Time-resolved in situ Raman spectroscopy of the nucleation and growth of siderite, magnesite and calcite and their precursors

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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. This study demonstrates that time-resolved Raman spectroscopic measurements can provide complementary and useful information on the nucleation and growth of particles and crystals from homogeneous and heterogeneous systems at different pressure-temperature conditions [1]. Three minerals were chosen for this study: siderite, magnesite and calcite, three carbonate minerals that are widespread in geological environments and have numerous industrial and medical applications. As expected, siderite and calcite can rapidly form via an amorphous precursor when using concentrated solutions of reactants directly mixed at ambient temperature (~25°C) and pressure (~1 bar) (i.e. via spinodal decomposition or when energetic barrier is close to zero). In addition, calcium carbonate clusters and/or probably also amorphous calcium carbonate (ACC) were detected in the first five minutes prior to calcite nucleation in a $Ca(OH)_2$-H_2O-CO_2 concentrated slurry at 25°C and 50bar. The calcite and siderite crystals, nucleated from their respective amorphous phases, grow by oriented aggregation of crystalline nanoparticles leading to porous spherical siderite-mesocrystals or non-porous rhombohedral calcite crystals after 24h of reaction, as deduced from FESEM images and X-ray diffraction analyses. Conversely, magnesite formation ($MgCO_3$: anhydrous Mg carbonate) was only measured under hydrothermal conditions (e.g. 90°C and 50bar of initial CO_2 pressure) and systematically a transient crystalline phase such as hydromagnesite was observed prior to magnesite nucleation and growth at the investigated conditions.

[1] G. Montes-Hernandez and F. REnard (2016) *Cryst. Growth Des.* 16, 7218-7230.