Triple Oxygen Isotopes: Fundamental Relationships and Applications

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Abstract

The element oxygen has three stable isotopes: ^{16}O, ^{17}O, and ^{18}O. For a defined process, a change in $^{18}O/^{16}O$ scales with the corresponding change in $^{17}O/^{16}O$, or the fractionation factors $^{18}\alpha$ and $^{17}\alpha$ have a relationship of $\theta = \ln^{17}\alpha/\ln^{18}\alpha$, in which the triple oxygen isotope exponent θ is relatively fixed but does vary with reaction path, temperature, and species involved. When the small variation is of interest, the distinction of three concepts—θ, S (a slope through data points in $\delta^{17}O$–$\delta^{18}O$ space), and C (an arbitrary referencing number for the degree of ^{17}O deviation)—becomes important. Triple oxygen isotope variations can be measured by modern instruments and thus offer an additional line of information on the underlying reaction processes and conditions. Analytical methods and Earth science applications have recently been developed for air oxygen, carbon dioxide, water, silicates, oxides, sulfates, carbonates, and phosphates.

1. INTRODUCTION

Isotopes refer to different nuclides of the same chemical element. Because they belong to the same element, the number of protons is fixed; therefore, isotopes differ only in the number of neutrons in the nuclides. There are stable and radiogenic isotopes, with the latter decaying spontaneously to daughter nuclides at certain fixed rates. Some elements, such as F and P, have only one stable isotope or a single stable nuclide. Others, such as H, O, S, and Fe, can have two, three, or more stable isotopes.

Oxygen's three stable isotopes, ^{16}O, ^{17}O, and ^{18}O, bear 8, 9, and 10 neutrons in their respective nuclides (**Table 1**). Chemically, they are almost identical because chemical properties are dominantly determined by the behavior of electrons in the atom. Thus, some might tend to think of them as three siblings in the oxygen family, with differences mainly in mass. But sibling would be a terribly wrong description of the three oxygen isotopes' original birth order or family line in the universe. In fact, ^{16}O is the parent of ^{17}O, and the birth of ^{18}O has nothing to do with either ^{16}O or ^{17}O. ^{16}O is the natural product of nuclear fusion of helium burning in stars. It is the most abundant nuclide synthesized in the stars and the third most abundant nuclide in the universe, next only to ^{1}H and ^{4}He, which were created just after the Big Bang (Clayton 2003). ^{17}O, formed via $^{16}O + {}^{1}H \rightarrow {}^{17}F \rightarrow {}^{17}O$, cannot be synthesized directly from H and He in stars, because H is consumed before the generation of ^{16}O and thus the ^{16}O never has a chance to meet hydrogen in the same primary star. Therefore, ^{17}O has to form in stars that have already acquired some ^{16}O from earlier dead stars. ^{17}O is thus a secondary nuclide, not a primary nuclide as ^{16}O is. Similarly, ^{18}O is not a primary nuclide. It is formed via $^{14}N + {}^{4}He \rightarrow {}^{18}F \rightarrow {}^{18}O$ in stars that already had initial ^{12}C or ^{14}N derived from earlier dead stars (Clayton 2003). Our solar nebula was a mixture of many sources and generations of stellar materials. The Solar System abundances of the three stable oxygen isotopes are shown in **Table 1**.

Triple oxygen isotope studies on meteorites in the Solar System have been previously synthesized (Clayton 1993, MacPherson et al. 2008, Thiemens et al. 2012, Wasson 2000). This review focuses on their fundamental relationships and on processes occurring within the Earth system. A subset of the triple oxygen isotope studies on Earth systems is focused on distinctly ^{17}O-anomalous atmospheric O_3 and its derivative gas and solid compounds. Thiemens' group and others have published thorough reviews on these observations, experiments, and mechanistic interpretations (Bao 2015; Brenninkmeijer et al. 2003; Thiemens 2003, 2006; Thiemens et al. 2001, 2012). Therefore, this review touches only lightly upon triple oxygen isotope studies pertinent to atmospheric chemistry.

There are many other elements that have three or more isotopes, and the relationships among multiple isotopes of the same element have been explored to variable degrees—for example, hydrogen (^{1}H, ^{2}H, and ^{3}H) (Hirschi & Singleton 2005, Kohen & Jensen 2002, Swain et al. 1958), sulfur (^{32}S, ^{33}S, ^{34}S, and ^{36}S) (Farquhar et al. 2000, 2007; Ono et al. 2006), silicon (^{28}Si, ^{29}Si, and ^{30}Si) (Armytage et al. 2012, Georg et al. 2007, Yeh & Epstein 1978), mercury (^{199}Hg, ^{200}Hg, ^{201}Hg, and ^{202}Hg) (Bergquist & Blum 2007), magnesium (^{24}Mg, ^{25}Mg, and ^{26}Mg) (Wiechert &

Table 1 The three stable isotopes of the element oxygen

Isotope	Symbol	Protons	Neutrons	Mass (u)	Spin	Solar System abundance (%)
Oxygen-16	^{16}O	8	8	15.9949146	0+	99.762
Oxygen-17	^{17}O	8	9	16.9991315	5/2+	0.038
Oxygen-18	^{18}O	8	10	17.9991604	0+	0.200

Halliday 2007, Young & Galy 2004), iron (^{54}Fe, ^{56}Fe, and ^{57}Fe) (Dauphas et al. 2009), and tin (^{116}Sn, ^{118}Sn, ^{120}Sn, and ^{124}Sn) (Osawa et al. 2009). Note that the three or more isotopes need not all be stable as long as the isotopes are stable within the time frame of interest. For example, ^{3}H (Kohen & Jensen 2002) and ^{14}C (Yankwich et al. 1954) are radioisotopes, or radionuclides, with half-lives of 12.32 years and 5,730 ± 40 years, respectively. Principles, concepts, and applications laid out in this review can be laterally applied to these other multiple isotope systems.

2. TERMINOLOGY AND FUNDAMENTAL RELATIONSHIPS

2.1. Two-Isotope System

Before we explore the triple oxygen isotope relationship, we first review the concept of isotope ratios used to describe isotope composition.

R denotes the ratio between the number of moles of a minor isotope and a reference isotope of an element. Conventionally, the reference isotope will have a much higher abundance than the minor isotope. For oxygen, ^{18}R (^{18}O/^{16}O) is a very small number, near 0.002. For analytical reasons and for convenience, the notation δ was introduced (McKinney et al. 1950) to denote the isotope composition of a compound, and it is widely used in Earth, environmental, and biological communities:

$$\delta \equiv (R_{\text{sample}}/R_{\text{reference}}) - 1. \tag{1}$$

The δ notation is just one of several ways to express a small difference in ratio with respect to that of a reference material. Another notation, δ′, was first introduced by Hulston & Thode (1965) and was subsequently adopted by others (e.g., Miller 2002, Ono et al. 2006, Young et al. 2002):

$$\delta' \equiv \ln(R_{\text{sample}}/R_{\text{reference}}). \tag{2}$$

This δ′ concept is the same as the concept of Ln*O (where * represents 17 or 18) from Angert et al. (2003). Although messy for mixing calculations, the δ′ notation simplifies most other mathematical treatments involving isotope fractionation processes. It is noted that

$$\delta' = \ln(\delta + 1). \tag{3}$$

To avoid messiness, we recommend that the × 1,000‰ factor be omitted from any of the derivations and reported only at the end of operations.

The fractionation factor α measures the degree of isotope fractionation between two compounds A and B:

$$\alpha \equiv R_{\text{A}}/R_{\text{B}}. \tag{4}$$

Only two αs have an intrinsic thermodynamic basis: equilibrium α (α_{eq}) and kinetic isotope effect (KIE). All other αs are apparent αs. Both α_{eq} and KIE can be calculated, and they are a function of temperature *T* once the process in question is defined. For example, $\alpha_{\text{eq(A-B)}} \equiv \beta_{\text{A}}/\beta_{\text{B}}$, in which β_{A} is the isotope fractionation factor between compound A and a hypothetical unbound monatomic oxygen. Thus, α is always associated with a process or a set of physicochemical processes, whereas *R* and δ′ are intensive properties of a compound and do not have to be associated with a process. For an equilibrium system A-B, with forward reaction(s) KIE as $\text{KIE}_{\text{TS-A}}$ and backward reaction(s) KIE as $\text{KIE}_{\text{TS-B}}$, we have

$$\alpha_{\text{eq(A-B)}} = \frac{\text{KIE}_{\text{TS-B}}}{\text{KIE}_{\text{TS-A}}}, \tag{5}$$

where TS stands for transition state.

2.2. Triple Isotope System

In addition to the concepts already used for a two-isotope system, a triple isotope system has at least four additional concepts: κ, θ, S, and C. The values of κ and θ are intrinsic properties of a compound and of a defined process, respectively; S is a phenomenological expression of a defined or undefined process; and C is an arbitrary reference number. The term κ is defined as $\kappa \equiv \ln^{17}\beta/\ln^{18}\beta$. It is a function of the mass and temperature (Cao & Liu 2011).The term θ is defined as $\theta \equiv \ln^{17}\alpha/\ln^{18}\alpha$. Similar to α, there are two intrinsic θs: θ_{eq} and θ_{KIE} ($\theta_{\mathrm{TS-A}}$ or $\theta_{\mathrm{TS-B}}$). The rest are apparent θs (Bao et al. 2015):

$$\theta_{\mathrm{TS\text{-}A}} \equiv \frac{\ln {}^{17}\mathrm{KIE}_{\mathrm{TS\text{-}A}}}{\ln {}^{18}\mathrm{KIE}_{\mathrm{TS\text{-}A}}}. \qquad (6)$$

This is one side of the reaction(s) for an equilibrium process. The other side is

$$\theta_{\mathrm{TS\text{-}B}} \equiv \frac{\ln {}^{17}\mathrm{KIE}_{\mathrm{TS\text{-}B}}}{\ln {}^{18}\mathrm{KIE}_{\mathrm{TS\text{-}B}}},$$

and therefore,

$$\theta_{\mathrm{eq}} = \frac{\ln^{17}\alpha}{\ln^{18}\alpha} = \frac{\ln\left(\frac{{}^{17}\mathrm{KIE}_{\mathrm{TS\text{-}B}}}{{}^{17}\mathrm{KIE}_{\mathrm{TS\text{-}A}}}\right)}{\ln\left(\frac{{}^{18}\mathrm{KIE}_{\mathrm{TS\text{-}B}}}{{}^{18}\mathrm{KIE}_{\mathrm{TS\text{-}A}}}\right)},$$

or

$$\theta_{\mathrm{eq}} = \theta_{\mathrm{TS\text{-}B}} + (\theta_{\mathrm{TS\text{-}B}} - \theta_{\mathrm{TS\text{-}A}})\frac{\ln {}^{18}\mathrm{KIE}_{\mathrm{TS\text{-}A}}}{\ln^{18}\alpha_{\mathrm{eq}}}. \qquad (7)$$

This θ_{KIE} concept is critical to understanding equilibrium and nonequilibrium processes in the framework of transition state theory.

The S value is a slope value in δ^{17}O–δ^{18}O or δ'^{17}O–δ'^{18}O space for a set of samples that may or may not be closely linked. As listed in the sidebar, many in the literature have used λ to represent this linear coefficient. Indeed, some of the S values are well defined. For example, if data pairs collected from a closed-system Rayleigh process are plotted, then $S = (\alpha^{17} - 1)/(\alpha^{18} - 1)$, from which intrinsic or apparent αs can be obtained (Barkan & Luz 2007, Blunier et al. 2002, Luz & Barkan 2010). There is an S (λ) value of 0.5179 for most organisms during ordinary respiration (Luz & Barkan 2005) and of 0.5228 for O_2 diffused into N_2 (Angert et al. 2003). An S value can also be obtained by plotting data pairs collected from a recovering system after it is perturbed, as is done in the terrarium experiment (Luz et al. 1999). For even more loosely related processes, researchers have often plotted δ^{17}O–δ^{18}O data pairs of the same group of chemical compounds from diverse space and time and obtained an S value (e.g., Rumble et al. 2007). Quite often, an S value represents the coefficient of triple oxygen isotope data pairs of undefined relationship, from which the underlying intrinsic or even apparent αs or θs are unlikely to be extracted.

Finally, C is an arbitrary number used to define a different reference frame. In order to compare triple oxygen isotope relationships to single out the ^{17}O deviation, researchers often shift to a new reference frame from which the deviation of ^{17}O can be quantified as Δ^{17}O, defined as $\Delta^{17}\mathrm{O} \equiv \delta^{17}\mathrm{O} - C \times \delta^{18}\mathrm{O}$ or $\Delta'^{17}\mathrm{O} \equiv \delta'^{17}\mathrm{O} - C \times \delta'^{18}\mathrm{O}$. Many values of C have been used in the literature, and four options stand out.

The first option is the use of a compound-specific S value as the reference slope C for a particular compound. For example, diverse water samples are measured for both δ^{17}O and δ^{18}O (or δ'^{17}O and δ'^{18}O), and then a slope is determined in δ^{17}O–δ^{18}O (or δ'^{17}O–δ'^{18}O) space (e.g., Angert et al. 2004, Luz & Barkan 2010, Meijer & Li 1998). The same practice has been performed for N_2O gas (Cliff & Thiemens 1997), sulfate (Bao et al. 2000), carbonate (Miller et al. 2002), and silicate

SUGGESTED USE OF θ, *S*, *C*, AND THEIR EQUIVALENTS IN THE LITERATURE

- **θ: defined as the ratio of $\ln^{17}\alpha/\ln^{18}\alpha$, an intrinsic fractionation relationship**
  - **θ_{eq} (triple oxygen isotope exponent for an equilibrium process):**
    - θ values for CO_2(g)-water, quartz-water, and calcite-water oxygen isotope exchange reactions at temperatures from 0°C to 100°C (Cao & Liu 2011)
    - $\theta = 0.529 \pm 0.001$ for water liquid-vapor equilibrium at temperatures from 11.4°C to 41.5°C (Barkan & Luz 2005)
    - *R*, ratio of liquid-vapor isotope fractionation factors (Chialvo & Horita 2009)
    - $\lambda_{33/34} = 0.551 \pm 0.010$ for SF_6 ice-vapor equilibrium at 155 K (Eiler et al. 2013)
    - Equilibrium β (Young et al. 2002)
    - $\theta = 0.522\mathrm{X}$ for CO_2-water equilibrium (Barkan & Luz 2012, Hofmann et al. 2012)
    - $\beta = 0.5240 \pm 0.0011$ at 685°C for CO_2(g)-CeO_2 oxygen exchange (Hofmann & Pack 2010)
  - **θ_{KIE} [triple oxygen isotope exponent for kinetic isotope effect (KIE)]:**
    - Kinetic β (Young et al. 2002)
  - **θ_{diff} (triple oxygen isotope exponent for a diffusion process):**
    - $\theta = 0.5185$ for water vapor diffusion in zero-relative-humidity air (Barkan & Luz 2007)
    - $\theta = 0.5228$ for O_2 diffusion into N_2 (Angert et al. 2003)
  - **θ_{appa} (an apparent triple oxygen isotope exponent for a process when elemental processes are not specified or difficult to delineate):**
    - θ (Mook 2001)
    - λ (Blunier et al. 2002)
- ***S*: a slope value in $\delta^{17}O$–$\delta^{18}O$ or $\delta'^{17}O$–$\delta'^{18}O$ space**
  - **For a defined process:**
    - $\gamma = 0.528 \pm 0.001$ for meteoric water experiencing Rayleigh distillation (Barkan & Luz 2007, Blunier et al. 2002, Luz & Barkan 2010)
    - $\gamma = 0.5179 \pm 0.0006$ for the kinetic respiration process for dominant O_2 consumers in aquatic systems (Luz & Barkan 2005)
    - $\theta = 0.515$ for O_2 in biological steady state with seawater (Luz & Barkan 2005)
    - $m = 1.00, 0.98$ during O_2 electrolysis (Heidenreich & Thiemens 1983, 1986; Thiemens & Heidenreich 1983)
    - Slope $= 0.5211 \pm 0.0005$ for O_2 evolving in a terrarium experiment when air O_2 is the reference (Luz et al. 1999)
    - $\lambda = 0.5111 \pm 0.0013$ to 0.5204 ± 0.0005 during the leaf transpiration process, increasing with decreasing atmospheric relative humidity (Landais et al. 2006)
    - Slope $= 0.5247 \pm 0.0007$ for carbonate thermolysis (0.5198 ± 0.0007 for protracted thermolysis) (Miller et al. 2002)
  - **For samples that may or may not be linked by a set of processes:**
    - Slope $= +1/2$ for a collection of terrestrial (rocks and water) and lunar samples (Clayton et al. 1973)
    - 0.5164 ± 0.0033 for 35 terrestrial waters and rocks (Matsuhisa et al. 1978)
    - λ' (Miller 2002)
    - $\lambda = 0.5259$ for terrestrial silicates (Spicuzza et al. 2007)
    - $C = 0.525$ for various natural water samples (Angert et al. 2004)
    - $\lambda = 0.5240$ to 0.5242 ± 0.0010 for hydrothermal quartz and 0.5262 ± 0.0008 to 0.5266 ± 0.0012 for high-temperature and high-pressure garnets (Rumble et al. 2007)

  - Slope $= 0.5244 \pm 0.0004$ for silicates and other oxides (Miller et al. 1999)
  - $\beta = 0.5237$ for terrestrial rocks and minerals (Pack et al. 2007)
  - $\lambda = 0.526 \pm 0.003$ for silicates and $\lambda = 0.528 \pm 0.001$ for waters (Kusakabe & Matsuhisa 2008)
  - $\lambda = 0.524$ as an assigned value for terrestrial silicates (Hallis et al. 2010)
  - $\beta = 0.5250 \pm 0.0007$, "analyses of terrestrial rocks and minerals ($n = 290$) including silicates, oxides, and phosphates" (Gehler et al. 2011)
  - $\lambda' = 0.5248 \pm 0.0003$ for terrestrial silicates (Ahn et al. 2012)
  - Slope $= 0.527$ for a set of silicates (Bindeman et al. 2014)
  - $\lambda = 0.5270 \pm 0.0005$ and $\Delta = -0.07‰ \pm 0.005‰$ for terrestrial silicates and oxides; $\lambda = 0.5285 \pm 0.0005$ and $\Delta = 0.03‰ \pm 0.02‰$ for meteoric water when λ is defined as $\ln(\delta^{17}O + 1) = \lambda \ln(\delta^{18}O + 1) + \Delta$ (Tanaka & Nakamura 2013)
  - $\lambda = 0.5281 \pm 0.0015$ for natural freshwaters and salt waters (Meijer & Li 1998)
  - $\lambda = 0.5279 \pm 0.0001$ between two water standards, Standard Light Antarctic Precipitation (SLAP) and Greenland Ice Sheet Precipitation (GISP) (Barkan & Luz 2005)
  - Slope $= 0.528$ for surface snow samples taken along an Antarctic transect (Landais et al. 2008a)
  - Slope $= 0.5280 \pm 0.0001$ for an expanded data set in δs (Luz & Barkan 2010)
- ***C*: an arbitrary number in the definition of $\Delta^{17}O$ ($\equiv \delta^{17}O - C\delta^{18}O$ or $\delta'^{17}O - C\delta'^{18}O$)**
  - 0.52, in $\Delta^{17}O \equiv \delta^{17}O - 0.52\delta^{18}O$ (Bao et al. 2000, Clayton & Mayeda 1988, Thiemens et al. 1995b)
  - 0.515 for N_2O in $\Delta^{17}O \equiv \delta^{17}O - 0.52\delta^{18}O$ (Cliff & Thiemens 1997)
  - $\beta = 0.516$ in $\Delta^{17}O \equiv \delta'^{17}O - \beta\delta'^{18}O$ (Kaiser et al. 2004)
  - 0.52, in a form of $\Delta^{17}O \equiv (\delta^{17}O + 1) - (1 + \delta^{18}O)^{0.52}$ (Farquhar et al. 1998, 1999)
  - $\lambda' = 0.52$ (Miller 2002)
  - $C = 0.525$ for water (Angert et al. 2004)
  - $\beta = 0.5305, 0.5288 \pm 0.0031$ (Wiechert et al. 2004)
  - $\beta = 0.5250 \pm 0.0007$ (Gehler et al. 2011)
  - $\beta = 0.528$ passing through San Carlos Olivine as the reference (Young et al. 2016)
  - $\lambda_{RL} = 0.5251 \pm 0.0007$ and $\gamma_{RL} = -0.048‰$ in a form of $\Delta^{17}O \equiv \delta'^{17}O - \lambda_{RL}\delta'^{18}O - \gamma_{RL}$ (Pack et al. 2013)
  - $\lambda_{ref} = 0.528$ in $\Delta^{17}O \equiv \delta'^{17}O - \beta\delta'^{18}O$ (Passey et al. 2014)
  - $\lambda_{RL} \equiv 0.5305$ (Pack & Herwartz 2014, 2015)
  - $\lambda = 0.524$–0.526 (Miller et al. 2015, Starkey et al. 2015)
  - $\lambda_0 = 0.516$ for atmospheric CO_2 (Boering et al. 2004, Liang & Mahata 2015)
  - $\lambda = 0.522 \sim 0.531$ for terrestrial silicates and oxides (Levin et al. 2014)

(Ahn et al. 2012, Kusakabe & Matsuhisa 2008, Miller et al. 2015, Rumble et al. 2007). This adoption of a compound-specific S as C appears to be practical. However, adjustment of the slope value can always be achieved by changing the sample size and/or coverage. There is no theoretical basis for picking a certain value as a reference C in this manner.

The second option is to use a process-specific S value as the C value for that specific process. When a process-specific S is used to define $\Delta'^{17}O$, one is comparing the $\delta'^{17}O$ deviation from a specific process that has a slope of S (also known as λ) and often a nonzero intercept in $\delta'^{17}O$–$\delta'^{18}O$ space. For example, the global meteorological cycle gives an S value of 0.528, with the line intercepting at approximately 0.04‰ on the $\delta'^{17}O$ axis when the $\delta'^{18}O$ is at 0 [i.e., at Vienna Standard Mean Ocean Water (VSMOW) (Luz & Barkan 2010)]. The advantage of using process-specific S (λ) is to see deviations from a typical set of processes more directly. However, both

S (λ) and the intercept of a specific process in question can change over time with improved measurement in both quantity and quality, and so will the corresponding Δ'^{17}O values. In addition, the term process-specific is loosely defined, and comparing Δ'^{17}O values among oxygen-bearing compounds involved in a set of different processes with different values of *S* will be confusing, as is demonstrated by photosynthesis and respiration cycles in the Earth system (Angert et al. 2003, Luz & Barkan 2005). The process-specific *S* value may also vary with initial conditions, reaction flux, temperature, and other variables. In addition, a pattern displayed on a δ'^{17}O–δ'^{18}O plot is more informative than Δ'^{17}O alone, and the pattern does not change under different reference frames.

Thus, the two options for *C* discussed above are not recommended as a Δ'^{17}O reference frame owing to their lack of stability or universality. In two-dimensional space, the position of a point can be mathematically defined by an origin and a line in either a Cartesian or a polar coordinate system. An obvious choice of the origin should be VSMOW with δ^{17}O and δ^{18}O (or δ'^{17}O and δ'^{18}O) defined as zero. So we are now left with the option of picking up a value for *C*. In this regard, one option is to use the value of 0.52, because historically the initial triple oxygen isotope analysis on terrestrial igneous samples gave a slope of 0.52 in δ^{17}O–δ^{18}O space (Clayton & Mayeda 1988). After all, the value 0.52 is the canonical slope value when looking at a wide spectrum of mass-dependent equilibrium and kinetic processes for oxygen. Effort to further calibrate the *C* value by covering as diverse samples as possible has been performed (Gehler et al. 2011, Miller et al. 1999, Rumble et al. 2007). This has resulted in only a slight change in the value of *C*, with most change reflected at the third or fourth decimal places. Another option for an arbitrary *C* value is 0.5305, the upper temperature limit for intrinsic equilibrium θ values for oxygen (Cao & Liu 2011, Matsuhisa et al. 1978), which is a number unbiased by the paradigms of any research community (Pack & Herwartz 2014, 2015). Whatever *C* value we pick, it is important that everyone use the same reference frame so that comparison of the Δ^{17}O values among different oxygen-bearing compounds or across different laboratories can be made. Using different reference frames for different systems only causes confusion. We are seeing the community coming to consensus on the referencing issue over the years, a process that is anticipated when a new field is first explored. Exemplifying this, the Pack group's view has undergone evolution over time, as evident from their 2011 (Gehler et al. 2011), 2013 (Pack et al. 2013), and 2014 (Pack & Herwartz 2014) papers.

To summarize, the conceptual differences among θ, *S*, and *C* should be stressed when working on a triple isotope system. These concepts and their differences can be visually displayed in δ'^{17}O–δ'^{18}O space (**Figure 1**). There has been considerable freedom as well as confusion in the literature concerning the use of Greek or Roman letters depicting higher-dimensional relationships among triple isotopes. This freedom and confusion are an inevitable stage in conceptual development. The sidebar is our attempt to compare and consolidate the use of these concepts. Note that, in our scheme, the concepts that *S* and *C* represent do not have a clear physical basis, and therefore these terms do not warrant a Greek letter.

3. THE δ'^{17}O DEVIATION: DIFFERENT Δ CONCEPTS AND DEFINITIONS

As we reasoned above, one way to define Δ'^{17}O, or the δ'^{17}O deviation, is

$$\Delta'^{17}\mathrm{O} \equiv \delta'^{17}\mathrm{O} - 0.5305 \times \delta'^{18}\mathrm{O}. \tag{8}$$

The Δ'^{17}O as defined in Equation 8 is with respect to a line going through the origin (e.g., VSMOW) with a slope of 0.5305. Similar to the concepts of *R* and δ′, Δ'^{17}O defined this way is an intensive property of a compound, independent of any processes involved. Treating Δ'^{17}O as an intensive variable of an oxygen-bearing compound alleviates many problems associated with

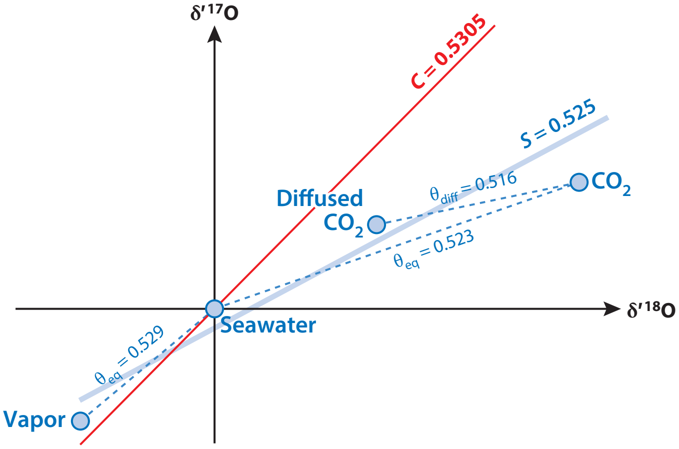

Figure 1

θ, *S*, and *C*: concepts and differences. The degrees of fractionation, slopes, and angles are not to scale. *S* is the slope of the line linearly fitting the four blue data points. Note that the point labeled "Seawater" may not be sitting exactly on the origin that is defined by Vienna Standard Mean Ocean Water (VSMOW). For example, modern seawater may have an average $\Delta'^{17}O$ of −0.005‰ ± 0.004‰ (1σ), a value reprocessed using $C = 0.5305$ based on data from Luz & Barkan (2010).

efforts trying to link $\Delta'^{17}O$ to a specific process and its specific θ as evident in some earlier studies (Assonov & Brenninkmeijer 2005, Miller 2002).

3.1. The Evolving Definition of $\Delta^{17}O$

There are four different $\Delta^{17}O$ definitions in the literature. First is the classical linear definition (Clayton & Mayeda 1988),

$$\Delta^{17}O \equiv \delta^{17}O - 0.52 \times \delta^{18}O; \tag{9}$$

second is the classical exponential definition (Farquhar et al. 1999),

$$\Delta^{17}O \equiv (\delta^{17}O + 1) - (\delta^{18}O + 1)^{0.52}; \tag{10}$$

third is the revised exponential definition (Miller 2002),

$$\Delta^{17}O \equiv [(1 + \delta^{17}O_{\text{classical}})/(1 + \delta^{18}O_{\text{classical}})^{0.52}] - 1; \tag{11}$$

and fourth is the logarithmic definition (Angert et al. 2004, Ono et al. 2006, Thode & Rees 1971; this article),

$$\Delta'^{17}O \equiv \delta'^{17}O - C \times \delta'^{18}O, \tag{12}$$

in which $\delta' \equiv \ln(R_{\text{sample}}/R_{\text{reference}})$. Angert et al.'s (2003) $^{17}\Delta$ used the same definition, but they claimed that this is the same definition as the one Miller (2002) used for $\Delta^{17}O$. This claim is not exactly accurate. In Miller's format, the logarithmic definition would be $\Delta^{17}O \equiv \ln(1 + k_{A,B})$ rather than Miller's (2002) $\Delta^{17}O \equiv k_{A,B}$.

The relationship between $\Delta'^{17}O$ in Equation 12 and the classical exponential one in Equation 10 (Δce) is

$$\Delta'^{17}O = \ln\left(1 + \frac{\Delta^{17}\text{ce}}{(1 + \delta^{18}\text{ce})^{0.52}}\right). \tag{13}$$

For the same pair of data points, the $\Delta'^{17}O$ value will be different under different reference systems [e.g., VSMOW, Vienna Pee Dee Belemnite (VPDB), or Holy Land Air (HLA)], as Miller (2002) pointed out. This is because the $\Delta'^{17}O$ scales with the $\delta'^{18}O$ value. When the fractionation or change in $\delta^{18}O$ is small, say, <10‰, the four different $\Delta^{17}O$ definitions above give nearly identical values at the third decimal place on the per mil scale. Even when the $\Delta\delta^{18}O$ is 30‰, the latter three $\Delta^{17}O$ definitions yield values that differ only at the second decimal place on the per mil scale. Because of these small differences, there was very little interest in evaluating these different definitions, especially when investigating large non-mass-dependent signatures. However, increasing analytical resolution is offering more information on the small differences in the triple oxygen isotope relationship. Thus, the choice of and unification to a proper reference frame are important.

3.2. Different Δ Concepts in Stable Isotope Geochemistry

There are many places the symbol Δ is used in stable isotope geochemistry. Therefore, it will be helpful for us to display how these Δs differ from one another in their underlying physiochemical meaning.

1. The "big delta": the difference in δ values for related pairs or the change in δ value through a fractionation process; for example, $\Delta\delta^{34}S_{\text{sulfate–sulfide}}$. This value is the difference in δ values, and therefore the "δ" must not be omitted.
2. The isotope ratio of mass 47 ($^{13}CO^{18}O$) over mass 44 (CO_2) can be measured by mass spectrometry. The difference between the measured $\delta^{47}CO_2$ and that calculated assuming a stochastic distribution of CO_2 isotopologues is gauged by the term Δ_{47}.
3. The deviation of a third isotope–to–reference isotope ratio from the expected one; for example, $\Delta^{17}O$, $\Delta^{33}S$, $\Delta^{36}S$, or $\Delta^{199}Hg$. There are four different physical meanings under this Δ category. We list them using the triple oxygen isotope system as an example.
    a. The triple isotope exponent θ varies in mass-dependent processes, largely from 0.51 to 0.53 for oxygen. When a $\delta'^{17}O$ and $\delta'^{18}O$ pair is evaluated against a reference frame, e.g., $C = 0.5305$, a small $\Delta'^{17}O$ value or ^{17}O excess can be calculated and compared.
    b. Non-mass-dependent processes generate $\delta'^{17}O$ and $\delta'^{18}O$ values that deviate significantly from a mass-dependent fractionation line. For example, the $\Delta^{17}O$ of O_3 formed in the atmosphere can be as high as +40‰ (Krankowsky et al. 2007).
    c. Atmospheric sulfate and nitrate have nonzero $\Delta^{17}O$ values. However, the anomalies are inherited from O_3 during reactions. The reaction processes that generate the anomalous atmospheric sulfate and nitrate are themselves mass dependent.
    d. Planets might form and inherit the initial triple oxygen isotope inhomogeneity of the solar nebula. The $\Delta^{17}O$ value is used to measure the inhomogeneity with respect to Earth. No specific chemical mechanism is implied in such a Δ usage.

4. LABORATORY $\Delta^{17}O$ MEASUREMENTS

4.1. Referencing

The primary reference point, or zero point, for oxygen isotopes was assigned to Pee Dee Belemnite (PDB) for carbonate minerals and to Standard Mean Ocean Water (SMOW) for oxygen-bearing compounds in general. For more ^{18}O-depleted samples, there is a second primary reference, Southern Latitude Antarctic Precipitation (SLAP). Historically, oxygen isotope composition means $\delta^{18}O$. The zero point for $\delta^{17}O$ was not explicitly defined, but logically, SMOW has a $\delta^{17}O$ value of zero. So does VSMOW, the redefined SMOW. For ^{18}O-depleted samples, SLAP's δ^{17}O can be calibrated when its δ^{18}O is defined as −55.50‰. Although SLAP's δ^{17}O was not defined initially (Coplen 1988, 1995; Gonfiantini 1978), it has been measured using different techniques in different laboratories since 1988 (Barkan & Luz 2005, Jabeen & Kusakabe 1997, Kusakabe & Matsuhisa 2008, Li et al. 1988, Lin et al. 2010, Schoenemann et al. 2013) and thus was recommended to be −29.6986‰, given its δ^{18}O is defined as −55.50‰ (Schoenemann et al. 2013). Thus, triple oxygen isotope measurement has a well-calibrated reference scale.

If a laboratory could easily convert VSMOW and SLAP into O_2 and measure this against an in-house tank O_2, triple oxygen isotope measurement and interlaboratory comparison would not be an issue. However, primary references are limited (Lin et al. 2010), and generating O_2 from liquid water with 100% yield is not a trivial task. When work is performed on silicates or oxides, suitable secondary mineral references are preferable. NBS-28 (quartz), NBS-30 (biotite), UWG-2 (garnet), and San Carlos Olivine are some of the common secondary mineral references that have been initially calibrated for δ^{18}O, but δ^{18}O only. For δ^{17}O of minerals, researchers either assumed a δ^{17}O versus δ^{18}O relationship for a secondary reference or ran against an arbitrarily defined O_2 reference with both δ^{17}O and δ^{18}O at the origin, e.g., HLA (Luz et al. 1999). If stated clearly, the reported δ^{17}O and δ^{18}O data can be recalibrated. For example, in our laboratory at Louisiana State University, we made it clear that the δ^{17}O value was initially calibrated against UWG-2, assuming its $\delta^{18}\text{O} = +5.80$‰ (VSMOW) and its $\delta^{17}\text{O} = 3.016$‰ ($0.520 \times \delta^{18}$O), which independently matches with the δ^{17}O calibration of the Thiemens group at the University of California, San Diego (Bao et al. 2004, 2007, 2010). Running a set of related samples may sound relevant to analyzed samples of interest—for example, silicates for silicates, CO_2 for CO_2—but the logic behind the calibrated reference is not sound. The slope will change with changing sample population size and will therefore change among laboratories at different times, as discussed in Section 2.

Therefore, there was a need to calibrate both δ^{17}O and δ^{18}O for the secondary mineral reference materials against VSMOW/SLAP directly. Work to this end has been done by several laboratories, and the results are listed in **Table 2**. These results indicate that the reported $\delta^{18}O_{VSMOW}$ values have a range beyond analytical errors (i.e., a spread of 1.06‰ for NBS-28, 0.59‰ for UWG-2, and 0.3‰ for San Carlos Olivine, respectively). Here we made an effort to normalize these measurements from different laboratories to the VSMOW or VSMOW/SLAP scale. After the normalization, the difference becomes smaller. Nevertheless, the calculated $\Delta^{17}O_{VSMOW}$ or $\Delta^{17}O_{VSMOW/SLAP}$ values from the different laboratories are not within analytical errors despite the normalization, especially in the case of San Carlos Olivine. Among the six different studies, three studies (Levin et al. 2014, Pack & Herwartz 2015, Tanaka & Nakamura 2013) yielded nearly identical δs and Δs with good consistency and precision with respect to VSMOW (**Table 3**). Their averaged δ^{18}O values agree with the recommended $\delta^{18}O_{VSMOW}$ very well (i.e., $\delta^{18}\text{O} = 9.6$‰ for NBS-28; $\delta^{18}\text{O} = 5.8$‰ for UWG-2), providing confidence that these data are useful references for triple oxygen isotope measurement.

4.2. Analytical Methods

The most accurate triple oxygen isotope data are obtained by analyzing O_2 with a dual-inlet setup on an isotope-ratio mass spectrometer, typically the MAT 253 model as of today. Therefore, much of the analytical effort has been focused on generating O_2 from oxygen-bearing compounds. **Table 4** summarizes the availability or lack of methods for different compounds. In particular, methods for quantitative (100% yield) conversion to oxygen for sulfate, phosphate, carbonate,

Table 2 Originally reported and recalibrated δs for NBS-28, UWG-2, and San Carlos Olivine[a]

Silicate	Reference	VSMOW			VSMOW/SLAP		
		δ^{17}O (‰)	δ^{18}O (‰)	Δ'^{17}O (‰)	δ^{17}O (‰)	δ^{18}O (‰)	Δ'^{17}O (‰)
NBS-28	Jabeen & Kusakabe 1997	**4.81**	**8.98**	0.0558	5.00	9.31	0.0714
	Kusakabe & Matsuhisa 2008	**4.76**	**9.04**	−0.0255	4.84	9.18	−0.0195
	Ahn et al. 2012	**4.52**	**8.69**	−0.0803	4.77	9.16	−0.0786
	Tanaka & Nakamura 2013	**4.96**	**9.56**	−0.0998	5.00	9.64	−0.1020
	Pack & Herwartz 2015	**5.06**	**9.75**	−0.1001	—	—	—
	Levin et al. 2014[b]	5.03	9.68	−0.0932	—	—	—
UWG-2	Kusakabe & Matsuhisa 2008	**2.91**	**5.50**	−0.0040	2.96	5.59	−0.0016
	Ahn et al. 2012	**2.81**	**5.40**	−0.0509	2.96	5.69	−0.0544
	Tanaka & Nakamura 2013	**2.93**	**5.71**	−0.0948	2.96	5.76	−0.0913
	Pack & Herwartz 2015	**3.06**	**5.99**	−0.1129	—	—	—
	Levin et al. 2014[b]	2.97	5.78	−0.0919	—	—	—
San Carlos Olivine	Kusakabe & Matsuhisa 2008	**2.84**	**5.19**	0.0898	2.89	5.27	0.0974
	Ahn et al. 2012	**2.56**	**4.98**	−0.0786	2.70	5.25	−0.0815
	Tanaka & Nakamura 2013	**2.70**	**5.28**	−0.0973	2.72	5.33	−0.1038
	Pack & Herwartz 2015	**2.69**	**5.28**	−0.1073	—	—	—
	Levin et al. 2014[b]	2.70	5.28	−0.0973	—	—	—

[a] All original δ^{17}O and δ^{18}O data except Levin et al.'s (2014) (see below) were calibrated to Vienna Standard Mean Ocean Water (VSMOW). Here we used $\delta^{17}O = -29.6986$‰ and $\delta^{18}O = -55.5$‰ for Southern Latitude Antarctic Precipitation (SLAP) to normalize the original data to the VSMOW/SLAP scale when the corresponding measurement for SLAP was available, and Δ'^{17}O was calculated using $\Delta'^{17}O = 1{,}000 \times \ln(\delta^{17}O/1{,}000 + 1) - 0.5305 \times 1{,}000 \times \ln(\delta^{18}O/1{,}000 + 1)$. Original data are in bold. A dash indicates that a measurement for SLAP was not available in the original experiments.

[b] Levin et al.'s (2014) δ^{17}O did not calibrate directly against VSMOW. Using Tanaka & Nakamura's (2013) results for San Carlos Olivine, we used Levin et al.'s raw data and recalibrated their δ^{17}O and δ^{18}O of tank O_2, and then the measured silicates against VSMOW. The recalibrated δ^{18}O values are nearly identical to Levin et al.'s original data (i.e., $\delta^{18}O_{VSMOW} = 9.663$‰, $\delta^{18}O_{VSMOW} = 5.756$‰, and $\delta^{18}O_{VSMOW} = 5.260$‰ for NBS-28, UWG-2, and San Carlos olivine, respectively).

nitrate, and perchlorate are lacking at this time, leaving room for further improvement of the accuracy and consistency of Δ^{17}O measurements.

Laser spectroscopy, an alternative method in measuring triple oxygen isotope composition, has recently been developed for water vapor. Despite its relative infancy for stable isotope ratio measurements, the laser spectroscopy method has improved tremendously in recent years in its precision, sensitivity, stability, and utility. In addition to having different sample pretreatment requirements, the laser spectroscopy method has a particular advantage over mass spectrometry

Table 3 Triple oxygen isotope compositions from three different research laboratories for NBS-28, UWG-2, and San Carlos Olivine, calibrated to Vienna Standard Mean Ocean Water (VSMOW)

Secondary silicate reference	$\delta^{17}O_{VSMOW}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	$\Delta'^{17}O_{VSMOW}$ (‰)
NBS-28	5.019	9.665	−0.096
UWG-2	2.986	5.825	−0.100
San Carlos Olivine	2.697	5.280	−0.100

The data are presented to the third decimal place to reduce rounding errors of the $\Delta'^{17}O_{VSMOW}$.

Table 4 Current status of analytical methods for triple oxygen isotope analysis of different compounds

Oxygen-bearing compound(s)	Analytical method(s)	Reference(s)
Solid		
Silicate, oxide, sulfate, phosphate	Fluorination using BrF_5 or F_2	Clayton & Mayeda 1963
Nitrate, perchlorate	Thermal decomposition	Bao & Gu 2004, Michalski et al. 2002
Carbonate	Acid digestion, direct CO_2 + BrF_5 fluorination	Clayton et al. 1984
	Acid digestion, CO_2-H_2O equilibrium + H_2O fluorination	Barkan & Luz 2012
	Acid digestion + methanation + H_2O fluorination	Passey et al. 2014
	Acid digestion + CO_2-O_2 exchange over catalysts	Mahata et al. 2013
Organic matter	Not developed	Not available
Liquid		
H_2O	Fluorination by BrF_5 in an Ni-metal tube	Tanaka & Nakamura 2013
	Fluorination by CoF_3 powder	Barkan & Luz 2005
Organic matter	Not developed	Not available
Gas		
O_3	Decomposition to O_2	Heidenreich & Thiemens 1983
CO_2	See methods listed above for carbonate after acid digestion	
CO	Oxidization to CO_2, followed by BrF_5 fluorination	Bhattacharya & Thiemens 1989
N_2O	Thermal decomposition with Au surface	Cliff & Thiemens 1994
H_2O	Condensation to liquid, followed by fluorination	See H_2O above
	Direct laser spectroscopy measurement	Berman et al. 2013, Steig et al. 2014
Organic volatiles	Not developed	Not available

in that spectroscopy measures gases in their nonfragmented states, a feature that opens up niches for future research.

5. UTILITY

Triple oxygen isotope composition has seen a great expansion in recent years in its utility in studying Earth processes. The following section outlines new developments and our assessment according to oxygen-bearing species.

5.1. O_3 and Its Derivatives

Atmospheric gases are the first terrestrial natural compounds to reveal non-mass-dependent ^{17}O anomalies. So far, atmospheric sulfate, nitrate, perchlorate, CO, CO_2, N_2O, and H_2O have been found to bear variably positive Δ^{17}O values. Ultimately, the source of these positive anomalies can be traced back to ozone (O_3) (Lyons 2001). There have been exciting discoveries and new applications along this productive line of research. Several excellent review papers have been written on the causes, distribution, and applications of these anomalies in O_3 and its derivatives (Brenninkmeijer et al. 2003; Thiemens 1999, 2003, 2006). One such derivative, sulfate (SO_4^{2-}), is particularly interesting because it carries not only the signature of O_3 but the signature of O_2 as well. For atmospheric O_3 and O_2 signatures of the geological past, sulfate currently seems to be our only safe bet (Bao 2015).

In this article, we add three new lines of development related to stratospheric O_3 chemistry to these previous reviews.

5.1.1. ^{17}O depletion in O_2. It had been an unconfirmed suspicion that atmospheric O_2 has a small, non-mass-dependent depletion in ^{17}O until Boaz Luz's team convincingly presented the result of their terrarium experiment, in which the $\Delta^{17}O$ of tropospheric O_2 was found to be approximately −0.20‰ relative to O_2 produced by photosynthesis (Luz et al. 1999). The source of the ^{17}O deficit was attributed to stratospheric O_3-CO_2-O_2 chemistry and stratosphere-troposphere exchange. Because of the small deviation as well as confusion with the choice of reference slope value for $\Delta^{17}O$ calculation, the community had debated the exact $\Delta^{17}O$ value and even the existence of ^{17}O depletion (Young et al. 2002), although today there seems to be agreement on the presence of a distinct ^{17}O depletion in tropospheric O_2 (Young et al. 2014).

The relationship between pCO_2 and $\Delta^{17}O_{O_2}$ is of great geological interest because atmospheric gas pCO_2 and $\Delta^{17}O_{O_2}$ can be measured directly from ice core records (Blunier et al. 2002, Luz et al. 1999) or inferred from geological sulfate deposits (Bao et al. 2008). There is a linear correlation between pCO_2 and $\Delta^{17}O_{O_2}$ in ice-core records, with $\Delta^{17}O_{O_2}$ reaching a maximum and pCO_2 a minimum at the peak of glacial times. What is striking is the sulfate ^{17}O modeling-based inferences that in the immediate aftermath of the Marinoan Snowball Earth meltdown approximately 635 million years ago, the $\Delta^{17}O_{O_2}$ may have reached −30‰ to −40‰ (Bao et al. 2009, Cao & Bao 2013), predicting a sizable range of triple oxygen isotope signatures that can be explored in geological atmospheric O_2 (Bao 2015, Bao et al. 2009).

5.1.2. Tropospheric CO_2. The $\Delta^{17}O$ of CO_2 has been measured or explored for mesospheric and stratospheric CO_2 (Boering et al. 2004; Thiemens et al. 1991, 1995a,b), tropospheric CO_2 (Hoag et al. 2005, Liang & Mahata 2015, Thiemens et al. 2014), and CO_2 generated from various combustion processes (Horvath et al. 2012). The stratospheric CO_2 has a distinctly positive $\Delta^{17}O$, reaching as high as approximately +12‰ (Thiemens et al. 1995a). What is most notable is that, even at ground level, the stratospheric CO_2 signature appears detectable at current analytical precision (Liang & Mahata 2015, Thiemens et al. 2014), which offers us a tool to study in high temporal and spatial resolution stratosphere-troposphere exchange, regional meteorology, and surface bioproductivity.

5.1.3. Possible stratospheric H_2O signature. The survival of a stratospheric CO_2 signature at ground level would certainly suggest that stratospheric H_2O may also survive in polar regions, where the tropospheric dilution effect is not as overwhelming as in low- to mid-latitude regions. Miller (2008) raised this possibility when he examined the first Antarctic ice snow triple oxygen data obtained by Landais et al. (2008a). Later, water vapor triple oxygen isotope data obtained from Alert, Canada (82°30′N, 62°19′W), suggested the presence of a small quantity of stratospheric H_2O based on a small positive $\Delta^{17}O$ value, of 0.076‰ ± 0.016‰ (2σ SE) relative to Chicago local precipitation (Lin et al. 2013a). However, a concern was raised and debated regarding the proper reference frame (Lin et al. 2013b, Miller 2013), casting doubt on the survivability of a stratospheric water signal at Alert, Canada. Subsequent triple oxygen isotope measurements of Antarctic snow ice transects seemed to reaffirm the possibility of stratospheric water input in polar snow (Pang et al. 2015, Winkler et al. 2013), although Schoenemann et al. (2014) argued that the observed $\Delta^{17}O$ change in Antarctic snow ice can be sufficiently explained by changes in temperature and in the KIE influenced by sea-ice coverage, and that stratospheric input is unnecessary.

5.2. H_2O

The first effort to measure the $\delta^{17}O$ of natural liquid water was made by Meijer & Li (1998), who converted liquid water to O_2 by electrolysis with an analytical precision reaching 0.1‰ and 0.07‰ for $\delta^{18}O$ and $\delta^{17}O$, respectively. They concluded that $\delta^{17}O$ yields no additional information for natural samples, due to its proportionality to $\delta^{18}O$ by a factor of 0.5281.

The discovery of small ($\Delta^{17}O$ within 0.3‰) non-mass-dependent ^{17}O depletion in tropospheric O_2 and its link to photosynthesis and bioproductivity has led to a demand for high precision in water $\delta^{18}O$ and $\delta^{17}O$ measurements (Blunier et al. 2002, Luz & Barkan 2000, Luz et al. 1999). A technique was developed in which water is converted completely to O_2 by reaction with CoF_3, and the generated O_2 is run on dual-inlet mode on a mass spectrometer; this technique achieved precisions for $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ of 0.01‰, 0.03‰, and <0.01‰, respectively (SE of the mean multiplied by Student's *t*-factor at a 95% confidence level) (Barkan & Luz 2005).

Angert et al. (2004) were the first to point out that the relationship between $\delta^{17}O$ and $\delta^{18}O$ for water may vary due to different θ values between vapor diffusion and vapor-liquid equilibrium. Relative humidity at initial vapor source regions is the predominant control of the $\Delta^{17}O$ of the subsequent precipitation. Thus, the $\Delta^{17}O$ of meteoric water complements the deuterium excess in studying hydrological cycling in that the $\Delta^{17}O$ is sensitive only to relative humidity, whereas the deuterium excess is sensitive to both relative humidity and temperature of the vapor source regions. Their predictions were confirmed and applied by measuring water $\delta^{17}O$ and $\delta^{18}O$ during leaf transpiration (Landais et al. 2006), during water evaporation (Barkan & Luz 2005, 2007), in monsoon rains (Landais et al. 2010), and in ice records (Landais et al. 2008a,b, 2012a,b; Risi et al. 2010, 2013; Winkler et al. 2012). Measurement of the triple oxygen isotope compositions of water, water vapor, and ice has provided additional constraints on moisture source, evaporation kinetics, re-evaporation, convection, and mixing processes among modern and recent hydrological cycles (**Figure 2**).

While the utility of water $\Delta^{17}O$ is promising, five issues remain.

1. **The $\Delta^{17}O$ of seawater over glacial-interglacial periods.** Landais et al.'s (2008a) main conclusion was that meteoric waters have an excess of ^{17}O of approximately 0.04‰ with respect to seawater. One of the uncertainties, however, comes from the lack of constraint on the $\Delta^{17}O$ of seawater during the last glacial maximum (LGM), as pointed out by Miller (2008). Later, Luz & Barkan (2010) measured the $\Delta^{17}O$ of water from the Atlantic Ocean, Pacific Ocean, eastern Mediterranean, and northern Red Sea and found that the $\Delta^{17}O$ of modern seawater is nonzero, at −0.005‰ ± 0.001‰, whereas the $\Delta^{17}O$ of meteoric water is 0.037‰ ± 0.004‰ (when a C value of 0.528 was used). The $\Delta^{17}O$ of the seawater at the LGM was implicitly assumed to be the same as that of present-day seawater (Blunier et al. 2002). For high-resolution $\Delta^{17}O$ studies, this assumption may need to be examined. Taking the $\delta^{18}O$ of LGM seawater to be 1‰ (Schrag et al. 1996) and the results of Luz & Barkan's (2010) open pan experiments, we estimate that the $\Delta^{17}O$ of seawater during the LGM should be approximately 0.010‰ (when $C = 0.528$) lower than the modern value. Of course, the uncertainty of this estimate comes mostly from the assumption that the evaporative conditions at the LGM were similar to the open-pan evaporation experimental conditions. Nevertheless, a 0.01‰ difference in seawater $\Delta^{17}O$ is not trivial given what is

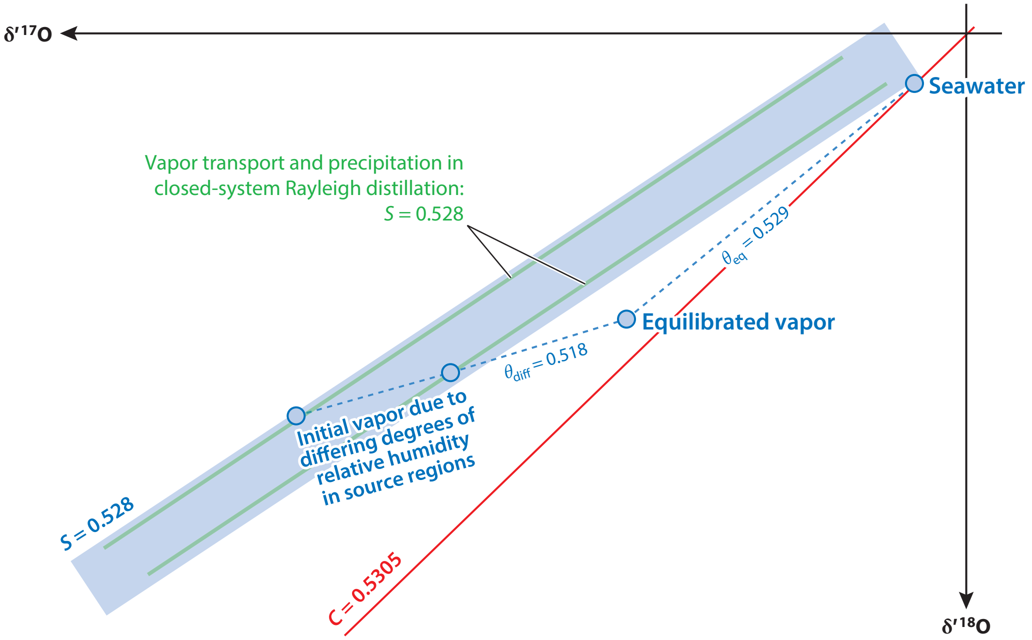

Figure 2

Triple oxygen isotope behavior of major processes the origin of the Δ^{17}O in meteoric water cycling (not to scale). Modified from Barkan & Luz (2007).

being measured. Currently, it is unknown how seawater Δ^{17}O varied throughout the past 800,000 or more years and how much this variation affects the interpretation of the Δ^{17}O record in ice cores.

2. **Relative humidity of the initial source region as the only factor for the Δ^{17}O of water vapor (before precipitation).** By measuring marine vapor directly, Uemura et al. (2010) found that marine vapor has a nonzero Δ^{17}O that negatively correlates with relative humidity. This direct measurement is consistent with previous theoretical considerations (Barkan & Luz 2007) and modeling results (Angert et al. 2004, Risi et al. 2010). However, other processes, such as re-evaporation, mixing, and convection, will influence the Δ^{17}O value during water vapor transportation (Landais et al. 2010; Li et al. 2015; Risi et al. 2010, 2013). These factors will vary among different moisture transport paths, and their impact on the Δ^{17}O of vapor is assumed to be small but has not been quantified.
3. **Validity of the θ_{eq} temperature insensitivity at low temperatures.** The equilibrium triple oxygen isotope behavior in the hydrological cycle can ultimately be reduced to the equilibrium triple isotope fractionation relationships—that is, θ_{eq}. It has been demonstrated theoretically that θ_{eq} is insensitive in the surface temperature range (Cao & Liu 2011, Chialvo & Horita 2009). Experimentally, it has been shown that θ_{eq} remains at 0.529 in the temperature range from 11.4°C to 41.5°C (Barkan & Luz 2005). However, experiments outside of this temperature range have been lacking. Landais et al. (2012b) claimed that the θ_{eq} between ice and water vapor at colder conditions should be 0.528, similar to that obtained from the 11.4°C to 41.5°C experiments. However, this conclusion is based on field observations with poor temperature constraints and no guarantee of isotope equilibrium between the ice and water vapor.

4. **The effect of precipitation kinetics on the $\Delta^{17}O$ of snow.** During nonequilibrium precipitation or condensation, the θ of vapor diffusion (θ_{diff}) plays an important role in the overall triple oxygen isotope composition of the precipitates. However, θ_{diff} may have a temperature sensitivity that is even less certain than that of θ_{eq}. The θ_{diff} value has been calibrated to be 0.5187 at 40°C and 0.5182 at 25°C (Barkan & Luz 2007), which means that there is a 0.0002/15°C decreasing trend if the trend is linear in this temperature range. If we extrapolate this trend, the θ_{diff} would be 0.5172 at −50°C, which would result in a more negative $\Delta^{17}O$ signal for ice that was precipitated at nonequilibrium. Angert et al. (2004) pointed out that the KIE associated with ice formation will lead to a negative $\Delta^{17}O$ value in ice, indicating that the relative humidity of the ocean source region may not be uniquely preserved in the ice core record if the degree of supersaturation is high during precipitation (Miller 2008). At very cold conditions, such as in remote regions of Antarctica, the $\Delta^{17}O$ in ice may not correlate well with the relative humidity of the ocean source, although the $\Delta^{17}O$ in ice at coastal locations may (Landais et al. 2012a,b; Winkler et al. 2012).
5. **Contribution of stratospheric water to surface ice.** Variations in the $\Delta^{17}O$ of polar ice may be introduced by mass-anomalous stratospheric water.

5.3. Silicates, Oxides, Carbonates, and Ancient Seawater

Common terrestrial minerals, such as silicates, oxides, and carbonates, have rarely been measured for their ^{17}O content, despite the fact that $\Delta^{17}O$ has been a powerful parameter in studying extraterrestrial materials since 1973 (Clayton et al. 1973). Because of the mass dependence of the fractionation law (Bigeleisen & Mayer 1947, Urey 1947), the $\delta^{17}O$ measurement was thought to offer no additional information. Here we review recent progress in $\Delta^{17}O$ measurements in silicates, oxides, and carbonates and their records in ancient seawater.

5.3.1. Silicate-water exchange: small $\Delta^{17}O$ as an extra constraint. Herwartz et al. (2015) presented an interesting application of high-resolution triple oxygen isotope analysis of terrestrial silicates. The central idea is that silicate rocks have triple oxygen isotope compositions that are approximately 0.20‰ lower than those of meteoric water. The silicates do not plot on the global meteoric water line (Pack & Herwartz 2014). Therefore, when partial exchange occurs between rock and water, "Rocks that have exchanged to variable degrees with meteoric water will define a mixing trend in a $\Delta'^{17}O$ versus $\delta'^{18}O$ diagram. The intersect between the mixing trend and the [meteoric water line] gives, along with a small offset due to equilibrium hydrothermal water-rock fractionation, the composition of the interacting water" (Herwartz et al. 2015, p. 5338). The idea's key assumption is that the water's $\delta'^{17}O$ and $\delta'^{18}O$ should fall on a line with a 0.528 slope even in the geological past. This idea offers an extra line of constraint and therefore a solution to an old problem: The $\delta'^{18}O$ of rock or silicate alone cannot tell us what the $\delta'^{18}O$ of the exchanged water is because we do not know the degree of exchange. In a recent Icelandic case, Herwartz et al. (2015) demonstrated the validity of this approach. Subsequently, they inferred very negative $\delta^{18}O$ values for the Neoproterozoic and Paleoproterozoic glacial meltwaters.

This application is the same as the three-isotope method in determining the equilibrium isotope fractionation factor, and it therefore shares the potential problems discussed in Section 5.5 below. Additional uncertainties come from the triple oxygen isotope composition of seawater in the distant past, as discussed in Section 5.3.4.

5.3.2. Carbonates. Carbonates are widely used minerals in stable isotope geochemistry and in paleotemperature reconstruction, through the measurement of their $\delta^{18}O$ or clumped isotopes (Eiler 2007, McCrea 1950). The measurement of $\delta^{17}O$ in carbonates was limited to extraterrestrial or potential atmospheric origins (e.g., Benedix et al. 2003; Clayton & Mayeda 1984; Farquhar et al. 1998, 1999; Shaheen et al. 2010, 2015). Passey et al. (2014) presented the first survey of $\Delta^{17}O$ in terrestrial carbonates using a newly developed sequential acid digestion/reduction/fluorination approach with a precision of 0.01‰ (1σ). The main idea is that triple oxygen isotopes in carbonates are related to those in parent water, and that the $\Delta^{17}O$ values for meteoric water, evaporated water (lake water, river water, soil water, or leaf water), and animal body water are measurably different. Evaporation conditions and the $\Delta^{17}O$ of atmospheric O_2 could thus be reconstructed by measuring the $\Delta^{17}O$ of carbonates. Their results indicated that the soil carbonates are formed in modestly evaporated waters, and carbonates in eggshells and tooth enamels carry signals from evaporated water and/or from atmospheric O_2, which confirms and expands earlier results on phosphate's triple oxygen isotope composition (see Section 5.4).

5.3.3. $\Delta^{17}O$ geothermometer. Because α and θ in a mineral-water system may have different temperature sensitivities, we may have a potential single-mineral geothermometer. We have three equations:

$$\ln\alpha^{18} = \delta'^{18}O_{\text{mineral}} - \delta'^{18}O_{\text{water}} = f(T), \tag{14}$$

$$\theta = \ln\alpha^{17}/\ln\alpha^{18} = (\delta'^{17}O_{\text{mineral}} - \delta'^{17}O_{\text{water}})/(\delta'^{18}O_{\text{mineral}} - \delta'^{18}O_{\text{water}}) = g(T), \tag{15}$$

$$\delta'^{17}O_{\text{water}} = 0.528\delta'^{18}O_{\text{water}} + \Delta'^{17}O. \tag{16}$$

Here $f(T)$ and $g(T)$ indicate two different functions of temperature. $\Delta'^{17}O$ is for coeval seawater, approximately −0.005‰ for modern seawater and approximately 0.04‰ for modern meteoric water. Among the five variables in Equations 14–16, $\delta'^{18}O_{\text{mineral}}$ and $\delta'^{17}O_{\text{mineral}}$ are measurable. Thus the three equations can uniquely solve all the other three variables: T, $\delta'^{18}O_{\text{water}}$, and $\delta'^{17}O_{\text{water}}$. Note that there are two critical assumptions here. One is that the θ value is known. Currently, we have θ_{eq} and its dependence on T for very limited mineral-water systems, and we do not know how the θ would vary if a mineral-water system were not in equilibrium. The second assumption is that the slope 0.528 for diverse meteoric water stays the same even in a very different Earth system in the distant past. This assumption has not been examined, and the possible range of this slope value and the $\Delta'^{17}O$ of coeval seawater in geological history are unknown at this time.

We have calculated the equilibrium $\Delta'^{17}O$ geothermometer for calcite-water systems at 0°C to 120°C. The plot (**Figure 3**) depicts a nearly linear relationship between the $\Delta\Delta'^{17}O$ (i.e., $\Delta'^{17}O$ difference between calcite and water) and precipitating temperature. Although for the calcite-water system with today's analytical techniques the uncertainty on estimated T is large (6°C to 10°C), further advancements in precision may allow this $\Delta'^{17}O$ thermometer to be viable. The concept of a $\Delta'^{17}O$ geothermometer is not limited to mineral-water systems, but currently high-precision calibration of θ is lacking for most processes.

The $\Delta'^{17}O$ values of diverse sedimentary cherts and oxides were recently measured with high precision (Levin et al. 2014). Archean and Phanerozoic cherts were found to have similar $\Delta'^{17}O$, whereas their corresponding $\delta^{18}O$ varied from 20.6‰ to 34.1‰. Because $\Delta'^{17}O$ should scale with $\delta^{18}O$ in their reference frame, this observation needs explanation. Four different scenarios were proposed, and some bear information on paleo-ocean temperature and/or the triple oxygen isotope composition of paleoseawater (Levin et al. 2014).

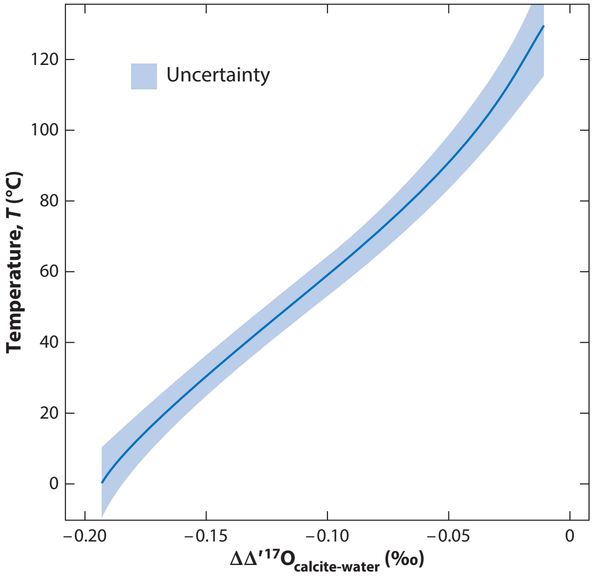

Figure 3

Calculated $\Delta\Delta'^{17}O_{\text{calcite-water}}$ versus temperature, T, for calcite-water equilibrium exchange based on data from Cao & Liu (2011), Hill et al. (2014), and Rosenbaum (1997). The corresponding uncertainty in T is approximated by the measurement uncertainty of 0.01‰ on $\Delta'^{17}O$ of calcite divided by the derivative of $\Delta\Delta'^{17}O$ with respect to T at the estimated temperature.

5.3.4. Constraints on triple isotope composition of ancient seawater. High-precision measurement of triple oxygen isotope composition for silicates, oxides, or carbonates offers a potential way to reconstruct the triple oxygen isotope composition of seawater in the distant past, a past much older than any ice core record could possibly reach. The approximately 0.10‰ lower $\Delta^{17}O$ value in silicates than in seawater was attributed to "the effect of kinetic isotope fractionation between minerals and fluid phase on a bulk Earth scale" that has a θ value smaller than 0.52 (Tanaka & Nakamura 2013, p. 295). Pack & Herwartz (2014) further elaborated the interpretation and argued that the seawater is buffered by low- and high-temperature isotope exchanges with mafic oceanic crust (Jaffres et al. 2007, Muehlenbachs & Clayton 1976). The high-temperature hydrothermal exchange processes bear a higher θ value than the low-temperature oceanic crust weathering processes, as depicted in **Figure 4**. This argument is consistent with theoretical estimations and empirical observations (Cao & Liu 2011, Matsuhisa et al. 1978, Pack & Herwartz 2014). Therefore, with improved measurement precision, we might be able to constrain the $\delta^{18}O$ and $\Delta^{17}O$ of ancient seawater by measuring the $\Delta^{17}O$ of old oceanic crusts (Pack & Herwartz 2014).

5.4. Phosphates

It has been known for some time that the phosphate ion (PO_4^{3-}), much like the sulfate ion, does not readily exchange oxygen isotopes with ambient water under most surface conditions (Chang & Blake 2015, Lecuyer et al. 1999). This property, combined with its tendency to form insoluble minerals, gives phosphate the ability to store the oxygen isotope signatures of its source over geological time. Although there are many studies investigating the $\delta^{18}O$ of phosphate as a proxy for meteoric water $\delta^{18}O$, mammalian body water, ocean temperature, bioproductivity,

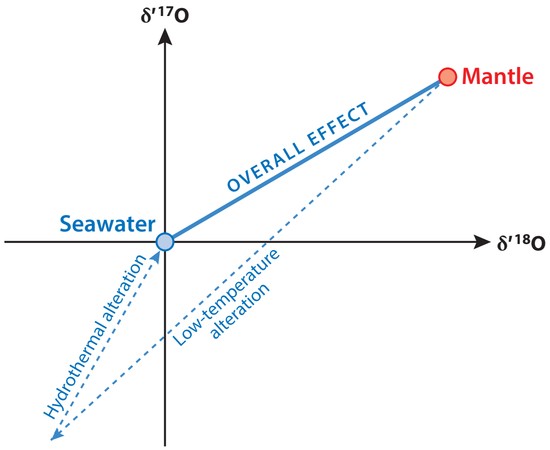

Figure 4

The triple oxygen isotope composition of seawater in geological history may have changed with changing ocean temperature or fraction of hydrothermal alteration versus low-temperature weathering of the ocean crust. The position of the mantle is fixed, but the position of seawater changes with changing slope and length of the dashed blue lines. Modified from Pack & Herwartz (2014).

or phosphorous cycling, there are so far only two studies looking into the triple oxygen isotope composition of phosphate.

Biogenic phosphate in the form of bones and teeth is believed to have its oxygen sourced from body water, which is itself composed dominantly of consumed water but also of water generated through respiration. Using $\delta^{18}O$ and $\delta^{17}O$ measurements, Gehler et al. (2011) showed that a portion of the atmospheric O_2 (recalculated $\Delta'^{17}O = -0.47‰$ when $C = 0.5305$) signal from respiration-sourced water can be recorded in the phosphate of teeth, particularly those of small mammals with high specific metabolic rates. In addition, they showed that the enamel, as opposed to the dentin, retained this signal through diagenesis. Using the results of Gehler et al. (2011) and an expected relationship between atmospheric $p\mathrm{CO}_2$ and the $\Delta^{17}O$ of air O_2, Pack et al. (2013) proposed a proxy based on the measurement of bioapatite from small mammals to reconstruct the ancient triple isotope composition of air O_2 and therefore to infer $p\mathrm{CO}_2$. Due to limits in analytical precision this technique is associated with significant uncertainty.

5.5. The Three-Isotope Method for Equilibrium Fractionation Determination

Calibrating equilibrium fractionation factors for mineral-water or mineral-mineral systems has been one of the first experimental endeavors in stable isotope geochemistry. The experiments, however, have been suffering from the lack of independent criteria for the attainment of true equilibrium (Chacko et al. 2001). The three-isotope exchange method was initially developed to determine the oxygen isotope equilibrium fractionation factor α_{eq} using one set of experiments instead of two sets that converge from two opposite fractionation directions when using $\delta^{18}O$ alone (Matsuhisa et al. 1978, Matthews et al. 1983). The three-isotope method has now been expanded to nontraditional isotope systems by several research groups (Beard et al. 2010, Guilbaud et al. 2011, Shahar et al. 2008, Williams et al. 2012).

In principle, the three-isotope method takes advantage of the fixed relationship between $\delta^{17}O$ and $\delta^{18}O$ during the exchange processes. Its trajectory in $\delta^{17}O$–$\delta^{18}O$ space reflects mixing between an equilibrium point and the initial point through an isotope exchange reaction. The equilibrium

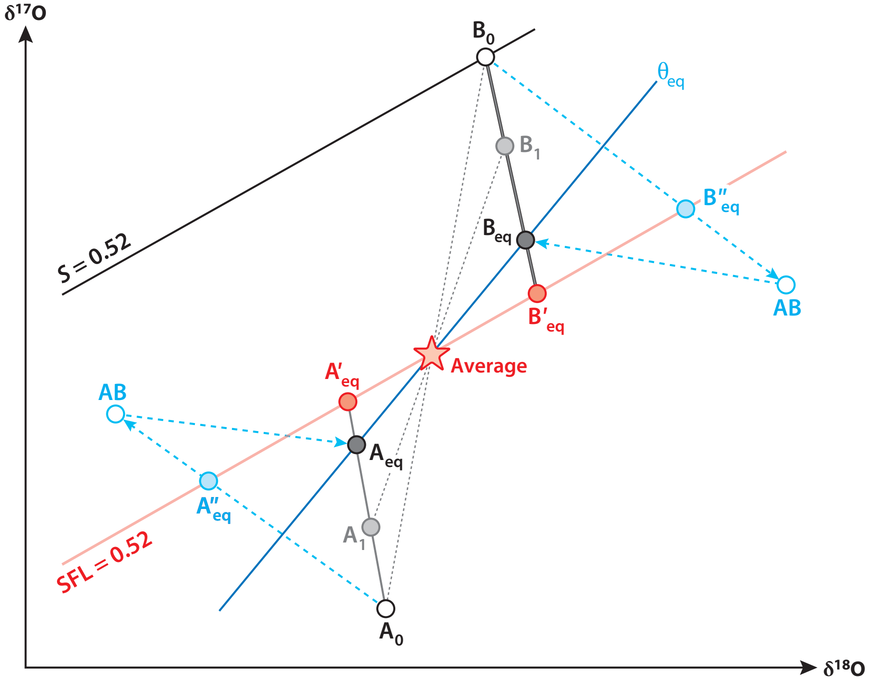

Figure 5

The three-isotope method for determining the equilibrium isotope fractionation factor. A_0 and B_0 are two initial points before exchange in the $\delta^{17}O$–$\delta^{18}O$ space, and the red star represents the average of the mixture. When the exchange progresses, the respective isotope compositions move to A_1 and B_1. The apparent equilibrium points A'_{eq} and B'_{eq} can be determined by linear extrapolation of these four points to their corresponding secondary fractionation line (SFL) (*red line*) with a predefined slope (e.g., 0.52). However, the true equilibrium points A_{eq} and B_{eq} are on a mass-dependent fractionation line (*dark blue line*) that may have a slope θ_{eq} that is different from the predefined slope. Most likely, however, is that the exchange process involves kinetic complexity. If the isotope exchange were to have a metastable intermediate phase AB, the initial exchange trajectory (*light blue dashed lines*) would not lead to the true equilibrium points but to one or more apparent equilibrium points (e.g., A''_{eq} and B''_{eq}).

points should fall on a parallel mass-dependent fractionation line, the secondary fractionation line (SFL), across the system average point (see **Figure 5**). Here we must caution the community that the three-isotope method is the same as the $\delta^{18}O$ approach in that both require the same set of assumptions. That is, the exchange has to be direct between two compounds and involve insignificant intermediates or no chemical changes. These conditions are in fact difficult to meet in most experiments because the kinetic pathway of exchange determines the trajectory in $\delta^{17}O$–$\delta^{18}O$ space and the kinetics of exchange is often not known a priori. Matsuhisa et al. (1978) warned of these pitfalls when the three-isotope method was first used in calibrating oxygen isotope equilibrium fractionation factors between quartz and water.

Even if an exchange experiment fits the conditions initially outlined by Matsuhisa et al. (1978), we argue here that the three-isotope method is inherently a method of approximation at best. This is because of two issues. First, a two-component, direct exchange process would produce data points on a straight line in $\delta^{17}O$–$\delta^{18}O$ space. However, the SFL is a straight line with a slope θ_{eq} in $\delta'^{17}O$–$\delta'^{18}O$ space, but would be curved in $\delta^{17}O$–$\delta^{18}O$ space. The mixing trajectory of the δs from initial point to equilibrium point would be slightly curved. For small δs, a linear relationship between an equilibrium point and the system average point can be approximated because $\ln(1+\delta) \approx \delta$. However, for experiments with large δs, this approximation will introduce uncertainties, as mentioned by other authors (Matsuhisa et al. 1978, O'Neil 1986). Second, θ_{eq} for the SFL is dependent on temperature and species involved (Cao & Liu 2011, Matsuhisa et al. 1978), which means that θ_{eq} or the SFL cannot be known before the equilibrium isotope fractionation is determined. If a fixed number such as 0.52 is assumed for oxygen, another source of uncertainty is introduced (**Figure 5**).

The kinetic complexity of the exchange reaction and the inherited curves in triple oxygen space (**Figure 5**) should have restrained us from being too optimistic when using the three-isotope method to calibrate equilibrium fractionation factors.

6. FUTURE RESEARCH

6.1. Nonequilibrium Processes: Kinetic Isotope Effects and Diffusion

Currently only a few triple oxygen isotope relationships have been calibrated computationally, experimentally, or observationally (e.g., Barkan & Luz 2007, Cao & Liu 2011, Helman et al. 2005, Luz & Barkan 2005). At equilibrium the α_{eq} and subsequently θ_{eq} can be determined for a defined process (Equations 5, 6, and 7). **Table 5** compares some of the key concepts and their corresponding physical meanings in two-isotope and three-isotope systems. Research efforts should begin to calibrate the θ_{eq} values of important processes. However, most natural processes are in a nonequilibrium state. At nonequilibrium, α or θ for a process is not fixed and is dependent on the deviation from equilibrium. For example, for equilibrium at 25°C, the CO_2(g)-H_2O system has an α of 1.041 and a θ of 0.5246 (Cao & Liu 2011). When equilibrium is not reached, the apparent α will be different from α_{eq}. This is similarly true for the apparent θ for a system at nonequilibrium. In order to predict the nonequilibrium α and θ, we must know the forward and backward reaction fluxes, and most importantly, the KIE and θ_{KIE} values for the forward and backward reactions.

As of today, physical and organic chemists are ahead of geochemists in the study of KIEs. Only very limited numbers of KIEs have been calibrated experimentally or computationally for important natural processes, including, for example, some steps in the CO_2-H_2O system (Clark et al. 1992, Clark & Lauriol 1992), microbial nitrite oxidation (Casciotti 2009), and N_2O oxidation (Yang et al. 2014) (although these may not be true KIEs, as admitted by the authors). Determination of θ_{KIE} for natural processes is otherwise nonexistent at this time. An entirely fundamental important field—determining KIE and θ_{KIE} for elemental steps in important natural processes, such as C, S, N, O, and H cycling—is open for exploration.

Diffusion is a nonequilibrium process. In the conceptual framework proposed in this review, we listed α_{diff} separately from KIE and θ_{diff} from θ_{KIE}. For diffusion in solid state or liquid state, transition state theory may be applicable (Eyring 1936, Wert & Zener 1949). Thus α_{diff} and θ_{diff} can be framed as KIE and θ_{KIE}, respectively. For diffusion in gas phase, there has not been a transition state theory–based approach. The values of α_{diff} and θ_{diff} have been experimentally determined for water vapor diffusion in air (Barkan & Luz 2007) but are scarce for other compounds at this time.

6.2. Reservoir Transport Complexity

Observed experimental processes or natural processes are often not elemental steps. What we see or measure is the result of multiple steps that often involve complex reservoir transport effects (Bao et al. 2015). A quantitative scheme is essential to deducing unique KIE, α, and θ for the

Table 5 Key concepts and their corresponding physical meanings in two-isotope and three-isotope systems

System	Concept	Equation (^{16}O-^{17}O-^{18}O system)	Description
Two-isotope	^{18}R, ^{17}R	$^{18}N/^{16}N$, $^{17}N/^{16}N$	The molar (N) ratio of the rare isotope to the reference isotope
	$\delta^{18}O$, $\delta^{17}O$	$(R_{sample}/R_{reference}) - 1$	The classical linear δ notation
	$\delta'^{18}O$, $\delta'^{17}O$	$\ln(R_{sample}/R_{reference})$	The logarithmic δ notation
	$^{18}\beta$, $^{17}\beta$	$^{18}Q/^{16}Q$, $^{17}Q/^{16}Q$	Equilibrium fractionation factor between a compound and an unbound oxygen atom, calculated as the ratio of partition functions (Q)
	$^{18}\alpha_{A\text{-}B}$, $^{17}\alpha_{A\text{-}B}$	β_A/β_B	Equilibrium fractionation factor between states or compounds A and B
	KIE	$\beta_{TS}/\beta_A = \alpha_{TS\text{-}A}$	Kinetic isotope effect (KIE), calculated as the equilibrium isotope fractionation factor between the transition state (TS) and its reactant A
	$\Delta\delta^{*}O_{A\text{-}B}$, $\Delta\delta'^{*}O_{A\text{-}B}$	$\delta_A - \delta_B$, $\delta'_A - \delta'_B$	The difference in δ or δ′ values between states or compounds A and B
Three-isotope	κ	$\ln^{17}\beta/\ln^{18}\beta$	Mass-dependence exponent describing the relationship between $^{17}\beta$ and $^{18}\beta$
	θ_{eq}	$\ln^{17}\alpha_{eq}/\ln^{18}\alpha_{eq}$	The intrinsic mass-dependence exponent describing the relationship between $^{17}\alpha$ and $^{18}\alpha$ for an equilibrium process
	θ_{KIE}	$\ln^{17}KIE/\ln^{18}KIE$	The intrinsic mass-dependence exponent describing the ^{17}KIE and ^{18}KIE relationship
	θ	$\ln^{17}\alpha/\ln^{18}\alpha$	Apparent θ; the αs are apparent αs
	S	Not applicable	The slope of measured points in $\delta'^{17}O$–$\delta'^{18}O$ space; the points can be tightly or loosely constrained by one process or a set of processes
	$\Delta^{17}O$, $\Delta'^{17}O$	$\delta^{17}O - C \times \delta^{18}O$, $\delta'^{17}O - C \times \delta'^{18}O$	Deviation of the measured $\delta^{17}O$ or $\delta'^{17}O$ from the predicted $\delta^{17}O$ or $\delta'^{17}O$ based on the measured $\delta^{18}O$ or $\delta'^{18}O$; the $\Delta^{17}O$ or $\Delta'^{17}O$ defined this way is a property (like δ or δ′) of a compound
	C (0.5305)	Not applicable	A slope value for normalizing the $\Delta^{17}O$ value of a compound; we recommend this value be set to the high-temperature limit value of 0.5305
	$\Delta\Delta^{17}O_{A\text{-}B}$, $\Delta\Delta'^{17}O_{A\text{-}B}$	$\Delta^{17}O_A - \Delta^{17}O_B$, $\Delta'^{17}O_A - \Delta'^{17}O_B$	The difference in $\Delta^{17}O$ or $\Delta'^{17}O$ values between states or compounds A and B

underlying elemental steps. Such a quantitative scheme is necessary not only in interpreting data but also in designing experiments. One of the most used schemes is Rayleigh distillation. In a closed system, many $\delta'^{17}O$ and $\delta'^{18}O$ data pairs from the leftover reservoir at different times can be plotted in $\delta'^{17}O$–$\delta'^{18}O$ space. The data points will line up in a straight line if the fractionation factor remains the same from time 1 (t_1) to time 2 (t_2). Thus, we have

$$\delta'^{18}O_{t_2} - \delta'^{18}O_{t_1} = ({}^{18}\alpha - 1)\ln f,$$

$$\frac{\delta'^{17}O_{t_2} - \delta'^{17}O_{t_1}}{\delta'^{18}O_{t_2} - \delta'^{18}O_{t_1}} = \frac{(\alpha^{18})^{\theta} - 1}{(\alpha^{18}) - 1} = S. \qquad (17)$$

From the observed $\delta'^{17}O$, $\delta'^{18}O$, and f (f is the mole fraction remaining) we can calibrate experimentally α and θ values of the elemental or at least the apparent elemental step of the Rayleigh distillation process.

However, many natural or laboratory processes are not easily reducible. Analytical numerical solutions can be obtained via existing quantification schemes developed in many disciplines, such as chemical engineering. The real challenge is to establish a unique relationship between the measured stable isotope compositions and the αs and θs of the underlying elemental steps. Much research effort is needed in this field.

DISCLOSURE STATEMENT

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LITERATURE CITED

Ahn I, Lee JI, Kusakabe M, Choi BG. 2012. Oxygen isotope measurements of terrestrial silicates using a CO_2-laser BrF_5 fluorination technique and the slope of terrestrial fractionation line. *Geosci. J.* 16:7–16

Angert A, Cappa CD, DePaolo DJ. 2004. Kinetic ^{17}O effects in the hydrologic cycle: indirect evidence and implications. *Geochim. Cosmochim. Acta* 68:3487–95

Angert A, Rachmilevitch S, Barkan E, Luz B. 2003. Effects of photorespiration, the cytochrome pathway, and the alternative pathway on the triple isotopic composition of atmospheric O_2. *Glob. Biogeochem. Cycles* 17:1030

Armytage RMG, Georg RB, Williams HM, Halliday AN. 2012. Silicon isotopes in lunar rocks: implications for the Moon's formation and the early history of the Earth. *Geochim. Cosmochim. Acta* 77:504–14

Assonov SS, Brenninkmeijer CAM. 2005. Reporting small $\Delta^{17}O$ values: existing definitions and concepts. *Rapid Commun. Mass Spectrom.* 19:627–36

Bao H. 2015. Sulfate: a time capsule for Earth's O_2, O_3, and H_2O. *Chem. Geol.* 395:108–18

Bao H, Cao X, Hayles JA. 2015. The confines of triple oxygen isotope exponents in elemental and complex mass-dependent processes. *Geochim. Cosmochim. Acta* 170:39–50

Bao H, Fairchild IJ, Wynn PM, Spoetl C. 2009. Stretching the envelope of past surface environments: Neoproterozoic glacial lakes from Svalbard. *Science* 323:119–22

Bao H, Gu BH. 2004. Natural perchlorate has a unique oxygen isotope signature. *Environ. Sci. Technol.* 38:5073–77

Bao H, Jenkins KA, Khachaturyan M, Diaz GC. 2004. Different sulfate sources and their post-depositional migration in Atacama soils. *Earth Planet. Sci. Lett.* 224:577–87

Bao H, Lyons JR, Zhou C. 2008. Triple oxygen isotope evidence for elevated CO_2 levels after a Neoproterozoic glaciation. *Nature* 453:504–6

Bao H, Rumble D III, Lowe DR. 2007. The five stable isotope compositions of Fig Tree barites: implications on sulfur cycle in ca. 3.2 Ga oceans. *Geochim. Cosmochim. Acta* 71:4868–79

Bao H, Thiemens MH, Farquhar J, Campbell DA, Lee CCW, et al. 2000. Anomalous ^{17}O compositions in massive sulphate deposits on the Earth. *Nature* 406:176–78

Bao H, Yu S, Tong DQ. 2010. Massive volcanic SO_2 oxidation and sulphate aerosol deposition in Cenozoic North America. *Nature* 465:909–12

Barkan E, Luz B. 2005. High precision measurements of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios in H_2O. *Rapid Commun. Mass Spectrom.* 19:3737–42

Barkan E, Luz B. 2007. Diffusivity fractionations of $H_2{}^{16}O/H_2{}^{17}O$ and $H_2{}^{16}O/H_2{}^{18}O$ in air and their implications for isotope hydrology. *Rapid Commun. Mass Spectrom.* 21:2999–3005

Barkan E, Luz B. 2012. High-precision measurements of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios in CO_2. *Rapid Commun. Mass Spectrom.* 26:2733–38

Beard BL, Handler RM, Scherer MM, Wu LL, Czaja AD, et al. 2010. Iron isotope fractionation between aqueous ferrous iron and goethite. *Earth Planet. Sci. Lett.* 295:241–50

Benedix GK, Leshin LA, Farquhar J, Jackson T, Thiemens MH. 2003. Carbonates in CM2 chondrites: constraints on alteration conditions from oxygen isotopic compositions and petrographic observations. *Geochim. Cosmochim. Acta* 67:1577–88

Bergquist BA, Blum JD. 2007. Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* 318:417–20

Berman ESF, Levin NE, Landais A, Li SN, Owano T. 2013. Measurement of $\delta^{18}O$, $\delta^{17}O$, and ^{17}O-excess in water by off-axis integrated cavity output spectroscopy and isotope ratio mass spectrometry. *Anal. Chem.* 85:10392–98

Bhattacharya SK, Thiemens MH. 1989. New evidence for symmetry dependent isotope effects: O+CO reaction. *Z. Naturforsch. Sect. B* 44:435–44

Bigeleisen J, Mayer MG. 1947. Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* 15:261–67

Bindeman IN, Serebryakov NS, Schmitt AK, Vazquez JA, Guan Y, et al. 2014. Field and microanalytical isotopic investigation of ultradepleted in ^{18}O Paleoproterozoic "Slushball Earth" rocks from Karelia, Russia. *Geosphere* 10:308–39

Blunier T, Barnett B, Bender ML, Hendricks MB. 2002. Biological oxygen productivity during the last 60,000 years from triple oxygen isotope measurements. *Glob. Biogeochem. Cycles* 16. doi: 10.1029/2001GB001460

Boering KA, Jackson T, Hoag KJ, Cole AS, Perri MJ, et al. 2004. Observations of the anomalous oxygen isotopic composition of carbon dioxide in the lower stratosphere and the flux of the anomaly to the troposphere. *Geophys. Res. Lett.* 31:L03109

Brenninkmeijer CAM, Janssen C, Kaiser J, Rockmann T, Rhee TS, Assonov SS. 2003. Isotope effects in the chemistry of atmospheric trace compounds. *Chem. Rev.* 103:5125–61

Cao XB, Bao HM. 2013. Dynamic model constraints on oxygen-17 depletion in atmospheric O_2 after a snowball Earth. *PNAS* 110:14546–50

Cao XB, Liu Y. 2011. Equilibrium mass-dependent fractionation relationships for triple oxygen isotopes. *Geochim. Cosmochim. Acta* 75:7435–45

Casciotti KL. 2009. Inverse kinetic isotope fractionation during bacterial nitrite oxidation. *Geochim. Cosmochim. Acta* 73:2061–76

Chacko T, Cole DR, Horita J. 2001. Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geologic systems. *Rev. Mineral. Geochem.* 43:1–81

Chang SJ, Blake RE. 2015. Precise calibration of equilibrium oxygen isotope fractionations between dissolved phosphate and water from 3 to 37°C. *Geochim. Cosmochim. Acta* 150:314–29

Chialvo AA, Horita J. 2009. Liquid-vapor equilibrium isotopic fractionation of water: How well can classical water models predict it? *J. Chem. Phys.* 130:094509

Clark ID, Fontes JC, Fritz P. 1992. Stable isotope disequilibria in travertine from high pH waters—laboratory investigations and field observations from Oman. *Geochim. Cosmochim. Acta* 56:2041–50

Clark ID, Lauriol B. 1992. Kinetic enrichment of stable isotopes in cryogenic calcites. *Chem. Geol.* 102:217–28

Clayton D. 2003. *Handbook of Isotopes in the Cosmos: Hydrogen to Gallium*. Cambridge, UK: Cambridge Univ. Press

Clayton RN. 1993. Oxygen isotopes in meteorites. *Annu. Rev. Earth Planet. Sci.* 21:115–49

Clayton RN, Grossman L, Mayeda TK. 1973. A component of primitive nuclear composition in carbonaceous meteorites. *Science* 182:485–88

Clayton RN, Mayeda TK. 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta* 27:43–52

Clayton RN, Mayeda TK. 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* 67:151–61

Clayton RN, Mayeda TK. 1988. Formation of ureilites by nebular processes. *Geochim. Cosmochim. Acta* 52:1313–18

Clayton RN, Mayeda TK, Rubin AE. 1984. Oxygen isotopic compositions of enstatite chondrites and aubrites. *J. Geophys. Res.* 89(S01):C245–249

Cliff SS, Thiemens MH. 1994. High-precision isotopic determination of the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios in nitrous oxide. *Anal. Chem.* 66:2791–93

Cliff SS, Thiemens MH. 1997. The $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios in atmospheric nitrous oxide: a mass-independent anomaly. *Science* 278:1774–76

Coplen TB. 1988. Normalization of oxygen and hydrogen isotope data. *Chem. Geol.* 72:293–97

Coplen TB. 1995. Discontinuance of SMOW and PDB. *Nature* 375:285

Dauphas N, Craddock PR, Asimow PD, Bennett VC, Nutman AP, Ohnenstetter D. 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth Planet. Sci. Lett.* 288:255–67

Eiler J, Cartigny P, Hofmann AE, Piasecki A. 2013. Non-canonical mass laws in equilibrium isotopic fractionations: evidence from the vapor pressure isotope effect of SF_6. *Geochim. Cosmochim. Acta* 107:205–19

Eiler JM. 2007. "Clumped-isotope" geochemistry—the study of naturally-occurring, multiply-substituted isotopologues. *Earth Planet. Sci. Lett.* 262:309–27

Eyring H. 1936. Viscosity, plasticity, and diffusion as examples of absolute reaction rates. *J. Chem. Phys.* 4:283–91

Farquhar J, Bao HM, Thiemens M. 2000. Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289:756–58

Farquhar J, Johnston DT, Wing BA. 2007. Implications of conservation of mass effects on mass-dependent isotope fractionations: influence of network structure on sulfur isotope phase space of dissimilatory sulfate reduction. *Geochim. Cosmochim. Acta* 71:5862–75

Farquhar J, Thiemens MH, Jackson T. 1998. Atmosphere-surface interactions on Mars: $\Delta^{17}O$ measurements of carbonate from ALH 84001. *Science* 280:1580–82

Farquhar J, Thiemens MH, Jackson TL. 1999. $\Delta^{17}O$ anomalies in carbonate from Nakhla and Lafayette and $\Delta^{33}S$ anomalies in sulfur from Nakhla: implications for atmospheric chemical interactions with the Martian regolith. *Lunar Planet. Sci. Conf. Abstr.* 30:1675

Gehler A, Tutken T, Pack A. 2011. Triple oxygen isotope analysis of bioapatite as tracer for diagenetic alteration of bones and teeth. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 310:84–91

Georg RB, Halliday AN, Schauble EA, Reynolds BC. 2007. Silicon in the Earth's core. *Nature* 447:1102–6

Gonfiantini R. 1978. Standards for stable isotope measurements in natural compounds. *Nature* 271:534–36

Guilbaud R, Butler IB, Ellam RM, Rickard D, Oldroyd A. 2011. Experimental determination of the equilibrium Fe isotope fractionation between Fe^{2+}_{aq} and FeSm (mackinawite) at 25 and 2°C. *Geochim. Cosmochim. Acta* 75:2721–34

Hallis LJ, Anand M, Greenwood RC, Miller MF, Franchi IA, Russell SS. 2010. The oxygen isotope composition, petrology and geochemistry of mare basalts: evidence for large-scale compositional variation in the lunar mantle. *Geochim. Cosmochim. Acta* 74:6885–99

Heidenreich JE III, Thiemens MH. 1983. A non-mass-dependent isotope effect in the production of ozone from molecular oxygen. *J. Chem. Phys.* 78:892–95

Heidenreich JE III, Thiemens MH. 1986. A non-mass-dependent oxygen isotope effect in the production of ozone from molecular oxygen: the role of molecular symmetry in isotope chemistry. *J. Chem. Phys.* 84:2129–36

Helman Y, Barkan E, Eisenstadt D, Luz B, Kaplan A. 2005. Fractionation of the three stable oxygen isotopes by oxygen-producing and oxygen-consuming reactions in photosynthetic organisms. *Plant Physiol.* 138:2292–98

Herwartz D, Pack A, Krylov D, Xiao Y, Muehlenbachs K, et al. 2015. Revealing the climate of snowball Earth from Δ^{17}O systematics of hydrothermal rocks. *PNAS* 112:5337–41

Hill PS, Tripati AK, Schauble EA. 2014. Theoretical constraints on the effects of pH, salinity, and temperature on clumped isotope signatures of dissolved inorganic carbon species and precipitating carbonate minerals. *Geochim. Cosmochim. Acta* 125:610–52

Hirschi J, Singleton DA. 2005. The normal range for secondary Swain-Schaad exponents without tunneling or kinetic complexity. *J. Am. Chem. Soc.* 127:3294–95

Hoag KJ, Still CJ, Fung IY, Boering KA. 2005. Triple oxygen isotope composition of tropospheric carbon dioxide as a tracer of terrestrial gross carbon fluxes. *Geophys. Res. Lett.* 32:L02802

Hofmann MEG, Horvath B, Pack A. 2012. Triple oxygen isotope equilibrium fractionation between carbon dioxide and water. *Earth Planet. Sci. Lett.* 319:159–64

Hofmann MEG, Pack A. 2010. Technique for high-precision analysis of triple oxygen isotope ratios in carbon dioxide. *Anal. Chem.* 82:4357–61

Horvath B, Hofmann MEG, Pack A. 2012. On the triple oxygen isotope composition of carbon dioxide from some combustion processes. *Geochim. Cosmochim. Acta* 95:160–68

Hulston JR, Thode HG. 1965. Variations in the ^{33}S, ^{34}S, and ^{36}S contents of meteorites and their relation to chemical and nuclear effects. *J. Geophys. Res.* 70:3475–84

Jabeen I, Kusakabe M. 1997. Determination of δ^{17}O values of reference water samples VSMOW and SLAP. *Chem. Geol.* 143:115–19

Jaffres JBD, Shields GA, Wallmann K. 2007. The oxygen isotope evolution of seawater: a critical review of a long-standing controversy and an improved geological water cycle model for the past 3.4 billion years. *Earth-Sci. Rev.* 83:83–122

Kaiser J, Rockmann T, Brenninkmeijer CAM. 2004. Contribution of mass-dependent fractionation to the oxygen isotope anomaly of atmospheric nitrous oxide. *J. Geophys. Res.* 109:D03305

Kohen A, Jensen JH. 2002. Boundary conditions for the Swain-Schaad relationship as a criterion for hydrogen tunneling. *J. Am. Chem. Soc.* 124:3858–64

Krankowsky D, Lammerzahl P, Mauersberger K, Janssen C, Tuzson B, Rockmann T. 2007. Stratospheric ozone isotope fractionations derived from collected samples. *J. Geophys. Res.* 112:D08301

Kusakabe M, Matsuhisa Y. 2008. Oxygen three-isotope ratios of silicate reference materials determined by direct comparison with VSMOW-oxygen. *Geochem. J.* 42:309–17

Landais A, Barkan E, Luz B. 2008a. Record of δ^{18}O and ^{17}O-excess in ice from Vostok Antarctica during the last 150,000 years. *Geophys. Res. Lett.* 35:L02709

Landais A, Barkan E, Luz B. 2008b. Reply to comment by Martin F. Miller on "Record of δ^{18}O and ^{17}O-excess in ice from Vostok Antarctica during the last 150,000 years." *Geophys. Res. Lett.* 35:L23709

Landais A, Barkan E, Yakir D, Luz B. 2006. The triple isotopic composition of oxygen in leaf water. *Geochim. Cosmochim. Acta* 70:4105–15

Landais A, Ekaykin A, Barkan E, Winkler R, Luz B. 2012a. Seasonal variations of ^{17}O-excess and d-excess in snow precipitation at Vostok station, East Antarctica. *J. Glaciol.* 58:725–33

Landais A, Risi C, Bony S, Vimuex F, Descroix L, et al. 2010. Combined measurements of $^{17}\mathrm{O}_{\mathrm{excess}}$ and d-excess in African monsoon precipitation: implications for evaluating convective parameterizations. *Earth Planet. Sci. Lett.* 298:104–22

Landais A, Steen-Larsen HC, Guillevic M, Masson-Delmotte V, Vinther B, Winkler R. 2012b. Triple isotopic composition of oxygen in surface snow and water vapor at NEEM (Greenland). *Geochim. Cosmochim. Acta* 77:304–16

Lecuyer C, Grandjean P, Sheppard SMF. 1999. Oxygen isotope exchange between dissolved phosphate and water at temperatures ≤135°C: inorganic versus biological fractionations. *Geochim. Cosmochim. Acta* 63:855–62

Levin NE, Raub TD, Dauphas N, Eiler JM. 2014. Triple oxygen isotope variations in sedimentary rocks. *Geochim. Cosmochim. Acta* 139:173–89

Li S, Levin NE, Chesson LA. 2015. Continental scale variation in ^{17}O-excess of meteoric waters in the United States. *Geochim. Cosmochim. Acta* 164:110–26

Li WJ, Ni B, Jin D, Zhang Q. 1988. Comparison of the oxygen-17 abundance in three international standard waters. *Huaxue Tongbao* 6:39–40 (in Chinese)

Liang MC, Mahata S. 2015. Oxygen anomaly in near surface carbon dioxide reveals deep stratospheric intrusion. *Sci. Rep.* 5:11352

Lin Y, Clayton RN, Groning M. 2010. Calibration of δ^{17}O and δ^{18}O of international measurement standards—VSMOW, VSMOW2, SLAP, and SLAP2. *Rapid Commun. Mass Spectrom.* 24:773–76

Lin Y, Clayton RN, Huang L, Nakamura N, Lyons JR. 2013a. Oxygen isotope anomaly observed in water vapor from Alert, Canada and the implication for the stratosphere. *PNAS* 110:15608–13

Lin Y, Clayton RN, Huang L, Nakamura N, Lyons JR. 2013b. Reply to Miller: Concerning the oxygen isotope anomaly observed in water vapor from Alert, Canada, and its stratospheric source. *PNAS* 110:E4568

Luz B, Barkan E. 2000. Assessment of oceanic productivity with the triple-isotope composition of dissolved oxygen. *Science* 288:2028–31

Luz B, Barkan E. 2005. The isotopic ratios ^{17}O/^{16}O and ^{18}O/^{16}O in molecular oxygen and their significance in biogeochemistry. *Geochim. Cosmochim. Acta* 69:1099–110

Luz B, Barkan E. 2010. Variations of ^{17}O/^{16}O and ^{18}O/^{16}O in meteoric waters. *Geochim. Cosmochim. Acta* 74:6276–86

Luz B, Barkan E, Bender ML, Thiemens MH, Boering KA. 1999. Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity. *Nature* 400:547–50

Lyons JR. 2001. Transfer of mass-independent fractionation in ozone to other oxygen-containing radicals in the atmosphere. *Geophys. Res. Lett.* 28:3231–34

MacPherson GJ, Mittlefehldt DW, Jones JH, eds. 2008. *Rev. Mineral. Geochem.* Vol. 68

Mahata S, Bhattacharya SK, Wang CH, Liang MC. 2013. Oxygen isotope exchange between O_2 and CO_2 over hot platinum: an innovative technique for measuring Δ^{17}O in CO_2. *Anal. Chem.* 85:6894–901

Matsuhisa Y, Goldsmith JR, Clayton RN. 1978. Mechanisms of hydrothermal crystallization of quartz at 250°C and 15 kilobars. *Geochim. Cosmochim. Acta* 42:173–82

Matthews A, Goldsmith JR, Clayton RN. 1983. On the mechanisms and kinetics of oxygen isotope exchange in quartz and feldspars at elevated temperatures and pressures. *Geol. Soc. Am. Bull.* 94:396–412

McCrea JM. 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* 18:849–57

McKinney CR, McCrea JM, Epstein S, Allen HA, Urey HC. 1950. Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios. *Rev. Sci. Instrum.* 21:724–30

Meijer HAJ, Li WJ. 1998. The use of electrolysis for accurate δ^{17}O and δ^{18}O isotope measurements in water. *Isot. Environ. Health Stud.* 34:349–69

Michalski G, Savarino J, Bohlke JK, Thiemens M. 2002. Determination of the total oxygen isotopic composition of nitrate and the calibration of a Δ^{17}O nitrate reference material. *Anal. Chem.* 74:4989–93

Miller MF. 2002. Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochim. Cosmochim. Acta* 66:1881–89

Miller MF. 2008. Comment on "Record of δ^{18}O and ^{17}O-excess in ice from Vostok Antarctica during the last 150,000 years" by Amaelle Landais et al. *Geophys. Res. Lett.* 35:L23708

Miller MF. 2013. Oxygen isotope anomaly not present in water vapor from Alert, Canada. *PNAS* 110:E4567

Miller MF, Franchi IA, Sexton AS, Pillinger CT. 1999. High precision δ^{17}O isotope measurements of oxygen from silicates and other oxides: method and applications. *Rapid Commun. Mass Spectrom.* 13:1211–17

Miller MF, Franchi IA, Thiemens MH, Jackson TL, Brack A, et al. 2002. Mass-independent fractionation of oxygen isotopes during thermal decomposition of carbonates. *PNAS* 99:10988–93

Miller MF, Greenwood RC, Franchi IA. 2015. Comment on "The triple oxygen isotope composition of the Earth mantle and understanding Δ^{17}O variations in terrestrial rocks and minerals" by Pack and Herwartz [Earth Planet. Sci. Lett. 390 (2014) 138–145]. *Earth Planet. Sci. Lett.* 418:181–83

Mook WG, ed. 2001. *Environmental Isotopes in the Hydrological Cycle: Principles and Applications*, Vol. I: *Introduction: Theory, Methods, Review*. Paris: UNESCO, IAEA

Muehlenbachs K, Clayton RN. 1976. Oxygen isotope composition of oceanic crust and its bearing on seawater. *J. Geophys. Res.* 81:4365–69

O'Neil JR. 1986. Theoretical and experimental aspects of isotopic fractionation. *Rev. Mineral. Geochem.* 16:1–40

Ono S, Wing B, Johnston D, Farquhar J, Rumble D. 2006. Mass-dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles. *Geochim. Cosmochim. Acta* 70:2238–52

Osawa T, Ono M, Esaka F, Okayasu S, Iguchi Y, et al. 2009. Mass-dependent isotopic fractionation of a solid tin under a strong gravitational field. *Europhys. Lett.* 85:64001

Pack A, Gehler A, Sussenberger A. 2013. Exploring the usability of isotopically anomalous oxygen in bones and teeth as paleo-CO_2-barometer. *Geochim. Cosmochim. Acta* 102:306–17

Pack A, Herwartz D. 2014. The triple oxygen isotope composition of the Earth mantle and understanding $\Delta^{17}O$ variations in terrestrial rocks and minerals. *Earth Planet. Sci. Lett.* 390:138–45

Pack A, Herwartz D. 2015. Observation and interpretation of $\Delta^{17}O$ variations in terrestrial rocks—response to the comment by Miller et al. on the paper by Pack & Herwartz (2014). *Earth Planet. Sci. Lett.* 418:184–86

Pack A, Toulouse C, Przybilla R. 2007. Determination of oxygen triple isotope ratios of silicates without cryogenic separation of NF_3—technique with application to analyses of technical O_2 gas and meteorite classification. *Rapid Commun. Mass Spectrom.* 21:3721–28

Pang H, Hou S, Landais A, Masson-Delmotte V, Prie F, et al. 2015. Spatial distribution of ^{17}O-excess in surface snow along a traverse from Zhongshan station to Dome A, East Antarctica. *Earth Planet. Sci. Lett.* 414:126–33

Passey BH, Hu HT, Ji HY, Montanari S, Li SN, et al. 2014. Triple oxygen isotopes in biogenic and sedimentary carbonates. *Geochim. Cosmochim. Acta* 141:1–25

Risi C, Landais A, Bony S, Jouzel J, Masson-Delmotte V, Vimeux F. 2010. Understanding the ^{17}O excess glacial-interglacial variations in Vostok precipitation. *J. Geophys. Res.* 115:D10112

Risi C, Landais A, Winkler R, Vimeux F. 2013. Can we determine what controls the spatio-temporal distribution of d-excess and ^{17}O-excess in precipitation using the LMDZ general circulation model? *Clim. Past* 9:2173–93

Rosenbaum JM. 1997. Gaseous, liquid, and supercritical fluid H_2O and CO_2: oxygen isotope fractionation behavior. *Geochim. Cosmochim. Acta* 61:4993–5003

Rumble D, Miller MF, Franchi IA, Greenwood RC. 2007. Oxygen three-isotope fractionation lines in terrestrial silicate minerals: an inter-laboratory comparison of hydrothermal quartz and eclogitic garnet. *Geochim. Cosmochim. Acta* 71:3592–600

Schoenemann SW, Schauer AJ, Steig EJ. 2013. Measurement of SLAP2 and GISP ^{17}O and proposed VSMOW-SLAP normalization for ^{17}O and $^{17}O_{\text{excess}}$. *Rapid Commun. Mass Spectrom.* 27:582–90

Schoenemann SW, Steig EJ, Ding QH, Markle BR, Schauer AJ. 2014. Triple water-isotopologue record from WAIS Divide, Antarctica: controls on glacial-interglacial changes in $^{17}O_{\text{excess}}$ of precipitation. *J. Geophys. Res. Atmos.* 119:8741–63

Schrag DP, Hampt G, Murray DW. 1996. Pore fluid constraints on the temperature and oxygen isotopic composition of the glacial ocean. *Science* 272:1930–32

Shahar A, Young ED, Manning CE. 2008. Equilibrium high-temperature Fe isotope fractionation between fayalite and magnetite: an experimental calibration. *Earth Planet. Sci. Lett.* 268:330–38

Shaheen R, Abramian A, Horn J, Dominguez G, Sullivan R, Thiemens MH. 2010. Detection of oxygen isotopic anomaly in terrestrial atmospheric carbonates and its implications to Mars. *PNAS* 107:20213–18

Shaheen R, Niles PB, Chong K, Corrigan CM, Thiemens MH. 2015. Carbonate formation events in ALH 84001 trace the evolution of the Martian atmosphere. *PNAS* 112:336–41

Spicuzza MJ, Day JMD, Taylor LA, Valley JW. 2007. Oxygen isotope constraints on the origin and differentiation of the Moon. *Earth Planet. Sci. Lett.* 253:254–65

Starkey NA, Jackson C, Greenwood RC, Parman S, Franchi IA, et al. 2015. Triple oxygen isotopic composition of the high-$^3He/^4He$ mantle. *Geochim. Cosmochim. Acta* 176:227–38

Steig EJ, Gkinis V, Schauer AJ, Schoenemann SW, Samek K, et al. 2014. Calibrated high-precision ^{17}O-excess measurements using cavity ring-down spectroscopy with laser-current-tuned cavity resonance. *Atmos. Meas. Tech.* 7:2421–35

Swain CG, Stivers EC, Reuwer JF, Schaad LJ. 1958. Use of hydrogen isotope effects to identify the attacking nucleophile in the enolization of ketones catalyzed by acetic acid. *J. Am. Chem. Soc.* 80:5885–93

Tanaka R, Nakamura E. 2013. Determination of ^{17}O-excess of terrestrial silicate/oxide minerals with respect to Vienna Standard Mean Ocean Water (VSMOW). *Rapid Commun. Mass Spectrom.* 27:285–97

Thiemens MH. 1999. Mass-independent isotope effects in planetary atmospheres and the early solar system. *Science* 283:341–45

Thiemens MH. 2003. Non-mass-dependent isotopic processes: mechanisms and recent observations in terrestrial and extra-terrestrial environments. In *Treatise on Geochemistry*, Vol. 4: *The Atmosphere*, ed. RF Keeling, HD Holland, KK Turekian, pp. 159–73. Amsterdam: Elsevier

Thiemens MH. 2006. History and applications of mass-independent isotope effects. *Annu. Rev. Earth Planet. Sci.* 34:217–62

Thiemens MH, Chakraborty S, Dominguez G. 2012. The physical chemistry of mass-independent isotope effects and their observation in nature. *Annu. Rev. Phys. Chem.* 63:155–77

Thiemens MH, Chakraborty S, Jackson TL. 2014. Decadal Δ^{17}O record of tropospheric CO_2: verification of a stratospheric component in the troposphere. *J. Geophys. Res. Atmos.* 119:6221–29

Thiemens MH, Heidenreich JE III. 1983. The mass-independent fractionation of oxygen: a novel isotope effect and its possible cosmochemical implications. *Science* 219:1073–75

Thiemens MH, Jackson T, Mauersberger K, Schueler B, Morton J. 1991. Oxygen isotope fractionation in stratospheric CO_2. *Geophys. Res. Lett.* 18:669–72

Thiemens MH, Jackson T, Zipf EC, Erdman PW, van Egmond C. 1995a. Carbon dioxide and oxygen isotope anomalies in the mesosphere and stratosphere. *Science* 270:969–72

Thiemens MH, Jackson TL, Brenninkmeijer CAM. 1995b. Observation of a mass independent oxygen isotopic composition in terrestrial stratospheric CO2, the link to ozone chemistry, and the possible occurrence in the Martian atmosphere. *Geophys. Res. Lett.* 22:255–57

Thiemens MH, Savarino J, Farquhar J, Bao HM. 2001. Mass-independent isotopic compositions in terrestrial and extraterrestrial solids and their applications. *Acc. Chem. Res.* 34:645–52

Thode HG, Rees CE. 1971. Measurement of sulphur concentrations and the isotope ratios ^{33}S/^{32}S, ^{34}S/^{32}S, and ^{36}S/^{32}S in Apollo 12 samples. *Earth Planet. Sci. Lett.* 12:434–38

Uemura R, Barkan E, Abe O, Luz B. 2010. Triple isotope composition of oxygen in atmospheric water vapor. *Geophys. Res. Lett.* 37:L04402

Urey HC. 1947. The thermodynamic properties of isotopic substances. *J. Chem. Soc.* 1947:562–81

Wasson JT. 2000. Oxygen-isotopic evolution of the solar nebula. *Rev. Geophys.* 38:491–512

Wert C, Zener C. 1949. Interstitial atomic diffusion coefficients. *Phys. Rev.* 76:1169–75

Wiechert U, Halliday AN. 2007. Non-chondritic magnesium and the origins of the inner terrestrial planets. *Earth Planet. Sci. Lett.* 256:360–71

Wiechert UH, Halliday AN, Palme H, Rumble D. 2004. Oxygen isotope evidence for rapid mixing of the HED meteorite parent body. *Earth Planet. Sci. Lett.* 221:373–82

Williams HM, Wood BJ, Wade J, Frost DJ, Tuff J. 2012. Isotopic evidence for internal oxidation of the Earth's mantle during accretion. *Earth Planet. Sci. Lett.* 321:54–63

Winkler R, Landais A, Risi C, Baroni M, Ekaykin A, et al. 2013. Interannual variation of water isotopologues at Vostok indicates a contribution from stratospheric water vapor. *PNAS* 110:17674–79

Winkler R, Landais A, Sodemann H, Dumbgen L, Prie F, et al. 2012. Deglaciation records of ^{17}O-excess in East Antarctica: reliable reconstruction of oceanic normalized relative humidity from coastal sites. *Clim. Past* 8:1–16

Yang H, Gandhi H, Ostrom NE, Hegg EL. 2014. Isotopic fractionation by a fungal P450 nitric oxide reductase during the production of N_2O. *Environ. Sci. Technol.* 48:10707–15

Yankwich PE, Promislow AL, Nystrom RF. 1954. C^{14} and C^{13} intramolecular isotope effects in the decarboxylation of liquid malonic acid at 140.5°. *J. Am. Chem. Soc.* 76:5893–94

Yeh HW, Epstein S. 1978. ^{29}Si/^{28}Si and ^{30}Si/^{28}Si of meteorites and Allende inclusions. *Lunar Planet. Sci. Conf. Abstr.* 9:1289–91

Young E, Galy A. 2004. The isotope geochemistry and cosmochemistry of magnesium. *Rev. Mineral. Geochem.* 55:197–230

Young ED, Galy A, Nagahara H. 2002. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim. Cosmochim. Acta* 66:1095–104

Young ED, Kohl IE, Warren PH, Rubie DC, Jacobson SA, Morbidelli A. 2016. Oxygen isotopic evidence for vigorous mixing during the Moon-forming giant impact. *Nature* 351:493–96

Young ED, Yeung LY, Kohl IE. 2014. On the Δ^{17}O budget of atmospheric O_2. *Geochim. Cosmochim. Acta* 135:102–25

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