



## Diffusion of hydrogen in $(\text{Mg,Fe})_2\text{SiO}_4$ and high pressure polymorphs refined by the $\text{cB}\Omega$ model

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### ARTICLE INFO

#### Article history:

Received 4 November 2011  
Received in revised form 21 January 2012  
Accepted 26 February 2012  
Available online 23 March 2012

#### Keywords:

Olivine  
Wadsleyite  
Ringwoodite  
Hydrogen diffusion  
 $\text{cB}\Omega$  model  
Point defect

### ABSTRACT

Diffusion of hydrogen in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs is critical for understanding and quantifying kinetic processes in Earth's interior. Here, we suggest an approach to reproduce the diffusion coefficient of hydrogen in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs as a function of temperature in terms of the bulk elastic and expansivity data. In particular, anisotropy of hydrogen diffusivity in olivine and forsterite was reproduced. On the other hand, the pressure dependence of hydrogen diffusion in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs is performed in this study. Our results show the refined diffusivities derived from the  $\text{cB}\Omega$  model agree well with the experimental data if the relevant uncertainties are considered. Furthermore, the  $\text{cB}\Omega$  model is also found to give a reasonable estimation of the activation enthalpy for hydrogen diffusion in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs.

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### 1. Introduction

$(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs (namely, olivine, wadsleyite and ringwoodite), nominally anhydrous mineral (NAMs), are considered as the major constituent minerals of the Earth's upper-mantle and transition zone (Ringwood, 1975). Solubility measurements have shown that olivine, wadsleyite and ringwoodite can incorporate significant amounts of water (Inoue et al., 1995; Kohlstedt et al., 1996; Ingrin and Skogby, 2000). Generally, water embedded as hydrogen (proton) defects in the structure of the nominally anhydrous minerals (NAMs) has a substantial effect, even at very low concentration levels, on many physical and chemical properties of the Earth's materials. For instance, a small amount of water attenuates seismic waves (Karato and Jung, 1998), reduces viscosity (e.g., Karato et al., 1986; Mei and Kohlstedt, 2000; Karato, 2008), enhances diffusivity (Wang et al., 2004; Demouchy et al., 2007; Shimojuku et al., 2010), and increases electrical conductivity (e.g., Karato, 1990; Huang et al., 2005; Wang et al., 2006; Yoshino et al., 2006, 2008). Therefore, knowledge of the mechanisms and rates of ionic diffusion in nominally anhydrous minerals, especially hydrogen diffusion in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs, is of fundamental importance for understanding the evolution and dynamics of the Earth.

Numerous experimental data of hydrogen diffusion in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs have been published for the last 20 years.

For example, the first extensive study on the kinetics of hydrogen uptake in olivine has been performed by Mackwell and Kohlstedt (1990). This study was later followed by more complete studies in olivine (Kohlstedt and Mackwell, 1998; Demouchy and Mackwell, 2006; Demouchy, 2010) and forsterite (Demouchy and Mackwell, 2003). In spite of the intensive experimental studies of hydrogen diffusion in  $(\text{Mg,Fe})_2\text{SiO}_4$  olivine several problems are still open: such as diffusivities determined in different labs/or different methods of measurement may differ by orders of magnitude and diffusion mechanisms are not well identified. In particular, the activation energies for hydrogen diffusion are not well constrained among these existing experiments. On the other hand, we note that most previous experiments were focused on olivine and forsterite, few researchers studied hydrogen diffusion in high pressure phases of  $(\text{Mg,Fe})_2\text{SiO}_4$  olivine except for two experiments, one for wadsleyite (Hae et al., 2006) and another for ringwoodite (Ohtani and Zhao, 2009). This is mainly due to the substantial difficulties of performing diffusion experiments at corresponding to the transition zone conditions in single-crystal or polycrystalline specimens.

Recently, a thermodynamical model, known as the  $\text{cB}\Omega$  elastic point defect model (Varotsos and Alexopoulos, 1986), that interconnects point defect parameters with the bulk properties has been employed for estimations of the diffusion coefficients in mantle minerals (Zhang et al., 2010, 2011; Zhang and Wu, 2011, 2012) and led to values in good agreement with the experimental data. Following the same idea, the main purpose of the present study is to examine whether the diffusion coefficient of hydrogen in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs can be reproduced on the basis of

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theoretical consequences of the  $cB\Omega$  model over a range of geologically relevant P–T conditions.

## 2. Method summary

Diffusion is a thermally activated process due to atomic-scale motion of a given species (atoms, ions and molecules) in solid phases, as well as liquids, and gases. In minerals, diffusive transport is the only mechanism for a given species to move from one location to another. If a single mechanism of diffusion is involved, the diffusivity increases with temperature following the Arrhenius relation (Shewmon, 1963):

$$D = fa^2 v \exp[-g^{\text{act}}/(k_B T)] \quad (1)$$

where  $f$  is a geometrical factor,  $a$  stands for the jump distance,  $v$  is the jump frequency (usually taken equal to the Debye frequency  $\nu_D$  [Varotsos and Alexopoulos, 1986]),  $k_B$  is Boltzmann constant,  $T$  is the absolute temperature, and  $g^{\text{act}}$  denotes the Gibbs free energy for the activation process.

According to the so-called  $cB\Omega$  model, the defect Gibbs free energy  $g^{\text{act}}$  is interconnected with the bulk expansivity and elastic data through the relation (Varotsos, 1976; Varotsos and Alexopoulos, 1977, 1979, 1980, 1984, 1986; Varotsos and Ludwig, 1978; Varotsos et al., 1978a, 1978b):

$$g^{\text{act}} = c^{\text{act}} B\Omega \quad (2)$$

where  $c^{\text{act}}$  is practically constant which can be considered as independent of temperature and pressure to the first approximation (Varotsos and Alexopoulos, 1986; Varotsos, 2007a),  $B$  is the isothermal bulk modulus,  $\Omega$  is the mean atomic volume per atom. The validity of the  $cB\Omega$  model has been checked for different defect processes (i.e., formation, migration and activation processes) in various categories of solids including metals (Varotsos and Alexopoulos, 1977, 1980; Varotsos et al., 1978a; Alexopoulos and Varotsos, 1981), rare gas solids (Varotsos and Alexopoulos, 1984, 1986), alkali and silver halides (Varotsos and Alexopoulos, 1986; Varotsos, 2007a; Dologlou, 2010a, 2010b), fluorides (Varotsos and Alexopoulos, 1986; Varotsos, 1976, 2007b, 2008) as well as diamond (Varotsos, 2007c; Zhang and Wu, 2012). In addition, the elastic model may provide a basis for the understanding of the compensation rules in carbon subgroup crystals (Papathanassiou et al., 2010) and diffusivity-density scaling function for viscous liquids (Papathanassiou and Sakellis, 2010). Furthermore, recent investigations (Zhang et al., 2010, 2011; Zhang and Wu, 2011, 2012) revealed that the  $cB\Omega$  model can successfully refine the self-diffusion and heterodiffusion coefficients for silicate minerals of geophysical interest.

Since the defect Gibbs energy  $g^{\text{act}}$  is proportional to the quantity  $B\Omega$ , by inserting Eq. (2) into Eq. (1) we can write  $D$  in terms of the  $cB\Omega$  model:

$$D = fa^2 v \exp[-c^{\text{act}} B\Omega/(k_B T)] \quad (3)$$

Obviously, if the diffusion coefficient  $D_1$  is known at a given temperature  $T_1$ , the value of  $c^{\text{act}}$  can be estimated from:

$$c^{\text{act}} = \frac{k_B T_1}{B_1 \Omega_1} \ln \frac{fa_1^2 v_1}{D_1} \quad (4)$$

where the subscript 1 stands for the value of each quantity measured ( $a_1$ ,  $v_1$ ,  $B_1$  and  $\Omega_1$ ) at  $T = T_1$ . Once the value of  $c^{\text{act}}$  has been determined through Eq. (4), Eq. (3) permits the refinement of the diffusion coefficient  $D$  at any temperature (or pressure) provided that appropriate values of  $f$ ,  $a$ ,  $v$ ,  $B$  and  $\Omega$  corresponding to each temperature are known. However, in order to obtain the correct value of  $c^{\text{act}}$  from Eq. (4) for the case of hydrogen diffusion in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs, here we must stress that the jump

frequency  $\nu$  depends roughly on the mass of the diffusant for a given matrix. Therefore, in the absence of any better approximation,  $\nu$  can be reasonably expressed by (Alexopoulos and Varotsos, 1981; Varotsos and Alexopoulos, 1986; Dologlou, 2010a; Zhang and Wu, 2011):

$$\nu = \nu_D (m_m/m_i)^{1/2} \quad (5)$$

where  $\nu_D$  denotes the Debye frequency of the host material,  $m_m$  and  $m_i$  represent the mass of the matrix ( $m$ ) and the diffusant ( $i$ ), respectively. Hereafter, the resulting values of  $c^{\text{act}}$  and  $D$  can only be correctly calculated from Eqs. (3) and (4) through employing the appropriate value of  $\nu$  which has to be determined from Eq. (5).

## 3. Uncertainty analysis

The refinement of diffusion coefficient from the elastic point defect viewpoint ( $cB\Omega$  model) is not a simple duplication for the experimentally available data. Zhang et al. (2010) have suggested that uncertainties in the refinement of diffusivity by means of the  $cB\Omega$  model mainly derive from the following aspects: (1) simplifying assumption for model parameters in Eqs. (3) and (4); (2) inherent errors in the experimentally measured diffusivity; (3) uncertainties related to the experimentally determined bulk properties of minerals.

Among many sources of uncertainty in the refinement of the diffusion coefficients of hydrogen, the influences of these potentially limiting factors in the framework of the  $cB\Omega$  model are considered in more detail below. The first parameter to determine is the geometrical factor  $f$  (also termed correlation factor) in Eqs. (1) and (3). In general, the geometrical factor  $f$  has a value between 0.2 and 1. Although a Random-Walk method was applied to calculate the correlation factors for the case of tracer diffusion by divacancy and impurity-vacancy pairs in cubic crystals (Howard, 1966) as well Mg–Fe interdiffusion in olivine (Hermeling and Schmalzied, 1984), neither experimental nor theoretical value of  $f$  is currently available for hydrogen diffusion in  $(\text{Mg,Fe})_2\text{SiO}_4$  polymorphs (olivine, wadsleyite and ringwoodite) discussed in this study. Probably, the geometrical factor would adopt various values for different element diffusion in the same mineral. In the absence of any direct determination for the value of  $f$ , we simply let the geometrical factor  $f$  be the same value as oxygen diffusion (Zhang et al., 2010, 2011). However, the approximation which are inherent in this calculation makes it somewhat inaccurate, it seems that this point is acceptable because the reproduced diffusivity only has a slight change (at most by a factor of 5) resulting from the variation of the geometrical factor, comparing to the relatively large uncertainty (usually by order of magnitude) in experimentally observed diffusivity.

Another source of error is the determination of constant " $c^{\text{act}}$ " in Eq. (4). This value is a key parameter of the  $cB\Omega$  model and its comparison to other quantities (e.g.,  $a_1$ ,  $v_1$ ,  $B_1$  and  $\Omega_1$ ) allows the refinement of diffusivity via Eq. (3). In most previous works (Varotsos and Alexopoulos, 1986; Varotsos, 2007a; Zhang et al., 2010, 2011; Zhang and Wu, 2011), the value of " $c^{\text{act}}$ " is often determined from a known data point (usually selected the lowest experimental temperature) and thought to be constant independent of temperature and pressure in Eqs. (2)–(4). In this case, in order to clarify the rationale of aforementioned assumption, Fig. 1 shows a comparison of the  $c^{\text{act}}$ -value resulting from a direct application of Eq. (4) for various temperature  $T_1$  (hydrogen diffusion in wadsleyite as an example). An inspection of Fig. 1 indicates that they scatter at most by 9%; this scatter is covered by the experimental error of 9% of the  $B\Omega$ -values involved in the calculation. In fact, the cause of the observed scattering in Fig. 1 is due to the experimentally

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