

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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20 **ABSTRACT**

21 Accurate and precise $\Delta^{17}\text{O}$ data are important for quantifying and understanding processes
22 responsible for variations of oxygen triple-isotope ratios in nature. Without universally agreed
23 numerical values of λ_{RL} and γ_{RL} in the definition $\Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - \lambda_{\text{RL}}\ln(1 + \delta^{18}\text{O}) - \gamma_{\text{RL}}$
24 however, as is currently the situation for measurements on rocks and minerals, reported $\Delta^{17}\text{O}$ data
25 may not be directly comparable. Furthermore, the accuracy of $\Delta^{17}\text{O}$ measurements is linked to
26 calibration (at the ppm level) of individual laboratory's 'working standard' O_2 relative to the
27 VSMOW water reference or to the VSMOW-SLAP scale, whereas few laboratories have the facility
28 to make high precision $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements on silicates and waters. Both points may be
29 addressed by defining a reference line from measurements of a pair of silicates which differ
30 substantially in oxygen isotopic composition (comparable to the difference between VSMOW and
31 SLAP), rather than by assigning λ_{RL} and γ_{RL} values arbitrarily. The resulting reference line has no
32 physical significance. However, because $\Delta^{17}\text{O}$ values reported relative to it are independent of the
33 calibration of the working standard O_2 , this greatly facilitates $\Delta^{17}\text{O}$ reproducibility and comparability.
34 We propose silicate standards for this purpose and report comparative measurements – from two
35 institutions – of the respective $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values relative to VSMOW, together with $\Delta^{17}\text{O}$ data
36 relative to various assigned reference lines. We also report $\Delta^{17}\text{O}$ measurements of UWG-2 garnet,
37 San Carlos olivine and NBS 28 quartz relative to our reference line. The proposed standards are: (1)
38 KRS (Khitostrov Rock Standard, $\delta^{18}\text{O} = -25.20 \text{ ‰}$), which consists of sintered, fine-grained
39 constituents (primarily garnet) of a very low- $\delta^{18}\text{O}$ amphibolite-grade Palaeoproterozoic rock from
40 Khitostrov, Karelia, Russia; (2) SKFS (Stevns Klint Flint Standard, $\delta^{18}\text{O} = 33.93 \text{ ‰}$), consisting of
41 thermally dehydrated grains of a high- $\delta^{18}\text{O}$ nodule of flint sampled from just below the exposed
42 Cretaceous–Palaeogene boundary at Stevns Klint, southeast Zealand Island, Denmark. Both silicates
43 fluorinate readily, using standard laser-assisted procedures, and the associated low blanks allow for
44 overnight pre-treatment. Small quantities of these materials may be supplied, on request, for
45 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	

53 1. Introduction

54 The occurrence of small but distinctive variations between the relative abundances of ^{17}O and ^{18}O
 55 in terrestrial rocks and minerals has been demonstrated from high precision measurements of the
 56 $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios (for example, Rumble et al, 2007; Tanaka and Nakamura, 2013; Pack and
 57 Herwartz, 2014; Levin et al., 2014; Starkey et al., 2016). Many processes during the formation history
 58 of individual samples may have contributed to their present isotopic composition. Chemical and
 59 isotopic characteristics of the interacting solids, melts and aqueous fluids are probably influential,
 60 together with the temperature under which isotopic exchange took place (Matsuhisa et al., 1978; Cao
 61 and Liu, 2011; Dauphas and Schauble, 2016).

62 For most process that modify oxygen isotope distributions in nature, $^{17}\text{O}/^{16}\text{O}$ changes by
 63 approximately half the corresponding change in $^{18}\text{O}/^{16}\text{O}$. This is because the mass difference between
 64 ^{17}O and ^{16}O (1.0042 Da) is approximately half as large as the mass difference between ^{18}O and ^{16}O
 65 (2.0042 Da). Isotope ratio modifications that follow this pattern of proportionality are usually referred
 66 to as ‘mass-dependent’ fractionations. Measurements of oxygen triple-isotope ratios are, by
 67 convention, reported as $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values, where:

$$68 \quad \delta^{17}\text{O} = \frac{{}^{17}\text{R}_{\text{sample}} - {}^{17}\text{R}_{\text{reference}}}{{}^{17}\text{R}_{\text{reference}}} \quad \text{and} \quad \delta^{18}\text{O} = \frac{{}^{18}\text{R}_{\text{sample}} - {}^{18}\text{R}_{\text{reference}}}{{}^{18}\text{R}_{\text{reference}}} \quad (1)$$

69 ${}^{17}\text{R}_{\text{sample}}$ and ${}^{18}\text{R}_{\text{sample}}$ are the respective abundances of the minor isotopes ^{17}O and ^{18}O relative to the
 70 ^{16}O abundance in the sample; ${}^{17}\text{R}_{\text{reference}}$ and ${}^{18}\text{R}_{\text{reference}}$ are the relative abundances in an international
 71 reference material, usually Vienna Standard Mean Ocean Water, VSMOW. Note that δ is a
 72 dimensionless quantity. Because it is of small magnitude ($\ll 1$) in natural systems, it is usually
 73 reported as parts per thousand (‘per mil’, ‰).

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

$$76 \quad \alpha_{\text{A-B}}^{17/16} = \frac{{}^{17}\text{R}_{\text{A}}}{{}^{17}\text{R}_{\text{B}}} = \frac{1 + \delta^{17}\text{O}_{\text{A}}}{1 + \delta^{17}\text{O}_{\text{B}}} \quad \text{and} \quad \alpha_{\text{A-B}}^{18/16} = \frac{{}^{18}\text{R}_{\text{A}}}{{}^{18}\text{R}_{\text{B}}} = \frac{1 + \delta^{18}\text{O}_{\text{A}}}{1 + \delta^{18}\text{O}_{\text{B}}} \quad (2)$$

77 are related by:

$$78 \quad \alpha_{A-B}^{17/16} = \left(\alpha_{A-B}^{18/16} \right)^\theta \quad (3)$$

79 Few experimental measurements of θ for the SiO_2 –water system have been made. Sharp et al. (2016)
80 reported that, at low temperatures (~ 0 to 50°C), $\theta \sim 0.523$ – 0.524 . The high temperature limit value of
81 θ for all oxygen isotope exchange processes under equilibrium conditions is 0.5305 (Matsuhisa et al.,
82 1978; Dauphas and Schauble, 2016, and references therein). For various kinetic fractionation
83 mechanisms, a comparable formalism (Young et al., 2002; Dauphas and Schauble, 2016) indicates
84 that θ varies between 0.501 and 0.516 , depending on molecular mass.

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

$$87 \quad \frac{{}^{17}\text{R}_{\text{sample}}}{{}^{17}\text{R}_{\text{reference}}} = (1 + \gamma) \left(\frac{{}^{18}\text{R}_{\text{sample}}}{{}^{18}\text{R}_{\text{reference}}} \right)^\lambda \quad (4)$$

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

$$93 \quad \ln(1 + \delta^{17}\text{O}) = \lambda \ln(1 + \delta^{18}\text{O}) + \ln(1 + \gamma) \quad (5)$$

94 It is useful to include a scaling factor of 10^3 so that the logarithmic terms involving $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$
95 are then of similar magnitude to the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values reported as ‰. The quantities
96 $10^3 \ln(1 + \delta^{17}\text{O})$ and $10^3 \ln(1 + \delta^{18}\text{O})$ are often denoted as $\delta'^{17}\text{O}$ and $\delta'^{18}\text{O}$ respectively, following
97 similar terminology introduced by Hulston and Thode (1965) in the context of sulphur multiple
98 isotope ratios. For a collection of samples characterized by a range of δ values, linear least squares
99 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
100 mean λ value for that particular group of samples; there is not necessarily an implied relationship

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

108 To quantify small deviations from an assigned reference line of slope λ_{RL} and ordinate axis offset
109 $10^3 \gamma_{\text{RL}}$ from the zero point of the δ scale (usually VSMOW), the parameter $\Delta^{17}\text{O}$ may be defined
110 from Eqn. (5) as:

$$111 \quad \Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - \lambda_{\text{RL}} \ln(1 + \delta^{18}\text{O}) - \gamma_{\text{RL}} \quad (6)$$

112 This definition (from Miller, 2002) has been widely adopted, with or without the inclusion of the γ_{RL}
113 term. The subscript ‘RL’ refers to ‘reference line’. We note that $\Delta^{17}\text{O}$ is sometimes referred to as ^{17}O -
114 excess, especially for waters, snow and ice cores. To avoid the implication that $\Delta^{17}\text{O} \geq 0$ in all cases,
115 and to avoid the incongruity of referring to a ‘negative excess’, that terminology is not used here.
116 Similarly, we avoid the term ‘ ^{17}O anomaly’, which is sometimes used in the context of non-mass-
117 dependent isotope distributions (e.g., Dauphas & Schauble, 2016). Inclusion of the ‘prime’ symbol in
118 $\Delta^{17}\text{O}$ notation has been widely adopted, to avoid confusion with the original definition of $\Delta^{17}\text{O}$ which
119 was based on the approximation of direct proportionality between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Clayton and
120 Mayeda, 1988). We use the $\Delta^{17}\text{O}$ notation for this paper, whilst acknowledging that this is not
121 universally accepted practice.

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

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

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129
$$\Delta^{17}\text{O} = \frac{1 + \delta^{17}\text{O}}{(1 + \gamma_{\text{RL}})(1 + \delta^{18}\text{O})^{\lambda_{\text{RL}}}} - 1 \quad (7)$$

130

131 Oxygen triple-isotope ratio measurements by mass spectrometry are conducted using O_2 as the
132 analyte gas, with $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ determined relative to a ‘working standard’ O_2 which should be
133 calibrated relative to a reference material with accurately known (or defined) $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values
134 relative to VSMOW. Currently, only IAEA water samples (not any silicate standards) are certified for
135 $\delta^{17}\text{O}$ value. Calibration of the working standard is difficult to achieve, to the degree of accuracy
136 required for many investigations. Furthermore, few laboratories have the facility to prepare O_2 from
137 both waters and silicates. As an alternative to direct calibration against VSMOW, the working
138 standard may be calibrated against an intermediate such as air O_2 (for example, Pack & Herwartz,
139 2014; Miller et al., 2015; Greenwood et al., 2018), although a complication is that different values for
140 the triple isotopic composition of air O_2 relative to VSMOW have been reported. An appraisal of
141 recent measurements is given by Pack et al. (2017).

142 **2. Rationale and methodology**

143 *2.1. Uncertainties in the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of silicate reference materials*

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

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

164 We provide in Figure 1 a ‘Caltech plot’ comparison of reported $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values (including
165 associated errors) for UWG-2, San Carlos olivine and NBS 28 from several recent publications. In
166 some of those reports, the silicate $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data have been normalized, but not necessarily to a
167 common procedure. Pack et al. (2016) reported their data on the VSMOW-SLAP scale using the
168 normalization recommended by Schoenemann et al. (2013). Kusakabe & Matsuhisa (2008) and Ahn
169 et al. (2012) also calibrated their $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data relative to VSMOW-SLAP, but using the
170 procedure adopted by Kusakabe and Matsuhisa (2008). In other reports, no direct calibration to
171 VSMOW or the VSMOW-SLAP scale was performed. Pack and Herwartz (2014), Starkey et al.
172 (2016) and Greenwood et al. (2018) related their $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data to VSMOW indirectly, by third
173 party calibration of the working standard O_2 against atmospheric oxygen. In other examples,
174 $\delta^{18}\text{O}_{\text{VSMOW}}$ values were calibrated on the basis of an assigned value for UWG-2 garnet (Levin et al.,
175 2014; Kim et al., 2019) or San Carlos olivine (Young et al., 2016), with the corresponding $\delta^{17}\text{O}_{\text{VSMOW}}$
176 value of UWG-2 or San Carlos olivine being derived by assuming a specified fractionation
177 relationship between the three oxygen isotopes. Ali et al. (2016) similarly calibrated the $\delta^{18}\text{O}_{\text{VSMOW}}$

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

184 Although the originally recommended $\delta^{18}\text{O}_{\text{VSMOW}}$ value of UWG-2 garnet (Valley et al., 1995) is
185 5.8 ‰, some reports have since proposed a slightly lower number. For example, Macpherson et al.
186 (2005) published a value of 5.71 ± 0.09 ‰ (1σ), calibrated to NBS 30 biotite $\delta^{18}\text{O} = 5.10$ ‰. For the
187 present work we assigned a value of 5.75 ‰, based on previous findings at Georg-August-Universität
188 Göttingen and at the University of Oregon.

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

194 2.2. $\Delta^{17}\text{O}$ measurements of silicate rocks and minerals

195 High precision measurements of oxygen triple-isotope ratios of silicate rocks and minerals at
196 various laboratories have resulted in a variety of ‘terrestrial fractionation lines’ being reported (Miller,
197 2002; Rumble et al., 2007; Pack et al., 2007; Spicuzza et al., 2007; Kusakabe and Matsuhisa, 2008;
198 Hofmann and Pack, 2010; Hofmann et al., 2012; Ahn et al., 2012; Tanaka and Nakamura, 2013; Pack
199 et al., 2013; Levin et al., 2014; Bindeman et al., 2014; Kim et al., 2019). Pack et al. (2013) suggested
200 that, based on their measurements of 1071 samples, the associated λ value of 0.5251 ± 0.0014 (2σ)
201 probably represents the mean isotopic fractionation between melts, minerals and fluids at various
202 temperatures and pressures.

203 Hallis et al. (2010), in the context of assigning a reference line for $\Delta^{17}\text{O}$ measurements of lunar
204 basalts, noted that the two silicate arrays compared by Rumble et al. (2007) were characterized by
205 different offsets from VSMOW. Subsequently, Tanaka and Nakamura (2013) demonstrated that an
206 array formed from a collection of (15) silicates, and characterized by a slope of 0.5270 ± 0.0005 (95%
207 confidence interval), was offset from VSMOW by $10^3\gamma = -0.070 \pm 0.005$ whereas, using the same
208 oxygen purification system and mass spectrometer, a set of four water samples including VSMOW,
209 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
210 important to recognize, however, that an array formed from least squares regression of $10^3\ln(1 +$
211 $\delta^{17}\text{O})$ versus $10^3\ln(1 + \delta^{18}\text{O})$ data from a group of silicate rocks and minerals will be characterized by
212 values of both slope and ordinate axis offset that are specific to that particular collection of samples.

213 The magnitude of λ is unaffected by the reference to which $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values are reported
214 (Miller, 2002); it is therefore invariant to the calibration of the laboratory working standard O_2 to any
215 specific reference material such as VSMOW. Clearly, however, this is not the case for γ . Furthermore,
216 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.
217 Wiechert et al., 2004; Herwartz et al., 2014; Pack and Herwartz, 2014), then the accuracy of the
218 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
219 working standard O_2 relative to VSMOW.

220 Hofmann et al. (2017) listed various different reference lines that have been used for reporting
221 $\Delta^{17}\text{O}$ measurements in a variety of applications. It was noted that, although there is not consensus on
222 a single selection, the choice is somewhat arbitrary because $\Delta^{17}\text{O}$ is not a measured quantity; it is
223 inferred from $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data. This point was also made by Kaiser (2008) and by Pack and
224 Herwartz (2014). Kaiser (2011) suggested that, regardless of the definition of $\Delta^{17}\text{O}$, all $\Delta^{17}\text{O}$ data are
225 ‘merely mathematical constructs’, in contrast to the relative $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratio
226 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
227 robust parameter (in principle, at least), that may be determined to higher accuracy and precision than
228 the associated $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. Furthermore, the latter are also ‘mathematical constructs’ in that

229 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
230 can be obtained on the selection of appropriate silicate rock or mineral samples for defining an
231 empirical, two-point reference line, then silicate or oxide $\Delta^{17}\text{O}$ data relative to that line would be
232 independent of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ calibration of individual laboratory's working standard O_2 to
233 VSMOW or to any other reference material. This confers a significant advantage over existing
234 methodology.

235 Because the fluorination of silicate rocks and minerals, to produce O_2 as the analyte for isotope
236 ratio measurements, requires a different procedure from that used for the fluorination of waters, there
237 is the possibility of systematic errors being introduced by the use of a water reference material for
238 reporting $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data of rocks and minerals. This point was made by Young et al. (2016),
239 who also noted that, as fractionation arrays from silicate rocks and minerals are now known
240 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
241 an additional complication. To eliminate such potential sources of error, Young et al. (2016)
242 chose to report their whole-rock and mineral $\Delta^{17}\text{O}$ results relative to a reference line derived
243 from $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data reported relative to San Carlos olivine (as representative of Earth's
244 mantle), with an assigned λ value of 0.528. A comparable approach was adopted by Cao et al.
245 (2019), in their investigation of ocean island basalts. Sharp et al. (2016) noted that, unfortunately,
246 oxygen triple-isotope ratio measurements of rocks are only peripherally linked to the VSMOW-SLAP
247 scale, because very few laboratories routinely measure the oxygen triple-isotope compositions of both
248 waters and silicates. Silicate oxygen triple-isotope data reported by Sharp et al. (2016) were
249 normalized to a $\delta^{18}\text{O}$ value for San Carlos olivine of 5.3 ‰ relative to VSMOW and corresponding
250 $\Delta^{17}\text{O}$ 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
251 ‰ than that reported by Pack et al. (2016) for San Carlos olivine relative to the same reference line.

252 2.3. $\Delta^{17}\text{O}$ of meteoric waters, snow and ice cores – comparison with silicates

253 Because the oxygen isotopic composition of rocks and minerals is reported relative to VSMOW,
254 with $\Delta^{17}\text{O}$ sometimes reported relative to the VSMOW-SLAP scale (with $\Delta^{17}\text{O}$ of SLAP defined to
255 be zero, as recommended by Schoenemann et al., 2013), it is relevant to consider such measurements
256 of waters. Meijer and Li (1998) first reported that natural waters from a wide range of sources,
257 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
258 the associated λ value was 0.5281 ± 0.0015 (standard error). Subsequently, Angert et al. (2004)
259 suggested, from theoretical considerations, that the array should be slightly offset (positive) from
260 VSMOW, with deviations being attributed primarily to kinetic fractionation during the diffusive
261 transport of water vapour from the evaporative source region into undersaturated air. That prediction
262 was later confirmed (Barkan and Luz, 2007; Landais et al., 2008; Luz and Barkan, 2010). Barkan and
263 Luz (2007) defined the ' ^{17}O -excess' ($\Delta^{17}\text{O}$) of meteoric precipitation as:

$$264 \Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - 0.528 \ln(1 + \delta^{18}\text{O}) \quad (8)$$

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

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

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

278 *2.4. Normalizing $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of waters and rocks to the VSMOW-SLAP*
 279 *scale*

280 A convention for optimizing inter-laboratory consistency of $\delta^{18}\text{O}$ measurements has long been
 281 established (Gonfiantini, 1978) and involves normalizing such measurements to the VSMOW-SLAP
 282 scale, with $\delta^{18}\text{O}$ of SLAP assigned as -55.5‰ (exactly) relative to VSMOW. By convention, the
 283 normalization requires that $\delta^{18}\text{O}$ data relative to VSMOW be adjusted by a factor of
 284 $(-55.5)/(\delta^{18}\text{O}_{\text{SLAP/VSMOW}})$, where $\delta^{18}\text{O}_{\text{SLAP/VSMOW}}$ is the measured value of SLAP relative to VSMOW.

285 Because the δ scale is non-linear, with $-1 < \delta < \infty$, ‘true’ linear scaling to VSMOW-SLAP
 286 requires that $\ln(1 + \delta^{18}\text{O})$ values be adjusted, rather than the corresponding $\delta^{18}\text{O}$ data. The associated
 287 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
 288 numerical differences between the conventional and logarithmic normalizations are generally small.
 289 An additional complication noted by Kaiser (2008) is that the assigned $\delta^{18}\text{O}$ value of SLAP relative to
 290 VSMOW may be significantly in error. Kaiser (2008) suggested that, on the basis of measurement
 291 comparisons reported in 2004, the ‘true’ value seems to be $-56.18 \pm 0.01\text{‰}$.

292 Kusakabe and Matsuhisa (2008) is the only publication we are aware of in which scaling of $\ln(1 +$
 293 $\delta^{18}\text{O})$ data to VSMOW-SLAP was implemented with the same factor $(-57.10)/(-56.20)$ being applied
 294 to scaling of the corresponding $\ln(1 + \delta^{17}\text{O})$ data. Kaiser (2008) recommended a similar normalization
 295 approach, but in power law format and with λ assigned to be 0.528:

$$296 \quad \delta^{17}\text{O}_{\text{VSMOW-SLAP normalized}}^{\text{sample}} = \delta^{17}\text{O}_{\text{VSMOW}}^{\text{sample}} \frac{(1 + \delta^{18}\text{O}_{\text{SLAP/VSMOW, assigned}})^{0.528} - 1}{(1 + \delta^{18}\text{O}_{\text{SLAP/VSMOW, measured}})^{0.528} - 1} \quad (9)$$

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

300 To improve the inter-laboratory consistency of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data from oxygen triple-isotope
301 ratio measurements of water samples, Schoenemann et al. (2013) proposed that $\delta^{17}\text{O}$ measurements be
302 normalized to the VSMOW-SLAP scale in similar fashion as the $\delta^{18}\text{O}$ data, with $\delta^{17}\text{O}$ of SLAP
303 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
304 resulting scale factor for the $\delta^{17}\text{O}$ measurements is therefore $(-29.6986)/\delta^{17}\text{O}_{\text{SLAP/VSMOW}}$,
305 approximately¹. Unlike the Kusakabe and Matsuhisa (2008) or Kaiser (2008) normalizing procedures,
306 the Schoenemann et al. (2013) recommendation involves scaling of the empirical $\delta^{17}\text{O}$ results
307 independently of the corresponding $\delta^{18}\text{O}$ data. Essentially, this adjusts the experimental data so that
308 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
309 the assigned λ_{RL} and γ_{RL} values.

310 2.5 A two-point silicate reference line for $\Delta^{17}\text{O}$ measurements of rocks and minerals

311 Pack et al. (2016) advocated that VSMOW-SLAP scaling should be applied to oxygen triple-
312 isotope measurements of silicate rocks and minerals, using the recommendation of Schoenemann et
313 al. (2013) originally devised for standardizing $\Delta^{17}\text{O}$ data obtained from waters. Whereas the
314 advantage of that approach for silicates has been demonstrated, it does require that any laboratory
315 undertaking high precision $\Delta^{17}\text{O}$ measurements of rocks and minerals must also have the capability of
316 making similar measurements on waters. There is also the implicit assumption that the water and
317 silicate fluorination procedures – although different – will essentially be characterized by the same
318 (low) processing errors. A simpler alternative, which obviates the requirement to make measurements
319 on waters, is to report rock and mineral $\Delta^{17}\text{O}$ measurements relative to an empirical reference line
320 constructed from two silicates, differing in $\delta^{18}\text{O}$ by a magnitude similar to (or greater than) that
321 between VSMOW and SLAP. The selected materials must be reasonably homogeneous in oxygen
322 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.

323 sputtering during laser-assisted reaction with BrF₅; also contribute a negligibly low oxygen ‘blank’
324 during pre-fluorination procedures. Furthermore, they need to be available in sufficient quantities to
325 allow distribution to other laboratories, on request.

326 This approach is advantageous to that of using a single silicate reference material of assigned
327 $\delta^{18}\text{O}_{\text{VSMOW}}$ value for normalizing $\delta^{18}\text{O}$ data to. A two-point scale enables any instrument-related
328 compression (or expansion) of the $\delta^{18}\text{O}$ scale to be identified and quantified; also whether identical
329 behaviour applies to the $\delta^{17}\text{O}$ scale. A difference between the respective linearities will cause the
330 slope of the two-point reference line to vary from the ‘true’ value, although $\Delta^{17}\text{O}$ values of silicates
331 reported relative to that reference line will be independent of any non-linearity of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$
332 scales. The respective $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of the two silicate standards may be anchored to the
333 VSMOW-SLAP scale using the procedure adopted by Pack et al. (2016), with inter-laboratory
334 comparison forming the basis of consensus values.

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

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

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

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

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

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

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

384 **4. Experimental procedures**

385 In this paper we report the results of oxygen triple isotope measurements, conducted at the Open
386 University and at Georg-August-Universität Göttingen, of the proposed silicate standards KRS and
387 SKFS together with comparable measurements of UWG-2 garnet, San Carlos olivine and NBS quartz.
388 Laser-assisted fluorination of silicate samples (~2 mg) is routinely performed at both institutions,
389 using a CO₂ infrared laser (10.6 μm wavelength) and with excess of BrF₅ vapour as the fluorinating
390 reagent. After isolation and purification of the O₂ formed, using cryogenic separation in conjunction
391 with trapping onto molecular sieve pellets, isotope ratio measurements are made using a Thermo
392 Fisher MAT 253 dual inlet mass spectrometer. The Open University facility is an updated version of
393 that described by Miller et al. (1999), with recent modifications as summarized by Greenwood et al.
394 (2018). A 'Fusions CO₂' (Teledyne CETAC Technologies) system is currently used for controlled
395 heating of the samples. The 55 W (maximum output) laser is integrated with a motorized zoom video
396 microscope, XYZ motion control stages, variable spot size and ring light illumination for line-of-sight
397 imaging and targetting. The laser is operated in continuous beam mode and the power is controlled
398 manually. Not reported previously is that, for optimal performance, the devised protocol is to use a

399 beam of 3 mm diameter initially, with the power gradually being increased to between ~25 and 30 %
400 of full rating. Once the fluorination reaction appeared to have ceased, the beam diameter is then
401 switched to 1 mm and heating continued, up to a maximum power output of ~15 to 20 %. To ensure
402 that no unreacted material remains, the sample stage is then rastered under the laser beam until no
403 further reaction is visible. In total, the time to complete the fluorination process is generally only a
404 few minutes. Greenwood et al. (2018) reported that the 2σ measurement precision for 39 replicate
405 analyses of an obsidian in-house laboratory standard gave ± 0.052 ‰ for $\delta^{17}\text{O}$, ± 0.094 ‰ for $\delta^{18}\text{O}$ and
406 ± 0.017 ‰ for $\Delta^{17}\text{O}$.

407 The silicate fluorination facility and procedures used at Georg-August-Universität Göttingen are
408 as documented by Pack et al. (2016). A significant difference from the Open University's system is
409 that an additional O_2 purification step is incorporated, whereby the gas is passed through a heated
410 (50°C) packed chromatograph column (3m length, 5\AA molecular sieve) prior to transfer to the mass
411 spectrometer. Further details are as given by Pack et al. (2016).

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

415 5. Data and discussion

416 Table 1 summarizes the results of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements on replicate samples of both
417 proposed standards together with comparable data on UWG-2 garnet, San Carlos olivine and NBS 28
418 quartz. Because of uncertainties in the accuracy of calibrating the respective O_2 working standards
419 relative to VSMOW, we normalized the raw data to UWG-2, with $\delta^{18}\text{O}_{\text{VSMOW}}$ assigned as 5.75 ‰ and
420 $\Delta^{17}\text{O}_{0.5305}$ as -60 ppm. The latter figure is based on the $\Delta^{17}\text{O}$ measurements of San Carlos olivine on
421 the VSMOW-SLAP scale as reported by Pack et al. (2016), together with the finding from the present
422 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
423 $\Delta^{17}\text{O}_{0.5305}$, the difference is 9 ppm (Georg-August-Universität Göttingen measurements) or 10 ppm

424 (Open University data). Although we suggest that our assigned $\delta^{18}\text{O}_{\text{VSMOW}}$ value of 5.75 ‰ is
425 accurate, normalizing to a slightly different $\delta^{18}\text{O}_{\text{VSMOW}}$ value for UWG-2 does not affect $\Delta^{17}\text{O}_{0.5305} =$
426 -60 ppm. The complete data set obtained for the present investigation, reported relative to the
427 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
428 normalizing to UWG-2, is provided in Appendix Table A.2.

429 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
430 corresponding $\Delta^{17}\text{O}$ values as derived from three different reference lines: (i). λ_{RL} assigned as 0.5305
431 (and $\gamma_{\text{RL}} = 0$), corresponding to the equilibrium high-temperature limit for θ ; (ii). λ_{RL} assigned as
432 0.528 (and $\gamma_{\text{RL}} = 0$), corresponding to the VSMOW-SLAP line; (iii). λ_{RL} assigned as 0.525, which
433 seems to be representative of large collections of silicate rocks and minerals of diverse origin (Miller,
434 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
435 selected so that San Carlos olivine (as representative of Earth's mantle) fits on the reference line.
436 No definition of $\Delta^{17}\text{O}$ is inherently superior to any other, although for identifying unusual isotopic
437 compositions it is advantageous to use a reference line of slope that is close to that of the fractionation
438 array given by the samples under consideration. So, for meteoric waters, snow and ice core samples,
439 assigning λ_{RL} as 0.528 (and $\gamma_{\text{RL}} = 0$), as is the established convention, is sensible. For investigations
440 involving oxygen isotopic exchange between waters and rocks, reporting both water and silicate $\Delta^{17}\text{O}$
441 values relative the VSMOW-SLAP line is advantageous. Empirical values of λ for silicate rocks and
442 minerals, however, generally range from 0.524 to 0.529 (as noted above) and there is currently no
443 consensus on a favoured reference line for defining $\Delta^{17}\text{O}$. Rather than be prescriptive, we use the
444 three different examples defined above to provide a comparison of our results in Figure 2.

445 *5.1 Data assessment and comparisons*

446 Table 1 shows that the standard deviation (1σ) of the mean $\delta^{18}\text{O}$ value of fourteen replicate
447 measurements of KRS at the Open University was less than 0.1 ‰, with the corresponding value for
448 $\delta^{17}\text{O}$ being less than 0.05 ‰. This indicates that the sintering procedure used to prepare KRS

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

453 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
454 of the other four silicates included in this investigation, which is probably related to the comparative
455 difficulty of fluorinating quartz (Spicuzza et al., 1998; Tanaka & Nakamura, 2013). Despite this, the
456 standard deviation of the associated $\Delta^{17}\text{O}_{0.5305}$ value as measured at either institution was <10 ppm.
457 Furthermore, it is particularly striking that, for a given $\Delta^{17}\text{O}$ definition, $\Delta^{17}\text{O}$ values determined at
458 the two institutions are in very good agreement. Similarly for $\Delta^{17}\text{O}$ values of KRS, with the very
459 small differences being essentially at or close to the measurement precision limit. For the purpose of
460 defining a two-point high precision reference line for silicate $\Delta^{17}\text{O}$ measurements, we therefore
461 consider that KRS and SKFS are both suitable materials, despite the measurement uncertainties
462 associated with the respective $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. In contrast, a difference of 11-12 ppm between
463 the two institutions was obtained for $\Delta^{17}\text{O}$ measurements of NBS 28 quartz. This may be related, at
464 least in part, to the small number of replicate measurements.

465 An additional point evident from Table 1 is that there is some compression of the $\delta^{17}\text{O}_{\text{VSMOW}}$ and
466 $\delta^{18}\text{O}_{\text{VSMOW}}$ scales as recorded by the mass spectrometer at Georg-August-Universität Göttingen
467 compared to the equivalent data measured on a nominally identical instrument at the Open University.
468 We cannot be confident, of course, that the Open University measurements are not also affected to
469 some extent by scale distortion. Because of the very close agreement obtained for $\Delta^{17}\text{O}$
470 measurements of SKFS and for KRS, the samples most enriched and depleted (respectively) in the
471 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
472 Göttingen instrument were of identical magnitude. Recently, Yeung et al. (2018) noted that pressure
473 baseline effects, resulting in scale distortion, are a potential source of inaccuracy in oxygen triple-
474 isotope measurements. The authors argued that the resulting non-linearity may be a contributory

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

480 Our results as presented in Table 1 demonstrate that the comparative $\Delta^{17}\text{O}$ data (regardless of
481 reference line assignment) are more robust, in terms of inter-laboratory reproducibility, than the $\delta^{17}\text{O}$
482 and $\delta^{18}\text{O}$ values from which they are derived. For consistency of numerical values, normalizing the
483 $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data is recommended. Although we have chosen to normalize to assigned $\delta^{18}\text{O}_{\text{VSMOW}}$
484 and $\Delta^{17}\text{O}_{0.5305, \gamma=0}$ for UWG-2, a similar exercise may be conducted by normalizing to, for example,
485 San Carlos olivine, with appropriate values. We note that the San Carlos olivine used at the Open
486 University is Type I (Macpherson et al., 2005; Thirlwall et al., 2006); it was supplied many years ago
487 by David Lowry (Royal Holloway, University of London). In contrast, the San Carlos olivine used at
488 Georg-August-Universität Göttingen appears to conform to the (more usual) Type II. Despite the $\delta^{18}\text{O}$
489 difference between Types I and II, we observed no distinction (within measurement precision)
490 between the respective $\Delta^{17}\text{O}$ values, when reported to a common reference line.

491 As an aside, we note that numerical inversion computations (performed by INB) similar to the
492 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
493 Table 1, in conjunction with quartz-water oxygen isotopic equilibrium fractionation data from Sharp
494 et al. (2016), give a formation temperature of approximately 35°C and with the $\delta^{18}\text{O}$ value of the
495 parent water being of the order -0.5 to -0.8 ‰ relative to VSMOW. This suggests that the flint nodule
496 closely represents the original precipitate from marine or near-coastal waters, fitting the quartz-water
497 fractionation line rather than a mixing curve connecting the primary value to low- $\delta^{18}\text{O}$ secondary
498 waters. Thus, the flint appears to have not interacted significantly with diagenetic or secondary
499 meteoric waters since nodule formation.

500 5.2 Evaluation of a KRS–SKFS reference line for silicate $\Delta^{17}\text{O}$ measurements

501 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
502 and SKFS produced a line characterized by $\lambda = 0.52720 \pm 0.00014$ (95% confidence) on the basis of
503 Open University measurements. The comparable result determined at Georg-August-Universität
504 Göttingen was very similar: $\lambda = 0.52727 \pm 0.00013$. Scatter of the individual measurements about the
505 respective regression line is illustrated in Figure 3. It is important to note that this λ value has no
506 inherent physical significance, as the two rocks are geologically unrelated. With $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data
507 reported relative to VSMOW, based on our normalizing to UWG-2 garnet, the corresponding $10^6\gamma$
508 value of the two-point line is -89 ± 4 (Open University) and -90 ± 4 (Georg-August-Universität
509 Göttingen), with uncertainties referring to the 95 % confidence interval. Clearly, there is very good
510 agreement about the definition of this potential reference line (KRS–SKFS), based on the
511 measurements made at the two institutions.

512 Table 2 reports the resulting $\Delta^{17}\text{O}$ values ($\pm 1\sigma$) of UWG-2, San Carlos olivine and NBS 28
513 relative to the KRS–SKFS line. The very small (2 ppm) difference between the Open University and
514 Georg-August-Universität Göttingen results for $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ of UWG-2 and for San Carlos olivine,
515 respectively, is significantly less than the associated measurement precision. Although comparative
516 measurements on NBS 28 showed a 12 ppm difference, this is the same as for the corresponding
517 $\Delta^{17}\text{O}$ data based on assigned (rather than empirical) reference lines, such as $\Delta^{17}\text{O}_{0.5305}$ and $\Delta^{17}\text{O}_{0.528}$
518 (Table 1) and might be related to the small number of replicate measurements, besides the inherent
519 difficulties of fluorinating NBS 28 without complications.

520 Because $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ data are independent of the isotopic composition of the reference gas
521 relative to which the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values are reported, there is no dependence on the
522 accuracy of calibration to the VSMOW scale, nor indeed to any other scale. Thus, as shown in Table
523 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
524 instead of the corresponding $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ results. Decoupling the accuracy of $\Delta^{17}\text{O}$
525 measurements from the accuracy of calibrating the working standard O_2 relative to VSMOW is a

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

529 The same methodology can be applied (for illustration of the principle) to the non-normalized
530 measurements of VSMOW and SLAP at Georg-August-Universität Göttingen reported by Pack et al.
531 (2016). Those data form a line characterized by $\lambda = 0.5270$ and $10^3\gamma = 0.340$ ‰, using $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$
532 data reported relative to the laboratory's working standard O_2 . Relative to this line as a reference,
533 $\delta^{17}\text{O}_{\text{WS}}$ and $\delta^{18}\text{O}_{\text{WS}}$ values of San Carlos olivine gave $\Delta^{17}\text{O} = -36 \pm 7$ ppm (1σ), which is identical to
534 the value obtained when the isotopic data were normalized to the VSMOW-SLAP scale. A similar
535 comparison can be made using the Okayama University data from the same study, giving $\Delta^{17}\text{O}$ of San
536 Carlos olivine = -39 ± 7 ppm (1σ).

537 It should be clear, however, that there is still a need for more laboratories to calibrate the $\delta^{17}\text{O}$ and
538 $\delta^{18}\text{O}$ values of their working standard gas relative to VSMOW and to check for instrument-related
539 non-linearity of the respective δ scales by measurements of VSMOW and SLAP. Every study that
540 utilizes oxygen triple isotope ratio measurements of silicates, oxides, phosphates, carbonates or other
541 solids for investigations involving interaction with water (e.g., Pack et al., 2013; Herwartz et al.,
542 2015; Bindemann et al., 2018) faces the problem that the water data may be accurately reported on the
543 VSMOW scale whereas data from the solids may be on a different scale. Therefore, even if the
544 measurements are of high precision, they might not be appropriate for investigating specific questions
545 in nature. Comparisons between theory (or modelling) and actual measurements require that all the
546 $\Delta^{17}\text{O}$ values are based on the same scale.

547 **6. Conclusions**

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

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

555 We have accurately characterized $\Delta^{17}\text{O}$ values of two silicates spanning a greater $\delta^{18}\text{O}$ range than
556 VSMOW–SLAP and suggest that these materials may be used for the reporting of $\Delta^{17}\text{O}$ data.
557 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
558 characterization of the oxygen isotopic composition of rocks and minerals than are the corresponding
559 $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values and can be determined to greater precision. Our flint standard, designated SKFS,
560 has $\Delta^{17}\text{O}_{0.528} = -114 \pm 2$ ppm (standard error). This material can therefore be used to calibrate the
561 position of a reference line of assigned slope such that it passes through the zero point of the
562 VSMOW scale. The accuracy of this calibration is dependent on the accuracy of our normalizing the
563 $\Delta^{17}\text{O}_{0.5305}$ value of UWG-2 garnet to -60 ppm (or $\Delta^{17}\text{O}_{0.528}$ to -46 ppm).

564 Alternatively, in combination with our low- $\delta^{18}\text{O}$ silicate standard, designated as KRS ($\Delta^{17}\text{O}_{0.528} =$
565 -69 ± 3 ppm, standard error), an empirical two-point silicate reference line may be defined from high
566 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
567 reported relative to this reference line are independent of whether $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data are reported
568 relative to VSMOW or to the ‘working standard’ O_2 , of any isotopic composition. This confers
569 significant advantages for inter-laboratory comparisons.

570 The $\delta^{18}\text{O}$ values of KRS and SKFS cannot be characterized as accurately or precisely as the
571 corresponding $\Delta^{17}\text{O}$ data relative to a reference line of assigned slope, such as $\Delta^{17}\text{O}_{0.528}$ or $\Delta^{17}\text{O}_{0.5305}$.
572 Some degree of inherent isotopic inhomogeneity undoubtedly contributes to the $\delta^{18}\text{O}$ variations. Our
573 ‘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)
574 for SKFS.

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

578 **Addendum**

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

587 For comparison with Table 2, the replicate $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements of KRS and SKFS
588 relative to the University of Oregon's working standard O_2 showed that least-squares linear regression
589 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
590 interval). With the working standard having been calibrated on the VSMOW-SLAP scale at the
591 Department of Earth and Space Sciences, University of Washington, Seattle, the ordinate axis offset
592 $10^3 \gamma$ of the KRS-SKFS line from VSMOW was -0.091 ± 0.009 (95 % confidence interval). Relative
593 to this reference line, the $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ mean and standard error values obtained for UWG-2, San
594 Carlos olivine and NBS 28, respectively, were: 51 ± 9 ($n = 7$), 51 ± 8 ($n = 5$) and $68 \pm 6 \text{ ppm}$ ($n = 3$).
595 All measurements were made later than at the Open University and at Georg-August-Universität
596 Göttingen because of INB being on six months sabbatical leave overseas during 2019.

597

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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.

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Figure Captions

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Figure 1

635 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

636 28 quartz, respectively – mostly from recent publications and using the original data. Error bars

637 represent $\pm 1\sigma$ (standard deviation). Infrared (10.6 μm) laser-assisted fluorination was used in all

638 cases, although heating protocols varied (focussed or defocussed beam; beam power; single step or

639 multi-step). Filled circles denote the use of BrF_5 for silicate fluorination; open circles indicate the use

640 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

641 replicates. Additional information:

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

643 ^b data obtained at Okayama University;

644 ^c measurements on Type I San Carlos olivine;

645 ^d measurements on Type II San Carlos olivine.

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Figure 2

649 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

650 of proposed silicate standards KRS and SKFS, together with corresponding results from San Carlos

651 olivine and NBS 28 quartz. Error bars represent \pm standard error of the mean, σ/\sqrt{n} . Key to symbols:

652 Open University data (●); Georg-August-Universität Göttingen data (◆). $\Delta^{17}\text{O}_{0.5305}$ results were

653 normalized to UWG-2 = -60 ppm (○ Open University, ◇ Georg-August-Universität Göttingen),

654 which provided the basis of the $\delta^{17}\text{O}_{\text{VSMOW}}$ data used for calculations of $\Delta^{17}\text{O}$ relative to other

655 reference lines, in conjunction with $\delta^{18}\text{O}_{\text{VSMOW}}$ values normalized to UWG-2 = 5.75 ‰.

656

657

Figure 3

658 Illustrating the deviation ($\Delta^{17}\text{O}_{\text{KRS-SKFS}}$) of individual data points from the linear least-squares
659 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
660 and SKFS. The $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ data are independent of the reference (such as VSMOW or the working
661 standard O_2) relative to which the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ are reported. The KRS–SKFS line as
662 measured at the Open University was characterized by slope (λ) of 0.52720 ± 0.00014 at the 95%
663 confidence interval. With $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ reported relative to VSMOW, on the basis of normalizing to
664 UWG-2 as discussed in the text, the corresponding $10^3\gamma$ value was -0.089 ± 0.004 . The comparable
665 findings from Georg-August-Universität Göttingen were: $\lambda = 0.52727 \pm 0.00013$ and $10^3\gamma = -0.090 \pm$
666 0.004 .

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Figure 4

670 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
671 NBS 28. Symbols are as for Figure 1. Associated error bars indicate standard error of the mean.
672 Where no error bars are shown, this indicates that the standard error is smaller than the size of the
673 associated data point symbol. The 95% confidence intervals of the reference line relative to which the
674 $\Delta^{17}\text{O}_{\text{KRS-SKFS}}$ values are calculated are also shown (----- Georg-August-Universität Göttingen;
675 Open University). The difference between the $\delta^{18}\text{O}_{\text{VSMOW}}$ values shown for San Carlos olivine is
676 attributed to Type I being used at the Open University whereas the sample analyzed at Georg-August-
677 Universität Göttingen was of Type II.

678

Table 1**A.** Open University measurements

Sample	n	$\delta^{17}\text{O}_{\text{VSMOW}}$ (‰)	σ (‰)	σ/\sqrt{n} (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	σ (‰)	σ/\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)	σ/\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 (‰)	σ/\sqrt{n} (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	σ (‰)	σ/\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)	σ/\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

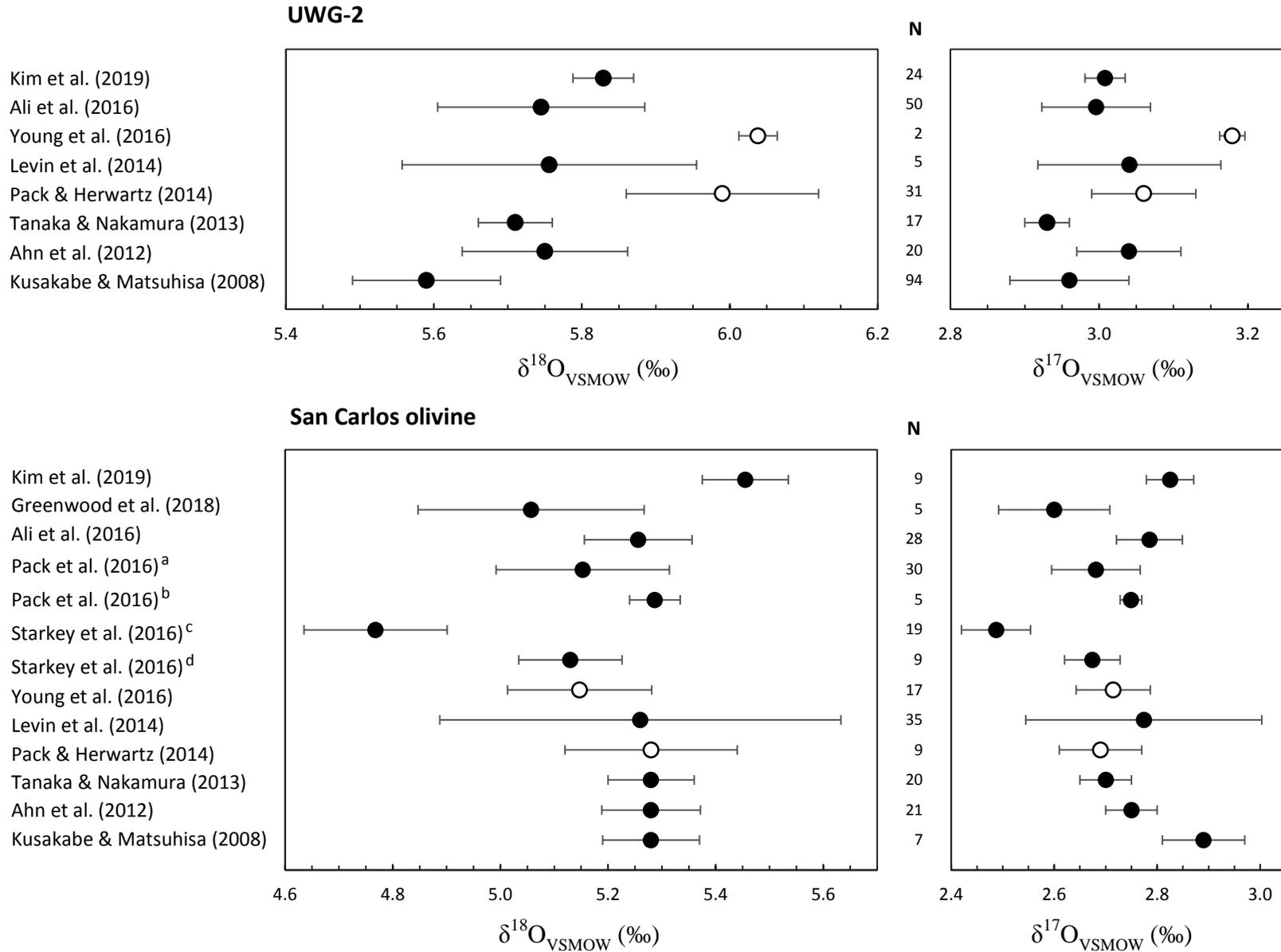


Figure 1

(Continued)

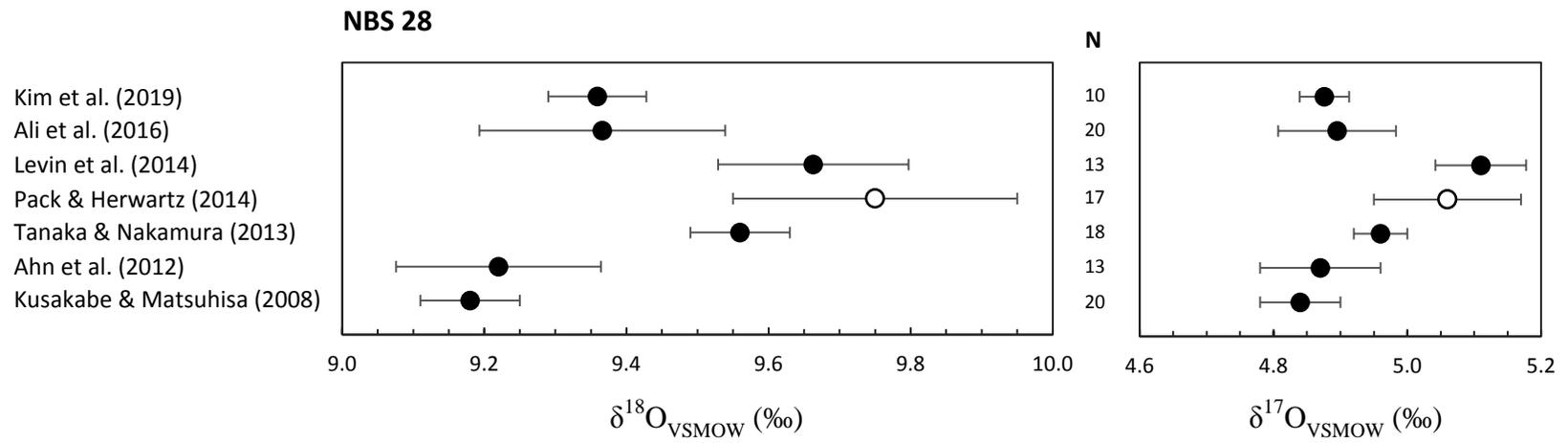


Figure 2

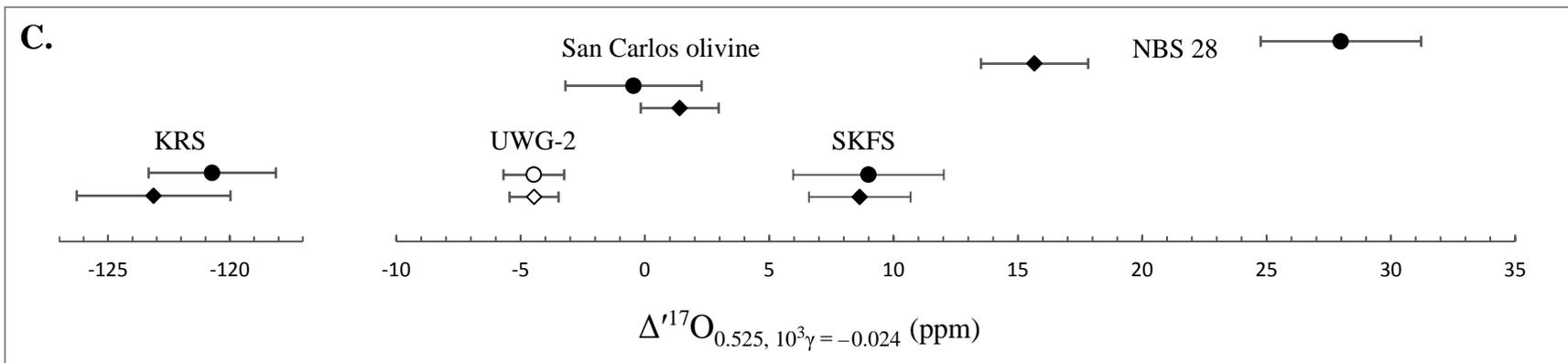
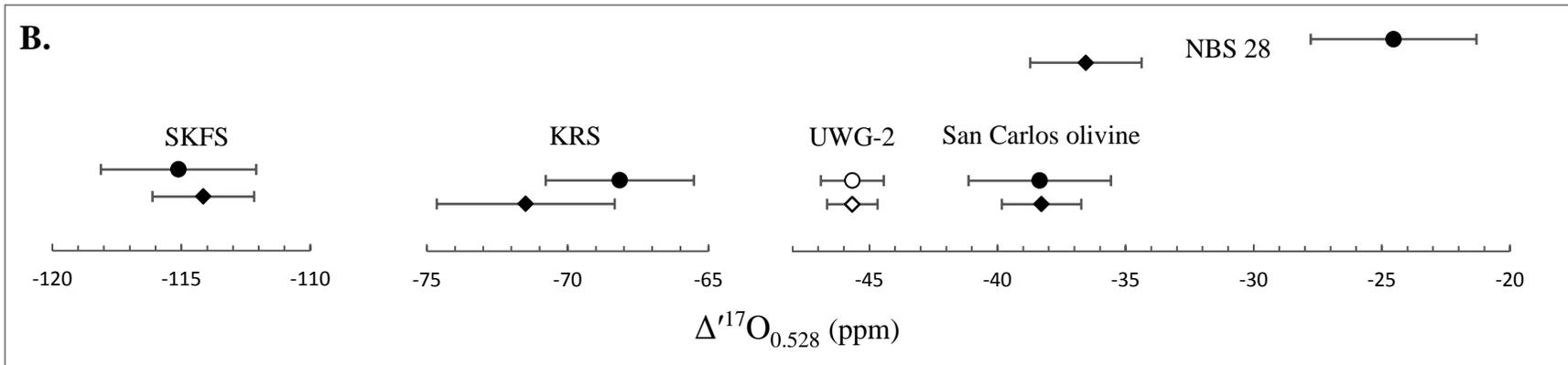
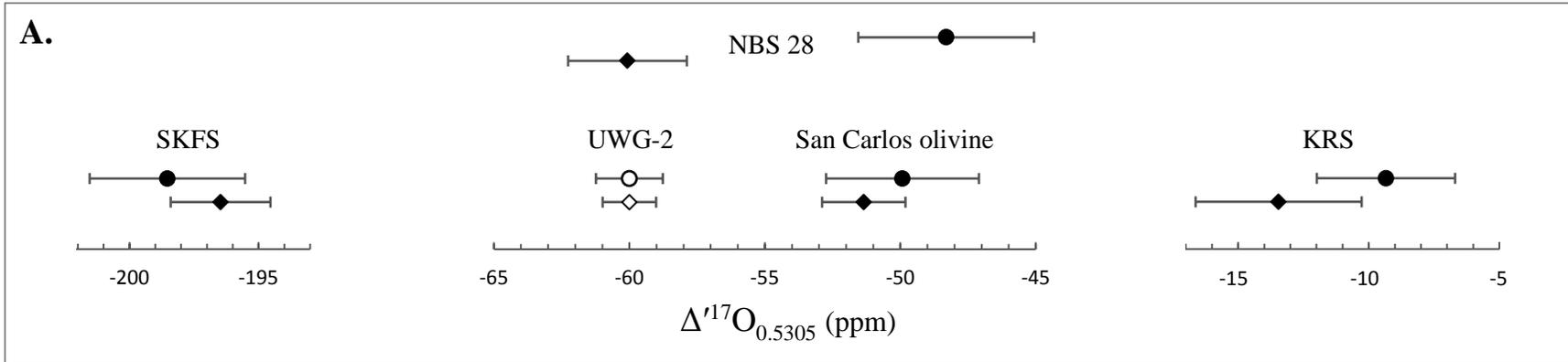
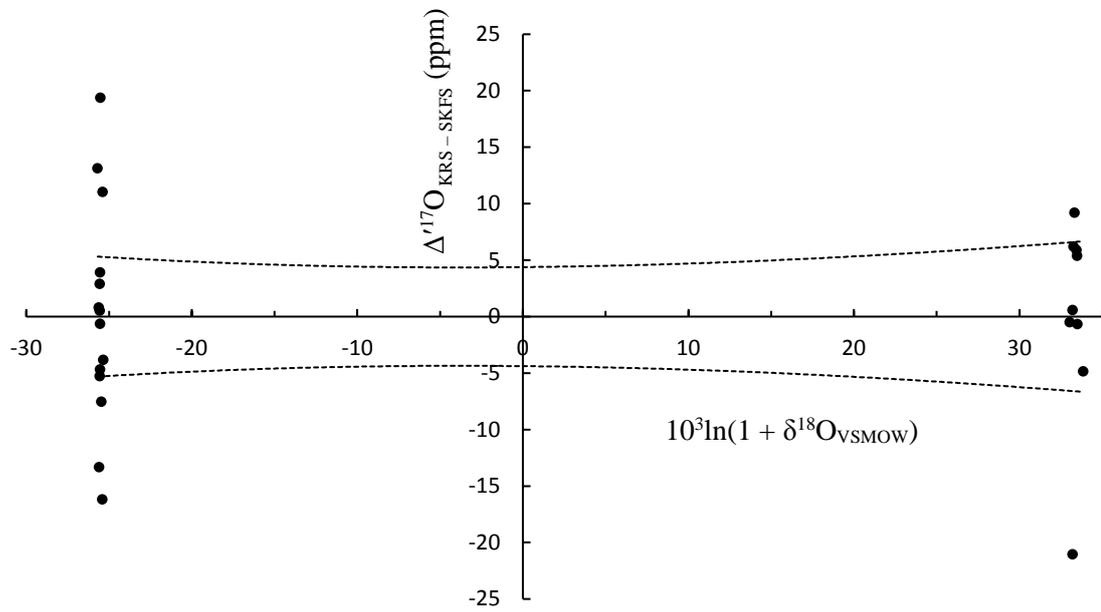


Figure 3

A. Open University measurements



B. Georg-August-Universität Göttingen measurements

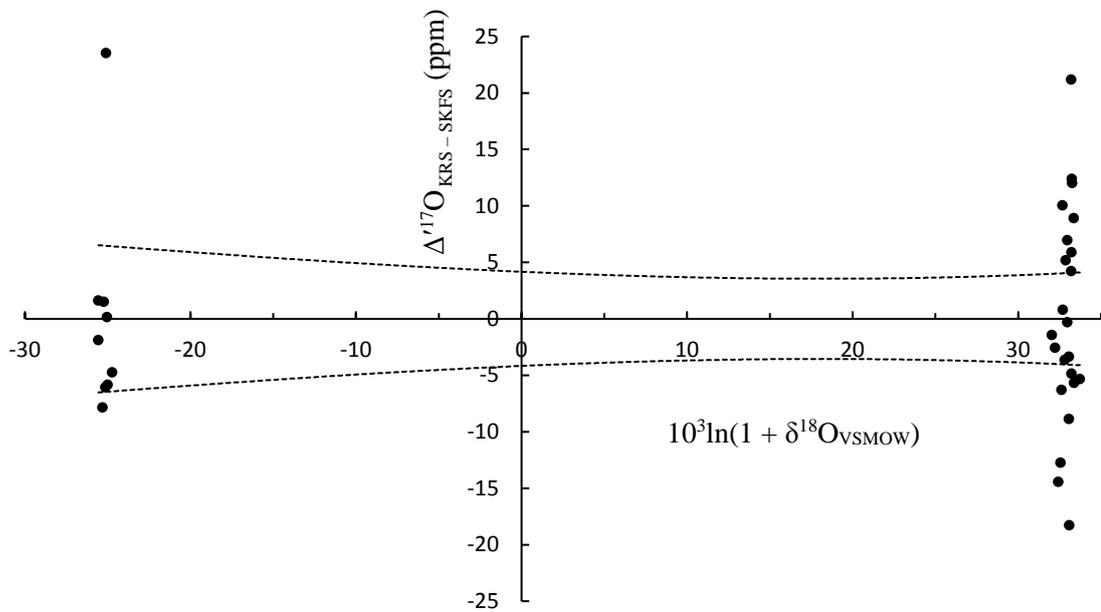
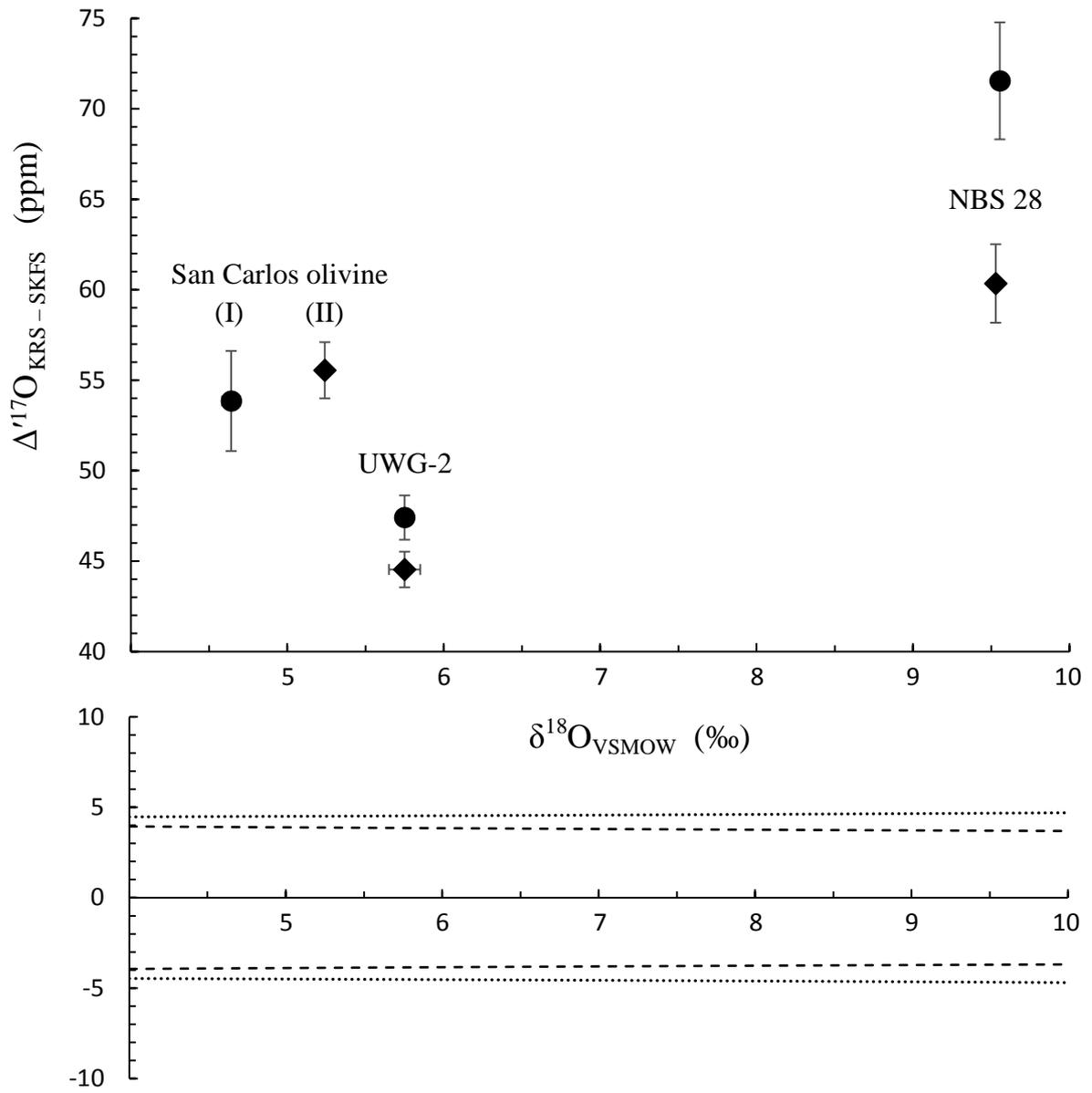


Figure 4



References

- Angert, A., Cappa, C.D., DePaolo D.J., 2004. Kinetic ^{17}O effects in the hydrologic cycle: indirect evidence and implications. *Geochim. Cosmochim. Acta* 68, 3487–3495.
- Ahn, I., Lee, J.I., Kusakabe, M., Choi, B.-G., 2012. Oxygen isotope measurements of terrestrial silicates using a CO_2 -laser BrF_5 fluorination technique and the slope of terrestrial fractionation line. *Geosci. J.* 16, 7–16.
- Bao, H., Cao, X., Hayles, J. A., 2016. Triple oxygen isotopes: fundamental relationships and applications. *Annu. Rev. Earth Planet. Sci.* 44, 463–492.
- Barkan, E., Luz B., 2007. Diffusivity fractionations of $\text{H}_2^{16}\text{O}/\text{H}_2^{17}\text{O}$ and $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$ in air and their implications for isotope hydrology. *Rapid Commun. Mass Spectrom.* 21, 2999–3005.
- Bindeman, I.N., Schmitt, A.K., Evans, D.A.D., 2010. Limits of hydrosphere-lithosphere interaction: Origin of the lowest known $\delta^{18}\text{O}$ silicate rock on Earth in the Paleoproterozoic Karelian rift. *Geology* 38, 631–634.
- Bindeman, I.N., Serebryakov, N.S., Schmitt, A.K., Vazquez, J.A., Guan, Y., Azimov, P.Ya., Astafiev, B.Yu, Palandri, J. Dobrzhinetskaya, L., 2014. Field and microanalytical isotopic investigation of ultradepleted in ^{18}O Paleoproterozoic “Slushball Earth” rocks from Karelia, Russia. *Geosphere* 10, 308–339.
- Bindeman, I.N., Zakharov, D.O., Palandri, J., Greber, N.D., Dauphas, N., Retallack, G.J., Hofmann, A., Lackey, J.S., Bekker A., 2018. Rapid emergence of subaerial landmasses and onset of a modern hydrologic cycle 2.5 billion years ago. *Nature* 557, 545–548.
- Cao, X., Bao, H., Gao, C., Liu, Y., Huang, F., Pen, Y., Zhang, Y., 2019. Triple oxygen isotope constraints on the origin of ocean island basalts. *Acta Geochim.* 38 (3), 327–334.
- Cao, X., Liu, Y., 2011. Equilibrium mass-dependent fractionation relationships for triple oxygen isotopes. *Geochim. Cosmochim. Acta* 75, 7435–7445.

- Clayton, R.N., Mayeda, T.K., 1988. Formation of ureilites by nebular processes. *Geochim. Cosmochim. Acta* 52, 1313–1318.
- Dauphas, N., Schauble E.A., 2016. Mass fractionation laws, mass-independent effects, and isotopic anomalies. *Annu. Rev. Earth Planet. Sci.* 44, 709–83.
- Gonfiantini, R., 1978. Standards for stable isotope measurements in natural compounds. *Nature* 271, 534–536.
- Greenwood, R.C., Barrat, J.-A., Miller, M.F., Anand, M., Dauphas, N., Franchi, I.A., Sillard, P., Starkey N.A., 2018. Oxygen isotopic evidence for accretion of Earth's water before a high-energy Moon-forming giant impact. *Sci. Adv.* 4, eaao5928.
- Hallis, L.J., Anand, M., Greenwood, R.C., Miller, M.F., Franchi, I.A., Russell S.S., 2010. The oxygen isotope composition, petrology and geochemistry of mare basalts: Evidence for large-scale compositional variation in the lunar mantle. *Geochim. Cosmochim. Acta* 74, 6885–6899.
- Herwartz, D., Pack, A., Friedrichs, B., Bischoff, A., 2014. Identification of the giant impactor Theia in lunar rocks. *Science* 344, 1146–1150.
- Herwartz, D., Pack, A., Krylov, D., Xiao, Y., Muehlenbachs, K., Sengupta, S., Di Rocco, T., 2015. Revealing the climate of snowball Earth from $\Delta^{17}\text{O}$ systematics of hydrothermal rocks. *Proc. Natnl. Acad. Sci. USA* 112, 5337–5341.
- Hofmann, M.E.G., Pack, A., 2010. Technique for high precision analysis of triple oxygen isotope ratios in carbon dioxide. *Anal. Chem.* 82, 4357–4361.
- Hofmann, M.E.G., Horváth B., Pack, A., 2012. Triple oxygen isotope equilibrium fractionation between carbon dioxide and water. *Earth Planet. Sci. Lett.* 319–320, 159–164.
- Hofmann, M.E.G., Horváth, B., Schneider, L., Peters, W., Schützenmeister, K., Pack, A., 2017. Atmospheric measurements of $\Delta^{17}\text{O}$ in CO_2 in Göttingen, Germany reveal a seasonal cycle driven by biospheric uptake. *Geochim. Cosmochim. Acta* 199, 143–163.

- Hulston, J.R., Thode H.G., 1965. Variations in S^{33} , S^{34} and S^{36} contents of meteorites and their relation to chemical and nuclear effects. *J. Geophys. Res.* 70, 3475–3484.
- Kaiser, J., 2008. Reformulated ^{17}O correction of mass spectrometric stable isotope measurements in carbon dioxide and a critical appraisal of historic ‘absolute’ carbon and oxygen isotope ratios. *Geochim. Cosmochim. Acta* 72, 1312–1334. Erratum: 73, 4616.
- Kaiser, J., 2011. Technical note: Consistent calculation of aquatic gross production from oxygen triple-isotope measurements. *Biogeosci.* 8, 1793–1811. Corrigendum: 8, 2561–2565.
- Kim, N.K., Kusakabe, M., Park, C., Lee, J.I., Nagao, K., Enokido, Y., Yamashita, S., Park, S.Y., 2019. An automated laser fluorination technique for high precision analysis of three oxygen isotopes in silicates. *Rapid Commun. Mass Spectrom.* 33, 641–649.
- Kusakabe, M., Matsuhisa, Y., 2008. Oxygen three-isotope ratios of silicate reference materials determined by direct comparison with VSMOW-oxygen. *Geochem. J.* 42, 309–317.
- Landais, A., Barkan, E., Luz, B., 2008. Record of $\delta^{18}\text{O}$ and ^{17}O -excess in ice from Vostok Antarctica during the last 150,000 years. *Geophys. Res. Lett.* 35, L02709.
- Landais, A., Steen-Larsen, H.C., Guillevic, M., Masson-Delmotte, V., Vinther, B., Winkler, R., 2012. Triple isotopic composition of oxygen in surface snow and water vapor at NEEM Greenland. *Geochim. Cosmochim. Acta* 77, 304–316.
- Luz, B., Barkan, E., 2010. Variations of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ in meteoric waters. *Geochim. Cosmochim. Acta* 74, 6276–6286.
- Macpherson, C.G., Hilton, D.R., Day, J.M.D., Lowry, D., Grönvold, K., 2005. High- $^3\text{He}/^4\text{He}$, depleted mantle and low- $\delta^{18}\text{O}$, recycled oceanic lithosphere in the source of central Iceland magmatism. *Earth Planet. Sci. Lett.* 233, 411–427.
- Matsuhisa, Y., Goldsmith, J.R., Clayton, R.N., 1978. Mechanisms of hydrothermal crystallization of quartz at 250°C and 15 kbar. *Geochim. Cosmochim. Acta* 42, 173–182.

- Meijer, H.A.J., Li, W.J., 1998. The use of electrolysis for accurate $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ isotope measurements in water. *Isotopes Environ. Health Stud.* 34, 349–369. Erratum: 35, 142 1999.
- Miller, M.F., 2002. Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochim. Cosmochim. Acta* 66, 1881–1889.
- Miller, M.F., Franchi, I.A., Sexton, A.S., Pillinger, C.T., 1999. High Precision $\delta^{17}\text{O}$ Isotope measurements of oxygen from silicates and other oxides: method and applications. *Rapid Commun. Mass Spectrom.* 13, 1211–1217.
- Miller, M.F., Greenwood, R.C., Franchi, I.A., 2015. Comment on “The triple oxygen isotope composition of the Earth mantle and understanding $\Delta^{17}\text{O}$ variations in terrestrial rocks and minerals” by Pack and Herwartz [*Earth Planet. Sci. Lett.* 390, 2014. 138–145]. *Earth Planet. Sci. Lett.* 418, 181–183.
- Pack, A., Herwartz, D., 2014. The triple oxygen isotope composition of the Earth mantle and understanding $\Delta^{17}\text{O}$ variations in terrestrial rocks and minerals. *Earth Planet. Sci. Lett.* 390, 138–145.
- Pack, A., Gehler, A., Süssenberger, A., 2013. Exploring the usability of isotopically anomalous oxygen in bones and teeth as paleo- CO_2 -barometer. *Geochim. Cosmochim. Acta* 102, 306–317.
- Pack, A., Höweling, A., Hezel, D.C., Stefanak, M.T., Beck, A-K., Peters, S.T.M., Sengupta, S., Herwartz, D., Folco, L., 2017. Tracing the oxygen isotope composition of the upper Earth’s atmosphere using cosmic spherules. *Nature Commun.* 8, 15702–15708.
- Pack, A., Tanaka, R., Hering, M., Sengupta, S., Peters, S., Nakamura, E., 2016. The oxygen isotope composition of San Carlos olivine on the VSMOW2-SLAP2 scale. *Rapid Commun. Mass Spectrom.* 30, 1495–1504.

- Pack, A., Toulouse, C., Przybilla, R., 2007. Determination of oxygen triple-isotope ratios of silicates without cryogenic separation of NF_3 – technique with application to analyses of technical O_2 gas and meteorite classification. *Rapid Commun. Mass Spectrom.* 21, 3721–3728.
- Rumble, D., Miller, M.F., Franchi, I.A., Greenwood, R.C., 2007. Oxygen three-isotope fractionation lines in terrestrial silicate minerals: an inter-laboratory comparison of hydrothermal quartz and eclogitic garnet. *Geochim. Cosmochim. Acta* 71, 3592–3600.
- Schoenemann, S.W., Schauer, A.J., Steig, E.J., 2013. Measurement of SLAP2 and GISP $\delta^{17}\text{O}$ and proposed VSMOW-SLAP normalization for $\delta^{17}\text{O}$ and $^{17}\text{O}_{\text{excess}}$. *Rapid Commun. Mass Spectrom.* 27, 582–590.
- Sharp, Z.D., Gibbons, J.A., Maltsev, O., Atudorej, V., Pack, A., Sengupta, S., Shock, E.L., Knauth, L.P., 2016. A calibration of the triple-isotope fractionation in the $\text{SiO}_2\text{--H}_2\text{O}$ system and applications to natural samples. *Geochim. Cosmochim. Acta* 186, 105–119.
- Sharp, Z.D., Wostbrock, J.A.G., Pack, A., 2018. Mass-dependent triple oxygen isotope variations in terrestrial materials. *Geochem. Persp. Lett.* 7, 27–31.
- Spicuzza, M., Day, J.M.D., Taylor, L.A., Valley J.W., 2007. Oxygen isotope constraints on the origin and differentiation of the Moon. *Earth Planet. Sci. Lett.* 253, 254–265.
- Spicuzza, M., Valley, J.W., Kohn, M.J., Girard, J.P., Fouillac, A.M., 1998. The rapid heating, defocused beam technique: a CO_2 -laser-based method for highly precise and accurate determination of $\delta^{18}\text{O}$ values of quartz. *Chem. Geol.* 144, 195–203.
- Starkey, N.A., Jackson, R.M., Greenwood, R.C., Parman, S., Franchi, I.A., Jackson, M., Fitton, J.G., Stuart, F.M., Kurz, M., Larsen, L.M., 2016. Triple oxygen isotopic composition of the high- $^3\text{He}/^4\text{He}$ mantle. *Geochim. Cosmochim. Acta* 176, 227–238.

- Tanaka, R., Nakamura, E., 2013. Determination of ^{17}O -excess of terrestrial silicate/oxide minerals with respect to Vienna Standard Mean Ocean Water VSMOW. *Rapid Commun. Mass Spectrom.* 27, 285–297.
- Thirlwall, M.F., Gee, M.A.M., Lowry, D., Matthey, D.P., Murton, B.J., Taylor, R.N., 2006. Low $\delta^{18}\text{O}$ in the Icelandic mantle and its origins: Evidence from Reykjanes Ridge and Icelandic lavas. *Geochim. Cosmochim. Acta* 70, 993–1019.
- Valley, J.W., Kitchen, N., Kohn, M.J., Niendorf, C.R., Spicuzza, M.J., 1995. UWG-2, a garnet standard for oxygen isotope ratios: Strategies for high precision and accuracy with laser heating. *Geochim. Cosmochim. Acta* 59, 5223–5231.
- Wiechert, U.H., Halliday, A.N., Palme, H., Rumble, D., 2004. Oxygen isotope evidence for rapid mixing of the HED meteorite parent body. *Earth Planet. Sci. Lett.* 221, 373–382.
- Winkler, R., Landais, A., Sodemann, H., Dümbgen, L., Prié, F., Masson-Delmotte, V., Stenni, B., Jouzel, J., 2012. Deglaciation records of ^{17}O -excess in East Antarctica: reliable reconstruction of oceanic normalized relative humidity from coastal sites. *Clim. Past* 8, 1–16.
- Yeung, L.Y., Hayles, J.A., Hu, H., Ash, J.L., Sun, T., 2018. Scale distortion from pressure baselines as a source of inaccuracy in triple-isotope measurements. *Rapid. Commun. Mass. Spectrom.* 32, 1811–1821.
- Young, E.D., Galy, A., Nagahara, H., 2002. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim. Cosmochim. Acta* 66, 1095–1104.
- Young, E.D., Kohl, I.E., Warren, P.H., Rubie, D.C., Jacobson, S.A., Morbidelli, A., 2016. Oxygen isotopic evidence for vigorous mixing during the Moon-forming giant impact. *Science* 351, 493–496.

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 $\text{O}_2\text{-8}$) 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
σ/\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
	σ/\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
σ/\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
σ/\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
σ/\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	
	Mean	-20.959	-39.874	-13.295	-24.899	
	σ	0.141	0.263	0.143	0.267	
	σ/\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	
10-2018		9.387	17.349	17.288	33.217	
		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	
		9.661	17.867	17.565	33.743	
05-2018		9.674	17.859	17.578	33.735	
Mean	9.520	17.605	17.422	33.477		
σ	0.216	0.408	0.218	0.414		
σ/\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
	09-2018 (A)	-4.702	-9.503	3.090	5.947
		-4.659	-9.404	3.133	6.047
		-4.835	-9.737	2.955	5.709
	09-2018 (B)	-4.795	-9.692	2.995	5.755
		-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	
-4.754		-9.607	3.037	5.841	
05-2018	-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
σ/\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
	σ/\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
	σ/\sqrt{n}	0.004	0.009	0.004	0.009