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Two-point normalization for reducing inter-laboratory discrepancies in $\delta^{17}O$, $\delta^{18}O$, and $\Delta'^{17}O$ of reference silicates

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Abstract

The $\delta^{17}O$ and $\delta^{18}O$ values of a number of terrestrial minerals and rocks have been determined using laser fluorination method worldwide. For the comprehensive and congruous interpretation of oxygen isotope data, the δ-values should be normalized by the two-point method (i.e., the VSMOW-SLAP scale) to eliminate inter-laboratory bias. In this study, the $\delta^{17}O$ and $\delta^{18}O$ values of VSMOW and SLAP were measured to calibrate our laboratory working standard O_2 gas. The O_2 gas liberated from the water samples was purified using the preparation line normally employed for solid samples, and analyzed by the same mass spectrometer. From the analyses of VSMOW and SLAP, the oxygen isotope compositions of the international silicate standards (UWG2 garnet, NBS28 quartz, and San Carlos olivine) were normalized to the VSMOW-SLAP scale (two-point calibration), and then the $\Delta'^{17}O$ values were determined. Using the δ-values obtained in this way, the inter-laboratory discrepancy of the $\delta^{17}O$ and $\delta^{18}O$ results of the silicate standards could be reduced. The VSMOW-SLAP scaling for $\delta^{17}O$ and $\delta^{18}O$ analysis of silicates provides the most effective way to obtain accurate and precise data. In reporting the $\Delta'^{17}O$ values, it is important to make the choice of the reference fractionation line into account because the $\Delta'^{17}O$ value is quite variable owing to the slope and y-intercept of the linear relation of the δ-values. The reference fractionation line obtained from the measurement of the low- and high-$\delta^{18}O$ reference silicates would help to compare $\Delta'^{17}O$ values. We confirmed that the $\Delta'^{17}O$ results of the international silicate standards based on the two-point silicate reference line were consistent with the results from other laboratories.

Keywords: Oxygen three isotope, Silicates, VSMOW-SLAP scaling, Inter-laboratory comparison, $\Delta'^{17}O$

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Introduction

Oxygen isotopic variations of rocks and minerals have been used in many fields of geo- and cosmochemistry. For the oxygen isotopic analysis of silicates, a laser fluorination method with dual-inlet mass spectrometry has been used for three decades, thereby contributing to the studies of terrestrial and extraterrestrial materials (Eiler 2001; Greenwood et al. 2017; Miller et al. 1999; Miller 2002; Sharp 1990; Spicuzza et al. 1998; Spicuzza et al. 2007). The oxygen isotope ratios of unknown samples are reported in delta (δ)-notation relative to the primary reference material, i.e., Vienna Standard Mean Ocean Water (VSMOW; Craig 1961). Many laboratories have calibrated their working standard O_2 gas against the VSMOW scale (Greenwood et al. 2018; Kusakabe and Matsuhisa 2008; Levin et al. 2014; Pack et al. 2016; Tanaka and Nakamura 2013). However, owing to different analytical settings, equipment, and calibration methods, discrepancies in the isotopic results of a given sample between laboratories have been noticed. Thus, it is necessary to reduce the potential analytical errors of each laboratory by introducing multiple reference materials. For water analysis, VSMOW and Standard Light Antarctica Precipitation (SLAP) are commonly used because the isotopic difference between VSMOW and SLAP is well established (Barkan and Luz 2005; Jabeen and Kusakabe 1997; Kusakabe and Matsuhisa 2008; Lin et al. 2010; Schoenemann et al. 2013). To achieve high precision and accuracy in the oxygen isotopic analysis of silicates, it is desirable to measure the oxygen isotope ratios of the silicates, VSMOW, and SLAP under the same analytical conditions, and then normalize the analytical results in the VSMOW-SLAP scale. However, some laboratories have indirectly calibrated their working standard O_2 gas using reference silicate standards only to which $\delta^{18}O$ values relative to VSMOW have been allocated (Ghoshmaulik et al. 2020; Levin et al. 2014; Miller et al. 2020; Young et al. 2014, 2016). This indirect calibration induces an inevitable inter-laboratory variability in the δ-values, because no consensus of δ-values for the silicate standards has been attained, and natural mineral samples may be isotopically heterogeneous.

Recently, precise $\delta^{17}O$ values of reference silicates have been reported (Miller et al. 2020; Wostbrock et al. 2020). The linear relationship between $\delta^{17}O$ and $\delta^{18}O$, defined as $\delta^{17}O = 0.52 \times \delta^{18}O$, has been known to follow a theoretical mass-dependent fractionation process (Matsuhisa et al. 1978). Since the development of the laser-based high-precision analytical method for three-oxygen isotopes, researchers have become interested in small variations in the $\delta^{17}O$ values of terrestrial silicates (Miller et al. 2020; Pack et al. 2016; Sharp et al. 2018; Tanaka and Nakamura 2013; Wostbrock et al. 2020). The small deviation of $\delta^{17}O$ is usually expressed as a vertical offset from the reference fractionation line, or $\Delta'^{17}O$. Thus, it is critical to evaluate how the reference line is obtained, as a small variability of the line arising from analytical systems used by different groups of people can induce a noticeable difference in $\Delta'^{17}O$.

Here, we present $\delta^{17}O$ and $\delta^{18}O$ values of VSMOW and SLAP that were determined by the conventional fluorination method that is used for the silicate analysis. Based on the standard water analyses, we normalized the oxygen isotope values of silicates relative to the VSMOW-SLAP scale. We propose that the VSMOW-SLAP normalization can reduce inter-laboratory differences in the $\delta^{17}O$ and $\delta^{18}O$ values of silicates. In addition, we support that a 2-point silicate reference line determined from low- and high-$\delta^{18}O$ silicates can be used for inter-laboratory comparison of the $\Delta'^{17}O$. Consequently, a systematic evaluation of the oxygen isotope compositions of silicates is necessary for an accurate inter-laboratory comparison.

Experimental method

After VSMOW was exhausted, the International Atomic Energy Agency (IAEA) has prepared VSMOW2, which is very close to the VSMOW in oxygen isotopic composition (Lin et al. 2010). Another international standard, SLAP2 (Standard Light Antarctic Precipitation 2), was also prepared by the IAEA to replace the SLAP which was also exhausted. The VSMOW2 and SLAP2 are isotopically indistinguishable from VSMOW and SLAP, respectively (Lin et al. 2010). In this work, we used VSMOW and SLAP as synonymous of VSMOW2 and SLAP2, respectively. To report the oxygen isotopic compositions of rocks and minerals relative to VSMOW, a working standard O_2 gas has to be calibrated by direct comparison with O_2 extracted from VSMOW. We decomposed the water by fluorination in a Ni reaction tube (Fig. 1). Two microliters of water sample was introduced into the reaction tube through a septum using a micro-syringe (Hamilton , USA). The water was rapidly condensed in the evacuated Ni reaction tube at liquid nitrogen temperature and then reacted with a sufficient amount of BrF_5 at 200 °C for 60 min. The product gases were passed through the purification line and purified using the same procedures as those followed for the silicate samples. The oxygen isotopic analysis of both the silicates and water was carried out at the Korea Polar Research Institute (KOPRI). The detailed analytical methods are described in Kim et al. (2019).

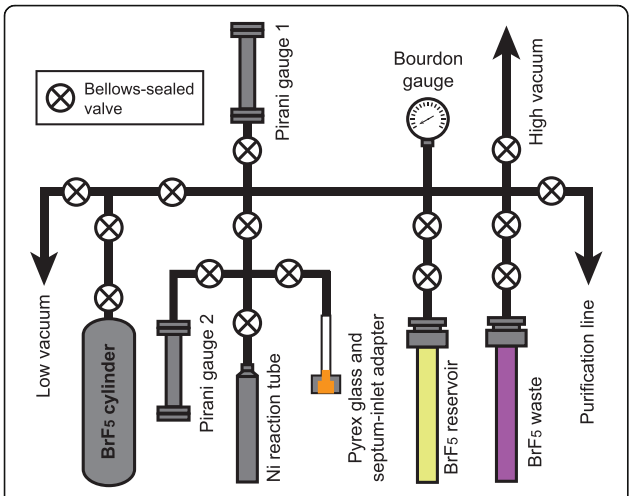

Fig. 1 Schematic diagram of BrF_5 introduction and water fluorination line modified from Kim et al. (2019). Two microliters of water was introduced into the vacuum line through a septum-inlet using a micro-syringe and then transferred in a Ni reaction tube with BrF_5 at liquid nitrogen temperature. The reaction was run at 200 °C for 1 h.

Results and discussion

Analysis of standard waters and VSMOW-SLAP normalization

Oxygen isotope ratios are conventionally reported as relative deviations from the standard water VSMOW in the delta notation $\delta^x O = (R^x_{sample}/R^x_{VSMOW}) - 1$, where $R = {}^xO/{}^{16}O$, $x = 17$ or 18. The $\delta^{17}O$ and $\delta^{18}O$ values of VSMOW are zero by definition. In order to report oxygen isotopic ratios of a sample in δ-notation, the measured raw δ-values need to be converted to the VSMOW scale. Normalization is achieved by direct determination of the δ-value of the working standard O_2 gas against that of VSMOW (Kusakabe and Matsuhisa 2008; Pack et al. 2016; Tanaka and Nakamura 2013). The results of the international standard waters are summarized in Table 1. The $\delta^{17}O$ and $\delta^{18}O$ values of VSMOW are zero by definition and the standard deviations were ± 0.030‰ and ± 0.056‰, respectively ($n = 11$) (Fig. 2 a). We obtained the oxygen isotopic composition of VSMOW-normalized SLAP as $\delta^{17}O = -29.148 \pm 0.082$‰ and $\delta^{18}O = -54.477 \pm 0.154$‰ ($n = 8$) (Fig. 2 b). The disagreement between the measured $\delta^{18}O$ value and the accepted value of − 55.5‰ strongly suggests the necessity of normalization of oxygen isotope data (Coplen 1988; Gonfiantini 1978). The difference between the measured and allocated values of SLAP is likely due to unknown isotopic fractionation during analytical operation and the system we used.

To ensure the accuracy of the isotopic results mainly for water samples, it is recommended to perform a 2-point normalization using VSMOW and SLAP (Coplen 1988; Gonfiantini 1978). By introducing the VSMOW-SLAP normalization, isotopic variations of a given sample that may arise from inter-laboratory differences in experimental settings and the use of different mass spectrometers can be minimized. There is, however, a problem when applying the normalization, as a consensus has not been attained for the $^{17}O/^{16}O$ ratio of SLAP (Barkan and Luz 2005; Jabeen and Kusakabe 1997; Kusakabe and Matsuhisa 2008; Schoenemann et al. 2013; Wostbrock et al. 2020). Although published $\delta^{17}O$ values of SLAP relative to VSMOW range from − 28.58 to − 29.74‰ (Jabeen and Kusakabe 1997; Kusakabe and Matsuhisa 2008; Pack et al. 2016; Wostbrock et al. 2020), ^{17}O-excess values, or $\Delta^{17}O$ (i.e., deviations of the $\delta^{17}O$ value from the global meteoric water line), for the published SLAP were close to zero (Schoenemann et al. 2013). The oxygen isotope data of meteoric water indicate that the global meteoric waters define a linear line with a slope (λ) of 0.528 in the plot of $\ln(\delta^{17}O + 1)$ vs. $\ln(\delta^{18}O + 1)$ (Kusakabe and Matsuhisa 2008; Luz and Barkan 2010; Schoenemann et al. 2013; Wostbrock et al. 2020). Therefore, we used a $\delta^{17}O$ value of SLAP of − 29.698‰ calculated using $\delta^{18}O^{assigned}_{VSMOW-SLAP} = -55.5$‰ and $^{17}O_{excess} = 0$ (Schoenemann et al. 2013).

We used the following equation to obtain the VSMOW-SLAP normalized δ-values:

$$\delta^x O^{normalized}_{sample/VSMOW-SLAP} = \exp\left[\ln\left(\delta^x O^{measured}_{sample/VSMOW} + 1\right) \frac{\ln\left(\delta^x O^{assigned}_{SLAP/VSMOW} + 1\right)}{\ln\left(\delta^x O^{measured}_{SLAP/VSMOW} + 1\right)}\right] - 1 \quad (1)$$

From the normalized $\delta^{17}O$ and $\delta^{18}O$ values, we report a $\Delta'^{17}O$ value which is the deviation of the $^{17}O/^{16}O$ ratio from the mass-dependent fractionation line defined by a linear function (Miller 2002):

$$\Delta'^{17}O = \ln(1 + \delta^{17}O) - \lambda_{RL} \times (1 + \delta^{18}O) - \gamma_{RL} \quad (2)$$

where λ_{RL} is the slope of the reference fractionation line in the linearized three-oxygen isotope plot and γ_{RL} is a y-axis offset of the line. The theoretical slope of mass-dependent fractionation line under thermodynamic equilibrium is 0.5305 (Matsuhisa et al. 1978; Wiechert et al. 2004). According to the oxygen isotope data of terrestrial rocks and minerals, the slope of the $\ln(1 + \delta^{17}O)$ versus $\ln(1 + \delta^{18}O)$ plot (i.e., the empirical fractionation line) is slightly smaller ($\lambda = 0.524$ to 0.528) than the theoretical value of 0.5305 (Ahn et al. 2012; Greenwood et al. 2018; Kusakabe and Matsuhisa 2008; Miller 2002; Miller et al. 2020; Spicuzza et al. 2007; Tanaka and Nakamura 2013). In our previous work, Kim et al.

Table 1 Individual standard water data of this study

Sample #	$\delta^{17}O_{VSMOW}$[a]	$\delta^{18}O_{VSMOW}$[a]	$\delta'^{17}O_{VSMOW}$[b]	$\delta'^{18}O_{VSMOW}$[b]	$\Delta'^{17}O$[c]
VSMOW					
VSMOW-42	− 0.045	− 0.099	− 0.045	− 0.099	0.007
VSMOW-43	− 0.030	− 0.044	− 0.030	− 0.044	− 0.007
VSMOW-44	0.047	0.086	0.047	0.086	0.001
VSMOW-45	− 0.003	0.015	− 0.003	0.015	− 0.011
VSMOW-47	− 0.036	− 0.064	− 0.036	− 0.064	− 0.002
VSMOW-48	0.009	0.030	0.009	0.030	− 0.006
VSMOW-49	− 0.014	− 0.030	− 0.014	− 0.030	0.002
VSMOW-50	0.034	0.064	0.034	0.064	0.000
VSMOW-51	0.024	0.035	0.024	0.035	0.005
VSMOW-52	− 0.005	− 0.017	− 0.005	− 0.017	0.005
VSMOW-53	0.019	0.025	0.019	0.025	0.006
Average	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
Standard deviation	**0.030**	**0.056**	**0.030**	**0.056**	**0.006**
SLAP					
SLAP-15	− 29.083	− 54.334	− 29.514	− 55.866	− 0.017
SLAP-16	− 29.256	− 54.685	− 29.692	− 56.237	0.001
SLAP-19	− 29.114	− 54.438	− 29.546	− 55.975	0.009
SLAP-20	− 29.276	− 54.713	− 29.713	− 56.267	− 0.005
SLAP-21	− 29.165	− 54.490	− 29.599	− 56.031	− 0.014
SLAP-23	− 29.079	− 54.347	− 29.510	− 55.879	− 0.006
SLAP-24	− 29.054	− 54.311	− 29.485	− 55.842	0.000
SLAP-25	− 29.155	− 54.499	− 29.588	− 56.041	0.001
Average	**− 29.148**	**− 54.477**	**− 29.581**	**− 56.017**	**− 0.004**
Standard deviation	**0.082**	**0.154**	**0.085**	**0.163**	**0.008**

Earlier results and 3σ outliers of VSMOW and SLAP analysis are not included due to analytical error
[a]δ-values are expressed as per mil relative to Vienna Standard Mean Ocean Water (VSMOW)
[b]Delta prime (δ') is defined as $10^3 \times \ln(\delta^x O + 1)$ by Miller (2002)
[c]Deviation of $^{17}O/^{16}O$ ratio of sample is estimated as: $\Delta'^{17}O = \delta'^{17}O_{VSMOW} - 0.528 \times \delta'^{18}O_{VSMOW}$

(2019) used λ_{RL} = 0.528 ± 0.020 and γ_{RL} = −0.040 ± 0.015 of the empirical fractionation line based on the data set for UWG2 garnet, NBS28 quartz, San Carlos olivine, basalt glass, and obsidian to calculate the $\Delta'^{17}O$ values. This empirical reference fractionation line was chosen to compare the $\Delta'^{17}O$ values determined from the reference lines based on a theoretical mass-dependent fractionation, meteoric waters, and two reference silicates as discussed in section "$\Delta'^{17}O$ of silicates".

$\delta^{17}O$ and $\delta^{18}O$ values of the international silicate standards on the VSMOW-SLAP scale

We measured the $\delta^{17}O$ and $\delta^{18}O$ values of the silicate minerals using the laser fluorination system (Kim et al., 2019). Table 2 shows the results normalized by the VSMOW-SLAP scale. Details of individual sample weight, oxygen yield, and δ-values relative to working standard O_2 gas are available in supplementary Table S1. The UWG2 garnet, NBS28 quartz, and San Carlos olivine have been widely used in laser fluorination oxygen isotope laboratories and can be used for inter-laboratory comparison. The recommended $\delta^{18}O$ values of UWG2 garnet and NBS28 quartz are 5.80 and 9.57‰ respectively (Hut 1987; Valley et al. 1995); however, no consensus has been reached yet on the San Carlos olivine. The $\delta^{18}O$ values of the San Carlos olivine vary widely compared to other natural mineral standards owing to its isotopic heterogeneity (Miller et al. 2020; Starkey et al. 2016).

Compilation of oxygen isotope data for the international silicate samples, i.e., UWG2 garnet, NBS28 quartz, and San Carlos olivine, over the last two decades shows a fairly wide variation in $\delta^{18}O$ values. They range from 5.40 to 6.04‰ for UWG2 garnet, 8.69 to 9.75‰ for

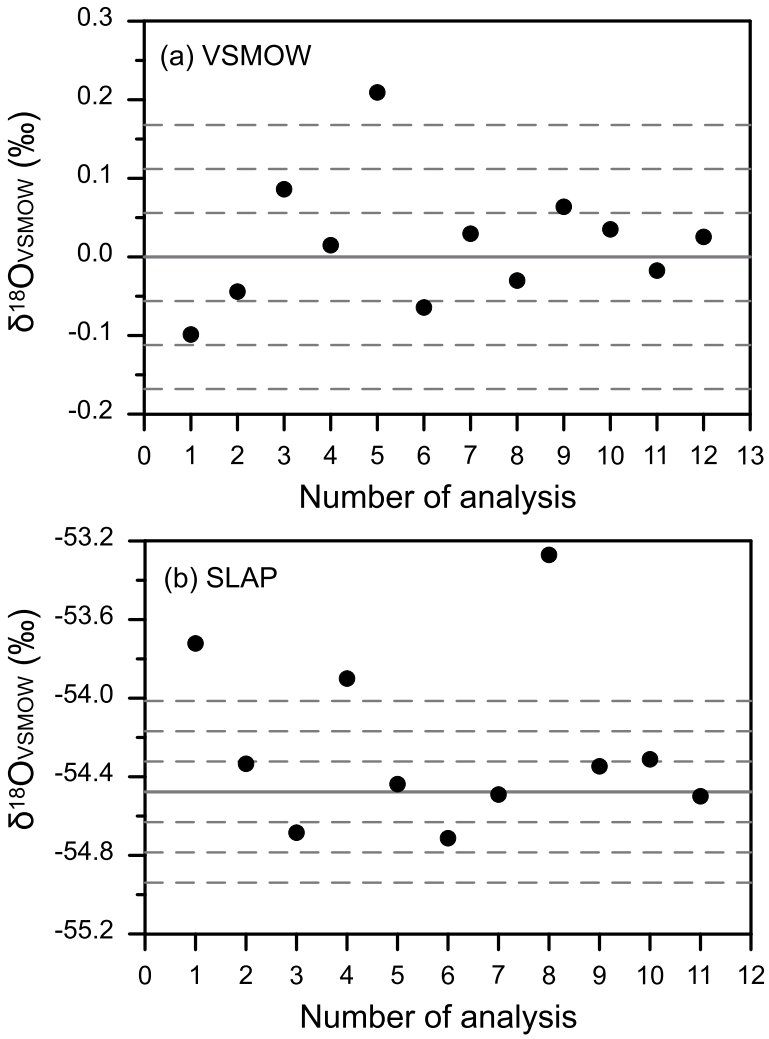

Fig. 2 Oxygen isotope compositions of **a** VSMOW and **b** SLAP. 3σ outliers are not included in the calculations of average and standard deviation. Solid gray lines indicate average values. Dashed gray lines display 1σ, 2σ, and 3σ standard deviations, respectively

NBS28 quartz, and 4.64 to 5.58‰ for San Carlos olivine as compiled in Table 3. The inter-laboratory reproducibilities which refer to the standard deviations of the compiled $\delta^{18}O$ values relative to VSMOW are 0.17‰ for UWG2 garnet, 0.30‰ for NBS28 quartz, and 0.21‰ for San Carlos olivine (Fig. 3 a–c). The ranges and reproducibilities of $\delta^{17}O$ for the international silicates are approximately one half of the $\delta^{18}O$ results because the oxygen isotopes normally follow mass-dependent rules (Fig. 4 a–c). Variability of $\delta^{17}O$ and $\delta^{18}O$ values likely arises from an analytical problem that is specific to experimental procedures for water and silicate analyses at each laboratory, as well as the way in which the working standard O_2 gas was calibrated against VSMOW. Several laboratories performed the calibration using the international silicate standards, such as UWG2 garnet (Levin et al., 2014; Miller et al., 2020), NBS28 quartz (Ghosh-maulik et al. 2020), and San Carlos olivine (Young et al., 2014, 2016) (Levin et al. 2014; Miller et al. 2020; Wostbrock et al. 2020; Young et al. 2016), or in some cases, atmospheric O_2 (Greenwood et al. 2018). Unlike the standard water (i.e., VSMOW) which is strictly homogeneous by its own nature, an isotopic heterogeneity of the natural mineral samples could cause analytical variability. In particular, the $\delta^{17}O$ values of silicate standards are still in poor agreement.

We have compiled the published oxygen isotope data of UWG2 garnet, NBS28 quartz, and San Carlos olivine on the VSMOW-SLAP scale (Table 3). In some cases, the measured $\delta^{18}O$ values of SLAP were so close to the value recommended by the IAEA that the VSMOW-SLAP normalization was not applied to the published

Table 2 $\delta^{17}O$ and $\delta^{18}O$ values of the waters and silicates measured in this study

Sample	Number of analysis	$\delta^{17}O_{VSMOW}$[a]	1SD[b]	$\delta^{18}O_{VSMOW}$[a]	1SD[b]	$\delta'^{17}O_{VSMOW\text{-}SLAP}$[c]	$\delta'^{18}O_{VSMOW\text{-}SLAP}$[c]	$\delta^{17}O_{VSMOW\text{-}SLAP}$[d]	$\delta^{18}O_{VSMOW\text{-}SLAP}$[d]	$\Delta'^{17}O$[e]	1SD[b]
Waters											
VSMOW	11	0.000	0.030	0.000	0.057	0.000	0.000	0.000	0.000		
SLAP	8	-29.148	0.083	-54.477	0.155	-30.148	-57.100	-29.698	-55.500		
Silicates											
UWG2 garnet	35	3.012	0.034	5.802	0.054	3.066	5.897	3.070	5.914	-0.007	0.011
NBS28 quartz	12	4.880	0.037	9.328	0.071	4.961	9.464	4.974	9.509	0.006	0.009
San Carlos olivine	9	2.835	0.046	5.436	0.080	2.885	5.526	2.889	5.541	0.008	0.011
Stenvs Klint Flint Standard	4	17.153	0.115	32.967	0.217	17.333	33.062	17.484	33.615	-0.077	0.012
Khitostrov Rock Standard	4	-12.947	0.181	-24.230	0.325	-13.282	-24.999	-13.194	-25.478	-0.046	0.009
Natural rocks											
Basalt glass	45	2.903	0.051	5.584	0.095	2.954	5.676	2.958	5.692	-0.002	0.010
Obsidian	127	4.384	0.075	8.404	0.144	4.459	8.531	4.469	8.568	-0.004	0.013
Working standard (O_2)		-5.071		-9.618		-5.181	-9.852	-5.168	-9.803		

[a]δ-values are expressed as per mil relative to Vienna Standard Mean Ocean Water (VSMOW)
[b]Standard deviation (SD) means an external reproducibility for each analyses
[c]Delta prime (δ') is defined as $10^3 \times \ln(\delta^x O+1)$ by Miller (2002). The VSMOW-SLAP scaling factor (1.019) is applied to linearized delta prime values
[d]δ-values are obtained from linearized delta values after normalization by the scaling factor
[e]Deviation of $^{17}O/^{16}O$ ratio of sample is estimated as: $\Delta'^{17}O = \delta'^{17}O_{VSMOW\text{-}SLAP} - 0.5278 \times \delta'^{18}O_{VSMOW\text{-}SLAP} + 0.040$

Table 3 Literature data of $\delta^{17}O$ and $\delta^{18}O$ for the international silicate standards and normalization methods

Sample	*n*	$\delta^{17}O_{VSMOW}$ (‰)	SD (1σ)	$\delta^{18}O_{VSMOW}$ (‰)	SD (1σ)	$\delta^{17}O$ VSMOW-SLAP	$\delta^{18}O$	Normalization	Reference
UWG2 garnet	38	2.808	–	5.443	–	–	–	SMOW	Franchi et al. (1999)
	94	2.91	0.08	5.50	0.08	2.96	5.59	VSMOW, SLAP (– 54.65‰)	Kusakabe and Matsuhisa (2008)
	20	2.81	0.07	5.40	0.11	3.04	5.73	VSMOW, SLAP (– 52.64‰)	Ahn et al. (2012)
	17	2.93	0.03	5.71	0.05	2.93[a]	5.71[a]	VSMOW, SLAP (– 55.11‰)	Tanaka and Nakamura (2013)
	31	–	–	5.756	0.119	–	–	UWG2 garnet (5.8‰)	Levin et al. (2014)
	5	3.06	0.07	5.99	0.13	–	–	VSMOW	Pack and Herwartz (2014)
	16	2.972	0.028	5.678	0.060	–	–	San Carlos olivine (5.3‰)	Young et al. (2014)
	50	2.996	0.073	5.745	0.14	–	–	VSMOW	Ali et al. (2016)
	20	3.011	0.029	5.779	0.061	–	–	VSMOW	Starkey et al. (2016)
	2	3.191	0.017	6.038	0.026	–	–	San Carlos olivine (5.2‰)	Young et al. (2016)
	16	2.986	0.023	5.75	0.046	–	–	UWG2 garnet (5.75‰)	Miller et al. (2020)[b]
	68	2.986	0.053	5.75	0.100	–	–	UWG2 garnet (5.75‰)	Miller et al. (2020)[c]
	9	–	0.057	–	0.115	2.932	5.696	VSMOW, SLAP (– 55.55‰)	Wostbrock et al. (2020)
	7	2.897	0.029	5.613	0.055	–	–	NBS28 quartz (9.577‰)	Ghoshmaulik et al. (2020)
	35	3.012	0.034	5.802	0.054	3.070	5.914	VSMOW, SLAP (– 54.477‰)	This study
NBS28 quartz	7	–	–	8.86	–	–	–	SMOW	Fouillac and Girard (1996)
	7	4.81	0.09	8.98	0.08	4.86	9.31	VSMOW, SLAP (– 53.54‰)	Jabeen and Kusakabe (1997)
	12	–	–	9.59	0.07	–	–	SMOW	Spicuzza et al. (1998)
	28	4.824	–	9.250	–	–	–	SMOW	Franchi et al. (1999)
	14	5.214	–	9.430	–	–	–	SMOW	Miller et al. (1999)
	20	4.76	0.06	9.04	0.07	4.84	9.18	VSMOW, SLAP (– 54.65‰)	Kusakabe and Matsuhisa (2008)
	13	4.52	0.09	8.69	0.14	4.86	9.18	VSMOW, SLAP (– 52.64‰)	Ahn et al. (2012)
	18	4.96	0.04	9.56	0.07	4.96[a]	9.56[a]	VSMOW, SLAP (– 55.11‰)	Tanaka and Nakamura (2013)
	17	–	–	9.633	0.138	–	–	UWG2 garnet (5.8‰)	Levin et al. (2014)
	13	5.06	0.11	9.75	0.20	–	–	VSMOW	Pack and Herwartz (2014)
	20	4.895	0.088	9.366	0.173	–	–	VSMOW	Ali et al. (2016)
	9	5.037	0.051	9.590	0.106	–	–	VSMOW	Starkey et al. (2016)
	5	5.009	0.021	9.555	0.040	–	–	UWG2 garnet (5.75‰)	Miller et al. (2020)[b]
	3	4.939	0.006	9.452	0.016	–	–	UWG2 garnet (5.75‰)	Miller et al. (2020)[c]
	13	–	0.055	–	0.106	4.986	9.577	VSMOW, SLAP (– 55.55‰)	Wostbrock et al. (2020)
	9	4.99	0.011	9.584	0.020	–	–	NBS28 quartz (9.577‰)	Ghoshmaulik et al. (2020)
	12	4.880	0.037	9.328	0.071	4.974	9.509	VSMOW, SLAP (– 54.477‰)	This study
San Carlos olivine	2	2.597	–	4.980	–	–	–	SMOW	Franchi et al. (1999)
	7	2.84	0.08	5.19	0.09	2.89	5.28	VSMOW, SLAP (– 54.65‰)	Kusakabe and Matsuhisa (2008)
	21	2.56	0.05	4.98	0.09	2.75	5.27	VSMOW, SLAP (– 52.64‰)	Ahn et al. (2012)
	20	2.70	0.05	5.280	0.08	2.70[a]	5.28[a]	VSMOW, SLAP (– 55.11‰)	Tanaka and Nakamura (2013)
	9	–	–	5.260	0.373	–	–	UWG2 garnet (5.8‰)	Levin et al. (2014)
	35	2.69	0.08	5.28	0.16	–	–	VSMOW	Pack and Herwartz (2014)
	24	2.726	0.06	5.177	0.113	–	–	San Carlos olivine (5.3‰)	Young et al. (2014)
	30	2.658	0.085	5.119	0.16	2.681	5.153	VSMOW, SLAP (– 55.143‰)	Pack et al. (2016)[d]

Table 3 Literature data of $\delta^{17}O$ and $\delta^{18}O$ for the international silicate standards and normalization methods *(Continued)*

Sample	*n*	$\delta^{17}O_{VSMOW}$ (‰)	SD (1σ)	$\delta^{18}O_{VSMOW}$ (‰)	SD (1σ)	$\delta^{17}O$ VSMOW-SLAP	$\delta^{18}O$	Normalization	Reference
	5	2.743	0.021	5.274	0.047	2.749	5.287	VSMOW, SLAP (− 55.366‰)	Pack et al. (2016)[e]
	5	2.785	0.064	5.256	0.100	–	–	VSMOW	Ali et al. (2016)
	19	2.487	0.067*	4.768	0.133*	–	–	VSMOW	Starkey et al. (2016)[f]
	9	2.674	0.054*	5.130	0.096*	–	–	VSMOW	Starkey et al. (2016)[g]
	17	2.714	0.072	5.148	0.135	–	–	San Carlos olivine (5.2‰)	Young et al. (2016)
	12	2.886	0.050	5.577	0.095	2.886[a]	5.577[a]	VSMOW, SLAP (− 55.394‰)	Sharp et al. (2016)
	9	2.409	0.089	4.641	0.173	–	–	UWG2 garnet (5.75‰)	Miller et al. (2020)[b, f]
	33	2.725	0.068	5.240	0.123	–	–	UWG2 garnet (5.75‰)	Miller et al. (2020)[c, g]
	18	–	0.048	–	0.096	2.720	5.268	VSMOW, SLAP (− 55.55‰)	Wostbrock et al. (2020)
	8	2.718	0.018	5.239	0.034	–	–	NBS28 quartz (9.577‰)	Ghoshmaulik et al. (2020)
	9	2.835	0.046	5.436	0.080	2.889	5.541	VSMOW, SLAP (− 54.477‰)	This study

[a]δ-values relative to the VSMOW-SLAP were assigned to the δ-values relative to VSMOW because measured oxygen isotope composition of SLAP was closed to − 55.5‰
[b]At Open University
[c]At Georg-August-Universitiät Göttingen
[d]At Geoscience Center (GZG), University of Göttingen
[e]At Institute for Study of the Earth's Interior (ISEI), Okayama University
[f]San Carlos olivine type 1
[g]San Carlos olivine type 2
*Errors are given as 2σ standard deviation or standard error of the mean
SD standard deviation, *SEM* standard error of the mean

data (Pack and Herwartz 2014; Tanaka and Nakamura 2013; Wostbrock et al. 2020). In other words, their δ-values were regarded as already normalized to the VSMOW-SLAP scale. Nevertheless, if we apply the VSMOW-SLAP normalization to their published $\delta^{17}O$ and $\delta^{18}O$ values of international silicate standards, the reproducibility of the reported values improved: 0.07 and 0.12‰ for UWG2 garnet, 0.07 and 0.20‰ for NBS28 quartz, and 0.09 and 0.15‰ for San Carlos olivine (Fig. 3 e, f and Fig. 4 e, f). The improved statistical indicator of the VSMOW-SLAP normalized values supports that the normalization can avoid the isotopic shrinking or stretching induced by analytical procedures and systems, leading to the correct isotopic ratios of natural rocks and minerals. For water analysis, this practice has provided good agreement with the $\delta^{17}O$ and $\delta^{18}O$ values of the Greenland Ice Sheet Precipitation (GISP) (Schoenemann et al. 2013). Consequently, the reporting of the δ-values normalized on the VSMOW-SLAP scale of silicates is required in order to make a valid comparison of the oxygen isotope data produced in different laboratories.

$\Delta'^{17}O$ of silicates

In oxygen isotope geochemistry, only $\delta^{18}O$ values are determined because $\delta^{17}O$ values are simply derived from the mass-dependent fractionation law, which has a slope of ~ 0.52 in a $\delta^{17}O$ vs. $\delta^{18}O$ diagram (Matsuhisa et al. 1978). $\Delta'^{17}O$, defined in Eq. 2, can display a vertical deviation of the $\delta^{17}O$ value from the reference fractionation line. Recently, it has been recognized that hydrothermally altered minerals and sediments have negative $\Delta'^{17}O$ values, which can be explained by water-rock interaction over a wide temperature range (Pack and Herwartz 2014; Sharp et al. 2018). This suggests that the precise determination of the $\Delta'^{17}O$ values of silicates may be used to establish new geochemical tracer. Published $\Delta'^{17}O$ values of the international reference silicates ranged from − 0.102 to 0.049‰ in UWG2 garnet, − 0.104 to 0.332‰ in NBS28 quartz, and − 0.103 to 0.12‰ in San Carlos olivine (Table 4, Fig. 5 a–c). The large variations may have arisen from the choice of different λ_{RL} and γ_{RL}. The literature values were obtained by assigning the slope and *y*-intercept of the linear equation based on the calculation of equilibrium oxygen isotope fractionation (Pack and Herwartz 2014; Wiechert et al. 2004), the measurements of arbitral silicate samples (Ahn et al. 2012; Kim et al. 2019; Kusakabe and Matsuhisa 2008; Miller 2002; Miller et al. 2020; Starkey et al. 2016; Tanaka and Nakamura 2013), and standard waters (Pack et al. 2016; Sharp et al. 2016; Wostbrock et al. 2020; Young et al. 2014). Recently, Miller et al. (2020) proposed an alternative

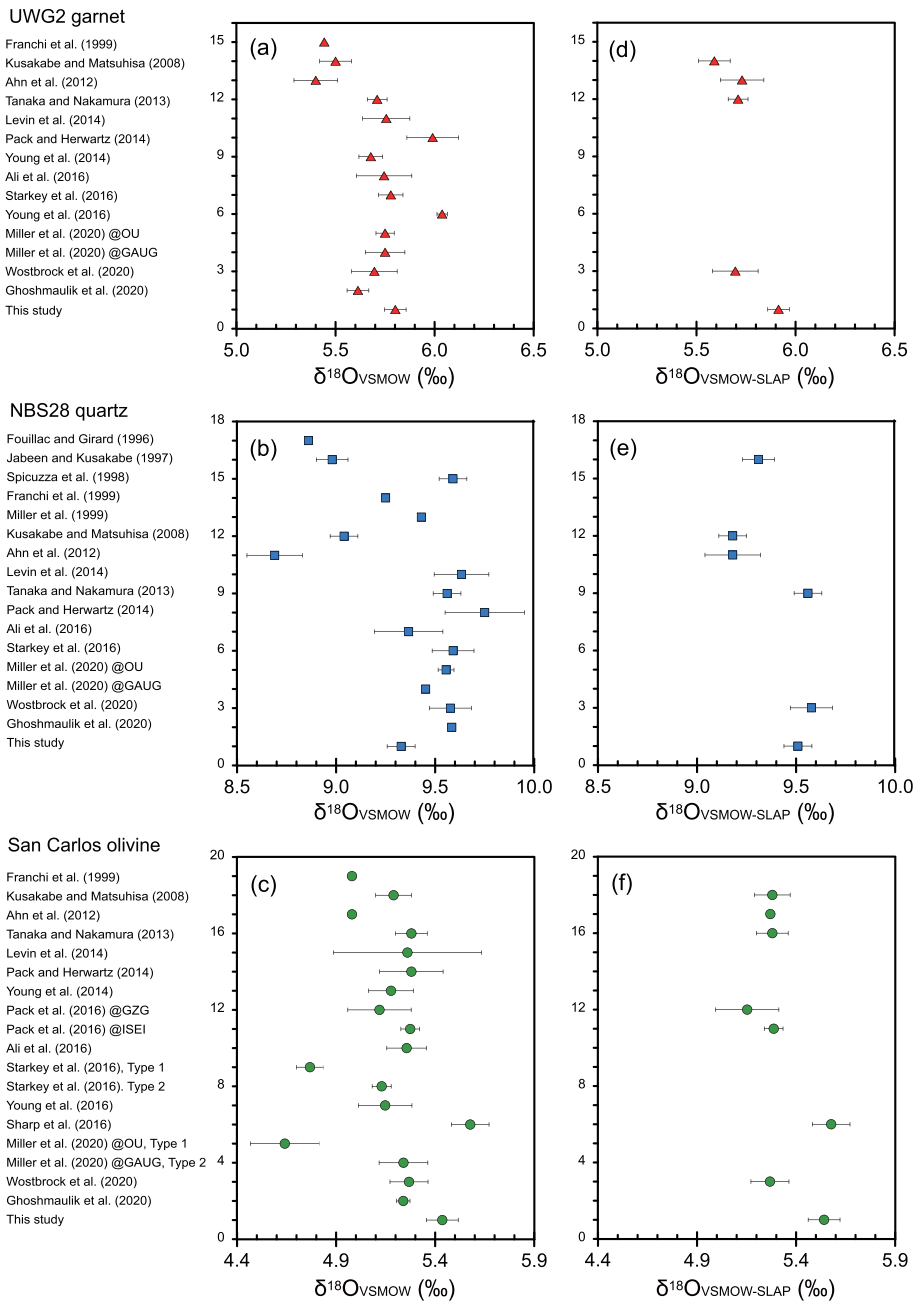

Fig. 3 Comparison of published $\delta^{18}O$ values relative to VSMOW (**a**–**c**) and VSMOW-SLAP (**e**–**f**) for international silicate standards

reference line using the low-$\delta^{18}O$ of KRS (Khitostorv Rock Standard, – 25.20‰) and high-$\delta^{18}O$ SKFS (Stevns Klint Flint Standard, 33.93‰) to report $\Delta'^{17}O$ values of UWG2 garnet, NBS28 quartz, and San Carlos olivine. The advantage of $\Delta'^{17}O$ values calculated from the KRS-SKFS 2-point reference line is that the $\Delta'^{17}O_{KRS\text{-}SKFS}$ can be reported without the careful calibration of the working standard O_2. Therefore, the measurements of KRS and SKFS may be useful for reporting a comparable $\Delta'^{17}O$ for oxygen isotope studies of silicates.

The different sets of λ_{RL} and γ_{RL} values may induce a misleading for the inter-laboratory comparison of $\Delta'^{17}O$. Therefore, we recalculated $\Delta'^{17}O$ values for the international silicate standards using four reference lines as follows: (i) λ_{RL} = 0.5305 and γ_{RL} = 0 for the equilibrium fractionation line; (ii) λ_{RL} = 0.528 and γ_{RL} = 0 for the VSMOW-SLAP line; (iii) λ_{RL} = 0.5278 and γ_{RL} = –

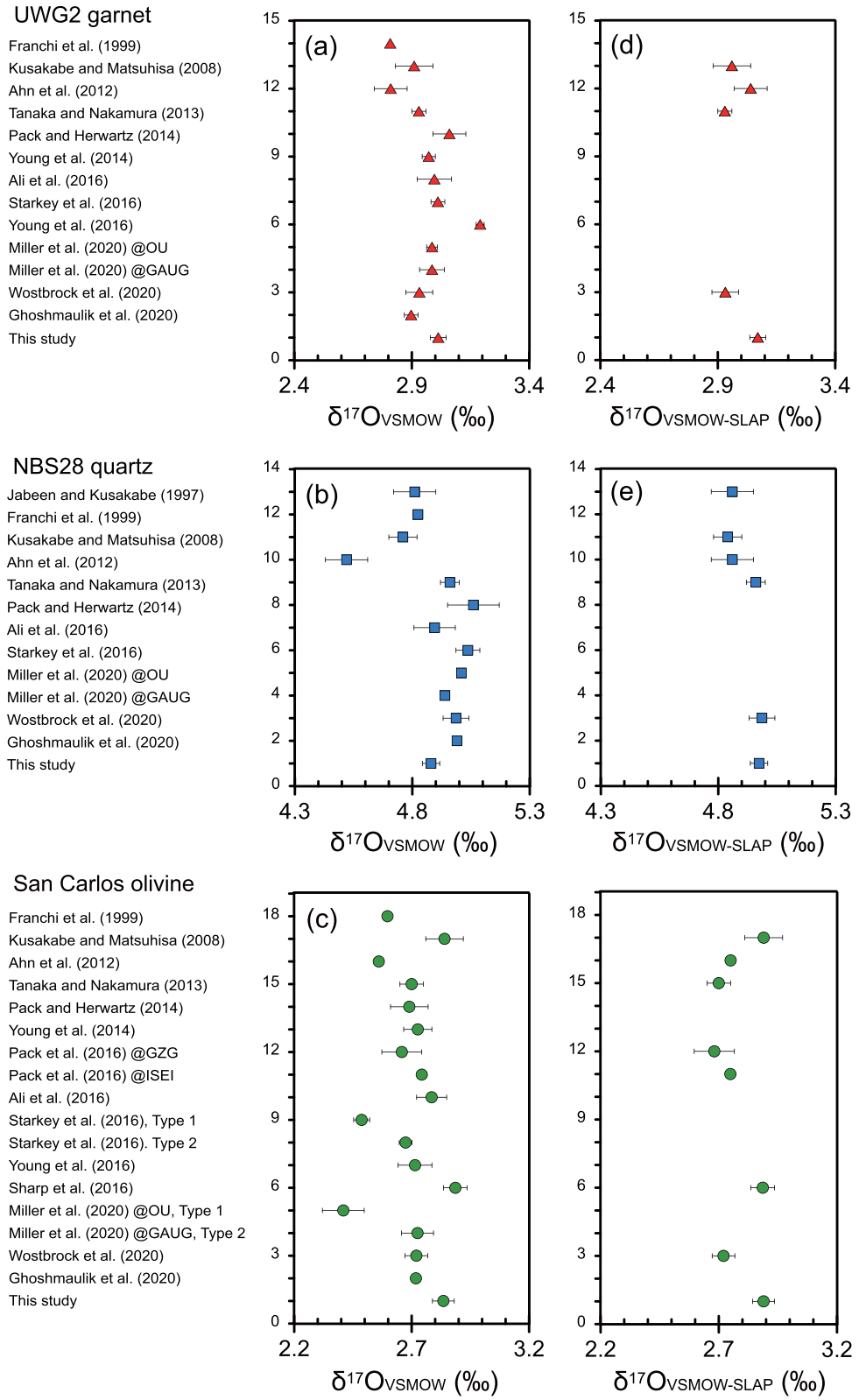

Fig. 4 Comparison of published $\delta^{17}O$ values relative to VSMOW (**a**–**c**) and VSMOW-SLAP (**e**–**f**) for international silicate standards

Table 4 Literature data of $\Delta'^{17}O$ and recalucalted $\Delta'^{17}O$ relative to different assigned reference lines

Sample	n	Literature data					Recalculated $\Delta'^{17}O$[a]				References
		$\Delta'^{17}O$ (‰)	SD (1σ)	SEM (1σ)	λ_{RL}	γ_{RL}	λ_{RL} = 0.5305 γ_{RL} = 0	λ_{RL} = 0.528 γ_{RL} = 0	λ_{RL} = 0.5278 γ_{RL} = -0.040	λ_{RL} = 0.5273 γ_{RL} = -0.099	
UWG2 garnet	38	-0.022	-	0.027	0.52	-	-0.076	-0.062	-0.021	0.041	Franchi et al. (1999)
	94	0.02	-	-	0.5263	-	-0.004	0.010	0.051	0.113	Kusakabe and Matsuhisa (2008)
	20	0.03	-	-	0.5248	-	-0.051	-0.037	0.004	0.065	Ahn et al. (2012)
	17	-0.008	0.029	-	0.5270	-0.07	-0.095	-0.081	-0.039	0.022	Tanaka and Nakamura (2013)
	5	-0.102	0.007	0.003	0.5305	-	-0.113	-0.098	-0.057	0.005	Pack and Herwartz (2014)
	16	-0.021	0.024	0.006	0.5280	-	-0.036	-0.022	0.019	0.081	Young et al., (2014)
	50	0.013	0.027	0.003	0.52	-	-0.047	-0.033	0.008	0.070	Ali et al. (2016)
	20	-0.017	0.010	0.002	0.5247	-	-0.050	-0.036	0.005	0.067	Starkey et al. (2016)
	2	-0.004	0.003	0.002	0.528	-	-0.008	0.007	0.049	0.111	Young et al. (2016)
	16	0.047	0.005	-	0.5272	0.282	-0.060	-0.046	-0.005	0.057	Miller et al. (2020)[b]
	68	0.049	0.008	-	0.5273	-0.089	-0.060	-0.046	-0.005	0.057	Miller et al. (2020)[c]
	9	-0.071	0.005	-	0.528	-	-0.085	-0.071	-0.030	0.032	Wostbrock et al. (2020)
	7	-0.062	0.001	-	0.528	-	-0.077	-0.063	-0.021	0.040	Ghoshmaulik et al. (2020)
	35	-0.007	0.011	-	0.528	-0.040	-0.061	-0.046	-0.007	0.057	This study
NBS28 qurartz	28	0.014	-	0.025	0.52	-	-0.072	-0.049	-0.007	0.056	Franchi et al. (1999)
	20	0.01	-	-	0.5263	-	-0.025	-0.003	0.039	0.102	Kusakabe and Matsuhisa (2008)
	13	0.04	-	-	0.5248	-	-0.080	-0.059	-0.017	0.046	Ahn et al. (2012)
	18	0.007	0.024	-	0.5270	-0.07	-0.100	-0.076	-0.034	0.030	Tanaka and Nakamura (2013)
	13	-0.104	0.008	0.002	0.5305	-	-0.100	-0.076	-0.034	0.030	Pack and Herwartz (2014)
	20	0.035	0.025	0.006	0.52	-	-0.062	-0.039	0.003	0.066	Ali et al. (2016)
	9	0.012	0.012	0.004	0.5247	-	-0.039	-0.016	0.026	0.090	Starkey et al. (2016)
	5	0.072	0.007	-	0.5272	0.282	-0.048	-0.025	0.017	0.081	Miller et al. (2020)[b]
	3	0.060	0.004	-	0.5273	-0.089	-0.064	-0.040	0.002	0.065	Miller et al. (2020)[c]
	13	-0.059	0.004	-	0.528	-	-0.083	-0.059	-0.017	0.047	Wostbrock et al. (2020)
	9	-0.059	0.006	-	0.528	-	-0.083	-0.059	-0.017	0.047	Ghoshmaulik et al. (2020)
	12	0.006	0.009	-	0.528	-0.040	-0.058	-0.035	0.006	0.071	This study
San Carlos olivine	2	0.007	-	0.019	0.52	-	-0.042	-0.029	0.012	0.073	Franchi et al. (1999)
	7	0.12	-	-	0.5263	-	0.090	0.103	0.144	0.205	Kusakabe and Matsuhisa (2008)
	21	0.01	-	-	0.5248	-	-0.079	-0.066	-0.025	0.036	Ahn et al. (2012)
	20	-0.006	-	-	0.5270	-0.07	-0.097	-0.084	-0.043	0.019	Tanaka and Nakamura (2013)
	35	-0.103	0.008	0.001	0.5305	-	-0.107	-0.094	-0.053	0.009	Pack and Herwartz (2014)
	24	-0.004	0.028	0.006	0.528	-	-0.017	-0.004	0.037	0.099	Young et al. (2014)
	30	-0.036	0.007	0.001	0.528	-	-0.054	-0.041	0.000	0.061	Pack et al. (2016)[d]
	5	-0.039	0.007	0.003	0.528	-	-0.051	-0.038	0.003	0.065	Pack et al. (2016)[e]
	5	0.055	0.084	0.038	0.52	-	0.000	0.013	0.054	0.116	Ali et al. (2016)
	19	-0.012	0.010[h]	0.002[h]	0.5247	-	-0.040	-0.028	0.013	0.075	Starkey et al. (2016)[f]
	9	-0.014	0.010[h]	0.003[h]	0.5247	-	-0.044	-0.031	0.010	0.071	Starkey et al. (2016)[g]
	17	0.000	0.005	0.001	0.528	-	-0.013	0.000	0.041	0.102	Young et al. (2016)
	12	-0.054	0.008	-	0.528	-	-0.069	-0.055	-0.014	0.048	Sharp et al. (2016)
	9	0.054	0.008	-	0.5272	0.282	-0.050	-0.039	0.002	0.064	Miller et al. (2020)[b, f]

Table 4 Literature data of $\Delta'^{17}O$ and recalucalted $\Delta'^{17}O$ relative to different assigned reference lines *(Continued)*

Sample	n	Literature data					Recalculated $\Delta'^{17}O$[a]				References
		$\Delta'^{17}O$ (‰)	SD (1σ)	SEM (1σ)	λ_{RL}	γ_{RL}	λ_{RL} = 0.5305 γ_{RL} = 0	λ_{RL} = 0.528 γ_{RL} = 0	λ_{RL} = 0.5278 γ_{RL} = -0.040	λ_{RL} = 0.5273 γ_{RL} = -0.099	
	33	0.056	0.009	-	0.5273	-0.089	-0.051	-0.038	0.003	0.064	Miller et al. (2020)[c, 9]
	18	-0.058	0.005	-	0.528	-	-0.071	-0.058	-0.017	0.045	Wostbrock et al. (2020)
	8	-0.045	0.002	-	0.528	-	-0.058	-0.045	-0.004	0.058	Ghoshmaulik et al. (2020)
	9	0.008	0.011	-	0.5278	-0.040	-0.045	-0.031	0.008	0.071	This study

SD standard deviation, *SEM* standard error of the mean
[a]Recalculated $\Delta'^{17}O$ values are from published δ-values relative to VSMOW and four different reference line as mentioned in the text
[b]At Open University
[c]At Georg-August-Universitiät Göttingen
[d]At Geoscience Center (GZG), University of Göttingen
[e]At Institute for Study of the Earth's Interior (ISEI), Okayama University
[f]San Carlos olivine type 1
[g]San Carlos olivine type 2
[h]Errors are given as 2σ standard deviation or standard error of the mean

0.040 for the terrestrial silicate line measured in this study; (iv) λ_{RL} = 0.5273 and γ_{RL} = −0.099 for the 2-point silicate reference line defined by the KRS and SKF measurements. The re-calculated $\Delta'^{17}O$ values indicate that the choice of λ_{RL} and γ_{RL} shows wide variation in $\Delta'^{17}O$ (Fig. 5 d–f). Although the reason for the $\Delta'^{17}O$ discrepancy is still uncertain, the different reference lines may interrupt a comparative study in a small $\Delta'^{17}O$ deviation of silicate. Each laboratory has calibrated its own reference O_2 gas in their own way as mentioned above. The oxygen isotopic ratios of these materials do not follow the theoretical mass-dependent fractionation line exactly. In other words, their $^{17}O/^{16}O$ ratios are fractionated, leading to a $\Delta'^{17}O$ shift from the fractionation line by physico-chemical processes such as evaporation, precipitation, and diffusion (Luz and Barkan 2010). The $^{17}O/^{16}O$ ratio of atmospheric O_2 also shows a variation at a given $^{18}O/^{16}O$ ratio relative to the water reference line due to photosynthesis, respiration, and photodissociation (Young et al. 2014). In silicates, hydrothermal alteration of the rocks and minerals produces a negative variation in $\Delta'^{17}O$ relative to the water reference line (Pack and Herwartz 2014; Sharp et al. 2018). Therefore, the different materials used to calibrate the working standard O_2 gas may lead to noticeable variability in the inter-laboratory comparison of $\Delta'^{17}O$. A reference line produced from the same materials and methods should be used for inter-laboratory comparison of $\Delta'^{17}O$ of silicates. Miller et al. (2020) suggested the use of the KRS and SKFS to define a 2-point silicate reference line and showed a superb agreement in $\Delta'^{17}O$ between the Open University and Georg-August-Universität Göttingen data based on the low- and high-$\delta^{18}O$ silicates reference line. In order to verify the 2-point silicate reference line, we measured the oxygen isotope compositions of two newly proposed silicate standards (KRS and SKFS) that are vastly different in δ-values and calculated $\Delta'^{17}O$ values of international silicate standards. They are $\Delta'^{17}O$ = 0.045 ± 0.011‰ for UWG2 garnet, 0.062 ± 0.009‰ for NBS28 quartz, and 0.060 ± 0.011‰ for San Carlos olivine. These values are in excellent agreement with the reported $\Delta'^{17}O$ values at Georg-August-Universität Göttingen: 0.049 ± 0.008‰ for UWG2 garnet, 0.060 ± 0.004‰ for NBS28 quartz, and 0.056 ± 0.009‰ for San Carlos olivine (Miller et al. 2020). Here we emphasize that $\Delta'^{17}O$ values should be evaluated by the identical reference fractionation line, that is the KRS-SKFS fractionation line. This approach can provide $\Delta'^{17}O$ results that are comparable with those calculated from the working standard O_2 calibrated by VSMOW-SLAP fluorination.

Conclusions

We determined the oxygen isotopic compositions of international standard waters (VSMOW and SLAP) and reference silicates (UWG2 garnet, NBS28 quartz, and San Carlos olivine) by fluorination using the same preparation line and mass spectrometer. According to the resulting oxygen isotope data of the above international reference silicates, we conclude that high precision $\delta^{17}O$ and $\delta^{18}O$ determination of silicates requires a 2-point calibration or VSMOW-SLAP scaling recommended by the IAEA for the analysis of water isotopes. Using this calibration, we can avoid instrumental bias and systematic differences between laboratories. The small variation in $\Delta'^{17}O$ with respect to the reference fractionation line is nowadays an important tool for investigating geological processes. We have confirmed that the $\Delta'^{17}O$ values of natural silicates calculated from 2-point reference line defined by low and high $\delta^{18}O$ silicates were consistent with the $\Delta'^{17}O$ values reported in other laboratories. Consequently, the VSMOW-SLAP normalization and two-point silicate

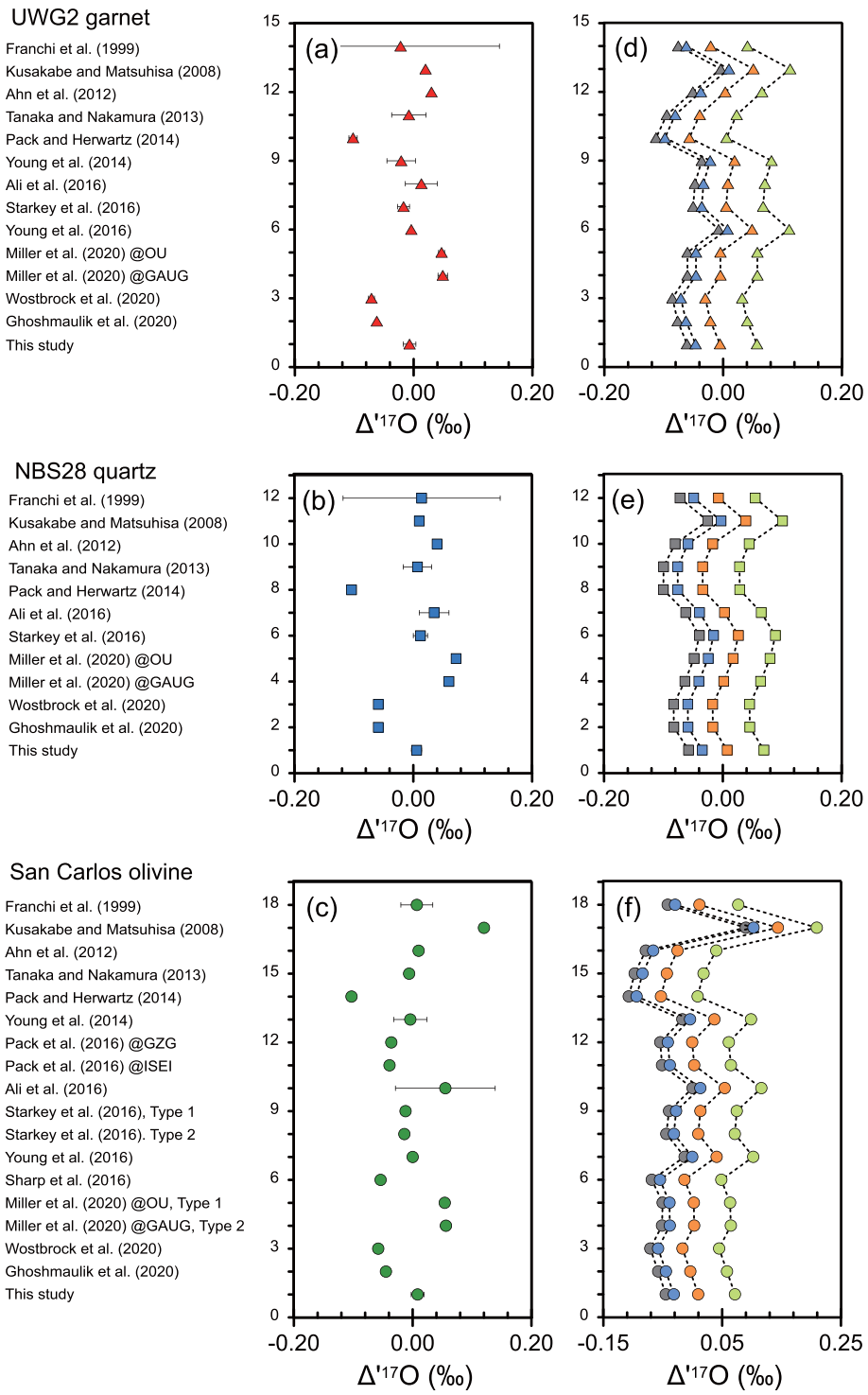

Fig. 5 Comparison of published $\Delta'^{17}O$ (**a**–**c**) and recalculated $\Delta'^{17}O$ using four different λ_{RL} and γ_{RL} (**d**–**f**). Gray symbol: $\lambda_{RL} = 0.5305$ and $\gamma_{RL} = 0$, light blue symbol: $\lambda_{RL} = 0.528$ and $\gamma_{RL} = 0$, orange symbol: $\lambda_{RL} = 0.5278$ and $\gamma_{RL} = -0.040$, light green: $\lambda_{RL} = 0.5273$ and $\gamma_{RL} = -0.099$ as mentioned in the text. The $\Delta'^{17}O$ values change significantly according to the different set of λ_{RL} and γ_{RL}

reference line can provide reliable data for $\delta^{17}O$, $\delta^{18}O$, and $\Delta'^{17}O$.

Abbreviations

VSMOW: Vienna Standard Mean Ocean Water; SLAP: Standard Light Antarctic Precipitation; IAEA: International Atomic Energy Agency; KOPRI: Korea Polar Research Institute; UWG: University of Wisconsin Garnet; NBS: National Bureau Standards; GISP: Greenland Ice Sheet Precipitation; KRS: Khitostorv Rock Standard; SKFS: Stevns Klint Flint Standard

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Authors' contributions

NKK and MK performed the measurements on waters and silicates and NKK wrote the draft of the manuscript. NKK, CP, and MK revised the manuscript critically. All authors read and approved the final version of the manuscript.

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Availability of data and materials

Research data have been provided in the manuscript and supporting information files.

Competing interests

The authors declare that they have no competing interests.

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