

Rapid measurement of carbonate clumped isotopes using tunable infrared laser spectroscopy

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Clumped isotope abundance in carbonates is an important paleothermometer, but measurement is difficult, slow, and subject to common-mass (*m/z*) interferences using isotope ratio mass spectrometry (IRMS). We present a fast method of clumped isotope measurement by laser spectroscopy that directly measures CO₂ isotopologue abundances rather than *m/z* ratios. We have adapted a tunable infrared laser differential absorption spectrometer (TILDAS) system to optically measure the abundances of four specific CO₂ isotopologues (¹⁶O¹²C¹⁶O, ¹⁶O¹³C¹⁶O, ¹⁶O¹²C¹⁸O, and ¹⁶O¹³C¹⁸O) used for clumped isotope thermometry. TILDAS achieves the same precision (0.01% S.E.) more rapidly (~50 minutes/ analysis) and on smaller samples (<2 mg calcite) compared to most widely used IRMS systems, without making assumptions about ¹⁷O abundance in the sample to correct for common-mass interference. A temperature calibration based on 406 analyses of CO₂ produced by acid digestion of 51 synthetic carbonates equilibrated at 6 °C to 1100 °C is consistent with results for natural carbonates and other published calibrations (Fig. 1), demonstrating the operational equivalence to IRMS systems. In addition, our TILDAS system results were indistinguishable from top performing IRMS systems after replicating the recent InterCarb interlaboratory calibration effort (Fig. 2). Finally, we demonstrate recent applications of the TILDAS system to geologic investigations. Measurement by TILDAS holds the potential to change the landscape for clumped isotope analysis.

Figure 2

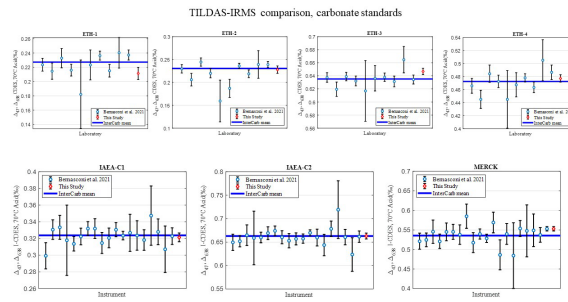


Figure 1

