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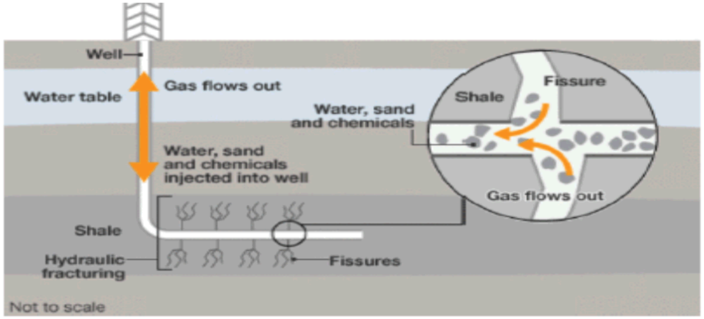
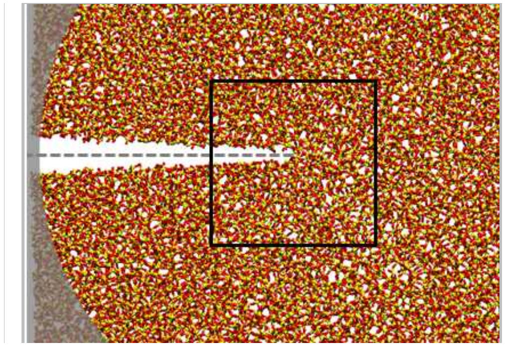
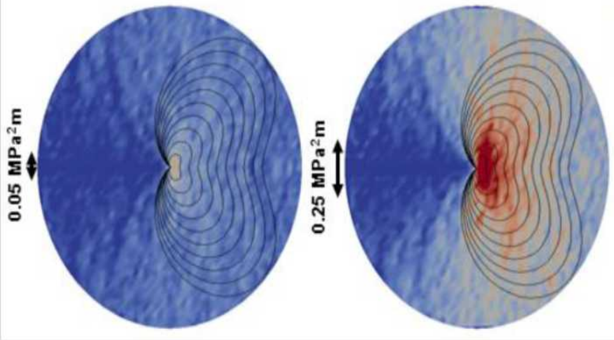




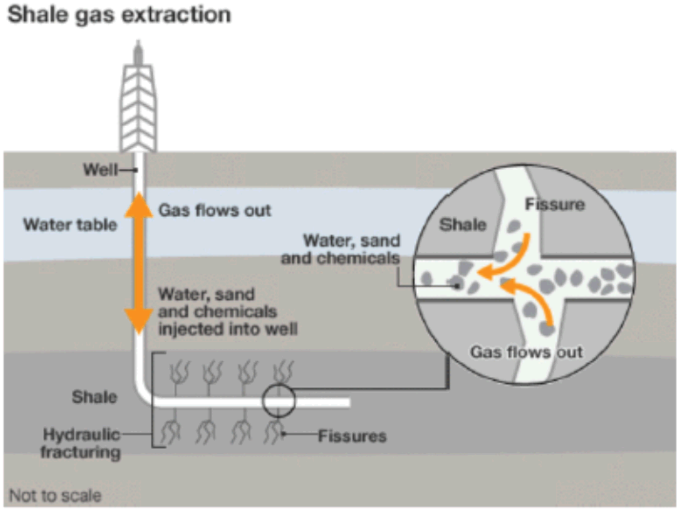


# Nanoscale Stress-Corrosion of Geo-materials in Aqueous Solutions

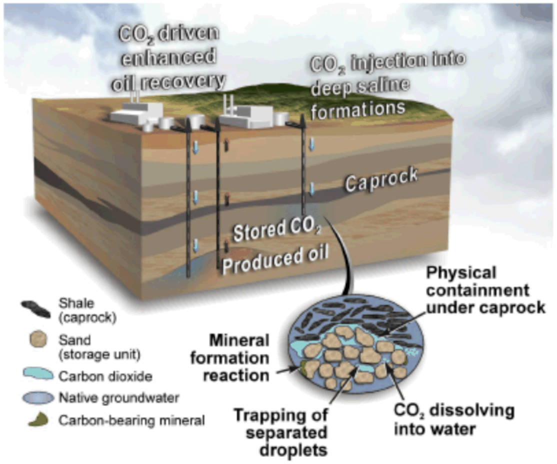
Louise J. Criscenti, Jessica M. Rimsza,
Edward N. Matteo, and Reese E. Jones

# Motivation

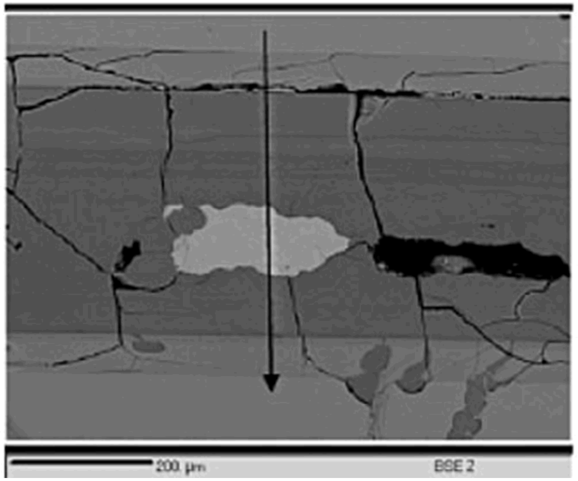
## Hydrofracking



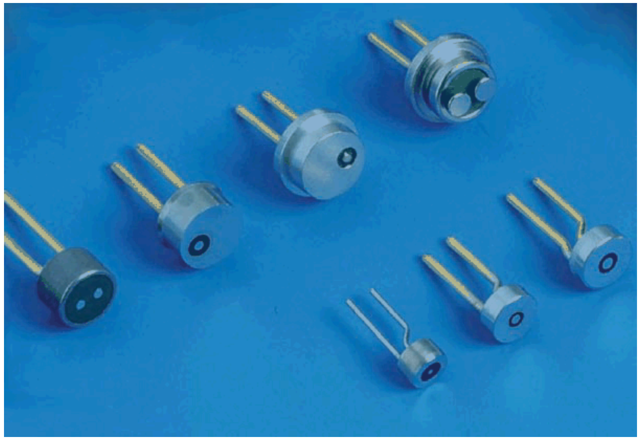
## Sequestration



## Crack in glass: analog for glass waste form



## Airbag feedthrough igniters



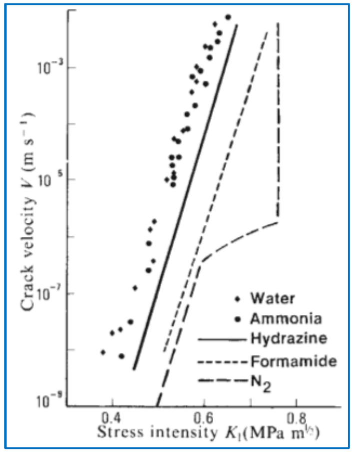
# Overview

- To develop a fundamental atomistic-level understanding of the chemical-mechanical mechanisms that control subcritical cracks in low-permeability geomaterials.
- To link atomic-scale insight to macroscale observables and directly address how chemical environment affects mechanical behavior.
- **Why Atomistic Simulation?**
  - Cracks start at the atomistic scale – a crack tip will be initiated by the breaking of bonds (e.g., Si-O) at the rock-fluid interface.
  - Crack tip formation and crack propagation is impacted by interfacial fluid and surface chemistry (e.g., development of surface charge, impact of adsorbed species along fracture surface).

# Chemical Effects on Subcritical Fracture

## Stress-Corrosion Cracking

Silica Glass

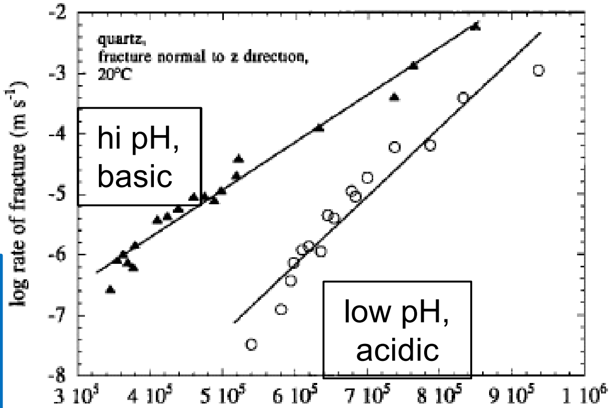


***T.A. Michalske & S.W. Freiman, Nature (1982)***

**$K_1$ = measure of stress field at crack tip.**

***Orders of magnitude Difference in the rate of fracture with chemical environment***

Quartz



$K_I$ = stress intensity factor (N m$^{-3/2}$)

***P. M. Dove, J. Geophys. Res. (1995)***

**Initial Objectives:**

- To calculate fracture toughness of dry silica glass from atomistic molecular simulation data
  - Start with a simple, well-studied isotropic material
  - Upscale atomistic data to macroscopic observable (fracture toughness)
- To calculate fracture toughness of wet silica glass from atomistic molecular simulation data
- To compare simulations with experimental observations.

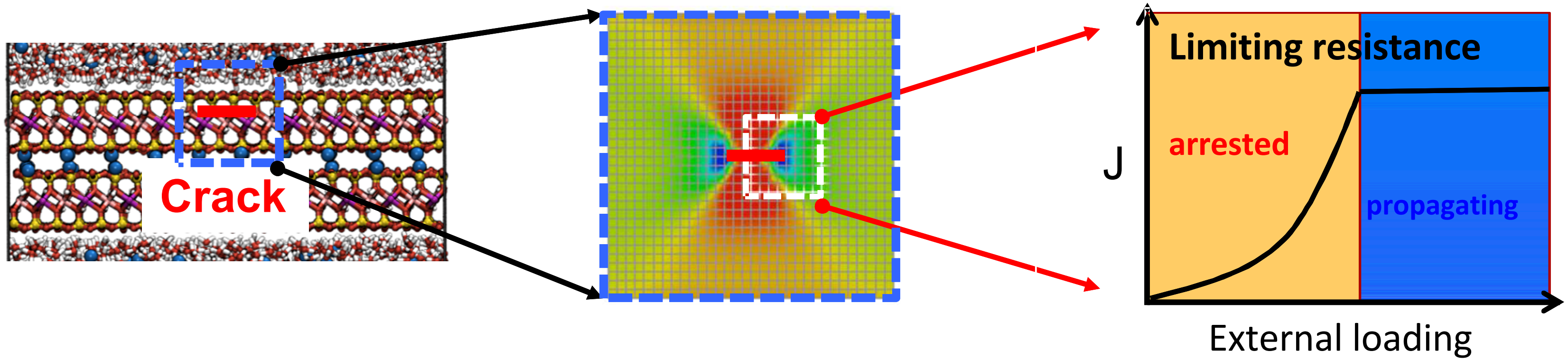
# Mechanical Fracture Models

## Upscaling Metrics: Atomistic to Continuum (AtC)

Molecular simulations sample atomic displacements, energies & forces

Eshelby stress fields use atomic data to characterize local energy available to move the crack (*in red*)

The J-integral is formed from the divergence of the Eshelby stress and determines if a crack will propagate

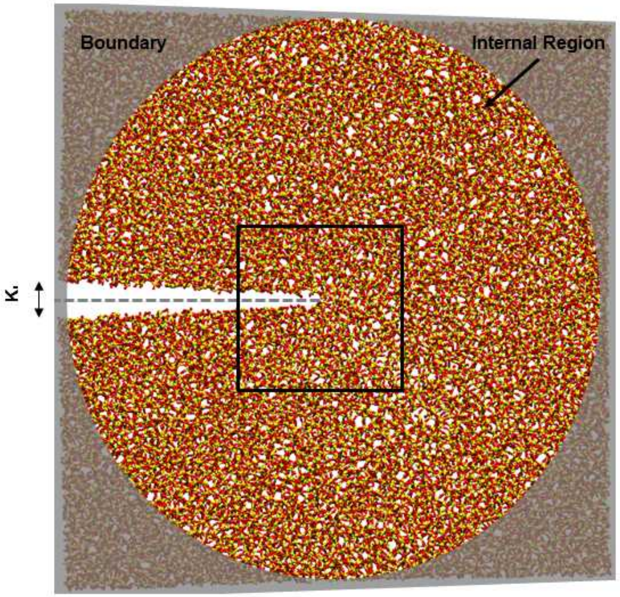


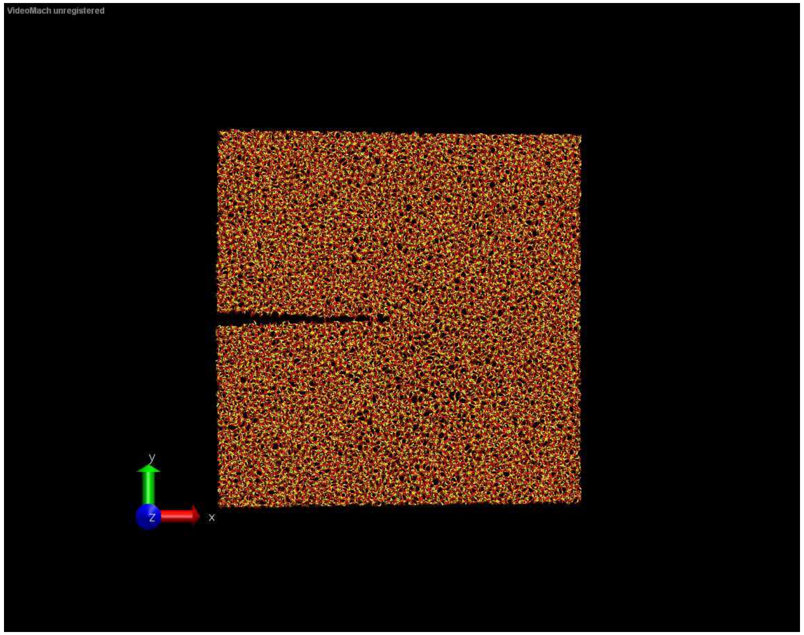
**Jones & Zimmerman: First to successfully apply continuum fracture theory to atomistic systems to estimate fracture toughness**

- The J-integral provides the characteristic crack tip driving force regardless of system configuration.
- **When J reaches the material's fracture toughness ($J_c$) , crack propagation begins**.
- $J/J_c$ can be measured experimentally using geometries and procedures specified in standards (e.g. ASTM E1820 - Standard Test Method for Measurement of Fracture Toughness)

# Simulation Set-Up for Dry Silica System

- ReaxFF Force Field, LAMMPS MD code (Plimpton, 1995)
- Amorphous silica, system size: 38,400 atoms (143 Å x 143 Å x 28 Å); Melt and quenched from β-cristobalite system; 12 replicas
- A slit crack is formed creating a singularity with highly concentrated stress
- Boundary atoms are fixed; Far-field loading as Mode I fracture
- Interior atoms are allowed to move freely
- Stress is introduced iteratively by increasing the crack width
- Atomic positions adjust to accommodate the added stress





# Silica Fracture and Energy Dissipation

- Fracture propagates in distinct steps when the stress at the crack tip exceeds the strength of the material
- Perfectly brittle fracture will have no dissipation energy, with all energy used to propagate the fracture
- Dissipation energy calculated from change in energy of the system over the added surface area

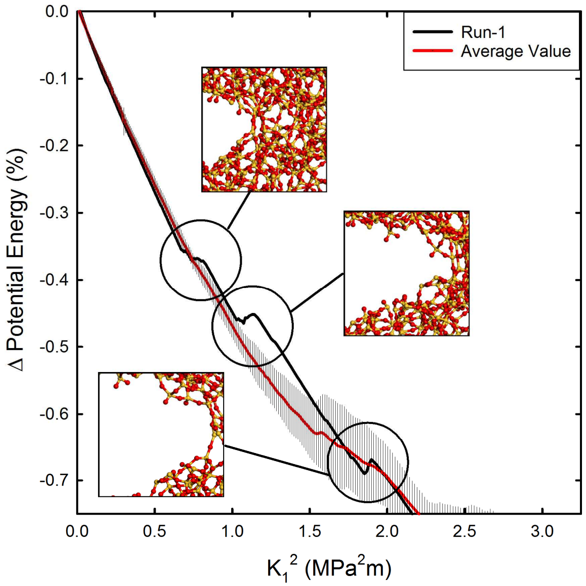
$$\frac{\Delta U}{\Delta S_A} = G_{diss}$$

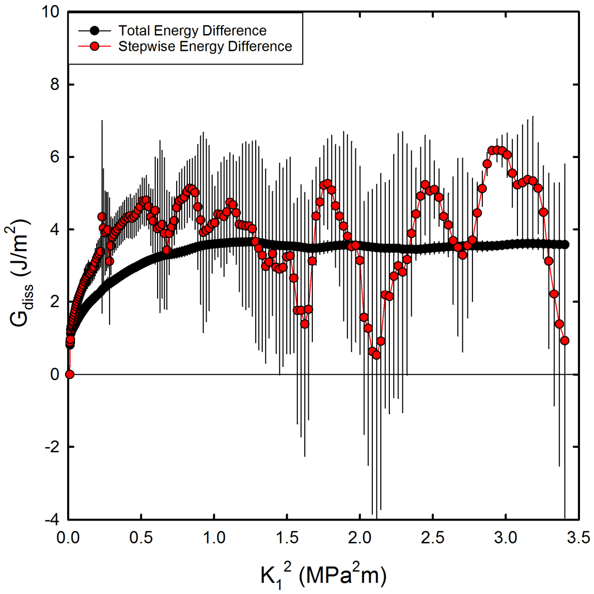
- Local inelastic behavior as energy is introduced into the silica during loading and not completely dissipated once fracture occurs

$$J_{IC} = G_{IC} = G_{diss} + 2\gamma_s$$

- Surface energies ($\gamma_s$): 1.2-2 J/m$^2$

Rimsza, J. M. et al. *Langmuir* (2017).





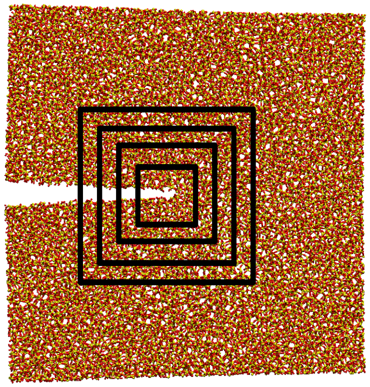
$G_{diss}$ = 3.5 J/m$^2$

Estimated $J_{IC}$ values are ~5.9-7.5 J/m$^2$

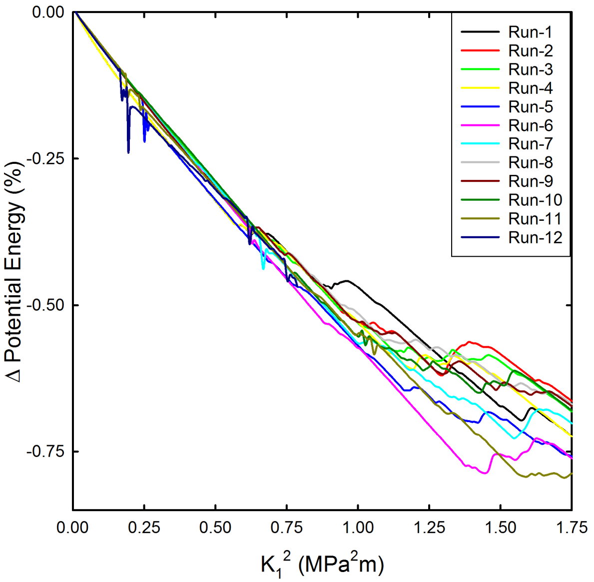
# J-Integral Calculation for Dry Silica

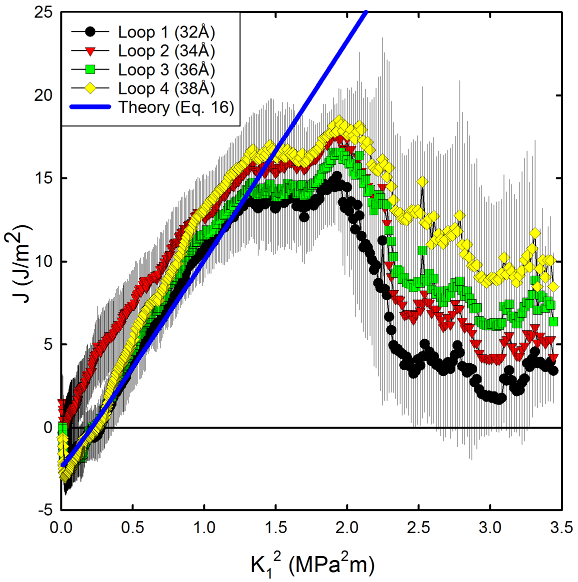
- Calculated via the AtC method through coarse graining energy, displacement, and stress *Jones, Reese E., et al. J. Phys.: Condens. Matter (2010)*

- J-integral converges at loop sizes of ~3 nm approximates the size of the inelastic zone



Schematic of increasing loop sizes for J-integral convergence test



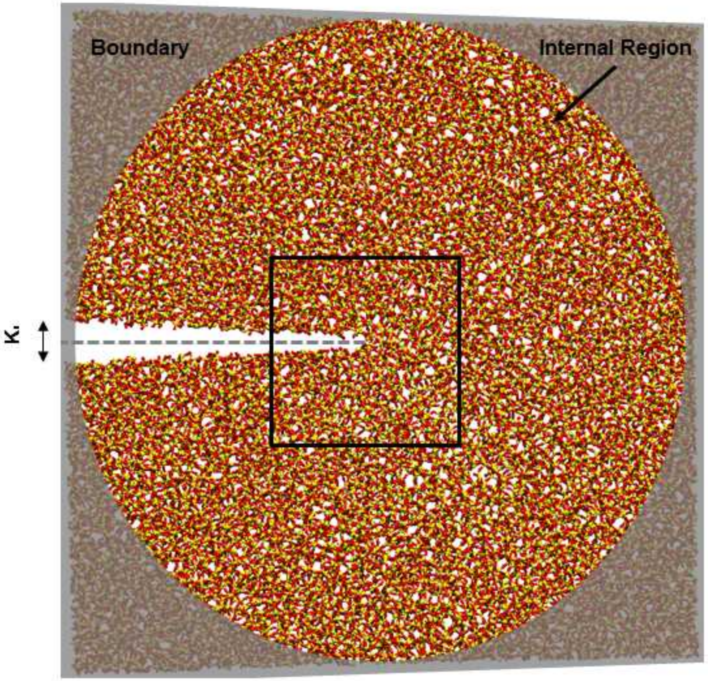


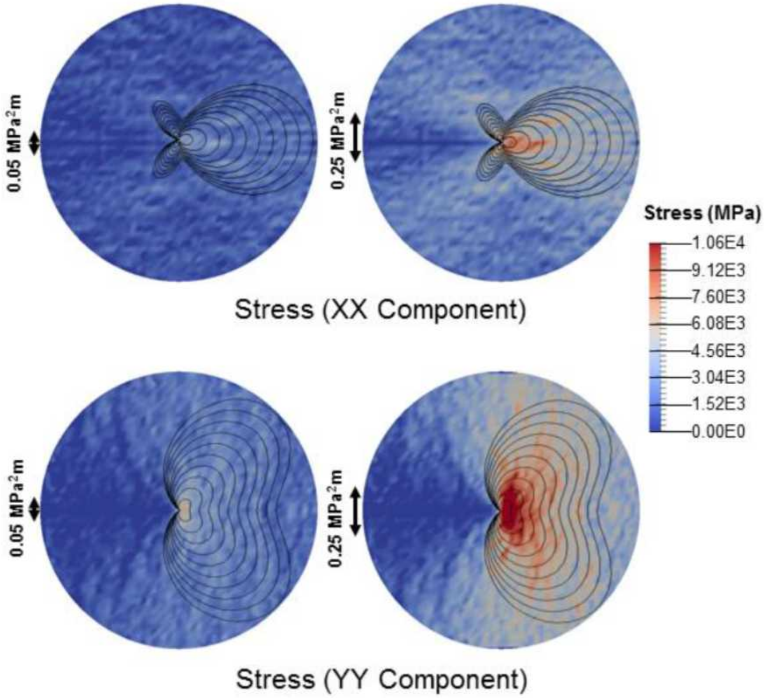
J-integrals with converged loop sizes

Calculated
$K_{IC}$=0.76±0.16 MPa√m
$J_{IC}$=6.16±4.34 J/m$^2$

Experimental
$K_{IC}$=0.78±0.04 MPa√m

# Simulated Stress Fields for Dry Silica



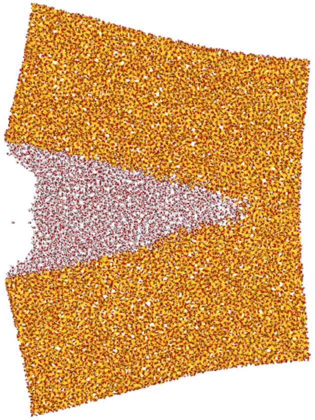


Crack tip stress fields in amorphous silica
at two loading levels ($K_I^2$ ~ 0.05 and 0.25 MPa$^2$m).
Black contours are from linear elastic solution.

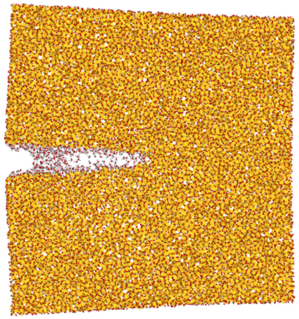
# Fracture of Silica in Water

**Three types of simulations performed:**

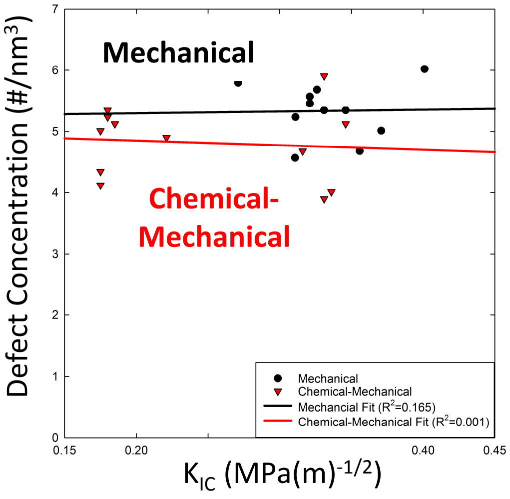
**Mechanical**



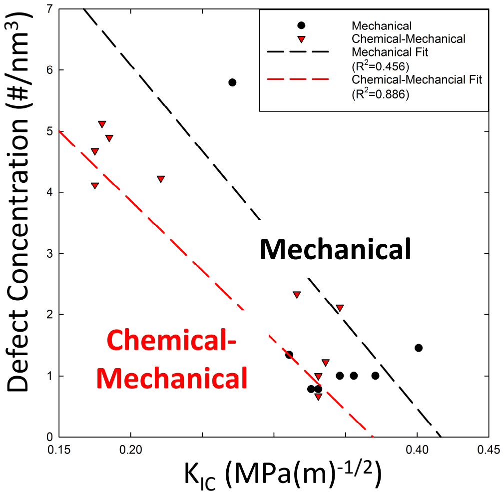
**Chemical-Mechanical**



**Chemical**



Initial structure



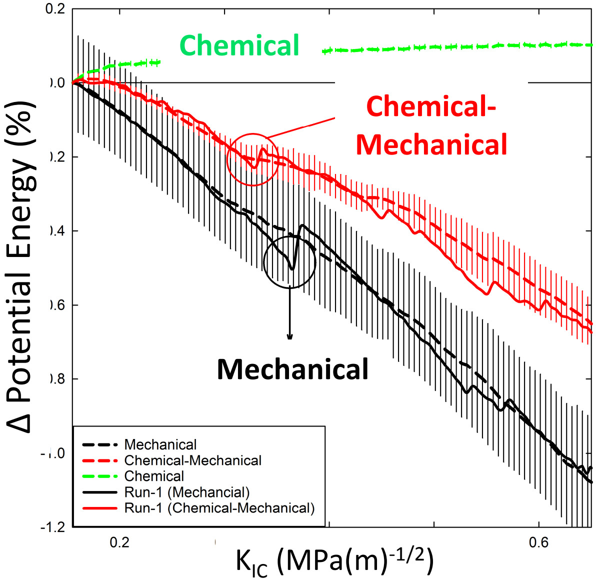
Immediately prior to propagation

## Defect Concentrations

Immediately prior to crack propagation, the defect concentration is higher for systems that fracture at $K_{IC}$ values of 0.25 Mpa√m or less.

# Fracture Toughness of Silica in Water

## Fracture Toughness ($K_{IC}$)



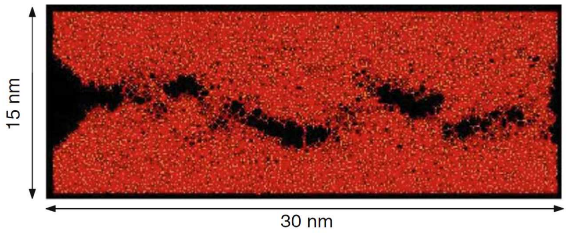
Mechanical $K_{IC}$ = 0.339* ± 0.37 MPa√m
Chemical-Mechanical $K_{IC}$ = 0.247 ± 0.074 MPa√m

- Fracture toughness ($K_{IC}$) is defined by the first deviation of the potential energy from the expected trend. Fracture from chemical ($H_2O$)-mechanical effects occurred at 75% of the $K_{IC}$ values from mechanical loading alone.

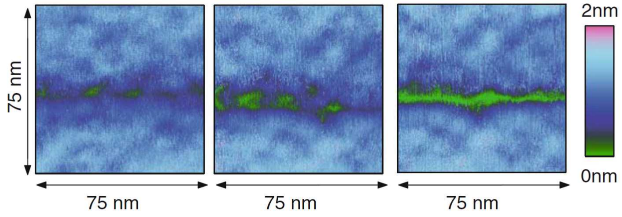
- Potential energy with loading for silica systems for mechanical, chemical, and mechanical-chemical conditions. Energies averaged over 12 runs with the average and standard deviations reported as well as data for one individual run.

- Lower $K_{IC}$ for dry systems is due to higher simulation temperature (300K vs. 0.1K) for direct comparison to aqueous systems which require higher temperatures to allow for water dynamics.

# Experimental Approach

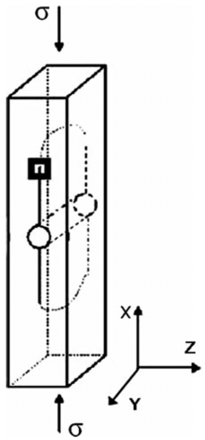


MD



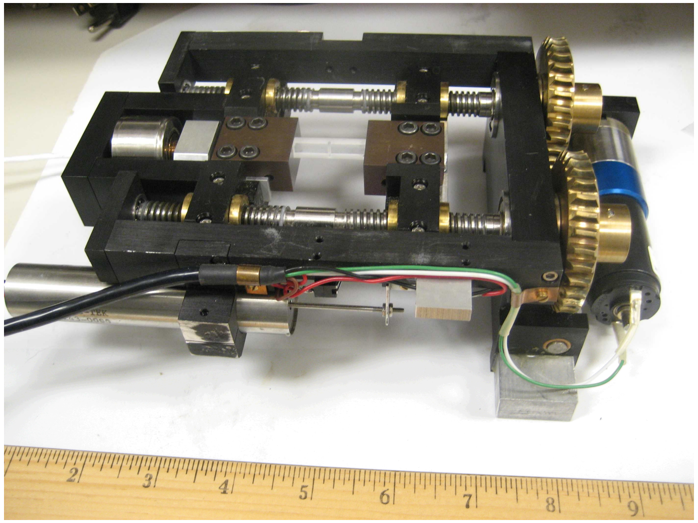
AFM

*Bonomay et al. Int. J. Fract. 2006*



DCDC = Double Cleavage Drilled Compression

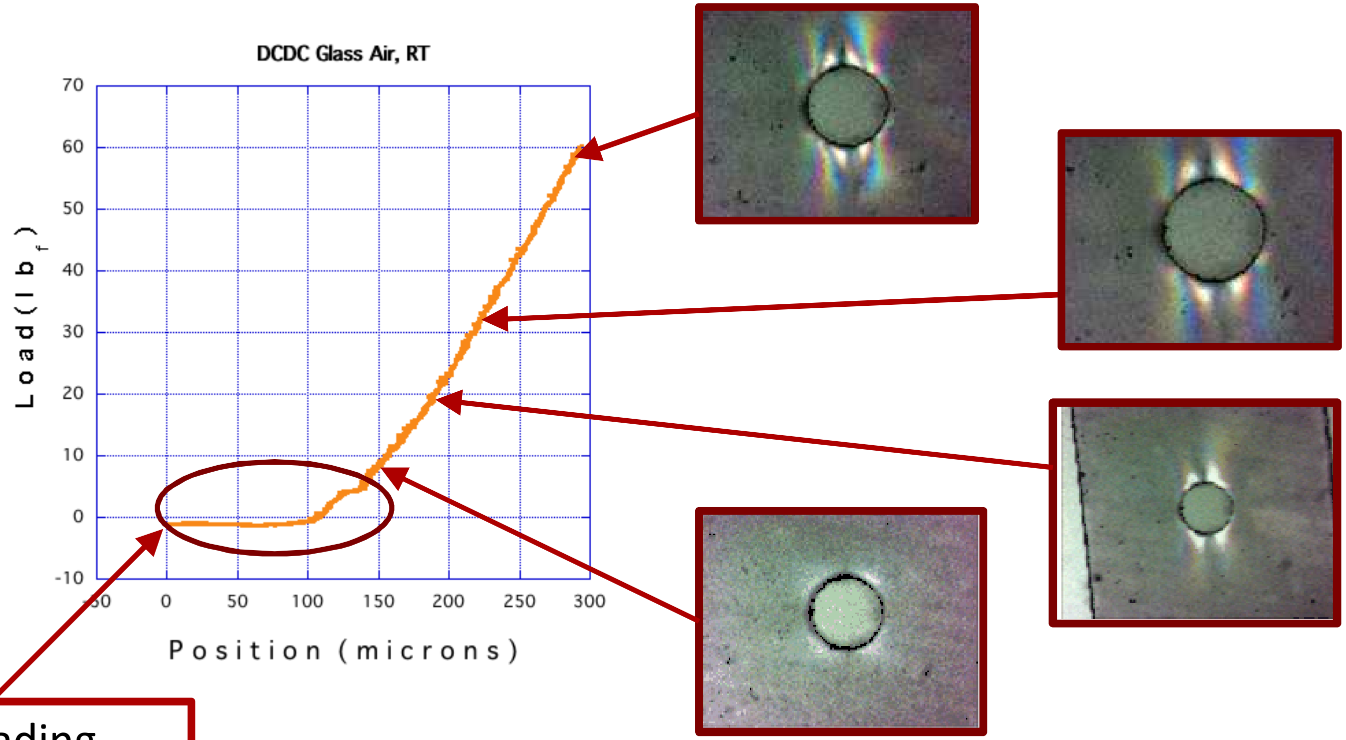
*Technique may also be implemented with confocal microscope.*



Load Frame

*Review articles: Ciccotti, J. Phys. D 2009, Ciccoti et al. JNCS 2008*

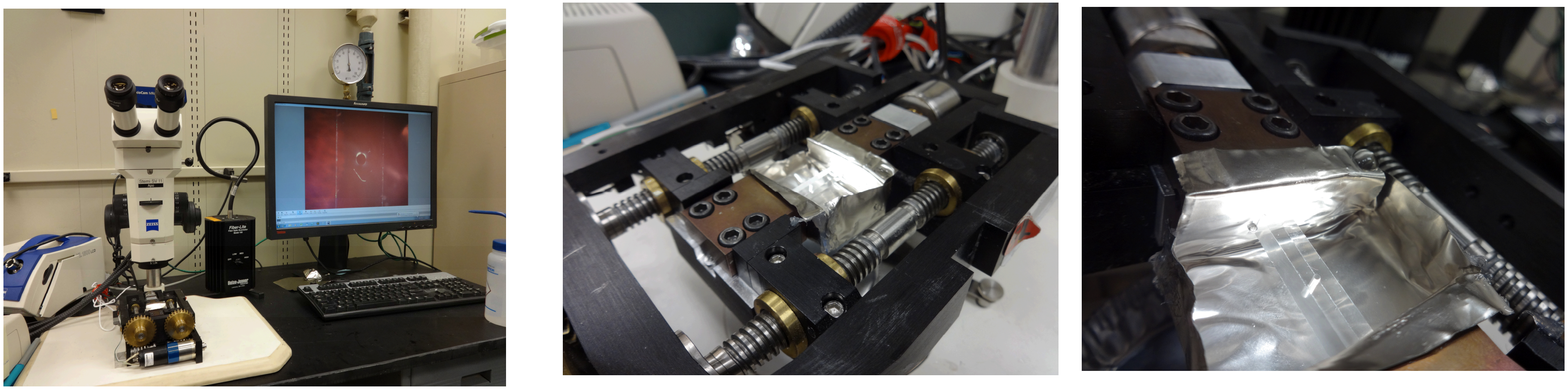
# Imaging Capabilities and Preliminary Results for Dry Silica



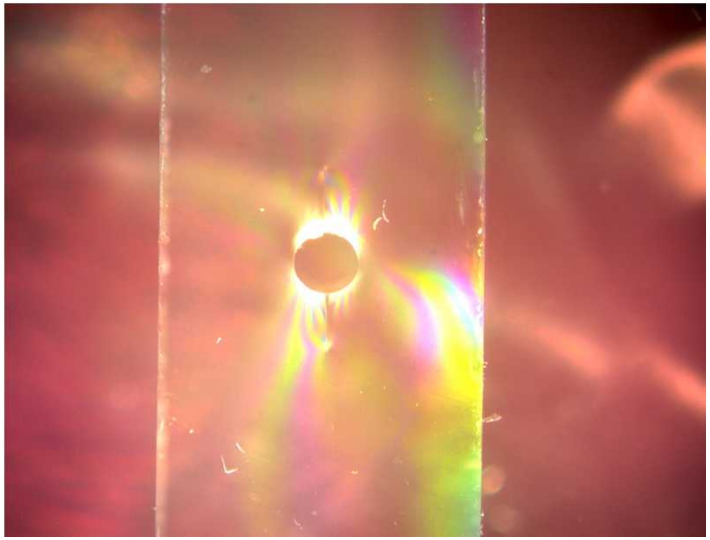
Sample loading and compliance of nickel foil

- Optical profilometry for post-test analysis and preliminary imaging of load frame tests of DCDC samples
- Polarized light microscopy for visualizing stress fields; will use Moiré analytical methods for stress field quantification

# Preliminary Results for Silica in Water



- Tested design for loading in liquids
- Repeatable loading of DCDC glass samples in DI water
- Air, DI, and 0.5 NaCl tested
- Upgraded test equipment for load frame and imaging
    - Software, updated laptop (Windows 10)
    - Time lapse software
    - Upgraded USB microscope



# Summary and Conclusions

- First time atomistic simulation data has been used to calculate the macroscopic J-integral and crack stress fields from atomistic data for an oxide in vacuum and in water.
- First time ReaxFF has been used to investigate subcritical crack propagation using a slit crack and Mode I tension.
- First time that a molecular-scale simulation method has been developed for stress-corrosion cracking in DI water.
- First time that DCDC experiments have been conducted in environmental chambers – new experimental design.

- Simulations for dry silica (T = 0.1K):
  - A localized high stress inelastic region develops prior to fracture with an estimated radius between 3-3.2 nm.
  - The calculated $K_{IC}$ of ~0.76 MPa√m is consistent with experimental data reported in the literature.
- Simulations for silica in water (T = 300K):
  - Immediately prior to crack propagation, the defect concentration is higher for systems that fracture at $K_{IC}$ values of 0.25 Mpa√m or less.
  - Fracture from chemical ($H_2O$)-mechanical effects occurred at 75% of the $K_{IC}$ values from mechanical loading alone.
- Preliminary experimental data is consistent with conceptual models and previously reported data.

## Acknowledgements

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

# Extra Slides

# Fracture Mechanics Theory: Fracture Toughness

***Griffith energy-balance:***

$$U = (U_E - W_L) + U_S$$

***Strain energy release rate*** (G) describes the energy stored in material prior to fracture

$$G = -d(U_E - W_L)/dc$$

A linear elastic solution for a slit crack in plane strain mode I leads to:

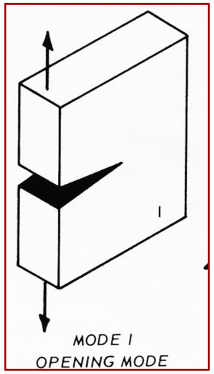
$$G_{IC} = J_{IC} = \frac{K_{IC}^2}{E^*} = 2\gamma_s$$

(brittle material)

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

(material with inelastic behavior)

***Fracture toughness ($K_{IC}$):*** **the energy required to propagate a crack in a material.**



γ = surface energy
$K_I$ = stress intensity factor
G = strain energy release rate
C = crack length

J-integral: a path independent contour integral used to calculate *G* for monotonic loading

$$J = \int_{\partial\Omega} S \cdot dA$$

Eshelby stress field:

$$S = WI - H^T P$$

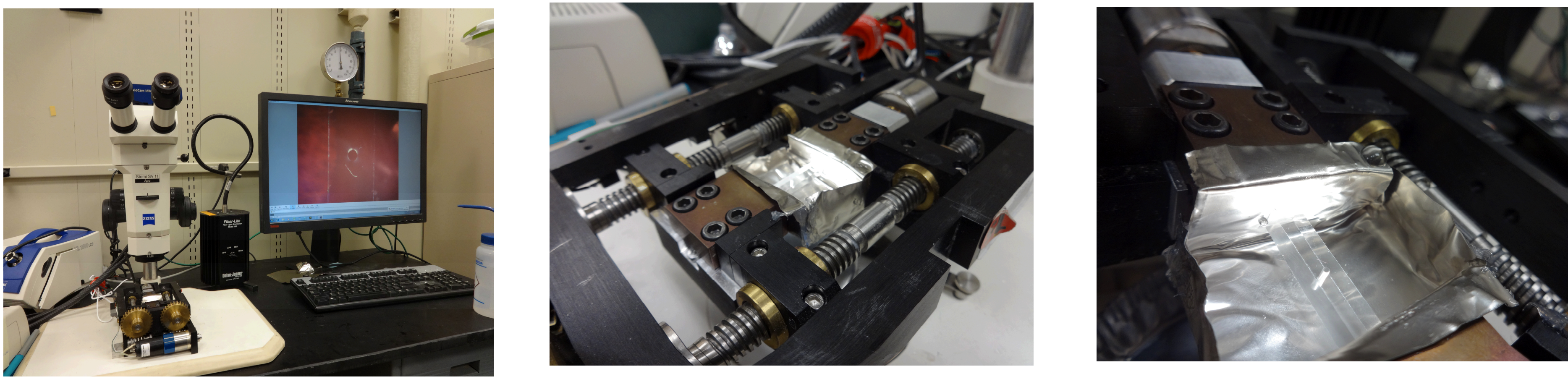
I is identity tensor

H = displacement gradient, measure of strain

P = stress

W = energy

# Experimental Results in Solution



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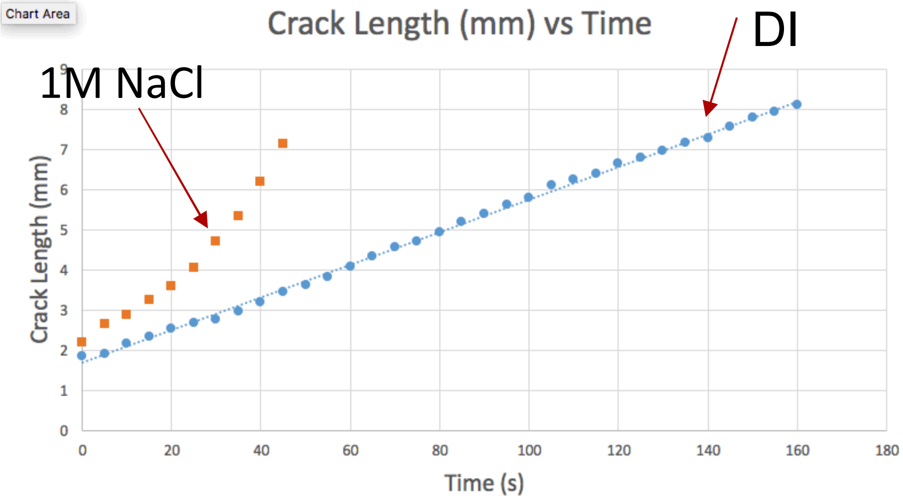
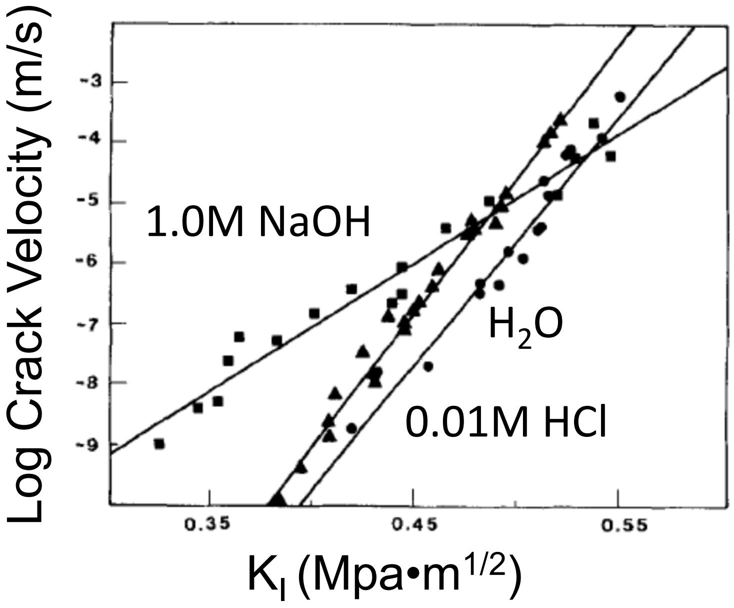


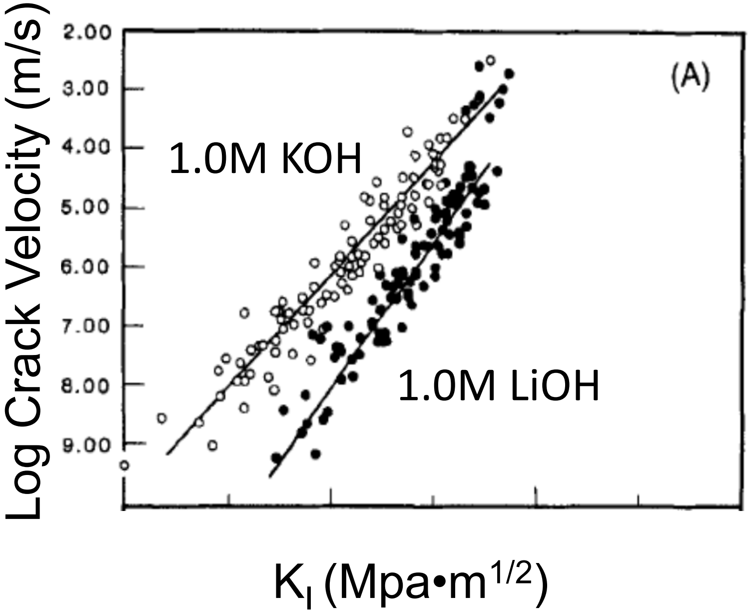
# Experimental Setup

## Objective: to obtain experimental data at the atomistic scale.

- Method: DCDC = Double Cleavage Drilled Compression
- Material:  Silica parallelepipeds with holes
- Technique may be implemented with confocal microscope or AFM.

# Effect of Counterions on Crack Growth in Vitreous Silica





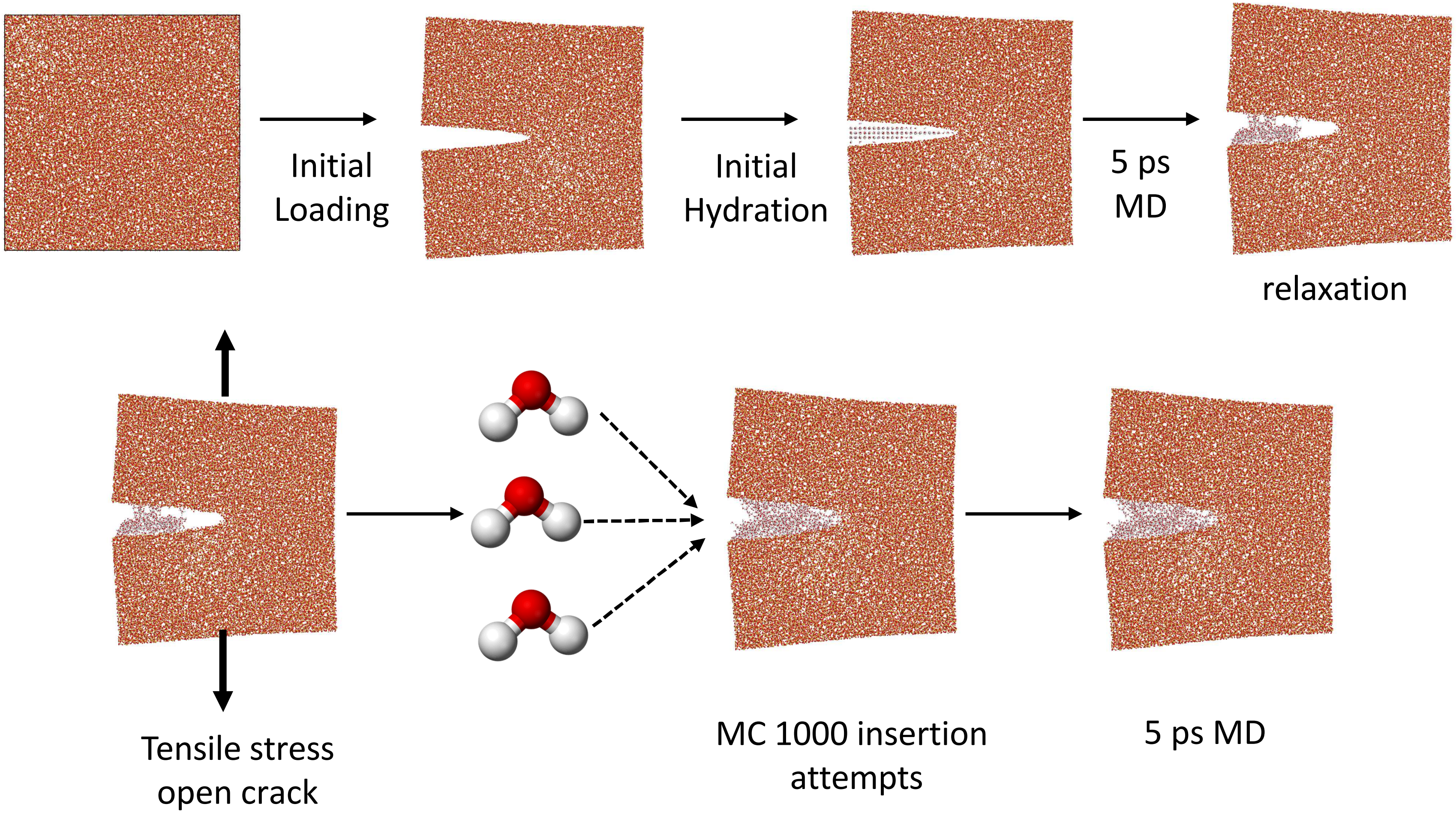
- The chemical activity of hydroxide is affected by the nature of the cation due to ion association.
- Hydroxide can penetrate the solvation shell of molecules.
- LiOH association decreases $OH^-$ activity in solution more than NaOH association.
- Dependence of applied stress on cation identity: NaOH ~ KOH ~ CsOH > LiOH

| | |
|---|---|
| 0.1M NaOH | pK = -0.7 |
| 0.1M LiOH | pK = -0.08 |

| | |
|---|---|
| 1M NaOH | 9% Associated |
| 1 M LiOH | 26% Associated |

*White et al., 1987*

# Silica Fracture in Water: Methodology



Initial Loading

Initial Hydration

5 ps MD

relaxation

Tensile stress open crack

MC 1000 insertion attempts

5 ps MD