

Advances in CaCO₃ clumped isotope analysis, using a custom extraction line and a dual inlet system

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We have designed and constructed a bespoke, fully automated, online carbonate acidification and CO₂ cleaning extraction line for clumped isotope analyses of CO₂. Several changes from previous designs have been made to improve data quality, understand the source of isobaric interferences, and optimize run parameters for the extraction line. The line is highly efficient, using minimal LN₂ and He, and creating highly pure CO₂. The line automatically passes purified CO₂ to the Thermo Scientific 253 *Plus*, which is outfitted with 10¹³ Ω amplifiers in the mass 47, 47.5, 48, and 49 positions, and thus allows for the analysis of smaller samples without loss of analytical precision.

Gas purification is accomplished through a series of custom built traps that cryogenically freeze, isolate, and distill CO₂ from water, SO₂, and organics. The design of the traps utilizes a spiral geometry, allowing for CO₂ to be entrained and removed from a He stream of about 10ml/min. The uptake in a He stream allows for conventional GC separation and additional chemical scrubbing. The line contains a residual gas analyzer (RGA) that scans an aliquot of the purified gas across the mass spectrum. We use this feature to ensure CO₂ purity prior to introduction of the gas into the mass spectrometer. In addition, we are actively building a library of contamination spectra to better identify the source of contamination, beyond the current understanding¹. The RGA also allows for the confirmation that individual cleaning steps are performing as expected. The line records many environmental variables, such as pressure, temperature, and valve timings, for later cross-referencing with RGA spectra and stable isotope analyses.

In addition to presenting the features discussed above, we will also show preliminary results of contaminants identified by the RGA, logged environmental variables, and Δ₄₈ excess in the final measurement. We will also present data from the 253 *Plus* that quantifies the signal-to-noise ratio, sample size reduction, and optimal run procedures for our new clumped isotope sample purification and measurement system.

[1]Huntington, K. W., et al. (2009), *J. Mass Spectrom.* 44.9, 1318-1329.