TECHNICAL REPORT

CO₂ Laser-BrF₅ Fluorination Technique for Analysis of Oxygen Three Isotopes of Rocks and Minerals

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Technical details of an on-line CO₂ laser-BrF₅ fluorination system, installed at Institute for Study of the Earth's Interior, Okayama University, were described. The system allows us precise determination of oxygen three isotope composition ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) of rocks and minerals. The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of some international and laboratory reference materials such as UWG2 garnet, NBS-28 quartz, NBS-30 biotite, San Carlos olivine, forsterite, fayalite, enstatite, augite, magnetite, zircon, and basalt glass from Juan de Fuca Ridge were determined with the precision of less than 0.1‰. The data plot well on the terrestrial fractionation line defined as $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$. The analytical system can be used for analysis of meteoritic materials. The results for international reference materials show generally good agreement with literature values. There exists, however, a small interlaboratory difference in $\delta^{18}\text{O}$ values of reference materials that reflects how standardization was made at each laboratory. A common standardization, such as comparison of reference materials with O₂ directly converted from VSMOW, is required to obtain better agreement within the international community.

1. Introduction

Variations of natural isotopic abundance of oxygen have been widely used in the field of stable isotope geochemistry and cosmochemistry, because oxygen is the most abundant element of planetary mantle and crust that consist mainly of silicates and oxides, and because the isotopic variations can give information of their origins and processes that they have experienced. It is well established that oxygen isotopic compositions of most of terrestrial materials plot on a straight line with a slope of $\sim 1/2$ in a $^{17}\text{O}/^{16}\text{O}$ – $^{18}\text{O}/^{16}\text{O}$ space.^{1), 2)} This relationship, often referred to as the terrestrial fractionation line or TF line, reflects mass dependent fractionation. Meteorites, however, have different isotopic characteristics that plot around the TF line and the mass independent fractionation (MIF) relationship^{1), 2)} with a slope of ~ 1 . The MIF relationship, sometimes called oxygen isotopic anomaly, has been interpreted to derive from either intrinsic isotopic heterogeneity and mixing between different oxygen isotopic reservoirs²⁾ or photochemical reactions between oxygen-bearing gases^{3), 4)} in the early solar system. For this reason the oxygen three-isotope plot has a special and unique importance in cosmochemistry.

Quantitative extraction of oxygen from silicates and oxides is accomplished by reaction with strongly oxidizing reagents such as fluorine or interhalogen fluorides (BrF₅, ClF₃). In early 60s, a mixture of F₂ and HF⁵⁾ and BrF₅^{6), 7)} were used for the oxygen extraction.

Conventionally the fluorination reaction is carried out in the atmosphere of either F₂ or BrF₅ in a Ni tube heated to 500–700°C using an external electric furnace. Of these BrF₅ was found to be an excellent reagent, because BrF₅ has physical properties easy to handle, e.g., vapor pressure of 438 hPa (mbar) at 20°C and freezing point at –61°C. A typical decomposition reaction for forsterite (Mg₂SiO₄) using BrF₅ is expressed by

The conventional method has been proven to give precise and accurate data, but requires relatively a large amount of sample (typically 5–30 mg) and is time-consuming. The resulting O₂ is recovered using a Hg Toepler pump and usually converted to CO₂ by the reaction with hot graphite^{5)–7)} for later mass spectrometric determination of $^{18}\text{O}/^{16}\text{O}$ ratios. With CO₂, however, an accurate $^{17}\text{O}/^{16}\text{O}$ ratio measurement is difficult to achieve due to high contribution of ^{13}C in mass 45 that is comprised of $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ and $^{13}\text{C}^{16}\text{O}^{16}\text{O}$. For this reason, we introduce O₂ directly into a mass spectrometer for precise measurement of m/z 33/32 ($=^{17}\text{O}/^{16}\text{O}$) and 34/32 ($^{18}\text{O}/^{16}\text{O}$) ratios. The choice of O₂ as an analyte has an advantage over CO₂ that a possible oxygen isotope fractionation during conversion of O₂ to CO₂ is avoided.

In early 90s laser extraction techniques were developed where IR laser (Nd:YAG or CO₂ laser) was used as a heat source.^{8), 9)} The techniques brought a revolution in the oxygen isotope geochemistry of rocks and minerals, because a required sample size was reduced to *ca.* 1/10 of the conventional methods, and more importantly, analysis of refractory minerals such as olivine, zircon, and garnet that were difficult to decompose with the conventional method was made possible. The

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Fig. 1. Schematic presentation of the laser fluorination line. An aliquot of BrF_5 is frozen into the cold finger (CF) attached to the reaction chamber. After evacuation and closing a valve next to the reaction chamber, the BrF_5 pressure inside the chamber becomes ~ 300 hPa. The sample is laser-heated and observed through the binocular microscope (see Fig. 2). After the reaction, the excess reagent and condensable gases are trapped in a cryogenic trap in the metal part of the line. The non-condensable gases are led to the glass part of the line for purification. Fluorine is removed at the KBr fluorine getter. Oxygen is further purified through a series of cryogenic traps. The purified O_2 is collected in the cold finger 2 that contains Molecular Sieve 13X. The O_2 pressure at room temperature is measured with a pressure transducer to calculate the reaction yield, and is admitted to the inlet system (Hg Toepler pump) of the mass spectrometer. The O_2 pressure inside the inlet system is finely adjustable by changing the volume of Hg-containing bellows. PG stands for Pirani gauge.

laser fluorination has several advantages over the conventional method in that (1) oxygen background is very small, (2) sample size is reduced to milligram to sub-milligram ranges, and (3) analytical efficiency is high keeping the analytical accuracy the same as the conventional method. In recent years UV laser (Kr-F_2 , Ar-F_2 laser) coupled with a continuous-flow mass spectrometry has been introduced for *in-situ* analysis of a minute amount of sample with spatial resolution as small as $50\text{ }\mu\text{m}$.^{10–12} Secondary ion mass spectrometry (SIMS) has also been used,^{13–15} because it has an extraordinarily high spatial resolution. The precision and accuracy of SIMS analysis, however, is still to be improved compared to the conventional and laser fluorination techniques.

In the present note we describe an oxygen isotope analytical system for rocks and minerals using a CO_2 laser- BrF_5 fluorination technique that has been installed at the Institute for Study of the Earth's Interior (ISEI), Okayama University at Misasa with an aim to achieve precise $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratio measurements. Although there are several laboratories in the world that use the laser fluorination techniques for oxygen isotopic analysis, the ISEI system is currently only one in Japan and has been applied to oxygen three isotope analysis of meteoritic materials in the community of Japanese cosmochemists.^{16, 17} We present some analytical results for silicate and oxide samples that are used as international and internal references using the system.

2. Experimental

2.1 System description

The configuration of our system is basically similar to that described in the literatures,^{8, 9} but some modifications have been made. Oxygen is extracted from sample in the form of O_2 and we use this O_2 as an analyzing gas for mass spectrometric measurement in order to obtain accurate $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios. An overall view of the oxygen extraction system is shown in Fig. 1. It basically consists of metal and glass parts; the reaction chamber and a purification line made of stainless steel (SUS316), and a purification line made of glass. The end of the glass line is directly connected to the inlet system of a mass spectrometer. Details of the reaction chamber will be described in Section 2.3. In the metal part where BrF_5 gas is in contact, stainless steel piping and high vacuum metal bellows valves (Nupro, SS-4H) are connected using Swagelok connectors. A fraction of BrF_5 in a metal cylinder is distilled into a Kel-F trap, stored and used for each analysis.

2.2 Laser

The laser used in this system is a CO_2 laser with a maximum power of 12 W and the wavelength of $10.6\text{ }\mu\text{m}$ (Japan Laser Co., Ltd., Model JLC-1250). The focal length is 10.2 cm and a minimum spot diameter is $100\text{ }\mu\text{m}$. A visible, coaxial He-Ne laser (wavelength of 633 nm) is attached in order to locate a target.

Fig. 2. (a) Schematic presentation of the reaction chamber with dimensions. Vacuum seal between the reaction chamber and BaF₂ window is attained with a KalRez® O-ring. Fluorination reaction is observed through a binocular microscope. (b) Schematic presentation of the sample holder. It is made of Ni.

2.3 Reaction chamber

The reaction chamber and its dimension are illustrated in Fig. 2a. It is made of stainless steel (SUS316), and connected to the purification line with a Cajon 1/4-inch flexible tubing. Since the laser beam radiates downward from a fixed position, the chamber needs to be movable and sits on a motor-driven XYZ stage. A stainless steel cold finger is attached to the chamber in order to collect and purify BrF₅ that is used for reaction. The chamber is covered with a BaF₂ window (50 mm in diameter and 5 mm thick) for vacuum sealing using a KalRez O-ring. BaF₂ is transparent to infrared and visible light. Sample is placed in a dimple of the sample holder made of Ni (Fig. 2b). The dimple size is 3 mm in diameter and 1.5 mm in depth. There are altogether 12 dimples in the sample holder, but currently we use 8 of them for a day work. A sample holder with steeply slanted holes may better be used

for some minerals to avoid sputtering of sample when laser-irradiated as mentioned later. Sample is laser-irradiated through the BaF₂ window. We observe the laser heating operation through a binocular microscope and a mirror that is placed above the chamber. It is important to observe how the reaction proceeds through a binocular microscope.

2.4 Oxygen extraction procedures

For analysis of silicate minerals and whole rocks, approximately 1.5–3 mg of sample is placed in one of the dimples of the sample holder. After loading samples the reaction chamber is evacuated. The chamber is preheated at ~180°C using heating tapes for several hours to overnight. Then the volume containing the chamber and cryogenic trap is filled with approximately 100 hPa of BrF₅ gas (measured with the Bourdon gauge) and is left for several hours to overnight (depending on a mineral type) to remove any atmos-

pheric moisture adsorbed on the surface of the BaF₂ window, reaction chamber and sample. Residual gases are then pumped out. Approximately 120 hPa of BrF₅ gas is expanded into the chamber and is frozen in a cold finger at liquid nitrogen temperature. After evacuation and closing the valve next to the chamber, the BrF₅ gas pressure inside the chamber becomes about 300 hPa at room temperature, high enough for the fluorination reaction. The chamber position is adjusted with the XYZ stage so that sample in a dimple is laser-heated (Fig. 2a). Initially, defocused low power laser beam is admitted. By rastering the laser beam, most of the sample in a dimple is decomposed. This is followed by final clean up with gradually increased laser power. A small fraction of the sample hiding underneath fluoride products needs to be irradiated with focused, high power beam. Visual observation helps these procedures.

After the laser fluorination the gases in the reaction chamber are expanded into the cryogenic trap kept at liquid nitrogen temperature where excess BrF₅, BrF₃, SiF₄, and other condensable gases (see reaction (1)) are trapped leaving only O₂ and a minute amount of F₂ in the line (Fig. 1). Metal fluorides such as MgF₂ remain in the reaction chamber. The O₂ is further purified cryogenically through a series of glass traps in the glass line. Gas transfer is monitored with Pirani gauges. A small amount of F₂, if any, is removed at the fluorine getter containing coarse grained KBr crystals kept at 150°C. The purified O₂ is finally adsorbed in a Molecular Sieve 13X cold finger 2 at liquid nitrogen temperature. In the case of nitrogen-containing sample, a trace amount of NF₃ may be formed. In the mass spectrometer ion source NF₃ is decomposed to form NF⁺ which has a mass number 33 interfering ¹⁷O/¹⁶O measurement.¹⁸⁾ The O₂ gas produced from such a sample is trapped in a Molecular Sieve 13X cold finger 1 at liquid nitrogen temperature, followed by preferential release of pure O₂ from the trap at −116°C, the melting temperature of ethanol.¹⁸⁾ After the manometric measurement of the O₂ amount using a pressure transducer, it is expanded into a mercury Toepler pump and admitted into the mass spectrometer through a capillary tubing after adjusting the O₂ pressure in the mercury Toepler pump of the mass spectrometer inlet system. With this system approximately 3/4 of the O₂ produced can be

introduced into the mercury Toepler pump.

2.5 Mass spectrometer

The mass spectrometer used in this study is SIRA12 (Micromass, UK). It is a dual-inlet, triple collector mass spectrometer for stable isotope measurement, but its original configuration has been drastically modified. The original electronics have been completely removed and replaced with a modern one (Linear Source Control, Europa Scientific, UK), a solenoid-type change-over valve with a pneumatically operated Kel-F sealed micro inlet (SIRA10-type), and the inlet variable volumes with handmade mercury Toepler pumps. The cross-seat leakage between reference and sample gases through the micro inlet is negligible. The effects of background and tailing of mass 32 on mass 33 have been corrected.¹⁹⁾ The data acquisition is made by WinIRMS, a Windows-based data collection software (Etchells, UK). The upper part of the Toepler pumps is thinner than the basal part in order to obtain a gas pressure high enough for mass spectrometric measurement of a small sample by raising a mercury level. With this inlet system sample weighing less than 1 mg can be run.

A commercially available high purity (99.999%) O₂ gas is used as a working standard. A bottle of another high purity O₂ gas named OKA-O is attached just before the Molecular Sieve 13X cold finger 2 (Fig. 1). OKA-O is measured daily to check the performance of the mass spectrometer.

3. Results and Discussion

3.1 Standardization

In reporting the ¹⁸O/¹⁶O and ¹⁷O/¹⁶O ratios a conventional δ notation is used as permil deviations from the Standard Mean Ocean Water standard (SMOW).²⁰⁾ They are defined as δ (‰) = $(R_s/R_{\text{SMOW}} - 1) \times 1000$, where R_s and R_{SMOW} are the ¹⁸O/¹⁶O or ¹⁷O/¹⁶O ratios of sample and SMOW, respectively. Since real SMOW is non-existent, VSMOW (Vienna-SMOW distributed by IAEA, Vienna) which is essentially the same as SMOW is taken as the standard. The absolute values of (¹⁸O/¹⁶O)_{VSMOW} and (¹⁷O/¹⁶O)_{VSMOW} have been reported to be $(2005.20 \pm 0.45) \times 10^{-6}$ ²¹⁾ and $(379.9 \pm 0.8) \times 10^{-6}$ ²²⁾. Oxygen isotope ratio of water is normally measured on CO₂ that has been equilibrated with reference water at a given temperature, hence any $\delta^{18}\text{O}$ value referred to

Table 1. Oxygen Isotopic Compositions of Some Reference Materials Analyzed in This Study

Sample	$\delta^{17}\text{O}$ (‰)	δ (‰)	$\delta^{18}\text{O}$ (‰)	δ (‰)	$\Delta^{17}\text{O}$ (‰)	<i>n</i>	O ₂ yield (Av. %)
UWG2 garnet (Gore Mountain, Adirondack, NY)	3.02 ^{a)}	0.09	5.80 ^{a)}	0.09	0.00	50	93
NBS-28 quartz (African galss sand)	4.88	0.07	9.45	0.07	−0.03	15	90
NBS-30 biotite (Lakeview tonalite, CA)	2.69	0.08	5.08	0.08	0.05	7	96
San Carlos olivine (Fo89.2)	2.91	0.09	5.44	0.10	0.08	9	90
Artificial forsterite (Fo100)	5.60	0.07	10.96	0.06	−0.10	6	89
Fayalite (pegmatite, Fukushima, manganoan)	3.08	0.10	5.68	0.12	0.12	6	87
Enstatite (En86.0, Wo0.8, Bamble, Norway)	4.98	0.12	9.58	0.13	0.00	6	92
Augite (Akita, Japan)	3.09	0.05	5.87	0.12	0.05	6	91
Magnetite (Shimonoseki, Japan)	−3.24	0.04	−6.48	0.07	0.13	4	94
Zircon (Baddeleyite, Minas Gerais, Brazil)	−1.69	0.06	−3.43	0.06	0.09	6	92
Juan de Fuca Ridge basalt glass	2.93	0.07	5.64	0.14	0.01	18	95

^{a)} $\delta^{18}\text{O}$ for UWG2 garnet is assigned to 5.80‰. $\delta^{17}\text{O}$ is assigned to 3.02‰ assuming the TF behavior (see the text).

Fig. 3. Long term variation (approximately 10 months) in the oxygen isotopic ratio of UWG2 garnet, showing reproducible $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values ($\pm 0.09\text{‰}$). Data obtained after a major modification of the SIRA12 mass spectrometer are plotted.

Fig. 4. $\delta^{18}\text{O}$ values of UWG2 garnet and NBS-28 quartz are plotted as a function of oxygen yield (a) and sample weight (b). Oxygen yield is usually between 90 and 98% for UWG2 garnet and around 90% for NBS-28 quartz, but it does not affect the $\delta^{18}\text{O}$ values. We usually use sample weighing between 1.5 and 3 mg. Sample size does not affect the $\delta^{18}\text{O}$ values in this range.

VSMOW for silicates and oxides inevitably includes the uncertainty of the equilibrium fractionation factor between H₂O and CO₂.²³⁾ For this reason $\delta^{18}\text{O}$ values of silicates and oxides are often normalized to a given value for a silicate reference material which is usually NBS-28 quartz. However, reflecting the above mentioned uncertainty in the CO₂-H₂O fractionation factor and difficulty of laser heating of quartz, $\delta^{18}\text{O}$ value of NBS-28 quartz has been variously reported as stated later. A $\delta^{18}\text{O}$ value of 5.80‰ has been recommended for garnet from mafic amphibolite from the Gore Mountain mine named as UWG2 by Valley *et al.*²⁴⁾ They pro-

posed this value based on $\delta^{18}\text{O}$ of 9.59‰ for NBS-28 quartz that resulted from compilation of the intercomparison program by IAEA.^{25), 26)} Note, however, that the compiled values range from 9.39 to 9.7‰, far from satisfactory agreement as discussed in Section 3.2. In addition the way how each $\delta^{18}\text{O}$ value was given in the SMOW scale is not shown in the compilation. In the present note, we *tentatively* report our $\delta^{18}\text{O}$ values taking 5.80‰ for UWG2 garnet, because it is most easily decomposed by laser fluorination with good reproducibility in $\delta^{18}\text{O}$ and oxygen recovery yield. Note that $\delta^{18}\text{O}_{\text{UWG2}} = 5.80\text{‰}$ may change slightly if $\delta^{18}\text{O}_{\text{NBS-28}} = 9.59\text{‰}$ is changed by direct comparison between O₂ from NBS-28 quartz and VSMOW or better determination of the CO₂-H₂O fractionation factor in the future. As stated earlier, oxygen isotopic compositions of most of terrestrial materials plot on a straight line with a slope of $\sim 1/2$ in a $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space, or more precisely $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$.²⁾ Accepting this relationship, we report our $\delta^{17}\text{O}$ values of any sample normalized to $\delta^{17}\text{O}_{\text{UWG2}} = 3.02\text{‰}$ calculated from the above equation.

It has been recommended by the Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations, IAEA, that $\delta^{18}\text{O}$ values of any material should be normalized to a scale that is defined as $\delta^{18}\text{O}_{\text{VSMOW}} - \delta^{18}\text{O}_{\text{SLAP}} = -55.5\text{‰}$.²⁶⁾ SLAP stands for Standard Light Antarctic Precipitation and is distributed by IAEA. This recommendation requires us to measure $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of O₂ directly converted from both VSMOW and SLAP. In the present study, we adopted the normalization factors of 1.002 for $\delta^{17}\text{O}$ and 1.037 for $\delta^{18}\text{O}$ which were used by Jabeen and Kusakabe,²⁷⁾ because the same mass spectrometer has been used in the present study. Note that the normalization factors include a small modification due to introduction of an instrumental factor which was not properly evaluated in Jabeen and Kusakabe.²⁷⁾

3.2 Analytical results

We have measured $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios of some silicate minerals, oxides, and basalt glasses, some of which are used widely as the international reference materials for oxygen isotopic measurement. The samples are UWG-2 garnet, NBS-28 quartz, NBS-30 biotite, San Carlos olivine, artificial forsterite, fayalite, ensta-

tite, augite, magnetite, zircon, and basalt glass from the Juan de Fuca Ridge. The analytical results are given in Table 1. The reproducibility of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ through the whole analytical procedures was evaluated by 50 replicate analyses of UWG2 garnet, and was found to be 0.09‰ (one sigma) for both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, as shown in Fig. 3. The average values of measured $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of UWG2 were assigned to 5.80‰²⁴⁾ and 3.02‰, respectively, as stated above, to obtain $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values in the VSMOW scale of any silicate/oxide sample in this study. Oxygen recovery yield is usually between 90 and 98%. Lower yields come out sporadically, reflecting sputtering of sample during laser irradiation and the weighing uncertainty. Lower oxygen yield, however, does not appear to affect the isotopic ratios in the case of UWG2 garnet and NBS-28 quartz as shown in Fig. 4a. The $\delta^{18}\text{O}$ values are also not affected by sample weight in the range between 1.5 and 3 mg that are normally used in this study (Fig. 4b).

NBS-28 quartz has been analyzed in many laboratories for $\delta^{18}\text{O}$. The data, as compiled in Table 2, vary from +8.8 to +10.0‰. Some of them were obtained using both the conventional and laser fluorination techniques. Our value, $9.45 \pm 0.07\text{‰}$ ($n=15$), is in the middle of the variations. Quartz grains tend to sputter when laser-heated and jump out of a dimple of the sample holder, sometimes contaminating the neighboring samples. In our method quartz sample is heated with defocused but high power laser beam followed by final rastering with focused beam at the same high power to decompose any remaining grains.²⁴⁾ A deep slanting sample holder rather than the sample holder shown in Fig. 2b is recommended for quartz. With this method sputter can be minimized. The $\delta^{18}\text{O}$ value of NBS-28 needs to be agreed upon by those who work in the field of oxygen isotope geochemistry. To avoid the ambiguity of the $\text{CO}_2\text{-H}_2\text{O}$ fractionation factor, comparison of NBS-28 with VSMOW that is directly converted to O_2 is preferred. This was attempted by Jabeen and Kusakabe.²⁷⁾ They reported NBS-28 quartz of 9.31‰ on the VSMOW- O_2 basis, but lower by 0.28‰ than the value compiled by IAEA.²⁵⁾ A mean $\delta^{18}\text{O}$ value of $5.59 \pm 0.16\text{‰}$ was given for UWG2 garnet by Jabeen²⁸⁾ using the same system. This value is also lower by 0.21‰ than that proposed by Valley *et al.*²⁴⁾ The relative difference in $\delta^{18}\text{O}$ between NBS-28 and UWG2 is 3.65‰ in the present study, which is consistent with 3.70‰ at the University of Wisconsin²⁴⁾ and 3.72‰ by Jabeen.²⁸⁾ This consistency and the variability in reported $\delta^{18}\text{O}_{\text{NBS-28}}$ values indicate that we need to constrain the $\delta^{18}\text{O}$ value of NBS-28 compared with O_2 directly converted from VSMOW. The variability in reported $\delta^{18}\text{O}_{\text{NBS-28}}$ values most probably stems from standardization of mass spectrometer reference material in each laboratory.

NBS-30 biotite is another international silicate reference material distributed by IAEA for stable isotope work. We obtained $\delta^{18}\text{O} = 5.08 \pm 0.08\text{‰}$ and $\delta^{17}\text{O} = 2.69 \pm 0.08\text{‰}$ ($n=7$) for this sample. Our $\delta^{18}\text{O}$ value agrees well with those obtained in other laboratories (Table 2). The IAEA compiled value is 5.2‰,²⁵⁾ but if an outlier (5.6‰) is excluded, it becomes 5.12‰. The biotite reacted easily with BrF_5 in our runs.

We also analyzed the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of laboratory reference samples, *i.e.*, San Carlos olivine, artificial forsterite (Fo100), fayalite, enstatite (En86), augite, magnetite, zircon, and basalt glass from Juan de Fuca Ridge as listed in Table 1. We obtained $\delta^{18}\text{O} = 5.44 \pm 0.10\text{‰}$ and $\delta^{17}\text{O} = 2.91 \pm 0.09\text{‰}$ ($n=9$) for San Carlos olivine. Our $\delta^{18}\text{O}$ value is higher than those obtained in other laboratories, and especially so when compared to $\delta^{18}\text{O}$ values reported by Jabeen *et al.*²⁹⁾ and by Matthey and Macpherson⁹⁾ whose isotopic standardization is based on NBS-19 calcite²⁵⁾ (see Table 2 for references). This suggests again the necessity of measurement of reference materials on the VSMOW- O_2 basis applied by the VSMOW-SLAP scaling at each laboratory. We noticed that Fe-rich minerals such as fayalite and magnetite produce fluorides that condense on the inside surface of the BaF_2 window during laser fluorination, sometimes making visual observation difficult.

The $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ relationship of the above reference materials is shown in Fig. 5. The data, spanning from -6.5‰ to 11.0‰ in $\delta^{18}\text{O}$ and from -3.2‰ to 5.6‰ in $\delta^{17}\text{O}$, plot nicely on the terrestrial fractionation line of $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ proposed by Clayton.²⁾ The $\Delta^{17}\text{O}$ values, defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$, of the reference materials analyzed in this study are very close to 0 (Table 1), confirming that their isotopic variations of our samples are governed by mass dependent fractionation. The line in Fig. 5 gives a basis for the oxygen isotopic study of extraterrestrial materials that display various $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ relationships and $\Delta^{17}\text{O}$ values.²⁾ The range of variation in the $\delta^{18}\text{O}$ values covers those for most of major stony meteorites.

Fig. 5. Oxygen three isotope plot of some international and intra-laboratory reference samples used in this study. The data lie on the terrestrial fractionation (TF) line with $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$.²⁾ Analytical error is smaller than the symbols. See Table 1 for analytical results of augite, UWG2 garnet, NBS-30 biotite, Juan de Fuca ridge basalt glass, San Carlos olivine and fayalite, since the data points are so crowded.

Table 2. Comparison of $\delta^{18}\text{O}$ Values of UWG2, NBS-28, San Carlos Olivine and NBS-30 Biotite Obtained by Different Laboratories

Sample	$\delta^{18}\text{O}$ (‰)	δ (‰)	n	Analyte	Method	Standardization	Reference
UWG2 garnet	5.80 ^{a)}	± 0.09	50	O ₂	CO ₂ laser-BrF ₅ , whole grain	UWG2=5.80	This study
	5.89	± 0.15	> 1000	CO ₂	CO ₂ laser-BrF ₅ , whole grain	NBS-28 = 9.58	Valley <i>et al.</i> (1995) ⁽²⁴⁾
	5.82	± 0.03	4	O ₂	UV laser-F ₂ , <i>in-situ</i>	Not given	Rumble <i>et al.</i> (1997) ⁽¹¹⁾
	5.77	± 0.07	5	CO ₂	CO ₂ laser-BrF ₅ , whole grain	NBS-28=9.58	Eiler <i>et al.</i> (1996) ⁽³⁰⁾
NBS-28 quartz	9.45	± 0.08	15	O ₂	CO ₂ laser-BrF ₅ , whole grain	UWG2=5.80	This study
	9.31	± 0.09	7	O ₂	CO ₂ laser-BrF ₅ , whole grain	VSMOW converted to O ₂	Jabeen and Kusakabe (1997) ⁽²⁷⁾
	9.23	± 0.05	18	CO ₂	Conventional	SMOW converted to O ₂ (?)	Clayton and Mayeda (1983) ⁽¹⁸⁾
	9.26	± 0.18	65	O ₂	CO ₂ laser-BrF ₅ , whole grain	Not given	Valley <i>et al.</i> (1995) ⁽²⁴⁾
	9.58	± 0.09	8	—	Compiled		Gonfiantini <i>et al.</i> (1995) ⁽²⁵⁾
	9.50	± 0.09	13	CO ₂	Conventional, $\alpha = 1.0407$ (25°C)	CO ₂ equilibrated with VSMOW	Matsuhisa (1974) ⁽³¹⁾
	9.0	± 0.10	3	CO ₂	Nd/YAG laser-ClF ₃	Not given	Akagi <i>et al.</i> (1995) ⁽³²⁾
	10.0	± 0.07	20	CO ₂	Conventional	VSMOW converted to CO ₂	Friedman and Gleason (1973) ⁽³³⁾
	9.46	± 0.19	44	CO ₂	CO ₂ laser-BrF ₅ , whole grain	Not given	Elsenhimer and Valley (1993) ⁽³⁴⁾
	9.39	± 0.10	7	CO ₂	CO ₂ laser-BrF ₅ , whole grain	NBS-28 and NBS-31	Kohn <i>et al.</i> (1993) ⁽³⁵⁾
	9.7	± 0.1	4	CO ₂	CO ₂ laser-BrF ₅ /ClF ₃ , whole grain	Not given	Sharp (1990) ⁽⁸⁾
	8.8	± 0.2	22	CO ₂	CO ₂ laser-BrF ₅ , whole grain	Not given	Fouillac and Girard (1996) ⁽³⁶⁾
	5.08	± 0.08	7	O ₂	CO ₂ laser-BrF ₅ , whole grain	UWG2=5.80	This study
	5.0	± 0.1	2	CO ₂	CO ₂ laser-BrF ₅ , whole grain	Not given	Sharp (1990) ⁽⁸⁾
NBS-30 biotite	5.03	± 0.08	82	CO ₂	Nd/YAG laser-ClF ₃	NBS-19 carbonate	Mattey and Macpherson (1993) ⁽⁹⁾
	5.24	± 0.24	4	CO ₂	Conventional	Compiled	Gonfiantini <i>et al.</i> (1995) ⁽²⁵⁾
San Carlos olivine	5.44	± 0.10	9	O ₂	CO ₂ laser-BrF ₅ , whole grain	UWG2=5.80	This study
	5.23	± 0.15	11	O ₂	UV laser-F ₂ , <i>in-situ</i>	Not given	Rumble <i>et al.</i> (1997) ⁽¹¹⁾
	4.70	± 0.18	5	O ₂	CO ₂ laser-BrF ₅ , whole grain	VSMOW converted to O ₂	Jabeen <i>et al.</i> (1998) ⁽²⁹⁾
	4.88	± 0.06	20	CO ₂	Nd/YAG laser-ClF ₃	NBS-19 carbonate	Mattey and Macpherson (1993) ⁽⁹⁾
	5.25	± 0.05	7	CO ₂	CO ₂ laser-BrF ₅ , whole grain	NBS-28=9.59	Eiler <i>et al.</i> (1996) ⁽³⁰⁾

^{a)}Assigned to 5.80. See the text.

4. Conclusion

The oxygen isotopic analytical system installed at the Institute for Study of the Earth's Interior, Okayama University has been described. The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of some international and laboratory reference materials such as UWG2 garnet, NBS-28 quartz, NBS-30 biotite, San Carlos olivine, forsterite, fayalite, enstatite, augite, magnetite, zircon and Juan de Fuca Ridge basalt glass were determined with the precision of less than 0.1‰ for most cases. The data plot nicely on the terrestrial fractionation line defined as $\delta^{17}\text{O}=0.52\times\delta^{18}\text{O}$. The system can be applied to the oxygen isotopic analysis of extraterrestrial materials with a good precision. The accuracy of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ analysis depends how standardization is made. Comparison of isotopic ratios of O_2 available from direct fluorination of VSMOW water with silicate/oxide samples is essential to obtain better accuracy.

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