

Rapid and precise carbon dioxide clumped isotope composition analysis by tunable infrared laser differential absorption spectroscopy

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Carbon dioxide clumped isotope thermometry is a relatively new and important technique in carbonate isotope geochemistry. The degree of heavy isotope clumping (e.g., $^{16}\text{O}^{13}\text{C}^{18}\text{O}$) beyond an expected random distribution can be related to the temperature of calcite precipitation. Unlike carbonate “paleotemperature” calculations, there is no need to constrain the isotopic composition of the water in which the carbonate grew. In addition, the independent temperature estimate, when combined with carbonate $\delta^{18}\text{O}$ values, allows us to constrain paleowater $\delta^{18}\text{O}$ values. However, the use of isotope ratio mass spectrometry (IRMS) to do these measurements remains relatively rare because it is time-consuming and costly. We have developed an isotope ratio laser spectrometry method using tunable infrared laser differential absorption spectroscopy (TILDAS) and describe our latest results using both gaseous carbon dioxide samples and CO_2 derived from carbonate minerals. The TILDAS instrument has two continuous wave lasers to directly and simultaneously measure four isotopologues involved in the $^{16}\text{O}^{13}\text{C}^{18}\text{O}$ equilibrium calculation. Because each isotopologue is independently resolved, this approach does not have to correct for isobaric peaks, i.e. separate families of absorbance peaks exist for $^{16}\text{O}^{13}\text{C}^{18}\text{O}$ and $^{17}\text{O}^{12}\text{C}^{18}\text{O}$, even though both molecules have a mass of 47 AMU. The gas samples are trapped in a low volume (~250 ml) optical multi-pass cell with a path length of 36 meters. Raw data are collected at 1.6 kHz, providing 96,000 peak-area measurements of each CO_2 isotopologue per minute. With a specially designed sampling system, each sample measurement is bracketed with measurements of a working reference gas, and a precision of 0.01‰ is achieved within 20 minutes, based on four repeated measurements. The total sample size needed for a complete measurement is approximately 15 μmol of CO_2 , or 1.5 mg of calcite equivalent. TILDAS reported $\Delta_{16\text{O}^{13}\text{C}^{18}\text{O}}$ values show a linear relationship with theoretical calculations, with a very weak dependence on bulk isotope composition. The performance of the TILDAS system demonstrated in this study is competitive with the best IRMS systems and surpasses typical IRMS measurements in several key respects, such as measurement duration and isobaric interference problems. This method can easily be applied more widely in stable isotope geochemistry by changing spectral regions and laser configurations, leading to rapid and high precision (0.01‰) measurement of conventional stable isotope ratios and $\delta^{17}\text{O}$ in CO_2 gas samples.

Keywords: clumped isotope, isotopologue, carbonate thermometry