illustrated with the common example of Fe here, it is apparent that the same situation may arise in the presence of any multivalent ion. Note that PED and TaMED as used here are similar to the "unconstrained extrinsic" and "constrained extrinsic" cases of *Jaoul et al.* [1995] but are not the same. We do not prefer the terminology of "constrained" versus "unconstrained" of *Jaoul et al.* [1995] because (1) the defect concentrations may be controlled by controlling the chemical potential in both cases, perhaps more easily in some than in others, and (2) there are other differences between the two kinds of diffusion behavior, as indicated above. In the above discussion it has been assumed that there is only one kind of majority defect which dominates the point defect population and controls diffusion at a particular thermodynamic condition.

Mechanism of Diffusion in Fe-Bearing Olivine

As diffusion rates in Fe-bearing olivines depend on the chemical potential of oxygen (f_{O_2}), diffusion in olivines must occur by the pure extrinsic (PED) or transition metal-extrinsic (TaMED) mechanisms. This is an expected behavior because intrinsic diffusion in silicates is energetically very unfavorable (e.g., see *Chakraborty et al.* [1994] for details). A number of independent and detailed studies of the point defect chemistry of olivines [e.g., *Nakamura and Schmalzried*, 1983; *Simons*, 1986; *Wanamaker*, 1994] allow us to further constrain the diffusion mechanism. From these studies we know that point defects related to the redox reaction of Fe are dominant in olivines, and their concentrations are proportional to $(f_{O_2})^{1/n}$. In essence, three Fe^{2+} may be replaced by a vacancy and two Fe^{3+} in a olivine crystal while maintaining charge balance. The exponent n appearing in the f_{O_2} dependence may vary somewhat depending on the details of the point defect model, temperature, silica activity, etc. but has been shown to remain between 4.5 and 6. Since the tracer as well as chemical diffusivity of various cations show a similar dependence on oxygen fugacity, it is concluded that diffusion in Fe-bearing olivines, as observed in laboratory experiments, proceeds by a transition metal-extrinsic (TaMED) mechanism. This implies, in turn, that the observed activation energies of diffusion are a sum of a defect formation and a migration energy. The important question then is to determine the relative contributions of these two terms to the total activation energy, because the magnitude of the formation energy in this case determines the likely temperature of a kink and its magnitude in the Arrhenius plot due to the PED-TaMED transition.

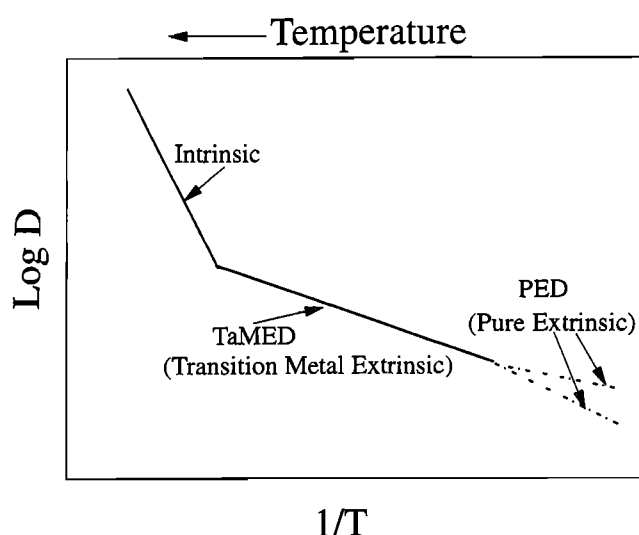


Figure 8. Schematic illustration of three possible diffusion regimes in Fe-bearing silicates and the expected relative temperature ranges of validity. Note that at the transition from transition metal extrinsic diffusion (TaMED) to pure extrinsic diffusion (PED) the change in slope is expected to be small; the slope in the PED regime may be higher or lower as indicated by the two dashed alternatives. Diffusion rates are sensitive to oxygen fugacity only in the TaMED regime.

For oxidation reactions of metals in divariant systems (e.g., involving solid solutions) the proportion of reduced metal usually increases with increasing temperature at constant oxygen fugacity. If reactions of this form occur within silicate crystals, then one would expect an increased concentration of cations of lower valence (e.g., Fe^{2+}) with increasing temperature, and consequently a reduction in the number of cation vacancies. This would lead to a negative formation enthalpy of vacancies; that is, the slope of diffusivity in the TaMED regime would be shallower (\sim difference between migration and formation energy) than that in the PED regime on an Arrhenius plot. Alternately, the energetics of oxidation along with vacancy formation within a crystal may be quite different from the simple oxidation reactions, and the enthalpy of formation of point defects may be positive, as in the intrinsic regime. For olivines we are able to estimate the magnitude of this effect from the work of *Nakamura and Schmalzried* [1983] and *Simons* [1986], who determined point defect concentrations in olivines as a function of temperature. In spite of the high sensitivity (allowing detection of changes in point defect concentrations <0.1 log unit due to small changes in ambient oxygen fugacity at a constant temperature), *Nakamura and Schmalzried* [1983] were unable to resolve any differences in point defect concentration between 1000°C and 1130°C and saw only very small differences between 1130°C and 1200°C. This points clearly to a very small enthalpy change in the defect formation reaction within the TaMED regime. This is confirmed by further coulometric titration measurements of *Simons* [1986], who combined his data with that of *Nakamura and Schmalzried* [1983] to quantify the small enthalpy change to be positive in most cases. The data of *Simons* [1986] show the enthalpy change determining the variation of octahedral vacancy concentration with temperature in fayalite between 900°–1130°C to be (1) of the order of 8–9 kJ/mol for olivine coexisting with one other oxide phase such as FeO or SiO_2 , (2) slightly negative of the order of -3.5 kJ/mol for olivine coexisting with magnetite, and (3) of the order of 12 kJ/mol for olivine coexisting with metallic Fe or two oxide phases (e.g., SiO_2 and Fe_3O_4). These results have a number of important implications.

First, we can infer that the observed activation energies of diffusion are essentially the migration energy and that the contribution of the formation energy is smaller in magnitude than the uncertainty in the knowledge of activation energy (± 20 kJ/mol). This, in turn, means that the size of the kink on the Arrhenius plot due to a transition from TaMED to PED would be beyond resolution (a change of ~ 8 – 12 kJ/mol in slope) with the commonly achieved accuracy of diffusion measurements. Thus extrapolation of diffusion data to lower temperatures than those of the measurements are unlikely to be affected by any major kinks; the main uncertainty arises from the scatter of the data itself. However, a sensitive monitor of the mechanism may be the oxygen fugacity dependence of transport rates. It is possible that at low temperatures point defect concentrations and diffusion rates become independent of oxygen fugacity as one crosses the TaMED–PED transition. To unequivocally document this transition, it would be necessary to demonstrate that the change in f_{O_2} dependence is not the result of kinetics of defect equilibration.

Second, the energetic data on defect formation provides us information about the nature of vacancies in these

crystals. The small enthalpy of defect formation indicates that the large energetic and entropic gain of trapping a free oxygen from the atmosphere into a crystal is practically offset by the formation of a vacancy within the crystal. Thus the region around the vacancy must involve major bond reorganizations/relaxations and be highly disordered with respect to the undisturbed crystal lattice. This has important consequences for computer simulations of point defect characteristics and transport properties of silicate minerals. For example, it is unlikely that intermolecular potentials derived from optimizing structural, thermodynamic, and physical characteristics of well-ordered bulk crystals would be very helpful in the calculation or simulation of diffusion or other transport properties which depend on the local structure around point defects. The important role of relaxations due to polarizability of ions around defects has already been discussed for simple ionic solids, most notably in important contributions by *Lidiard* [1981] and *Gillan* [1981] and many others following them. The important new result here is the derivation of this conclusion from purely macroscopic considerations and the implication that simulation of transport in transition metal-bearing silicates must consider the role of variable valence cations (both their concentration and effect on local geometry), even when these are present in low concentrations. The mechanisms of transport in idealized, transition metal-free systems and real, transition metal-bearing systems will be quite different qualitatively and energetically.

The third implication of the data on energetics points to a result we have already obtained experimentally; as long as f_{O_2} , P , and T are fixed, the number of majority point defects in the crystal will be fixed within narrow limits, and so the abundance of other trace elements ("impurities") will not play a major role in controlling transport rates. This may change, however, when one enters the pure extrinsic regime (PED), presumably at lower temperatures or for minerals with very low concentrations of transition metals. Such a case was observed by *Chakraborty et al.* [1994] for diffusion in nominally pure forsterite, if their Model -I (one of two alternatives) explaining the observations is the correct explanation of their data.

Finally, it is interesting to note that cation diffusion rates depend on oxygen fugacity only in the TaMED regime (excepting some rather forced scenarios involving diffusion via oxygen interstitials). Consequently, when one goes through a transition marked by a kink in the Arrhenius plot, diffusion rates are unlikely to be oxygen fugacity dependent on both sides of the transition. The exception is when the transition is from one transition metal-related defect to another in a crystal containing more than one kind of transition metal ion (e.g., from Fe^{3+} control to Mn^{3+} control). In this case one may observe a kink in the Arrhenius plot within the TaMED regime. Thus it is difficult to explain the observations of *Buening and Buseck* [1973] that diffusion rates were oxygen fugacity dependent both above and below the observed kink in their Arrhenius plot in terms of any change of mechanism occurring within the crystal itself (unless the minor Mn content of San Carlos olivine is invoked in the explanation somehow; the fayalite used by *Buening and Buseck* was synthetic, and hence presumably free of Mn). Based on this line of reasoning as well, then, it appears likely that the transition observed by *Buening and Buseck* was related somehow to an interplay between grain boundary and volume diffusion rates. On the basis of this

analysis of diffusion mechanisms and our data we would recommend that when necessary, a simple Arrhenius expression without any kink in it should be used for low-temperature extrapolation of diffusion rates.

Implications for Modeling Natural Processes

The implication of the present data in terms of modeling natural processes is that timescales of natural processes inferred from compositional zoning in olivine will be longer, cooling rates will be slower, and calculated temperatures will be higher than those obtained using previously available diffusion data. Closure temperatures of element exchange thermometers involving olivine may be higher in cases where diffusion of divalent cations in olivine is the rate-determining step. Two recent examples from the literature may illustrate these aspects. In their study on compositional zoning of olivines from the Allende meteorite, Weinbruch *et al.* [1994] concluded that temperature estimates from element exchange geothermometers (at least 800 K, from olivine-spinel pairs) and compositional zoning in olivine (~600 K) were inconsistent with each other for reasonable estimates of the duration of metamorphic event in the parent body (based on the decay rate of ^{26}Al and assuming this to be the major heat source). With the present data set this inconsistency disappears and the peak metamorphic temperatures are found to be ~800 K or even higher; the mean olivine-spinel temperatures of ~900 K are consistent with the information obtained from compositional zoning in olivines.

In a second example, Nakamura [1995] estimated the residence times of olivines in magmas that erupted from the northern Yatsugatake volcanoes in Japan using compositional zoning. Some of the details of his modeling rely on the difference between Fe-Mg interdiffusion and Ni tracer diffusion rates in olivines and are questionable based on recent measurements of Ni tracer diffusion rates [Petry *et al.*, 1996]. However, just from the results of modeling the Fe/Mg compositional profiles he concluded that the residence times of type-I olivines were between 10 days and 1 year, whereas for type-II olivines the timescales were 10 to 100 times longer. With the present diffusion data, although the relative timescales remain unaffected, the absolute duration would be revised upward to about 3-100 years for the type-I olivines.

Summary

The main finding of this work is that Fe-Mg interdiffusion in olivine is slower by about 2 orders of magnitude than that measured in most previous studies in the temperature range of 980°-1300°C. Data obtained by Misener [1974] for Mg-rich olivines (not included in his Arrhenius fit) agree well with diffusion coefficients obtained in this study. The compositional dependence and activation energy of diffusion determined here are similar to those found earlier, and a few exploratory experiments indicate that the dependence on crystallographic orientation and oxygen fugacity are consistent with previous determinations. We do not find a change in temperature dependence (activation energy) over the range of measurement, and it is shown that a large change of activation energy is not anticipated at lower temperatures. It is also pointed out that

the point defect systematics of Fe-bearing silicates allow the separation of at least three distinct diffusion regimes, which have been termed intrinsic, pure extrinsic (PED), and transition metal-extrinsic (TaMED) in this work. After discussing the characteristics of diffusion in these three regimes, it is shown that observed diffusion in olivine occurs in the TaMED regime.

Fe-Mg interdiffusion coefficients at typical mantle olivine compositions of about Fo_{90} are measured directly over a wide range of temperature for the first time in this work, and diffusion rates at compositions in the range Fo_{85-88} are tightly constrained by bracketing these compositions using two different diffusion couples. These results also show that diffusion rates are uniquely defined as long as the relevant thermodynamic parameters are well characterized (P, T, composition, and oxygen fugacity in this case), and concerns about the lack of portability of diffusivities between different crystals with variable trace element contents, etc. are unfounded. This conclusion is not only limited to the crystals used in this study but is more general, because this behavior (diffusion in the TaMED regime, as discussed above) has been rationalized in terms of the reasonably well understood point defect chemistry of olivines. The present data set implies that closure temperatures and timescales of processes determined using previously available diffusion coefficients would have to be revised upward; cooling rates and estimated length scales of diffusion in a given time would decrease.

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