Measurements of Drift in the Stable Isotopic Composition of Atmospheric CO_2 inside Storage Flasks
Study performed as a Bachelor Research Project

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Abstract

Previous research has indicated that drift occurs in the stable isotope (si) composition of atmospheric CO_2 (atm-CO_2) inside storage flasks over time. A similar drift has been found at the CIO labs, when research regarding this occurrence was conducted. However, the ICOS-CAL lab in Jena claims that there is not such a drift present in their Kel-F storage flasks. Kel-F flasks have a different seal material (PCTFE), with a lower permeation coefficient than the standard CIO flasks, which have Viton O-rings as a seal. Therefore this research aims to answer the question; are the drifts of si atm-CO_2 mole fractions over time in flasks filled with discrete air samples caused by permeation of water through Viton O-ring seals? The research consisted of 3 experiments, to provide an answer to the research question. From the first experiment it was concluded that there is a drift in both the Viton-flasks, as well as, in the PCTFE-flasks, although the Viton-flasks show a drift approximately 10 times as large as that of the PCTFE-flasks. From the second experiment it was determined that the difference in drift between the ICOS-CAL and the CIO lab was not caused by the different conditioning method, as the extreme conditioning method used by the ICOS-CAL lab did not result in a significant decrease in drift, but only caused the different flask measurements to be closer to each-other. From the third experiment it was concluded that permeation of water occurs in both flask types, however the Viton-flasks showed a significant larger drift by permeation (approximately 3.5 times as large). Therefore, the conclusion of this report is that the drift in si atm-CO_2 mole fractions over time in flasks filled with discrete air samples at the CIO labs are most likely caused by permeation of water through Viton O-ring seals.

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Contents

1 Acknowledgements

This research was carried out at the CIO labs at the University of Groningen, which provided the space and materials to perform the experiments. Firstly, I would like to thank prof. dr. H.A.J. Meijer for providing helpful feedback during the process of this research. Secondly, I must acknowledge that my research would have been impossible without the aid of all the CIO staff members who helped me at the labs, with a special thanks to B.A.M Kers who gave me invaluable help during the setup of the experiments. Thirdly, a special thanks goes to dr. ir. H.A. Scheeren for providing preliminary research data, which was used as a comparison for results and which provided enough data for a hypothesis. At last I am sincerely grateful for all the help and advice that I received from P.M. Steur to be able to conduct this research and to improve the overall quality of this report.

2   Introduction

2.1   The importance of air samples

Climate change is one of the most pressing issues of modern times. Global warming results in the warming of the atmosphere and oceans, the diminishing of snow and ice and in a rise of the sea level. This consequently results in the destruction of ecosystems which might have disastrous consequences. Research indicates that climate change has been extensively enhanced by humans through the emission of greenhouse gases like CO_2, CH_4, and N_2O, resulting in enhanced radiative forcing or "a change in energy flux in the atmosphere". Essentially, the excessive greenhouse gases in the atmosphere create a blanket trapping outgoing radiative energy, resulting in a rise in temperature on earth (IPCC, 2014). The earth actually depends on this blanket to a certain extent, as the natural concentration of greenhouse gases, together with H_2O, warm up the temperature of the earth to 16°C instead of -17°C, which would be the average temperature on earth if no greenhouse gases were present at all, making the earth more or less inhabitable (Marshall and Plumb, 2008). Greenhouse gases are thus not exclusively bad; however, the industrial revolution has resulted in a tremendous increase in the burning of fossil fuels and therefore the emission of greenhouse gases into the atmosphere. This has resulted in an over-plus of greenhouse gases, trapping more heat, resulting in enhanced global warming.

CO_2 is by far the largest contributor of all the greenhouse gases in global warming. For comparison, CO_2 has had the largest increase in absolute atmospheric concentration since the industrial revolution: 105000 parts per billion (ppb) versus 1050 ppb and 25 ppb for CH_4 and N_2O respectively (Marshall and Plumb, 2008). Furthermore, CO_2 has a significant higher lifetime than CH_4 and N_2O, specifically CO_2 has a lifetime of 300-1000 years compared to 12.4 and 121 years for CH_4 and N_2O respectively (IPCC, 2014; Ciais et al., 2013). It is therefore paramount to keep track of sources and sinks in atmospheric CO_2 (atm-CO_2) all over the globe, by analysing collected air samples. A viable way to monitor atm-CO_2 is to measure the stable isotope (si) composition of atm-CO_2. The stable isotopes of atm-CO_2 are expressed as $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$, where the delta values stand for the ratios of a sample over the ratios of a reference value. The stable isotopes can be used as an additional tool to distinguish between anthropogenic emissions and the influence of the biosphere on varying CO_2 mole fractions (Pataki et al., 2003; Zhou et al., 2005). Air samples can be taken at measurement locations all around the world and analysed in isotopic research labs. To exactly map out the effects of global warming, communication and exchange of data between labs around the globe is key. Air samples, saved in flasks, are therefore often exchanged between multiple science labs.

2.2   Drift in isotopic composition

The Centre for Isotope Research (CIO) lab in Groningen is such a science lab. The CIO focuses on improving existing measuring instruments and methods and carries out research regarding radiocarbon dating, stable isotopes and atmospheric measurements amongst others (RUG, 2022). At the CIO labs, it has been noted that in sample flasks, when storage times are long, the isotopic composition changes, which might lead to incorrect results if not corrected (Steur et al., 2021). This is an occurrence often referred to as 'drift', which is also mentioned in Sturm et al. (2004), Rothe et al. (2003) and Keeling et al. (1998). More specific, the most notable drift that is often found inside storage flasks is a decrease of the $\delta^{18}O$ value over time. According to Sturm et al. (2004); Rothe et al. (2003); Keeling et al. (1998) the drift can be caused by multiple sources, such as permeation of water through O-ring seals (reacting with the air sample), remaining water inside the flasks (reacting with the air sample), leakage, oxidation of grease for lubrication of the O-rings or OH-binding inside the flask from the borosilicate glass itself. However, they can all agree that water inside the flask, whether through permeation or by already being present from the start, causes the largest change in $\delta^{18}O$. It can be assumed that water is the cause when the depletion in $\delta^{18}O$ is twice as large as the depletion in $\delta^{17}O$, indicating an equilibration of CO_2 with H_2O (Steur et al., 2021).

It is a recurring problem, which has resulted in confusion between labs in the past, as different measurements from the same sample tanks have resulted in varying si atm-CO_2 concentrations in different labs (Wendeberg et al., 2013). Consequently, multiple measurements were done at the CIO-labs to find out if there are indeed drifts present and if they are caused by permeation through O-rings or that there might be another possible explanation.
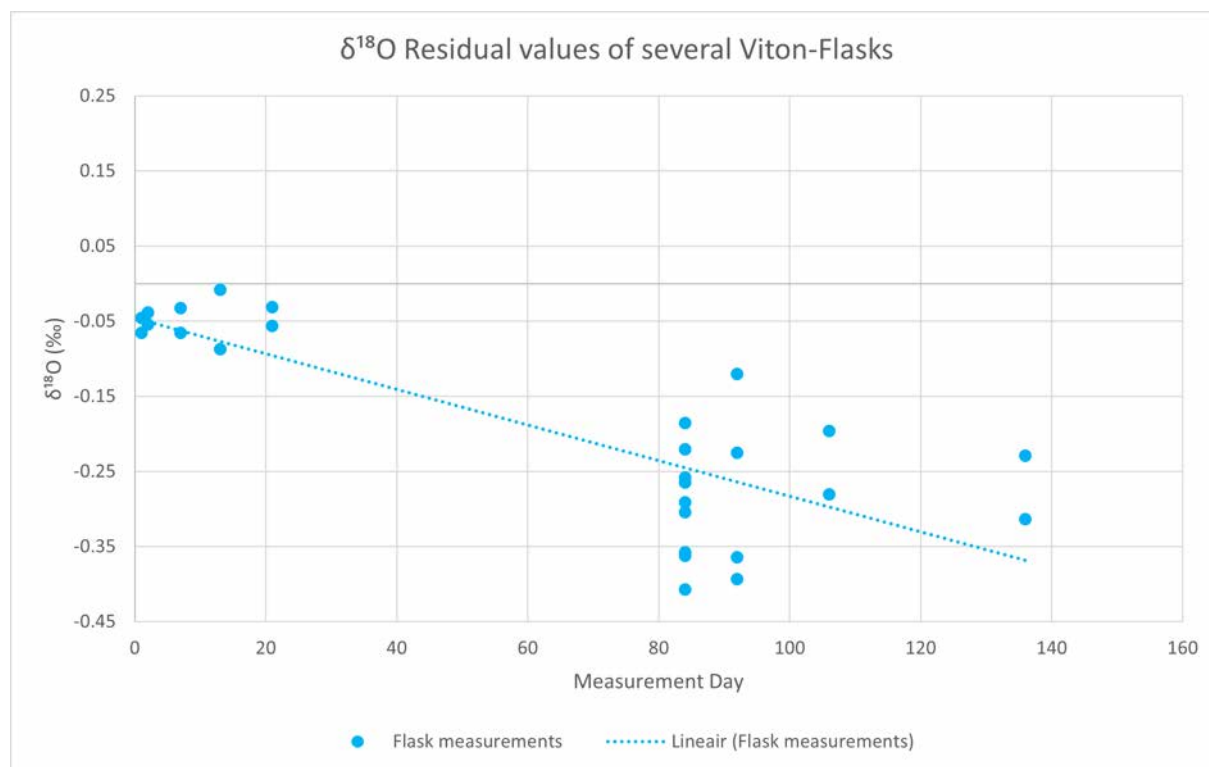
Figure 1: Preliminary research results from a research carried out by P.M. Steur. A total of 15 flasks with Viton-seals were measured over a maximum of 136 days. A linear approximation was added to give a clear indication of the total $\delta^{18}O$ change.

In figure 1 and table 1 some results of these experiments can be seen. Figure 1 presents the $\delta^{18}O$ results of an experiment carried out by P.M. Steur to indicate whether a drift was present in the storage flasks. Table 1 presents the results of another experiment carried out by P.M. Steur to confirm that permeation through Viton O-rings occurs. This was researched by exposing the flasks with Viton seals to a beaker with water highly enriched in ^{18}O, which should be noticeable in the $\delta^{18}O$ values inside the flasks after a certain amount of time. The results are shown in a table instead of a figure, as there were only two data-sets consisting of two flasks. It can be noted that there was indeed a drift detected over time, as seen as the decrease in $\delta^{18}O$ of -0.0024 ± 0.0004 ‰ per day in figure 1 and that there also occurs permeation through Viton seals, as can be seen in table 1 (the increases of 2.50 ± 0.08 and 1.93 ± 0.08 ‰ in $\delta^{18}O$ for the flasks with Viton seals (also referred to as Viton-flasks from now) compared to the reference gas). For simplicity only the $\delta^{18}O$ measurement results were added as figures, as they show the most notable change (for the other stable isotope measurements see appendix 8.1.1). It must be noted that the $\delta^{17}O$ graph in appendix 8.1.1 shows a decline approximately half of the $\delta^{18}O$ value change, indicating that water most certainly equilibrated with CO_2. Also note that the drift is calculated from the linear approximation as the data-points are to scattered to use any hard measurement numbers.

Preliminary research results for experiment with enriched water			
Sample	$\delta^{13}C$ value (‰)	$\delta^{17}O$ value (‰)	$\delta^{18}O$ value (‰)
Reference gas (Tank)	-9.14 ± 0.02	19.71 ± 0.06	38.08 ± 0.04
Viton-flask (9271) Residual value change	0 ± 0.04	-0.04 ± 0.10	2.50 ± 0.08
Viton-flask (9272) Residual value change	0.02 ± 0.04	0.01 ± 0.11	1.93 ± 0.08

Table 1: Stable isotopes of atm-CO_2 measurements of 2 Viton flasks exposed to water highly enriched in ^{18}O, given as residual values with respect to the reference gas. The time between the first and last measurements was 66 days. Preliminary research results of experiment carried out by P.M. Steur

The Integrated Carbon Observation System - Central Analytical Laboratories (ICOS-CAL) lab in Jena, Germany is another science lab, which tracks carbon fluxes in Europe and adjacent regions by monitoring the atmosphere and its greenhouse gas exchange fluxes with ecosystems and the oceans through integrated networks (ICOS-CAL, 2022).

The ICOS-CAL lab, in contrast with the CIO findings and previous research, claims that their flasks do not show any sign of drift. At the ICOS-CAL lab, polychlorotrifluoroethylene-seals (PCTFE-seals) are used instead of the Viton seals used at the CIO labs. The flasks with PCTFE-seals will be referred to as PCTFE-flasks from now on. This is another method/material to seal the flasks. Instead of sealing the flask off with two Viton O-rings between the glass and the pin (Viton-flasks), the PCTFE-flasks uses a system where the seal is the pin. This pin can be closed thoroughly resulting in a different closing mechanism. Furthermore, the seal is, as the name suggests, made of a different material, namely PCTFE. According to Rothe et al. (2003); Sturm et al. (2004) the difference in drift might be caused by the difference in permeation coefficients (the rate of molecular penetration of gases, vapours or fluids through the material membrane of a solid) between the flasks. Viton has a permeation coefficient varying from 40 to 216 $*10^{15}m^2s^{-1}hPa^{-1}$, whereas PCTFE has a permeation coefficient of 0.22 $*10^{15}m^2s^{-1}hPa^{-1}$ (Sturm et al., 2004). To exclude that the found drift at the CIO-labs was caused by measurements errors or coincidence and to find out more about the mechanism behind the drift, new measurements were taken, as seen in figure 2. In this new experiment both Viton- and PCTFE-flasks were used to explore if there is indeed a difference between the flask types, which could provide insight in whether permeation of water through the seals or water already inside the flask might cause the drift. Furthermore, a distinction between Viton-flasks with an extra cap and without the extra cap was made as well. This is an experiment (except for the Viton-flasks with extra caps) comparable to an experiment carried out by Rothe et al. (2003), where PFA-flasks (Viton) were compared to PCTFE-flasks, as can be seen in figure 3.
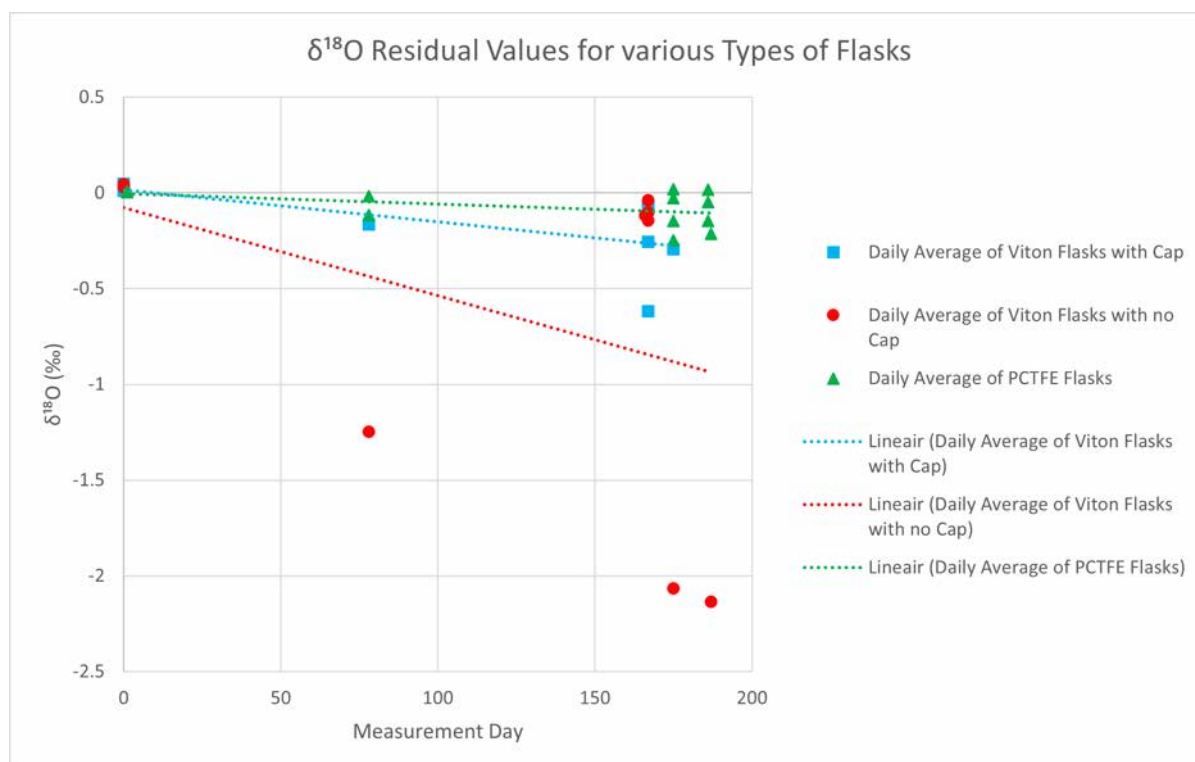

Figure 2: Preliminary research results from dr. ir. H.A. Scheeren. 3 different types of flasks were measured and graphed over a total of 187 days, indicated by the different colours and mark types, as seen in the legend. Also note that linear approximations are added to give a general overview of the values over time.

As can be noted in figure 2, a significant difference in drift of $\delta^{18}O$ over time between flask types can be found. This might be the direct consequence of varying permeation coefficients, however as there are also multiple Viton-flask data points that suggest that there is no significant difference, these results are therefore not conclusive. The PCTFE-flasks show a daily decline of 0.0006 ± 0.0004 ‰. The other stable isotope measurements of this experiment can be found in appendix 8.1.2. It must be noted that adding an extra cap might reduce the drift, as indicated by the flatter graph.
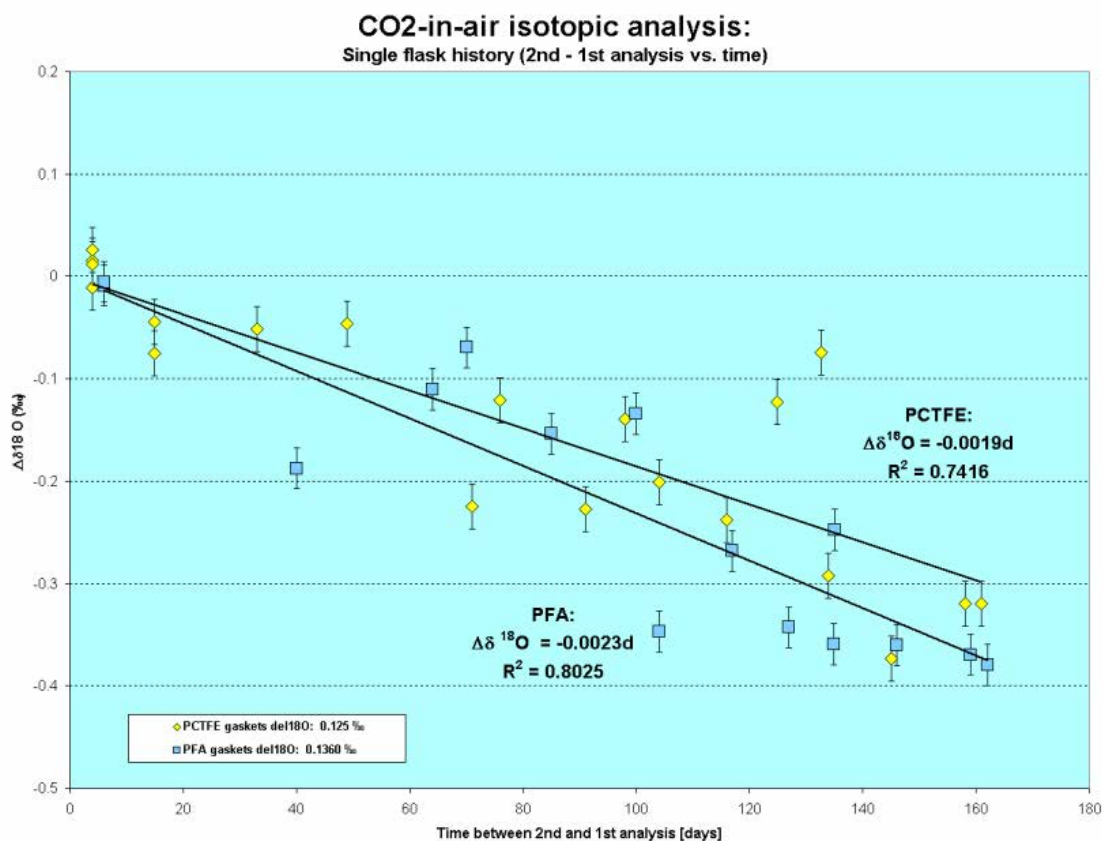

Figure 3: A $\delta^{18}O$ value change comparison of PFA-flasks (Viton) and PCTFE-flasks from Rothe et al. (2003). Figure adapted from (Rothe et al., 2003).

In figure 3 it can be noted that the daily $\delta^{18}O$ value change for PFA/Viton-flasks is -0.0023 ± 0.02 ‰, which is almost the same result (excluding errors) as the found decline of the $\delta^{18}O$ values in figure 1. The daily $\delta^{18}O$ value change for PCTFE-flasks is -0.0019 ± 0.02 ‰. The PCTFE-flask value change is almost equal to the PFA/Viton-flask value change, which is in contrast to the results seen in figure 2.

2.3   Aim of the research

The aim of this research is therefore to provide a clear insight in the isotopic behaviour in stored flasks over time at the CIO labs and to find out what exactly causes this drift. Furthermore, this report will provide an insightful comparison between Viton and PCTFE-flasks regarding their capacity to prevent drift. The main research question that this report will answer is:

- Are the drifts of si atm-CO_2 mole fractions over time in flasks filled with discrete air samples caused by permeation of water through Viton O-ring seals?

3   Theory

3.1   Storage and Flask types

As mentioned in the introduction, the main research question is; if the difference in flask types (specifically the Viton O-rings) causes the difference in drift. For the experiment, the Viton and PCTFE-flasks are used for comparison, as seen in figure 4. The PCTFE-flasks are from the brand Kel-F and are closed with a valve of the PCTFE material that seals the tapered shaft of the flask. Each flask has two shafts and thus 2 inlets, as well as 2 valves. Although the Viton-flask types (glassware factories, where they were made or repaired) differ, the glass is comparable, both to each-other, as well as, to the PCTFE-flasks. All of the Viton-flask types use the same double Viton O-rings to seal off the cylindrical Louwers Hapert shaft of the flask (Sturm et al., 2004). Viton is a specific brand of synthetic rubber and fluoropolymer elastomer. Both the Viton- and the PCTFE-flasks have no extra buffer volume. Furthermore, it must be noted that the PCTFE-flasks are relatively new compared to the Viton-flasks, which might affect the smoothness of the glass and therefore possibly affect the amount of remaining water after conditioning.

Figure 4: Figures showing the 2 types of flasks; Viton-flask on the left and PCTFE-flask on the right

All the flasks (when not being measured) were stored in closed Zarges boxes (normally- and extremely conditioned flasks in separate boxes), at standard room temperature and pressure. The flasks used for the enriched water experiment were stored in a special foam box, for the purpose of containing the enriched water vapour more proficiently.

3.2   Permeation process

As mentioned in paragraph 2.2 permeation is the molecular penetration of gases, vapours or fluids through the material membrane of a solid. The permeation coefficient differs significantly for different materials. For instance, the permeation coefficient for H_2O varies between 40 to $216 *10^{-15}$ $m^2s^{-1}hPa^{-1}$ (Viton) and $0.22 *10^{-15}$ $m^2s^{-1}hPa^{-1}$ (PCTFE) (Sturm et al., 2004). Permeation is therefore a process not to be overlooked during the design of storage flasks and it possibly contributes significantly to the drifts. It is thus paramount to understand the principle of permeation. The permeation process can be quantitatively described as following: First of, the flux of diffusing species is given by Fick's first law:

$$J = -D\nabla c \tag{1}$$

Where D is the concentration-independent, isotropic diffusion coefficient and c the concentration of diffusing species. This equation can be simplified to an approximation for high concentrations or a longer period of time to:

$$J = -D\frac{(c_2 - c_1)}{d} \tag{2}$$

Where d is the membrane thickness. The solubility coefficient, S is given by:

$$S = \frac{c}{p} \tag{3}$$

Here p is the gas pressure. Rewriting equation 2 then gives:

$$J = DS\frac{(p_1 - p_2)}{d} \qquad (4)$$

Where the permeation coefficient, K is then given by:

$$K = DS \qquad (5)$$

The permeation coefficient is therefore dependent on the pressure difference, but also, because of the diffusion coefficient, on temperature (approximately exponential) (Rothe et al., 2003). It is therefore paramount to keep conditions as constant as possible, to prevent differences in pressure or temperature during filling and storage, which might affect the permeation process and therefore drift.

3.3 Measurement Systems

3.3.1 SICAS

There are multiple ways to measure the si atm-CO_2 mole fractions in an air sample, such as isotope ratio mass spectrometry (IRMS) and Fourier-transform infrared spectroscopy (FTIR spectroscopy) (Allison and Francey, 1995). Traditionally IRMS is used for high-precision stable isotope measurements, however this method requires the extraction of CO_2 from the air sample before measurement. Furthermore, very strict, 100 % extraction procedures need to be applied to acquire an adequate sample (Wendeberg et al., 2013). This is often where random and systematic errors occur. Therefore, FTIR spectroscopy or laser absorption spectrometry has been preferred in recent research as smaller sample sizes suffice, $\delta^{17}O$ in addition to $\delta^{13}C$ and $\delta^{18}O$ can be directly measured and the possibility to leakage or change in composition due to exposure to other gases or water is smaller (Steur et al., 2021).

At the CIO labs in Groningen laser absorption spectroscopy has the preference as well, for the reasons listed above. Since September 2017 an Aerodyne dual-laser optical spectrometer (CW-IC-TILDAS-D) is used for the measurements of the si of CO_2, therefore also referred to as the Stable Isotopes of CO_2 Absorption Spectrometer (SICAS) (Steur et al., 2021). The isotopologues that are measured are $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$ and $^{12}C^{16}O^{17}O$ also referred to as 626, 636, 628 and 627 respectively, using the HITRAN database notation(Gordon et al., 2017). All the sample values are calibrated against a reference value, resulting in the previous mentioned delta values. The $\delta^{13}C$ values are calibrated against the VPDB (Vienna Pee Dee Belemnite) scale and the $\delta^{18}O$ and $\delta^{17}O$ are calibrated against the VSMOW (Vienna Standard Mean Ocean Water) scale (Steur et al., 2021). The SICAS will be used in this research to analyse the isotopic behaviour within flasks over time. See the report of Steur et al. (2021) for more details about the working system of the SICAS.
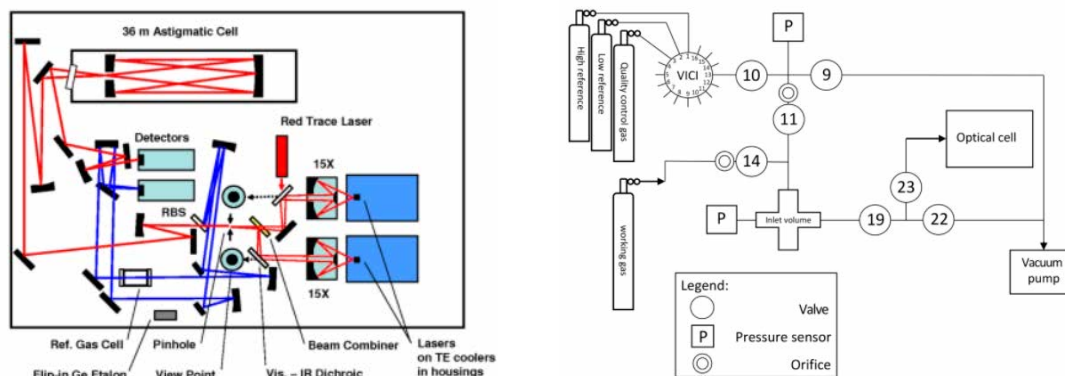
Figure 5: On the left, a scheme of the optical board of the SICAS (figure adapted from (McManus et al., 2015)). Two pathways are shown, both consisting of signals from both lasers: the sample measurement beam in red and the reference beam in blue. The reference pathway is in our case only used for fitting purposes. RBS stands for reference beam splitter. One of the detectors is used to read the signal of the sample beam, the other for the reference beam. The red trace laser is co-aligned with the sample path to visualize the sample pathway to ease alignment. On the right, a scheme of the gas inlet system of the SICAS with one VICI multi-valve inlet port, connected to three high-pressure natural-air tanks and 12 free ports for samples. It includes an extra inlet port for the working gas, also a high-pressure natural-air tank. Figure adapted from (Steur et al., 2021).

3.3.2   EN PICARRO

During this research the EN PICARRO G2401 gas mole fraction analyser was added to the flushing setup to measure the H_2O concentration of the flushing air. The PICARRO can be used to simultaneously measure the mole fractions of CO_2 (parts per million (ppm)), H_2O (%) and CH_4 (ppm) of a connected sample. At the CIO labs it is often used to give an indication of the composition of the outside air, next to the standard use for experiments, as for instance described by Steur et al. (2021).

4   Methods

4.1   Research Plan

The research consists of 3 different experiments. The first experiment is to explore the difference of drift between the Viton and the PCTFE-flask types. The flasks will be stored and measured every 2 weeks, to see if there is a depletion of $\delta^{18}O$. There will be a total of 5 measurements, 1 start measurement and 4 follow-up measurements. This will thus take 8 weeks or 56 days in total.

The second experiment is to check whether the different method of conditioning (used by the ICOS-CAL lab in Jena) makes any difference in drift. This is done at the same time as the storage experiment, by simply dividing the stored flasks into 2 sub-groups. The first group consisting of both Viton, as well as, PCTFE-flasks will be normally conditioned (following the normal conditioning standards of the CIO)(see paragraph 4.2.1 for further explanation). The second group will be 'extremely' conditioned (following the conditioning strategy of the ICOS-CAL lab, or an approach of it)(see paragraph 4.2.2 for further explanation). This group will also consist of both Viton and PCTFE-flasks.

The third experiment is to check whether permeation actually occurs. This experiment will be carried out by exposing both PCTFE and Viton-flasks to water, highly enriched in $\delta^{18}O$ (for further explanation see paragraph 4.2.3). If permeation occurs a clear signal (substantial increase of $\delta^{18}O$) should be noticeable when the flasks are measured. These flasks will only be measured at the start and again after approximately one month.

4.2   Experimental Setup

A total of 12 PCTFE-flasks were available during the time of the experiments and therefore also 12 Viton-flasks were used for clear comparison. These 24 flasks were divided over separate groups to ensure that all 3 experiments could be performed, as shown in Table 2.

Flask Group Division					
Flask Group	Evacuated in Oven (72 hours)	Thoroughly Flushed (2-3 hours)	Normally Flushed (1 hour)	Exposed to Enriched Water	Total Preparation Time (Including Setup)
PCTFE group 1 (5 flasks)	X	X	-	-	$\approx$ 4 days
PCTFE group 2 (5 flasks)	-	-	X	-	$\approx$ 3 hours
PCTFE group 3 (2 flasks)	-	-	X	X	$\approx$ 1 day
Viton group 1 (5 flasks)	X	X	-	-	$\approx$ 4 days
Viton group 2 (5 flasks)	-	-	X	-	$\approx$ 3 hours
Viton group 3 (2 flasks)	-	-	X	X	$\approx$ 1 day

Table 2: Flask Group Division

4.2.1   Normal conditioning (CIO standard)

Flask conditioning at the CIO labs is done according to a standard conditioning procedure, where the flasks are firstly dried and flushed with dried outside air and after that flushed and filled with a "CIO test cylinder gas" of which the isotopic composition is known. During the process of flask conditioning at the CIO labs, an "old air percentage" of 0.1 % is aimed at. This percentage can be acquired for 10 flasks within an hour of dry air flushing together with 25 minutes of flushing with the test cylinder, assuming a flow of 2.5 litre/minute.

During this research an apparatus, named the EN PICARRO, was added to the flushing setup to measure the H_2O concentration of the flushing air. The water concentration was narrowly monitored and it was observed that H_2O concentrations could be as low as 0.001 $\pm$ 0.001 % instead of 0.015 $\pm$ 0.005 % when 2 hours of dry air flushing, instead of the normal 1 hour of dry air flushing was implemented, as can be seen in appendix 8.2.1. Therefore the 2 hours were taken as the standard during this research, as the 2 hours of dry air flushing ensures a significant decrease in water concentrations. The flushing setup can be seen in figure 6.
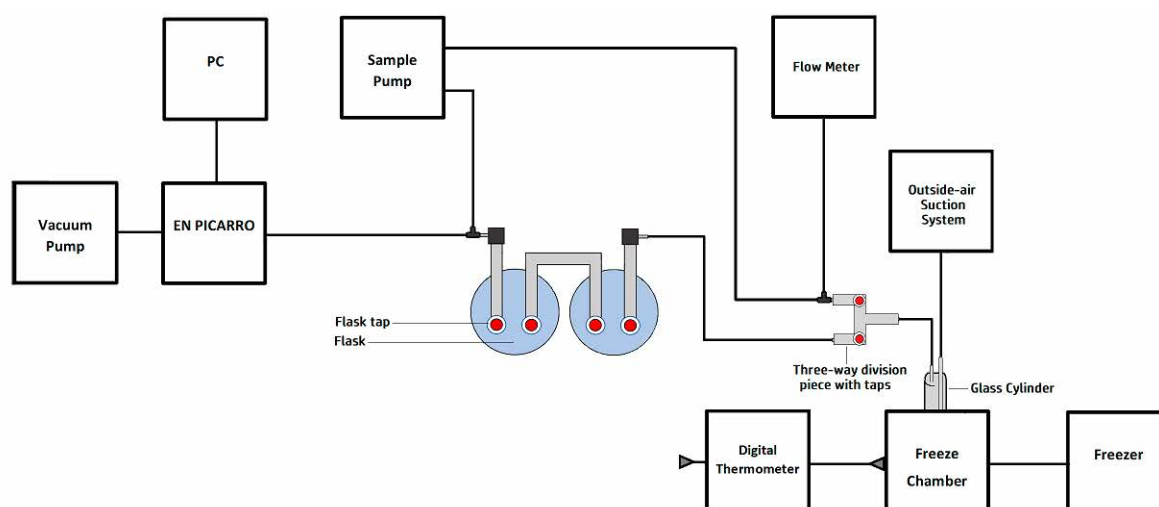

Figure 6: Experimental Setup of the Flushing Process

The sample pump ensures a round going air flow, which can be adjusted and is measured with the flow meter. Outside air is sucked into the system and is cooled and therefore dried in the glass cylinder, which is placed in the freeze chamber. The freeze chamber is connected to a digital thermometer and to a freezer, which cools the chamber to almost -60°C. The EN PICCARO is connected to a vacuum pump, which sucks in the air from the system, which can then be measured. It is also connected to a PC to do the readings and data analysis. When the flushing is finished, the flasks can be filled with air from a reference gas tank, of which the composition is known. The flasks were all filled with a flow of 2.5 litre/minute.

4.2.2   Extreme conditioning (ICOS-CAL standard)

The ICOS-CAl labs warm their flasks to ensure that water bounded to the sides of the flasks is loosened and can therefore be evacuated. This might result in less drift as water bounded to the flask surface could equilibrate with CO_2 over time (as mentioned in paragraph 2.2). The ICOS-CAL labs use a special flask conditioning oven (ICOS-CAL, 2022). The CIO does not possess such a system, however its operation can be approached, with the vacuum system and normal oven available at the CIO labs. The setup of this system can be seen in figure 7.
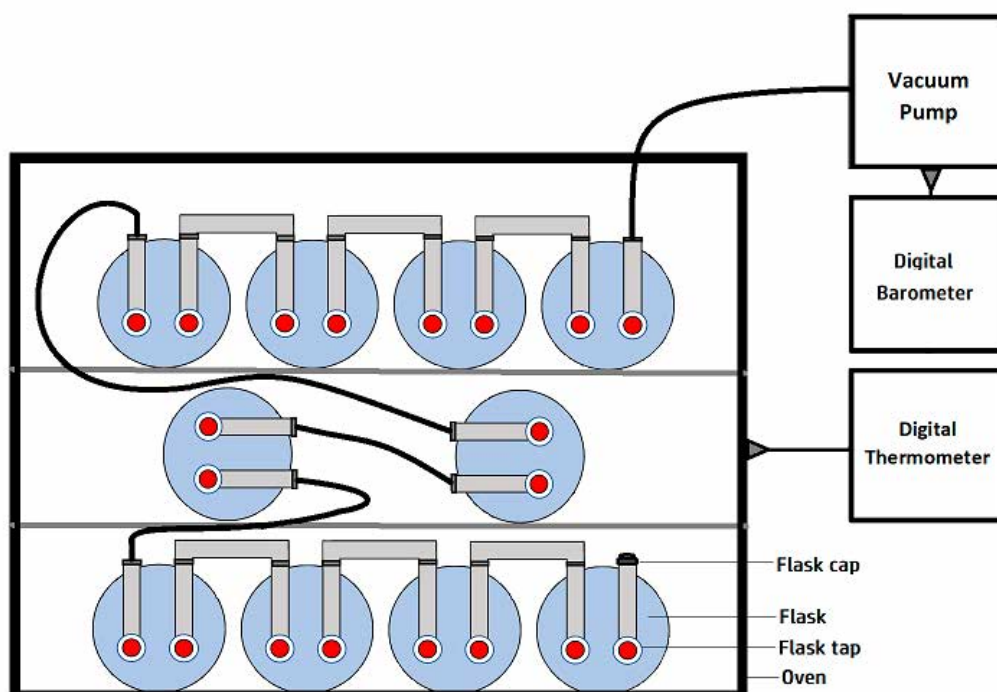

Figure 7: Experimental Setup of the Oven

The flasks are all connected to each-other, except for the last one which is sealed off with a flask cap and the first flask, which is connected to the vacuum pump of the CIO lab. The vacuum pump can be operated using a digital barometer. The oven is set to a temperature of 60°C, which can be adjusted and operated with a digital thermometer. The flasks needed to be evacuated inside the oven for a period of at least 72 hours (according to ICOS-CAL lab standards), this was eventually increased to 144 hours due to unforeseen circumstances, however this could have only been beneficial to the results and is therefore not considered as a problem. After this time period the flasks will be flushed and filled using the normal system of the CIO lab, as seen in figure 6.

4.2.3   Enriched water experiment

For the enriched water experiment an abundant amount of water highly enriched in ^{18}O was required. A total of 90226.9 mg was produced by mixing a 100 mL flask full of demineralized water with a small flask full of water with an isotopic abundance of 0.98 for ^{18}O and 0.004 for ^{17}O. The aim was to acquire at least an enrichment of 1000 ‰ of δ^{18}O. Eventually the enrichment was calculated to be 1072.9034 ‰. For δ^{17}O the enrichment was 19.7802 ‰. The small flask was chosen to be small enough to be thrown directly inside the 100 mL beaker to avoid spillage and left-over enriched water inside the small flask. The beaker only had a small opening to ensure that evaporation happened slowly. The beaker was placed in a foam box, together with 2 Viton and 2 PCTFE-flasks, of which the isotopic composition was measured with the SICAS before the start of the experiment. The box was closed off with its lid and taped shut with sticky foil, to provide a nearly hermetically sealed environment. The box was placed into storage for a total period of 35 days, after which the flasks could be measured again.

4.3   Data Processing

The SICAS and EN PICARRO measurement systems provided large data sets, which were treated and analysed using Excel. A combined uncertainty was given directly from the measurements, which could be used as the errors in the created graphs. However, due to 10 flasks being measured at the same time, which resulted in the same value on the x-axis in the graphs, it became quite incomprehensible. Therefore, the errors were omitted in the graphs and average errors are given in the text. The errors were very close to each other, making an average error an appropriate choice. The calculation of the average errors is given by the standard formula:

$$\bar{\Delta} = \sum_{i=1}^{n} \frac{\Delta_i}{n} \tag{6}$$

Where $\bar{\Delta}$ is the new average error, $\sum_{i=1}^{n} \Delta_i$ is the sum of all the measurement error values and n is the total number of measurements. The average uncertainty represents measuring errors, systematic errors and the precision of the measurement apparatus. The spread of the measurements can be easily seen from the graphs.

Instead of plotting the standard δ^{18}O, δ^{17}O and δ^{13}C values, the choice was made to use the residuals. This displays the change with respect to the tank value in a clearer fashion. The residuals are calculated by the following formula:

$$R = \bar{x}_t - x_m \tag{7}$$

Where R is the Residual value, $\bar{x}_t$ is the average specific delta value of the tank during the measurement and x_m is the absolute delta measurement value.

Different flasks are indicated in the graphs with different colours and mark types to give a clear distinction between them. Linear approximations are added as well for each flask to give a general overview of the flask drifts over time. The graphs all have the same maximum and minimum values for the axis for easy comparison.

5   Results

5.1   Normally conditioned flasks

The results of the normally conditioned δ^{18}O flask measurements can be found in figures 8 and 9. The results of the δ^{17}O and δ^{13}C measurements can be found in the appendix 8.2.2.
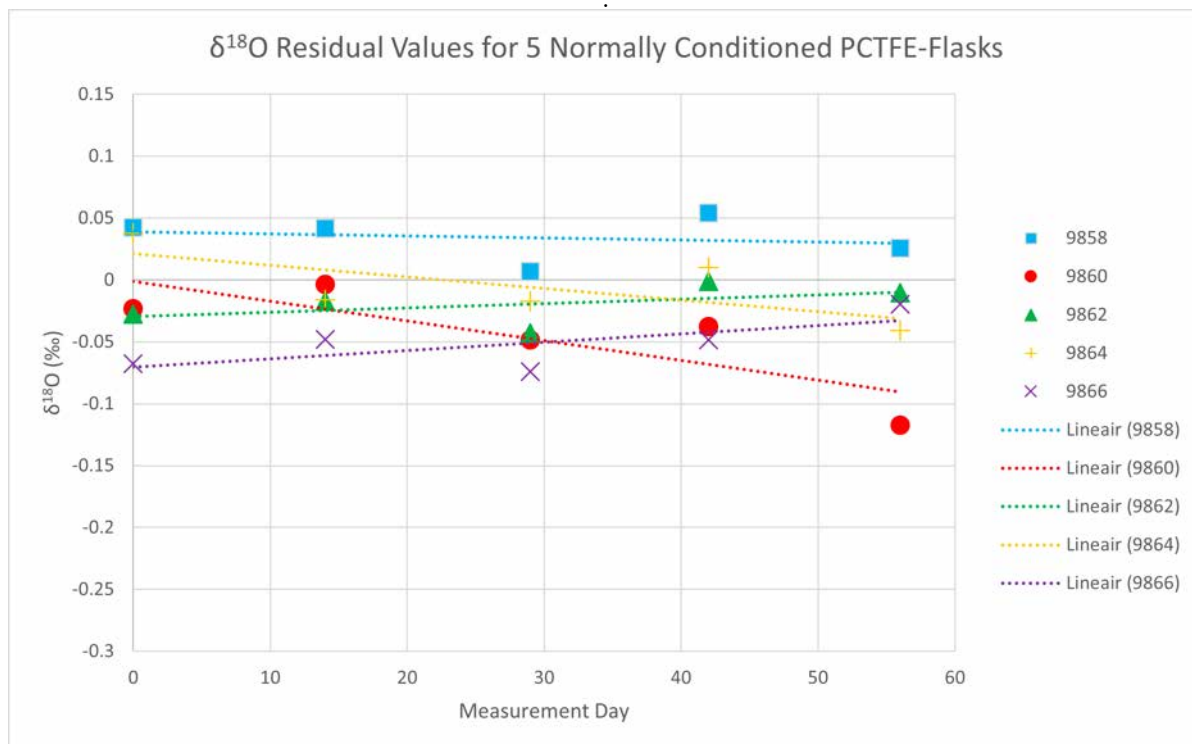
Figure 8: Normally conditioned PCTFE-flask results for $\delta^{18}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.
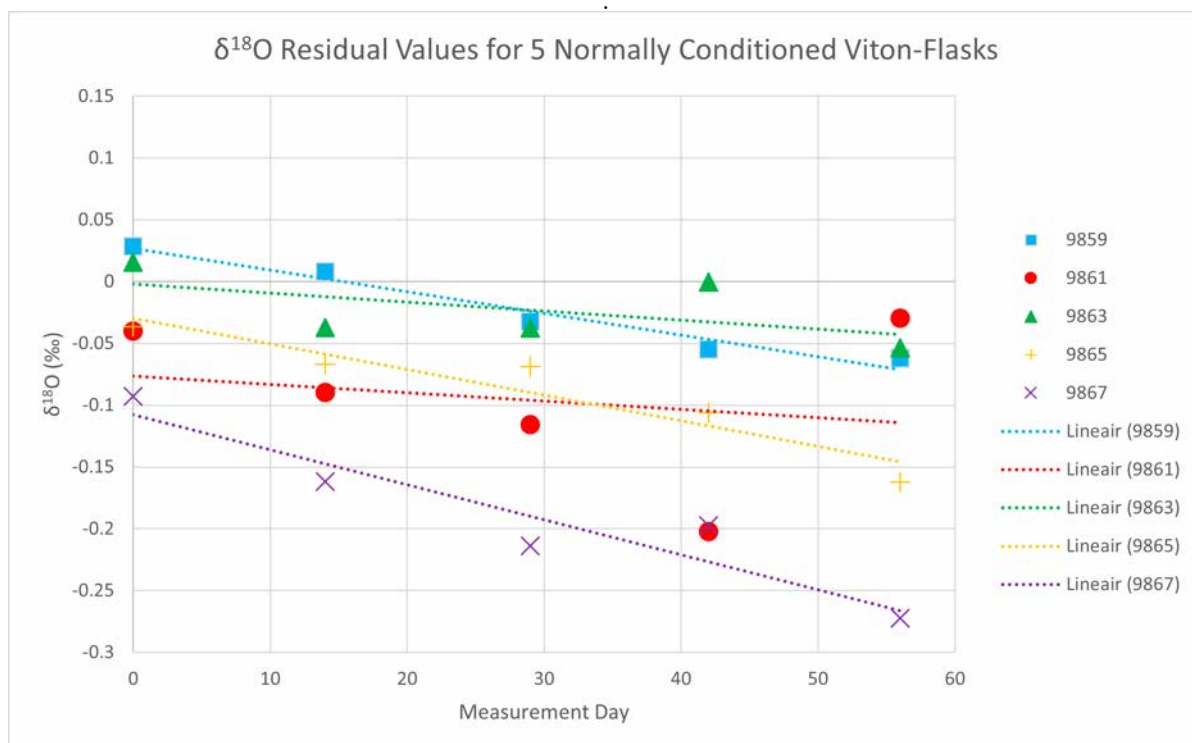

Figure 9: Normally conditioned Viton-flasks results for $\delta^{18}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.

The normally conditioned PCTFE-flasks can be considered as approximately constant. Two flasks show a sign of decrease (flasks 9860 and 9864), however flask 9862 and 9866 even show small increases in $\delta^{18}O$ values. Flask 9858 remains almost perfectly constant over time. The residual change over time therefore lays between -0.0944 and 0.0477 $\pm$ 0.0751 ‰. Where the average error is calculated with equation 6 and the residual values with equation 7. An average daily change can therefore be calculated by taking the average residual change and dividing it by the total number of measurement days (56), which is equal to -0.000417 $\pm$ 0.001341 ‰ per day.

A relatively steep decrease in the normally conditioned Viton-flask $\delta^{18}O$ values can be noted. All flasks show a decrease, although for flask 9861 the last measurement indicates that the $\delta^{18}O$ value has suddenly risen. This measurement might be considered as invalid. The largest decrease can be seen for flask 9867, where the smallest decrease is shown by flask 9865. The residual change over time therefore lays between -0.1792 and -0.0692 $\pm$ 0.0751 ‰. Where the average error is calculated with equation 6 and the residual values with equation 7. The average daily change is equal to -0.002218 $\pm$ 0.001341‰ per day.

5.2 Extremely conditioned flask

The results of the extremely conditioned $\delta^{18}O$ flask measurements can be found in figures 10 and 11. The results of the $\delta^{17}O$ and $\delta^{13}C$ measurements can be found in the appendix 8.2.3.
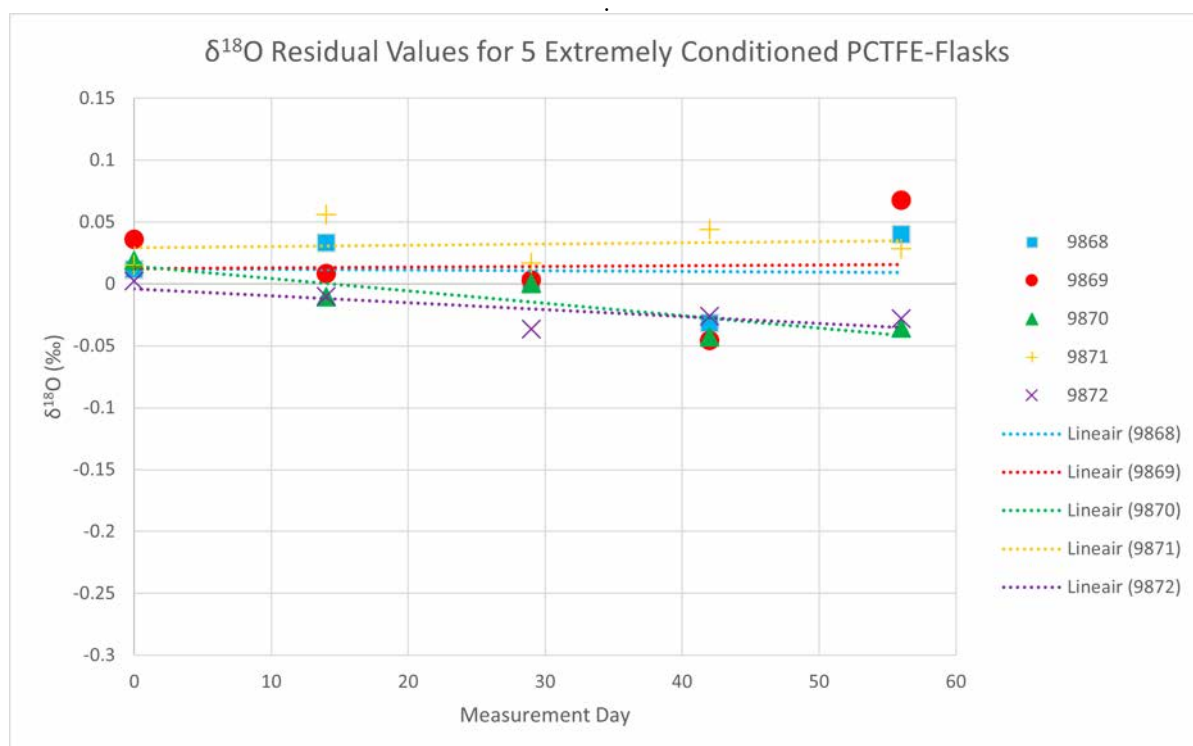

Figure 10: Extremely conditioned PCTFE-flask results for $\delta^{18}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number. A linear approximation for each flask can be seen as well, serving as a general overview of the $\delta^{18}O$ values over time.
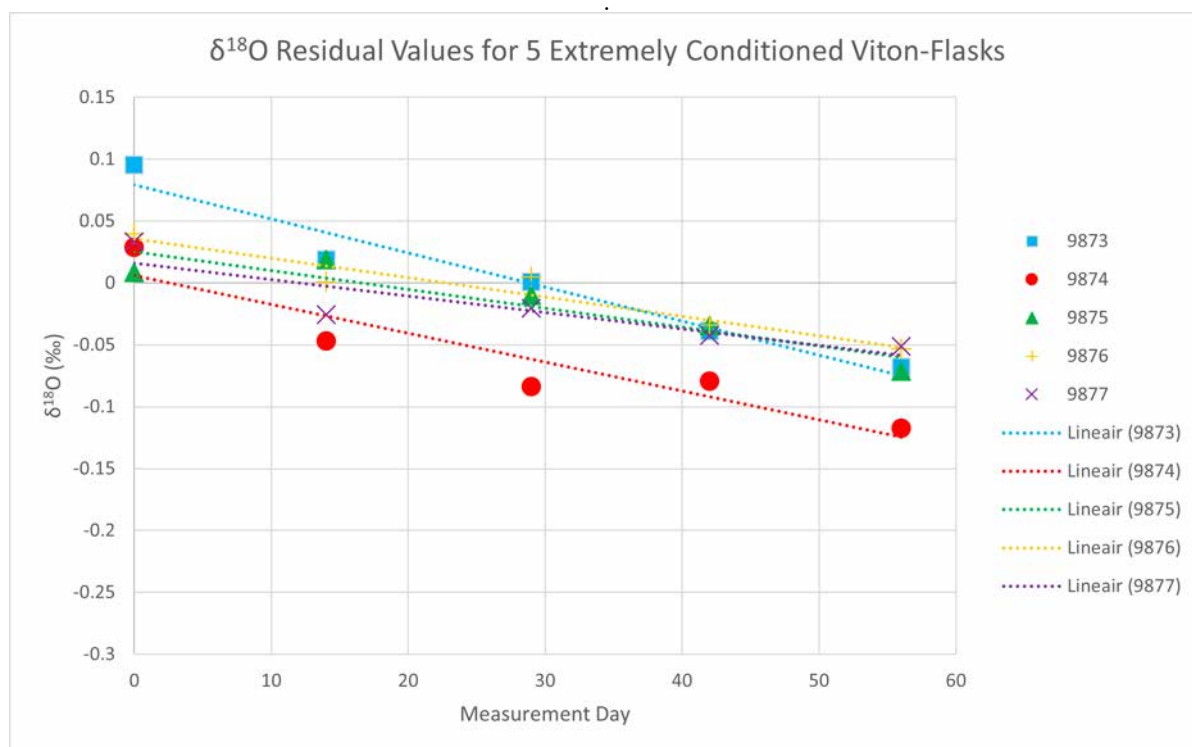
Figure 11: Extremely conditioned Viton-flasks results for $\delta^{18}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number. A linear approximation for each flask can be seen as well, serving as a general overview of the $\delta^{18}O$ values over time.

The extremely conditioned PCTFE-flask values can be considered as approximately constant again. Some small decreases in flasks 9870 and 9872 can be found. The other flasks remain almost perfectly constant. It must be noted that flask 9869 has a large deviation in the last measurement, which might therefore be considered as invalid. The largest decrease can be seen for flask 9870, where the smallest decrease (or in this case even a small increase) is shown by flask 9868. The residual change over time therefore lays between -0.0252 and 0.0286 ± 0.0760 ‰. Where the average error is calculated with equation 6 and the residual values with equation 7. The average daily change is equal to -0.000030 ± 0.001357 ‰ per day.

A relatively steep decrease in the extremely conditioned Viton-flask $\delta^{18}O$ values can be noted. All flasks show a significant decrease, where flask 9873 shows the largest and flask 9876 the smallest. The residual change over time therefore lays between -0.1636 and -0.0930 ± 0.0759 ‰. Where the average error is calculated with equation 6 and the residual values with equation 7 again. The average daily change is equal to -0.002291 ± 0.001355 ‰ per day.

5.3 Enriched water experiment

The results of the $\delta^{13}C$, $\delta^{17}O$ and $\delta^{18}O$ flask measurements for the enriched water experiment can be found in table 3. The results are again shown in a table instead of a graph as the measurements only provided two data-sets of two flasks, which is better shown in a table. As there is no interest in the exact data points, but rather in the change of the delta values, the residuals of the start measurement (day 0) are subtracted from the residuals of the end measurement (day 35), giving a residual value change.

Research results for experiment with enriched water			
Sample	$\delta^{13}C$ value (‰)	$\delta^{17}O$ value (‰)	$\delta^{18}O$ value (‰)
Reference gas (Tank)	-9.17 ± 0.08	19.70 ± 0.07	38.07 ± 0.07
PCTFE-flask (9879) Residual value change	-0.02 ± 0.07	0.05 ± 0.06	0.08 ±0.06
PCTFE-flask (9881) Residual value change	0.00 ± 0.08	-0.11 ± 0.07	0.13 ± 0.06
Viton-flask (9878) Residual value change	0.13 ± 0.07	0.04 ± 0.07	0.45 ± 0.04
Viton-flask (9880) Residual value change	-0.03 ± 0.07	-0.17 ± 0.06	0.32 ± 0.06

Table 3: Stable isotopes of atm-CO_2 measurements of 2 Viton-flasks exposed to water highly enriched in $\delta^{18}O$, given as residual values with respect to the reference gas.

As can be seen in table 3, increases in $\delta^{18}O$ were measured after 35 days for the Viton-flask specifically. The $\delta^{13}C$ and $\delta^{17}O$ values remain more or less the same with a maximum deviation of -0.17 ± 0.06 ‰ for the $\delta^{17}O$ value of the 9880 Viton-flask. In contrast to the Viton-flasks $\delta^{18}O$ values, which change with 0.45 ± 0.04 and 0.32 ± 0.06 ‰ for flask 9878 and 9880 respectively. This is a significant change with respect to the almost constant $\delta^{18}O$ values of the PCTFE-flasks. The average increases over 35 days for the $\delta^{18}O$ values are 0.39 ± 0.05 and 0.11 ± 0.07 for the Viton- and PCTFE-flasks respectively.

5.4 Summarized results

In table 4 below the summarized results of all the experiment can be seen. The value changes and uncertainties are given units of per meg (where 1 per meg = 0.001‰), instead of the previously used parts per thousand (denoted as ‰). This was done for clearer comparison.

Results Comparison			
Flask group	Description	Daily change in $\delta^{18}O$ value (per meg)	Uncertainty (per meg)
PCTFE group 1 (5 flasks)	Normally conditioned	- 0.42	± 1.34
PCTFE group 2 (5 flasks)	Extremely conditioned	- 0.03	± 1.36
Viton group 1 (5 flasks)	Normally conditioned	- 2.22	± 1.34
Viton group 2 (5 flasks)	Extremely conditioned	- 2.29	± 1.36
PCTFE group 3 (2 flasks)	Enriched with $\delta^{18}O$	+ 3.14	± 1.71
Viton group 3 (2 flasks)	Enriched with $\delta^{18}O$	+ 11.14	± 1.43

Table 4: Summarized results of storage-, conditioning- and enriched water experiments (for comparison)

6   Discussion

6.1   Drift in isotopic composition

From the results of the normally- and extremely conditioned flasks (paragraph 5.1 and 5.2/ table 4) it can be found that there is indeed a noticeable drift in $\delta^{18}O$ over time. Furthermore, a significant difference in daily change in $\delta^{18}O$ value can be noted between the Viton- and PCTFE-flasks. Where the Viton- and PCTFE-flasks have an average daily change of -2.26 $\pm$ 1.35 and -0.23 $\pm$ 1.35 per meg respectively. By subtraction, an average difference of 2.03 $\pm$ 1.35 per meg between the flasks can be found. Where all the averages (both errors and delta values) are calculated with equation 6. Over longer periods of time, this will result in significant differences. From previous results, such as the experiments executed by P.M. Steur and dr. ir. H.A. Scheeren it was already expected that there would be a difference between the flasks over time. The results met the expectations and provided a clear insight in the distinctive isotopic behaviour over time for both flasks.

From the storage experiment alone it was concluded that there occurs a drift over time and that the drift is significantly steeper for the Viton-flasks in comparison with the PCTFE-flasks. However, without the other 2 experiments no valid conclusions can be made regarding the cause of the drift.
Looking at the summarized results (table 4), extremely conditioning (the ICOS-CAL lab strategy), resulted in no significant difference in the daily change in $\delta^{18}O$ values for the Viton-flasks. However, according to table 4 it did reduce drift in the PCTFE-flasks. Remarkably, when figures 8, 9, 10 and 11 are further inspected it can be noticed that there is a noteworthy difference between the two conditioning methods. It appears as if extreme conditioning reduces the amount of large deviations in measurements, which results in a smaller spread of results. This makes the results more precise (closer to each other), giving the opportunity to make harder conclusions when the results are accurate as well.
When table 4 and figure 8 are compared it might be concluded that the reduction in drift by extreme conditioning instead of normal conditioning for the PCTFE-flasks might be caused by the last data point of flask 9860, which results in a steeper decline for the $\delta^{18}O$ value of which the average daily residual change eventually was calculated. Neglecting this data-point it can be concluded that extreme conditioning increases the precision of results, however it does not reduce drift necessarily. This conclusion disproves the possibility that the different conditioning methods between the ICOS-CAL and CIO-labs is the source of the difference in drift between the PCTFE- and Viton-flask types.

6.2   Permeation through O-rings

From the results of the enriched water experiment (paragraph 5.3 and table 4), it can be noticed that the $\delta^{18}O$ value increases tremendously over time. A daily increase of 3.14 $\pm$ 1.71 and 11.14 $\pm$ 1.43 per meg can be noticed for the PCTFE- and Viton-flasks respectively. As the $\delta^{17}O$ value barely increases (flasks 9879 and 9878) or even decreases (flasks 9881 and 9880)(see table 3), it can be concluded that the increase is induced by the beaker with enriched water and not by water already present inside the flasks, as then a comparable change of approximately half the change in $\delta^{18}O$ should have been noticeable in $\delta^{17}O$ as well, due to equilibration of CO_2 with H_2O, as mentioned in paragraph 2.2. Therefore, permeation through O-rings does indeed occur. The difference in the value shift between the 2 flask types is significant, which is in line with the varying permeation coefficients of both flask seal materials, as mentioned in paragraph 2.2. It is also analogous to the difference in drift found in the storage experiment and therefore it is plausible that permeation is the cause of the drifts.

6.3   Comparison with previous research

The results from the experiments were broadly speaking, as expected. Of course expectations can only come from previous experiences or in this case research. According to the preliminary research results of P.M. Steur a serious decline in $\delta^{18}O$ values should have been noticeable in the storage experiment. P.M. Steur recorded an average daily decrease of -2.4 $\pm$ 0.4 per meg for Viton-flasks. Furthermore, Rothe et al. (2003) recorded a daily decrease of -0.0023 $\pm$ 0.02 ‰, which is equal to -2.3 $\pm$ 20 per meg. For the storage experiment conducted during this research an average daily decrease of -2.3 $\pm$ 1.4 was recorded, which can therefore definitely be considered as a comparable result. Comparing the results for both enriched water experiments a noticeable difference is found, P.M. Steur recorded an average daily increase in the $\delta^{18}O$ values of Viton-flasks of 33.56 $\pm$ 1.21 per meg, whereas this research concluded an

average daily increase of just 11.14 $\pm$ 1.43. This is a significant difference, which might be contributed to differences in ^{18}O enrichment or possibly to the difference in measurement time (66 versus 35 days). However, from both results it can be concluded that a large shift in the $\delta^{18}O$ values occurs, which is the most important result here.

Dr. ir. H.A. Scheeren conducted a follow-up research of the storage experiment with both flasks. The average daily changes in $\delta^{18}O$ values that were recorded during this experiment were -4.28 $\pm$ 0.39 and -0.53 $\pm$ 0.35 per meg for Viton- and PCTFE-flasks respectively. Compared to the average found values in this experiment (-2.26 $\pm$ 1.35 and -0.23 $\pm$ 1.35 per meg for Viton- and PCTFE-flasks respectively), it can be noticed that the Viton-flask values fall just outside each-others errors, but that the PCTFE-flask values are comparable. Furthermore, looking at the ratios between the Viton- and PCTFE-flasks for both researches, they actually are comparable to each-other. The research of dr. ir. H.A. Scheeren provided a ratio of 8.08 (the Viton-flask value divided by the PCTFE-flask value), whereas this research gave a ratio of 9.83. Compared to previous research of Rothe et al. (2003), the Viton-flasks show a larger decline again. The PCTFE-flasks in the research of Rothe et al. (2003) showed a daily decline of -0.0019 $\pm$ 0.02 for the $\delta^{18}O$ values, which is equal to -1.9 $\pm$ 20 per meg per day, which is a significant larger decrease compared to this research. However as the errors are large, it might be that the results are comparable.

According to (Sturm et al., 2004), the permeation coefficients of Viton and PCTFE for water are 40-216 and 0.22 respectively (as also mentioned in paragraph 2.2), which is equal to a ratio between 181.8 and 981.8, which is significantly higher than the found ratios in this experiment. However it must be considered that the permeation rate and therefore possibly the drift are also dependent on the surface area and thickness of the sealing material and not only the material itself, which varies with different valve types (such as Viton- and PCTFE-flasks).

6.4   Errors, mistakes and recommendations

Overall, the research was executed quite fluently after the experiments were all laid-out. However, in the start-up of the research there were some minor issues, which took a lot of time and effort to resolve. Especially, with the warming system for the extreme conditioning process. The first setup (as seen in figure 26, appendix 8.3.1) was too complex for its service and resulted in a lot of inaccurate and imprecise measurements, as there was a lot of room for systematical, and random errors. The setting up of this experimental setup was also time consuming, which resulted in a significant delay of the experiments. Eventually, it was replaced with the oven (as seen in figure 7, paragraph 4.2.2), which served its purpose a lot better.

The 3 final experiments were conducted with great precision, resulting in few accidental errors. However some minor errors must be mentioned. First of before the first measurement of the normally conditioned flasks, one of the Viton-flasks broke, which meant that it had to be replaced. Therefore the replacement flask was not conditioned at the same time as the other normally conditioned flasks. This could have resulted in a different environment and therefore it could have affected the results. However, there was no clear effect noticeable and therefore the flask was considered as equal for the rest of the experiment. Secondly, the pressure in the flasks logically decreased during the experiment, as for each measurement a little bit of air from the samples was needed. This might or might not have influenced permeation, as permeation is dependent on the pressure difference between the sample and the outside air, as mentioned in paragraph 3.2.

To increase the precision, accuracy and results of the experiments, some improvements can be recommended. To get more results and therefore possibly to increase the validity of the results, it might be suggested to measure over a longer period of time or to increase the number of measured flasks. Furthermore, it might be possible that there is a difference in the smoothness of the flasks, resulting in more water remaining in small cavities. This difference might be mostly due to the newness of the flasks, where a substantial difference appears between the relatively new PCTFE-flasks and the older Viton-flasks. This may or may not have affected the results and therefore for follow-up research it is suggested to use only new flasks to eliminate this bias. Furthermore, as the results from the research of dr. ir. H.A. Scheeren suggest that adding a cap to the Viton-flasks reduces the drift as well, it may be suggested to implement this for longer storage experiments for the time being. At last, although the

extreme conditioning of the flasks did not necessarily result in less drift of the mole fractions of the stable isotopes, it did induce a significant reduction in large measurement deviations, resulting in more similar results between the flasks. It might thus be recommended to implement this conditioning method in the standard procedure at the CIO labs to reduce the amount of deviating results, resulting in more stable results.

7   Conclusion

By measuring the values of the si of atm-CO_2 over a period of 56 days it was concluded that there is a drift in isotopic composition. Although the $\delta^{13}C$ and the $\delta^{17}O$ values remain relatively constant, an average daily depletion of -2.26 $\pm$ 1.35 and -0.23 $\pm$ 1.35 per meg were found in the $\delta^{18}O$ values for the Viton- and PCTFE-flasks respectively. This tends to a reaction between the air sample and either water already inside the flask or water from outside the flask. It seemed that extreme conditioning did not necessarily result in a lower depletion of the $\delta^{18}O$ values, from which it might be concluded that the differences in drift between the ICOS-CAL lab in Jena and the CIO-lab in Groningen was not caused by the different conditioning methods. However, it did provide the insight that extreme conditioning can increase the stability of the air sample measurements. By performing the enriched water experiment it was found that permeation through flask seals indeed occurs, where there was a significant difference noticeable between the Viton- and the PCTFE-flasks. The PCTFE-flasks had an average daily increase of 3.14 $\pm$ 1.71 per meg in $\delta^{18}O$, where the Viton-flasks had an increase of 11.14 $\pm$ 1.43 per meg.
From these two experiments it was concluded that permeation through flask seals occurs and although a drift can be found for PCTFE-flasks as well, it is a much weaker signal than that of the Viton-flasks. The Viton-flask showed a clear signal of permeation and this is most certainly the reason for the drift in isotopic composition within the CIO storage flasks over time.

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M. Wendeberg, J. M. Richter, M. Rothe, and W. A. Brand. Jena. reference air set (jras): A multi-point scale anchor for isotope measurements of co2 in air. *Atmos. Meas. Tech.*, 6:817–822, 2013.

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8   Appendix

8.1   Preliminary research results

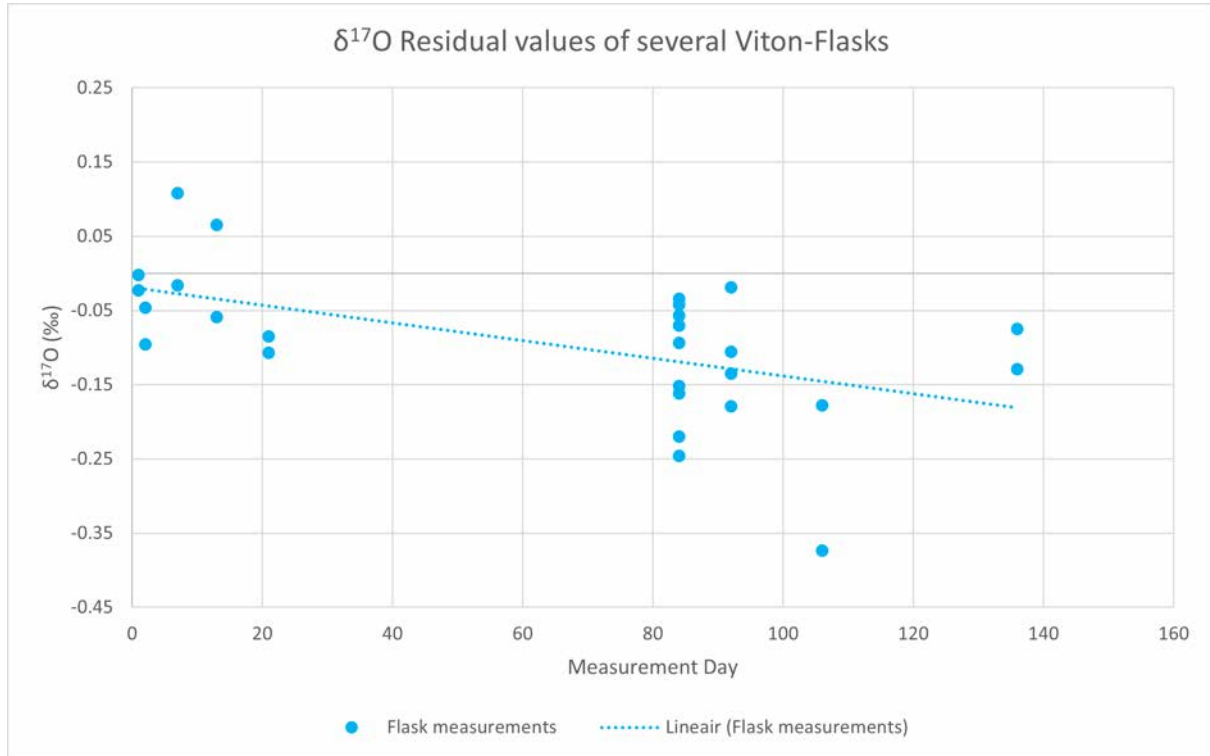### 8.1.1   Preliminary research results from experiment conducted by P.M. Steur

Figure 12: Preliminary research results from experiment conducted by P.M. Steur
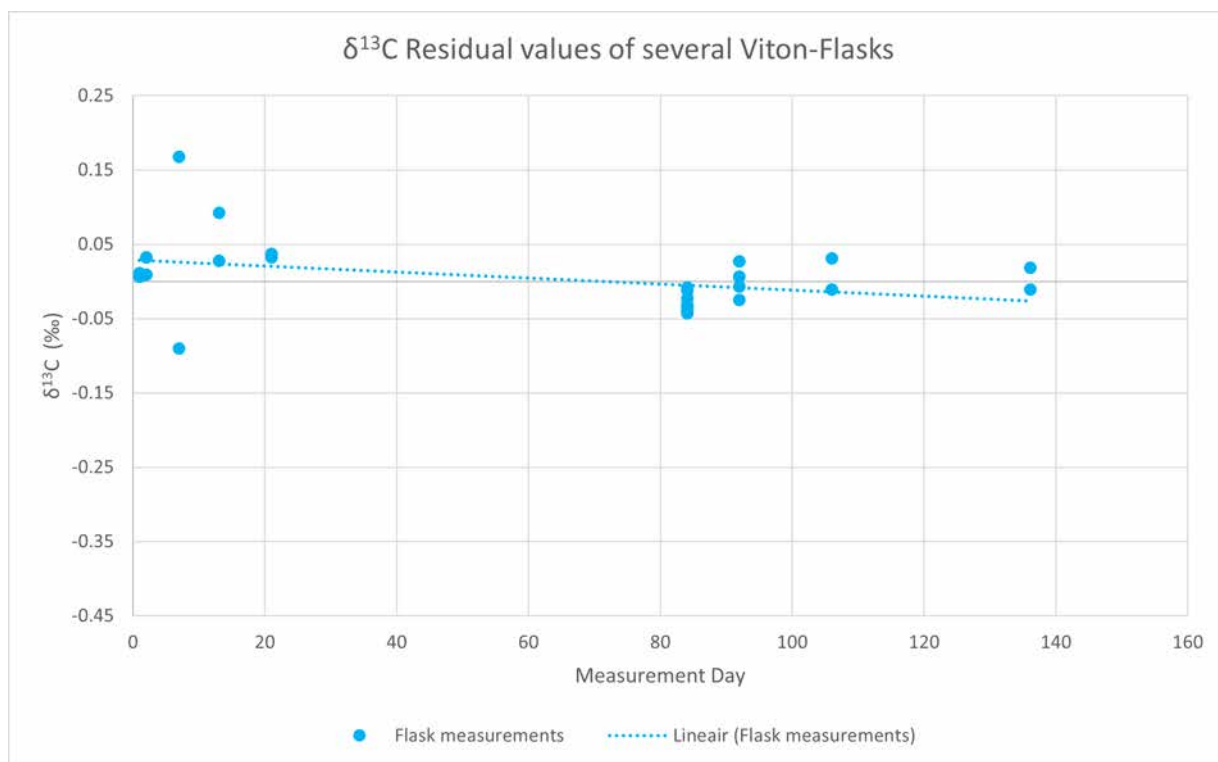
Figure 13: Preliminary research results from experiment conducted by P.M. Steur

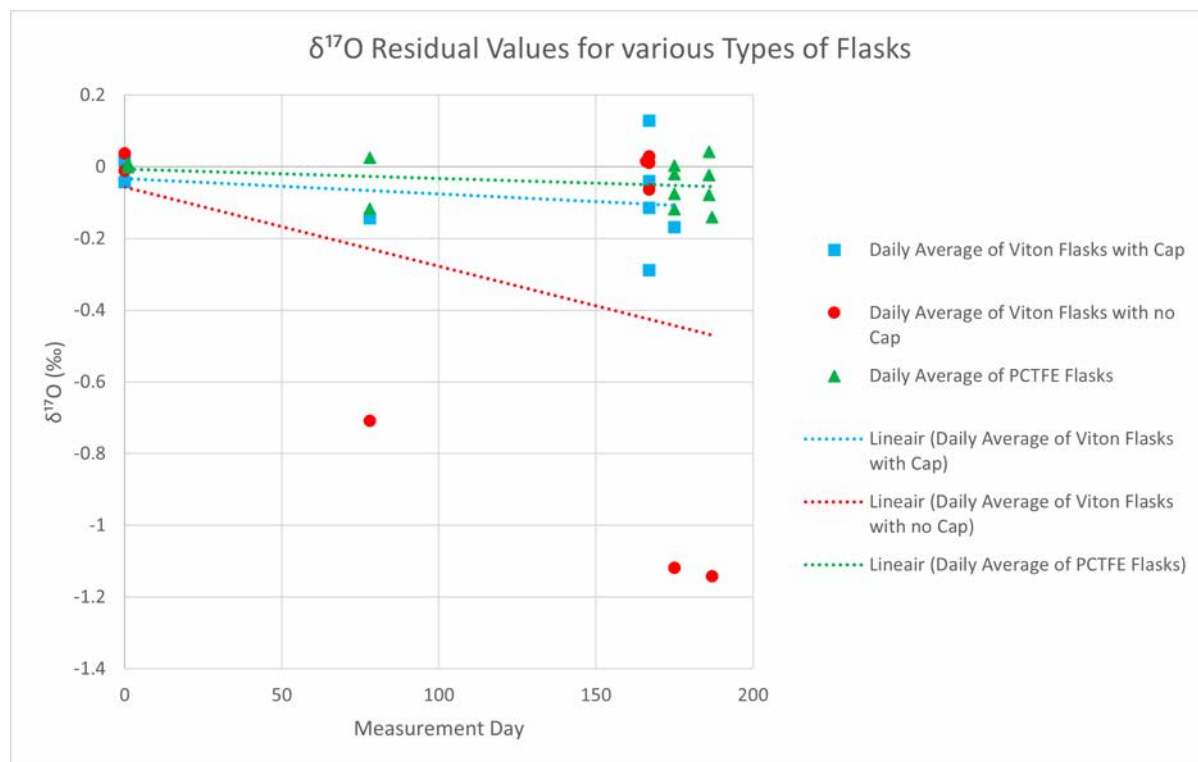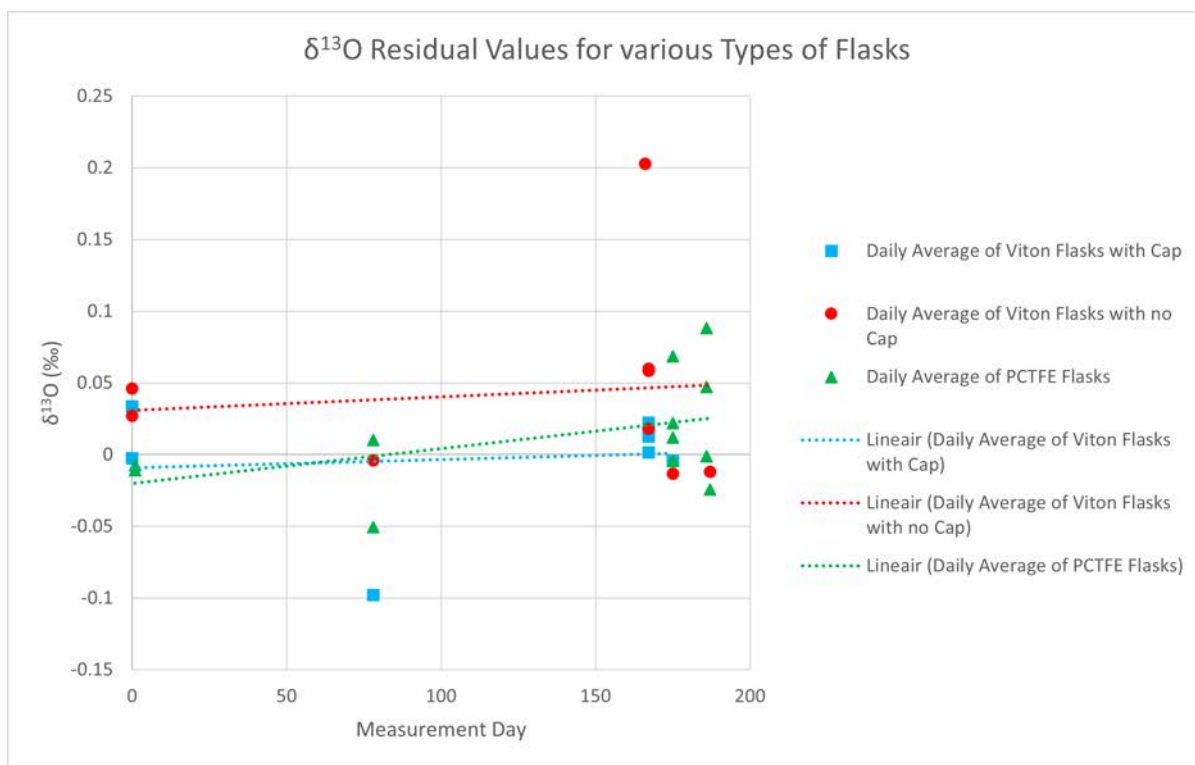### 8.1.2 Preliminary research results from experiment conducted by dr. ir. H.A. Scheeren

Figure 14: Preliminary research results from experiment conducted by dr. ir. H.A. Scheeren

Figure 15: Preliminary research results from experiment conducted by dr. ir. H.A. Scheeren

8.2 Experiment results

8.2.1 Picarro measurements
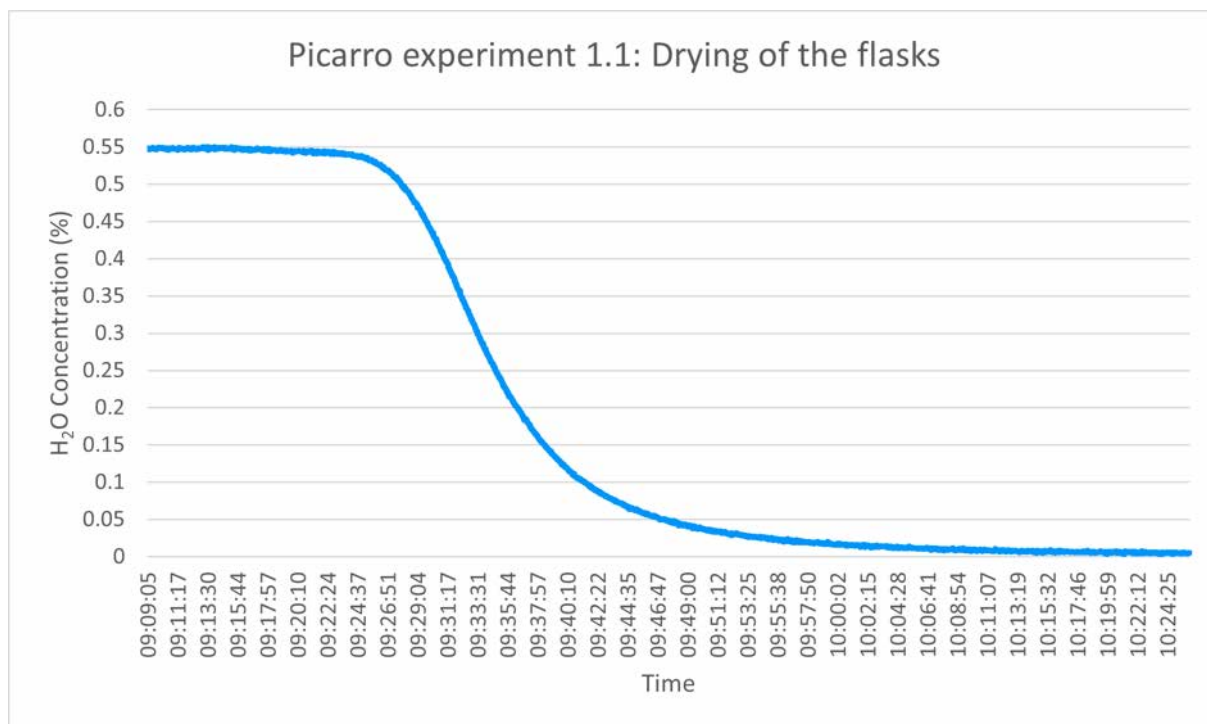
Figure 16: Picarro H_2O measurement 1, start of the flask drying
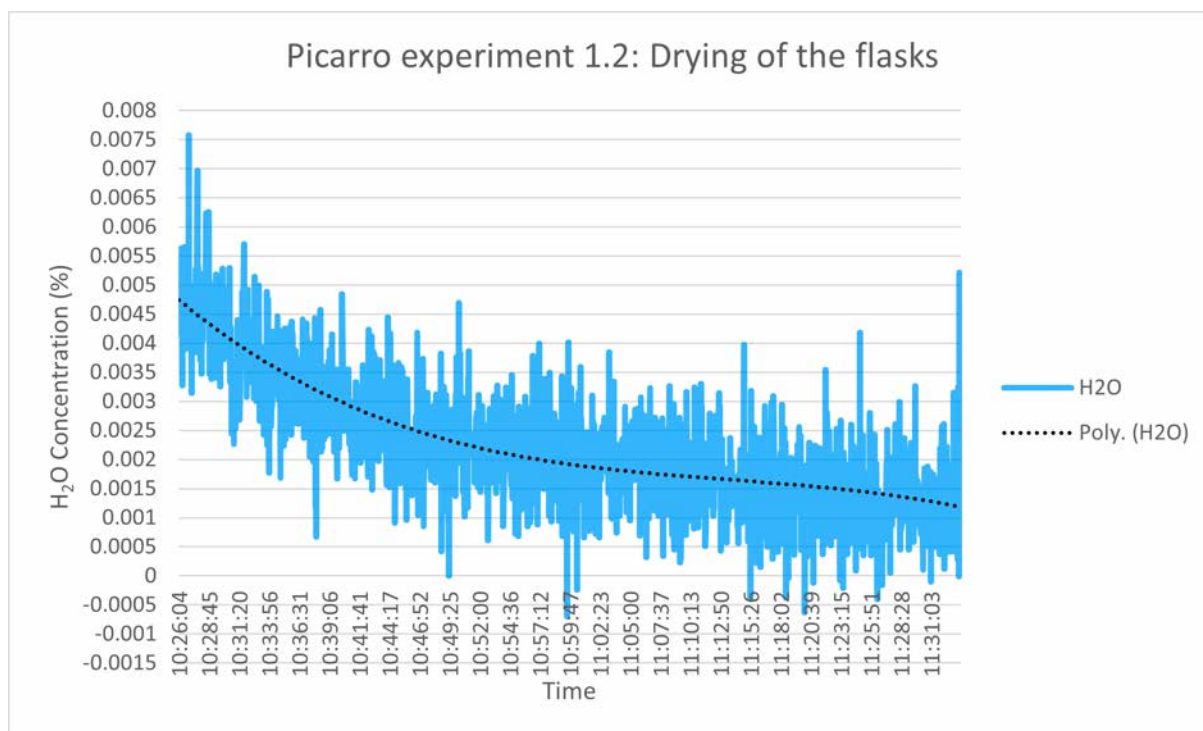
Figure 17: Picarro H_2O measurement 2, continuation of the flask drying
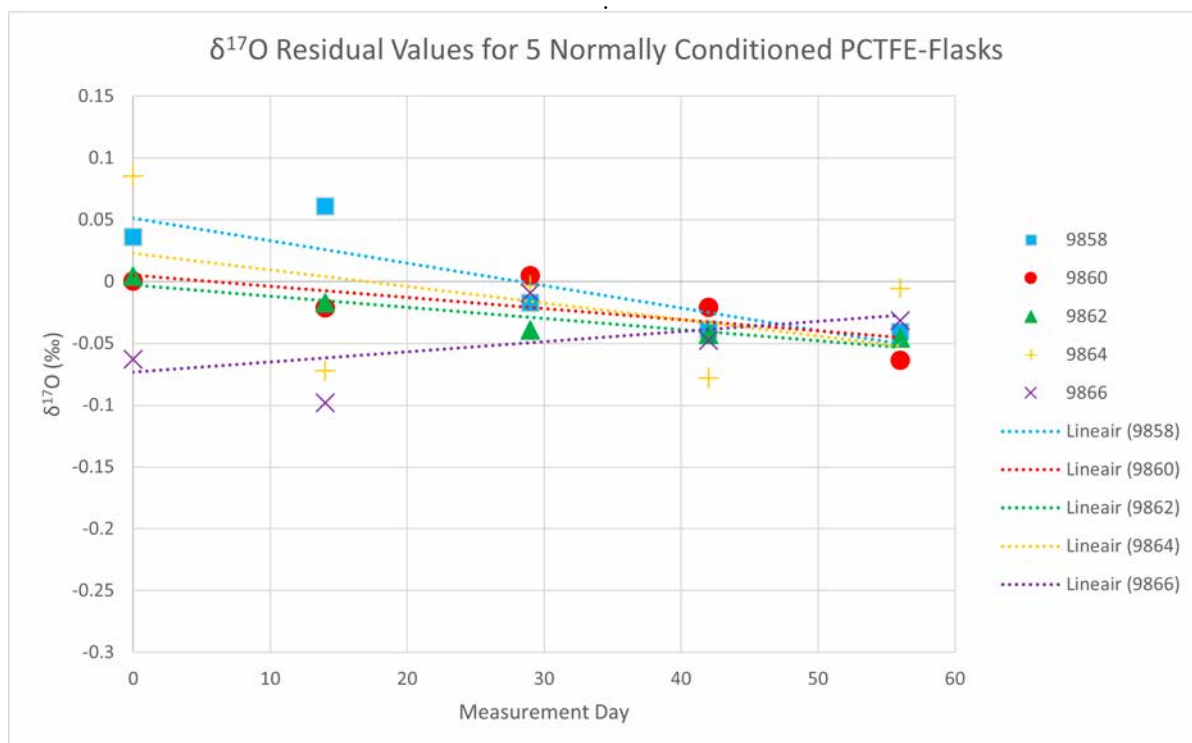
8.2.2 Normally conditioned flasks
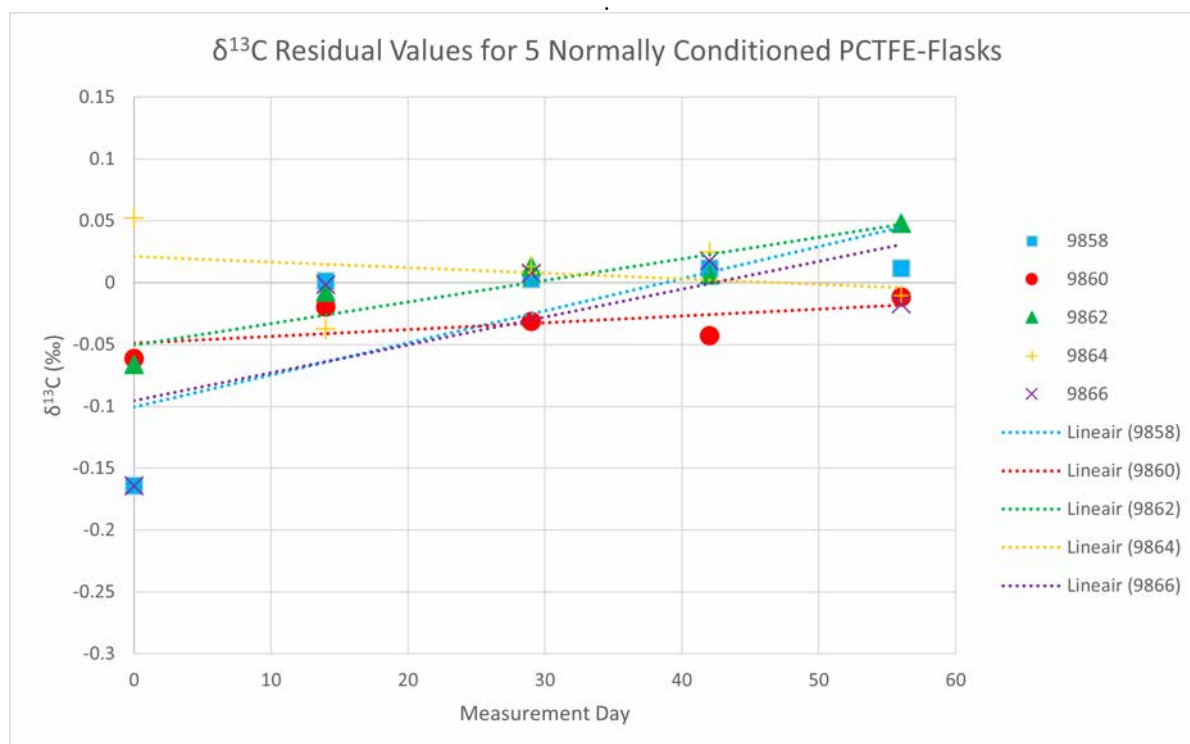
Figure 18: Normally conditioned PCTFE-flask results for $\delta^{13}C$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.
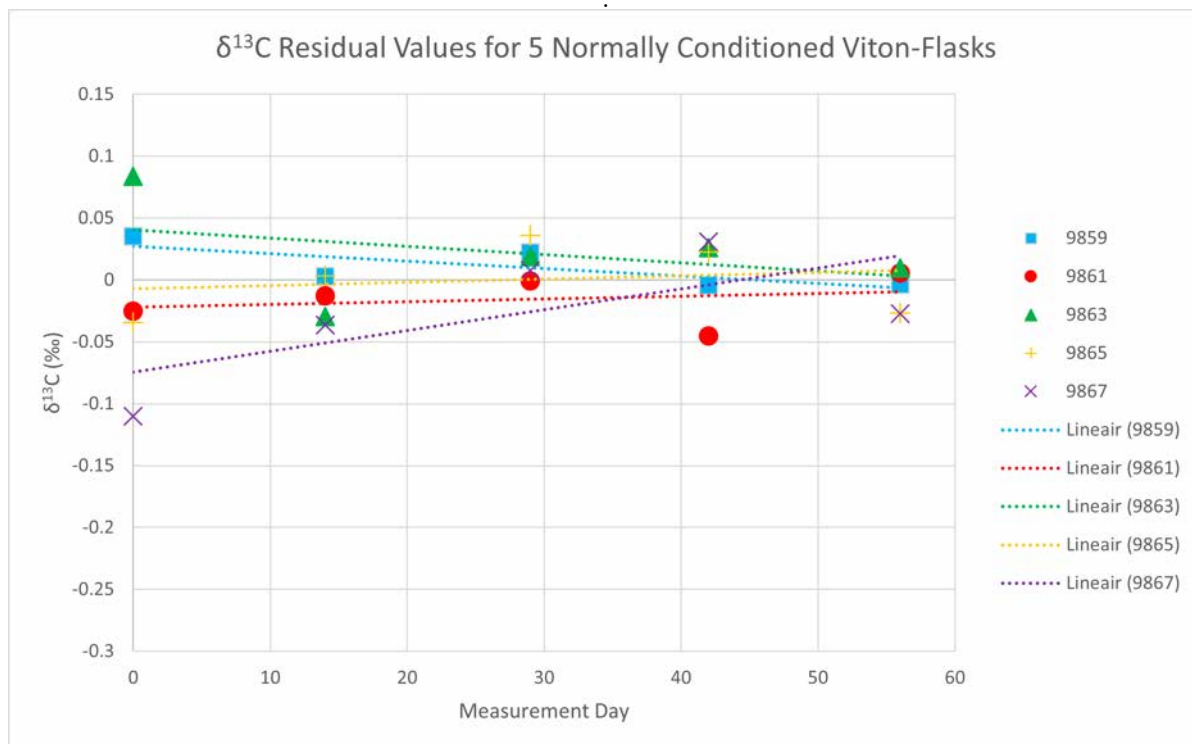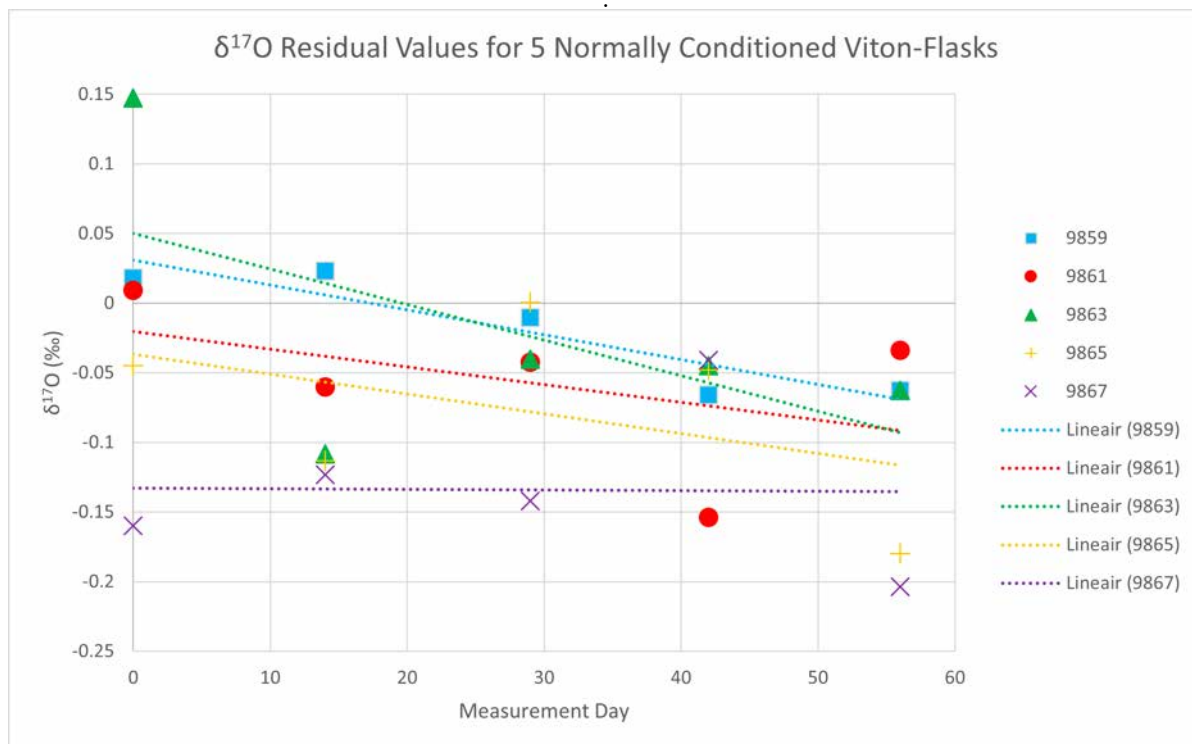
Figure 19: Normally conditioned Viton-flask results for $\delta^{13}C$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.

Figure 20: Normally conditioned PCTFE-flask results for $\delta^{17}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.

Figure 21: Normally conditioned Viton-flask results for $\delta^{17}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.
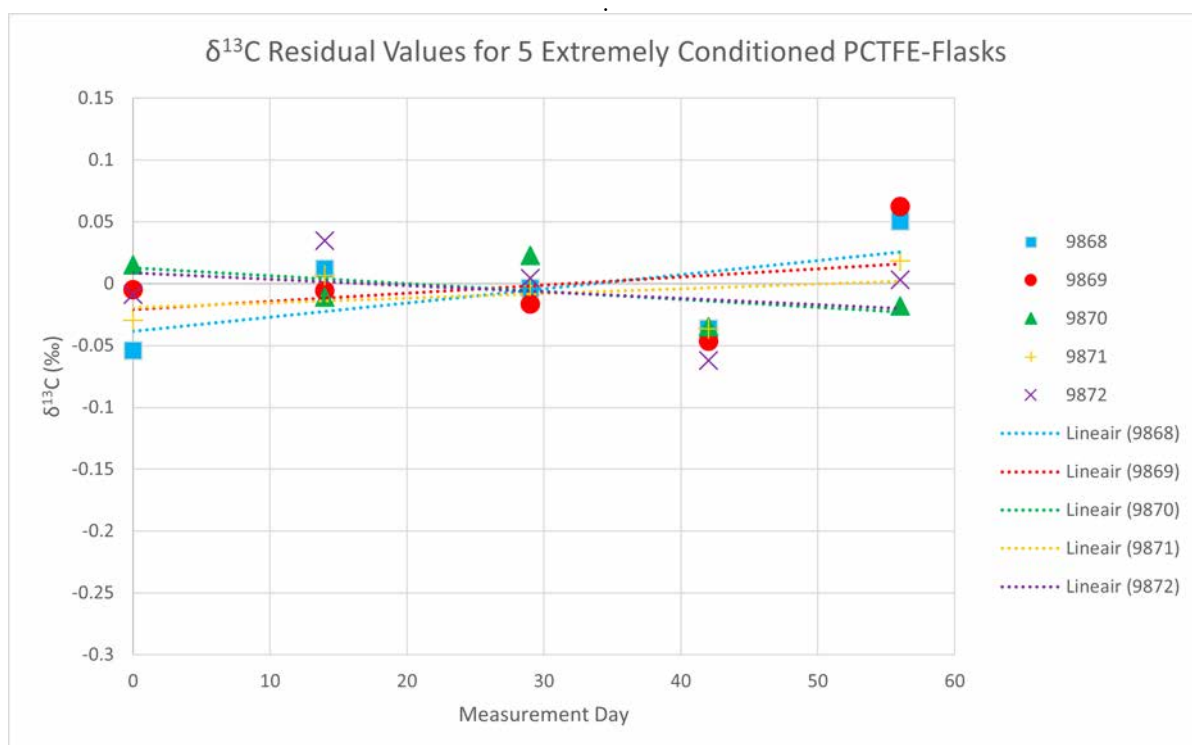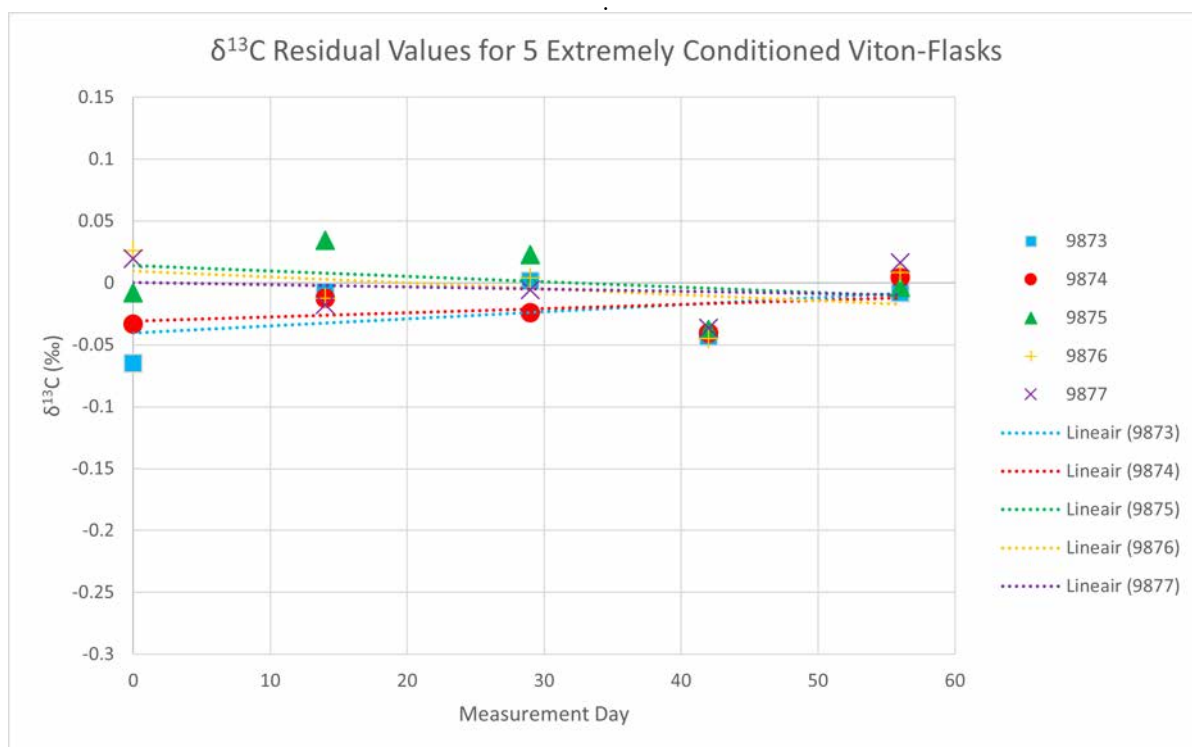
8.2.3   Extremely conditioned flasks

Figure 22: Extremely conditioned PCTFE-flask results for $\delta^{13}C$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.
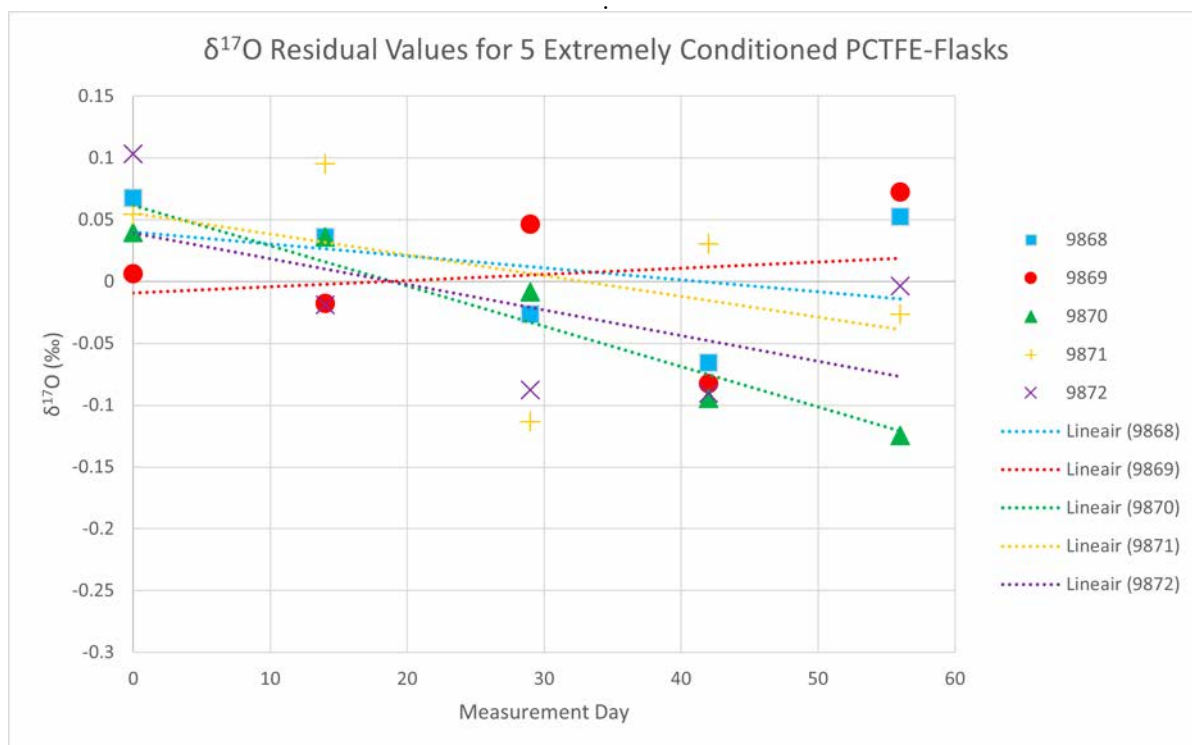
Figure 23: Extremely conditioned Viton-flask results for $\delta^{13}C$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.

Figure 24: Extremely conditioned PCTFE-flask results for $\delta^{17}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.
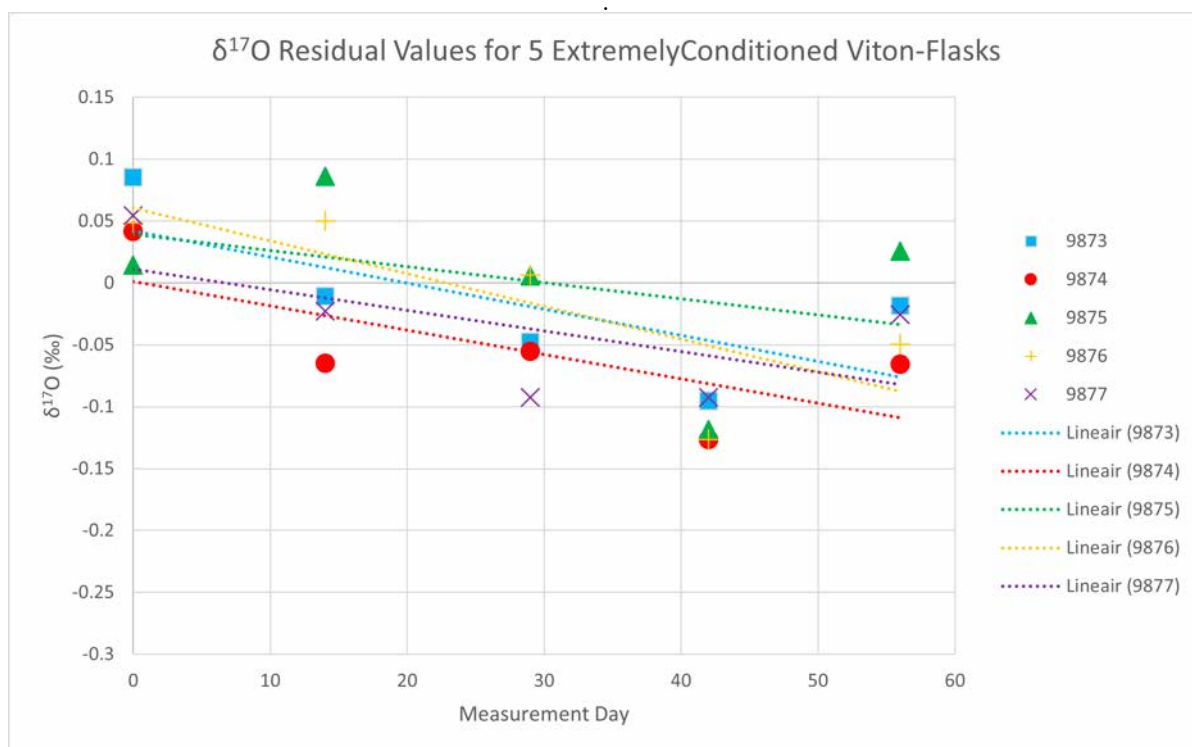
Figure 25: Extremely conditioned Viton-flask results for $\delta^{17}O$. The different numbers in the legend (together with the varying colours and mark types) stand for the 5 flasks used in this experiment, all indicated by their own flask number.

8.3 Experimental Setups

8.3.1 First experimental setup for warming of the flasks

The first try to warm the flasks was done using a warming blanket, however as it turned out this was not practical at all and the flasks could not be evacuated at the same time. After this realisation the setup was changed to the setup of figure 7.
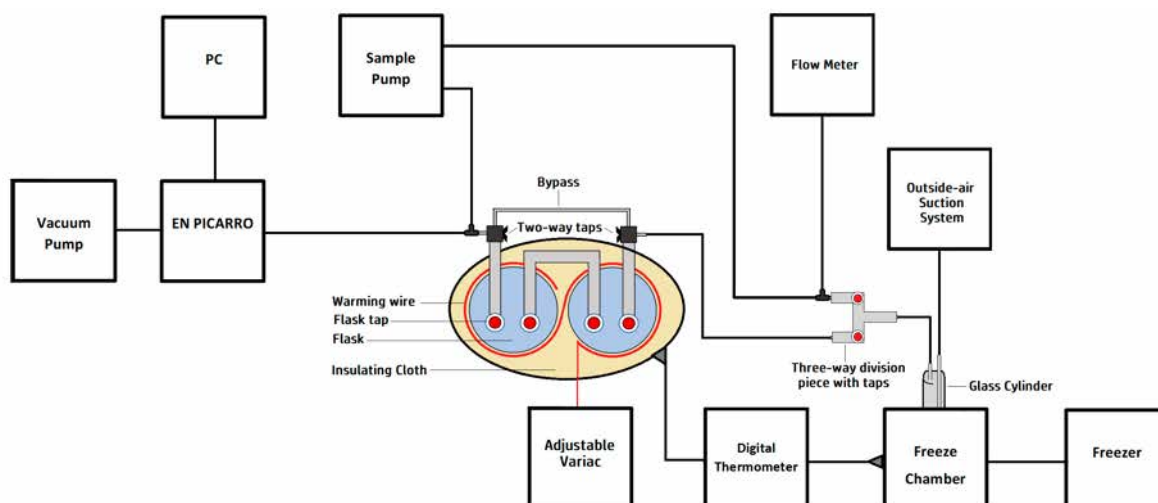

Figure 26: First experimental setup for warming of the flasks