Geophysical Research Abstracts
Vol. 20, EGU2018-3972-3, 2018
EGU General Assembly 2018

Optical measurements of carbonate "clumped" isotope signatures

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The "clumped" isotope composition $\Delta^{16}O^{13}C^{18}O$ of CO_2 liberated from carbonates is a new analytical tool for temperature dependent processes in a variety of environmental systems, e.g. paleoclimate reconstruction, speleothem sciences, biogeochemistry. Meaningful resolution requires the analysis of multiple carbon dioxide isotopologues at the level of few tens ppm (parts-per-million). Conventional mass-spectrometric methods provide precise rare isotopologue measurements that suffer, however, from isobaric interferences. We present a laser-based measurement technique that is intrinsically free of isobaric interferences and offers a virtually non-destructive analysis of pure carbon dioxide samples.

The prototype of the absorption spectrometer uses two intra-band cascade lasers (ICL) tuned at 4.3 and 4.4 μm to detect CO_2 absorption lines in the fundamental ν_3 band. Dry pure carbon dioxide samples ($\leq$100 μmol) are analysed in a custom built multipass Herriot type cell equipped with two optical paths of 9 cm and 9 m. MIR optical fibers are used to deliver laser light to the cell preventing unwanted absorption in ambient air. The instrument has an augmented temperature stabilisation system, achieved temperature stability is on the level of $\pm$2 mK, despite ambient temperature variations of $\pm 1^{\circ}$C. An integrated sample extraction and purification line is designed for preparation and repetitive measurements of carbonate CO_2 samples.

Spectra are obtained at a sweeping rate of 1.56 kHz. Recorded spectra are integrated and fitted at a rate of 1 Hz. The instrumental precision of 20 ppm is achieved after 20 seconds of data acquisition. A full operation cycle consists of several comparisons of the sample gas with the working reference, each cycle includes zero absorption level measurements, sample analysis, and cell evacuation. Within one hour of measurements, a reproducibility of 50 ppm (1SEM) is obtained.

To demonstrate the performance of the instrument and prove its applicability to environmental applications we conducted a series of reproducibility tests and analysed the isotopic composition of conventional carbonate standards, including NBS-18 and NBS-19.