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Direct, Precise Measurements of Oxygen-17 Anomalies in CO2 Using VCOF-CRDS

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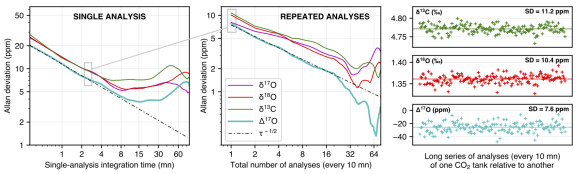

Triple oxygen isotope analyses of CO2 are a challenge for mass spectrometers because of isobaric interference between 16O13C16O and 16O12C17O. Using spectroscopic methods, each CO2 isotopologue is uniquely described by its distribution of masses and roto-vibrational frequencies, potentially providing simple, direct, non-destructive measurements of δ13C, δ18O and Δ17O on small samples of CO2. It remains technically challenging, however, to constrain istopologue abundances from infra-red absorption spectra with precision levels of <10 ppm, as required by many geochemical applications. Here we report the latest results documenting the repeatability, linearity and accuracy of Δ17O measurements by V-shaped Cavity Optical Feedback Cavity Ring-Down Spectroscopy (VCOF-CRDS), a novel technique combining the excellent absorption linearity of CRDS with state-of-the art spectral stability and selectivity [1,2].

By using different laser diodes, all locked to a single ultra-stable V-shaped cavity, we are able to select optimal absorption lines to probe each isotopologue of interest. Our instrument currently performs simultaneous analyses of δ13C, δ18O and δ17O with external repeatabilities of 10 ppm and Δ17O at 8 ppm by alternating 150-s-long measurements between unknown samples and a working reference gas, with each unknown-to-unknown cycle requiring 10 min. Analyses of one pressurized tank of CO2 against another one over long time series display excellent Δ17O stability (SD = 7.6 ppm) at time scales exceeding 24 h (155 analyses). We will also report the results of our ongoing tests of linearity and accuracy, based on carbonate reference materials and CO2 isotopically equilibrated with independently-constrained waters with known Δ17OVSMOW values ranging from -95 to +32 ppm.

[1] T. Stoltmann, M. Casado, M. Daëron, A. Landais & S. Kassi (2017). Direct, Precise Measurements of Isotopologue Abundance Ratios in CO2 Using Molecular Absorption Spectroscopy : Application to Δ17O. Analytical Chemistry. 10.1021/acs.analchem.7b02853

[2] S. Kassi, T. Stoltmann, M. Casado, M. Daëron & A. Campargue (2018). Lamb dip CRDS of highly saturated transitions of water near 1.4 μm. The Journal of Chemical Physics. 10.1063/1.5010957