Influence of Organic Ligands on Mineral Carbonation Kinetics

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Abstract

Recent field tests at the Wallula Basalt Pilot Project and CarbFix pilot project have successfully demonstrated carbonate mineralization due to injection of supercritical CO₂ and aqueous-dissolved CO₂, respectively. Basalt also host significant biomass that can supply organic ligands and impact fluid-rock interactions. In this study, we explored the influence of organic ligands on forsterite (Mg₂SiO₄) carbonation in nanoscale interfacial water films in contact with water-saturated supercritical CO₂ (scCO₂) fluids (90 bar) by conducting time-resolved in situ X-ray diffusion (XRD) experiments at 50 °C. Synthetic forsterite was exposed to water-saturated scCO₂ that had been equilibrated with acetate, malonate, oxalate, and citrate solutions of varying concentrations (0.01-0.5 M) to determine how organic ligands influence carbonate pathways and pathways. The experimental results demonstrated that greater concentrations of citrate in the nanoscale interfacial water film promoted the precipitation of magnesite (MgCO₃) relative to nesquehonite (MgCO₃·3H₂O). The enhancement of magnesite precipitation also correlates with the equilibrium constant for the ligand-Mg²⁺ association reactions, with trivalent citrate most effectively dehydrating Mg²⁺. At the highest concentrations of citrate tested, magnesite nucleation and growth were inhibited, lowering the carbonation rate constant from 9.1 × 10⁻⁹ to 3.6 × 10⁻⁹ M⁻¹ s⁻¹. These impacts of citrate were due to partial dehydration of Mg²⁺(aq) and the adsorption of citrate onto nuclei and magnetic surfaces. This type of information may be used to predict and tailor subsurface mineralization rates and pathways.

Organic ligands influence reaction pathways

- Propagation of magnesite precipitation enhanced when air organics are present relative to control experiment
- Mg²⁺-organic ligand comprising partially dehydrated citrate
- Complex stability/strength correlates with magnesite enhancement trend
- NSE/HEX identification of secondary carbonate and silicates
- Radiating prismatic blades of nesquehonite, submicroscopic magnesium rhombohedra, and distinctive amorphous silica observed
- Distinct morphologies of precipitates correlate with expected chemistry (EDS)
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Citrate influences carbonate formation and reaction pathways

- Citrate promotes amphoteric Mg-carbonate precipitation
- Citrate complexes with Mg in the water film, displacing water of hydration
- At high concentrations, carbonation reaction is inhibited due to citrate adsorption on magnetic

Influence of nanon confinement on reaction kinetics

- Higher energy barrier and subsequent slower kinetics due to impacts on diffusion and ligand-exchange
- Apparent activation energy of forsterite carbonation more than double when water film thickness decreases by <1 nm

Materials

- Synthetic Model Minerals: Forsterite (Mg₂SiO₄)
- Reactive on laboratory timescale (27 m/s/g surface area)

Model

- Three overall reaction listed below
- Carbonation may proceed in an autocatalytic, hydrothermal carbonate mechanism
- Carbonation proceeds as Reaction 1 and Reaction 2 and/or Reaction 3 followed by Reaction 3

1) $\text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 \rightarrow 2\text{MgCO}_3 + \text{SiO}_2 (am)$

2) $2\text{MgCO}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{MgCO}_3\cdot\text{H}_2\text{O} + \text{SiO}_2 (am)$

3) $\text{Mg}_2\text{CO}_3\cdot3\text{H}_2\text{O} \rightarrow \text{Mg}_2\text{CO}_3 + 3\text{H}_2\text{O}$

Conceptual Model

- CO₂-H₂O-rock-organic interactions

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