静岡大学地球科学研究報告 31（2004年7月）73頁～76頁
Geosci. Repts. Shizuoka Univ., 31 (July, 2004), 73-76

Optimum experimental conditions for the conversion of oxygen to carbon dioxide for the precise oxygen isotope analysis of rock forming minerals

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Abstract This study describes the optimum experimental conditions required for the conversion of oxygen to carbon dioxide produced in the laser ablation oxygen extraction system (Matsui *et al.*, 2003). Purity of carbon used in the converter, duration of preheating between sample conversions (1hour at ~630℃) and careful temperature control during conversion (600 ℃) can yield high reproducibility. Experimental runs with oxygen gas from cylinder gave a reproducibility for $\delta^{18}O$ values of ± 0.1‰ ($n = 4$).

Key words: laser ablation, oxygen isotopes, $O_2 \rightarrow CO_2$ converter, silicate minerals

Introduction

Oxygen isotope is one of the important tools used for investigating the origin and the evolution of rocks. The history of oxygen isotope analyses for silicate minerals started more than 70 years ago (Manian *et al.*, 1934) and experimental procedure for the separation of oxygen from rock forming minerals were revised and modified until the recent laser based technique was introduced (Sharp *et al.*, 1990). Laser ablation oxygen extraction system for silicate minerals was installed in Shizuoka University and its instrumentation, initial settings and operational procedure were reported in Matsui *et al.* (2003). Oxygen is separated from mineral grains by ablation using a CO_2 laser in a BrF_5 atmosphere and is then converted to CO_2 using a converter. CO_2 gas is analyzed for oxygen isotopes. However, the reproducibility of the system as a whole, especially of the converter, reported by Matsui *et al.* (2003), was not satisfactory for the precise measurement of the small volume of CO_2 gas using the modified inlet system of the mass spectrometer at Shizuoka University (Wada *et al.*, 1982). The purpose of this study is to reexamine the reproducibility of the $O_2 \rightarrow CO_2$ converter, so that the results of the oxygen isotope laser ablation system for silicate minerals could give precise isotopic determinations. We reexamined the experimental conditions, such as conversion temperature, duration of pre-heating and grain size of graphite, using oxygen gas samples.

$O_2 \rightarrow CO_2$ Converter

CO_2 is generated from O_2 in the $O_2 \rightarrow CO_2$ converter using a heater comprising of a self resistant platinum foil for increasing temperature, within which

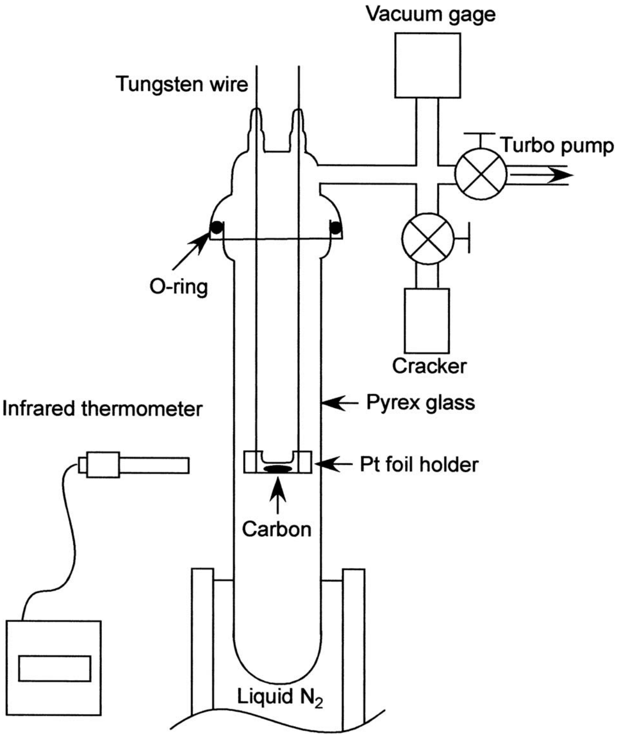

Fig. 1 The oxygen to carbon dioxide converter in the laser ablation oxygen extraction system.

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graphite is placed (Matsui *et al.*, 2003). The conversion apparatus used is shown in Figure 1. Through the tungsten wire, electric current flows to the Pt (platinum) foil holder where the graphite is loaded. Based on the difference of resistance between the wire and the foil, the temperature in the foil is increased. The temperature is continuously measured using an infrared remote thermometer while the graphite in Pt the foil is heated. The temperature is adjusted by varying the current. Oxygen reacts with carbon at temperatures higher than 550℃. Before conversion, pre-heating of the converter is necessary in order to remove adsorbed gases. The vacuum inside the converter is monitored using a capacitance manometer (Fig. 1). O_2 gas released from minerals using laser ablation is introduced into the converter. As soon as the gas enters the converter, it starts reacting with carbon to form CO_2. The resulting CO_2 is trapped in the cold slush of liquid N_2 and sealed in ampoules, which are cracked open to the inlet system of the mass spectrometer (Wada *et al.*, 1982) to measure the stable isotopes of the carbon and oxygen using Finnigan MAT 250 mass spectrometer.

Results and discussion

Matsui *et al.* (2003) carried out experiments with oxygen gas from cylinder and obtained a reproducibility of ± 0.33‰ ($n = 22$). The carbon used in their conversion experiments was a crushed carbon rod (JEOL), normally used for carbon coating of thin section. The reaction temperature for conversion was about 650℃ and the reaction time was 15 minutes.

In this study, carbon in the converter was changed to SP-2 (Nihon Carbon Co. Ltd), which is graphite carbon chemically purified from coal and used as photospectroscopic anode. According to Wada & Ito (1990) SP-2 graphite has a homogenous carbon isotope composition.

O_2 gas from cylinder, expanded in about 72 cm long 6ϕ glass tube (we call a batch) and cut into six tubes of almost same volume of O_2, and were then used for the conversion into CO_2. This O_2 tube is cracked open in to the converter to react with the graphite in the converter. The vacuum inside the converter decreases after reaching a maximum value, indicating that most of the O_2 has already reacted with carbon to form CO_2 (Fig. 2). The decrease in the minimum value of the vacuum inside the converter indicates the release of gases which can not be trapped by liquid N_2. Especially, if CO is produced, it causes fractionation of isotopes and should be avoided.

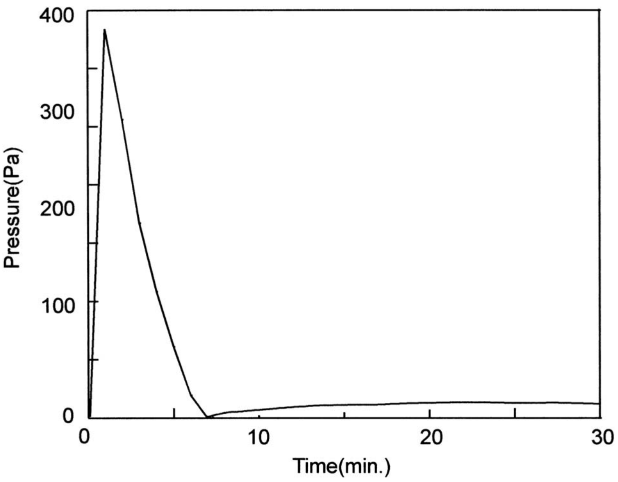

Fig. 2 Trend of vacuum condition inside the converter after reaching the maximum value.

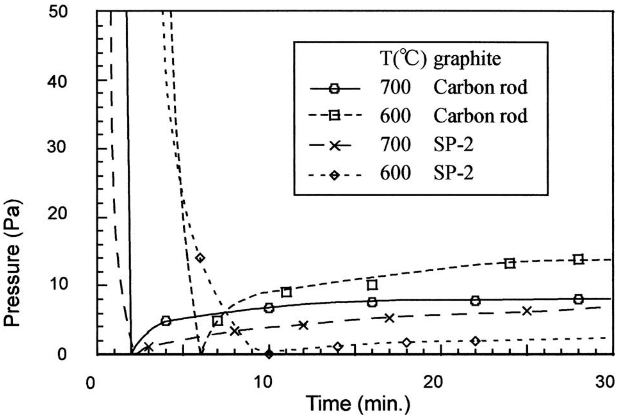

Fig. 3 Vacuum condition inside the converter during experimental runs at varying temperatures and different carbon materials.

Results of O_2 batch experiments are given in Figure 3. When the SP-2 graphite were used, the decrease in vacuum condition after reaching the high vacuum at about 10 minutes was not so large when compared with the experiments using the carbon rod. Experiments were carried out with different temperatures of conversion and the vacuum inside the converter was monitored (Fig. 3). The best temperature condition to form CO_2 gas without forming any other gases was confirmed by this experiment. When the temperature is over 600℃, the gas pressure of the converter rises suddenly, after reaching the minimum. Therefore, based on the results of the experiments, ~600℃ is considered to be optimum reaction temperature. 15 minutes after attaining a high vacuum condition, the vacuum inside the converter became constant. Experiments were carried out using this reaction condition show that the $\delta^{18}O$ values have a regular change for the samples converted in a sequence, *i.e.* later converted sample gave heavier $\delta^{18}O$ values (Table 1). This means that there is a "memory effect" remaining in the converter. The adsorption of heavier oxygen inside the converter can cause such a shift. The most

Table 1 Results of conversion experiments of pure oxygen gas from cylinder.

O2 sample no.	yeild (%)	$\delta^{13}C$ (‰, PDB)	$\delta^{18}O$ (‰, SMOW)	Pressure increase (Pa)	Carbon used	Temperature of conversion	Pre-heating temperaure	Pre-heating time (min.)
A-2	93	-25.82	14.48		Carbon rod	680	--	--
A-3	96	-25.85	14.77			680	--	--
A-4	93	-25.83	15.10			680	--	--
A-5	94	-25.94	14.99			680	--	--
A-6	85	-25.82	14.78			680	--	--
	1σ	**0.05**	**0.24**					
B-1	94	-25.77	15.82		Carbon rod	680	540	43
B-2	93	-25.79	15.87			680	540	32
B-3	94	-25.76	15.89			680	500	25
B-4	91	-25.78	16.48			680	540	22
B-5	89	-25.83	16.37			680	540	32
B-6	93	-25.80	16.21			680	510	35
	1σ	**0.02**	**0.28**					
C-1	79	-25.76	16.22	10.3	Carbon rod	700	510	38
C-2	79	-25.82	16.36	8.0		700	490	33
C-3	81	-25.70	15.45	4.2		600	510	65
C-4	81	-25.61	15.64	14.7		600	520	45
	1σ	**0.09**	**0.44**					
F-1	94	-24.64	27.95	4.1	SP-2	600	520	101
F-2	105	-24.64	27.87	3.9		600	540	255
F-3	105	-24.61	28.17	3.5		600	520	41
F-4	110	-25.01	27.97	6.9		700	540	73
F-5	105	-24.96	27.60	4.7		700	510	70
F-6	96	-24.85	27.64	5.0		700	550	49
	1σ	**0.18**	**0.22**					
I-1	--	-24.49	29.72	5.4	SP-2	600	550	49
I-2	--	-24.48	29.71	6.4		600	550	44
I-3	--	-24.49	29.94	4.8		600	540	89
I-4	--	-24.49	30.11	6.4		600	540	33
I-5	--	-24.45	30.04	3.0		600	550	65
I-6	--	-24.48	30.31	3.0		600	540	79
	1σ	**0.01**	**0.23**					
J-1	91	-24.57	29.34	4.8	SP-2	600	630	145
J-2	101	-24.59	29.28			600	620	51
J-3	102	-24.50	29.45	1.1		600	620	57
J-4	102	-24.50	29.57	1.3		600	620	63
J-5	99	-24.47	29.26	1.5		600	640	49
J-6	88	-24.51	29.34	1.2		600	630	35
	1σ	**0.05**	**0.12**					
M-1	99	-24.50	29.83	2.0	SP-2	600	630	120
M-2	104	-24.49	29.81	1.3		600	630	160
M-3	105	-24.50	29.87	0.9		600	630	54
M-4	105	-24.45	29.89	1.3		600	630	50
	1σ	**0.02**	**0.04**					

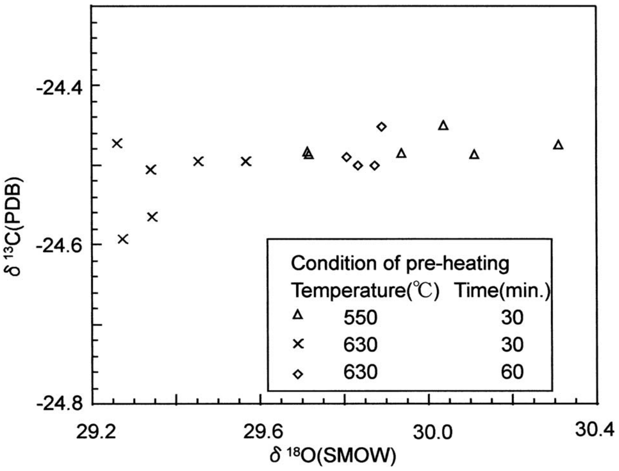

Fig. 4 Carbon versus oxygen isotope results of a single batch of six oxygen gas samples. Same symbols indicate a sequence of conversion and the numbers indicate the order in which the experiments were carried out.

possible site of adsorption may be the graphite itself. Lighter isotopes move faster than heavier ones. If isotopically heavy O_2 remains in the converter, $\delta^{18}O$ value of the sample measured later could be higher than the value of last sample (Fig. 4).

Based on the above results, the graphite in the Pt foil holder needs to be preheated before each conversion in order to remove the memory effect of the earlier sample. The pre-heating temperature was set at ~630℃, which is higher than the reaction temperature and the time required for preheating was one hour (Fig. 5). Experiments using this condition gave good vacuum condition after the conversion (increase was less than 2 Pa). The oxygen isotope results of experiments carried out using a single batch of oxygen gas gave a reproducibility within ±0.1‰ ($n = 4$). This accuracy is as best as that of oxygen isotope machine constant of MAT250 mass spectrometer (Wada *et al.*, 1982).

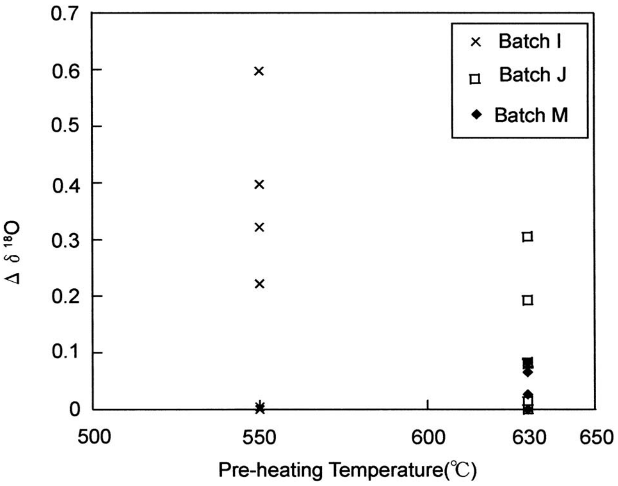

Fig. 5 Relationship between oxygen isotopes of oxygen gas converted under different temperature conditions and duration of pre-heating between sample conversions.

Thus, in summary, the experiments presented here were helpful in finding out the best condition to convert O_2 to CO_2 reproducibility necessary for small volume isotope measurements.

Acknowledgements

We would like to express our gratitude to Prof. Nobuaki Niitsuma for the advices and encouragements. Dr. Kazuhiro Kato, Mr. Youhei Tada, Mr. Yoshiaki Araki and Mr. Takafumi Matsui are thanked for their perpetual helps. Financial support through Ministry of Education, Science and Culture (No. 10440160 to HW), JSPS research grant (No. 15740302 to MS-K) and field research grant (No. 15403016 to HW) are acknowledged.

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