

# Modification of Calcite Surface Reactivity Driven by Dissolved Pb<sup>2+</sup> during Advective Reactive Transport under Far-From-Equilibrium Conditions

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Reactions at the mineral–water interface play a central role in natural and engineered environments. Many previous studies have characterized the surface reactivity of powdered minerals with stirred bulk solutions. However, chemical reactions commonly occur under dynamic flow conditions where these interfacial reactions are controlled by advective–diffusive transport (e.g., during flow of reactive fluids through interconnected pore spaces in soils and rocks). Reactive transport during advection-dominated conditions in far-from-equilibrium mineral–water systems can be affected by steep concentration gradients that alter transport processes. Here we present the results of a digital holographic microscopy study where we used a simple millifluidic reaction cell to examine the effects of variations in flow rate and total dissolved Pb<sup>2+</sup> concentration on calcite (104) surface reactivity in acidic aqueous conditions (i.e., initial pH = 3.7). Dissolution rates were obtained from measurements of surface-normal retreat of the surface from its initial position as a function of time, using a gold-plated portion of the surface as a fiducial reference marker. The flow rate was varied from 1.66 to 53.3 mm sec<sup>-1</sup> and total dissolved Pb<sup>2+</sup> ([Pb<sup>2+</sup>]<sub>tot</sub>) was varied from 5 nM to 50 mM. Experiments were conducted at ambient temperature (~22 °C). The Damköhler numbers for our experimental setup ( $3.6 \times 10^{-3}$ – $1.2 \times 10^{-4}$ ) indicating surface reaction limited conditions. Under a constant flow rate of 6.66 mm sec<sup>-1</sup>, the calcite dissolution rates in [Pb<sup>2+</sup>]<sub>tot</sub> = 5 nM to 5 μM were similar to that in Pb-free solution, but became significantly smaller when [Pb<sup>2+</sup>]<sub>tot</sub> was increased to values of 0.05 to 50 mM, and dissolution rate decreased with increasing [Pb<sup>2+</sup>]<sub>tot</sub> over this concentration range. We also observed emergent behavior in calcite surface morphology patterns as a function of flow rate and [Pb<sup>2+</sup>]<sub>tot</sub>. Understanding these effects will enable progress toward the development of a predictive understanding of emergent phenomena in geochemical reactive transport processes involving metal-carbonates.

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