Fe-Mg diffusion in spinel: New experimental data and a point defect based model

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Abstract

We have measured Fe-Mg interdiffusion rates ($D_{Fe-Mg}$) in synthetic Mg-Al spinel and a natural (Mg,Fe) aluminous spinel from Sri Lanka ($X_{Fe} \approx 0.07$) at atmospheric pressure over a range of different oxygen fugacities ($\log_{10}(fO_2 [Pa]) = -14$ to -10) and temperatures (750-900 °C). Diffusion couples made of single crystal spinel and thin films of hercynitic composition ($X_{Fe} \approx 0.5$) were used for the diffusion anneals. The experimentally induced diffusion profiles were analyzed by Rutherford Backscattering Spectroscopy to retrieve true depth concentration profiles for Fe. These were fitted numerically by an explicit finite difference scheme that allows compositionally dependent interdiffusion processes to be modelled by relating self- and interdiffusion coefficients. Synthesis of data from the two diffusion couples indicate that: (a) $D_{Fe-Mg}$ depends on $X_{Mg}$ of spinel, with increasing diffusion rates with increasing $X_{Mg}$. This behaviour is opposite of that found in silicates. (b) Self diffusion coefficients could not be determined from these experiments, but the results indicate that $D_{Fe}/D_{Mg} > 100$. (c) $D_{Fe-Mg}$ in Mg-spinel is independent of oxygen fugacity whereas it depends strongly and non-linearly on oxygen fugacity for the natural spinel. This observation indicates that the mechanisms of diffusion are different in the two kinds of spinel (Fe-bearing vs. Fe-free), which is also seen in the difference in activation energy obtained for these. Moreover, the non-linear dependence on oxygen fugacity indicates that diffusion occurs by an interstitial mechanism at low oxygen fugacities and by a vacancy mechanism at high oxygen fugacities in natural, Fe-bearing spinel. (d) Simple Arrhenius relations that describe the data within the range of experimental conditions are - Synthetic magnesium spinel: $Q_{FeMg}$
26 \[ Q_{FeMg} = 139 \pm 18 \text{ kJ/mol}, \log_{10} D_{Fe-Mg} = -12.33 \pm 0.85 [\text{m}^2/\text{s}] \]. A model based on point defect considerations, that describes the temperature as well as oxygen fugacity dependence of \( D_{Fe-Mg} \) in Fe-bearing spinel is:

\[
D[\text{m}^2/\text{s}] = D_v[\text{m}^2/\text{s}/\text{O}_2[\text{Pa}]]^m \exp(-Q_v[J/\text{mol}]/RT[K]) + D_i[\text{m}^2/\text{s}/\text{O}_2[\text{Pa}]]^m \exp(-Q_i[J/\text{mol}]/RT[K]),
\]

with \( D_v = 1.07 \times 10^{-09} \pm 1.55 \times 10^{-09} \text{ m}^2/\text{s}, \quad Q_v = 131 \pm 66 \text{ kJ/mol}, \quad D_i = 1.03 \times 10^{-17} \pm 7.32 \times 10^{-17} \text{ m}^2/\text{s}, \quad Q_i = 130 \pm 80 \text{ kJ/mol} \) and \( m = 0.34 \pm 0.18 \). Poor coverage of T-\( fO_2 \) space by available experimental data results in large uncertainties in the fit parameters. As a result, these expressions are useful for understanding the diffusion behaviour in spinels, but not for extrapolation and calculation of diffusion coefficients for cooling rate or other related calculations. Until the parameters can be better constrained through the availability of more data, we recommend that for such calculations, the parameters noted above for Fe-bearing spinels be used for compositions and \( fO_2 \) conditions that are close to those of the experiments. (e) \( D_{Fe-Mg} \) in spinel is faster than \( D_{Fe-Mg} \) in olivines, pyroxenes and garnets at most conditions.

**Keywords:** Spinel; diffusion coefficient; diffusion mechanism; point defect; thin films; pulsed laser deposition; Rutherford Backscattering Spectroscopy;

**Introduction**

Spinel (Fe\(_x\)Mg\(_{1-x}\)Al\(_2\)O\(_4\)) is one of the major minerals in Earth’s uppermost mantle, a common mineral in a wide range of metamorphic and ultramafic rocks, an important mineral inclusion found in chondritic meteorites of the early solar system, and it has also been found in lunar rocks (see references in the review by Van Orman and Crispin, 2010). Because of its wide range of thermodynamic solid solutions, spinel may form in a variety of different tectonic environments and its chemical composition has been used to infer the physicochemical conditions under which its host rocks have formed (e.g. Irving, 1965; O’Neill and Wall, 1987; Ballhaus, 1991). Hence, knowledge of diffusion rates in spinel is of interest in a number of geological and planetary science problems. For example, Sheng et al., (1992) studied the
Mg isotopic variations in spinel and coexisting silicates of the plagioclase-olivine inclusions in the Allende meteorite to evaluate cooling rates based on Mg-self diffusion in spinel and equilibrium melt. Ozawa (1983) used zoning patterns in spinel and coexisting olivine to constrain cooling rates of ultramafic rocks of the Miyamori ultramafic complex. Similarly, Coogan et al. (2007) used the partitioning of Mg and Fe$^{2+}$ between olivine and spinel to infer cooling rates of the lower oceanic crust and upper mantle, whereas Liemann and Ganguly (2002) studied the partitioning between spinel and orthopyroxene to study the thermal history of diogenites. Apart from these, diffusion of Fe$^{2+}$ in spinel is believed to be a major process controlling maghemitization, by which magnetic minerals with spinel structure become progressively oxidized but remain single phase spinels, which is an important feature of submarine weathering (Freer and O'Reilly, 1980).

Although much emphasis has been placed on the temperature dependent exchange of Fe$^{2+}$ and Mg between olivine and spinel (e.g. Lehmann et al., 1983; Ozawa, 1983; Ozawa, 1984; Kessel et al., 2006; Coogan et al., 2007) and orthopyroxene and spinel (e.g. Liemann and Ganguly, 2001, 2002, 2003) in order to constrain complex thermal histories and cooling rates, aspects of Fe$^{2+}$-Mg interdiffusion in spinel, such as the nature of dependence of diffusion rates on oxygen fugacity, still remain unclear. Freer and O'Reilly (1980) were the first to determine the activation energy and the Fe$^{2+}$-Mg interdiffusion coefficient, $D_{Fe-Mg}$ in aluminous spinel as a function of temperature (800-1034 °C) and composition (FeAl$_2$O$_4$-MgAl$_2$O$_4$) using diffusion couples composed of synthetic pellets. Their data reveals a strong compositional dependency where $D_{Fe-Mg}$ increases with decreasing Fe$^{2+}$ content in spinel. Sheng and co-workers (1992) measured Mg self diffusion ($D_{Mg}$) in aluminous spinel (MgAl$_2$O$_4$) and coexisting melt at bulk chemical equilibrium using an isotopic tracer at 1261-1553 °C. More recently Liemann and Ganguly (2002) have determined the diffusion kinetics of Fe$^{2+}$ and Mg in spinel (Mg$_{0.99}$Fe$_{0.01}$Al$_{1.997}$Cr$_{0.003}$O$_4$) using diffusion couples at 2 GPa, 950-1325 °C and at 3 GPa and 1125 °C. Comparison of their data with those of Freer and O'Reilly implies that Fe$^{2+}$-Mg interdiffusion might be much slower than previously thought. Also, in contrast to the complex profiles measured by
Freer and O’Reilly (1980), Liermann and Ganguly (2002) found simple symmetric diffusion profiles that indicate a weak compositional dependency. Suzuki et al. (2008) found that Fe-Mg interdiffusion might be strongly dependent on the Cr-Al ratio in spinel, but the authors based their inference on a single experiment and assumed $D_{Mg}$ and $D_{Fe}$ to be equal and thus independent of Mg/(Mg+Fe).

However, none of these studies considered the effect of varying oxygen fugacity upon the rate of diffusion, which could have a significant effect not only on the diffusion rate itself but also on the point defect chemistry and hence diffusion mechanisms, as has been reported for magnetite based spinels (e.g. Dieckmann and Schmalzried, 1977a,b; Hallron and Bowen, 1980; Dieckmann and Schmalzried, 1986; Dieckmann et al., 1987; Töpfer et al., 1995, Aggarwal and Dieckmann, 2002a, Aggarwal and Dieckmann, 2002b). It would also be useful to extend the data set to lower temperatures to obtain better constraints on activation energies of diffusion. The aim of this study is to characterize the temperature dependent Fe$^{2+}$-Mg interdiffusion in aluminous spinel in particular at temperatures below 1000 °C and to verify possible effects of oxygen fugacity and composition on the diffusion mechanism. Here we present an experimental study on Fe$^{2+}$-Mg interdiffusion in spinel as a function of oxygen fugacity (log$_{10}$ [$f_{O_2}$ Pa] =-14 to -10), temperature (750-900 °C) and composition and discuss mechanisms of diffusion. In the process, we explore whether it is possible to reconcile the various data sets that are available in the literature in the framework of one consistent model.

**Methods**

**Starting material**

We have prepared diffusion couples made of single crystals of Mg-rich aluminous spinel and 30-80 nm thick films of synthetic Fe$^{2+}$-rich spinel. Crystals of two different compositions were used for the experiments –a synthetic aluminous spinel (Sp1: MgAl$_2$O$_4$) and a natural gem-quality spinel (Sp2: (Mg$_{0.93}$Fe$_{0.07}$)(Al$_{1.997}$Cr$_{0.003}$)O$_4$) from Sri Lanka. The synthetic crystals were obtained from CrysTec GmbH (Berlin, Germany). The compositional difference between diffusion couples involving Sp1 and
Sp2 enable a test of the role of Fe in influencing diffusion rates in spinel. All crystals were cut into pieces with dimensions of approximately 1-2 mm x 2 mm x 2 mm and polished mechanically using diamond compounds, followed by a final step of mechano-chemical polishing using colloidal silica. Thin films of Fe$^{2+}$-rich spinel were deposited on these polished samples using Pulsed Laser Deposition (PLD). The source material (target) used for all depositions was a polycrystalline spinel pellet with a hercynite content of 50% ($\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Al}_2\text{O}_4$) synthesized from powdered oxide mixes. A detailed description of the method, experimental setup and target preparation used in similar studies in our laboratory is given in Dohmen et al. (2002) and Dohmen et al. (2007). To ensure that the polished crystal surfaces are free of any volatile absorbents, all samples were heated in vacuum ($<6 \times 10^{-1}$ Pa) at 600 °C for 15-20 minutes before the deposition. The synthetic target, ($\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Al}_2\text{O}_4$), was ablated using an ArF-excimer laser with a wavelength of 193 nm at laser fluences of a few J/cm$^2$ which formed a stoichiometric conversion of all components of the target into a plasma that finally condenses on the substrate (single crystal spinel). Typically 4 samples were deposited at the same time of which one was used as a reference sample to infer the film thickness and initial composition of the deposited film. Previous studies have shown that the variations in film thickness among those crystals are less than 10% (Dohmen et al., 2002). Likewise, no compositional variations have been detected for any given deposition. A detailed list of the deposition conditions is given in Table 1.

**Diffusion Anneal**

All diffusion anneals were carried out in a gas-mixing furnace at atmospheric pressure under controlled oxygen fugacity. To induce Fe$^{2+}$-Mg interdiffusion, the diffusion couples were annealed at temperatures between 750-900°C for varying lengths of time, during which the oxygen fugacity was buffered using a continuously flowing gas mixture of CO-CO$_2$ ($10^{-14}-10^{-10}$ Pa). Both, temperature and oxygen fugacity, were continuously monitored in situ by a type B thermocouple (Pt/Rh6%-Pt/Rh30%) and a $f_{O_2}$-sensor ($\text{ZrO}_2$) and controlled within ± 1 °C and ± 0.1 log$_{10}$ units, respectively. The
reproducibility of the data was tested by repeating experiments at 800 °C and for different durations. Conditions of all diffusion anneals are summarised in Table 2.

The surface topography of the samples was analysed using reflected light microscopy and some selected samples were investigated using scanning electron microscopy and white-light phase-shifting interference microscopy. The structure of the initially amorphous thin layer was also analysed using electron backscatter diffraction (EBSD).

**Rutherford Backscattering Spectroscopy and measurement of diffusion profiles**

Film thickness and composition of the reference samples and detailed analysis of the compositional changes of spinel across the interface of the diffusion couples were measured using Rutherford Backscattering Spectroscopy (RBS). RBS is widely used for near surface analysis of solids and there is a growing number of studies that use RBS for diffusion related problems in the earth sciences (e.g. see Cherniak et al., 1991; Jaoul et al., 1991; and Dohmen et al., 2002; Dohmen et al., 2007 for related studies from our laboratory). The analyses shown in this study were performed at the Dynamitron Tandem Accelerator Laboratory of the Ruhr-University of Bochum. The 4 Mev tandem accelerator was used to generate a beam of α-particles at 2 MeV that was focused onto the spinel samples. A final aperture of 0.5 mm diameter enables to analyze samples with surface areas as small as 1 mm². A beam current of 20-50 nA was typically used for the measurement. To prevent charging of samples, the sides of sample crystals were coated with an Ag solution to allow for direct contact with the metallic sample holder. The backscattered particles were detected at an angle of 170 ° with a silicon particle detector at an energy resolution of about 16-20 keV. The sample surface was tilted at 5 ° relative to the beam to prevent channeling.

Element distributions and film thicknesses were simulated by an iterative procedure to fit the measured spectra using the software RBX (Kótai, 1994), which enabled us to retrieve true concentration depth profiles for Fe and Mg spanning up to 400 nm. Because the depth profiles of
heavier elements are better constrained using RBS, only the well-defined Fe concentration profiles were fitted in the following. A typical RBS spectrum is shown in Fig. 1.

**Fitting of Diffusion Profiles and calculation of Diffusion Coefficients.**

In a binary diffusion process, the net flux of Fe$^{2+}$ and Mg$^{2+}$ in a binary solid solution such as spinel must be zero at any given point in order to maintain charge balance and stoichiometry. It is governed by the same diffusion coefficient, which represents the interdiffusion coefficient of the two components, $D_{Fe-Mg}$:

\[
\frac{\partial c^{Sp}_{Fe}}{\partial t} = \frac{\partial}{\partial x} \left[ D_{Fe-Mg} \frac{\partial c^{Sp}_{Fe}}{\partial x} \right] \tag{1}
\]

We have used an explicit finite difference scheme (e.g. see Costa et al., 2008) to solve for equation (1) in order to calculate compositionally dependent interdiffusion coefficients to fit the concentration depth profiles extracted from the RBS spectra. A compositionally dependent $D_{Fe-Mg}$ is calculated at each grid point to calculate concentration profiles according to:

\[
C_{i}^{n+1} = C_{i}^{n} + \Delta t \left( \frac{D_{i+1}^{n} - D_{i}^{n}}{\Delta x} \right) \left( \frac{C_{i+1}^{n} - C_{i}^{n}}{\Delta x} \right) + D_{i}^{n} \Delta t \left( \frac{C_{i+1}^{n} - 2C_{i}^{n} + C_{i-1}^{n}}{\Delta x^2} \right)
\]

$C_{i}^{n}$ represents the concentration at the location $i$ at the current timestep, $n$, whereas $n+1$ represents the new (future) concentration ($C_{i}^{n+1}$), $\Delta t$ is the timestep, $\Delta x$ is the grid spacing and $D_{i}^{n}$ refers to the diffusion coefficient, $D_{Fe-Mg}$, at a given composition (at node $i$) and time-step,$n$. We assume constant grid spacing, zero flux at the top of the thin film and constant flux at the bottom i.e. the interior of the crystal.
The interdiffusion coefficient is related to the self-diffusion coefficients $D_{Mg}$, $D_{Fe}$ and the thermodynamic properties of the silicate / oxide according to (e.g.: Barrer, 1963):

$$D_{Fe-Mg}^{Sp} = \frac{D_{Fe}^{Sp}D_{Mg}^{Sp}}{X_{Fe}D_{Fe}^{Sp} + X_{Mg}D_{Mg}^{Sp}} \left[ 1 + \frac{\partial \ln y_{Fe}^{Sp}}{\partial \ln x_{Fe}^{Sp}} \right]$$

(2)

where $D_{Fe-Mg}^{Sp}$ is the interdiffusion coefficient at a given composition, $D_{Fe}^{Sp}$ and $D_{Mg}^{Sp}$ are the self-diffusion coefficients of Fe$^{2+}$ and Mg$^{2+}$, $X_i$ is the mole fraction of a component $i$, where $i = Fe^{2+}$ or Mg$^{2+}$ in this study, and $\gamma_{Fe}^{Sp}$ is the thermodynamic activity coefficient of the Fe-component, all at the same composition at which $D_{Fe-Mg}$ is to be calculated. This relationship provides a theoretical basis for describing the compositional dependence of $D_{Fe-Mg}$ that is used in Eqn. (1) and is more meaningful than using arbitrary functions such as polynomials or power laws. It should be noted that the self-diffusion coefficients $D_{Fe}$ and $D_{Mg}$ themselves might also depend on the major element composition, in which case the compositional dependence of $D_{Fe-Mg}$ is even stronger. The term in parentheses, called the thermodynamic factor, is equal to one if the solid solution behaves ideally (or nearly ideally), which is the case for the mixing of Fe$^{2+}$- and Mg-components in spinel (Liermann and Ganguly, 1999; Liermann and Ganguly, 2003).

In a situation where Fe$^{2+}$ and Mg are exchanged, the shapes and lengths of concentration profiles are controlled by the interdiffusion coefficient, $D_{Fe-Mg}$, and its compositional dependence as given, for example, by Eqn. 2. However, as the relationship between $D_{Fe-Mg}$, $D_{Fe}$ and $D_{Mg}$ is non-linear, it is worth exploring the sensitivity of the different diffusion parameters in Eqn. (2) to compositional variation, particularly if $D_{Fe}$ and $D_{Mg}$ are not similar to each other. A question that will become particularly relevant is: To what extent may the quantities $D_{Fe}$ and $D_{Mg}$ be constrained from the profile shapes in different compositions and for different $(D_{Fe}/D_{Mg})$?
If $D_{Fe}$ and $D_{Mg}$ are similar to each other, then it follows from Eqn. (2) that in the limiting case when one of the components is dilute (e.g. $X_{Fe} \to 0$), the interdiffusion coefficient approaches the self-diffusion coefficient of the dilute component (i.e. $D_{Fe-Mg} \approx D_{Fe}$). To illustrate the total range of possibilities, we have plotted the relationship between $D_{Fe-Mg}$, $D_{Fe}$ and $D_{Mg}$ for a wide range of values of $D_{Fe}$ and $D_{Mg}$ for different compositions, with these quantities, and hence also ($D_{Fe}/D_{Mg}$), varying over 10 orders of magnitude (Fig. 2). The median values of $D_{Fe-Mg}$, $D_{Fe}$ and $D_{Mg}$ are arbitrarily chosen to be $1 \times 10^{-18} \text{ m}^2/\text{s}$ for the purpose of illustration – the choice of this value has no effect on the discussion that follows.

For a given spinel composition ($X_{Fe}$) and $D_{Fe}/D_{Mg}$ there exists a minimum value of the ratio where $D_{Fe-Mg}$ is effectively equal to $D_{Fe}$ and a maximum where $D_{Fe-Mg}$ approaches $D_{Mg}$. These two ratios delineate a band (Fig. 2) within which $D_{Fe-Mg}$ (and hence profile lengths) are determined by both $D_{Fe}$ and $D_{Mg}$. Conversely, a given profile can be fitted to retrieve both $D_{Fe}$ and $D_{Mg}$ only if $D_{Fe}/D_{Mg}$ lies within this band. If $D_{Fe}$ and $D_{Mg}$ differ by more than a couple of orders of magnitude, then the profile lengths and shapes become effectively independent of one of the quantities and this quantity cannot be constrained from the data. See also Borinski et al. (2012) for a related discussion on multicomponent systems. With increasing molar fraction of the hercynite component ($X_{Fe}$), the band shifts to lower values. We have illustrated this behaviour for four spinel compositions in Figs. 2.

For example for $X_{Fe} = 0.001$, the composition of Sp1 in this study, for $D_{Fe}/D_{Mg} < 100$, $D_{Fe-Mg} \approx D_{Fe}$, but for $D_{Fe}/D_{Mg} > 10000$ one has $D_{Fe-Mg} = D_{Mg}$ (Fig. 2a). In between these two ratios $D_{Fe-Mg}$ is dependent on both tracer diffusion coefficients. It follows that diffusion profiles in Sp1 can be used to extract $D_{Fe-Mg}$ and this quantity is essentially $D_{Fe}$, whereas $D_{Mg}$ cannot be constrained (unless $D_{Mg}/D_{Fe} < 0.001$). With incorporation of Fe, at $X_{Fe} = 0.07$ (the composition of Sp2) if $D_{Fe}/D_{Mg} < \sim 1$, $D_{Fe-Mg} = D_{Fe}$, and if $D_{Fe}/D_{Mg} > \sim 100$, $D_{Fe-Mg} = D_{Mg}$ (Fig. 2b). Similarly, for $X_{Fe} = 0.5$ (the composition of the thin film) the band lies between $D_{Fe}/D_{Mg}$ 0.1 and 10 (Fig. 2c). Therefore, assuming that $D_{Fe}$ and $D_{Mg}$ are constant, different diffusion profile shapes and lengths can be expected depending on $D_{Fe}/D_{Mg}$ and the
initial chemical gradient as defined by the diffusion couple in the experiment. If \( \frac{D_{\text{Fe}}}{D_{\text{Mg}}} > 100 \) for the diffusion couple Sp2/thin film, \( D_{\text{Fe-Mg}} \) would be effectively constant and equal to \( D_{\text{Mg}} \). However, if in addition \( \frac{D_{\text{Fe}}}{D_{\text{Mg}}} < 10000 \) (i.e. \( 100 < \frac{D_{\text{Fe}}}{D_{\text{Mg}}} < 10000 \)), then for the diffusion couple Sp1/thin film \( D_{\text{Fe-Mg}} \) would depend strongly on composition. \( D_{\text{Fe-Mg}} \) changes by about two orders of magnitude between Sp1 and the thin film ends of the diffusion couple and distinctly asymmetric profile shapes would be observed. In addition \( D_{\text{Fe-Mg}} \) of Sp1 would depend on \( D_{\text{Fe}} \) and \( D_{\text{Mg}} \) and the two quantities cannot be constrained independently of each other. At \( X_{\text{Fe}} \sim 0.999 \), the roles of \( D_{\text{Mg}} \) and \( D_{\text{Fe}} \) are reversed from that discussed for \( X_{\text{Fe}} \sim 0.001 \) (Fig. 2d).

Results and discussion

Sample characterization: Stoichiometry, structure and topography

Surface topography, film thickness and stoichiometry of the samples were analysed before and after the diffusion anneal using reflected light spectroscopy, scanning electron microscopy, EBSD, white light interference microscopy, and RBS.

No substantial differences have been observed between the surfaces of the polished single crystals and the coated samples using reflected light microscopy and white light interference microscopy (Fig. 3 a and b). Structural characterization of the samples before and after the diffusion anneal have been performed using EBSD. Distinct diffraction patterns obtained from the annealed samples show that the initially amorphous thin film crystallized during the diffusion anneal. SEM images show that when rare scratches were present on the sample surface, these are still visible after coating and subsequent annealing. This implies that the thin film follows the surface topography of the substrate (single crystal) and that crystallization does not change the surface topography of the sample. Measurement of topographic variations using white light interference microscopy in different regions of the surfaces of samples (e.g. two examples shown in Fig. 3 a and b) reveal that the total variation of topography is on
the order of ± 1.5 nm (Sp1) to ± 6-10 nm (Sp2). The film thickness, measured by RBS analysis, varied in the range 25-85 nm (Table 2) in different samples. Compositional analysis of the nominally pure spinels (Sp1) revealed moreover that these contain minor Fe ($X_{Fe}=0.001$) that could be detected using RBS.

**Diffusion Profiles**

Fe$^{2+}$ concentration profiles found in the diffusion couples of Sp1 (Fig. 4a) show a marked asymmetry around the inflection point (where the sign of the second derivative of C(x) changes), whereas profiles in Sp2 (Fig. 4b) are less asymmetric. The asymmetry indicates a compositional dependence of $D_{Fe-Mg}$.

In both cases, Fe$^{2+}$-Mg interdiffusion appears to be faster (i.e. slopes of concentration profiles are gentler) on the iron-poor side of the diffusion couple. This behaviour is opposite of the behaviour seen in silicates such as olivine or garnet, where diffusion rates tend to increase with Fe-content. The difference may arise because diffusion in spinel can occur by vacancy as well as interstitial mechanisms; this aspect will be discussed in more detail below. The asymmetric diffusion profile shapes could be reproduced by assuming constant self diffusion coefficients (insensitive to compositional changes) in Eqn. (2), with $D_{Fe}$ greater than $D_{Mg}$. It is found that fits to the observed profile shapes can be obtained for $D_{Fe}/D_{Mg} \geq 100$ for Sp1 and $D_{Fe}/D_{Mg} \geq 10$ for Sp2, as discussed above. Under these circumstances the diffusion couple Sp2/thin film does not provide a strong constraint on compositional dependence of diffusion coefficients. Fig. 2 indicates that for Sp1, if $D_{Fe}/D_{Mg} \sim 100$, then $D_{Fe-Mg} \sim D_{Fe}$; if $D_{Fe}/D_{Mg} > 10000$, then $D_{Fe-Mg} \sim D_{Mg}$. It is not possible to distinguish between these scenarios (i.e. whether $D_{Fe}$ or $D_{Mg}$ or both control the observed profiles) based on our data, although $D_{Fe-Mg}$ itself can be determined robustly. For Sp2, with $D_{Fe} > D_{Mg}$ as indicated by the asymmetry of the profile, $D_{Fe-Mg}$ lies within an order of magnitude of $D_{Mg}$ (Fig. 2). The values of $D_{Fe-Mg}$ that are obtained from calculated profiles that best describe the observed profile lengths and shapes for both compositions are reported in Table 2. Variations in D values obtained from different crystals annealed...
at the same conditions over different lengths of time indicate a reproducibility of 0.11 log\(_{10}\) units for the measured D values (Fig. 5) and this provides a useful estimate of the uncertainty in D.

**Dependence of diffusion coefficients \(D_{\text{Fe-Mg}}\) on oxygen fugacity and temperature**

The retrieved \(D_{\text{Fe-Mg}}\) values as a function of oxygen fugacity (log\(_{10}\) \((fO_2[\text{Pa}]) = -14\) to -10 at constant pressure (10\(^5\) Pa) and temperature (800 °C) are shown in Fig 6. In the nominally pure spinel Sp1 diffusion coefficients are independent of oxygen fugacity within the uncertainty of the data. In the Fe-bearing spinel Sp2 there is a clear dependence of diffusion rates on oxygen fugacity and the dependence of log\(_{10}\) D on log\(_{10}\)\(fO_2\) is not linear (Fig. 6).

While there is extensive work in the literature on cation diffusion in magnetite-based spinels, comparably little is known about Fe\(^{2+}\)-Mg interdiffusion in aluminous spinels (e.g. Van Orman and Crispin, 2010). Because there are two different cation sublattices in spinel, a number of different migration mechanisms are possible (Dieckmann and Schmalzried, 1977a,b; Murphy et al., 2009). A direct comparison of the point defect chemistry of magnetite and (Fe,Mg)Al\(_2\)O\(_4\) should therefore be considered with caution because magnetite and aluminous spinel have different crystal structures. In MgAl\(_2\)O\(_4\)–spinel, Mg\(^{2+}\) occupies the tetrahedral and Al\(^{3+}\) the octahedral sites. Magnetite, on the other hand, has an inverse spinel structure at low temperatures. Fe\(^{2+}\) and Fe\(^{3+}\) occupy the octahedral sites in equal proportions, and Fe\(^{3+}\) is the sole occupant of the tetrahedral sites (e.g. Verwey, 1947). Bearing this caveat in mind, it is worthwhile nevertheless to compare the dependence of diffusion rates found in this study with those obtained for magnetite. Diffusivities in magnetite have been reported to vary non-linearly as a function of oxygen fugacity according to the expression of the form:

\[
D = D_v(T) fO_2^{2/3} + D_i(T) fO_2^{-2/3} \tag{3}
\]
where \( D \) is the total diffusivity and \( D_v(T) \) and \( D_i(T) \) refer to temperature dependent components of diffusivity by the vacancy (\( v \)) and interstitial (\( i \)) mechanisms, respectively. The inferred \( f_{O_2} \) exponents of \(-\frac{2}{3}\) at low and \(\frac{2}{3}\) at high oxygen fugacities were used to demonstrate that cation vacancies and cation interstitials were the majority defects at high and low oxygen fugacities, respectively (Dieckmann and Schmalzried, 1977a,b; Hallron and Bowen, 1980; Dieckmann, 1982; Dieckmann and Schmalzried, 1986; Dieckmann et al., 1987; Töpfer et al., 1995; Aggarwal and Dieckmann, 2002a, Aggarwal and Dieckmann, 2002b; see also Van Orman and Crispin, 2010 for a review). Our data on Fe\(^{2+}\)-Mg diffusion in Sp2 shows a dependence on oxygen fugacity that is practically identical to the dependence observed for magnetite (Fig. 6) – lines drawn according to Eqn. 3 with slopes of \(\frac{2}{3}\) and \(-\frac{2}{3}\) describe the data set very well, indicating that in spite of the structural differences between magnetite and Fe\(^{2+}\)-Mg spinel, diffusion by an interstitial mechanism at low oxygen fugacities and by a vacancy mechanism at higher oxygen fugacities occurs in (Fe\(^{2+}\),Mg)Al\(_2\)O\(_4\) as well. Therefore, unlike in other systems such as olivine, it is not possible to use a single \(f_{O_2}\)-exponent to correct for the effect of \(f_{O_2}\) on diffusion rates in spinels over the entire range of their stability. In contrast to the behaviour of Sp2, the data on nominally Fe-free spinel Sp1 show no resolvable dependence on \(f_{O_2}\) (Fig. 6), showing that diffusion occurs in the two spinels by different mechanisms.

The temperature dependence of diffusion coefficients obtained from all experiments on Mg-spinel (Sp1) and the natural Fe-bearing spinel (Sp2) at \(\log_{10}[f_{O_2} \text{ Pa}] = -12\) are shown in Fig. 7 in the form of an Arrhenius plot (750-900 °C). It is seen that over the experimental range of temperature, diffusion in the Mg-rich spinel Sp1 is faster than in the Fe-bearing spinel Sp2. The slopes of the best-fit lines to the data indicate that the activation energy for diffusion in Sp1 is higher than for diffusion in Sp2. The difference in activation energy implies that there will be a crossover at lower temperatures where diffusion in the Fe-bearing spinel may become faster. A linear least squares fit yields the following
values of the pre-exponential factor, $D_0$, and the activation energy, $Q$, in the Arrhenius relation: $D = D_0 \exp(-Q/RT)$, where $R$ is the gas constant and $T$ is the absolute temperature:

Synthetic magnesium spinel (Sp1)

$Q_{FeMg} = 213 \pm 14$ kJ/mol

$\log_{10}(D_{0FeMg} [m^2/s]) = -8.02 \pm 0.67$

Natural Fe-bearing spinel (Sp2)

$Q_{FeMg} = 139 \pm 18$ kJ/mol

$\log_{10}(D_{0FeMg} [m^2/s]) = -12.33 \pm 0.85$

The activation energies in the two spinels differ, as has been found in other studies as well (e.g. Sheng et al., 1992, Liermann and Ganguly, 2002), because diffusion occurs by different mechanisms in the two spinels, as discussed above. Similar differences in diffusion behaviour between Fe-bearing and Fe-free crystals have also been found in the olivine solid solution series (e.g. see Chakraborty et al., 1994; Chakraborty, 2010). Consequently, an interim conclusion is that for applications dealing with natural, Fe-bearing spinels, the Arrhenius relation obtained for Sp2 should be used. This aspect is considered in more detail below.

**Comparison with Fe, Mg, Cr and Al diffusion rates in spinels from other studies**

Fig. 8 shows a comparison of the Arrhenius relations reported in different studies on $D_{Mg}$ and $D_{Fe-Mg}$ in aluminous spinel. Sheng et al (1992) determined Mg tracer diffusion coefficients in pure Mg-spinel at temperatures between 1260 – 1550 °C with an activation energy of 384 kJ/mol. Our data on $D_{Fe-Mg}$ in pure Mg-spinel at lower temperatures yield a much lower activation energy of 219 kJ/mol. This difference can result from one of three reasons: (a) If $D_{Fe}/D_{Mg} \sim 100$, then $D_{Fe-Mg} \sim D_{Fe}$ (Fig. 2) and we have no information on $D_{Mg}$, or (b) the addition of Fe during diffusion in our experiments alters the
point defect chemistry and diffusion mechanism, or (c) If $D_{Fe}/D_{Mg} > 300$, then $D_{Fe-Mg} \sim D_{Mg}$ (Fig. 2), and the difference could result from a transition from an intrinsic diffusion mechanism at high temperatures (Sheng et al., 1992) to extrinsic diffusion at lower temperatures (this study). To choose between these alternatives it is necessary to obtain data at intermediate temperatures or determine $D_{Mg}$ directly at low temperatures.

Liermann and Ganguly (2002) determined $D_{Fe-Mg}$ at high temperatures and pressures in a spinel of very similar composition to Sp2, whereas Freer and O’Reilly (1980) determined $D_{Fe-Mg}$ as a function of composition using diffusion couples made of pure Mg- and Fe-spinels enclosed in evacuated silica tubes. Van Orman and Crispin (2010) and Liermann and Ganguly (2002) argue that the presence of oxidizing conditions and extended defects in the crystals may have affected the results of the study of Freer and O’Reilly (1980). Liermann and Ganguly (2002) fit their interdiffusion profiles using $D_{Fe}$ and $D_{Mg}$ that were related by Equation (2). Based on the observed symmetry of their profile shapes, they inferred that there was no significant compositional dependence and that $D_{Fe} \sim D_{Mg}$. However, our analysis above indicates that $D_{Fe} \sim D_{Mg}$ need not be necessarily fulfilled for spinels of composition Sp2, and that symmetric profile shapes may be produced even when $D_{Fe} \neq D_{Mg}$ (Fig. 2). To illustrate this aspect (Fig. 9), we have calculated a synthetic profile (points in Fig. 9) with $D_{Fe} = D_{Mg}$ using one of the data points of Liermann and Ganguly (2002): 21.4x10^8 Pa, 1125 °C, 51 hours (Sp-diff05d). Next, we have produced “best fit” profiles to this data set (Fig. 9) using (a) $D_{Fe}/D_{Mg} = 1$, (b) $D_{Fe}/D_{Mg} = 10$ and (c) $D_{Fe}/D_{Mg} = 100$. It is seen that there is very little difference in the calculated profile shapes and in particular, there is no pronounced asymmetry even when $D_{Fe}/D_{Mg} = 100$. Although it is possible to distinguish the quality of fit in this perfectly ideal calculated profile shape, it is conceivable that with real analytical data showing some scatter it would be difficult to distinguish between these possibilities. This happens because at these conditions ($X_{Fe} \sim 0.01$, $D_{Fe} > D_{Mg}$), $D_{Fe-Mg}$ is always essentially equal to $D_{Mg}$ and is insensitive to the value of $D_{Fe}$ (Fig. 2). Therefore, the data set of Liermann and Ganguly (2002) is also consistent with our inference that $D_{Fe} > D_{Mg}$, by a factor of 100 or more. In the subsequent
discussion, therefore, we consider the $D_{Fe-Mg}$ values obtained by Liermann and Ganguly (2002) and not the $D_{Fe}$ and $D_{Mg}$ values that they extracted from the profiles (see discussion above related to profile shape and length in an interdiffusion experiment and the role of $D_{Fe-Mg}$, $D_{Fe}$ and $D_{Mg}$).

As the study of Liermann and Ganguly (2002) was carried out in graphite capsules in a piston cylinder apparatus, the oxygen fugacity of their experiments was constrained to be between the C-O buffer and the $fO_2$ given in the C-O-H system with H:O = 2:1 (i.e. constrained by the presence of some water and graphite in the piston cylinder cell); see Chakraborty and Ganguly (1992) for more details for a similar setup. However, oxygen fugacity along a buffer reaction curve is not constant at different temperatures and therefore the temperature dependence of the buffer reaction gets incorporated into the calculated apparent activation energy of diffusion. Moreover, as seen above, the oxygen fugacity dependence of $D_{Fe-Mg}$ is non-linear. This makes it difficult to compare the Arrhenius relation of Liermann and Ganguly (2002) directly with our data. We have chosen an alternative option to analyse the data. Considering the nature of $fO_2$ dependence of $D_{Fe-Mg}$ in Fe-bearing spinel (Fig. 6), which can be rationalized by a point defect thermodynamic model, we have explored whether it is possible to describe both sets of $D_{Fe-Mg}$ data taken together (i.e. Liermann and Ganguly, 2002; this study) in the framework of one comprehensive model:

$$D[m^2/s] = D_v[m^2/s]fO_2[Pa]^m \exp(-Q_v[J/mol]/RT[K]) + D_i[m^2/s]fO_2[Pa]^{-m} \exp(-Q_i[J/mol]/RT[K])$$

We obtain the following fit parameters:

$D_v = 1.07x10^{-09} \pm 1.55x10^{-09} \text{ m}^2/\text{s} \quad \log_{10}D_v = -9.0 \text{ [m}^2/\text{s}]$

$Q_v=131 \pm 66 \text{ kJ/mol}$

$D_i=1.03x10^{-17} \pm 7.32x10^{-17} \text{ m}^2/\text{s} \quad \log_{10}D_i = -17.0 \text{ [m}^2/\text{s}]$

$Q_i=130 \pm 80 \text{ kJ/mol}$

$m=0.34 \pm 0.18,$
where \( R \) [J K\(^{-1}\)mol\(^{-1}\)] is the universal gas constant.

The resulting fit to the data is shown in Fig. 10. In spite of the relatively large uncertainties resulting from the limited body and spread of data, it is seen that the results are consistent with the general behaviour predicted by the point defect model. In particular, the fit parameters also describe other data sets (e.g. Freer and O’Reilly, 1980 and Suzuki et al., 2008), that were not included in the fitting procedure, quite well (see below). The best fit \( f_\text{O}_2 \) exponent is different from 2/3 in the magnetite model. This could be because Fe-Mg spinel behaves differently from magnetite, or simply the result of scatter of our data – detailed experiments as a function of \( f_\text{O}_2 \) at several temperatures would be required to adequately quantify this aspect. The limited spread of data in T-\( f_\text{O}_2 \) space results in high uncertainties in the fit-parameters so that these are not suitable for calculation of diffusion coefficients at extrapolated conditions. However, the mean values of the fit-parameters provide several important insights into the diffusion behaviour of Fe-Mg in Fe-bearing spinel. For example, a consequence of this analysis is the recognition that although the \( f_\text{O}_2 \) dependence of \( D_{\text{Fe-Mg}} \) in spinel is non-linear, for the range of temperatures and oxygen fugacity conditions that are relevant for at least most applications to terrestrial samples, a positive dependence of \( D_{\text{Fe-Mg}} \) on \( f_\text{O}_2 \) (corresponding to diffusion by dominantly a vacancy mechanism) is adequate. The activation energy of 130 kJ/mol is slightly higher than the 50 – 100 kJ/mol migration energy of diffusion that is calculated in computer simulations (e.g. Murphy et al., 2009). This fact, combined with the observed dependence of diffusion rates on oxygen fugacity (i.e. an externally imposed chemical potential), indicates that Fe-Mg diffusion in spinels occurs by a transition metal extrinsic diffusion (TaMED) mechanism (see Chakraborty, 1997 for details on the characteristics of TaMED mechanism).

Fig. 10 shows calculated diffusion coefficients using the mean values of the fit parameters as a function of temperature and oxygen fugacity with the experimentally measured data points from different studies shown as well for comparison. Fig. 10a shows individual data points from our study as well as all earlier studies in Fe-bearing spinel (Freer and O’Reilly, 1980; Liermann and Ganguly, 2002;
Suzuki et al., 2008) as a function of temperature in an Arrhenius diagram. For the inferred $f_O^2$
condition of each study, we have calculated diffusion coefficients at each experimental condition using
the fit parameters above (shown as red squares in Fig. 10a). It is seen that all of the experimentally
measured data are consistent with the above relationship. Moreover, we have fit Arrhenius type
relationships to the calculated dataset for each study (i.e. Freer and O’Reilly, 1980, Liermann and
Ganguly, 2002, and for Sp2 data from this study), shown as dashed red lines. It is seen that the apparent
mismatch between studies and the scatter seen in Fig. 8 is almost completely reproduced. This indicates
that results from all experimental studies are in fact consistent with each other and may be described by
the model above; there is no need to invoke enhanced diffusion due to artefacts such as oxidation of
spinels. This exercise also underscores the need to consider the effect of oxygen fugacity in dealing
with diffusion in Fe-bearing spinels – the non-linear dependence can lead to a wide range of behaviour
so that simple linear extrapolations in Arrhenius plots can lead to incorrect results.

The diffusivities reported by Freer and O’Reilly (1980) (for a spinel composition of FeO= 25
wt% and FeO= 5 wt%) are 3 to 4 orders of magnitude higher than those obtained in this study (Fig. 8,
10a) but can be reproduced using the relationship given above (Eqn. 4, Fig. 10). Suzuki et al (2008)
obtained two data points for $D_{Fe-Mg}$ (Fig. 8, 10a) which indicates that in addition to the factors
considered here, $D_{Fe-Mg}$ also depends on Cr-content of spinel. $D_{Fe-Mg}$ in Cr-free spinel is about a factor
of 7.5 smaller than in spinel with Cr# (= Cr/Cr+Al) = 0.9. Their diffusion coefficient for Cr-free spinel
can be reproduced using our expression (Eqn. 4). Therefore, for applications to mantle spinels
containing Cr, it should be considered that diffusion coefficients calculated using our expression could
be slightly smaller than the real values. Suzuki et al. (2008) measured Al-Cr interdiffusion in chromite
spinel at high pressure (9-7 GPa) and temperatures ranging from 1400-1700 °C by using diffusion
couples of natural single crystals of MgAl$_2$O$_4$ spinel and chromite. Fig. 8 shows a comparison of the
diffusivities obtained in this study with the Al-Cr interdiffusion coefficients for Cr# =0.8 and self
diffusion coefficients for Cr in spinel (Cr#=0) obtained by Suzuki et al. (2008). Extrapolation of the
data implies that Fe-Mg interdiffusion is faster than Al-Cr interdiffusion or Cr self diffusion in spinel at temperatures relevant for the upper mantle. Empirical observations on diffusion in spinel at upper mantle conditions confirm that Cr is the slowest diffusing species among all the cations (e.g. Ozawa, 1984; Suzuki et al., 2008). However one should note in view of the non-linear dependencies described above that these relationships could be reversed at certain $T$-$fO_2$ conditions. Notwithstanding the excellent consistency of diffusion behavior calculated using the mean values of the fit parameters and various experimental data sets, the large uncertainties on the fit parameters make them poorly suited for large extrapolations. Therefore, for the purpose of cooling rate or closure temperature calculations, we recommend the direct fit to our data ($Q_{FeMg}=139 \pm 18 \text{ kJ/mol}$, $\log_{10}(D_{0FeMg} [\text{m}^2/\text{s}]) = -12.33 \pm 0.85$) for Fe-bearing spinel, to be used for compositions and $fO_2$ conditions similar to those of the experiments, until availability of more data allow the model based on point defects to be better constrained.

Comparison with Fe-Mg diffusion in other related minerals (olivine, pyroxene and garnet)

Data for diffusion of Fe-Mg in all the phases that might coexist with spinel in the mantle are now available. We compare the rates of Fe-Mg diffusion in Mg-Al spinel, olivine, garnet, clinopyroxene and orthopyroxene in Fig. 11. For the purpose of comparison, we have calculated diffusion rates at a constant composition of $X_{Fe} = 0.07$ where composition dependence is known to play a role (e.g. olivine, garnet), although these are not necessarily the compositions that coexist in nature. It is found that Fe-Mg diffusion in spinel is among the fastest among these under most circumstances.

$Fe^{2+}$-Mg interdiffusion in olivine has recently been summarized by Dohmen et al. (2007), Dohmen and Chakraborty (2007) and Chakraborty (2010). The set of experiments presented in Dohmen et al. (2007) was carried out following the same experimental procedure as described in this study. Their data for diffusion along the c-axis are shown in Fig. 11 for an olivine composition of $X_{Fe}=0.07$ (Fo93) at oxygen fugacities less than $\log [fO_2 \text{ Pa}] = -10$, by using the Arrhenian relation given by these authors (Dohmen and Chakraborty, 2007). Diffusion in olivine is anisotropic and to obtain
diffusion coefficients parallel to the \( a \) and \( b \) axis one needs to subtract \( \log(6) \) from the relation shown in Fig.11., which decreases the \( \log D_{Fe-Mg} \) values for olivine by 0.78 log units. Thus, at temperatures less than 900 °C interdiffusion of \( Fe^{2+} \) and Mg is faster in spinel than in olivine (given \( X_{Fe} = 0.07 \)). Only at temperatures above 900 °C \( D_{Fe^{2+}-Mg} \) may become faster in olivine, depending on the ambient \( fO_2 \).

Based on an empirical study of compositional gradients in olivine and coexisting spinel, Ozawa (1984) concluded that \( D_{Fe-Mg} \) in spinel (\( Cr# < 0.6 \)) is a factor of 100 greater than that of olivine and that only for \( Cr \) rich spinels (\( Cr# > 0.7 \)) \( Fe-Mg \) interdiffusion in spinel is the same order or smaller than that of olivine. Depending on the ambient \( fO_2 \) and crystallographic orientation of olivine, this observation could be consistent with the experimental data from this study, although more recent findings (Suzuki et al., 2008) suggest that diffusion in \( Cr \)-bearing spinel is actually faster than in \( Cr \)-free spinel; the influence of \( Cr \) on \( Fe-Mg \) diffusion needs to be studied through further detailed experiments.

\( Fe-Mg \) diffusion in spinel is at least two orders of magnitude faster than diffusion rates of \( Fe-Mg \) in garnets (Borinski et al., 2012) and pyroxenes (Müller et al., 2013, Dohmen et al., 2014), although the difference decreases at higher temperatures because of the low activation energy of \( D_{Fe-Mg} \) in spinel (\( \sim 130 \) kJ/mol) compared to those in other phases (\( > 200 \) kJ/mol).

**Conclusions**

We have carried out a set of diffusion experiments on \( Fe^{2+}-Mg \) interdiffusion in a pure Mg-spinel and a natural spinel from Sri Lanka (\( X_{Fe} \sim 0.07 \)). The measured concentration profiles were treated using an explicit finite difference scheme to obtain diffusion coefficient as a function of temperature (750-900 °C), oxygen fugacity (\( \log [fO_2 \text{ Pa}] = -14 \) to -10) and composition. The main findings are as follows:

1) \( D_{Fe-Mg} \) in spinel is faster in more Mg-rich compositions.

2) Although it is not possible to constrain the exact values of the tracer diffusion coefficients \( D_{Fe} \) and \( D_{Mg} \), results from both crystals indicate that \( D_{Fe}/D_{Mg} > 100 \).
3) Diffusion rates are independent of oxygen fugacity in the nominally pure Mg-spinel (although it contains detectable amounts of Fe) within the resolution of measurement of this study. In contrast, diffusion rates in the Fe-bearing spinel are a non-linear function of oxygen fugacity. The dependence is consistent with models that predict that diffusion occurs by an interstitial mechanism at low oxygen fugacities and by a vacancy mechanism at high oxygen fugacities.

4) The consequence of the above observations is that the mechanism of diffusion is different in Fe-free spinel from that in Fe-bearing spinel (different activation energy and Arrhenius parameters); and different in Fe-bearing spinel at low vs. high oxygen fugacities. For most terrestrial processes, the vacancy mechanism of diffusion should dominate.

5) A comprehensive model (Eqn. 4) accounting for variations caused by all these factors is able to reproduce all existing experimental data on Fe-Mg diffusion in Fe-bearing spinels (this study, Liermann and Ganguly, 2002, Freer and O'Reilly, 1980).

6) The model developed in this study (Eqn. 4) may be used to calculate $D_{Fe-Mg}$ for modelling natural processes. In addition, it should be considered that $D_{Fe-Mg}$ depends substantially on the Cr-content of spinel (Cr-#), as discussed above. As diffusion by the vacancy mechanism should dominate in most terrestrial processes, diffusion rates in spinels should increase with oxygen fugacity. In most circumstances, diffusion rates of Fe-Mg in spinels will be faster than that in coexisting mafic minerals (olivines, orthopyroxenes, clinopyroxenes and garnets).

**Implications**

The new diffusion data on Fe-Mg spinel and the point defect model that evolved from these data help to explain earlier diffusion data that were apparently discrepant, and provides a means of calculating diffusion related properties (closure temperatures, timescales from modelling concentration gradients) that vary over a considerable range depending on the Fe concentration of the spinel crystal and oxygen fugacity in the environment, in addition to factors such as temperature and likely, pressure.
Acknowledgment

This study evolved from the M.Sc thesis of KV and was supported by funds from the Ruhr Universität Bochum. Hans-Werner Becker helped with the RBS analyses and Rolf Neuser with the SEM observations. Joana Polednia took the photographs with the interference microscope. We thank Katherine Crispin, Daniele Cherniak and associate editor John Ferry for their constructive reviews and comments.

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**Figure captions**

**Figure 1.** RBS spectra of sample number Sp2Her50-3 (annealed at 10\(^0\) Pa, T= 800 °C, Log\(_{10}\)f\(_{O_2}\) = -12 Pa) and the corresponding reference (i.e. unannealed sample showing the initial condition) showing normalized counts vs. energy of backscattered alpha particles (grey circles: reference sample; blue circles: Sp2Her50-3). Simulations of the spectra are shown as solid lines (yellow: reference sample,
red: Sp2Her50-3). The marked region in a) is drawn to a larger scale in b). Note the decrease of Fe in
the thin layer after the diffusion anneal.

Figure 2. Calculated interdiffusion coefficients $D_{Fe-Mg}$ as a function of varying iron content and
differing self-diffusion coefficients $D_{Fe}$ and $D_{Mg}$ using Eqn. (2) for an ideal solid solution. The plots
show a variation in the relationship over ten orders of magnitude of each self-diffusion coefficient. The
color gradient represents $\log_{10} D_{Fe-Mg}$, with warmer colors representing higher values. Contour lines
denote interdiffusion coefficients of equal value. The white band represents an area, where $D_{Fe-Mg}$ is
represented by both $D_{Fe}$ and $D_{Mg}$. Red solid lines denote equal ratios of $D_{Fe}/D_{Mg}$. a) $X_{Fe}=0.001$, b)
$X_{Fe}=0.07$, c) $X_{Fe}=0.5$, d) $X_{Fe}=0.999$.

Figure 3. Reflected light microscopy and white light interference microscopy images of a) Sp1 and b)
Sp2. Total variations of topography measured in different regions are shown to be on the order of ± 1.5
nm (Sp1) to ± 6-10 nm (Sp2).

Figure 4. Experimental data (symbols) and simulations (solid lines) of diffusion profiles in a) Sp1
(Sample no. Sp1Her50-10, 10$^{05}$ Pa, $T= 900 \degree C$, $\log_{10}O_2 = -10$ [Pa]) and b) Sp2 (Sp2Her50-13, 10$^{05}$ Pa,
$T= 800 \degree C$, $\log_{10}O_2 = -12$ [Pa]). Both diffusion profiles are matched assuming constant self-diffusion
coefficients, where $D_{Fe} > D_{Mg}$. The asymmetric profile in a) is best described for $D_{Fe}/D_{Mg}$ ≥ 100. The
less asymmetric profile shown in b) is well described for $D_{Fe}/D_{Mg}$ ≥ 100 as well.

Figure 5. Time sequence. Variations in $D_{Fe-Mg}$ values obtained from different crystals annealed at the
same conditions over different lengths of time (Sp2Her50-1, -2, -3, -14). The data indicate a
reproducibility of $1\sigma = 0.11 \log_{10}$ units for the measured $D_{Fe-Mg}$ values.
**Figure 6.** $D_{\text{Fe-Mg}}$ in Sp1 and Sp2 at $T = 800 \, ^\circ\text{C}$ and $10^5 \text{ Pa}$ as a function of oxygen fugacity: $\log_{10} f_{\text{O}_2}$ in Pa = $10^{-14} - 10^{-10}$. Diffusion coefficients in Sp1 are independent of oxygen fugacity within the uncertainty of the data. In contrast, diffusion coefficients in Sp2 are dependent on oxygen fugacity in a non-linear manner. The blue dashed line represents a constant value of Log$_{10} D = -18.37 \, [\text{m}^2/\text{s}]$, which describes $D_{\text{Fe-Mg}}$ in Sp1 within the uncertainty of the data. The red dashed line represents the “best fit” to $D_{\text{Fe-Mg}}$ in Sp2, based on Eqn. 3. The inferred $f_{\text{O}_2}$ exponents of $-2/3$ at low and $2/3$ at high oxygen fugacities were used in accordance to the $f_{\text{O}_2}$ dependence described for magnetite (e.g. Dieckmann and Schmalzried, 1977a,b). See text for further discussion.

**Figure 7.** Arrhenius plot showing diffusion coefficients ($D_{\text{Fe-Mg}}$) retrieved from Sp1 and Sp2. All experiments were performed at atmospheric pressure and controlled oxygen fugacity. Because diffusion in Sp1 is independent of oxygen fugacity, all data are plotted in this figure. Diffusion in Sp2 is shown for $\log_{10} f_{\text{O}_2} = -12[\text{Pa}]$. Dashed lines denote self-diffusion coefficients $D_{\text{Fe}}$ and $D_{\text{Mg}}$, solid lines represent best fits to the interdiffusion coefficients for a given composition of $X_{\text{Fe}} = 0.001$ (Sp1) and $X_{\text{Fe}} = 0.07$ (Sp2).

**Figure 8.** Arrhenius diagram showing diffusion coefficients determined in aluminous spinel in earlier studies: Fe-Mg interdiffusion (dots), Mg self-diffusion (squares) and Cr-Al interdiffusion (stars) coefficients. The symbols represent the experimental data. The data by Freer and O’Reilly (1980) is shown for a composition of FeO = 5 wt% and FeO = 25wt%, respectively. Data obtained from Suzuki et al (2008) is shown for Cr#=0 and Cr#=0.9 at $3 \times 10^9 \text{[Pa]}$. For a better comparison of the interdiffusion data given by Liermann and Ganguly (2002) with those obtained in this study, all data are shown for a composition of $X_{\text{Fe}} = 0.07$ (dots). Note that Liermann and Ganguly (2002) performed their study in the presence of graphite at an oxygen fugacity of approx. $2 \times 10^9 \text{[Pa]}$ (black dashed line).
The black solid line denotes the Arrhenius relation obtained by Liermann and Ganguly (2002) at atmospheric pressure.

**Figure 9.** Synthetic profile (dots) based on one of the best fit data points of Liermann and Ganguly (2002): 21.4x10^8 Pa, 1125 °C, 51 hours (Sp-diff05d). Solid lines represent “best fit” profiles to this data for $D_{Fe}/D_{Mg}=1,10$ and 100, with $D_{Fe-Mg}$ determined using Eqn. (2) in the text.

**Figure 10.** Fe-Mg diffusion coefficients calculated using the best fit parameters in the point defect model (Eqn. 4) compared to measured data from different studies. a) Arrhenius relation showing the diffusion data measured by Liermann and Ganguly (2002) (grey dots), Freer and O’Reilly (1980) (green dots), Suzuki et al. (2008) (blue dots) and our data on interdiffusion in Sp2 (red dots) for a given composition of $X_{Fe}=0.07$. Red lines are calculated using equation 4. b) $D_{Fe-Mg}$ in Sp2 at $T=800 \, ^{\circ}C$ and 1005 Pa as a function of oxygen fugacity (red dots) in comparison to the calculated value according to equation 4. c) is a 3D plot, to illustrate the dependence of the interdiffusion coefficient $\log_{10} D_{Fe-Mg}$ [m^2/s] on temperature and oxygen fugacity based on equation 4.

**Figure 11.** Comparison of the Fe-Mg interdiffusion data in spinel obtained in this study with those in olivine [Dohmen et al. (2007a)], garnet [Borinski et al., 2012], clinopyroxene [Müller et al., 2012] and orthopyroxene [Dohmen et al., 2014].
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<th>film [nm]</th>
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<th>DMg [m²/s]</th>
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Table 2.
Sp1-Her50-ref-B

Sp1-Her50-10

Reflected light microscopy

White light interference microscopy

Sp2-Her50-ref-E

Sp2-Her50-13

Reflected light microscopy

White light interference microscopy
a) Sp1
- $DFe/DMg = 10$
- $DFe/DMg = 100$
- $DFe/DMg = 1000$

b) Sp2
- $DFe/DMg = 10$
- $DFe/DMg = 100$
- $DFe/DMg = 1000$