**Atmospheric
Measurement
Techniques
Discussions**

A new CF-IRMS system for the quantification of the stable isotopes of carbon monoxide from ice cores and small air samples

Z. Wang and J. E. Mak

Institute for Terrestrial and Planetary Atmospheres/School of Marine and Atmospheric
Sciences, Stony Brook University, Stony Brook, NY 11794-5000, USA

Correspondence to: Z. Wang (zhihui.wang@stonybrook.edu)

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

A new simultaneous analysis technique for stable isotope ratios (δ^{13}C and δ^{18}O) of atmospheric carbon monoxide (CO) from ice core samples and small air samples is presented, based on an on-line cryogenic vacuum extraction followed by continuous-flow isotope ratio mass spectrometry (CF-IRMS). The CO extraction system includes two multi-loop cryogenic cleanup traps, a chemical oxidant for oxidation to CO_2, a cryogenic collection trap, a cryofocusing unit, purification by gas chromatography, and subsequent injection into a Finnigan Delta Plus IRMS. Analytical precision of 0.2‰ ($\pm 1\sigma$) for δ^{13}C and 0.6‰ ($\pm 1\sigma$) for δ^{18}O can be obtained for 100 mL (STP) air sample with CO mixing ratio ranging from 60 to 140 ppbv ($\sim$268–625 pmol CO). Six South Pole ice core samples with depth ranging from 133 to 177 m are also processed for CO isotope analysis based on a wet extraction line attached to the above cryogenic vacuum system. This is the first report on measuring isotope ratios of CO in ice core samples.

1 Introduction

As the major sink for hydroxyl radicals (OH), carbon monoxide plays a key role in global atmospheric chemistry and strongly affects the oxidizing capacity of the atmosphere. The major sources of atmospheric CO in the modern atmosphere are known and incorporation of stable isotopes (^{13}C and ^{18}O) renders inverse model results for CO budget estimates much more robust compared to inversions of CO mixing ratios only (Bergamaschi et al., 2000a,b). The stable isotopes of CO (^{13}C and ^{18}O) from air bubbles trapped in ice cores provide valuable information of CO source strength for the past atmosphere, which will enhance the understanding of atmospheric chemistry in the past. However, essentially no observations exist from which the relative source strengths can be estimated. Haan et al. studied the CO mixing ratio in both Antarctic and Greenland ice cores by reduction gas detector (RGD) (Haan et al., 1996, 1998), which gives

insight to measure ice core CO isotopes. Unfortunately, the volume of air trapped in ice cores is only around 100 mL (STP) per kg ice, and the ice core CO mixing ratio is previously reported to be only ~50 ppbv (Haan et al., 1996, 1998). Measuring CO isotope composition in ice core is extremely challenging since the sample size is very limited, in which case the conventional dual inlet micro-volume analysis method is not applicable.

Continuous-flow isotope ratio mass spectrometry (CF-IRMS) systems have been developed for measuring atmospheric CH_4 (Rice et al., 2001; Merritt et al., 1995; Lowe et al., 1991), atmospheric N_2O (Röckmann et al., 2003) and volatile organic compounds (VOC) in ambient air (Rudolph et al., 1997). The primary advantage of using CF-IRMS for CO isotope analysis by monitoring the relative abundance of masses 44, 45, and 46 has been shown by Mak and Yang (1998). A recent study by Tsunogai et al. (2002) has shown the advantage of isotope analysis for atmospheric CO using CF-IRMS by simultaneously monitoring the CO^+ ion currents at masses 28, 29, and 30. However, preparing CO standard gas with known isotope ratios and purifying CO presents challenges. In this study, a new cryogenic vacuum extraction system, which is principally based on the approach originally outlined in previous study (Brenninkmeijer et al., 1993), is designed to analyze isotope ratios of CO for small air samples (~268–625 pmol CO), specifically for CO in air bubbles trapped in Antarctic ice core by measuring CO-derived CO_2.

2 Methodology

2.1 Instrumentation and procedure

A schematic diagram of the online extraction and preconcentration method for carbon and oxygen isotope analyses of ice core CO is shown in Fig. 1. A wet extraction system for ice cores is combined with a cryogenic vacuum system for CO extraction. The cryogenic vacuum extraction line and a stripped down commercially available PreCon

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►I

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A new CF-IRMS system for the quantification of the stable isotopes

Z. Wang and J. E. Mak

(Finnigan MAT), is attached to a Delta Plus IRMS through a customized open split. The cryogenic vacuum system in this study includes dual four loop 1/4 inch OD glass coil cryogenic cleanup traps held at liquid nitrogen temperature, a Schütze reactor (1/4 inch OD U tube, 15 cm long) and a four loop glass CO_2 collection trap which is also held at liquid nitrogen temperature.

Ambient air samples are run by filling the sample canisters with air and attaching to the inlet of the cryogenic vacuum system. After passing through the cryogenic cleanup traps with a flow rate of 50 mL/min, atmospheric CO_2, H_2O, N_2O and other condensable species present in air samples are removed due to condensation at liquid nitrogen temperature (Brenninkmeijer, 1993). The purified CO is then selectively and quantitatively oxidized to CO_2 by the Schütze reagent, retaining the original ^{18}O signature of CO (Brenninkmeijer et al., 1993). The Schütze reagent is prepared according to the method described by previous studies (Schütze, 1949; Smiley, 1949). A bypass is installed for the Schütze reactor tube as well, allowing the postrun flushing with helium. The degradation of Schütze is indicated by its color change, e.g. from yellow to brown, which informs of the replacement (Mak and Yang, 1998).

The CO-derived CO_2 collected in trap3 is then eluted with cryogenically purified ultrapure helium with flow rate of 40 mL/min for 5 min and cryogenically focused in a microvolume trap of the modified Finnigan Preconcentration unit through a Valco six-port valve (Fig. 1). The cryofocus trap is then heated to room temperature and the CO_2 is loaded into the GC column (25 m×0.25 mm ID Poraplot Q capillary) with helium flow of 1 mL/min from back inlet of GC (Fig. 1). The resolved CO_2 then passes through an open split into the Finnigan MAT Delta-plus isotope ratio mass spectrometer at a flow rate of about 0.4 mL/min.

The detailed calculation of $\delta^{13}C$ and $\delta^{18}O$ is based on the two observable ion-current ratios (45/44 and 46/44) as discussed in previous study (Santrock et al., 1985). $\delta^{13}C$ of the original CO is determined by the $\delta^{13}C$ of derived CO_2, whereas $\delta^{18}O$ is determined based on calibration gas (Brenninkmeijer et al., 1993). The mixing ratio of CO for an air sample is determined by the ratio of peak areas between a sample and a cal-

A new CF-IRMS system for the quantification of the stable isotopes

Z. Wang and J. E. Mak

ibration gas. The precision of CO mixing ratios for air samples results reported in this study is better than 5% ($\pm 1\sigma$) based on reproducibility of 4 to 10 runs for field samples.

The Finnigan Precon system (Mak and Yang, 1998) is replaced by a new cryogenic vacuum system for measuring CO in air bubbles of ice core samples. A further de-
5 tailed procedure for ice extraction will be discussed later in this paper. The ice core sample is placed in a 1.2 L glass container with a 4.5 inch glass flange, viton o-ring and horseshoe clamp. A four-loop coil trap between the container and the inlet of the cryogenic vacuum system is used to remove water vapor. Upon melting, the air sample released from around 1 kg ice core is around 100 mL (STP), giving an initial pressure in
10 the headspace of about 300 mbar. This pressure drops to 60 mbar after air sample is processed for 5 min. A 150 mL glass flask filled with zero air (CO free air) is expanded to the ice container for building up pressure to around 500 mbar after processing the air sample for 5 min. The disadvantage for this method is the large blank from Schütze reagent due to long process time, which largely limits the precision of isotope ratios
15 measured using this technique. We tested the use of molecular sieve 5A and 13X held at liquid nitrogen temperature is used to condense air released from ice cores in order to shorten the process time and decrease the Schütze blank, however isotopic fractionation of both carbon (2–3‰) and oxygen (1–4‰) was evident during the elution process. This isotopic fractionation was not reported in Tsunogai et al. (2002). Use of
20 a Teflon beaker liner (Welch Fluorocarbon Inc.) was also investigated as its volume is adjustable and thus builds up pressure in the headspace by shrinking and pushing water upward. This can counteract the pressure reduction during processing. However, permeability of CO across Teflon film limits the use of this material. Similarly, Tedlar (polyvinyl fluoride, PVF), another polyfluorocarbon but with low CO permeability, was
25 also tested. However, it is quite difficult to engineer a Tedlar liner because of its rigidity. In the end, while the idea is intriguing and may warrant further study, we opted to keep our sampling protocol simple with the dilution process and characterize the Schütze blank to a high degree of precision. Clearly, an old fashioned mercury toepler pump could be ideal to solve this problem by reducing extraction time and Schütze blank.

2.2 Diagnostic experiments

Diagnostic experiments have been conducted on the cryogenic extraction system, and results indicate this new technique produces reliable isotope ratios for 100 mL air samples with CO mixing ratio as low as 60 ppbv (∼268 pmol CO). The diagnostic tests include analytical blank tests, precision tests and accuracy tests. Analytical blank is lower than 40 pmol CO for 100 mL air sample (see Table 3). Analytical precision of 2 ppb (±1σ) for CO mixing ratio, 0.2‰ (±1σ) for δ^{13}C and 0.6‰ (±1σ) for δ^{18}O can be obtained for sample size of 268 pmol CO (100 mL with CO mixing ratio of 60 ppbv). Meanwhile, both δ^{13}C and δ^{18}O from CF-IRMS were compared with those from dual inlet IRMS to examine the accuracy of this new technique (Table 1).

As for ice core analysis, the system blank includes the Schütze blank and ice blank. The former is 60 pmol for 10 min collection time. The latter is determined by tests base on artificial bubble free ice from LGGE, France (Table 4). High ice blank of 140 pmol CO was found resulting from CO adsorption on the ice surface, which decreased significantly after the ice was flushed with zero air for a few times to a level of 20 pmol CO. The ice blank was subjected to light tests as well. Sample environment with or without light exposure were compared. The isotope composition (δ^{13}C=−15‰) of the ice blank and the slight difference of blank signal between light and dark environment (Table 4) indicates the ice blank is from air diffusion/adsorption not in situ photochemical production.

2.3 Ice core introduction

South Pole ice core samples provided by National Ice Core Lab (NICL) were dry drilled in 2004 by Jihong Cole-Dai. They contain very low contamination since no fluid was used for drilling. The ice core samples are semi cylindrical with average length of 17 cm and radius of 5 cm. The ice core samples were first trimmed with a band saw to remove several mm of surface, and then scraped with a stainless steel disposable scalpel to remove additional 1–2 mm of surface. Prior to use, the container was cleaned with

acetone and rinsed with deionized water, then heated overnight at 90°C. The ice core sample was weighted and sealed in the container and immersed in cooling bath held at −20°C. The ice and the container were repeatedly evacuated and flushed with zero air for 30 min. After final pumping, the ice was melted in hot water bath held at temperature of 60–70°C. The occluded air extracted from the ice was then processed through the cryogenic extraction line and followed CF-IRMS.

3 Results and discussion

3.1 Calibration gas test

Experiments were performed to check the reliability and precision of stable C and O isotope data using a calibration gas of known concentration and isotopic composition (130 ppbv; $\delta^{13}C=-45.56‰$ VPDB; $\delta^{18}O=-1.94‰$ VSMOW). Concentration and $\delta^{13}C$ and $\delta^{18}O$ values were determined by using whole air extraction of several hundred liters of air for [14]CO analysis (Mak et al., 1994) followed by dual-inlet microvolume analysis with the Delta Plus IRMS (Mak et al., 1994). The $\delta^{18}O$ of Schütze reagent is derived with the $\delta^{18}O$ of CO for the calibration gas and the $\delta^{18}O$ of the produced CO_2 in cryogenic vacuum extraction system. As shown in Fig. 2, the mean value of $\delta^{13}C(CO)$ is −45.40‰ (VPDB) with a standard deviation of 0.33‰ ($\pm1\sigma$), for 47 runs of the measurements with CO amount ranging from 232 pmol to 4 nmol, and the mean value of $\delta^{18}O(CO_2)$ is 0.42‰ (VSMOW) with a standard deviation of 0.32‰ ($\pm1\sigma$). This $\delta^{18}O(CO_2)$ value was used for determining the $\delta^{18}O$ of the Schütze reagent and $\delta^{18}O(CO)$ for samples based on the following equation:

$$\delta^{18}O(‰, \text{VSMOW})_{\text{sample}} = 2\delta^{18}O_{CO_2} - \left(2\delta^{18}O_{\text{Cal } CO_2} - \delta^{18}O_{\text{Cal CO}}\right) \tag{1}$$

where $\delta^{18}O_{CO_2}$ is the isotopic signature of the CO-derived CO_2 with one of the oxygen atoms from the Schütze reagent, $\delta^{18}O_{\text{Cal } CO_2}$ is the average value obtained from the

A new CF-IRMS system for the quantification of the stable isotopes

Z. Wang and J. E. Mak

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

calibration runs (0.42‰), and $\delta^{18}O_{Cal\ CO}$ is the isotopic signature of the CO calibration runs (−1.94‰, VSMOW), which was determined based on conventional dual inlet micro-volume analysis method (Brenninkmeijer et al., 1993; Mak and Brenninkmeijer, 1998).

3.2 Field sample measurement

The accuracy and reproducibility of the above analysis method was also tested in processing field samples. Air samples collected from two sites: the Mauna Loa Observatory and Westmann Islands, Iceland, with the whole volume on the order of 600 L (STP) were collected into high pressure aluminum air cylinders using a previously published protocol (Mak and Brenninkmeijer, 1998). These field samples were first processed with off-line extraction and analyzed with conventional dual inlet-microvolume method. Aliquot of remaining samples were then processed with the new on-line analysis. Measurements based on the on-line extraction CF-IRMS are compared with the off-line results (Table 1). The 0.2‰ standard deviation for $\delta^{13}C$ and 0.6‰ standard deviation for $\delta^{18}O$ obtained from the new on-line analysis method for these field samples indicate reliable reproducibility. Moreover, no significant difference for $\delta^{13}C$ or $\delta^{18}O$ is found between the off-line dual inlet microvolume analysis and the on-line extraction CF-IRMS analysis, implying the reliable accuracy of the new on-line method.

3.3 South Pole ice core measurement

As described in the methodology section, six South Pole ice core samples (∼1 kg for each sample, with depth ranging from 133 to 177 m) were processed with this on-line technique. Results including both CO mixing ratios and isotope ratios were shown in the following table (Table 2). All these CO mixing ratio and isotope data are raw data and have not been calibrated for gravitational fractionation. The consistency of CO mixing ratio and isotope ratios between the duplicate South Pole ice core samples (165 m) indicate the above analytical technique produces consistent results for ice core

samples with CO amount as low as 223 pmol.

4 Conclusions

A new simultaneous analysis technique for stable isotope ratios (δ^{13}C and δ^{18}O) of atmospheric carbon monoxide (CO) from small air samples has been presented. This new technique produces reliable and precise mixing ratio, δ^{13}C and δ^{18}O values for atmospheric CO with sample size as small as 220 pmol, making it especially useful in analyzing air samples with very limited amount, such as measuring stable isotopes for atmospheric CO trapped in ice core. Six South Pole ice core samples were measured for CO mixing ratio, δ^{13}C(CO) and δ^{18}O(CO) based on this new on-line technique. This is the first report on measuring ice core samples for CO isotopes.

References

Bergamaschi, P., Hein, R., Brenninkmeijer, C. A. M., and Crutzen, P. J.: Inverse modeling of the global CO cycle 2. Inversion of C-13/C-12 and O-18/O-16 isotope ratios, J. Geophys. Res.-Atmos., 105, 1929–1945, 2000a.

Bergamaschi, P., Hein, R., Heimann, M., and Crutzen, P. J.: Inverse modeling of the global CO cycle 1. Inversion of CO mixing ratios, J. Geophys. Res.-Atmos., 105, 1909–1927, 2000b.

Brenninkmeijer, C. A. M.: Measurement of the abundance of ^{14}CO in the atmosphere and the ^{13}C/^{12}C and ^{18}O/^{16}O ratio of atmospheric CO with applications in New Zealand and Antarctica, J. Geophys. Res., 98, 10595–10614, 1993.

Haan, D., Martinerie, P., and Raynaud, D.: Ice core data of atmospheric carbon monoxide over Antarctica and Greenland during the last 200 years, Geophys. Res. Lett., 23, 2235–2238, 1996.

Haan, D. and Raynaud, D.: Ice core record of CO variations during the last two millennia: atmospheric implications and chemical interactions within the Greenland ice, Tellus, 50B, 253–262, 1998.

Lowe, D. C., Brenninkmeijer, C. A. M., Tyler, S. C., and Dlugkencky, E. J.: Determination of the isotopic composition of atmospheric methane and its application in the Antarctic, J. Geophys. Res.-Atmos., 96, 15455–15467, 1991.

Mak, J. E. and Brenninkmeijer, C. A. M.: Compressed-air sample technology for isotopic analysis of atmospheric carbon-monoxide, J. Atmos. Ocean. Tech., 11, 425–431, 1994.

Mak, J. E., Brenninkmeijer, C. A. M., and Tamaresis, J.: Atmospheric (Co)-C-14 observations and their use for estimating carbon-monoxide removal rates, J. Geophys. Res.-Atmos., 99, 22915–22922, 1994.

Mak, J. E. and Brenninkmeijer, C. A. M.: Measurement of ^{13}CO and C^{18}O in the free troposphere, J. Geophys. Res., 103, 19347–19358, 1998.

Mak, J. E. and Yang, W.: Technique for analysis of air samples for ^{13}C and ^{18}O in carbon monoxide via continuous-flow isotope ratio mass spectrometry, Anal. Chem., 70, 5159–5161, 1998.

Merritt, D. A., Hayes, J. M., and Marias, D. J. D.: Carbon isotopic analysis of atmospheric methane by isotope-ratio-monitoring gas-chromatography mass-spectrometry, J. Geophys. Res.-Atmos., 100, 1317–1326, 1995.

Rice, A. L., Gotoh, A. A., Ajie, H. O., and Tyler, S. C.: High-precision continuous-flow measurement of delta C-13 and delta D of atmospheric CH$_4$, Anal. Chem., 73, 4104–4110, 2001.

Rockmann, T., Kaiser, J., Brenninkmeijer, C. A. M., and Brand, W. A.: Gas chromatography/isotope-ratio mass spectrometry method for high-precision position-dependent N-15 and O-18 measurements of atmospheric nitrous oxide, Rapid Commun. Mass Sp., 17, 1897–1908, 2003.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Rudolph, J., Lowe, D. C., Martin, R. J., and Clarkson, T. S.: A novel method for compound specific determination of delta C-13 in volatile organic compounds at ppt levels in ambient air, Geophys. Res. Lett., 24, 659–662, 1997.

Santrock, J., Studley, S. A., and Hayes, J. M.: Isotopic analyses based on the mass spectrum of carbon dioxide, Anal. Chem., 57, 1444–1448, 1985.

Schütze, M.: Ein neues Oxidationsmittel für die quantitative Überführung von Kohlenmonoxyd in Kohlendioxyd. Ein Beitrag zur Chemie des Jodpentoxids, Ber. Dtsch. Chem. Ges., 77b, 484–487, 1949.

Smiley, W. G.: Note on a reagent for oxidation of carbon monoxide, Nucl. Sci. Abstr., 3, p. 391, 1949.

Tsunogai, U., Nakagawa, F., Komatsu, D. D., and Gamo, T.: Stable carbon and oxygen isotopic analysis of atmospheric carbon monoxide using continuous-flow isotope ratio MS by isotope ratio monitoring of CO, Anal. Chem., 74, 5659–5700, 2002.

A new CF-IRMS system for the quantification of the stable isotopes

Z. Wang and J. E. Mak

A new CF-IRMS system for the quantification of the stable isotopes

Z. Wang and J. E. Mak

Table 1. Comparison of δ^{13}C and δ^{18}O results of field CO samples obtained by dual inlet microvolume analysis and on-line extraction CF-IRMS.

Sample ID	Collection date	CO mixing ratio (ppbv)	Dual inlet microvolume analysis						On-line extraction CF-IRMS				
			δ^{13}C (‰, VPDB)	SD[a]	δ^{18}O (‰, VSMOW)	SD[a]	Sample volume (L, STP)		δ^{13}C (‰, VPDB)	SD	δ^{18}O (‰, VSMOW)	SD	Sample volume (mL, STP)
315MLCO (12)[b]	28-Aug-07	61	−30.996	0.021	−1.27	0.043	286		−30.80	0.17	−1.33	0.61	100
393ICE(5)	24-Jan-07	126	−27.188	0.019	8.74	0.125	658		−27.45	0.28	8.49	0.20	100
394ICE(7)	31-Jan-07	128	−27.245	0.028	8.25	0.04	678		−27.36	0.24	8.35	0.38	100
396ICE(4)	17-Jan-07	137	−27.627	0.034	9.16	0.097	662		−27.84	0.19	9.39	0.36	100
397ICE(4)	07-Feb-07	134	−27.577	0.086	8.19	0.194	602		−27.71	0.10	8.32	0.21	100
398ICE(5)	28-Feb-07	139	−26.928	0.034	9.64	0.064	674		−27.15	0.28	9.43	0.38	100

Note: [a] this standard deviation for dual inlet is analytical error for mass spectrometric analysis only, and no sample preparation error is taken into account; [b] the number in parentheses next to sample ID is the number of analyses by on-line extraction CF-IRMS.

Table 2. On-line extraction CF-IRMS measurements for South Pole ice core CO.

Sample ID	CO mixing ratio (ppbv)	SD (ppbv)	$\delta^{13}C$ (‰, VPDB)	SD (‰)	$\delta^{18}O$ (‰, VSMOW)	SD (‰)
135	57	4.8	−28.83	0.3	−1.79	0.7
147	39	4.8	−29.40	0.3	−1.89	0.7
157	37	4.8	−29.15	0.3	−1.02	0.7
165T[a]	42	4.8	−28.47	0.3	−0.49	0.7
165B[b]	46	4.8	−28.95	0.3	−0.96	0.7
177	57	4.8	−27.40	0.3	1.43	0.7

Note: [a] 165 m top; [b] 165 m bottom. Standard deviation is based on the results from calibration runs with bubble free ice processed the same way as that for real ice core samples.

Title Page

Abstract   Introduction

Conclusions   References

Tables   Figures

◄◄   ►►

◄   ►

Back   Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A new CF-IRMS system for the quantification of the stable isotopes

Z. Wang and J. E. Mak

Table 3. Schütze blank of the cryogenic system tested with zero air.

Date	Sample volume (mL)	Collection time (min)	CO blank (pmol)	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)
30.7.2008	100	2	38	−14.8	33.7
30.7.2008	100	2	38	−15.4	33.0
30.7.2008	250	5	49	−15.6	33.0
30.7.2008	500	10	68	−15.2	34.2
30.7.2008	750	15	89	−15.3	33.9
30.7.2008	1500	30	145	−15.0	33.8
14.5.2009	100	2	39	−15.2	33.1
20.5.2009	100	2	39	−15.0	33.1
21.5.2009	100	2	38	−15.3	33.6
22.5.2009	100	2	37	−15.4	33.0
10.6.2009	100	2	40	−14.9	33.6
13.6.2009	100	2	34	−15.2	33.9
14.6.2009	100	2	32	−15.6	33.8
15.6.2009	100	2	39	−14.7	33.4

A new CF-IRMS system for the quantification of the stable isotopes

Z. Wang and J. E. Mak

Table 4. Ice blanks tested with calibration gas and artificial bubble free ice from LGGE, France.

Artificial ice type	Weight (g)	CO blank (pmol)	$\delta^{13}C$ (‰, VPDB)	$\delta^{18}O$ (‰, VSMOW)
Polycrystalline ice	256	22	−15.8	33.2
Polycrystalline ice	385	31	−15.6	33.3
Monocrystalline ice	200	9	−14.9	33.7
Monocrystalline ice[a]	275	22	−15.2	32.3
Monocrystalline ice	150	31	−15.2	33.4
Monocrystalline ice	347	18	−15.9	33.3

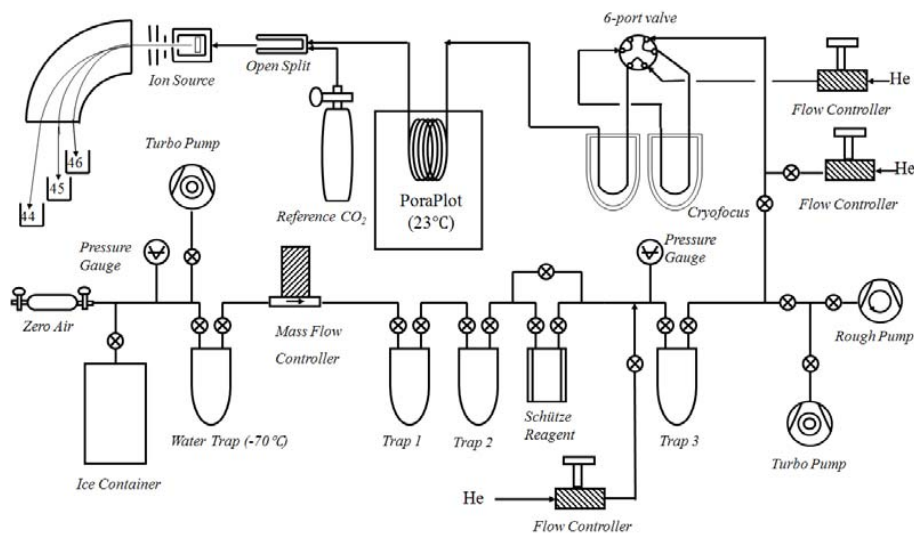Note: [a] Dark test: glass container was wrapped with aluminum foil during the experiment.

Fig. 1. A schematic diagram of the system used for mixing ratio, $\delta^{13}C$ and $\delta^{18}O$ analysis of atmospheric CO and ice core CO. See details in the text.
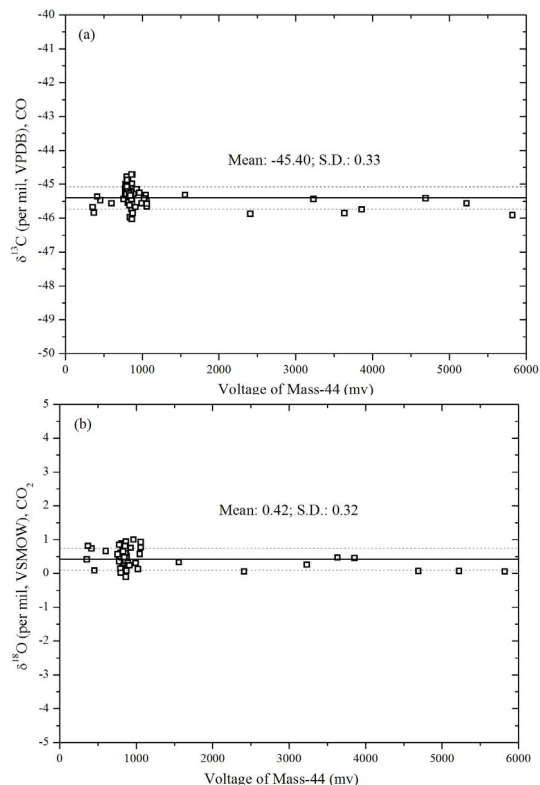
Fig. 2. Measurements of **(a)** δ^{13}C and **(b)** δ^{18}O for calibration gas versus voltage mass-44 ranging from 400 mv to 6 V. Mean value of δ^{13}C(CO): −45.40‰ (with standard deviation 0.33‰); mean value of δ^{18}O(CO$_2$): 0.42‰ (with standard deviation 0.32‰). Sample size is linear with voltage of mass-44 and 700 pmol CO gives 1 V for the signal of voltage mass-44.