The isotope effect for Mg-Fe interdiffusion in olivine and its dependence on crystal orientation, composition and temperature

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Abstract

Isotopic fractionation associated with diffusion in crystals is the most reliable means of understanding the origin of mineral zoning in igneous and metamorphic rocks. We have experimentally determined the relative diffusivities of iron isotopes in olivine as a function of crystallographic orientation, composition, and temperature. For two isotopes \(i\) and \(j\) of an element, the isotope effect for diffusion is parameterized as 
\[
\frac{D_i}{D_j} = \left(\frac{m_j}{m_i}\right)^b
\]
where \(b\) is a dimensionless parameter, and \(D\) and \(m\) stand for diffusivity and mass, respectively. A series of single crystal diffusion couple experiments were conducted at an oxygen fugacity of QFM – 1.5 at temperatures of 1200, 1300, and 1400 °C. For the Fo 83.4–Fo 88.8 composition pair, \(b_{Fe}\) is isotropic and a value of 0.16 ± 0.09 can be used to describe diffusion along all major crystallographic axes in olivine. Based on our experiments and previously reported coupled Mg-Fe isotopic data, we also estimate \(b_{Mg} = 0.09 ± 0.05\) for this range of olivine composition. For the Fo 88.8–Fo 100 composition pair, \(b_{Fe}\) becomes anisotropic with \(b_{Fe} [100] = 0.11 ± 0.03\) and \(b_{Fe} [010] = 0.14 ± 0.03\) (both within error of the value measured for the Fo 83.4–Fo 88.8 pair), and \(b_{Fe} [001] = 0.03 ± 0.03\). For Fo# between 83.4 and 100, \(b_{Fe} [100]\) and \(b_{Fe} [010]\) are thus independent of composition. The reason why \(b_{Fe} [001]\) transitions from ~0.16 to ~0.03 close to the Mg-endmember is unclear. Over the temperature range studied, a dependence of \(b_{Fe}\) on temperature was not resolved. General analytical expressions are introduced to calculate isotopic fractionation as a function of distance, time, \(b\), and the concentration contrast between the diffusing media for spherical, cylindrical, and planar geometries.

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1. INTRODUCTION

Chemical profiles in crystals and melts have been used to extract timescales of magmatic processes with the assumption that these profiles were diffusion-driven (e.g., Rubin et al., 2017; Ruprecht and Plank, 2013; Saunders et al.,...
Recognizing diffusive transport, however, is challenging because chemical profiles in crystals and melts can arise from chemical diffusion or crystal growth. Chemical diffusion is associated with isotopic fractionation as the light isotopes diffuse faster than their heavier counterparts (e.g., Schoen, 1958; Mullen 1961; Peterson, 1975; Tsuyiyyama et al., 1994; Richter et al., 1999, 2003, 2008; Roskosz et al., 2006; Goel et al., 2012; Mueller et al., 2014; Watson et al., 2016). These large isotopic fractionations provide a means to identify diffusive transport in nature (Lundstrom et al., 2005; Beck et al., 2006; Tang et al., 2017; Dauphas, 2007; Jeffcoate et al., 2007; Parkinson et al., 2007; Gallagher and Elliott, 2009; Gao et al., 2011; Chopra et al., 2012; Sio et al., 2013; Pogge von Strandmann et al., 2015; Oeser et al., 2015, 2018; Richter et al., 2016; Collinet et al., 2017; Teng et al., 2006, 2011).

Olivines are particularly useful for diffusion-based geospeedometry studies due to their common occurrence in planetary materials and the observation that they are commonly zoned in Mg and Fe. Dauphas et al. (2010) and Teng et al. (2011) first showed that zoned olivines in natural settings were isotopically fractionated in Mg and Fe and that the fractionations could be attributed to diffusive transport. These first studies were bulk measurements on mineral fragments. Sio et al. (2013), Oeser et al. (2015, 2018), and Collinet et al. (2017) subsequently measured the isotopic compositions of Mg and Fe along chemical profiles in zoned olivines and demonstrated that these were consistent with diffusion-driven isotopic fractionations.

The net isotope fractionation measured in chemically zoned olivine depends on the rate of crystal growth relative to the rate of diffusion within olivine (i.e., the Péclet number; Sio and Dauphas, 2017; see Watson and Mueller, 2009 for the case of diffusion-limited growth in crystals). If the crystal grows quickly relative to diffusion, then zoning is driven by crystal growth associated with magmatic differentiation and little isotopic fractionation is expected. This is because at magmatic temperatures, the equilibrium olivine-melt fractionations are small and thus olivine and melt have roughly the same Mg and Fe isotopic compositions (Teng et al., 2010; Dauphas et al., 2014). Conversely, if crystal growth is slow relative to diffusion, zoning is generated during diffusive re-equilibration with an evolving melt, which strongly fractionates Mg and Fe isotopes. To assess the relative contributions of diffusion and crystal growth to chemical zoning in olivine, the magnitude of the isotopic fractionation imparted by diffusion must be experimentally determined. This is termed the isotope effect for diffusion and the relevant parameter, $\beta$ in $D_i/D_j = (m_i/m_j)^{\beta}$, is the focus of this study. In addition to teasing apart the effects of crystal growth from diffusion, knowledge of $\beta$ can be used to extract thermal histories for unknown samples. The importance of $\beta$ has been illustrated in Sio and Dauphas (2017), where an inverse-modeling method was used to reconstruct the cooling and crystallization histories of a magmatic system using estimated $\beta$-values. They used the olivine phenocryst characterized by Sio et al. (2013) to ground-truth this approach as the thermal history of this sample is independently well constrained. The authors demonstrated that while many thermal histories provided good fits to the chemical profile, only the true thermal history provided a good fit to both the chemical and isotopic profiles measured in the crystal. In other words, if $\beta$ is known, isotopic profiles can be used to constrain cooling and crystallization histories of samples.

Extending the inverse-modeling method to systems with different olivine compositions and cooling histories will require knowledge of the factors that control $\beta$. Accordingly, the goal of this study is to experimentally determine the effects of crystallographic orientation, composition, and temperature on $\beta$ for Fe and $\delta^{26}$Mg in olivine. The ratio of $\beta_{Fe}/\beta_{Mg}$ is well constrained from the correlation between $\delta^{56}$Fe and $\delta^{26}$Mg in natural olivines (Dauphas et al., 2010; Sio et al., 2013; Oeser et al., 2015). Therefore, experimentally constraining $\beta_{Fe}$ will also help establish the value of $\beta_{Mg}$.

### 2. THEORETICAL BACKGROUND

The isotope effect for diffusion exists in materials because the light isotopes of an element diffuse faster than their heavier counterparts. Extensive work has been done on diffusion in metals in an effort to identify diffusion mechanisms. In that context, the mass-dependence of diffusion-driven isotopic fractionation is expressed using the isotope effect:

$$E = \frac{(D_i/D_j) - 1}{(m_i/m_j)^{\beta} - 1}$$

(1)

where $D_i$ and $D_j$ are diffusivities, and $m_i$ and $m_j$ are the masses of isotopes $i$ and $j$ of an element. ($E \approx 2\beta$; Van Orman and Krawczynski, 2015; Watkins et al., 2017). Mullen (1961) showed that $E$ could be expressed as the following:

$$E = fK$$

(2)

where $f$ is a correlation factor and $K$ is a kinetic energy factor. The correlation factor, $f$, represents the extent to which an atom’s exchange with a vacancy is correlated to its previous jump. If there is a high tendency for the atom to return to where it came from (i.e., making a reverse jump), then the jump is said to be highly correlated, described by a small $f$ and thus a small isotope effect for diffusion. The kinetic energy factor, $K$, describes the coupling between the diffusing atom and the surrounding atoms and typically ranges from 0.5 to 1.0 (Van Orman and Krawczynski, 2015) where a small $K$ signifies a large coupling effect.

Using a simple model for diffusion via the vacancy mechanism in concentrated systems, Manning (1971) derived an expression of $f$, which is presented in Van Orman and Krawczynski (2015):

$$f_a = 1 - \frac{(D_i)(1 - f_a)}{\sum C_i D_i}$$

(3)

where $f_a$ is the correlation factor for self-diffusion and $C_i$ is the mole fraction of the diffusing species. In deriving Eq. (3), Manning (1971) assumed that vacancies and atoms are randomly distributed and that there is no atom-vacancy attraction. Substituting in parameters relevant to the olivine binary solid solution, we have:
where \( f_{Fe} \) and \( f_{Mg} \) are the correlation factors, \( D_{Fe} \) and \( D_{Mg} \) are the self-diffusivities for Fe and Mg, respectively, \( C_{Fe} \) is the molar Fe/(Fe + Mg) ratio in olivine, and \( f_o \) is the correlation factor for both Fe and Mg in their pure end-member forms (\( f_o \approx 0.745 \) Hermalng and Schmalzried, 1984). When \( D_{Fe}/D_{Mg} \approx 1 \), the correlation factors are functions of composition. Hermalng and Schmalzried (1984) studied the self-diffusion of Fe in olivine for \( 0.2 < C_{Fe} < 0.9 \) and suggested that \( D_{Fe}/D_{Mg} \approx 3.6 \) at 1130 °C. Details on the determination of \( D_{Mg} \), however, were not given. Chakraborty et al. (1994) and Chakraborty (1997) studied Mg self-diffusion (\( D_{Mg} \)) and Mg-Fe interdiffusion in olivine (\( D_{Mg-Fe} \)) respectively, at identical experimental conditions for the same composition (Fo 92), allowing the Fe self-diffusion (\( D_{Fe} \)) to be calculated via (e.g., Dohmen and Chakraborty, 2007; Van Orman and Krawczynski, 2015):

\[
D_{Mg-Fe} = \frac{D_{Mg} D_{Fe}}{C_{Fe} D_{Fe} + (1 - C_{Fe}) D_{Mg}}
\]

Using the data of Chakraborty et al. (1994) and Chakraborty (1997) and Eq. (6), \( D_{Fe}/D_{Mg} \) is calculated to be 3.5 at 1400 °C, and it increases to 5.2 at 1300 °C and to 8.2 at 1200 °C. Qualitatively, Manning’s model predicts that \( f_{Fe} \) and \( f_{Mg} \) increase with increasing \( C_{Fe} \) (see Fig. 9 in Van Orman and Krawczynski, 2015) and with increasing temperature. However, at \( D_{Fe}/D_{Mg} > 5.2 \) (i.e., temperatures below 1300 °C) at \( C_{Fe} = 0.08 \) (Fo082), Manning’s model fails as Eq. (4) would give a negative \( f_{Fe} \), which is physically impossible. Furthermore, Manning’s model also predicts that at all \( C_{Fe}, f_{Fe}/f_{Mg} < 1 \), which is in contradiction with the natural samples showing \( \beta_{Fe}/\beta_{Mg} \approx 2 \) (Sio et al., 2013; Osier et al., 2015). A possible reason for the discrepancy is that there is a Fe-vacancy binding energy in olivine (Van Orman and Krawczynski, 2015), which is not incorporated into Manning’s model. A difference in the kinetic energy factor, \( K \), for Mg and Fe in olivine may account for some of the discrepancy. However, there is currently no theoretical constraint to help assess how different \( K \) could be for Mg and Fe in olivine.

Recently, Watson et al. (2016) studied the Fe and Ni isotope effect for diffusion in Fe-Ni metallic alloys and also noted that Manning’s model was inadequate to fully describe their results. Modification of Manning’s model is outside the scope of this study but should be a goal of future work. Until a suitable model is available, experiments are the most direct way to study diffusive isotope effects in olivine.

### 3. EXPERIMENTAL PROCEDURE

Single crystals of Fo83.4 were obtained from the Smithsonian Institution (catalogue# 170992 and 170985, Shush-Bemah Mine, Peridot Mesa at San Carlos, Arizona). These crystals were oriented by optically examining and cutting parallel to the most prominent crystal faces. These crystal faces were determined to be orthogonal to [010], or the b-axis (10.2 Å), by XRD (Bruker D8 Discover) at the Carnegie Institution of Washington. The [100] (or the a-axis) and [001] (or the c-axis) orientations were found using a petrographic microscope and confirmed by XRD. Two other crystallographically oriented crystals were used in the experiments: San Carlos olivine (Fo88.8) from Dr. David Kohlstedt, the University of Minnesota and synthetic Fo100 from Roditi International Corp. All crystallographic orientations were confirmed by electron backscatter diffraction (EBSD) characterization post-experiment, using a Bruker e-FlashHR connected to a FEI Inspect F scanning electron microscope (SEM) at the Lawrence Livermore National Laboratory.

Crystallographically oriented crystals were polished (final polish with 1 μm diamond suspension) and cut into pieces of about 2 mm × 1.5 mm × 1 mm. Two configurations were used and compared with regard to their effectiveness in keeping the crystals in contact during and after the experimental runs (Fig. 1). In the first configuration, the polished crystal faces were pressed together, then wrapped in a piece of Re ribbon to maintain the arrangement, while leaving enough exposed crystal surfaces to facilitate equilibration with the imposed \( f_{O2} \). Rhenium was used rather than Pt because the former helps limit the loss of iron during the high temperature annealing step (e.g., Borisov and Jones, 1999). Once wrapped, crystal pairs were inserted into alumina crucibles and further pushed together using an alumina rod that extended beyond the crucible length (Fig. 1c). The whole assemblage was then tied using Pt wires to maintain pressure. In the second configuration, the alumina crucibles were filled with an oxide mixture (90 wt% FeO + 10 wt% MgO) that sintered upon heating and thus kept the crystals in place. After the oxides were hand-packed, the crucibles were closed with alumina lids and tied with Pt wires (Fig. 1d). About half of the experiments were done using each configuration. These configurations introduced different silica activities (\( a_{SiO2} \)) with the Re ones being unbuffered and the FeO-MgO ones being buffered at low \( a_{SiO2} \). It has been shown that the diffusion of Ni, Co (Zhukova et al., 2014) and Zr, Hf (Jollands et al., 2014) depend on \( a_{SiO2} \) due to its control on vacancy concentration. However, its effect on Mg-Fe interdiffusion and the associated isotope effect in olivine has not been studied systematically. As the Re configuration is buffered in \( a_{SiO2} \), effects of \( a_{SiO2} \) may not be pinned down in this study.

Experiments were run at ambient pressure in a Deltech furnace at the Carnegie Institution of Washington. The temperature in the furnace was calibrated using the melting points of Au and Pd and was accurate to ±5 °C. Thermal gradients were absent in the experiments as the diffusion couple assemblies were always placed within the furnace hotspot, which is ~2 cm long with temperature varying by only 2 °C across this length. CO-CO\( \text{g} \) gas mixtures were used to control the oxygen fugacity (\( f_{O2} \)), which was set to 1.5 log units below the quartz-fayalite-magnetite (QFM) buffer for all experiments. The oxygen fugacity was monitored throughout the experiments using a yttrium-doped...
zirconia oxygen sensor. To investigate the temperature dependence of $\beta_{Fe}$, five sets of Fo$_{88.8}$-Fo$_{100}$ experiments were done at 1400 °C, two at 1300 °C, and one at 1200 °C. To investigate the compositional dependence of $\beta_{Fe}$, two sets of Fo$_{83.4}$-Fo$_{88.8}$ diffusion couples were run at 1300 °C. Each set of experiments consisted of crystals aligned along [100], [010], and [001] in 3 separate crucibles, yielding a total of 30 experiments.

4. ANALYTICAL METHODS

4.1. Chemical and isotopic analyses

The experimental run-products were first mounted in epoxy, then sectioned perpendicular to the diffusion interfaces. They were then remounted in either epoxy or indium and polished for chemical and isotopic analyses.
The chemical profiles were measured using a JEOL JXA-8530F field emission electron probe microanalyzer (FE-EPMA) at the Carnegie Institution of Washington. Springwater olivine was used as a standard for Fe and a synthetic Fo100 crystal for Mg and Si. Analyses were done at 15 kV and 20 nA with 20 s on-peak counting times using a 1 μm spot size. Only analyses with atomic (Mg + Fe)/Si ratios between 1.95 and 2.05 corresponding to the stoichiometry of olivine were kept.

Isotopic analyses were performed by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) using a Photon Machines 193 nm Excimer laser ablation system equipped with a 2-volume HelEx cell coupled to a Nu Plasma II at the Carnegie Institution of Washington. Analyses were acquired at 40 Hz with energy readings of ~5 mJ. Data were collected with the sample stage moving at 25 μm/s parallel to the diffusion interfaces. After each line analysis was done, the stage was moved to a distance comparable to the spot diameter, in a direction perpendicular to the diffusion interface, and the procedure was repeated. Line analyses, rather than stationary spot analyses, were used in order to maximize analysis times while avoiding downhole effects (Eggins et al., 1998).

Analysis times were typically 40–60 s and washout times were 20 s, although 8 s was enough for signals to fall back to background levels. These ablation conditions generated laser t trenches of ~3 μm in depth, measured using a Zygo interferometer at the Carnegie Institution of Washington.

The He carrier gas flow rates were ~0.35 L/min and ~0.45 L/min in the cup insert and sample (outer) cell of the 2-volume HelEx cell system, respectively, and the Ar make-up gas flow rate was ~0.8 L/min. At these flow rates, positional effects were absent (i.e., isotopic compositions analyzed over a large area on a standard did not change as a function of position in the sample chamber).

The Nu Plasma II mass spectrometer was used to measure ion beams of \(^{57}\text{Fe}, {^{56}\text{Fe}, {^{54}\text{Fe} + {^{54}\text{Cr}}, and {^{55}\text{Cr}, which were collected on H9, H6, Ax, and L3 Faraday cups in pseudo-high resolution mode. Natural olivines used in this study contain \(^{54}\text{Cr} that can contribute to up to 0.06% of the mass 54 signal so that simultaneous collection of \(^{53}\text{Fe} was required. Signal intensities from the interfering isotope, \(^{54}\text{Cr}, were calculated from those of \(^{53}\text{Cr} assuming natural abundances of Cr isotopes, and were subtracted from \(^{54}\text{Fe} + {^{54}\text{Cr} signal intensities to obtain \(^{54}\text{Fe} signals. All data, once corrected for \(^{54}\text{Cr} interferences, plot on the expected mass-dependent fractionation line (Fig. S1).

During continuous ablation, the signals (measured using 10\(^{11}\ Ω resistors) were integrated over 1 s intervals so that each line analysis consisted of 40–60 measurement cycles. At the end of each line analysis, constant background signals were measured with no ablation and were subtracted from the measured signals for each isotope. The transient points, typically the first 6 and the last 4 points of each traverse, were discarded manually as isotope ratios deviated from a plateau value. The ratios of averaged isotopic signals were used to calculate the Fe isotopic composition, reported as \(\delta^{56}\text{Fe} (an abbreviation of \(\delta^{56/54}\text{Fe}; see Teng et al., 2017 for a discussion of this notation):

\[
\delta^{56}\text{Fe}(\%) = 1000 \times \left( \frac{^{56}\text{Fe}}{^{54}\text{Fe}_{\text{sample}}} \right) \left( \frac{^{54}\text{Fe}_{\text{standard}}} {^{54}\text{Fe}_{\text{sample}}} \right) - 1 \]  

(7)

where \(^{56}\text{Fe}_{\text{standard}} is the average of two isotopic ratios of a bracketing standard (see below), measured before and after each line analysis on the sample.

Sample-standard signal mismatch is known to cause analytical artifacts for MC-ICPMS isotopic analyses (e.g., Dauphas et al., 2009; Teng and Yang, 2014). To minimize this effect, ablation characteristics are typically adjusted to match signal intensities for the sample and the standard. Adjustment in ablation characteristics was unnecessary for the Fo88.8-Fo88.8 diffusion couples, as the bracketing standards used were the diffusion-unaffected areas of the same crystal where analyses were being made. That is, the diffusion-unaffected part of the Fo83.4 crystal served as the bracketing standard for its diffusion-affected part (20 μm spot diameter for both) and the same procedure was applied to Fo88.8 (25 μm spot diameter for both). This procedure produced a sample-standard signal mismatch that is at most 1.2:1.0, corresponding to a correction of <0.01\(\delta\) (see supplementary file; Fig. S2). This is negligible given the precisions reported and thus no correction was made.

For the Fo88.8-Fo100 diffusion couples, the bracketing standard was always the diffusion-unaffected region of Fo88.8. When analyzing the diffusion-affected parts of the Fo100 crystals (using a 15 μm spot diameter), a smaller spot diameter (10 μm) was used on the bracketing standard (Fo88.8). This produced signal mismatch between sample and standard that was at most 1:4, which occurred close to Fo99. At such low Fe-concentration, the 2 SD uncertainty is ~3.7\(\delta\), which is large compared to the applied correction of ~0.7\(\delta\) from signal mismatch (see supplementary file; Fig. S2). The difference in laser spot size for the samples vs. the bracketing standard may introduce artificial fractionations arising from wall effects. If this effect was significant, then a plot of \(\delta^{56}\text{Fe} vs. \text{Fo8}\# would show an offset across the interface at ~Fo94, but such an offset was not detected.

Matrix effects were evaluated by measuring Fo95 against Fo92 in line traverses using a spot diameter of 15 μm for both matrix standards located in the same mount. The LA-MC-ICPMS measured difference between the isotopic compositions of Fo95 and Fo92 (or \(\Delta^{56}\text{Fe}_{\text{Fo95,Fo92}}\) was ~0.06 ± 0.54\(\delta\) after applying the signal mismatch correction discussed above (2 SD, n = 8), which agrees well with the solution value of ~0.09 ± 0.06\(\delta\). As a result, matrix effects were considered negligible at the precision reported and no matrix correction was made beyond matching approximately the Fo content of the bracketing standard with that of the sample analyzed.

For the Fo88.8-Fo100 diffusion couples, analyses were done until there was insufficient signal on \(^{54}\text{Fe} (the low abundance isotope in Eq. (7)) to produce a meaningful measurement. All data with \(^{54}\text{Fe} signals falling below 4 mV were discarded. Based on the measured instrumental noise and counting statistics, the theoretical 2 SD uncertainty (John and Adkins, 2010) on \(\delta^{56}\text{Fe} should be ~2\(\delta\) with 4 mV on \(^{54}\text{Fe}. The true uncertainty, however, was determined experimentally by analyzing our in-house San
Carlos olivine standard at different frequencies of ablation to generate 4 mV to 80 mV signals on $^{54}\text{Fe}$. At each frequency, the sample was analyzed 8 times and the 2 SD of these measurements was calculated. The uncertainties determined in this manner is always larger than the theoretical uncertainty (Fig. S2). Therefore, the interpolation between the empirically determined analytical uncertainty (2 SD) and the corresponding voltage on $^{54}\text{Fe}$ was used to give an estimated 2 SD error for data collected for the Fo$_{88.4}$Fo$_{100}$ diffusion couples. For the Fo$_{88.4}$Fo$_{88.8}$ diffusion couples, $^{54}\text{Fe}$ signals were between 100 mV and 400 mV and uncertainties were simply reported as the 2 SD of the bracketing standards.

Some diffusion couples were analyzed multiple times. After each analysis, the samples were coated in Ir and put into the SEM to obtain the distances of the laser trenches from the diffusion interface. The location of the diffusion interface is usually apparent because either the contact did not stay intact after the experiment or there are imperfections (submicron holes and cracks) along the contact. We assigned an Fo# to each of the laser trenches based on the model fits to the Fo# vs. distance profiles previously measured using EPMA. The Fo# obtained this way was always close to that estimated by LA-MC-ICPMS (calculated by referencing the measured signal to that of the bracketing standard), except in areas when the line analyses passed through large cracks. After studying the laser trenches in the SEM, the samples were re-polished for further isotopic analysis.

4.2. Modeling approach

The equation governing chemical diffusion as a function of composition for a planar infinite geometry is (Crank, 1979):

$$\frac{\partial C}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} \right).$$

For our purpose, $C$ is the molar Fe/(Mg + Fe) ratio in olivine, $x$ is distance, $D$ is the Mg-Fe interdiffusion coefficient, and $t$ is time. Eq. (8) is solved numerically using the finite difference method in Fortran (for details, see the supplementary material in Sio and Dauphas, 2017), with the initial condition $C = C_0$ at $t \geq 0$ and $C = C_1$ at $x < 0$ at $t = 0$, and boundary conditions $C = C_0$ at $x = +\infty$ and $C = C_1$ at $x = -\infty$ at $t \geq 0$. For the Fo$_{88.4}$Fo$_{88.8}$ couples, $C_0 = 0.112$ and $C_1 = 0.166$; for the Fo$_{88.8}$Fo$_{100}$ couples, $C_0$ is assumed to be 0.00001 and $C_1 = 0.112$. The Mg-Fe interdiffusion rate along [001] at ambient pressure, as a function of temperature, composition, and $\gamma$O$_2$ is taken and modified from Dohmen and Chakraborty (2007):

$$D_{[001]} (m^2/s) = \kappa \times 10^{-3.21 \gamma \text{O}_2 \left( \frac{R}{T} \right) \frac{T}{T_0} \left( \frac{t}{t_0} \right)},$$

where $\kappa$ is a multiplication factor (introduced in this study), $R$ is the gas constant in J mol$^{-1}$ K$^{-1}$, $T$ is in Kelvin, $\gamma$O$_2$ is the oxygen fugacity in Pascal, $\gamma$ represents the strength of the composition dependency, and $D_{[001]} = 6 \times D_{[100]} = 6 \times D_{[001]}$. In Dohmen and Chakraborty (2007) $\gamma = 3$ but it is treated here as a free parameter in order to fit the measured chemical profiles (see Section 5.1). Additionally, we have introduced $\kappa$ as a free parameter to improve the fit between measured and modelled diffusion profiles. Note that details of the fit to the chemical profiles are largely inconsequential for assessing the value of $\beta$Fe.

Isotopic profiles were modeled by calculating the $^{54}\text{Fe}$ and $^{56}\text{Fe}$ profiles individually. The ratio of the isotope concentrations at each position is calculated to give $\delta^{56}\text{Fe}$ using the following equation:

$$\delta^{56}\text{Fe} = 1000 \times \left( \frac{C_{56}\text{Fe}}{C_{54}\text{Fe}} - 1 \right).$$

The Mg-Fe interdiffusion rate in Eq. (9) represents that for $^{56}\text{Fe}$ (i.e., $D_{56\text{Fe}}$). After fitting the chemical profiles with the free parameters ($\gamma$ and $\kappa$) highlighted above, the isotopic profiles are fit by adjusting $\beta$Fe to minimize the difference between measured and calculated isotopic compositions. If $\beta$Fe is treated as a constant, the Mg-Fe interdiffusion rate for $^{54}\text{Fe}$ is calculated using the relationship $D_{54\text{Fe}} = D_{56\text{Fe}} \times (56/54)^{\beta\text{Fe}}$.

We also evaluated the possibility that $\beta$Fe is not constant and instead varies linearly as a function of composition. In this case, the calculation for $D_{56\text{Fe}}$ is still the same as that presented in Eq. (9). To calculate $D_{54\text{Fe}}$, we assign a $\gamma$-value that is slightly different from that used for $D_{56\text{Fe}}$ (by <0.2%). Additionally for $D_{54\text{Fe}}$, the right hand side of Eq. (9) is multiplied by $(56/54)^{\beta\text{Fe}(c-n)}$, where $\beta$Fe ($c$=0.1) is the input $\beta$Fe at $C = 0.1$ (or Fo90).

The best fits were given by the minimization of the reduced Chi-square, $\chi^2$, calculated using the following equation (Sio and Dauphas, 2017):

$$\chi^2 = \frac{1}{v} \sum \frac{(\delta^{56}\text{Fe}_{\text{model}} - \delta^{56}\text{Fe}_{\text{measured}})^2}{\sigma_{\text{unknown}}^2 + \sigma^2_i},$$

where $v$ is the number of degrees of freedom and $\sigma_i$ is the 1 SD uncertainty on the isotopic measurement at position $i$ across a profile, $\sigma_{\text{unknown}}$ is a constant which is chosen to make $\chi^2 = 1$ for the $\beta$Fe value that gives the best isotopic profile fit. Values of $\sigma_{\text{unknown}}$ are given in Table S1. The number of degrees of freedom is equal to $N - n - 1$, where $N$ is the number of data points, and $n$ is the number of parameters. When $\beta$Fe is treated as a constant, the only variable parameter in fitting isotopic profiles is $\beta$Fe so $n = 1$. When $\beta$Fe varies as a function of composition, $n = 2$. Values of $\chi^2$ were calculated at 0.05 one-sided significance level, and these values served as the $\chi^2$ cut-offs to give 95% confidence intervals for $\beta$Fe. For some experiments, the number of data points ($N$) is as high as 75. Binning tests with various bin sizes were done to confirm that the best-fit $\beta$Fe and its uncertainty did not change as a result of binning. This is because while binning decreases the uncertainty at each distance bin, $N$ was also decreased, which increased the $\chi^2$ cut-off value.

5. RESULTS

5.1. Chemical profiles

Chemical profiles for diffusion couples can be modeled using Eqs. (8) and (9). When the multiplication factor, $\kappa$, is unity, the diffusion coefficient is perfectly described by
the formulation of Dohmen and Chakraborty (2007). Due to the low degree of reproducibility of Mg-Fe interdiffusion coefficients, the uncertainty in $D_\text{Mg-Fe}$ is half an order of magnitude (Dohmen and Chakraborty, 2007), which is represented by $\kappa$ in this study. As discussed in Section 4.2, this multiplication factor was treated as a fitting parameter in our diffusion models. It averaged 1.1 for diffusion along $[100]$, 4.5 for diffusion along $[010]$ and 1.9 for diffusion along $[001]$. Only 4 out of the 25 modeled profiles required $\kappa$ values greater than the uncertainty quoted by Dohmen and Chakraborty (2007). Some of the discrepancies may be explained by not having the diffusion couples sectioned directly perpendicular to the diffusion interface (note that post-experiment sectioning effects do not affect $\beta_{\text{Fe}}$ as diffusion still occurred only along a particular crystallographic direction). The reason for the discrepancy in $\kappa$ is unclear, but contributions of diffusive flux from the other sides of the crystals are ruled out.

All profiles have been modeled using a composition-dependent diffusion coefficient. The exponent $\gamma$ in Eq. (9) describes the compositional dependence of the Mg-Fe inter-diffusion coefficient and a constant value of $\gamma$ has been observed for compositions more Fe-rich than Fo$_{95}$ (Misener, 1973, 1974; Buening and Buseck, 1973; Chakraborty, 1997). For olivines more Mg-rich than Fo$_{95}$, however, this simple compositional behavior appears insufficient to fully describe the data. Misener (1973) conducted an Fo$_{92.7}$-Fo$_{100}$ diffusion couple experiment and found that $\gamma$ takes a value of $\approx 8$. His 8 other diffusion experiments done using Fo$_{90.8}$ immersed in MgO powder also generated $\gamma$ values of greater than 6 (Misener, 1973; 1974). We note that assigning a single value to $\gamma$ of either 3 or 8 for modeling all of our profiles does not allow us to provide the optimum model fits. The improvement in the quality of fit by selecting one value for $\gamma$ over the other is subtle (Fig. 2), but significant. There is no correlation between which $\gamma$ provides the best quality of fit and the EPMA session, allowing us to exclude the possibility that this is an analytical artifact. There is also no correlation with $\gamma$ and the nature of the quenched contact (cracked vs. intact) or the experimental configuration (Re vs. FeO-MgO). Furthermore, run-product characterization by EBSD confirms that all crystals were well-aligned in their crystallographic orientations (Fig. 1a and b) so the difference in $\gamma$ between experiments cannot be explained by crystallographic misalignments of the crystals. We have not yet found a satisfactory explanation for the range of $\gamma$ values required to fit the models, but rather have simply treated it as a fitting parameter.

5.2. Isotopic profiles fit using a constant $\beta_{\text{Fe}}$ vs. $\beta_{\text{Fe}}$ as a function of composition

A feature of isotope profiles modeled using a constant $\beta_{\text{Fe}}$ is that isotopes are always unfractionated (i.e., $\delta^{56}\text{Fe} = 0 \%$) at the diffusion interface. The effect of using a $\beta_{\text{Fe}}$ that changes linearly with composition is that this unfractiated position shifts toward the side of the diffusion couple that has a higher $\beta_{\text{Fe}}$ (Fig. 3). The amplitude of the fractionation does not change, as long as the average $\beta_{\text{Fe}}$ is the same as the model ran using a constant $\beta_{\text{Fe}}$. In all of our profiles, there is no significant improvement in fits modeled using a composition-dependent $\beta_{\text{Fe}}$. Therefore, constant values of $\beta_{\text{Fe}}$ are used to model all profiles.

5.3. The nature of post-experiment crystal-crystal contacts

SEM investigation revealed that only some of the diffusion couples displayed intact contacts after quenching while others showed cracks along the diffusion interfaces (Fig. 1). Only 33% (5/15) of the Re-wrapped experiments and 50% (5/10) of experiments using the FeO-MgO configuration have intact contacts (Table 1; some experiments done using the FeO-MgO were not counted or modeled at all due to the prevalence of oxides throughout the contacts). Chemical analyses done across either the intact or cracked contacts in the same diffusion couple show identical profiles, suggesting that the cracks formed by the mechanical stress produced by quenching.

With the high number of repeat experiments at 1400 °C (and 1388 °C), we were able to assess whether the lack of intact contacts in the presence of an otherwise smooth chemical profile was demonstrably a quench effect. In a plot of $\delta^{56}\text{Fe}$ vs. Fo# of these experiments all plot on the same trend that can be modeled using the same $\beta_{\text{Fe}}$, regardless of the nature of the contact (Fig. 4). This observation gives us confidence that although the crystals separated during quenching, a good contact was established at high temperature and maintained throughout the experimental duration. Thus, we are confident that even when recovered experiments lacked an intact contact, the derived $\beta_{\text{Fe}}$ is correct.

5.4. Dependence of the isotope effect on crystal orientation, composition, and temperature

Our data show that $\beta_{\text{Fe}}$ is a function of crystallographic orientation for the Fo$_{88.8}$-Fo$_{100}$ composition pair, with $\beta_{\text{Fe}}[100] \approx \beta_{\text{Fe}}[010] \geq \beta_{\text{Fe}}[001]$ (Fig. 4). At 1400 °C, where

![Graph](image-url)
the most repeat experiments and measurements were done, we obtained weighted averages of $b_{\text{Fe}[100]} = 0.10 \pm 0.03$, $b_{\text{Fe}[010]} = 0.14 \pm 0.03$, and $b_{\text{Fe}[001]} = 0.03 \pm 0.03$ (Table 2). At 1300 °C, the error bars are larger but the relative order of $b_{\text{Fe}}$ remains the same.

For the composition pair Fo$_{83.4}$-Fo$_{88.8}$, $b_{\text{Fe}}$ appears to be isotropic. A value of $b_{\text{Fe}} = 0.16 \pm 0.09$ can be used to describe diffusion along all major crystallographic axes (Fig. 5). Experimental evidence for the isotropy of $b_{\text{Fe}}$ at higher Fe content is not strong, as only one set of Fo$_{83.4}$-Fo$_{88.8}$ diffusion couple has been analyzed, and the relatively modest fractionations in this composition pair resulted in a large uncertainty of $b_{\text{Fe}}$.

The compositional dependence of $b_{\text{Fe}}$ is evaluated two ways. First, we compare the $b_{\text{Fe}}$ values extracted from the Fo$_{83.4}$-Fo$_{88.8}$ and Fo$_{88.8}$-Fo$_{100}$ diffusion couples that were annealed at the same temperature, 1300 °C (Table 2). Between the two composition pairs, the best-fit $b_{\text{Fe}[100]}$ differs by $0.01 \pm 0.16$, that of $b_{\text{Fe}[010]}$ differs by $0.02 \pm 0.17$, and that of $b_{\text{Fe}[001]}$ differs by $0.13 \pm 0.11$. Therefore, $b_{\text{Fe}[001]}$ may be composition-dependent, such that it decreases with decreasing Fe content in the olivine. A second way of evaluating the composition-dependency of $b_{\text{Fe}}$ is to examine the isotope profile in each experiment. The measured profiles do not discriminate between a composition-dependent and a constant $b_{\text{Fe}}$ (Fig. 3). Using this method, a compositional dependence of $b_{\text{Fe}}$ could not be resolved with the current analytical precision. Further work is required to ascertain the compositional dependency of $b_{\text{Fe}[001]}$.

The temperature dependence of $b_{\text{Fe}}$ is evaluated from 1200 °C to 1400 °C for diffusion along [001] for the Fo$_{88.8}$-Fo$_{100}$ diffusion couples (Fig. 6). The difference of the best-fit $b_{\text{Fe}[001]}$ values between 1200 °C and 1400 °C is $0.03 \pm 0.09$, suggesting little temperature dependence of
Fe$^{56}$ in this temperature range. Therefore, we have provided in Table 2 the weighted average values of $\beta_{\text{Fe}}$ for the Fo$^{88.8}$-Fo$^{100}$ diffusion couples. In Fig. 7, we summarize the results for the crystallographic orientation, composition, and temperature dependences of $\beta_{\text{Fe}}$.

6. DISCUSSION

Estimating $\beta_{\text{Fe}}$ from natural samples requires that initial and boundary conditions be well-constrained. Sio and Dauphas (2017) demonstrated how using a single $\beta_{\text{Fe}}$, core-rim iron isotope fractionations ranging from -0.8 to -3% could be generated depending on the choice of cooling and crystallization histories used in the model. In other words, if the cooling and crystallization histories are not well constrained, $\beta_{\text{Fe}}$ estimated from natural samples can potentially be off by a factor of 3. Experimentally determined values of $\beta_{\text{Fe}}$ are based on well-controlled conditions and therefore supersede $\beta_{\text{Fe}}$ values estimated from natural samples. Knowledge of how $\beta_{\text{Fe}}$ may change as a function of crystallographic orientation, composition, and temperature is essential for modeling chemically and/or isotopically zoned olivines.

6.1. Crystallographic dependence of $\beta_{\text{Fe}}$ in experiments and natural samples

Our experimental dataset shows that $\beta_{\text{Fe}}$ is anisotropic in olivine for the Fo$^{88.8}$-Fo$^{100}$ diffusion couples with $\beta_{\text{Fe}}$ [001] being significantly smaller than $\beta_{\text{Fe}}$ [100] and $\beta_{\text{Fe}}$ [010]. Such anisotropy was not detected in the Fo$^{88.4}$-Fo$^{88.8}$ diffusion couples but the uncertainties are larger so some anisotropy might still be present.

The Mg-Fe interdiffusion rate along [001] is six times higher than that along [100] and [010]. Accordingly, for isotopic profiles measured along a random crystallographic orientation, $\beta_{\text{Fe}}$ [001] will generally exert a strong control on the Fe isotope fractionation. That is, if anisotropy is present in a natural sample (i.e., $\beta_{\text{Fe}}$ [100] ≈ $\beta_{\text{Fe}}$ [010] ≈ $\beta_{\text{Fe}}$ [001]), then isoipetic fractionation for a traverse close to [001] will be less pronounced than for a traverse that is far from [001]. Collinet et al. (2017) presented data for the martian meteorite NWA 1068 where semi-orthogonal $\delta^{56}$Fe profiles were analyzed in a single olivine (ol A2; Fo$^{63}$-Fo$^{76}$), with “ip1” being 46° and “ip2” being 78° from [001]. The measured $\delta^{56}$Fe fractionations for the two profiles are identical, suggesting $\beta_{\text{Fe}}$ [100] ≈ $\beta_{\text{Fe}}$ [010] ≈ $\beta_{\text{Fe}}$ [001] for natural, Fe-bearing olivines, in agreement with our experimental data on the Fo$^{88.4}$-Fo$^{88.8}$ diffusion couple.

The reason why $\beta_{\text{Fe}}$ would show some anisotropy in the Fo$^{88.8}$-Fo$^{100}$ couples but none or a more subtle effect in the Fo$^{88.4}$-Fo$^{88.8}$ couple is unclear. Chakraborty et al. (1994) and Petry et al. (2004) suggested that cation diffusion in very Mg-rich olivine may exhibit a different diffusion mechanism. Exactly where the transition occurs in the olivine solid solution is unknown (Chakraborty, personal communication). Therefore, the discussion of compositional dependency of $\beta_{\text{Fe}}$ presented in this study may result from a change in diffusion mechanism within the studied range and any trend (or the lack thereof) may not be extended to olivines more Fe-rich than Fo$^{88.4}$.

The apparent lack of anisotropy in $\beta_{\text{Fe}}$ for compositions more Fe-rich than Fo$^{88.8}$ (and possibly Fo$^{88.4}$, as Fe isotope fractionations in the Fo$^{88.4}$-Fo$^{100}$ couples were controlled by compositions more Mg-rich than Fo$^{88.4}$; see Fig. 4) is convenient for modeling diffusion-driven isotopic fractionation in natural olivines. In most instances, a $\beta_{\text{Fe}}$ of 0.16 ± 0.09 (Fig. 5) can be used for modeling Fe isotope profiles in any crystallographic direction. For the more Mg-rich composition (Fo# > 94), the isotopic effect along the analytical traverse may need to be calculated. First, we define the chemical diffusion coefficient as a function of crystallographic orientation (Costa et al., 2008):

$$D_{\text{traverse}} = D_{[100]} \cos^2 \theta_{[100]} + D_{[010]} \cos^2 \theta_{[010]} + D_{[001]} \cos^2 \theta_{[001]}$$

where $D_{[100]}$, $D_{[010]}$, and $D_{[001]}$ are the diffusion coefficients along the crystallographic axes, $\theta_{[100]}$, $\theta_{[010]}$, and $\theta_{[001]}$ are the angles between the traverse and the axes. The $\beta_{\text{traverse}}$ is then calculated as follows (Batra, 1967):

$$\beta_{\text{traverse}} = \frac{\beta_{[100]} D_{[100]} \cos^2 \theta_{[100]} + \beta_{[010]} D_{[010]} \cos^2 \theta_{[010]} + \beta_{[001]} D_{[001]} \cos^2 \theta_{[001]}}{D_{\text{traverse}}}$$

Table 1

<table>
<thead>
<tr>
<th>Run#</th>
<th>Fo#</th>
<th>Time (hr)</th>
<th>Temp (°C)</th>
<th>ΔΩM</th>
<th>$\alpha^*$</th>
<th>$\gamma^*$</th>
<th>$\beta_{\text{Fe}}$ [001]</th>
<th>$\beta_{\text{Fe}}$ [100]</th>
<th>$\beta_{\text{Fe}}$ [010]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>1400</td>
<td>-1.48</td>
<td>1.5</td>
<td>0.8</td>
<td>1</td>
<td>0.12 ≥ 0.07</td>
<td>1.2 ± 0.03</td>
<td>1.2 ± 0.03</td>
<td>Fo-MgO</td>
</tr>
<tr>
<td>2</td>
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<td>1400</td>
<td>-1.51</td>
<td>2.5</td>
<td>2</td>
<td>3</td>
<td>0.16 ≥ 0.02</td>
<td>1.2 ± 0.00</td>
<td>1.2 ± 0.00</td>
<td>Fo-MgO</td>
</tr>
<tr>
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<td>1400</td>
<td>-1.51</td>
<td>3.0</td>
<td>2</td>
<td>3</td>
<td>0.23 ≥ 0.09</td>
<td>1.3 ± 0.01</td>
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<td>Fo-MgO</td>
</tr>
<tr>
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</tr>
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<td>3</td>
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<td>Fe</td>
</tr>
<tr>
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<td>2.0 ± 0.01</td>
<td>2.0 ± 0.02</td>
<td>Fe</td>
</tr>
</tbody>
</table>

Run-products with an intact contact after quench are highlighted in grey.
6.2. Estimation of $\beta_{\text{Mg}}$ in olivines

While the absolute values of $\beta_{\text{Fe}}$ and $\beta_{\text{Mg}}$ extracted from natural samples depend highly on the modeling parameters, the $\beta_{\text{Fe}}/\beta_{\text{Mg}}$ ratio is a robust estimate that is constrained only by the chemical and isotopic compositions of Fe and Mg measured in the sample (see Section 6.4). Observations from natural samples constrain $\beta_{\text{Fe}}/\beta_{\text{Mg}}$ to be $\sim 1.8 \pm 0.3$ for compositions between Fo$_{80}$ and Fo$_{95}$ (Sio et al., 2013), $\sim 2.05 \pm 0.45$ for compositions between Fo$_{83.4}$ and Fo$_{91}$ (Oeser et al., 2015), and $\sim 1.7 \pm 0.2$ for compositions between Fo$_{52}$ and Fo$_{78}$ (Collinet et al., 2017; using the second values of $\beta_{\text{Mg}}$ from their Table 2). Combining our best estimate $\beta_{\text{Fe}}$ value of $0.16 \pm 0.09$ together with the weighted average ratio $\beta_{\text{Fe}}/\beta_{\text{Mg}} = 1.77 \pm 0.16$ from Sio et al. (2013), Oeser et al. (2015) and Collinet et al. (2017), we calculate $\beta_{\text{Mg}} = 0.09 \pm 0.05$ for Mg-Fe interdiffusion in olivines with compositions approximately between Fo$_{83.4}$ and Fo$_{88.8}$.

Near the Mg endmember, which is seldom encountered in nature, $\beta_{\text{Fe}}/\beta_{\text{Mg}}$ may depart from $\sim 2$. Indeed, at the pure end-member Fo$_{100}$, the correlation factor for Mg in olivine is estimated to be 0.745 (Hermeling and Schmalzried, 1984), calculated based on crystal structure and diffusion via a vacancy mechanism. Assuming that $K$ in Eq. (1) is between 0.5 and 1 (Van Orman and Krawczynski, 2015), $\beta_{\text{Mg}}$ should then be between 0.19 and 0.37 near the pure Fo$_{100}$ endmember.

Yet, using the experimentally determined $\beta_{\text{Fe}}$ and a $\beta_{\text{Fe}}/\beta_{\text{Mg}}$ ratio of $\sim 2$, a $\beta_{\text{Mg}}$ of $<0.08$ is obtained near the pure Fo$_{100}$ endmember. The discrepancy in the theoretically expected and our inferred $\beta_{\text{Mg}}$ highlights the fact that we do not yet have a complete understanding of Mg-Fe interdiffusion in olivine near the pure Fo$_{100}$ endmember. Magnesium isotope analyses on these diffusion couples will provide critical constraints on $\beta_{\text{Fe}}/\beta_{\text{Mg}}$ as a function of composition and therefore elucidate the mechanism by which Mg-Fe interdiffusion occurs near Fo$_{100}$.

6.3. Improvements in cooling rates and timescales of magmatic processes

Common applications of diffusion-based geospeedometry include determinations of cooling rates and timescales of magmatic processes. Chemical profiles found in crystals
Fig. 5. Chemical-isotopic profiles for Run# 8 (Fo83.4–Fo88.8, 1300 °C). β_{Fe} is found by minimizing \( \chi^2 \) (black curves), bound by 95% confidence intervals (grey curves). There is no resolvable crystallographic dependence in this composition range.

Fig. 6. Temperature dependence of δ_{Fe} along [001] in the experimental run products. Differences in β_{Fe} [001] could not be resolved across the 1200 °C to 1400 °C temperature range.
are sometimes assumed to be purely driven by diffusion with crystal growth ignored (e.g., Mikouchi and Miyamoto, 2002; Costa and Dungan, 2005). These modeling approaches result in calculated cooling timescales that represent maximum values. Isotopes provide information on the contribution of crystal growth in generating a chemical profile. At magmatic temperatures, crystal growth imparts little isotope fractionation to olivines (Dauphas et al., 2014; Teng et al., 2010). The small equilibrium fractionation means that the olivine will incorporate unfracti- onated isotopes during crystal growth, as long as the surrounding medium is well-mixed. Therefore, any crystal growth will dilute diffusive isotope fractionations.

Illustrated in Fig. 8 is an example of the effect of crystal growth on a hypothetical olivine. A crystal with an initial composition of Fo_{85.5} is allowed to cool linearly from 1230 °C to 1140 °C; the relationship with rim Fo# and temperature (i.e., the boundary condition) is taken from MELTS using a starting composition shown in Sio and Dauphas (2017). Two models are used to fit the hypothetical chemical profile. The “no growth” model assumes no crystal growth so that the chemical profile results entirely from diffusive re-equilibration with the changing boundary condition. Fractionation in this case is large with δ^{56}Fe fractionated by −0.55% in this crystal. The “growth” model assumes the same boundary condition, while the crystal grows at 5 × 10^{-11} m/s. The incremental growth layers have compositions that reflect changes in the boundary condition, while diffusive relaxation takes place simultaneously. In this case, the δ^{56}Fe is only fractionated by −0.03%. The isotope profiles readily distinguish the two scenarios, but the chemical profiles do not. The “no growth” model requires a cooling timescale that is 42 times longer to generate a fit to the hypothetical chemical profile than the “growth” model (Fig. 8). Significant improvement in diffusion-based geospeedometry can therefore be realized if isotope profiles are measured and β-values can be experimentally determined.

Recently, Sio and Dauphas (2017) introduced an inverse modeling technique where β_{Fe} and β_{Mg} are input parameters and the time–temperature history of a sample is calculated by fitting the chemical-isotopic profiles from inverse modeling. In that study, β_{Fe} was assumed to be ~0.25. Armed with experimental data, we have now re-run those models by restricting β_{Fe} to 0.16 and β_{Mg} to 0.09. Modeling results show that the best time–temperature path overlap with the acceptable paths obtained previously using higher β_{Fe} and β_{Mg} values. This means that to first order, the reconstructed time–temperature histories are not overly sensitive to the value of β_{Fe} used and an uncertainty of ±0.09 in β_{Fe} does not affect the veracity of the inverse modeling approach (see Fig. S3).

6.4. Modeling methods and expected diffusion-driven isotope fractionations

We now present the general equations for modeling isotope profiles and show how the expected isotope fractionations change given compositional contrast and diffusion geometry. As done in this study, diffusion-driven isotopic profiles are typically computed independently for each isotope (e.g., δ^{54}Fe, δ^{56}Fe) using a slightly different diffusivity for each isotope. The isotopic profile is then calculated by taking the ratio of the isotopic concentrations at the same distance in the profile (Eq. (10)). Below, we present analytical expressions that directly give the isotopic fractionation as a
Similarly, the concentrations can represent the molar Mg/(Mg + Fe) ratio and can be calculated by multiplying the y-axes values by \((56/54 – 1)\).

The maximum isotopic fractionation occurs at 0.134 \(s\) and is

\[
\frac{C}{C_0} = f(D),
\]

where \(C_0\) and \(C_1\) are constants and correspond to concentrations at the beginning and/or at some boundaries (see Appendix A), \(C\) is the evolving concentration and \(D\) is the diffusion coefficient. In Appendix A, we show the derivation for the general analytical expression:

\[
\frac{\delta^{15}C}{C_0} \approx -1000\beta D \left( \frac{m_j}{m_i} - 1 \right) \frac{\partial C}{\partial D} \left[ \frac{C_0}{C_1} - f(D) \right]
\]

where \(m_i\) and \(m_j\) are the isotopic masses of an element. It can be seen from this equation that the magnitude of the fractionation correlates linearly with \(\beta\) and the relative mass difference of the isotopes involved \((m_j/m_i – 1)\). Isotopic fractionation also increases with compositional contrast of the different media. Changing \(D\) will change the time-scales required to fit diffusion profiles, but it will not change the isotopic fractionation for a given \(\beta\).

The derivation of analytical solutions for the slab, cylindrical, and spherical geometries are given in Appendix A for a compositionally homogeneous material in contact with a well-mixed medium whose composition does not change with time. We compared these equations with the traditional method of calculating isotopic profiles (discussed above), and the agreement is excellent for all except for the single slab geometry (see Fig. A1), which shows a discrepancy that decreases with decreasing compositional contrast.

Using Eq. (15), the ratio of \(\beta\)-values for the inter-diffusing elements in a binary solid solution can be calculated. For an ideal binary solution, we have the relationship \(C_a + C_b = 1\), where \(a\) and \(b\) are the inter-diffusing elements and \(C\) is their molar fraction. We may take measured isotopic compositions of \(a\) and \(b\) at any point in the profile to estimate the ratios of their \(\beta\)-values. To do this, we take the ratio of Eq. (15) written for \(a\) and \(b\). As these elements have the same \(D\) and hence \(\delta f/\delta D\), these terms cancel out and we have:

\[
\frac{\delta^{15}C/a}{\delta^{15}C/b} = \frac{\beta_{i,a}}{\beta_{i,b}} \left( \frac{m_{j,a}/m_{j,b} - 1}{\frac{1}{C_a} - f(D)} \right)
\]

where \(m_{j,a}\) and \(m_{j,b}\) are the masses of isotopes \(i\) and \(j\) for element \(a\), \(m_{j,b}\) and \(m_{j,b}\) are those of element \(b\), and \(C_j\) is the mole fraction of \(a\) at the same location in the profile where the isotopic measurements are taken. This is the relationship that was given in Dauphas et al. (2010) and used to estimate \(\beta_{Fe}/\beta_{Mg}\) in Sio et al. (2013). It can be extended to any binary diffusion system to estimate the ratios of \(\beta\)-values of the inter-diffusing elements.

A virtue of Eq. (15) is that it can be used to rapidly investigate how changes in some parameters affect the computed isotopic profile. Using Eq. (A12), the expected isotopic fractionations have been calculated for an initially homogenous spherical crystal in contact with an infinite hypothetical reservoir of diffusant (i.e., a small crystal in a large volume of a well-mixed medium). The maximum isotopic fractionation is achieved when the concentration, \(C\), at the center is halfway between the boundary concentration, \(C_1\) and the initial concentration, \(C_0\) (Fig. 9a and b). This maximum fractionation is plotted as a function of distance for a series of diffusion problems with constant diffusion coefficients (applicable to Mg-Fe in an olivine crystal with little variation in Fo#). As shown below, these can be advantageous to directly see how model parameters affect isotopic fractionation associated with diffusive transport. A feature of all these problems is that they assume an analytical solution of the form:

\[
\frac{C - C_0}{C_1 - C_0} = f(D),
\]

Fig. 9. Expected diffusion profiles (a, b) as a function of time for a given \(C_i/C_0\) ratio of 1.5 and a \(\beta\) of 0.16. \(C_0\) is the initial concentration, which is in contact with a well-mixed reservoir of diffusant with a concentration of \(C_i\). \(C_i\) is the evolving concentration, which is in contact with a well-mixed reservoir of diffusant with a concentration of \(C_i\). Models are calculated using Eqs. (A2) and (A10) (chemical profiles) and Eq. (A12) (isotopic profiles) with a constant \(D\). For application to olivine, the concentrations \((C, C_0, C_1)\) represent the molar Fe/(Fe + Mg) ratio and \(\delta^{15}Fe\) can be calculated by multiplying the y-axes values by \((56/54 – 1)\). Similarly, the concentrations can represent the molar Mg/(Mg + Fe) ratio and \(\delta^{26}Mg\) can be calculated by multiplying the y-axes values by \((26/24 – 1)\).
the ratio \( C_1/C_0 \) (Fig. 9c). It should be noted that it is not the absolute difference of concentration, but rather, it is the ratio of concentration (i.e., \( C_1/C_0 \)) in the diffusing media that will determine the magnitude of isotope fractionation (also see Richter et al., 2003). For example, a Fo84-Fo89 composition pair will generate the same Fe isotopic fractionation as a Fo89-Fo85 pair. This is because for the Fe-rich pair, the diffusive signal is diluted by a large background of unfractonated material so that a larger diffusive flux is required to see the same magnitude of Fe isotopic fractionation.

The same plot can be created for semi-infinite slab + semi-infinite slab geometry (i.e., the diffusion couples in this study and in natural samples where a compositionally homogeneous mantle is grown instantaneously onto a pre-existing crystal) using Eq. (A16; Fig. 10). For this geometry, the maximum isotopic fractionation does not change with time. The position associated with maximum isotopic fractionation simply moves away from the interface.

7. CONCLUSION

We have experimentally determined the iron isotope effect (\( \beta_{Fe} \)) for Mg-Fe interdiffusion in olivine, as a function of crystallographic orientation, composition, and temperature. For olivine compositions from Fo0.3 to Fo0.8, \( \beta_{Fe} \) is isotropic and a value of \( \sim 0.16 \) can be used. Within this composition range, we calculate a \( \beta_{Mg} \) value of \( \sim 0.09 \) based on coupled Mg-Fe isotopic variations in natural olivines. For more Mg-rich compositions, \( \beta_{Fe} \) decreases from \( \sim 0.16 \) to \( \sim 0.03 \), while \( \beta_{Fe} \) and \( \beta_{Fe} \) are unchanged. No temperature dependence of \( \beta_{Fe} \) was resolved from 1200 °C to 1400 °C in the Fo0.8-Fo0.9 diffusion couples. This study provides the first experimentally determined isotope effect for Fe during Mg-Fe interdiffusion in olivine and some critical constraints for future theoretical investigations of the process by which Mg-Fe inter-diffuse in olivine.

Finally, we derived analytical expressions for calculating isotopic profiles for various crystal geometries. The general expression shows that diffusion-controlled isotopic fractionation scales linearly with \( \beta \) and increases with increasing compositional contrast between the diffusing media. The isotope effect for diffusion may be exploited to retrieve robust thermal histories from chemical-isotopic profiles in zoned minerals in magmatic and metamorphic systems.

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APPENDIX A. ANALYTICAL SOLUTIONS FOR DIFFUSION-DRIVEN ISOTOPIC FRACTIONATION

Several diffusion problems with constant diffusion coefficients have analytical solutions that give the concentration as a function of distance and time. The manner in which the associated isotopic fractionation is usually computed is to independently calculate diffusion profiles for two isotopes \( i \) (e.g., \( ^{56}\text{Fe} \)) and \( j \) (e.g., \( ^{54}\text{Fe} \)) using the relationship:

\[
D_i/D_j = (m_i/m_j)^\theta
\]  

(A1)

The isotopic composition is calculated by taking the ratio of the concentration-distance profiles for the two isotopes. Below, we derive analytical expressions that directly give the isotopic fractionation as a function of distance for a series of diffusion problems with constant diffusion coefficients. A feature of all these problems is that they assume an analytical solution of the form,

\[
C - C_0 \quad \text{or} \quad C_1 - C_0 = f(D)
\]

(A2)

where \( C_0 \) and \( C_1 \) are constant and correspond to concentrations at the beginning and/or at some boundaries. If the difference in mass of the two isotopes is small, we can take a series expansion truncated to the first order to calculate the concentration of isotope \( i \),

\[
\frac{C_i - C_{i,0}}{C_{i,1} - C_{i,0}} \approx f(D_i) + (m_j - m_i) \frac{\partial f(m_i)}{\partial m_j}
\]

(A3)
which can be rewritten as,
\[
\frac{C_i - C_i,0}{C_i,1 - C_i,0} = f(D) + \left(\frac{m_i}{m_j} - 1\right) \frac{\partial f}{\partial D}\frac{\partial D_j}{\partial m_j}.
\]
(A4)

Because \(\partial D_j/\partial m_j = -\beta f \left(\frac{m_i}{m_j}/\beta\right)^2 \approx -\beta D/m_j\),
\[
\frac{C_i - C_i,0}{C_i,1 - C_i,0} = \frac{C_i - C_i,0}{C_i,1 - C_i,0} - \beta D \left(\frac{m_i}{m_j} - 1\right) \frac{\partial f}{\partial D}.
\]
(A5)

Below, we rearrange this equation to reformulate it in terms of isotopic ratio,
\[
\frac{C_i/C_i,0 - 1}{C_i,1/C_i,0 - 1} = \frac{C_i/C_i,0 - 1}{C_i,1/C_i,0 - 1} - \beta D \left(\frac{m_i}{m_j} - 1\right) \frac{\partial f}{\partial D}.
\]
(A6)

The isotopic composition is uniform at the beginning. Furthermore, in slab, cylindrical, and spherical geometries, the surrounding medium is assumed to have uniform and constant isotopic composition. We therefore have \(C_i,0/C_i,0 = C_i/C_i,0 = C_i,1/C_i,0\), and
\[
\frac{C_i/C_i,0 - C_j/C_j,0}{C_j,1/C_j,0 - 1} = \left(\frac{C_i/C_i,0}{C_i,1/C_i,0} - 1\right) - \beta D \left(\frac{m_i}{m_j} - 1\right) \frac{\partial f}{\partial D}.
\]
(A7)

Introducing the notation \(\delta^{ij}(\%) = 1000 \left(\frac{C_i/C_i,0}{C_i,1/C_i,0} - 1\right)\), we have,
\[
\delta^{ij}(\%) = -1000 \beta D \left(\frac{m_i}{m_j} - 1\right) \frac{C_i - C_i,0}{C_i,1 - C_i,0} \frac{\partial f}{\partial D}
\]
or equivalently,
\[
\delta^{ij}(\%) = -1000 \beta D \left(\frac{m_i}{m_j} - 1\right) \frac{\partial f}{\partial D} \left(\frac{1}{C_i - C_i,0} + f\right)
\]
(A8)

We see from this equation that the magnitude of the fractionation depends on the isoce effect (\(\beta\)), the relative mass difference of the isotopes involved \(\left(\frac{m_i}{m_j} - 1\right)\), and the contrast in concentrations of the different media \([C_i/C_i,0]/(C_i,1/C_i,0)\). Below, we calculate analytical expressions for several diffusion geometries.

a. Diffusion in a sphere in contact with a well-mixed medium

Initial and boundary conditions:
\(t = 0\): \(C = C_0\) at \(x > x_0\) and \(C = C_1\) at \(x < x_0\)
\(t \geq 0\): \(C = C_0\) at \(x = +\infty\) and \(C = C_1\) at \(x = -\infty\)

\[
f(D) = \frac{1}{2} \text{erfc}\left(\frac{x - x_0}{2\sqrt{D}t}\right)
\]
(A13)

\[
\frac{\partial f}{\partial D} = \frac{e^{-\left(x-x_0\right)^2}}{4D\sqrt{\pi}Dt} \left(\frac{C_0}{C_1 - C_0}\right) + \frac{1}{2} \text{erfc}\left(\frac{x + x_0}{2\sqrt{D}t}\right).
\]
(A14)

\[
\delta^{ij}(\%) = -250 \left(\frac{m_i}{m_j} - 1\right) \frac{e^{-\left(x-x_0\right)^2}}{\sqrt{\pi}Dt} \left(\frac{C_0}{C_1 - C_0}\right) + \frac{1}{2} \text{erfc}\left(\frac{x + x_0}{2\sqrt{D}t}\right).
\]
(A15)

b. 1D diffusion between 2 semi-infinite media (slab + slab)

Initial and boundary conditions:
\(t = 0\): \(C = C_0\) at \(x > x_0\) and \(C = C_1\) at \(x < x_0\)
\(t \geq 0\): \(C = C_0\) at \(x = +\infty\) and \(C = C_1\) at \(x = -\infty\)

\[
f(D) = \frac{1}{2} \text{erfc}\left(\frac{x - x_0}{2\sqrt{D}t}\right)
\]
(A13)

\[
\frac{\partial f}{\partial D} = \frac{e^{-\left(x-x_0\right)^2}}{4D\sqrt{\pi}Dt} \left(\frac{C_0}{C_1 - C_0}\right) + \frac{1}{2} \text{erfc}\left(\frac{x + x_0}{2\sqrt{D}t}\right).
\]
(A14)

\[
\delta^{ij}(\%) = -250 \left(\frac{m_i}{m_j} - 1\right) \frac{e^{-\left(x-x_0\right)^2}}{\sqrt{\pi}Dt} \left(\frac{C_0}{C_1 - C_0}\right) + \frac{1}{2} \text{erfc}\left(\frac{x + x_0}{2\sqrt{D}t}\right).
\]
(A15)

c. Diffusion in a slab in contact with a well-mixed medium

Initial and boundary conditions:
\(t = 0\): \(C = C_0\) at \(-l < x < +l\)
\(t \geq 0\): \(C = C_1\) at \(x = -l\) and \(x = +l\); (a half-space can be modeled by using the no-flux boundary condition \(\partial C/\partial x = 0\) at \(x = 0\))

\[
f(D) = 1 - \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-\frac{n(2n+1)^2\pi^2}{4Dt}} \cos\left(\frac{2n+1}\pi x\right)
\]
(A16)

\[
\frac{\partial f}{\partial D} = \sum_{n=0}^{\infty} (-1)^n (2n+1) e^{-\frac{n(2n+1)^2\pi^2}{4Dt}} \cos\left(\frac{2n+1}\pi x\right)
\]
(A17)

\[
\delta^{ij}(\%) = -1000 \left(\frac{m_i}{m_j} - 1\right) \frac{\pi \beta Dt}{l^2} 
\]
(A18)
d. Diffusion in a cylinder in contact with a well-mixed medium

Initial and boundary conditions:

\[ t = 0: C = C_0 \text{ at } -R < r < +R \]
\[ t \geq 0: C = C_1 \text{ at } r = -R \text{ and } r = +R; \text{ (a half-space can be modeled by using the no-flux boundary condition } \partial C / \partial r = 0 \text{ at } r = 0) \]

\[ f(D) = 1 - 2 \frac{R}{\lambda_n} \sum_{n=1}^{\infty} e^{-\lambda_n r} J_0(r \lambda_n) J_1(R \lambda_n) \tag{A19} \]

where \( J_0(x) \) and \( J_1(x) \) are the 0 and 1 integer orders of the Bessel function, and \( \lambda_n \) is the \( n^{th} \) root of \( J_0(\lambda) = 0 \).

\[ \frac{\partial f}{\partial D} = \frac{2t}{R} \sum_{n=1}^{\infty} \lambda_n e^{-\lambda_n r} J_0(r \lambda_n) J_1(R \lambda_n) \tag{A20} \]

\[ \delta^{(1)}(\%o) = -1000 \beta \left( \frac{m_i}{m_j} - 1 \right) \frac{2D}{R} \sum_{n=1}^{\infty} \lambda_n e^{-\lambda_n R} \frac{1}{J_1(R \lambda_n)} \left( \frac{\lambda_n}{e^{\lambda_n r} - \frac{2}{R} \sum_{m=1}^{\infty} e^{-\lambda_m r} J_0(r \lambda_m) J_1(R \lambda_m)} \right) \tag{A21} \]

The analytical solutions for isotopic fractionations as a function of distance for the 4 geometries have been calculated and compared to the traditional way calculating isotopic profiles (discussed in the text). The results are presented in Fig. A1.

**APPENDIX B. SUPPLEMENTARY MATERIAL**

Supplementary data associated with this article can be found, in the online version, at [https://doi.org/10.1016/j.gca.2018.06.024](https://doi.org/10.1016/j.gca.2018.06.024).

**REFERENCES**


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