

A Thin Film Approach for Producing Mineral Diffusion Couples

CRAIG S. SCHWANDT,¹ RANDALL T. CYGAN¹ and HENRY R. WESTRICH¹

Abstract—Few diffusion coefficient values have been measured for silicate minerals at pertinent geologic conditions because of experimental restrictions. Until recently, analysis of diffusion couples was conducted principally with electron microprobes which have rather poor spatial resolution (micrometer scale). Ion microprobe analyses, however, eliminate many of the previous experimental restrictions; in depth profile mode they have excellent spatial resolution (tens of angstroms) and diffusion couples can be analyzed normal to the interface. Diffusion couples analyzed by ion microprobe must be well-defined and uniform; previous methods using solution precipitates to form the diffusion couples were heterogeneous and had limited success. A new approach, the thermal evaporation of ^{25}MgO under high vacuum onto a crystalline substrate (oxide, silicate), produces a 1000 Å thick $^{25}\text{MgO}_x$ ($x < 1$) thin film. This method yields an excellent diffusion couple for low-temperature diffusion experiments. Diffusion anneal experiments using this approach for garnet provide a Mg self-diffusion coefficient of $D = 0.60 \pm 0.09 \times 10^{-21} \text{ m}^2/\text{s}$ at 1000°C ($\log f\text{O}_2 = -11.3$, $P = 1 \text{ atm}$, $X_{\text{Almandine}} = 0.24$).

Key words: Thin film, diffusion coefficients, ion microprobe.

Introduction

Understanding and modeling geochemical, nuclear waste, and materials science systems require accurate diffusion coefficient data for silicate minerals. Diffusion coefficients and the concentration gradient of the species determine the migration rates of a component through a material. Commonly, a silicate glass or mineral of one composition is placed in contact with a sample having a different composition, forming a diffusion couple that will generate concentration gradients. The couple is annealed at temperature for a given time and then penetration profiles in response to diffusion are measured. Diffusion follows the Arrhenius-type behavior typical for thermally-activated kinetic processes. Therefore, diffusion data should be determined for a range of geologically-relevant temperatures to evaluate the temperature dependence of the diffusion process. Minerals that have especially small diffusion coefficients often exhibit compositional zoning that can yield thermal history

¹ Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico 87185-0750, U.S.A.

information if appropriate diffusion models are used and the temperature dependence of diffusion is known. Natural garnets commonly exhibit compositional zoning that can typically be modeled as a diffusion process, however, only limited diffusion data are available and only for restricted conditions (FREER, 1979, 1981; ELPHICK *et al.*, 1985; CYGAN and LASAGA, 1985; CHAKRABORTY and GANGULY, 1992). The preservation of compositional zoning in garnets, but not in the minerals that coexist with garnet, suggests garnet possesses some of the smallest silicate mineral diffusion coefficients. Accordingly, we developed a method for measuring diffusion coefficients in garnet, as they should be the most difficult to determine at temperatures representative of metamorphic conditions in the crust of the earth. A technique that works for garnet should be suitable for other minerals with larger diffusion coefficients.

Previous investigators (FREER, 1979; ELPHICK *et al.*, 1985; CHAKRABORTY and GANGULY, 1992) conducted cation diffusion experiments on garnet at temperatures of 1000°C and higher to experimentally compensate for the slow diffusion rates and inherently-small penetration distances. Also, the spatial resolution of electron microprobes requires diffusion penetration distances of tens of micrometers, thereby limiting diffusion experiments to high temperatures for moderate laboratory anneal times. The existing high-temperature data are limited in extent, and have inconsistent temperature trends; activation energies range from 100 to 285 kJ/mole (FREER, 1979; ELPHICK *et al.*, 1985; CHAKRABORTY and GANGULY, 1992) with very limited information regarding compositional and oxygen fugacity dependencies (c.f. BUENING and BUSECK, 1973; RYERSON *et al.*, 1989). Therefore, extrapolation of the high-temperature data to lower temperatures is questionable.

The introduction of the ion microprobe provided a means of resolving spatial information to the tens-of-angstroms level in depth profiling mode (WILSON *et al.*, 1989). Shorter experimental penetration distances permit diffusion experiments to be conducted at relatively low temperatures and shorter anneal durations. CYGAN and LASAGA (1985) took advantage of this approach and conducted self-diffusion experiments in the temperature range of 750°C to 900°C. Self-diffusion is the migration of an isotope due to an isotopic gradient, rather than a chemical gradient. Self-diffusion coefficients are approximately the same order of magnitude as chemical diffusion coefficients (CYGAN and LASAGA, 1985; CHAKRABORTY and GANGULY, 1992). CYGAN and LASAGA (1985) investigated magnesium self-diffusion using diffusion couples formed by dissolving ^{25}MgO in oxalic acid and precipitating $^{25}\text{MgC}_2\text{O}_4$ on the surfaces of single-crystal garnets. The ^{25}Mg isotope was enriched to 97.8 percent of total magnesium in the oxide. The natural abundance of ^{25}Mg is 10 percent of total magnesium. This approach, although successful, produced a ^{25}MgO source that was very heterogeneous on the garnet surface (Fig. 1a). The oxalate decomposes to the oxide during the initial heating period of the diffusion anneal yielding a nonuniform distribution of the source material and subsequent difficulty in obtaining reproducible depth profile analyses.

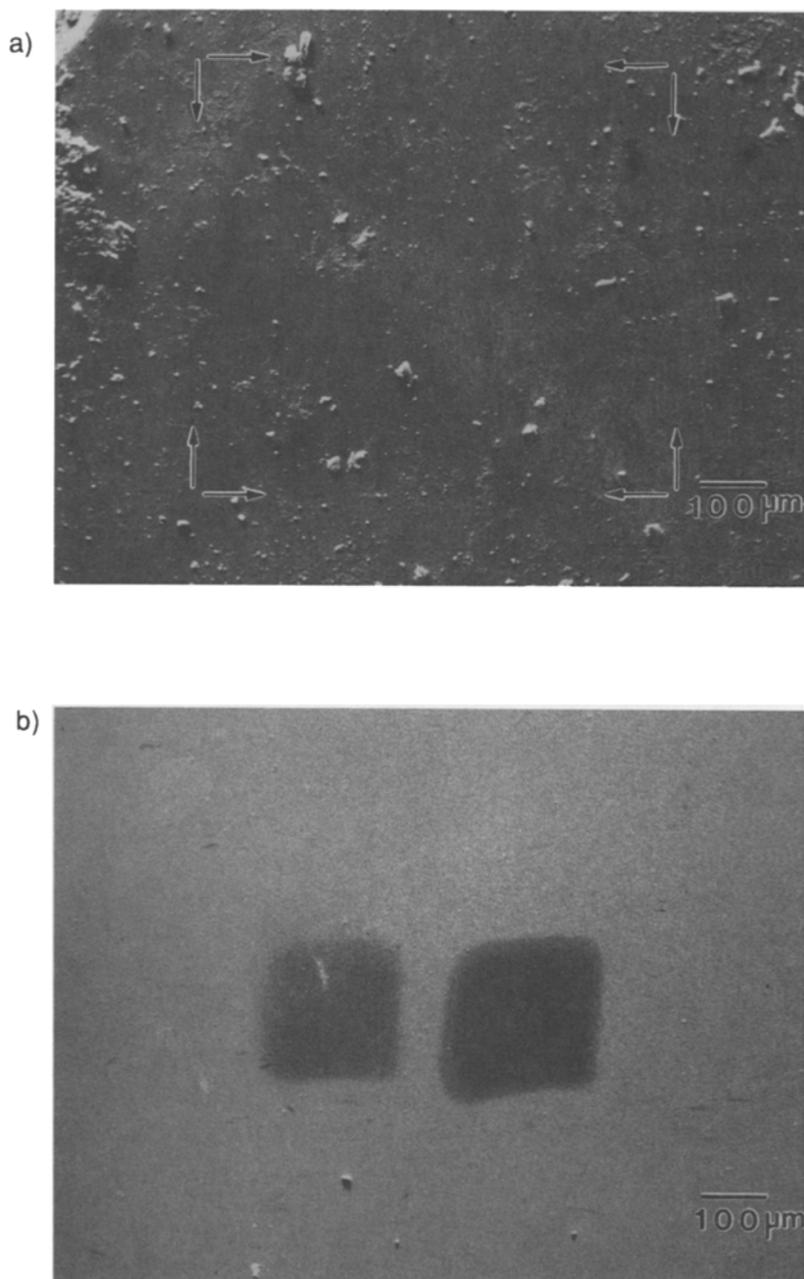


Figure 1

a) SEM photomicrographs of garnet surface with ^{25}MgO layer formed by precipitation of ^{25}Mg oxalate and diffusion anneal. Large amounts of MgO are observed in the $750\ \mu\text{m} \times 750\ \mu\text{m}$ ion microprobe crater. b) SEM photomicrographs of ^{25}MgO thin film on garnet. The uniform ion microprobe craters are $150\ \mu\text{m} \times 150\ \mu\text{m}$. Scale bars are $100\ \mu\text{m}$.

The inconsistencies of the previous high-temperature data underscore the need for determining accurate diffusion data in the range of 700°C to 1000°C. Whereas, the ion microprobe provides the analytical means for these experiments, an improved technique for creating diffusion couples that provides and maintains the uniformity of the diffusion interface is needed, thereby improving analytical precision. Because precipitation techniques (CYGAN and LASAGA, 1985; CHAKRABORTY *et al.*, 1992) have serious limitations, we initially explored the use of molten salts, precipitated metal chlorides, and evaporative thin films as alternative diffusion couple preparation methods. The molten salt and metal chloride techniques proved to be inappropriate, as the presence of these compounds corrodes the garnet surface during the diffusion anneal.

Evaporative Thin Film Techniques

Self-diffusion experiments impose several restrictions on the choice of a diffusion couple. Foremost, it is important that the distribution of source material closely approximates a finite plane source to simplify the diffusion models used to obtain the diffusion coefficients. Second, to avoid disruption or destruction of the diffusion interface, the source material must not chemically react, outside of ion exchange, with the silicate substrate. Synthesis of the diffusion couple should occur at a low enough temperature to avoid premature diffusion or reaction. Finally, the technique must be efficient to minimize expense when utilizing enriched stable isotope compounds that can cost as much as \$10 to \$20 per milligram.

Although various physical vapor deposition techniques are available to produce thin films, not all of the techniques are appropriate for preparing garnet diffusion couples. JAOU *et al.* (1981) and HOULIER *et al.* (1990) utilized radio-frequency sputtering techniques to produce an amorphous thin film (100 Å to 200 Å) for examining silicon diffusion in olivine. However, thin film dimensions and the cost of producing an enriched film severely limit the use of this technique for examining diffusion in garnet. Two other vapor deposition techniques, electron beam evaporation and thermal evaporation (SURDASHAN, 1989; OHRING, 1992; GEORGE, 1992), were considered for creation of an oxide thin film on a garnet substrate to form a diffusion couple. Both methods use a vacuum evaporation apparatus which includes a cryogenic pump, a quadrupole residual gas analyzer, and a film-thickness monitor. The vacuum chamber is pumped down to 1.1×10^{-4} MPa and typically increases to 1.3×10^{-4} MPa during thin film deposition.

The vacuum evaporator can be set to operate in either electron beam or thermal-resistive evaporation mode (Fig. 2). Samples are mounted in an inverted position above either evaporation source. The distance between the source and samples is approximately 40 cm. This configuration provides a uniformly thick thin film over an area several square centimeters (OHRING, 1992; GEORGE, 1992). An

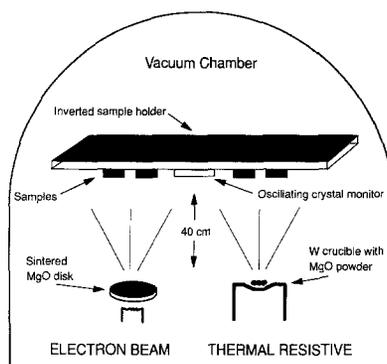


Figure 2
Schematic of the vacuum evaporation apparatus.

oscillating quartz crystal positioned in the plane of the sample holder monitors film thickness during either mode of operation. Silicon wafers act as control samples for convenient analysis of the thin films with standard energy dispersive spectrometry (EDS) and scanning electron microscope (SEM) imaging techniques. Silicon wafers from both evaporation methods were examined to determine which was more appropriate.

Electron beam bombardment of a pressed MgO pellet, using a 10 kV gun potential and about 200 mA of current, produces uniform thin films of high quality MgO about 2000 Å thick in approximately 30 seconds. However, this technique requires a source pellet with a mass of at least 10 grams, and is prohibitively expensive if using enriched stable isotope materials. We also explored the possible use of sintered pellets comprised of an oxide mixture, with a pyrope composition ($3\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$), for evaporation to produce thin films with the appropriate pyrope garnet compositions. However, evaporation of the oxide mixture was nonstoichiometric and produced a silica-rich thin film.

The thermal-resistive evaporation technique requires less material and is therefore more economical. A residual gas analyzer monitored the composition of the vapor throughout the evaporation process. Thermal evaporation of a mixture of oxides with pyrope composition ($3\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) in tungsten crucibles also failed to produce thin films with the appropriate composition. Results of the vapor analysis and subsequent EDS analysis of the thin film/silicon wafer assemblages confirm the absence of Mg evaporation from the oxide mixture.

Given that garnet-like thin films were not obtained, we investigated the thermal evaporation of pure MgO. Although the melting point of pure MgO is 2852°C, under high vacuum the MgO sublimates at a much lower temperature. Sintered MgO pellets appear to evaporate nonuniformly as a result of uneven heating of the pellets. In contrast, MgO in powder form evaporates uniformly.

We made use of these latter results to prepare thermally-evaporated $^{25}\text{MgO}_x$ ($x < 1$) thin films for the garnet diffusion application. Polished, gem-quality, single-crystal, pyrope garnet crystals ($\approx 1 \text{ mm} \times 4 \text{ mm} \times 4 \text{ mm}$) are mounted to glass slides with double-sided tape; a frame holds the inverted glass slides above the thermal source. Thermal evaporation of 100–140 milligrams of ^{25}MgO (^{25}Mg enriched to 94.5% of total Mg) powder using a tungsten crucible yields thin films of $^{25}\text{MgO}_x$ ($x < 1$) approximately 1000–2000 Å thick, depending on the current and length of time. The typical deposition rate varies from 2 to 15 Å/s and results in a thin film with a submetallic luster. Subsequent SEM/EDS examination confirms the presence of magnesium and oxygen on the silicon wafer used as a control substrate. The temperatures sustained by the garnets during thin film production are too low ($< 40^\circ\text{C}$) to produce any premature self-diffusion of ^{25}Mg into the garnet. Survival of the double-sided tape, and previous depositions that utilized thermocouples with the vacuum chamber, support the estimate of low temperatures at the sample holder.

^{25}MgO Thin Films as Diffusion Source Material

Secondary ion mass spectrometry (SIMS) depth-profile analysis with an ion microprobe confirms that the ^{25}Mg content of the thin film is equivalent to the enrichment of the source powder (94.5%). Therefore, the thermal evaporation process does not result in observable isotopic fractionation with the formation of the oxide thin film. Ion microprobe sputtering and surface contact profilometry indicate the film thickness increases to approximately 3000 Å during annealing. The change in thickness is consistent with the approximate difference in molar volumes of Mg metal and MgO. Thermodynamic calculations suggest the Mg-MgO transition occurs at very reducing conditions, much more reducing than those of the self-diffusion experiments ($\log f\text{O}_2 = -10$ to -18 depending on the anneal temperature). Therefore, the magnesium metal present in the thin film is likely to be metastable and will tend to oxidize upon annealing. The luster of the thin film changes from submetallic to nonmetallic during experimental anneal. These observations are consistent with oxidation of the thin film during experimental anneal and suggest that the ^{25}MgO thin film is nonstoichiometric before the diffusion anneal. OHRING (1992) and GEORGE (1992) also believe that thermal evaporation is ineffective in producing stoichiometric thin films. The thin film is probably in the form of $^{25}\text{MgO}_x$ ($x < 1$) before the diffusion anneal.

SEM observation of the thin film before the diffusion anneal indicates the film is smooth and uniform (Fig. 3a). During diffusion anneal the $^{25}\text{MgO}_x$ ($x < 1$) film recrystallizes into “islands” (Figs. 3a–f) that appear to grow slowly with time as a function of temperature. Longer diffusion anneal times and higher temperatures produce fewer but larger islands. Mechanisms of island generation and coalescence

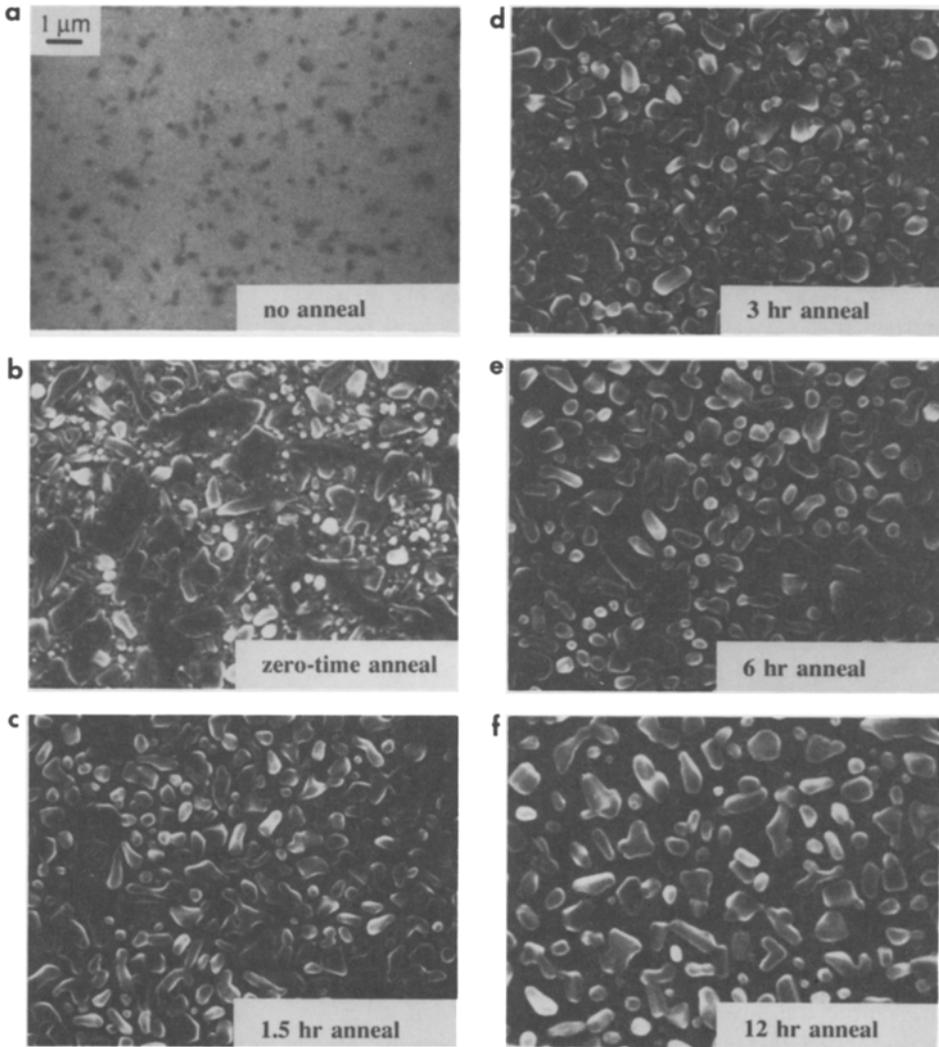


Figure 3

Secondary electron photomicrographs of ^{25}MgO thin film-garnet diffusion anneals at 1000°C , $\log f\text{O}_2 = -11.3$, for different anneal durations. The $1\ \mu\text{m}$ scale bar in a) is representative of that for photomicrographs a-f).

are not completely understood, but island formation is a common phenomenon of sintered thin films on substrate materials (HOULIER *et al.*, 1990; OHRING, 1992). Island formation is a combination of: 1) nucleation and growth of crystallites; 2) the result of Ostwald ripening or the minimization of surface-free energy of the thin film material; and 3) coalescence as the result of collisions between islands as they

execute random motion. It is difficult to distinguish which of the processes is dominant (OHRING, 1992). TANNHAUSER (1956) demonstrated that a distribution of source material similar to that of the island material provides an adequate supply of source ^{25}Mg throughout the duration of the diffusion anneals, and yields the same effective diffusion coefficient that an ideal thin film would.

The ablation or sputtering process of the ion microprobe removes material from the sample according to the original topography of the sample surface (Fig. 4). This topographic phenomenon persists throughout the depth profile analysis (WILSON *et al.*, 1989; KING, 1992). Therefore, the part of the rastered ion beam between islands sputters the garnet surface earlier (Fig. 4b) than for the case of an ideal ablation front. Similarly, the peaks of the islands sputter longer beyond the interface than they would for a planar ablation front. This type of hummocky sputter topography effectively thickens the thin film/garnet interface. Additionally, the sputtering process does not produce depth profiles that are step-like even when penetrating a perfect planar interface into a compositionally different substrate (WILSON *et al.*, 1989). Because the diffusional penetration distance is proportional to the square root of time ($d \approx (4Dt)^{1/2}$) short anneal times will produce very small diffusion distances. If the distances are too small ($< 500 \text{ \AA}$), then the thickened interface contributes a greater amount of ^{25}Mg signal from residual thin film islands relative to the ^{25}Mg signal due to diffusional penetration (Fig. 4). For small penetration distances the interface thickening contributes a ^{25}Mg signal for most of the penetration distance, ultimately producing an artificial time dependence for the diffusion coefficients (Fig. 5). The time dependence is the result of this interference from the thickened interface and the sputtering process. However, with diffusional penetration distances of at least 0.1 micrometer obtained with longer anneal times, the diffusion coefficients obtained for 1000°C anneals asymptotically approach the "true" diffusion coefficient value (Fig. 5). The diffusion coefficients (and their associated standard deviations) for different anneal times follow a $1/t$ curve. The longer anneal times which provide more accurate diffusion coefficient values, are given more weight in the $1/t$ curve fit by use of a $1/D$ weighting factor. The choice of the $1/t$ curve is entirely empirical and permits prediction of the true diffusion

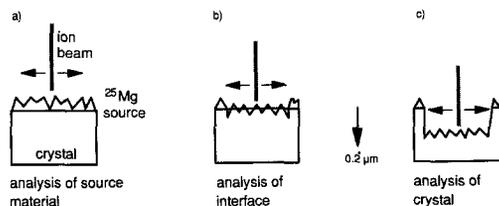


Figure 4

Schematic diagram of sputtering process for annealed thin film on crystalline substrate diffusion couples. Note the retention of the original topography throughout the sputtering process.

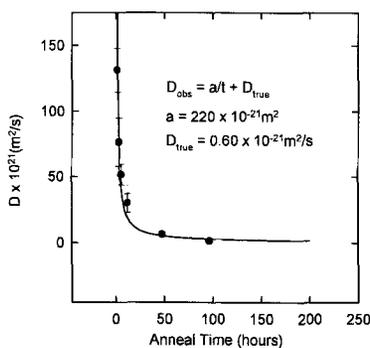


Figure 5

Log D versus anneal time at 1000°C for a ^{25}MgO thin film on pyrope. Error bars, shown when larger than symbol size, equal one standard deviation associated with replicate analyses for each anneal time. The weighted curve fit provides an estimate for the limiting value of the self-diffusion coefficient, D .

coefficient given infinite anneal time. Longer anneal times provide deeper diffusional penetration distances, which can be analyzed more accurately, as the interferences contribute less to the measured profile and therefore provide better evaluations of the diffusion coefficients.

Pyrope garnet ($X_{\text{Almandine}} = 0.24$) samples for our diffusion experiments are held at the anneal temperature and oxygen fugacity for 24 hours to remove surface defects that may have formed during the polishing process and to equilibrate the bulk point defect structure to the conditions of the diffusion anneal (Ryerson *et al.*, 1989). After the preanneal, a ^{25}MgO thin film is applied to the garnets, and then the diffusion couples are annealed at 1000°C and atmospheric pressure; a $\text{CO}-\text{CO}_2$ gas mixture provides a $\log f_{\text{O}_2} = -11.3$ (QFM buffer). Diffusion anneal times ranged from 1.5 hours to 4 days. Replicate analyses were obtained for each anneal time. A best fit value was determined for the Mg self-diffusion coefficient for each replicate analysis using a thin film diffusion model:

$$C_x = C_b + (C_s - C_b)\exp(-x^2/4Dt)$$

where C_x is ^{25}Mg concentration at a distance x , C_b is the bulk concentration of the garnet, and C_s is the surface concentration (CRANK, 1975). The uncertainty in the diffusion coefficient for the best fit of each replicate is about two percent relative. However, because there is more variation among the replicates, the means and standard deviations for each of the anneal times are used to represent the uncertainty in the diffusion coefficient measurement (see Fig. 5). The standard deviations for each anneal time are roughly 15 percent relative, but absolute values for the standard deviations decrease with increasing anneal time. Therefore, the $1/t$ approach can be used to estimate the diffusion coefficient at infinite time and the relative uncertainty should not exceed 15 percent.

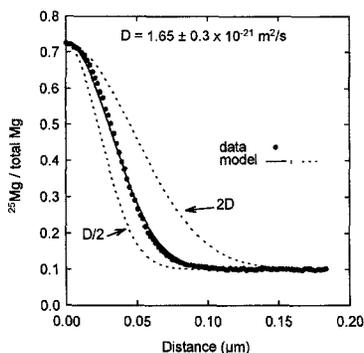


Figure 6

Best fit of the thin film diffusion model for the 96.5 hour 1000°C anneal ($\log f_{\text{O}_2} = -11.3$).

The depth profile for the 4-day diffusion experiment is shown in Figure 6 with the best fit of the model providing a Mg self-diffusion coefficient of $1.65 \pm 0.30 \times 10^{-21} \text{ m}^2/\text{s}$. The fit in Figure 6 is quite good ($r^2 = 0.97$), supporting the use of the simple diffusion model to simulate the observed diffusion profile. The residuals, portions of data with a poor match to the diffusion model, are probably related to the remnant interface thickening not yet corrected by the asymptotic fit presented in Figure 5. The analytical precision determined from replicate analyses is much less than the envelope formed by the $D/2$ and $2D$ curves also presented in Figure 6. The $1/t$ curve fit for the diffusion coefficients, obtained for the various anneal times (Fig. 5), yields a limiting value of $0.60 \pm 0.09 \times 10^{-21} \text{ m}^2/\text{s}$ for the Mg self-diffusion coefficient at 1000°C. The values for the Mg self-diffusion coefficient, both measured and empirically fit, are smaller by 3 orders of magnitude than the extrapolated value from the data of CYGAN and LASAGA (1985), though garnet composition and oxygen fugacity conditions are different. The present data are about 1.5 to 2 orders of magnitude smaller than the extrapolated values from the data of CHAKRABORTY and GANGULY (1992), again for different garnet compositions. Comparison of the present data with these earlier studies suggests that the present experimental approach is viable.

Conclusions

Precipitation of tracer compounds from solution produces a nonuniform distribution of the source material that complicates subsequent analysis of diffusion profiles. The use of molten salts or the precipitation of metal chlorides as diffusion source material generates a disrupted diffusion couple interface that complicates interpretation of the diffusion profiles. Thermal vacuum evaporation is the most

economical option for the preparation of enriched stable isotope thin films. Electron beam vacuum evaporation is a better choice when source materials are more readily available.

The evaporative thin film technique, used in conjunction with ion microprobe analysis, allows for the experimental determination of diffusion coefficients at much lower temperatures than previously performed. The improved uniformity of the diffusion interface permits precise measurement of much shorter diffusional penetration depths than previous studies. Evaporative thin film methods eliminate numerous problems experienced in making viable diffusion couples by providing a uniform source with no destruction of the couple interface. This type of diffusion couple is especially amenable to depth-profile mass analysis with an ion microprobe.

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