S1 Supplementary material on analysis of CRDS data

In order to find the best strategy for the data interpretation and a suitable cut-off point presented in Sect. 3.1.1 , three methods were applied.

(i) using CO measurements and set the end point when the CO amount fraction starts to increase

5   (ii) setting a minimum gas inflow to the analyzer limiting the residence time in the cavity.

(iii) applying a method using the correlation between an internal variable of the analyzer (outlet valve) and measured variables (low pressure reading of the pressure regulator).

Since (ii) is already explained in Sect. 3.1.1, the details of the two other methods are presented here.

S1.1 Using CO measurements

10 The method is based on the assumption that the measurements of CO should not show an increase due to adsorption/desorption processes. This is a reasonable assumption considering previous experiments with big cylinders (unpublished data).

For each of the gas species, the deviation from the mean of the first hour of measurements was calculated, and then this was divided by the maximum of the calculated differences to obtain the normalized species (Fig. S1). For the low pressure side of the pressure regulator, the difference was calculated relative to the highest pressure, whereas for the outlet valve the

15 minimum value of 17500 was taken. A similar strategy to time of emergence (ToE), used in climate sciences to distinguish natural variability from climate change (Hawkins and Sutton, 2012), was adopted to separate instrumental noise of the CO measurements from the increasing signal. Firstly, a cubic smoothing spline was fitted to CO measurements. Then the point in time was calculated in which the difference between the smooth CO signal and the CO measurements was higher than the standard deviation of CO data during the first hour of the experiment. This time gave the 1-σ cut-off point, and the method is

20 called σ-method from here on. The analysis was done for all experiments which resulted in individual cut-off points for each experiment.

Relying on CO measurements has the disadvantage of the high noise level of > 5 nmol mol^{-1}. Applying this method on CH$_4$ measurements would be an alternative. However, implementation on CH$_4$ did not improve the results. Moreover, CH$_4$ measurements showed the decrease in amount fractions later than the increase in CO. The differences in the onset of the

25 increase or decrease can be related to the underlying mechanisms in the CRDS analyzer, such as outgassing of CO followed by a dilution effect in the cavity for CH$_4$. However, as already discussed in Sect. 3.1.1, the reason of this effect in the CRDS analyzer is unclear and needs further investigation of the materials surrounding the cavity as well as the cavity itself.
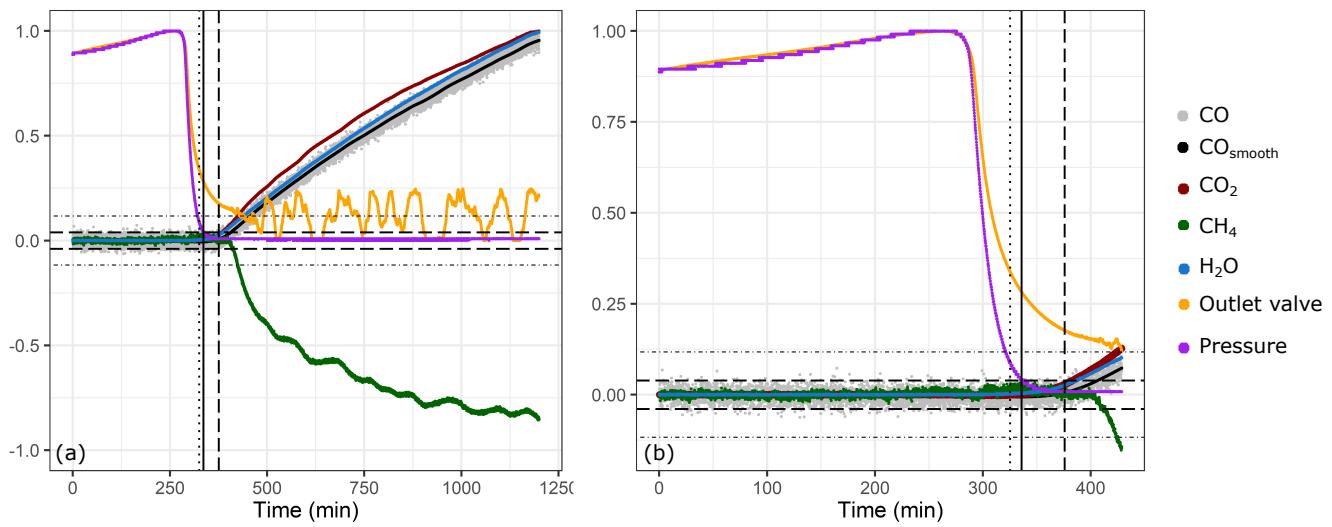
Figure S1. Normalized values of measured species, outlet valve and low pressure reading of the pressure regulator during the course of the experiment (**a**), and a zoom-in to first 450 minutes (**b**). Dot-dash lines indicate 3-σ of the CO measurements, dashed lines indicate 1-σ, solid lines show the 25000 outlet valve cut-off point and dotted lines denotes the correlation method

S1.2 Using correlation between two measured variables

This method is based on the correlation between the outlet valve value and the low pressure reading of the pressure regulator (Fig. S2). As the inlet pressure to the analyzer decreases, the CRDS analyzer regulates its cavity pressure through closing the outlet valve. These two variables are linked to each other as long as there is enough flow coming into the analyzer for the proportional valve to regulate. Towards the end of the measurements, the correlation between the outlet valve and the pressure reading breaks, and these parameters are not physically linked anymore. In order to calculate the point in time where the measurements were still correlated, an algorithm was constructed. The algorithm is based on maximizing the coefficient of determination (r^2). It started by calculating the linear regression parameters between the low pressure and the outlet valve data for the range where the outlet valve values are between 30000 and 40000, indicated by the blue region in the Fig. S2a. In this region these two parameters should be correlated, and sufficient flow conditions should be present. To this interval, consecutive data points were added step-by-step, and the fit was recalculated. From the calculated fits, the range which yields the highest r^2 was selected. The last data point added to this range determined the cut-off point. Then, to this range, the measurements at the beginning of the experiment was added, since under the initial conditions there was sufficient flow through the analyzer. This yielded the total range of included data for this method (Fig. S2b). Since the correlation method is based on maximizing the coefficient of determination (r^2) for the linear fit, it is capable of capturing the linear relation, however the validity of such linear dependency is not confirmed. For instance, a time lag in the response of the outlet valve would not follow linear response. Moreover, a cut-off point based on low pressure reading would incorporate the variations in the pressure measurements, since the pressure data is measured relative to atmospheric pressure.

In order to highlight the differences between the three methods, Fig. S1 shows all cut-off points as vertical lines. Using the σ-method resulted in cut-off points later in time, whereas using the correlation approach was the most conservative approach in cutting the data. The methods excluding the 25000 cut-off point yieldeed individual cut-off points for each experiment. In Fig. S3 the distribution of the cut-off points is presented. This clearly illustrates the difference between the two approaches, whereas the value 25000 is closer to outlet valve-low pressure correlation method.

As explained in Sect. 3.1.2, we have validated that using the CO amount fractions did not act early enough to distinguish the instrument related effects from the desorption signal. Nevertheless, we present the results for these two other methods (Fig. S4 and Fig. S5). These results can be interpreted by using Fig. 3: the later the cut-off point, the larger will be the enrichments in the amount fractions of CO_2 and H_2O. One-hour difference between the cut-off points from the σ-method and the outlet valve low pressure method explains the observed differences between the maximum amount fractions observed for the experiments. The difference between the methods were up to 1.1 μmol mol^{-1} for CO_2 (14 bar experiment after heating) and up to 300
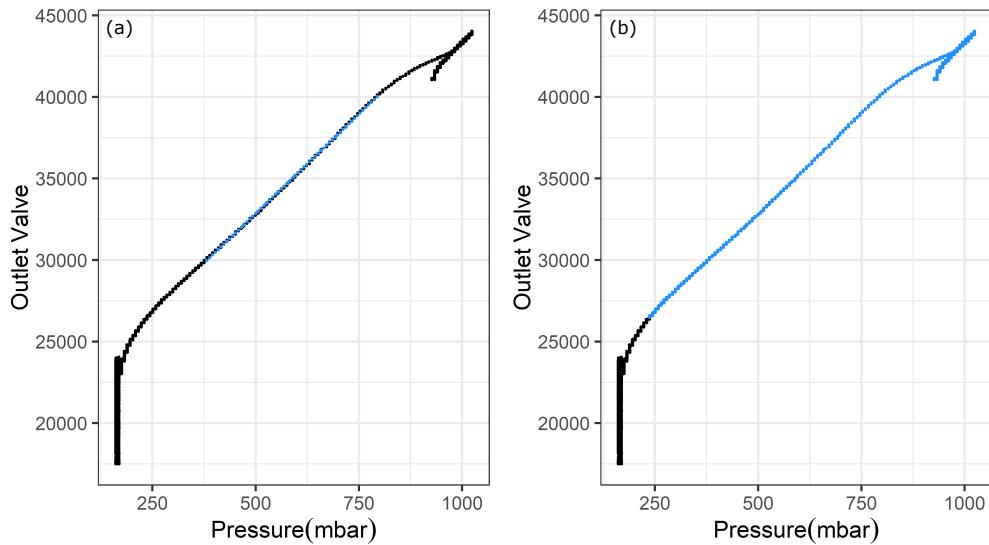
Figure S2. The initial conditions for the correlation method. Blue region indicates the included data at the beginning **(a)**, and data to be included after the algorithm **(b)**
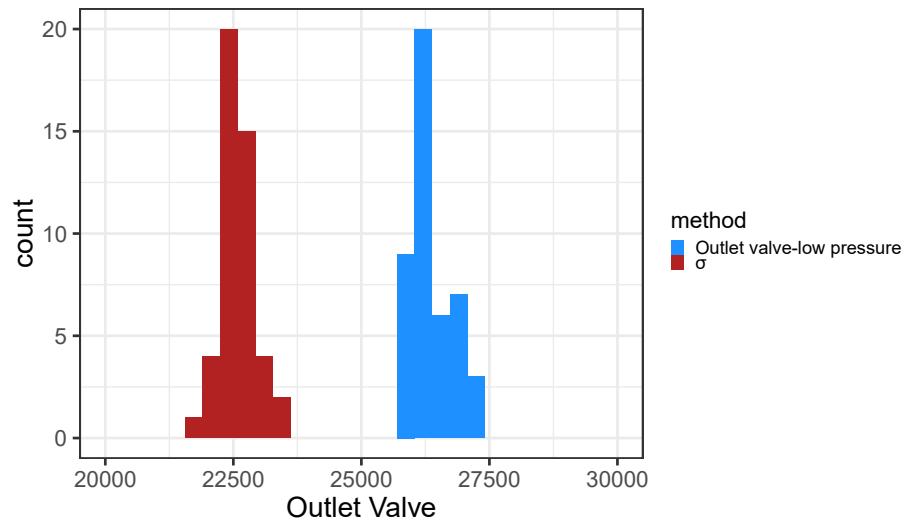
Figure S3. Distribution of the cut-off points using the two methods

µmol mol^{-1} for H_2O (3.5 bar experiment with mass flow meter). Using the σ-method should limit any significant enrichments of CO, since the method is based on tracking the increase in CO amount fractions. However, a slight difference of 2 nmol mol^{-1} is observed for CO measurements between the two methods (Fig. S4 and Fig. S5).

On the hand, the differences between the correlation method and the fixed outlet valve value of 25000 are small. For CO_2, the differences for the aluminum cylinder were less than 0.1 µmol mol^{-1}, whereas for the steel cylinder they were slightly bigger amounting to 1.25 µmol mol^{-1}. The mean of the differences between the two methods were 0.3 nmol mol^{-1} and 0.1 nmol mol^{-1} for CO and CH_4 respectively. For H_2O a mean difference of 6 µmol mol^{-1} was calculated when all experiments except the runs with mass flow meter were taken into account. The runs with MFM showed differences as high as 40 µmol mol^{-1}. The higher increase was related to steeper slope of H_2O enrichment when MFM was placed prior to the analyzer. It is important to note that the differences between the fixed outlet value of 25000 and the outlet valve pressure correlation method do not result in significant changes in the interpretation of data presented in Sect. 3.2.
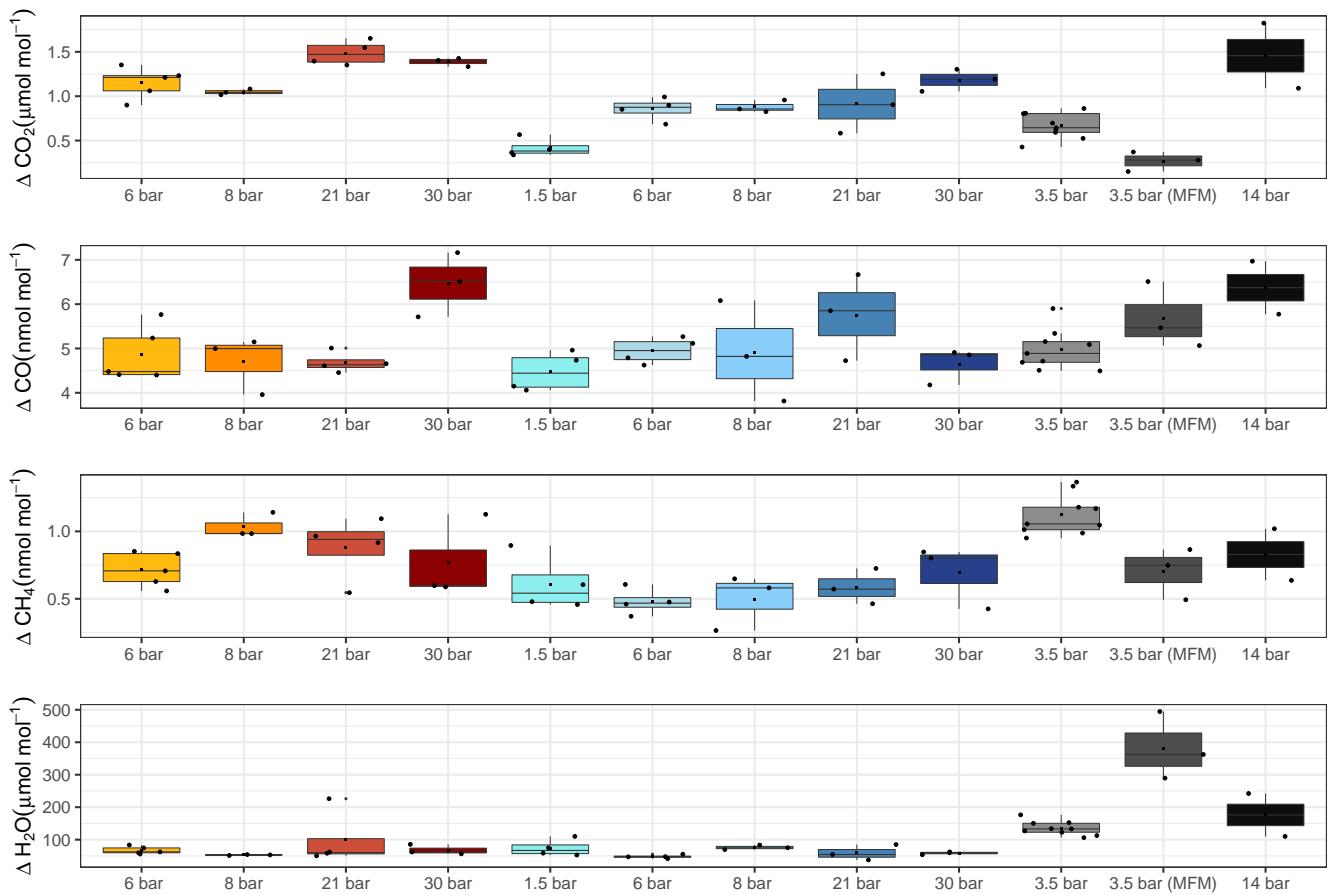
Figure S4. Box plots for all experiments for the species CO_2, CO, CH_4 and H_2O using the σ-method
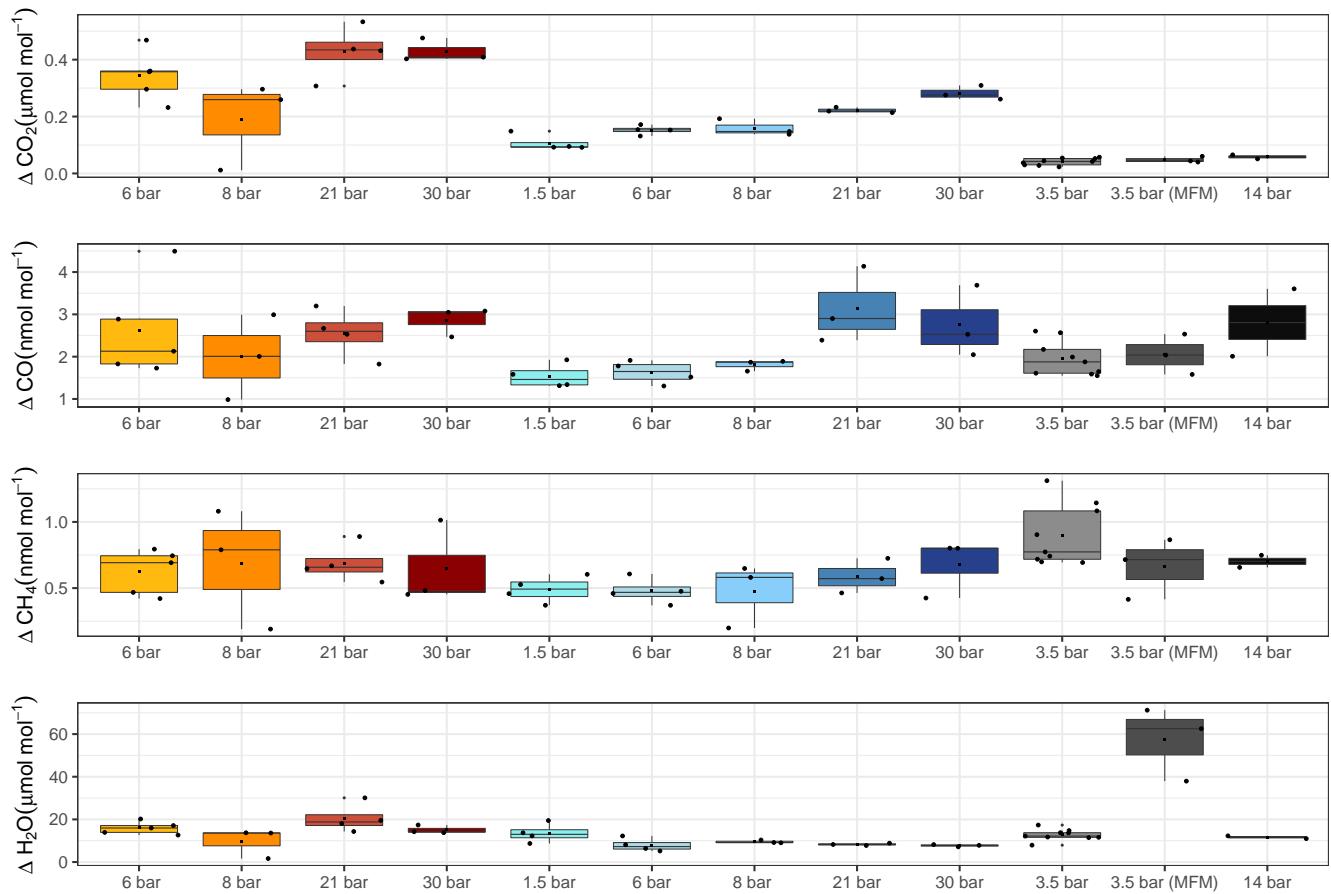
Figure S5. Box plots for all experiments for the species CO_2, CO, CH_4 and H_2O using the outlet valve - low pressure method

S2   Correction for the measurements

As explained in Sect. 3.2, the measurements after heating for the aluminum cylinder showed a downwards trend in the amount fractions of CO_2. Figure S6 and S7 show the evolution of this downward trend for experiments with aluminum cylinder before and after the temperature experiments. The evolution of the cavity pressure with respect to cylinder pressure and the outlet

5   valve value was similar in both cases, which supported that this behavior was related to a lag in response time of the outlet valve. However, the enrichment in the amount fractions was significantly different among the two cases. The measurements at 8 bar before heating showed a dip in the measured amount fraction in the order of 0.05 µmol mol^{-1}. This negative difference was compensated by a steep increase in the amount fraction of CO_2. Whereas, for the experiments after heating the dip in the observations was as high as 0.1 µmol mol^{-1} and the decrease was not recovered as fast as in the previous experiments. This is

10   presumably related to the lower amount of CO_2 molecules adsorbed to the surface.

A linear correction based on the cavity pressure and the observed negative deviations from the starting amount fractions was applied. The deviations were corrected with slopes varying from -1.93 to -0.75 µmol mol^{-1} Torr^{-1} for the experiments after the heating. Figure S8b shows the corrected amount fractions. The application of a correction function is non-trivial, since the amount fraction response at lower cavity pressures cannot be explained in its full extent by a linear function. Therefore, despite

15   the correction function, a slight decrease (in the order of 0.05 µmol mol^{-1}) in the amount fractions of CO_2 is still present.
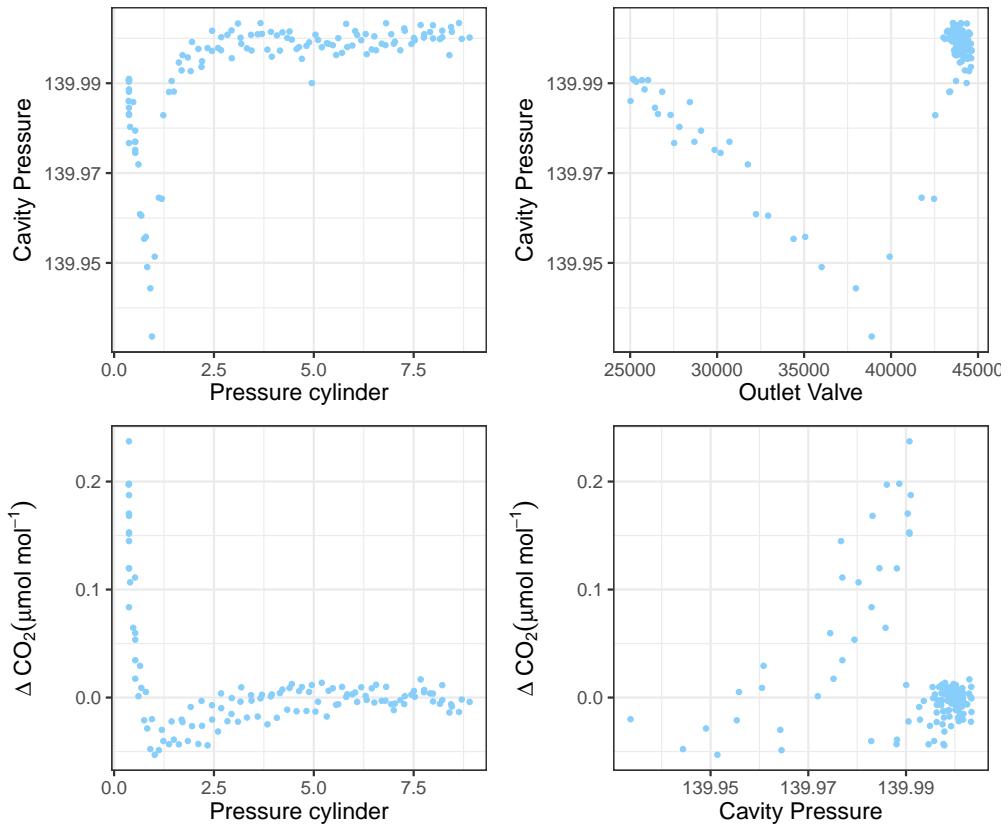
Figure S6. Response of CO_2 amount fraction to changes in cavity pressure for the aluminum cylinder filled at 8 bar before heating. To make it easier to follow, same color codes are used for all experiments presented in this study.
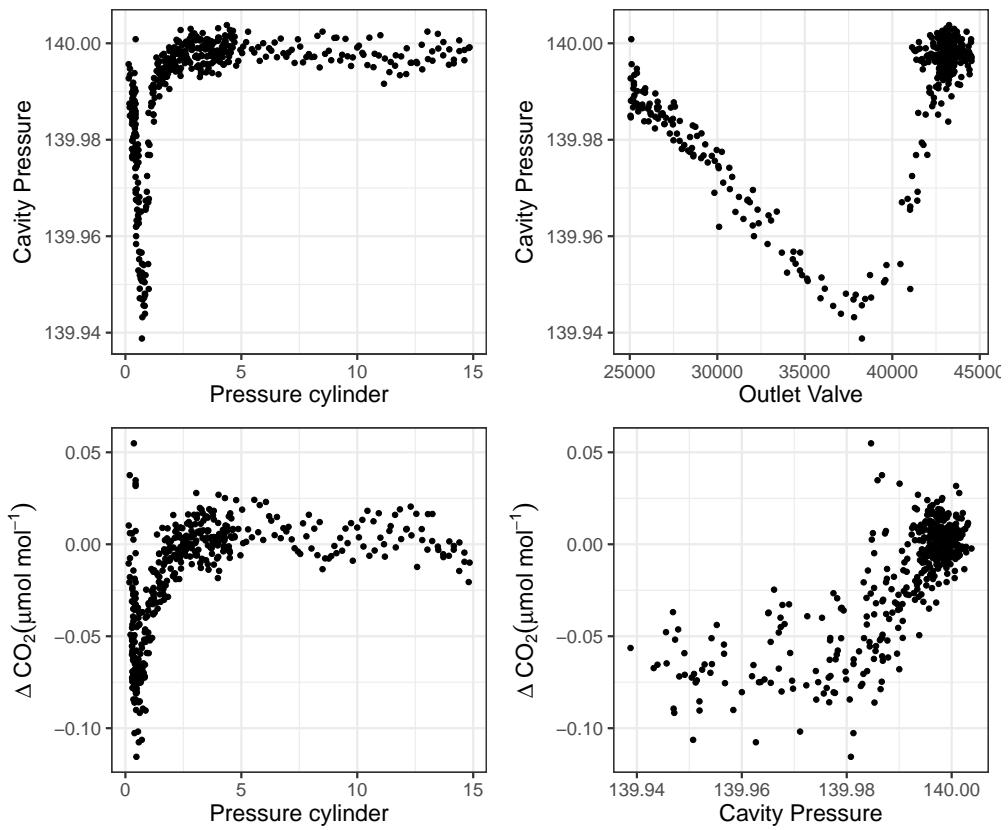
Figure S7. Response of CO_2 amount fraction to changes in cavity pressure for all experiments after the heating for the aluminum cylinder. To make it easier to follow, same color codes are used for all experiments presented in this study.
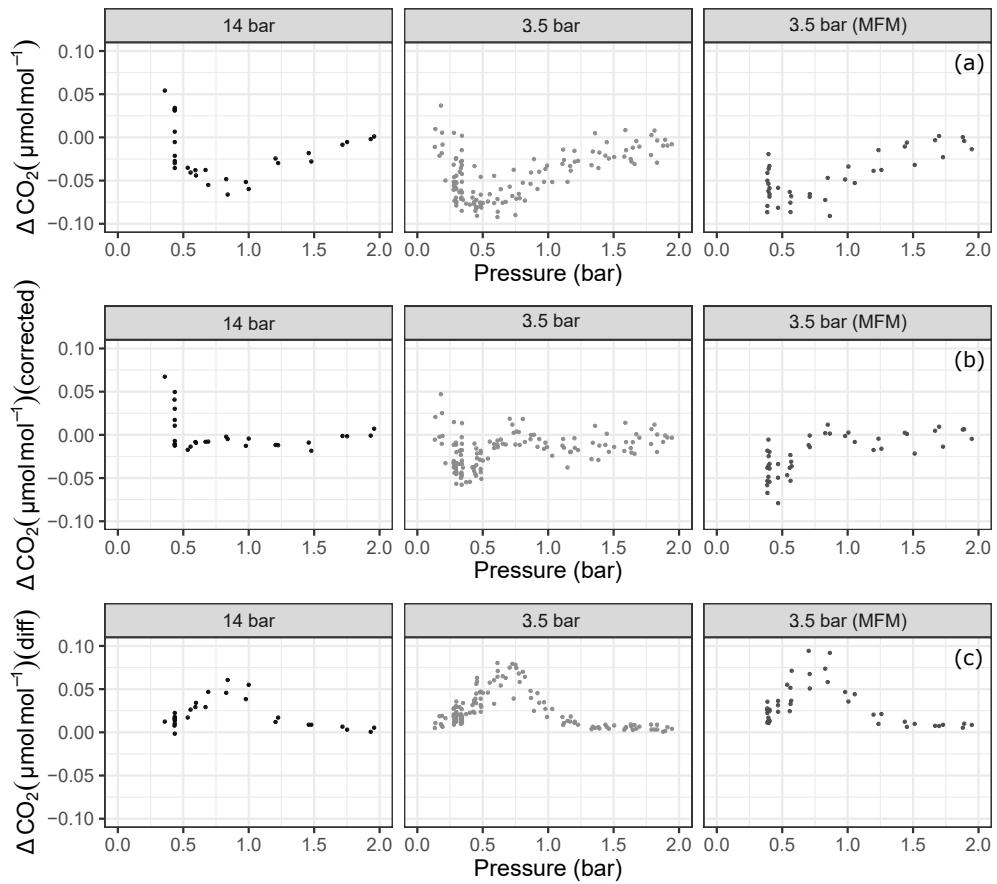
Figure S8. Zoom-in to the region in which the correction is significant. **(a)** Uncorrected, **(b)** corrected, and **(c)** the difference between the two values for the CO_2 amount fractions. To make it easier to follow, same color codes are used for all experiments presented in this study.

References

Hawkins, E. and Sutton, R.: Time of emergence of climate signals, Geophysical Research Letters, 39, L01 702, https://doi.org/10.1029/2011gl050087, 2012.