PhD Supervisor

Name	Musset Olivier
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Projet

Title	*Laser calcination of carbonates for isotopic measurements of Carbon and Oxygen – Coupling with LIBS analysis and on field measurement*
Acronym	ISOLASER

Research groups in the project

CNRS unit	Laboratory	Name
UMR6303	**ICB** – Université de Bourgogne	Mr. Musset Olivier
UMR 6282	**Biogéoscience** - Université de Bourgogne	Mr. Christophe Thomazo
UMR 7590	**IMPMC** – Université Sorbonne / Muséum d'Histoire Naturelle de Paris	Mr Pierre Sansjofre

CV of the directors

The thesis director is Olivier Musset, professor at the University of Burgundy and researcher at the ICB laboratory within the Saphir team (formerly SLCO). It is initially specialized in the development of custom laser sources for specific applications including industrial, defense or industrial. These developments include the production of demonstrators adapted to research initially very focused on the economic world. He has to his credit about thirty contracts and three operating licenses with companies ranging from start-ups to industrial groups (examples IVEA Solutions, Bertin Tech., Thalès/TDA, Sagem, etc.). For some time now, and in the continuity of his secondary research activities, Mr Musset has reoriented his work towards the fields of biology and geology within the framework of multidisciplinary studies integrating laser processes or optical instrumentation systems. Currently in CRCT (year 2022), Mr Musset now devotes himself to two main activities which are the preparation of geological samples by laser for analyzes either isotopic (infrared spectrometry) or elementary (LIBS spectroscopy) and the study of the host / parasite link in animal biology (an article published in 2021). It nevertheless retains other activities, particularly in LIBS analysis in the context of nuclear material analyzes (5 articles) and in the development of custom laser sources. This more academic and much less restrictive work in terms of communication has thus enabled the filing of two patents and the publication of 6 articles (LIBS analysis, laser preparation of carbonate samples, treatment of host/parasite pair by laser, etc.). This thesis project is part of the partnership with the Biogeosciences laboratory (UMR 6282) and focuses on laser-induced calcination for in situ isotopic analyzes of carbonates.
The first codirector within the UB partner team is Christophe Thomazo, MCF at the Biogeosciences laboratory (UMR 6282) at the University of Burgundy. His main research themes centered on geochemistry are: Biogeochemical Cycles, Biosphere-Geosphere interactions, Early Earth Environment, Isotope Biomarkers, Sedimentology and Isotope Geochemistry. He specializes in - Geochemistry of stable isotopes (C, O, N, S and Fe), microbiology, sedimentology and astrobiology. His skills are mainly focused on mass spectrometry in dynamic mode (continuous flow, dual inlet) and in static mode with magnetic sector and infrared, mineral and gaseous chemistry, mineral speciation of iron by sequential extraction, optical microscopy and electronics, and field sedimentology. He is the author or co-author of 66 publications (including: Science, Scientific report, Science advances, Nature communications) and a patent in collaboration with the ICB. He has been a junior IUF member since 2020 after being awarded a CNRS/UB chair of excellence over the period 2010-2015.

The second codirector, Pierre Sansjofre, within the IMPC laboratory of Sorbonne University has been a lecturer and member of the ROCKS team since 2019. He is also responsible for the geology collections of the National Museum of Natural History in Paris. Previously he was MCF at the University of Bretagne Ouest for 6 years after two postdocs in Canada and Brazil, respectively at Mc Gill University and the University of Sao Paolo. His research themes are: Sedimentology and Geochemistry of Precambrian environments, Biosphere - Geosphere Interaction, Isotope Geochemistry (N, C, O and S), Redox Conditions, Extreme Glaciations, Carbon Cycle, and Diagenetic Processes. He is responsible for the ISOMAP project, which aims to provide Île-de-France with an innovative isotopic analysis technique making it possible to obtain the carbon (C) and oxygen (O) isotopic compositions of carbonates using a method that is not very destructive and portable, but also to obtain the isotopic compositions in C and O of the Dissolved Inorganic Carbon (DIC) of the water continuously. He is co-author of several patents.

PROJET DE RECHERCHE

1 - Context

The isotopic analyzes of Carbon and Oxygen of carbonates of geological origin correspond to a major challenge in the knowledge of the geological and climatic history of the earth (in particular the evolution of the carbon cycle and surface temperatures since 4.5 Ga). If the analysis process has progressed a lot in recent years with the improvement of devices, particularly optical ones, allowing field analysis to be considered, the chemical preparation aspect of the samples remains cumbersome and complex. The principle proposed by the researchers, validated by a patent and supported by SATT Sayens funding, is based on locally induced calcination by laser. This method has proven its effectiveness for carbon but still requires work on oxygen to obtain results of metrological quality. The first part of this thesis will therefore aim to improve the metrological performances of existing demonstrators in order to refine the reproducibility parameters as well as the analysis precision for its in situ type analyses. A second part will explore the possibilities of coupling this method to a portable LIBS (Laser Induced Breakdown Spectroscopy) analysis to expand the isotopic measurements of a routine elementary chemical analysis.

2 – Keyworlds

Laser calcination / sample preparation / geological carbonates / isotopic analysis / in situ isotopic analysis / in situ LIBS

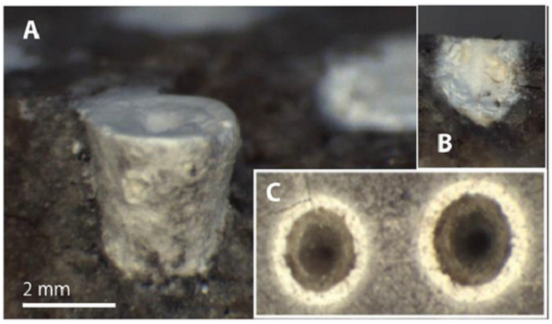
3 – Scientific project:

The study of the carbon and oxygen isotopic composition of carbonate rocks is a subject of great interest for geologists and geochemists with the aim of reconstructing the secular evolution of the carbon cycle and terrestrial paleo-temperatures. The "classic" method is based on mechanical grinding followed by hot acid digestion of the samples and purification using a liquid nitrogen trap, to produce CO_2 whose isotopic stoichiometry must be representative of that of the sample (ie complete conversion without isotopic fractionation). The gas thus produced is then sent to a mass spectrometer. The cost, size and mass, as well as the consumption (electricity + chemical consumables) strongly limit the analysis yield of this technique and do not allow considering relocating the measurement from the laboratory to the field. In recent years, new CO_2 isotopic analysis systems, based on optical absorption, have been developed. These spectrometers are more compact and make it possible to envisage deployment in the field for the first time. However, the gas production part from the sample remains problematic due to the acid digestion prior to gas analysis here too. The partners in this project have developed a new laser preparation technique based on calcination induced by the absorption of a laser beam from a fiber multimode laser diode. The chemical reaction is shown below.

$$CaCO_{3\ \text{mineral or rock}} \rightarrow CaO_{\text{solid}} + CO_{2\text{gas}}$$

NB: the reaction is complete for C (100% yield of the solid-gas reaction), for oxygen the reaction is not complete (1/3 remains in the solid and 2/3 are degassed)

This technique was patented and then published in 2021 (ref. [1] [2]). An example of the results obtained is shown in Figure 1a with a photo of the zone calcined by the laser and in Figure 2 with a comparison with the conventional so-called “acid” measurement technique.



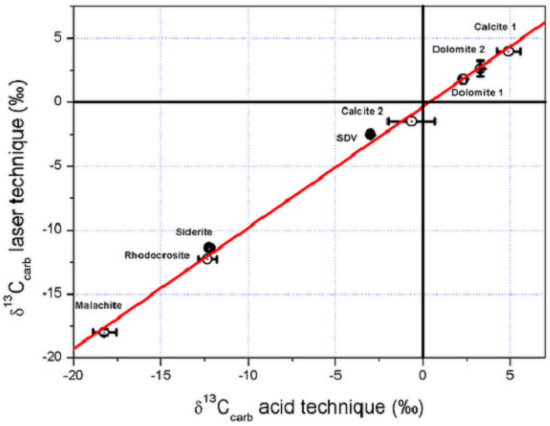


Figure 1a: Photograph of the zone calcined by laser on a carbonate, Figure 1b: Comparison of the preparation technique by laser / usual technique by acid digestion.

This work has already been presented at several conferences with very keen interest from users and manufacturers in the field. Thanks to maturation funding from SATT Sayens, the ICB laboratory was able to develop three analysis systems, each with different possibilities and missions, two of these demonstrators are presented in Figure 2.

Until now, the development of this project has only been carried out by permanent staff from the ICB and Biogeosciences and the IMPMC. These first results and developments showed that the method was functional and made it possible to consider isotopic analyzes of rocks directly in the field. The objective of this request is therefore to: (1) specify the medium and long-term reproducibility of the Laser-Laser analyses, (2) Validate the "portable" nature of the analyzes under different measurement conditions (eg matrix effect , topography of the sample, temperature, partial pressure of gas, etc.) and (3) to couple this isotopic analysis to a LIBS analysis in order to specify the elementary chemistry for each isotopic analysis and to explore the relationships between these two parameters on the scale of a hundred microns for natural carbonates.

This thesis will be organized in two tasks: a first experimental and metrological centered on the isotopy of carbon and oxygen and a second more prospective to evaluate the potential of coupling between laser calcination / optical isotopy and LIBS analysis.

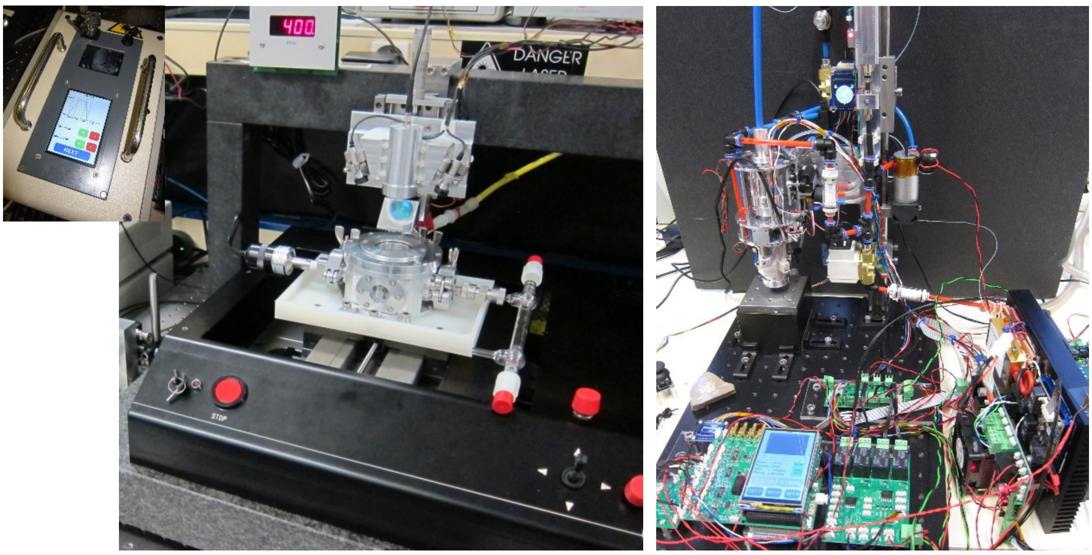


Figure 2: Initial laser calcination device, tabletop demonstrator for a transportable system for in situ analysis.

Task I: Process improvement and advanced metrological study of laser calcination

The doctoral student will be responsible for designing, defining and manufacturing internal standards in association with an engineer from the Biogeosciences laboratory (I. Jovovic) to verify the accuracy and reproducibility of the analyses. He will also have to carry out a critical expertise on families of samples (composition, color, hydration, density, etc.) and the influence of the experimental conditions on the results obtained (gas conditions: nature of the gas, pressure, etc.). These studies should thus help to build robust protocols and consist of help in defining standard experimental conditions adapted to the types of samples and field analysis. The laser calcination system will be coupled with the optical isotopic spectrometers of the Biogeosciences laboratories (Delta Ray) and the Natural History Museum of Paris (LGR). This metrology work will be associated with the development of an internal database covering the known terrestrial carbonate diversity (C. Thomazo, P. Sansjofre). The experimental device will also be improved and made more reliable at the ICB laboratory with its designer (O. Musset) with a view to in situ measurement campaigns (South Africa, Canada, etc. from 2022 to 2024). A modified version capable of automatic analysis of drill cores will also be developed for installation at the MNHN (P. Sansjofre, head of the geology collections at the Paris Natural History Museum) with the aim of processing reference cores of geological time currently stored in the museum. Finally, the analysis capacities of this isotopic technique will be explored to develop an "isotopic mapping" type analysis of the surface of the samples. Obstacles such as the evaluation of point-to-point gaseous interferences and of the treatment process on the reliability of the measurements will again have to be lifted. It is also planned to assess the potential of the technique under conditions equivalent to those of Mars (i.e. under an atmosphere containing 96% CO_2 at 6 mbar) to test the relevance of future space applications.

The doctoral student will also have the opportunity to evaluate the possibilities of the technique and the system developed for more varied fields of application such as, for example, archeology (collaboration with the ArtéHis laboratory via F. Monna) and biology (analysis of corals, sea urchins etc., see example figure 3). This last action of task 1 therefore aims to open up the application potential. The applications of this technique could here again be important, particularly on issues of biodiversity in the context of past and present climate change.

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Figure 3: Example of preliminary tests on biological samples treatable via laser calcination for isotopic analysis (sea urchin radiole from New Caledonia, cuttlefish bone from the Atlantic).

Task II: Coupling of isotopic analysis by laser calcination with LIBS analysis:

The ICB and Biogeosciences have significant joint experience in LIBS analysis of geological samples (sorting by rock families, for example, see references [3] to [5]). The ICB laboratory thus has a prototype portable LIBS analyzer system and compact triggered laser sources for LIBS (Figure 4). It was also equipped very recently (2021) with a transportable system of spectrometers adapted to LIBS (6 triggerable fiber spectrometers in a volume of 10 liters).

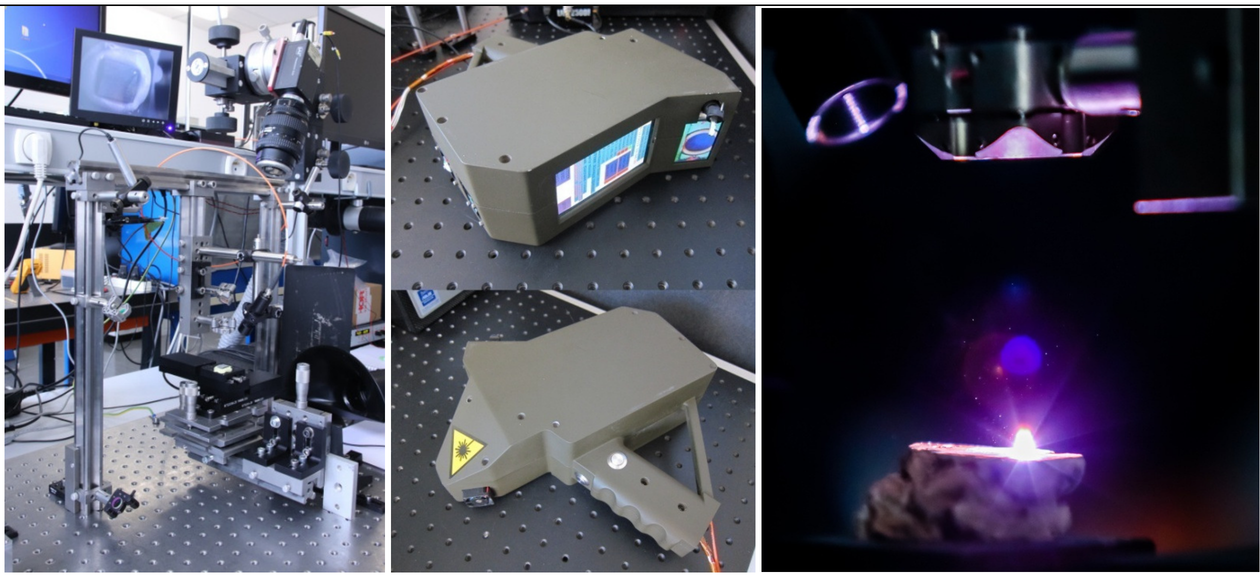

Figure 4: From left to right, ICB LIBS ban, portable LIBS analyzer developed at ICB and example of plasma generated on a carbonate sample (Pyramid lake, Nevada, USA).

The objective will therefore be to combine the two analysis methods (laser calcination and plasma generation by laser) to compile the results obtained in situ and gain spatially resolved information. Since the conditions of laser-matter interaction are very different, their coupling raises many questions in terms of experimental devices and the exploitation of the measurements obtained. Ideally, the doctoral student will therefore be in charge of producing the first coupled "elementary chemical" and "isotopic" surface images (see figure 5).

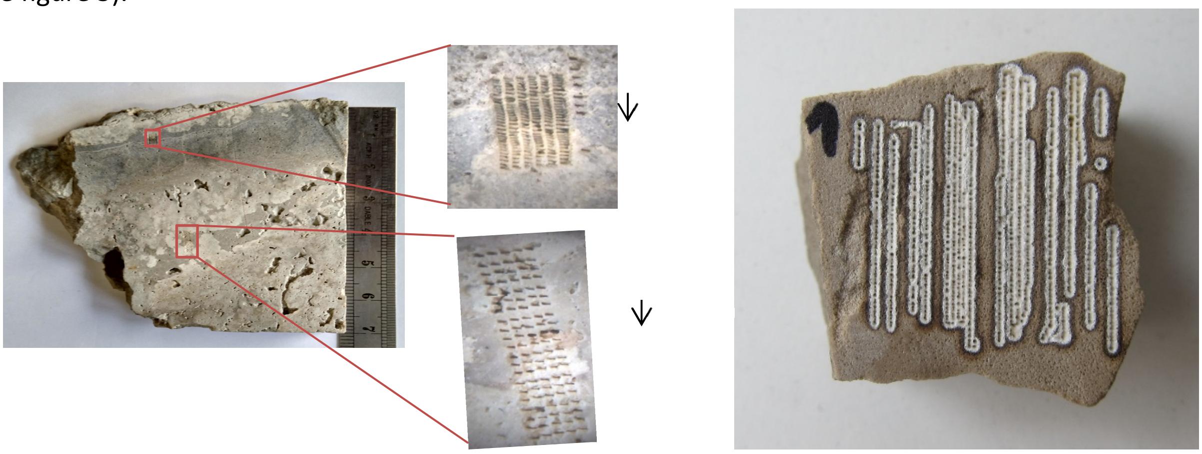

Figure 5: On the left, example of LIBS mapping on a Nevada carbonate (USA), on the right example of scanning by laser calcination on a dolomite.

The ISOLASER project therefore has significant development potential in academic terms because it should make it possible to greatly increase the speed and resolution of isotopic measurements on carbonates, all at a reduced cost. The opening of this technique to continuous in situ analysis also makes it possible to envisage economic development, for example via industrial transfer in the medium term.

[1] **"**In situ carbon and oxygen isotopes measurements in carbonates by fiber coupled laser diode-induced calcination: A step towards field isotopic characterization**"**, C. Thomazo, P. Sansjofre; O. Musset; T. Cocquerez; S. Lalonde, Chemical Geology, Volume 578, 20 September 2021, 120323, https://doi.org/10.1016/j.chemgeo.2021.120323
[2] "Dispositif de production de CO_2 gazeux à partir de carbonates pour analyse isotopique ($\delta^{13}C$ et $\delta^{18}O$) sur site et procédé associé", O. Musset, C. Thomazo, P. Sans Jofre, T. Coquerez, S. Lalonde, FR1907289 -3098300, WO 2021/001344A1
[3] **-**"In situ Laser Induced Breakdown Spectroscopy as a tool to discriminate volcanic rocks and magmatic series, Iceland", C. Roux, J. Rakovsky, **O. Musset**, F. Monna, JF. Buoncristianni, C. Thomazzo, P. Pellenard, *Spectrochimica Acta Part B: Atomic Spectroscopy,* Volume 103-104, pp. 63-69, 2015, https://doi.org/10.1016/j.sab.2014.11.013
[4] "Testing a portable Laser-induced Breakdown Spectroscopy system on geological samples ", Rakovský J., Musset O., Buoncristiani JF**.**, BichetV., Monna F., Neige P. et Veis P. 2012.. *Spectrochimica Acta Part B: Atomic Spectroscopy*, Volume 74-75, pp. 57-65. https://doi.org/10.1016/j.sab.2012.07.018

[5] - "A compact, high-efficiency, quasi-continuous wave mini-stack diode pumped, actively Q-switched laser source for laser-induced breakdown spectroscopy", C. Alvarez Llamas, C. Roux, O. Musset, Spectrochimica Acta Part B, 148 (2018), 118-128. https://doi.org/10.1016/j.sab.2018.06.012
[6] **"**A review of the development of portable laser induced breakdown spectroscopy and its applications", J. Rakovsky, P. Cermak, O. Musset, P. Veis, *Spectrochimica Acta Part B: Atomic Spectroscopy,* Volume 101, pp. 269-287, 2014, https://doi.org/10.1016/j.sab.2014.09.015