Influence of CO_2 adsorption on cylinders and fractionation of CO_2 and air during preparation of a standard mixture

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Abstract: We conducted a study to evaluate carbon dioxide (CO_2) adsorption on a cylinder's internal surface and fractionation of CO_2 and air during the preparation of standard mixtures of atmospheric CO_2 levels through a multistep dilution. It became clear that the CO_2 molar fractions in standard mixtures prepared by diluting pure CO_2 with air three times deviated by -0.207 ± 0.060 μmol mol^{-1} on average from the gravimetric values. It indicates that the deviation is larger than a compatibility goal of 0.1 μmol mol^{-1}, which has been recommended by the World Meteorological Organization (WMO). The deviation was consistent with those calculated from two fractionation factors of 0.99968 ± 0.00010 and 0.99975 ± 0.00004; one was estimated by mother–daughter transfer experiment that transfer CO_2/air mixtures from a cylinder to another evacuated receiving cylinder and another was computed by applying the Rayleigh model to the increase in CO_2 molar fractions in a source gas as its pressure depleted from 11.5 MPa to 1.1 MPa. Both fractionation factors also agree within their uncertainties. Additionally, the mother–daughter transfer experiments shows that the deviation is caused by the fractionation of CO_2 and air in the process of transferring a source gas (a CO_2/air mixture with a higher CO_2 molar fraction than that in the prepared gas mixture). The fact that the CO_2 fractionation effect was less significant when the transfer speed decreased less than 3 L min^{-1} suggested that the main factor of the fractionation could be thermal diffusion. Experiments were conducted that a CO2 in air mixture (CO_2/Air mixture) was emitted from a cylinder to evaluate the CO_2 adsorption to the internal surface of the cylinder. When the cylinder pressure was reduced

from 11.0 to 0.1 MPa, the CO_2 molar fractions in the mixture stream exiting the cylinder increased by 0.16 ± 0.04 μmol mol^{-1}. By applying the Langmuir adsorption-desorption model to the measured data, the amount of CO_2 adsorbed on the internal surfaces of a 10 L aluminum cylinder when preparing a standard mixture with atmospheric CO_2 level was estimated to be 0.027 ± 0.004 μmol mol^{-1} at 11.0 MPa.

Keywords: standard mixture, atmospheric CO_2, gravimetric method, fractionation

1 Introduction

Carbon dioxide (CO_2) is an important greenhouse gas that contributes significantly to the radiative forcing of the atmosphere. Numerous laboratories conduct systematic measurements of atmospheric CO_2 to better understand its sources and sinks. The measurements are typically performed using analyzers calibrated by working standards traceable to the CO_2 scale of the World Meteorological Organization (WMO). The WMO has recommended a compatibility goal of 0.1 μmol mol^{-1} for CO_2 measurements based on the WMO CO_2 scale in the Northern Hemisphere (WMO, 2019) to address small and globally significant gradients over large spatial scales. The WMO CO_2 scale has been determined only by standard gas mixtures prepared using manometry. It is necessary to validate by standard mixtures prepared using other method such as gravimetry to make the scale more robust. However, the scale of standard mixtures prepared by gravimetry are not consistent among respective laboratories (Tsuboi et al., 2017, Flores et al., 2019), preventing the WMO CO_2 scale to precisely validate.

Recently, several studies have shown that CO_2 adsorbed on the internal surface of a high-pressure cylinder and desorbed from the surface, as the internal pressure decreases (Langenfelds et al., 2005, Leuenberger et al., 2015, Brewer et al., 2018, Schibig et al., 2018, Hall et al., 2019). These studies also provided a method to determine the amount of CO_2 adsorbed on the internal surface of a cylinder using a "decanting" experiment to continuously measure the CO_2 molar fraction in a CO_2 in air mixture (CO_2/air mixture) exiting a cylinder. For example, Leuenberger et al. (2015) estimated the amount of CO_2, expressed as a fraction of the total gas in a cylinder, to be 0.028 μmol mol^{-1} at 6 MPa by applying the Langmuir model (Langmuir, 1918) to the results as 30 L aluminum cylinders were emptied from 6.0 MPa to 0.1 MPa. Schibig

et al (2018) also estimated the amount of CO_2 to be 0.0165 ± 0.0016 μmol mol^{-1} at 15.0 MPa as 29.5 L aluminum cylinders were emptied from 15.0 MPa to 0.1 MPa. These values cause a small bias in the gravimetrically assigned CO_2 molar fraction in standard mixtures. However, Miller et al. (2015) conducted a series of "mother−daughter" experiments in which they transferred half of a CO_2/air mixture from a "mother" cylinder into an evacuated "daughter" cylinder. They reported that CO_2 molar fractions in the mother cylinders were 0.02%−0.03% higher than those in the daughter cylinders. The values were greater than the amounts of adsorbed CO_2 estimated by the decanting experiments. According to Hall et al. (2019), CO_2 molar fractions in the mother and daughter cylinders after the mother−daughter experiment were 0.06 μmol mol^{-1} higher and 0.10 μmol mol^{-1}−0.13 μmol mol^{-1} lower, respectively, than CO_2 molar fractions in the mother cylinders before the transfer. The increasing and decreasing amounts were 5 to 10 times larger than the adsorbed amount estimated from their decanting experiments. They proposed that the detected CO_2 change was due to thermal fractionation rather than adsorption of CO_2 on the internal surface of a cylinder. Langenfelds et al. (2005) also assumed diffusive fractionation due to pressure diffusion, thermal diffusion, and effusion were factors that changed CO_2 molar fraction observed in CO_2/air mixtures due to gas handling. If the CO_2 changes in the transfer are caused by a kinetic process such as the diffusive fractionation, the fractionation factor is considered to be constant regardless of the CO_2 molar fraction. In gravimetry, standard mixtures with atmospheric CO_2 levels are typically prepared through a multistep dilution, which involves diluting pure CO_2 with air two or three times. Each step of dilution is accomplished by transferring a source gas from a "mother" cylinder into an evacuated "daughter" cylinder and pressurizing it with dilution gas air. The fractionation of CO_2 and air (nitrogen, oxygen, argon, and trace impurities other than CO_2) is likely to occur in the second and third step dilutions because a CO_2/air mixture with a higher CO_2 molar fraction than that in the prepared standard mixture is used as the source gas. The fractionation process decreases the CO_2 molar fraction in the source gas transferred into the daughter cylinder which causes an increase in the CO_2 molar fraction in the remaining source gas in the mother cylinder because of its consumption. This could be a factor that deteriorates the reproducibility of the assigned CO_2 molar fractions because CO_2 molar fractions in the prepared standard mixtures are biased by the decrease and increase in

CO_2 in the transferred gas mixture and the remaining pre-mixture, respectively. To avoid fractionation in each step dilution, one method is to gravimetrically prepare standard mixtures by one-step dilution to mix pure CO_2 and air directly, as there is no process to transfer a CO_2/air mixture into another cylinder (Hall et al., 2019). Tohjima et al. (2005) developed a technique to gravimetrically prepare standard mixtures by one-step dilution. However, they did not discuss fractionation and adsorption that occurs during the multistep dilution process.

To accurately determine the CO_2 molar fraction, we must understand the adsorption and fractionation effects on the preparation process of standard mixtures with atmospheric CO_2 levels. Therefore, this study evaluated the systematic error of CO_2 molar fraction in the standard mixtures prepared by multistep dilution and the contribution of its factors. CO_2 adsorption and fractionation are assumed to depend on the type and size of a cylinder (Leuenberger et al, 2015). The evaluation was performed using 10 L aluminum cylinders which are often used for preparation of gravimetric standard mixtures because previous studies only evaluated CO_2 adsorption and CO_2 and air fractionation in 29.5 L aluminum and 50 L steel cylinders. Based on decanting experiments, we evaluated the amount of CO_2 adsorbed on the internal surface of a 10 L aluminum cylinder. The fractionation of CO_2 and air in the transfer of CO_2/air mixtures were then evaluated in detail based on mother–daughter experiments using the cylinders, and the fractionation factor in the transfer of a source gas was estimated on the basis of the results. Finally, we demonstrated that standard mixtures gravimetrically prepared by three-step dilutions had a systematic error of CO_2 molar fractions by comparing them with the standard mixtures prepared by one-step dilution.

2 Methods

2.1 Decanting and mother–daughter experiments

We conducted decanting and mother−daughter experiments to estimate CO_2 adsorption on the internal surface of a cylinder, and the fractionation of CO_2 and air during the transfer of a CO_2/air mixture into an evacuated cylinder.

The decanting experiments were performed using 10 L aluminum cylinders (Luxfer Gas Cylinders, UK) with a brass diaphragm valve (G-55, Hamai Industries Limited, Japan). The cylinders were evacuated to ~10^{-4} Pa using a turbo molecular pump and pressurized to 11.0 MPa by CO_2/air mixtures with CO_2 molar fractions ranging from 350 μmol mol^{-1} to 450 μmol mol^{-1}. The CO_2/air mixtures were decanted using single stage regulators (Torr 1300, NISSAN TANAKA Co., Japan) attached to the cylinders from 11.0 MPa to 0.1 MPa at total flow rates of 80 ml min^{-1}, 150 ml min^{-1}, and 300 ml min^{-1}. After flowing through the regulator, the mixture flow was branched in two ways by T-pieces. The branched flows were controlled by two mass flow controllers (SEC-Z512MGX 100 SCCM, and 1SLM, Horiba STEC Co., Ltd., Japan); one was introduced as sample gas into a Picarro G2301 (Picarro, Inc., USA) at a flow rate of 80 ml min^{-1}, and the other was exhausted to the surroundings at rates of 0 ml min^{-1}, 70 ml min^{-1}, and 220 ml min^{-1}. An absolute pressure gauge of flush diaphragm type (PPA-33X, KELLER AG, Switzerland) attached to the regulator was used to measure the pressures in the cylinders. The Picarro G2301 output was linearly calibrated using one standard mixture containing atmospheric CO_2 levels with a standard uncertainty of less than 0.1 μmol mol^{-1} as the signal was assumed to be zero when the CO_2 molar fraction was zero. After calibrating the Picarro G2301 for 20 min, the process of measuring CO_2 in the decanting flow for 100 min was repeated. The decanting flow was stopped while the Picarro G2301 was calibrated using the standard mixture.

The mother−daughter experiment was performed using 10 L or 48 L aluminum cylinders (Luxfer Gas Cylinders, UK) with a brass diaphragm valve. These cylinders were filled with CO_2/air mixtures with CO_2 molar fractions ranging from 380 μmol mol^{-1} to 460 μmol mol^{-1} and 3.2 MPa to 13.9 MPa; some of these mixtures were purchased from a gas supplier (Japan Fine Products, Japan), while others were prepared at our laboratory. The CO_2/air mixtures were prepared using pure CO_2 and purified air which was removed CO_2, CH_4, CO, H_2O etc. from ambient air. In this experiment, the cylinders containing the mixtures were referred to as the mother cylinder, while the receiving cylinders into which the mixture was transferred were referred to as the daughter cylinder. The mixtures in the mother cylinders with vertical or horizontal placements were transferred into the evacuated daughter cylinder with vertical placement through a

manifold made of a 1/4-inch o.d. stainless steel line, diaphragm valves (FUDDF-716G, Fujikin Incorporated, Japan) and the absolute pressure gauge as shown in Fig. 1a. The sheet, diaphragm, and body of the valve were made from Polychlorotrifluoroethylene (PCTFE), nickel-cobalt alloy, and stainless steel, respectively. The mother and daughter cylinders were connected and then the manifold was evacuated to ~10^{-4} Pa by a turbo molecular pump after all diaphragm valves opened (A1−A4 or a1−a6). The valve of the mother cylinder opened after the valves of A3 or a3 closed, and then the mixture was expanded from the mother cylinder to the daughter cylinder by opening the valve of the daughter cylinder. The transfer speed was controlled by degree of opening the diaphragm valve of the daughter cylinders and calculated roughly from the transfer time and volume. The valves of the mother and daughter cylinders closed immediately after the transfer volume reached the desired level which was confirmed by monitoring the weight of the daughter cylinder using a balance of load cell type (BW22KH, SHIMADZU Corporation, Japan) as shown in Fig. 1a. The transfer time and the pressure of the daughter cylinders were measured using a clock of PC and the absolute pressure gauge, respectively. The transfer volume was computed using the inner volume and the pressure of the daughter cylinder. Molar fractions of CO_2 in the mother cylinders were measured using the Picarro G2301 before starting each experiment, and after each experiment, those in the mother and daughter cylinders were measured several hours to half a day after the mixtures were transferred. The Picarro G2301 was calibrated using standard mixtures with atmospheric CO_2 levels before and after each transfer experiment. We also measured $\delta(^{29}N_2/^{28}N_2)$, $\delta(^{34}O_2/^{32}O_2)$, $\delta(^{32}O_2/^{28}N_2)$, $\delta(^{40}Ar/^{28}N_2)$, and $\delta(^{40}Ar/^{36}Ar)$ in the mother and daughter cylinders using a mass spectrometer (Delta-V, Thermo Fisher Scientific Inc., USA) to clarify the mechanism(s) of diffusive fractionation during the mother−daughter experiment based on relationships between the measured elemental and isotopic ratios (e.g., Langenfelds et al., 2003; Ishidoya et al., 2013). The measurement details of the technique were provided in Ishidoya and Murayama (2014). The value of $\delta(CO_2/N_2)$ was calculated using the ratio of CO_2/N_2 obtained from Eq. (1) assuming that minor components except CO_2 can be ignored (N_2+O_2+Ar+ CO_2=1).

$$CO_2/N_2 = \frac{CO_2}{N_2} \times \frac{1-CO_2}{1-CO_2} = \frac{CO_2}{N_2} \times \frac{N_2+O_2+\mathrm{Ar}}{1-CO_2} = \frac{CO_2}{1-CO_2} \times \left(1 + \frac{O_2}{N_2} + \frac{Ar}{N_2}\right). \quad (1)$$

Where CO_2 molar fractions measured using Picarro G2301 were used as values of CO_2. The ratios of O_2/N_2 and Ar/N_2 were computed using values measured using the mass spectrometer (Aoki et al., 2019).

2.2 Preparation of standard mixtures

2.2.1 Starting Materials for preparation

Standard mixtures were gravimetrically prepared using the one-step and the three-step dilution in accordance with ISO 6142-1:2015. Pure CO_2 (>99.998 %, Nippon Ekitan Corp., Japan) and purified air (G1-grade, Japan Fine Products, Japan) were used as a source gas. The purity of pure CO_2 and N_2 molar fraction in the air was determined using a subtraction method in which the sum of molar fractions of impurities was subtracted from 1 (ISO 19229:2015). Impurities in the source gases were identified and quantified using gas chromatography (GC). A GC with a thermal conductivity detector (TCD) was used to analyze N_2, O_2, CH_4, and H_2 in pure CO_2. Ar in the air was analyzed using GC-TCD with an oxygen absorber. A paramagnetic oxygen analyzer was used to quantify O_2 in the air. A Fourier-transform infrared spectrometer was used to detect trace amounts of CO_2, CH_4, and CO in the air. A capacitance type moisture sensor was used to measure H_2O in pure CO_2, and a cavity ring-down moisture analyzer was used to measure H_2O in the air.

2.2.2 Balances and weighing sequence

A 0.8-L aluminum cylinder and a 10-L aluminum cylinder were used for preparing standard mixtures with atmospheric CO_2 levels using a one-step dilution, while a 10-L cylinder was used for preparing a three-step dilution. The two types of cylinders were weighed using two different balances (mass comparators). One is AX2005 (Mettler Toledo, Switzerland) used for weighing the 0.8-L cylinder, of which resolution and maximum load are 0.01 mg and 2 kg, respectively. Another is the XP26003L (Mettler Toledo, Switzerland) used for weighing the 10-L cylinder, of which the resolution and maximum load are 1 mg and 26 kg (Matsumoto et al., 2004, Aoki et al., 2019), respectively. The mass measurement of each cylinder, which was performed in a weighing room controlled at temperature and humidity 26ºC ± 0.5ºC and 48 % ± 1 %,

respectively, was conducted with respect to a nearly identical reference cylinder to reduce any influence exerted by zero-point drifts, sensitivity issues associated with the mass comparator, changes in buoyancy acting on the cylinder, or adsorption effects on the cylinder's surface because of the presence of water vapor (Alink et al., 2000; Milton et al., 2011). This was performed based on several consecutive weighing operations in the ABBA order sequence, where "A" and "B" denote the reference and sample, respectively. The process of loading and unloading the cylinders was automated, and one complete cycle of the ABBA sequence took five minutes. The mass difference, which was calculated by subtracting the reference cylinder from the sample cylinder readings, provided the mass reading recorded from the weighing system. Aoki et al. (2019) reported that the mass reading deviates in relation to temperature differences between the sample and the surrounding air. In this study, the mass measurement was performed at the sample and the surrounding areas at the same temperature to reduce the deviation.

2.2.3 Preparation process by one-step dilution

Standard mixtures were gravimetrically prepared by mixing pure CO_2 and air using stainless steel manifolds (Fig 1b and Fig 1c) in the process shown in Fig. 2a. The pure CO_2 cylinder and the 0.8-L aluminum cylinder were connected at the position of valve 2 (V2) and valve 5 (V5) to the stainless-steel manifold (Fig. 1b) the internal surface of which was electropolished. The 0.8-L aluminum cylinder was evacuated to ~ 5.0×10^{-5} Pa via the manifold by opening V2, V4, V5, and V6. The pure CO_2 was added to the 0.8-L aluminum cylinder after closing V4. Furthermore, we connected the 0.8-L cylinder and the evacuated 10-L cylinder at the position of V8, and then evacuated the manifold to ~ 5.0×10^{-5} Pa by opening V4, V7, and V8. The movement of the 0.8-L cylinder was made to reduce the dead volume when the pure CO_2 was transferred to 10-L cylinder. The valves of the 0.8-L and 10-L cylinders were opened after closing V8, allowing the pure CO_2 to expand into the 10-L cylinder. Both cylinder valves were closed, and then the remaining CO_2 in the manifold was moved into the 10-L cylinder by alternating the pressurization−expansion operation that pressurizes the manifold to ~1.5 MPa with air and open the valve of the 10-L cylinder. The 10-L cylinder was connected to other manifold shown in Fig. 1c after the CO_2 was completely transferred into

the cylinder by repeating this pressurization expansion process 300 times. The manifold was evacuated to ~ 1.5×10^{-4} Pa and then the cylinder was further pressurized to ~10.0 MPa with air using the manifold. The CO_2 mass filled into the 10-L cylinder was determined by weighing the 0.8-L cylinder before and after pure CO_2 was transferred, whereas the mass of air was calculated by subtracting the CO_2 mass from the difference in the 10-L cylinder mass before and after transferring pure CO_2 and air into the 10-L cylinder.

2.2.4 Preparation process by three-step dilution

Fig. 2b shows that the standard mixtures were gravimetrically prepared into the 10-L cylinders by diluting pure CO_2 with air three times in the process by using the manifold shown in Fig. 1c. The preparation technique detail was provided in Matsumoto et al. (2004 and 2008) and Aoki et al. (2019). In the first step dilution, a gas mixture with a CO_2 molar fraction of 65000 μmol mol^{-1}, referred to as a 1st gas mixture, was prepared from pure CO_2 and air. The pure CO_2 was transferred into the 10-L cylinder evacuated to 1.5×10^{-4} Pa, which was then pressurized to 10.0 MPa with air using the manifold shown in Fig. 1c. The masses of pure CO_2 and air were approximately 110 and 1100 g, respectively. In the second step, a gas mixture with a CO_2 molar fraction of 5000 μmol mol^{-1}, referred to as a 2nd gas mixture, was prepared from the 1st gas mixture and air. The 1st gas mixture was transferred into the 10-L cylinder evacuated to 1.5×10^{-4} Pa, which was then pressurized to 10.0 MPa by air. The masses of the 1st gas mixture and air were approximately 100 and 1200 g, respectively. In the third step, a gas mixture with atmospheric CO_2 level, referred to as a 3rd gas mixture, was gravimetrically prepared from the 2nd gas mixture and air. The 2nd gas mixture was transferred into the 10-L cylinder evacuated to 1.5×10^{-4} Pa, which was then pressurized to 10.0 MPa with air. The masses of the 2nd gas mixture and air were approximately 100 and 1200 g, respectively. The mass of pure CO_2, CO_2/air mixture, and air used as source gases was determined by weighing the cylinder before and after filling each source gas.

2.2.5 Analysis of standard mixtures

The gravimetrically prepared standard mixtures (3rd gas mixtures) were measured using the Picarro G2301 equipped with a multiport valve (Valco Instruments Co. Inc., USA) for gas introduction and a mass flow controller (SEC-N112, 100SCCM, Horiba STEC, CO., Ltd, Japan). The output of the Picarro G2301 was calibrated using standard mixtures prepared by the one-step dilution. CO_2 molar fractions in the 3rd gas mixtures were calculated from the calibration line obtained by applying the Deming least-square fit to the measured data. In the calibration, two series of standard mixtures were used. One series was composed of four standard mixtures with the range from 390 μmol mol^{-1} to 430 μmol mol^{-1} and another series was composed of five standard mixtures from 390 μmol mol^{-1}to 420 μmol mol^{-1}.

3 Result and discussion

3.1 Adsorption and fractionation of CO_2/air mixtures

As described in the introduction, the adsorption of CO_2 on a cylinder's internal surface causes a small bias on the gravimetrically assigned CO_2 molar fraction. Furthermore, the transfer of CO_2/air mixture changed CO_2 molar fractions by about 0.10 μmol mol^{-1}. This allows transfer of source gases to have a larger impact on the CO_2 molar fractions than the bias on adsorption process. Therefore, we estimated the amount of CO_2 adsorbed on the internal surface of a 10-L aluminum cylinder, and then fully evaluated the amount of fractionation caused by the transfer of CO_2/air mixtures used as source gases in the evacuated cylinders.

3.1.1 Amount of CO_2 adsorbed on the internal surface of a cylinder

Previous studies have shown that by applying the Langmuir adsorption-desorption model to the results of decanting experiments, it is possible to determine the amount of CO_2 adsorbed on the internal surface of a cylinder. In this method, the amount of CO_2 adsorbed on the internal surfaces at the initial pressure of the decanting experiment is expressed as a molar fraction. For example, Schibig et al. (2018) performed a decanting experiment, emptying 29.5 L aluminum cylinders at a low flow rate of 300 mL min^{-1} and high flow rate of 5 L min^{-1}, which is estimated to be 0.0165 ± 0.0016 μmol mol^{-1} and 0.043 ± 0.008 μmol mol^{-1}

at 15.0 MPa, respectively. Leuenberger et al. (2015) also performed the decanting experiment, emptying 30 L aluminum cylinders at a low flow rate of 250 mL min^{-1} and high flow rate of 5 L min^{-1}, which is estimated to be 0.028 μmol mol^{-1} at 6.0 MPa and 0.047 μmol mol^{-1} at 9.0 MPa, respectively. The low-flow decanting experiments indicated that less CO_2 was adsorbed on the internal surfaces of cylinders compared to the high-flow decanting experiments. They pointed out that the enrichment of CO_2 molar fraction detected in the high flow decanting experiment was related to thermal diffusion and fractionation in the cylinder. Previous studies showed that a low flow decanting experiment is suitable for evaluating the amount of CO_2 adsorbed on a cylinder internal surface in the case of 29.5 L and 30 L aluminum cylinders (Schibig et al., 2018; Leuenberger et al., 2015). It is not known whether this applies to the experiment using 10-L aluminum cylinders. Therefore, we investigated the optimum flow rate to evaluate the adsorbed amount by measuring CO_2 molar fraction in a gas mixture exiting from the 10-L cylinder at low flow rates of 80 mL min^{-}, 150 mL min^{-}, and 300 mL min^{-1} during the decrease in pressure from 11.0 MPa to 0.1 MPa. The deviations in CO_2 molar fractions from initial values against relative cylinder pressure (P/P_0) at different flow rates are shown in Fig. 3a. Where P is the actual pressure of the cylinder in MPa and P_0 is the initial pressure of the cylinder in MPa before the decanting experiment. The CO_2 in the gas mixture flow increased by 0.16 ± 0.04 μmol mol^{-1} as the cylinder pressure decreased from 11.0 MPa to 0.1 MPa. Unless otherwise noted, the numbers following the symbol ± represent standard deviation. The increase in CO_2 molar fraction is the same as flow rates of 80 mL min^{-1}, 150 mL min^{-1}, and 300 mL min^{-1}, indicating that the contribution of thermal fractionation is negligible at a flow rate of 300 mL min^{-1} or less. The amount adsorbed on the internal surface of the cylinder ($X_{CO_2,ad}$) was calculated using the following equation based on the Langmuir model as derived by Leuenberger et al. (2015) (Fig. 3b).

$$X_{CO_2,meas} = X_{CO_2,ad} \cdot \left(\frac{K \cdot (P - P_0)}{1 + K \cdot P} + (1 + K \cdot P_0) \cdot \ln \left(\frac{P_0 \cdot (1 + K \cdot P)}{P \cdot (1 + K \cdot P_0)} \right) \right) + X_{CO_2,initial} \quad (2)$$

Where $X_{CO_2,ad}$ is expressed as the CO_2 molar fraction multiplied by the occupied adsorption sites at pressure P_0. $X_{CO_2,meas}$ corresponds to the measured molar fraction. $X_{CO_2,initial}$ is the CO_2 molar fraction measured in the cylinder at a pressure P_0. K is the ratio of the adsorption and desorption rate constants, and its unit is MPa^{-1}. $X_{CO_2,ad}$ and K was obtained from the least square fit to the results. These experiments were performed seven times, and the average of $X_{CO_2,ad}$ was 0.027 ± 0.004 μmol mol^{-1}, corresponding to 0.030 mL standard temperature and pressure (STP) or 1.2 micromoles or 7.3×10^{17} molecules. There was no difference among the values of $X_{CO_2,ad}$ in range of CO_2 from 350 to 450 μmol mol^{-1}. The ratio of the adsorption of CO_2 to total CO_2 in the cylinder is 0.008 % ± 0.001 % at a unit of mole. The inner diameter of 0.16 m, length of 0.56 m, and the internal surface area are roughly calculated to be 0.32 m^2. The occupied area of CO_2 adsorbed on the internal surface was estimated to be 0.06 m^2, assuming a molecule diameter of 0.34 nm, corresponding to approximately 20 % of the inner area by a monolayer of adsorbed CO_2 molecules. The CO_2 molar fractions in 3rd gas mixtures gravimetrically determined in the following section were computed considering the adsorbed amount by the third step dilution because the adsorption of CO_2 causes a small bias of CO_2 molar fraction in a cylinder. However, the amount was neglected in the case of the 1st and 2nd gas mixtures. This is because the CO_2 molar fraction is significantly higher than the atmospheric CO_2 level by 10 and 100 times or more. In the Langmuir model, the increase rate of the amount adsorbed on the internal surface with increasing the molar fraction of CO_2 becomes small as that of CO_2 is higher. The adsorbed amount is assumed to be lower than the adsorption ratio of 0.008 % ± 0.001 % in the case of the 1st and 2nd gas mixtures with a high molar fraction of CO_2.

3.1.2 Mother–daughter experiment.

The fractionation of CO_2 and air is expected to result from the diffusive fractionation process based on the three types of diffusion, i.e., pressure diffusion, thermal diffusion, and effusion as described by Langenfelds et al. (2005) and Moore et al. (1962). The pressure diffusion is driven by a pressure gradient. The diffusion caused heavier molecules to be preferentially accumulated in the region of higher pressure. The thermal diffusion is driven by a temperature gradient. Heavier molecules are preferentially accumulated in the

colder region. The effusion is known as Knudsen diffusion. Gas molecules escaping from a pressurized vessel through a tiny orifice are subject to molecule effusion. However, the effusion was negligible in our mother–daughter experiments since this Knudsen diffusion occurs when the size of the orifice is small compared to the mean free path among molecular collisions. On the other hand, the temperature decreases of 2−8 K for the mother cylinders were observed during our mother–daughter experiments. This may allow the fractionation of CO_2 and air by the adsorption process. It is because the fractionation of the adsorption process is assumed to be caused by the increase in the amount of CO_2 adsorbed on the internal surface according to the cooling of the mother cylinder in the transfer of the gas mixture. Leuenberger et al. (2015) identified the temperature dependence in the amount of CO_2 adsorbed on the internal surface of an aluminum cylinder to be in a range from −0.0002 μmol mol^{-1} K^{-1} to −0.0003 μmol mol^{-1} K^{-1}. This corresponded to the decrease in 0.0004 μmol mol^{-1}–0.0024 μmol mol^{-1} for CO_2 molar fractions in the mixtures transferred from the mother cylinder, which is significantly lower than the changes in CO_2 molar fractions in the transfer of CO_2/air mixtures detected by Hall et al. (2019).

Mother–daughter experiments of gas mixtures with atmospheric CO_2 levels were performed in fifteen sets using 48-L and 10-L aluminum cylinders as mother cylinders and 10-L aluminum cylinders as daughter cylinders: three sets were performed with horizontal placement of mother cylinders and twelve sets were with vertical placement. All transfers of the mixtures performed with horizontal placement increased the CO_2 molar fractions in the daughter cylinders from those before the transfer as shown in Fig. 4, while all transfer with vertical placement decreased the CO_2 molar fractions in the daughter cylinders. The CO_2 molar fractions deviated inversely in the transfers from the vertical mother cylinder and the horizontal mother cylinder. The difference in the deviations indicated that the fractionations occurred rather in the mother cylinders than in the transfer line and manifold since the pressure and thermal gradient in the mixtures in transfer line and manifold are determined regardless of the vertical and horizontal placement of mother cylinders. The direction of the pressure gradient does not change even if the placement of the mother cylinder changes the magnitude of the pressure gradient in the mother cylinder. The fact that the deviation of CO_2 molar fraction was opposite suggests that the fractionation of CO_2 and air was caused based on

rather the thermal diffusion than the pressure diffusion. A source gas used for preparation of standard mixtures are generally transfers into a vertical receiving cylinder from a vertical mother cylinder. The experiments for the mother cylinders with vertical placement were conducted at different mother cylinder's pressure, transfer gas amount, and transfer gas speed corresponding to transfer conditions of a source gas, to understand the contributions of the fractionation to CO_2 molar fraction in general preparation process. The mother–daughter experimental results performed with vertical placement are summarized in Table 1. Here, CO_2 molar fractions in the daughter cylinders were corrected by the amount of CO_2 absorbed on the internal surface based on the value of 0.027 ± 0.004 μmol mol^{-1} determined by the decanting experiment. The dependence of CO_2 molar fractions in the daughter cylinders relative to transfer volume, cylinder pressure, and transfer speed is shown in Fig. 4. The closed circles in Fig. 4 represent values in the transfer speed of more than 19 L min^{-1}, whereas open triangles represent values in the transfer speed of less than 3 L min^{-1}. All CO_2 molar fractions in the mixtures transferred into the daughter cylinders decreased from the CO_2 molar fraction before the transfer of the mixtures as shown in Fig. 4. The decrease in CO_2 molar fractions mixtures for the daughter cylinders was 0.122 ± 0.040 μmol mol^{-1} on average at a transfer speed of more than 19 L min^{-1}, whereas the decrease in CO_2 molar fractions for daughter cylinders from initial values became significantly small as 0.036 ± 0.027 μmol mol^{-1} (0.008 % ± 0.006 %) on average when the mixtures were transferred at an extremely slow transfer speed of less than 3 L min^{-1}. The decreased values at the transfer speed of more than 19 L min^{-1} agreed with previous values of 0.10 and 0.13 μmol mol^{-1} reported by Hall et al. (2019), who reported that the decrease could be related to thermal diffusion. Correspondingly, the remaining mixtures in all vertical mother cylinders provided higher CO_2 molar fractions than before the transfer of the mixture, contrary to the daughter cylinders. The amount of substance (n) for increased and decreased CO_2 in the mother and daughter cylinders was computed from the change amount of CO_2 molar fraction (c_{CO_2}) to evaluate the mass balance of CO_2 corresponding to increase and decrease in CO_2 molar fractions, which is related to the initial value before the transfer of the mixture, and the cylinder volume (V) and pressure (p) in the daughter cylinder using the ideal gas low; $n = c_{CO_2} \times p \times V/(\mathrm{R} \times \mathrm{T})$. Where R and T express gas constant (0.082057 L atm K^{-1} mol^{-1}) and gas

temperature (298 K), respectively. The mass balance between the increase and decrease was consistent within uncertainties in each experiment (Table 1), indicating that the changes of CO_2 were caused by the diffusive fractionation rather than CO_2 adsorption.

As shown in Fig. 4, the CO_2 decrease does not depend on the transfer volume and initial pressure of the mother cylinder, but it becomes significantly smaller below flow rates of 19 L min^{-1}. The fact that the amount of CO_2 molar fractions decreased was constant regardless of the transfer volume, indicates that the fractionation factor did not change at the beginning and end of the transfer. The change of CO_2 decreased amounts due to transfer speed also support that the fractionation is caused by thermal diffusion because the transfer speed determines the thermal gradient. Source gases transfer into daughter cylinders at the transfer speed of more than 19 L min^{-1} in general preparation process. Therefore, CO_2 molar fractions in standard mixtures with accurate atmospheric CO_2 level are influenced by the fractionation in transfer of the source gas but it may be significantly suppressed by the transfer of the mixture at a lower transfer speed. However, it is difficult to transfer source gases at the transfer speed presented in this experiment because the speed is much lower than the normal transfer speed in the preparation process of the standard mixtures. We must acquire a technique to control the transfer speed of source gas.

A fractionation factor (α) in the transfer of a source gas was estimated from the results for the transfer speed of more than 19 L min^{-1} because a source gas in the actual preparation of standard mixtures is transferred at the transfer speed larger than 19 L min^{-1}. CO_2 molar fraction in the gas mixture in the cylinder (X_{out}) is modified by the fractionation factor to the ratio in the cylinder as the following equation.

$$X_{out} = \alpha X_0. \quad (3)$$

Where X_0 is the initial CO_2 molar fractions. The fractionation factor (α) was estimated to be X_{out}/X_0 = 0.99968 ± 0.00010 using only values with transfer speeds of more than 19 L min mol^{-1} in Table 1. If a standard mixture with a CO_2 molar fraction of 400 μmol mol^{-1} is prepared by a three-step dilution, the CO_2 molar fraction in the standard mixture is predicted to decrease by 0.252 ± 0.082 μmol mol^{-1} by the

fractionation effect in the second and third step dilutions. Additionally, the CO_2 molar fraction in a source gas (X) can be expressed using pressure (P) and initial pressure (P_0) of the source gas by the Rayleigh fractionation model.

$$\frac{X}{X_0} = \left(\frac{P}{P_0}\right)^{\alpha-1} \quad (4)$$

According to equation (4), the CO_2 molar fraction in the source gas is estimated to be 1.00076 ± 0.00024 against an initial value with a decrease in pressure from 11.0 to 1.0 MPa. This value corresponds to the increase in 0.30 ± 0.09 μmol mol^{-1} from the initial value in a standard mixture with a CO_2 molar fraction of 400 μmol mol^{-1} prepared from the source gas.

We also measured different molecular pairs, $^{32}O_2/^{28}N_2$, $^{40}Ar/^{28}N_2$, and CO_2/N_2, and the same molecular pairs, $^{29}N_2/^{28}N_2$, $^{34}O_2/^{32}O_2$, and $^{40}Ar/^{36}Ar$ to confirm if the fractionating process discussed above occurred by the transfer of mixture. The relationship of the deviations of $\delta(^{32}O_2/^{28}N)_2$, $\delta(^{40}Ar/^{28}N_2)$, $\delta(CO_2/N_2)$, $\delta(^{34}O_2/^{32}O_2)$, and $\delta(^{40}Ar/^{36}Ar)$ with deviations of $\delta(^{29}N_2/^{28}N_2)$ in the daughter cylinders relative to their mother cylinders are shown in Fig. 5. The black line represents the values obtained from the mother–daughter experiment using 10 and 48 L cylinders. The red dotted line represents the theoretical value of thermal diffusion, which was calculated using the equations provided by Langenfelds et al. (2005). Red solid lines represent the deviations due to thermal diffusion experimentally estimated by Ishidoya et al. (2013, 2014). The deviation of molecular pairs in the daughter cylinders relative to their mother cylinders occurred between not only different molecular pairs, $\delta(^{32}O_2/^{28}N)_2$, $\delta(^{40}Ar/^{28}N_2)$, and $\delta(CO_2/N_2)$ but also the same molecular pairs, $\delta(^{29}N_2/^{28}N_2)$, $\delta(^{34}O_2/^{32}O_2)$, and $\delta(^{40}Ar/^{36}Ar)$, suggesting that the deviation corresponded to the mass number of the molecules. The relationship of the deviations closed to the experimental thermal diffusion, supporting that the fractionation occurs due to thermal diffusion. The deviations of $\delta(CO_2/N_2)$ were more than the values expected from theorical and experimental thermal diffusions. It may be because the deviation of the experimental thermal diffusion for $\delta(CO_2/N_2)$ had larger uncertainty than those of other species. The values

of $\delta(^{32}O_2/^{28}N)_2$ and $\delta(^{40}Ar/^{28}N_2)$ scattered more than their uncertainties. Further studies are needed to understand the mechanism(s) of the fractionation in detail.

3.2 Comparation between one-step dilution and three-step dilutions

In the previous section, we determined the fractionation factor in the transfer of a source gas to be 0.99968 ± 0.00010. This indicates that the CO_2 molar fraction in gravimetrically prepared standard mixture with atmospheric CO_2 level has a systematic error by the fractionation in the dilution process by the transfer of CO_2/air mixture used as a source gas to an evacuated daughter cylinder in the second and third step dilution. Two types of experiments were conducted to confirm the systematic error. One evaluated the fractionation in the second and third step dilutions based on the increase in CO_2 molar fractions in 1st and 2nd gas mixtures due to the fractionation with their consumption. Another demonstrated that CO_2 molar fractions in 3rd gas mixtures deviate from their gravimetric values by measuring 3rd gas mixtures based on standard mixtures prepared by one-step dilution, which can avoid the fractionation.

Two series of standard mixtures were prepared by one-step dilution to determine CO_2 molar fractions in the 3rd gas mixtures used in the two experiments. The CO_2 molar fractions were corrected on the basis of the adsorption of CO_2 to the internal surface using the $X_{CO_2,ad}$ of 0.027 ± 0.004 μmol mol^{-1}. Four standard mixtures were prepared as the first series to evaluate the fractionation in the second and third steps, and the CO_2 molar fractions were 390.687 ± 0.077 μmol mol^{-1}, 402.253 ± 0.078 μmol mol^{-1}, 415.452 ± 0.080 μmol mol^{-1}, and 426.602 ± 0.082 μmol mol^{-1}. Five standard mixtures were prepared as the second series to demonstrate the deviations of CO_2 molar fractions in the 3rd gas mixtures in which the CO_2 molar fractions were 390.599 ± 0.078 μmol mol^{-1}, 399.807 ± 0.094 μmol mol^{-1}, 402.724 ± 0.094 μmol mol^{-1}, 406.021 ± 0.094 μmol mol^{-1}, and 419.618 ± 0.098 μmol mol^{-1}. The numbers following the symbol ± denote expanded uncertainty, which was mainly associated with the mass of source gases, CO_2 and air. The molar mass of air also contributes to the uncertainty of the CO_2 molar fraction because the composition of the air is different among individual cylinders purchased from the same gas manufacturer. For example, O_2 molar fractions in the air which our laboratory uses, ranges from 208000 μmol mol^{-1} to 209600 μmol mol^{-1}. This

difference causes the CO_2 molar fraction to deviate by 0.09 μmol mol^{-1}. Therefore, the molar fractions of N_2, O_2, and Ar in the air used in this experiment were determined based on standard mixtures composed of N_2, O_2, Ar, and CO_2. Ar molar fractions were determined to range from 9300 μmol mol^{-1} to 9360 μmol mol^{-1} using GC-TCD, and their largest standard uncertainty was 6 μmol mol^{-1}, whereas O_2 molar fractions were determined to range from 208804 μmol mol^{-1} to 209276 μmol mol^{-1} using the paramagnetic O_2 analyzer and their largest standard uncertainty was 6 μmol mol^{-1}. N_2 molar fractions in the air were calculated by subtracting the Ar and O_2 molar fractions from 1. The first and second series were measured using the Picarro G2301, showing the results in Fig. 6a. The line represents the Deming least-square fit to the data. The residuals from the line are shown in Fig. 6b. The error bar is expressed as the expanded uncertainty of gravimetric values. The residual ranges from −0.014 μmol mol^{-1} to 0.008 μmol mol^{-1} for the first series and from −0.057 μmol mol^{-1} to 0.054 μmol mol^{-1} for the second series. The measured molar fractions were consistent with the line within the expanded uncertainties.

To evaluate the increase in CO_2 molar fraction in 2nd gas mixture as the source gas, six reference mixtures (3rd gas mixtures) with approximately 400 μmol mol^{-1} were prepared from a common 2nd gas mixture, which had a gravimetric value of 5022.46 ± 0.18 μmol mol^{-1} for CO_2 in the process shown in Fig. 7a. The number following the symbol ± denotes the expanded uncertainty. The pressure of the 2nd gas mixture used for the preparation of the 3rd gas mixtures was 11.5 MPa, 9.7 MPa, 8.05 MPa, 4.2 MPa, 2.75 MPa, and 1.1 MPa. The increase in CO_2 molar fractions in the 2nd gas mixture was evaluated by measuring the 3rd gas mixtures using the Picarro G2301 based on the first series because the increase in the 2nd gas mixture directly reflects them in the 3rd gas mixtures prepared from the 2nd gas mixture. The fractionation in the transfer of the 2nd gas mixture into the daughter cylinder contributes to not the increase of CO_2 molar fraction in the 3rd gas mixture but that of CO_2 molar fraction in the remaining 2nd gas mixture because the effects on the transferred mixtures act similarly on all 3rd gas mixtures. The relationship of the deviations from the gravimetric values in the 3rd gas mixtures and the pressure of the 2nd gas mixture is shown in Fig. 8a. The vertical axis is expressed as the deviation values to subtract the measured values from the gravimetric values for the 3rd standard mixtures. The error bars represent the expanded uncertainties

calculated based on combining the standard uncertainty of the measurement with that of the gravimetric values for the standard mixtures prepared by a three-step dilution. The known negative offset from the gravimetric value caused by the fractionation process in the gas transfer during the 3rd gas mixture preparation is observed for the 3rd gas mixture prepared from the 2nd at 11.5 MPa. With decreasing the pressure of 2nd gas mixture to 1.1 MPa, CO_2 increased in the 3rd gas mixture by 0.25 ± 0.10 μmol mol^{-1}, which agrees with the increased value of 0.30 ± 0.10 μmol mol^{-1} predicted from Eq. (4) using the fractionation factor of 0.99968 ± 0.00010 determined in section 3.1. However, we estimated the fractionation factor in the third step dilution by applying the Rayleigh fractionation model [the Eq. (4)] to the increase of the CO_2 mole fraction with the decrease of inner pressure, as shown in the solid line in Fig. 8a. The estimated fractionation factor was 0.99975 ± 0.00004, which was consistent with the fractionation factor of 0.99968 ± 0.00010 estimated in section 3.1. This consistency indicates that the fractionation detected in the mother–daughter experiment also occurs in the transfer of a source gas in the preparation process of the 3rd gas mixtures.

The fractionation of CO_2 and air is also assumed to occur in the second step dilution in which the 1st gas mixture composed of CO_2 and air was transferred to the evacuated cylinder. We evaluated the fractionation based on the change in the deviations from the gravimetric values in 3rd gas mixtures prepared using the process shown in Fig. 7b. Two 3rd gas mixtures with a CO_2 molar fraction of approximately 400 μmol mol^{-1} were prepared from two 2nd gas mixtures, which were prepared using a common 1st gas mixture having a CO_2 molar fraction of 65164.9 ± 1.9 μmol mol^{-1}. The 2nd gas mixtures had CO_2 molar fractions of 5022.46 ± 0.18 μmol mol^{-1} and 4824.67 ± 0.35 μmol mol^{-1}, which were prepared from the 1st gas mixture at a pressure of 7.8 and 0.8 MPa. The 2nd gas mixtures were used only for the preparation of the 3rd gas mixtures. The number following the symbol ± denotes the expanded uncertainty. The CO_2 molar fractions in the 3rd gas mixtures were determined using the Picarro G2301, which is based on the first series. The contribution of the fractionation of CO_2 in the daughter cylinder was canceled because of the reasons described in the previous paragraph. The relationship of the deviations in the measured values from the corresponding gravimetric values and pressure of the 1st gas mixture is shown in Fig. 8b. The solid and dotted lines in Fig.

8b represent the Rayleigh model line, which was calculated based on the fractionation factor of 0.99975 ± 0.00004 and 0.99968 ± 0.00010. The error bars represent the expanded uncertainties calculated based on the combination of standard uncertainty of the measurement with that of the gravimetric values for the 3rd gas mixtures. The deviations increased by 0.16 ± 0.10 μmol mol^{-1} as the pressure decreased from 7.8 MPa to 0.8 MPa. Both lines agree with the deviations within the uncertainties. The results mean that the fractionation factor in the second step dilution is equivalent to the fractionation factor in the third step dilution. This means that fractionation occurs regardless of the CO_2 molar fraction of a source gas.

Finally, we demonstrated that the CO_2 molar fraction in the 3rd gas mixture deviated from its gravimetric value according to the fractionation factors described above. In this demonstration, four 3rd gas mixtures for atmospheric CO_2 levels were newly prepared by three-step dilutions. The increase in CO_2 molar fractions in the 1st and 2nd gas mixtures with their consumption were corrected on the basis of the decrease in their pressures from the initial values. The decreases in CO_2 molar fractions by the adsorption of CO_2 to the internal surface for 3rd gas mixtures were corrected based on the $X_{CO_2,ad}$ of 0.027 ± 0.004 μmol mol^{-1}. These corrections allow for extracting only the deviations from gravimetric values caused by fractionation in the transfer of 1st and 2nd gas mixtures. The CO_2 molar fractions in the 3rd gas mixtures were measured using the Picarro G2301 based on the second series. The measured values of CO_2 molar fractions were calculated based on the calibration line obtained by applying the Deming least-square fit to the measured values. The error bars represent the expanded uncertainties of the gravimetric values. The deviations were −0.207 ± 0.060 μmol mol^{-1} on average. The deviation was dropped between −0.252 ± 0.082 μmol mol^{-1} and −0.200 ± 0.032 μmol mol^{-1} calculated using the fractionation factor of 0.99968 ± 0.00010 and 0.99975 ± 0.00004, and it was consistent with both values within their uncertainty. This indicates that the fractionation of CO_2 and air occurs according to our estimated fractionation factor in each dilution process.

4 Conclusion

CO_2 adsorption on cylinder and fractionation of CO_2 and air were used to evaluate systematic deviations during the preparation of a standard mixture with atmospheric CO_2 levels. Decanting experiments were

performed to evaluate the amount of CO_2 adsorbed on the internal surface of a 10-L aluminum cylinder during the preparation of CO_2/air mixtures at the atmospheric level. The amount of adsorbed CO_2 was determined to be 0.027 ± 0.004 μmol mol^{-1} at 11.0 MPa, resulting in a small bias in the gravimetric value. The mother–daughter experiments were performed to understand the fractionation of CO_2 and air when a CO_2/air mixture used was transferred into an evacuated cylinder as a source gas. CO_2 molar fractions in the mother and daughter cylinders increased and decreased, respectively, indicating that fractionation causes not only a decrease in CO_2 molar fraction in the prepared standard mixture but also an increase in CO_2 molar fraction in a remaining source gas. The decreases of CO_2 mole fractions in the daughter cylinders were constant regardless of the transfer volume, the initial pressure of the mother cylinder, and the transfer speeds at flow rate exceeding 19 L min^{-1} which are in range of conditions used in preparation of the standard mixtures. This indicates that the degree of fractionation in transfer of a source gas is constant. We demonstrated that CO_2 molar fractions in standard mixtures by three-step dilutions decreased by −0.207 ± 0.060 μmol mol^{-1} from gravimetric values based on source gas fractionation, which is greater than the compatibility goal of 0.1 μmol mol^{-1}. The decrease was between the values calculated using two fractionation factors of 0.99976 ± 0.00004 and 0.99968 ± 0.00010; one was estimated in mother–daughter transfer experiment and another was computed by applying the Rayleigh model to the increase in CO_2 molar fractions in source gas. Fractionation at different stages of a multi-step dilution can result in CO_2 increases as well as in CO_2 decreases of the final gas mixture. This affects the reproducibility and accuracy of CO_2 molar fractions in gravimetric standard gases. CO_2 molar fractions in standard mixtures prepared by multistep dilutions were identified as including systematic error according to the fractionation of CO_2 and air. Therefore, we must consider the fractionation when determining CO_2 molar fraction in standard mixtures gravimetrically prepared by multistep dilutions.

Code availability

Data availability. The data presented in this article are available upon request to Nobuyuki Aoki (aoki-nobu@aist.go.jp).

Author contribution. NA designed the study. NA performed the experiment and drafted the paper. SI carried out measurement by a mass spectrometry. NM helped with the preparation of standard mixtures. SM helped with determination of CO_2 molar fraction. All were actively involved with the final version of the paper.

Competing interests. The authors declare that they have no conflict of interest.

Disclaimer

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Table 1. Results of the mother–daughter experiment on 10-L and 48-L aluminum cylinders which were performed the mother cylinder with vertical placement. CO_2/air mixtures at atmospheric level were transferred from 10-L or 48-L aluminum cylinders (mother) to 10-L aluminum cylinders (daughter) at different mother cylinder's pressure, transfer volume, and transfer speed.

Cylinder			*Pressure* [a]		*molar fraction* [b]		*Drift* [c]		*Transfer* [d]
	number	Size (L)	Before (MPa)	After (MPa)	Before (μmol/mol)	After (μmol/mol)	Amount (μmol)	Molar fraction (μmol/mol)	Speed (L/min)
Mother	CPC00878	10	9.8	4.4	379.138	379.322	3.15 ± 0.73	0.18	62
Daughter	CPC00875	10		4.5		379.034	−1.82 ± 0.74	−0.10	
Mother	CPD00092	10	10.5	4.8	458.611	458.715	1.96 ± 0.79	0.10	211
Daughter	CPD00093	10		4.4		458.487	−2.12 ± 0.73	−0.12	

Mother	CPD00076	10	4.1	2.0	378.103	378.243	1.09 ± 0.33	0.14	27
Daughter	CPB28688	10		2.0		377.982	−0.94 ± 0.33	−0.12	
Mother	CPD00069	10	13.5	8.0	377.523	377.602	2.46 ± 1.32	0.08	216
Daughter	CPD00072	10		4.5		377.333	−3.31 ± 0.74	−0.19	
Mother	CPD00070	10	13.2	7.8	377.936	378.026	2.73 ± 1.29	0.09	24
Daughter	CPD00074	10		5.1		377.751	−3.68 ± 0.84	−0.19	
Mother	CPB16349	10	8.8	7.0	419.319	419.350	0.84 ± 1.16	0.03	54
Daughter	CPC00484	10		1.7		419.135	−1.21 ± 0.28	−0.19	
Mother	CPD00069	10	6.6	5.6	377.602	377.635	0.72 ± 0.93	0.03	19
Daughter	CPD00072	10		0.8		377.463	−0.43 ± 0.13	−0.14	
Mother	CQB15834	48	14.5	8.6	376.876	376.950	12.49 ± 7.18	0.07	167.7
Daughter	CPD00072	10		8.1		376.780	−3.01 ± 1.33	−0.10	55.2
	CPD00074	10		8.0		376.792	−2.60 ± 1.31	−8.54 ± 2.33	−0.08	54.5
	CPD00073	10		8.5		376.787	−2.93 ± 1.40		−0.09	57.9
Mother	CQB15808	48	13.9	8.5	377.200	377.255	9.18 ± 7.10	0.05	291.6
Daughter	CPD00070	10		8.3		377.127	−2.34 ± 1.37		−0.07	99.6
	CPD00069	10		7.8		377.093	−3.24 ± 1.29	−8.83 ± 2.32	−0.11	93.6
	CPD00076	10		8.2		377.098	−3.25 ± 1.36		−0.10	98.4
Mother	CPB31362	10	4.13	3.3	441.693	441.722	0.37 ± 0.54	0.03	2.8

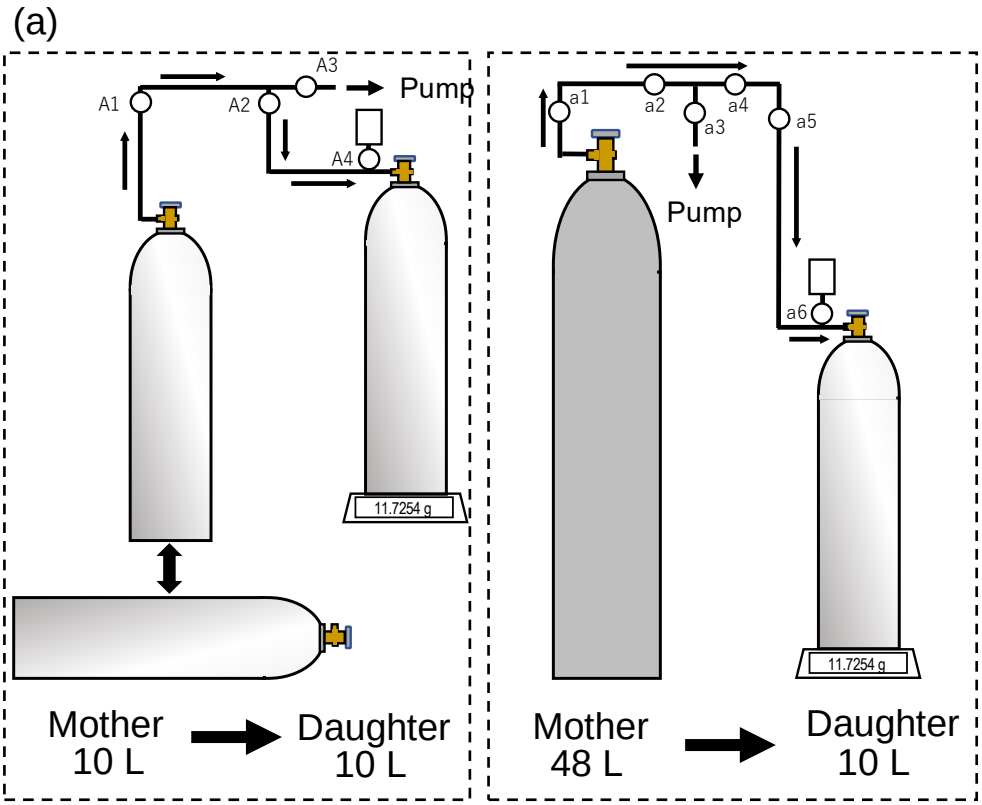
Daughter	CPB16311	10		0.86		441.641	−0.17 ± 0.14	−0.05	
Mother	CPB31362	10	3.2	1.6	406.184	406.223	0.24 ± 0.26	0.04	1.1
Daughter	CPB16311	10		1.5		406.179	−0.03 ± 0.25	−0.004	
Mother	CPB28912	10	8.5	4.5	419.853	419.908	0.95 ± 0.74	0.06	2.2
Daughter	CPB16463	10		4.0		419.801	−0.82 ± 0.66	−0.05	

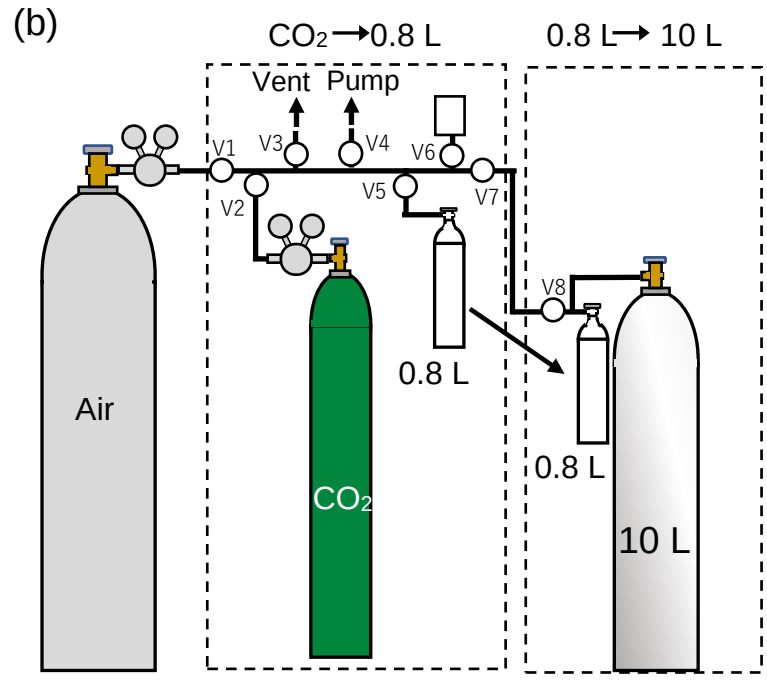
[a] Pressures were measured using the pressure gauge attached the regulator.

[b] CO_2 molar fractions in mother and daughter cylinders were measured after several hours to half of a day of transferring the mixtures. These values have a measurement uncertainty of 0.030 μmol/mol.

[c] The change in the amount of substance (n) for CO_2 were computed from the change in the amount of CO_2 molar fraction ($\boldsymbol{c_{CO_2}}$), the cylinder volume (V) and pressure (p) in the daughter cylinder using the ideal gas low; $\boldsymbol{n = c_{CO_2} \times p \times V/(R \times T)}$. Numbers following the symbol ± denote the standard uncertainties calculated based on the measurement uncertainty.

[d] Transfer speeds were roughly computed by dividing transfer volume by transfer time.


(a)
A1
A2
A3
A4
Pump
11.7254 g
Mother
10 L
Daughter
10 L
a1
a2
a3
a4
a5
a6
Pump
11.7254 g
Mother
48 L
Daughter
10 L


(b)
CO2 → 0.8 L
0.8 L → 10 L
Vent
Pump
V1
V2
V3
V4
V5
V6
V7
V8
Air
CO2
0.8 L
0.8 L
10 L

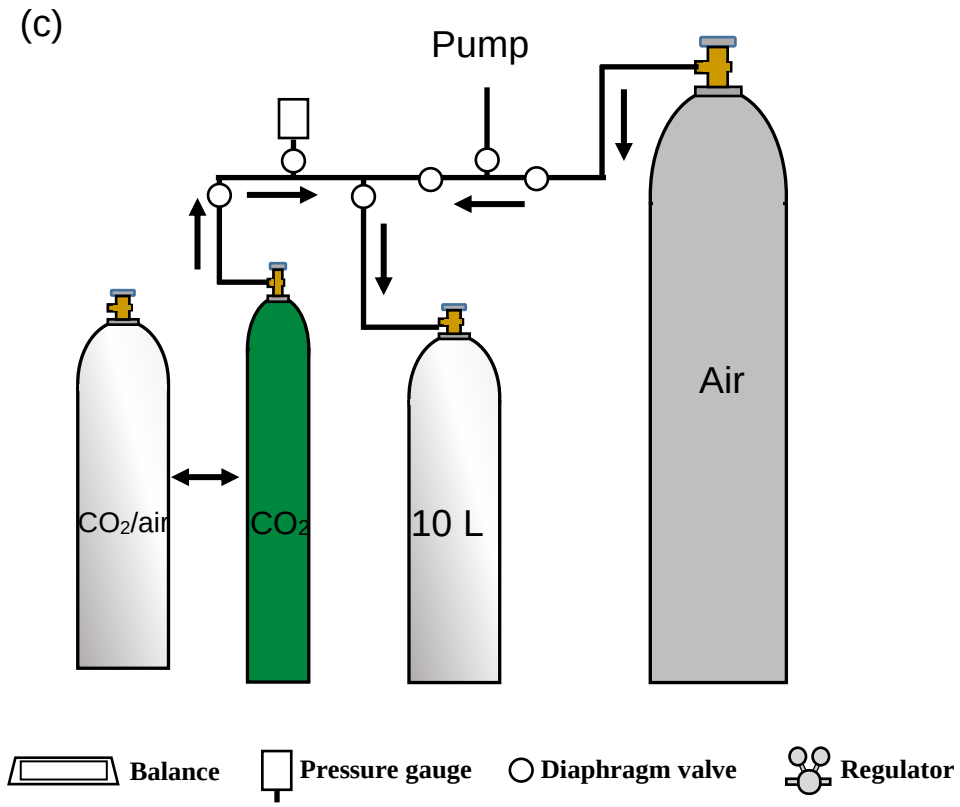


Figure 1 (a) Schematic of the manifold used to transfer a CO_2/air mixture from a mother cylinder to a daughter cylinder in a mother–daughter experiment, (b) the manifold used to transfer pure CO_2 to a 0.8-L aluminum cylinder and from a 0.8-L aluminum cylinder to a 10-L aluminum cylinder for preparing a standard mixture via one-step dilution and (c) the manifold used to transfer source gas (pure CO_2 or a CO_2/air mixture) and dilution gas (purified air).

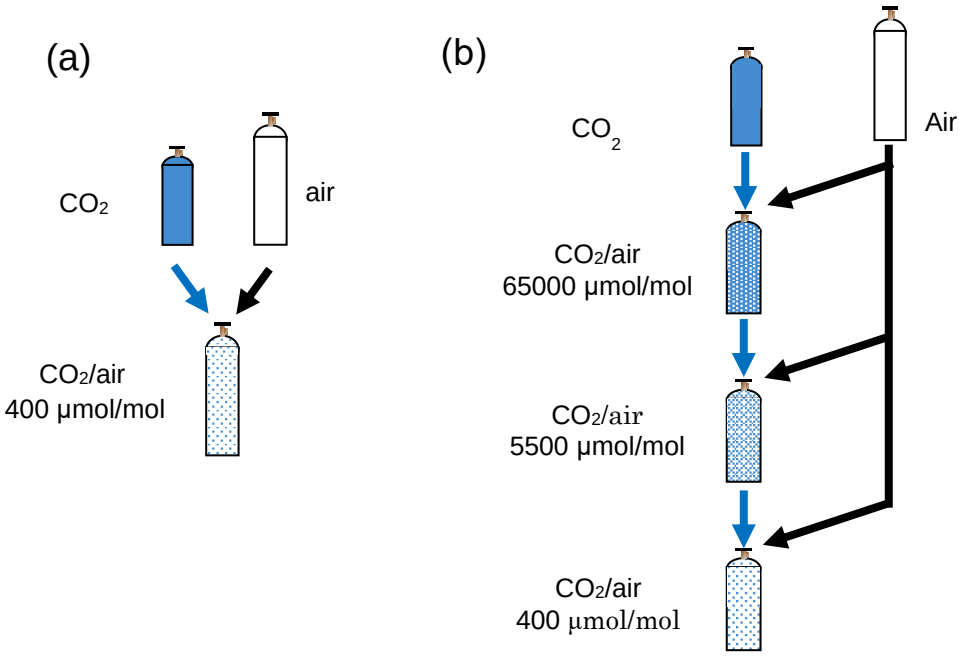
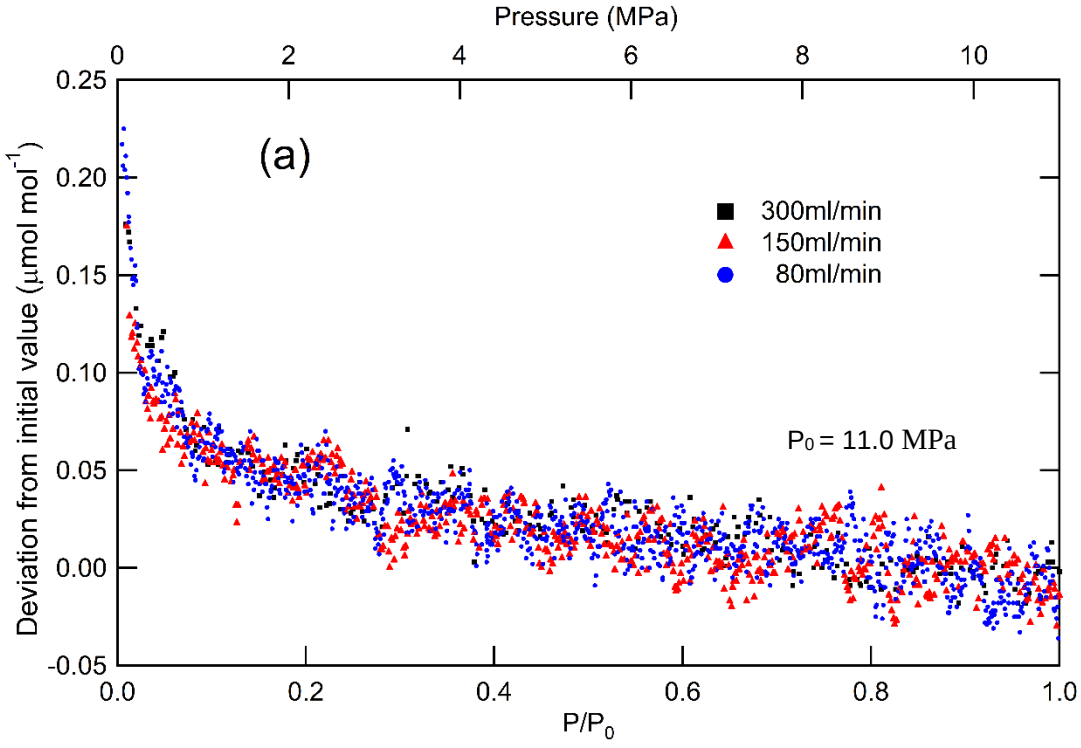


Figure 2 (a) Preparation process of standard mixtures under atmospheric CO_2 level via one-step dilution. (b) Preparation process of 3rd gas mixtures under atmospheric CO_2 level via three-step dilutions.



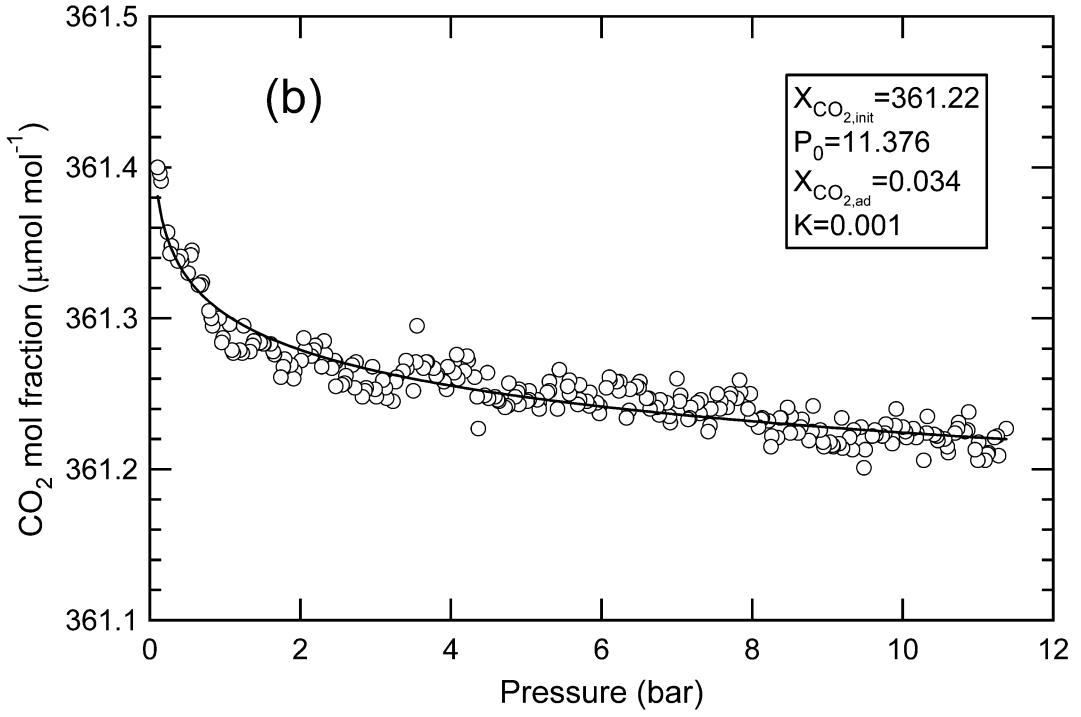


Figure 3 (a) Change of the CO_2 molar fractions from initial value in CO_2/air mixtures under atmospheric CO_2 level against relative pressure as the cylinder was emptied at the flow rates of 80 mL min^{-1}, 150 mL min^{-1}, and 300 mL min^{-1} from 11.0 MPa to 0.1 MPa. (b) Typical results obtained by applying the Langmuir model to the change of CO_2 molar fractions from initial value in CO_2/air mixture as the cylinder was emptied from 11.0 MPa to 0.1 MPa.

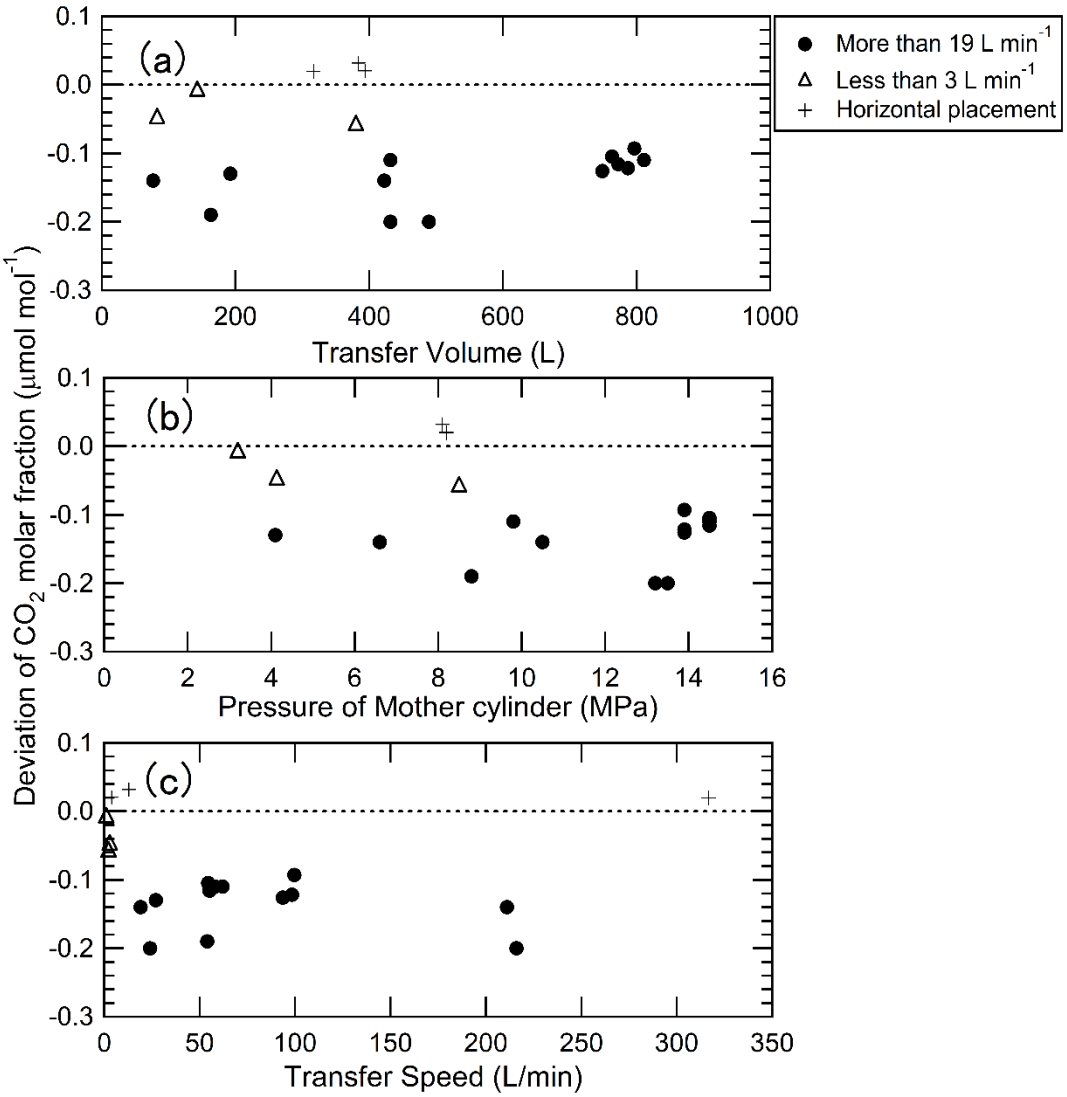


Figure 4 Deviations of CO_2 molar fractions in daughter cylinders from initial values against (a) transfer volume (b) mother cylinder's pressure, and (c) transfer speed when the CO_2/air mixtures under atmospheric level were transferred from the mother cylinder to the daughter cylinder. The closed circles represent the results measured at a transfer speed of more than 19 L min^{-1}, while the open triangles represent the results measured at a transfer speed of less than 3 L min^{-1}. These were performed with the vertical mother cylinders plus signs represent the results performed with the horizontal mother cylinders

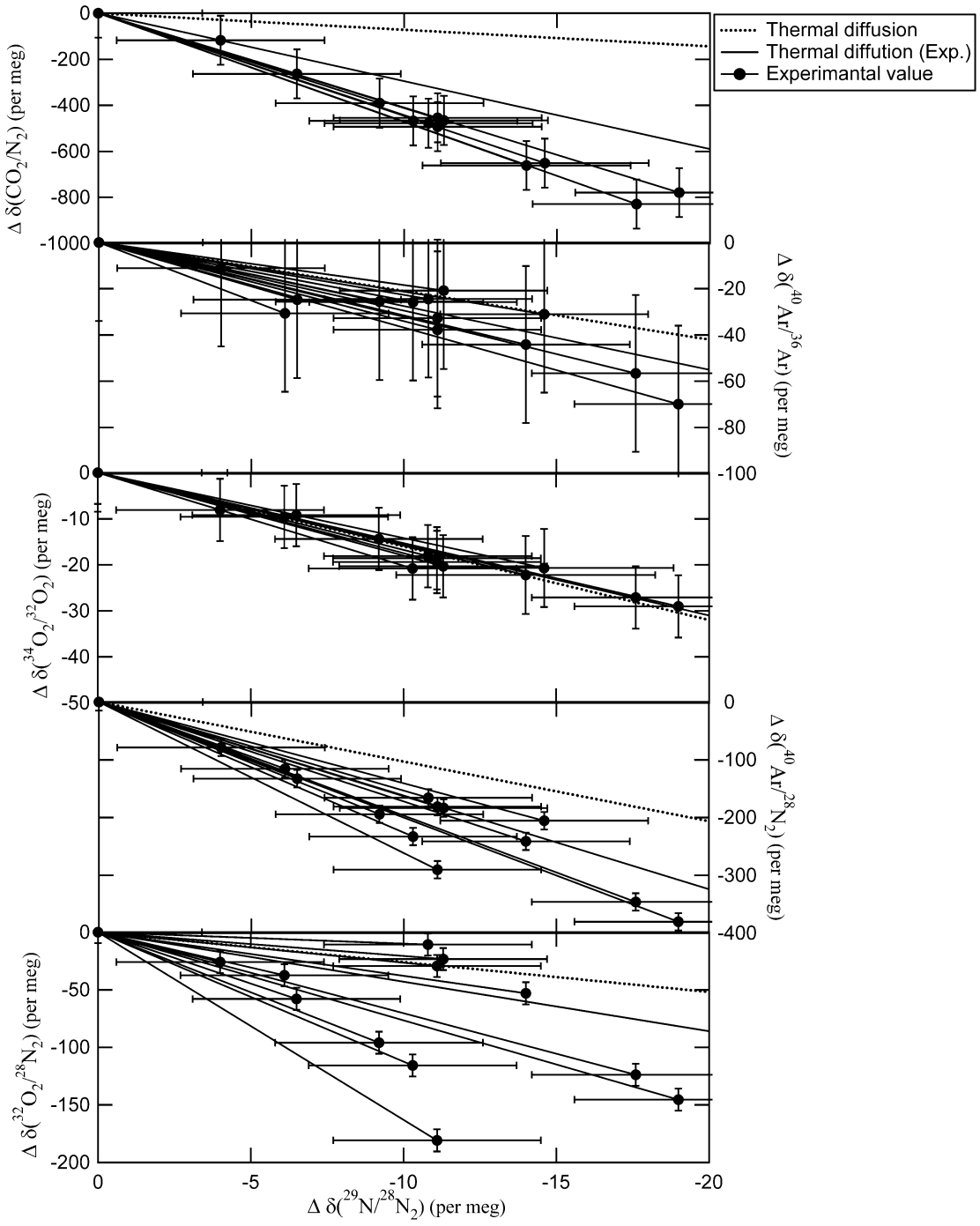


Figure 5 Relationship between the deviations of $\delta(^{44}CO_2/^{28}N_2)$, $\delta(^{40}Ar/^{36}Ar)$, $\delta(^{34}O_2/^{32}O_2)$, $\delta(^{40}Ar/^{28}N_2)$, and $\delta(^{32}O_2/^{28}N_2)$ with the deviations of $\delta(^{29}N_2/^{28}N_2)$ in the daughter cylinders relative to their mother cylinders after the CO_2/air mixtures under atmospheric level were transferred from the mother cylinder to the daughter cylinder. Error bar expresses expanded uncertainty of the deviations. The red dotted line represents the theoretical value of thermal diffusion, respectively, (Langenfelds et al. 2005). The red solid lines represent the deviations due to thermal diffusion, experimentally estimated by Ishidoya et al. (2013, 2014).

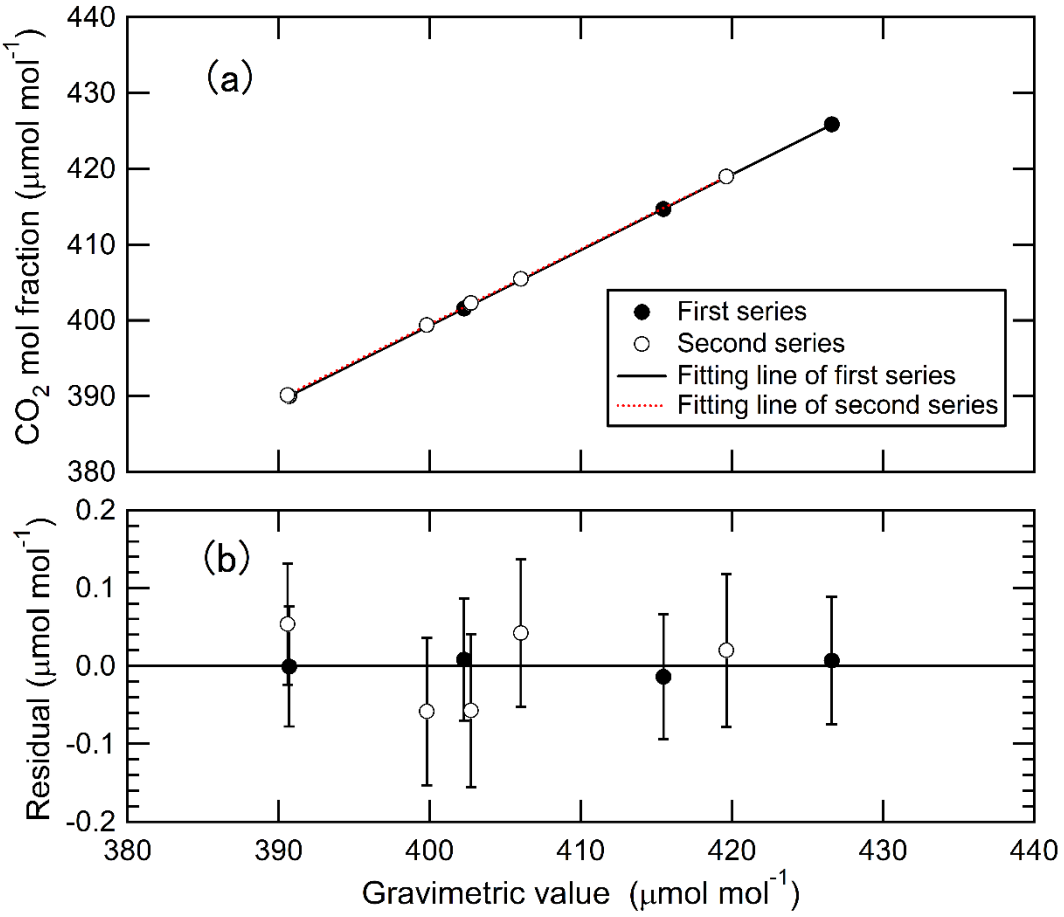


Figure 6 (a) Relationships between the measured CO_2 molar fractions and the gravimetric values for two series of standard mixtures prepared via one-step dilution. (b) Residuals from the Deming least-square fit shown in (a).

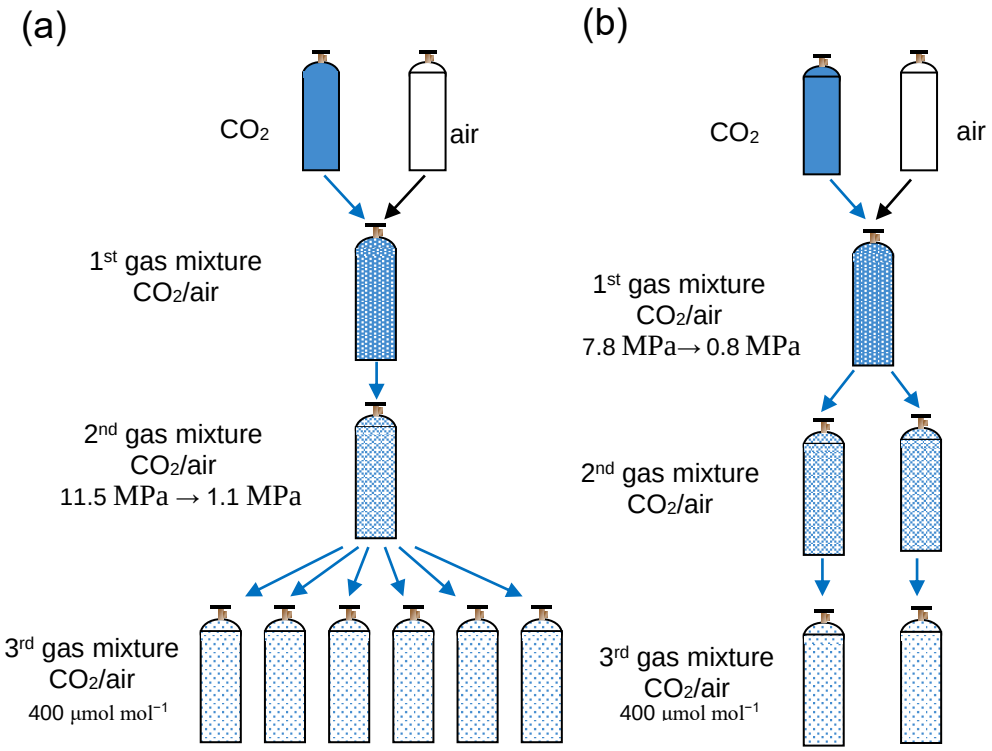


Figure 7 (a) Preparation process of the 3rd gas mixtures under atmospheric CO_2 level via three-step dilutions to evaluate the fractionation in the third step and (b) second step dilutions.

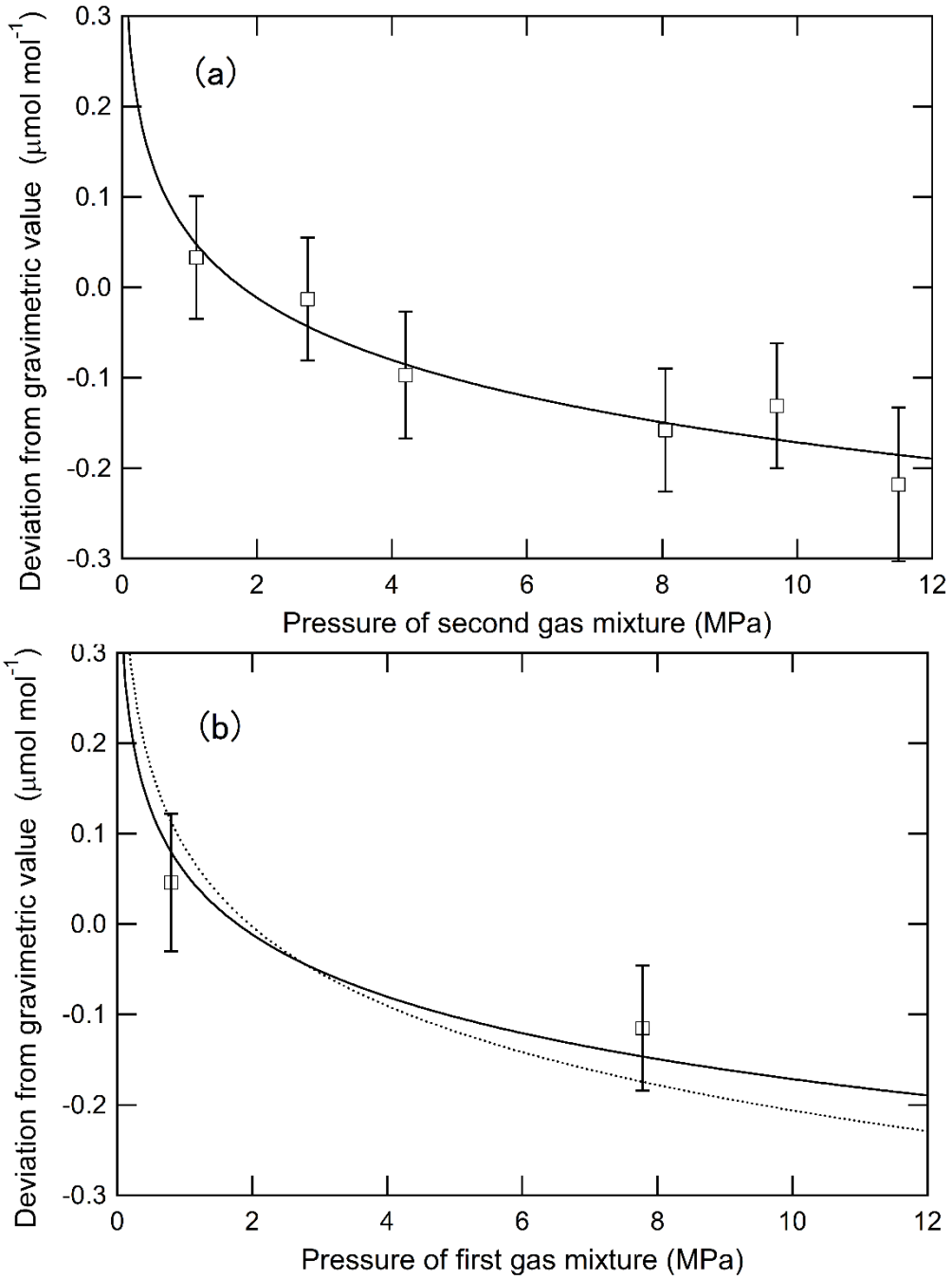


Figure 8 (a) Deviations of the measured CO_2 molar fractions from the gravimetric values against the pressure of the 2nd gas mixture. CO_2 molar fractions determined on the basis of the standard mixtures prepared via one-step dilution. The solid line represents the Rayleigh model fit for the plots. (b) Deviations of the measured CO_2 molar fractions from the gravimetric values against the pressure of the 1st gas mixture. The CO_2 molar fractions determined on the basis of the standard mixtures prepared via one-step dilution. The solid and dotted lines represent the Rayleigh model fit based on the fractionation factor of 0.99975 ± 0.00004 and 0.99968 ± 0.00010.

Re

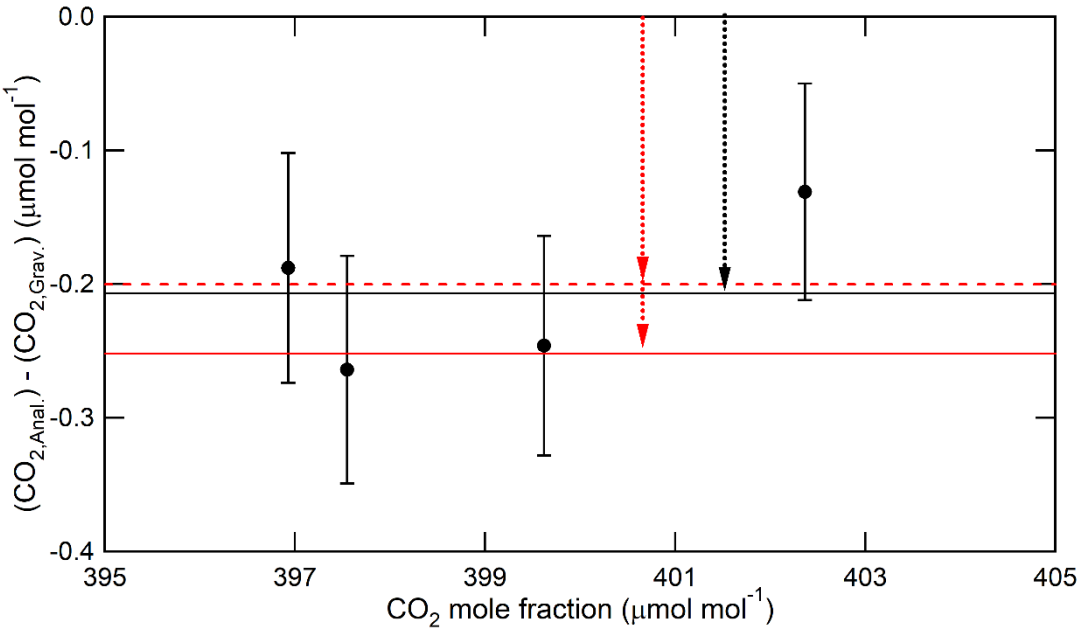


Figure 9 Deviations of the measured values from the gravimetric values of CO_2 molar fractions in the standard mixtures (3^{rd} gas mixtures) prepared via three-step dilutions. The measured values were calculated from the calibration line obtained by applying the Deming least square fit to the measured data. The black line represents the average value of the deviations. The red solid and dotted lines represent the values calculated using fractionation factors of 0.99968 ± 0.00010 and 0.99975 ± 0.00004, respectively. The red and black arrows represent the deviation of CO_2 molar fraction in the 3^{rd} gas mixtures according to the fractionation of CO_2 and air.