Influence of Organic Ligands on Mineral Carbonation Kinetics

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Abstract

Quin Miller^a, Todd Schaef^a, John Kaszuba^b, Mark Bowden^c, Pete McGrail^a

Recent field tests at the Wallula Basalt Pilot Project and CarbFix pilot project have successfully demonstrated carbonate mineralization due to injection of supercritical CO_2 and aqueous-dissolved CO_2 , respectively. Basalts 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 (Mg_2SiO_4) 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 diffraction (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 carbonation rates 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 \cdot 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^{-6} to 3.6×10^{-6} s⁻¹. These impacts of citrate were due to partial dehydration of $Mg^{2+}(aq)$ and the adsorption of citrate onto nuclei and magnesite surfaces. This type of information may be used to predict and tailor subsurface mineralization rates and pathways.

High Pressure X-ray Diffraction (HXRD)

- Powerful *in situ* experimental technique
- **•** Time series of mineral abundances at 50 °C and 90 atm
- **Definitive mineral identification**

^aPacific Northwest National Laboratory, Richland, WA ^bUniversity of Wyoming, Laramie, WY ^cEnvironmental Molecular Sciences Laboratory, Richland, WA

- Quantitative (Rietveld), ± 5 wt % uncertainty
- Rated to 225 °C and 207 bar
- Either pure water or NaCl solutions placed in reservoir to control water activity of system

Materials

- Synthetic Model Mineral: Forsterite (Mg₂SiO₄)
- Reactive on laboratory timescales (27 m²/g surface area)
- Well-studied carbonation behavior

Forsterite Carbonation in CO₂ Fluids

- Water dissolves into the scCO₂ and then partitions onto mineral surfaces to form thin $(\sim 1-4 \text{ nm})$ water films
- Carbonation reaction (forsterite dissolution and carbonate precipitation) occurs in the thin water film environment
- Amorphous silica not detectable with XRD due to noncrystalline structure



Reaction Pathways

- Three overall reactions listed below
- Carbonation may proceed via an intermediate hydrated magnesium carbonate (nesquehonite)
- **Carbonation proceeds as Reaction 1 and Reaction 2** and/or Reaction 2 followed by Reaction 3
- $Mg_2SiO_4 + 2CO_2 = 2MgCO_3 + SiO_2(am)$ Forsterite
- $Mg_2SiO_4 + 2CO_2 + 6H_2O = 2MgCO_3 \cdot 3H_2O + SiO_2(am)$ 2)
- 3) $MgCO_3 \cdot 3H_2O = MgCO_3 + 3H_2O$ _{Nesquehonite}

Conceptual Model



CO₂-H₂O-rock-organic interactions

Organic ligands influence reaction pathways

Forsterite 🔵 Nesquehonite 🔺 Magnesite



Proportion of magnesite precipitation enhanced when are organics are present relative to control experiment

-10

-11

-15

-16

2.7

[(-12 -13 -13 -14

- ▶ Mg²⁺-organic ligand complexing partially dehydrates cation
- Complex stability/strength correlates with magnesite enhancement trend



- acetate<oxalate~malonate<citrate
- Organics help overcome kinetic barriers to magnesite precipitation





Impacts of Organic Ligands on Forsterite Reactivity in Supercritical CO₂ Fluids

Quin R. S. Miller,*,[†] John P. Kaszuba,^{†,‡} Herbert T. Schaef,[§] Mark E. Bowden,^{II} and Bernard P. McGrail[⊥]

malonate ($C_3H_2O_4^{2-}$) citrate ($C_6H_5O_7^{3-}$)

acetate ($C_2H_3O_2^{-}$) oxalate $(C_2O_4^{2-})$



Citrate influences carbonation rates and reaction pathways



- **SEM/EDS** identification of secondary carbonate and silica
- Radiating prismatic blades of nesquehonite, submicron magnesite rhombohedrals, and discontinuous amorphous silica observed
- **Distinct morphologies of precipitates correlate with expected chemistry (EDS)**



