SAND2022-6903C

Sandia National Laboratories

Slow Crack Growth in Sodium-Modified Silicate Glasses

Jessica Rimsza , Kevin Strong, Craig Nakakura, Jessica Durree, Kelly Stephens, and Scott Grutzik

Sandia National Laboratories, Albuquerque, NM

U.S. DEPARTMENT OF ENERGY | NNSA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

ADD

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Technical Motivation – Stress Intensity Threshold

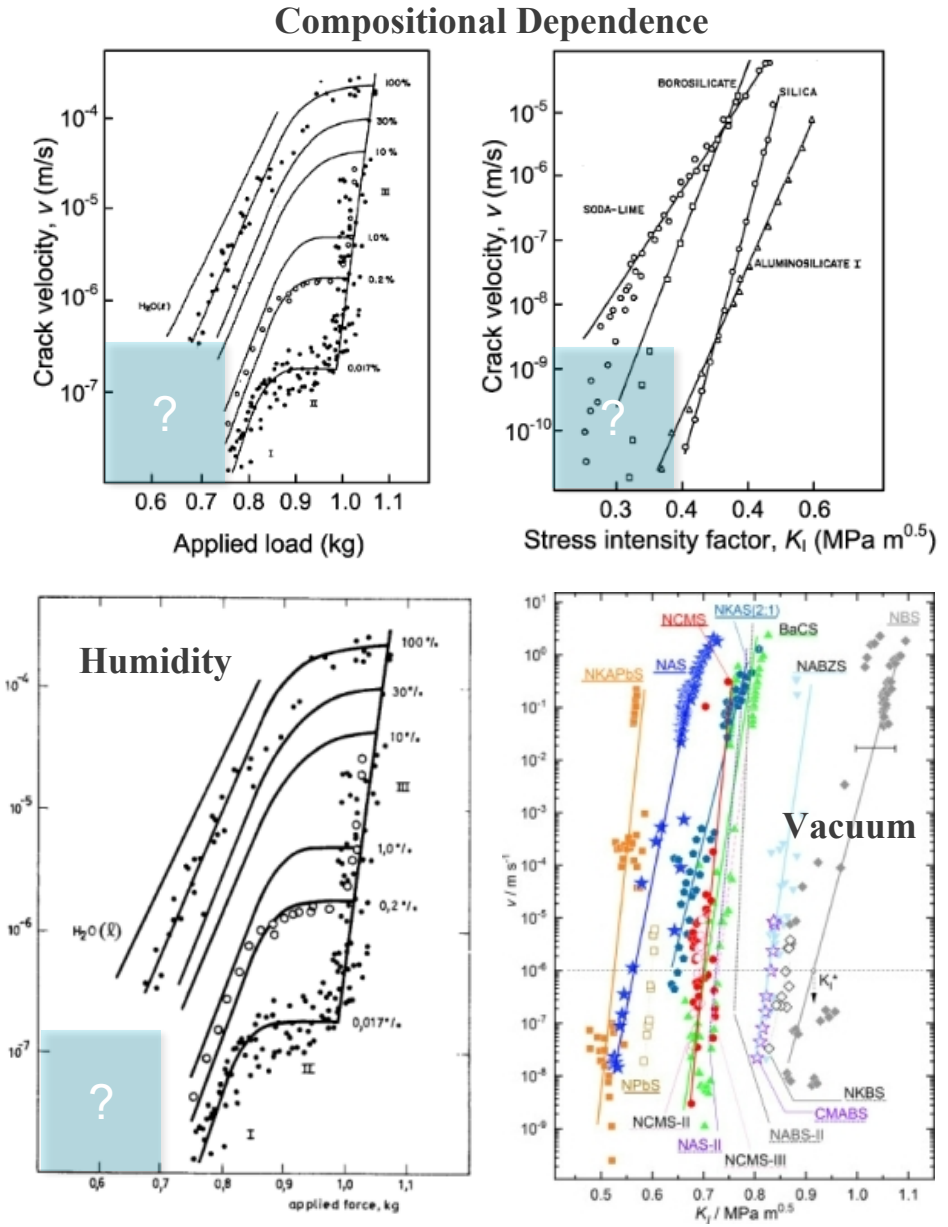
- Brittle fracture of silicates affect the stability and reliability of amorphous systems making prediction of the mechanical response difficult
- Even slow crack growth rates, 10^{-10} m/s and 10^{-11} m/s can cause significant crack propagations over years of service

Crack Velocity (m/s)	Fracture Length (m)	
	10 Years	30 Years
10^{-8}	31.5400	94.6100
10^{-10}	0.3154	0.9461
10^{-12}	0.0031	0.0094

10^{-13} m/s velocity is reported for silica fibers and soda-lime silicate glass from post-fracture analysis of surfaces

1. Crack velocity decreases with applied load, but data becomes more scarce at lower load rates
2. Crack growth increases with increasing humidity, but still exists in vacuum conditions

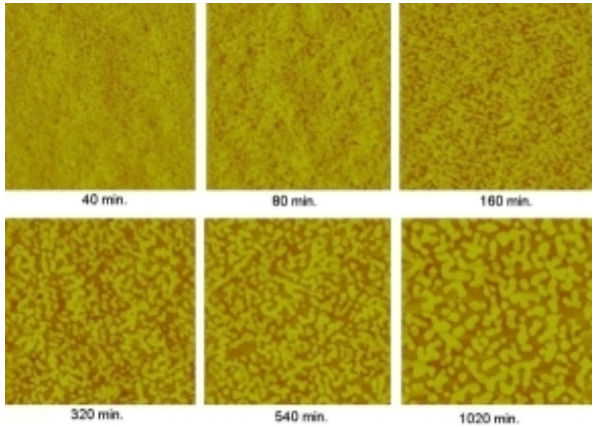
Do cracks continue to propagate? Or is there a stress-intensity threshold below which the crack no longer propagates?



References: Wiederhorn, S. M. *J. Amer. Ceram. Soc. (*1967), Wiederhorn and Bolz. *J. Amer. Ceram. Soc.* (1970), Muraoka and Abe *J. Am. Ceram. Soc. (1996),* Kocer and Collins J. Am. Ceram. Soc. (2001), Waurischk et al. *J. Non-Cryst. Solids* 572 (2021): 121094. Wiederhorn *Int. J. Frac. Mech.* 4.2 (1968): 171-177.

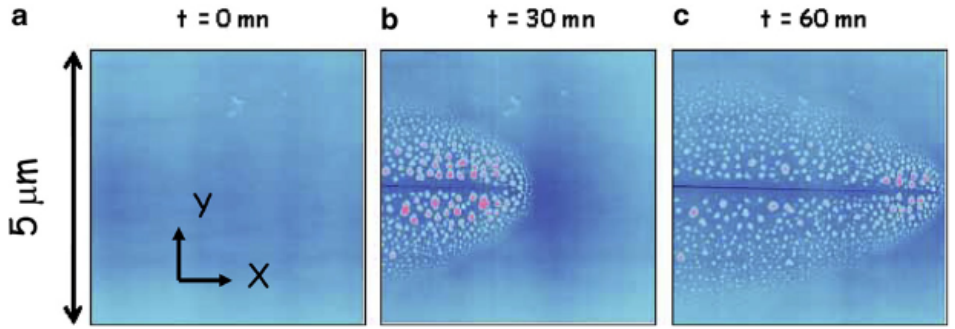
Monitoring Crack Growth

- Optically tracking crack growth is challenging at slow crack growth rates
- Need to have a stable crack with known loading conditions
- AFM provides resolution with sensitivity to surface features for monitoring crack growth
- Bi-beam with varying CTE



AFM images of 12.5%Na_2O · 87.5%SiO_2 glass at 650 °C

Wheaton and Clare. *J. Non-Crystl. Solids* 353.52-54 (2007): 4767-4778.

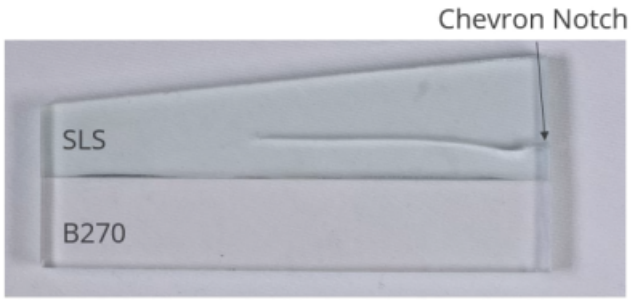


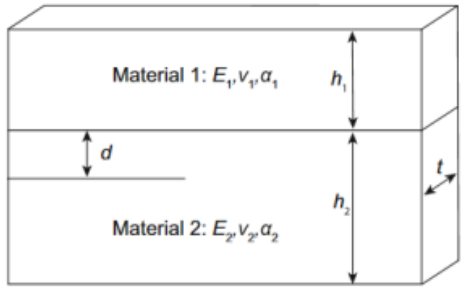
Sequence of successive AFM height images a soda–lime glass at RH = 45%. The vertical range is 10 nm.

Célarié et al. (2007). *J. Non-Cryst. Solids. 353*(1), 51-68.

Bi-beam Specimens

- Bi-beam samples based on mis-match of CTE
  - Pilkington soda-lime silicate (CTE = 9.1x10^{-6}/°C)
  - Schott B270 (CTE = 10.12x10^{-6}/°C)
- Diffusion bonded edges with mirror finish

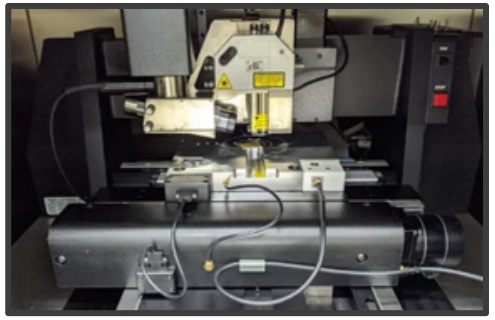




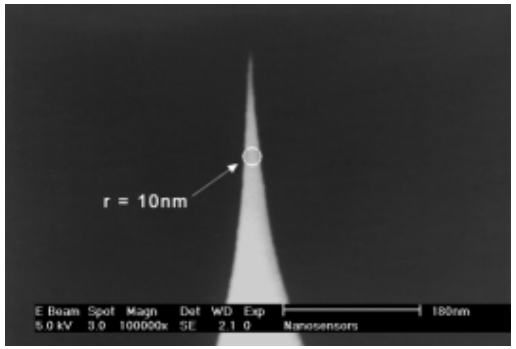
Grutzik et al. *Exp. Mech.* 61.2 (2021): 411-418.

Atomic Force Microscopy

- AFM (Veeco D5000) - high aspect ratio AFM probes
- Plastic environmental enclosure w/ humidity source
  - 15, 23, 25, 32, 33, 37 and 40% RH
- 512 x 512 pixel resolution; ~28 min per image, continuously imaged

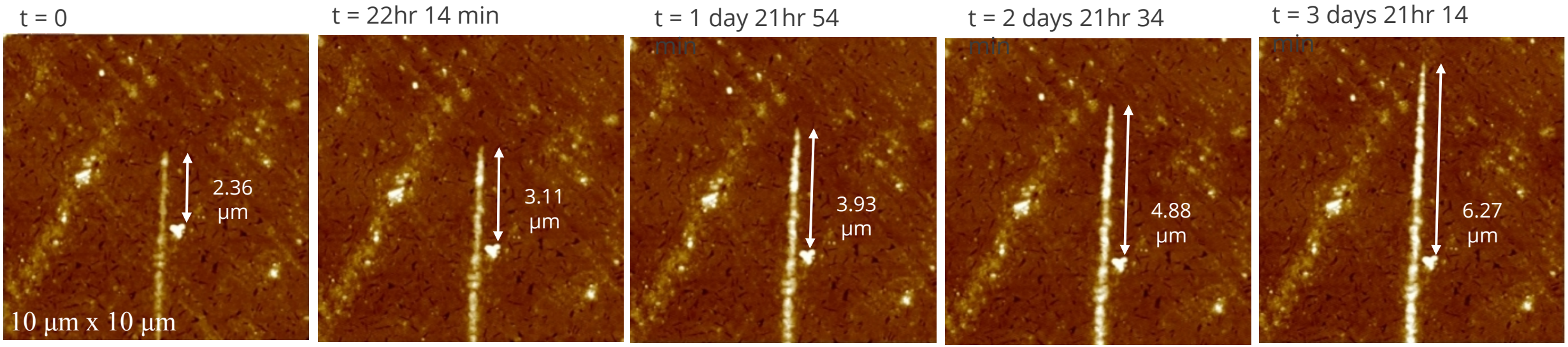


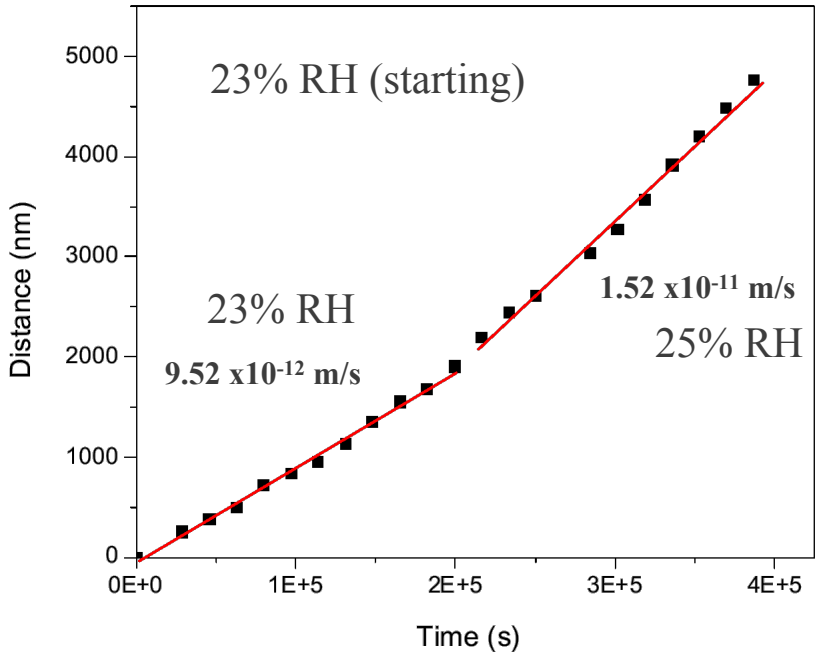
Veeco Dimension 5000 AFM

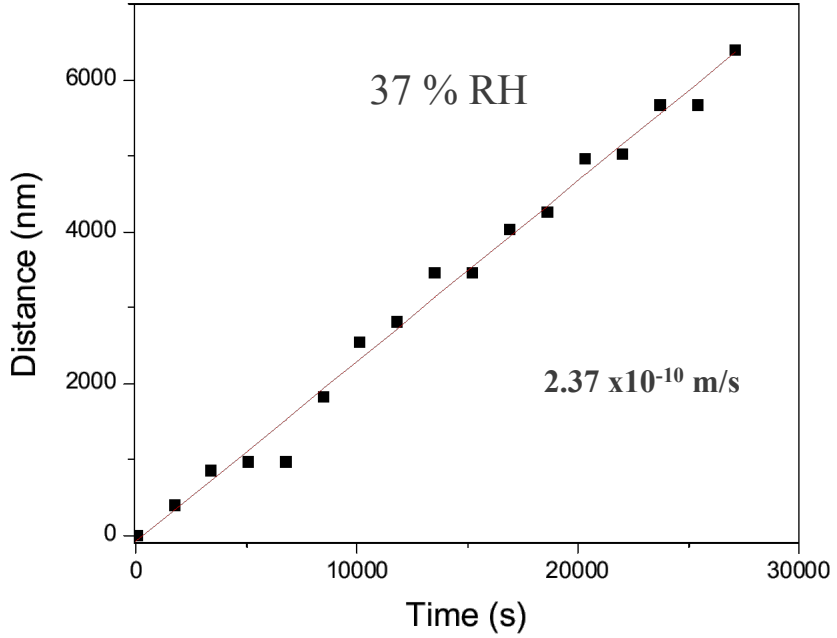


Nanosensors SuperSharpSilicon AFM Tip

Crack Growth in Sodium-Silicate Glasses

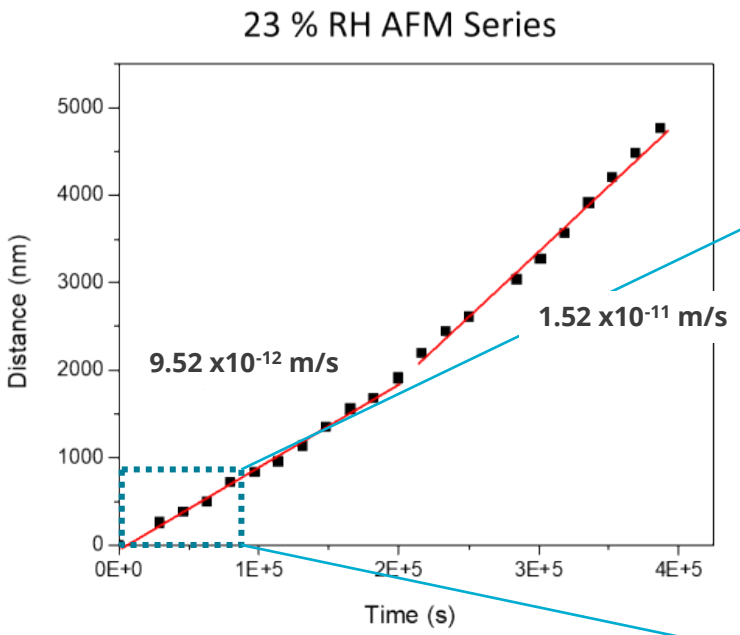


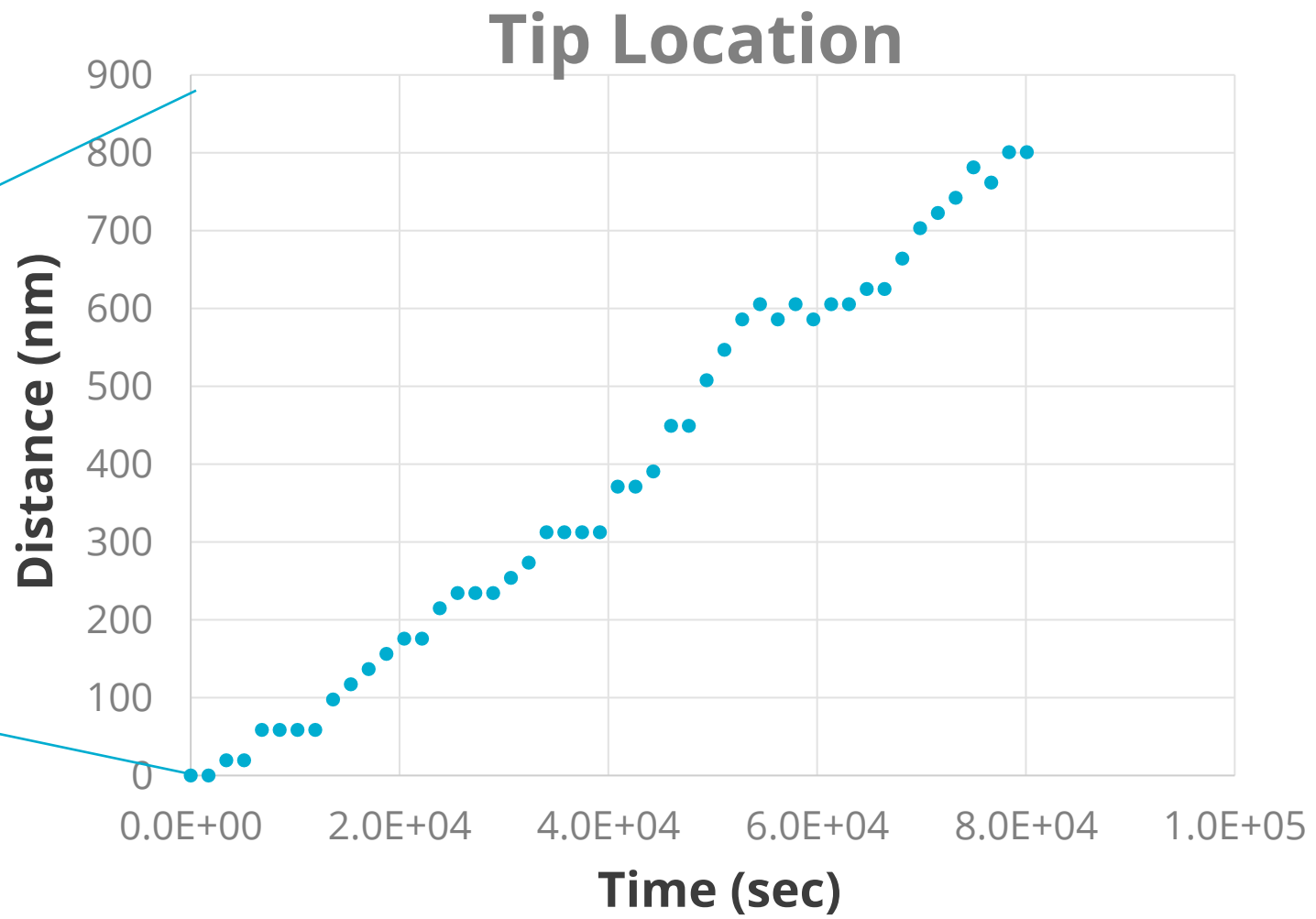




Relative Humidity (%)	Crack Tip Velocity (pm/sec)
15	4.0
23	9.5
25	15.2
32	100.9
33	162.0
37	237.4
40	368.1

Stepwise Crack Propagation

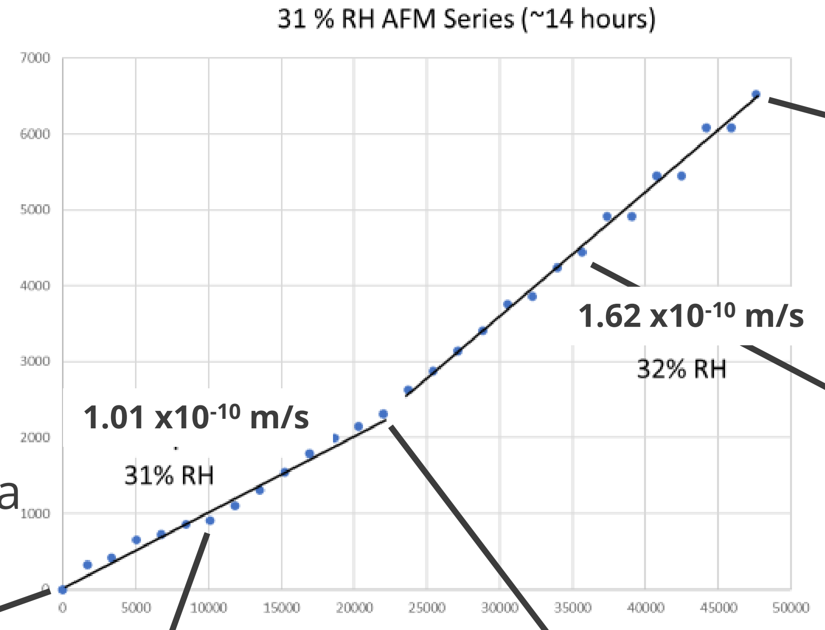


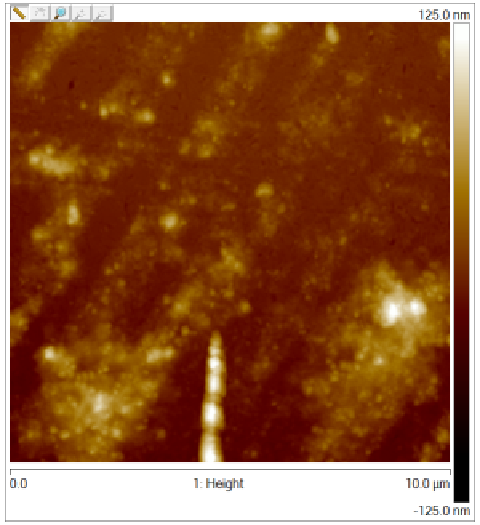


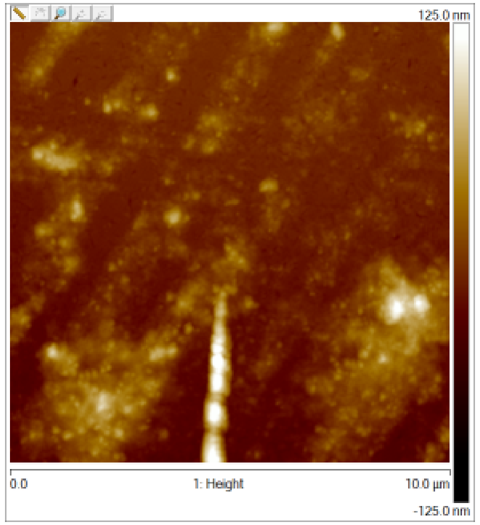
Single frame analysis shows evidence of step-wise propagation

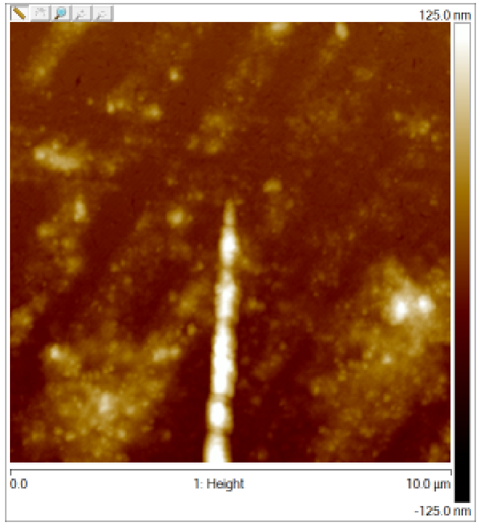
Stepwise Crack Propagation

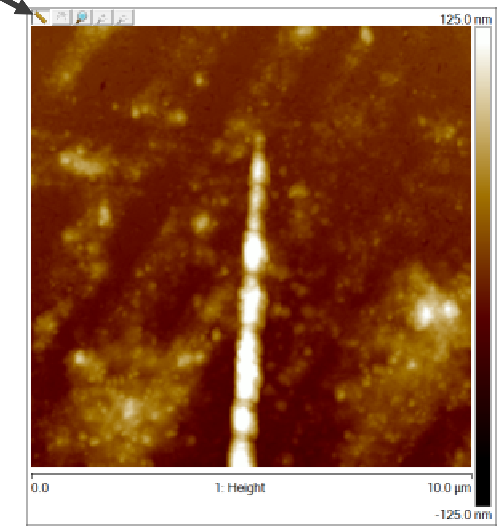
AFM images are height data

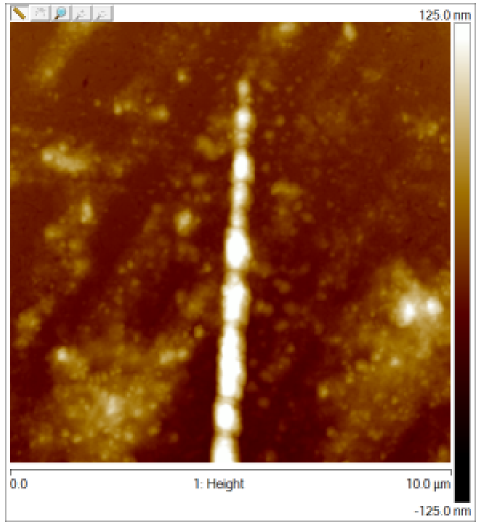






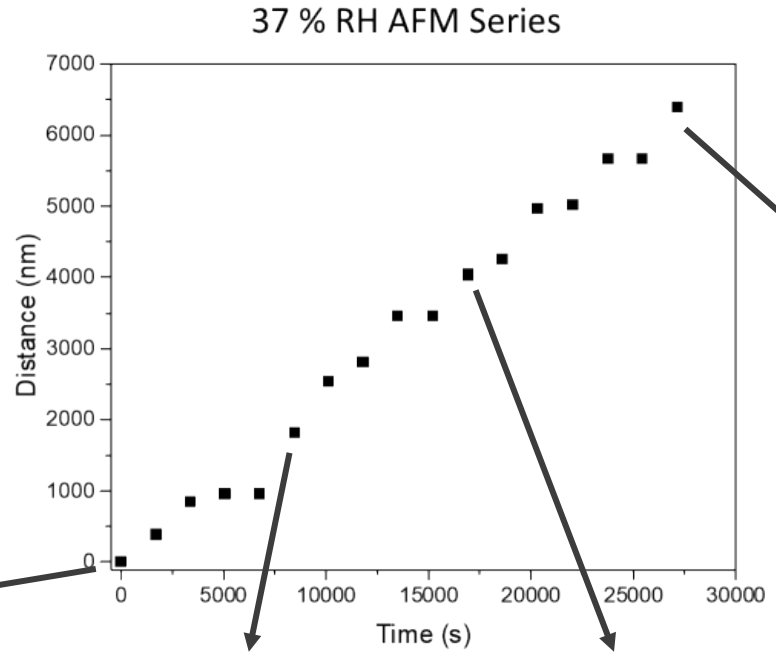


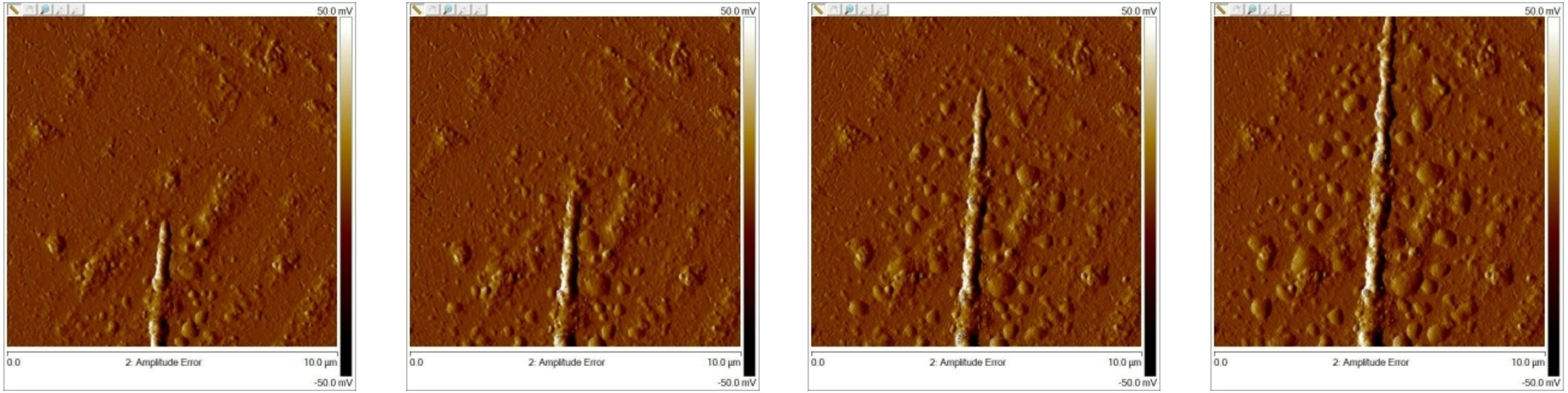




Results – 37% RH

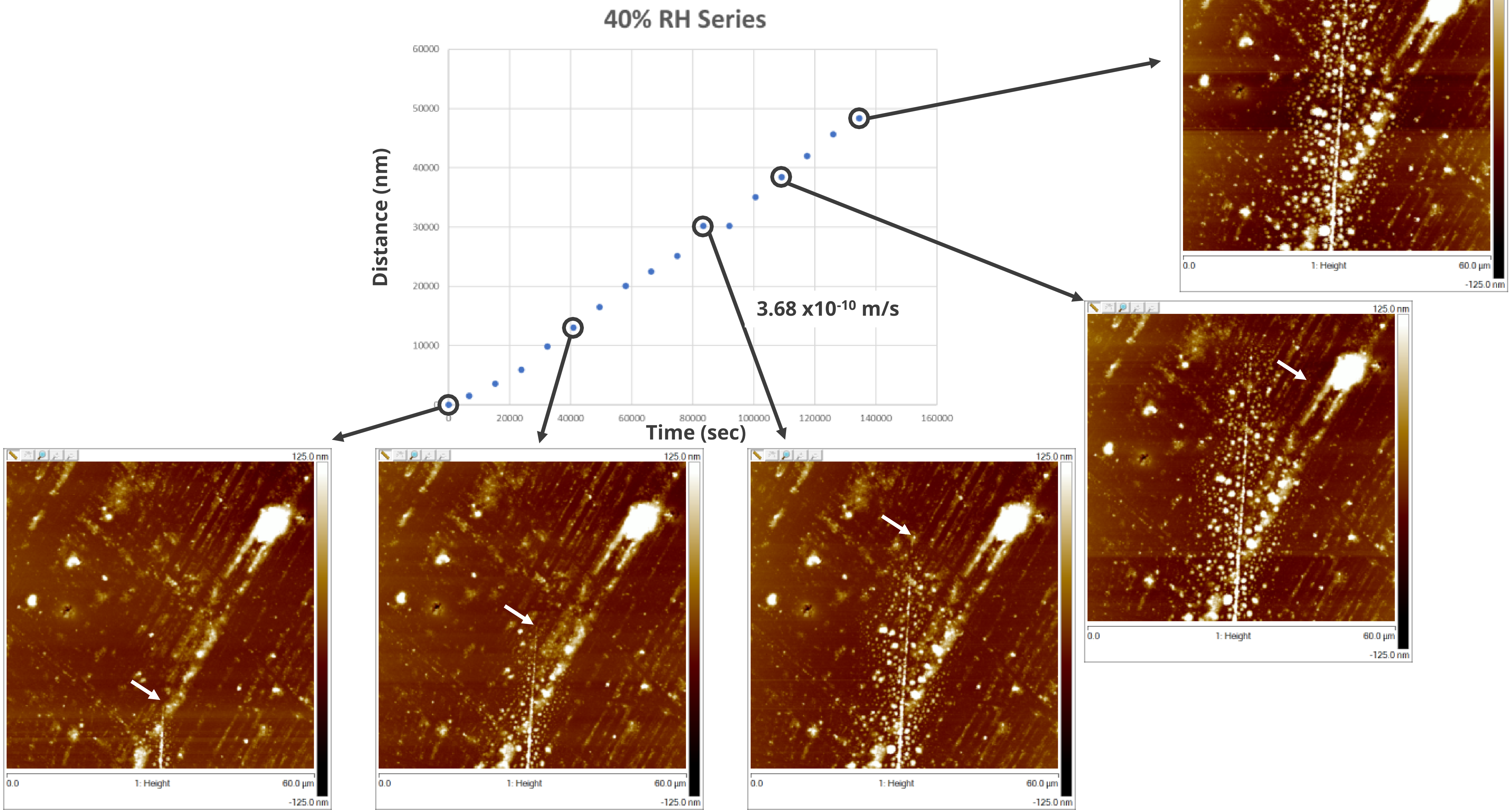
Growth of surface features surrounding fracture observed at higher relative humidity





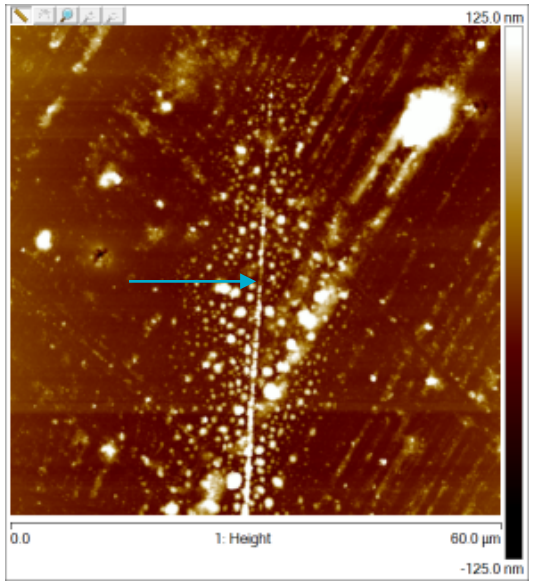
AFM images are amplitude channel to highlight features

Results – 40% RH



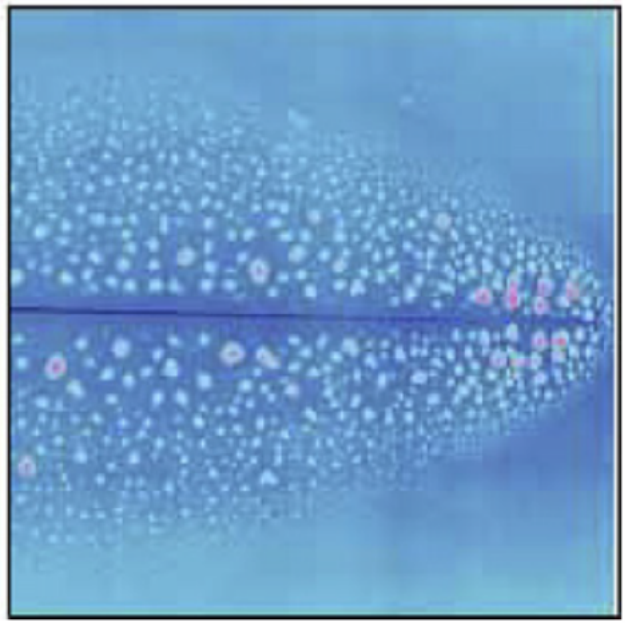
Formation of Surface Features during Fracture

40% RH



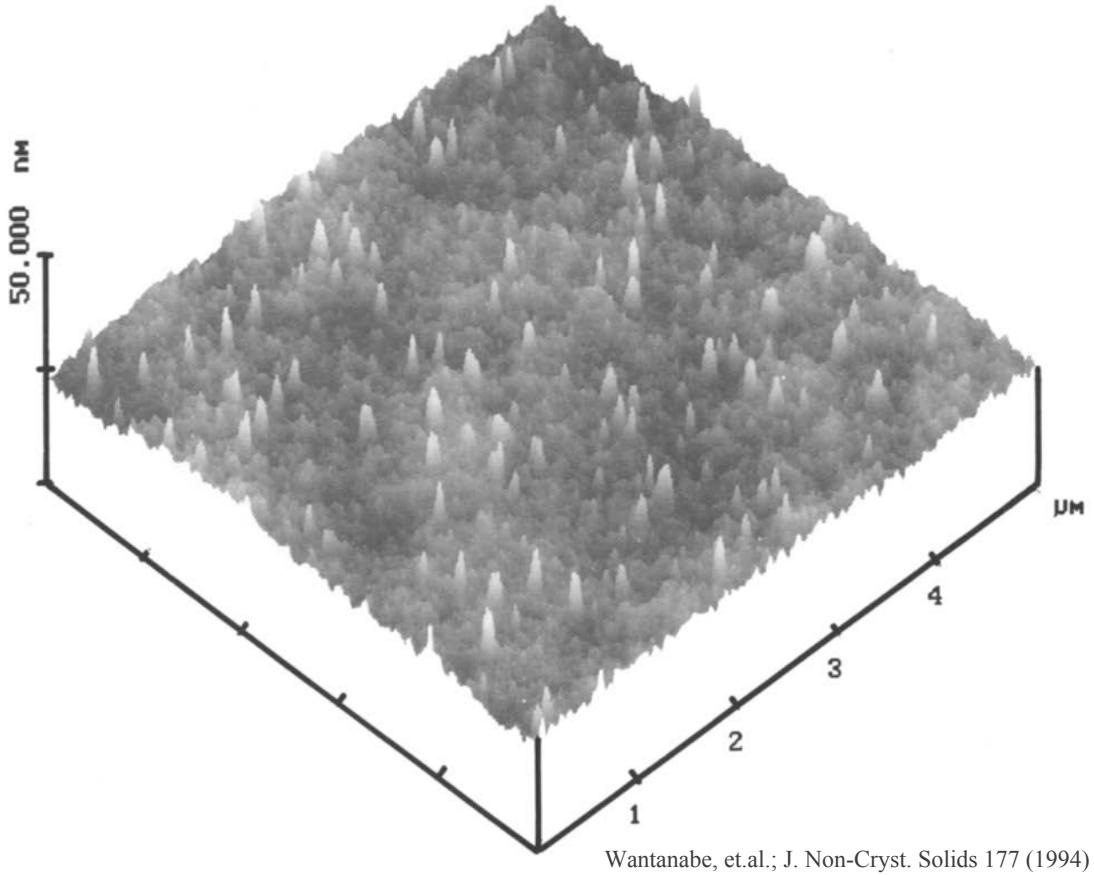
37% RH

45% RH



Celarie, Ciccotti, and Marliere, J. Non-Cryst. Solids **353** (2007)

Fracture Surface



Wantanabe, et.al.; J. Non-Cryst. Solids 177 (1994)

Are similar phenomena present at the atomistic scale?

Why atomistic simulations?

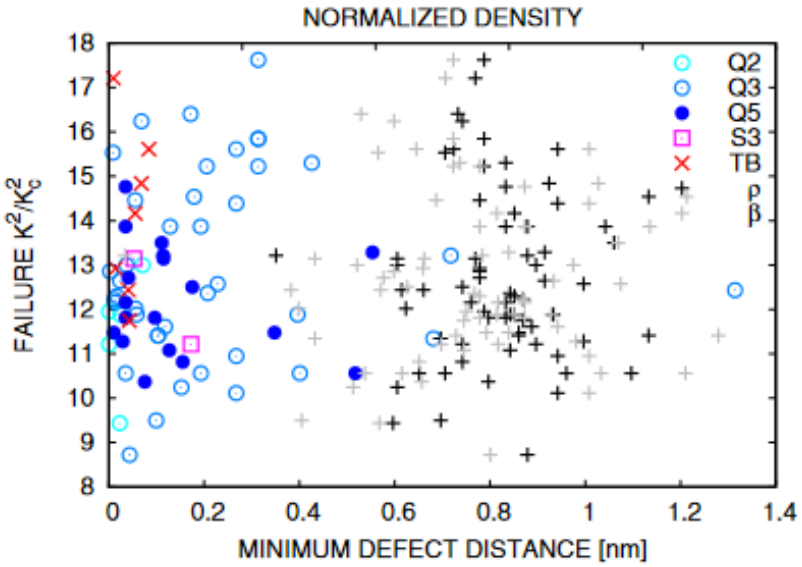
- Subcritical crack growth fundamentally occurs on a nanometer scale
- Fracture mechanisms occur through a bond breakage and formation process

- Molecular scale simulations have replicated the fracture toughness of the bulk material
- Fracture propagation is stepwise for silica from far-field loading and notched geometries
- Fractures propagate when loading exceeds the fracture toughness

Sources of Fracture Propagation?

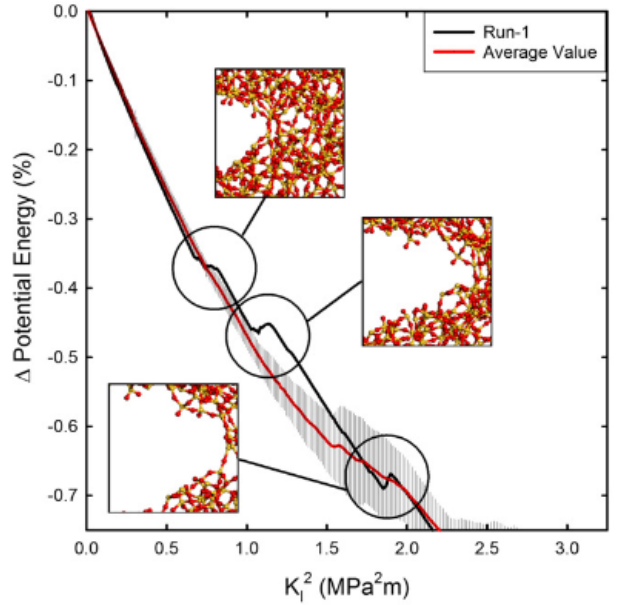
- Typically structures are single component so little/no changes in local composition
- No variation with minimum defect distance

What other types of structural factors could be influencing crack propagation?



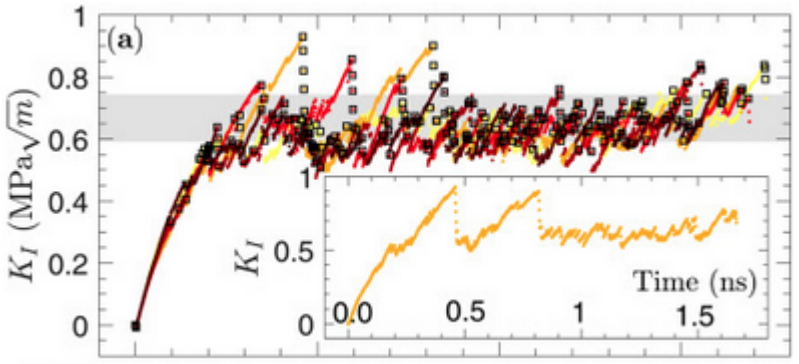
Correlation of K_{Ic} with distance to closest defect to crack tip for in silica during far-field loading.

Jones et al. *J. Phys.: Condens.Matter* 30.24 (2018): 245901.



Percent change in potential energy in silica during far-field loading

Rimsza et al. *J. Amer. Ceram. Soc.* 101.4 (2018): 1488-1499.



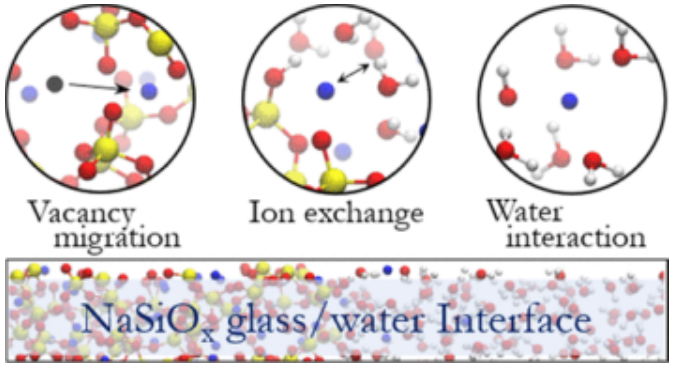
Calculated K_{IC} for a-SiO. Data are reported for five samples at applied strain of 0.22.

Wilson et al. *Comput. Methods Appl. Mech. Eng.* 354 (2019): 732-749.

Computational Methods

- Classical molecular dynamics for large scale simulation of silica fracture
- ReaxFF: bond order based forcefield including silica bond breakage and formation

$$E_{Total} = E_{Bond} + E_{Over} + E_{Under} + E_{LP} + E_{Val} + E_{Pen} + E_{Tors} + E_{Conj} + E_{VDW} + E_{Coul} \quad (1)$$



Hahn et al. *J. Phys. Chem. C* 122.34 (2018): 19613-19624.

Two-step methodology for structure generation developed by Deng et al.:

Deng et al. *J. Amer. Ceram. Soc.* 103.3 (2020): 1600-1614.

1. Melt and quench with a non-reactive forcefield
   - Melting at 3500 K for 100 ps
   - Cool to 300 K at a rate of 5 K/ps
   - Final 100 ps equilibration at 300 K
   - NPT ensemble and 1.0 fs time step

   Pedone et al. *J. Phys. Chem. B.* 110.24 (2006): 11780-11795.

2. Annealing with Na/Si/O/H ReaxFF
   - Heat to 1500 K at 5 K/ps
   - Hold at 1500 K for 80 ps
   - Cool to 300 K at a rate of 5 K/ps
   - NPT ensemble and a 0.25 fs time step

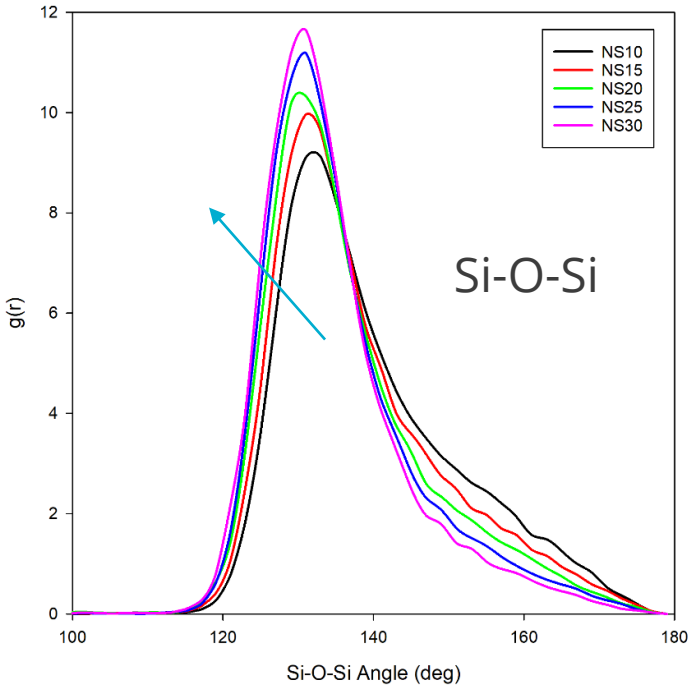
   Hahn et al. *J. Phys. Chem. C* 122.34 (2018): 19613-19624.

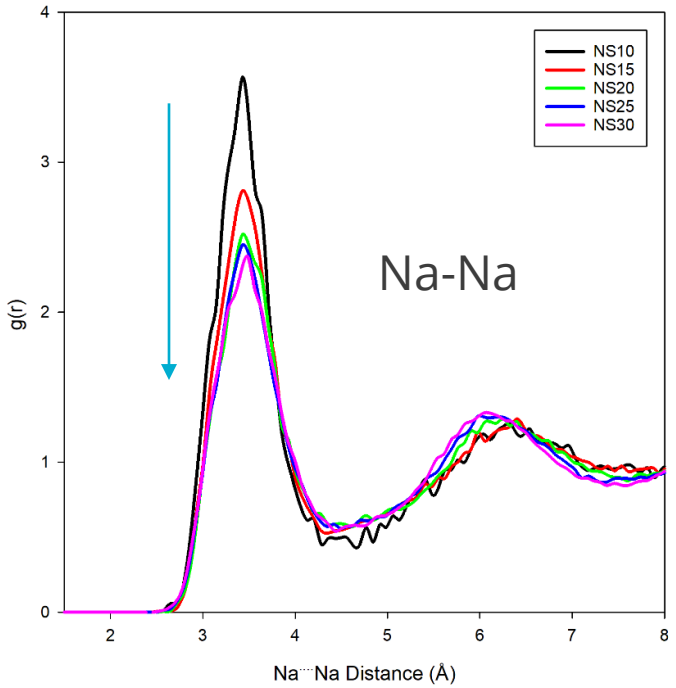
	Composition (atoms)			Density (g/cm³)	
	Na	Si	O	This Work	Ref
NS10	2550	11525	24325	2.42	2.30
NS15	3850	10875	23675	2.44	2.34
NS20	5100	10250	23050	2.45	2.38
NS25	6400	9600	22400	2.46	2.43
NS30	7700	8950	21750	2.46	2.47

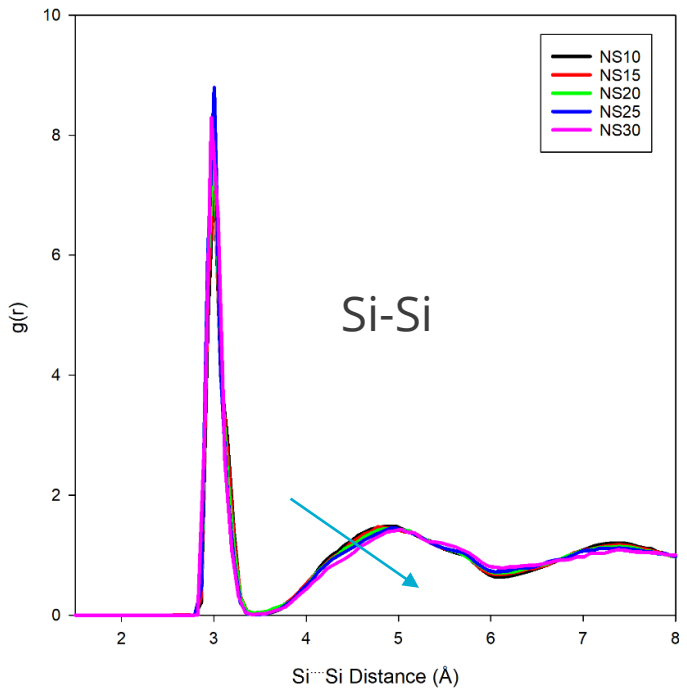
Ref: Lower et al. *J. Non-Rryst. Solids* 349 (2004): 168-172.

Bulk Sodium Silicate Properties

Structural and mechanical properties of sodium silicates are consistent with previous work

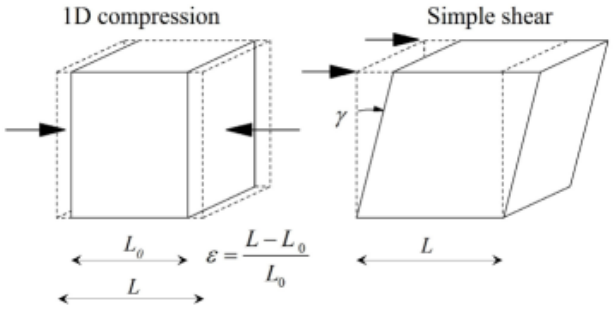






Elastic (E) and shear (G) modulus and surface energy for sodium silicate glass models and comparison experimental results

	E (GPa)		G (GPa)		v		Surface Energy (J/m²)
	This Work	Ref	This Work	Ref	This Work	Ref	This Work
NS10	82.7	73.4	32.6	29.9	0.27	0.22	1.74
NS15	74.9	65.1	29.2	29.2	0.29	0.21	1.53
NS20	67.1	59.9	25.7	25.4	0.30	0.22	1.27
NS25	68.3	59.7	26.1	24.3	0.31	0.23	1.37
NS30	64.5	59.0	24.1	23.3	0.34	0.25	1.26



Ref: Molnár et al. *J. Non-Cryst. Solids* 440 (2016): 12-25.

Selection of Fracture Methodology

Multiple crack tip geometries and loading conditions have been explored including:

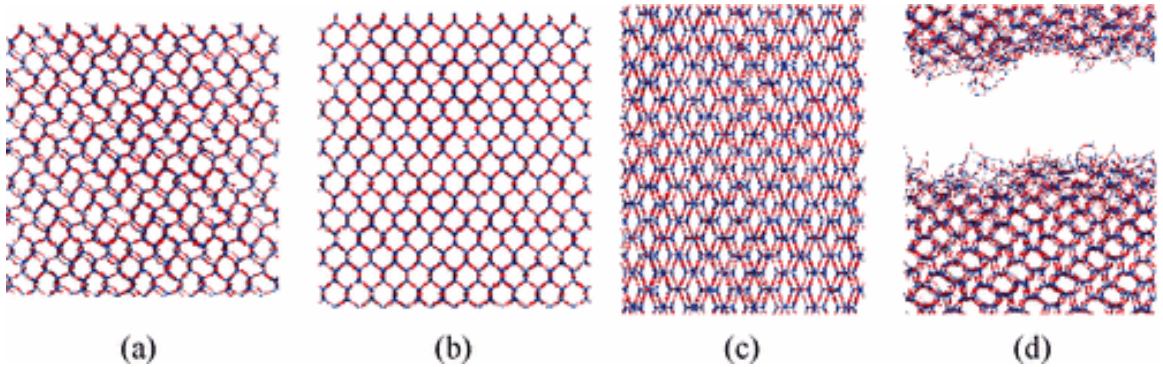
- Tensile loading of the bulk phase
- Tensile loading with an internal void
- Tensile loading with initial notch/fracture

Benefits:

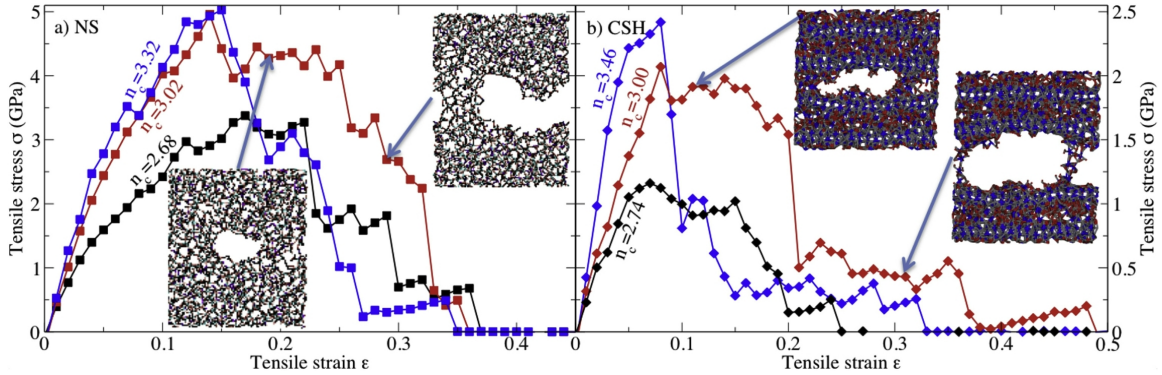
- Known loading conditions
- Simple to implement
- Adjustable system size

Drawbacks:

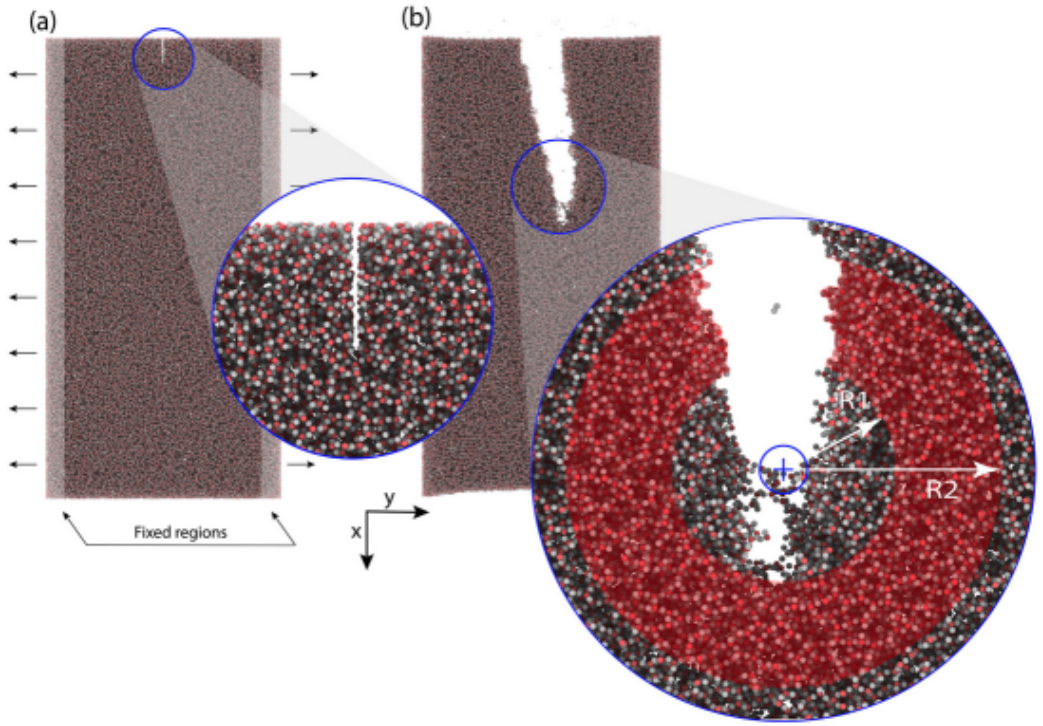
- Connection to LEFM solutions / J-integral
- Changes the charge balance
- Variation from crack size and geometry



Pedone et al. *Chemistry of Materials* 20.13 (2008): 4356-4366.



Bauchy et al. *Acta Materialia* 121 (2016): 234-239.



Wilson, Grutzik, and Chandross. *Comput. Methods Appl. Mechs. Eng.* 354 (2019): 732-749.

Mechanical Loading Conditions

Irwin near-field solution for crack tips:

- Analytical solution for displacement field around a crack tip
- Assumes a slit-like plane crack
- Creates a stress singularity at the crack tip

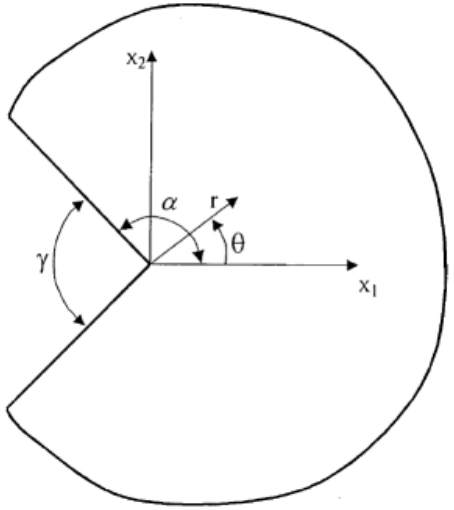
Lawn, Brian R. "Fracture of brittle solids." *Cambridge Solid State Science Series* (1993).

$$\begin{Bmatrix} u_r \\ u_\theta \end{Bmatrix} = \frac{K_I}{2E}\left\{\frac{r}{2\pi}\right\}^{\frac{1}{2}} \begin{Bmatrix} (1+\nu)[(2k-1)\cos(\theta/2) - \cos(3\theta/2)] \\ (1+\nu)[-(2k+1)\sin(\theta/2) + sin(3\theta/2)] \end{Bmatrix}$$

K_I = loading, E = elastic modulus, ν = Poisson's ratio

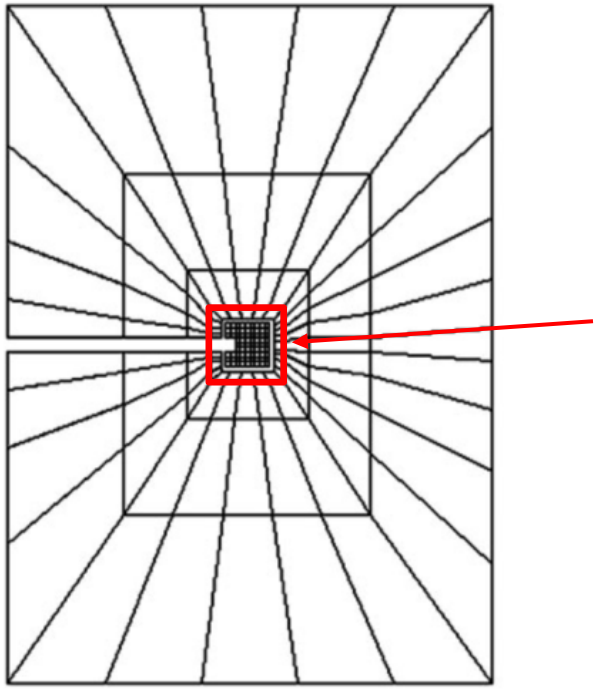
- Previously used in multi-scale simulations to connect the internal MD simulation sections to the external FEM simulation in MgO, Si, and $BaTiO_3$

Chen and Niemkiewicz. *Z. Angew. Math. mech.* 95.2 (2015): 165-172. Gleizer et al. *Physical Review Letters* 112.11 (2014): 115501. Chen and Lee. *Theo. Appl. Fract. Mech.* (2010): 74-79.



Geometry of the notch tip and the coordinate system.

Suwito et al. *J. Appl. Phys.* 83.7 (1998): 3574-3582.

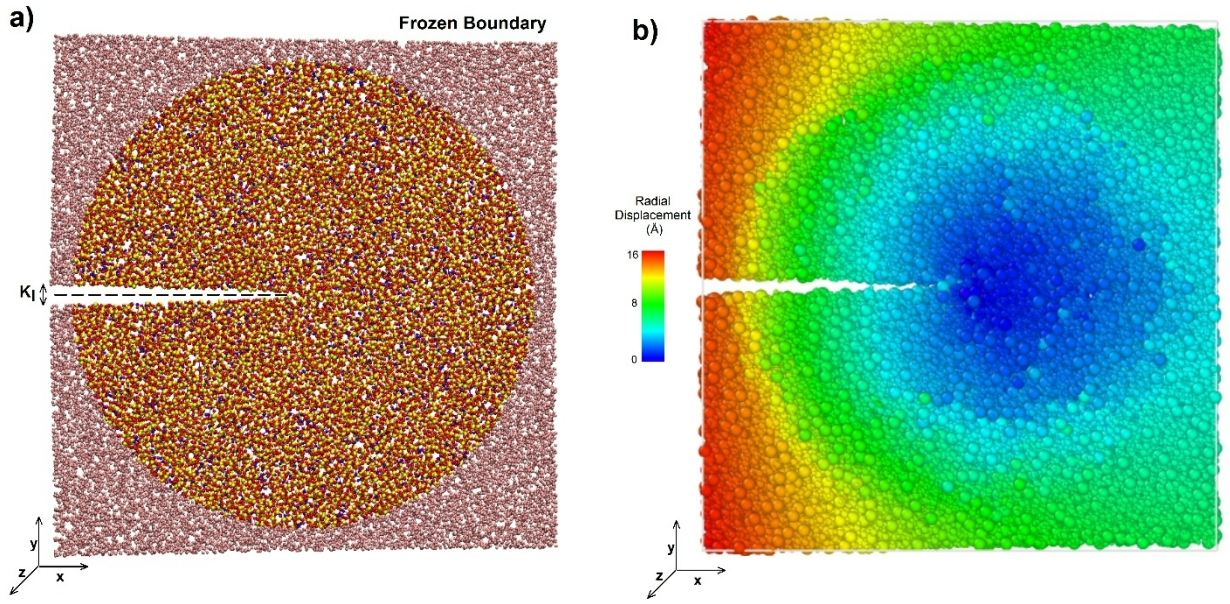


Finite element mesh for near field (FEM) and atomic region (classical MD simulations).

Chen and Lee. *Theo. Appl. Fract. Mech.* (2010): 74-79.

Simulation Details

- 38,400 atom structure, 150 Å x 150 Å x 30 Å
- Slit crack is introduced by removing neighboring
- Structure is rotated 3x to get 4 distinct initial cracks
- Boundary atoms are fixed and atomic positions are adjusted to introduce far-field loading
- Interior atoms (radius = 6.5 nm) are integrated with a canonical (NVT) ensemble
- Initial loading was 0.18 MPa√m



(a) Snapshot of the NS10 sodium silicate glass structure with a loaded slit crack. (b) Radial displacement field from far-field loading conditions in NS10 sodium silicate glass structure.

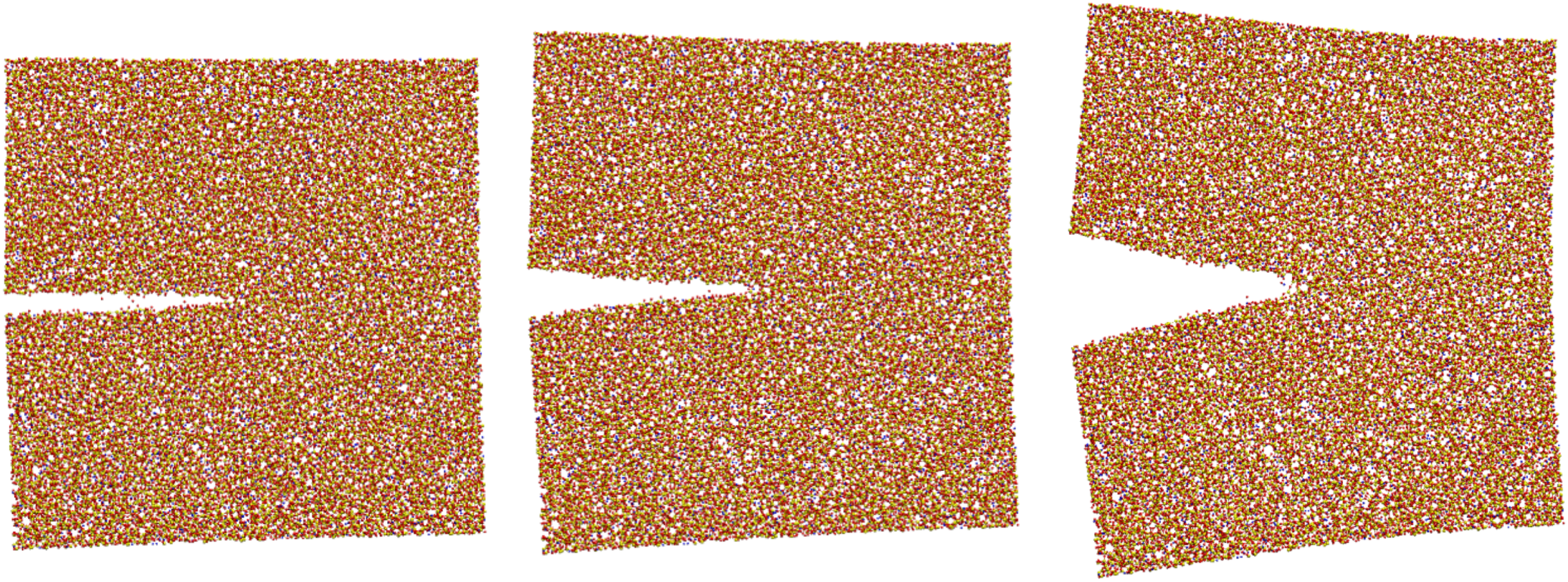
Rimsza and Jones (2022). *Int. J. Appl. Glass Sci* submitted

- Quasistatic loading = loading increases of 0.01 MPa√m followed by 5ps of NVT to a final loading of 1.2 MPa√m
- Similar methods have been used for fracture simulations of silica in vacuum, water, and aqueous electrolyte solutions

Rimsza et al. (2018). *J. Amer. Ceram. Soc. 101*(4), 1488-1499., Rimsza, J. M. et al. (2018). *J. Geophys. Res.: Solid Earth*, *123*(11), 9341-9354., Rimsza et al. (2019). *Front. Mater. 6*, 79

From this methodology we can identify mechanisms of fracture in sodium silicate glasses.

Example of Fracture Growth in NS10



0.18 MPa√m

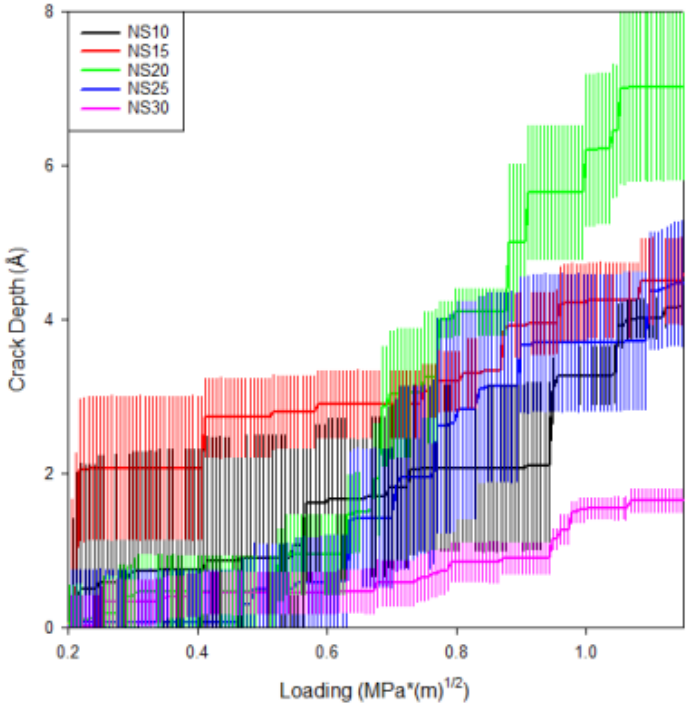
0.50 MPa√m

1.2 MPa√m

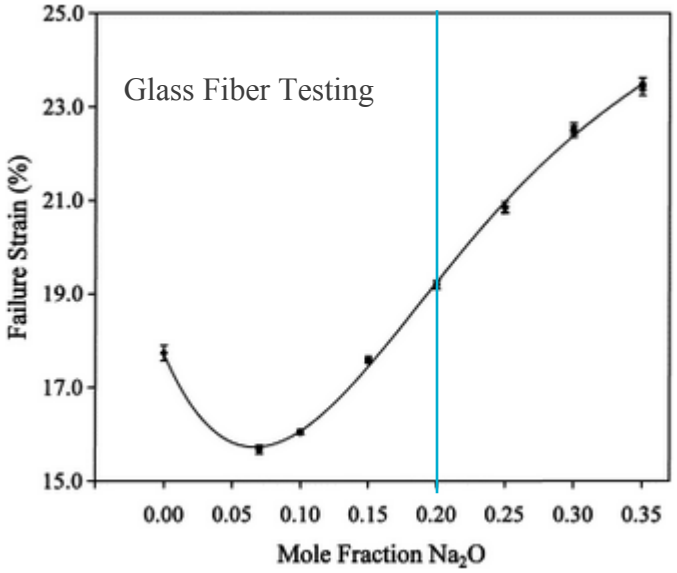
Fracture Growth

- Fracture growth peaks at 20 mole % Na content (NS20)
- Driven primarily by more fracture events than at lower Na concentrations

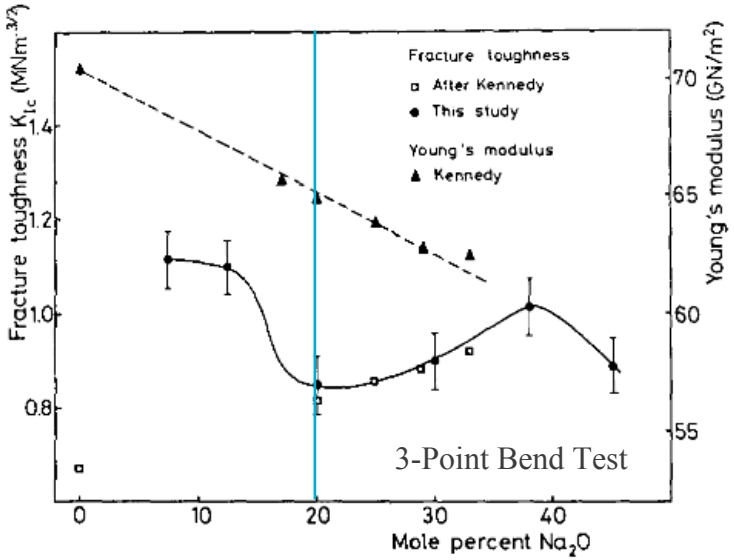
1.2 MPa√m	Total Crack Growth (Å)	Fracture Events (#)	Average Fracture Length (Å)	Longest Fracture (Å)
NS10	4.60±0.82	7.00±2.92	0.71±0.13	2.87±0.84
NS15	3.95±0.74	3.50±1.50	1.27±0.37	3.57±0.66
NS20	7.02±1.51	10.25±4.44	0.78±0.29	2.60±0.46
NS25	5.67±2.51	8.50±2.06	0.65±0.19	2.70±0.93
NS30	3.15±1.42	5.25±1.48	0.70±0.38	2.00±0.98



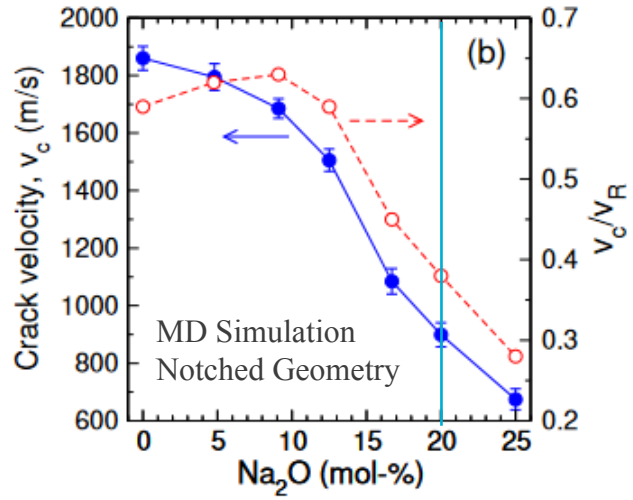
- Consistent with previous reports?



Lower, Brow, and Kurkjian. *J. Non-Cryst. Solids* 349 (2004): 168-172.



Vernaz, Larche, and Zarzycki. *J. Non-Cryst. Solids* 37.3 (1980): 359-365.



Zhang, Ispas, and Kob. *arXiv preprint arXiv:2205.02461* (2022).

Brittleness and Energy Dissipation

- Does the increased fracture growth in NS20 composition relate to the brittleness of the material?

- A *perfectly* brittle material will convert all excess energy into new fracture surface energy

$$G = 2\gamma_s$$

- For systems with some amount of non-ideal behavior an energy dissipation term (G_{DISS}) can capture these additional effects

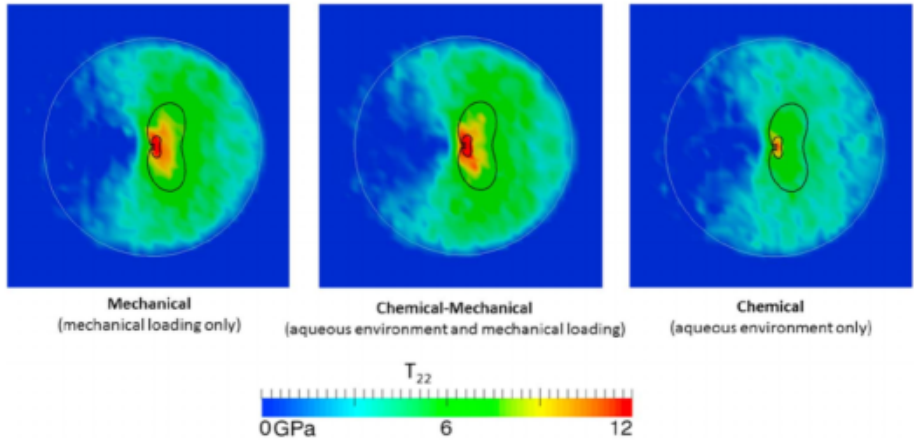
$$G = G_{diss} + 2\gamma_s$$

- By using the change in energy and added surface area of the value is calculated

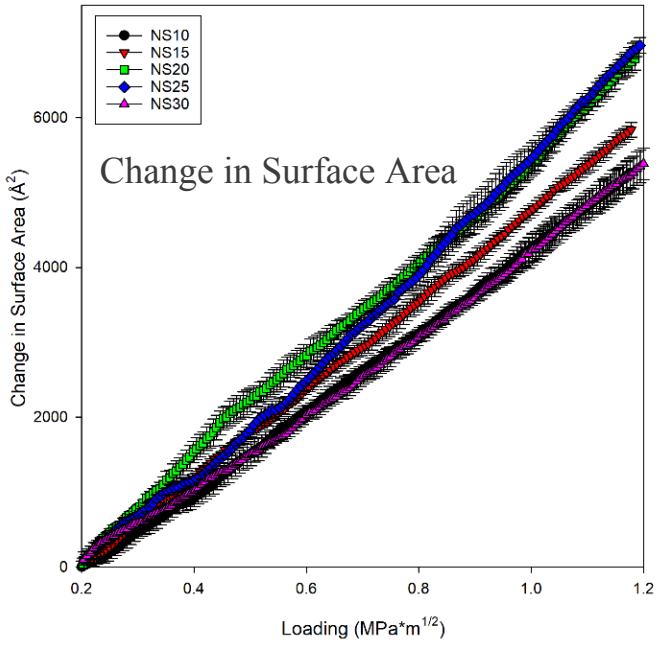
$$\Delta U - \Delta U_s = -(G_{DISS} + 2\gamma_s)\Delta c$$

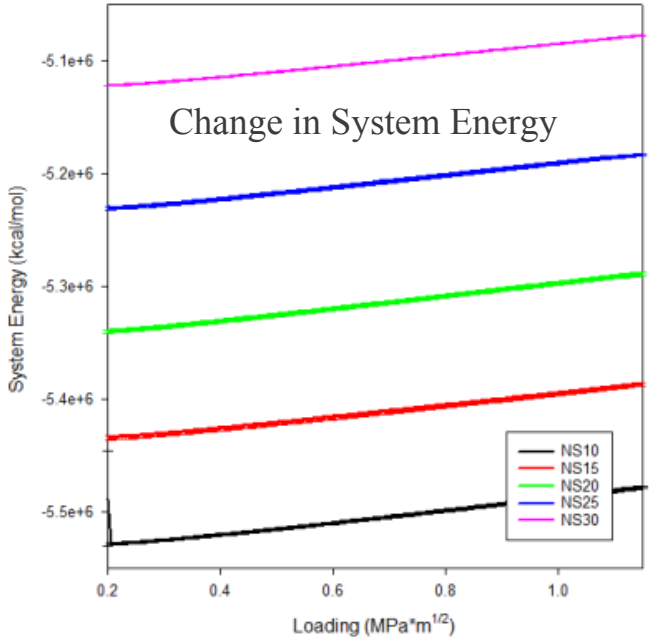
$$G_{DISS} = \frac{\Delta U}{\Delta S_A}$$

- A derivation is included in: 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* 101.4 (2018): 1488-1499.



Rimsza et al. (2018). *J. Geophys. Res.: Solid Earth*, *123*(11), 9341-9354.

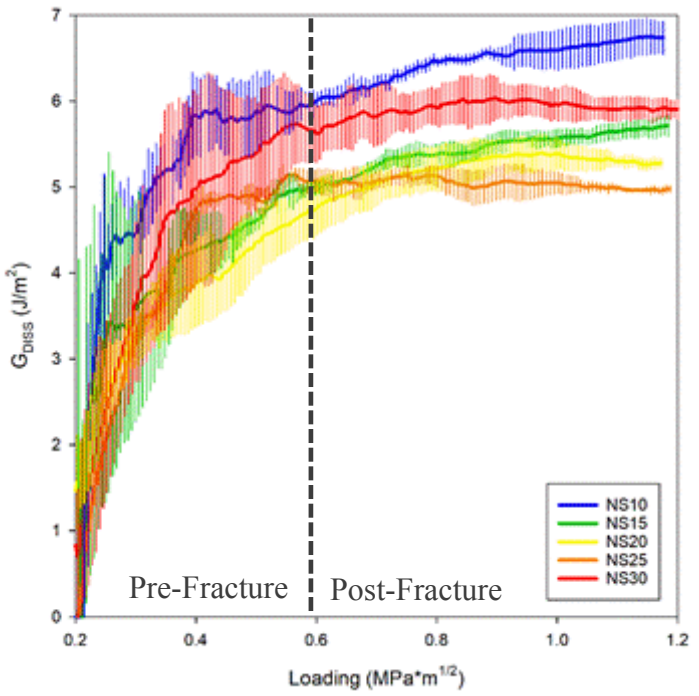


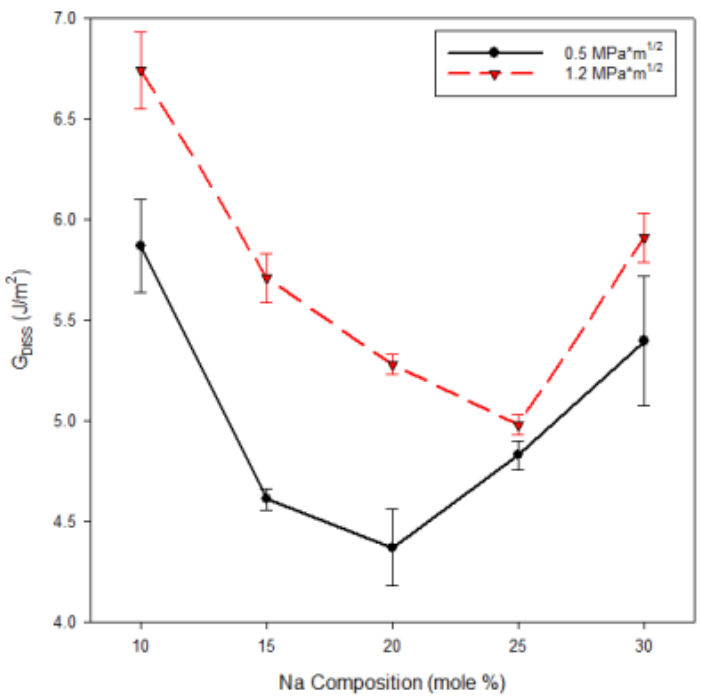


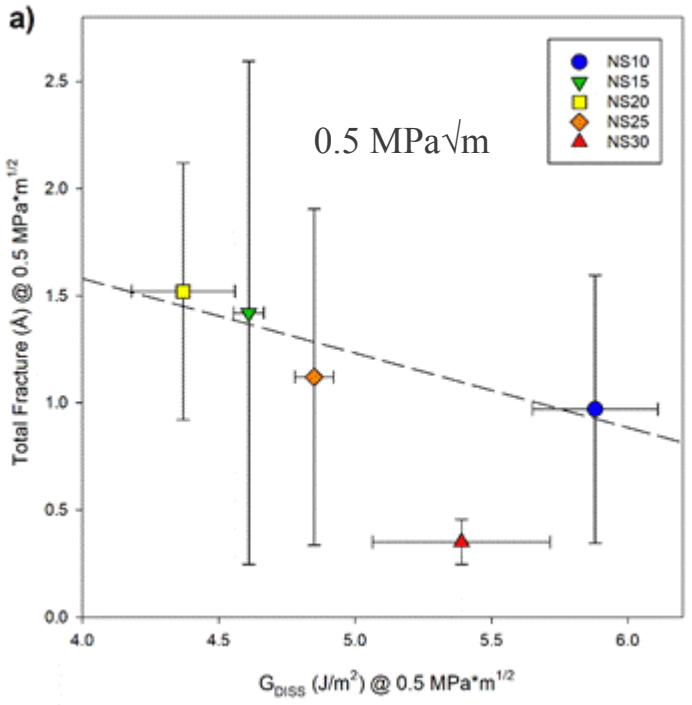
Energy Dissipation

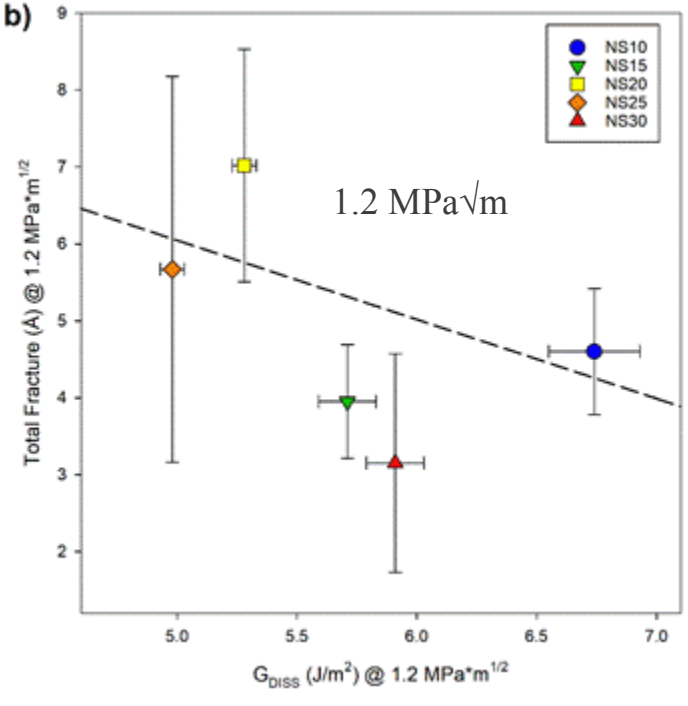
- Energy dissipation follows a pattern similar to fracture growth
  - Pre-Fracture: NS10 > NS30 > NS25 > NS15 > NS20
  - Post-Fracture: NS10 > NS30 > NS15 > NS20 > NS25
- The trend is more distinct pre-fracture, and fracture propagation may be complicating the analysis
- Plotting *total fracture* versus G_{DISS} results in a loose linear fit, with increasing fracture growth with decreasing G_{DISS}
- For pre-fracture conditions, NS30 is an outlier

What structural changes may be causing differences in energy dissipation?

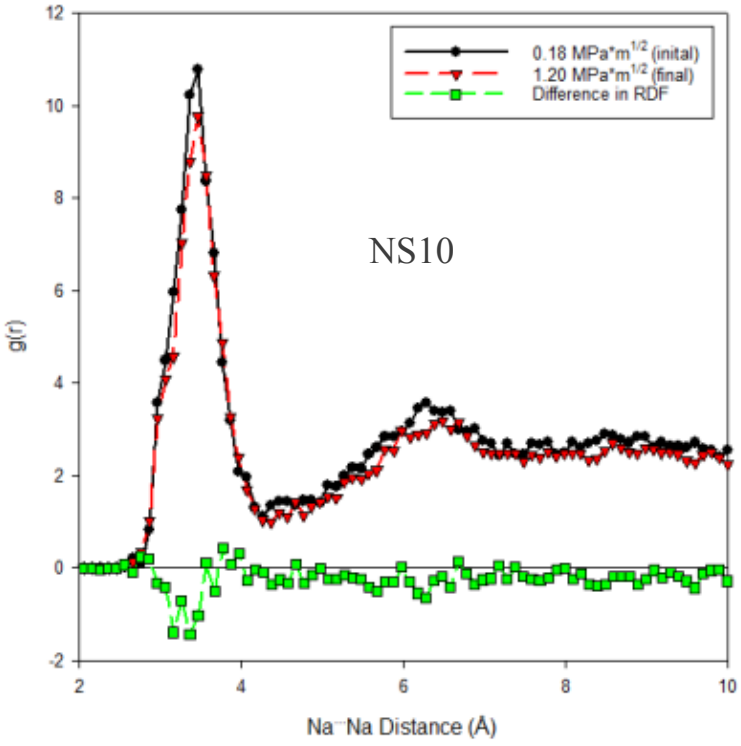


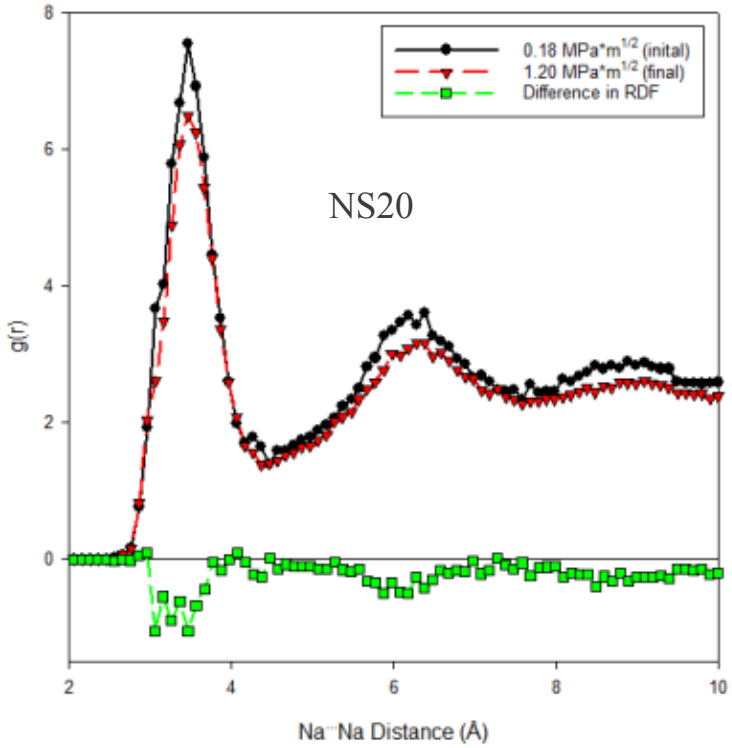


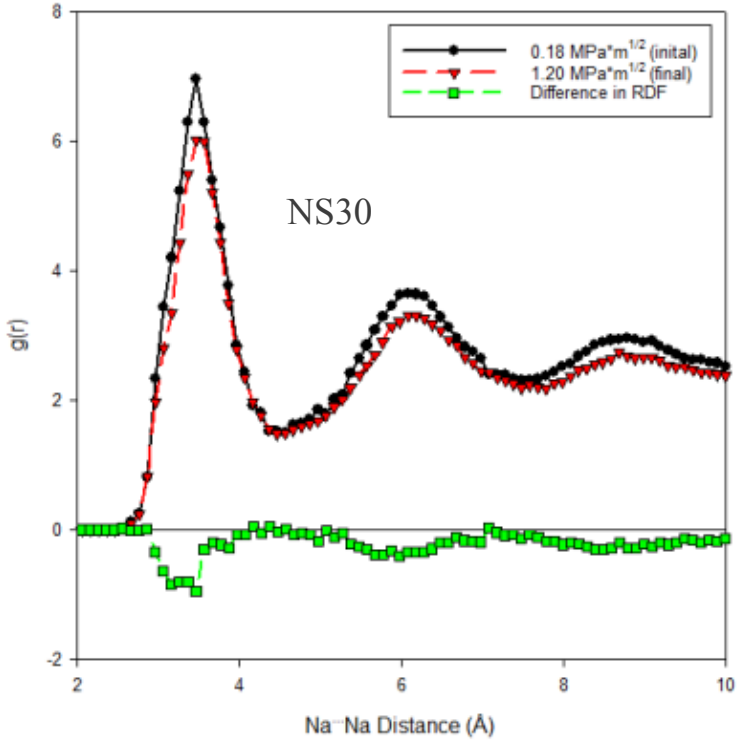




Na clustering during fracture?





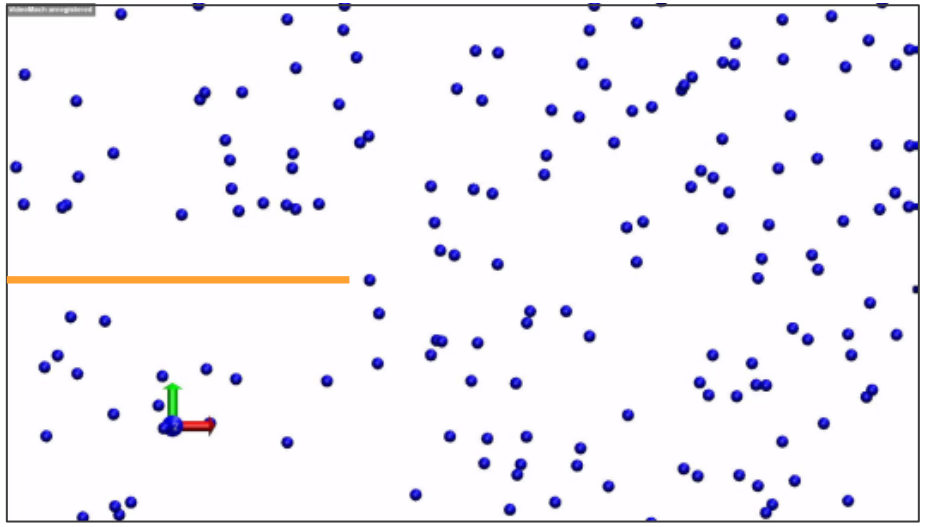


- Limited variation in Na-Na distances with composition during loading
- Small decreases in the peaks at ~3.8 Å and at ~6.0 Å due to the overall stretching of the system during loading

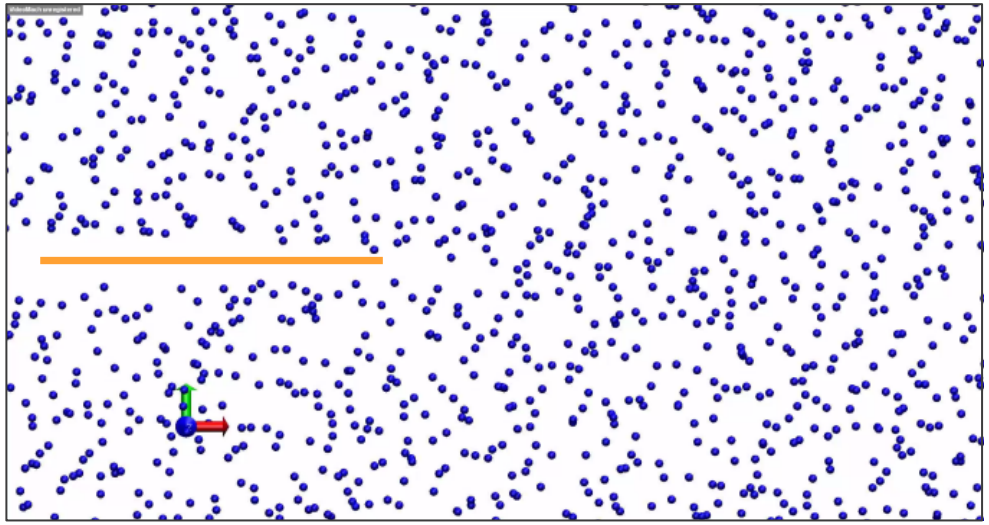
What about Na movement?

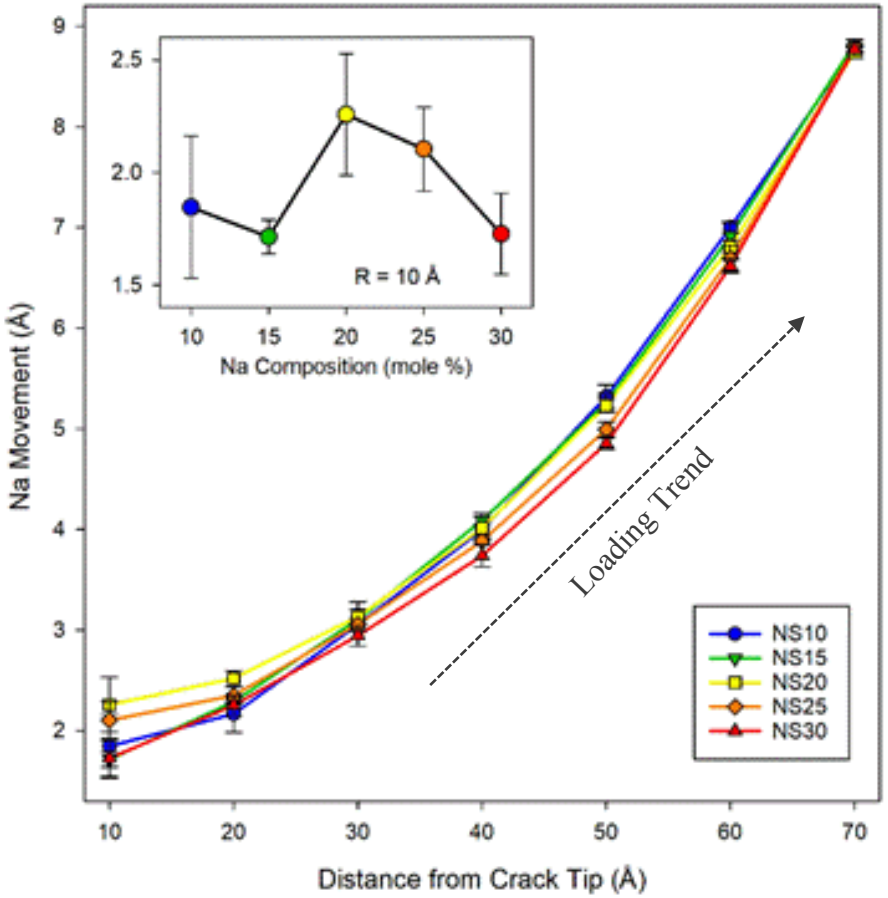
Sodium Movement During Loading

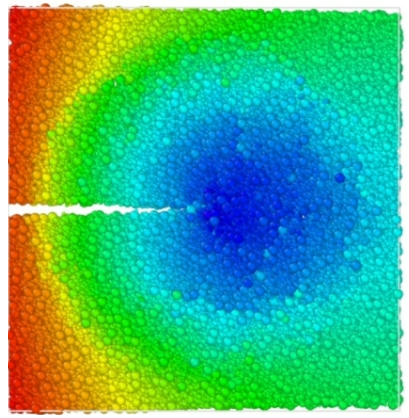
NS10



NS30



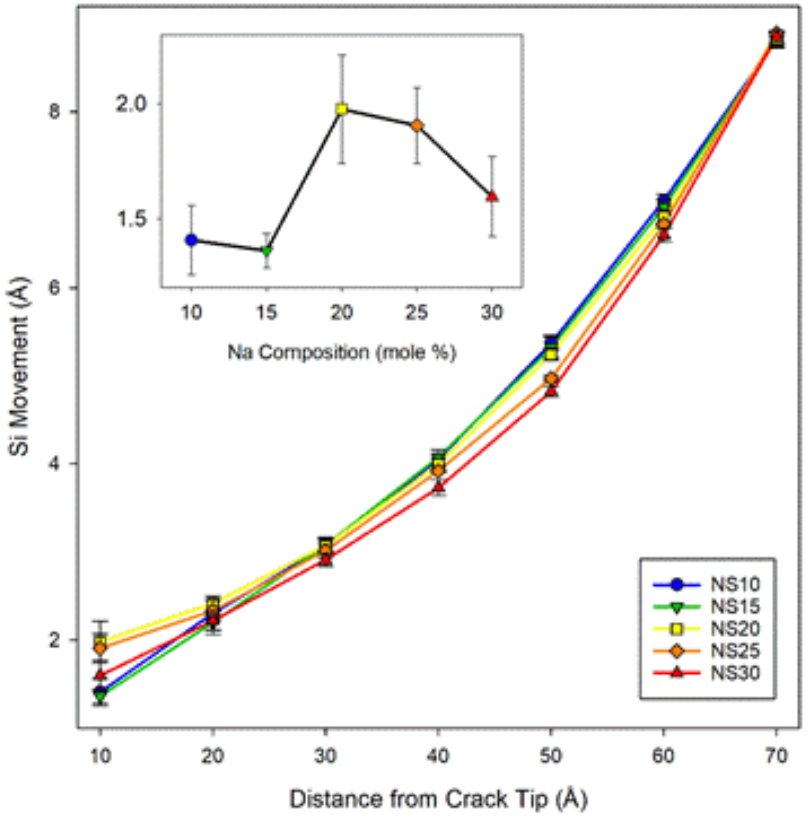




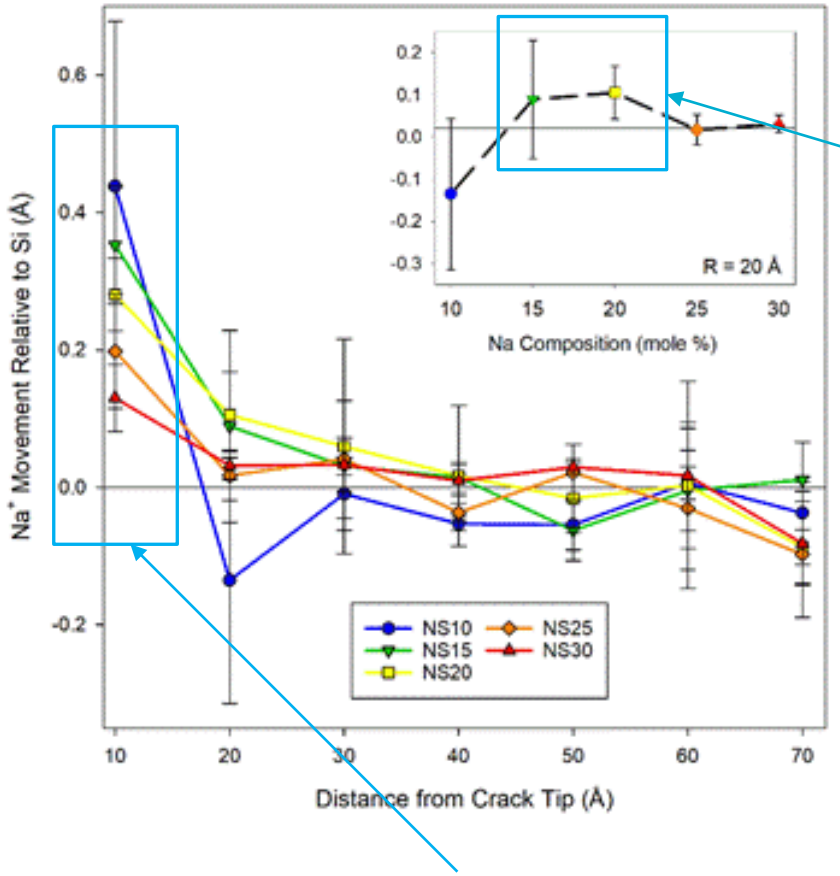
Displacement field
(red = high, blue = low)

- Na movement deviates from loading trend near the crack tip
- Na movement is highest for NS20 composition

Network Movement During Loading



Si movement (e.g., the network) is *also* elevated near the crack tip

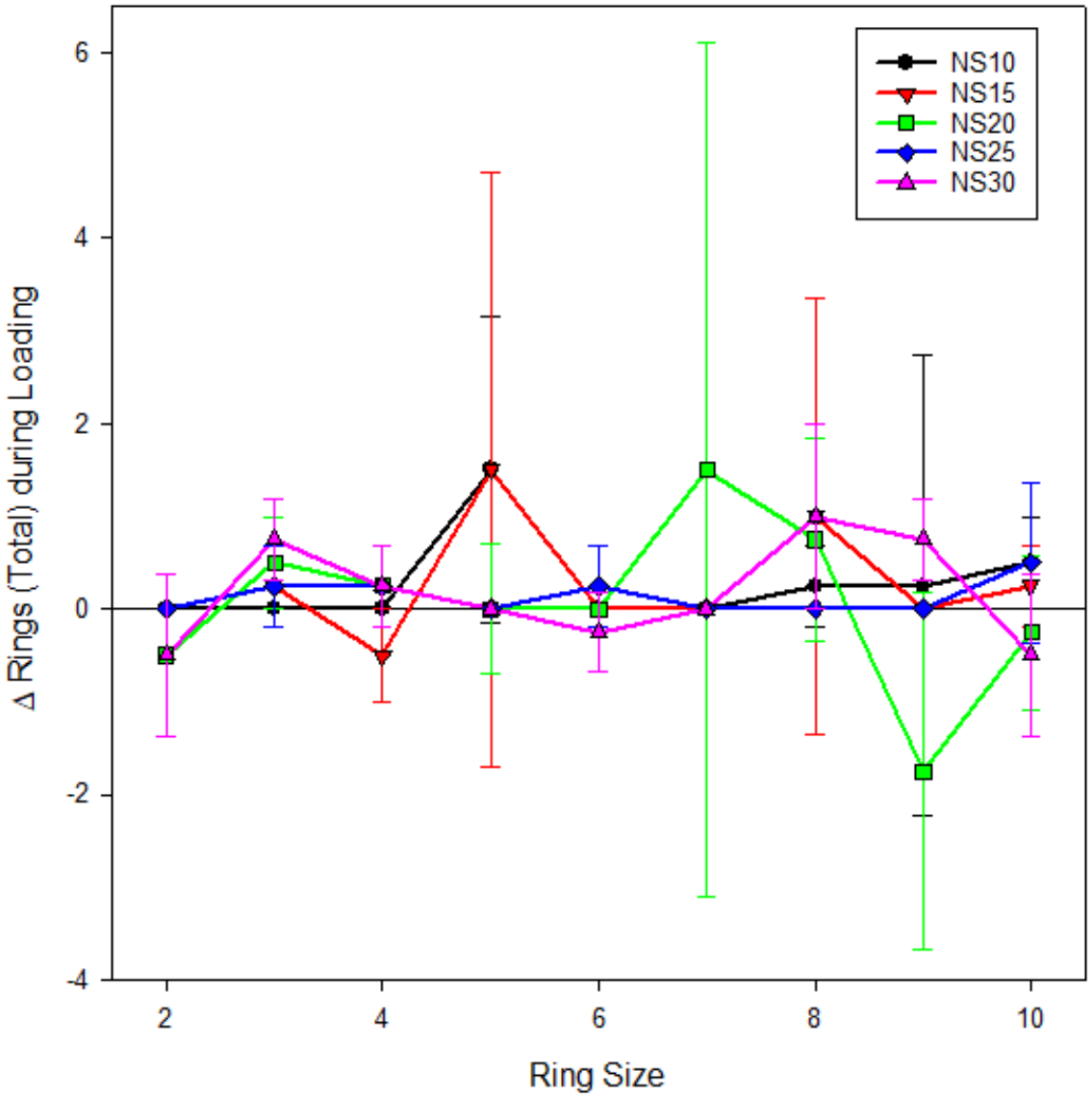


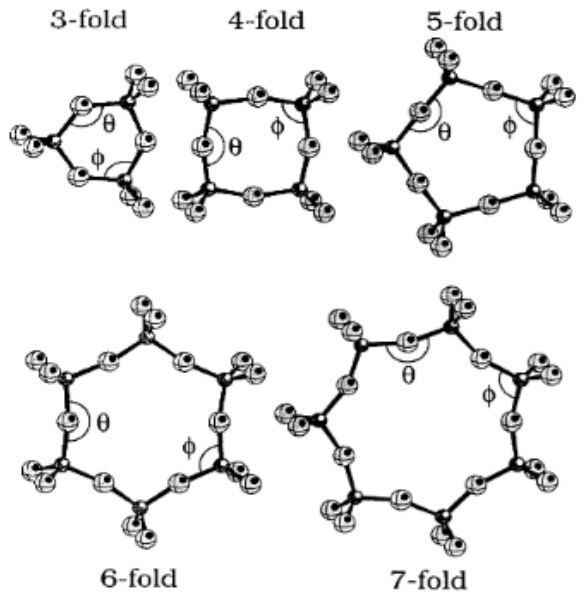
Relative movement of Na results in a compositional trend of increased Na movement for lower Na concentrations

Sodium movement is still faster in the NS20 structure, even if the movement of the framework is removed

What about the change in the network structure?

Change in Intermediate Range Structure





Regular planar n-fold rings in vitreous silica

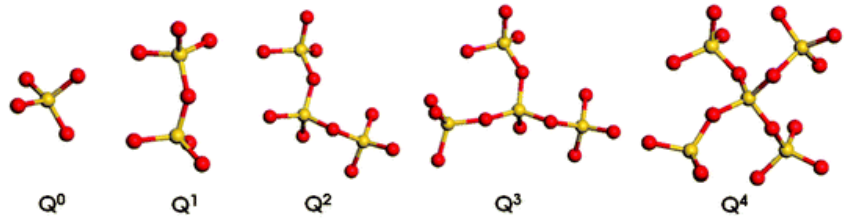
Rino et al. *Phys. Rev. B* 47.6 (1993): 3053.

Kings ring sizes calculated via R.I.N.G.S. code

King *Nature* 213.5081 (1967): 1112-1113. and Le Roux and Jund. " *Comput. Mater. Sci.* 49.1 (2010): 70-83.

Change in Q_n Distribution

- Changes in Q_n distribution of up to 0.08% (or ~4-8 Si with different coordination structures)
- Change in Q_n cancel each other out, causing less change in the connectivity



Chaprntier et al. RSC Adv. (2013)

	Loading (MPa√m)	Q_1	Q_2	Q_3	Q_4	Q_5	Connectivity
NS10	0.2	0.08±0.02	1.57±0.08	20.20±0.06	77.92±0.17	0.23±0.06	3.766
	1.2	0.08±0.02	1.58±0.10	20.22±0.07	77.89±0.16	0.23±0.06	3.766
	Diff	**0.0**	**0.01**	**0.02**	**0.03**	**0.00**	**0.000**
NS15	0.2	0.13±0.01	3.58±0.06	28.35±0.10	67.78±0.06	0.16±0.03	3.643
	1.2	0.17±0.03	3.60±0.08	28.35±0.24	67.72±0.35	0.17±0.03	3.641
	Diff	**0.04**	**0.02**	**0.00**	**0.06**	**0.01**	**-0.002**
NS20	0.2	0.58±0.01	6.28±0.06	37.16±0.17	55.83±0.15	0.15±0.07	3.473
	1.2	0.58±0.01	6.27±0.06	37.18±0.14	55.81±0.16	0.16±0.07	3.473
	Diff	**0.00**	**0.01**	**0.02**	**0.02**	**0.01**	**0.000**
NS25	0.2	1.12±0.02	10.81±0.10	41.32±0.08	46.66±0.17	0.09±0.04	3.338
	1.2	1.12±0.01	10.96±0.28	41.29±0.12	46.54±0.33	0.09±0.04	3.335
	Diff	**0.00**	**0.07**	**-0.02**	**-0.08**	**0.00**	**-0.003**
NS30	0.2	2.20±0.01	16.87±0.09	44.99±0.05	35.88±0.03	0.06±0.02	3.147
	1.2	2.20±0.01	16.87±0.09	45.01±0.05	35.86±0.03	0.06±0.02	3.147
	Diff	**0.00**	**0.00**	**0.02**	**-0.02**	**0.00**	**0.000**

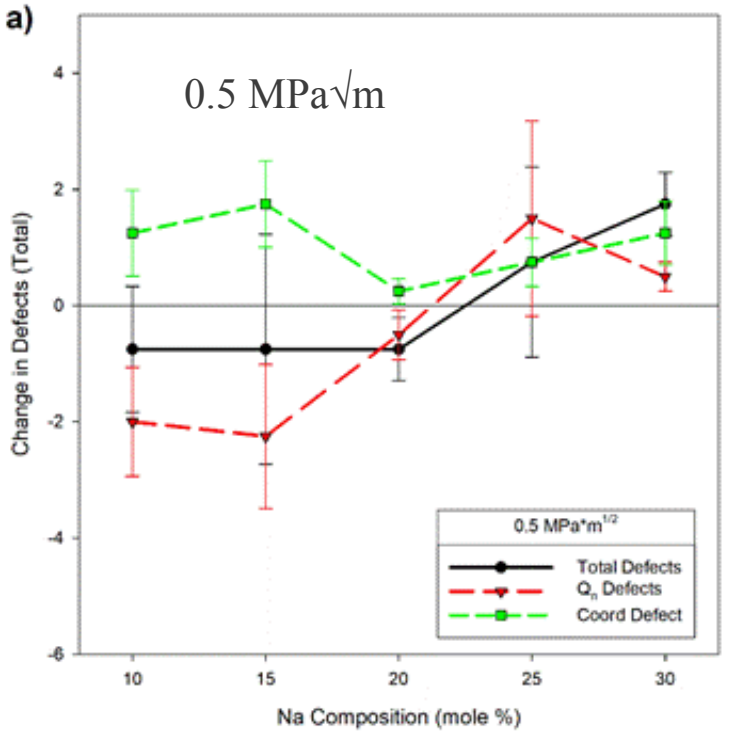
How does the change in defects change with composition?

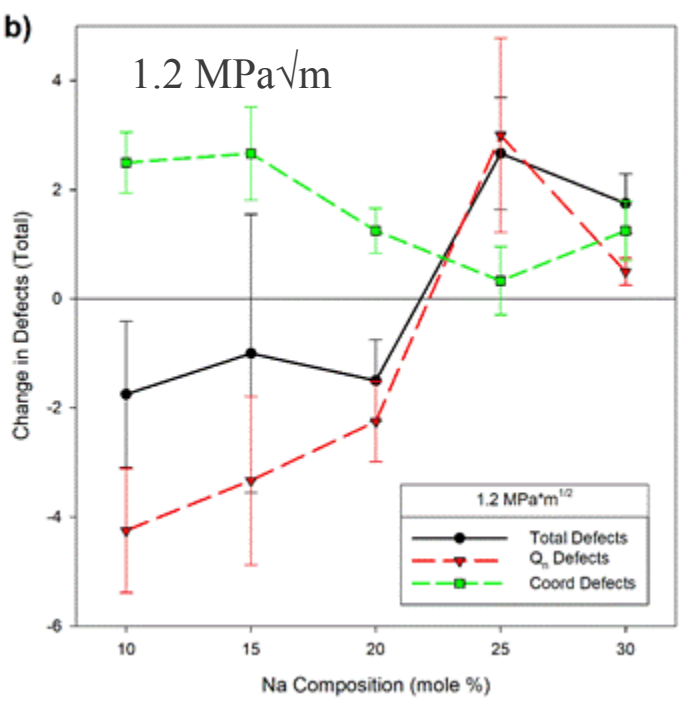
Separate out structural defects by type:

- Q_n Defects: Q_1, Q2, Q_3, Q_5
- Coordination Defects: Si^2, Si^3, non-bridging oxygen (NBO), three-bonded oxygen (TBO)

- For NS10-NS20 the defects cancel each other out (one Q_n defect is removed for each coordination defect formed)
- For NS25-NS30 compositions, both coordination and Q_n defects are introduced for an overall increase in defect concentration despite less formation of surface area

Two different mechanisms? Structural relaxation and sodium migration?





	Total Crack Growth (Å)
NS10	4.60±0.82
NS15	3.95±0.74
NS20	7.02±1.51
NS25	5.67±2.51
NS30	3.15±1.42

Conclusions

- Through continuous scanning with the AFM crack velocities as low as 1x10-11 m/s were measured
- Crack propagation was stepwise, with fracture events dispersed with periods of loading
- Strong humidity dependence is observed, as seen with previous studies
- Classical molecular dynamics modeling also exhibited similar step-wise fracture properties
- Most crack growth occurred for the NS20 simulation, which was also the sodium-silicate composition with the lowest amount of stress dissipation
- Two different energy dissipation mechanisms, one through sodium migration and one through structural rearrangement, are reported
- Elevated structural rearrangement in the NS30 simulation accounted for the high energy dissipation and low amount of fracture growth

Additional information:

- Rimsza, Grutzik, and Jones "Inelastic relaxation in silica via reactive molecular dynamics", (2021) *J. Amer. Ceram. Soc.*
- Rimsza, Jones, and Criscenti, "Mechanisms of fracture in aqueous electrolyte solutions", (2019) *Front. Mater.*
- Rimsza, Jones, and Criscenti. "Chemical effects on subcritical fracture in silica from reactive molecular dynamics simulations", (2018) *J. Geophys. Res.*
- Rimsza, Jones, and Criscenti. "Crack propagation in silica from reactive classical molecular dynamics simulations", (2018) *J. Amer. Ceram. Soc.*

Funding: SNL LDRD Program

jrimsza@sandia.gov

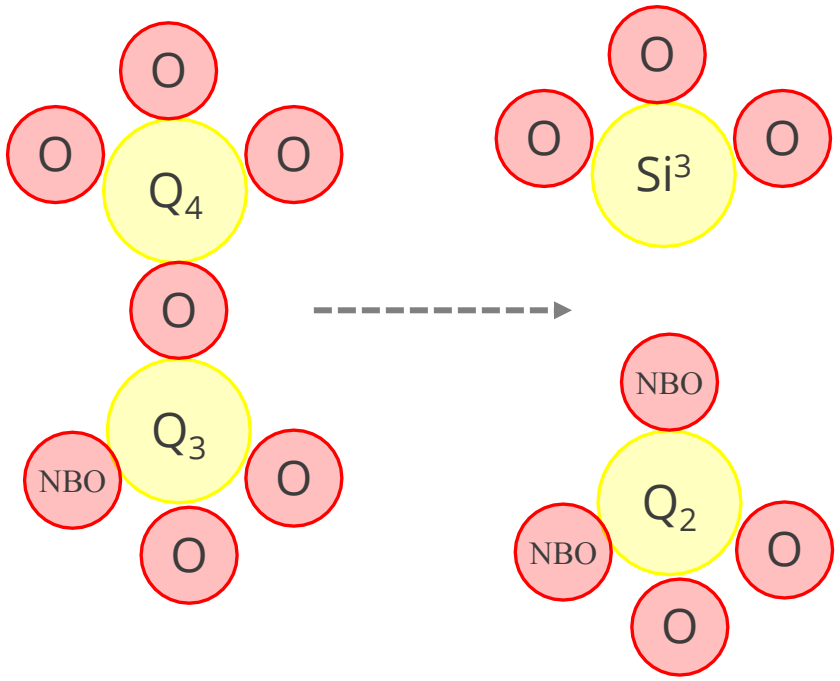
Questions



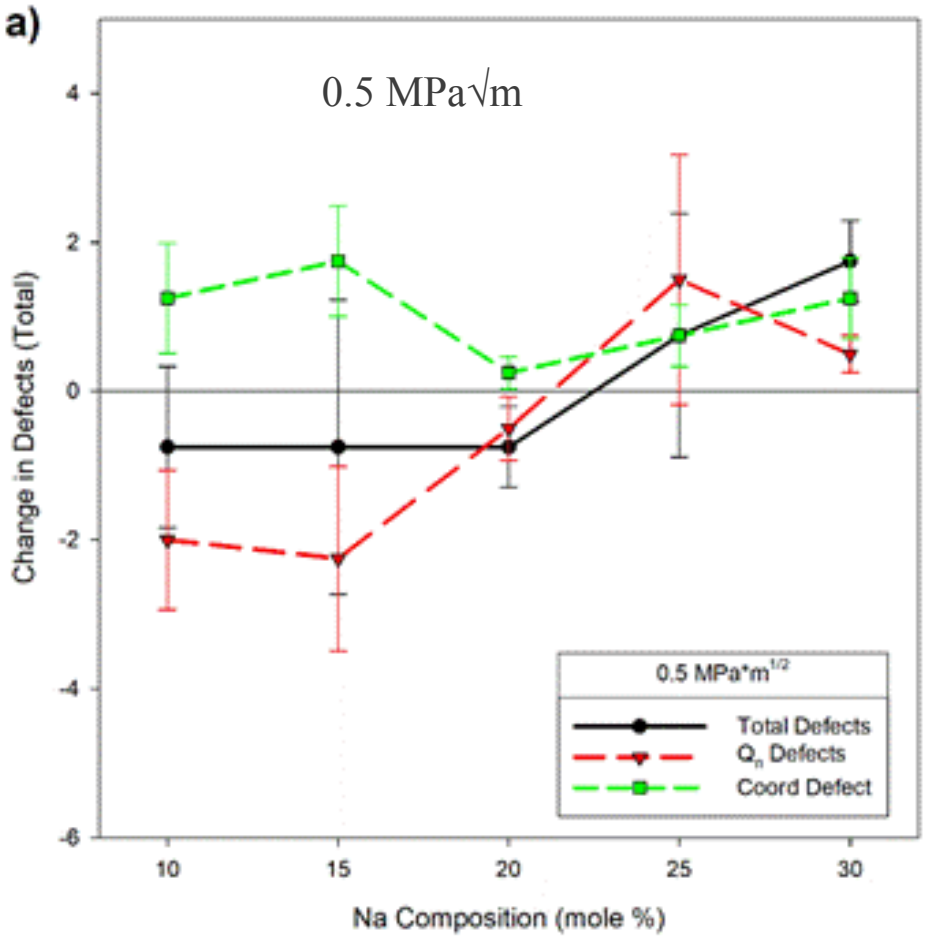

How does the change in defects change with composition?

Separate out structural defects by type:

- Q_n Defects: Q_1, Q2, Q_3, Q_5
- Coordination Defects: Si^2, Si^3, non-bridging oxygen (NBO), three-bonded oxygen (TBO)



- Surface area adds coordination defect and one Q_n defect per each bond breakage event



- For NS10-NS20 the added defects are primarily surface area
- For NS25-NS30 compositions, both coordination and Qn defects are introduced