Characterization of reaction fronts associated with mineral carbonation of fractured basalts

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Basalt reservoirs could enable secure long-term carbon sequestration whereby divalent cations released from acid-driven dissolution of the host rock combine with injected CO_2 to form stable carbonates. Understanding the mechanisms driving carbonation reactions at microscales is necessary to assess the viability of large-scale CO_2 mineralization.

Here, high-pressure flow-through experiments were coupled with reactive transport modeling to evaluate how transport limitations and geochemical gradients drive precipitation reaction fronts in fractured basalts. To isolate advection- and diffusion-controlled transport, saw-cut basalt cores were surface milled to create one primary flow channel adjoined by four dead-end pathways. In the first experiment, slightly alkaline water (6.3 mM $NaHCO_3$) equilibrated with CO_2 (100˚C, 10MPa) was injected at 1 mL/hr under 20 MPa confining stress. The second was conducted under the same conditions but at lower temperature (20˚C) within an x-ray computed tomography (xCT) scanner to monitor real-time reaction progress. Effluent chemistry data was used to calibrate reactive transport models in CrunchTope. Reacted cores were characterized using optical microscopy, scanning electron microscopy, and Raman spectroscopy.

Minimal carbonation occurred at 20˚C despite a longer reaction time. Reactivity was significantly enhanced at 100˚C, where diverse secondary precipitates coated fracture surfaces. Thin amorphous layers formed on the milled fractures; the appearance and composition of reaction fronts notably varied with distance along dead-end fractures. Small (~20μm-1mm) carbonate crystals of varying compositions and morphologies formed predominantly within small pores or vesicles in the confined unmilled regions between the two core halves. Carbonate nucleation was closely associated with reactive primary mineral grains contributing critical dissolved cations; calcite and aragonite formed on Ca-rich pyroxene while (Ca,Mn)-carbonates precipitated on Mn-bearing olivine. Complementary reactive transport models elucidated the role of geochemical gradients (e.g. pH, CO_2) in controlling the location and extent of basalt dissolution and secondary precipitation reactions within diffusion-limited fractures.