Theoretical calibration of the triple oxygen isotope thermometer

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Abstract

The field of isotope geochemistry began with the study of oxygen isotope geothermometry, most notably for carbonates. For traditional oxygen isotope geothermometry only the relationship between one rare isotope, oxygen-18, and the common isotope, oxygen-16, is used because for most terrestrial processes the ^{17}O-^{16}O relationship scales with the ^{18}O-^{16}O relationship and is thought to not grant any new information. However, theoretical analysis predicts a small temperature-dependence of the equilibrium triple oxygen isotope relationship and instrumentation and techniques now allow for high-precision determination of the oxygen isotope composition for all three oxygen isotopes for a variety of sample types. To set the groundwork for triple oxygen isotope geothermometry, here we present new calibrations based on statistical thermodynamics and density functional theory for both the traditional two isotope and the recently introduced triple isotope thermometer for pairs of quartz, calcite, dolomite, fluorapatite, hematite, magnetite and liquid water. The results compare well with previous studies on $^{18}O/^{16}O$ fractionation where theoretical and experimental data are available. Of the models given here, pairs of quartz, calcite, dolomite and fluorapatite with water, hematite or magnetite show promising temperature sensitivities as triple isotope thermometers with acceptable uncertainties for surface and low-T hydrothermal environments.
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1. INTRODUCTION

The potential for isotope fractionation to be used as a geothermometer dates back to the work of Harold Urey who recognized the temperature dependence of oxygen isotope fractionation between carbonate and water (Urey, 1947). At the time, isotope ratio mass spectrometry was in its infancy and precisions of only one part per thousand were possible for the ratio of the two most abundant isotopes of oxygen, ^{16}O and ^{18}O. For low temperatures, this precision allowed for the carbonate geothermometer, with assumptions on the isotope composition of the water (Urey, 1947). Early on, it was assumed that isotope

fractionation for the ^{17}O-^{16}O system would scale with ^{18}O-^{16}O system due to the mass dependent isotope fractionation (Clayton et al., 1973) and so it was thought that measuring the $^{17}O/^{16}O$ ratio would provide no useful further information. The discovery of ^{17}O deviation in meteorites from the terrestrial fractionation line and later large non-mass-dependent isotope effects associated with ozone chemistry in Earth's atmosphere changed this paradigm and led to a newfound need in measuring the triple isotope composition of various oxygen reservoirs (Clayton et al., 1973; Heidenreich and Thiemens, 1983; Thiemens, 2013). Over time, analytical precision and techniques improved to the point where much smaller mass-dependent variations are resolvable and can be related to chemically and geochemically relevant parameters (Pack and Herwartz, 2014; Liang and Mahata, 2015; Bao et al., 2016; Sharp et al., 2016). What has become apparent is that much like with

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the two isotope systems, fractionation in triple isotope systems is temperature dependent (Cao and Liu, 2011; Pack and Herwartz, 2014; Bao et al., 2016; Hayles et al., 2017). This extra dimension of temperature dependency led to the suggestion by Pack and Herwartz (2014) that the value of the mass dependence exponent, θ, can be used as a separate geothermometer for low temperature systems.

For the oxygen triple isotope system, θ is given by;

$$\theta = \frac{ln\,^{17}\alpha_{A-B}}{ln\,^{18}\alpha_{A-B}} \qquad (1)$$

where α is the fractionation factor which for measurement purposes is given by:

$$^{18}\alpha_{A-B} = \frac{^{18}\beta_A}{^{18}\beta_B} = \frac{\left[^{18}n/^{16}n\right]_A}{\left[^{18}n/^{16}n\right]_B} \qquad (2)$$

where $\left[^{18}n/^{16}n\right]$ is the molar ratio of the rare/heavy isotope ^{18}O and the common/light isotope ^{16}O, which can be measured relative to a standard and β is a theoretical parameter relating to a hypothetical equilibrium between the phase in question and an oxygen species with no thermodynamic bias for one oxygen isotope over another. β is therefore a theoretical parameter which describes the "affinity" of a species for one oxygen isotope relative to another. In both equations, the superscript indicates the isotope system and the subscript indicates the species involved in equilibrium (e.g. A-B => Calcite-H₂O(L)).

Not long after the introduction of the θ based triple isotope thermometer, the concept of using the temperature dependence of the difference in $\Delta'^{17}O$ between minerals and water as a geothermometer was introduced. This was independently suggested by Bao et al. (2016) based on previous theoretical work for calcite-water equilibrium and Sharp et al. (2016) based on measurements of natural quartz and silica. The core concept of $\Delta'^{17}O$ is given by the equation:

$$\Delta'^{17}O = \delta'^{17}O - 0.5305\delta'^{18}O \qquad (3)$$

where isgivenby :is given by:

$$\delta'^{18}O = ln\frac{\left[^{18}n/^{16}n\right]_{sample}}{\left[^{18}n/^{16}n\right]_{standard}} \qquad (4)$$

Using Eqs. (2) and (4), the difference on $\delta'^{18}O$ (or $\Delta\delta^{18}O$) between two phases given by;

$$\Delta\delta'^{18}O_{A-B} = ln\,^{18}\alpha_{A-B} \qquad (5)$$

The similar expression for the difference in $\Delta'^{17}O$ (or $\Delta\Delta^{17}O$) between two phases is then given by;

$$\Delta\Delta'^{17}O = \Delta\delta'^{17}O - 0.5305\Delta\delta'^{18}O \qquad (6)$$

Based on prior use (Pack and Herwartz, 2014; Wiechert et al., 2004) as well as the arguments put forth by Hayles et al. (2017) and Bao et al. (2016), here the suggested 0.5305 is used for Eqs. (3) and (6) as opposed to other commonly used values (e.g. 0.52, 0.528). This value is very nearly equal to the high-temperature limit of θ for oxygen isotope fractionation under the harmonic approximation and allows for a monotonic, or very near monotonic behavior for the temperature dependence of $\Delta\Delta'^{17}O$.

Although mathematically equivalent, in practice, the use of $\Delta\Delta'^{17}O$ has three primary advantages over the use of θ. (1) Application of simple the $\Delta^{17}O$ thermometer is similar in practice to the commonly used $\delta^{18}O$ thermometer. (2) Covariance between the measurements of $\delta'^{18}O$ and $\delta'^{17}O$ lead to a higher precision for $\Delta'^{17}O$ than would be expected from the uncertainties of $\delta'^{18}O$ and $\delta'^{17}O$. (3) The temperature dependency of $\Delta\Delta'^{17}O$ is simple and does not deviate from a finite range for small values of $\Delta\delta'^{18}O$. This is as opposed to θ which can be very uncertain and fundamentally hold any value for small enough values of $\Delta\delta'^{18}O$ (Hayles et al., 2017).

Sharp et al. (2016) empirically calibrated the SiO₂-H₂O system and compared to natural samples. A sound interpretation, however, would first require the confirmation of the mineral-water equilibrium, for which a reliable theoretical calibration of both α and θ variability with T is a prerequisite. Furthermore, to extend triple oxygen isotope thermometer to the diverse mineral assemblages in surface-temperature or hydrothermal systems, we need equilibrium θ-T or $\Delta\Delta'^{17}O$-T relationships for many other common oxygen-bearing minerals. At this time, however, we only have theoretical predictions for quartz and calcite without the needed models at the same level of theory for liquid water (Cao and Liu, 2011; Hill et al., 2014).

Therefore, in this study we investigate the viability of a triple isotope thermometer based on the ^{16}O-^{17}O-^{18}O system from a theoretical perspective. Here the temperature dependency of $\Delta\Delta'^{17}O$ (Bao et al., 2016; Sharp et al., 2016) is used as a mass-dependent fractionation descriptor for its ease of use. New theoretical calculations for equilibrium pairs of hematite, magnetite, fluorapatite, calcite, dolomite, quartz and liquid water and water vapor were carried out for both the $\delta^{18}O$ and $\Delta^{17}O$ systems. The structures for minerals and liquid water are represented by molecular clusters, and the Volume Variable Cluster Method is adopted here to allow for optimizing the structures for minerals at different theoretical levels (Li and Liu, 2015). It is found that using the assumption of isotope equilibrium: fluorapatite-H₂O(L), calcite-H₂O(L), dolomite-H₂O(L), and quartz-H₂O(L) can be effective triple isotope thermometers for surface to hydrothermal environments. Both hematite and magnetite can be used in place of H₂O(L) for the above pairs with only minor reduction in temperature sensitivity.

2. METHODS

2.1. Calculation of β_h for minerals

Periodic boundary conditions are typically used to represent the crystal environment and have been used to predict inter-minerals isotope fractionation factors for many systems (Schauble, 2011; Huang et al., 2013). However, this method is challenged when dealing with systems involving aqueous species. In order to use consistent methods for the representation of both minerals and aqueous species, molecule-like clusters were introduced to predict mineral-aqueous isotope fractionation factors (Gibbs, 1982;