The statistical mechanical basis of the triple isotope fractionation relationship

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Abstract

Multiple stable isotope relationships have found a growing variety of uses in geochemistry and cosmochemistry. Approximations to the statistical-mechanical models for predicting isotope effects have led to the notion that mass fractionation laws are constrained to a "canonical" range of possible values. Despite previous work indicating that these mass fractionation exponents can be highly variable, the concept of a constant relationship remains common. In this study, we demonstrate generically that the mass fractionation exponent, θ, can take *any* value for small fractionations and that these deviations are measurable. In addition, we characterise and advocate the use of the change/difference in cap-delta as a necessary and more reliable descriptor of multiple isotope fractionation relationships. Deviations from the "canonical" range are demonstrated by experimental data in the geochemically relevant haematite-water system.

Introduction

Despite roots in physical chemistry, the study of triple isotope relationships has found its most widespread and varied footing in the realm of geochemistry and cosmochemistry. Multiple stable isotope ratios have, among other uses, found utility as tools to elucidate photochemical (Farquhar *et al.*, 2000; Bao *et al.*, 2008) or magnetic isotope effects (Blum *et al.*, 2014) and as an identifying marker for extraterrestrial materials (Clayton *et al.*, 1973). Because of advances in analytical resolution, now more than ever, it is critical to understand the natural range of multiple isotope relationships to further these pursuits. The three isotope relationship was recently re-investigated for complex processes by Bao *et al.* (2015) using a broadly approximate treatment for elemental processes (*i.e.* equilibrium

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and kinetic isotope effects). The intrinsic relationships among temperature (T), isotope fractionation factor (α), and three-isotope exponent (θ) in mass-dependent elemental processes at equilibrium have not been explored theoretically.

The first accurate model for predicting the separation of isotopes for equilibrium processes was published independently by Urey (1947) and Bigeleisen and Goeppert-Mayer (1947; the B-GM-U model). Their development of the concept of reduced partition function ratio (*RPFR* or *(s/s')f*) allowed for the calculation of α between two species using only the harmonic vibrational frequencies for each degree of freedom and temperature.

$$\alpha_{A-B} = \frac{\beta_A}{\beta_B} \qquad \text{Eq. 1}$$

where A and B indicate different chemical species. Using oxygen as an example, $^{18}\alpha_{A-B} = ([^{18}O]/[^{16}O])_A/([^{18}O]/[^{16}O])_B$ and $^{18}\beta_A = ([^{18}O]/[^{16}O])_A/([^{18}O]/[^{16}O])_{Atomic-O}$. Under the harmonic approximation, β can be calculated by

$$\beta_{harm}^* = \prod_i^{3n-6(5)} \left(\frac{u_i^*}{u_i}\right)_{TRPR} \left(\frac{e^{-u_i^*/2}}{e^{-u_i/2}}\right)_{ZPE} \left(\frac{1-e^{-u_i}}{1-e^{-u_i^*}}\right)_{EXC} \qquad \text{Eq. 2}$$

$$u_i^* = \frac{hv_i^*}{k_B T} \qquad \text{Eq. 3}$$

Here, h is the Planck constant, k_B is Boltzmann's constant and T is temperature in kelvin, v is the harmonic vibrational frequency for a specific vibrational degree of freedom and the product is taken over all vibrational degrees of freedom, the number of which is given by $3n$-6 for non-linear molecules and $3n$-5 for linear molecules where n is the number of atoms in that molecule. The heavy isotope substituted state is indicated by "*" and the lack of a superscript indicates the reference isotope (commonly the most abundant isotope). The harmonic contribution can be separated into the product of three terms: (a) the Teller-Redlich product rule *(TRPR)* term; (b) the zero-point energy (*ZPE*) contribution; and (c) non-zero point energy contributions (*EXC*) (Wolfsberg, 1972). Importantly, the β in Equation 2 is modified with a subscript "*harm*" to indicate that this term only represents the contributions to isotope partitioning from the harmonic portions of molecular vibrations. The B-GM-U model is successful as it gives the dominant contribution to the value of β to a point near or better than analytical precision for most isotope systems. However, for molecules bearing light isotopes, particularly hydrogen, contributions from anharmonicity, non-classical rotations and rotational-vibrational interactions become significant. Modifications of the B-GM-U model in the form of multiplicative terms have been developed to correct these inaccuracies. Here we use the term "contribution" to specifically indicate multiplicative terms. Each contribution (*e.g.*, harmonic vibrational, anharmonic vibrational, rotational, imaginary *etc.*) is treated as having its own parameter, such as β, which is only a portion of the complete parameter.

Extension to Three Isotope Effects

Transformation of a two-isotope model to a three-isotope model involves combining two independently calculated models that use the same reference isotope. A key aspect for the B-GM-U model is the mass dependence of isotope fractionation due to the mass dependence of vibrational frequencies. This relationship can be described by an exponent θ where

$$\theta = \frac{\ln a^{\ddagger}_{A-B}}{\ln a^{*}_{A-B}} \qquad \text{Eq. 4}$$

where "$\ddagger$" and "$*$" indicate the respective parameters for two different isotope ratios of the same element. Due to the use of the "low-u" (see Eq. 3) approximation of Equation 2, it was commonly believed that the value of the three isotope exponent was somewhat constant and later thought to be constrained to a finite, "canonical", range for mass-dependent processes which remains as an accepted idea (Swain *et al.*, 1958; Matsuhisa *et al.*, 1978; Young *et al.*, 2002, 2016; Kaiser *et al.*, 2004). Here, "canonical" refers to a θ value being within certain range represented by most of the observed cases and theoretical justifications (*e.g.*, 0.50-0.5305 for the ^{16}O-^{17}O-^{18}O system; Eiler *et al.*, 2013).

Using a theoretical framework which represented strictly mass dependent scenarios, Skaron and Wolfsberg (1980) showed theoretically for oxygen isotope partitioning that θ can vary from positive to negative infinity for crossover scenarios, situations where the fractionation factor α for transitions from greater than 1 (heavier isotopes partitioned to A) to less than 1 (heavier isotopes partitioned to B) or *vice-versa* with changing temperature. Studies investigating these scenarios for sulphur (Deines, 2003; Otake *et al.*, 2008) and hydrogen (Kotaka *et al.*, 1992) have come to the same conclusion.

Analogously to the concept of β, Cao and Liu (2011) first introduced the concept of κ defined as the one species analogue of θ, or

$$\kappa = \frac{\ln\beta^{\ddagger}}{\ln\beta^{*}} \qquad \text{Eq. 5}$$

where β is the one species fractionation factor for the two-isotope system. The complete value of κ including all contributions can be calculated by

$$\kappa_{Complete} = \frac{\Sigma_i \kappa_i \ln\beta^{*}_i}{\Sigma_i \ln\beta^{*}_i} \qquad \text{Eq. 6}$$

where the sums are taken over all contributions whether they are from corrections (rotational, anharmonic *etc.*) to the B-GM-U model, from the imaginary frequency contribution for a transition state or from independent vibrational degrees of freedom. As long as all values of $\ln\beta$ have the same sign, such as for

harmonic vibrational degrees of freedom, the value of κ for a complex molecule is equal to the $\ln\beta$ weighted mean of the κ values from each contribution. The relationship between κ and θ is given by (Cao and Liu, 2011)

$$\theta = \kappa_A + (\kappa_A - \kappa_B)\frac{\ln\beta^{*}_B}{\ln\alpha^{*}_{A-B}} \qquad \text{Eq. 7}$$

From Equation 7, a large difference in the values of κ between phases A and B allows for a larger variability in the value of θ particularly where α is near unity. The only scenario which would not allow the above conditions to occur for any system would be if the values of κ and β were related by an explicit function of one-another which could be universally applied to all species. This hypothetical case is invalid (see Fig. 1a) because the relationship between vibrational frequencies of differently substituted molecules is a function of not only the mass of the substituted atom, but also the molecular configuration, bond force constants, and masses of secondary, non-substituted atoms. Additional evidence against a universal κ - β^{*} relationship can be found in studies implicating crossovers for θ values approaching infinity (Kotaka *et al.*, 1992; Deines, 2003; Otake *et al.*, 2008).

Theoretical Values of κ

The complete equation for the harmonic contribution to κ for a single degree of freedom is given by

$$\kappa_{harm} = \frac{\left(\ln\left(u^{\ddagger}\right) - \ln(u)\right)_{TRPR} + \left(u/2 - u^{\ddagger}/2\right)_{ZPE} + \left(\ln\left(1-e^{-u}\right) - \ln\left(1-e^{-u^{\ddagger}}\right)\right)_{EXC}}{\left(\ln\left(u^{*}\right) - \ln(u)\right)_{TRPR} + \left(u/2 - u^{*}/2\right)_{ZPE} + \left(\ln\left(1-e^{-u}\right) - \ln\left(1-e^{-u^{*}}\right)\right)_{EXC}} \qquad \text{Eq. 8}$$

which can be separated into terms that correspond to the contributions from *TRPR*, *ZPE* and *EXC* with each having their own mass dependence. At high temperatures, the contribution from energised states (*EXC*) dominates the harmonic κ. In this instance the values of u become very small and

$$\kappa_{HTL} = \frac{1/m - 1/m^{\ddagger}}{1/m - 1/m^{*}} \qquad \text{Eq. 9}$$

where m, $m^{\ddagger}$ and m^* are the masses of the light, middle and heavy isotopes respectively. Equation 9 serves as an upper bound of its value for diatomic molecules at all temperatures (*e.g.*, $\kappa_{HTL} \approx 0.5305$ for the $^{16}O\text{-}^{17}O\text{-}^{18}O$ system). At low temperatures, the contribution from *ZPE* dominates the harmonic κ. For a diatomic molecule under these conditions

$$\kappa_{LT-D} = \frac{1/\sqrt{\mu} - 1/\sqrt{\mu^{\ddagger}}}{1/\sqrt{\mu} - 1/\sqrt{\mu^*}} \qquad \text{Eq. 10}$$

where μ is the reduced mass ($\mu = m\,M\,/\,[m + M]$ for a diatomic molecule where M is the secondary, non-substituted mass). In this case, the value of κ decreases with increasing mass of the non-substituted atom (Cao and Liu, 2011). The limit of Equation 10 as the non-substituted mass approaches infinity is then

$$\kappa_{LL} = \frac{1/\sqrt{m} - 1/\sqrt{m^{\ddagger}}}{1/\sqrt{m} - 1/\sqrt{m^*}} \qquad \text{Eq. 11}$$

which serves as an unattainable lower boundary of κ for diatomic molecules (*e.g.*, $\kappa_{LL} \approx 0.5232$ for the $^{16}O\text{-}^{17}O\text{-}^{18}O$ system). Equation 10 is the same as the approximation to the mass fractionation law used by Swain *et al.* (1958) for triple-hydrogen system. Using the arguments of Swain *et al.* (1958), it is expected that polyatomic molecules will behave within or near the diatomic boundaries of κ_{harm} presented here. For all calculated results for hypothetical diatomic molecules, the values of κ_{harm} are found to not exceed the boundaries given by Equations 9 and 11.

Figure 1 displays the relationships between (a) β and κ and (b) θ and α for equilibrium between hypothetical diatomic molecules containing oxygen under the harmonic approximation with temperature plotted as colour. A key finding here is that the diatomic model allows θ to hold any value for small fractionations. Polyatomic molecules incorporate additional degrees of freedom which will weaken the relationship between κ and β. Therefore, this result is a conservative estimate of the distribution of θ. Much like values of α for a two isotope system, the variability of θ becomes greater at lower temperatures. Because anharmonic corrections are small relative to the harmonic contribution and have a similar mass dependency, anharmonic corrections do not have a significant effect on the distribution of θ values. The effects of anharmonic corrections are addressed in more depth in the Supplementary Information. For kinetic isotope effects, the value of κ for the transition states imaginary frequency contribution is also discussed in the Supplementary Information. The results indicate that values of θ for kinetic isotope effects are more variable and on average, but not strictly, lower than those of equilibrium isotope effects.
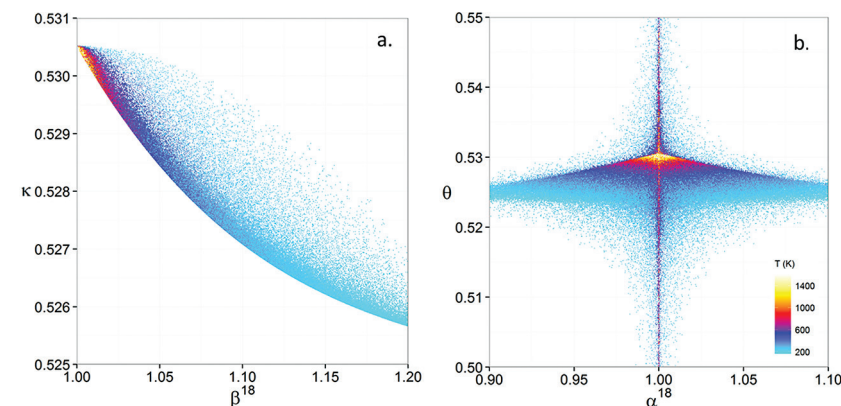
Figure 1 **(a)** β^{18} *vs.* κ and **(b)** Equilibrium α^{18} *vs.* θ plots for randomly selected hypothetical diatomic molecules under the harmonic approximation in the $^{16}O\text{-}^{17}O\text{-}^{18}O$ system. Temperature is plotted as colour on the same scale for both plots. The model uses 1,000,000 evenly distributed randomly generated values for the secondary mass (0-300 AMU), the bond force constant (0-κ_{UL}), and temperature (200-1600 °K). The bond force constant for carbon monoxide (CO) is used as an arbitrary upper limit (UL) for the bond force constant for diatomic oxygen species.

Change/Difference in Cap-Delta

Although κ is expected to be bounded to a first-order approximation by the high temperature and lower limits as described above, the more common mass-dependent fractionation exponent, θ, is not. What is needed is an additional descriptor for multiple isotope fractionation relationships that is bounded for small isotope effects.

Measured multiple isotope relationships are commonly expressed in the "cap-delta" notation.

$$\Delta^{\ddagger}M = \ln\left(R^{\ddagger}_{sample}/R^{\ddagger}_{standard}\right) - C\ln\left(R^{*}_{sample}/R^{*}_{standard}\right) \qquad \text{Eq. 12}$$

typically either in "per mille" or "per meg", where C is a somewhat arbitrary constant and R is the molar ratio of one isotope and a reference isotope of the same element. For example, $\Delta^{\ddagger}M$ becomes $\Delta^{17}O$ for the $^{16}O\text{-}^{17}O\text{-}^{18}O$ system and $\ln\left(R^{\ddagger}_{sample}/R^{\ddagger}_{standard}\right) = \delta'^{17}O$.

The change, or difference in cap-delta, *i.e.* $\Delta(\Delta^{\ddagger}M)$ through a fractionation process is then

$$\Delta\left(\Delta^{\ddagger}M\right) = \ln\alpha^{\ddagger}_{A-B} - C\ln\alpha^{*}_{A-B} \qquad \text{Eq. 13}$$

or reduced to more fundamental parameters

$$\Delta\left(\Delta^{\ddagger}M\right)=\left(C-\kappa_{B}\right)\ln\beta_{B}^{*}-\left(C-\kappa_{A}\right)\ln\beta_{A}^{*} \qquad \text{Eq. 14}$$

Current analytical precision for $\Delta^{\ddagger}M$ can be as low as 0.002 ‰ depending on the element, technique, and species analysed allowing for the resolution of $\Delta(\Delta^{\ddagger}M)$ well within the natural range for many commonly explored light elements (*e.g.*, for oxygen in Fig. 2). Using the $^{16}O\text{-}^{17}O\text{-}^{18}O$ system as an example, if the arbitrary upper limit of β is given as 1.100 and using the boundaries of κ proposed above for equilibrium (0.5232 to 0.5305), a potential range of $\Delta(\Delta^{17}O)$ is then about ±0.7 ‰ ($C = 0.5305$). The ends of this range are not realistic except at very low temperatures (<<0 °C) where values of β become larger and more variable and the lower boundary of κ becomes more obtainable. A more realistic range for equilibrium between natural samples is likely in the vicinity of ±0.3 ‰ ($C = 0.5305$). This value is comparable to measured values for silica-water fractionation near 0 °C (Sharp *et al.*, 2016). Kinetic isotope effects should have more variable $\Delta(\Delta^{17}O)$ values because of their more variable κ values, however the range is expected to be similar to that of equilibrium isotope effects.
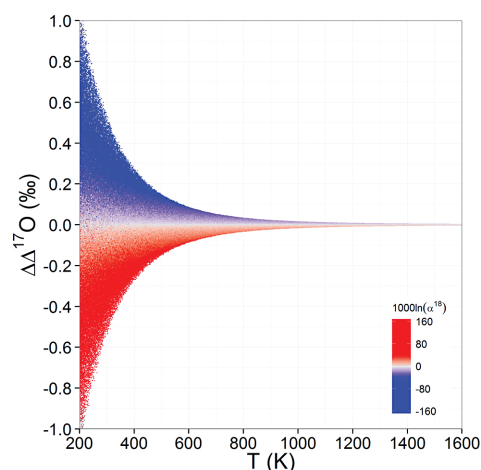

Figure 2   Temperature *vs.* $\Delta(\Delta^{17}O)$ plot for equilibrium between randomly selected diatomic molecules under the harmonic approximation in the $^{16}O\text{-}^{17}O\text{-}^{18}O$ system. A *C* value of 0.5305 (HTL) is used for the $\Delta(\Delta^{17}O)$ definition. $1000 \ln \alpha^{18}$ is plotted as colour. The range of $\Delta(\Delta^{17}O)$ values in this plot is expected to be an overestimate for natural samples. The points in this model each correspond to a point in Figure 1a.

Regardless of the value of *C*, $\Delta(\Delta^{\ddagger}M)$ will approach a high temperature limit of 0 because both β values approach a high temperature limit of 1.000. We recommend the use of the high temperature limit of κ for *C* which will ensure that the $(C-\kappa)$ terms in Equation 14 remain positive. For sufficiently different β values (*i.e.* non-small values of $\ln\alpha_{A\text{-}B}^{*}$) the sign of $\Delta(\Delta^{\ddagger}M)$ will be determined

by the larger β. For positive $\ln\alpha_{A\text{-}B}^{*}$ values, $\Delta(\Delta^{\ddagger}M)$ will tend to be negative and *vice-versa*. This trend is not necessarily expected when α is near unity, particularly at low temperatures.

Haematite-Water Fractionation

For crossover scenarios, there is a guarantee that the determined α value will be near unity. In Bao and Koch (1999) haematite (Fe_2O_3)-water fractionation was measured over a range of near-surface temperatures. Nine samples are selected from this study for new triple oxygen isotope analysis. Details of the analysis and the tabulated results can be found in the Supplementary Information. The new calculated fractionation parameters with their uncertainties and best fits are illustrated in Figure 3.
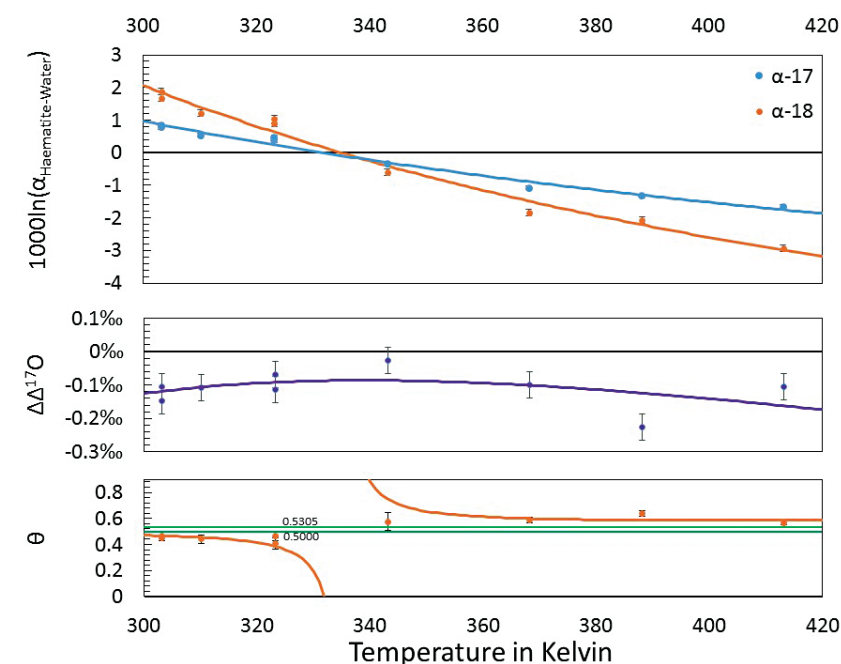

Figure 3   Three isotope fractionation parameters for haematite synthesis conducted by Bao and Koch (1999). Values are calculated from newly measured $\delta^{18}O_{haematite}$ and $\delta^{18}O_{water}$ values, and an assumed $\Delta^{17}O$ ($C = 0.528$) of 0.02 ‰ for the water based on reported Baltimore tap water from Li *et al.* (2015). $\Delta(\Delta^{17}O)$ are reported using $C = 0.5305$. The method for calculating uncertainties can be found in the Supplementary Information. Best fit curves for the $\ln(\alpha)$ values are second order polynomials of $1/T$. The best fit curves for $\Delta(\Delta^{17}O)$ and θ are calculated from the fits to $\ln(\alpha)$.

From the calculated haematite fractionation parameters, it is clear that the crossover temperature is different for α^{17} and α^{18}. With one exception, every experimentally measured θ value exists outside of the typical "canonical" range of θ (approximately 0.5000 to 0.5305) to beyond 1 σ uncertainties. Despite the variability in θ, $\Delta(\Delta^{17}O)$ values remain within a range of -0.026 ‰ to -0.226 ‰ within the theoretically predicted mass dependent range.

Conclusions

Using the simplest application of the B-GM-U model, it is shown theoretically that values of the mass fractionation exponent, θ, are unbounded and particularly variable for small fractionations and at low temperatures. This is in contrast to the mass-fractionation exponent, κ, which is bounded by upper and lower limits. As a supplemental mass-fractionation descriptor, $\Delta(\Delta^{\ddagger}M)$ is suggested on a theoretical basis because it remains within a finite range for mass-dependent fractionations. The haematite-water system at near surface temperatures is cited as an example of deviations from the "canonical" range of θ for oxygen. These deviations are found to be consistent with a finite range of $\Delta(\Delta^{17}O)$. It is our opinion based on the results of this study that even for elemental processes the concept of a "canonical" range of θ values is not well founded and should be applied with caution.

Acknowledgements

Additional Information

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■ The statistical mechanical basis of the triple isotope fractionation relationship

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▎ Supplementary Information

The Supplementary Information includes:

➤   Anharmonic Correction

➤   Kinetic Isotope Effects

➤   Experimental Methods

➤   Calculation of Parameters for Haematite Water Fractionation

➤   Computational Methods

➤   Tabulated Oxygen Isotope Results for Haematite Precipitation (Table S-1)

➤   Supplementary Information References

Anharmonic Correction

The harmonic approximation yields the largest contributions to both β and κ for any isotope system. However, for hydrogen bearing molecules, corrections for anharmonicity become significant enough to consider. The complete expression, accounting for anharmonicity, for the vibrational contribution to the energy levels of a diatomic molecule is given by

$$E_n^* = G_0^* + \left(\frac{1}{2} + n\right)h\omega^* - \left(\frac{1}{2} + n\right)^2 \omega^* x^* + Higher\ Order\ Terms \qquad \text{Eq. S-1}$$

where the second term corresponds to harmonic vibrations (Wolfsberg, 1969). The first and third terms give the anharmonic correction and

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$$G_0^* = \frac{21}{2}\gamma + \frac{1}{2}\delta \qquad\qquad \text{Eq. S-2}$$

$$\omega^* x^* = -90\gamma - 2\delta \qquad\qquad \text{Eq. S-3}$$

where δ and γ are functions of the parameters of the anharmonic potential, and μ the bond force constant. Because both δ and γ are proportional to $1/\mu$, both G_0 and ωx are proportional to $1/\mu$ (Wolfsberg, 1969). The value of κ for the G_0 contribution for a diatomic molecule is then simply given by

$$\kappa_{G_0 - D} = \frac{1/\mu - 1/\mu^\ddagger}{1/\mu - 1/\mu^*} = \frac{1/m - 1/m^\ddagger}{1/m - 1/m^*} \qquad\qquad \text{Eq. S-4}$$

which has a constant value equal to the high-temperature limit for harmonic vibrations. The zero-point energy of the remaining anharmonic term, which gives the majority of the correction, is given by $\omega x/4$ which yields a κ value also equal to the correction from G_0. The constancy of this value, although treated as the complete correction, was originally determined by Cao and Liu (2011). The κ values for the excited state contributions to this term as well as higher order corrections are not calculated here but have respective β values that are expected to be small enough to mostly be neglected for any system.

The effect of anharmonic corrections on the value of κ is treated in the same manner as additional vibrational degrees of freedom so that the final κ value is equal to the sum of the $\ln\beta$ weighted contributions from the anharmonic correction and harmonic κ values. Because the anharmonic corrections are small (<5 % for hydrogen) relative to the harmonic contribution and have a predictable and equal κ value, incorporation of the anharmonic correction yields only a slightly lower value of κ than the harmonic model. Although the small percent change in the value of κ is valid for polyatomic molecules, the value of κ may not necessarily be equal to the harmonic high temperature limit. As a result, incorporation of the anharmonic correction may not strictly decrease κ relative to the harmonic model for polyatomic molecules, but its effect will still be small.

Kinetic Isotope Effects

Kinetic isotope effects can be modelled as equilibrium between the relevant reactant and the transition state with the modification that one degree of freedom for the transition state corresponds to the decomposition mode (Bigeleisen and Wolfsberg, 1958). This can be described as a two mass harmonic oscillator with a negative bond force constant, and hence an imaginary frequency, and is applied by multiplying Equation 2 in the main text (minus one degree of freedom) by the ratio of the imaginary frequencies for the differently substituted states (Bigeleisen and Wolfsberg, 1958). The value of κ for the imaginary frequency contribution is then given by

$$\kappa_{IF} = \frac{\ln(\mu^\ddagger) - \ln(\mu)}{\ln(\mu^*) - \ln(\mu)} \qquad\qquad \text{Eq. S-5}$$

where μ corresponds to the reduced mass of the decomposition fragments. Because the imaginary frequency contribution to β is always less than 1.000, the result of Equation S-5, on average, results in higher values of κ for transition states, but a higher value is not necessarily the case. Because of this, κ for the transition state including the imaginary frequency contribution does not remain bounded by the harmonic limits described above but should remain within or near those boundaries for species with large contributions from other vibrational degrees of freedom. The result is that θ for kinetic isotope effects have a wider distribution than for equilibrium isotope effects. As previous research has shown, normal kinetic isotope effects are expected to exhibit, on average, lower values of θ (Young et al., 2002; Bao et al., 2015). However, we emphasise that kinetic isotope effects should not be strictly associated with low θ values, but rather, more variable θ values.

Experimental Methods

The iron oxide materials used for this study were originaly precipitated for a study by Bao and Koch (1999). The iron oxides were stored as dry powders for nearly a decade and a half in centrifuge tubes since their original precipitation and processing. All processing of the samples apart from the new triple oxygen isotope analysis were conducted for the original study (Bao and Koch, 1999). From the available samples, 9 synthetic haematite samples were selected based on the process used. All selected samples were precipitated from $NaOH + HCO_3^-$ solutions (molar ratios OH / Fe $\approx$ 3, HCO_3^- / Fe $\approx$ 0.7) at various temperatures for times ranging from 24 hours to 190 days depending on reaction temperature. Samples using this precipitation procedure were chosen because this procedure consistently generated haematite (as opposed to goethite and akaganeite) over the entire temperature range. The samples were then washed in a HCl solution to eliminate amorphous phases and then dried. XRD results for the selected samples show that the samples were pure haematite with the exception of sample CH-19A which may contain trace goethite (Bao and Koch, 1999).

In the 1999 study, haematite samples were converted to O_2 by CO_2-laser fluorination and analysed for $\delta^{18}O$ on a Thermo Finnigan MAT 252 isotope ratio mass spectrometer at the Geophysical Laboratory, Carnegie Institute, Washington. The O_2 yields were at or near 100 % for these samples with a precision of ±0.05 ‰ and duplicate analyses being within 0.3 ‰ for $\delta^{18}O$ (Bao and Koch, 1999). Water with a known $\delta^{18}O$ composition (-8.0 ‰ ± 0.1 ‰) was used for all synthesis solutions. The water that was used is doubly deionised New Jersey tap water. The $\delta^{18}O$ of the water was determined by CO_2 equlibration on a Micromass Isoprep 18 automated water analysis system interfaced with an Optima isotope

ratio mass spectrometer at the Department of Geosciences, Princeton University (Bao and Koch, 1999). Further details, descriptions and notes on the above procedures can be found in Bao and Koch (1999).

New analysis of the haematite samples from Bao and Koch (1999) was conducted at Louisiana State University. Haematite samples were analysed for triple oxygen isotope composition as O_2 on a Thermo Finnigan MAT 253 isotope ratio mass spectrometer. Precision of O_2 isotope analysis is on the order of 0.03 ‰ or better for both the $\delta^{18}O$ and $\Delta'^{17}O$. Prior to conversion to O_2, haematite samples were placed in a 20 torr BrF_5 atmosphere overnight to eliminate adsorbed water. Haematite samples were converted to O_2 by laser fluorination in a ~20 torr BrF_5 atmosphere. The resulting O_2 gas was purified using a series of LN_2 cooled U-traps before being collected into 5 Å molecular sieve for transfer to the mass spectrometer. The triple oxygen isotope composition of the O_2 derived from each haematite sample is initialy measured in dual inlet mode relative to a house standard, LSU-O_2 ($\delta^{18}O$ = 17.540 ‰; $\delta^{17}O$ = 8.84 ‰). The house standard was initially calibrated to VSMOW using O_2 gas derived from BrF_5 laser fluorination of a dozen of UWG-2 samples using the same procedure described above. The $\delta^{18}O$ (5.800 ‰) for UWG-2 is taken from Valley *et al.* (1995) and an assigned $\delta^{17}O$ value of 3.016 ‰. These values give UWG-2, according to our lab reference scale, a $\Delta'^{17}O$ (C = 0.5305) of -0.057 ‰ which is between the reported values of -0.019 ‰ and -0.113 ‰ from Young *et al.* (2016) and Pack and Herwartz (2014, 2015) respectively.

Calculation of Parameters for Haematite Water Fractionation

Values for θ, $\Delta\delta'^{18}O$ (=1000 ‰ ln α^{18}), $\Delta\delta'^{17}O$ and $\Delta(\Delta'^{17}O)$ are calculated using the equations

$$\delta'^{17}O_{water} = 0.528 * \delta'^{18}O_{water} + \Delta'^{17}O_{water(C=0.528)} \qquad \text{Eq. S-6}$$

$$\Delta'^{17}O_{water(C=0.5305)} = \delta'^{17}O_{water} - 0.5305 * \delta'^{18}O_{water} \qquad \text{Eq. S-7}$$

$$\delta'^{17}O_{haematite} = 0.5305 * \delta'^{18}O_{haematite} + \Delta'^{17}O_{haematite(C=0.5305)} \qquad \text{Eq. S-8}$$

$$\Delta\delta'^{17}O_{haematite-water} = \delta'^{17}O_{haematite} - \delta'^{17}O_{water} \qquad \text{Eq. S-9}$$

$$\Delta\delta'^{18}O_{haematite-water} = \delta'^{18}O_{haematite} - \delta'^{18}O_{water} \qquad \text{Eq. S-10}$$

$$\theta_{haematite-water} = \frac{\Delta\delta'^{17}O_{haematite-water}}{\Delta\delta'^{18}O_{haematite-water}} \qquad \text{Eq. S-11}$$

and

$$\Delta\left(\Delta'^{17}O\right)_{haematite-water} = \Delta'^{17}O_{haematite(C=0.5305)} - \Delta'^{17}O_{water(C=0.5305)} \qquad \text{Eq. S-12}$$

Uncertainties for each fractionation parameter are calculated using a Monte Carlo method. The method uses the above equations, inputs for each known parameter and their respective 1 σ uncertainties. These input uncertainties include those for the new haematite $\delta^{18}O$ and $\Delta'^{17}O$ measurements (±0.03 ‰), the uncertainty of the original water $\delta^{18}O$ measurement (±0.1 ‰) and an assumed uncertainty of the $\Delta'^{17}O$ of the water used for precipitation (±0.02 ‰; C = 0.528). The uncertainty for the $\Delta'^{17}O$ of the water was chosen so that nearly all reported values for the $\Delta'^{17}O$ for tap waters in the continental United States lie within 1 σ of the central value (Li *et al.*, 2015). A distribution of 1000 values are generated for each parameter with the same statistics as the respective parameter. These values are then processed through Equations S-6 through S-12 and the mean and standard deviation are calculated for the results. The distributions for $\Delta\delta'^{17}O$, $\Delta\delta'^{18}O$ and $\Delta(\Delta'^{17}O)$ are found to be normal in all cases, but the distributions of θ are slightly skewed. For θ, the central value is the median and the uncertainties correspond to the 84.1 % and 15.9 % quantiles giving the boundaries of the central 68.2 % of the distribution. The median is chosen, as opposed to the mean for θ, because it gives the same result as the solution using only the central values of the inputs. As a caveat, the results of the calculated haematite-water fractionation parameters given here assume that the calibrations of Li *et al.* (2015) and Bao and Koch (1999) for water isotope analysis are consistent with our calibration. Slight differences in calibration to SMOW/VSMOW between studies may have an effect on the calculated values of each parameter but this is not expected to be significant for the range of θ values.

Computational Methods

We utilise a Monte Carlo approach to provide a visual representation of the results of this study (Main Text, Figs. 1 and 2). The Monte Carlo models use the diatomic special case for ease of calculation because the vibrational frequency can be simply described as a function of the bond force constant and reduced mass. The model uses 1,000,000 evenly distributed randomly generated values for the secondary mass (0-300 AMU), the bond force constant (0-κ_{UL}), and temperature (200-1600 °K). The bond force constant for carbon monoxide (CO) is used as an arbitrary upper limit (UL) for the bond force constant for diatomic oxygen species. All calculations were performed in R (R Core Team, 2012).

Tabulated Oxygen Isotope Results for Haematite Precipitation

Table S-1 Results from both previous δ^{18}O (converted to logarithmic definition) measurements from Bao and Koch (1999) and new δ'^{18}O and Δ^{17}O analysis from this study. δ'^{17}O values for the water are calculated using the δ'^{18}O values for the water measured by Bao and Koch (1999) and published Δ^{17}O values for Baltimore tap water (Li *et al.*, 2015). Values of α are for haematite precipitation with oxygen sourced from water (α$_{haematite-water}$). The method for determining uncertainties is described in the text of the Supplementary Information. All uncertainties are 1 σ.

Sample Name	T in K	Previous δ'^{18}O (‰) SMOW	δ'^{18}O (‰) VSMOW	δ'^{17}O (‰) VSMOW	Δ^{17}O (‰) VSMOW	1000 ln (α^{18})	1000 ln (α^{17})	θ	Δ(Δ^{17}O) (‰) VSMOW
CH-20A	303.15	-6.9239	-6.1482	-3.369	-0.1074	1.8828 ± 0.1067	0.8513 ± 0.0653	0.4525 (+0.0197; -0.0207)	-0.1475 ± 0.0398
CH-20B	303.15	-6.9239	-6.3531	-3.4352	-0.0649	1.6778 ± 0.1067	0.785 ± 0.0653	0.468 (+0.0226; -0.0226)	-0.105 ± 0.0398
CH-19A	310.15	-7.7298	-6.8148	-3.6828	-0.0675	1.2161 ± 0.1067	0.5375 ± 0.0653	0.4428 (+0.0302; -0.033)	-0.1077 ± 0.0398
CG-13A	323.15	-7.8305	-7.1179	-3.8504	-0.0743	0.913 ± 0.1067	0.3699 ± 0.0653	0.4067 (+0.0409; -0.0462)	-0.1145 ± 0.0398
CG-13B	323.15	-7.8305	-6.9974	-3.7403	-0.0282	1.0335 ± 0.1067	0.4799 ± 0.0653	0.465 (+0.0361; -0.038)	-0.0683 ± 0.0398
CG-12B	343.15	-8.5363	-8.6214	-4.5597	0.0139	-0.5904 ± 0.1067	-0.3394 ± 0.0653	0.5761 (+0.0689; -0.065)	-0.0262 ± 0.0398
CH-15A	368.15	-9.9493	-9.8669	-5.2947	-0.0603	-1.8359 ± 0.1067	-1.0744 ± 0.0653	0.5859 (+0.0212; -0.0225)	-0.1004 ± 0.0398
CH-17A	388.15	-10.2524	-10.0992	-5.5437	-0.1861	-2.0682 ± 0.1067	-1.3234 ± 0.0653	0.6404 (+0.02; -0.0207)	-0.2262 ± 0.0398
CH-16A	413.15	-10.5555	-10.9575	-5.8772	-0.0643	-2.9265 ± 0.1067	-1.657 ± 0.0653	0.5664 (+0.0131; -0.0136)	-0.1044 ± 0.0398

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