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13C and 18O isotope effects resulting from high pressure regulation and CO_2 cylinder depletion

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Global observatories and research stations measure atmospheric gases, such as CO_2, to provide critical data for global climate change models. The models rely on precise and accurate isotopic measurements to help differentiate the various CO_2 sources and sinks. These measurements are typically made with an Isotope Ratio Mass Spectrometer (IRMS) which requires stable isotopic standards of CO_2.
An equilibrium isotope fractionation within the liquid-vapor system of carbon dioxide as a function of temperature for both C and O isotopes is well established and has been for many years (i.e. Grootes, et. al. [1969], Z. Physik 221). Carbon isotopes tend to be enriched in 13C in the vapor phase while Oxygen isotopes tend to be depleted in 18O in the vapor phase. This observation has particular relevance in contemporary stable isotope laboratory practices due mainly to the advent of Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS) techniques. For 13C and 18O measurements, CF-IRMS relies almost exclusively on incorporating a high pressure cylinder of CO_2 as a calibrated internal reference gas. If reference gas contains a liquid phase, the laboratory's ability to produce reliable isotope data will be dependent on whether the isotopic composition of the CO_2 vapor phase will change during depletion of that CO_2. Intuitively, one may presume that as the liquid CO_2 within that cylinder decreases, the vapor produced from that liquid will change isotopically to reflect known isotopic fractionation between those phases.

This presentation will quantify isotopic fractionations for both 13C and 18O as a function of CO_2 cylinder depletion. CO_2 vapor samples from the cylinder that contains both liquid and vapor phases will be taken regularly and measured for both 13C and 18O via Dual Inlet-Isotope Ratio Mass Spectrometry. The carbon dioxide will be depleted during sequential sampling and resulting cylinder contents monitored gravimetrically. Observed isotopic effects (fractionation) of the vapor from the depleted CO_2 cylinder will be reflected in the 13C and 18O composition of that vapor. Thus the last remaining liquid within the cylinder, as confirmed gravimetrically, will likely show the largest isotope effect. Additionally, data will be presented to illustrate with selection of the appropriate regulator, pressure reduction can be achieved without fractionation. This data will help to ensure that data of the highest quality data is obtained from these measurements.