SAND2019-9712C

Sandia National Laboratories

Molecular Simulation of Geochemical Reactions in Subcritical Fractures

PRESENTED BY

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Goldschmidt, August 2019

Funding: Laboratory Directed Research and Development
Sandia National Laboratories, Albuquerque, NM

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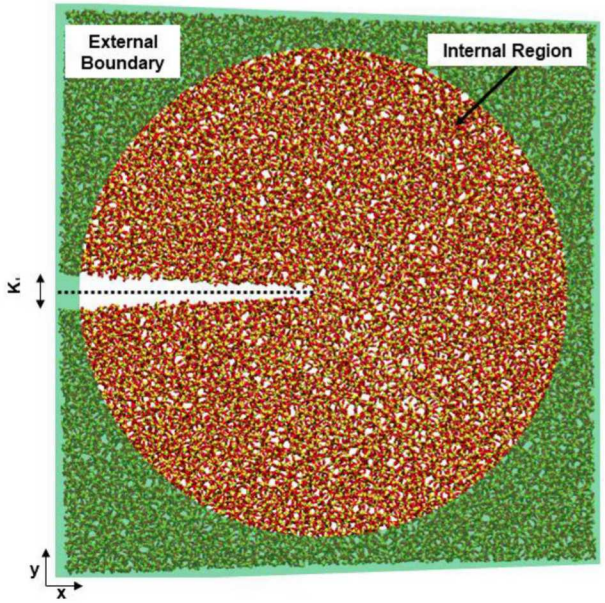
Geochemical Reactions in Subcritical Fracture

Subcritical fracture is an example of a nano-confined space – a location where the chemistry of reactions will be impacted by:

- Proximity of two surfaces
- Changes in water structure
- Changes in ion adsorption mechanisms

Fracture geometries are wedge-shaped, introducing the effects of nanoconfinement on geochemical fluids over a range of pore sizes from the tip to the bulk solution.

The chemical reactions that occur in a subcritical fracture impact the mechanical properties of the material and influence fracture propagation.



- Schematic of the quasi-2D silica system with a slit crack.
- Bonds are severed to form a slit crack.
- Atoms in the boundary region are fixed to the displacement proscribed by mode I loading (radius 3.2 nm).
- In the cylindrical region, the atoms are free to relax to a minimum energy configuration
- The axis of the cylinder is out-of-plane and the thickness of the system is 2.8 nm.

Project Objectives

- Develop a fundamental, atomistic-level understanding of the *chemical-mechanical* processes that **control subcritical cracks** in low-permeability geomaterials.
- Link atomic-scale insight to macroscale observables.
- Address how **chemical environment** affects **mechanical behavior**.

Definitions:

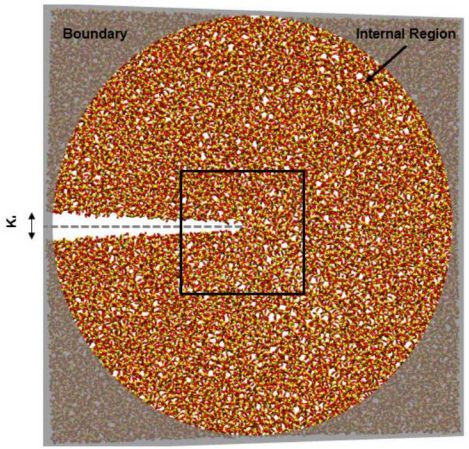
- Classical fracture mechanics: the fracture toughness, K_{IC} is the point at
- which a pre-existing fracture converts from subcritical to critical behavior.
- Our definition(eK_{IC}): the loading at which the first fracture event occurs.
- Our eK_{IC} is impacted by the chemical environment unlike the strict K_{IC} which is defined as an intrinsic material property.

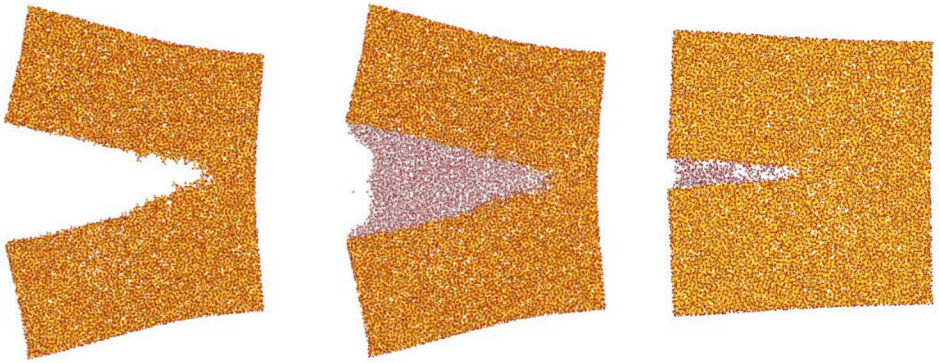
Computational Methods

- Classical molecular dynamics for large scale simulation of silica fracture
- ReaxFF: Bond-order based forcefield including reactive water and silica bond breakage and formation (Fogarty et al. *J. Chem. Phys.* (2010), Yeon and van Duin, *J. Phys. Chem. C.* (2015)

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

- 2D silica structures (12-replicates) were used.
- Investigated 3 different conditions to isolate chemical and mechanical effects on fracture
- Protocol: Apply initial loading (0.15 MPa$\sqrt{m}$) and relax fracture tip
  - Mechanical: increase loading (stepwise), relax for 5ps at 300K, repeat
  - Chemical-Mechanical: increase loading, add in water, relax for 5ps at 300K, repeat
  - Chemical: maintain loading, relax for 5ps at 300K, repeat





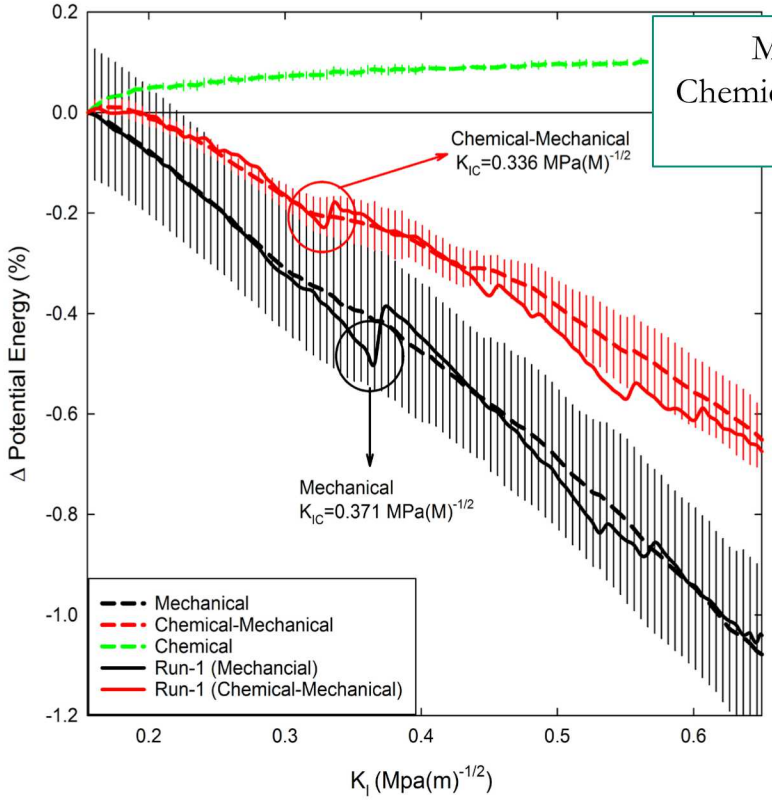
Mechanical
(mechanical loading only)

Chemical-Mechanical
(aqueous enviorment and mechanical loading)

Chemical
(aqueous enviorment only)

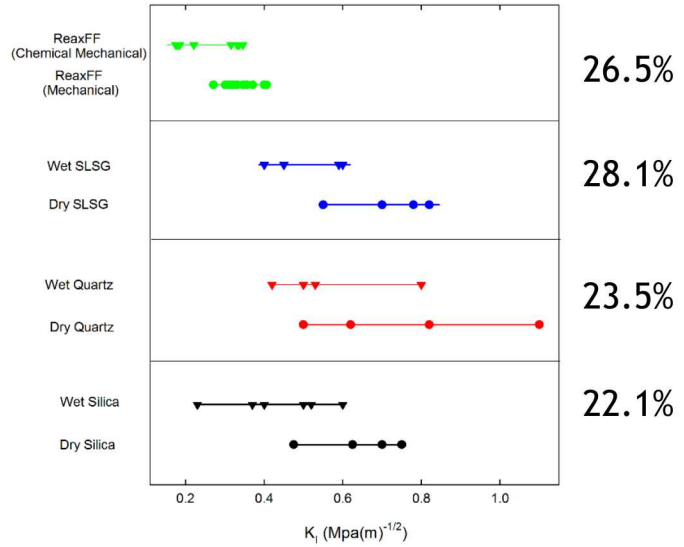
Fracture Toughness in Vacuum and Water

- 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



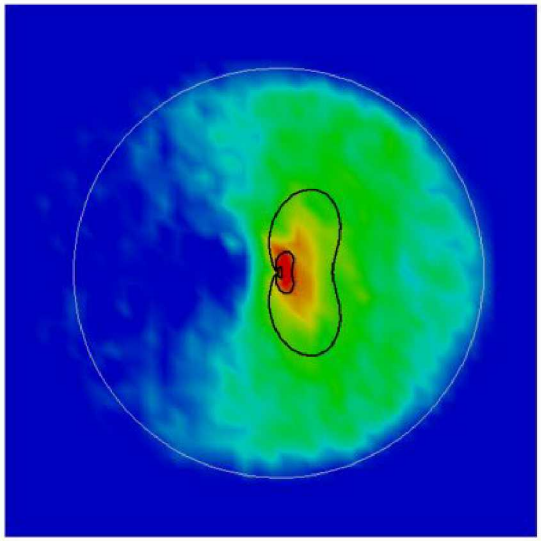
Change in potential energy for silica systems in mechanical, chemical, and chemical-mechanical conditions.

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

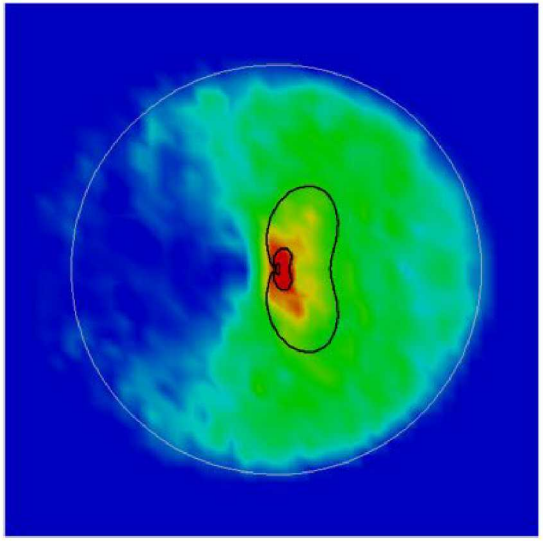


Experimental K_{IC} data for amorphous silica, quartz, and soda-lime silicate glasses in dry and aqueous environments compared with current data.

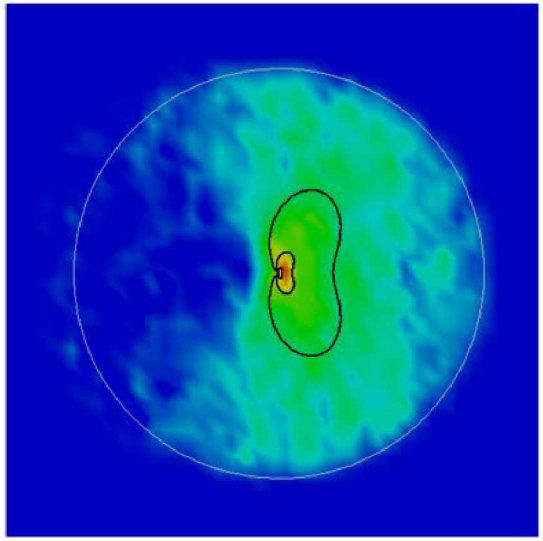
Stress Distributions



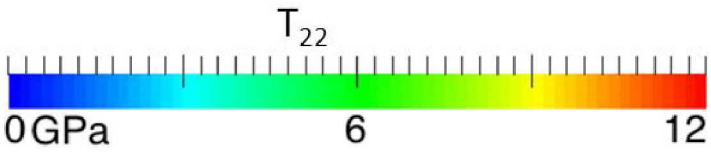
Mechanical
(mechanical loading only)



Chemical-Mechanical
(aqueous environment and mechanical loading)



Chemical
(aqueous environment only)



Stresses from the atomistic simulations were coarse grained to describe the stress states surrounding the fracture tip. Stress fields for silica systems in mechanical (K_I=0.2 MPa$\sqrt{m}$), chemical-mechanical (K_I=0.2 MPa$\sqrt{m}$), and chemical conditions (K_I=0.15 MPa$\sqrt{m}$).

Energy Dissipation

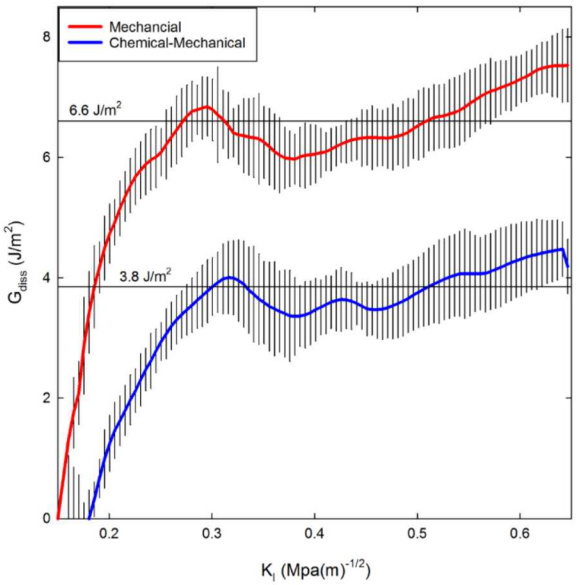
- G is related to both the surface energy and dissipative energy (unrecoverable inelastic character around the fracture tip)

$$G = G_{diss} + 2\gamma_s$$

- G_{diss} is calculated from energy and surface area of the fracture:

$$\frac{\Delta U}{\Delta S_A} = G_{diss}$$

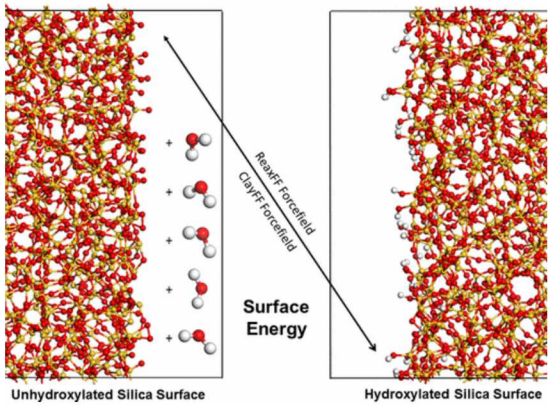
  - Surface energy (γ) = related to hydroxylation of the surface
  - Wet fracture results in a lower K_{IC} value and lower G_{IC}, due to larger dissipation energy
  - Larger G_{diss} relates to the strain distribution surrounding the fracture tip



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

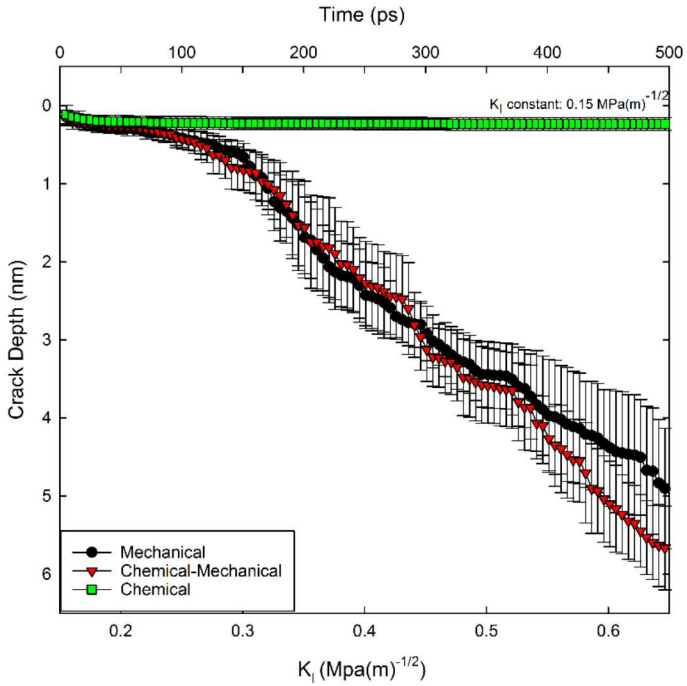
Fracture properties of silica in mechanical and chemical-mechanical conditions.

	K_{IC} (MPa√m)	G_{IC} (J/m²)	G_{diss} (J/m²)	Si-OH (#/nm²)	γ (J/m²)
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



Fracture Propagation in Water

- 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 effects 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

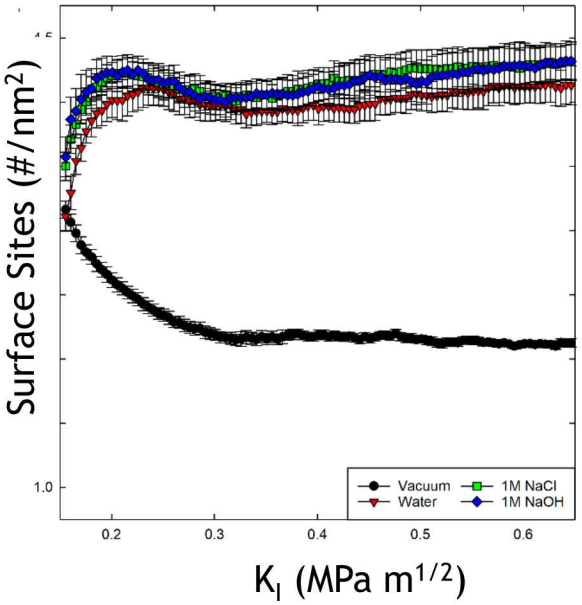


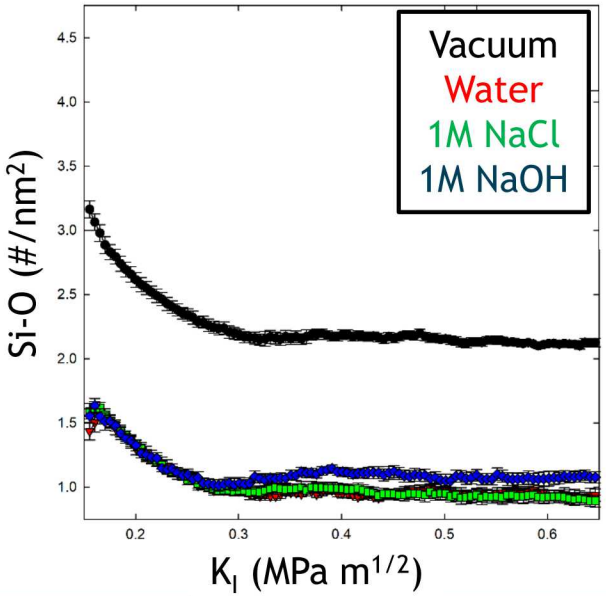
Crack depth for silica systems in mechanical, chemical, and chemical-mechanical conditions.

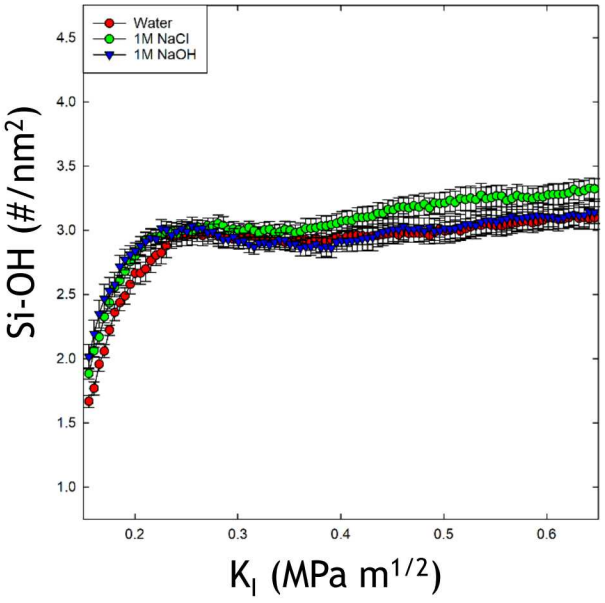
Crack propagation data for silica systems under different conditions.

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

Silica Surface Sites in 1M NaCl and 1 M NaOH Solutions





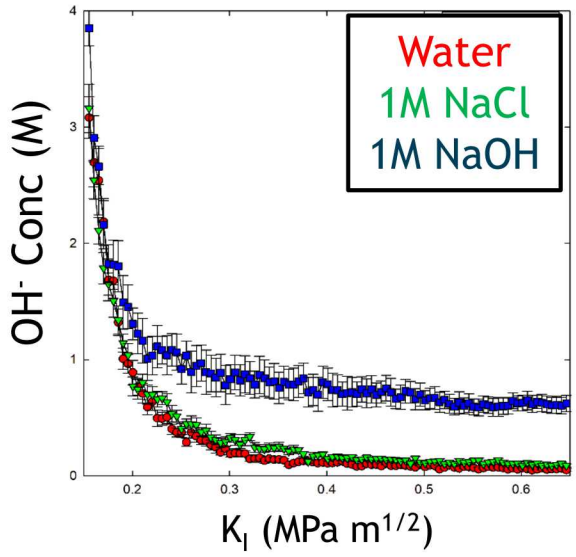


- In vacuum, there are no Si-OH surface sites.
- In vacuum, surface relaxation causes some surface sites to reconnect and form siloxane bonds.
- Silica surfaces exposed to salt solutions exhibit more surface sites than those in pure water suggesting a higher concentration of broken Si-O- bonds.
- More Si-OH sites form in 1M NaCl solutions; more $Si\text{-}O^-$ sites form in 1M NaOH solutions.

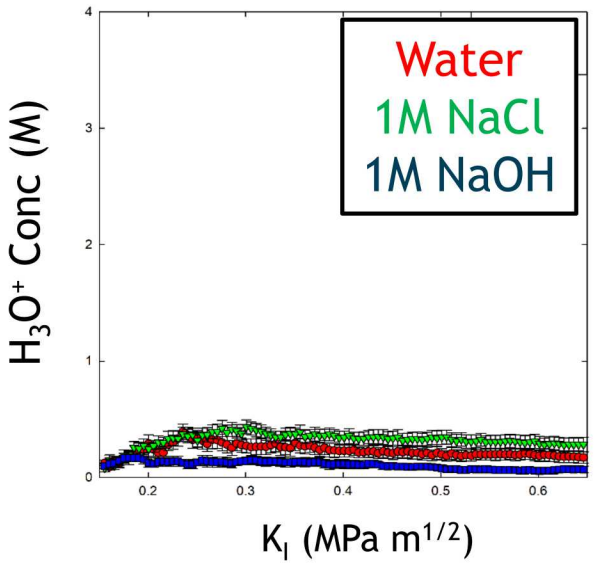
- Surface structure is influenced by solution composition.

Solution Composition in Fracture

OH^- Concentration in Solution



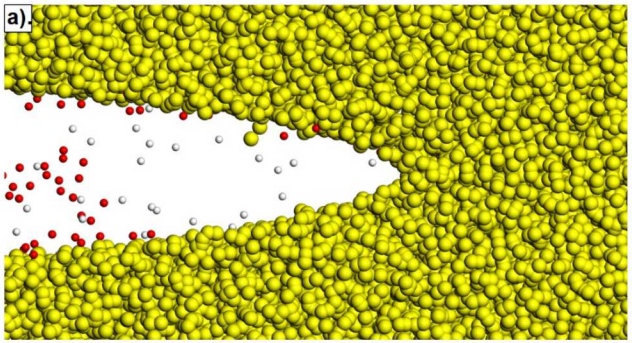
H_3O^+ Concentration in Solution



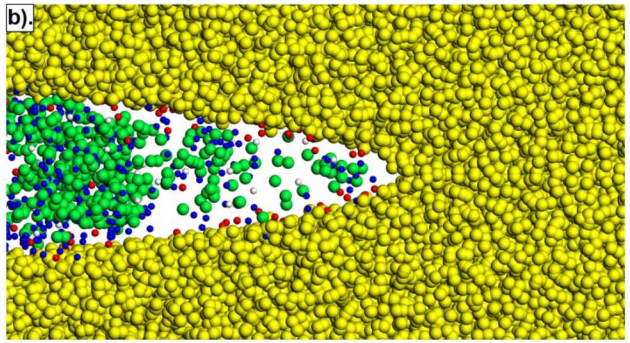
- Rapid change in concentrations occurs with initial loading before crack propagation
- Steady-state concentration occurs at ~0.25-0.3 MPa$\sqrt{m}$ due to balance of rate of water infiltration and addition of NaCl or NaOH molecules as fracture is loaded
- Concentration of $H3O^+$ increases with decreasing pH: 1 M NaOH < water < 1 M NaCl.
- Silica dissolution should be higher in both NaCl and NaOH solutions than in pure water.

Accessibility of Fracture Tip to Different Ions

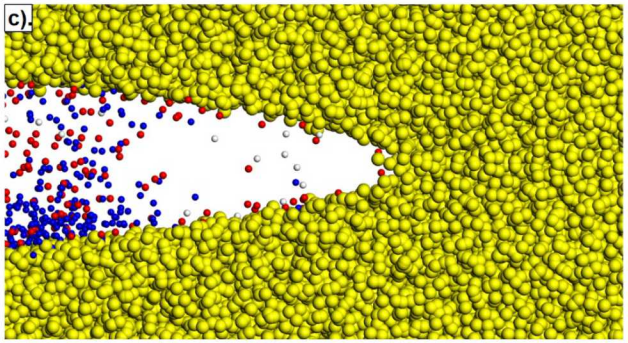
Water



1M NaCl



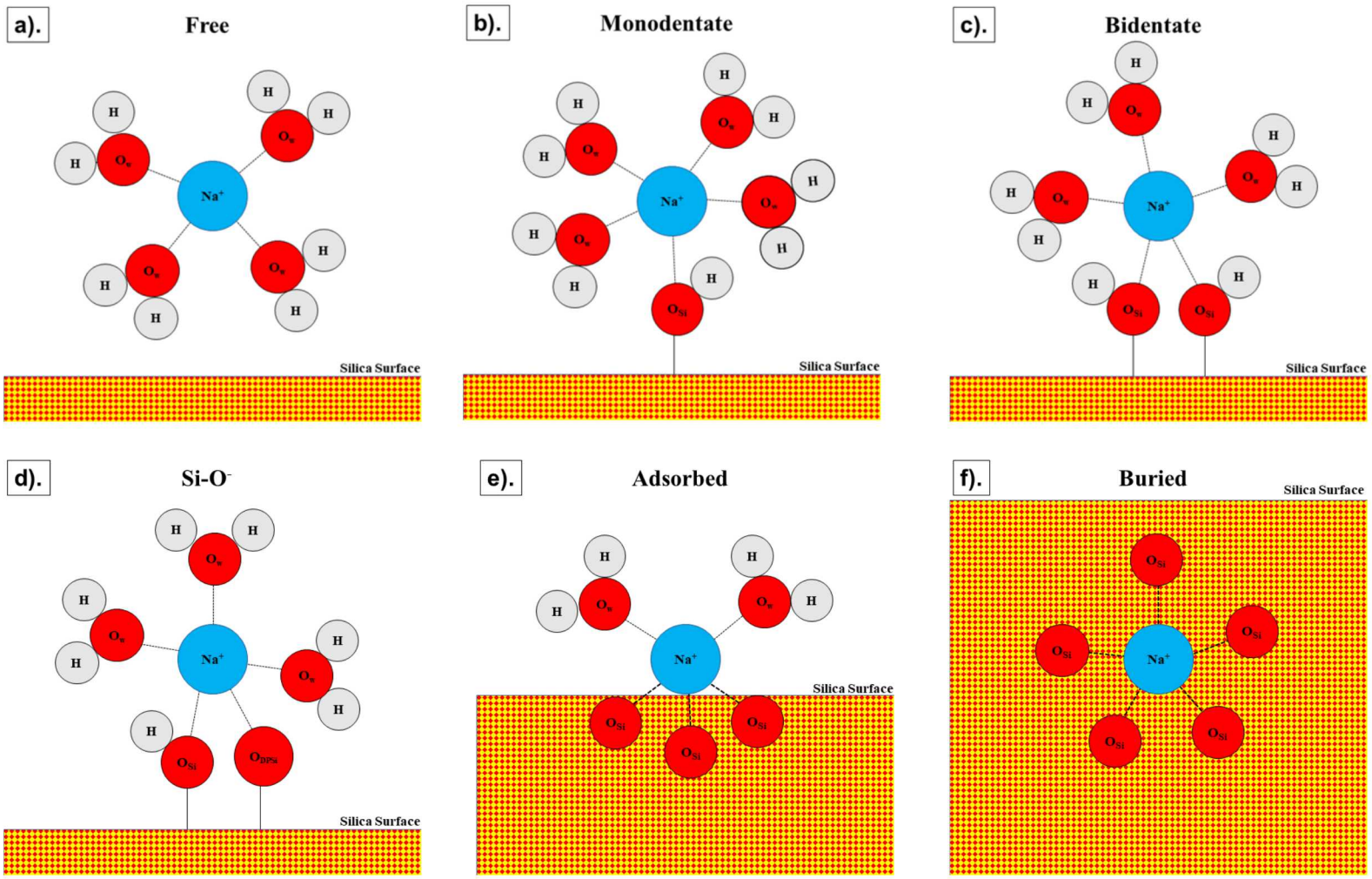
1M NaOH



Si H_3O^+ OH^- Na^+ Cl^-

- NaCl and NaOH molecules were added at the widest point in the fracture to emulate diffusion of ions from the bulk fluid
- For silica fracture in H_2O, the crack tip is filled with H_2O and a few H_3O^+
- OH^- migrates to fracture tip in both NaCl and NaOH solutions
- In NaCl solutions, the tip is filled with Na^+, Cl^- and some OH^-, H_3O^+
- Limited Na^+ diffusion into crack tip from NaOH solution; crack tip contains surface coordinated OH^- or free H_3O^+.

Na^+ Coordination Structures



Structure (d) does not occur on flat surfaces: nanoconfinement effect of fracture tip

Fracture Properties of Silica for Different Environmental Conditions

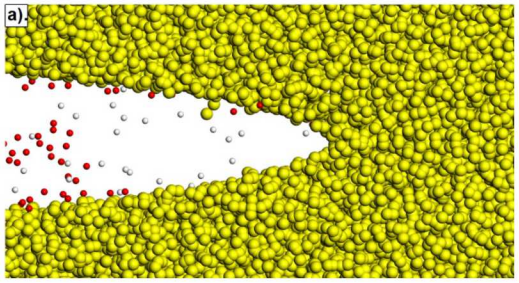
	eK_{IC} (MPa√m)		Fracture Events (#)	G_{IC} (J/m²)	G_{diss} (J/m²)	Si-OH (#/nm²)	γ (J/m²)
	First	Average					
Vacuum	0.34±0.04	0.43±0.04	3.67±1.18	7.91	6.78	0.00	1.13
Water	0.20±0.06	0.37±0.05	4.33±1.03	4.59	4.21	3.10	0.38
1M NaCl	0.28±0.09	0.41±0.05	5.42±1.66	5.14	4.75	3.04	0.39
1M NaOH	0.19±0.05	0.37±0.05	6.00±1.41	5.47	5.06	2.95	0.41

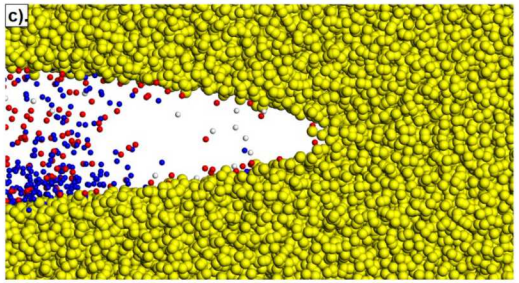
Ranking of factors that influence environmentally assisted fracture

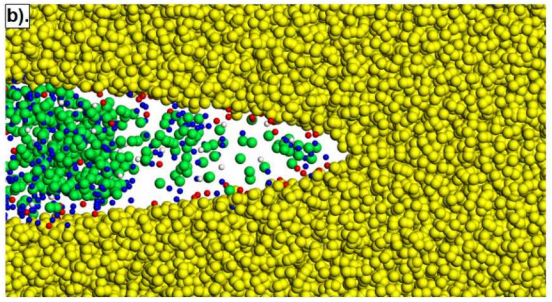
	eK^*_{IC}	Fracture events	Dissolution	Si-O^- #	Tip access	Radius of curvature
Water	2	3	3	3	3	3
1M NaCl	1	2	1	2	1	1
1M NaOH	3	1	2	1	2	2

Conclusions

- Amorphous silica is substantially weaker when in contact with aqueous solutions than in vacuum due to chemical reactions with preexisting cracks.
- Fracture toughness is lowest for silica in 1M NaOH solutions. The basic solution leads to higher surface deprotonation, less dissolution, and a narrower radius of curvature than in an acidic environment.
- The 1M NaCl solution causes more silica dissolution than pure water or a 1M NaOH solution and changes the geometry of the fracture tip. In addition Q^0 silica species are observed in solution.
- The nanoconfinement at the fracture tip results in different Na^+ adsorption mechanisms than on a flat surface.







This work was fully supported by the Laboratory Directed Research and Development (LDRD) program of Sandia National Laboratories.