In Situ carbon and oxygen isotopes measurements in carbonates using laser-induced calcination: A step forward field isotopic characterization

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Stable isotopes ratios ($\delta^{13}C$ and $\delta^{18}O$) of carbonates archived in the rock records are routinely used to reconstruct paleo-temperatures and the secular evolution of the biogeochemical carbon cycle through Earth History. The state-of-the-art technique, developed since the mid 19th century, to measure these isotopic ratios includes: micro-drilling and/or sawing and crushing, CO_2 release by wet acid digestion, gas equilibration, purification and transfer, before gas phase IRMS measurements. While these steps are time and resources consuming, they provide accurate measurements of the rock record.

This study presents a new protocol involving a laser calcination system that allows to decrease drastically the analyses time by reducing the number of preparations steps together with offering the possibility of performing punctual analyses at the mm scale. This original setting is based on the use of a fiber laser diode device emitting in near infrared at 880nm and inducing the decomposition of calcium carbonate into lime and carbon dioxide.

We analyzed 9 different types of carbonate encompassing a range of isotopic composition between -18.2 and+3.3 and between -1.7 and -14.6‰ for the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ VPDB, respectively. The comparison of isotopic results is performed after both micro-drilling before acid digestion and laser calcination and considers samples isotopic inhomogeneity. The resulting isotopic cross-calibration shows a direct positive co-variation between both methods with a correlation coefficient of 0.99 and a regression slope of 1 within uncertainties for the $\delta^{13}C_{carb}$. The $\delta^{18}O_{carb}$ also compared well with a correlation coefficient of 0.96 suggesting a constant gas-solid phases isotopic equilibrium. The reproducibility of our laser calcination method shows a 1σ standard deviation of 0.31 and 0.77 for the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$, respectively.

We demonstrate that (i) laser calcination gives accurate and reproducible C and O isotopes characterization of carbonates, (ii) the physical effect during calcinations does not introduce any isotopic fractionation for C and is accompanied with a constant isotopic equilibrium of O. These findings paved the way to a renewed range of possibilities for carbonate isotopic measurements using rapid, punctual and easy to manipulate laser preparation device.

Mots-clés : stable isotope, carbonate, laser, punctual analyses