

Reply to the review of Anonymous Referee #1

The authors would like to thank Anonymous Referee for the valuable comments. In the following, referee's comments are given in bold and author's responses in plain text. Suggested new text is quoted in italics together with page and line numbers.

This paper described the testing of various materials in an aluminum chamber designed such that various materials can be inserted in the chamber and tested for adsorption effects. This paper is a follow-on from a previous paper that described the testing chamber and analytical challenges (10.5194/amt-2019-197). The paper is well-written and contains informative figures. For many of the materials tested, desorption of CO₂, CH₄, and CO were minimal, which is good news for the measurement community. However, it is not exactly clear how the results of these experiments relate to atmospheric trace gas analysis due to significant differences between this work and how compressed gas standards are used in practice.

We understand the concern of our reviewer. The idea behind the setup and the material experiments is the following: compared to a standard cylinder (e.g. 29.5 L or 50 L) the surface to volume ratio of the small cylinders is bigger, and one can further increase the surface area by inserting materials. By testing materials at various pressure and temperature ranges, problematic materials can be identified. The following assumption lies behind these experiments: if the material has adsorbed significant amount of gas while filling the cylinder, this should be desorbed towards the end of the experiments controlled by desorption. The controlled experiments and the numerous materials tested in this study showed even under increased surface areas and lower than normally employed pressure ranges, surface effects for most materials were minimal, meaning that currently used materials are well-suited for their applications in atmospheric measurement community.

The following paragraphs will be added in discussion:

“The presented setup enabled the investigation of surface effects under “extreme” conditions which favored adsorption/desorption. Compared to common usage in the atmospheric measurement and gas metrology communities, our study has differed in cylinder size, geometric surface to volume ratios, pressure and temperature ranges. Previous studies (Leuenberger et al. 2015, Brewer et al. 2018, Schibig et al. 2018) investigating surface effects in compressed gas cylinders have used (50 L, 10 L, or 29.5 L) cylinders. The geometric surface of the small (5 L) aluminum cylinder used in this study is 0.18 m², which results in a surface to volume ratio of 35.7 for the unloaded cylinder. Compared to 29.5 L Luxfer cylinders, the small cylinders are estimated to be more prone to adsorption by 40 %. Inserting material blocks into the aluminum cylinder further increased the surface area. Therefore, the setup allows to test materials under increased surface to volume ratios in which the surface effects should be stronger and dominant. However, despite our efforts of increasing the surface material effects were minor. In addition to the properties of the materials, pressure and temperature play a role on surface effects. The following assumption lies behind the pressure experiments: if the material has adsorbed a significant amount of gas while filling the cylinder, this should be desorbed towards the end of the experiments controlled by desorption. The onset of the desorption for all tested materials except Dursan and partly DLC was observed well-below atmospheric pressures. Increasing temperature is expected to facilitate desorption by providing the required energy to desorb the gas molecules from the surface and mix into gas phase. On the contrary, cooling the cylinder and its content favor adsorption and it is expected that this results in a decrease in the measured amount fraction.”

General comments: You mention that you did not subtract the background, or blank (empty) run from the experiments. In figure 5, it would seem that the empty run shows much the same signals as the materials tested, which I suppose is why you state that only Dursan showed significant difference. I think this needs further explanation related to the other Satar et al 2019 paper (10.5194/amt-2019-197).

We thank our reviewer for pointing this out. In order to clarify this point, the following will be added on page 9, at line 10 and the corresponding paragraph will be rearranged:

“For CO₂ measurements, the amount fraction differences for all materials except Dursan were less than 0.17 μmol mol⁻¹, with slight differences among the various loadings. Of this difference, 0.05 μmol mol⁻¹ is related to the blank cylinder (background effect). The blank cylinder corresponded to the “14 bar after heating” case presented in Satar et al. (2019). More information on the blank cylinder and its filling history is provided in the above-mentioned publication. It is also crucial to consider that during all material block experiments, glass pieces were also present in the small measurement chamber. When the material runs were compared to the experiments with glass, except the DLC loading, the remaining differences were in the order of 0.02 μmol mol⁻¹, which corresponded to the 5 minute-standard deviation of the measured data. Moreover, during the evacuation of the measurement chamber with the DLC loading, a slightly increasing trend of -0.004 μmol mol⁻¹ bar⁻¹ was observed. For the steel loaded cylinder, the experiments where a multiport valve was upstream of the analyzer showed slightly more variation both for final amount fractions and during the pressure run. Whereas, the mass flow controller employed did not have a significant effect on the CO₂ measurements.”

On page 12, you mention that you measured the "blank" or background at the beginning at the end of the experiments, and the "blank" shown in figure 6 is the mean. How for this impact the conclusions? Do you know if the background changed smoothly over time, or abruptly as a results of adding Dursan or DLC?

Our concern about the repeated heating cycles on page 12 line 6, was the change of the background effect of the measurement chamber only due to heating. Inserting any of the materials should not have changed the background effect of the cylinder. During the experiments the blank cylinder has evolved to be better after re-use and refilling with the same gas. Therefore, we don't think that the inserted materials can result in irreversible effects.

For clarity the sentence on page 12 line 6 is modified to:

“This presumably resulted in a change of the background effect over the course of the presented analysis in the range of 0.04 μmol mol⁻¹.”

Further, I think you can better explain why you chose the maximum deviation (page 7, line 9), given that making measurements at sub-ambient pressure introduces complications, as described in the other Satar et al 2019 paper.

In our opinion, the maximum deviation is the most suitable parameter, since we are interested in the maximum possible effect which might occur related to the desorption process. Moreover, all data was processed using the same criterion cancelling out the effects originating from the analyzer and enable to focus on the differences between the materials.

The following will be added on page 7, line 9:

“Maximal difference was chosen to highlight the maximum possible effect related to desorption. Since all data was processed using the same criterion, the effects originating from the analyzer is cancelled out and we focus on the differences between the materials.”

How do these results compare with others studies (Leuenberger et al 2015; Schibig et al 2018) that suggest that a Langmuir isotherm can be used to model the physical adsorption? Your tests seem to show a much steeper increase at the lowest pressures. Is the abrupt increase at the lowest pressure related to desorption, or is it complicated by analysis at low pressure? I realize the analysis is discussed in the first Satar et al 2019 paper, but I think some important aspects need to be repeated here.

We understand the view of our reviewer that this point needs further explanation, we have already provided more information on this comparison in the revised version of the Satar et al 2019 paper and its supplementary material. However, it is crucial to note that the aluminum cylinder without loading presented in this study corresponds to the case “14 bar aluminum after heating” and showed a maximal deviation from the initial amount fraction as low as $0.05 \mu\text{mol mol}^{-1}$ making the modelling of this increase extremely difficult. For the material loadings, adsorbed amounts should be distributed between the blank cylinders and the material blocks. However as previously explained, subtracting the maximal amount fraction difference of the glass loaded cylinder from the material loaded cylinder resulted in amount fractions in the order of the standard deviation of the measured data. Therefore, for the majority of the materials fitting the Langmuir isotherm is not reasonable.

Since it not common to use a cylinder of gas down to less than 10% of the fill pressure, what would these results say about that practice?

These results highlight that the currently used materials are non-problematic at various temperature and pressure ranges, which is good news for the atmospheric measurements community and gas applications. The experiments were conducted under “extreme” conditions to understand possible surface effects to its full extent. Please see the explanation on the first paragraph of the replies.

I am also concerned about how to interpret the results with respect to materials used by the scientific community. The inside of an aluminum cylinder, for example, does not typically look like the outside. Presumably the process of manufacturing a cylinder (using a ram rod) alters the surface roughness of the inside, and may deposit trace elements on the internal surface. While you tested the same aluminum alloy used for cylinders, the tested materials might not be representative of actual cylinders. Have you tested pieces of material cut from aluminum or steel cylinders? Maybe it doesn't matter since the results don't show significant desorption, but this should at least be discussed.

We thank our reviewer for pointing this out. We have not tested materials cut from aluminum or steel cylinders. This can be done within the scope of another study. Regarding other tested materials, commercial coatings aiming to provide an inert surface undergo specific cleaning and chemical or physical vapor deposition of processes, which should be consistent regardless of the coated piece. Concerning copper and brass, these materials might be used in regulators or as seals, and not commonly used for cylinders. Unfortunately, one individual study with a new setup is not capable of answering of all questions about materials employed in the atmospheric measurement community. The study was a first step in understanding surface effects by increasing surface areas, for a significant number of materials under various pressure and temperature ranges with a sufficient number of replicates.

The following will be added into discussion:

“Testing pieces cut from the aluminum and steel cylinders commonly used in the community would be a valuable addition to enable direct comparison between the commonly used cylinder materials and the produced material blocks at low pressures and high temperatures. “

Specific Comments

P1, L5: suggest: “For this study we used small-volume chambers designed to be used for adsorption studies”. – text modified accordingly

P3, L30: suggest: “A mother cylinder was....” – text modified accordingly

Figure 4: Minor point: I’m not sure of the significance of the box plots based on only 3 data points. I guess you are assuming normal distributions and assigning quartiles based on the standard deviation.

We thank our reviewer for this comment. In the box plots R uses the “fivenum” function which is the descriptive statistics for minimum, 1st quartile, median, 3rd quartile and the maximum. In case of 3 data points, the 1st quartile is the mean of the minimum value and the median, whereas the 3rd quartile is the mean of the median and the maximum value. Therefore, the whiskers extend to the minimum and the maximum values, respectively. Since in Fig. 4 and Fig. 7, all data points are shown in addition to the box plots, using box plots for the figures is non-problematic.

On page 7, at line 10, we will add the following:

“The median is denoted by the horizontal line, whereas the mean is shown by the square. Since for most cases only 3 replicates are present, the 1st quartile is the mean of the minimum and the median, whereas the 3rd quartile is the mean of the median and the maximum value. For clarity, data points used for the box plots are also shown and they are denoted by the black points. “

We have also rearranged Fig.4 to better distinguish the mean (denoted by the squares) from the results of the replicates (denoted by the black points)

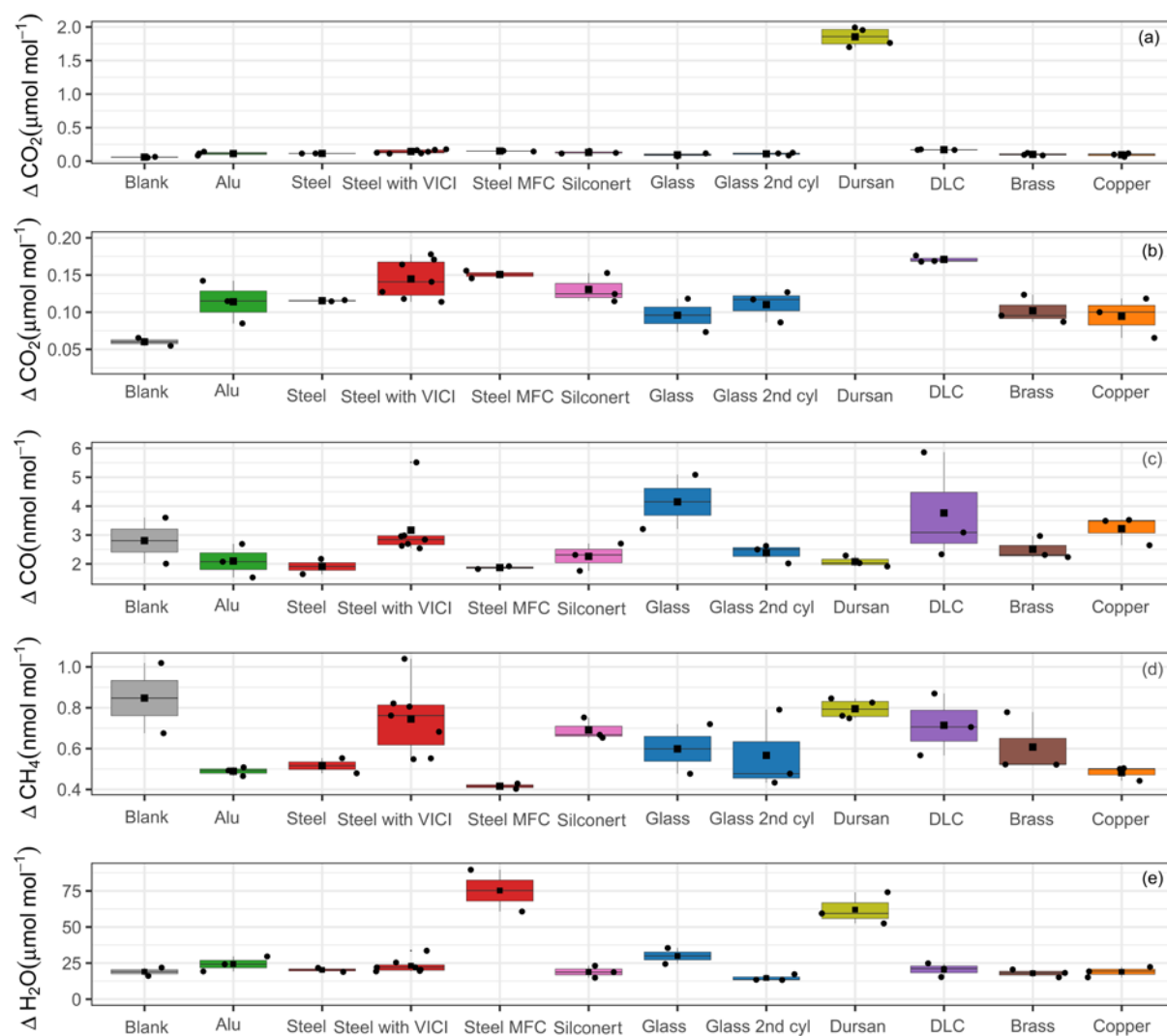


Figure 4. Box plots for all materials for the species (a) CO_2 , (b) zoom-in for CO_2 , (c) CO , (d) CH_4 and (e) H_2O . y-axes show the maximal amount fraction difference relative to the initial amount fraction. Horizontal lines in each box plot shows the median, whereas the square in the center of the box is the mean of the maximal amount fractions of the replicates.

Reply to the review of Anonymous Referee #2

The authors would like to thank Anonymous Referee for the valuable comments. In the following, referee's comments are given in bold and author's responses in plain text. Suggested new text is quoted in italics together with page and line numbers.

1 General comments

This manuscript deals with adsorption/desorption of trace gases in air on various metal surfaces. While many existing studies have focused on real cases, testing types of cylinders in use in the atmospheric measurement community, this manuscript on the contrary describes experiments performed using specifically designed test cylinders, filled with an air mixture and various materials, to study potential adsorption phenomenon of gases (CO₂, CO, CH₄, water vapour) on the tested surfaces. The results presented in this manuscript represent many hours of preparation and measurement, and are surely of value for the community measuring trace gases in the atmosphere and preparing reference gas mixture for this purpose. In particular, this study reports detectable and quite large effects for the coating Dursan for CO₂, which was unexpected, Dursan being advertised as a passivation treatment. Irreversible alteration of the amount fraction for most species and materials at temperatures equal or above 80 °C are also reported. In many other cases, no clear adsorption/desorption effect can be seen, which is at the same time a bit disappointing for process analysis but also good news from the user's point of view. The manuscript is well organised and figures in particular have been prepared with great care and display the results very clearly. Some descriptions in the text may gain in clarity (suggestions hereafter under 'specific comments').

2 Specific comments

What is your method's limit of detection, i.e. the smallest adsorption/desorption effect that could be detected using the chosen measuring instrument? What does the thresholds of 0.2 µmol/mol you mention for CO₂ p. 9 l. 9, 6 nmol/mol for CO and 1 nmol/mol for CH₄ (p. 7 l. 15) represent? If these questions are answered in the companion paper, please cite it.

We agree with our reviewer that this point needs further clarification. The word "threshold" is not correctly used in this context, therefore we replace it with the following phrasing on page 9 line 10:

"For CO₂ measurements, the amount fraction differences for all materials except Dursan were less than 0.17 µmol mol⁻¹, with slight differences among the various loadings."

For the presented experiments, we have used a Picarro G2401 CRDS analyzer. According to the specification sheet, the 5-minute, 1-σ precision of the instrument is <0.02 µmol mol⁻¹, <1.5 nmol mol⁻¹ and <0.5 nmol mol⁻¹, for CO₂, CO and CH₄, respectively. The numbers presented in our study (0.17 µmol mol⁻¹, 6 nmol mol⁻¹ and 1 nmol mol⁻¹, for CO₂, CO and CH₄, respectively) were reported to highlight that the observed changes have not exceeded these values but are higher than instrument precision stated in the specification sheet. These values can further be compared to the 5-minute standard deviation of measured data for CO₂, CO and CH₄ which in our case corresponded to 0.02 µmol mol⁻¹, 5 nmol mol⁻¹, and 0.2 nmol mol⁻¹, respectively. For CO₂ measurements, an explanation is already provided to clarify the significance of the observed changes within the reply to the anonymous referee#1. For CO and CH₄ considering the standard deviation of the measurements and the specifications of the analyzer, the observed maximal amount fractions are not significant and do not show material dependency.

We will add and rearrange the paragraph on page 7 line 13:

“For CO and CH₄, the maximum difference in the amount fractions did not exceed 6 nmol mol and 1 nmol mol⁻¹, respectively. According to the analyzer (Picarro G2401) specification sheet, the 5-minute, 1-σ precision of the instrument is <1.5 nmol mol⁻¹ and <0.5 nmol mol⁻¹, whereas the 5-minute standard deviation of measured data corresponded to 5 nmol mol⁻¹ and 0.2 nmol mol⁻¹, for CO and CH₄, respectively. Therefore, we have concluded that no significant change was observed in the final amount fractions for any of the materials during the course of the pressure experiments for the species CO and CH₄.”

For the pressure tests in particular, very little adsorption/desorption effect is seen, making likely very hard to actually estimate a number of molecules adsorbed per unit of surface area and/or to compare with theoretical adsorption curves (even if, from the user’s point of view, this is actually good news). This stated, it seems also clear that a new design allowing to cause larger adsorption effect would demand a substantial work and is beyond the scope of this manuscript. Still, how would you design a new test chamber / test material or how would you conceptually modify the present equipment to provoke a larger effect that could then be better analysed? I would suggest to add a few lines discussing this in the discussion and/or conclusion.

We thank our reviewer for appreciating the difficulty of estimating the number of adsorbed molecules. In order to increase adsorption, we would recommend inserting materials of very high surface areas into the measurement chambers. Some ideas would be using thin metal plates, metal spheres or metal pieces resulting from manufacturing processes (e.g. metal chips).

We will add the following statement at the end of the discussion:

“Moreover, in order to observe significant surface effects, materials of very high surface areas can be inserted into the measurement chamber. Some ideas would be using thin metal plates, metal spheres or metal pieces resulting from manufacturing processes (e.g. metal chips).”

Distinction container/content: I would suggest making clear reference to a gas mixture when writing of measuring, spiking or being adsorbed (e.g.: working gas, mother mixture), and to a gas container when writing of evacuating, cleaning, connecting, etc. (e.g.: working cylinder, mother cylinder). A few examples:

p. 3 l. 29: The fillings were done using compressed air from high pressure 50 l aluminum cylinders (LUX3586 and LUX 3575). – text modified accordingly

p. 3 l. 29-30: These two cylinders are called the mother cylinders and their air content the mother mixture from here on. – text modified accordingly

p.3 l. 31: In addition to the mother mixture, another mixture of comparable content and from a cylinder of comparable material and equipment to the mother cylinder was measured [...]. – text modified accordingly

p. 3 l. 33: This mixture (from cylinder LUX3579) is referred to as the working gas. – text modified accordingly

p. 4 l. 2-4: [...], the mother mixtures we spiked [...] using another compressed air mixture as carrier gas. – text modified accordingly

Please check that this distinction is clear through the manuscript.

p.5 l. 6: ‘empty cylinder’: it is still filled using the mother mixture so it is not empty strictly speaking. Maybe ‘blank cylinder’ (with the same meaning as ‘blank measurement’) would be more precise. Please modify through the manuscript (text, Tables, Figures).

We understand the concern of our reviewer, we have changed “empty cylinder” to “blank cylinder” throughout the manuscript.

p. 7 l. 12: ‘end amount fraction’: I would suggest replacing by ‘final amount fraction’. Please check through the text. – “end amount fraction” was changed to “final amount fraction” in the manuscript.

3 Technical corrections, phrasing

Abstract: a direct mention of adsorption right at the beginning would be more clear. Suggestion: A critical issue [...] employed. Both measuring and preparing reference gas mixtures for trace gases are challenging due to e.g. adsorption/desorption of the substances of interest on surfaces; this is particularly critical at low amount fraction and/or for reactive gases. Therefore, to ensure [...]. This study focuses on testing potential adsorption/desorption effects for different materials [...].

We agree with our reviewer that an earlier mentioning of adsorption is essential, we have changed the text accordingly.

Abstract l. 10: [...] to investigate the pressure dependency of adsorption up to 15 bar, and its temperature dependency [...]. – text modified accordingly

p. 1 l. 18, suggestion: In order to achieve a high level of compatibility for data obtained at different sites and/or at different time, the World Meteorological Organisation [...]. – text modified accordingly

p.1 l. 22: [...] but also by limiting any cause of molar fraction alteration. – text modified to “*but also by limiting any cause of amount fraction alteration.*”

p. 1 l. 22: maybe mention an order of magnitude for the lifetime of a standard cylinder?

On page 1 at line 22, the sentence is modified accordingly:

“During their relatively long lifetime in the order of decades, standard gas cylinders [...].”

p. 2 l. 8: larger volume – text modified accordingly

p. 2 l. 18: we aim at distinguishing these effects – text modified accordingly

p. 2 l. 28: on various surfaces. – text modified accordingly

p. 2 l. 30: According to the current literature, – text modified accordingly

p. 2 l. 34: the adsorption loss on the stainless steel surface – text modified accordingly

p. 3 l. 14: [...] we used the aluminium cylinder only. – text modified accordingly

p. 3 l. 17: [...] used in the atmospheric measurement community. This custom-made[...] – text modified accordingly

p. 5, legend of Fig. 2: related to the cleaning procedure – text modified accordingly

p. 7 l. 2: For the data analysis, for each temperature step the first 10 minutes of the measurements were not included in order to allow time for equilibration; the mean of the remaining 25 minutes was calculated. – text modified accordingly

p. 9 legend of Fig 5: whereas in the second and third panels – text modified accordingly

p. 9 l. 10 For example, [...] analyser showed [...] pressure run, whereas the mass flow[...]. – text modified accordingly

p. 10 l. 6: Based on the results of the pressure tests, the temperature experiments were conducted within a pressure range for which no pressure effect should occur, [...]. – text modified accordingly

p. 10, legend of Fig. 6: The x-axes correspond to the temperature cycles (cf. Fig. 3), – text modified accordingly

p. 10, legend of Fig. 6: does the y-axis show the amount fraction differences relative to the first measurement bloc done at 20°C? (There are three measurement blocs done at 20°C.)

We thank our reviewer for pointing this out. We changed the legend accordingly:

“the y-axes show the amount fraction differences relative to the first measurement block at 20 °C.”

p. 10 l. 7: In order to graphically distinguish [...] – text modified accordingly

p. 11 l. 9: remove 'Please' (check through the text). – text removed accordingly

Suggestion: displaying Fig. 6 and 7 on the same page.

We agree with our reviewer and combined the two figures into one.

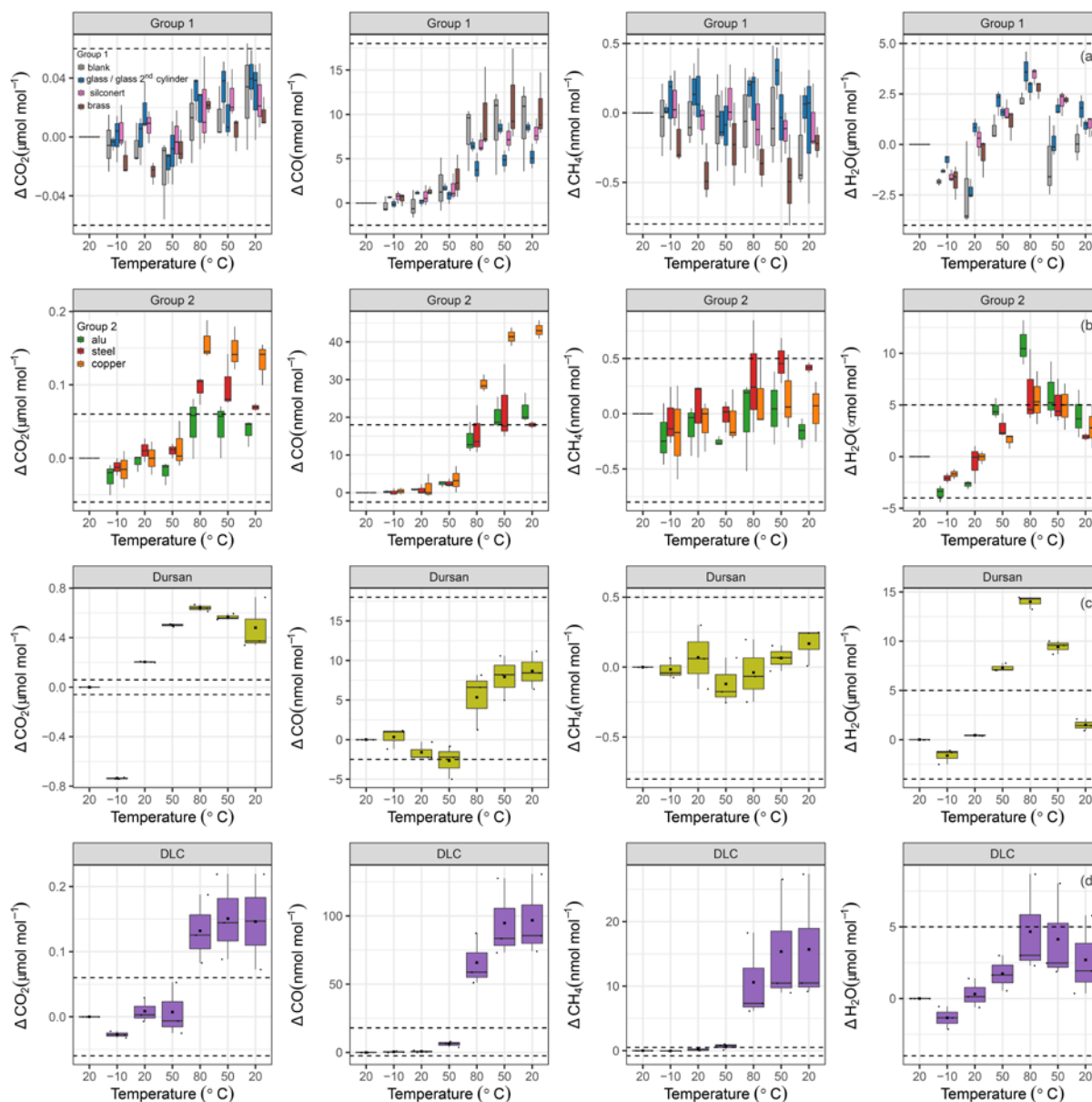


Figure 6. Temperature experiments grouped according to temperature response. (a) Group 1 materials are blank cylinder (gray), glass (blue), SilcoNert®2000-coated steel (pink), and brass (brown). (b) Group 2 materials are aluminum (green), stainless steel (red), and copper (orange). (c) Dursan® (light green) and (d) DLC (purple) coatings on stainless steel. Dashed lines indicate the same ranges for each species. The x-axes correspond to the temperature cycles (cf. Fig.3), and the y-axes show the amount fraction differences relative to the first measurement block at 20 °C.

Reply to the review of Anonymous Referee #3

The authors would like to thank Anonymous Referee for the valuable comments. In the following, referee's comments are given in bold and author's responses in plain text. Suggested new text is quoted in italics together with page and line numbers.

General comments:

This paper describes a series of experiments aimed at comparing the adsorption of some atmospheric trace gases in various materials. Experiments were planned in a very structured way to allow meaningful observations. The study was part of a larger study on adsorptions, and it is clear that authors chose to limit this paper to one main variable: the surface material. A good number of different materials were chosen, and all of them appear to be of interest to the community. The paper is generally well written, well-structured, clear, and provides a number of details on the instruments and methods, with some further details missing. However, the discussion part of the paper is quite limited. The results need to be put in perspective with other published work, in particular on CO₂ with aluminium. It also misses explanation and assumptions on the phenomena at work. Previous work by Leuenberger included a complete model with an attempt to fit the results during similar experiment in large cylinders. This paper should at least summarise this effort and explain if such attempt was also made here, and why it does not appear. Considering the type of comments provided below, I recommend a major revision before the paper can be published.

We would like to thank our reviewer for the insights and opinions. As already stated by the reviewer, this study focuses on surface material. The previous study on these small cylinders (Satar et al. 2019, 10.5194/amt-2019-197) have already concentrated on comparing the newly built small cylinders with the existing literature. In the presented work, we aimed at going a step further and have used the aluminum cylinder as the measurement chamber. We'll include a separate discussion section (presented as well in the replies to anonymous referee #1). Regarding a model of fit for the results presented in this study, the observed maximal deviation from the initial amount fraction for the blank cylinder was as low as 0.05 $\mu\text{mol mol}^{-1}$ making modelling of this increase extremely difficult. For the material loadings, adsorbed amounts should be distributed between the blank cylinders and the material blocks. However, subtracting the maximal amount fraction difference of the glass loaded cylinder from the material loaded cylinder resulted in amount fractions in the order of the standard deviation of the measured data. Therefore, for the majority of the materials fitting the Langmuir isotherm is not reasonable (presented as well in the replies to anonymous referee #1).

Please see point by point comments for the comparison between this work and the previous studies.

Specific comments by section:

Section 1. Introduction:

-Cylinders volume in this study compared to others: the introduction mentions this difference but does not state the potential impact on observations. In Schibig 2018 it is explained that cylinders smaller than 30 L should present larger effects, due to the surface to volume ratio. This should be observed and reflected through the introduction and the rest of the paper, in terms of the magnitude of observed effects compared to cylinders commonly used as standards.

Despite our efforts of increasing the surface area the material effects were minor, the geometric surface to volume ratio in the material experiments were 71.4, whereas this ratio is only 25.4 in Schibig et al. (2018). Our study with various different materials have revealed that even by increasing the

surface areas the desorbed amount at the end of the experiment until sub-atmospheric pressures is not significant for the materials except Dursan and DLC.

In the discussion part the following paragraph will be added (already presented in the replies to anonymous referee#1):

“The presented setup enabled the investigation of surface effects under “extreme” conditions which favored adsorption/desorption. Compared to common usage in the atmospheric measurement and gas metrology communities, our study has differed in cylinder size, geometric surface to volume ratios, pressure and temperature ranges. Previous studies (Leuenberger et al. 2015, Brewer et al. 2018, Schibig et al. 2018) investigating surface effects in compressed gas cylinders have used (50 L, 10 L, or 29.5 L) cylinders. The geometric surface of the small (5 L) aluminum cylinder used in this study is 0.18 m², which results in a surface to volume ratio of 35.7 for the unloaded cylinder. Compared to 29.5 L Luxfer cylinders, the small cylinders are estimated to be more prone to adsorption by 40 %. Inserting material blocks into the aluminum cylinder further increased the surface area. Therefore, the setup allows to test materials under increased surface to volume ratios in which the surface effects should be stronger and dominant. However, despite our efforts of increasing the surface material effects were minor.”

Section 2.1:

-Small chambers in aluminium and steel cylinders were designed, but this study only reports observations with the aluminium cylinder. The rationale behind this choice should be added. Was it after the conclusions of the other paper?

For the material experiments we have chosen to use the cylinder with the smallest background effect. We will add the following on page 3 line 14:

“Since the aluminum cylinder showed smaller effects with respect to surface effects in the previous study (Satar et al, 2019), we have chosen to use the aluminum cylinder only for the material experiments in order to minimize the background effect related to the measurement chamber.”

-The analyser is mentioned line 27 without a description. Please add the model and the performances which are relevant to the study. In particular one needs to pay attention to the sensitivity for the compounds measured, to demonstrate that observations are meaningful (or not). The claimed repeatability of the instrument appears sometimes on the same order as the changes measured during the study.

We will mention the name of the analyzer earlier on page 3 line 27:

“On the measurement line between the pressure regulator and the Picarro Cavity-Ring Down Spectroscopy analyzer (CRDS) G2401 either an electropolished stainless steel 1/4” tubing ,...”

On page 5 at line 3, we will add the following:

“The experiments were conducted using a Picarro G2401 CRDS analyzer enabling measurements of CO₂, CO, CH₄ and H₂O. According to the specification sheet of the analyzer, 5 minute, 1-σ standard deviation is <0.02 μmol mol⁻¹, <1.5 nmol mol⁻¹, <0.5 nmol mol⁻¹ and <50 μmol mol⁻¹ for the species CO₂, CO, CH₄ and H₂O, respectively. In order to investigate the material’s pressure dependency, the cylinder was filled through expansion from the mother cylinder to around 15 bar, and was evacuated through the Picarro analyzer.”

-Compressed air used for the study: more details on the composition are clearly needed, at least nominal values provided by the company. The water content in particular is under question, as some

of the observed differences are of the order of 70 $\mu\text{mol}/\text{mol}$. Does this mean the water amount fraction was even higher than this? This is important to clarify, considering that the work of Brewer et al. showed how water can be preferably adsorbed on surfaces, decreasing the adsorption of other compounds such as CO_2 .

The observed differences of the 70 $\mu\text{mol mol}^{-1}$ were not related to the water content of the mother mixtures, but were related to the equipment or material involved in the experiments. This is already explained on page 9 at lines 14-18 for the runs with mass flow controller.

On page 4 at line 4 the following will be added:

“After spiking the mother mixture, the composition of LUX3575 was 428.59 $\mu\text{mol mol}^{-1}$, 1083.73 nmol mol^{-1} , 2132.93 nmol mol^{-1} and <15 $\mu\text{mol mol}^{-1}$ for CO_2 , CO, CH_4 and H_2O .”

On page 9 at line 18, we will add the following:

“Similar to the CO_2 response of Dursan loading, the increase in H_2O amount fraction is most probably a combination of both desorption of newly adsorbed molecules and, desorption from the coated layer. It is unlikely that the enrichment of H_2O is related to the mother mixture since all other materials resulted in significantly lower amount fraction differences.”

Section 2.2:

-Flow rate: previous studies of Schibig et al. and Brewer et al. mentioned an influence of the flow rate at which cylinders are being emptied. How was this taken into account? What was the flow rate during the measurements? Some consideration on this point should be provided.

Schibig et al. (2018) and Brewer et al. (2018) have conducted their measurements at high and low flow rates. In Schibig et al. (2018), low and high flow conditions were 0.3 L min^{-1} and 5.0 L min^{-1} , whereas in Brewer et al. (2018) the low and high flow rates were 0.7 L min^{-1} and 5.5 L min^{-1} , respectively. The flow rate in the presented experiments in this study as well as Satar et al. (2019) are comparable to the low flow conditions. In contrast to the above-mentioned previous studies, there was no excess flow prior to the analyzer. At the beginning of the experiment, the flow rate was 220 mL min^{-1} (STP) and towards the end of the experiment it was 15 mL min^{-1} (STP). More information on flow rate is included in Sect. 3.1.1 of Satar et al. (2019). Since we have conducted the measurements at low flow conditions, other fractionation effects due to a temperature gradient in the cylinder are not expected.

We will add the following flowrate information on page 6 line 1:

“There was no flow regulation after the pressure regulator prior to the analyzer inlet. At the beginning of the experiment the flow rate was 220 mL min^{-1} (STP) and towards the end of the experiment it decreased to 15 mL min^{-1} .”

-Pressure values during temperature studies: table 1 shows that the pressure could change when changing the temperature. Consider explaining the reason and potential impact on the results.

We think there was a misunderstanding in the interpretation of the values presented in Table 1. The three pressure values shown in the table only show the starting pressures of each experiment, and does not give information on pressure change related to temperature change. Regarding pressure changes during the temperature experiments, these changes can be estimated using the ideal gas equation. For example, for a filling of 15 bar pressure and 20 °C temperature a pressure of 18.1 bar at 80 °C and 13.5 bar at -10 °C is expected. At these ranges, no pressure effect is expected. This point is already taken into account and discussed for the temperature experiments (on page 10 line 6).

For clarification, we will add the following in the caption of Table 1:

“The pressure values indicate the pressure in the small cylinder at the beginning of each replicate run.”

-It is explained that in this study, all reported values are in amount fraction difference. It can be assumed that this choice was made to plot all data together and be able to compare different observations. This might be a good reason, but absolute values should also be provided, at least once, to be able to compare the results in this study with others.

Indeed, similar to other studies we have preferred to plot our results in amount fraction differences. This approach enables to compare different observations and also highlights the measured differences. The mother cylinder content is compressed natural air. We have added the composition of the cylinder to section 2.1.

-Temperature cycle: please clarify that the container was refilled at the beginning of each new temperature step. This information could also be added on figure 3.

We think that there is a misunderstanding at this point. The cylinder was not filled at the beginning of each new temperature step. The cylinder was filled to about 15 bar at the beginning of the temperature cycle (Fig. 3) and refilled after a full temperature cycle.

Section 3:

-It is said several times that changes observed with CO₂ are significant only for Dursan. However, differences of the order of 0.15 μmol/mol were observed with other materials and this is comparable with the compatibility goal within GAWG. In other studies, similar changes were not considered negligible. Some analysis in view of already published work should be added and made more consistent.

We thank our reviewer for pointing this out. It should be noted that the differences observed in this study were observed at sub-atmospheric pressures, other studies including Leuenberger et al. (2015), Schibig et al. (2018) and Brewer et al. (2018) observed these differences at an earlier onset at higher pressures. In our opinion, this study should be seen independently from the existing literature due to the following reasons: (i) the experimental setup used in this study is not comparable to previously published work in terms of inserting different materials in a measurement chamber, (ii) an introduction into the blank cylinders and their comparison to existing literature is already presented in detail within the scope of Satar et al. (2019), (iii) the surface to volume ratios in the current study is increased on purpose to increase adsorption/desorption effects.

In the previous study in which the cylinders were introduced (Satar et al., 2019), a discussion on how the small cylinders behave in comparison to other studies has already been included for the blank cylinders. In our opinion the focus of the presented work is to understand the effects of different materials. Nevertheless, we suggest to add the following the paragraph to discussion (presented as well in the replies to anonymous referee #1):

“The presented setup enabled the investigation of surface effects under “extreme” conditions which favored adsorption/desorption. Compared to common usage in the atmospheric measurement and gas metrology communities, our study has differed in cylinder size, geometric surface to volume ratios, pressure and temperature ranges. Previous studies (Leuenberger et al. 2015, Brewer et al. 2018, Schibig et al. 2018) investigating surface effects in compressed gas cylinders have used (50 L, 10 L, or 29.5 L) cylinders. The geometric surface of the small (5 L) aluminum cylinder used in this study is 0.18 m², which results in a surface to volume ratio of 35.7 for the unloaded cylinder. Compared to 29.5 L Luxfer cylinders, the small cylinders are estimated to be more prone to adsorption by 40 %. Inserting material

blocks into the aluminum cylinder further increased the surface area. Therefore, the setup allows to test materials under increased surface to volume ratios in which the surface effects should be stronger and dominant.”

Regarding the significance of $0.15 \mu\text{mol mol}^{-1}$, we clarify as follows on page 9, at line 10 (presented as well in the replies to anonymous referee #1):

“For CO_2 measurements, the amount fraction differences for all materials except Dursan were less than $0.17 \mu\text{mol mol}^{-1}$, with slight differences among the various loadings. Of this difference, $0.05 \mu\text{mol mol}^{-1}$ is related to the blank cylinder (background effect). The blank cylinder corresponded to the “14 bar after heating” case presented in Satar et al. (2019). More information on the blank cylinder and its filling history is provided in the above-mentioned publication. It is also crucial to consider that during all material block experiments, glass pieces were also present in the small measurement chamber. When the material runs were compared to the experiments with glass, except the DLC loading, the remaining differences were in the order of $0.02 \mu\text{mol mol}^{-1}$, which corresponded to the 5-minute standard deviation of the measured data.”

-The “empty” case needs further clarification. First on the term itself which is badly chosen as the container is always filled with gas. Second on the values compared to the other paper of the authors. They are apparently those of the case “aluminium, filled at 14 bar, after heating”. This should be clarified and related to the choice of this material (best results?).

In order to avoid this misunderstanding, we have changed “empty” to “blank” as suggested by the anonymous reviewer 2.

Aluminum cylinder was chosen as a measurement chamber for the presented study, since aluminum is the commonly used material in the atmospheric measurement community. Since all material experiments were conducted after the temperature experiments presented in Satar et al. (2019), we have naturally used the “aluminum cylinder after heating”. The choice of the cylinder is already clarified above (Section 2.1), and the blank results are linked to the 14 bar after heating case in the discussion section (please see the suggestions above).

-The “steel” results can be confusing when compared to the other paper, where a difference of $0.5 \mu\text{mol/mol}$ was observed. The setup is of course not the same, but this would need some consideration and some assumptions to explain those discrepant results.

We thank our reviewer for his/her attention. The discrepancy between the two steel result is most likely related to the different composition of steel used in these two studies. In the presented study stainless steel blocks of (316L) are used, whereas the previous study uses a steel cylinder of hardened and tempered steel (1.7218 / 25CrMo4 EN AW-6061) This information is already presented at the respective papers.

-Results on water: figure 4 shows up to $60 \mu\text{mol/mol}$ changes, which would mean quite large water content to start with. Was it the case? If not, where does the water come from?

The two cases with high water changes were already explained in the manuscript on page 9 at line 14 and with the suggestions above. It is important to note that the big differences in the amount fractions are observed towards the end of the experiments where desorption is expected to be at play. We relate the high water content with the mass flow controller and the Dursan blocks. For the remaining runs, considering the low flow rate and the duration of the high water vapor content episodes, the

integrated amount of water vapor is reasonable since there is a trace amount of water available in the mother cylinder which will be adsorbed at high pressures.

Comments on figures:

Figure 5: consider splitting in different figures to allow a larger front. This is currently far too small.

We understand the reviewer's concern. We will increase the font size, but will keep all subfigures.

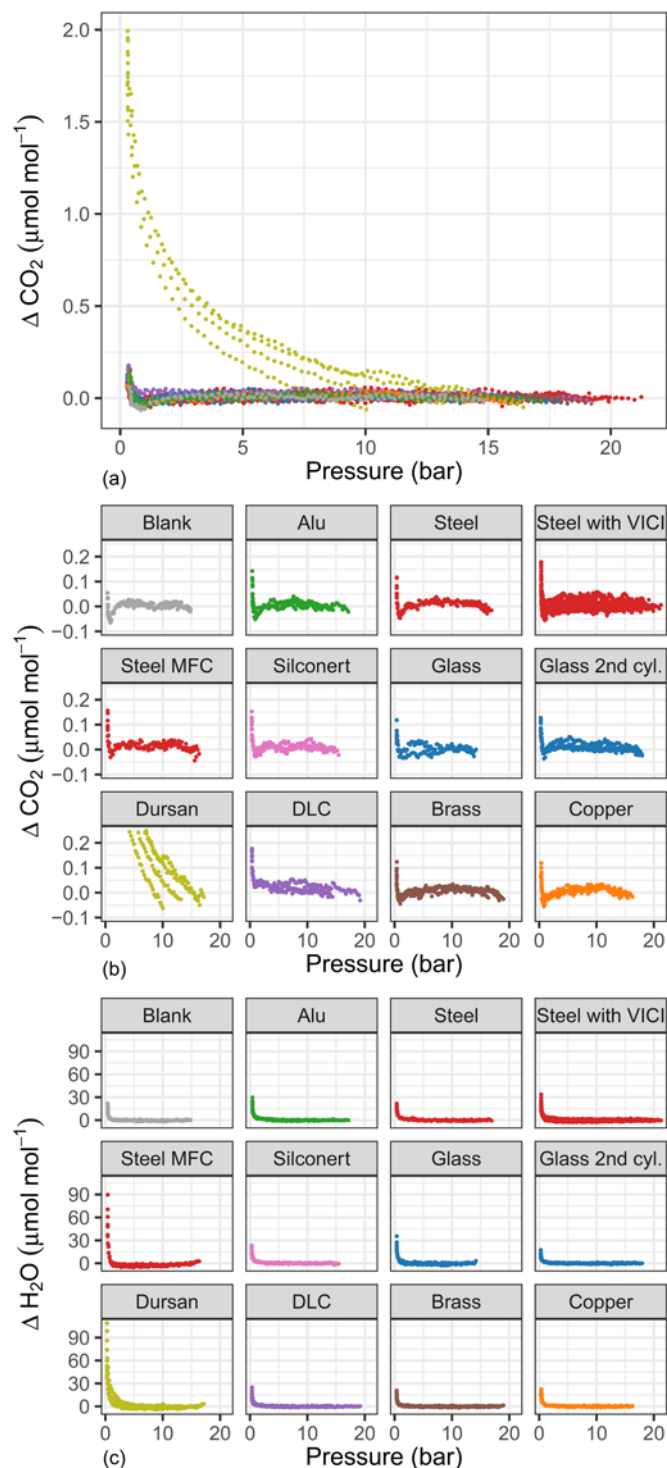


Figure 5. Amount fraction difference relative to the start of the experiment for (a, b) CO_2 and (c) H_2O with respect to pressure for all tested materials. The first panel shows all materials together, whereas in the second and third panels, each material is plotted separately. Consistent color codes are used throughout the study.

Figures 6: the x-axis is very disturbing, even after the highlight in the text noting that it indicates the temperature cycle, which is why the scale is not linear. There is some logic in this choice, but it discards the possibility to clearly see the temperature effect. Consider plotting with a linear temperature scale using a color code or different shapes to show the time. Another option is to use time as x-axis and superpose the temperature cycle.

We respect our reviewers view on Figure 5 and Figure 6. However, in our opinion the plots are clearly showing both the reversibility (e.g. H₂O) and the irreversibility (e.g. CO and CO₂) of the temperature effect. Superposing a temperature cycle would pack more information on already full plots especially in the case of group 1 plots (Fig. 6a).

Towards an understanding of surface effects: Testing of various materials in a small volume measurement chamber and its relevance for atmospheric trace gas analysis

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Abstract. A critical issue for the long-term monitoring of atmospheric trace gases is precision and accuracy of the measurement systems employed. ~~To Both measuring and preparing reference gas mixtures for trace gases are challenging due to e.g. adsorption/desorption of the substances of interest on surfaces; this is particularly critical at low amount fraction and/or for reactive gases. Therefore, to~~ ensure the best preparation and measurement conditions for trace gases in very low amount fractions, usage of coated materials is in demand in gas metrology and atmospheric measurement communities. This study focuses on ~~the testing of~~ testing potential adsorption/desorption effects for different materials or coatings that are currently used, or may be relevant in future for the measurements of greenhouse gases. For this study ~~, we used the previously tested small volume cylinders, which were constructed such that they can serve as adsorption test chambers~~ we used small volume chambers designed to be used for adsorption studies. Various materials with or without coatings were loaded into the small cylinder to test their adsorption/desorption behavior. We used the aluminum cylinder as the measurement chamber, and glass, aluminum, copper, brass, steel and three different commercially available coatings as test materials. Inserting the test materials into the measurement chamber doubles the available geometric area for the surface processes. The presented experiments were designed to investigate the pressure dependency of adsorption up to 15 bar, and its temperature dependency up to 80 °C for the test materials placed in the measurement chamber. Here, we focused on the species CO₂, CH₄, CO and H₂O measured by a cavity ring down spectroscopy analyzer. Our results show that the materials currently used in atmospheric measurements are well-suited. The investigated coatings were not superior to untreated aluminum or to stainless steel at the tested pressure ranges, whereas under changing temperature aluminum showed better performance for CO₂ (< 0.05 μmol mol⁻¹ change in measured amount fractions) than stainless steel (> 0.1 μmol mol⁻¹). To our knowledge, this study is one of the first attempts to investigate surface effects of different materials in such a setup for the above-mentioned gases.

20 1 Introduction

Long term atmospheric monitoring of trace gases requires great attention to precision and accuracy. In order to achieve a ~~globally integrated and well-established greenhouse gas observation network~~ high level of compatibility for data obtained at

different sites and/or at different time, the World Meteorological Organization (WMO) has recommended compatibility goals for measurements of trace gases within its Global Atmosphere Watch (GAW) Programme (2016). These challenging limits can be achieved not only by regular calibration with standard gases of known composition, but also by ~~careful material selection~~limiting any cause of amount fraction alteration. During their relatively long lifetime, in the order of decades, standard gas cylinders may not be stable due to diffusion, leakage, regulator effects, gravimetric fractionation and surface processes (Keeling et al., 2007; Langenfelds et al., 2005). The latter, which encompass adsorption/desorption, are also dependent on temperature, pressure and surface properties. Currently there exists only limited data and a few attempts to quantify these surface processes for CO₂ and CH₄ (Leuenberger et al., 2015; Miller et al., 2015; Brewer et al., 2018; Schibig et al., 2018). These studies use Langmuir (1918) adsorption theory (Leuenberger et al., 2015; Schibig et al., 2018) and Rayleigh fractionation (Schibig et al., 2018) to explain the enrichment in the amount fractions towards the end of the cylinder lifetime with respect to different flow rates.

Key results of the above-mentioned studies point out that the adsorption behavior is pressure- and temperature- dependent. All mentioned studies used ~~bigger~~larger volume (~~10 or 30 L~~, 29.5 or 50 L) cylinders, which were already in use as standard cylinders. Their approach on filling varied from compressing natural air (Schibig et al., 2018) to gravimetric preparation in synthetic air or in nitrogen (Brewer et al., 2018). In their study, neither Brewer et al. (2018) nor Schibig et al. (2018) observed that their passivation treatment for the aluminum cylinder decreased the surface interaction of CO₂.

Langmuir (1918) defines adsorption as the time lag between the condensation of a molecule and its evaporation from a surface. The simplest relation which can be linked to adsorption is the pressure dependency. At higher pressures, the gas molecules are pressed to the cylinder walls, where they are adsorbed to the cylinder surface. As the pressure decreases during the lifetime of a cylinder, these molecules are desorbed from the surface and lead to an enhancement in the amount fraction of the gas. Changes in temperature also affect the equilibrium amount fraction of the adsorbed molecules by varying temperature dependent rate constants of adsorption and desorption.

In this study, we aim ~~to distinguish the~~at distinguishing these effects among various materials under controlled conditions in a previously characterized measurement chamber (Satar et al., 2019). We limited ourselves to a selection of materials ranging from materials frequently used in atmospheric measurement community to commercially available coatings. Aluminum cylinders are now the state of the art for the measurements of greenhouse gases such as CO₂ and CH₄ (WMO, 2018). Although not recommended anymore for above-mentioned species, some steel cylinders may still be in use. Additionally, stainless steel pieces are very commonly used as tubings and in pressure regulators, and have contact with the measured gases. Some regulators are made of brass (WMO, 2018), and copper is commonly used as seals in vacuum applications of atmospheric trace gas measurements (Behrens et al., 2008). Moreover, commercially available coatings are increasingly interesting for both atmospheric measurement and metrology communities, since with the improvement of experimental techniques, the demand for higher precision and accuracy in trace gas analysis is growing.

The affinity of adsorption/desorption deviates largely for different species ~~at~~on various surfaces. Some coatings may provide inert, corrosion resistant, or hydrophobic surfaces, and enable usage of metals instead of polymers with ambiguous outgassing effects. ~~In~~According to the current literature, surface losses are critical especially for more reactive gases during the prepara-

tion of the standards. In gas metrology community, this issue has already been investigated in more detail i.e. for species such as ammonia using test tubes with various coatings (Vaittinen et al., 2014), for propane and benzene (Lee et al., 2017), and for monoterpenes in cylinders (Allen et al., 2018). In their study, Vaittinen et al. (2014) observed that some of the commercial coatings reduced the adsorption loss ~~of stainless steel on the stainless steel surface~~ by a factor of ten or more. The atmospheric measurement community makes use of inert coatings of chemically protective barrier of amorphous silicon (Silcotek Corporation) in air core applications (Karion et al., 2010; Andersen et al., 2018), where the surface to volume ratio is large. Diamond-like carbon coatings are not yet commonly used in trace gas analysis, but have found their place in many applications in a range varying from wear and corrosion protection of magnetic storage media to biological implantations (Grill, 1999).

This study contributes to the limited literature on the discussion of surface effects of different materials for the species CO₂, CH₄, CO and H₂O. It is one of the first attempts to systematically investigate the differences among various materials in a reproducible way using a relatively small custom-made aluminum measurement chamber requiring less gas and time for the measurements. In this study, we briefly introduce the setup and the established procedure for the measurements. Then, we proceed with eight material loadings to the measurement chamber, and test their response to pressure and temperature variations.

2 Data and Methods

2.1 Measurement setup and used materials

In order to understand adsorption/desorption behavior of various materials, high pressure (up to 130 bar) and small volume (5 L) cylinders of aluminum and steel were designed. These cylinders served as measurement chambers in which various test materials can be inserted. ~~In this study, we used~~ Since the aluminum cylinder showed smaller effects with respect to surface effects in the previous study (Satar et al., 2019), we have chosen to use the aluminum cylinder only for the material experiments in order to minimize the background effect related to the measurement chamber. More information and details on the filling history of the cylinders were previously explained (Satar et al., 2019). Here we provide a brief summary: The aluminum cylinder is made of the aluminum alloy AlMg1SiCu (EN AW-6061), and its composition is specifically chosen that it corresponds to the aluminum commonly used in the atmospheric measurement community. ~~The~~ This custom-made cylinder consists of three pieces: a body part in the middle with two caps on the sides (Fig. 1a). These pieces are joined by twelve necked-down bolts on each side, and Inconel X750 seals with silver coating are placed in the caps. It is equipped with four stainless steel bellows sealed valves (SS-4H from Swagelok), where the wetted surfaces are solely of stainless steel and do not include any polymers. The connections are from stainless steel and all tubings are of electropolished stainless steel 1/4". At the outlet, the cylinders are equipped with dual stage pressure regulators made of a stainless steel body with a polychlorotrifluoroethylene (PCTFE) seat (64-3441KA412 from Tescom). Pressure transducers are used at low (PTU-S-AC6-31AC from Swagelok), and high (PTU-S-AC160-31AC from Swagelok) pressure sides of the pressure regulators. Temperature sensors spanning a range from -35 °C to +100 °C (AF25.PT100 from Thermokon) are placed on the outer cylinder surfaces. All measured temperature and pressure data were read and logged by a signal converter (midi logger GL820 from Graphtec).

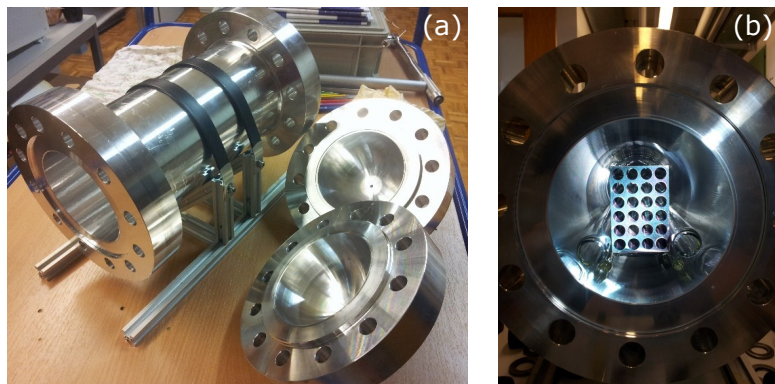


Figure 1. (a) Custom made cylinder of three pieces. (b) Material loading into the cylinder. The metal blocks are placed on the glass ladder, and two rod shaped glass pieces support the material from the sides.

On the measurement line between the pressure regulator and the [analyzer-Picarro Cavity-Ring Down Spectroscopy analyzer \(CRDS\) G2401](#) either an electropolished stainless steel 1/4" tubing, a mass flow controller (358 Series from ANALYT-MTC) or a multiport valve (EMT2CSD6MWE from VICI AG) was placed.

The fillings were done using [compressed air from high pressure 50 L aluminum cylinders with compressed air L aluminum cylinders](#) (LUX3586 and LUX3575). These [two](#) cylinders are called the mother cylinders [and their air content the mother mixture](#) from here on. ~~The A~~ mother cylinder was directly connected to a small expansion volume (0.5 L) made of stainless steel (316L-HDF4-500 from Swagelok). In addition to the mother ~~eylinders, another mixture, another mixture of comparable content and from a~~ cylinder of comparable material and equipment to the mother cylinder was measured to check the stability of the measurement device. This ~~eylinder (mixture from cylinder~~ LUX3579) is referred to as the working gas. All three
 5 [cylinders](#) were filled by Carbagas, Switzerland with compressed air according to their own protocol. The filling history of the cylinders is known only to the extent that the cylinders were filled with compressed air only. In order to test for higher amount fractions of CO, ~~mother eylinders the mother mixtures~~ were spiked: a known amount of pure CO gas was injected into a known volume (60 [mL](#)), and was pushed into the sample cylinder using another compressed air ~~eylinder mixture~~ as carrier gas.
 10 [For example, after spiking the mother mixture, the composition of LUX3575 was 428.59 \$\mu\text{mol mol}^{-1}\$, 1083.73 \$\text{nmol mol}^{-1}\$, 2132.93 \$\text{nmol mol}^{-1}\$, <15 \$\mu\text{mol mol}^{-1}\$ for CO₂, CO, CH₄ and H₂O.](#)

Material loadings into the cylinder were conducted as follows: glass pieces were inserted in order to avoid sharp metal-metal contact points between the sample pieces and the cylinder inner surface. These consisted of a ladder and two rod shaped glass pieces (Fig. 1b). Then, on top of the ladder-shaped glass piece, two metal blocks were placed. Each metal block has the dimensions 100x74x50 mm, and has 24 drill holes of 1 cm in diameter. The two blocks have in total comparable (factor of 1.17)
 20 geometric area to the cylinder inner surface. Aluminum (AlMgSi1), copper (CuETP), brass (CuZn39Pb3), steel (316L), and three different commercially available coatings on steel (SilcoNert®2000, Dursan®, and CERODEM® diamond-like carbon (DLC)) were used as test materials. Glass pieces and metal blocks without coatings underwent a cleaning procedure consisting

of ultrasonic bath with a diluted solution of a mildly alkaline commercial cleaning agent (Deconex HT1201), and vacuum oven drying at 120 °C.

Since the cylinder was exposed to outside air in between loadings of different materials, a specific cleaning procedure was applied to eliminate water vapor. The measurement chamber was first pumped down to 0.05 mbar using a dry piston vacuum pump (EcoDry M15 from Leybold), and then filled with 2 bar of N₂, and pumped again while heating with a heat gun. After three fill-pump-heat cycles of 30 minutes each, the cylinder was filled with N₂, and left for cooling overnight. During these heating cycles, the surface temperature of the sample cylinder increased up to 60 °C. The following morning, the cylinder was pumped down to 0.05 mbar, and filled with compressed air through expansion. The desired pressure in the small cylinder was achieved by repeating the expansion step several times. An hour was allowed for equilibration prior to starting the measurements.

2.2 Measurement sequence and data collection

Figure 2 shows a scheme of the measurement setup. For each material loading, temperature and pressure experiments were conducted using the same procedure as before (Satar et al., 2019). The experiments were conducted using a Picarro G2401 CRDS analyzer enabling measurements of CO₂, CO, CH₄ and H₂O. According to the specification sheet of the analyzer, 5-minute, 1- σ standard deviation is <0.2 $\mu\text{mol mol}^{-1}$, <1.5 nmol mol^{-1} , <0.5 nmol mol^{-1} , and <50 $\mu\text{mol mol}^{-1}$ for the species CO₂, CO, CH₄ and H₂O, respectively. In order to investigate the material's pressure dependency, the cylinder was filled through expansion from the mother cylinder to around 15 bar, and was ~~measured with a Picarro Cavity Ring-Down Spectroscopy analyzer (CRDS) G2401~~ evacuated through the Picarro analyzer. Each sample material loading had at least three replicates for both temperature and pressure runs with the exception of the ~~empty blank~~ cylinder (Table 1). Bracketing each measurement, the working gas cylinder was measured to check the stability of the measurement device. The measurement sequence for an individual loading was established in the following order: The first two runs were pressure experiments. These were followed by three cycles of temperature experiments. Lastly, the cylinder underwent the third pressure experiment. This order enables the detection of any changes in pressure response after heating cycles. Table 1 shows an overview of the experiments presented in this study.

For the pressure dependency experiments, data analysis was based on Satar et al. (2019). There was no flow regulation after the pressure regulator prior to the analyzer inlet. At the beginning of the experiment the flow rate was 220 mL min^{-1} (STP) and towards the end of the experiment it decreased to 15 mL min^{-1} (STP). The end point of the experiments was set to a fixed internal parameter of the measurement device called the "outlet valve". This value can easily be linked to the outflow from the instrument, which corresponds to about 15 ~~mL~~ mL min^{-1} at STP. For better comparability among the measurements, measured amount fractions were subtracted from the mean of the first hour of measurements for each run. In order to eliminate instrumental noise, 5-minute means of these differences were calculated. In this study, all reported values are in amount fraction differences (ΔCO_2 , ΔCH_4 , ΔCO , $\Delta\text{H}_2\text{O}$).

In order to investigate the temperature dependency, the cylinder was placed into a climate cabinet (ACS Challenge 600) at the Swiss Federal Institute of Metrology (METAS). The temperature of the cabinet was set to -10 °C, 20 °C, 50 °C and 80 °C,

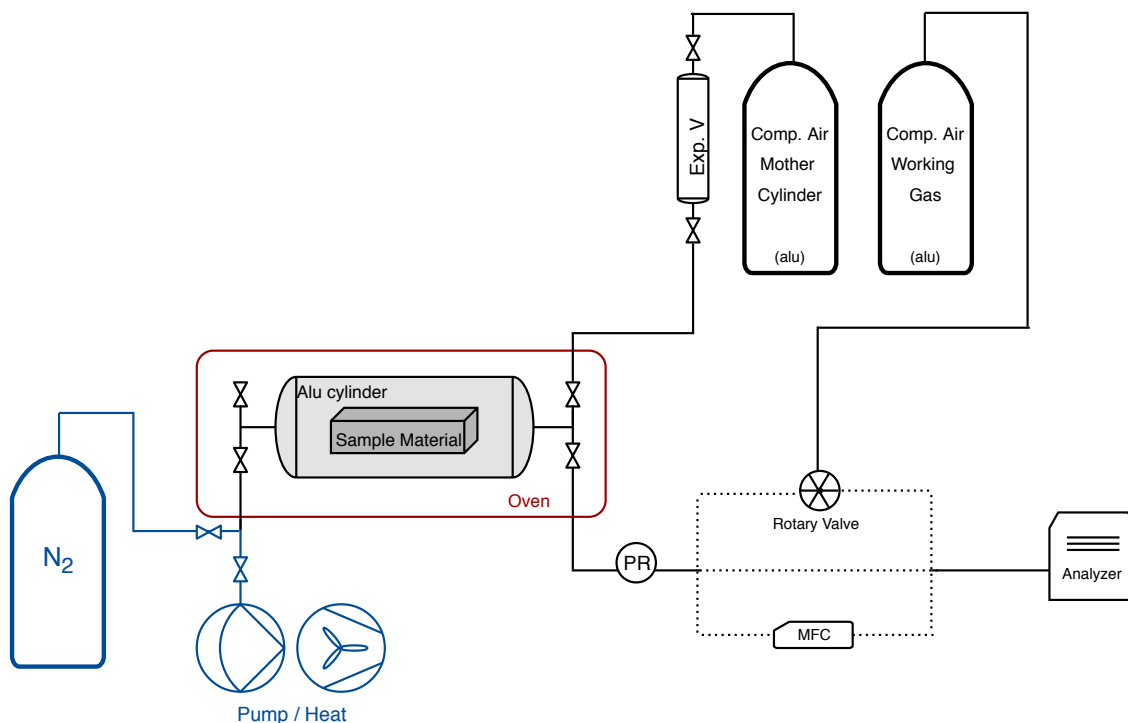


Figure 2. Schematic of the experimental setup. The aluminum cylinder is placed in the oven (denoted by the red box). The cylinder is filled through the expansion volume from the mother cylinder. At the outlet of the cylinder, the dashed lines show the three possible paths into the analyzer: through the rotary valve, direct tubing or mass flow controller (MFC). The equipment related to the cleaning procedure is denoted in blue.

with 30 °C increments, heated or cooled within an hour (Fig. 3). The temperature was kept constant for four hours at each level, of which during the last 35 minutes the material loaded cylinder was measured. These measurements were bracketed by working gas measurements which had not experienced any temperature changes. A multiport valve was used to switch between the small cylinder and the working gas. A full temperature cycle lasted 34 hours. For the data analysis, ~~the first ten for each~~
 5 temperature step the first 10 minutes of the measurements were not included in order to allow time for equilibration. ~~For each~~
~~temperature step,~~ the mean of the remaining 25 minutes was calculated. Then, differences for each temperature level were calculated with respect to the measurements at 20 °C.

Table 1. An overview of data included in this study. The pressure values indicate the pressure in the small cylinder at the beginning of each replicate run.

Experiment	Type	Pressure [bar]	Number of replicates	Mother cylinder
<u>EmptyBlank</u>	Pressure	13.9; 13.9	2	LUX3575
<u>EmptyBlank</u>	Temperature	15.8; 15.0; 16.7	3	LUX3586
Glass	Pressure	13.3; 13.0	2	LUX3586
Glass	Temperature	15.3; 14.7; 14.5	3	LUX3586
Aluminum	Pressure	13.6; 13.0; 16.3	3	LUX3575
Aluminum	Temperature	15.3; 14.7; 14.7	3	LUX3586
Steel	Pressure	16.0; 15.4	2	LUX3586
Steel with VICI	Pressure	16.4 - 20.3	7	LUX3586
Steel MFC	Pressure	15.5; 15.0	2	LUX3586
Steel	Temperature	12.7; 18.5; 18.3	3	LUX3586
SilcoNert@2000	Pressure	14.5; 13.7; 14.0	3	LUX3586
SilcoNert@2000	Temperature	13.9; 14.0; 16.1	3	LUX3586
Glass	Pressure	17.1; 16.7; 16.0	3	LUX3575
Glass	Temperature	16.8; 16.9; 16.7	3	LUX3575
Dursan®	Pressure	16.3; 9.2; 15.5; 12.3	4	LUX3575
Dursan®	Temperature	15.8; 15.5; 15.0	3	LUX3575
DLC	Pressure	13.0; 13.5; 18.3	3	LUX3575
DLC	Temperature	13.9; 19.6; 19.5	3	LUX3575
Copper	Pressure	15.4; 14.9; 13.4	3	LUX3575
Copper	Temperature	15.5; 14.7; 14.6	3	LUX3575
Brass	Pressure	18.1; 17.3; 15.4	3	LUX3575
Brass	Temperature	18.4; 17.3; 16.9	3	LUX3575

3 Results and Discussion

3.1 Pressure experiments

In Fig. 4, an overview of all measured species is shown. For each run, we calculated the amount fraction differences with respect to the initial amount fraction and selected the maximal difference. ~~Then, we~~ Maximal difference was chosen to highlight the maximum possible effect related to desorption. Since all data was processed using the same criterion, the effects originating from the analyzer is cancelled out and we focus on the differences between the materials. We grouped replicate runs of each material loading together and showed the calculated maximal differences in the boxplots. The median is denoted by the horizontal

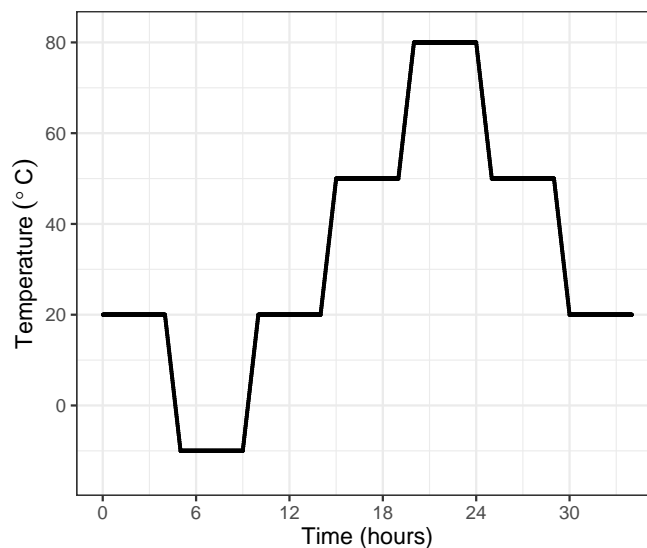


Figure 3. Temperature cycle set at the climate cabinet

line, whereas the mean is shown by the square. Since for most cases only 3 replicates are present, the 1st quartile is the mean of the minimum and the median, whereas the 3rd quartile is the mean of the median and the maximum value. For clarity, data points used for the box plots are also shown and they are denoted by the black points. In Fig. 4a and b, CO₂ amount fractions are plotted: the first panel includes all materials, whereas the second is a zoom-in aiming to distinguish smaller differences among the material loadings. For CO₂, we were able to detect significant changes only for Dursan®, where the end-final amount fraction was about 10 times higher than all other materials. For CO and CH₄, we did not observe any significant change in the end-the maximum difference in the amount fractions did not exceed 6 nmol mol⁻¹ and 1 nmol mol⁻¹, respectively. According to the analyzer (Picarro G2401) specification sheet, the 5-minute, 1-σ precision of the instrument is <1.5 nmol mol⁻¹ and <0.5 nmol mol⁻¹, whereas the 5-minute standard deviation of measured data corresponded to 5 nmol mol⁻¹ and 0.2 nmol mol⁻¹ for CO and CH₄, respectively. Therefore, we have concluded that no significant change was observed in the final amount fractions for any of the materials during the course of the pressure experiments. The maximum difference did not exceed 6 nmol mol⁻¹ and 1 nmol mol⁻¹, for CO and CH₄ respectively for the species CO and CH₄. For H₂O, steel with mass flow controller and Dursan® loading showed significantly higher maximal amount fractions, corresponding to about 3 times higher enhancements than other species.

In order to highlight the changes during the emptying of the measurement chamber, we show differences of the measured amount fractions from the initial amount fraction (ΔCO_2 and $\Delta\text{H}_2\text{O}$) with respect to pressure for each material loading (Fig. 5). The first panel shows all materials together, whereas in the second and the third panels, individual runs are grouped together for each material loading. As indicated in Fig. 2, we made some changes to the measurement line in order to distinguish whether various equipment upstream of the analyzer had an influence on the measurements. Therefore, for the steel loading,

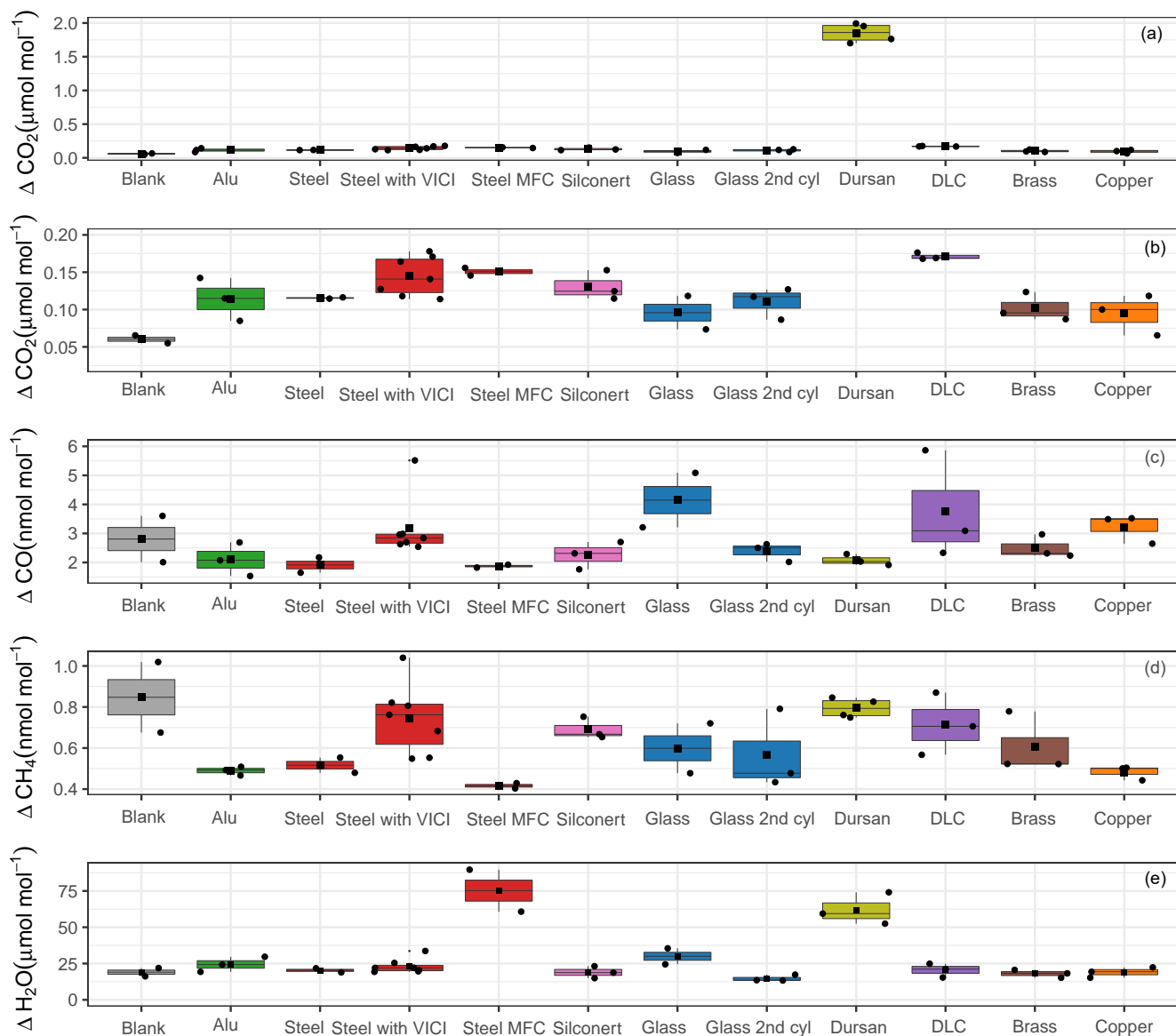


Figure 4. Box plots for all materials for the species (a) CO_2 , (b) zoom-in for CO_2 , (c) CO , (d) CH_4 and (e) H_2O . y-axes show the maximal amount fraction difference relative to the initial amount fraction. Horizontal lines in each box plot shows the median, [whereas the square in the center of the box is the mean of the maximal amount fractions of the replicates.](#)

we show results of the pressure experiments with a mass flow controller, and a multiport valve. For CO_2 , only Dursan® showed a significant difference as high as $1.85 \pm 0.14 \mu\text{mol mol}^{-1}$ in the [end-final](#) amount fractions. The enrichment in the CO_2 measurements started significantly earlier, and followed a distinctly different evolution compared to all other tested

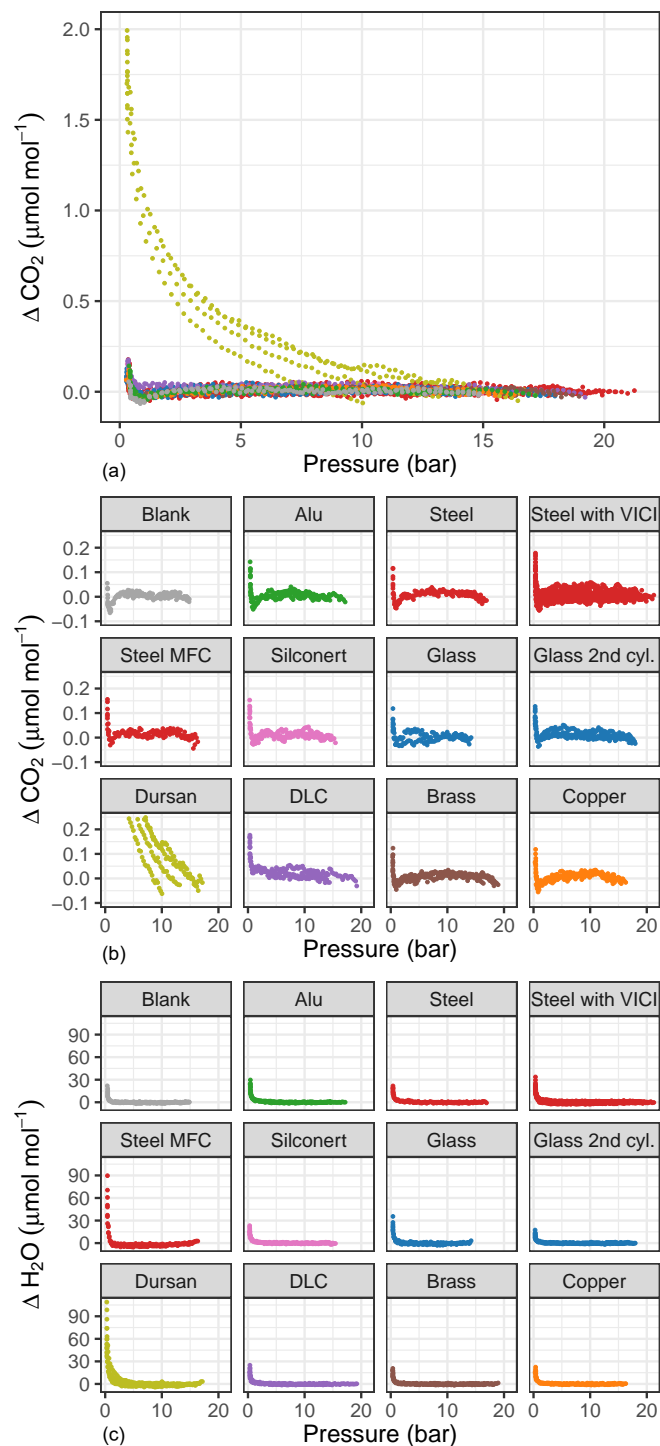


Figure 5. Amount fraction difference relative to the start of the experiment for (a, b) CO_2 , and (c) H_2O with respect to pressure for all tested materials. The first panel shows all materials together, whereas in the second and third panels, each material is plotted separately. Consistent color codes are used throughout the study.

materials. We do link this enhancement to desorption from the surface of the material. Besides being resistant to adsorption of corrosive and reactive media, the coating layer consists of amorphous silicon, oxygen and carbon (Silcotek Corporation). The desorption from the material to the gas mixture is most probably a combination of both desorption of newly adsorbed molecules after the filling, and desorption of already existing carbon in form of CO₂ on the coating. In order to distinguish this difference, fillings containing no CO and CO₂ such as synthetic air or N₂ would be worthwhile.

For CO₂ measurements, the amount fraction differences for all ~~other materials were under a threshold of 0.2 materials except Dursan® were less than 0.17~~ $\mu\text{mol mol}^{-1}$, with slight differences among the various loadings. ~~In example, the experiments Of this difference, 0.05 $\mu\text{mol mol}^{-1}$ is related to the blank cylinder (background effect). The blank cylinder corresponded to the “14 bar after heating” case presented in Satar et al. (2019). More information on the blank cylinder and its filling history is provided in the above-mentioned publication. It is also crucial to consider that during all material block experiments, glass pieces were also present in the small measurement chamber. When the material runs were compared to the experiments with glass, except the DLC loading, the remaining differences were in the order of 0.02 $\mu\text{mol mol}^{-1}$, which corresponded to the 5-minute standard deviation of the measured data. Moreover, during the evacuation of the measurement chamber with the DLC loading, a slightly increasing trend of $-0.004 \mu\text{mol mol}^{-1} \text{ bar}^{-1}$ was observed. For the steel loaded cylinder, the experiments where a multiport valve was upstream of the analyzer, showed slightly more variation both for end-final amount fractions and during the pressure run. Whereas, the mass flow controller employed did not have a significant effect on the measurements. Moreover, during the evacuation of the measurement chamber, DLC loading showed a slightly increasing trend of $-0.004 \mu\text{mol mol}^{-1} \text{ bar}^{-1}$. CO₂ measurements.~~

H₂O measurements (Fig. 5) showed greater differences than CO₂ measurements, corresponding to $19.05 \pm 2.84 \mu\text{mol mol}^{-1}$ for the ~~empty-blank~~ cylinder. Compared to other materials, Dursan® loading and the measurements with the mass flow controller showed significantly higher ~~end-final~~ amount fractions of $73.71 \pm 12.55 \mu\text{mol mol}^{-1}$, and $75.22 \pm 14.45 \mu\text{mol mol}^{-1}$, respectively. The difference observed for the mass flow controller was most probably related to a memory effect combined with teflon tape, since it was used for humid air prior to these measurements. ~~Similar to the CO₂ response of Dursan® loading, the increase in H₂O amount fraction is most probably a combination of both desorption of newly adsorbed molecules and, desorption from the coated layer. It is unlikely that the enrichment of H₂O is related to the mother mixture since all other materials resulted in significantly lower amount fraction differences.~~

Since CO and CH₄ (Fig. 4c-d) showed no distinct differences in amount fractions with decreasing cylinder pressure, we include their analog plots in Fig. A1 for completeness. Under these "extreme" conditions of cylinder evacuation, the observed effects were minimal for most of the investigated materials. However, the Dursan® loading showing a difference revealed that the measurement chamber and the established procedure were successful to detect changes.

3.2 Temperature experiments

~~Temperature experiments grouped according to temperature response. (a) Group 1 materials are empty cylinder (gray), glass (blue), SilcoNert®2000-coated steel (pink), and brass (brown). (b) Group 2 materials are aluminum (green), stainless steel~~

(red), and copper (orange). Dashed lines indicate the same ranges for each species. The x-axes correspond to temperature cycles, and the y-axes show the amount fraction differences relative to the measurements at 20 °C.

All of the shown amount fraction differences during Based on the results of the pressure tests, the temperature experiments were in the conducted within a pressure range for which no pressure effect should occur, with the exception of Dursan®.

5 In order to graphically distinguish the temperature effect on various materials, data was split into four different groups (Fig. 6): group 1 corresponded to materials showing the least response, group 2 were materials showing a significant temperature response, and group 3 and 4 corresponded to Dursan® and DLC separately, since they showed an order of magnitude higher differences for some of the measured species. Figure ?? shows the first two groups. Note that all x-axes correspond to in Fig. 6 correspond to a temperature cycle. Empty Blank cylinder, glass, SilcoNert®2000 and brass loadings (Fig. ??6a) showed the
10 least response to temperature variations between -10 °C and 80 °C. For CO₂, the observed mean differences per material were less than 0.05 μmol mol⁻¹. However, this difference was as high as 11 nmol mol⁻¹ for CO. At 80 °C, there was a clear change in the amount fractions of CO, whereas this step change was not as clear in CO₂ measurements. The reason of this behavior is most probably related to the cylinder itself, which points to an irreversible chemical reaction, since the enhancement in amount fraction stayed prominent even when the cylinder was cooled back down to 20 °C. For CH₄, temperature variations resulted
15 in non-significant amount fraction differences, and they stayed in a narrow range from -0.75 nmol mol⁻¹ to 0.5 nmol mol⁻¹. All material loadings showed an effect with respect to H₂O measurements. This effect was reversible: lower H₂O amount fractions were observed at colder temperatures, and higher amount fractions at higher temperatures. This is an indication of adsorption/desorption, in which at colder temperatures desorption rate is lower, and the system equilibrates at lower amount fractions in the gas mixture. As the temperature increases, desorption rate increases, resulting temporally in higher amount
20 fractions in water vapor. For the first group of materials, H₂O measurements were within the range of -5 μmol mol⁻¹ to 5 μmol mol⁻¹. After cooling the cylinder to 20 °C, a slight change of 1 μmol mol⁻¹ compared to the initial amount fraction was observed.

Figure ??6b shows steel, aluminum and copper. These loadings showed a more significant temperature response compared to group 1. Please note Note that the dashed lines represent the ranges from the first group of materials. For CO₂, all materials
25 showed a clear increase when the temperature was increased to 80 °C. This increase corresponded to 0.16 ± 0.02 μmol mol⁻¹, 0.10 ± 0.01 μmol mol⁻¹, and 0.05 ± 0.02 μmol mol⁻¹, for copper, steel, and aluminum respectively. After cooling back to 20 °C, the amount fraction increase in aluminum and steel dropped back to less than 0.07 μmol mol⁻¹, whereas for copper the difference persisted and was 0.13 ± 0.02 μmol mol⁻¹. For CO, the effects were even more significant. At 80 °C, ΔCO for the copper loading increased to 29 ± 1 nmol mol⁻¹, and was followed by 16 ± 4 nmol mol⁻¹ and 14 ± 2 nmol mol⁻¹ for
30 aluminum and steel respectively. Aluminum and steel loadings reached their maximum increase at 50 °C after cooling down from 80 °C, and stayed at that level even with further cooling. The increase in CO amount fraction for the copper loading continued and reached 43 ± 1 nmol mol⁻¹. This might be an indication of an irreversible chemical reaction happening after the threshold of 80 °C which uses copper as a catalyst. This is further supported by the fact that the amount fraction enhancement after each temperature cycle was reproducible. Similarly to the first group, CH₄ measurements of the second
35 group stayed in the narrow window of -0.75 nmol mol⁻¹ to 0.5 nmol mol⁻¹. For H₂O, group 2 materials showed a slightly

greater effect than group 1 materials with a mean of $7.55 \pm 2.88 \mu\text{mol mol}^{-1}$ at 80°C , and reached $11 \pm 1 \mu\text{mol mol}^{-1}$ for aluminum. After cooling to 20°C , a difference over $2 \mu\text{mol mol}^{-1}$ compared to the beginning was observed.

Figure ?? shows 6c-d show Dursan® and DLC on separate panels for each of the measured species. For CO_2 , Dursan® showed differences as high as $0.64 \pm 0.02 \mu\text{mol mol}^{-1}$. A fraction of this difference was related to the pressure decrease of the cylinder from 15 bar to 5 bar. However, during most of the temperature cycle including measurements at 80°C , the pressure in the cylinder was over 9.5 bar, corresponding to a pressure effect of less than $0.25 \mu\text{mol mol}^{-1}$. Even when this difference was considered, the temperature effect of this material was an order of magnitude greater than group 1 materials at 80°C . Whereas at 20°C at the end of the temperature cycle, the pressure contribution was as high as $0.5 \mu\text{mol mol}^{-1}$. CO and CH_4 did not show any significant difference in their response compared to group 1 and group 2 materials. H_2O measurements were higher than in the other groups, but reversible.

The DLC loading clearly showed different temperature response compared to all other materials, especially with regard to the variability of its replicates. CO_2 showed a mean difference of $0.15 \pm 0.04 \mu\text{mol mol}^{-1}$ compared to the beginning of the cycle. For CO and CH_4 , the differences from the starting amount fractions were 10 and 20 times larger than the differences observed for other tested materials. At each temperature cycle, the measured CO difference at 80°C decreased, for the first and last cycle, this difference corresponded to 87 nmol mol^{-1} and 51 nmol mol^{-1} , respectively. This feature was observed in CH_4 and H_2O measurements as well. During the first temperature cycle at 80°C , CH_4 and H_2O showed an increase of 18 nmol mol^{-1} and $8 \mu\text{mol mol}^{-1}$, whereas during the third temperature cycle, CH_4 and H_2O showed an increase of 6 nmol mol^{-1} and $3 \mu\text{mol mol}^{-1}$, respectively. This behavior in DLC measurements showed that the underlying reason of the enhancement in the amount fractions were substances on the surface of the DLC coating, which by repeated heating were depleted. According to Grill (1999), thermal relaxation of the DLC film may occur at temperatures as low as 100°C .

Moreover, it should be noted that during the set of the measurements presented in this study, the aluminum cylinder experienced the temperature cycle 30 times. This presumably resulted in a change of the background effect for the material loadings over the course of the presented analysis in the range of $0.04 \mu\text{mol mol}^{-1}$. We measured the empty blank cylinder at the very beginning and at the end of the material set. The empty blank cylinder results shown in the Fig. ??(a)-6a is a mean of the former and latter temperature experiments, therefore resulted in a higher variation. Due to the observed variation, we did not subtract the background to avoid disturbing other measurements. More detailed information on heating experiments and its consequences were presented in Satar et al. (2019).

4 Discussion

The presented setup enabled the investigation of surface effects under “extreme” conditions which favored adsorption/desorption. Compared to common usage in the atmospheric measurement and gas metrology communities, our study has differed in cylinder size, geometric surface to volume ratios, pressure and temperature ranges. Previous studies (Leuenberger et al., 2015; Brewer et al. investigating surface effects in compressed gas cylinders have used (50 L, 10 L, or 29.5 L) cylinders. The geometric surface of the small (5 L) aluminum cylinder used in this study is 0.18 m^2 , which results in a surface to volume ratio of 35.7 for the

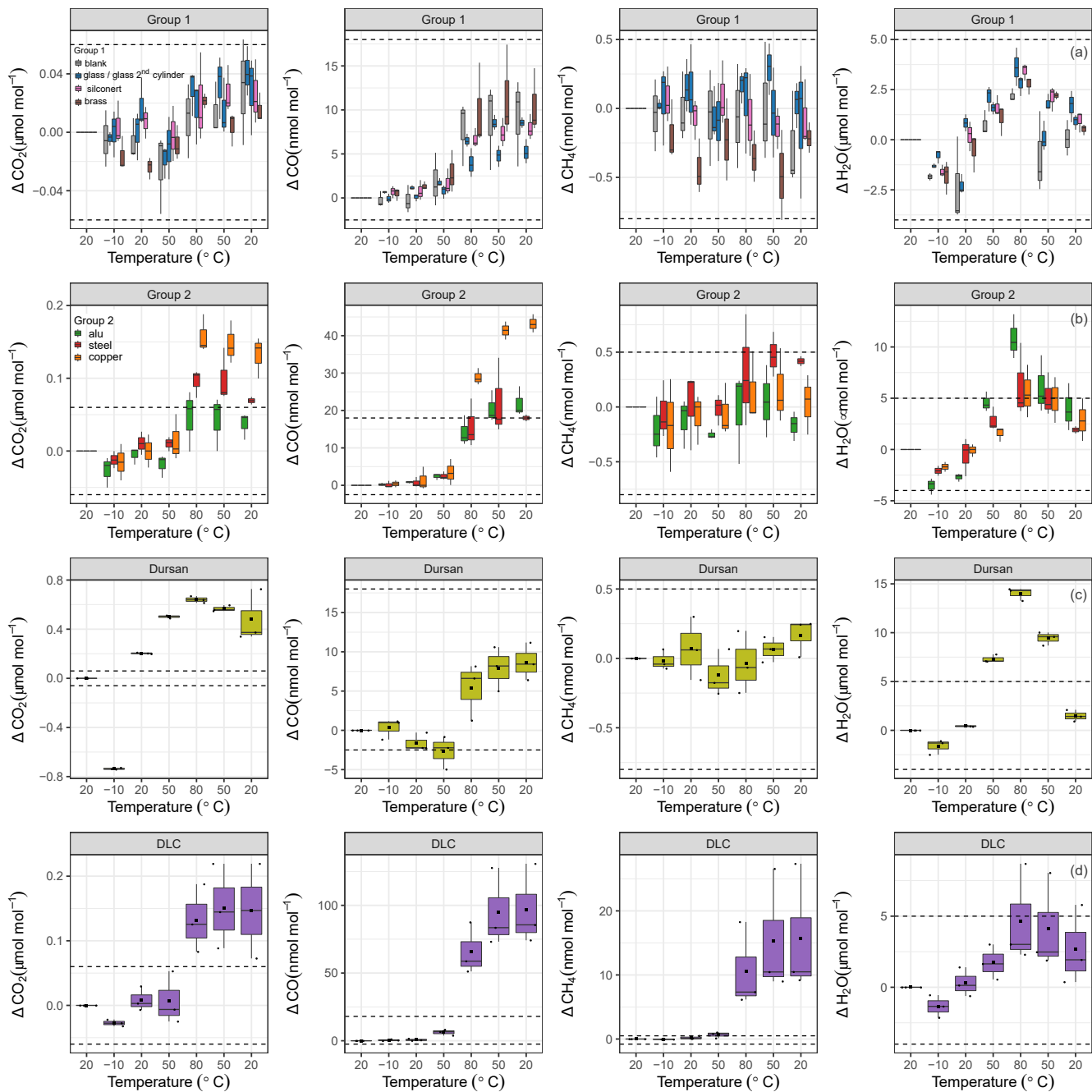


Figure 6. Temperature experiments for-grouped according to temperature response. (a) Group 1 materials are blank cylinder (gray), glass (blue), SilcoNert®2000-coated steel (pink), and brass (brown). (b) Group 2 materials are aluminum (green), stainless steel (red), and copper (orange). (c) Dursan® (light green) and (b) (d) DLC (purple) coatings on stainless steel. Dashed lines indicate the same ranges for each species. The x-axes correspond to the temperature cycles (cf. Fig. 3), and the y-axes show the amount fraction differences relative to the measurements-first measurement block at 20 °C.

unloaded cylinder. Compared to 29.5 L Luxfer cylinders, the small cylinders are estimated to be more prone to adsorption by 40 %. Inserting material blocks into the aluminum cylinder further increased the surface area. Therefore, the setup allows to test materials under increased surface to volume ratios in which the surface effects should be stronger and dominant. However, despite our efforts of increasing the surface material effects were minor.

5 In addition to the properties of the materials, pressure and temperature play a role on surface effects. The following assumption lies behind the pressure experiments: if the material has adsorbed a significant amount of gas while filling the cylinder, this should be desorbed towards the end of the experiments controlled by desorption. The onset of the desorption for all tested materials except Dursan® and partly DLC was observed well-below atmospheric pressures.

10 Increasing temperature is expected to facilitate desorption by providing the required energy to desorb the gas molecules from the surface and mix into gas phase. On the contrary, cooling the cylinder and its content favor adsorption and it is expected that this results in a decrease in the measured amount fraction.

15 Testing pieces cut from the aluminum and steel cylinders commonly used in the community would be a valuable addition to enable direct comparison between the commonly used cylinder materials and the produced material blocks at low pressures and high temperatures. Moreover, in order to observe significant surface effects, materials of very high surface areas can be inserted into the measurement chamber. Some ideas would be using thin metal plates, metal spheres or metal pieces resulting from manufacturing processes (e.g. metal chips).

5 Conclusions

We have presented the pressure and temperature dependent response of the species CO₂, CH₄, CO and H₂O with respect to glass, aluminum, copper, brass, steel, and three different commercially available coatings on stainless steel (Dursan®, 20 SilcoNert®2000 and DLC). For the pressure response, under the circumstances of our experimental setup and procedure, within the pressure range varying from 15 bar to 200 mbar absolute, we were only able to detect changes for CO₂ in the loading with Dursan® coated stainless steel reaching 2 μmol mol⁻¹ enrichment in the amount fractions. All other materials showed effects less than 0.2-0.17 μmol mol⁻¹ for CO₂. Under exposure to temperatures from -10 °C to 80 °C, the response of glass, brass and SilcoNert®2000 coated steel were minimal, whereas DLC and Dursan® showed distinctly different temperature effects than 25 all other tested materials. For most materials, including stainless steel, copper, aluminum, DLC and Dursan® a step change in the measured amount fractions were observed after 80 °C.

30 These experiments show that all coatings not necessarily enable more passive surfaces, and might result in enhancements when exposed to pressure and temperature changes. Materials currently used by the atmospheric measurement community for storing standard gases are well suited under 80 °C, which are typical utilisation temperatures. Moreover, the materials presented in this study are not only relevant for measurements of standard gases, but also of interest for other gas handling and measuring applications.

Appendix A

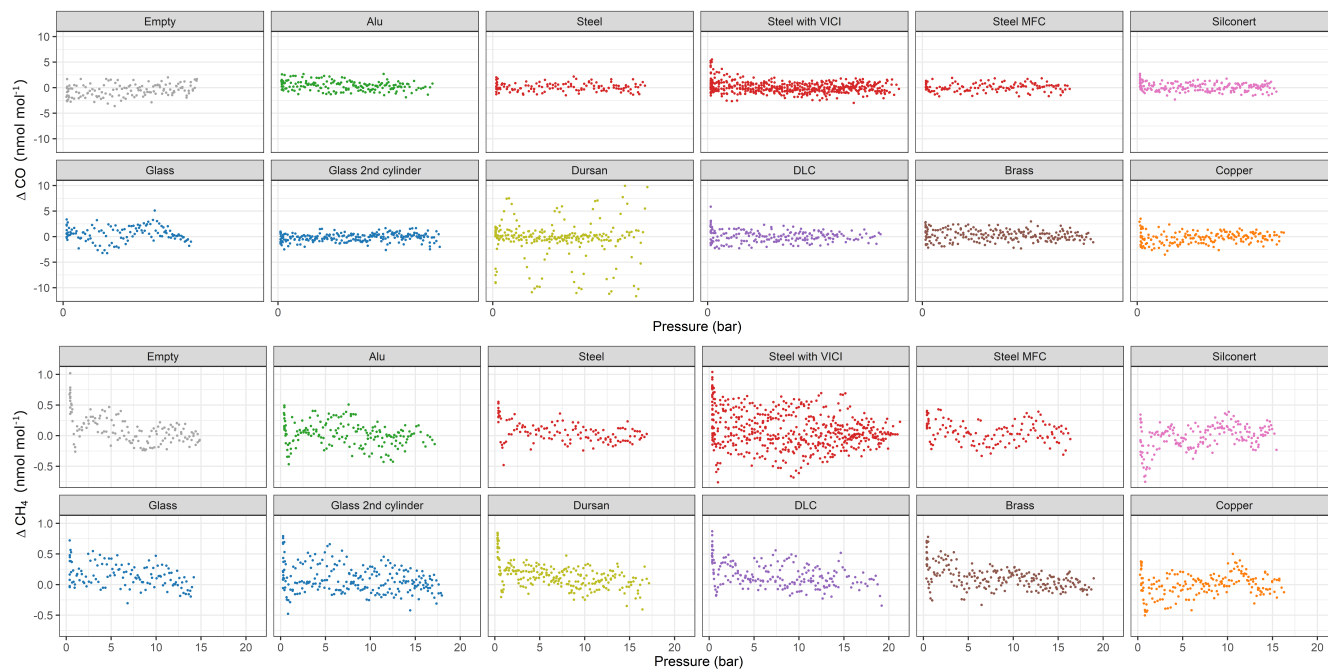


Figure A1. Amount fraction differences compared to the start of the experiment for CO, and CH₄ for all tested materials

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