Responses to Review of Referee 2 (AMTD-8-8083-2015)

We would like to sincerely thank reviewer 2 for his excellent comments and suggestions. It improved the manuscript again by giving the reader more in-depth information about how the experiments were performed and which materials were in use.

In the following we reply to every point raised by the reviewer 2. Our answers are given in red, whereas changes made to the manuscript are given in blue.

General Comments
The manuscript is describing an experimental approach to investigate effects of sorption processes of various gaseous species on high pressure air cylinder walls. It is providing an introduction in the theoretical description of physisorption and evaluates the obtained experimental results from the perspective of this theoretical framework. The subject is of significance for high accuracy trace gas analysis as these measurements generally are based on referencing to air standards that are stored in such high pressure cylinders. Any composition change in the extracted air from these reference gas cylinders throughout the lifetime of such a standard as observed by the authors would introduce a bias in the measurement data. The authors conclude by raising the need for further experiments using a better defined experimental set-up. I highly welcome such efforts to quantify these phenomena and elucidate their mechanistic background.

However, I do have substantial questions on the presented data material as well as the interpretation of these data by the authors. The presented material seems insufficient to justify the conclusions drawn by the authors. I am not convinced that the interpretation of the experimental data is focussing on the correct processes but rather feel that it might be biassed by the adopted theoretical framework. I would rate a revised version of the manuscript ready for publication only if the authors can exclude any ambiguity in the experimental set-up. The authors should also be conclusive in responding to questions raised to their interpretation of the data.
In addition, there are several specific comments that I would ask the authors to consider for a revision of the manuscript.
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Specific and Technical Comments with respect to the experimental data:

- The description of the material involved in the experiments is incomplete with respect to the characterization of the cylinders (p.8088, l.13-15). The volume and the supplier are not an exhausting characterization of the cylinders: the kind of steel and the aluminium alloy (probably 6061) should be mentioned and most importantly the cylinder head valve mounted on the cylinder. While Scott Marin aluminium cylinders are commonly equipped with packless diaphragm valves, steel cylinders from gas companies could have various types of valves. In packed valves or O-ring sealed valves the pressurized gas is in contact to sealing polymers (like PTFE, Viton, EPDM). We have made the experience that there are cylinders valve types with the potential to significantly modify the gas composition specifically for CO_2. This most likely is due to permeation and sorption effects on sealing polymers that are inappropriate. Such effects have the potential to be significantly larger than sorption on cylinder walls and therefore would completely mix up the experiment. The authors therefore should specify the valve type specifically the sealing type (O-ring/packed/packless) and wetted materials. The value of the entire study is at stake if the possibility that this component interferes in the experiment cannot be excluded.

This is a valid point. We updated the information for the cylinders in use. We used 50 liter tempered steel (34CrMo4) cylinders equipped with a standard brass valve K44-8 from VTI with Peek as spindle sealing material. The regulator connection type is G 5/8" RH female thread from Carbagas Switzerland. Gas wetted materials for these cylinders are steel, brass and Peek. The aluminium cylinders are 30 liter Scott-Marrin Luxfer (AA 6061 T6) cylinders equipped with a brass valve D 202 from Rotarex with PA as spindle material. The regulator connection type is CGA-590. Gas wetted materials are aluminium, stainless steel, brass and PA.

We used 50 liter tempered steel (34CrMo4) cylinders equipped with a standard brass valve K44-8 from VTI with Peek as spindle sealing material. The regulator connection type is G 5/8" RH female thread from Carbagas Switzerland sealed with a PA disk. Gas wetted materials for these cylinders are steel, brass and Peek. The aluminium cylinders are new 30 liter Scott-Marrin Luxfer (AA 6061 T6) cylinders equipped with a brass valve D 202 from Rotarex with PA as spindle material. The regulator connection type is CGA-590. Gas wetted materials are aluminium, stainless steel, brass and PA. No additional pre-treatment of the inner surfaces were applied except these applied by the supplier and producer that we do not know in detail and these given above. The steel cylinders were filled by Carbogas according to their protocol. We do not know the filling history of these cylinders except that they are used for compressed air fillings only. The aluminium cylinders were pumped to roughly 10 mbars and then flushed and pressurised to 10 to 15 bars using dry compressed air with ambient concentrations three times and then filled with dry compressed air from another cylinder again at ambient concentrations. CB09877 prepared similarly at Empa and was additionally blended by a second compressed air. CA03901 was prepared at Boulder by NOAA/CMDL according their protocol.

Additionally, we added the following statement to the Result section based on experiments that we did in the climate chamber.

Furthermore, we investigated whether the sealing material in use at the cylinder valve as well as at the connection to the pressure regulator (PEEK, PA) has an influence on our findings. An aluminium cylinder equipped with a VTI K44-8 (PEEK as spindle sealing material) and a PA sealing at the regulator connection (G 5/8" RH female thread), as used for the steel cylinders, showed a similar behaviour as a different aluminium cylinder equipped with a Rotarex D 202 valve (PA as spindle sealing material) with a gold ring as sealing material at the CGA 590 connection.

- p.8089, l. 10f: "Unfortunately, the electronics of the Vici valve was malfunctioning after the first night and therefore we had to replace it." The reader does not get an idea what relevance this problem has for the experiment and the validity of its results: if the valve remained at one position for a longer period, or no gas was flowing during the period of the valve defect.

Indeed, the Vici valve was not switching between the cylinders. It remained on one single position for four hours. This sequence was neglected in the evaluation. We changed this part as follows:

Unfortunately, the electronics of the Vici valve was malfunctioning after the first night (remained at the same position) and therefore we had to replace it. This sequence was neglected in the evaluation. The experiment was extended in order to have two full temperature cycles for data evaluation.

- In experiment 2 the CRDS instrument was calibrated measuring one external reference gas every two hours. The authors specify the set of calibration coefficients for CO2 which I would consider as an irrelevant information because it is a characteristic of the individual instrument (and why only CO2 and not CH4 or CO?). More relevant

would be the presentation of the reference measurement data to document the stability of the measurement throughout the experiment. Fig. 6 presents data with <0.005 ppm resolution whereas Fig. 4 (lower panel) indicates temporary fluctuations on a time scale of 20 min in the 0.03 ppm range (based on 480 min for 80 bar decrease = 8 min /bar), which raises the question what minimum signal actually can be taken as significant.

We agree with the reviewer 2 that the calibration is not the most relevant information (also mentioned by reviewer 1) therefore, we removed it and replaced it with information about the reference measurements as follows in the method section:

Both instruments are frequently calibrated with known standard gas admissions, i.e. in the case of experiment 1 before and after the experiment and in the case of experiment 2 during the complete experiment. Though, of more importance for these experiments that are designed to be short-term measurements are the repeatability and drift rates. The repeatability can be accessed by the short-term measurement variability and corresponds to < 0.01 ppm (averaged over 5 minutes) whereas the drift rate has been estimated from the standard cylinder CA03901 to be 0.0041 ppm/day (see also Results section).

Addition under Results (experiment 2):
The different sign of the dependencies for steel and aluminium cylinder is a first hint that these dependencies are not originating from instrument drift. This is supported by the measurements of cylinder 3901 acting as a reference that was not exposed to the temperature variations but placed just beside the instrument in an anteroom. This measurements done throughout the experiment showed rather constant values with a standard deviation of 5-minute averages of 0.009 ppm. There is only a small trend of +0.0041 ppm/day. Excluding the trend, the standard deviation reduces to 0.006 ppm. Furthermore, even with this small constant drift of the analyser, only the scatter of the data but not the temperature dependence itself would be affected. Actually, large instrument drifts could potentially be estimated from the scatter of the data. Therefore, the temperature dependencies seen for steel and aluminium cylinders are most certainly not due to drifts of the analyser.

Comments to Fig. 4 and Fig. 6. First of all, our description of the decanting experiment was not complete. The high (5 l/min) and low (0.25 l/min) flow emptying experiment took 8 and 120 hours, respectively, to empty the two aluminium cylinders from their initial pressures 97 bar (cylinder CB09790) and 58 bar (cylinder CB09880) to 1 bar as given in table 1. We changed the caption of Figure 4 accordingly.

Figure 4: Fast and slow emptying experiment within 8 (upper panel) and 120 (lower panel) hours, respectively:

The question which minimal signal can actually be taken as significant is an important point that requires some additional attention. As mentioned above the standard deviation of 5-minute averages of the reference tank is 0.006 ppm. Since the evaluation of the measurements during experiment 2 is based on 10-minute averages the observed variations are significant.

- p.8103 (Table 1): Surprisingly, the pressure drop for the cylinder described as leaky is the same as for the two other steel cylinders. The leaking cylinder has been replaced during the experiment but apparently not been excluded, as the results are listed anyhow in Table 2. This leaves the reader with the question whether the leak does not have the potential to provoke an additional drift.

This is an interesting remark. Indeed the pressure drop is the same but within a much shorter time and indicates a leak indeed. It is surprising that this does obviously not lead to a strong

difference in the derived thermal dependence, though the value for CO_2 is the highest observed. A reason for this behaviour might be that there is no fractionation associated with the leak or it remains constant and lead only to a common shift of the concentration values but would not alter the temperature induced values. We have included the following sentences in the main text under the Results section (experiment 2).

All other measured gas species, i.e. CO, CH_4 and H_2O showed no temperature dependence as documented in Table 2, except for H_2O of the steel cylinder LK548528 that had to be replaced due to a leak. It is surprising that the leak obviously had no or at least not a strong effect on the derived thermal dependence, though the value for CO_2 is the highest observed. A reason for this behaviour might be that there is no fractionation associated with the leak (less plausible) or it remains constant and led only to a common shift of the concentration values but would not alter the temperature dependence.

- The pressure drop for the replacement cylinder is more than double compared to the other three steel cylinders although it is stated that it was included only for part of the time.

There was a mistake in table 1. The correct pressures for the replacement cylinder LK535353 are >170 bars at the start of its usage during the experiment and 155.5 bars after it. Since the first pressure was taken at 45°C it is higher than the other pressures taken at 22°C. We added the following note to the caption of table 1.

[#] The pressure reading was made at 45°C, the pressure comparable to the other pressure readings taken at 22°C will be lower.

- p. 8092, l. 19-22: "Unlike the steel cylinder, aluminium cylinder did not show any desorption effect for H2O and CO and a hardly visible effect for CH4 as displayed in Figure 5. However, it has to be stressed that the H2O and CO mole fraction were very low and further experiment should be done in particular for CO including steel and aluminium cylinders." The CO and H2O diagrams in Figure 5 show negative mole fractions (raw reading from the analyzer) which do not make physical sense. These data show that the instrument is at its limit of detection or that its precision is not sufficient at that level to make a meaningful measurement. I do not see the information content in displaying these data. They should be removed.

We only partly agree with the reviewer 2. Negative raw readings of the analyser are not necessary meaningless. It depends on the factory calibration or user settings. Low concentrations can easily be offset by an insufficient calibration in this low range and lead to negative readings. Only when a blank is included in the calibration curve one can exclude it, but this rarely done. Therefore, we would like to keep the data and the explanations.

- p. 8094, l. 11f: "..which might point to a small contribution of thermal diffusion on measured CO2 mole fraction.." It is not clear to me on what basis the argument is made that the impact of this phenomenon has a small impact on the observed small changes.

We agree with the reviewer 2 that the statement requires additional explanation. Therefore, we added the following sentences to the revised manuscript:

The significantly lower correlation ($r^2 < 0.75$) than for the steel cylinder (Figure 7) can only partly be explained by the very small effects observed for the aluminium cylinders ($\Delta CO_2 < 0.04$ ppm) since the measurement repeatability is below 0.006 ppm as documented by the reference cylinder (CA03901). This calls for additional influences. The fact that there are small offsets observed for the CO_2 concentrations for positive and negative temperature gradients (dotted red lines in Figure 8) may indicate a temperature driven influence. A small

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contribution of thermal diffusion on measured CO_2 mole fraction [Keeling et al., 2007] as discussed above can therefore not be excluded and requires further attention, e.g. regarding temperature distribution on regulators.

- In the caption of Table 1 the statement is made: "Note that no pretreatment of the cylinder has been applied, i.e. no steam cleaning,..". One step in the production of aluminium high-pressure cylinders is a heating and subsequent quenching using water, new cylinders are generally hydrostatically tested, there are proprietary cleaning procedures employed by manufacturers. So the quote from the caption rather states that the cylinder pretreatment is not known. The question would rather be if the cylinders had been new or what has been their filling history.

We fully agree with the reviewer 2 and re-formulated the caption as follows:

Table 1. Cylinders used for the two experiments with their identification and trace gas mole fractions. Note that the absolute values of both CO and H_2O are of lower quality due to values close to the lower end of the measurement range. * Due to a leak cylinder LK548528 had to be exchanged with cylinder LK535353 during the experiment. Note that no pretreatment of cylinders has been applied by us, i.e. no steam cleaning, surface conditioning or finishing except those applied by the supplier (see main text). Values displayed in Figures are non-calibrated values.

Furthermore, we re-formulated the description in the Method section:

We used 50 liter tempered steel (34CrMo4) cylinders equipped with a standard brass valve K44-8 from VTI with Peek as spindle sealing material. The regulator connection type is G 5/8" RH female thread from Carbagas Switzerland. Gas wetted materials for these cylinders are steel, brass and Peek. The aluminium cylinders are new 30 liter Scott-Marrin Luxfer (AA 6061 T6) cylinders equipped with a brass valve D 202 from Rotarex with PA as spindle material. The regulator connection type is CGA-590. Gas wetted materials are aluminium, stainless steel, brass and PA. No additional pre-treatment of the inner surfaces were applied except these applied by the supplier and producer that we do not know in detail and these given above. The steel cylinders were filled by Carbogas according to their protocol. We do not know the filling history of these cylinders except that they are used for compressed air fillings only. The aluminium cylinders were pumped to roughly 10 mbars and then flushed and pressurised to 10 to 15 bars using dry compressed air with ambient concentrations three times and then filled with dry compressed air from another cylinder again at ambient concentrations. CB09877 prepared similarly at Empa and was additionally blended by a second compressed air. CA03901 was prepared at Boulder by NOAA/CMDL according their protocol.

- The caption of Figure 4 explains that the Joule-Thompson cooling effect. The cooling takes place at the point of the pressure expansion of the gas, i.e. the pressure regulator; why is the regulator temperature above the cylinder temperature?

As obvious from Figure 1, the temperature is always in a transient situation since the time of two hours is obviously too short to guarantee a thermal equilibrium of the whole system, cylinder, regulator etc. The present setup does not exclude that the cylinders and regulator exhibit different temperatures. Due to the smaller heat capacity of the regulator, we expect a faster equilibration than for cylinders.

- Fig. 6: The CO2-deviation for aluminium cylinders is between +0.01 ppm at cold and -0.01 ppm at warm temperatures. Despite the known precision and stability of the CRDS analyzers this is a very small signal and it would be more convincing if also the actual data and not only the linear correlation line were presented also for the aluminium cylinders, not only for steel cylinder 1 (e.g. as supplemental material - for

clarity reasons, the figures could be split in a and b).

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We do not agree with the reviewer in this point. In our view all relevant information is given in the manuscript. In Figure 6, there is the scatter of data given for cylinder 1 (steel cylinder) which is similar for the other steel cylinders. Similar, in Figure 8 the scatter of the data is given for cylinder 2 (aluminium cylinder) which again is similar to the other aluminium cylinders. However, we changed the caption of Figure 6 as follows to accommodate this information of the aluminium cylinder 2.

Figure 6: Temperature dependence for the CO_2 mole fraction deviations from their corresponding value at 20°C (T_0) for the steel cylinders 1, 3, 5, 5*, increasing values (left y-axis) as well as for aluminium cylinders 2, 4, 6, decreasing values (right y-axis). The y-axes are different by a factor of 40. For clarity reasons measurements are only given for cylinder 1 (measurements for cylinder 2 are displayed in Figure 8) together with its linear correlation line, whereas for the other cylinders linear correlations lines are given only. The temperature dependencies vary between 0.0014 to 0.0184 ppm / °C for steel and -0.0002 to -0.0003 ppm / °C for aluminium cylinders

Specific and Technical Comments with respect to the discussion of the results:

The experimental observations are directly put in the context of the theoretical framework considered in the introduction assuming that surface physisorption on a metal surface is the dominant effect:

- p. 8090, l. 22: "..where CO2, ad corresponds to the adsorbed CO2 molecules on the wall.."
- p. 8091, l. 3f: "These values can be compared with a monomolecular layer of CO2 molecules on the inner cylinder wall area.."
- p. 8091, l. 22-25f: " The effect of adsorption is significantly less on aluminium than on steel surface, only about 35% of the adsorption sites are occupied. This further supports our approach to use the Langmuir model for a monomolecular layer in contrast to a multi-layer coverage."
- p. 8095, l. 12f: "The determined energy value underpins that the observed adsorption mechanism is physisorption only."
The perception of the inner surface of an aluminum cylinder as a metal surface is not appropriate. Aluminium surfaces are generally covered by a small aluminium oxide layer that may contain hydroxyl groups. Such a surface clearly has a large potential to rather form strong chemisorption (hydrogen bonds, lewis acid - base bonds) particularly with water molecules. Yet, these processes are not considered at all. Therefore, the following conclusion seems premature:

p. 8094, l. 18-20: " The experiments performed clearly demonstrate that the aluminium cylinders are significantly more robust against adsorption/desorption processes for CO2, CO, CH4 and H2O than steel cylinders."

We only partly agree with the reviewer 2. Of course the aluminium surface is by far not sufficiently characterised by a metal surface and we actually expected for our experiments chemisorption effects with higher energies involved than physisorption. However, observations are in agreement with an adsorption by physisorption based on the low energies involved that are significantly lower than energies for chemisorption. Furthermore, we expected higher adsorption rates for CO than CO_2, but again this was not the case, at least with our limited experiments.

In the introduction section, the authors have listed the assumptions that are the basis for the Langmuir model (p. 8087, l.4-7) and concede that these assumptions are often not fulfilled (p. 8087, l.15). This simplification of the Langmuir model is not at all

discussed in the results section, e.g. the competition of different gas species (like H2O and CO2 molecules) on surface sorbent sites is not considered. The different air mixtures used in the test had varying water contents (as specified in Table 1) and this could have an influence on the CO2 sorption in each test gas.

Such the validity of the conclusions drawn is questionable. The fact that the model provides a formula that can be used to fit the data by itself is no convincing proof.
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We do not agree with the reviewer 2 that the conclusion is questionable. However, it is simply not possible to investigate all of the many different facets of adsorption/desorption phenomena. We were already happy to come up with a convincing explanation for the steel cylinders which also seems to be valid for the aluminium cylinders. Of course there will be a competition between the molecules for the adsorption sites. But again, we were very much surprised that CO (with our limitation regarding the concentration range) exhibiting a lower tendency for adsorption. We added the following remark to the introduction:

The four assumptions listed by Langmuir are often not fulfilled, in particular assumption (iv), but a in depth discussion of this issues would exceed the scope of this publication. Yet in our experiments we found a good agreement with this simplified adsorption theory.

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Further Technical Comments:

- p. 8084, l. 11: " We proved the pressure effect on physisorption..". The statement should be modified or removed as the presented evidence in the manuscript is no real proof.

We see the argumentation of reviewer 2 and modified the sentence to:

Our observations from decanting one steel and two aluminium cylinders completely are in agreement with the pressure dependence of physisorption for CO_2, CH_4 and H_2O.

- p. 8084, l. 13: Inaccurate language generates an ambiguity, either: "The CO2 results for both aluminium cylinders ..." or "The CO2 results for both cylinder types are in excellent agreement ..."

thank you, done (second choice is correct)

- p. 8084, l. 15f: The language is inaccurate: describing adsorption in units of ppm does not make sense: all quantitative statements only have a meaning in combination with dimensions of the used cylinders. It is disputable that there is no sorption of H2O on the aluminium cylinder inner surface (0 ppm), and 0 ppm is not 10 times less than < 2.5 ppm.

We agree with the reviewer 2 and reformulated it. It reads now:

However, concentration changes due to adsorption on aluminium (< 0.05 ppm and 0 ppm for CO_2 and H_2O) were significantly lower than on steel (< 0.41 ppm and about < 2.5 ppm, respectively).

- p. 8084, l. 16: "The CO2 amount adsorbed..."

done

- p. 8084, l. 20: Inaccurate language: the reference for "latter dependence" is not clear

Yes, we agree and reformulated this part. It reads now.

Adsorption/desorption effects were minimal for CH_4 and for CO but requires further attention since it was only studied on one aluminium cylinder with a very low mole fraction.

- p. 8084, l. 25-28: "The reversed temperature dependence for aluminium cylinders point to significantly lower desorption energies than for steel cylinders and might at least partly be due to temperature and gas consumption induced pressure changes."
I was confused why there would be a difference in temperature and gas consumption induced pressure changes between aluminium and steel cylinders and therefore suggest to re-phrase this like e.g.:
"The reversed temperature dependence for aluminium cylinders may point to significantly lower desorption energies than for steel cylinders that are covered by temperature and gas consumption induced pressure changes within the experimental set-up."

Principally we agree but the reviewer's suggestion is not adequate. It reads now:

The reversed temperature dependence for aluminium cylinders point to significantly lower desorption energies than for steel cylinders and due to the small values they might at least partly be influenced by temperature, permeation from/to sealing materials and gas consumption induced pressure changes.

- p. 8089, l. 19: "Both CRDS instruments were frequently calibrated.."

done

- p. 8091, l. 8f: "It is interesting to note that the adsorbed water amount is about five times bigger.."

done

- p. 8090, l. 22: "CO2, ad corresponds to the adsorbed CO2 molecules on the wall, expressed as CO2 mole fraction times the occupied adsorption sites."
The description of the term CO2, ad is confusing; if this quantity means a number of molecules but is expressed as mole fraction any number can only be referred to a particular point of time within the decanting experiment. So the statement p. 8091, l. 22 has to be specified:

We agree, $CO_{2,ad}$ corresponds to the value at pressure P_0. See also eq. (A3), in which we defined it. We change it accordingly.

…where $CO_{2, ad}$ corresponds to the adsorbed CO_2 molecules on the wall, expressed as CO_2 mole fraction times the occupied adsorption sites at pressure P_0.

p. 8091, l. 22: "derived values of 0.047 ppm for CO2, ad at the start of the experiment ..."
No, we disagree. $CO_{2,ad}$ is not changing during the experiment. The adsorbed CO_2 does, but this is expressed by the first term of eq. 5.

- p. 8093, l. 5f: "Hence no influence on the temperature dependencies is expected for steel cylinders."
I was confused why the physical processes described in p. 8092, l. 29 - p. 8093, l. 8 should depend on the metal. A rephrasing could help: "The relative influence on the temperature dependency observed for steel cylinders is expected to be minor."

We agree and changed it accordingly.

- p. 8095, l. 1-2: "The community is generally aware of this influence but it has not yet been quantified properly." There has been an evaluation of this effect by the WMO central calibration laboratory (Huilin Chen: Long-term stability of calibration gases in cylinders for CO2, CH4, CO, N2O, and SF6; http://ggmt-2013.cma.gov.cn/dct/page/70029). This evaluation did not find a generally very large increase in CO2 mole fractions in cylinders vented to low pressures.

Thank you, we reference it and reformulated the sentence to:

Therefore, special attention has to be given to which end pressure the cylinders should be used for calibration purposes. The community is generally aware of this influence that has been investigated Chen et al., 2013 but it has not yet been quantified properly.

- Table 1: Are two decimals in bar for the pressure meaningful?

We agree and changed it accordingly.

- Figure 1: The definition of "actual temperature" and "set temperature" is not selfexplaining; re-phrasing the caption would make it easier to understand: "the actual temperature follows the set temperature with a delay of 2.75 h (bold blue line accounting for the time shift)

Thank you, done

- Figure 4 last line of caption: "..cannot be determined.."

done

- Figure 5: The displayed uncalibrated data for CO and H2O are partly negative mixing ratios (raw reading from the analyzer); the relative precision of the analyzer at these mole fractions is on the order of tens of percents compared to 0.01% relative for CO2 and 0.02% relative for CH4. Therefore the statement "CO and H2O show no ...desorption effect" should be replaced by "no effect of CO and H2O can be detected given the limitations of the analyzers signal-to-noise at that level". There appears to be a pretty similar increase of CH4 and CO2 below mole fractions of 404.4 ppm CO2 i.e. for the first 80 bars of pressure release. It is when venting the last 20 bar where the CO2 increase is decoupled from the CH4 trend.

We agree and reformulated the caption.

Figure 5: Emptying experiment within 8 hours: no effect of CO and H_2O can be detected given the limitations of the analyzers signal-to-noise at that level on this aluminium cylinder compared to the CO_2 mole fraction.

- Figure 6: The CO2-deviation for aluminium cylinders is between +0.01 ppm at cold and -0.01 ppm at warm temperatures. Despite the know precision of the CRDS analyzers this is a very small signal and it would be more convincing if also the actual data and not only the linear correlation line were presented also for the aluminium cylinders, not only for steel cylinder 1 (for clarity reasons, the figures could be split in a and b).

For clarity reasons we would keep it like this but referenced to the measurements of cylinder 2 (aluminium cylinder) in the Figure caption 6.

Figure 6: Temperature dependence for the CO_2 mole fraction deviations from their corresponding value at 20°C (T_0) for the steel cylinders 1, 3, 5, 5*, increasing values (left y-axis) as well as for aluminium cylinders 2, 4, 6, decreasing values (right y-axis). The y-axes are different by a factor of 40. For clarity reasons measurements are only given for cylinder 1 (measurements for cylinder 2 are displayed in Figure 8) together with its linear correlation line, whereas for the other cylinders linear correlations lines are given only. The temperature dependencies vary between 0.0014 to 0.0184 ppm / °C for steel and -0.0002 to -0.0003 ppm / °C for aluminium cylinders

- Figure 7, caption l. 3: "The slopes are corresponding.."

done

- Figure 8, caption l. 6-8: Suggestion for re-phrasing: "The correlation is rather bad (r2 = 0.6). Part of the variability might be due to temperature induced effects that are independent of adsorption/desorption phenomena."

Thank you, accepted.

- Figure 8, caption l. 8: "Hence desorption energies have to be taken with care." This should be reflected in the number of decimals of the slopes that are displayed.

Done.