

Effects of ferrous iron on the precipitation and growth of CaCO₃ in slightly basic aqueous solutions, from macro to nanoscale

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The precipitation of CaCO₃ and further growth of calcite has been studied in aqueous solutions containing ferrous iron (Fe²⁺). Two different types of bulk experiments have been carried out. Nucleation experiments have been conducted at pH 9 with five different Ca_{TOT}/Fe_{TOT} ratios: 10, 5, 2.5, 1.25 and 0.625. As well, calcite growth experiments have been conducted at pH 8.5 (following the constant composition method) with Ca_{TOT}/Fe_{TOT} ratios: 100, 50 and 25; this higher dilution partially reduces the impact of inhibition on growth of calcite occurring when Ca_{TOT}/Fe_{TOT} ≤ 25. Parameters such as the solution pH, [Ca²⁺], conductivity, solution transmittance (610 nm), and volume added were continuously monitored by a Titrino 905 system (Metrohm, Switzerland). After the experiments, the CaCO₃ precipitates were collected, filtered, dried and characterized by powder-XRD, HRTEM, FESEM-EDX, EMPA. Solution composition was determined by ICP-MS. Additionally, in-situ Atomic Force Microscopy (AFM) flow-through growth experiments were conducted in a sealed fluid cell using freshly cleaved natural calcite (Iceland spar). The solution composition in AFM experiments was analogous to the bulk growth experiments. The results of these experiments reveal the significant influence of ferrous iron on nucleation and growth in the CaCO₃-H₂O system, reflected as well in polymorphic selection in this system. Finally, thermodynamic considerations for the system Ca-Fe-CO₂-H₂O are discussed that allow the modelling of geochemical processes involving this system, such as geological carbon storage in basaltic rocks.