

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

Louise J. Criscenti

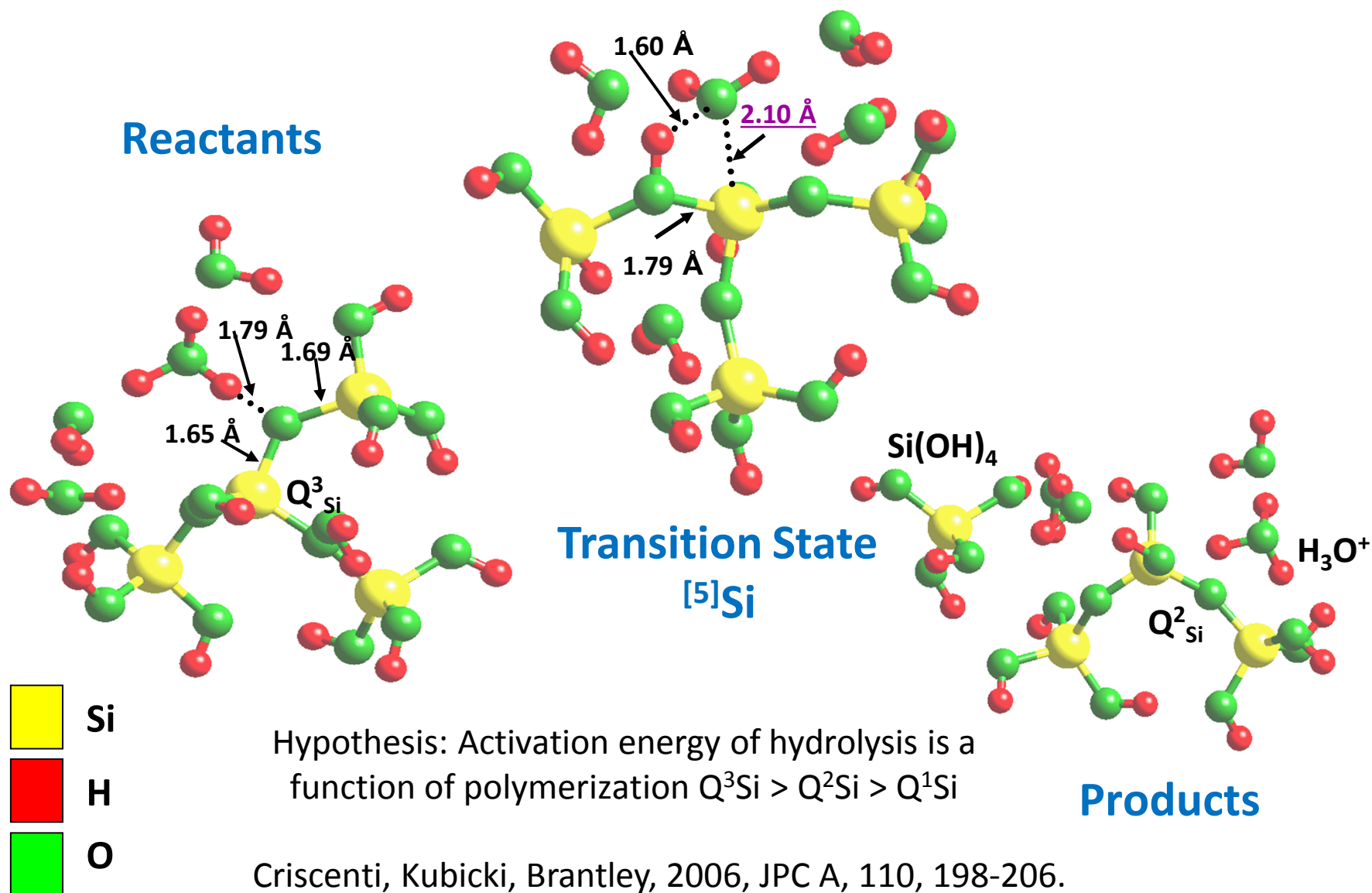
Sandia National Laboratories

ACS Spring 2017



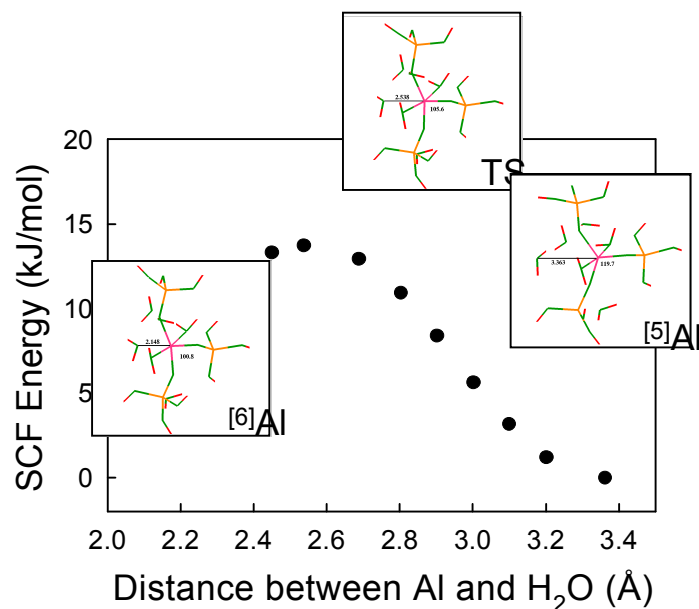
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Silicate Hydrolysis Reaction: Q^3_{Si} Cluster



Al-Si Cluster Energies and ^{27}Al Chemical Shifts

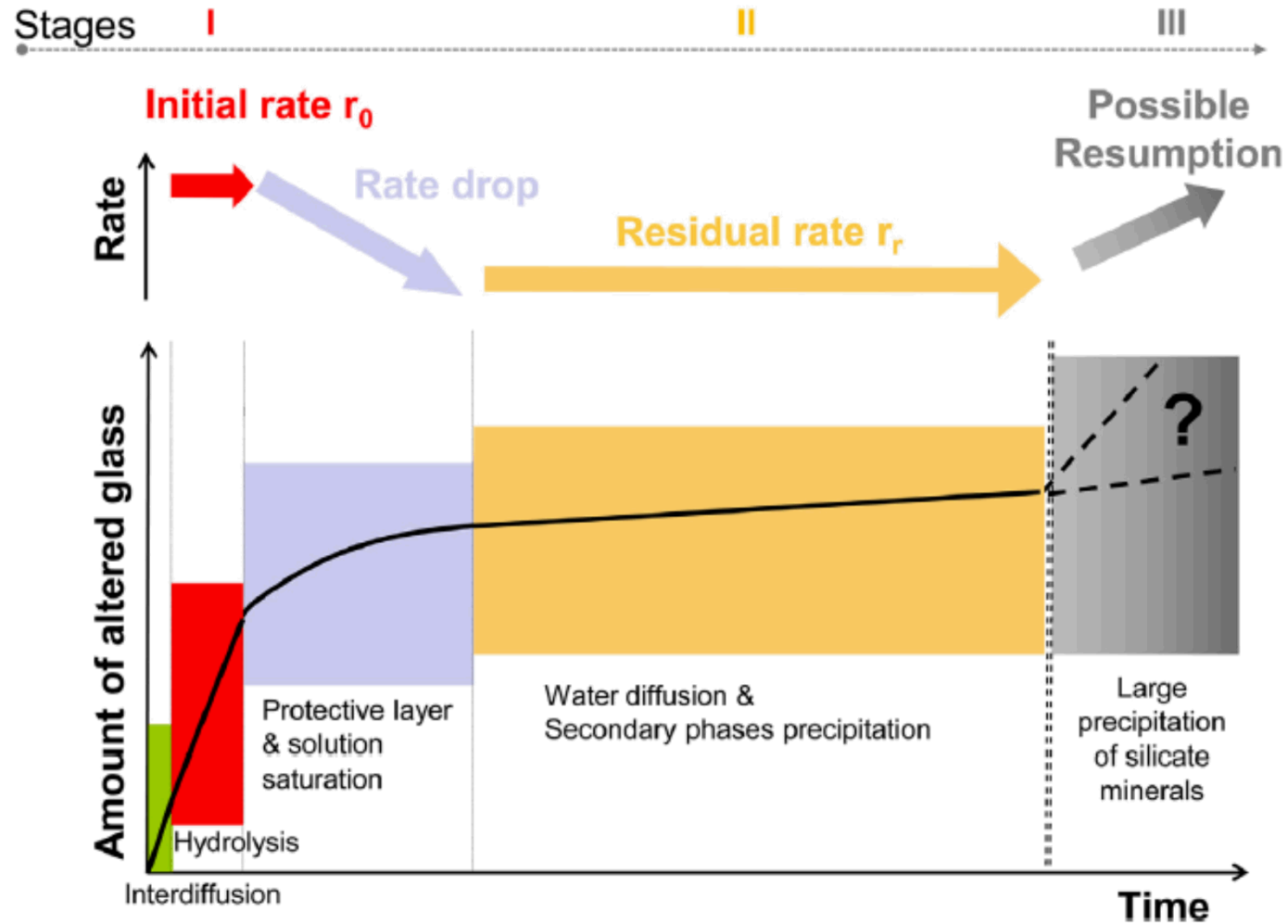
- Coordination change from $^{[4]}\text{Al}$ to $^{[6]}\text{Al}$ in feldspar composition crystals and glasses must occur during acidic dissolution (*Hellman et al., 1990*).
- Evidence for $^{[6]}\text{Al}$ on the surface of some leached aluminosilicates has been observed in NMR spectra (*Hamilton, 1999;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



	CALCULATED		EXPERIMENTAL
Al CN ^a	Relative Energy ^b (kJ/mol)	δ_{iso}	δ_{obs}
4	20	68	58-63.5 ^c
5	0	37	36 ^d
6	20	13	0-10 ^c

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

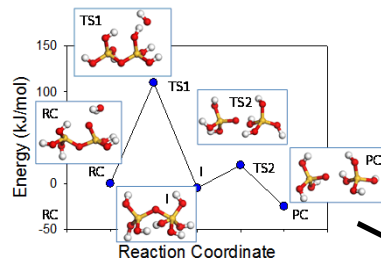
Nuclear Waste Glass Dissolution



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

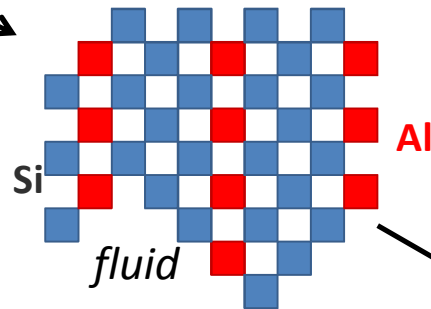


Stochastic Monte Carlo
Modeling of the dissolution
and re-precipitation of
crystal units SiO_4 and AlO_4

Constitutive equations
developed to fit leach
data from bulk
experiments.

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

Gap 1 "Mesoscale"



Continuum

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

Gap 1

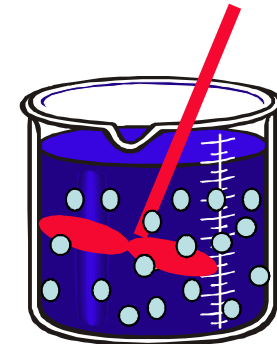
- ❖ No consensus on how activation energies for bond-breaking should be modeled in QM/DFT calculations
- ❖ Not clear how to go from the energy of breaking one bond to dissolving "crystal units"

Gap 2

- ❖ 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.

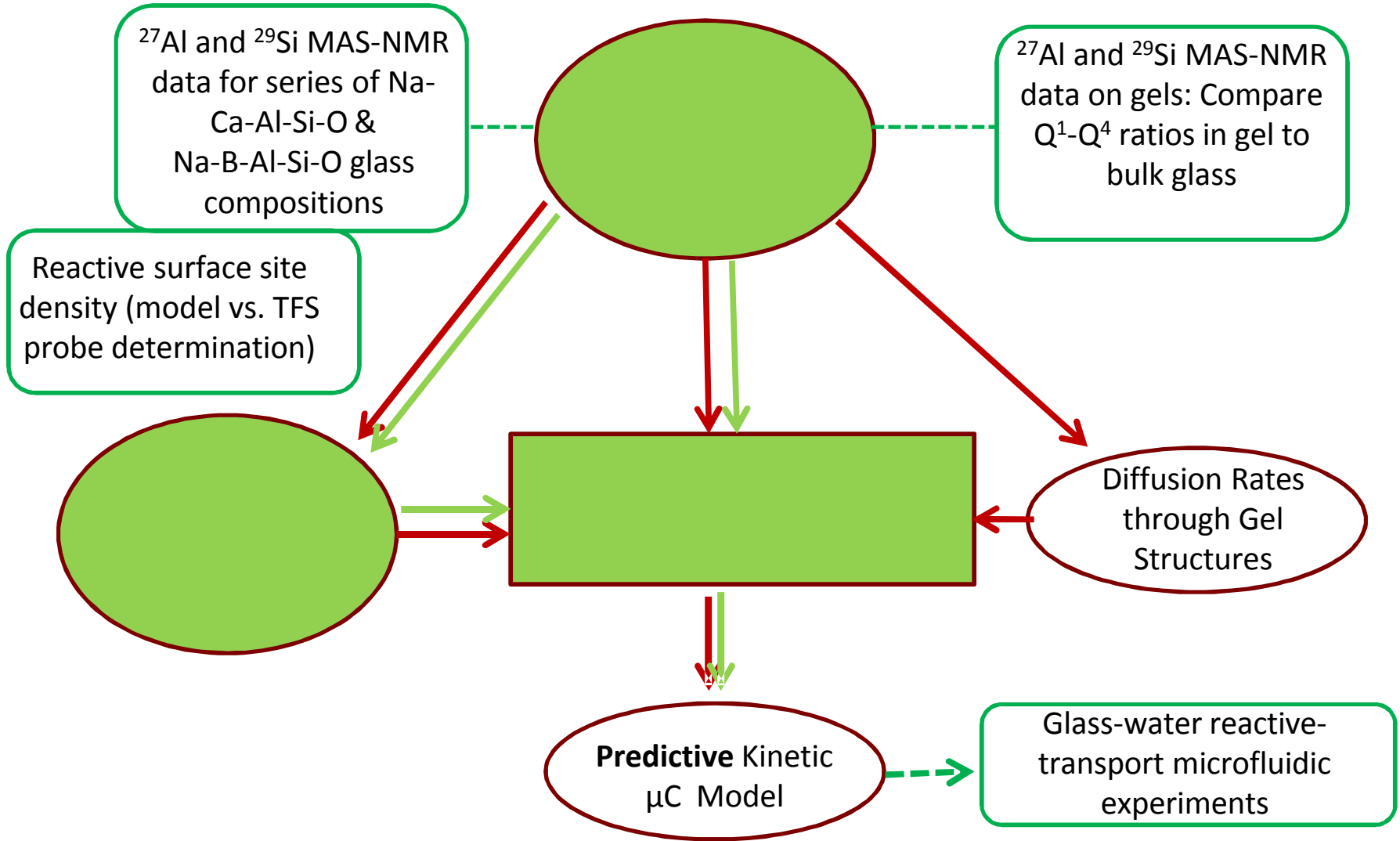
Gap 3

- ❖ Aluminosilicate crystal dissolution → Nuclear Waste Glass Dissolution



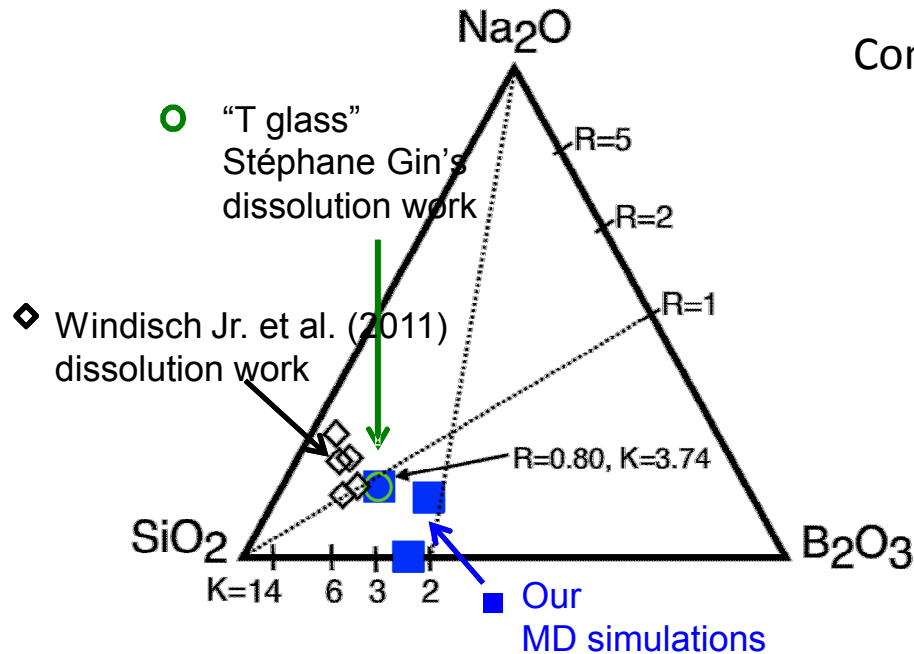
Criscenti, L.J. and Sassani, D. 2010. Upscaling Atomistic Mechanisms to Continuum Models for Nuclear Waste Glass Dissolution, FMM NEAMS Project Report/SAND Report 2010-6707P

Integrated Modeling & Experimental Plan



Criscenti et al. 2011, Progress toward Bridging from Atomistic to Continuum Modeling to Predict Nuclear Waste Glass Dissolution, SAN2011-8250.

Gap 3: Adding Boron to Glass Modeling



Composition-dependent FF (Kieu et al. 2011)

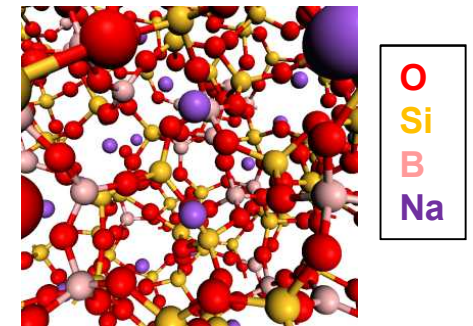
$$U(r_{ij}) = \frac{z_i z_j e^2}{r} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

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

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

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

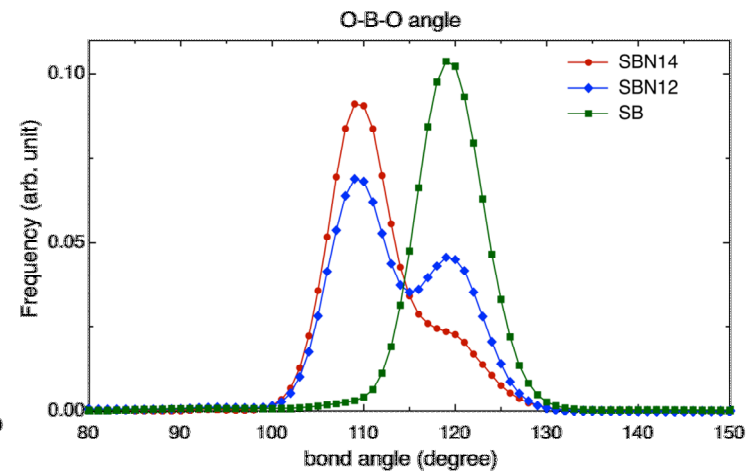
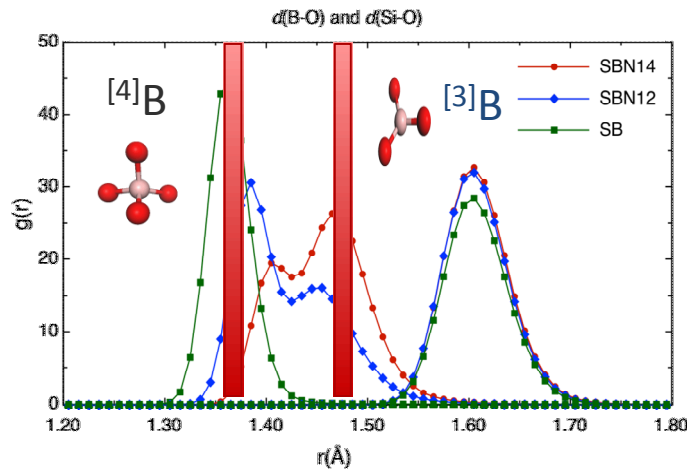
	SiO ₂ (mol%)	B ₂ O ₃ (mol%)	Na ₂ O (mol%)	R	K	Density (g/cm ³)	
						EXP.*	Our MD
SB	69.5	30.5	0	0	2.28	2.04	2.01
SBN12	59.66	28.14	12.20	0.43	2.11	2.37	2.39
SBN14	67.73	18.04	14.23	0.80	3.74	2.45	2.44



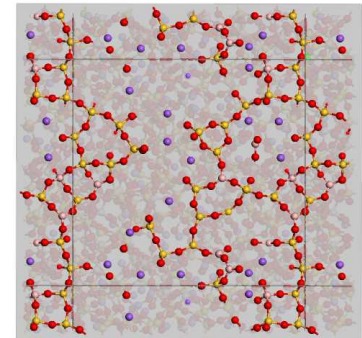
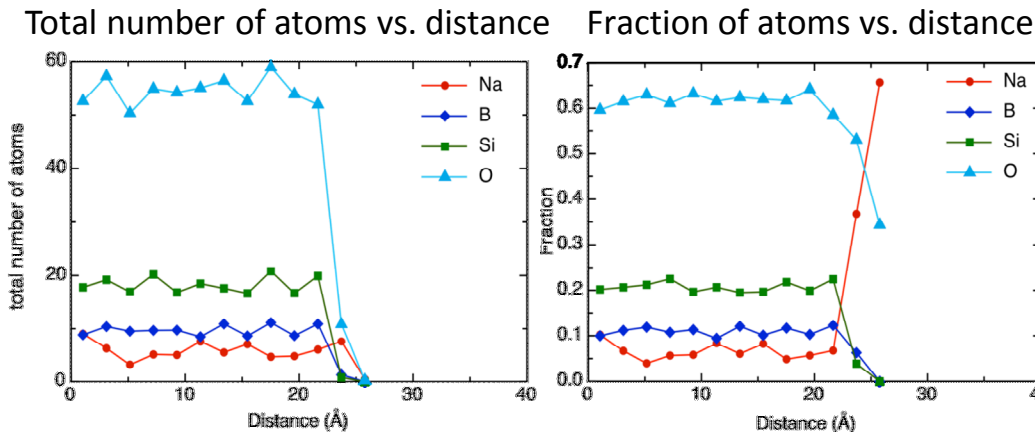
LAMMPS code with
1,004 or 1,005 atoms

Molecular Modeling of Na-Borosilicate Glass

Bulk
Glass



Glass
Surface
SBN-14

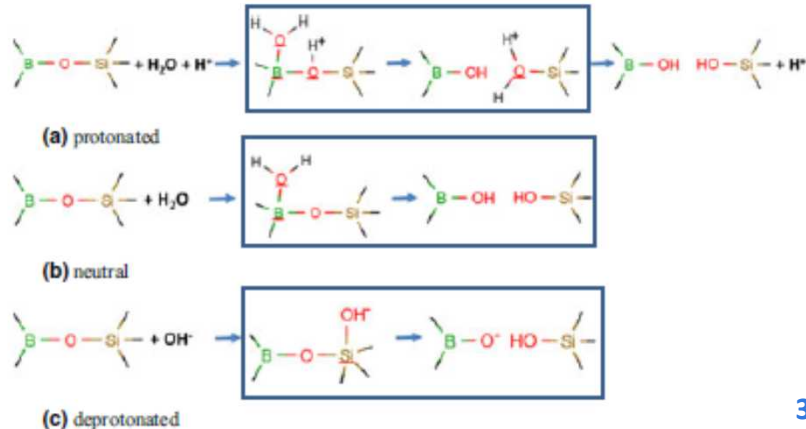


Kwon, K.D. and **L.J. Criscenti** (2013) Na borosilicate glass surface structures: A classical molecular dynamics simulations study. Journal of the Mineralogical Society of Korea, 26, 119-127.

Pierce et al., 2014. Modeling the Glass-Water Reaction from Interface to Pore-Scale: Recent Advances and Current Limitations, IJAGS, DOI: 10.111/ijag.12077.

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

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



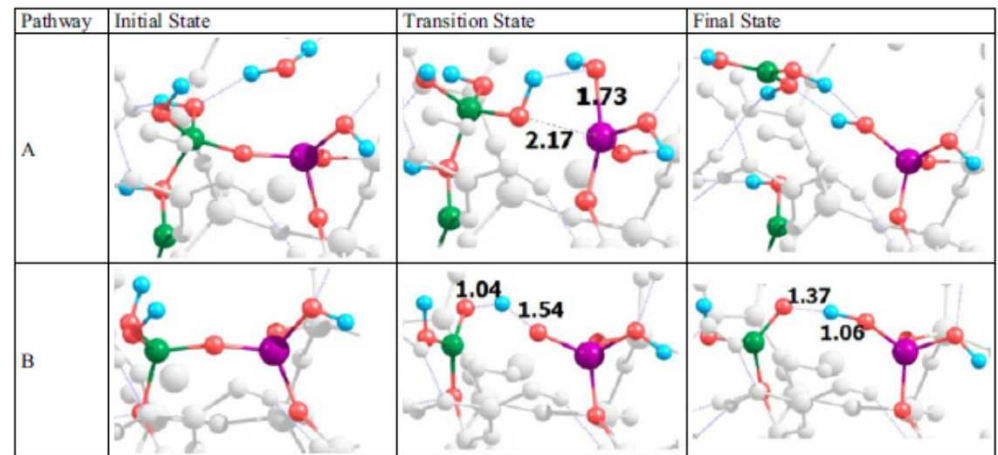
SUMMARY

- 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.

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)

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



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

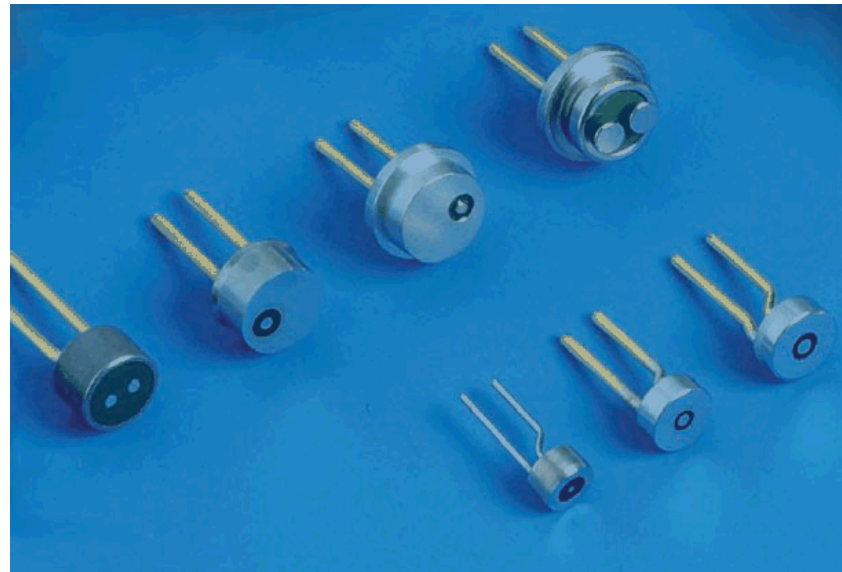
- Air bags “motors”
- Medical implants
- Microelectronics

■ 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

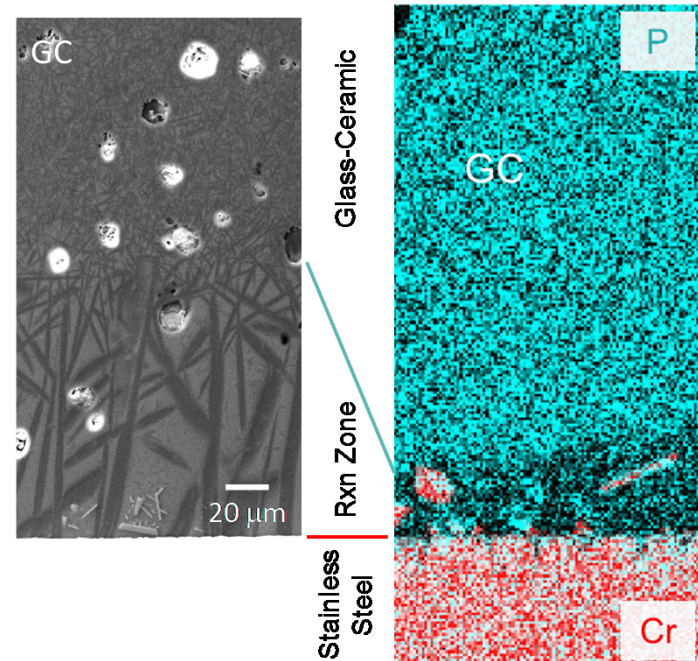
Characterize & model glass chemistry-structure-property relations

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

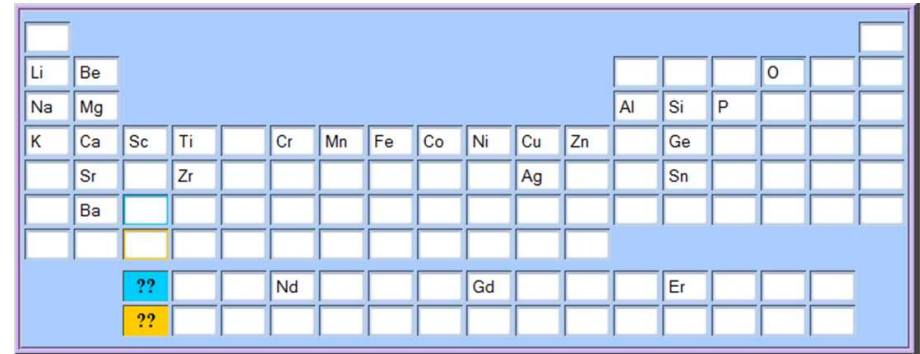


Molecular Dynamics Simulation Methods I

- 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

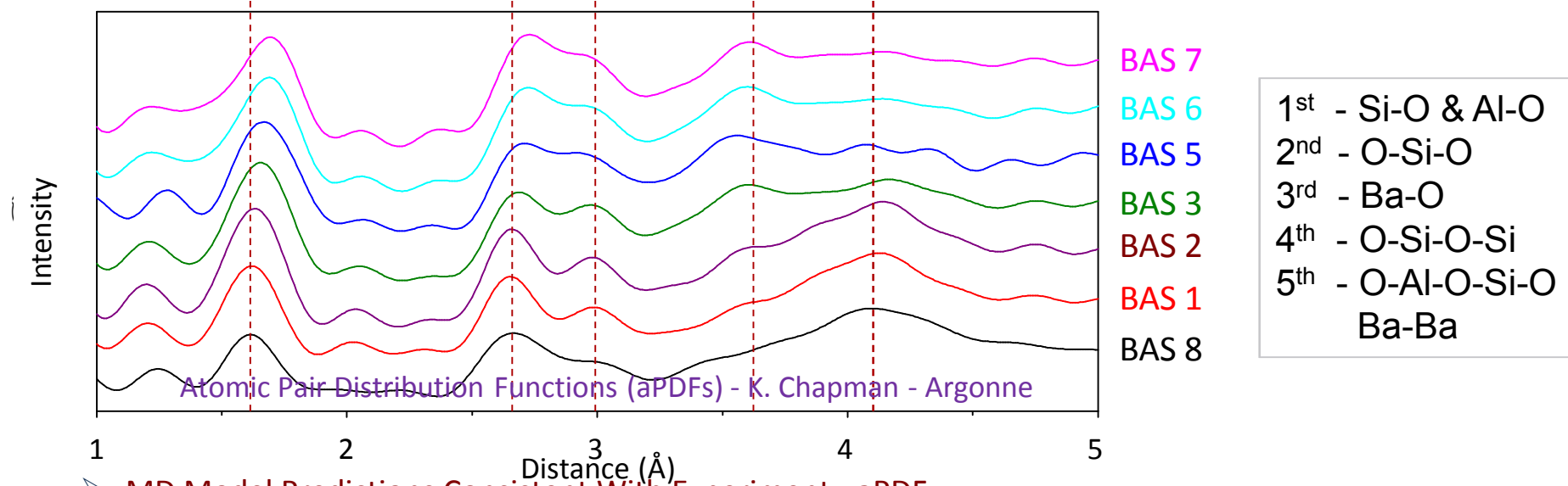
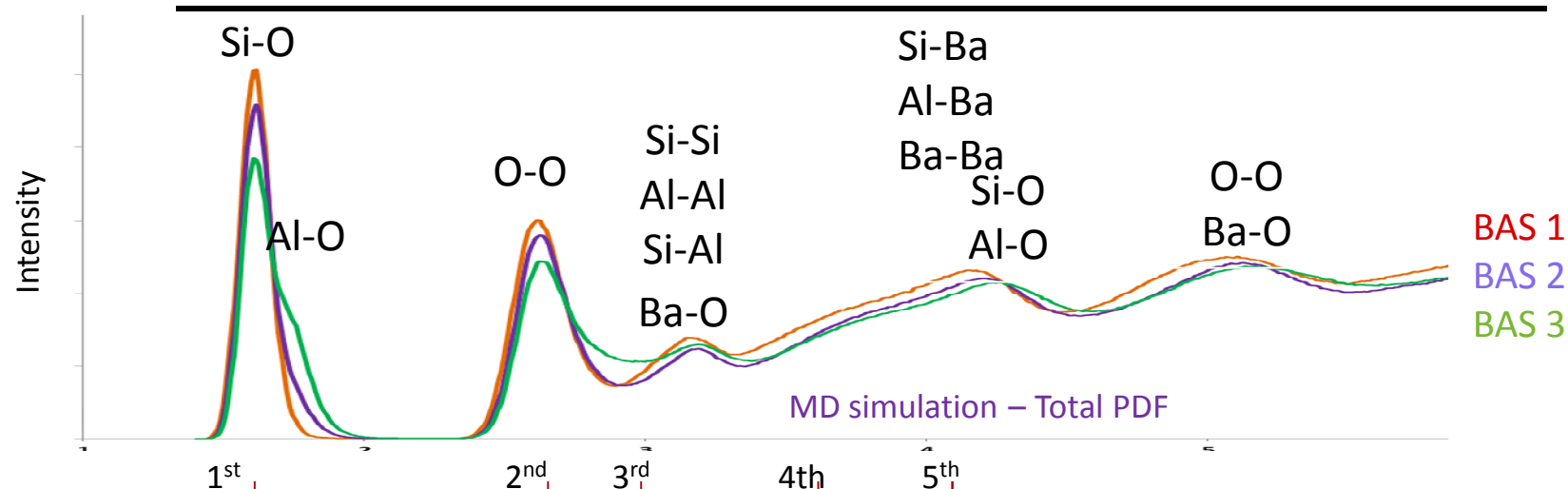


Glass	SiO ₂	Al ₂ O ₃	BaO/CaO
BAS1	75	0	25
BAS2	70	5	25
BAS3	60	15	25
BAS8	66.7	0	33.3
CAS1	75	0	25
CAS2	70	5	25
CAS3	60	15	25

*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).

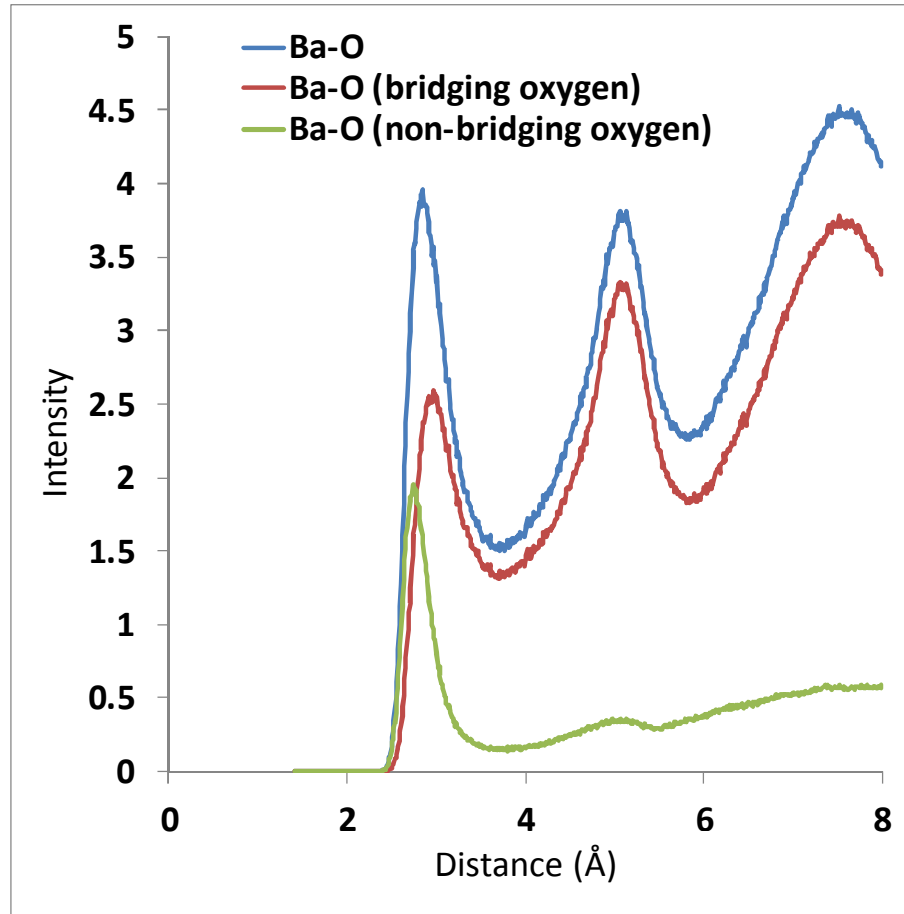
Measured aPDF Peaks Are Consistent With Nearest Neighbor (NN) Distances From MD Simulations



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

Ba-O Distances

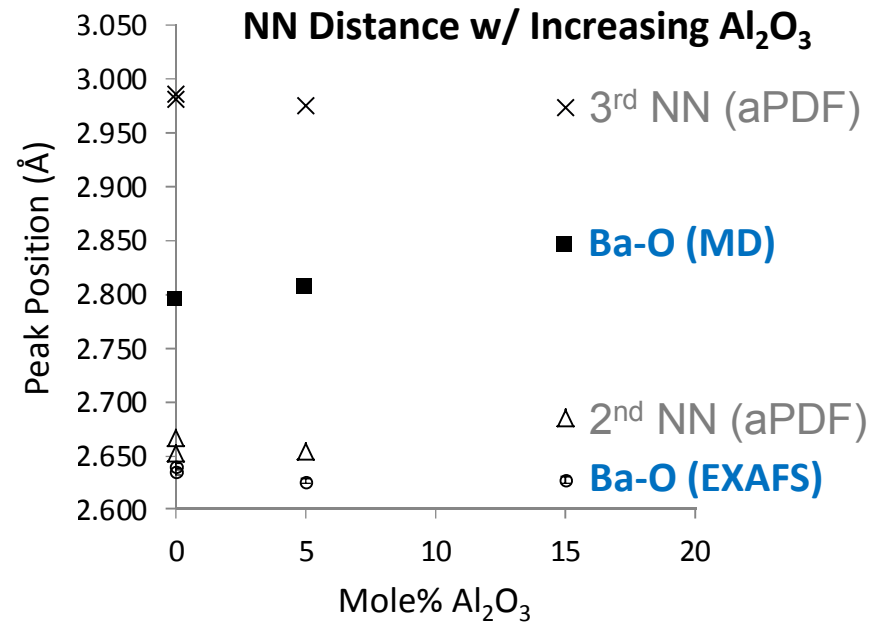
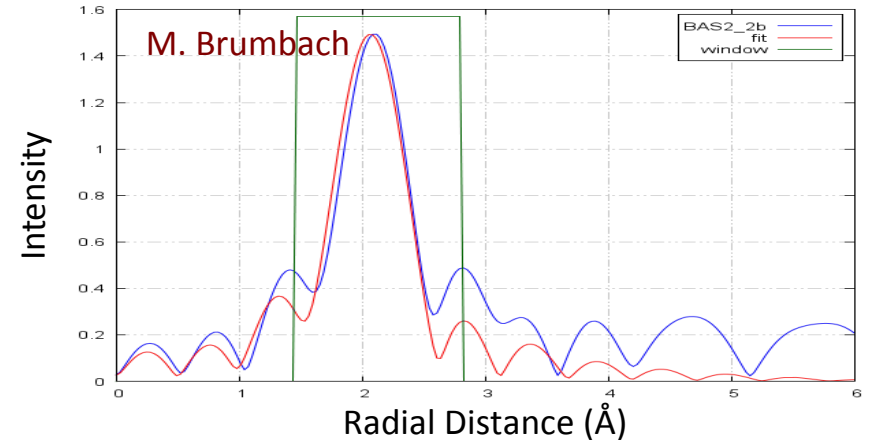
MD pair distribution function



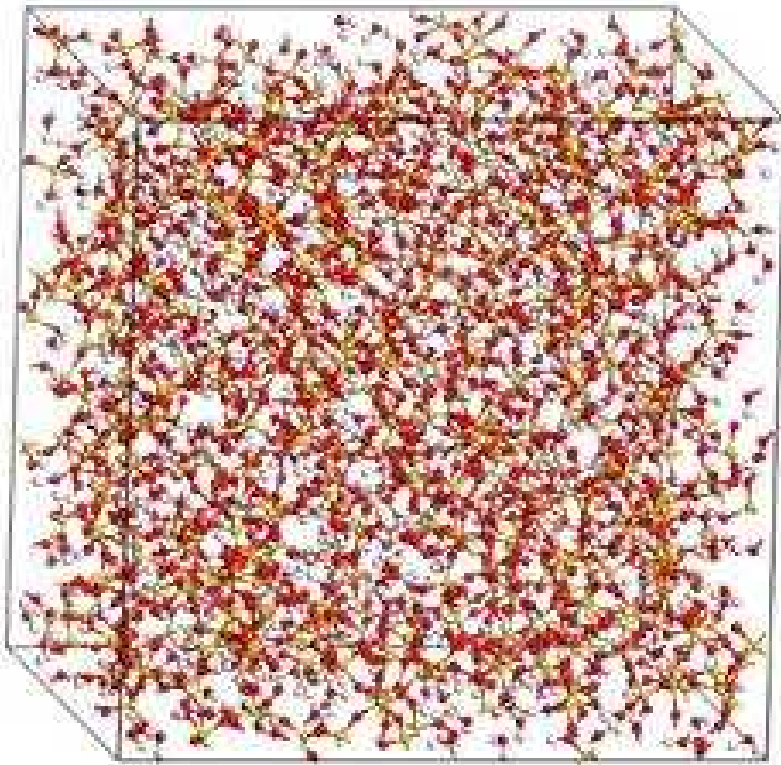
- Ba creates NBOs
- MD & experiment indicate poorly-defined CNs

Rai and Mountjoy (2014) Ba-O = 2.79 Å

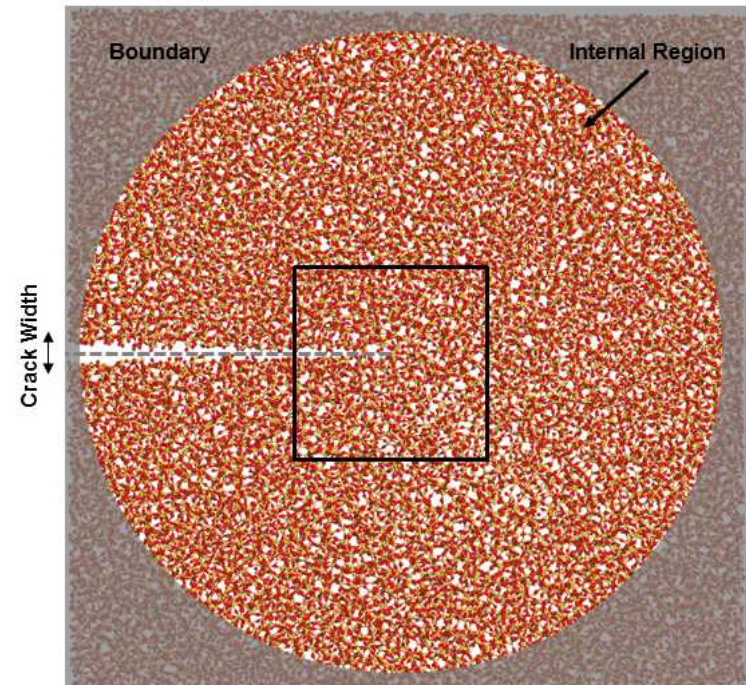
Uncorrected EXAFS Radial distribution function



Ongoing Work: Silica Gel and Fracture Modeling



Rimsza and Du, in press, Langmuir



Rimsza et al. (this afternoon)!

Acknowledgments

- Carlo Pantano, Jorge Sofo, James Kubicki, Nathan Mellott, Alem Leed
- Karl Mueller, Nancy Washton, Joe Ryan, John Vienna (PNNL)
- Peter Schultz, David Sassani (Sandia National Laboratories)
- Kevin Ewsuk, Todd Alam, Todd Zeitler, Michael Brumbach, Mark Rodriguez (SNL)
- Jincheng Du (UNT)

THANKS SUE!!



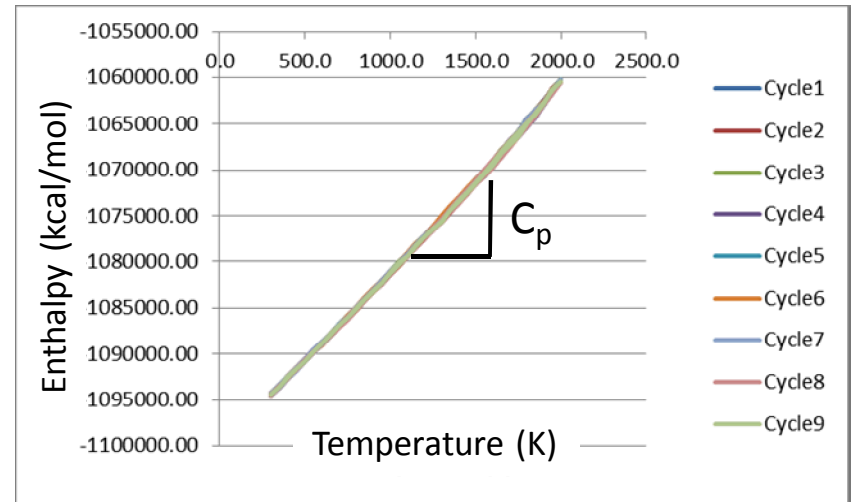
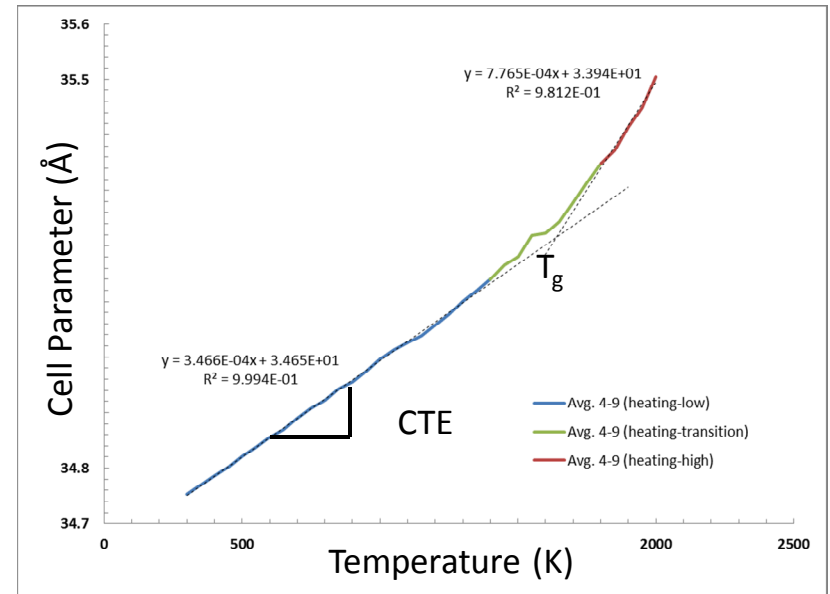
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Nuclear Energy

Sandia LDRD Program

Molecular Dynamics Simulation Methods II

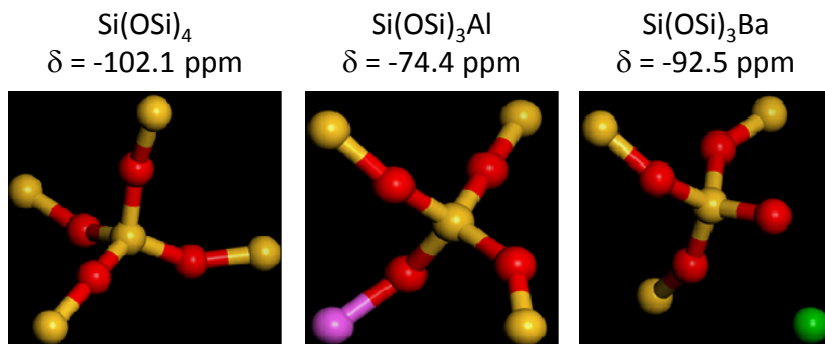
- Glass created:
 - Based on desired composition
 - Through a typical melt-quench process (NVT, NVE) *Xiang, Y. et al. 2013
- Structural data includes:
 - Radial distribution functions
 - Bond angle distributions
 - Q^n distributions ($Q = \text{Al or Si}$; $n = \text{number of bridging oxygens}$)
- 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 LiAlF₄ glass", *J. Non-Crystalline Solids*, **358, 1917-1923, (2012).

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



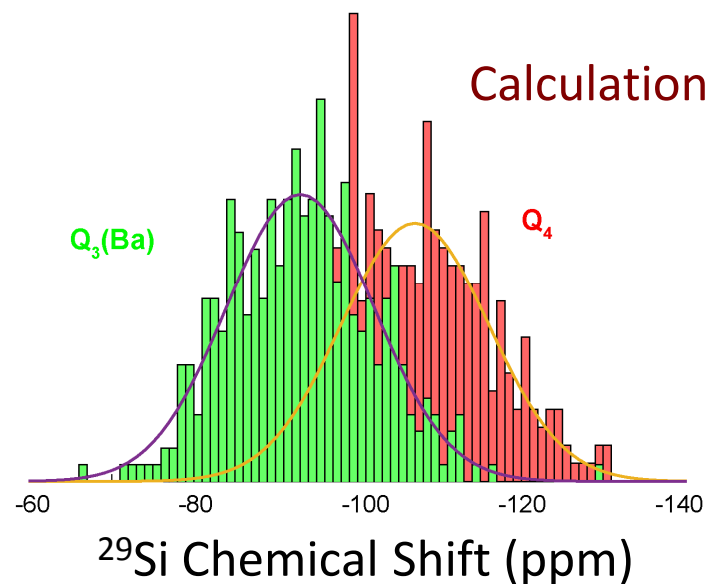
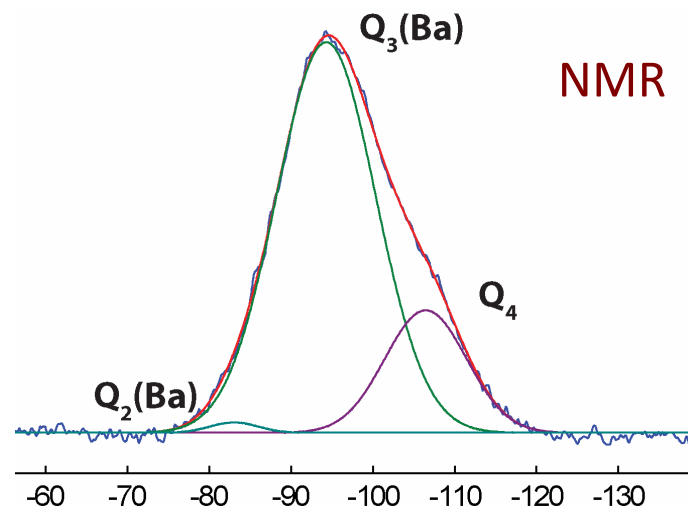
- Calculated ^{29}Si chemical shifts using MD coordinates.
- Employed correlation from Sherrif et al. (1991) based on silicate mineral structures.
- Factors included bond valence (s_i), angle of the bridging oxygen, Si-O bond distance, and distance to the 2nd nearest neighbors.

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

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

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

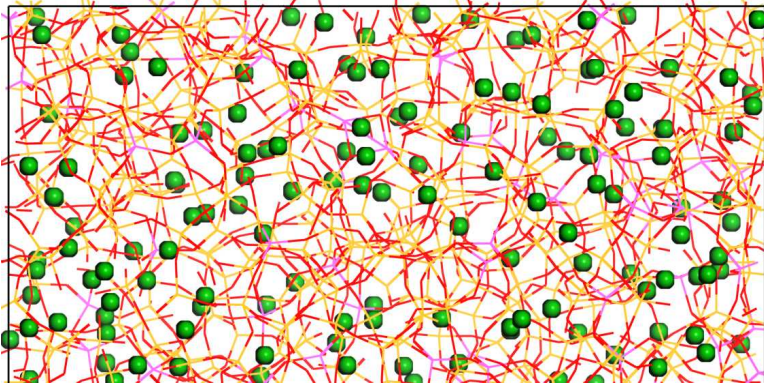
T. Alam



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

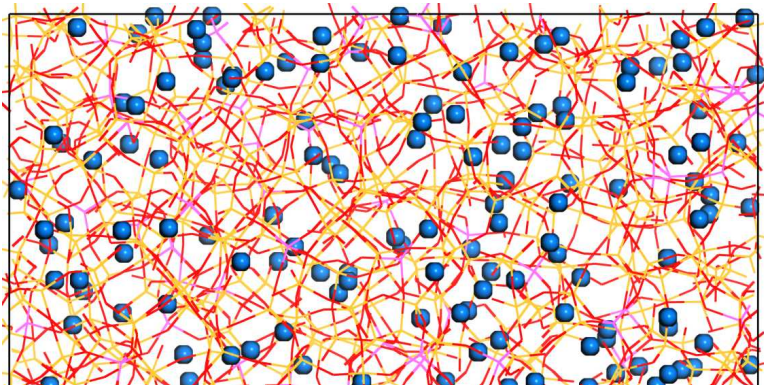
BAS 2

25 BaO - 5 Al₂O₃ - 70 SiO₂

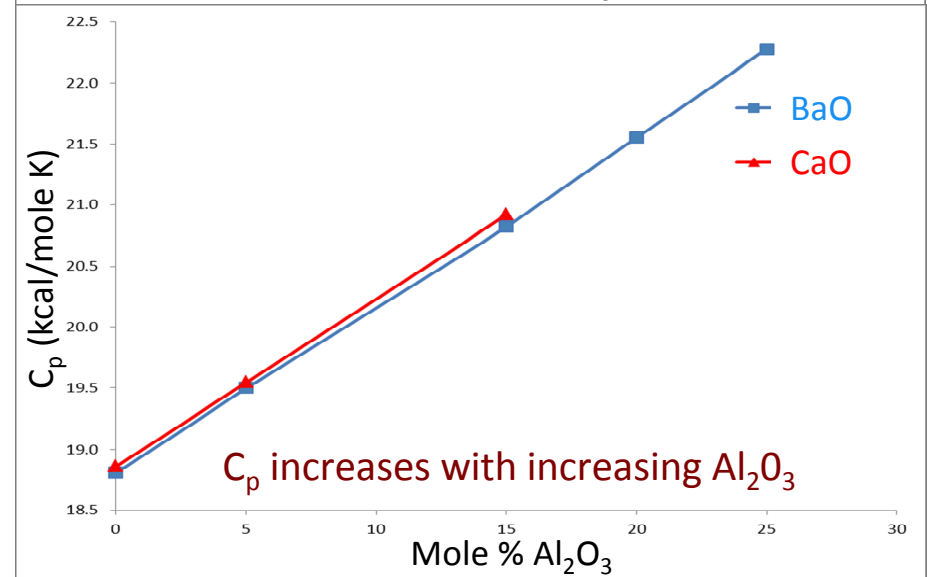
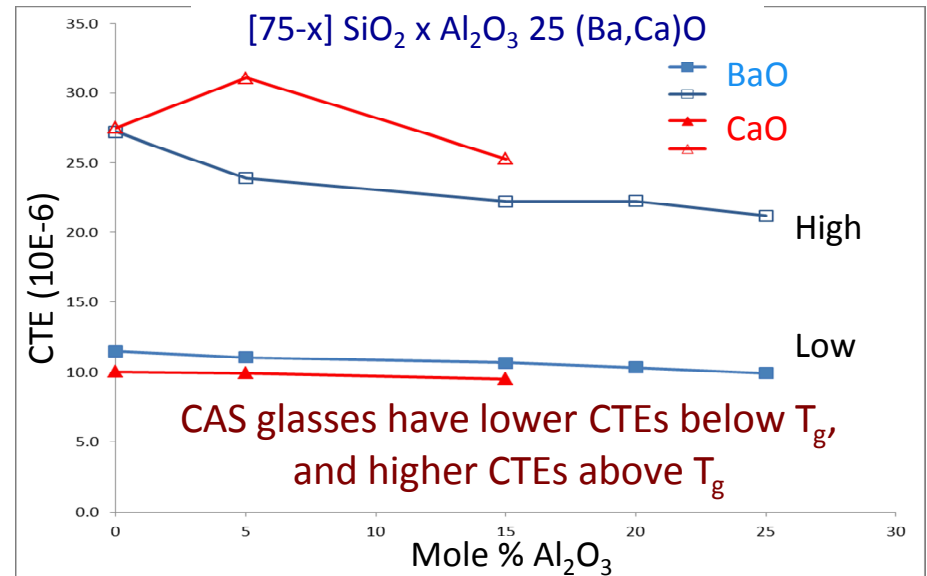


CAS 2

25 CaO - 5 Al₂O₃ - 70 SiO₂



T. Zeitler



- 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.