

Thesis title: *Time-resolved in situ Raman spectroscopy of the nucleation and growth of particles and crystals under hydrothermal conditions*

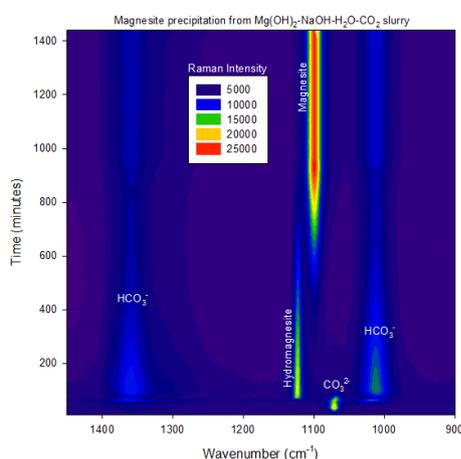
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Important advances have been made in our understanding of mineral formation. Both, experimental and computational data collected for various systems (e.g. calcite, apatite, gypsum), have revealed a number of alternative – often called “non-classical” – perspectives on the mechanisms underlying the birth, growth and transformation of mineral phases (e.g. Gebauer et al., 2008; Dey et al., 2010; Van Driessche et al., 2012; Wallace et al., 2013; Nielsen et al., 2014). However, there is still a long way to go until we fully and quantitatively understand how minerals nucleate and grow from solution (e.g. Van Driessche et al., 2017). Moreover, most experimental observations were done at room temperature and atmospheric pressure, and many common minerals such as magnesite, siderite, goethite, dolomite, magnetite, chrysotile and anhydrite predominantly form at significantly higher temperatures and pressures.

A recently developed in-situ Raman monitoring system (Montes-Hernandez and Renard, 2016) is a powerful real-time technique to monitor reactions in aqueous, organic and multi-phasic media, which allows us to probe in situ the early stages of mineral formation for both



homogenous (solution-solution interactions) and heterogeneous (solid-fluid interactions) systems. The present PhD thesis proposes the coupling of this in-situ Raman spectroscopy technique with a hydrothermal reaction cell (autoclave) in order to monitor the solution chemistry (e.g. speciation, nature and fate of organic matter...) and the nucleation and growth processes of minerals. This will allow us to probe the early stages of mineral formation for wide T and P range, representative of environmental/industrial conditions. For example, preliminary experiments have revealed a detailed reaction mechanism of

precipitation of magnesite from brucite slurry under hydrothermal conditions (90°C and 50bar of CO₂) that implies the CO₂ dissolution in carbonate species (fast CO₃²⁻ formation followed by its protonation in HCO₃⁻), transient precipitation of hydro-magnesite mineral phase and finally nucleation of magnesite (more stable mineral phase in the system) by progressive consumption of hydro-magnesite via a dissolution-reprecipitation process (above figure; see also [Montes-Hernandez and Renard, 2016](#)).

We expected that this coupling experimental setup will allow extending this investigation to other low-temperature and hydrothermal minerals such as siderite,

dolomite, anhydrite, zeolites, allophanes, etc. Moreover, Raman in-situ detection (immersed probe into slurry phase) will allow obtaining realistic data on the pH behaviour (in specific cases), carbonate speciation, nature of the first nucleating particles and fate of organic molecules during crystal growth of carbonates, sulphates, serpentines and oxyhydroxides. Note that the ex-situ measurements of fluid properties generally performed at ambient conditions after filtration, cooling, depressurization, and degasification are not representative of in-situ fluid properties behavior during nucleation-growth of solids in multiphasic systems under hydrothermal conditions. Thus, in situ Raman monitoring will provide key insights to improve our understanding of classical and/or non-classical crystallization pathways taking place beyond room temperature and atmospheric pressure. When required, the data Raman will be complemented with (cryo) TEM imaging and *in situ* SAXS/WAXS experiments, using a custom-build hydrothermal flow-through cell.

PhD candidate will require a solid background in material sciences, physico-chemistry or applied physics and, a good motivation to lab experimentation and numerical simulation. For complementary details on the experimentation kind, solid/fluid characterization and numerical simulation to be performed refers to the following some references:

- **G. Montes-Hernandez**, F. Renard. Time-resolved in situ Raman spectroscopy of the nucleation and growth of siderite, magnesite and calcite and their precursors. *Crystal Growth & Design* 16 (2016) 7218-7230.
- **G. Montes-Hernandez**, G. Sarret, R. Hellmann, N. Menguy, D. Testemale, L. Charlet, F. Renard. Nanostructured calcite precipitated under hydrothermal conditions in the presence of organic and inorganic selenium. *Chemical Geology* 290 (2011) 109-120.
- **G. Montes-Hernandez**, F. Renard, R. Chiriac, N. Findling, F. Toche. Rapid precipitation of magnesite micro-crystals from $Mg(OH)_2$ - H_2O - CO_2 slurry enhanced by NaOH and a heat-ageing step (from ~20 to 90°C). *Crystal Growth & Design* 12 (2012) 5233-5240.
- **G. Montes-Hernandez**, F. Renard, R. Chiriac, N. Findling, J. Ghanbaja, F. Toche. Sequential precipitation of a new goethite-calcite nanocomposite and its possible application in the removal of toxic ions from polluted water. *Chemical Engineering Journal* 214 (2013) 139-148.
- B. Fritz, A. Clément, **G. Montes-Hernandez**, C. Noguera. Calcite formation by hydrothermal carbonation of portlandite: Complementary insights from experiment and simulation, *CrystEngComm* 15 (2013) 3392-3401.
- **A. E. S. Van Driessche**, L. G. Benning, J. D. Rodriguez-Blanco, M. Ossorio, P. Bots and J. M. García-Ruiz. The Role and Implications of Bassanite as a Stable Precursor Phase to Gypsum Precipitation. *Science*, 336, 69-72, 2012.
- T. Stwaski, **A.E.S. Van Driessche***, M. Ossorio, J.D. Rodriguez-Blanco, R. Besselink, L. Benning. Formation of calcium sulfate through the aggregation of sub-3 nm primary species. *Nat. Comm.* 7, 11177, 2016.
- J. Scheck, B. Wu, M. Dreschler, R. Rosenberg, **A.E.S. Van Driessche**, T.M. Stwaski, D. Gebauer. The molecular mechanisms of iron(III) oxide nucleation. *J. Phys. Chem. Lett.* 7, 3123, 2016.