

Mechanistic Insights into the Water-Film Threshold for Silicate Carbonation in Wet-scCO₂

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In geologic carbon sequestration, anthropogenic-sourced CO₂ is injected into a deep geologic reservoir for long-term storage. Olivines, pyroxenes and serpentines are among the silicates present in these formations and have high reactive potential for CO₂-mineral trapping due to their abundance of divalent-cations. At injection depths, the CO₂ will spread through the formation initially as a buoyant supercritical fluid that will solubilize small amounts of water ("wet" scCO₂). Variably wet scCO₂ has been shown to cause rapid carbonation reactions of silicate minerals, but little is known about the interfacial mechanisms controlling the unique chemistry in these supercritical fluid-mineral systems.

In this study, we investigated the carbonation of a nanometer-sized synthetic forsterite using *in situ* high pressure infrared (IR) spectroscopy. Experiments were conducted at 50°C and 90 bar by titrating water into a vessel containing forsterite and pressurized with either scCO₂ or supercritical argon (scAr). Transmission IR measurements of the supercritical fluid phases allow quantification of water partitioned to the forsterite surface, and attenuated total reflection (ATR) IR spectra enable monitoring of water adsorption, mineral dissolution, and carbonate/silica precipitation reactions. Post-reacted samples were analyzed by *ex-situ* XRD, TGA, SEM, and FIB-TEM.

Our results reinforce the concept of a minimum threshold in the adsorbed water concentration at which carbonation occurs. Before ~5 monolayers of water, ATR IR spectra show that H₂O and HCO₃⁻ are primarily adsorbed inner-spherically to surface Mg²⁺. However, beyond this adsorbed water concentration, continuous carbonate precipitation takes place, and magnesite is the dominant product. Using evidence from novel experiments in scAr, we demonstrate that a dramatic change in water/metal/carbonate speciation beyond the water film threshold is the mechanistic trigger that enables the continuous carbonation reaction.

This study provides important insights that will enhance modelling efforts designed to predict the fate and transport of subsurface stored CO₂. More broadly, our results fill a major scientific knowledge gap concerning interfacial chemistry in thin water films and mineral reactions in high-pressure fluids.