1   **Revision 2#**

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

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6

7   **Abstract**

8   We have measured Fe-Mg interdiffusion rates (D_{Fe-Mg}) in synthetic Mg-Al spinel and a natural (Mg,Fe)

9   aluminous spinel from Sri Lanka ($X_{Fe} \sim 0.07$) at atmospheric pressure over a range of different oxygen

10   fugacities ($\log_{10}(fO_2 [Pa]) = -14$ to -10) and temperatures (750-900 °C). Diffusion couples made of

11   single crystal spinel and thin films of hercynitic composition ($X_{Fe} \sim 0.5$) were used for the diffusion

12   anneals. The experimentally induced diffusion profiles were analyzed by Rutherford Backscattering

13   Spectroscopy to retrieve true depth concentration profiles for Fe. These were fitted numerically by an

14   explicit finite difference scheme that allows compositionally dependent interdiffusion processes to be

15   modelled by relating self- and interdiffusion coefficients. Synthesis of data from the two diffusion

16   couples indicate that: (a) D_{Fe-Mg} depends on X_{Mg} of spinel, with increasing diffusion rates with

17   increasing X_{Mg}. This behaviour is opposite of that found in silicates. (b) Self diffusion coefficients

18   could not be determined from these experiments, but the results indicate that $D_{Fe}/D_{Mg} > 100$. (c) D_{Fe-Mg}

19   in Mg-spinel is independent of oxygen fugacity whereas it depends strongly and non-linearly on

20   oxygen fugacity for the natural spinel. This observation indicates that the mechanisms of diffusion are

21   different in the two kinds of spinel (Fe-bearing vs. Fe-free), which is also seen in the difference in

22   activation energy obtained for these. Moreover, the non-linear dependence on oxygen fugacity

23   indicates that diffusion occurs by an interstitial mechanism at low oxygen fugacities and by a vacancy

24   mechanism at high oxygen fugacities in natural, Fe-bearing spinel. (d) Simple Arrhenius relations that

25   describe the data within the range of experimental conditions are - Synthetic magnesium spinel: Q_{FeMg}

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26    $=213 \pm 14$ kJ/mol, $\log_{10}D_{Fe\text{-}Mg}=-8.02\pm0.67$[m^2/s]. Natural Fe-bearing spinel for $\log_{10}$ (fO$_2$ [Pa]) = -12):

27    $Q_{FeMg}=139 \pm 18$ kJ/mol, $\log_{10}D_{Fe\text{-}Mg}=-12.33\pm 0.85$[m^2/s]. A model based on point defect considerations,

28   that describes the temperature as well as oxygen fugacity dependence of $D_{Fe\text{-}Mg}$ in Fe-bearing spinel is:

29   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]),

30   with D$_v$ = 1.07x10^{-09} ± 1.55x10^{-09} m^2/s , Q_v=131 ± 66 kJ/mol, D_i=1.03x10^{-17} ± 7.32x10^{-17} m^2/s,

31   Q_v=130 ± 80 kJ/mol and m=0.34 ±0.18. Poor coverage of T-fO$_2$ space by available experimental data

32   results in large uncertainties in the fit parameters. As a result, these expressions are useful for

33   understanding the diffusion behaviour in spinels, but not for extrapolation and calculation of diffusion

34   coefficients for cooling rate or other related calculations. Until the parameters can be better constrained

35   through the availability of more data, we recommend that for such calculations, the parameters noted

36   above for Fe-bearing spinels be used for compositions and fO$_2$ conditions that are close to those of the

37   experiments. (e) $D_{Fe\text{-}Mg}$ in spinel is faster than $D_{Fe\text{-}Mg}$ in olivines, pyroxenes and garnets at most

38   conditions.

39   **Keywords:** Spinel; diffusion coefficient; diffusion mechanism; point defect; thin films; pulsed laser

40   deposition; Rutherford Backscattering Spectroscopy;

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42   **Introduction**

43   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

44   a wide range of metamorphic and ultramafic rocks, an important mineral inclusion found in chondritic

45   meteorites of the early solar system, and it has also been found in lunar rocks (see references in the

46   review by Van Orman and Crispin, 2010). Because of its wide range of thermodynamic solid solutions,

47   spinel may form in a variety of different tectonic environments and its chemical composition has been

48   used to infer the physicochemical conditions under which its host rocks have formed (e.g. Irving, 1965;

49   O'Neill and Wall, 1987; Ballhaus, 1991). Hence, knowledge of diffusion rates in spinel is of interest in

50   a number of geological and planetary science problems. For example, Sheng et al., (1992) studied the

51 Mg isotopic variations in spinel and coexisting silicates of the plagioclase-olivine inclusions in the

52 Allende meteorite to evaluate cooling rates based on Mg-self diffusion in spinel and equilibrium melt.

53 Ozawa (1983) used zoning patterns in spinel and coexisting olivine to constrain cooling rates of

54 ultramafic rocks of the Miyamori ultramafic complex. Similarly, Coogan et al. (2007) used the

55 partitioning of Mg and Fe^{2+} between olivine and spinel to infer cooling rates of the lower oceanic crust

56 and upper mantle, whereas Liermann and Ganguly (2002) studied the partitioning between spinel and

57 orthopyroxene to study the thermal history of diogenites. Apart from these, diffusion of Fe^{2+} in spinel is

58 believed to be a major process controlling maghemitization, by which magnetic minerals with spinel

59 structure become progressively oxidized but remain single phase spinels, which is an important feature

60 of submarine weathering (Freer and O'Reilly, 1980).

61   Although much emphasis has been placed on the temperature dependent exchange of Fe^{2+} and

62 Mg between olivine and spinel (e.g. Lehmann et al., 1983; Ozawa, 1983; Ozawa, 1984; Kessel et al.,

63 2006; Coogan et al., 2007) and orthopyroxene and spinel (e.g. Liermann and Ganguly, 2001, 2002,

64 2003) in order to constrain complex thermal histories and cooling rates, aspects of Fe^{2+}-Mg

65 interdiffusion in spinel, such as the nature of dependence of diffusion rates on oxygen fugacity, still

66 remain unclear. Freer and O'Reilly (1980) were the first to determine the activation energy and the

67 Fe^{2+}-Mg interdiffusion coefficient, D_{Fe-Mg} in aluminous spinel as a function of temperature (800-1034

68 °C) and composition ($FeAl_2O_4$-$MgAl_2O_4$) using diffusion couples composed of synthetic pellets. Their

69 data reveals a strong compositional dependency where D_{Fe-Mg} increases with decreasing Fe^{2+} content in

70 spinel. Sheng and co-workers (1992) measured Mg self diffusion (D_{Mg}) in aluminous spinel

71 ($MgAl_2O_4$) and coexisting melt at bulk chemical equilibrium using an isotopic tracer at 1261-1553 °C.

72 More recently Liermann and Ganguly (2002) have determined the diffusion kinetics of Fe^{2+} and Mg in

73 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

74 1125 °C. Comparison of their data with those of Freer and O'Reilly implies that Fe^{2+}-Mg interdiffusion

75 might be much slower than previously thought. Also, in contrast to the complex profiles measured by

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76   Freer and O'Reilly (1980), Liermann and Ganguly (2002) found simple symmetric diffusion profiles

77   that indicate a weak compositional dependency. Suzuki et al. (2008) found that Fe-Mg interdiffusion

78   might be strongly dependent on the Cr-Al ratio in spinel, but the authors based their inference on a

79   single experiment and assumed D_{Mg} and D_{Fe} to be equal and thus independent of Mg/(Mg+Fe).

80   However, none of these studies considered the effect of varying oxygen fugacity upon the rate

81   of diffusion, which could have a significant effect not only on the diffusion rate itself but also on the

82   point defect chemistry and hence diffusion mechanisms, as has been reported for magnetite based

83   spinels (e.g. Dieckmann and Schmalzried, 1977a,b; Hallron and Bowen, 1980; Dieckmann and

84   Schmalzried, 1986; Dieckmann et al., 1987; Töpfer et al., 1995, Aggarwal and Dieckmann, 2002a,

85   Aggarwal and Dieckmann, 2002b). It would also be useful to extend the data set to lower temperatures

86   to obtain better constraints on activation energies of diffusion. The aim of this study is to characterize

87   the temperature dependent Fe^{2+}-Mg interdiffusion in aluminous spinel in particular at temperatures

88   below 1000 °C and to verify possible effects of oxygen fugacity and composition on the diffusion

89   mechanism. Here we present an experimental study on Fe^{2+}-Mg interdiffusion in spinel as a function of

90   oxygen fugacity ($\log_{10}$ [fO_2 Pa] =-14 to -10), temperature (750-900 °C) and composition and discuss

91   mechanisms of diffusion. In the process, we explore whether it is possible to reconcile the various data

92   sets that are available in the literature in the framework of one consistent model.

93

94   **Methods**

95   **Starting material**

96   We have prepared diffusion couples made of single crystals of Mg-rich aluminous spinel and 30-80 nm

97   thick films of synthetic Fe^{2+}-rich spinel. Crystals of two different compositions were used for the

98   experiments –a synthetic aluminous spinel (Sp1: $MgAl_2O_4$) and a natural gem-quality spinel (Sp2:

99   $(Mg_{0.93}Fe_{0.07})(Al_{1.997}Cr_{0.003})O_4$) from Sri Lanka. The synthetic crystals were obtained from CrysTec

100 GmbH (Berlin, Germany). The compositional difference between diffusion couples involving Sp1 and

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101   Sp2 enable a test of the role of Fe in influencing diffusion rates in spinel. All crystals were cut into

102   pieces with dimensions of approximately 1-2 mm x 2 mm x 2 mm and polished mechanically using

103   diamond compounds, followed by a final step of mechano-chemical polishing using colloidal silica.

104   Thin films of Fe^{2+}-rich spinel were deposited on these polished samples using Pulsed Laser Deposition

105   (PLD). The source material (target) used for all depositions was a polycrystalline spinel pellet with a

106   hercynite content of 50% $(Fe_{0.5}Mg_{0.5})Al_2O_4$ synthesized from powdered oxide mixes. A detailed

107   description of the method, experimental setup and target preparation used in similar studies in our

108   laboratory is given in Dohmen et al. (2002) and Dohmen et al. (2007). To ensure that the polished

109   crystal surfaces are free of any volatile absorbents, all samples were heated in vacuum (<6 x 10^{-1}Pa) at

110   600 °C for 15-20 minutes before the deposition. The synthetic target, $(Fe_{0.5}Mg_{0.5})Al_2O_4$, was ablated

111   using an ArF-excimer laser with a wavelength of 193 nm at laser fluences of a few J/cm^2 which formed

112   a stoichiometric conversion of all components of the target into a plasma that finally condenses on the

113   substrate (single crystal spinel). Typically 4 samples were deposited at the same time of which one was

114   used as a reference sample to infer the film thickness and initial composition of the deposited film.

115   Previous studies have shown that the variations in film thickness among those crystals are less than

116   10% (Dohmen et al., 2002). Likewise, no compositional variations have been detected for any given

117   deposition. A detailed list of the deposition conditions is given in Table 1.

118

Diffusion Anneal

120   All diffusion anneals were carried out in a gas-mixing furnace at atmospheric pressure under controlled

121   oxygen fugacity. To induce Fe^{2+}-Mg interdiffusion, the diffusion couples were annealed at

122   temperatures between 750-900°C for varying lengths of time, during which the oxygen fugacity was

123   buffered using a continuously flowing gas mixture of CO-CO_2 (10^{-14}-10^{-10} Pa). Both, temperature and

124   oxygen fugacity, were continuously monitored in situ by a type B thermocouple (Pt/Rh6%-Pt/Rh30%)

125   and a fO_2-sensor (ZrO_2) and controlled within ± 1 °C and ± 0.1 $\log_{10}$ units, respectively. The

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126 reproducibility of the data was tested by repeating experiments at 800 °C and for different durations.

127 Conditions of all diffusion anneals are summarised in Table 2.

128   The surface topography of the samples was analysed using reflected light microscopy and some

129 selected samples were investigated using scanning electron microscopy and white-light phase-shifting

130 interference microscopy. The structure of the initially amorphous thin layer was also analysed using

131 electron backscatter diffraction (EBSD).

132

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

134 Film thickness and composition of the reference samples and detailed analysis of the compositional

135 changes of spinel across the interface of the diffusion couples were measured using Rutherford

136 Backscattering Spectroscopy (RBS). RBS is widely used for near surface analysis of solids and there is

137 a growing number of studies that use RBS for diffusion related problems in the earth sciences (e.g. see

138 Cherniak et al., 1991; Jaoul et al., 1991; and Dohmen et al., 2002; Dohmen et al., 2007 for related

139 studies from our laboratory). The analyses shown in this study were performed at the Dynamitron

140 Tandem Accelerator Laboratory of the Ruhr-University of Bochum. The 4 Mev tandem accelerator was

141 used to generate a beam of α-particles at 2 MeV that was focused onto the spinel samples. A final

142 aperture of 0.5 mm diameter enables to analyze samples with surface areas as small as 1 mm^2. A beam

143 current of 20-50 nA was typically used for the measurement. To prevent charging of samples, the sides

144 of sample crystals were coated with an Ag solution to allow for direct contact with the metallic sample

145 holder. The backscattered particles were detected at an angle of 170 ° with a silicon particle detector at

146 an energy resolution of about 16-20 keV. The sample surface was tilted at 5 ° relative to the beam to

147 prevent channeling.

148   Element distributions and film thicknesses were simulated by an iterative procedure to fit the

149 measured spectra using the software RBX (Kótai, 1994), which enabled us to retrieve true

150 concentration depth profiles for Fe and Mg spanning up to 400 nm. Because the depth profiles of

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151 heavier elements are better constrained using RBS, only the well-defined Fe concentration profiles

152 were fitted in the following. A typical RBS spectrum is shown in Fig. 1.

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

155 In a binary diffusion process, the net flux of Fe^{2+} and Mg^{2+} in a binary solid solution such as spinel

156 must be zero at any given point in order to maintain charge balance and stoichiometry. It is governed

157 by the same diffusion coefficient, which represents the interdiffusion coefficient of the two

158 components, $D_{Fe\text{-}Mg}$:

159

160
$$\frac{\partial C_{Fe}^{Sp}}{\partial t} = \frac{\partial}{\partial x}\left[D_{Fe-Mg}^{Sp}\frac{\partial C_{Fe}^{Sp}}{\partial x}\right] \quad (1)$$

161

162 We have used an explicit finite difference scheme (e.g. see Costa et al., 2008) to solve for equation (1)

163 in order to calculate compositionally dependent interdiffusion coefficients to fit the concentration depth

164 profiles extracted from the RBS spectra. A compositionally dependent $D_{Fe\text{-}Mg}$ is calculated at each grid

165 point to calculate concentration profiles according to:

166

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

167

168 C_i^n represents the concentration at the location i at the current timestep, n, whereas $n+1$ represents the

169 new (future) concentration (C_i^{n+1}), Δt is the timestep, Δx is the grid spacing and D_i^n refers to the

170 diffusion coefficient, $D_{Fe\text{-}Mg}$, at a given composition (at node i) and time-step,n. We assume constant

171 grid spacing, zero flux at the top of the thin film and constant flux at the bottom i.e. the interior of the

172 crystal.

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173   The interdiffusion coefficient is related to the self-diffusion coefficients D_{Mg}, D_{Fe} and the

174   thermodynamic properties of the silicate / oxide according to (e.g.: Barrer, 1963):

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176
$$D_{Fe-Mg}^{Sp} = \frac{D_{Fe}^{Sp} D_{Mg}^{Sp}}{X_{Fe} D_{Fe}^{Sp} + X_{Mg} D_{Mg}^{Sp}} \left[1 + \frac{\partial ln \gamma_{Fe}^{Sp}}{\partial ln X_{Fe}^{Sp}} \right] \quad (2)$$

177

178   where D_{Fe-Mg}^{Sp} is the interdiffusion coefficient at a given composition, D_{Fe}^{Sp} and D_{Mg}^{Sp} are the self-

179   diffusion coefficients of Fe^{2+} and Mg^{2+}, X_i is the mole fraction of a component i, where i = Fe^{2+} or

180   Mg^{2+} in this study, and γ_{Fe}^{Sp} is the thermodynamic activity coefficient of the Fe-component, all at the

181   same composition at which D_{Fe-Mg} is to be calculated. This relationship provides a theoretical basis for

182   describing the compositional dependence of D_{Fe-Mg} that is used in Eqn. (1) and is more meaningful than

183   using arbitrary functions such as polynomials or power laws. It should be noted that the self-diffusion

184   coefficients D_{Fe} and D_{Mg} themselves might also depend on the major element composition, in which

185   case the compositional dependence of D_{Fe-Mg} is even stronger. The term in parentheses, called the

186   thermodynamic factor, is equal to one if the solid solution behaves ideally (or nearly ideally), which is

187   the case for the mixing of Fe^{2+}- and Mg-components in spinel (Liermann and Ganguly, 1999; Liermann

188   and Ganguly, 2003).

189   In a situation where Fe^{2+} and Mg are exchanged, the shapes and lengths of concentration

190   profiles are controlled by the interdiffusion coefficient, D_{Fe-Mg}, and its compositional dependence as

191   given, for example, by Eqn. 2. However, as the relationship between D_{Fe-Mg}, D_{Fe} and D_{Mg} is non-linear,

192   it is worth exploring the sensitivity of the different diffusion parameters in Eqn. (2) to compositional

193   variation, particularly if D_{Fe} and D_{Mg} are not similar to each other. A question that will become

194   particularly relevant is: To what extent may the quantities D_{Fe} and D_{Mg} be constrained from the profile

195   shapes in different compositions and for different (D_{Fe}/D_{Mg})?

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196   If D_{Fe} and D_{Mg} are similar to each other, then it follows from Eqn. (2) that in the limiting case

197   when one of the components is dilute (e.g. $X_{Fe} \rightarrow 0$), the interdiffusion coefficient approaches the self-

198   diffusion coefficient of the dilute component (i.e. $D_{Fe\text{-}Mg} \sim D_{Fe}$). To illustrate the total range of

199   possibilities, we have plotted the relationship between $D_{Fe\text{-}Mg}$, D_{Fe} and D_{Mg} for a wide range of values

200   of D_{Fe} and D_{Mg} for different compositions, with these quantities, and hence also (D_{Fe}/D_{Mg}), varying

201   over 10 orders of magnitude (Fig. 2). The median values of $D_{Fe\text{-}Mg}$, D_{Fe} and D_{Mg} are arbitrarily chosen

202   to be 1 x 10^{-18} m^2/s for the purpose of illustration – the choice of this value has no effect on the

203   discussion that follows.

204   For a given spinel composition (X_{Fe}) and D_{Fe}/D_{Mg} there exists a minimum value of the ratio

205   where $D_{Fe\text{-}Mg}$ is effectively equal to D_{Fe} and a maximum where $D_{Fe\text{-}Mg}$ approaches D_{Mg}. These two ratios

206   delineate a band (Fig. 2) within which $D_{Fe\text{-}Mg}$ (and hence profile lengths) are determined by both D_{Fe}

207   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

208   within this band. If D_{Fe} and D_{Mg} differ by more than a couple of orders of magnitude, then the profile

209   lengths and shapes become effectively independent of one of the quantities and this quantity cannot be

210   constrained from the data. See also Borinski et al. (2012) for a related discussion on multicomponent

211   systems. With increasing molar fraction of the hercynite component (X_{Fe}), the band shifts to lower

212   values. We have illustrated this behaviour for four spinel compositions in Figs. 2.

213   For example for $X_{Fe} = 0.001$, the composition of Sp1 in this study, for $D_{Fe}/D_{Mg} < 100$, $D_{Fe\text{-}Mg} \approx$

214   D_{Fe}, but for $D_{Fe}/D_{Mg} > 10000$ one has $D_{Fe\text{-}Mg} = D_{Mg}$ (Fig. 2a). In between these two ratios $D_{Fe\text{-}Mg}$ is

215   dependent on both tracer diffusion coefficients. It follows that diffusion profiles in Sp1 can be used to

216   extract $D_{Fe\text{-}Mg}$ and this quantity is essentially D_{Fe}, whereas D_{Mg} cannot be constrained (unless $D_{Mg}/D_{Fe} <$

217   0.001). With incorporation of Fe, at $X_{Fe} = 0.07$ (the composition of Sp2) if $D_{Fe}/D_{Mg} < \sim 1$, $D_{Fe\text{-}Mg} = D_{Fe}$,

218   and if $D_{Fe}/D_{Mg} > \sim 100$, $D_{Fe\text{-}Mg} = D_{Mg}$ (Fig. 2b). Similarly, for $X_{Fe} = 0.5$ (the composition of the thin

219   film) the band lies between D_{Fe}/D_{Mg} 0.1 and 10 (Fig. 2c). Therefore, assuming that D_{Fe} and D_{Mg} are

220   constant, different diffusion profile shapes and lengths can be expected depending on D_{Fe}/D_{Mg} and the

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221   initial chemical gradient as defined by the diffusion couple in the experiment. If $D_{Fe}/D_{Mg} > 100$ for the

222   diffusion couple Sp2/thin film, $D_{Fe\text{-}Mg}$ would be effectively constant and equal to D_{Mg}. However, if in

223   addition $D_{Fe}/D_{Mg} < 10000$ (i.e. $100 < D_{Fe}/D_{Mg} < 10000$), then for the diffusion couple Sp1/thin film

224     $D_{Fe\text{-}Mg}$ would depend strongly on composition. $D_{Fe\text{-}Mg}$ changes by about two orders of magnitude

225   between Sp1 and the thin film ends of the diffusion couple and distinctly asymmetric profile shapes

226   would be observed. In addition $D_{Fe\text{-}Mg}$ of Sp1 would depend on D_{Fe} and D_{Mg} and the two quantities

227   cannot be constrained independently of each other. At $X_{Fe} \sim 0.999$, the roles of D_{Mg} and D_{Fe} are

228   reversed from that discussed for $X_{Fe} \sim 0.001$ (Fig. 2d).

229

230   **Results and discussion**

231

232   **Sample characterization: Stoichiometry, structure and topography**

233   Surface topography, film thickness and stoichiometry of the samples were analysed before and after the

234   diffusion anneal using reflected light spectroscopy, scanning electron microscopy, EBSD, white light

235   interference microscopy, and RBS.

236   No substantial differences have been observed between the surfaces of the polished single crystals and

237   the coated samples using reflected light microscopy and white light interference microscopy (Fig. 3 a

238   and b). Structural characterization of the samples before and after the diffusion anneal have been

239   performed using EBSD. Distinct diffraction patterns obtained from the annealed samples show that the

240   initially amorphous thin film crystallized during the diffusion anneal. SEM images show that when rare

241   scratches were present on the sample surface, these are still visible after coating and subsequent

242   annealing. This implies that the thin film follows the surface topography of the substrate (single crystal)

243   and that crystallization does not change the surface topography of the sample. Measurement of

244   topographic variations using white light interference microscopy in different regions of the surfaces of

245   samples (e.g. two examples shown in Fig. 3 a and b) reveal that the total variation of topography is on

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246   the order of ± 1.5 nm (Sp1) to ± 6-10 nm (Sp2). The film thickness, measured by RBS analysis, varied

247   in the range 25-85 nm (Table 2) in different samples. Compositional analysis of the nominally pure

248   spinels (Sp1) revealed moreover that these contain minor Fe (X_{Fe}=0.001) that could be detected using

249   RBS.

250

251   **Diffusion Profiles**

252   Fe^{2+} concentration profiles found in the diffusion couples of Sp1 (Fig. 4a) show a marked asymmetry

253   around the inflection point (where the sign of the second derivative of C(x) changes), whereas profiles

254   in Sp2 (Fig. 4b) are less asymmetric. The asymmetry indicates a compositional dependence of D_{Fe-Mg}.

255   In both cases, Fe^{2+}-Mg interdiffusion appears to be faster (i.e. slopes of concentration profiles are

256   gentler) on the iron-poor side of the diffusion couple. This behaviour is opposite of the behaviour seen

257   in silicates such as olivine or garnet, where diffusion rates tend to increase with Fe-content. The

258   difference may arise because diffusion in spinel can occur by vacancy as well as interstitial

259   mechanisms; this aspect will be discussed in more detail below. The asymmetric diffusion profile

260   shapes could be reproduced by assuming constant self diffusion coefficients (insensitive to

261   compositional changes) in Eqn. (2), with D_{Fe} greater than D_{Mg}. It is found that fits to the observed

262   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.

263   Under these circumstances the diffusion couple Sp2/thin film does not provide a strong constraint on

264   compositional dependence of diffusion coefficients. Fig. 2 indicates that for Sp1, if $D_{Fe}/D_{Mg} \sim$ 100, then

265     $D_{Fe-Mg} \sim D_{Fe}$; if $D_{Fe}/D_{Mg} >$ 10000, then $D_{Fe-Mg} \sim D_{Mg}$. It is not possible to distinguish between these

266   scenarios (i.e. whether D_{Fe} or D_{Mg} or both control the observed profiles) based on our data, although

267   D_{Fe-Mg} itself can be determined robustly. For Sp2, with $D_{Fe} > D_{Mg}$ as indicated by the asymmetry of the

268   profile, D_{Fe-Mg} lies within an order of magnitude of D_{Mg} (Fig. 2). The values of D_{Fe-Mg} that are obtained

269   from calculated profiles that best describe the observed profile lengths and shapes for both

270   compositions are reported in Table 2. Variations in D values obtained from different crystals annealed

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271 at the same conditions over different lengths of time indicate a reproducibility of 0.11 $\log_{10}$ units for the

272 measured D values (Fig. 5) and this provides a useful estimate of the uncertainty in D.

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

275 The retrieved $D_{Fe\text{-}Mg}$ values as a function of oxygen fugacity ($\log_{10} (fO_2[Pa]) = $ -14 to -10 at constant

276 pressure (10^5 Pa) and temperature (800 °C) are shown in Fig 6. In the nominally pure spinel Sp1

277 diffusion coefficients are independent of oxygen fugacity within the uncertainty of the data. In the Fe-

278 bearing spinel Sp2 there is a clear dependence of diffusion rates on oxygen fugacity and the

279 dependence of $\log_{10}$ D on $\log_{10} fO_2$ is not linear (Fig. 6).

280 While there is extensive work in the literature on cation diffusion in magnetite-based spinels,

281 comparably little is known about Fe^{2+}-Mg interdiffusion in aluminous spinels (e.g. Van Orman and

282 Crispin, 2010). Because there are two different cation sublattices in spinel, a number of different

283 migration mechanisms are possible (Dieckmann and Schmalzried, 1977a,b; Murphy et al., 2009). A

284 direct comparison of the point defect chemistry of magnetite and $(Fe,Mg)Al_2O_4$ should therefore be

285 considered with caution because magnetite and aluminous spinel have different crystal structures. In

286 $MgAl_2O_4$ –spinel, Mg^{2+} occupies the tetrahedral and Al^{3+} the octahedral sites. Magnetite, on the other

287 hand, has an inverse spinel structure at low temperatures. Fe^{2+} and Fe^{3+} occupy the octahedral sites in

288 equal proportions, and Fe^{3+} is the sole occupant of the tetrahedral sites (e.g. Verwey, 1947). Bearing

289 this caveat in mind, it is worthwhile nevertheless to compare the dependence of diffusion rates found in

290 this study with those obtained for magnetite. Diffusivities in magnetite have been reported to vary non-

291 linearly as a function of oxygen fugacity according to the expression of the form:

292

293 $D = D_v(T) fO_2^{2/3} + D_i(T) fO_2^{-2/3}$ (3)

294

12

295   where D is the total diffusivity and $D_v(T)$ and $D_i(T)$ refer to temperature dependent components of

296   diffusivity by the vacancy (v) and interstitial (i) mechanisms, respectively. The inferred fO_2 exponents

297   of $-^2/_3$ at low and $^2/_3$ at high oxygen fugacities were used to demonstrate that cation vacancies and

298   cation interstitials were the majority defects at high and low oxygen fugacities, respectively

299   (Dieckmann and Schmalzried, 1977a,b; Hallron and Bowen, 1980; Dieckmann, 1982; Dieckmann and

300   Schmalzried, 1986; Dieckmann et al., 1987; Töpfer et al., 1995; Aggarwal and Dieckmann, 2002a,

301   Aggarwal and Dieckmann, 2002b; see also Van Orman and Crispin, 2010 for a review). Our data on

302   Fe^{2+}-Mg diffusion in Sp2 shows a dependence on oxygen fugacity that is practically identical to the

303   dependence observed for magnetite (Fig. 6) – lines drawn according to Eqn. 3 with slopes of $^2/_3$ and $^{-2}/_3$

304   describe the data set very well, indicating that in spite of the structural differences between magnetite

305   and Fe^{2+}-Mg spinel, diffusion by an interstitial mechanism at low oxygen fugacities and by a vacancy

306   mechanism at higher oxygen fugacities occurs in $(Fe^{2+},Mg)Al_2O_4$ as well. Therefore, unlike in other

307   systems such as olivine, it is not possible to use a single fO_2-exponent to correct for the effect of fO_2 on

308   diffusion rates in spinels over the entire range of their stability. In contrast to the behaviour of Sp2, the

309   data on nominally Fe-free spinel Sp1 show no resolvable dependence on fO_2 (Fig. 6), showing that

310   diffusion occurs in the two spinels by different mechanisms.

311

312   The temperature dependence of diffusion coefficients obtained from all experiments on Mg-spinel

313   (Sp1) and the natural Fe-bearing spinel (Sp2) at $\log_{10} [fO_2\ Pa] = -12$ are shown in Fig. 7 in the form of

314   an Arrhenius plot (750-900 °C). It is seen that over the experimental range of temperature, diffusion in

315   the Mg-rich spinel Sp1 is faster than in the Fe-bearing spinel Sp2. The slopes of the best-fit lines to the

316   data indicate that the activation energy for diffusion in Sp1 is higher than for diffusion in Sp2. The

317   difference in activation energy implies that there will be a crossover at lower temperatures where

318   diffusion in the Fe-bearing spinel may become faster. A linear least squares fit yields the following

13

319   values of the pre-exponential factor, D_0, and the activation energy, Q, in the Arrhenius relation: $D =$

320     $D_0 exp(-Q/RT)$, where R is the gas constant and T is the absolute temperature:

321

322   Synthetic magnesium spinel (Sp1)

323   Q_{FeMg} =213 ± 14 kJ/mol

324     $Log_{10} (D_{0FeMg} [m^2/s]) = -8.02±0.67$

325

326   Natural Fe-bearing spinel (Sp2)

327   Q_{FeMg}=139 ± 18 kJ/mol

328     $Log_{10} (D_{0FeMg} [m^2/s]) = -12.33± 0.85$

329

330   The activation energies in the two spinels differ, as has been found in other studies as well (e.g. Sheng

331   et al., 1992, Liermann and Ganguly, 2002), because diffusion occurs by different mechanisms in the

332   two spinels, as discussed above. Similar differences in diffusion behaviour between Fe-bearing and Fe-

333   free crystals have also been found in the olivine solid solution series (e.g. see Chakraborty et al., 1994;

334   Chakraborty, 2010). Consequently, an interim conclusion is that for applications dealing with natural,

335   Fe-bearing spinels, the Arrhenius relation obtained for Sp2 should be used. This aspect is considered in

336   more detail below.

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

338   Fig. 8 shows a comparison of the Arrhenius relations reported in different studies on D_{Mg} and D_{Fe-Mg} in

339   aluminous spinel. Sheng et al (1992) determined Mg tracer diffusion coefficients in pure Mg-spinel at

340   temperatures between 1260 – 1550 °C with an activation energy of 384 kJ/mol. Our data on D_{Fe-Mg} in

341   pure Mg-spinel at lower temperatures yield a much lower activation energy of 219 kJ/mol. This

342   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

343   have no information on D_{Mg}, or (b) the addition of Fe during diffusion in our experiments alters the

14

344   point defect chemistry and diffusion mechanism, or (c) If $D_{Fe}/D_{Mg} > 300$, then $D_{Fe-Mg} \sim D_{Mg}$ (Fig. 2),

345   and the difference could result from a transition from an intrinsic diffusion mechanism at high

346   temperatures (Sheng et al., 1992) to extrinsic diffusion at lower temperatures (this study). To choose

347   between these alternatives it is necessary to obtain data at intermediate temperatures or determine D_{Mg}

348   directly at low temperatures.

349   Liermann and Ganguly (2002) determined D_{Fe-Mg} at high temperatures and pressures in a spinel

350   of very similar composition to Sp2, whereas Freer and O'Reilly (1980) determined D_{Fe-Mg} as a function

351   of composition using diffusion couples made of pure Mg- and Fe-spinels enclosed in evacuated silica

352   tubes. Van Orman and Crispin (2010) and Liermann and Ganguly (2002) argue that the presence of

353   oxidizing conditions and extended defects in the crystals may have affected the results of the study of

354   Freer and O'Reilly (1980). Liermann and Ganguly (2002) fit their interdiffusion profiles using D_{Fe} and

355   D_{Mg} that were related by Equation (2). Based on the observed symmetry of their profile shapes, they

356   inferred that there was no significant compositional dependence and that $D_{Fe} \sim D_{Mg}$. However, our

357   analysis above indicates that $D_{Fe} \sim D_{Mg}$ need not be necessarily fulfilled for spinels of composition Sp2,

358   and that symmetric profile shapes may be produced even when $D_{Fe} \neq D_{Mg}$ (Fig. 2). To illustrate this

359   aspect (Fig. 9), we have calculated a synthetic profile (points in Fig. 9) with $D_{Fe} = D_{Mg}$ using one of

360   the data points of Liermann and Ganguly (2002): 21.4×10^8 Pa, 1125 °C, 51 hours (Sp-diff05d). Next,

361   we have produced "best fit" profiles to this data set (Fig. 9) using (a) $D_{Fe}/D_{Mg} = 1$, (b) $D_{Fe}/D_{Mg} = 10$

362   and (c) $D_{Fe}/D_{Mg} = 100$. It is seen that there is very little difference in the calculated profile shapes and

363   in particular, there is no pronounced asymmetry even when $D_{Fe}/D_{Mg} = 100$. Although it is possible to

364   distinguish the quality of fit in this perfectly ideal calculated profile shape, it is conceivable that with

365   real analytical data showing some scatter it would be difficult to distinguish between these possibilities.

366   This happens because at these conditions ($X_{Fe} \sim 0.01$, $D_{Fe} > D_{Mg}$), D_{Fe-Mg} is always essentially equal to

367   D_{Mg} and is insensitive to the value of D_{Fe} (Fig. 2). Therefore, the data set of Liermann and Ganguly

368   (2002) is also consistent with our inference that $D_{Fe} > D_{Mg}$, by a factor of 100 or more. In the subsequent

15

369 discussion, therefore, we consider the D_{Fe-Mg} values obtained by Liermann and Ganguly (2002) and not

370 the D_{Fe} and D_{Mg} values that they extracted from the profiles (see discussion above related to profile

371 shape and length in an interdiffusion experiment and the role of D_{Fe-Mg}, D_{Fe} and D_{Mg}).

372   As the study of Liermann and Ganguly (2002) was carried out in graphite capsules in a piston

373 cylinder apparatus, the oxygen fugacity of their experiments was constrained to be between the C-O

374 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

375 water and graphite in the piston cylinder cell); see Chakraborty and Ganguly (1992) for more details for

376 a similar setup. However, oxygen fugacity along a buffer reaction curve is not constant at different

377 temperatures and therefore the temperature dependence of the buffer reaction gets incorporated into the

378 calculated apparent activation energy of diffusion. Moreover, as seen above, the oxygen fugacity

379 dependence of D_{Fe-Mg} is non-linear. This makes it difficult to compare the Arrhenius relation of

380 Liermann and Ganguly (2002) directly with our data. We have chosen an alternative option to analyse

381 the data. Considering the nature of fO_2 dependence of D_{Fe-Mg} in Fe-bearing spinel (Fig. 6), which can be

382 rationalized by a point defect thermodynamic model, we have explored whether it is possible to

383 describe both sets of D_{Fe-Mg} data taken together (i.e. Liermann and Ganguly, 2002; this study) in the

384 framework of one comprehensive model:

385

386 $D[m^2/s] = D_v[m^2/s]fO_2[Pa]^m\exp(-Q_v[J/mol]/RT[K]) + D_i[m^2/s]fO_2[Pa]^{-m}\exp(-Q_i[J/mol]/RT[K])$ (4)

387

388 We obtain the following fit parameters:

389 $D_v = 1.07\times10^{-09} \pm 1.55\times10^{-09}$ m^2/s $\log_{10}D_v = -9.0$ [m^2/s]

390 $Q_v = 131 \pm 66$ kJ/mol

391 $D_i = 1.03\times10^{-17} \pm 7.32\times10^{-17}$ m^2/s $\log_{10}D_i = -17.0$ [m^2/s]

392 $Q_v = 130 \pm 80$ kJ/mol

393 m=0.34 ±0.18,

16

394   where R [J K^{-1}mol^{-1}] is the universal gas constant.

395   The resulting fit to the data is shown in Fig. 10. In spite of the relatively large uncertainties resulting

396   from the limited body and spread of data, it is seen that the results are consistent with the general

397   behaviour predicted by the point defect model. In particular, the fit parameters also describe other data

398   sets (e.g. Freer and O'Reilly, 1980 and Suzuki et al., 2008), that were not included in the fitting

399   procedure, quite well (see below). The best fit fO_2 exponent is different from 2/3 in the magnetite

400   model. This could be because Fe-Mg spinel behaves differently from magnetite, or simply the result of

401   scatter of our data – detailed experiments as a function of fO_2 at several temperatures would be required

402   to adequately quantify this aspect. The limited spread of data in T-fO_2 space results in high

403   uncertainties in the fit-parameters so that these are not suitable for calculation of diffusion coefficients

404   at extrapolated conditions. However, the mean values of the fit-parameters provide several important

405   insights into the diffusion behaviour of Fe-Mg in Fe-bearing spinel. For example, a consequence of

406   this analysis is the recognition that although the fO_2 dependence of D_{Fe-Mg} in spinel is non-linear, for the

407   range of temperatures and oxygen fugacity conditions that are relevant for at least most applications to

408   terrestrial samples, a positive dependence of D_{Fe-Mg} on fO_2 (corresponding to diffusion by dominantly a

409   vacancy mechanism) is adequate. The activation energy of 130 kJ/mol is slightly higher than the 50 –

410   100 kJ/mol migration energy of diffusion that is calculated in computer simulations (e.g. Murphy et al.,

411   2009). This fact, combined with the observed dependence of diffusion rates on oxygen fugacity (i.e. an

412   externally imposed chemical potential), indicates that Fe-Mg diffusion in spinels occurs by a transition

413   metal extrinsic diffusion (TaMED) mechanism (see Chakraborty, 1997 for details on the characteristics

414   of TaMED mechanism).

415   Fig. 10 shows calculated diffusion coefficients using the mean values of the fit parameters as a

416   function of temperature and oxygen fugacity with the experimentally measured data points from

417   different studies shown as well for comparison. Fig. 10a shows individual data points from our study as

418   well as all earlier studies in Fe-bearing spinel (Freer and O'Reilly, 1980; Liermann and Ganguly, 2002;

17

419   Suzuki et al., 2008) as a function of temperature in an Arrhenius diagram. For the inferred fO_2

420   condition of each study, we have calculated diffusion coefficients at each experimental condition using

421   the fit parameters above (shown as red squares in Fig. 10a). It is seen that all of the experimentally

422   measured data are consistent with the above relationship. Moreover, we have fit Arrhenius type

423   relationships to the calculated dataset for each study (i.e. Freer and O'Reilly, 1980, Liermann and

424   Ganguly, 2002, and for Sp2 data from this study), shown as dashed red lines. It is seen that the apparent

425   mismatch between studies and the scatter seen in Fig. 8 is almost completely reproduced. This indicates

426   that results from all experimental studies are in fact consistent with each other and may be described by

427   the model above; there is no need to invoke enhanced diffusion due to artefacts such as oxidation of

428   spinels. This exercise also underscores the need to consider the effect of oxygen fugacity in dealing

429   with diffusion in Fe-bearing spinels – the non-linear dependence can lead to a wide range of behaviour

430   so that simple linear extrapolations in Arrhenius plots can lead to incorrect results.

431   The diffusivities reported by Freer and O'Reilly (1980) (for a spinel composition of FeO= 25

432   wt% and FeO= 5 wt%) are 3 to 4 orders of magnitude higher than those obtained in this study (Fig. 8,

433   10a) but can be reproduced using the relationship given above (Eqn. 4, Fig. 10). Suzuki et al (2008)

434   obtained two data points for D_{Fe-Mg} (Fig. 8, 10a) which indicates that in addition to the factors

435   considered here, D_{Fe-Mg} also depends on Cr-content of spinel. D_{Fe-Mg} in Cr-free spinel is about a factor

436   of 7.5 smaller than in spinel with Cr# (= Cr/Cr+Al) = 0.9. Their diffusion coefficient for Cr-free spinel

437   can be reproduced using our expression (Eqn. 4). Therefore, for applications to mantle spinels

438   containing Cr, it should be considered that diffusion coefficients calculated using our expression could

439   be slightly smaller than the real values. Suzuki et al. (2008) measured Al-Cr interdiffusion in chromite

440   spinel at high pressure (9-7 GPa) and temperatures ranging from 1400-1700 °C by using diffusion

441   couples of natural single crystals of $MgAl_2O_4$ spinel and chromite. Fig. 8 shows a comparison of the

442   diffusivities obtained in this study with the Al-Cr interdiffusion coefficients for Cr#=0.8 and self

443   diffusion coefficients for Cr in spinel (Cr#=0) obtained by Suzuki et al. (2008). Extrapolation of the

18

444   data implies that Fe-Mg interdiffusion is faster than Al-Cr interdiffusion or Cr self diffusion in spinel at

445   temperatures relevant for the upper mantle. Empirical observations on diffusion in spinel at upper

446   mantle conditions confirm that Cr is the slowest diffusing species among all the cations (e.g. Ozawa,

447   1984; Suzuki et al., 2008). However one should note in view of the non-linear dependencies described

448   above that these relationships could be reversed at certain T-fO_2 conditions. Notwithstanding the

449   excellent consistency of diffusion behavior calculated using the mean values of the fit parameters and

450   various experimental data sets, the large uncertainties on the fit parameters make them poorly suited for

451   large extrapolations. Therefore, for the purpose of cooling rate or closure temperature calculations, we

452   recommend the direct fit to our data (Q_{FeMg}=139 ± 18 kJ/mol, $Log_{10} (D_{0FeMg} [m^2/s]) = -12.33± 0.85$) for

453   Fe-bearing spinel, to be used for compositions and fO_2 conditions similar to those of the experiments,

454   until availability of more data allow the model based on point defects to be better constrained.

455

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

457   Data for diffusion of Fe-Mg in all the phases that might coexist with spinel in the mantle are now

458   available. We compare the rates of Fe-Mg diffusion in Mg-Al spinel, olivine, garnet, clinopyroxene and

459   orthopyroxene in Fig. 11. For the purpose of comparison, we have calculated diffusion rates at a

460   constant composition of $X_{Fe} = 0.07$ where composition dependence is known to play a role (e.g.

461   olivine, garnet), although these are not necessarily the compositions that coexist in nature. It is found

462   that Fe-Mg diffusion in spinel is among the fastest among these under most circumstances.

463   Fe^{2+}-Mg interdiffusion in olivine has recently been summarized by Dohmen et al. (2007),

464   Dohmen and Chakraborty (2007) and Chakraborty (2010). The set of experiments presented in

465   Dohmen et al. (2007) was carried out following the same experimental procedure as described in this

466   study. Their data for diffusion along the c-axis are shown in Fig. 11 for an olivine composition of X_{Fe}=

467   0.07 (Fo93) at oxygen fugacities less than log [fO_2 Pa] = -10, by using the Arrhenian relation given by

468   these authors (Dohmen and Chakraborty, 2007). Diffusion in olivine is anisotropic and to obtain

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469   diffusion coefficients parallel to the a and b axis one needs to substract log(6) from the relation shown

470   in Fig.11., which decreases the $LogD_{Fe-Mg}$ values for olivine by 0.78 log units. Thus, at temperatures

471   less than 900 °C interdiffusion of Fe^{2+} and Mg is faster in spinel than in olivine (given X_{Fe}=0.07). Only

472   at temperatures above 900 °C $D_{Fe2+-Mg}$ may become faster in olivine, depending on the ambient fO_2.

473   Based on an empirical study of compositional gradients in olivine and coexisting spinel, Ozawa (1984)

474   concluded that D_{Fe-Mg} in spinel (Cr#<0.6) is a factor of 100 greater than that of olivine and that only for

475   Cr rich spinels (Cr#>0.7) Fe-Mg interdiffusion in spinel is the same order or smaller than that of

476   olivine. Depending on the ambient fO_2 and crystallographic orientation of olivine, this observation

477   could be consistent with the experimental data from this study, although more recent findings (Suzuki

478   et al., 2008) suggest that diffusion in Cr-bearing spinel is actually faster than in Cr-free spinel; the

479   influence of Cr on Fe-Mg diffusion needs to be studied through further detailed experiments.

480   Fe-Mg diffusion in spinel is at least two orders of magnitude faster than diffusion rates of Fe-

481   Mg in garnets (Borinski et al., 2012) and pyroxenes (Müller et al., 2013, Dohmen et al., 2014),

482   although the difference decreases at higher temperatures because of the low activation energy of D_{Fe-Mg}

483   in spinel (~ 130 kJ/mol) compared to those in other phases (> 200 kJ/mol).

484

485   **Conclusions**

486   We have carried out a set of diffusion experiments on Fe^{2+}-Mg interdiffusion in a pure Mg-spinel and a

487   natural spinel from Sri Lanka (X_{Fe} ~ 0.07). The measured concentration profiles were treated using an

488   explicit finite difference scheme to obtain diffusion coefficient as a function of temperature (750-900

489   °C), oxygen fugacity (log [fO_2 Pa] = -14 to -10) and composition. The main findings are as follows:

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

491   2) Although it is not possible to constrain the exact values of the tracer diffusion coefficients D_{Fe}

492   and D_{Mg}, results from both crystals indicate that $D_{Fe}/D_{Mg} > 100$.

20

493   3) Diffusion rates are independent of oxygen fugacity in the nominally pure Mg-spinel (although it

494   contains detectable amounts of Fe) within the resolution of measurement of this study. In

495   contrast, diffusion rates in the Fe-bearing spinel are a non-linear function of oxygen fugacity.

496   The dependence is consistent with models that predict that diffusion occurs by an interstitial

497   mechanism at low oxygen fugacities and by a vacancy mechanism at high oxygen fugacities.

498   4) The consequence of the above observations is that the mechanism of diffusion is different in Fe-

499   free spinel from that in Fe-bearing spinel (different activation energy and Arrhenius

500   parameters); and different in Fe-bearing spinel at low vs. high oxygen fugacities. For most

501   terrestrial processes, the vacancy mechanism of diffusion should dominate.

502   5) A comprehensive model (Eqn. 4) accounting for variations caused by all these factors is able to

503   reproduce all existing experimental data on Fe-Mg diffusion in Fe-bearing spinels (this study,

504   Liermann and Ganguly, 2002, Freer and O'Reilly, 1980).

505   6) The model developed in this study (Eqn. 4) may be used to calculate $D_{Fe\text{-}Mg}$ for modelling

506   natural processes. In addition, it should be considered that $D_{Fe\text{-}Mg}$ depends substantially on the

507   Cr-content of spinel (Cr-#), as discussed above. As diffusion by the vacancy mechanism should

508   dominate in most terrestrial processes, diffusion rates in spinels should increase with oxygen

509   fugacity. In most circumstances, diffusion rates of Fe-Mg in spinels will be faster than that in

510   coexisting mafic minerals (olivines, orthopyroxenes, clinopyroxenes and garnets).

<div align="center">Implications</div>

512   The new diffusion data on Fe-Mg spinel and the point defect model that evolved from these data

513   help to explain earlier diffusion data that were apparently discrepant, and provides a means of

514   calculating diffusion related properties (closure temperatures, timescales from modelling

515   concentration gradients) that vary over a considerable range depending on the Fe concentration of

516   the spinel crystal and oxygen fugacity in the environment, in addition to factors such as temperature

517   and likely, pressure.

21

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518

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634

635   **Figure captions**

636   **Figure 1.** RBS spectra of sample number Sp2Her50-3 (annealed at 10^{05} Pa, T= 800 °C, $Log_{10}fO_2$ = -12

637   Pa) and the corresponding reference (i.e. unannealed sample showing the initial condition) showing

638   normalized counts vs. energy of backscattered alpha particles (grey circles: reference sample; blue

639   circles: Sp2Her50-3). Simulations of the spectra are shown as solid lines (yellow: reference sample,

26

640   red: Sp2Her50-3). The marked region in a) is drawn to a larger scale in b). Note the decrease of Fe in

641   the thin layer after the diffusion anneal.

642

643   **Figure 2.** Calculated interdiffusion coefficients D_{Fe-Mg} as a function of varying iron content and

644   differing self-diffusion coefficients D_{Fe} and D_{Mg} using Eqn. (2) for an ideal solid solution. The plots

645   show a variation in the relationship over ten orders of magnitude of each self-diffusion coefficient. The

646   color gradient represents $\log_{10} D_{Fe-Mg}$, with warmer colors representing higher values. Contour lines

647   denote interdiffusion coefficients of equal value. The white band represents an area, where D_{Fe-Mg} is

648   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)

649     $X_{Fe}=0.07$, c) $X_{Fe}=0.5$, d) $X_{Fe}=0.999$.

650

651   **Figure 3.** Reflected light microscopy and white light interference microscopy images of a) Sp1 and b)

652   Sp2. Total variations of topography measured in different regions are shown to be on the order of ± 1.5

653   nm (Sp1) to $\pm$ 6-10 nm (Sp2).

654

655   **Figure 4.** Experimental data (symbols) and simulations (solid lines) of diffusion profiles in a) Sp1

656   (Sample no. Sp1Her50-10, 10^{05}Pa, T= 900 °C, $\log_{10}fO_2 = -10$ [Pa]) and b) Sp2 (Sp2Her50-13, 10^{05} Pa,

657   T= 800 °C, $\log_{10}fO_2 = -12$ [Pa]). Both diffusion profiles are matched assuming constant self-diffusion

658   coefficients, where $D_{Fe} > D_{Mg}$. The asymmetric profile in a) is best described for $D_{Fe}/D_{Mg}\geq 100$. The

659   less asymmetric profile shown in b) is well described for $D_{Fe}/D_{Mg}\geq 100$ as well.

660

661   **Figure 5.** Time sequence. Variations in D_{Fe-Mg} values obtained from different crystals annealed at the

662   same conditions over different lengths of time (Sp2Her50-1,-2,-3,-14). The data indicate a

663   reproducibility of $1\sigma = 0.11 \log_{10}$ units for the measured D_{Fe-Mg} values.

664

27

665 **Figure 6.** D_{Fe-Mg} in Sp1 and Sp2 at T= 800 °C and 10^{05} Pa as a function of oxygen fugacity: $log_{10} fO_2$ in

666 Pa = 10^{-14} – 10^{-10}. Diffusion coefficients in Sp1 are independent of oxygen fugacity within the

667 uncertainty of the data. In contrast, diffusion coefficients in Sp2 are dependent on oxygen fugacity in a

668 non-linear manner. The blue dashed line represents a constant value of $Log_{10}D=-18.37$ [m^2/s], which

669 describes D_{Fe-Mg} in Sp1 within the uncertainty of the data. The red dashed line represents the "best fit"

670 to D_{Fe-Mg} in Sp2, based on Eqn. 3. The inferred fO_2 exponents of $-^2/_3$ at low and $^2/_3$ at high oxygen

671 fugacities were used in accordance to the fO_2 dependence described for magnetite (e.g. Dieckmann and

672 Schmalzried, 1977a,b). See text for further discussion.

673

674 **Figure 7.** Arrhenius plot showing diffusion coefficients (D_{Fe-Mg}) retrieved from Sp1 and Sp2. All

675 experiments were performed at atmospheric pressure and controlled oxygen fugacity. Because

676 diffusion in Sp1 is independent of oxygen fugacity, all data are plotted in this figure. Diffusion in Sp2

677 is shown for $log_{10}fO_2 = -12$[Pa]. Dashed lines denote self-diffusion coefficients D_{Fe} and D_{Mg}, solid lines

678 represent best fits to the interdiffuion coefficients for a given composition of $X_{Fe}=0.001$ (Sp1) and

679 $X_{Fe}=0.07$ (Sp2).

680

681 **Figure 8.** Arrhenius diagram showing diffusion coefficients determined in aluminous spinel in earlier

682 studies: Fe-Mg interdiffusion (dots), Mg self-diffusion (squares) and Cr-Al interdiffusion (stars)

683 coefficients. The symbols represent the experimental data. The data by Freer and O'Reilly (1980) is

684 shown for a composition of FeO = 5 wt% and FeO = 25wt%, respectively. Data obtained from Suzuki

685 et al (2008) is shown for Cr#=0 and Cr#=0.9 at $3x10^{09}$ [Pa]. For a better comparison of the

686 interdiffusion data given by Liermann and Ganguly (2002) with those obtained in this study, all data

687 are shown for a composition of $X_{Fe}=0.07$ (dots). Note that Liermann and Ganguly (2002) performed

688 their study in the presence of graphite at an oxygen fugacity of approx. $2x10^{09}$ [Pa] (black dashed line).

28

689   The black solid line denotes the Arrhenius relation obtained by Liermann and Ganguly (2002) at

690   atmospheric pressure.

691

692   **Figure 9.** Synthetic profile (dots) based on one of the best fit data points of Liermann and Ganguly

693   (2002): 21.4×10^8 Pa, 1125 °C, 51 hours (Sp-diff05d). Solid lines represent "best fit" profiles to this

694   data for D_{Fe}/D_{Mg}=1,10 and100, with D_{Fe-Mg} determined using Eqn. (2) in the text.

695

696   **Figure 10.** Fe-Mg diffusion coefficients calculated using the best fit parameters in the point defect

697   model (Eqn. 4) compared to measured data from different studies. a) Arrhenius relation showing the

698   diffusion data measured by Liermann and Ganguly (2002) (grey dots), Freer and O'Reilly (1980)

699   (green dots), Suzuki et al. (2008) (blue dots) and our data on interdiffusion in Sp2 (red dots) for a given

700   composition of X_{Fe}=0.07. Red lines are calculated using equation 4. b) D_{Fe-Mg} in Sp2 at T= 800 °C and

701   10^{05} Pa as a function of oxygen fugacity (red dots) in comparison to the calculated value according to

702   equation 4. c) is a 3D plot, to illustrate the dependence of the interdiffusion coefficient $\log_{10} D_{Fe-Mg}$

703    $[m^2/s]$ on temperature and oxygen fugacity based on equation 4.

704

705   **Figure 11.** Comparison of the Fe-Mg interdiffusion data in spinel obtained in this study with those in

706   olivine [Dohmen et al. (2007a)], garnet [Borinski et al., 2012], clinopyroxene [Müller et al., 2012] and

707   orthopyroxene [Dohmen et al., 2014].

708

29

Table 1.

Sample	Substrate	Target	Laser energy [mJ]	time [min]	Vacuum [bar]
A	Sp1	Her50	156	20	3.30E-06
B	Sp1	Her50	156	20	3.50E-06
C	Sp1	Her50	144	12	6.00E-06
D	Sp2	Her50	144	10	3.50E-06
E	Sp2	Her50	152	15	4.00E-06
F	Sp2	Her50	152	15	3.50E-06
G	Sp2	Her50	152	15	6.00E-06
H	Sp2	Her50	120	30	6.60E-06

	XFe=0.001								
Sample	**Temp**	**fO$_2$**	**time**	**film**	**DFe**	**DMg**	**DFeMg**	**Log$_{10}$(DFeMg)**	
	[^{o}C]	**[bar]**	**[s]**	**[nm]**	**[m2/s]**	**[m^2/s]**	**[m^2/s]**	**[m^2/s]**	
Sp1Her50-5	802	-15	7200	80	6.0E-19	6.0E-21	5.5E-19	**-18.3**	A
Sp1Her50-6	803	-16	7200	85	5.0E-19	5.0E-21	4.5E-19	**-18.3**	
Sp1Her50-7	804	-18	7200	85	4.0E-19	4.0E-21	3.6E-19	**-18.4**	
Sp1Her50-8	805	-19	7200	85	4.0E-19	4.0E-21	3.6E-19	**-18.4**	B
Sp1Her50-9	855	-15	1800	80	1.4E-18	1.4E-20	1.3E-18	**-17.9**	
Sp1Her50-10	900	-15	1800	70	2.6E-18	2.6E-20	2.4E-18	**-17.6**	
Sp1Her50-g	750	-17	81000	35	1.0E-19	1.0E-21	9.1E-20	**-19.0**	C
Sp1Her50-h	850	-17	3600	30	1.5E-18	1.5E-20	1.4E-18	**-17.9**	
SP2	**XFe=0.07**								
Sample	**Temp**	**fO$_2$**	**time**	**film**	**DFe**	**DMg**	**DFeMg**	**Log$_{10}$(DFeMg)**	
	[^{o}C]	**[bar]**	**[s]**	**[nm]**	**[m2/s]**	**[m^2/s]**	**[m^2/s]**	**[m^2/s]**	
Sp2Her50-1	805	-17	1800	25	1.10E-18	1.10E-20	1.39E-19	**-18.9**	D
Sp2Her50-2	805	-17	7200	25	8.00E-19	8.00E-21	1.01E-19	**-19.0**	
Sp2Her50-3	805	-17	29160	25	6.50E-19	6.50E-21	8.20E-20	**-19.1**	
Sp2Her50-12	801	-15	21600	40	1.20E-18	1.20E-20	1.51E-19	**-18.8**	E
Sp2Her50-13	801	-16	21600	50	6.00E-19	6.00E-21	7.57E-20	**-19.1**	
Sp2Her50-14	801	-17	21600	45	7.00E-19	7.00E-21	8.83E-20	**-19.1**	
Sp2Her50-15	801	-18	21600	40	2.50E-18	2.50E-20	3.15E-19	**-18.5**	F
Sp2Her50-16	801	-15.5	21600	45	1.10E-18	1.10E-20	1.39E-19	**-18.9**	
Sp2Her50-17	797	-16.5	21600	35	7.00E-19	7.00E-21	8.83E-20	**-19.1**	
Sp2Her50-c	750	-17	90000	35	3.00E-19	3.00E-21	3.78E-20	**-19.4**	G
Sp2Her50-d	750	-17	52000	40	2.10E-19	2.10E-21	2.65E-20	**-19.6**	
Sp2Her50-19	800	-17.5	21600	30	1.20E-18	1.20E-20	1.51E-19	**-18.8**	
Sp2Her50-e	850	-17	4320	35	1.10E-18	1.10E-20	1.39E-19	**-18.9**	H
Sp2Her50-f	900	-17	3780	30	2.10E-18	2.10E-20	2.65E-19	**-18.6**	
Sp2Her50-g	760	-17	81000	35	3.60E-19	3.60E-21	4.54E-20	**-19.3**	

Table 2.

a)

reference sample Sp2
Sp2 after diffusion anneal

35 nm

Sp2

a-particles

$Mg_{0.5}Fe_{0.5}Al_2O_4$

O

Al

Mg

b)

Fe

norm. Counts

Energy of scattered a-particles [keV]

b)

reference sample Sp2
Sp2 after diffusion anneal

film

Substrate Sp2

Fe diffuses
into the substrate

norm. Counts

Energy of scattered a-particles [keV]

a)

Sp1-Her50-ref-B Sp1-Her50-10

Reflected light microscopy

2 mm

White light interference microscopy

Sp1-Her50-ref-B Sp1-Her50-10

b)

Sp2-Her50-ref-E Sp2-Her50-13

Reflected light microscopy

White light interference microscopy

Sp2-Her50-ref-E Sp2-Her50-13

a)
- Sp1
- DFe/DMg =10
- DFe/DMg =100
- DFe/DMg =1000

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

a)

b) Temp = 800 °C

c)