

Nucleation and growth mechanisms and kinetics of environmentally important oxides and carbonates

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Nucleation and growth of hydrous oxide or carbonate nanoparticles can significantly influence the fate and transport of organic and heavy metal contaminants in the environment. Their particles' formation and transport can alter the porosity and permeability of geo-media. Therefore, more accurate quantitative and qualitative information about mineral nucleation and growth is required.

In this work, we used a time-resolved simultaneous small angle x-ray scattering (SAXS)/grazing incidence (GISAXS) setup for real-time monitoring of water-mineral interfacial reactions. To observe the size, shape, distribution, and phase of hydrous iron oxide and calcium carbonate nanoparticles on quartz and mica surfaces as well as in solutions, we also used complementary techniques, such as atomic force microscopy, high resolution transmission electron microscopy, high resolution X-ray diffraction, and grazing incidence wide angle x-ray scattering. The solutions included different ionic strengths of sodium nitrate, arsenate, aluminum, and polyaspartate. The mineral nucleation and growth modes were monitored as a function of exposure time. We delineated the quantitative contributions between homogenous and heterogeneous mechanisms at varied environmental conditions. Hydrous iron oxide nanoparticles formed preferentially along steps rather than terraces, while amorphous calcium carbonate did not show any clear preference. Under aqueous conditions, newly formed nanoparticles did not exhibit any facets. The presence of arsenate and aluminum ions significantly influenced the sizes and crystallinities of hydrous iron oxide nanoparticles and altered their nucleation and growth kinetics. This study provides more accurate depiction of nucleation and growth of environmentally important minerals in solution as well as at active interfaces. Our findings have implications not only for hydrous oxide- or carbonate-containing biogeochemical systems, but also for environmental remediation (heavy metal removal and nuclear waste deposition site remediation) and geoenvironmental applications (geologic CO₂ sequestration).

Effects of organic ligands on supercritical CO₂-induced phlogopite dissolution and secondary mineral formation

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To evaluate the long-term and short-term risks associated with geologic CO₂ sequestration (GCS), we need to understand both the reactions at supercritical CO₂ (scCO₂)-saline water-rock interfaces and the environmental factors affecting these interactions.[1, 2] This research investigated the effects of four organic ligands (oxalate, malonate, acetate, and propionate) on the dissolution and surface morphological changes of phlogopite [KMg_{2.87}Si_{3.07}Al_{1.23}O₁₀ (F, OH)₂] under GCS conditions (in particular, 95°C and 102 atm). Phlogopite was chosen as a model clay mineral in potential GCS sites.

After CO₂ injection, the dissolution of CO₂ causes a pH decrease in saline water, which increases phlogopite dissolution, but this effect can be minimized by the buffering capacity of organic ligands. However, in this study, for ligands forming a strong complexation with surface metals, phlogopite dissolution rates (especially for Al) are increased by ligand-promoted dissolution, even though the pH increases. The experimentally observed dissolution rates of phlogopite were in the order: oxalate > malonate > acetate ≈ propionate. Based on results from ion-exchange chromatography, oxalate and malonate were stable in our reaction system; however, acetate and propionate concentrations continuously decreased due to the solvent extraction of acetic acid and propionic acid by scCO₂ at 95°C and 102 atm. After 159 h, all of the acetate and propionate had disappeared from the aqueous solutions.

Interestingly, in the presence of oxalate, nanoscale precipitation of amorphous silica and fibrous illite was observed only three hours after CO₂ injection. At this early reaction time, illite fibers formed a honeycomb structure on phlogopite basal surfaces, but at a later reaction time these structures detached from the surface and triggered the formation of dissolution channels. In addition, kaolinite, boehmite, diaspore, and gibbsite were also identified. These results provide new information for understanding reactions at scCO₂-saline water-rock interfaces in deep saline aquifers.

[1] Shao, Ray & Jun (2010) *ES&T* **44**, 5999–6005. [2] Shao, Ray & Jun (2011) *ES&T* **45**, 1737–1743.