

Progress Toward a Carbon Dioxide Laser Isotope Analyzer for Oxygen-17 Excess and Three Clumped Isotopologues: 638, 828 and 637

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Isotopic analysis using high resolution laser spectroscopy has been shown to be advantageous to multiple geochemical applications during the last decade. These advances include isotopic analysis of the bulk isotopic compositions of water, carbon dioxide, methane and nitrous oxide. More recently, laser spectroscopy has been used by several groups to examine the isotopic compositions of methane, carbon dioxide and nitrous oxide when carrying two rare isotopes (so called clumped isotopes). Our recent work has demonstrated highly accurate (~0.01 ‰) measurements of the clumped (¹⁶O¹³C¹⁸O or 638 in HITRAN isotope notation) isotopic composition of carbon dioxide derived from carbonate samples with spectroscopic measurement times of ~30 minutes using a dual laser spectrometer. That spectrometer is optimized for the measurement of the four isotopologues required to calculate δ_{638} . In this paper we present our parallel efforts to develop a novel dual laser isotope analyzer capable of measuring multiple carbon dioxide isotopic signatures simultaneously. Specifically, we aim to simultaneously measure the isotopic abundances of the three most abundant clumped isotopologues (δ_{638} , δ_{637} and δ_{828}) as well as ¹⁷O oxygen excess or $\delta^{17}\text{O}$. δ_{638} and δ_{828} correspond to the quantities δ_{47} and δ_{48} when measured by isotope ratio mass spectroscopy (IRMS). $\delta^{17}\text{O}$ is very difficult to measure with IRMS and δ_{637} has not been previously measured with any technique to the best of our knowledge. The new instrument utilizes carefully chosen spectral windows, operates at low sample pressure and exploits automated laser frequency hopping. In the attached figure we show our preliminary results for δ_{637} from a novel prototype instrument which is simultaneously measuring 626, 636, 628, 627, 638, 637 and 828. These preliminary results are displayed as an Allan-Werle plot which shows that the precision in the measurement of δ_{637} is 0.1‰ for a single 5 minute measurement referenced to a working reference gas. The plot shows that instrumental drift is very small over periods of days and that the precision can be improved to 0.03‰ by processing 10 samples or to 0.01‰ by processing 100 samples. These measurements are preliminary and somewhat idealized but show promise for this new technique.

