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メタデータ	言語: eng 出版者: 公開日: 2008-01-25 キーワード (Ja): キーワード (En): 作成者: Matui, Takafumi, Satish-Kumar, M., Kato, Kazuhiro, Wada, Hideki メールアドレス: 所属:
URL	https://doi.org/10.14945/00000398

Laser fluorination oxygen extraction system for stable isotope analysis of rock forming minerals

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Abstract High vacuum line made of stainless steel and computer controlled pneumatic valves attached with a 40W CO₂ laser system capable of extracting oxygen from rock forming silicate and oxide minerals in a BrF₅ atmosphere was fabricated. The vacuum line can resist the hazardous BrF₅ reagent used for disintegrating the Si=O bonds in minerals. The oxygen, thus released, is converted to CO₂ in an O₂→CO₂ converter using graphite heated at ~ 650°C in a platinum foil holder. We present here the results on vacuum checks, initial setting of laser, reproducibility of the O₂→CO₂ converter, background measurements during fluorination and precautions in handling the BrF₅ reagent. The present system can withstand high vacuum conditions without appreciable leaks for intervals required to complete one cycle of measurement. However, due to the toxic nature of BrF₅ reagent, sizeable amount of background O₂ was released during the pre-fluorination of the system (~ 0.2-0.3 μmoles of O₂ for 30 minutes of fluorination). Repeated fluorination of the system considerably reduced the background O₂, however, could not be completely eliminated. Tests were also made for the functional setting of the O₂→CO₂ converter using ampoules of external O₂ gas. Optimum conditions for conversion were determined; temperature of ~ 650°C, graphite grain size fraction of 1 ~ 2 mm and reaction time of 15 minutes. NBS-28 quartz standard were pre-fluorinated overnight in the reaction chamber in order to reduce the background effect. δ¹⁸O_{SNOW} values of 14 measurements with varying amounts of NBS-28 quartz gave 10.06 ± 1.15‰. The results indicate that a minimum sample size of 250 μg is essential to overcome the background effects. However, this amount is almost four times less than the usual amount of sample used in laser fluorination laboratories elsewhere. Also, it was found that the laser beam should be defocused for precise measurement of small grain size samples. Thus, at present, the presence of background O₂ released in the reaction chamber is hindering the application of micrometer scale measurement of oxygen isotope measurements in minerals. In order to improve the present system, the background within the reaction chamber should be reduced further.

Key Words: laser ablation, oxygen isotopes, silicate mineral, BrF₅, O₂-CO₂ converter

Introduction

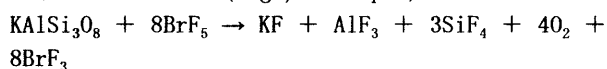
Oxygen is the most abundant element in the Earth's crust and mantle, and forms an important stable isotope tracer in various geological processes. Oxygen isotope analysis of rock forming minerals is considered to be one of the most important geochemical techniques to elucidate the origin and evolution of rocks. However, oxygen, especially in silicate minerals, is strongly bonded with silicon and other cations, and extremely difficult to separate. Furthermore, oxygen is present in most of the chemical reagents and in the atmosphere so that it needs extreme care to analyze it without

contamination.

Until 1960s, two type of reactions were used to analyze oxygen isotope ratios of silicate minerals: (1) reduction by carbon at high temperature (1,600-2,000°C) to yield carbon monoxide (Manian *et al.*, 1934) and (2) deoxygenation by fluorine or halogen fluorides to produce O₂ (Clayton & Mayeda, 1963). The pioneering work on oxygen isotope analyses in silicate was reported by Manian *et al.* (1934), making use of the reduction method. It was Baertschi & Silverman (1951) who for the first time used the deoxygenation method. They employed fluorine or chlorine trifluoride (ClF₃) as reagent. Taylor & Epstein (1962) described that the de-

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oxygenation method with fluorine is better than reduction with carbon at high temperature. Clayton & Mayeda (1963) found that bromine pentafluoride (BrF_5) is preferred to fluorine as the reagent. This study adopts BrF_5 as the reagent for the laser ablation and the following equation illustrates a typical reaction of bromine pentafluoride with a silicate mineral (e.g., feldspar).



The conventional fluorination technique, reacting silicate or oxide with fluorine or fluoride gas in the nickel vessel at moderate temperature (200–650°C), normally need 12–18 hrs to liberate O_2 and large sample sizes (5–30 mg), since the background is normally high. Thus, precise small volume isotope analysis is impossible by conventional method. On the other hand, laser ablation technique is superior to the conventional method with respect to smaller sample size, shorter reaction time, less blank, and high accuracy (e.g., Sharp, 1990; Spicuzza *et al.*, 1998). With the advancement of high precision micro-analytical systems for stable isotope measurements and its widespread application in geology, it is essential to accurately measure small volume samples (Kyser, 1995).

The purpose of this study is to establish a laser ablation system for the accurate measurement of oxygen isotopes in rock forming minerals at Shizuoka University. With the modified inlet system of the Finnigan MAT 250 mass spectrometer, measurement of ultra-micro volume of carbon dioxide (up to 0.1 μmoles) with high precision is possible (Wada *et al.*, 1982). The laser ablation system is therefore expected to establish the oxygen isotope analysis for ultra-small silicate samples.

Present status of oxygen isotope analysis of silicate minerals

Conventional fluorination techniques for oxygen extraction had been established and employed in laboratories, several decades ago and is still the most commonly used method (e.g., Baertschi & Silverman, 1951; Clayton & Mayeda, 1963; Borthwick & Harmon, 1982). This technique is useful to liberate O_2 in most common silicates, except for the highly refractory minerals (e.g., forsterite, kyanite, coesite, corundum, zircon). However, 5–30 mg samples are commonly needed for accurate and reproducible result, because of large blank. This large amount of blank is due to the production of hygroscopic NiF_2 that affect stable isotope ratio. When small sample size analysis is performed, an arbitrary blank correction is essential (Lee *et al.*, 1980), which reduces the accuracy of the measurement considerably.

The laser ablation techniques to extract oxygen

from silicate minerals were first reported by Sharp (1990), and several modifications and refinements made in the system thereon (Chamberlain & Conrad, 1991; Conrad & Chamberlain, 1992; Chamberlain & Conrad, 1993; Sharp, 1992; Kohn *et al.*, 1993; Matthey & Macpherson, 1993; Young & Rumble, 1993; Akagi *et al.*, 1995; Valley *et al.*, 1995; Spicuzza *et al.*, 1998). The advantages of this technique are (1) refractory minerals can be analyzed, (2) it takes only seconds to minutes for completing the extraction (< 15 min for one sample preparation, Valley *et al.*, 1995) (3) small sample size (as low as 0.1 mg, Sharp, 1990), and (4) high precision can be achieved ($\pm 0.1\%$, Spicuzza *et al.*, 1998). By employing a remote laser for heating, it is not difficult to rapidly increase the temperature to > 1,300°C, whereby, the refractory minerals can easily react in short time under this intense heat. Another benefit of using laser ablation method is that the sample is directly heated, which reduces the amount of background considerably, and the blank is much less than conventional methods. Thus, the analysis on small sample size can be performed without any corrections, and is expected to achieve high accurate measurement. Sharp (1990) achieved high precision ($\pm 0.1\%$) for many minerals (quartz, feldspar, kyanite, olivine, diopside, garnet, muscovite, biotite, MnO_2) using CO_2 laser, and in situ spot-analysis (< 300 μm in diameter) on the polished thick section was also successful (< 0.5%).

The most commonly used CO_2 laser emits radiation ($\lambda=10.6 \mu\text{m}$) which is well absorbed by all silicate minerals (Fouillac & Girard, 1996). Other types of lasers were also recently tested for oxygen extraction. The Nd-YAG laser could not successfully heat the transparent samples, because the emitted radiation ($\lambda=1.064 \mu\text{m}$) could not be absorbed by transparent minerals (Elsenheimer & Valley, 1992; Akagi *et al.*, 1993, 1995). For the in situ measurements, Wiechert & Rumble (1993) and Rumble *et al.* (1997) have succeeded in vaporizing in-situ spots without fractionation of isotopes using KrF UV laser ($\lambda=248 \text{ nm}$), however could not ablate transparent minerals such as quartz. This was overcome by Fiebig *et al.* (1999) by using ArF laser ($\lambda=193 \text{ nm}$), whereby precise in situ analysis of quartz was made possible.

The purification of O_2 gas extracted from minerals is a difficult task, because of the low freezing point of oxygen and the presence of toxic reagents. Liquid nitrogen can condense almost all of the toxic reagent and by-product gases except O_2 . However, as an unwanted by-product, small amounts of F_2 is produced, when silicate minerals react with BrF_5 . F_2 gas cannot be cryogenically separated from O_2 gas and corrodes the $\text{O}_2 \rightarrow \text{CO}_2$ conversion system. Sharp (1990, 1992) introduced a mercury diffusion pump as a fluorine remover. However, mercury is very

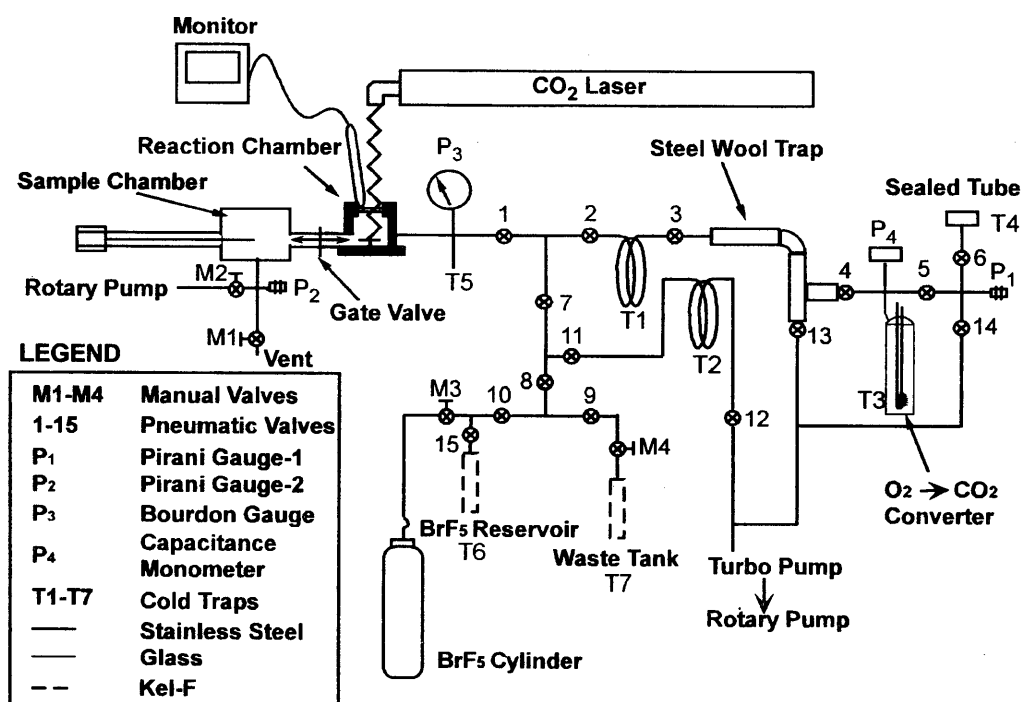


Fig. 1 Schematic layout of the vacuum line for laser fluorination system and associated instrumentation.



Fig. 2 Photograph showing the general setup of the vacuum line and laser. The pneumatic valves are controlled by the computer with the labVIEW software. Laser generating system is placed on top of the line by means of steel frame with adjustable bolts to fix the distance between the outlet lens and the sample holder.

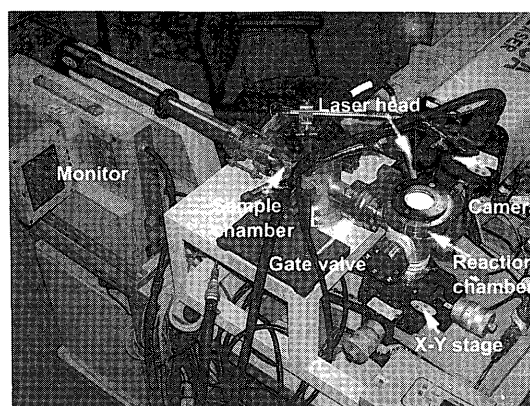


Fig. 3 The reaction chamber and the sample chamber of the system, separated by a gate valve. The sample holder is fixed on an X-Y stage (25 mm X 25 mm). Sample holder with sample is placed in the sample chamber and evacuated using a rotary pump. After evacuation, the gate valve is open and the holder is pushed by the magnetic piston rod and fixed in the reaction chamber.

likely to absorb not only fluorine but also oxygen (Akagi *et al.*, 1995). Akagi *et al.* (1995) reported that steel wool trap was effective in removing F_2 .

Fouillac & Girard (1996) and Kirschner & Sharp (1997) reported that $\delta^{18}O$ values obtained by laser analysis of fine (>250 μm) splits of quartz were up to 0.8‰ lower than the accepted values. Fouillac & Girard (1996) called it 'grain size effect'. Spiccuza *et al.* (1998) succeeded to resolve the 'grain size effect' adopting the rapid heating, defocused beam technique instead of slow heating,

focused beam technique usually used for extraction. They achieved high accuracy ($\pm 0.1\%$) for NBS-28 quartz standard samples (100–250 μm).

Laser ablation system in Shizuoka University

Instrumentation

Laser fluorination vacuum line at Shizuoka University is shown schematically in Fig. 1. This line is equipped with a 40W- CO_2 laser (ONZCA PIN-40S), which uses helium-neon laser for target

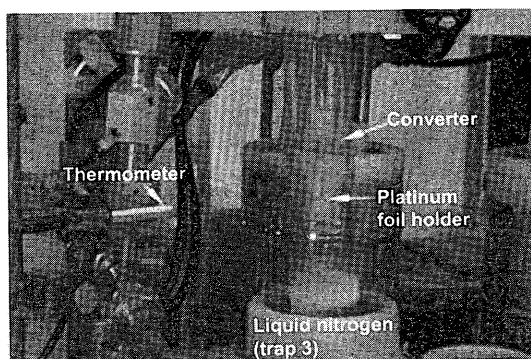


Fig. 4 The $O_2 \rightarrow CO_2$ converter, made of Pyrex glass, comprises of a platinum foil (0.1 mm thick) holder designed to keep graphite and give self resistance for increasing the temperature in the order $500 \sim 700^\circ C$.

location (CHINO NEO-1M) (Fig. 2). The reaction chamber is made of stainless steel and has a BaF_2 window for uninterrupted laser passage and to view the sample holder during lasing (Fig. 3). A high magnification camera is connected with the monitor (KEYENCE VH-6300) and it is possible to observe the laser ablation reaction. An infrared remote thermometer (CHINO IR-FB with a range of 1,100 to 3,000 $^\circ C$), equipped with a guide laser to locate the point of measurement, measures the temperature during laser ablation. Sample holder (2.5 cm diameter) is made of nickel and has ~ 3 mm deep nine sample pits.

The main line is evacuated using a combination of turbo pump (PFEIFFER TPH060DN40KF) and a rotary pump. Pre-evacuation of the sample chamber is carried out using a rotary pump. Samples are placed in the sample holder and kept in the sample holder in the sample chamber and pre-evacuated. The sample holder is moved into the reaction chamber through the gate valve using a magnetic piston "rod". There are four pressure gauges (P_1 - P_4) located at different segments in the line. P_1 and P_2 are pirani gauges (WAKAIDA PG-2B). P_3 and P_4 are bourdon gauge and capacitance monometer (PFEIFFER CMR263) respectively. 15 pneumatic valves are controlled by computer used the programming software, LabVIEW $^\circledR$. Furthermore, 4 manual valves (M_1 - M_4) are also included in the line for specific operations.

The line has 7 cold traps (T_1 - T_7) and a stainless steel wool trap. The liquid nitrogen, cold traps are capable to condense BrF_5 , CO_2 , SiF_4 and BrF_3 gas, while the steel wool trap can remove the F_2 gas. T_1 and T_2 , made of double ring steel pipe, are designed to remove efficiently any remaining reagent or by-product gas. T_3 gathers CO_2 generated at the $O_2 \rightarrow CO_2$ converter (Fig. 4). T_4 is the place to seal the CO_2 gas in 6 mm Pyrex $^\circledR$ ampoules. T_5 is used for shifting the required aliquot of BrF_5 to the reaction chamber from BrF_5 tank. T_6 is Kel-F (Chlorotrifluoroethylene) waste tank, where unreacted BrF_5 and by-product gases are stored and T_7

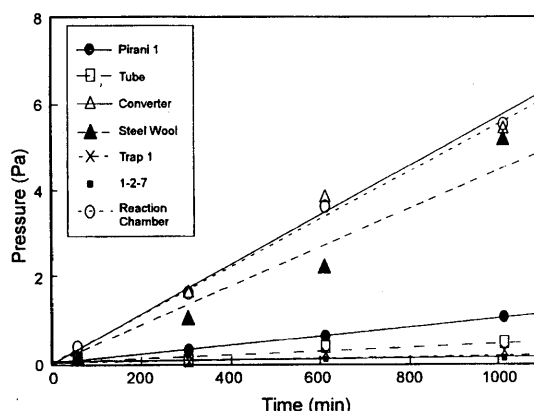


Fig. 5 Results showing the segment wise leak check for the oxygen extraction line plotted as a function of pirani gauge reading (P_1) with time. Note that the steel wool, $O_2 \rightarrow CO_2$ converter and the reaction chamber can not withstand high vacuum condition for long, however is capable to keeping high vacuum until the completion of a single sample extraction.

is the Kel-F reservoir tank for storing BrF_5 .

In the reaction chamber, the silicate sample is ablated by CO_2 laser in a BrF_5 atmosphere, and O_2 gas is liberated from the sample. The O_2 gas is purified from other gases through the liquid N_2 cold traps and stainless steel wool trap. At the converter, CO_2 is generated from O_2 by heating graphite in a platinum heating foil holder. The temperature is measured using an infrared remote thermometer (CHINO IR-FA in the range of 300 to 1300 $^\circ C$). The temperature can be adjusted by resistance controller and oxygen can react with graphite at $> 560^\circ C$. The resulting CO_2 gas is sealed in 6 mm Pyrex $^\circledR$ ampoule which is cracked open to the inlet system of Finnigan MAT 250 (Wada *et al.*, 1982) and the stable isotopes of the carbon and oxygen are measured.

Vacuum condition

Most of the vacuum line of the present oxygen isotope preparation system is made up of stainless steel except the converter, which is made of Pyrex $^\circledR$ glass, in order to resist corrosion by fluorine-bearing gases (Fig. 1). Initial vacuum check of the system was carried out in order to determine whether the line can withstand high vacuum condition for intervals of time required for completion of a single sample. The system was evacuated to the minimum pressure ($P_1 \sim 2.55$ Pa). Vacuum check of this line was carried out based on the following procedure. Firstly, the valves were held closed for a specific time (e.g., 5 hours) and then, starting from the valve near to P_1 , valves are opened one by one, while reading the shift in P_1 values. For example, in the case of $O_2 \rightarrow CO_2$ converter segment's vacuum check, it is kept in the closed condition with the valves No. 4 and No. 5 closed and No. 6 and No. 14 kept opened. Subsequently, No. 6 and No. 14

Table 1 Results of laser intensity measurements

laser current (mA)	intensity (W)
3.0	17.6
3.5	18.6
4.0	22.9±0.5

Table 2 Laser diameter measurements based on the insitu ablation of mica flake.

Distance between sample holder and laser outlet lens (mm)	laser current (mA)	time (sec.)	hole diameter (μm)
150	2.9	<1	200
157	2.9	<1	400
163	3.9	<1	700
153.5	3.0	<1	1200
147.8	3.0	<1	400

are closed and No. 5 is opened the shift in P_1 value is measured. The relation between the time and the shift in P_1 reading for each segment of the line is shown in Fig. 5. At all segments can essentially keep high vacuum condition ($P_1 < 2.55$ Pa) for more than 30 min., the maximum time required during one sample analysis. Keeping the valve closed for a long time (e.g., 12 hours), some parts loose the vacuum considerably. Because of their large internal volume, steel wool trap, reaction chamber and $O_2 \rightarrow CO_2$ converter are such portions in the line. This decrease in vacuum condition is probably caused by adsorption of H_2O etc. in the walls, or minute leaks along the large 'O' rings and gaskets connections.

Laser settings

The present system adopts a 40W CO_2 laser. Two fundamental experiments were performed in order to check the power of the laser beam and its diameter. Table 1 shows the relation between the current and the intensity. Table 2 illustrates the variation of laser diameter by changing the distance between the lens and the sample holder (using a thin mica flake). The results suggest that the laser beam can be defocused from its focal position (laser outlet lens at ~ 80 mm above the BaF_2 window, see Fig. 1) either by moving the laser equipment upward or downward, which apparently changes the working distance of the laser outlet lens. Although an increase in working distance could defocus the beam to the required 1 mm diameter (Table 2), the beam gets focused near the BaF_2 window, causing damage in the window glass. This can be avoided by a shorter working distance than the focus. However, the present design of the line and the optical system restricts the defocusing of the laser to a maximum

of 400 μm. Finally, the laser equipment was positioned at ~ 15 cm above the sample holder for achieving a laser diameter of about 200 μm (Table 2). The position of the laser equipment was shifted 2 cm lower to defocus the beam to a diameter of about 400 μm. At both the positions the power of the laser was kept at 3.5–4.0 mA for obtaining enough power for extraction.

Handling of BrF_5

Bromine pentafluoride (BrF_5) is liquid at room temperature and highly toxic reagent, which reacts with organic matters and H_2O explosively, and with any material except for selected metals and alloys, such as nickel or stainless steel. Thus, extreme care is needed while handling BrF_5 . Fortunately, BrF_5 can be condensed in a liquid N_2 cold slush.

At the beginning of the experiments, it is necessary to shift an aliquot of BrF_5 (10–15 ml) from the cylinder (1 kg) to the reservoir tank made of Kel-F (~ 13.5 cm long and ~ 2.5 cm diameter). Transferring BrF_5 is possible using liquid nitrogen cold trap. After evacuating the line to high vacuum, liquid nitrogen is set at the tank (T_7). Stopcock of the cylinder and M_3 is opened, while keeping valve No. 10 closed. The BrF_5 vapor gets condensed at the reservoir tank (T_7). 15–20 min. is required to gather ~ 10 ml liquid BrF_5 . To condense BrF_5 efficiently, it is necessary to increase the level of the liquid nitrogen slowly every 2–3 min. After completion, the valves of the cylinder and M_3 are closed. During the shifting of BrF_5 , it was found that there is non-condensable gas inside the BrF_5 cylinder, part of which will expand to the line and the Kel-F reservoir along with BrF_5 . This non-condensable gas was evacuated through the T_2 trap set with liquid nitrogen.

For each measurement of sample, an aliquot of BrF_5 equivalent to about 94 hPa (~ 70 mm Hg) inside the reaction chamber has to be transferred to the reaction chamber. For this, BrF_5 in the reservoir tank is expanded in the line between valves No. 1, No. 2, No. 11, M_4 and M_3 and after closing valve No. 15, while T_5 cold trap is used to condense the BrF_5 at the reaction chamber. The reagent pressure of BrF_5 is usually kept at above 94 hPa (70 mmHg) and lower pressure cause incomplete yield and considerably low $\delta^{18}O$ values (Spiccuza *et al.*, 1998). If there isn't sufficient pressure of BrF_5 in the reaction chamber, a second expansion of BrF_5 is needed. While keeping the required aliquot of BrF_5 at T_5 , the line is completely evacuated through T_2 liquid N_2 trap, in order to clean the system of any non-condensable gases that may increase the background oxygen gas.

$O_2 \rightarrow CO_2$ converter conditions

The oxygen to carbon dioxide converter is one of

Table 3 Results of experiments carried out for investigating the reproducibility of the O₂-CO₂ converter. External oxygen gas was expanded in respective segments of the vacuum line to be verified. C corresponds to the converter, SW the steel wool trap and RC the reaction chamber.

Run No.	gas volume (μl)	yeild (%)	δ ¹³ C‰ (PDB)	δ ¹⁸ O‰ (SMOW)	batch No.	segment
No.1	174	99±4	-25.40	37.66	0	C
No.2	98.7	83±6	-25.51	38.00	0	C
No.3	204	100±3	-25.55	38.72	0	C
No.4	192	100±4	-25.56	38.57	0	C
No.5	174	87±4	-25.57	38.55	0	C
No.11	58.7	33±4	-25.62	10.29	1	C
No.12	53.1	31±4	-25.59	12.33	1	C

Table 4 Results of O₂-CO₂ conversion experiments carried out with large size graphite gains (carbon L+). Abbreviations are same as in Table 3.

Run No.	gas volume (μl)	yeild (%)	δ ¹³ C‰ (PDB)	δ ¹⁸ O‰ (SMOW)	batch No.	segment
No.13	184	103±4	-25.61	37.93	1	C
No.14	144	84±4	-25.52	36.36	1	C
No.18	191	108±4	-25.52	42.58	2	C
No.21	121	68±4	-25.50	41.33	3	C
No.22	184	95±4	-25.50	41.52	3	S.W
No.19	197	112±4	-25.49	39.54	3	R.C
No.16	119	68±4	-25.51	42.31	2	C
No.17	119	68±4	-25.52	41.37	2	C
No.31	82.8	89±6	-25.53	35.40	5	C
No.32	61.3	66±6	-25.66	25.90	5	R.C
No.33	62.5	65±6	-25.58	24.15	5	R.C
No.34	89.2	95±6	-25.52	38.07	6	C
No.36	44.3	48±6	-25.56	21.05	6	R.C

Table 5 Results of O₂-CO₂ conversion experiments carried out with small size graphite gains (carbon S+). Abbreviations are same as in Table 3.

O ₂ No.	gas volume (μl)	yeild (%)	δ ¹³ C‰ (PDB)	δ ¹⁸ O‰ (SMOW)	batch No.	segment
No.37	82.5	93±7	-25.41	37.78	6	C
No.38	85.0	93±6	-25.56	37.90	6	R.C
No.39		n.d.			5	R.C
No.40	86.3	94±6	-25.50	38.42	5	R.C
No.41	91.0	96±6	-25.58	38.27	5	C

the most important components in this system. This is the only part of the system made of glass, so as to be visible to measure the temperature of the platinum foil. Oxygen liberated from the silicates is reacted with carbon at temperatures >550°C to produce carbon dioxide, based on the simple reaction O₂ + C → CO₂. In the present study two fundamental tests were carried out for confirming the reproducibility of the converter; so that there is no fractionation of isotopes while O₂ gas is converted to CO₂.

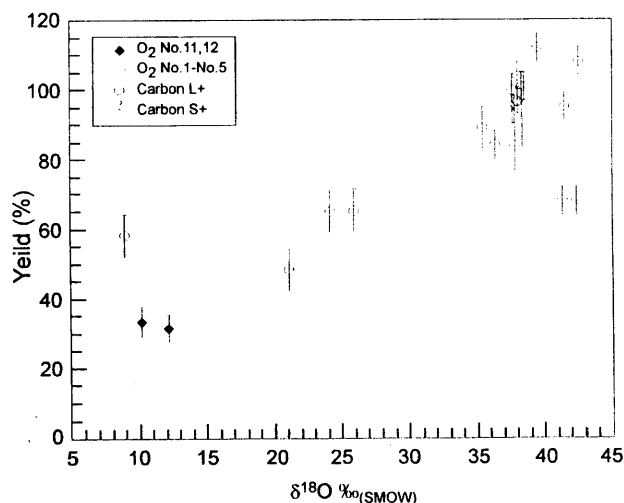


Fig. 6 Results showing the converter reproducibility experiments carried out on O₂ gas inlet externally. The low oxygen isotope values show systematic relation against the yield, which indicates that lower yields cause selective lighter isotope conversion.

Table 6 A. Selected (with all experimental conditions satisfied) experimental results on reproducibility of O₂-CO₂ conversion experiments using external oxygen gas.

Run No.	Gas volume (μl)	Yield (%)	δ ¹³ C‰ (PDB)	δ ¹⁸ O‰ (SMOW)	Batch No.	Segment	Reaction temperature (°C)	Time
No.47	115.8	95±5	-25.80	38.69	7	C	640	
No.48	118.7	96±5	-25.81	38.74	7	C	640	
No.49	114.8	96±6	-25.78	38.62	7	C	630	
No.50	147.2	112±5	-25.62	39.13	7	R.C.	630	
No.51	116.7	100±5	-25.64	38.62	7	R.C.	620	
No.52	84.0	91±6	-25.68	38.42	9	R.C.	600	
No.53	87.0	92±6	-25.71	38.80	9	R.C.	580	
No.54	83.8	86±6	-25.59	39.44	9	R.C.	625	
No.62	138.2	108±5	-25.60	39.24	11	R.C.	620	15min
No.63	128.1	101±5	-25.64	39.13	11	R.C.	640	10min
No.65	135.5	107±5	-25.57	38.96	11	R.C.	615	10min
No.67	136.8	105±5	-25.56	39.21	11	R.C.	625	15min
No.68	67.1	85±6	-25.70	38.98	10	R.C.	605	
No.69	90.3	93±6	-25.58	39.22	9	R.C.	577.5	
No.70	110.1	108±6	-25.55	39.29	12	R.C.	580	
No.72	106.4	108±6	-25.70	38.96	12	R.C.	661.5	
No.73	90.1	92±6	-25.64	38.98	12	R.C.	675	
No.74	71.5	94±6	-25.80	38.33	12	S.W.	605	
No.76	71.4	104±6	-25.64	39.04	13	S.W.	580	
No.78	61.1	101±6	-25.72	39.56	13	S.W.	600	
No.82	86.6	109±6	-25.83	39.24	14	S.W.	675	
No.84	85.6	103±6	-25.69	39.35	14	R.C.	660	
Average δ ¹³ C			-25.68±0.09	Average δ ¹⁸ O	39.00±0.33 (n=22)			

Results and discussion

Reproducibility of the O₂→CO₂ conversion

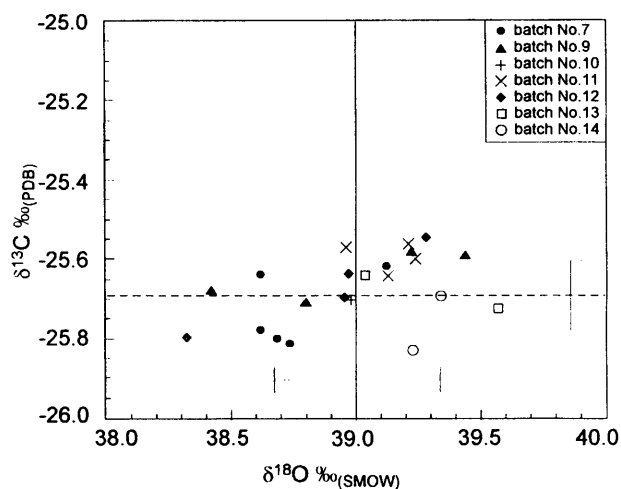
Oxygen gas from an external cylinder was utilized for this experiment. From the cylinder, O₂ was expanded in a glass vacuum line directly to about 1500-2000 hPa (~1.5-2.0 atm). After removing the possible impurities such as H₂O by cleaning through the cooled pentane trap (-130°C), the O₂ gas was expanded in ~72 cm long 6 mm Pyrex® glass tube at a reduced pressure of 55-90 hPa (~40-70 mmHg) and sealed. This "long" tube is then cut into 3-6 almost

Table 6 B. Results of 5 minutes conversion experiments.

Run No.	Gas volume (μl)	Yield (%)	$\delta^{13}\text{C}\text{‰}$ (PDB)	$\delta^{18}\text{O}\text{‰}$ (SMOW)	Batch No.	Segment	Reaction temperature (°C)	Time
No.64	129.5	102±5	-25.57	38.21	11	R.C.	n.d.	5min
No.66	144.6	105±5	-25.57	37.12	11	R.C.	n.d.	5min

Table 6 C. Results of experimental runs having specific reasons for isotopic variations. Abbreviations are same as in Table 3.

Run No.	Gas volume (μl)	Yield (%)	$\delta^{13}\text{C}\text{‰}$ (PDB)	$\delta^{18}\text{O}\text{‰}$ (SMOW)	Batch No.	Segment	Reaction temperature (°C)	Time
No.45	89.8	91±6	-26.17	37.72	8	C	n.d.	
No.46	89.4	92±6	-25.89	38.35	8	C	n.d.	
No.55	85.3	88±6	-25.60	38.30	9	R.C.	n.d.	
No.56	60.0	64±6	-28.06	39.35	9	C	n.d.	
No.57	55.5	75±8	-26.38	39.30	10	R.C.	n.d.	
No.58	65.4	82±8	-25.82	39.05	10	R.C.	n.d.	
No.59	67.0	84±8	-25.96	39.35	10	R.C.	n.d.	
No.60	67.0	85±8	-25.77	39.48	10	R.C.	n.d.	
No.61	63.1	77±6	-25.91	39.26	10	R.C.	n.d.	
No.71	99.95	97±6	-25.44	38.66	12	R.C.	560	
No.75	122.23	94±6	-25.62	39.84	12	R.C.	590	
No.77	129.67	n.d.	-25.60	39.72	13	R.C.	595	
No.79	129.5	101±6	-25.60	38.88	13	R.C.	600	
No.80	122.35	101±6	-25.78	37.84	13	R.C.	670	
No.81	55.85	68±6	-25.88	37.47	14	R.C.	680	
No.82	86.64	109±6	-25.83	39.24	14	S.W.	675	
No.83	109.6	n.d.	-25.48	39.97	14	R.C.	670	
No.84	85.63	103±6	-25.69	39.35	14	R.C.	660	
No.85	71.3	109±6	-25.80	36.67	14	S.W.	655	
No.87	105.14	112±6	-25.69	37.51	15	S.W.	675	
No.89	100.56	104±6	-25.66	37.92	15	S.W.	650	
No.91	112.61	109±6	-25.66	38.51	15	S.W.	680	
No.93		n.d.			16	S.W.	n.d.	
No.94	68.75	100±6	-25.80	37.52	16	S.W.	660	
No.96	83.77	108	-25.69	38.49	16	S.W.	650	

Fig. 7 $\delta^{13}\text{C} - \delta^{18}\text{O}$ covariance plot showing the results of seven "batches" of external O_2 gas converted to CO_2 . Reproducibility of oxygen isotope is seen within a single batch of samples.

equal parts and grouped as 'a batch', each of which has identical oxygen isotope ratios. Different batches have slightly different oxygen isotopes because of the oxygen isotope fractionation caused by molecular flow resulting from the large pressure difference between the parent storage cylinder (> 100 atm) and the ampoules. The prepared oxygen tubes

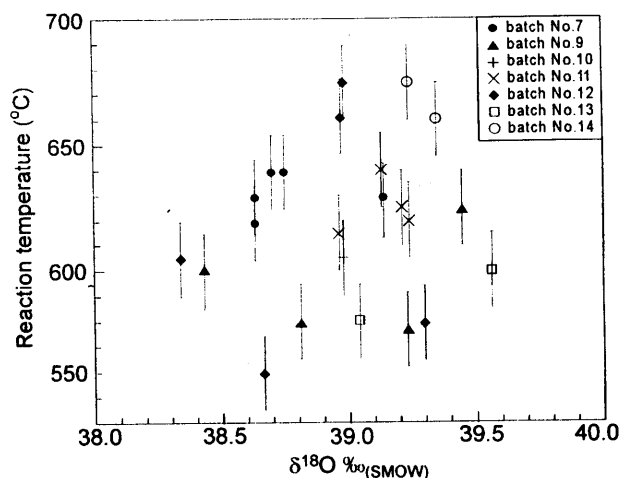
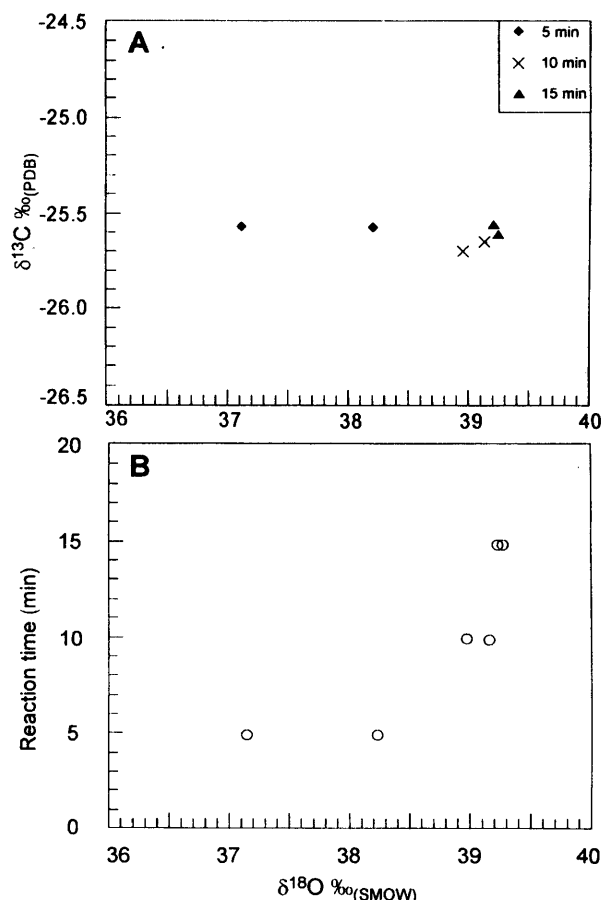


Fig. 8 The relation between converter temperature and oxygen isotope for seven batches of oxygen gas.

Fig. 9 Results of conversion time experiments. A. $\delta^{13}\text{C} - \delta^{18}\text{O}$ covariance plot showing a constant carbon isotope value in spite of a decreased oxygen isotope values for less conversion time. This suggests that lighter isotopes react with carbon faster than the heavier isotopes. B. Oxygen isotope variation in relation with conversion time.

are attached to T_4 with a Cajon® tube cracker, and evacuated for about 15 min. The tube is cracked open and the O_2 gas is inlet into the laser ablation line. The O_2 gas is expanded up to the converter or till

Table 7 Results of blank measurements.

Blank run number	Fluorination time(min)	CO ₂ gas volume(μ l)	$\delta^{13}\text{C}\%$ (PDB)	$\delta^{18}\text{O}\%$ (SMOW)	Running day
2	30	24.1	-25.50	5.44	2002/5/26
3	30	n.d.	n.d.	n.d.	2002/5/27
4	30	n.d.	n.d.	n.d.	2002/5/28
5	45	n.d.	n.d.	n.d.	2002/5/28
6	35	n.d.	n.d.	n.d.	2002/5/28
7	889	n.d.	n.d.	n.d.	2002/5/29
8	30	15.5	-25.73	-15.83	2002/5/29
9	860	n.d.	n.d.	n.d.	2002/5/30
10	35	n.d.	n.d.	n.d.	2002/5/30
11	35	n.d.	n.d.	n.d.	2002/5/30
12	995	278	-25.58	-1.67	2002/5/31
13	30	9.5	-25.24	9.28	2002/5/31
14	832	90.9	-25.58	-5.95	2002/6/1
15	30	10.8	-25.28	6.07	2002/6/1
16	10	n.d.	n.d.	n.d.	2002/6/1
17	747	43.3	-25.67	-9.09	2002/6/2
18	30	5.3	-24.04	7.08	2002/6/2
21	1268	69.8	-25.54	-8.80	2002/6/2
22	6600	n.d.	n.d.	n.d.	2002/6/8
23	30	6.7	-25.78	4.91	2002/6/8
24	2065	n.d.	n.d.	n.d.	2002/6/10
25	30	n.d.	n.d.	n.d.	2002/6/10
26	6.5	6.9	-25.45	14.00	2002/6/10

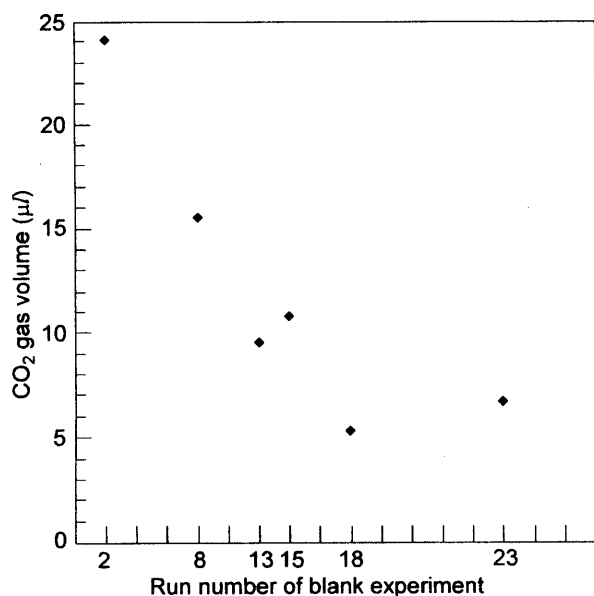


Fig. 10 Systematic variation in the volume of blank gas released from the reaction chamber for 30 min. fluorination experiments. The number in the abscissa corresponds to the order in which blank was measured.

the steel wool trap, or to the reaction chamber, depending upon the purpose of the experiment. The converter is then put on and O₂ is converted to CO₂, which is collected in a new ampoule at T₄ (liquid nitrogen trap), and measured for isotopes.

The results of the reproducibility tests are given in Table 3. The proper functioning of the converter can be easily checked by the yield of the CO₂ produced. For example, the low yields in the experiment run No. 11 and 12 are, indicative of the inefficiency of the converter, caused by the reduced activity of graphite to react with O₂. This

is obvious when compared with the run Nos. 1-5 (Table 3), which was performed with exactly the same graphite. Although the presence of graphite in the holder can be visible, after several conversion experiments the surface area of the graphite efficient to the reaction decreases, resulting in diminished reactivity with oxygen. Therefore, it is necessary to replace the graphite with the new one (Taylor & Epstein, 1962; Clayton & Mayeda, 1963).

Experimental runs were carried out with the introduction of new graphite grains of varying size and the results are presented in Tables 4 and 5. Initially, the graphite gave yields greater than 100%, caused by the release of adsorbed gases, which can be reduced by storing graphite crystals in a vacuum desiccator. The relation between $\delta^{18}\text{O}$ and yield (%) is shown in Fig. 6. 'Carbon L+' is the result after the large graphite pieces (2-4 mm) were added, and 'Carbon S+' is the one with small size graphite (< 2 mm) added. 'Carbon L+' has scattered $\delta^{18}\text{O}$ values and yield, on the contrary, 'Carbon S+' shows only a narrow spread in the values. This indicates a greater efficiency of small sized graphite because of the increase in reactive surface area. Furthermore, this tendency also suggests that a lower yield will result in lower $\delta^{18}\text{O}$ value. Thus, if the yield is lowered, the fractionation of oxygen isotope occur, since the lighter oxygen gets easily converted to CO₂, resulting in lower $\delta^{18}\text{O}$ values.

Fig. 7 illustrates the stable isotope result of the trustworthy data ($n=22$) using graphite grain size of 0.5-1.0 mm. The average $\delta^{18}\text{O}$ value is $39.00 \pm 0.33\%$, whereas the average of $\delta^{13}\text{C}$ value is $-25.68 \pm 0.09\%$ (Table 6). The absence of apparent correlation between oxygen and carbon isotope ratios suggests that the converter works efficiently without any fractionation. The variation of $\delta^{13}\text{C}$ values is very nominal, within the error of mass spectrometer measurement, whereas the variations in the $\delta^{18}\text{O}$ values are considered to be related to the batch-to-batch difference in the initial values. If a single batch is considered, the $\delta^{18}\text{O}$ values are as constant as $\pm 0.2\%$.

According to Taylor & Epstein (1962), higher converter temperature may result in the formation of carbon monoxide and cause simultaneous lowering of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. The result of the experiment with varying converter temperature (550 ~ 700°C) indicates no correlation with $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ values, which indicate that carbon monoxide was not produced at the range of the temperature investigated (Fig. 8).

Fig. 9 shows the relation between $\delta^{18}\text{O}$ values and reaction time of the converter using the same batch of O₂ gas (batch No.14). Although the yield is thought to be sufficient (Table 6B), reaction that terminated after 5 minutes gave lower $\delta^{18}\text{O}$ values. This indicates that O₂ was not completely reacted

Table 8 The results of $\delta^{18}\text{O}$ values in relation with fluorination experiments.

Run number	CO ₂ gas volume(μl)	$\delta^{13}\text{C}\text{‰}$ (PDB)	$\delta^{18}\text{O}\text{‰}$ (SMOW)	O ₂ batch number	Reaction temperature (°C)	Pre-fluorination time
86	113.7	-25.68	30.50	14	650	
88	166.8	-25.54	34.24	15	670	
90	157.2	-25.64	36.42	15	675	
92	161.3	-25.40	39.16	15	670	
95	114.1	-25.64	38.03	16	650	4h
97	124.8	-25.53	38.63	16	650	11h

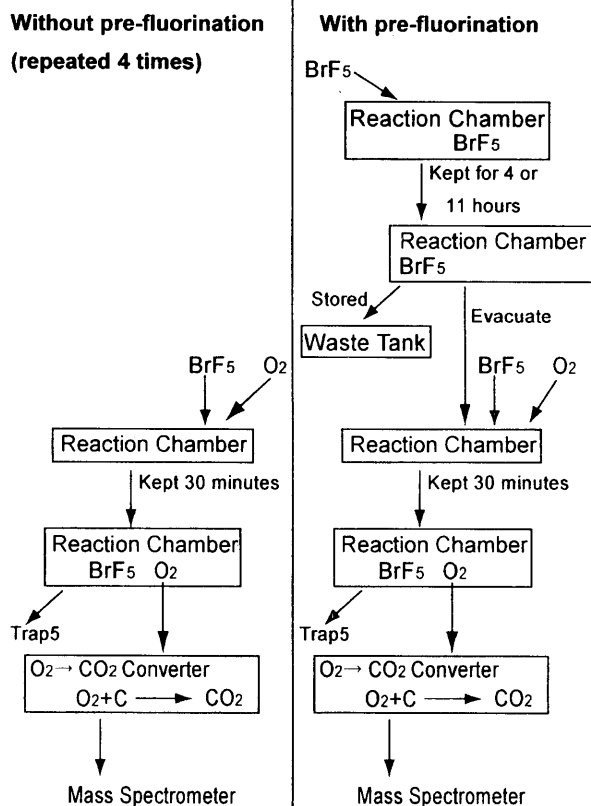
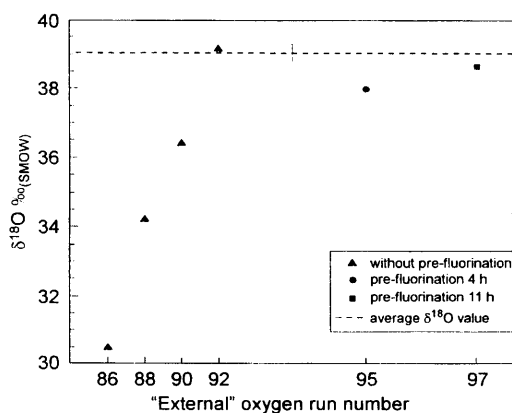
Fig. 11 Flow chart showing the procedure for pre-fluorination experiments to check the impact of the blank gas release on sample O₂ gas.

Fig. 12 Variation in oxygen isotope values with and without pre-fluorination experiment. When oxygen gas was measured continuously for 4 times, the isotope value of the last measurement gave expected values. Overnight pre-fluorination is recommended for the system.

and the remaining fraction of O₂ carried heavier $\delta^{18}\text{O}$ values. This fraction of O₂ is volumetrically insignificant to cause reduced yields, however can cause isotope variations. From these results it was concluded that a conversion time of 15 minutes is necessary to complete the reaction without any detectable fractionation of oxygen isotopes.

Blank check

Several earlier studies have reported the release of considerable blank oxygen gas (background), when BrF₅ is expanded in the reaction chamber. Signifying that the potential of the present system lies in the measurement of small volume of oxygen extracted from minerals, it is crucial to quantify the background and reduce it to a minimum as possible, because it is directly related to the minimum limit of sample size for analysis. Background check was performed by expanding BrF₅ in the reaction chamber at 100–135 hPa (76–100 mmHg) for a specific time and then condensing it in T₅ liquid nitrogen cold trap. The released gas is passed through T₁ (liquid nitrogen) and steel wool trap and reacted with graphite that generates carbon dioxide, which is sealed in an ampoule and measured for oxygen and carbon isotopes.

The results of the blank measurements are given in Table 7 and selected data corresponding to 30 minutes fixed fluorination results are illustrated in Fig. 10. During early stages of BrF₅ expansion, the amount of background was high and after repeated 'cleaning up' of the reaction chamber the blank O₂ gas reduced considerably. To verify the effect of blank on $\delta^{18}\text{O}$ values, the experiment of mixing 'external' oxygen gas and the oxygen blank released from the reaction chamber was carried out. Oxygen gas used was the same as that used for the converter reproducibility experiments. The procedure of the experiment is shown in Fig. 11. 'External' O₂ and BrF₅ are mixed and kept for 30 min in the reaction chamber and then the BrF₅ was condensed at T₅. The total O₂ in the reaction chamber was converted to CO₂ and stable isotope ratios were measured. Although the yields were satisfactory, lower values of $\delta^{18}\text{O}$ (30.5–39.16‰) than expected value (39.0 ± 0.3‰) are noticeable (Table. 8). This is likely to be caused by the influence of the blank, which has lower values (~15–20‰, based on the blank measurements made simultaneously with NBS-28 standard measurements; see section below) than the O₂ gas values. The mixing experiments were repeated 4 times. The $\delta^{18}\text{O}$ values become progressively heavier and the last result corresponds well within the expected value of 39.0 ± 0.33‰ (Fig. 12). This result indicates that the blank effect reduces with repetition of fluorination runs.

Spiccuza *et al.* (1998) found that pre-fluorination is an efficient method to reduce the blank. Pre-fluorination is the process of

Table 9 Results of laser ablation experiments of internal quartz standard samples.

Quartz run number	Sample weight (mg)	CO ₂ gas volume(μl)	Yield (%)	δ ¹³ C‰ (PDB)	δ ¹⁸ O‰ (SMOW)
No.1	0.273	68.7	67.9	-25.67	-6.78
No.2	0.320	13.0	11	-25.70	-10.10
No.3	0.481	48.8	27	-25.59	11.50
No.4	0.515	38.0	20	-25.64	9.29
No.21	0.321	115.1	96.8	-25.64	14.17
No.22	0.207	68.8	90	-25.62	14.87
No.23	0.112	32.4	78	-25.68	15.20
No.24	0.216	70.3	88	-25.65	13.70
No.25	0.188	29.6	43	-25.53	16.27

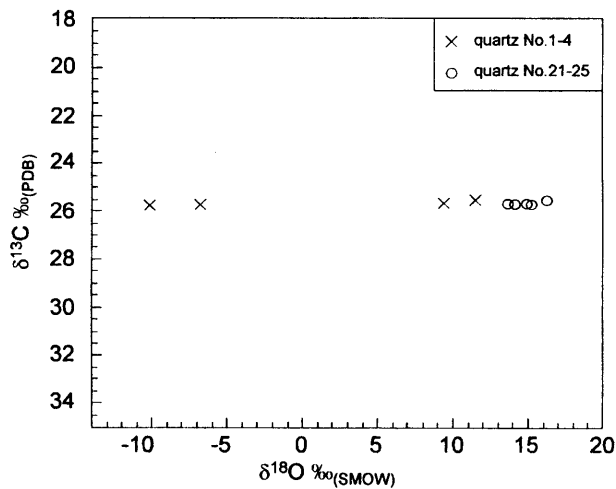


Fig. 13 $\delta^{13}\text{C} - \delta^{18}\text{O}$ covariance plot of quartz sample used for testing the functioning of the laser and the converter. Samples 1-4 show large isotope heterogeneity because of the malfunctioning of the O₂ CO₂ converter.

keeping BrF₅ expanded in the reaction chamber for a specific time for the purpose of minimizing the blank. The results of blank experiments described above also suggest that a long time exposure to BrF₅ in the reaction chamber can reduce the blank. As a confirmation for this test in our system, the same mixing experiments were carried out after pre-fluorination. The procedure is illustrated in Fig. 11, in which 4 hrs or 11 hrs pre-fluorination were carried out, and the results are shown in Fig. 12. The 4 hrs run has lower $\delta^{18}\text{O}$ value compared to the expected value indicating that considerable effect of blank still remains in the system. On the contrary, the 11 hrs run produced almost the same $\delta^{18}\text{O}$ value as expected for the 'external' oxygen gas. Thus, it was confirmed that over night pre-fluorination is necessary before laser ablation to reduce the effect of blank.

Preparation of quartz samples

Initial tests of the laser ablation system for the measurement of silicate minerals were performed

Table 10 NBS-28 measurement results. The accepted value is 9.64‰ (Friedman & Gleason, 1973).

	Sample weight (mg)	CO ₂ gas volume (μmol)	Yield (%)	δ ¹³ C‰ (PDB)	δ ¹⁸ O‰ (SMOW)	Difference from recommended value
Blank No.38	-	0.25	-	-24.42	19.88	-
NBS28 No.1	0.235	2.01	52	-25.77	10.99	1.35
NBS28 No.2	0.182	2.02	67	-25.70	10.63	0.99
Blank No.39	-	0.29	-	-25.13	18.44	-
NBS28 No.3	0.209	2.09	60	-25.83	9.60	-0.04
NBS28 No.4	0.293	2.41	50	-25.80	9.95	0.31
Blank No.40	-	0.15	-	-24.06	17.77	-
Blank No.43	-	0.21	-	-27.48	14.80	-
NBS28 No.5	0.349	3.98	69	-25.83	8.94	-0.70
Blank No.44	-	0.22	-	-26.73	17.79	-
NBS28 No.6	0.336	3.44	62	-25.66	9.82	0.17
NBS28 No.7	0.229	3.25	86	-25.66	9.78	0.14
NBS28 No.8	0.155	0.96	37	-25.64	11.76	2.12
NBS28 No.9	0.437	5.71	79	-25.65	8.97	-0.67
NBS28 No.10	0.104	1.18	69	-25.48	12.95	3.31
Blank No.45	-	0.11	-	-25.72	19.18	-
NBS28 No.11	0.666	11.07	101	-25.70	9.44	-0.20
NBS28 No.12	0.598	8.65	88	-25.62	9.52	-0.12
NBS28 No.13	0.544	7.61	85	-25.69	9.40	-0.24
NBS28 No.14	0.629	7.98	77	-25.51	9.07	-0.57

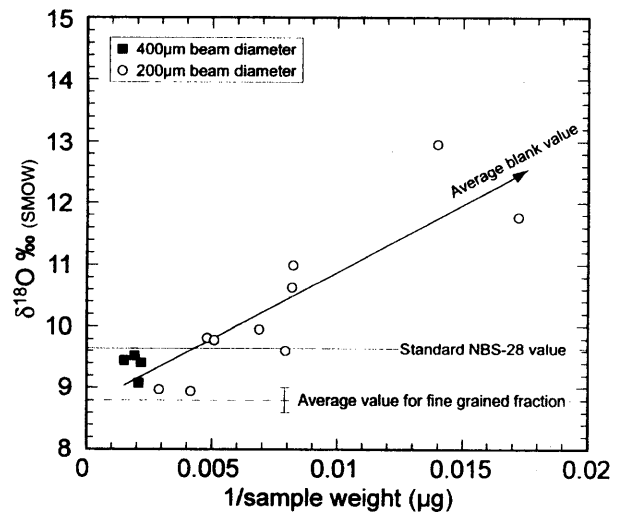


Fig. 14 Oxygen isotope values of NBS-28 in relation with the quantity of sample used (estimated from the amount of CO₂ produced). The recommended $\delta^{18}\text{O}$ value for NBS-28 and the small grain size fraction value of Fouillac & Girard (1996) are also plotted. The results show that there is a simple mixing of isotope values between the NBS-28 and blank for small volume measurements, associated with a "grain size effect".

using quartz fragments taken from a transparent single crystal. Although the isotope value and its homogeneity are unknown for this quartz crystal, it was utilized for the scrutiny of yield, laser power, and other tests in our oxygen extraction procedure.

The quartz crystal was crushed and sieved to 100-250 μm grain size. The sample was then cleaned with 2N HCl and distilled water. After rinsing with ethanol, the sample was dried in an oven at 110°C. The nickel sample holder was also cleaned in HCl, distilled water and ethanol and dried in an oven. The weight of sample was measured using an ultra-micro balance (Sartorius Surpermicro S4;

precision of 0.1 μg). Approximately 100–500 μg of quartz samples were placed in the eight sample pits in the holder. Each pit is ~ 2 mm in diameter at the surface and taper to < 1 mm at the bottom to a depth of about ~ 2 mm. This tapering design helps to observe the inner side of the sample pit using video camera without the dead angle.

Oxygen extraction

The sample holder containing the quartz samples in the pits is set in the sample preparation chamber and evacuated with a rotary pump. The holder is brought in to the reaction chamber through the gate valve and kept in a BrF_5 atmosphere (Pre-fluorination) overnight. After an initial 30 min. blank run, BrF_5 is expanded at 100–135 hPa (76–100 mmHg) in the reaction chamber. The sample is now ready for the laser ablation.

Initially, laser was set at a low power (~ 2.0 mA) to melt only the surface of the quartz grains. The X-Y stage is used to move the holder to completely fuse the sample surface. The process of surface melting is needed to prevent sample from spattering. It is reported that the ejecta of unreacted minerals can occur during the laser ablation (Spiccuza *et al.*, 1998), and can result in isotope variation or inter-sample contamination if the laser is focused and the power is too strong. After melting the surface of the sample, the power of laser was increased to 2.3–3.0 mA and the sample was made to react with BrF_5 as quickly as possible. However, the laser should not be continuously ablated more than ~ 15 seconds, because of the likelihood of breaking the BaF_2 window of the reaction chamber. The total time of oxygen extraction by laser ablation varied between 6–27 min in the present suite of ablation experiments. The liberated O_2 was converted to CO_2 and sealed in an ampoule and measured for carbon and oxygen isotopes.

Reproducibility of $\delta^{18}\text{O}$ values of internal quartz standard

It is necessary to check the reproducibility of $\delta^{18}\text{O}$ values determined by the present procedure for silicate minerals before the analysis of the natural sample. Oxygen was extracted from the quartz sample as described in the former section. The results are given in Table 9, and illustrated in Fig. 13 in a covariance diagram between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. Initial measurements of the quartz samples (1 to 4) gave a large range of $\delta^{18}\text{O}$ values (-10.1 – 11.5 ‰) and low yields (11–68%), since the $\text{O}_2 \rightarrow \text{CO}_2$ converter did not work well. On the other hand, runs 21 to 25 show less scatter in $\delta^{18}\text{O}$ values (13.7–16.3‰) with acceptable yields (78–97%), except for run 25 (43%) (Table 9). This indicates that relatively good reproducibility is achieved by the experiments, although there was still ~ 3 ‰ spread for the $\delta^{18}\text{O}$ values.

Measurement of NBS-28 quartz standard

Since accurate $\delta^{18}\text{O}$ value of the internal quartz is unknown and its homogeneity in isotope values is not clear, it is necessary to measure standard material with well-specified $\delta^{18}\text{O}$ value in order to evaluate further the accuracy of the system. NBS-28 quartz (SiO_2) is the international reference standard for oxygen isotope ratio provided by the National Institute of Standard and Technology (NIST), Geithersburg, Maryland, USA. The accepted $\delta^{18}\text{O}$ value for this standard is 9.64‰ (VSMOW), analyzed by conventional methods (Friedman & Gleason, 1973). The grain size of the quartz is 100–250 μm . The weight of sample used in this study varied between 100–440 μg . The procedure followed was the same as that of internal quartz standard.

Table 10 shows the $\delta^{18}\text{O}$ results of the measurement of NBS-28 and intermittent blank, which is tabulated in the order of extraction day and time. 0.96 – 11.07 μmoles of CO_2 gas were produced corresponding to the yields between 50–101%, except for run No. 8 (37%). It may be noted that in most of the experiments, the yields are not close to 100% and are varies randomly. Microscopic observation after completion of the extraction revealed that significant amount of sample remains in the sample holder. Thus, the low yield seems to result from incomplete sample reaction during the laser ablation.

The $\delta^{13}\text{C}$ values remained constant at -25.68 ± 0.11 ‰ ($n = 14$) in these experiments. However, the $\delta^{18}\text{O}$ values for the NBS-28 gave a considerable range (8.97‰ – 12.95‰). A comparison with the recommended value (9.64‰) shows that most of the values are heavier, while two samples show lighter value (Fig. 14). The relation between $\delta^{18}\text{O}$ values and the sample size estimated from the yield of CO_2 indicates that the $\delta^{18}\text{O}$ values for small size samples are affected more strongly by the blank and can be explained by simple mixing. However, the variation in the isotope values is considered to reflect the large range of blank values as well as the proportion of the blank in the total oxygen. Blank runs were carried out before, in between and after NBS-28 sample measurements (Table 10). The $\delta^{18}\text{O}$ values of blanks are in the range of 14.80‰ – 19.88‰ (17.98 ± 1.76 ‰, $n = 6$). Although the observed $\delta^{18}\text{O}$ values of NBS-28 is lower than accepted values, it should be noted that corresponding to a larger sample size, more reliable $\delta^{18}\text{O}$ values were obtained. This indicates that larger sample size reduces the effect of blank. Based on the available results, at present, at least 250 μg of quartz is needed for one analysis in order to obtain reliable $\delta^{18}\text{O}$ values. This sample size is less than one fourth of the commonly used sample size used for laser ablation elsewhere in other laboratories (e.g., Fouillac & Girard, 1996,

Spiccuza *et al.*, 1998).

Most of the $\delta^{18}\text{O}$ values obtained for NBS-28 with larger sample sizes are slightly lower than the recommended value (9.64‰). Fouillac & Girard (1996) suggested that $\delta^{18}\text{O}$ values are lowered by "grain size effect" that occurs when grains are smaller than 250 μm and laser is sharply focused. In our system, we used focused CO_2 laser ($\sim 200 - 400 \mu\text{m}$) and fine grain samples (100–250 μm). Hence, the lowering of $\delta^{18}\text{O}$ values may correspond to the "grain size effect". The fine grains are supposed to cause 'slow heating', the difficulty to absorb the laser energy than the larger grains, because of transparency. Further experiments are necessary to confirm the causes of lowering of $\delta^{18}\text{O}$ values of small grain size.

Summary of experiments and concluding remarks

Based on the experimental results described above, the recommended procedure for oxygen extraction using laser ablation system is summarized in Fig. 15. Sample should be cleaned with 2N HCl, distilled water, rinsed with ethanol and dried in an oven at 110°C over night. The nickel sample holder should also be cleaned in a similar manner. After weighing the samples by ultra-micro balance, they are placed in the conical pits in the nickel sample holder. The sample holder is then kept in the sample chamber and evacuated using a rotary pump. After evacuating, sample holder is transferred to the high vacuum reaction chamber from the sample chamber with a magnetic piston 'rod' passing through the gate valve.

It is necessary to run pre-fluorination at least 3 times, before analysis. First, BrF_5 is expanded for 5 min in the reaction chamber and deposited to waste tank. The second run is for 30 min and the third run for over night. After the third pre-fluorination is completed, new aliquot of BrF_5 is expanded in the reaction chamber at 100–135 hPa (76–100 mmHg). Checking the point to irradiate by target laser, the operator adjust sample holder using X-Y stage. Then, the laser is turned on to heat the sample instantaneously high enough to react (for quartz it is about 1,100–1,300°C). The power of the laser is fixed depending upon the beam diameter and the mineral to be ablated (refractory minerals need high power). In the case of small grain size samples, initial surface melting is necessary, so as to reduce the chance of sputtering of the samples from the sample pits. Viewing at the monitor, the sample is reacted under the laser beam until no more reaction is visible.

After completion of the reaction, excess BrF_5 gas and by-product gases (SiF_4 , BrF_3) are removed using liquid N_2 cold traps T_5 and T_1 , and steel wool trap is used to absorb the minor amounts of F_2 . Thus, only pure O_2 gas is allowed to reach the $\text{O}_2 \rightarrow \text{CO}_2$ converter

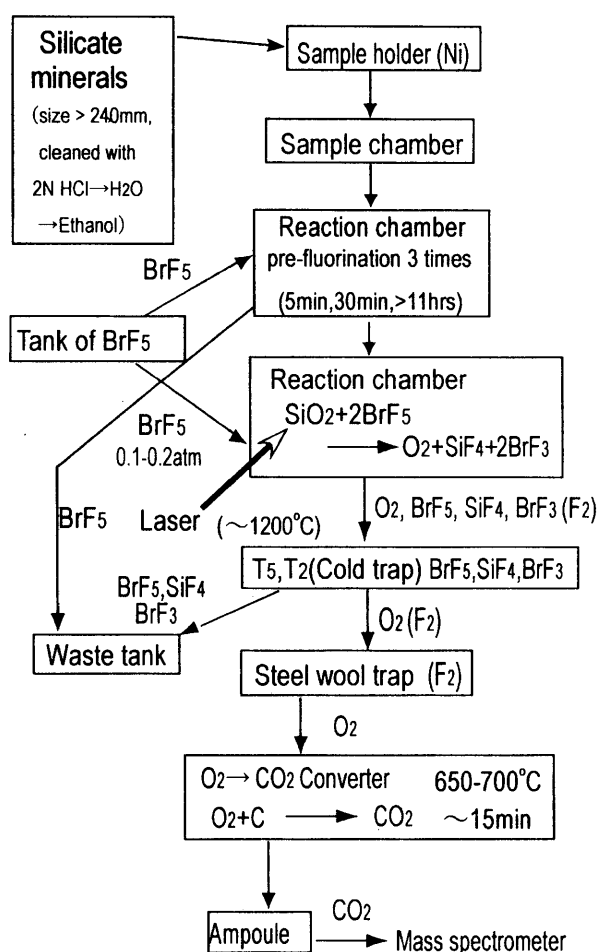


Fig. 15 Flowchart showing the recommended procedure for oxygen extraction and conversion to CO_2 for stable isotope measurements of rock forming minerals at Shizuoka University. The total time required for single average size sample extraction is about 30 minutes.

from reaction chamber. At the converter ' $\text{O}_2 + \text{C} \rightarrow \text{CO}_2$ ' reaction takes place with the help of heated graphite in a platinum foil holder at $\sim 650^\circ\text{C}$. Generally the reaction finishes by 8–10 min., as can be observed from the reduction of gas pressure in the capacitance monometer. However, 5–7 min. more time is given to complete the reaction of the remaining O_2 at a slightly lower temperature ($\sim 600^\circ\text{C}$). Thus, the total reaction time is about 15 min. The product gas (CO_2), as soon as formed, is condensed by liquid N_2 cold trap T_3 and is finally shifted to trap T_4 to be sealed in 6 mm Pyrex® glass ampoules. The CO_2 gas is then cracked open in vacuum to the inlet system of the Finnigan MAT 250 mass spectrometer and measured for carbon and oxygen isotope ratios.

In summary, the best reaction conditions for $\text{O}_2 \rightarrow \text{CO}_2$ converter are $\sim 650^\circ\text{C}$ for 15 min. with < 2 mm graphite grain size. It is effective to run pre-fluorination in order to reduce the quantity of blank oxygen gas. The measurements of NBS-28 quartz standard shows about 4‰ spread for $\delta^{18}\text{O}$ values, basically caused by the 'blank' effect. Using the

present laser ablation system, at least $\sim 250 \mu\text{g}$ of quartz is needed for one analysis in order to obtain reliable values. Based on the results of NBS-28 analyses, a defocused laser beam ($\sim 1\text{mm}$ diameter, Spiccuza *et al.*, 1998), which can completely react the sample, is most suited for oxygen extraction.

Tips for further improvement

In order to establish the micro-sample analysis ($< 250 \mu\text{g}$ of quartz), it is necessary to reduce the blank to as minimum as possible. Since the present reaction chamber has high volume, it is difficult to achieve this reduction. It is expected that replacing the present chamber with a new reaction chamber, which has small volume and more simple structure, the 'blank' effect can be minimized. In order to reduce 'grain size effect' a defocused beam technique ($\sim 1\text{mm}$ diameter) is required to completely react the samples. To achieve this, either the working distance between laser and the sample holder has to be decreased considerably or equip the laser outlet with a lens with a shorter focal length than the present one. Some part of the sample remains in the holder after the analysis obviously causing reduced yield and depletion in $\delta^{18}\text{O}$ values. Therefore it is necessary to improve the sample pits in the holder and to reconsider the monitoring system, so that the sample can be viewed more clearly during laser fluorination.

Acknowledgements

We thank Dr. T. Ishikawa for his valuable review comments. The authors also wish to acknowledge Prof. N. Niitsuma for his advice during the course of this study. T. M. wish to thank Mr. Y. Tada, Y. Yoshida, Ms. M. Matsunaga, Mr. Binu-Lal and M. Mochizuki for encouragements. H. W. acknowledges JSPS for special grant (10440160) support through which the oxygen extraction system was installed.

References

- Akagi T., Franchi I. A. & Pillinger C. T. (1995), Isotope analysis of oxygen in minerals using Nd/YAG laser-fluorination: The use of stainless-steel wool trap as a fluorine remover. *Geochemical Journal*, **29**, 115-122.
- Akagi T., Franchi I. A. & Pillinger T. (1993), Oxygen isotope analysis of quartz by neodymium-yttrium aluminum garnet laser-fluorination. *Analyst*, **118**, 1507-1510.
- Baertschi P. & Silverman S. R. (1951), The determination of the relative abundance of the oxygen isotopes in silicate rocks. *Geochimica et Cosmochimica Acta*, **1**, 317-328.
- Borthwick J. & Harmon R. S. (1982), A note regarding CIF_3 as an alternative to BrF_5 for oxygen isotope analysis. *Geochimica et Cosmochimica Acta*, **46**, 1665-1668.
- Chamberlain C. P. & Conrad M. E. (1991), Oxygen isotope zoning in garnet. *Science*, **254**, 403-406.
- Chamberlain C. P. & Conrad M. E. (1993), Oxygen isotope zoning in garnet: a record of volatile transport. *Geochimica et Cosmochimica Acta*, **57**, 2613-2629.
- Clayton R. N. & Mayeda T. K. (1963), The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta*, **27**, 43-52.
- Conrad M. E. & Chamberlain C. P. (1992), Laser-based, in situ measurements of fine-scale variations in the $\delta^{18}\text{O}$ values of hydrothermal quartz. *Geology*, **20**, 812-816.
- Elsenheimer D. & Valley J. W. (1992), In situ oxygen analysis of feldspar and quartz by Nd: YAG laser microprobe. *Chemical Geology*, **101**, 21-42.
- Fiebig J., Wiechert U., Rumble D. III. & Hoefs J. (1999), High-precision in situ oxygen isotope analysis of quartz using an ArF laser. *Geochimica et Cosmochimica Acta*, **63**, 687-702.
- Fouillac A. M. & Girard J. P. (1996), Laser oxygen analysis of silicate/oxide grain separates: evidence for a grain size effect? *Chemical Geology*, **130**, 31-54.
- Friedman I. & Gleason J. D. (1973), A new silicate intercomparison standard for ^{18}O analysis. *Earth and Planetary Science Letters*, **18**, 124.
- Kohn M. J., Valley J. W., Elsenheimer D. & Spiccuza M. J. (1993), O isotope zoning in garnet and staurolite: evidence for closed-system mineral growth during regional metamorphism. *American Mineralogist*, **78**, 988-1001.
- Krischner D. L. & Sharp Z. D. (1997), Oxygen isotope analysis of fine-grained minerals and rocks using the laser-extraction technique. *Chemical Geology*, **137**, 109-115.
- Kyser T. K. (1995), Micro-analytical techniques in stable-isotope geochemistry. *Canadian Mineralogist*, **33**, 261-278.
- Lee T., Mayeda T. K. & Clayton R. N. (1980), Oxygen isotopic anomalies in Allende inclusion HAL. *Geophysical Research Letters*, **7**, 493-496.
- Manian S. H., Urey H. C. & Bleakney W. J. (1934), An investigation of the relative abundance of the oxygen isotopes $^{18}\text{O}/^{16}\text{O}$ in stone meteorites: *American Chemical Society Journal*, **56**, 2601-2609.
- Mattey D. & Macpherson C. (1993), High-precision oxygen isotope microanalysis of ferromagnesian minerals by laser fluorination. *Chemical Geology*, **105**, 305-318.
- Rumble D. III., Farquhar J., Young E. D. & Christensen C. P. (1997), In situ oxygen isotope analysis with an excimer laser using F_2 and BrF_5 and oxygen gas as analyte. *Geochimica et Cosmochimica Acta*, **61**, 4229-4234.
- Sharp Z. D. (1990), A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides. *Geochimica et Cosmochimica Acta*, **54**, 1353-1357.
- Sharp Z. D. (1992), In situ laser microprobe techniques for stable isotope analysis. *Chemical Geology*, **101**, 3-19.
- Spiccuza M. J., Valley J. W., Kohn M. J., Girard J. P. & Fouillac A. M. (1998), The rapid heating,

- defocused beam technique: A CO₂- laser based method for highly precise and accurate determination of $\delta^{18}\text{O}$ values of quartz. *Chemical Geology*, **144**, 195-203.
- Taylor H. P. & Epstein S. (1962), The relationship between $^{18}\text{O} / ^{16}\text{O}$ ratios in coexisting minerals of igneous and metamorphic rocks. *Geological Society of America Bulletin*, **73**, 461-480.
- Valley J. W., Kitchen N., Kohn M. J., Niendorf C. R. & Spicuzza M. J. (1995), UWG-2, a garnet standard for oxygen isotope ratios: strategies for high precision and accuracy with laser heating. *Geochimica et Cosmochimica Acta*, **59**, 5223-5231.
- Wada H., Niitsuma N. & Saito T. (1982), Carbon and oxygen isotopic measurements of ultra-small samples. *Geoscience Reports of Shizuoka University*, **7**, 35-50 (in Japanese with English abstract).
- Wiechert U. & Rumble D. III. (1993), An excimer laser-based microanalytical preparation technique for in-situ oxygen isotope analysis of silicate and oxide minerals. *Geochimica et Cosmochimica Acta*, **59**, 4093-4100.
- Young E. D. & Rumble D. III. (1993), The origin of correlated variations in in-situ $^{18}\text{O}/^{16}\text{O}$ and elemental concentrations in metamorphic garnet from southeastern Vermont, USA. *Geochimica et Cosmochimica Acta*, **57**, 2585-2597.