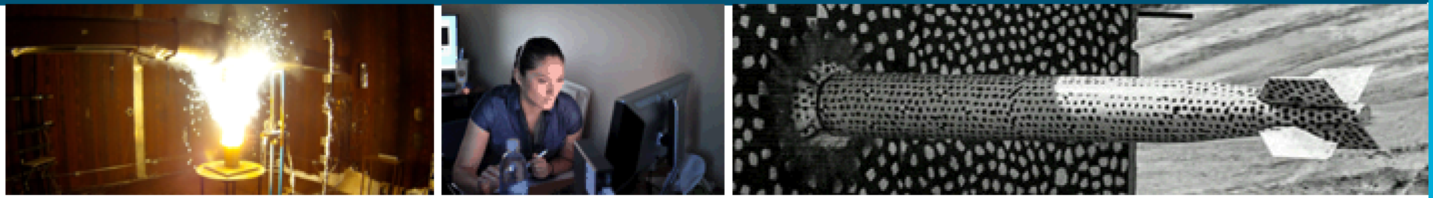
SAND2018-2666C

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



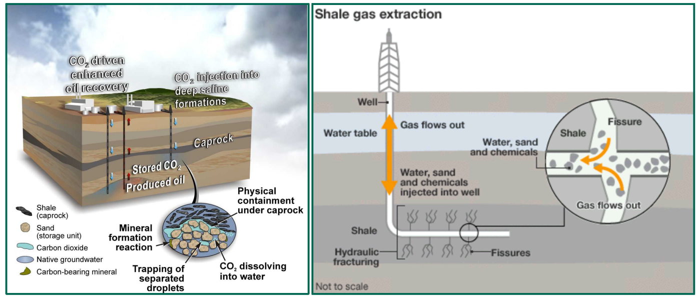
PRESENTED BY

Jessica M. Rimsza, Reese E. Jones, Louise J. Criscenti

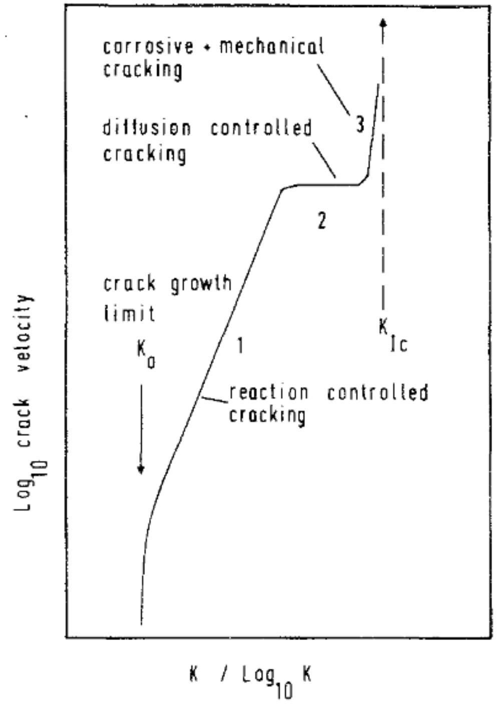
ACS SPRING 2018, NEW ORLEANS LA

Technical Motivation

- Brittle fracture of silicates affect the stability and reliability of subsurface systems, making prediction of the mechanical response to fracking and carbon sequestration difficult
- Develop fundamental understanding of the chemical-mechanical mechanisms that control subcritical cracks in silicates.
- Link atomic-scale insight to macroscale observables and directly address how chemical environment alter mechanical behavior.



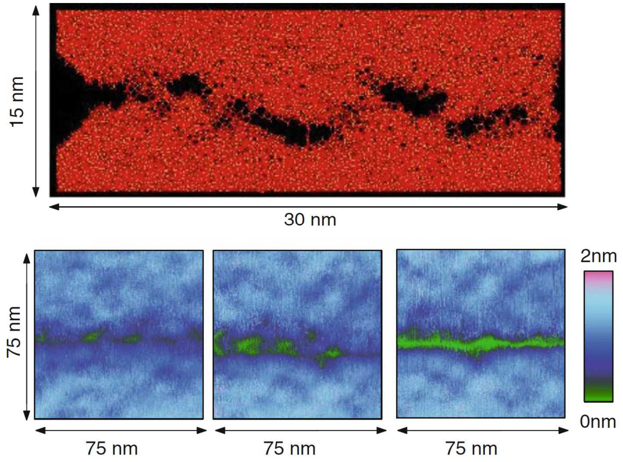
Figures: Fracking (http://www.bbc.com/news/uk-14432401) carbon sequestration (https://www.arb.ca.gov/cc/sequestration/seq.htm)



Atkinson, Barry Kean. "A fracture mechanics study of subcritical tensile cracking of quartz in wet environments." *Pure and Applied Geophysics* 117.5 (1979): 1011-1024.

What are the chemical and mechanical aspects of fracture?

- Why atomistic simulations?
    - Cracks start at the atomistic scale by the breaking of bonds at the solid-fluid interface.
    - Crack tip formation & crack propagation is influenced by fluid and surface chemistry
    - Isolation of chemical and mechanical effects on fracture



Bonamy, Daniel, et al. *Int. J. Fract.* (2006)

Introduction to geomechanics

Cracks propagate when the stress at the crack tip exceeds the strength of the material (Griffith criterion)

$$\sigma = \left(\frac{2E\gamma}{\pi a}\right)^{\frac{1}{2}}$$

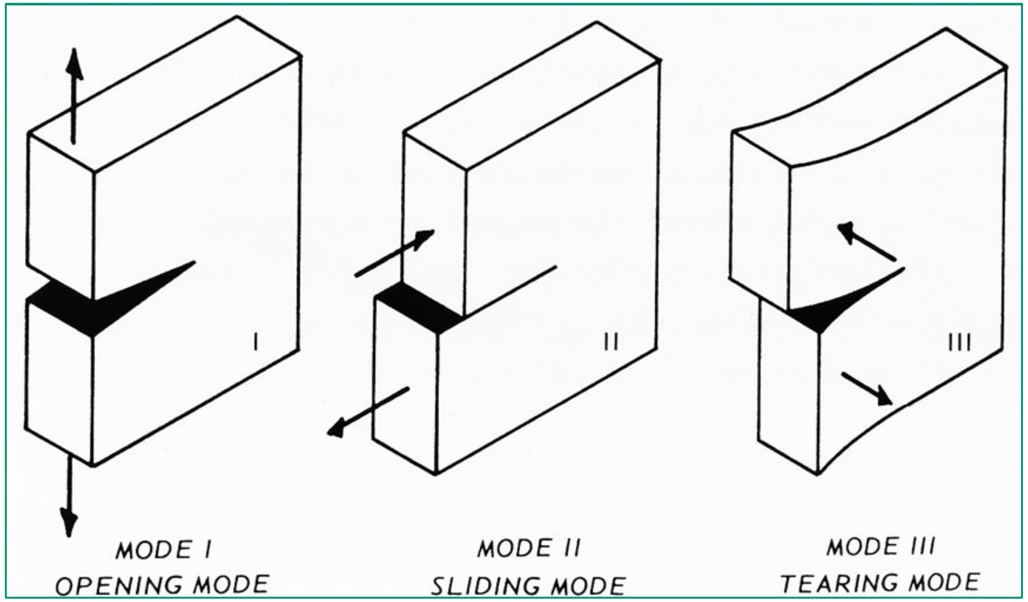
A.A. Griffith, *Phil. Trans. R. Soc. A* (1921)

Fracture toughness (K): the energy required to propagate a crack in a material

$$G = \frac{K_c^2(1-\nu)^2}{E} = 2\gamma_s \qquad \text{(brittle material)}$$

$$G = G_{diss} + 2\gamma_s \qquad \text{(material with inelastic behavior)}$$

Strain energy release rate (G): energy dissipated during fracture per unit of surface area



http://thediagram.com/12_3/thethreemodes.html

Computational Methods

- Classical molecular dynamics for large scale simulation of silica fracture

Fogarty, Joseph C., et al. *J. Chem. Phys.* (2010), Yeon, Jejoon, and Adri CT van Duin. *J. Phys. Chem. C.* (2015)

- ReaxFF: bond order based forcefield including reactive water and silica bond breakage and formation

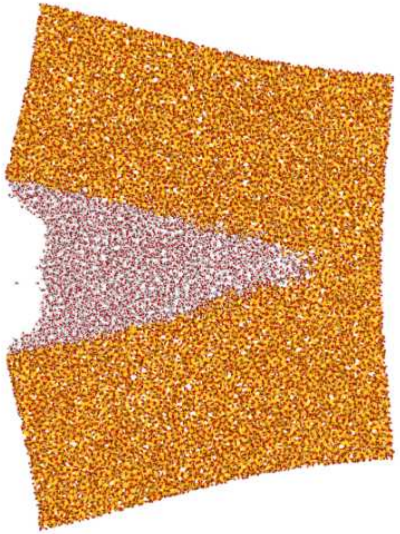
$$E_{Total} = E_{Bond} + E_{Over} + E_{Under} + E_{LP} + E_{Val} + E_{Pen} + E_{Tors} + E_{Conj} + E_{VDW} + E_{Coul}$$

- 2D silica structures (12-replicates) were used as the brittle system

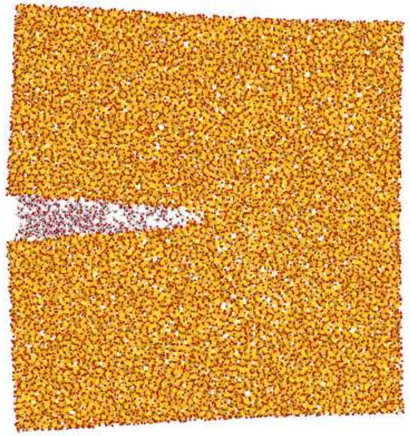
Separation of Chemical and Mechanical Impact on Fracture

- Investigated three different conditions to isolate chemical and mechanical effects on fracture
- Protocol: Apply initial loading (0.15 MPa√m) and relax fracture tip
  - Mechanical: increase loading (stepwise), relax for 5ps at 300K, repeat
  - Chemical-Mechanical: Increasing loading, add in water molecules, relax for 5ps at 300K, repeat
    - Requires GCMC (Grand canonical Monte Carlo) method of inserting water into the fracture to maintain surface wetting
  - Chemical: maintain loading, relax for 5ps at 300K, repeat

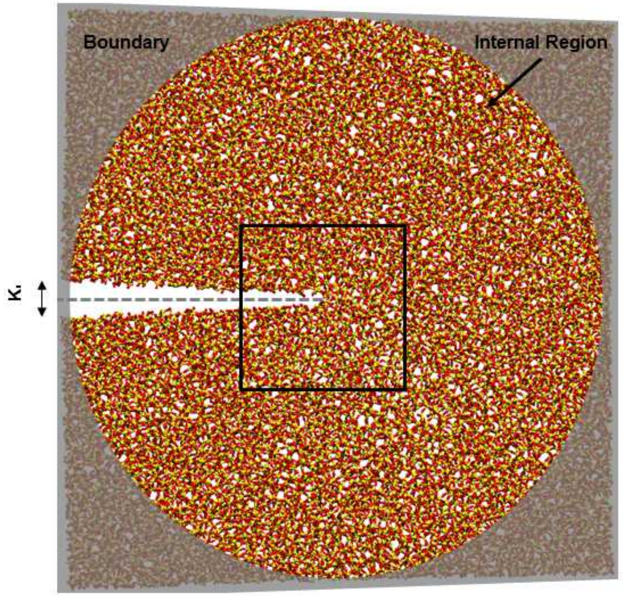
Mechanical
(mechanical loading only)



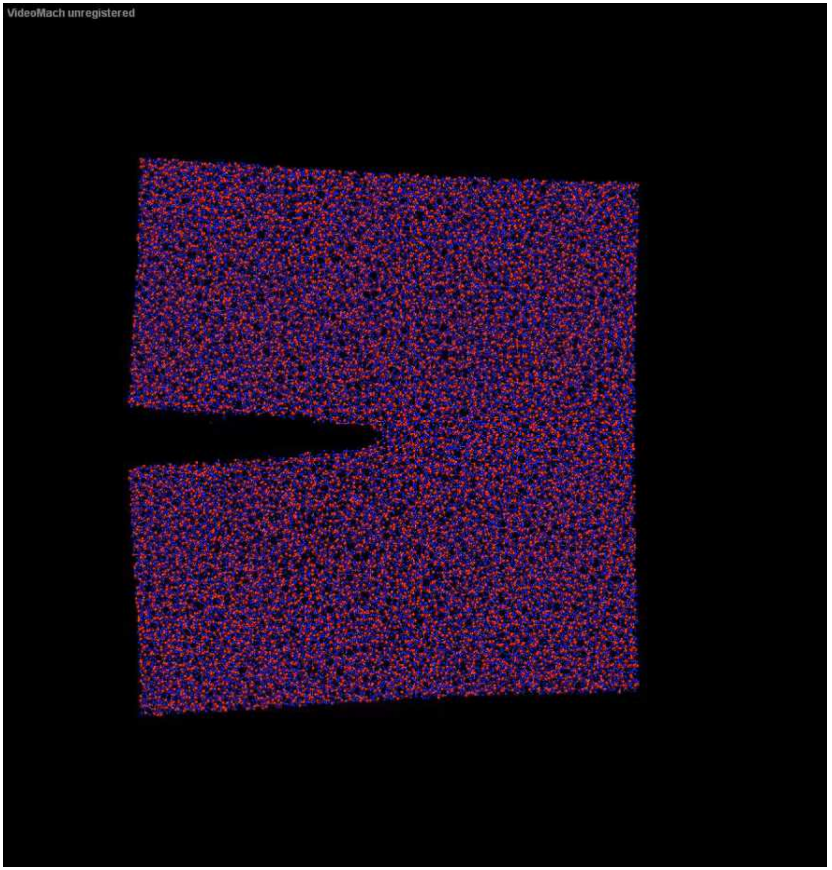
Chemical-Mechanical
(aqueous enviorment and mechanical loading)



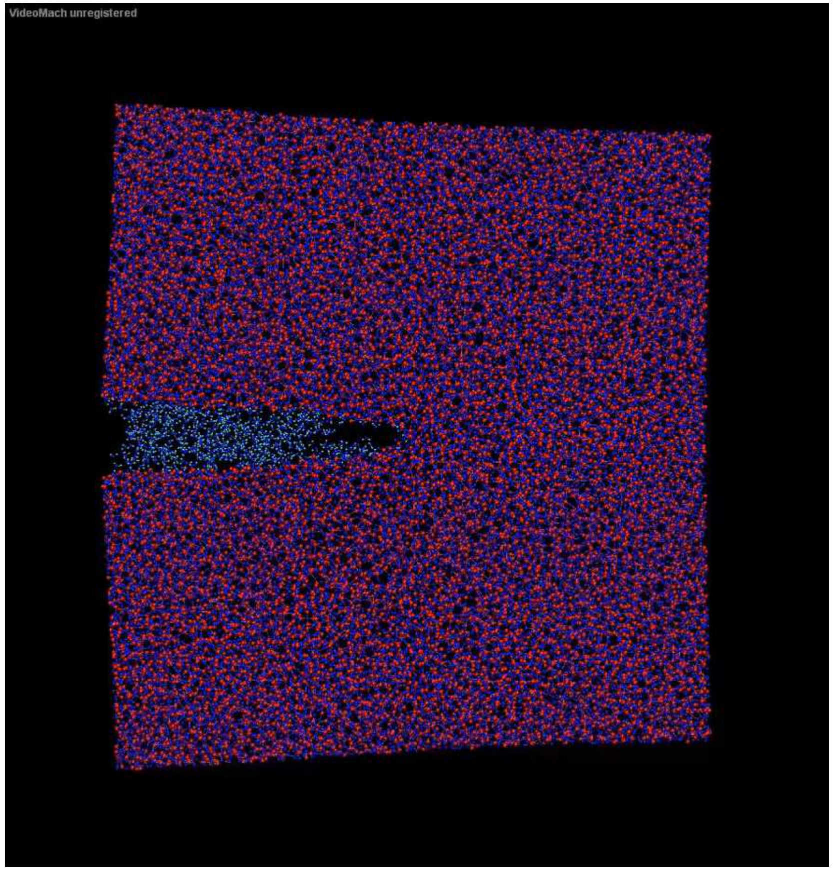
Chemical
(aqueous enviorment only)



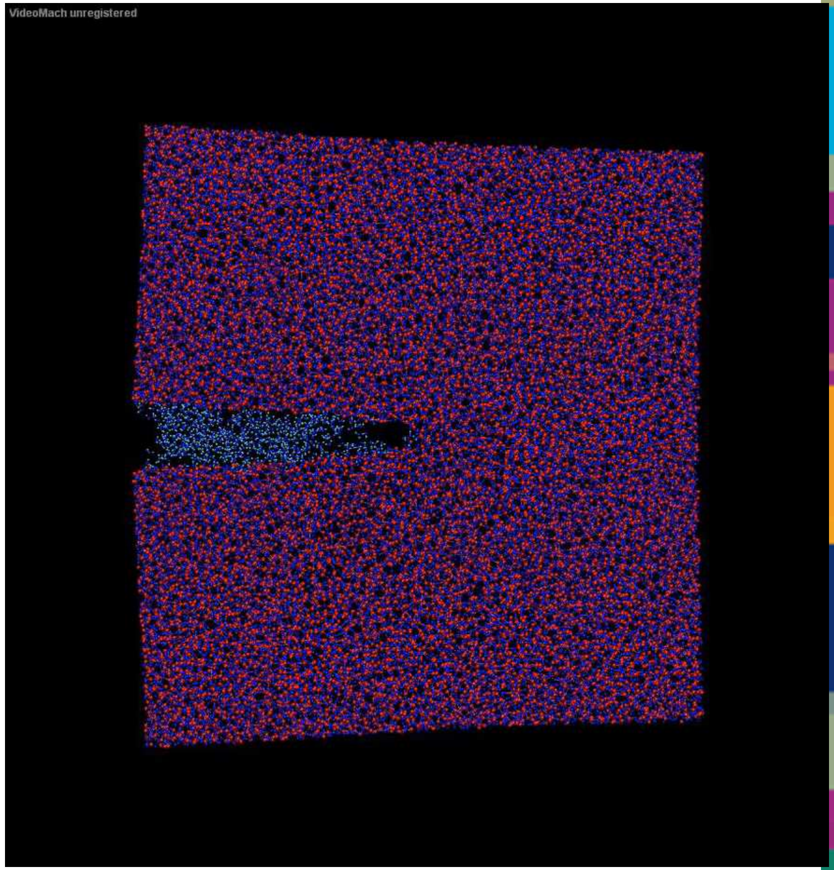
Example Simulations



Mechanical
(mechanical loading only)



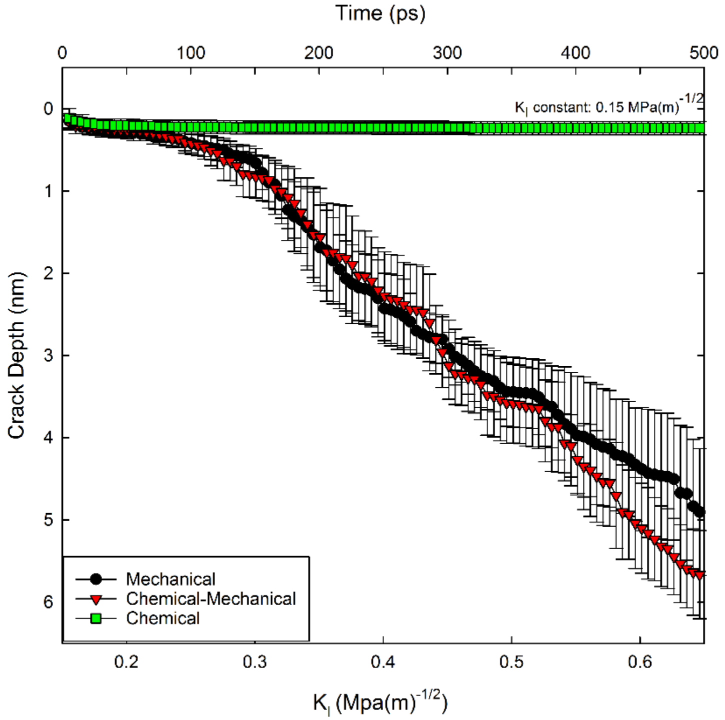
Chemical-Mechanical
(aqueous environment and mechanical loading)



Chemical
(aqueous environment)

Fracture Depth

- Fracture depth identifies aggregate effect of aqueous environment on fracture
- Chemical-mechanical conditions: longer fracture propagation, larger number of fracture events and slightly shorter average fracture length
- Chemical affects become more prominent as the fracture propagates
- May be altering the conditions for fracture (bond stretching, stress states etc.)
- Chemical impact is more than additive on fracture growth



Crack depth for silica systems in mechanical, chemical, and chemical-mechanical conditions.

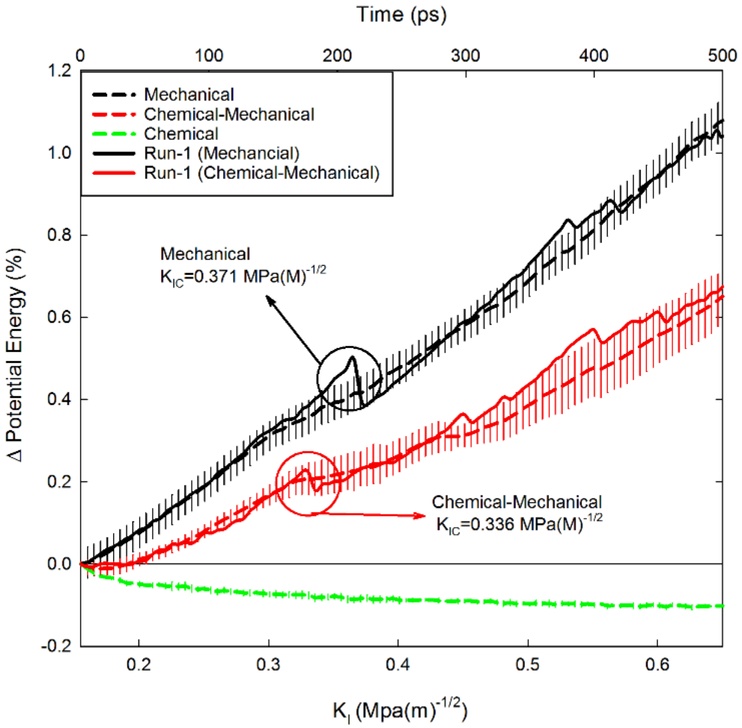
Crack propagation data for silica systems in mechanical, chemical, and chemical-mechanical conditions.

Conditions	Propagation (nm)	Fracture Events* (#)	Average Fracture Length (nm)	Longest Fracture (nm)	Fracture Velocity (m/s)
Mechanical	4.92±0.76	11.50±2.06	0.35±0.08	0.90±0.23	9.85±1.51
Chemical	0.23±0.07	0.50±0.50	0.16±0.08	0.10±0.08	0.47±0.16
Chemical-Mechanical	5.69±0.53	14.83±2.41	0.32±0.06	0.97±0.38	11.38±1.07

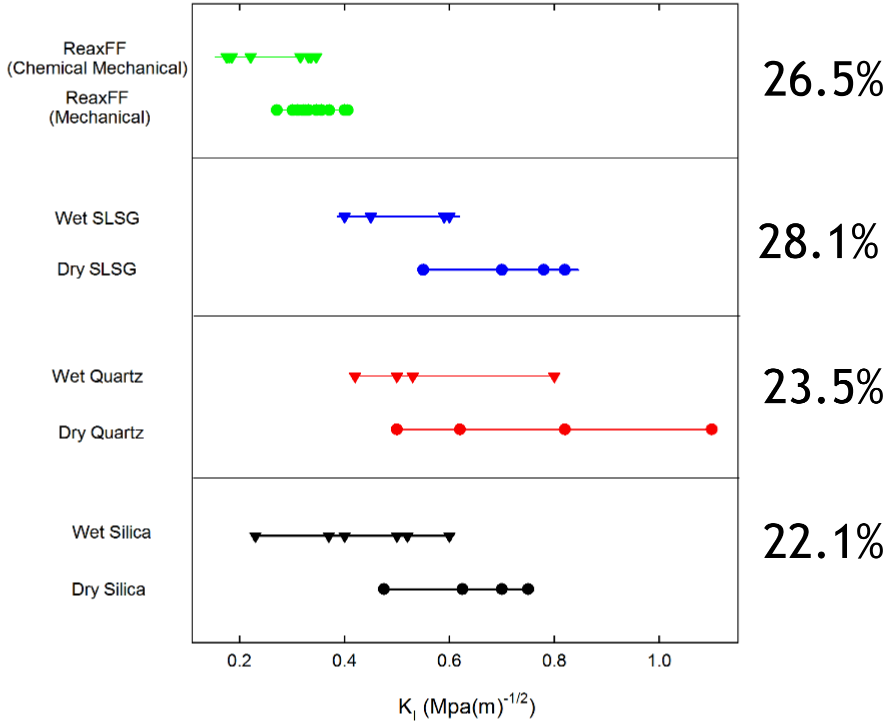
Fracture Toughness

- Identified from variation in the potential energy of the silica during loading
- Earlier fracture of silica in aqueous conditions
- No fracture in chemical-only systems (dissolution)
- K_{IC} is lower than in experimental systems (0.78 MPa√m) due to resolution and temperature effects

Mechanical: 0.339±0.037 MPa√m
Chemical-Mechanical: 0.246±0.074 MPa√M
Reduction in K_{IC}: ~26.5%



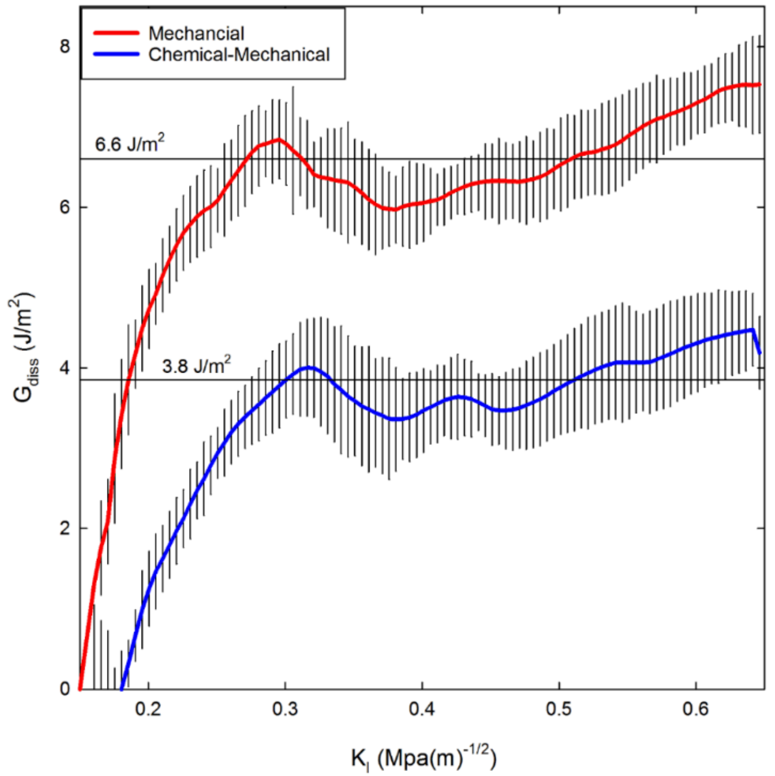
Change in potential energy for silica systems in mechanical, chemical, and chemical-mechanical conditions.



Experimental K_{IC} data for amorphous silica, quartz , and soda-lime silicate glasses in dry and aqueous environments compared with current data.

Energy Dissipation

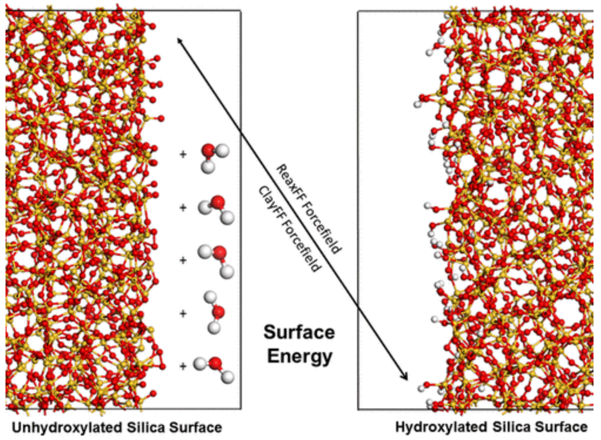
- G is related to both the surface energy and dissipative energy (unrecoverable inelastic character around the fracture tip) $G = G_{diss} + 2\gamma_s$
- G_{diss} is calculated from energy and surface area of the fracture: $\frac{\Delta U}{\Delta S_A} = G_{diss}$
- Surface energy (γ) = related to hydroxylation of the surface
- Wet fracture results in a lower K_{IC} value and lower G_{IC}, due to larger dissipation energy
- Larger G_{diss} relates to the strain distribution surrounding the fracture tip



Energy dissipation (G_{diss}) during crack loading and subsequent crack propagation for silica systems

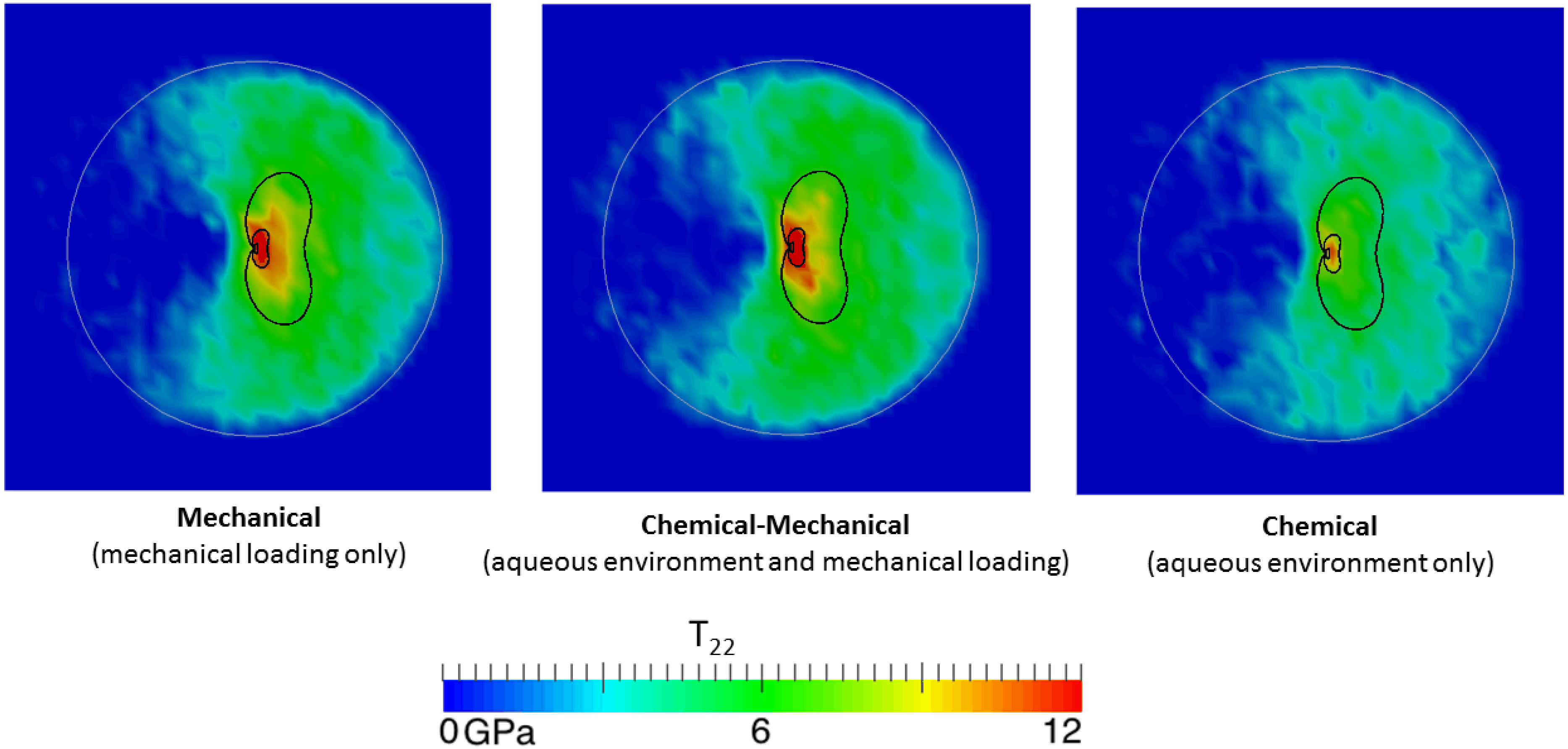
Fracture properties of silica in mechanical and chemical-mechanical conditions.

	K_{IC} (MPa√m)	G_{IC} (J/m^2)	G_{diss} (J/m^2)	Si-OH (#/nm^2)	γ (J/m^2)
Mechanical	0.339±0.037	8.8	6.6	0.0	1.1
Chemical-Mechanical	0.246±0.074	4.6	3.8	3.1	0.4



Stress Distribution

- Stresses from the atomistic simulations were coarse grained and averaged over the twelve replicates to describe the stress states surrounding the fracture tip



Mechanical
(mechanical loading only)

Chemical-Mechanical
(aqueous environment and mechanical loading)

Chemical
(aqueous environment only)

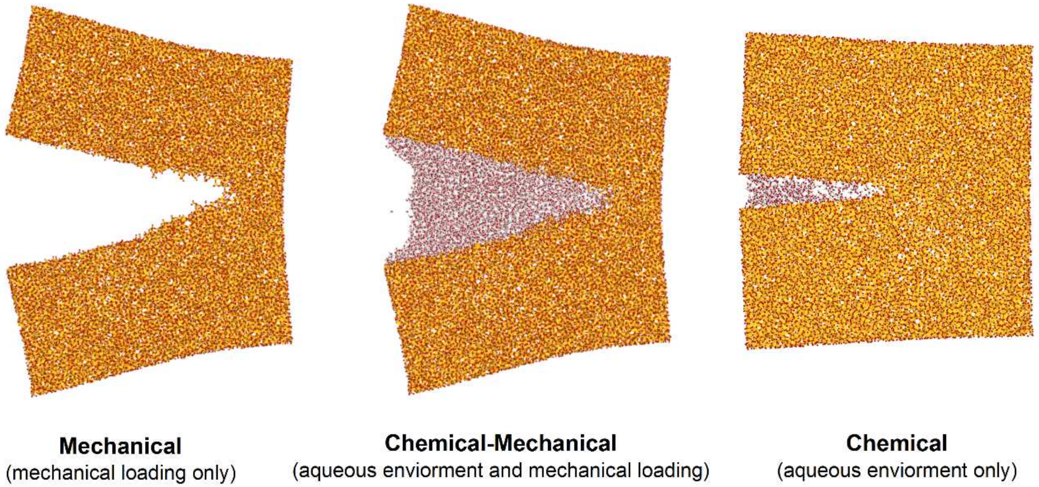
Stress fields for silica systems in mechanical (K_I=0.2 MPa√m), chemical-mechanical (K_I=0.2 MPa√m), and chemical conditions (K_I=0.15 MPa√m).

Conclusions

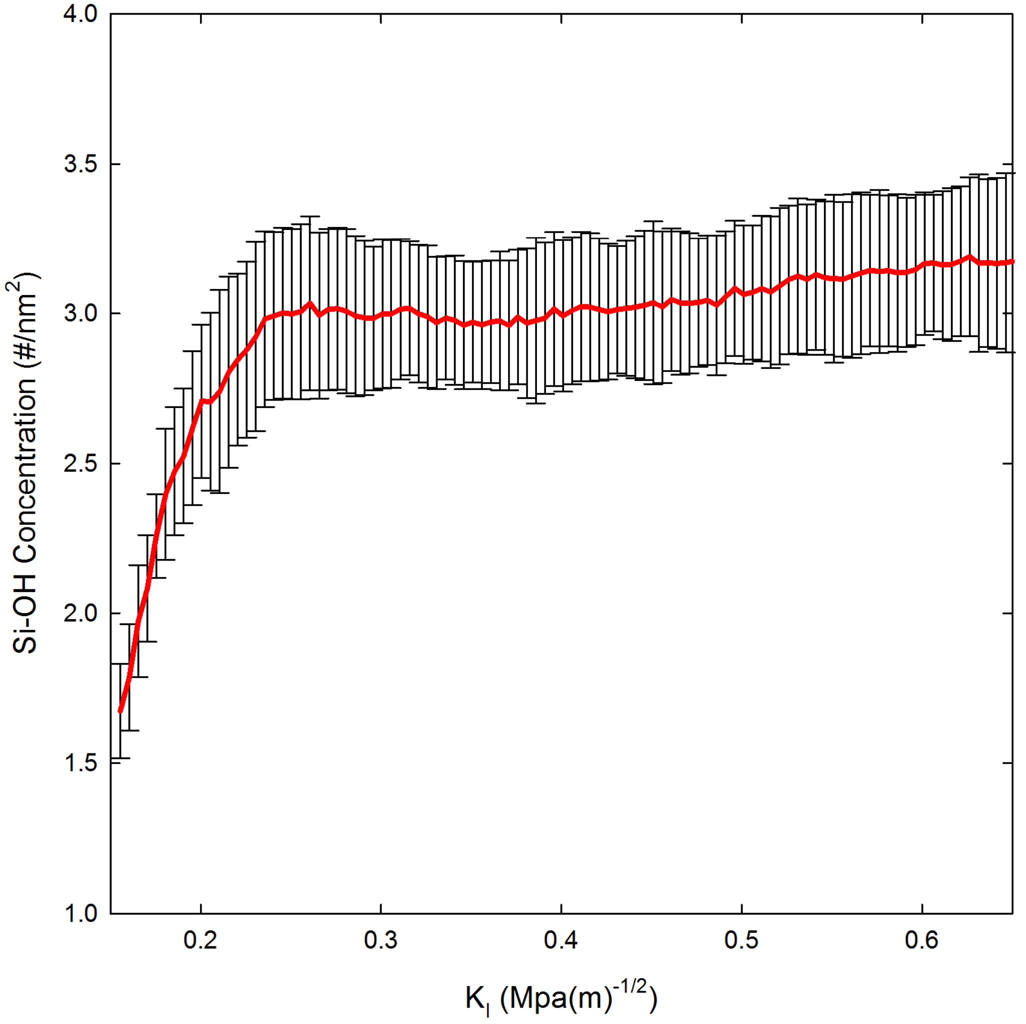
- Atomistic simulations of silica fracture in aqueous environments were used to isolate the chemical and mechanical effects of fracture
- Chemical-mechanical systems exhibited increased fracture growth due to higher number of fracture events (and possibly lower threshold for fracture)
- Fracture toughness was decreased by ~25% between vacuum and water conditions, consistent with reported experimental data
- G_{IC} (strain energy release rate) was decreased by ~50% in chemical-mechanical systems due to decreased dissipation energy and surface energy
- Stress fields indicate relaxation of the process zone surrounding the fracture in aqueous conditions, suggesting that the starin effects are even more localized at the fracture tip
- Thresholds for fracture may be decreased in the presence of water, even on extremely local distance and time scales, and chemical affects are not additive

Acknowledgements

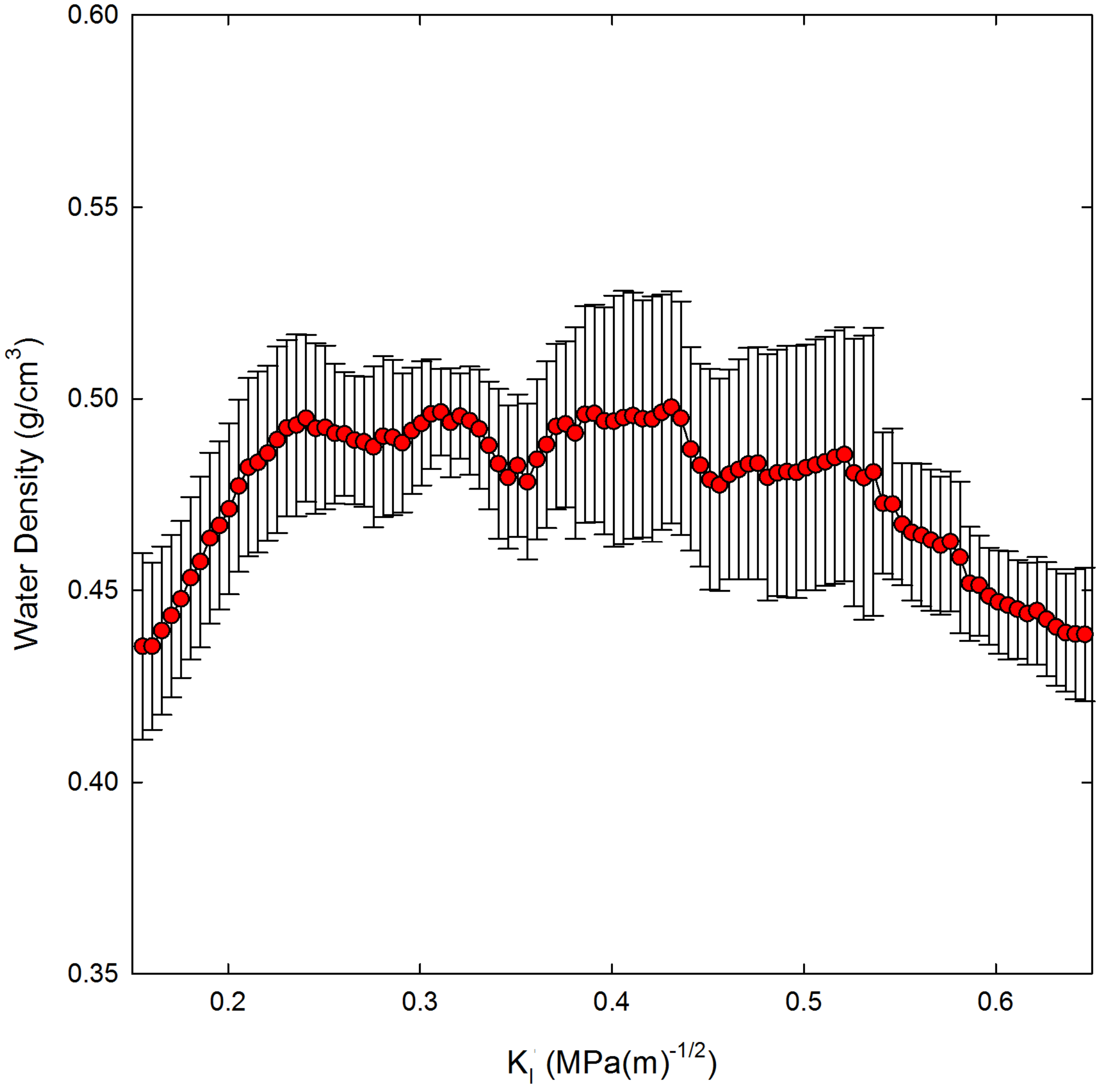
This work was fully supported by the Laboratory Directed Research and Development (LDRD) program of Sandia National Laboratories. Special thanks to Mark Wilson (SNL) for LAMMPS support.



Back-Up Data



Si-OH Concentration (#/nm^2)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.2
0.3
0.4
0.5
0.6
K_I (Mpa(m)$^{-1/2}$)



Water Density (g/cm^3)
0.60
0.55
0.50
0.45
0.40
0.35
0.2
0.3
0.4
0.5
0.6
K_I (MPa(m)$^{-1/2}$)