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Application of the $cB\Omega$ model for the calculation of oxygen self-diffusion coefficients in minerals

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The $cB\Omega$ model, which suggests the defect Gibbs energy is proportional to the isothermal bulk modulus and the mean volume per atom, is first introduced to predict self-diffusion coefficients of oxygen in various silicate and oxide minerals in terms of available elastic data. We develop a new approach to determine constant c in the $cB\Omega$ model on the basis of the observed compensation effect between the activation energies and pre-exponential factors, which is critical to the diffusivity prediction. Under anhydrous conditions, the validity of this model is tested by the experimentally determined oxygen self-diffusion coefficients. Our results show that the absolute oxygen diffusion rates derived from the $cB\Omega$ model are in agreement with experimental data in a variety of rock-forming minerals including olivine, MgSiO_3 perovskite, spinel, and zircon. © 2010 American Institute of Physics. [doi:10.1063/1.3476283]

I. INTRODUCTION

Oxygen is the most abundant element in the Earth. Study of the rates of oxygen isotope exchange by self-diffusion in rock-forming minerals is of fundamental importance for understanding the thermal histories in geological processes.^{1,2} With the rapid development of high-pressure research in the geosciences over the past several decades, there has been a large number of experimental studies on the diffusion rate of oxygen in a wide range of silicate minerals (e.g., see Refs. 3–13). Nevertheless, those available diffusion data are still considerably less abundant than what is required in geochemical applications. This is mainly due to the substantial difficulties of performing diffusion experiments at high-pressure and high-temperature conditions in a single crystal or polycrystalline specimens.

In the absence of direct experimental determination, an empirical method of predicting diffusion coefficients without having to measure them would be of great value. Voltaggio¹⁴ presented a method of estimating diffusion coefficients by the compensation law, which relies on an observed correlation between the natural logarithm of the pre-exponential factor ($\ln D_0$) and the activation energy (E) in the Arrhenius diffusion relation $D = D_0 \exp(-E/k_B T)$. The approach makes use of a compensation relation for both the species and the minerals of interest, which requires considerable experimental data. In addition, diffusion compensation rests on the assumption that the diffusion mechanism is the same for all the minerals and species being considered.¹⁵ On the other hand, theoretical prediction of the thermodynamic and diffusion properties in diverse minerals has been approached by means of atomistic or molecular dynamics simulation methods.^{16,17} By calculating the free energy of formation and modeling the motion of both Mg and O vacancies in MgO , lattice dynamics simulation technique has been employed by Vocadlo *et*

*al.*¹⁶ to investigate the diffusion of Mg and O in a wide range of temperature. Likewise, the above-mentioned theoretical methods for predicting diffusion properties in minerals have already shown some promise but this example involves a simple oxide mineral and the methodology used does not allow the calculation of absolute diffusion rates. To our knowledge, the application of such theoretical models to complex minerals is not yet practical.

Almost 30 years ago, a theoretical model (usually called the $cB\Omega$ model) has been proposed by Varotsos and Alexopoulos,^{18–22} which results from thermodynamic considerations that lead to a connection between defect parameters and the bulk properties of solids. Significant success in the $cB\Omega$ model has been found to calculate defect parameters (i.e., formation, migration, and activation processes), and to predict the self-diffusion coefficients for metals,^{19,20} rare gas solids,^{21,22} alkali and silver halides,^{22–25} fluorides^{26,27} at any temperature and pressure where all the necessary elastic and expansivity data are available. Recently, the validity of the $cB\Omega$ model was further verified by the calculation of point defect parameters in diamond.²⁸ However, this potentially valuable $cB\Omega$ model has scarcely been applied to predict elemental diffusion coefficients in geologic materials so far (such as silicate minerals). Therefore, the present study is the first attempt of the application of the $cB\Omega$ model in a geochemical problem. Our intention is also to test whether oxygen self-diffusion coefficients in a variety of minerals can be independently reproduced on the basis of theoretical consequences of the $cB\Omega$ model over a range of geologically relevant temperatures.

II. THEORETICAL BACKGROUND

A. The $cB\Omega$ model

The thermodynamic model, so-called the $cB\Omega$ model, was proposed by Varotsos and Alexopoulos,^{18–22} in which

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TABLE I. Parameters used in the calculation of anhydrous oxygen self-diffusivities in minerals as predicted from the $cB\Omega$ model.

Mineral	f	a (Å)	$B(T)$		$V(T)$		$c^{\text{act } c}$
			B_0 (GPa)	$(\partial B / \partial T)_P$ (GPa K ⁻¹)	V_0 (Å ³)	α_0 ($\times 10^{-5}$ K ⁻¹)	
Olivine ^a	0.745 ^b	4.7656 ^c	128	-0.0223	292.13 ^c	2.73 ^c	0.6814
Spinel ^a	1	8.0832	207.9	-0.0338	528.14	2.68	0.4853
Zircon ^a	1	6.6042	227	-0.021	260.80	1.23	0.3106
Perovskite ^a	1	4.7754	263.86 ^d	-0.0272 ^d	162.35	2.53 ^d	0.3606

^aReference 30.^bReference 31.^cReference 32.^dReference 33.^e c^{act} represents the calculated value of c^{act} from the characteristic temperature $T_c=2358$ K using Eq. (4).

the defect Gibbs free energy g^{act} is interconnected with the bulk properties of the solid through the relation:

$$g^{\text{act}} = c^{\text{act}} B \Omega, \quad (1)$$

where B is the isothermal bulk modulus, Ω is the mean volume per atom, and c^{act} is dimensionless factor which considered to be independent of temperature and pressure to the first approximation. The self-diffusion or tracer-diffusion coefficients for a single diffusion mechanism are described by the Arrhenius equation:^{22,29}

$$D = f a^2 \nu \exp[-g^{\text{act}}/(k_B T)], \quad (2)$$

where f is a correlation factor depending on the diffusion mechanism and structure, a stands for the lattice constant (which should be actually the jump distance), ν is the jump frequency (usually taken equal to the Debye frequency ν_D),²² k_B is Boltzmann's constant, and g^{act} denotes the Gibbs free energy for activation process. From Eq. (1), we rewrite Eq. (2) as:

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

in which f , a , ν are approximately considered as constants, B and Ω are experimentally available elastic data, so c^{act} is only unknown constant in Eq. (3). As mentioned by Varotsos and Alexopoulos,^{20,22} given a single measurement of diffusion D_1 at temperature T_1 , the value of c^{act} can be calculated by following equation:

$$c^{\text{act}} = \frac{k_B T_1}{B_1 \Omega_1} \ln \frac{f a_1^2 \nu_1}{D_1}, \quad (4)$$

where a_1 , ν_1 , B_1 , and Ω_1 are corresponding values at T_1 . Hence, Eq. (3) permits the calculation of self-diffusion coefficients D at any temperature (for $P=\text{constant}$) provided that the appropriate values of f , a , ν , B , and Ω are available at the corresponding temperature (see Table I).

Before we calculate the self-diffusion coefficients by Eq. (3), several points should be noted: (1) The value of c^{act} in $cB\Omega$ model is considered to be a constant independent of temperature and pressure, which may result in an uncertainty of around 3% mainly due to error in the determination of the isothermal bulk modulus B .^{22,25,34} (2) Most of previous studies on rare gas solids, metals, alkali and silver halides, fluorides with the cubic crystal structure (see Refs. 19–27) imply

the same lattice constant a in different directions. However, in this study, the lattice constants in various minerals are all chosen to be the values along the a -axis at ambient condition regardless of crystallographic direction as we focus on estimation of isotropic oxygen diffusion in minerals, the anisotropic diffusion are much complicated and not the topic in present study. (3) B is expressed by a linear approximation:^{22,30}

$$B(T) = B_0 + (\partial B / \partial T)_P (T - T_0), \quad (5)$$

where B_0 is the value at ambient conditions $T_0=300$ K and $(\partial B / \partial T)_P$ is the temperature derivative of the bulk modulus which is assumed to be constant below the melting temperature. The experimental data of B for different minerals are usually obtained at fairly limited range of temperatures, we actually neglect the possible nonlinear change at lower temperature or higher temperature (near the melting point) in Eq. (5). Meanwhile, the pressure dependence of the isothermal bulk modulus has not been considered here because the pressure derivative of the bulk modulus is usually not available at high temperatures for many minerals. (4) The mean volume per atom Ω is calculated by $\Omega(T) = V(T) / (nZ)$, where $V(T)$ is the unit cell volume (in Å³) at temperature T , Z is the number of formula units per cell and n is the total number of atoms in the formula unit. $V(T) = V_0 [1 + \alpha_0 (T - T_0)]$, in which V_0 is the volume of the unit cell at room temperature and α_0 the thermal expansion coefficient. As a result, the mean volume per atom Ω can be written as:

$$\Omega(T) = V_0 [1 + \alpha_0 (T - T_0)] / (nZ). \quad (6)$$

A summary of the $cB\Omega$ model parameters is given in Table I.

Now the problem is to find a value of diffusion coefficient, such as D_1 at T_1 , to determinate c^{act} , which will be solved next through the compensation effect.

B. The compensation effect

For diffusion coefficient $D = D_0 \exp(-E/k_B T)$, the relation of the natural logarithm of the pre-exponential factor $\ln D_0$ (D_0 in m²/s) and activation energy E (in kJ/mol) takes an approximate linear form:

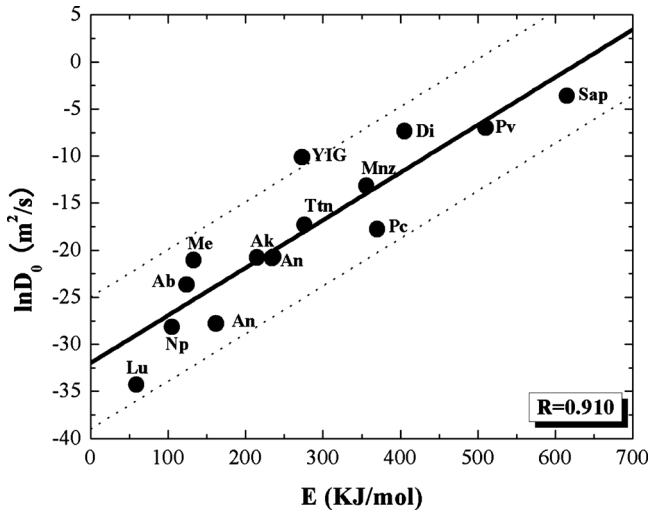


FIG. 1. Compensation plots of pre-exponential ($\ln D_0$) vs activation energy (E) for oxygen self-diffusion under anhydrous conditions, modified after Zheng and Fu (Ref. 38). Solid line denotes the best fit to the experimental data [Eq. (8)] and dotted lines are used to bracket the variation range in the intercept of the compensation line. Abbreviations: Ab—albite (Ref. 36); Ak—akermanite (Ref. 39); An—anorthite (Refs. 9 and 40); Di—diopside (Ref. 6); Lu—leucite (Ref. 41); Me—melilite (Ref. 42); Mnz—monazite (Ref. 12); Np—nepheline (Ref. 6); Pc—periclase (Ref. 43); Pv—perovskite (Ref. 13); Sap—sapphire (Ref. 44); Ttn—titanite (Ref. 45); YIG—yttrium iron garnet (Ref. 46).

$$\ln D_0 = \alpha + \beta E, \quad (7)$$

where α and β are constants. Equation (7) is generally referred to the compensation effect which was observed in many silicate glasses and minerals.^{15,35–37} Thus the diffusion can be written as

$$\ln D = \ln D_0 - E/kT = \alpha + (\beta - 1/kT)E.$$

Suppose we write:

$$\beta - 1/kT_c = 0,$$

then

$$T_c = (\beta k)^{-1},$$

where T_c is called “characteristic temperature.” This implies that the diffusion tends to converge to a constant $D_c = \exp(\alpha)$ at the characteristic temperature T_c .

Zheng and Fu³⁸ illustrated a common compensation trend for oxygen diffusion in minerals under both anhydrous and hydrothermal conditions. On this basis, we revisit the available experimental data resulting in a better compensation trend for oxygen diffusion in minerals under anhydrous conditions (see Fig. 1). The compensation relation is:

$$\ln D_0 = 0.051(\pm 0.006)E - 31.99(\pm 1.98). \quad (8)$$

As above, it implies that the oxygen diffusion converges to a constant $D_c = 1.28_{-1.10}^{+7.99} \times 10^{-14}$ m²/s at $T_c = 2358_{-248}^{+315}$ K in all minerals. Therefore, the value of c^{act} can be reasonably estimated if set $T_1 = T_c$ and $D_1 = D_c$ in Eq. (4), respectively.

III. RESULTS AND DISCUSSION

As above mentioned, let us now determine the value of c^{act} from the characteristic temperature ($T_1 = T_c = 2358$ K).

For $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ olivine, at this temperature the elastic and expansivity data were calculated to be $B = 82.1$ GPa and $\Omega = 11.02 \times 10^{-24}$ cm³ by extrapolation these parameters (given in Table I) according to Eqs. (5) and (6), respectively. The correlation factor $f = 0.745$ (Ref. 31) and the Debye frequency ν_D is $\sim 1.27 \times 10^{13}$ s⁻¹ (see Ref. 30). By inserting these values and $D_1 = D_c = 1.28 \times 10^{-14}$ m²/s into Eq. (4) for $T_1 = 2358$ K, we find $c^{\text{act}} = 0.6814$. The same approach is also applied for other minerals (MgSiO₃ perovskite, spinel, and zircon), hence the value of c^{act} can be determined (see the last column of Table I). Since c^{act} is now known, the diffusion coefficient D can be calculated by means of Eq. (3) at various temperatures (pressure remains constant) where all the necessary elastic and expansivity data are available.

In order to check the validity of the $cB\Omega$ model in this study, comparison can be made between the predicted diffusivities and the existing experimental data for various minerals (Fig. 2). In particular, it should be noted that the compensation law is the foundation of the $cB\Omega$ model. The experimental data for oxygen self-diffusion in olivine, spinel, and zircon are not included in the compensation effect (Fig. 1). The main purpose for this is to test whether the $cB\Omega$ model can independently provide a reasonable estimate of oxygen diffusivity in these minerals. Nevertheless, inclusion of the experimental data for olivine, spinel, and zircon does not considerably improve the compensation trend in Fig. 1.

In Fig. 2, we compare the “independently” theoretical results of the $cB\Omega$ model with previous experimental measurements for anhydrous oxygen self-diffusion in olivine, spinel, and zircon. Here, the meaning of independently has already been pointed out above, although these minerals are not included in the compensation law but we shall assume all of these minerals satisfy the common compensation trend. In the present study, the theoretical values of oxygen diffusion coefficients in olivine derived from the $cB\Omega$ model are comparable with the experimental measurements^{4,11,47,48} at higher temperature in Fig. 2(a). However, extrapolating both the calculated and experimental data to lower temperature, it is clear that our predicted diffusivity yields several orders of magnitude lower than those of experimental measurements. In fact, Ryerson *et al.*⁷ found a dependence of oxygen diffusion on oxygen fugacity for olivine. Some factors such as oxygen fugacity, water fugacity and diffusion mechanism, are ignored in the current $cB\Omega$ model. Therefore, the experimental activation energies for olivine are much smaller than that stemmed from the $cB\Omega$ model. For oxygen self-diffusion in MgSiO₃ perovskite shown in Fig. 2(b), comparison of the theoretically calculated and experimental diffusivity D values¹³ reveals that the $cB\Omega$ model is quite successful in predicting oxygen diffusivity where the uncertainty is within one order of magnitude. We also noted that the experimental measurement was conducted at 25 GPa, whereas data on elasticity properties of perovskite at this pressure are unavailable in this case. Therefore, the effect of pressure on diffusivity was not considered, this goal remains for further work. As seen in Fig. 2(c), the independently theoretical predictions of anhydrous oxygen self-diffusion in spinel from the $cB\Omega$ model agree reasonably well with the experimental determinations.^{3,9,49} Furthermore, the independent estimates

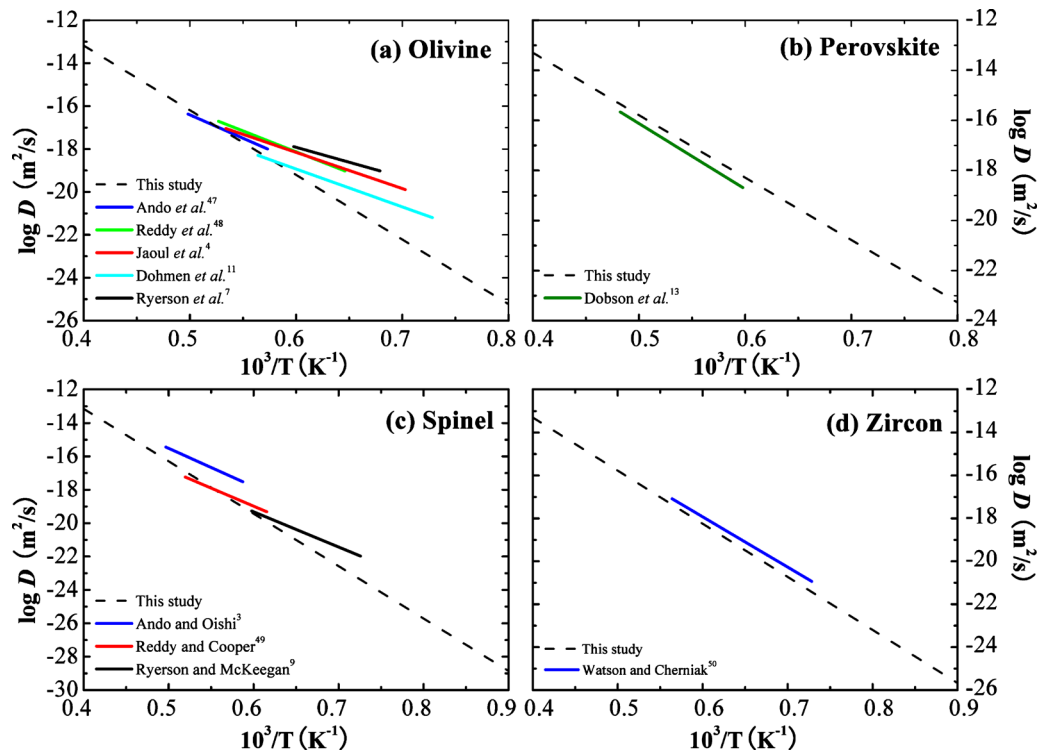


FIG. 2. (Color online) Comparison of the theoretical results derived from the $cB\Omega$ model with the experimental data for oxygen self-diffusion in minerals: (a) olivine, (b) perovskite, (c) spinel, and (d) zircon.

of oxygen diffusivity (3.98×10^{-4} m²/s and 474 kJ/mol) in zircon from the $cB\Omega$ model are identical within error to those of Watson and Cherniak,⁵⁰ with $D_0 = 1.33 \times 10^{-4}$ m²/s and $E = 448.3$ kJ/mol under anhydrous conditions [Fig. 2(d)].

By comparison of our independently theoretical predictions from the $cB\Omega$ model with experimental data (Fig. 2), we find that the $cB\Omega$ model is valid in calculating oxygen self-diffusion for all these cases presented here. However, the key part of success in the $cB\Omega$ model lies on the accurately calculated model parameters, including a , ν , c , B , and Ω . This is also why, although some minerals (e.g., anorthite, monazite, melilite, titanite, etc.) are included in the compensation effect (Fig. 1), the $cB\Omega$ model cannot be checked for these minerals because the necessary elastic data are not available. In addition, the present study is mainly focused on the investigation of the validity of the $cB\Omega$ model in temperature dependence of oxygen diffusivity. As indicated above, the pressure dependence of diffusivity in the $cB\Omega$ model remains for future study, the main reasons are still because the lack of the necessary elastic data for most minerals.

We now turn to origin of the uncertainties. In the framework of $cB\Omega$ model, the uncertainties in calculating self-diffusion coefficients of oxygen under the anhydrous conditions based on Eq. (3) or Eq. (4) are mainly from several sources: (1) assumption of linear compensation effects; (2) is c^{act} in the $cB\Omega$ model constant? (3) uncertainties arising in the calculation of the elastic and expansivity data of minerals.

First, the compensation law is an empirical correlation between $\log D_0$ and E observed for many thermally activated

processes and, in particular, atomic diffusion.^{35,51} It is known that there are two types of compensation effects. One is referred to the same diffusing species in different minerals,^{14,37,38,52,53} the other is for different diffusants in the same mineral.^{14,15,35,36} Although the compensation effect is primarily an empirical of observation, several theories have been tried to propose physical explanation for it.^{37,54,55} Unfortunately, the origin of compensation effect is still not well understood. Lasaga⁵⁶ has noted that the application of the compensation law in silicates and other complex phases must be modified to account for the variations in mineral structure and the types of defects. Nevertheless, Zheng and Fu³⁸ claimed if the common compensation trend is assumed to hold for all of the minerals, a similar mechanism of oxygen diffusion may be operative in these diverse minerals regardless of the diffusion medium. Moreover, inspection of all the available experimental data does not allow the establishment of separate compensation lines for oxygen diffusion in different mineral groups.

Secondly, to elucidate whether c^{act} in the $cB\Omega$ model remain constant in Eq. (4), we rewrite Eq. (4) in the form: $c^{\text{act}} = AT_c \ln(B/D_c)$, where $A = k_B/B_1\Omega_1$ and $B = fa_1^2\nu_1$ are constants. Now the following three steps are considered: (1) if D_c is unchanging, the relative uncertainty of c^{act} because of the change in T_c can be directly calculated by: $|(dc^{\text{act}}/c^{\text{act}})| = |(dT_c/T_c)|$. In this case, the characteristic temperature $T_c = 2358^{+315}_{-248}$ K and $D_c = 1.28^{+7.99}_{-1.10} \times 10^{-14}$ m²/s are based on the compensation effect [Eq. (8)]. It is obvious that the relative uncertainty of c^{act} is not more than 10% when T_c has a change of 10%. (2) If assuming D_c has a change (labeled as $D_c^* = nD_c$) while T_c remains constant, then the relative uncer-

tainty of c^{act} because of the change in D_c can be expressed by: $|((c^{\text{act}})^* - c^{\text{act}}/c^{\text{act}})| = |(\ln n / \ln(B/D_c))|$, where $(c^{\text{act}})^*$ is the value of c^{act} when $D_c = D_c^*$. Usually, $B(=fa_1^2\nu_1)$ is approximately 10^{-6} and $D_c \sim 10^{-14}$, thus $1/\ln(B/D_c)$ is $\sim(1/20)$. Here, we show a calculated example to demonstrate the relative uncertainty of c^{act} derived from the change in D_c . For example, if let $D_c^* = 2.4 \times 10^{-14} \text{ m}^2/\text{s} \approx 2D_c$, the relative uncertainty of c^{act} is calculated to be $1/20 \ln 2$ ($\approx 3\%$). (3) If both T_c and D_c remain constant in Eq. (4), the relative uncertainty of c^{act} because of the change in elastic data ($B_1\Omega_1$) can also be calculated by $|dc^{\text{act}}/c^{\text{act}}| = |dT_c/T_c|$. Therefore, the relative uncertainty of c^{act} is also less than 3% when $B_1\Omega_1$ -value has a change of 3%. In fact, the central viewpoint, whether the value of c^{act} in the $cB\Omega$ model remains constant, has been extensively investigated for self-diffusion data in rare gas solids, metals, alkali, and silver halides, fluorides (see Refs. 19–27). More recently, the same problem has been once more discussed by Varotsos²⁵ in fcc, bcc, and tetragonal metals. All of previous studies indicate that the c^{act} value has an uncertainty of not more than 3% mainly due to the experimental error in the determination of the elastic and expansivity data of solids. Therefore, to a first approximation, c^{act} can be reasonably considered to a constant which is independent of the temperature and pressure.

Finally, it is worthwhile to consider the errors associated with the experimental bulk properties of minerals. In general, compressibility and expansivity of minerals are determined in quite limited temperature and pressure ranges, and thus extrapolation of the available bulk properties to the desired temperature in the term of Eqs. (5) and (6) is needed. Varotsos and Alexopoulos²² have already pointed out that Eq. (5) is valid between the room temperature and below the melting temperature, whereas the isothermal bulk modulus B decreases with temperature in a nonlinear way at very low and near the melting point temperatures. This means that linear extrapolation to higher or lower temperature regions may be not appropriate for the isothermal bulk modulus B in this study. Compression and thermal expansion of the unit cell of the minerals would largely affect the mean volume per atom Ω under high temperatures and high pressures, because any mineral has a large or nonlinear change in volume with increasing temperatures. Thus, it is very difficult to evaluate whether the mean volume per atom Ω really changes with the temperatures and pressures.

The only up to date application of $cB\Omega$ model to problems of geophysical and geochemical interest and in particular to rock-forming minerals, as already mentioned in Refs. 25 and 27, is the following: The $cB\Omega$ model was found to be consistent with the parameters that describe the time-dependent polarization⁵⁷ arising when changing the rate of uniaxial stress in ionic crystals or by the indenter penetration into its surface (before the material failure). Since the same may happen at the ionic inclusions in the rock-forming minerals in the earth when the stress gradually increases in the focal region before an earthquake,⁵⁷ this might explain why transient electric signals, termed seismic electric signals, are observed before earthquakes.^{58,59} Such a possibility, in view of its practical importance, should be further investigated.

IV. SUMMARY AND OUTLOOK

On the basis of the universal compensation effect, the most key constant c^{act} in the $cB\Omega$ model was determined by a new approach proposed in this case. Examples have been presented here for olivine, spinel, zircon, and MgSiO_3 perovskite. Without using any adjustable parameter, the $cB\Omega$ model successfully reproduces the self-diffusion coefficients of oxygen in all these minerals. A comparison of the theoretically calculated diffusivity with the experimental data, suggests that the $cB\Omega$ model is valid for various silicate and oxide minerals.

Although we have demonstrated in this work that it is possible to obtain a reasonable estimation of diffusion coefficients over the wide range of temperatures for various rock-forming minerals, many assumptions and simplifications have been made in the $cB\Omega$ model. However, accurate prediction of element diffusivity from the $cB\Omega$ model remains challenging, and a number of issues need to be explored in more detail. Here we will list some of the major limitations that are critical to make further progress in employing the $cB\Omega$ model to geoscience materials:

- (1) The effects of pressure and oxygen fugacity on the diffusion were ignored in this case, in fact experimental measurements have indicated that pressure and oxygen fugacity may have a considerable influence on the diffusivity, especially for high-pressure phase and for Fe-bearing minerals.
- (2) It should be mentioned that this model has been applied to different kinds of diffusion, including self-diffusion and heterodiffusion in several monocrystalline materials.^{22,60} The point that seems to be still open is whether the $cB\Omega$ model can be applicable to complicated-structure minerals under extreme conditions.
- (3) In this case, the diffusion coefficients were calculated from the $cB\Omega$ model only under anhydrous conditions, can it be used to water-saturated conditions? The role of water on diffusion processes in mantle minerals must be clarified.
- (4) We select a -axis for diffusion calculation in this case and do not consider the anisotropic diffusion for complicated-structure minerals regardless of the different crystallographic orientations. However, the calculation using one crystallographic axis should be modified for high anisotropic mineral in future work.

In view of above, solving these difficult problems is a key to improve upon the agreement between the calculation-derived models and those determined through experimental measurements. It is hoped that the approach proposed here will be of considerable interest in obtaining reliable estimates of diffusion coefficients in a variety of mantle minerals.

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