

Standardization for the Triple Oxygen Isotope System: Waters, Silicates, Carbonates, Air, and Sulfates

Zachary D. Sharp, Jordan A.G. Wostbrock

*Department of Earth and Planetary Sciences
University of New Mexico
Albuquerque, NM, 87131
USA*

zsharp@unm.edu

INTRODUCTION

Stable isotope analyses are a relative measurement. The precision is far higher than the accuracy, so that subtle isotopic differences must be made relative to a reference. Modern mass spectrometers can routinely measure the $\delta^{18}\text{O}$ value of a gas with a precision of 0.01‰. This is 20 times more precise than the accuracy of the $^{18}\text{O}/^{16}\text{O}$ ratio of VSMOW (Baertschi 1976). It is for this reason that isotope analyses, like most analytical measurements, are reported relative to standards. The problem faced by the stable isotope community is that different materials are measured using different techniques, and direct comparison between them is difficult. Heroic efforts have been made to align the different types of analyses to the same scale, so that data collected on different materials in different laboratories can be directly compared. For traditional $\delta^{18}\text{O}$ analyses, coalescence around common standards took decades. Triple oxygen isotope studies ($\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) of terrestrial materials is a relatively new discipline, and agreement on standardization is only recently achieving a high level of conformity. In this chapter, we first consider the historical path towards standardization for the well-established $^{18}\text{O}/^{16}\text{O}$ ratios. Then the extension to standardization to $^{17}\text{O}/^{16}\text{O}$ is discussed with a goal of presenting a uniform set of standard values for commonly used reference materials.

There was a time when stable isotope standards didn't exist. Consider the classic paper by Dole (1936), in which he determined the oxygen isotope composition of air relative to water. "*The atomic weight of oxygen in air is 0.000108 atomic weight units heavier than Lake Michigan water*". This was a high precision analysis, considering that it was determined by density measurements, but it was far lower precision than what is achievable using modern extraction methods and modern mass spectrometers. Precise determinations of relative isotopic differences only began in earnest in the 1950s following the development of a dual inlet mass spectrometer (McKinney et al. 1950) under the direction of Harold Urey. Urey's desire to develop a carbonate paleothermometer necessitated highly precise oxygen isotope analyses in order to obtain temperature estimates in the 1 °C range. This led to the University of Chicago group creating what is essentially the modern high precision mass spectrometer (McKinney et al. 1950). McKinney's mass spectrometer measured the ratios of the voltages of $^{18}\text{O}/^{16}\text{O}$ of a sample gas relative to a reference gas using a set of changeover valves that allowed for rapid switching between the two gases. This reduced errors associated with the inevitable drift of the sensitive electronics. The $^{18}\text{O}/^{16}\text{O}$ ratios were presented by McKinney in what is now the ubiquitous delta notation in per mil units as

$$\delta^{18}\text{O} = \left(\frac{R_{\text{sa}}}{R_{\text{std}}} - 1 \right) 1000 \quad (1)$$

In more general terms, delta is given by

$$\delta^{18}\text{O} = \frac{R_{\text{sa}}}{R_{\text{std}}} - 1 \quad (2)$$

and indeed, early hydrogen isotope measurements were given in ‰ (e.g., Friedman 1953) rather than per mil and recent publications have presented $\Delta^{17}\text{O}$ values in parts per million (ppm or per meg). In this contribution, all additional equations (e.g., Eqn. 7) and delta values are given in terms of Equation (1).

While it is generally assumed that the first measurements of oxygen isotope ratios were made on CO_2 gas, interestingly, McKinney's original mass spectrometer was used for measuring both the isotope ratios of CO_2 (the ratio $\text{C}^{16}\text{O}^{18}\text{O}/\text{C}^{16}\text{O}_2$) and O_2 ($^{16}\text{O}^{18}\text{O}/^{16}\text{O}_2$) gas. Today, O_2 gas is the primary analyte for triple oxygen isotope analyses in order to be able to measure the $\delta^{17}\text{O}$ value. It is perhaps surprising to see that, from the very beginning, O_2 gas was considered as a viable gas for the classic dual-inlet mass spectrometer.

Some of the first high-precision measurements were made by Epstein et al. (1951, 1953) on natural waters and carbonates, which led to the carbonate–water oxygen isotope thermometer. Their paleotemperature equation is given as

$$t \text{ (}^\circ\text{C)} = 16.5 - 4.3 \delta + 0.14 \delta^2 \quad (3)$$

In this equation δ is the difference in the $\delta^{18}\text{O}$ value of CO_2 (in per mil) produced by reaction of carbonates with 100% phosphoric acid and the working standard CO_2 gas. The reference gas was CO_2 produced by the reaction of *Belemnitella americana* from the Peedee formation of South Carolina (Urey et al. 1951). They did not measure the $\delta^{18}\text{O}$ values of either the water or the carbonate—only the small difference between the CO_2 gases obtained by decarbonating the calcite and equilibrating CO_2 with water, respectively. As long as their temperature equation was calibrated to their own internal reference gas, they would encounter no problems.

Silverman (1951) measured the oxygen isotope composition of silicate rocks. The reference gas he used in all analyses was oxygen derived from quartz from the Randville pegmatite (Randville, Michigan, USA). In setting the standard for future measurements, he adjusted all of his silicate analyses to Hawaii seawater, with an arbitrary $\delta^{18}\text{O}$ value of 0‰. (Hawaii seawater is 0.17‰ heavier than SMOW, Epstein and Mayeda 1953). Presumably Silverman fluorinated his water sample to quantitatively extract oxygen (Baertschi 1950). In those early years the different laboratories had good communication, and the standards were commonly exchanged for cross-comparison. At the Caltech laboratory, for example, Potsdam sandstone was the unofficial internal standard for years (Clayton 1959; Taylor and Epstein 1962) and was calibrated relative to Hawaiian water and, later, mean ocean water.

As the number of stable isotope laboratories grew, it became increasingly imperative to develop a coordinated intercalibration so that the data from all labs could be compared with one another. Harmon Craig published a detailed presentation of stable isotope standards, combining existing standards from the University of Chicago laboratory with samples from the newly created National Bureau of Standards, NBS (Craig 1957). These included the NBS Solnhofen limestone and NBS 1 (water from the Potomac River, Maryland, Fig. 1). The oxygen isotope values of carbonates were reported relative to the PDB carbonate standard, whereas waters were reported relative to the NBS 1 water standard. Craig later defined the average ocean water (mean ocean water of Epstein and Mayeda 1953) in terms of NBS 1, giving the relationship

$$\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{(SMOW-Standard Mean Ocean Water)}} \equiv 1.008 \times \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{(NBS1)}} \quad (4)$$

NBS 1 was distributed widely by the National Bureau of Standards and could be used for interlaboratory calibration. Later, Harmon Craig collected, distilled and adjusted ocean water at the request of the International Atomic Energy Agency (IAEA) to match the original SMOW so that it conformed to the definition in terms of NBS 1 (Craig 1961). The new reference material was called VSMOW (shortened from Vienna SMOW—Fig. 2) to distinguish it from the original SMOW (Gonfiantini 1978). At the same time, a second light water standard, SLAP (for Standard Light Antarctic Precipitation) was developed, allowing for laboratories to have two different water standards with $\delta^{18}\text{O}$ and δD values that were far apart. The $\delta^{18}\text{O}$ and δD values of VSMOW, by definition, are 0‰. Although not envisioned at the time, by analogy the $\delta^{17}\text{O}$ value is also 0‰. SLAP has a $\delta^{18}\text{O}$ value of -55.5‰ and a δD value of -428‰ . There is some indication that the actual value of SMOW may be closer to -56.18‰ (Verkouteren and Klinedinst 2004). We will stick with the IAEA convention of -55.5‰ for SLAP and SLAP2 (IAEA 2006, 2017). An intermediate standard GISP (Greenland Ice Sheet Precipitation) has a $\delta^{18}\text{O}$ value of -24.76‰ and a δD value of -189.5‰ (IAEA 2006). GISP is now discontinued and has been replaced with GRESP with a $\delta^{18}\text{O}$ value of -33.39‰ and δD value of -257.8‰ (IAEA 2020). The absolute values for the $^{18}\text{O}/^{16}\text{O}$ and D/H ratios of VSMOW are $2005.20 \pm 0.45 \times 10^6$ and $155.76 \pm 0.05 \times 10^{-6}$ (see compilation in Table 2.5 of Sharp 2013).



Figure 1. Unopened sealed vial of NBS 1.



Figure 2. The SMOW-1 standard (VSMOW). Why, if it is not to be moved, does it have handles? [USGS Public Domain].

Two formally adopted carbonate standards followed (Friedman et al. 2007). The first, NBS 19, essentially replaced PDB as the benchmark marine carbonate value, while the second, NBS 18, is a carbonate of igneous origin which has a lower $\delta^{18}\text{O}$ value, much closer to that of the mantle. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of NBS 19 are defined as $\delta^{18}\text{O} \equiv -2.20\text{‰}$ and $\delta^{13}\text{C} \equiv +1.95\text{‰}$ (where \equiv indicates that these values are exact by definition to the VPDB scale). NBS 19 is no longer available and has been replaced by IAEA 603 with $\delta^{18}\text{O} \equiv -2.37\text{‰}$ and $\delta^{13}\text{C} \equiv +2.46\text{‰}$ (Assonov et al. 2020).

The relationship between VPDB and VSMOW is given by the equation (Kim et al. 2015)

$$\delta^{18}\text{O}_{\text{VSMOW}} = 1.03092 \delta^{18}\text{O}_{\text{VPDB}} + 30.92 \quad (5)$$

updated from the long-used equation (Coplen et al. 1983)

$$\delta^{18}\text{O}_{\text{VSMOW}} = 1.03091 \delta^{18}\text{O}_{\text{VPDB}} + 30.91 \quad (6)$$

As we will see, the difference between these two equations is significantly less than the total uncertainties in the fractionation factors necessary to construct them.

Equation (5) allows a comparison of the $\delta^{18}\text{O}$ values of waters reported to the VSMOW scale with carbonates reported to the VPDB scale. Silicates are also anchored to the VSMOW scale by the quartz sand reference material NBS 28, a sand donated by Corning Glass Co. Friedman and Gleason (1973) introduced this standard and determined its $\delta^{18}\text{O}$ value relative to VSMOW by fluorinating both the quartz and VSMOW to quantitatively extract O_2 , which was then converted to CO_2 for isotopic analysis. Their measured $\delta^{18}\text{O}$ value for NBS 28 was $10.0\text{‰} \pm 0.12$ (2σ). Friedman and O'Neil (1977) presented a range of published $\delta^{18}\text{O}$ values for NBS 28 of 9.5 to 9.9‰ from different laboratories (the IAEA reference sheet for NBS 28 presents a literature range of 8.8 to 10.0‰). There is clearly uncertainty in the $\delta^{18}\text{O}$ value of NBS 28 relative to VSMOW. This illustrates one of the most fundamental problems facing the triple oxygen isotope community with regards to standardization—*intercalibrating reference samples that are traditionally measured using different methods tied to different standards.*

INTERCALIBRATING WATERS, CARBONATES AND SILICATES FOR $\delta^{18}\text{O}$

In order to report the $\delta^{18}\text{O}$ values of different materials relative to each other, it is critical to have all types of phases calibrated to the same standard. The problem is that the methods for analyzing carbonates, water, and silicates are completely different. Waters are generally analyzed by equilibration with CO_2 gas which is then measured on the mass spectrometer (although laser spectroscopy methods are now commonly employed, e.g., Steig et al, 2014); carbonates are reacted with phosphoric acid to produce CO_2 ; silicates are fluorinated to quantitatively produce O_2 . The results from these three methods are not directly comparable and require a correction factor to bring them into agreement. As explained below, the errors in these correction factors are far larger than the uncertainty of the analyses themselves.

Water

The standard method for analyzing the $\delta^{18}\text{O}$ value of water was developed by the biochemist and National Medal of Science recipient Mildred Cohn and Nobel laureate coauthor Harold Urey over 80 years ago (1938), and is used today virtually unchanged. A trace amount of CO_2 is added to the water sample. The mixture is held at a constant temperature (generally 25°C) for hours to days in order to allow the two phases to come into oxygen isotope equilibrium. The CO_2 is removed from the reaction vessel, purified and measured on the mass spectrometer. Although there is a large fractionation between the water and CO_2 gas, as long as there is a large excess of H_2O and the equilibration process is performed using identical protocol at constant temperature, the isotope fractionation between the equilibrated water and CO_2 gas should be constant. Epstein and Mayeda (1953) compared the $\delta^{18}\text{O}$ values of many natural waters relative to the average of deep marine waters from the different oceans. All of their data were therefore relative to MOW (mean ocean water). This ultimately led to the formation of the SMOW and later VSMOW and still later VSMOW2 standards.

The isotopic fractionation between CO_2 and water is given by

$$\alpha_{\text{CO}_2\text{-water}} = \frac{1000 + \delta^{18}\text{O}_{\text{CO}_2}}{1000 + \delta^{18}\text{O}_{\text{water}}} \quad (7)$$

This is thought to be an equilibrium fractionation (unlike the acid digestion of carbonates—see below). It therefore can be determined theoretically as well as experimentally. Theoretical determinations give $\alpha_{\text{CO}_2\text{-water}}$ values of 1.042 (Urey and Greiff 1935), 1.039 (Urey 1947) and 1.0411 (Bottinga and Craig 1969). The difficulty in making this calculation is in the complexity of structure of liquid water in comparison to simple diatomic gaseous species from a statistical mechanical perspective (Cao and Liu 2011; Hayles et al. 2018).

Experimental determinations of the alpha value for Equation (7) require a quantitative conversion of H₂O to CO₂ so that the δ¹⁸O value of the CO₂ derived from the H₂O can be compared directly to the CO₂ equilibrated with the water. At least nine experimental determinations of the α_{CO₂-water} fractionation at 25 °C have been made using a variety of different methods based on carbon reduction or fluorination (see Brenninkmeijer et al. 1983 for a summary). The α_{CO₂-water} values range from 1.0407 to 1.0424 (Fig. 3) and have a standard deviation in the α values that corresponds to a 1σ uncertainty in the δ¹⁸O value of ~0.4‰. The general consensus is that α_{CO₂-water} = 1.0412 (Friedman and O'Neil 1977; Kim et al. 2015).

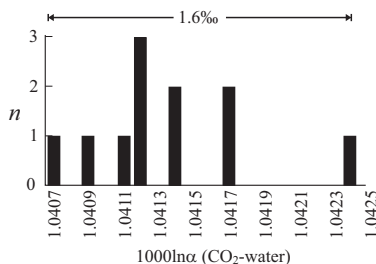


Figure 3. Published estimates of experimental α_{CO₂-water}. From (Friedman and O'Neil 1977; Brenninkmeijer et al. 1983).

Carbonates

The method for analyzing carbonate, like water, is also an indirect measure. Developed by John McCrea (1950) as part of Urey's project to develop a paleotemperature scale, calcite (and later other carbonates) is reacted with 100% phosphoric acid at a controlled temperature. The reaction liberates CO₂ gas, which is purified and analyzed on the mass spectrometer. As is the case for CO₂-water equilibration, the δ¹⁸O value of the evolved CO₂ gas is not equal to that of the actual carbonate. It is offset by the acid-liberated CO₂-calcite fractionation. By reacting all samples in controlled, repeatable conditions, the δ¹⁸O values of the CO₂ from different samples can be compared relative to each other.

Acid digestion of carbonates liberates only 2/3 of the total oxygen. The isotope fractionation during this process is the α_{CO₂(ACID)-carbonate} value. It is worth pointing out that the α_{CO₂(ACID)-carbonate} value is not the same as the α_{CO₂-carbonate} value. The latter is the equilibrium oxygen isotope fractionation between CO₂ gas and the carbonate, while the former is not (Guo et al. 2009). The equilibrium α(¹⁸O/¹⁶O)_{CO₂-calcite} value is between 1.0014 and 1.0119 (O'Neil and Epstein 1966b; Bottinga 1968), over 1‰ greater than the average α_{CO₂(ACID)-calcite} value. The α_{CO₂(ACID)-carbonate} value is therefore determined experimentally, and can only be quantified and tied to the VSMOW scale if the δ¹⁸O value of the total carbonate is known. This is determined by quantitatively extracting 100% of the oxygen from a sample by high temperature fluorination (e.g., Sharma and Clayton 1965). The extracted O₂ is then converted to CO₂ by high temperature reaction with a graphite rod. Comparison of this CO₂ gas with the CO₂ liberated by reaction of the same carbonate by phosphoric acid gives the α_{CO₂(ACID)-carbonate} value. There have been five independent determinations of this value (see Kim et al. 2015 Table 2 for compilation). They range from α_{CO₂(ACID)-calcite} = 1.01015 to 1.01058 (average is 1.01036 ± 0.00017), corresponding to an uncertainty of 0.18‰ (1σ). The generally accepted α_{CO₂(ACID)-calcite} value at 25 °C is 1.01025 as determined by Sharma and Clayton (1965) and amended by Friedman and O'Neil (1977).

Silicates

Silicates were first analyzed with high precision using the method of fluorination (Baertschi and Silverman 1951; Silverman 1951). Unlike the techniques for carbonates and water, the fluorination method is *quantitative* in the sense that 100% of the oxygen in the silicate is released by the fluorination reaction. The early studies measured the $^{18}\text{O}/^{16}\text{O}$ ratios of the O_2 gas produced by the fluorination (Baertschi and Silverman 1951). Most laboratories subsequently added a combustion step where O_2 was quantitatively converted to CO_2 by high temperature reaction with spectroscopic graphite in the presence of a Pt catalyst (Taylor and Epstein 1962). CO_2 could be purified more easily and moved throughout a vacuum line by freezing with liquid nitrogen. It is ironic that, after more than a half a century of analyzing silicate oxygen in the mass spectrometer using CO_2 as the analyte, we have returned to analyzing O_2 gas in order to also obtain the $^{17}\text{O}/^{16}\text{O}$ ratios of samples. There are two IAEA silicate standards: NBS 28 (quartz) with a defined $\delta^{18}\text{O}$ value of 9.57‰ and NBS 30 (biotite) with a $\delta^{18}\text{O}$ value of 5.12‰ (https://nucleus.iaea.org/rpst/Documents/NBS28_NBS30.pdf). There are 16 tabulated $\delta^{18}\text{O}$ values for NBS 28 in the abovementioned IAEA report with a standard deviation of 0.3‰ (1σ). Two recent studies have measured the $\delta^{18}\text{O}$ values of both NBS 28 and VSMOW. The results are 9.56‰ (Tanaka and Nakamura 2013) and 9.58‰ (Wostbrock et al. 2020a) on the VSMOW scale, in excellent agreement with the recommended IAEA value. Note: NBS 30 is no longer distributed from IAEA.

Comparison of all data

The crucial fractionation factors that are required to place waters, carbonates and silicates on the same scale are the equilibrium $\alpha_{\text{CO}_2\text{-water}}$ and kinetic $\alpha_{\text{CO}_2(\text{ACID})\text{-calcite}}$ fractionation factors (Fig. 4). From the above discussion it is clear that there is a significant degree of uncertainty when comparing waters to carbonates to silicates. Only silicates (and air O_2) are routinely determined quantitatively. The accuracy of carbonates and silicates on the VSMOW scale (relative to water) is dependent on the accuracy of the alpha factors and overall translates to an uncertainty as high as 0.5‰. This number may be slightly lower if we cull some of the experimental fractionation values that have been published. The most widely accepted values are $\alpha_{\text{CO}_2\text{-water}} = 1.0412$ and for $\alpha_{\text{CO}_2(\text{ACID})\text{-calcite}} = 1.01025$ (at 25 °C). These values may be refined by future researchers, but at present, the techniques available for analysis are essentially the same that were used in previous studies. Thus the ~0.5‰ uncertainty when comparing carbonates to waters to silicates remains.

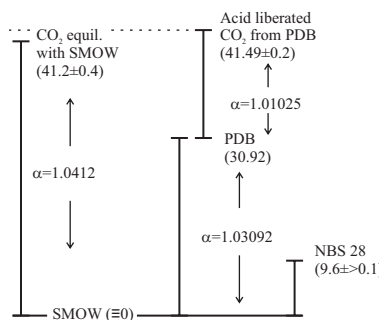


Figure 4. Fractionation factors and relative effects for comparing waters to carbonates to silicates. Uncertainties discussed in text.

STANDARDIZATION FOR $\delta^{17}\text{O}$ VALUES OF SELECTED REFERENCE MATERIALS

All of the same problems and obstacles for calibrating standards for $^{18}\text{O}/^{16}\text{O}$ exist for $^{17}\text{O}/^{16}\text{O}$ as well, with several additional complications. Proper standardization for $^{17}\text{O}/^{16}\text{O}$ ratios is particularly critical because the differences that are measured in natural materials are so small. While the $\delta^{18}\text{O}$ value of a material can be measured on either CO_2 , CO gas or O_2 gas, $\delta^{17}\text{O}$ values generally must be measured on O_2 gas. Converting samples quantitatively to O_2 gas can be extremely challenging, as in the case of carbonates.

The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of most terrestrial (Earth) materials co-vary, such that they follow the relationship $\delta^{17}\text{O} \approx 0.52x \times \delta^{18}\text{O}$ (see Miller and Pack 2021, this volume for a more detailed discussion). Plotting all Earth materials on a $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$ plot results in a linear trend that is often called the ‘Terrestrial Fractionation Line’ or TFL, especially in the meteoritic literature (e.g., McKeegan and Leshin 2001). The importance of measuring the $\delta^{17}\text{O}$ values of terrestrial materials becomes relevant only when we determine small deviations from some reference line that is representative of natural materials. This offset is the $\Delta^{17}\text{O}$ value, where

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda_{\text{RL}} \delta^{18}\text{O} - \gamma_{\text{RL}} \quad (8)$$

Here λ_{RL} is the assigned slope of a reference line (hence the RL subscript) and γ_{RL} is the y intercept. λ is commonly chosen to be 0.528 with $\gamma = 0$. The δ' notation refers to the linearized form of δ , such that $\delta' = 1000 \times \ln(\delta/1000+1)$ in per mil notation (Hulston and Thode 1965; Miller 2002). The advantage of the linearized notation is that the $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ relationship is close to linear, unlike $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$. The precision of $\Delta^{17}\text{O}$ measurements is on the order of $\pm 0.005\text{‰}$, when appropriate protocols are followed. These include extreme gas purification and long counting times on the mass spectrometer. This precision is significantly higher than what can be obtained for either the $\delta^{18}\text{O}$ or $\delta^{17}\text{O}$ value. The higher precision is obtained because the errors in the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values covary and therefore tend to cancel each other out (see appendix of Wostbrock et al. 2018 for details).

Method of measurement

In conventional mass spectrometry, $\delta^{18}\text{O}$ values can be measured on O_2 , CO_2 or even CO gas. The $\delta^{17}\text{O}$ value, however, must be determined using O_2 as an analyte, where the $[33]/[32]$ ratio ($^{17}\text{O}^{16}\text{O}/^{16}\text{O}^{16}\text{O}$) is measured. CO_2 cannot be used because of the interference from ^{13}C . Consider that 45/44 is both $^{12}\text{C}^{17}\text{O}^{16}\text{O}/^{12}\text{C}^{16}\text{O}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}^{16}\text{O}/^{12}\text{C}^{16}\text{O}^{16}\text{O}$. The mass resolution necessary to separate $^{12}\text{C}^{17}\text{O}^{16}\text{O}$ from $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ is over 50,000, far above that attainable with any commercially available gas-source mass spectrometer. There are several other analytical options in place of the conventional mass spectrometer. The $\delta^{17}\text{O}$ value of $\text{H}_2\text{O}_{\text{vapor}}$ is now routinely measured using cavity ringdown spectroscopy (Steig et al. 2014) with precision that rivals conventional mass spectrometry measurements. Promising preliminary data have also been made measuring the $\delta^{17}\text{O}$ value of CO_2 gas in a laser spectroscopy system (Sakai et al. 2017; Stoltmann et al. 2017). A different approach is to measure the O^+ fragment of CO_2 produced in the source of an electron impact isotope ratio mass spectrometer (Adnew et al. 2019). Extremely high mass resolution (4700) is required to separate the $^{17}\text{O}^+$ fragment (16.9991 amu) from the ubiquitous OH^+ ion (17.0027 amu). This high mass resolution requires an expensive doubly focusing mass spectrometer (e.g. Thermo Fisher 253 Ultra) and has significantly reduced transmission, necessitating counting times in excess of 20 hours for high precision.

Water

Ultimately all samples are related to VSMOW, using a stretching factor based on the difference between VSMOW and SLAP2. Therefore, it is critical to calibrate the working gas of a mass spectrometer and ultimately all materials to the VSMOW and SLAP2 scale. Water was first analyzed for the $\delta^{17}\text{O}$ value using electrolysis (Meijer and Li 1998) to produce

the O_2 from the water samples, which was then analyzed by conventional mass spectrometry. These authors recognized the relationship $\delta^{17}O = (1 + \delta^{18}O)^\lambda - 1$ ($\lambda = 0.5281 \pm 0.015$) by analyzing waters of very different isotope compositions, but their precision for $\Delta^{17}O$ was far lower than what would be attainable with fluorination systems.

Precise measurements for triple isotope analyses of water are made by either fluorination of water to O_2 , followed by analysis on a conventional dual inlet mass spectrometer, or, in recent years, by direct analysis of water vapor using either laser absorption cavity ringdown spectroscopy (Steig et al. 2014) or off-axis integrated cavity output spectroscopy (Tian et al. 2016). The latter gives precise analyses, but is not quantitative, and generally requires a correction due to the machine-related non-linearities. Fluorination methods are, in principle, quantitative, as 100% of the oxygen is converted to O_2 . Fluorination is accomplished either by passage of water through a CoF_3 heated reaction chamber in a He flow (Barkan and Luz 2005; Schoenemann et al. 2013) or by reaction with BrF_3 in a steel or nickel reaction vessel (O'Neil and Epstein 1966a; Jabeen and Kusakabe 1997; Pack et al. 2016; Wostbrock et al. 2020a). The data of Barkan and Luz (2005) may suffer from a slight $\Delta^{18}O$ compression observed in the CoF_3 method (Schoenemann et al. 2013; Passey et al. 2014). Figure 5 shows all published estimates for SLAP2 relative to VSMOW using the methods of fluorination. The vertical black line represents the accepted $\delta^{18}O$ value of SLAP2 of -55.5‰ . Three analyses are close to this value, with $\Delta^{17}O$ values averaging $-0.011 \pm 0.003\text{‰}$ (1σ). All other studies report $\delta^{18}O$ values that are higher than the accepted value. It has been shown that analysis of light waters suffers from a memory effect, and that the lightest (and presumably correct) values are only obtained after multiple injections (Barkan and Luz 2005; Schoenemann et al. 2013; Wostbrock et al. 2020a). While it has been suggested that the $\Delta^{17}O$ value of SLAP should be assigned a value of 0‰ because the measured value is close to 0‰ (Schoenemann et al. 2013), we argue that, while this may be a useful convention, accepting a 0‰ value is not necessarily correct. The clustering of data at $\delta^{18}O = -55.5\text{‰}$ and -0.011‰ implies that the $\Delta^{17}O$ value of SLAP2 is $-0.011 \pm 0.005\text{‰}$. The $\Delta^{17}O$ value of -0.006‰ from Schoenemann et al. (2013) agrees with our suggested estimate for SLAP2 within error.

One of the subtle complexities of accurately measuring $\Delta^{17}O$ values of samples with very different $\delta^{18}O$ values is the possibility of scale distortion resulting from a pressure baseline effect (Yeung et al. 2018). Because the effect can be non-mass-dependent, it may lead to non-trivial errors in the measured $\Delta^{17}O$ value of SLAP2 relative to VSMOW. The magnitude

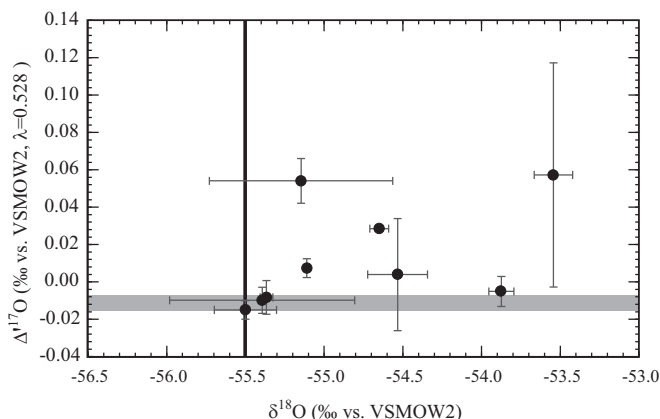


Figure 5. Published values for SLAP2 on the VSMOW2 scale. The accepted $\delta^{18}O$ value is -55.5‰ (vertical line). We suggest a $\Delta^{17}O$ value of $-0.011 \pm 0.005\text{‰}$. See Wostbrock et al. (2020a, Table 2) for sources.

of this effect was evaluated by Wostbrock et al. (2020a), who reported a SLAP2 value of $\delta^{18}\text{O}_{\text{SLAP2/VSMOW2}} = -55.55\text{‰}$ and $\Delta^{17}\text{O} = -0.015 \pm 0.005\text{‰}$. They found no pressure-baseline effect in their mass spectrometer (Thermo Scientific™ 253 Plus). Two gases with $\delta^{18}\text{O}$ values that differed by 25‰ were analyzed against each other at operating pressures of 3, 5 and 10 V [mass 32]. The measured $\Delta^{17}\text{O}$ values varied by no more than 0.002‰ over the entire pressure range. We therefore determine that the measured values are accurate and that the $\Delta^{17}\text{O}$ value of SLAP2 is between -0.015 and -0.010‰ . The number is not very different from 0‰, and whether a $\Delta^{17}\text{O}$ value of -0.011 or 0.0‰ is used will have a negligible effect for most samples when adjusted to the VSMOW-SLAP2 scale. Nevertheless, it appears that the -0.011‰ is a closer fit to the true value of SLAP2 on the VSMOW scale relative to $\lambda = 0.528$. Our best estimate for VSMOW and SLAP2 (and presumably the original SLAP, Lin et al. 2010) is given in Table 1.

Table 1. Triple oxygen isotope values of various reference standards.

Standard	Material	$\delta^{17}\text{O}$ (‰ relative to VSMOW-SLAP2)	$\delta^{18}\text{O}$ (‰ relative to VSMOW-SLAP2)	$\Delta^{17}\text{O}$ ($\lambda = 0.528$)
VSMOW	water	$\equiv 0$	$\equiv 0$	$\equiv 0$
SLAP & SLAP2	water	-29.709 ± 0.006	$= -55.5^a$	-0.011 ± 0.006
San Carlos Olivine (SCO)	olivine	2.75 ± 0.08	5.32 ± 0.16	-0.052 ± 0.014
UWG garnet	garnet	2.94^b	5.7^c	-0.064^b
NBS 28 ^b	quartz	4.991^b	9.57^a	-0.050^b
KRS ^d	garnet	-13.34 ± 0.11	-24.95 ± 0.21	-0.091 ± 0.003
SKFS ^d	chert	17.57 ± 0.13	33.81 ± 0.26	-0.137 ± 0.004
air	O ₂ gas	12.09 ± 0.11	23.88 ± 0.21	-0.447 ± 0.034
NBS 18	calcite	3.636 ± 0.009	6.99^a	-0.048 ± 0.009
NBS 19, 19A	calcite	14.92 ± 0.010	28.65^a	-0.102 ± 0.010
IAEA603	calcite	14.83 ± 0.007	28.47^a	-0.100 ± 0.007
NBS 127	sulfate	4.57	8.67 ± 0.02^a	0.003 ± 0.02
IAEA-SO-5	sulfate	6.14	12.07 ± 0.02^a	-0.217 ± 0.02
IAEA-SO-6	sulfate	-6.21	-11.36 ± 0.02^a	-0.204 ± 0.02
$\alpha_x\text{OCO}_2(\text{ACID})\text{-calcite}$	acid fractionation factor @25 °C	$1.00535 \pm (3.55 \times 10^{-6})$	1.01025^a	

Note: ^aIAEA defined value; ^bdetermined relative to SCO (see Fig. 6); ^cin relation to VSMOW-SLAP (see text);

^ddeveloped by Miller et al. (2020), reporting new average of four labs (Table 3).

Silicates

Determination of the $\delta^{17}\text{O}$ values of silicates is straightforward because O₂ is produced during fluorination and the conversion from the silicate solid to O₂ gas is quantitative (i.e., 100% of the silicate oxygen is converted to O₂). The problem, of course, is calibration to VSMOW, and to a lesser extent, to the stretching factor VSMOW-SLAP2. That requires fluorination of water and silicate standards in the same extraction line and mass spectrometer, something that, until recently, has rarely been done.

Early analyses calibrated their $\delta^{17}\text{O}$ value to SMOW by assuming that the $\delta^{17}\text{O}$ value of NBS-28 was equal to $0.52 \times \delta^{18}\text{O}$ (Clayton and Mayeda 1983). Franchi et al. (1999) were perhaps the first to fluorinate both the NBS 28 standard and SMOW. Unfortunately, the errors

in the analyses were high in comparison to more recent results. A number of more recent studies have been made in which the IAEA standard NBS 28 and two commonly used informal standards San Carlos olivine (SCO) and UWG garnet (Valley et al. 1995) have been analyzed relative to VSMOW and SLAP. One problem is that all researchers get their SCO from any one of a number of sources. It has been shown that there are at least two different populations of SCO with different $\delta^{18}\text{O}$ values (Macpherson et al. 2005; Starkey et al. 2016). Nevertheless, in general, the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values from recent calibration papers give consistent values for SCO data, as shown in Table 2. The data in Table 2 are all corrected to the SLAP2 value in Table 1. The correction procedure involves the following standardization of each laboratories data:

1) The delta values for VSMOW, SLAP (or SLAP2) and SCO are converted to prime values where $\delta' = 1000 \times \ln(\delta/1000 + 1)$.

2) A constant given by $\delta'^x\text{O}_{\text{VSMOW-accepted}} - \delta'^x\text{O}_{\text{VSMOW-measured}}$ is added to all data ($\delta'^x\text{O}_{\text{VSMOW-accepted}} = 0$).

3) A stretching factor is applied such that all data are multiplied by

$$\frac{\delta'^x\text{O}_{\text{SMOW-accepted}} - \delta'^x\text{O}_{\text{SLAP-accepted}}}{\delta'^x\text{O}_{\text{SMOW-measured}} - \delta'^x\text{O}_{\text{SLAP-measured}}}, \text{ which reduces to } \frac{57.100}{\delta'^{18}\text{O}_{\text{SMOW-measured}} - \delta'^{18}\text{O}_{\text{SLAP-measured}}}$$

and $\frac{30.159}{\delta'^{17}\text{O}_{\text{SMOW-measured}} - \delta'^{17}\text{O}_{\text{SLAP-measured}}}$.

The small differences seen in Table 2 may be due to slight differences in the oxygen isotope compositions of the olivine samples or slight miscalibrations to VSMOW-SLAP2. The San Carlos olivine measured in Wostbrock et al. (2020a) comes from a large aliquot of pure olivine and is available for others to calibrate their system. Samples of this standard can be obtained from the UNM CSI laboratory (csi.unm.edu) allowing for precise interlaboratory calibration. Widescale use of this particular batch of SCO could potentially reduce the interlaboratory discrepancies and result in further refinements of this value in the future.

NBS 28 quartz and UWG garnet (Valley et al. 1995) are two other commonly measured reference silicates. There are only two direct comparisons of these two standards to VSMOW and SLAP (Tanaka and Nakamura 2013; Wostbrock et al. 2020a). Both obtain a $\delta^{18}\text{O}$ value of 5.70 (± 0.01)‰ for UWG, in good agreement with the original published values of 5.74 to 5.8‰ (Valley et al. 1995). The reported $\Delta^{17}\text{O}$ values are -0.078 ‰ (Tanaka and Nakamura 2013) and -0.071 ‰ (Wostbrock et al. 2020a). For both studies, the $\delta^{18}\text{O}$ values for NBS 28 are within 0.01‰ of the accepted IAEA value of 9.57‰, with $\Delta^{17}\text{O}$ values of -0.063 ‰ (Tanaka and Nakamura 2013) and -0.059 ‰ (Wostbrock et al. 2020a).

Table 2. Triple isotope data for San Carlos Olivine. Data are corrected for $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ SLAP2 = -55.5 and -0.011 ‰.

Laboratory/reference	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$
GZG, Goettingen ¹	2.682	5.153	-0.036
ISIE, Okayama ¹	2.750	5.287	-0.038
ISIE, Okayama ²	2.717	5.294	-0.075
CSI, UNM ³	2.717	5.263	-0.058
CSI, UNM ⁴	2.892	5.588	-0.054
<i>Average</i>	<i>2.75 ± 0.08</i>	<i>5.32 ± 0.16</i>	<i>-0.052 ± 0.014</i>

Note: ¹ Pack et al. (2016), ²Tanaka and Nakamura (2013), ³Wostbrock et al. (2020a), ⁴Sharp et al. (2016).

The $\Delta^{17}\text{O}$ values of UWG and NBS 28 can also be further refined by using additional published data. There are a large number of studies where UWG and NBS 28 are compared directly to SCO (see Fig. 6 caption for references). From Figure 6, we obtain a $\Delta\Delta^{17}\text{O}_{\text{UWG-SCO}}$ value of -0.012‰ and a $\Delta\Delta^{17}\text{O}_{\text{NBS 28-SCO}}$ value of 0.002‰ . We use the IAEA-accepted $\delta^{18}\text{O}$ value of 9.57‰ for NBS 28 and a $\delta^{18}\text{O}$ value of 5.7‰ for UWG and the difference in the $\Delta^{17}\text{O}$ values between SCO and NBS 28 (Fig. 6) to determine the $\Delta^{17}\text{O}$ value and ultimately the $\delta^{17}\text{O}$ value of these two standards (Table 1).

Two additional standards with extremely different $\delta^{18}\text{O}$ values have recently been developed (Miller et al. 2020). The first is an extremely light garnet from Karelia, Russia (KRS) and the second is a heavy chert from Denmark (SKFS). The purpose of developing standards with such different $\delta^{18}\text{O}$ values is to allow laboratories that are not set up to fluorinate waters to be able to determine a stretching factor based on two silicate samples with very different $\delta^{18}\text{O}$ values. The standards were originally analyzed at Georg-August-Universität, Goettingen, Germany, and The Open University, UK and have subsequently been analyzed at The Center for Stable Isotopes, University of New Mexico, USA and The University of Oregon, USA (Table 3). All data were corrected to the common value of UWG given in Table 1. (This is because the SCO standard at Open University appears to have a different $\delta^{18}\text{O}$ value from the other labs and what is seen in Table 2). Correcting all data to a common value of UWG (Table 1) allows for a common standardized value for these two light and heavy standards (Table 1).

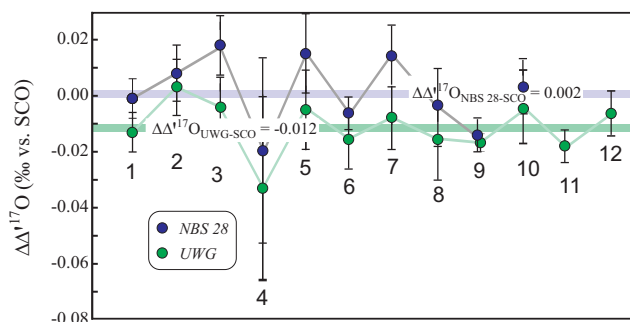


Figure 6. Published $\Delta\Delta^{17}\text{O}$ values for UWG garnet and NBS 28 relative to San Carlos olivine values from Table 1. The average $\Delta^{17}\text{O}$ value of UWG is -0.012‰ less than SCO while the average $\Delta^{17}\text{O}$ value for NBS 28 is 0.002‰ heavier than SCO (pale horizontal lines). Data sources: 1 (Wostbrock et al. 2020a); 2 (Tanaka and Nakamura 2013); 3 (Pack and Herwartz 2014); 4 (Franchi et al. 1999); 5 (Starkey et al. 2016); 6 (Cowie and Johnston 2016); 7 (Miller et al. 2020); 8 (Kim et al. 2019); 9 (Ghoshmaulik et al. 2020); 10 (I. Bindeman, pers. comm.); 11 (Young et al. 2016); 12 (Yeung et al. 2018).

Air

There are three direct comparisons between atmospheric oxygen (O_2) and VSMOW-SLAP (Barkan and Luz 2005; 2011; Wostbrock et al. 2020a) and three additional comparisons of O_2 with secondary standards, either UWG or SCO (Young et al. 2014; Pack et al. 2017; Yeung et al. 2018). Accurate $\Delta^{17}\text{O}$ analyses of air require the separation of N_2 and especially Ar from O_2 , which is done using a long gas chromatographic column chilled to $\sim -80^\circ\text{C}$. All studies removed Ar from the O_2 gas except for two (Barkan and Luz 2005, 2011) in which an empirical correction was applied (Luz and Barkan 2005). All studies results were corrected to VSMOW-SLAP2 using the data for standards UWG, SCO and VSMOW-SLAP2 in Table 1. The newly normalized results are shown in Table 4.

Table 3. Triple isotope data for light and heavy standards KRS and SKFS from four different laboratories. Data are corrected to UWG values given in Table 1. OU–Open University, UK; Goet–Georg-August-Universität Göttingen, Germany; CSI–Center for Stable Isotopes, U. New Mexico, USA; Or–University of Oregon, USA.

Laboratory/ reference	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$
KRS			
OU	-13.50 ± 0.05	-25.25 ± 0.09	-0.088 ± 0.010
Goet	-13.34 ± 0.14	-24.95 ± 0.27	-0.091 ± 0.010
CSI	-13.31 ± 0.06	-24.87 ± 0.12	-0.096 ± 0.010
Or	-13.23 ± 0.05	-24.74 ± 0.03	-0.090 ± 0.015
<i>Average</i>	-13.34 ± 0.11	-24.95 ± 0.21	-0.091 ± 0.003
SKFS			
OU	17.61 ± 0.13	33.88 ± 0.24	-0.135 ± 0.009
Goet	17.38 ± 0.22	33.43 ± 0.41	-0.134 ± 0.009
CSI	17.68 ± 0.08	34.03 ± 0.11	-0.142 ± 0.005
Or	17.62 ± 0.12	33.90 ± 0.38	-0.136 ± 0.007
<i>Average</i>	17.57 ± 0.13	33.81 ± 0.26	-0.137 ± 0.004

Table 4. Compilation of published triple oxygen isotope analyses of Air corrected to VSMOW-SLAP2.

Reference	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$
Barkan and Luz 2005 ^{1,2}	12.08 ± 0.01	23.88 ± 0.02	-0.453
Barkan and Luz 2011 ^{1,2}	12.03	23.88	-0.507
Young et al. 2014 ³	11.94 ± 0.02	23.57 ± 0.05	-0.429 ± 0.01
Pack et al. 2017 ^{1,5}	12.25 ± 0.02	24.15 ± 0.05	-0.432 ± 0.019
Yeung et al. 2018 ^{3,4}	12.03 ± 0.01	23.73 ± 0.01	-0.429 ± 0.007
Wostbrock et al. 2020a ¹	12.18 ± 0.07	24.05 ± 0.11	-0.441 ± 0.012
<i>Average</i>	12.09 ± 0.11	23.88 ± 0.21	-0.447 ± 0.034

Note: ¹Measured directly to VSMOW-SLAP; ²Did not remove Ar from O₂ sample; ³Corrected to SCO; ⁴Includes pressure baseline correction; ⁵Corrected to SCO, A. Pack, pers. comm., (2020)

Carbonates

The only way in which the $\delta^{17}\text{O}$ of carbonates can be directly determined is by complete conversion to O₂ by the method of fluorination. 100% oxygen retrieval requires high temperature fluorination in nickel reaction vessels. The difficulty with this method is that other intermediate oxygen-bearing compounds, such as CO, CO₂ and COF_x, are produced in the fluorination process and they are difficult to react completely to O₂ (and CF₄). In the one high-precision study of this type, Wostbrock et al. (2020a) fluorinated carbonates at 750 °C for four days with a large excess of BrF₅. Yields approached 100%, but the $\delta^{18}\text{O}$ values were often less than the accepted values determined by phosphoric acid digestion. It was found, however, that the lower $\delta^{18}\text{O}$ also had proportionally lower $\delta^{17}\text{O}$ values, such that the measured λ was 0.528, identical to our reference slope λ . The measured $\Delta^{17}\text{O}$ values were therefore constant within $\pm 0.01\%$ (Fig. 7). Wostbrock et al. (2020a) therefore used the conventionally accepted values for the $\delta^{18}\text{O}$ values of IAEA carbonate standards and the measured $\Delta^{17}\text{O}$ values to

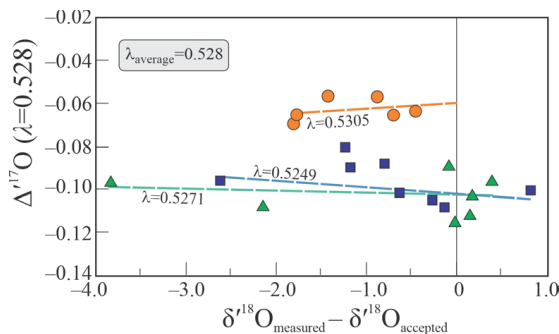


Figure 7. Plot of $\Delta^{17}\text{O}$ value of an individual analysis vs the difference in the accepted $\delta^{18}\text{O}$ value and the measured $\delta^{18}\text{O}$ value for carbonate samples. Extrapolation of 2‰ for the $\delta^{18}\text{O}$ value will change the $\Delta^{17}\text{O}$ value by less than 0.006‰. The average of these three samples give a $\lambda = 0.528$. Data from Wostbrock et al. (2020b).

back-calculate the $\delta^{17}\text{O}$ values of the samples. This same correction to the endmember $\Delta^{17}\text{O}$ values has been used for sulfates (Cowie and Johnston 2016) and CO_2 gas (Farquhar et al. 1998). Results are given in Table 1.

Wostbrock et al. (2020a) also fluorinated the CO_2 released by phosphoric acid digestion from calcite at 25 °C. Their calculated $\theta_{\text{CO}_2(\text{ACID})-\text{calcite}}$ value is 0.5230 ± 0.0003 , where $\theta = \ln \alpha^{17}\text{O}_{\text{CO}_2(\text{ACID})-\text{calcite}} / \ln \alpha^{18}\text{O}_{\text{CO}_2(\text{ACID})-\text{calcite}}$. This corresponds to an $\alpha^{17}\text{O}_{\text{CO}_2(\text{ACID})-\text{calcite}}$ value of $1.00535 \pm 3.55 \times 10^{-6}$ relative to an $\alpha^{18}\text{O}_{\text{CO}_2(\text{ACID})-\text{calcite}}$ value of 1.01025. Using this fractionation factor, laboratories that measure the $\Delta^{17}\text{O}$ value of CO_2 released from carbonates by phosphoric acid digestion (at 25 °C) can back-calculate to the original $\Delta^{17}\text{O}$ value of the carbonate.

There are a number of indirect measurements of the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of carbonates obtained by measuring the CO_2 gas liberated by phosphoric acid digestion. The CO_2 is analyzed for the triple oxygen isotope composition using one of several methods: conversion to H_2O followed by fluorination (Passey et al. 2014); equilibration with O_2 in the presence of a Pt catalyst (Mahata et al. 2013; Barkan et al. 2015; Fosu et al. 2020); or by direct analysis of the O^+ fragment of CO_2 using a high resolution mass spectrometer (Adnew et al. 2019). With accurate determinations of the triple oxygen isotope composition of IAEA calcite standards, researchers who measure the CO_2 released by phosphoric acid digestion can easily use the $\alpha_{\text{CO}_2(\text{ACID})-\text{calcite}}$ values in Table 1 or determine an appropriate α value that brings their measurements into agreement with the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of the carbonate standards.

A compilation of $\Delta^{17}\text{O}$ values of IAEA standards and their relative values from different studies is given in Table 5. Although the measured $\Delta^{17}\text{O}$ values may be different depending on the analytical procedure used, the difference in the $\Delta^{17}\text{O}$ values between any two standards should be the same for all laboratories. The community is coming to consensus on the $\Delta\Delta^{17}\text{O}$ of standards, although there are still large outliers, potentially due to issues with exchanging $\text{CO}_2\text{-O}_2$.

Sulfates

The triple oxygen isotope composition of sulfates is measured by laser fluorination with either BrF_5 (Bao and Thiemens 2000) or F_2 with additional gas purification using a GC column (Cowie and Johnston 2016). The laser fluorination methods result in molar yields of 25–35% when using BrF_5 and ~50% when using F_2 as reaction reagents. Measured $\delta^{18}\text{O}$ values can be as much as 15–20‰ below the accepted values. Due to the low yields, triple oxygen isotope compositions are corrected based on the measured $\Delta^{17}\text{O}$ value from fluorination and the $\delta^{18}\text{O}$ value obtained by thermal conversion elemental analyzer (TC/EA) method (Kornexl et al. 1999;

Table 5. Published $\Delta^{17}\text{O}$ values of carbonate and CO_2 liberated from phosphoric acid digestion and $\Delta\Delta^{17}\text{O}_{\text{NBS 19-NBS 18}}$ and $\Delta\Delta^{17}\text{O}_{\text{IAEA 603-NBS 18}}$ values.

Study	CO_2			calcite			$\Delta\Delta^{17}\text{O}$	
	NBS 19	IAEA 603	NBS 18	NBS 19	IAEA 603	NBS 18	NBS 19 -NBS 18	IAEA 603 -NBS 18
Wostbrock et al. 2020a ^a	-0.155	-0.147	-0.100	-0.102	-0.100	-0.048	-0.055 ^b -0.054 ^c	-0.047 ^b -0.052 ^c
Barkan et al. 2019	-0.182	-0.194	-0.163				-0.019 ^b	-0.023 ^b
Passey et al. 2014	-0.135 ^d		-0.098 ^d				-0.037 ^b	
Fosu et al. 2020	-0.169		-0.119				-0.050 ^b	
Passey and Ji 2019	-0.143 ^d		-0.088 ^d				-0.055 ^b	
Barkan et al. 2015	-0.227 ^e		+0.003 ^e				-0.230 ^{b,e}	
Sha et al. 2020		-0.267	-0.225					-0.042 ^b

Notes: ^afluorination; ^b CO_2 gas extracted from carbonate; ^cdirect carbonate fluorination; ^dextracted at 90 °C. All others extracted at 25 °C; ^eBarkan et al. (2019) suggest that the analyzed samples may have been contaminated.

Savarino et al. 2001). Using a calculated θ_{LF} value (the fractionation associated with incomplete fluorination) of 0.5301, Cowie and Johnston (2016) were able to extrapolate their measured $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ to obtain the $\Delta^{17}\text{O}$ value of their sulfate standards NBS 127, IAEA-SO-5, and IAEA-SO-6. The $\delta^{18}\text{O}$ values of these standards are tied to the VSMOW-SLAP scale using waters analyzed by $\text{CO}_2\text{-H}_2\text{O}$ equilibration (Brand et al. 2009). The reported $\Delta^{17}\text{O}$ values in Cowie and Johnston (2016) are relative to their $\delta^{17}\text{O}$ values for the UWG standard. We recalculate the $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ values of these standards using the difference between Cowie and Johnston's $\Delta^{17}\text{O}$ values for UWG, San Carlos olivine and NBS 28 and those reported in the present communication (Table 1). The reported $\delta^{18}\text{O}$ values are those given in Johnston et al. (2014). Results are presented in Table 1 calibrated to the VSMOW-SLAP scale based on the fluorination of VSMOW and SLAP2 .

CONCLUSION

Mass dependent triple oxygen isotope geochemistry is a relatively new field. Until recently, laboratories generally measured variations in the $\Delta^{17}\text{O}$ values of materials without a proper interlaboratory calibration scheme. In some cases, the $\delta^{17}\text{O}$ values of their samples were estimated, with no direct ties to VSMOW and SLAP (SLAP2). While this did not affect the results from an 'isolated' publication, it made intercomparisons between laboratories extremely difficult. The problems in standardizing different materials to the same scale is related to the different methods employed for analysis. Silicates and waters are both fluorinated, but relatively few laboratories are set up to do both. More challenging is the total fluorination of carbonates, which requires high temperatures and long reaction times in order to approach 100% recovery.

In this communication, we have attempted to calibrate all standards relative to VSMOW and SLAP2 as presented in Table 1. Standards include waters, silicates, carbonates, sulfates and air. We also provide the acid fractionation factor data for CO₂-calcite as reported in Wostbrock et al. (2020a), so that laboratories that determine the triple isotope values of CO₂ liberated by phosphoric acid digestion of calcite can back calculate the isotope values of the calcite relative to VSMOW-SLAP2. With this internally consistent standards table, practitioners can directly compare their data for different materials with different laboratories. Invariably, adjustments will be made to these suggested standard values. Nevertheless, the triple oxygen isotope geochemical community is reaching consensus on standards that makes possible direct comparison of the very subtle differences that are seen in natural materials.

ACKNOWLEDGEMENTS

We would like to thank S.W. Schoenemann and M. Miller for their constructive reviews, and the editors I.N. Bindeman and A. Pack for their comments and support during this work. David Johnston provided us with unpublished sulfate data. Support for this study comes from the following grants: NSF-EAR 1551226 and NSF-EAR 1903852 to ZDS and NSF GRFP Grant DGE-1418062 to J.A.G.W.

REFERENCES

- Adnew GA, Hofmann ME, Paul D, Laskar A, Surma J, Albrecht N, Pack A, Schwieters J, Koren G, Peters W, Röckmann T (2019) Determination of the triple oxygen and carbon isotopic composition of CO₂ from atomic ion fragments formed in the ion source of the 253 Ultra high-resolution isotope ratio mass spectrometer. *Rapid Commun Mass Spectrom* 33:1363–1380
- Assonov S, Groening M, Fajgelj A, Hélie J-F, Hillaire-Marcel C (2020) Preparation and characterization of IAEA-603, a new primary reference material aimed at the VPDB scale realisation for δ¹³C and δ¹⁸O determination. *Rapid Commun Mass Spectrom* 34:e8867
- Baertschi P (1950) Isotopic composition of the oxygen in silicate rocks. *Nature* 166:112–113
- Baertschi P (1976) Absolute ¹⁸O content of Standard Mean Ocean Water. *Earth Planet Sci Lett* 31:341–344
- Baertschi P, Silverman SR (1951) The determination of relative abundances of the oxygen isotopes in silicate rocks. *Geochim Cosmochim Acta* 1:4–6
- Bao H, Thieme MH (2000) Generation of O₂ from BaSO₄ using a CO₂-laser fluorination system for simultaneous analysis of δ¹⁸O and δ¹⁷O. *Anal Chem* 72:4029–4032
- Barkan E, Luz B (2005) High precision measurements of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios in H₂O. *Rapid Commun Mass Spectrom* 19:3737–3742
- Barkan E, Luz B (2011) The relationships among the three stable isotopes of oxygen in air, seawater and marine photosynthesis. *Rapid Commun Mass Spectrom* 25:2367–2369
- Barkan E, Musan I, Luz B (2015) High-precision measurements of δ¹⁷O and ¹⁷Oexcess of NBS19 and NBS18. *Rapid Commun Mass Spectrom* 29:2219–2224
- Barkan E, Affek HP, Luz B, Bergel SJ, Voarintsoa NRG, Musan I (2019) Calibration of δ¹⁷O and ¹⁷Oexcess values of three international standards: IAEA-603, NBS19 and NBS18. *Rapid Commun Mass Spectrom* 33:737–740
- Bottinga Y (1968) Calculation of fractionation factors for carbon and oxygen isotopic exchange in the system calcite-carbon dioxide-water. *J Phys Chem* 72:800–808
- Bottinga Y, Craig H (1969) Oxygen isotope fractionation between CO₂ and water, and the isotopic composition of marine atmospheric CO₂. *Earth Planet Sci Letters* 5:285–295
- Brand WA, Coplen TB, Aerts-Bijma AT, Böhlke JK, Gehre M, Geilmann H, Gröning M, Jansen HG, Meijer HA, Mroczkowski SJ, Qi H (2009) Comprehensive inter-laboratory calibration of reference materials for δ¹⁸O versus VSMOW using various on-line high-temperature conversion techniques. *Rapid Commun Mass Spectrom* 23:999–1019
- Brenninkmeijer CAM, Kraft P, Mook WG (1983) Oxygen isotope fractionation between CO₂ and H₂O. *Chem Geol* 41:181–190
- Cao X, Liu Y (2011) Equilibrium mass-dependent fractionation relationships for triple oxygen isotopes. *Geochim Cosmochim Acta* 75:7435–7445
- Clayton RN (1959) Oxygen isotope fractionation in the system calcium carbonate-water. *J Chem Phys* 30:1246–1250

- Clayton RN, Mayeda TK (1983) Oxygen isotopes in eucrites, shergottites, nakhlites, and chassignites. *Earth Planet Sci Lett* 62:1–6
- Cohn M, Urey HC (1938) Oxygen exchange reactions of organic compounds and water. *J Am Chem Soc* 60:679–687
- Coplen TB, Kendall C, Hopple J (1983) Comparison of stable isotope reference samples. *Nature* 302:236–238
- Cowie BR, Johnston DT (2016) High-precision measurement and standard calibration of triple oxygen isotopic compositions ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) of sulfate by F_2 laser fluorination. *Chem Geol* 440:50–59
- Craig H (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim Cosmochim Acta* 12:133–149
- Craig H (1961) Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* 133:1833–1834
- Dole M (1936) The relative atomic weight of oxygen in water and air. A discussion of the atmospheric distribution of the oxygen isotopes and of the chemical standard of atomic weights. *J Chem Phys* 4:268–275
- Epstein S, Mayeda T (1953) Variation of O^{18} content of waters from natural sources. *Geochim Cosmochim Acta* 4:213–224
- Epstein S, Buchsbaum R, Lowenstam HA, Urey HC (1951) Carbonate–water isotopic temperature scale. *Geol Soc Am Bull* 62:417–426
- Epstein S, Buchsbaum R, Lowenstam HA, Urey HC (1953) Revised carbonate–water isotopic temperature scale. *Geol Soc Am Bull* 64:1315–1326
- Farquhar J, Thiemens MH, Jackson TL (1998) Atmosphere–surface interactions on Mars: $\Delta^{17}\text{O}$ measurements of carbonate from ALH 84001. *Science* 280:1580–1582
- Fosu BR, Subba R, Peethambaran R, Bhattacharya SK, Ghosh P (2020) Technical Note: Developments and applications in triple oxygen isotope analysis of carbonates. *ACS Earth Space Chem* doi.org/10.1021/acsearthspacechem.9b00330:9 p.
- Franchi IA, Wright IP, Sexton AS, Pillinger CT (1999) The oxygen-isotopic composition of Earth and Mars. *Meteorit Planet Sci* 34:657–661
- Friedman I (1953) Deuterium content of natural waters and other substances. *Geochim Cosmochim Acta* 4:89–103
- Friedman I, Gleason JD (1973) A new silicate intercomparison standard for ^{18}O analysis. *Earth Planet Sci Lett* 18:124
- Friedman I, O'Neil JR (eds) (1977) Compilation of stable isotope fractionation factors of geochemical interest. Washington, D.C.
- Friedman I, O'Neil JR, Cebula G (2007) Two new carbonate stable-isotope standards. *Geostand Geoanal Res* 6:11–12
- Ghoshmaulik S, Bhattacharya SK, Roy P, Sarkar A (2020) A simple cryogenic method for efficient measurement of triple oxygen isotopes in silicates. *Rapid Commun Mass Spectrom* 34:e8833
- Gonfiantini R (1978) Standards for stable isotope measurements in natural compounds. *Nature* 271:534–536
- Guo W, Mosenfelder JL, Goddard WA, Eiler JM (2009) Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements. *Geochim Cosmochim Acta* 73:7203–7225
- Hayles JA, Gao C, Cao X, Liu Y, Bao H (2018) Theoretical calibration of the triple oxygen isotope thermometer. *Geochim Cosmochim Acta* 235:237–245
- Hulston JR, Thode HG (1965) Variations in the S^{33} , S^{34} , and S^{36} contents of meteorites and their relation to chemical and nuclear effects. *J Geophys Res* 70:3475–3484
- IAEA (2006) Reference values for the relative difference in hydrogen and oxygen stable isotope-amount ratio for the international measurement standards [1] IAEA Reference Sheet https://nucleus.iaea.org/rpst/documents/VSMOW_SLAP.pdf:5
- IAEA (2017) Reference Sheet for International Measurement Standards VSMOW2 Vienna Standard Mean Ocean Water 2, water, SLAP2 Standard Light Antarctic Precipitation 2, water. IAEA Reference Sheet https://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf:8
- IAEA (2020) Reference Sheet for Certified Reference Material GRESP Greenland Summit Precipitation, water. IAEA Reference Sheet https://nucleus.iaea.org/sites/ReferenceMaterials/Shared%20Documents/ReferenceMaterials/StableIsotopes/Gresp/RS_GRESP-2020.pdf:5
- Jabene I, Kusakabe M (1997) Determination of $\delta^{17}\text{O}$ values of reference water samples VSMOW and VSLAP. *Chem Geol* 143:115–119
- Johnston DT, Gill BC, Masterson A, Beirne E, Casciotti KL, Knapp AN, Berelson W (2014) Placing an upper limit on cryptic marine sulphur cycling. *Nature* 513:530–533
- Kim NK, Kusakabe M, Park, Lee JJ, Nagao K, Enokido Y, Yamashita S, Park SY (2019) An automated laser fluorination technique for high-precision analysis of three oxygen isotopes in silicates. *Rapid Commun Mass Spectrom* 33:641–649
- Kim S-T, Coplen TB, Horita J (2015) Normalization of stable isotope data for carbonate minerals: Implementation of IUPAC guidelines. *Geochim Cosmochim Acta* 158:276–289
- Kornel BE, Gehre M, Höfling R, Werner RA (1999) On-line $\delta^{18}\text{O}$ measurement of organic and inorganic substances. *Rapid Commun Mass Spectrom* 13:1685–1693

- Lin Y, Clayton RN, Grönning M (2010) Calibration of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of international measurement standards—VSMOW, VSMOW2, SLAP, and SLAP2. *Rapid Commun Mass Spectrom* 24:773–776
- Luz B, Barkan E (2005) The isotopic ratios $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ in molecular oxygen and their significance in biogeochemistry. *Geochim Cosmochim Acta* 69:1099–1110
- Macpherson CG, Hilton DR, Day JMD, Lowry D, Grönvold K (2005) High- $^3\text{He}/^4\text{He}$, depleted mantle and low- $\delta^{18}\text{O}$, recycled oceanic lithosphere in the source of central Iceland magmatism. *Earth Planet Sci Lett* 233:411–427
- Mahata S, Bhattacharya SK, Wang C-H, Liang M-C (2013) Oxygen isotope exchange between O_2 and CO_2 over hot platinum: An innovative technique for measuring $\Delta^{17}\text{O}$ in CO_2 . *Anal Chem* 85:6894–6901
- McCrea JM (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J Chem Phys* 18:849–857
- McKeegan KD, Leshin LA (2001) Stable isotope variations in extraterrestrial materials. *Rev Mineral Geochem* 43:279–318
- McKinney CR, McCrea JM, Epstein S, Allen HA, Urey HC (1950) Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios. *Rev Sci Instrum* 21:724–730
- Meijer HAJ, Li WJ (1998) The use of electrolysis for accurate $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ isotope measurements in water. *Isot Environ Health Stud* 34:349–369
- Miller MF (2002) Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochim Cosmochim Acta* 66:1881–1889
- Miller MF, Pack A (2021) Why measure ^{17}O ? Historical perspective, triple-isotope systematics and selected applications. *Rev Mineral Geochem* 86:1–34
- Miller MF, Pack A, Bindeman IN, Greenwood RC (2020) Standardizing the reporting of $\Delta^{17}\text{O}$ data from high precision oxygen triple-isotope ratio measurements of silicate rocks and minerals. *Chem Geol* 532:119332
- O'Neil JR, Epstein S (1966a) A method for oxygen isotope analysis of milligram quantities of water and some of its applications. *J Geophys Res* 71:4955–4961
- O'Neil JR, Epstein S (1966b) Oxygen isotope fractionation in the system dolomite–calcite–carbon dioxide. *Science* 152:198–200
- Pack A, Herwartz D (2014) The triple oxygen isotope composition of the Earth mantle and $\Delta^{17}\text{O}$ variations in terrestrial rocks. *Earth Planet Sci Lett* 390:138–145
- Pack A, Tanaka R, Hering M, Sengupta S, Peters S, Nakamura E (2016) The oxygen isotope composition of San Carlos olivine on the VSMOW2–SLAP2 scale. *Rapid Commun Mass Spectrom* 30:1495–1504
- Pack A, Höweling A, Hezel DC, Stefanak MT, Beck A-K, Peters STM, Sengupta S, Herwartz D, Folco L (2017) Tracing the oxygen isotope composition of the upper Earth's atmosphere using cosmic spherules. *Nature Communications* 8:15702
- Passey BH, Ji H (2019) Triple oxygen isotope signatures of evaporation in lake waters and carbonates: A case study from the western United States. *Earth Planet Sci Lett* 518:1–12
- Passey BH, Hu H, Ji H, Montanari S, Li S, Henkes GA, Levin NE (2014) Triple oxygen isotopes in biogenic and sedimentary carbonates. *Geochim Cosmochim Acta* 141:1–25
- Sakai S, Matsuda S, Hikida T, Shimono A, McManus JB, Zahniser M, Nelson DD, Dettman DL, Yang D, Ohkouchi N (2017) High-precision simultaneous $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, and $^{17}\text{O}/^{16}\text{O}$ analyses for microgram quantities of CaCO_3 by tunable infrared laser absorption spectroscopy. *Anal Chem* 89:11846–11852
- Savarino J, Alexander B, Darmohusodo V, Thiemens MH (2001) Sulfur and oxygen analysis of sulfate at micromole levels using a pyrolysis technique in a continuous flow system. *Anal Chem* 73:4457–4462
- Schoenemann SW, Schauer AJ, Steig EJ (2013) Measurement of SLAP2 and GISP $\delta^{17}\text{O}$ and proposed VSMOW–SLAP normalization for $\delta^{17}\text{O}$ and ^{17}O excess. *Rapid Commun Mass Spectrom* 27:582–590
- Sha L, Mahata S, Duan P, Luz B, Zhang P, Baker J, Zong B, Ning Y, Brahim YA, Zhang H, Edwards RL (2020) A novel application of triple oxygen isotope ratios of speleothems. *Geochim Cosmochim Acta* 270:360–378
- Sharma T, Clayton RN (1965) Measurement of $\text{O}^{18}/\text{O}^{16}$ ratios of total oxygen of carbonates. *Geochim Cosmochim Acta* 29:1347–1353
- Sharp ZD (2013) *Principles of Stable Isotope Geochemistry*, 2nd Edition. Open Educational Resources, Albuquerque, NM
- Sharp ZD, Gibbons JA, Maltsev O, Atudorei V, Pack A, Sengupta S, Shock EL, Knauth LP (2016) A calibration of the triple oxygen isotope fractionation in the SiO_2 – H_2O system and applications to natural samples. *Geochim Cosmochim Acta* 186:105–119
- Silverman SR (1951) The isotope geology of oxygen. *Geochim Cosmochim Acta* 2:26–42
- Starkey NA, Jackson CRM, Greenwood RC, Parman S, Franchi IA, Jackson M, Fitton JG, Stuart FM, Kurz M, Larsen LM (2016) Triple oxygen isotopic composition of the high- $^3\text{He}/^4\text{He}$ mantle. *Geochim Cosmochim Acta* 176:227–238
- Steig EJ, Gkinis V, Schauer AJ, Schoenemann SW, Samek K, Hoffnagle J, Dennis KJ, Tan SM (2014) Calibrated high-precision ^{17}O -excess measurements using cavity ring-down spectroscopy with laser-current-tuned cavity resonance. *Atmos Measur Tech* 7:2421–2435
- Stoltmann T, Casado M, Daëron M, Landais A, Kassi S (2017) Direct, precise measurements of isotopologue abundance ratios in CO_2 using molecular absorption spectroscopy: Application to $\Delta^{17}\text{O}$. *Anal Chem* 89:10129–10132
- Tanaka R, Nakamura E (2013) Determination of ^{17}O -excess of terrestrial silicate/oxide minerals with respect to Vienna Standard Mean Ocean Water (VSMOW). *Rapid Commun Mass Spectrom* 27:285–297

- Taylor HP, Jr., Epstein S (1962) Relationship between O^{18}/O^{16} ratios in coexisting minerals of igneous and metamorphic rocks: Part 1: Principles and experimental results. *Geol Soc Am Bull* 73:461–480
- Tian C, Wang L, Novick KA (2016) Water vapor δ^2H , $\delta^{18}O$ and $\delta^{17}O$ measurements using an off-axis integrated cavity output spectrometer—sensitivity to water vapor concentration, delta value and averaging-time. *Rapid Commun Mass Spectrom* 30:2077–2086
- Urey HC (1947) The thermodynamic properties of isotopic substances. *J Chem Soc*:562–581
- Urey HC, Greiff LJ (1935) Isotopic exchange equilibria. *J Am Chem Soc* 57:321–327
- Urey HC, Epstein S, McKinney CR (1951) Measurement of paleotemperatures and temperatures of the Upper Cretaceous of England, Denmark, and the southeastern United States. *Geol Soc Am Bull* 62:399–416
- Valley JW, Kitchen N, Kohn MJ, Niendorf CR, Spicuzza MJ (1995) UWG-2, a garnet standard for oxygen isotope ratios; strategies for high precision and accuracy with laser heating. *Geochim Cosmochim Acta* 59:5223–5231
- Verkouteren RM, Klinedinst DB (2004) Value assignment and uncertainty estimation of selected light stable isotope reference materials: RMs 8543–8545, RMs 8562–8564, and RM 8566. NIST Spec Publ 260–149 2004 ED:58
- Wostbrock JAG, Sharp ZD, Sanchez-Yanez C, Reich M, van den Heuvel DB, Benning LG (2018) Calibration and application of silica–water triple oxygen isotope thermometry to geothermal systems in Iceland and Chile. *Geochim Cosmochim Acta* 234:84–97
- Wostbrock JAG, Cano EJ, Sharp ZD (2020a) An internally consistent triple oxygen isotope calibration of standards for silicates, carbonates and air relative to VSMOW2 and SLAP2. *Chem Geol* 533:119432
- Wostbrock JAG, Brand U, Coplen T, Swart PK, Carlson SJ, Brearley AJ, Sharp ZD (2020b) Calibration of carbonate–water triple oxygen isotope fractionation: seeing through diagenesis in ancient carbonates. *Geochim Cosmochim Acta* 288:369–388
- Yeung LY, Hayles JA, Hu H, Ash JL, Sun T (2018) Scale distortion from pressure baselines as a source of inaccuracy in triple-isotope measurements. *Rapid Commun Mass Spectrom* 32:1811–1821
- Young ED, Yeung LY, Kohl IE (2014) On the $\Delta^{17}O$ budget of atmospheric O_2 . *Geochim Cosmochim Acta* 135:102–125
- Young ED, Kohl IE, Warren PH, Rubie DC, Jacobson SA, Morbidelli A (2016) Oxygen isotopic evidence for vigorous mixing during the Moon-forming giant impact. *Science* 351:493–496