Oxygen-17 excess ($\Delta^{17}O$) in carbonate minerals can provide valuable insights into past continental and marine environments, long-term trends in the temperature and oxygen-isotope composition of ancient oceans, isotopic disequilibrium effects in biogenic and abiotic carbonates, and cryptic diagenesis. Triple oxygen isotope analyses of carbonates and/or CO$_2$ using isotope-ratio mass spectrometers (IRMS) remain challenging, however, because of isobaric interference between 16O13C16O and 16O12C17O. Using spectroscopic methods, the abundance of each CO$_2$ isotopologue may be directly quantified, potentially providing simple, non-destructive measurements of $\delta^{13}C$, $\delta^{18}O$ and $\Delta^{17}O$ on small samples of CO$_2$.

Here we report new data characterizing the application of VCOF-CRDS (V-shaped Cavity Optical Feedback - Cavity Ring Down Spectroscopy [1]) to the analysis of small samples (<40 μmol) of pure CO$_2$, as typically produced by phosphoric acid digestion of carbonate minerals.

Instrumental drifts from various sources are observed to bias apparent isotopic abundances by a few tens of ppm, but these drifts are slow enough that they may be precisely monitored and corrected for by repeated analyses of a working gas interspersed between other analyses, requiring only ~8 mn per aliquot and 30 mn between consecutive “unkown” analyses. This approach was tested by analyzing repeated aliquots of another CO$_2$ tank with a different isotopic composition, yielding instrumental repeatabilities of 12 ppm, 13 ppm and 7.4 ppm for $\delta^{13}C$, $\delta^{18}O$ and $\Delta^{17}O$, respectively (95 % CL, Nf = 66).

The accuracy of our measurements was tested over a wide range of $\Delta^{17}O$ values spanning 130 ppm, by analyzing CO$_2$ equilibrated at 25 °C with different waters whose triple oxygen compositions were independently constrained in the SMOW-SLAP scale by IRMS measurements and by simple nonlinear mixing predictions. We find that our $\Delta^{17}O$ measurements are well within analytical uncertainties of predicted values (RMSE = 1.2 ppm), with analytical repeatabilities (including isotopic equilibration and gas manipulation) of 8.6 ppm (95 % CL, Nf = 27).

We will also report the results of our ongoing investigation regarding the isotopic fractionation and analytical noise associated with different acid digestion protocols at different reaction temperatures, and the triple oxygen composition of various international reference materials.
already used for δ13C, δ18O, and clumped-isotope measurements.

Based on these results, we conclude that VCOF-CRDS offers excellent accuracy, along with state-of-the-art levels of analytical precision/linearity, for straightforward analyses of 17O excess in CO2, water, and carbonate minerals.

[1] Stoltmann et al. (2017) 10.1021/acs.analchem.7b02853