

# 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 CO<sub>2</sub> laser system capable of extracting oxygen from rock forming silicate and oxide minerals in a BrF<sub>5</sub> atmosphere was fabricated. The vacuum line can resist the hazardous BrF<sub>5</sub> reagent used for disintegrating the Si=O bonds in minerals. The oxygen, thus released, is converted to CO<sub>2</sub> in an O<sub>2</sub>→CO<sub>2</sub> 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 O<sub>2</sub>→CO<sub>2</sub> converter, background measurements during fluorination and precautions in handling the BrF<sub>5</sub> 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 BrF<sub>5</sub> reagent, sizeable amount of background O<sub>2</sub> was released during the pre-fluorination of the system (~ 0.2-0.3 μmoles of O<sub>2</sub> for 30 minutes of fluorination). Repeated fluorination of the system considerably reduced the background O<sub>2</sub>, however, could not be completely eliminated. Tests were also made for the functional setting of the O<sub>2</sub>→CO<sub>2</sub> converter using ampoules of external O<sub>2</sub> 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. δ<sup>18</sup>O<sub>SNOW</sub> 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 O<sub>2</sub> 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, BrF<sub>5</sub>, O<sub>2</sub>-CO<sub>2</sub> converter

## Introduction

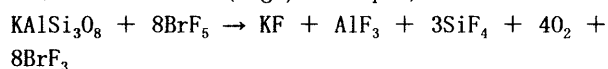
Oxygen is the most abundant element in the Earth's crust and mantle, and forms an important stable isotope tracer in various geological processes. Oxygen isotope analysis of rock forming minerals is considered to be one of the most important geochemical techniques to elucidate the origin and evolution 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 O<sub>2</sub> (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 (ClF<sub>3</sub>) 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 ( $\text{BrF}_5$ ) is preferred to fluorine as the reagent. This study adopts  $\text{BrF}_5$  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  $\text{O}_2$  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  $\mu\text{moles}$ ) 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  $\text{O}_2$  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  $\text{NiF}_2$  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,  $\text{MnO}_2$ ) using  $\text{CO}_2$  laser, and in situ spot-analysis (< 300  $\mu\text{m}$  in diameter) on the polished thick section was also successful (< 0.5%).

The most commonly used  $\text{CO}_2$  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  $\text{O}_2$  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  $\text{O}_2$ . However, as an unwanted by-product, small amounts of  $\text{F}_2$  is produced, when silicate minerals react with  $\text{BrF}_5$ .  $\text{F}_2$  gas cannot be cryogenically separated from  $\text{O}_2$  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

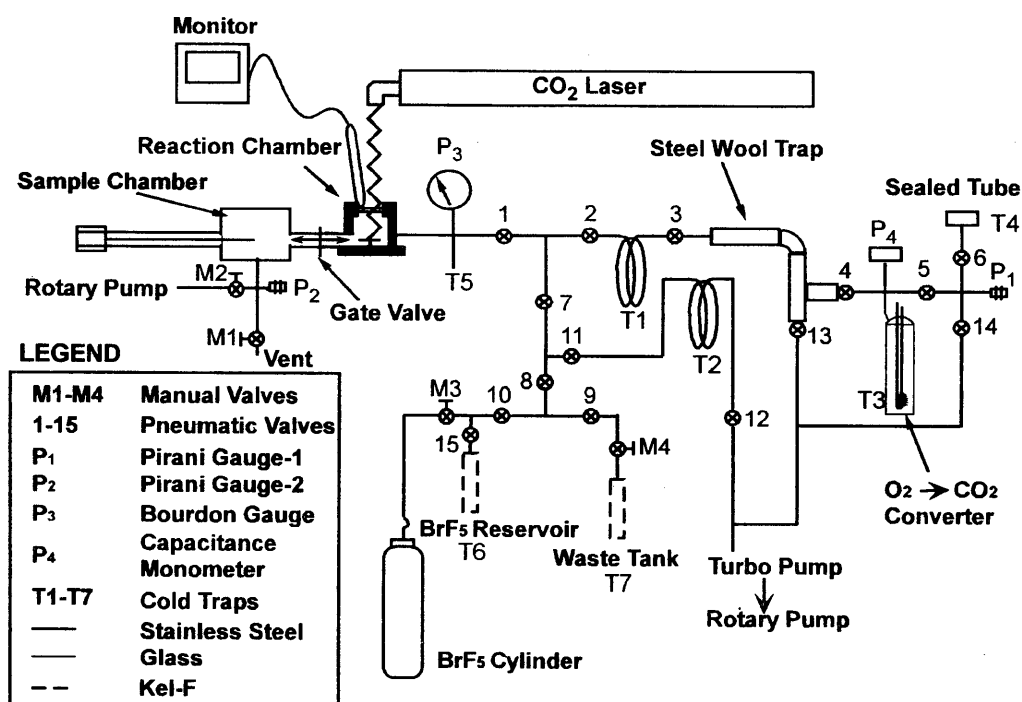


Fig. 1 Schematic layout of the vacuum line for laser fluorination system and associated instrumentation.



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.

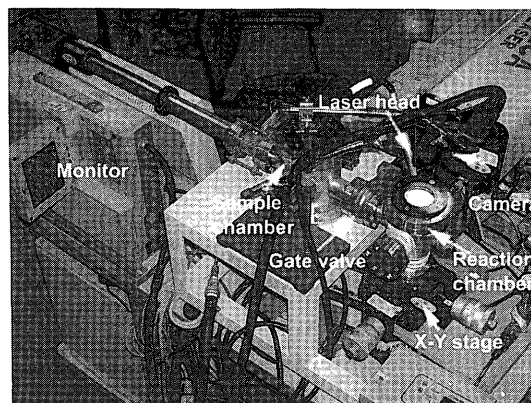


Fig. 3 The reaction chamber and the sample chamber of the system, separated by a gate valve. The sample holder is fixed on an X-Y stage (25 mm X 25 mm). Sample holder with sample is placed in the sample chamber and evacuated using a rotary pump. After evacuation, the gate valve is open and the holder 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 ( $>250 \mu m$ ) 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  $\mu m$ ).

#### 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

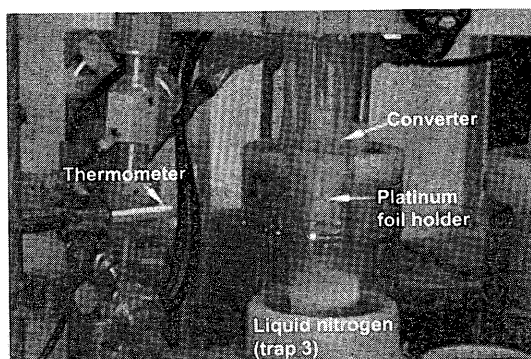


Fig. 4 The  $O_2 \rightarrow CO_2$  converter, made of Pyrex glass, comprises of a platinum foil (0.1 mm thick) holder designed to keep graphite and give self resistance for increasing the temperature in the order  $500 \sim 700^\circ C$ .

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  $\sim 3$  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  $T_7$

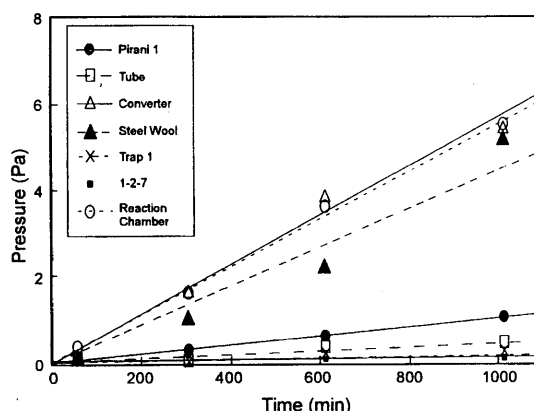


Fig. 5 Results showing the segment wise leak check for the oxygen extraction line plotted as a function of pirani gauge reading ( $P_1$ ) with time. Note that the steel wool,  $O_2 \rightarrow CO_2$  converter and the reaction chamber can not withstand high vacuum condition for long, however is capable 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  $\sim 80$  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  $\sim 15$  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 ( $\sim 13.5$  cm long and  $\sim 2.5$  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  $\sim 10$  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 ( $\sim 70$  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

