Measuring the clumped isotopic composition of carbon dioxide with mid-infrared laser spectroscopy

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We present Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) measurements of the clumped isotope ratio of gaseous carbon dioxide samples and describe our plans to extend this technique to the measurement of carbon dioxide samples derived from carbonate minerals. Our method uses two lasers to measure the four isotopologues involved in the $^{16}O^{13}C^{18}O$ isotope exchange equilibrium. Our samples consist of carbon dioxide diluted in nitrogen. These samples are trapped at low pressure (40 to 75 mbar) in a low volume (~200 ml) optical multi-pass cell with a path length of 36 meters. Each sub-sample is probed for <2 minutes. Each sub-sample measurement is bracketed with measurements of a working reference gas. A complete sub-cycle requires a measurement time of ~4 minutes and consumes 3.8 micro-moles of CO_2. These measurements show repeatability of 0.015‰ for Δ638 which is the infrared spectroscopic equivalent of Δ47. Furthermore, when we execute multiple sub-cycles drawing from the same original sample mixture, we observe noise reduction consistent with random noise statistics. Hence, after averaging 3 sub-cycles we observe repeatability of 0.009‰. This requires 12 minutes of time and 11.5 micro-moles of CO_2. Recent measurements of temperature equilibrated CO_2 samples show excellent results.