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Preface

Physicochemical reactions at the solid-fluid interfaces play a crucial role in the global cycle of major and trace elements in the Earth and other telluric planets. Thus, chemical weathering at the Earth's surface, metamorphic reactions in the continental and oceanic crusts, diagenetic reactions in sedimentary basins, hydrothermalism in oceanic ridge and Earth crust, and crystal-melt reactions in magmas are critical processes that control the evolution of the Earth and shape its surface and sub-surface. However, many physicochemical and microtextural aspects of these so-called rock-fluid interactions are still poorly understood. Experimental and numerical-modelling studies of these interactions are fundamental to understand and predict the fate and transport of chemical elements in natural and engineered geo-environments. The chemical form and the speciation of these elements control their chemical reactivity. In this general picture, I am convinced that the nucleation, growth and dissolution of minerals are among the most fundamental global Earth processes in the first deep-km (including the so-called critical zone, several natural and/or engineered fluid storage systems and formation of mineral deposits under hydrothermal sites). Concerning the formation of minerals, numerous experimental and theoretical studies in the past decade have provided evidence for the existence of multi-step nucleation pathways and aggregation processes that take place during the early stages of mineral formation. These multi-step pathways contrast with the over-simplified traditional models described by the classical mineral nucleation theory than is based on the nucleation of seed entities (clusters or nuclei of nanometric size) from a given oversaturated system followed by crystal growth via ion-by-ion or molecule-by-molecule (unit formula) attachment to existing nuclei; such formalism is exclusively based on the size notion and a single energetic barrier. Experiments tracking these pathways are challenging because of the small size − in the nm range − and short lifetimes of some of the precursor species. Such experiments have recently been the focus a wide interest in geosciences, chemistry and material sciences. In this way, from my arrival to Grenoble I have initiated this new research topic at ISTerre and in this manner I have focused my research work in the past years on the experimental measurement and detection of multi-step nucleation pathways of carbonate, phosphate and iron hydro(oxides) minerals, using particularly time-resolved Raman spectroscopic measurements. In parallel, I have investigated the simultaneous carbonation and serpentinization of ultrabasic minerals (olivine model) and the transfer of ionic pollutants (Se, Sb, As, Fe, Cr, Cu and Cd) at the mineral-solution interfaces under mild and hydrothermal conditions, using conventional and unconventional experimental setups such as hydrothermal autoclaves and reaction cells connected to atomic force microscopy (AFM) or infrared spectroscopy. My main goal is to progress on a holistic understanding of the nucleation, growth and transformation (including dissolution-recrystallization processes) of minerals from solutions far from equilibrium and/or near of equilibrium, as summarized in the figure below and reflected by my recent scientific production. I underline that during my head-responsibility of geochemistry team at ISTerre (three years in total), the topic on the nucleation, growth and transformation of minerals was claimed as a priority inside of geochemistry team because it is actively developed using a diversified panel of in-situ techniques as commented below and particularly in my research program/outlook for the next 5-10 years.
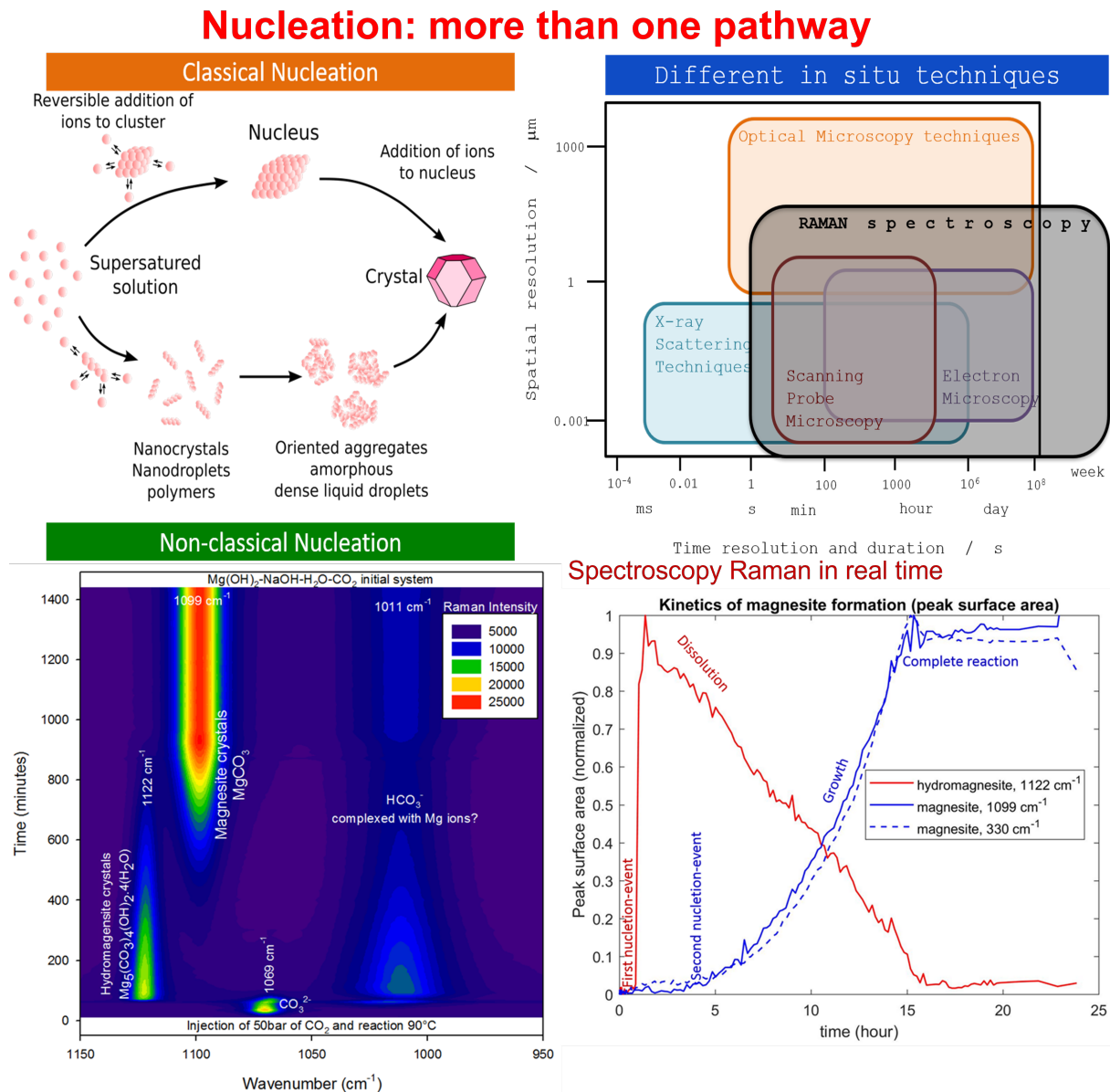
Nucleation: more than one pathway

Figure 1. Current perspective on the nucleation and growth of minerals via classical or non-classical crystallization pathways. Current in-situ techniques being developed to track experimentally the nucleation events. Magnesite nucleation tracked with spectroscopy Raman monitored in real-time at 90°C from a heterogenous system (brucite slurry carbonated with compressed CO_2 using NaOH as sequestering carbon dioxide agent).

In the past twenty-four years (from 1999 to 2023; including my PhD thesis), I have developed my research on the experimental and numerical simulation of physicochemical reactions at the solid-fluid interfaces. Herein, I have worked on four main research topics during my doctoral and post-doctoral periods:

1- Osmotic swelling of clays (Ph. D. in Strasbourg, 1999-2002); **6 publications** as first author

2- Modelling of reactive transport in saturated clay barriers (post-doc in Strasbourg, 2003-2005); **4 publications** as first author

3- Hydrothermal alteration/precipitation of minerals in CO_2-rich systems (post-doc in Nancy, 2005-2006); **2 publications** as first author

4- Mineralization, capture and valorisation of CO$_2$ (post-doc in Grenoble, 2007-2009); **9 publications** as first author

      Since my CNRS recruitment as CR1 in 2009 and my HDR obtained the same year in Grenoble, a significant part of my research was oriented on the CO$_2$ capture, utilization and storage (CCUS) and in a most general picture on the nucleation, growth and transformation of minerals under mild and hydrothermal conditions, in several contexts of basic and applied research. I have also developed various complementary/collaborative studies such as water aqueous alteration of meteorites and experimental alteration of ultrabasic minerals, including trace elements partitioning. I have trained 7 PhD students and 15 B.S and M.S students. The supervision of students, the management and partner of research projects (CEMENTO PEPS-INSIS CNRS (2023), (European ACT program FUNMIN (2019-2023), ANR Coro (2012-2015), ANR Spring (2011-2014), Labex OSUG@2020 (2012), Labex Serenade (2016-2017) and other local projects), the collaborations with various foreign and French researchers, have contributed considerably to my scientific impact. My scientific production includes **81** international peer-reviewed publications (**43 as first author**) in the domains of Earth and Planetary sciences, Material sciences and Chemical Engineering, **5** contributions to books and **5** patents as first inventor (see also my website: https://www.isterre.fr/annuaire/pages-web-du-personnel/german-montes-hernandz-1397/). My citation metrics includes more of **3700** citations and h-index of **35** in google scholar (see annual citation behavior below).
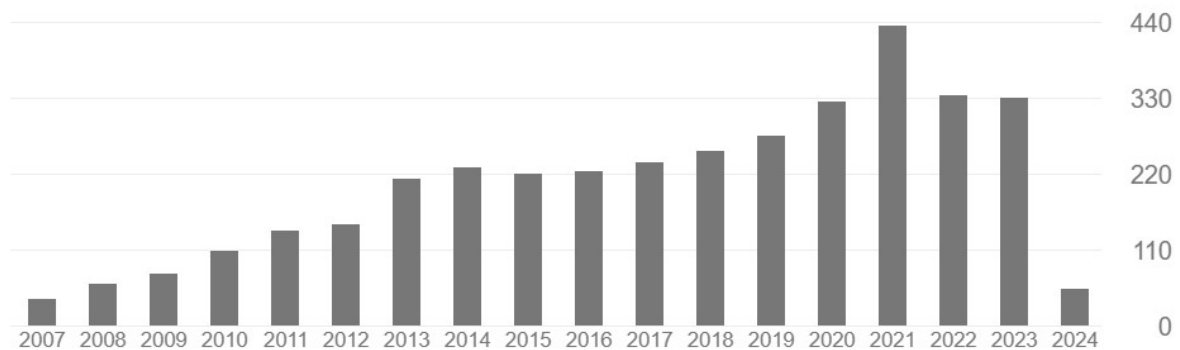

Figure 2: German Montes-Hernandez's impact over time (citation number by year), record: total citations = 3780 and H-INDEX = 35.

The present document summarizes below my research and synergetic activities, including a short descriptive CV (**Part I**) and three important current research topics than I have developed in the past seven years (**Part II**).

Part I: Summary of activities related to research work

Since my arrival as postdoc in 2006 and my recruitment in CNRS in 2009, I have built a cross-disciplinary research group in Grenoble, with national and international collaborations, on topics related to nucleation, growth and transformation processes of minerals and I have also pioneered several studies on the CO_2 capture, utilisation and storage (CCUS). My experimental research is then relevant to fundamental processes in the Earth systems such as mineral formation in hydrothermal systems, CO_2 impact in drink water aquifers, gas-solid carbonation in soils and aerosols widespread in cold natural environments; and societal applications such as Ca looping process, synthesis of nanostructured minerals and composites, CO_2 capture by alkaline sorbents and particularly direct or indirect transformation of CO_2 gas to solidified added-value carbonates such as magnesite and dolomite (permanent CO_2 storage) and/or production of very-high used carbonates such as nano-calcite, siderite, eitelite, hydromagnesite, etc.

(a) Supervision/co-supervision of students

PhD. Students: I have supervised or co-supervised the PhD thesis of eight students. **Romain Lafay** (doctoral fellowship from the University Grenoble Alpes, 8 publications, thesis defended October, 3rd, 2013) worked on the partition of trace elements during nucleation and growth processes of serpentines and competitive serpentinization and carbonation of ultrabasic rocks (San Carlos olivine model). **Alexandre Garenne** (doctoral fellowship from ANR Spring, thesis defended December 10th, 2014, 4 publications) conducted research on the hydration and carbonation processes at the surface of Mars and asteroids. I have supervised this work in collaboration with Pierre Beck. **Ayumi Koishi (**doctoral fellowship from the University Grenoble Alpes, thesis defended October, 30th 2017, 2 publications) worked on the amorphous calcium carbonate (ACC) precursors to crystalline calcium carbonate phases in a context of biomineralization. She has obtained relevant insights on the water dynamic in partially stabilized amorphous phases by using synchrotron and conventional tools. I have co-supervised this work with A. Fernandez-Martinez.

In collaboration with the Natural Water Treatment Laboratory, Water Research and Technologies Center (CERTE) in Tunisia, **Afef Hamdouni** (PhD student in Tunisia, thesis defended in April 2017) has carried out a 6-months research internship in Grenoble under my supervision and published one article on the trapping of Fe(II) as oxyhydroxide during carbonation process. In the same way, **Sabah Hajji** (PhD student in Tunisia, thesis defended in July 2018) has finished a 6 months research internship on the sequestration of toxic ions in/on nanostructured iron minerals, published in one high-level international publication.

Before covid19 pandemic situation. I have hosted two other foreign PhD students at ISTerre (geochemistry group) for 6 months to deepen their research work on the calcium-silicates nucleation under hydrothermal conditions (Xonotlite model) (**Felipe Marti Montava**, grant from Spain) and on the removal of ferrous iron contained in groundwater from Niger: Experimental approach (**Mamane Imrana Chaibou Ousmane**, grant from "Campus France" program). I have also hosted **Marthe Guren** in 2019 (PhD student, University of Oslo) for a short research stay that led to an article published in Chemical Geology on the sequestration of chromium on calcite.

Master, Bachelor and ungraduated students: I have supervised 15 B.S, M.S and ungraduated students and various of them are co-authors of articles written using the main results of their research.

1. **Nicolas Concha-Lozano:** Incorporation/sequestration of oxyanions during nucleation and growth of calcite crystals (G. Montes-Hernandez, N. Concha-Lozano, F. Renard, E. Quirico, Removal of oxyanions from synthetic wastewater via carbonation process of calcium hydroxide: Applied and fundamental aspects. *Journal of Hazardous Materials 166* (2009) 788-795).

2. **Alexandre Garenne:** Gas-solid carbonation of alkaline minerals under cold planetary conditions (A. Garenne, G. Montes-Hernandez, P. Beck, B. Schmitt, O. Brissaud, A. Pommerol. Gas-solid carbonation as a possible source of carbonates in cold planetary environments. *Planetary and Space Science 76* (2013) 28-41).

3. **Mahaut Di Girolamo**: AgNPs precipitation on textile fibers and their oxidative dissolution using flow-through reactors (G. Montes-Hernandez, M. Di Girolamo, G. Sarret, S. Bureau, A. Fernandez-Martinez, C. Lelong, E. Eymard Vernain. In situ Formation of Silver Nanoparticles (Ag-NPs) onto Textile Fibers. *ACS Omega* 6 (2021) 1316-1327.

4. **Mamadou Bah**: Séquestration minérale directe et indirecte du CO_2 : Approches expérimentales et apport des ligands organiques. (Stay in 2018). This experimental study has demonstrated how magnesite (strategic mineral to storage permanently CO_2) can be precipitated at moderate temperature (G. Montes-Hernandez, M. Bah, F. Renard. Mechanism of the formation of engineered magnesite: A useful mineral to mitigate CO_2 industrial emissions. *Journal of CO_2 Utilization 35* (2020) 272-276).

5. **Alix Tordo**: Removal of As from water using nanostructured minerals, some results were incorporated in an important recent study on the removal of As(III) and Cr(VI) from water (S. Hajji, G. Montes-Hernandez, G. Sarret, A. Tordo, G. Morin, G. Ona-Nguema, S. Bureau, T. Turki, M. Nzoughi. Arsenite and chromate sequestration onto ferrihydrite, siderite and goethite nanostructured minerals: Isotherms from flow-through reactor experiments and XAS measurements. *Journal of Hazardous Materials* 362 (2019) 358-367).

6. **Manon Revol**: Removal of Ag, Cr and As from water using nano-magnetite, hematite, pyrrhotite and hydroxyapatite using flow-through experiments.

7. **Clara Vernier**: Removal of amoxicillin from water using nano-magnetite, adsorption and Fenton reaction experiments using flow-through reactors. Some of obtained results were integrated in a recent paper on the removal of antibiotics from water (G. Montes-Hernandez, L. Feugueur, C. Vernier, A. Van Driessche, F. Renard. Efficient Removal of Antibiotics from Water via Aqueous Portlandite Carbonation. *Journal of Water Process Engineering* 51 (2023) 103466.)

8. **Michelle Garcia Salinas**: Precipitation of Mg-Fe-Ca Carbonates from indirect carbonation of peridotite and steel slag waste (confidential report).

9. **Elodie David**: Optical real-time monitoring of salts and calcite crystallization from drying drops (topic in developing)

10. **Noémie Bouchard**: Capture of carbon dioxide using NaOH and lysine compounds (confidential report).

11. **Lola Feugueur**: Removal of As(III) and antibiotics from groundwater using nanominerals and mineral nanoparticles. These results were shared in important publication on the antibiotic removal from water mainly concerning the work of two bachelor students (G. Montes-Hernandez, L. Feugueur, C. Vernier, A. Van Driessche, F. Renard. Efficient Removal of Antibiotics from Water via Aqueous Portlandite Carbonation. *Journal of Water Process Engineering* 51 (2023) 103466.)

12. **Sarah Clavier (M2R, Lille)** Indirecte carbonation of peridotite and use of synthesized Fe-magnesite (Confidential Report). The obtained data have completed the results obtained in the las five years and achieved in a patent on the indirect carbon dioxide mineralization and its application.
13. **Amethys Brioudes (BUT, Grenoble)** Optical real-time monitoring of calcite crystallization on hydrophilic and hydrophobic surfaces (topic in developing)
14. **Jules Collion (BUT, Grenoble)** Removal of ammonium and nitrate ions from water: real-time monitoring by using an multi-ionic probe (topic in developing)
15. **Suzanne Marchaland Le Bihan (L2, Paris)** Optical real-time monitoring of CO2 capture from air using µ-drops of NaOH and Ca(OH)$_2$ solutions (topic in developing).

(b) Projects management and lab infrastructure

       Since 2009, I have participated as principal investigator (PI) or co-PI to national and international projects. Currently, I am PI of a PRC ANR project (called PERTINENT) than was submitted for assessment such project concerns my achievement on the carbon dioxide mineralization actively investigated in the last ten years. In summary, the proposal **PERTINENT** presents a compelling plan conducting both basic and applied research in order to produce high-purity magnesite crystals through indirect carbonation of peridotite and/or serpentine-rich rocks (raw or mining wastes). Additionally, we will investigate the potential of magnesite to serve as a partial substitute (up to 30%) of traditional cement in concrete production with a particular focus on its mechanical and textural impact on concrete. This multi-disciplinary project will integrate two main research topics by (1) pinpointing the optimal mild conditions for magnesite production through indirect carbonation of peridotite and serpentine, and (2) meticulously assessing the incorporation of fabricated magnesite as a partial cement replacement in concrete manufacturing. To implement this project, researchers from various disciplines such as geochemistry, mineralogy, material sciences and civil engineering will be involved as shown in Figure 3.
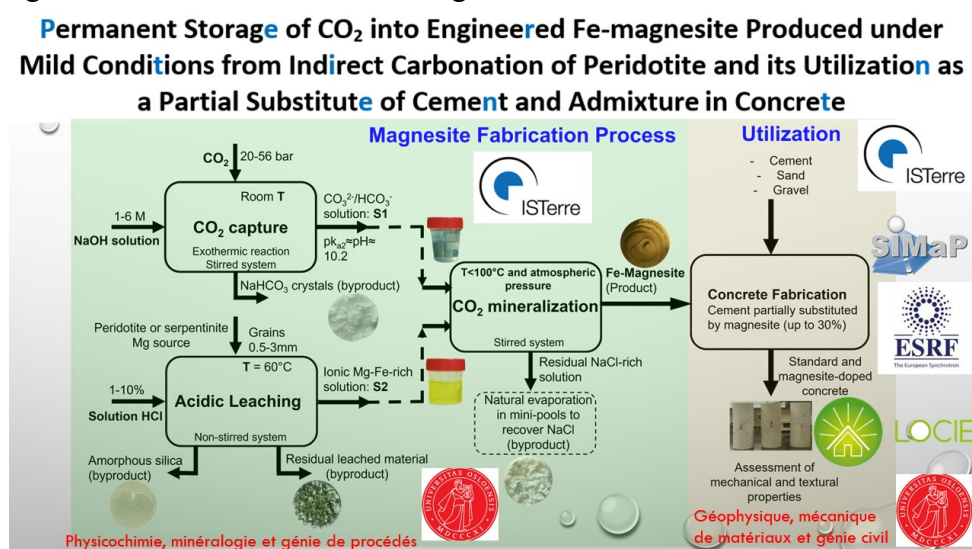

Figure 3. Graphical summary of PERTINENT project indicating process steps and partners

Historically, thanks to various grants obtained between 2009 and 2023 (CEMENTO PEPS-INSIS CNRS (2023), European ACT program FUNMIN (2019-2023), ANR Coro (2012-2015), ANR Spring (2011-2014), Labex OSUG@2020 (2012), Labex Serenade (2016-2017) and other local or ISTerre internal (BQR) projects), I have built a state-of-the-art moderate-temperature (up to 400°C) and moderate-pressure (up to 500bar) geochemistry experimental

room (about 40m^2) in Grenoble through the acquisition of various experimental setups that include:

1. A cryogenic reaction cell for *in situ* infrared measurement (investment: **10 kEuros**): Project in collaboration with Pierre Beck, Olivier Brissaud et Bernard Schmitt at Institut d'Astrophysique et Planétologie de Grenoble (IPAG).

2. A hydrothermal autoclave made of titanium with pH sensor (investment: **35 kEuros**): Collaboration with CiNAM center. Coro ANR project in collaboration with Daniel Vielzeuf Group.

3. A hydrothermal autoclave made of Hastelloy C22 for *in situ* Raman measurements (investment: **33 kEuros**): Collaboration between the Fault Mechanics and Mineralogy groups at ISTerre, Labex OSUG project: PIs: German Montes-Hernandez and François Renard.

4. A hydrothermal autoclave made of Hastelloy for simple mineral alteration and mineral hydrothermal syntheses (investment: **11 kEuros**). Project in collaboration with Alexander Van Driesche, ISTerre.

5. A multi-oven for hydrothermal experiments (investment: **10 kEuros**). Project in collaboration with Emilie Janots, ISTerre.

6. Several percolation reactors made of plastic for breakthrough curves and isotherms of pollutants, including pump and connectors (investment: **14 kEuros**). EU FUNMIN project.

7. Small equipments (peristaltic pumps, flow-through reactors, analytical balance, etc.) (investment: **20 kEuros**). EU FUNMIN project.

8. A Raman spectrometer (RXN Kaiser Optical Systems) with optical fiber probe (investment: **90 kEuros**): Collaboration between Faults Mechanics, Geochemistry and Mineralogy groups at ISTerre (GDF-SUEZ industry grant and Labex Serenade). PIs: German Montes-Hernandez and François Renard.

9. A Raman probe and optical dispositive for Raman measurements onto powdered samples (investment: **20 kEuros**). FUNMIN project.

My experimental room is also equipped of 4 tubular hydrothermal reactors with three independent zones of heating for hydrothermal experiments up to 400°C and 500bar inherited from (J. P. Gratier) and reaction cells connected to one inverted optical microscope for nucleation experiments at room T inherited from (F. Renard) as illustrated in some compiled photos below.

Figure 4. Experimental room for mineral-fluid interactions under mild and hydrothermal condition (up to 400°C and 500bar). All these experimental setups are also summarized in some slides available in my page web (https://www.isterre.fr/IMG/pdf/experimental-setups-in-my-lab.pdf)

In the past years, using this equipment, I have pioneered a new experimental technique: the time-lapse measurements of the nucleation and growth of crystals and non-crystalline mineral particles (e.g., carbonates, phosphates, sulfates, iron oxyhydroxides and oxides, etc.) under hydrothermal conditions (Figure 4). This laboratory technique is the only one so far with enough time resolution and precision to identify the formation and dissolution of chemical species and solid phases during a series of interacting hydrothermal reactions. These results have been disseminated in various international publications and recently also in a press communication: La nucléation de la magnétite analysée grâce à la spectroscopie Raman | INSU (cnrs.fr)

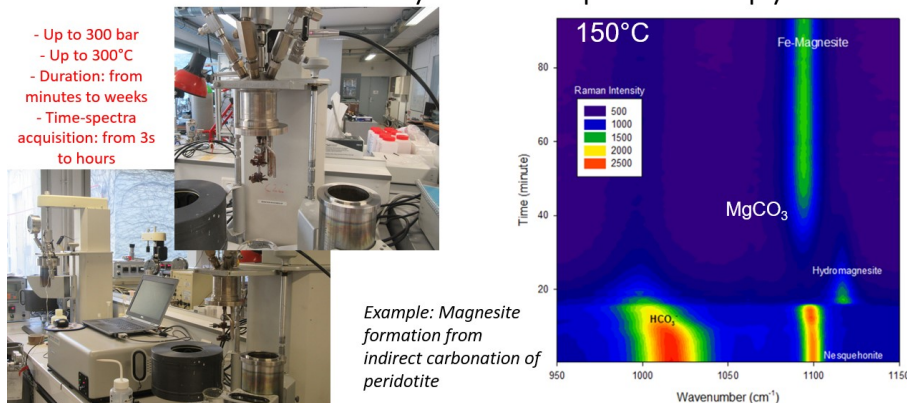Real-time monitoring of gas-solid and/or gas-liquid-solid reactions by Raman spectroscopy

Figure 5. Time-resolved in situ Raman spectroscopy of nucleation and growth of crystals and particles. Left: reactor coupled to a Raman spectrometer developed at ISTerre. Right: Time-lapse Raman spectroscopy data show magnesite nucleation and growth from a complex hydrothermal system (Montes-Hernandez and Renard, 2016 and 2020; Montes-Hernandez et al., 2020 and 2021 and Montes-Hernandez 2024).

(c) Synergetic activities

1. From January 2017 to November 2019, I was the leader of the Geochemistry team at ISTerre. This multi-disciplinary group (from mantle rocks to biosphere) federated 10 researchers, 4 engineers, 3 invited researchers and 10-15 students (B. Sc., M. Sc. and PhD). This is a very important management task in France because the team leader prepares decisions and proposes scientific directions concerning the allocation of PhD thesis grants, the definition of scientific priorities, and the allocations of local grant projects. As group leader, I was responsible of the technical staff (responsible of annual interview imposed by professional organization) and I coordinated the preparation of the national assessment of the group (HCERES). In this way, my most important task was the preparation and supervision of summary (five past years) and prospective document for the next five years program for HCERES assessment. I coordinated and wrote the general items of five-year summary (2015-2019) and project and strategy for the next five years (2020-2024). See: https://www.isterre.fr/IMG/pdf/e2_geochimie_self_assessment_document_vague_a_rech_ur_.pdf

2. From January 2016 to December 2016, I was elected as active member of the department board at ISTerre.

3. With Mexican colleagues, I participated to the creation to an informative French network "Red de Talentos, Capitulo Francia" for Mexicans working or studying in France. This network, supported by the Mexican embassy in France, facilitates the scientific and business exchange between France and Mexico.

4. From January 2015 to December 2018, I co-supervised the "axe transverse" on the geo-resources at ISTerre, a cross-disciplinary action at the department scale. The goal was firstly to identify potential cross-disciplinary local activities concerning geo-resources in order to create new collaborations and develop new research topics relevant for both basic research and societal needs. I coordinated various activities such as seminars and workshops during these three years.

5. In 2014, I organized one scientific session on the reactivity of CO_2 in aquifers during RST French meeting at Pau.

(d) Teaching activities

As Mexican citizen and ex-fellow of CONACYT in Mexico, I contribute annually with 8-16h teaching in the Master of Chemical Engineering in the University in Tlaxcala (UAT), Mexico (https://piq-uatx.mx/maestria.php). I am teaching:

- Synthesis and applications of nanostructured minerals
- Wastewater and solid waste treatment and management
- Removal of toxic ions and organic molecules from water
- Storage, mineralization, capture and reactivity of CO_2

(e) International and national collaborations

I participated to the European consortium on CO_2 mineralization via the project FUNMIN (2019-2023), as PI in France various actions (e.g., student formation, annual report for ADEM French agency, seminars, etc.) and preparation of one international publication. I have also developed several collaborations on the processes of crystal growth, that have allowed me to publish in the best journals of Earth Science and Chemical Engineering such as Chemical Geology, Geochimica et Cosmochimica Acta, Environmental Science & Technology

andCrystEngComm. These publications involve international collaborations with co-authors in, e.g., Germany, Spain, Switzerland, The Netherlands, Norway, England, USA and Tunisia.

(f) Peer-review of publications, projects and thesis

1. I am reviewing around 15 publications every year in the domains of Earth Sciences and Inorganic Chemistry, including articles in the best journals in these domains such as Angewandte Chemie, Advanced Materials, Small, Environmental Science & Technology, Geochimica et Cosmochimica Acta, Journal of Hazardous Materials, Water Research, Journal of Colloid & Interface Sciences, Chemical Geology, Langmuir, Applied Clay Science, Journal of Crystal Growth, Crystal Growth & Design, Chemical Engineering Journal, Energy & Fuels, American Mineralogist, others.

2. I have reviewed four research projects (ANR and European)

3. I was invited to participate to evaluation committees of two Ph. D. thesis (Spain and France), one committee Ph.D. thesis (France) and two M. Sc. thesis (France).

Part II: Summary of research work

Here I describe three main research topics than I have carried out in the last eight years and present a coherent and small subset of my **43 international publications as first author** (over **81 in total**, see my complete list of publications).

My main research work at ISTerre in the past seven years concerns the experimental measurement and detection of the multi-step nucleation pathways during the formation of several magnesium and calcium carbonates, various calcium phosphates and various magnetic and not-magnetic iron oxides (hydro-), using particularly time-resolved Raman spectroscopy technique, with the aim of obtaining a new holistic model of the formation of these minerals from the supersaturated solution to the final crystal as thermodynamically expected by Ostwald repining rule, but transient steps kinetically poorly characterized (see Figure 6).
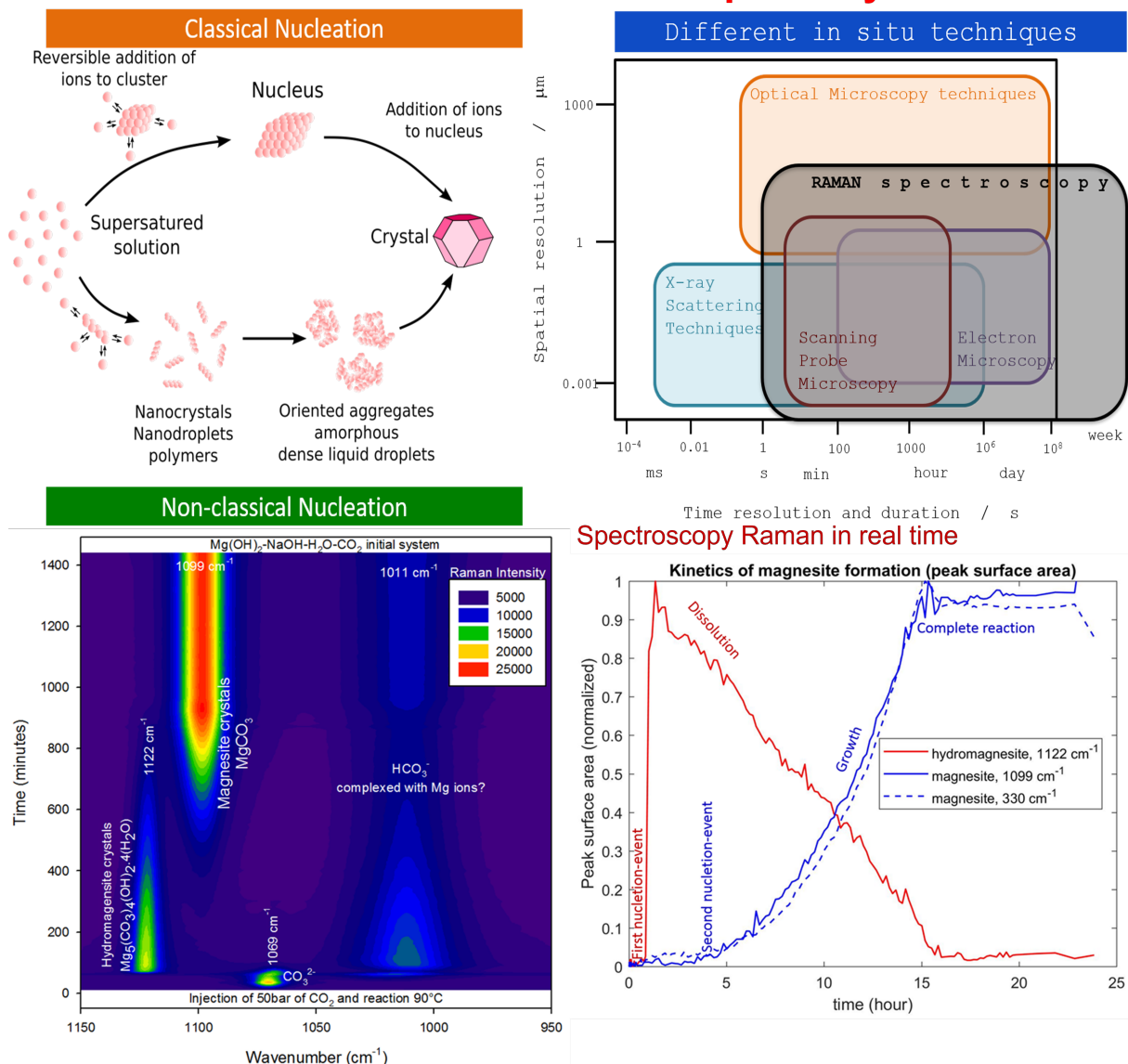

Figure 6. Current perspective on the nucleation and growth of minerals via classical or non-classical crystallization pathways. Current in-situ techniques being developed to track experimentally the nucleation events. Magnesite nucleation tracked with spectroscopy Raman monitored in real-time at 90°C from a heterogenous system (brucite slurry carbonated with compressed CO₂ using NaOH as sequestering carbon dioxide agent).

In parallel, I have investigated on the competitive carbonation and serpentinization of ultrabasic rocks (olivine model) and the transfer of pollutants (Se, Sb, As, Fe, Cr, Cs, Cu and Cd) at the mineral-solution interfaces under mild and hydrothermal conditions. My aim was to obtain original and novel insights, as demonstrated by my recent scientific production, listed at the end of each topic. All these studies on the mineral nucleation have direct relevance in natural environments, but systematically, some applications are also researched such as adsorbents in the water treatment, recycling and storage of CO_2, mineral filler and/or additive in widespread used materials, etc.

Topic 1: Nucleation, Growth and Transformation of Mineral Phases by Using Time-Resolved *in situ* Raman Spectroscopy

I have developed and used a unique laboratory technique – time-lapse Raman monitoring of fluid-mineral interactions under *in situ* conditions. This technique was initially developed for chemical engineering applications and I have imported and developed it further for fundamental studies in moderate temperature (up to 300°C) geochemistry. This technique is very reliable, relatively cheap, with data interpretation that do not require intermediate modelling steps and is complementary to other laboratory techniques that image reaction products (e.g., Transmission Electron Microscopy) and synchrotron *in situ* spectroscopy (e.g. small and wide-angle X-ray scattering SAXS/WAXS).

In the scientific community, the nucleation and growth processes of particles and crystals from aqueous systems are actively investigated and occasionally open to debate because multi-step nucleation and pre-nucleation events often exist (see my project). One main challenge is that several observations of these pre-nucleation events are made by stopping the reaction and using high resolution microscopy to search for amorphous precursor phases. However, stopping the reaction may produce additional phases, making the interpretation of the results challenging. My studies overcome this challenge by demonstrating that time-resolved *in situ* Raman spectroscopy measurements provide complementary and useful information to study the nucleation, growth and transformation of particles and crystals from homogeneous (i.e., solution-solution interactions) and heterogeneous (i.e., solution-substrate(solid) interactions) systems at different pressure-temperature conditions. I have performed a comprehensive and extensive exploration of the nucleation and growth processes of Ca, Mg and Fe carbonate minerals (including solid solutions such as Mg-calcite, dolomite and ankerite) using *in situ* time-resolved Raman spectroscopy, from surface ambient conditions to hydrothermal conditions. These studies have direct implications for the understanding of natural systems as well as for the synthesis of nanostructured carbonate minerals (e.g. mesocrystals) with economical interest (retarding flame agents, CO_2 mineral sequestration, excipients, additives in foods, paper, paints, etc.). Here, I provide only three examples of carbonate nucleation monitored in real time, but, various other carbonates, phosphates and iron oxides (Hydro-) were also investigated as illustrated in the publication list at the end of this sub-section:

Magnesite (MgCO₃)

Magnesite formation from brucite carbonation was rapidly obtained at 90°C and only 15h were required to produce up to ~6 kg/m³h high-purity magnesite (Figure 7). This important study has direct implications on the permanent storage of industrial carbon dioxide because the magnesite is the more stable carbonate under surface conditions and it can be used as substituting (up to 30%) of fresh cement in the concrete fabrication (potential application currently in investigation at ISTerre under my leadership (one patent submitted)).
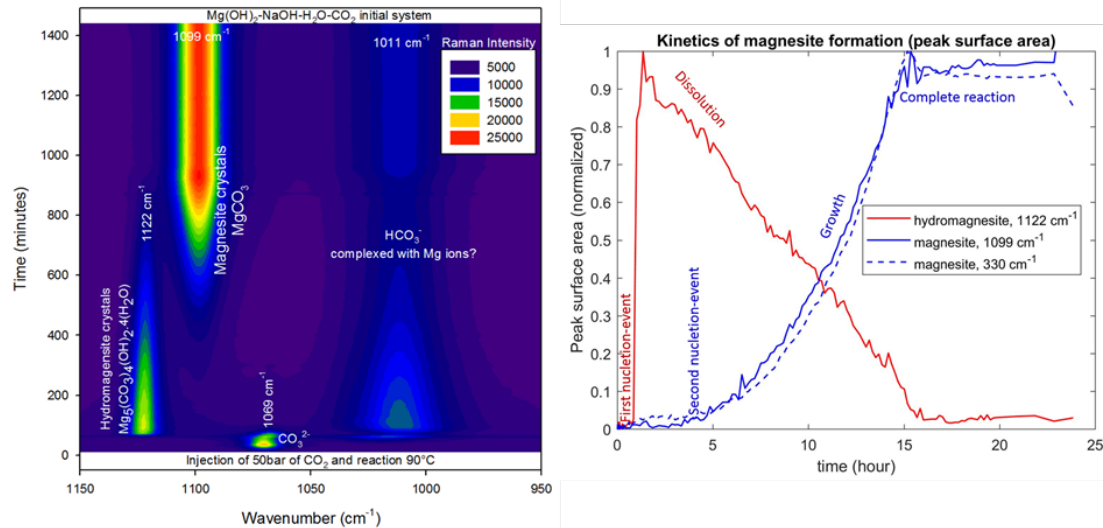
Figure 7. a) Zoom between 950 and 1150 cm^{-1} of the time-resolved Raman spectroscopy data of magnesite nucleation and growth from hydrothermal carbonation of brucite (Montes-Hernandez et al., 2020). b) Surface areas of the two peaks of magnesite and the main peak of hydromagnesite, a transient phase, as a function of time during the reaction.

The overall reaction summarizes the process:

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$
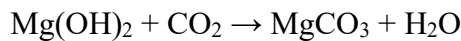
A complete aqueous carbonation reaction was obtained at 90°C exclusively when using NaOH as the CO_2 sequestering agent (or additive). The detailed reaction mechanism and kinetics was demonstrated from the time-resolved *in situ* Raman spectroscopy measurements and all temporal reaction events are shown in Montes-Hernandez et al., 2020 (see also Figure 7). Here, the aqueous carbon dioxide ($CO_{2(gas)} \leftrightarrow CO_{2(aq)}$) was rapidly dissociated into CO_3^{2-} ($CO_{2(aq)} + 2NaOH \rightarrow CO_3^{-2} + H_2O + 2Na^+$), but this reaction remained active only during the first 100 minutes. Then, carbonate ions were rapidly protonated, forming bicarbonate ions ($CO_3^{-2} + H^+ \rightarrow HCO_3^-$) that may complex with Mg^{2+}, leading to a shift of the maximum of the Raman peak of HCO_3^- from 1020 cm^{-1} to 1011 cm^{-1}. After 150 minutes, aqueous carbon dioxide and bicarbonate ions were the dominant species in the reactor, which induced a significant pH change in the interacting solution as suggested from carbonate speciation in relation with pH (inorganic carbonate fraction vs. pH diagram). Under these conditions, the dissolution of magnesium hydroxide ($Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$) was enhanced, and the release of magnesium ions generated oversaturation states with respect to several magnesium carbonates. Consequently, the nucleation of hydromagnesite was detected *in situ* after 60 minutes of reaction and correspond to a first nucleation-event.

$$5Mg^{2+} + 4HCO_3^- + 6H_2O \rightarrow Mg_5(CO_3)_4(OH)_2.4H_2O + 6H^+$$
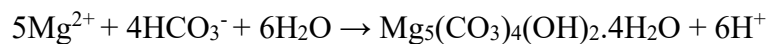
Hydromagnesite formed as a transient mineral phase that reached a maximum spectral intensity after 120 minutes. Then, this mineral dissolved in a destabilization process through a decrease of integrated surface spectral peak, a proxy for the concentration in solution (right panel in Figure 7) progressively before the nucleation of magnesite that was detected after 240 minutes of reaction. This mineral formed during this second nucleation-event.

$$Mg^{2+} + HCO_3^- \rightarrow MgCO_3 + H^+ \quad \text{(nucleation of magnesite)}$$

After the magnesite nucleation event, the growth of magnesite was mainly nourished by progressive dissolution of hydromagnesite. The temporal evolution of Raman peak surface areas of hydromagnesite and magnesite minerals suggest that this reaction included a coupled dissolution-reprecipitation pathway. Hydromagnesite serves as transient phase and it facilities

the magnesium dehydration at the hydromagnesite-interacting solution interfaces, it was completely consumed after 15 h (Figure 7).

In an environmental or engineered context, formation of magnesite at room temperature (<30°C) from the aqueous carbonation of magnesium hydroxide is too slow to be developed widely. The study I have performed shows that magnesite precipitation may have important environmental advantages if NaOH is used as additive and a moderate temperature (90°C) is applied:

1- reduction of CO_2 emissions from the industrial sector (e.g., steel and cement industry, coal-fired power);

2- production of magnesite-rich or high-purity magnesite materials with an aggregate value (e.g., fabrication of roadbed materials, bricks, granular fill, fire-retardant building material, substituting a proportion of fresh cement in the concrete fabrication…) at low or moderate temperature and reduced time (<24 h);

3- use of mine solid wastes (e.g., mines in ultrabasic rocks) or widely available Mg-silicates as a magnesium source to capture CO_2.

In practice, the residual alkaline-solution used during magnesite production could be recycled for future carbonation experiments or re-used in other chemical processes, and these options will be assessed in further studies.

Siderite (FeCO₃)

Siderite is a common constituent of low-grade iron-rich sedimentary formations and of some hydrothermal veins; it is found in a broad range of geo-environments including lake sediments, estuaries, carbonate-rich springs and shallow to deeply buried sediments and rocks. Siderite is also a common corrosion product in anoxic engineered environments and has relevance in Fe/CO₂ fuel cells. This means that siderite can form in a wide temperature range, from ambient to 200°C in alkaline carbonate solutions. However, little is known on the nature of the first precipitating particles, the role of amorphous ferrous carbonate (AFC) and/or other precursors, and the reaction kinetics. For example, recent studies have suggested that the AFC precursor provides a low-energy pathway for siderite crystallization (See Montes-Hernandez and Renard, 2016 and references therein). Assuming this hypothesis to be true, I have confirmed that adding ferrous chloride salt (FeCl₂) to a concentrated HCO_3^- solution (1mol/L) leads to the spontaneous condensation of amorphous ferrous carbonate ($Fe^{2+}+HCO_3^- \Rightarrow FeCO_{3(amorphous)}+H^+$), as attested by a broad peak at 1098 cm⁻¹, corresponding to the υ_1 vibration mode (Figure 8) and the absence of crystal lattice vibration modes (active at lower wavenumbers in the 300-200 cm⁻¹ region). This transient condensate phase persists for about 10 minutes in the system prior to siderite nucleation from AFC, as reflected by a progressive shift and thinning of the υ_1 vibration mode peaking at 1084 cm⁻¹ after about 17 minutes of reaction (Figures 8b and 8c) and the detection of crystal lattice vibration modes peaking at 283 cm⁻¹ (libration mode) and 206 cm⁻¹ (translation mode). The low intensity and broad Raman signature are mainly related to nanosized particles (<100nm) as observed by FESEM. The υ_1 peak position then shifts slightly from 1084 cm⁻¹ to 1085.5 cm⁻¹ after 24h of reaction. During this period from 20min to 24h, periodic intensity variations and slight progressive thinning of υ_1 peak were monitored, probably indicating a crystal growth process by Ostwald ripening.
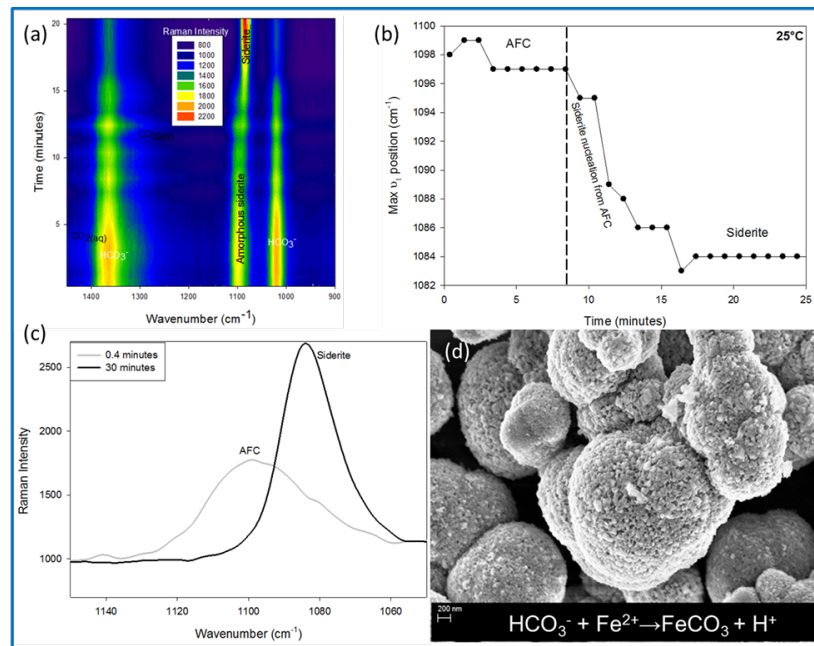
Figure 8. Time-resolved Raman spectroscopy measurements of siderite nucleation by two sequential steps: 1) Carbon dioxide capture using NaOH concentrated solution and 2) siderite formation by adding FeCl$_2$. (Montes-Hernandez and Renard, 2016). a) Time-lapse Raman data. b) Evolution of the position of the peak of siderite and its precursor (Amorphous Ferrous Carbonate: AFC). c) Raman peaks of AFC after 0.4 minutes and siderite after 30 minutes demonstrating that siderite formed from the dissolution-precipitation of AFC, an amorphous precursor. d) Scanning electron microscopy of siderite aggregates.

Oriented aggregation of crystalline nanoparticles is suggested, based on the high-resolution Field Emission Scanning Electron Microscopy (FESEM) images of recovered precipitates after 24h of reaction. The images clearly show micrometer-size spherical aggregates (e.g., Figure 8d) composed of crystalline siderite nanoparticles (size<100nm) as confirmed by ex-situ X-ray diffraction (XRD) and *in situ* Raman measurements. As a consequence, we consider that these data (broad Raman peak, nano-particles of siderite, and aggregation of them into micrometer-size aggregates) provide three circumstantial evidences that, together, point to a self-assembly aggregation process, whose mechanism remains to be understood.

In summary, *in situ* Raman monitoring data reveal a complex kinetic behavior during siderite crystallization from AFC. I discovered a siderite nucleation event detected after about 10 minutes of reaction and the complete transformation of AFC into siderite takes place in only 7 minutes. Oriented aggregation, leading to siderite mesocrystals, and Ostwald ripening mechanisms are proposed as the main processes of crystalline siderite growth at the investigated conditions.

Calcite (CaCO$_3$)

I have used concentrated ionic solutions to form amorphous calcium carbonate (ACC) by a spontaneous (spinodal) decomposition. Then, the rapid transformation of ACC into calcite was monitored by *in situ* Raman spectroscopy. Calcite (ν_1 peaking at 1089 cm^{-1}) and ACC (ν_1 peaking at 1079 cm^{-1}) were detected after 10s (Figure 9a). However, the librational/rotational and, more particularly, the translational vibration modes (lattice vibration modes) of calcite, are not clearly detected. This observation supports the fact that calcite nanoparticles coexist with ACC in the first minute of reaction and the first particles precipitated (e.g., calcite nanoparticles and ACC) are metastable, i.e., they can dissolve or transform (ACC particularly) in short times. After one minute, an effective calcite nucleation

event from ACC-calcite nanoparticle bulk phases was monitored as attested by the clear detection of two calcite lattice vibrational modes (a librational mode peaking at 283 cm^{-1} and a translational mode peaking at 157 cm^{-1}). Their Raman intensity values increased with time and the peak position shifted slightly during the experiment, in particular the librational mode from 283 to 285 cm^{-1}. On the other hand, the ACC remained detectable in the system for about five minutes. This means that calcite grows from ACC consumption in the first 5-10 minutes. Then, it subsequently grows by oriented aggregation of crystalline calcite nanoparticles, as suggested by the non-classical crystallization pathway and as also deduced from FESEM observations that show non-continuous layers at grain scale (Figure 9b). However, crystal growth by Ostwald ripening process cannot be excluded.
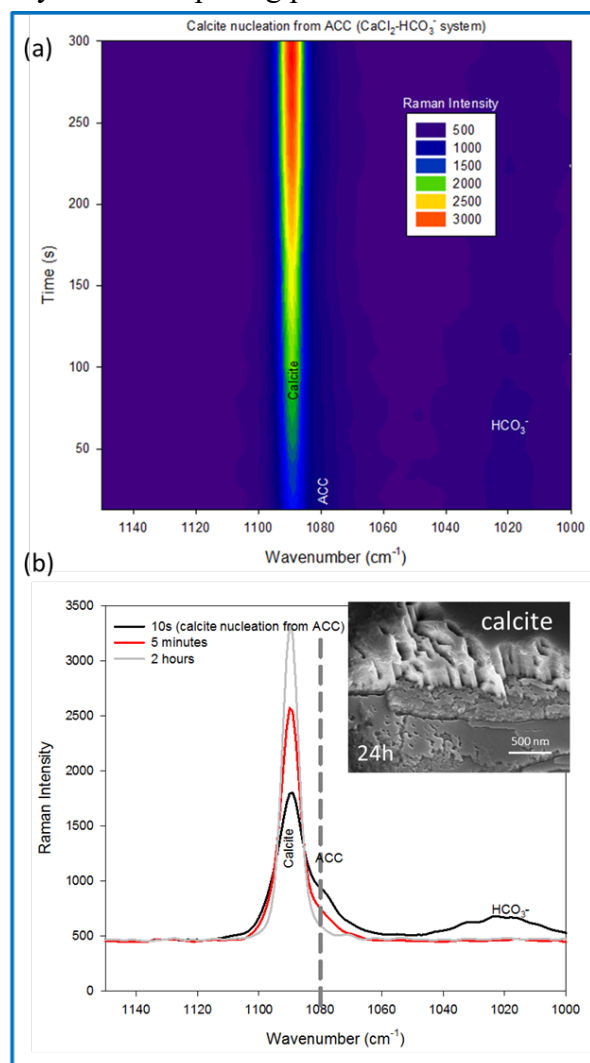

Figure 9. Time-resolved Raman spectroscopy measurements of calcite nucleation and growth from amorphous calcium carbonate (ACC) (Montes-Hernandez and Renard, 2016). a) Raman data. b) Evolution of the peak of calcite at three different times. The shoulder on this peak (gray dashed line) corresponds to Amorphous Calcium Carbonate (ACC). Inset: scanning electron microscopy image of calcite crystals produced during the reaction.

The data acquired in this study suggest that oriented aggregation and Ostwald ripening mechanisms can take place simultaneously during calcite crystal growth when ACC exists or when it is voluntarily used as precursor. The formation of so-called clusters and ACC prior to calcite nucleation is still a debated question. Complementary studies by aqueous carbonation of calcium hydroxide (Ca(OH)$_2$) was also reinvestigated by using time-resolved Raman spectroscopy. Here, the investigated overall reaction can be written as follows:

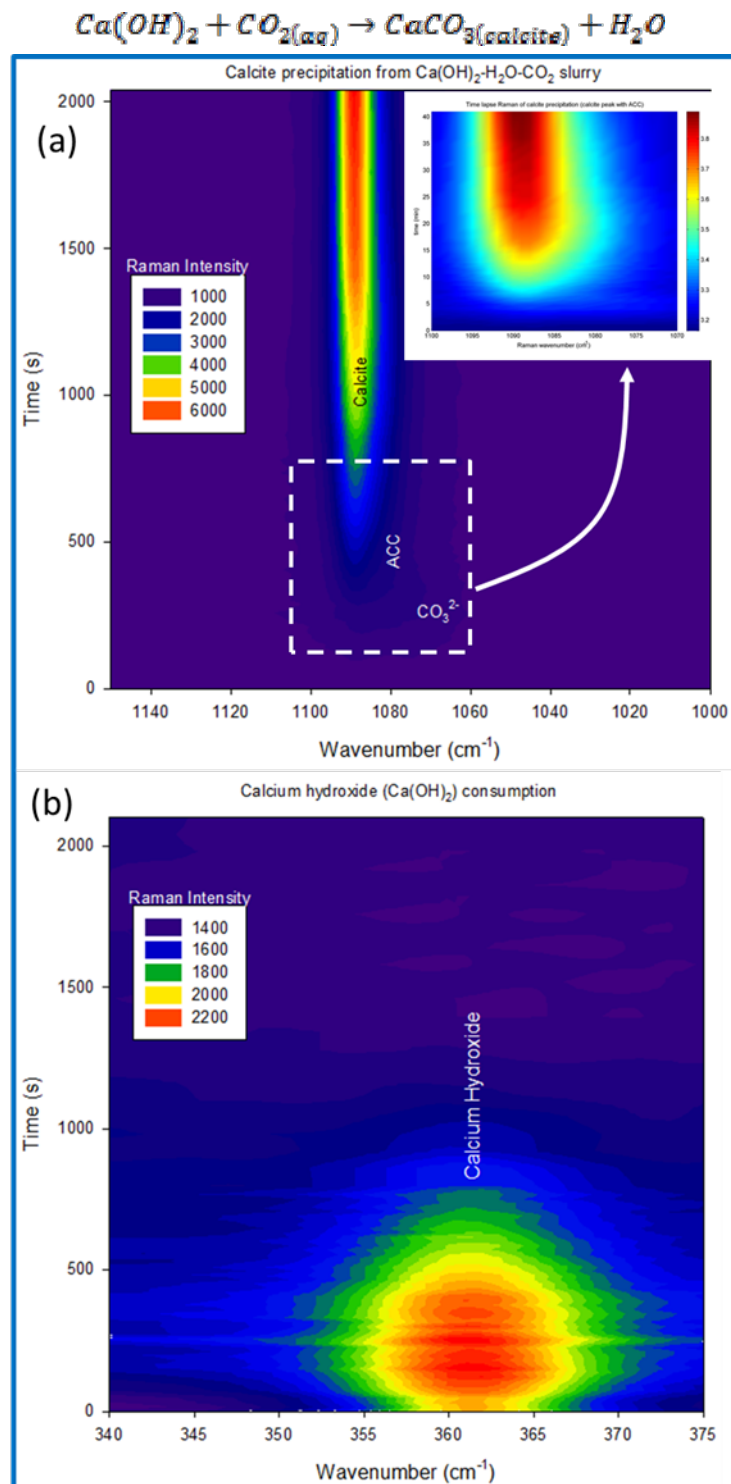$$Ca(OH)_2 + CO_{2(aq)} \rightarrow CaCO_{3(calcite)} + H_2O$$

Figure 10. Time-resolved Raman spectroscopy measurements of calcite nucleation from portlandite aqueous carbonation (Montes-Hernandez and Renard, 2016). a) Main peak of calcite as a function of time, with a shoulder corresponding to ACC. b) Growth and dissolution of calcium hydroxide, a transient phase.

Previous studies have shown that the absorption of CO_2 is the limiting step for carbonation of available calcium hydroxide ($Ca(OH)_2$). Note that calcium hydroxide is initially present in large excess (74 g/L or 1mol/L) with respect to its solubility (1.73 g/L at 20°C), and consequently this strong base maintains a high pH (~12.2) after CO_2 injection until it is completely transformed or carbonated after a given time t_c . This critical time corresponds to a

sudden drop in pH during the experiments. In practice, calcium hydroxide is completely consumed in the first 20 minutes by a carbonation process at 25°C, as attested by Raman monitoring (see Fig. 10b). Under these particular conditions, it is possible to determine whether calcium carbonate clusters and/or ACC are formed prior to calcite nucleation. Calcium carbonate nucleation is clearly detected after about 3 minutes of reaction (i.e. 3 minutes after CO_2 injection in the system), as demonstrated by the clear appearance of two υ_1 vibration modes, characteristic of the carbonate group, one peaking at $1087 cm^{-1}$ attributed to calcium carbonate and the other peaking at $1073 cm^{-1}$, this latter probably related to carbonate ions forming a complexation with calcium ions and water, given that a single carbonate ion (CO_3^{2-}) peaks at $1069 cm^{-1}$ in the measuring instrument used. This first nucleation step probably involves calcium carbonate clusters because the lattice vibration modes for calcite, vaterite or aragonite were not detected at this time. In fact, lattice vibration modes for calcite were exclusively detected after 5 minutes of reaction. Prior to this second nucleation event ($3<t<5$minutes), ACC is present (slight bump at $1079 cm^{-1}$) and coexists with calcite for about 2 minutes (Fig. 10a). After calcite nucleation (t=5minutes), calcite growth and eventually the nucleation of new calcite particles remain active processes until the complete consumption of calcium hydroxide, i.e. after about 20 minutes of reaction (see Fig. 10). When calcium hydroxide is completely consumed in the system, calcite grows by an Ostwald ripening process at 25°C for 24h, as suggested by a progressive thinning of all calcite vibrational modes, but reaching a spectroscopic equilibrium (not more significant variation of Raman intensity) after about 2h of reaction. This is also supported by the integrated peaks for calcite that reach equilibrium after about 2h. In this particular case, oriented aggregation of calcite nanoparticles is excluded, except when organic additives are used leading calcite mesocrystals as displayed in the following illustration (Fig. 11).
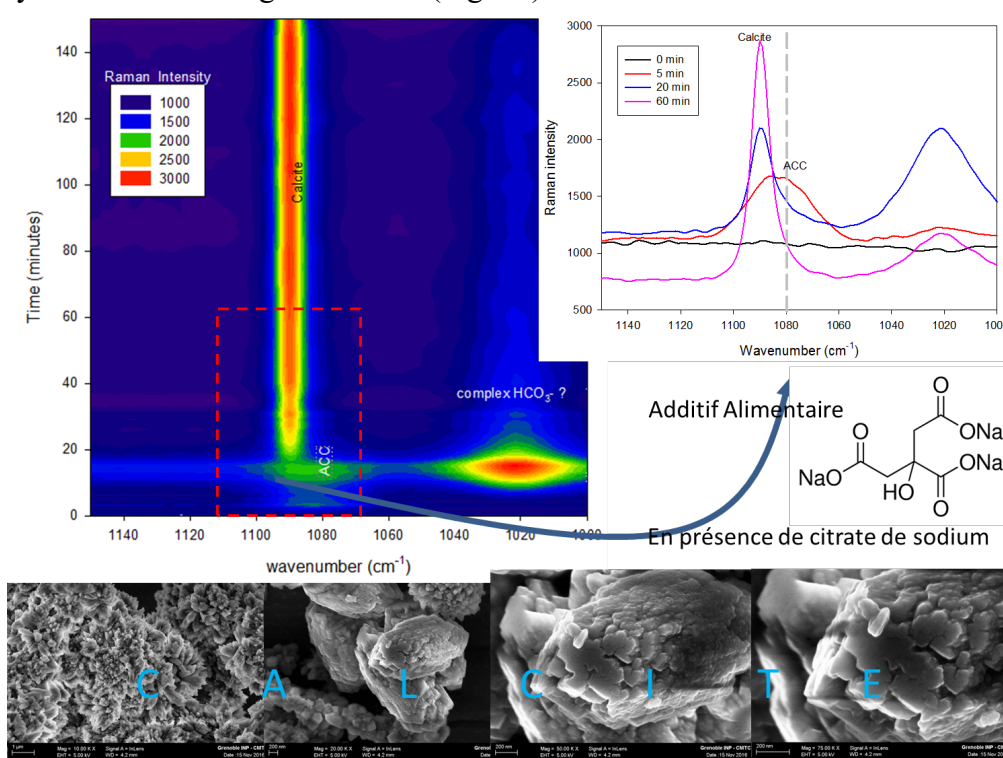

Figure 11. Time-resolved Raman spectroscopy measurements of calcite nucleation from portlandite aqueous carbonation in presence of sodium citrate (Montes-Hernandez et al., unpublished data). Top left: Time-lapse Raman data showing the peaks corresponding to the main species present in solution. Top right: Raman peaks of Amorphous Calcium Carbonate (ACC) and calcite as a function of time and in the presence of sodium citrate, where a complexation occurs with HCO_3^-. Lower images: scanning electron microscopy images of calcite formed during this experiment.

More recent studies concerning the nucleation of magnesite, Sr and Ca sulphates, proto-dolomite, Mg-calcite, magnetite and calcium phosphates (brushite and hydroxyapatite) were not summarized in the present report, but these references are listed below. Moreover, some recent results are used to illustrate my research program and/or strategy for the next 5-10 years (additional document for this competition).

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Topic 2. Hydrothermal alteration of ultrabasic minerals: competitive serpentinization and carbonation processes

This topic was started during the PhD thesis of R. Lafay who investigated the partioning of some trace elements during serpentine formation and he also investigated on the competitive serpentinization and carbonation processes during the alteration of olivine (Lafay et al., 2014). Such impressive results were shared in 6 international publications from 2012 to 2016. The results were expanded in three other recent publications (Lafay et al., 2018, Fritz et al., 2018, Denys et al., 2024) and this topic continue to be investigated using milli-metric grains and higher pressure-temperature conditions (up to 400°C and 400bar). In order to investigate the effect of supercritical water and carbon dioxide states during the olivine alteration and also determine if serpentinization is active at such conditions and finally characterize the fracture propagation at the millimetric grain scale.

In general, when mantle peridotite rocks are tectonically exposed with (sub-) surface fluids (e.g., seafloor water), olivine and pyroxene anhydrous minerals are far-from-equilibrium with respect to aqueous fluid composition. Numerous physicochemical reactions at peridotite-fluid interfaces may take place, such as hydration (-OH incorporation and serpentinization) and carbonation processes, and depend on temperature and fluid composition. Some of these reactions involve the production of natural H$_2$ and abiotic methane via redox reactions and the formation of secondary minerals, such as those observed in various natural hydrothermal sites (e.g. Logatchev, Rainbow, The Lost City). Such reducing systems may represent analogues to early Earth environments and may provide insights into requirements for the emergence of life, probably initiated at the sea floor. Field monitoring and ex-situ characterization of rock and fluid samples have revealed complex fluid chemistry and generally low pH (in the range 2.8-4.3) and high temperature (in the range 275-365°C) of the expelled fluids from various ultramafic-hosted hydrothermal systems in the Mid-Atlantic Ridge. Conversely, expelled fluids at the Lost City field and other less investigated sites (e.g. Samail Ophiolite in Oman) are highly alkaline (pH>9) and lower temperatures have been observed, in the range 55-90°C. These measurements and the recent discovery of spectacular carbonate towers at the Lost City hydrothermal field have stimulated interest in the role of serpentinization and carbonation processes on the production of hydrogen- and methane-rich fluids and on the biological communities that develop in these environments (Lafay et al., 2014 and references threrein).

The technologies of *ex situ* and *in situ* carbonation of mafic and ultramafic rocks (e.g., basalts and peridotite), extensively available in the oceanic crust and ophiolites, have been proposed as promising solutions to mitigate global warming. Indeed, Mg- Ca- or Fe-carbonates resulting from mineral carbonation of atmospheric CO$_2$ can remain stable over geological time scales, as frequently observed in the Earth surface and/or sub-surface. In this general context, numerous experimental studies concerning the serpentinization or carbonation of peridotite (or single olivine) have been recently performed using batch, semi-continuous or flow-through reactors in order to better understand the reaction mechanisms and kinetics, reaction and microfracture propagation from the grain boundaries, nature and role of secondary phase formation, potential of hydrogen production, potential for mineral sequestration of CO$_2$ and role of P, T, pH, solid/fluid ratio and fluid chemistry. However, the competitive and/or coexistence between serpentinization and carbonation along peridotite-fluid interfaces have been rarely investigated at the laboratory scale. Serpentinization and carbonation of peridotite, leading to precipitation of serpentine (e.g. lizardite, chrysotile…)

and magnesite (or hydrated Mg carbonates), could occur simultaneously in natural hydrothermal systems if the interacting solution is supersaturated with respect to both minerals (Lafay et al., 2014 and 2018, Fritz et al., 2018 and references therein).

For this reason, the main goal of my studies was targeted to determine the competitive precipitation of serpentine and magnesite from hydrothermal alteration of olivine under high-carbonate alkalinity. In the first time, I have identified specific experimental conditions (200°C, saturation vapour pressure ($\approx$16bar), solution/solid weigh ratio (=15), olivine grain size (<30μm) and high-carbonate alkalinity solution (1M $NaHCO_3$)). These experimental conditions were selected based on previous-experimental studies, investigating independently the serpentinization or the carbonation of olivine. Some of these results are reported in this no-exhaustive summary. As above mentioned, complementary experiments using now milli-metric olivine grains and higher pressure-temperature conditions continue to be investigated and one publication is in preparation.

High-purity synthetic chrysotile and serpentinized olivine (chrysotile + brucite mineral + small amount of residual olivine) obtained in my laboratory were also used as starting solids in complementary-similar experiments in order to determine their reactivity under high-alkalinity. As expected, the chrysotile was slightly altered and brucite quickly transformed to magnesite at the investigated conditions. Various analytical tools such as X-ray diffraction (XRD), Field Emission Gun Scanning Electron Microscopy (FESEM), Thermogravimetric analyses (TGA/SDTA) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the solid products. TGA analyses and the respective 1st derivative curves were particularly used to determine with high accuracy the temporal variation of magnesite and serpentine during olivine alteration. Finally, in a specific study the olivine alteration at 200°C in alkaline fluids was numerically simulated using Nanokin code (Fritz et al., 2018).

Reaction steps

　　　In Lafay et al. (2012), we reported that the serpentinization of San Carlos olivine under high-hydroxyl alkalinity (pH of 13.5, measured at 20°C) takes place via mineral replacement of olivine by chrysotile and brucite assemblage. The spatial and temporal couplings of dissolution and precipitation reactions at the interface between olivine and chrysotile–brucite minerals lead to the preservation of the external shape of olivine grains (Figure 12a). Conversely, using the same pressure-temperature conditions, but, also now CO_2-rich alkaline solutions producing a high-carbonate alkalinity, the above mineral replacement reactions did not take place. In other terms, the original external shape of olivine grains was not preserved as observed by FESEM observations (Figure 12, Lafay et al., 2014).
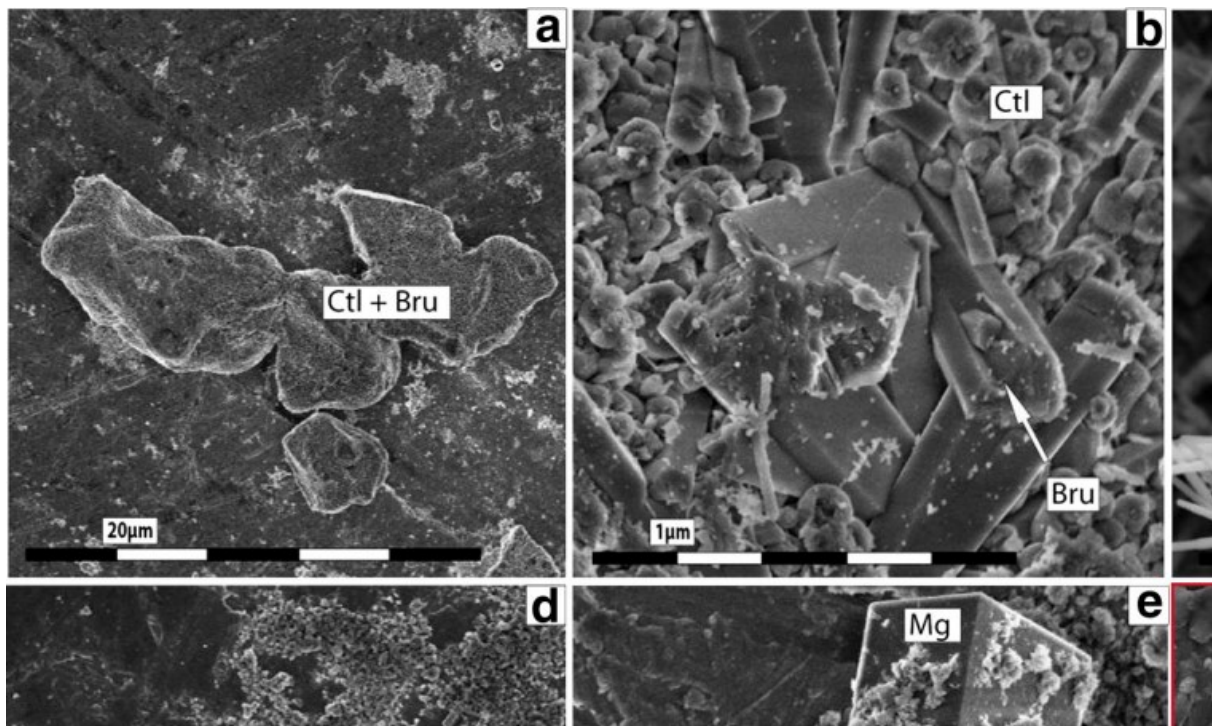
Figure 12. FESEM images of alteration of olivine in hydrothermal experiments. (a), (b) and (c) show mineral replacement of olivine by chrysotile and brucite under high-hydroxyl alkalinity, implying the preservation of original external shape of olivine grains (image (a), see also Lafay et al. 2012). (d), (e) and (f) show the coexistence of magnesite and serpentine precipitates during olivine alteration under high-carbonate alkalinity without preservation of original external shape of olivine grains (Lafay et al. 2014).

These observations suggest that super-saturation is also reached into the bulk interacting solution and not only at the fluid-olivine interface, leading to the precipitation of single magnesite crystals and fine particles of serpentine from solution. However, nucleation and epitaxial growth processes at the olivine-fluid interface cannot be excluded in our investigated system. Herein, competitive precipitation of magnesite and serpentine was clearly determined on solid products using TGA measurements and recently numerically modeled using Nanokin code (Fritz et al., 2018) as illustrated in Figure 13.
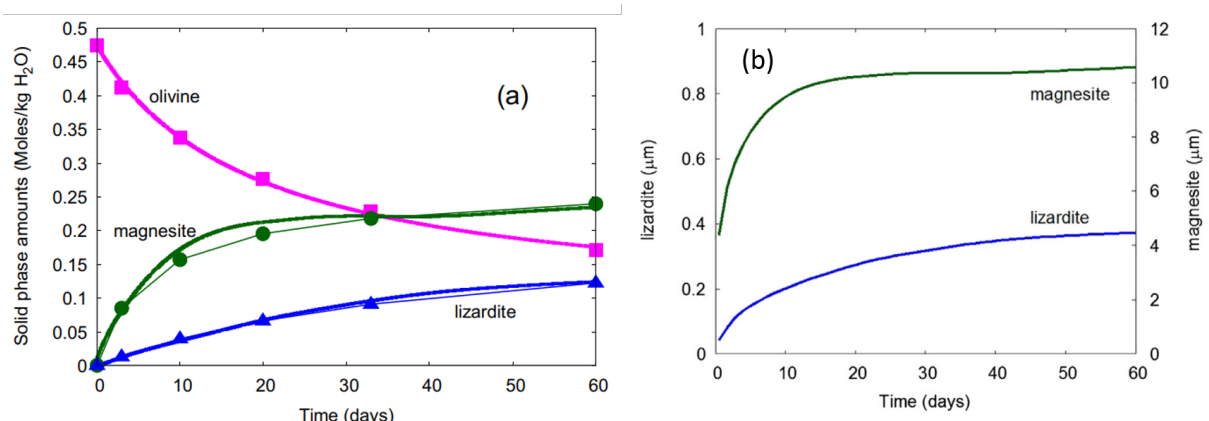

Figure 13. (a) Time evolution of the amounts of forsterite, magnesite and lizardite obtained from NANOKIN simulations (thick lines) and from the TGA analysis (symbols and thin lines); (b) Time evolution of the mean particle size of lizardite (left scale) and magnesite (right scale) (microns).

When excluding the fate of the iron initially contained in olivine (for simplicity), the alteration reaction for olivine under high-carbonate alkalinity can be expressed as follows:

$$2Mg_2SiO_4 + 2H_2O + HCO_3^- \rightarrow MgCO_3 + Mg_3Si_2O_5(OH)_4 + OH^-$$

This reaction mechanism implied a dissolution process, releasing Mg and Si ions into solution until supersaturation of solution with respect to magnesite and/or serpentine. The kinetics behavior of these minerals depends directly on the fluid chemistry such as gradual consumption of dissolved carbonate species and *in situ* OH⁻ regeneration in this close system. This change of fluid chemistry can probably promote the formation of chrysotile at the end of experiment, as observed on FESEM images (Lafay, 2013, PhD thesis). This is possibly due to a decrease of carbonate alkalinity (consumption of HCO_3^-) which is directly proportional to an increase of hydroxyl alkalinity as illustrated in the reaction above. Moreover, Lafay et al. (2012) reported that chrysotile formation is favored under high-hydroxyl alkalinity.

On the other hand, the release of iron contained in the olivine did not lead to the precipitation of iron oxides or (oxy)hydroxides under carbonate alkaline conditions. The released iron was partially oxidized (about 50%) via a simple reduction of water as follows:

$$2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^-$$
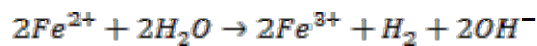
leading to the production of hydrogen. In this way, the released iron was incorporated in serpentine as Fe(II) and Fe(III), and in magnesite as Fe(II) only. This latter step was clearly demonstrated by FESEM/EDS chemical analysis on single magnesite crystals (Figure 14).
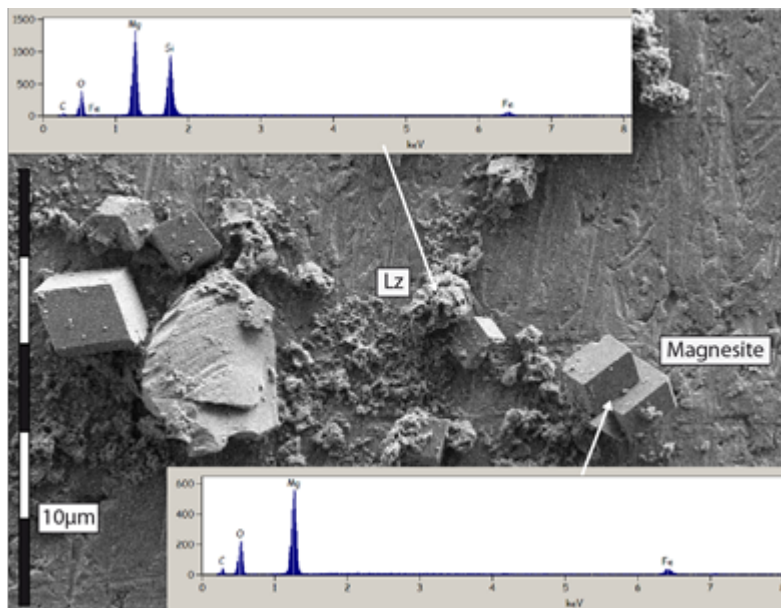

Figure 14. FESEM/EDS chemical analyses have revealed complex fate of released iron initially contained in San Carlos olivine. Iron content in magnesite suggests partial iron oxidation via water reduction. Iron may be incorporated into lizardite (Lz).

Kinetics of reaction

The kinetic pseudo-first-order and pseudo-second-order models have been widely used to describe several physicochemical reactions at solid-fluid interfaces such as uptake processes of ions and molecules, photocatalytic oxidation of organic molecules, sorption of

vapor water in/on clays, osmotic swelling process of clays, aqueous carbonation of alkaline minerals and crystal growth processes. In the present study, the kinetic pseudo-second-order model was specifically used to describe the kinetic behavior of olivine alteration under hydrothermal conditions by using the variation of formed mineral(s) content or the alteration extent ξ_{extent} (%) with time t (day). As mentioned previously, the temporal variation of magnesite and serpentine was directly determined by using thermogravimetric measurements (Lafay et al., 2012 and PhD thesis of Lafay, 2013). These kinetic data were successfully fitted using a kinetic pseudo-second-order model. This simple model predicts a fast mass transfer followed by a slow equilibration of mass transfer in closed systems. Its integrated form can be expressed as follows:

$$\xi_{extent} = \frac{\xi_{extent,\max}t}{t_{1/2} + t}$$

where $t_{1/2}$ is called the "half-extent time" and is used to calculate the initial-rate of olivine alteration [1/day], $\xi_{extent,max}$ is the maximum value of formed mineral(s) content or alteration extent at apparent equilibrium [%] and ξ_{extent} is the formed mineral(s) content or alteration extent [%] at any time t [day].

A non-linear regression by the least-squares method was performed to determine these two kinetic parameters ($\xi_{extent,max}$ and $t_{1/2}$) from the equation above.

Competitive carbonation (or magnesite formation) and serpentinization (are displayed in Figure 15a and confirm a retarding process of serpentine formation with respect to magnesite (about three times slower). In fact, the magnesite seems to reach an apparent stabilization after about 20 days of reaction while the serpentine follows a progressive slower evolution. We assumed that the magnesite reaches a fast-apparent equilibrium with solution because the available carbonate species are not renewed from gas phase, as typically constrained in aqueous carbonation experiments where a given CO_2 pressure is imposed in the system. In this way, the serpentinization process remains active until the end of experiment and carbonation process seems to be inhibited after about 30 days in the system as shown in Figure 15a. On the other hand, the alteration rate of olivine in presence of dissolved CO_2 or under high-carbonate alkalinity ($1.9x10^{-9}$ mol/m^2 s) is significantly retarded with respect to a CO_2-free system or under high-hydroxyl alkalinity at the same P-T-grain size-solid/fluid ratio conditions ($1.7x10^{-8}$ mol/m^2 s) as shown in Figure 15b. The chrysotile and brucite were preferentially formed under high-hydroxyl alkalinity and the original external shape of olivine grains was preserved (Lafay et al., 2012). Conversely, under high-carbonate alkalinity, lizardite and magnesite were preferentially formed and the original external shape of olivine grains was not preserved as recently also demonstrated for milli-metric olivine grains (Lafay et al. 2018).
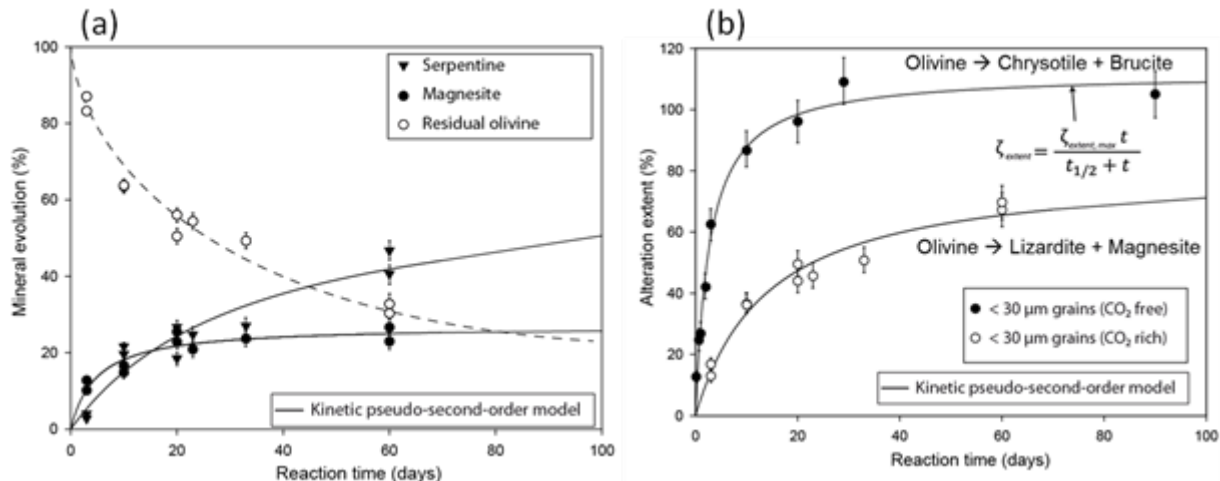
Figure 15. (a) Competitive kinetic behavior of magnesite and serpentine during olivine alteration under high-carbonate alkalinity (Lafay et al., 2014). (b) Alteration kinetic of olivine under high-hydroxyl alkalinity (filled circles) (Lafay et al., 2012) and under high-carbonate alkalinity (open circles) (Lafay et al., 2014). Experimental kinetic data were fitted by using a kinetic pseudo-second-order model.

The coexistence of serpentinization and aqueous carbonation of ultrabasic rocks has investigated for the first time by Lafay et al., 2014 at laboratory scale and various questions still remain unanswered concerning its mechanistic pathways in natural systems, mainly under high alkalinity. In response to this scientific gap, my results provide new insights on competitive serpentinization and aqueous carbonation of olivine under high-carbonate alkalinity. As above mentioned, our studies are now focused on the milli-metric olivine grains and particularly at higher pressure-temperature conditions (up to 400°C and 400bar). In order to determine the effect of supercritical water and carbon dioxide states and also to determine if serpentinization is still active at such conditions that have not been reported in the literature.

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Topic 3. Mobility of ionic and organic pollutants at the mineral-solution interfaces under mild and hydrothermal conditions

The investigation on the mobility of the heavy metals, metalloids and rare elements at the mineral-solution interfaces under hydrothermal conditions have important implications on the formation of ionic-enriched mineral phases and/or formation of solid solutions such as carbonates (bastnäsite) or phosphates (monazite) of rare elements (so-called strategic elements). In this way, my research group has determined that cerium carbonate (bastnäsite-Ce type) can be formed from 90°C to 300°C in hydrothermal systems (Montes-Hernandez et al., 2013). In this same context, the allanite alteration under hydrothermal conditions and role of ligands was also recently investigated (see Denys et al., 2024). The mobility of Sb, Cs and As was also determined during experimental serpentinization of Olivine San Carlos at 200°C (Lafay et al. 2016) and during chrysotile formation at 300°C (Lafay et al., 2014). In this later study, the partitioning coefficients were determined from simple fitting of Langmuir equation. This experimental research topic offers an original perspective to determine specific hydrothermal conditions on the formation of mineral deposits, i.e., minerals enriched in the so-called strategic chemical elements poorly documented in the literature. This topic will continue to be developed in the coming years via PhD students and postdoctoral grants as proposed in my outlook for the next 5-10 years.

On the other hand, the ionic-pollutant sequestration during nucleation or during dissolution (creating sequestration sites) by time-lapse imaging in atomic force microscopy (AFM) was widely investigated in collaboration with C. Putnis and F. Renard (see below the publication list at the end of this section). In the same context, the sequestration by sorption an/or sequestration crystal processes is also being actively investigated by my group by using flow-through reactor experiments as reported recently in Hajji *et al*., 2019 and Montes-Hernandez et al., 2023. All these fundamental results related to wastewater treatment and/or fate of ionic and organic pollutants in the environment. I note for example that heavy metals, metalloids and antibiotic are often released into the environment as a result of industrial, medical and agricultural activities such as mining industrial activities, microelectronics, electroplating, metal finishing, battery manufacture, tannery, metallurgical, pharmaceutical, textile, fertilizer, etc. industries. Toxic ions and organic molecule can be transferred into the human and other life organisms via inhalation, ingestion, and skin adsorption, causing irreversible disruptions. They are bio- not biodegradable and, hence, may cause long-term contamination of aquatic ecosystems. In this way, the development of efficient techniques for the removal of ionic (As, Sb, Se, Cr, Cd, Pb…) and emerging (e.g., antibiotics) pollutants from water and wastewater is an important task in terms of protection of public health and environment.

In practice, several simple and sophisticated methods are available to remove the toxic ions and organic pollutants from wastewater, such as chemical precipitation, ion exchange, membrane filtration, electrocoagulation, phytoremediation, oxidation-reduction processes, reverse osmosis, chemical coagulation followed by filtration and adsorption. Among these methods, the sorption by using non-expensive solid-adsorbents remains efficient and its

functioning and technological requirements are also simple. Significant advantages of the adsorption method are a high efficiency in removing very low levels of heavy metals from dilute solutions, an easy handling, a high selectivity, low operating costs, a minimization of chemical or biological sludge, and in some cases the adsorbent can be regenerated or simply confined in controlled disposal systems (See Montes-Hernandez and Rihs, 2010, Montes-Hernandez et al., 2014 and 2015 and references therein).

Extensive research has been performed on the removal of toxic ions from wastewater by sorption processes, i.e., by using simple adsorbent-solution interactions in batch stirred reactors, from which the concept of sorption isotherm has been defined. Back in the 1990's, experimental methods using stirred flow-through reactors were develop to measure the sorption isotherms and offered a more realistic interpretation linking the kinetic to equilibrium behavior for a well-defined adsorbent-solution system in percolation mode. Unfortunately, this efficient method was not popularized and rare studies are found in the literature. Besides, several studies were performed to determine the fixation mechanism of ions and/or pollutants onto/into solid phases at the atomic level by using synchrotron-based X-ray absorption spectroscopy (XAS). Such studies have significantly contributed to existing knowledge on the sorption and/or sequestration mechanism of toxic ions at the mineral-solution interfaces. Nevertheless, the "sorption/sequestration isotherms", a curve describing the retention of pollutants on a solid at various concentrations, remains a major tool to describe and predict the mobility of chemical species in natural and anthropogenic environments (e.g., Hajji et al., 2019, Montes-Hernandez et al., 2023). I have developed a series of experimental studies to characterize the sequestration of Se, As, Cr, Sb, Cd, Cu, Fe and antibiotics in/on some nanostructured minerals (calcite, 6L-ferrihydrite, goethite, siderite and portlandite) freshly synthesized using in-house methods. I have used batch and stirred flow-through reactor experiments and combined these studies with *in situ* time-lapse atomic force microscopy experiments performed in collaboration with the group of C. Putnis in Münster. Herein, various significant studies were published from 2013 in top journals such as ES&T, GCA and Chem. Geol.

The stirred flow-through reactor technique offers a direct monitoring of pollutants sequestration performance for a given adsorbent by comparing the breakthrough curves for inert and reactive tracers. Moreover, the integrated surface comprised between these experimental breakthrough curves (retarding effect) enables the determination of sequestration isotherms for pollutants in a broad concentration range from a single experiment as illustrated in figure 16.
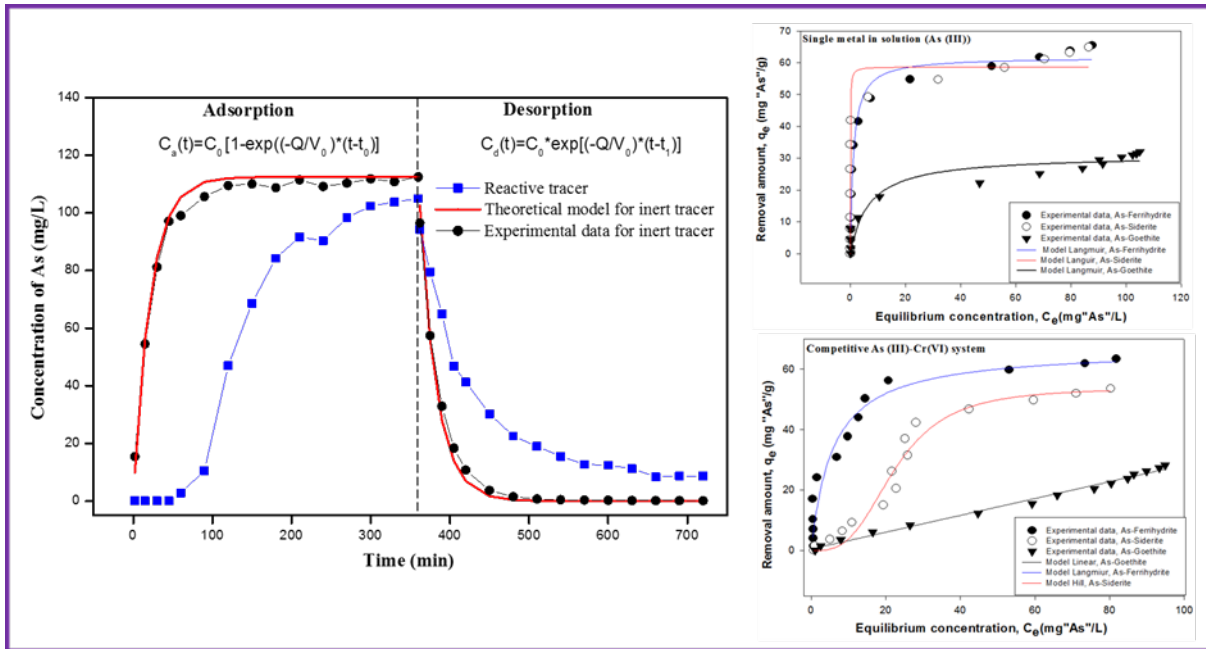
Figure 16. Sorption isotherms from the breakthrough curves of an inert and a reactive tracer obtained with the stirred flow-through reactor, assuming that the reaction is instantaneous. The relation between the hatched surface area Ai of the breakthrough curve and the solid concentration Qi is given by $Q_i = \frac{Flow\ rate}{Solid\ mass} A_i = \frac{Flow\ rate}{Solid\ mass} (\int_{t=0}^{t=t_i} C_{inert\ tracer}\ dt - \int_{t=0}^{t=t_i} C_{reactive\ compound}\ dt)$.

Flow through reactors appear then as efficient tools for the screening of their efficiency on large series of pollutants and sorbents, and can be considered as high throughput methods. Spectroscopic measurements (XAS, FTIR, XPS, Raman, etc.) and microscopic (e.g. AFM) are ideal complementary tools to determine the fixation mechanisms of pollutants at the nano- and/or atomic scales. In this way, I have performed various studies using *in situ* time-lapse atomic force microscopy experiments in collaboration with the group of C. Putnis in Münster.

For example, the selenite incorporation during calcite growth perturbs a pyramidal typical growth for calcite (Figure 17).
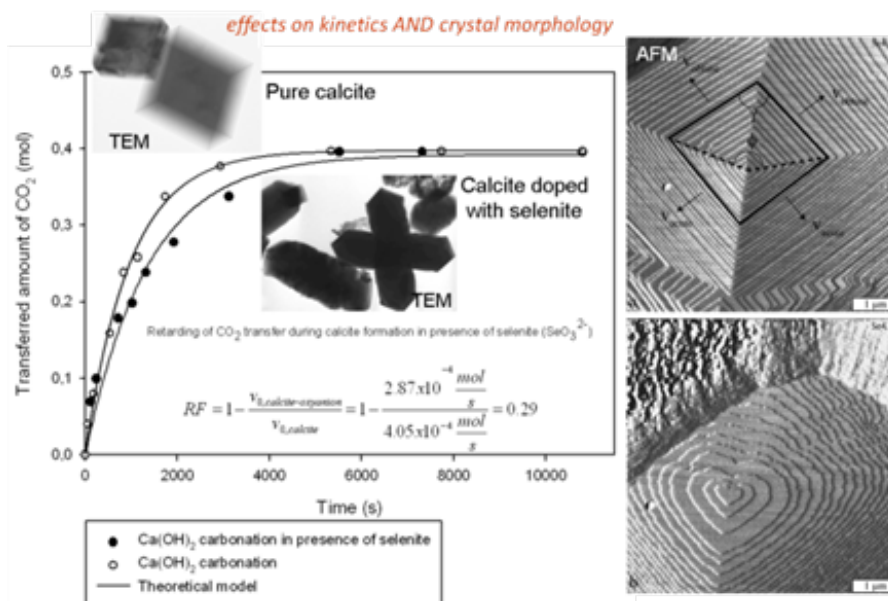
Figure 17. Left: Kinetic effect of selenite oxyanion (SeO_3^{2-}) on the CO_2 consumption during nucleation-growth of calcite in triphasic gas-liquid-solid system under hydrothermal conditions (on the left). The selenite incorporation during calcite growth perturbs a pyramidal typical growth for calcite as measured by in situ time-lapse atomic force microscopy experiments. Right: Atomic force microscopy imaging of the effect of selenite on the growth of calcite (Renard et al., 2013).

In this way combining batch and flow-through experiments with time-resolved AFM observations, was possible to investigate on the physicochemical interactions of Se, Sb, Fe, As, Cr and antibiotics during nucleation and/or dissolution of carbonate phases. All these data were shared in top journals as illustrated in my publication list and/or page-web https://www.isterre.fr/annuaire/pages-web-du-personnel/german-montes-hernandez-1397/article/publications.html

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Scientific production in addition to the three topics described previously

In the past ten years, I have collaborated and contributed to mineral characterization of extra-terrestrial objects in order to understand their mineral aqueous alteration. In this context, I have supervised the PhD thesis of Alexandre Garenne and co-authored four publications in this domain. In parallel, several studies on the synthesis and applications of mineral nanocomposites, mesocrystals and nanomaterials (geo-inspired and engineered systems) continue to be developed as illustrated in the following list:

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2. **G. Montes-Hernandez**. Synthesis of Magnetite, Ceria and Magnetite-Ceria Materials by Calcination of Nanostructured Precursor-Minerals. *Materials Letters 276* (**2020**) 128246.

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