The authors would like to thank Referee#1 and Referee# for their valuable comments and suggestions on this manuscript. Below we have addressed the individual remarks by each reviewer. The Referee's comments and questions are blue, the authors' replies are formatted as plain text, and excerpts from the manuscript as well as changes to the manuscript are given in italics.

Reply to Anonymous Referee #1

The manuscript "Experiments with CO_2 -in-air reference gases in high-pressure aluminium cylinders" of M. Schibig et al. studies the stability of CO_2 in air mixtures at ambient mole fractions. The topic is relevant, since accurate and reproducible measurements with traceability to standard scales are needed to detect changes in regional sources and sinks of CO_2.

The manuscript is generally well written and concise. The chain of arguments is sound, and the topic is relevant for the scientific community. I therefore do recommend publication in AMT after addressing the following concerns.

General comments

The experiments carried out are clearly relevant for laboratory studies using large amount of standard gases within a short time period. However, this is mostly not the case for long-term monitoring of CO_2 and other research projects, where the gas of a standard cylinder is used over a much longer time period and in intervals. During period without use of standard gas, re-equilibration might take place, and the effect of changing CO_2 mole fraction during the use of a standard that was observed in this study will in many cases not happen or be much less pronounced in a normal measurements set-up for ambient CO_2.

We disagree with the referee. The adsorption/desorption effect is mainly pressure driven and not dependent on time. According to Langmuir's adsorption/desorption equation, the equilibrium between the molecules on the cylinder wall and in the air has to change with changing pressure.

Stability is much better for low flow conditions, but again, in reality, it might even be worse due to effects of the regulators. Especially in realistic measurement set-ups, this can be a problem, since only small aliquots of standard gases are used in longer time intervals, and the air is mostly sampled from the regulator and not directly from the cylinder. I recommend adding a few words on this issue.

In realistic measurement set-ups at an e.g. atmospheric measurement station, the main valve of a cylinder remains open and therefore the gas in the stem and the regulator can equilibrate with the gas in the cylinder body. Then, when a cylinder is measured e.g. to calibrate or as a target, the first few minutes are usually discarded to make sure the regulator is flushed properly and to avoid such effects. This is recommended good practice in every WMO/GAW report. If a cylinder is used only sporadic, the regulator should be flushed several times anyway. Therefore, we do not think that this makes a big difference if best practice recommendation for trace gas measurements are followed properly.

The study was carried out with dry air mixtures (H_2O < 1 µmol mol^{-1}). Residual water content might have a significant impact on the behavior of CO_2 absorption. Has the low water content be verified by measurements or other means?

The water content is ensured by the drying system NOAA uses to fill the calibration gas tanks at Niwot Ridge station and is continually measured (Meeco Waterboy, Meeco Inc., USA) during the filling procedure. For further information such as the setup and specifications of the filling station and the procedure see: https://www.esrl.noaa.gov/gmd/ccl/ccl.html and https://www.esrl.noaa.gov/gmd/ccl/airstandard.html.

What will be the effect of residual water, even if less than 1 µmol mol^{-1}? Could it be that differences in the residual water content explain at least partly the difference between individual cylinders or fillings?

At such low water contents, we do not expect any significant influence of the water on the CO_2 adsorption/desorption effects, because CO_2 molecules occupy only a fraction of the available active sites on the cylinder wall as shown in the paper. It would be different if there were more water in the cylinder, because the water molecules would compete with the CO_2 molecules for the available active sites and hinder CO_2 molecules to adsorb to the cylinder wall.

A very recent publication studies similar effects including the influence of water on the stability of gaseous reference materials (Brewer et al., 2018). Citation of this work should be made in the final AMT version of the paper.

The publication was added to the references.

SGS (Superior Gas Stability) cylinders are mentioned in the introduction and methods, but no results are shown in the paper. In the conclusions, they are mentioned again, saying that they behave in the same way as untreated cylinders. This should also be shown and discussed in the results. E.g. individual fits could be shown for SGS and untreated cylinders in a separate figure similar to Fig.6.

We added the following sentence to section 3.2:

"*The two SGS cylinders do not show a significantly different behavior, the form of the* CO_2 *enrichment with decreasing pressure as well as the amount is the same as for the normal cylinders within the given uncertainty (Fig. 6 b).*"

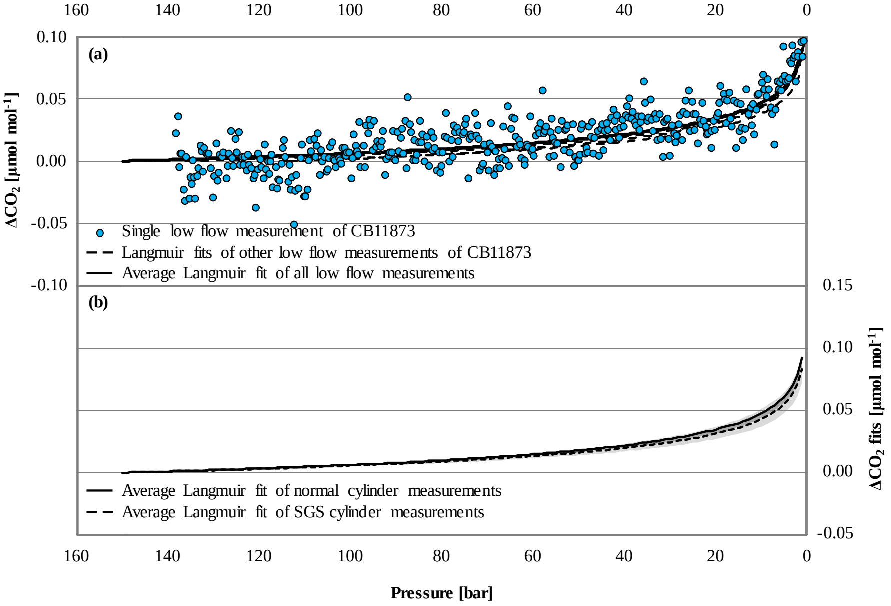
and we changed the sentence at page 10, line 34 from:

"*Two additional low flow measurements with horizontally positioned cylinders were done.*"

to:

"*Additionally, a low flow run with two horizontally positioned cylinders (one normal and one SGS cylinder) was done.*"

Additionally we expanded figure 6 that shows all low flow measurements of one cylinder (panel a) with a second panel that shows the average fit of all low flow measurements of the normal and SGS cylinders, respectively, with the uncertainties given as greyed area (panel b).



"*Figure 6: a) The blue circles represent the* CO_2 *mole fraction measurement of a low flow experiment started on 17.10.2016 with CB11873 vertically positioned as a function of pressure, note the inverse pressure scale. The black dashed lines are the individual fits following the Langmuir model of the other low flow experiments done with CB11873 vertically positioned, the black solid line represents the average Langmuir fit using all low flow experiments with the* *cylinders vertically positioned. b) The black solid and dashed line correspond to the average Langmuir fit of all normal and SGS cylinder measurement, respectively, that were done under low flow conditions, the greyed area corresponds to the standard deviation of the averages. In order to plot all data in one plot, the corresponding ($CO_{2,ini}$ – $CO_{2,ad}$) was subtracted from the measurements and the fits in both panels.*"

In section 3.3, we replaced the first sentence

"*In the high flow mode, eight complete drainings were done with cylinders vertically positioned…*"

with

"*In high flow mode, each of the six normal and the two SGS cylinders were drained once with cylinders vertically positioned…*"

In section 4, the first sentence

"*The low flow measurements with cylinders vertically positioned show repeatedly comparable CO_2 enrichment with decreasing pressure, no matter which cylinder was measured.*"

was shortened and a second sentence was added, it reads now:

"*The low flow measurements with cylinders vertically positioned show repeatedly comparable CO_2 enrichment with decreasing pressure. Neither the normal nor the SGS cylinders showed any unique features with respect to CO_2 enrichment.*"

I don't see much additional value of the experiments with heating and changing the orientation of the cylinders during venting. The results of the heating experiments were not consistent between different runs, and probably more experiments would be needed to get a clear picture. For example, the mole fraction change after the start of the heating shown in Fig. 15 is not significantly different from changes observed at higher pressures during the same run. The results of the experiments with changing orientation during the draining are also based on only one run for each experiment, and it is unsure if they can be reproduced. The paper could be shortened and would improve if only the results of the low and high flow experiments, including different cylinder orientation and treatment, are presented.

We disagree with the referee that the heating experiments and changing the position do not add any value to the manuscript. However, we agree that more experiments are needed, which is also stated in the manuscript. This is also why we would like to keep these experiments in the manuscript. These tests with no clear result might inspire other laboratories to do more experiments in this direction to solve this issue. However, we shortened the paragraph at page 17, line 22 from

"*With the three cylinders that were moved upside down, the picture is not very clear. Because of a logger failure , there are no temperature measurements on the first cylinder, which is why it will not be discussed here. The second and the third cylinders put upside down show a drop in the CO_2 mole fraction after they have been moved. While the second cylinder remains stable at the slightly lower CO_2 mole fraction, the CO_2 mole fraction of the last cylinder goes up first by about 0.07µmol mol^{-1} from 30 to 15 bar and falls back by roughly the same amount until the end of the experiment. The temperature measurements of the two cylinders look the same. The only small difference between the two is the pressure when they were turned, the second cylinder was turned at 32.2 bar, the third cylinder was turned at 27.8 bar. However, whether this caused the different behavior in the CO_2 measurements remains unclear. The results from the experiments with constant heating…*"

to

"*With the three cylinders that were moved upside down, the picture is not very clear. Also the results from the experiments with constant heating…*"

I further recommend re-writing the conclusions. Currently, they are difficult to read without the full context of the paper, and present results which are not mentioned previously (e.g. SGS cylinders). Furthermore, the statement 'This opens the possibility to use a general correction function in case a calibration cylinder on a field station runs empty' should be made in the results section because it needs more careful discussion. Most likely, corrections will be associated with high uncertainties, since the calibration sequence at stations is different from your experiments in which the cylinders were emptied with a constant flow.

We changed the conclusion from:

"*The tested aluminum cylinders behaved always the same within uncertainties, the individual cylinders did not show distinct unique features. This is also true for the SGS cylinders, indicating no benefit in using these tanks in CO_2 measurements at ambient level. To describe the CO_2 enrichment in low flow settings, the Langmuir adsorption/desorption model using averaged coefficients is sufficient to describe the CO_2 enrichment effects in aluminum cylinders. This opens the possibility to use a general correction function in case a calibration cylinder on a field station runs empty. However, we still recommend changing calibration cylinders before the pressure drops below 30 bar in order to avoid the steepest part of the enrichment at the lowest pressures, and the corrections that add uncertainty to the measurements. At the same time the currently* *recommended threshold of 20 bar (WMO, 2016) is supported by measurements of this study. Using the low flow coefficients for the Langmuir model, a drop from 150 to 20 bar results in a* CO_2 *enrichment of about 0.036* $\mu mol\ mol^{-1}$*, which is still well within the WMO compatibility goal between laboratories.*

In high flow settings additional thermal diffusion effects and Rayleigh fractionation come into play that overrule the simultaneously ongoing Langmuir adsorption/desorption. Depending on the positioning of the cylinder, CO_2 *can be increasing or decreasing with decreasing pressure. However, this might be only the case for systems with a steady high flow. If cylinders are decanted in quick bursts with enough time in between to allow them to equilibrate thermally, thermal fractionation should not be able to develop and only Langmuir adsorption/desorption effects have to be taken into account. Some of the observed effects remain unexplained because the measurements were inconsistent, or the behavior of air in the cylinder needs to be modelled explicitly. To answer these questions additional controlled experiments would be necessary. A further benefit could be gained by using a CRDS (cavity ring down spectroscopy) gas analyzer because it does not need to be calibrated as often as an NDIR analyzer and it could measure several gas species simultaneously.*"

to

"*Six 29.5 L Luxfer L6X® as well as two 29.5 L Luxfer L6X® SGS aluminum cylinders were used to investigate the stability of the* CO_2 *mole fraction of ambient level* CO_2*-in-air mixtures with decreasing pressure. In low flow settings (0.3* $L\ min^{-1}$*), the Langmuir adsorption/desorption model using averaged coefficients is sufficient to describe the* CO_2 *enrichment. With this function, the* CO_2 *enrichment over a pressure range of 150 to 1 bar was calculated to be* $0.090 \pm 0.009\ \mu mol\ mol^{-1}$*, where the given error corresponds to the standard deviation (1-sigma) of the fitted* CO_2 *enrichment of the individual cylinder drainings. The tested aluminum cylinders behaved always the same within uncertainties, the individual cylinders did not show distinct unique features. This is also true for the SGS cylinders, indicating no benefit in using these tanks for* CO_2 *measurements at ambient level. This opens the possibility to use a general correction function in case a calibration cylinder on a field station runs empty. However, we still recommend changing calibration cylinders before the pressure drops below 30 bar in order to avoid the steepest part of the enrichment at the lowest pressures, and the corrections that add uncertainty to the measurements. At the same time the currently recommended threshold of 20 bar (WMO,* *2016) is supported by measurements of this study. Using the low flow coefficients for the Langmuir model, a drop from 150 to 30 bar results in a CO_2 enrichment of about 0.026 µmol mol^{-1}, whereas a drop from 150 to 20 bar yields a CO_2 enrichment of 0.34 µmol mol^{-1}.which is still well within the WMO compatibility goal between laboratories. By using bigger cylinders (e.g. 50 L) the surface to volume ratio becomes smaller compared to the 29.5 L cylinders used in this study, which might be beneficial in minimizing the CO_2 enrichment effect at lower pressures. We discourage the use of smaller cylinders as their surface-to-volume ratio increases. Approximating the top and bottom area of a cylinder as a disk perpendicular to the cylinder length (L), and assuming that the effective adsorption area remains the same where the cylinder diameter (R) has been compressed, the surface to volume scales as $(2\pi RL + 2\pi R^2)/(\pi R^2 L) = (L+R)/RL$. We expect a commonly used Luxfer N060 (internal volume 10.7 liter) to be worse by ~30%.*

In high flow settings (5.0 L min^{-1}), additional thermal diffusion effects and Rayleigh fractionation come into play that add to, or can overrule the simultaneously ongoing Langmuir adsorption/desorption. Depending on the positioning of the cylinder, CO_2 can be increasing or decreasing with decreasing pressure. We have demonstrated that these effects very likely do play a role, but before a satisfactory explanation can be attempted a considerable number of additional controlled experiments, as well as modeling of the flow and mixing in cylinders will be necessary. A further benefit could be gained by using a CRDS (cavity ring down spectroscopy) gas analyzer because it does not need to be calibrated as often as an NDIR analyzer and it could measure several gas species, such as CH_4 or CO, simultaneously."

Specific comments

Page 2, line 13: kilogram is a SI unit, despite the fact that it is still based on an artifact. It should be removed from the list of examples in parenthesis.

"…, the kilogram or…" was removed

Page 3, line 21ff: Add a short description of the performance of the analytical system (repeatability, drift etc.) here. This could be done by moving paragraph 3.1 to the method section.

We moved paragraph 3.1 to the method section and changed the paragraph and figure numbering accordingly.

Page 3, line 34: According to Fig. 1, C1 is repeatedly measured, not C2. Page 9, first lines of result section and section 3.1 would better fit in the method section.

Correct, changed to C1.

Page 10, section 3.2.: The low flow experiments are probably the most relevant for most users of standard gases. Beside the average of all cylinders, the result of only one (representative) standard is shown, while in total 38 experiments of the same type were made. It would be valuable to see the variation between different cylinders / fillings, which could be added in either an additional figure or Fig. 6 (e.g. individual fits for all experiments). I recommend to also show and discuss the similar behavior of SGS and untreated cylinders could here.

We added a second panel to Fig. 6, that shows the average fits of the low flow experiments of the normal and the SGS cylinders with the uncertainty given as greyed area (see also similar question above).

Figures 6 and 8: The y-axis shows ΔCO_2, and not CO_2 mole fraction, which needs to be corrected.

We replaced "*CO_2 mole fraction…*" with "*ΔCO_2…*" in Figure 6 and 8. The same is true for Figure 12, which was changed in the same manner on the authors' behalf.

Why do the measurements at higher pressures show a negative delta? Especially in Fig. 8 all ΔCO_2 as well as the fits at higher pressures are negative. Is this correct?

($X_{CO2,ini}$ and $X_{CO2,ad}$ correspond to $CO_{2,ini}$ and $CO_{2,ad}$, respectively, see also reply to Referee#2)

It is correct but might be misleading. For this figures, the term $CO_{2,ini}$ was subtracted from the Langmuir-equation (equation 1) and the remainder with the corresponding coefficients was plotted. $X_{CO2,ini}$ corresponds to the CO_2 mole fraction before adsorption to the walls occurs, therefore it is slightly higher than the CO_2 average value at the beginning of the measurements. This results in negative ΔCO_2 values in the beginning of the measurements. For clarity we shifted the values by adding $X_{CO2,ad}$, this shifts the fits upwards so that the initial value is exactly 0. This was done for Fig 6, 8, and 12. In all three captions we changed

"*...the corresponding $CO_{2,ini}$ was subtracted…*"

to

"*…the corresponding ($X_{CO2,ini} – X_{CO2,ad}$) was subtracted…*",

accordingly.

Technical corrections

Page 2, line 24: the latest available GGMT report is not cited (WMO, 2016). It should be added. The format of the citations of the WMO reports needs also to be changed.

The latest GGMT report was added and the format of the citations were changed.

Page 2, line 28: replace 'SI values' with 'SI traceable values'.

Done.

Page 2, line 35: Cite the latest GGMT report here.

Done.

Page 3, line 36: Change to ‘An additional full calibration was made at the end of each experiment’.

Done.

Page 6, line 25: Kitzis (2017) is missing in the references.

Correct, we added the reference.

References

Brewer, P. J., Brown, R. J. C., Resner, K. V., Hill-Pearce, R. E., Worton, D. R., Allen, N. D. C., Blakley, K. C., Benucci, D., and Ellison, M. R.: Influence of Pressure on the Composition of Gaseous Reference Materials, Analytical Chemistry, 90, 3490-3495, 2018.

WMO: 18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13-17 September 2015, GAW Report No. 229, World Meteorological Organization, Geneva, Switzerland, 2016.

Corrections on the authors’ behalf:

We replaced all symbols for liter “l” with a capital L for better readability (also in the figures).

As mentioned above, the y-axis of Fig. 12 was changed from “*CO_2 mole fraction…*” to “*ΔCO_2…*” as requested by Referee#1 for Fig. 6 and Fig. 8.

Page 5 line 21: For consistency, we changed “*normal flow*” to “*low flow*”

Page 9, line 27: For clarity, we changed the first sentence from:

“*No general filtering was applied to the measured data.*”

To

“*No data selection was applied to the measured data.*”

Page 10, line 32 ff: We replaced the two sentences

“*The standard deviation of the average α is very low. If the measurement system’s repeatability as deduced from the target gas measurements is taken into account, a realistic error of α should be about four times bigger*.”

with

“*The given uncertainty range of 0.000004 corresponds to about 9.3 % of (1-0.999957). Considering the calculated CO_2 enrichment of 0.085 µmol mol^{-1}, 9.3 % equates to about*

0.008 µmol mol^{-1}, which is consistent with the measurement system's repeatability of 0.01 µmol mol^{-1} as deduced from the target gas measurements before the analyzer change."

Page 13, line 6: For better readability the two sentences were shortened from

"*If only the CO_2 measurements below 50 % of the cylinder's pressure are used to calculate α, then the average fractionation factor for the outflow becomes 1.00021 ± 0.00004, indicating an even stronger fractionation. When the Rayleigh fractionation with the stronger fractionation factor is only applied after the cylinder is half empty, when the temperature difference between the upper and the lower side of the cylinder body reaches its final value of 0.3 K, the average final depletion is -0.26 ± 0.07 µmol mol^{-1}.*"

to

"*If only the CO_2 measurements below 50 % of the cylinder's pressure are used to calculate α, then the average fractionation factor for the outflow becomes 1.00021 ± 0.00004, indicating an even stronger fractionation with a final average depletion of -0.26 ± 0.07 µmol mol^{-1}.*"

Page 15 line 7: "*vertically*" was replaced with "*horizontally*".

Page 16, line 24: For clarity reasons we changed the sentence from

"*This is also the moment when the temperature difference between…*"

to

"*This is also the reason when the measured temperature difference between…*"

Page 18, line 18:We replaced 0.036 µmol mol^{-1} with 0.034 µmol mol^{-1}

Page 24: For clarity reasons, the caption of figure 3 (now figure 2) was changed from

"*Flow schematic of the high flow inlet system. The sample gas enters on the left side at 5.0 l min^{-1}. A small aliquot of 0.3 l min^{-1} goes to the analyzer, the vast remainder of 4.7 l min^{-1} goes to the exhaust. The ratio between the gas going to the analyzer and the exhaust, respectively, can be adjusted by the needle valve on the exhaust side.*"

to

"*Flow schematic of the high flow inlet system. The sample gas enters on the right side at 5.0 L min^{-1}. A small aliquot of 0.3 L min^{-1} goes to the analyzer, the remainder of 4.7 L min^{-1} goes to the exhaust. The ratio between the gas going to the analyzer and the exhaust, respectively, is set by the dimensions of the inner and outer tube and can be adjusted by the needle valve on the exhaust side.*"

Page 28, line 4: "*vertically*" was replaced with "*horizontally*"

Page 34: We changed the colors of figure 13 for better readability and changed the caption accordingly.

Page 35: The x-axis title of figure 14 was corrected.

Page 37, line 5: “*vertically*” was replaced with “*horizontally*”, the x-axis title of figure 16 was corrected.

The authors would like to thank Referee#1 and Referee#2 for their valuable comments and suggestions on this manuscript. Below we have addressed the individual remarks by each reviewer. The Referee's comments and questions are given in blue, the authors' replies are formatted as plain text, and excerpts from the manuscript as well as changes to the manuscript are given in italics.

Reply to Anonymous Referee#2

General comments:

This paper describes a series of experiments performed to better understand previously observed drifts in the CO_2 mole fraction measured during the lifetime of reference gases in high pressure cylinders. The subject is of interest for worldwide measurements of atmospheric CO_2 mole fractions, which make use of such reference gases for their calibration. The authors have planned a consistent number of experiments to study the impact of various conditions. The measurements themselves appear robust, and all plots clearly summarise the observations. There is however some issue with the overall presentation, the organisation of the results, the link with the equations developed to fit the measurement results, and the relevance of some of the experiments. I therefore recommend a major revision before the paper can be published in AMT.

Although the general aim of the study appears to be a better understanding of already observed effects when using CO_2 in air standards, it is not so clear which particular questions are answered. For example, it is already recommended to leave not less than 20 bars in those cylinders, and this recommendation is again confirmed here. If that was the goal, it should be stated.

It was not the goal of this study to confirm the 20 bar recommendation, however, since this threshold is confirmed by the measurements done for this study we thought it worth mentioning.

The study also looked at the influence of the flow rate at which the gas is used, but the conclusions are never actually linked with some recommendation. Does this have any impact on their usage? Similarly, a big part of the paper is devoted to the analysis of thermal convections inside the cylinders. What is the impact here? Should this be followed by any recommendation, or was it only performed to better understand the process?

The high flow experiments were done to reach a better understanding of the processes involved. As described in the introduction (page 3, line 8) the high flow measurements were done to find out whether adsorption/desorption processes are the only ones changing the CO_2 mole fraction of the sample gas with decreasing pressure. However, while doing these experiments, we found that Rayleigh fractionation is at work as well and that this effect is stronger than the Langmuir adsorption/desorption when decanting at high flow. Since we found this thermally induced fractionation process to play a major role in altering the CO_2 mole fraction at high flow rates, we wanted to investigate it further and be able to give a possible explanation for the measured effects as well.

The organisation, terminology and wording of the paper can be improved. The description of the experiment is not very well structured and information on a same aspect is sometimes separated in different sections. At several occasions, words have been omitted, resulting in sentences which can still be understood but belong to oral language rather than a written paper.

We replaced all contracted forms such as e.g. didn’t, isn’t etc. with their longer forms (did not, is not etc.). We also changed phrases throughout the whole manuscript to improve readability, e.g. page 7, line 15 “…*where the* CO_2 *increase is more pronounced…*” reads now “…*where the increase of the* CO_2 *mole fraction is more pronounce*d…”

Authors also chose to sometimes use their own terminology, not following recommendations from international bodies such as IUPAC. It would be easier to follow with a more common terminology. It is also suggested to write all symbols for quantities in italic.

All symbols of quantities are now in italic and we changed some of the symbols used in the manuscript (e.g. $CO_{2,ad}$ is now $X_{CO2,ad}$, N_a was changed to n_a in order to prevent confusion with the Avogadro number, l (liter) was changed to L etc.)

Finally, a recent paper dealing with the same subject was published earlier in 2018. It should be mentioned in the introduction and results compared in the discussion: Brewer, P. J., R. J. C. Brown, K. V. Resner, R. E. Hill-Pearce, D. R. Worton, N. D. C. Allen, K. C. Blakley, D. Benucci and M. R. Ellison (2018). "Influence of Pressure on the Composition of Gaseous Reference Materials." Analytical Chemistry 90(5): 3490-3495.

We added this paper to the references.

Specific comments by section:

1. Introduction: the end of that section needs to be revised to state more clearly which questions are being answered, which experiments were performed to do so, and which theory was applied. It is suggested to replace the assumptions with questions, such as i) is the effect cylinder−dependent? ii) in which conditions is the Langmuir model sufficient, and when does this need to be completed with the other effects already mentioned earlier in the section? iii) are SGS cylinders any better?

We changed the wording of our hypotheses from

"*In this study the following hypotheses were tested, i) the* CO_2 *increase with decreasing pressure is different for each individual cylinder, ii) the* CO_2 *enrichment follows the Langmuir monolayer adsorption/desorption model and iii) the stability of the* CO_2 *mole fraction is better in SGS (Superior Gas Stability®, Luxfer, USA) cylinders.*"

to

"*In this study, three hypotheses were tested, i) the increase of the* CO_2 *mole fraction in the sample gas with decreasing pressure is different for each individual cylinder, ii) at low flow rates, the Langmuir monolayer adsorption/desorption model is sufficient to describe the observed* CO_2 *enrichment in the sample gas with decreasing pressure and iii) the stability of the* CO_2 *mole fraction with decreasing pressure is better in SGS (Superior Gas Stability®, Luxfer, USA) cylinders than in untreated aluminum cylinders.*"

In addition, other questions may be added if there are parts of the goal of the study, such as the influence of the flow rate at which the gas is sampled from cylinders, or the influence of the cylinder position.

Since most measurement systems use calibration gases at low flow rates, our focus is on the low flow rates. It was not the goal of this study to show that different flow rates as well as changing the orientation alter the CO_2 mole fraction of the sample gas. We used the different flow rates and orientations to see whether adsorption/desorption processes are the only effects influencing the CO_2 mole fraction of the sample gas or whether temperature gradients and thereby induced fractionation also plays a role. This is also described briefly on page 3, line 10 ff. However, since we found that a high flow rate in combination with different orientations of the cylinders has an influence on the CO_2 mole fraction of the sample gas, we thought it worth mentioning.

To make it more clear that we will ad change hypothesis two from

"*…ii) the* CO_2 *enrichment follows the Langmuir monolayer adsorption/desorption model…*"

to

"*…ii) at low flow rates, the Langmuir monolayer adsorption/desorption model is sufficient to describe the observed* CO_2 *enrichment with decreasing pressure…*"

Finally, it is recommended to add a summary of the following sections, to clarify for the reader which information is provided in each section.

We think by rearranging the sections as recommended by Referee#1 and Referee#2 the manuscript should be much easier to follow and therefore we do not think that this is necessary anymore.

2. Section 2:

a. The title (“methods”) appears unclear. It actually contains information on the cylinders and analytical equipment, the measurement protocol, but also some theory to describe all processes at work.

We changed it to “*Material and methods*”

To our understanding the purpose of the methods section is to describe the used materials, the analytical equipment, the measurement protocol, how the data was analyzed and what type of fit functions were used and why.

b. It is suggested to modify the organisation, starting with a section only devoted to the description of the theory, then the equipment (cylinders plus gas lines plus instruments), and finally the measurement protocol. Within the protocol, the description of the measurement sequence can come first, followed by the explanation of the different conditions chosen to test the various assumptions.

We reorganized the method section to the following order: Sample cylinders, Measurement system with subsections protocol, low flow measurement and high flow measurement, system performance, temperature measurement, heating system, CO_2 enrichment estimates.

2.1 Sample cylinders
2.2 Measurement system
2.2.1 Low flow measurements
2.2.2 High flow measurements
2.2.3 Measurement protocol (with explanation of the different conditions to test the various assumptions)
2.2.4 System performance
2.3 Auxiliary systems
2.3.1 Temperature measurement
2.3.2 Heating system
2.4 CO_2 enrichment estimates
2.4.1 Langmuir adsorption/desorption model I
2.4.2 Langmuir adsorption/desorption model II

2.4.3 Estimating *K* based on the CO_2 measurements

2.4.4 Rayleigh distillation model and its combination with the Langmuir adsorption/desorption model I

The reasoning behind this order is: We are interested in the stability of CO_2-in-dry-air mixtures in high pressure aluminum cylinders at low flow rates, therefore the cylinders should be described first, followed by the sections where we show how we measured it and how good the performance of the measurement system is. After that, auxiliary systems (temperature measurements of the cylinders and heating) are described. The last step of this work, and therefore presented last, are the different functions of known effects we used to fit to the measured data, to find out which effect is most probably responsible for the observed CO_2 enrichment.

c. The description of the protocol needs to be revised. Table 1 and figure 1 are clear and almost describe it completely, but the text brings more confusion. Specific words need to be chosen for each series of measurement (block, cycle, run), defined and further used with always the same meaning.

We changed the description of the measurement cycle from

"*The calibrations and measurements were done in a cyclic sequence defined in the control program. The cycles were divided in blocks of 5 minutes each, during which gas from a single cylinder (sample, calibration or target gas) was measured. The data was read every 5 seconds, but data reported to the log file were 30 s averages yielding 10 values per block. In the very beginning of each cycle, a full calibration with all four calibration gases (C1, C2, C3, C4) as well as a target gas measurement were done. Then the program cycled through all samples several times, before C1 was measured again to catch short term drifts in the measurement system (Fig. 1).*"

to

"*The CO_2-analyzer reported 5 s values to the data logger, which in turn logged 30 s averages. Ten of these 30 s averages were taken together into one 5 minute block that formed the basic unit used for the measurement sequence. The calibration, target and sample gas measurements were done in a repetitive cyclic sequence that was made up of the aforementioned 5 minute blocks and whose order was defined in the control program. In the very beginning of each cycle, a full calibration with a single block of each calibration gas (C1, C2, C3, C4) as well as a block of target gas measurement were done. Then, the program switched through all connected samples several times,* *measuring a block C1 in between to catch short-term drifts of the measurement system (Fig. 3). When a cycle was finished, a new cycle was started, again by measuring blocks of all four calibration gases first. At the end an additional calibration with all four calibration gases and the target gas was made.*"

A block is a 5 min interval during which a single gas is measured, the measurement cycles are made up of blocks.

A cycle starts by measuring all calibration gases, each during a 5 minute block, and subsequent sample gas measurements and some blocks of C1 to catch short term drifts of the analyzer.

A "cylinder measurement" refers to all measured blocks of one individual cylinder during one run. During a run, one or several sample cylinders are drained from their filling pressure down to the preset pressure threshold, when the measurement is stopped (usually 1 or 1.5 bar)

d. First part of the section 2 describes the measurement sequence, also displayed in Figure 1. Sequences were apparently setup to obtain both calibrated and a drift corrected values. This could be stated first, before providing the details of how this goal was achieved.

We changed the wording, see previous reply.

3. Section 2.4: is it relevant to show the equation used to determine the temperature? This cannot be checked and the only interesting value in that case seems to be the temperature.

The equation was removed and the sentence

"*The voltage was converted into temperature values by using the Steinhart-Hart (Steinhart and Hurt, 1968):*

$$\frac{1}{T} = A + B \cdot \ln R + C \cdot (\ln R)^3 \qquad (1)$$

where T is the Temperature, A, B and C are the Steinhart-Hart coefficients provided by the manufacturer of the thermistors and R is the measured resistance."

reads now

"*The voltage was converted into temperature values by using the Steinhart-Hart equation (Steinhart and Hart, 1968).*"

4. Section 2.6: it is indicated that the filling was done at Niwot Ridge Station. Was this the case every time a cylinder was emptied? Was it sent back and refilled there? Please clarify.

Yes, it was always the case. Niwot Ridge Station is very close to the NOAA Campus in Boulder. It is run by our group, which is why we filled the cylinders always there using the same equipment and procedure as for the NOAA standard cylinders.

5. Section 2.7: the entire section is difficult to follow, partly due to some considerations on unsuccessful attempt to fit the data. Even if some choices were justified by the observations, it would be easier to read if the different models were presented independently. The section could be divided in three parts, each of them presenting the assumptions, which part of the information comes from previous work (seems to be all in model 1 for example), which is the equation used during the fits, which parameters were assumed and which were fitted. The presentation of the maths could be better balanced: while some common knowledge is sometimes detailed (such as the definition of the Avogadro number), some more expert information is not fully described (such as the Rayleigh distillation function).

We merged other sections and split this section in four parts, it is now:

2.4 CO_2 enrichment estimates

2.4.1 Langmuir adsorption/desorption model I

2.4.2 Langmuir adsorption/desorption model II

2.4.3 Estimating K based on the CO_2 measurements

2.4.4 Rayleigh distillation model and its combination with the Langmuir adsorption/desorption model I

There we moved the explanations about the difficulties of fitting the K value into the according section, which reads:

"2.4.3 Estimating K based on the CO_2 measurements

"To find a value for K, a process of elimination was used. Given that the residuals between the data and the fit function of a good fit are normally distributed, K can be found by fitting the adsorption/desorption equation but with a fixed K value, starting with a value close to 0. Then, K is increased step wise, until the residuals are not normally distributed anymore. To improve the sensitivity of this method, only CO_2 measurements below 30 bar were taken into account, where the increase of the CO_2 mole fraction is more pronounced. These calculations were done for ten different low flow cylinder measurements. The resulting K values were averaged and the standard deviation was calculated. This K value might not be the best fit, but it gives a good estimate about the upper boundary of possible K values. To make sure the residuals of all fits stay well within the normally distributed range, the *K* value was considered to be the difference "average *K* value minus standard deviation", which resulted in 0.002 bar^{-1}. To be on the safe side, *K* was set in the nls algorithm to 0.001 bar^{-1}."

a. Model 1: Langmuir. Equation (2) comes from Leuenberger 2015 where it was derived from the Langmuir model. This should be stated clearly.

We changed the sentence

"*…based on the Langmuir adsorption/desorption model (Langmuir, 1918, 1916; Leuenberger, 2015):…*"

to

"*…based on the Langmuir adsorption/desorption model (Langmuir, 1918, 1916) as derived by Leuenberger et al. (2015):…*"

In addition, the Langmuir model normally uses partial pressure, not total pressure. Some consideration on the choice of using total pressure and its impact should be provided. The explanation on the difficult fitting may be moved to the results, to limit this section to the theory. The quantity K was fixed at the same value than in the Leuenberger paper. Is that a coincidence? This should be better explained, but again not in this section, which should only state that K was fixed to find $CO_{2,ad}$.

The assumption that the CO_2 partial pressure is proportional to the total pressure is valid in our case because the CO_2 mole fraction varies by at most a few tenths of 1 ppm out of 400 ppm. Method II does not make that assumption.

We decided against moving the explanation to the results section but we split the section in four subsections, one of these subsections explains how K was determined.

We shortened the following sentence

"*Therefore the algorithm wasn't able to find K values with a high confidence level and the output corresponded mostly to the lower boundary, even when it was set to 0, meaning no exchange between the cylinder wall and the gas.*"

to

"*Therefore the algorithm was not able to find K values with a high confidence level and ultimately K was fixed at 0.001 bar^{-1} to find the other coefficients of the model, as will be explained later.*"

The rest of the explanation will follow in a separate section "*2.4.3 Estimating K based on the CO_2 measurements*". The content of this new section is given above at comment 5.

It is true that K was fixed at the same value as in Leuenberger et al. (2015) but the K value was estimated independently. However, the value used here only represents a rough estimate and was fixed for all the further calculations.

b. Model 2: in this approach, it is stated that the fraction of occupied sites does not depend on the total pressure. Note that the CO_2 mole fraction varies with the total pressure, as demonstrated by the paper. It is certainly negligible but this should be explained. This section introduces the symbol Na for a number of moles. This symbol being commonly chosen for the Avogadro number, it is recommended to replace with na. The derivation of Equation (9) from (8) is not straightforward, compared to equation (5) for example which is very straightforward. It is suggested to provide the steps in annex, limiting this section to the model description and the equation used later on to fit the data. The formalism could also be improved, avoiding a sentence such as "total trace gas" to replace a quantity. Why not defining ntot = nad+ngas. Finally, like for the first model, considerations on results of the fit should be kept for the results analysis.

To make it easier to follow the derivation of equation 9, we added the following steps between Eq. (8) and Eq. 9 and changed the numbering of the equations accordingly:

"*…which we rearranged into the following equation*

$$-\rho_a dX = \frac{a}{V}\left(\frac{K d\rho_x}{1+K\rho_x} - \frac{K\rho_x K d\rho_x}{(1+K\rho_x)^2}\right) = \frac{a}{V}\frac{K d\rho_x}{1+K\rho_x}\left(1 - \frac{K\rho_x}{1+K\rho_x}\right) \qquad (9)$$

and subsequently into

$$-\rho_a dX = d\rho_x \frac{a}{V}\frac{K}{(1+K\rho_x)^2} \qquad (10)$$

By substituting $d\rho_x$ in Eq. (10) with $Xd\rho_a + \rho dX$, it can be rearranged to…"

We added "$n_{tot} = n_{ad}+n_{gas}$" as equation 5 and replaced the term "*Total trace gas*" with "n_{tot}" in the other formulas accordingly. "N_a" was replaced with "n_a" as suggested.

c. Model 3: in the third part, a Rayleigh distillation function is introduced. Some more explanation would be needed here, describing in one sentence the process and its expected impact on the CO_2 mole fraction. The formalism may also be improved here: equation (12) introduces a mole fraction with the symbol X, where equation (13) uses CO_2, meas. It is suggested to always use x for mole fractions.

The sentence

"*The outflowing gas is depleted in CO_2 if $\alpha < 1$ and vice versa.*"

was changed to

"*The outflowing gas is depleted in CO_2 if $\alpha < 1$, leaving the gas in the cylinder slightly enriched in CO_2 (and vice versa). With ongoing outflow, the effect gets stronger because the gas in the cylinder becomes more and more enriched. However, to make Rayleigh distillation possible, a fractionating process has to be involved, namely that the CO_2 mole fraction of outflowing gas is either enriched or depleted with respect to the cylinder average. A possible reason for fractionation in the cylinders is a temperature gradient in the cylinder. Heavier molecules tend to accumulate at the cooler end of a gas reservoir, while the lighter molecules are slightly more represented at the warmer end. If the sample air is taken from e.g. the warmer part of the gas column, it will be slightly depleted in the heavier molecule while the gas in the cylinder becomes enriched.*"

We replaced "$CO_{2,meas}$" with "$X_{CO2,meas}$"

6. Section 3:

a. This section is quite long and it is not always easy to distinguish the conclusions that are derived from each particular experiment. It is suggested to revise the structure, splitting in sub– sections to clearly identify what is the tested assumption, what were the observations, and the preliminary conclusion.

We split section 3.2 High flow measurements (formerly 3.3, see reply to 7) and merged it with "Moving cylinders into different orientations while measuring" and the "Heating cylinders" section, it is now:

3.2 High flow measurements

3.2.1 Vertically positioned cylinders

3.2.2 Horizontally positioned cylinders

3.2.3 Moving cylinders into different orientations while measuring

3.2.4 Heating cylinders

To clarify the tested assumption we changed:

The first sentence of Section 3.1 Low flow measurements (formerly 3.2) from

"*In the low flow mode, 38 full tanks were depleted with vertically positioned cylinders.*"

to

"*In the low flow mode, 38 full tanks were depleted with vertically positioned cylinders to see whether the* CO_2 *mole fraction change with decreasing pressure is different in each individual cylinder and whether SGS cylinders perform better than normal cylinders.*"

At Section 3.2 High flow measurements (formerly 3.3) we changed the first sentence from

"*In the high flow mode, eight complete drainings were done with cylinders vertically positioned.*"

to

"*In high flow mode, each of the six normal and the two SGS cylinders were drained once with cylinders vertically positioned, to find out whether Langmuir adsorption/desorption is the only process enriching the* CO_2 *mole fraction with decreasing pressure.*"

At page 11, line 34 we changed the sentence from

"*Three more complete drainings were done with the cylinders horizontally positioned.*"

to

"*Three more complete drainings were done with the cylinders horizontally positioned to measure the* CO_2 *changes with different temperature gradients compared to the vertically positioned cylinders. In case the temperature gradient has no influence on the observed* CO_2 *changes with decreasing cylinder pressure, the outcome of these measurements should be the same as with vertically positioned cylinders.*"

At Page 13, line 13 we added a sentence, it reads now

"*…at about 30 bar and vice versa. If there are different air masses in the cylinder with different temperatures and therefore depleted/enriched* CO_2 *mole fractions, moving the cylinder should cause a sudden change in the temperature measurements as well as in the* CO_2 *measurements of the sample gas. The tank that was first…*"

At page 14, line 7 we added a sentence, it reads now

"*…at a cylinder pressure of 30 bar. In case the heating induces convection in the cylinder, we expect the sample gas to become well mixed and no* CO_2 *enrichment besides Langmuir adsorption/desorption as in the low flow. The first cylinder showed…*"

To emphasize the preliminary conclusions we changed:

Page 10, line 22ff from

“*A fit following Langmuir’s adsorption/desorption model was calculated for each measurement. The fit functions were used to calculate the average CO_2 enrichment with decreasing pressure using the pressure measurements, it is 0.089 ± 0.013 µmol mol^{-1} (Fig. 6), the given error corresponds to the standard error (1-sigma) of the average. Since each cylinder started with a different pressure, the averages could be not entirely comparable. However, if the enrichment is calculated over the same pressure span of 150 to 1 bar, the result is again 0.090 ± 0.009 µmol mol^{-1}, which is the same within the given uncertainty.*”

to

“*A fit following Langmuir’s adsorption/desorption model was calculated for each measurement and used to estimate the average CO_2 enrichment with decreasing pressure. Using the actual pressure measurements, the average CO_2 enrichment is 0.089 ± 0.013 µmol mol^{-1} (Fig.6 a), the given error corresponds to the standard deviation (1-sigma) of individual cylinder drainings. However, values for the CO_2 enrichment of the individual cylinder measurements might be not entirely comparable, since each cylinder had a different initial pressure. Therefore, we calculated the CO_2 enrichment for each cylinder measurement using the same pressure span of 150 to 1 bar. This results in an average CO_2 enrichment of 0.090 ± 0.009 µmol mol^{-1}, which is the same within the given uncertainty. The variation of the enrichment was very low, indicating that the CO_2 enrichment with decreasing pressure is not cylinder dependent. The two SGS cylinders do not show a significantly different behavior, the shape of the CO_2 enrichment with decreasing pressure as well as the amount is the same as for the normal cylinders within the given uncertainty (Fig. 6 b).*”

7. Section 3.1: there are many details in this section which may not be relevant for the understanding of the measurements. If the change of the analyser was not an issue, this should not be highlighted so strongly. The term accuracy does not seem appropriate, as the analyser was regularly calibrated. In addition it is noted at the end of the section that only relative measurements were performed. Then why not starting with this statement, and explaining that the repeatability (expressed with the standard deviation) of the measurements was evaluated, as this is the quantity which matters.

Following the recommendation of referee#1, this section was moved to the methods part and renamed system performance.

The change of the analyzer is not a big issue, however, it’s still visible in the histogram and we wanted to explain, why the histogram shows two peaks with the second one having a higher variation.

In our opinion, the statement about the measurement performance fits better at the end of the section.

8. Section 3.2: it is mentioned here that the values $CO_{2,ini}$ and $CO_{2,ad}$ had a fix value. This was not so clear in the section on methods. It was also not clear how their values were actually chosen.

In the low flow experiments, $CO_{2,ini}$ and $CO_{2,ad}$ are not fixed, only K was fixed as mentioned in the method section. In section 3.2 (now 3.1) we state that the values we found for $CO_{2,ad}$ are almost the same in all low flow experiments but they were calculated for each run of each cylinder separately (page 10, line 27).

9. Section 3.3: it is suggested to separate this section in two, to treat vertical and horizontal cylinders separately. Also the reference to figure 9 appears too early, as this figure contains results with both positions of the cylinders. The clear distinction between them helps the understanding of the analysis, but maybe this could come after. Some effort to reduce the text, summarising each observation and drawing conclusions by step would be very much appreciated as well.

We split section 3.2 High flow measurements (formerly 3.3) and merged it with “Moving cylinders into different orientations while measuring” and the “Heating cylinders” section, it is now:

3.2 High flow measurements
3.2.1 Vertically positioned cylinders
3.2.2 Horizontally positioned cylinders
3.2.3 Moving cylinders into different orientations while measuring
3.2.4 Heating cylinders

10. Section 3.4: please indicate which assumption was tested here and also when the cylinders were put upside−down. Certainly the idea of moving cylinders came from the observations during previous measurements, but this is not very clear.

The respective pressures when the cylinders were moved can be found on page 13, line 32, line 34 and line 36 respectively.

At page 13, line 13 We added the following sentence to clarify why these experiments were done:

"If there are different air masses in the cylinder with different temperatures and therefore depleted/enriched CO_2 mole fractions, moving the cylinder should cause a sudden change in the temperature measurements as well as in the CO_2 measurements of the sample gas."

11. Section 3.5: Some effort to reduce the text, summarising each observation and drawing conclusions by step would be very much appreciated as well here.

We shortened a few sentences and added a brief conclusion after the experiments with the constant heating as well as after the experiments with the burst heating.

Page 14, line 8ff was shortened from

"The first cylinder showed a stable CO_2 mole fraction before heating, it was 410.36 ± 0.03 µmol mol^{-1}. The resumed CO_2 measurement after the cylinder temperature reached 30 °C showed a drop of about 0.09 µmol mol^{-1} and remained stable at 410.27 ± 0.02 µmol mol^{-1} until the cylinder was empty (Fig. 15). The second cylinder showed no changes in the CO_2 mole fraction before and during the heating. The average CO_2 mole fraction down to 30 bar was 410.99 ± 0.03 µmol mol^{-1}, after the temperature reached the preset value it was at 410.99 ± 0.02 µmol mol^{-1}."

to

"The mole fraction of the first cylinder was stable before and after the heating was started at 410.36 ± 0.03 µmol mol^{-1} and 410.27 ± 0.02 µmol mol^{-1}, respectively (Fig. 15). The second cylinder showed no changes in the CO_2 mole fraction before and during the heating. The average CO_2 mole fraction coming out of the cylinder before and after heating was 410.99 ± 0.03 µmol mol^{-1}and 410.99 ± 0.02 µmol mol^{-1}, respectively."

Page 14, line 18ff was shortened from

"The cylinder wall is slightly thicker at the shoulder resulting in a bigger thermal mass. That, and the fact that there was a heat band at the bottom, might be why the temperature is higher at the bottom than at the shoulder and why the temperature overshot in the beginning of the heating."

to

"A possible reason for the cylinder being warmer at the bottom end might be the thicker wall at the shoulder that results in a bigger thermal mass and the additional heat band at the bottom of the cylinder."

Page 14, line 33ff was shortened from

"*Then, after the heating was switched on, the temperature gradient was turned upside down almost immediately. The set temperature of 30 °C was reached after about one hour, which corresponds to a pressure decrease of about 10 bar.*"

to

"*After the heating was switched on, the temperature gradient was inverted almost immediately and after about one hour the set temperature was reached.*"

Two brief conclusions were added at page 14, line 20

"*Due to the inconsistency of the two runs, it is impossible to tell whether the mixing induced by convection prevented thermal fractionation or not.*"

and at page 15, line 2

"*The two experiments showed, that quick heat bursts have only a short effect on the sampling gas and are not sufficient to produce much mixing the cylinder gas.*"

12. Section 4: it is suggested to also reshape this section, starting from each conclusion drawn during section 3, and summarising. At the end, some consideration on the impact should be given. For example, a possible small bias in the calibration of CO_2 measurement is mentioned. What is the conclusion? Will it be followed by further recommendation?

We split the section in

4 Discussion

4.1 Low flow measurements

4.2 High flow measurements

On page 15, line 29 we changed the sentence

"*This effect is likely worse with smaller cylinders, where the surface to volume ratio is bigger*"

to

"*This effect is likely worse with smaller cylinders, where the surface to volume ratio is bigger and should be taken into account when preparing CO_2 standards gravimetrically or when preparing mother/daughter cylinder sets for comparison projects between different analyzing systems and/or laboratories.*"

At the end of page 15, it seems that some inconsistency is noted between the observations made when sampling the gas with low and high flow rates, as they would lead to two different values of the amount of CO_2 adsorbed on the wall. This appears quite serious. What is the conclusion? Does this question the entire model?

At page 15, line 30 ff, we state that the observed CO_2 enrichment in vertically positioned cylinders in the high flow setup is about 2.5 times higher compared to vertically positioned cylinders in the low flow setup. In the same paragraph we explain that the reason for this higher enrichment can be attributed to Rayleigh distillation processes, which do not occur under low flow conditions. Since most gas measurement systems have a low calibration gas flow, or if they have a high calibration gas flow, it is only for a few minutes, too short to induce a temperature gradient, this shouldn't be a problem.

At page 15, line 30 we changed the sentence from

"*…in the high flow measurement was on average…*"

to

"*…in the high flow measurement with vertically positioned cylinders was on average…*" for clarity reasons.

This is also stated as a conclusion in section "5. Conclusions", page 18, line 20 ff.

13. Section 5: the first conclusion from the low flow experiment appears to diminish the importance of the study. Indeed, if it is already recommended to stop using calibration gases when the pressure is below 20 bar, what was the purpose of this study? The second part would need to be strengthened; bringing more sounds conclusions and consideration on the implication (if any) on the usage of calibration gases.

At page 18, line 9 to 13 we verify/falsify the three hypotheses from the introduction. These are the most important findings of this study. The most important implications are given at line 13-15 (possibility to correct if necessary) and that recommendation from the WMO, to change cylinders when they reach 20 bar should be changed, still holds true, even though we recommend to change the cylinders when they reach 30 bar to minimize the effect of the enrichment.

Additionally, we added the sentence

"*By using bigger cylinders (e.g. 50 l) the surface to volume ratio becomes smaller compared to the 29.5 l cylinders used in this study, which might be beneficial in minimizing the* CO_2 *enrichment effect at lower pressures.*"

at page 18, line 19.

The whole rest of this paragraph are additional findings we didn't look actively for but thought worth mentioning.

Line-by-line comments:

Page 1

Line 20: "…In this study we found that during low flow conditions". As this is the first mention of low flow rates, it should be stated more clearly that this is the flow rate used to sample the gas inside the standard.

We replaced the sentence

"*In this study we found that during low flow conditions (0.3 l min^{-1}) the tested vertically positioned aluminum cylinders always showed similar CO_2 enrichment of 0.090 ± 0.009 µmol mol-1 as the cylinder was emptied from about 140 to 1 bar above atmosphere, following Langmuir's adsorption/desorption model.*"

with the following sentence

"*In this study the tested vertically positioned aluminum cylinders showed similar CO_2 enrichment during low flow conditions (0.3 l min^{-1}), which are similar to flows often used for calibration gases in practical applications. The average CO_2 enrichment was 0.090 ± 0.009 µmol mol^{-1} as the cylinder was emptied from about 150 to 1 bar above atmosphere. However, it is important to note that the enrichment is not linear but follows Langmuir's adsorption/desorption model, where the CO_2 enrichment is almost negligible at high pressures but much more pronounced at low pressures.*"

Note that we corrected 140 to 150 bar, which is the pressure the calculations were based on. At the same time, this change should also address the next remark of Referee#2.

Line 21: "showed similar CO_2 enrichment of 0.090 ± 0.009 µmol mol^{-1} as the cylinder was emptied from about 140 to 1 bar above atmosphere". This is misleading, because the increase happens only after a certain pressure, not gradually during the cylinder was emptied. This is quite important as users could be afraid of using the standards.

We disagree, according to Langmuir's adsorption/desorption model, the CO_2 starts to desorb as soon as the pressure starts to decrease. However, in the beginning (at high pressures) the number of CO_2 molecules desorbing from the walls is very small compared to the number of CO_2 molecules present in the cylinder air. At the end of the sentence, we state that the enrichment follows the Langmuir model, which should be a clear indicator, that the CO_2 enrichment does not follow a linear function.

This is the exact reason why the WMO states in its GAW reports: "In the case of CO_2 the calibration standards should be replaced once the cylinder pressure has decreased to 20 bar.".

(e.g. WMO: 18th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13-17 September 2015, GAW Report No. 229, World Meteorological Organization, Geneva, Switzerland, 2016.)

Line 28: "In case they are used in high flow experiments that involve significant cylinder temperature changes, special attention has to be paid to possible fractionation effects". This is the only statement in the entire paper about possible impacts of sampling gas from the standards at a high flow rate. Some more consideration should be provided, both in the introduction to explain the current situation, and in the conclusion to provide a recommendation.

The high flow experiments were only done to understand the involved processes better. For most applications, the low flow experiments are much more important. However, since we found these effects, we thought it worth mentioning, in case somebody actually uses cylinders at such high flows over a period long enough to induce temperature gradients.

The possible impacts are mentioned in the discussion page 15, line 30 ff, where we explain what the possible reason for this observation is, as well as in the conclusions page 18, line 20 ff.

Page 2

Line 14-17: the sentence about the traceability explains the situation within WMO/GAW. It may not be extended to all CO_2 measurements in the world.

We changed the sentence from

"*In the case of GHGs traceability is maintained by the use of a unique hierarchy of CO_2-in-(dry)-air mixtures (and similarly for CH_4, N_2O) in high pressure cylinders starting from the primary standards (with link to SI) to secondaries and tertiaries, all with known CO_2 mole fraction derived from the higher level, ultimately calibrating the instrument making air measurements.*"

to

"*Within the WMO/GAW network, GHGs traceability is maintained by the use of a unique hierarchy of CO_2-in-(dry)-air mixtures (and similarly for CH_4, N_2O) in high pressure cylinders. The hierarchy starts from the primary standards (with link to SI) to secondaries and tertiaries, all with known CO_2 mole fraction derived from the higher level, ultimately calibrating the instrument making air measurements.*"

Line 18:"The resulting…" this sentence describes a goal rather than an observation. In addition the word "true" should be avoided and could be replaced with "unbiased".

Gas analyzers with well known characteristics should indeed not depend on priori estimates or models. A suite of calibration gases that covers the range in which the analyzer will be used is usually enough. Of course, this is different for e.g. remote sensing data such as satellite data, FTIR systems measuring the total column etc., these systems depend on modelling and a priori estimates of the column.

As suggested, we replaced "*true*" with "*unbiased*".

Line 28:" SI values". Incorrect terminology. May be replaced with "values traceable to the SI".

We changed "*SI values*" to "*SI traceable values*"

Line 32:"accuracy". Incorrect terminology. To be replaced with Data Quality Objective or compatibility.

"accuracy" was replaced with "compatibility"

Page 3

Line 17: "To check the third hypothesis, two SGS cylinders were added to the set…" this would mean that 8 + 2 = 10 cylinders were tested. Table 1 shows only 8 cylinders (not considering the one which was replaced).

For clarity reasons, the sentence was changed from

"*To check the third hypothesis, two SGS cylinders were added to the set but used exactly the same way as the ordinary cylinders.*"

To

"*To check the third hypothesis, two of the eight tested cylinders were SGS cylinders, but they were used exactly the same way as the ordinary cylinders.*"

Line 30 and 32: the term "block" seems to indicate 10 measurements recorded during 5 minutes. Later in the text, the same quantity is sometimes only referred to as "a measurement". It can be understood to define a measurement as a 5 minute average, but this should be stated and always used in the same way.

For consistency reasons we applied the following changes:

Page 4, line 16, we replaced "*…and the target gas…*" with "*…a block of target gas measurements…*"

Page 4, line 20, we replaced "*measurement*" with "*run*"

Page 4, line 29, we changed "*…resulted in about 12 additional target gas measurements…*" to "*…resulted in about 12 additional blocks of target gas measurements…*"

Page 5, line 2, we changed “*…about 4 target gas measurements…*” to “*…about 4 blocks of target gas measurements…*”

Page 10, line 2, we changed “*…to the measurements…*” to “*…to the measurement sequence…*”

Page 10, line 5, we changed “*…were calculated for each target gas measurement…*” to “*…were calculated for each block of target gas measurement…*”

Page 10, line 20, we changed “*…All measurements followed a similar pattern…*” to “*…All low flow measurements followed a similar pattern …*”

Page 10, line 22, we changed “*…for each measurement…*” to “*…for each cylinder measurement…*”

Page 10, line 22, we changed the “*Two additional low flow measurements with horizontally positioned cylinders were done. Again the Langmuir fit functions of the two measurements were used…*” to “*Additionally, a low flow run with two horizontally positioned cylinders (one normal and one SGS cylinder) was done. Again the Langmuir fit functions of the two cylinder measurements were used…*”

Page 11, line 4, we changed “*…at the same time the only low flow measurement with temperature…*” to “*…at the same time the only low flow run with temperature…*”

Page 12, line 36, we changed “*…until the end of the measurement, the* CO_2*…*” to “*…until the end of the run, the* CO_2*…*”

Page 13, line 4: We changed “*In all three measurements the logarithmic plots show a flat plateau in the beginning. The decrease starts in all three measurements at* $-\ln(P/P_0)\approx 0.7$*…*” to “*In all three runs the logarithmic plots show a flat plateau in the beginning. The decrease starts in all three runs at* $-\ln(P/P_0)\approx 0.7$*…*”

Page 13, line 20, we changed “*…the two measurements seem to mirror…*” to “*…the two cylinder measurements seem to mirror…*”

Page 14, line 27, we changed “*In the second measurement, the* CO_2 *mole fraction…*” to “*In the second run, the* CO_2 *mole fraction…*”

Page 16, line 10, we replaced “*…at the end of the measurement.*” *with* “*…at the end of the run.*”

Page 16, line 26, we replaced “*…which is maintained until the end of measurement.*” *with* “*…which is maintained until the end of run.*”

Page 17, line 4, we replaced "*At the end of the measurement, the most…*" *with* "*At the end of the run, the most…*"

Page 4

Line 2:" continuously at 10 ml min-1 flowing reference cell signals". Revise the order of words in the sentence.

We changed the sentence from

"*The values reported by the LI-7000 are Δ-signals which are basically the difference between the sample and the continuously at 10 mL min*$^{-1}$ *flowing reference cell signals.*"

to

"*The values reported by the LI-7000 are the difference between the signals of the sample and the reference cell, which is flushed continuously with a reference gas at a flow rate of 10 mL min*$^{-1}$."

Line 16: C2 was measured twice? Should this be C2, C3?

This is a mistake, it was changed from "*C2*" to "*C1*".

Line 17: define what is "one run"

"One run" is when one or several cylinders are measured from their initial pressure down to pressure 1 (or 1.5 bar in the high flow setup).

We changed the sentence at page 4, line 17 from (first appearance of "run")

"*…which allowed measuring all sample cylinders in one run. With the new 16-port…*"

to

"*…which allowed measuring all sample cylinders from their initial pressure down to their final pressure in one single run. With the new 16-port…*"

Line 19: "secondary". This term may be replaced here as it was already used previously in the traceability hierarchy.

We replaced "*secondary*" with "*working*". For consistency reasons also at page 5, line 18 and deleted "*primary*" at page 3, line 28.

Line 26:"before a block of C2 was measured". As the word "block" is not so appropriate to a 5 minute average, the entire sentence is difficult to understand.

This whole section was changed, the sentence

“*In the low flow measurements with multiple samples, all samples were subsequently measured twice before a block of C2 was measured, and this was repeated three times, before another full calibration was done.*”

reads now

“*In the low flow setup with multiple samples, the sequence cycled between the sample cylinders until two blocks of every sample cylinder were subsequently measured. Then a block of C1 was measured to catch the analyzers short term drift. This was repeated three times, before another full calibration was done.*”

Line 31:”lasts” should be “lasted”.

Done.

Page 5

Line 28: “showed that they perform even slightly better.” Sounds more like an opinion than an observation. Values should be provided, or the statement can simply be removed as it does not bring additional value.

The sentence was removed.

Page 6

Line 15:”as soon as the cylinder reached 30 bar”. Omission of the word “pressure”, to be included.

Done.

Page 7

Equation (2): using the symbol of the molecule for its mole fraction is confusing when it is used in the text. It is recommended to follow IUPAC terminology.

This is how Leuenberger et al., (2015) give the formula in their publication. However we changed “$CO_{2,meas}$“ to “$X_{CO2,meas}$”, “$CO_{2,ini}$“ to “$X_{CO2,ini}$“ and “$CO_{2,ad}$“ to “$X_{CO2,ad}$“ in the whole manuscript. For consistency, “$CO_{2ad,lf}$“ was changed to “$X_{CO2ad,lf}$“ as well.

Line 23:”amount density”. This should be “amount concentration”.

Done.

Line 24: “function of CO_2 only”. This illustrates the problem of using the molecule’s name instead of a symbol for its mole fraction.

We changed the sentence

“*In this approach θ is a function of CO_2 only, not of total gas pressure.*”

to

"*In this approach, θ is a function of the amount of CO_2 only, not of total gas pressure.*"

Page 8

Line 2:"available". The term can be misleading, as it could indicate non occupied sites. May be replaced with "total number of sites".

We changed it from

"*…with θ the fraction available wall space that is occupied…*"

to

"…*with θ the fraction of total number of available sites that are occupied…*"

Line 2:"amount of sites, expressed in moles". The mole is limited to an amount of molecules, atoms, ions, electrons, or other particles. This may be replaced with "maximum amount of adsorbed molecules", which also corresponds to the total number of sites.

Done.

Page 10

Line 23 to 25: revise the sentence, maybe using two distinct sentences.

We changed

"*A fit following Langmuir's adsorption/desorption model was calculated for each measurement. The fit functions were used to calculate the average CO_2 enrichment with decreasing pressure using the pressure measurements, it is 0.089 ± 0.013 μmol mol^{-1} (Fig.6 a), the given error corresponds to the standard deviation (1-sigma) of the average. Since each cylinder started with a different pressure, the averages could be not entirely comparable. However, if the enrichment is calculated over the same pressure span of 150 to 1 bar, the result is again 0.090 ± 0.009 μmol mol^{-1}, which is the same within the given uncertainty.*"

to

"*A fit following Langmuir's adsorption/desorption model was calculated for each cylinder measurement and used to estimate the average CO_2 enrichment with decreasing pressure. Using the actual pressure measurements, the average CO_2 enrichment is 0.089 ± 0.013 μmol mol^{-1} (Fig.6 a), the given error corresponds to the standard deviation (1-sigma) of individual cylinder drainings. However, values for the CO_2 enrichment of the individual cylinder measurements might be not entirely comparable, since each cylinder had a different initial pressure. Therefore, we calculated the CO_2 enrichment for each cylinder measurement using the same pressure span of 150 to 1 bar. This results in an average CO_2 enrichment of 0.090 ± 0.009 μmol mol^{-1}, which is the* *same within the given uncertainty. The variation of the enrichment was very low, indicating that the CO_2 enrichment with decreasing pressure is not cylinder dependent. The two SGS cylinders do not show a significantly different behavior, the form of the CO_2 enrichment with decreasing pressure as well as the amount is the same as for the normal cylinders within the given uncertainty (Fig. 6 b).*"

Line 24:"standard error". A better term would be "standard deviation", as used later on in the text.

True, the value given corresponds to the standard deviation, not to the standard error. We changed it accordingly.

Page 11

Line 15: revise the last part of the sentence. It seems that some words are missing.

We changed

"*The average fractionation factor α is 0.99993 ± 0.00002, which means CO_2 depletion in the outflowing gas.*"

to

"*The average fractionation factor α is 0.99993 ± 0.00002, which corresponds to a CO_2 depletion in the outflowing gas.*"

Page 12

Line 11:"errors". To be replaced with "uncertainties".

Done.

Page 14

Line 13: "are the virtually". Remove "the" and consider replacing the word "virtually", which seems more appropriate for a talk than for a paper.

We changed the sentence from

"*The temperature measurements of the two cylinders are the virtually the same (Fig. 16 a).*"

to

"*The temperature measurements of the two cylinders are in good agreement (Fig. 16 a).*"

Page 15

Line 15: "By using a ….the number becomes even smaller". Consider revising the sentence, first because the fraction of occupied sites goes from 13% to 37%, secondly because the second calculation seems to be an alternative one, so that two models are compared.

The sentence

“*By using a very simplified geometrical approach, this number becomes even smaller*.”

was changed to

“*Using a very simplified geometrical approach results in a higher estimate of the occupied wall spaces*.”

Line 17: “the number of molecules…Avogadro number”. Is it really needed to state what is the Avogadro number?

“*…(Avogadro’s number)…*” has been removed and we changed the line to “*…*$N_A = 6.022 \cdot 10^{23}\ mol^{-1}$*, a pressure of* $P = 150\ bar$*, a volume of* $V_{cyl} = 29.5\ l$*, a temperature of* $T = 293.15\ K$*…*”

Line 24:”a second conclusion”: what was the first conclusion?

We changed the sentence (page 15, line 5)

“*That suggests that the observed* CO_2 *enrichment may be universal for this type of aluminum cylinder.*”

to

“*Therefore the conclusion can be drawn that the observed* CO_2 *enrichment for ambient level* CO_2*-in-dry-air mixtures stored in this type of aluminum cylinder is universal.*”

Page 17

Lines 9 to 12: consider splitting the sentence. This is currently difficult to understand.

We changed the sentence from

“*If it is laid down from vertical, the vanishing gradient along the cylinder and the emerging temperature difference between the now lower and upper side are proof of that the jump in the* CO_2 *mole fraction when a cylinder is laid down is in accordance with the aforementioned thermal diffusion fractionation that* CO_2 *gets enriched in cool air that accumulates at the bottom of the cylinder.*”

to

“*If a cylinder’s orientation is changed from a vertical to a horizontal position, the temperature gradient initially remains the same along the cylinder. A temperature difference between the now lower and upper cylinder wall starts to build up. The conservation of the gradient’s vertical orientation proves that the jump in the* CO_2 *mole fraction that occurs when a cylinders orientation is changed is in accordance with the aforementioned thermal diffusion fractionation, where* CO_2 *gets enriched in cool air that accumulates at the bottom of the cylinder.*”

Page 18

Line 12 and 13: “to describe the CO_2 enrichment”. Consider removing one of the appearances of this part of the sentence.

Referee#1 suggested to rewrite the conclusions, this statement reads now:

“*In low flow settings (0.3 L min*$^{-1}$*), the Langmuir adsorption/desorption model using averaged coefficients is sufficient to describe the* CO_2 *enrichment.*”

Figures 6, 8, 12: the y-axis is a difference, not the CO_2 mole fraction. From the legend it seems that the first value was subtracted from the set, but then why is the first point not at zero?

(A similar answer was given to Referee#1)

The y-axis corresponds to the ΔCO_2 and was changed accordingly. For this figures, the term $X_{CO2,ini}$ ($CO_{2,ini}$ in the unrevised manuscript) was subtracted from the Langmuir-equation and the remainder with the corresponding coefficients was plotted. Because $X_{CO2,ini}$ corresponds to the CO_2 mole fraction before adsorption to the walls occurs, it is slightly higher than the average CO_2 mole fraction at the beginning of the measurements. This results in negative ΔCO_2 values in the beginning of the measurements. For clarity we shifted the values by adding $X_{CO2,ad}$, this shifts the fits upwards so that the initial value is exactly 0. This was done for Fig 6, 8, and 12. In all three captions we changed

“*...the corresponding* $X_{CO2,ini}$ *was subtracted…*”

to

“*…the corresponding* ($X_{CO2,ini} – X_{CO2,ad}$) *was subtracted…*”,

accordingly.

Experiments with CO_2 -in-air reference gases in high-pressure aluminum cylinders

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Abstract

Long term monitoring of carbon dioxide (CO_2) in the atmosphere is key for a better understanding of the processes involved in the carbon cycle that have a major impact on further climate change. Keeping track of large-scale emissions and removals (“sources and sinks”) of CO_2 requires very accurate measurements. They all have to be calibrated very carefully and have to be traceable to a common scale, the WMO CO_2 X2007 scale, which is maintained by NOAA/ESRL (Oceanic and Atmospheric Administration/Earth System Research Laboratory) in Boulder, CO, USA. The international WMO/GAW (World Meteorological Organization/Global Atmosphere Watch) program sets as compatibility goals for the required agreement between different methods and laboratories ± 0.1 µmol mol^{-1} for the northern hemisphere and ± 0.05 µmol mol^{-1} for the southern hemisphere. The reference gas mixtures used to pass down and distribute the scale are stored in high pressure aluminum cylinders. It is crucial that the standards remain stable during their entire time of use. In this study the tested vertically positioned aluminum cylinders showed similar CO_2 enrichment during low flow conditions (0.3 L min^{-1}), which are similar to flows often used for calibration gases in practical applications. The average CO_2 enrichment was 0.090 ± 0.009 µmol mol^{-1} as the cylinder was emptied from about 150 to 1 bar above atmosphere. However, it is important to note that the enrichment is not linear but follows Langmuir’s adsorption/desorption model, where the CO_2 enrichment is almost negligible at high pressures but much more pronounced at low pressures. ~~In this study we found that during low flow conditions (0.3 l min^{-1}) the tested vertically positioned aluminum cylinders always showed similar CO_2 enrichment of 0.090 ± 0.009 µmol mol^{-1} as the cylinder was emptied from about 140 to 1 bar above atmosphere, following Langmuir’s adsorption/desorption model.~~ When decanted at a higher rate of 5.0 L~~l~~ min^{-1} the enrichment becomes 0.22 ± 0.05 µmol mol^{-1} for the same pressure drop. The higher enrichment is related to thermal diffusion and fractionation effects in the cylinder, which were also dependent on the cylinder’s orientation and could even turn negative. However, the low amount of CO_2 adsorbed on the cylinder wall as well as the fact that the main increase happens at low pressure lead to the conclusion that aluminum cylinders are suitable to store ambient CO_2-in-dry-air mixtures provided they are not used below 20 bar. In case they are used in high flow experiments that involve significant cylinder temperature changes, special attention has to be paid to possible fractionation effects.

1. Introduction

The amount of the emissions in combination with the radiative forcing makes carbon dioxide (CO_2) the most important anthropogenic greenhouse gas (GHG) (IPCC, 2013; Hofmann et al., 2006). CO_2 exchanges rapidly between the atmosphere, oceans and terrestrial biosphere (the "fast exchange"), and very slowly with carbonate rocks. The current combustion of coal, oil, and natural gas constitutes a large scale transformation of fossilized organic matter to CO_2 gas that is now overwhelming natural exchange processes. The CO_2 emissions are practically irreversible; removal from the atmosphere and oceans by natural sedimentation and erosion will take thousands of years. The fast exchange implies that not only does CO_2 influence climate, but the oceans as well as the terrestrial biosphere can gain or lose carbon as climate change unfolds, which is often called the "carbon-climate feedback". This feedback constitutes a major uncertainty for climate projections. We need to create an accurate record of changing sources/sinks to the atmosphere in order to diagnose and quantify these feedbacks as they occur.

Downwind of a source region atmospheric CO_2 is enhanced relative to upwind. However such enhancements/depletions due to regional sources/sinks are typically very small on regional to continental scales, so that long term monitoring with very accurate measurements is necessary. Small systematic errors between measurement stations can lead to mis-assignment of sources or sinks, noisy measurements might obscure interesting signals that could help to identify processes and calculate their contribution to the carbon cycle (e.g. Masarie et al., 2011). High quality measurements start with careful calibrations, preferably traceable to the International System of Units (SI), or if not possible as in the case of isotopic ratios, to an artifact chosen by convention (e.g.~~, the kilogram, or~~ VPDB for $^{13}C/^{12}C$). ~~In the case of~~Within the WMO/GAW network, GHGs traceability is maintained by the use of a unique hierarchy of CO_2-in-(dry)-air mixtures (and similarly for CH_4, N_2O) in high pressure cylinders.~~,~~ The hierarchy starts~~ing~~ from the primary standards (with link to SI) to secondaries and tertiaries, all with known CO_2 mole fraction derived from the higher level, ultimately calibrating the instrument making air measurements. Careful calibration procedures make the result independent of which instrument or method is used. The resulting data stand on their own feet; they do not depend on models or a-priori estimates and assumptions, and are unbiased~~true~~ within a known uncertainty range.

The World Meteorological Organization (WMO) coordinates GHG measurements around the world, through its Global Atmosphere Watch Program (GAW), and during biannual meetings of the international participating laboratories ("the community") goals have been set for the level of compatibility between different stations. The community recommends the WMO CO_2 X2007 scale (WMO, 2016), and they defined a compatibility goal of ± 0.1 µmol mol^{-1} (1 standard deviation) for CO_2 datasets of the northern hemisphere (WMO, 2016, 2014, 2012, 2011, 2007, 2006; Zellweger et al., 2016). For the southern hemisphere this number is even lower at ± 0.05 µmol mol^{-1} because smaller source intensities, due to the large proportion of ocean surface, give rise to smaller spatial gradients than in the northern hemisphere. The WMO CO_2 X2007 scale is embodied in 15 primary standards, which are measured once every two years on a manometric system that provides SI traceable values by NOAA/ESRL (National Oceanic and Atmospheric Administration/Earth System Research Laboratory) in Boulder, USA (Zhao and Tans, 2006; Zhao et al., 1997). The primary standards are used to transfer the calibration scale to secondary and subsequently to tertiary standards. The tertiary standards are sent to the different laboratories around the world to calibrate their CO_2

measurements. To meet the WMO's ~~accuracy~~compatibility goal of 0.1 (or 0.05) µmol mol^{-1}, it is crucial that the standards remain stable during their entire time of use, and/or that they are re-calibrated at reasonable intervals, and that appropriate laboratory practices are being followed. The latter are included in the biannual WMO reports as "Expert Group Recommendations". At field stations (Schibig et al., 2015) but also in laboratory experiments (Langenfelds et al., 2005; Leuenberger et al., 2015; Miller et al., 2015; Brewer et al., 2018), standard gases typically show some CO_2 enrichment with decreasing pressure. Those studies attributed the CO_2 enrichment to different effects such as Langmuir monolayer adsorption/desorption, gravimetric fractionation, thermal fractionation or Rayleigh distillation related effects for example. Evaluating 10 years of calibration tank measurements, Keeling et al. (2007) found a downward drift in their aluminum calibration tanks relative to steel, which they attributed to surface conditioning.

In this study, ~~the following~~three hypotheses were tested, i) the ~~CO_2~~ increase of the CO_2 mole fraction in the sample gas with decreasing pressure is different for each individual cylinder, ii) at low flow rates, the Langmuir monolayer adsorption/desorption model ~~the~~ is sufficient to describe the observed CO_2 enrichment with decreasing pressure ~~follows the Langmuir monolayer adsorption/desorption model~~ and iii) the stability of the CO_2 mole fraction with decreasing pressure is better in SGS (Superior Gas Stability®, Luxfer, USA) cylinders than in untreated aluminum cylinders. To check the first hypothesis, eight cylinders were repeatedly filled and decanted and the CO_2 enrichment of the individual measurements ~~was~~ were compared. The second hypothesis was investigated by decanting the cylinders at different flow rates. At low flow the temperature changes due to the decreasing pressure are negligible, whereas at a high flow setting the fast pressure decrease induces cooling and substantial temperature gradients in the cylinder. If only adsorption and desorption effects are at work, the CO_2 enrichment of the high flow experiments can be expected to be the same as with the low flow experiments, unless the wall equilibration times are long (at least several hours) such that during high flow experiments the walls do not equilibrate as during low flow experiments. In that case one could expect to see a smaller wall effect. Additionally, the cylinders were positioned in different orientations, which again should not~~n't~~ have any influence on the measured CO_2 mole fraction of the outflowing gas if only adsorption/desorption effects are involved. Furthermore, heating bands were used to alter the temperature of the cylinder wall to learn more about potential temperature issues. To check the third hypothesis, two of the eight tested cylinders were SGS cylinders, ~~were added to the set~~ but they were used exactly the same way as the ordinary cylinders. If their surface treatment is beneficial to the CO_2 stability, the experiments with SGS cylinders should stand out clearly.

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2. Material and ~~M~~methods

2.1 Sample cylinders

To measure the CO_2 development over the lifetime of a cylinder eight cylinders were repeatedly filled to about 130 bar at Niwot Ridge Station, CO, USA. The filling was done the exact same way as for the standard cylinders NOAA fills to be used as calibration gas tanks (Kitzis, 2017). Six of the eight cylinders were Luxfer L6X® aluminum

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cylinders, which are the same type NOAA uses for the CO_2 standards, two were Luxfer L6X® SGS (Superior Gas Stability) aluminum cylinders (Table 1). Cylinder CB11876 was excluded from the set and was replaced with CB11941 after the first run, because the cylinder valve's sealing surface got scratched badly. The 29.5 L cylinders were fitted with Rotarex Series D200 brass packless valves (Rotarex, Luxembourg) to be used with two stage pressure reducers (Scott Specialty model 51-14B-590) and chromed brass CGA connection. The regulators were connected to the measurement system by Quick-Connects (SS-QC4-B-4PM and SS-QC4-D-400 for the samples and SS-QM2-B-2PM and SS-QM2-D-200 for the standards, respectively, Swagelok, USA) and 1/8" stainless steel tubing (Swagelok, USA).

2.2 Measurement system

The CO_2 measurement system was based on a customized replacement unit of NOAA's tall tower network (Andrews et al., 2014). To measure CO_2 mole fractions a nondispersive infrared gas analyzer (LI-7000, LI-COR, USA) was used. In March 2017, the original CO_2 analyzer stopped working and had to be replaced by a spare analyzer of the same make and model. The system was controlled by CR-1000 measurement and control data logger (Campbell Scientific, USA), a Windows laptop was used to communicate with the CR-1000 and to store the data. The pressure regulators were equipped with digital pressure readers on the high pressure side (EW-68075-10, Cole-Parmer Instrument Company, USA), the pressure is measured relative to atmospheric pressure. To avoid complete drainage, the sample cylinders were excluded from the measurement sequence as soon as the ~~primary~~ pressure dropped below a preset threshold.

2.2.2 Low flow measurements setup

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In the low flow setting the cylinders were hooked to a VICI multiport valve, which was used to switch between the different calibration gases and the sample gas cylinders. Until 8.11.2016, it was a 10-port valve (EMT2SD10MWE, Valco Instruments Co. Inc., USA), where ports 1 to 5 were used for the sample gases and ports 6 to 10 were connected to the calibration gases C1, C2, C2, C4 and the target gas. The valve was later upgraded to a 16-port valve (EMT2SD16MWE, Valco Instruments Co. Inc., USA), which allowed measuring all sample cylinders from their initial pressure down to their final pressure in one single run. With the new 16-port valve ports 1 to 8 were used for the samples, ports 9 to 13 were used for the calibration and target gases. The working pressure for the calibration as well as the target and sample gas was set to about 1 bar. To allow a constant flow out of the sample cylinders throughout the whole run, solenoids were used in each sample line to open by-pass lines for the cylinders that were not currently measured. The by-pass lines led to needle valves, where the flow was adjusted to 0.3 L min^{-1} for each sample cylinder individually. The by-pass line of the cylinder currently measured remained closed. This ensured that all the gas flowed through the analyzer, kept the flow rate coming out of the cylinder stable and avoided potential fractionation at the tee unions due to pressure and/or temperature gradients between the arm and the runs of the tee unions (Fig. 1 a).

2.2.3 High flow measurements setup

In the high flow setting, the gas was drained out of the cylinder at 5.0 L min^{-1}, which is why a cylinder lasted only about 12 to 13 hours. Only one sample tank was measured per run, otherwise too much detail might be lost, especially towards the end of the experiment, where we expected the enrichment to happen (Fig. 1 b). Originally the measurement system was designed to operate with sample gas flows of about 0.2-0.3 L min^{-1}. To achieve a flow of 5.0 L min^{-1} out of a sample cylinder, 4.7-4.8 L min^{-1} had to be bypassed in a non-fractionating manner. To do so an inlet system similar to an open-split design was built (Fig. 2). The gas enters the inlet system on one end at a flow rate of 5.0 L min^{-1} and flows through a 0.5 inch stainless steel union and then through a 0.5 inch synflex tube. In the center of 0.5 inch tube, a $^{1}/_{8}$ inch stainless steel tube takes an aliquot of air to the measurement system, the rest leaves at the other end through the exhaust. The length of the outer tube is 0.25 m, which in combination with the high flow is sufficient to avoid back diffusion of outside air through the open split. Because the ambient pressure is too low for the pressure controller to maintain the set pressure of 1030 mbar, the secondary pressure of the pressure regulator of the sample gases was increased to 1.5 bar and a needle valve was used to provide a small backpressure. The needle valve increased or decreased the resistance of the exhaust to the lab and thereby the ratio of the flows. Measurements of the same cylinder connected to the high flow inlet and the normal flow inlet resulted in the same CO_2 mole fraction proving that the sampled small flow is not fractionated from the large bypass flow.

2.2.3 Measurement protocol

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The CO_2-analyzer reported 5 s values to the data logger, which in turn logged 30 s averages. Ten of these 30 s averages were taken together into one 5 minute block that formed the basic unit used for the measurement sequence. The calibration, target~~s~~ and sample gas measurements were done in a repetitive cyclic sequence that was made up of the aforementioned 5 minute blocks and whose order was defined in the control program. In the very beginning of each cycle, a full calibration with a single block of each calibration gas (C1, C2, C3, C4) as well as a block of target gas measurement were done. Then, the program switched through all connected samples several times, measuring a block C1 in between to catch short-term drifts of the measurement system (Fig. 3). When a cycle was finished, a new cycle was started, again by measuring blocks of all four calibration gases first. At the end an additional calibration with all four calibration gases and the target gas was made. ~~The cycles were divided in blocks of 5 minutes each, during which gas from a single cylinder (sample, calibration or target gas) was measured. The data was read every 5 seconds, but data reported to the log file were 30 s averages yielding 10 values per block. In the very beginning of each cycle, a full calibration with all four calibration gases (C1, C2, C3, C4) as well as a target gas measurement were done. Then the program cycled through all samples several times, before C2 was measured again to catch short term drifts in the measurement system (Fig. 1).~~

In the low flow setup with multiple samples, the sequence cycled between the sample cylinders until two blocks of every sample cylinder were subsequently measured. Then a block of C1 was measured to catch the analyzer's short term drift. This was repeated three times, before another full calibration was done. In case all eight sample lines were used, one cycle took 275 min, a whole run, where the cylinders were measured from full until empty, lasted about 9 to 10 days. In the low flow measurements, the target gas block was added every 1000th minute, which resulted in about

12 additional blocks of target gas measurements in one complete run. To avoid contamination, the sample cylinders were excluded from the sequence as soon as their high pressure reached 1 bar.

In the high flow setup, the calibration sequence was similar to the low flow measurements. In the beginning of every cycle, there was again a complete calibration sequence. After the calibration, the sample block was repeated 10 times followed by one block of C1 and again 10 blocks of sample gas that completed the cycle. This was repeated until the sample cylinder's high pressure reached the preset pressure threshold of 1.5 bar. A target gas block was added every 150th minute, which yielded about additional 4 target gas measurements per run. In order to catch as much sample measurements within the last few bars of the sample cylinders lifetime, some additional conditions related to the sample pressure were added to the measurement sequence: i) no full calibration below 35 bar sample pressure, ii) no target gas measurement below 15 bar and iii) no C1 below 8 bar. A run was finished by measuring all 4 calibration gases as well as the target gas. The initial calibration in the low flow measurements sometimes showed noisy measurements, most probably due to run-in effects of the whole system. While four hours in the low flow measurements corresponds only to a fraction of the whole run, it would be about a third of a high flow run. To avoid run-in effects, a two hour flush cycle with gas similar to the sample gases was added prior to the first calibration measurement.

In some high flow runs, heat was applied to the sample cylinder. In case the heating system was used to apply heat over a longer time period and keep the sample cylinder at a certain temperature, the heating started as soon as the cylinder reached 30 bar pressure. Heating the whole cylinder to 30 °C took about 1 hour. To avoid losing a lot of gas while the set temperature was not reached, the sample gas flow was shut off during this period and the idle time was used to measure all calibration gases. During the remaining time, flush gas was measured in order to keep the system in steady state. For the heat bursts, the setup was slightly different. The heating started when the cylinder pressure reached 50 bar and lasted until the thermostat measured 30 °C, usually at about 40 bar. During the heating, the measurement cycle continued without any further changes.

~~For quality control, the target gas block was also measured in between the samples. An additional full calibration was measured at the end of each experiment.~~ The values reported by the LI-7000 are the difference between the signals of the sample and the reference cell, which is flushed continuously with a reference gas at a flow rate of 10 mL~~l~~ min^{-1}.~~Δ-signals which are basically the difference between the sample and the continuously at 10 ml min^{-1} flowing reference cell signals.~~

To calculate the CO_2 mole fractions of the sample and target measurements, the raw Δ-signals of the calibration gas measurements were interpolated over time and together with the assigned values of the calibration gases a quadratic calibration function was calculated for each individual sample or target measurement. To guarantee a proper flushing in between different gases and to avoid memory and mixing effects, only the last 2 minutes of each 5 minute block were averaged into one CO_2 mole fraction value and used for further calculations. Since we were only dealing with dry cylinder gases (H_2O < 1 µmol mol^{-1}), the drying unit was bypassed and no water correction was applied.~~ The measurements were done in two different flow settings, a low flow setting with 0.3 l min^{-1} drain and a high flow setting with 5.0 l min^{-1}. The different settings required some adjustments of the hardware and calibration procedure, which will be explained in the following sections.~~

~~2.1 Low Flow measurements~~

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~~In the low flow setting the cylinders were hooked to a VICI multiport valve, which was used to switch between the different calibration gases and the sample gas cylinders. Until 8.11.2016, it was a 10-port valve (EMT2SD10MWE, Valco Instruments Co. Inc., USA), where ports 1 to 5 were used for the sample gases and ports 6 to 10 were connected to C1, C2, C2, C4 and the target gas. The valve was later upgraded to a 16-port valve (EMT2SD16MWE, Valco Instruments Co. Inc., USA), which allowed measuring all sample cylinders in one run. With the new 16-port valve ports 1 to 8 were used for the samples, ports 9 to 13 were used for the calibration and target gases. The secondary pressure for the calibration as well as the target and sample gas was set to about 1 bar. To allow a constant flow out of the cylinder throughout the whole measurement, solenoids were used in each sample line to open by-pass lines for the cylinders that weren't currently measured. The by-pass lines led to needle valves, where the flow was adjusted to 0.3 l min^{-1} for each sample cylinder individually. The by-pass line of the cylinder currently measured remained closed. This ensured that all the gas flowed through the analyzer, kept the flow rate coming out of the cylinder stable and avoided potential fractionation at the tee unions (Fig. 2 a) due to pressure and/or temperature gradients between the arm and the runs of the tee unions. In the low flow measurements with multiple samples, all samples were subsequently measured twice before a block of C2 was measured, and this was repeated three times, before another full calibration was done. In case all eight sample lines were used, one cycle took 275 min, a whole run lasted about 9 to 10 days. In the low flow measurements, the target gas block was added every 1000th minute, which resulted in about 12 additional target gas measurements in one complete run.~~

~~2.2 High flow measurements~~

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~~In the high flow setting, the gas was drained out of the cylinder at 5.0 l min^{-1}, which is why a cylinder lasts only about 12 to 13 hours. Only one sample tank was measured per run, otherwise too much detail might be lost, especially towards the end of the experiment (Fig. 2 b). The calibration sequence was similar to the low flow measurements with some minor changes. In the beginning of every cycle there was again a complete calibration sequence. After the calibration, the sample block was repeated 10 times followed by one block of C2 and again 10 blocks of sample gas that completed the cycle. A target gas block was added every 150th minute, which added about 4 target gas measurements. In order to catch as much sample measurements within the last few bars of the sample cylinders lifetime, some additional conditions related to the sample pressure were added to the measurement sequence: i) no full calibration below 35 bar sample pressure, ii) no target gas measurement below 15 bar and iii) no C2 below 8 bar. The initial calibration in the low flow measurements sometimes showed noisy measurements, most probably due to run-in effects of the whole system. While four hours in the low flow measurements corresponds only to a fraction of the whole run, it would be about a third of a high flow run. To avoid these effects a two hour flush cycle with gas similar to the sample gases was added prior to the first calibration measurement.~~

~~2.3 High flow inlet system~~

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~~Originally the measurement system was designed to operate with sample gas flows of about 0.2-0.3 l min^{-1}. To achieve a flow of 5.0 l min^{-1} out of a sample cylinder, 4.7-4.8 l min^{-1} had to be bypassed in a non-fractionating manner. To do so an inlet system similar to an open-split design was built (Fig. 3). The gas enters the inlet system on one end at a flow rate of 5.0 l min^{-1} and flows through a 0.5 inch stainless steel union and then through a 0.5 inch synflex tube. In~~

~~the center of 0.5 inch tube union, a $^1/_8$ inch stainless steel tube takes an aliquot or air to the measurement system, the rest leaves at the other end through the exhaust. The length of the outer tube is 0.25 m, which in combination with the high flow is sufficient to avoid back diffusion of outside air through the open split. Because the ambient pressure is too low for the pressure controller to maintain the set pressure of 1030 mbar, the secondary pressure of the pressure regulator of the sample gases was increased to 1.5 bar and a needle valve was used to provide a small backpressure. The needle valve increased or decreased the resistance of the exhaust to the lab and thereby the ratio of the flows. Measurements of the same cylinder connected to the high flow inlet and the normal flow inlet resulted in the same~~ ~~CO_2 mole fraction proving that the sampled small flow is not fractionated from the large bypass flow.~~

2.2.4 System performance

To estimate the accuracy and repeatability of the system, differences of target $X_{CO2,measured}$ minus target $X_{CO2,assigned}$ were calculated for each block of target gas measurement. The differences show a normal distribution with a small positive bias of 0.02 ± 0.02 µmol mol^{-1}. There seems to be a difference in the target gas measurements before and after the end of March 2017 (Fig. 4 a). Between these two periods C1 had to be changed because it reached the end of its lifetime. A few days later the CO_2 analyzer had to be changed as well due to a malfunction. Before that period, the average of the target gas differences was 0.01 ± 0.01 µmol mol^{-1}. After the C1 and the CO_2 analyzer were replaced, it became 0.03 ± 0.02 µmol mol^{-1} (Fig. 4 a and b). The assigned values of the calibration gases have currently a reproducibility of 0.01 µmol mol^{-1} (1-sigma). If we assume independent errors between the old C1 and the replacement C1, their difference can be expected to be within $0.01 \cdot \sqrt{2} = 0.014\ \mu mol\ mol^{-1}$ at 1-sigma, which is smaller than the difference between the two periods. Because of that and since the noise grew as well, the change is most likely caused by the exchange of the analyzer. A change of the C3 at the end of September 2017 did not have any significant influence on the precision or accuracy. However, despite the small bias, the accuracy and precision are still excellent for a NDIR CO_2 measurement system. Furthermore, since we are only interested in the changes of the CO_2 mole fraction over the life time of a cylinder, the small bias is only of minor importance. The repeatability is much more meaningful because it shows the detection limit of our experiment.

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2.3 Auxiliary systems

2.3.14 Temperature measurement

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Thermistors were used during the high flow experiments to measure the temperature development of the cylinder surface and on the pressure regulator. The used thermistors were negative temperature coefficient (NTC) sensors (PR103J2, U.S. Sensor Corp., USA) with an accuracy guaranteed by the manufacturer of ± 0.05 °C. ~~Testing the thermistors against a NIST (National Institute of Standards and Technology, USA) calibrated platinum probe showed that they perform even slightly better.~~ The voltages of the thermistors were measured by a Keysight 34901A Data acquisition/switch unit with a 34908A 40-channel multiplexer module (Keysight Technologies, USA) and logged on a laptop PC. During high flow measurements, the temperature was read once a minute, during the one low flow experiment with temperature measurement once every five minutes. The voltage was converted into temperature values by using the Steinhart–Hart equation (Steinhart and Hart, 1968).~~:~~

$$\cancel{\frac{1}{T} = A + B \cdot \ln R + C \cdot (\ln R)^3} \qquad \cancel{(1)}$$

~~where T is the Temperature, A, B and C are the Steinhart-Hart coefficients provided by the manufacturer of the thermistors and R is the measured resistance.~~ To fix the thermistors to the regulator (T1–T6), the cylinder valve (T7–T8) as well as the cylinder (T9–T18) and insulate them from influences from room air, small pieces of rubber foam and duct tape were used. To detect potential biases in the temperature measurement, two thermistors were fixed at similar positions opposing each other, and the thermistors (T19–T25) not attached to the cylinder were bundled and used as background measurement (Fig. 5~~4~~ a and b).

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To learn more about the involved processes, heat was applied in some measurements, steadily over a longer time period or as a single burst. To do so, small heating bands (Minco, USA) with an overall heating power of 110 watts were attached to the cylinder by using aluminum foil tape. Eight bands were equally distributed in pairs on four levels along the cylinder, the ninth band was attached to the bottom of the cylinder (Fig. ~~4~~5 a). The heaters were switched on and off by the measurement sequence, the end temperature was set to 30 °C and regulated by a control unit with a thermostat. For safety reasons the cylinders were wrapped in a thin fire proof glass wool mat during these experiments, the insulating effect of the glass wool mat should be negligible.

~~In case the heat was applied over a longer time period, the heating started as soon as the cylinder reached 30 bar. Heating the whole cylinder to 30 °C took about 1 hour. To avoid losing a lot of gas while the set temperature was not reached, the sample gas flow was shut off during this period and the idle time was used to measure all calibration gases. During the remaining time, flush gas was measured in order to keep the system in steady state.~~

~~For the heat bursts, the setup was slightly different. The heating started when the cylinder pressure reached 50 bar and lasted until the thermostat measured 30 °C, usually at about 40 bar. During the heating, the measurement cycle continued without any further changes.~~

~~2.6 Sample cylinders~~

~~To measure the CO_2 development over the lifetime of a cylinder eight cylinders were repeatedly filled to about 130 bar at Niwot Ridge Station, CO, USA. The filling was done the exact same way as for the standard cylinders NOAA fills to be used as calibration gas tanks (Kitzis, 2017). Six of the eight cylinders were Luxfer L6X® aluminum cylinders, which are the same type NOAA uses for the CO_2 standards, two were Luxfer L6X® SGS (Superior Gas Stability) aluminum cylinders (Table 1). Cylinder CB11876 was excluded from the set and was replaced with CB11941 after the first run, because the cylinder valve's sealing surface got scratched badly. The 29.5 l cylinders were fitted with Rotarex Series D200 brass packless valves (Rotarex, Luxembourg) to be used with two stage pressure reducers (Scott Specialty model 51-14B-590) and chromed brass CGA connection. The regulators were connected to the measurement system by Quick-Connects (SS-QC4-B-4PM and SS-QC4-D-400 for the samples and~~

~~SS-QM2-B-2PM and SS-QM2-D-200 for the standards, respectively, Swagelok, USA) and 1/8” stainless steel tubing (Swagelok, USA).~~

2.4~~7~~ CO_2 enrichment estimates

2.4.1 Langmuir adsorption/desorption model I

Each low flow measurement run of every cylinder was used to fit individually a function based on the Langmuir adsorption/desorption model (Langmuir, 1918, 1916) as derived by Leuenberger et al. (2015):

$$\cancel{CO}X_{CO2,meas} = \cancel{CO}X_{CO2,ad} \cdot \left(\frac{K \cdot (P - P_0)}{1 + K \cdot P} + (1 + K \cdot P_0) \cdot \ln\left(\frac{P_0 \cdot (1 + K \cdot P)}{P \cdot (1 + K \cdot P_0)}\right) - 1\right) + \cancel{CO}X_{CO2,ini} \qquad (\cancel{2}1)$$

where $X_{CO2,meas}$ corresponds to the measured CO_2 mole fraction, $X_{CO2,ad}$ stands for the CO_2 molecules adsorbed by the cylinder wall expressed as a mole fraction, $X_{CO2,ini}$ is the CO_2 mole fraction at the start pressure P_0 in bar, P is the actual pressure in bar and K is the ratio of the adsorption and desorption rate constants and has the units bar^{-1} (see Leuenberger et al. (2015) for more information). To find K, $X_{CO2,ad}$ and $X_{CO2,ini}$, a R script using the Nonlinear Least Square fitting algorithm (nls) was used. Because the CO_2 enrichment in aluminum cylinders was small, the fit seems to be relatively insensitive to K. Therefore the algorithm was not~~n’t~~ able to find K values with a high confidence level and ultimately K was fixed at 0.001 bar^{-1} to find the other coefficients of the model, as will be explained later. ~~and the output corresponded mostly to the lower boundary, even when it was set to 0, meaning no exchange between the cylinder wall and the gas. To find a value for *K* nonetheless, a different approach was used. Given that the residuals of a good fit are normally distributed, *K* can be found by fitting the adsorption/desorption equation but with a fixed *K* value, starting at a value close to 0 and increase it step wise, until the residuals are not normally distributed anymore. To improve the sensitivity, only CO2 measurements below 30 bar were taken into account, where the CO2 increase is more pronounced. This was done for ten different low flow cylinder measurements. The resulting *K* values were averaged and the standard deviation was calculated. To make sure the residuals of all fits stay well within the normally distributed range, the K value was considered to be difference “average - standard deviation”, which resulted in 0.002 bar-1. To make sure, the residuals are normally distributed, *K* was set in the nls algorithm to 0.001 bar-1.~~

2.4.2 Langmuir adsorption/desorption model II

We also took a different approach to find values for the adsorbed CO_2 and the exchange rate K starting from a slightly altered Langmuir’s adsorption desorption model (Langmuir, 1918, 1916):

$$\theta = \frac{K\rho_x}{1 + K\rho_x} \qquad (\cancel{3}2)$$

with θ the fraction of total number of available sites~~available wall space~~ that ~~is~~are occupied (dimensionless), K corresponds again to the ratio of the adsorption and desorption rate constants here in the units m^3 mol^{-1} and ρ_x is the average amount density (mol m^{-3}) of CO_2 in the gas phase. In this approach θ is a function of CO_2 only, not of total

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Formatted: Font: Italic, English (United States) gas pressure. With the trace gas mole fraction X and the average amount density ρ_a of air molecules, ρ_x can be written as the product of two independent variables:

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$$\rho_x = X \cdot \rho_a \qquad (\cancel{4}3)$$

Assuming the ideal gas law with P the pressure, V the volume, R the gas constant, T the temperature, and ~~N~~n_a the total amount of air (moles) in the gas phase, we also have

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$$\rho_a = \frac{\cancel{N}n_a}{V} = \frac{P}{R \cdot T} \quad and \quad \rho_x = \frac{X \cdot P}{R \cdot T} \qquad (\cancel{5}4)$$

The total amount of trace gas n_{tot} can be written as the sum of the amount of trace gas adsorbed to the walls n_{ad} and the amount of trace gas in the cylinder air n_{gas}:

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$$n_{tot} = n_{ad} + n_{gas} \qquad (5)$$

The amount of molecules adsorbed to the wall n_{ad} can be expressed as:

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$$n_{ad} = \theta \cdot a \qquad (6)$$

in which a is the available wall space (maximum amount of adsorbed molecules~~amount of sites~~, expressed in moles), a number that we do not know, so that we have for the total amount of trace gas, in the gas phase and on the wall divided by the volume:

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$$\frac{\cancel{Total\ trace\ gas}n_{tot}}{V} = X\rho_a + \theta \cdot \frac{a}{V} \qquad (7)$$

By draining some air ($d\rho_a$, which is negative) with its current mole fraction X out of a cylinder, a certain amount of trace gas will be removed ($Xd\rho_a$) and the partitioning between the gas phase and the wall will change. If we also assume that the relevant quantities are uniform inside the cylinder, the corresponding change of trace gas per volume can be written as

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$$\frac{d(\cancel{Total\ trace\ gas}n_{tot})}{V} = Xd\rho_a = d(X\rho_a) + d\left(\frac{a}{V} \cdot \theta\right) = \rho_a dX + Xd\rho_a + d\left(\frac{a}{V} \cdot \frac{K\rho_x}{1 + K\rho_x}\right) \qquad (8)$$

which we rearranged into the following equation

$$-\rho_a dX = \frac{a}{V}\left(\frac{Kd\rho_x}{1 + K\rho_x} - \frac{K\rho_x Kd\rho_x}{(1 + K\rho_x)^2}\right) = \frac{a}{V}\frac{Kd\rho_x}{1 + K\rho_x}\left(1 - \frac{K\rho_x}{1 + K\rho_x}\right) \qquad (9)$$

and subsequently into

$$-\rho_a dX = d\rho_x \frac{a}{V} \frac{K}{(1+K\rho_x)^2}$$ (10)

By substituting $d\rho_x$ in Eq. (10) with $Xd\rho_a + \rho_a dX$, it can be rearranged to

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$$\frac{dX}{X} = -\frac{d\rho_a}{\rho_a} \cdot \frac{\frac{a}{V} \cdot K}{(1+K\rho_x)^2 + \frac{a}{V} \cdot K}$$ (11~~9~~)

The gas pressure (and the amount density) varies over a large range from 150 to 1 bar, whereas the quotient $\frac{\frac{a}{V} \cdot K}{(1+K\rho_x)^2 + \frac{a}{V} \cdot K}$ varies only little. Therefore we can integrate Eq. (11~~9~~) numerically in successive steps from 150 bar to 1 bar, as follows:

$$X_i = X_{i-1} \left(\frac{\rho_{a,i}}{\rho_{a,i-1}} \right)^{\frac{-\frac{a}{V} \cdot K}{(1+K\rho_{x,i-1})^2 + \frac{a}{V} \cdot K}}$$ (12~~0~~)

Assuming the ideal gas law, it could also be rewritten as

$$X_i = X_{i-1} \left(\frac{P_i}{P_{i-1}} \right)^{\frac{-\frac{a}{V} \cdot K}{(1+K\rho_{x,i-1})^2 + \frac{a}{V} \cdot K}}$$ (13~~1~~)

with P being the pressure (bar). However, also with this different approach, it was not~~n't~~ possible to determine K and a independently. There is not enough information in the data at the low observed enrichments. A range of solutions, in which there is a tight anti-correlation between K and a, can reproduce the enrichment at a pressure of 1 bar. However, with higher K values the enrichment effect becomes more and more concentrated at low pressures, so that at some point the observed shape of the observations can not be met. Therefore K and the corresponding coverage factor θ (at 150 bar) have to be low.

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2.4.3 Estimating *K* based on the CO_2 measurements

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To find a value for *K*, a process of elimination was used. Given that the residuals between the data and the fit function of a good fit are normally distributed, *K* can be found by fitting the adsorption/desorption equation but with a fixed *K* value, starting with a value close to 0. Then, *K* is increased step wise, until the residuals are not normally distributed anymore. To improve the sensitivity of this method, only CO_2 measurements below 30 bar were taken into account, where the increase of the CO_2 mole fraction is more pronounced. These calculations were done for ten different low flow cylinder measurements. The resulting *K* values were averaged and the standard deviation was calculated. This *K* value might not be the best fit, but it gives a good estimate about the upper boundary of possible K values. To make sure the residuals of all fits stay well within the normally distributed range, the *K* value was considered to be the

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difference "average *K* value minus standard deviation", which resulted in 0.002 bar^{-1}. To be on the safe side, *K* was set in the nls algorithm to 0.001 bar^{-1}.

2.4.4 Rayleigh distillation model and its combination with the Langmuir adsorption/desorption model I

Additionally to the Langmuir adsorption/desorption model, a Rayleigh distillation function (Langenfelds et al., 2005; Matsubaya and Matsuo, 1982; Rayleigh, 1902) was fitted to the data as well, it had the form:

$$\frac{X}{X_0} = \left(\frac{P}{P_0}\right)^{\alpha-1} \qquad (14\cancel{2})$$

where *X* corresponds to the measured CO_2 mole fraction, X_0 to the initial CO_2 mole fraction, *P* and P_0 correspond to the actual and initial pressure, respectively, and α is the fractionation factor for the gas leaving the cylinder. The outflowing gas is depleted in CO_2 if $\alpha < 1$, leaving the gas in the cylinder slightly enriched in CO_2 (and vice versa). With ongoing outflow, the effect gets stronger because the gas in the cylinder becomes more and more enriched. However, to make Rayleigh distillation possible, a fractionating process has to be involved, namely that the CO_2 mole fraction of outflowing gas is either enriched or depleted with respect to the cylinder average. A possible reason for fractionation in the cylinders is a temperature gradient in the cylinder. Heavier molecules tend to accumulate at the cooler end of a gas reservoir, while the lighter molecules are slightly more represented at the warmer end. If the sample air is taken from e.g. the warmer part of the gas column, it will be slightly depleted in the heavier molecule while the gas in the cylinder becomes enriched. If only low flow experiments are considered, it is not possible to distinguish between Langmuir adsorption/desorption effects and Rayleigh fractionation, both functions give equally reasonable ~~results~~fits, which is one reason the high flow experiments were needed (see hypothesis ii in the introduction). To each of the high flow measurements a fit based on the Langmuir adsorption/desorption as well as a fit based on the combination of the Langmuir and Rayleigh distillation function were calculated. The Langmuir fit was again calculated with *K* fixed at 0.001 bar^{-1}, $X_{CO2,ad}$ and $X_{CO2,ini\cancel{t}}$ were estimated by a non-linear least squares (nls) algorithm in a R script. In case of the combination, the Langmuir part was calculated with fixed coefficients that correspond to the averaged coefficients of the low flow experiments. The coefficients X_0 and α of the Rayleigh distillation term were again determined using R's nls algorithm using the following equation:

$$\cancel{CO}X_{CO2,meas} = \overline{\cancel{CO}X_{CO2,ad,lf}} \cdot \left(\frac{K \cdot (P - P_0)}{1 + K \cdot P} + (1 + K \cdot P_0) \cdot \ln\left(\frac{P_0 \cdot (1 + K \cdot P)}{P \cdot (1 + K \cdot P_0)}\right) - 1\right) + X_0 \cdot \left(\frac{P}{P_0}\right)^{(\alpha-1)} \qquad (15\cancel{3})$$

~~W~~where $X_{CO2,ad,lf}$ is the average $X_{CO2,ad}$ coefficient of the low flow experiments, *K* is again the ratio of the adsorption and desorption rate constants (fixed at 0.001 bar^{-1}), *P* is the actual pressure, P_0 is the initial pressure, X_0 corresponds to the CO_2 mole fraction before the enrichment and α is the fractionation factor, close to one. To test whether the enrichment follows a Rayleigh fractionation, ln(X/X_0) can be plotted against -ln(P/P_0) after the data has been corrected

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Formatted: Font: Italic, English (United States) for Langmuir adsorption/desorption effects. If there is Rayleigh fractionation, the points should line up, following a line with a slope of 1-α.

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3. Results

No data selection~~general filtering~~ was applied to the measured data. However, in the beginning of these experiments, some ~~measurements~~ runs showed run-in effects between the first two calibration points, most probably due to an insufficiently flushed reference line due to the very small flow. These measurements were excluded from any further calculations. The run-in effects vanished mostly when an additional flush gas cylinder with a 2 hour flushing sequence was added to the measurement sequence.

~~3.1 Accuracy and precision~~

~~To estimate the accuracy and repeatability of the system, differences of target $CO_{2,measured}$ minus target $CO_{2,assigned}$ were calculated for each target gas measurement. The differences show a normal distribution with a small positive bias of 0.02 ± 0.02 µmol mol^{-1}. There seems to be a difference in the target gas measurements before and after the end of March 2017 (Fig. 5 a). Between these two periods C2 had to be changed because it reached the end of its lifetime. A few days later the CO_2 analyzer had to be changed as well due to a malfunction. Before that period, the average of the target gas differences was 0.01 ± 0.01 µmol mol^{-1}. After the C2 and the CO_2 analyzer were replaced, it became 0.03 ± 0.02 µmol mol^{-1} (Fig. 5 a and b). The assigned values of the calibration gases have currently a reproducibility of 0.01 µmol mol^{-1} (1-sigma). If we assume independent errors between the old C2 and the replacement C2, their difference can be expected to be within $0.01 \cdot \sqrt{2} = 0.014\, \mu mol\, mol^{-1}$ at 1-sigma, which is smaller than the difference between the two periods. Because of that and since the noise grew as well, the change is most likely caused by the exchange of the analyzer. A change of the C3 at the end of September 2017 didn't have any significant influence on the precision or accuracy. However, despite the small bias, the accuracy and precision are still excellent for a NDIR CO_2 measurement system. Furthermore, since we are only interested in relative changes of CO_2 over the life time of a cylinder, the small bias is only of minor importance. The repeatability is much more meaningful because it shows the detection limit of our experiment.~~

3.1~~2~~ Low flow measurements

In the low flow mode, 38 full tanks were depleted with vertically positioned cylinders to see whether the CO_2 mole fraction change with decreasing pressure is different in each individual cylinder and whether SGS cylinders perform better than normal cylinders. All low flow measurements followed a similar pattern with a very small, almost linear CO_2 mole fraction increase down to about 30 bar that becomes much stronger from there. A fit following Langmuir's adsorption/desorption model was calculated for each cylinder measurement and used to estimate the average CO_2 enrichment with decreasing pressure. Using the actual pressure measurements, the average CO_2 enrichment is 0.089 ± 0.013 µmol mol^{-1} (Fig.6 a), the given error corresponds to the standard deviation (1-sigma) of individual cylinder drainings. However, values for the CO_2 enrichment of the individual cylinder measurements might be not

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entirely comparable, since each cylinder had a different initial pressure. Therefore, we calculated the CO_2 enrichment for each cylinder measurement using the same pressure span of 150 to 1 bar. This results in an average CO_2 enrichment of 0.090 ± 0.009 µmol mol^{-1}, which is the same within the given uncertainty. The variation of the enrichment was very low, indicating that the CO_2 enrichment with decreasing pressure is not cylinder dependent. The two SGS cylinders do not show a significantly different behavior, the shape of the CO_2 enrichment with decreasing pressure as well as the amount is the same as for the normal cylinders within the given uncertainty (Fig. 6 b). ~~The fit functions were used to calculate the average CO_2 enrichment with decreasing pressure using the pressure measurements, it is 0.089 ± 0.013 µmol mol^{-1} (Fig.6), the given error corresponds to the standard error (1-sigma) of the average. Since each cylinder started with a different pressure, the averages could be not entirely comparable. However, if the enrichment is calculated over the same pressure span of 150 to 1 bar, the result is again 0.090 ± 0.009 µmol mol^{-1}, which is the same within the given uncertainty.~~ As mentioned ~~in the methods~~above, the coefficient K of the Langmuir model had a fixed value of 0.001 bar^{-1}, but also the value of the initially adsorbed CO_2, $X_{CO2,ad}$ was relatively constant throughout all measurements, the average was 0.0165 ± 0.0016 µmol mol^{-1} at the initial pressure. When fitting a function based on Rayleigh distillation, the average of the fractionation factor α is 0.999957 ± 0.000004, which would cause a CO_2 increase of about 0.085 µmol mol^{-1} ~~if~~when the pressure drops from 150 to 1 bar. The given uncertainty range of 0.000004 corresponds to about 9.3 % of (1-0.999957). Considering the calculated CO_2 enrichment of 0.085 µmol mol^{-1}, 9.3 % equates to about 0.008 µmol mol^{-1}, which is consistent with the measurement system's repeatability of 0.01 µmol mol^{-1} as deduced from the target gas measurements before the analyzer change.~~The standard deviation of the average α is very low. If the measurement system's repeatability as deducted from the target gas measurements is taken into account, a realistic error of α should be about four times bigger.~~

~~Two additional low flow measurements with horizontally positioned cylinders were done.~~ Additionally, a low flow run with two horizontally positioned cylinders (one normal and one SGS cylinder) was done. Again the Langmuir fit functions of the two cylinder measurements were used to estimate the average CO_2 enrichment, which was 0.019 ± 0.003 µmol mol^{-1} for the measured pressure drop and 0.021 ± 0.004 µmol mol^{-1} for a pressure drop from 150 to 1 bar, respectively, which is a hardly significant considering the detection limit of the measurement system. One of the two cylinders was equipped with thermistors, similar to the high flow setup, representing at the same time the only low flow ~~measurement~~ run with temperature measurements (Fig. 5~~4~~ b). The temperature measurements did not~~n't~~ reveal any features related to the pressure drop in the cylinder. The observed periodical cylinder temperature changes with an amplitude of about 1 K were mainly driven by changes of the room temperature due to the air conditioning regulation and not by the gas decanting (Fig. 7).

3.2~~3~~ High flow measurements

3.2.1 Vertically positioned cylinders

~~In the high flow mode, eight complete drainings were done with cylinders vertically positioned.~~ In high flow mode, each of the six normal and the two SGS cylinders were drained once with cylinders vertically positioned, to find out whether Langmuir adsorption/desorption is the only process enriching the CO_2 mole fraction with decreasing pressure. The average enrichment calculated from the Langmuir-only fits corrected to a pressure drop from 150 to 1 bar was

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0.24 ± 0.04 µmol mol^{-1} (Fig. 8). The average value for $X_{CO2,ad}$ was 0.043 ± 0.008 µmol mol^{-1}, which is about 2.5 times bigger than the value found in the low flow experiments (K was again fixed at 0.001 bar^{-1}). If the combined Langmuir/Rayleigh fit is used with the Langmuir coefficients fixed from the low flow measurements, the enrichment adjusted to a pressure drop of 150 to 1 bar is 0.22 ± 0.05 µmol mol^{-1}, which is basically the same within the uncertainties. The average fractionation factor α is 0.99993 ± 0.00002, which ~~means~~corresponds to a CO_2 depletion in the outflowing gas. Subtracting the Langmuir function with the low flow coefficients from the measurements and using the residuals to plot ln(X/X_0) against -ln(P/P_0) yields an elongated cloud with slope of 1-α, indicating that Rayleigh distillation might be responsible for the additional CO_2 enrichment seen in the high flow measurements (Fig. 9). At the same time, the temperature development of the cylinder and the pressure regulator were measured (Fig. 10 a). At the front end of the regulator, where the secondary pressure reduction happens, the temperature dropped rapidly by about 6.76 ± 0.59 K within 94 ± 22 min with the given errors being the standard error (1-sigma) of the ~~average~~ mean of all runs. The thermistors indicate also a slightly bigger temperature drop of 7.01 ± 0.62 K within 98 ± 23 min at the first stage compared to the second stage, although the difference is hardly significant. The stem of the regulator showed a reduced temperature drop of about 4.58 ± 0.44 K with the minimum delayed by about 133 ± 33 min. The cylinder valve follows much closer the temperature of the cylinder body than the temperature of the regulator. It shows a drop of 2.33 ± 0.25 K with the minimum occurring 234 ± 25 min after the beginning of the gas flow. The temperature of the cylinder was measured at five evenly distributed ~~levels~~distances. The average temperature drops from the top to the bottom level were 2.29 ± 0.23 K, 2.40 ± 0.19 K, 2.53 ± 0.17 K, 2.58 ± 0.18 K and 2.55 ± 0.21 K, respectively, with the minima occurring at 251 ± 29 min, 266 ± 23 min, 281 ± 17 min, 286 ± 16 min and 283 ± 22 min after the gas flow was initiated. The temperatures of the different levels of the cylinder body follow each other closely until one after the other reaches the minimum. Then they start to fan out until the end of the experiment, reaching a spread of 0.55 ± 0.13 K with the level near the ground showing the lowest temperature and the level near the shoulder showing the highest temperature.

3.2.2 Horizontally positioned cylinders

Three more ~~complete drainings~~runs were done with the cylinders horizontally positioned to measure the CO_2 changes with different temperature gradients compared to the vertically positioned cylinders. In case the temperature gradient has no influence on the observed CO_2 changes with decreasing cylinder pressure, the outcome of these measurements should be the same as with vertically positioned cylinders. In the beginning of the experiments, the temperature of the regulator, the stem and the valve show a fast drop to minimal temperatures followed by a slow gradual temperature increase, similar as with the vertically positioned cylinders. Also the cylinder valve follows closely the temperature of the cylinder body, although it seems to cool down a bit more and appears to be slightly more influenced by the regulator stem compared to the measurements with the vertical cylinders. The maximal temperature drops of the regulator from the front end to the stem are 6.40 ± 0.18 K, 6.72 ± 0.22 K and 4.66 ± 0.31 K, respectively with delay times of 112 ± 16 min, 109 ± 21 min and 194 ± 43 min after starting the gas flow. The cylinder valve shows a temperature drop of 2.81 ± 0.52 K with a time delay of 251 ± 15 min. The temperatures of the cylinder body show a different behavior. If the corresponding thermistors of the lower and the upper side are averaged, similarly to the

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measurements with vertically positioned cylinders, the temperature drop seems to be the same everywhere within the uncertainties. From the valve end to the bottom end of the cylinder the average temperature drops of the three measurements are 2.82 ± 0.64 K, 2.80 ± 0.59 K, 2.83 ± 0.67 K, 2.80 ± 0.67 K, and 2.78 ± 0.67 K, with time delays of 292 ± 38 min, 292 ± 36 min, 291 ± 35 min, 299 ± 33 min and 299 ± 35 min, respectively (Fig. 10 b). The given uncertainties~~errors~~ correspond to the standard deviation (1-sigma) of the average over the three runs. However, if the temperature development of each thermistor is evaluated individually, interesting details can be found. Since the three cylinders had slightly different starting pressures, the pressures had to be converted into a relative pressure measure in order to make them comparable. To do so the pressure at each measurement was divided by the initial pressure (P/P_0) ~~which means~~where 1 (or 100 %) stands for a full cylinder, 0 means the cylinder is empty. The temperature measurements of each thermistor during the three runs were matched according to the relative pressure and to make the temperatures comparable, the difference of the temperature measured by the individual thermistor minus the cylinder body average (including the valve) was calculated. The results of the three runs were averaged and the standard deviation calculated. On the cylinder body, the temperature of the upper thermistor is usually higher than the temperature of its counterpart at the lower side (Fig. 11). The temperatures of the two thermistors at the valve are the same within uncertainty. In the beginning~~ at 100 % relative pressure~~, there is no significant temperature gradient along the cylinder body. At 75 % relative pressure, the front end is cooler than the cylinder body and the difference between the upper and the lower side starts to grow with the largest difference of 0.25 K ~~being~~ in the middle of the cylinder body. At 50 % relative pressure the temperature distribution becomes symmetrical, with the lowest difference at the front end and the largest difference still in the middle of the cylinder body. There the temperature difference is about 0.3 K and remains stable for the rest of the experiment. This is also the point where the CO_2 depletion starts to follow the 1-α slope in the logarithmic plot indicating Rayleigh fractionation as will be shown later in this section (Fig. 9). At 25 % relative pressure the valve and the shoulder start to warm up (Fig. 11). While the temperature gradient along the cylinder becomes smaller on the upper side, the gradient along the lower side is increasing. The largest difference is again at the middle of the body, it is still about 0.30 K. At 1 % relative pressure, the temperature gradient at the upper side almost vanished while it is the largest now for the lower side. The largest temperature difference of about 0.30 K is still at the middle of the cylinder body. The mole fraction measurements of these cylinders looked completely different. From the start of the measurement down to about 30 bar, the CO_2 mole fraction of all three cylinders showed first a slight decrease of about 0.05 µmol mol^{-1}, followed by a small increase back to the original CO_2 level. From 30 bar until the end of the measurement, the CO_2 measurements show a steep CO_2 depletion (Fig. 12). If only the Langmuir function was used, $X_{CO2,ad}$ had to become negative, which is physically impossible. Using the combined Langmuir/Rayleigh fit function with the Langmuir coefficients fixed to the value from the low flow setting gives us an average CO_2 depletion of 0.20 ± 0.03 µmol mol^{-1} over a pressure drop from 150 to 1 bar. The average fractionation factor α is 1.00014 ± 0.00003 indicating a CO_2 enrichment in the outflowing sample gas, in contrast to the vertical cylinders (Fig. 9). The slope still follows 1-α, consistent with Rayleigh fractionation. In all three ~~measurements~~ runs the logarithmic plots show a flat plateau in the beginning. The decrease starts in all three ~~measurements~~ runs at -ln(P/P$_0$)≈0.7, which corresponds roughly to a half empty cylinder. If only the CO_2 measurements below 50 % of the cylinder's pressure are used to calculate α, then the average fractionation factor for the outflow becomes

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1.00021 ± 0.00004, indicating an even stronger fractionation~~. When the Rayleigh fractionation with the stronger fractionation factor is only applied after the cylinder is half empty, when the temperature difference between the upper and the lower side of the cylinder body reaches its final value of 0.3 K, the average~~ with a final average depletion ~~is~~ of -0.26 ± 0.07 µmol mol^{-1}.

3.2.34 Moving cylinders into different orientations while measuring

One high flow run each was done with a cylinder being in horizontal position and then put into vertical position at about 30 bar and vice versa. If there are different air masses in the cylinder with different temperatures and therefore depleted/enriched CO_2 mole fractions, moving the cylinder should cause a sudden change in the temperature measurements as well as in the CO_2 measurements of the sample gas. The tank that was first in horizontal position showed a very stable CO_2 mole fraction (411.00 ± 0.02 µmol mol^{-1}) down to 32.7 bar when it was put up into a vertical position (Fig. 13). With the movement, the CO_2 mole fraction dropped within 15 min by about 0.08 µmol mol^{-1} and from there on, it showed similar enrichment behavior as the other measurements of vertically positioned cylinders with a CO_2 increase of about 0.12 µmol mol^{-1}. Also the opposite experiment showed stable CO_2 mole fractions (401.90 ± 0.02 µmol mol^{-1}) until it was laid down at 32.1 bar. As soon as it was in a horizontal position the CO_2 mole fraction jumped up within 25 min by about 0.13 µmol mol^{-1} and decreased in a similar manner as the other horizontally positioned cylinders with a CO_2 decrease of about 0.14 µmol mol^{-1}. Interestingly, the two cylinder measurements seem to mirror each other pretty well (Fig. 13). The temperature development of the regulators looks the same as for other high flow measurements and the temperature of the cylinder body shows similar main characteristics, such as a fast drop in the beginning and a slow increase after reaching a minimum. However, there are some interesting differences. Until the cylinders are moved, the temperature measurements follow the usual individual pattern, the temperatures of the vertical cylinder drop and fan out, the ones of the horizontal cylinder drop but stay together. After the cylinders are moved, the temperature measurements of the cylinder that is now horizontal converge (Fig. 14 a) while the ones of the cylinder that is now vertical fan out (Fig. 14 b).

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Three additional runs were done, where the cylinders were first in horizontal position, and then put in a vertical position but with their valves at the bottom. During the first run, the handling of the cylinder did not~~n’t~~ go as smooth as planned and the turning of the cylinder took several attempts. Also the data logger for the thermistors stopped after about two hours. The CO_2 mole fraction of the first run is stable at 401.74 ± 0.02 µmol mol^{-1}, after the manipulation at 30.7 bar it stepped up by 0.05 µmol mol^{-1} and remained stable at 401.79 ± 0.02 µmol mol^{-1} until the cylinder was empty. The second cylinder was also stable at 401.85 ± 0.02 µmol mol^{-1} until it was put up on its valve side at 32.2 bar, then the CO_2 mole fraction dropped by 0.08 µmol mol^{-1} to 401.77 ± 0.02 µmol mol^{-1} were it remained stable until the cylinder was empty. The third cylinder again showed stable CO_2 mole fractions in the beginning it was at 401.83 ± 0.02 µmol mol^{-1}. At 27.8 bar it was put up and the CO_2 mole fraction dropped by 0.10 µmol mol^{-1} were it stayed at 401.72 ± 0.02 µmol mol^{-1} until the cylinder was empty. The temperature measurements of the two cylinders show the same behavior and they are comparable to the ones where the horizontal cylinder was brought into a vertical position. The only difference is that after the fanning out of the different temperature levels, the temperatures at the bottom of the cylinder are the highest, the temperatures at the valve, which is here the lower end, are the lowest (Fig. 14 c).

3.2.4~~5~~ Heating cylinders

Two horizontally positioned cylinders were measured with constant heating up to 30 °C starting at a cylinder pressure of 30 bar. In case the heating induces convection in the cylinder, we expect the sample gas to become well mixed and no CO_2 enrichment besides Langmuir adsorption/desorption as in the low flow experiments. The mole fraction of the first cylinder was stable before and after the heating was started at 410.36 ± 0.03 µmol mol^{-1} and 410.27 ± 0.02 µmol mol^{-1}, respectively (Fig. 15). ~~The first cylinder showed a stable CO_2 mole fraction before heating, it was 410.36 ± 0.03 µmol mol^{-1}. The resumed CO_2 measurement after the cylinder temperature reached 30 °C showed a drop of about 0.09 µmol mol^{-1} and remained stable at 410.27 ± 0.02 µmol mol^{-1} until the cylinder was empty (Fig. 15).~~ The second cylinder showed no changes in the CO_2 mole fraction before and during the heating. The average CO_2 mole fraction coming out of the cylinder before and after heating was ~~down to 30 bar was~~ 410.99 ± 0.03 µmol mol^{-1}~~, after the temperature reached the preset value it was at~~ and 410.99 ± 0.02 µmol mol^{-1}, respectively. The temperature measurements of the two cylinders are ~~the virtually the same~~in good agreement (Fig. 16 a). In the beginning, they show the same pattern as the other high flow measurements with horizontally positioned cylinders, a temperature drop with the onset of the gas flow and almost no dispersion of the temperatures along the cylinder. At 30 bar, the heating began and the temperature increased and overshot slightly. Since the thermostat was attached to the shoulder of the cylinder, the temperature measured there is closest to the preset 30 °C. From there it increased by about 4.5 K with a maximum at the bottom of the cylinder. A possible reason for the cylinder being warmer at the bottom end might be the thicker wall at the shoulder that results in a bigger thermal mass and the additional heat band at the bottom of the cylinder. Due to the inconsistency of the two runs, it is impossible to tell whether the mixing induced by convection prevented thermal fractionation or not. ~~The cylinder wall is slightly thicker at the shoulder resulting in a bigger thermal mass. That, and the fact that there was a heat band at the bottom, might be why the temperature is higher at the bottom than at the shoulder and why the temperature overshot in the beginning of the heating.~~

Two vertically positioned cylinders were measured with burst heating up to 30 °C, starting at 50 bar. The first cylinder did not~~n’t~~ seem to be affected by the heat burst, before heating the CO_2 mole fraction was stable at 401.91 ± 0.02 µmol mol^{-1}, after heating the CO_2 mole fraction followed the same pattern as with vertically positioned high flow experiments with no heating, resulting in a CO_2 enrichment of 0.15 µmol mol^{-1}. Unfortunately, the measurement cycle started a full calibration at about 52 bar, which is why there are no CO_2 data while heating. Also the temperature data logging stopped working after four hours, missing the interesting part of the experiment. In the second~~ measurement~~ run, the CO_2 mole fraction was stable at 401.71 ± 0.02 µmol mol^{-1} before the heating was switched on. With the beginning of the heating, the CO_2 mole fraction increased by about 0.10 µmol mol^{-1}, but again a full calibration obscures partly what happened during the heat burst. When the heaters were turned off, the CO_2 mole fraction fell back on values similar to high flow runs with vertical cylinders without heating and followed their enrichment pattern from there. The enrichment from the beginning of the heating until the cylinder was empty corresponded to 0.13 µmol mol^{-1} (Fig. 17). Initially the temperature development looks about the same as for other

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vertically positioned cylinders, the temperature is coolest at the bottom and highest at the shoulder. ~~Then, a~~After the heating was switched on, the temperature gradient was ~~turned upside down~~inverted almost immediately~~. The set~~ and after about one hour the set temperature ~~of 30 °C~~ was reached. ~~after about one hour which corresponds to a pressure decrease of about 10 bar.~~ As soon as the heat bands were switched off, the temperature began to sink and the temperature gradient turned back eventually (Fig. 16 b). The two experiments showed, that quick heat bursts have only a short effect on the sampling gas and are not sufficient to produce much mixing of the cylinder gas.

4. Discussion

4.1 Low flow measurements

The low flow measurements with cylinders vertically positioned show repeatedly comparable CO_2 enrichment with decreasing pressure.~~, no matter which cylinder was measured.~~ Neither the normal nor the SGS cylinders showed any unique features with respect to CO_2 enrichment. ~~That suggests~~Therefore the conclusion can be drawn that the observed CO_2 enrichment ~~may be universal~~ for ambient level CO_2-in-dry-air mixtures stored in this type of aluminum cylinder is universal. The only low flow temperature measurement available was done on one of two ~~vertically~~horizontally positioned cylinders. Towards the end of these measurements, the laboratory's air conditioning was not~~n't~~ very stable, varying by up to 1.5 K. The temperature variation is also visible in the CO_2 mole fraction of two cylinders measured, making it impossible to calculate the CO_2 enrichment of this run properly. However, during the first few days, when the background temperature was more stable, the temperature measurements also reveal that the slow pressure drop of the low flow setting does not cause a big temperature drop in the cylinders. Therefore, the CO_2 enrichment in the low flow experiments is most probably not temperature driven, but rather caused by CO_2 desorbing from the walls with decreasing pressure, following Langmuir's adsorption/desorption model. Assuming a pressure of 150 bar, a K value of 0.001 bar^{-1} and using these values in Langmuir's equation predicts occupation of the available wall spaces of about 13 %. ~~By u~~Using a very simplified geometrical approach~~,~~ results in a higher estimate of the occupied wall spaces. ~~this number becomes even smaller.~~ Assuming the inner surface of the cylinder A_{cyl} is 0.75 m^2, the area a CO_2 molecule occupies corresponds to the collision diameter squared (D_{CO2} =0.39 $\cdot 10^{-9}$ m), the number of molecules per mole is defined as $N_A = 6.022 \cdot 10^{23}$ mol^{-1} ~~(Avogadro's number),~~ a pressure of $P =$ 150 bar, a volume of $V_{cyl} = 29.5$ l, a temperature of $T =$ 293.15 K, and using the $X_{CO2,ad}$ = 0.0165 µmol mol^{-1} from the low flow measurements, the fraction of occupied spaces can be calculated to be $\frac{CO_{2,ad} \cdot D_{CO2}{}^2 \cdot P \cdot V_{cyl} \cdot N_A}{A_{cyl} \cdot R \cdot T} = 37\ \%$. There is not enough information in the data to determine which of the two numbers is closer to reality. As mentioned in the methods section, a range of solutions can reproduce the observed enrichment at a pressure of 1 bar. But since with higher K values the enrichment effect becomes more and more pronounced at lower pressures, so that the observed shape can not be met, K and the corresponding coverage factor θ (at 150 bar) have to be low. A second conclusion is that the aluminum cylinders are a good choice to store CO_2-in-dry-air mixtures. In the case of gravimetrically prepared standards, the CO_2 mole fraction is calculated by weighing the CO_2 and the air that have been added to the cylinder. Because part of the CO_2 is adsorbed by the cylinder wall, the assigned CO_2 mole fraction of the sample gas might be overestimated, leading to a small bias in the calibration of CO_2 measurements if not corrected properly. This effect is

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likely worse with smaller cylinders, where the surface to volume ratio is bigger and should be taken into account when preparing CO_2 standards gravimetrically or when preparing mother/daughter cylinders for comparison projects between different analyzers and/or laboratories.

4.2 High flow measurements

The CO_2 enrichment in the high flow measurement with vertically positioned cylinders was on average 2.5 times higher than in the low flow measurements. This corresponds well with the $X_{CO2,ad}$ value of 0.047 µmol mol^{-1} found by Leuenberger et al. (2015) in a similar experiment. However, since the cylinders for the low flow and the high flow experiments were prepared the same way, there is no reason why the CO_2 adsorbed by the wall should be that much higher. Also the ratio of the adsorption/desorption rate (K), although slightly temperature dependent, does not~~n't~~ explain the difference of the CO_2 enrichment between the low and the high flow experiments. Following the van't Hoff equation $K(T) = K(T_0) \cdot e^{\frac{E}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_0}\right)}$ (van't Hoff, 1900), assuming a desorption energy of -10 kJ mol^{-1} and using the maximum measured temperature drop of about 10 K, the coefficient K would only vary by about 10 %. But as mentioned in the methods section, the fit function is very insensitive to K anyway. A possible explanation for the stronger CO_2 enrichment might be thermally driven processes. As the air expands inside the cylinder because the pressure drops, it will undergo adiabatic cooling. The cooling will be partially shared with the cylinder wall through circulation and diffusion of the air. The air will circulate because the air near the walls will tend to remain warmer than in the core. The temperature measurements during the high flow experiments with vertically positioned cylinders show a temperature drop of about 2.5 K at the cylinder surface caused by the pressure drop. The temperature difference between the different levels becomes gradually bigger and is about 0.5 K between the top and the bottom end at the end of the ~~measurement~~run. This is consistent with cool air sinking in the cylinder while warmer air is rising. Assuming that there are only slow laminar flows in the cylinder and because air is a poor heat conductor, it is likely that the air inside the cylinder is forming a considerably cooler core. In equilibrium CO_2 will be depleted slightly in air that is warmer and in contact with air that is cooler by ~0.06 ppm/K at 400 ppm (Chapman and Cowling, 1970). The upright position of the cylinder might add to the effect by separating the warm and the cool end spatially. By draining gas from the cylinder, the warm depleted air comes out first and leaves slightly CO_2 enriched air in the cylinder. The cooler CO_2 enriched air follows later. Plotting $\ln(X/X_0)$, corrected for Langmuir desorption using the low flow coefficients, against $-\ln(P/P_0)$, the points line up nicely with a slope of $1-\alpha$, supporting the idea of Rayleigh fractionation being partly responsible for the CO_2 enrichment in the high flow experiments (Fig. 9). We also have to remember that in this situation the cylinder air is not perfectly mixed any more, and the air leaving the cylinder does not sample the cylinder uniformly.

Besides adsorption/desorption effects, Rayleigh fractionation seems to be at work in the high flow measurements with horizontal positioned cylinder as well, causing a net decrease in the CO_2 mole fraction with decreasing pressure. When looking at the logarithmic plot (Fig. 9), the points form first a plateau with stable CO_2 mole fractions. The points seem to indicate an onset of Rayleigh fractionation when the cylinder is half empty. This is also the moment when the measured temperature difference between the lower and the upper side reaches its maximum, which is maintained

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until the end of the measurement. An approximate possible explanation might be found by consulting the temperature measurements (Fig. 11). The temperature gradients along the cylinder and between the upper and the lower side change with decreasing pressure. At the very start there is almost no gradient visible, neither along the cylinder nor between the upper and the lower side. Between the start and 75 % of the initial pressure, the temperature measurements indicate a cooling at the cylinder's shoulder and at the lower side. The cooling of the shoulder is most probably induced by heat conduction from the cylinder through the cylinder valve to the even cooler regulator. When the cylinder is half empty, the whole temperature distribution starts to shift. The temperature gradient along the upper side seems to mirror the temperature gradient along the lower side with the difference in the middle of the cylinder body being highest. Until now, the cooler air was always close to the valve, while the warmer air was at the upper bottom end of the cylinder. In the cooler air, CO_2 becomes enriched and is drained out first based on its proximity to the valve. Thereby the air remaining in the cylinder becomes slowly depleted in CO_2. Additionally, the warmer air at the upper bottom side might impair or even block off convection, enhancing the depletion. As the pressure drop in the regulator becomes gradually less the cooling at the valve end becomes weaker and it starts to warm up, slightly affecting the shoulder, too. With the pressure decreasing further and the air at the valve end being removed steadily, the warmer air from the upper bottom of the cylinder that is now depleted in CO_2 gradually becomes sample air. A second factor might be that the colder air has slightly lower viscosity. At the end of the ~~measurement~~run, the most depleted air from the farthest end of the cylinder is moved to the valve by expansion and causes the lower most CO_2 measurements. This observation will need to be explained by a model of the expansion and outflow, combined with circulation, heat conduction, and diffusive mixing in the cylinder.

When the cylinders are moved during the measurements, it becomes obvious that the air in the cylinder is separated into different air masses of different temperatures. If a cylinder's orientation is changed from a vertical to a horizontal position, the temperature gradient initially remains the same along the cylinder body. A temperature difference between the now lower and upper cylinder wall starts to build up. The conservation of the gradient's vertical orientation proves that the jump in the CO_2 mole fraction that occurs when a cylinders orientation is changed is in accordance with the aforementioned thermal diffusion fractionation, where CO_2 gets enriched in cool air that accumulates at the bottom of the cylinder.~~If it is laid down from vertical, the vanishing gradient along the cylinder and the emerging temperature difference between the now lower and upper side are proof of that the jump in the CO_2 mole fraction when a cylinder is laid down is in accordance with the aforementioned thermal diffusion fractionation that CO_2 gets enriched in cool air that accumulates at the bottom of the cylinder.~~ By laying it down, the cool CO_2 enriched air flows along the cylinder to the valve and is drained, while the CO_2 depleted warmer air goes to the upper side of the cylinder. The cool air gets warmed by the cylinder wall and a weak convection is started that mixes the lower layers of air in the cylinder. With further decreasing pressure and gas expansion, the depleted air from the upper side gets mixed into the drained air, thereby causing the CO_2 decrease measured by the system. In the opposite case in which the cylinder is horizontal first and then put up into a vertical position, the cool air sinks to the bottom and the warm depleted air goes up to the top where it gets drained first. That causes the initial CO_2 drop after the repositioning. The cooler CO_2 enriched air at the bottom gets again warmed by the cylinder walls, inducing a weak convection. Due to the convection and the gas expansion caused by the decreasing pressure, CO_2 enriched air gets increasingly mixed into the drained air causing the measured increase of the CO_2 mole fraction.

With the three cylinders that were moved upside down, the picture is not very clear. ~~Because of a logger failure, there are no temperature measurements on the first cylinder, which is why it will not be discussed here. The second and the third cylinders put upside down show a drop in the CO_2 mole fraction after they have been moved. While the second cylinder remains stable at the slightly lower CO_2 mole fraction, the CO_2 mole fraction of the last cylinder goes up first by about 0.07µmol mol^{-1} from 30 to 15 bar and falls back by roughly the same amount until the end of the experiment. The temperature measurements of the two cylinders look the same. The only small difference between the two is the pressure when they were turned, the second cylinder was turned at 32.2 bar, the third cylinder was turned at 27.8 bar. However, whether this caused the different behavior in the CO_2 measurements remains unclear.~~

~~T~~Also the results from the experiments with constant heating from a pressure of 30 bar to 1 bar do not~~n't~~ draw a distinct picture. While the first cylinder does not~~n't~~ seem to be affected by the heating, the second shows a drop in the CO_2 mole fraction and remains stable until the end of the experiment. Since the temperature gradient between the bottom and the valve end is quite large while heating, the CO_2 drop could be caused by mixing of the air masses due to convection induced by the heating. But why only one cylinder shows that feature, while the other has a stable CO_2 mole fraction throughout the whole experiment remains unclear. Burst heating has only a short-term effect. Since the heat burst is not able to penetrate deep into the air in the cylinder it affects only the outermost layers. The temperature measurements show that the cylinder becomes warmer at the bottom than at the valve end, probably due to the ninth heat band at the bottom and the slight cooling of the regulator at the valve end. This might cause the outermost CO_2 enriched layers from the bottom to rise and generate the measured CO_2 peak when it reaches the valve. The effect is transient, finishing before the heating is finished. Shortly after the heating is stopped, the inversed temperature gradient returns to its usual distribution, supporting the assumption that the heat burst did not~~n't~~ penetrate deeply into the cylinder gas. This is also backed by the measurements of the CO_2 mole fraction that besides the short spike show a similar CO_2 increase as with vertically positioned cylinder in high flow mode.

5. Conclusion

Six 29.5 L Luxfer L6X® as well as two 29.5 L Luxfer L6X® SGS aluminum cylinders were used to investigate the stability of the CO_2 mole fraction of ambient level CO_2-in-air mixtures with decreasing pressure. In low flow settings (0.3 L min^{-1}), the Langmuir adsorption/desorption model using averaged coefficients is sufficient to describe the CO_2 enrichment. With this function, the CO_2 enrichment over a pressure range of 150 to 1 bar was calculated to be 0.090 ± 0.009 µmol mol^{-1}, where the given error corresponds to the standard deviation (1-sigma) of the fitted CO_2 enrichment of the individual cylinder drainings. The tested aluminum cylinders behaved always the same within uncertainties, the individual cylinders did not show distinct unique features. This is also true for the SGS cylinders, indicating no benefit in using these tanks for CO_2 measurements at ambient level. This opens the possibility to use a general correction function in case a calibration cylinder on a field station runs empty. However, we still recommend changing calibration cylinders before the pressure drops below 30 bar in order to avoid the steepest part of the enrichment at the lowest pressures, and the corrections that add uncertainty to the measurements. At the same time

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the currently recommended threshold of 20 bar (WMO, 2016) is supported by measurements of this study. Using the low flow coefficients for the Langmuir model, a drop from 150 to 30 bar results in a CO_2 enrichment of about 0.026 µmol mol^{-1}, whereas a drop from 150 to 20 bar yields a CO_2 enrichment of 0.34 µmol mol^{-1}, which is still well within the WMO compatibility goal between laboratories. By using bigger cylinders (e.g. 50 L) the surface to volume ratio becomes smaller compared to the 29.5 L cylinders used in this study, which might be beneficial in minimizing the CO_2 enrichment effect at lower pressures. We discourage the use of smaller cylinders as their surface-to-volume ratio increases. Approximating the top and bottom area of a cylinder as a disk perpendicular to the cylinder length (l), and assuming that the effective adsorption area remains the same where the cylinder diameter (r) has been compressed, the surface to volume scales as $(2\pi rl + 2\pi r^2)/(\pi r^2 l) = (l+r)/rl$. We expect a commonly used Luxfer N060 (internal volume 10.7 L) to be worse by ~30%.

In high flow settings (5.0 L min^{-1}), additional thermal diffusion effects and Rayleigh fractionation come into play that add to, or can overrule the simultaneously ongoing Langmuir adsorption/desorption. Depending on the positioning of the cylinder, CO_2 can be increasing or decreasing with decreasing pressure. We have demonstrated that these effects very likely do play a role, but before a satisfactory explanation can be attempted a considerable number of additional controlled experiments, as well as modeling of the flow and mixing in cylinders will be necessary. A further benefit could be gained by using a CRDS (cavity ring down spectroscopy) gas analyzer because it does not need to be calibrated as often as an NDIR analyzer and it could measure several gas species, such as CH_4 or CO, simultaneously. ~~The tested aluminum cylinders behaved always the same within uncertainties, the individual cylinders didn't show distinct unique features. This is also true for the SGS cylinders, indicating no benefit in using these tanks in CO₂ measurements at ambient level. To describe the CO₂ enrichment in low flow settings, the Langmuir adsorption/desorption model using averaged coefficients is sufficient to describe the CO₂ enrichment effects in aluminum cylinders. This opens the possibility to use a general correction function in case a calibration cylinder on a field station runs empty. However, we still recommend changing calibration cylinders before the pressure drops below 30 bar in order to avoid the steepest part of the enrichment at the lowest pressures, and the corrections that add uncertainty to the measurements. At the same time the currently recommended threshold of 20 bar (WMO, 2014) is supported by measurements of this study. Using the low flow coefficients for the Langmuir model, a drop from 150 to 20 bar results in a CO₂ enrichment of about 0.036 µmol mol-1, which is still well within the WMO compatibility goal between laboratories.~~

~~In high flow settings additional thermal diffusion effects and Rayleigh fractionation come into play that overrule the simultaneously ongoing Langmuir adsorption/desorption. Depending on the positioning of the cylinder, CO₂ can be increasing or decreasing with decreasing pressure. However, this might be only the case for systems with a steady high flow. If cylinders are decanted in quick bursts with enough time in between to allow them to equilibrate thermally, thermal fractionation shouldn't be able to develop and only Langmuir adsorption/desorption effects have to be taken into account. Some of the observed effects remain unexplained because the measurements were inconsistent, or the behavior of air in the cylinder needs to be modelled explicitly. To answer these questions additional controlled experiments would be necessary. A further benefit could be gained by using a CRDS (cavity ring down spectroscopy)~~

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~~gas analyzer because it doesn’t need to be calibrated as often as an NDIR analyzer and it could measure several gas species simultaneously.~~

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

Data availability: https://doi.org/10.15138/G3263N

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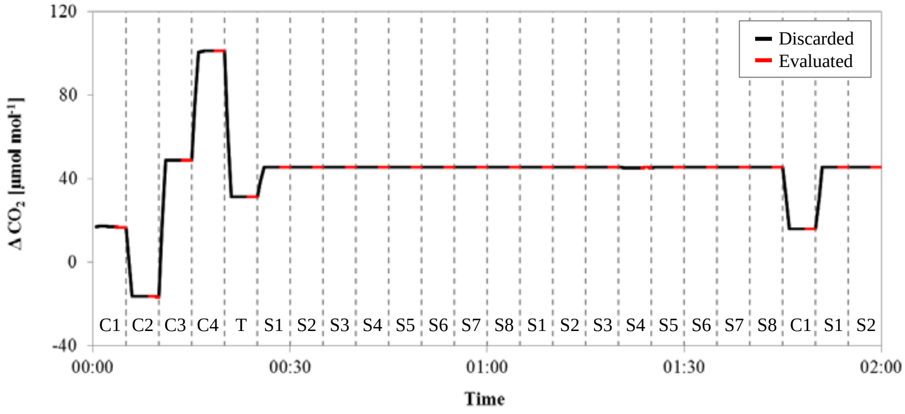
Table 1 List of the cylinders used in this study and numbers and types of experiments done with each of them.

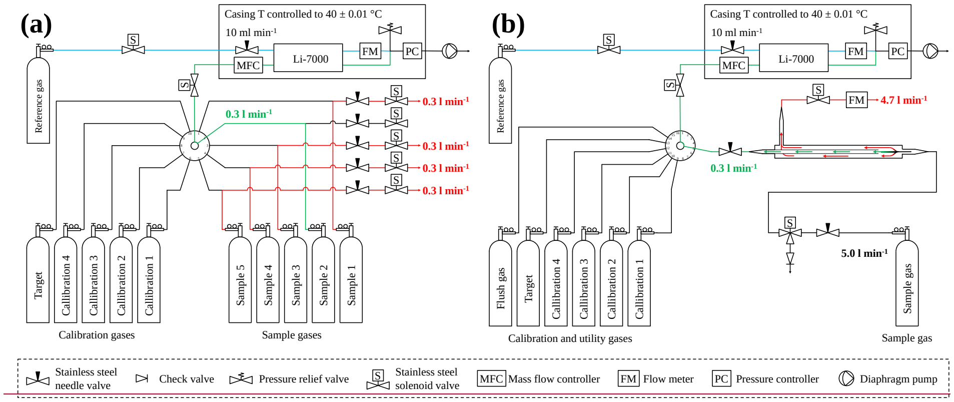
		Cylinder Nr.									
		CB11795	**CB11873**	**CB11876[1]**	**CB11906**	**CB11941**	**CB11976**	**CB12009**	**CC505453[2]**	**CC505457[2]**	**Total Nr. of measurements per setup**
Low flow	**vertical**	**5**	**5**	**1**	**5**	**4**	**5**	**5**	**4**	**4**	**38**
	horizontal	**1**								**1**	**2**
High flow	**vertical**	**1**	**1**		**1**	**1**	**1**	**1**	**1**	**1**	**8**
	horizontal		**1**					**1**	**1**		**3**
	Vertical to horizontal		**1**								**1**
	Horizontal to vertical						**1**				**1**
	Horizontal to vertical upside down					**1**	**1**		**1**		**3**
	Horizontal with heating				**1**	**1**					**2**
	Vertical with burst heating							**1**		**1**	**2**
	Total Nr. of measurements per cylinder	**7**	**8**	**1**	**7**	**7**	**8**	**8**	**7**	**7**	**60**

[1] *Because of a scratched cylinder valve the cylinder was replaced after the first measurement*

[2] *SGS (Superior Gas Stability) cylinders*



~~**Figure 1: Example of a calibration sequence from a low flow measurement. The x-axis represents time, the y-axis the delta signal of the NDIR analyzer. The gas measured is indicated by the codes at the top of the figure (C = Calibration, T = Target, S = sample), the switching of the valve is marked by the dashed vertical lines. Each gas was measured for 5 minutes, to avoid mixing and memory effects, the first 3 minutes were discarded (black lines) and only the last 2 minutes (red lines) were used for further evaluation.**~~



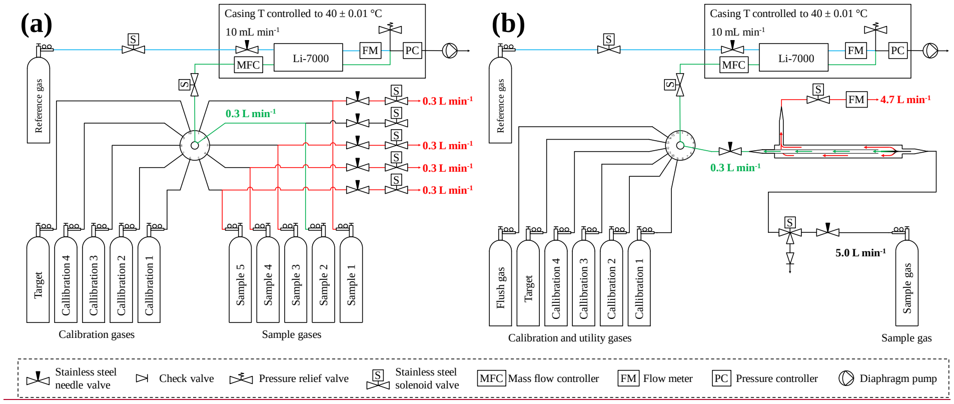
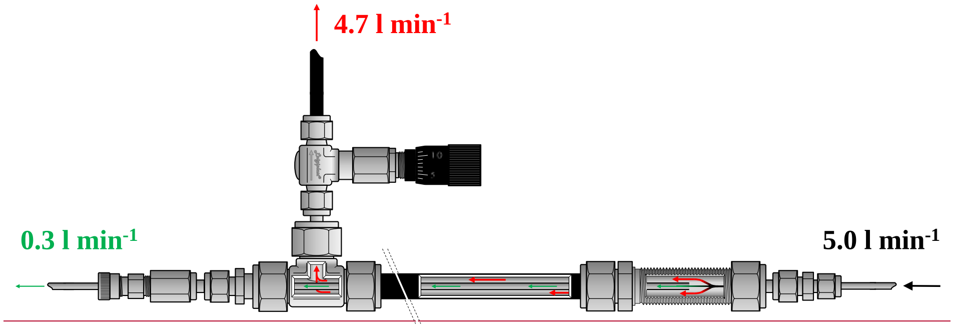


Figure 1: Schematic of the low flow measurements system setup, here with the 10-port vici valve (a) and the high flow measurement system setup with the 16-port VICI valve (b). The red lines and numbers indicate the gas that is drained to the room to maintain a steady flow out of the cylinder, the green lines and numbers are what goes into the analyzer, the blue lines are the reference gas flow.



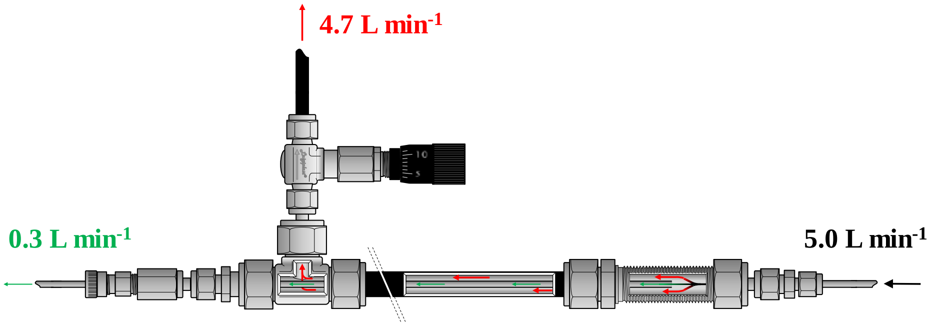


Figure 2: Flow schematic of the high flow inlet system. The sample gas enters on the right ~~left~~ side at 5.0 ~~l~~ L min^{-1}. A small aliquot of 0.3 ~~l~~ L min^{-1} goes to the analyzer, the ~~vast~~ remainder of 4.7 ~~l~~ L min^{-1} goes to the exhaust. The ratio between the gas going to the analyzer and the exhaust, respectively, is set by the dimensions of the inner and outer tube and can be ~~set by~~ adjust~~eding~~ by the needle valve on the exhaust side.

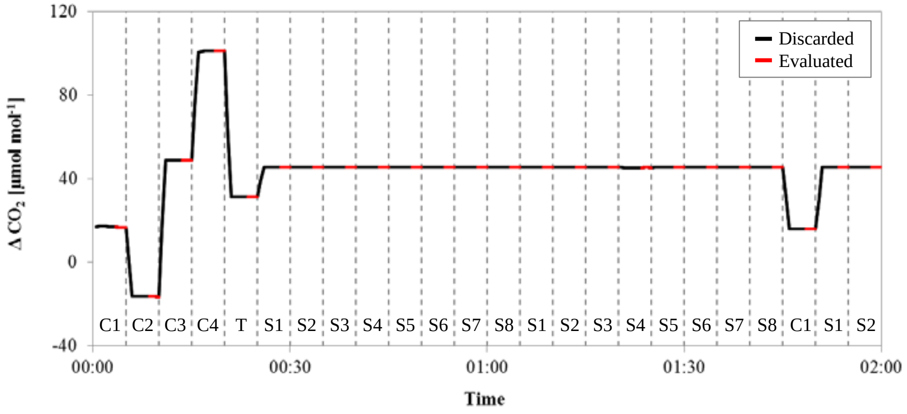


Figure 3: Example of a calibration sequence from a low flow measurement. The x-axis represents time, the y-axis the delta signal of the NDIR analyzer. The gas measured is indicated by the codes at the top of the figure (C = Calibration, T = Target, S = sample), the switching of the valve is marked by the dashed vertical lines. Each gas was measured for 5 minutes, to avoid mixing and memory effects, the first 3 minutes were discarded (black lines) and only the last 2 minutes (red lines) were used for further evaluation.

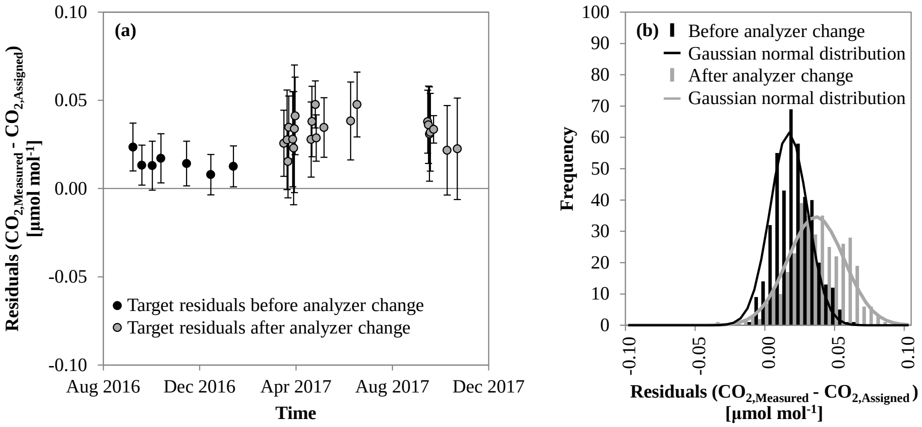


Figure 4: Panel (a): Average of the difference of the target gas measurement minus the assigned CO_2 mole fraction for each run against time, black indicates the measurements before the analyzer change, grey after the analyzer change in March 2017. The error bars correspond to the standard deviation of the individual target gas measurements within each run. Panel (b): Histogram of the residuals of the target gas measurements, again, black stands for the measurements before, grey after the analyzer change.

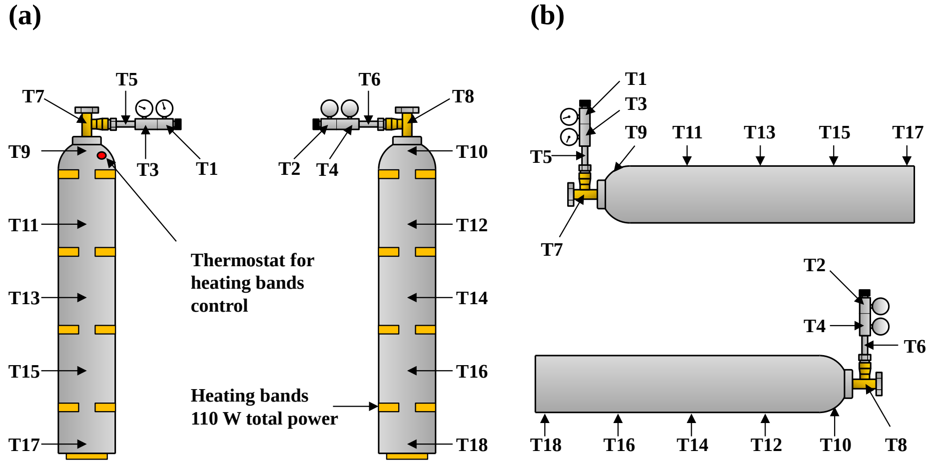
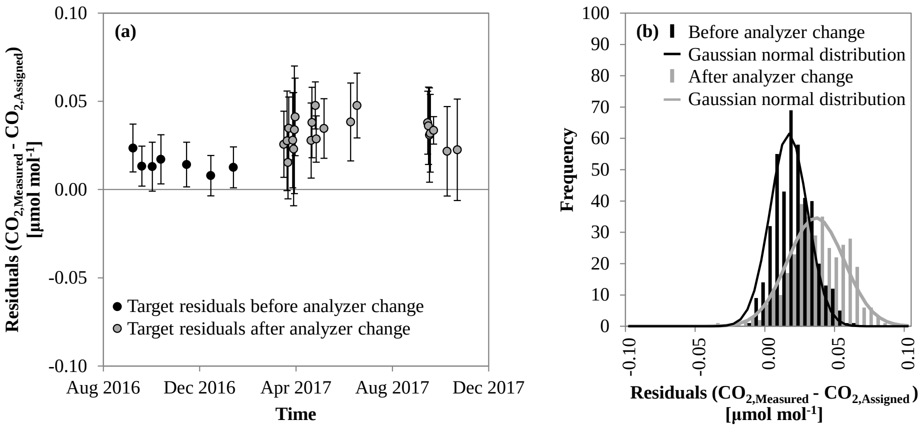
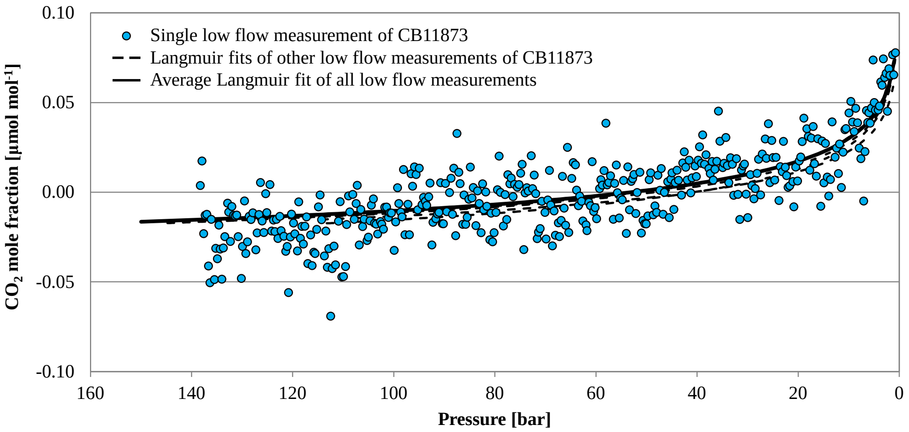


Figure 5: Schematic of the locations of the thermistors on the cylinder in vertical (a) and horizontal positon (b) as well as the heating bands if used. Thermistors 19 to 25 were bundled and used to measure the background temperature of the laboratory.



~~**Figure 5: Panel (a): Average of the difference of the target gas measurement minus the assigned CO_2 mole fraction for each run against time, black indicates the measurements before the analyzer change, grey after the analyzer change in March 2017. The error bars correspond to the standard deviation of the individual target gas measurements within each run. Panel (b): Histogram of the residuals of the target gas measurements, again, black stands for the measurements before, grey after the analyzer change.**~~



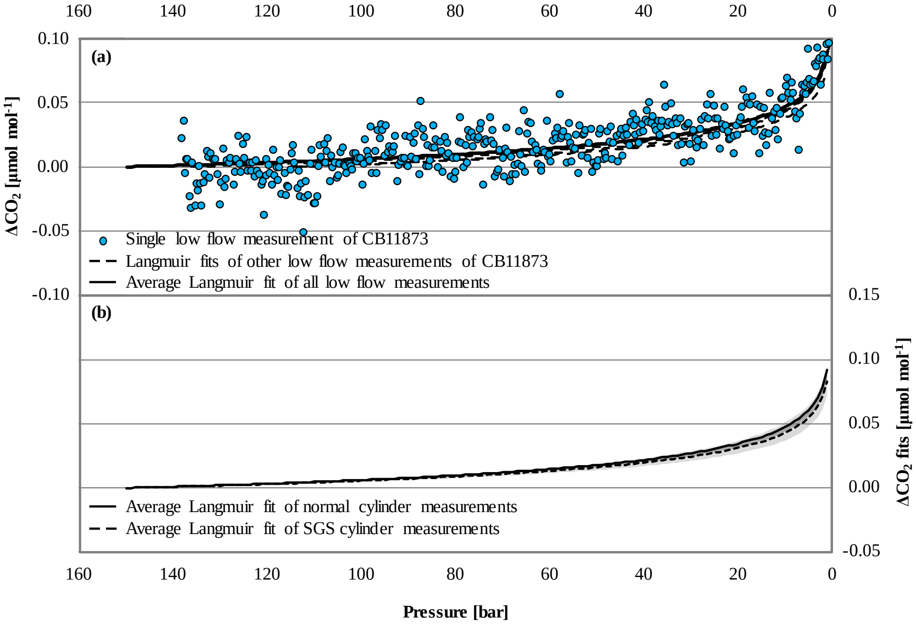


Figure 6: a) The blue circles represent the CO$_2$ mole fraction measurement of a low flow experiment started on 17.10.2016 with CB11873 vertically positioned as a function of pressure, note the inverse pressure scale. The black dashed lines are the individual fits following the Langmuir model of the other low flow experiments done with CB11873 vertically positioned, the black solid line represents the average Langmuir fit using all low flow experiments with the cylinders vertically positioned. b) The black solid and dashed line correspond to the average Langmuir fit of all normal and SGS cylinder measurement, respectively, that were done under low flow conditions, the greyed area corresponds to the standard deviation

of the averages. In order to plot all data in one plot, the corresponding $(X_{CO2,ini} - X_{CO2,ad})$ was subtracted from the measurements and the fits in both panels.

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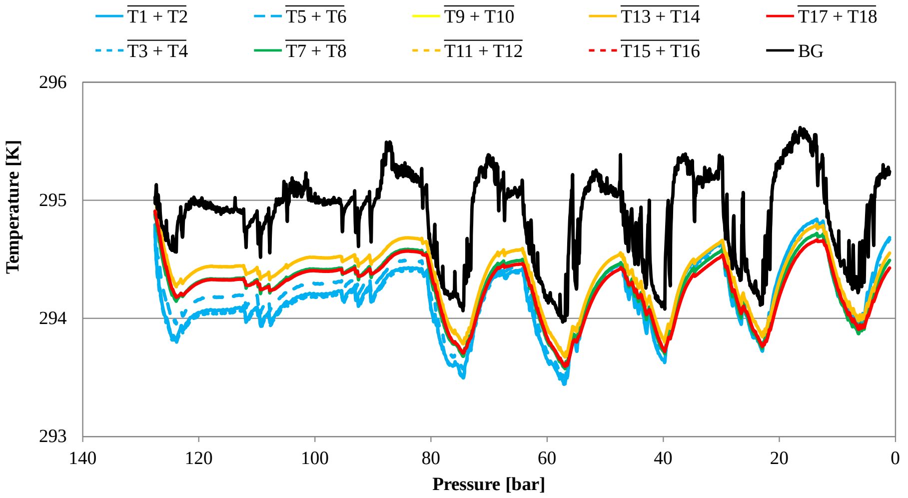

Figure 7: Temperature development of CB11795 during the low flow measurement with ~~vertically~~ horitontally positioned cylinders as a function of pressure, note the inverse pressure scale. The lines represent averages of the following thermistors: Pressure regulator to stem: Solid blue: T1 and T2; dotted blue: T3 and T4; dashed blue: T5 and T6; Cylinder valve: green: T7 and T8; Cylinder body: yellow: T9 and T10; dashed orange: T11 and T12; solid orange: T13 and T14; dashed red: T15 and T16; solid red: T17 and T18; laboratory background: black: T19 to T25.

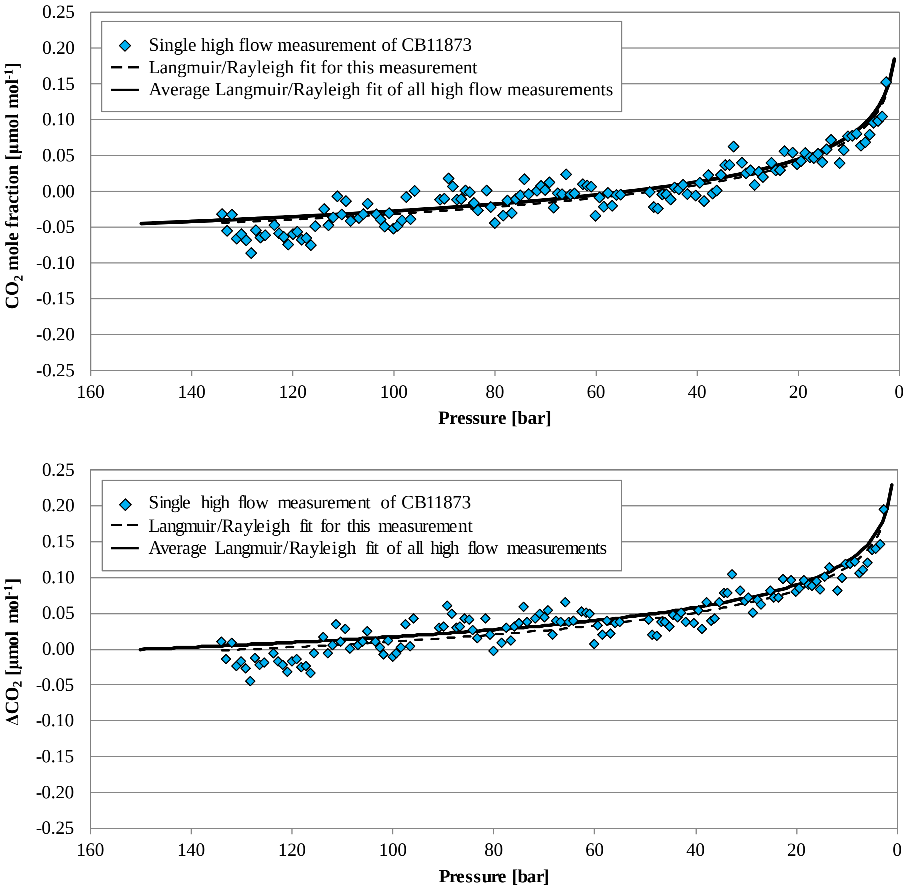

Figure 8: The blue diamonds represent the CO_2 mole fraction measurement of the high flow experiment done on 5.4.2017 with CB11873 vertically positioned as a function of pressure, note the inverse pressure scale. The black dashed line is a fit following the combined Langmuir adsorption/desorption and Rayleigh distillation model, the black solid line represents the average of the combined Langmuir and Rayleigh fit using all high flow experiments with vertically positioned cylinders. In order to plot all data in one plot, the corresponding ~~$CO_{2,ini}$~~$(X_{CO2,ini} - X_{CO2,ad})$ ~~-~~ was subtracted from the measurements and the fits.

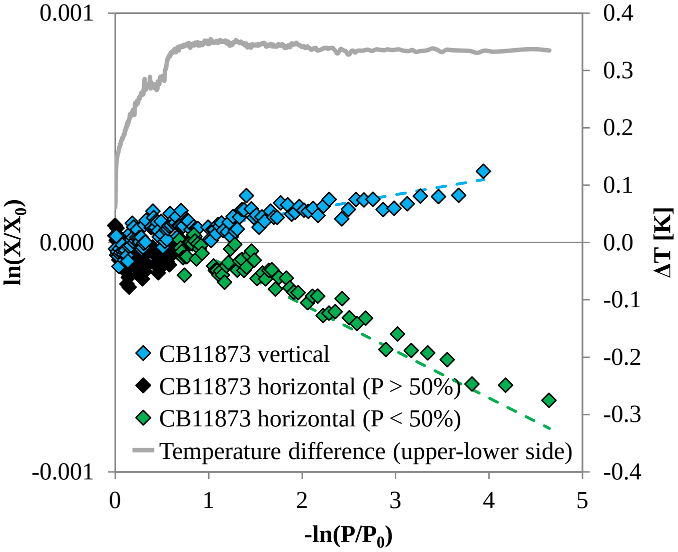

Figure 9: CO_2 measurements of high flow experiments with CB11873 corrected for Langmuir adsorption/desorption effects based on the low flow experiments, vertically positioned cylinder in blue and horizontally positioned cylinder in black for the first half and green for the second half of the run. The data is plotted such that fractionations caused by Rayleigh distillation would follow a line with slope 1-α with α being the fractionation factor. These lines are indicated by the dashed lines in corresponding colors that were calculated based on an averaged α from all available experiments. The grey line plotted on the secondary y-axis is the temperature difference between T15 and T16 corresponding to the upper and the lower side of the horizontally positioned cylinder. It reaches its maximum after the cylinder is about half empty, which is when the fractionation seems to start.

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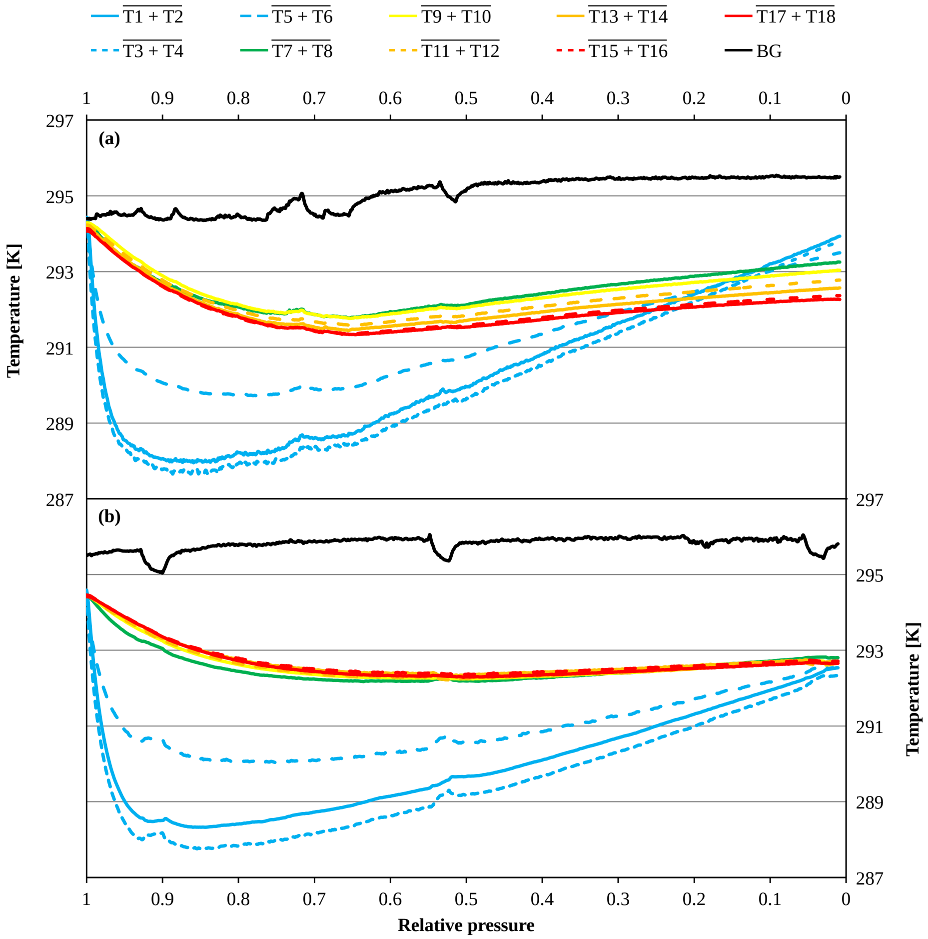

Figure 10: Temperature measurements against relative pressure, note the inverse x-axis. Because the initial pressures of the two cylinders were slightly different (CB11873 at 140.0 bar and CB12009 at 128.2 bar), the pressure is expressed as relative pressure (P/P_0) in order to use the same x-axes for both panels. The measurements in panel (a) come from a high flow experiment with vertically positioned cylinder (CB11873 on 4.5.2017), the temperatures in panel (b) were measured during a high flow experiment with horizontally positioned cylinder (CB12009 on 8.5.2017). The lines represent averages of the following thermistors: Pressure regulator to stem: Solid blue: T1 and T2; dotted blue: T3 and T4; dashed blue: T5 and T6; Cylinder valve: green: T7 and T8; Cylinder body: yellow: T9 and T10; dashed orange: T11 and T12; solid orange: T13 and T14; dashed red: T15 and T16; solid red: T17 and T18; laboratory background: black: T19 to T25.

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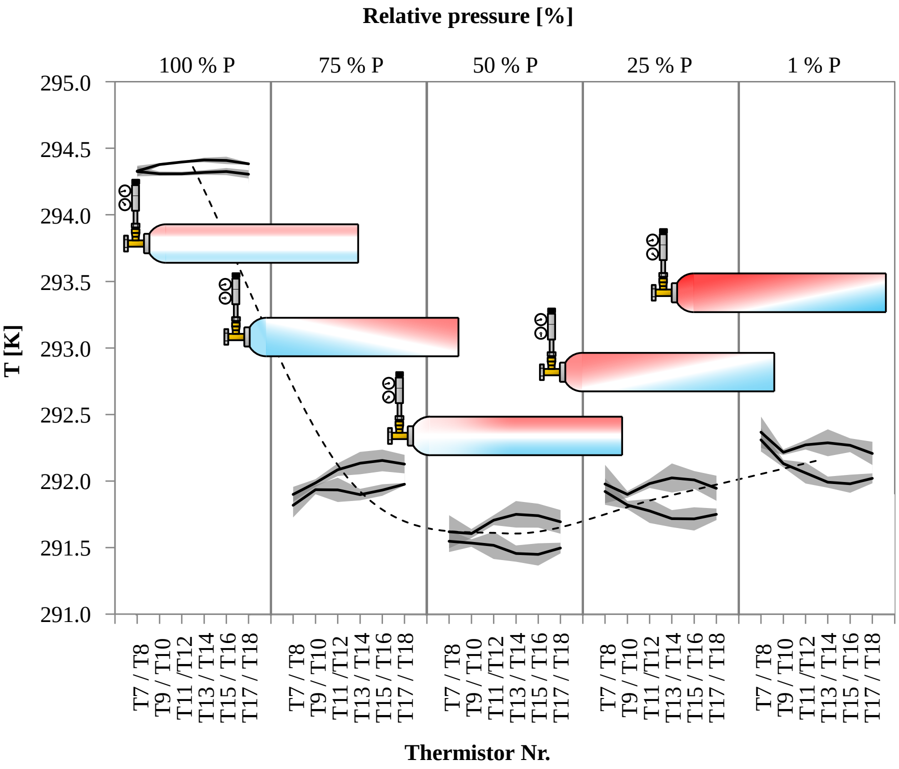


Figure 11: Temperature difference between the upper and the lower side of the cylinder (in horizontal position) at five different stages of decanting. The temperature is given on the y-axis, the black lines are the average temperature along the upper and lower side of the cylinder derived from three runs, the shaded areas correspond to the standard deviation. The position of the temperature measurement along the cylinder is given for each stage individually on the x-axis in form of the thermistor number (see Fig. 54), the relative pressure is given as bins on the secondary x-axis. The black dashed line serves as an indicator for the general temperature development of the cylinder, it corresponds to the average of T11 to T14. The red and blue colors in the cylinders represent a possible distribution of warm (red) and cool (blue) air within the cylinder derived from the temperature measurements on the outside of the cylinder.

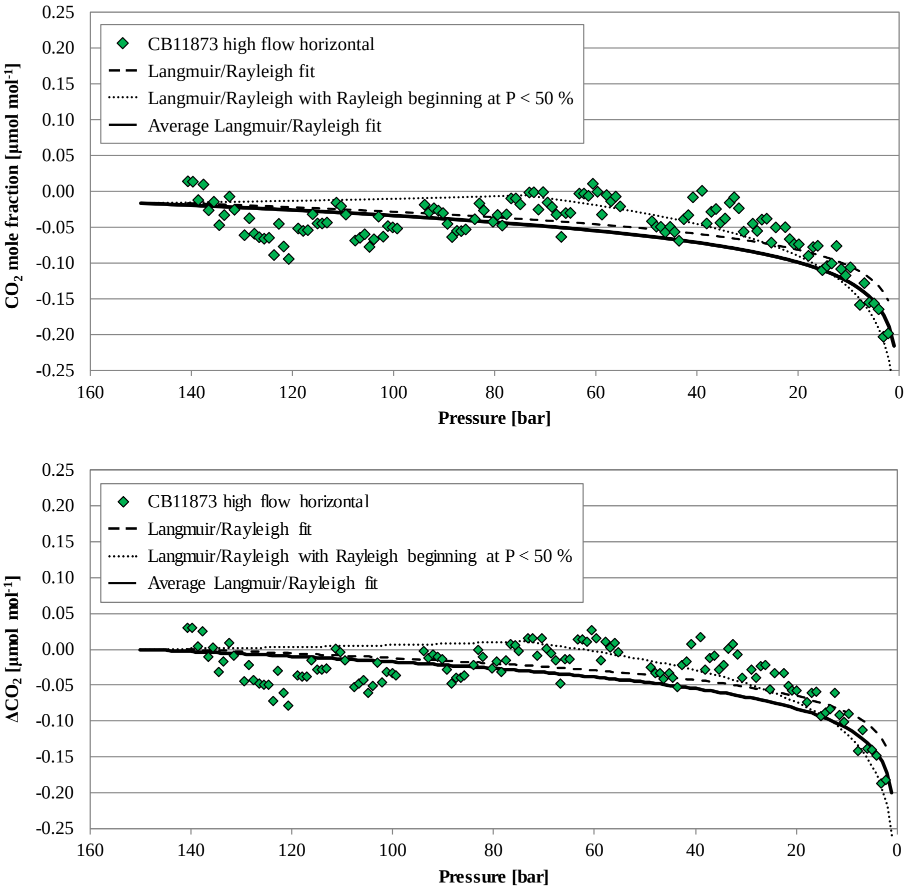


Figure 12: The green diamonds represent the CO_2 mole fraction measurement of the high flow experiment done on 4.5.2017 with CB11873 horizontally positioned as a function of pressure, note the inverse pressure scale. The black dashed line is a fit following the combined Langmuir adsorption/desorption and Rayleigh distillation model, the black dotted line is a fit following the combined Langmuir adsorption/desorption and Rayleigh distillation model with the Rayleigh distillation starting when the cylinder is half empty, the black solid line represents the average of the combined Langmuir and Rayleigh fit using all high flow experiments with horizontally positioned cylinders. In order to plot all data in one plot, the corresponding ~~$CO_{2,ini}$~~ ($X_{CO2,ini} - X_{CO2,ad}$) was subtracted from the measurements and the fits.

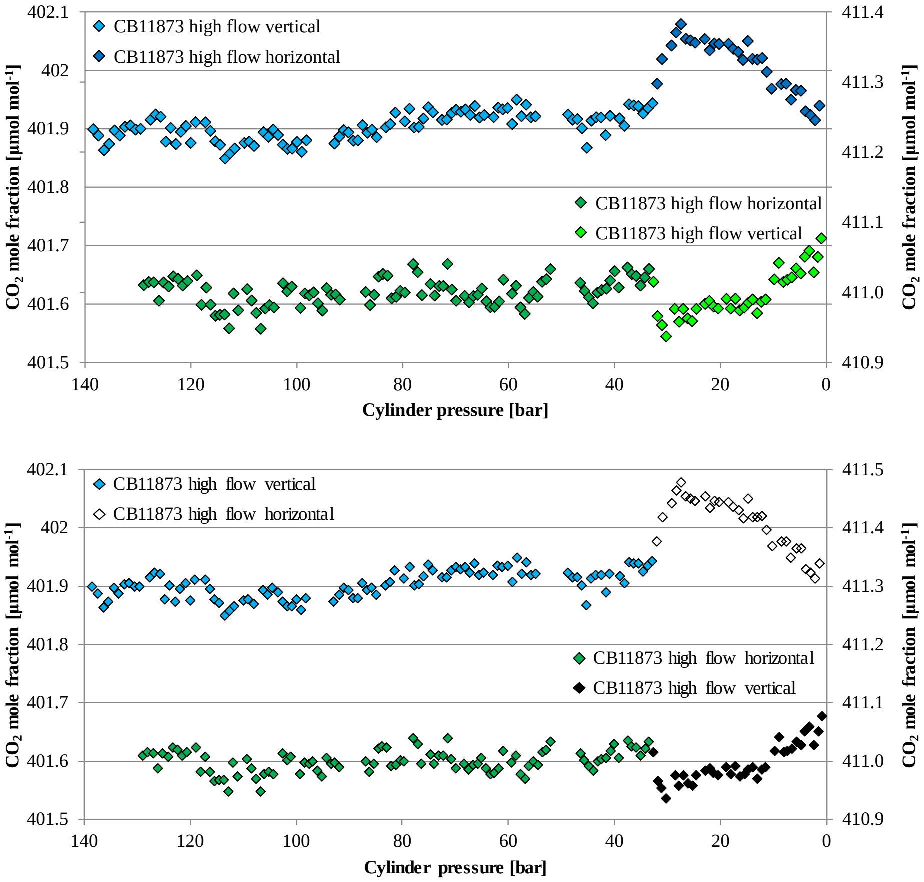
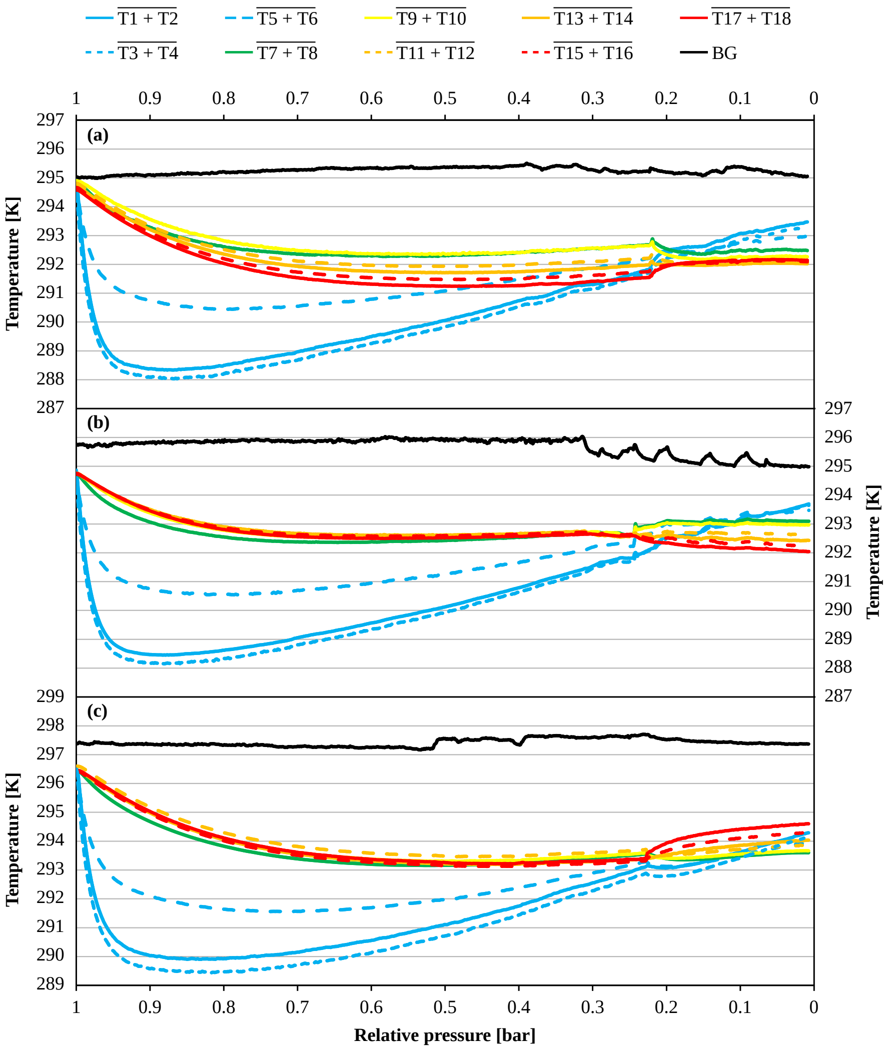


Figure 13: CO_2 mole fraction as a function of pressure, note the inverse x-axis. The blue and empty diamonds belong to the primary y-axis and were measured on CB11873 during a high flow experiment, where the cylinder was first vertically positioned and then laid down at 32.1 bar (indicated by the ~~darker blue~~empty diamonds). The green and black diamonds belong to the secondary y-axis and were measured on CB11976 during a high flow experiment, where the cylinder was first horizontally positioned and then put up at 32.7 bar (indicated by the ~~brighter green~~ black diamonds).


T1 + T2
T5 + T6
T9 + T10
T13 + T14
T17 + T18
T3 + T4
T7 + T8
T11 + T12
T15 + T16
BG
(a)
(b)
(c)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
297
296
295
294
293
292
291
290
289
288
287
299
298
Temperature [K]
Relative pressure [bar]

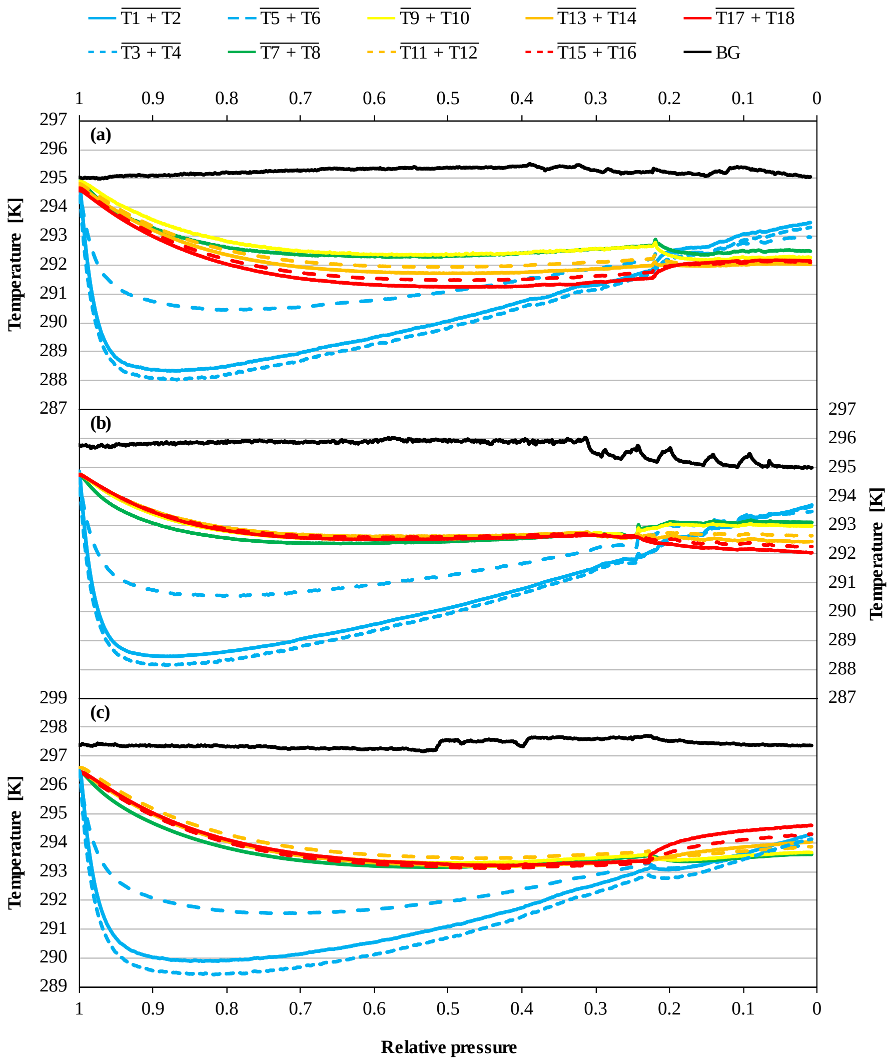


Figure 14: Temperature measurements against relative pressure, note the inverse x-axis. Because the initial pressures of the cylinders were slightly different (CB11873 in panel (a) at 138.4 bar, CB11976 in panel (b) at 128.9 bar and CB11976 in panel (c) at 133.9 bar, respectively), the pressure is expressed as relative pressure (P/P_0) in order to use the same x-axes for all three panels. Panel (a) shows the temperature measurements of a high flow experiment where a vertically positioned cylinder was laid down (CB11873 at 32.1 bar), panel (b) shows a high flow experiment, where a horizontally positioned cylinder was put up (CB11976 at 32.7 bar) and panel (c) shows the temperature of a cylinder that was horizontally positioned and then put upside down (CB11976 at 32.2 bar). The lines represent averages of the following thermistors: Pressure regulator to stem: Solid blue: T1 and T2; dotted blue: T3 and T4; dashed blue: T5 and T6; Cylinder valve: green:

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T7 and T8; Cylinder body: yellow: T9 and T10; dashed orange: T11 and T12; solid orange: T13 and T14; dashed red: T15 and T16; solid red: T17 and T18; laboratory background: black: T19 to T25.

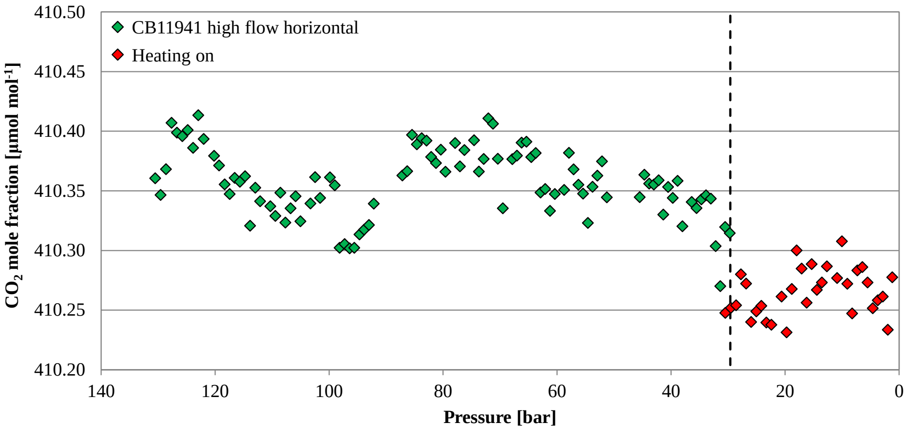
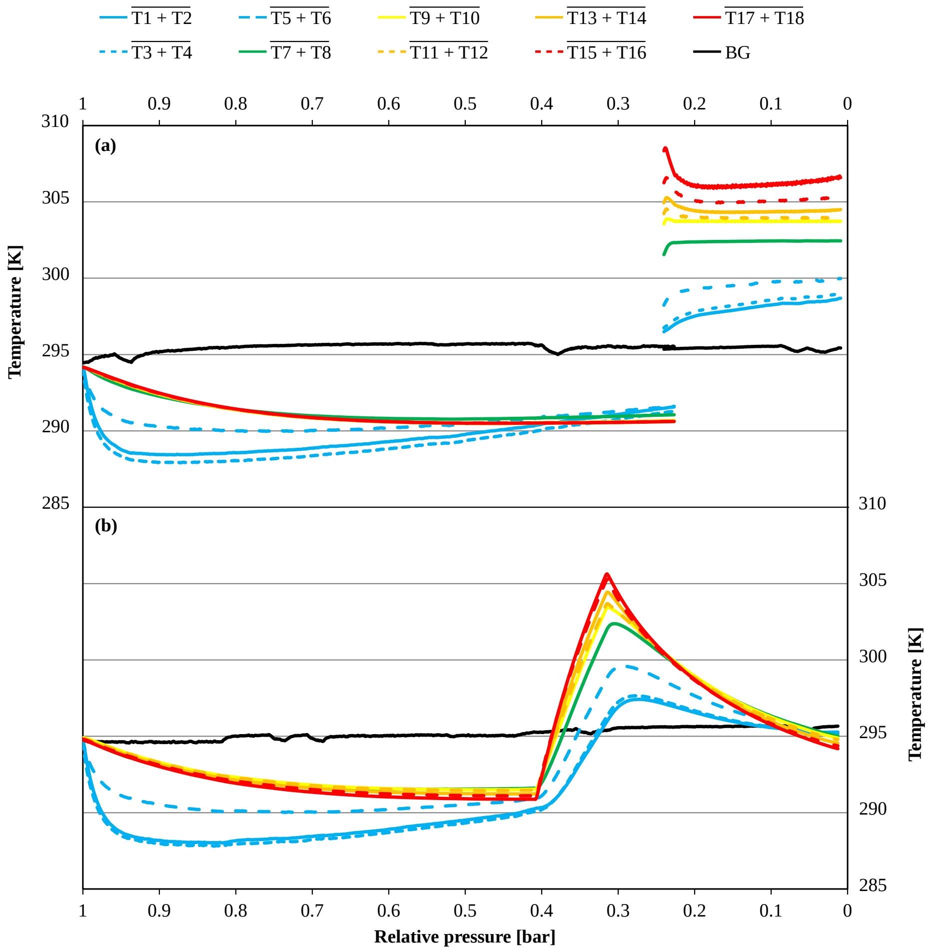


Figure 15: CO_2 mole fraction of a high flow experiment as a function of pressure, note the inverse x-axis. The cylinder (CB11941 on 22.6.2017) was horizontally positioned throughout the whole experiment. The CO_2 mole fraction was measured down to 30 bar (green diamonds). At 30 bar (indicated by the dashed line), the flow was interrupted and the cylinder was heated up to 30°C, after the set temperature was reached, the CO_2 measurement continued (red diamonds). The heating caused a small pressure increase, which is why the first two points of the resumed measurements appear slightly above the pressure threshold of 30 bar ~~threshold~~.


$\overline{T1 + T2}$
$\overline{T5 + T6}$
$\overline{T9 + T10}$
$\overline{T13 + T14}$
$\overline{T17 + T18}$
$\overline{T3 + T4}$
$\overline{T7 + T8}$
$\overline{T11 + T12}$
$\overline{T15 + T16}$
BG
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
310
305
300
295
290
285
(a)
Temperature [K]
(b)
310
305
300
295
290
285
Temperature [K]
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Relative pressure [bar]

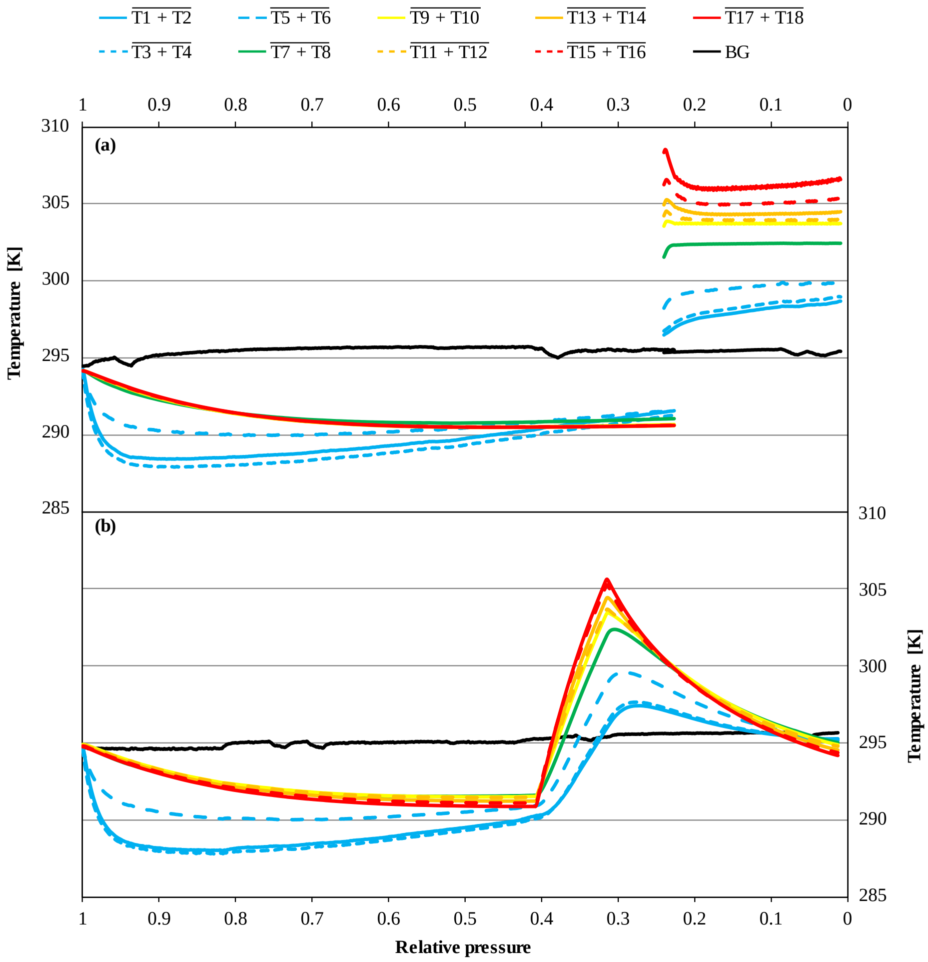


Figure 16: Temperature measurements against relative pressure, note the inverse x-axis. Because the initial pressures of the cylinders were slightly different (CB11941 at 130.5 bar and CB12009 at 124.0 bar, respectively), the pressure is expressed as relative pressure (P/P_0) in order to use the same x-axes for both panels. Panel (a) shows the temperature measurements of a high flow experiment where a ~~vertically~~ horizontally positioned cylinder (CB11941 on 21.6.2017) was measured until it reached 30 bar. At 30 bar, the flow was stopped and the heating turned on. After the thermostat read 30°C, the flow was switched back on and the measurement continued with the heating keeping it at a steady temperature until the end. The heating created a small pressure increase which is responsible for the small overlap in the x-axis, clearly visible in the background temperature. Panel (b) shows a high flow experiment, where a vertically positioned cylinder (CB12009 on 26.9.2017) got a burst of heat at 50 bar. The heating was maintained until the thermostat read 30°. After reaching the threshold, the heating was switched off (at 40.8 bar). During the burst heating, the CO_2 measurements continued. The lines represent averages of the following thermistors: Pressure regulator to stem: Solid blue: T1 and T2; dotted blue: T3 and T4; dashed blue: T5 and T6; Cylinder valve: green: T7 and T8; Cylinder body: yellow: T9 and T10; dashed orange: T11 and T12; solid orange: T13 and T14; dashed red: T15 and T16; solid red: T17 and T18; laboratory background: black: T19 to T25.

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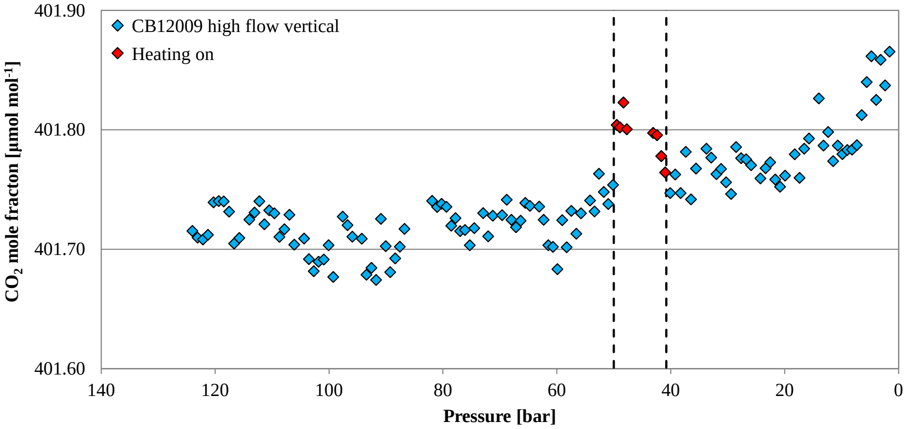

Figure 17: CO$_2$ mole fraction of a high flow experiment as a function of pressure, note the inverse x-axis. The cylinder (CB12009 on 26.9.2017) was vertically positioned throughout the whole experiment. The CO$_2$ mole fraction was measured down to 50 bar (blue diamonds). At 50 bar (indicated by the first dashed line), the heating was switched on but the CO$_2$ measurements continued during the heating phase (red diamonds). After the heating's thermostat indicated that the cylinder reached 30°C the heating was switched off (indicated by the second dashed line) and the CO$_2$ mole fraction was measured until the end (again blue diamonds).