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Standardizing the reporting of ^{17}O data from high precision oxygen triple isotope ratio measurements of silicate rocks and minerals.

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1 Standardizing the reporting of $\Delta^{17}\text{O}$ data from high
2 precision oxygen triple-isotope ratio measurements of
3 silicate rocks and minerals

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ABSTRACT

Accurate and precise $\Delta^{17}\text{O}$ data are important for quantifying and understanding processes responsible for variations of oxygen triple-isotope ratios in nature. Without universally agreed numerical values of λ_{RL} and γ_{RL} in the definition $\Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - \lambda_{\text{RL}}\ln(1 + \delta^{18}\text{O}) - \gamma_{\text{RL}}$ however, as is currently the situation for measurements on rocks and minerals, reported $\Delta^{17}\text{O}$ data may not be directly comparable. Furthermore, the accuracy of $\Delta^{17}\text{O}$ measurements is linked to calibration (at the ppm level) of individual laboratory's 'working standard' O_2 relative to the VSMOW water reference or to the VSMOW-SLAP scale, whereas few laboratories have the facility to make high precision $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements on silicates and waters. Both points may be addressed by defining a reference line from measurements of a pair of silicates which differ substantially in oxygen isotopic composition (comparable to the difference between VSMOW and SLAP), rather than by assigning λ_{RL} and γ_{RL} values arbitrarily. The resulting reference line has no physical significance. However, because $\Delta^{17}\text{O}$ values reported relative to it are independent of the calibration of the working standard O_2 , this greatly facilitates $\Delta^{17}\text{O}$ reproducibility and comparability. We propose silicate standards for this purpose and report comparative measurements – from two institutions – of the respective $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values relative to VSMOW, together with $\Delta^{17}\text{O}$ data relative to various assigned reference lines. We also report $\Delta^{17}\text{O}$ measurements of UWG-2 garnet, San Carlos olivine and NBS 28 quartz relative to our reference line. The proposed standards are: (1) KRS (Khitostrov Rock Standard, $\delta^{18}\text{O} = -25.20 \text{ ‰}$), which consists of sintered, fine-grained constituents (primarily garnet) of a very low- $\delta^{18}\text{O}$ amphibolite-grade Palaeoproterozoic rock from Khitostrov, Karelia, Russia; (2) SKFS (Stevens Klint Flint Standard, $\delta^{18}\text{O} = 33.93 \text{ ‰}$), consisting of thermally dehydrated grains of a high- $\delta^{18}\text{O}$ nodule of flint sampled from just below the exposed Cretaceous–Palaeogene boundary at Stevens Klint, southeast Zealand Island, Denmark. Both silicates fluorinate readily, using standard laser-assisted procedures, and the associated low blanks allow for overnight pre-treatment. Small quantities of these materials may be supplied, on request, for standardizing $\Delta^{17}\text{O}$ measurements of silicate rocks and minerals according to the proposed procedure.

46	Key words:
47	Oxygen triple isotopes
48	Silicates
49	Khitostrov rock standard
50	Stevns Klint flint standard
51	$\Delta^{17}\text{O}$ standardization
52	

1. Introduction

The occurrence of small but distinctive variations between the relative abundances of ^{17}O and ^{18}O in terrestrial rocks and minerals has been demonstrated from high precision measurements of the $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios (for example, Rumble et al, 2007; Tanaka and Nakamura, 2013; Pack and Herwartz, 2014; Levin et al., 2014; Starkey et al., 2016). Many processes during the formation history of individual samples may have contributed to their present isotopic composition. Chemical and isotopic characteristics of the interacting solids, melts and aqueous fluids are probably influential, together with the temperature under which isotopic exchange took place (Matsuhisa et al., 1978; Cao and Liu, 2011; Dauphas and Schauble, 2016).

For most process that modify oxygen isotope distributions in nature, $^{17}\text{O}/^{16}\text{O}$ changes by approximately half the corresponding change in $^{18}\text{O}/^{16}\text{O}$. This is because the mass difference between ^{17}O and ^{16}O (1.0042 Da) is approximately half as large as the mass difference between ^{18}O and ^{16}O (2.0042 Da). Isotope ratio modifications that follow this pattern of proportionality are usually referred to as ‘mass-dependent’ fractionations. Measurements of oxygen triple-isotope ratios are, by convention, reported as $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values, where:

$$\delta^{17}\text{O} = \frac{{}^{17}\text{R}_{\text{sample}} - {}^{17}\text{R}_{\text{reference}}}{{}^{17}\text{R}_{\text{reference}}} \quad \text{and} \quad \delta^{18}\text{O} = \frac{{}^{18}\text{R}_{\text{sample}} - {}^{18}\text{R}_{\text{reference}}}{{}^{18}\text{R}_{\text{reference}}} \quad (1)$$

${}^{17}\text{R}_{\text{sample}}$ and ${}^{18}\text{R}_{\text{sample}}$ are the respective abundances of the minor isotopes ^{17}O and ^{18}O relative to the ^{16}O abundance in the sample; ${}^{17}\text{R}_{\text{reference}}$ and ${}^{18}\text{R}_{\text{reference}}$ are the relative abundances in an international reference material, usually Vienna Standard Mean Ocean Water, VSMOW. Note that δ is a dimensionless quantity. Because it is of small magnitude ($\ll 1$) in natural systems, it is usually reported as parts per thousand (‘per mil’, ‰).

For two chemical entities or phases A and B, the equilibrium fractionation factors for oxygen isotope exchange, defined by:

$$\alpha_{\text{A-B}}^{17/16} = \frac{{}^{17}\text{R}_{\text{A}}}{{}^{17}\text{R}_{\text{B}}} = \frac{1 + \delta^{17}\text{O}_{\text{A}}}{1 + \delta^{17}\text{O}_{\text{B}}} \quad \text{and} \quad \alpha_{\text{A-B}}^{18/16} = \frac{{}^{18}\text{R}_{\text{A}}}{{}^{18}\text{R}_{\text{B}}} = \frac{1 + \delta^{18}\text{O}_{\text{A}}}{1 + \delta^{18}\text{O}_{\text{B}}} \quad (2)$$

are related by:

$$\alpha_{A-B}^{17/16} = \left(\alpha_{A-B}^{18/16} \right)^{\theta} \quad (3)$$

Few experimental measurements of θ for the SiO_2 –water system have been made. Sharp et al. (2016) reported that, at low temperatures (~ 0 to 50°C), $\theta \sim 0.523$ – 0.524 . The high temperature limit value of θ for all oxygen isotope exchange processes under equilibrium conditions is 0.5305 (Matsuhisa et al., 1978; Dauphas and Schauble, 2016, and references therein). For various kinetic fractionation mechanisms, a comparable formalism (Young et al., 2002; Dauphas and Schauble, 2016) indicates that θ varies between 0.501 and 0.516 , depending on molecular mass.

The distribution of the three stable isotopes of oxygen in individual silicate samples also conforms to a power law relationship:

$$\frac{{}^{17}\text{R}_{\text{sample}}}{{}^{17}\text{R}_{\text{reference}}} = (1 + \gamma) \left(\frac{{}^{18}\text{R}_{\text{sample}}}{{}^{18}\text{R}_{\text{reference}}} \right)^{\lambda} \quad (4)$$

where the $(1 + \gamma)$ term quantifies any deviation of $\frac{{}^{17}\text{R}_{\text{sample}}}{{}^{17}\text{R}_{\text{reference}}}$ from unity when ${}^{18}\text{R}_{\text{sample}} = {}^{18}\text{R}_{\text{reference}}$. Whereas θ refers to a specific process, λ is a more general and empirical term, the magnitude of which is determined by the cumulative effects of individual (unspecified) fractionation processes associated with the history of the sample. Converting Eqn. (4) to linear format, and expressing the result in terms of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values rather than absolute ratios, gives:

$$\ln(1 + \delta^{17}\text{O}) = \lambda \ln(1 + \delta^{18}\text{O}) + \ln(1 + \gamma) \quad (5)$$

It is useful to include a scaling factor of 10^3 so that the logarithmic terms involving $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ are then of similar magnitude to the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values reported as ‰. The quantities $10^3 \ln(1 + \delta^{17}\text{O})$ and $10^3 \ln(1 + \delta^{18}\text{O})$ are often denoted as $\delta'^{17}\text{O}$ and $\delta'^{18}\text{O}$ respectively, following similar terminology introduced by Hulston and Thode (1965) in the context of sulphur multiple isotope ratios. For a collection of samples characterized by a range of δ values, linear least squares regression of the $10^3 \ln(1 + \delta^{17}\text{O})$ versus $10^3 \ln(1 + \delta^{18}\text{O})$ data gives an array of slope representing the mean λ value for that particular group of samples; there is not necessarily an implied relationship

between the individual silicates. Despite this, such arrays have frequently been designated as a ‘terrestrial fraction line’ in the literature. Empirical data (discussed in Section 2.1) have shown that, for individual collections of silicate rocks and minerals, λ generally ranges from ~ 0.524 to 0.529 . Measurements have shown that the fractionation arrays are slightly offset from VSMOW (Tanaka and Nakamura, 2013; Miller et al., 2015), with the magnitude of the offset, as quantified by $10^3 \ln(1 + \gamma)$, being of the order of -0.03 to -0.07 , depending on the samples (Miller et al., 2015). Thus, $\ln(1 + \gamma)$ may be substituted by γ in Eqn. (5) without loss of accuracy.

To quantify small deviations from an assigned reference line of slope λ_{RL} and ordinate axis offset $10^3 \gamma_{\text{RL}}$ from the zero point of the δ scale (usually VSMOW), the parameter $\Delta'^{17}\text{O}$ may be defined from Eqn. (5) as:

$$\Delta'^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - \lambda_{\text{RL}} \ln(1 + \delta^{18}\text{O}) - \gamma_{\text{RL}} \quad (6)$$

This definition (from Miller, 2002) has been widely adopted, with or without the inclusion of the γ_{RL} term. The subscript ‘RL’ refers to ‘reference line’. We note that $\Delta'^{17}\text{O}$ is sometimes referred to as ^{17}O -excess, especially for waters, snow and ice cores. To avoid the implication that $\Delta'^{17}\text{O} \geq 0$ in all cases, and to avoid the incongruity of referring to a ‘negative excess’, that terminology is not used here. Similarly, we avoid the term ‘ ^{17}O anomaly’, which is sometimes used in the context of non-mass-dependent isotope distributions (e.g., Dauphas & Schauble, 2016). Inclusion of the ‘prime’ symbol in $\Delta'^{17}\text{O}$ notation has been widely adopted, to avoid confusion with the original definition of $\Delta^{17}\text{O}$ which was based on the approximation of direct proportionality between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Clayton and Mayeda, 1988). We use the $\Delta'^{17}\text{O}$ notation for this paper, whilst acknowledging that this is not universally accepted practice.

The magnitude of $\Delta'^{17}\text{O}$ is not necessarily of physical significance, as a proportion may be attributed simply to the divergence (or convergence) of the reference line from that which is characteristic of the collection of samples under investigation (Miller et al., 2015). Whereas a scaling factor of 10^3 or 10^6 may usefully be applied to $\Delta'^{17}\text{O}$ data, to give numerical values that are not $\ll 1$,

the reporting of $\Delta^{17}\text{O}$ data as ‘per mil’ or ‘ppm’ (as has been widely adopted) is technically correct only if $\Delta^{17}\text{O}$ is expressed in ratio format, similar to that as used for defining the δ value:

$$\Delta^{17}\text{O} = \frac{1 + \delta^{17}\text{O}}{(1 + \gamma_{\text{RL}})(1 + \delta^{18}\text{O})^{\lambda_{\text{RL}}}} - 1 \quad (7)$$

Oxygen triple-isotope ratio measurements by mass spectrometry are conducted using O_2 as the analyte gas, with $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ determined relative to a ‘working standard’ O_2 which should be calibrated relative to a reference material with accurately known (or defined) $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values relative to VSMOW. Currently, only IAEA water samples (not any silicate standards) are certified for $\delta^{17}\text{O}$ value. Calibration of the working standard is difficult to achieve, to the degree of accuracy required for many investigations. Furthermore, few laboratories have the facility to prepare O_2 from both waters and silicates. As an alternative to direct calibration against VSMOW, the working standard may be calibrated against an intermediate such as air O_2 (for example, Pack & Herwartz, 2014; Miller et al., 2015; Greenwood et al., 2018), although a complication is that different values for the triple isotopic composition of air O_2 relative to VSMOW have been reported. An appraisal of recent measurements is given by Pack et al. (2017).

2. Rationale and methodology

2.1. Uncertainties in the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of silicate reference materials

Considerable variations exist between published $\delta^{18}\text{O}_{\text{VSMOW}}$ values (i.e. $\delta^{18}\text{O}$ values reported relative to VSMOW) of individual silicates commonly used as standards in oxygen triple isotope studies. Similarly, there are discrepancies for the corresponding $\delta^{17}\text{O}$ values. Compilations of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values reported for UWG-2 garnet, San Carlos olivine and NBS 28 quartz have been provided in several publications; recent examples are Supplementary Table S2 of Kim et al. (2019) and Table 2 of Bao et al. (2016). In the latter publication, the authors observed that the $\delta^{18}\text{O}_{\text{VSMOW}}$ variations from recent studies were greater than the associated analytical errors. Specifically, the range reported was 1.06 ‰ for NBS 28, 0.59 ‰ for UWG-2 and 0.3 ‰ for San Carlos olivine,

respectively. Even after attempting to normalise the data to VSMOW or VSMOW-SLAP, thereby reducing the discrepancies, Bao et al. (2016) found that the revised values were still not within analytical errors, especially in the case of San Carlos olivine. If silicate oxygen is quantitatively and completely extracted, using established procedures of laser heating in the presence of an excess of BrF_5 vapour or F_2 , variations in the isotopic composition of the resulting O_2 should be minimal. However, Kim et al. (2019) showed that automating the laser heating step and using a high density beam in conjunction with a short irradiation time usually led to significantly improved precision of the isotopic data, compared to their results obtained when the laser was operated manually. The authors postulated that partial vapourization of SiO_2 occurs to greater extent when samples are irradiated at low power density, resulting in isotopic fractionation. Any loss of partially-reacted material by sample grain sputtering during the heating process would also be expected to adversely affect the isotopic measurements.

We provide in Figure 1 a ‘Caltech plot’ comparison of reported $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values (including associated errors) for UWG-2, San Carlos olivine and NBS 28 from several recent publications. In some of those reports, the silicate $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data have been normalized, but not necessarily to a common procedure. Pack et al. (2016) reported their data on the VSMOW-SLAP scale using the normalization recommended by Schoenemann et al. (2013). Kusakabe & Matsuhisa (2008) and Ahn et al. (2012) also calibrated their $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data relative to VSMOW-SLAP, but using the procedure adopted by Kusakabe and Matsuhisa (2008). In other reports, no direct calibration to VSMOW or the VSMOW-SLAP scale was performed. Pack and Herwartz (2014), Starkey et al. (2016) and Greenwood et al. (2018) related their $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data to VSMOW indirectly, by third party calibration of the working standard O_2 against atmospheric oxygen. In other examples, $\delta^{18}\text{O}_{\text{VSMOW}}$ values were calibrated on the basis of an assigned value for UWG-2 garnet (Levin et al., 2014; Kim et al., 2019) or San Carlos olivine (Young et al., 2016), with the corresponding $\delta^{17}\text{O}_{\text{VSMOW}}$ value of UWG-2 or San Carlos olivine being derived by assuming a specified fractionation relationship between the three oxygen isotopes. Ali et al. (2016) similarly calibrated the $\delta^{18}\text{O}_{\text{VSMOW}}$

value of their working standard O₂ on the basis of UWG-2 measurements, but calibrated the corresponding $\delta^{17}\text{O}_{\text{VSMOW}}$ value using that of UWG-2 as reported by Pack and Herwartz (2014). Whereas the analyte O₂ was isolated from other fluorination products by cryogenic separation and selective desorption from molecular sieve pellets in most of the investigations referred to in Figure 1, Pack and Herwartz (2014) and Pack et al. (2016) additionally utilized gas chromatography for a final purification step.

Although the originally recommended $\delta^{18}\text{O}_{\text{VSMOW}}$ value of UWG-2 garnet (Valley et al., 1995) is 5.8 ‰, some reports have since proposed a slightly lower number. For example, Macpherson et al. (2005) published a value of 5.71 ± 0.09 ‰ (1σ), calibrated to NBS 30 biotite $\delta^{18}\text{O} = 5.10$ ‰. For the present work we assigned a value of 5.75 ‰, based on previous findings at Georg-August-Universität Göttingen and at the University of Oregon.

A complication with San Carlos olivine is that different populations have been distinguished, on the basis of distinct $\delta^{18}\text{O}$ values. Macpherson et al. (2005) reported that ‘Type I’ is characterized by a value of 4.84 ± 0.09 ‰, whereas the (more commonly used) ‘Type II’ is 5.22 ± 0.08 ‰. Thirlwall et al. (2006) reported a $\delta^{18}\text{O}$ value of 4.88 ‰ for Type I. It is probable that other variations of San Carlos olivine also exist.

2.2. $\Delta^{17}\text{O}$ measurements of silicate rocks and minerals

High precision measurements of oxygen triple-isotope ratios of silicate rocks and minerals at various laboratories have resulted in a variety of ‘terrestrial fractionation lines’ being reported (Miller, 2002; Rumble et al., 2007; Pack et al., 2007; Spicuzza et al., 2007; Kusakabe and Matsuhisa, 2008; Hofmann and Pack, 2010; Hofmann et al., 2012; Ahn et al., 2012; Tanaka and Nakamura, 2013; Pack et al., 2013; Levin et al., 2014; Bindeman et al., 2014; Kim et al., 2019). Pack et al. (2013) suggested that, based on their measurements of 1071 samples, the associated λ value of 0.5251 ± 0.0014 (2σ) probably represents the mean isotopic fractionation between melts, minerals and fluids at various temperatures and pressures.

Hallis et al. (2010), in the context of assigning a reference line for $\Delta^{17}\text{O}$ measurements of lunar basalts, noted that the two silicate arrays compared by Rumble et al. (2007) were characterized by different offsets from VSMOW. Subsequently, Tanaka and Nakamura (2013) demonstrated that an array formed from a collection of (15) silicates, and characterized by a slope of 0.5270 ± 0.0005 (95% confidence interval), was offset from VSMOW by $10^3\gamma = -0.070 \pm 0.005$ whereas, using the same oxygen purification system and mass spectrometer, a set of four water samples including VSMOW, GISP and SLAP gave an array characterized by $\lambda = 0.5285 \pm 0.0005$ and $10^3\gamma = 0.03 \pm 0.02$. It is important to recognize, however, that an array formed from least squares regression of $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ data from a group of silicate rocks and minerals will be characterized by values of both slope and ordinate axis offset that are specific to that particular collection of samples.

The magnitude of λ is unaffected by the reference to which $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values are reported (Miller, 2002); it is therefore invariant to the calibration of the laboratory working standard O_2 to any specific reference material such as VSMOW. Clearly, however, this is not the case for γ . Furthermore, if $\Delta^{17}\text{O}$ data are reported relative any other reference line, such as $\lambda_{\text{RL}} = 0.5305$, $\gamma_{\text{RL}} = 0$ (e.g. Wiechert et al., 2004; Herwartz et al., 2014; Pack and Herwartz, 2014), then the accuracy of the resulting $\Delta^{17}\text{O}$ values is still inextricably linked to the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ calibrations of the laboratory working standard O_2 relative to VSMOW.

Hofmann et al. (2017) listed various different reference lines that have been used for reporting $\Delta^{17}\text{O}$ measurements in a variety of applications. It was noted that, although there is not consensus on a single selection, the choice is somewhat arbitrary because $\Delta^{17}\text{O}$ is not a measured quantity; it is inferred from $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data. This point was also made by Kaiser (2008) and by Pack and Herwartz (2014). Kaiser (2011) suggested that, regardless of the definition of $\Delta^{17}\text{O}$, all $\Delta^{17}\text{O}$ data are ‘merely mathematical constructs’, in contrast to the relative $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratio differences, reported as $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. We suggest, however, that $\Delta^{17}\text{O}$ is potentially a more robust parameter (in principle, at least), that may be determined to higher accuracy and precision than the associated $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. Furthermore, the latter are also ‘mathematical constructs’ in that

they relate $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios to those in an artificial seawater proxy (VSMOW). If consensus can be obtained on the selection of appropriate silicate rock or mineral samples for defining an empirical, two-point reference line, then silicate or oxide $\Delta^{17}\text{O}$ data relative to that line would be independent of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ calibration of individual laboratory's working standard O_2 to VSMOW or to any other reference material. This confers a significant advantage over existing methodology.

Because the fluorination of silicate rocks and minerals, to produce O_2 as the analyte for isotope ratio measurements, requires a different procedure from that used for the fluorination of waters, there is the possibility of systematic errors being introduced by the use of a water reference material for reporting $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data of rocks and minerals. This point was made by Young et al. (2016), who also noted that, as fractionation arrays from silicate rocks and minerals are now known to be offset from VSMOW on the $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ plot, this introduces an additional complication. To eliminate such potential sources of error, Young et al. (2016) chose to report their whole-rock and mineral $\Delta^{17}\text{O}$ results relative to a reference line derived from $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data reported relative to San Carlos olivine (as representative of Earth's mantle), with an assigned λ value of 0.528. A comparable approach was adopted by Cao et al. (2019), in their investigation of ocean island basalts. Sharp et al. (2016) noted that, unfortunately, oxygen triple-isotope ratio measurements of rocks are only peripherally linked to the VSMOW-SLAP scale, because very few laboratories routinely measure the oxygen triple-isotope compositions of both waters and silicates. Silicate oxygen triple-isotope data reported by Sharp et al. (2016) were normalized to a $\delta^{18}\text{O}$ value for San Carlos olivine of 5.3 ‰ relative to VSMOW and corresponding $\Delta^{17}\text{O}$ value of -0.054 ‰, relative to $\lambda_{\text{RL}} = 0.528$, $\gamma_{\text{RL}} = 0$. This $\Delta^{17}\text{O}$ value is more negative by 0.016 ‰ than that reported by Pack et al. (2016) for San Carlos olivine relative to the same reference line.

2.3. $\Delta^{17}\text{O}$ of meteoric waters, snow and ice cores – comparison with silicates

Because the oxygen isotopic composition of rocks and minerals is reported relative to VSMOW, with $\Delta^{17}\text{O}$ sometimes reported relative to the VSMOW-SLAP scale (with $\Delta^{17}\text{O}$ of SLAP defined to be zero, as recommended by Schoenemann et al., 2013), it is relevant to consider such measurements of waters. Meijer and Li (1998) first reported that natural waters from a wide range of sources, spanning nearly 60 ‰ in $\delta^{18}\text{O}$, formed a linear array in $\ln(1 + \delta^{17}\text{O})$ versus $(1 + \delta^{18}\text{O})$ space and that the associated λ value was 0.5281 ± 0.0015 (standard error). Subsequently, Angert et al. (2004) suggested, from theoretical considerations, that the array should be slightly offset (positive) from VSMOW, with deviations being attributed primarily to kinetic fractionation during the diffusive transport of water vapour from the evaporative source region into undersaturated air. That prediction was later confirmed (Barkan and Luz, 2007; Landais et al., 2008; Luz and Barkan, 2010). Barkan and Luz (2007) defined the ‘ ^{17}O -excess’ ($\Delta^{17}\text{O}$) of meteoric precipitation as:

$$\Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - 0.528 \ln(1 + \delta^{18}\text{O}) \quad (8)$$

This convention, and the associated terminology, has since been widely adopted in studies of oxygen triple-isotope ratios in meteoric precipitation and in ice cores.

Inter-laboratory reproducibility of $\Delta^{17}\text{O}$ data from waters, at the ppm level, is challenging. Small differences in the operational details of the water fluorination technique or the isotope ratio measurements may result in significant inter-laboratory offsets. This is especially true for samples from the polar regions, characterized by substantial depletion of ^{17}O and ^{18}O . For example, Winkler et al. (2012) reported a 22 ppm difference between $\Delta^{17}\text{O}$ measurements of a surface snow sample from Dome F in Antarctica, as given by two different laboratories. The magnitude of the discrepancy diminished with increasing $\delta^{18}\text{O}$. Similar findings were reported by Landais et al. (2012). This observation is consistent with instrument non-linearity (isotope scale compression) for $\delta^{17}\text{O}$ differing from that for $\delta^{18}\text{O}$. A solution to this problem was proposed by Schoenemann et al. (2013), who

introduced a VSMOW-SLAP normalization procedure for $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$. Their recommendation has since been widely adopted and is considered further in Section 2.3.

2.4. Normalizing $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of waters and rocks to the VSMOW-SLAP scale

A convention for optimizing inter-laboratory consistency of $\delta^{18}\text{O}$ measurements has long been established (Gonfiantini, 1978) and involves normalizing such measurements to the VSMOW-SLAP scale, with $\delta^{18}\text{O}$ of SLAP assigned as -55.5‰ (exactly) relative to VSMOW. By convention, the normalization requires that $\delta^{18}\text{O}$ data relative to VSMOW be adjusted by a factor of $(-55.5)/(\delta^{18}\text{O}_{\text{SLAP/VSMOW}})$, where $\delta^{18}\text{O}_{\text{SLAP/VSMOW}}$ is the measured value of SLAP relative to VSMOW.

Because the δ scale is non-linear, with $-1 < \delta < \infty$, ‘true’ linear scaling to VSMOW-SLAP requires that $\ln(1 + \delta^{18}\text{O})$ values be adjusted, rather than the corresponding $\delta^{18}\text{O}$ data. The associated factor is thus $\ln(1 - 0.0555)/\ln(1 + \delta^{18}\text{O}_{\text{SLAP/VSMOW}}^{\text{sample}})$. Fortunately, as noted by Kaiser (2008), the numerical differences between the conventional and logarithmic normalizations are generally small. An additional complication noted by Kaiser (2008) is that the assigned $\delta^{18}\text{O}$ value of SLAP relative to VSMOW may be significantly in error. Kaiser (2008) suggested that, on the basis of measurement comparisons reported in 2004, the ‘true’ value seems to be $-56.18 \pm 0.01\text{‰}$.

Kusakabe and Matsuhisa (2008) is the only publication we are aware of in which scaling of $\ln(1 + \delta^{18}\text{O})$ data to VSMOW-SLAP was implemented with the same factor $(-57.10)/(-56.20)$ being applied to scaling of the corresponding $\ln(1 + \delta^{17}\text{O})$ data. Kaiser (2008) recommended a similar normalization approach, but in power law format and with λ assigned to be 0.528:

$$\delta^{17}\text{O}_{\text{VSMOW-SLAP normalized}}^{\text{sample}} = \delta^{17}\text{O}_{\text{VSMOW}}^{\text{sample}} \frac{(1 + \delta^{18}\text{O}_{\text{SLAP/VSMOW, assigned}})^{0.528} - 1}{(1 + \delta^{18}\text{O}_{\text{SLAP/VSMOW, measured}})^{0.528} - 1} \quad (9)$$

These scaling procedures preserve the oxygen triple-isotope ratio relationship of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements, whilst ensuring that the measured $\delta^{18}\text{O}$ values are normalized to the VSMOW-SLAP scale.

To improve the inter-laboratory consistency of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data from oxygen triple-isotope ratio measurements of water samples, Schoenemann et al. (2013) proposed that $\delta^{17}\text{O}$ measurements be normalized to the VSMOW-SLAP scale in similar fashion as the $\delta^{18}\text{O}$ data, with $\delta^{17}\text{O}$ of SLAP defined to give $\Delta^{17}\text{O}$ of exactly zero, relative to a reference line of $\lambda_{\text{RL}} = 0.528$ and $\gamma_{\text{RL}} = 0$. The resulting scale factor for the $\delta^{17}\text{O}$ measurements is therefore $(-29.6986)/\delta^{17}\text{O}_{\text{SLAP/VSMOW}}$, approximately¹. Unlike the Kusakabe and Matsuhisa (2008) or Kaiser (2008) normalizing procedures, the Schoenemann et al. (2013) recommendation involves scaling of the empirical $\delta^{17}\text{O}$ results independently of the corresponding $\delta^{18}\text{O}$ data. Essentially, this adjusts the experimental data so that linear least squares regression of $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ of VSMOW and SLAP gives the assigned λ_{RL} and γ_{RL} values.

2.5 A two-point silicate reference line for $\Delta^{17}\text{O}$ measurements of rocks and minerals

Pack et al. (2016) advocated that VSMOW-SLAP scaling should be applied to oxygen triple-isotope measurements of silicate rocks and minerals, using the recommendation of Schoenemann et al. (2013) originally devised for standardizing $\Delta^{17}\text{O}$ data obtained from waters. Whereas the advantage of that approach for silicates has been demonstrated, it does require that any laboratory undertaking high precision $\Delta^{17}\text{O}$ measurements of rocks and minerals must also have the capability of making similar measurements on waters. There is also the implicit assumption that the water and silicate fluorination procedures – although different – will essentially be characterized by the same (low) processing errors. A simpler alternative, which obviates the requirement to make measurements on waters, is to report rock and mineral $\Delta^{17}\text{O}$ measurements relative to an empirical reference line constructed from two silicates, differing in $\delta^{18}\text{O}$ by a magnitude similar to (or greater than) that between VSMOW and SLAP. The selected materials must be reasonably homogeneous in oxygen isotopic composition and have desirable fluorination characteristics – such as not being prone to

¹ In the abstract of Schoenemann et al. (2013), the normalized $\delta^{17}\text{O}$ value of SLAP is reported as being approximately -29.6968 ‰, instead of approximately -29.6986 ‰ as stated in the text of the paper.

sputtering during laser-assisted reaction with BrF_5 ; also contribute a negligibly low oxygen ‘blank’ during pre-fluorination procedures. Furthermore, they need to be available in sufficient quantities to allow distribution to other laboratories, on request.

This approach is advantageous to that of using a single silicate reference material of assigned $\delta^{18}\text{O}_{\text{VSMOW}}$ value for normalizing $\delta^{18}\text{O}$ data to. A two-point scale enables any instrument-related compression (or expansion) of the $\delta^{18}\text{O}$ scale to be identified and quantified; also whether identical behaviour applies to the $\delta^{17}\text{O}$ scale. A difference between the respective linearities will cause the slope of the two-point reference line to vary from the ‘true’ value, although $\Delta^{17}\text{O}$ values of silicates reported relative to that reference line will be independent of any non-linearity of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ scales. The respective $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of the two silicate standards may be anchored to the VSMOW-SLAP scale using the procedure adopted by Pack et al. (2016), with inter-laboratory comparison forming the basis of consensus values.

3. High- and low- $\delta^{18}\text{O}$ silicate standards for defining a $\Delta^{17}\text{O}$ reference line

Reported $\delta^{18}\text{O}$ values of terrestrial silicate rocks and minerals vary from -27.3‰ (Bindeman et al., 2010; Bindeman et al., 2014), in the most extreme example of interaction with ‘Snowball Earth’-derived synglacial meteoric waters at depth, to as high as $\sim 43\text{‰}$ in some sedimentary quartz samples precipitated from synglacial seawater at low temperature (Sharp et al., 2018). For a high- $\delta^{18}\text{O}$ silicate standard, we selected a flint from one of several nodules collected (by RCG) near the exposed Cretaceous–Palaeogene boundary at Stevns Klint, southeast Zealand Island, Denmark. A quantity of this nodule (designated K-1B) was crushed and sieved to 0.25–0.5 mm grain size, then heated in air to remove aqueous micro inclusions. Initial tests at 600°C and then 800°C , followed by washing in 0.1M HCl at 60°C , showed that a higher temperature was needed to ensure that the flint grains were free of aqueous content. Initially, the flint contained 0.83 wt % water, as determined by high temperature conversion elemental analyzer (TC/EA) at the University of Oregon. Besides ensuring that quartz is the only oxygen-bearing phase in the flint, complete removal of aqueous fluid inclusions also

minimizes the potential for grains to move energetically during the laser-assisted fluorination process. Subsequent heating to 1000°C for an hour, followed by washing in boiling deionized water to remove any released salts, then drying at 100°C, resulted in the flint being virtually anhydrous (< 0.1 wt %). Approximately 50 g was prepared in total, at the Open University. We designate this proposed standard as the Stevns Klint Flint Standard, SKFS.

The 1.85 Ga Belomorian Belt at Khitostrov, Karelia (Russia) hosts rocks characterized by exceptionally low $\delta^{18}\text{O}$ values, down to -27.3 ‰ relative to VSMOW (Bindeman et al., 2010; Bindeman et al., 2014; Herwartz et al., 2015). Approximately 50 g of sample K1-3 from Bindeman et al. (2010) was selected (by INB) as a potential low- $\delta^{18}\text{O}$ silicate standard, after metamict zircon, plagioclase and biotite had been removed. The residual material consisted primarily of garnet (~90%) together with rutile, amphibole, ilmenite and corundum. These minerals are lower in $\delta^{18}\text{O}$ than the original bulk rock and are resistant to secondary alteration. After crushing to a fine powder, 15 g was fused to a sintered block by heating at 1100°C in a (Pt + 5% Au) alloy crucible, placed in the centre of a horizontally-aligned alumina tube (50 mm internal diameter, 1 m length). The heating was conducted in a constant flow ($100\text{ cm}^3\text{ min}^{-1}$) of nitrogen (Technical grade, Air Products, Code 14626) to exclude atmospheric oxygen. Silica wool plugs, 200 mm long, were positioned at each end of the heated zone, to minimize the thermal gradient and to avoid back-diffusion of air. The temperature was ramped up from ambient at a rate of 100°C per hour, held for 2 hours at 1100°C, then ramped down to ambient at the same rate. Oxygen isotopic exchange between the constituent minerals would have occurred during this procedure. Measurements of the resulting sintered material (discussed below) indicated that it is essentially homogeneous in $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$. The sintered block was subjected to crushing and sieving to 0.25-0.5 mm grain size. We designate the resulting material the Khitostrov Rock Standard, KRS. All the remaining unfused material was subsequently divided equally into two (Pt + 5% Au) alloy crucibles which were heated together in the same tube furnace, using the procedure as described. The fused and sintered content of one of these two crucibles (designated as 'Batch C') was found to be of indistinguishable isotopic composition from that of KRS, whereas the

other (designated 'Batch B') was slightly different, although characterized by the same $\Delta^{17}\text{O}$ result. We do not know the reason for the small discrepancy in isotopic composition.

Whereas heating powdered K1-3 to melting was considered initially, with the objective of obtaining a homogeneous glass on cooling, technical considerations associated with the very high temperature required – whilst avoiding chemical reaction and/or isotopic exchange with the containing crucible – prevented that approach from being adopted.

X-ray fluorescence measurements of elemental abundances in KRS and flint sample K-1B (prior to heating the latter in air at 1000°C) were made at the University of Oregon. Those results are reported in Appendix Table A.1 and confirm, in particular, that the flint sample consists essentially of quartz only.

4. Experimental procedures

In this paper we report the results of oxygen triple isotope measurements, conducted at the Open University and at Georg-August-Universität Göttingen, of the proposed silicate standards KRS and SKFS together with comparable measurements of UWG-2 garnet, San Carlos olivine and NBS quartz. Laser-assisted fluorination of silicate samples (~2 mg) is routinely performed at both institutions, using a CO₂ infrared laser (10.6 μm wavelength) and with excess of BrF₅ vapour as the fluorinating reagent. After isolation and purification of the O₂ formed, using cryogenic separation in conjunction with trapping onto molecular sieve pellets, isotope ratio measurements are made using a Thermo Fisher MAT 253 dual inlet mass spectrometer. The Open University facility is an updated version of that described by Miller et al. (1999), with recent modifications as summarized by Greenwood et al. (2018). A 'Fusions CO₂' (Teledyne CETAC Technologies) system is currently used for controlled heating of the samples. The 55 W (maximum output) laser is integrated with a motorized zoom video microscope, XYZ motion control stages, variable spot size and ring light illumination for line-of-sight imaging and targetting. The laser is operated in continuous beam mode and the power is controlled manually. Not reported previously is that, for optimal performance, the devised protocol is to use a

beam of 3 mm diameter initially, with the power gradually being increased to between ~25 and 30 % of full rating. Once the fluorination reaction appeared to have ceased, the beam diameter is then switched to 1 mm and heating continued, up to a maximum power output of ~15 to 20 %. To ensure that no unreacted material remains, the sample stage is then rastered under the laser beam until no further reaction is visible. In total, the time to complete the fluorination process is generally only a few minutes. Greenwood et al. (2018) reported that the 2σ measurement precision for 39 replicate analyses of an obsidian in-house laboratory standard gave ± 0.052 ‰ for $\delta^{17}\text{O}$, ± 0.094 ‰ for $\delta^{18}\text{O}$ and ± 0.017 ‰ for $\Delta^{17}\text{O}$.

The silicate fluorination facility and procedures used at Georg-August-Universität Göttingen are as documented by Pack et al. (2016). A significant difference from the Open University's system is that an additional O_2 purification step is incorporated, whereby the gas is passed through a heated (50°C) packed chromatograph column (3m length, 5Å molecular sieve) prior to transfer to the mass spectrometer. Further details are as given by Pack et al. (2016).

At both institutions, silicate fluorination proceeds only after the oxygen 'blank' has been reduced to a negligible amount (typically $< \sim 0.15$ $\mu\text{mol O}_2$ at the Open University, equivalent to $< \sim 0.5$ % of the O_2 yield from 2 mg of silicate), obviating the need for any correction to be applied.

5. Data and discussion

Table 1 summarizes the results of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements on replicate samples of both proposed standards together with comparable data on UWG-2 garnet, San Carlos olivine and NBS 28 quartz. Because of uncertainties in the accuracy of calibrating the respective O_2 working standards relative to VSMOW, we normalized the raw data to UWG-2, with $\delta^{18}\text{O}_{\text{VSMOW}}$ assigned as 5.75 ‰ and $\Delta^{17}\text{O}_{0.5305}$ as -60 ppm. The latter figure is based on the $\Delta^{17}\text{O}$ measurements of San Carlos olivine on the VSMOW-SLAP scale as reported by Pack et al. (2016), together with the finding from the present study that the $\Delta^{17}\text{O}_{0.528}$ value of UWG-2 is 8 ppm more negative than that for San Carlos olivine. For $\Delta^{17}\text{O}_{0.5305}$, the difference is 9 ppm (Georg-August-Universität Göttingen measurements) or 10 ppm

(Open University data). Although we suggest that our assigned $\delta^{18}\text{O}_{\text{VSMOW}}$ value of 5.75 ‰ is accurate, normalizing to a slightly different $\delta^{18}\text{O}_{\text{VSMOW}}$ value for UWG-2 does not affect $\Delta^{17}\text{O}_{0.5305} = -60$ ppm. The complete data set obtained for the present investigation, reported relative to the respective working standard O_2 , together with the $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values based on our normalizing to UWG-2, is provided in Appendix Table A.2.

As well as the $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ mean values and associated errors, Table 1 reports the corresponding $\Delta^{17}\text{O}$ values as derived from three different reference lines: (i). λ_{RL} assigned as 0.5305 (and $\gamma_{\text{RL}} = 0$), corresponding to the equilibrium high-temperature limit for θ ; (ii). λ_{RL} assigned as 0.528 (and $\gamma_{\text{RL}} = 0$), corresponding to the VSMOW-SLAP line; (iii). λ_{RL} assigned as 0.525, which seems to be representative of large collections of silicate rocks and minerals of diverse origin (Miller, 2002; Pack et al., 2013), and with $10^3\gamma_{\text{RL}} = -0.024$ relative to VSMOW. This $10^3\gamma_{\text{RL}}$ value was selected so that San Carlos olivine (as representative of Earth's mantle) fits on the reference line. No definition of $\Delta^{17}\text{O}$ is inherently superior to any other, although for identifying unusual isotopic compositions it is advantageous to use a reference line of slope that is close to that of the fractionation array given by the samples under consideration. So, for meteoric waters, snow and ice core samples, assigning λ_{RL} as 0.528 (and $\gamma_{\text{RL}} = 0$), as is the established convention, is sensible. For investigations involving oxygen isotopic exchange between waters and rocks, reporting both water and silicate $\Delta^{17}\text{O}$ values relative the VSMOW-SLAP line is advantageous. Empirical values of λ for silicate rocks and minerals, however, generally range from 0.524 to 0.529 (as noted above) and there is currently no consensus on a favoured reference line for defining $\Delta^{17}\text{O}$. Rather than be prescriptive, we use the three different examples defined above to provide a comparison of our results in Figure 2.

5.1 Data assessment and comparisons

Table 1 shows that the standard deviation (1σ) of the mean $\delta^{18}\text{O}$ value of fourteen replicate measurements of KRS at the Open University was less than 0.1 ‰, with the corresponding value for $\delta^{17}\text{O}$ being less than 0.05 ‰. This indicates that the sintering procedure used to prepare KRS

produced a material that is sufficiently homogenous in oxygen isotopic composition for the intended purpose. Although greater variability was apparent from the corresponding measurements at Georg-August-Universität Göttingen, the associated $\Delta^{17}\text{O}_{0.5305}$ value was of very similar precision to that obtained at the Open University.

For the SKFS flint, Table 1 shows that variations in $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ were notably higher than in any of the other four silicates included in this investigation, which is probably related to the comparative difficulty of fluorinating quartz (Spicuzza et al., 1998; Tanaka & Nakamura, 2013). Despite this, the standard deviation of the associated $\Delta^{17}\text{O}_{0.5305}$ value as measured at either institution was <10 ppm. Furthermore, it is particularly striking that, for a given $\Delta^{17}\text{O}$ definition, $\Delta^{17}\text{O}$ values determined at the two institutions are in very good agreement. Similarly for $\Delta^{17}\text{O}$ values of KRS, with the very small differences being essentially at or close to the measurement precision limit. For the purpose of defining a two-point high precision reference line for silicate $\Delta^{17}\text{O}$ measurements, we therefore consider that KRS and SKFS are both suitable materials, despite the measurement uncertainties associated with the respective $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. In contrast, a difference of 11-12 ppm between the two institutions was obtained for $\Delta^{17}\text{O}$ measurements of NBS 28 quartz. This may be related, at least in part, to the small number of replicate measurements.

An additional point evident from Table 1 is that there is some compression of the $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ scales as recorded by the mass spectrometer at Georg-August-Universität Göttingen compared to the equivalent data measured on a nominally identical instrument at the Open University. We cannot be confident, of course, that the Open University measurements are not also affected to some extent by scale distortion. Because of the very close agreement obtained for $\Delta^{17}\text{O}$ measurements of SKFS and for KRS, the samples most enriched and depleted (respectively) in the minor isotopes of oxygen, it is evident that $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ scale compressions on the Göttingen instrument were of identical magnitude. Recently, Yeung et al. (2018) noted that pressure baseline effects, resulting in scale distortion, are a potential source of inaccuracy in oxygen triple-isotope measurements. The authors argued that the resulting non-linearity may be a contributory

factor to literature disagreements on the oxygen triple-isotope differences between Earth's mantle, air O₂ and VSMOW, and could also perhaps explain the frequent revisions to the isotopic composition of some standards. Fortunately, however, Yeung et al. (2018) concluded that the linear stretching corrections for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ (as commonly adopted) are rigorous for pressure baseline-induced errors, if the analyte O₂ is of high purity.

Our results as presented in Table 1 demonstrate that the comparative $\Delta^{17}\text{O}$ data (regardless of reference line assignment) are more robust, in terms of inter-laboratory reproducibility, than the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values from which they are derived. For consistency of numerical values, normalizing the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data is recommended. Although we have chosen to normalize to assigned $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\Delta^{17}\text{O}_{0.5305, \gamma=0}$ for UWG-2, a similar exercise may be conducted by normalizing to, for example, San Carlos olivine, with appropriate values. We note that the San Carlos olivine used at the Open University is Type I (Macpherson et al., 2005; Thirlwall et al., 2006); it was supplied many years ago by David Lowry (Royal Holloway, University of London). In contrast, the San Carlos olivine used at Georg-August-Universität Göttingen appears to conform to the (more usual) Type II. Despite the $\delta^{18}\text{O}$ difference between Types I and II, we observed no distinction (within measurement precision) between the respective $\Delta^{17}\text{O}$ values, when reported to a common reference line.

As an aside, we note that numerical inversion computations (performed by INB) similar to the approach used by Bindeman et al. (2018), with $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}_{0.5305}$ values for SKFS as reported in Table 1, in conjunction with quartz-water oxygen isotopic equilibrium fractionation data from Sharp et al. (2016), give a formation temperature of approximately 35°C and with the $\delta^{18}\text{O}$ value of the parent water being of the order –0.5 to –0.8 ‰ relative to VSMOW. This suggests that the flint nodule closely represents the original precipitate from marine or near-coastal waters, fitting the quartz-water fractionation line rather than a mixing curve connecting the primary value to low- $\delta^{18}\text{O}$ secondary waters. Thus, the flint appears to have not interacted significantly with diagenetic or secondary meteoric waters since nodule formation.

5.2 Evaluation of a KRS–SKFS reference line for silicate $\Delta^{17}\text{O}$ measurements

Linear least-squares regression of replicate $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ values of KRS and SKFS produced a line characterized by $\lambda = 0.52720 \pm 0.00014$ (95% confidence) on the basis of Open University measurements. The comparable result determined at Georg-August-Universität Göttingen was very similar: $\lambda = 0.52727 \pm 0.00013$. Scatter of the individual measurements about the respective regression line is illustrated in Figure 3. It is important to note that this λ value has no inherent physical significance, as the two rocks are geologically unrelated. With $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data reported relative to VSMOW, based on our normalizing to UWG-2 garnet, the corresponding $10^6\gamma$ value of the two-point line is -89 ± 4 (Open University) and -90 ± 4 (Georg-August-Universität Göttingen), with uncertainties referring to the 95 % confidence interval. Clearly, there is very good agreement about the definition of this potential reference line (KRS–SKFS), based on the measurements made at the two institutions.

Table 2 reports the resulting $\Delta^{17}\text{O}$ values ($\pm 1\sigma$) of UWG-2, San Carlos olivine and NBS 28 relative to the KRS–SKFS line. The very small (2 ppm) difference between the Open University and Georg-August-Universität Göttingen results for $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ of UWG-2 and for San Carlos olivine, respectively, is significantly less than the associated measurement precision. Although comparative measurements on NBS 28 showed a 12 ppm difference, this is the same as for the corresponding $\Delta^{17}\text{O}$ data based on assigned (rather than empirical) reference lines, such as $\Delta^{17}\text{O}_{0.5305}$ and $\Delta^{17}\text{O}_{0.528}$ (Table 1) and might be related to the small number of replicate measurements, besides the inherent difficulties of fluorinating NBS 28 without complications.

Because $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ data are independent of the isotopic composition of the reference gas relative to which the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values are reported, there is no dependence on the accuracy of calibration to the VSMOW scale, nor indeed to any other scale. Thus, as shown in Table 2, the values as measured relative to the working standard O_2 ($\delta^{17}\text{O}_{\text{WS}}$ and $\delta^{18}\text{O}_{\text{WS}}$ data) may be used instead of the corresponding $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ results. Decoupling the accuracy of $\Delta^{17}\text{O}$ measurements from the accuracy of calibrating the working standard O_2 relative to VSMOW is a

major advantage of this approach, leading to greater confidence in the comparison of $\Delta^{17}\text{O}$ data from different laboratories. Figure 4 illustrates our $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ data for UWG-2, San Carlos olivine and NBS 28, relative to the corresponding $\delta^{18}\text{O}_{\text{VSMOW}}$ values.

The same methodology can be applied (for illustration of the principle) to the non-normalized measurements of VSMOW and SLAP at Georg-August-Universität Göttingen reported by Pack et al. (2016). Those data form a line characterized by $\lambda = 0.5270$ and $10^3\gamma = 0.340\text{‰}$, using $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data reported relative to the laboratory's working standard O_2 . Relative to this line as a reference, $\delta^{17}\text{O}_{\text{WS}}$ and $\delta^{18}\text{O}_{\text{WS}}$ values of San Carlos olivine gave $\Delta^{17}\text{O} = -36 \pm 7\text{ ppm (1}\sigma\text{)}$, which is identical to the value obtained when the isotopic data were normalized to the VSMOW-SLAP scale. A similar comparison can be made using the Okayama University data from the same study, giving $\Delta^{17}\text{O}$ of San Carlos olivine = $-39 \pm 7\text{ ppm (1}\sigma\text{)}$.

It should be clear, however, that there is still a need for more laboratories to calibrate the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of their working standard gas relative to VSMOW and to check for instrument-related non-linearity of the respective δ scales by measurements of VSMOW and SLAP. Every study that utilizes oxygen triple isotope ratio measurements of silicates, oxides, phosphates, carbonates or other solids for investigations involving interaction with water (e.g., Pack et al., 2013; Herwartz et al., 2015; Bindemann et al., 2018) faces the problem that the water data may be accurately reported on the VSMOW scale whereas data from the solids may be on a different scale. Therefore, even if the measurements are of high precision, they might not be appropriate for investigating specific questions in nature. Comparisons between theory (or modelling) and actual measurements require that all the $\Delta^{17}\text{O}$ values are based on the same scale.

6. Conclusions

High precision $\Delta^{17}\text{O}$ determinations of silicate rocks and minerals depend on relating the isotopic measurements accurately to the VSMOW-SLAP scale, or to accurately calibrating the isotopic composition of the laboratory working standard O_2 to VSMOW, if $\Delta^{17}\text{O}$ data are reported relative to a

reference line characterized by assigned values of λ_{RL} and γ_{RL} . These calibration requirements are technically challenging. Furthermore, many laboratories which report oxygen triple-isotope ratio measurements of rocks and minerals do not have the facility for making similar measurements on waters.

We have accurately characterized $\Delta^{17}\text{O}$ values of two silicates spanning a greater $\delta^{18}\text{O}$ range than VSMOW–SLAP and suggest that these materials may be used for the reporting of $\Delta^{17}\text{O}$ data. Because of the mass-dependent variation of $^{17}\text{O}/^{16}\text{O}$ with $^{18}\text{O}/^{16}\text{O}$, $\Delta^{17}\text{O}$ is a more robust characterization of the oxygen isotopic composition of rocks and minerals than are the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values and can be determined to greater precision. Our flint standard, designated SKFS, has $\Delta^{17}\text{O}_{0.528} = -114 \pm 2$ ppm (standard error). This material can therefore be used to calibrate the position of a reference line of assigned slope such that it passes through the zero point of the VSMOW scale. The accuracy of this calibration is dependent on the accuracy of our normalizing the $\Delta^{17}\text{O}_{0.5305}$ value of UWG-2 garnet to -60 ppm (or $\Delta^{17}\text{O}_{0.528}$ to -46 ppm).

Alternatively, in combination with our low- $\delta^{18}\text{O}$ silicate standard, designated as KRS ($\Delta^{17}\text{O}_{0.528} = -69 \pm 3$ ppm, standard error), an empirical two-point silicate reference line may be defined from high precision $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements of these two materials. $\Delta^{17}\text{O}$ data of rock and mineral samples reported relative to this reference line are independent of whether $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data are reported relative to VSMOW or to the ‘working standard’ O_2 , of any isotopic composition. This confers significant advantages for inter-laboratory comparisons.

The $\delta^{18}\text{O}$ values of KRS and SKFS cannot be characterized as accurately or precisely as the corresponding $\Delta^{17}\text{O}$ data relative to a reference line of assigned slope, such as $\Delta^{17}\text{O}_{0.528}$ or $\Delta^{17}\text{O}_{0.5305}$. Some degree of inherent isotopic inhomogeneity undoubtedly contributes to the $\delta^{18}\text{O}$ variations. Our ‘best estimates’ are: $\delta^{18}\text{O}_{\text{VSMOW}} = -25.20 \pm 0.09$ ‰ (1σ) for KRS; $\delta^{18}\text{O}_{\text{VSMOW}} = 33.93 \pm 0.24$ ‰ (1σ) for SKFS.

Samples of KRS and SKFS may be obtained, on request, from any of the authors (contact email addresses: m.f.miller@open.ac.uk; andreas.pack@geo.uni-goettingen.de; bindeman@uoregon.edu; r.c.greenwood@open.ac.uk).

Addendum

While this paper was in review, oxygen triple isotope measurements of KRS and SKFS were made at the University of Oregon, concurrently with either or both UWG-2 garnet and San Carlos olivine. The fluorinating reagent was BrF_5 and a Thermo Fisher MAT 253 was used for the isotope ratio measurements. Details of the the experimental procedure are described in the Supplementary Information to Bindeman et al. (2018). For comparison with the data shown in Table 1, we report here the normalized $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}_{0.5305}$ mean and standard error values obtained for KRS and SKFS, respectively: $-24.702 \pm 0.086 \text{ ‰}$, $-11 \pm 6 \text{ ppm}$ (KRS, $n = 9$); $33.936 \pm 0.150 \text{ ‰}$, $-205 \pm 7 \text{ ppm}$ (SKFS, $n = 9$). Additionally, for NBS 28: $\delta^{18}\text{O} = 9.388 \pm 0.200$, $\Delta^{17}\text{O}_{0.5305} = -62 \pm 3 \text{ ppm}$ ($n = 3$).

For comparison with Table 2, the replicate $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements of KRS and SKFS relative to the University of Oregon's working standard O_2 showed that least-squares linear regression of the $10^3 \ln(1 + \delta^{17}\text{O}_{\text{ws}})$ versus $10^3 \ln(1 + \delta^{18}\text{O}_{\text{ws}})$ data gave $\lambda = 0.52719 \pm 0.00032$ (95 % confidence interval). With the working standard having been calibrated on the VSMOW-SLAP scale at the Department of Earth and Space Sciences, University of Washington, Seattle, the ordinate axis offset $10^3 \gamma$ of the KRS-SKFS line from VSMOW was -0.091 ± 0.009 (95 % confidence interval). Relative to this reference line, the $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ mean and standard error values obtained for UWG-2, San Carlos olivine and NBS 28, respectively, were: 51 ± 9 ($n = 7$), 51 ± 8 ($n = 5$) and $68 \pm 6 \text{ ppm}$ ($n = 3$). All measurements were made later than at the Open University and at Georg-August-Universität Göttingen because of INB being on six months sabbatical leave overseas during 2019.

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Table Captions

Table 1

Open University and Georg-August-Universität Göttingen measurements of $\delta^{17}\text{O}_{\text{VSMOW}}$, $\delta^{18}\text{O}_{\text{VSMOW}}$ and derived $\Delta^{17}\text{O}$, with associated errors, of proposed silicate standards KRS and SKFS, together with comparative data from UWG-2, San Carlos olivine and NBS 28. $\Delta^{17}\text{O}$ are reported relative to three different reference lines as discussed in the text. To eliminate uncertainties associated with calibration of the individual working standard O_2 relative to VSMOW, the isotopic data were normalized to UWG-2, with $\delta^{18}\text{O}_{\text{VSMOW}}$ assigned to be 5.75 ‰ and $\Delta^{17}\text{O}_{0.5305}$ assigned as –60 ppm. The standard deviation values (1σ) reported for $\Delta^{17}\text{O}$ refer specifically to $\Delta^{17}\text{O}_{0.5305}$. For $\Delta^{17}\text{O}_{0.528}$ and $\Delta^{17}\text{O}_{0.525}$, $10^3\gamma = -0.024$ data, the 1σ values are of very similar magnitude.

Table 2

$\Delta^{17}\text{O}$ and associated standard deviation ($\pm 1\sigma$), rounded to integer values, of UWG-2, San Carlos olivine and NBS 28 reported relative to the KRS–SKFS reference line. The slope (λ_{RL}) of the line is independent of the isotopic composition of the O_2 relative to which all $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data are reported, whereas γ_{RL} , the ordinate offset of the line from the zero point of the scale, is not. The precision values of the slope and intercept refer to the 95 % confidence interval. The $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ data were normalized to measurements of UWG-2, $\delta^{18}\text{O}_{\text{VSMOW}} = 5.75$ ‰, $\Delta^{17}\text{O}_{0.5305} = -60$ ppm.

Figure Captions

Figure 1

Illustrating $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta^{17}\text{O}_{\text{VSMOW}}$ values reported for UWG-2 garnet, San Carlos olivine and NBS 28 quartz, respectively – mostly from recent publications and using the original data. Error bars represent $\pm 1\sigma$ (standard deviation). Infrared (10.6 μm) laser-assisted fluorination was used in all cases, although heating protocols varied (focussed or defocussed beam; beam power; single step or multi-step). Filled circles denote the use of BrF_5 for silicate fluorination; open circles indicate the use of F_2 , generated by thermal decomposition of Asprey's salt, $\text{K}_2\text{NiF}_6 \cdot \text{KF}$. 'N' denotes the number of replicates. Additional information:

^a data obtained at Georg-August-Universität Göttingen;

^b data obtained at Okayama University;

^c measurements on Type I San Carlos olivine;

^d measurements on Type II San Carlos olivine.

Figure 2

Comparison of $\Delta^{17}\text{O}_{0.5305}$, $\Delta^{17}\text{O}_{0.528}$ and $\Delta^{17}\text{O}_{0.525, 10^3\gamma = -0.024}$ determined from replicate measurements of proposed silicate standards KRS and SKFS, together with corresponding results from San Carlos olivine and NBS 28 quartz. Error bars represent $\pm$ standard error of the mean, $\sigma/\sqrt{n}$. Key to symbols: Open University data (●); Georg-August-Universität Göttingen data (◆). $\Delta^{17}\text{O}_{0.5305}$ results were normalized to UWG-2 = -60 ppm (○ Open University, ◇ Georg-August-Universität Göttingen), which provided the basis of the $\delta^{17}\text{O}_{\text{VSMOW}}$ data used for calculations of $\Delta^{17}\text{O}$ relative to other reference lines, in conjunction with $\delta^{18}\text{O}_{\text{VSMOW}}$ values normalized to UWG-2 = 5.75 ‰.

Figure 3

Illustrating the deviation ($\Delta^{17}\text{O}_{\text{KRS-SKFS}}$) of individual data points from the linear least-squares regression line of $10^3\ln(1 + \delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ defined by replicate measurements of KRS and SKFS. The $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ data are independent of the reference (such as VSMOW or the working standard O_2) relative to which the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ are reported. The KRS–SKFS line as measured at the Open University was characterized by slope (λ) of 0.52720 ± 0.00014 at the 95% confidence interval. With $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ reported relative to VSMOW, on the basis of normalizing to UWG-2 as discussed in the text, the corresponding $10^3\gamma$ value was -0.089 ± 0.004 . The comparable findings from Georg-August-Universität Göttingen were: $\lambda = 0.52727 \pm 0.00013$ and $10^3\gamma = -0.090 \pm 0.004$.

Figure 4

Illustrating a comparison of $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ versus $\delta^{18}\text{O}_{\text{VSMOW}}$ values of UWG-2, San Carlos olivine and NBS 28. Symbols are as for Figure 1. Associated error bars indicate standard error of the mean. Where no error bars are shown, this indicates that the standard error is smaller than the size of the associated data point symbol. The 95% confidence intervals of the reference line relative to which the $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ values are calculated are also shown (---- Georg-August-Universität Göttingen; Open University). The difference between the $\delta^{18}\text{O}_{\text{VSMOW}}$ values shown for San Carlos olivine is attributed to Type I being used at the Open University whereas the sample analyzed at Georg-August-Universität Göttingen was of Type II.

Table 1

A. Open University measurements

Sample	n	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	σ (‰)	$\sigma/\sqrt{n}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	σ (‰)	$\sigma/\sqrt{n}$ (‰)	$\Delta^{17}\text{O}_{0.5305, \gamma=0}$ (ppm)	$\Delta^{17}\text{O}_{0.528, \gamma=0}$ (ppm)	$\Delta^{17}\text{O}_{0.525, 10^3\gamma=-0.024}$ (ppm)	σ (ppm)	$\sigma/\sqrt{n}$ (ppm)
UWG-2 garnet	16	2.986	0.023	0.006	5.750	0.046	0.011	-60	-46	-4	4.9	1.2
KRS	14	-13.453	0.048	0.013	-25.200	0.093	0.025	-4	-68	-121	9.9	2.7
SKFS	9	17.658	0.127	0.042	33.932	0.242	0.081	-199	-115	9	9.0	3.0
San Carlos olivine	9	2.409	0.089	0.030	4.641	0.173	0.058	-50	-38	0	8.5	2.8
NBS 28 quartz	5	5.009	0.021	0.010	9.555	0.040	0.018	-48	-25	28	7.3	3.2

B. Georg-August-Universität Göttingen measurements

Sample	n	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	σ (‰)	$\sigma/\sqrt{n}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	σ (‰)	$\sigma/\sqrt{n}$ (‰)	$\Delta^{17}\text{O}_{0.5305, \gamma=0}$ (ppm)	$\Delta^{17}\text{O}_{0.528, \gamma=0}$ (ppm)	$\Delta^{17}\text{O}_{0.525, 10^3\gamma=-0.024}$ (ppm)	σ (ppm)	$\sigma/\sqrt{n}$ (ppm)
UWG-2 garnet	68	2.986	0.053	0.006	5.750	0.100	0.012	-60	-46	-4	8.1	1.0
KRS	9	-13.295	0.143	0.048	-24.899	0.267	0.089	-8	-71	-123	9.5	3.2
SKFS	23	17.422	0.218	0.045	33.477	0.414	0.086	-196	-114	9	9.3	1.9
San Carlos olivine	33	2.725	0.068	0.012	5.240	0.123	0.021	-51	-38	1	8.8	1.5
NBS 28 quartz	3	4.939	0.006	0.004	9.452	0.016	0.009	-60	-37	16	3.8	2.2

Table 2

	λ	$10^3\gamma$	$\Delta'^{17}\text{O}_{\text{KRS-SKFS}}$ (ppm)		
			UWG-2	San Carlos olivine	NBS 28
Open University measurements					
Using $\delta^{17}\text{O}_{\text{WS}}$ and $\delta^{18}\text{O}_{\text{WS}}$ data	0.52720 ± 0.00014	0.282 ± 0.004	47 ± 5	54 ± 8	72 ± 7
Using $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ data	0.52720 ± 0.00014	-0.089 ± 0.004	47 ± 5	54 ± 8	72 ± 7
Georg-August-Universität Göttingen measurements					
Using $\delta^{17}\text{O}_{\text{WS}}$ and $\delta^{18}\text{O}_{\text{WS}}$ data	0.52727 ± 0.00013	0.273 ± 0.003	49 ± 8	56 ± 9	60 ± 4
Using $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ data	0.52727 ± 0.00013	-0.090 ± 0.004	49 ± 8	56 ± 9	60 ± 4

Figure 1

Figure 1

(Continued)

Figure 2

Figure 3

A. Open University measurements

B. Georg-August-Universität Göttingen measurements

Figure 4

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APPENDIX

Table A.1

Results of XRF measurements, at the University of Oregon, of major, minor and trace (ppm) element abundances in KRS and in Stevns Klint flint K-1B prior to heating the flint in air at 1000°C to form the proposed standard SKFS.

	KRS	K-1B	AGV-2 Standard		
SiO ₂	34.71	99.83	60.45	60.46	60.48
TiO ₂	3.07	0.01	1.05	1.05	1.05
Al ₂ O ₃	22.34	0.00	16.98	16.99	16.98
Fe ₂ O ₃	28.40	0.04	6.78	6.79	6.79
MnO	0.30	0.00	0.10	0.10	0.10
MgO	7.57	0.00	1.76	1.76	1.76
CaO	3.26	0.09	5.24	5.23	5.23
Na ₂ O	0.03	0.00	3.89	3.89	3.88
K ₂ O	0.01	0.00	2.94	2.94	2.94
P ₂ O ₅	0.03	0.02	0.48	0.47	0.47
Total (%)	99.71	99.99	99.69	99.68	99.69
Rb	1	0	68	68	68
Sr	5	1	666	668	664
Ba	66	22	1123	1134	1137
Zr	143	19	221	220	221
Y	47	0	20	19	20
Nb	36	16	18	24	17
Cs	0	0	0	0	0
Sc	74	0	16	11	13
V	148	4	119	121	123
Cr	527	4	16	20	19
Ni	83	0	13	15	13
Cu	852	0	50	51	50
Zn	85	2	92	91	90
Ga	22	4	21	21	20
La	8	0	45	33	44
Ce	46	0	72	76	74
Pr	3	4	7	7	6
Nd	15	0	13	28	23
Hf	8	4	0	5	5
Pb	11	3	17	17	19
Th	0	0	4	5	4
U	15	0	11	12	10

Table A.2

Measurements made at the Open University, and at Georg-August-Universität Göttingen, of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of proposed silicate standards KRS and SKFS, together with comparable data from UWG-2 garnet, San Carlos olivine and NBS28 silica. We report the results relative to the respective laboratory's working standard O_2 (these are the $\delta^{17}\text{O}_{\text{WS}}$ and $\delta^{18}\text{O}_{\text{WS}}$ data) and relative to VSMOW ($\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$). For the latter, we normalized to UWG-2, with $\delta^{18}\text{O}_{\text{VSMOW}}$ assigned to be 5.75 ‰ and $\Delta^{17}\text{O}_{0.5305} = -60$ ppm. Justification for the -60 ppm value is discussed in the main text. For comparison with previously published (and not normalized) $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ data from the same institutions, we report that the composition of the Open University's working standard O_2 relative to VSMOW was assigned as $\delta^{17}\text{O}_{\text{VSMOW}} = 4.308$ and $\delta^{18}\text{O}_{\text{VSMOW}} = 8.873$ ‰. Apart from in a recent comparison of lunar and Earth mantle proxy samples at the Open University (Greenwood et al., 2018), these values have been used since 29th November 2006, pending direct calibration against O_2 derived from the fluorination of VSMOW. For the Greenwood et al. (2018) investigation, values of 4.361 and 9.046 ‰, were assigned. Similarly, the $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values of the working standard O_2 used at Georg-August-Universität Göttingen were also not determined by direct measurement against O_2 derived from the fluorination of VSMOW, but were assigned as 7.795 and 15.635 ‰. The $\delta^{17}\text{O}_{\text{VSMOW}}$ figure of 7.795 is known to be ~0.050 ‰ lower than the true value. Normalizing to UWG-2 on the basis described required that the isotopic composition of the Open University's working standard (referred to as O_2 -8) be revised to $\delta^{17}\text{O}_{\text{VSMOW}} = 4.29366$ ‰, $\delta^{18}\text{O}_{\text{VSMOW}} = 8.86855$ ‰. The number of decimal places reported here is for calculation purposes only; it does not imply measurement to such accuracy. At Georg-August-Universität Göttingen, the isotopic composition of the working standard O_2 as derived from 68 replicate measurements of UWG-2 was $\delta^{17}\text{O}_{\text{VSMOW}} = 7.82825$ ‰, $\delta^{18}\text{O}_{\text{VSMOW}} = 15.59785$ ‰.

A. Open University measurements

Silicate standard	Date	$\delta^{17}\text{O}_{\text{WS}}$ (‰)	$\delta^{18}\text{O}_{\text{WS}}$ (‰)	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
KRS	17-08-2018	-17.583	-33.597	-13.364	-25.026
	17-08-2018	-17.653	-33.771	-13.435	-25.202
	17-08-2018	-17.696	-33.806	-13.478	-25.237
	17-08-2018	-17.720	-33.838	-13.503	-25.269
	17-08-2018	-17.721	-33.866	-13.504	-25.297
	17-08-2018	-17.680	-33.793	-13.462	-25.224
	22-01-2019	-17.647	-33.711	-13.429	-25.141
	22-01-2019	-17.586	-33.632	-13.368	-25.061
	22-01-2019	-17.684	-33.794	-13.467	-25.225
	23-01-2019	-17.686	-33.798	-13.468	-25.229
	23-01-2019	-17.681	-33.779	-13.463	-25.210
	23-01-2019	-17.623	-33.650	-13.405	-25.080
	30-01-2019	-17.689	-33.808	-13.471	-25.239
	30-01-2019	-17.744	-33.929	-13.526	-25.361
	Mean	-17.671	-33.769	-13.453	-25.200
	σ	0.048	0.092	0.048	0.093
	$\sigma/\sqrt{n}$	0.013	0.025	0.013	0.025
SKFS	29-10-2018	13.200	24.679	17.550	33.766
	30-10-2018	13.222	24.679	17.572	33.766
	22-01-2019	13.366	24.947	17.717	34.036
	22-01-2019	13.263	24.746	17.613	33.834
	22-01-2019	13.292	24.796	17.642	33.884
	23-01-2019	13.128	24.502	17.478	33.587
	23-01-2019	13.560	25.337	17.911	34.430
	30-01-2019	13.378	24.981	17.729	34.071
	30-01-2019	13.352	24.919	17.703	34.008
	Mean	13.307	24.843	17.658	33.932
	σ	0.126	0.240	0.127	0.242
	$\sigma/\sqrt{n}$	0.042	0.080	0.042	0.081
	30-01-2019	13.352	24.919	17.727	34.060
	30-01-2019	13.352	24.919	17.727	34.060
UWG-2 garnet	10-10-2017	-1.259	-3.020	3.030	5.822
	10-10-2017	-1.277	-3.043	3.011	5.799
	10-10-2017	-1.293	-3.067	2.995	5.775
	11-10-2017	-1.324	-3.144	2.964	5.697
	11-10-2017	-1.332	-3.157	2.956	5.684

(continued)

Table A.2
(continued)

Silicate standard	Date	$\delta^{17}\text{O}_{\text{WS}}$ (‰)	$\delta^{18}\text{O}_{\text{WS}}$ (‰)	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
	11-10-2017	-1.330	-3.134	2.958	5.707
	05-04-2018	-1.327	-3.140	2.961	5.701
	05-04-2018	-1.326	-3.144	2.962	5.697
	05-04-2018	-1.294	-3.089	2.994	5.753
	23-04-2018	-1.289	-3.057	2.999	5.785
	23-04-2018	-1.318	-3.109	2.970	5.732
	21-08-2018	-1.299	-3.101	2.989	5.740
	21-08-2018	-1.318	-3.115	2.970	5.726
	22-01-2019	-1.281	-3.048	3.007	5.794
	23-01-2019	-1.276	-3.037	3.013	5.805
	30-01-2019	-1.285	-3.053	3.003	5.788
Mean		-1.302	-3.091	2.986	5.750
σ		0.023	0.045	0.023	0.046
$\sigma/\sqrt{n}$		0.006	0.011	0.006	0.011
San Carlos olivine	06-02-2018	-1.837	-4.126	2.449	4.706
	06-02-2018	-1.810	-4.040	2.476	4.793
	05-04-2018	-1.846	-4.135	2.440	4.697
	05-04-2018	-1.762	-3.965	2.524	4.869
	20-09-2018	-2.061	-4.537	2.224	4.292
	25-09-2018	-1.857	-4.179	2.429	4.653
	25-09-2018	-1.899	-4.217	2.387	4.615
	25-09-2018	-1.963	-4.366	2.323	4.464
	25-09-2018	-1.851	-4.147	2.435	4.685
Mean		-1.876	-4.190	2.409	4.641
σ		0.089	0.171	0.089	0.173
$\sigma/\sqrt{n}$		0.030	0.057	0.030	0.058
NBS28 quartz	17-08-2018	0.683	0.636	4.979	9.511
	21-08-2018	0.739	0.730	5.036	9.605
	20-09-2018	0.702	0.641	4.999	9.516
	24-09-2018	0.713	0.696	5.010	9.571
	25-09-2018	0.724	0.697	5.021	9.572
Mean		0.712	0.680	5.009	9.555
σ		0.021	0.040	0.021	0.040
$\sigma/\sqrt{n}$		0.010	0.018	0.010	0.018

(continued)

B. Georg-August-Universität Göttingen measurements

Silicate standard	Date	$\delta^{17}\text{O}_{\text{WS}}$ (‰)	$\delta^{18}\text{O}_{\text{WS}}$ (‰)	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
KRS	08-2018	-20.882	-39.731	-13.217	-24.752
	10-2018 (B)	-20.892	-39.791	-13.227	-24.814
		-21.158	-40.240	-13.495	-25.270
		-21.157	-40.245	-13.495	-25.275
	02-03-2019	-20.722	-39.425	-13.056	-24.442
		-20.942	-39.831	-13.278	-24.854
		-20.986	-39.927	-13.322	-24.952
		-21.030	-39.991	-13.366	-25.017
		-20.865	-39.689	-13.201	-24.710
		-20.959	-39.874	-13.295	-24.899
	Mean				
	σ	0.141	0.263	0.143	0.267
	$\sigma/\sqrt{n}$	0.047	0.088	0.048	0.089
SKFS	05-2018	9.571	17.739	17.474	33.613
		9.580	17.727	17.483	33.601
		9.575	17.727	17.478	33.602
	06-2018	9.339	17.271	17.240	33.139
		9.441	17.461	17.343	33.331
	07-2018	9.130	16.864	17.029	32.725
		9.223	17.065	17.123	32.929
	07-08-2018	9.930	18.401	17.836	34.285
		9.295	17.200	17.196	33.067
	09-2018 (A)	9.525	17.616	17.428	33.488
		9.030	16.672	16.929	32.530
	09-2018 (B)	9.379	17.317	17.271	33.185
		9.539	17.629	17.442	33.501
		9.480	17.519	17.382	33.390
		9.387	17.349	17.288	33.217
	10-2018	9.661	17.884	17.564	33.760
		9.740	18.036	17.644	33.916
	02-03-2019	9.684	17.895	17.588	33.772
		9.671	17.882	17.575	33.759
		9.745	18.018	17.650	33.897
		9.691	17.909	17.595	33.786
	05-2018	9.661	17.867	17.565	33.743
		9.674	17.859	17.578	33.735
		9.520	17.605	17.422	33.477
		0.216	0.408	0.218	0.414
	Mean				
	σ	0.216	0.408	0.218	0.414
	$\sigma/\sqrt{n}$	0.045	0.085	0.045	0.086

(continued)

Table A.2
(continued)

Silicate standard	Date	$\delta^{17}\text{O}_{\text{ws}}$ (‰)	$\delta^{18}\text{O}_{\text{ws}}$ (‰)	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
UWG-2 garnet	05-2018	-4.840	-9.773	2.950	5.672
		-4.809	-9.704	2.981	5.743
		-4.844	-9.743	2.946	5.703
		-4.756	-9.599	3.035	5.849
		-4.749	-9.578	3.042	5.871
	06-2018	-4.894	-9.857	2.896	5.587
		-4.826	-9.709	2.964	5.738
		-4.758	-9.608	3.033	5.840
		-4.839	-9.753	2.952	5.693
	07-2018	-4.795	-9.698	2.996	5.748
		-4.748	-9.584	3.043	5.864
		-4.739	-9.581	3.052	5.867
		-4.861	-9.808	2.929	5.637
	07-08-2018	-4.736	-9.571	3.055	5.877
		-4.766	-9.643	3.025	5.804
		-4.869	-9.836	2.921	5.608
		-4.745	-9.583	3.046	5.865
	07-08-2018	-4.722	-9.538	3.069	5.911
		-4.751	-9.598	3.040	5.850
		-4.702	-9.503	3.090	5.947
	09-2018 (A)	-4.659	-9.404	3.133	6.047
		-4.835	-9.737	2.955	5.709
		-4.795	-9.692	2.995	5.755
	09-2018 (B)	-4.830	-9.751	2.960	5.695
		-4.857	-9.812	2.933	5.633
		-4.888	-9.868	2.902	5.576
		-4.692	-9.513	3.100	5.937
	10-2018	-4.734	-9.576	3.057	5.873
		-4.710	-9.576	3.081	5.872
		-4.820	-9.733	2.971	5.713
		-4.826	-9.721	2.964	5.725
	02-03-2019	-4.808	-9.694	2.983	5.753
		-4.742	-9.568	3.049	5.881
		-4.820	-9.721	2.970	5.726
		-4.838	-9.753	2.952	5.693
	05-2018	-4.754	-9.607	3.037	5.841
		-4.752	-9.605	3.039	5.843
		-4.907	-9.907	2.883	5.536

(continued)

Table A.2
(continued)

Silicate standard	Date	$\delta^{17}\text{O}_{\text{WS}}$ (‰)	$\delta^{18}\text{O}_{\text{WS}}$ (‰)	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
	05-2018	-4.856	-9.821	2.934	5.623
		-4.802	-9.679	2.989	5.768
		-4.786	-9.669	3.005	5.778
		-4.830	-9.759	2.960	5.686
		-4.815	-9.716	2.975	5.730
		-4.776	-9.618	3.015	5.830
		-4.793	-9.675	2.997	5.772
		-4.787	-9.664	3.004	5.783
		-4.821	-9.748	2.969	5.698
		-4.836	-9.740	2.955	5.706
		-4.823	-9.721	2.967	5.726
		-4.822	-9.728	2.969	5.718
		-4.824	-9.723	2.967	5.723
		-4.811	-9.716	2.980	5.731
		-4.823	-9.727	2.967	5.719
		-4.830	-9.739	2.960	5.707
		-4.811	-9.699	2.980	5.748
		-4.825	-9.727	2.965	5.720
		-4.802	-9.710	2.988	5.737
		-4.861	-9.799	2.929	5.646
		-4.844	-9.765	2.947	5.681
		-4.842	-9.742	2.948	5.704
		-4.834	-9.761	2.956	5.684
		-4.906	-9.868	2.884	5.576
		-4.819	-9.738	2.971	5.708
		-4.858	-9.774	2.932	5.671
		-4.844	-9.770	2.946	5.675
		-4.785	-9.655	3.006	5.793
		-4.750	-9.575	3.041	5.874
		-4.875	-9.838	2.916	5.606
Mean		-4.805	-9.697	2.986	5.750
σ		0.053	0.098	0.053	0.100
$\sigma/\sqrt{n}$		0.006	0.012	0.006	0.012
San Carlos olivine	06-2018	-4.958	-9.978	2.831	5.464
		-4.983	-10.038	2.806	5.403
		-5.106	-10.273	2.682	5.165
		-4.982	-10.058	2.808	5.383
		-5.013	-10.069	2.776	5.372

(continued)

Table A.2
(continued)

Silicate standard	Date	$\delta^{17}\text{O}_{\text{ws}}$ (‰)	$\delta^{18}\text{O}_{\text{ws}}$ (‰)	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
		-4.980	-10.040	2.809	5.401
	07-2018	-4.916	-9.943	2.874	5.500
	10-2018	-5.012	-10.113	2.777	5.327
		-4.996	-10.084	2.793	5.356
		-5.008	-10.105	2.781	5.336
		-4.994	-10.118	2.795	5.322
		-4.993	-10.093	2.796	5.347
	02-03-2019	-5.084	-10.244	2.704	5.194
		-5.063	-10.211	2.725	5.228
		-5.052	-10.182	2.737	5.257
		-4.997	-10.085	2.792	5.355
		-5.134	-10.319	2.654	5.118
		-5.134	-10.337	2.654	5.099
		-5.143	-10.351	2.645	5.086
		-5.051	-10.173	2.738	5.267
		-5.138	-10.334	2.650	5.103
		-5.080	-10.226	2.708	5.213
		-5.108	-10.278	2.680	5.160
		-5.081	-10.227	2.707	5.211
		-5.132	-10.325	2.656	5.111
		-5.113	-10.275	2.675	5.163
		-5.131	-10.336	2.657	5.100
		-5.154	-10.350	2.634	5.087
		-5.117	-10.291	2.671	5.146
		-5.158	-10.380	2.630	5.056
		-5.119	-10.288	2.669	5.150
		-5.116	-10.277	2.672	5.160
		-5.056	-10.163	2.732	5.276
Mean		-5.064	-10.199	2.725	5.240
σ		0.067	0.122	0.068	0.123
$\sigma/\sqrt{n}$		0.012	0.021	0.012	0.021
NBS28 quartz	02-03-2019	-2.862	-6.056	4.944	9.448
		-2.858	-6.034	4.948	9.470
		-2.870	-6.065	4.936	9.438
Mean		-2.863	-6.052	4.943	9.452
σ		0.006	0.016	0.006	0.016
$\sigma/\sqrt{n}$		0.004	0.009	0.004	0.009