SAND2012-4018C

Bridging from Atomistic to Continuum Modeling to Better Predict Nuclear Waste Glass Dissolution:

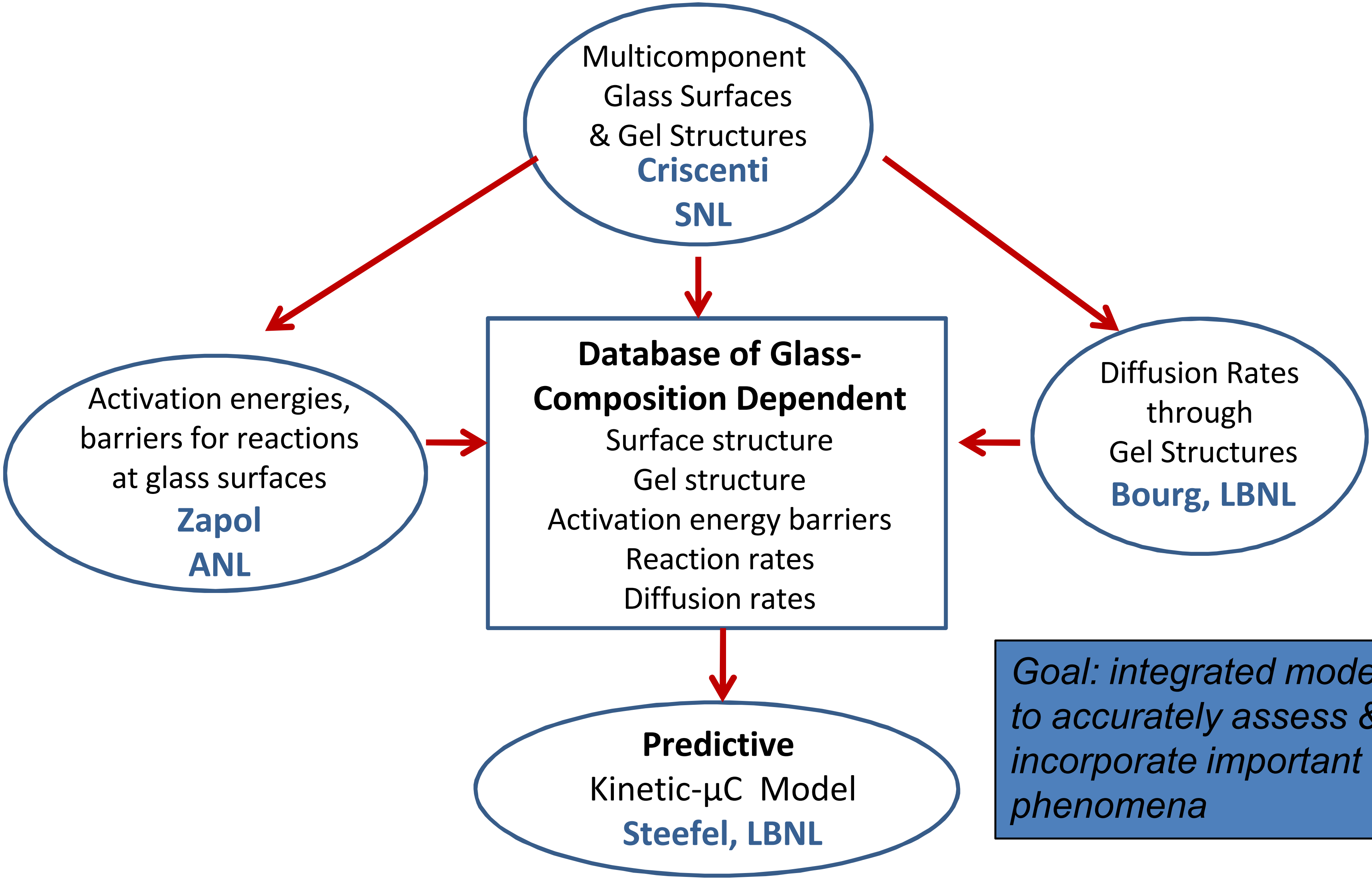
Bulk glass, glass surfaces, and gels

Louise J. Criscenti and Kideok Kwon
Sandia National Laboratories
Albuquerque, NM

Collaborators: Peter Zapol and Haiying He (ANL)

May 24, 2012

Integrated Multiscale Modeling Approach



Multicomponent
Glass Surfaces
& Gel Structures
Criscenti
SNL

Activation energies,
barriers for reactions
at glass surfaces
Zapol
ANL

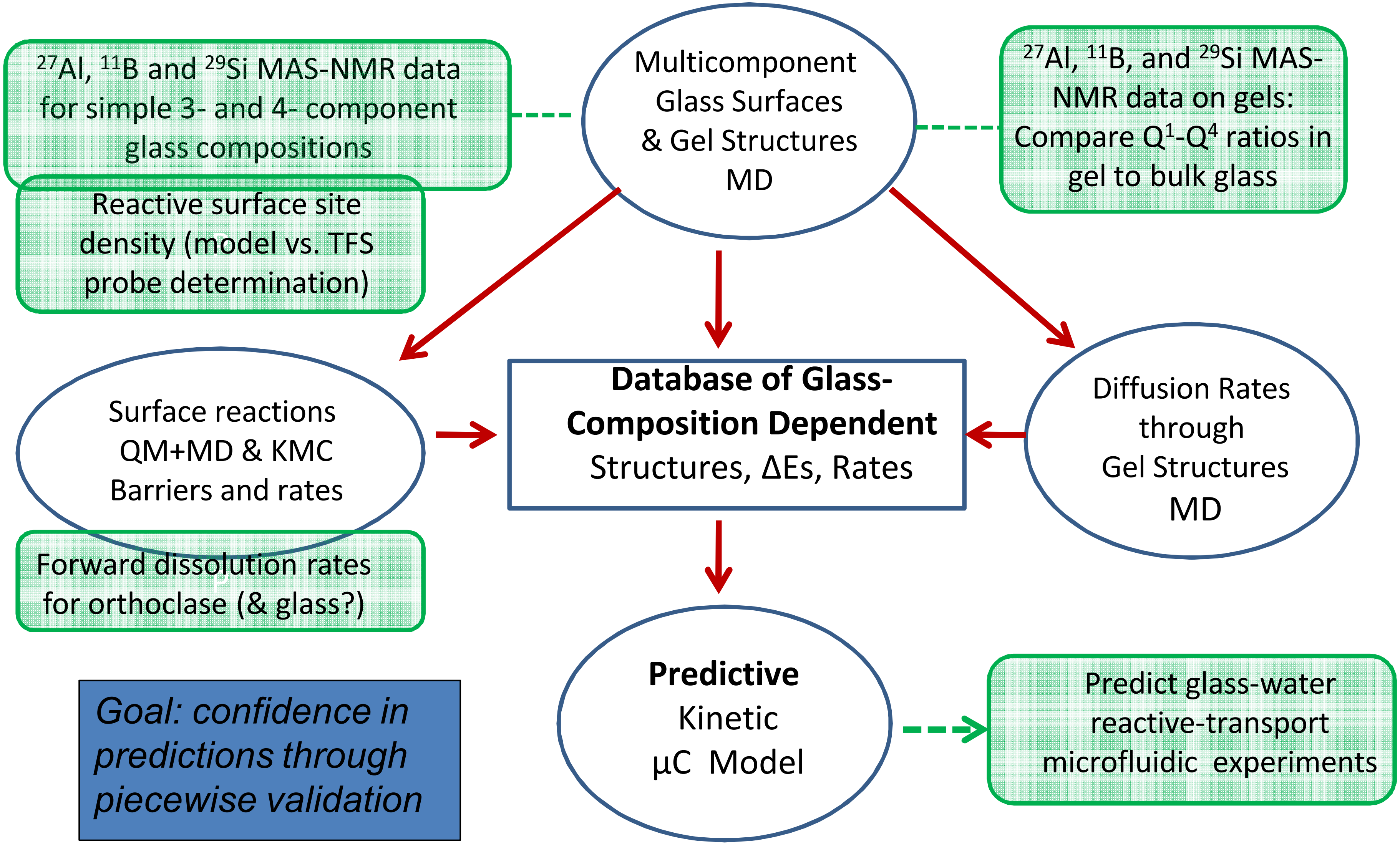
Database of Glass-Composition Dependent
Surface structure
Gel structure
Activation energy barriers
Reaction rates
Diffusion rates

Diffusion Rates
through
Gel Structures
Bourg, LBNL

Predictive
Kinetic-μC Model
Steefel, LBNL

Goal: integrated model to accurately assess & incorporate important phenomena

Joint modeling-experiment efforts



^{27}Al, ^{11}B and ^{29}Si MAS-NMR data for simple 3- and 4- component glass compositions

Reactive surface site density (model vs. TFS probe determination)

Multicomponent Glass Surfaces & Gel Structures MD

^{27}Al, ^{11}B, and ^{29}Si MAS-NMR data on gels: Compare Q^1-Q^4 ratios in gel to bulk glass

Surface reactions QM+MD & KMC Barriers and rates

Database of Glass-Composition Dependent Structures, ΔEs, Rates

Diffusion Rates through Gel Structures MD

Forward dissolution rates for orthoclase (& glass?)

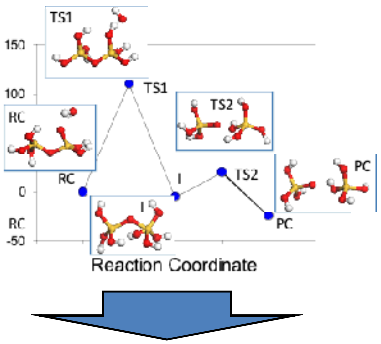
Predictive Kinetic µC Model

Predict glass-water reactive-transport microfluidic experiments

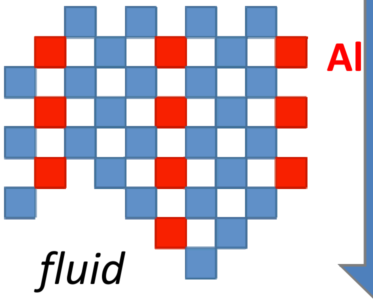
Goal: confidence in predictions through piecewise validation

Upscaling strategy: Assess

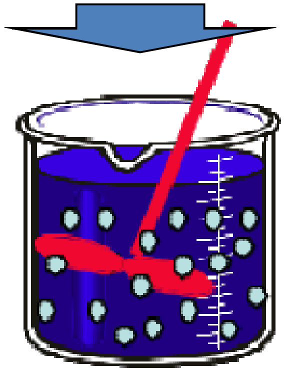
Atomic/
Quantum:
- Energies



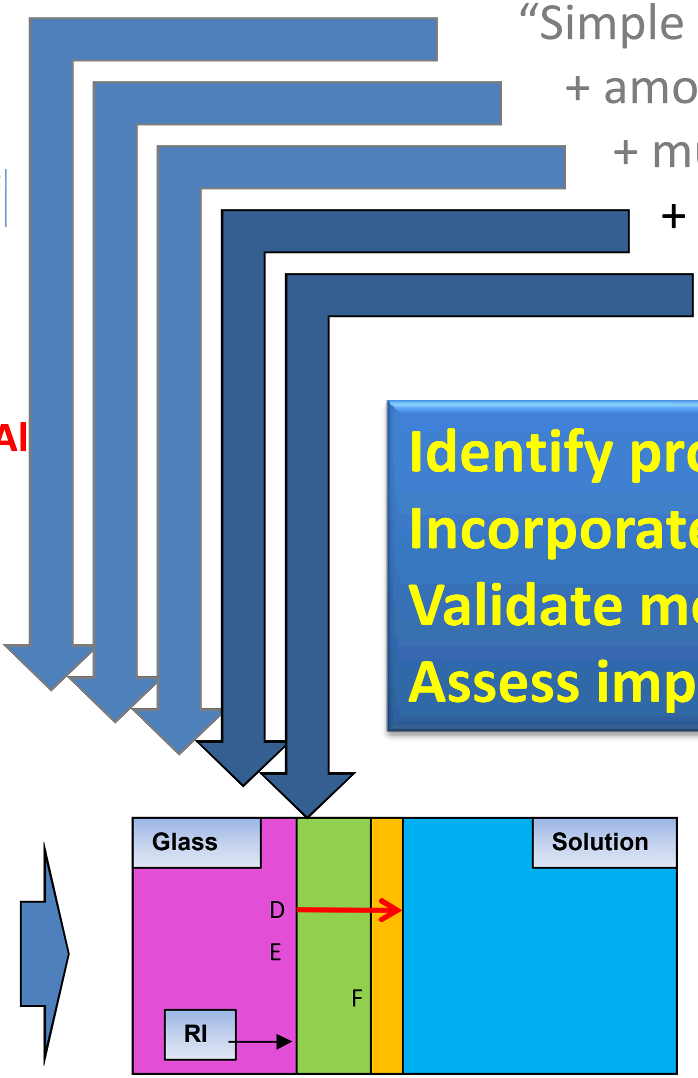
"Mesoscale"/
KMC:
- Statistics
& rates



Continuum:
Reactive
transport/
Kinetic-μC

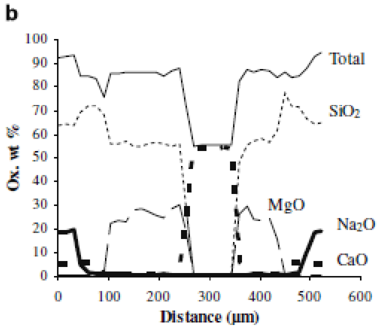


"Simple dissolution": orthoclase
+ amorphous glass
+ multicomponent glass
+ comformational (gels)
+ secondary phases
…



Identify process
Incorporate into model
Validate model vs. data
Assess impact of process

?
=



Upscaling strategy - incremental *validated* complexity

- Start with feldspar/orthoclase …
  - Simple crystalline structure - well controlled model system
  - Good experimental characterization - validate key elements of upscaling
- …**add amorphous character**
  - **Glass introduces structural complexity, statistical behavior**
  - **Similar chemistry, test-verify/validate another element of upscaling**
- **… add multicomponent**
  - **Test-verify/validate another element of upscaling**
- … add conformational complexity
  - Bulk/surface/gel … cracking, porosity contributions to surface area,
  - Test-verify/validate conformational models
- … connect to downscaling continuum models

- … develop/refine constitutive models for continuum scale dissolution

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?
- 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 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
- Teter Potentials
- **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

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

Long-range Coulombic interaction

Short-range repulsion

Dispersion

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

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

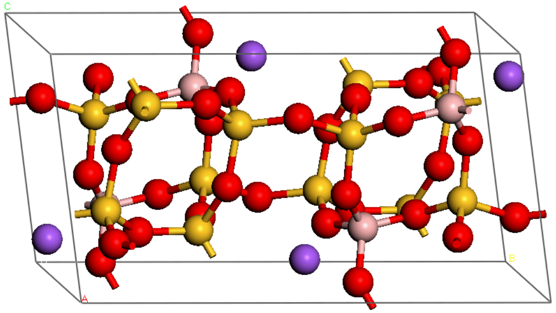
Molecular Dynamics Simulations of Na-borosilicate Glass

Na-borosilicate crystal

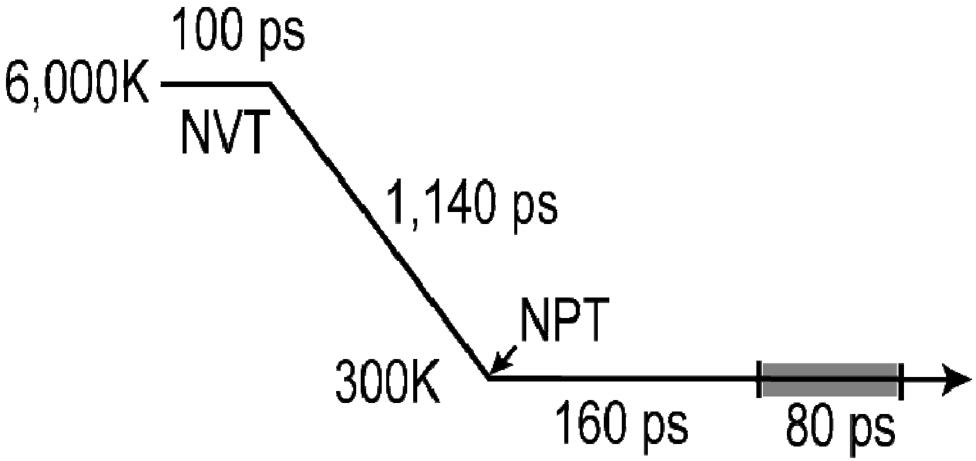
Structural parameters	EXP[a]	Our MD results	DFT[b]
a, *b*, *c* (Å)	7.84, 12.37, 6.81	7.77, 12.55, 6.83	7.89, 12.46, 6.84
α, *β*, *γ* (°)	93.3, 116.4, 92.0	93.7, 116.8, 91.9	93.4, 116.2, 91.8
density (g/cm^3)	2.78	2.76	2.72
d(Si-O) (Å)	1.61	1.60	1.60
d(B-O) (Å)	1.47	1.47	1.49
d(Na-O) (Å)	2.54	2.60	2.53

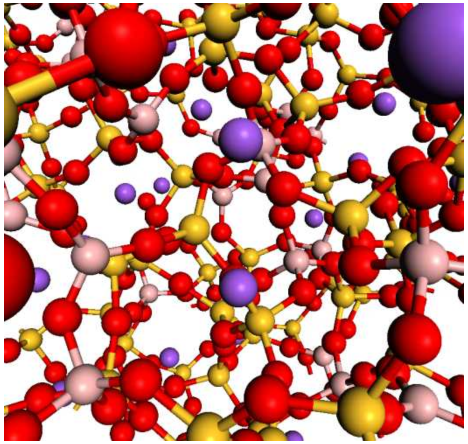
[a] Downs et al. (1999) Am. Mineral. 84, 333.
[b] GGA/PW91 (Argonne National Laboratory)

Reedmergnerite ($NaBSi_3O_8$)



MD Simulations of Na Borosilicate Glass



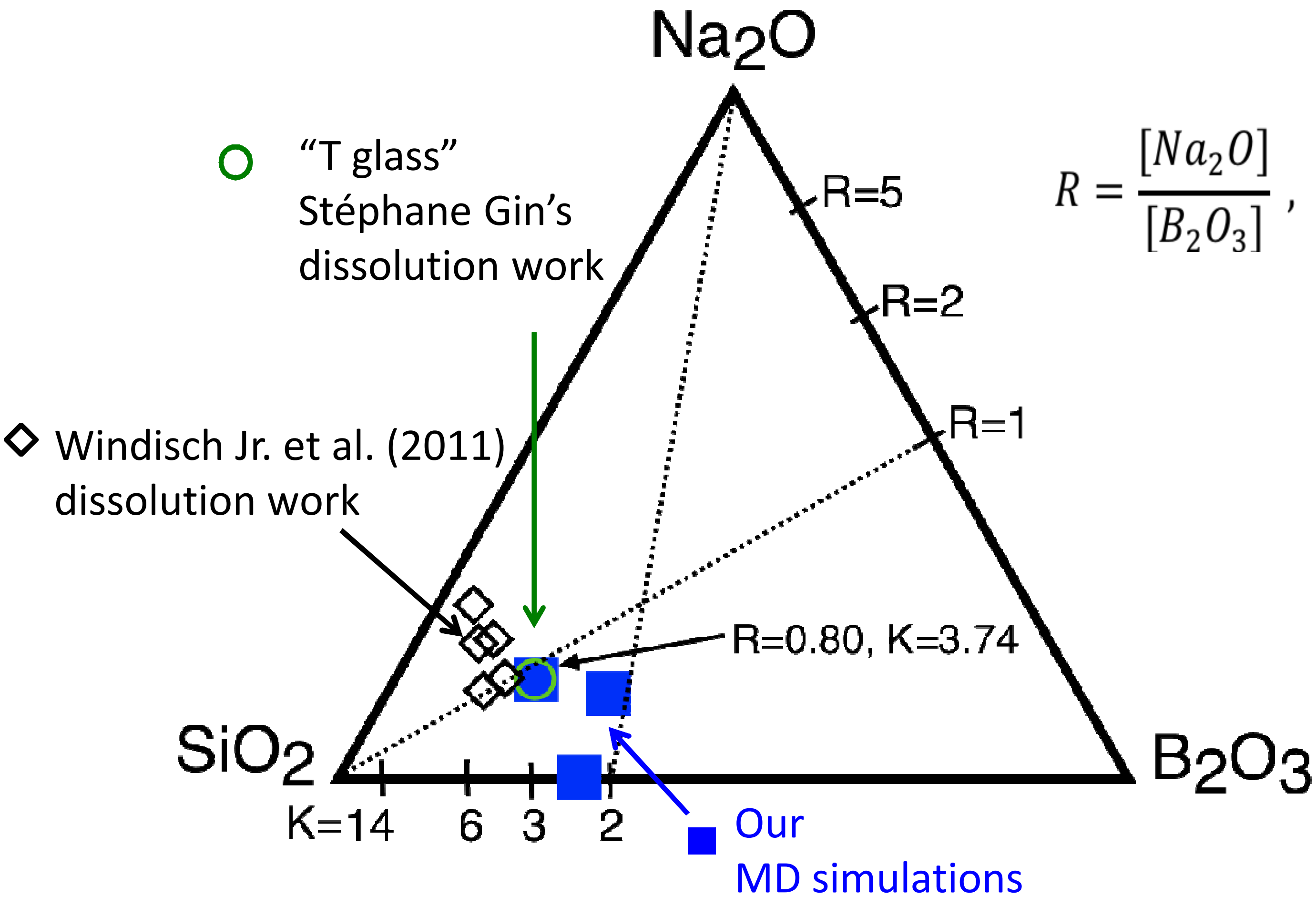


LAMMPS code with
1,004 or 1,005 atoms

	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.

Composition of simulated glass models



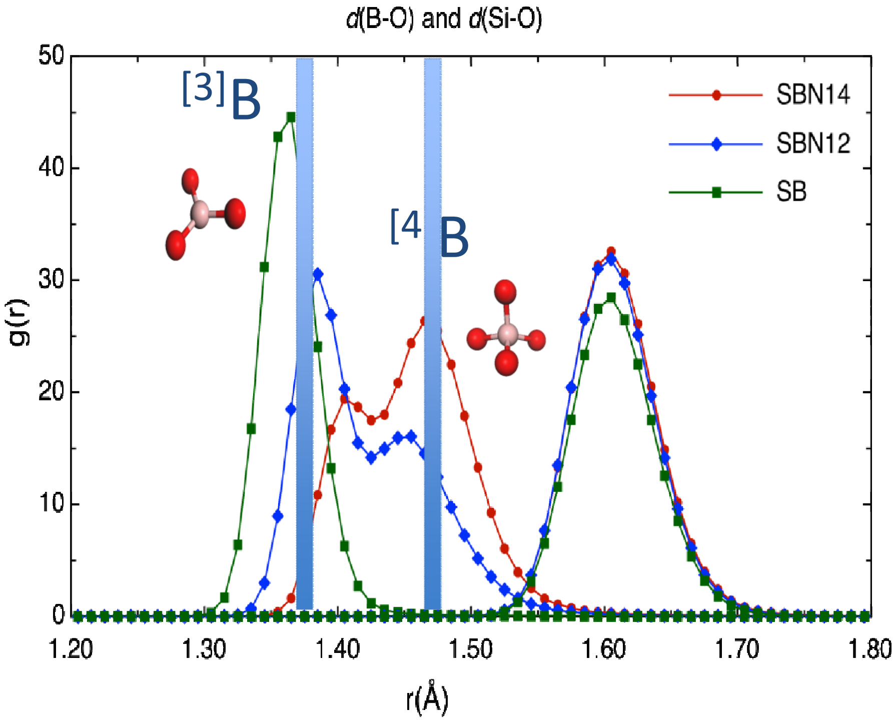
○ "T glass"
Stéphane Gin's
dissolution work

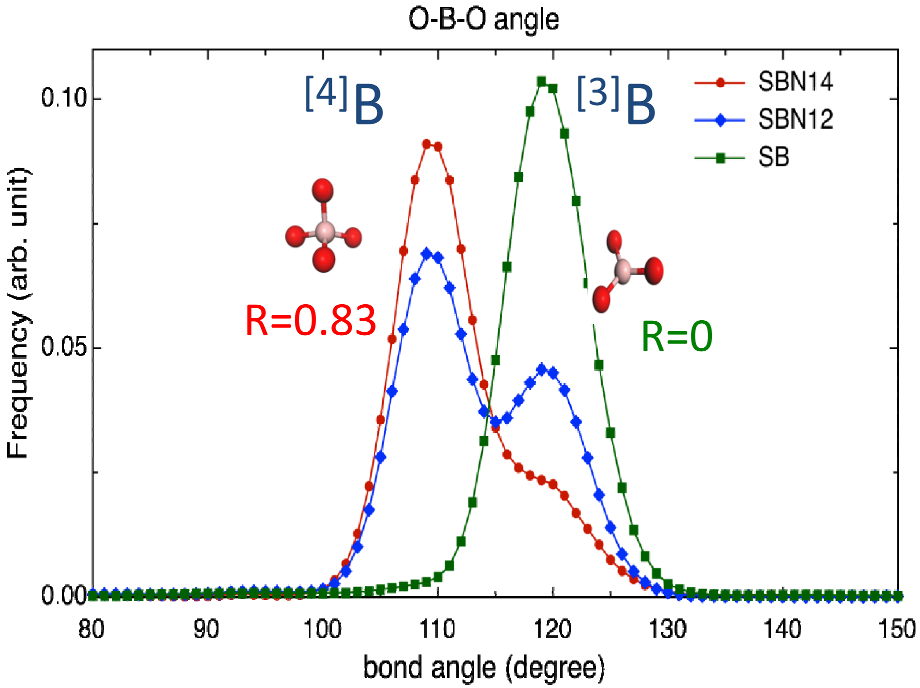
◇ Windisch Jr. et al. (2011)
dissolution work

■ Our
MD simulations

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

Detailed structures

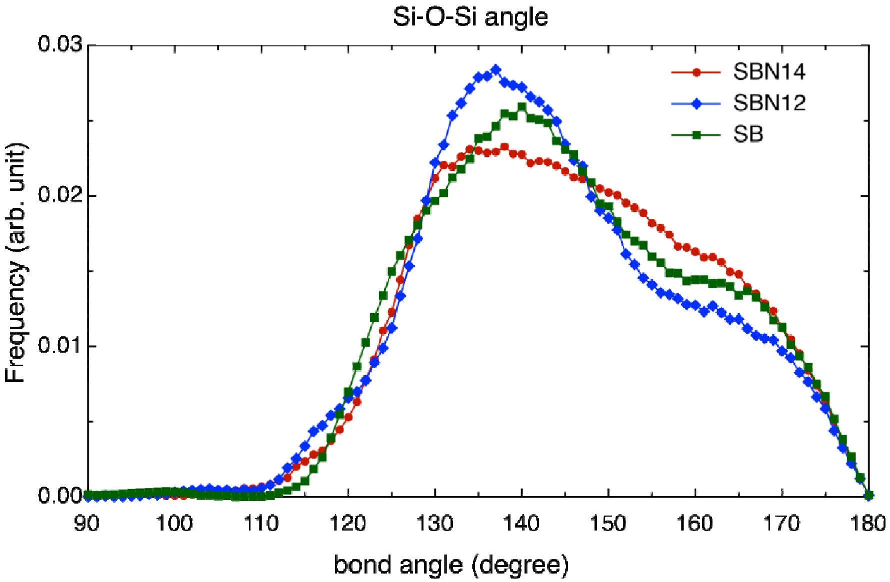


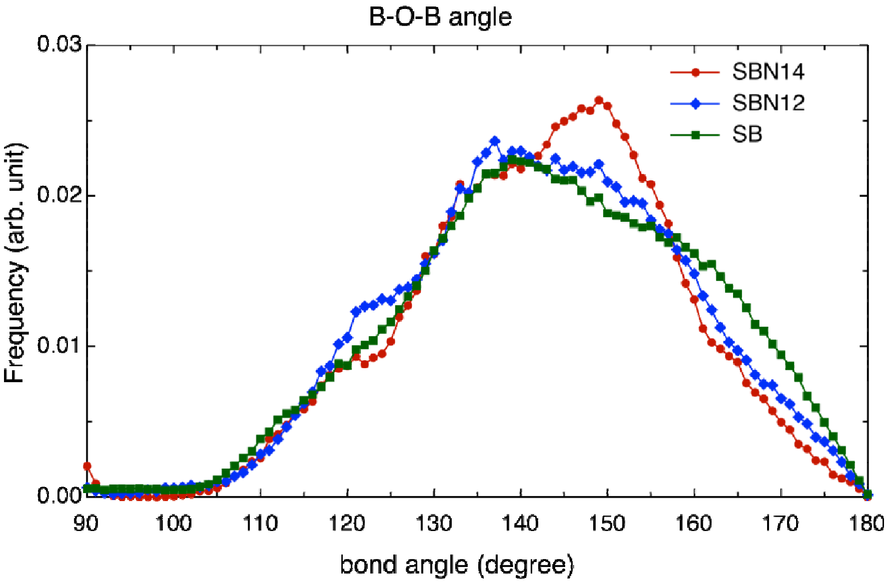


Glass	*d*(B-O)		CN_B		$^{[4]}$B	NBO		Q_3 (Si)
	MD	EXP	MD	Theory	MD	MD	Theory	MD
SB	1.36	1.37	3.0	3.0	0 %			
SBN12	1.42	1.41	3.42	3.43	42 %	3 %	0 %	2 %
SBN14 (“T glass”)	1.45	1.44	3.62	3.73	62 %	5 %	1 %	3 %

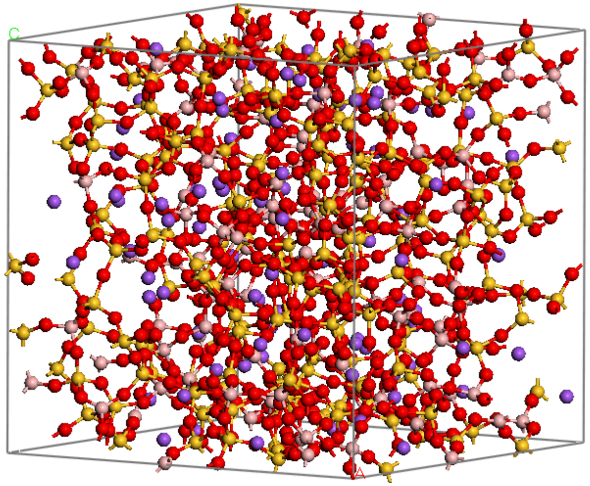
Detailed structures

Glass	*d*(Si-O)	*d*(Na-O)	*d*(Si-Si)	*d*(B-B)	*d*(Si-B)	∠(O-Si-O)	∠(Si-O-Si)	∠(O-B-O)	∠(B-O-B)
SB						109.3	145.3	119.2	143.9
SBN12	1.61	2.54	3.03	2.66	2.86	109.5	144.0	113.5	142.6
SBN14	1.61	2.51	3.05	2.71	2.88	109.4	145.8	111.7	142.8
EXP	1.61	2.29-2.62	3.08			109.5-109.7	144-147	111.6-118.6	129.4-143

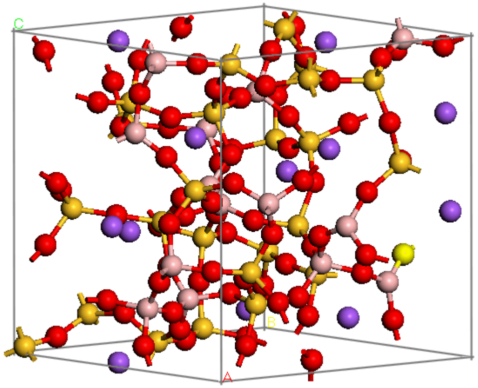




Glass structure for Argonne’s DFT work



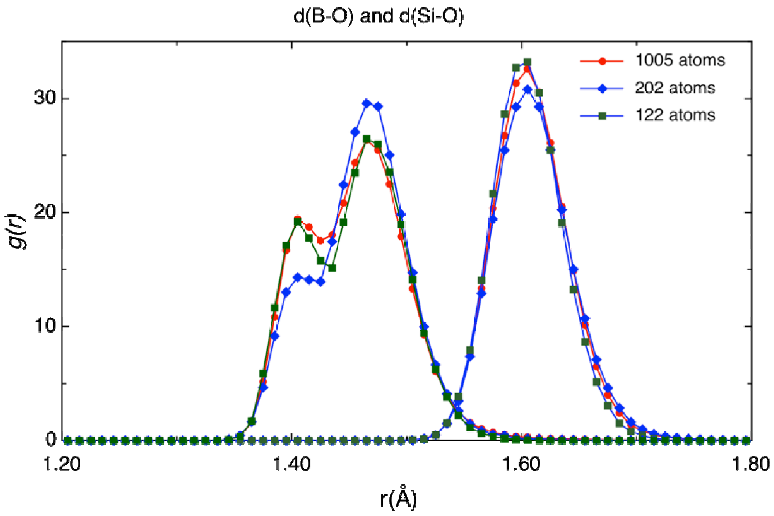
T_glass
(1005 atoms)

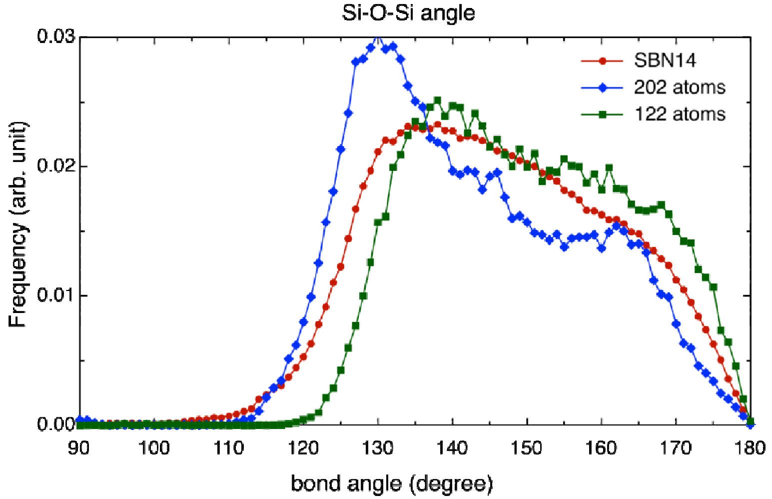


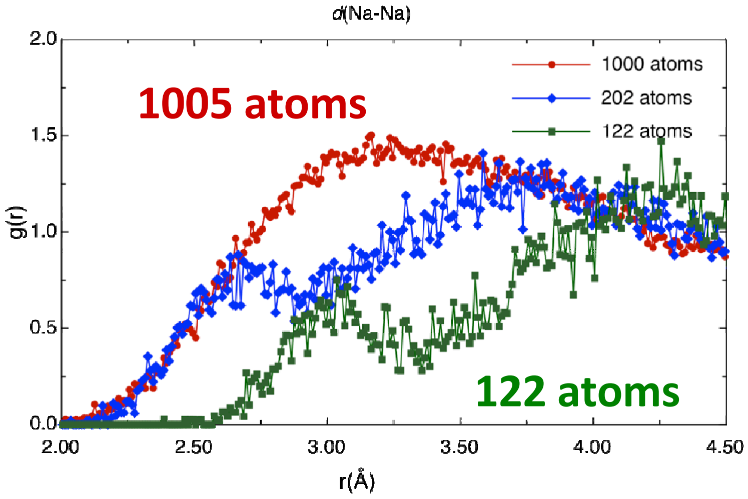
T_glass_122
(122 atoms)

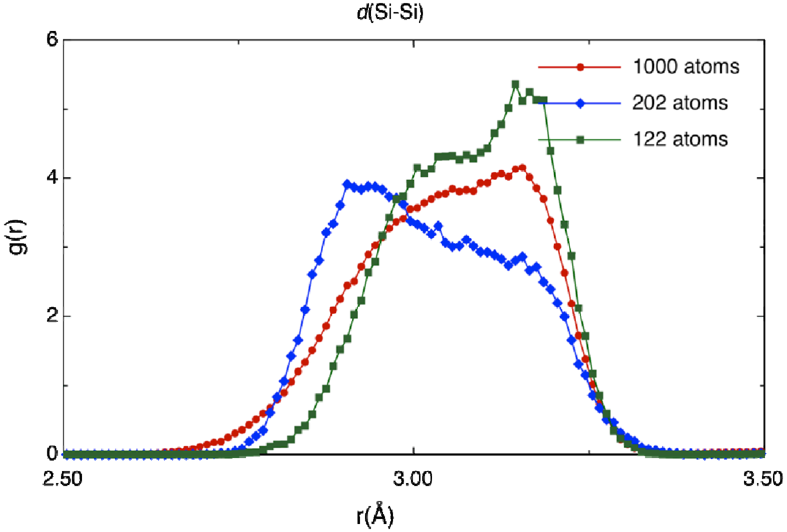
Glass	density		*d*(B-O)		CN_B		$^{[4]}$B	NBO	
	MD	Exp	MD	Exp	MD	Theory	MD	MD	Theory
T_glass	2.44	2.45	1.45	1.44	3.62	3.73	62 %	4.7 %	1 %
T_glass_122	2.46	2.45	1.45	1.44	3.64	3.73	64 %	1.4 %	1 %

SBN14 glass 1005 atoms vs. 122 atoms



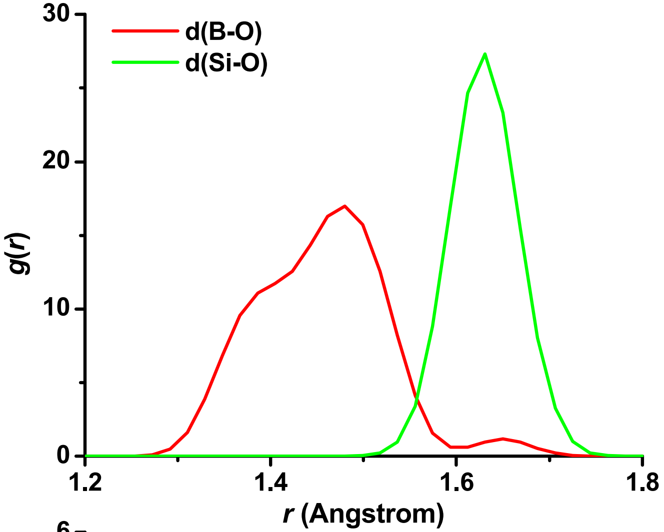


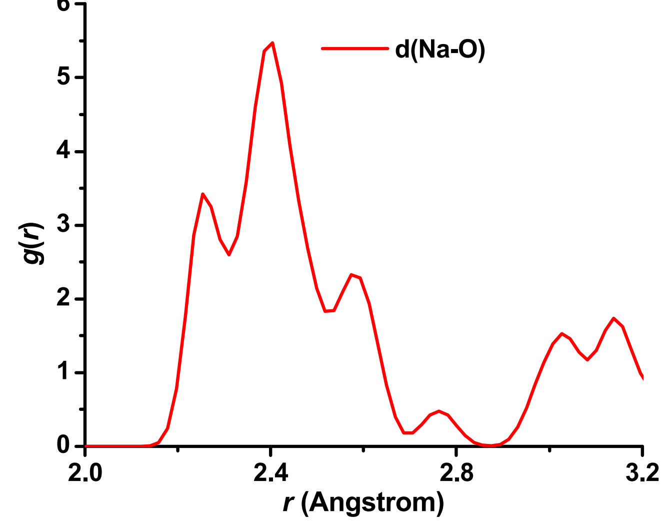




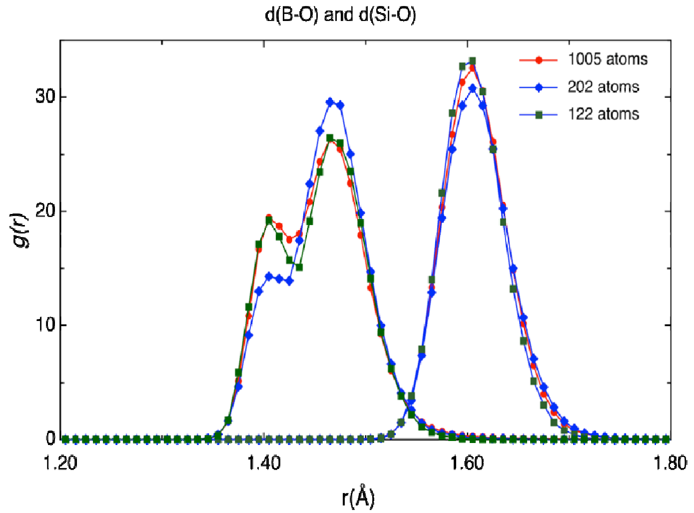
DFT geometry optimization of T-glass (ANL)

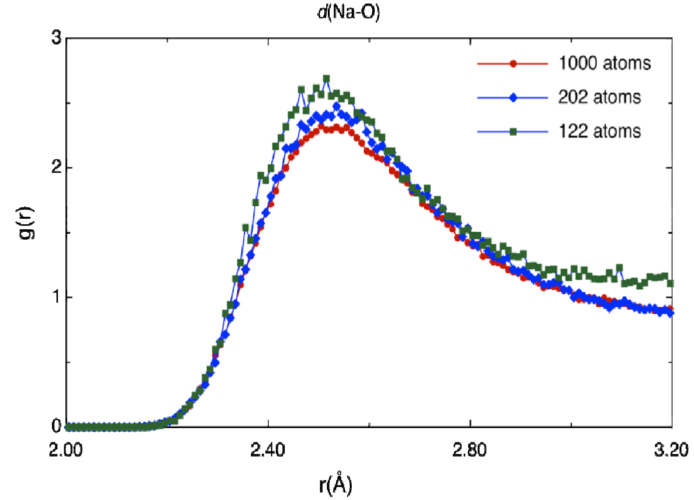
DFT (Argonne) of 1 configuration



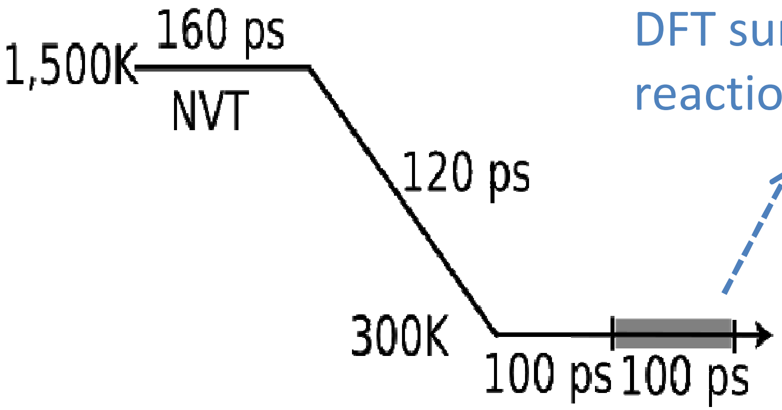


MD simulations (Sandia) of 1600 conf.

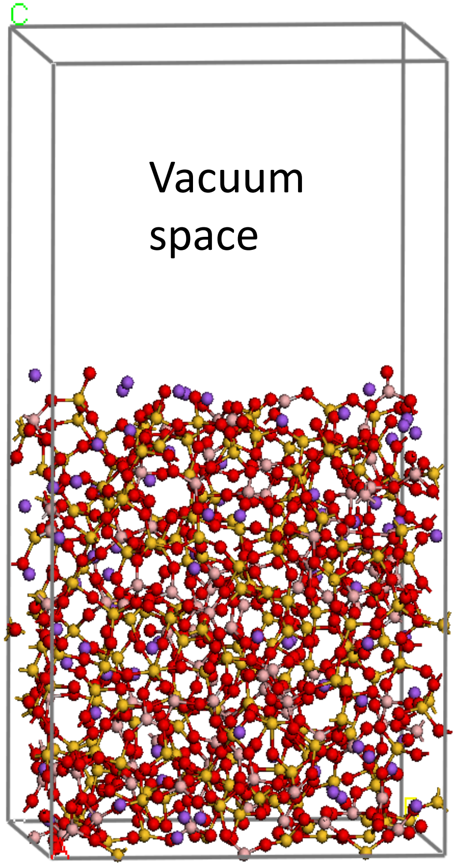




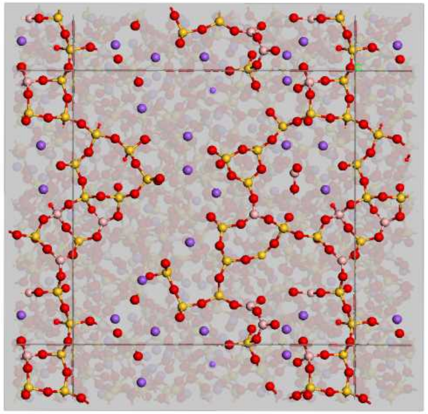
MD simulations of glass surfaces



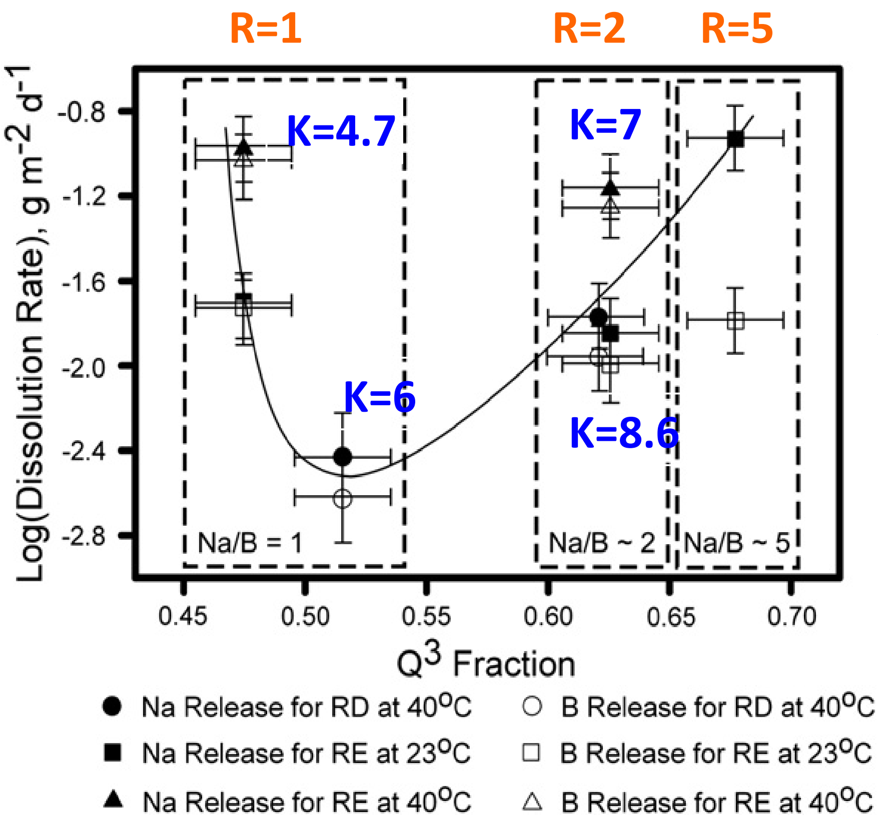
DFT surface
reactions study (ANL)

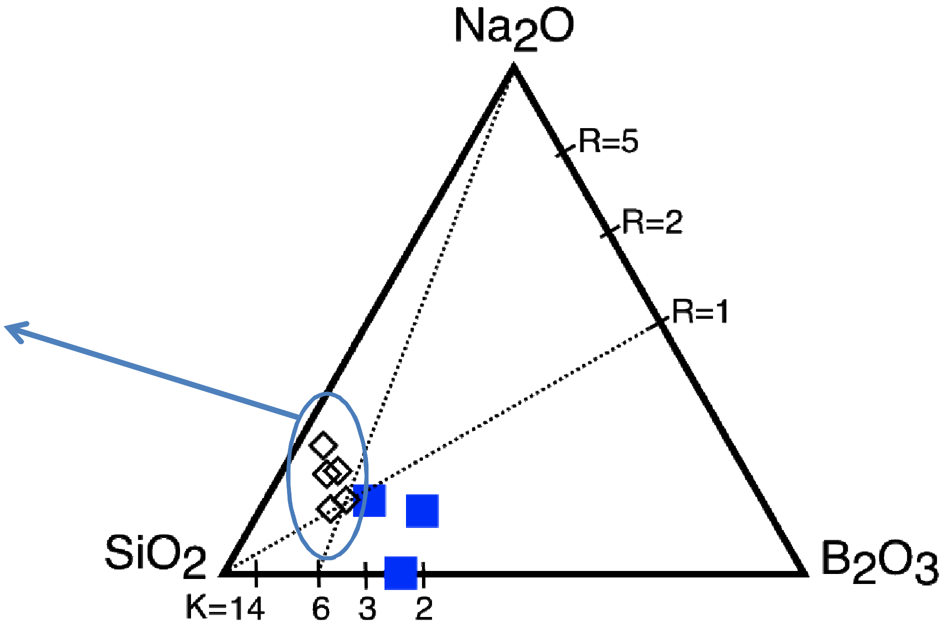


Top 4 Å

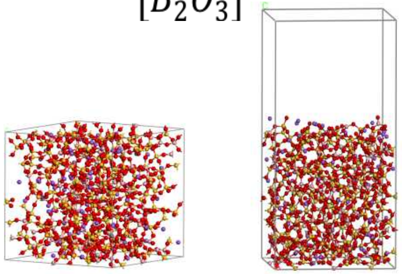


Composition, dissolution, and structures





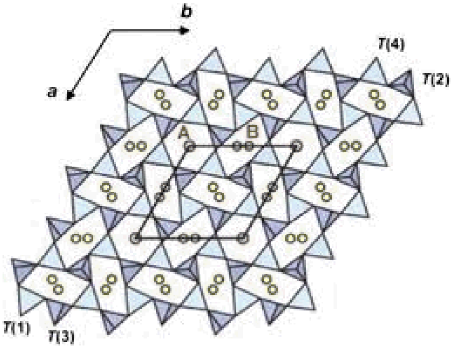
$$R = \frac{[Na_2O]}{[B_2O_3]}, \qquad K = \frac{[SiO_2]}{[B_2O_3]}$$

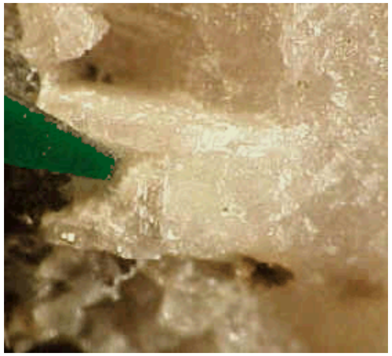


Windisch Jr. et al. (2011) *J. Non-Cryst. Solids*, 2170.

Future Work: Add Al_2O_3 to Force Field

- 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).



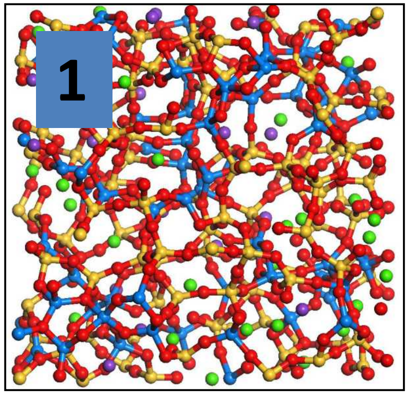


Future Work: Add Al_2O_3 to Force Field

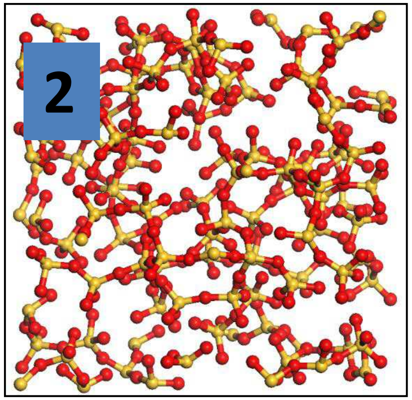
- Simulate NaO-Al_2O_3-B_2O_3-SiO_2 glasses along nepheline-malinkoite join studied by ***Pierce et al***.
- Examine simulated bulk and surface structures, and determine relationships between structure, composition, and dissolution.
- Evaluate hypothesis based on NMR TFS probe determinations (***Washton***) 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).
- DFT results will inform Kinetic Monte Carlo models (***Kerisit***) to calculate overall rate without prior assumption of the dissolution reaction mechanisms.

Model (?) Gel Structure from MD Simulations

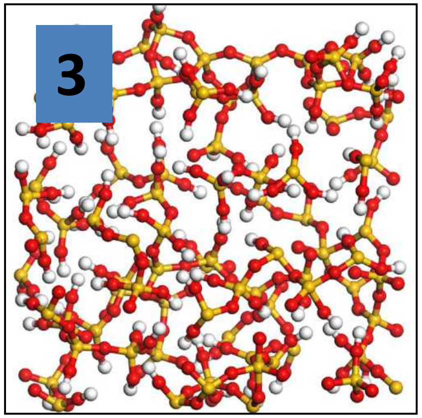
Mellott and Pantano, 2003



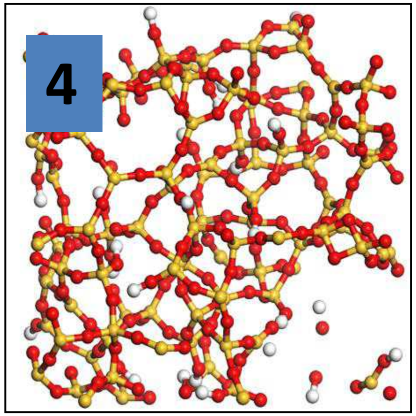
Fully polymerized glass structure



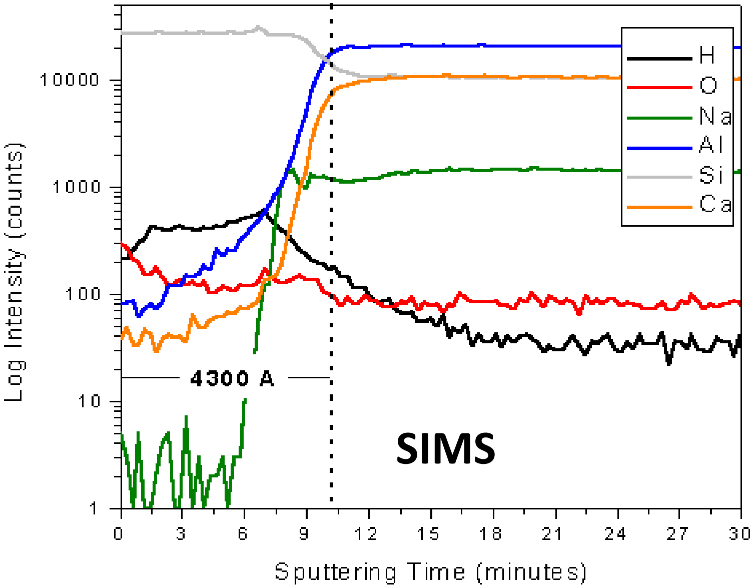
Remove Al, Na, Ca

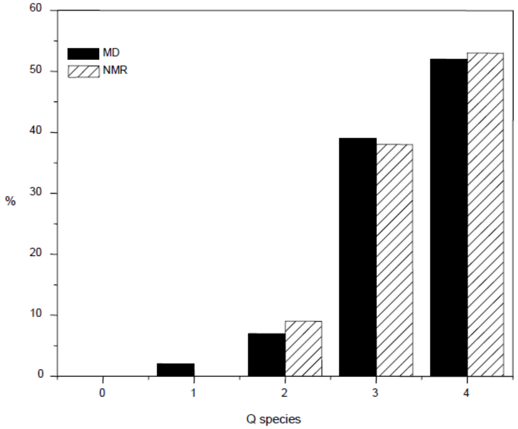


Hydroxylate NBOs



Condensation to form SiO_2 gel layer

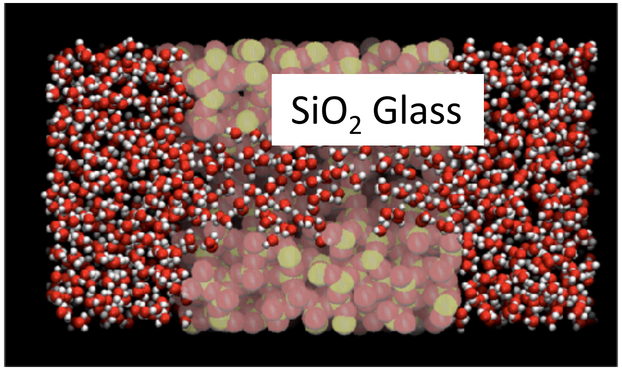


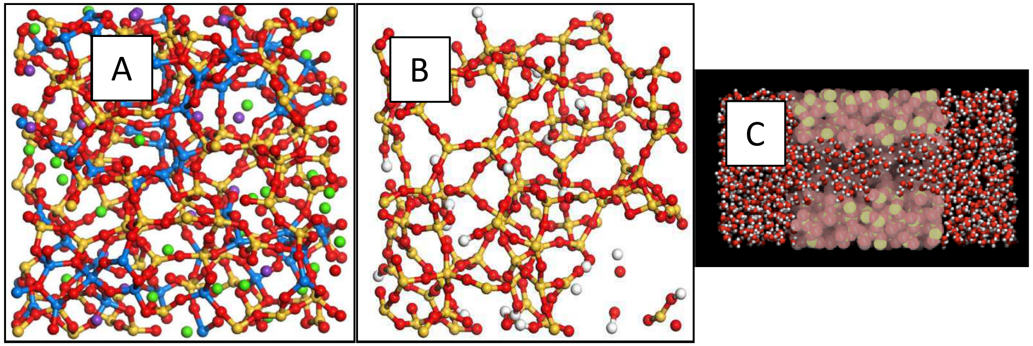


Figures fr. Mellott, 2003

Gel Porosity and Diffusion

Bourg and Steefel, in press





Distance from glass → bulk solution
Time zero → aged gel

Gel Characterization by *Cailleteau et al. (2011)*

- Composition determined by ToF-SIMS: Sharp compositional boundary analogous to that of Mellott
- Morphology determined by SAXS.
- Pore diameters from 10 Å– 45 Å in diameter
- Pore sizes increase over time

Diffusion Rates of H_2O through pores (*B & S*): $0.28 – 1.54 \times 10^{-9}$ m^2 s^{-1}

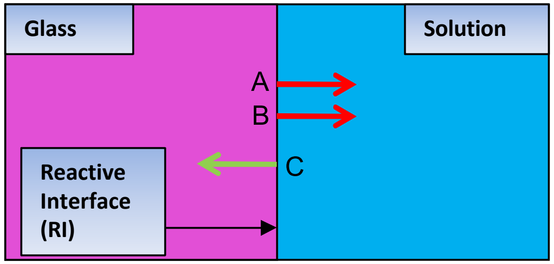
Diffusion is not rate-limiting in pores > 1 nm diameter

How should I characterize simulated gel structures (B) to compare with experimental analyses?

Pores < 1 nm diameter

Fractal dimension
Pore Volume
Skeletal Structure: (polymerization?)

Incorporating Molecular-Level Information into KμC for $NaO\text{-}B_2O_3\text{-}SiO_2$ Glass Dissolution



Assume same general form of constitutive expression for glass

Questions:

1. Can we incorporate this expression into KμC?

2. With continued dissolution do we multiply this expression by (1-Q/K) to account for SiO_2 saturation?

3. This is a surface-site specific model for dissolution. Analogous to MUSIC surface complexation model?

Constitutive Expression from 1st Principles For Orthoclase (Zapol, ANL)

$$k = \sum_{\text{structure}(Q)} \sum_{\text{protonation}(i)} n_Q f_{Qi} k_{Qi}$$

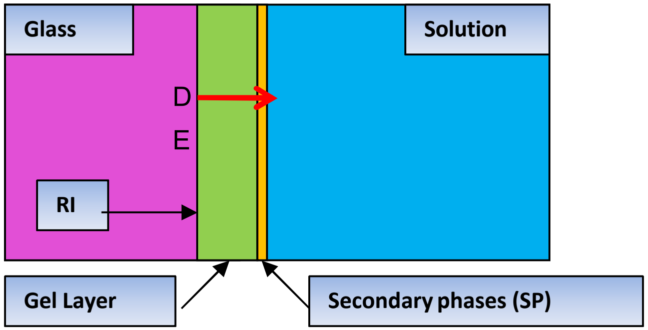
$$f_{Qi} = f\,(Q\,, i\,, \text{aq}, \ \text{pH}\ )$$

$$k_{Qi} = A_{Qi} e^{-E_a(Q,i)/RT}$$

$i = SiOH_2^+, SiOH, SiO^-$

- Overall rate *k* is a linear combination of rates for all exposed sites
- Fractional distribution of three sites *fQi* varies with pH
- Each different type of sites (*Q, i*) has different rate constant *kQi*

Gel Layer Formation and Evolution



•Dissolution (i.e., bond-breaking) at glass surface

•Diffusion of glass components through gel layer (limited?)

H4SiO4 (aq)?

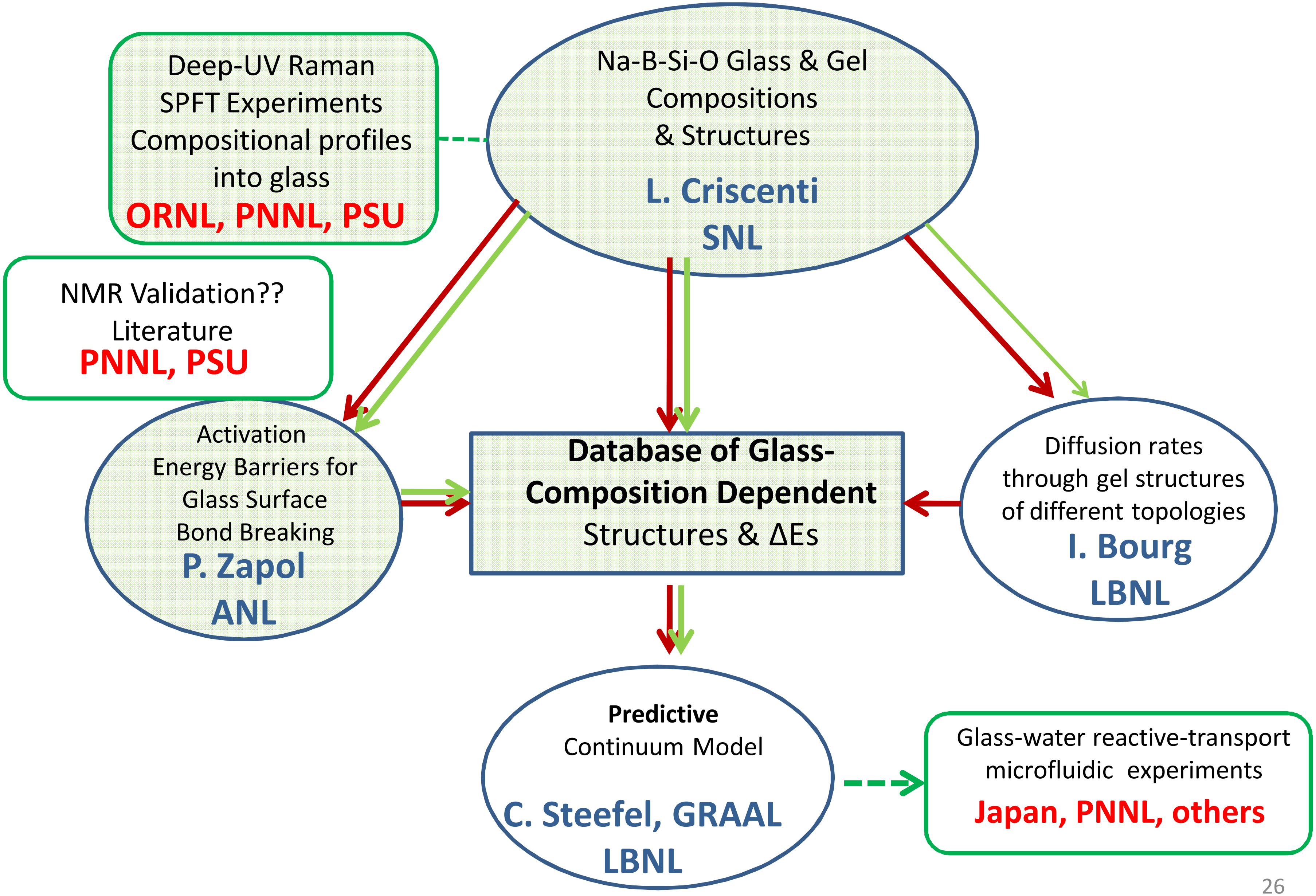
Recondensation of gel layer

- Pore size and connectivity for diffusion of chemical components into glass surface and out into bulk solution
- H^+ migration in gel – through large pores or silica matrix? Na^+ can also “hop” in silica glass.
- Activation energy barriers within gel structure for dissolution (bond-breaking) and recondensation (bond-making)?
- Dual porosity transport model?

Incorporate Molecular-Level Information into KμC for NaO-B_2O_3-SiO_2 Glass Dissolution

- Complete the “upscaling” between from first principles to micro-continuum KμC calculations for a simple 3-component glass.
  - Provide constitutive equations for activation energy barriers as a function of surface composition
  - Provide diffusion rates for solutes through gel structures with < 1 nm pores
- Use KμC in both standard and new predictive approaches to model experimental data from ORNL (Pierce) for 3-component glasses (and Gin’s T-glass)
  - SPFT leachates for NaO-B2O3-SiO2 glass dissolution
  - Leached glass surface to depth profiles
  - UV-Raman Spectroscopy on glass structure
- Determine strengths and weaknesses of 1st principles informed model.
- Reiterate.

Integrated Modeling Plan



Deep-UV Raman
SPFT Experiments
Compositional profiles
into glass
ORNL, PNNL, PSU

Na-B-Si-O Glass & Gel
Compositions
& Structures
L. Criscenti
SNL

NMR Validation??
Literature
PNNL, PSU

Activation
Energy Barriers for
Glass Surface
Bond Breaking
P. Zapol
ANL

Database of Glass-
Composition Dependent
Structures & ΔEs

Diffusion rates
through gel structures
of different topologies
I. Bourg
LBNL

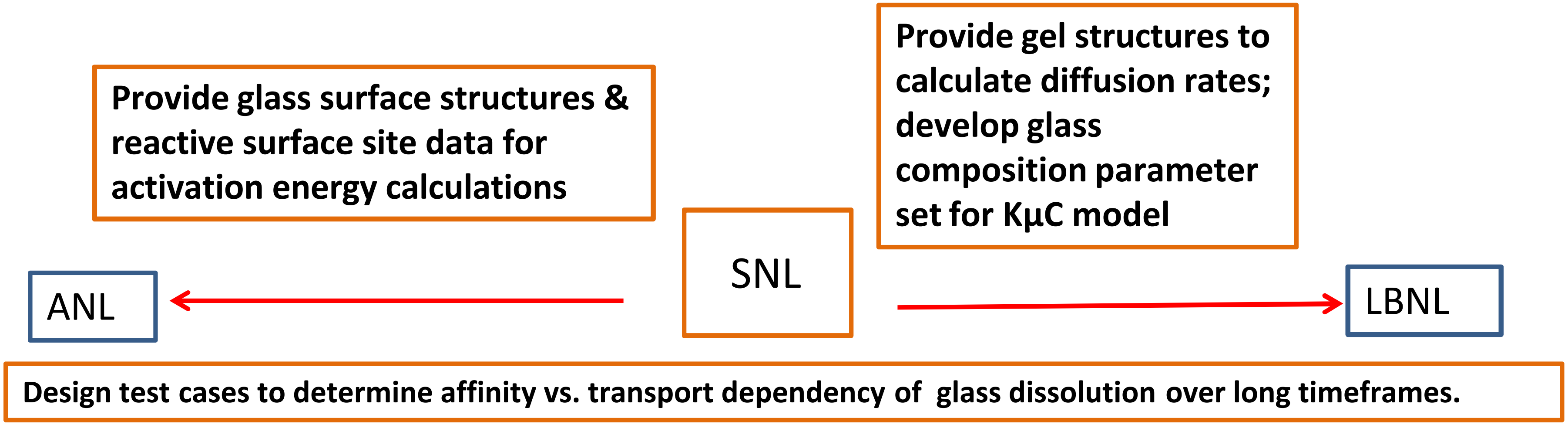
Predictive
Continuum Model
C. Steefel, GRAAL
LBNL

Glass-water reactive-transport
microfluidic experiments
Japan, PNNL, others

EXTRAS

Next Steps Continued

- Examine how Kieu et al. (2011) reproduces surface structure of Na-borosilicate glasses
  - Changes in bond length and bond angle distribution
  - Changes in Si and B coordination
  - Depth of variation due to surface
- Validate Na-borosilicate glass bulk and surface structures with neutron diffraction and NMR data where possible.
- Create representative 100-atom glass surface structures to hand off to Peter Zapol (ANL) for activation energy barrier calculations.



Provide glass surface structures & reactive surface site data for activation energy calculations

Provide gel structures to calculate diffusion rates; develop glass composition parameter set for KμC model

ANL

SNL

LBNL

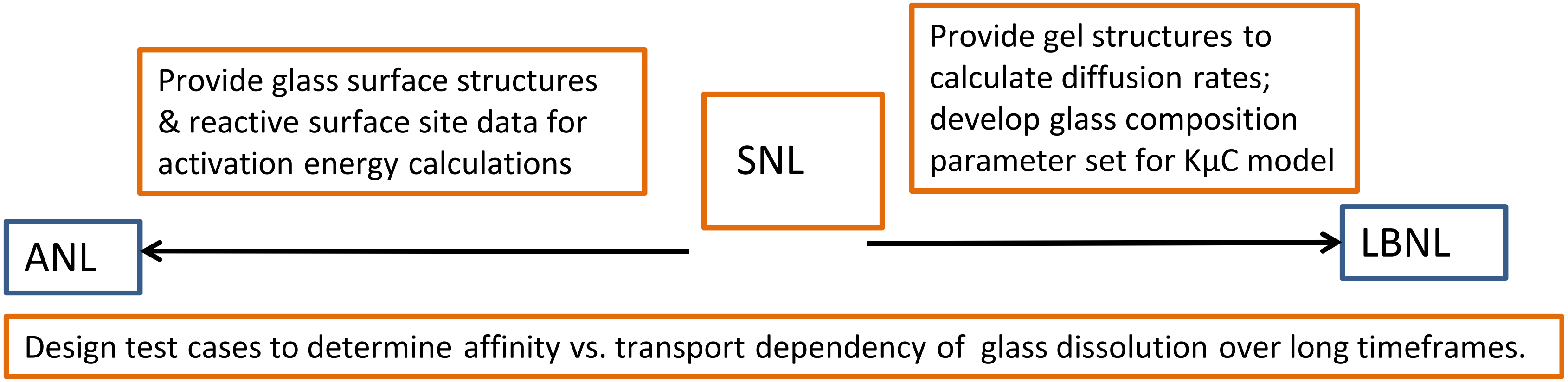
Design test cases to determine affinity vs. transport dependency of glass dissolution over long timeframes.

Incorporating Molecular-Level Information into KμC for NaO-B_2O_3-SiO_2 Glass Dissolution

- *Windisch et al. (2011):* Na_2O-xB_2O_3-(3-x)SiO_2 glass structure correlated to dissolution rates in SPFT testing.
- SPFT leach tests and ToF SIMMS data collection for Na_2O-xB_2O_3-(3-x)SiO_2 currently underway at ORNL (***Pierce***).
- Can we reproduce ORNL data using constitutive expression for glass dissolution obtained by SNL/ANL?
- By using KμC using both empirical and predictive approaches, we will be able to assess and improve upscaling approach before moving on to more complex glasses.
- This would be the first time an atomistic-based constitutive equation for dissolution kinetics would be incorporated into a reactive-transport model.

Interactions

- *Collaboration* with K. Murphy, C. Pantano, and K. Mueller to coordinate the simulation of glass structures that are simultaneously being investigated by NMR spectroscopy.
- *Handoff* to P. Zapol of glass surface structures for 1st principles calculations of activation energy barriers.
- *Collaboration* with J. Icenhower to investigate the importance of ion exchange on the long-term dissolution rate of glasses.
- *Handoff* to I. Bourg of gel surface structures for diffusion studies.
- *Collaboration* with C. Steefel to create a database of kinetic reaction and transport parameters that can be used with KμC. Further collaboration to design test cases for KμC that can be validated against experiment.



Provide glass surface structures & reactive surface site data for activation energy calculations

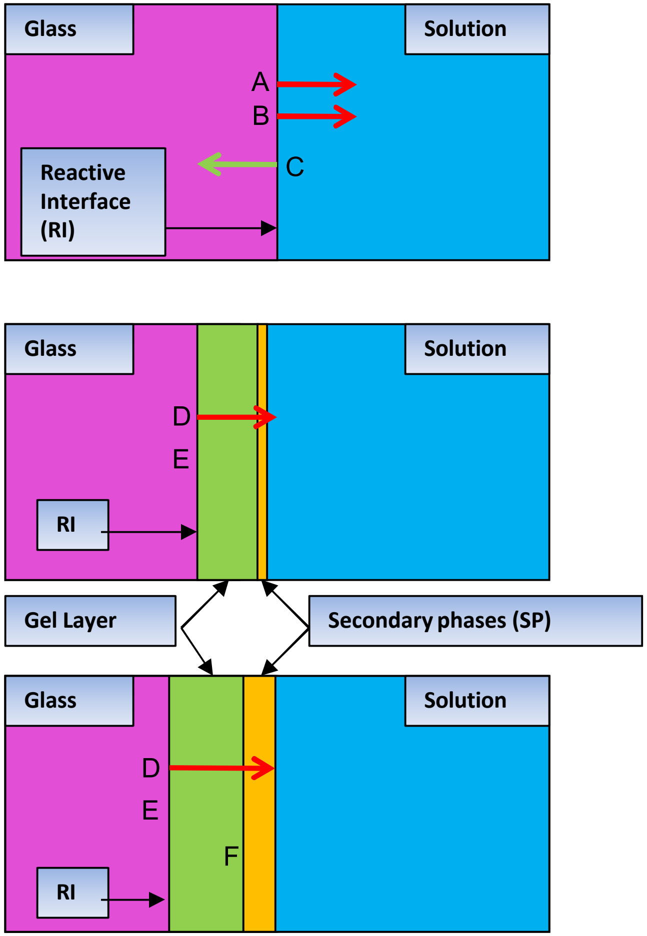
SNL

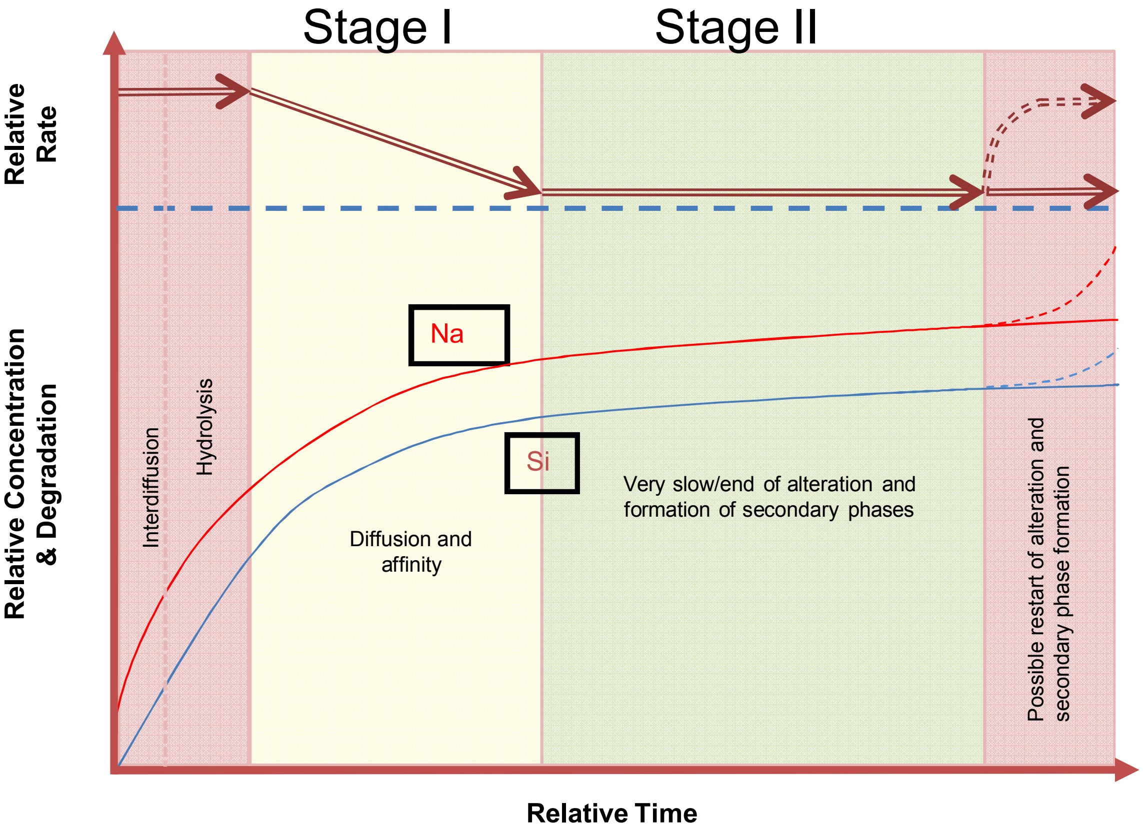
Provide gel structures to calculate diffusion rates; develop glass composition parameter set for KμC model

ANL

LBNL

Design test cases to determine affinity vs. transport dependency of glass dissolution over long timeframes.





A – rate of alkali surface release
B – rate of Si, Al surface detachment (tends to be limiting)
C – rate of H_2O diffusion into glass

D – rate of silica diffusion through the gel (± SP) layer (at least partially limiting). Other constituents mass transport rates may also be important.
E – the aqueous composition at the RI is not the same as the Solution (aqueous silica concentration especially) and the surface area of the RI may be reduced by glass-gel contact area.
F – the gel and secondary phase layers may be acting as a mantle, in part isolating the fresh glass from the Solution.

- Fraction of dissolved boron, which is the yardstick of the degree of glass corrosion, decreased as the Ca content increased in the glass.

Long-term Behavior Science: The cornerstone approach for reliably assessing the long-term performance of nuclear waste (Gin et al., 2011) A large multi-scale approach is required and involves a mechanistic understanding of the key phenomena controlling the source term (i.e. the flux of radionuclides released from the waste as a function of time), as well as parametric studies, integrated and in situ tests. As a result, it is eventually possible to develop an operational model based on clever simplifications of a very complex reality, ensuring that predictions will always remain conservative despite conceptual and numerical uncertainties. Finally, predictive models must be validated based on the study of natural or archaeological analogues.