

Molecular Simulation of Geochemical Reactions in Subcritical Fractures

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Geochemical reactions in nanoconfined geometries such as fracture tips differ from those at flat mineral-water interfaces and may contribute to changes in effective fracture toughness (eK_{IC}). Using reactive molecular dynamics (MD) simulations, we investigate fracture propagation with a slit crack in vacuum, pure water, and electrolyte solutions (1M NaCl, 1M NaOH) to evaluate how solution composition alters silica fracture. Although all three aqueous environments weaken silica, the addition of 1M NaOH led to the most significant decrease in the effective fracture toughness (eK_{IC}). This system is characterized by a more alkaline pH within the fracture, higher surface deprotonation, less silica dissolution and a narrower crack tip radius of curvature. The nanoconfined environment of the fracture tip led to the formation of adsorption complexes not seen on flat surfaces and unexpected ion inaccessibility to the fracture tip. The reaction mechanisms leading to bond breaking differ in the two electrolyte solutions, in pure water and in vacuum. The divergent results from the two electrolyte solutions correspond to phenomena observed in experiments and provide insight into how anions alter the chemical-mechanical fracture response of silica. Fracture tip geometries are wedge-shape, introducing the effects of nanoconfinement on geochemical fluids over a range of pore sizes – that is, the effects of nanoconfinement will vary from the fracture tip into the bulk solution. More detailed research on the specific coupled effects of geochemical reactions, ion and water molecule transport, and mechanical stress are needed to fully understand how fluid composition influences fracture propagation.

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