Laser Ablation – Cavity Ring Down Spectrometry, a new method for the *in-situ* analysis of $\delta^{13}C$ of organic and inorganic carbonates

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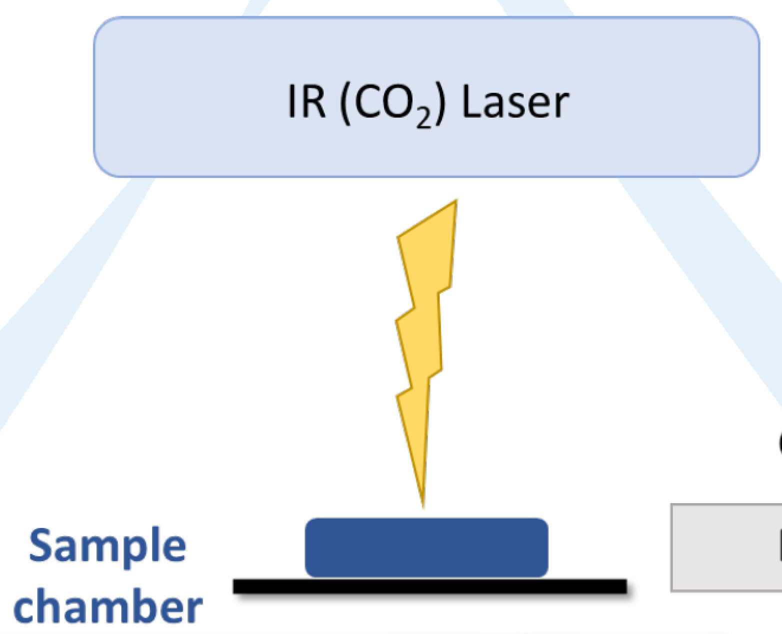
Introduction

Elemental analyzers (EA) are the go-to sample introduction instrument for light stable isotope analyses of solid materials. Sample preparation is labor intensive and time consuming, with high associated consumable and equipment cost. Sample recovery is impossible in case of malfunctioning, i.e., no repeat analysis when sample amount is restricted.

In the same way, Laser ablation (LA) is traditionally considered a sample introduction technique for Inductively Coupled Plasma Mass Spectrometry (ICP MS) where plasma-based instrumentation will ionize and measure with a high degree of accuracy and precision the aerosol generated during the ablation process.

In this contribution we present an innovative method of measuring C stable isotopic ratios of carbonates by hyphening two instruments that are not usually found in the same lab. We coupled a laser ablation system (Teledyne Photon Machines Fusions CO2) equipped with a specially designed ablation chamber (Terra Analitic isoScell Δ100) to a Cavity Ring Down Spectrometer (Picarro G2201-i) to perform spatially resolved, highly accurate and precise measurements of both inorganic (stalagmite) and bioaccumulated (freshwater bivalve) carbonate samples. This novel system requires minimal sample preparation, allows for in-situ sequential and repeat sampling, all while eliminating the need to individually prepare samples.

Instrumental setup



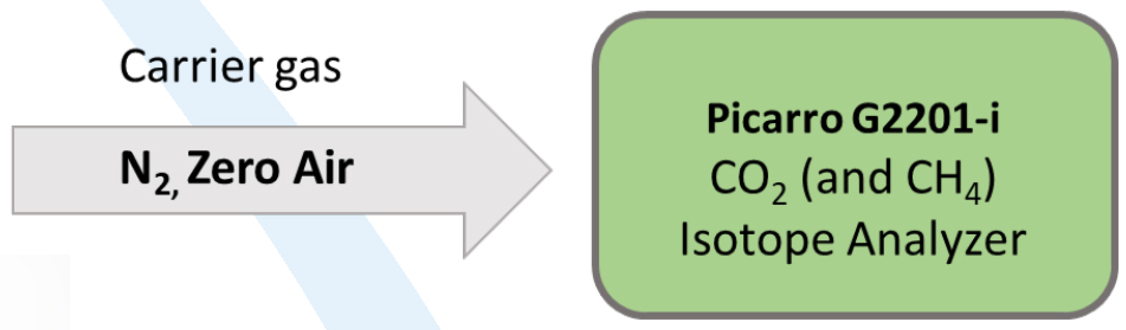


Figure 1. Analytical setup schematics.

Figure 2. The isoScell Δ100 – bespoke stable isotope ablation chamber.

Parameter	Unit	Value
Carrier gas (N2, ZeroAir)	mLPM	26
Energy output	W	3.6
Spot size	µm	150
Ablation time	seconds	3,5

Table 1. Physical parameters set for the analyses.

Figure 3. Instrument line-up.

Preliminary results

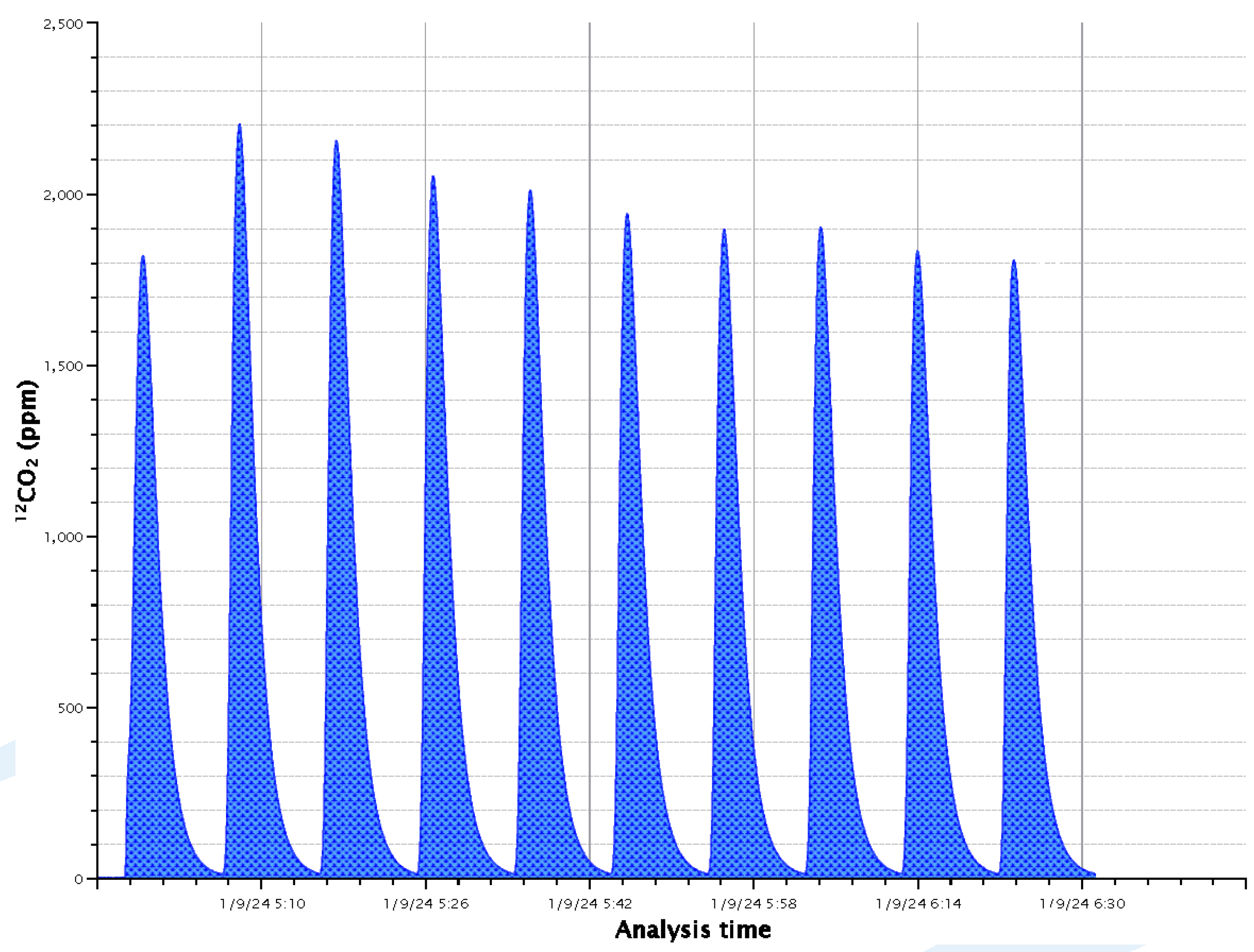


Figure 4. CO_2 signal intensity acquired on a natural sample (V11 Stalagmite, Bihor Mts, Romania; Tămaș *et al.* 2005). Even though the sample is intrisically heterogeneous, the reproducibility of the signal is very good. Laser parameters were adjusted to optimize sample removal, without thermally affecting adjacent areas in order to minimize ablation-induced isotopic fractionation.

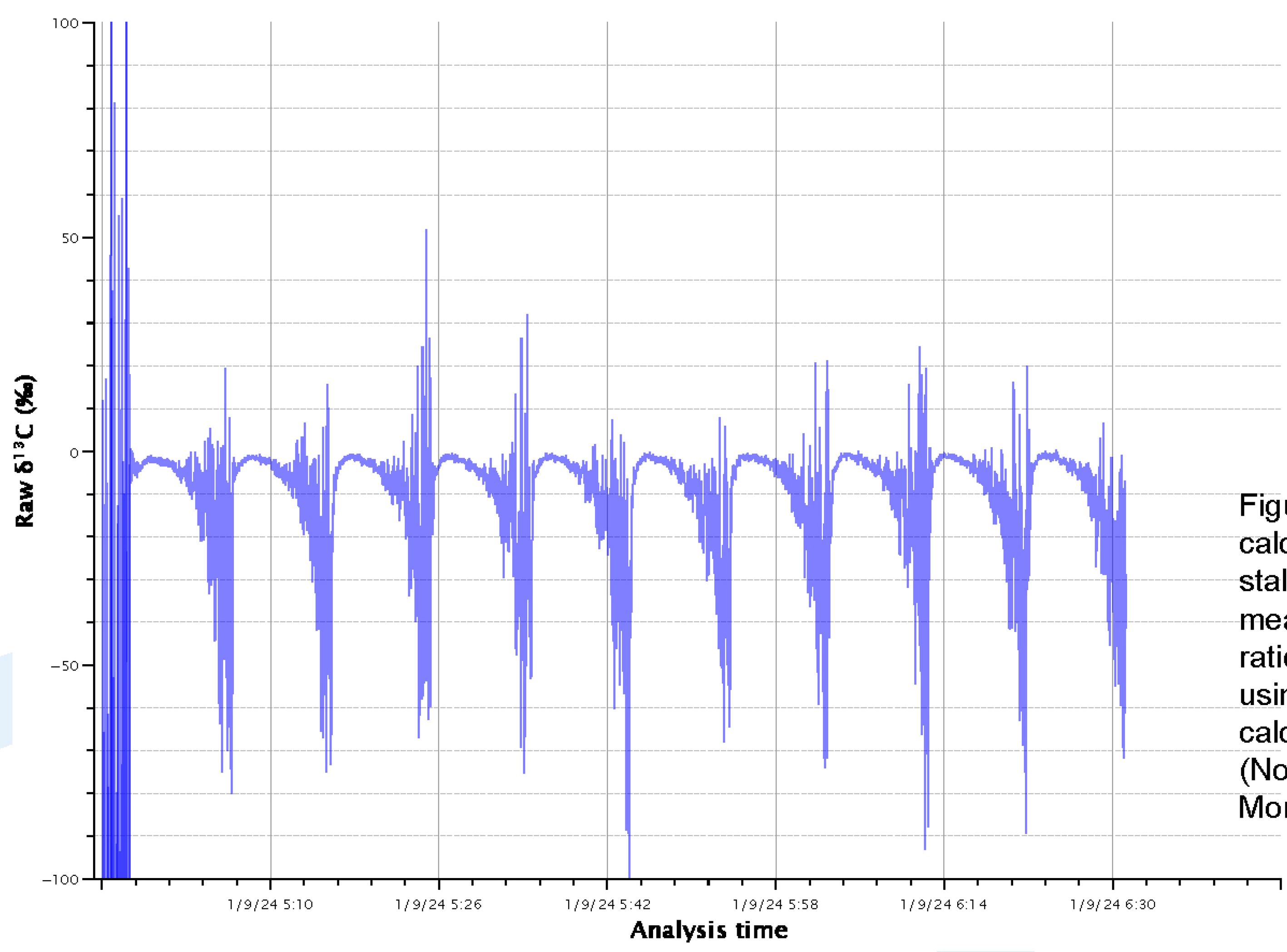


Figure 5. On-line $\delta^{13}C$ calculation for the V11 stalagmite measurements. The ratios were calculated using an in-house calcite standard (Nowa Ruda calcite; Morawiecki 1962).

Preliminary results

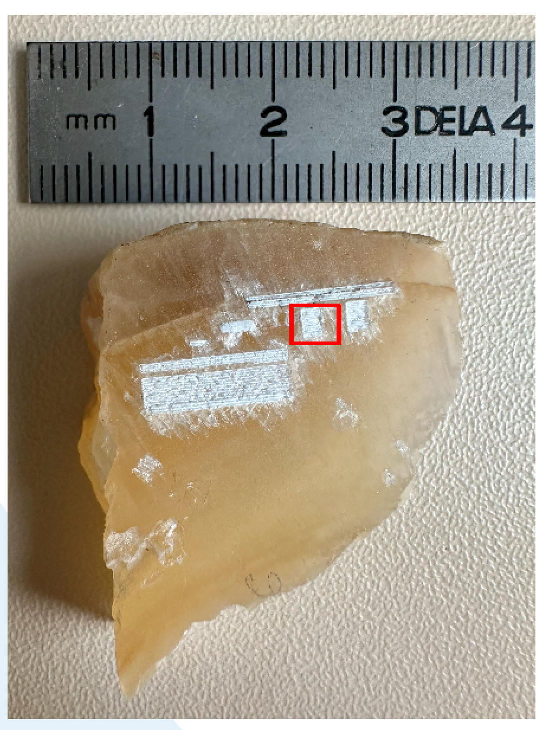


Figure 6. V11 Stalagmite (Bihor Mts., Romania) fragment used for the preliminary testing. Ablated area highlighted by the red rectangle.

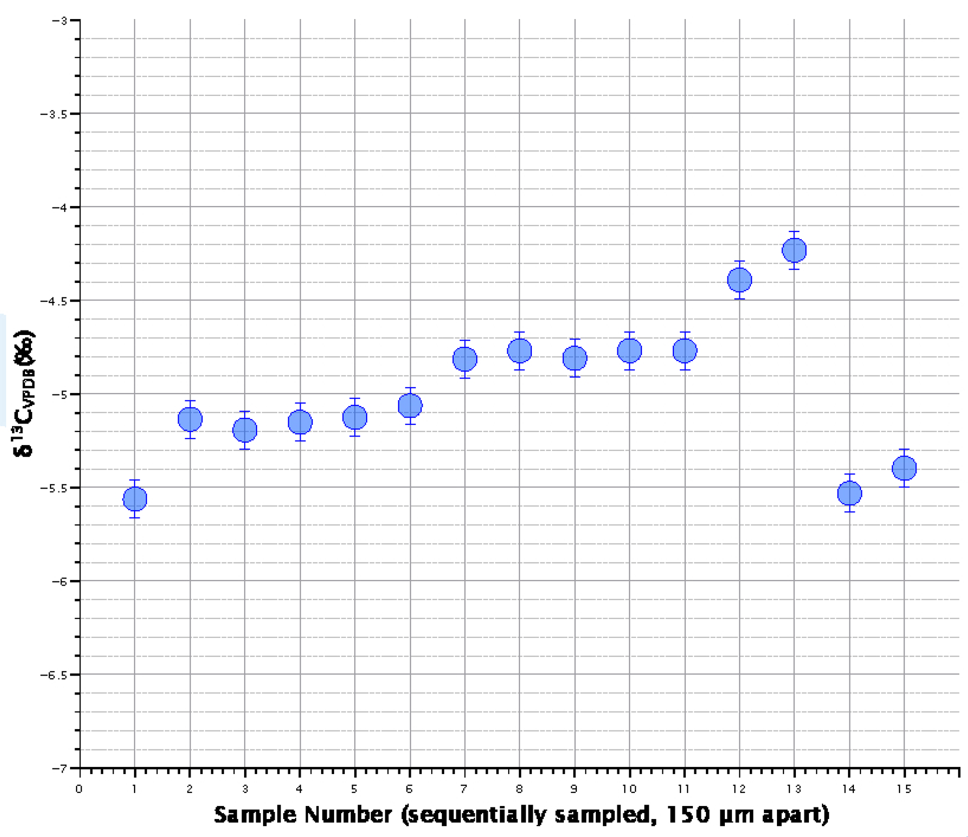


Figure 7. Drift corrected $\delta^{13}C$ values for the V11 Stalagmite. Error bars represent analytical precision calculated on the in-house standard reference and expressed as 1std (0.1 ‰)

Conclusion

Preliminary data shows that LA CRDS can reliably be used for high spatial resolution, *in situ,* measurements of $\delta^{13}C$ in both organic and inorganic carbonates. The analysis is fast (10 minutes per measurement), cost effective (carrier gas can be N_2 or ZeroAir) and requires minimal sample preparation.

The high spatial resolution measurements enabled by the laser ablation system allows the user to resolve changes in isotopic composition at micron scale.

Tămaș, Tudor & Onac, Bogdan & Bojar, Ana-Voica. (2005). Late Glacial-Middle Holocene stable isotope records in two coeval stalagmites from the Bihor Mountains, NW Romania. *Geological Quarterly*. 49. 185 – 194.

Skrzypek, G., & Paul, D. (2006). $\delta^{13}C$ analyses of calcium carbonate: comparison between the GasBench and elemental analyzer techniques. *Rapid Communications in Mass Spectrometry*, 20(19), 2915–2920.

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