



Bridging the water solubility and ion diffusivity in the mantle silicates by a thermodynamic model

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Abstract

Water solubility in Mg-endmember silicates is suggested to correlate with cation diffusivity. This study proposes a thermodynamic model by introducing the concept of transient Frenkel defect for Mg ions to quantify the relationship between water solubility and Mg diffusivity in mantle silicates. The formation of the Mg transient Frenkel defect is regarded as the escape of Mg from Mg-O polyhedron, and the concentration of Mg transient vacancy is considered as its statistical probability in silicate minerals. The proposed thermodynamic model reveals that the formation energy for Mg transient vacancy (ΔG_{tr}) is approximately $\Delta G/6$ (ΔG is activation energy for Mg diffusion in silicates) for silicates with Mg-O₆ octahedra, such as enstatite, forsterite, wadsleyite, and ringwoodite, and $5\Delta G/12$ for bridgmanite and post-perovskite. This observation implies a possible diffusion mode of Mg through transient vacancies. Our model connects water solubility and ion diffusivity in silicates.

Keywords Water solubility · Diffusivity · Thermodynamic model · Mantle silicate

Introduction

Water structurally bound as hydroxyl defects in mineral lattice is considered crucial in dynamic processes in the Earth's interior. Numerous studies have demonstrated that even tens of ppm of water by weight also exerts considerable effect on the transport properties of mantle minerals such as diffusion (Costa and Chakraborty 2008; Demouchy et al. 2007; Hier-Majumder et al. 2005; Wang et al. 2004), rheology (Mei and Kohlstedt 2000; Xu et al. 2013) and electrical conductivity (Wang et al. 2006; Yoshino et al. 2006; Zhang et al. 2012), though there is still a considerable debate about the magnitude of the effects (Demouchy et al. 2013; Faul et al. 2016; Fei et al.

2013). Therefore, an understanding of water dissolution in nominally anhydrous minerals at the atomic level is fundamental for development of dynamic models of the Earth's mantle.

Theoretical and experimental studies have demonstrated that water can be incorporated into silicate minerals by a variety of potential atomistic mechanisms, such as metal site vacancy, Si site vacancy, and O ions (Griffin et al. 2013; Grüninger et al. 2017, 2018; Karato 2008; Panero 2010; Wright 2006; Xue et al. 2017). Among these mechanisms, despite of Si site vacancy arguments for the main mechanism of water incorporation in olivine and ringwoodite (Grüninger et al. 2017, 2018; Padrón-Navarta and Hermann 2017; Xue et al. 2017), the metal site vacancy shows the most favorable positions at high temperatures as numerous studies revealed a direct relationship between water solubility and Mg diffusivity in olivine (Costa and Chakraborty 2008; Demouchy and Mackwell 2006; Fei et al. 2018; Kohlstedt and Mackwell 1998) and ringwoodite (Kudoh et al. 2000). Therefore, a comprehensive understanding of the detailed mechanisms of water correlating with ion vacancy and diffusivity not only aids to investigate the water solubility by ion diffusion coefficient in one mineral but also helps to determine the effect of water on ion diffusivity. Until now, the details of these mechanisms are still not well understood.

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Here, a thermodynamic model that introduces the concept of transient Frenkel defects is developed to determine the essential correlation between the formation of Mg vacancy and the effect of water on ion diffusivity. This model provides new insights into the understanding of water solubility in Mg-endmember silicate minerals, especially the high water solubility of silicates in the transition zone (i.e., wadsleyite and ringwoodite). The model also suggests the essentially nearly dry nature of the lower mantle and high water solubility in the lowermost mantle, where post-perovskite is dominant.

Thermodynamic model

Theoretical background

According to the classical random walk theory, the diffusion coefficient can be expressed by Eq. (1) (Poirier 1985; Varotsos and Alexopoulos 1986):

$$D = fa^2vC\exp\left(-\frac{\Delta G_m}{RT}\right) \quad (1)$$

where f refers to the correlation factor (usually smaller than 1 for tracer diffusion and equal to 1 for self-diffusion), v denotes the jump frequency (s^{-1}), a represents the jump distance (m), T represents the absolute temperature (K), R is the gas constant (J/mol/K), C specifies the defect concentration (dimensionless), and ΔG_m is the migration Gibbs free energy (kJ/mol). The defect concentration C at equilibrium is represented by the following:

$$C = \exp\left(-\frac{\Delta G_f}{RT}\right) \quad (2)$$

where ΔG_f corresponds to the Gibbs free energy of the defect formation. A direct relationship between ion diffusion coefficient and vacancy concentration is given in Eq. (1). In general, distinguishing both ΔG_f and ΔG_m from experimentally determined diffusion activation energy ($\Delta G = \Delta G_f + \Delta G_m$) is difficult. Previous computational simulations showed that the ΔG_f values for Mg vacancy are considerably higher for both Schottky and Frenkel defects than the ΔG_m value for Mg migration (Béjina et al. 2009; Karki and Khanduja 2007; Verma and Karki 2009; Walker et al. 2009; Watson et al. 2000; Wright and Price 1993). The higher vacancy formation energy of Mg cannot explain the water solubility in Mg-endmember silicates. Even when the most probable Si vacancy mechanism in olivine (e.g., Berry et al. 2005, 2007a; Lemaire et al. 2004; Walker et al. 2007) is considered, it remains unworkable due to its considerably higher vacancy formation energy than that of Mg. Therefore, the existing model (Eqs. 1 and 2) cannot effectively explain the relationship between ion diffusivity and water solubility. In simple terms,

both processes may not need to be correlated due to a similar reason as suggested by Jollands et al. (2016), where the bulk amount of hydrogen is controlled by different defects but the diffusivity of hydrogen is controlled only by Mg vacancies. However, this can be well explained by the following proposed thermodynamic model.

Mg transient Frenkel defect

In this study, a thermodynamic model, which considers the formation of Mg vacancy as a transient Frenkel defect, is proposed to address the above issue. Different from the concept of transient defect in the study of Fair et al. (1984), the transient Frenkel defect of Mg in silicates is explained as follows. The formation energy for the Mg transient vacancy (denoted as ΔG_{tr} , where tr is transient) indicates the escaping difficulty of Mg from the Mg-O polyhedra by thermal activation. Once Mg escapes from Mg-O polyhedra, it will form the transient Frenkel defect pair (transient Mg interstitial and transient Mg vacancy). This transient defect is unstable due to charge imbalances, and Mg shortly returns to its original site. In this case, the vacancy concentration expressed by Eq. (2) indicates the probability of the transient Frenkel defect where Mg escapes from Mg-O octahedra. This value is also statistical when the numbers of transient Frenkel defect reach a dynamic equilibrium in minerals at a given temperature.

Mg migration and diffusion

The migration of Mg from one site to a vacancy usually occurs between neighboring octahedral sites. The connections of octahedra in silicate minerals mainly appear in two forms: edge-shared and corner-shared as shown in Fig. 1a and b, respectively. In both forms, the migration of Mg to neighboring octahedral sites is more difficult than the escape of Mg from octahedral sites as ΔG_m is larger than ΔG_{tr} . Mg diffusion in silicates can occur in the following steps. (1) Vacancies are formed in the type of transient Frenkel defects. (2) Mg migrates to its neighboring transient vacancy. (3) Two possible results may be obtained. i) Mg jumps to the adjacent transient vacancies and finishes the exchange with its neighbor (denoted as Route-1, as shown in Figs. 2 and 3). ii) Mg fails to jump to its adjacent transient vacancy (the exchange with its neighbor fails), and a normal Frenkel defect is formed (denoted as Route-2, as shown in Figs. 2 and 3). However, the contribution of normal Mg Frenkel defect to Mg vacancy concentration is limited compared with that of transient Mg Frenkel defect. One reason is the larger formation energy of the former, and the other reason is that the normal Mg Frenkel defect cannot only be produced but also annihilated during Mg diffusion. Caution must be exercised that Mg diffusion process does not always lead to the formation of normal Mg Frenkel defect.

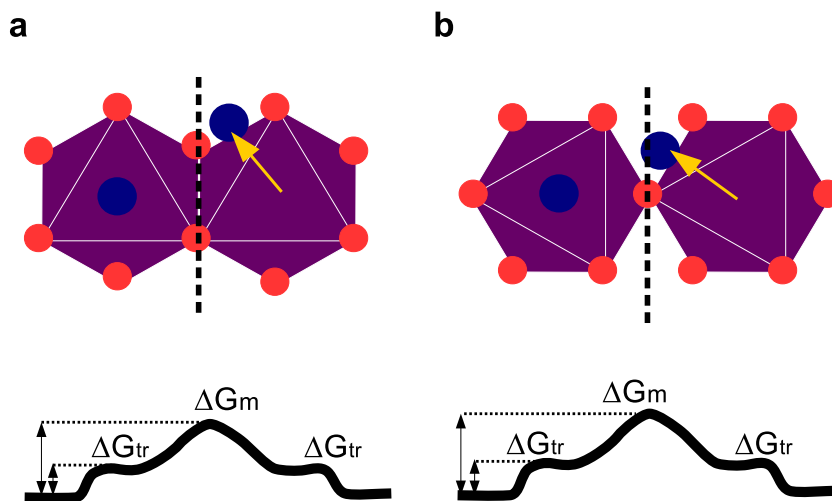


Fig. 1 Schematic description of Mg transient Frenkel defect at edge-shared and corner-shared octahedral sites in Mg-endmember silicates (enstatite, olivine, wadsleyite, ringwoodite). The blue and red balls represent the Mg and O ions, respectively. **(a)** Transient Frenkel defect at an edge-shared octahedral site and its schematic levels of ΔG_{tr} and ΔG_m . **(b)**

Transient Frenkel defect at a corner-shared octahedral site and its schematic levels of ΔG_{tr} and ΔG_m . Note that ΔG_m is the required migration energy as Mg moves from one octahedral site to a neighboring vacancy, and the values of ΔG_m should be different for both types of octahedral sites

Model quantification

To quantify the Gibbs free energy of transient Frenkel defect, Varotsos and Alexopoulos (1977, 1980, and 1986) suggested that the defect activation for diffusion (ΔG , kJ/mol) is interconnected with the bulk expansivity and elasticity of solids by the $cB\Omega$ model:

$$\Delta G = cB\Omega \tag{3}$$

where B refers to the isothermal bulk modulus (GPa), Ω denotes the mean volume per atom (m^3), and c is a dimensionless factor that is considered independent of temperature and pressure to the first approximation. Note that the unit of ΔG is kJ/mol, and here, the value of c is different from those of

previous studies with factor N_A (Avogadro constant). Based on the $cB\Omega$ model, the diffusion coefficient D can be predicted by the following relationship (Varotsos and Alexopoulos 1980, 1986; Zhang et al. 2010; Zhang and Shan 2015):

$$D = fa^2v \exp\left(-\frac{cB\Omega}{RT}\right) \tag{4}$$

Equations (3) and (4) indicate that the activation energy for ion diffusion (ΔG) is related to the mean atom volume (Ω). Following this point, it is supposed that the formation energy of Mg transient vacancy (Frenkel defects) in the mineral lattice is also related to a volume term. In the case of diffusion, Mg needs to jump between two Mg site volumes (ΔV). By contrast, for the formation of Mg transient vacancy, Mg only

Fig. 2 Schematic description of Mg diffusion to its neighboring edge-shared octahedral site. The blue and red balls represent the Mg and O ions, respectively. **(a)** Edge-shared octahedral sites. **(b)(c)** Formation of transient Frenkel defects for both octahedral sites and Mg migration along different routes. **(d)** Formation of Frenkel defect for Mg. Two diffusion route circles: Route-1 (a)-(b)-(a) and Route-2 (a)-(c)-(d)

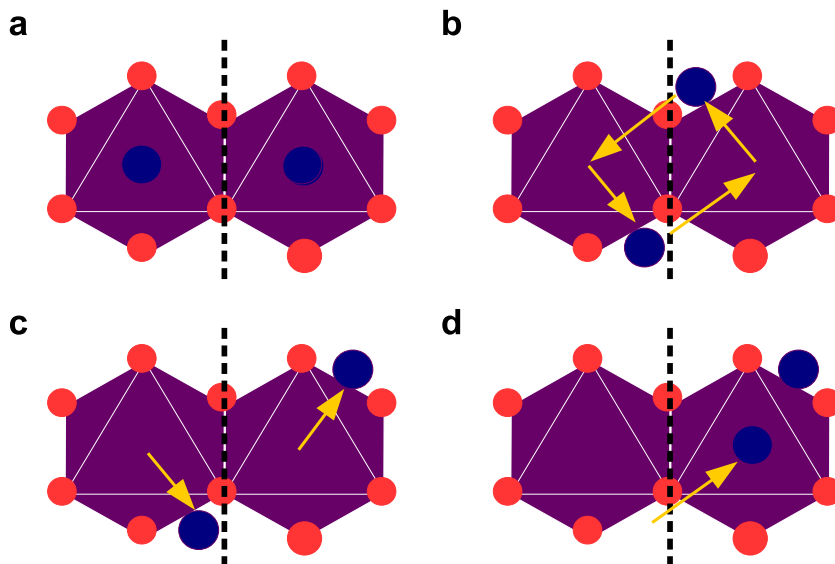
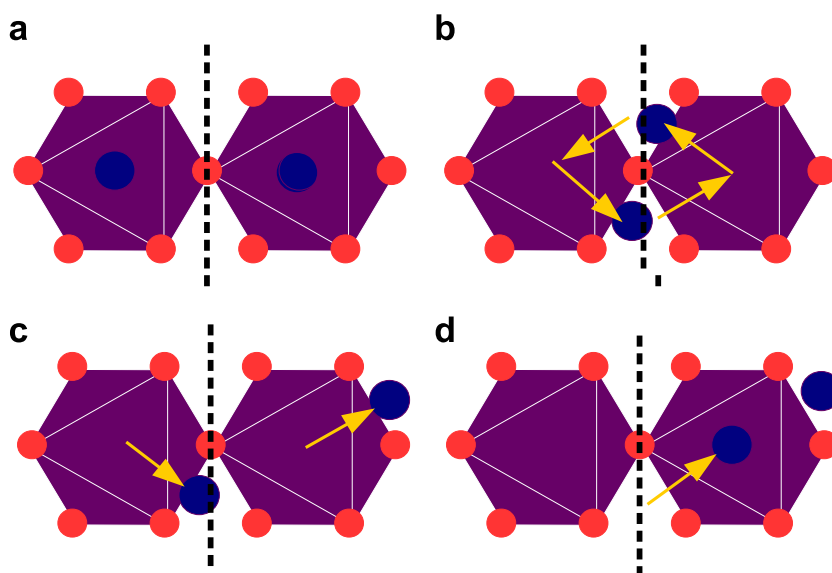


Fig. 3 Schematic description of Mg diffusion to its neighboring corner-shared octahedral site. The blue and red balls represent the Mg and O ions, respectively. **(a)** Corner-shared octahedral sites. **(b)(c)** Formation of transient Frenkel defects for both octahedral sites and Mg migration along different routes. **(d)** Formation of Frenkel defect for Mg. Two diffusion route circles: Route-1 **(a)-(b)-(a)** and Route-2 **(a)-(c)-(d)**



needs to jump in a volume (ΔV_{tr}) slightly larger than that of Mg-O polyhedra (Fig. 4). Therefore, the required formation energy for Mg transient vacancy (ΔG_{tr}) is thought to meet the following relationship:

$$\Delta V_{tr}/\Delta V = \Delta G_{tr}/\Delta G \quad (5)$$

Equation (5) indicates that the relative magnitude of energy for different types of behavior of Mg is proportional to the ratio of their related volumes. Therefore, the formation energy for Mg transient vacancy (ΔG_{tr}) can be obtained by Eq. (5) through calculation of the relative volume ratios, as shown in Fig. 4, which is schematic for Mg-O polyhedral volumes (shaded areas) and the mean volumes for Mg diffusion (cuboids bounded by dashed lines) in silicate structures. In each figure, ΔV_{tr} refers to the volume of one shaded polyhedron, whereas ΔV refers to that of two cuboids bordered by dashed lines. Consequently, the ratios of $\Delta V_{tr}/\Delta V$ are calculated to be 1/6 (for Fig. 4a and b), 1/2 and 1/4 (for Fig. 4c and d), and 5/12 (bridgmanite and post-perovskite for Figs. 4e), respectively. Therefore, the ΔG_{tr} of Mg transient vacancy in silicates with Mg-O₆ octahedra is $\Delta G/6$ (Fig. 4a and b), which is between $\Delta G/4$ and $\Delta G/2$ in silicates with Mg-O₈ (e.g., bridgmanite and post-perovskite) polyhedra (Fig. 4c and d). Considering that both bridgmanite and post-perovskite are based on MO₁₂-coordinated perovskite structure, the ΔG_{tr} in both of them is determined to be $5\Delta G/12$ (Fig. 4e). Thus, Eq. (5) can be rewritten as:

$$\Delta G_{tr} = n\Delta G \quad (6)$$

where n is a dimensionless constant. For silicates with Mg-O₆ octahedra, n is 1/6, whereas for bridgmanite and post-perovskite, n is 5/12.

Results

To verify this thermodynamic model, the published data of water solubility and Mg diffusion for the major Mg-endmember silicates of the Earth's mantle were used. All experimental data on Mg-endmember silicates were obtained in the stability fields of each constituent under mantle conditions. ΔG_{tr} can be calculated from the activation energy for Mg diffusion (ΔG). The water solubility data were transferred from the form of ppm weight into the form of site fraction by supposing that the maximum water content in silicate minerals is constrained by Mg defect concentration, though Mg defects are not the only mechanism for water incorporation in some silicates. Then, the formation energy of Mg vacancy ($\Delta G_{f,ws}$) can be calculated from the water solubility data from Eq. (2).

Table 1 summarizes the published water solubility data in Mg-endmember silicates together with the pressures, temperatures, the activation energies for Mg diffusion (ΔG) and hydrogen migration. Water solubility data indicate the maximum water contents under the conditions in which samples were synthesized. It is thought to be under a relatively water equilibrium condition. Those studies (e.g., Enstatite: Rauch and Keppler 2002; Olivine: Kohlstedt et al. 1996; Mosenfelder et al. 2006; Wadsleyite: Jacobsen et al. 2005; Kawamoto et al. 1996; Kohlstedt et al. 1996; Ringwoodite: Kawamoto et al. 1996; Kohlstedt et al. 1996; Smyth et al. 2003) have been conducted to investigate the maximum solubility of water in silicate minerals under various P-T conditions. Excess water (a few of wt% water to tens of wt% water) was added to the starting materials, which means that all these experiments were performed under water saturated conditions. For example, Rauch and Keppler (2002) used the mixture of Mg(OH)₂ and SiO₂ as the starting materials with about 10 wt% water to

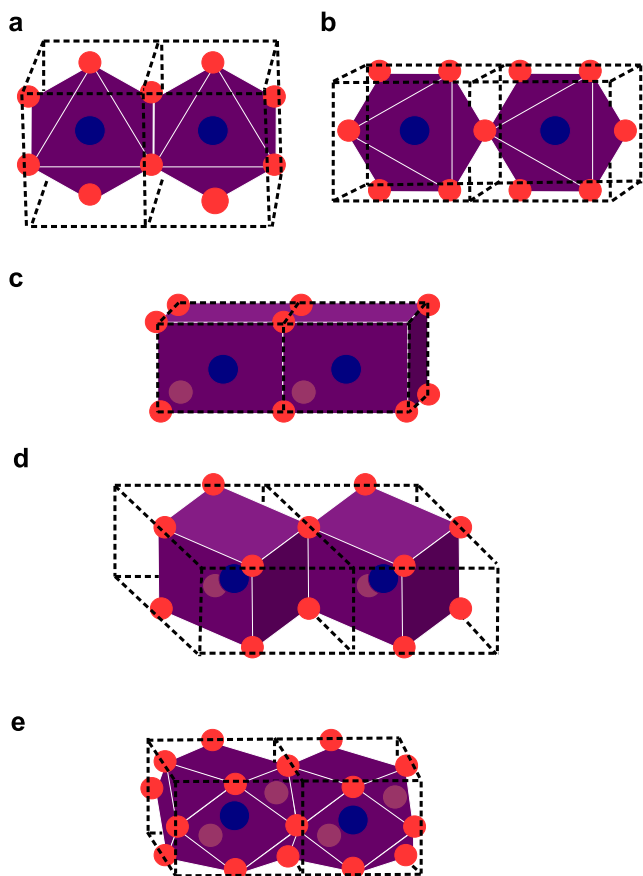


Fig. 4 Schematic for Mg-O polyhedral volumes and the mean Mg atom volume (dashed line) in silicate structures. The blue and red balls represent the Mg and O ions, respectively. **(a)** Edge-shared octahedral sites (Mg-O₆). **(b)** Corner-shared octahedral sites (Mg-O₆). **(c)** Face-shared eight-coordinated sites (Mg-O₈). **(d)** Edge-shared eight-coordinated sites (Mg-O₈). **(e)** Perovskite-type polyhedral site (Mg-O₁₂). For Mg diffusion, Mg needs to jump within the volume (ΔV) containing two Mg atoms. Hence, ΔV equals that of two cuboids bordered by dashed lines. For the formation of Mg transient Frenkel defect, it only needs to jump in a volume (ΔV_{tr}) slightly larger than Mg-O polyhedron. ΔV_{tr} equals the volume of one shaded polyhedron. The required activation energy ΔG_{tr} for transient Frenkel defect is considered to be $\Delta V_{tr}/\Delta V = \Delta G_{tr}/\Delta G$. Therefore, for Fig. 4a and b, $\Delta G_{tr} = \Delta G/6$. For Fig. 4c and d, $\Delta G_{tr} = \Delta G/2$ and $\Delta G_{tr} = \Delta G/4$, respectively. For Fig. 4e, $\Delta G_{tr} = 5\Delta G/12$

explore the maximum water solubility in orthopyroxene. Kawamoto et al. (1996) employed KLB-1 plus brucite as water source (about 13.7 wt% water) to investigate the maximum water solubility in wadsleyite and ringwoodite. Similar experiments were also carried out in olivine, wadsleyite and ringwoodite by Kohlstedt et al. (1996), Jacobsen et al. (2005) and Mosenfelder et al. (2006). Water solubility data were selected also by considering the following rules: (1) For the study that showed different results under nearly the same conditions, the relatively high values were selected. With respect to the results from different studies, different data were also considered. (2) For the water content data obtained through different calibrations (e.g., Mosenfelder et al. 2006),

the data by Paterson (1982) calibration were preferred. (3) For the samples analyzed for water content measurements, single crystals were preferred. Furthermore, the results from Mg-endmember silicates were preferred because Fe (or other impurities) content may affect the results. The data for the diffusion activation energies of Mg were selected based on two rules: (1) The results in Mg-endmember silicates were preferred as Fe may lower the activation energy. E.g., for enstatite in Schwandt et al. (1998), considering the effects of Fe content, the highest value among the results along the axes was selected. (2) The results under dry conditions (usually water content <50 ppm by weight) were preferred because transient Frenkel defect is thought to be an intrinsic mechanism, and water may largely affect the diffusion activation energy.

Both the calculated formation energies for Mg vacancy (ΔG_{f_ws}) from water solubility data and the calculated activation energies for Mg migration (ΔG_m) (using the relationship $\Delta G_m = \Delta G - \Delta G_{f_ws}$) are listed in Table 1. The table also shows the calculated formation energies for Mg transient vacancy (ΔG_{tr}) from our model based on Eq. (6). The value of ΔG_{f_ws} in olivine is around 59 kJ/mol, which is similar to that in enstatite (around 66 kJ/mol). However, the ΔG_{f_ws} (~130 kJ/mol) values in bridgmanite and post-perovskite are considerably larger than those (~30 kJ/mol) in wadsleyite and ringwoodite, and also larger than those (59–66 kJ/mol) in olivine and enstatite. The ΔG_{f_ws} values in silicates are only one-fifth or even near one order of magnitude lower than those calculated ΔG_f values using first-principles (e.g., Ammann et al. 2010; Béjina et al. 2009; Karki and Khanduja 2007; Verma and Karki 2009; Walker et al. 2009; Watson et al. 2000; Wright and Price 1993), indicating that the normal Mg vacancies cannot well explain the water solubility in Mg-endmember silicates. Remarkably, the ΔG_{f_ws} values were found to be consistent with those of ΔG_{tr} calculated using our model. These findings demonstrate that Mg transient vacancy can be used to illustrate the water solubility in Mg-endmember silicates. Thus, water solubility (C_{H_2O}) in silicates can be connected with the Mg transient vacancy concentration using Eq. (7):

$$C_{H_2O} = \exp(-\Delta G_{tr}/RT) \quad (7)$$

Therefore, the water solubility and Mg diffusivity [$D = D_0 \exp(-\Delta G/RT)$] can be bridged by combining Eqs. (6) and (7):

$$C_{H_2O} = (D/D_0)^n \quad (8)$$

where D_0 represents a pre-exponential factor. The smaller values of ΔG_{tr} compared with ΔG_m for Mg in silicates demonstrate that the formation of Mg transient vacancy is easier than the migration of Mg, indicating the high possibility for the Mg transient vacancy to incorporate with OH groups. The ΔG_m values in silicates with Mg-O₆ octahedra are several

Table 1 Collected data of water solubility and hydrogen (H) migration in enstatite (En), olivine (Ol), wadsleyite (Wds), ringwoodite (Rwd), bridgmanite (Br) and post-perovskite (pPv), estimated formation energies for Mg vacancy ($\Delta G_{F_{\text{Mg}}}$) and activation energies for Mg migration (ΔG_m) from water solubility data, formation energies for Mg transient vacancy (ΔG_{tr}), and activation energies for Mg diffusion (ΔG)

Minerals	Water solubility (ppm wt) ^a	P (GPa)	T (K)	$\Delta G_{F_{\text{Mg}}}$ (kJ/mol) ^b	ΔG_m (kJ/mol) ^c	Calculated ΔG_{tr} from ΔG by our model (kJ/mol) ^d	ΔG for Mg diffusion (kJ/mol) ^e	ΔG_m for H (kJ/mol) ^f
En	714–867	7.5–10	1370	66 ± 1	294 ± 54	60 ± 9	360 ± 52	213–295
Ol	950–2267	8–12	1270–1470	59 ± 9	306 ± 104 (Fo) 216 ± 34 (Ol)	61 ± 16 (Fo)	365 ± 95 (Fo) 275 ± 25 (Ol)	110–258
Wds	15,000–31,000	14–16	1370–1770	29 ± 12	172 ± 41	33 ± 7	200 ± 29	123 ± 32
Rwd	7300–27,000	15–20	1370–1770	35 ± 10	169 ± 39	38 ± 7	200 ± 29	101–140
Br	15–40	25	1570–1770	134 ± 15	171 ± 92	139 ± 9	305 ± 77	–
pPv	446–2763	120–130	2500–3500	–	–	132	–	–

a. Water content data obtained by considering both direct data and estimated results based on those following references: enstatite (Rauch and Keppeler 2002), olivine (Kohlstedt et al. 1996; Mosenfelder et al. 2006), wadsleyite (Demouchy et al. 2005; Kawamoto et al. 1996; Kohlstedt et al. 1996), ringwoodite (Kawamoto et al. 1996; Kohlstedt et al. 1996; Smyth et al. 2003) and bridgmanite (Litasov et al. 2003; Xu et al. 2011). Water solubility in post-perovskite is estimated using our model based on the diffusion energy of Mg from (Ammann et al. 2010) and temperature range (Nomura et al. 2014; Townsend et al. 2016)

b. Calculated by Eq. (2) after water solubility data being transferred from form of ppm wt to form of Mg site fraction

c. Calculated by the equation of $\Delta G_m = \Delta G - \Delta G_{F_{\text{Mg}}}$

d. Calculated by Eq. (6). n is 1/6 for En, Ol, Wds and Rwd, and it is 5/12 for Br and pPv

e. The references are as following: enstatite (Schwandt et al. 1998), forsterite and olivine (Charkraborty et al. 1994; Fei et al. 2018), wadsleyite and ringwoodite (Farber et al. 2000; Kubo et al. 2004); Holzappel et al. 2009). Suppose ΔG is the same for both wadsleyite and ringwoodite), and bridgmanite (Xu et al. 2011)

f. The migration energies of hydrogen (H) are from enstatite (Stalder and Skogby 2003), olivine (Demouchy and Mackwell 2003, 2006; Du Frane and Tyburczy 2012; Jollands et al. 2016; Kohlstedt and Mackwell 1998), wadsleyite (Hae et al. 2006), ringwoodite (Kudo et al. 2006; Sun et al. 2015)

times larger than those of ΔG_{tr} , whereas they are comparable in bridgmanite. However, the ΔG_m value for Fe-bearing olivine is smaller than that for forsterite, which may indicate that Fe content can reduce the diffusion activation energy (ΔG) through decreasing the migration energy (ΔG_m).

On the other hand, the migration energy of hydrogen in silicates is relatively smaller than that of Mg (see Table 1), implying that hydrogen migrates within the mineral lattice is easier or faster than that of Mg. We also notice that Padrón-Navarta et al. (2014) reported very high energy (461 kJ/mol) for hydrogen diffusion in forsterite when it diffuses via Si vacancy, indicating that diffusion for some of them may be controlled by the migration of Si.

Discussion

Errors and effects of data selection on the transient vacancy model

In this study, an Mg transient vacancy model is proposed to understand the water solubility from Mg diffusion data for the major Mg-endmember silicates in the Earth's mantle. The errors for the ΔG_{tr} values were calculated directly from those of the ΔG values, whereas the errors for the ΔG_{f_ws} values were calculated from Eq. (2) by considering the range of water solubility data (Table 1). Owing to the difficulties of performing diffusion experiments especially at high pressures, the ΔG values of Mg diffusion in silicates usually has relatively large errors with tens of kJ/mol. Consequently, a greater uncertainty of ΔG will lead to imprecise estimations of ΔG_{tr} and water solubility. Notably, some silicates with higher water solubility have small ΔG_{tr} . For example, the ΔG_{tr} values in wadsleyite and ringwoodite are very small (30 kJ/mol), while only 10 kJ/mol of errors will lead to significant changes in water content at a range of 0.8–4.7 wt.%. In addition to the abovementioned, the other factors, such as P-T conditions, impurity contents, and methods of water calibration (which directly determine the estimated values of ΔG_{f_ws}), also affect the prediction of water solubility in the present model. Especially, if the Si vacancy is the dominant mechanism for water incorporated into olivine as suggested by recent studies (Padrón-Navarta and Hermann 2017; Tollan et al. 2017; Xue et al. 2017), the corresponding value of the G_{f_ws} in olivine can change from ~60 kJ/mol to ~70 kJ/mol due to the change of four hydrogens corresponding one Si vacancy instead of two Mg vacancies. The value of the G_{f_ws} in ringwoodite can change from ~35 kJ/mol to ~40 kJ/mol if considering that half amount of water solubility values are contributed by Si vacancy mechanism suggested by (Grüniger et al. 2018). Though the above suggested errors caused by Si vacancy mechanism are still consistent with the error ranges of G_{f_ws} shown in Table 1, we have to state that the values of G_{f_ws} were obtained

based on the suppose of Mg vacancy dominant mechanism for water incorporation in silicates. Despite the existence of large errors, better consistency between the values of ΔG_{tr} and ΔG_{f_ws} for all the silicates in Table 1 verifies the reliability of the transient vacancy model developed in this study.

Role of normal mg vacancy in mg diffusion

Our model describes an Mg transient vacancy model for water solubility and Mg diffusion, and it also provides insights into the behavior of normal Mg vacancy. Figure 5 shows the calculated ΔG_{tr} (that approximately equals the ΔG_{f_ws} in Table 1) in Mg-endmember silicates with Mg-O₆ octahedra and migration activation energies ($\Delta G_m = \Delta G - \Delta G_{f_ws}$). Clearly, ΔG_m is almost five times higher than that of ΔG_{tr} for Mg in Mg-endmember silicates with Mg-O₆ octahedra. Thus, the migration energy from the Mg site to an Mg transient vacancy is approximately five times larger than that of Mg transient formation, in which a Frenkel defect pair of Mg is simultaneously formed (Route-2 in Figs. 2 and 3). Consequently, the formation energy of a normal Mg vacancy as a Frenkel defect is at a similar level to that of Mg diffusion in silicates. Figure 5 also indicates that the lowest value of ΔG_m is at least thrice larger than that of ΔG_{tr} . The lowest ΔG_m value may correspond to the migration of Mg ions from the octahedral sites to the normal Mg vacancies instead of to the transient ones. The normal Mg vacancies are also expected to form by thermal activation through either Frenkel defect or Schottky defect. However, the concentration of normal Mg vacancy is limited due to its larger formation energy compared

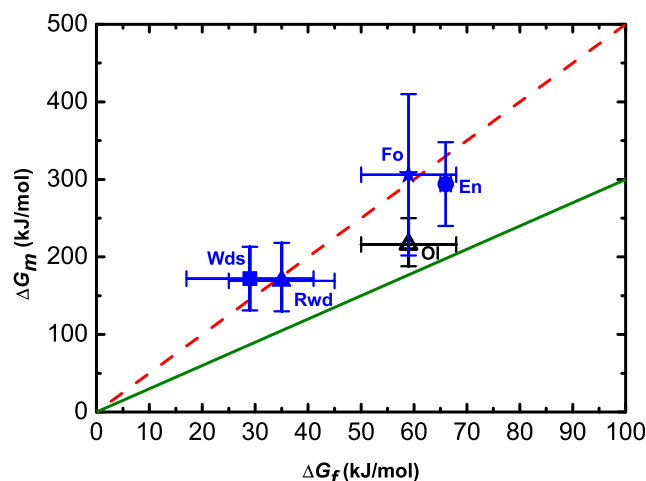


Fig. 5 Plots of the ΔG_f (close to ΔG_{tr} in our model) and ΔG_m of Mg in Mg-silicates (enstatite, olivine, wadsleyite, ringwoodite), which are calculated from water solubility data. The slopes for the dotted and solid lines are 5 and 3, respectively. Mg migration has lower activation energy in olivine than in forsterite. This is an example of the effect of Fe content on water solubility and Mg diffusion, which ultimately reduces the activation energy of Mg diffusion rather than increases the water solubility

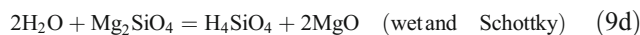
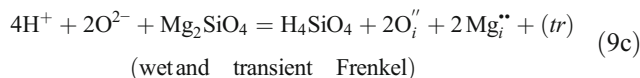
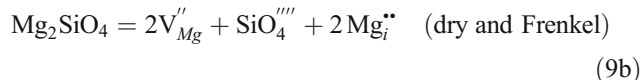
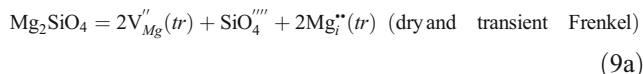
with that of Mg transient vacancy. Therefore, Mg diffusion in silicate minerals might be dominated by the transient vacancy form.

Water solubility in silicates

Under dry conditions, Mg vacancy is mainly formed by thermal activation as a form of transient Frenkel defect. Under wet conditions, water incorporates as OH defects into the lattice of silicate minerals, and ions of hydrogen occupy Mg transient vacancies. In this case, Mg ion preferentially exists as an interstitial atom because its migration to the neighboring vacancy is considerably more difficult than that by hydrogen (Table 1). Furthermore, molecular dynamics simulations (Caracas and Panero 2017; Grüninger et al. 2018) have demonstrated the rapid mobility of hydrogen in wadsleyite and ringwoodite. Although many mechanisms for the entry of water into the ringwoodite lattices (Grüninger et al. 2017, 2018) are known, half of the total water content is related to Mg vacancies. According to our model, hydrogen continually migrates between vacancies and shortly affects the return of transient Mg interstitial. This may favor the escape of Mg from the mineral structures to generate normal Mg vacancy in the form of Schottky defect. Subsequently, water content and Mg defect reach an equilibrium.

In this configuration, each Mg site features a high possibility of forming a transient vacancy whose formation energy is lower than that for hydrogen migration (ΔG_{tr} for Mg < ΔG_m for hydrogen) (Table 1). Large amounts of Mg transient vacancies provide the possibility of hydrogen migration and avoid the diffusion constraint by Mg vacancy mobility. The maximum water content (water solubility) depends on the concentration of transient Mg Frenkel defect. By contrast, water (hydrogen) can also occupy the Si vacancy (e.g., olivine: Lemaire et al. 2004; Matveev et al. 2001; Padrón-Navarta and Hermann 2017; Yang and Keppler 2011; ringwoodite: Grüninger et al. 2017, 2018). Recent studies suggest that Si vacancy may be the dominant mechanism for water incorporated into olivine under high pressure (> 3 GPa) (Padrón-Navarta and Hermann 2017; Tollan et al. 2017; Xue et al. 2017). Even in ringwoodite, Si vacancy is also important and at a similar concentration level to Mg vacancy. Various mechanisms for water incorporation in silicates imply that the precise interconnection between water solubility and the diffusion coefficients is difficult. It is worth noting that our model may not be suitable for olivine when Si vacancy is the dominant mechanism. In addition, the latest first-principle calculations (Qin et al. 2018) as well as Mg diffusion experiments (Fei et al. 2018) have demonstrated that hydrous Mg defects is more stable than hydrous Si defect at high temperatures (>1000 K). Whether the incorporated mechanism transfers from Mg vacancy to Si vacancy during the quench of synthetic sample remains unclear. Future studies, especially in-situ

NMR measurement, may be necessary. Starting from our model, during the formation of Mg transient Frenkel defect and incorporation of water in silicate minerals, the following reactions can occur.



Reactions (9a) and (9c) reveal the main defect forms of Mg under dry and wet conditions, respectively, whereas reactions (9b) and (9d) indicate the possible existing defect forms.

Our model suggests similar water solubility for enstatite and olivine, due to the similar activation energies for Mg diffusion in enstatite (360 kJ/mol, Schwandt et al. 1998) and forsterite (400 kJ/mol, Chakraborty et al. 1994). The water solubilities of olivine and orthopyroxene (Al-free) are comparable and increase with pressure and temperature (Hirth and Kohlstedt 1996; Karato and Jung 1998; Kohlstedt et al. 1996; Mierdel and Keppler 2004; Rauch and Keppler 2002; Zhao et al. 2004). However, the higher water solubilities of wadsleyite and ringwoodite are related to the low formation energies of Mg transient vacancy, which can be estimated from the Mg diffusion activation energies from our model (Farber et al. 2000; Holzapfel et al. 2009; Kubo et al. 2004). Unlike the hydrated mechanism in wadsleyite where Mg vacancy defects are dominant (Griffin et al. 2013), the hydrated mechanism in ringwoodite demonstrates similar importance for the Si and Mg vacancies (Grüninger et al. 2018), suggesting the difficulty for the understanding of the water solubility in ringwoodite through ion diffusivity.

The water solubilities of bridgmanite and post-perovskite differ from those of olivine and its high-pressure polymorphs. The diffusion model proposed by Xu et al. (2011) suggested that the movement of Mg ion in bridgmanite occurs in a different manner (coupling with Si) due to a close-packed structure. In bridgmanite, Mg ion can hardly escape from the wrapping polyhedra formed by the O ion. This structural feature implies the low concentration of Mg transient vacancy and the essentially dry nature of bridgmanite structures. Similar to bridgmanite, Mg in post-perovskite is also eight-coordinated with O (Murakami et al. 2004), thereby suggesting an Mg-Si coupled diffusion mechanism. This hypothesis has been verified by the first-principle calculations of Si and Mg diffusion in post-perovskite (Ammann et al. 2010), in which the diffusion coefficients of Mg are smaller than those of Si. However, given the considerably lower diffusion activation energy at

similar pressure conditions compared with that of bridgmanite (Ammann et al. 2010), post-perovskite may contain up to 2000 ppm wt. water (Table 1), indicating a considerably larger water solubility in the D'' region than in the lower mantle.

Factors influencing water solubility

In addition to temperature, water solubility in silicates can be influenced by other factors, such as cation substitutions (e.g., Fe, Al, and Ti) (Berry et al. 2004, 2007b; Férot and Bolfan-Casanova 2012; Hirschmann et al. 2005; Mierdel et al. 2007; Mosenfelder et al. 2006; Rauch and Keppler 2002; Padrón-Navarta et al. 2014; Padrón-Navarta and Hermann 2017), redox conditions (Yang 2015, 2016; Yang et al. 2014, 2016), and pressure (Demouchy et al. 2005; Rauch and Keppler 2002). These substitutions affect water solubility mainly by charge compensation, which requires the compensation of charge balance by approaches, such as H, hydroxyl, or vacancy (Berry et al. 2004, 2007b; Férot and Bolfan-Casanova 2012; Hirschmann et al. 2005; Mierdel et al. 2007; Mosenfelder et al. 2006; Rauch and Keppler 2002). The anhydrous forsterite that contains Ti (usually substitutes the Si site) is hydrated, and its defect structure will be rearranged, with Ti moving from the Si site to an Mg site, thereby creating the Ti-OH point defect (Berry et al. 2004, 2007b; Padrón-Navarta et al. 2014; Padrón-Navarta and Hermann 2017). If the valence of the cation is the same, the change in water solubility by cation substitutes (e.g., substitution of Mg by Fe) is relatively small. In olivine, Fe content influences water solubility mainly at low pressures (<1 GPa) (Férot and Bolfan-Casanova 2012; Zhao et al. 2004) but causes no influence on water solubility in wadsleyite (Demouchy et al. 2005; Smyth 1987). Water solubility in hydrous forsterite is similar to that in olivine (Keppler and Bolfan-Casanova 2006; Kohlstedt et al. 1996; Mosenfelder et al. 2006). It may be only underlying low pressures and low water contents that the dissolution of water in olivine is related to minor chemical impurities. However, Fe content ultimately reduces the activation energy for Mg diffusion, as experimentally reported for olivine (Fig. 5) (Chakraborty et al. 1994) and Fe-bearing wadsleyite (Chakraborty et al. 1999; Kubo et al. 2004). Therefore, contrary to Fe-bearing silicates, Fe-free ones show better correlation between the water solubility data and the activation energy of Mg diffusion.

Water solubility in silicates can also be influenced by redox conditions. Under reducing conditions, the water content is considerably lower than that under oxidizing conditions (Keppler and Bolfan-Casanova 2006; Yang et al. 2014, 2016; Yang 2015, 2016). In particular, molecular hydrogen can be dissolved in differently structured minerals with similar solubility, although their solubility values are one order smaller than those under oxidizing conditions (Yang 2016). This finding suggests that the measured water content in previous

studies may be lower than the actual water solubility. Our model may explain this issue as that the transient vacancy indicates the basic water content but trivalent cations require extra defects, such as OH⁻ and H⁺, to balance charges (Keppler and Bolfan-Casanova 2006). Therefore, we suggest that water solubility in silicates with other cations can be understood by using both the transient model and chemical stoichiometry.

Experimental and theoretical studies indicated an increase in the activation energies of Mg diffusion with increasing pressures for silicates such as olivine (Béjina et al. 2009; Chakraborty et al. 1994; Zhang and Shan 2015), wadsleyite (Holzapfel et al. 2009; Zhang and Shan 2015), bridgmanite (Ammann et al. 2010; Zhang and Shan 2015), and post-perovskite (Ammann et al. 2010). According to our model, the increase in diffusion activation energies with increasing pressure reveals a decrease in water solubility in silicates. However, this finding is contrary to experimental observations (e.g., in olivine Mosenfelder et al. 2006). This discrepancy may be due to the effects of the second critical endpoint in the ultramafic system (Padrón-Navarta and Hermann 2017). The effect of pressure on water solubility can be combined with other factors. Contrary to the observations at low pressures (<1 GPa, Zhao et al. 2004), water solubility in olivine decreases with increasing temperatures (Litasov et al. 2007; Smyth et al. 2006). This is probably due to the dissolution of silicates into the fluid water until formation of a supercritical fluid or melt (Mibe et al. 2007; Stalder et al. 2001). Before the supercritical fluid reaches the second critical endpoint at higher pressure, water solubility increases with pressure as observed by Mosenfelder et al. (2006). Once the supercritical fluid is beyond the second critical endpoint at high pressure, the activity of water in melts decreases with increasing temperature and causes a decrease in the water solubilities of olivine (Litasov et al. 2007; Smyth et al. 2006), enstatite (Bali et al. 2008; Withers and Hirschmann 2007), wadsleyite (Demouchy et al. 2005), and ringwoodite (Bolfan-Casanova 2005; Ohtani et al. 2000). Although precise determination of water solubility in silicates is difficult in the Earth's actual interiors because of various influencing factors, our model provides a thermodynamic understanding for the basic water solubility in silicates. In particular, the present model can be used to understand or estimate water solubility in the silicates in the deep mantle, in which the surrounding conditions are relatively simple but experimentally difficult to achieve, as opposed to the upper mantle above the 200-km or subduction zones.

Effect of water on ion diffusivity

Previous studies have demonstrated that water can strongly enhance element diffusivity in silicate minerals, such as olivine (Hier-Majumder et al. 2005; Wang et al. 2004) and its high

pressure polymorphs (Kubo et al. 2004; Shimojuku et al. 2010; Zhang et al. 2019), although the extent has recently been questioned (Fei et al. 2013, 2014). However, the magnitude for enhancements of different elements diffusivities is different. Costa and Chakraborty (2008) have indicated that Si diffusivity in olivine can be enhanced by several orders of magnitude due to the presence of water, whereas the hydrated effect on O diffusivity is within one order of magnitude and considerably smaller for Mg diffusivity. Under wet conditions, water causes no effect in the diffusion mechanisms and remains vacancy related (Costa and Chakraborty 2008; Walker et al. 2003). Thus, water possibly increases the vacancy concentration by reducing the vacancy formation energies of ions, thereby leading to orders of magnitude of differences in the vacancy concentration of forsterite (Brodholt 1997) and considerable contributions to diffusion (Jaoul et al. 1995).

The energies of vacancy formation and ion migration are usually related to their atomic and electronic structures. One approach for the effect of water on vacancy formation is the distortion of the Mg-O and Si-O polyhedra. When water is incorporated into the silicate structure, hydrogen can occupy the Mg site, and MgO interstitial is simultaneously formed. The Mg-O bond is then lengthened, loosening the Si-O polyhedra. This process is demonstrated in wadsleyite (Holl et al. 2008; Jacobsen et al. 2005), in which the bond lengths increase with increasing water content. Thus, Si can easily escape. However, the magnitude of the increase in the bond length is highly limited owing to the presence of water. For example, 1 wt% water can lead to a ~0.1% increase in the bond length (Holl et al. 2008; Jacobsen et al. 2005), which is approximately one order of magnitude smaller than the original differences among Mg-O bonds (~1%). Our model provides another viewpoint to understand the effect of water on ion diffusion from the aspect of transient vacancy formation. Reduced formation energy of ion vacancy derived from water content occurs by breaking the local charge balance. The hydrogen that occupies Mg vacancy will prolong the duration of Mg transient Frenkel defect. After the hydrogen jumps to the next neighboring transient vacancy, Mg will return to its original site owing to the lower migration energy of hydrogen to the neighboring site. The negligible effect of water content on Mg-O and Si-O polyhedra cannot significantly contribute to the increasing concentration of transient ion vacancy. The fast mobility of hydrogen (due to small radius and charge) within the lattice structure (Demouchy and Mackwell 2006; Hae et al. 2006; Ingrin and Blanchard 2006; Kohlstedt and Mackwell 1998) may disturb the local charge balance of the Si-O tetrahedron at the atomic scale and lower the barrier of Si and O, allowing these ions to escape from their original positions and migrate within structures. Thus, the local charge imbalance caused by hydrogen mobility is expected to be the main factor for the significant strengthening of the effect of water on the diffusion rate of ions.

Conclusions

A quantified relationship between water solubility and Mg diffusivity for mantle silicates was established based on the transient Frenkel defect model. The transient vacancy concentration of Mg indicates the probability of the escape of Mg from Mg-O polyhedra. The formation energy of the transient Frenkel defect for Mg can be estimated from the diffusion activation energy. Our model reveals a possible diffusion mode of Mg by transient vacancy. Water solubility in silicates can be connected with ion diffusivity with the help of our model. A higher water solubility in the D'' layer is expected owing to the relatively low diffusion activation energy of Mg in post-perovskite. The enhancement of ion diffusivity by water content is probably due to the high mobility of H, which can disturb the local charge balance and decrease the vacancy formation energy.

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