

Equilibrium mass-dependent fractionation relationships for triple oxygen isotopes

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Abstract

With a growing interest in small ^{17}O -anomaly, there is a pressing need for the precise ratio, $\ln^{17}\alpha/\ln^{18}\alpha$, for a particular mass-dependent fractionation process (MDFP) (e.g., for an equilibrium isotope exchange reaction). This ratio (also denoted as “ θ ”) can be determined experimentally, however, such efforts suffer from the demand of well-defined process or a set of processes in addition to high precision analytical capabilities. Here, we present a theoretical approach from which high-precision ratios for MDFPs can be obtained. This approach will complement and serve as a benchmark for experimental studies. We use oxygen isotope exchanges in equilibrium processes as an example.

We propose that the ratio at equilibrium, $\theta^E \equiv \ln^{17}\alpha/\ln^{18}\alpha$, can be calculated through the equation below:

$$\theta_{a-b}^E = \kappa_a + (\kappa_a - \kappa_b) \frac{\ln^{18}\beta_b}{\ln^{18}\alpha_{a-b}}$$

where $^{18}\beta_b$ is the fractionation factor between a compound “b” and the mono-atomic ideal reference material “O”, $^{18}\alpha_{a-b}$ is the fractionation factor between a and b and it equals to $^{18}\beta_a/^{18}\beta_b$ and κ is a new concept defined in this study as $\kappa \equiv \ln^{17}\beta/\ln^{18}\beta$. The relationship between θ and κ is similar to that between α and β . The advantages of using κ include the convenience in documenting a large number of θ values for MDFPs and in estimating any θ values using a small data set due to the fact that κ values are similar among O-bearing compounds with similar chemical groups.

Frequency scaling factor, anharmonic corrections and clumped isotope effects are found insignificant to the κ value calculation. However, the employment of the rule of geometric mean (RGM) can significantly affect the κ value. There are only small differences in κ values among carbonates and the structural effect is smaller than that of chemical compositions. We provide κ values for most O-bearing compounds, and we argue that κ values for Mg-bearing and S-bearing compounds should be close to their high temperature limitation (i.e., 0.5210 for Mg and 0.5159 for S). We also provide θ values for $\text{CO}_2(\text{g})$ –water, quartz–water and calcite–water oxygen isotope exchange reactions at temperature from 0 to 100 °C.

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1. INTRODUCTION

The sole mass-dependent fractionation law of oxygen isotopes, predicted by an approximate solution of the Bigeleisen–Mayer equation (Bigeleisen and Mayer, 1947; Urey, 1947), had resulted in a lack of interest in other rare

isotopes of the same element for a long time (e.g., Clayton, 2008). Clayton et al. (1973) first discovered deviations of ^{17}O abundance from the terrestrial fractionation line (TFL) in meteorites. The slope value of 0.52 has been commonly used for TFL to depict the $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$ space. Later, Thiemens and Heidenreich (1983) observed large mass-independent fractionations (MIF) of ozone caused by electrical discharge in laboratory. The abnormal MIF signal of ozone in the stratosphere can be transferred to carbon dioxide and oxygen (Wen and Thiemens, 1993; Bender et al., 1994; Yung et al., 1997), and then may be conserved

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in terrestrial samples which can be used to study biosphere productivity, climate changes and ancient atmosphere composition, etc. (e.g., Luz et al., 1999; Bao et al., 2008, 2010).

Even within the realm of mass-dependent fractionation, small deviations have been recognized both theoretically and experimentally depending on what exact slope value is used (Young et al., 2002; Luz and Barkan, 2005). Often small ^{17}O excesses or depletions can provide new insights on reaction pathways that have climate and environmental implications (e.g., Angert et al., 2003, 2004; Luz and Barkan, 2005, 2010; Landais et al., 2006, 2007, 2008, 2010; Risi et al., 2010; Uemura et al., 2010).

A precise $(\ln^{17}\alpha/\ln^{18}\alpha)$ ratio, so-called θ value, is critical to the utility of small ^{17}O variation signals. Boaz Luz's group has set examples on how this ratio can be determined precisely by experiments (e.g., Luz et al., 1999; Angert et al., 2003; Barkan and Luz, 2005, 2007; Luz and Barkan, 2005; Landais et al., 2006). Hofmann and Pack (2010) have also determined this ratio for $\text{CO}_2\text{-CeO}_2$ system experimentally. Often the experiments require well-defined process or a set of processes in addition to high-precision analytical capabilities. While more experimental calibrations are needed, a sound theoretical framework for predicting process-specific θ values can complement and serve as a benchmark for experimental studies. The lack of θ values has become a limiting factor in further expansion of the small ^{17}O deviation study in many other systems.

In this study, we introduce a theoretical method to determine θ values for MDFFPs. We focus on oxygen isotopes in equilibrium exchange processes, although similar approach can be applied to other isotope systems (e.g., Mg and S). We propose a new concept κ , the ratio of an equilibrium isotope exchange process between a specific O-bearing compound and the ideal gaseous mono-atomic material "O". This new method provides equilibrium θ values with the precision to the third decimal number (i.e., 0.5xx) and should satisfy most of the studies on small ^{17}O deviation.

2. THEORY AND METHODS

2.1. Theoretical methods of equilibrium θ values

In a triple oxygen isotope system, when it is in equilibrium, the θ value is equal to (e.g., Mook, 2000; Angert et al., 2003; Luz and Barkan, 2005):

$$\theta_{a-b}^E = \frac{\ln^{17}\alpha_{a-b}}{\ln^{18}\alpha_{a-b}} \quad (1)$$

where θ_{a-b}^E represents the ratio for an equilibrium isotope exchange reaction between compounds a and b . θ is different from the concept " λ " used by previous researchers (e.g., Meijer and Li, 1998; Rumble et al., 2007; Luz and Barkan, 2010). As suggested by most of people, λ represents a statistical $\delta^{17}\text{O}-\delta^{18}\text{O}$ result of one compound from different sources, which includes reservoir effect or kinetic effect. While θ is not a slope but only two points in $\delta^{17}\text{O}-\delta^{18}\text{O}$ space to describe triple oxygen isotopes relationship between two compounds in a specific process.

The equilibrium isotope fractionation factor α can be calculated from

$$\alpha_{a-b} = \beta_a/\beta_b \quad (2)$$

where β defined in Richet et al. (1977) is an isotopic fractionation between a compound and its reference as an ideal gaseous mono-atomic material, for example, a dissociated and non-interacting atom O or C, etc. (e.g., Schauble, 2004). If we ignore rare isotopologues (i.e., those with multiple heavy isotopes), the β value will be represented as (use $^{18}\beta$ of any O-bearing compound "XO $_n$ " as an example):

$$\begin{aligned} {}^{18}\beta_{\text{XO}_n} &= \frac{({}^{18}\text{O}/{}^{16}\text{O})_{\text{XO}_n}}{({}^{18}\text{O}/{}^{16}\text{O})_{\text{O}}} \approx \frac{[\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O}]/(n \cdot [\text{X}^{16}\text{O}_n])}{[{}^{18}\text{O}]/[{}^{16}\text{O}]} \\ &= \frac{1}{n} f(\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O}) \end{aligned} \quad (3)$$

where $f(\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O})$ is the partition function ratio of $\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O}$ to X^{16}O_n , which can be obtained at harmonic approximation level (Bigeleisen and Mayer, 1947; Urey, 1947):

$$\left(\frac{s^*}{s}\right) f(\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O}) = \prod_i^l \frac{u_i^* e^{-u_i^*/2}}{u_i e^{-u_i/2}} \frac{1 - e^{-u_i}}{1 - e^{-u_i^*}} \quad (4)$$

where s is symmetry number, l is the number of freedom for vibration mode ($l = 3N - 5$ for linear molecule and $l = 3N - 6$ for non-linear molecule, N is the number of atoms in the molecule), u_i is equal to $hc\omega_i/k_bT$, h is the Planck constant, c is the speed of light, ω_i is the i th normal vibration mode, k_b is Boltzmann constant and T is temperature in Kelvin, the terms with star (*) refer to the isotopologues containing one heavy isotope (i.e., $\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O}$). The left side of Eq. (4) is often called reduced partition function ratio (RPFR) of $\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O}$ to X^{16}O_n .

When u is small (e.g., at high temperatures) and at first-order approximation, Eq. (4) can be approximated to a simple form (Bigeleisen and Mayer, 1947):

$$\left(\frac{s^*}{s}\right) f(\text{X}^{16}\text{O}_{n-1}{}^{18}\text{O}) = 1 + \sum_i^l \frac{\Delta(u_i^2)}{24} \quad (5)$$

In this case, θ_{a-b}^E is equal to $(1/^{16}m - 1/^{17}m)/(1/^{16}m - 1/^{18}m) = 0.5305$ for all equilibrium oxygen isotope exchange reactions (e.g., Matsuhisa et al., 1978; Criss, 1999; Weston, 1999; Young et al., 2002). However, this approximation, leading to the sole mass-dependent law, is no longer adequate for the studies of small ^{17}O deviations.

Note that using theoretical methods beyond harmonic approximations, β value (or RPFR) can be calculated more precisely. There are also a series of higher-order corrections can be applied to the Bigeleisen–Mayer equation (i.e., Eq. (4)). Readers are referred to Richet et al. (1977) and Liu et al. (2010) for the detailed formalism of those higher-order corrections. Detailed discussion about the effect of anharmonic corrections on equilibrium θ value calculation will be shown in Section 4.2.

2.2. The concept of κ

If θ value, which is related to two O-bearing compounds, is used directly, it will need a very large data

set to document triple oxygen isotopes relationships in nature and more efforts to calculate $\ln\alpha$ precisely due to the high order corrections to Bigeleisen–Mayer equation (i.e., Eq. (4), Richet et al., 1977; Liu et al., 2010). We found that κ values of compounds with similar chemical groups are very similar, providing an easy way to estimate κ values of a large number of compounds, and scaling factor effects and anharmonic corrections are insignificant to κ calculations (see discussions below), if we define a new concept κ as

$$\kappa = \frac{\ln^{17}\beta}{\ln^{18}\beta} \quad (6)$$

which is the equilibrium θ value of an isotope exchange reaction between any O-bearing compound and the ideal gaseous mono-atomic reference material “O”.

From Eq. (2), $\ln\alpha_{a-b} = \ln\beta_a - \ln\beta_b$. From Eq. (6), $\ln^{17}\beta = \kappa \times \ln^{18}\beta$. Substituting these relationships into Eq. (1), we obtain:

$$\begin{aligned} \theta_{a-b}^E &= \frac{\kappa_a \ln^{18}\beta_a - \kappa_b \ln^{18}\beta_b}{\ln^{18}\beta_a - \ln^{18}\beta_b} \\ &= \frac{\kappa_a (\ln^{18}\beta_a - \ln^{18}\beta_b) + (\kappa_a - \kappa_b) \ln^{18}\beta_b}{\ln^{18}\beta_a - \ln^{18}\beta_b} \\ &= \kappa_a + (\kappa_a - \kappa_b) \frac{\ln^{18}\beta_b}{\ln^{18}\beta_a} \end{aligned} \quad (7)$$

where $^{18}\alpha_{a-b}$ is the commonly used $^{18}\text{O}/^{16}\text{O}$ fractionation factor between phase a and phase b and $\ln^{18}\alpha_{a-b} \equiv \ln^{18}\beta_a - \ln^{18}\beta_b$. Eq. (7) suggests that θ_{a-b}^E can be obtained from κ and $^{18}\beta$ values of two O-bearing compounds.

2.3. Quantum chemistry calculation

It has become a routine practice to obtain β and α values through quantum chemistry calculations (e.g., Driesner et al., 2000; Schauble et al., 2001; Liu and Tossell, 2005; Schauble et al., 2006; Méheut et al., 2007; Rustad and Zarzycki, 2008; Li et al., 2009; Rustad and Yin, 2009; Li and Liu, 2010, 2011; Liu et al., 2010; Zeebe, 2010; Rustad et al., 2010a,b; Schauble, 2011). At harmonic approximation level, the Bigeleisen–Mayer equation is often used and pure harmonic frequencies of interested isotopologues are the only unknown variables. Both the Hartree–Fork (HF) and the Becke three-parameter Lee–Yang–Parr (B3LYP) methods (Lee et al., 1988; Becke, 1993) are used in this study to obtain harmonic frequencies. The triple-zeta with diffusion and polarization functions basis set 6-311 + G(2df,p) is used according to the recommendation by Andersson and Uvdal (2005) for frequency calculation. Gaussian03 software package (Frisch et al., 2004) is used for all calculations in this study. Frequency scaling factors are often used in the community when theoretical levels are not sufficiently high (e.g., Scott and Radom, 1996; Irikura et al., 2009). We use 0.9268 for HF/6-311 + G(2df,p) and 0.9889 for B3LYP/6-311 + G(2df,p) as recommended by Merrick et al. (2007) (i.e., the scaling factor for zero point energy, ZPE). In fact, it will be shown in Section 4.1 that the effect of scaling factors for the equilibrium κ value calculation is negligible.

2.4. Einstein–Debye model

The β values for carbonates are calculated here using the Einstein–Debye model, which has been used for isotope fractionation calculation since 1950s (e.g., McCrea, 1950; Bottinga, 1968; O’Neil et al., 1969; Kawabe, 1978; Chacko et al., 1991; Deines, 2004; Chacko and Deines, 2008). Readers are referred to Deines (2004) for detailed description of the method. In brief, the vibrations of minerals are divided into two parts (1) internal vibration modes, which are described by discrete Einstein oscillators and (2) lattice vibration modes, which are modeled by Debye spectrum approximation (e.g., O’Neil et al., 1969). However, the vibration frequency is not discrete and the Debye model is inadequate to obtain thermodynamic properties of solids (e.g., Kieffer, 1979). Furthermore, this model could only carry out calculations under the rule of geometric mean (RGM), which is an approximation and is questionable for the κ calculation (see Section 4.3 for details). Therefore, we will not use Einstein–Debye model to produce absolute κ values but rather differences or trends of κ values between a series of structurally similar minerals (i.e., a group of carbonates) by assuming they are still observable when with systematic errors.

3. RESULTS

Eq. (7) shows that θ values of equilibrium processes can be calculated using κ and $^{18}\beta$ values. $^{18}\beta$ can be obtained from either previous experimental data or theoretical calculations. Therefore, we will focus on discussing κ values hereafter.

Fig. 1 displays the κ values of some representative gaseous O-bearing molecules using different theoretical methods (i.e., HF vs. B3LYP). Table 1 shows some of those κ results at B3LYP/6-311 + G(2df,p) level as a function of temperature. Our results of water molecule are close to the results of Matsuhisa et al. (1978). Our results of CO_2 , however, are larger than theirs. Matsuhisa et al. (1978) employed the rule of geometric mean approximation, which is improper for the κ calculation (see Section 4.3). The results of Table 1 are plotted in Fig. 1A ($\text{CO}_3^{2-}(\text{g})$, SiO_2 and Si–O–Al are not included). From Fig. 1A, we find all κ values are quite close to each other except for H_2O molecule. Fig. 1B–D shows the differences between different theoretical methods or scaled/un-scaled treatments. Here, “scaled” means using frequency scaling factor, “un-scaled” means not using frequency scaling factor. The differences between scaled and un-scaled results of the same theoretical level are found to be extremely small (on the order of 10^{-5}) (Fig. 1B). However, the differences between theoretical methods are larger (see Fig. 1C and Fig. 1D, on the order of 10^{-4}). Because the harmonic frequencies of B3LYP methods are generally considered more accurate than those of HF methods (see the Supplemental file), we only used the B3LYP frequencies in later calculations.

For the calculations of κ values of silicates, we used a series of cluster models to simulate silicate structures (see Fig. 2 and the Supplemental file). The κ values of quartz at different sizes of cluster models are very similar, the

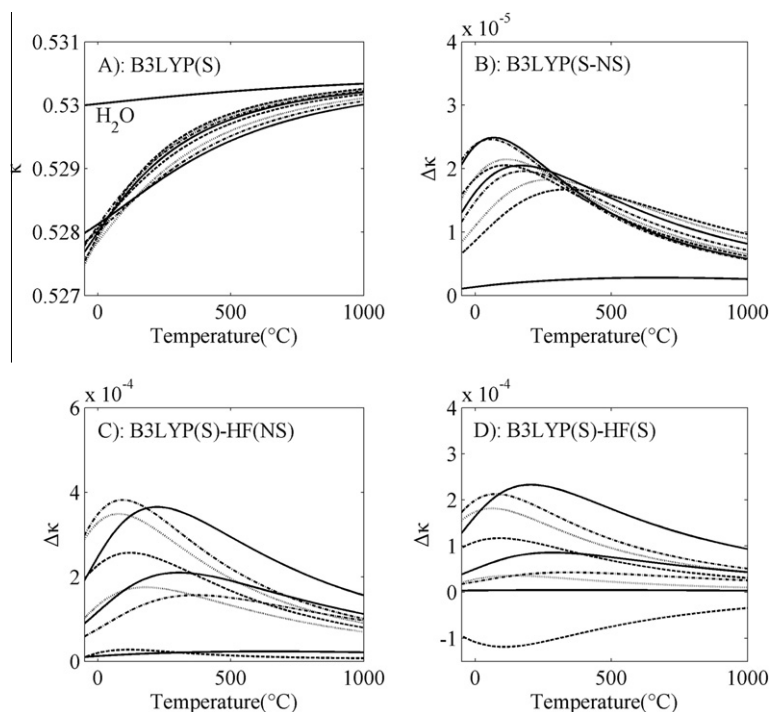


Fig. 1. Calculated κ values using different theoretical methods (all with the same 6-311 + G(2df,p) basis-set). Fig. 1A is for the scaled results of B3LYP method (Results of $\text{CO}_3^{2-}(\text{g})$, SiO_2 and SiOAl are not included). Fig. 1B shows the κ value differences between scaled and un-scaled results of B3LYP method (scaled = using frequency scaling factor, un-scaled = not using frequency factor, see the main text for details). Their differences are on the order of 10^{-5} , which implies that the choice of scaling factor does not cause significant effect on the κ results. Fig. 1C shows the κ value differences between scaled B3LYP method and un-scaled HF method. Fig. 1D shows the κ value differences between scaled B3LYP method and scaled HF method. The κ value differences in Fig. 1C and Fig. 1D are on the order of 10^{-4} .

Table 1

Formula of κ of several representative O-bearing molecules at different temperatures, calculated at B3LYP/6-311 + G(2df,p) level. The frequency scaling factor is 0.9889. $\text{CO}_3^{2-}(\text{g})$ stands for the free carbonate-ion in gas phase.

$$\kappa = A \times 10^{-12} \times T^3 + B \times 10^{-9} \times T^2 + C \times 10^{-6} \times T + D$$

($223.15\text{K} \leq T \leq 1273.15\text{K}$; $\text{K} = 273.15 + ^\circ\text{C}$)

| | A | B | C | D |
|-----------------------------------|---------|----------|---------|---------|
| CO | -0.0149 | -1.4742 | 4.1857 | 0.52708 |
| O ₂ | 1.7253 | -6.3723 | 8.4475 | 0.52619 |
| NO | 0.55727 | -3.2083 | 5.8678 | 0.52663 |
| CO ₂ | 1.8974 | -6.8631 | 9.0062 | 0.52586 |
| N ₂ O | 2.6719 | -8.8680 | 10.480 | 0.52575 |
| NO ₂ | 2.6258 | -8.6612 | 10.165 | 0.52592 |
| H ₂ O | 0 | -0.14615 | 0.54363 | 0.52988 |
| SO ₂ | 3.7970 | -11.882 | 13.002 | 0.52516 |
| SO ₃ | 3.8249 | -11.894 | 12.918 | 0.52524 |
| CO ₃ ²⁻ (g) | 3.6517 | -10.854 | 11.078 | 0.52636 |
| SiO ₂ | 4.5855 | -13.814 | 14.268 | 0.52511 |
| SiOAl | 4.5689 | -13.549 | 13.682 | 0.52550 |

difference between them is only 0.0001. We also find that the change of κ values caused by the Al^{3+} substitution of Si^{4+} is on the order of 10^{-4} (see Fig. 2).

For the calculations of κ values of carbonates, we used the Einstein–Debye model to obtain β values for calcite, magnesite, aragonite, dolomite, and witherite. The frequency data are taken from Chacko and Deines (2008). Previous studies suggested that oxygen isotope fractionations

are similar among carbonate minerals, i.e. the CO_3^{2-} ion dominates the oxygen isotope fractionation (Chacko and Deines, 2008). We also found that the κ values of carbonates are controlled by CO_3^{2-} ion (see Fig. 3), with the κ values varying in a small range (less than 0.001) for different carbonates as calculated using the Einstein–Debye model.

In Fig. 3, $\text{CO}_3^{2-}(\text{g})$ stands for the results of free CO_3^{2-} ion gas with only one oxygen atom exchanged (i.e.,

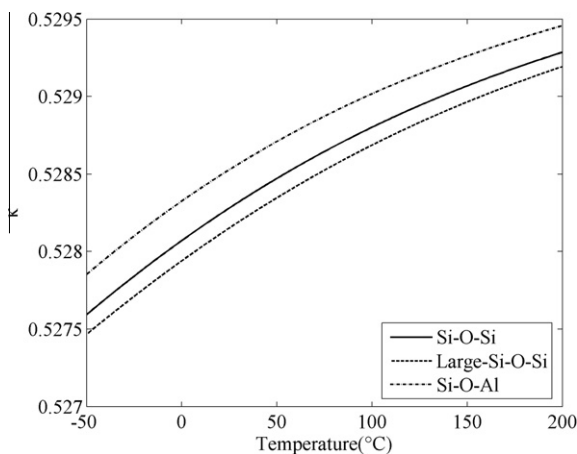


Fig. 2. Calculated κ values of simple cluster models (Si–O–Si and Si–O–Al) and a large cluster model (Large-Si–O–Si) (see Supplement file for details). The simple cluster models are calculated at B3LYP/6-311 + G(2df,p) level (scaling factor: 0.9889), and the large cluster model is calculated at B3LYP/6-311 + G(d,p) level (scaling factor: 0.9887). The differences between results of Si–O–Si and Large-Si–O–Si are about 0.0001. The differences between Si–O–Si and Si–O–Al are about 0.0003. These results imply that the structural effect is smaller than that of chemical composition.

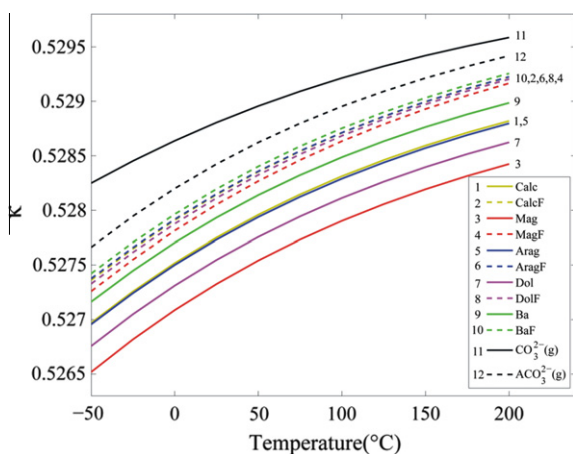


Fig. 3. The comparison of κ values of carbonates calculated by different methods. Calc, Mag, Arag, Dol and Ba (solid lines) stand for κ values calculated by the Einstein-Debye model of calcite, magnesite, aragonite, dolomite and witherite, respectively. CalcF, MagF, AragF, DolF and BaF (dash lines) stand for the κ values obtained by using only internal vibration frequencies of carbonate ion in corresponding minerals. $\text{CO}_3^{2-}(\text{g})$ and $\text{ACO}_3^{2-}(\text{g})$ stand for the results calculated by cluster-model method for free carbonate ion gases. Except for $\text{CO}_3^{2-}(\text{g})$, all the other cases are using the rule of geometric mean to obtain β values because all their oxygen atoms are exchanged during the calculation. The results of RGM are only used to explore general trends of these carbonates and they will not be used to estimate absolute θ values.

$^{12}\text{C}^{16}\text{O}_3^{2-}$ to $^{12}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$). $\text{ACO}_3^{2-}(\text{g})$ stands for the results of free CO_3^{2-} ion gas with three oxygen atom exchanged (i.e., $^{12}\text{C}^{16}\text{O}_3^{2-}$ to $^{12}\text{C}^{18}\text{O}_3^{2-}$) and use the rule of geometric mean (RGM) to obtain its κ values. There is a surprisingly large difference between the results of these two treatments.

4. DISCUSSION

4.1. Frequency scaling factor effects on the κ calculation

In isotopic fractionation calculation one often needs to use an appropriate frequency scale factor when the method used for harmonic frequency is not of sufficiently high accuracy. This often occurs to isotopic fractionation involving larger molecules. There are many kinds of scaling factors for different purposes, such as for ZPE, for harmonic frequency or for fundamental frequency corrections (e.g., Scott and Radom, 1996; Andersson and Uvdal, 2005; Merrick et al., 2007). We use a scaling factor for ZPE correction recommended by Liu et al. (2010).

From the scaled or un-scaled results in Fig. 1, we find the effect of frequency scaling factor will be largely canceled in the case of κ calculation. Therefore, the choice of scaling factor does not significantly affect κ results. Here, we provide a theoretical analysis to prove this hypothesis.

A good approximation used for the calculation of β value is (Bigeleisen and Mayer, 1947):

$$\ln \beta \approx \sum_i \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{\exp(u_i) - 1} \right) \Delta u_i = \sum_i k_i \Delta u_i \quad (8)$$

where:

$$k_i = \frac{1}{2} - \frac{1}{u_i} + \frac{1}{\exp(u_i) - 1}$$

and $\Delta u = u - u^*$, where u^* is for the isotopically substituted case.

We use lower case “s” to denote items scaled by the frequency scaling factor, such as $u_s = S \times u$ and $\Delta u_s = S \times \Delta u$; the “S” means scaling factor (usually a number close to 1). The scaled $\ln \beta$ can be approximated as

$$\begin{aligned} \ln \beta_s &\approx \sum_i \left(\frac{1}{2} - \frac{1}{u_{si}} + \frac{1}{\exp(u_{si}) - 1} \right) \Delta u_{si} \\ &\approx \ln \beta + \sum_i (p_i(1 - S)u_i \Delta u_i + k_i(S - 1)\Delta u_i) \\ &= \ln \beta(S + (1 - S) \sum_i p_i u_i \Delta u_i / \sum_i k_i \Delta u_i) \end{aligned} \quad (9)$$

where:

$$p_i = \frac{\exp(u_i)}{(\exp(u_i) - 1)^2} - \frac{1}{u_i^2}$$

When u is large enough (e.g., at low temperatures), the value of $\sum_i p_i u_i \Delta u_i / \sum_i k_i \Delta u_i$ tends to be zero, and $(1 - S)$ is close to zero too, thus:

$$\ln \beta_s \approx S \cdot \ln \beta \quad (10)$$

which is similar to what Méheut et al. (2009) found in their study of solids. When we calculate the κ , the scaling factor will be canceled:

$$\kappa_s = \frac{\ln^{17} \beta_s}{\ln^{18} \beta_s} \approx \frac{S \cdot \ln^{17} \beta}{S \cdot \ln^{18} \beta} = \kappa \quad (11)$$

Therefore, frequency scaling factors have little effect on the κ value calculation. They can only marginally change κ values, especially at low temperature (i.e., when u is large).

4.2. Effects of anharmonic corrections on the κ calculation

The above discussions are about isotope fractionation calculation under harmonic approximation. One important question is whether higher-order anharmonic corrections will significantly change the value of κ or not. Here, we present a theoretical analysis about anharmonic effects on κ value using diatomic molecules as an example.

Anharmonic corrections can affect β values significantly. For example, there is about 4 percent anharmonic correction to $\ln\beta$ for $^{18}\text{O}/^{16}\text{O}$ exchanges in H_2O (i.e., $\ln\beta_{\text{AnhC}} \approx 4\% \times \ln\beta$, see Table 3 in Liu et al. (2010)). The dominating anharmonic correction for a non-H/D isotope exchange reaction is the anharmonic corrections on ZPE (e.g., Richet et al., 1977; Liu et al. 2010). For diatomic molecules, the anharmonic corrections to $\ln\beta$ of a non-H/D isotope exchange can be simplified as (Richet et al., 1977; Liu et al. 2010):

$$\ln\beta_{\text{AnhC}} = \frac{1}{4} \frac{hc}{k_B T} (\omega_e^* \chi_e^* - \omega_e \chi_e) \quad (12)$$

where χ_e is anharmonic constant. For diatomic molecules, $\omega_e^* \chi_e^* / \omega_e \chi_e = \mu / \mu^*$ (Dunham, 1932), and μ is the reduced mass (i.e., $\mu = M \times m / (M + m)$, M is the atomic mass which bonds to oxygen atom, m is oxygen atomic mass). Here, the higher-order energy part (G_0) of ZPE is ignored as suggested by Liu et al. (2010) for non-H/D exchanges. Then, the anharmonic correction to κ is:

$$\begin{aligned} \Delta\kappa &= \frac{\ln^{17}\beta + \ln^{17}\beta_{\text{AnhC}}}{\ln^{18}\beta + \ln^{18}\beta_{\text{AnhC}}} - \frac{\ln^{17}\beta}{\ln^{18}\beta} \\ &= \frac{(\kappa_{\text{AnhC}} - \kappa) \ln^{18}\beta_{\text{AnhC}}}{\ln^{18}\beta + \ln^{18}\beta_{\text{AnhC}}} \end{aligned} \quad (13)$$

where

$$\kappa_{\text{AnhC}} = \frac{\ln^{17}\beta_{\text{AnhC}}}{\ln^{18}\beta_{\text{AnhC}}} = \frac{m_{18}(m_{17} - m_{16})}{m_{17}(m_{18} - m_{16})} = 0.5305$$

Because κ values are generally in the range from 0.5275 to 0.5305 (e.g., Fig. 1A), the difference between κ_{AnhC} and κ should be less than 0.003. Considering $\ln\beta_{\text{AnhC}}$ is less than 5% of $\ln\beta$ for non-H/D exchanges (Liu et al., 2010), the $\Delta\kappa$ value could not exceed 0.00015. Using the frequencies and ZPEs data of Wang et al. (2004), we calculated the anharmonic effects for CO_2 and N_2O . These calculated corrections to κ are all less than 0.0001, agreeing with what we

Table 2

κ values of CO_2 calculated at different temperatures. κ_{all} represents results of including all isotopologues into the calculation, κ_{SS} represents results of including only the singly substituted isotopologue (i.e., $^{18}\text{O}^{12}\text{C}^{16}\text{O}$ and $^{17}\text{O}^{12}\text{C}^{16}\text{O}$) and κ_{RGM} represents results of employing the rule of geometric mean (i.e., using fully substituted isotopologues: $^{18}\text{O}^{12}\text{C}^{18}\text{O}$ and $^{17}\text{O}^{12}\text{C}^{17}\text{O}$).

| Temp. (°C) | κ_{all} | κ_{SS} | κ_{RGM} |
|------------|-----------------------|----------------------|-----------------------|
| −50 | 0.52759 | 0.52759 | 0.52698 |
| 0 | 0.52785 | 0.52785 | 0.52738 |
| 50 | 0.52812 | 0.52812 | 0.52775 |
| 100 | 0.52837 | 0.52837 | 0.52808 |
| 500 | 0.52960 | 0.52960 | 0.52956 |

* Frequencies data are from Wang et al. (2004).

estimated. Therefore, we conclude that anharmonic corrections will be insignificant in the calculation of κ value.

4.3. Effects of clumped isotopes and the rule of geometric mean (RGM)

The clumped isotope study considers isotopologues with more than one rare isotope (Wang et al., 2004; Eiler, 2007). Nevertheless, the abundance of multiple-substituted isotopologues is usually very low. The bulk isotope composition mainly reflects the abundance of singly-substituted isotopologue (i.e., Eq. (3)). Here, we check whether rare, multiple-substituted isotopologues should be considered in the calculation of κ or not.

Taking CO_2 as an example, there is no difference between the calculated κ value including all isotopologues and the one including only singly substituted isotopologues (see Table 2). Therefore, the exclusion of rare isotopologues in the κ calculation will be reasonable.

Another issue is related to the use of the rule of geometric mean (RGM). RGM is an approximation by assuming there is no energy difference for grouping heavy isotopes into bonds other than let them bond to light isotopes (e.g. the energy of H_2 and D_2 is equal to 2 times of HD, Eiler, 2007). This assumption is not reasonable at low temperature (e.g., Urey, 1947; Bigeleisen, 1955; Eiler, 2007). We find that the employing of RGM in the κ calculation is improper. The results for both CO_2 and CO_3^{2-} are quite different by whether RGM was employed or not. The difference between the results becomes larger with decreased temperature (see Table 2 or Fig. 3). Therefore, in the case of κ calculation, we recommend not using the RGM especially when it is at lower temperatures (e.g., less than 500 °C).

4.4. Effects of structure and chemical composition on κ values

The carbonate κ results calculated by the Einstein–Debye model suggest that the structural effect might be smaller than that of chemical composition, which is similar to the results of silicates (see Figs. 2 and 3). For example, with different structures but the same chemical composition, the κ values of calcite and aragonite are almost identical (e.g., the difference is on the order of 10^{-5} or less). On the other hand, with the same structure but different chemical compositions, the κ values of calcite, magnesite and dolomite can differ by the order of 10^{-4} .

Table 3

$\theta_{\text{X-water}}^{\text{E}}$ values of several equilibrium processes at given temperatures, calculated by Eq. (15).

| | 0 °C | 25 °C | 50 °C | 75 °C | 100 °C |
|--|--------|--------|--------|--------|--------|
| $\theta_{\text{CO}_2\text{-water}}^{\text{E}}$ | 0.5242 | 0.5246 | 0.5250 | 0.5253 | 0.5255 |
| $\theta_{\text{Quartz-water}}^{\text{E}}$ | 0.5242 | 0.5246 | 0.5249 | 0.5252 | 0.5255 |
| $\theta_{\text{Calcite-water}}^{\text{E}}$ | 0.5233 | 0.5235 | 0.5237 | 0.5238 | 0.5239 |

* κ_{water} is supposed to be 0.5299. κ_{calcite} is calculated by $\kappa_{\text{calcite}} = \kappa_{\text{CO}_3^{2-}(\text{g})} - 0.0007$. $\kappa_{\text{CO}_2(\text{g})}$, κ_{quartz} and $\kappa_{\text{CO}_3^{2-}(\text{g})}$ can be found in Table 1. $^{18}\beta_{\text{water}}$, $^{18}\beta_{\text{CO}_2}$, $^{18}\beta_{\text{quartz}}$ and $^{18}\beta_{\text{calcite}}$ are taken from Rosenbaum (1997), Richet et al. (1977), Méheut et al. (2007) and Schauble et al. (2006).

Similar to the analysis of anharmonic effects, the β value of carbonates can be divided into two parts: one part related to internal vibrations of CO_3^{2-} ion (i.e., $\kappa_{\text{CO}_3^{2-}}$) and the other part related to external lattice vibration modes (i.e., κ_{LM}). The difference between κ value of carbonates and CO_3^{2-} ion is:

$$\begin{aligned} \Delta\kappa &= \frac{\kappa_{\text{CO}_3^{2-}} \cdot \ln^{18}\beta_{\text{CO}_3^{2-}} + \kappa_{\text{LM}} \ln^{18}\beta_{\text{LM}}}{\ln^{18}\beta_{\text{CO}_3^{2-}} + \ln^{18}\beta_{\text{LM}}} - \kappa_{\text{CO}_3^{2-}} \\ &= \frac{(\kappa_{\text{LM}} - \kappa_{\text{CO}_3^{2-}}) \times \ln^{18}\beta_{\text{LM}}}{\ln^{18}\beta_{\text{CO}_3^{2-}} + \ln^{18}\beta_{\text{LM}}} \end{aligned} \quad (14)$$

where the subscript “LM” represents the external lattice modes, the $\ln^{18}\beta_{\text{LM}}$ stands for the lattice modes’ contributions to the β of carbonates. In carbonates, interactions between CO_3^{2-} ion and outside structures (i.e., network modifier cations) are weak, leading to relatively low frequencies of corresponding vibration modes. It suggests the dominant contribution to β value will come from the internal vibrations of CO_3^{2-} ion (Chacko and Deines; 2008; Zeebe, 2009). The value of κ_{LM} is calculated by Debye model, and its value varies from 0.522 to 0.523. The total difference, $\Delta\kappa$, should therefore be small (e.g., on the order of 10^{-4} , see Fig. 3), which indicates that CO_3^{2-} ion dominates the κ value of carbonates.

However, the Einstein–Debye model could only carry out κ calculation under RGM, and RGM would cause errors at low temperature. Therefore, the results of carbonates could not be used for θ^E calculations directly. Considering the general trends (see Fig. 3), it is possible to evaluate $\kappa_{\text{carbonates}}$ values from $\kappa_{\text{CO}_3^{2-}(\text{g})}$. For example, κ_{calcite} is generally 0.0007 smaller than $\kappa_{\text{ACO}_3^{2-}(\text{g})}$ from -50 to 200 °C (see Fig. 3), and its value could be calculated by $\kappa_{\text{calcite}} = \kappa_{\text{CO}_3^{2-}(\text{g})} - 0.0007$.

The discussions above indicate that the κ values of $\text{CO}_3^{2-}(\text{g})$, $\text{CO}_3^{2-}(\text{aq})$, and carbonates only vary on the order of 10^{-4} . This is very different from the β value. Previous studies shown that different carbonates have different β values and even the same carbonate will have different β values if using different number of wave vectors (Schauble et al., 2006). However, for the κ values, even isolated CO_3^{2-} in gas phase would have a κ value very closed to those of other carbonates. This finding suggests that a meaningful κ value could be obtained via the calculation on very simple cluster models.

Similar to carbonates, $[\text{SiO}_4^{4-}]$ tetrahedron networks control the oxygen isotope effect in silicates (Chacko et al., 2001). It is therefore possible to use simple cluster models to represent numerous silicates with quite different structures and chemical compositions.

4.5. General rules for κ values

We use diatomic molecules as examples to explore the general rules for κ values. It is because κ values of diatomic molecules can be easily calculated by using this relationship $(\omega^*/\omega) = (\mu/\mu^*)^{1/2}$, where μ is the reduced mass (Dunham, 1932). O-bearing, Mg-bearing and S-bearing diatomic molecules are studied (Fig. 4). κ values of them are plotted against atomic mass (M) of the bonded atoms with O, Mg

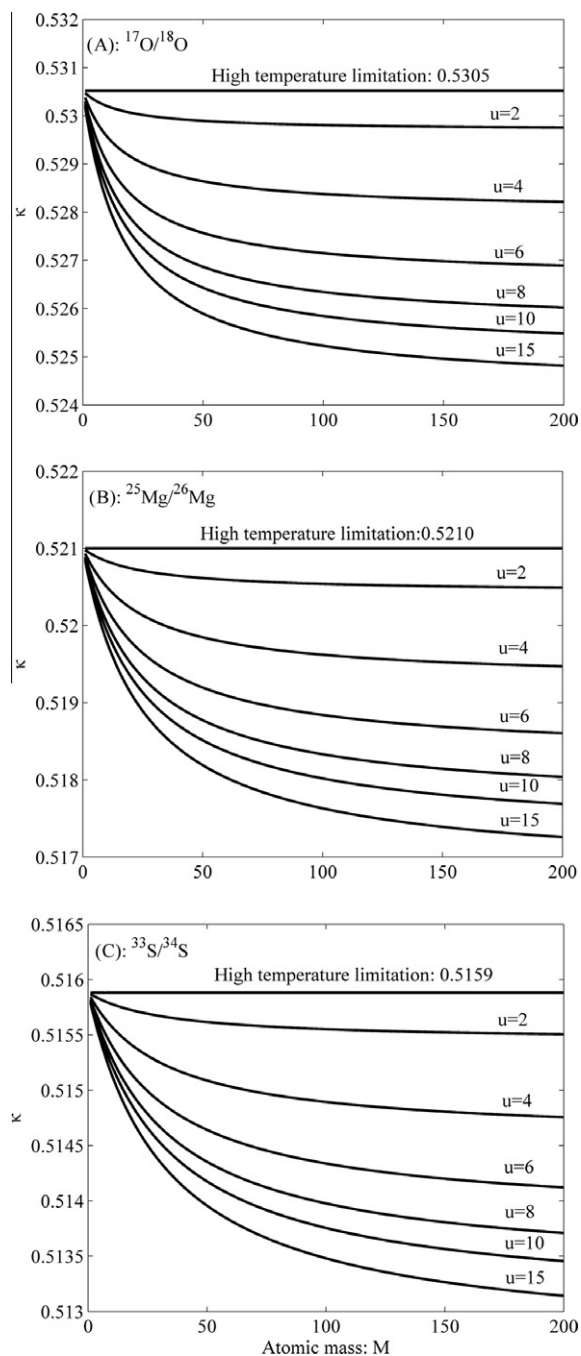


Fig. 4. The behaviors of κ for O-, Mg- and S-bearing isotopic systems. X-axis is for the M value that is the atomic mass of the bonded atom with O, Mg or S. u is equal to $hc\omega_j/k_bT$. (see the text for details).

or S, respectively. For example, when the bonded atom is hydrogen, $M = 1$; when the bonded atom is iron, $M = 56$. From Fig. 4, several general rules can be observed:

(1) Rule 1: When M are small (i.e., the bonded atoms are light elements), the effects of u ($u = hc\omega_j/k_bT$) to κ values decreases rapidly. Different lines of u numbers are converged to a very small region. At that situation, κ values can only be varied slightly no matter how large changes

of vibrational frequencies and temperatures will be. We call it as the “light mass limitation” (LML) rule. The unusual behavior of κ of H₂O (see Fig. 1A) is caused by the LML rule.

(2) Rule 2: When u is small (i.e., at high temperatures), the κ value is relatively insensitive to the bonded atomic mass. We call it as the “high temperature limitation” (HTL) rule.

(3) Rule 3: The range of κ values for heavier isotope systems will be smaller (e.g., S < Mg < O). The range of κ values for S isotopes should be small due to their large atomic mass (see Fig. 4C). Previous theoretical estimations on θ values of S isotopes suggested the similar conclusion (Farquhar et al., 2003; Otake et al., 2008). For Mg isotope systems, given low frequencies usually related to Mg–X bondings (e.g., $u < 3$ at room temperature, Schauble, 2011), the variation of κ for Mg isotopes should be very small too. If consider the HTL rule, all θ values for Mg isotopes will be very close to 0.5210 in equilibrium processes. This is very different from the θ value (0.510) of evaporation process (i.e., kinetic process, Young et al., 2002), providing a way to distinguish equilibrium or kinetic processes.

4.6. Estimation of θ value for the CO₂–CeO₂ isotope exchange reaction

Hofmann and Pack (2010) determined a high-precision θ value for the CO₂–CeO₂ exchange experimentally. If we use their θ value (0.5240) and $\ln^{18}\alpha_{\text{CO}_2\text{-CeO}_2}$ at 685 °C, we can obtain the κ_{CeO_2} value from Eq. (7) by using well-accepted $\ln^{18}\beta_{\text{CO}_2}$ (e.g., Richet et al. (1977)) and our calculated κ_{CO_2} values. However, the κ_{CeO_2} value (0.5407) from this way is very strange. It is even larger than that of LML or HTL rule (i.e., 0.5305).

We can use another way to estimate the κ_{CeO_2} value and the $\theta_{\text{CO}_2\text{-CeO}_2}$ value. From Fig. 4, κ_{CeO_2} should be very close to the high temperature limitation value 0.5305 since the frequencies of CeO₂ compound is low (Weber et al., 1993) and this isotope exchange reaction is at high temperature (i.e., 685 °C). Using Eq. (7), we obtain $\theta \approx 0.5294$ for the CO₂–CeO₂ exchange reaction at 685 °C. The experimental θ value (0.5240) of Hofmann and Pack (2010) is obviously too small. We doubt that such value reflects a set of combined processes but not the single equilibrium exchange reaction of CO₂–CeO₂. There are several processes actually taking place on the CO₂–CeO₂ interaction surface simultaneously (Assonov and Brenninkmeijer, 2001 and references therein).

4.7. θ values of several equilibrium exchange processes

The equilibrium processes related to water are always important because water is the most important medium of numerous processes in hydrosphere, biosphere, atmosphere, hydrothermal system and even in extraterrestrial environments (e.g., Luz et al., 1999; Luz and Barkan, 2005; Landais et al., 2006, 2008; Shaheen et al., 2010; Kohl and Bao, 2011). We therefore provide here some equilibrium θ values related to liquid water.

Rewriting Eq. (7), we obtain:

$$\theta_{\text{X-water}}^E = \kappa_{\text{X}} + (\kappa_{\text{X}} - \kappa_{\text{water}}) \frac{\ln^{18}\beta_{\text{water}}}{\ln^{18}\alpha_{\text{X-water}}} \quad (15)$$

where X is any oxygen-bearing compound; κ_{X} and κ_{water} are the κ values of X and liquid water; $^{18}\beta_{\text{water}}$ is the reduced partition function ratio (RPF) of ¹⁸O/¹⁶O for liquid water (Rosenbaum, 1997), $^{18}\alpha_{\text{X-water}}$ is the ¹⁸O/¹⁶O isotope fractionation factor between X and liquid water. $^{18}\beta_{\text{water}}$ and $^{18}\alpha_{\text{X-water}}$ can be obtained from previous experimental results or through theoretical calculations (e.g., Richet et al., 1977; Horita and Wesolowski, 1994; Rosenbaum, 1997; Schauble et al., 2006; Méheut et al., 2007).

The κ_{water} value should be very similar to that of $\kappa_{\text{H}_2\text{O(g)}}$ (see Table 1) because similar κ values are expected for similar compounds or species as discussed in Section 4.4. In that case, the $(\kappa_{\text{H}_2\text{O(g)}} - \kappa_{\text{water}})$ term in Eq. (15) will be close to zero. No matter what the values of $^{18}\beta_{\text{water}}$ and $^{18}\alpha_{\text{vapor-water}}$ are, the $\theta_{\text{L/V}}^E$ of equilibrium liquid water–vapor exchange reaction should be very close to $\kappa_{\text{H}_2\text{O(g)}}$, which is about 0.5300. This estimation is very close to the theoretical estimation of Angert et al. (2004) and the experimental results of Barkan and Luz (2005).

If using the $^{18}\beta_{\text{water}}$ and $^{18}\alpha_{\text{vapor-water}}$ values from Rosenbaum (1997) and Horita and Wesolowski (1994) and also the experimental $\theta_{\text{L/V}}^E$ value (0.529), the κ_{water} is determined to be 0.5299 at 0–50 °C. This is very close to our theoretically estimated κ_{water} value (i.e., 0.5299 vs. 0.5300).

Using $^{18}\beta$ values from previous studies (Richet et al., 1977; Schauble et al., 2006; Méheut et al., 2007) and κ_{X} values from our theoretical estimations ($\kappa_{\text{CO}_2(\text{g})}$ and κ_{quartz} can be found in Table 1, κ_{calcite} is calculated by $\kappa_{\text{calcite}} = \kappa_{\text{CO}_3^{2-}(\text{g})} - 0.0007$ (see Section 4.4)), we can obtain several equilibrium θ^E values (Table 3). Table 3 shows that θ^E values are only slightly dependent on temperatures. Such temperature dependences are consistent with what Farquhar et al. (2003) found for sulfur isotope systems, in which the variation is on the order of 10^{-4} from 0 to 100 °C.

The water–CO₂(g) equilibrium exchange reaction was examined for the possibility of extracting small ¹⁷O-excess information of water (Uemura et al., 2010). The $\theta_{\text{CO}_2(\text{g})\text{-water}}^E$ value of this process, however, has not been determined. Our results suggest that $\theta_{\text{CO}_2(\text{g})\text{-water}}^E$ value is 0.5246 at room temperature, compared to 0.5 used in Uemura et al. (2010).

Although our results for $\theta_{\text{quartz-water}}^E$ and $\theta_{\text{calcite-water}}^E$ are very close to the experimental data (Rumble et al., 2007; Shaheen et al., 2010), they actually cannot be directly compared with each other. This is because our results are for single equilibrium exchange reactions between minerals and water, while the experimental data are statistical results for minerals from different locations. Only if many other effects (e.g., kinetic effect, reservoir effect, etc.) have been excluded, their results can be compared to ours.

5. CONCLUSIONS

We have introduced a theoretical approach in calculating equilibrium θ value, which is the relationship between ¹⁷ α and ¹⁸ α as in triple oxygen isotope fractionation

processes. A new concept κ is defined and recommended for calculating a large number of equilibrium θ values in nature. We find that similar chemical groups in molecules or minerals will have similar κ values. For example, the difference between κ values of different carbonates is on the order of 10^{-4} , providing a simple way to estimate equilibrium θ values by applying a small data set. The structural effect might be smaller than that of chemical composition. Frequency scaling factor, anharmonic corrections and clumped isotopes, have little effect on κ calculations. However, the use of rule of geometric mean (RGM) will significantly affect the κ results, suggesting not use such approximation at low temperatures.

Based on the new method, equilibrium θ values for $\text{CO}_2(\text{g})$ -water, quartz-water, and calcite-water equilibrium isotope exchange reactions are provided. These ratios are temperature dependent but the dependency is insensitive.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.09.048.

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