The mechanism of Mg diffusion in forsterite and the controls on its anisotropy

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Abstract

Mg diffusion is important for explaining many rheological properties in forsterite but its mechanism is unknown. Without knowing a mechanism the effect of variables such as pressure are hard to constrain. In this study we used Density Functional Theory (DFT) to calculate the diffusivity of Mg vacancies and interstitials in forsterite and thus the diffusion rate of Mg in forsterite. We predict vacancy diffusion to be highly anisotropic with considerably faster diffusion in the [001] direction while interstitial diffusion is predicted to be more isotropic. Thus we predict that a combination of interstitial and vacancy diffusion is required to reproduce experimentally derived anisotropies. Interstitial diffusion is predicted to be highly pressure dependant such that with increasing pressure the anisotropy of Mg diffusion decreases while temperature has little effect on this anisotropy. Substances like Fe and water likely cause increases in Mg diffusion rate through the creation of extrinsic Mg vacancies and we predict that without modifications to the inherent mobility of Mg vacancies these cause small increases to diffusional anisotropy at 1300 and 1600 K but very large increases at 1000 K.

Keywords: Forsterite; Mg Diffusion; DFT

Word Count: 7504

1 Introduction

Diffusion of cations occupying the octahedral metal sites in olivine controls processes that are active in the Earth's crust and upper mantle, and which underpin a range of geophysical and geochemical techniques. In the upper mantle, where olivine with composition close to $(Mg_{0.9,}Fe_{0.1})_2SiO_4$ is the dominant phase, the diffusivity of Mg is important in understanding electrical conductivity (Fei et al., 2018, Yoshino et al., 2009, Yoshino et al., 2017, Schock et al., 1989) and could influence deformation even though Mg is a rapidly diffusing species as argued in Jaoul (1990). Anisotropic Mg diffusion could be an important factor in explaining the anisotropic conduction seen in high conductivity layers underneath young oceanic plates (Fei et al., 2018) and, if Mg diffusion is important in forming olivine textures, could also help explain the variety of textures that are formed by olivine under different conditions (Karato et al., 2008). Mg-Fe interdiffusion occurring in zoned phenocrysts from volcanic products is increasingly used as a petrological tool (diffusion chronometry) to understand the timescales of pre-eruptive processes operating in the days and weeks prior to eruption (e.g. Hartley et al. 2016 and Pankhurst et al. 2018). On a longer timescale diffusion-controlled exchange between Mg and Fe in olivine and spinel can be used to infer the post-crystallisation thermal history of ultramafic igneous bodies (Ozawa, 1984). Diffusion can also lead to magnesium and iron isotope fractionation (Teng et al., 2011).

Our understanding and ability to model all of these processes relies on accurate determination of the Mg self-diffusion and Fe-Mg interdiffusion coefficients in olivine and thus this has been the focus of a range of experimental and computational studies reviewed by Chakraborty (2010). However, details of the atomic scale basis of Mg self and inter-diffusion in olivine have thus far eluded a full atomistic explanation and this limits our ability to confidently make use of this data under the wide range of conditions where diffusion is important. In this work we shall study the atomistic mechanisms of Mg self-diffusion as the more straightforward of these two processes.

Experimental measures of Mg diffusion

Previous experimental studies have identified several key features of Mg self-diffusion as well as questions that remain unanswered. Despite early uncertainty, it is clear that magnesium self-diffusion is faster than the self-diffusion of oxygen or silicon (for a review of this history see Chakraborty (2010)). Diffusion can be described by a basic equation $D^{sd} = D_0 \exp\left(-\frac{E_{act}}{k_B T}\right)$ where D^{sd} is the rate of self-diffusion, D_0 is a preexponential factor, E_{act} is the activation energy, k_B is the Boltzmann constant and T is the temperature. D_0 and E_{act} can then be treated as fitting factors for experiments run at different temperatures. Recent experimental estimates of E_{act} and D_0 for Mg tracer diffusion in forsterite are 9.6×10^{-4} m^2/s and 4.15 ± 0.17 eV (Chakraborty et al., 1994) or 4.0×10^{-9} m^2/s or 2.59 ± 0.31eV (Fei et al., 2018). The diffusion rate D_{sd} at 1300 K and 0 GPa is $3.6x10^{-19}$ m^2/s in Fei *et al.* (2018a) or $2\text{-}6x10^{19}$ m^2/s in Chakraborty *et al.* 1994. More generally there is broad agreement as to the Mg diffusion parameters in anhydrous forsterite though there is around half an order of magnitude discrepancy between different experimental predictions, some of which are plotted in Figure 5 (Andersson et al., 1989, Chakraborty et al., 1994, Fei et al., 2018, Jollands et al., 2020, Morioka, 1981) .

In detail, magnesium self-diffusivity is found to be mildly sensitive to pressure, to be anisotropic and to depend on the chemistry of the olivine crystal. Diffusion along [001] has been found to be faster than diffusion along [100], which is faster than diffusion along [010] (Chakraborty et al., 1994) though other studies have found diffusion along [010] to be faster than diffusion along [100] (Andersson, 1987, Jollands et al., 2020). There are some differences in experimental activation volumes 1-3.5 cm^3/mol (Chakraborty et al., 1994) or 4.0-4.6 cm^3/mol (Fei et al., 2018) but in all cases these are small and so pressure has little effect on diffusion rates. These activation volumes come from data solely in the [001] direction which is important because they do not reflect all processes that occur in the crystal as shall be explored in the text.

Although these experiments provide the critical data needed to model diffusion-controlled processes in olivine, several aspects of Mg diffusion remain enigmatic and some parameters have not been fully established. For example, the reason for the anisotropy of diffusion is not clear and the effect of pressure or other elements on this anisotropy has not yet been determined. An argument has been made that diffusional anisotropy is related to Mg hopping distance (Brodholt, 1997) but in a highly anisotropic crystal like forsterite the difficulty of Mg hopping is unlikely to be a simple function of distance. By using *ab-initio* calculations we can explore atomistic mechanisms by which these processes could occur.

Crystal structure of olivine

In order to understand diffusion in olivine it is first necessary to consider the crystal structure, how this permits point defect mobility and the chemistry that controls the defect concentration. This will allow us to formulate possible atomistic mechanisms by which diffusion can occur. Olivine's distorted hexagonal close packed oxygen sublattice contains two distinct octahedrally co-ordinated M sites: M1, on an inversion centre, and the less symmetric M2, which sits on a mirror plane. M1 sites share edges and form continuous chains along [001] while M2 sites are isolated from each other (sharing an edge with an M1 site and corners with other M1 and M2 sites). This structural anisotropy hits at a possible reason for the directional dependence of Mg diffusion in forsterite: vacancy mobility along chains of M1 sites could be high compared to more tortuous pathways between M1 and M2 sites. There are also two normally unoccupied octahedral sites in the olivine structure. Each is located half way between two occupied M sites (and shares faces with them) along [100]. We call the unoccupied octahedral site midway between two M1 sites I1, and the unoccupied octahedral site midway between two M2 sites I2.

Theoretical Studies of Mg defects and their diffusion in Forsterite

Using this knowledge of forsterite crystal structure previous work has attempted to address the structure and mobility of point defects in forsterite. This largely consists of two parts, first identifying the points defects of forsterite and then their mobility.

Simulations using interatomic potentials (Wright and Catlow, 1994, Walker et al., 2009, Jaoul et al., 1995, Bejina et al., 2009), density functional theory (Brodholt, 1997) and QM/MM embedded clusters (Walker et al., 2009, Braithwaite et al., 2003) suggest that the most important defects are Mg vacancies which are most stable on M1 rather than M2 sites and octahedrally coordinated Mg interstitials which form a split-interstitial structure (two magnesium ions in tetrahedral coordination located on opposite sides of the M1 site) is stable (Walker et al., 2009). The mobility of some of these defects has been studied using interatomic potentials (Bejina et al., 2009, Jaoul et al., 1995, Walker et al., 2009) where it was found that Mg vacancies are more mobile than Mg interstitials (Walker et al., 2009), that pressure has a limited effect on mobility along the M1 chain as was found in experiments (Jaoul et al., 1995, Bejina et al., 2009) and that vacancies overwhelmingly diffuse along the [001] M1 chain (Bejina et al., 2009). These studies have neglected important effects. First, interatomic potentials often behave poorly in unusual geometries and these are often formed during diffusion. Second, these studies consider only activation energies and not the time taken for diffusing point defects to overcome these barriers. And third, they do not convert their diffusion pathways into a macroscopic diffusion model and thus calculate rates of diffusion.

Thus there exists no detailed exploration of Mg diffusion in forsterite using electronic structure methods. In the following we make use of atomic scale simulation to understand the atomic scale mechanism of Mg diffusion in forsterite, determine the absolute diffusivity as a function of direction and how this is altered by pressure and how extrinsic defects could affect this picture.

2 Methods

Compared to the timescale accessible to direct atomic scale simulation using molecular dynamics, point defect diffusion in minerals is usually slow. Methods available to simulate diffusion thus seek to describe diffusion by repeated rare events which can be studied in detail, and then combined in order to describe diffusion on a meaningful timescale. The rare events are typically hops of point defects between adjacent sites. For example, one of a number of atoms could migrate into a vacancy, effectively moving the vacancy and permitting diffusion via a vacancy mechanism, or an interstitial atom could move into one of a number of different interstitial sites, permitting diffusion via an interstitial mechanism. Repeated occurrences of these hops leads to a random walk of the defect and bulk self-diffusion (Tilley, 1987). Our approach to simulating Mg diffusion in forsterite thus follows three steps. First, we make use of density functional theory to determine the structure and relative stability of stable Mg point defects in forsterite. These models represent the ground state end-points of the hops leading to diffusion. Second, we probe the energy landscape that must by traversed by the defect during a hop. This provides us with the energy barrier that must be overcome for the hop to proceed and the structure of the transition state (the configuration with maximum energy on the minimum energy pathway between the start and the end point). Boltzmann statistics tell us how likely it is for a point defect to have enough energy at a given temperature to overcome the energy barrier while simulation of the lattice vibrations of the ground and activated state allow us to calculate the frequency at which each hop is attempted. Third, we combine information about multiple hops between different ground states using a kinetic Monte Carlo approach to access timescales long enough to observe the random walk and measure Mg diffusion in forsterite.

2.1 Defect calculations using density functional theory

All input parameters to our models of magnesium diffusion in forsterite are derived from atomic scale simulations. Specifically, we use a “planewave and pseudopotentials” approach (Payne et al., 1992), where density functional theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965) allows us to probe the energy of periodic boxes of simulated atoms. We use this to evaluate the ground state defect structures and energies, the structures and energies of the transition states, and the way atoms vibrate in these configurations. This approach allows us to calculate the hop activation energies and rates as a function of temperature and pressure. These calculations were undertaken using version 16.11 of the CASTEP code (Clark et al., 2005), which makes use of a plane wave basis for valence electrons (a cut off energy of 1000 eV was used throughout) and pseudopotentials to describe core electrons (on-the-fly ultra soft pseudopotentials were used with 2s, 3p and 3s, 2s and 2p, 3s and 3p, and 1s in the valence for Mg, O, Si and H, respectively). The PBE (Perdew et al., 1996) exchange correlation functional (a revised GGA functional) was used and, Kohn-Sham wavefunctions were represented on a (4x4x4) k-point grid in reciprocal space (Monkhorst and Pack, 1976).

We created models of Mg vacancies by removing an Mg^{2+} ion from an M1 or M2 site in a (2x1x2) forsterite super cell. Interstitial defects were created by inserting an extra Mg^{2+} ion into potential interstitial sites in the structure. In both cases the cell parameters were always fixed to those of the defect free crystal to approximate the dilute limit. To account for atomic relaxation around the defects, the structure was then relaxed until the forces on all atoms were less than 0.01 eV/Å and an energy change between different geometric steps was less than 1×10^{-5} eV/atom. Repeating calculations with increased cutoffs changed the energy of the supercell by <0.1 meV/atom. A (2x1x2) forsterite supercell was used to ensure that there was roughly 10 Å between repeating vacancies in all directions, a distance we found to be sufficient to contain the important atomic relaxations. Simulation cells containing vacancies or interstitials have a net charge and so the energy calculated by CASTEP includes a defect-defect interaction term between adjacent supercells which does not reflect our desired energy of a charged defect in an infinite medium. We can approximately correct for this interaction by assuming it is the energy of a periodic array of point charges in a uniform neutralising background charge. This was done using the method of Leslie and Gillan (1985), first used for forsterite by Brodholt (1997). To use this method the relative permittivity of the cell needs to be set - we used a value of 6.2 (Weast, 1981). We repeated these calculations for a (4x2x4) supercell containing a Mg vacancy, and the vacancy energy changed by <0.01 eV, suggesting that our simulation cell size and energy corrections are sufficient for our needs.

Knowing the energy of defects allows us to calculate their population with assumptions about their formation reactions. The Mg Frenkel reaction ($Mg_{Mg}^{X} \rightarrow V_{Mg}'' + Mg_{I}^{\bullet\bullet}$) is the likely formation reaction for Mg vacancies (Dohmen and Chakraborty, 2007). This will be the source of defects in this work and the number of defects can be calculated from the knowledge of the defect energies of Mg vacancies and interstitials. This assumption is explored later in the text.

Once ground state structures and energies for the defects had been determined, we enumerated the possible hops (where a defect moves from location to location) and for each hop we determined the pathway and found the transition state structure and energy. We did this by using a constrained optimisation approach. We first determined an approximate path for the hop (for vacancy diffusion this consists of two vacancies with a Mg atom at a point between the vacancies, for interstitial diffusion the interstitial atom is located between stable interstitial sites). For each hop we tried multiple paths, but direct paths proved to have the lowest transition state energy in all cases. A path was defined by at least 10 images (with the Mg atom in different locations between the start and end point) and each image was relaxed with the migrating Mg fixed to the path by preventing its movement in one direction ([100] or [010] or [001]) with the fixed direction being that which has the longest distance along the path. This provides an energy profile along the path and a maximum energy point. We then searched for the transition state by moving along the path from the maximum energy point in 0.1 Å steps in both directions until a maximum was found. This is the candidate transition state. While this method may not definitely find the transition state our frequency calculations (below) typically returned a single imaginary eigenvalue of the dynamical matrix, as expected for a transition state. In the few cases, which were all for interstitial diffusion, where this was not the case the candidate transition state was found by manual adjustment based on visualising the eigenvectors of the imaginary phonon frequencies until a single imaginary eigenvalue was found. It turned out that this manual adjustment changed the activation energy of the hop by <0.01 eV suggesting that the constrained optimisation method is highly reliable for finding activation energies even if they are in complex parts of the energy hypersurface.

We repeated the calculations described above at 0, 5 and 10 GPa and 1000, 1300 and 1600 K by setting the simulation cell dimensions to minimise the Gibbs free energy of the defect free cell. The effect of pressure is easily accounted for by adding the PV term to the internal energy of the system. The effect of temperature requires consideration of the thermal motion of the atoms. We include this effect by making use of lattice dynamics to evaluate the phonon frequencies and then use these to evaluate the vibrational entropy of the crystal. Phonon frequencies were determined using the finite displacement method of CASTEP with finite displacements of 0.01 bohr. All lattice dynamics calculations were performed solely at the q=(0,0,0) point. While this calculation at a single q-point may introduce a significant sampling error all of our calculations involve comparisons between two very similar structures – the start/end point of a diffusion step and its transition state – and so the effect of sampling errors are likely to be small but this is a limitation of the method. For lattice dynamics we tightened the convergence criteria on the forces and energy for the geometry optimisation to 0.001 eV/Å and 1×10^{-9} eV/atom, respectively. A few end points and transition states were sampled with 0.00075 eV/Å and 5x10-^{10} eV/atom cuts off and the change in free energy caused by these increased cutoffs was <1 meV/atom. We determined the Gibbs free energy at a wide range of temperatures and at least 5 different volumes and then the energy at each volume with the following equations:

$$G(P,T,V) = U(V) + PV + E_{ZP}(V) - TS(T,V) \quad \text{Equation 1}$$

$$E_{ZP}(V) = \sum_{k,i} \frac{1}{2} \hbar\nu_{k,i}(V) \quad \text{Equation 2}$$

$$S(V) = -\sum_{k,i} \ln\left[1 - \exp\left(-\frac{\hbar\nu_{k,i}(V)}{k_B T}\right)\right] - \frac{1}{T}\sum_{k,i} \hbar\nu_{k,i}(V) \left[\exp\left(\frac{\hbar\nu_{k,i}(V)}{k_B T}\right) - 1\right]^{-1} \quad \text{Equation 3}$$

Where U(V) is the internal energy and $\nu_{k,i}(V)$ is the frequency of the phonon with wave vector *k* in the *i*-th band at volume V. At the pressure and temperature of interest the appropriate volume and energy was determined by fitting 2nd order polynomials across our volume range and minimising Equation 1. This method is quasi-harmonic as it ignores anharmonic effects beyond those caused by thermal expansion.

2.3 From defects to diffusion

The self-diffusion of a Mg by a vacancy mechanism can be represented by:

$$D_{Mg}^{sd-vac} = D_{Mg}^{Vac} N_{Vac} \quad \text{Equation 4}$$

Where D_{Mg}^{Vac} is the diffusion coefficient of Mg vacancies and N_{Vac} is the atomic fraction of Mg vacancies.

As shown below, our atomic scale simulations suggest that diffusion of both interstitials and vacancies can be important for magnesium diffusion in pure forsterite. To account for this possibility we use the assumption that vacancies and interstitials diffuse independently of each other, which means that the total self-diffusion of Mg in forsterite is given by:

$$D_{Mg}^{sd} = D_{Mg}^{Vac} N_{Vac} + D_{Mg}^{Int} N_{Int} \text{ Equation 5.}$$

Other diffusing species (which are not considered in this paper) would have their own term if present. For systems with simple geometry, the diffusion coefficients can be found analytically from the attempt frequency, the migration entropy, the activation energy and the crystal structure. For example, for a single hop the coefficient is given by (Poirier, 1985):

$$D_{Mg}^{Vac} = \frac{\alpha}{q} l^2 v exp\left(\frac{\Delta S_m}{k_B}\right) exp\left(-\frac{\Delta H_m}{k_B T}\right) \text{ Equation 6}$$

where α is a geometric prefactor to account for the degeneracy of the hop, q is a dimensionality constant (q = 2, 4 or 6 for 1, 2 or 3D diffusion), *l* is the length of the hop and the two exponential terms are the migration entropy and the migration enthalpy, respectively. This approach has been used to determine diffusion coefficients in a number of minerals including MgO, bridgmanite and post-perovskite (e.g. Vocaldo et al. 1995; Ammann et al. 2010). However, forsterite diffusion involves defects moving from one site to an inequivalent site via multiple different hops and so it becomes cumbersome to attempt to develop equations of this type. Instead we seek a numerical estimate of the diffusion coefficients by implementing a kinetic Monte-Carlo (KMC; Bortz et al. (1975)) simulation of the motion of a defect in a forsterite crystal.

For our KMC method we need to know the concentration of defects and the rate at which each Mg hop can occur. As explained above the concentration of intrinsic defects (vacancies and interstitials) were determined by minimising the free energy of the Frenkel reaction at the appropriate P and T. To determine the rate of hopping we used lattice dynamics to probe the vibration of atoms around the point defects in their ground state and transition state configurations. This allows us to model the effect of temperature on point defect mobility. The rate, *k*, at which a defect hops from one location to another is given by:

$$k = v exp\left(\frac{\Delta S_m}{k_B}\right) exp\left(-\frac{\Delta H_m}{k_B T}\right) \text{ Equation 7}$$

where v is the attempt frequency (in Hz). The activation energy term was calculated from our constrained optimisation. In order to calculate the attempt frequency and activation entropy we used Vineyard theory (Vineyard, 1957) which is based on absolute rate theory. Both of the temperature-based factors (vibrational entropy and attempt frequency) are combined into a modified attempt frequency (v*) which is found from the ratio of the calculated phonon frequencies:

$$v^* = vexp\left(\frac{dS}{k_B}\right) = \frac{\prod_{j=1}^{N} \mathrm{v}_j}{\prod_{j=1}^{N-1} \mathrm{v}_{j'}} \text{ Equation 8}$$

where v_j are the lattice frequencies of a defect in its stable starting position and v_j' are the real lattice frequencies of the defect at the transition state of its hop. The latter has one imaginary frequency and so one less real frequency. Similarly to our method for the treatment of thermal expansion this theory assumes harmonic small oscillations near the saddle point and thus assumes the system operates as a harmonic oscillator. Once activation energies and modified attempt frequencies have been calculated for each hop (and at each temperature and pressure of interest), we can calculate the rate of each hop and have all the atomic scale information in hand to evaluate the absolute diffusivity of magnesium in forsterite. These single hop parameters are then fed into our KMC algorithm.

First developed to allow the efficient simulation of Ising spin systems, KMC works by simulating the time evolution of a system between a collection of states, with transitions between states governed by a set of rules that includes a probability of that transition occurring in a given amount of time. Transitions between states are selected randomly (preserving the relative probability of each transition) and a clock is advanced by an appropriate amount after the state transition has been determined. This makes it useful for simulating complex transitions with many possible motions as the properties of each transition can be calculated independently and then put collectively into a KMC algorithm. KMC has found a number of applications in extending atomic scale simulations to macroscopic behaviour, including the simulation of dislocation motion (Bulatov and Cai, 2006), chemical vapour deposition (Bagatur'yants et al., 2003) and point defect diffusion (Voter, 2007).

For our simulations, we followed the rejection-free residence time method of Voter (2007). A brief overview of this method shall be given here, with more detail in the Supplementary Information. For each state in the system (e.g. a vacancy on M1) we enumerate all possible hops from that state and then calculate the rate of each hop (k^i) (equation 7 using equation 8), the sum of the rates of all the hops (k^{tot}) and the probability of each hop occurring $p^i = \frac{k^i}{k^{tot}}$. We then use the weighted probability of each hop to randomly select a hop. We also randomly select a time for that hop to occur (the escape time):

$t^i = -\left(\frac{1}{k_{tot}}\right) \ln{(r^2)}$ Equation 9

Where r^2 is a random number between 0 and 1. At each stage of the calculation the randomly selected hop moves our defect a certain distance in a certain direction and the randomly determined escape time advances the clock. Thus as this algorithm progresses, we build a list of positions of the defect as a function of time as it undergoes a random walk through the (infinite) crystal structure. We then calculate the mean-squared displacement (MSD) of our defect (using the method of Leetmaa and Skorodumova (2015) as explained in the supplementary information) as a function of time. This can then be converted to diffusion:

$\langle x^2 \rangle = qDt$ Equation 10

Where q is the dimensionality constant as above.

3 Results

3.1 Defect Energies and Concentrations

There are two sites for Mg vacancies in forsterite – the M1 and the M2 sites. We calculate that M1 sites are strongly favoured over M2 sites with pressure increasing the vacancy preference for M1 sites (Table S1). This preference for M1 over M2 vacancies agrees with previous calculations though there is some difference in the energy of this preference (0.9-1.2 eV in this work, ~1.9 eV with forcefield calculations (Walker et al., 2009) or ~0.8 eV previously using DFT (Brodholt, 1997)).

We have also considered Mg interstitials. As with Walker et al. (2009) we found that the most stable position is a split interstitial at the M1 site with 2 Mg atoms displaced from the centre of this site in opposite [010] directions (shown in Figure S1). This arrangement is very stable with alternative arrangements of the Mg at this site all relaxing into this one. Even placing a Mg atom in an I1 site causes it to relax into this split interstitial arrangement. The other stable configuration is found by placing an additional Mg in the I2 site. The Mg interstitial in the I2 site has an octahedral coordination like the M1 and M2 and is thus geometrically similar to them. At 0 GPa the split M1 interstitial is slightly favoured over the I2 arrangement (~0.2 eV) but with increasing pressure the I2 configuration is favoured (Table S1) as the split M1 arrangement is larger than the I2 arrangement. In QM-MM embedded cluster calculations (Walker et al., 2009) the split M1 geometry was found to be favoured over an I1 interstitial geometry by ~4.4 eV but an I2 geometry was not reported. In our own forcefield calculations we were unable to stabilise an I2 arrangement as I2 arrangements always relaxed into M1 arrangements. Forcefields are thus likely poor at calculating these interstitial structures.

To calculation diffusion rates the concentration of vacancies is required (Equation 5). For intrinsic diffusion we have assumed this comes from minimising the free energy of the Frenkel reaction ($Mg_{Mg}^{X} \rightarrow V_{Mg}^{\prime\prime} + Mg_{I}^{\bullet\bullet}$). When this reaction proceeds forward the positive enthalpy and the negative configurational entropy term both increase and at some concentration this provides a minimum energy. As the Mg interstitial is able to occupy two sites solving analytically for the free energy minimum is awkward. Instead we calculate the number of different arrangements of Mg vacancies and defects in the crystal considering all M1, M2, I1 and I2 sites and then calculate the probability of their occurrence and thus their configurational entropy. The steps for this are given in the supplementary information but the final result is that the equilibrium concentration in the intrinsic case comes from minimising Equation 11:

$\Delta G = \Delta E \times a - TS_{confa}$ Equation 11 where a is a reaction vector for the Frenkel reaction (between 0 and 1), ΔE is the energy of the Frenkel reaction and S_{confa} is the configurational entropy after the reaction has proceeded forward by a. The results of this minimisation are given in Table 1. Pressure strongly decreases the number of defects (by increasing the positive formation energy) whereas temperature increases the number of defects (as the configuration entropy is multiplied by -T).

To test the assumption that only the Frenkel reaction is important we looked at the following intrinsic reactions that produce Mg defects:

R1) $Mg_{Mg}^{X} \rightarrow V_{Mg}'' + Mg_{I}^{\bullet\bullet}$

R2) $Mg_{Mg}^{X} + O_{O}^{X} \rightarrow V_{Mg}'' + V_{O}^{\bullet\bullet} + MgO$

R3) $MgO \rightarrow Mg_{I}^{\bullet\bullet} + O_{I}''$

R4) $2V_{Mg}'' + Si_{Si}^{X} + 4MgO \rightarrow V_{Si}'''' + 2Mg_{Mg}^{X} + Mg_2SiO_4$

R5) $Si_{Si}^{X} + 4MgO \rightarrow V_{Si}'''' + 2Mg_{I}^{\bullet\bullet} + Mg_2SiO_4$

R6) $Mg_2SiO_4 + Si_{Si}^{X} + 2Mg_{Mg}^{X} \rightarrow 2V_{Mg}'' + Si_{I}^{\bullet\bullet\bullet\bullet} + Si_{Si}^{X} + 4MgO$

To simulate the other defects we probed all likely sites, found the sites with the minimum enthalpy and then calculated their high temperature energy through Equation 1-3. The energy of these reactions is shown in Table S2 but all reactions have substantially higher energies than the Frenkel reaction (R1). By including these other reactions, which also compete in configurational entropy space, we change the concentration of Mg defects by less than 0.001% and thus these can safely by ignored and we shall only consider the Frenkel reaction R1 from now on.

3.2 Vacancy Hops

For Mg diffusion by vacancy hopping we found six different vacancy diffusion hops for which we calculated the geometries and energies of hopping. The hops that we have considered are shown and labelled in Figure 1 with their dimensions listed in Table S3 and described in the SI.

The activation energies and frequencies of these hops are presented in Table 2 and the barriers to diffusion are shown in Figure 2. Notably the A hop which is directly along the [001] direction has a substantially lower activation energy than all other M1 hops. The easiest hop from an M2 site is the C hop back to an M1 site. These two effects combine such that vacancies will diffuse easily along the [001] direction when in a M1 site and will have difficulty escaping to an M2 site. If they do escape to an M2 site they will be converted quickly back to an M1 site. The weighted probability of these hops is shown in Figure 2 and an alternative representative in Figure S2 demonstrating the overwhelming dominance of the A hop.

Comparing our activation energies to published values we find that our value for the favoured A hop of 0.75 eV is similar to literature values of 0.72 (Walker et al., 2009) and 0.62 eV (Bejina et al., 2009). Our other hops have some variation with those found in Walker et al. (2009). To test whether this was an effect of simply using DFT as against using forcefields we recalculated our results using GULP with a TBH1 forcefield (Wright and Catlow, 1994) (Table S4, computational details in supplementary information). We find that generally DFT produces lower barriers than forcefield calculations but that the order of the hops is the same with both DFT and forcefield calculations. Crucially the activation energy of the easiest A hop (which largely controls the overall diffusion) is very similar with both methods 0.77/0.75 eV which means that both DFT and forcefield calculations return a very similar diffusivity for anhydrous vacancy diffusion.

We also considered the effect of pressure on the activation energies of these vacancies. As shown in Table S5 and Table S6 going from 0 to 10 GPa makes negligible differences to the activation energy or v^* of any of the hops. The small differences seen are miniscule compared to the effect pressure has on the vacancy concentration as described above.

3.3 Mg interstitial hops

As Mg interstitials occupy M1 and I2 sites- the latter of which are simply shifted M2 sites- the relative geometry of interstitial hops are identical to those of vacancies. These hops are pictured and labelled in Figure 3 and their barriers in Figure 4 (and tabulated in Table S7) with their energies and frequencies in Table 2 (and more pressure derivatives listed in Table S6 and S8). The probability of any of the hops occurring is shown in Figure 4 and alternatively in Figure S3. These are again described in the supplementary information.

Interstitial hops I and J, which are between M1 and I2 sites, are the most favourable with activation energies <0.6 eV. In part this is because in the split M1 configuration one Mg at the M1 site is already close to an I2 site. Pressure has a small effect on the attempt frequency (Table S6) but a relatively large effect on the activation energy of these hops (Table S8) with hop I becoming nearly barrierless by 10 GPa. Interstitial hops from the split M1 configuration have considerably lower attempt frequencies than the typical values between 1×10^{-12} and 1×10^{-13} Hz whereas hops from the I2 site show more typical attempt frequencies.

3.4 Diffusion

Using our KMC algorithm we can convert hops into diffusion rates. The diffusion coefficients for both vacancy and interstitial hopping are presented in Table 3 (these are listed at 5 and 10 GPa in Table S9 and S10). Vacancy diffusion is highly anisotropic with diffusion along [001] being orders of magnitude faster than diffusion along [100] or [010]. This is an outcome of diffusion where the hop directly along [001] is ~0.75 eV easier than any other M1 hop. In the absence of any additional undiscovered hops/mechanisms this will always hold. Interstitial diffusion is much more isotropic than vacancy diffusion due to the favourability of M1 to I2 hops (I and J) which go in all three primary directions.

To calculate total diffusion of Mg in forsterite we added together the rates of Mg vacancy and interstitial diffusion. This assumes that Mg Frenkel pairs are not associated with each other. To test this assumption, we calculated the binding energy of this pair by running separate simulations with isolated Mg vacancies and interstitials and then calculations with them adjacent in the same unit cell and comparing the difference in enthalpy. We find that the binding energy is approximately -1.9 eV with a negative number indicating that bound defects are more stable than unbound defects. This is a large number but it is much smaller than the configurational energy gains of randomly scattering Mg vacancy and interstitial pairs for low concentrations. For the pairing energy to exceed this configuration entropy, the defect concentration would need to be above 1.2x10^{-3} defects per unit cell at 1300 K, many orders of magnitude larger than the predicted vacancy concentrations (Table 1). Thus the Mg vacancy and interstitial pairs are unlikely to be associated with each other and can be modelled individually here.

Figure 5 compares our pressure corrected (see supplementary information) results with some experimental measures of Mg self-diffusion at 0 GPa. We only plotted results for experiments buffered with MgO because enstatite has been observed (in one case) to increase Mg diffusion rates by nearly 1 order of magnitude (Jollands et al., 2020). For Chakraborty *et al.* 1994 we plotted the results without buffer as the SiO_2 activity of these experiments is likely controlled by MgO (Jollands et al., 2020). In the [001] direction our results are very similar to those of Jollands *et al.* 2020. The absolute value of our results, however, is somewhat unreliable as it is largely dependent on the choice of V_0^{exp} and thus the pressure correction. This is shown in Figure S4 where a larger (-5 GPa) pressure correction was applied and we find diffusion rates in the [001] direction very similar to those of Chakraborty *et al.* 1994. The results presented in Figure 5 use what we consider the most reliable pressure correction. Regardless our calculated [001] diffusion lies in the experimental range. In the [100] and [010] direction our results are within the experimental scatter of Andersson et al. (1989) but not that of Jollands *et al.* 2020. The experimental results have considerable differences from each other. While partly this is due to self-diffusion experiments being very difficult there is another possible cause. The most likely cause of these discrepancies is the presence of different extrinsic defects across different systems. Different extrinsic defects even if they do not diffuse themselves could vary the N_{vac} and N_{Int} terms in Equation 5 and thus vary the diffusion rate. Such a variation would only have a very small effect on the experimentally determined activation energy unless the extrinsic defects were themselves produced thermally. Traditional measures of crystal purity are not adequate to accurately judge this effect as the key parameter is not so much the presence of different extrinsic defects but how these defects affect the intrinsic defects on a sub ppb level. To fully address this a large thermodynamic model needs to be built which is beyond the scope of this work. Another possibility is that there exists some factor of diffusion- such as an additional method of defect production- that is not replicated in this study.

Our ability to replicate the results of Jollands et al. (2020) suggests that our model for diffusion in anhydrous forsterite accurately captures its diffusion in at least one case. Critically if interstitials are not included in our model while [001] diffusion can be modelled accurately, [100] and [010] diffusion would be orders of magnitude slower than has been observed by any experiment.

We next consider the effect of pressure. Figure 6 shows our anhydrous [001] diffusion rates (with values listed in Table S11) as a function of pressure. Notably we find a larger pressure derivative for intrinsic diffusion coefficients than has been seen in the literature (Chakraborty et al., 1994, Fei et al., 2018). Our activation volumes are 6.69 cm^3/mol at 1000 K, 7.51 cm^3/mol at 1300 K and 7.84 cm^3/mol at 1600 K. The pressure dependence of diffusion is strongly controlled in our calculations by the pressure dependence of defect concentration (Table 1) with little effect of the defect mobility (Table 3). Small changes to the formation energy of the Frenkel defect can have a strong effect on this dependence. If the number of defects is held constant across pressure then the calculated activation volumes are much smaller, ranging from -0.30 to 0.15 cm^3/mol. These lower activation volumes are of relevance for cases where pressure does not alter the number of vacancies. For example, in an extrinsic regime (where vacancies form to charge balance impurities) the vacancy concentration is not temperature or pressure dependent and only the direct effect of pressure on vacancy mobility is important. In a real crystal with few impurities there will be a balance between the number of vacancies formed intrinsically via Frenkel pairs and the number of vacancies associated with impurities. In such a case, the effective activation volume will fall between our high and low values as is observed experimentally.

4. Discussion

4.1 Anistropic intrinsic diffusion

One of the most notable features of our results is that Mg diffusion can be strongly anisotropic. Figure 7 shows the anisotropy of this diffusion as a function of pressure. We find that anisotropy decreases with pressure due to the increasing importance of interstitial diffusion, which is less anisotropic, while temperature has little effect on anisotropy. At 1600 K and 0 GPa (corrected) we find the ratio of diffusion in different directions [001]:[100] to be ~15 and [001]:[010] to ~6. Experimental measures of these ratios have produced lower results with [001]:[100] having values of ~3 (Chakraborty et al., 1994), 3.5-7 (Jollands et al., 2020) and 7-40 (Andersson, 1987), and [001]:[010] having values of 4.5 (Chakraborty et al., 1994), 1.5-3.5 (Jollands et al., 2020) and 5-13 (Andersson, 1987). These experimental measurements were all at ambient pressure. Our calculated values for diffusional anisotropy are somewhat larger than has been seen experimentally. Our pressure correction method has not been calibrated for defect production and mobility and if the pressure correction was somewhat larger our anisotropies would approach the experimental range albeit its top end. One possible way to reduce the anisotropy would be to increase the ratio of Mg interstitials to Mg vacancies which could occur in the presence of extrinsic sources of Mg interstitials or impurities that fill Mg vacancies. Alternatively, there could be some macroscopic effect that reduces diffusional anisotropy in real crystals and that we do not model.

Another issue is the order of diffusional speeds in different directions. Our calculations and some experiments (Andersson et al., 1989, Jollands et al., 2020) predict diffusion rates to be ordered [001]>[010]>[100] while Chakraborty et al. (1994) measured diffusion rates to be [001]>[100]>[010]. We do not have a source for this discrepancy as in our model both [010] and [100] diffusion are almost entirely controlled by interstitial I and J hops and thus their relative rate is fixed by the geometry of the crystal and not by any variable parameter. We have no hops that could selectively increase the [100] diffusion rate that are even close to being viable. Thus the presence of evidence suggesting that diffusion along [100] can be faster than diffusion along [010] suggests some kind of atomistic or macroscopic effect that is not being modelled in our system.

4.2 Anisotropy Changes in the Upper Mantle

While the dependence of anisotropy on pressure is large this probably has little implication in the upper mantle. After applying pressure corrections a 0-10 GPa range in the upper mantle would be equivalent to ~4-16 GPa in our pressure scales. The largest changes in anisotropy come at the lowest pressures and so across the pressure range of the upper mantle, changes in Mg diffusional anisotropy with depth will typically be up to an order of magnitude except at the coldest temperatures (1000 K) where this could reach 1.5 orders of magnitude. These changes are likely to too small to have any major effects on mantle rheology that change with depth.

4.3 The effect of extrinsic vacancies

Other substances such as iron (Chakraborty, 2010, Dohmen et al., 2007, Dohmen and Chakraborty, 2007) or water (Fei et al., 2018) that are in olivine can substantially change the diffusion rate. Without substantial changes to the diffusion mechanism there are two ways this can happen 1) through modifying the concentration of defects (N_{Vac}, N_{Int}) or 2) through modifying the mobility (D_{Mg}^{Vac}, D_{Mg}^{Int}) of defects. All substances that modify the diffusion rate likely do the former while only some do the latter. Iron can increase the number of Mg vacancies through the following reaction (Dohmen and Chakraborty, 2007, Chakraborty, 2010):

R7) $6Fe_{Mg}^{X} + SiO_2 + O_2(g) \rightarrow 2V_{Mg}'' + 4Fe_{Mg}^{\bullet} + Fe_2SiO_4$

whereas water can produce $(2H)_{Mg}^{X}$ vacancies. R7 has been invoked as the controlling reaction in Mg diffusion at intermediate temperatures in what is known as the Transition Metal Extrinsic Domain (TAMED) (Chakraborty, 2010). In the Fe-Mg interdiffusion case the mobility of vacancies is also modified as they include Fe self-diffusion coefficients. In the case of water the mobility of $(2H)_{Mg}^{X}$ could be different to V_{Mg}'' but likely similar. In these and other cases we expect the change in the concentrations of vacancies to generally outweigh the changes to the mobility of vacancies due to the small number of intrinsic defects produced by the Frenkel reaction (Table 1). Extrinsic Mg vacancy concentrations can be many orders of magnitude higher than our predicted intrinsic Mg vacancy concentration in many systems. This is seen in iron-containing olivine (Dohmen and Chakraborty, 2007) where the Mg vacancy concentration is many orders higher than predicted here due to R7. Thus the prime reason that various contaminants cause an increase in Mg diffusion rates is likely to be the production of more Mg vacancies. Critically Mg vacancies can be produced in this way but producing extrinsic Mg interstitials is much more difficult. This means that extrinsic defects are likely to produce a strong imbalance in the Mg vacancy vs Mg interstitial ratio.

Producing Mg vacancies in excess of Mg interstitials would cause strong changes to the anisotropy of diffusion. This effect is explored in Figure 8 where we plot how increasing the diffusion rate solely by adding Mg vacancies changes the anisotropy of diffusion. We are not aware of any studies on diffusional anisotropy in forsterite with large amounts of defects so instead we use our model to predict the anisotropy from the measured diffusion rates. We do this by assuming two things: 1) any change in Mg diffusion rate from the Mg self diffusion rate (D_{sd}) in Equation 5 is due to extrinsic Mg vacancies and 2) that extrinsic Mg vacancies do not bind to any charge balancing impurities that produce them (D_{Mg}^{Vac} is identical for intrinsic and extrinsic Mg vacancies). Then we use Equation 12:

$D_x = D_{sd} + D_{Mg}^{Vac} N_{Vacex}$ Equation 12

where D_x is the target diffusion rate, D_{sd} is determined from Equation 5 and N_{vacex} is the concentration of extrinsic Mg vacancies that is varied until D_x matches the desired value. Using this framework we explore the effects of two defective elements Fe (1-20%) (Dohmen and Chakraborty (2017) and water (1-100 ppm) (Fei *et al.* 2018). At 1300 K we predict these defects to increase diffusional anisotropy (compared to perfect forsterite) by 2-5 times at 5-10 GPa (uncorrected). As temperature increases this effect decreases such that by 1600 K iron and water increase diffusional anisotropy by less than 1.2 times. Thus at the high pressures and temperatures of the upper mantle the measured experimental diffusion rates of both water and iron containing forsterite can be matched by adding in extrinsic Mg defects without large increases in diffusional anisotropy. Thus for these compositional ranges we do not expect extrinsic vacancies to lead to significant anisotropy for Mg diffusion in the upper mantle.

Conclusions

We find that the anisotropy of Mg diffusion in forsterite is heavily dependent upon conditions with pressure strongly decreasing the anisotropy while temperature only weakly affects it. In the presence of extrinsic vacancies temperature strongly controls diffusional anisotropy with samples at low temperatures having potentially extremely high diffusional anisotropy (>500 times faster in the [001] direction). This has strong implications for diffusion chronometry and conductivity (and other properties dependant on Mg diffusion rates) which need to include corrections for pressure and impurity content alongside orientation to account for this effect.

In this work we outline a simple atomistic model which is able to replicate measured experimental diffusion rates along the [001] direction. We find that to explain experimental diffusion rates in the [100] and [010] directions interstitial diffusion is required alongside Mg diffusion.

The next step is to consider how other components could affect this diffusion such as has been seen with enstatite (Jollands et al., 2020) and with our simple extrinsic vacancy model in Figure 8. Additional components can either affect the number and balance of Mg vacancies and interstitials or they can affect the intrinsic diffusion of Mg vacancies and interstitials. The former effect can be considered by examining the energetics of defect forming reactions and how contaminants change these energetics- particularly through changing the configurational entropy balances- and the latter can be considered for contaminants that directly change Mg vacancies or interstitials by interacting with them.

Acknowledgments

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Figure 1:

Diagram of possible vacancy hops between M1 and M2 sites. The absolute distances of these hops are listed in Table S3. Mg atoms are brown, Si atoms are blue with their tetrahedrons highlighted, oxygen atoms are red.

Figure 2: Plot of the activation energy barriers to Mg vacancy hopping in anhydrous forsterite. The energy of a vacancy is plotted at M1 (blue) (defined as 0 eV) and M2 (green) sites and at 7 points in-between each site with both the site and the intermediate points plotted with the same relative energy bar as shown. Many more intermediate points were used to determine the activation energy maximum than are shown here(see text for details). Hops in the [100] direction (hops B and F) are not shown but both of these hops have activation energies higher than all the hops pictured here. The black box represents a forsterite unit cell. For a sample M1 and an M2 site we have shown the main hops with a percentage likelihood of selecting this hop that was determined at 1300 K and 0 GPa (uncorrected).

Figure 3:

Diagram of interstitial hops between M1 and I2 sites. The absolute distances of these hops are listed in Table S7. Octahedral holes are green.

Figure 4: As Figure 2 but for interstitial hops between M1 and I2 sites with the M1 sites being defined as 0 eV. The layer closer to the bottom of the graph are M1 and then I2 and M1 layers alternate going up the page. These sites are much closer in energy than the M1 and M2 sites for vacancy migration. Again hops along the [100] axis (H and L) are not shown but are very high in energy. With this projection I and I* and J and J* hops are on top of each other (as they are only varied along the [100] direction) but we have pictured the lower energy paths (I and J respectively).

Fig 5: Plot of experimental Mg self diffusion rates in MgO-buffered forsterite at 0 GPa alongside our predicted rates at 0 GPa (corrected- see supplementary information) determined by fitting between our pressure corrected values (the same plot with a 5 GPa pressure correction is shown in Fig S4). Rates have been separated by diffusion direction (colour- red= [001], green= [010], blue= [100]) and by the work they come from (symbol-see below). The lines represent our own calculations. In this collection we have excluded work in olivine and work buffered by enstatite. The mark for Fei *et al.* (2018a) was determined by our own extrapolation of the high temperature data across different pressures, all other points were as measured in the experiment. References are Morioka *et al.* 1981 triangles, Jollands *et al.* 2020 squares, Chakraborty *et al.* 1994 circles, Fei *et al.* (2018a) cross, Andersson *et al.* 1987 diamonds.

Figure 6: [001] Mg diffusion rates in perfect forsterite as a function of pressure at fixed temperatures (blue=1000 K, green=1300 K, red=1600 K) compared to results from Chakraborty *et al.* (1994) and Fei *et al.* (2018a). Model predictions are uncorrected (solid line) or pressure corrected (dotted line). For experimental data data points are plotted and then a line is constructed using activation volumes of

1.1 cm^3/mol for Fei *et al.* (1994) and 4.3 cm^3/mol for Fei *et al.* (2018a). The results from Chakraborty *et al.* (1994) are those with no buffer with an f_{O_2} of 10^{-12}. In these results a higher activation volume (~3.4) was determined in air. The oxygen fugacity of Fei *et al.* (2018a) is unknown due to the complicated presence of water.

Figure 7: Log of the ratios of C/A ([001]/[100]) (dotted lines, circles) and C/B ([001]/[010]) Mg diffusion (solid line, squares) in perfect olivine as a function of pressure at different temperatures (blue 1000 K, green 1300, red 1600). Two pressure scales are shown, the pressure scale from DFT and one that has been corrected as per the text.

Fig 8 Comparision of anisotropy (defined as diffusion in the [001] direction/ diffusion in the [110] direction) for different diffusion rates (D_x) in a system of self diffusion+extrinsic vacancies. Anistropy is relative to pure forsterite which is 1. This was determined by solving Equation 13 as a function of diffusion rate. Lines are at 1000 (blue), 1300 (orange) and 1600 K and solid lines represent 5 GPa, dotted lines 10 GPa (uncorrected) which correct to around 1 and 6 GPa respectively.

The dark region represent the range of D_x between Fe=1-20% for olivine at 0 GPa, 1300 K and $fO^2=10^{-7}$ Dohmen and Chakraborty (2017). The ligt region represents the range of D_x for water ranging between 1-150 wt. ppm at ~8 GPA and 1300 K (Fei *et al.* 2018).

Table 1: Free energy of the Frenkel reaction at various pressures and temperatures and the corresponding concentration of vacancies and interstitials (in defects/unit cell) in a pure forsterite crystal where only the Mg Frenkel reaction forms significant defects- this concentration is for each defect type so the concentration of total defects (vacancies+interstitials) is twice this number. Also shown is the concentration of hydrous vacancies formed by water assuming water solely forms hydrous Mg vacancies (γ=1). All pressures are uncorrected.

Table 2: Activation energy and modified attempt frequency v* of various hops (shown in Figure 1 and 3 with the hop distances outlined in Table S4 and S8) for hydrous and anhydrous forsterite at 0 GPa uncorrected. Hop L could not be stabilised but is very high in energy. Hops with an asterisk go in the reverse direction where this is not equivalent.

Table 3: Diffusion coefficients (m^2/s) of vacancies and interstitials in three directions at 0 GPa (uncorrected) with 5 and 10 GPa (uncorrected) [001] diffusion coefficients also listed. For the other coefficients in [100] and [010] at 5 and 10 GPa see Table S10 and S11.

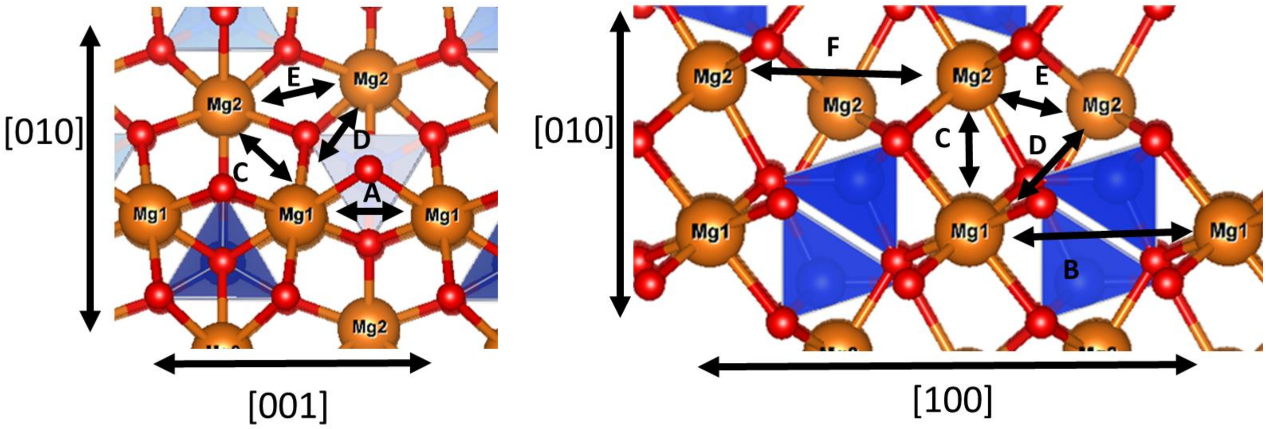

Figure 1:

Diagram of possible vacancy hops between M1 and M2 sites. The absolute distances of these hops are listed in Table S3. Mg atoms are brown, Si atoms are blue with their tetrahedrons highlighted, oxygen atoms are red.

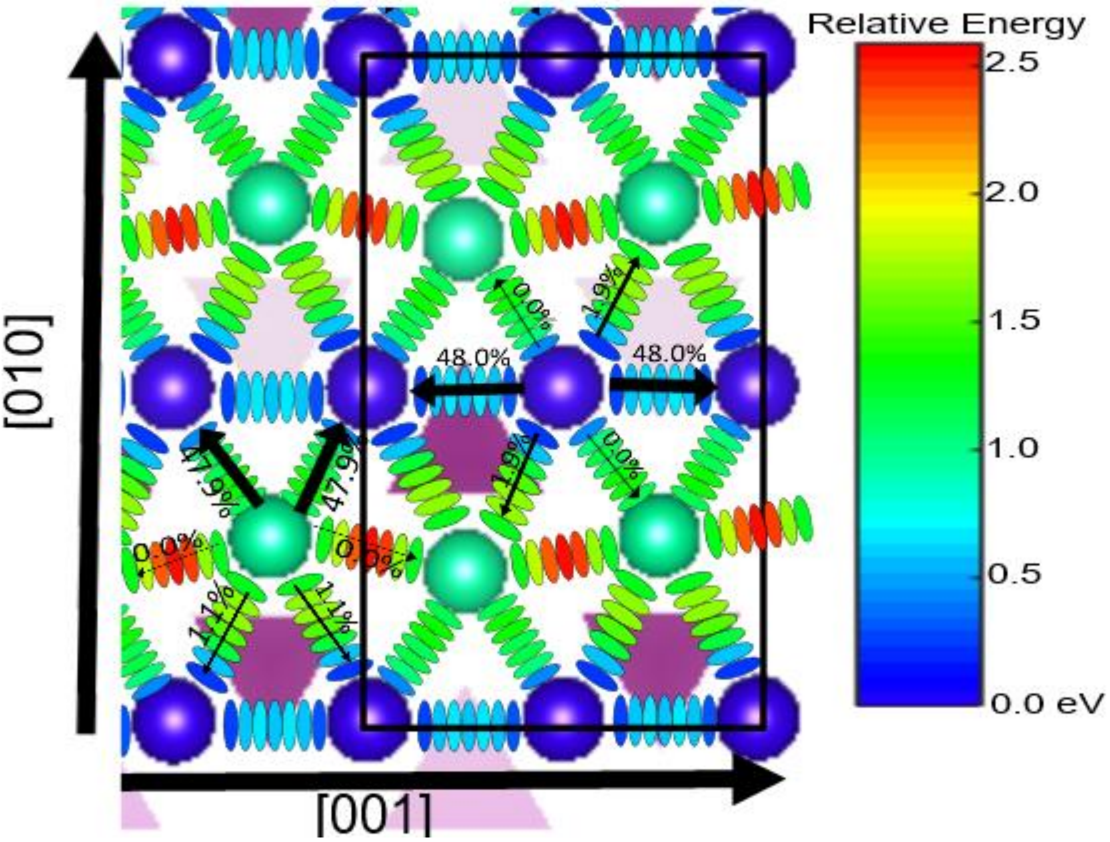

Figure 2: Plot of the activation energy barriers to Mg vacancy hopping in anhydrous forsterite. The energy of a vacancy is plotted at M1 (blue) (defined as 0 eV) and M2 (green) sites and at 7 points in-between each site with both the site and the intermediate points plotted with the same relative energy bar as shown. Many more intermediate points were used to determine the activation energy maximum than are shown here(see text for details). Hops in the [100] direction (hops B and F) are not shown but both of these hops have activation energies higher than all the hops pictured here. The black box represents a forsterite unit cell. For a sample M1 and an M2 site we have shown the main hops with a percentage likelihood of selecting this hop that was determined at 1300 K and 0 GPa (uncorrected).

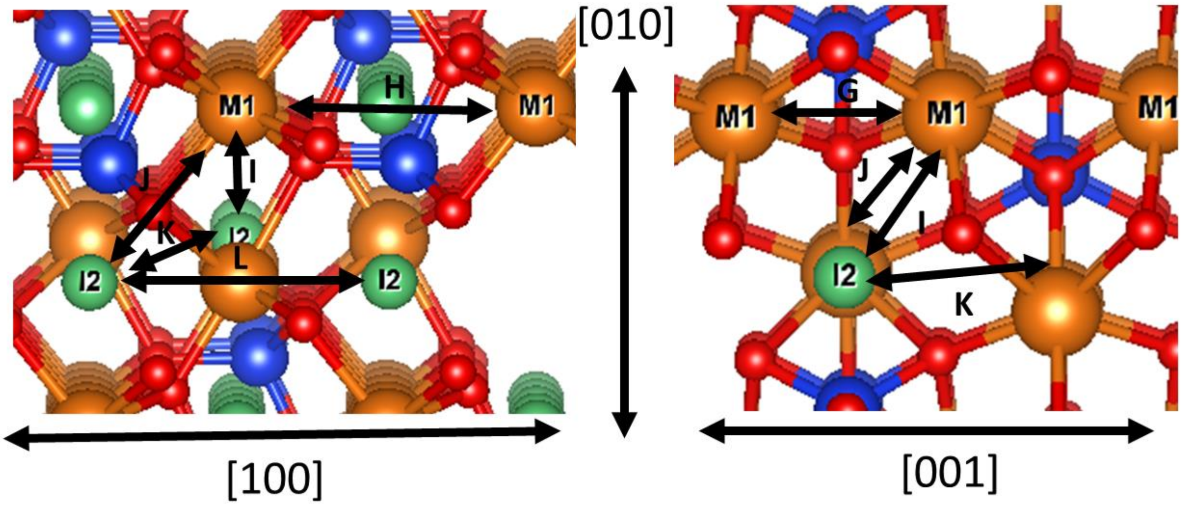

Figure 3:

Diagram of interstitial hops between M1 and I2 sites. The absolute distances of these hops are listed in Table S7. Octahedral holes are green.

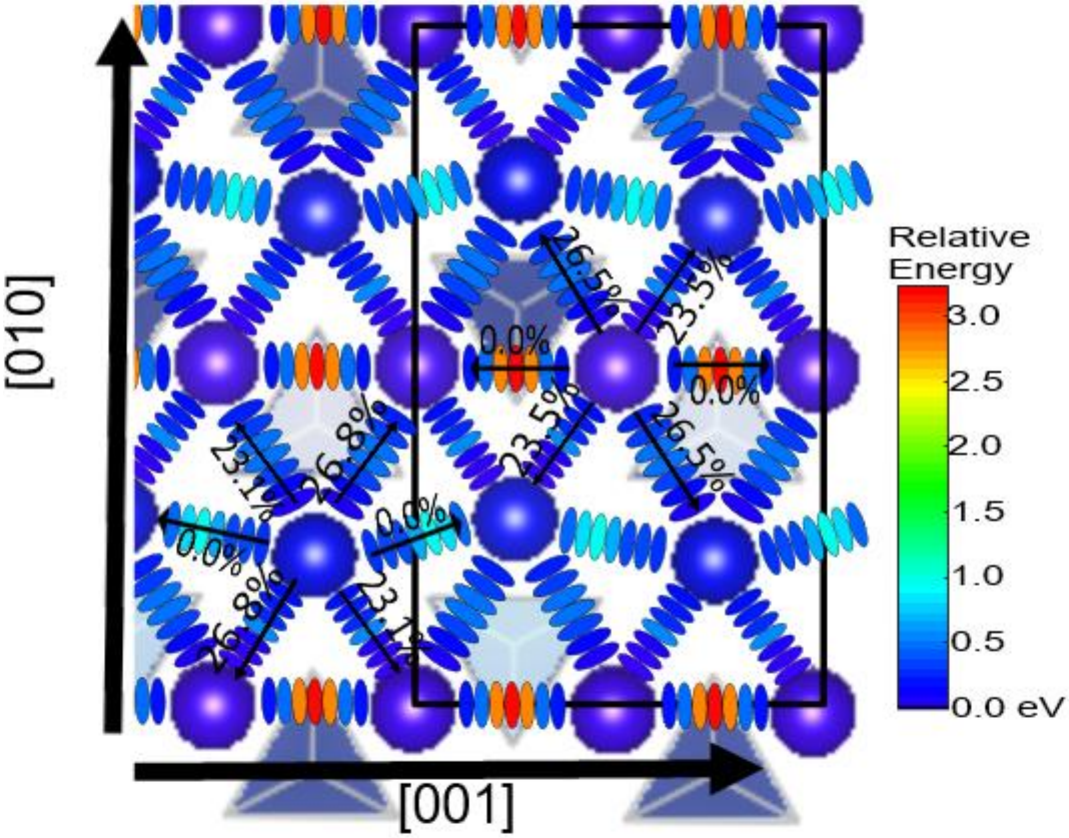

Figure 4: As Figure 2 but for interstitial hops between M1 and I2 sites with the M1 sites being defined as 0 eV. The layer closer to the bottom of the graph are M1 and then I2 and M1 layers alternate going up the page. These sites are much closer in energy than the M1 and M2 sites for vacancy migration. Again hops along the [100] axis (H and L) are not shown but are very high in energy. With this projection I and I* and J and J* hops are on top of each other (as they are only varied along the [100] direction) but we have pictured the lower energy paths (I and J respectively).

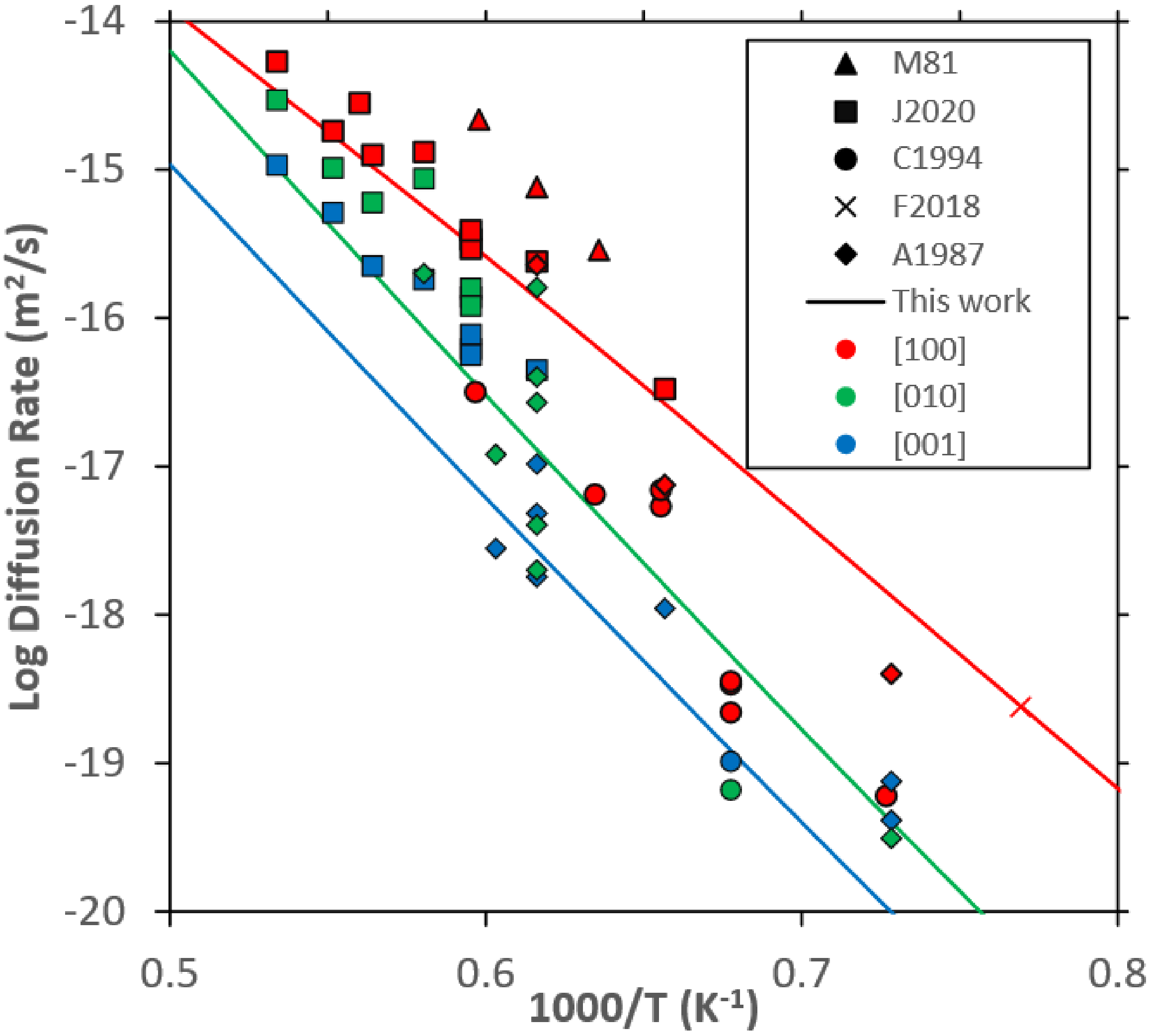

Fig 5: Plot of experimental Mg self diffusion rates in MgO-buffered forsterite at 0 GPa alongside our predicted rates at 0 GPa (corrected- see supplementary information) determined by fitting between our pressure corrected values (the same plot with a 5 GPa pressure correction is shown in Fig S4). Rates have been separated by diffusion direction (colour- red= [001], green= [010], blue= [100]) and by the work they come from (symbol-see below). The lines represent our own calculations. In this collection we have excluded work in olivine and work buffered by enstatite. The mark for Fei *et al.* (2018a) was determined by our own extrapolation of the high temperature data across different pressures, all other points were as measured in the experiment. References are Morioka *et al.* 1981 triangles, Jollands *et al.* 2020 squares, Chakraborty *et al.* 1994 circles, Fei *et al.* (2018a) cross, Andersson *et al.* 1987 diamonds.

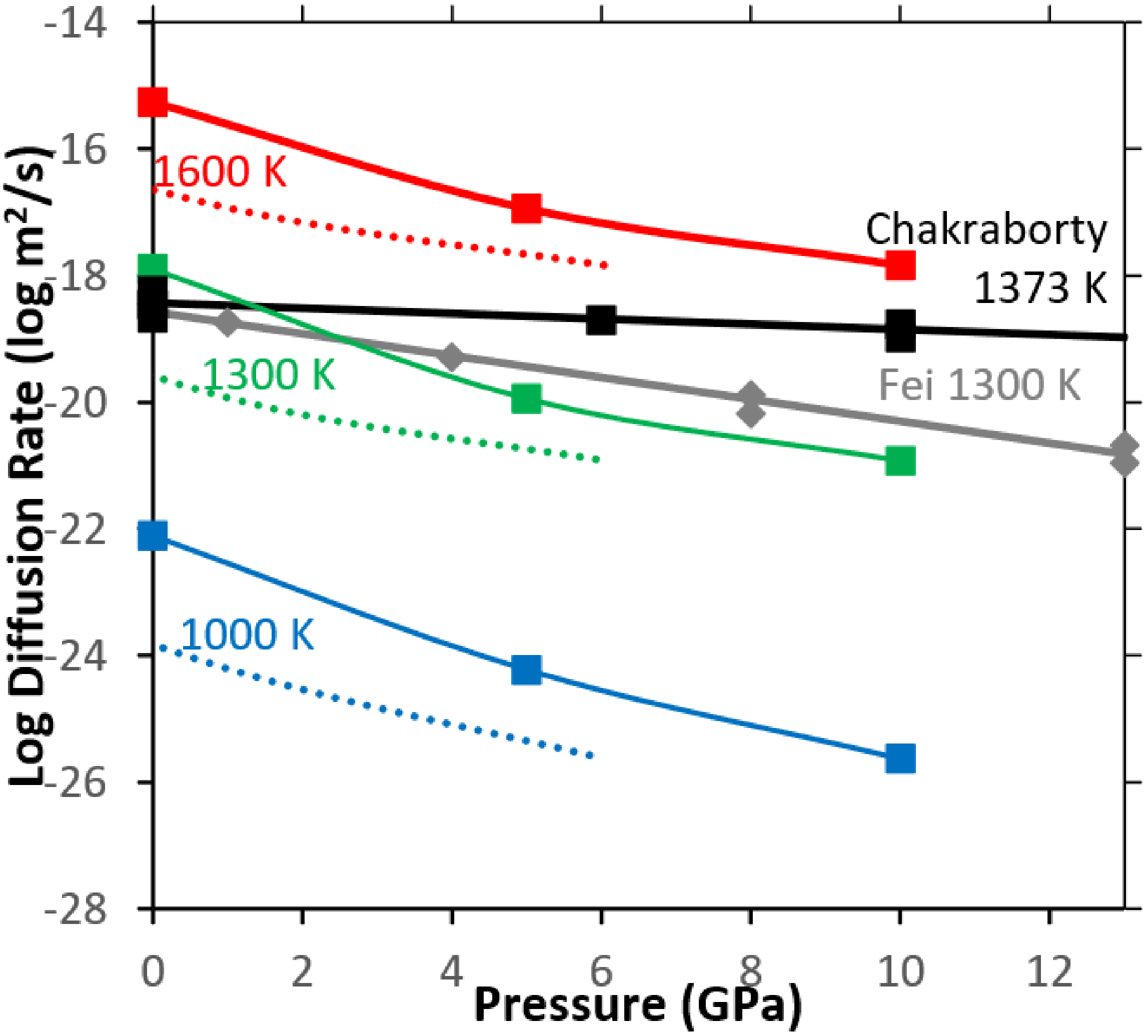

Figure 6: [001] Mg diffusion rates in perfect forsterite as a function of pressure at fixed temperatures (blue=1000 K, green=1300 K, red=1600 K) compared to results from Chakraborty *et al.* (1994) and Fei *et al.* (2018a). Model predictions are uncorrected (solid line) or pressure corrected (dotted line). For experimental data data points are plotted and then a line is constructed using activation volumes of 1.1 cm^3/mol for Fei *et al.* (1994) and 4.3 cm^3/mol for Fei *et al.* (2018a). The results from Chakraborty *et al.* (1994) are those with no buffer with an f_{O_2} of 10^{-12}. In these results a higher activation volume (~3.4) was determined in air. The oxygen fugacity of Fei *et al.* (2018a) is unknown due to the complicated presence of water.

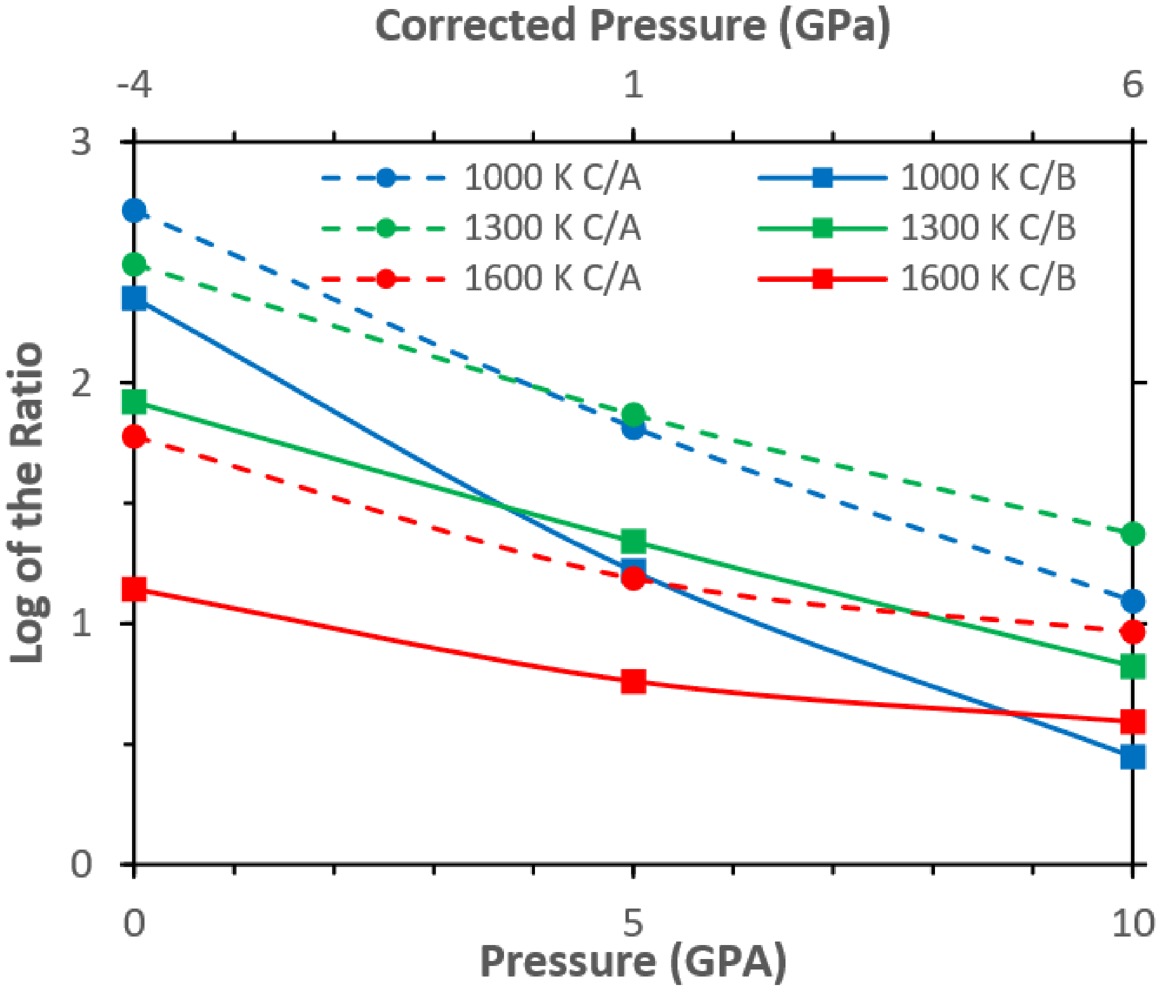

Figure 7: Log of the ratios of C/A ([001]/[100]) (dotted lines, circles) and C/B ([001]/[010]) Mg diffusion (solid line, squares) in perfect olivine as a function of pressure at different temperatures (blue 1000 K, green 1300, red 1600). Two pressure scales are shown, the pressure scale from DFT and one that has been corrected as per the text.

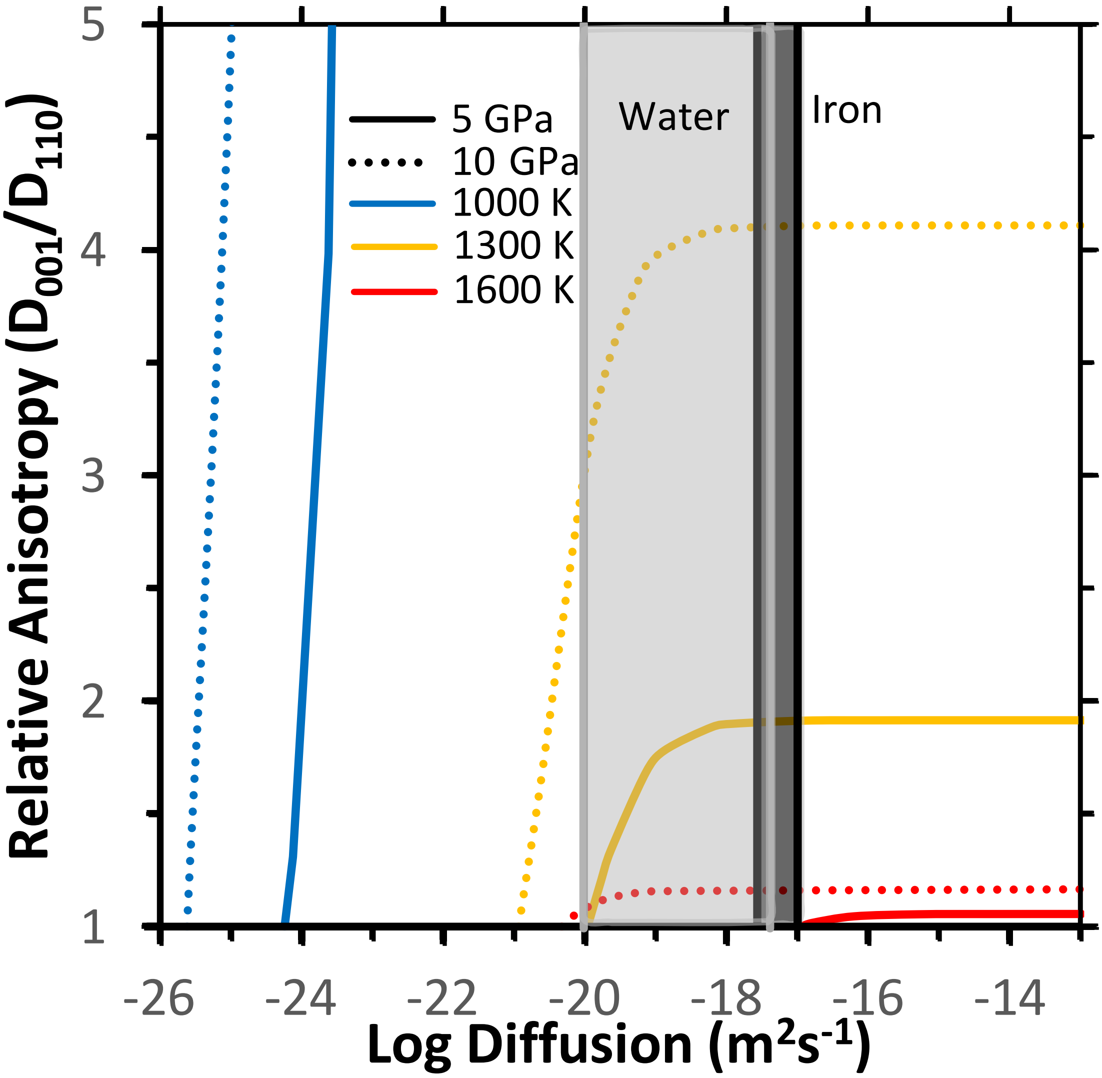

Fig 8 Comparision of anisotropy (defined as diffusion in the [001] direction/ diffusion in the [110] direction) for different diffusion rates (D_x) in a system of self diffusion+extrinsic vacancies. Anistropy is relative to pure forsterite which is 1. This was determined by solving Equation 13 as a function of diffusion rate. Lines are at 1000 (blue), 1300 (orange) and 1600 K and solid lines represent 5 GPa, dotted lines 10 GPa (uncorrected) which correct to around 1 and 6 GPa respectively.

The dark region represent the range of D_x between Fe=1-20% for olivine at 0 GPa, 1300 K and $fO^2=10^{-7}$ Dohmen and Chakraborty (2017). The ligt region represents the range of D_x for water ranging between 1-150 wt. ppm at ~8 GPA and 1300 K (Fei *et al.* 2018).

	0 GPa	5	10
	Formation Energy (eV)		
0 K	5.65	6.43	6.54
1000	4.94	5.96	6.37
1300	4.73	5.78	6.27
1600	4.52	5.60	6.13
	Vacancy Concentration		
1000	4.13×10^{-13}	3.06×10^{-15}	9.23×10^{-17}
1300	8.51×10^{-10}	8.81×10^{-12}	9.37×10^{-13}
1600	9.59×10^{-08}	2.14×10^{-09}	2.89×10^{-10}

Table 1: Free energy of the Frenkel reaction at various pressures and temperatures and the corresponding concentration of vacancies and interstitials (in defects/unit cell) in a pure forsterite crystal where only the Mg Frenkel reaction forms significant defects- this concentration is for each defect type so the concentration of total defects (vacancies+interstitials) is twice this number. Also shown is the concentration of hydrous vacancies formed by water assuming water solely forms hydrous Mg vacancies (γ=1). All pressures are uncorrected.

		Anhydrous Vacancy		Anhydrous Interstitial	
		E_a (eV)	ν^* (Hz)	E_a (eV)	ν^* (Hz)
Hops from M1 Site					
A/G	M1-M1	0.75	1.01×10^{13}	3.22	9.11×10^{08}
B/H	M1-M1	4.12	3.71×10^{15}	3.16	1.22×10^{10}
C/I	M1-M2/I2	1.45	2.37×10^{14}	0.59	3.01×10^{09}
I*	M1-I2			1.35	2.38×10^{08}
D/J	M1-M2/I2	1.91	4.39×10^{14}	0.56	2.02×10^{09}
D*/J*	M1-M2/I2	1.91	4.39×10^{14}	1.29	2.80×10^{09}
Hops From M2/I2 Site					
C/I	M2/I2-M1	0.45	1.15×10^{14}	0.39	1.41×10^{13}
I*	M1-I2			1.15	1.11×10^{12}
D/J	M2/I2-M1	1.00	2.13×10^{14}	0.36	9.46×10^{12}
D*/J*	M2/I2-M1	1.00	2.13×10^{14}	1.09	1.31×10^{13}
E/K	M2/I2-M2/I2	1.65	4.27×10^{14}	1.08	5.53×10^{12}
F/L	M2/I2-M2/I2	2.82	2.31×10^{15}	N/A	N/A

Table 2: Activation energy and modified attempt frequency v* of various hops (shown in Figure 1 and 3 with the hop distances outlined in Table S4 and S8) for hydrous and anhydrous forsterite at 0 GPa uncorrected. Hop L could not be stabilised but is very high in energy. Hops with an asterisk go in the reverse direction where this is not equivalent.

		[100]	[010]	[001]	[001] 5 GPa	[001] 10 GPa
Anhydrous vacancy	1000 K	1.58 X 10^{-14}	6.61 X 10^{-14}	1.91 X 10^{-10}	1.88 x 10^{-10}	1.88 x 10^{-10}
	1300	3.37 X 10^{-12}	1.42 X 10-^{11}	1.48 X 10^{-09}	1.27 x 10^{-09}	1.19 x 10^{-09}
	1600	9.15 X 10^{-11}	4.02 X 10^{-10}	5.71 X 10^{-09}	5.30 x 10^{-09}	4.93 x 10^{-09}
Interstitial	1000	3.47 X 10^{-13}	7.58 X 10-13	2.65 X 10^{-13}	6.13 x 10^{-12}	6.66 x 10^{-11}
	1300	1.39 X 10^{-12}	3.62 X 10-12	1.18 X 10^{-12}	1.39 x 10^{-11}	8.44 x 10^{-11}
	1600	3.83 X 10^{-12}	7.86 X 10-12	3.96 X 10^{-12}	2.46 x 10^{-11}	1.01 x 10^{-10}

Table 3: Diffusion coefficients (m^2/s) of vacancies and interstitials in three directions at 0 GPa (uncorrected) with 5 and 10 GPa (uncorrected) [001] diffusion coefficients also listed. For the other coefficients in [100] and [010] at 5 and 10 GPa see Table S10 and S11.