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Geochemistry, Geophysics, Geosystems

RESEARCH ARTICLE

10.1002/2014GC005551

Key Points:

- A simple model was used to calculate Si diffusivity based on MNR
- This model reproduces T and P dependence of Si diffusivity in silicates
- This model provides a reasonable activation volume estimate for Si diffusion

Supporting Information:

- Supporting Information
- ms_similarity_data

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Application of the $cB\Omega$ model to the calculation of diffusion parameters of Si in silicates

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Abstract Silicon diffusion in major mantle minerals plays an important role in understanding a number of physical and chemical processes in the Earth's interior. Inspection of existing experimental data reveals linear compensation law between the preexponential factors and the activation energies for Si diffusion in various minerals by focusing on those of geophysical interest. On the basis of the observed compensation relationship, here we propose a thermodynamic model, the so-called $cB\Omega$ model that interconnects point defect parameters with the bulk properties to reproduce the Si self-diffusion coefficients in different rock-forming minerals. When the uncertainties are considered, the predicted results show that the temperature and pressure dependences of self-diffusion coefficients concur with existing experimental data and theoretical calculations in most cases.

1. Introduction

In the Earth's mantle, ionic or atomic diffusion in minerals is the most fundamental process that controls a number of transport properties, such as rheology [Yamazaki *et al.*, 2000; Karato, 2008; Xu *et al.*, 2011], chemical heterogeneity [Farber *et al.*, 1994], and electrical conductivity [Kostopoulos *et al.*, 1975; Farber *et al.*, 2000; Dobson *et al.*, 2008]. Therefore, understanding and quantifying these processes require knowledge on the diffusion coefficients for mantle minerals over the range of pressure-temperature conditions encompassed by the Earth's mantle.

Silicon is the lowest diffusion species [Chakraborty, 2010] for most mantle silicates. The Si diffusion rate is thought to control the creep behavior of rocks containing these silicates [Houlier *et al.*, 1990; Yamazaki *et al.*, 2000; Xu *et al.*, 2011] in the Earth's mantle. A large number of experimental data [e.g., Freer, 1981; Brady, 1995; Béjina and Jaoul, 1997; Béjina *et al.*, 2003; Brady and Cherniak, 2010] and theoretical studies [e.g., Karki and Khanduja, 2007; Verma and Karki, 2009; Ammann *et al.*, 2009, 2010; Ito and Toriumi, 2010] on Si diffusion in silicate minerals have been reported. However, some unresolved issues remain. Significant discrepancies extensively exist for Si diffusion in different laboratories and between experimental and theoretical findings because of materials and methodologies used or subtle variations in experimental conditions (e.g., fO_2 , P , and C_{OH}). By contrast, available experimental data are limited to the uppermost pressure area in the lower mantle because of the difficulty of performing experiments at high pressures. Most published studies focus on the temperature dependence (usually very limited temperature range) of diffusion rates, while few experimental measurements have been conducted to determine the diffusion activation volume (i.e., pressure dependence), which plays an important role in extrapolating laboratory measurements of diffusivities to a wide variety of geological and geophysical problems.

A thermodynamic method can satisfactorily predict the diffusion behaviors of some fundamental elements (e.g., Si) using the pressure-volume-temperature (P - V - T) equation in a complicated system or under extreme conditions. In the absence of a direct experimental or theoretical calculation, this thermodynamic method may produce predictions that can potentially provide useful constraints on future experiments and further practical applications where no experimental data exist.

This study presents a thermodynamic model (so-called $cB\Omega$ model) that interconnects the point defect parameters to the bulk and elastic properties, which allows the extraction of the experimental diffusion data, activation energy, and theoretical activation volume estimate. Without having to measure them experimentally, the $cB\Omega$ model reasonably predicts diffusion coefficients and point defect parameters for

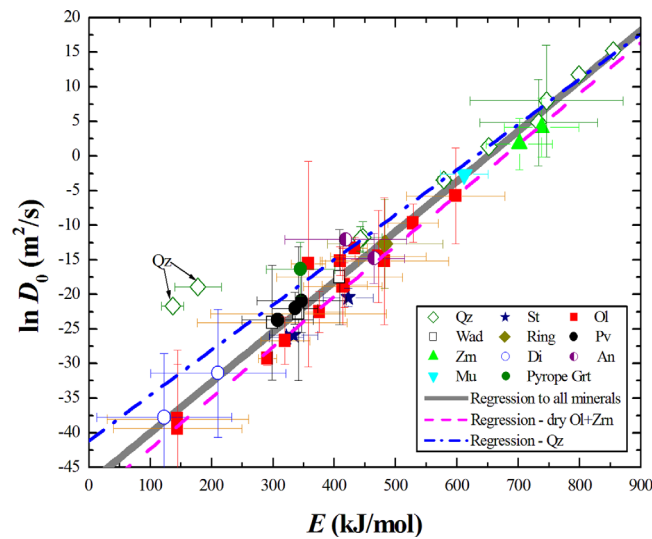


Figure 1. Compensation plots of the experimentally determined preexponential factor ($\ln D_0$) versus activation energy (E) for the diffusion of Si in a selected group of minerals. Solid lines denote the best linear fit to the experimental diffusion data. Two points (for Si self-diffusion) represent quartz for which diffusion data were not included in the regression (see the text for explanation). The dashed and dash-dotted lines show the regression to mineral subgroups, for example, dry olivine + zircon: $\ln D_0$ (m^2/s) = $0.07332(\pm 0.00112)E$ (kJ/mol) - $49.6464(\pm 0.5222)$ ($R \approx 0.998$), and quartz: $\ln D_0$ (m^2/s) = $0.06531(\pm 0.00214)E$ (kJ/mol) - $41.1419(\pm 1.4379)$ ($R \approx 0.997$). Mineral abbreviations and data references are given in Table S1.

factor, E is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. The compensation law, which is often called the “isokinetic effect” or Meyer-Neldel rule (MNR), refers to a positive linear relationship between the activation energy (E) and the natural logarithm of the preexponential factor ($\ln D_0$). The MNR is demonstrated to be upheld for a wide variety of activated processes, such as diffusion [Winchell, 1969; Hart, 1981; Voltaggio, 1985; Béjina and Jaoul, 1997; Zheng and Fu, 1998; Zhao and Zheng, 2007; Brady and Cherniak, 2010] and electrical conductivity [Wu and Zheng, 2003; Zhang et al., 2011]. The compensation law is expressed as follows:

$$\ln D_0 = \alpha + \beta E \tag{2}$$

where α and β are constants. If equations (1) and (2) are combined in light of the compensation law, then we can get $T_C = (\beta k_B)^{-1}$, here T_C is called the “characteristic temperature.” This implies that if the compensation law exists in the substance, the diffusion tends to converge to a constant $D_C = \exp(\alpha)$ at T_C .

Béjina and Jaoul [1997] observed a linear compensation trend for Si diffusion in minerals. They proposed that this compensation law outlines a unique interstitial mechanism for Si migration in all silicate minerals with the SiO_4 tetrahedron-based structure. On this basis, we recheck numerous diffusion data resulting in a better positive correlation between $\ln D_0$ and E for Si diffusion in minerals (Figure 1). The Si compensation trend in Figure 1 is represented by the following linear equation:

$$\ln D_0 (\text{m}^2/\text{s}) = 0.07267(\pm 0.00214)E (\text{kJ}/\text{mol}) - 47.26815(\pm 1.03520) \tag{3}$$

where regressed values of parameters α and β are shown with their 1σ statistical errors in equation (3). A significant compensation law for Si self-diffusion in minerals is shown by statistically good correlations (correlation factor $R > 0.98$) between $\ln D_0$ and E (Figure 1). However, the data on Si self-diffusion in quartz [Farver and Yund, 2000] significantly deviate from the compensation trend (Figure 1). This departure implies that the Si diffusion rates may be overestimated in natural quartz aggregates under hydrothermal conditions. Si diffusion tends to intersect at a constant $D_C = 2.96_{-1.89}^{+5.36} \times 10^{-21} \text{ m}^2/\text{s}$ at $T_C = 1655_{-50}^{+48} \text{ K}$ as a result of the compensation law (Figure 1).

different crystalline mineral structures and compositions using elastic properties [Varotsos and Alexopoulos, 1982, 1986; Varotsos, 2007a; Dologlou, 2011; Zhang et al., 2010, 2011]. Therefore, this study is offered as a test to further examine whether the Si diffusion coefficients in various minerals can be reproduced based on the theoretical consequences of the $cB\Omega$ model.

2. Theoretical Methods

2.1. Investigation of Compensation Law

Diffusion is a thermally activated process in which particles (i.e., atoms, ions, and molecules) migrate randomly within a medium. In general, the diffusivity increases rapidly with temperature in accordance with the Arrhenius relation, which is expressed as follows:

$$D = D_0 \exp\left(-\frac{E}{k_B T}\right) \tag{1}$$

where D is the diffusivity at a certain temperature, D_0 is the preexponential

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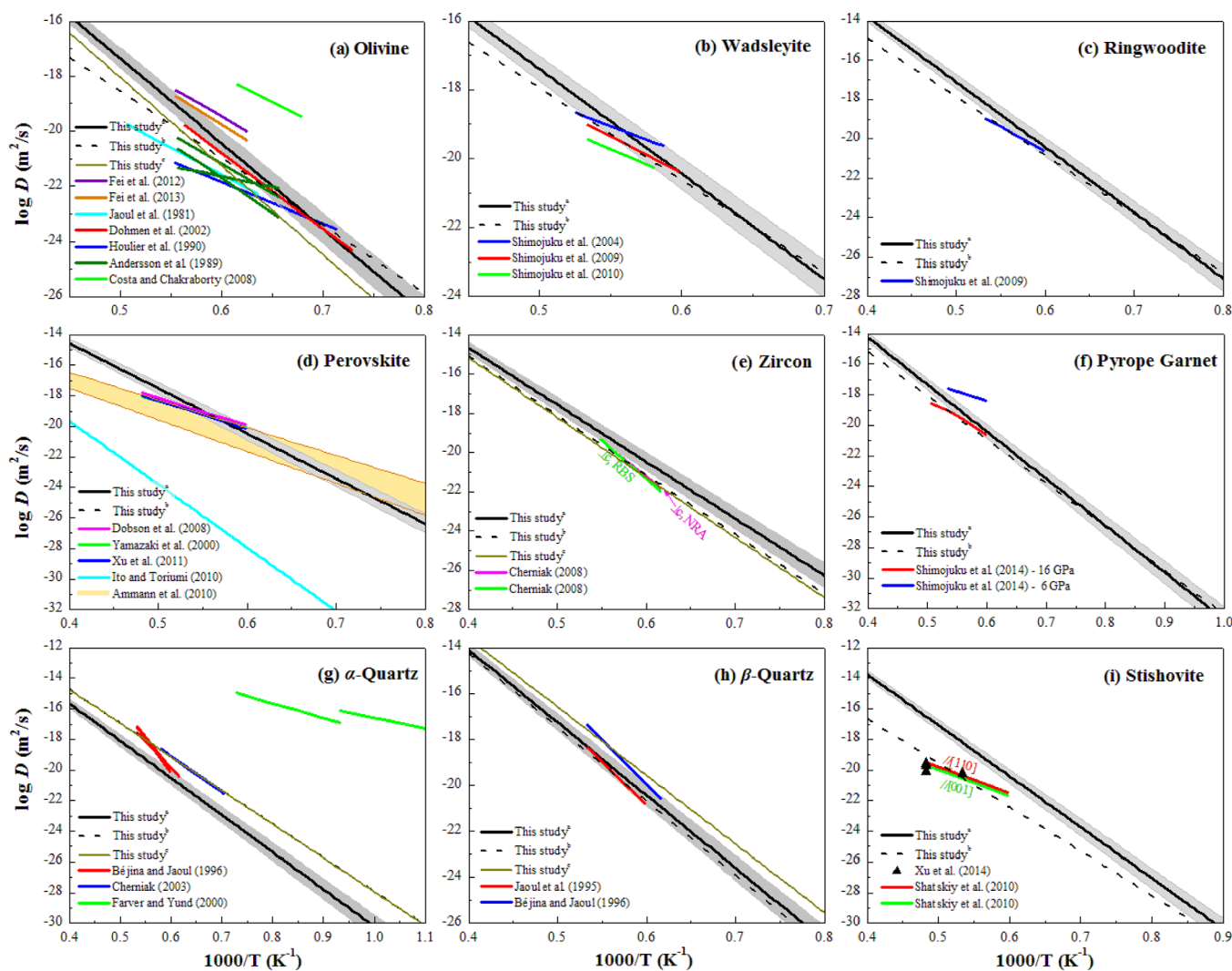


Figure 2. Comparison of the calculated results derived from the $cB\Omega$ model with the experimental data for Si self-diffusion in minerals: (a) olivine; (b) wadsleyite; (c) ringwoodite; (d) perovskite; (e) zircon; (f) pyrope garnet; (g) α -quartz; (h) β -quartz; and (i) stishovite. Note that, the superscripts “a, b, c” of “this study” represent the diffusivities, were calculated from the equation (3), mean value method, and linear regression to mineral subgroups (shown in Figure 1), respectively.

It is worth noting that, as shown in equation (3) and Figure 1, the present observed “universal” compensation law for Si self-diffusion includes all minerals (listed in Table S1) but which have diverse structure. For example, silicon is in six coordination in perovskite and stishovite, whereas four coordination in other minerals in this study. Therefore, different compensation trends may be upheld in one mineral set because the diffusivity of Si was mainly controlled by the lattice structure of host material. However, to elucidate this issue, we also undertook least squares linear regressions on selected subsets for individual minerals (see Figure 1). The resulting predictions were compared with the existing data in Figure 2. 89
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Although the origin of the MNR remains unclear, solid state physicists have discussed the physical meaning of the MNR for many years. Some physicists have concluded that it is a consequence of a one phonon-activated process [Yelon *et al.*, 1992, 2006]. Shimakawa and Aniya [2013] recently presented a new model to explain the MNR in the condensed matter atomic diffusion, taking into account the phonon absorption and emission processes by diffusing atoms. This empirically observed rule is currently demonstrated to be upheld in many cases. Moreover, this rule is used to check laboratory observations and provide fundamental constraints on the derivation and estimation of D_0 and E from experimental data given their interrelationship through the MNR. This relationship is also used to calibrate and validate laboratory experiments. Some examples for proton conduction in olivine [Jones, 2014a] and H diffusion in minerals [Jones, 2014b] have recently been provided. 96
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2.2. The $cB\Omega$ Model

If a single-diffusion mechanism is involved, the self-diffusion coefficient D is described in terms of the activation Gibbs energy g^{act} as follows [Shewmon, 1963; Varotsos and Alexopoulos, 1986]:

$$D = fa^2 \nu \exp\left(-\frac{g^{\text{act}}}{k_B T}\right) \quad (4)$$

where f is a geometric factor, a is the jump distance equal to the lattice constant [Dologlou, 2011; Vallianatos and Saltas, 2014], ν is the jump frequency in the order of the Debye frequency ν_D [Varotsos and Alexopoulos, 1986; Varotsos, 2007a], k_B is the Boltzmann constant, T is the absolute temperature, and g^{act} is the Gibbs free energy for the activation process.

According to the $cB\Omega$ model, g^{act} is interconnected with the bulk expansivity and elastic data through the following relation [Varotsos, 1976; Varotsos and Alexopoulos, 1977a, 1986]:

$$g^{\text{act}} = c^{\text{act}} B \Omega \quad (5)$$

where c^{act} is a practical constant independent of temperature and pressure in the first approximation [Varotsos and Alexopoulos, 1986; Varotsos, 2007a], B is the isothermal bulk modulus, and Ω 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) in various solid categories such as rare gas solids [Varotsos and Alexopoulos, 1986], fluorides [Lazaridou et al., 1985; Varotsos, 2007b, 2008], diamond [Varotsos, 2007c; Zhang and Wu, 2012], and viscous liquids [Papathanassiou and Sakellis, 2010], as well as in mixed ionic solids [Varotsos, 1981]. Furthermore, this model has been successfully applied for self-diffusion and heterodiffusion coefficient refinement of silicate minerals of geophysical interest [Dologlou, 2011; Zhang et al., 2010, 2011; Zhang and Wu, 2011, 2012, 2013; Zhang, 2012, 2014; Vallianatos and Saltas, 2014].

By substituting equation (5) into equation (4), the following equation is obtained:

$$D = fa^2 \nu \exp\left(-\frac{c^{\text{act}} B \Omega}{k_B T}\right) \quad (6)$$

If the diffusion coefficient D_1 is known at a given temperature T_1 , then the value of c^{act} is estimated from

$$c^{\text{act}} = \frac{k_B T_1}{B_1 \Omega_1} \ln \frac{fa_1^2 \nu_1}{D_1} \quad (7)$$

where subscript 1 is the value of each measured quantity (a_1 , ν_1 , B_1 , and Ω_1) at $T = T_1$. Once the value of c^{act} has been determined through equation (7), equation (6) permits the diffusion coefficient D refinement at any temperature (or pressure) provided that appropriate f , a , ν , B , and Ω values for each temperature are available.

Now the critical problem is finding an appropriate data point (D_1 and T_1) to determine the c^{act} value in equation (7). Several approaches have been used to achieve the appropriate point including a single experimental measurement [Alexopoulos and Varotsos, 1981; Varotsos and Alexopoulos, 1980, 1986; Varotsos, 2007a; Zhang and Wu, 2011; Zhang, 2012; Varotsos, 2009], mean value method [Dologlou, 2011; Zhang and Wu, 2012; Zhang, 2012], and compensation law [Zhang et al., 2010, 2011]. A robust compensation trend has been established for Si diffusion in various minerals, as shown in equation (3). The most outstanding advantage of the compensation law is that all diffusing species of interest have the same diffusion rates D_C at the particular temperature T_C regardless of the diffusion medium or mechanism. Therefore, the c^{act} value is reasonably determined using the compensation law. The value is set at $T_1 = T_C$ and $D_1 = D_C$ in equation (7). By contrast, the mean value method is used to calculate the c^{act} value in the present case. The predicted diffusion data comparison derived from different approaches shows the better method for the correct $cB\Omega$ model implementation.

All model parameters (a , ν , B , and Ω) used for the c^{act} calculation (equation (7)) and the diffusion coefficient D_{calc} prediction (equation (6)) are recalculated at each corresponding temperature and pressure in light of the P - V - T equation of state of the mineral.

2.3. Uncertainties and Limitations

Zhang et al. [2010] have suggested that uncertainties in the self-diffusion coefficient refinement using the $cB\Omega$ model are mainly attributed to the following three factors: (1) assumption of linear compensation effects; (2) simplified assumption for model parameters (f , a , v , c^{act} , B , and Ω) in equations (6) and (7) in the $cB\Omega$ model framework; and (3) uncertainties in calculating the elastic and expansivity data of referenced minerals. For the first issue, more uncertainty details that originate from the compensation law are found in previous studies [Zheng and Fu, 1998; Zhao and Zheng, 2007; Zhang et al., 2010]. Here we have to mention that data selection can change the resulting compensation line and should be done with caution. As stated by Brady and Cherniak [2010] in their examination of adherence to the compensation law by diffusion of various species in various minerals: "Compilation, establishment, and interpretation of diffusion compensation relations face two distinct difficulties: (1) the selective exclusion of data that are perceived as 'outliers' without strong justification for their exclusion, and (2) the inclusion of diffusion data that may be compromised by nondiffusional processes or experimental artifacts that render Arrhenius relations nondescriptive of volume diffusion." For these reasons, the employment of compensation lines to predict diffusion coefficients is likely to be at best a rough approximation.

This study focuses on the potential error sources from the $cB\Omega$ model inheritance itself. The c^{act} value is determined by equation (7) to predict the self-diffusion coefficients from equation (6). As mentioned, the value of c^{act} in this study is determined by a novel method based on the compensation law [Zhang et al., 2010, 2011]. The advantage of this improved approach is that it enables the use of the data point (D_C and T_C) to determine the c^{act} value in equation (7) regardless of the diffusion medium or mechanism. The second parameter to determine is the jump distance a , the value of which is related to the diffusion mechanism. In particular, Béjina and Jaoul [1997] argued that the jump distance of the Si diffusion has a similar value (~ 5 Å) close to a mean distance between the SiO_4 tetrahedra for all silicate minerals. Therefore, a unique diffusion mechanism by interstitials is highly probable among these silicates strongly controlled by the SiO_4 tetrahedron. In the absence of an experimental or theoretical determination, the jump distance is simply assumed to be similar to the lattice constant value in this calculation. Moreover, the uncertainties from both the appropriate choice of the Debye frequency (optic or acoustic frequency) and the correlation factor, which is not always known, are incorporated into equation (7).

Another potential error in the self-diffusion coefficient refinement in terms of the $cB\Omega$ model is caused by the experimental elastic and expansivity data of minerals, particularly B and Ω . An experimental study frequently determines the bulk properties (e.g., compressibility and expansivity) of the minerals in limited temperature and pressure ranges. The extrapolation of these available bulk properties to a relatively higher or lower temperature of geological interest is required in practical application. The bulk mineral properties, especially volume V and isothermal bulk modulus B , often vary with temperature and pressure in a nonlinear manner at temperatures relatively lower and near the melting point [Varotsos and Alexopoulos, 1986; Zhang et al., 2010]. Thus, such an extrapolation easily introduces an additional uncertainty in the $cB\Omega$ model framework. However, previous studies [Varotsos, 2007a; Zhang et al., 2010; Zhang, 2012] have indicated that the c^{act} value has an uncertainty of not more than 3% mainly because of the experimental error in the elastic and expansivity data determination of solids.

3. Results and Discussion

Considering the aforementioned approaches, we compared the predicted self-diffusivities (D_{calc}) with available data, including experimental (D_{exp}), theoretical, and other empirical ones. The comparison was conducted to check whether the $cB\Omega$ model successfully reproduced the whole experimental diffusion behavior and to test the validity of the current thermodynamic approach.

3.1. Temperature Dependence of Diffusivities

First the temperature dependence of Si self-diffusion in olivine was refined to show how D was determined at any temperature and pressure based on the $cB\Omega$ model. The c^{act} value in equation (7) was calculated at the characteristic temperature ($T_1 = T_C = 1655$ K) to do the refinement. As described in section 2.2, $f = 0.745$ for olivine at 8 GPa and 1655 K. This result was based on the assumption that Si diffusion via interstitials [Béjina and Jaoul, 1997]. In addition, $a_1 = 4.7437$ Å [Liu and Li, 2006], $v_1 = 1.35 \times 10^{13} \text{ s}^{-1}$ [Liu and Li, 2006], $B_1 = 137.21$ GPa [Fabrichnaya et al., 2004], and $\Omega_1 = 10.16$ Å³ [Liu and Li, 2006]. Finally, one gets

Table 1. Parameters Used in the Calculation of Diffusivities in Minerals as Predicted From cB Ω Model

Mineral [Reference]	f	a (Å)	B (T)		V (T)	
			B_0 (GPa)	$(\partial B/\partial T)_P$ (GPa K $^{-1}$)	V_0 (Å 3)	α_0 ($\times 10^{-5}$ K $^{-1}$)
Olivine [Liu and Li, 2006]	0.745 ^a	4.7656	129	-0.019	292.13	2.73
Wadsleyite [Katsura et al., 2009]	0.745 ^a	5.7015	169.2	-0.021	538.49	2.31
Ringwoodite [Katsura et al., 2004]	1	8.0663	182	-0.029	524.8	2.57
Perovskite [Fiquet et al., 1998]	1	4.7765	261	-0.027	162.6	1.19
Pyrope Garnet [Zou et al., 2012]	1	11.4482	167	-0.021	1500.43	2.89
Stishovite [Wang et al., 2012]	1	4.179	294	-0.0788	46.55	1.86

^aReference: Hermeling and Schmalzied [1984].

$c^{\text{act}} = 0.5616 (\pm 0.0035)$ when these values and $D_1 = D_C = 2.96 \times 10^{-21}$ m 2 /s were inserted into equation (7). By contrast, the calculated c^{act} value obtained as a “mean value” from one set of available experimental diffusion data [Dohmen et al., 2002, Table 1] was 0.5531 (± 0.0026) if the appropriate parameters (f , a , v , B , and Ω) in equation (7) were used at the P - T conditions similar to those in the diffusion experiment. The c^{act} value was already known, the diffusion coefficient D_{calc} from equation (6) was calculated using the appropriate elastic and expansivity data (Table 1) for each temperature. The same procedure for the pressure dependence was applied to the other selected minerals [Zhang et al., 2010, 2011; Zhang and Wu, 2012; Zhang, 2012].

The calculated diffusion coefficient values D_{calc} using the cB Ω model and the experimental/theoretical data were separately plotted as a function of the inverse temperature (Figure 2). The empirical estimates agreed with the experimental data in most cases except for stishovite. Costa and Chakraborty [2008] showed that water considerably enhanced the Si diffusion rate compared with the rates measured in anhydrous minerals. Thus, it is clear that Si diffusion in anhydrous olivine was significantly faster by 2–3 orders of magnitude than the calculated results and existing data (Figure 2a) [Jaoul et al., 1981; Andersson et al., 1989; Houlier et al., 1990; Dohmen et al., 2002]. By contrast, Fei et al. [2012, 2013] measured the Si self-diffusion coefficients in single crystals of forsterite under dry and wet ($C_{\text{H}_2\text{O}}$ up to 800 ppm) conditions. They concluded that the effect of water on Si diffusion in forsterite was minimal. This effect was overestimated in the study conducted by Costa and Chakraborty [2008]. The calculations matched the experimental results well for Si diffusion in (Mg,Fe) $_2$ SiO $_4$ high-pressure polymorphs (i.e., wadsleyite and ringwoodite, as shown in Figures 2b and 2c). A recent high-pressure experiment indicated that Si self-diffusion in single crystals of perovskite was almost isotropic. Moreover, the diffusion rates were similar to those in the polycrystals [Xu et al., 2011]. As shown in Figure 2d, the thermodynamic predictions are comparable to the existing experimental [Yamazaki et al., 2000; Dobson et al., 2008; Xu et al., 2011] and theoretical [Ammann et al., 2010] data. However, the molecular dynamic calculations by Ito and Toriumi [2010] are several orders of magnitude lower than the thermodynamic estimates and previous experimental results. For Si diffusion in zircon, the experimental results from different analytical methods (i.e., nuclear reaction analysis and Rutherford backscattering spectrometry) are comparable to each other [Cherniak, 2008]. The results are also close to the empirical predictions (Figure 2e). Similarly, the calculated D_{calc} for pyrope garnet at 16 GPa is comparable to the experimental data [Shimojuku et al., 2014]. For Si diffusion in the quartz group (i.e., α - β -stishovite), the empirical estimates of Si diffusivities for the α -quartz reasonably match the laboratory results [Béjina and Jaoul, 1996; Cherniak, 2003]. The experimental data of Farver and Yund [2000] disagree with the empirical estimates (Figure 2g) and deviate significantly from the compensation trend (Figure 1). This discrepancy is mainly due to the grain boundary diffusion that dominates the effective diffusion rates in quartz aggregates. Farver and Yund [2000] showed that the Si grain boundary diffusion rates in quartz were more than 12 orders of magnitude faster than the Si volume diffusion rates under anhydrous conditions. As illustrated in Figure 2h, for β -quartz, a comparison of the empirically estimated diffusivities with the experimental data [Jaoul et al., 1995; Béjina and Jaoul, 1996] reveals a good agreement when the uncertainties are considered. For stishovite (Figure 2i), the empirical diffusivities are several orders higher than the experimental data [Shatskiy et al., 2010; J. S. Xu et al., manuscript in preparation, 2014]. This discrepancy may be caused by the slight deviation of experimental data from the compensation line in Figure 1, which led to an imprecise estimate for the value of c^{act} . Alternatively, experimental uncertainties on the elastic and expansivity data of minerals would also affect the degree of accuracy of the calculated results D_{calc} . Particularly, the importance

Table 2. Summary of the Predicted Results Derived From the cB Ω Model

References	T (K)	P (GPa)	$\ln D_0$ (m ² /s)	E (kJ/mol)	ΔV (cm ³ /mol)	Remarks
<i>Olivine</i>						
Fei et al. [2012]	1600–1800	0–13	-15.20 ± 2.07	410 ± 30	1.7 ± 0.4	Dry Fo ₁₀₀
Fei et al. [2013]	1600–1800	8	-13.35 ± 1.61	434 ± 20		Wet Fo ₁₀₀
Costa and Chakraborty [2008]	1473–1623	2	-15.60 ± 1.13	358 ± 28		Wet, // and \perp [001]
Houlier et al. [1990]	1403–1803	1 atm	-29.30 ± 1.00	291 ± 15	0.7 ± 2.3^a	Dry, // and \perp [001]
Farver and Yund [2000]	1173–1473	1 atm	-19.04	203 ± 36		Dry Fo ₁₀₀
Dohmen et al. [2002]	1373–1773	1 atm	-9.67 ± 2.76	529 ± 41		Dry, // [001]
This study	1000–1900	0–14	-4.84 ± 0.18	583 ± 17	1.20 ± 0.13	cB Ω model
This study	1000–1900	1 atm	-6.055	467 ± 20		Mean value method
<i>Wadsleyite</i>						
Shimojuku et al. [2004]	1703–1903	18	-24.09 ± 8.29	299 ± 122	6.1^b	Wet, polycrystal
Shimojuku et al. [2009]	1723–1873	18	-22.79 ± 9.77	342 ± 143		Wet, polycrystal
Shimojuku et al. [2010]	1673–1873	16	-17.50 ± 6.91	409 ± 103	-1.57^c	Wet, polycrystal
This study	1000–1900	10–20	-4.97 ± 0.22	583 ± 12	6.21 ± 0.35	cB Ω model
This study	1000–1900	18	-10.46 ± 0.35	513 ± 18		Mean value method
<i>Ringwoodite</i>						
Shimojuku et al. [2010]	1673–1873	22	-12.66 ± 6.44	483 ± 94	3.86^d	Wet, polycrystal
This study	1000–1900	16–24	-1.14 ± 0.32	636 ± 20	2.25 ± 0.13	cB Ω model
This study	1000–1900	22	-6.83 ± 0.18	570 ± 16		Mean value method
<i>Perovskite</i>						
Xu et al. [2011]	1673–2073	25	-23.70	308 ± 58		dry, single crystal
Dobson et al. [2008]	1673–2073	25	-20.91 ± 4.42	347 ± 73	3.5^e	dry, polycrystal
Yamazaki et al. [2000]	1673–2073	25	-22.02	366 ± 37	3.0^f	dry, polycrystal
Karki and Khanduja [2007]		0–120		657	$0.87–2.48$	first-principle calculation
This study	1000–2400	0–60	-6.34 ± 0.24	565 ± 18	5.08 ± 0.27	cB Ω model
This study	1000–2400	25	-6.33 ± 0.21	564 ± 15		Mean value method
<i>Pyrope Garnet</i>						
Shimojuku et al. [2014]	1673–2073	6–25	-16.35 ± 3.91	345 ± 56	4.70 ± 0.50	Single crystal
This study	1000–1900	0–20	-4.51 ± 0.22	588 ± 18	5.62 ± 1.21	cB Ω model
This study	1000–1900	16	-8.65 ± 1.35	547 ± 11		Mean value method
<i>Stishovite</i>						
Xu et al. [2014] ^g	1873–2073	13–23	-20.45 ± 1.34	423 ± 41	5.18 ± 0.26	Single crystal
Shatskiy et al. [2010]	1673–2073	14	-26.23 ± 1.82	322 ± 28		// [110]
Shatskiy et al. [2010]	1673–2073	14	-25.90 ± 2.53	334 ± 39		// [001]
This study	1000–2500	0–60	-0.96 ± 0.19	638 ± 21	7.38 ± 0.31	cB Ω model
This study	1000–2500	14	-11.69 ± 1.32	552 ± 30		Mean value method

^aReference: Béjina et al. [1999].^bEstimated from Mg-Fe interdiffusion [Farver and Yund, 2000].^cCalculated at 10 GPa [Verma and Karki, 2009].^dCalculated at 20 GPa [Verma and Karki, 2009].^eCalculated at 25 GPa [Ammann et al., 2009].^fReference: Yamazaki and Karato [2001].^gReference: Xu et al. (manuscript in preparation, 2014).^hSupporting Information: xxxx

of the influence of the anharmonic effects on elastic properties of solids becomes evident with increasing temperature [Varotsos, 2009].

In testing the validity of the cB Ω model, the preexponential factors D_0 and the activation energies E derived from different approaches (i.e., cB Ω model and experimental measurement) are summarized in Table 2. Furthermore, the advantages and disadvantages of using different methods to calculate the c^{act} value with the experimental results are compared. In this study, we randomly choose one experimental result to determine the mean c^{act} value if two or more sets of experimental data exist for a given mineral. The inspection in Figure 2 and Table 2 shows that in all cases, the predicted D_{calc} and activation energy E using the “mean value method” are closer to the D_{exp} than those predicted by the compensation law. However, an inherent difference between these two approaches is observed. The keyword is “general” when the c^{act} value is calculated using the compensation law. This condition indicates that the diffusion coefficient D_{calc} can be predicted for a wide variety of minerals even if no experimental data are available. The “mean value method” considerably depends on the choice of experimental diffusion data. Thus, the keyword is “specific.” In cases where numerous experimental results are obtained for a given mineral (e.g., olivine in Figure 2a), large discrepancies exist in different laboratory measurements, and no experimental data are available, the “mean value method” faces serious difficulty in practical use.

3.2. Pressure Dependence of Diffusivities

Knowledge on the pressure dependence of Si diffusion in mantle minerals is crucial in quantifying and understanding the geodynamic processes in the Earth's mantle. Laboratory measurement (e.g., extremely limited pressure range) diffusion data is frequently extrapolated to the conditions of the deep Earth. Unfortunately, only a few experimental studies have focused on the pressure dependence of Si diffusion in the mantle minerals because of the substantial diffusivities of simultaneously performing diffusion experiments at high-pressure and high-temperature conditions. If the activation volume definition is recalled (i.e., $v^{act} = -\left(\frac{dg^{act}}{dP}\right)_T$) and equation (4) is differentiated with respect to pressure, then the activation volume can be expressed as

$$v^{act}(P, T) = -k_B T \left(\frac{\partial \ln D}{\partial P} \right)_T \quad (8)$$

The quantity v^{act} can be determined using the slope of $\ln D$ versus P plot [Varotsos *et al.*, 1978; Varotsos and Alexopoulos, 1986; Zhang *et al.*, 2011; Zhang, 2012; Zhang and Wu, 2012].

The thermodynamic estimates with the existing experimental and theoretical results on the Si self-diffusion pressure dependence in (Mg,Fe)₂SiO₄ polymorphs, MgSiO₃ perovskite, stishovite, and pyrope garnet under several temperatures are presented in Figure 3. The thermodynamic model used in this study provides first-order approximations of Si experimental diffusivities in these minerals. In (Mg,Fe)₂SiO₄ olivine (0–14 GPa and 1000–1900 K), the empirical estimates agree well with the experimental results obtained by Fei *et al.* [2012] at lower pressure, Dohmen *et al.* [2002] at ambient pressure, and other researchers [Jaoul *et al.*, 1981; Houlier *et al.*, 1990; Andersson *et al.*, 1989; Béjina and Jaoul, 1997] (data not shown in Figure 3a). Nevertheless, the thermodynamic wadsleyite (10–20 GPa and 1000–1900 K) and ringwoodite (16–24 GPa and 1000–1900 K) calculations are slightly lower than those experimentally obtained [Shimojuku *et al.*, 2004, 2009, 2010]. The experimental determinations for Si self-diffusion in MgSiO₃ perovskite are completely close to each other [Yamazaki *et al.*, 2000; Dobson *et al.*, 2008; Xu *et al.*, 2011] at 25 GPa. These results match our thermodynamic calculations at the 1600–2100 K temperature range (Figure 3b) if one considers the experimental error in the elastic data at high pressure. However, the theoretical calculations on the Si diffusion pressure dependence in perovskite using the first-principle calculations [Ammann *et al.*, 2010] and molecular dynamic simulation [Ito and Toriumi, 2010] are several orders of magnitude higher than our thermodynamic estimates and those that have been reported experimentally. As illustrated in Figures 3c and 3d, the calculated Si diffusion coefficients, as a function of pressure, are in good agreement with the experimental results for stishovite [Shatskiy *et al.*, 2010; Xu *et al.*, manuscript in preparation, 2014] and pyrope garnet [Shimojuku *et al.*, 2014].

Furthermore, an inspection of the calculated $\log D$ versus P plots (Figure 3) shows a slight upward curvature that is effectively described by equation (8). Considering the preceding reservations on the pressure dependence of the diffusion data, we can combine the various pressure results to obtain the activation volume estimate of Si self-diffusion. Therefore, a comparison of our estimated activation volume (Table 2) and the experimental and theoretical ones is possible. A positive activation volume of 1.2 cm³/mol for Si self-diffusion in olivine is comparable to a previous experimental value of 1.7 cm³/mol [Fei *et al.*, 2012] for dry synthetic forsterite single crystals and 0.7 cm³/mol [Béjina *et al.*, 1999] for San Carlos olivine. The agreement on the activation volume between the thermodynamic calculations and the existing experimental and theoretical data can be similarly observed in other cases (Table 2). This result suggests that the thermodynamic cBΩ model can provide a reasonable activation volume estimate for Si diffusion in most silicates.

3.3. Comparison of Estimated Diffusivities

In principle, the thermodynamic calculations can be performed for any mineral if only the bulk elastic properties of the given minerals and the key data point (i.e., D_1 and T_1 in equation (7), which are crucial to determine the c^{act} value) are available. In this study, the c^{act} value was computed from the observed compensation trend between the logs of the preexponential factor (D_0) and the activation energy (E) for a particular diffusing (Si) species in all minerals.

The thermodynamic diffusivity calculations for Si in a selected group of rock-forming minerals as Arrhenius functions of temperature are shown in Figure 4. All the Arrhenius lines of $\log D$ versus $1/T$ tend to intersect at a single diffusion coefficient value at a given critical temperature ($T_c = 1655$ K). Given these trends, the

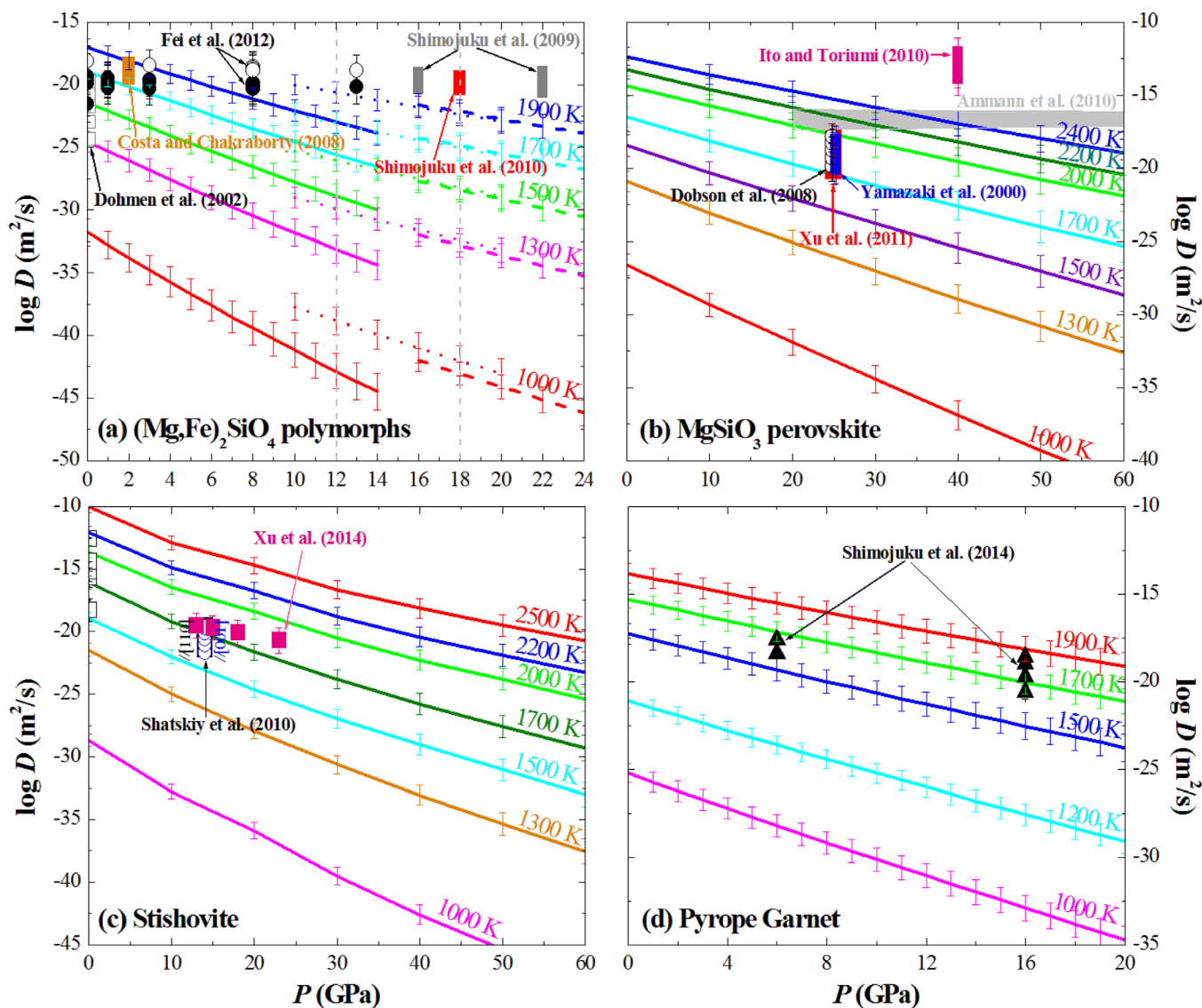


Figure 3. Pressure dependence of Si self-diffusion coefficients D at various temperatures. (a) $(\text{Mg,Fe})_2\text{SiO}_4$ polymorphs; (b) MgSiO_3 perovskite; (c) stishovite; and (d) pyrope garnet. The light gray dashed lines represent the phase boundary between olivine/wadsleyite and wadsleyite/ringwoodite in Figure 3a.

estimated diffusion rates were systematized using the $cB\Omega$ model for the respective minerals (Figure 4 and 305
 Table 2). The thermodynamic predicted sequences of the Si diffusivity are listed from high to low as follows: 306
 α -quartz > zircon > perovskite > wadsleyite \approx pyrope garnet > olivine > β -quartz > ringwoodite > stishovite. 307
 However, the aforementioned sequence is reversed when the temperature is higher than the critical value. 308

3.4. Calculation of Point Defect Parameters Based on $cB\Omega$ Model

The point defect parameters (i.e., activation volume v^{act} and activation enthalpy h^{act}) are estimated for the 310
 Si diffusion process in silicates. Differentiating equation (5) with respect to pressure, we find that the activa- 311
 tion volume $v^{act} = -\left(\frac{dg^{act}}{dP}\right)_T$ is given as 312

$$v^{act} = c^{act} \Omega \left(\frac{dB}{dP} \Big|_T - 1 \right) \quad (9)$$

Similarly, when equation (5) is differentiated with respect to the temperature for $P = \text{constant}$ and the defini- 313
 tions of defect entropy ($s^{act} = -\frac{dg^{act}}{dT} \Big|_P$) and defect enthalpy (h^{act}) are considered, the value of h^{act} can be 314

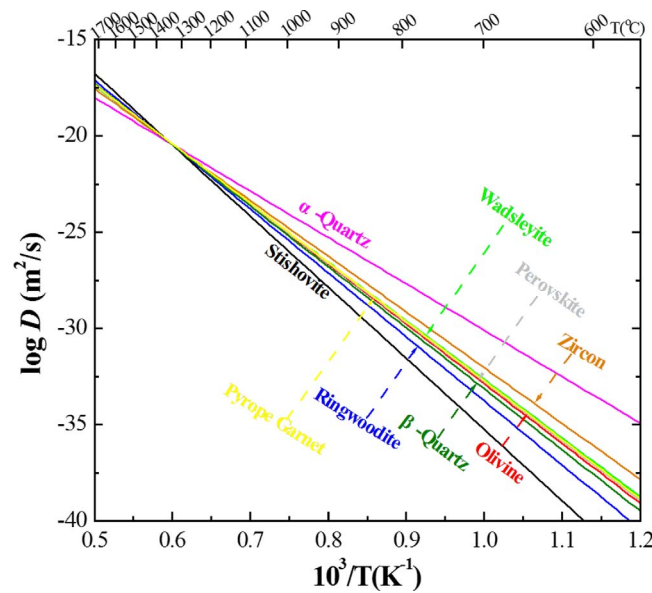


Figure 4. Arrhenius plots of thermodynamically calculated diffusivities (Table 2) of Si in selected minerals.

2006]. By substituting the preceding values in equations (9) and (10) and the estimated c^{act} values, $\Omega(T)$ and $B(T)$ for Si diffusion in olivine are in the 1000–2000 K temperature range. The v^{act} and h^{act} values are calculated as 1.22–1.25 (± 0.27) cm^3/mol and 390–425 (± 24) kJ/mol [(4.04–4.40) ± 0.25 eV], respectively. These values are in good agreement with the experimentally reported activation volume (i.e., $\Delta V = 1.7 \text{ cm}^3/\text{mol}$) [Fei et al., 2012] and activation energy (i.e., $E = 358\text{--}434 \text{ kJ/mol}$) [Costa and Chakraborty, 2008; Fei et al., 2012, 2013]. However, these values disagree with other experimental data [Houlier et al., 1990; Farver and Yund, 2000; Dohmen et al., 2002] (Table 2). The ratio $v^{act}/h^{act} = 0.0287\text{--}0.0321 \text{ cm}^3/\text{kJ}$ is obtained if the preceding elastic parameters are used in equation (11). This ratio is comparable to that derived from equations (9) and (10).

Furthermore, Figure 5 shows a direct comparison of the calculated values of v^{act} , h^{act} , and v^{act}/h^{act} from equations (9)–(11), with the experimental or theoretical results for all minerals referenced in this study. The calculated v^{act} value is in good agreement with previously published data (Figure 5a). The calculated h^{act} value falls in the range of that determined experimentally or theoretically (Figure 5b). Meanwhile, the calculated ratios of $(v^{act}/h^{act})_{\text{Calc}}$ for olivine, wadsleyite, and perovskite indicate a satisfactory agreement with the reported data. However, a large deviation ranging from 34% to 47% can be observed in wadsleyite, pyrope garnet, and stishovite (Figure 5c). The discrepancy in h^{act} and v^{act}/h^{act} may have resulted from the inherent uncertainty of the cB Ω model and the experimental errors in the quantities (i.e., B , $\frac{dB}{dT}|_P$, $\frac{dB}{dP}|_T$, and β) used in this calculation.

4. Concluding Remarks

The cB Ω thermodynamic model successfully reproduces the temperature and pressure dependence of the Si self-diffusion coefficients in various mantle minerals with the aid of the established compensation law and the available bulk and elastic properties. In most cases, the calculated diffusivities favorably agree with the existing experimental or other empirical or theoretical data over the investigated temperature-pressure range. The cB Ω model provides a reasonable activation volume estimate for Si diffusion in silicate minerals. A critical point for evaluating the effectiveness of an empirical or theoretical method is based on the fact that such a method can reproduce the existing data and deliver the predictions that can be confirmed by subsequent observations.

The cB Ω thermodynamic model systematically and reasonably calculates the Si diffusion properties in a number of geoscience materials and systems based on their bulk properties over wide ranges of

directly calculated at any temperature using the following equation [Varotsos and Alexopoulos, 1977b, 1979, 1986]:

$$h^{act} = c^{act} \Omega \left(B - T \beta B - T \frac{dB}{dT} \Big|_P \right) \quad (10)$$

where β is the thermal (volume) expansion coefficient.

Taking the ratio of equations (9) and (10), we obtain

$$\frac{v^{act}}{h^{act}} = \left(\frac{dB}{dP} \Big|_T - 1 \right) / \left(B - T \beta B - T \frac{dB}{dT} \Big|_P \right) \quad (11)$$

If we consider the case of olivine at ambient pressure, then the corresponding parameters (Table 1) are as follows: $\frac{dB}{dT} \Big|_P = -0.019 \text{ (2) GPa K}^{-1}$, $\frac{dB}{dP} \Big|_T = 4.61 \text{ [Liu and Li, 2006]}$, and $\beta = 2.73 \text{ (34)} \times 10^{-5} + 2.22 \text{ (81)} \times 10^{-8} T - 0.538 T^{-2} \text{ (K}^{-1})$ [Liu and Li,

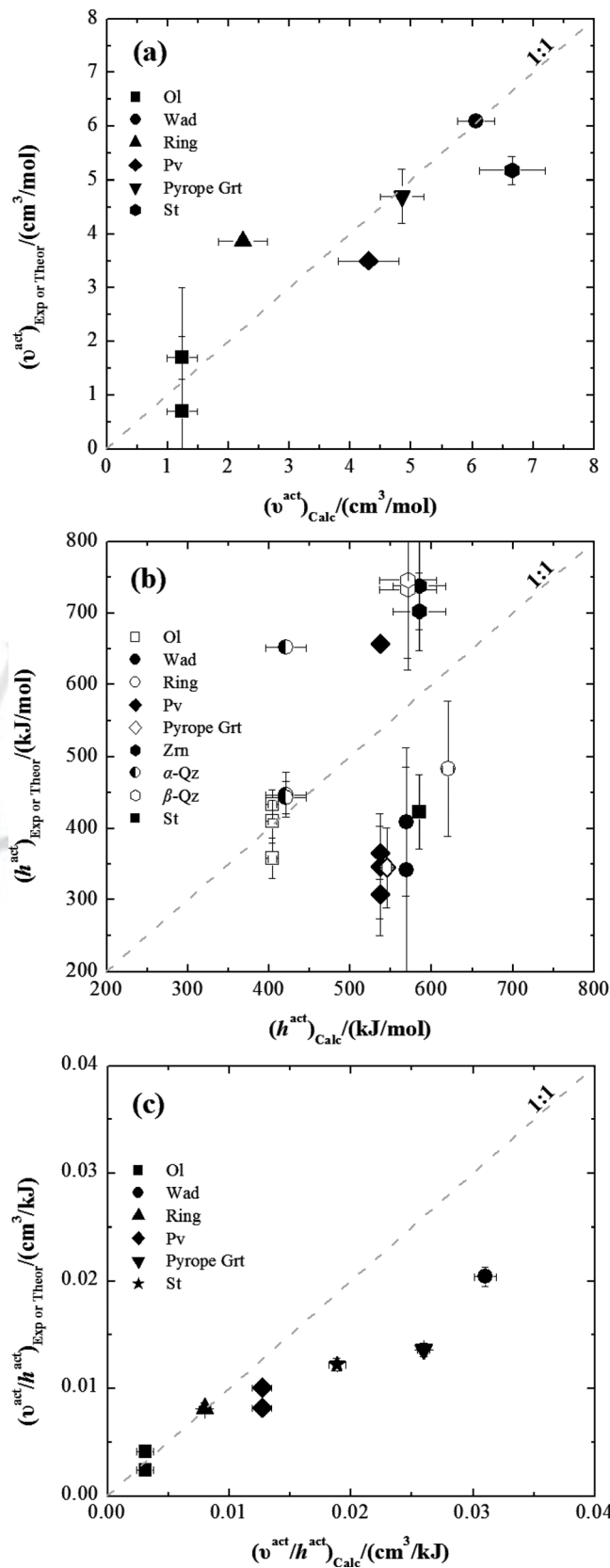


Figure 5. Comparison of the calculated point defect parameters based on the $cB\Omega$ model with the experimental or theoretical data for Si diffusion in minerals: (a) Activation volume v^{act} ; (b) activation enthalpy h^{act} ; (c) the ratio v^{act}/h^{act} .

temperature and pressure. Based on the assumptions and simplifications of the cB Ω model framework, the degree of accuracy of the predicted diffusivities and point defect parameters is not as good as that determined using experimental measurements. The present calculations are valuable in guiding and extending experimental diffusion investigations to real natural systems. Future challenges include the expanding the scope of the thermodynamic approach (i.e., the cB Ω model) to include other important phase categories, such as silicate melts, liquid, and metallic systems, which are relevant to the transport properties in the Earth's interior. These categories will enable the exploration of other geological processes, including melt generation and differentiation, which have played major roles in geological history.

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