Trace gases, δ^{13}C and δ^{18}O of CO$_2$-in-air samples:

Storage in glass flasks using PCTFE seals and other effects

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Abstract

The storage properties of air in borosilicate glass flasks have been studied over extended periods of time. Changes of the trace gas composition as well as the stable isotope ratios of CO$_2$ have been observed and quantified. Different types of sealing materials are discussed and the role of permeation is reiterated. The effects of two types of sealing materials (PFA and PCTFE) have been investigated more closely. Except for a small increase in the CO concentration over time, PCTFE in general seems much better suited than PFA owing to the much lower permeation rates for most gases. In particular, no change could be detected for the CO$_2$ mixing ratio over a time period of 250 days.

The isotopic composition of CO$_2$ remains constant for δ^{13}C in both materials. δ^{18}O, on the other hand, exhibits a pronounced change over time with a trend close to -0.2 ‰ in 100 days. Possible causes are discussed including traces of H$_2$O or exchange with OH bonds inside the borosilicate glass.

Introduction

Owing to the small size of seasonal and longer term alterations trace gas measurements as well as CO$_2$ carbon and oxygen isotope ratios in air samples collected in glass flasks require the highest attainable precision.[1] Among the limitations to improve such measurements is the integrity of the samples during storage. The option to measure samples within a short time period following collection is not always given. Logistical problems in sample transport from the often remote sampling stations (e.g. Siberia, Antarctica) require that samples remain unaltered over months before analysis can be made. On top of the time aspect, temperatures during storage as well as outside pressures may vary considerably.

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Samples are usually collected in duplicate in order to exclude results from flask pairs that differ by more than a certain margin. Systematic errors, however, that arise during storage and alter the respective sample air in a similar fashion in both flasks, are not detectable using such a strategy. Loss of air through the O-ring seals via diffusion is such a case.

Diffusion through O-rings

Permeation is a function of the sealing material, the geometry of the seal, the temperature, partial pressure difference and, most importantly, of the molecular species diffusing through the seal[2]. Diffusion through a single O-ring can be described by

(1) $d(pV)/dt = D_g(T) \bullet A/d_y \bullet (p_i-p_A)$

with A= exhibited O-ring area, d_y = O-ring diffusion length, $D_g(T)$ = Gas diffusion constant, T = Temperature and (p_i-p_A) denoting the pressure difference between the inside and outside of the flask. The gas diffusion constant or permeation coefficient $D_g(T)$ differs widely for the diffusing gas and for the O-ring material. Some literature constants have been compiled in reference 2. For CO_2 the permeation coefficient for instance varies between $4 \bullet 10^{-17}$ m^2/s mb^{-1} (PCTFE) and $2.3 \bullet 10^{-12}$ m^2/s mb^{-1} (Silicone), i.e. 5 orders of magnitude. For other gases the situation is similar and the relevance of the effect for flask sampling of air has been recognized[2].

Flask conditioning

Measurements of trace gases in atmospheric air as well as determination of isotopic composition of CO_2 in air samples must be made with a high focus on precision and accuracy. In order to avoid a spill over of 'bad' air into the next sample (we have seen samples with organic material from a spill over of kerosene in air campaigns, we occasionally have samples with a considerable water background and we often have flasks filled with soil or close-to-ground air) or other forms of memory we have installed a routine flask conditioning unit where all flasks have to pass through in between sampling. Figure 1 depicts the major components of the unit. Dry conditioning air (clean air, originally manufactured for scuba diving) is dried further with $Mg(ClO_4)_2$. A backpressure regulator and mass flow controller bracket the flask 'sausages' (series of flasks connected with Cajon Ultratorr adapters) attached to a wide-bore Valco 6-port valve.
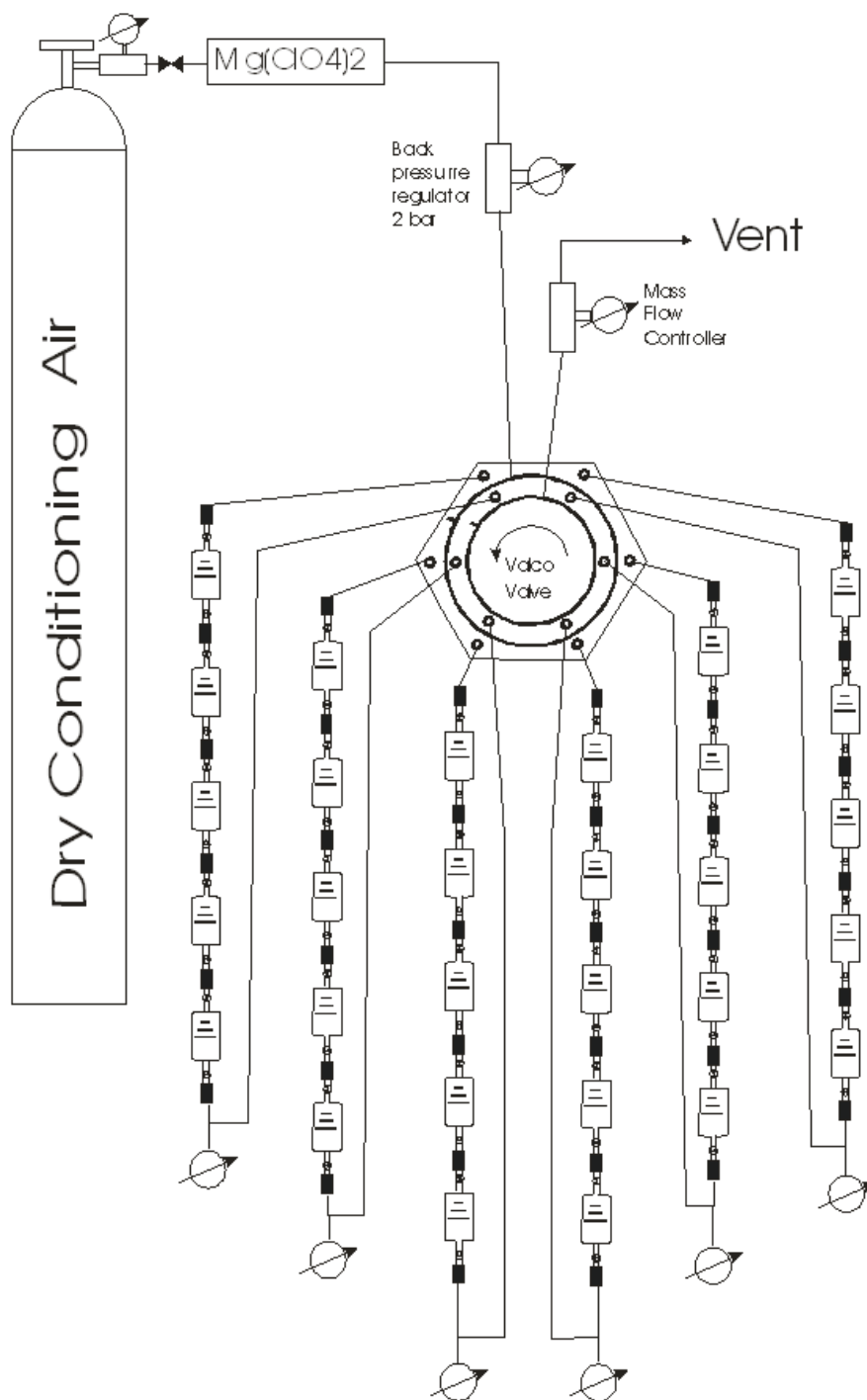
Figure 1; Layout of the flask conditioning station at MPI-BGC Jena. Five flasks in a row are flushed with dry air at the final pressure of 2 bar (3 l/min, ½ h).

Conditioning is made at the final pressure of 2 bar using a flow of 3 l/min for 1/2 h for every 5-flask sausage. Hence, a total amount of 90 l of conditioning air passes the 1-liter flasks, thereby exchanging the total volume 9 times. We have carefully checked whether the flasks within a sausage differ for instance from the first to the last, but we have never found any significant difference for any of the measurements we routinely perform, including O_2/N_2 ratios (see reference 3 in this volume). We also have occasionally checked for deviations from one sausage to the next for adjacent fillings. Also here, we were unable to find differences so far.

Trace gas stability

A number of our standard flasks have been filled with dry air using the procedure described above in order to study the stability of trace gas mixing ratios over elongated periods of time.

Figure 2; Glass flask with PCTFE-on-glass seat[4]. The shaft seal is made using two Viton O-rings. The flasks are protected against ex- or implosion hazards by a heat shrink hose (black).

Some of the flasks were equipped with PFA O-rings, another set of flasks had a PCTFE seal as shown in Figure 2. The storage tests were made by analysing flasks from a common sausage at different times. The data are shown in Figure 3 for CO_2, CH_4 and N_2O and in Figure 4 for CO.
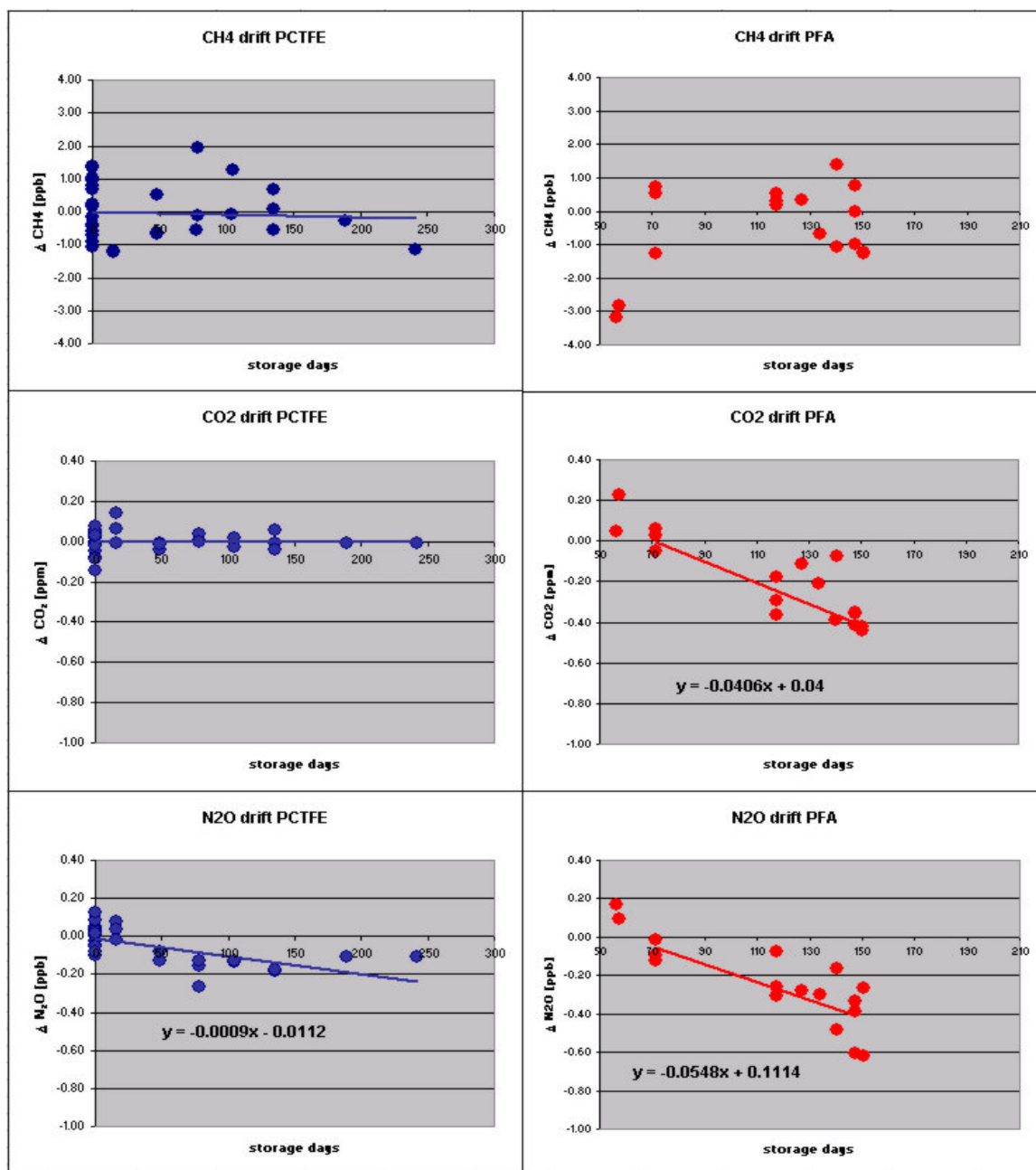

Figure 3; Storage data for the mixing ratios of CO_2, CH_4, and N_2O. The right hand panels are for PFA O-rings, results for the new PCTFE flasks are on the left.

Each data point in these figures represents the mean of triplicate analsis of a single flask, i.e. all flasks were stored under the pressure of 2 bar until measurement. The PFA flasks were part of an ongoing bilateral intercomparison program filled in Heidelberg by I. Levin using a procedure close to the one described above. The PFA flasks exhibit a clear preferential loss of CO_2 (about -0.4 ppm in 100 days) and of N_2O (about 0.5 ppb in 100 days) over time. The mixing ratio of CH_4 seems to be stable. For the flasks equipped with PCTFE the trend in CO_2 is completely eliminated, CH_4 is again stable over time and the drift in the N_2O mixing ratio has declined to less than $1/5^{th}$ (if any) of the PFA value. The stability of CO, however, seems to deteriorate slightly when replacing PFA O-rings with PCTFE (Figure 4). An increase of CO of almost 6 ppb in 100 days is observed. The phenomenon has first been noticed by Ray Langenfelds of the CSIRO Atmospheric Research division in Aspendale, Australia. He observed a growth of about 7 ppb in 100 days in flasks equipped with a different geometry of the PCTFE seal[5]. The origin of the finding is not clear and warrants further observation. We speculate that it may be an outgassing effect that should decline over time.
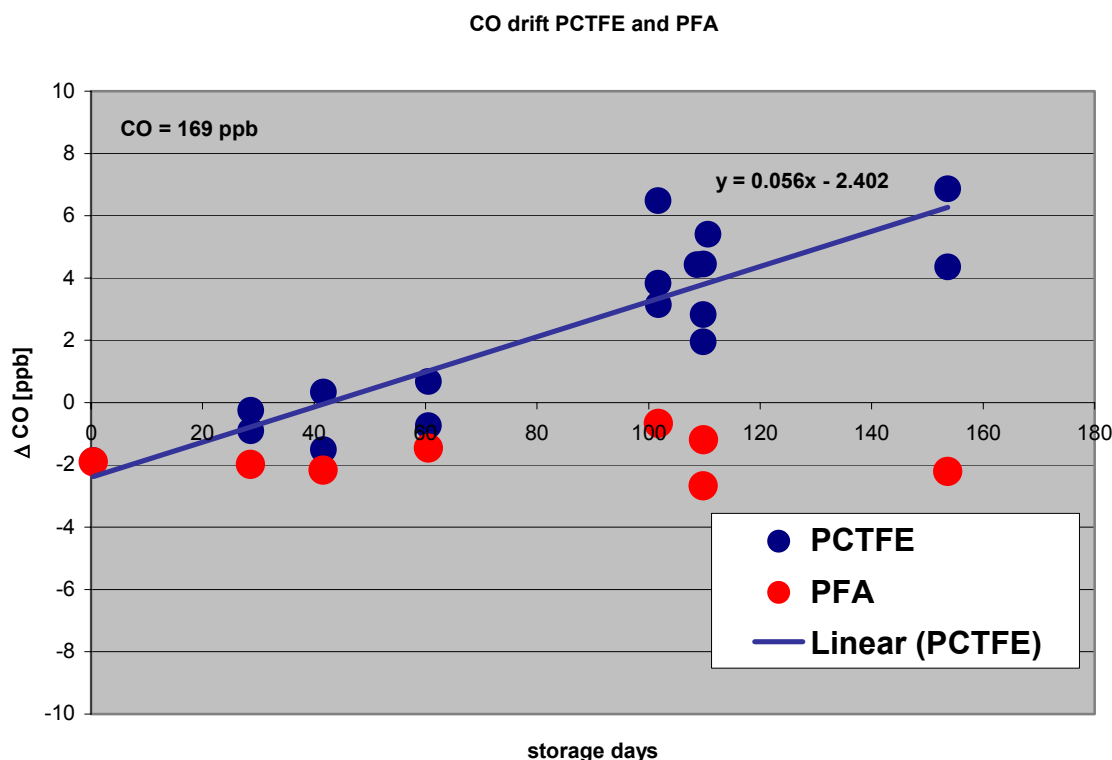
CO drift PCTFE and PFA

Figure 4; Storage data for the CO mixing ratio in air samples. PCTFE sealed flasks seem to develop CO over time. An outgassing effect of the polymer is suspected to be the cause.

In any case: The effect is small in comparison to the observed variability of CO in atmospheric samples. The data for H_2 and for SF_6 are not shown in the figures. Within measurement precision these data were essentially flat with time for both types of sealing materials.

Storage effects for the stable isotope ratios of CO_2 in air

Measurements of $^{13}C/^{12}C$ ratios from air-CO_2 stored in glass flasks have mostly been reliable in the past. Extensive intercomparison programs have revealed a high level of comparablity of such data and exchange of air in glass flasks is used to monitor and diagnose mutual drifts caused by either the measurement equipment or by the standardization procedures in the participating laboratories[6].

CO_2-in-air isotopic analysis:
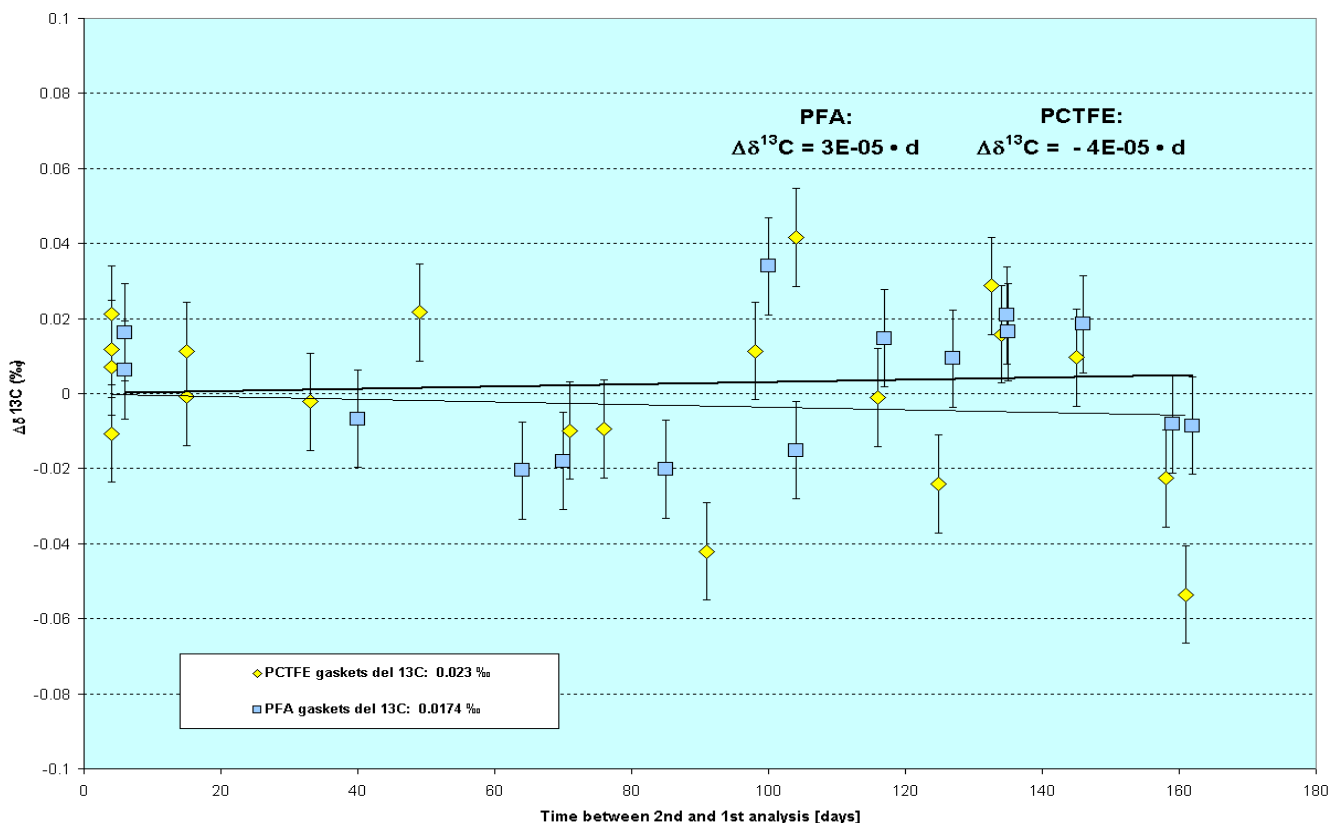Single flask history (2nd - 1st analysis vs. time)

PFA:
$\Delta\delta^{13}C = 3E\text{-}05 \cdot d$

PCTFE:
$\Delta\delta^{13}C = -4E\text{-}05 \cdot d$

◇ PCTFE gaskets del 13C: 0.023 ‰

☐ PFA gaskets del 13C: 0.0174 ‰

Figure 5; $^{13}C/^{12}C$ isotope ratio results for CO_2 in air samples. Two measurements per sample with the difference between the second and the first determination plotted as a function of time.

It is therefore not surprising that our findings confirm that there is no change of the measured $\delta^{13}C$ values over longer periods of time (Figure 5). Each sample was measured twice with the corresponding storage time in between the two determinations. The error bars represent the average long term single measurement precision of our isotopic measurements. $\Delta\delta^{13}C$ denotes again the difference between the first and the second determination of the isotopic composition. The trendlines are not significant. Although there seems to be an increase in the scatter of the data points as a function of time, we believe that this is not significant. The overall precision of about 0.02 ‰ for both types of flasks is in line with our normal flask pair deviation. Figure 6 shows the corresponding situation for $\Delta\delta^{18}O$ of CO_2 in the same samples.
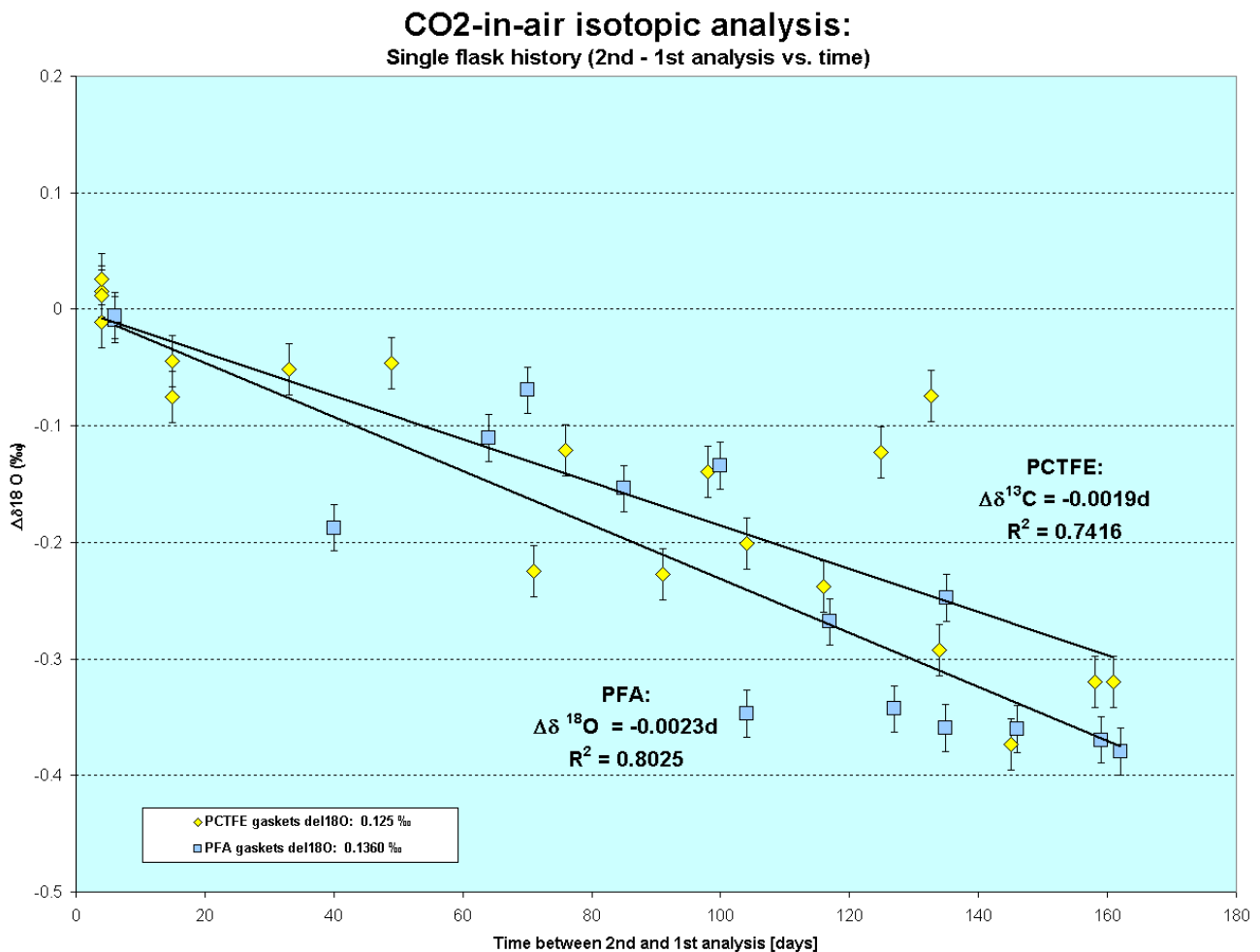

CO2-in-air isotopic analysis:
Single flask history (2nd - 1st analysis vs. time)

PCTFE:
$\Delta\delta^{13}C = -0.0019d$
$R^2 = 0.7416$

PFA:
$\Delta\delta^{18}O = -0.0023d$
$R^2 = 0.8025$

◇ PCTFE gaskets del18O: 0.125 ‰
☐ PFA gaskets del18O: 0.1360 ‰

Figure 6; $^{18}O/^{16}O$ isotope ratio results for CO_2 in air samples. Data are from the same measurements as those in figure 5

Contrary to ^{13}C there is a clear negative trend with a slope of about -0.2 ‰ in 100 days. In light of the single determination measurement precision indicated by the error bars, the trend is statistically significant with $R^2 > 0.7$ for both types of flasks. The trend is also large in comparison to the measurement precision that is necessary for explaining the fate of CO_2 regarding the cycling through different compartments of the environment. Moreover, there is an increase in the scatter of the data over time, rendering a possible drift correction almost impossible. We believe that the observed trend is in line with the inconsistencies observed in ^{18}O records and in intercomparisons between laboratories. If we find a cure for this behaviour we will certainly improve on these issues and make better use of ^{18}O data in the future.

One of the prime candidates for causing ^{18}O drifts is water in the flasks, present either from the start or added over time through permeation. The latter should show up in the data as a pronounced difference in the ^{18}O behaviour between the PFA and the PCTFE flasks owing to the differences in permeation rates. Such differences are not seen (yet) in the data set. Water on the glass walls, on the other hand, should come to an equilibrium with the CO_2 in the flasks within a rather short period of time. Complete exchange of large amounts of CO_2 with liquid water is achieved within less than a single day. Hence, if water is responsible for the observed change of $\delta^{18}O$ over time, it must reside inside the glass, not on the surface and diffuse slowly from there. Alternatively, the rate limiting step can also be a diffusion of CO_2 in and back out of the glass. Exchange then must take place inside the glass. Borosilicate glass (Pyrex®, Duran®, our flasks are made from the latter) is carrying a large number of OH groups which are part of the glass structure and not mobile. We suspect that this structure itself, not water trapped inside, is able to slowly exchange oxygen isotopes with CO_2. Whether other types of glass are better suited or whether a coating of the surface with another type of glass would be a solution remains to be seen in the future.

Acknowledgments

We also would like to thank QVF AG, Ilmenau (www.glasapparate.de), the manufacturers of our flasks for developing the PCTFE valve with us and make it available commercially.

References

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[5] Ray Langenfelds, personal communication

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