Mg diffusion in forsterite from 1250-1600 °C

Michael C. Jollands, Irina Zhukova, Hugh St.C O’Neill, Jörg Hermann

1Research School of Earth Sciences, Australian National University, 142 Mills Rd, ACT 0200, Australia.

2Institute of Earth Sciences, Géopolis Building, University of Lausanne, 1015 Lausanne, Switzerland.

3State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan), 388 Lumo Rd, Hongshan, Wuhan, Hubei, China 430074

4Institute of Geology, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland.

corresponding author: michael.jollands@unil.ch

Abstract

26Mg tracer diffusion coefficients were determined in single crystals of pure synthetic forsterite (Mg2SiO4). Isotopically-enriched powder sources both acted as the 26Mg source and buffered the activities of silica (aSiO2) at forsterite+protoenstatite (Mg2Si2O6) (high aSiO2) and forsterite+periclase (MgO) (low aSiO2). Experiments were conducted at atmospheric pressure between 1250 and 1600 °C, and at oxygen fugacities (fO2s) between 10⁻¹² bars (CO-CO2 mix) and 10⁻⁰.⁷ bars (air). The resulting diffusion profiles were measured along the three principal crystallographic axes (a, b and c; ||[100], ||[010], ||[001]) using laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS), with a quadrupole mass spectrometer. These
measurements were corroborated by ion microprobe using the Sensitive High Resolution Ion Microprobe-Reverse Geometry (SHRIMP-RG) instrument.

Mg tracer diffusion is anisotropic, with $D_{[001]} > D_{[010]} > D_{[100]}$, the difference in diffusion coefficients varying by about one order of magnitude at a given temperature with crystallographic orientation. Diffusion is faster in protoenstatite-buffered than periclase-buffered conditions, again with around one order of magnitude difference in diffusivity between buffering conditions. There is no apparent effect of $fO_2$ on diffusion. A global fit to all data, including data from Chakraborty et al. (1994) and Morioka (1981) yields the relationship:

$$\log_{10} D = \log_{10} D_0 (\text{m}^2 \text{s}^{-1}) + 0.61(\pm0.03) \log_{10} a_{\text{SiO}_2} + \frac{-359(\pm10) \text{kJmol}^{-1}}{2.303RT}$$

where $\log_{10} D_0$ is $-3.15(\pm0.08)$, $-3.61(\pm0.02)$ and $-4.01(\pm0.05) \text{m}^2\text{s}^{-1}$ for the [001], [010] and [100] directions, respectively (1 s.d.). The LA-ICP-MS technique reproduces diffusion coefficients determined by SHRIMP-RG, albeit with slightly different absolute values of isotope ratios. This shows that LA-ICP-MS, which is both accessible and rapid, is a robust analytical method for such tracer diffusion studies.

**Keywords:** Diffusion, olivine, forsterite, magnesium, experimental petrology

**Introduction**

The prominence of olivine, $(\text{Mg, Fe}^{2+})_2\text{SiO}_4$, as the dominant mineral in the Earth’s upper mantle, coupled with its experimental accessibility, has led to its transport properties being the most intensively studied of all silicate minerals. Diffusion especially has received much attention. Following several decades of research, there is generally good agreement that of the major elements in $(\text{Mg, Fe}^{2+})_2\text{SiO}_4$ olivine, Si diffusion is the slowest of the major elements (Bejina et al., 1999; Costa and
Chakraborty, 2008; Dohmen et al., 2002b; Fei et al., 2012), Mg self/tracer or Fe-Mg inter-diffusion (Chakraborty, 1997; Dohmen et al., 2007; Dohmen and Chakraborty, 2007, Buening and Buseck, 1973; Hier-Majumder et al., 2005; Wang et al., 2004) is the fastest, and O diffusion is intermediate (Ando et al., 1981; Dohmen et al., 2002b; Jaoul et al., 1980; Reddy et al., 1980). However, there still remain many contentious and important issues, including the effects of water (Costa and Chakraborty, 2008; Fei et al., 2018; Fei et al., 2013; Hier-Majumder et al., 2005; Wang et al., 2004), pressure (Bejina et al., 1999; Chakraborty et al., 1994; Fei et al., 2018), and silica activity (Zhukova et al., 2014) on diffusion, especially of trace-elements (Spandler and O’Neill 2010; Zhukova et al, 2017; Jollands et al. 2014, 2016).

From an experimental and analytical perspective, studies of diffusion in olivine have been central to developing and testing the advantages and drawbacks of different approaches and procedures. Experimental anneals to produce measurable diffusion profiles have employed diffusion couples consisting of crystal-melt (Jurewicz and Watson, 1988; Spandler and O’Neill, 2010); crystal-crystal (Chakraborty, 1997); crystal-polyphase powder (Jollands et al., 2014; Zhukova et al., 2014); crystal-film (Dohmen et al., 2002a); polycrystalline aggregates (Fei et al., 2018); crystal-fluid (Demouchy and Mackwell, 2003; Demouchy and Mackwell, 2006; Jollands et al., 2016b); and crystal-gas (e.g. Ryerson et al., 1989), while analytically the diffusion profiles have been measured using the electron microprobe (Chakraborty, 1997); Rutherford Backscattering Spectroscopy (Cherniak, 2010; Cherniak and Liang, 2014; Dohmen et al., 2007); Nuclear Reaction Analysis (Ryerson et al., 1989; Cherniak and Watson, 2012); LA-ICP-MS (Spandler and O’Neill, 2010; Spandler et al., 2007); SIMS depth-profiling (Ito and Ganguly, 2006) and Local Electrode Atom Probe...
(LEAP; Bloch et al., 2019). Many of these approaches were developed, or refined, using natural or synthetic olivine of various compositions. Diffusivities in crystals are sensitive to their point-defect structures, which in turn depend on their thermodynamic states. While the thermodynamic state of a crystal in a diffusion experiment would ideally be completely determined, this is impractical in most chemical diffusion experiments due to the large number of thermodynamic components present. It is feasible, however, in the study of tracer diffusion in forsterite, which exists in a three-component system, Mg-Si-O (barring considerations of isotopic components), so that the equilibrium thermodynamic state of the forsterite is uniquely defined by the coexistence of two additional phases. Here, we expand on previous studies (Andersson, 1987; Chakraborty et al., 1994; Fei et al., 2018; Morioka, 1981; Sockel et al., 1980) by reconsidering the effects of major-element chemical potentials (notably the activity of silica (aSiO$_2$)) on Mg tracer diffusion, defining the equilibrium thermodynamic state of forsterite using a gas phase (air or a CO-CO$_2$ mix) plus either MgO or an Mg$_2$Si$_2$O$_6$-pyroxene. We also demonstrate that laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) with a simple quadrupole mass spectrometer, used previously for analysing trace-element diffusion profiles (e.g., Spandler and O’Neill 2010), can successfully measure experimental isotope diffusion profiles.

**Methods**

**Experimental**

Czochralski-grown single crystals of forsterite supplied by the Solix Corporation, Belarus, were cut into cubes of approximate dimension 2.5 x 2.5 x 2.5 mm. The cut surfaces were oriented parallel to the (001), (010) or (100) planes. Full trace-element contents of the forsterite from the same supplier are given in Zhukova et al. (2014);
the impurities include around 20-30 wt. ppm Al with <5 wt. ppm Fe. These cubes were mounted in epoxy and polished down to 1 μm diamond (cloth lap), then recovered from the resin for diffusion experiments. Further information regarding the experimental and analytical methodology is presented in Supplementary Figure 1.

Isotopically-distinctive buffering phase assemblages were synthesised from $^{26}$MgO (99.62% $^{26}$Mg, obtained from Isoflex USA), mixed with reagent grade MgO and SiO$_2$ in proportions calculated to give either Mg$_2$SiO$_4$-Mg$_2$Si$_2$O$_6$ (forsterite-protoenstatite, herein fo-prEn) or Mg$_2$SiO$_4$-MgO (forsterite-periclase, herein fo-per) assemblages to buffer aSiO$_2$ (and aMgO). The mole fractions of each phase and by-weight isotopic enrichments were: fo-prEn: 43.1 mol% Mg$_2$Si$_2$O$_6$, 56.9 mol % Mg$_2$SiO$_4$, 44.7 wt. % $^{24}$Mg, 5.7 wt. % $^{25}$Mg, 49.6 wt. % $^{26}$Mg (4.5x enrichment); fo-per: 32.9 mol% MgO, 67.1 mol % Mg$_2$SiO$_4$, 46.2 wt. % $^{24}$Mg, 5.9 wt. % $^{25}$Mg, 47.9 wt. % $^{26}$Mg (4.3x enrichment). Relative isotopic abundances are calculated assuming both that the non-enriched MgO, and the remaining 0.38% of MgO in the enriched material has the natural abundances.

The mixes were ground under acetone in an agate mortar, pressed into pellets in a tungsten carbide dye and sintered in air at 1300 °C. These were then re-ground, mixed with polyethylene oxide glue and pasted onto polished surfaces of the forsterite crystals. The glue-powder-crystal assemblage was then dried for ~12 h at ~100 °C, then the crystals were placed onto a bed of non-isotopically-enriched MgO or Mg$_2$SiO$_4$-Mg$_2$Si$_2$O$_6$ (matched to the buffering assemblage adhered to the crystal) in a Pt crucible and annealed in either air in a high temperature box furnace or a gas-mixing furnace (O’Neill and Eggins 2002) under CO-CO$_2$ gas flow, to control the oxygen fugacity at lower values than that of air (see Table 1). Temperatures were
monitored and controlled using type B Pt-Rh thermocouples, with an estimated accuracy of 2 °C.

Following the diffusion anneals, the recovered crystals were mounted in epoxy on a plane perpendicular to the diffusion interface, ground down by around 500 µm, and polished with 6 µm then 3 µm diamond paste on cloth laps for LA-ICP-MS analysis. Some visible surface degradation always occurred. However, the roughness associated with this is <5 µm (an example experimental charge is shown in Figure 1 and Supplementary Figure 2), considerably shorter than the length scales of diffusion.

For SHRIMP-RG analysis, several crystals were selected and cut from different mounts, remounted together in epoxy in one mount, and repolished. The mount was then degassed for ~100 hours in a vacuum oven at 60 °C and coated with 50 nm Au.

Analytical

LA-ICP-MS Measurements were conducted using a 193 nm LambdaPhysik Complex ArF excimer laser coupled to an Agilent 7700x quadrupole ICP-MS via He-Ar carrier gas. The laser beam was apertured to give an on-sample slit-shaped beam with approximate dimensions 6x100 µm, with the long axis parallel to the diffusion interface. The slit was scanned along the diffusion profile from low to high \(^{26}\text{Mg}\) concentration (core to rim). The pulse rate was 5 Hz and laser energy was maintained at 50-60 mJ at point of exit. \(^{24}\text{Mg}, \(^{25}\text{Mg}\) and \(^{26}\text{Mg}\) were counted for 0.1, 0.1 and 0.3 s per sweep, respectively. \(^{29}\text{Si}\) was used as an internal standard (dwell time 0.01s) and \(^{57}\text{Fe}\) and \(^{27}\text{Al}\) (potential contaminants) counted for 0.05 s each. NIST 610 glass (Jochum et al. (2011) values) was used as the primary standard to quantify Fe and Al only – these data were reduced using Iolite freeware (Paton et al., 2011).
Isotopic concentrations of Mg ($^{24}\text{Mg}$, $^{25}\text{Mg}$ and $^{26}\text{Mg}$) along the diffusion profiles were extracted from the raw data in two ways. Firstly, data were converted to counts per second, then background corrected and normalised to $^{29}\text{Si}$, i.e. $^{26}\text{Mg}(\text{cps})/^{29}\text{Si}(\text{cps})$. In lieu of a true external standard, a correction was applied using the crystal core as an isotopic standard, assuming it has the natural isotope ratio (modified from Longerich et al., 1996).

$$C_{\text{Mg}_{\text{sample}}} = \frac{R_{\text{Mg}_{\text{sample}}} C_{\text{Mg}_{\text{core}}}}{R_{\text{Mg}_{\text{core}}}} \quad (1)$$

Where $C$ is the content (expressed as isotopic abundance, i.e. 0.1101 for $^{26}\text{Mg}$) and $R$ is the Si-and background corrected count rate. Subscript ‘core’ represents a mean of the 50 innermost points of the transect (around 25 µm), and ‘sample’ is the whole profile. For the second reduction method, all above steps were done, then the fraction of the isotope $^{x}\text{Mg}$ ($x = 24, 25$ or $26$) was calculated from:

$$\frac{^{x}\text{Mg}}{\sum\text{Mg}} = \frac{^{26}\text{Mg}}{^{24}\text{Mg} + ^{25}\text{Mg} + ^{26}\text{Mg}} \quad (2)$$

Processed data are available in Supplementary dataset 1. Visual inspection of comparisons of D for $^{26}\text{Mg}$ determined following the two different methods of data reduction (either normalised, or not, to $\sum\text{Mg}$) suggest a good correlation (Supplementary Figure 3). However, the reduced chi-squared ($\chi^2$) between a 1:1 line and the data (determined using total least squares to account for uncertainties in x and y, without incorporating the uncertainty on the interface position) is high ($\chi^2 = 3.4$ or 15.7, depending on whether eq. (3) or (5) is used), suggesting that the imposition of the $\sum\text{Mg}$ condition affects the Ds in a non-negligible way. This is likely due to $^{24}\text{Mg}$ profiles being quite poorly resolved relative to $^{26}\text{Mg}$ profiles (probably a consequence...
of short counting times), and showing resolvably (but not systematically so) different
diffusivities (see Supplementary Figure 4 for more information). Therefore, we chose
to not apply the $\Sigma \text{Mg} = ^{24}\text{Mg} \cdot ^{25}\text{Mg} \cdot ^{26}\text{Mg}$ correction.

For each profile, the crystal-powder interface was located by inspection of the
analytical data. This was generally done using the major drop in Si counts associated
with the laser beam moving into the epoxy resin. In some cases, this was also
associated with a large jump in Al and Fe counts, and/or a large change in slope of
$^{26}\text{Mg}$. The potential effect of this partially subjective choice of position is a function
of the length of the diffusion profile and it is minimal with respect to the estimated
diffusion coefficients associated with the profile lengths in this study. For example, a
~10 micron misplacement of the assigned interface, on a 150-200 µm long profile
leads to ~0.05 logD unit variation (Supplementary Figure 5). This was also discussed
by Zhukova et al. (2014), who concluded that the effect of changing the interface
position, when converting time to distance during data processing, has a much larger
effect on the interface concentration than the extracted diffusion coefficient.

**SHRIMP-RG** The reverse-geometry sensitive high-resolution ion microprobe
(SHRIMP-RG) was used for secondary ion mass spectrometry (SIMS) measurements.
Secondary ions were sputtered by an O$^-$ primary beam 5 µm in diameter. The 45°
incidence angle of the primary beam in SHRIMP-RG results in a transformation of
the analytical spot to a slightly elongated ellipse, hence samples were oriented such
that the short axis of the ellipse was parallel to the diffusion direction to obtain the
optimal spatial resolution. Following a two-minute raster of the beam over the sample
to clean the surface, the nominal masses analysed were 24, 25 and 26 and 28, counted
for 2, 2, 3 and 1 seconds, respectively.
The positions of the SHRIMP-RG spots were determined post-analysis by taking high resolution photomicrographs and measuring distances from the interface using ImageJ (Schindelin et al., 2015). Where spots overlapped, the spacing was assumed to be equidistant between each analysis.

For the shortest profiles (<20 µm), the stage was moved 1 step (~3 µm) between each analysis, such that adjacent analyses partially overlap. To determine if this overlap affected the measured ratios, one profile (1250 °C, forsterite-periclase buffered experiment) was measured both forwards (away from the interface) and backwards (towards the interface).

The data were processed similarly to the LA-ICP-MS data, by normalising to $^{28}\text{Si}$ then correcting to the natural ratio using the count rate ratio in the crystal core. Data were either normalised or not to $\sum\text{Mg}$, as for the LA-ICP-MS data.

**Extraction of diffusion coefficients**

Two methods were used for extracting diffusion coefficients, with all fitting done using non-linear least squares regression with MATLAB. Interpretation of the observed diffusion profiles is complicated by the decrease of $^{26}\text{Mg}$ in the diffusant source as it exchanges with Mg in the crystal, causing $^{26}\text{Mg}/\sum\text{Mg}$ at the crystal interface to decrease continuously during the diffusion anneal. Because of the large number of profiles, and to reduce operator bias, all curve fitting was done automatically. To enhance the probability of achieving global minima, multi-start algorithms with at least ten random seeds were used, and all fits were visually inspected.

Initially, all data were fitted to the constant diffusion coefficient, constant interface, one dimensional, semi-infinite medium solution to Fick’s second law (Crank, 1975), i.e. fitting directly to an error function-shaped curve:
\[ C(x,t) = (C_{\text{rim}} - C_{\text{core}}) \cdot \text{erfc}\left( \frac{x}{\sqrt{4Dt}} \right) + C_{\text{core}} \]  

where \( C_{\text{rim}} \) and \( C_{\text{core}} \) are the concentrations at the interface and in the crystal core, \( D \) is the diffusion coefficient (m\(^2\) s\(^{-1}\)), \( t \) is the time (s) and \( x \) is the distance from the visually identified interface (m). Eq. (3) rarely gave a satisfactory fit to the whole profile – the regression biases the fit towards the high concentration end, such that the fitted curve overestimates the diffusivity. This is likely due to depletion at the interface, also observed by Chakraborty et al., 1994 and Zhukova et al., 2014 in similar diffusion experiments. To account for this, only the tail end of each profile was fitted. This was done as follows: firstly, the whole profile was fitted to give initial estimates of \( D \), \( C_{\text{core}} \), \( C_{\text{rim}} \), allowing the characteristic diffusion length scale of \( 2\sqrt{Dt} \) to be calculated. Then, all data points closer to the interface than half of this length scale (cutoff point = \( \sqrt{Dt} \)) were removed, and the residual profile re-fitted. The cut-off position was chosen as a compromise between uncertainties, which increase as the number of data points decrease, and a fit to the tail-end of the profile, which gets better as the cut-off point gets further from the interface. This method is appropriate for processing the SHRIMP-RG data, where the distance from the interface corresponding to each analysis was directly measured after the analytical session. For the LA-ICP-MS data the situation is slightly more complex – we make the assumption that the long axis of the slit shaped laser beam is exactly perpendicular to the crystal edge (alignment is done manually), and that the decrease of Si counts is associated with the first point at which the laser samples a mix of crystal and resin / buffer. Therefore, we have extra uncertainty relating to the difference between the position of the interface assigned in the ICP-MS data and the actual interface position. We estimate this conservatively as ±10 µm (c.f. the laser
width of 6 µm). This was taken into account by adding an interface term ($x_0$) to (3), fitting the data for $x_0$ between -10 and +10 µm, then taking the maximum and minimum ±1 s.d. values for the variables $D$, $C_{\text{rim}}$ and $C_{\text{core}}$.

$$C(x,t)=(C_{\text{rim}}-C_{\text{core}}).\text{erfc}\left(\frac{x-x_0}{\sqrt{4Dt}}\right)+C_{\text{core}} \quad (4)$$

To account for the depletion at the interface, another analytical solution to Fick’s second law was used (Crank, 1975, eq. 3.26, modified for a non-zero core composition), which assumes a constant rate of decrease of $^{26}\text{Mg}$ at the interface:

$$C(x,t)=[C_{\text{rim}}(t=0)-C_{\text{core}}].\left(\text{erfc}\left(\frac{x-x_0}{\sqrt{4Dt}}\right)+4kt_i \text{erfc}\left(\frac{x-x_0}{\sqrt{4Dt}}\right)\right)+C_{\text{core}} \quad (5)$$

where $i^2\text{erfc}(z)$ is calculated using:

$$i^2\text{erfc}(z)\frac{1}{4}\left(\text{erfc}(z)-2z\left(\frac{1}{\sqrt{\pi}}e^{-z^2}-z.\text{erfc}(z)\right)\right) \quad (6)$$

(Crank, 1975, Table 2.1) and $k$ is a constant describing the rate of decrease/increase of $^{26}\text{Mg}/\text{Si}$ at the interface (Crank, 1975, eq. 3.25). Again, the $x-x_0$ term in eq. (5) can be replaced by $x$ to remove uncertainty in the position of the assigned interface. The interface concentration of $^{26}\text{Mg}$ ($C_{\text{rim}}$) is assumed to decrease linearly away from its initial state ($C_{\text{rim}}(t=0)$) as a function of time. Changing $k$ leads to a stronger or weaker depletion at the interface, but does not change the length-scale of diffusion, hence the extracted $D$. This solution gives a good fit to more of the observed diffusion profile than eq. (3), which translates into smaller uncertainties in $D$. Details of both fitting procedures are shown in Figure 2. Supplementary dataset 1 contains fits to all $^{26}\text{Mg}$ profiles with both methods, along with the processed data.
The two fitting methods – depleting source (eq. (5)) or partial fit to error function (eq. (3)), give Ds within 0.1-0.2 log units, with the partial fit method generally giving slightly lower Ds than the depleting source model (Supplementary Figure 6).

However, a total least squares regression of the two sets of Ds to a y=x curve gives $\chi^2 = 132$, and a y=x+c fit yields c=-0.11 (y=partial fit, x=depleting source), but with $\chi^2 = 73$, so it is clear that we cannot use the methods interchangeably and extract the same Ds within uncertainty. The extremely high $\chi^2$ is due to using only the small uncertainties derived from curve fitting. In terms of selecting which method to use herein, both have advantages and drawbacks. The depleting source model is more physically reasonable, but sometimes does not satisfactorily fit all sections of the profiles. It makes the assumption that the decrease at the interface is linear, but this is highly unlikely – conservation of mass in a closed system would predict instead $^{26}$Mg versus time relationship that is closer to logarithmic (numerical modelling is presented in Supplementary Figure 7). As a further complication, the system is not closed – there exists a large bed of fo-prEn or fo-per powder below the crystal that should be able to isotopically exchange with the $^{26}$Mg-doped source via diffusion along the crystal surface. The partial fit method is good in that it does not make assumptions about the nature of the profile, but effectively just fits its length-scale. The main drawback is the large uncertainties associated with fitting a relatively small number of data points. Therefore, to avoid definitively choosing one method over the other, each curve was fitted by each method then means and uncertainties were combined.

When the uncertainty on the interface position is applied (the $x_0$ term in eq. (4) and (5)), the uncertainties (calculated as described above) derived from this treatment naturally increase as profiles get shorter (Supplementary Figure 8).
Results

SHRIMP-RG forward versus backwards profiling

A profile measured both forwards (away from the interface) and backwards (towards the interface) are shown in Figure 3a, showing good agreement. This suggests that the SHRIMP-RG is capable of quantifying precisely such short profiles despite considerable spot overlap, albeit for samples where the isotopic enrichment is extreme.

LA-ICP-MS vs SHRIMP-RG

Figure 3 shows $^{26}$Mg profiles from the experiment successfully measured by both SHRIMP-RG and LA-ICP-MS. For consistency with the LA-ICP-MS data, the SHRIMP-RG data were not normalised to $\sum$Mg. The concentrations in the crystal cores are in agreement – this is due to the normalisation method used, but the rims are not. Importantly, the diffusion coefficients from the fits fall within uncertainty (1 s.d. shown in the figure) of one another.

Mg diffusion

Following the methodology laid out above, extracted diffusion coefficients and their relevant experimental conditions are presented in Table 1. Example profiles are presented in Figure 4.
The effect of aSiO$_2$

Diffusivity is consistently higher, by around one order of magnitude, in experiments buffered by Mg$_2$SiO$_4$-Mg$_2$Si$_2$O$_6$ (high aSiO$_2$) than in those buffered by Mg$_2$SiO$_4$-MgO (low aSiO$_2$) at otherwise identical conditions.

The effect of crystal orientation

Mg diffusion is anisotropic, with $D_{[001]} > D_{[010]} > D_{[100]}$. The difference is around 0.5 log units between $D_{[001]}$ and $D_{[010]}$, and between $D_{[010]}$ and $D_{[100]}$, that is, a total of around one order of magnitude difference in diffusion coefficients. This is consistent with anisotropy of diffusion of M-site vacancies in pure forsterite (Demouchy and Mackwell, 2003; Jollands et al., 2016), and diffusion of other divalent M-site cations (e.g. Spandler and O’Neill 2010).

The effect of $f$O$_2$

There is no discernible effect of $f$O$_2$ on Mg diffusion in pure forsterite, over ~12 orders of magnitude $f$O$_2$. This is consistent with the previous experiments in the same system of Chakraborty et al., (1994), which also used forsterite of high purity (11 ppm Fe, approximately similar to ours), and contrasts with the positive $f$O$_2$-D relationship from that same study where less pure forsterite was used (120-180 ppm Fe). We note, however, that these Fe values are those of the starting material and do not account for any potential Fe enrichment or depletion occurring during the diffusion experiments.

Fitting to the Arrhenius relationship

Diffusion coefficients as a function of temperature for each aSiO$_2$-orientation condition were fitted individually to the general Arrhenius relationship:
\[ \log_{10} D = \log_{10} D_0 + \frac{-E_a}{2.303RT} \]  

(7)

where \( \log_{10} D_0 \) is the logarithm of the diffusion coefficient \( (m^2/s) \) at \( 1/T=0 \) \((T=\infty)\), \( E_a \) is the activation energy for diffusion \( \text{in kJmol}^{-1} \), \( R \) is the gas constant \( \text{(kJmol}^{-1} \) and \( T \) is the temperature \( \text{(K)} \). Values of \( E_a \) and \( \log D_0 \) for each axis-buffer pair are presented in Table 2.

An adequate fit of the \( D_s \) to eq. (7), as judged from the reduced chi-square of the regression, is not obtained if the uncertainties in \( \log_{10} D \) are taken simply as those listed in Table 1, which are from fitting the profiles alone. These uncertainties do not include contributions from (1) uncertainties in temperature; (2) relative uncertainties (between experiments) in the position of the crystal interface; (3) deviations from the assumed constant rate of decrease of \(^{26}\text{Mg} \) at the interface (4) non-oblique (to interface) mounting and polishing during post-experiment sample preparation; (5) non-oblique profile measurements and (6) deviations from the principal crystallographic planes.

To obtain a realistic estimate of the total uncertainty, the best fits to eq. (7) were recalculated assuming uncertainties of \( \log D \pm 0.1 \) and \( \pm 0.2 \) (1 s.d.), or as observed, whichever was larger. The resulting values of \( \chi^2 \) are given in Table 2, for six series of data (three orientations times two \( \text{aSiO}_2 \) values). Realistic uncertainties, incorporating all experimental, analytical and sample-preparation based issues thus appear to fall within the 0.1-0.2 \( \pm \log D \) range.

**A global fit**

\( E_a \) values estimated from Arrhenius plots are between 250-400 kJ mol\(^{-1}\), except for diffusion in enstatite buffered conditions along the \( a \) and \( b \) axes, for which the temperature range is quite limited. Whilst these activation energies are quite varied,
visual inspection of the trends in Figure 5 suggests that a global fit to eq. (7) may be reasonable, where $Q$ is fixed and $\log D_0$ changes for each $\alpha SiO_2$-orientation condition. This assumes the $1/T$ versus $\log D$ relationships are parallel, based on previous work in similar systems (e.g. Dohmen and Chakraborty, 2007; Zhukova et al., 2014). Thus, all data were fitted by weighted least-squares regression to the equation:

$$\log_{10} D = \log_{10} D_0(a,b,c) + \frac{-E_a}{2.303RT} + m\log a_{SiO_2}$$

This equation contains five parameters to be determined, namely $E_a$, $m$, and the three values of $D_0$ for each crystallographic orientation, $D_0[001]$, $D_0[010]$, $D_0[100]$. Values of $\alpha SiO_2$ for the fo-prEn and fo-per buffers were determined from the free energies of the reactions $\text{Mg}_2\text{Si}_2\text{O}_6 = \text{Mg}_2\text{SiO}_4 + \text{SiO}_2$ and $\text{Mg}_2\text{SiO}_4 = 2\text{MgO} + \text{SiO}_2$, respectively, using the data from Holland and Powell (2011). The silica activity for each buffer as a function of temperature is shown in Figure 6. Two data (MFO3, pericline-buffered, parallel to $[010]$, MFO9, enstatite-buffered, parallel to $[010]$) were found to be unusually aberrant (calculated value $> 5$ s.d. from observed) and were eliminated from the fitting, leaving 47 data. In both cases, there may have been an orientation mix-up – the $D$s $\|[010]$ are extremely similar to those $\|[001]$. Again, the uncertainties as defined in Table 1 give unreasonably high $\chi^2$, so these were adjusted as to ±0.15 $m^2 s^{-1}$, or as observed, if the latter was higher. The best fit gave $E_a = 298 \pm 19 \text{kJmol}^{-1}$, $m = 0.59 \pm 0.04$ and $\log D_0$ parallel to $[001] = -5.01 \pm 0.02$; $[010] = -5.50 \pm 0.02$; and $[100]: -5.90 \pm 0.05 m^2 s^{-1}$. The reduced chi-square ($\chi^2_r$) for the assumed weighting was 1.1. The uncertainties on the three values of $\log_{10} D_0$ were calculated in two stages, to mitigate the effects of covariance between the parameters, which are large. Firstly, the global best fit was obtained, secondly the fitting was repeated for the three orientations separately, constraining $E_a$ and $m$ at the global best-fit values. These three uncertainties therefore do not include the contribution from their covariances.
with $E_a$ and $m$. We therefore emphasise that the *differences* in the three values of $D_0$ are very well resolved. A comparison between the final model and the data is given in Figure 7. The value of $m$ is close to that found by Zhukova et al. (2014) for Ni ($m = 0.58 \pm 0.03$), although their value of $m$ for Co was higher ($0.80 \pm 0.03$). Note that these values are switched relative to those given by Zhukova et al. (2014) in their eqs. (9) and (10) due to a mix-up – the $E_a$ and $n_{SiO_2}$ given in their Eq. 10 are meant for their Eq. 9, and vice versa. This does not affect the fit parameters ($D_0$, $E_a$, $n_{SiO_2}$) from their combined fit (their Eq. 11).

To test our assumption that $E_a$ is constant, independent of crystal orientation, we repeated the fitting allowing $E_a$ to vary with orientation as well as $D_0$ (7 parameters). However, no improvement in the fit was observed.

**Discussion**

**Comparison with previous studies**

Mg diffusion in forsterite has been the subject of several decades of study. Diffusion coefficients from published studies are presented in Figure 8, as a function of temperature. Hallwig et al. (1979), Sockel and Hallwig (1977) and Sockel et al. (1980) measured experimental $^{26}$Mg profiles using SIMS depth profiling. They used a thin film of Mg$_2$SiO$_4$ composition enriched in $^{26}$Mg as the diffusant source, hence aSiO$_2$ was unconstrained. Morioka (1981) conducted three experiments at 1300-1400 °C by evaporating, from solution, $^{26}$MgO onto the surface of a crystal and then placing the crystal – film couples into quartz crucibles for annealing. The use of quartz crucibles may have buffered the experiment at high aSiO$_2$, i.e. corresponding to the Mg$_2$SiO$_4$ – Mg$_2$Si$_2$O$_6$ equilibrium. Andersson (1987) (PhD Thesis, then published as Andersson and Borchardt (1989) and Andersson et al. (1989)) used
NPB-SIMS (Neutral Primary Beam SIMS) depth profiling to measure $D_{Si}$, $D_O$ and $D_{Mg}$ simultaneously, in fully $\alpha$SiO$_2$-buffered experiments between 1100-1450 °C.

Whilst diffusive anisotropy is reported (Andersson et al., 1989), with $D_c > D_b > D_a$, the raw data (Andersson, 1987) do not support this well – the data show over one order of magnitude discrepancy between replicate experiments and time series steps. The sensitivity of the then newly developing analytical technique was likely insufficient to distinguish these order-of-magnitude variations, although they did successfully demonstrate that $D_{Si}<< D_{Mg}$. Chakraborty et al. (1994) revisited the problem, studying the two different forsterite crystals, one with very low Fe (<10 ppm), the other with >100 ppm Fe, and $fO_2$ and $\alpha$SiO$_2$. They found no $\alpha$SiO$_2$ dependence within the sensitivity of their analytical technique, hence conducted most experiments in $\alpha$SiO$_2$-unbuffered conditions. An $fO_2$ dependence was observed in the less pure forsterite (probably due to $Fe^{3+}$-associated M-site vacancies), whereas no dependence was seen in the very pure forsterite, in line with this study. Fei et al. (2018) extended the dataset to higher pressures (up to 13 GPa) using polycrystalline forsterite aggregates rather than single crystals, and also considered the effect of $fH_2O$ on $D_{Mg}$. They found $D_{Mg}$ broadly in agreement with previous data, but also showed a pressure effect ($\Delta V$=4.3 cm$^3$/mol$^{-1}$), and that $D_{Mg}$ is positively dependent on $fH_2O$. Whilst outside the scope of this work, it is curious to note that this $D_{Mg}$-$fH_2O$ dependence exists despite the infrared spectra of their experimental olivine showing no O-H stretching bands associated with hydrogen on the M-sites, only H associated with T-site vacancies (e.g. Lemaire et al., 2004; Matveev et al., 2001; Tollan et al., 2017).

Despite both Chakraborty et al. (1994) and Andersson (1987) conducting experiments with explicit $\alpha$SiO$_2$ buffering, no $\alpha$SiO$_2$ dependence was found. The results from Andersson (1987) showed scatter so considerable (Figure 8) that this is not surprising.
– the ~1 order of magnitude effect of $a\text{SiO}_2$ would not be resolvable. The reason Chakraborty et al. (1994) saw no effect is less obvious. Their replicate measurements on the same sample differ by up to ~0.3 log units, but this is still smaller than the effect of $a\text{SiO}_2$ found in this study.

An insight is provided by our experiences in this study. In several preliminary experiments, we found that buffering $a\text{SiO}_2$ under the constraints of economizing on high-cost materials like isotopically enriched sources can be troublesome, if there are multiple parts of the experimental charge attempting to impose different $a\text{SiO}_2$ on the crystal. In these problematic experiments, all crystals were placed onto a bed of nominally pure forsterite powder, synthesised from MgO and SiO$_2$. However, because the nominally pure forsterite most likely has some deviation from perfect (2:1) Mg:Si stoichiometry, it will have an intrinsic, if unknown, capacity to buffer the $a\text{SiO}_2$. In previous experimental campaigns by our group studying chemical, not tracer diffusion (Zhukova et al., 2014, 2017, 2018, Jollands et al., 2014, 2018) we did not encounter this problem because we were able to use large amounts of inexpensive buffering powder for each experiment. In the present study, we initially used the minimum possible volume of $^{26}\text{Mg}$-doped powder for each experiment, which apparently led to the buffering capacity of the powder glued onto the crystal surface being overwhelmed by that of the powder bed, thus several of these early experiments gave identical results for the fo-per and fo-prEn buffered runs. When the experimental design was modified, making use of a forsterite-enstatite or periclase bed, the differences between the buffering conditions systematically appeared.

This may have been the case in the Chakraborty et al. (1994) experiments, where the $^{26}\text{Mg}$ source was a MgO film (low $a\text{SiO}_2$), and then the crystal-film couples were surrounded by MgO or Mg$_2$Si$_2$O$_6$ powder, or nothing. Potentially, the MgO film was
able to buffer the near-surface region (i.e. at least the top micrometres) of the crystals to low $a$SiO$_2$, even if Mg$_2$Si$_2$O$_6$ was present nearby. If their Mg$_2$Si$_2$O$_6$ powder was acting as a true buffer, the MgO film should have fully reacted to Mg$_2$SiO$_4$ – it is not clear whether this occurred.

In any case, our data show, for the first time, that $D_{Mg}$ is a function of $a$SiO$_2$, as would be expected from general considerations of the effect of $a$SiO$_2$ on M-site vacancy concentration in forsterite (e.g. Plushkell and Engell, 1968; Smyth and Stocker, 1975; Stocker and Smyth, 1978). We may suggest that the Morioka (1981) experiments were unintentionally conducted at high $a$SiO$_2$ (quartz crucibles) and the Chakraborty et al. (1994) experiments at low $a$SiO$_2$ (MgO film), and even that the Sockel and Hallwig (1977) experiments were at high $a$SiO$_2$ due to Si-enrichment during film deposition, if this process produced effects similar to those of pulsed laser deposition (Dohmen et al., 2002a). This would explain the sequence of results in which $D_{Mg}$(Morioka) $\approx D_{Mg}$(Sockel,Hallwig) > $D_{Mg}$(Chakraborty), and why the Chakraborty et al. (1994) data agree, when extrapolated in temperature, with our low $a$SiO$_2$ series (Figure 9), and the Morioka (1981) experiments agree with our fo-prEn buffered data. An enlarged comparison of our data and that of Chakraborty et al. (1994) and Morioka (1981) is shown in Figure 9. If our interpretation is correct, then an extended global fit, incorporating their data, is possible. Utilising the results of Chakraborty et al. (1994) considerably extends the range of temperature covered, resulting in improved accuracy of the activation energy (Ea) from the global fit, giving:

$$E_a = 359 \pm 10 \text{ kJ mol}^{-1},$$

$$m = 0.61 \pm 0.03 \text{ m}^2\text{s}^{-1}$$

$$\log D_0 \||[001]\| = -3.15 \pm 0.08; \||[010]\| = -3.61 \pm 0.02; \||[100]\|: -4.01 \pm 0.05 \text{ m}^2\text{s}^{-1}.$$

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Point defects and charge neutrality conditions

The global best fit, including previously published data, gave $m = 0.61 \pm 0.03$, that is,

$$D_{Mg}^* \propto a_{SiO_2}^{0.61},$$

similar to that found for Ni chemical diffusion by Zhukova et al. (2014).

Assuming that the diffusivity of Mg is proportional to the concentration of M-site vacancies, it allows a relationship between externally imposed chemical activities and the population of point defects in the crystal to be described.

The relationship between the concentration of M-site vacancies and $a_{SiO_2}$ in pure, Fe-free forsterite has been proposed to be related either to the concentration of interstitial Si$^{4+}$, $\{Si_i^{••••}-2V_M^{••}\}^×$, or to O vacancies $\{V_O^{••}V_M^{••}\}^×$ (Smyth and Stocker, 1975; Stocker and Smyth, 1978). In the first case, $[V_M^•] \propto a_{SiO_2}^{2/3}$, and in the latter, $[V_M^{••}] \propto a_{SiO_2}^{1/4}$, with no relationship between $[V_M^{••}]$ and $fO_2$ in either case. While the present results are closer to the former, the best-fit exponent is resolvably lower than 2/3. A possible explanation may be that M-site vacancies are produced by both mechanisms.

This assertion could be independently tested by determining the tracer diffusivity of O in pure forsterite as a function of $a_{SiO_2}$ at constant $fO_2$: the creation of O vacancies implies $D_O^* \propto a_{SiO_2}^{1/4}$, whereas if $D_O^* \propto a_{SiO_2}^0$ (no relationship) at constant $fO_2$, this would support the apparently favoured $[V_M^{••}] = 2[Si_i^{••••}]$ charge neutrality condition (Smyth and Stocker, 1975; Stocker and Smyth, 1978).

It might also be the case that trace elements control the defect population to some extent, as recently demonstrated using forsterite from the same supply (Le Losq et al., 2019). The $fO_2$ independence of $^{26}$Mg diffusion suggests Fe is not a likely candidate for controlling Mg diffusion in these experiments. Al (present at the level of several tens of wt. ppm in our crystals) could be a potential candidate, especially given its ability to reside on both the tetrahedral and octahedral sites in forsterite. For example,
a reaction that enables Al to move from the tetrahedral site to the octahedral site, forming M-site vacancies ([vac]), in the presence of enstatite can be written:

$$2\text{MgAl}_2\text{O}_4 + 4\text{Mg}_2\text{Si}_2\text{O}_6 = 3\left(\frac{\text{Al}_2[\text{vac}]}{5}\right)\text{SiO}_4 + 5\text{Mg}_2\text{SiO}_4$$  \hspace{1cm} (9)

However, this reaction is formulated for the crystal-buffer interface. Similar reactions rearranging Al from the tetrahedral to octahedral site within the crystal, where site balance has to be maintained, are much more complex and would likely have to involve other point defects. For example, (10) is an interaction between the Al Tschermak’s type defect and an interstitial $\text{Si}^{4+}$ charge-balanced by two M-site vacancies (presented in Kröger-Vink notation):

$$\{\text{Al}_T^{-\text{Al}_M}\}^\times + \{\text{Si}_{i}^{----2\text{V}_M}\}^\times = \{2\text{Al}_M^{-\text{V}_M}\}^\times + \text{Si}_{\text{Si}}^\times$$  \hspace{1cm} (10)

Thus, in order for Al to control the defect population within the crystal by rearrangement, there must either be some complex interaction with other defects, or Al diffusion must be fast enough to modify the M-site vacancy population via diffusion of the $\{2\text{Al}_M^{-\text{V}_M}\}^\times$ association. The latter could be possible- the fast mechanism for Al diffusivity in forsterite (Zhukova et al., 2017) is at least two orders of magnitude higher than that of Mg (this study). In terms of concentrations, 30 wt. ppm of Al in $\{2\text{Al}_M^{-\text{V}_M}\}^\times$ configuration, in pure forsterite, is equivalent to around $1.6\times10^{-4}$ apfu Al, i.e. $[\text{V}_M]^\times \approx 8\times10^{-5}$, which is in the same order of magnitude as $[\text{V}_M]^\times$ associated with Fe$^{3+}$ in Fe-bearing olivine (Dohmen and Chakraborty, 2007), which is well known to affect Fe-Mg inter-diffusion. Thus, even ten, or tens of wt. ppm Al could considerably alter the point defect population of pure forsterite, which will have a lower background vacancy population than Fe-bearing olivine.
The effect of $a\text{SiO}_2$ on diffusion of different cations in forsterite

Following several similar experimental campaigns where different trace/minor elements have been diffused into forsterite/olivine at fully buffered $a\text{SiO}_2$ conditions, some observations can be compiled. One first order observation is that the effect of $a\text{SiO}_2$ is not equal for all trace elements. The largest effects of $a\text{SiO}_2$ (>2 orders magnitude) on D were observed for $\text{Al}^{3+}$ (Zhukova et al., 2017) although some of this effect may be due to higher diffusant concentration in high $a\text{SiO}_2$ experiments, and concentration-dependent diffusion. The smallest effects (approximately no effect) were observed for $\text{Ca}^{2+}$ (Bloch et al., 2019). The notable difference between these cations is their octahedrally-coordinated ionic radii ($\text{Al}^{3+}$:0.54; $\text{Cr}^{3+}$:0.62; $\text{Ca}^{2+}$:1), where the larger cations are preferentially ordered into the M2 site, and smaller cations the M1 (although ionic radius is not the only parameter controlling site preference-crystal field effects (e.g. Burns, 1970) and covalent bond strength (e.g. Ghose and Wan, 1974) are also important).

The link between M-site preference and effect of $a\text{SiO}_2$ on diffusivity could be explained by the M1 preference of M-site vacancies (Brodholt, 1997; Walker et al., 2009). Large M2 site cations are less likely to encounter M-site vacancies than smaller M1-site cations. Therefore, M2 site cations may be relatively immune to external variations in $a\text{SiO}_2$, whereas M1 cations would be readily affected.

Figure 10 shows the difference between logD at high $a\text{SiO}_2$ and at low $a\text{SiO}_2$ for a series of cations, firstly against ionic radii, then qualitatively against likely site preference. Where available, references describing site preference are given in the caption. Figure 10 suggests that there is some relationship between the effect of $a\text{SiO}_2$ on D and M site preference. However, the inability to place a quantitative constraint
on site preference, and (possibly) hence the data scatter, makes describing this
important relationship in any physical sense premature at this time.

This relationship could be explored further by considering the effect of $a\text{SiO}_2$ on
diffusive anisotropy in a simple system with diffusants showing M1 site preference
(e.g. Ni, Co in forsterite) where no complications from concentration-dependent
diffusion exist (Zhukova et al. 2014) only considered Ni and Co diffusion parallel to
[100] in forsterite). Given that the M1 sites form chains parallel to [001], it may be
that the response of D to $a\text{SiO}_2$ is greater parallel to [001] than [010] or [100]. This
would also depend, for example, on the extent to which macroscopically measurable
diffusion parallel to [001] is the sum of diffusive hops occurring only $\sim||[001]$ – such
experiments would help shed light on this question as well. Alternatively, the effect of
$a\text{SiO}_2$ on the diffusion of the trivalent cations could be studied systematically – it may
be expected that La (1.03 Å) is less sensitive to $a\text{SiO}_2$ than Lu (0.89 Å) or Sc (0.75
Å).

**Implications**

Mg diffusion in forsterite, like many other cations, is a function of silica activity,
along with temperature, pressure, crystallographic orientation, and water fugacity
(Chakraborty et al., 1994; Fei et al., 2018). This dependence will propagate forwards
into any geochemical transport behaviour that depends on Mg diffusion. Apparent
discrepancies between diffusion studies may potentially be explained by differences
in the buffering of major element chemical potentials, as in this study, or could
alternatively be related to differences in impurities such as Al and Fe that can have a
large influence on the number and positions of point defects.
Regarding the usefulness of various cations for diffusion chronometry, not all cations can be considered equal. The best should be those where diffusivity is a function of temperature, but little else. The safest element in olivine is probably calcium, which is unaffected by silica activity (Bloch et al., 2019), is approximately isotropic (Coogan et al., 2005), often shows simple diffusion profiles (Qian et al., 2010), and is generally easy to measure in natural systems (De Hoog et al., 2010). To be truly useful, Ca diffusion must also be unaffected by the fugacity of water in the system – this remains to be explored. However, we note that most applications of olivine diffusion chronometry have been done on olivine crystals in systems where the activity of silica is high enough (e.g. in basalt, kimberlite, dolerite etc) that an olivine-pyroxene simple system is a good approximation.

Looking forwards, for systems where the chemical activities are unknown, there exists the tantalising possibility that relative profile length scales could be used as activity monitors.

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Figure Captions

Figure 1: Backscattered electron images (obtained using an Oxford Instruments CamScan scanning electron microscope (SEM) at the University of Lausanne) of a fo-prEn buffered sample post-experiment and post-analysis, mounted in, and impregnated with epoxy. (a) Wide view, showing the nature of the buffering layer, several laser tracks scanning from core to rim (and into the epoxy) with arrows denoting the direction of laser movement relative to the sample surface, and two single laser shots, used for orientation before analysis. (b) is a closer view of the area in (a) delimited by the white square. Larger versions of the same figure, and other SEM images, can be found in Supplementary Figure 2.

Figure 2: Details regarding the fitting procedures for $^{26}$Mg, to show the different model geometries from the three methods. The profile is from a 1500 °C, fo-prEn buffered, diffusion ||[001] experiment. (a) Fit of the whole profile to eq. (3). The fitted curve fails to adequately model the whole profile, notably at the tail-end. (b) Partial fit using eq. (3), where all data before the $\sqrt{Dt}$ point, from (a), have been removed from fitting. (c) Fit of the full profile to eq. (5), although without the $x_0$
term. The best-fit values of logD using the three methods, associated with the three figures are (a) -13.98 m²s⁻¹; (b) -14.14 m²s⁻¹ and (c) -14.13 m²s⁻¹, respectively.

Figure 3: (a) comparison between a forward and backward profile measured by SHRIMP-RG, showing within uncertainty agreement (1 s.d. shown). (b) comparison between LA-ICP-MS and SHRIMP-RG data for the 1250 °C, forsterite-periclase buffered (846720 s, air, [001]) experiment successfully measured by both techniques, showing within-uncertainty agreement in diffusivity, but a slight disagreement in concentrations.

Figure 4: Some example LA-ICP-MS profiles from this study, including fits to eq. (5). Panels are arranged such that temperature increases from top to bottom, with the two left columns representing diffusion along [001] and the right columns representing diffusion along [100] or [010] (except for the bottom row). For each orientation, profiles are shown for the two buffering conditions, with a profile from the other buffering condition shown in grey (i.e. the greyed profile in (a) is the main profile in (b), etc.). Enstatite-buffered experiments suffered partial melt at >1500°C, so only periclase-buffered experiments are shown in the lowermost row.

Figure 5: The effects of chemical activities, crystal orientation, oxygen fugacity and temperature on Mg diffusion. (a) Diffusion along [001] for experiments buffered either by fo-per or fo-prEn. Despite the scatter, there is a clear difference of around one order of magnitude between the datasets. (b) fo-per buffered experiments for diffusion along the [001], [010] and [100] directions. Diffusion is fastest along [001] and slowest along [100]. (c) No apparent effect of oxygen fugacity on diffusion in either buffering condition.
Figure 6: Silica activity ($aSiO_2$) as a function of inverse temperature. Grey areas: ranges of experimental conditions. The liquidus of fo-prEn is from Andersen and Bowen (1914).

Figure 7: Comparison of measured versus model diffusion coefficients, including a 1:1 line and 1:1±0.25 logD lines.

Figure 8: Diffusion coefficients from previous published studies of $^{26}$Mg diffusion in forsterite, and ///[001] diffusion coefficients from this study, with conditions described in the text. Abbreviations: C94: Chakraborty et al. (1994); S80: Sockel et al. (1980); M81: Morioka et al. (1981), A87: Andersson (1987); F18: Fei et al. (2018).

Figure 9: Data from this study (diffusion ///[001]), along with the data from Morioka (1981) and Chakraborty et al. (2004). (a) shows the best fits to all data. Dashed lines represent the best fits to only the dataset from this study. Solid lines also include the data from Chakraborty et al. (1994) and Morioka (1981), assuming that the former was fo-per buffered (MgO thin films) and the latter was fo-prEn buffered (quartz crucible). The global best fit incorporating the other studies requires a slightly higher activation energy. (b) shows the comparison between model and data, according to the global fit including the three studies. Most data fall within ±0.25 log units (dashed lines).

Figure 10: (a) The relationship between ionic radii and difference in diffusion coefficients between high $aSiO_2$ (enstatite-buffered) and low $aSiO_2$ (periclas buffered) for various elements where fully-buffered experiments have been conducted. Most data are at 1300 °C, or the closest temperature available. $Al^{3+}$: (Zhukova et al., 2017); $Cr^{3+}$, $Cr^{2+}$: (Jollands et al., 2018); $Rh^{3+}$: (Zhukova et al., 2018); $Ni^{2+}$, $Co^{2+}$: (Zhukova et al., 2018); $Hf^{4+}$, $Zr^{4+}$: (Jollands et al., 2014); $Mg^{2+}$:
this study; Y\(^{3+}\): (Crépisson et al., 2012); Ca\(^{2+}\): (Bloch et al., 2019). (b) Effect of aSiO\(_2\)
on diffusion as a function of site preference. Ni: M1 (Burns, 1970; Matsui and Syono, 1968); Co: M1 (Ghose and Wan, 1974); Ca\(^{2+}\): M2 (Lumpkin et al., 1983; Mukhopadhyay and Lindsley, 1983); Cr\(^{2+}\): M1 (Burns, 1970) or M2 (Li et al., 1995); Cr\(^{3+}\): slight M1 preference (Petričević et al., 1988). Zr\(^{4+}\), Hf\(^{4+}\), REE\(^{3+}\), Al\(^{3+}\), Rh\(^{3+}\): assumed to be ordered based on ionic radii for lack of quantitative data.

Table Captions

Table 1: Experimental conditions and results. Values of the quartz-fayalite-magnetite (QFM) equilibrium are from (O'Neill, 1987). Bold, italic values are from SHRIMP-RG, all others are from LA-ICP-MS. Values and uncertainties (1 s.d.) are weighted based on fit quality from ~five repeat profiles. *=reverse profile (see Figure 3). Note that these uncertainties likely underestimate the true uncertainty – this is described in more detail in the text. Missing data are usually due to profiles being too short to satisfactorily resolve, or issues with sample preparation leading to unrecoverable interfaces.

Table 2: Arrhenius parameters for fits to each condition (buffer+axis), calculated imposing different minimum uncertainties. Numbers in parentheses are 1σ. The bold values are the reduced chi squared closest to one from the different fits for each condition.

Supplementary Figure Captions

Supplementary Figure 1: Cartoon experimental and analytical procedure. 1) ~cubes of forsterite cut from a larger crystal, then polished on one face. Not shown: following cutting, forsterite was mounted in epoxy, ground and polished, then removed from the...
resin. 2) Buffer powder, sintered then re-ground, was mixed with polyethylene oxide
glue, then pasted onto the crystal surface. The thickness was generally around 1 mm,
which decreases considerably when the glue is dried, then devolatilised at run
conditions. 3) Charge dried at 100 °C. 4) Diffusion experiment conducted in a tube or
box furnace, with conditions described in the text. 5) Following the experiment, the
charge was mounted in epoxy, and vacuum impregnated. This was often done with
several other charges in the same mount. Sometimes the buffering powder was
removed prior to mounting, other times it was not. 6) The mount was ground down on
a diamond wheel by at least 1 mm, to expose the crystal core. Then, the mount was
diamond polished. 7) The sample was analysed by traversing a slit-shaped beam
across the surface, from core to rim (i.e. from low $^{26}$Mg to high $^{26}$Mg). Note: no depth
profiling was done in this study.

Supplementary Figure 2: Backscatter electron (BSE) images of the diffusion interface
and buffering powder taken post-experiment using an Oxford Instruments CamScan
scanning electron microscope (SEM) at the University of Lausanne. (a) fo-per
buffered experiment, showing laser tracks. (b) enlargement of (a), showing surface
roughness on the order of <10 μm. (c) and (d): as for (a) and (b), but for an enstatite-
buffered experiment. Note the longer laser tracks in (c) versus (a), given that
diffusivity is higher when buffered by fo-prEn compared to by fo-per.

Supplementary Figure 3: Comparison of diffusion coefficients ($^{26}$Mg) determined
following data reduction by the two methods. In both figures, the x axis is the
diffusion coefficient determined after normalising to $\Sigma$Mg, and the y axis is the
diffusion coefficient determined when the data are not normalised to $\Sigma$Mg. Reduced
chi-squared are calculated from a 1:1 correlation. (a) is determined using the depleting
interface solution (eq. (5)) and (b) using the fit to only part of the curve (eq. (4)).
Supplementary Figure 4: Extracted diffusion coefficients for $^{26}$Mg versus $^{24}$Mg, with uncertainties derived by combining the diffusion coefficients determined using the two fitting methods. Whilst the data cluster around the 1:1 line, the disagreement between diffusivities, and small uncertainties associated with $^{26}$Mg, make the reduced chi squared too high to suggest a meaningful correlation.

Supplementary Figure 5: The effect of chosen interface position on the outputted logD values. (a) Example $^{29}$Si and $^{26}$Mg profiles, and the chosen interface position associated with a drop in $^{29}$Si counts. (b) the effect of moving the interface in either direction on diffusion coefficients, and their uncertainties.

Supplementary Figure 6: Comparing the diffusivities extracted by fitting only the tail end of the diffusion profiles (partial fit) versus those determined using eq. (5), which assumes a linearly decreasing boundary condition. (a) histogram of the difference between Ds determined using the two methods, showing a mean offset to around -0.1 (i.e. the partial fit method gives Ds around 0.1 orders of magnitude lower than the depleting source method, when comparing medians). (b) all fits from the two methods, compared. Whilst the correlation appears strong, the reduced chi squared is extremely high, regardless of the fitting method used. This is because the errors from curve fitting are generally smaller than the discrepancy between Ds from the two methods.

Supplementary Figure 7: Considering the validity of eq. (5) to such a system as studied in this work. (a) schematic of the (1D) model used. A 0.1 mm thick buffer powder, with infinitely fast diffusion (no Mg isotopic gradient within the buffer at any time) and enriched $^{26}$Mg, is attached to a 1 mm long crystal, with defined D and the natural abundance of $^{26}$Mg. For simplicity we assume length is proportional to mass.
The model assumes no isotopic fractionation between buffer and crystal. All
modelling is done using an explicit finite difference approximation of Fick’s second
law. (b) Comparison of the evolution of the boundary conditions over time. The
dashed line shows the linear decrease assumed by eq. (5), whereas the solid line
describes the evolution of the boundary when mass is conserved in the whole system,
with a shape close to logarithmic. This was calculated by subtracting the total amount
of $^{26}$Mg in the crystal from the total $^{26}$Mg in the whole system at every time step. (c)
Diffusion profiles generated using the two boundary conditions. The linear decrease
model predicts a slight inflexion in the near boundary, whereas the mass conservation
model does not. (d) The total amount of $^{26}$Mg in the system (given as mean isotopic
ratio) over the duration of the model. The linear decrease boundary condition leads to
$^{26}$Mg increasing then decreasing, which is clearly not feasible in a closed system.

Supplementary Figure 8: The relationship between uncertainties and diffusion profile
length. Uncertainties are calculated as described in the text, combining fits determined
using the two solutions to the diffusion equation, and incorporating the x0 term that
accounts for uncertainty on the interface position. The diffusion lengthscale is
calculated using the $4\sqrt{Dt}$ approximation, which is an estimate of the distance over
which the concentration decays by erf(2), i.e. by around 99.5%. (a) includes all fits,
(b) is the data after multiple fits have been combined.

Supplementary dataset 1: All $^{26}$Mg profiles and fits. See the _README document for
more information.
Figure 2

(a) Full fit to error function

(b) Partial fit to error function

(c) Depleting source error function
Figure 3

(a) Mg (normalised) vs. distance from interface (µm)

-16.37±0.10 m²s⁻¹
-16.41±0.09 m²s⁻¹

(b) Mg (normalised) vs. distance from interface (µm)

logD_{SHRIMP-RG} = -14.21±0.04 m²s⁻¹
logD_{LA-ICP-MS} = -14.27±0.09 m²s⁻¹
Figure 4
Figure 6

Successful experimental range

liquid

fo-prEn

fo-per

1000/T(K)

ln a_{SiO_2}

T (°C)
Figure 7

The graph shows a plot of logD (m²s⁻¹) [data] versus logD (m²s⁻¹) [model]. The data points are aligned relatively close to the 45-degree line, indicating a strong correlation. Two dashed lines are drawn, one at +0.25 and the other at -0.25, which serve as reference lines for comparison. One data point is excluded from the fit, as indicated by the label "excluded from fit."
Figure 8

This study, fo-prEn

Chakraborty et al. (1994)
Fo1 (120-180 ppm Fe)
MgSiO$_3$
- ///[001], fO$_2$ = 10$^{-12}$ bars
- ///[001], fO$_2$ = 10$^{-6}$ bars
- ///[001], fO$_2$ = 10$^{-0.7}$ bars

MgO
- ///[001], fO$_2$ = 10$^{-12}$ bars
- ///[001], fO$_2$ = 10$^{-0.7}$ bars

No buffer
- ///[100], fO$_2$ = 10$^{-12}$ bars
- ///[010], fO$_2$ = 10$^{-12}$ bars
- ///[001], fO$_2$ = 10$^{-12}$ bars
- ///[001], fO$_2$ = 10$^{-0.7}$ bars

MgSiO$_3$
- ///[001], fO$_2$ = 10$^{-12}$ bars
- ///[001], fO$_2$ = 10$^{-6}$ bars
- ///[001], fO$_2$ = 10$^{-0.7}$ bars

Morioka (1981)
- ///[001], no buffer

Andersson (1987)
MgSiO$_3$
- ///[100]
- ///[010]
- ///[001]

MgO
- ///[100]
- ///[010]
- ///[001]

Fei et al. (2018)
- 'Wet', 8 GPa
- 'Dry', 1-13 GPa

Sokel et al. (1980)
- ///[001], no buffer
- ///[010],[100], no buffer

Fo2 (11 ppm Fe)
No buffer
- ///[001], fO$_2$ = 10$^{-12}$ bars
- ///[001], fO$_2$ = 10$^{-0.7}$ bars
Figure 9

(a) $\log_{10} D \left( m^2 s^{-1} \right)$ vs $10000/T$ (K) for different datasets:
- **This study (fo-prEn)**
- **This study (fo-per)**
- **Morioka (1981)**
- **Chakraborty et al. (1994)**

(b) Global fit for this study (+M81, C94)
Figure 10

(a) (b)

Difference in logD between high and low \( a_{SiO2} \)

Increasing preference for M2

Octahedral ionic radius

M1 equal M2
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<th>Time (s)</th>
<th>Absolute</th>
<th>ΔQFM</th>
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Using $\sigma$ from Table 1

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