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Why Measure ^{17}O? Historical Perspective, Triple-Isotope Systematics and Selected Applications

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INTRODUCTION

For many years, it was considered that measurements of the least abundant stable isotope of oxygen, ^{17}O, would not provide any information additional to that obtainable from determinations of the ^{18}O/^{16}O abundance ratio, which, by being a factor of ~5.2 larger than ^{17}O/^{16}O, can be measured more easily. Here, we summarize significant events in the historical development of oxygen stable isotope ratio measurements and their application to Earth and planetary sciences, leading to a consideration of the potential information to be gained from high precision measurements of the 'third isotope'. This is followed by a short description of triple oxygen isotope systematics, together with notation and definitions. In turn, this leads to a discussion of how improvements in measurement precision, coupled with recent theoretical developments and empirical findings, have enabled small variations in the ^{17}O/^{16}O isotope abundance ratio relative to ^{18}O/^{16}O to provide new insights to a remarkable diversity of applications.

The foundations of stable isotope geochemistry can arguably be traced to the year 1947, when a theoretical framework for calculating equilibrium constants and their temperature dependence for isotopic exchange reactions was proposed by Urey (1947) and independently by Bigeleisen and Göppert-Mayer (1947). The partitioning of isotopes at equilibrium results was considered as a quantum mechanical process; reduced partition function ratios, in conjunction with the Teller–Redlich approximation (Redlich 1935) formed the basis of the calculations. The latter approximation allowed the rotational partition function contribution to be eliminated from the calculations and it was also assumed that isotope substitution has no direct effect on electronic energies. Thus, equilibrium fractionation factors could be determined from consideration of the respective molecular vibration frequencies only. From the reported results, Urey (1947) also suggested that, as a temperature increase from 0 °C to 25 °C should change the equilibrium ^{18}O abundance in carbonate by a factor of 1.004 relative to that in coexisting water, accurate determination of the ^{18}O/^{16}O ratio in natural carbonates could be used to determine the

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temperature at which they formed. Fortunately, these theoretical advances coincided with of the development by Nier (1947) of a gas source mass spectrometer suitable for routine analyses of isotope ratios of the lighter elements. Modifications of the Nier mass spectrometer to increase the precision in relative abundance measurement by an order of magnitude were subsequently proposed by McKinney et al. (1950). Amongst these, a change-over valve was incorporated, to permit rapid switching between sample and reference gases being admitted to the ion source.

Furthermore, the delta notation for reporting stable isotope relative abundances was introduced. Thus, for oxygen:

$$\delta^{18}\mathrm{O} = \frac{{}^{18}R_{\mathrm{sample}} - {}^{18}R_{\mathrm{reference}}}{{}^{18}R_{\mathrm{reference}}} \tag{1}$$

where ${}^{18}R_{\mathrm{sample}}$ is the ${}^{18}\mathrm{O}/{}^{16}\mathrm{O}$ abundance ratio in the sample; ${}^{18}R_{\mathrm{reference}}$ is the corresponding ratio in a reference material. The δ value, being a ratio of dimensionless quantities, is also dimensionless. Because it is of small magnitude ($\ll 1$) in natural systems, it is usually reported as parts per thousand (designated 'per mil', or '‰').

The developments in mass spectrometry instrumentation enabled McCrea (1950), Urey et al. (1951) and Epstein et al. (1951) to investigate the carbonate-water isotopic temperature exchange scale in detail. It was shown that δ^{18}O measurements of marine carbonates could be used to determine the ocean water temperatures to ±1 °C on a geologic timescale. Urey et al. (1951) already noted that the approach requires knowledge of the past seawater composition and that the δ^{18}O of the carbonate did not change with time. These two factors persist to be the most important unknowns in paleo-thermometry. Epstein and Mayeda (1953) extended the measurements to include various natural waters and detail the effects of glaciation. Following a preliminary investigation by Baertschi (1950), Baertschi and Silverman (1951) extracted oxygen from silicate crustal rocks by fluorination (with HF and either ClF_3 or F_2) and reported a δ^{18}O range of 24‰. They also noted that their measurements (made on O_2 as the analyte gas) could be used to determine the temperature of equilibration and mineral closure. Conversion of extracted O_2 to CO_2, by reaction with a heated graphite rod (Clayton 1955) was generally adopted for δ^{18}O measurements in future studies. This was because CO_2 molecular ions occur in a region of the mass spectrum not coinciding with the major background ions from air O_2 and N_2. Furthermore, CO_2 is less corrosive to the mass spectrometer filament than is O_2. Later, Clayton and Mayeda (1963) used BrF_5 as the fluorination reagent for extracting oxygen from silicate rocks, for improved oxygen yields and reduced systematic errors in the isotope data.

Besides equilibrium exchange, variations of light element stable isotope ratios in nature may also result from kinetic effects, with the rates of chemical reactions (or physical processes, such as diffusion) differing for isotopically substituted molecules. Early theoretical considerations for quantifying the effects of isotopic substitution on the rates of chemical reactions were published by Bigeleisen (1952) and by Bigeleisen and Wolfsberg (1957).

Despite the existence of the least abundant stable isotope of oxygen, ^{17}O, having been suggested and confirmed as early as 1924 (Blackett 1925), and its presence identified in Earth's atmosphere (Giauque and Johnston 1929) before the discovery of deuterium by H. C. Urey in 1931, no mention of ^{17}O was made in the early calculations of equilibrium constants and their temperature dependence for isotope exchange reactions. This was also true for a review three decades later (Richet et al. 1977). The first application of ^{17}O in the isotope geochemistry literature was the 'Craig correction' (Craig 1957) for quantifying the contribution of ${}^{12}\mathrm{C}^{16}\mathrm{O}^{17}\mathrm{O}^{+}$ isotopologues[1] to the mass 45 ion beam when deriving δ^{13}C values from measurements on CO_2. Based on Craig's (1957) data on CO_2 extracted from Peedee Formation calcite by concentrated H_3PO_4 at 25.2 °C (McCrea 1950), ~6.3% was attributable to ${}^{12}\mathrm{C}^{16}\mathrm{O}^{17}\mathrm{O}^{+}$. In formulating the

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[1] Isotopologues (a contraction of *isotopic homologues*) are molecular entities that differ only in isotopic composition, e.g. $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$.

correction procedure, Craig (1957) postulated that: “For systems in thermodynamic equilibrium, consideration of the vibrational frequency decrease for the addition of one and of two neutrons to a nucleus indicates that the fractionation factor for the distribution of ^{18}O between two compounds should be the square of the fractionation factor for ^{17}O”. The relative abundances of the three oxygen isotopes should therefore follow a simple power law:

$$\frac{^{17}R_{\text{sample}}}{^{17}R_{\text{reference}}} = \left(\frac{^{18}R_{\text{sample}}}{^{18}R_{\text{reference}}} \right)^{0.5} \tag{2}$$

In delta notation

$$1 + \delta^{17}\text{O} = (1 + \delta^{18}\text{O})^{0.5} \tag{3}$$

Using the Maclaurin series expansion

$$\ln(1+x) = x - \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 - \ldots \cong x \tag{4}$$

and neglecting higher order terms, this relationship between the three isotopes can thus be approximated to:

$$\delta^{17}\text{O} \approx 0.5\delta^{18}\text{O} \tag{5}$$

Isotope ratio modifications that follow this pattern of proportionality are commonly referred to as ‘mass-dependent’ fractionations. Essentially, they result from the mass difference between ^{17}O and ^{16}O (1.0042 Da) being approximately half the mass difference between ^{18}O and ^{16}O (2.0042 Da). Clearly, if all processes that modify $\delta^{18}O$ values followed this simple law exactly, then indeed nothing would be learned from also measuring $\delta^{17}O$. Fortunately, however, oxygen triple-isotope distributions in natural systems are more variable than is suggested by this simple analysis.

Non-mass-dependent oxygen triple-isotope distributions

In a study of refractory calcium-aluminum-rich inclusions, fragments, chondrules and isolated crystals in type-2 and type-3 (C2 and C3) carbonaceous chondritic meteorites, Clayton et al. (1973) made the surprising discovery that the apparent $\delta^{13}C$ of the CO_2 used as the analyte gas for isotope ratio measurements was negatively correlated with the $\delta^{18}O$ value, which varied by nearly 40‰. As the standard (heated graphite rod) method for the conversion of O_2 to CO_2 had been used, the authors correctly attributed the apparent change in $\delta^{13}C$ to a change in $\delta^{17}O$. Assuming that the $\delta^{13}C$ value was constant, Clayton et al. (1973) found that the oxygen triple-isotope distributions conformed to $\delta^{17}O \approx \delta^{18}O$, rather than to a mass-dependent trend with $\delta^{17}O \approx 0.5\,\delta^{18}O$. Approximately half of the samples were from the Allende meteorite (a type CV3). In addition to the data forming an array of slope one on a $\delta^{17}O$ versus $\delta^{18}O$ plot, the samples were strongly depleted in both minor isotopes. This led the authors to suggest that the oxygen isotopic compositions probably resulted from the admixture of a component of almost pure ^{16}O, of nucleosynthetic origin. That explanation was abandoned almost three decades later (Clayton 2002), however, in favor of a CO ‘self-shielding’ mechanism. This is now widely accepted and involves optical shielding of ultraviolet radiation by the most abundant isotopologue of carbon monoxide, $^{12}C^{16}O$. Such a mechanism had previously been suggested by Thiemens and Heidenreich (1983), although uncertainty about the chemical speciation of oxygen in the presolar nebula prevented those authors from assigning specifically which oxygen-bearing gas-phase molecule was most likely to be implicated. Other mechanisms to explain the $\delta^{17}O \approx \delta^{18}O$ relationship observed in many meteoritic components continue to be discussed, however (e.g., Chakraborty et al. 2013; Thiemens and Lin 2021, this volume).

Following the discovery of the unusual relationship between $\delta^{17}O$ and $\delta^{18}O$ in the high-temperature phases of Allende and other carbonaceous chondrites, further work (with O_2 as the analyte) led to the suggestion by Clayton et al. (1976) and Clayton and Mayeda (1983) that groups of meteorites whose $\delta^{18}O$ and $\delta^{17}O$ values plot on a distinct mass-dependent fractionation line (displaced from one another) originated on separate planetary bodies. The characterization and classification of meteorites on the basis of oxygen triple-isotope measurements (nowadays at significantly higher levels of precision) continues to be of fundamental importance to meteoritics and studies of the solar system.

The next major discovery to stimulate interest in ^{17}O was when Thiemens and Heidenreich (1983) showed that the generation of ozone from molecular oxygen by electrical discharge also produces a slope one array on a $\delta^{17}O$ versus $\delta^{18}O$ plot. This demonstration that mass-independent (also referred to as 'non-mass-dependent') isotopic fractionation of oxygen can result from a chemical process was of far-reaching significance. At the time, it was suggested that the effect may result from self-shielding by the major isotopologue, $^{16}O_2$, although that was subsequently shown to be improbable (Navon and Wasserburg 1985). Heidenreich and Thiemens (1986) then suggested that stabilization of the excited transition state during ozone formation is where the anomalous isotope effect occurs and that symmetry may play a role, as may isotope-specific reaction rates. The empirical findings have been discussed from a theoretical perspective in numerous subsequent publications, but details of the mechanism are still not fully understood. See Thiemens and Lin (2021, this volume) for further information.

The laboratory findings were followed by the discovery that stratospheric ozone is also characterized by a mass-independent ^{17}O enrichment (Schueler et al. 1990; Krankowsky et al. 2000; Mauersberger et al. 2001), as are stratospheric CO_2 (Thiemens et al. 1991, 1995a,b; Lämmerzahl et al. 2002) and stratospheric nitrous oxide (Cliff et al. 1999). Lämmerzahl et al. (2002) showed a tight coupling of the $\delta^{17}O$ and $\delta^{18}O$ values of stratospheric CO_2, with the ratio being surprisingly high, at 1.70 ± 0.03, for the altitude range sampled (19 to 33 km). As shown in the same paper, ozone at this altitude range was found to exhibit a $\delta^{17}O$ versus $\delta^{18}O$ slope of 0.62 ± 0.06, which was probably controlled largely by the local temperature (Krankowsky et al. 2000). Tropospheric ozone was also found to be unusually enriched in ^{17}O (Krankowsky et al. 1995; Johnston and Thiemens 1997), as was tropospheric nitrous oxide (Cliff and Thiemens 1997). Transfer of ^{17}O enrichment, directly or indirectly, from stratospheric ozone into most other oxygen-bearing constituents of the atmosphere has since been documented (and reviewed by Thiemens 2013; Thiemens and Lin 2019). Stratospheric–tropospheric exchange results in tropospheric O_2 being depleted in ^{17}O (Luz et al. 1999) relative to the mass-dependent composition of photosynthetic O_2. Stratospheric CO_2 entering the troposphere (Boering et al. 2004; Thiemens et al. 2014; Liang and Mahata 2015) may experience successive isotopic exchange with water, especially leaf water, where the process is promoted by the presence of carbonic anhydrase. The isotopic exchange reduces—and may eventually eliminate—departure from non-mass-dependent composition.

Few other occurrences of the generation (rather than inheritance) of mass-independent oxygen isotopic composition have been documented. The fractionation in atmospheric CO as a result of the CO + ·OH reaction (Röckmann et al. 1998) is one example. A second is photodissociation of CO_2 by of 185 nm wavelength (ultraviolet) radiation, generating CO and O_2 which are unusually enriched in ^{17}O (Bhattacharya et al. 2000). Carbon monoxide photodissociation at shorter wavelengths (90–108 nm) in vacuum leads to atomic oxygen formation, which reacts with CO to produce CO_2 enriched in ^{17}O (Chakraborty et al. 2012). Of considerable significance in a cosmochemical context is the discovery that silica formed during gas phase oxidation of silicon monoxide by OH is characterized by a slope one array on the $\delta^{17}O$ versus $\delta^{18}O$ plot (Chakraborty et al. 2013).

The first examples of rocks or minerals on Earth that are characterized by non-mass-dependent oxygen isotope composition were discovered by Bao et al. (2000a) in massive sulfate deposits (gypcretes from the central Namib Desert and sulfate-bearing Miocene volcanic ash-beds in North America); also in sulfates from Antarctic dry valley soils (Bao et al. 2000b) and in desert varnish sulfates from Death Valley, USA (Bao et al. 2001). Substantial non-mass-dependent oxygen isotope distributions were subsequently found in atmospheric nitrate aerosols, sampled at coastal La Jolla, California (Michalski et al. 2003). Nitrate minerals (and, to a lesser extent, sulfates) of the Atacama Desert, northern Chile, also exhibit substantial enrichments of ^{17}O (Michalski et al. 2004), as do nitrates sampled in the dry valleys of Antarctica (Michalski et al. 2005). Modelling indicated that these unusual isotopic compositions could be traced to photochemical reactions in the troposphere and stratosphere.

Sulfate in snow and ice sampled at the South Pole (Savarino et al. 2003) was found to be characterized by strongly non-mass-dependent oxygen isotopic compositions. The authors suggested that SO_2 from explosive volcanic eruptions which ejected substantial quantities of material into the stratosphere was probably responsible and that reaction with O(^{3}P) in the stratosphere, rather than with coexisting ·OH, was the most likely mechanism. Similarly, volcanic sulfate from volcanic supereruption ash deposits sampled from dry lake beds in the Tecopa basin, California, contain strong enrichments in ^{17}O relative to mass-dependent isotopic composition (Martin and Bindeman 2009), indicative of the photolysis and oxidation of volcanic SO_2 by ^{17}O-enriched ozone or ·OH, in the stratosphere. Eruptions which did not eject material higher than the troposphere, however, produced sulfate of, or very close to, mass-dependent oxygen isotopic composition (Martin et al. 2014).

Non-mass-dependent oxygen triple-isotope distributions generated by processes not involving photochemical reactions

There are three reported examples of non-mass-dependent fractionation of oxygen isotopes—and not involving photochemistry—having been demonstrated in the laboratory. The first is that of ozone thermal decomposition (Bhattacharya and Thiemens 1988; Wen and Thiemens 1990, 1991). Equal ^{17}O and ^{18}O enrichments were found in the product O_2 when the decomposition was performed at 110 °C (Wen and Thiemens 1991). In contrast, photolyic decomposition by visible light gave a $\delta^{17}O/\delta^{18}O$ slope of ~0.53 at room temperature; this increased to ~0.65 if ultraviolet radiation was used.

The second example is that associated with the thermal decomposition of divalent metal carbonate minerals (calcite, magnesite and dolomite were the examples used), under conditions that prevent back-reaction and isotopic exchange between the resulting metal oxide and released CO_2 gas. For a collection of carbonates covering a wide range of $\delta^{18}O$ values (and including NBS 18 carbonatite and NBS 19 calcite), it was found that the decomposition products fitted parallel mass-dependent fractionation arrays, offset from each other by ~0.4‰ (Miller et al. 2002). The metal oxides were anomalously depleted in ^{17}O relative to mass-dependent composition, whereas the CO_2 was enriched by a corresponding amount (half the magnitude of the depletion in the metal oxide). There is still no satisfactory explanation for the empirical findings. It has been suggested (J. R. Hulston, *pers. comm.*) that Fermi resonance might be an influential factor. However, the theoretical analysis required to investigate that hypothesis has yet to be performed. Fermi resonance occurs when two vibrational energy levels associated with different diatomic or polyatomic vibrations have nearly the same energy, that is, may be 'accidentally degenerate'. It occurs in CO_2, where the υ_1 vibration at 1337 cm^{-1} is close to twice the υ_2 vibration at 667 cm^{-1}. A splitting of the 1337 cm^{-1} line results, as observed in the Raman spectrum. Essentially, Fermi resonance causes shifting of the energies and intensities of absorption bands; this has implications for isotope effects. Fermi resonance might be expected to occur during vibrational excitation of carbonates. In calcite, for example, υ_3 occurs at 1432 cm^{-1}, which is very close to twice the υ_4 value of 714 cm^{-1}

(both bands are Raman active). Depending on whether or not there is a linear progression in vibrational energy levels associated with substituting ^{16}O by ^{17}O or ^{18}O in the crystalline carbonate lattice could have significant implications for the isotopic composition of the thermal decomposition products, if the reaction pathway is influenced by Fermi resonance.

The third example—which does not involve any chemical reaction—is that the diffusion of molecular O_2 gas, at low pressure and in a closed volume, defies mass-dependent isotopic distributions when a thermal gradient is applied (Sun and Bao 2011a). In contrast to the more abundant stable isotopes of oxygen, ^{17}O has a non-zero nuclear spin value (5/2). In a follow-up paper, Sun and Bao (2011b) postulated that a—usually negligible—nuclear spin effect on the gas diffusion coefficient, amplified by the temperature gradient, may be responsible for the empirical observations. Such an effect had been predicted, from theoretical considerations, some 35 years earlier (Zel'dovich and Maksimov 1976).

OXYGEN TRIPLE-ISOTOPE SYSTEMATICS

The equilibrium mass-dependent distribution of the three stable isotopes of oxygen resulting from isotopic exchange between two chemical entities A and B may be described in terms of the ^{17}O and ^{18}O abundance ratios relative to ^{16}O as

$$\frac{^{17}R_{\mathrm{A}}}{^{17}R_{\mathrm{B}}} = \left(\frac{^{18}R_{\mathrm{A}}}{^{18}R_{\mathrm{B}}}\right)^{\theta} \tag{6}$$

which, by definition, gives the relationship between the respective fractionation factors as

$$\alpha^{17/16}_{\mathrm{A-B}} = \left(\alpha^{18/16}_{\mathrm{A-B}}\right)^{\theta} \tag{7}$$

and as expressed in delta values:

$$\frac{1+\delta^{17}\mathrm{O_A}}{1+\delta^{17}\mathrm{O_B}} = \left(\frac{1+\delta^{18}\mathrm{O_A}}{1+\delta^{18}\mathrm{O_B}}\right)^{\theta} \tag{8}$$

The exact magnitude of the exponent θ depends on the identity of A and B, since the energy differences between the various isotopically-substituted molecules depends not only on the respective masses of ^{16}O, ^{17}O and ^{18}O, but on the reduced masses in the molecular vibrations. The first investigation of such variations, and their temperature dependence, was by Matsuhisa et al. (1978). Calculations were performed according to the procedure of Urey (1947), i.e. with θ obtained as the ratio of natural logarithms of reduced partition function ratios, and with vibrational frequencies for ^{17}O-containing species calculated from published values for the corresponding ^{16}O- and ^{18}O-bearing entities. The harmonic oscillator approximation for molecular vibrations was assumed throughout. The authors reported that, for gas phase equilibrium exchange between CO_2 and water, θ ranges from 0.5233 at 0 °C to 0.5251 at 727 °C. This variation appears small, compared with the corresponding $\ln(\alpha^{18/16})$ varying by a factor of approximately twenty, and illustrates that the magnitude of θ is not particularly sensitive to temperature. For large changes in δ^{18}O, however, small variations in θ become important and the resulting influence on oxygen triple-isotope distributions is usually measurable, at current levels of precision.

Matsuhisa et al. (1978) also noted that, at low temperatures, the natural logarithm of the ratio of partition function ratios for CO_2 and water approach limiting values given by the respective ratios of the zero-point energy differences between the isotopically substituted molecules. For isotope exchange between water vapor and atomic oxygen, this is 0.53052; the comparable figure for CO_2 is 0.52554. At high temperatures, the ratio approaches a constant value of 0.53053 for all oxygen-bearing molecules, as derived from equation 8 of Urey (1947) and is in accord with the simple expression

$$\frac{\ln\left(\dfrac{^{17}Q}{^{16}Q}\right)}{\ln\left(\dfrac{^{18}Q}{^{16}Q}\right)}=\frac{\dfrac{1}{m_{16}}-\dfrac{1}{m_{17}}}{\dfrac{1}{m_{16}}-\dfrac{1}{m_{18}}} \tag{9}$$

where m_{16}, m_{17} and m_{18} are the atomic masses of ^{16}O, ^{17}O and ^{18}O respectively. Matsuhisa et al. (1978) observed that, for temperatures of interest, ratios of the natural logarithms of partition function ratios for oxygen-bearing molecules vary from about 0.527 to 0.530. In exchange reactions, however, the θ values will be somewhat lower and more variable, depending on the specific reaction considered. The authors reported that a range of 0.520 to 0.528 was obtained from various representative reactions (unspecified) for which calculations were made. This was a highly significant finding, which has since been shown experimentally to be largely true. In the same paper, the authors also reported an experimental determination of $10^3\ln(\alpha^{17/16})$ and $10^3\ln(\alpha^{18/16})$ for oxygen isotope exchange at equilibrium in the quartz–water system at 250 °C. The respective values of 4.75 and 9.03 gave θ as 0.526. This number has been confirmed by more recent theoretical calculations (Cao and Liu 2011) and empirical data (Sharp et al. 2016).

In addition to considering equilibrium processes, Matsuhisa et al. (1978) reported that kinetic processes involving isotope exchange can be examined using a comparable formalism. Their calculations for the example of pinhole (Graham's law) diffusion, however, seem to have been based on an erroneous algorithm; the reported results are at variance with more recent discussions of the same example (Young et al. 2002; Dauphas and Schauble 2016). The relationship as derived in the later works is:

$$\theta_{\text{diffusion}}=\frac{\ln\left(\dfrac{M_{16}}{M_{17}}\right)}{\ln\left(\dfrac{M_{16}}{M_{18}}\right)} \tag{10}$$

where M_i refers to the masses of the isotopically substituted molecules. This gives values ranging from 0.516, for the diffusion of atomic oxygen, to 0.501 in the high molecular mass limit. As noted by Dauphas and Schauble (2016), the latter value also corresponds to

$$\theta_{\text{diffusion}}=\frac{m_{16}-m_{17}}{m_{16}-m_{18}} \tag{11}$$

Clayton and Mayeda (2009) showed experimentally that the lower limit value of θ for a kinetic process was approached during thermal dehydration, in vacuum, of Mg–O–H units in the minerals serpentine and brucite.

The oxygen isotopic compositions of crustal silicates on Earth generally results from interactions between solids, melts and aqueous fluids, involving many individual processes and with temperature playing an influential role. Therefore, it is to be expected that, as suggested by Matsuhisa et al. (1978), collections of silicate rocks and minerals will be characterized by oxygen triple-isotope distributions that result from the average of the many individual slopes for specific processes. Measurements on diverse rock and mineral samples reported during the past decade (and discussed below) indicate that, as expected, equilibrium processes dominate the slope value and there seems to be little evidence to suggest that the simple diffusion model is relevant in this context.

Experimental measurements of $\ln({}^{17/16}\alpha)/\ln({}^{18/16}\alpha) = \theta$

Few experimental measurements of the equilibrium exponent θ for oxygen triple-isotope exchange have been reported to date. Pack and Herwartz (2014) found that, for SiO_2 as chert in equilibration with water at ~50 °C, θ is 0.5235 ± 0.003. At 8 °C, a lower value of 0.5212 ± 0.0008 was determined from opal equilibrated with water. Data from high temperature rock assemblages (granite and San Carlos lherzolite) as reported in the same paper indicated that θ was of the order of 0.528 to 0.529, but the associated error bars were significantly larger because of the very limited $\delta^{18}O$ ranges of the samples investigated. Sharp et al. (2016) found that, for the temperature range ~0 to 50 °C, θ in the SiO_2–water system is 0.523–0.524 (see also Wostbrock and Sharp 2021, this volume). Taken together, these findings are consistent with the value at 250°C being 0.526, as determined experimentally by Matsuhisa et al. (1978). Oxygen triple-isotope exchange between biogenic apatite and water under equilibrium conditions has also been investigated experimentally (Pack et al. 2013), with θ reported to be 0.523 at 37 °C.

Barkan and Luz (2005) measured the fractionation factors ${}^{17/16}\alpha$ and ${}^{18/16}\alpha$ for water liquid–vapor exchange at equilibrium and found the $\ln({}^{17/16}\alpha)/\ln({}^{18/16}\alpha)$ ratio, θ, to be 0.529 ± 0.001 over the temperature range 11.4 to 41.5°C. The same authors subsequently conducted evaporation experiments to investigate the relative diffusivities of water vapor isotopologues in air and derived values for the diffusion fractionation coefficients ${}^{17/16}\alpha_{\text{diffusion}}$ and ${}^{18/16}\alpha_{\text{diffusion}}$ (Barkan and Luz 2007). The ratio $\ln({}^{17/16}\alpha_{\text{diffusion}})/\ln({}^{18/16}\alpha_{\text{diffusion}})$ was found to be 0.5185 ± 0.0002, in very good agreement with the theoretical value and significantly smaller than the corresponding ratio reported by the same authors for water liquid–vapor equilibrium.

For CO_2–H_2O equilibrium exchange, θ was determined by Barkan and Luz (2012) as 0.5229 ± 0.0001 at 25 °C, which is in good agreement with the value of 0.522 ± 0.002 for the temperature range 2 to 37 °C as reported by Hofmann et al. (2012). Both values, however, are notably lower than the 0.5246 calculated from theoretical considerations by Cao and Liu (2011)[2] and also somewhat less than 0.5235 as calculated by Matsuhisa et al. (1978).

Defining and quantifying deviations from a reference fractionation relationship

To quantify departures from a specific fractionation relationship between ${}^{17}O/{}^{16}O$ and ${}^{18}O/{}^{16}O$, Clayton and Mayeda (1988) proposed the term $\Delta^{17}O$, which they defined as:

$$\Delta^{17}O = \delta^{17}O - 0.52\delta^{18}O \tag{12}$$

This famous equation has since been used routinely in studies of meteorites; also for quantifying terrestrial non-mass-dependent isotope effects. It is based on approximating a power law relationship, as discussed above. Assigning 0.52 as the constant of proportionality was attributed to measurements made more than a decade earlier (Clayton et al. 1976; Matsuhisa et al. 1978) of 35 terrestrial samples—including various rocks and waters—which were found to form an array of slope 0.5164 ± 0.0033 (standard error of the mean, SEM) on a $\delta^{17}O$ versus $\delta^{18}O$ plot. Unfortunately, no details of the samples, nor the actual isotope data, were reported. Matsuhisa et al. (1978) mentioned that, on the basis of those measurements, a slope of 0.520 was chosen for the quartz–water system as a reasonable compromise between theoretical calculations and empirical observations. This defined a reference (terrestrial) fractionation line; the extent to which meteorite samples deviated from this was quantified by the parameter $\Delta^{17}O$. Definitions of $\Delta^{17}O$ using different constants of proportionality have since appeared in the literature, according to the particular application and associated mass fractionation characteristics. For example, Cliff and Thiemens (1997) used 0.515 in defining the $\Delta^{17}O$ of atmospheric nitrous oxide; Boering et al. (2004) assigned 0.516 for defining the $\Delta^{17}O$ of stratospheric carbon dioxide; Luz et al. (1999) used 0.521 as determined from the fractionation of O_2 during respiration.

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[2] The θ_{CO_2}–water value at 25 °C was later recalculated as 0.523 (Y. Liu, *pers. comm.* in Hofmann et al. 2012).

A consequence of the δ^{17}O versus δ^{18}O relationship not being truly linear is that the slope given by a collection of data points on such a plot is dependent on the range of δ values associated with the group of samples and on the isotopic composition of the reference material. An example of this is shown in Figure 1. For consistency of reporting and comparison of data sets, it is therefore advantageous to avoid the approximation. The oxygen triple-isotope distributions in a collection of silicate rock and mineral samples (or waters) of diverse origin will generally conform to the mass-dependent fractionation relationship

$$\frac{^{17}R_{\text{sample}}}{^{17}R_{\text{reference}}} = \left(\frac{^{18}R_{\text{sample}}}{^{18}R_{\text{reference}}}\right)^{\lambda} \tag{13}$$

as shown experimentally by Meijer and Li (1998) for natural waters. The exponent term in this case is designated as λ rather than θ, to indicate that the isotope exchange processes are undefined. Thus, λ is a purely empirical parameter, the magnitude of which results from the cumulative effects of (unspecified) fractionations associated with the history of the individual samples. To quantify deviations from a specific mass-dependent fractionation curve, an additional term is needed:

$$\frac{^{17}R_{\text{sample}}}{^{17}R_{\text{reference}}} = (1+k)\left(\frac{^{18}R_{\text{sample}}}{^{18}R_{\text{reference}}}\right)^{\lambda} \tag{14}$$

With δ values rather than absolute ratios, and with k defined to be Δ^{17}O, then, as suggested by Miller (2002)

$$\Delta^{17}\text{O} = \frac{1+\delta^{17}\text{O}}{\left(1+\delta^{18}\text{O}\right)^{\lambda}} - 1 \tag{15}$$

which is of a similar form to the definition of the δ value. In linear format,

$$\ln(1+\Delta^{17}\text{O}) = \ln\left(1+\delta^{17}\text{O}\right) - \lambda\ln\left(1+\delta^{18}\text{O}\right) \tag{16}$$

It needs to be remembered that the δ^{17}O and δ^{18}O data here are not 'per mil' values, as conventionally reported, but the absolute numbers ($\ll 1$). Therefore, it is useful to include a multiplier of 10^3 so that the logarithmic terms involving δ^{17}O and δ^{18}O are then of similar magnitude to the corresponding δ^{17}O and δ^{18}O data reported as 'per mil':

$$10^3\ln(1+\Delta^{17}\text{O}) = 10^3\ln\left(1+\delta^{17}\text{O}\right) - \lambda 10^3\ln\left(1+\delta^{18}\text{O}\right) \tag{17}$$

Following similar terminology introduced by Hulston and Thode (1965) in the context of sulfur multiple isotope ratios, the quantities $10^3\ln(1 + \delta^{17}\text{O})$ and $10^3\ln(1 + \delta^{18}\text{O})$ are sometimes denoted as δ'^{17}O and δ'^{18}O respectively. As reported by Miller (2002), a plot of $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ data obtained from a collection of silicate rocks and minerals (for example) thus gives a linear array of slope λ, invariant to the range of δ values and to the isotopic composition of the reference, and with the ordinate deviation of an individual sample from the mass-dependent reference fractionation line being quantified by $10^3\ln(1 + \Delta^{17}\text{O})$. With $10^3\ln(1 + \Delta^{17}\text{O})$ written as Δ'^{17}O, similar to the definitions of δ'^{17}O and δ'^{18}O, we then obtain the simple, non-approximated relationship:

$$\Delta'^{17}\text{O} = \delta'^{17}\text{O} - \lambda\delta'^{18}\text{O} \tag{18}$$

This definition is used throughout this volume. What is perhaps not immediately intuitive is that, instead of assigning the magnitude of λ from a set of measurements, a value may alternatively be assigned arbitrarily. For example, reference lines of slope 0.528 (as used throughout this volume) or 0.5305—and passing through VSMOW—have been defined for the reporting of $\Delta'^{17}O$ in various recent studies. Not accounted for in this $\Delta'^{17}O$ definition, however, is the magnitude of any offset of a reference line from the zero point of the δ scale. At the time that the definition of $\Delta'^{17}O$ was proposed, it was considered that fractionation arrays formed from silicates (or meteoric waters) were not offset from VSMOW. This was subsequently found to be incorrect, although quantifying the small magnitude of the offsets generally requires the highest levels of precision and accuracy. Defining a reference line that is offset from the zero point of the δ scale by a specified amount may also be useful under some circumstances. Therefore, an additional term is required in the definition of $\Delta'^{17}O$; it is usually designated as γ, and with $\gamma' \equiv 10^3\ln(1 + \gamma)$. Thus, we now have:

$$\Delta'^{17}O = \delta'^{17}O - \lambda\delta'^{18}O - \gamma' \tag{19}$$

If defined from an empirical data array, the exact magnitude of λ is representative of the particular group; there is not necessarily an implied relationship between the individual samples. Different collections of silicate rock and mineral samples generally give slightly different values of λ (usually between 0.522 and 0.529) and of γ′. Recalibration more accurately to the VSMOW scale, on the basis of Pack et al. (2016) and Miller et al. (2020), of Open University measurements of the two silicates arrays reported by Rumble et al. (2007) results in γ′ values of +8 ± 19 ppm (95% confidence interval) for the hydrothermal quartz and chalk flint array; –38 ± 5 ppm for the eclogite garnets. These values are 12 ppm lower than given by Hallis et al. (2010). Similarly, recalibration by Tanaka and Nakamura (2017) of the γ′ value the same authors reported in 2013, results in a revised γ′ value of –33 ± 5 ppm. This small number of examples is probably not indicative of the γ′ range limits. Despite the variations of λ and γ′, individual arrays have frequently been referred to as a ‘Terrestrial Fractionation Line’ (TFL).

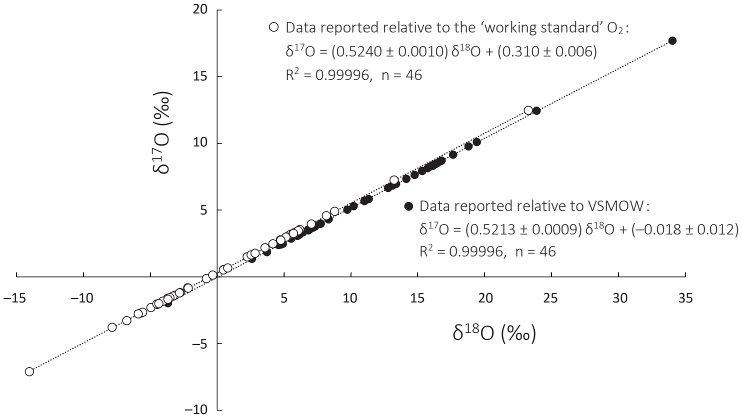

Figure 1. Illustrating that a change of reporting reference for $\delta^{17}O$ and $\delta^{18}O$ measurements (from the laboratory ‘working standard’ O_2 to VSMOW, in this example) may be associated with a changed regression line slope and ordinate offset on a $\delta^{17}O$ versus $\delta^{18}O$ plot. This is caused by the δ scale being non-linear, leading to non-linearity of $\delta^{17}O$ versus $\delta^{18}O$ data arrays. The extent of non-linearity increases with distance from the zero point of the scale. For this example, the data are from Miller et al. (1999). The $\delta^{18}O$ value of the ‘working standard’ O_2 was 10.34‰ relative to VSMOW, with corresponding $\Delta'^{17}O_{0.528} = +0.387$‰ (as derived from Miller et al. 2015). Converting to the VSMOW scale, from data (shown as **open circles**) reported relative to the working standard O_2, therefore involves substantial positive shifts of the respective $\delta^{18}O$ and $\delta^{17}O$ values. This results in best linear fit to the converted data (**filled circles**) requiring a different regression line, as shown. Precision values refer to the 95% confidence interval.

The terminology λ_{RL} and γ_{RL} has recently been introduced to denote that λ_{RL} and γ_{RL} are defined quantities (with RL referring to 'reference line') and is gaining acceptance. The respective values need to be clearly stated, as there is currently no consensus. This is discussed by Hofmann et al. (2017), who identified six different reference lines used in various studies. An advantage of writing $\Delta'^{17}O$ rather than $\Delta^{17}O$ is that it provides a clear distinction from the original definition introduced by Clayton and Mayeda (1988). For simplicity, the 10^3 multiplier term is usually omitted from the definition and γ'_{RL} approximated as γ_{RL}, on the basis that $|\gamma|$ is usually $< 10^{-4}$ or is defined to be zero. Thus,

$$\Delta'^{17}O = \ln\left(1+\delta^{17}O\right) - \lambda_{RL}\ln\left(1+\delta^{18}O\right) - \gamma_{RL} \tag{20}$$

This definition is becoming generally adopted (e.g., Hofmann et al. 2017) and is advocated for future reporting of $\Delta'^{17}O$ data. As a ratio, it may be written (in non-approximated form) as:

$$\Delta'^{17}O = \frac{1+\delta^{17}O}{\left(1+\gamma_{RL}\right)\left(1+\delta^{18}O\right)^{\lambda_{RL}}} - 1 \tag{21}$$

A graphical representation of the relationship between the various parameters is shown in Figure 2. Because of the small magnitude of $\Delta'^{17}O$ in many studies, it is usually reported as parts per million (ppm). In some of the earlier literature, the term 'per meg' is used instead of ppm.

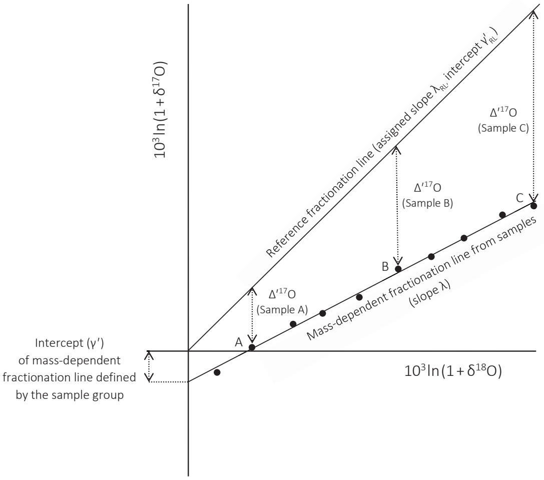

Figure 2. Schematic illustration of the relationship between $\Delta'^{17}O$ values for a set of rock, water or gas samples and: (i) the reference mass-dependent fractionation line characterized by assigned slope λ_{RL} (0.528, for the VSMOW-SLAP scale) and assigned ordinate axis intercept value γ'_{RL} (zero, in this example) on the $10^3\ln(1 + \delta^{17}O)$ versus $10^3\ln(1 + \delta^{18}O)$ plot; (ii) the mass-dependent fractionation line of slope λ and ordinate axis intercept value γ' formed by the collection of samples. Unlike λ, the value of γ' will depend on the isotopic composition of the reference material (usually VSMOW) relative to which $\delta^{17}O$ and $\delta^{18}O$ values are reported; also on the accuracy of the calibration of the 'working standard' O_2 relative to that reference. If λ_{RL} differs significantly from λ, $\Delta'^{17}O$ will vary with increasing $\delta^{18}O$ as an artefact of the increasing divergence (or convergence) of the two mass-dependent fractionation lines.

For completeness, we note that an earlier definition used by Farquhar et al. (1998) also avoided the approximation of a linear relationship between $\delta^{17}O$ and $\delta^{18}O$:

$$\Delta^{17}O = 1+\delta^{17}O-(1+\delta^{18}O)^{0.52} \tag{22}$$

With $\lambda_{\text{RL}} = 0.52$ and $\gamma_{\text{RL}} = 0$, this expression gives very similar results to those obtained from the recommended Δ'^{17}O definition, for a given triple-isotope data set. We also note that (rather confusingly) Angert et al. (2003) defined $\delta'^{17}\text{O} - \lambda\,\delta'^{18}\text{O}$ as $^{17}\Delta$. The $^{17}\Delta$ notation has not gained general acceptance, however.

In much of the literature reporting oxygen triple-isotope ratio measurements of waters, snow and ice cores, Δ'^{17}O is referred to as '^{17}O-excess', a term introduced by Luz and Barkan (2000) and subsequently defined by the same authors (Barkan Luz 2007) as

$$^{17}\text{O-excess} = \ln\left(1+\delta^{17}\text{O}\right) - 0.528\ln\left(1+\delta^{18}\text{O}\right) \tag{23}$$

This does indicate that ^{17}O-excess is ≥ 0 in all cases, otherwise there is the incongruity of a 'negative excess'. The definition of ^{17}O-excess is identical to the definition of Δ'^{17}O used throughout this volume. The expression '^{17}O anomaly' is also sometimes adopted (e.g., Thiemens et al. 1995b; Dauphas and Schauble 2016), to describe non-mass-dependent isotope distributions. For simplicity and consistency, we suggest that it is preferable to use the term Δ'^{17}O universally and with the values of λ_{RL} and γ_{RL} clearly stated. For consistency throughout this volume, the Editors have recommended that Δ'^{17}O be defined using $\lambda_{\text{RL}} = 0.528$ and $\gamma_{\text{RL}} = 0$.

It should be noted that Δ'^{17}O does not behave linearly with regard to mixing calculations, unlike Δ^{17}O as defined by Clayton and Mayeda (1988). It is therefore necessary to use the associated δ^{17}O and δ^{18}O data for calculating changes in Δ'^{17}O resulting from the mixing of fluids characterized by different isotopic compositions. Finally, a detailed discussion of the theoretical principles and calculations of mass-dependent fractionation processes in the oxygen triple-isotope system is beyond the scope of this introductory section. For further reading, see Schauble and Young (2021, this volume); Yeung and Hayles (2021, this volume); Brinjikji and Lyons (2021, this volume); Thiemens and Lin (2021, this volume). The review by Dauphas and Schauble (2016) is also recommended. Cao and Liu (2011) and Bao et al. (2016) provide additional insights.

REFERENCE MATERIALS AND STANDARDS

Early measurements of oxygen triple-isotope ratios (e.g., Clayton et al. 1973) were reported relative to the Standard Mean Ocean Water (SMOW) standard described by Craig (1961); this practice continued for some considerable time. In 1968, the International Atomic Energy Agency (IAEA) began distributing two new water reference materials, Vienna Standard Mean Ocean Water (V-SMOW) and Standard Light Antarctic Precipitation (SLAP). Both were prepared by H. Craig at the University of California San Diego: V-SMOW by mixing distilled Pacific Ocean water (collected in July 1967) with small amounts of other waters in order to make the isotopic composition as close as possible to that of SMOW. V-SMOW is also referred to as RM 8535 by the US National Institute of Standards and Technology (NIST). SLAP was prepared from a firn sample collected in 1967 at Plateau Station, Antarctica, by E. E. Picciotto of the Université Libre de Bruxelles. On the basis of comparative measurements by 36 different institutions, the δ^{18}O value of SLAP was assigned in 1976 as –55.5‰ exactly, by the IAEA (Gonfiantini 1978), with V-SMOW (subsequently re-designated as VSMOW) defined as the zero point of the scale. SLAP is also referred to as RM 8537 by NIST.

For improved consistency of reporting δ^{18}O measurements, it was recommended that data be normalized to the VSMOW-SLAP scale (Gonfiantini 1978). Thus, δ^{18}O data (relative to VSMOW) should be scaled by a factor of $(-55.5)/(\delta^{18}\text{O}_{\text{SLAP/VSMOW}})$ where $\delta^{18}\text{O}_{\text{SLAP/VSMOW}}$ is the measured value of SLAP relative to VSMOW. It has since been suggested that the assigned δ^{18}O value of SLAP may be significantly in error, however. On the basis of a report by Verkouteren and Klinedinst (2004), Kaiser (2008) noted that the 'true' δ^{18}O value seems to be –56.18 ± 0.01‰, illustrating that the VSMOW-SLAP δ^{18}O scale is associated with significant uncertainties for values far removed from VSMOW. Because measurement artefacts such as cross-contamination generally lead to a compression of the δ scale, the value of –56.18 ± 0.01‰ for SLAP is likely to be more accurate. Nevertheless, the value of –55.5‰ has been retained for calibration to the VSMOW-SLAP scale.

With stocks of VSMOW and SLAP becoming low, the IAEA ceased to distribute those reference waters after November 2006. However, successor materials VSMOW2 and SLAP2, prepared to have nominally identical isotopic characteristics to VSMOW and SLAP respectively, were produced at the IAEA Isotope Hydrology Laboratory and made available from 2007 onwards. Details of the respective preparations are given by Harms and Gröning (2017). It is important to recognize that the reporting scale for δ^{18}O (and for δ^{2}H) is still denoted and referred to as the VSMOW–SLAP scale, despite VSMOW and SLAP being no longer available. The non-availability of VSMOW and SLAP doesn't prevent calibration (or normalizing) measurements to VSMOW and SLAP using VSMOW2 and SLAP2, which provide suitable traceability to VSMOW and SLAP respectively (Dunn et al. 2020).

Oxygen triple-isotope ratio measurements (especially at high precision) are generally performed using molecular oxygen as the analyte gas and reported relative to the equivalent ratios in a reference material (usually VSMOW). For investigations involving rocks and minerals, the use of a water reference material causes significant calibration challenges. The accuracy of reported δ^{17}O and δ^{18}O data is critically dependent, however, on the accuracy of calibration (relative to VSMOW) of a laboratory 'working standard' O_2 against which the isotopic composition of molecular oxygen extracted from silicates (or waters) is compared. The extent of instrumental scale compression should also be established, from measurements of molecular oxygen extracted from SLAP. A few silicates, such as the University of Wisconsin garnet standard UWG-2 (Valley et al. 1995) and San Carlos olivine, are widely used for calibrating the δ^{18}O value of individual laboratory's 'working standard' O_2, although there remains a lack of consensus about the exact δ^{18}O values of those silicates relative to VSMOW. Furthermore, there are currently no standards for δ^{17}O and recent attempts to characterize the δ^{17}O values of UWG-2 and San Carlos olivine have not resulted in consensus (Pack et al. 2016; Sharp et al. 2016; Miller et al. 2020; Wostbrock et al. 2020). Table 1 lists those recent results. It should be noted that two distinct variations of San Carlos olivine have been identified (designated as Type I and Type II); these are characterized by different δ^{18}O values. It is probable that other variations also exist. Type I is characterized by δ^{18}O = 4.88‰ (Mattey and Macpherson 1993; Thirlwall et al. 2006). Macpherson et al. (2005) reported a value of 4.84 ± 0.09‰, together with 5.22 ± 0.08‰ for the more commonly-used Type II. In a more recent investigation, Starkey et al. (2016) compared δ^{18}O and also δ^{17}O measurements of Types I and II San Carlos olivine. They noted that, despite the variations in δ^{18}O, the corresponding Δ'^{17}O value seemed to be constant. This latter finding was subsequently confirmed by Miller et al. (2020). For further discussion on standardizing oxygen triple-isotope data, see Sharp and Wostbrock (2021, this volume).

Despite atmospheric O_2 having a deficit of ^{17}O relative to mass-dependent composition, a number of studies have used it as a standard, notably in investigations of the triple-isotope composition of dissolved O_2 for estimating global and oceanic biological productivity (e.g., Luz et al. 1999; Luz and Barkan 2000). Because δ^{17}O and δ^{18}O measurements of air O_2 are affected by the presence of argon (which was not removed in those investigations), corrections needed to be applied (Barkan and Luz 2003)[3]. Converting the resulting isotope data to the VSMOW-SLAP scale, however, is complicated by the δ^{17}O and δ^{18}O values of air O_2 relative to the VSMOW reference water not having been universally agreed, as discussed below.

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[3] In more recent studies involving isotopic measurements of air O_2 (Yeung et al. 2012; Young et al. 2014; Pack et al. 2017; Wostbrock et al. 2020), all other atmospheric constituents were removed, including Ar.

Table 1. Recent high-precision oxygen triple-isotope measurements of widely-used silicate standards San Carlos olivine and UWG-2 garnet.

Institution	***n***	**$\delta^{18}O_{VSMOW}$ (‰)**	**$\Delta'^{17}O_{0.528}$ (ppm)**	**Reference**
San Carlos olivine				
Georg-August-Universität	30	5.153 ± 0.161	–36 ± 7	Pack et al. (2016)
Okayama University	5	5.287 ± 0.047	–39 ± 7	Pack et al. (2016)
University of New Mexico	12	5.577 ± 0.095	–54 ± 8	Sharp et al. (2016)
University of New Mexico	18	5.268 ± 0.023	–58 ± 5	Wostbrock et al. (2020)
UWG-2 garnet				
University of New Mexico	9	5.696 ± 0.115	–71 ± 5	Wostbrock et al. (2020)

Notes: Measurement precision data are 1σ. All data were calibrated directly to VSMOW and SLAP. With the $\delta^{18}O_{VSMOW}$ and $\Delta'^{17}O_{0.528}$ values of UWG-2 garnet assigned as 5.75‰ and –46 ppm respectively, for calibration purposes, Miller et al. (2020) reported that the $\Delta'^{17}O_{0.528}$ value of San Carlos olivine is –38 ± 9 ppm (1σ) as measured at Georg-August-Universität Göttingen, with comparable measurements at The Open University giving –38 ± 8 ppm (i.e., in accord with the inter-laboratory comparison reported by Pack et al. 2016).

For maximum accuracy, linear scaling to VSMOW-SLAP requires that ln(1 + $\delta^{18}O$) values be adjusted, rather than the corresponding $\delta^{18}O$ data, because of the non-linearity of the δ scale. The 'true' scaling factor is therefore ln(1 – 0.0555)/ln(1 + $\delta^{18}O_{SLAP/VSMOW}$), with $\delta^{18}O_{SLAP/VSMOW}$ referring to the measured value of SLAP relative to VSMOW. Fortunately, as noted by Kaiser (2008), the numerical differences between the conventional and logarithmic normalization procedures are generally small. Kusakabe and Matsuhisa (2008) did normalize their ln(1 + $\delta^{18}O$) data to VSMOW-SLAP, with the same scale factor of (–57.10)/(–56.20) being applied to their ln(1 + $\delta^{17}O$) results. The same approach was adopted by Ahn et al. (2012). Kaiser (2008) recommended a similar normalization, but in power law format and with λ assigned to be 0.528, as shown to apply to natural waters (Meijer and Li, 1998):

$$\delta^{17}O^{\text{sample}}_{\text{VSMOW-SLAP normalized}} = \delta^{17}O_{\text{VSMOW}}\,\frac{(1+\delta^{18}O_{\text{SLAP/VSMOW, measured}})^{0.528}-1}{(1+\delta^{18}O_{\text{SLAP/VSMOW, assigned}})^{0.528}-1} \tag{24}$$

These scaling procedures preserve the oxygen triple-isotope ratio relationship of the $\delta^{17}O$ and $\delta^{18}O$ measurements, whilst ensuring that the measured $\delta^{18}O$ values are normalized to the VSMOW-SLAP scale. To improve inter-laboratory consistency of $\Delta'^{17}O$ data from measurements of water samples, Schoenemann et al. (2013) proposed that $\delta^{17}O$ measurements be normalized to the VSMOW-SLAP scale in the same way as recommended by Gonfiantini (1978) for normalizing $\delta^{18}O$ data, with the $\delta^{17}O$ value of SLAP *defined* to give $\Delta'^{17}O$ of exactly zero, relative to a reference line of $\lambda_{RL} = 0.528$ and $\gamma_{RL} = 0$. Schoenemann et al. (2013) reported that the resulting scale factor for the $\delta^{17}O$ measurements is therefore approximately (–29.6986)/$\delta^{17}O_{SLAP/VSMOW}$. This recommendation involves scaling of the empirical $\delta^{17}O$ results independently of the corresponding $\delta^{18}O$ data. Essentially, the experimental data are adjusted so that the measurements of SLAP fit exactly on a reference line of slope 0.528 and which passes through VSMOW on a ln(1 + $\delta^{17}O$) versus ln(1 + $\delta^{18}O$) plot. The two-point calibration also addresses other instrument-related effects, as discussed by Yeung et al. (2018) and by Pack (2021, this volume). Recent measurements of SLAP indicate that it is characterized by a $\Delta'^{17}O$ value slightly less than zero. Schoenemann et al. (2013) obtained a value of –6 ± 8 ppm (1σ). Wostbrock et al. (2020) reported that averaging their own measurements (–15 ± 5 ppm) with the –9 ± 7 ppm result reported by Sharp et al. (2016) and –8 ± 9 ppm obtained at Okayama University (Pack et al. 2016) gives a value of –11 ± 4 ppm.

^{16}O, ^{17}O AND ^{18}O ABUNDANCES AND ISOTOPE RATIO RANGES IN NATURALLY OCCURRING TERRESTRIAL MATERIALS

Oxygen is characterized by atomic number 8 and is the third most abundant element in the solar system, after hydrogen and helium. It is the most abundant element on Earth, with silicate and oxide minerals of the crust and mantle comprising by far the largest terrestrial reservoir (~99.5% by mass). Table 2 lists the masses of three stable isotopes of oxygen (Holden et al. 2018), together with their natural abundance ranges (Meija et al. 2016) and abundance ratios in VSMOW (IAEA reference sheet on VSMOW and SLAP 2006).

Table 2. Mass, natural abundance range, and abundance ratio in the VSMOW reference material, of the three stable isotopes of oxygen.

Isotope	Mass (Da)	Natural abundance range (atom%)	Abundance ratio (ppm) in VSMOW, relative to ^{16}O
^{16}O	15.994914619	99.738–99.776	10^6
^{17}O	16.999131757	0.0367–0.400	379.9 ± 0.8
^{18}O	17.999159613	0.187–0.222	2005.2 ± 0.45

Although ^{17}O is a factor of ~5.3 less abundant than ^{18}O in seawater, it is nevertheless approximately twice as abundant as deuterium. Reported $\delta^{18}O$ values of terrestrial silicate rocks and minerals vary from –27.3‰ (Bindeman et al. 2010, 2014), in the most extreme example of interaction with 'Snowball Earth'-derived synglacial meteoric waters at depth, to as high as 60.2‰ (and with $\Delta^{17}O$ ranging from 14–21‰) in nitrate deposits from the Atacama desert (Michalski et al. 2004). However, the largest known ^{18}O enrichments occur in stratospheric ozone ($\delta^{18}O$ up to ~110‰), with only slightly lower values in tropospheric ozone and nitrate aerosols. Isotopic data for these three species scatter about a slope one line on a $\delta^{17}O$ versus $\delta^{18}O$ array (Thiemens 2013). At the other end of the scale, a $\delta^{18}O$ value as low as –81.9‰ has been measured in precipitation collected at Dome Fuji, East Antarctica (Fujita and Abe 2006).

Oxygen triple-isotope measurements of atmospheric O_2

M.H. Thiemens (comment reported in Bender et al. 1994) first suggested that there should be a deficiency of ^{17}O in atmospheric O_2, relative to mass-dependent composition. This was based on a consideration of stratospheric photochemical reactions and mass exchange between the stratosphere and troposphere (Thiemens et al. 1991). The magnitude of the deviation from mass dependent composition was subsequently documented from experiments by Luz et al. (1999). The first high precision $\delta^{18}O$ and $\delta^{17}O$ measurements of atmospheric O_2 relative to VSMOW directly, however, were by Barkan and Luz (2005), who obtained $\delta^{18}O = 23.88 \pm 0.02‰$, $\delta^{17}O = 12.08 \pm 0.01‰$. Measurements on SLAP were reported in the same paper as –55.11 ± 0.01‰ and –29.48 ± 0.03‰, respectively, giving a $\Delta'^{17}O$ value (relative to $\lambda_{RL} = 0.528$) of 0.007‰. The air O_2 $\delta^{18}O$ value was in agreement with 23.79 ± 0.06‰ as obtained by Horibe et al. (1973) and also with the 23.8 ± 0.14‰ value (Coplen et al. 2002) obtained by recalibrating the measurements of Kroopnick and Craig (1972). The measurements by Horibe et al. (1973) and Kroopnick and Craig (1972) were made on CO_2 equilibrated with water of air O_2 isotopic composition. In none of those three studies was instrument-related contraction of the δ scale corrected for, however, which would increase the respective magnitudes of the $\delta^{17}O$ and $\delta^{18}O$ data. Relative to a reference line of $\lambda_{RL} = 0.528$ and passing through VSMOW, $\Delta'^{17}O$ for air O_2 as obtained from the Barkan and Luz (2005) data is –0.453‰. Normalizing their data to the VSMOW-SLAP scale as recommended by Schoenemann et al. (2013) shifts the $\Delta'^{17}O$ value by only 2 ppm, to –0.451‰, despite the corresponding $\delta^{18}O$ and $\delta^{17}O$ values being increased to 24.05‰ and 12.17‰ respectively. This illustrates the comparative robustness of $\Delta'^{17}O$ (resulting from the correlation of $\delta^{17}O$ and $\delta^{18}O$ measurement errors) relative to the $\delta^{17}O$ and $\delta^{18}O$ data.

Kaiser (2008) considered how 'true' linear scaling (i.e., of $\delta'^{17}O$ and $\delta'^{18}O$ values rather than $\delta^{17}O$ and $\delta^{18}O$) affects the isotope data from Barkan and Luz (2005). If a scaling factor of $\ln(1 - 0.0555))/\ln(1 - 0.05511) = 1.00728$ is applied to the $\delta'^{17}O$ and $\delta'^{18}O$ values, then $\Delta'^{17}O$ becomes –0.456‰. Again, the resulting change is very small. Performing the same scaling but with $\delta^{18}O_{SLAP/VSMOW} = -56.18‰$ as recommended by Kaiser (2008) gives $\Delta'^{17}O = -0.462‰$. This latter value is in close agreement with subsequent measurements by Kaiser and Abe (2012), which gave $\Delta'^{17}O = -0.460‰$. The corresponding $\delta^{17}O$ and $\delta^{18}O$ data were 12.25 ± 0.03‰ and 24.22 ± 0.04‰, corrected for a 0.8% scale contraction (which the authors noted may be typical for the type of instrument used).

Assigning the $\Delta'^{17}O$ value of San Carlos olivine on the VSMOW-SLAP scale as –0.051‰ (based on averaging the data from Pack et al. 2016; Sharp et al. 2016; and Wostbrock et al. 2020), the $\Delta'^{17}O$ value of air O_2 relative to VSMOW as reported by Pack et al. (2017) becomes –0.422‰ (it is –0.409‰ if based on Pack 2016, alone). Applying the same San Carlos calibration to measurements reported by Young et al. (2014) gives the $\Delta'^{17}O$ value of air O_2 as –0.425‰. If the Yeung et al. (2018) $\Delta'^{17}O$ value of UWG-2 garnet relative to air O_2 is revised to –0.061‰ (i.e., 10 ppm lower than that of San Carlos olivine), the derived $\Delta'^{17}O$ of air O_2 is –0.435‰. Anchoring recent data by Wostbrock et al. (2020) to both San Carlos olivine at $\Delta'^{17}O = -0.051‰$ and UWG-2 garnet at –0.061‰ results in the $\Delta'^{17}O$ value of air O_2 as –0.433‰. Data from different laboratories are thus converging, but more measurements of air O_2, silicates and waters (using similar extraction protocols and the same mass spectrometers) are needed for consensus values to emerge. At present, is evident that anchoring the $\Delta'^{17}O$ value of air O_2 to measurements of silicates results in more positive values than as obtained by direct measurements of VSMOW relative to air O_2. The reason for this is currently unknown.

Oxygen triple-isotope measurements of terrestrial silicates

The first investigation of oxygen triple-isotope mass fractionation relationships in terrestrial rocks since that reported by Matsuhisa et al. (1978) was by Robert et al. (1992). Modern cherts were compared with well-preserved examples of age up to 3.5 Ga (Precambrian), together with mantle-derived rocks (mid-ocean ridge basalts, ocean island basalts and continental flood basalts). No statistically meaningful distinction was apparent, on a $\delta^{17}O$ versus $\delta^{18}O$ plot, between the fractionation line derived from the modern cherts and that derived from the Precambrian samples. The authors interpreted this as showing that oxygen isotopic homogeneity between the Precambrian ocean and the Earth's mantle (through which the modern ocean has been extensively recycled) was already attained by 3.7 ± 0.1 Ga ago. A corollary was that the Precambrian sedimentary rocks presented no evidence for the delivery of extraterrestrial (cometary) water.[4] Within measurement error, the mantle-derived rocks all fitted on the mass-dependent fractionation line defined by the cherts. Meijer and Li (1998) noted that if the chert data reported by Robert et al. (1992) are re-formulated to obtain the corresponding λ values, the result is the same (although at significantly lower precision) as that determined by Meijer and Li (1998) for meteoric waters.

A significant technical advance in oxygen triple-isotope measurements of rocks and minerals was the demonstration by Sharp (1990) that fluorination of silicates and oxides by BrF_5 vapor could be achieved rapidly and quantitatively using a CO_2 laser beam (10.6 μm wavelength) as the heat source, directed onto the sample through a BaF_2 window in a purpose-designed fluorination cell. Far smaller quantities of material were needed than for the conventional (Clayton and Mayeda 1963) procedure and the attendant blanks were very much reduced. Furthermore, even the most refractory minerals could be fluorinated, by heating to incandescence and without heating the surrounding chamber. In that initial report, the resulting oxygen gas was converted into CO_2 by reaction with a hot graphite rod (catalyzed by Pt wire),

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[4] Rumble (2018) reported that the isotopic homogeneity has since been extended back to 4.3 Ga before present, i.e. earlier than the beginning of the Archean Eon.

for $\delta^{18}O$ analysis only. Rumble and Hoering (1994) showed that a similar procedure but using F_2 as the fluorinating agent (derived from heating Asprey's salt, $K_2NiF_6 \cdot KF$) was also possible and with the extracted O_2 used as the analyte gas for mass spectrometric measurements. Oxygen triple-isotope data from quartz and spinel samples were reported by those authors. Laser-assisted fluorination of silicates using focused spot heating by an excimer laser (pulsed, ultraviolet radiation) was also developed during the 1990s (Wiechert and Hoefs 1995; Rumble et al. 1997; Young et al. 1998). This technique, however, was limited to spot sizes in the range ~80–300 µm, was very sensitive with respect to reactive materials in the samples (e.g., carbonates, resin, clay minerals), and has thus been largely discontinued.

The development of laser-based silicate fluorination procedures, together with use of O_2 as the analyte for oxygen triple-isotope measurements, coincided with new designs of gas source mass spectrometers which were better able to resolve the $^{17}O^{16}O$ ion beam from that of the major isotopologue, $^{16}O^{16}O$, thus facilitating ^{17}O relative abundance measurements at higher precision. At several laboratories where a laser-based silicate fluorination facility was installed, an investigation was made of the mass-dependent fractionation characteristics of a collection of terrestrial rocks and minerals spanning a wide range of $\delta^{18}O$ values (Miller et al. 1999[5]; Miller 2002; Rumble et al. 2007; Pack et al. 2007, 2013; Spicuzza et al. 2007; Kusakabe and Matsuhisa 2008; Ahn et al. 2012; Hofmann et al. 2012; Tanaka and Nakamura 2013; Levin et al. 2014; Kim et al. 2019). In many of these studies, an objective was to define a 'Terrestrial Fractionation Line' for use as a $\Delta'^{17}O$ reference. Despite the diversity of rock and mineral types in most cases, the slope (λ) obtained from $10^3\ln(1 + \delta^{17}O)$ versus $10^3\ln(1 + \delta^{18}O)$ data regression in all of the above-mentioned examples were within the range of 0.5240–0.5270. Furthermore, in several reports the associated 95% confidence interval was better than 0.001. Such λ variations are within the range of theoretical θ values calculated by Matsuhisa et al. (1978) for various oxygen isotope exchange reactions under equilibrium conditions, thus indicating that kinetic fractionation does not play a significant role in rock-forming processes.

Rumble et al. (2007), in an inter-laboratory comparison, showed that a mass fractionation line formed from eclogite facies garnets (high-pressure, medium- to high-temperature metamorphism) was statistically distinguishable from a comparable array formed from hydrothermal quartz samples. The respective (best precision) slope values were 0.5262 ± 0.0008 for the garnets and 0.5240 ± 0.0008 (95% confidence interval) for the quartz. This was the first empirical demonstration that the concept of a single 'Terrestrial Fractionation Line' for rocks and minerals is inaccurate, and that distinct mass fractionation arrays exist. It was later noted (Hallis et al. 2010) that the two fractionation arrays discussed by Rumble et al. (2007) were offset from one another. At VSMOW, the origin of the δ scale, the $10^3\ln(1 + \delta^{17}O)$ difference was 0.046‰. The precision (95% confidence interval) of the intercept value of the eclogite garnets line was 0.005; that of the hydrothermal quartz line was 0.019. This demonstrated that mass fractionation arrays from silicate rocks and minerals are offset from VSMOW, by an amount dependent on the specific fractionation array. This finding, though important, was overlooked until Tanaka and Nakamura (2013) similarly identified an offset between VSMOW and a fractionation array formed from a collection of silicate and oxide mineral samples. Measurements of VSMOW, SLAP and GISP (Greenland Ice Sheet Precipitation) were made, using the same oxygen purification system and mass spectrometer for the reference waters as for the mineral and oxide samples. The laboratory 'working standard' O_2 was calibrated against O_2 obtained from the fluorination of VSMOW and the magnitude of the ordinate offset (γ') of

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[5] Miller et al. (1999) reported the slope in $\delta^{17}O$ versus $\delta^{18}O$ format. Taking the mean of duplicate measurements (46 samples), the equivalent λ value is 0.5247 ± 0.0010 (95% confidence interval). The same data set was subsequently extended and discussed by Miller (2002), with all raw data being published in Miller et al. (2015). A statistically identical slope value of 0.5251 ± 0.0014 (SEM multiplied by Student's *t* factor for a 95% confidence limit) was reported by Hofmann et al. (2012) from >700 measurements. This was unchanged (0.5251 ± 0.0014, 2σ) by increasing the number of samples to 1071 (Pack et al. 2013).

the silicate array from VSMOW was reported to be –0.070 ± 0.005‰ at the 95% confidence interval, for the specific collection of samples selected (λ value of 0.5270 ± 0.0005). The reported γ' value was later found to be significantly in error (Pack et al. 2016). Tanaka and Nakamura (2017) subsequently gave a revised figure of –33 ppm.

Further confirmation that distinct mass fractionation lines are associated with specific rock- and mineral-forming processes was provided by Pack and Herwartz (2014) and, independently, by Levin et al. (2014). Pack and Herwartz (2014) demonstrated that variations in $\Delta'^{17}O$ relate to the temperature dependence of α and θ for specific fractionations and/or mixing between reservoirs with different isotopic compositions. They suggested that even a fractionation line defined by data points from coexisting and well-equilibrated minerals in a rock is conceptually incorrect, as θ values (by analogy to α values) are specific to two phases that are in equilibrium. Furthermore, low-temperature (4–50 °C) equilibration between silica and water was shown to be associated with low (and temperature-dependent) values of θ (0.5211 at ~8 °C), whereas high-temperature mineral–mineral equilibria in metamorphic and igneous felsic and mafic rocks are characterized by θ values of the order of 0.528–0.529. In their investigation of oxygen triple-isotope variations in sedimentary rocks, including Archean and Phanerozoic cherts, Levin et al. (2014) noted that, although their complete data set produced a fractionation array of λ value 0.523 ± 0.001, different groups gave distinctive slopes (non-overlapping at the 95% confidence level). In accord with Pack and Herwartz (2014), Levin et al. (2014) noted that the slope variations were the result of processes including mass fractionation associated with low-temperature precipitation during the growth of authigenic minerals; variation in the triple-isotope composition of the waters from which the sedimentary minerals precipitated; and equilibrium exchange after initial authigenic formation. The observations collectively provided further confirmation that no single fractionation line exists for terrestrial materials. Pack and Herwartz (2014) and Levin et al. (2014) also noted that oxygen triple-isotope studies are particularly appropriate for investigating (mass-dependent) low-temperature processes. This is because small variations in θ cause large variations in $\Delta'^{17}O$ when the isotope fractionation factors ($^{18/16}\alpha$ and $^{17/16}\alpha$) between water and the mineral of interest are large, as at low temperature. Comparisons of empirical and predicted triple-isotope arrays can therefore, in principle, be used to test hypotheses of chert formation and thus inform long-standing debates on the trends in chert $\delta^{18}O$ values, from the Archean through the Phanerozoic.

Oxygen triple-isotope distributions in meteoric waters, snow and ice cores

In much of the literature, the relative abundance of the isotopologues $H_2{}^{16}O$, $H_2{}^{17}O$ and $H_2{}^{18}O$ in meteoric precipitation and in the cryosphere has been quantified using the dimensionless parameter ^{17}O-excess (Angert et al. 2004), which was later defined as $\ln(1 + \delta^{17}O) - 0.528\ln(1 + \delta^{18}O)$ by Barkan and Luz (2007). The ^{17}O-excess parameter is therefore identical to the definition of $\Delta'^{17}O$ used throughout this volume. The rationale for the approach introduced by Barkan and Luz (2007) is that, as first shown by Meijer and Li (1998) and subsequently confirmed by higher precision measurements (Barkan and Luz 2007; Landais et al. 2008; Luz and Barkan 2010), oxygen triple-isotope distributions in precipitation seemed to conform closely, on a global scale, to the relationship $\ln(1 + \delta^{17}O) = 0.528\ln(1 + \delta^{18}O)$, with only small deviations from this trend.

Angert et al. (2004) predicted ppm-scale positive deviations from the array, resulting from kinetic fractionation during the diffusive transport of water vapor from the (marine) source region into undersaturated air. This causes the $\ln(1 + \delta^{17}O)$ versus $\ln(1 + \delta^{18}O)$ array for natural waters to be slightly offset from VSMOW. In the same paper it was also suggested that normalized relative humidity at the vapor source largely controls—and inversely correlates with—the magnitude of ^{17}O-excess, if turbulence in the marine boundary layer is taken into consideration. These theoretical predictions could not be tested, however, until a procedure for making oxygen triple-isotope measurements of waters at the required precision (5 ppm) had been devised.

That was achieved by Barkan and Luz (2005), who developed further a fluorination technique described by Baker et al. (2002). Small (~2 μL) samples of water samples were injected into a helium carrier stream which passed through a heated nickel tube containing CoF_3 at 370 °C. The resulting O_2 was isolated from the HF also formed, prior to $\delta^{17}O$ and $\delta^{18}O$ measurements. The same fluorination method was subsequently established at a small number of other laboratories.

Barkan and Luz (2007) suggested that the difference between the $\ln(^{17/16}\alpha)/\ln(^{18/16}\alpha)$ value for water vapor diffusion in air (0.5185 ± 0.0002) and the corresponding ratio (0.529) for vapor–liquid equilibrium is responsible for the presence of ^{17}O-excess in meteoric waters. This explanation is in accord with that originally proposed by Angert et al. (2004), although the relevant fractionation factors were not known accurately in 2004.

Many studies, as reported elsewhere in this volume, have since used ^{17}O-excess measurements of precipitation as a temperature-insensitive proxy for the humidity at the vapor source region, above the ocean. Experimental evidence for a non-zero value of ^{17}O-excess in water vapor of marine air, and a negative correlation between ^{17}O-excess and relative humidity, was first presented by Uemura et al. (2010). Uechi and Uemura (2019) demonstrated a similar finding, from a two-year record of ^{17}O-excess in precipitation at the sub-tropical maritime island of Okinawa, Japan (in the East Asian monsoon region), in conjunction with the corresponding normalized relative humidity back-calculated from a simple model of evaporation. Their results were in accord with ^{17}O-excess in the precipitation being determined largely by diffusional fractionation during evaporation from the surrounding ocean.

From recently published data sets (Li et al. 2015; Tian et al. 2018, 2019), it is evident that precipitation in the temperate and tropical regions actually conforms to a slightly lower and more variable proportionality constant than the 0.528 value used in the ^{17}O-excess definition. Furthermore, it is the inclusion of samples from the polar regions in the earlier data sets of oxygen triple-isotope ratios in meteoric precipitation that essentially constrained the slope to be 0.528. Removal of polar data from the sample collection used by Meijer and Li (1998), and that reported by Luz and Barkan (2010), lowers the slope value significantly (Miller 2018). Nevertheless, a definition based on a λ value of exactly 0.528 and with the corresponding $\Delta'^{17}O$ of the VSMOW and SLAP reference waters defined to be zero (Schoenemann et al. 2013) provides the basis of a VSMOW-SLAP scale for reporting $\Delta'^{17}O$ values to, as well as the corresponding $\delta^{18}O$ data. This is now widely accepted practice for standardizing the reporting of oxygen triple-isotope data from waters.

Uechi and Uemura (2019) showed that lowering the proportionality constant slightly from 0.528 in the ^{17}O-excess definition does not generally affect the robustness of using ^{17}O-excess data for normalized relative humidity reconstruction for tropical and subtropical regions (i.e., between 35°S and 35°N), where precipitation $\delta^{18}O$ values are generally >–10‰. This is because the resulting change in ^{17}O-excess is generally <10 ppm, i.e. close to the analytical uncertainty of such measurements. The authors noted, however, that this is not the case if the $\delta^{18}O$ values are significantly lower. For example, the anti-correlation between ^{17}O-excess and $\delta^{18}O$ noted by Li et al. (2015) from their measurements of meteoric waters sampled across the USA (with $\delta^{18}O$ values ranging from –5 to –25‰) is reduced if a slope value of 0.527 is adopted instead of 0.528.

Although initially applied to ice core data from Vostok, on the Antarctica plateau (Landais et al. 2008), doubts have since been raised about the interpretation of ^{17}O-excess data from the polar regions, especially the interior of Antarctica (Shoenemann et al. 2014; Miller 2018). As noted by Schoenemann and Steig (2016), although the use of ^{17}O-excess measurements has become quite common, the factors that control its spatial and temporal variability are not fully understood. Antarctic snowfall is largely controlled by meteorological conditions over the Southern Ocean and the penetration of marine air into the continental interior. There is frequent clear-sky precipitation and occasional, more massive falls from intrusions of maritime air. The extreme precipitation events play a dominant role in controlling Antarctic snowfall variability (Turner et al. 2019). Whereas the proportionality constant of 0.528 for the slope of the $\ln(1 + \delta^{17}O)$ versus $\ln(1 + \delta^{18}O)$ relationship characterizes many triple-isotope measurements of Antarctic snow, firn and ice cores, even for $\delta^{18}O$ values as low as –70‰ relative to VSMOW (Miller 2018), with correspondingly low temperatures of formation, precipitation over much of the Antarctic plateau, including at Vostok, occurs almost daily from a clear sky (nucleation and growth of 'diamond dust' ice crystals), rather than being cloud-derived. In this case, the associated proportionality constant seems to be significantly higher than 0.528. From the Vostok ice core measurements of Landais et al. (2008), covering the period 5–150 ka before present, an empirical λ value of 0.5310 ± 0.0004 (95% confidence interval) can be derived (Miller 2008, 2018); this is also in accord with modern precipitation at the same locality (Miller 2018).

Measurement procedures. More recently, spectroscopic techniques that require no chemical conversion of the water have been developed. Specifically, these are based on either or cavity ring-down spectroscopy with laser-current-tuned cavity resonance (Steig et al. 2014), or off-axis integrated cavity output spectroscopy (Tian et al. 2016). The attainable precision of such instrumentation is approaching that of the Barkan and Luz (2005) fluorination method. Another alternative, recently proposed by Affek and Barkan (2018), involves equilibrated CO_2–H_2O isotope exchange followed by oxygen isotope exchange between the CO_2 and O_2 over hot platinum, prior to triple-isotope measurements of the O_2. The authors reported that the accuracy and precision of this procedure are similar to those of the fluorination method described by Barkan and Luz (2005).

STANDARDIZING $\Delta'^{17}O$ DATA FROM ROCKS AND MINERALS

Pack et al. (2016) advocated that VSMOW-SLAP scaling should be applied to oxygen triple-isotope measurements of rocks and minerals, using the recommendation of Schoenemann et al. (2013) as devised for standardizing $\Delta'^{17}O$ data from waters. The principal advantage of this approach is that measurements of waters and rocks are then reported on the same scale. However, it does require that any laboratory undertaking high precision $\Delta'^{17}O$ measurements of rocks and minerals must also have the capability of making similar measurements on waters. Few laboratories currently have such a capability. There is also the implicit assumption that the water and silicate fluorination procedures—although different—will be characterized by the same (low) processing errors. In only a few studies reporting oxygen triple-isotope measurements of rocks or minerals were the data calibrated by direct measurements on VSMOW and SLAP (Kusakabe and Matsuhisa 2008; Ahn et al. 2012; Tanaka and Nakamura 2013; Pack et al. 2016; Sharp et al. 2016; Wostbrock et al. 2020).

The $\Delta'^{17}O$ values of silicates can currently be determined to a precision of 10 ppm or less (standard deviation, 1σ), as reported in several recent studies (e.g., Pack et al. 2016; Sharp et al. 2016; Kim et al. 2019; Miller et al. 2020; Wostbrock et al. 2020). This is significantly better than for the corresponding $\delta^{17}O$ and $\delta^{18}O$ measurements, as a result of the high degree of correlation between the respective errors in $\delta^{17}O$ and $\delta^{18}O$. Variations of the latter shift the associated data point along a mass-dependent fractionation line on the $\ln(1 + \delta^{17}O)$ versus $\ln(1 + \delta^{18}O)$ plot, causing little or no change to the corresponding $\Delta'^{17}O$ value. The accuracy of $\Delta'^{17}O$ data, however, is dependent on the accuracy of calibration of the $\delta^{17}O$ and $\delta^{18}O$ values of the 'working standard' O_2 gas to VSMOW, together with any corrections needed (as identified and quantified from measurements of SLAP) to compensate for compression of the $\delta^{17}O$ and $\delta^{18}O$ scales and to ensure that $\Delta'^{17}O_{0.528}$ of SLAP is zero, i.e., relative to a reference line of slope 0.528 and having no offset from VSMOW on the $\ln(1 + \delta^{17}O)$ versus $\ln(1 + \delta^{18}O)$ plot.

Even for the highest precision measurements, there is as yet no consensus on the $\Delta'^{17}O$ values of widely used silicate standards UWG-2 garnet, San Carlos olivine and NBS quartz on the VSMOW-SLAP scale. This illustrates the challenging nature of such measurements. Pack et al. (2016), in an inter-laboratory comparison and with calibration to VSMOW-SLAP, reported a $\Delta'^{17}O_{0.528}$ value of –36 ± 7 ppm (1σ) for San Carlos olivine as measured at one institution, with –39 ± 7 ppm being recorded by the other laboratory in that study. Clearly, these values are indistinguishable, within experimental precision. In contrast, Sharp et al. (2016) reported that their oxygen triple-isotope measurements of San Carlos olivine gave a $\Delta'^{17}O_{0.528}$ value of –54 ± 8 ppm (1σ), calibrated to measurements of VSMOW and SLAP. The reason for the discrepancy between that result and the –37 ± 7 ppm (weighted mean value) reported by Pack et al. (2016) on the same calibrated scale is not clear. More recently, Wostbrock et al. (2020) reported oxygen triple-isotope measurements of San Carlos olivine, UWG-2 garnet and NBS 28 quartz, calibrated to the VSMOW-SLAP scale. The respective $\Delta'^{17}O_{0.528}$ values were given as –58 ± 5 ppm, –71 ± 5 ppm and –59 ± 4 ppm (1σ). The San Carlos olivine and UWG-2 data are clearly different from (more negative) those reported by Pack et al. (2016) and Miller et al. (2020), with the respective discrepancies being 20 ppm and 25 ppm respectively. The Wostbrock et al. (2020) result for NBS 28 is also more negative, by a similar amount, than as obtained at the two institutions in the study reported by Miller et al. (2020). Possible explanations for such discrepancies are discussed by Pack (2021, this volume) and by Wostbrock and Sharp (2021, this volume).

As an alternative to the need for every laboratory to calibrate directly to the VSMOW-SLAP scale, Miller et al. (2020) suggested that a two-point empirical reference line defined by measurements of silicates which differ in $\delta^{18}O$ by a similar (or greater) amount than VSMOW and SLAP could be used for the measurements. Two such samples were described (referred to as the Khitostrov Rock Standard, KRS, and the Stevns Klint Flint Standard, SKFS), covering a $\delta^{18}O$ range of 59.1‰, based on provisional measurements of –25.20 ± 0.09‰ (1σ) for KRS and 33.93 ± 0.24‰ for SKFS. $\Delta'^{17}O$ data of rock and mineral samples reported relative to this reference line are independent of whether the $\delta^{17}O$ and $\delta^{18}O$ data are reported relative to VSMOW or to the 'working standard' O_2, of any isotopic composition. This confers significant advantages for inter-laboratory comparisons. For converting the data into the VSMOW-SLAP reference frame, it is necessary to calibrate the position of the KRS-SKFS line accurately line on the $\ln(1 + \delta^{17}O)$ versus $\ln(1 + \delta^{18}O)$ plot relative to VSMOW. Miller et al. (2020) reported that such measurements conducted at two laboratories gave very good agreement. The accuracy of those calibrations is dependent, however, on the accuracy of the calibration of San Carlos olivine to the VSMOW-SLAP scale as reported by Pack et al. (2016).

In addition to reporting their measured $\delta^{18}O$ and $\Delta'^{17}O$ values for San Carlos olivine, UWG-2 garnet and NBS 28 quartz on the VSMOW-SLAP scale, Wostbrock et al. (2020) also proposed a higher $\delta^{18}O$ quartz standard, 18.070 ± 0.136‰ (1σ), designated NM-Q. The corresponding $\Delta'^{17}O$ value, on the VSMOW-SLAP scale, was given as –81 ± 5 ppm. Although not spanning as large a $\delta^{18}O$ range as KRS and SKFS (Miller et al. 2020), all these materials are useful for laboratories not able to calibrate directly to the VSMOW-SLAP scale.

SOME EXAMPLES OF THE APPLICATION OF OXYGEN TRIPLE-ISOTOPE RATIO MEASUREMENTS

We provide here an indication of how oxygen triple-isotope ratio measurements have contributed to a diverse range of research areas in the geosciences. The list includes only a selection of examples and is by no means exhaustive. Several of the topics are discussed in detail elsewhere in this volume.

Corrections to $\delta^{13}C$ measurements of CO_2

As noted above, the contribution of $^{12}C^{17}O^{16}O$ isotopologues to the CO_2 *m/z* 45 ion beam current needs to be quantified and subtracted from the measured total value, during stable isotope ratio measurements of CO_2. Different data reduction procedures have long been adopted for this correction, notably based on either that proposed by Santrock et al. (1985) or by Allison et al. (1995). The latter procedure was subsequently recommended by the IAEA. Differences between the algorithms lead to small but potentially significant discrepancies in the magnitude of the resulting correction. Furthermore, neither allows changes to the assigned values of λ (0.516 and 0.5, respectively) in the mass-dependent relationship between the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios. Nor can non-mass-dependent distributions be accommodated. Röckmann and Brenninkmeijer (1998) implemented a simple and approximate additional correction for $\delta^{13}C$ measurements of tropospheric CO, which was known to contain a non-mass-dependent enrichment of ^{17}O (Huff and Thiemens 1998; Röckmann et al. 1998). The authors estimated that not taking account of the enhanced ^{17}O abundance resulted in a systematic error of the order of 0.08 to 0.25‰ in the corresponding $\delta^{13}C$ values. Assonov and Brenninkmeijer (2003) suggested that discrepancies between published values for $^{17}R_{\text{VPDB-CO}_2}$ in different correction algorithms were a major source of the $\delta^{13}C$ biases. The authors also suggested that the value of the mass-dependent fractionation exponent λ should be set to 0.528, on the basis that H_2O-CO_2 oxygen isotope exchange probably controls the triple-isotope composition of CO_2 in nature, and natural waters fit an array characterized by a λ value of 0.528 (Meijer and Li, 1998). Brand et al. (2010) also endorsed the adoption of 0.528 for λ and proposed a simplified ^{17}O correction procedure which the authors suggested was sufficiently accurate for many cases. Non-mass-dependent oxygen triple-isotope distributions were not accommodated, however. Miller et al. (2007) modified the Allison et al. (1995) algorithm to allow for user-defined values of λ and $\Delta'^{17}O$. Kaiser (2008) gave a very detailed appraisal of ^{17}O correction procedures and showed that the correction could be framed in terms of relative isotope ratio differences (δ values), although inaccuracy would still result from assigning an inappropriate value of λ.

More recently, measurements of the equilibrium $\theta_{CO_2-H_2O}$ value for oxygen isotope exchange show that the value is 0.5229 ± 0.0015 (SEM multiplied by Student's *t* factor for a 95% confidence limit) at 23 °C (Hofmann et al. 2012); an identical value at 25 °C (0.5229 ± 0.0001) was obtained by Barkan and Luz (2012). Furthermore, the same θ value applies to CO_2 formed from phosphoric acid digestion (McCrea 1950) of calcite at 25 °C (Wostbrock et al. 2020). It seems, therefore, that 0.523 is the most appropriate λ value for use in ^{17}O correction algorithms for $\delta^{13}C$ measurements of CO_2 and also for carbonates equilibrated with water characterized by $\delta^{18}O \approx \Delta'^{17}O \approx 0‰$. Freshwater carbonates or eggshell calcite would deviate from such trends, however, therefore independent assessment of $\delta^{17}O$ needs to be made for such materials.

With the development of gas source mass spectrometers of sufficiently high resolution, isotope measurements on atomic ions formed from fragmenting the CO_2^+ molecular ion can now be used, in principle, to determine the carbon and oxygen triple-isotopic composition of CO_2, without chemical processing or corrections for mass interferences (Adnew et al. 2019). However, because the signal intensities are very small, long measurement times are required. At the present state of development, 12 hours of measurement are required to determine the $\Delta'^{17}O$ of CO_2 to a precision of the order of 37 ppm, with $\lambda_{RL} = 0.528$. Nevertheless, this technique demonstrates a capability that offers new possibilities for the future.

Comparisons of the oxygen triple-isotope compositions of the Earth and Moon

It is widely accepted that the Moon was most likely formed from debris produced by a Mars-sized body, named Theia, colliding with the proto-Earth. Whether or not the Moon has an identical oxygen triple-isotope composition to that of Earth's mantle has important implications for refining this (and other) models of the Moon's origin. The first high precision oxygen triple-isotope measurements to investigate this question were by Wiechert et al. (2001), using CO_2 laser-assisted fluorination and with BrF_5 as the fluorinating reagent. Previous reports, as noted by the authors, gave a $\Delta^{17}O$ range of 0.30‰ for lunar samples. Such a range is of similar magnitude to the $\Delta^{17}O$ distinction between the Earth and Mars (0.321 ± 0.013‰, 1σ), as inferred from measurements of Shergotty–Nakhla–Chassigny (SNC) meteorites (Franchi et al. 1999); similarly between the Earth and the asteroid Vesta (–0.26 ± 0.08‰), as inferred from measurements of Howardite–Eucrite–Diogenite (HED) meteorites (Clayton and Mayeda 1996)[6]. From measurements on a lunar collection of mare basalts, KREEP basalts, highland rocks, volcanic glasses, breccias, and a single lunar meteorite, Wiechert et al. (2001) found that all the lunar oxygen isotope compositions plotted within ±0.016‰ (2σ) on a single mass-dependent fractionation line on the $\delta^{17}O$ versus $\delta^{18}O$ plot. The array was identical—within analytical uncertainties—to that produced from 11 terrestrial minerals with $\delta^{18}O$ values ranging from 0 to 12‰ and forming a $\delta^{17}O$ versus $\delta^{18}O$ slope of 0.5245. Thus, $\Delta^{17}O$ was defined as $\delta^{17}O - 0.5245\,\delta^{18}O$ for that particular study.

Spicuzza et al. (2007) similarly found that their measurements of lunar basalts and soils (plotted in $10^3\ln(1 + \delta^{17}O)$ versus $10^3\ln(1 + \delta^{18}O)$ format) showed no statistically significant deviation from an empirically-derived terrestrial reference line (details as given above). $\Delta'^{17}O$ values of all the lunar samples were within uncertainty of the reference line measurements and averaged 0.008 ± 0.022‰ (2σ). Consistent with this finding, and with that of Wiechert et al. (2001), an investigation by Hallis et al. (2010) of the oxygen triple-isotope characteristics, titanium content and modal mineralogy of five different types of lunar basalts revealed no $\Delta'^{17}O$ deviation (0.006 ± 0.021, 2σ) for the average of the lunar basalts, relative to a reference line obtained from the set of eclogite garnets described by Rumble et al. (2007).

Herwartz et al. (2014) reported the surprising finding that their measurements of lunar basalts gave a $\Delta'^{17}O$ value distinctive from that of mantle xenoliths and MORB (from seven different localities). Correcting the published data for recalibration to San Carlos olivine on the VSMOW-SLAP scale (Pack et al. 2016), but keeping $\lambda_{RL} = 0.5305$ as assigned by the authors for $\Delta'^{17}O$ reporting, the Earth mantle-derived samples gave a weighted average $\Delta'^{17}O$ value of –49 ± 0.003 ppm (1σ) whereas –37 ± 0.008 ppm was the comparable result obtained from replicate measurements of the (three) lunar basalts. This remarkable finding was disputed by Young et al. (2016), who performed a similar comparison, using seven lunar samples and one lunar meteorite, together with a suite of terrestrial igneous samples. The $\Delta'^{17}O$ difference between the lunar and terrestrial data sets was reported to be −1 ± 5 ppm (2 × SEM), i.e. indistinguishable. For $\Delta'^{17}O$ reporting, Young et al. (2016) used a reference fractionation line with $\lambda_{RL} = 0.528$ and passing through the San Carlos olivine datum point instead of VSMOW.

A possible reason for the discrepancy between Herwartz et al. (2014) and Young et al. (2016) about whether or not there is an oxygen isotopic distinction between lunar samples and 'bulk silicate Earth', as represented by terrestrial, mafic rocks, has been revealed by more recent studies, which involved more extensive suites of lunar samples. Greenwood et al. (2018) included 17 lunar whole-rocks, representing all main lithological units, together with 14 lunar mineral separates. Terrestrial mafic rocks were represented by 20 basalts and a mantle xenolith, together with previously-published data on high-$^3He/^4He$ olivines, measured in the same laboratory. From the oxygen triple-isotope data, it was seen that the set of lunar samples as a whole was characterized by a 3 to 4 ppm, statistically resolvable, $\Delta'^{17}O$ difference relative to the terrestrial basalts. However, no such distinction was found between the terrestrial olivines and lunar rocks.

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[6] The corresponding $\Delta'^{17}O_{0.528}$ value for Mars is 0.286 ± 0.016‰ (1σ). From a recent compilation of oxygen isotope data from early-formed differentiated meteorites (Greenwood et al. 2017), the $\Delta'^{17}O_{0.528}$ value for Vesta, as determined using results from (26) eucrite or diogenite falls only (thereby minimizing the effects of terrestrial weathering), is –0.252 ± 0.007‰ (1σ).

The latest investigation of the Earth–Moon $\Delta'^{17}O$ comparison is by Cano et al. (2020). Their oxygen triple-isotope measurements of a range of lunar lithologies (and reported on the VSMOW-SLAP scale) showed that the Earth and Moon have slightly different $\Delta'^{17}O$, if measurements of all (23) lunar samples were averaged to determine a 'bulk silicate Moon' value. This procedure gave $\Delta'^{17}O = -0.056 \pm 0.010$‰ (1σ), whereas the 'bulk silicate Earth' value was –0.060 ± 0.004‰ (22 samples). The magnitude of the difference is in accord with the findings of Greenwood et al. (2018). What is particularly noteworthy, however, is that lunar samples analyzed by Cano et al. (2020) showed nearly three times the $\Delta'^{17}O$ variability (0.0103‰, 1σ) when compared with Earth (0.0037‰). Furthermore, the mean $\Delta'^{17}O$ value for low-Ti lunar basalts showed a more positive $\Delta'^{17}O$ value than that of the 'bulk silicate Earth' samples—as did Herwartz et al. (2014)—with the magnitude of the discrepancy being comparable to the difference reported by Herwartz et al. (2014). Cano et al. (2020) reported that their oxygen isotope data variations for lunar samples correlated with lithology; it was proposed that the differences were evidence for mixing between isotopically light vapor, generated by the impact of Theia, and the outermost portion of the early lunar magma ocean.

Thus, whereas details of the 'Giant Impact' hypothesis of the Moon's formation are still being refined, high precision oxygen triple-isotope measurements during the past two decades have contributed significantly to these developments and stimulated the emergence of new ideas.

Investigating the climate of 'Snowball Earth' from hydrothermal rocks

A novel application of $\Delta'^{17}O$ systematics was described by Herwartz et al. (2015). Noting that the oxygen isotopic compositions of hydrothermally-altered rocks originate partly from interactions with the associated aqueous fluid, oxygen triple-isotope measurements of hydrothermally-altered Proterozoic rocks were used to estimate the $\delta^{18}O$ value of the associated water. The calculations were based on the assumption that the rocks would define a mixing trend with the meteoric waters on a $\Delta'^{17}O$ versus $\delta'^{18}O$ plot and that the waters actually describe a parabolic array in $\delta^{17}O$ versus $\delta^{18}O$ space, thus giving resolvable mixing trajectories. The isotopic composition of the water may then be estimated from the intersect between the mixing trend and the meteoric waters array on this plot. For waters derived from Paleoproterozoic (age ~2.3 – 2.4 Ga) 'snowball Earth' glaciers at low paleo-latitudes (<35°N), a $\delta^{18}O$ value of –43 ± 3‰ was derived. Precipitation characterized by such depletion of ^{18}O currently occurs only in central Antarctica. A similar analysis of a Neoproterozoic example (age ~0.6 – 0.7 Ga) indicated a meltwater $\delta^{18}O$ value of –21 ± 3‰, implying less extreme climate conditions at similar paleo-latitude. As noted by the authors, such estimates essentially represent 'single snapshots' of ancient water samples and may not be representative of peak 'snowball Earth' conditions. A further point is that the derived $\delta^{18}O$ value is dependent on the calibration of the triple-isotope composition of the 'working standard' O_2 relative to VSMOW. If the assigned $\delta^{17}O$ value was 0.050‰ too low, as inferred from Pack et al. (2016), then the calculated $\delta^{18}O$ values of the meteoric waters will need to be adjusted accordingly. For the Paleoproterozoic example mentioned above, the revised value is –38 ± 3‰.

The same methodology has been adopted in more recent studies. For example, Zakharov et al. (2017, 2019) also showed that the $\delta^{18}O$ of glacial meltwaters during two separate and individually dated episodes of snowball Earth glaciation was approximately –40‰ relative to VSMOW. The authors noted that the presence of Paleoproterozoic glacial diamictites deposited at low latitudes on different continents indicated that three or four worldwide glaciations occurred between 2.45 and 2.22 Ga before present. Subglacial hydrothermal alteration was induced by intrusions of high-Mg and high-Fe gabbros during the early Paleoproterozoic rifting on the Baltic Shield, which at the time was located at low latitudes. The low $\delta^{18}O$ values of hydrothermally altered rocks associated with these intrusions were attributed to high-temperature isotopic exchange with glacial meltwater, indicating the presence of glacial ice globally.

Zakharov and Bindeman (2019) reported that oxygen triple-isotope analyses of hydrothermally altered rocks (well-preserved pillow structures, hyaloclastites and komatiitic basalts) of age 2.43–2.41 Ga from the Vetreny belt, Baltic Shield, Russia, provide a record of high-temperature water-rock interaction induced by contemporaneous seawater. Comparison with modern oceanic crust examples implied that the Vetreny belt examples formed in equilibrium with seawater-derived fluids of $\Delta'^{17}O$ value very close to zero, i.e. that early Paleoproterozoic seawater was characterized by a $\Delta'^{17}O$ value indistinguishable from that of modern-day seawater. Further information on the use of oxygen triple-isotope measurements in hydrothermal systems is given by Herwartz (2021, this volume).

Insights from $\Delta'^{17}O$ measurements on basalts, shales and fluvial sediments

Several novel applications of high precision measurements of oxygen triple-isotope ratios to the Earth sciences have recently been presented in the literature. Here, three examples are described, briefly.

Quantifying the crustal component in ocean island basalts. A consequence of plate tectonics is that subducted oceanic crust contributes to the formation of ocean island basalt (OIB), although its actual fraction in the mantle source is not well established. Cao et al. (2019) proposed that, on the basis of their theoretical calculations, $\Delta'^{17}O$ values of olivine should be unaffected by crystallization and partial melting. This feature permits the use of oxygen triple-isotope ratio measurements of olivine to identify subducted oceanic crustal material in the mantle source region from which OIB is believed to originate. A quantitative assessment of the respective fractions of subducted ocean sediments and hydrothermally altered oceanic crust in OIB mantle source was made by the authors, using $\Delta'^{17}O$ data from the literature. It was estimated that the fraction of subducted oceanic crust was as high as 22.3% in some examples, although the affected region in the respective mantle plume is likely to be limited.

Constraints on the emergence of continents—evidence from the shale record. Bindeman et al. (2018) used oxygen triple-isotope measurements of shales, from every continent and spanning an age of 3.7 billion years, to provide constraints on the emergence of continents over time. A stepwise total decrease of 80 ppm in the average $\Delta'^{17}O$ value across the Archaean–Proterozoic boundary was reported, using a reference line slope of 0.5305 to define $\Delta'^{17}O$. However, because of $\delta^{18}O$ variations in the dataset, the change in $\Delta'^{17}O$ is reduced when reporting relative to a reference line of slope 0.528. An increase in $\delta^{18}O$ value of 10‰ results in a $\Delta'^{17}O$ change of –25 ppm when switching from a reference line slope of 0.528 to 0.5305. Thus, changes in $\Delta'^{17}O$ should always be discussed in the context of changes of $\delta^{18}O$. In this case, however, defining $\Delta'^{17}O$ using a reference line of slope 0.528 clearly does not obliterate the trend observed by Bindeman et al. (2018). It was suggested that this was most probably caused by a shift in the nature of water–rock interactions, from near-coastal in the Archaean to predominantly continental (and diverse in $\delta^{18}O$) from the Proterozoic era, and accompanied by a decrease in average surface temperatures. Furthermore, this shift may have coincided with the onset of a modern hydrological cycle, owing to the rapid emergence of continental crust with a diversity of hydrologic conditions (continents with near-modern average elevation and with mountain ranges, spreading across a range of latitudes) and aerial extent, approximately 2.5 billion years ago. For further details, see Bindeman (2021, this volume).

Fluvial sediments—insights into weathering processes. Bindeman et al. (2019) conducted an investigation of oxygen triple-isotope ratios in fluvial sediments, using samples from 45 rivers worldwide, cumulatively representing ~25% of the area—from the tropics to the polar regions—associated with continental transport into the oceans. $\Delta'^{17}O$ determinations of the clay-sized fraction indicated that the values were essentially controlled almost exclusively by the associated meteoric waters at the respective temperature of weathering, together with minor effects related to evaporation. The majority of the clays were consistently characterized by high-δ^{18}O signatures, regardless of the bedrock type, as weathering involves very high water/rock ratios. The clays appeared to be in oxygen isotopic equilibrium with local meteoric waters. Lack of significant isotopic variation between clays from different climatic regions was attributed to the opposing effects of temperature on clay–water fractionation, on the one hand, and the global relationship between temperature and δ^{18}O of the local meteoric waters (e.g., Dansgaard 1964; Rozanski et al. 1993). Bindeman et al. (2019) concluded that the Δ'^{17}O values of shales in the geological record provide a measure of the evolving global hydrologic cycle during continental emergence; also of a decrease in global mean annual temperatures or diagenetic conditions, together with decreasing ocean mass caused by rehydration of the mantle from the subduction of hydrated, low-δ^{18}O, high-Δ'^{17}O slabs.

Quantifying gross photosynthetic oxygen production in the oceans

Oxygen triple-isotope measurements of dissolved O_2 in marine environments have been widely adopted during the past two decades for estimating gross photosynthetic O_2 production (i.e., the rate prior to any respiratory O_2 consumption) in oceanic surface waters, on temporal and spatial scales. Such information contributes to an understanding of both the present-day global carbon cycle and also to predictions of how carbon cycling might respond to future climate forcing. The principle was originally suggested by Luz and Barkan (2000) and uses the distinction in triple-isotope composition between dissolved oxygen of atmospheric origin (non-mass-dependent, $\Delta'^{17}O_{0.528} = -0.469 \pm 0.007‰$) and that produced during photosynthesis (mass-dependent and essentially the same as that of the water). The Δ'^{17}O value of dissolved O_2 depends on: (1) the rate of air–water gas exchange which, in the absence of biological activity, tends towards an equilibrium value with air; (2) the rate of *in situ* production of photosynthetic O_2, which tends to increase Δ'^{17}O of dissolved O_2 to a maximum value (close to zero) and equivalent to that of the substrate water. Using measurements of surface seawater oxygen triple-isotope ratios, together with estimates of the air–sea gas transfer of O_2 via a windspeed-based parameterization, it is possible to estimate the rate of photosynthetic O_2 contribution to the surface mixed layer budget. As respiration has no impact on the measured isotopic anomaly in the mixed layer, the measured rate equates to the gross photosynthetic production (GPP).

Various revisions to the calculation procedure have been proposed (e.g., Kaiser 2011; Kaiser and Abe 2012; Prokopenko et al. 2011), to improve the accuracy of the GPP estimates. Manning et al. (2017) adapted the method to incorporate the local isotopic composition of the water. Advances that this use of oxygen triple-isotope measurements has contributed to improved understanding of biological carbon cycling have been reviewed by Juranek and Quay (2013).

Oxygen triple-isotope ratios in bio-apatite: a proxy for CO_2 partial pressure in paleo atmospheres

Gehler et al. (2011) described the use of oxygen triple-isotope analysis to identify diagenetic changes of δ^{18}O in the skeletal apatite of small mammals. The method is based on the Δ'^{17}O of atmospheric oxygen being partially transferred from inhaled air O_2, via body water, to the skeletal and tooth apatite of terrestrial mammals—especially small mammals (body mass < ~1 kg). In larger mammals, low specific metabolic rates result in a lower fraction of oxygen inhaled via breathing, relative to oxygen from other sources in the body water. The authors reported that remnant negative Δ'^{17}O values were detected in the apatite of rodent tooth enamel of Eocene to Miocene age. The distinctive isotopic pattern was not present in dentine of the same teeth, however; this was presented as evidence for diagenetic alteration.

Because the Δ'^{17}O value of air O_2 is coupled with the partial pressure of atmospheric CO_2 and gross primary productivity (Luz et al. 1999; Bao et al. 2008), oxygen triple-isotope analyses of bioapatite from fossil mammals can also be used as a proxy for paleo-CO_2 partial pressure

(Pack et al. 2013). Tooth enamel was used, as it is less prone to diagenetic alteration than is dentine or bone material. Examples from Cenozoic (age <65 Ma) fossil small mammals agree (within uncertainty) with other proxies and geochemical modelling for p_{CO_2}, if gross primary production was similar to present-day values. The uncertainty intrinsic to the proxy is mainly due to uncertainties in physiological parameters: the total water flux, the metabolic rate and the evaporative water flux.

Gehler et al. (2016) adopted the same principle to investigate p_{CO_2} during the Paleocene–Eocene transition (56 Ma ago), which is known from other proxies to have been accompanied by a rapid temperature rise, contemporaneous with a large negative carbon isotope excursion. The latter indicates a massive release of carbon-containing gas(es) into the atmosphere, although the carbon source and speciation were not well documented. Oxygen triple-isotope measurements of mammalian tooth enamel indicated that the sudden rise in atmospheric temperature during the Paleocene–Eocene transition was not accompanied by the elevated concentrations (>~2,500 ppm) of CO_2 needed to explain the temperature profile. Instead, the low $^{13}C/^{12}C$ ratios during the Paleocene–Eocene thermal maximum were most likely caused by a massive release of seabed methane to the atmosphere.

CONCLUSIONS AND OUTLOOK

The application of oxygen triple-isotope ratio measurements, long established for the characterization of meteorites and other extraterrestrial samples, has also contributed valuable new insights to a diversity of research investigations involving the lithosphere, hydrosphere, cryosphere and atmosphere of Earth. In some cases, it is the presence and magnitude of non-mass-dependent distributions of the isotopes that has provided unique tracer information; in other instances it is variations in isotopic composition resulting from mass-dependent fractionation that facilitated new inferences. In much of the rock record, oxygen triple-isotope compositions seem to be consistent with equilibrium θ values for SiO_2–water exchange at various temperatures. The high levels of precision currently possible on $\Delta'^{17}O$ determinations of rocks, minerals and waters, in conjunction with a robust and consistent reporting framework, allow remarkably small differences to be identified. Despite these advances, the calibration of rock and mineral data to a water-based reporting scale (VSMOW-SLAP), to a degree of accuracy commensurate with the associated precision, continues to be challenging. At present, additional measurements are needed on the oxygen triple-isotope compositions of widely-used silicate standards for $\delta^{18}O$ measurements (such as San Carlos olivine, UWG-2 garnet and NBS 28 silica), from which consensus $\Delta'^{17}O$ values will eventually be agreed. Furthermore, a two-point silicate calibration, with widely-separated δ values that encompass most of the range encountered in natural samples, is highly desirable. As a first step, inter-laboratory comparison of two potential silicate standards for this purpose have recently been made, resulting in agreement of the $\Delta'^{17}O_{0.528}$ values to within 3 ppm. Meanwhile, recent high precision measurements of the corresponding value for ‘bulk silicate Earth’, exemplified by San Carlos olivine as a proxy, suggest that it lies within the range –36 to –58 ppm; a recent model prediction suggests that the value should be close to –40 ppm. A challenge for the cosmochemistry research community is to agree on a definition of $\Delta'^{17}O$ (or, indeed, whether to just continue with the long-established $\Delta^{17}O$ definition) for standardizing the reporting of measurements on meteorites and, especially, compilations of such measurements in reference databases. Clearly, there is no single ‘correct’ or ‘incorrect’ definition; it is for meteoriticists to debate the respective merits of various alternative options and to reach a consensus view.

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