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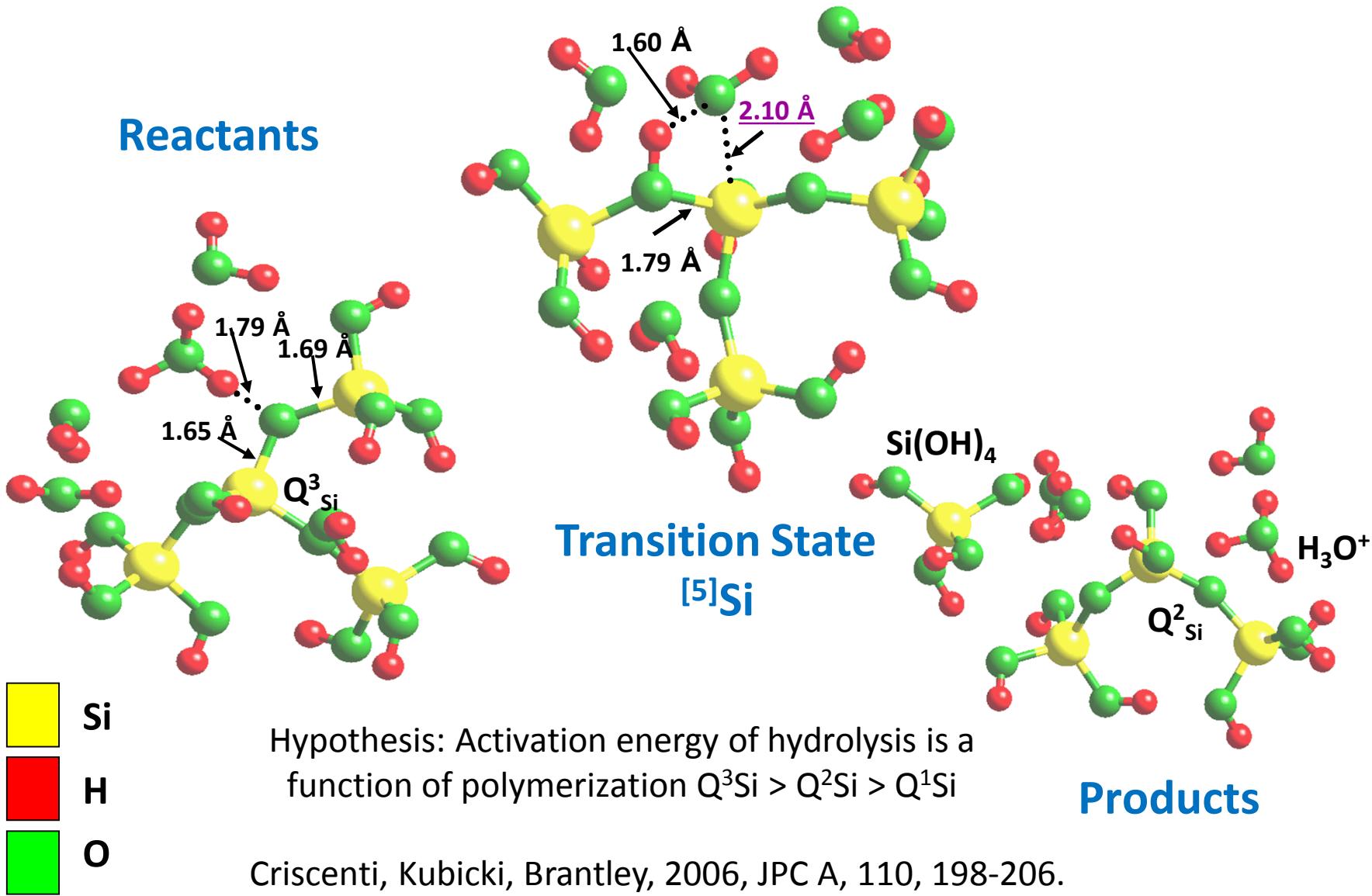
# **Molecular modeling of multicomponent glass and glass surfaces for nuclear waste glass dissolution and glass-to-metal seals applications**

**Louise J. Criscenti**  
**Sandia National Laboratories**  
**ACS Spring 2017**



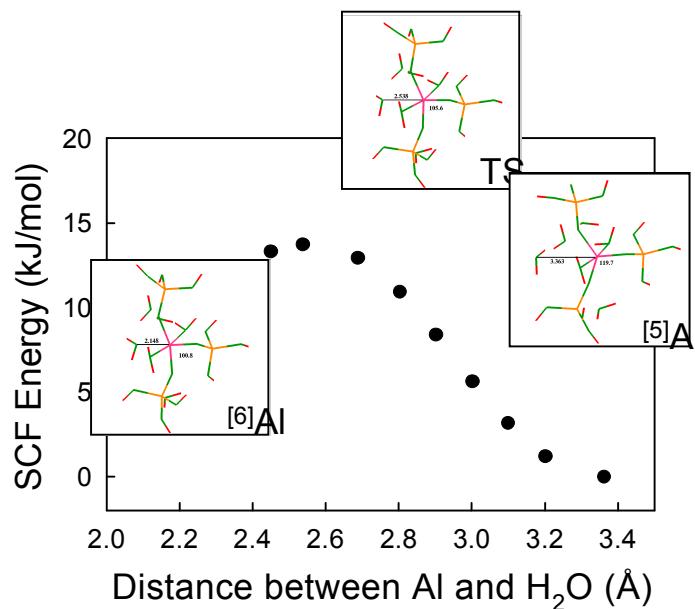
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# Silicate Hydrolysis Reaction: $Q^3\text{Si}$ Cluster



# Al-Si Cluster Energies and $^{27}\text{Al}$ Chemical Shifts

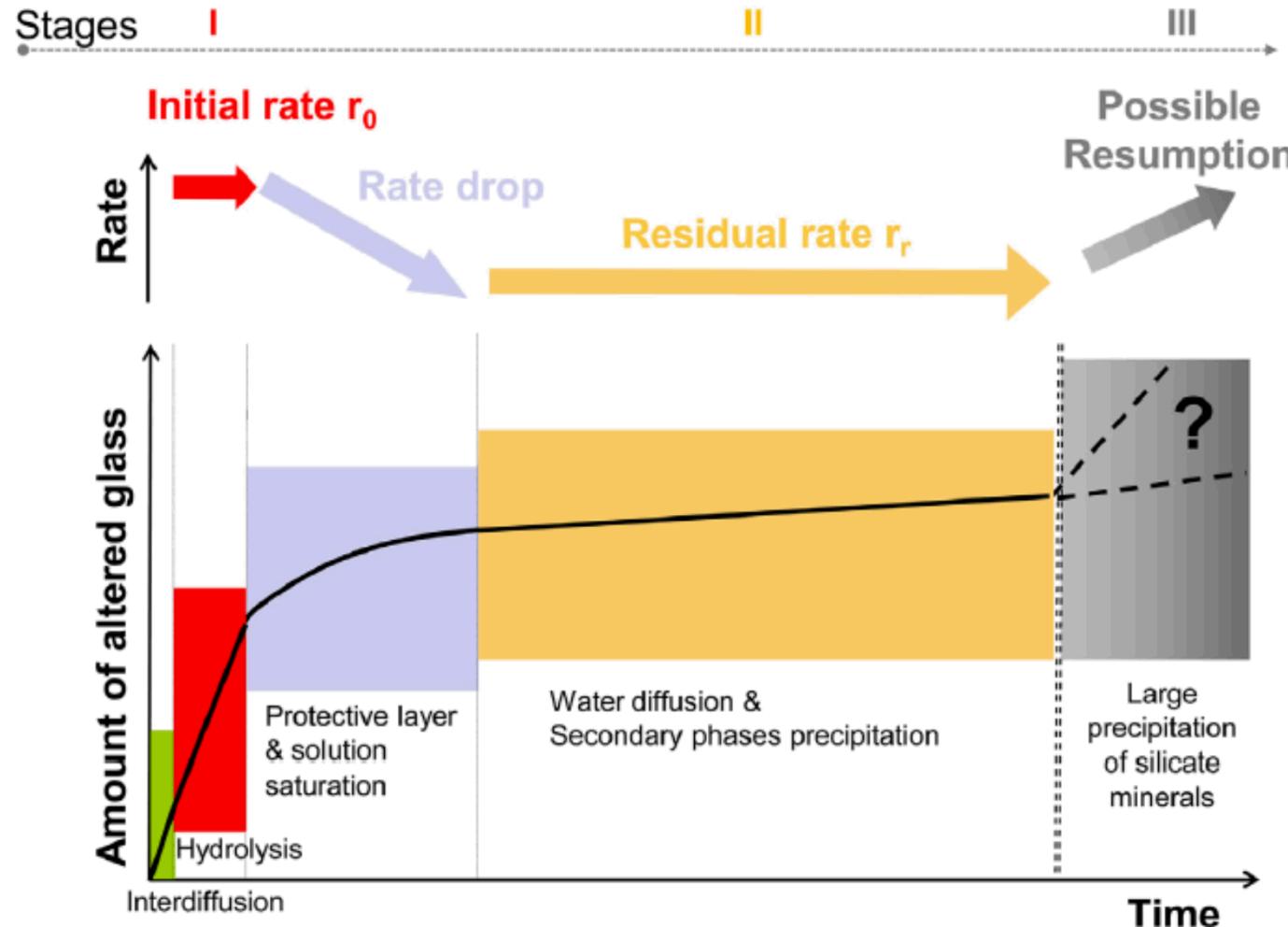
- Coordination change from  $^{[4]}\text{Al}$  to  $^{[6]}\text{Al}$  in feldspar composition crystals and glasses must occur during acidic dissolution (*Hellman et al., 1990*).
- Evidence for  $^{[6]}\text{Al}$  on the surface of some leached aluminosilicates has been observed in NMR spectra (*Hamilton, 1999; Tsomaia et al., 2002*).
- **Hypothesis:** This coordination change takes place at the surface while the Al-tetrahedron is linked to other tetrahedra.
- **Conclusion:** Energy difference between  $\text{Q}^3\text{ }^{[4]}\text{Al}$  and  $\text{Q}^3\text{ }^{[6]}\text{Al}$  linked to three Si-tetrahedra is small enough to allow for the conversion of  $\text{Q}^3\text{ }^{[4]}\text{Al}$  to  $\text{Q}^3\text{ }^{[6]}\text{Al}$  in a hydrated layer of feldspar.



Al CN <sup>a</sup>	CALCULATED		EXPERIMENTAL
	Relative Energy <sup>b</sup> (kJ/mol)	$\delta_{\text{iso}}$	$\delta_{\text{obs}}$
4	20	68	58-63.5 <sup>c</sup>
5	0	37	36 <sup>d</sup>
6	20	13	0-10 <sup>c</sup>

Criscenti, Brantley, Mueller, Tsomaia, Kubicki, 2005, GCA, 69, 2205-2220.

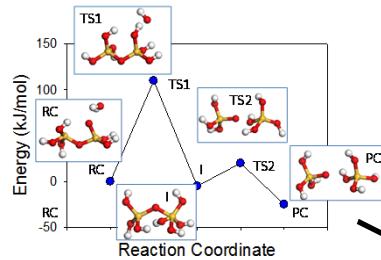
# Nuclear Waste Glass Dissolution



Gin et al., 2013, An international initiative on long-term behavior of high-level nuclear waste glass, Materials Today, 16, 243-248.

# Upscaling: Glass Dissolution Gaps

## Atomic/Quantum

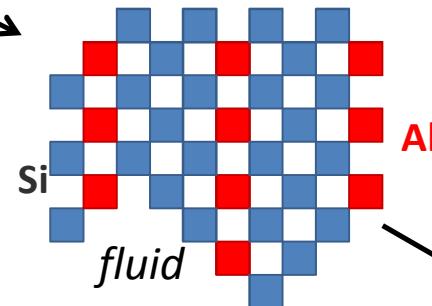


Ab initio (QM/DFT) calculations to determine bond-breaking energies

Stochastic Monte Carlo Modeling of the dissolution and re-precipitation of crystal units  $\text{SiO}_4$  and  $\text{AlO}_4$

## Gap 1 “Mesoscale”

Constitutive equations developed to fit leach data from bulk experiments.

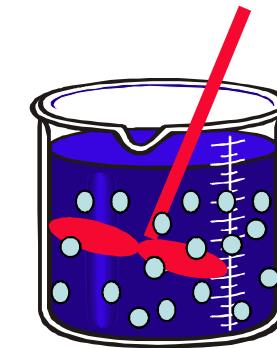


## Continuum

$$r = k \prod_{i=1, i \neq k}^i \left[ \frac{K_i \left( \frac{v_i}{a_{H^+}} \right)^s}{\left( 1 + K_i \left( \frac{v_i}{a_{H^+}} \right)^s \right)} \right]$$

## Gap 2

- ❖ No consensus on how activation energies for bond-breaking should be modeled in QM/DFT calculations
- ❖ Not clear how to go from the energy of breaking one bond to dissolving “crystal units”
- ❖ Mesoscale models are used to test dissolution scenarios – not completely predictive.
- ❖ Not clear how to link mesoscale models directly to continuum models or develop new constitutive equations from them.

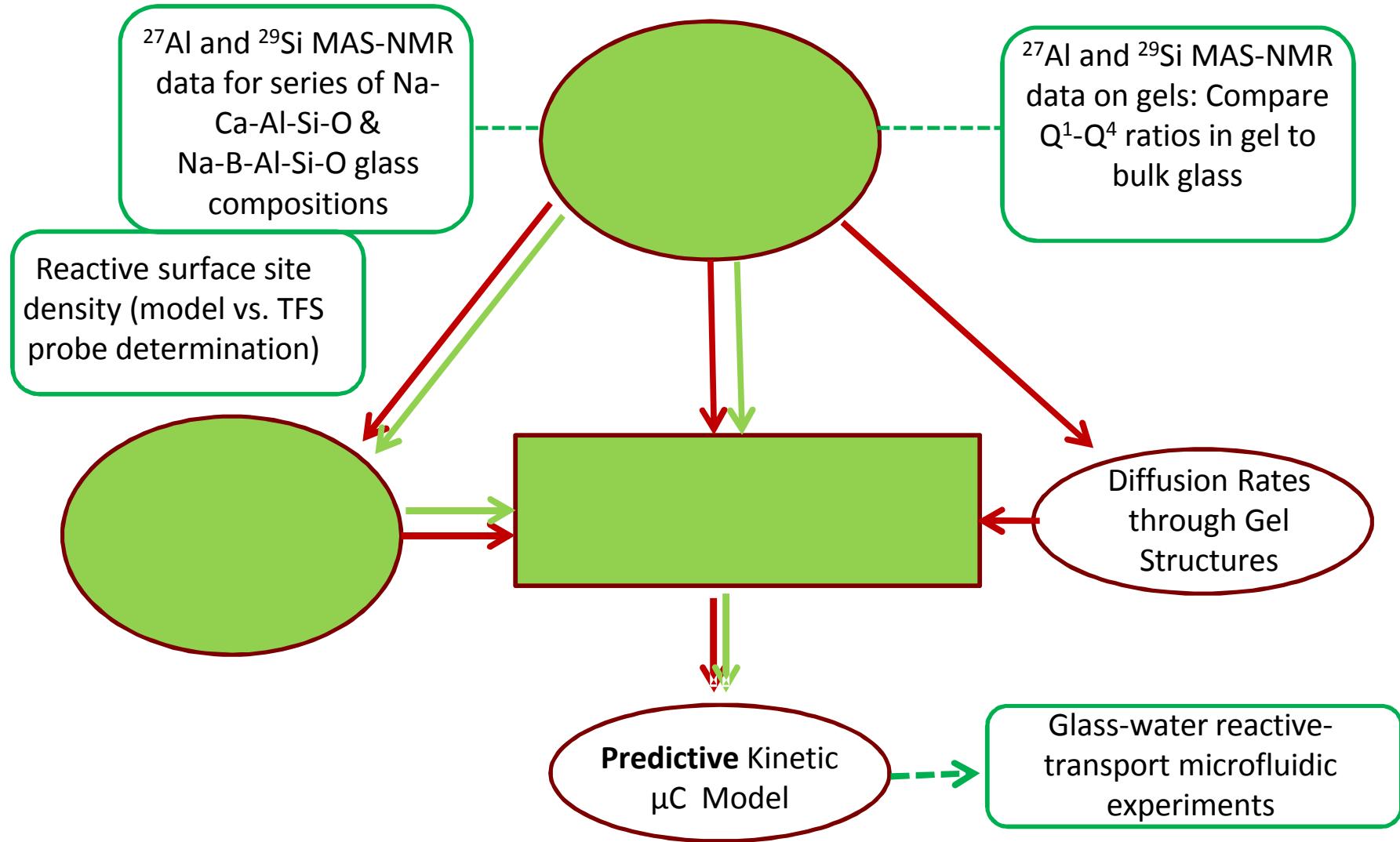


## Gap 3

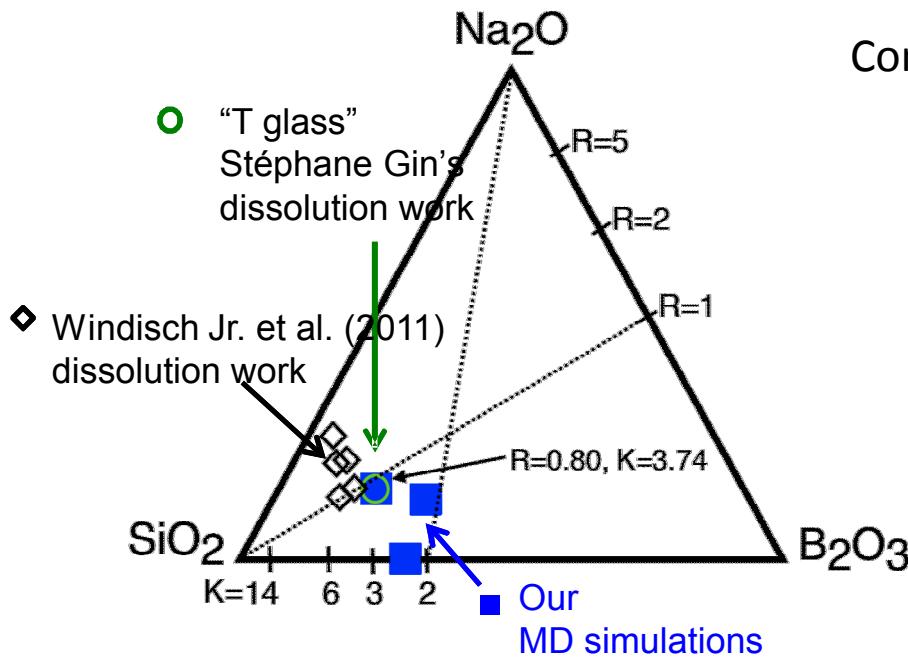
- ❖ Aluminosilicate crystal dissolution → Nuclear Waste Glass Dissolution

Criscenti, L.J. and Sassani, D. 2010. Upscaling Atomistic Mechanisms to Continuum Models for Nuclear Waste Glass Dissolution, FMM NEAMS Project Report/SAND Report 2010-6707P

# Integrated Modeling & Experimental Plan



# Gap 3: Adding Boron to Glass Modeling



Composition-dependent FF (Kieu et al. 2011)

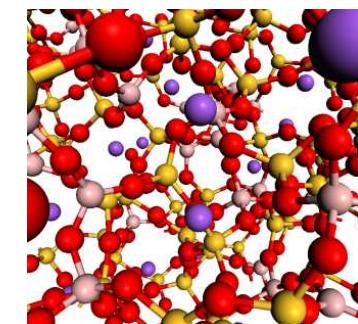
$$U(r_{ij}) = \frac{z_i z_j e^2}{r} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

$$q'_B = -q'_0 \left( C_6 K^2 + \sum_{i=1}^5 C_i R^i + C_0 \right)$$

$$q'_i = q_i - N_B \frac{q'_B - q_B}{N_B + N_O + N_{Na}}, \text{ where } i = Si, O, Na$$

$$R = \frac{[Na_2O]}{[B_2O_3]}, \quad K = \frac{[SiO_2]}{[B_2O_3]}$$

	SiO <sub>2</sub> (mol%)	B <sub>2</sub> O <sub>3</sub> (mol%)	Na <sub>2</sub> O (mol%)	R	K	Density (g/cm <sup>3</sup> )	
						EXP.*	Our MD
SB	69.5	30.5	0	0	2.28	2.04	2.01
SBN12	59.66	28.14	12.20	0.43	2.11	2.37	2.39
SBN14	67.73	18.04	14.23	0.80	3.74	2.45	2.44

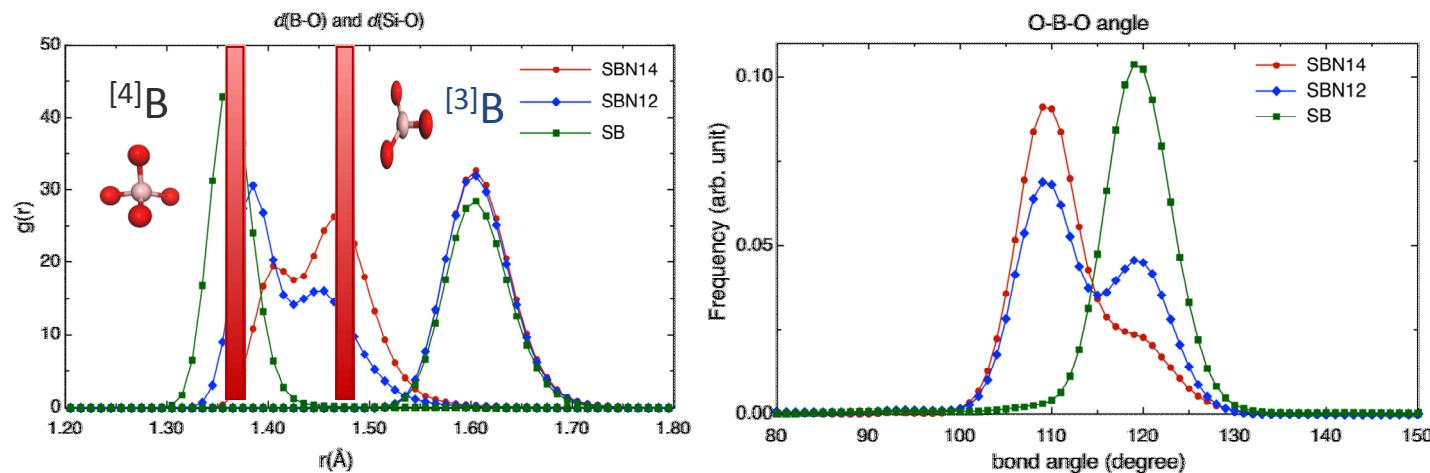


O  
Si  
B  
Na

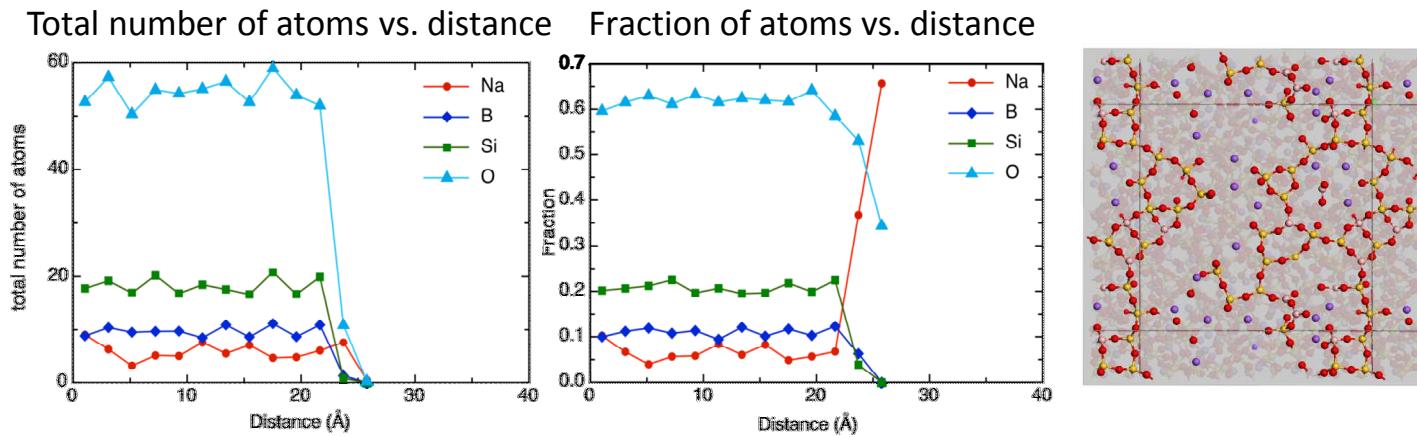
LAMMPS code with  
1,004 or 1,005 atoms

# Molecular Modeling of Na-Borosilicate Glass

Bulk  
Glass



Glass  
Surface  
SBN-14

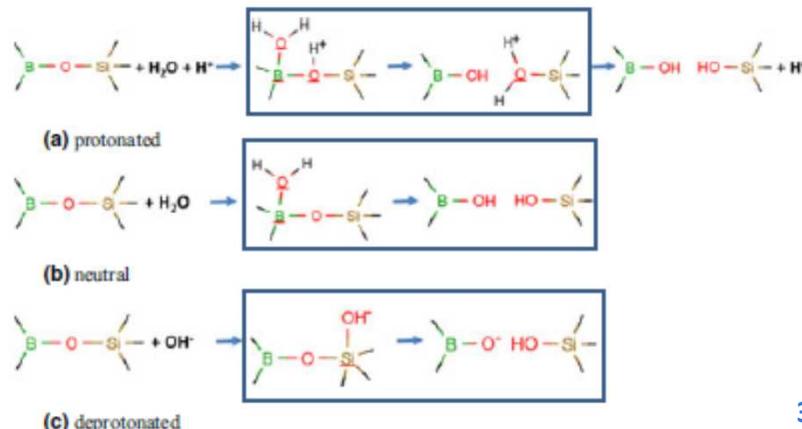


Kwon, K.D. and L.J. Criscenti (2013) Na borosilicate glass surface structures: A classical molecular dynamics simulations study. Journal of the Mineralogical Society of Korea, 26, 119-127.

Pierce et al., 2014. Modeling the Glass-Water Reaction from Interface to Pore-Scale: Recent Advances and Current Limitations, IJAGS, DOI: 10.1111/ijag.12077.

# First Principles Study of Hydrolysis Reaction Barriers in a Na-Borosilicate Glass

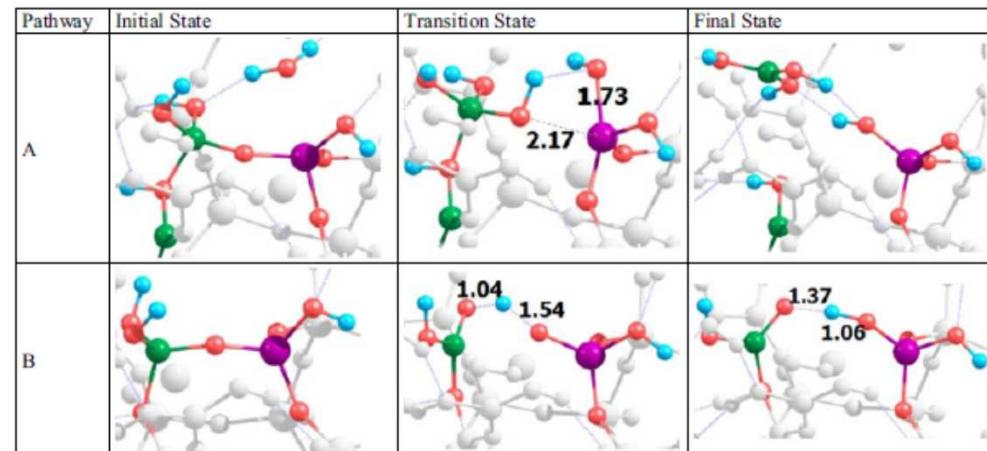
## Hydrolysis reactions at the ${}^3\text{B}-\text{O}-\text{Si}$ bridge



## SUMMARY

- Reaction barriers in acidic conditions for dissolution of B-O-B and B-O-Si bridges are lower than in neutral and basic conditions.
- Barriers for B-O-B and B-O-Si hydrolysis lower than for Si-O-Si hydrolysis in acidic conditions but more similar in basic conditions.

## ${}^3\text{B}(\text{Q}^2)-\text{O}-\text{Si}(\text{Q}^3)$ bridge - deprotonated conditions



## FUTURE WORK

- Reaction energies and barriers may be used to construct constitutive models for the dissolution and alteration of borosilicate glasses
- Fenter et al., GCA, 2014, 598-611 Orthoclase (001)

Zapol, He, Kwon, Criscenti (2013) First-Principles Study of Hydrolysis Reaction Barriers in a Sodium Borosilicate Glass, International Journal of Applied Glass Science, 4, 395-407.

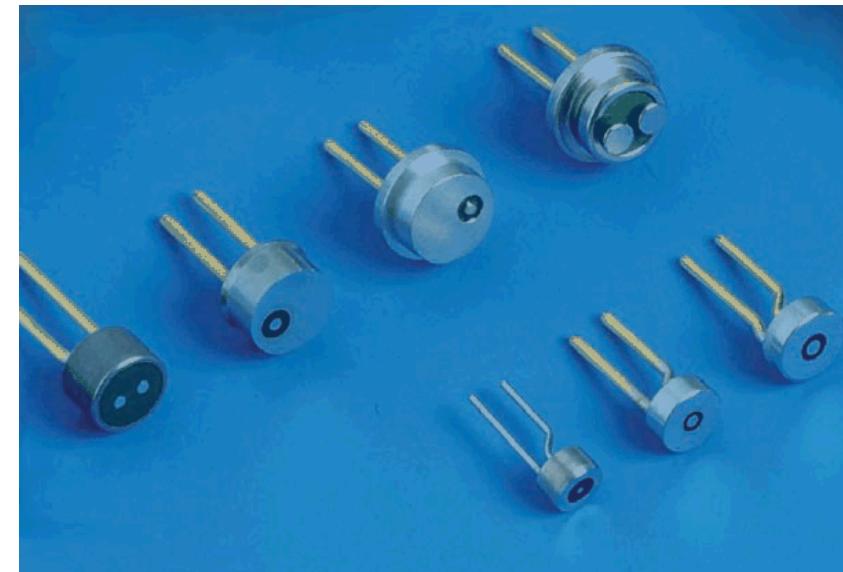
# Glass is Used to Bond/Join Materials

## ■ Glass bonding/joining Applications

- Glass-bonded composites
  - Glass-bonded alumina
  - Low temperature co-fired ceramic (LTCC) electronic packaging
- Seals
  - Hermetic glass to metal (GtM) seals
    - Air bags “motors”
    - Medical implants
    - Microelectronics
  - Energy conversion
    - Solid oxide fuel cells (SOFCs)
    - Concentrated solar



Feedthroughs for  
pressure & flow sensors  
(Schott Electronic Packaging)



Airbag igniter feedthroughs  
(Schott Electronic Packaging)

# Glass-Metal Interface

- To design/develop advanced filled glass composites.
- To develop experimentally-validated modeling/simulation tools to predict glass chemistry-structure-property relations.

## Approach

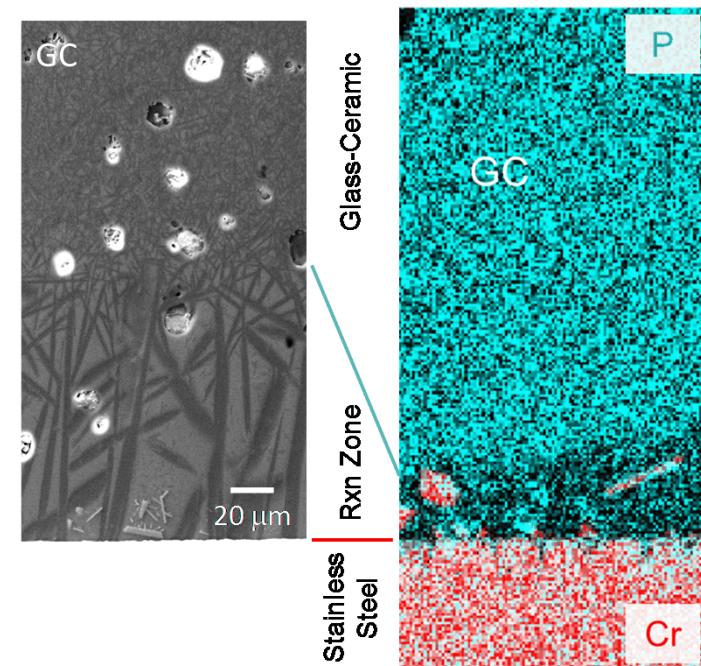
Characterize & model glass chemistry-structure-property relations

In a simple/model 3-component barium alumino-silicate (BAS) glasses

In more complex, commercial-like 6-7 component glasses

Test, refine, & validate modeling/simulation by comparison to experiment

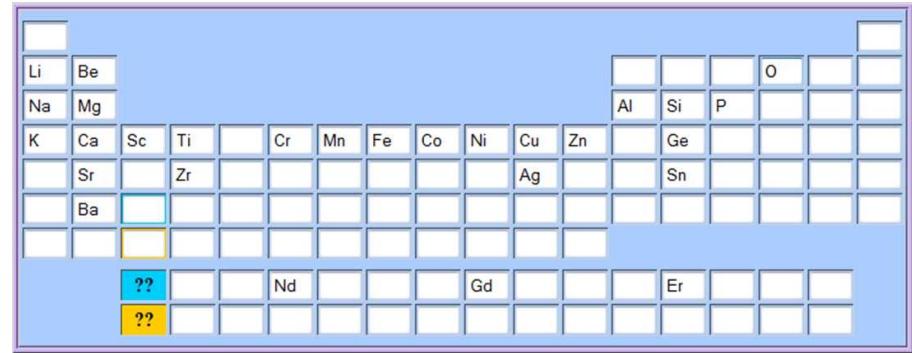
Characterize & model glass chemistry-structure-property relations at interfaces



# Molecular Dynamics Simulation Methods I

- Classical Molecular Dynamics
- Simulation Cell Size:
  - 3000 for 3-component glasses
  - 12000 for 6-7 component glasses
- LAMMPS\* MD software
- Pedone\*\* Interatomic Potentials used because parameters available for multi-component glasses like those used commercially.
- $$U(r) = \frac{z_i z_j e^2}{r} + D_{ij} \left[ \left\{ 1 - e^{-a_{ij}(r-r_0)} \right\}^2 - 1 \right] + \frac{C_{ij}}{r^{12}}$$

Long-range Coulomb	Short-range Morse	Repulsive Contribution
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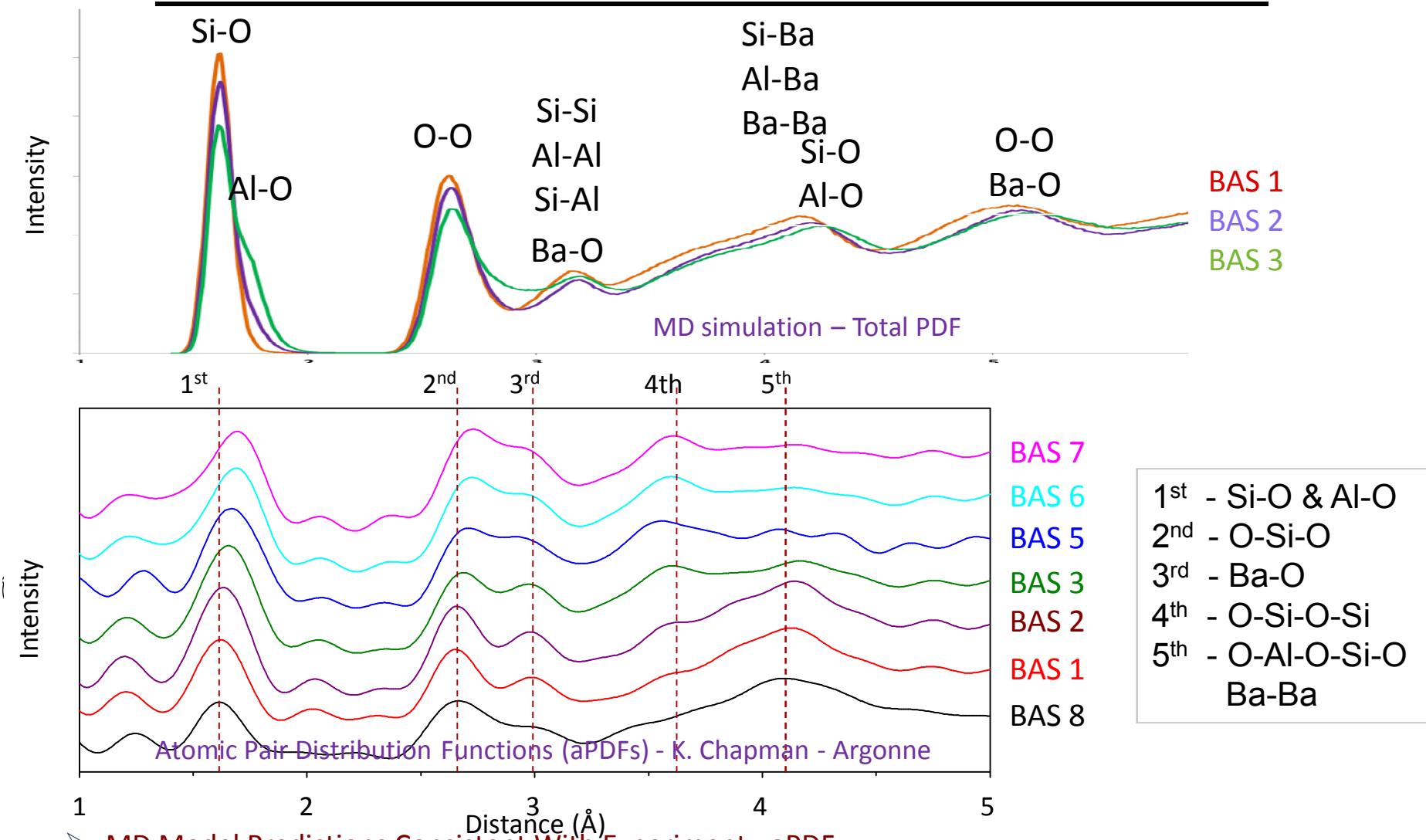


Glass	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	BaO/CaO
BAS1	75	0	25
BAS2	70	5	25
BAS3	60	15	25
BAS8	66.7	0	33.3
CAS1	75	0	25
CAS2	70	5	25
CAS3	60	15	25

\*S Plimpton, "Fast Parallel Algorithms for Short-Range Molecular-Dynamics", *J Comp Phys*, **117** [1], 1-19 (1995).

\*\*A Pedone et al., "A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses", *J Phys Chem B*, **110**, 11780-11795 (2006).

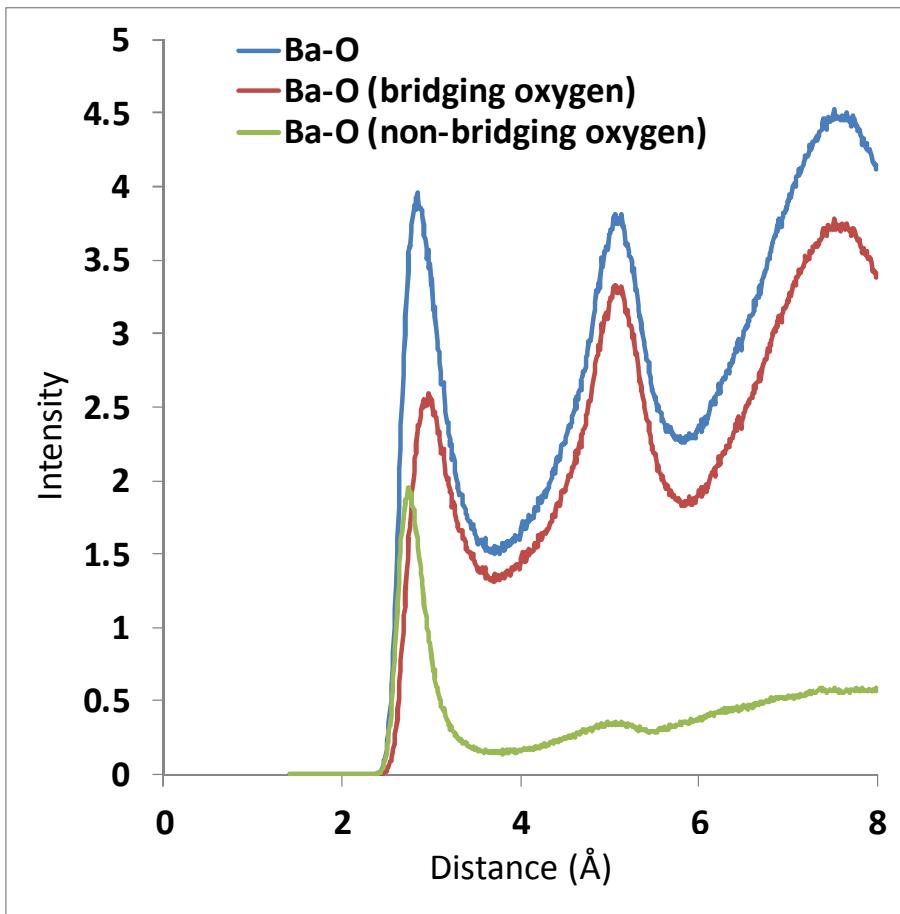
# Measured aPDF Peaks Are Consistent With Nearest Neighbor (NN) Distances From MD Simulations



- MD Model Predictions Consistent With Experiment - aPDF
- Modeling Captures Structural Detail Not Possible Experimentally

# Ba-O Distances

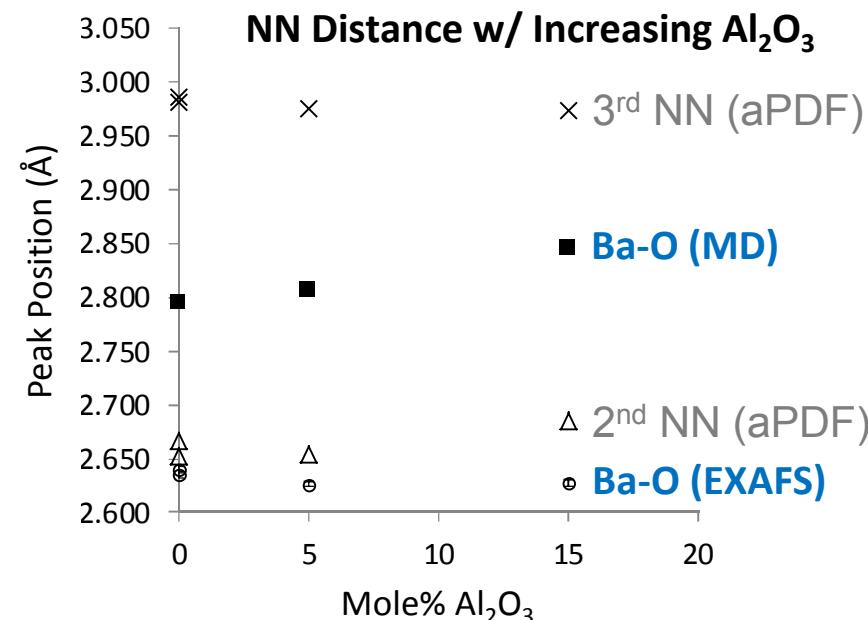
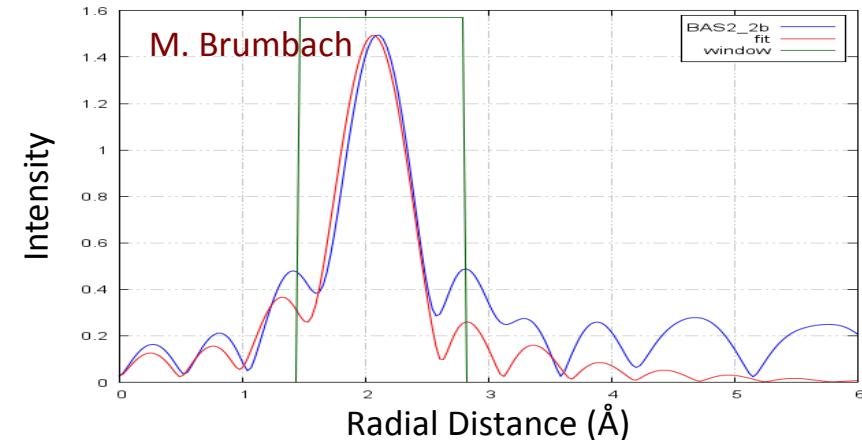
MD pair distribution function



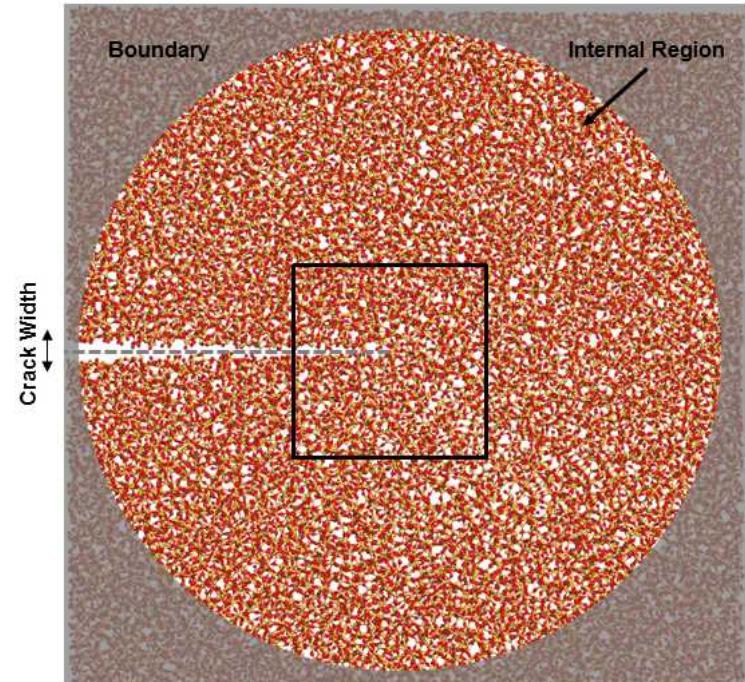
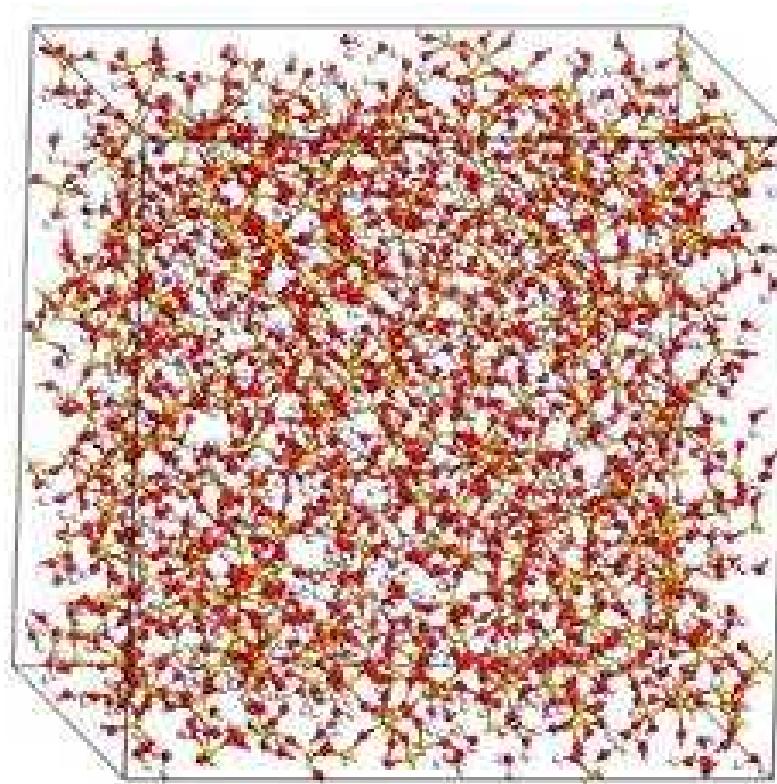
- Ba creates NBOs
- MD & experiment indicate poorly-defined CNs

*Rai and Mountjoy (2014) Ba-O = 2.79 Å*

Uncorrected EXAFS Radial distribution function



# Ongoing Work: Silica Gel and Fracture Modeling



Rimsza and Du, in press, Langmuir

Rimsza et al. (this afternoon)!

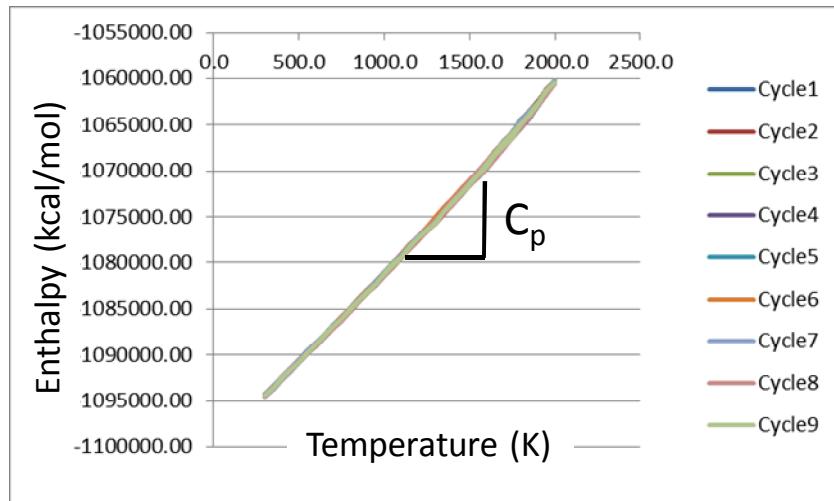
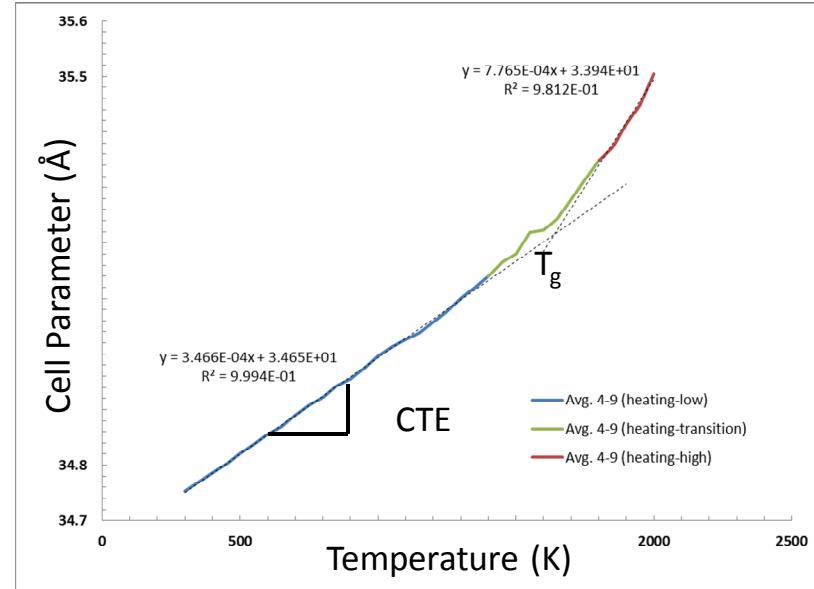
# Acknowledgments

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- Peter Schultz, David Sassani (Sandia National Laboratories)
- Kevin Ewsuk, Todd Alam, Todd Zeitler, Michael Brumbach, Mark Rodriguez (SNL)
- Jincheng Du (UNT)

**THANKS SUE!!**

# Molecular Dynamics Simulation Methods II

- Glass created:
  - Based on desired composition
  - Through a typical melt-quench process (NVT, NVE) \*Xiang, Y. et al. 2013
- Structural data includes:
  - Radial distribution functions
  - Bond angle distributions
  - $Q^n$  distributions ( $Q = \text{Al}$  or  $\text{Si}$ ;  $n = \text{number of bridging oxygens}$ )
- Property calculations:
  - Coefficient of thermal expansion (CTE) calculated from heating and cooling cycles under the NPT ensemble. \*\*Stechert et al. 2012
  - Heat capacity calculated as slope of enthalpy vs. temperature from same heating/cooling simulations.

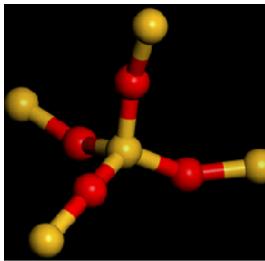


\*Xiang, Y. et al. "Structure and properties of sodium aluminosilicate glasses from molecular dynamics simulations", *J. Chem. Phys.*, **139**(7), 044507 (2013).

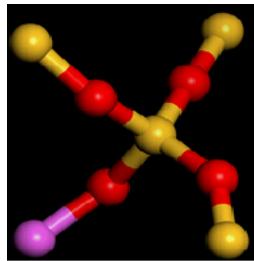
\*\*Stechert, T.R. et al. "Predicted structure, thermo-mechanical properties and Li ion transport in LiAlF<sub>4</sub> glass", *J. Non-Crystalline Solids*, **358**, 1917-1923, (2012).

# $^{29}\text{Si}$ MAS-NMR $Q_3$ & $Q_4$ Peaks Are Accurately Predicted From MD Coordinates, But The $Q_3$ : $Q_4$ Ratio Differs

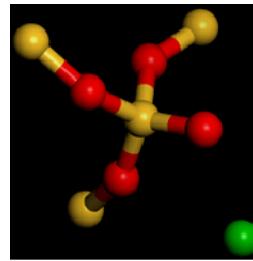
$\text{Si}(\text{OSi})_4$   
 $\delta = -102.1$  ppm



$\text{Si}(\text{OSi})_3\text{Al}$   
 $\delta = -74.4$  ppm



$\text{Si}(\text{OSi})_3\text{Ba}$   
 $\delta = -92.5$  ppm



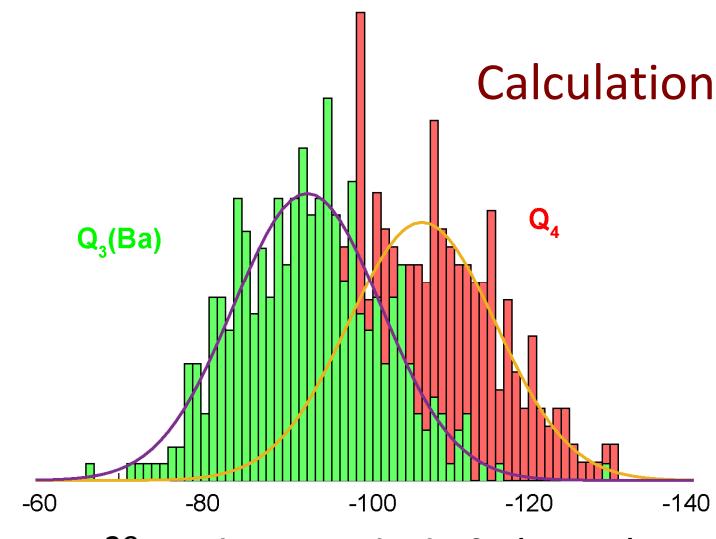
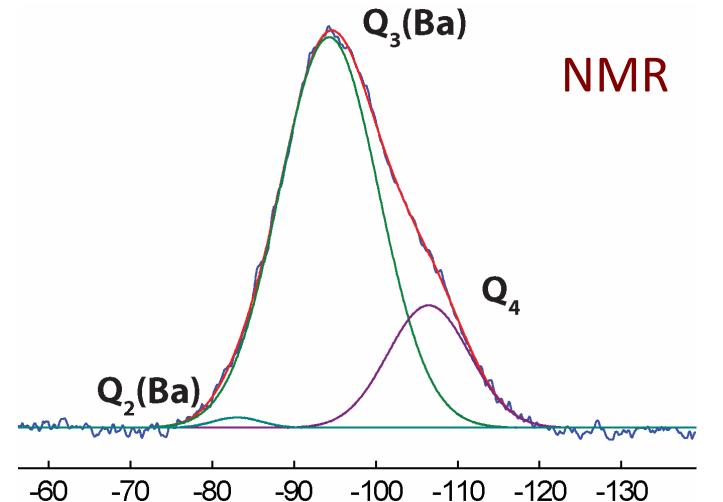
- Calculated  $^{29}\text{Si}$  chemical shifts using MD coordinates.
- Employed correlation from Sherrif et al. (1991) based on silicate mineral structures.
- Factors included bond valence ( $s_i$ ), angle of the bridging oxygen, Si-O bond distance, and distance to the 2<sup>nd</sup> nearest neighbors.

$$s_i = \left( \exp \left[ (r_0 - r_i) / 0.37 \right] \right)$$

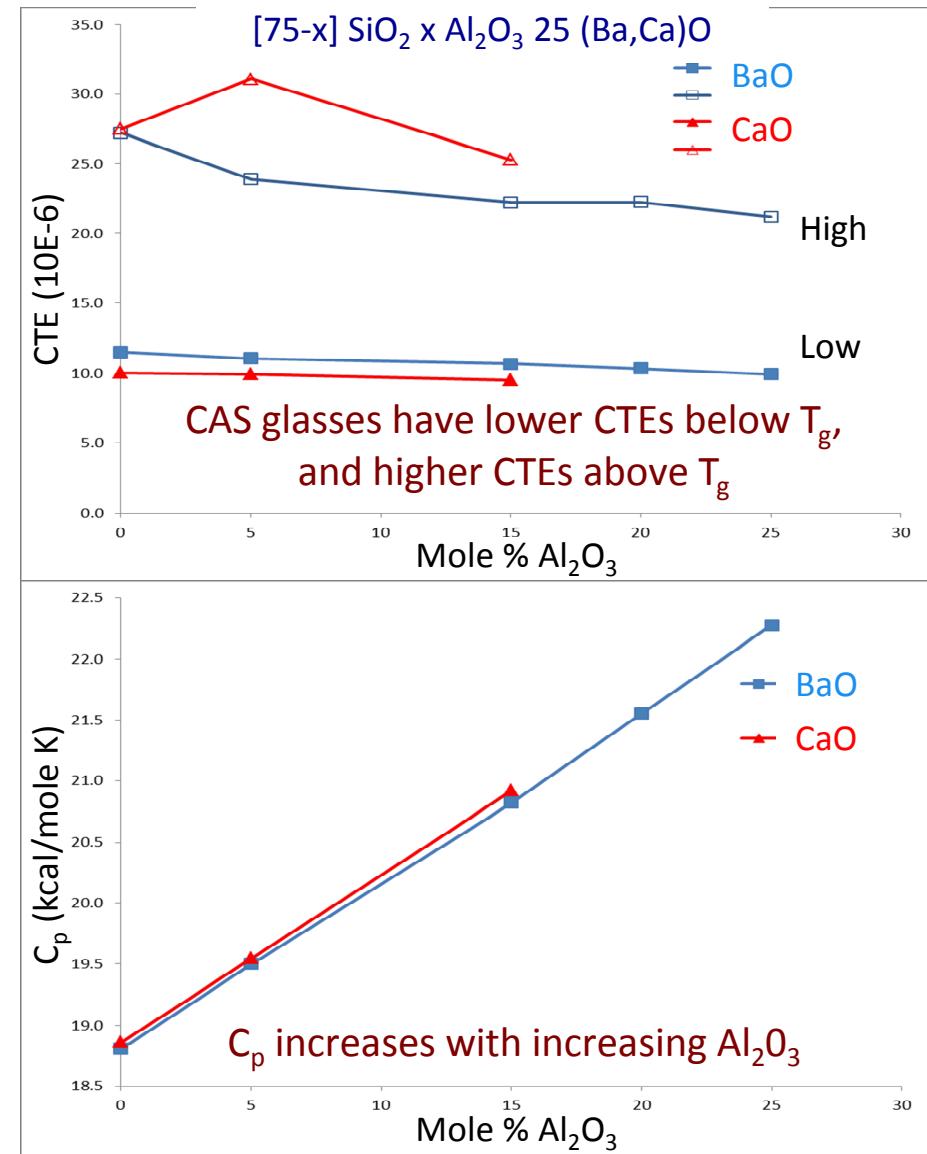
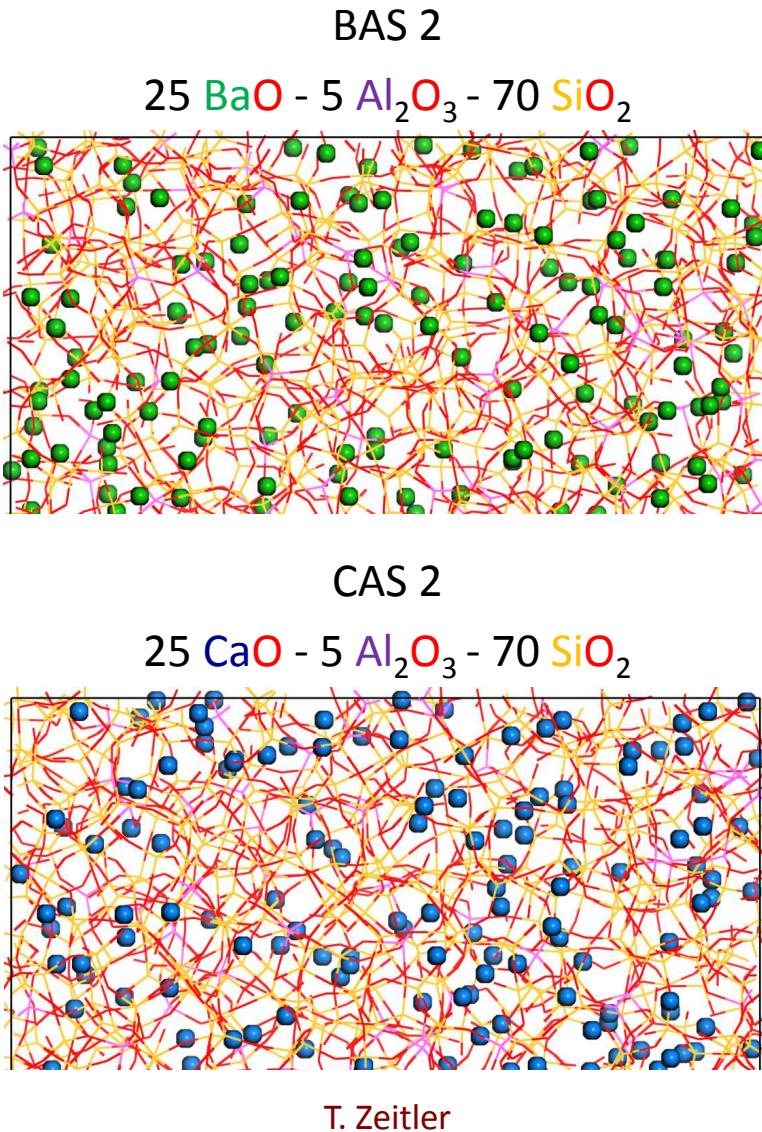
$$\Omega = \sum_{i=1}^N \left[ s_i \left( 1 - 3 \cos^2 \theta_i \right) / 3R_i^3 \right] \log D_i$$

$$\delta(^{29}\text{Si}) = 701.6\Omega - 45.7$$

T. Alam



# Simulated BAS And CAS Glasses Have Similar But Different Structures And Properties



- **Glass Structure & Properties Can Be Modeled With MD Code and the Pedone FF**
  - Good first-order agreement between experiment & model structures
  - Good agreement between experiment & model densities
  - Modeling is an efficient means to assess chemistry-structure relations
- **There is Room for Improvement in Modeling & Experiment**
  - Differences between modeling and experiment suggest room to improve potentials
  - Property predictions are challenging, and may be limited to predicting trends
  - Modeling low concentration constituents in the bulk is not practical
  - Modeling Interface segregation may be a practical approach for surface active elements
  - Enhanced experimental technique & analysis are needed to test/validate modeling

Acknowledgement: Funded by Sandia National Laboratories, Laboratory Directed Research and Development (LDRD) Program.