

Atomistic-scale evaluation of the fracture toughness of silicates in aqueous solutions

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Objectives and Introduction

- Develop a fundamental, atomistic-level understanding of the chemical-mechanical processes that control subcritical cracks in low-permeability geomaterials.
- Link atomic-scale insight (reaction mechanisms, diffusion) to macroscale observables (rate of crack propagation, fracture toughness)
- Address how chemical environment affects mechanical behavior.

Computational Details

Simulation methods:

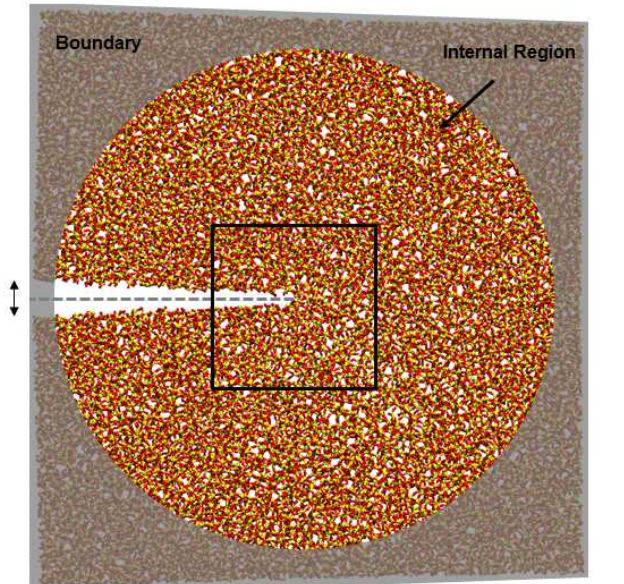
- Classical molecular dynamics with a reactive bond-order-based force field (ReaxFF) for evaluation of atomic level evaluation of stress and energies

Atomistic-to-Continuum method:

- A far-field continuum displacement boundary is applied to an annulus of atoms.
- Stress, displacement, and energy density fields are coarse-grained on a grid.
- Eshelby stress is formed and the J-integral is evaluated on the contour.

Slit cracks:

- Develops a singularity at the crack tip
- Inserted by breaking bonds along a half plane of atoms
- Cracks are opened in mode I fracture through adjustment of boundary atoms and relaxing the interior region



Schematic of mechanical loading of silica systems

Fracture of Dry Silica

Fracture Events

Fracture is identified by distinct jumps in the potential energy of the silica, indicating a divergence from energy gains due to mechanical loading

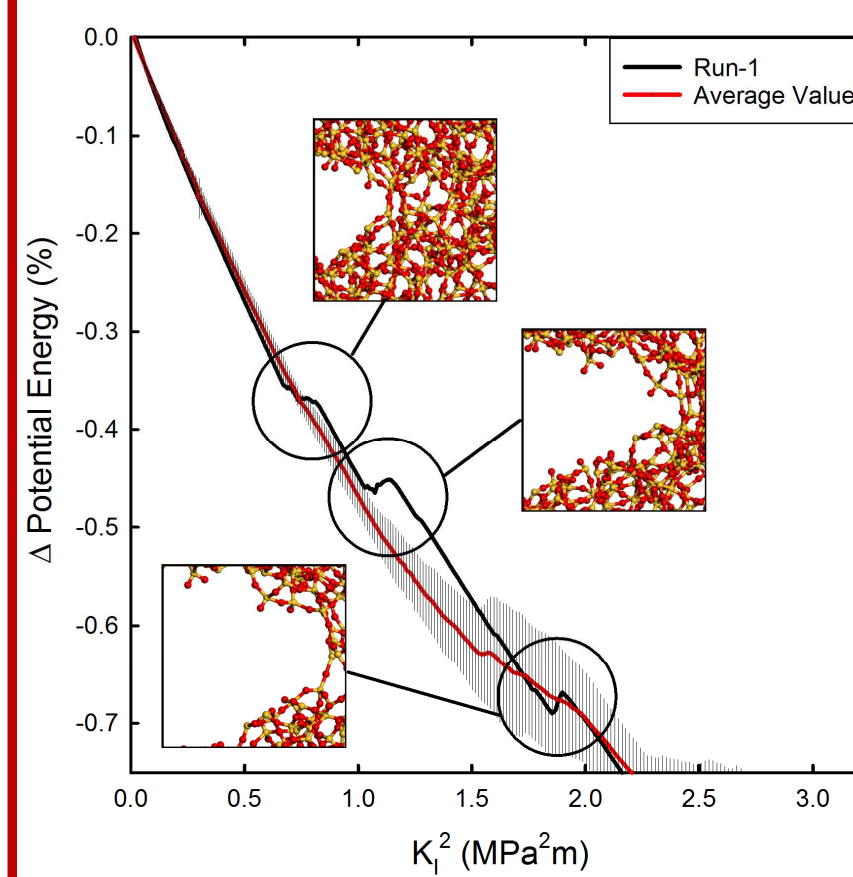


Fig. 1: Change in potential energy with increasing loading. The average over 12 replicas (red) with the standard deviation (gray) are shown, as is a single simulation (Run-1, black). Snapshot dimensions: 25Åx25Å.

J-Integral and the Process Zone

Loading results in increasing J-integral values until fracture. J-integrals converged at loop sizes of 32Å-38Å, indicating the size of the process zone (~3-4 nm)

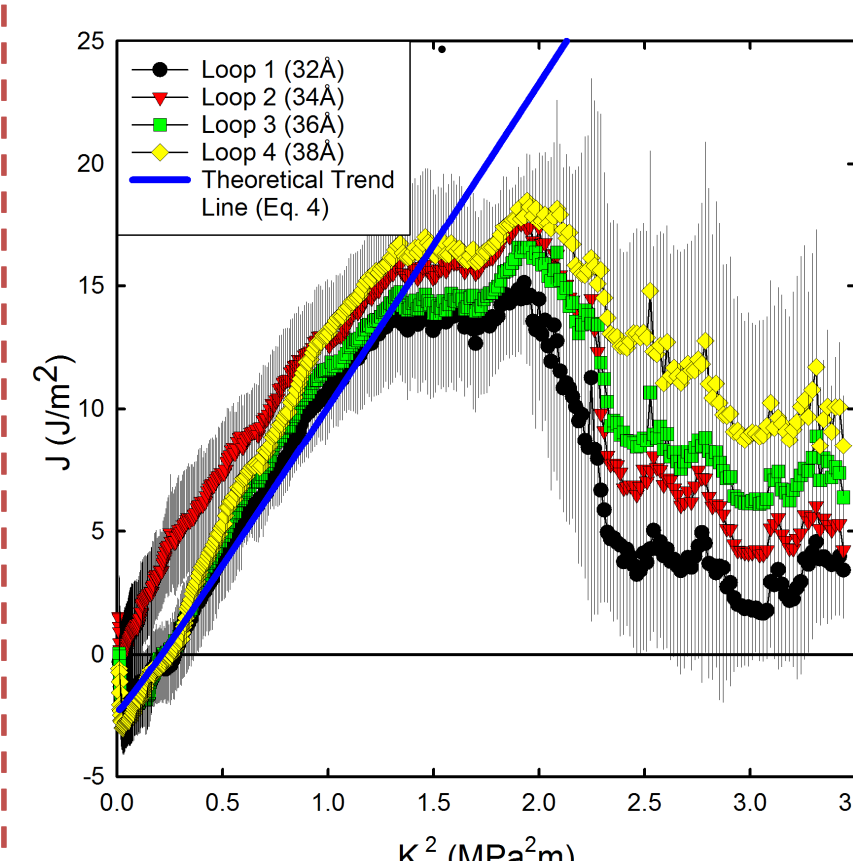


Fig. 2: Change in J-integral values with increased loading. The average over 12 replicas is included with standard deviation (gray). The theoretical trend line has been offset by -2.4 J/m² to be consistent with the minimum of the J-integral curves.

Fracture Toughness (K_{IC})

K_{IC} and the maximum J-integral (J_{IC}) is from the first fracture event identified by deviation of the potential energy by 1.5%. All four loop sizes (32Å-38Å) are included. Scatter is due to variation in the atomic structure at the crack tip.

$$K_{IC} = 0.76 \pm 0.16 \text{ MPa}\sqrt{\text{m}} \quad J_{IC} = 6.16 \pm 4.34 \text{ J/m}^2$$

*At 0K

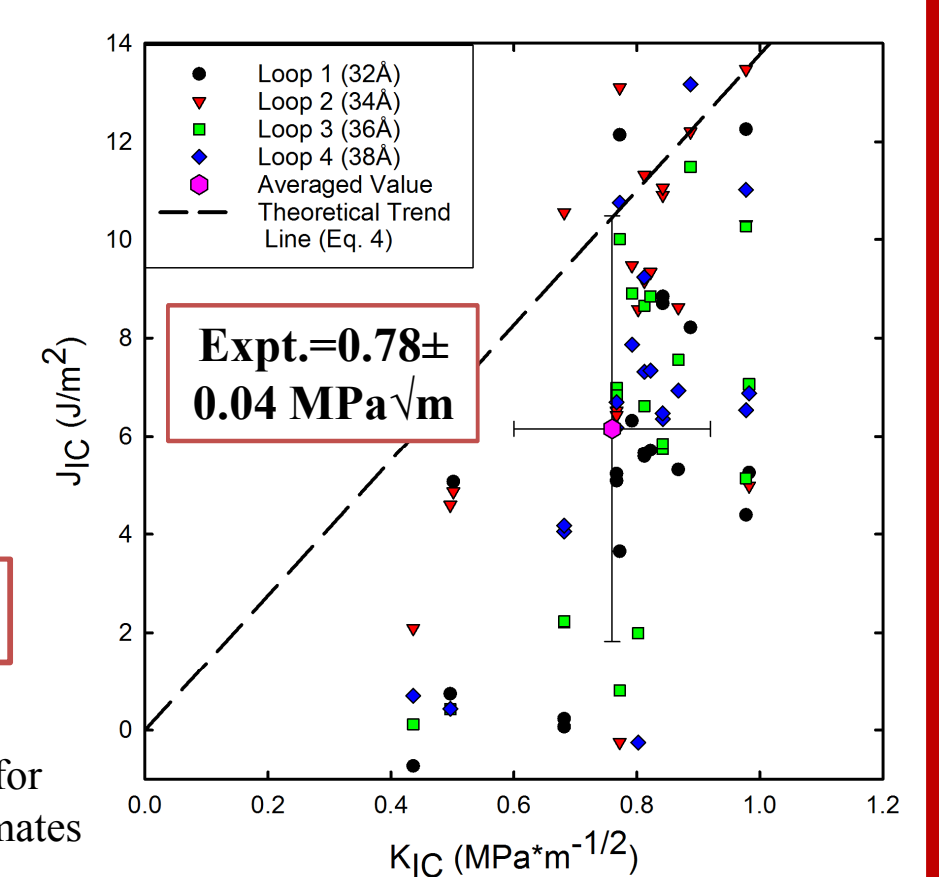


Fig. 3: K_{IC} and J_{IC} values for the initiation of crack propagation. The individual estimates for the various loop sizes are shown as points and value averaged over all the individual estimates as a point with error bars.

Dissipation Energy

In non-ideal brittle solids, localized unrecoverable inelastic processes can occur, resulting in a dissipative energy term (G_{diss}): $G_{IC} = G_{diss} + 2\gamma_s$

G_{diss} is calculated from the amount of energy in the energy which exceeds the energy from the added surface area: $G_{diss} = \frac{\Delta U}{\Delta A} = 3.5 \text{ J/m}^2$

Surface energy (γ_s) = 1.2-2.0 J/m² (Rimsza et al. Langmuir 2017)

$$G_{IC} = 5.9 - 7.5 \text{ J/m}^2$$

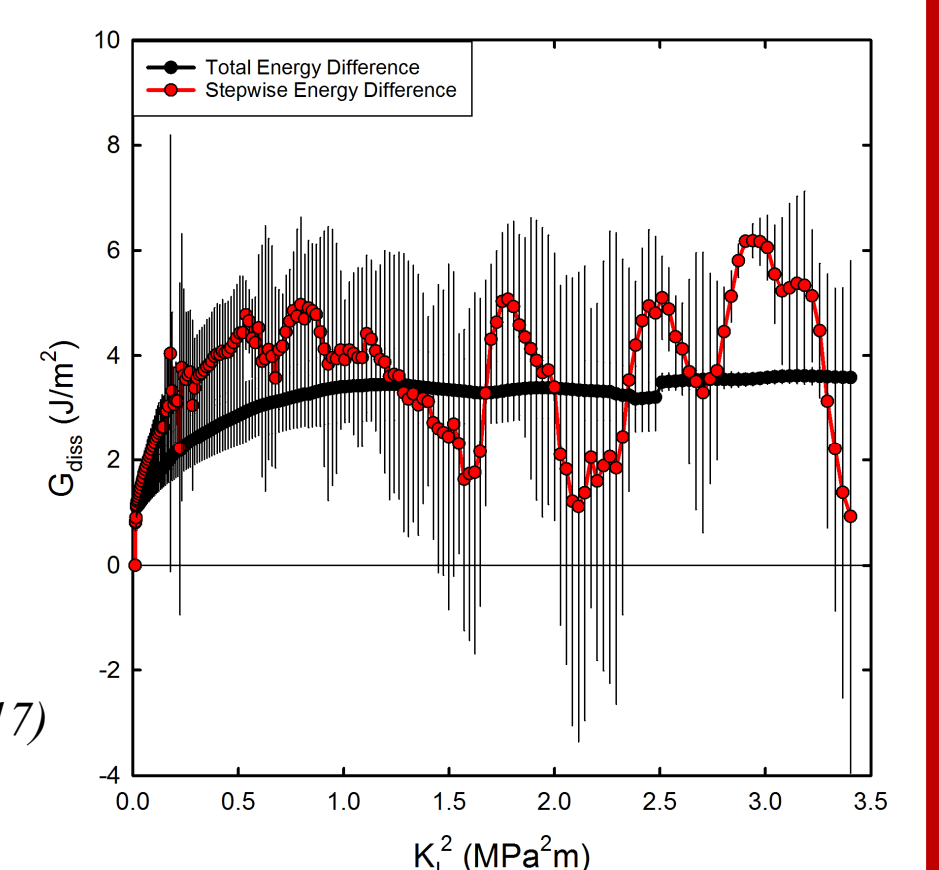
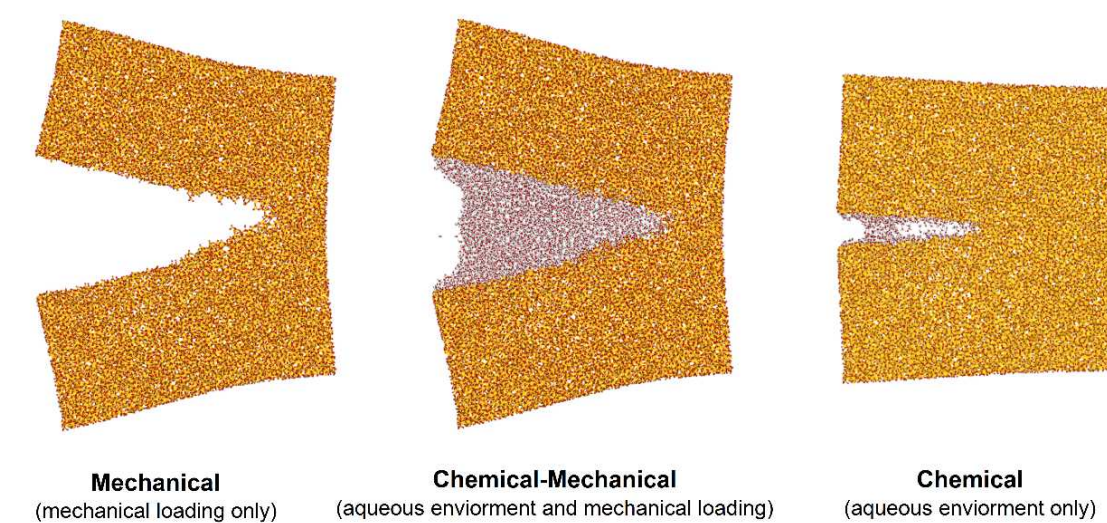


Fig. 4: Energy dissipation during crack loading and subsequent crack propagation in amorphous silica including both the total and stepwise change in G_{diss} with respect to crack surface area.

Silica Fracture in Aqueous Environments

Fracture Conditions

Three different conditions were selected to isolate variables influencing fracture: 1) mechanical loading only, 2) chemistry only (i.e., dissolution), 3) mechanical loading in aqueous solution



Defect Concentrations

On the atomistic scale does the defect concentration near the crack tip control fracture?

Initial structure: no (or very weak) correlation between defect concentration and fracture toughness in mechanical and chemical-mechanical systems

Prior to fracture: The defect concentration is higher for systems that fracture at K_{IC} values of 0.25 Mpa√m or less and follows a clear trend for both mechanical and chemical-mechanical systems

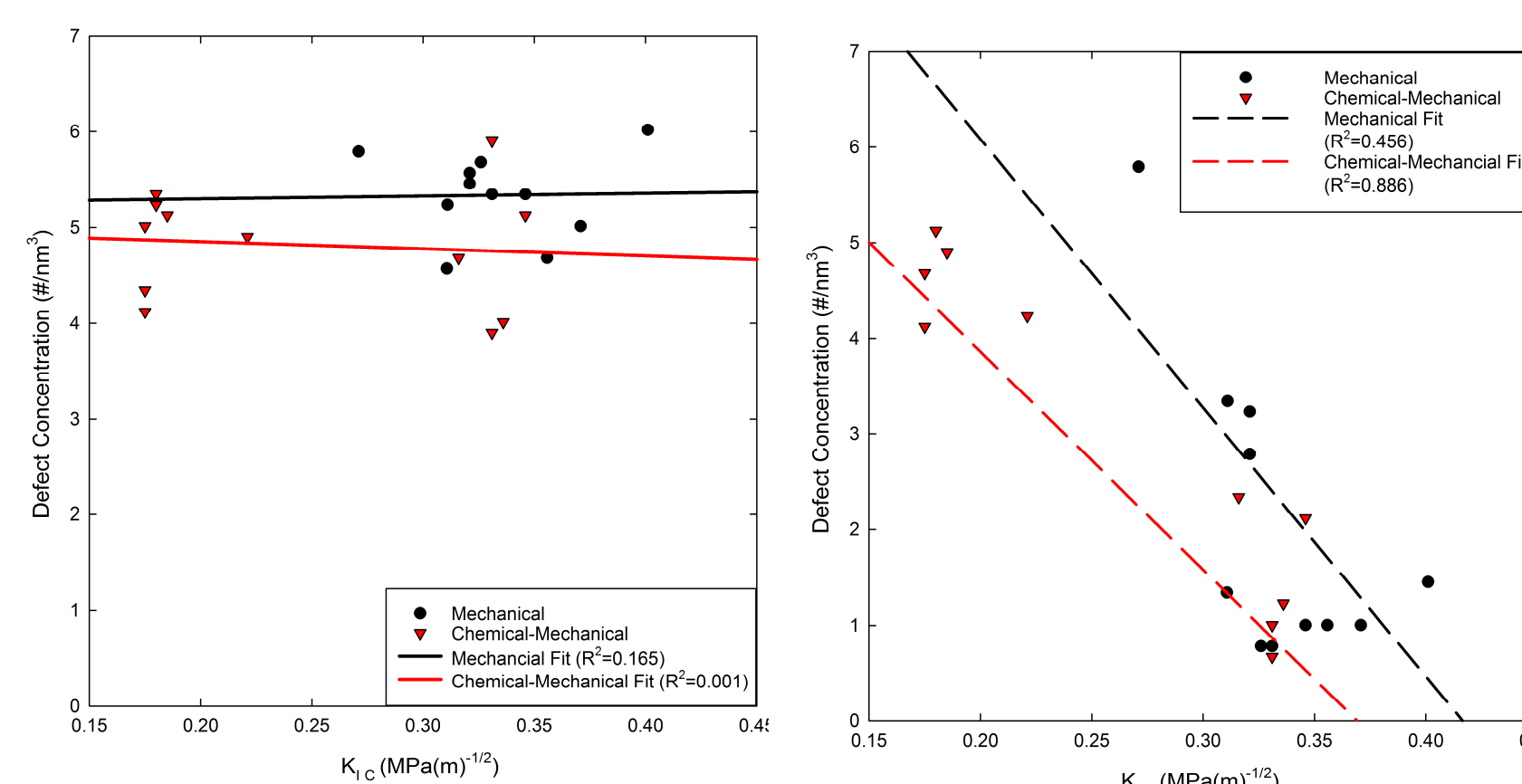


Fig. 5: Defect concentration around the crack tip (10Å radius) correlated with fracture toughness of the silica systems for (left) the initial structures and (right) just before the fracture event.

If the defects are not present at the crack tip before loading, are the defects diffusing through the systems or forming around the crack tip? (Future Work)

Fracture Toughness (K_{IC})

K_{IC} is identified by the first deviation of the potential energy from the expected trend. Fracture from chemical-mechanical effects occurred at ~75% of the K_{IC} values from mechanical loading alone. Dissolution did not result in any fracture events.

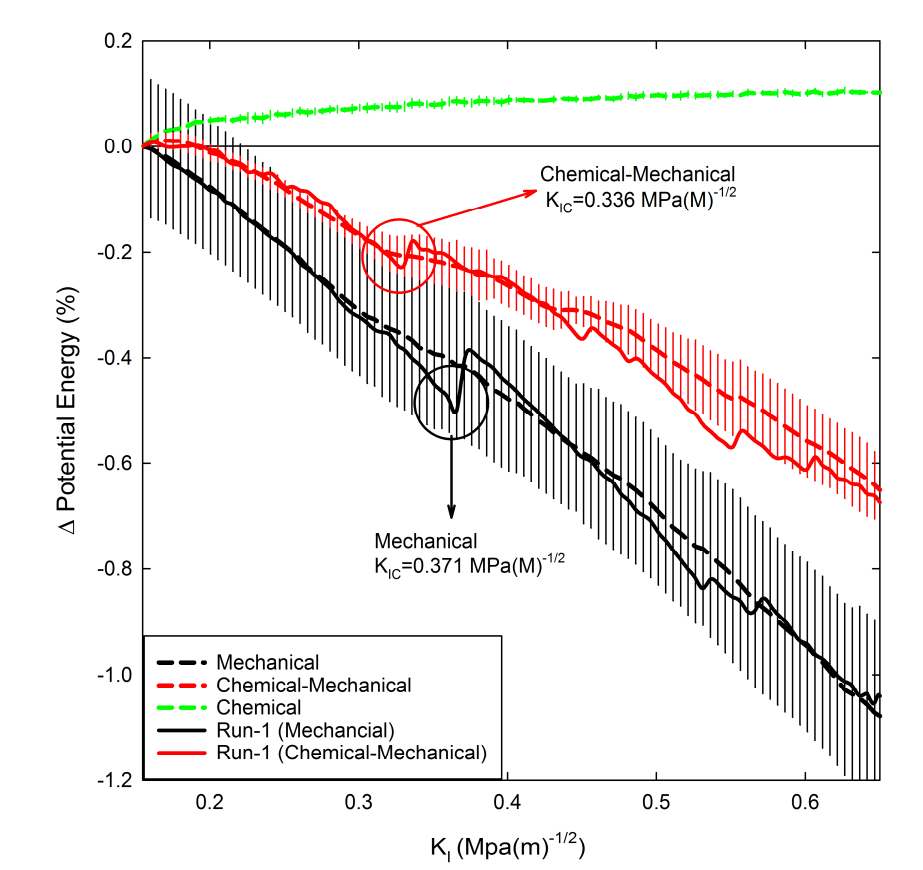


Fig. 6: Potential energy with loading for silica systems for mechanical, chemical, and mechanical-chemical conditions. Energies are averaged over 12 runs with the average and standard deviation reported, as well as data for one individual run.

$$\text{Mechanical } K_{IC} = 0.339 \pm 0.037 \text{ MPa}\sqrt{\text{m}} \\ \text{Chemical-Mechanical } K_{IC} = 0.246 \pm 0.074 \text{ MPa}\sqrt{\text{m}}$$

*Lower K_{IC} for dry systems than indicated above is due to higher simulation temperature (300K v. 0.1K) to allow for water dynamics in aqueous conditions

Conclusions

- Molecular dynamics simulations with a reactive force field (ReaxFF) are capable of simulating silica fracture in the presence of a reactive fluid
- Silica fracture at the atomistic level is highly variable, due to differences in the local structure at the crack tip
- In water, silica fractures ~25% earlier than systems that are mechanically loaded in a vacuum (consistent with experimental data)
- Fracture is correlated to the defect concentration at the crack tip immediately prior to fracture propagation, but not to the initial defect concentration

Future Work

- Introduce electrolytes (NaCl, LiCl) in varying concentrations to identify their role on the fracture properties of silica
- Increase temperature of the systems to increase dissolution effects on fracture

References

- [1] Reese E Jones et al. (2016) Multiscale Materials Modeling for Nanomechanics. 223-259 [2] Yeon, J. and Adri CT van Duin. (2015) The Journal of Physical Chemistry C 120.1 305-317. [3] Rimsza, Jessica M., Reese E. Jones, and Louise J. Criscenti. "Crack propagation in silica from reactive classical molecular dynamics simulations." *Journal of the American Ceramic Society*.

