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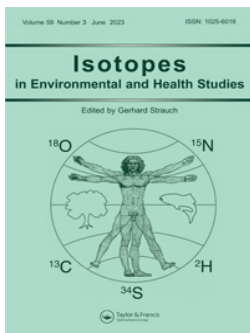
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Preventing drift of oxygen isotopes of CO₂-in-air stored in glass sample flasks: new insights and recommendations*

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ABSTRACT

It is known that the oxygen isotope composition of CO₂-in-air, when stored over longer time periods in glass sample flasks, tends to drift to more negative values while the carbon isotope composition remains stable. The exact mechanisms behind this drift were still unclear. New experimental results reveal that water already inside the flasks during sampling plays a major role in the drift of the oxygen isotopes. A drying method to remove any water sticking to the inner walls by evacuating the flasks for more than 72 h while heating to 60 °C significantly decreases drift of the oxygen isotopes. Moreover, flasks not dried with this method showed higher differences among drift rates of individual flasks. This is explained through the buildup of H₂O molecules sticking to the inner walls. Humidity of the air samples in the flasks as well as surface characteristics will lead to differences among flasks. Results also show that permeability of water is higher through Viton O-ring flask seals than through polychlorotrifluoroethylene (PCTFE) shaft seals, and that the stability of flasks sealed with the latter is significantly better over time.

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Glass sample flasks; oxygen-18; oxygen-16; CO₂; atmospheric samples; PCTFE; Viton; storage

1. Introduction

The ratio of the heavy to the light isotope, i.e. ¹³C/¹²C and ¹⁸O/¹⁶O, provides additional information on carbon fluxes, as they are essential for flux partitioning [1–7]. However, the isotope signals in atmospheric CO₂ are relatively small, therefore the Global Atmosphere Watch programme of the World Meteorological Organisation (WMO/GAW) inter-laboratory compatibility goals for δ¹³C and δ¹⁸O of atmospheric CO₂ (defined in the usual way with respect to VPDB(–CO₂)) were set at 0.01 and 0.05 ‰ for the Northern Hemisphere [8], respectively. The compatibility goal in this definition is the maximum bias between measurement records that should be aimed for when we want to

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capture the small variations that occur in the atmosphere [8]. Considering these stringent goals, the combined uncertainty of stable isotope measurements of atmospheric CO₂, including the stability of the isotopic composition of air samples, should be reduced to its minimum. Air samples are often collected in glass sample flasks, and, depending on the accessibility of the sample site and turnaround time of the measurement lab, can be stored for weeks or even months before their isotopic compositions are measured. For accurate and compatible measurement results it is therefore crucial that the stability of the isotopic composition in the sample flask is guaranteed. However, especially the oxygen isotopes of CO₂ are quite susceptible for drifts. Generally, they tend to drift towards more negative isotope values when stored in glass sample flasks for longer periods [9,10]. This is consistent with the assumption that this is caused by exchange of oxygen isotopes with (condensed or adsorbed) water vapour, having a much lower ¹⁸O content than atmospheric CO₂ [11].

The potential causes for depletion over time of the oxygen isotopes of atmospheric CO₂ in glass sample flasks have been studied by some groups [9,10]. Humid sample air can lead to condensation of water on the glass walls which will lead to exchange of oxygen between the H₂O and CO₂ molecules, altering the oxygen isotope composition of the CO₂ [9]. Drying the sample air is therefore crucial to ensure the stability of oxygen isotopes values over time. The influence of glass seal materials, contaminants in sample flasks or water sticking to the glass walls as potential causes for alterations of the oxygen isotope composition of CO₂ have been suggested in several studies [12,13]. The permeation of atmospheric gases through flask-sealing polymer O-rings was studied by Sturm et al. [14] and showed significant differences of water vapour pressure and CO₂ concentration in glass flasks after storage times of a few weeks. The empirical results were compared to theoretical calculations of the permeation flux for the various types of flasks used. Calculations of the permeation flux were done using the following equation:

$$F = K \frac{A(p_1 - p_2)}{d}, \quad (1)$$

in which F is the permeation flux ($\text{m}^3 \text{s}^{-1}$), K is the permeation coefficient ($\text{m}^2 \text{s}^{-1} \text{hPa}^{-1}$) of the material for a specific gas, A is the surface area (m^2) of the seal, $p_1 - p_2$ is the difference in partial pressure (hPa) of the gas and d is the membrane thickness (m). In Sturm et al. [14] a recommendation for the use of polychlorotrifluoroethylene (PCTFE) as a sealing material was made, based on the much lower permeation coefficient for H₂O of PCTFE in comparison to Viton ($0.22 \cdot 10^{-15}$ and $40\text{--}216 \cdot 10^{-15} \text{m}^2 \text{s}^{-1} \text{hPa}^{-1}$ at 25 °C, respectively). A follow-up study was performed at the Stable Isotope Laboratory at the Max Planck Institute for Biogeochemistry in Jena (BGC-IsoLab) to compare the stability of trace gas amount fractions and the stable isotope composition of CO₂ in flasks sealed with perfluoralkoxy alkane (PFA) O-rings in a cylindrical shaft and flasks with a tapered shaft with PCTFE sealing tips [10]. Although the PCTFE-sealed flasks showed a higher stability in the amount fractions of most of the analysed trace gases (CO₂, CH₄, N₂O), no significant difference was observed in the stability of the stable isotope composition of CO₂. $\delta^{18}\text{O}$ values of the CO₂ in the flasks changed with average rates of 0.0019 and 0.0023 ‰ per day for the PCTFE and the PFA-sealed flasks, respectively. This resulted in average changes of 0.3 and 0.4 ‰ from their original

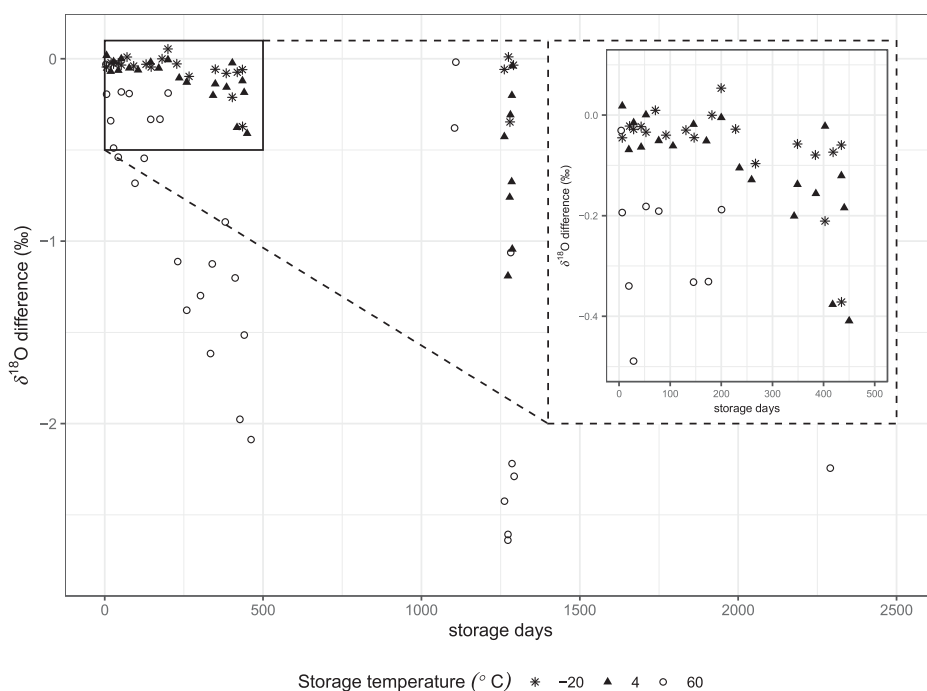


Figure 1. Differences between two $\delta^{18}\text{O}$ measurements of the same flask at different dates as a function of storage time in days. Three groups of flasks, stored at different temperatures (stars for -20°C , circles for 4°C and triangles for 60°C), are shown. The period until 500 days is displayed in a bigger format on the right side of the figure.

values over a period of 160 days for the PCTFE and PFA sealed flasks, respectively. Carbon isotopes showed no significant changes over the total storage period for both flask types. These results tend to point towards a change of oxygen isotopes of CO_2 in glass air sample flasks due to exchange with water, or anything else containing oxygen atoms, which is already present inside the flasks during sampling.

The BGC-IsoLab has studied the stability of the isotope composition of CO_2 -in-air in their glass sample flasks extensively [10] and developed a flask conditioning method that improved the stability significantly. Long-time storage experiments of flasks stored at different temperatures are presented in this paper, as well as storage experiments testing the effectivity of the drying procedure that was developed. At the Centre for Isotope Research (CIO) changes of the oxygen isotopes of CO_2 -in-air in glass sample flasks that occur already after time periods of several weeks were observed. Experiments conducted at the CIO show the difference of permeability of H_2O through different flask seals and the combined effect of thorough drying of the flasks, using the method developed at the BGC-IsoLab, and the use of flask seal material on the long-time stability of the oxygen isotope composition of CO_2 -in-air. The experimental results presented here are used to make a recommendation for long-time storage of air samples in glass flasks to ensure stability of the isotopic composition of the CO_2 -in-air within the WMO/GAW inter-laboratory compatibility goals.

2. BGC-IsoLab experiments

2.1. Flask conditioning and filling

The flasks used at the BGC-IsoLab for experiments described here are all 1-L flow through glass flasks (borosilicate 3.3) equipped with tapered shafts with PCTFE sealing tips produced by Pfaudler Normag Systems GmbH (Ilmenau, Germany). 102 flasks were flushed with dried and filtered atmospheric air from a high-pressure tank for half an hour at a flow of 3 L/min [10]. The air was commercially bought as high-pressurised air certified for scuba diving. Flasks were filled with the same air to a maximum pressure of 2 bar absolute. The $\delta^{13}\text{C}$ - and $\delta^{18}\text{O}$ -CO₂-in-air values of that atmospheric air are 8.86 ± 0.01 ‰ and -0.50 ± 0.02 ‰, respectively, on the JRAS-06 scale [15].

2.2. Stable isotope measurements

All stable isotope ratio measurements of CO₂-in-air at the BGC-IsoLab were done on two MAT252 isotope ratio mass spectrometers (ThermoFinnigan, Bremen, Germany). The IRMS instruments are equipped with custom-made CO₂ extraction autosamplers (BGC-AirTrap). Air flows over a water trap (-70 °C) and subsequently over a CO₂ trap (-196 °C) before it enters the IRMS instrument. For detailed descriptions of the systems we refer the reader to Werner et al. [16] and Ghosh et al. [17]. A subset of 12 flasks that were used for the long-time storage experiment, described below, was stored at room temperature and analysed twice within the first week of the experiment to assess the measurement stability. The average standard deviation of these measurements was better than 0.02 and 0.03 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO₂-in-air, respectively.

2.3. Long-time storage experiment

A large-scale storage experiment was set up with the aim to further study the mechanisms behind the drift of oxygen isotopes observed in a storage experiment conducted earlier at the BGC-IsoLab [10]. From that experiment, the conclusion was drawn that equilibration of CO₂ with water or OH-bonds, already present in the flask at the moment of sampling, is the most important reason for the observed drift. Expectations were therefore that drift would occur faster at high temperatures compared to low temperatures. Also, it was expected that, if permeation of water through the PCTFE seals is not of significance for the drift, an equilibrium should be reached when the CO₂ equilibrated with all exchangeable oxygen atoms in the flask.

90 flasks, filled with clean dried air as using the method described above, were analysed for trace gas concentrations and for the isotopic composition of the CO₂-in-air within several days after filling. The flasks were divided into three groups of 30 flasks and stored at different storage temperatures, being -20 , 4 and 60 °C, with the aim to test the hypothesis that oxygen isotopes drift faster with increasing temperatures as the result of a higher equilibration rate of CO₂ and H₂O at higher temperatures. One flask from each group was analysed every 7–14 days, later this period was extended to one month. From the 90, 8 flasks are not included in the analysis because leakages or contamination occurred. After 460 days the main part of the experiment was finished, but

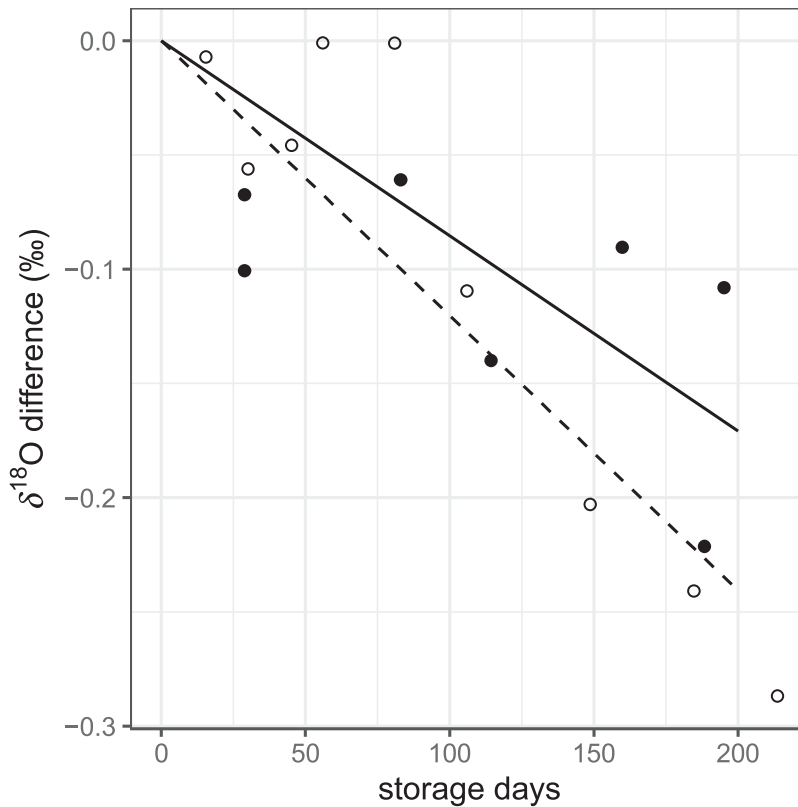


Figure 2. Differences between two $\delta^{18}\text{O}$ measurements of the same flask at different dates as a function of storage time in days. Open circles for the flasks that were evacuated for 24 h while heated to 60 °C and stored at 23 °C. Closed circles for the flasks that were evacuated for 72 h while heated to 60 °C and stored at 60 °C. The dashed line is the linear fit, with intercept set at 0, of the open circle data points, the black line for the closed circles.

the remaining flasks were kept at their storage temperatures so measurements after longer storage periods could be conducted as well.

Over the whole storage period, $\delta^{13}\text{C}$ values did not show any significant drifts. Differences between the first and the second (after variable storage time for the different flasks) $\delta^{18}\text{O}$ measurement as a function of the storage time are shown in Figure 2. It is clear that the flasks stored at 60 °C drift at higher rates than the flasks stored at lower temperatures. The flasks stored at 60 °C show a steep, linear drift over the first 500 storage days. After 500 days the drift seems to slow down and eventually stop, possibly because an equilibrium was reached. It is, on the other hand, striking that 3 of the flasks show lower deviations after storage times of more than 3 years, not following the general trend of steep linear drift in the first 500 days. It has to be considered that the flasks stored at 60 °C are exposed to extreme storage conditions and that leakages or permeation through the flask seals can occur, resulting in deviating oxygen isotope compositions. When also considering the results of the flasks stored at lower temperatures after 1300 days we must conclude that the spread in drifting rates between flasks is very high. This points towards the same conclusion drawn by Gemery et al. [9] that individual flasks can show

different drifting rates due to differences in surface characteristics. One of these characteristics could be the presence of water molecules sticking to the inner glass surface of the flasks. A lower amount of water molecules present in the flasks during sampling would cause a lower total drift of the flasks when equilibration is reached, and can, therefore, explain the lower drift of three out of 9 flasks after ~ 1000 days.

We conducted linear fits on the $\delta^{18}\text{O}$ results from the first 500 storage days of the various storage temperatures, giving a slope of -0.0034 ‰ per day and an R2 of 0.76, a slope of -0.0005 ‰ per day and an R2 of 0.50 and a slope of -0.0003 ‰ per day and an R2 of 0.34 for 60, 4 and -20 °C, respectively. The storage experiment conducted earlier by BGC-IsoLab over a period of 160 days with flasks stored at room temperature resulted in a slope of -0.0019 ‰ per day and an R2 of 0.74 [10]. We can therefore conclude that the storage temperature enhances the drift of oxygen isotopes of CO_2 in glass sample flasks. Permeation of water through the PCTFE flask seals is very likely of marginal importance for the drift, as permeation would continue as long as the partial pressure of water inside the flask is (much) lower than outside the flask. A minimal drift is observed after a storage time of p500 days and this period is certainly not long enough to eliminate this difference in partial pressure [14].

2.4. Drying procedure

The BGC-IsoLab developed a drying procedure that significantly improves the long-term stability of the oxygen isotope composition of CO_2 -in-air in their glass sample flasks. Storage experiments were conducted to develop the procedure and test its effectiveness for higher stability of oxygen isotopes of CO_2 . The drying procedure implies evacuation of flasks, connected in series of 8 flasks inside an oven set at 60 °C, to a pressure of 0.3 mbar using membrane pumps. To test the required period that the flasks should be evacuated, two sets of flasks were prepared and monitored for their trace gas concentrations and stable isotope composition of CO_2 . One set consisted of 9 flasks that were evacuated for 24 h, and another set of 7 flasks that were evacuated for 72 h. The flasks were all flushed and filled using the method described in Section 2.1, and their trace gas concentration and the isotopic composition of CO_2 was analysed. The 9 flasks that were evacuated for 24 h were stored at 23 °C. One of the flasks, each time a different one, was analysed again every 2–4 weeks over a period of 214 days in total.

The carbon isotopes remained stable within the measurement uncertainty. The oxygen isotopes drifted with a rate of -0.0012 ‰ per day, as presented in Figure 2. From storage experiments conducted earlier by BGC-IsoLab we know that in similar flasks, that were dried only by flushing with dried air, the drift over a period of 160 days was 0.0019 ‰ per day [10]. Evacuating the flasks for 24 h while heating to 60 °C hence gives an improvement of 25 %.

The other set of 9 flasks, evacuated for 72 h, were stored in an incubation oven at 60 °C. As CO_2 in flasks stored at higher temperatures will equilibrate faster with any oxygen-containing molecules within the flask (as described in Section 2.3), this procedure was chosen as a rapid test for the stability of the oxygen isotopes of CO_2 . A lower drift rate of 0.0009 ‰ per day compared to the 24 h evacuated flasks stored at 23 °C was observed. Considering the high temperature at which equilibration of CO_2 and oxygen atoms will be faster, this test showed that evacuating the flasks for 72 h considerably improves

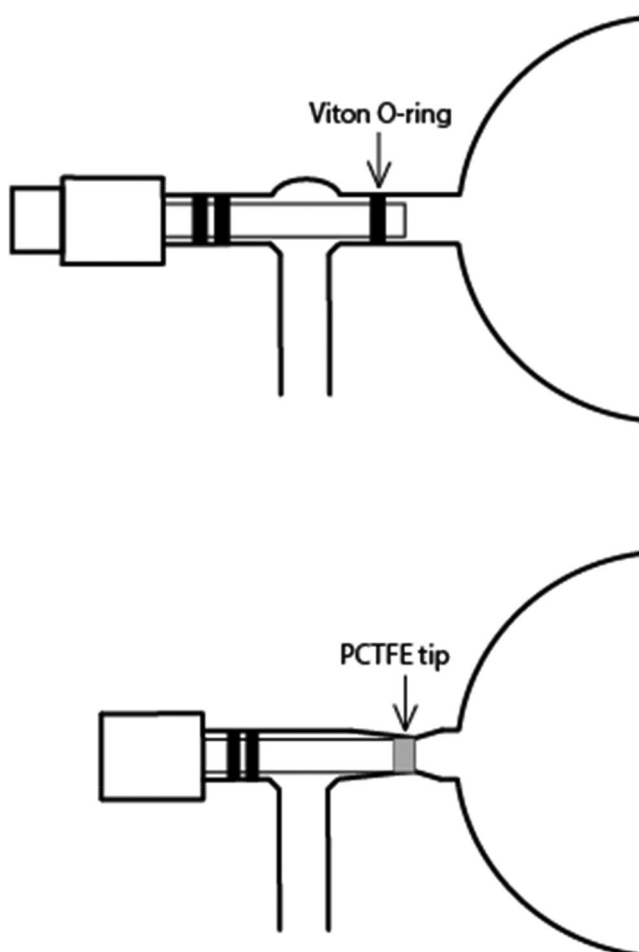


Figure 3. Scheme of the two different glass valves used for the CIO experiments. Top figure shows LouwersHanique cylindrical glass valves sealed with a Viton O-ring. The lower Figure shows the tapered shaft with a PCTFE sealing tip, produced by Pfaudler Normag Systems GmbH.

the stability compared to an evacuation time of 24 h. For accurate results of the CO_2 oxygen isotopes it is, however, of importance to do the measurements soon after sampling, especially when flasks are stored at higher temperatures, for instance in the tropics. At the BGC-IsoLab the drying procedure was implemented as described in this section, using an evacuation period of at least 72 h.

3. CIO experiments

3.1. Flask conditioning and filling

At the CIO 2.3-L glass (borosilicate 3.3 Duran, Schott®) flow-through flasks with cylindrical high vacuum glass valves (LouwersHanique, Hapert, Netherlands) sealed with Viton O-rings (from now on called 'CIO Viton flasks') are normally used for the sampling of atmospheric air. 12 similar flasks with tapered shafts with PCTFE sealing tips (produced by

Pfaunder Normag Systems GmbH), from now on called 'CIO PCTFE flasks', were bought to facilitate the comparison of the stability of oxygen isotopes in similar flasks with different valves. A schematic of the valves is shown in [Figure 3](#).

Before air sampling, all flasks at the CIO are routinely dried by flushing with cryogenically (60 °C) dried air, ensuring a maximum of 0.1 % of 'old air' in the downstream flask. Flushing of multiple flasks is done by flushing the same air through flasks connected in series. Flushing and filling of flasks is always done at atmospheric pressure. The required flushing time for a flask is determined by iterative numeric calculation of the percentage of old air (C_o) per time step (dt) with the equation:

$$C_o^i = C_{o(t-1)}^i + dt * \frac{1}{\tau} * (C_{o(t-1)}^{i-1} - C_{o(t-1)}^i), \quad (2)$$

in which C_o is the percentage of old air in the flask, and the superscript i stands for the position of the flask, with $i = 1$ for the flask positioned most upstream and $i = n$ for the flask positioned most downstream. τ is the volume of the flasks (in L) divided by the flow rate in L/s (the flow rate that was used was always 0.042 L/s). For a system containing only 1 flask the term $C_{o(t-1)}^i$ is cancelled out. This method is a modified version of the model for integration of *in situ* measurements as described by Chen et al. [18]. The method described here assumes no flow of air from downstream flasks into upstream flasks, an adequate assumption given the design of the flasks (with one of the valves connected to a dip-tube inside the flask).

For the experiments described below, we used a flushing time twice as long as routinely used to ensure dry air conditions inside the flasks. Sampling from reference air cylinders is done by using the same flushing method as for drying the flasks.

3.2. Measurement of stable isotope composition

Stable isotope composition measurements are conducted directly on atmospheric air samples with the Stable Isotopes of CO₂ Absorption Spectrometer (SICAS), a dual-laser spectrometer (CW-IC-TILDAS-D, Aerodyne) operating in the mid-infrared range of the electromagnetic spectrum. The measurement procedure and calibration method are extensively described by Steur et al. [19]. In brief, measurements are performed in static mode and are repeated for nine aliquots per sample. Gas consumption per aliquot is 20 mL, so measuring one sample requires 180 mL of air. Drift correction is carried out by measuring a working reference gas continuously, alternating with every aliquot measurement. Reference gases in high-pressure gas cylinders that bracket the isotopologue mole fractions of the measured samples are measured four times throughout a measurement series. Quadratic calibration curves for all measured isotopologues are determined from a minimum of three reference gas cylinders, including the working gas. Calibrated isotopologue mole fractions are subsequently used to calculate the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and the CO₂ mole fraction, according to the calculations in [20]. From the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ composition the $\Delta^{17}\text{O}$ is calculated by

$$\Delta^{17}\text{O} = \ln(\delta^{17}\text{O} + 1) - \lambda * \ln(\delta^{18}\text{O} + 1), \quad (3)$$

where we use for λ the value 0.5229, after the triple oxygen isotope composition of CO₂ equilibrated with water measured by Barkan and Luz [21].

Table 1. Mean differences between the CIO flask measurements 1 day after filling the flasks with gas from the QC, and the QC measurements. Also, the standard deviations of all differences are shown. In this analysis measurements of the 20 flasks used for the storage experiment were included. The values in brackets in the $\delta^{13}\text{C}$ column show values of measurements conducted after 15–20 days of storage.

| | CO_2 (ppm) | $\delta^{13}\text{C}$ (‰) | $\delta^{18}\text{O}$ (‰) | $\delta^{17}\text{O}$ (‰) | $\Delta^{17}\text{O}$ (‰) |
|--------------------|------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| mean difference | −0.06 | −0.03 (−0.01) | 0.016 | 0.00 | 0.00 |
| Standard deviation | 0.1 | 0.07 (0.019) | 0.03 | 0.068 | 0.05 |

A quality control cylinder (QC), or a known unknown, is always included in the measurement series and is measured, just like the reference cylinders, four times throughout the series. As it is not used to determine the calibration curves it is an indicator for the quality of the measurement. Per measurement series the repeatability, being the standard deviation of the QC measurements conducted in one measurement series, and the accuracy, defined as the difference between the mean of the QC measurements and the assigned value of the QC, can be determined. In the experiments presented in this study flasks filled with gas from the QC are used and the difference between the values of gas in the flasks and in the original cylinder are studied. The QC contains gas with a CO_2 amount fraction of $417.11 \mu\text{mol mol}^{-1}$, and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -9.13 and -3.25 ‰ on the VPDB($-\text{CO}_2$) scale, respectively. Flask measurements are compared to QC measurements of that same measurement series and are therefore independent of scale uncertainties or instrumental inaccuracies of the QC measurements. QC measurements of the total measurement period, the first 5 months of 2022, were analysed and no drifts were detected that would influence the comparison between the flasks and the QC measurements. The measurement uncertainty of the filled flasks (including the measurement stability and the uncertainty introduced by sampling of the air) is determined by analysing differences between flask measurements 1 day after filling the flasks and the measurements of the QC from that same measurement series. The mean and standard deviations of the differences are shown in Table 1. Two out of 20 flasks showed deviating CO_2 mole fractions higher than 0.5 ppm, which could be the result of incomplete flushing of the flasks. Results from these 2 flasks are therefore not included in determination of the measurement uncertainty. When the two deviating flasks are included in the uncertainty analysis this results in a mean difference of -0.12 and a standard deviation of 0.22, instead of the values of -0.06 and 0.1 that are presented in Table 1. Hence the sampling method is a potential source for inaccuracies when doing measurements of atmospheric samples in glass sample flasks.

Under normal conditions, the SICAS shows repeatabilities of 0.03, 0.02, 0.04 and 0.04 ‰ for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$, respectively. Overall the standard deviations of the differences of the 20 flasks samples are slightly higher (lower than twice as high), which we attribute to the overall increase in uncertainty as a consequence of the sampling method. The measurement uncertainty of the $\delta^{13}\text{C}$ measurements is, however, more than twice as high than usual as the result of low repeatability of the measurement instrument during the period right after filling the flasks. This deviating repeatability is only persistently present in the $\delta^{13}\text{C}$ values, indicating that the $^{13}\text{C}^{16}\text{O}_2$

absorption peak was slightly misfitted during that period. Repeatability is better, and more representative for $\delta^{13}\text{C}$ measurements of the SICAS, during the period 15–20 days after filling of the flasks (shown in brackets in Table 1).

3.3. Enriched water experiment

To study the difference in permeability of the CIO Viton and PCTFE flasks, an experiment was set up in which two flasks of each type were stored in a styrofoam box, together with an open beaker containing 100 mL of isotope-enriched water, exposing the flasks to an isotopically enriched high humidity environment. From own observations and earlier studies [9,10] it can be concluded that the drift in oxygen isotopes, when stored under normal circumstances in the lab, is negative. By using enriched water for this experiment it was ensured that any drift towards a heavier oxygen isotope composition of CO_2 in the flasks can be unambiguously linked to permeation of the enriched water into the flasks. The enriched water was prepared by gravimetrically mixing demineralised water with a smaller amount of water highly enriched in $\delta^{18}\text{O}$ (^{18}O abundance is 0.98, ^{17}O abundance is 0.004). With the exact weight of the two components and their isotope compositions, it was calculated that the mixture has a $\delta^{18}\text{O}$ value of 1073 ‰ and a $\delta^{17}\text{O}$ value of 19.8 ‰ on the VSMOW scale. The $\delta^{17}\text{O}$ value does not differ much from natural waters and, therefore, it is expected that the drift in $\delta^{17}\text{O}$ of the CO_2 in the flasks will not deviate from normal storage conditions. The four flasks were dried following the routine method and were subsequently sampled with air from the QC as described in Section 3.1. Measurements were conducted on the SICAS 1 day after sampling, before the flasks were put in the box together with the enriched water to check the sampling process, and 35 days after sampling, to check whether a drift in oxygen isotopes is observed that can be linked to the enriched water.

The results of the enriched water experiment are summarised in Table 2 showing the differences between the flask measurements and the QC measurements for CO_2 mole fractions and the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$. Day 0 measurements are shown to check the quality of the filling of the flasks as well as the quality of the measurements and the reliability of the estimated uncertainties. A significant difference of -0.65 ppm is observed in the CO_2 mole fraction of one of the PCTFE flasks. Despite this difference in CO_2 , all isotopic compositions of the same flask at day 0 are as expected. The difference in CO_2 might be due to insufficient flushing of the flask, as its position during filling was the flask furthest from the cylinder. A leak with the consequence of lab air leaking into the flask does not seem plausible as we would then expect a higher CO_2 mole fraction than

Table 2. Differences between QC and flask CO_2 mole fraction and stable isotope composition measurements of the enriched water experiment at the day of filling the flasks and after 35 days of storage in the vicinity of enriched water.

| Flask type | CO_2 (ppm) | | $\delta^{13}\text{C}$ (‰) | | $\delta^{18}\text{O}$ (‰) | | $\delta^{17}\text{O}$ (‰) | | $\Delta^{17}\text{O}$ (‰) | |
|------------|---------------------|--------|---------------------------|--------|---------------------------|--------|---------------------------|--------|---------------------------|--------|
| | Day 0 | Day 35 | Day 0 | Day 35 | Day 0 | Day 35 | Day 0 | Day 35 | Day 0 | Day 35 |
| Viton | -0.03 | 0.00 | 0.003 | -0.02 | 0.01 | 0.33 | 0.06 | -0.1 | 0.04 | -0.28 |
| Viton | -0.01 | -0.07 | -0.15 | -0.03 | -0.03 | 0.41 | -0.03 | 0.00 | -0.04 | -0.2 |
| PCTFE | -0.65 | -0.21 | -0.02 | -0.02 | 0.04 | 0.17 | 0.05 | -0.06 | 0.05 | -0.16 |
| PCTFE | -0.05 | -0.03 | -0.15 | -0.04 | 0.00 | 0.08 | -0.11 | -0.06 | -0.11 | -0.11 |

the QC. It has been acknowledged that flasks containing more than 1.7 % absolute humidity can exhibit CO₂ depletion [22]. The air from the QC has a humidity of >0.002 %, and CO₂ depletion due to increased humidity should therefore not play a role.

The repeatability of the $\delta^{13}\text{C}$ measurements of the QC at times of the measurement at day 0 was worse than usual, as discussed in Section 3.2. The higher deviations of $\delta^{13}\text{C}$ values of two of the four flasks at day 0 are therefore most likely due to instrumental instabilities, and not due to sampling problems. $\delta^{18}\text{O}$ measurements at day 0 show very small deviations from the QC measurements, ranging from 0.03 to 0.04 ‰. The $\delta^{17}\text{O}$ measurements deviate more, as can be expected from the measurement uncertainty of 0.07 ‰ (Table 1). This also applies to the $\Delta^{17}\text{O}$ measurements.

After 35 days of storage with the enriched water, the flasks were taken out of the styrofoam box and analysed. The CO₂ mole fraction of the same PCTFE flask that showed a high negative deviation from the QC at day 0 increased by 0.44 ppm. This change is much higher than the change observed in the other flasks. A small leak in the PCTFE shaft seal could explain this difference, although we would then also expect a higher leak-in of H₂O, and therefore a strong drift in the oxygen isotopes. Drift in oxygen isotopes is slightly stronger than the other PCTFE flask but still much lower than the Viton flasks. Therefore, a leak is not very plausible and the increase in CO₂ remains unexplained. The $\delta^{13}\text{C}$ flask values show very low differences with the QC measurements, ranging from 0.04 to 0.02 ‰, so storage had no effect on the $\delta^{13}\text{C}$ values. The $\delta^{18}\text{O}$ flask measurements show a 0.33 and 0.41 ‰ increase for the Viton flasks and a 0.17 and 0.08 ‰ increase for the PCTFE flasks. As under normal storage conditions a depletion in the $\delta^{18}\text{O}$ values is observed [9,10], we conclude that the enrichment is due to water vapour permeating into the flasks and equilibrating with the CO₂ inside the flasks. The Viton flasks show an enrichment approximately three times higher in $\delta^{18}\text{O}$ than the PCTFE flasks. The PCTFE flasks are hence less susceptible to permeation of water vapour than the Viton flasks, as would be expected from the lower permeation coefficient and the configuration of the valves. As there might have been water present inside the flasks before sampling which counteracted the observed positive change in $\delta^{18}\text{O}$ values, the total change is actually an under-estimation of the equilibration with the enriched water. It is therefore not possible to quantify the difference in change in $\delta^{18}\text{O}$ values using Equation (1). The differences in $\delta^{17}\text{O}$ are in the same order of magnitude as the measurement uncertainties and are therefore not significant. This is as expected since the $\delta^{17}\text{O}$ values of the enriched water do hardly deviate from natural waters, and significant changes would therefore occur only after longer storage times. As $\delta^{17}\text{O}$ values do not change, but $\delta^{18}\text{O}$ values point to significantly more ¹⁸O enrichment, the $\Delta^{17}\text{O}$ values all more to ¹⁷O depletion after 35 days and the $\Delta^{17}\text{O}$ of the Viton flasks changed twice as much.

3.4. Storage experiment

The storage experiment was set up to study the influence of the use of cylindrical flask valves sealed with Viton O-rings on the stability of the oxygen isotopes, in comparison with shaft valves with PCTFE seal tips, and in addition, the influence of drying the flasks using the method developed and implemented at the BGC-IsoLab and described in Section 2.4. 20 flasks in total were used for this experiment, of which 10 with Viton valves and 10 with PCTFE valves. Five of the Viton and five of the PCTFE flasks were initially

conditioned using the BGC-IsoLab method. The ten flasks were, interconnected in series, put in an oven set at a temperature of 60 °C, while evacuating the flasks with a membrane pump (KNF, model N86) for at least 3 days. All 20 flasks were subsequently flushed with dry air (using the method described in Section 3.1), and then filled with gas from the QC according to the standard sampling procedure. Their initial isotopic composition was measured the next day. Subsequently, the flasks were measured approximately every 2–4 weeks over a period of 144 days to monitor any changes in the isotopic composition and CO₂ mole fraction.

The CO₂ mole fraction results for the four categories of the storage experiment are shown in Figure 4. In the four categories, different symbols are used for individual flasks. Repeatability of the four QC measurements of the same measurement series is shown as the grey ribbon. Due to two deviating flasks showing strong depletions (>0.5 ppm) at day 0, all CO₂ mole fractions were normalised to 0 difference at day 0. The two deviating flasks do not show significant deviations in the measured isotope compositions, so their results are still included in the experiment. In the 'Viton unconditioned' group, 4 out of 5 flasks show an increase of CO₂ mole fractions inside the flasks after 114 days, with a maximum increase of 1.45 ppm. In the other groups, no general trend of increasing or decreasing CO₂ mole fractions is observed, but individual flasks show deviations that increase over time. The increasing CO₂ mole fractions in the 'Viton unconditioned' group can be explained by outgassing of ad/absorbed CO₂ from the Viton O-rings. Viton is shown to be more susceptible to outgassing effects than PCTFE [23,24]. Outgassing rates are thereby reduced by baking the material in vacuum [24,25], which is essentially being done when conditioning the flasks. This explains why no increasing trend of CO₂ mole fractions is observed in the 'Viton conditioned' group. Although CO₂ originating from the outgassing processes will be fractionated, additional CO₂ from this source does not impact the stability of the δ¹³C. This is expected as the amount of additional CO₂ derived from the sealing material is very small compared to the amount of CO₂ in the analysed QC air.

Despite the fact that the stability in the PCTFE groups and the conditioned Viton flasks is rather good (when disregarding the flasks showing high deviations at day 0), staying within 0.25 ppm difference from the QC, it is striking that the variability of the flask CO₂ mole fractions is always higher than the measurement uncertainty. CO₂ mole fractions in glass flasks are hence highly sensitive to sampling and storage effects. It should be noted that the pressure in the flasks is lowered by 0.08 bar (equivalent to 180 mL) after every measurement on the SICAS. This causes the pressure in the flasks to drop from ~1 bar to 0.4 bar over the total storage time, thereby increasing the $p_1 - p_2$ term in Equation (1), and thus increasing the permeation flux. Under normal circumstances the $p_1 - p_2$ term would remain stable over time. At low pressures it is, thereby, more likely that species desorb from a surface [26] which could be true for CO₂ adsorbed to the glass walls.

Results of the isotope composition measurements of the storage experiment are shown in Figure 5. As already described in 3.1, the δ¹³C measurements at days 1 and 2 after sampling show a high measurement uncertainty of 0.1 ‰. Subsequent measurements have lower uncertainties between 0.01 and 0.05 ‰ and show excellent agreement of the QC and flask values. In other words, the δ¹³C values do not show any significant drift over the whole storage period in all four groups of flasks.

The $\delta^{18}\text{O}$ measurements show large variations between the groups of flasks that were studied. The highest drifts are observed in the unconditioned Viton flasks. The highest residual is 0.48 ‰ after a storage time of 114 days. Not all flasks from this group show high drifts as two of the flasks show drifts not higher than 0.06 ‰. Hence, again it is clear that differences in surface characteristics of individual flasks have a great influence on the expected drift of $\delta^{18}\text{O}$ values. When the 'Viton unconditioned' group is compared to the 'Viton conditioned' group we see that the scatter between flasks for the latter is much lower. The unconditioned flasks show a standard deviation of the residuals of 0.23 ‰ after 114 days, the conditioned flasks 0.08 ‰ after 107 days. Also, the maximum drift of -0.26 ‰ after 107 days is lower in the conditioned flasks. Because of the smaller scatter, however, it is clear that the drift is systematic and shared between the individual flasks. The size of this drift is about 0.15 ‰ per 100

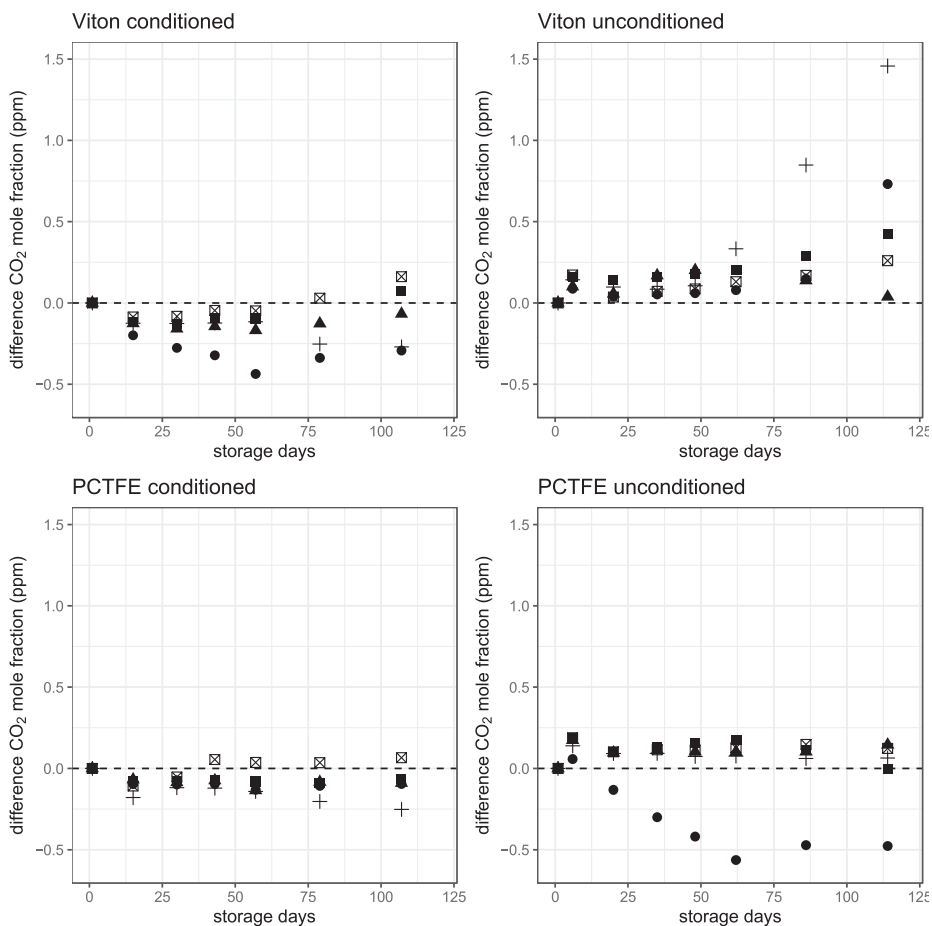


Figure 4. The difference between measured CO₂ mole fraction of the flasks and the QC over time (values are normalised to day 0 measurements). Five times four flasks are shown in the figure, grouped as 'Viton conditioned', 'Viton unconditioned', 'PCTFE conditioned' and 'PCTFE unconditioned', respectively. The different symbols in the groups represent individual flasks. The dashed lines show the position of 0 difference.

days. This is clearly detrimental to achieving the WMO targets of ≤ 0.05 ‰ regardless of the precision of the analytical instrument used. The PCTFE flasks also show differences between the conditioned and unconditioned flasks. The maximum drift for the unconditioned flasks is -0.22 ‰ after 114 days, for the conditioned flasks it is -0.13 ‰ after 107 days. There is a small difference in the scatter of the flasks between the groups being 0.11 ‰ after 114 days for the unconditioned flasks and 0.08 ‰ after 107 days for the conditioned flasks. Whereas there seems to be a systematic drift over time for the unconditioned flasks, such a drift is barely visible (if at all) for the conditioned flasks. In the study by Rothe et al. [10] an average drift rate of -0.0019 ‰ per day was found for the $\delta^{18}\text{O}$ values stored for 160 days in the 1-L PCTFE sealed glass flasks. This is the same average drift of -0.22 ‰ after 114 days as found in the CIO experiment of the unconditioned PCTFE flasks. Results from Figure 1 show that the same BGC-IsoLab flasks continued to drift for more than 500 days at storage temperatures of 60 °C before saturation was

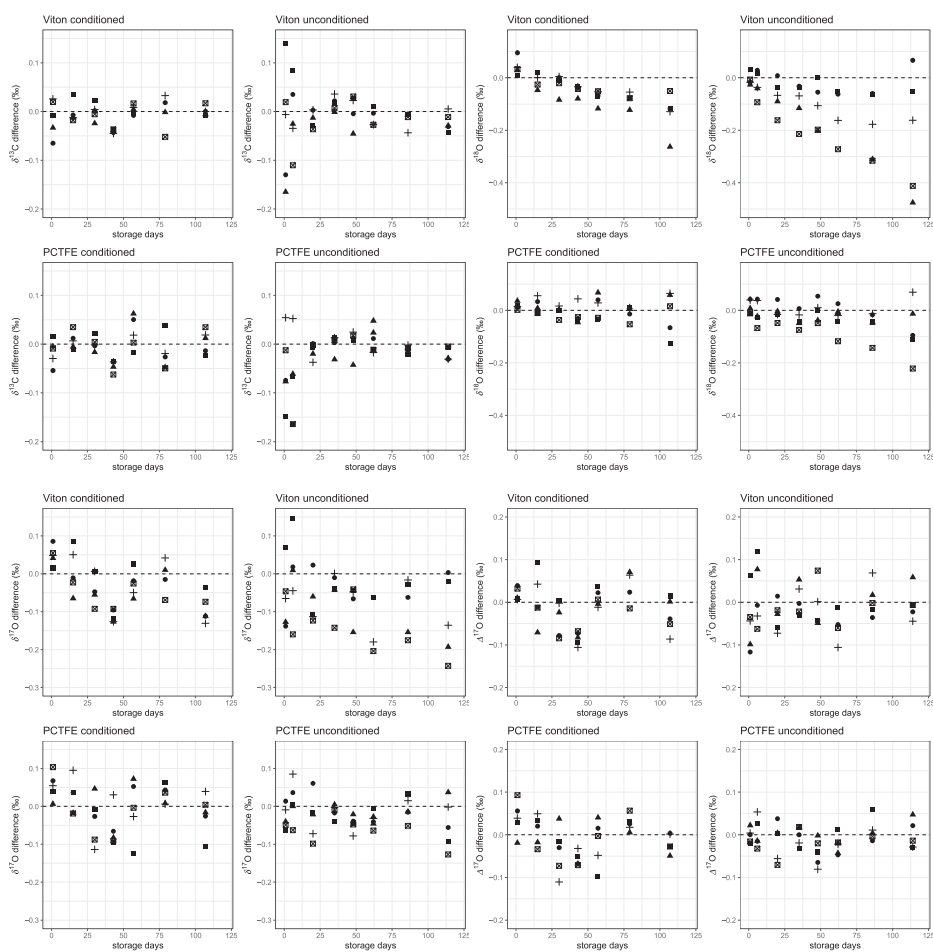


Figure 5. Differences between individual flask measurements and QC measurements over time for (top left) $\delta^{13}\text{C}$, (top right) $\delta^{18}\text{O}$, (bottom left) $\delta^{17}\text{O}$ and (bottom right) $\Delta^{17}\text{O}$. The different shapes in the groups represent individual flasks, shapes are used consistently in Figure 5. The dashed line shows the position of 0 difference.

reached with a maximum drift of -2.64 ‰. It is therefore expected that the drift in $\delta^{18}\text{O}$ in the CIO unconditioned PCTFE flasks will continue until saturation is reached. For a similar maximum drift of -2.64 ‰, as found in the long-time storage experiment conducted at the BGC-IsoLab, with the average drift rate of -0.0019 ‰, continuation of the drift for almost 1400 days would be expected. It is clear that conditioning the flasks before sampling and using PCTFE flask seals is the most effective method to reduce the drift in $\delta^{18}\text{O}$. This results in stable $\delta^{18}\text{O}$ values over a period of 75 days, after this period drifts are observed in two of the five flasks. The $\delta^{17}\text{O}$ differences are typically twice as low as the $\delta^{18}\text{O}$ differences in all groups. This is according to expectations with a drift due to the exchange of CO_2 with water. Also, in accordance with this is the fact that there are no significant drifts observed in the $\Delta^{17}\text{O}$ values in any of the four groups. As the $\Delta^{17}\text{O}$ of the QC is very close to 0, which is per definition the $\Delta^{17}\text{O}$ value that we chose for CO_2 equilibrated with water, there are no significant drifts observed in the $\Delta^{17}\text{O}$ values.

Rothe et al. [10] observed no significant difference in drift of $\delta^{18}\text{O}$ between PCTFE and PFA-sealed flasks. As the permeation coefficient of PCTFE for water is much lower than for PFA they concluded that water permeating into the flasks would not be the major cause of the drift. As the drift increases over a period of several months, while equilibration of CO_2 with water inside the flasks should occur within a short time period, they argued that an exchange of CO_2 can potentially occur with $-\text{OH}$ bonds in the glass structure. However, the large differences in drift between the 'Viton conditioned' and 'Viton unconditioned' group observed in the results of the CIO storage experiments point to a strong influence of the amount of water sticking to the glass walls at the moment of sampling. In the results, contrary to the results in [10], there is a difference in drift of $\delta^{18}\text{O}$ values between the Viton and PCTFE flasks. As both flasks are made out of borosilicate glass, this difference cannot be explained by exchange of CO_2 with $-\text{OH}$ bonds in the glass structure. As permeation occurs through both of the sealing materials but much slower through the PCTFE than the Viton valves, the picture arising from the four cases is consistent: both water inside the flasks and water permeating into the flasks contribute to the drift in oxygen isotopes, the former being equal in both the Viton and PCTFE flasks, the latter much more severe in the Viton flasks. Still, water permeation into the flasks also plays a role for the PCTFE flasks, as the enriched water experiment shows. Even for PCTFE, the effect of water permeation through the seals will, under normal storage conditions, result in drifts in the oxygen isotope composition of CO_2 higher than the WMO/GAW compatibility goals after storage times longer than 100 days.

Contrary to the Viton flasks, which have been in use for air sampling for a longer time, the PCTFE flasks were bought new for this experiment. Older flasks can have different surface characteristics, for instance, the presence of (micro-)cracks or contaminated walls which can influence the effectiveness of removing precipitated water/water molecules adsorbed to the glass surface. This could then also explain the higher difference in drift between the Viton conditioned and unconditioned flasks, in comparison to the PCTFE conditioned and unconditioned flasks. From tests with a glass cold trap in a glass vacuum system for the collection of CO_2 at the CIO, it is known that micro-cracks cause higher CO_2 memory of the glass. The CO_2 memory of the glass cold trap gradually increases when it is exposed to frequent temperature change cycles from -190 °C to room temperature and *vice versa*. CIO flasks are normally not exposed to high-

temperature gradients nor put under vacuum. It is therefore not expected that micro-cracks play a significant role in changing the surface area characteristics. It is more plausible that the flasks are contaminated with (sea) salt particles from frequent sampling at atmospheric measurement stations, for instance, the two coastal stations Lutjewad (Netherlands) and Mace Head (Ireland) which are both permanently monitored at CIO using flask samples. Adsorption of sea salt particles on the glass surface can, under ambient conditions, lead to a thin film of water forming on the salt [27].

4. Conclusions

Long-time storage experiments conducted at the BGC-IsoLab show that storage temperature enhances the drift rate of oxygen isotopes of CO₂-in-air stored in glass sample flasks. Drift rates differ strongly between different flasks, and drifts slow down and eventually stop after very long storage times (more than 500 days for flasks stored 60 °C). A drying method has been successfully developed and implemented by the BGC-IsoLab that limits the drift of CO₂ oxygen isotopes in glass flasks significantly. The enriched water experiment conducted at the CIO shows that water permeates into glass sample flasks, at a rate that is dependent on the used seal material as well as the geometry. Water permeates at a higher rate through cylindrical Viton O-ring seals than through PCTFE shaft seals, but even in the latter, the effect is not negligible. Furthermore, water is usually already present at or in the walls of glass flasks. This water equilibrates with the CO₂ inside the flasks, thereby changing the oxygen isotope composition of the air which is detrimental to achieving the WMO accuracy goal for $\delta^{18}\text{O}$ measurements for atmospheric CO₂. For $\delta^{13}\text{C}$, and also for $\Delta^{17}\text{O}$, the influence of water is far less critical. For the conducted experiments there was no focus on the preservation of the CO₂ mole fraction (it was used only as a quality check for filling the flasks) and our results are inconclusive.

The drying method as developed at BGC-IsoLab to remove adsorbed water sticking to the glass walls is very effective in enhancing the stability of the oxygen isotopes of CO₂-in-air in the flasks. High storage temperatures speed up the drift rates of oxygen isotopes as seen in PCTFE shaft sealed flasks that were dried according to the BGC-IsoLab drying method (evacuating while heating to 60 °C for more than 72 h) and stored at 60 °C: a drift rate of -0.0004 ‰ per day is still observed. CIO flasks with PCTFE shaft seals stored at room temperature and dried following the BGC-IsoLab drying method show no drifts of oxygen isotopes higher than the WMO/GAW compatibility goals of 0.05 ‰ until 75 days of storage. CIO flasks with Viton seals, dried following the same method, still show drifts higher than 0.05 ‰ of oxygen isotopes already after 2 weeks. This difference is caused by the higher permeation of water through the Viton O-rings in comparison to the PCTFE shaft seals, but in addition, the surface characteristics of the used Viton flasks (salt particles sticking to the glass wall), in contrast with the new PCTFE ones, might play a role. The flasks sealing materials and conditioning regimes tested here do not remove the storage-induced $\delta^{18}\text{O}$ -CO₂ drift completely, but it is possible to significantly reduce such a drift. Thus we propose the following sampling guidelines when sampling for high-precision measurements of isotopes of atmospheric CO₂:

- Use flasks that are fitted with PCTFE seals

- Condition the flasks using the BGC-IsoLab drying method
- Flush the glass flasks with dried air before sampling
- If possible aim to analyse the flasks as soon as possible, but certainly within 75 days of taking the sample

These suggestions may be of particular importance where very humid air is sampled or a drying mechanism not working very efficiently, or in situations where the time between sampling and analysis is very long (e.g. sample collection in Antarctica).

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

The data that support the findings of this study are available via <https://surfdrive.surf.nl/files/index.php/s/viSubY0ySMTaWo1>.

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