**Pressure Dependent $CO_2$ Enrichment in High-pressure Aluminum Cylinders**

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The primary standards to maintain the World Meteorological Organization (WMO) carbon dioxide ($CO_2$) X2007 scale as well as the secondary and the tertiary $CO_2$ standards to pass the scale down are stored in high-pressure aluminum cylinders. To meet the WMO's accuracy goal of ± 0.1 µmol mol$^{-1}$, it is crucial that the standards are stable during their whole life time. At field stations but also in laboratory experiments, standard gases showed $CO_2$ enrichment with decreasing pressure, which was most probably caused by either desorption of $CO_2$ from the cylinder walls with decreasing pressure or Rayleigh distillation. If these enrichment effects are reproducible, a function could be applied to correct the enrichment effects of the cylinders and improve the accuracy of the $CO_2$ measurements calibrated with these standards.

To investigate the $CO_2$ enrichment effects, a batch of eight high-pressure aluminum cylinders is repeatedly filled at NOAA's Niwot Ridge station with pressurized ambient air. After delivery to the laboratory and reaching thermal equilibrium, they are decanted while the $CO_2$ mole fraction is measured continuously. The obtained data is used to prove whether the $CO_2$ enrichment is reproducible or not, and to determine whether it is possible to find a useful general correction function.

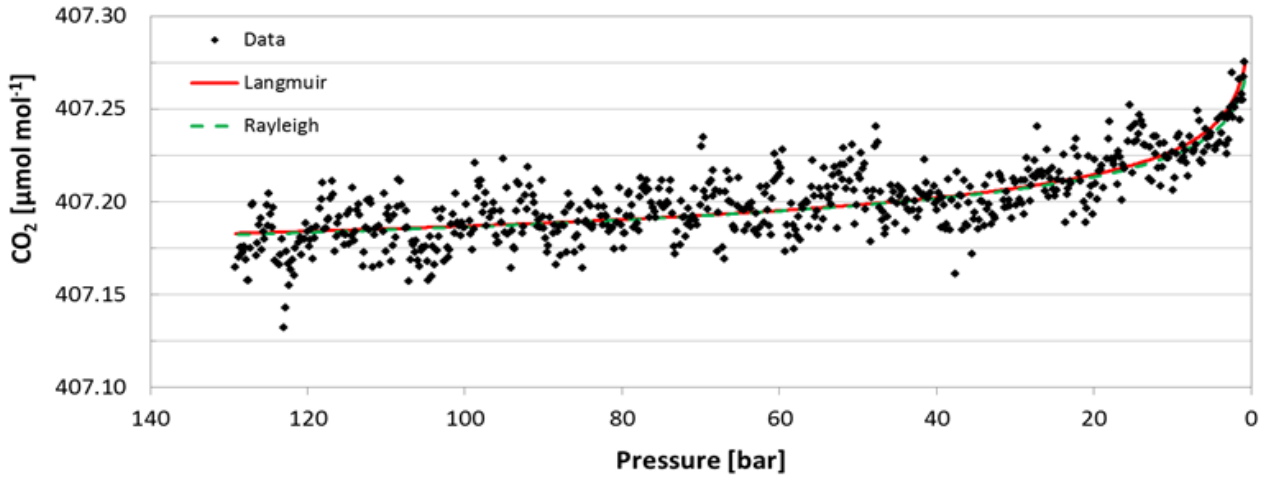


**Figure 1.** Example for the enrichment of the $CO_2$ mole fraction with decreasing pressure in air decanted from an aluminum cylinder as used to store $CO_2$ standards. The black dots represent measurements, the red line corresponds to a best fit according to the Langmuir adsorption/desorption function, and the green dashed line represents a best fit according to the Rayleigh distillation function.