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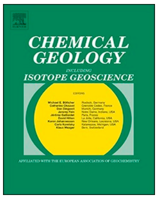

An internally consistent triple oxygen isotope calibration of standards for silicates, carbonates and air relative to VSMOW2 and SLAP2

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ABSTRACT

High precision triple oxygen isotope measurements are becoming a more common analysis in laboratories. There is a lack of calibrated standards to use for triple oxygen isotope measurements and this has led to data being presented on different scales rather than to the traditional VSMOW2-SLAP2 scale. Here we present triple oxygen isotope values of standard carbonates, CO_2 liberated from carbonates, silicates and air calibrated to the VSMOW2-SLAP2 scale. We analyzed VSMOW2 and SLAP2 to calibrate our reference gas. Our measured $\delta^{18}O$ value of SLAP2 is −55.55‰, indistinguishable from the accepted value of −55.5‰. Our $\Delta'^{17}O$ value of SLAP2 ($\lambda = 0.528$) is not zero, but rather −0.015‰, corresponding to a $\delta^{17}O$ value of −29.741‰. The $\Delta'^{17}O$ values of carbonate standards NBS19, IAEA603 and NBS18 are −0.102, −0.100 and − 0.048‰, respectively (± 0.010). For CO_2 of calcite liberated by phosphoric acid digestion at 25 °C, the θ_{ACID} value at 25 °C is 0.5230 ± 0.0003. These results can be used to correct triple oxygen isotope measurements of CO_2 released by phosphoric acid digestion in other laboratories. We present triple oxygen isotope values for UW Garnet-2, NBS-28, San Carlos Olivine (NM-SCO), and our in-house quartz standard (NM-Q). Aliquots of NM-Q and NM-SCO are available from the Center for Stable Isotopes (CSI), New Mexico for interlaboratory comparison. Our $\delta^{17}O$ and $\delta^{18}O$ values for air are 12.178‰ (± 0.066) and 24.046‰ (± 0.117), respectively, with a corresponding $\Delta'^{17}O$ value of −0.441 ± 0.012‰. With the availability of common standards, all laboratories making $\delta^{17}O$-$\delta^{18}O$ measurements can calibrate their reference gas relative to the VSMOW2-SLAP2 scale. Laboratories making triple oxygen isotope measurements on CO_2 released from carbonates using phosphoric acid digestion can correct to the bulk carbonate value.

1. Introduction

The IAEA working group (e.g., Gonfiantini, 1978; Hut, 1987) recognized the necessity of having well-characterized stable isotope standards to allow all laboratories to be calibrated to the same scale. In the case of oxygen, samples are ultimately related to VSMOW (or VSMOW2), defined as having a $\delta^{18}O$ value of 0‰. To correct for possible instrumental compression of stable isotope analyses made over a wide range of isotopic compositions, a second light water standard with a $\delta^{18}O$ value of −55.5‰, called SLAP (or SLAP2), is used to correct for different laboratory 'stretching factors'. Original batches of VSMOW and SLAP are extinguished, and another batch of standards is currently distributed under the names VSMOW2 and SLAP2 with essentially identical $\delta^{18}O$ values as their original counterpart. A second oxygen scale is related to PDB, defined relative to the carbonate standard NBS-19 with a $\delta^{18}O$ value of −2.20‰ on the VPDB scale. The carbonate standard is ultimately related to VSMOW2 by laboratories that have quantitatively extracted total oxygen from carbonates by fluorination and O_2 of water by fluorination or CO_2-H_2O equilibration (Kim et al., 2007; Kim and O'Neil, 1997; Sharma and Clayton, 1965). The VSMOW2 and VPDB scales are related by the equation by Friedman and O'Neil (1977) corrected in Coplen et al. (1983)

$$\delta^{18}O_{VSMOW} = 1.03091\ \delta^{18}O_{VPDB} + 30.91 \tag{1}$$

All laboratories are now able to report their oxygen isotope data relative to VSMOW2 by calibrating their secondary standards to widely available IAEA reference materials.

There has been a recent interest in measuring the $^{17}O/^{16}O$ ratio of terrestrial materials with high precision (e.g., Pack and Herwartz, 2014). A number of studies have calibrated silicate materials relative to VSMOW or VSMOW2 by fluorinating both the solids and VSMOW or VSMOW2 in the same extraction system (Kusakabe and Matsuhisa, 2008; Pack et al., 2016; Sharp et al., 2016; Tanaka and Nakamura, 2013). There is some disagreement as to the accepted $\delta^{17}O$ value of

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these standards, but more importantly, there is no direct calibration to VSMOW2 for the $\delta^{17}O$ value of carbonates. In this work, we calibrate silicate and carbonate standards to VSMOW2 by directly fluorinating water, silicates and carbonates using the same extraction line. We also measure $\delta^{17}O$ and $\delta^{18}O$ values of air on the same extraction line. The work provides $\delta^{17}O$ values of IAEA carbonate references materials and calibrates new silicate standards that can be requested from the Center for Stable Isotopes (CSI) at the University of New Mexico (see csi.unm.edu for details).

Inter-calibration of water, carbonates and silicates is complicated due to the different methods traditionally used for their analysis. The $\delta^{18}O$ values of silicates are measured directly on O_2 gas quantitatively extracted from the sample by fluorination in nickel bombs (Clayton and Mayeda, 1963) or by laser fluorination (Sharp, 1990). Waters and carbonates, on the other hand, are commonly measured indirectly. Waters are generally analyzed using the CO_2 equilibration method originally developed by Cohn and Urey (1938) or, rarely, directly using the fluorination method of O'Neil and Epstein (1966) or the CoF_3 method by Baker et al. (2002) and modified by Barkan and Luz (2005). Carbonates are analyzed as CO_2 using the phosphoric acid digestion method developed by McCrea (1950). Only 2/3 of the oxygen is liberated during phosphoric acid digestion and the $\delta^{18}O$ value of the CO_2 gas is not the same as that of the original sample. A correction factor (α value) must be applied in order to relate the sample back to the VSMOW2 scale. In order to determine the appropriate α value, waters and carbonates have been analyzed quantitatively using fluorination methods to extract 100% of the oxygen (e.g., O'Neil and Epstein, 1966; Sharma and Clayton, 1965). Even after a sizeable number of studies aimed at determining the phosphoric acid digestion fractionation factor (α_{ACID}), variations of up to 0.5‰ for the carbonate-CO_2 and H_2O-CO_2 fractionation factor still exist (Blattner, 1973; Bottinga and Craig, 1969; Compston and Epstein, 1958; Kim et al., 2007; Kim and O'Neil, 1997; Majzoub, 1966; Matsuhisa et al., 1971; O'Neil et al., 1975; O'Neil et al., 1969; O'Neil and Epstein, 1966; Sharma and Clayton, 1965; Staschewski, 1964). These uncertainties translate into similar uncertainties for the conversion from the VPDB to VSMOW scale (Coplen et al., 1983; Craig, 1957; Craig, 1961; Friedman and O'Neil, 1977).

Calibration for the $\delta^{17}O$ values of reference materials is much more limited. Several studies have fluorinated waters and silicates (Kusakabe and Matsuhisa, 2008; Pack and Herwartz, 2014; Pack et al., 2016; Sharp et al., 2016; Tanaka and Nakamura, 2013) in order to determine the $\delta^{17}O$ value on the VSMOW-SLAP scale. In studies where water was also fluorinated, published $\delta^{18}O$ and $\Delta^{17}O$ values of San Carlos olivine vary by 0.36 and 0.168, respectively (Kusakabe and Matsuhisa, 2008; Pack et al., 2016; Sharp et al., 2016; Tanaka and Nakamura, 2013). The problem is further compounded due to variability in the $\delta^{18}O$ values of different aliquots of San Carlos olivine (Starkey et al., 2016). There are several published $\delta^{18}O$ and $\Delta^{17}O$ values of air (Barkan and Luz, 2003; Barkan and Luz, 2011; Pack et al., 2017; Yeung et al., 2012; Young et al., 2014) ranging between 23.4 and 24.15 and −0.363 and −0.453‰, respectively (Note, Young et al. (2014) published $\Delta'^{17}O$ values of air relative to a San Carlos olivine $\Delta'^{17}O$ value of 0‰ and not directly to VSMOW). Since the troposphere is expected to be homogenous, the variations are probably related to slight differences in analytical technique and calibration.

To date, no direct calibration of the $\Delta'^{17}O$ values of carbonates have been made using the method of fluorination. Barkan et al. (2019, 2015) and Passey et al. (2014) presented triple oxygen isotope values of CO_2 of common standards NBS-18, NBS-19 and IAEA-603 for CO_2 released using phosphoric acid digestion at 25 °C and 90 °C, respectively. The authors used different methods for analyzing for triple oxygen isotope values as well as different temperatures of acid digestion. Barkan et al. (2019, 2015) determined the $\delta^{17}O$ value using a CO_2-O_2 equilibration method modelled after Mahata et al. (2013). Passey et al. (2014) used methanation to convert the CO_2 to H_2O and then fluorinated the H_2O using the CoF_3 method of Barkan and Luz (2005). Although helpful for standardizing laboratories making these measurements, the standards reported are for CO_2 only and not the total carbonate value.

By having a wide suite of $\delta^{18}O$ values of silicates, carbonates, and air that have been analyzed on the same mass spectrometer using the same reference gas and inlet systems and that are calibrated to VSMOW2-SLAP2, we hope to reduce interlaboratory errors discussed earlier. Laboratories can calibrate and stretch their own working reference gas to the sample values and report all values relative to the VSMOW2-SLAP2 scale. We present common silicate standards (NBS-28, UW-Gore Mountain Garnet 2, and San Carlos Olivine) as a complete dataset to any laboratory making triple oxygen isotope measurements to calibrate their reference gas to the VSMOW2-SLAP2 scale. All labs conducting oxygen isotope analyses for either $\delta^{18}O$ or paired $\delta^{17}O$-$\delta^{18}O$ measurements, can use these standards to calibrate their reference gas on the VSMOW2-SLAP2 scale. We also present the carbonate triple oxygen isotope composition of NBS-18, NBS-19, and IAEA-603 measured by total fluorination so laboratories measuring the triple oxygen isotope composition of CO_2 evolved by phosphoric acid digestion can correct directly to the oxygen isotope values of the total carbonate.

2. Isotope systematics

The isotopic abundance ratio is reported in standard δ-notation (McKinney et al., 1950) and defined as:

$$\delta^{x}O = \left(\frac{{}^{x}R_{sample}}{{}^{x}R_{VSMOW}} - 1\right) \times 1000 \tag{2}$$

${}^{x}R = {}^{x}O / {}^{16}O$ and x is either mass 17 or 18. In this study, all samples are reported in linearized notation relative to the VSMOW2-SLAP2 scale. We use linear notation to remove curvature effects that exist when comparing $\delta^{18}O$ and $\delta^{17}O$ values across a large scale and is defined as (Hulston and Thode, 1965; Miller, 2002):

$$\delta'^{x}O = 1000\ln\left(\frac{\delta^{x}O}{1000} + 1\right) \tag{3}$$

where x refers to ^{17}O or ^{18}O. By combining and rewriting the equilibrium fractionation equation with δ′ notation, the mass-dependent equilibrium fractionation between two phases can be written as $1000\ln\alpha_{a\text{-}b} = \delta'^{x}O_a - \delta'^{x}O_b$ (where x is either mass 17 or 18 and $\alpha = {}^{17}R / {}^{18}R$). Deviations of $\delta'^{17}O$ from a reference slope are expressed as $\Delta'^{17}O$, given by,

$$\Delta'^{17}O = \delta'^{17}O - \lambda_{RL} \times \delta'^{18}O + \gamma \tag{4}$$

where λ_{RL} is the reference slope and γ is the y-intercept (for this study $\gamma = 0$). In this work, we use a λ_{RL} value of 0.528 to keep in line with the original literature reporting triple oxygen isotope standards and align geological papers with the broader triple oxygen isotope community (Barkan et al., 2019; Meijer and Li, 1998; Passey et al., 2014; Sharp et al., 2018).

While λ is used to describe the slope of the best fit, we use θ to describe processes controlled by thermodynamic equilibrium, defined for the triple oxygen isotope system as:

$$\theta_{a-b} = \frac{\delta'^{17}O_a - \delta'^{17}O_b}{\delta'^{18}O_a - \delta'^{18}O_b} \tag{5}$$

where a and b are any two phases.

3. Methods

All samples (except air) were fluorinated using BrF_5 as the fluorinating agent. The fluorination procedures for waters, silicates and carbonates are slightly different, but the post-fluorination O_2 purification and analysis were identical for all methods and all samples were measured on the same mass spectrometer relative to the same working gas.

3.1. Waters

Waters were fluorinated using a modification of the procedure outlined in O'Neil and Epstein (1966). 1.8 µl of water were injected through a Valco® 1/8″ septum injector nut with support and low bleed septum using a 2 µl Hamilton© series 7000 Gastight® syringe into an evacuated glass U-trap. The H_2O was cryogenically transferred into a ¼″ Ni U-trap bounded on either side by a Swagelok SS-4H welded bellows valve. 500–550 µmol of BrF_5 were then frozen into the U-trap. The volume was isolated and the entire region (including the bellows valve block) was heated for 5 min using a heat gun. The reaction products were expanded into the laser fluorination chamber for further purification. Precision of analyses is 0.091 and 0.164‰ for $\delta^{17}O$ and $\delta^{18}O$ respectively and 0.006 for $\Delta'^{17}O$ values. The higher precision for $\Delta'^{17}O$ is due to the fact that small uncertainties in the $\delta^{17}O$ and $\delta^{18}O$ are correlated (Wostbrock et al., 2018).

3.2. Silicates

Silicates were reacted using the standard laser fluorination procedure of Sharp (1990). Two mg sized samples were loaded onto a Ni sample block with individual holes for up to 44 samples. The block was evacuated in the heated reaction chamber using a turbomolecular pump for 24 h while being heated by an external halogen heat lamp. Samples were then prefluorinated for about 1 h at room temperature to remove any adsorbed water or other contaminants. Samples were heated with a 50 W CO_2 laser in the presence of 100 torr BrF_5 (~500 µmol) until the sample was completely fluorinated. Purification of the O_2 gas is described below.

3.3. Carbonates

Carbonates were quantitatively fluorinated at high temperatures using the conventional ‘Ni bomb’ method, similar to a method used by Sharma and Clayton (1965). The procedure involves loading 5–6 mg of carbonate into Ni tubes and heating under vacuum at ~100 °C for 12 h to remove any adsorbed H_2O. A 30-times excess of BrF_5 (30× more gas than stoichiometrically necessary for complete reaction) is then added as an oxidizing reagent and the tubes are heated to 750 °C for 4 days to ensure complete fluorination. The bombs are frozen with liquid nitrogen and O_2 is quantitatively released into the laser fluorination chamber/cleanup line. The bombs are then isolated, warmed and refrozen to release any remaining O_2 that might have been trapped in the residual BrF_x ice. A Pfeiffer PrismPlus quadrupole mass spectrometer was used to test the presence of unreacted COF_2.

3.4. CO_2 gas

The CO_2 released via phosphoric acid digestion at 25 °C from the 3 standards was also fluorinated using the same method as the carbonates. To release the CO_2, 8–10 mg of carbonate were loaded into glass tubes along with a smaller tube containing 3 ml of 102% phosphoric acid (McCrea, 1950). Samples were degassed for 12 h and then placed in a water bath for 1 h to equilibrate to 25 °C. The phosphoric acid was then reacted with the carbonate for ~15 h in the water bath. The released CO_2 was purified using cryogenic traps to remove H_2O and non-condensable gases and transferred cryogenically into Ni tubes for fluorination. The same Ni tubes were used for both CO_2 and carbonate fluorination. After BrF_5 was added to the Ni tube, the tubes were heated to 750 °C for 4 days. Released O_2 was transferred into the mass spectrometer following the exact same purification process as the O_2 released from carbonate fluorination.

3.5. Oxygen gas purification and O_2 analysis

Following fluorination of a sample, the O_2 gas was passed over two traps cooled with liquid nitrogen and then through a warmed (~100 °C) NaCl trap to remove traces of F_2. The gas passed through an additional cold trap and was adsorbed onto a 5 Å mol sieve cooled to liquid nitrogen temperature. The sample gas was transferred through a 6′, 1/8″ diameter, 5× mol sieve gas chromatograph in a He stream set at a constant flow of 6.0 ml/min at room temperature and collected on a second mol sieve trap at the inlet of the mass spectrometer (the high purity He was first passed through a large U-trap filled with activated 5 Å mol sieve cooled to liquid nitrogen temperatures for further purification and removal of any trace O_2). Excess He was pumped away, and the O_2 was expanded into a Thermo-Finnegan MAT 253+ mass spectrometer at the Center for Stable Isotopes at the University of New Mexico specifically configured for O_2 gas. The oxygen was measured using long integration (26 s) with 30 iterations per analysis and measured against the same O_2 reference gas. The instrument was checked for any pressure effects described by Yeung et al. (2018) and no pressure effect was found so no correction was applied. The test involved measuring two different gases ($\Delta\delta^{18}O \approx 25‰$) at 3 V, 5 V, and 10 V intensities on mass 32 and the resulting $\Delta'^{17}O$ value varied by 0.002‰, and $\delta^{18}O$ value varied by < 0.04‰ (see Supplementary material). Nevertheless, we made every attempt to run our samples at a constant intensity of 5.5 V on mass 32, corresponding to a pressure of ~55 mbar in the bellows and 6.8 × 10^{-6} mbar in the source.

3.6. Air

For air analyses, 3 ml of outside Albuquerque air was injected into a vacuum line, frozen into a 4-way valve with a liquid nitrogen trap filled with 5 Å mol sieve. Purified He was used to carry the sample through a 4-meter 1/8″ packed 5× mol sieve column cooled with a mixture of dry ice-ethanol (−80 °C) with a He flow rate of 12.8 ml/min. The O_2 was collected on a second mol sieve liquid nitrogen trap and excess He was pumped away before being expanded into the mass spectrometer. Argon and O_2 separation was complete (Fig. 1) with ~10 s between argon and the beginning of the O_2 peak. The Ar concentration remaining in the O_2 sample gas was ~0.05% based on relative peak intensities for masses 32 and 40.

4. Results/discussion

All results are reported in Tables 1, 3, 5, and 6.

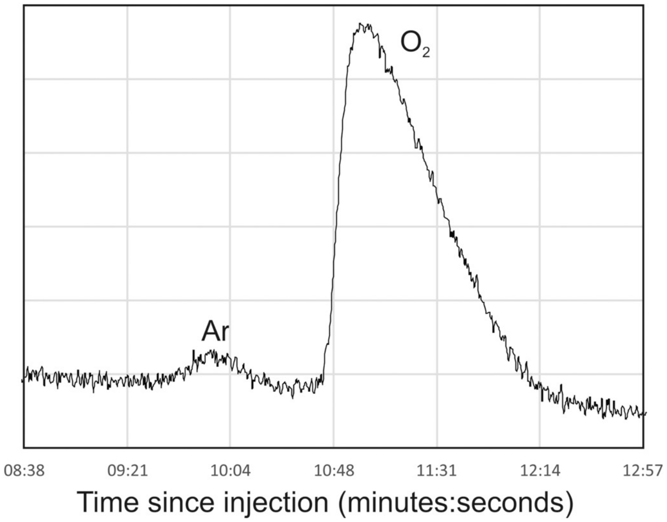

Fig. 1. Separation of Ar and O_2 in our chilled GC column during an air sample injection.

Table 1
Individual and average VSMOW2-SLAP2 data of this study reported in ‰ notation. All data have been normalized to VSMOW2 having a $\delta^{17}O = \delta^{18}O = 0.000‰$.

Sample	$\delta^{17}O$ (VSMOW2)	$\delta^{18}O$ (VSMOW2)	$\delta'^{17}O$ (VSMOW2)	$\delta'^{18}O$ (VSMOW2)	$\Delta'^{17}O$ (VSMOW2, $\lambda = 0.528$)
VSMOW2_1	−0.085	−0.163	−0.085	−0.163	0.001
VSMOW2_2	−0.116	−0.204	−0.116	−0.204	−0.008
VSMOW2_3	−0.017	−0.027	−0.017	−0.027	−0.002
VSMOW2_4	0.108	0.194	0.108	0.194	0.006
VSMOW2_5	0.102	0.194	0.102	0.194	0.000
VSMOW2_6	−0.097	−0.169	−0.097	−0.169	−0.008
VSMOW2_7	0.063	0.105	0.063	0.105	0.008
VSMOW2_8	0.040	0.070	0.040	0.070	0.003
Average	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
St. Dev (± 1σ)	**0.091**	**0.164**	**0.091**	**0.164**	**0.006**
SLAP2_1*	−28.205	−52.689	−28.611	−54.128	−0.031
SLAP2_2*	−28.504	−53.244	−28.918	−54.714	−0.029
SLAP2_3*	−29.452	−54.991	−29.895	−56.561	−0.031
SLAP2_4	−29.850	−55.761	−30.305	−57.376	−0.010
SLAP2_5	−29.633	−55.355	−30.081	−56.946	−0.013
SLAP2_6	−29.792	−55.651	−30.245	−57.259	−0.012
SLAP2_7	−29.637	−55.349	−30.085	−56.939	−0.021
SLAP2_8	−29.792	−55.635	−30.245	−57.242	−0.021
Average	**−29.741**	**−55.550**	**−30.192**	**−57.153**	**−0.015**
St. Dev (± 1σ)	**0.100**	**0.187**	**0.103**	**0.198**	**0.005**

* denotes samples of observed consecutive memory effect after earlier VSMOW2 injections and are not included in averages or standard deviation.

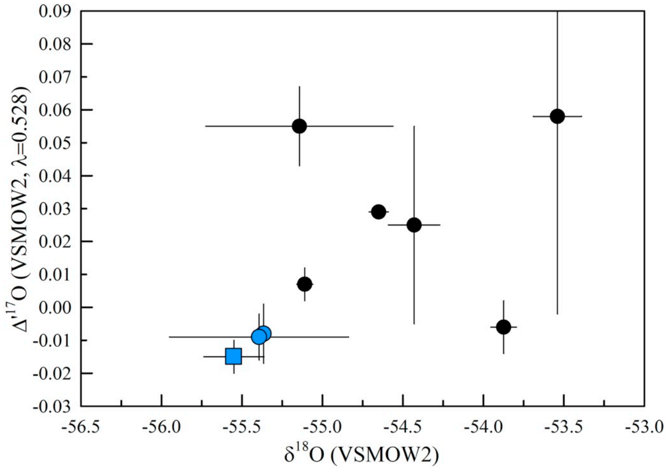

Fig. 2. Triple oxygen isotope composition of SLAP2. A literature compilation (Table 2) of $\Delta'^{17}O$ values shows a relationship with $\delta^{18}O$ values for SLAP2 where higher $\delta^{18}O$ values result in higher $\Delta'^{17}O$ values. This study (blue square) is the closest $\delta^{18}O$ value to IAEA. Studies with $\delta^{18}O$ values close to the IAEA accepted value of −55.5 (blue) were used to define SLAP2 values. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

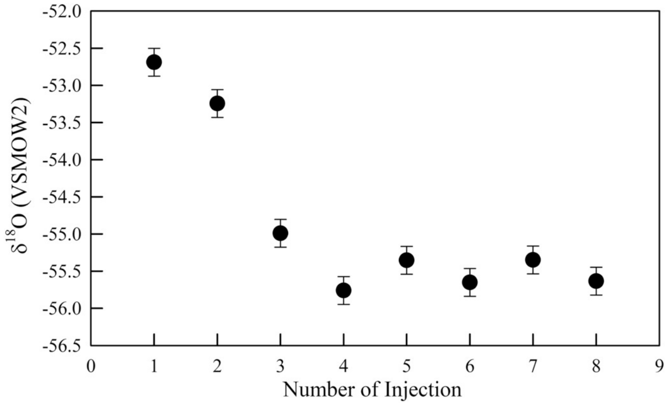

Fig. 3. Memory effect of switching from VSMOW2 samples to SLAP2 samples for analysis. The first three injections of SLAP gave high $\delta^{18}O$ values.

4.1. Water standards

All data are reported normalized to VSMOW2 with oxygen isotope values ≡ 0‰. Our analyses for VSMOW2 have the following uncertainty (1σ, $n = 8$): $\delta^{18}O \pm 0.16‰$, $\delta^{17}O \pm 0.09‰$, $\Delta'^{17}O \pm 0.006‰$ (Table 1). The average oxygen isotope values of SLAP2 are $\delta^{17}O = -29.74 \pm 0.10‰$, $\delta^{18}O = -55.55 \pm 0.19$ and $\Delta'^{17}O = -0.015 \pm 0.005‰$ ($n = 5$), nearly identical to the accepted

Table 2
Compilation of published triple oxygen isotope values of SLAP2 on the VSMOW2 scale, all values are reported in ‰.

	$\delta^{17}O$ (VSMOW2)	$\delta^{18}O$ (VSMOW2)	$\delta'^{17}O$ (VSMOW2)	$\delta'^{18}O$ (VSMOW2)	$\Delta'^{17}O$ (VSMOW2, $\lambda = 0.528$)
Jabeen and Kusakabe (1997)	−28.58 (± 0.13)	−53.54 (± 0.15)	−28.996	−55.027	0.058 (± 0.06)
Barkan and Luz (2005)	−29.48 (± 0.03)	−55.11 (± 0.05)	−29.923	−56.687	0.007 (± 0.005)
Kusakabe and Matsuhisa (2008)	−29.21 (± 0.07)	−54.65 (± 0.06)	−29.645	−56.200	0.029[a]
Lin et al. (2010)[b]	−29.10 (± 0.10)	−54.43 (± 0.16)	−29.529	−55.972	0.025 (± 0.030)
Schoenemann et al. (2013)	−28.822 (± 0.04)	−53.874 (± 0.08)	−29.245	−55.380	−0.006 (± 0.008)
Pack et al. (2016) - GZG	−29.451 (± 0.314)	−55.143 (± 0.582)	−29.893	−56.722	0.055 (± 0.012)
Pack et al. (2016) - ISEI	**−29.633 (± 0.028)**	**−55.366 (± 0.044)**	**−30.089**	**−56.958**	**−0.008 (± 0.009)**
Sharp et al. (2016)	**−29.650 (± 0.296)**	**−55.394 (± 0.556)**	**−30.099**	**−56.987**	**−0.009 (± 0.007)**
This study	**−29.741 (± 0.100)**	**−55.550 (± 0.187)**	**−30.192**	**−57.153**	**−0.015 (± 0.005)**

Bolded studies are 3 lowest SLAP values which averages $\delta^{18}O = -55.438 \pm 0.099$ and $\Delta'^{17}O = -0.011 \pm 0.004$

[a] standard deviation unreported in publication

[b] SLAP2 corrected to VSMOW2

Table 3

Triple oxygen isotope data for carbonate standards and CO_2 extracted by phosphoric acid digestion at 25°C. The measured $\Delta'^{17}O$ value and accepted $\delta^{18}O$ value of the standards were used to calculate the $\delta^{17}O$ value relative to the accepted $\delta^{18}O$ value (corr data). The θ and α values are for CO_2-calcite. All samples are reported in ‰ relative to VSMOW2-SLAP2.

Sample	Type	$\delta^{17}O$	$\delta^{18}O$	$\delta'^{17}O$	$\delta'^{18}O$	$\Delta'^{17}O$ ($\lambda = 0.528$)	$\delta^{17}O_{corr}$ [a]	$\delta^{18}O_{corr}$ [b]	$\delta'^{17}O_{corr}$ [c]	$\delta'^{18}O_{corr}$
NBS18_1	calcite	3.795	7.286	3.787	7.260	–0.046	3.749	7.200	3.742	7.174
NBS18_2	calcite	3.484	6.692	3.478	6.670	–0.043	3.752	7.200	3.745	7.174
NBS18_3	calcite	3.772	7.273	3.765	7.247	–0.062	3.733	7.200	3.726	7.174
NBS18_4	calcite	3.539	6.793	3.532	6.770	–0.042	3.753	7.200	3.746	7.174
	Average	**3.647**	**3.641**	**7.011**	**6.986**	**–0.048**	**3.747**	**7.200**	**3.740**	**7.174**
	± 1σ	**0.159**	**0.158**	**0.313**	**0.311**	**0.009**	**0.010**	**0.010**	**–**	**–**
	St. err[d]	**0.079**	**0.079**	**0.156**	**0.155**	**0.005**	**0.005**	**0.005**	**–**	**–**
NBS18_1	CO_2	9.049	9.008	17.400	17.250	–0.100	9.114	9.072	17.524	17.372
		$\theta = 0.52294$, $^{17}\alpha = 1.00538$, $^{18}\alpha = 1.01032$					**$\theta_{corr} = 0.52291$, $^{17}\alpha_{corr} = 1.00535$, $^{18}\alpha_{corr} = 1.01025$**			
NBS19_1	calcite	15.139	29.055	15.026	28.641	–0.097	14.928	28.650	14.818	28.247
NBS19_2	calcite	14.888	28.560	14.778	28.160	–0.090	14.935	28.650	14.825	28.247
NBS19_3	calcite	15.014	28.827	14.903	28.419	–0.103	14.922	28.650	14.812	28.247
NBS19_4	calcite	14.894	28.622	14.784	28.220	–0.116	14.909	28.650	14.799	28.247
NBS19_5	calcite	14.761	28.341	14.653	27.947	–0.103	14.922	28.650	14.812	28.247
NBS19A_1	calcite	14.510	27.830	14.406	27.450	–0.088	14.937	28.650	14.827	28.247
NBS19A_2	calcite	12.891	24.744	12.809	24.443	–0.097	14.928	28.650	14.818	28.247
NBS19A_3	calcite	13.775	26.462	13.681	26.118	–0.109	14.915	28.650	14.805	28.247
NBS19A_4	calcite	14.992	28.803	14.880	28.396	–0.112	14.912	28.650	14.802	28.247
	Average	**14.541**	**27.916**	**14.436**	**27.533**	**–0.102**	**14.923**	**28.650**	**14.813**	**28.247**
	± 1σ	**0.741**	**1.423**	**0.730**	**1.385**	**0.010**	**0.010**	**–**	**0.010**	**–**
	St. err	**0.247**	**0.474**	**0.243**	**0.462**	**0.003**	**0.003**	**–**	**0.003**	**–**
NBS19A_1	CO_2	19.188	36.955	19.006	36.288	–0.154	20.349	39.194	20.145	38.445
NBS19A_2	CO_2	19.749	38.030	19.556	37.325	–0.151	20.352	39.194	20.148	38.445
NBS19A_3	CO_2	19.709	37.964	19.517	37.261	–0.157	20.346	39.194	20.142	38.445
NBS19A_4	CO_2	19.817	38.175	19.624	37.464	–0.158	20.346	39.194	20.141	38.445
	Average	**19.616**	**37.781**	**19.426**	**37.085**	**–0.155**	**20.348**	**39.194**	**20.144**	**38.445**
	± 1σ	**0.289**	**0.558**	**0.283**	**0.538**	**0.003**	**0.003**	**–**	**0.003**	**–**
	St. err	**0.144**	**0.279**	**0.142**	**0.269**	**0.001**	**0.001**	**–**	**0.001**	**–**
		$\theta = 0.52241$, $^{17}\alpha = 1.00500$, $^{18}\alpha = 1.00960$					**$\theta_{corr} = 0.52276$, $^{17}\alpha_{corr} = 1.00535$, $^{18}\alpha_{corr} = 1.01025$**			
IAEA603_1	calcite	15.266	29.307	15.151	28.885	–0.101	14.830	28.47	14.722	28.072
IAEA603_2	calcite	14.213	27.263	14.113	26.898	–0.090	14.841	28.47	14.732	28.072
IAEA603_3	calcite	14.746	28.322	14.638	27.928	–0.108	14.823	28.47	14.714	28.072
IAEA603_4	calcite	14.674	28.179	14.567	27.789	–0.105	14.826	28.47	14.717	28.072
IAEA603_5	calcite	13.442	25.797	13.352	25.470	–0.096	14.835	28.47	14.726	28.072
IAEA603_6	calcite	14.497	27.832	14.393	27.452	–0.102	14.829	28.47	14.720	28.072
	Average	**14.473**	**27.783**	**14.369**	**27.404**	**–0.100**	**14.831**	**28.470**	**14.722**	**28.072**
	± 1σ	**0.612**	**1.182**	**0.604**	**1.150**	**0.007**	**0.007**	**–**	**0.007**	**–**
	St. err	**0.250**	**0.483**	**0.247**	**0.470**	**0.003**	**0.003**	**–**	**0.003**	**–**
IAEA603_1	CO_2	19.446	37.417	19.260	36.734	–0.136	20.273	39.012	20.071	38.270
IAEA603_2	CO_2	19.358	37.245	19.173	36.568	–0.135	20.275	39.012	20.072	38.270
IAEA603_3	CO_2	19.709	37.964	19.517	37.261	–0.157	20.252	39.012	20.050	38.270
IAEA603_4	CO_2	19.817	38.175	19.624	37.464	–0.158	20.251	39.012	20.049	38.270
IAEA603_5	CO_2	19.847	38.215	19.653	37.503	–0.149	20.260	39.012	20.058	38.270
	Average	**19.635**	**37.803**	**19.445**	**37.106**	**–0.147**	**20.262**	**39.012**	**20.060**	**38.270**
	± 1σ	**0.221**	**0.446**	**0.217**	**0.429**	**0.011**	**0.011**	**–**	**0.011**	**–**
	St. err	**0.099**	**0.199**	**0.097**	**0.192**	**0.005**	**0.005**	**–**	**0.005**	**–**
		$\theta = 0.52319$, $^{17}\alpha = 1.00509$, $^{18}\alpha = 1.00975$					**$\theta_{corr} = 0.52342$, $^{17}\alpha_{corr} = 1.00535$, $^{18}\alpha_{corr} = 1.01025$**			

[a] – corrected using Eq. (3)

[b] – IAEA accepted values

[c] – corrected using Eq. (4)

[d] – St. err = Stdev/√n, where n is number of analyses

value for $\delta^{18}O = -55.5$‰ (Gonfiantini, 1978), but with a $\Delta'^{17}O$ value slightly less than the recommended value of 0.00‰ (Schoenemann et al., 2013). It should be pointed out that the measured $\Delta'^{17}O$ value of SLAP2 by Schoenemann et al. (2013) is -0.005‰. The $\Delta'^{17}O$ value of 0‰ is an artificial one that is taken for convenience only. A clear trend exists where lower published $\delta^{18}O$ values correspond to lower $\Delta'^{17}O$ values (Fig. 2). In studies where VSMOW2 and SLAP2 are analyzed for triple oxygen isotope analyses, most $\delta^{18}O$ values are higher than the IAEA value of -55.5‰ (Table 2). Measurement of SLAP2 is notoriously difficult due to a persistent memory effect. Our memory effect was minimal after 4 iterations (Fig. 3). We suggest that other studies may not have completely erased the memory effect or suffer from an unidentified compression factor. Given that the lowest $\delta^{18}O$ values of SLAP are most likely to be the closest to reality, the corresponding $\Delta'^{17}O$ values should also be closest to the true value. Even small traces of meteoric/atmospheric water in the fluorination line will result in higher measured SLAP $\delta^{18}O$ and $\Delta'^{17}O$ values. Traces of NF_3 in the sample gas also increase the measured $\Delta'^{17}O$ values. In our procedure, we use a GC column to completely eliminate any traces of NF_3.The three lowest published $\delta^{18}O$ and $\Delta'^{17}O$ values are shown as the bolded samples in Table 2. The $\Delta'^{17}O$ values of these three studies average -0.011‰ ($\pm$ 0.003), corresponding to a $\delta^{17}O$ and $\delta^{18}O$ value of SLAP2 = -29.7093‰ and -55.5‰ relative to $\delta^{17}O$ and $\delta^{18}O$ value of VSMOW ≡ 0‰. We suggest that the average values of the three studies that gave the nearly-correct $\delta^{18}O$ values more accurately reflect the true $\Delta'^{17}O$ values of SLAP2. The effect of using a $\Delta'^{17}O$ value of -0.011‰ (or -0.015‰) for SLAP rather than 0.00‰ is negligible for all but extremely light or heavy $\delta^{18}O$ values. The difference between the two calibrations for a carbonate with a $\delta^{18}O$ value of 30‰ is only 0.006‰ so that either reference gives the same $\Delta'^{17}O$ values, within error, for most natural materials.

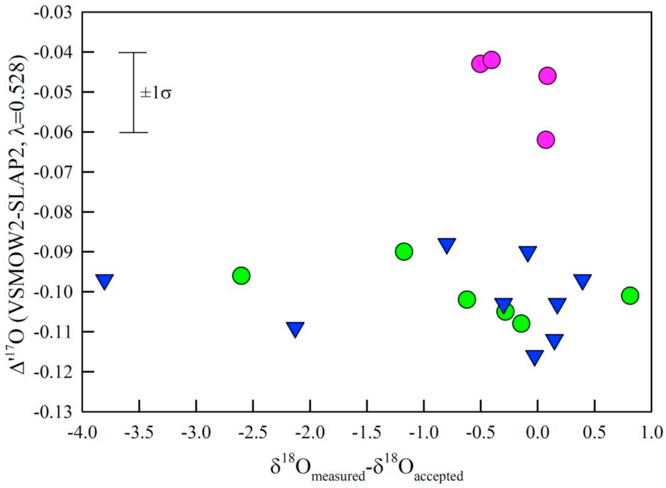

Fig. 4. $\Delta'^{17}O$ vs. the difference between the $\delta^{18}O_{measured}$ and the $\delta^{18}O_{accepted}$ value ($\delta^{18}O_{measured}$ - − $\delta^{18}O_{accepted}$). Regardless of the measured $\delta^{18}O$ value, the $\Delta'^{17}O$ values are within our reported error and do not correlate with $\delta^{18}O$ value. NBS18 (magenta), NBS19/NBS19A (blue) and IAEA603 (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
$\delta^{17}O$ and $\delta^{18}O$ values of IAEA carbonate standards. $\delta^{18}O$ values are accepted IAEA values. $\delta^{17}O$ values are calculated from the measured $\Delta'^{17}O$ values using Eqs. (3) and (4).

Sample	$\delta^{17}O$	$\delta^{18}O$	$\Delta'^{17}O$ (± 1σ) (λ = 0.528)
NBS 18*	3.636	6.99	-0.048 (± 0.009)
NBS 18**	3.747	7.20	-0.048 (± 0.009)
NBS19, 19a**	14.923	28.65	-0.102 (± 0.010)
IAEA603*	14.831	28.47	-0.100 (± 0.007)

* Value given by IAEA data sheet (https://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/13C18and7Li/NBS_18.htm)

** Value of IUPAC technical report (Brand et al., 2014; Coplen et al., 1983)

4.2. Calcite standards

Three methods have been used to quantitatively extract oxygen from carbonates (Sharma and Clayton, 1965). The first involves low temperature fluorination at 125 °C to produce CO_2 and O_2; the latter is then combusted to CO_2 and all CO_2 is recombined for the total $\delta^{18}O$ analysis. This procedure is not applicable for triple isotope analyses as the ultimate product, CO_2, is not easily measured for $^{17}O/^{16}O$ ratio (see however, Adnew et al., 2019). The second is complete fluorination in nickel bombs run at temperatures in excess of 700 °C. Sharma and Clayton (1965) found that the $\delta^{18}O$ value from this method were 0.5‰ lower than for the low-T fluorination method. They hypothesized that the lower $\delta^{18}O$ values are due to the presence of COF_2 that produced an ion beam at mass 47 (COF^+), which was collected along with mass 44 in the large cup of their double-collector mass spectrometer. The third method involves thermal decarbonation in a vacuum producing CO_2 followed by fluorination of the remaining oxide. The oxygen is reacted with carbon to form CO_2 and the two extracted CO_2 gases are combined for the total $\delta^{18}O$ value. Sharma and Clayton (1965) did not use this method for calcite, but interestingly obtained the same result using decarbonation-fluorination and total fluorination (methods 2 and 3) for most other divalent cation carbonates. All other studies (Das Sharma et al., 2002; Kim et al., 2007; Kim and O'Neil, 1997) used the third technique for $\delta^{18}O$ determinations of calcite.

We measured NBS18, NBS19 (and NBS19a), and IAEA603 carbonate standards using high temperature fluorination at 750 °C (Table 3). We tested for unreacted COF_2 (mass 66) by analyzing the reaction products left in the nickel tubes after O_2 removal using a Pfeiffer PrismPlus Quadrapole. There was a very small peak at mass 47 (COF^+), but almost undetectable COF_2 at mass 66 (see Supplementary material). Therefore, we consider that the reaction is extremely close to completion and we are measuring total O_2 content of the carbonates reacted at high temperatures.

Table 5
Triple oxygen isotope data for silicate standards. All samples are reported in ‰ relative to VSMOW2-SLAP2.

Sample	Weight (mg)	$\delta^{17}O$	$\delta^{18}O$	$\delta'^{17}O$	$\delta'^{18}O$	$\Delta'^{17}O$ (λ = 0.528)
UWG_1	2.7	2.909	5.645	2.904	5.629	−0.068
UWG_2	2.5	2.964	5.768	2.960	5.752	−0.077
UWG_3	2.5	2.961	5.769	2.956	5.752	−0.081
UWG_4	3.4	2.913	5.649	2.909	5.633	−0.066
UWG_5	2.1	2.912	5.651	2.908	5.635	−0.068
UWG_6	2.4	3.047	5.922	3.043	5.905	−0.075
UWG_7	2.2	2.948	5.728	2.943	5.712	−0.073
UWG_8	2.3	2.884	5.598	2.880	5.582	−0.067
UWG_9	2.1	2.851	5.534	2.847	5.519	−0.067
	Average	**2.932**	**5.696**	**2.928**	**5.680**	**−0.071**
	± 1σ	**0.057**	**0.115**	**0.056**	**0.114**	**0.005**
NBS28_1	1.4	4.951	9.518	4.939	9.473	−0.063
NBS28_2	1.0	4.947	9.500	4.935	9.455	−0.057
NBS28_3	1.5	4.923	9.450	4.910	9.405	−0.056
NBS28_4	1.5	4.976	9.555	4.964	9.510	−0.057
NBS28_5	1.3	4.961	9.537	4.948	9.491	−0.063
NBS28_6	1.3	5.071	9.735	5.058	9.688	−0.057
NBS28_7	1.2	5.079	9.743	5.066	9.696	−0.053
NBS28_8	1.2	5.046	9.702	5.033	9.656	−0.065
NBS28_9	1.2	4.990	9.576	4.978	9.530	−0.054
NBS28_10	1.2	5.050	9.706	5.037	9.659	−0.063
NBS28_11	1.5	4.934	9.474	4.922	9.430	−0.057
NBS28_12	1.4	4.944	9.494	4.932	9.449	−0.057
NBS28_13	1.3	4.951	9.516	4.939	9.471	−0.062
	Average	**4.986**	**9.577**	**4.974**	**9.532**	**−0.059**
	± 1σ	**0.055**	**0.106**	**0.055**	**0.105**	**0.004**
NM-SCO-1	2.2	2.746	5.336	2.742	5.321	−0.067
NM-SCO_2	2.3	2.749	5.338	2.746	5.324	−0.065
NM-SCO_3	2.1	2.660	5.148	2.657	5.134	−0.054
NM-SCO_4	2.0	2.805	5.424	2.801	5.410	−0.055
NM-SCO_5	1.6	2.742	5.326	2.738	5.312	−0.067
NM-SCO_6	1.7	2.806	5.428	2.802	5.413	−0.056
NM-SCO_7	2.4	2.721	5.264	2.717	5.250	−0.055
NM-SCO-8	1.8	2.765	5.373	2.761	5.359	−0.068
NM-SCO_9	1.8	2.688	5.209	2.684	5.196	−0.059
NM-SCO_10	1.4	2.738	5.298	2.734	5.284	−0.055
NM-SCO_11	1.7	2.763	5.357	2.759	5.343	−0.062
NM-SCO_12	2.2	2.668	5.165	2.665	5.152	−0.055
NM-SCO_13	2.1	2.667	5.155	2.664	5.142	−0.051
NM-SCO_14	2.3	2.652	5.136	2.648	5.123	−0.057
NM-SCO-15	1.9	2.730	5.279	2.726	5.265	−0.054
NM-SCO_16	2.2	2.652	5.125	2.649	5.112	−0.050
NM-SCO_17	2.1	2.714	5.259	2.710	5.246	−0.060
NM-SCO_18	2.2	2.687	5.213	2.684	5.199	−0.062
	Average	**2.720**	**5.268**	**2.716**	**5.255**	**−0.058**
	± 1σ	**0.048**	**0.096**	**0.048**	**0.095**	**0.005**
NM-Q_1	1.3	9.405	18.032	9.362	17.871	−0.075
NM-Q_2	1.4	9.350	17.945	9.306	17.786	−0.085
NM-Q_3	1.3	9.458	18.158	9.414	17.995	−0.087
NM-Q_4	1.4	9.521	18.260	9.476	18.096	−0.078
NM-Q_5	1.5	9.359	17.957	9.315	17.798	−0.082
	Average	**9.419**	**18.070**	**9.375**	**17.909**	**−0.081**
	± 1σ	**0.072**	**0.136**	**0.071**	**0.133**	**0.005**

The $\delta^{18}O$ values measured using the high temperature fluorination method in this study have a variability as high as 1‰ (1σ) and a standard error of 0.5‰, making the data unsuitable for accurate determinations of the $\delta^{18}O$ value (Table 3). However, $\delta^{18}O$ and $\delta^{17}O$ covary with a λ = 0.528, so that the $\Delta'^{17}O$ value is constant with a standard deviation of 0.01‰ or less. There is no trend for the $\Delta'^{17}O$

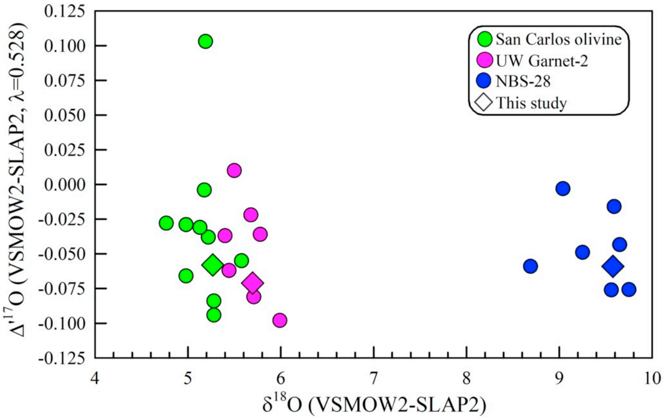

Fig. 5. Values of published (circles) and this study (diamonds) for the three silicate standards San Carlos olivine (green), UWG (magenta), and NBS-28 (blue). Data from Ahn et al. (2012), Franchi et al. (1999), Kusakabe and Matsuhisa (2008), Pack et al. (2016), Pack et al., 2017, Pack and Herwartz (2014), Sharp et al. (2016), Starkey et al., 2016, Tanaka and Nakamura (2013), and Young et al. (2014). Error bars are smaller than the symbols. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 6

Triple oxygen isotope data for individual air analyses. All samples are reported in ‰ relative to the VSMOW2-SLAP2 scale.

Sample	$\delta^{17}O$	$\delta^{18}O$	$\delta'^{17}O$	$\delta'^{18}O$	$\Delta'^{17}O$ ($\lambda = 0.528$)
Air_1	12.283	24.212	12.208	23.923	−0.424
Air_2	12.136	23.958	12.063	23.676	−0.437
Air_3	12.132	23.978	12.059	23.695	−0.452
Air_4	12.136	23.987	12.063	23.704	−0.453
Air_5	12.205	24.095	12.131	23.809	−0.440
Average	**12.178**	**24.046**	**12.105**	**23.761**	**−0.441**
± 1σ	**0.066**	**0.107**	**0.065**	**0.104**	**0.012**

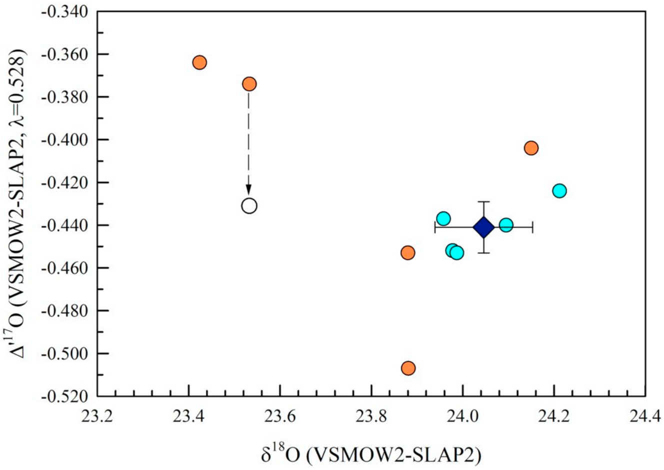

Fig. 6. $\Delta'^{17}O$ and $\delta^{18}O$ values of air from individual analyses of this study (light blue circles) and the average (dark blue diamond, with error bars) and previous work (orange circles). Data from Barkan and Luz (2005); Barkan and Luz (2011), Pack et al., 2017, Yeung et al. (2012), and Young et al. (2014). Note, Young et al. (2014) reported data relative to San Carlos olivine $\Delta'^{17}O$ value of 0.0‰. When corrected to the $\Delta'^{17}O$ value of San Carlos olivine reported in this paper, the data in Young et al. (2014) becomes a lower $\Delta'^{17}O$ value (arrow and open circle). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

value vs the $\delta^{18}O$ value, giving us high confidence on the accuracy of the $\Delta'^{17}O$ value (Fig. 4). The $\Delta'^{17}O$ values of the sedimentary carbonates are consistent with low temperatures of formation with seawater whereas the carbonatite (NBS-18) has a higher $\Delta'^{17}O$ typical of mantle origin (Sharp et al., 2018). Our $\Delta'^{17}O_{NBS\text{-}19} - \Delta'^{17}O_{NBS\text{-}18}$ value (the $\Delta\Delta'^{17}O_{NBS\text{-}19-NBS\text{-}18}$ value) is −0.054‰, in agreement with the expected differences for a low temperature calcite (NBS-19) and an igneous carbonatite (NBS-18). Other published values for this difference are −0.037 (Passey et al., 2014) and −0.019 (Barkan et al., 2019), both measured on CO_2 extracted from carbonate at 90 and 25 °C, respectively. The $\Delta\Delta'^{17}O_{NBS\text{-}19-NBS\text{-}18}$ value should be constant, regardless of extraction procedure.

We report the IAEA recommended $\delta^{18}O$ values and calculated $\delta^{17}O$ values from our data in Table 4. The corrected $\delta^{17}O$ are determined from the measured $\Delta'^{17}O$ values and the accepted $\delta^{18}O$ value using Eq. (4) ($\delta'^{17}O = \Delta'^{17}O_{(avg)} + 0.528 \times \delta'^{18}O_{IAEA\ value}$).

4.3. CO_2 from calcite

The $\delta^{17}O$ and $\delta^{18}O$ values of CO_2 extracted from calcite using phosphoric acid digestion at 25 °C are determined in a similar manner to calcite. The $\delta^{18}O$ value of the CO_2 extracted using phosphoric acid digestion was measured before fluorination. The $\Delta'^{17}O$ values determined from the measured $\delta^{17}O$ and $\delta^{18}O$ are constant for all analyses, so that we can use the calculated average $\Delta'^{17}O$ values to back-calculate the $\delta^{17}O$ value from the $\delta^{18}O$ value determined conventionally. These data are reported in Table 3. The calculated θ_{ACID} value for CO_2-calcite extracted by phosphoric acid digestion at 25 °C is 0.5230 ± 0.0003, where $\theta = \ln\alpha^{17}O_{CO2\text{-}calcite(ACID)} / \ln\alpha^{18}O_{CO2\text{-}calcite(ACID)}$, corresponding to an $^{18}\alpha_{CO2\text{-}calcite(ACID)}$ value of 1.01025 and an $^{17}\alpha_{CO2\text{-}calcite(ACID)}$ value of 1.0053 ± 3.55×10^{-6} (note that the error of the corrected $^{17}\alpha_{CO2\text{-}calcite(ACID)}$ is influenced by the error on $\Delta'^{17}O$ values).

Laboratories that make triple oxygen isotope measurements of carbonates commonly measure the CO_2 liberated via phosphoric acid digestion (Barkan et al., 2019; Barkan et al., 2015; Passey et al., 2014; Passey and Ji, 2019) using the methods described in the introduction. Laboratories can now use one of the reported carbonate standards and the measured θ_{ACID} value presented here to correct for the fractionation that occurs for $\delta^{17}O$ during phosphoric acid digestion.

4.4. Silicate standards

We analyzed 3 commonly used silicate standards (San Carlos Olivine, NBS 28, and UW-Gore Mountain Garnet-2), and our laboratory inhouse quartz standard (NM-Q, Table 5). We estimated yield based on measured weight of each sample and the pressure in the bellows of the mass spectrometer. Analyses with low yields were removed from the dataset. Lower yields generally corresponded to higher $\delta^{18}O$ and lower $\Delta'^{17}O$ values. The average $\delta^{18}O$ and $\Delta'^{17}O$ values of the silicate standards changed by < 0.05 and 0.002‰, respectively, after data removal.

Five previous publications calibrated silicate standards relative to a gas that was calibrated to VSMOW-SLAP using the same fluorination line (Ahn et al., 2012; Kusakabe and Matsuhisa, 2008; Pack et al., 2016; Sharp et al., 2016; Tanaka and Nakamura, 2013). Four other papers have published various silicate standard using either oxygen gas calibrated to reference gas that is calibrated to VSMOW2-SLAP2 (Pack and Herwartz, 2014), oxygen gas calibrated to a combination of UWG-2, NBS-28 and San Carlos Olivine (Starkey et al., 2016), oxygen gas calibrated in respect to San Carlos Olivine with an assumed $\Delta'^{17}O$ value of 0.0‰ (Young et al., 2014), or have run only SMOW to calibrate the reference gas (Franchi et al., 1999). The average $\delta^{18}O$ and $\Delta'^{17}O$ values of previous studies for San Carlos olivine are 5.19 ± 0.20 and –0.014 ± 0.056, respectively. It has been demonstrated that not all San Carlos olivine has the same $\delta^{18}O$ (Starkey et al., 2016) which may explain some of the spread. Removal of studies reporting $\delta^{18}O$ value of < 5.0‰, yields an average of 5.27 ± 0.129 and –0.010 ± 0.057 for $\delta^{18}O$ and $\Delta'^{17}O$ values, respectively. Our average $\delta^{18}O$ and $\Delta'^{17}O$ values are 5.268‰ ± 0.096 and –0.058‰ ± 0.005. We analyzed San Carlos Olivine over two analytical sessions separated by 2 months. The average $\Delta'^{17}O$ values between the two analytical sessions varied by 0.005‰. Our NBS-28 $\delta^{18}O$ value of 9.577‰ ± 0.105 and is indistinguishable from the IAEA reported value of 9.6‰. The $\Delta'^{17}O$ value is −0.059‰ ± 0004. Lastly, the UWG-2 garnet has a $\Delta'^{17}O$ value of −0.071 ± 0.005‰ and a $\delta^{18}O$ value of 5.696‰ ± 0.115, slightly lower but within error of the reported interlaboratory average of 5.78‰ (commonly rounded to 5.8‰) and the University of Wisconsin laboratory's average of 5.74‰ (Valley et al., 1995). Our and previously measured values are shown in Fig. 5.

We have made a clean size-fractioned mineral separate of a large aliquot of San Carlos olivine. No obvious heterogeneity in different aliquots has been found. We are making this standard available (NM-SCO) to other laboratories to ensure that all laboratory calibrations of San Carlos olivine are made on samples with the same isotopic composition. This will minimize the problem of sample-to-sample heterogeneity (Starkey et al., 2016) and allow laboratories that do not fluorinate waters to calibrate their silicate data to the VSMOW2-SLAP2 scale. Our average NM-Q values for $\delta^{18}O$ and $\Delta'^{17}O$ values are 18.070 (± 0.136) and –0.081 (± 0.005), respectively. Common silicate standards are all < 10‰. Using a silicate sample that is heavier than most samples analyzed will allow laboratories to now calibrate their mass spectrometer without the need to analyze water. We see this as an essential way to improve interlaboratory calibration. Interested parties should go to www.csi.unm.edu to request an aliquot of NM-SCO or NM-Q. The silicate standard, NBS-28, is available for purchase from the IAEA.

4.5. *Air*

Air O_2 is, in theory, an attractive standard for triple oxygen isotope analysis. It is homogeneous and is readily available. The difficulty with using air as a standard is that the O_2 must be purified of Ar (Barkan and Luz, 2003) which requires passing the air sample through a long, chilled GC column. We analyzed 5 samples of outside air near Northrop Hall, University of New Mexico using cryogenic GC purification. Average $\delta^{17}O$, $\delta^{18}O$, and $\Delta'^{17}O$ values are 12.178 ± 0.066, 24.046 ± 0.107, and –0.441 ± 0.012‰, respectively (Table 6). Ar/O_2 ratios averaged 0.0005, sufficiently low enough to not affect the $\Delta'^{17}O$ value (Barkan and Luz, 2003).

Our results agree well with the average of published values in laboratories where VSMOW2 and SLAP2 were also measured (Fig. 6). The data from Young et al. (2014) and Yeung et al. (2012) are significantly lighter in $\delta^{18}O$ and heavier in $\Delta'^{17}O$ than the other calibrations, but are calibrated only to their San Carlos olivine standard, likely explaining the discrepancy. When correcting the data from Young et al. (2014) to the San Carlos olivine reported in this study, the $\Delta'^{17}O$ value is −0.436‰, within error of our reported $\Delta'^{17}O$ value of air. Assuming that air is homogenous, then laboratories that are able to separate O_2 and Ar using a GC column are encouraged to use air as a high $\delta^{18}O$ value reference.

5. Conclusion

In this communication we present triple oxygen isotope data for standard carbonate, silicate and air samples all calibrated to VSMOW2 and SLAP2. All analyses were made on the same Thermo Finnigan 253 Plus mass spectrometer using the same inlet system and reference gas. Most of the samples are available from the IAEA website. An aliquot of our San Carlos olivine standard and quartz standard (NM-SCO and NM-Q) can be requested from csi.unm.edu. The calibration presented here will allow laboratories measuring carbonates for triple oxygen isotope ratios to be calibrated directly to waters and silicates. This internally consistent data set, tied to VSMOW2 and SLAP2, should lead to improved intercalibration for triple oxygen isotope analyses.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

All data used in this study are available in the research paper and Supplementary file.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2019.119432.

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