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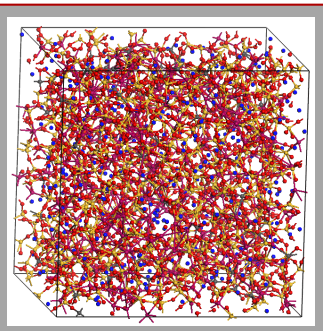
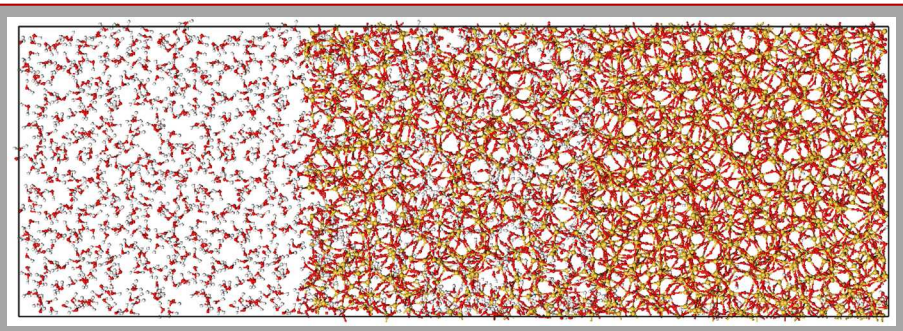
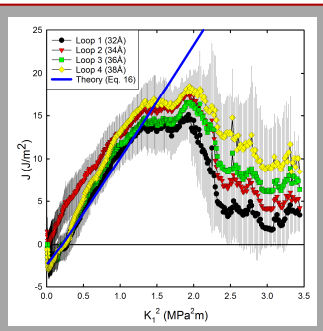

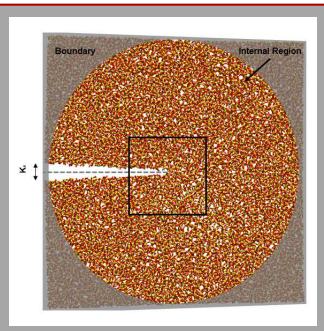

Dissolution and fracture of amorphous silica

J.M. Rimsza

SNL: Louise Criscenti, Reese Jones
UNT: Jincheng Du, Jeffrey Kelber, Lu Deng
UNT/Lam Research: Haseeb Kazi, Frank Pasquale
Penn. St: Adri van Duin, Seung Ho, Jejoon Yun (U.C. Merced)

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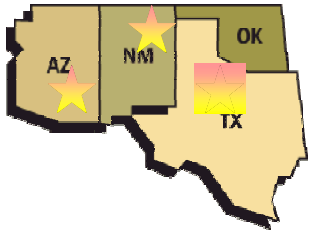
Outline

- Introduction
- Computational methods
- Silica glass dissolution
- Silica glass fracture
- Conclusions

Background



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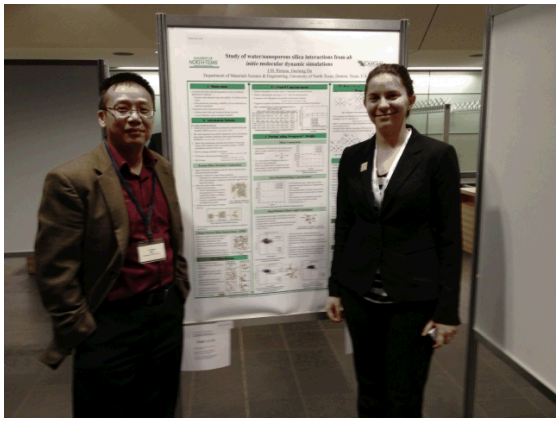
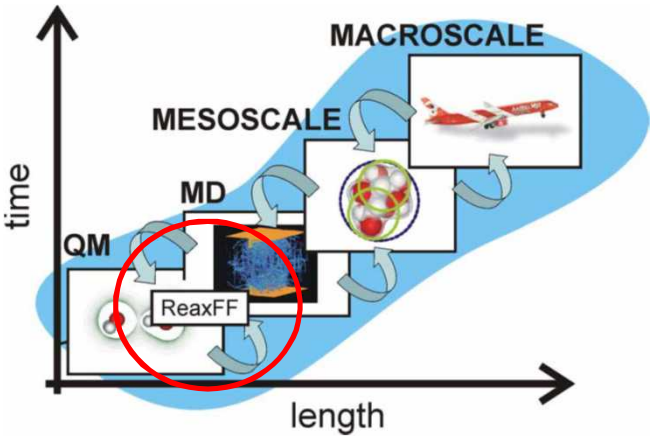


Classical molecular dynamics (MD)

- User generated forcefield (ex. Lennard-Jones)

$$V = \epsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right]$$

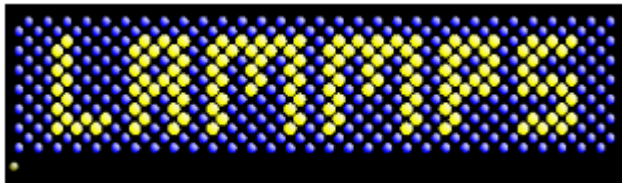
- Efficient simulation method
- Requires knowledge of the system
- Difficulty with calculating reactions
- Reactive Force Field (ReaxFF):



Markus J. Beuhler, Lecture, MIT . (2006).

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

- Bond order based potential
- Simulates changing coordination environments
- Geometry dependent charges
- Accuracy between *ab initio* and other classical MD potentials



http://lammps.sandia.gov/

- Implemented in the LAMMPS code distributed by Sandia National Labs

Yeon, J. and Adri CT van Duin. "ReaxFF molecular dynamics simulations of hydroxylation kinetics for amorphous and nano-silica structure, and its relations with atomic strain energy." *J. Phys. Chem. C* 120.1 (2015): 305-317.

Dissolution of Amorphous Silica

Jessica M. Rimsza (Sandia National Laboratories)

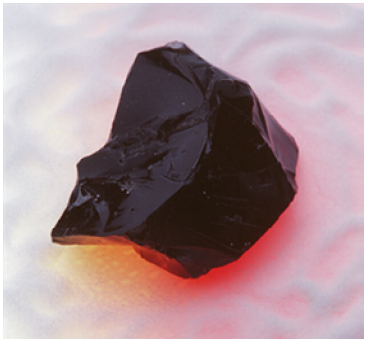
Co-Authors: Jincheng Du (UNT), Jeffrey Kelber (UNT), Lu Deng (UNT), Haseeb Kazi, (UNT, Lam Research), Adri van Duin (Penn. St.), Jejoon Yun (Penn. St., U.C. Merced)

Funding: This work was supported through the DOE Nuclear Energy University Partnership (NEUP), the Semiconductor Research Corporation (SRC), and the NSF Graduate Research Fellowship Program (GRFP)

Vitrification of nuclear waste glasses

- How to store nuclear waste without impacting the environment?
- Vitrification - immobilize nuclear waste in a stable amorphous network
- Composition: borosilicate glasses

Liquid nuclear waste in barrels



Vitrified nuclear waste

Table 1: International simple glass (ISG) and SON68 nuclear waste glasses compositions *Gin et al. Materials Today (2013)*

Composition (Mole %)	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2	Other
ISG	60.2	16.0	12.6	3.8	5.7	1.7	0.0
SON68	45.5	14.0	9.9	4.9	4.0	2.7	19.0*

*Other elements: Li_2O, Fe_2O_3, P_2O_5, NiO, Cr_2O_3, Cs_2O, SrO, Y_2O_3, MoO_3, MnO_2, CoO, Ag_2O, CdO, SnO_2, Sb_2O_3, TeO_2, BaO, La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3, UO_2, and ThO_2

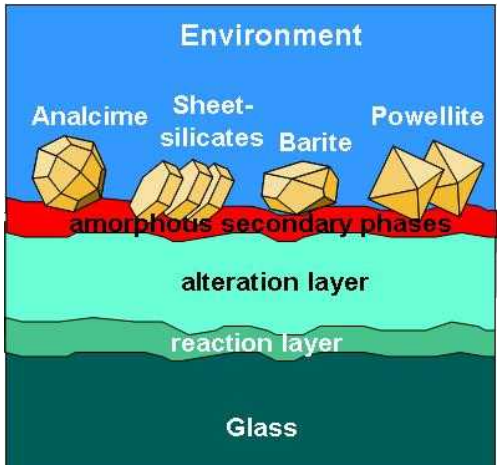
Hanford Plant, Washington state

What are the mechanisms and processes which govern the dissolution of silicate glasses in aqueous environments?

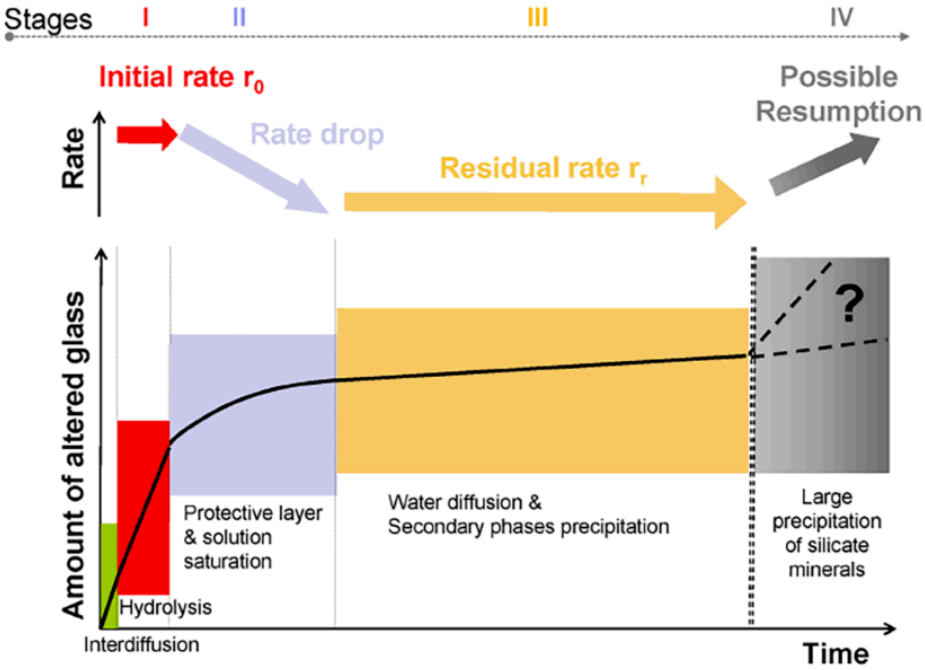
Images: http://www.hanfordvitplant.com/about-project http://www.hanford.gov/page.cfm/AdvancesinGlassChemistry https://www.sheffield.ac.uk/news/nr/nuclear-waste-storage-glass-sheffield-1.203561

Stages of glass dissolution

1. Interdiffusion between water and network modifiers
2. Hydrolysis of Si-O-Si bonds
3. Formation of a protective layer
4. Development of a residual dissolution rate
5. Precipitation of large silicate minerals



https://www.ine.kit.edu/english/417.php



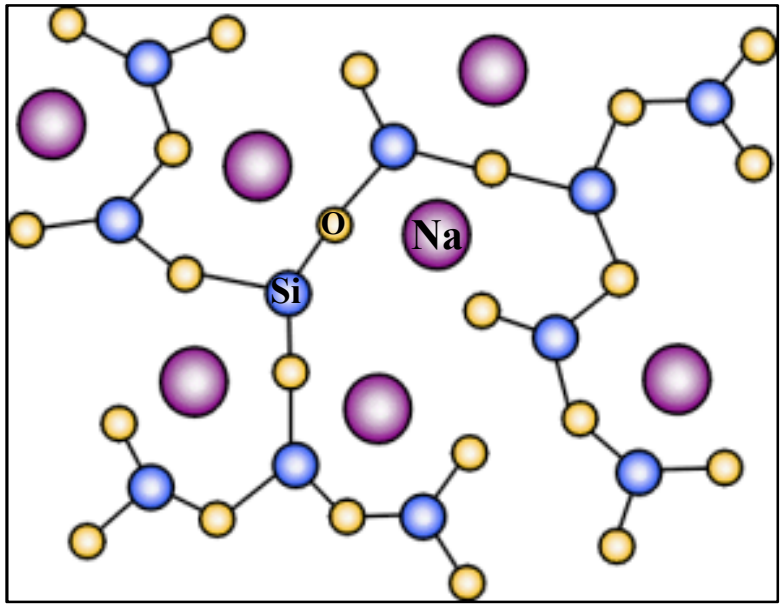
Gin et al. Procedia Mat. Sci. (2014)

Silica gel alteration layer

Silica gel alteration layer affects the dissolution rate due to:

- Slowing water diffusion
- Acting as a molecular sieve
- Providing more reactive sites for water
- Re-polymierizing silica from solution

Schematic of interdiffusion and hydrolysis



http://www.materials.unsw.edu.au/tutorials/online-tutorials/1-atomic-structure

Creation of the remnant silica gel structures

1. Generated a 3396 atom multi-component glass structure using a classical MD potential by Deng and Du

   Deng, Lu, and J. Du. *J. Non-Crys. Slds.* 453 (2016): 177-194.

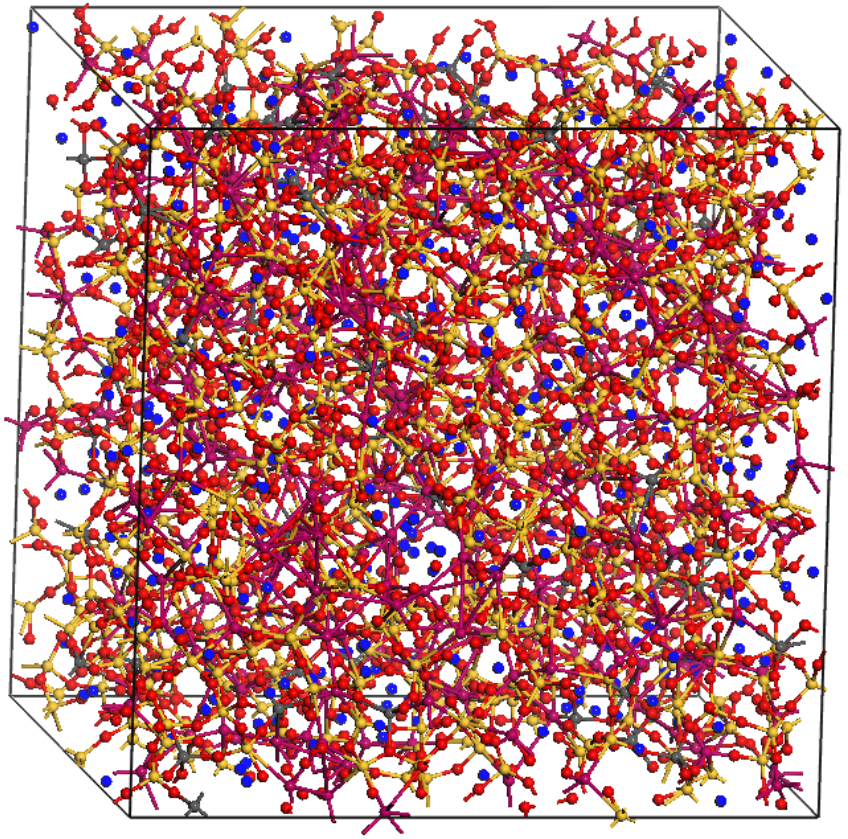
Composition of sodium aluminoborosilicate structure model

SiO_2 (wt%)	B_2O_3 (wt%)	Na_2O (wt%)	Al_2O_3 (wt%)
54.6	23.6	16.3	5.5

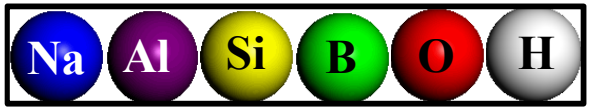
2. Remove sodium, boron, and aluminum atoms from the system (interdiffusion)

3. Terminate non-bridging oxygen with hydrogen to form silanols

4. Hydrate the hydroxylated silica system forming a gel structure

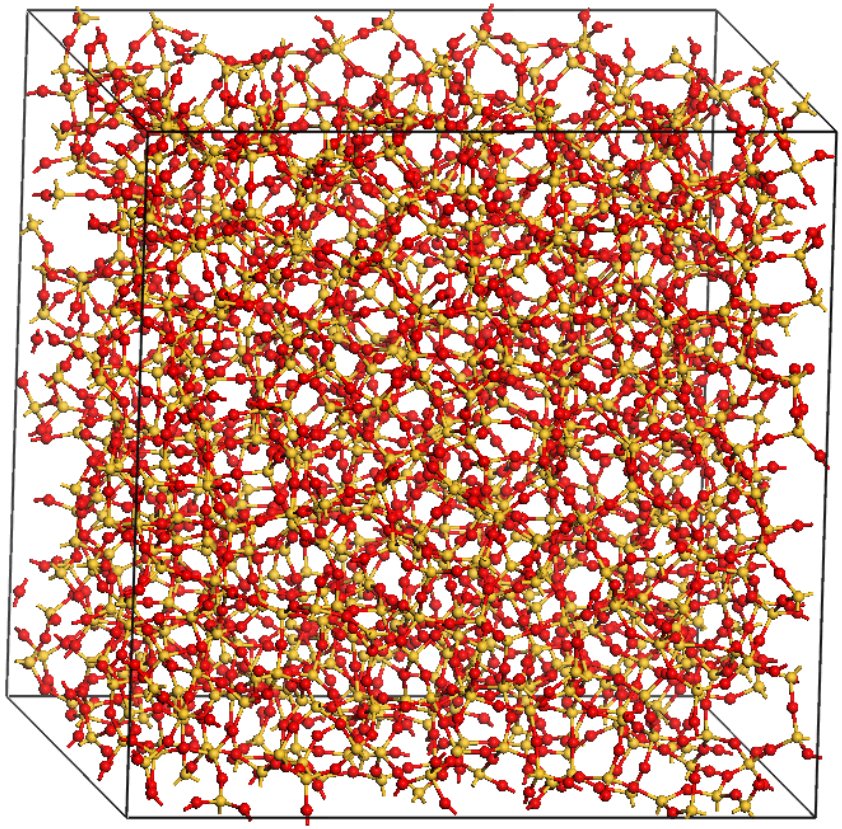


Sodium aluminoborosilicate glass structure model

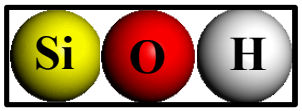


Depolymerized silica gel structures

1. Generated dense silica structure (3000 atoms)
2. Remove silicon and form four non-bridging oxygen
3. Terminate non-bridging oxygen with hydrogen to form silanols
4. Repeat until x number of silicon have been removed (40%, 60%, 80%) forming a hydroxylated nanoporous silica structure
5. Hydrate the system forming a silica gel



3000 atom dense silica (SiO_2) structure



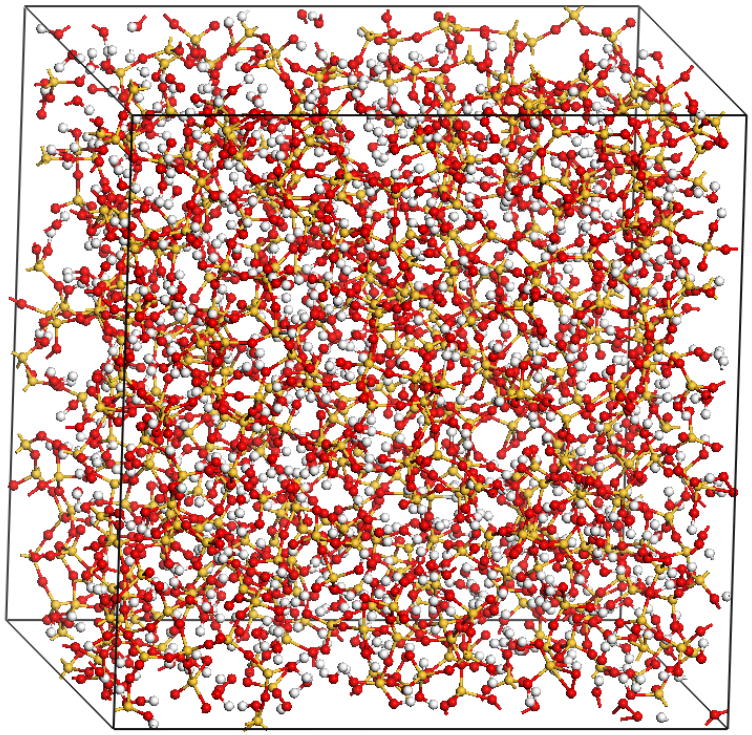
Composition and density for DSG silica gel structures.

	% Si Removed	Mole % SiO_2	Density (g/cm^3)
DSG-20	20 (Si)	62.26±1.19	1.91±0.01
DSG-40	40 (Si)	40.77±0.06	1.57±0.01
DSG-60	60 (Si)	23.66±0.07	1.25±0.01

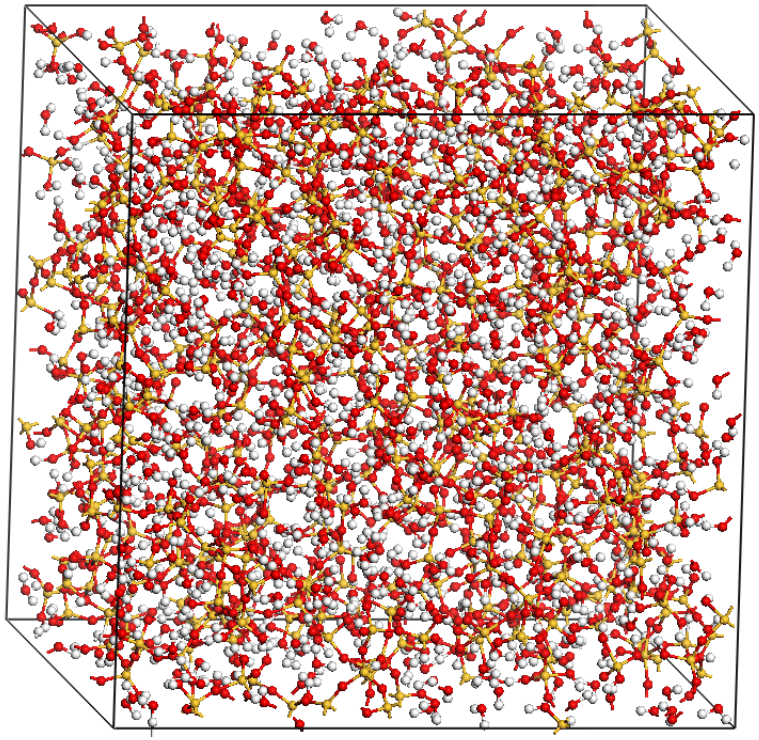
Simulation details

- Create silica gel as a remnant of the multicomponent glass (RSG) or from the de-polymerization of silica gel (DSG)

- MD simulation for 30ps using a 0.25 fs time step at 300K to allow for structural relaxation



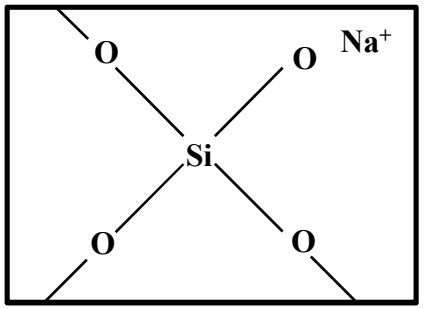
Remnant silica gel (RSG) structure model

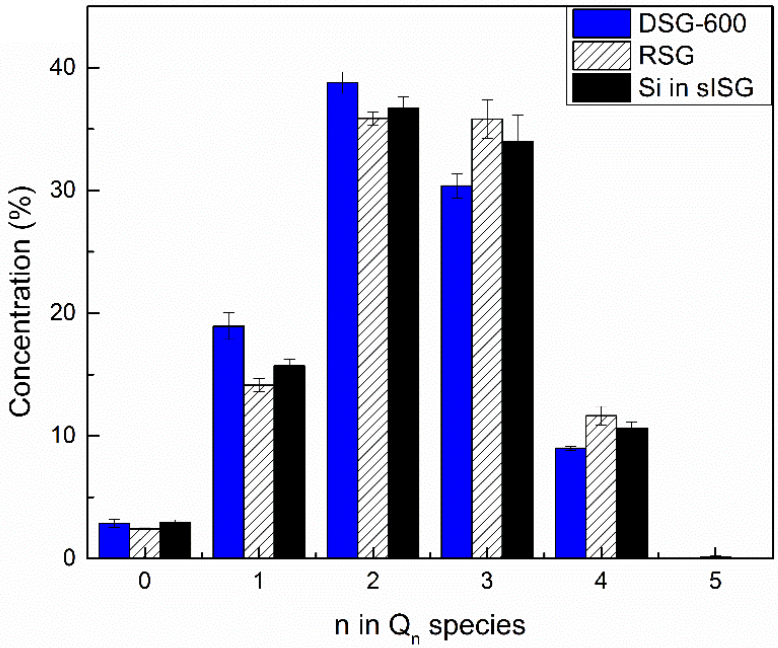


Hydrated silica gel structure with 40% (400) of the silicon removed.

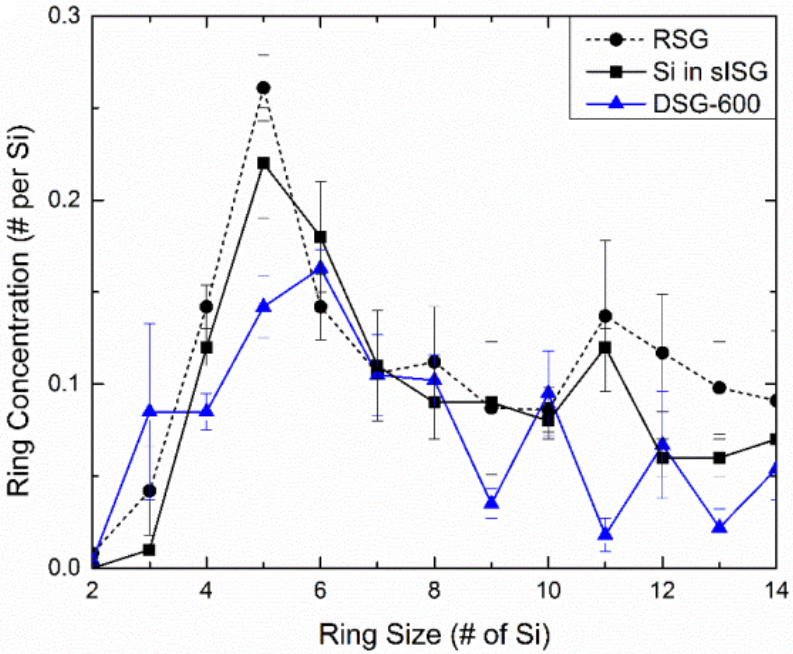
Silica gel intermediate range structure

- Q_n distribution: difference in Q_3 concentration is from the initial Na^+ concentration in the RSG structure
- Ring structure: small difference in the five-membered ring concentration
- DSG-40 (40% of silicon removed) matches best with Q_n distribution for the RSG structure





Q_n distribution of silica gel structures



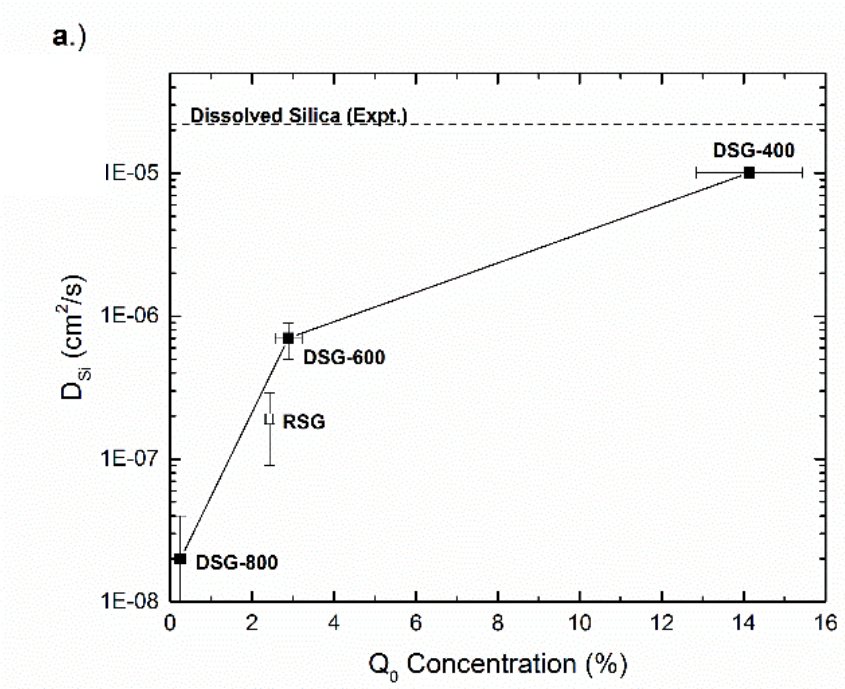
Ring size distribution of silica gel structures

Water and silicon diffusion

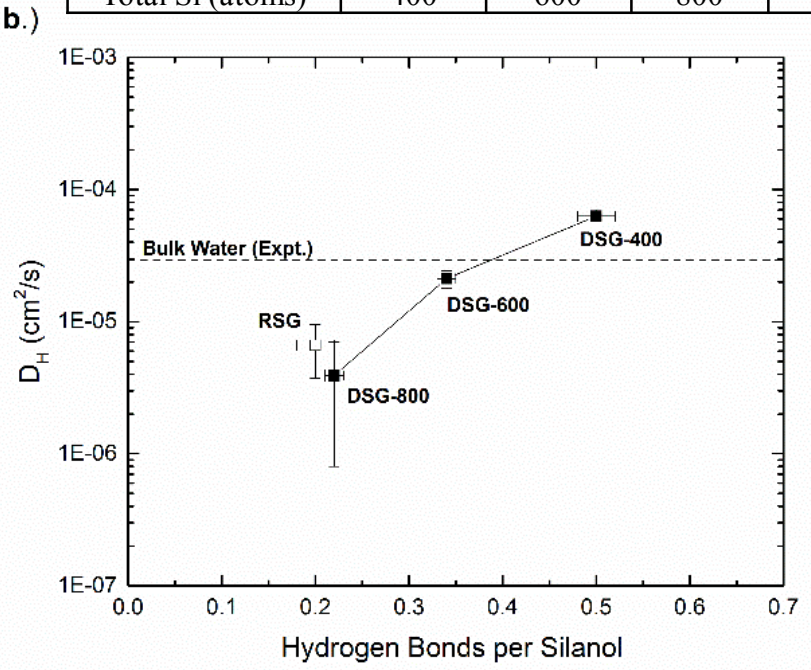
- Low silica concentration decreases D_{si}, possibly forming water-silica suspension
- RSG systems contain fewer H-bonds per Si-OH resulting lower D_H values

System size, composition and density for de-polymerized silica gel (DSG) and remnant silica gel (RSG) structures

Structure	DSG-400	DSG-600	DSG-800	RSG
Density (g/cm^3)	1.25 ±0.00	1.57 ±0.00	1.91 ±0.00	1.62 ±0.01
Remaining Si (%)	40.0	60.0	80.0	60.9
Total Si (atoms)	400	600	800	618



Silicon diffusion with Q_0 concentration

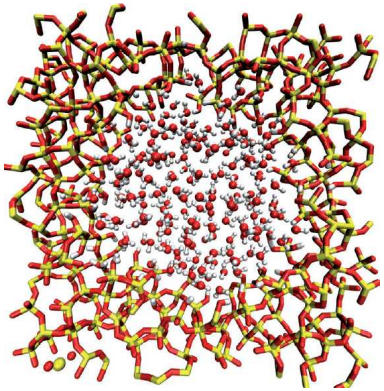


Water diffusion with hydrogen bond concentration

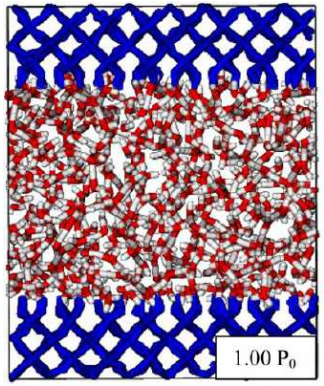
How would the gel impact silica dissolution in an interface model?

Water-silica surfaces

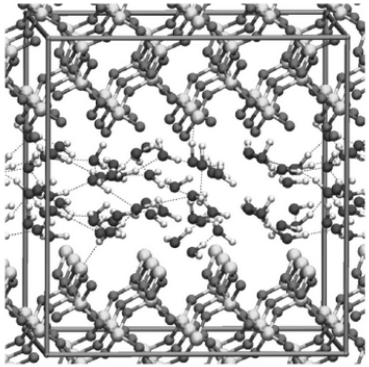
- Computational analysis has focused on water interaction with: flat silica surfaces, well ordered pore structures, and clusters
- Do not account for:
  - Nanoporous silica gel structure
  - Prescence of interfaces



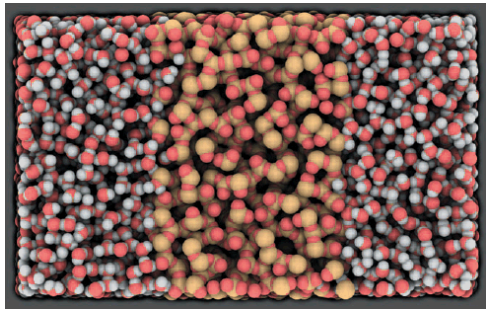
Allolio, Christoph, et al. ChemPhysChem (2014)



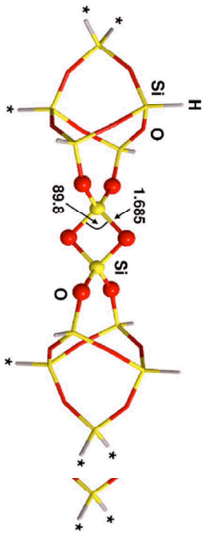
Bonnaud, P. A. et al. J. Phys.: Condens. Matter (2010)



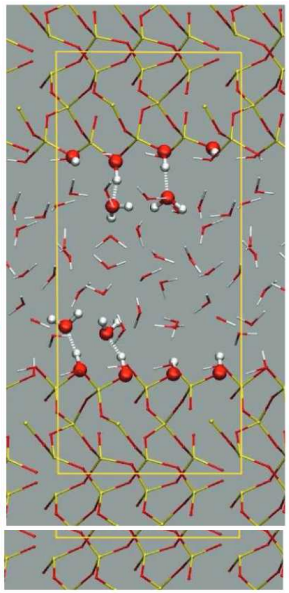
Adeagbo, et al. ChemPhysChem (2008)



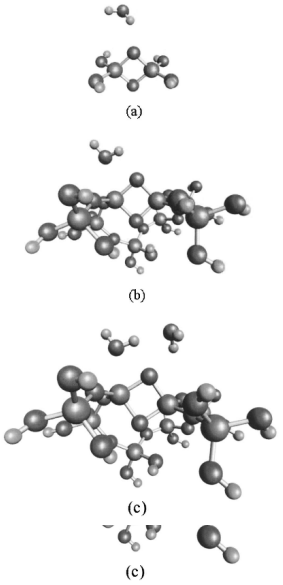
Fogarty, Joseph C., et al. J. Chem. Phys. (2010)



Rimola et al. J. Chem. Phys. (2008)



Sulpizi, et al. J. Chem. Theory Comput. (2012)

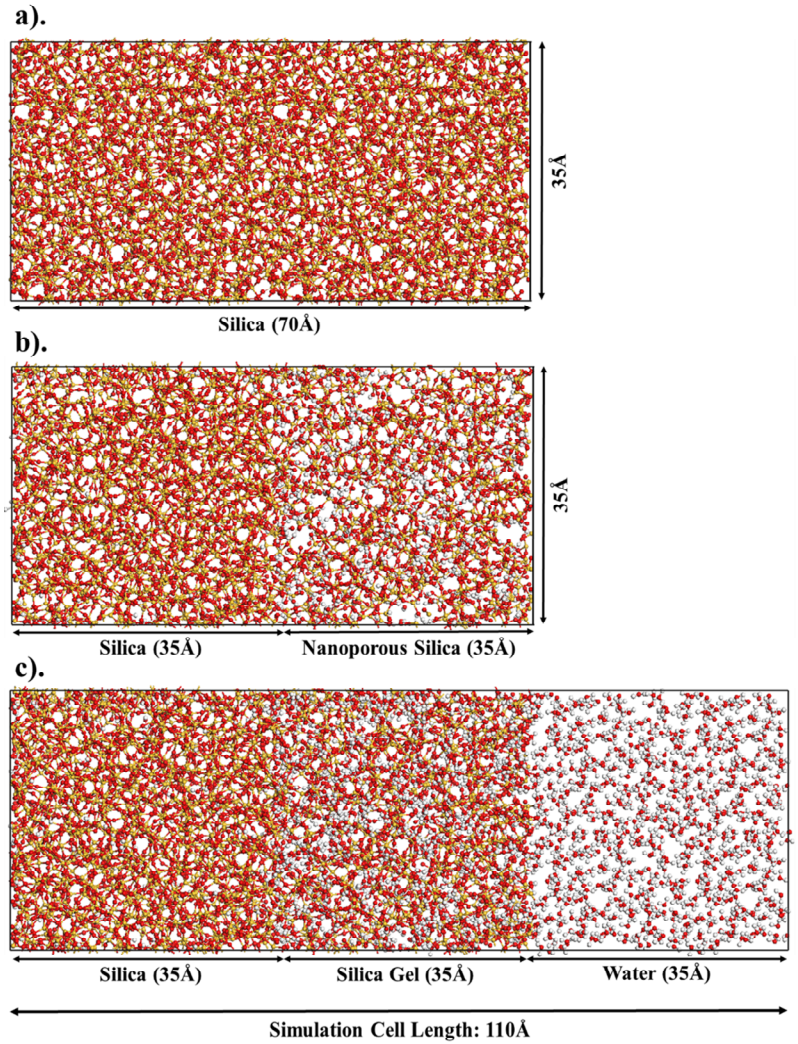


Du, M-H., et al. Eur. Phys. J. D (2003)

Creating realistic complex structure models, to investigate the mechanisms and process which govern silica dissolution

Development of silica-gel-water (SGW) model structure

- Begins with a dense silica structure
- ½ becomes the dense silica region and ½ is the silica gel
- 400 of the 1000 silica in the gel region are removed
- Non-bridging oxygen are hydrogen terminated
- Structure is hydrated and bulk water region is added
- Forms a three component model consisting of silica-gel-water and silica-gel and gel-water interfaces



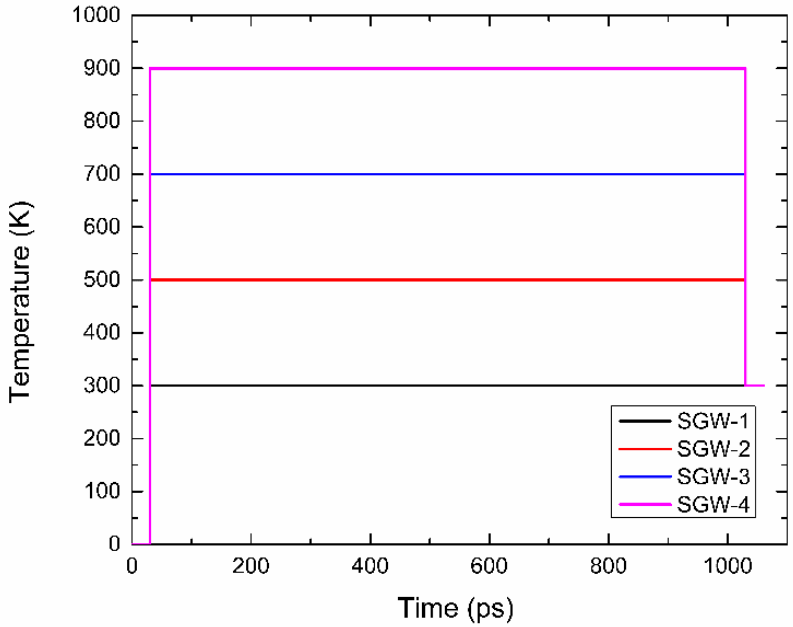
Schematic of the creation of a silica-gel-water (SGW) dissolution model

Simulation details

- High temperature simulation for structural evolution
- 1 ns of simulation with a 0.25 fs time step at 300K, 500K, 700K, or 900K
- After high temperature simulation temperature was decreased to 300K for 30ps
- Low temperature simulations:
  - Deconvolution of high temperature structures
  - Standardize analysis of the structure

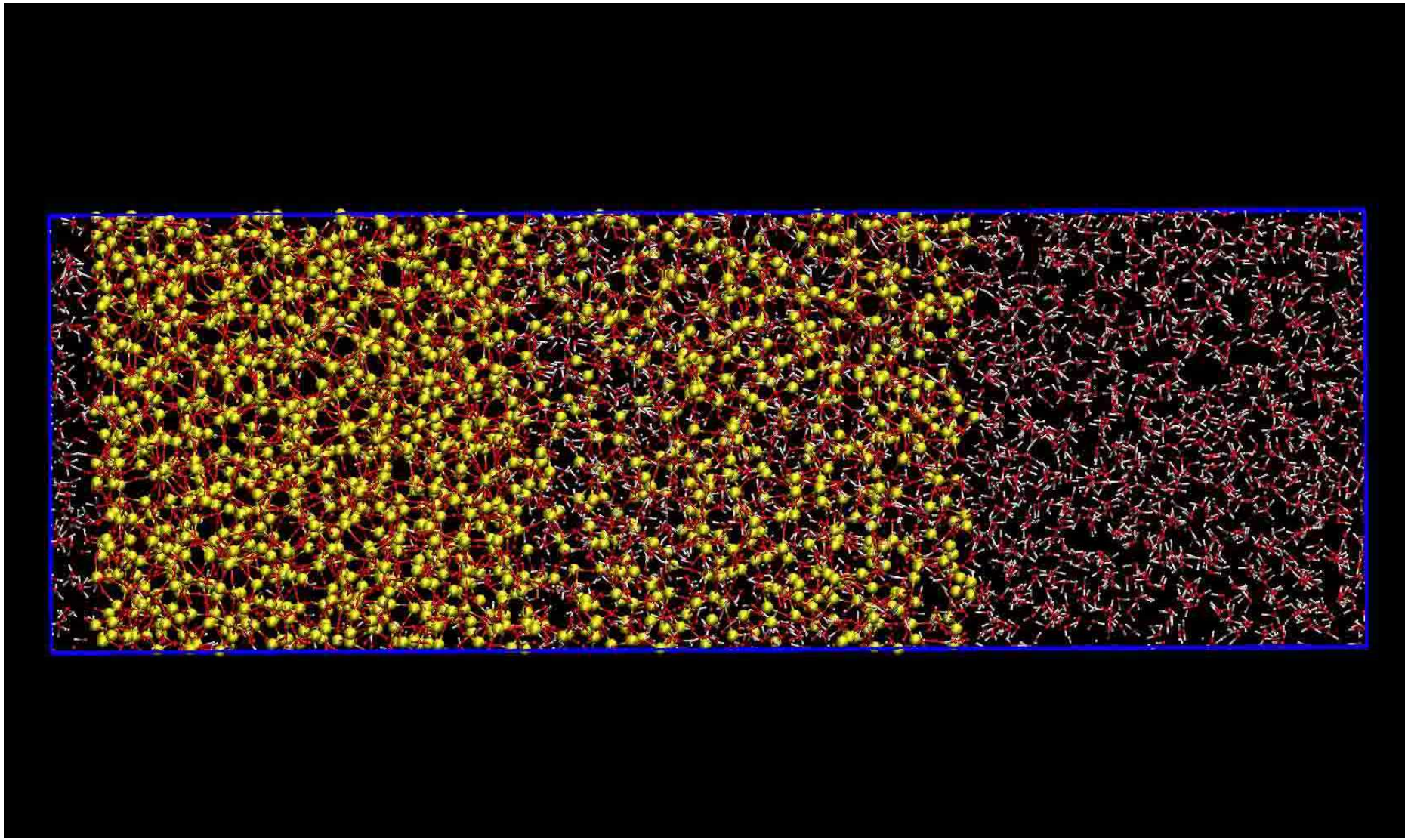
Model number and temperature for 1 ns simulation

Model	Initial	SGW-1	SGW-2	SGW-3	SGW-4
Temperature (K)	N/A	300K	500K	700K	900K



Changing temperature with time for the four different SGW model structures.

SGW model structure: simulated at 900K



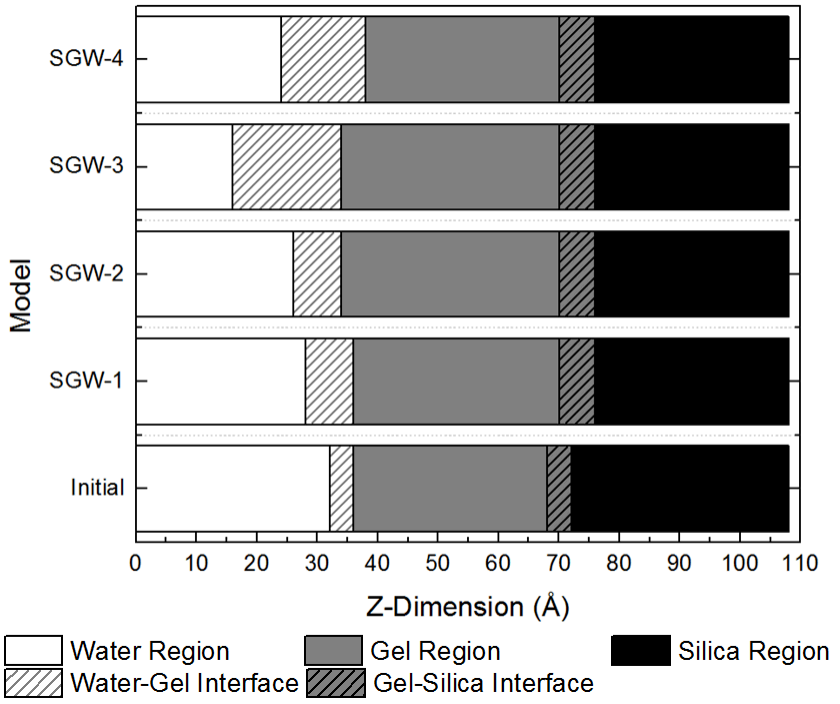
1 ns classical MD simulation of the SGW model at 900K

Growth of silica-gel-water regions

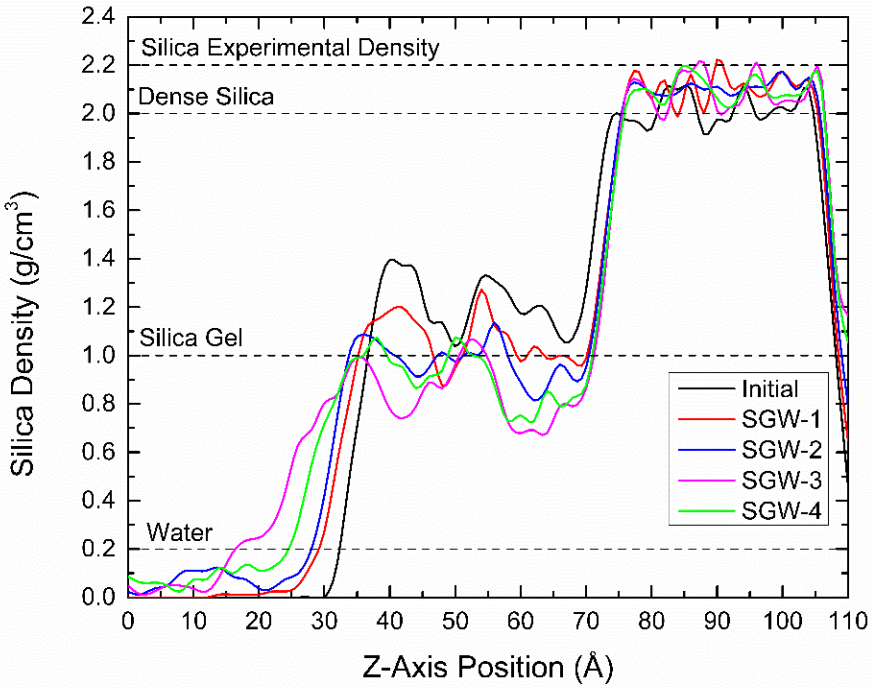
- Silica gel grows into the water region
- Gel-water interfaces thicken
- Silica and silica-gel regions remain stable

Silica density cut-off values for different regions

Region	Silica Cut-off (g/cm^3)
Silica	2.0
Gel	0.9
Water	0.2



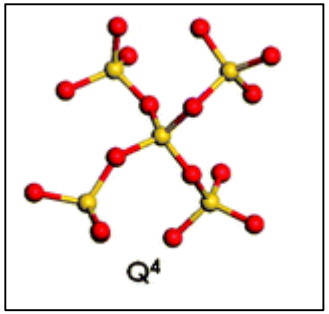
Schematic outline of width of the silica, gel, and water regions



Z-density profile of silica density in SGW models

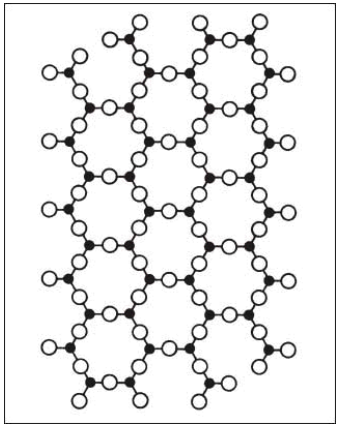
Intermediate range order of silica

- Primarily composed of Q_4 species, Q_3, Q_2, and Q_1 concentration is due to the interfaces
- Very little change as the structure evolves

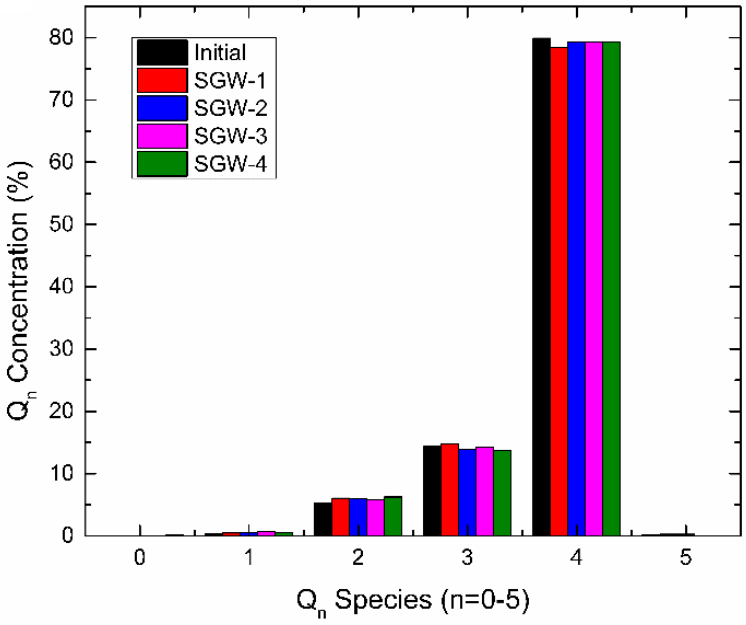


Chaprentier et al. RSC Adv. (2013)

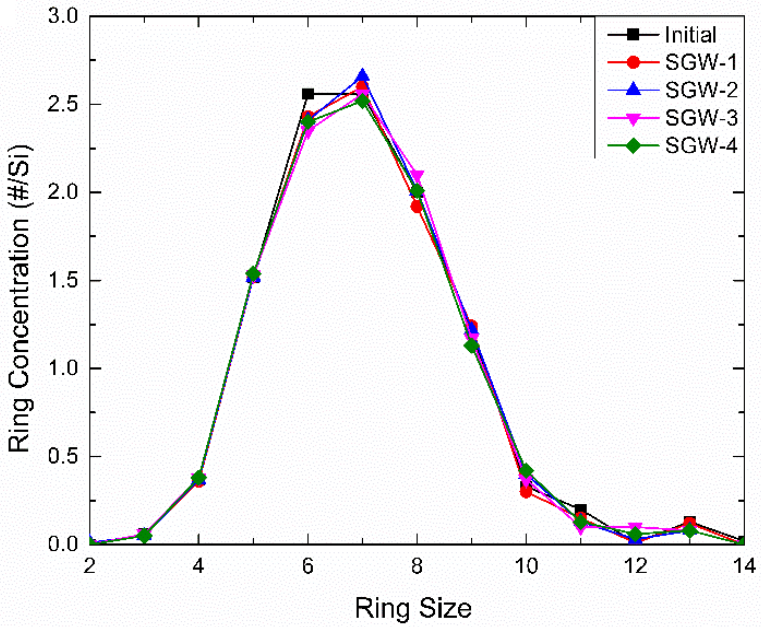
- Composed six-membered and seven-membered rings
- Expected for bulk dense silica



Kinegery et al. Glass-Ceramic Materials (1976)



Q_n distribution of the silica region of the SGW model

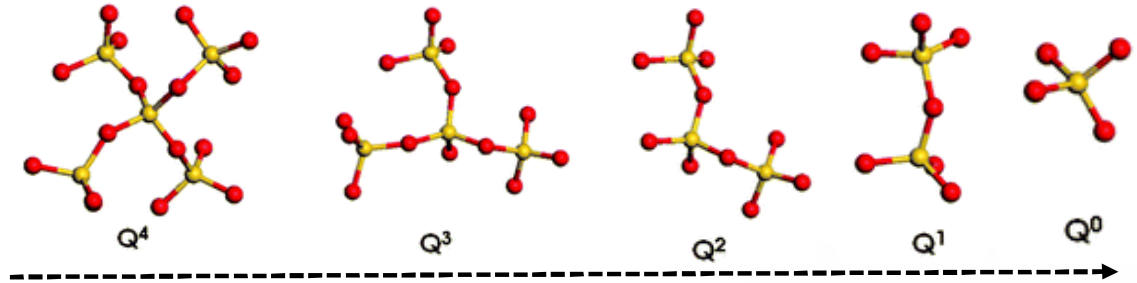


Ring size distribution of the silica region of the SGW model

Q_n distribution of the silica gel

- Stability of Si-O bonds in SiO_4 tetrahedron is affected by the number of bridging oxygen
- Dissolution occurs with the conversion of $Q_4 \rightarrow Q_3 \rightarrow Q_2 \rightarrow Q_1 \rightarrow Q_0$ species in a step-wise fashion

Kagan and Garofalini. Phys. Chem. Chem. Phys. (2014)

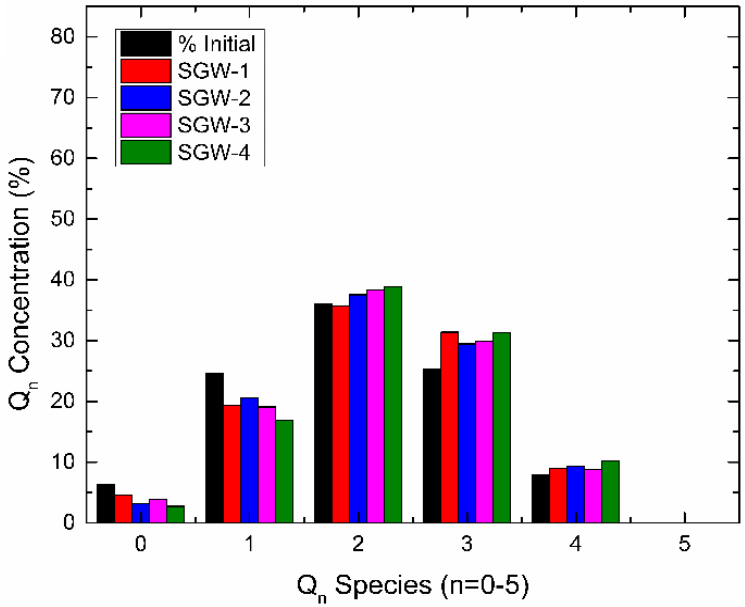


Chaprentier et al. RSC Adv. (2013)

- Highest energy barriers have been reported for the $Q_3 \rightarrow Q_2$ and $Q_2 \rightarrow Q_1$ transitions

Kagan and Garofalini. Phys. Chem. Chem. Phys. (2014)
Criscenti et al. J. of Phys. Chem. C (2006)

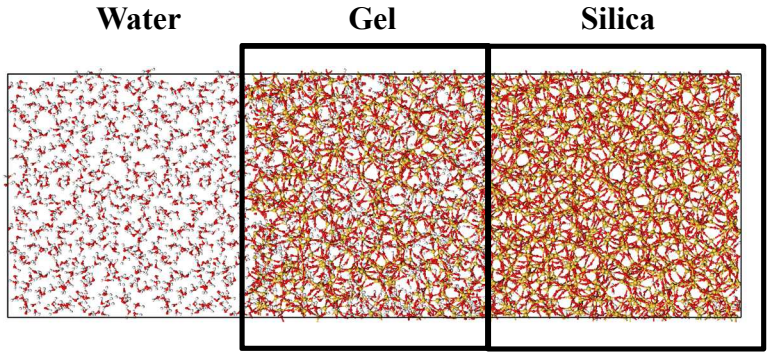
- Silica gel Q_n distribution:
  - Increases in Q_2, Q_3, and Q_4, concentrations
  - Decreases in Q_0 and Q_1 species
- Lower Q_n species are dissolved into the bulk water, increasing in higher Q_n species in the gel

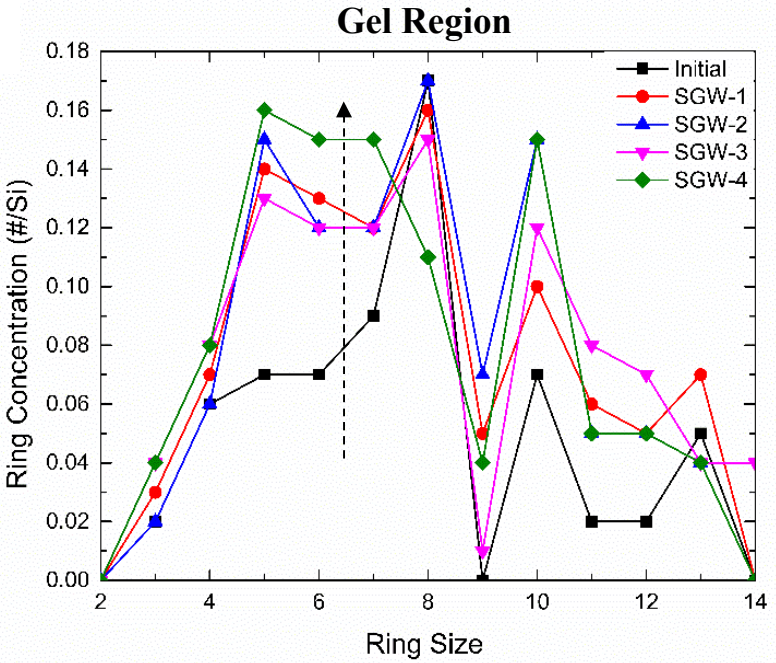


Q_n distribution of the gel region of the SGW models.

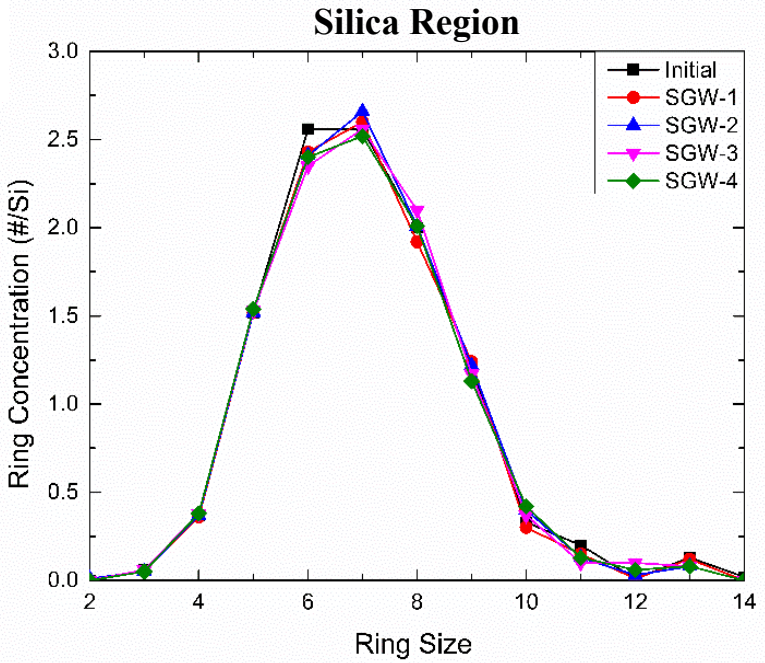
Ring size distribution of silica gel

- Initial gel structure has a fragmented ring structure
- After evolution the five-membered, six-membered, and seven-membered rings concentrations increase
- Trends toward the distribution seen in bulk silica
- Over time, would a silica backbone structure similar to dense silica form?





Ring size distribution of the gel region of the SGW model



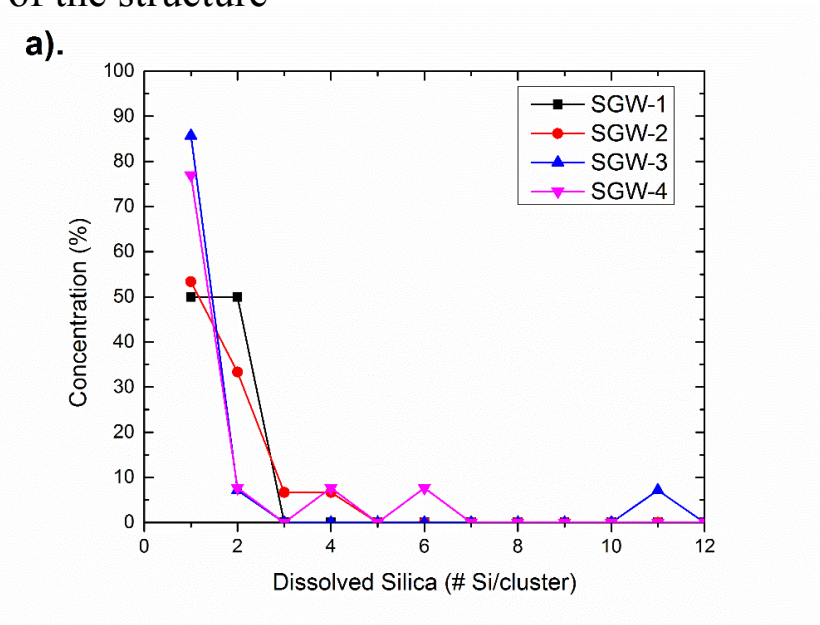
Ring size distribution of the silica region of the SGW model

Concentration of dissolved silica

- Primarily silica monomers occur in water (Raman spectroscopy) *Gunnarsson et al. Geochim. Cosmochim. Acta. (2000)*
- Water region: 50%+ silica monomers
- Silica concentration is higher than in experiments (1.5 g/L for pure amorphous silica at 300K)
  Dolstsinis et al. J. of Theo. Comp. Chem. (2007)
- Monomeric silica consistently increases with evolution of the structure

Dissolved silica in the water region

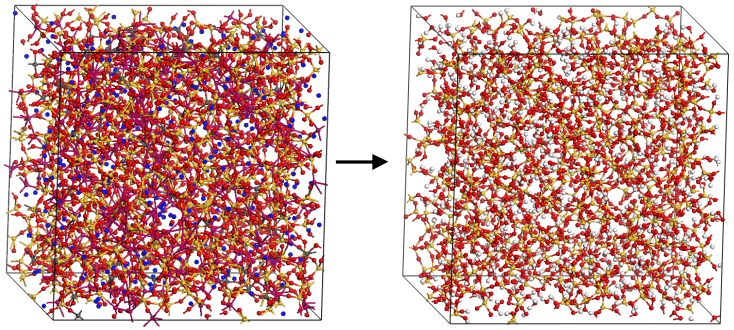
	All Si (g/L)	Monomers (g/L)
Initial	0.00±0.00	0.00±0.00
SGW-1	4.94±1.73	3.47±0.87
SGW-2	31.89±4.65	8.77±1.65
SGW-3	19.71±3.57	11.00±1.87
SGW-4	40.49±4.44	11.90±1.93



(a) Dissolved silica concentration in the SGW models as either monomers or larger silica polymer chains, and (b) distribution of dissolved silica molecules by the number of silicon atoms in a cluster.

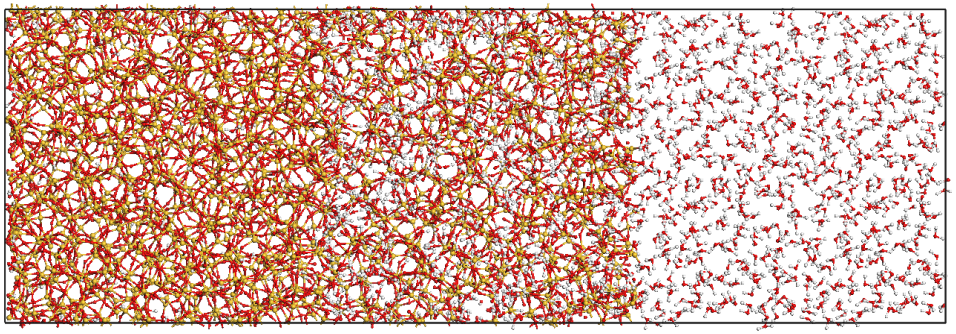
Conclusions

- Developed silica gel structure models to mimic the dissolution process
- Differences in intermediate range structure occur with silica concentration and impact water diffusion



Remnant and de-polymerized silica gel structure models

- Created a silica-gel-water interfacial model
- Tendency of the silica gel to form dense silica intermediate range structure
- Dissolved silica increases with gel dissolution and is composed of silica monomers



Silica-gel-water structure model

Related work

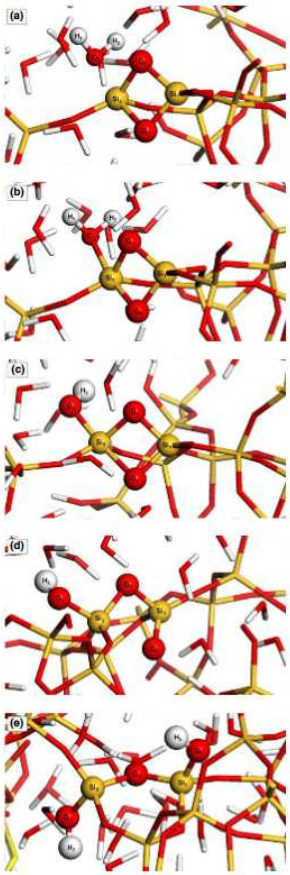


Fig. 2. Snapshots of the five representing steps of the mechanism of two-membered ring breakage in a 60% nanoporous silica system in the presence of water.

Rimsza, J. M., and J. Du. *J. Amer. Ceram. Soc.* 98.12 (2015): 3748-3757.

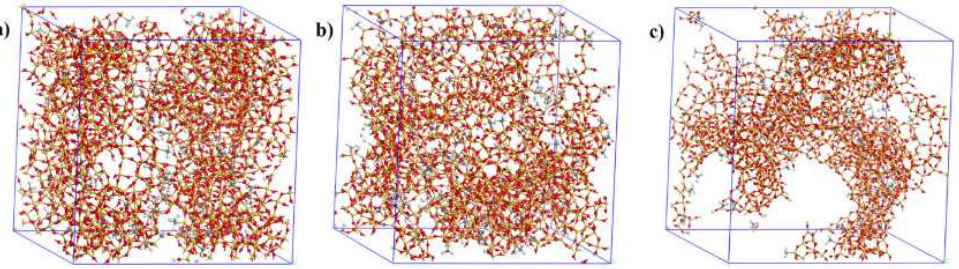
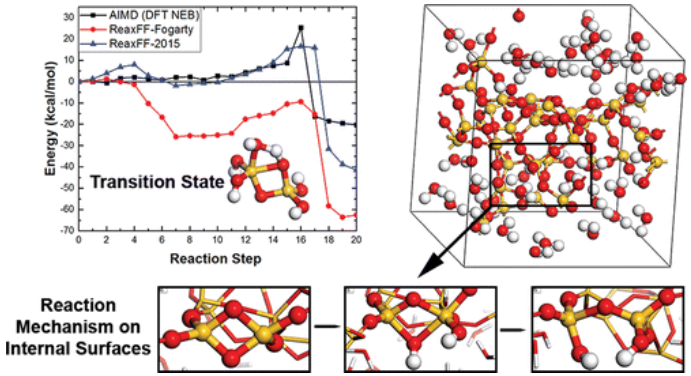
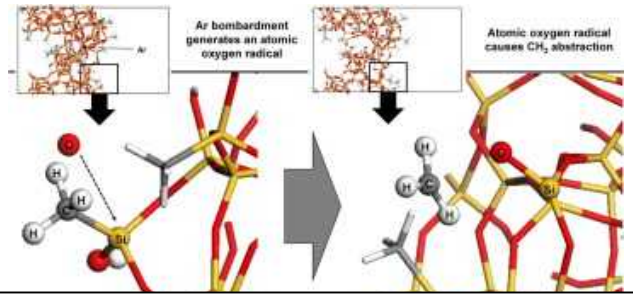


Fig. 3. Simulated nanoporous OSG structures using ReaxFF for the lattice expansion (LE) method at a) 32.94%, b) 46.29%, and c) 73.08% porosity. The red is the oxygen atoms and the yellow is silicon.

Rimsza, J. M., L. Deng, and J. Du. *J. Non-Crys. Solids* 431 (2016): 103-111.



Rimsza, J. M., et al. *J. Phys. Chem. C* 120.43 (2016): 24803-24816.



Rimsza, J. M., and J. Du. *Comput. Mater. Sci.* 110 (2015): 287-294.

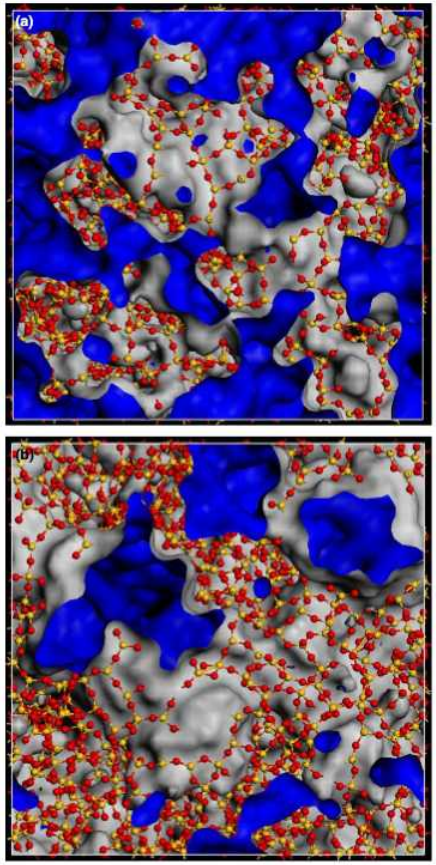


Fig. 2. Snapshot of the cross-section views of porous silica structures developed with the (a) volume scaling and (b) charge scaling simulation methods with around 42% porosity. Yellow atoms are silicon, red atoms are oxygen, and the Connolly surface (as described in section II) is outlined in blue (internal surface) and gray (external surface). The simulation cell size of (a) is 42.79 A, × 42.79 A × 42.79 A and that for (b) is 42.88 A × 42.88 A × 42.88 A.

Rimsza, J. M., and J. Du. *J. Amer. Ceram. Soc.* 97.3 (2014): 772-781.

Fracture of Amorphous Silica

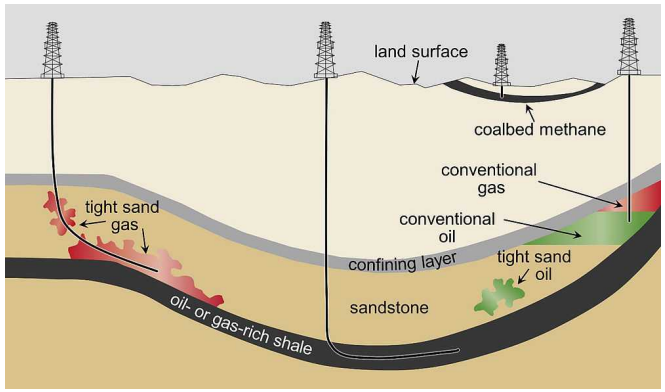
Jessica M. Rimsza (Sandia National Laboratories)

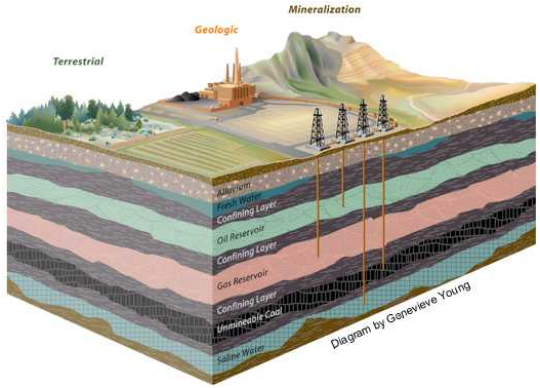
Co-Authors: Louise Criscenti (SNL), Reese Jones (SNL), Adri van Duin (Penn. St.), Seung Ho (Penn. St.)

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

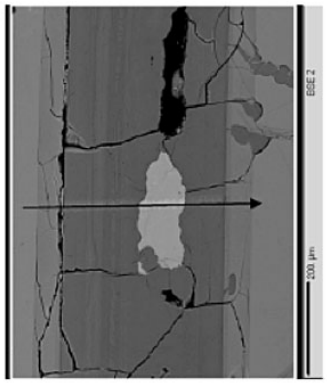
Technical motivation

Natural systems: hydrocracking, carbon sequestration





Engineered systems: nuclear glass waste forms, glass-to-metal hermetic seals



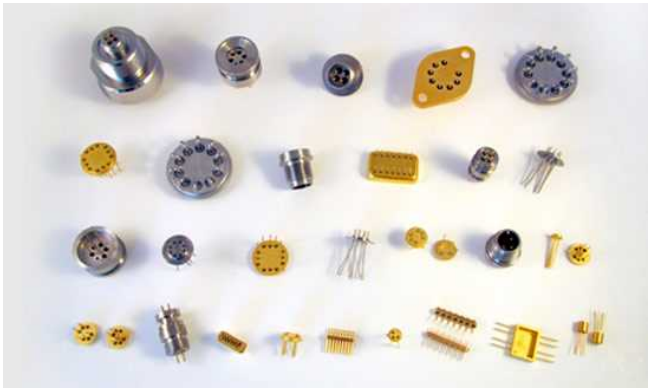


Image References: *http://wikivisually.com/wiki/Fracking, http://co2.egi.utah.edu/, https://eesa.lbl.gov/projects/waste-form-degradation-modeling/ , http://www.completehermetics.com/glass-to-metal-seals-and-feedthroughs/*

Introduction to fracture mechanics

- 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)

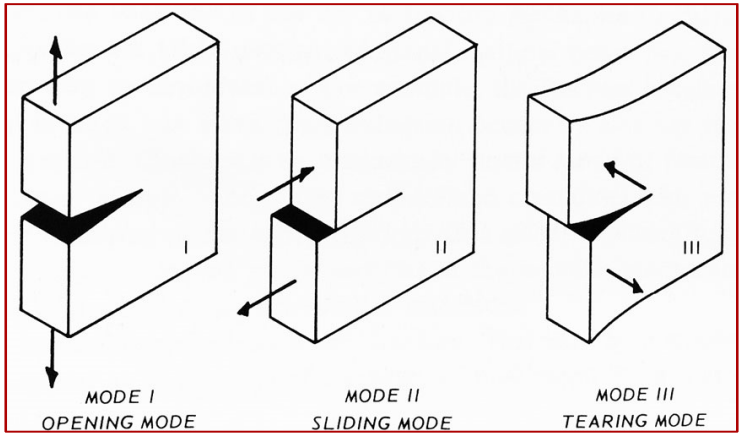
- Fracture toughness (K): the energy required to propagate a crack in a material

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

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

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

- J-integral: method of calculating G for monotonic loading through a path independent contour integral
  - For a linear elastic (non-yielding) material G=J
  - Bulk material property
  - In Mode I: $J_{IC} = G_{IC} = K_{IC}^2\left(\frac{1-\nu^2}{E}\right)$
    - E: elastic modulus
    - ν: poission's ratio
- Modes of loading
  - Mode 1: Opening
  - Mode 2: Sliding
  - More 3: Tearing



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

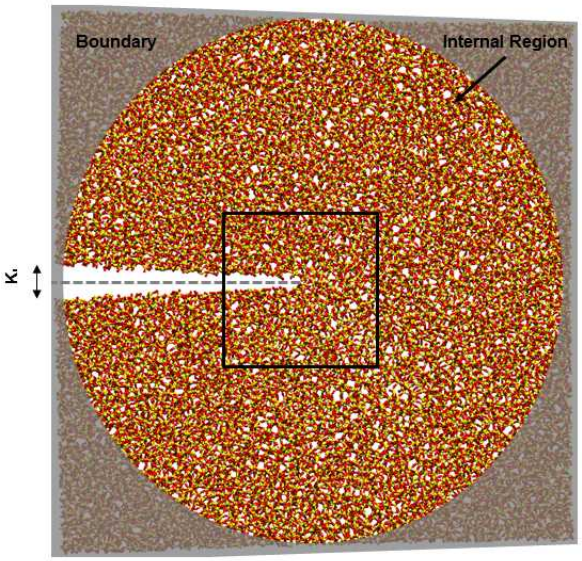
Zhu, X, and J.A. Joyce. Eng. Fract. Mech. (2012)

Computational methods

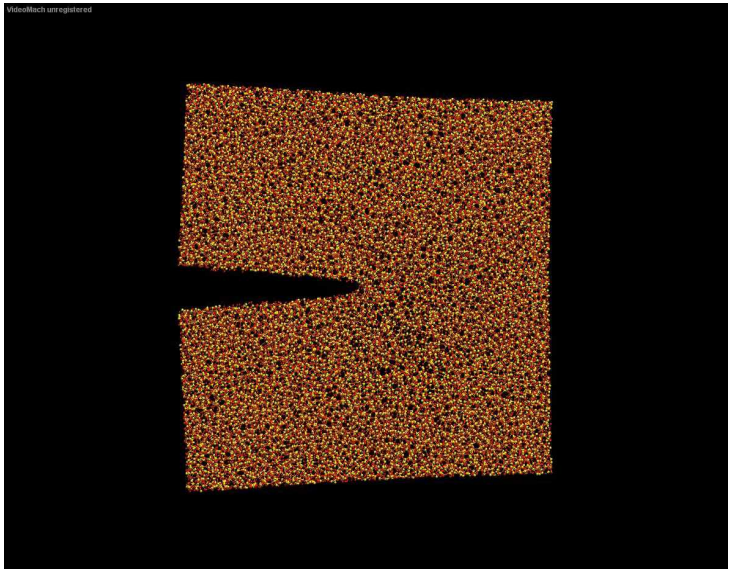
- J-integral and the fracture toughness calculated from stress, displacement and energy densities of atomistic system coarse grained onto a grid
  Jones, Reese E., et al. *J. Phys.: Condens. Matter* (2010)
- Eshelby stress (S) is calculated and the J-integral is evaluated around a loop around the crack tip
- Atoms-to-Continuum (ATC) package calculates the J-integral and the fracture toughness from atomic stresses and is available as a USER-ATC LAMMPS Package

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

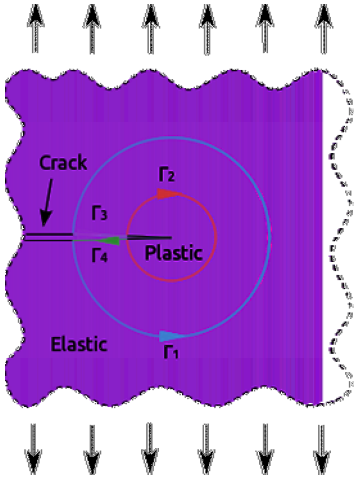
- Slit crack created forming a high stress condition
- Far-field loading through fixed boundary atoms with mode I stress
- Stress is introduced iteratively by increasing the crack width



Schematic of silica slit crack, crack width, as well as boundary and internal regions. Atoms: oxygen (red), silicon (yellow)



Opening of silica slit crack
Atoms: oxygen (red), silicon (yellow)



Bhanerje, "J-integral contours for an elastic material" 9/4/2013

Schematic of J-integral demonstrating the inclusion of the plastic region inside an elastically responding matrix

Crack tip blunting

- Crack tip blunting indicates an even stress distribution and local inelastic behavior
- Strength of a material is proportional to the radius of curvature of the crack tip (ρ):

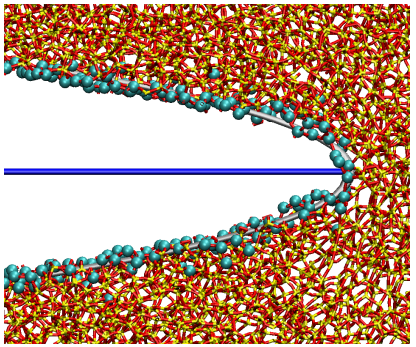
$$\sigma_{max} \propto \sqrt{\frac{1}{\rho}}$$

C.E. Inglis, Spie Milestone series MS (1997)

- To calculate ρ the internal atoms of the crack tip are fit with a parabolic function, from which ρ is calculated:

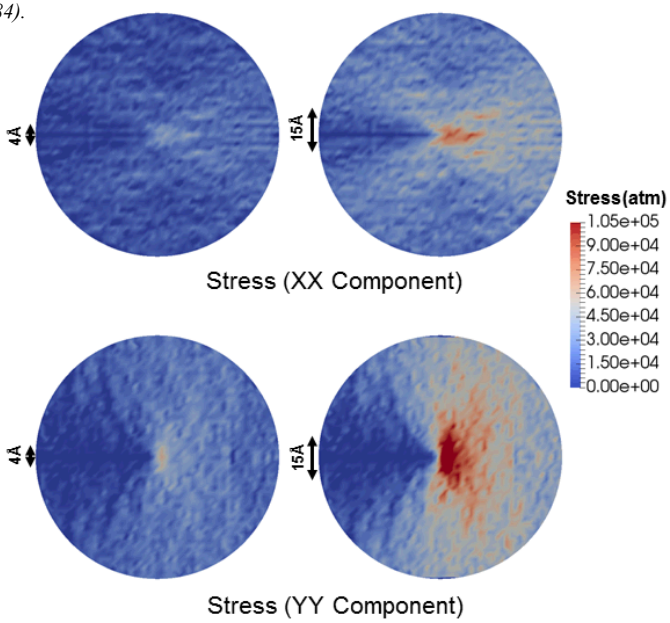
A. Howard, Calculus: With analytic geometry, John Wiley 1988.

$$\rho = \frac{(1 + f'(x)^2)^{\frac{3}{2}}}{f''(x)}$$

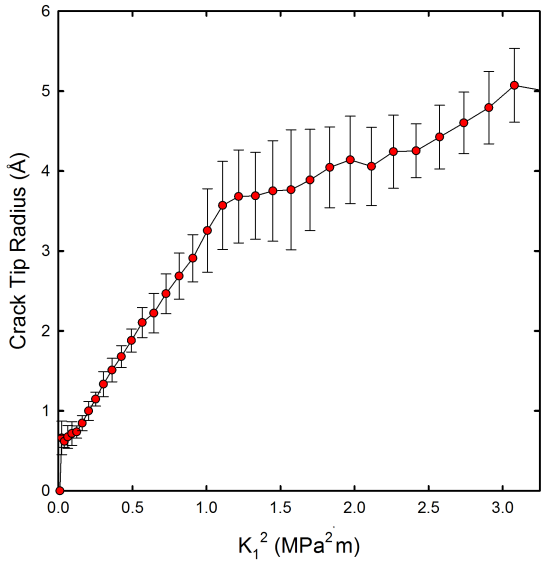


Silica structure (red and yellow) atoms in quadratic fit (turquoise), parabola estimating the shape of the crack tip (silver), and horizontal axis (blue)

- Radius of curvature: 0.1Å-5Å, experimental value: 15Å *Bando et al. J. Amer. Cera. Soc. 67.3 (1984).*
- Increasing stress around the crack tip prior to fracture
- Identifies size of the inelastic zone and development of a high stress conditions ahead of the crack tip



Stress fields calculated from individual atomic stresses. Averaged over twelve different trajectories.

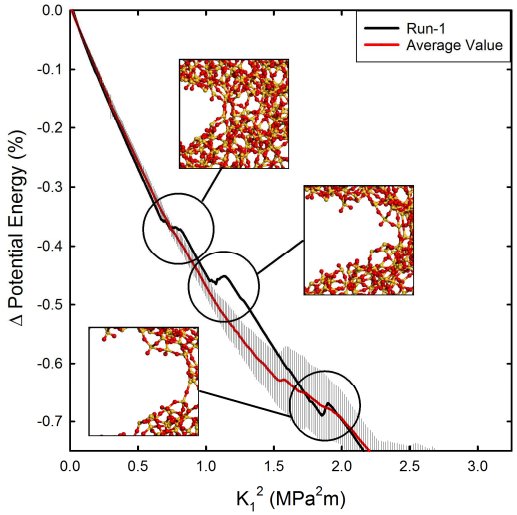


Radius of curvature and crack length during brittle fracture in silica

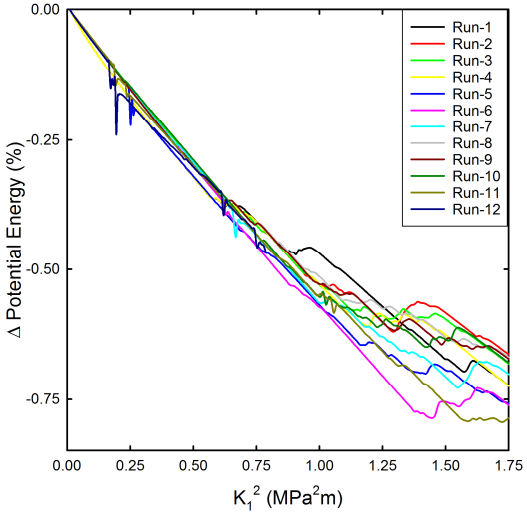
Fracture and energy dissipation

- Fracture propagates in distinct steps
- Perfectly brittle fracture will have no dissipation energy, with all energy used to propagate the fracture
- Dissipation energy calculated from the total energy of the system and added surface energy

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



Potential energy change with loading for a single simulation (Run-1) and averaged



Potential energy change for individual simulations with loading of 0-1.75 K_I^2 (MPa^2m)

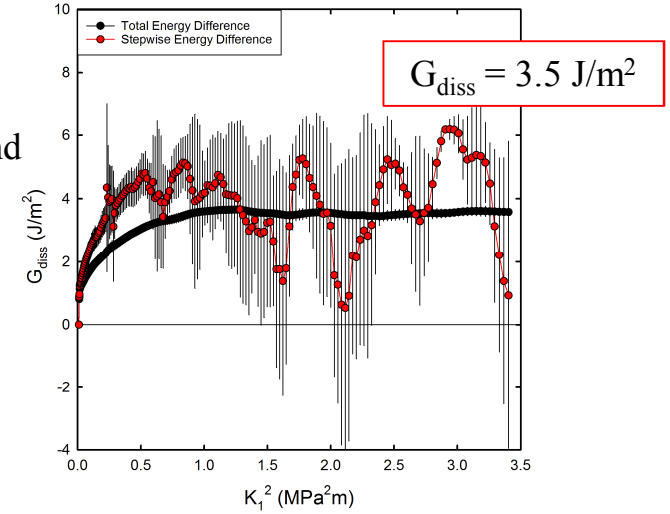
- Local inelastic behavior is introduced into the matrix during loading and not completely dissipated once fracture occurs

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

- Surface energies (γ_s): 2-1.2 J/m^2 varying with surface structure and relaxation

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

Estimated G values are ~5.9-7.5 J/m^2



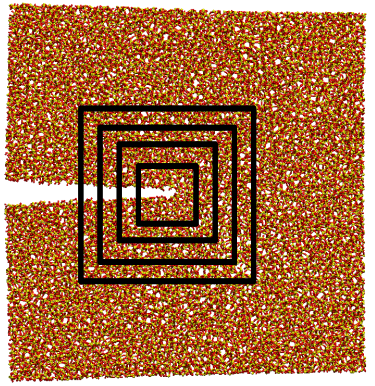
Energy dissipation (G_{diss}) during loading and subsequent crack propagation in amorphous silica

J-integral calculation

- Calculated via the AtC method through coarse graining energy, displacement, and stress
  Jones, Reese E., et al. *J. Phys.: Condens. Matter* (2010)
- J_{IC} value = J-integral when the crack begins propagating

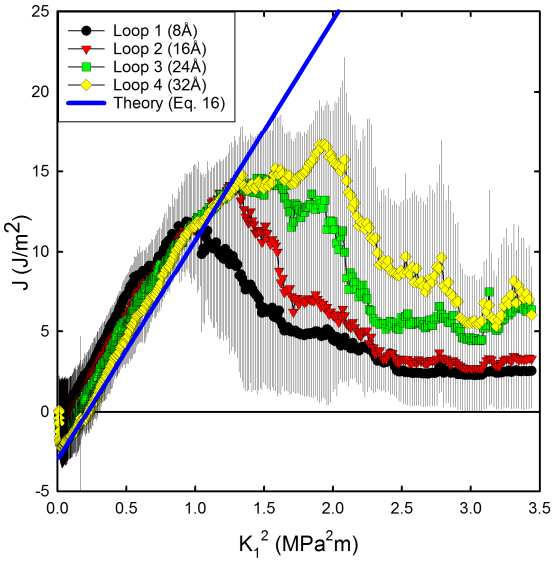
$$J_{IC} = \frac{K_{IC}^2}{E^*} \qquad E^* = \frac{2\mu}{1-\nu}$$

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

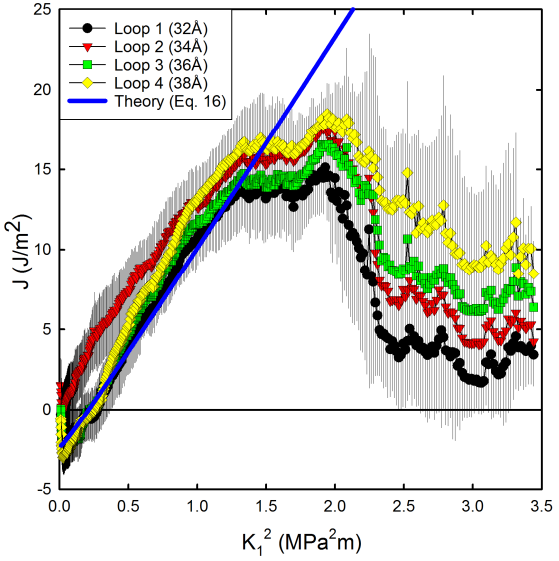


Schematic of increasing loop sizes for J-integral convergence test

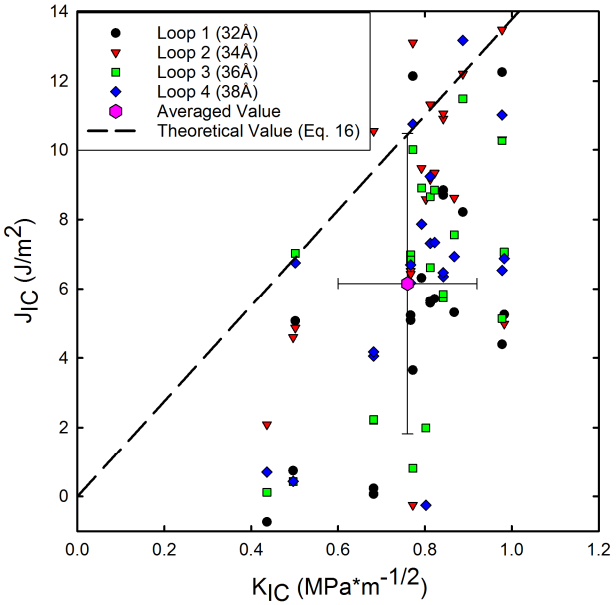
K_{IC}=0.76±0.16 MPa√m
J_{IC}=6.16±4.34 J/m^2



J-integral with increasing loop sizes



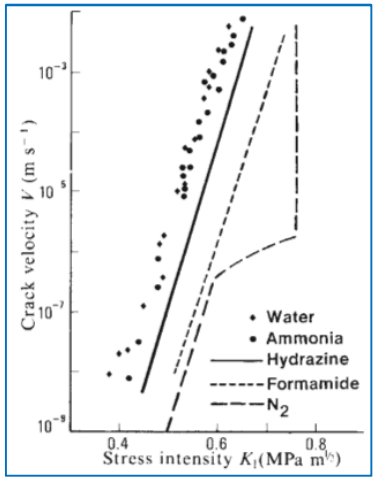
J-integrals with converged loop sizes



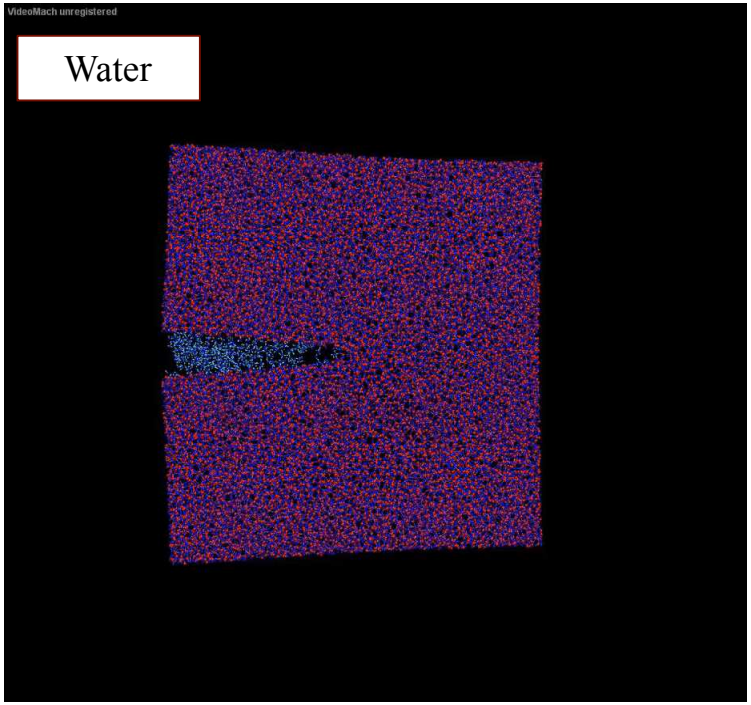
K_{IC} and J_{IC} values for the initiation of crack propagation in amorphous silica

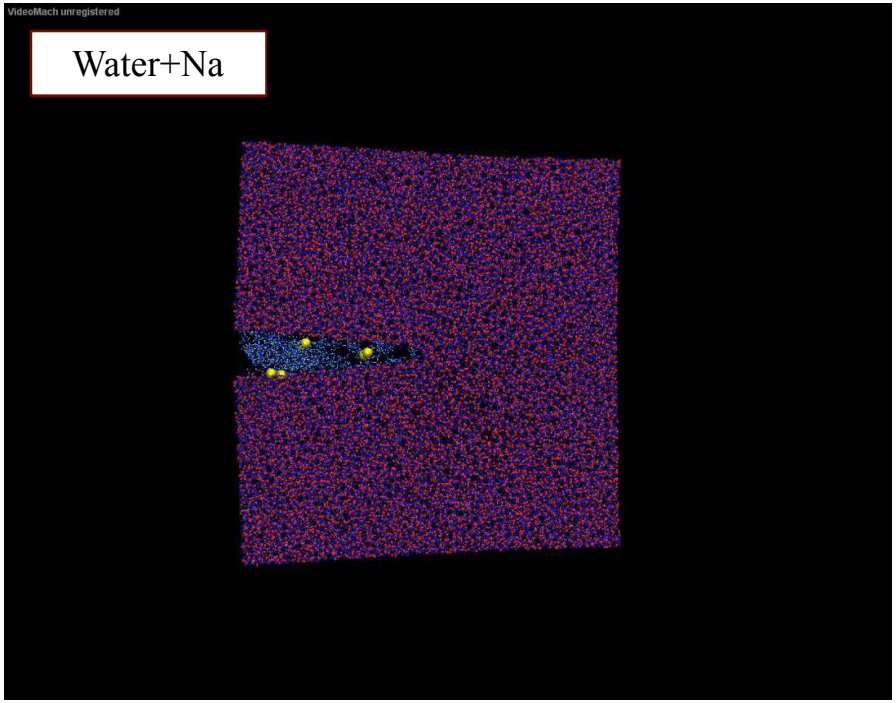
Fracture: aqueous conditions

- Coupled chemical-mechanical processes inside the crack chances crack velocity in silicates
- Method:
  - Introduce thin film of water which wets the crack surfaces
  - Water molecules added via GCMC to maintain surface wetting
  - Can vary the fluid composition to investigate the effect of dissolved salts on fracture (dissolved NaCl, pH)



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



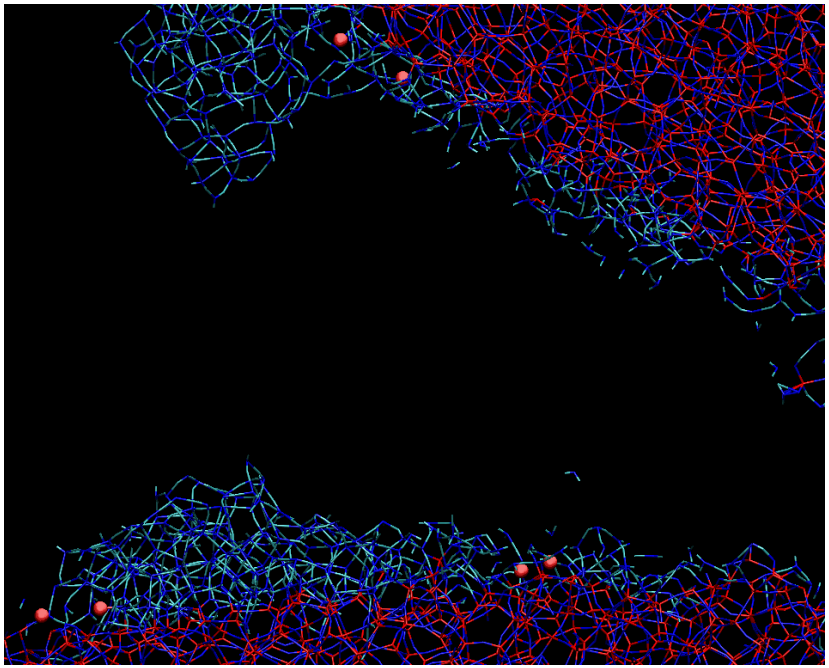


Opening of silica slit crack in a hydrated environment
Atoms: oxygen (red), silicon (purple), hydrogen (blue), sodium (yellow)

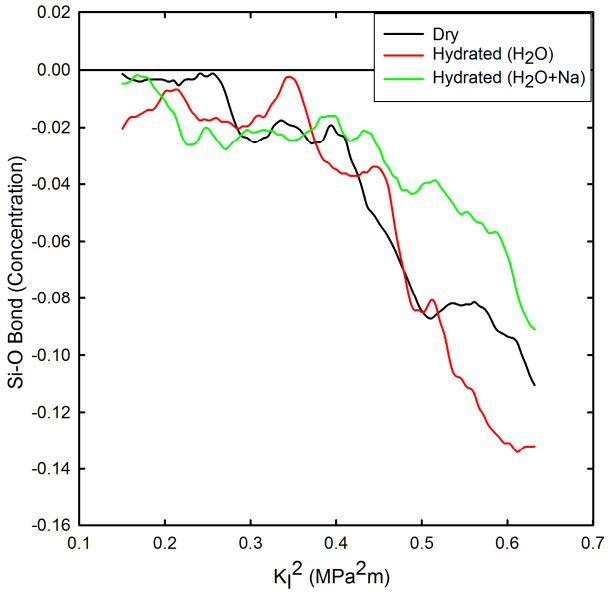
Bond concentration and Na environment

- Bond concentration:
  - Environment alters rate of bond breakage and formation
  - Sodium results in earlier fracture
  - Investigation of statistical variation of fracture with different environments is ongoing

- Na Environment:
  - Sodium does not migrate to the crack tip, but may be impacting the composition of the solution, altering fracture properties



Snapshot of water-Na+ solution inside the fracture



Si-O bond concentration of the system with loading for silica in three different environments (dry, hydrated, hydrated with sodium)

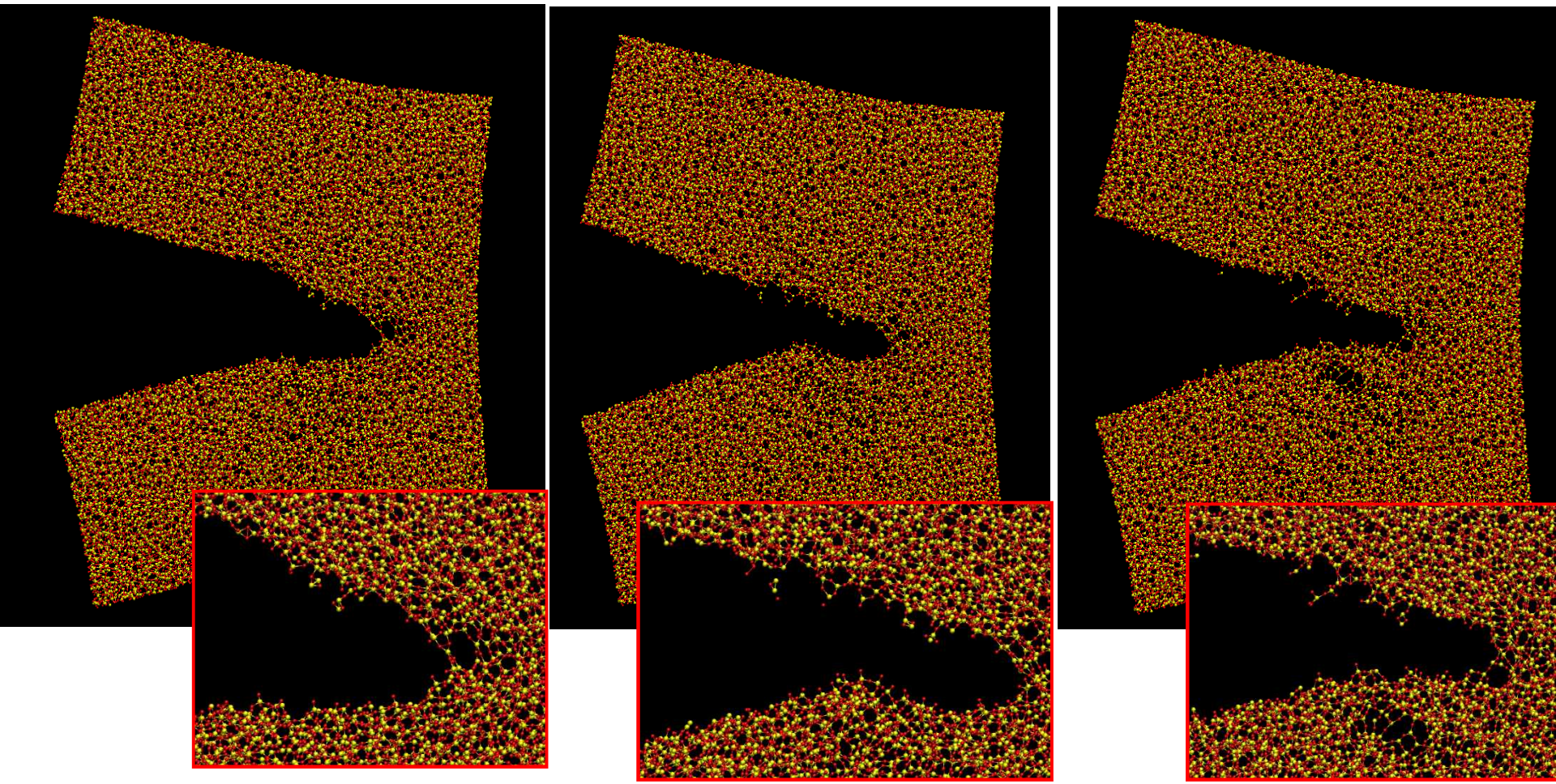
Na Environment

Coordination Number	5
Charge	0.83-0.92
Na-O distance	2.64±0.18 Å

Crack tip shape

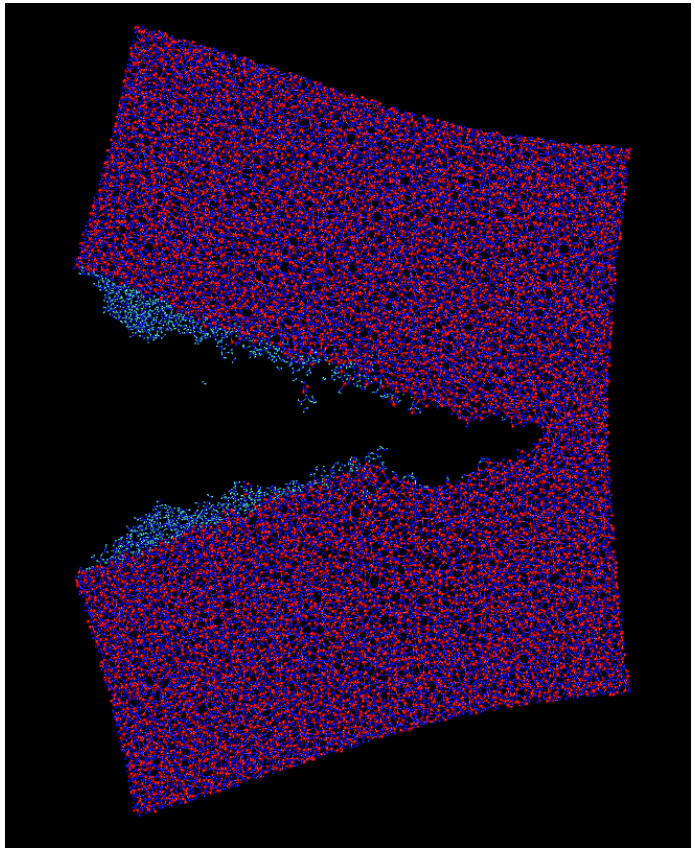
- Narrowing of crack tip with hydration and introduction of cations
- Possible capillary effects altering surface structure and stability during fracture

Dry | **Hydrated (H_2O)** | **Hydrated (H_2O+Na)**



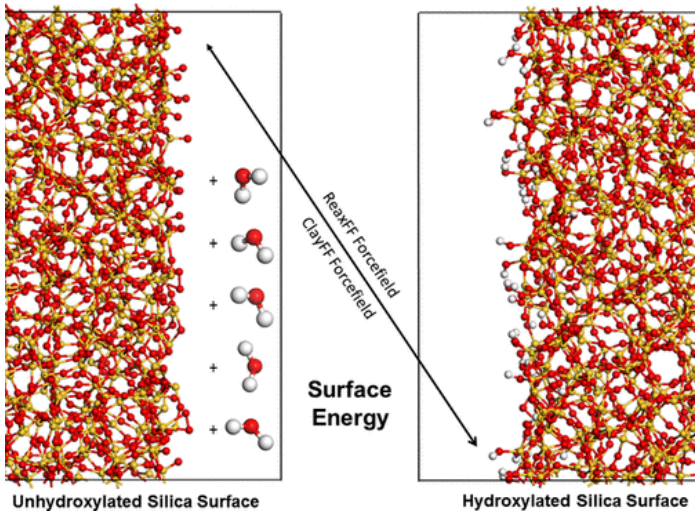
Conclusions

- Dry silica fracture:
  - Development of localized high stress inelastic region prior to fracture
  - Inelastic zone estimated with a radius between 3-3.2 nm
  - K_{IC} of ~0.78 MPa$\sqrt{m}$ consistent with experimental results
- Atoms-to-Continuum methods appropriate for evaluating macroscopic fracture properties from atomistic scale information
- Hydrated silica fracture:
  - Decreasing connectivity of the structure during crack propagation
  - Changing morphology of the crack tip

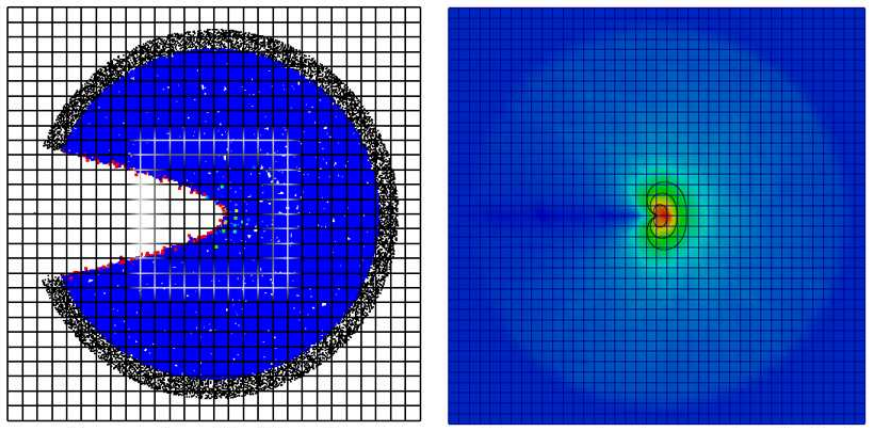


Snapshot of fracture silica in a hydrated environment

Ongoing work related to fracture



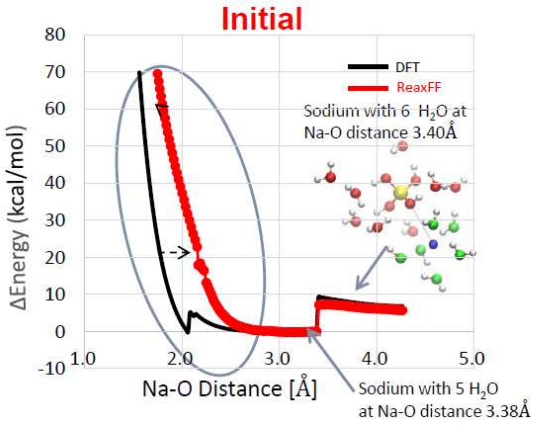
Rimsza, J. M., R. E. Jones, and L. J. Criscenti. "Surface structure and stability of partially hydroxylated silica surfaces." *Langmuir* 33.15 (2017): 3882-3891.

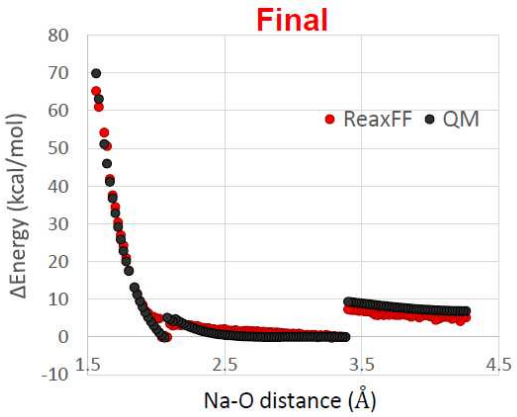


Atoms colored by PE, notice significant surface energy

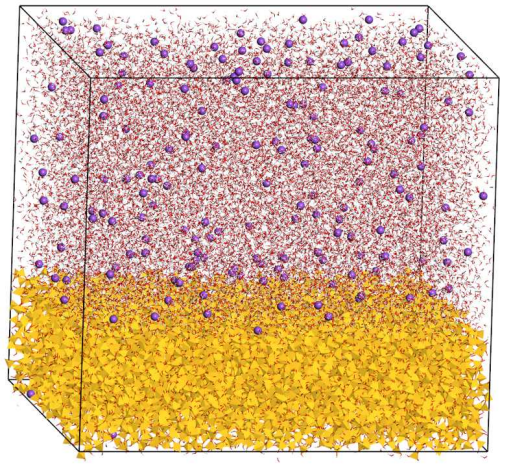
Coarse-grained energy density (color) corresponds well to theory (contours)

R. E. Jones, J.M. Rimsza, and L. J. Criscenti. "At atomic-scale evaluation of the fracture toughness of silica glass" *In preparation*





Seung Ho, J.M. Rimsza, L. J. Criscenti, ACT van Duin et al. "Silica dissolution in electrolyte solutions by ReaxFF classical MD simulations " *In preparation*



J.M. Rimsza, R.E. Jones, and L.J. Criscenti "Sodium Adsorption on Silica Surfaces " *In preparation*

Thank you for your attention!

Dissolution of Amorphous Silica

Jessica M. Rimsza (SNL) Jincheng Du (UNT), Jeffrey Kelber (UNT), Lu Deng (UNT), Haseeb Kazi, (UNT, Lam Research), Adri van Duin (Penn. St.), Jejoon Yun (Penn. St., U.C. Merced)

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Fracture of Amorphous Silica

Jessica M. Rimsza (SNL) Louise Criscenti (SNL), Reese Jones (SNL), Adri van Duin (Penn. St.), Seung Ho (Penn. St.)

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