

Crystallization Experiments in the MgO-CO₂-H₂O system: Role of Amorphous Magnesium Carbonate Precursors in Magnesium Carbonate Hydrated Phases and Morphologies in Low Temperature Hydrothermal Fluids

Manolis Giampouras, Juan Manuel Garcia-Ruiz, and Carlos J. Garrido

Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC & UGR, Avd. Palmeras 4, 18100 Armilla, Granada, Spain

Numerous forms of hydrated or basic magnesium carbonates occur in the complex MgO-CO₂-H₂O system. Mineral saturation states from low temperature hydrothermal fluids in Semail Ophiolite (Oman), Prony Bay (New Caledonia) and Lost City hydrothermal field (mid-Atlantic ridge) strongly indicate the presence of magnesium hydroxy-carbonate hydrates (e.g. hydromagnesite) and magnesium hydroxides (brucite). Study of formation mechanisms and morphological features of minerals forming in the MgO-CO₂-H₂O system could give insights into serpentinization-driven, hydrothermal, alkaline environments, which are related to early Earth conditions. Temperature, hydration degree, pH and fluid composition are crucial factors regarding the formation, coexistence and transformation of such mineral phases. The rate of supersaturation, on the other hand, is a fundamental parameter to understand nucleation and crystal growth processes. All these parameters can be examined in a solution using different crystallization techniques.

In the present study, we applied different crystallization techniques to synthesize and monitor the crystallization of Mg-bearing carbonates and hydroxides under abiotic conditions. Various crystallization techniques (counter-diffusion, vapor diffusion and unseeded solution mixing) were used to screen the formation conditions of each phase, transformation processes and structural development. Mineral and textural characterization of the different synthesized phases were carried out by X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy coupled to dispersive energy spectroscopy (FE-SEM-EDS). Experimental investigation of the effect of pH level and silica content under variable reactant concentrations revealed the importance of Amorphous Magnesium Carbonate (AMC) in the formation of hydroxy-carbonate phases (hydromagnesite and dypingite). Micro-structural resemblance between AMC precursors and later stage crystalline phases highlights the critical role of internal molecule re-organization to form crystalline structures. Aggregation of AMC spherulites triggers biomimetic morphologies forming curling laminar structures and rings. The size and number of nesquehonite (MgCO₃·3H₂O) crystals are controlled by pH and Mg²⁺ ions at pH < 9. As pH increases, nesquehonite transforms to spherical, rosette-like dypingite and/or hydromagnesite. Crystallization experiments within silica gel impedes the normal growth of prismatic nesquehonite crystals and generates peculiar dendritic crystalline structures. Finally, vapor diffusion techniques resulted in synthesis of NH₄⁺-bearing hydrated compounds after ammonium incorporation when [NH₄⁺]/[Mg²⁺] ≥ 1 and ≥ 0.5M [NH₄⁺].

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