

Oxygen isotope measurements of terrestrial silicates using a CO₂-laser BrF₅ fluorination technique and the slope of terrestrial fractionation line

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ABSTRACT: Here we report oxygen isotopic compositions (both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) of San Carlos olivine, Juan de Fuca basalt glass, garnet standard at University of Wisconsin (UWG-2 garnet), National Bureau of standard #28 quartz (NBS-28 quartz), a hydrothermal quartz from China (CQ4 quartz), chert flint standard and a serpentine measured with a CO₂-laser BrF₅ fluorination system installed at Korea Polar Research Institute. In addition we measured VSMOW (Vienna standard mean ocean water) and SLAP (standard light Antarctic precipitation) with the same line; a scaling factor of 1.056 was obtained to fit the measured SLAP data to the recommended value of $\delta^{18}\text{O}_{\text{SMOW}} = -55.5\text{‰}$. All the other data were corrected using the VSMOW-SLAP scaling factor. Majority of the samples in this work have been measured by several laboratories; our data in general agree very well with previous data. We report data using the delta prime notation, since linearity of a mass-dependent fractionation line holds in $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ diagram for wide range of oxygen isotopic compositions. Average $\delta^{18}\text{O}$ values and 2σ standard error of means are $5.27 \pm 0.04\text{‰}$ for San Carlos olivine, $5.49 \pm 0.02\text{‰}$ for Juan de Fuca basalt glass, $5.73 \pm 0.05\text{‰}$ for UWG-2 garnet, $9.18 \pm 0.08\text{‰}$ for NBS-28 quartz, $23.14 \pm 0.36\text{‰}$ for CQ4 quartz, $33.97 \pm 0.16\text{‰}$ for chert flint standard and $0.78 \pm 0.07\text{‰}$ for the serpentine. Slope of terrestrial fractionation was obtained using these data, which is 0.5248 ± 0.0003 ($R^2 = 0.99992$).

Key words: oxygen isotopes, laser-fluorination, terrestrial fractionation line

1. INTRODUCTION

Oxygen, the third abundant element in the solar system and the most in Earth's crust and mantle, is one of the key elements in the fields of isotope geochemistry and cosmochemistry. Oxygen has three stable isotopes ^{16}O , ^{17}O and ^{18}O with respective terrestrial abundances of approximately 99.76%, 0.04% and 0.20%. Oxygen isotope compositions of rocks and minerals varies due to (1) initial heterogeneities, (2) mixing of two or more distinct reservoirs and/or (3) isotopic fractionation during physico-chemical processes, thus give critical clues to understand the origins and processes that formed the samples.

Oxygen isotopic compositions of oxygen-bearing sam-

ples have been measured using fluorination techniques and secondary ion mass spectrometry (SIMS). While with SIMS one can measure oxygen isotopic compositions with high spatial resolution, fluorination techniques give high precision data. In fluorination techniques, F₂ and BrF₅ have been used as most common oxidants (e.g., Clayton and Mayeda, 1963; Young et al., 1998; Kusakabe et al., 2004). Since F₂ and BrF₅ react sufficiently with oxygen-bearing phases only at high temperature, it is required to heat the sample in the presence of F₂ or BrF₅. In so-called conventional fluorination technique, samples are heated using external furnace to ~500–700 °C (e.g., Clayton and Mayeda, 1963), while in laser-fluorination technique either IR or UV laser is used to heat the sample locally (e.g., Young et al., 1998; Sharp, 1990; Elsenheimer and Valley, 1992; Mathey and Macpherson, 1993). Currently, IR (CO₂ or Nd:YAG) laser fluorination either by F₂ or BrF₅ is the most common method to sample oxygen from solid materials for mass spectrometric measurements. The technique provides high precision (<0.1‰) data from relatively small amount (~2 mg for typical silicates or oxides) of sample (e.g., Miller et al., 1999; Kusakabe et al., 2004; Rumble et al., 2007).

A CO₂-laser BrF₅ fluorination system was installed in 2007 at Korea Polar Research Institute (KOPRI). In this paper, we report data obtained using the system for various terrestrial solid samples that have been used as standard reference materials of many laboratories, including San Carlos (SC) olivine, Juan de Fuca basalt (JFB) glass (Kusakabe et al., 2004), garnet standard at University of Wisconsin (UWG-2 garnet, Valley et al., 1995), a hydrothermal quartz from China (CQ4 quartz, Rumble et al., 2007) and chert flint standard at Open University (CFS, Rumble et al., 2007). We also measured oxygen isotopic compositions of VSMOW (Vienna standard mean ocean water) and SLAP (standard light Antarctic precipitation) with the same line. A scaling factor was obtained using the VSMOW and SLAP data which applied to the other measurements. Analytical procedures and data reduction processes are also discussed. We also report the slope of terrestrial mass fractionation line obtained using our data and compare it with the previously reported values.

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2. TERMINOLOGY

Since the range of oxygen isotope compositions found in majority of terrestrial and solar system materials is within a few % (a few tens of ‰), their oxygen isotopic compositions have been reported using delta notation that is part per thousand of the sample ratio relative to the reference ratio, i.e., $\delta^x\text{O} (\text{‰}) = [\{({}^x\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^x\text{O}/{}^{16}\text{O})_{\text{reference}}\} - 1] \times 1000$, where ${}^x\text{O}$ is either ${}^{17}\text{O}$ or ${}^{18}\text{O}$. The most widely used reference in the equation is SMOW (standard mean ocean water). SMOW is no longer available and thus replaced by VSMOW that has the identical oxygen isotope composition with SMOW. Coplen (1995) suggested that the oxygen isotope abundance should be scaled in to the SLAP having a $\delta^{18}\text{O}_{\text{SMOW}}$ of -55.5‰ in order to minimize possible inter-laboratory bias. This has been done by Kusakabe and Matsuhisa (2008) and we also normalized our data using the VSMOW-SLAP scaling with the analyzed oxygen isotopic compositions of VSMOW and SLAP using the same line for the analysis of the solid samples.

In $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ diagram (oxygen three-isotope plot), oxygen isotopic compositions of any samples derived from a homogenous oxygen reservoir by common physical and chemical processes, such as evaporation, condensation, melting, crystallization, etc., fall along a mass-dependent fractionation line with a slope (λ) of ~ 0.52 (e.g., Matsuhisa et al., 1978). The trend for the terrestrial samples is called as terrestrial fractionation (TF) line (Clayton et al., 1973). It has been well known that majority of extraterrestrial-solar-system materials measured, i.e., meteorites, do not fall along the TF line (Clayton, 1993 and references therein). The deviation from the TF line is defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ (e.g., Clayton and Mayeda, 1988). Since the linear relation is an approximation derived from a power law relation, Miller (2002) proposed to use delta prime notation: $\delta^x\text{O} = 1000 \times \ln(1 + \delta^x\text{O}/1000)$. They also defined the slope of a mass-dependent fractionation line in $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ diagram as δ' that they reported as 0.5247 ± 0.0007 for terrestrial rocks and minerals. The deviation from the TF line is then defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda' \times \delta^{18}\text{O}$. In this paper, we report oxygen isotope data using delta prime notation. If necessary, we put both delta and delta prime values side by side. Also in order to avoid any ambiguity, we use δ , Δ and λ for the traditional notation and δ' , Δ' , and λ' for the log-scale notation in the paper. We will discuss about delta and delta prime notations in more detail at discussion.

3. ANALYTICAL PROCEDURES

The KOPRI CO_2 -laser BrF_5 fluorination system is similar to those described in Kusakabe et al. (2004) and Kusakabe and Matsuhisa (2008). The system consists of three major parts: (1) reaction chamber for fluorination reaction of oxygen-bearing solid samples using BrF_5 as oxidation agent

and CO_2 -laser as heat source, (2) purification line made of stainless steel and Pyrex[®] glass for recovering pure O_2 gas, and (3) mass spectrometer to measure oxygen isotope ratio. For analysis of water sample, a Ni reaction tube is directly connected to the purification line. The Ni tube is heated up to 300°C using an external furnace to fluorinate H_2O with BrF_5 . Some details of these analytical steps are described below.

3.1. The Reaction Chamber and Fluorination

The reaction chamber for solid samples is made of stainless steel and has a BaF_2 window that is nearly transparent to the wavelength of CO_2 laser. A sample holder made of pure Ni and having eight dimples (2.5 mm in diameter and 1.5 mm in depth each) on the surface is placed in the reaction chamber. The laser used in the system is a CO_2 laser (wavelength of $10.6 \mu\text{m}$) having a maximum of 20 W and a beam spot of $\sim 100 \mu\text{m}$ in diameter on the sample surface when focused (Model PIN-10R, Onizuka Glass Co. Ltd.).

About 2 mg of solid sample (from 1.5 to 4 mg) was placed in each dimple on the Ni holder. The reaction chamber having samples was evacuated and preheated at $\sim 180^\circ\text{C}$ for overnight, followed by pre-fluorination with BrF_5 for about one hour at room temperature in order to remove any surface contamination such as adsorbed moisture of samples and reaction chamber.

After this cleaning step, approximately 100 mbar of BrF_5 gas was introduced into the reaction chamber. Each sample is gently heated with minimum power (~ 3 W) of the laser, in order to avoid to jumping out of fine-grained samples from the dimple. Laser beam power is gradually increased until all solid grains react with BrF_5 .

Fluorination of water sample is also similar to that described in Kusakabe and Matsuhisa (2008). About $1.8 \mu\text{l}$ of reference water (VSMOW and SLAP) is inserted in Pyrex[®] glass ball in the water fluorination system. After evacuation (the water is frozen by liquid Nitrogen during the evacuation), the water is released into pure Ni tube. The Ni tube is heated up to 300°C for one hour using an external furnace in the presence of BrF_5 .

3.2. Purification Line and Extraction of O_2

The purification line has three cryogenic traps using liquid nitrogen and one KBr trap and is connected to one diffusion pump and two rotary pumps that maintain the line at pressure less than 1.0×10^{-4} mbar. Gaseous species at room temperature liberated from a sample by the fluorination are expanded into the purification line. All gaseous species except O_2 are expected to be trapped either cryogenically or by KBr. At the end of the purification line, pure O_2 gas is adsorbed by Molecular Sieve 13X at liquid Nitrogen temperature. Pressure of O_2 gas released from the Molecular Sieve at

room temperature was measured in order to calculate the reaction oxygen yield (Kusakabe et al., 2004). Oxygen yield (%) is defined as (amount of O₂ gas recovered)/(amount of O₂ in the sample) × 100. The amount of recovered O₂ gas is calculated from the pressure and temperature of the O₂ gas in a constant volume and that in the sample calculated from chemical composition and weight. The calculated oxygen yields for the solid samples we measured range from 89 to 102%.

3.3. Mass Spectrometer and Measurement of Isotopic Ratio

The mass spectrometer (PRISM, VG Isotech) with a dual inlet system is on-line connected to the purification line. Every manipulation and data acquisition is controlled by OS/2 based computer program (Dual Inlet Software, ver. 2.4).

Two bellows of the dual-inlet system differ in volume: the larger one is used for standard gas and the smaller for sample gas. High purity (99.999%) O₂ gas, whose oxygen isotopic composition has been determined against VSMOW, was used as working standard. Every day prior to the sample measurements, the working standard O₂ gas was inserted into both bellows and the isotopic ratios in the mass spectrometer were compared. Any systematic bias between the same O₂ gas in the two bellows was applied to the sample results, however, was typically less than ±0.05‰.

The isotopes, ¹⁶O, ¹⁷O and ¹⁸O of the ionized gas were analyzed by three Faraday cups as ¹⁶O¹⁶O⁺ (mass 32), ¹⁶O¹⁷O⁺ (mass 33) and ¹⁶O¹⁸O⁺ (mass 34), respectively. Backgrounds and tailing effects on these masses were carefully checked and corrected.

It has been known that NF₃ gas, if any, can reach to the molecular sieve and gives potential interference for the oxygen isotope measurement with mass spectrometry (Rumble et al., 1997). If there is nitrogen in the chamber by any reasons, NF₃ can be formed during the fluorination and is decomposed into some ionic gases such as NF⁺ and NF₂⁺ by electron beam in the mass spectrometer (Clayton and Mayeda, 1983). The mass number of ¹⁴N¹⁹F⁺ ion is 33, the same mass number with the ¹⁷O¹⁶O⁺, thus any NF₃ reaches to the bellows of the mass spectrometer results in false ¹⁷O excess (Rumble et al., 1997). Fortunately, the presence of NF⁺ on mass analyzer can be checked with NF₂⁺. We have checked the presence NF₂⁺ for any suspicious samples and found no NF₂⁺.

4. DATA REDUCTION AND RESULTS

4.1. Data Reduction Process

Any isotopic measurements suffer from various analytical bias that result not only in increasing analytical uncertainty but also in systematic discrepancy in data reported from dif-

ferent laboratories (e.g., Fouillac and Girard, 1996; Kohn et al., 1993; Sharp, 1990; Matthey and MacPherson, 1993; Kusakabe and Matsuhisa, 2008).

As noted by various previous studies in the case of oxygen isotope measurements using the fluorination technique, the bias could be generated by (1) contamination due to passive partial reaction of neighboring samples in the holder or by fluorides and bromides accumulated in the cleanup section of the vacuum line, (2) method of defining the VSMOW-scale and correction procedures for the instrumental mass fractionation.

The first factor can be minimized by careful treatment of the line and is reflected in the analytical errors reported. The second factor could result in systematic bias of data obtained from different laboratories. In order to minimize the systematic bias, Kusakabe and Matsuhisa (2008) adopted VSMOW-SLAP scaling method that has been recommended by Coplen (1995). We also normalized our data by applying the same scaling factor to make our SLAP measurement match with the recommended value by Coplen (1995) that is δ¹⁸O = -55.5‰ (δ¹⁸O = -57.1‰). Our SLAP data (n = 9) after SMOW-scaling is δ¹⁸O = -54.08 ± 0.17‰. The ratio between two values, i.e., scaling factor (-57.1/-54.08 = 1.056) was applied to the other analyzed samples. The effect of this scaling is minor for the samples close to the origin (δ¹⁸O = 0‰) and increases with increasing distance from that, for instance, the corrected δ¹⁸O values will be increased by 0.28, 0.56 and 1.11‰ when δ¹⁸O values before the corrections are 5, 10 and 20‰, respectively.

The mass spectrometer, PRISM has the dual-inlet system that was initially designed to provide the identical flow rate for a known isotope composition of reference gas and the unknown sample gas as long as sufficient gas pressures. In order to verify whether two inlets give the identical flow, we monitor the system every day prior to sample measurements by measuring the same reference oxygen gas from both bellows. When the gas pressure at one of the bellows is not high enough to give the identical flow rate, instrumental mass fractionation may occur. This gives the lower limit of sample oxygen we can measure with the system without any bias. In order to find the limit, we calculated the slope from a δ¹⁸O value (‰) vs. amount of oxygen (μmol) diagram using our JFB glass data. The slope should be zero if there was no instrumental fractionation due to the sample size, however in our data it was 0.012. The slope becomes smaller by removing smaller samples from the diagram and approaches nearly zero (<0.004) for samples having ≥29 μmol of O₂. That amount of oxygen can be extracted from about 2 mg of typical silicates. It is thus desirable to use more than 2 mg of samples (in the case of typical silicates) in order to measure the oxygen isotopic composition using the KOPRI system. On occasion, however, it is necessary to measure small amount of samples of less than 2 mg, especially the precious ones. We obtained a calibration curve to

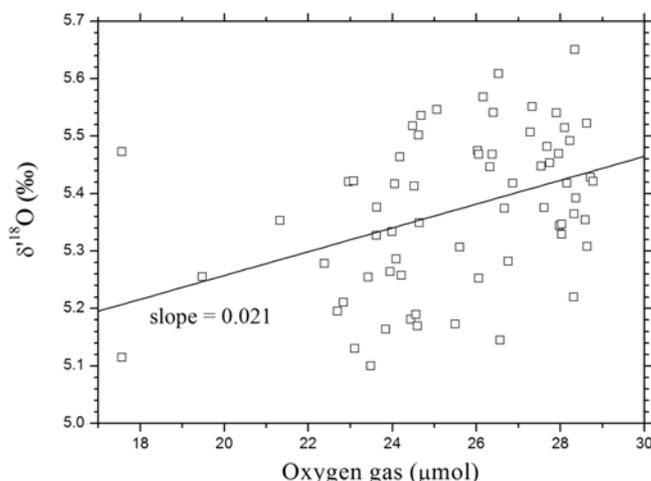


Fig. 1. Measured $\delta^{18}\text{O}$ vs. amount of recovered oxygen (open symbol) for Juan de Fuca basalt glass having oxygen less than 29 μmol . The smaller O_2 tends to give lower $\delta^{18}\text{O}$, suggesting instrumental bias due to sample size. A regression line was obtained to correct the instrumental mass fractionation for samples having less than 29 μmol of oxygen.

correct any instrumental fractionation due to sample size from the data of JFB glass having $<29 \mu\text{mol}$ of O_2 (Fig. 1). The slope from Figure 1 was used to correct the instrumental mass fractionation due to sample size for the samples having $<29 \mu\text{mol}$ of O_2 . No such correction was applied to the samples having $\geq 29 \mu\text{mol}$ of oxygen.

In order to validate the correction method, we compare the JFB data having $\geq 29 \mu\text{mol}$ of O_2 (no correction) with those having $<29 \mu\text{mol}$ of O_2 after the correction. After the correction for the samples $<29 \mu\text{mol}$, the mean value ($\delta^{18}\text{O} = 5.44\text{‰} \pm 0.03$, $n = 67$) is only slightly lower than those for the samples $\geq 29 \mu\text{mol}$ ($\delta^{18}\text{O} = 5.53\text{‰} \pm 0.03$, $n = 81$), where the errors are 2-sigma standard error of mean. The slope was applied for the other solid samples. The $\delta^{18}\text{O}$ values of samples $<29 \mu\text{mol}$ and those $\geq 29 \mu\text{mol}$ are $5.23 \pm 0.11\text{‰}$ ($n = 4$) and $5.28 \pm 0.04\text{‰}$ ($n = 17$) for SC olivine, $5.68 \pm 0.06\text{‰}$ ($n = 10$) and $5.79 \pm 0.06\text{‰}$ for UWG-2 garnet ($n = 10$) and $23.21 \pm 0.57\text{‰}$ ($n = 3$) and $23.08 \pm 0.46\text{‰}$ for CQ4 quartz ($n = 3$), respectively. CQ4 data has larger errors than the others not only because of smaller number of measurements but also probably due to CQ4 quartz is rather heterogeneous in oxygen isotopic composition.

4.2. Results

The averages of the solid samples we measured are summarized in Table 1. The ranges of literature values of these samples measured by laser-fluorination techniques are also shown in Table 1 for comparison. Note that all values in tables, figures and text are shown as delta prime values and errors are given as 2-sigma standard error of mean, unless specified. In general, our data fall in the ranges occupied by

the previously reported values (Fig. 2).

Among others, SC olivine, UWG-2 garnet and NBS-28 quartz have been the most widely used as solid standards by many laboratories using laser-fluorination techniques. Literature $\delta^{18}\text{O}$ values for SC olivine vary from 4.69‰ (Jabeen et al., 1998) to 5.26‰ (Kusakabe and Matsuhisa, 2008). Our value of $\delta^{18}\text{O} = 5.27 \pm 0.04\text{‰}$ is the same as that of Kusakabe and Matsuhisa (2008) and agrees well with those by Eiler et al. (1996) and Larson and Sharp (2005). The other two literature values (Jabeen et al., 1998; Franchi et al., 1999) are slightly lower than these.

Valley et al. (1995) measured $\delta^{18}\text{O}$ of UWG-2 garnet as 5.65‰ (weighted mean of data in their Table 1, $\delta^{18}\text{O} = 5.67\text{‰}$) and recommended to use 5.78‰ (given as $\delta^{18}\text{O} = 5.8\text{‰}$). After that several other authors reported oxygen isotopic compositions of UWG-2, where $\delta^{18}\text{O}$ values vary from 5.43‰ (Franchi et al., 1999) to 5.75‰ (Eiler et al., 1996). Our value of $5.73 \pm 0.05\text{‰}$ agrees well with these values.

Gonfiantini et al. (1995) compiled literature data for NBS-28 quartz and suggested to use $\delta^{18}\text{O}$ of as 9.53‰ (given as $\delta^{18}\text{O} = 9.58\text{‰}$). However, most data for NBS-28 quartz measured by laser fluorination techniques since then are somewhat lower than 9.53‰ and ranging from 8.76‰ (Fouillac and Girard, 1996) to 9.47‰ (Spicuzza et al., 1998). If we consider only literature data analyzed using O_2 gas, the range is smaller from 9.14‰ to 9.39‰, giving an average of 9.25‰. Our value of $9.18 \pm 0.08\text{‰}$ is very similar to these literature data.

JFB glass has been measured by Kusakabe and Matsuhisa (2008) and the oxygen isotopic composition was reported as $\delta^{18}\text{O} = 5.31 \pm 0.04\text{‰}$. We used JFB glass as our primary solid standard to check daily performance of the system. Our value of $5.49 \pm 0.02\text{‰}$ is slightly higher than Kusakabe and Matsuhisa (2008).

CQ4 quartz has been measured by Rumble et al. (2007), where the measured values have relatively large range from 22.21 to 23.80‰. Our data for CQ4 quartz also show larger variation than the other samples and give the average of $23.14 \pm 0.36\text{‰}$. As mentioned above, it is possible that the CQ4 quartz is not as homogenous in oxygen isotopic composition as the others.

Rumble et al. (2007) also reported the averages of CFS measured at Geophysical Laboratory, Carnegie Institute of Washington and at Open University, $\delta^{18}\text{O} = 32.68 \pm 0.84\text{‰}$ and $33.99 \pm 0.04\text{‰}$, respectively. Our value of $33.97 \pm 0.16\text{‰}$ is identical to that measured at Open University.

Figure 3 shows daily performance of the KOPRI system, in which we plot individual $\delta^{18}\text{O}$ values of SC olivine ($n = 21$), UWG-2 garnet ($n = 20$), NBS-28 quartz ($n = 13$) and JFB glass ($n = 148$) for 117 days we operated the system since year 2007. Figure 4 shows deviations of individual data from the averages of SC olivine, UWG-2 garnet, NBS-28 quartz and JFB glass. Their 2-sigma standard deviations are similar in these four samples (Fig. 4). Typical daily performance mon-

Table 1. VSMOW normalized $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values (‰) and VSMOW-SLAP scaled $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of reference minerals and rocks in this study

Samples	n	$\delta^{17}\text{O}^a$	$\delta^{18}\text{O}^a$	$\delta^{17}\text{O}^b$	$\delta^{18}\text{O}^b$	$\Delta^{17}\text{O}^c$	Published mean $\delta^{18}\text{O}$	References
San Carlos olivine	21	2.56	4.98	2.75 ± 0.02	5.27 ± 0.04	0.01	4.69–5.26	Jabeen et al. (1998); Eiler et al. (1996); Franchi et al. (1999); Larson and sharp (2005); Kusakabe and Matsuhisa (2008).
Juan de Fuca basalt glass	148	2.66	5.17	2.88 ± 0.01	5.49 ± 0.02	0.00	5.31	Kusakabe and Matsuhisa (2008).
UWG-2 garnet	20	2.81	5.40	3.04 ± 0.03	5.73 ± 0.05	0.03	5.43–5.75	Valley et al. (1995); Eiler et al. (1996); Franchi et al. (1999); Larson and sharp (2005); Kusakabe and Matsuhisa (2008).
NBS-28 quartz	13	4.52	8.69	4.86 ± 0.05	9.18 ± 0.08	0.04	8.76–9.53	Rumble and Hoering (1994); Fouillac and Girard (1996); Jabeen and Kusakabe (1997); Spiccuza et al. (1998); Franchi et al. (1999); Miller et al. (1999); Larson and sharp (2005); Kusakabe and Matsuhisa (2008).
CQ4 quartz	6	11.27	21.88	12.15 ± 0.18	23.14 ± 0.36	0.01	22.21–23.80	Rumble et al. (2007)
Chert flint standard (CFS)	4	16.54	32.18	17.78 ± 0.09	33.97 ± 0.16	0.04	32.68–33.99	Rumble et al. (2007)

In general, our results agree with published results measured using IR laser as heat source and O₂ as analytical gas.

Errors are given as 2 σ standard error of mean.

^aNormalized δ values of VSMOW as working standard O₂.

^bDetermined VSMOW-SLAP scale values, given by $\delta^{17}\text{O}$ or $\delta^{18}\text{O}$ × scaling factor.

^c $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5248 \times \delta^{18}\text{O}$; 0.5248 is the slope of TF from this study.

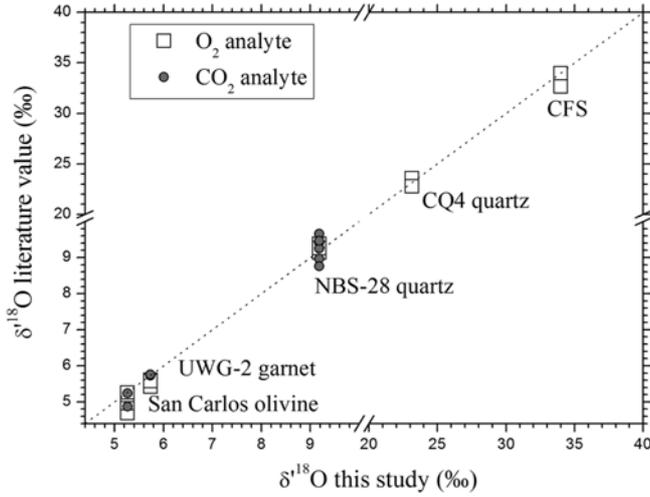


Fig. 2. Comparison our results with literature data. The dotted line represents that literature value equals KOPRI value. Our data agree well with the previously reported values throughout wide range of oxygen isotopic compositions. See the text for the sources of literature data.

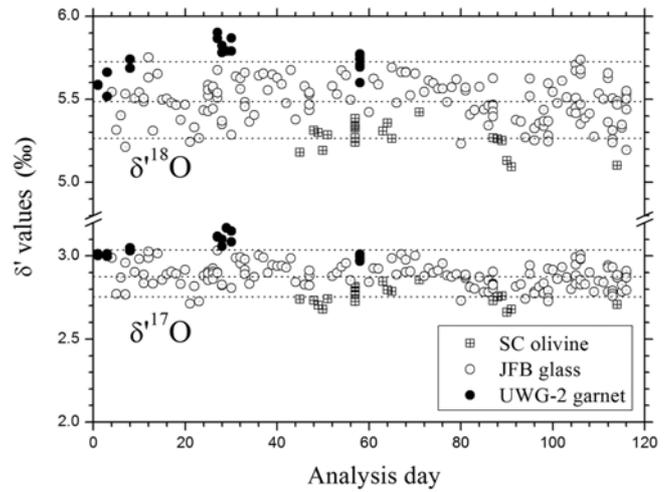


Fig. 3. The reproducibility of KOPRI laser fluorination system showing as daily variations $\delta^{18}\text{O}$ values of UWG-2 garnet, SC olivine and JFB glass measured. Dash lines are mean $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of them.

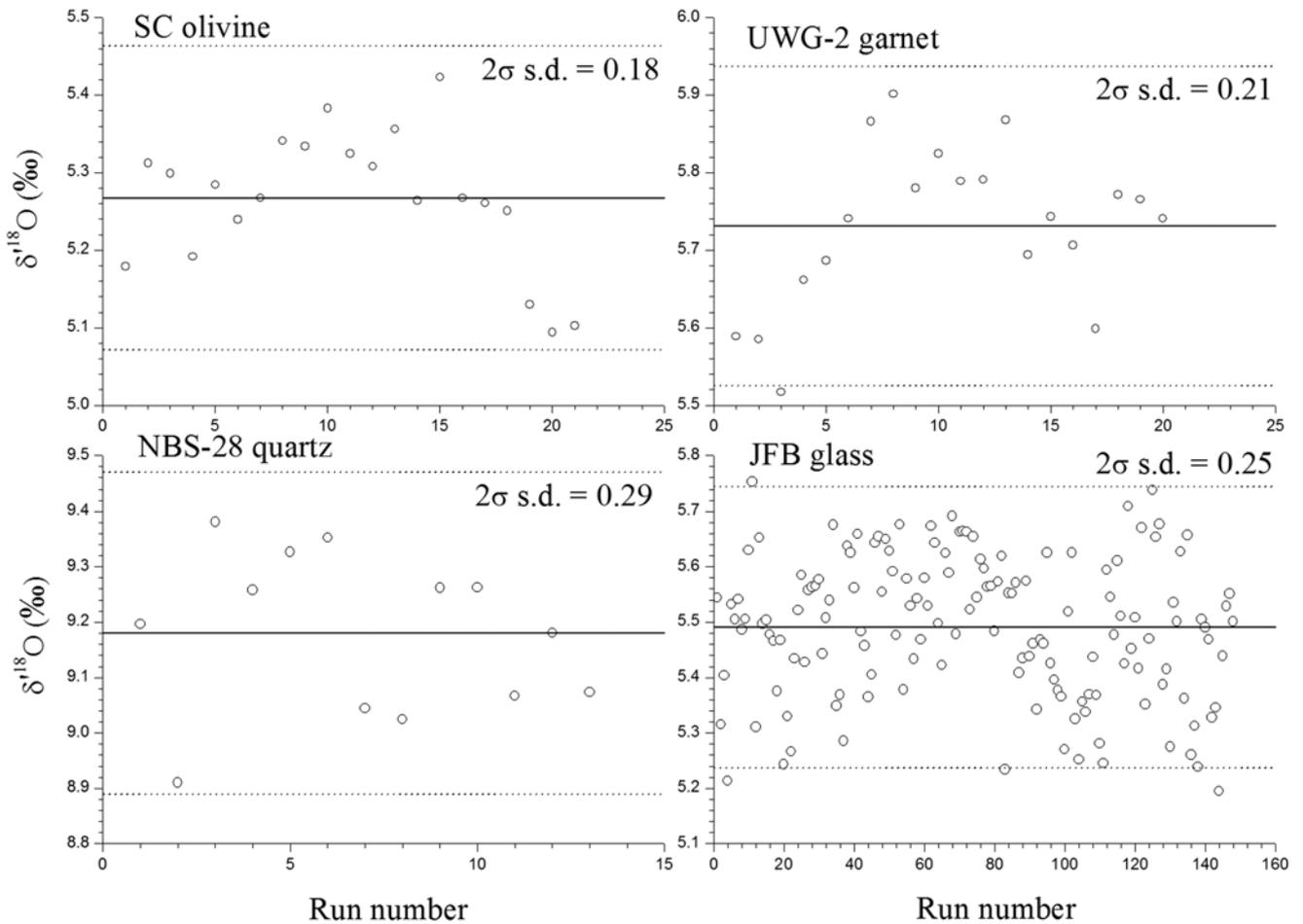


Fig. 4. Deviations of individual measurements from the average of each sample. Averages are shown as solid lines and 2σ standard deviations as dotted lines.

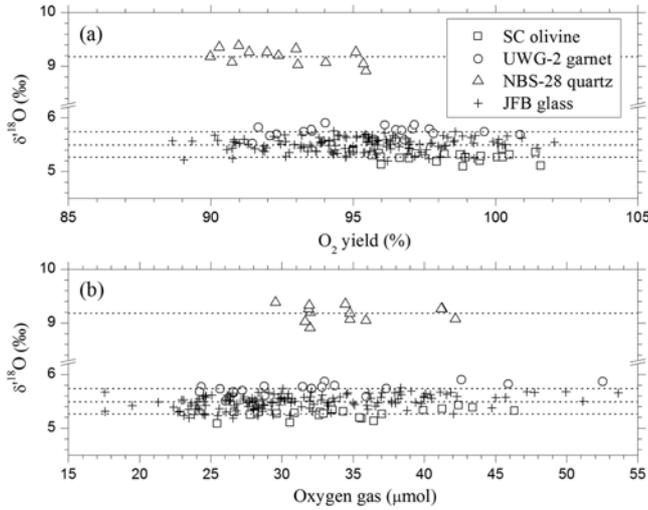


Fig. 5. $\delta^{18}\text{O}$ values vs. amount of oxygen as (a) relative yield and (b) absolute amount for SC olivine, UWG-2 garnet, NBS-28 quartz and JFB glass. Dash lines are mean $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of them. After the correction we described in text, $\delta^{18}\text{O}$ values are independent to amount of oxygen.

itored by measuring JFB glass is approximately less than $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ and less than $\pm 0.02\text{‰}$ for $\Delta^{17}\text{O}$.

In Figure 5, we plot individual $\delta^{18}\text{O}$ values of SC olivine, UWG-2 garnet, NBS-28 quartz and JFB glass against their oxygen yield (Fig. 5a) and the amount of O₂ recovered (Fig. 5b). There seems to be no analytical bias related to these factors after the corrections we described in the previous chapter.

It is challenging to measure oxygen isotopic composition of hydrous minerals or rocks having such minerals by laser-fluorination techniques, since some oxygen in O-H bond seems to be released by reacting with BrF₅ or F₂ even at room temperature. We measured oxygen isotopic composition of a serpentine sample collected from serpentinized ultramafic rocks in the Precambrian Kyeonggi gneiss complex, Korea (Song et al., 2004). In order to avoid any partial loss of oxygen during the cleaning step, we only evacuated the chamber having the serpentine samples for overnight and their oxygen isotopic compositions were measured without the pre-fluorination step. Table 2 shows 5 measurements for the serpentine sample, where the average gives $\delta^{18}\text{O} = 0.78 \pm 0.07\text{‰}$. Reproducibility of the serpentine is similar to those

Table 2. Bulk oxygen isotope compositions of KOPRI serpentine from Kwangcheon mine in Hongseong area, Korea

Sample weight (mg)	O ₂ yield (%)	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
2.11	97.7	0.47	0.91	0.01
2.05	94.3	0.37	0.70	0.00
2.45	96.3	0.41	0.76	0.01
1.86	101.1	0.41	0.80	0.01
1.97	100.8	0.35	0.72	0.02
averages	98.0 ± 2.6	0.40 ± 0.04	0.78 ± 0.07	0.01 ± 0.01

Errors are given as 2σ standard error of mean.

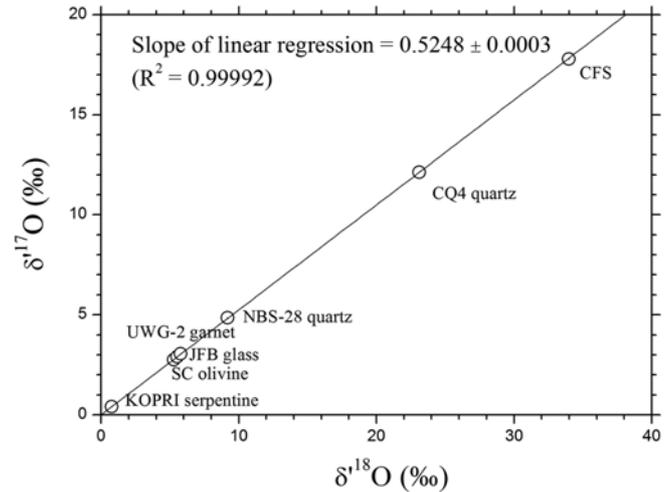


Fig. 6. A plot of mean $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ for KOPRI serpentine, SC olivine, JFB glass, UWG-2 garnet, NBS-28 quartz, CQ4 quartz, CFS measured in this study. The slope of TF line (λ') as regression line for these data is 0.5248 ± 0.0003 ($R^2 = 0.99992$).

of the other solid samples, demonstrating that the system is capable of measuring oxygen isotopic compositions of hydrous samples with similar precision of anhydrous samples.

Oxygen isotopic compositions of these terrestrial solid samples are plotted in a $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ diagram (Fig. 6), in which they fall on almost perfect linear line. The slope (λ') of the terrestrial fractionation (TF) line was calculated from them as 0.5248 ± 0.0003 ($R^2 = 0.99992$), which is very similar to previously reported values (Table 3) ranging from 0.5237 (Pack et al., 2007) to 0.5262 ± 0.0008 (Rumble et al., 2007).

Table 3. Summary of previously reported λ' values (slopes of TF line) obtained from terrestrial rocks and minerals and that of this study

Methods	λ' value	References
Fluorination with BrF ₅	0.5247 ± 0.0007	Miller (2002)
Fluorination with BrF ₅	0.5259 ± 0.0008	Spicuzza et al. (2007)
Fluorination with BrF ₅	0.5240 ± 0.0010 (Silica)	Rumble et al. (2007)
	0.5262 ± 0.0008 (Garnet)	
Fluorination with BrF ₅	0.526 ± 0.003	Kusakabe and Matsuhisa (2008)
Fluorination with F ₂	0.5237	Pack et al. (2007)
Fluorination with BrF ₅	0.5248 ± 0.0003	This study

5. DISCUSSION

In this chapter we will discuss the difference between delta and delta prime notation, merit of VSMOW-SLAP scaling and the slope of the mass-dependent fractionation in a three oxygen isotope plot.

5.1. Delta vs. Delta Prime

Delta prime (δ') notation was proposed by Miller (2002) to replace the delta (δ) notation. Let us briefly summarize the definition of δ' and the difference between two notations. For any phase in isotopic equilibrium with phase a , the following equation can be written:

$$\left(\frac{R^{18}}{R_a^{18}}\right)^\lambda = \left(\frac{R^{17}}{R_a^{17}}\right),$$

where R^{18} and R^{17} are the ratios ($^{18}\text{O}/^{16}\text{O}$) and ($^{17}\text{O}/^{16}\text{O}$) of the phase respectively. If we take a as reference, e.g., SMOW, by the definition of delta the above equation is replaced by,

$$\left(\frac{\delta^{18}\text{O}}{1000} + 1\right)^\lambda = \left(\frac{\delta^{17}\text{O}}{1000} + 1\right).$$

Taking natural log and multiplying 1000,

$$\lambda \times 1000 \times \ln\left(\frac{\delta^{18}\text{O}}{1000} + 1\right) = 1000 \times \ln\left(\frac{\delta^{17}\text{O}}{1000} + 1\right).$$

Miller (2002) defined $1000 \times \ln\left(\frac{\delta^{18}\text{O}}{1000} + 1\right)$ as $\delta'^{18}\text{O}$. In a $\delta'^{18}\text{O}$ vs. $\delta'^{17}\text{O}$ diagram, λ is the slope of mass dependent fractionation line.

When $x^2 < 1$, $\ln(x+1) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \frac{1}{4}x^4 + \dots$. Since the second term and after that can be ignored, if $x \ll 1$, i.e., $\left(\frac{\delta^{18}\text{O}}{1000}\right) \ll 1$, the following approximation can be made,

$$\lambda \times \delta^{18}\text{O} \cong \delta'^{18}\text{O}$$

Thus, in a $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ diagram (traditional three-isotope plot), oxygen isotopic compositions of phases derived by mass-dependent fractionation fall on a linear line when $\delta^{18}\text{O}$ values are only close to the origin.

Delta and delta prime values for the same oxygen isotopic ratio are slightly different from each other. Any ratios of $-20\% < \delta^{18}\text{O} < +20\%$, the difference is relatively insignificant ($< 0.20\%$), however the difference is getting larger with increasing absolute values of $\delta^{18}\text{O}$; for instance, -50% as $\delta^{18}\text{O}$ is equal to -51.29% as $\delta'^{18}\text{O}$, and $+50\%$ as $\delta^{18}\text{O}$ is equal to $+48.79\%$ as $\delta'^{18}\text{O}$ (Fig. 7). Because of such difference, we converted literature data to δ' values, if they were given as δ values, in order to compare with our data.

Delta and delta prime values differ not only in $\delta^{18}\text{O}$ ($\delta'^{18}\text{O}$) but also in $\Delta^{17}\text{O}$ ($\Delta'^{17}\text{O}$) for the same oxygen isotopic

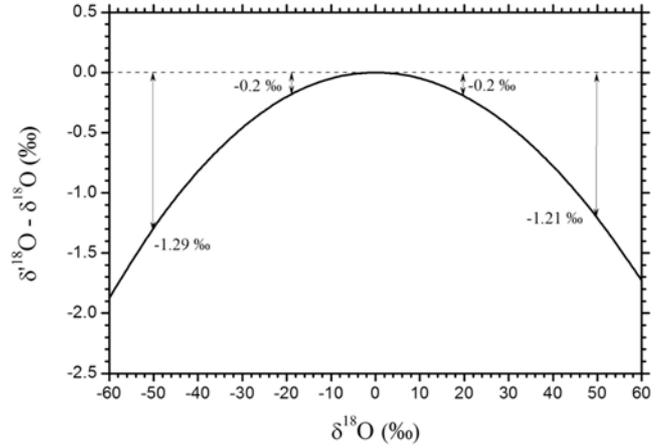


Fig. 7. Difference between $\delta'^{18}\text{O}$ and $\delta^{18}\text{O}$ that is relatively small near the origin ($< 0.2\%$ when $-20\% < \delta^{18}\text{O} < 20\%$) and increases with increasing distance from the origin.

composition (Fig. 2 in Miller, 2002); the difference between $\Delta^{17}\text{O}$ and $\Delta'^{17}\text{O}$ is negligible, only when $\delta^{18}\text{O}$ (or $\delta'^{18}\text{O}$) values are close to the origin.

5.2. VSMOW-SLAP Scaling

The VSMOW-SLAP scaling factor of we used in this paper is 1.056 that was calculated as the ratio between the recommended and measured $\delta^{18}\text{O}$ values of SLAP. Merits of the VSMOW-SLAP scaling are that any bias generated among different laboratories can be minimized after the scaling and one can easily recalibrate the scaled data if new SLAP data is available. Prior to this study only Kusakabe and Matsuhisa (2008) clearly stated that they used the scaling.

In Figure 8, we compare the $\delta'^{18}\text{O}$ differences between NBS-28 quartz and SC olivine (or UWG-2 garnet) reported from various laboratories. Two data sets with the VSMOW-SLAP scaling, Kusakabe and Matsuhisa (2008) and this study, are most similar to each other.

5.3. Slope of the Mass Fractionation Line

Recent high precision data suggest that the slope, λ' might differ for the samples derived from different physico-chemical processes. Rumble et al. (2007) obtained λ' values of 0.5240 ± 0.0010 and 0.5242 ± 0.0010 from hydrothermal quartz together with chert flint sample, while those of 0.5262 ± 0.0008 and 0.5266 ± 0.0012 from high-temperature eclogitic garnet using two laser fluorination systems at the Open University and Geophysical Laboratory, Carnegie Institute of Washington. The δ' values obtained by analyzing meteoric water samples are even higher: 0.528 ± 0.001 (Kusakabe and Matsuhisa, 2008) and 0.5279 ± 0.0001 (Barkan and Luz, 2005). It was also pointed out that equilibrium

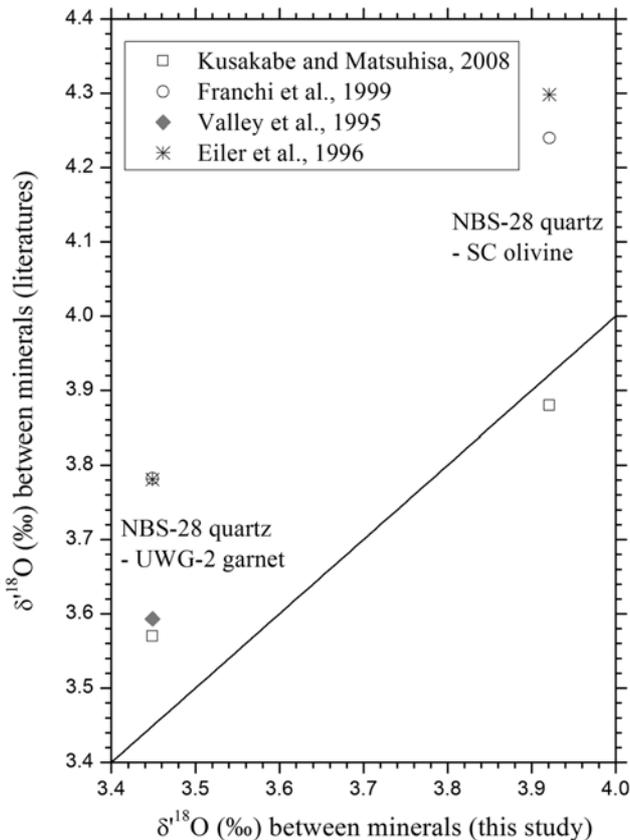


Fig. 8. Comparison of differences between $\delta^{18}\text{O}$ values of mineral pairs (NBS-28 quartz – UWG-2 garnet or NBS-28 quartz – SC olivine) plotted as literature values vs. KOPRI values. Note that two data sets with VSMOW-SLAP scaling (Kusakabe and Matsuhisa, 2008 and this study) are similar to each other: fall close to the slope-1 line.

and kinetic processes result in different mass-dependent fractionation line (e.g., Rumble et al., 2007; Young et al., 2002). In this paper, we simply assume that the samples we measured fall on a single mass-dependent fractionation line and calculated the slope of TF line using the averages of 8 terrestrial solid samples as 0.5248 ± 0.0003 with $R^2 = 0.99992$ (Fig. 6). Note that $\Delta^{17}\text{O}$ values of the samples in Figure 6 are less than ± 0.04 . Table 3 compares the slopes of the TF line obtained from terrestrial rocks and minerals from various laboratories.

6. SUMMARY AND CONCLUSIONS

We measured oxygen isotopic compositions of various terrestrial solid samples by a CO₂-laser BrF₅ fluorination system installed at Korea Polar Research Institute since year 2007. Various solid materials including SC olivine, JFB glass, UWG-2 garnet, NBS-28 quartz, CQ4 quartz and CFS were measured to check precision and reproducibility of the system. These samples were chosen because they are most widely used solid standards at the laboratories with similar

system, thus we can compare our data with previously reported values. Among them we use JFB glass as our primary solid standard to monitor daily performance.

Typical weight of silicates consumed by individual analysis in our system is 2 mg (equivalent to 29 μmol). Smaller samples may cause instrumental fractionation, since the pressure at the inlet system is not high enough to give the identical flow rate for dual-inlet system. However, in some case it is necessary to measure samples having less than 29 μmol of oxygen, especially very precious ones, such as meteorites. We have tested our system for the samples of less than 2 mg and obtained a correction function.

All data here are reported as $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values following Miller (2002) and were scaled using the measured VSMOW and SLAP data as suggested by Kusakabe and Matsuhisa (2008) and Coplen (1995).

Average $\delta^{18}\text{O}$ values and 2σ standard error of means are $5.27 \pm 0.04\text{‰}$ for SC olivine, $5.49 \pm 0.02\text{‰}$ for JFB glass, $5.73 \pm 0.05\text{‰}$ for UWG-2 garnet, 9.18 ± 0.08 for NBS-28 quartz, 23.14 ± 0.36 for CQ4 quartz and $33.97 \pm 0.16\text{‰}$ for CFS. Five measurements for the serpentine give similar reproducibility with the anhydrous standard materials, and the average $\delta^{18}\text{O}$ is $0.78 \pm 0.07\text{‰}$. All these data nicely fall along a linear line on a $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ diagram giving the slope of terrestrial fractionation as 0.5248 ± 0.0003 ($R^2 = 0.99992$). Our data agree in general with recently published data and are most similar to those reported by Kusakabe and Matsuhisa (2008) whose data was also scaled by VSMOW-SLAP.

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