SAND2013-4600C

Impact of Multicomponent Glass Composition on Glass Dissolution

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Albuquerque, NM

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Sandia National Laboratories

National Nuclear Security Administration

Glass Projects

- Na-borosilicate glass dissolution
  - U.S. DOE NE
  - Collaborators:
    - Kideok Kwon, Kangwon National University, Korea
    - Peter Zapol, ANL
    - Haiying He, ANL
- Metal to Glass Seals
  - U.S. DOE Advanced Simulations and Computing Physics and Engineering Models (ASC PEM)

Molecular Models of Bulk Glass, Glass Surfaces and Surface Gels

- How does the glass composition influence long-term glass dissolution rates?
  - How are changes in glass composition reflected in the glass surface?
  - How do changes in surface site types and densities influence glass dissolution rates?
  - How do changes in glass composition impact ion diffusion to the glass surface?
- Does bulk glass composition influence gel structure?
  - What role does condensation play in gel formation?
  - How does this impact the transport of ions and water through the gel?

Approach:

- Develop bulk and surface models for multicomponent (B, Al, Si, O, Na) glass compositions representative of nuclear waste glasses through molecular dynamics simulations
- Validate calculated glass structures and surfaces with experimental data such as ^{27}Al and ^{29}Si MAS-NMR data from Pierce et al. (2010).
- Compare NMR-determined and calculated surface density of reactive sites for different glass compositions.
- Use molecular dynamics simulation techniques to evaluate the impact of glass composition on gel layer formation and structure.

Force Field Models For Glass

Composition	Form of Potential	Authors
Na, K, Ca, Si, B, O	Modified BMH used by Busing w/o dispersion terms	Soules (1979)
SiO_2, $AlPO_4$	Buckingham form Known as BKS	Van Beest, Kramer & van Santen (1990)
Al, O	Modified BMH	Blonski and Garofalini (1993)
Li, Cs, B, O	BMH	Verhoef & den Hartog (1995)
Mg, Ca, Al, Si, O	Modified BMH used by Busing w/o dispersion terms	Okuno & Kawamura (1995)
Na, Ca, Al, Si, B, Zr, O	BMH	Delaye & Ghaleb (1996)
Na, Ca, Al, Si, B, O	BMH – improvement on D&G (1996)	Abbas et al. (2003); Cormier et al. (2003)
Na, Si, O, -OH	Buckingham + Si-OH 3-body screened harmonic form	Du and Cormack (2004)
Al, O	Buckingham	Adiga et al. (2006)

Force Field Models for Glass-Water Interaction

Composition	FF for Glass	FF for –OH and H_2O	Authors
Si, Na, H_2O	BMH	Shell Model for H_2O -OH: Morse potential	Leed and Pantano (2003)
Si, O, Si-OH, H_2O	Buckingham (Teter's)	3-body term for Si-O-H; Coulomb subtracted Morse potential for –OH group	Du and Cormack (2005)
Si, O, Si-OH, H_2O	BMH + 3-bond angle terms	Rahman, Stillinger & Lemberg form for Si-H, O-H and H-H	Feuston and Garofalini (1990)
Si, O, Si-OH, H_2O	Modified BMH + 3-body potential	Modified BMH + 3-body potential	Litton and Garofalini (2001)
Si, O, Si-OH, H_2O		New dissociative H_2O model	Mahadevan and Garofalini (2008)

No force fields available that include B, Al, Si, O, Na, -OH, and H_2O

Force Field Models For Glass Structures and Glass-Water Interaction

State-of-the-art force field models for multi-component glasses:

- Pedone et al. (2006)
  - Self-consistent empirical interatomic potential model for silica-based glasses
  - Can model structures and mechanics of multicomponent glasses with different compositions
  - Published papers are on alkali silicate glasses (Li, Na, K) and Na-Ca silicate glasses.
- Garofalini (1990s)
  - Reactive force field model that provides good structural results
  - Dissociation of water
- **Kieu, Delaye, Cormier, Stoltz (2011)**
  - Delaye and Galeb have been collecting NMR, WAXS, and other analytical data on nuclear waste glass for over 15 years.
  - Developed a force field to look at multicomponent nuclear waste glass compositions (Na, Ca, Al, Si, B, Zr, O.).
  - Kieu et al. (2011) is a new NaO-B2O3-SiO2 force field.

Molecular Dynamics Simulations of Na-borosilicate Glass

Kieu et al. (2011)'s composition-dependent pair potential

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

Long-range Coulombic interaction

Short-range repulsion

Dispersion

* q_i, A_{ij}, ρ_{ij}, C_{ij} depend on R & K (i.e., composition dependent)

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

LAMMPS, Plimpton, SNL

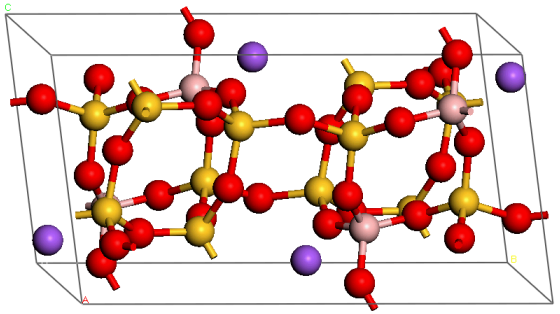
Molecular Dynamics Simulations of Na-borosilicate Glass

Na-borosilicate crystal

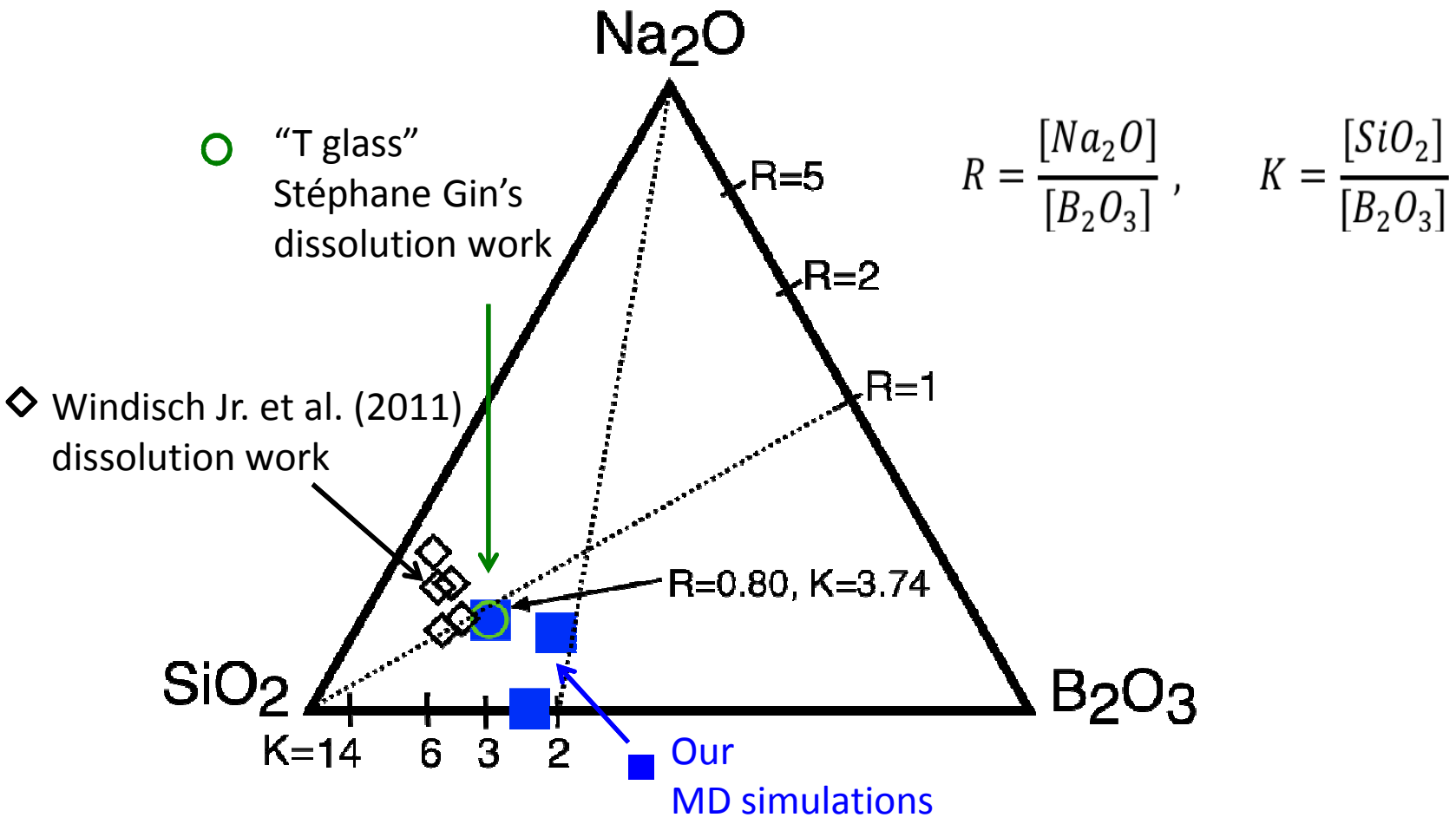
Structural parameters	EXP[a]	Our MD results	DFT[b]
a, b, c (Å)	7.84, 12.37, 6.81	7.77, 12.55, 6.83	7.89, 12.46, 6.84
α, β, γ (°)	93.3, 116.4, 92.0	93.7, 116.8, 91.9	93.4, 116.2, 91.8
density (g/cm^3)	2.78	2.76	2.72
d(Si-O) (Å)	1.61	1.60	1.60
d(B-O) (Å)	1.47	1.47	1.49
d(Na-O) (Å)	2.54	2.60	2.53

[a]Downs et al. (1999) Am. Mineral. 84, 333.
[b]GGA/PW91 (Argonne National Laboratory)

Reedmergnerite ($NaBSi_3O_8$)



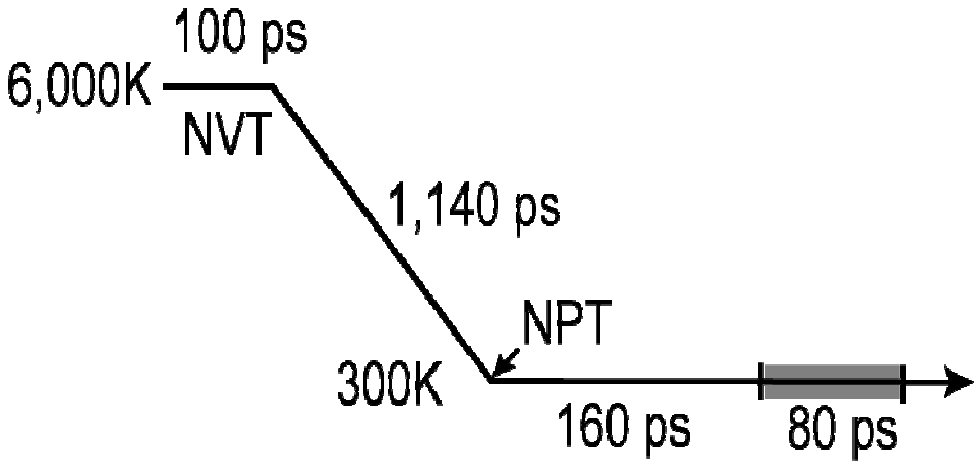
Composition of simulated glass models

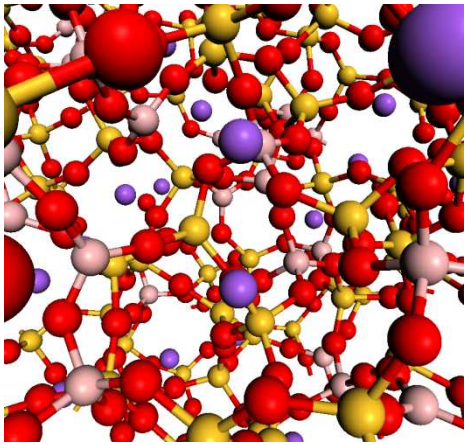


$$R = \frac{[Na_2O]}{[B_2O_3]}, \qquad K = \frac{[SiO_2]}{[B_2O_3]}$$

MD (NPT) Simulations of Na Borosilicate Glass

Composition-dependent FF (Kieu et al. 2011)



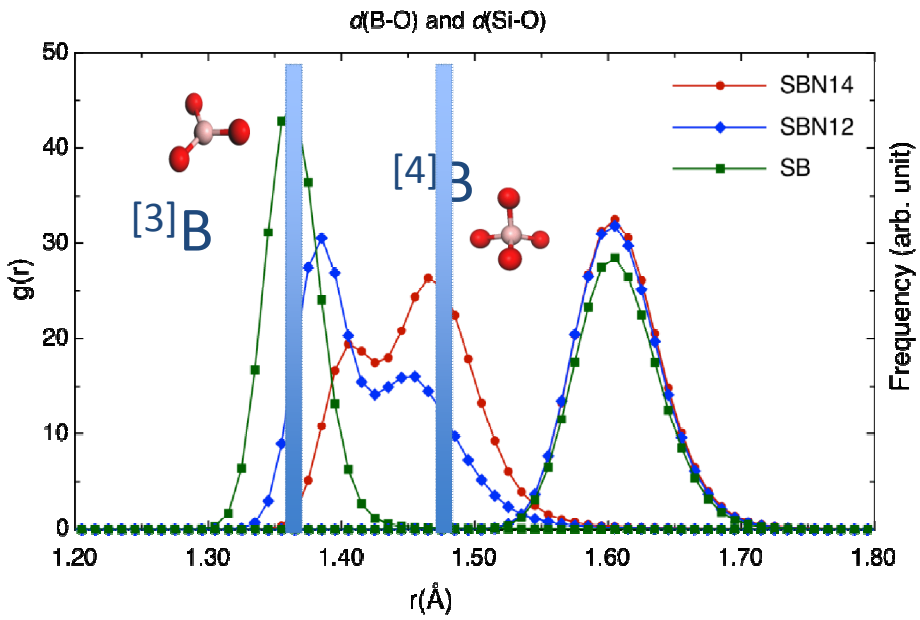


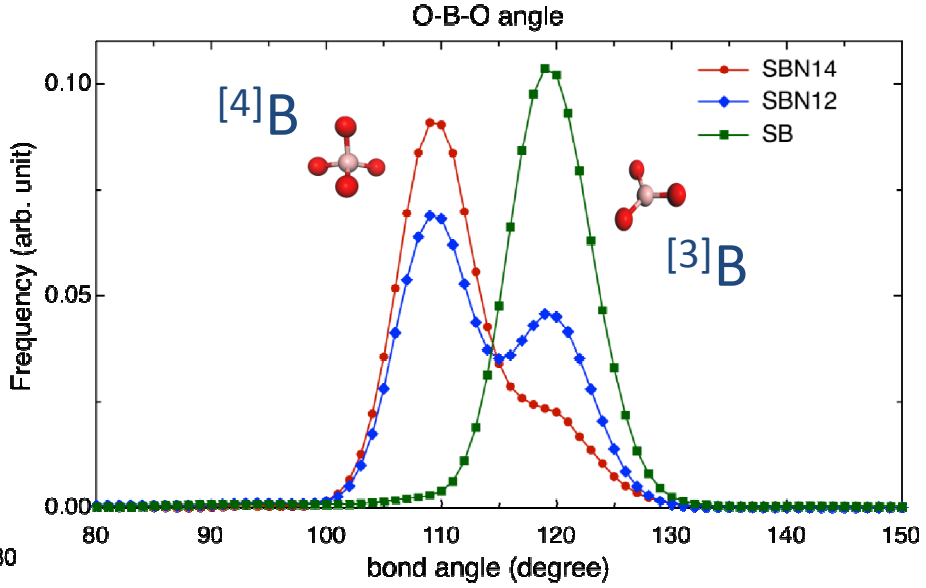
LAMMPS code with
1,004 or 1,005 atoms

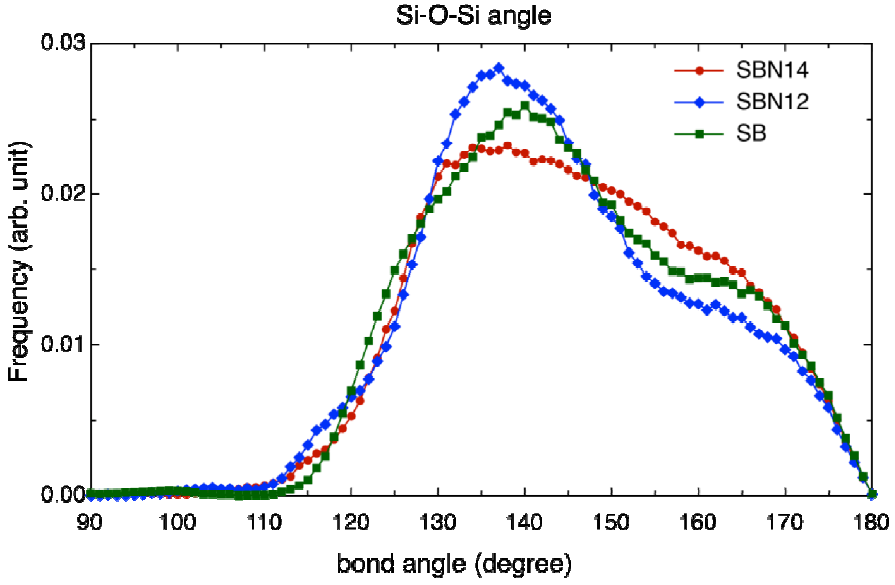
	SiO_2 (mol%)	B_2O_3 (mol%)	Na_2O (mol%)	*R*	*K*	density (g/cm^3)	
						EXP.*	Our MD
SB	69.5	30.5	0	0	2.28	2.04	2.01
SBN12	59.66	28.14	12.20	0.43	2.11	2.37	2.39
SBN14	67.73	18.04	14.23	0.80	3.74	2.45	2.44

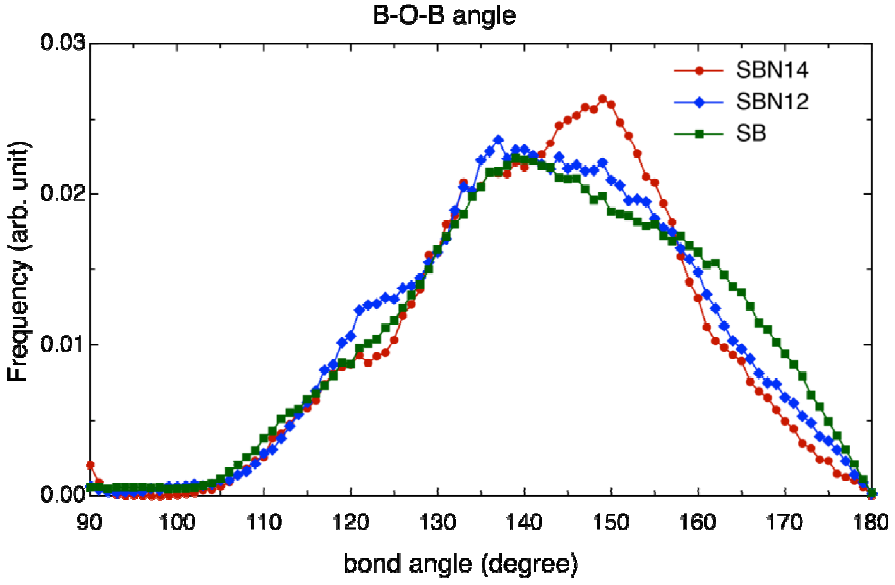
*Kieu et al. (2011) and references therein.

Analysis of NPT simulations of Na borosilicate glass

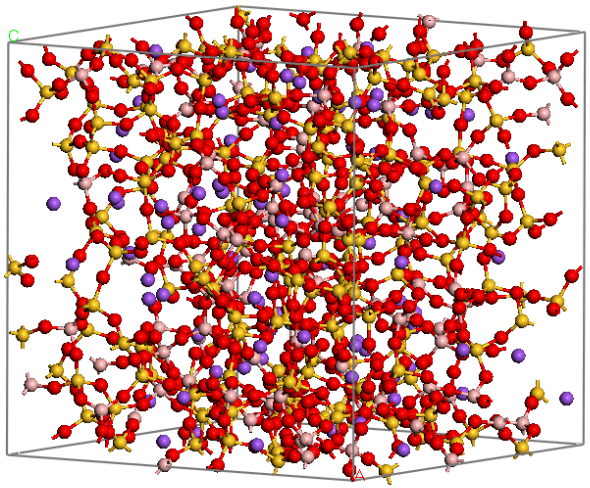




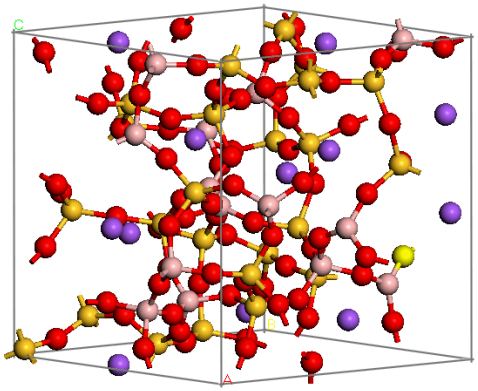




Glass structure for Argonne's DFT (Zapol) work



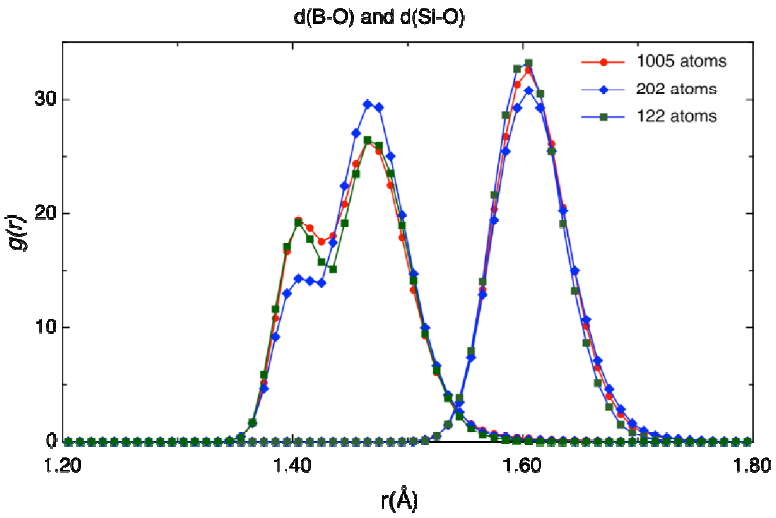
T_glass
(1005 atoms)

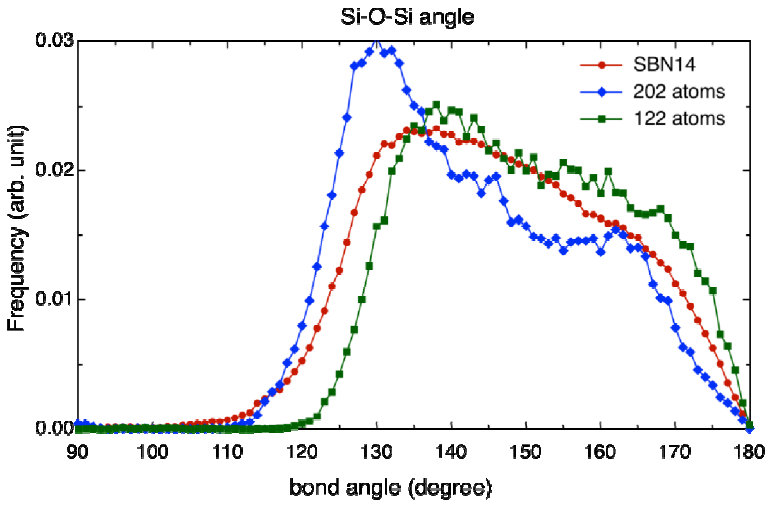


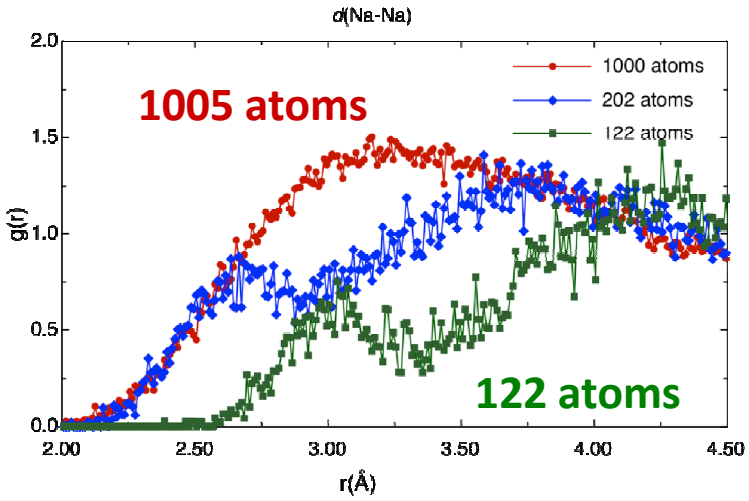
T_glass_122
(122 atoms)

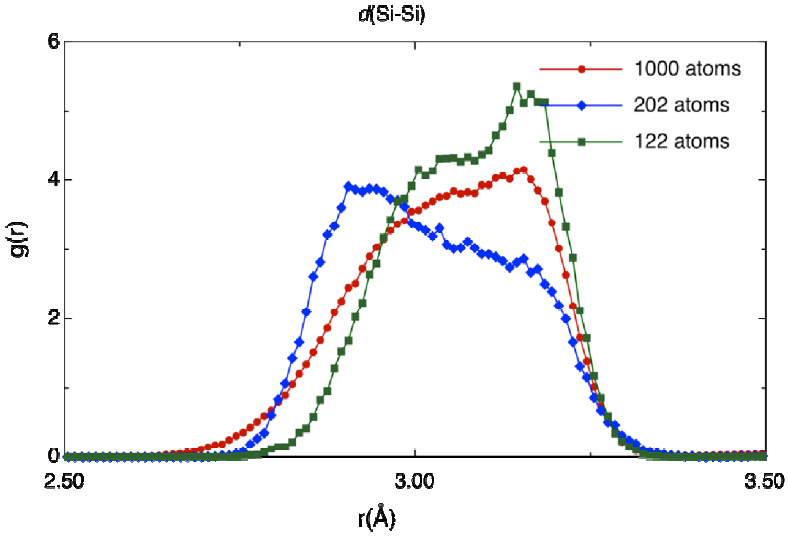
Glass	density		d(B-O)		CN_B		$^{[4]}$B	NBO	
	MD	Exp	MD	Exp	MD	Theory	MD	MD	Theory
T_glass	2.44	2.45	1.45	1.44	3.62	3.73	62 %	4.7 %	1 %
T_glass_122	2.46	2.45	1.45	1.44	3.64	3.73	64 %	1.4 %	1 %

SBN14 glass 1005 atoms vs. 122 atoms



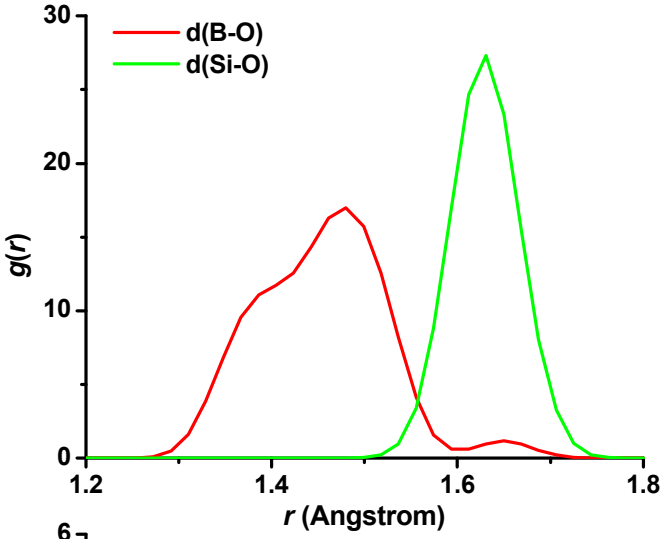


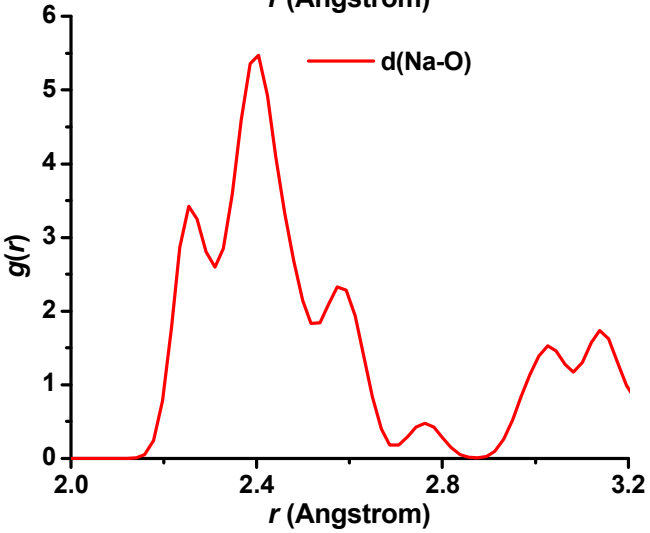




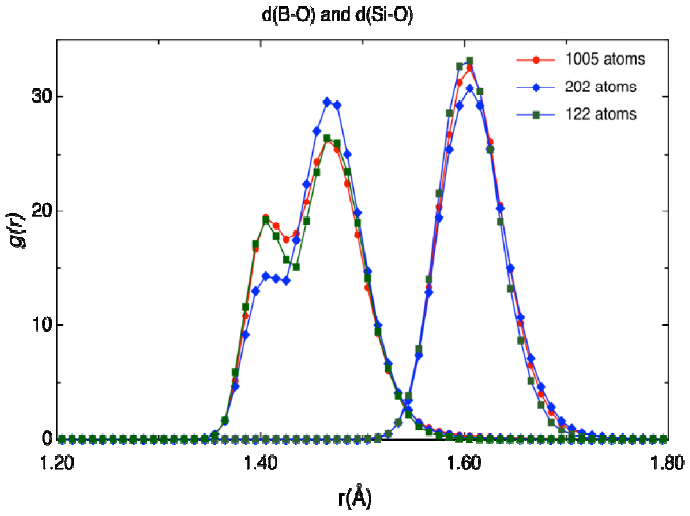
DFT geometry optimization of T-glass (ANL)

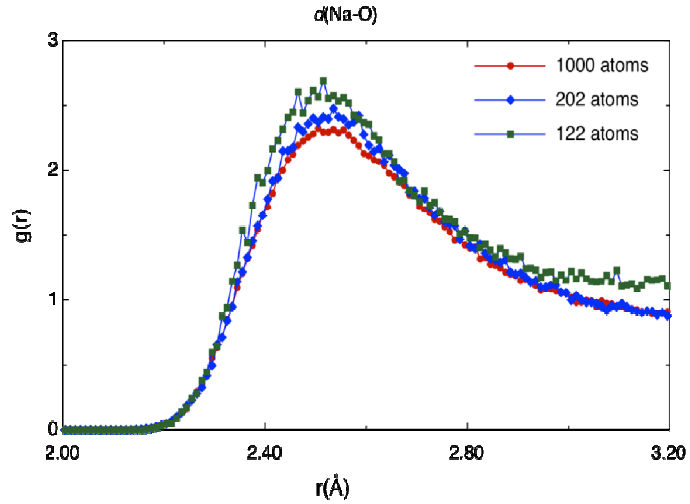
DFT (Argonne) of 1 configuration



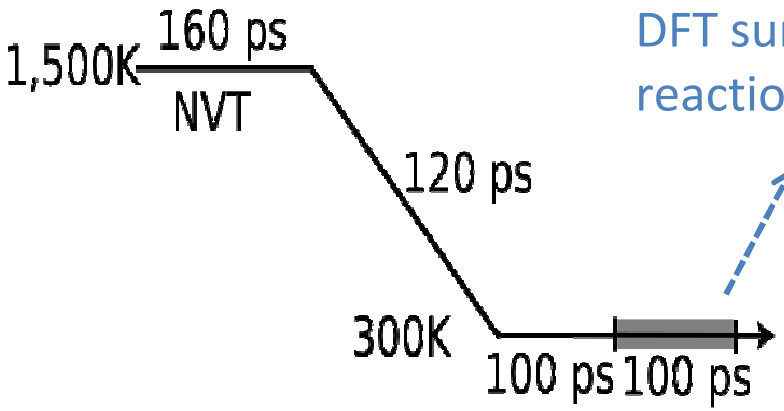


MD simulations (Sandia) of 1600 conf.

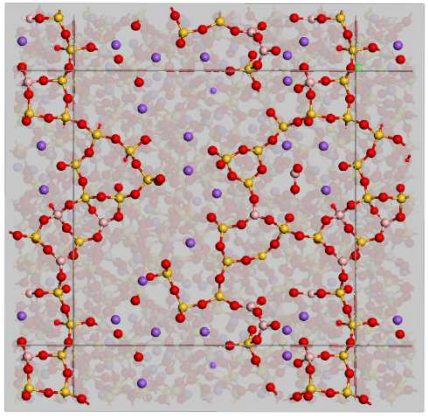




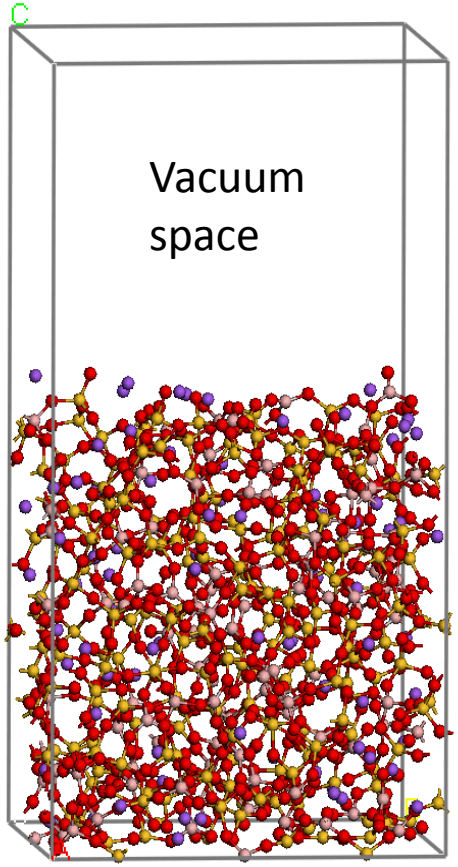
MD simulations of glass surfaces



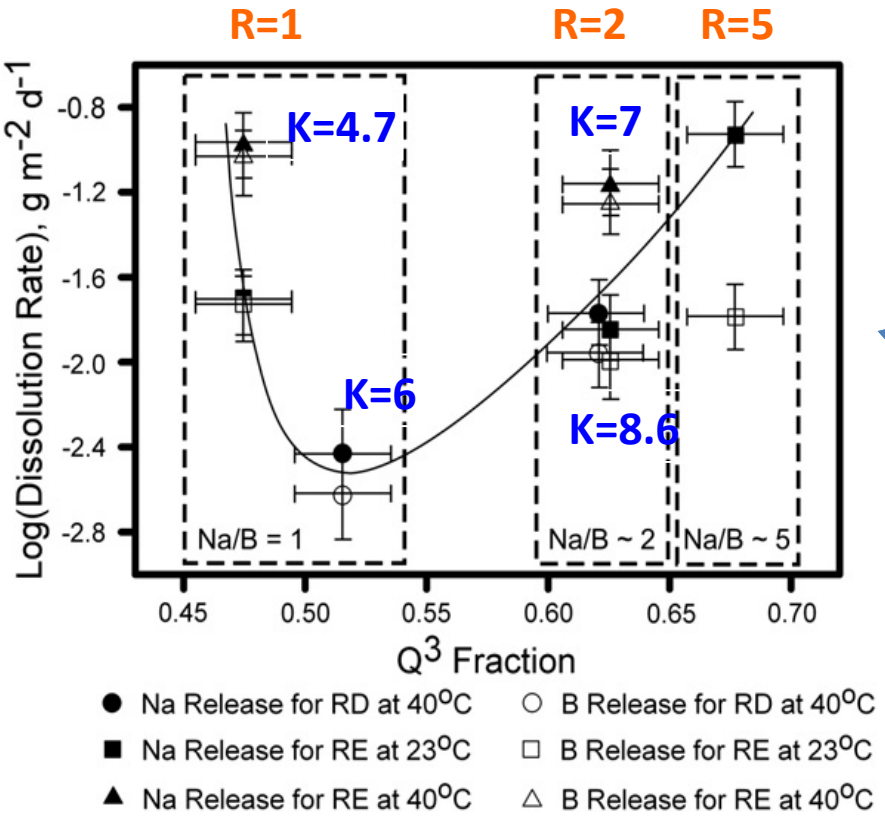
DFT surface reactions study (ANL)

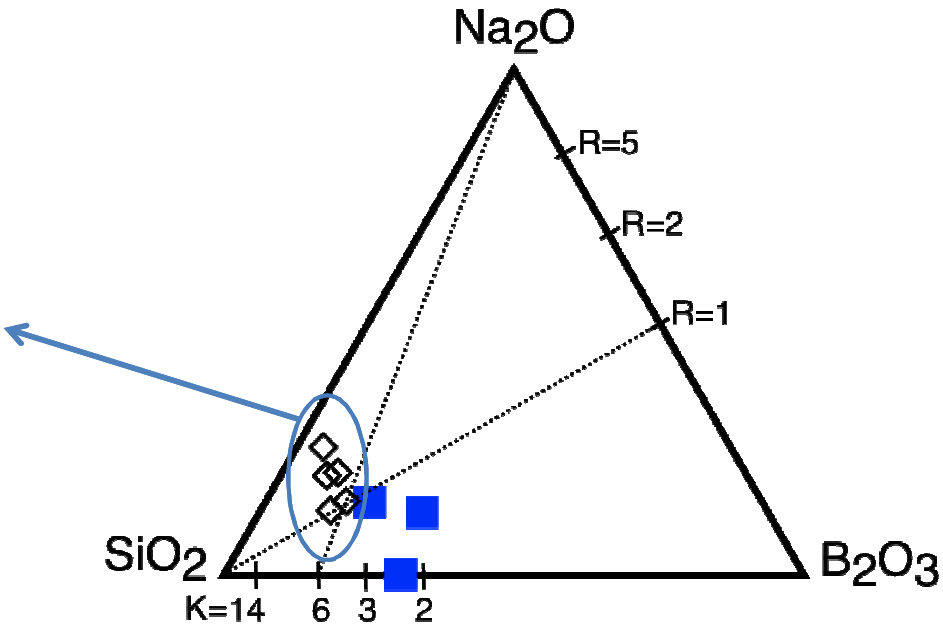


Top 4 Å

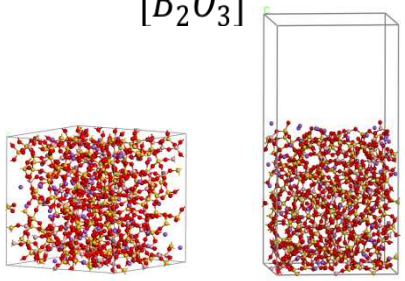


Composition, dissolution, and structures



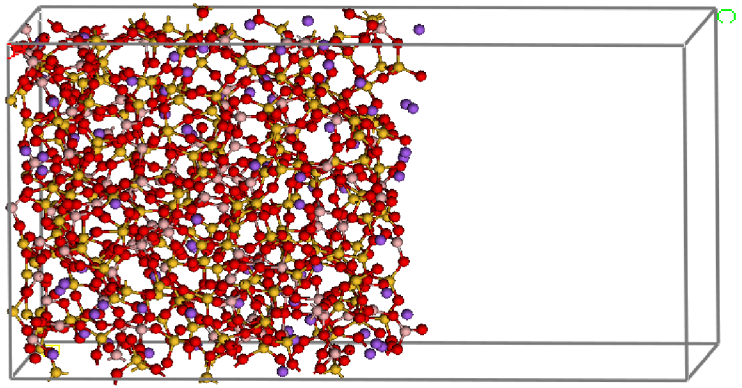


$$R = \frac{[Na_2O]}{[B_2O_3]}, \qquad K = \frac{[SiO_2]}{[B_2O_3]}$$



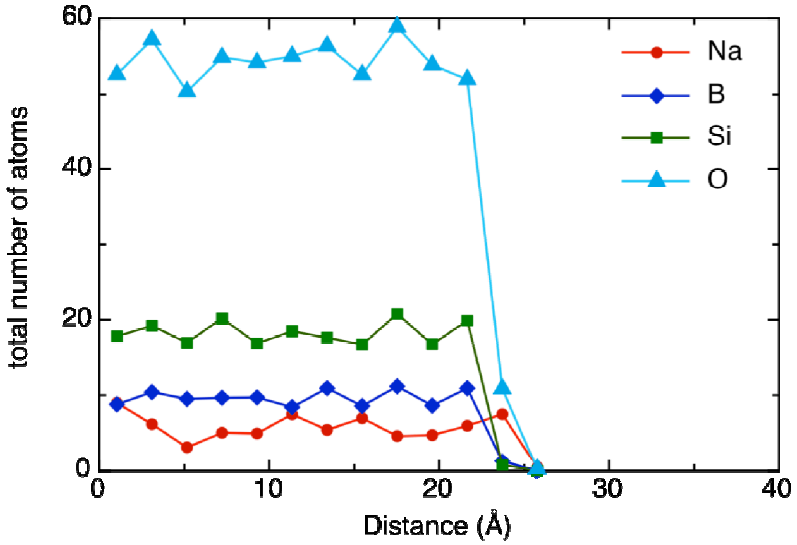
Windisch Jr. et al. (2011) *J. Non-Cryst. Solids*, 2170.

Concentration z-profile

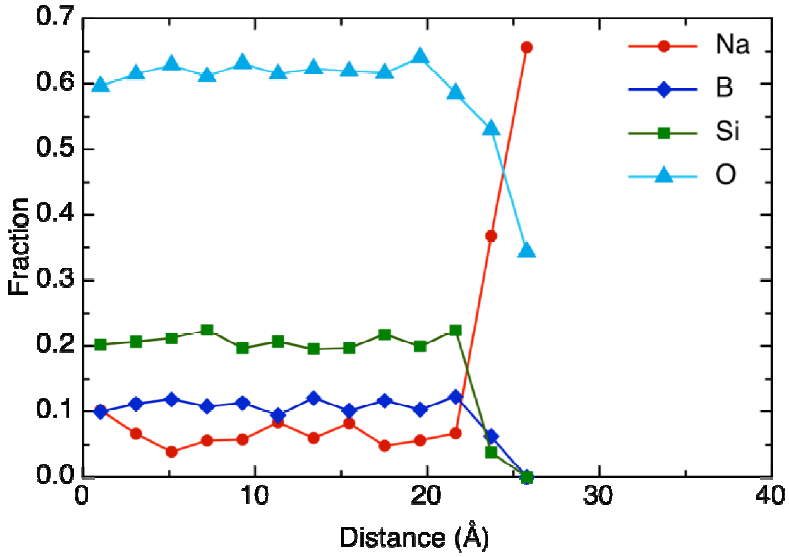


Significant enrichment of Na at the surface!

Total number of atoms vs. distance

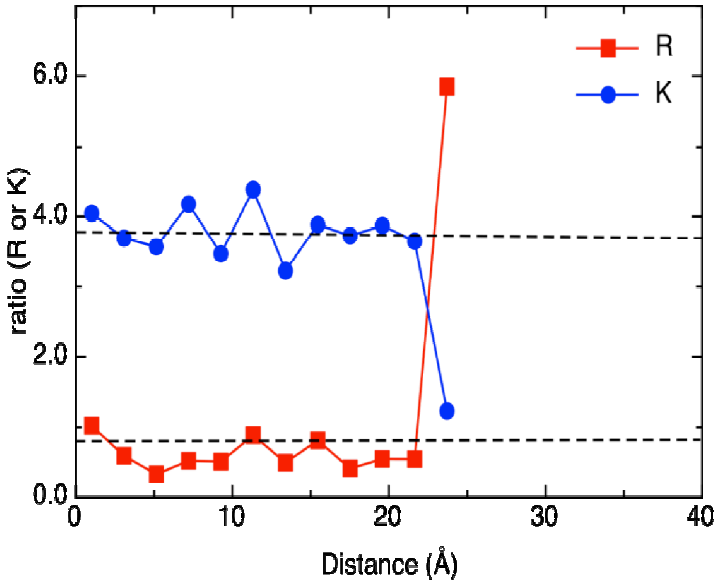


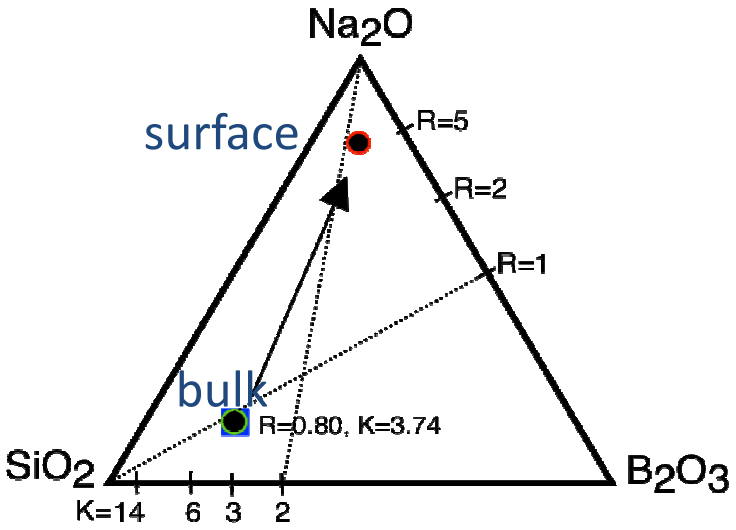
Fraction of atoms vs. distance



Dramatic changes at the surface

The trends in observed dissolution rates of glasses are often described by their bulk composition/structure. But, our results imply that the glass surface, which is interfaced with solution, can take significantly different composition and structure from the bulk. Careful interpretation is required in any attempt to correlate glass dissolution behavior with the composition.





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

Submitted Journal Article

Kwon, K.D. and Criscenti, L.J.

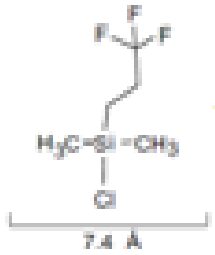
- **Na borosilicate glass surface structures: A classical molecular dynamics simulations study**
- 소듐 봉규산염 유리의 표면 구조에 대한 분자 동역학 시뮬레이션 연구

The Journal of the Mineralogical Society of Korea

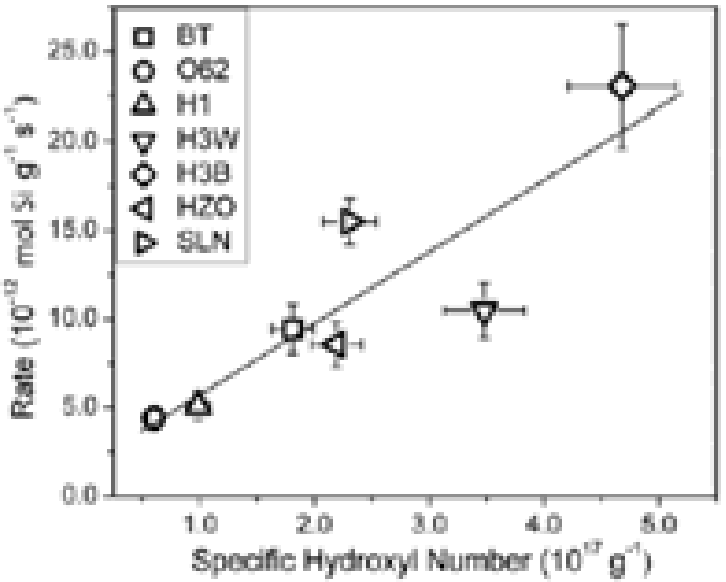
Determining Reactive Sites on Glass Surfaces

Washton et al. (2008)

- Studied volcanic aluminosilicate glasses
- Measured the reactive sites for covalent attachment of the fluorine containing TFS probe molecule by quantitative ^{19}F NMR spectroscopy.
- Dissolution rates scaled directly with the surface density of TFS-reactive sites as measured by solid-state NMR.
- The TFS-reactive M-OH species on the glass surface are known to be non-H-bonded Q^3 groups, & may represent loci accessible to and affected by proton-mediated dissolution.



TFS probe molecule

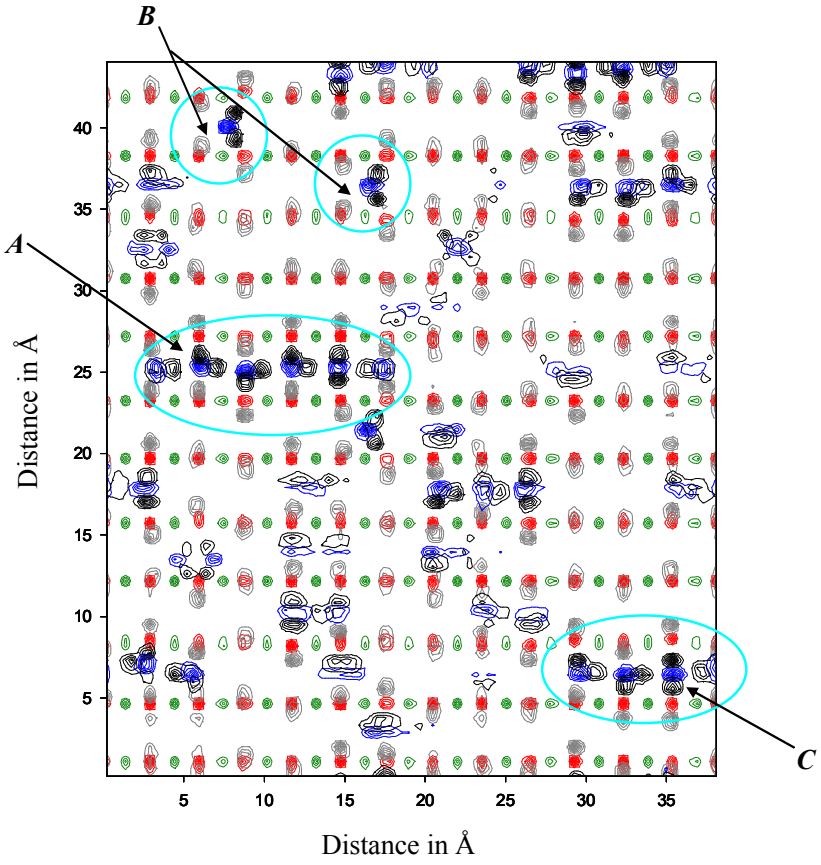


Compare availability of non-H-bonded Q^3 groups from calculation with results from PNNL (Mueller and Washton on elected multicomponent glasses

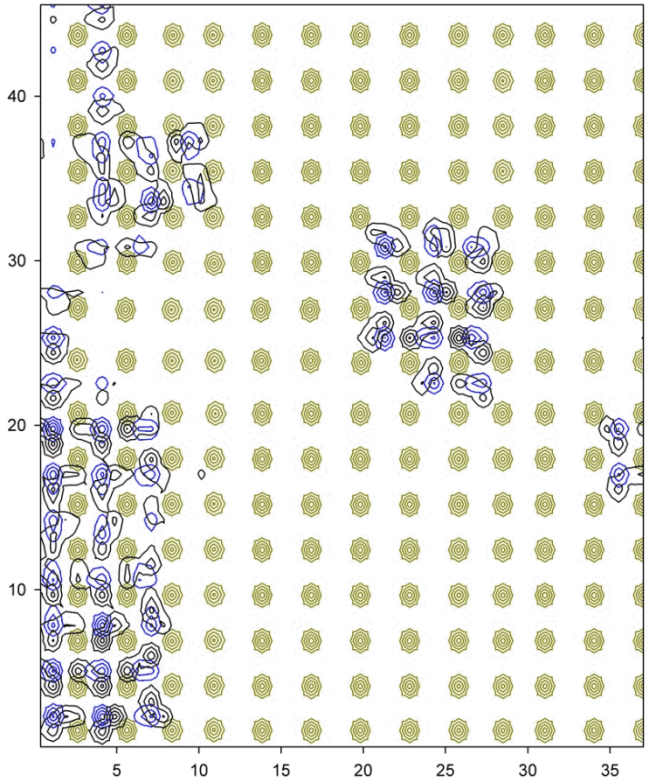
Rates of dissolution exhibit dependence on the # of TFS-reactive hydroxyl groups on an Icelandic suite of glasses.
Dissolution data from Wolff-Boenisch et al. (2004)

Water structure on 2 Surfaces

Boehmite



Gold



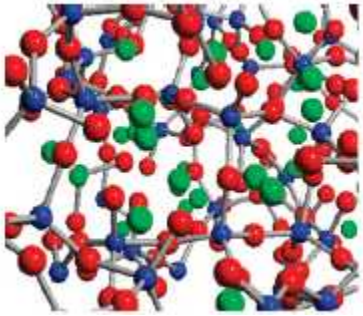
Criscenti et al. 2008

Research on Glass to Metal Seals

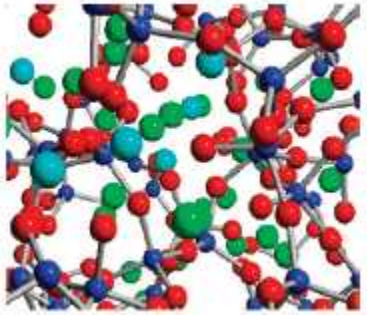
- General Problems:
  1. Brittle fracture of alkali barium silicate glass at the glass-metal interface.
  2. Debonding or loss of hermeticity between glass-ceramic materials and stainless steel.

Problem #1

- State-of-the-art study of brittle fracture in silica glass at the silica-copper interface.
- How does Na^+, Ba^{2+} impact glass structure and fracture? How do concentrations of Na_2O impact stress level required for fracture to occur?



$25Na_2O{\cdot}75SiO_2$



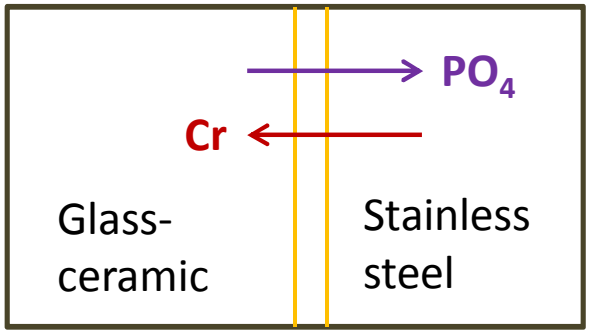
$15Na_2O{\cdot}10CaO{\cdot}75SiO_2$

Snapshots of channels created by (a) Na ions and (b) Ca and Na. Network modifiers cluster around NBOs.

Pedone 2009

Glass-Ceramic to Metal Seal

Reaction zone = 100 μm



Glass-Ceramic contains:
SiO_2, Li_2O, P_2O_5, Al_2O_3, K_2O, B_2O_3, ZnO.

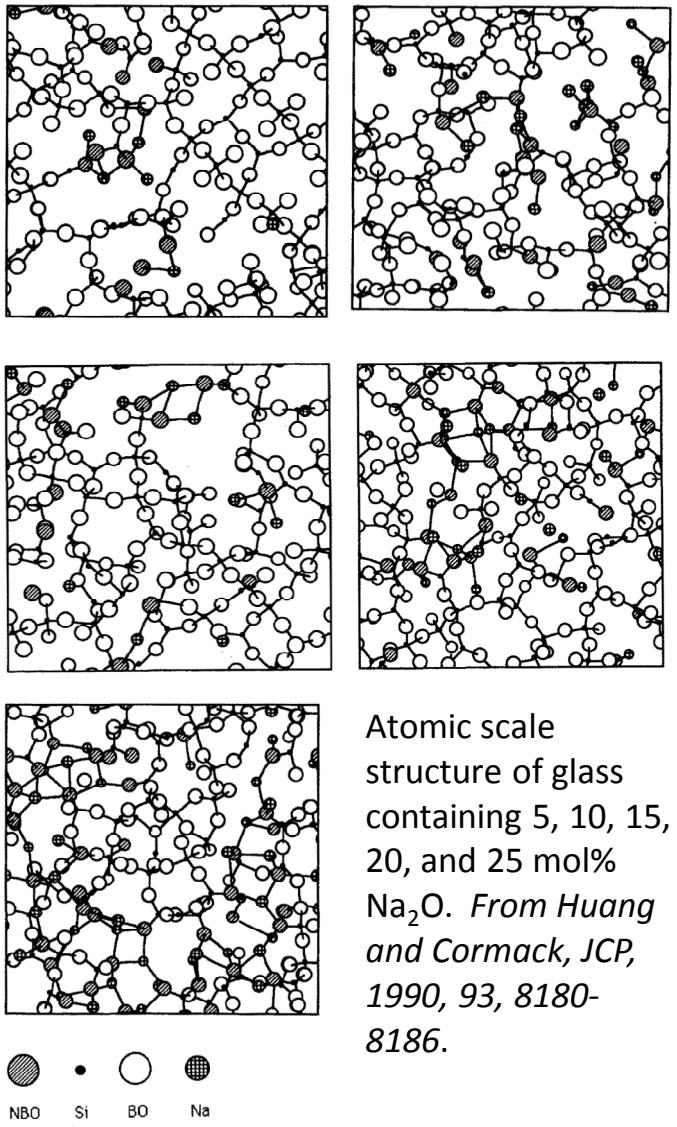
Pedone et al. (2009)

- We can model structures and mechanics of multicomponent glasses with different compositions (PO_4, Cr^{3+} included in FF)
- Interatomic potential parameters derived by fitting mechanical properties such as Young's modulus, the shear and bulk moduli, and Poisson's ratio.

First Question to Address:
How does phosphate migrate through glass to glass surface?

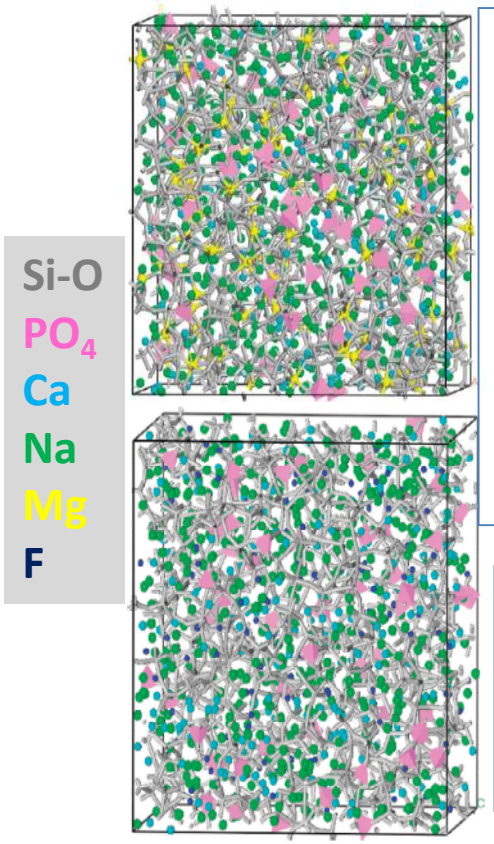
Effect of Glass Composition on Glass Structure

Na_2O-SiO_2 Glass



Atomic scale structure of glass containing 5, 10, 15, 20, and 25 mol% Na_2O. *From Huang and Cormack, JCP, 1990, 93, 8180-8186.*

$46.2SiO_2$-$24.3Na_2O$-$16.9CaO$-$2.6P_2O_5$-$10(MgO/CaF_2)$



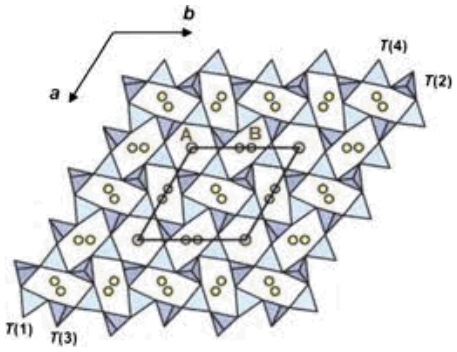
CaO replaced by MgO leads to larger ring structures.
Rough correlation between ring size and Young's modulus. Min YM for 10 MgO.
Mg is homogeneously distributed in Si-rich region with Ca, Na and is totally absent from Ca-Na-PO_4-rich regions.
Separation of PO4 and SiO4-rich sections.

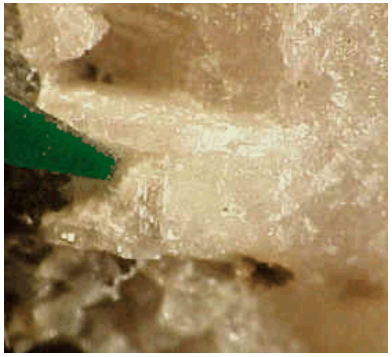
Add F to glass; NaF, CaF attraction leads to separation of phospho-silicate matrix from ionic-rich phase rich in F

Tilocca et al., 2007

Future Work: Add Additional Chemical Components to Kieu et al. (2011) → IGS

- Add additional chemical components to Kieu et al. force field.
  - NaO-B_2O_3-SiO_2 force field was derived from a multi-component potential for silicate melts (*Guillot and Sator, 2007*) that includes:
    - **Al_2O_3**
    - **CaO**, K_2O, MgO, FeO, Fe_2O_3, TiO_2
  - Provides starting point for adding these elements to the NaO-B_2O_3-SiO_2 force field.
- Adjust force field parameters to fit:
  - Crystal structure data for nepheline ($NaAlSiO_4$) and malinkoite ($NaBSiO_4$) to prepare to study Pierce et al. NaO-Al_2O_3-B_2O_3-SiO_2 glasses.
  - Experimental structure factors of aluminosilicate glass compositions obtained by different spectroscopic techniques (e.g., WAXS, Delaye et al., 2001).





Future Work Continued

- Simulate NaO-Al_2O_3-B_2O_3-SiO_2 glasses along nepheline-malinkoite join studied by ***Pierce et al***.
- Examine simulated bulk and surface structures, and determine relationships between structure, composition, and dissolution.
- Evaluate hypothesis based on NMR TFS probe determinations (***Washton***) that the non-H-bonded Q^3 groups are the most reactive by examining accessibility and calculated activation energy barriers.
- Provide surface structures to ***Zapol*** for DFT calculations of glass dissolution (i.e., bond-breaking at glass surfaces).