

Rapid and Precise Clumped Isotope Composition Analysis by Tunable Infrared Laser Differential Absorption Spectroscopy

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Carbonate clumped isotope thermometry is one of the most developed applications of the geochemistry of multiply substituted isotopologues. The degree of heavy isotope clumping (e.g., $^{16}\text{O}^{13}\text{C}^{18}\text{O}$) provides an independent temperature estimate. We have developed an isotope ratio laser spectrometry method using tunable infrared laser differential absorption spectroscopy (TILDAS) and describe our latest results of gaseous CO_2 samples and CO_2 derived from carbonate minerals. The TILDAS instrument directly and simultaneously measure four isotopologues involved in the $^{12}\text{C}^{16}\text{O}_2 + ^{13}\text{C}^{16}\text{O}^{18}\text{O} \leftrightarrow ^{13}\text{C}^{16}\text{O}_2 + ^{12}\text{C}^{16}\text{O}^{18}\text{O}$ exchange reaction, it does not need isobaric correction as in isotope ratio mass spectrometry (IRMS). The clumped isotopologue precision of 0.01‰ (1 S.E.) is achieved within 20 minutes using 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 values, with a very weak dependence on bulk isotope composition. This method can be broadened to other areas of carbonate isotope geochemistry, such as rapid and high precision (0.01‰) measurement of conventional stable isotope ratios and $\delta^{17}\text{O}$ in CO_2 gas samples.

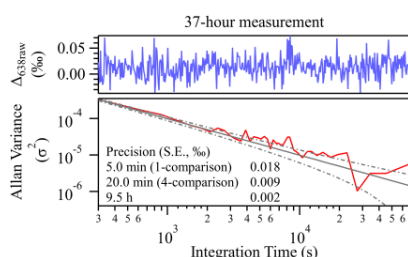


Fig. 1. sample-working reference comparison measurement.