

In Situ Laser-Laser C- and O- isotopes measurements in carbonates

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Stable isotopes ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of carbonates are central to our understanding of Earth climate and carbon cycle evolutions. These classical geochemical measurements have been developed in the mid 19th century building on the advance of gas phase IRMS laboratory instruments. With the recent development of a new generation of instruments based on laser spectroscopy (Isotope Ratio Infrared Spectroscopy and Cavity Ring-Down Spectroscopy), that can be operate remotely and directly on the field due to their small architecture, a renew range of applications has been developed in the last decade such as continuous monitoring of atmospheric CO_2 isotopes. On site isotopic characterization of carbonates is however not easily achievable because several preliminary steps (micro-drilling or crushing, CO_2 release by wet acid digestion, gas equilibration, purification and transfer) are usually needed to provide accurate measurements whether using both a classical IRMS or laser spectroscopy system.

We report a new transportable sample preparation setup involving a fiber laser diode, emitting in the near infrared at around 900nm, that induces the decomposition (calcination) of calcium carbonate into lime and carbon dioxide¹. The latter being directly introduced into an IRIS instrument for isotopic measurements. Using this setup, we analyzed different types of carbonate including inhouse isotopic standards, calcite, dolomite, siderite and malachite. Cross calibration with state of the art IRMS shows a correlation coefficient of 0.99 and 0.96 within uncertainties for the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ VPDB, respectively, over a large range of isotopic compositions (>20 ‰ for C isotope and 15 ‰ for O isotope). The reproducibility (evaluated on calcite inhouse standard material) of our Laser-Laser isotopes setup shows a 1s standard deviation of 0.09 and 0.19 ‰ (n=52) for the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$, respectively. Accordingly, we show that (i) laser calcination of carbonates releases CO_2 than gives accurate and reproducible isotopic determination and that (ii) Laser-Laser isotopic measurements can be performed at reduce time and cost and in field lab conditions. Finally, the ability of the Laser-Laser setup to produce spatially resolved isotopic mapping of heterogenous samples will also be presented.

¹Thomazo, C. et al., (2021). *Chemical Geology*, 578, 120323.