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Validating the use of VCOF-CRDS for precise & accurate triple oxygen isotope analyses of CO2, H2O and carbonates

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Oxygen-17 excess (Δ17O) 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. Using spectroscopic methods, the abundance of each CO2 isotopologue may be directly quantified measurements of δ13C, δ18O and Δ17O on small samples of CO2.

Here we report new data characterizing the application of VCOF-CRDS (V-shaped Cavity Optical Feedback - Cavity Ring Down Spectroscopy) to the analysis of small samples (<40 µmol) of pure CO2, 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. This approach was tested by analyzing repeated aliquots of another CO2 tank with a different isotopic composition, yielding instrumental repeatabilities of 12 ppm, 13 ppm and 7.4 ppm for δ13C, δ18O and Δ17O, respectively.

The accuracy of our measurements was tested over a wide range of Δ17O values spanning 130 ppm, by analyzing CO2 equilibrated at 25 °C with different waters whose Δ17O were independently constrained in the SMOW-SLAP scale by IRMS measurements and by simple nonlinear mixing predictions. We find that our Δ17O measurements are well within analytical uncertainties of predicted values (RMSE = 1.2 ppm), with analytical repeatabilities of 8.6 ppm (95 % CL, Nf = 27). We also present the results of our investigations regarding the isotopic fractionation and analytical noise associated with the acid reaction used to convert carbonate minerals into CO2. 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 Δ17O.

Finally, we report VCOF-CRDS measurements of the triple oxygen composition of various international reference materials already used for δ13C, δ18O, and/or clumped-isotope measurements, with non-trivial implications regarding the realization of the VPDB scale for δ13C values when using spectroscopic versus spectrometric methods.