

## Oxygen three-isotope ratios of silicate reference materials determined by direct comparison with VSMOW-oxygen

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The  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of some international silicate reference materials such as NBS-28 quartz, NBS-30 biotite, UWG2 garnet, San Carlos olivine and some mineral separates of terrestrial origin were re-evaluated on the VSMOW-SLAP scale using the  $\text{CO}_2$ -laser fluorination technique. To report their  $\delta^{18}\text{O}$  values on the VSMOW-SLAP scale, the  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of  $\text{O}_2$  directly derived from VSMOW and SLAP were measured using the same preparation line as used for the silicates. Application of the VSMOW-SLAP scale to the above silicate reference samples resulted in the  $\delta^{18}\text{O}$  values of NBS-28 quartz, NBS-30 biotite, UWG2 garnet and San Carlos olivine that are 9.18, 4.88, 5.59 and 5.28‰, respectively. The data form a straight line in the  $10^3 \ln(1 + \delta^{17}\text{O}/10^3)$  vs.  $10^3 \ln(1 + \delta^{18}\text{O}/10^3)$  plot with a slope of  $0.526 \pm 0.003$  (standard error at 95% confidence limit), but the line for the waters (VSMOW, GISP, SLAP and MSA-6) seems to have a slightly steeper slope of  $0.528 \pm 0.001$ , although difference of the slopes is not statistically significant.

Keywords: oxygen three-isotope ratios, silicate reference materials, VSMOW-SLAP normalization, terrestrial fractionation line,  $\text{BrF}_5$  fluorination

### INTRODUCTION

Oxygen isotopic ratios of natural materials of geochemical interest are nowadays reported relative to Vienna Standard Mean Ocean Water or VSMOW (Coplen, 1995). The VSMOW-scale for reporting oxygen isotopic ratios of silicates and oxides contains ambiguity as large as 0.5‰ due mainly to various procedures of oxygen extraction from samples and the method of defining the VSMOW-scale in individual laboratories. For water samples oxygen isotopic comparison between a sample and VSMOW is precisely done by means of the  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibration method (Epstein and Mayeda, 1953), because the equilibrium fractionation factor of oxygen isotopes between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  ( $\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ ) is cancelled out as long as the equilibration is performed at a constant temperature. For silicates and oxides, however, the situation is different. Oxygen is liberated from samples in the form of  $\text{O}_2$  using fluorination techniques (Clayton and Mayeda, 1963; Sharp, 1990; and later development summarized in Taylor, 2005). Many workers convert this  $\text{O}_2$

to  $\text{CO}_2$  to compare its oxygen isotopic ratio with  $\text{CO}_2$  that has been equilibrated with reference water of a known isotopic composition (such as VSMOW). In this comparison, the equilibrium fractionation factor  $\alpha_{\text{CO}_2\text{-H}_2\text{O}}$  comes into the calculation. Since the reported values of  $\alpha_{\text{CO}_2\text{-H}_2\text{O}}$  at 25°C range from 1.0407 to 1.0412 (Friedman and O'Neil, 1977; Chako *et al.*, 2001), this variability causes serious uncertainty in  $\delta^{18}\text{O}$  values of minerals relative to VSMOW, if the oxygen isotopic ratios are determined using  $\text{CO}_2$  as an analytical gas for mass spectrometry. To avoid the ambiguity, direct comparison of  $\text{O}_2$  liberated from reference water samples with that from minerals is preferable. In the present note, we show the results of oxygen isotopic ratios of some international reference minerals by direct comparison of oxygen isotopic ratios of VSMOW and SLAP.

### ANALYTICAL PROCEDURES

Oxygen was extracted in the form of  $\text{O}_2$  from silicate and oxide minerals using a laser fluorination system with  $\text{BrF}_5$  as a reagent (Sharp, 1990). The laser used in our system was a  $\text{CO}_2$  laser with a maximum power of 12W and the wavelength of 10.6  $\mu\text{m}$  (Model JLC-1259, Japan Laser). The focal length was 10.2 cm and a minimum spot diameter was 100  $\mu\text{m}$ . A visible, coaxial He-Ne laser (wavelength of 633 nm) was attached to locate a target. The technical details of the laser fluorination system have

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been described by Kusakabe *et al.* (2004). The system consists basically of metal and glass parts; the reaction chamber and the purification line made of stainless steel (SUS316), and the purification line made of Pyrex® glass after the fluorination gases have been removed. The end of the glass line is connected on-line to the inlet system of an isotope ratio mass spectrometer equipped with triple collectors (modified SIRA12, VG Micromass). The modification of SIRA12 included (1) replacement of all electronic units (high voltage supply, source control unit, and vacuum gauge control) with modern ones supplied by Europa Scientific (UK), (2) replacement of the original dual inlet system with hand-made, dual mercury Toepler pumps, (3) replacement of the original solenoid type change-over valve with a pneumatically operated Kel-F seated micro inlet (VG Micromass), and (4) installation of WinIRMS, a Windows-based data acquisition software (Etchells, pers. commun.). With the micro inlet, the cross-seat leakage of reference and sample gases is negligible. The instrumental factors such as the effects of tailing of  $m/z$  32 and of background on  $m/z$  33 were evaluated following the method described by Horibe (1966). The intensity ratio of the  $m/z$  32 tailing to the  $m/z$  33 output was  $\sim 3 \times 10^{-3}$ , and the background over  $m/z$  33 was  $\sim 8 \times 10^{-4}$  based on the replicate analysis. Thus  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios are calculated from simultaneous measurement of  $m/z$  33/32 and 34/32 beam intensity ratios after the instrumental corrections. The  $\text{O}_2$  from sample was measured against a working standard  $\text{O}_2$  gas which is commercially available and 99.999% pure. The working standard has  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of 14.59‰ and 28.34‰ with respect to VSMOW, respectively, with a  $^{17}\text{O}$  excess of  $-0.28‰$  relative to the terrestrial fractionation line, which indicates its tropospheric origin (Miller, 2002).

Approximately 2 mg of sample was used for the analysis of silicate and oxide minerals. The sample was placed in a hole of a sample holder made of Ni, which was held in the reaction chamber. In our system, 8 samples can be loaded in a reaction chamber at one time. The samples were preheated at  $\sim 180^\circ\text{C}$  for several hours to overnight. Pre-fluorination at room temperature was applied for several hours to overnight (depending on mineral type) to remove any atmospheric moisture adsorbed on the surface of the sample, reaction chamber and a  $\text{BaF}_2$  window. Bromine pentafluoride gas of about 300 hPa was used for the fluorination reaction using the laser as a heat source. Reaction was visually observed through a binocular microscope. After purification of  $\text{O}_2$  gas through a series of cryogenic traps and a  $\text{KBr}$  trap for  $\text{F}_2$  removal, purified  $\text{O}_2$  was finally adsorbed in a calibrated cold finger containing Molecular Sieve 13X at liquid nitrogen temperature. From the pressure of  $\text{O}_2$  gas released from the Molecular Sieve 13X cold finger at room temperature, the

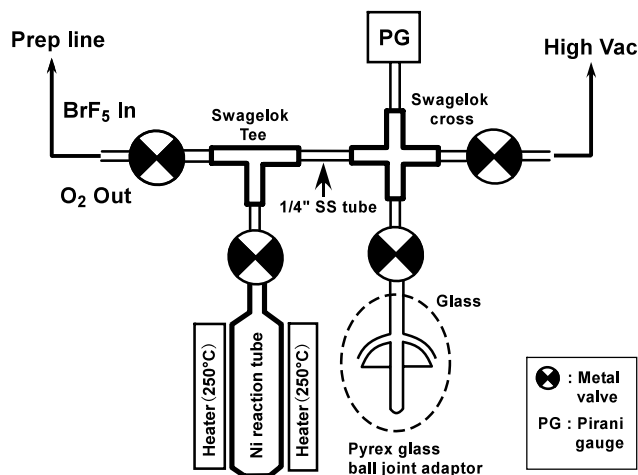


Fig. 1. Ni reaction tube used to decompose water to  $\text{O}_2$  by reaction with  $\text{BrF}_5$ . Two mg of water was taken in the Pyrex glass ball joint adaptor using a micro syringe. After evacuation of air the water was thoroughly distilled into the Ni reaction tube. Reaction temperature and duration were  $250^\circ\text{C}$  and 60 minutes, respectively.

reaction yield was calculated before isotopic measurement by the mass spectrometer.

For analysis of water samples the reaction chamber for minerals was replaced by a small Ni reaction tube with a capacity of 25 ml (Fig. 1). Two  $\mu\text{l}$  of water sample was distilled into the Ni reaction tube and reacted with  $\text{BrF}_5$  at  $250^\circ\text{C}$  for 60 min to liberate oxygen. The oxygen was purified in the same manner as  $\text{O}_2$  from minerals. A commercially available stainless steel reaction tube used in an early stage of the water fluorination runs was found to give a poor reproducibility of  $\delta$  values due probably to progressive fluoride formation on inner wall of the reaction tube, and thus abandoned.

## RESULTS AND DISCUSSION

$\delta$  notation was originally used as deviation in parts per thousand (permil) from those of Standard Mean Ocean Water (SMOW) (Craig, 1961) to report  $^{18}\text{O}/^{16}\text{O}$  ratio of sample. It was defined as  $\delta^{18}\text{O} (\text{‰}) = (R_S/R_{\text{SMOW}} - 1) \times 1000$ , where  $R_S$  and  $R_{\text{SMOW}}$  are the  $^{18}\text{O}/^{16}\text{O}$  ratios of sample and SMOW, respectively. The  $\delta$  notation is also used to report the  $^{17}\text{O}/^{16}\text{O}$  ratios. Since real SMOW is non-existent, VSMOW (Vienna-SMOW distributed by IAEA, Vienna) which is essentially the same as SMOW in the  $^{18}\text{O}/^{16}\text{O}$  and  $D/H$  ratios is taken as the standard (Gonfiantini, 1984; Hut, 1987). The absolute values of  $(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}$  and  $(^{17}\text{O}/^{16}\text{O})_{\text{VSMOW}}$  have been reported to be  $(2005.20 \pm 0.45) \times 10^{-6}$  (Baertschi, 1976) and  $(379.9 \pm 0.8) \times 10^{-6}$  (Li *et al.*, 1988), respectively. In the present

Table 1.  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of reference waters and minerals on the VSMOW-SLAP scale

Sample	Number of analysis	$\delta^{17}\text{O}_{\text{wst}}$	$1\sigma^{(a)}$	$\delta^{18}\text{O}_{\text{wst}}$	$1\sigma^{(a)}$	$\delta^{17}\text{O}_{\text{VSMOW}}^{(b)}$	$\delta^{18}\text{O}_{\text{VSMOW}}^{(b)}$	$10^3 \ln [1 + \delta^{17}\text{O}_{\text{VSMOW}} * 10^{-3}]$	$10^3 \ln [1 + \delta^{18}\text{O}_{\text{VSMOW}} * 10^{-3}]$
<b>Waters</b>									
VSMOW	7	-14.15	0.04	-27.13	0.06	0.00	0.00	0.00	0.00
SLAP	5	-42.95	0.07	-80.30	0.06	-29.21	-54.65	-29.64	-56.20
GISP	6	-26.88	0.08	-50.88	0.07	-12.91	-24.41	-12.99	-24.72
MSA6	2	-18.30	—	-35.06	—	-4.21	-8.15	-4.21	-8.19
<b>Minerals</b>									
NBS-28 quartz	20	-9.46	0.06	-18.34	0.07	4.76	9.04	4.75	9.00
NBS-30 biotite	7	-11.62	0.08	-22.45	0.08	2.57	4.81	2.57	4.80
UWG-2 garnet	94	-11.28	0.08	-21.78	0.10	2.91	5.50	2.91	5.48
San Carlos olivine	7	-11.35	0.08	-22.08	0.09	2.84	5.19	2.84	5.18
Augite	5	-11.23	0.05	-21.71	0.11	2.97	5.57	2.96	5.55
Enstatite	5	-9.37	0.12	-18.23	0.13	4.85	9.15	4.84	9.11
Fayalite	6	-11.24	0.10	-21.89	0.12	2.96	5.39	2.95	5.37
Forsterite	5	-8.79	0.04	-16.97	0.03	5.44	10.44	5.43	10.39
Magnetite	4	-17.43	0.04	-33.30	0.07	-3.32	-6.35	-3.33	-6.37
Zircon	6	-15.91	0.06	-30.44	0.06	-1.78	-3.40	-1.78	-3.41
Juan de Fuca basalt glass	37	-11.42	0.07	-22.03	0.12	2.77	5.24	2.77	5.23
Working standard (O <sub>2</sub> )						14.36	27.89	14.26	27.50

Sample	$10^3 \ln [1 + \delta^{17}\text{O}_{\text{VSMOW-SLAP}} * 10^{-3}]$	$10^3 \ln [1 + \delta^{18}\text{O}_{\text{VSMOW-SLAP}} * 10^{-3}]$	$\delta^{17}\text{O}_{\text{VSMOW-SLAP}}^{(c)}$	$\delta^{18}\text{O}_{\text{VSMOW-SLAP}}^{(c)}$	$\Delta^{17}\text{O}_M^{(d)}$
<b>Waters</b>					
VSMOW	0.00	0.00	0.00	0.00	0.00
SLAP	-30.12	-57.10	-29.67	-55.50	0.04
GISP	-13.20	-25.11	-13.11	-24.80	0.07
MSA6	-4.28	-8.32	-4.27	-8.28	0.11
<b>Minerals</b>					
NBS-28 quartz	4.83	9.14	4.84	9.18	0.01
NBS-30 biotite	2.61	4.87	2.61	4.88	0.04
UWG-2 garnet	2.95	5.57	2.96	5.59	0.02
San Carlos olivine	2.89	5.26	2.89	5.28	0.12
Augite	3.01	5.64	3.02	5.66	0.04
Enstatite	4.92	9.25	4.93	9.30	0.05
Fayalite	3.00	5.46	3.01	5.47	0.13
Forsterite	5.52	10.55	5.53	10.61	-0.04
Magnetite	-3.38	-6.47	-3.38	-6.45	0.02
Zircon	-1.81	-3.46	-1.81	-3.45	0.01
Juan de Fuca basalt glass	2.81	5.31	2.81	5.33	0.01
Working standard (O <sub>2</sub> )	14.48	27.95	14.59	28.34	-0.28

<sup>(a)</sup>Standard deviation of the distribution of analyses of each sample including chemical preparation.

<sup>(b)</sup> $\delta^{17}\text{O}_{\text{VSMOW}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  are calculated from  $\delta^{17}\text{O}_{\text{wst}}$  and  $\delta^{18}\text{O}_{\text{wst}}$ , respectively.

<sup>(c)</sup> $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  and  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  were obtained after normalizing  $10^3 \ln [10^{-3} \delta^{18}\text{O}_{\text{VSMOW-SLAP}} - 1]$  to -30.12 and  $10^3 \ln [10^{-3} \delta^{18}\text{O}_{\text{VSMOW-SLAP}} - 1]$  to -57.10, respectively. -57.10 is  $10^3 \ln [1 + (-55.50) * 10^{-3}]$ , and -30.12 is  $10^3 \ln [1 + \delta^{17}\text{O}_{\text{SLAP}} * 10^{-3}]$  of SLAP multiplied by (-57.10/-56.20).

<sup>(d)</sup> $\Delta^{17}\text{O}_M$  is the offset from a reference fractionation line (calculated according to Miller, 2002). Slope values of 0.5282 and 0.5263 were used for waters and silicates, respectively, using isotopic data scaled to VSMOW-SLAP.

study, we have measured  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  ratios of O<sub>2</sub> recovered from international reference water samples, i.e., VSMOW, SLAP and GISP, and from some international reference silicate minerals, to report their  $\delta$  values on the VSMOW-SLAP normalized scale as recommended by IAEA (Gonfiantini, 1978; Coplen, 1988, both recom-

mended only for  $\delta^{18}\text{O}$ ). Some of the samples analyzed here are widely used for inter-laboratory comparison of oxygen isotopic ratios of silicate minerals and rocks. They include NBS-28 quartz, NBS-30 biotite, UWG-2 garnet, and San Carlos olivine. Some mineral separates of forsterite, fayalite, enstatite, augite, magnetite, zircon, and

basalt glass from the Juan de Fuca Ridge were also analyzed to examine the  $^{18}\text{O}/^{16}\text{O}$ – $^{17}\text{O}/^{16}\text{O}$  relationship for terrestrial materials. The analytical results are given in Table 1. The reproducibility of the  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  measurements of silicates and oxides is generally smaller than  $\pm 0.1\text{‰}$  as evaluated through 94 replicate analyses of UWG-2 garnet which was found to be  $\pm 0.08\text{‰}$  for  $\delta^{17}\text{O}$  and  $\pm 0.09\text{‰}$  for  $\delta^{18}\text{O}$  (one sigma of the distribution of analyses including chemical preparation). The reproducibility applies to the period of more than a year. It was better than  $\pm 0.1\text{‰}$  for waters (Table 1).

The  $\delta^{17}\text{O}_{\text{VSMOW}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values in Table 1 were calculated relative to  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios of  $\text{O}_2$  directly derived from VSMOW and SLAP and thus VSMOW-SLAP scaled, following the procedures stated later. The VSMOW-SLAP scaling to any sample has been recommended in order to eliminate an instrumental bias characteristic to a mass spectrometer used. In other words, the measured  $\delta^{18}\text{O}$  value of SLAP should be normalized to  $-55.50\text{‰}$  (Gonfiantini, 1978; Coplen, 1988). The scaling factor calculated from the  $\delta^{18}\text{O}$  measurement can be applied to  $\delta^{17}\text{O}$ , because a good linearity is guaranteed when  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  are plotted on the  $10^3 \ln(1 + \delta^{17}\text{O}/10^3)$  vs.  $10^3 \ln(1 + \delta^{18}\text{O}/10^3)$  space (Miller, 2002). We assumed the VSMOW-SLAP scaling factors are applicable to silicates that have usually  $\delta$  values higher than waters.

The  $\delta^{18}\text{O}$  values of NBS-28 quartz, NBS-30 biotite, UWG-2 garnet and San Carlos olivine obtained by different laboratories were compared (Table 2). The range of reported  $\delta^{18}\text{O}$  values of NBS-28 quartz is surprisingly big, i.e., 8.8 to 10.0‰. The variability results from different methods of oxygen extraction, choice of analytical gas for mass spectrometric analysis and whether the VSMOW-SLAP scaling has been applied (mostly not). Historically,  $\text{O}_2$  was extracted using  $\text{BrF}_5$  as a fluorination reagent in an externally heated Ni reaction tube (e.g., Clayton and Mayeda, 1963). The use of an infrared laser as a heating device was later introduced (Sharp, 1990). Laser heating has become popular because it has advantages to give temperatures high enough to decompose most refractory minerals under  $\text{BrF}_5$  atmosphere and to give high analytical efficiency. The choice of an external or laser heating does not matter for decomposition of quartz which reacts with  $\text{BrF}_5$  at temperatures as low as 500°C. Many researchers who are interested only in  $\delta^{18}\text{O}$  values convert  $\text{O}_2$  to  $\text{CO}_2$  for isotopic analysis with a mass spectrometer. The isotopic composition of the  $\text{CO}_2$  is then compared with that of  $\text{CO}_2$  that has been equilibrated with a reference water like VSMOW. The oxygen isotopic fractionation factor between  $\text{CO}_2$  and water ( $\alpha_{\text{CO}_2\text{-H}_2\text{O}}$ ) has to be applied to calculate  $\delta^{18}\text{O}$  values of silicates and oxides relative to VSMOW from measured  $m/z$  46/44 ratios of the equilibrated  $\text{CO}_2$ . It should be noted that the value of  $\alpha_{\text{CO}_2\text{-H}_2\text{O}}$  has not been agreed upon among re-

searchers; it ranges from 1.0407 to 1.0417 at 25°C (summarized by Chako *et al.*, 2001), resulting in an uncertainty of silicate  $\delta^{18}\text{O}$  as much as  $\pm 0.5\text{‰}$ . It should also be noted that many papers describing silicate  $\delta^{18}\text{O}$  values obtained through the  $\text{CO}_2$  method do not mention which of the  $\text{CO}_2$ – $\text{H}_2\text{O}$  fractionation factors was used. This makes the choice of the best  $\delta^{18}\text{O}$  value for NBS-28 quartz difficult on the VSMOW scale. Valley *et al.* (1995) recommended a  $\delta^{18}\text{O}$  value of +5.8‰ relative to VSMOW for UWG-2, a garnet standard now widely used as a reference for oxygen isotopic analysis of silicates by laser fluorination techniques. For the  $\delta^{18}\text{O}$  value of UWG-2 garnet on the VSMOW-scale, they assumed  $+9.59 \pm 0.12\text{‰}$  for NBS-28 based on a compilation of literature values reported by various laboratories (Hut, 1987; Gonfiantini *et al.*, 1995). In the data compilation, it is not clear which methods were used for determining the VSMOW-scale in individual laboratories.

As shown in Table 2, our  $\delta^{18}\text{O}$  values of NBS-28 quartz, NBS-30 biotite, UWG-2 garnet and San Carlos olivine relative to VSMOW (VSMOW-SLAP scaled) were  $9.18 \pm 0.07\text{‰}$  ( $1\sigma$ ,  $n = 20$ ),  $+4.88 \pm 0.08\text{‰}$  ( $n = 7$ ),  $+5.59 \pm 0.09\text{‰}$  ( $n = 94$ ) and  $+5.28 \pm 0.10\text{‰}$  ( $n = 7$ ), respectively. These standard deviations for the above samples will reduce to 0.02, 0.03, 0.01, and 0.04‰, respectively, if expressed in the standard error of the mean of the measurements. The use of  $\text{O}_2$  directly converted from VSMOW in the scaling reduces the uncertainties mentioned above. It is noted that the  $\delta^{18}\text{O}$  values of NBS quartz obtained using  $\text{O}_2$  as the analytical gas are generally lower than those using  $\text{CO}_2$ . The  $\delta^{18}\text{O}$  values of 9.23–9.43‰ have been reported for NBS-28 quartz when  $\text{O}_2$  directly derived from VSMOW is used as reference (Clayton and Mayeda, 1983; Rumble and Hoering, 1994; Jabeen and Kusakabe, 1997; Miller *et al.*, 1999). The  $\delta^{18}\text{O}$  values of 9.22–9.34‰ have been obtained for NBS-28 quartz with the conventional technique with  $\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 1.0407$  (25°C) (Ito and Clayton, 1983; Matsuhisa and Aoki, 1993). Coplen *et al.* (1983) suggested that the  $\delta^{18}\text{O}$  value of NBS-28 quartz would be 9.19‰ if  $\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 1.04073$  (25°C) is used, and similarly the value for NBS-30 biotite would be 4.65‰. As has been mentioned before, Valley *et al.* (1995) recommended a  $\delta^{18}\text{O}$  value of 5.8‰ for UWG-2 garnet by normalizing their data for NBS-28 quartz to  $\delta^{18}\text{O} = 9.59\text{‰}$ , which was compiled by IAEA (Hut, 1987; Gonfiantini *et al.*, 1995). However, Table 1 of Valley *et al.* (1995) shows that the average  $\delta^{18}\text{O}$  value for UWG-2 reported on their own SMOW scale is 5.59‰, which is identical to the value obtained by the present study. Table 1 of Valley *et al.* (1995) also shows that the average  $\delta^{18}\text{O}$  value for NBS-28 is 9.29‰, which is closer to our value than to the IAEA value. Integrating above, the  $\delta^{18}\text{O}$  value of 9.58‰ for NBS-28 quartz compiled by IAEA (Hut, 1987; Gonfiantini *et al.*, 1995) appears to be too

Table 2. Comparison of  $\delta^{18}\text{O}$  values of NBS-28, NBS-30 biotite, UWG2 garnet and San Carlos olivine obtained by different laboratories

Sample	$\delta^{18}\text{O}$ ‰	$\sigma$ ‰	n	Analytical gas	Method	Standardization	Reference	
NBS-28 quartz	9.18	± 0.07	20	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub> , VSMOA-SLAP normalized	This study	
	9.23	± 0.05	18	O <sub>2</sub>	Conventional	VSMOW converted to O <sub>2</sub>	Clayton and Mayeda (1983)	
	9.31	± 0.09	7	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub>	Jabeen and Kusakabe (1997)	
	9.43	± 0.09	14	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub>	Miller <i>et al.</i> (1999)	
	9.25	± 0.1	28	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub>	Franchi <i>et al.</i> (1999)	
	9.30	± 0.2	—	O <sub>2</sub>	CO <sub>2</sub> laser-F <sub>2</sub> , <i>in situ</i>	Not given	Rumble and Hoering (1994)	
	9.7	± 0.1	4	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> /ClF <sub>3</sub> , whole grain	Not given	Sharp (1990)	
	9.46	± 0.19	44	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	Not given	Eisenheimer and Valley (1993)	
	9.29 <sup>(a)</sup>	± 0.18	65	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	Not given (table 1 of Valley <i>et al.</i> , 1995)	Valley <i>et al.</i> (1995)	
	9.0	± 0.10	3	CO <sub>2</sub>	Nd/YAG laser-ClF <sub>3</sub>	Not given	Akagi <i>et al.</i> (1995)	
	8.8	± 0.2	22	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	Not given	Fouillac and Girard (1996)	
	9.51	± 0.07	9	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	UWG2 = 5.80‰	Spicuzza <i>et al.</i> (1998)	
	9.22	± 0.14	7	CO <sub>2</sub>	Conventional	CO <sub>2</sub> equilibrated with VSMOW	Ito and Clayton (1983)	
NBS-30 biotite	9.19 <sup>(b)</sup>	± 0.06	7	CO <sub>2</sub>	Conventional	CO <sub>2</sub> equilibrated with VSMOW with $\alpha = 1.04073$ (25°C)	Coplen <i>et al.</i> (1983)	
	9.34	± 0.09	13	CO <sub>2</sub>	Conventional	CO <sub>2</sub> equilibrated with VSMOW with $\alpha = 1.0407$ (25°C)	Matsuhisa and Aoki (1993)	
	10.0	± 0.07	20	CO <sub>2</sub>	Conventional	VSMOW converted to CO <sub>2</sub>	Friedman and Gleason (1973)	
	9.58	± 0.09	8	—	Conventional	Compiled	Gonfiantini <i>et al.</i> (1995)	
	4.88	± 0.08	7	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub> , VSMOA-SLAP normalized	This study	
	5.0	± 0.1	2	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	Not given	Sharp (1990)	
	5.03	± 0.08	82	CO <sub>2</sub>	Nd/YAG laser-ClF <sub>3</sub>	NBS-19 calcite	Mattey and Macpherson (1993)	
	4.65 <sup>(b)</sup>	± 0.02	2	CO <sub>2</sub>	Conventional	CO <sub>2</sub> equilibrated with VSMOW with $\alpha = 1.04073$ (25°C)	Coplen <i>et al.</i> (1983)	
	5.24	± 0.24	4	CO <sub>2</sub>	Conventional	Compiled	Gonfiantini <i>et al.</i> (1995)	
	UWG2 garnet	5.59	± 0.09	94	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub> , VSMOA-SLAP normalized	This study
		5.44	± 0.10	38	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub>	Franchi <i>et al.</i> (1999)
		5.82	± 0.03	4	O <sub>2</sub>	UV laser-F <sub>2</sub> , <i>in situ</i>	Not given	Rumble <i>et al.</i> (1997)
		5.63	± 0.04	—	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	Not given	Larson and Sharp (2005)
5.89		± 0.15	>1000	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	NBS-28 = 9.58‰	Valley <i>et al.</i> (1995)	
5.77		± 0.07	5	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	NBS-28 = 9.58‰	Eiler <i>et al.</i> (1996)	
San Carlos olivine	5.28	± 0.10	7	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub> , VSMOA-SLAP normalized	This study	
	5.23	± 0.15	11	O <sub>2</sub>	UV laser-F <sub>2</sub> , <i>in situ</i>	Not given	Rumble <i>et al.</i> (1997)	
	4.70	± 0.18	5	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub>	Jabeen <i>et al.</i> (1998)	
	4.98	—	2	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	VSMOW converted to O <sub>2</sub>	Franchi <i>et al.</i> (1999)	
	5.20	± 0.05	—	O <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	Not given	Larson and Sharp (2005)	
	4.88	± 0.06	20	CO <sub>2</sub>	Nd/YAG laser-ClF <sub>3</sub>	NBS-19 calcite	Mattey and Macpherson (1993)	
	5.25	± 0.05	7	CO <sub>2</sub>	CO <sub>2</sub> laser-BrF <sub>3</sub> , whole grain	NBS-28 = 9.58‰	Eiler <i>et al.</i> (1996)	

<sup>(a)</sup>Averaged  $\delta^{18}\text{O}$  value for NBS-28 quartz given in Table 1 of Valley *et al.* (1995). It was reported on their own SMOW scale.

<sup>(b)</sup>Recalculated from the values given in Table 1 of Coplen *et al.* (1983) using  $\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 1.04073$  (25°C).

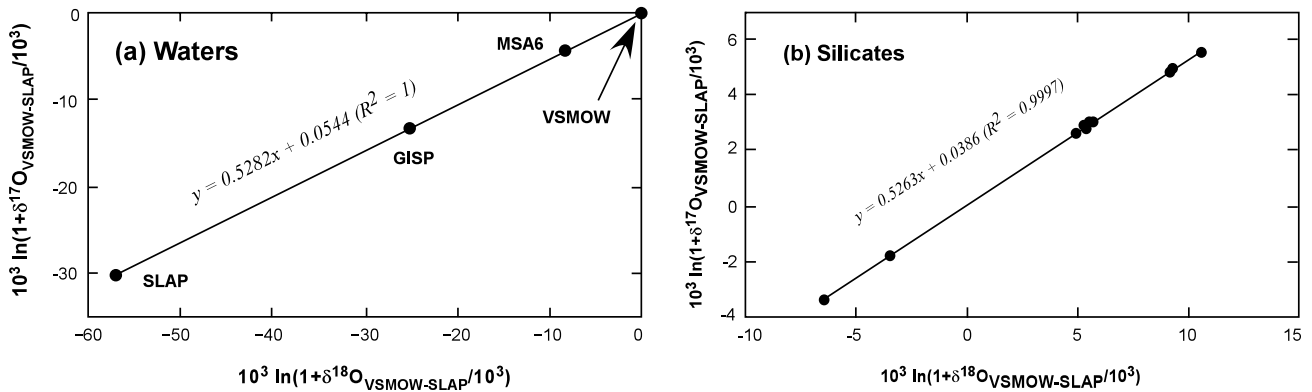


Fig. 2. (a) Regression of  $10^3 \ln(1 + \delta^{17}O_{\text{VSMOW-SLAP}}/10^3)$  vs.  $10^3 \ln(1 + \delta^{18}O_{\text{VSMOW-SLAP}}/10^3)$  plot for waters (VSMOW, SLAP, GISP and MSA-6) using the averaged values shown in Table 1. The slope 0.528 is associated with the standard error of  $\pm 0.001$ . (b) Regression of  $10^3 \ln(1 + \delta^{17}O_{\text{VSMOW-SLAP}}/10^3)$  vs.  $10^3 \ln(1 + \delta^{18}O_{\text{VSMOW-SLAP}}/10^3)$  plot for silicates and oxides using the averaged values shown in Table 1. The slope 0.526 is associated with the standard error of  $\pm 0.003$ .

high by  $\sim 0.4\%$ . We recommend to accumulate more  $\delta^{18}\text{O}$  data of reference silicate materials based on the  $\text{O}_2$  method, and to use  $\alpha_{\text{CO}_2\text{-H}_2\text{O}} = 1.04073$  ( $25^\circ\text{C}$ ) if  $\delta^{18}\text{O}$  is calculated via  $\text{CO}_2$  equilibrated with VSMOW.

We also measured  $\delta^{17}\text{O}$  values for the samples in Table 1. The relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of terrestrial minerals and rocks are known to form a “terrestrial fractionation line”, approximated by  $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$  (Clayton *et al.*, 1973; Clayton, 1993). The slope of the line 0.52 represents a best fit value for natural rocks and waters including some theoretical considerations (Matsuhisa *et al.*, 1978). Our mineral data in Table 1 just plot on the terrestrial fractionation line (Kusakabe *et al.*, 2004), confirming the above relationship. Recently, Miller (2002) has noted that the linearity of this mass-dependent relationship is only satisfactory when the range of  $\delta^{18}\text{O}$  values is within those normally encountered in terrestrial and extraterrestrial minerals and rocks. He stresses that the linearity is really guaranteed if the data are plotted in the  $10^3 \ln(1 + \delta^{17}\text{O}/10^3)$  vs.  $10^3 \ln(1 + \delta^{18}\text{O}/10^3)$  space. The regression equation with a proportionality constant “ $\lambda$ ” is linear for a much wider range of delta values. Miller proposes  $\lambda = 0.5247 \pm 0.0007$  for terrestrial silicates based on 104 data points (47 samples) that span from  $\delta^{18}\text{O} = -15 \sim +24\%$  relative to the reference gas used by Miller *et al.* (1999). A recent inter-laboratory comparison of hydrothermal quartz that has a range in  $\delta^{18}\text{O}$  of  $31\%$  yielded very good agreement of  $\lambda$  values of  $0.5240 \sim 0.5242$  regardless of the difference in mass spectrometers used and in analytical techniques (Rumble *et al.*, 2007). A similar value of 0.5237 for terrestrial rocks and minerals has been reported by Pack *et al.* (2007). A slightly higher  $\lambda$  value of  $0.526 \pm 0.001$  has been suggested for garnet from high  $P$ - $T$  metamorphic facies by Rumble *et al.* (2007).

The  $\lambda$  values for water samples, however, appear to be higher than those for silicates. Meijer and Li (1998) published a  $\lambda$  value of  $0.5281 \pm 0.0015$  for meteoric waters (VSMOW and SLAP included), with  $\delta^{18}\text{O}$  ranging from  $-55$  to  $+9\%$ . A similar value of  $0.527 \pm 0.002$  can be calculated using the data for VSMOW, GISP and SLAP in Jabeen and Kusakabe (1997). Recently Barkan and Luz (2005) have shown a very similar value of  $\lambda = 0.5279 \pm 0.0001$  for VSMOW, GISP and SLAP using their very precise data set. A significantly lower value of 0.5179 has been reported for oxygen involved in respiration pathways (Luz and Barkan, 2005).

We evaluated our  $\lambda$  values for waters and silicates using the data in Table 1 which shows the mean values for each sample. The procedures are as follows. First, raw  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values relative to the working standard gas were converted to  $\delta^{17}\text{O}_{\text{VSMOW}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values (columns 7 and 8). The  $\delta^{17}\text{O}_{\text{VSMOW}}$  and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values were then converted to a logarithmic format, i.e.,  $10^3 \ln(1 + \delta^i\text{O}/10^3)$  (where  $i$  is 17 or 18. See columns 9 and 10). Since very good linearity is guaranteed in the  $10^3 \ln(1 + \delta^{17}\text{O}/10^3)$  vs.  $10^3 \ln(1 + \delta^{18}\text{O}/10^3)$  plot, the same VSMOW-SLAP scaling factor should hold for  $^{17}\text{O}$ . The scaling factor is simply given by  $-57.10/-56.20 = 1.0160$ , where  $-57.10 = 10^3 \ln(1 + (-55.5)/10^3)$  for SLAP and  $-56.20 = 10^3 \ln(1 + (-54.65)/10^3)$ , calculated from the observed  $\delta^{18}\text{O}_{\text{VSMOW}}$  of SLAP. This way of VSMOW-SLAP scaling is more reasonable than using a ratio of  $-55.5/\delta^{18}\text{O}_{\text{SLAP-observed}}$  as initially recommended by IAEA (Gonfiantini, 1978). The values of  $10^3 \ln(1 + \delta^{17}\text{O}_{\text{VSMOW-SLAP}}/10^3)$  and  $10^3 \ln(1 + \delta^{18}\text{O}_{\text{VSMOW-SLAP}}/10^3)$  in Table 1 (columns 11 and 12) were obtained by multiplying the scaling factor of 1.0160 to the values of  $10^3 \ln(1 + \delta^{17}\text{O}_{\text{VSMOW}}/10^3)$  and  $10^3 \ln(1 + \delta^{18}\text{O}_{\text{VSMOW}}/10^3)$  (columns 9 and 10), respectively. Assuming the same scaling fac-

tor can be applied to silicate samples that have generally  $\delta$  values higher than those of waters, this practice resulted in  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values on the VSMOW-SLAP scale as given in columns 13 and 14, respectively.

Figure 2 shows plots of  $10^3 \ln(1 + \delta^{17}\text{O}_{\text{VSMOW-SLAP}}/10^3)$  vs.  $10^3 \ln(1 + \delta^{18}\text{O}_{\text{VSMOW-SLAP}}/10^3)$  for waters (Fig. 2a) and for silicates and oxides (Fig. 2b). We have separated the waters from silicates, because the slope of the regression line  $\lambda$  is likely different as stated above. The waters (VSMOW, GISP, SLAP and MSA6 (a laboratory standard)) plot on a regression line with a slope of  $0.528 \pm 0.001$  (standard error at 95% confidence limit). This value is in good agreement with  $\lambda$  values for waters reported by Meijer and Li (1998) and Barkan and Luz (2005), confirming that meteoric waters are characterized by  $\lambda = 0.528$ . The silicate and oxide samples with  $\delta^{18}\text{O}$  values ranging from  $-6.5\text{‰}$  to  $10.5\text{‰}$  (Table 1) plot on a regression line with  $\lambda = 0.526 \pm 0.003$ . The standard error at 95% confidence limit for the silicates and oxides is greater than that for water, probably because a span of the  $\delta^{18}\text{O}$  values of the silicate and oxide samples used here ( $17\text{‰}$  in  $\delta^{18}\text{O}$ ) is narrower than that for the waters ( $55\text{‰}$  in  $\delta^{18}\text{O}$ ), and poor analytical reproducibility of enstatite and fayalite relative to the others (Table 1). If our standard error at 95% confidence limit for the slope ( $\pm 0.003$ ) is taken into account, our  $\lambda$  value of 0.526 is consistent with the  $\lambda$  value of  $0.524 \pm 0.001$  for silicates reported by Miller (2002), Pack *et al.* (2007) and Rumble *et al.* (2007). The above statement that waters and silicates appear to have different  $\lambda$  values confirms that  $\lambda$  values are process-dependent as initially pointed out by Matsuhisa *et al.* (1978), because mechanisms of natural isotopic variations for water (e.g., evaporation, condensation, diffusion) are quite different from those for silicates and oxides (e.g., crystallization, melting, fluid-rock interaction). Thus precisely determined  $\lambda$  values will be used to clarify the processes in which oxygen isotopic variations have taken place as suggested in Luz and Barkan (2005) and Rumble *et al.* (2007).

As shown in Table 1, the  $\delta^{17}\text{O}$  value of SLAP, which has rarely been reported, is  $-29.67 \pm 0.07\text{‰}$  on the VSMOW-SLAP scale. The value given by Barkan and Luz (2005) is  $-29.48\text{‰}$ , which becomes  $-29.69\text{‰}$  if VSMOW-SLAP scaled. Our  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  and  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  values for GISP were calculated likewise to be  $-13.11 \pm 0.08\text{‰}$  and  $-24.80 \pm 0.07\text{‰}$ , respectively. They agree quite well with the Barkan and Luz (2005) values and also with the reported  $\delta^{18}\text{O}$  value for GISP (Gonfiantini *et al.*, 1995).

It is well known that extraterrestrial materials do not follow the above mentioned mass-dependent fractionation (e.g., Clayton, 1993). The deviation from the terrestrial fractionation line is expressed by  $\Delta^{17}\text{O}$  which is often expressed by  $\Delta^{17}\text{O}_\text{C} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$  (Clayton, 1993,

the subscript C of  $\Delta^{17}\text{O}_\text{C}$  stands for Clayton). The “accuracy” of  $\Delta^{17}\text{O}_\text{C}$  becomes increasingly worse as  $\delta^{18}\text{O}$  value goes away from that used for a standard. If a new definition of the big delta is taken as  $\Delta^{17}\text{O}_\text{M} = 10^3 \ln(1 + \delta^{17}\text{O}/10^3) - \lambda \times 10^3 \ln(1 + \delta^{18}\text{O}/10^3)$  (Miller, 2002, the subscript M of  $\Delta^{17}\text{O}_\text{M}$  stands for Miller), the accuracy of  $\Delta^{17}\text{O}_\text{M}$  is guaranteed for a much wider range of  $\delta^{18}\text{O}$ . Of course, the magnitude of  $\Delta^{17}\text{O}_\text{M}$  thus calculated depends on  $\lambda$ . Considering a small difference of  $\lambda$  values for waters and silicates as stated above,  $\Delta^{17}\text{O}_\text{M}$  values of our samples have been calculated using  $\lambda = 0.528$  for waters and  $\lambda = 0.526$  for silicates and oxides in Table 1. Although our  $\lambda$  for silicates is slightly greater than the value (0.524) proposed by Miller (2002), Pack *et al.* (2007) and Rumble *et al.* (2007), the  $\Delta^{17}\text{O}_\text{M}$  values are close to zero with few exceptions and can be used to evaluate the offset of most extraterrestrial materials from the terrestrial fractionation line.

## CONCLUSIONS

Oxygen isotopic ratios of natural waters have been reported on the VSMOW-SLAP scale as recommended by IAEA. Since  $\delta^{18}\text{O}$  values of silicates and oxides are usually calculated relative to VSMOW through indirect ways, e.g., adoption of a given silicate reference material of which oxygen isotopic value has been published or comparison of  $\delta^{18}\text{O}$  of  $\text{CO}_2$  with that derived from international reference waters and carbonates. To avoid any uncertainties potentially involved in such indirect ways, we recommend to measure oxygen isotopic ratios of  $\text{O}_2$  directly derived from VSMOW and SLAP at the same time when oxygen isotopic ratio of silicates are measured. From the data obtained the oxygen isotopic ratios should be reported on the VSMOW-SLAP scale as we did. Such exercise is particularly important for international reference silicate materials such as NBS-28 quartz and NBS-30 in the community of oxygen isotope geochemists, for they are often taken as a reference material for reporting on the VSMOW basis. Based on our results a choice of the  $\text{CO}_2\text{-H}_2\text{O}$  fractionation factor of 1.0407 is recommended, if oxygen isotopic ratios are referred to that of VSMOW using a conventional system with  $\text{CO}_2$  as the analyzing gas.

When the “big delta” ( $\Delta^{17}\text{O}$ ) of sample under consideration, a deviation of  $\delta^{17}\text{O}$  from the terrestrial fractionation line, is calculated using equation  $\Delta^{17}\text{O} = 10^3 \ln(1 + \delta^{17}\text{O}/10^3) - \lambda \times 10^3 \ln(1 + \delta^{18}\text{O}/10^3)$  as given by Miller (2002), the most appropriate proportionality constant  $\lambda$  has to be chosen, for it is depending on the isotopic fractionation process concerned.

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