

SELF-DIFFUSION OF MAGNESIUM IN GARNET AT 750° TO 900°C

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ABSTRACT. The self-diffusion of magnesium in pyrope garnet was experimentally determined at temperatures of 750° to 900°C and a pressure of 200 MPa. Diffusion couples consisted of natural single crystal pyrope and ²⁵Mg-enriched polycrystalline magnesium oxide. A SIMS ion microprobe was utilized to determine the induced depth profiles of ²⁴Mg and ²⁵Mg which extended to a depth of approx 0.3 μm. A semi-infinite medium chemical diffusion model was used to extract the Mg self-diffusion coefficients from the ²⁵Mg/²⁴Mg mass ratio versus depth profiles. The results obtained at the different temperatures follow the Arrhenius relation, $D = D_0 \exp(-E_a/RT)$, with an activation energy, E_a of 239 ± 16 kJ/mole and a pre-exponential factor, D_0 , of 9.8×10^{-9} m²/sec. The results are in excellent agreement with the garnet diffusivities deduced from kinetic models for natural occurrences of garnet compositional zoning. Only limited agreement occurs for extrapolated high-temperature (T greater than 1000°C) garnet diffusion data. Extrapolation of high-temperature data to lower temperatures may be hampered by changes in diffusion mechanism and activation energies. Knowledge of these transport properties of Mg in garnet at metamorphic conditions is necessary for determining the reliability of T and P estimates based on mineral pair geothermometry and geobarometry, especially when compositional zoning is present. Homogenization times and closure temperatures derived from the experimental diffusion rates provide valuable tools for investigating time-temperature relations in petrologic processes.

INTRODUCTION

The transport properties of major cations in silicate minerals are of major concern to the petrologist in the utilization of geothermometers and geobarometers. The occurrence of compositional zoning in one or both phases of a mineral pair can lead to ambiguous and uncertain equilibration temperature and pressure estimates for a particular mineral assemblage. Although it is possible to compare mineral pair core and rim concentrations in deriving a thermal history of the crystallizing phases (Tracy, Robinson, and Thompson, 1976; Dahl, 1979), it is necessary to have some knowledge of the diffusion rates of the particular cations that are inhomogeneously distributed in the minerals. It is the presence of the compositional gradient that provides the force to drive the diffusion process and therefore is responsible for modifying intra-mineral compositions during or after mineral formation or equilibration. The role of

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chemical diffusion is especially important at the temperatures of metamorphism where numerous examples of compositional zoning have been reported, especially for the ferromagnesian phases (see Tracy, 1982).

Lasaga (1983) has recently extended geothermometry theory by introducing diffusional transport terms to account for the observed disequilibrium zoning. This kinetic model, referred to as geospeedometry, requires the input of diffusion rates for cations in each phase of a mineral pair. The paucity of such diffusion data in the geochemical literature puts severe limitations on the application of such kinetic models to geological field problems. It was the obvious need of such data that led to the present study of determining cation diffusion data for garnet, a major silicate mineral, at reasonable metamorphic conditions. The accurate quantification of cation diffusion in garnet would provide the necessary input terms for refining the application of kinetic and diffusion models, such as those of Anderson and Buckley (1973), Loomis (1975, 1977), Lasaga, Richardson, and Holland (1977), and Tracy and Dietsch (1982), to metamorphic rocks.

Of all the major silicate phases in metamorphic terranes, garnet is the mineral that almost ubiquitously exhibits compositional zoning. The fact that zoning is so well preserved in garnet suggests that the chemical diffusion coefficients have an extremely small value at these metamorphic temperatures. However, there have been no previous experimental determinations of the diffusion coefficient for any component in garnet at any metamorphic temperatures (less than 900°C). This can be attributed to the difficulty of inducing a chemical zoning profile with a penetration distance large enough to be resolved easily using conventional micro-analytical techniques such as the electron microprobe analyzer. Obviously, the experimentalist will be limited at these relatively low temperatures by the length of practical run times permitted in the laboratory. For these reasons previous garnet diffusion studies (Freer, 1979; Duckworth and Freer, 1981; Elphick, Ganguly, and Loomis, 1981, 1982) have been restricted to temperatures above 900°C.

Recent studies of chemical diffusion in silicate minerals and glasses have utilized an ion microprobe to determine the chemical profile of the diffusing species. This technique, often referred to as SIMS (Secondary Ion Mass Spectrometry), has a depth resolution of 50 to 100 Å. This high resolution provides a means of determining accurately the small diffusion coefficients of minerals at the lower geological temperatures. The majority of the ion microprobe studies of minerals have concentrated on oxygen transport in feldspar (Giletti, Semet, and Yund, 1976, 1978; Freer and Dennis, 1982) and olivine (Giletti, Semet, and Kasper, 1974; Giletti, Hickey, and Tullis, 1979; Jaoul and others, 1980; Hallwig, Schactner, and Sockel, 1982). The ion microprobe has also been used for determining major cation diffusion coefficients in silicates, such as potassium in biotite (Hofmann and others, 1974); magnesium (Hallwig, Schactner, and Sockel, 1982; Morioka, 1981) and silicon (Hallwig, Schactner, and Sockel, 1982) in forsterite; and calcium, magnesium (Freer and others, 1982), and strontium (Sneeringer, Hart, and Shimizu, 1981) in diopside.

In SIMS analysis, a primary beam of ions is accelerated and focused onto the sample surface allowing the high kinetic energy of the primary ions to be transferred to the sample atoms. This process causes some of the sample atoms in the surface region to be ejected or sputtered away in essentially monolayer increments. A portion of the sputtered atoms is ionized in the process (termed secondary ions) and is then collected and analyzed by a mass spectrometer. If the rate of sputtering is known, it is possible to obtain a mass (chemical) versus depth profile. An excellent summary of SIMS theory, instrumentation, and general application is provided by Colby (1975) while Shimizu and Hart (1982a) present a more specific review of SIMS techniques as applied to geochemical problems. The principles of SIMS depth profiling, necessary for diffusion studies, are discussed by Zinner (1980).

In this paper we present data obtained by SIMS technique for the self-diffusion of magnesium in natural pyrope garnet obtained at 750° to 900°C and 200 MPa (2 kb). The run conditions were selected to reflect a near-metamorphic environment. The data are compared to the previous high-temperature cation diffusion determinations. A discussion of crystal chemistry and defect theory is presented in light of the determined diffusion rates. The application of these lower temperature diffusion data to garnets of metamorphic terranes is also presented.

EXPERIMENTAL PROCEDURE

Samples of pyrope-rich garnet were obtained from a kimberlite diatreme located at Green Knobs on the Navajo Indian Reservation in New Mexico. O'Hara and Mercy (1966) and Smith and Levy (1976) provide discussions of the possible sources for the basic xenolithic material. The garnets are optically pure and free of major fractures and inclusions. An average chemical composition of the garnets is presented in table 1 and in endmember proportions corresponds to that of $\text{Py}_{74}\text{Alm}_{15}\text{Gr}_{10}\text{Ur}_1$. Garnet, possessing a cubic crystal structure, can have its transport properties described by a single isotropic diffusion coefficient (Nye, 1957). Therefore,

TABLE 1
Mean chemical composition of pyrope garnet used in diffusion runs
determined by electron microprobe analyses

Oxide	Wt Percent	Standard Error	Cations/12 Oxygen
SiO ₂	42.09	0.62	3.005
TiO ₂	0.02	0.01	0.001
Al ₂ O ₃	22.27	0.26	1.875
Cr ₂ O ₃	1.84	0.07	0.104
Fe ₂ O ₃ *	0.26	0.01	0.014
FeO	7.61	0.24	0.454
MnO	0.64	0.02	0.039
MgO	20.58	0.25	2.190
CaO	4.14	0.07	0.317
Total	99.45		7.999

* Determined by nonstoichiometry.

the samples were arbitrarily cut into rectangular blocks of approx $6 \times 3 \times 3$ mm dimensions. The largest surface of each crystal was ground with SiC powders and then polished successively with alumina powders, the final stages utilizing $0.05 \mu\text{m}$ gamma alumina, to provide a smooth surface, free of visually observed defects. All samples were then ultrasonically cleaned in, successively, acetone, soapy water, distilled water, and ethanol. It should be noted that considerable care is required in this stage of sample preparation in order to avoid surface damage (see Reed and Wuensch, 1980). This is of particular importance with the use of the SIMS ion microprobe for the analysis of very short zoning profiles.

The diffusion couples were prepared by applying a magnesium-25 tracer to the surface of each garnet crystal. The ^{25}Mg tracer was supplied by Merck Sharp and Dohme Canada Limited and was in the form of MgO powder at 97.8 atomic percent ^{25}Mg . The oxide was dissolved in oxalic acid to produce a solution of $2.8 \times 10^{-3} \text{ M } ^{25}\text{MgC}_2\text{O}_4$. This solution was allowed to evaporate on the surface of each garnet to provide a thin (approx $2.0 \mu\text{m}$) uniform distribution of polycrystalline $^{25}\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precipitate. The samples were then treated at 250°C for 12 hrs in order to remove the structural and absorbed water and to provide the necessary binding of the single crystal garnet-polycrystalline oxide couple together.

The diffusion couples were housed in open (crimped, not welded) $\text{Ag}_{50}\text{Pd}_{50}$ capsules of 4.8 mm inside diameter and 18 mm length. The capsules were then brought to temperature and pressure conditions in an internally heated pressure vessel (Holloway, 1971) using argon as the pressure medium. The oxalate decomposes during the run up at approx 400°C to produce ^{25}MgO which is maintained on the garnet surface. Run durations were timed from the point when the temperature was within 50°C of run temperature. Usually the run temperature was obtained several minutes after this initial time. An effort was made to equilibrate thermally the diffusion couple as quickly as possible (usually less than 10 min) once a diffusion closure temperature (approx 700°C) was exceeded. This closure temperature defines the limit where diffusion becomes measurable under the considered experimental times. The quench was relatively fast and occurred within 30 sec of removing power from the furnace.

Temperatures were recorded by three calibrated chromel-alumel thermocouples positioned about the run capsule. The temperature readings are believed to be accurate to within $\pm 5^\circ\text{C}$. Proportional controllers provided a means of minimizing any temperature gradient in the double resistance furnace assembly. Pressure was measured with a manganin cell calibrated against a Heise bourdon-tube gauge. The pressure of all the diffusion runs was 200 MPa (2 kb) with an uncertainty of ± 4 MPa (40 bar). Although there was no specific buffering of the oxygen fugacity in these runs, the reaction vessel possesses an inherent f_{O_2} buffer that approximately follows the magnetite-hematite buffer assemblage. However, it is important to note that there was no evidence of oxidation or garnet reaction, as determined by optical and scanning electron microscopy, for any of the samples after completion of the diffusion run.

Diffusion runs were performed at 900°, 850°, 800°, and 750°C, all at a pressure of 200 MPa. Two couples were annealed for a given run time at each temperature except at 900°C where runs were repeated for three different anneal times. Anneal times were selected to provide a diffusion penetration depth of approx 0.2 μm based upon an estimated garnet diffusivity from Lasaga, Richardson, and Holland (1977). An additional run was performed for 24 hrs at 450°C, well below the closure temperature, as a check on the experimental technique. Upon completion of the diffusion anneal, the samples were removed from the capsules and examined with an optical microscope. It was necessary to remove as much of the polycrystalline MgO layer as possible by rubbing the garnet surface on a felt pad. Although not successful in providing a completely clean surface, this process did provide a suitable garnet surface necessary for SIMS analysis, without destroying the interface.

The garnet samples were analyzed on a Gatan SIMS ion microprobe at the Materials Research Laboratory of The Pennsylvania State University. The instrument was operated with 7.0 kV Ar⁺ primary ion beam which was electrostatically focused to provide an 80 μm diameter beam at the sample surface. The beam is rastered upon the surface of the sample to produce a homogeneously sputtered flat-bottomed crater of approx 750 \times 750 μm area. A beam current of 0.48 μA was maintained for all analyses as determined by a Faraday cup located at the sample. The samples are positioned to intercept the primary ion beam at a 45° angle of incidence. The secondary ions are detected by an Extranuclear Laboratories quadrupole mass spectrometer positioned directly behind the sample. A resistive disk energy filter is used to energy select and bend the path of the emitted secondary ions to the mass spectrometer entrance. The detector is electronically gated so that only the signal from the central portion (approx 200 \times 200 μm area) of the rastered area is recorded. This process removes any edge effects created by secondary ions emitted from the edge of the rastered crater. An electron gun is used for charge neutralization at the garnet surface to prevent charge buildup and eventually signal loss and primary beam deflection.

The sputtering rate for pyrope garnet was determined by monitoring crater depth as a function of time. A Talysurf profilometer, incorporating a mechanical diamond stylus and an optical transducer, is used to measure the depth and roughness of sputtered areas. A linear sputtering rate of 2.07 ± 0.04 Å/sec was determined for pyrope garnet with a primary beam operating at 7 kV and 0.085 mA/cm². This rate was found to be linear over crater depths ranging from 0.42 to 0.95 μm in depth. Similar linear behavior was found for feldspars by Giletti, Semet, and Yund (1978) and appears to be true for silicates, in general. The crater bottoms of garnet show no major roughness or inhomogeneity above the detection limit of the profilometer.

It is necessary to monitor the ²⁵Mg/²⁴Mg ratio as a function of depth in the garnet for the determination of the diffusion coefficient. This is not a straightforward procedure using the SIMS technique due to mass inter-

ferences and restrictions imposed by the sputtering/ionization process. Mass separation of small mass differences (less than 0.1 atomic mass unit) is difficult due to the low mass resolution ($M/\Delta M = 300$) of the quadrupole mass spectrometer. Doubly charged ions and molecular ionic species can therefore contribute to the mass spectrometer signal, especially if a natural composition is being analyzed with a wide variety of chemical components. For the masses analyzed in this study, these interferences are negligible when compared to the major masses. For instance, ^{48}Ca and ^{48}Ti and ^{50}Ti and ^{50}Cr will contribute, respectively, to the mass 24 and 25 intensities as doubly charged species. But these components are insignificant due to either their relatively low concentrations in the garnet (see table 1) or the insignificant natural abundance of that particular isotope. In addition, oxide systems inherently produce secondary ions dominated by singly charged species (C. Pantano, personal commun.). Shimizu and Hart (1982a) discuss some of the problems associated with the molecular interferences. While analyzing an untreated garnet the energy filter of the secondary ion detection system was adjusted to remove all these interferences and to produce an intensity ratio ($^{25}\text{I}/^{24}\text{I}$) equivalent to that expected for the natural abundance of magnesium isotopes ($^{25}\text{Mg}/^{24}\text{Mg} = 0.13$). It is assumed in the following discussion that the measured intensity ratio is equivalent to the magnesium isotopic concentration ratio. It is also believed that this assumption holds true for all isotopic compositions and depths of the garnet.

A garnet depth profile consists of monitoring the intensities of ^{16}O , ^{24}Mg , ^{25}Mg , ^{28}Si , and ^{56}Fe signals as the primary ion beam sputters into the garnet. The signal from each mass was monitored for 2 sec to provide a statistically significant count rate. Each signal is sequentially monitored every 10 sec. It was necessary to search for a clean area on the garnet surface for a good analysis spot in order to avoid the interference of the remnant polycrystalline MgO layer. The true garnet interface was determined by monitoring $^{25}\text{Mg}/^{24}\text{Mg}$ and the ^{28}Si signal. The former value decreases sharply once the interface is intercepted and is accompanied by a substantial increase of the ^{28}Si signal. Sputtering was allowed to proceed for about 40 min (0.5 μm depth) so as to define the complete diffusion profile and the expected $^{25}\text{Mg}/^{24}\text{Mg}$ bulk composition. Analysis of an untreated sample produced a homogeneous $^{25}\text{Mg}/^{24}\text{Mg}$ composition to a depth of 0.45 μm . A relative standard error of 6 percent was determined for the isotope ratio from this bulk composition data. The scatter in the bulk isotope ratio is reflected in the large distance sections of the SIMS profiles presented in figures 1 and 2.

Representative depth profiles of $^{25}\text{Mg}/^{24}\text{Mg}$ in garnet as measured by the SIMS ion microprobe are presented in figures 1 and 2. The change in intensity ratio with depth is as one would expect for a volume diffusion process (see later discussion). It is important, though, to examine other processes that may contribute to the measured profile which can be an artifact of the measurement technique. Implantation of ions from the primary beam into the sample during the sputtering process can create an

enhanced near-surface intensity. This was a major problem in the oxygen diffusion work of Giletti, Semet, and Yund (1978) using an O^- primary beam but poses no significant problem in the present study in which Ar^+ is used. On the other hand, the sputtering does produce a knock-on effect in which near surface atoms are knocked deeper into the sample during a primary ion-sample atom collision. This process, discussed by Colby (1975) and Ishitani, Shimizu, and Tamura (1975), would produce a broadened depth profile. Another potential problem is isotopic fractionation during sputtering or ionization (Slodzian, Lorin, and Havette, 1980). The light isotope will be enhanced relative to the heavy isotope and provide an invalid isotope ratio. Shimizu and Hart (1982b) examined this effect for Mg isotopes in silicates and found the fractionation to be insignificant at less than 1 percent per atomic mass unit. The use of an electron gun, for analyzing insulating materials, may stimulate desorption of ions from the surface. This effect was found to be negligible by checking mass signals while the primary ion beam was blocked. Zinner (1980) reviews other factors, such as primary beam uniformity, crater micro-roughness, primary beam heating, and enhanced diffusion, among others, which may affect the measured depth profile. Unfortunately, very little is known of the physics of the sputtering and ionization processes and still less for the specific case

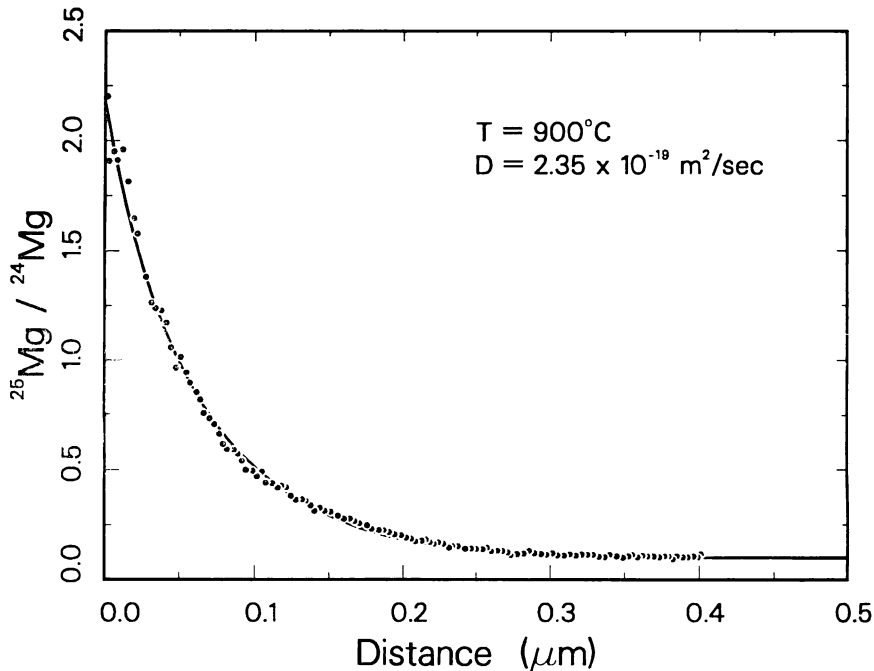


Fig. 1. Depth profile of $^{25}\text{Mg}/^{24}\text{Mg}$ in pyrope garnet after an anneal time of 12.10 hrs at 900°C (run PYR9LL900-5). The smooth curve is the best fit of the SIMS data to the diffusion model.

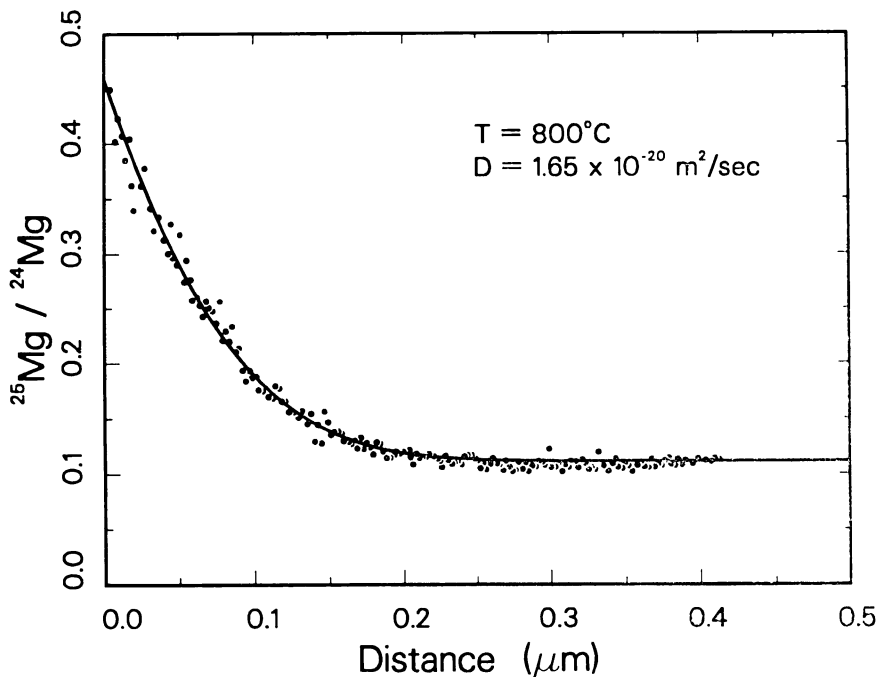


Fig. 2. Depth profile of $^{25}\text{Mg}/^{24}\text{Mg}$ in pyrope garnet after an anneal time of 70.57 hrs at 800°C (run PYR3CC800-7). The smooth curve is the best fit of the SIMS data to the diffusion model. Note the different scale for the $^{25}\text{Mg}/^{24}\text{Mg}$ axis in comparison with figure 1.

of silicate minerals. Obviously, it is very difficult to quantify the contribution of each effect in modifying the true diffusion profile. In this respect, it was necessary to analyze a blank diffusion couple run at 450°C (well below the experimental closure temperature) in order to examine the experimental and instrumental contributions to a depth profile. The resulting $^{25}\text{Mg}/^{24}\text{Mg}$ profile is equivalent to that obtained for an untreated garnet except for the near surface region (less than 100 Å) in which all mass signals were attenuated. Diffusion runs repeated at 900°C for different anneal times also suggest negligible contributing effects. It is, therefore, reasonable to suggest that *only* a diffusion process was responsible for creating the measured $^{25}\text{Mg}/^{24}\text{Mg}$ depth profiles.

ANALYSIS OF DIFFUSION PROFILES

The measured $^{25}\text{Mg}/^{24}\text{Mg}$ depth profiles can be used to extract the Mg self-diffusion coefficient in garnet. The diffusive transport that generated the observed SIMS profiles is modeled as diffusion in a semi-infinite medium with a constant isotopic surface composition. The garnet medium has an initially homogeneous isotopic composition. The solution to the Fickian diffusion equations for a single component in this type of model is given by Crank (1975) as:

$$\frac{C_x - C_s}{C_b - C_s} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (1)$$

C_x , C_b , and C_s refer to the concentration of the component respectively at a distance x from the surface, at $x = \infty$ (the bulk composition), and at the surface ($x = 0$). D is the diffusion coefficient, t is the run duration time, and erf is the error function.

It is necessary to modify eq (1) to obtain an equation for the variation in the isotopic ratios. Besides the diffusion of ^{25}Mg into the garnet, there is an outward flux of ^{24}Mg from the garnet and hence a complementary diffusion profile. Eq (1) can be rewritten for each of the diffusion species,

$$^{25}C_x = ^{25}C_s + (^{25}C_b - ^{25}C_s) \operatorname{erf}(Fx) \quad (2)$$

$$^{24}C_x = ^{24}C_s + (^{24}C_b - ^{24}C_s) \operatorname{erf}(Fx) \quad (3)$$

where,

$$F \equiv \frac{1}{2\sqrt{Dt}} \quad (4)$$

The numerical superscripts refer to the specific Mg isotope. D is actually a binary or inter-diffusion coefficient but is referred to as the self-diffusion coefficient for the isotopic exchange and diffusion process (see Freer, 1981).

Figure 3 presents a schematic representation of the diffusion couple depicting the initial and boundary conditions for the model. As there is only a limited amount of isotope exchange between the oxide and garnet, especially in view of the small SIMS depths required, the concentrations in the oxide remain essentially unchanged during the experiment. This would suggest a constant isotope partitioning between oxide and garnet

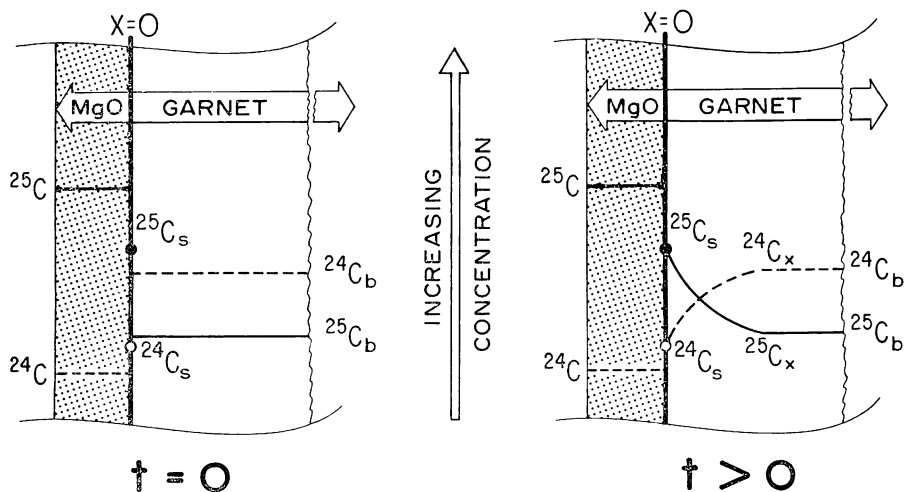


Fig. 3. Schematic representation of the initial and boundary conditions imposed for the diffusion model of ^{25}Mg and ^{24}Mg in garnet. The drawing on the right also depicts the isotope profiles after some finite time of annealing.

and therefore a constant surface concentration. In addition, there will be a homogeneous distribution of ^{25}Mg and ^{24}Mg in the MgO layer due to the relatively fast transport of the isotopes to and from the garnet surface through the polycrystalline oxide. Grain boundary diffusion in the oxide layer is assumed to be much more efficient than the volume diffusion in the single crystal garnet (Manning, 1974). The oxide layer can therefore be considered in the diffusion model as an infinite well-stirred reservoir.

The possibility of other diffusing species contributing to the observed depth profiles was investigated. Limitations upon a given mass analysis were imposed by low intensities and mass interferences, so not all available garnet masses were monitored. For those masses that permitted SIMS analysis, especially ^{56}Fe (the second major cation in the pyrope samples), there was no evidence of any zonation throughout the entire analyzed depth. The contribution of ^{26}Mg , the third stable Mg isotope, was considered negligible although ^{26}Mg is similar in natural abundance to ^{25}Mg . Mass 26 was monitored during several SIMS depth analyses and was found to be insignificant in mass signal when compared to the enriched ^{25}Mg and natural ^{24}Mg intensities. It is, therefore, assumed that ^{25}Mg and ^{24}Mg are the only diffusing species in the pyrope garnet and that the Mg self-diffusion coefficient can be determined directly from the $^{25}\text{Mg}/^{24}\text{Mg}$ profiles using the present diffusion model.

As we are measuring the ratio of isotope concentrations in the SIMS analysis, it is necessary to form the ratio of eqs (2) and (3). This ratio can be rearranged into,

$$R_x = \frac{R_i + A \operatorname{erf}(Fx)}{1 - A \operatorname{erf}(Fx)} \quad (5)$$

where,

$$A \equiv \frac{R_b - R_i}{1 + R_b} \quad (6)$$

The R terms represent $^{25}\text{Mg}/^{24}\text{Mg}$ intensity or concentration ratios and the subscripts refer to positions as defined previously. The A term results from the imposed boundary conditions for the diffusion model. Eq (5) presents R_x as a function of position x for a given D (see eq 4) since all other terms are defined by the initial, boundary, and run conditions. Because D is a constant during the garnet diffusion run (see below), this expression ultimately allows us to extract the self-diffusion coefficient from the best fit of the model to the observed SIMS profiles. A similar technique was incorporated by Coles and Long (1974) for lithium isotopes diffusing in lithium fluoride.

It is desirable to rearrange the theoretical diffusion model expression, eq (5), into a form useful for the least-squares fitting. The resulting function is given by:

$$\operatorname{erf}(Fx) = \frac{1}{A} \frac{R_x - R_i}{1 + R_x} \quad (7)$$

The measured diffusion profiles were fitted to this equation using a least-

squares method and the simultaneous optimization of D and R_s values. A Newton-Raphson iterative technique was implemented in this effort. The reason for varying the R_s value is due to the characteristic large slope for the $^{25}\text{Mg}/^{24}\text{Mg}$ profile which occurs immediately below the garnet surface. The optimized R_s value would therefore reflect the true surface value ($x = 0$) and not the first analyzed depth. This effort was a major concern during the SIMS analysis due to the nature of the garnet surface and the necessity of defining a proper oxide-garnet interface. The bulk garnet composition, R_b , was determined by averaging the $^{25}\text{Mg}/^{24}\text{Mg}$ values from the last section of the diffusion profile, essentially at $x = \infty$.

Two representative best fits of the diffusion model to the observed profiles are presented in figures 1 and 2 for runs at respectively 900° and 800°C. The diffusion model is represented by the smooth curve and is in remarkable agreement with the SIMS data. Similar theoretical profiles, although not always providing as excellent a fit, were obtained for the other SIMS profiles. These additional theoretical and SIMS profiles are provided in Cygan (ms). Values of the Mg self-diffusion coefficient, derived from the best fits, are presented in table 2 along with a summary of run conditions and SIMS analysis particulars. A relative standard error of 20 percent for the diffusion coefficient values was determined by an error propagation technique based upon the measurement uncertainties in mass intensity ratio, run duration, and sputtered depth. A similar error estimate was determined by Giletti, Semet, and Yund (1978) for oxygen diffusion coefficients in feldspar using a similar experimental approach.

It was not possible to obtain SIMS profiles for both crystals from a common temperature run because of the hindrance created by the incomplete removal of the MgO layer. When a clean surface permitted multiple analyses of a single crystal, the determined diffusion coefficients are in agreement within the estimated uncertainties. Only one successful SIMS analysis was performed on the 750°C garnets because of the surface oxide problem. A noteworthy feature of the oxide-garnet diffusion couple is demonstrated by the variation in the measured interface ratio. R_s values ranged from a maximum of 2.5 to as low as 0.45 (see fig. 2) and presu-

TABLE 2
Summary of SIMS analyses for magnesium self-diffusion coefficient determinations in pyrope garnet

Run and analysis number	Run temperature (°C)	Run duration (hr)	Crater depth (μm)	Diffusion coefficient (m^2/sec)
PYR1BB900-1	900	9.08	0.415	2.29×10^{-19}
PYR1BB900-3	900	9.08	0.403	2.06×10^{-19}
PYR8KK900-2	900	7.00	0.379	2.26×10^{-19}
PYR9LL900-5	900	12.10	0.401	2.35×10^{-19}
PYR4FF850-2	850	22.47	0.329	8.56×10^{-20}
PYR4FF850-3	850	22.47	0.358	7.10×10^{-20}
PYR3CC800-2	800	70.57	0.370	2.48×10^{-20}
PYR3CC800-7	800	70.57	0.413	1.65×10^{-20}
PYR7GG750-2	750	309.57	0.400	9.75×10^{-21}

ably reflect the extent of cohesion of the couple and the communication or partitioning of isotopes between oxide and garnet. In addition, the partitioning and fractionation of Mg isotopes may have occurred during the preparation of the oxalate-garnet couple to produce significant variations in the initial isotopic ratio at the garnet surface. There appears to be no correlation between the value of R_s and temperature or time.

Diffusion runs were repeated at 900°C for several anneal times as a check on the diffusion process and the time independence of D . The self-diffusion coefficients derived from these runs are presented in figure 4. Longer times of annealing were restricted by mass absorption problems associated with SIMS analysis of the deeper diffusion profiles and the greater depth of the sputtered craters. The results indicate that there is no major variation in the diffusion coefficient with run duration. All the 900°C diffusion coefficients are in agreement within experimental error and therefore support the assumption of a time-independent diffusion coefficient.

Noteworthy of all the SIMS depth profiles are their smooth and continuous nature without any major breaks in slope. These data suggest the occurrence of a true bulk diffusion process and not one interrupted or enhanced by major line dislocations which may have been introduced during initial sample polishing. Because of the lack of cleavage in garnet, it was not possible to compare diffusion rates obtained from prepared surfaces and cleavage planes. Giletti, Semet, and Yund (1978) utilized this latter procedure to support the bulk diffusion assumption in their ion microprobe analysis of oxygen diffusion in feldspars. It appears reasonable that the denser garnet structure would behave similarly and not

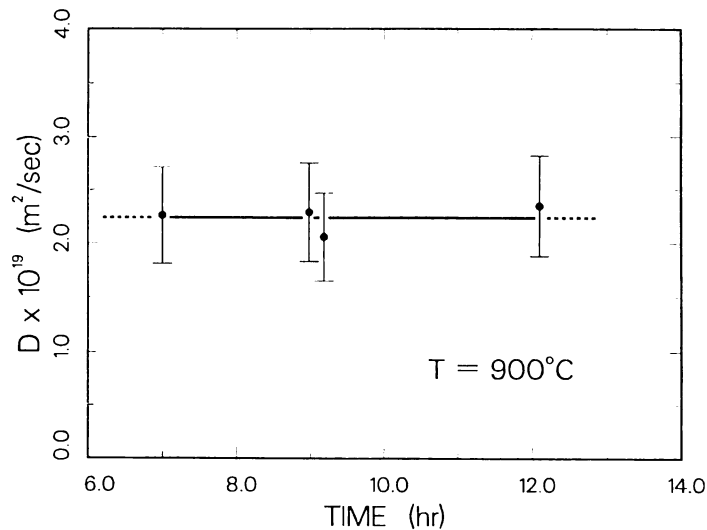


Fig. 4. Plot of Mg self-diffusion coefficient versus anneal time for the 900°C garnet data demonstrating the time independency of D . The two data points at 9.08 hrs have been offset for clarity. The error bars represent the estimated uncertainty in D .

develop a line defect and dislocation altered surface region. Additional work is presently being performed in order to elucidate the effect of polishing and preannealing upon the diffusional properties of garnet.

RESULTS AND DISCUSSION

The results of the garnet diffusion experiments performed at 900°, 850°, 800°, and 750°C, all at a pressure of 200 MPa, are presented in table 2. Because garnet is cubic, the diffusion coefficient (a second-rank tensor) is necessarily isotropic, and so it is necessary to determine only a single diffusion coefficient in garnet for a given temperature and oxygen fugacity in order to describe completely the volume self-diffusion behavior of Mg or any other component.

The temperature dependence of the Mg self-diffusion coefficient can be investigated by examining chemical diffusion or, in this case, self-diffusion as a thermally activated process. Therefore the temperature dependence will be described by an exponential or Arrhenius-type relation:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

Here, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. The pre-exponential term, D_0 , is a function of the diffusive jump distance and a mean atomic vibrational frequency (Jost, 1960). D_0 is commonly referred to as the frequency factor. By taking the natural logarithm of both sides of this equation and converting to common logarithms for convenience, a linear relation between $\log D$ and $1/T$ is obtained:

$$\log D = \log D_0 - \frac{E_a}{2.3026 R} \left(\frac{1}{T}\right) \quad (9)$$

A linear regression of the experimental diffusion data was performed to determine the best fit for this relation. The associated error in each diffusion coefficient was included in this regression. The results are plotted in figure 5. The activation energy, E_a , can be determined from the slope of this line, and the $T = \infty$ intercept provides a value for the frequency factor, D_0 . The best fit values are $E_a = 239 \pm 16$ kJ/mole and $\log D_0 = -8.01 \pm 0.75$, with the diffusion coefficients being expressed in units of m^2 /sec. Although the Arrhenius line is not that well constrained at the lower temperatures, the calculated activation energy is in the approximate range for diffusion in silicate minerals (see Freer, 1981). The single 750°C diffusion value lies above the Arrhenius line and may suggest the onset of a new mechanism of diffusion in garnet. Lasaga (1980) discusses the systematics of a change in diffusion mechanism, such as from an intrinsic to extrinsic region with a decrease in the activation energy. The more favorable extrinsic process would be reflected in an Arrhenius plot by a break in slope to a smaller slope value at the lower temperatures. This may not necessarily be the case for the present diffusion data (see below), and the faster transport value at 750°C may just reflect a larger error or uncertainty.

A comparison of all available diffusion data on natural garnet is presented in the Arrhenius plot of figure 6. The majority of the studies have been completed at high temperatures for reasons mentioned earlier, while only two studies, those utilizing an ion microprobe, are at lower temperatures. The oxygen diffusion data of Freer and Dennis (1982) are presented for comparison of cation and anion diffusion. The diffusion data of Lasaga, Richardson, and Holland (1977), derived from a kinetic model of naturally zoned garnets, are also included. Pressure effects have been ignored in this comparison of diffusion data. (The activation volume for diffusion in garnet as determined by Elphick, Ganguly, and Loomis (1982) suggests the pressure correction for the activation energy to be of the same magnitude as the uncertainty in the experimental activation energy.) The wide range of activation energies and log D intercepts indicates the possible complexities of diffusion as well as the difficulty of experimentally measuring small diffusion coefficients. Obviously compositional and structural differences play an important role in the comparison of self, tracer, and binary diffusion data, but one would expect similar

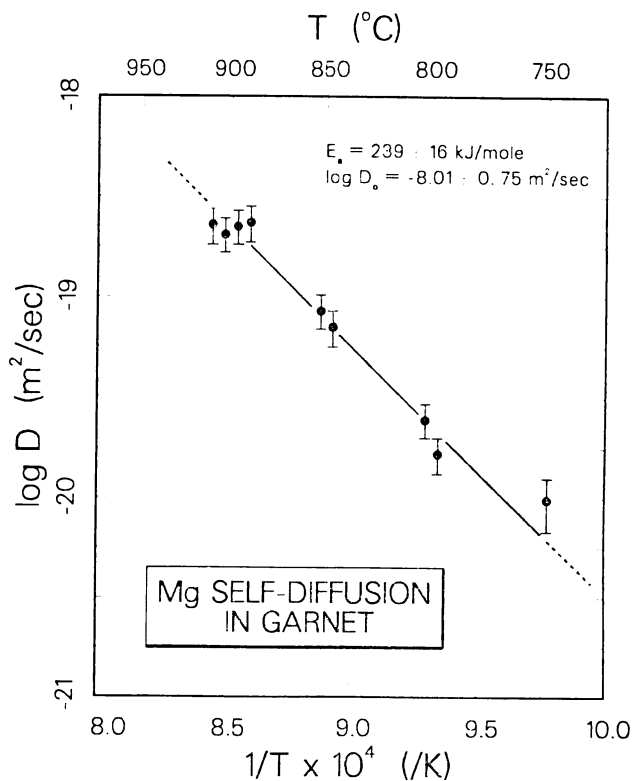


Fig. 5. Arrhenius plot showing the variation of Mg self-diffusion with temperature. The solid line represents the linear regression of the data to eq (9). Data obtained at identical temperatures have been offset for clarity. The error bars represent the estimated uncertainty in log D.

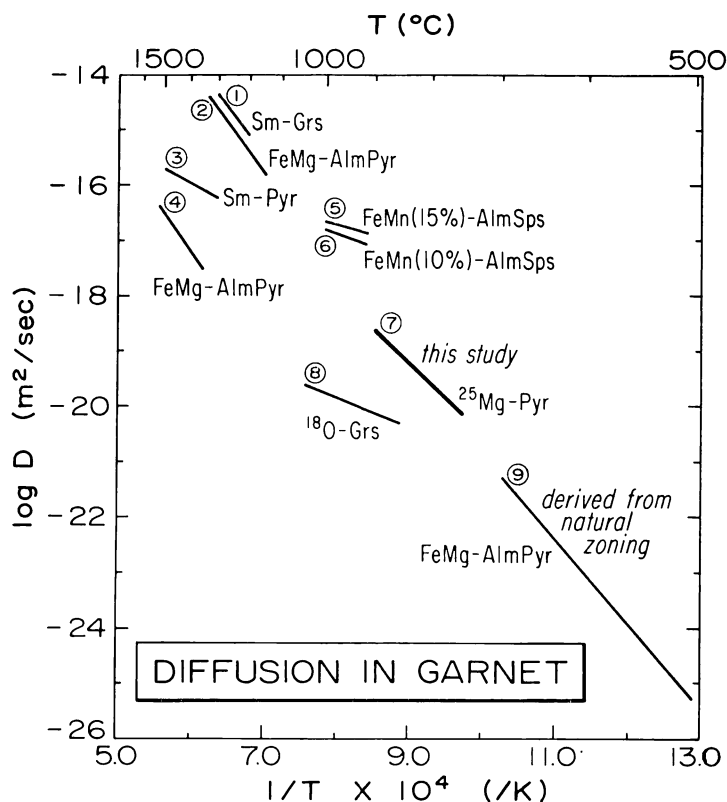


Fig. 6. Arrhenius plot presenting the available chemical diffusion data on garnets. The labels correspond to the following studies: (1) and (3) Harrison and Wood (1980), (2) Duckworth and Freer (1981), (4) Elphick, Ganguly, and Loomis (1981), (5) and (6) Freer (1979), (7) this study, (8) Freer and Dennis (1982), and (9) Lasaga, Richardson, and Holland (1977).

activation energies if equally sized cations diffuse by equivalent mechanisms. Such would be the case for the interpretation of Fe-Mg data in pyrope which is depicted in figure 6 from four separate studies. There is excellent agreement between the Mg self-diffusion data from this study and the Fe-Mg binary diffusion values derived from the natural zoning study. This agreement gives major credence to the theoretical model of Lasaga, Richardson, and Holland (1977) and supports its use for extracting other useful kinetic data. In addition, the activation energy derived in this study may be used to extrapolate the experimental diffusion data to temperatures as low as 500°C as constrained by the kinetic model. In view of this low-temperature agreement, it seems unlikely that the 750°C self-diffusion value would constitute a change of diffusion mechanism.

There is only limited agreement between the Mg self-diffusion data and the high-temperature Fe-Mg binary diffusion data of Duckworth and Freer (1981). Extrapolation of their experimental data to the temperatures

of this study provides approximate agreement for the diffusion coefficients, although they measured a larger activation energy (344 kJ/mole). The difference in E_a values would suggest a change in diffusion mechanism occurring between 900° and 1150°C in accord with a possible intrinsic-extrinsic transition. The diffusion data of Elphick, Ganguly, and Loomis (1981) provide the greatest disagreement with the lower temperature data of this study. Extrapolation of their 1350° to 1525°C values to temperatures below 900°C provides diffusion coefficients approximately four orders of magnitude lower than our values. These comparisons demonstrate some of the pitfalls encountered in extrapolating high-temperature data to lower temperatures (that is, metamorphic regime). In attempting to determine the thermal history of a mineral assemblage based upon compositional zoning in garnet, caution must therefore be employed that the necessary diffusion coefficients have been derived at temperatures close to those of the application.

The concept of a compensation effect between diffusion activation energy and pre-exponential factor has been suggested by Winchell (1969). A positive linear relation was found to hold for diffusion in silicates:

$$E_a = a + b \log D_0 \quad (10)$$

An improved correlation results if only glass and melt data are included. Hart (1981) and Lasaga (1981) determined that the compensation effect was best examined for a single crystal structure and that the available feldspar and olivine diffusion data clearly exhibited this behavior. A similar examination of the garnet diffusion values shows additional support of a compensation law (see fig. 7). Note that the garnet diffusion data cover a wide range of pressure and temperature conditions and generally represent unknown defect concentrations. A linear regression of the garnet data provides values for the parameters in eq (10); $a = 423$ kJ/mole and $b = 23$ kJ/mole with D_0 expressed in units of m^2/sec (linear correlation factor, r , is 0.95). An interesting characteristic of the compensation effect is the existence of a critical temperature, T^* , at which all diffusion values are equivalent:

$$T^* = \frac{b}{2.3026 R} \quad (11)$$

At this point there is a crossover of the Arrhenius lines for the different diffusing species. For this sort of analysis it is necessary to extrapolate the experimental data beyond the measured temperatures. The critical temperature derived from eq (11) for the garnet diffusion data of figure 6 is 930°C. Hart (1981) provides an analysis of critical temperatures derived from natural silicate diffusion data. Although no garnet data were included in that study, the data for a similar orthosilicate mineral, olivine, produce a higher critical temperature ($T^* = 1360^\circ C$). The garnet critical temperature is significant in the fact that it lies at the upper reaches of crustal conditions and will not be a major factor in interpreting the relative diffusion rates of chemical species in metamorphic rocks. How-

ever, at the higher temperatures of mantle rocks one can expect a reversal of relative diffusion rates for species derived at temperatures less than this critical temperature (see Hart, 1981) as long as the diffusion mechanisms do not change.

An examination of the crystal structure of garnet is useful in order to analyze the possible mechanisms by which diffusion of Mg can occur. The crystal structure and chemistry have been described in detail by Novak and Gibbs (1971), so only a brief summary is presented here. The general formula for the silicate garnets is $X_3Y_2Si_3O_{12}$ where the X represents a triangular dodecahedron (distorted cube) site for divalent cations (namely, Mg^{2+}), and Y represents a slightly distorted octahedron site for the smaller trivalent cations (namely, Al^{3+}). The isotropic garnet structure possesses $Ia\bar{3}d$ space group symmetry and as an orthosilicate is characterized by isolated SiO_4^{4-} tetrahedra. The X dodecahedron shares common edges with two tetrahedra, four octahedra, and four other triangular dodecahedra. The oxygens are nearly in cubic closest packing and provide a dense sublattice. For the present discussion we are concerned with the crystal structure of the pure endmember, pyrope, $Mg_3Al_2Si_3O_{12}$.

For diffusion to occur in pyrope it is necessary for the crystal lattice to possess a significant number of point defects. For the case of Mg trans-

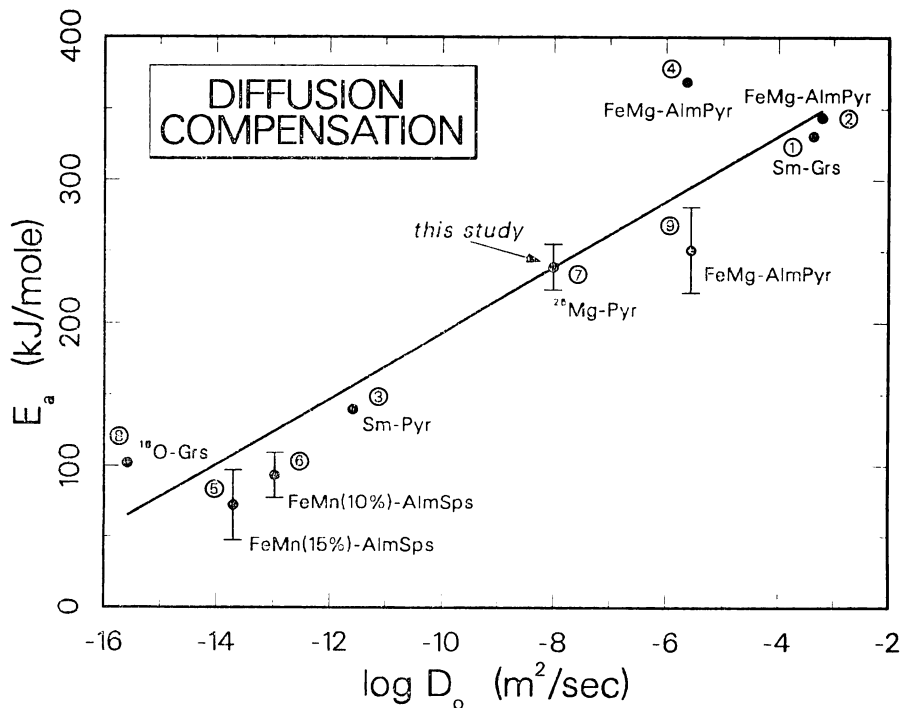


Fig. 7. Compensation plot of E_a versus $\log D_0$ for the available diffusion data in garnet. The numbers refer to the studies listed in the caption of figure 6. Uncertainties in E_a are presented when available.

port and in the presence of multivalent iron these defects will most probably be of the vacancy or Schottky type. Cation interstitials, unless they are situated in unoccupied dodecahedron sites, would not be energetically favored due to the dense packing of the oxygens. Of course, diffusion rates may be enhanced by extended defects such as dislocations and line defects. In a vacancy mechanism the migrating Mg^{2+} would pass from an occupied dodecahedron site, through a shared edge, and into a vacant neighboring dodecahedron site. The energy requirements of such a process would include the formation of the point defect (in the intrinsic region) and the migration barrier of the Mg cation. Electrostatic and short-range interactions among the ions during these processes must be analyzed to provide a determination of site preference for the defect and an estimate of the potential barriers that must be surmounted (see Miyamoto and Takeda, 1983). In more sophisticated studies (for example, Lasaga, 1980), polarization or relaxation of the ionic lattice has been examined and found to be significant in contributing to the ease of defect formation. The polarization energy will account for the induced dipoles among the ions, as well as electronic clouds of these ions, as the local electric field is perturbed by the defect or migrating cation. Ultimately, these energies can be linked to the temperature dependence of the diffusion coefficient and the experimentally derived activation energy.

The Mg self-diffusion data have provided an activation energy of 239 kJ/mole which can be compared to the dissociation energy (3930 kJ/mole) of a crystalline Mg-O bond. The latter value, often referred to as the lattice binding energy, was determined using eq (1) of Lasaga and Cygan (1982) for the case of periclase. These values suggest that there exists some *partial* breaking (stretching) of Mg-O bonds as the Mg cation migrates from site to site. Actually, at the top of the migration potential barrier, Mg^{2+} will exist as an activated complex coordinated by the common edge oxygens. So one could expect a partial stabilization and not require as large an amount of thermal energy as expected if complete bonds were severed. In general, the measured activation energy may represent the migration enthalpy in an extrinsic diffusion process (that is, impurity defect controlled) or a combination of defect formation and migration enthalpies in an intrinsic diffusion process (that is, thermally generated defects). Barr and Lidiard (1971) provide a discussion of these diffusion energy relations for simple ionic crystals, while Lasaga (1980) examines silicate minerals, in particular, olivine. It is most likely that the Mg self-diffusion data are representative of an extrinsic diffusion process where the defect equilibria is controlled by the impurity and f_{O_2} levels. This mechanism is also suggested by the high-temperature data, in particular that of Duckworth and Freer (1981), for which larger activation energies were derived as in an intrinsic diffusion process. One would expect a "kink" in the Arrhenius plot as temperature is decreased, so that the migration energy barrier would become the only limiting diffusion factor.

Extrinsic diffusion behavior is common for most minerals at metamorphic and most igneous temperatures and is primarily attributed to

the impurity or minor element content of natural samples (Lasaga, 1981). The multivalency of the transition elements (that is, Fe and Mn) will usually dictate the diffusion mechanism and will therefore create an oxygen fugacity dependency. Buening and Buseck (1973) examined Fe-Mg diffusion in natural olivines and defined both intrinsic and extrinsic regions; the latter diffusion coefficients were proportional to $f_{O_2}^{1/6}$ and were explained theoretically by a simple Fe oxidation-vacancy defect equilibrium model. In the present case of Mg diffusion in pyrope, the defect equilibria would be more complex due to the presence of Fe, Cr, and Mn which can exist in several valence states in the garnet structure (for example, the Y octahedron). Future investigations of diffusion in garnet should entail an analysis of the role of impurities, composition, and oxygen fugacity in the diffusion process. Only then would we be able to elucidate fully the defect structure and the exact mechanism(s) of the diffusion in garnet.

APPLICATIONS TO PETROLOGY

An important aspect of the present study is that the garnet diffusion data were experimentally obtained at near metamorphic conditions and may prove valuable in applications to metamorphic processes. The homogenization of chemically zoned garnets and the concept of closure temperature play integral parts in evaluating the attainment of equilibrium, so necessary for applying thermodynamic models. On the other hand, the persistence of compositional zoning in garnet provides a medium by which the petrologist can extract useful thermal history data.

An estimate of garnet homogenization time or equilibration rate can be obtained from the Mg self-diffusion data. This would necessarily be for the case of binary diffusion (for example, the counter diffusion of Fe and Mg) in which Mg transport is the rate determining step. The approximate penetration distance of a diffusing species is given by Crank (1975) as:

$$x = \sqrt{4Dt} \quad (12)$$

This relation can be applied to the case of a Mg zoned garnet of 5 mm diam (that is, $x = 2.5 \times 10^{-3}$ m). Using the Mg diffusion coefficient derived at 750°C ($D = 9.75 \times 10^{-21}$ m²/sec) the garnet would require 5 my in order to equilibrate and homogenize. If the garnet were maintained at 900°C ($D = 2.24 \times 10^{-19}$ m²/sec) the homogenization time is cut to two hundred twenty thousand yrs, indicating the sensitivity of the diffusion process to temperature. It is assumed that the garnet is maintained at that temperature throughout the homogenization period and that regional metamorphic conditions are constant.

In order to examine a more realistic metamorphic scenario it would be beneficial to include cooling effects that would occur with regional uplift and erosion. Dodson (1973) has derived the following expression for describing a diffusion process limited by a closure temperature, T_c :

$$\frac{E_a}{RT_c} = \ln \left(- \frac{ART_c^2 D_0}{a^2 E_a s} \right) \quad (13)$$

The linear cooling rate is denoted by s , and a is the radius of a sphere; A is a geometric factor which has a value of 55 for a spherical grain. T_c is representative of the temperature region at which a crystal is unable to respond and reequilibrate to temperature changes (Lasaga, 1983). This expression can be applied to the case of zoned almandine-pyrope garnets from central Massachusetts which crystallized during the Acadian orogeny and for which a minimum cooling rate is known (see Lasaga, Richardson, and Holland, 1977; Cygan and Lasaga, 1982). For 3.5-mm-diameter garnet cooled at the metamorphically rapid rate of 100°/my and incorporating the experimental diffusion values, eq (13) provides a 740°C closure temperature. It is noteworthy that the maximum geologic temperature for the area was 675°C, and therefore the higher T_c value would indicate that the composition of the particular size garnet would be maintained at its 675°C values (that is, no diffusion modification during cooling). In contrast for a 0.5-mm-diameter garnet at the same conditions, a closure temperature of 630°C is obtained. Therefore the smaller garnets would be able to reequilibrate to a limited extent by volume diffusion during the initial cooling stages. Lasaga, Richardson, and Holland (1977) and Cygan and Lasaga (1982) discuss the particulars of applying such diffusion data to the mineral assemblage of this regionally metamorphosed area and provide more refined kinetic models for predicting the chemical zoning observed in the different size garnets. Finally, it would be important in the future to examine and apply other sophisticated kinetic and diffusion models, such as those of Tracy and Dietsch (1982) and Lasaga (1983), to metamorphic garnets in view of the experimental garnet diffusion data.

CONCLUSION

We have experimentally determined the self-diffusion coefficients for Mg in natural pyrope garnet at 750° to 900°C and 200 MPa (2 kb). A SIMS ion microprobe has been successfully utilized for explicitly measuring the induced depth profiles of ^{24}Mg and ^{25}Mg in the garnets. The best fit of the observed $^{25}\text{Mg}/^{24}\text{Mg}$ profiles to a semi-infinite medium diffusion model provides a helpful method for determining the diffusion coefficients. Such techniques are preferred when compared to bulk exchange methods (for example, Harrison and Wood, 1980) in which certain vulnerable assumptions are necessary and in which a diffusion profile is implied and not directly measured.

An Arrhenius relation describes the temperature dependence of the diffusion process. The activation energy for Mg diffusion in garnet, derived from the slope of the Arrhenius plot ($\log D$ versus $1/T$), is comparable to cation diffusion in other dense silicate minerals. A comparison of the data with other garnet diffusion measurements, primarily obtained at temperatures greater than 1000°C, suggests an extrinsic or impurity controlled diffusion mechanism. An investigation of composition and oxygen fugacity effects would be necessary in order to elucidate the actual diffusion mechanism.

The determination of accurate volume diffusion data for cations and oxygen in minerals, specifically in the crystalline silicates, is a major task

for the experimental mineralogist. The void in accurate diffusion data under a variety of geological conditions must be remedied in order to provide the petrologist with the necessary tools for understanding such geological phenomena as compositional zoning, crystallization and nucleation processes, geochronology and paleo-temperatures, and isotope equilibration. This is especially true at the temperatures of metamorphism where disequilibrium processes abound. The use of the ion microprobe is obviously a necessity in deriving diffusion coefficients of silicate minerals at these lower temperatures.

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