



U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Environmental Management

DOE Studies to Improve Understanding of Rate-Limiting Mechanisms under Varying Conditions

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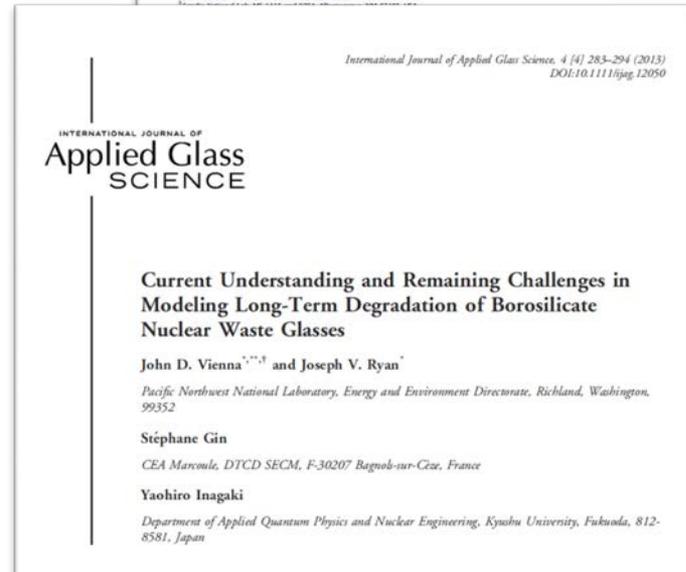
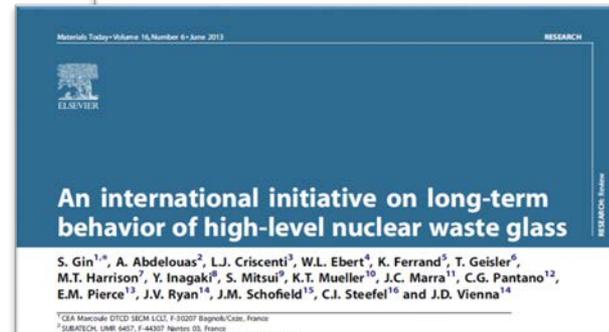
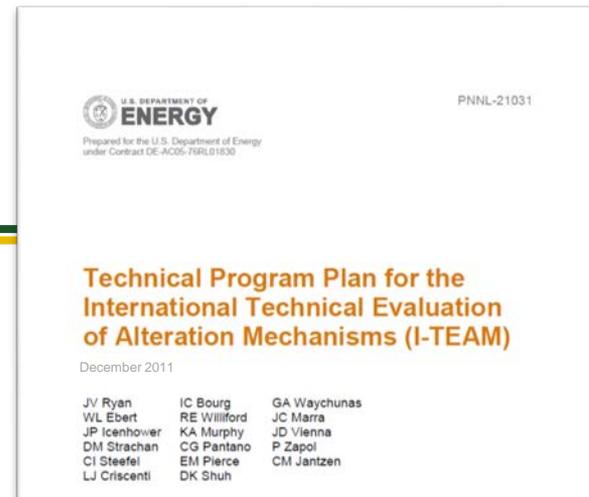
Background

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■ The most current international collaboration on long-term glass corrosion (**many prior incarnations from as early as the 1970's**) was organized in 2010 to develop the data and understanding necessary for an international consensus on the behavior of glass over geologic time scales in a variety of disposal environments

■ The team has worked collaboratively to:

- Identify the key mechanisms that can control the long-term dissolution rate of glass
- Perform fundamental and applied research using modern materials science techniques to understand the mechanisms in question
- Critical evaluation of test methods, data, interpretations, and models



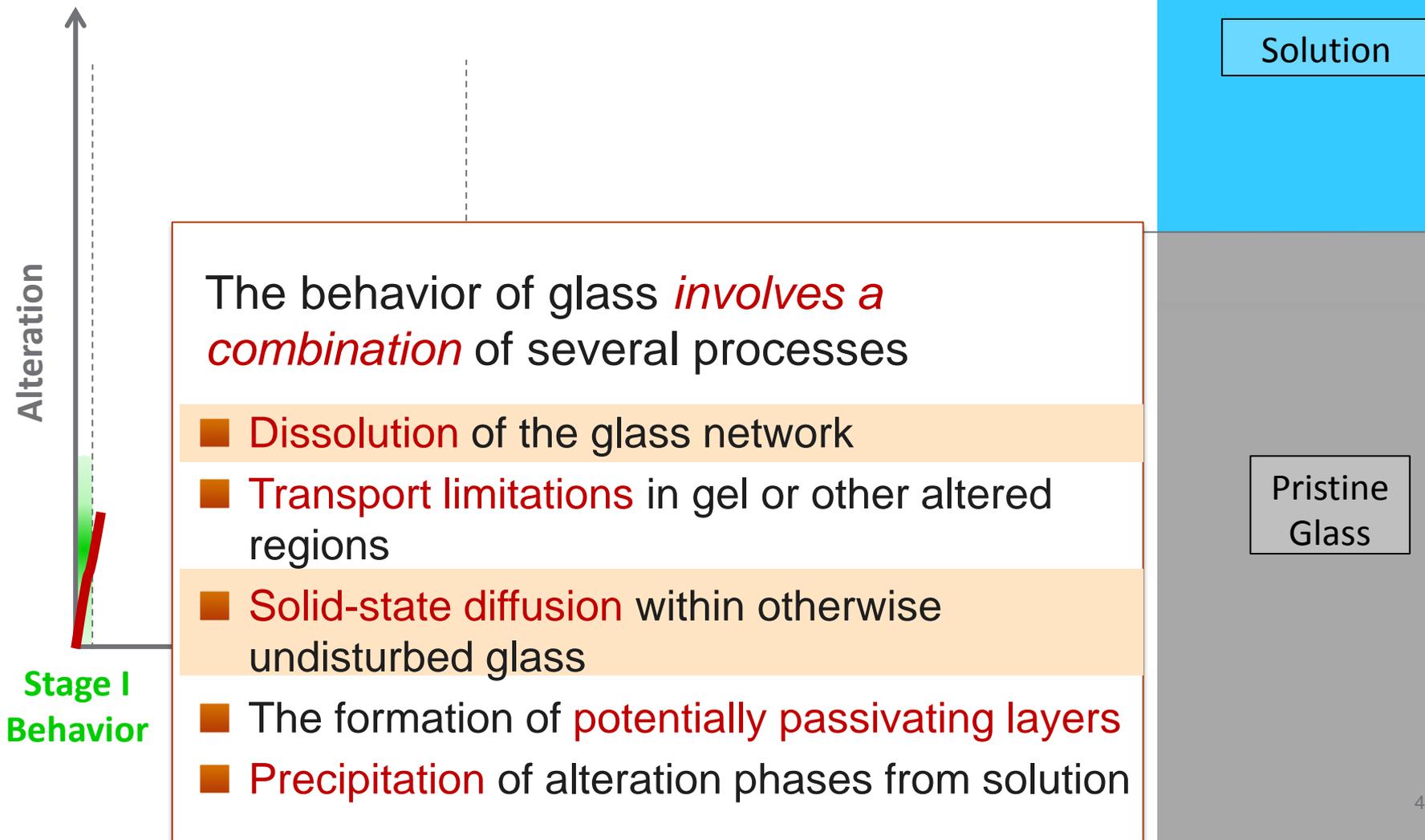


What are the rate-limiting mechanisms for **radionuclide release** from a glass waste form and how should models represent them?

- The corrosion behavior of glass results from a combination of several simultaneously-occurring processes
- More remains to be known about which processes dominate under different conditions and how they should be represented in models
- **A coordinated approach leveraging particular national and international expertise**



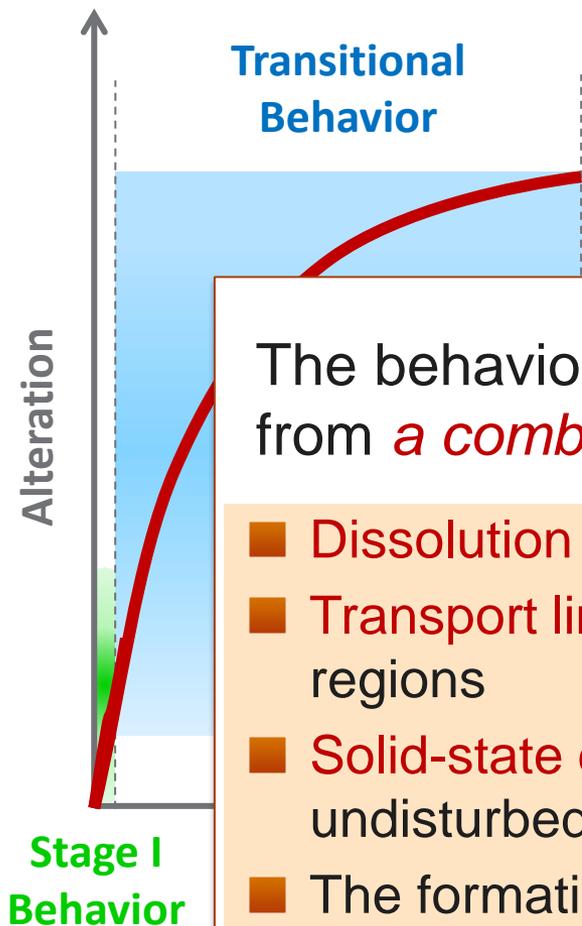
Current understanding of glass corrosion mechanisms





Current understanding of glass corrosion mechanisms

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The behavior of glass *at all times* results from *a combination* of several processes:

- **Dissolution** of the network
- **Transport limitations** in gel or other altered regions
- **Solid-state diffusion** within otherwise undisturbed glass
- The formation of **potentially passivating layers**
- **Precipitation** of alteration phases from solution

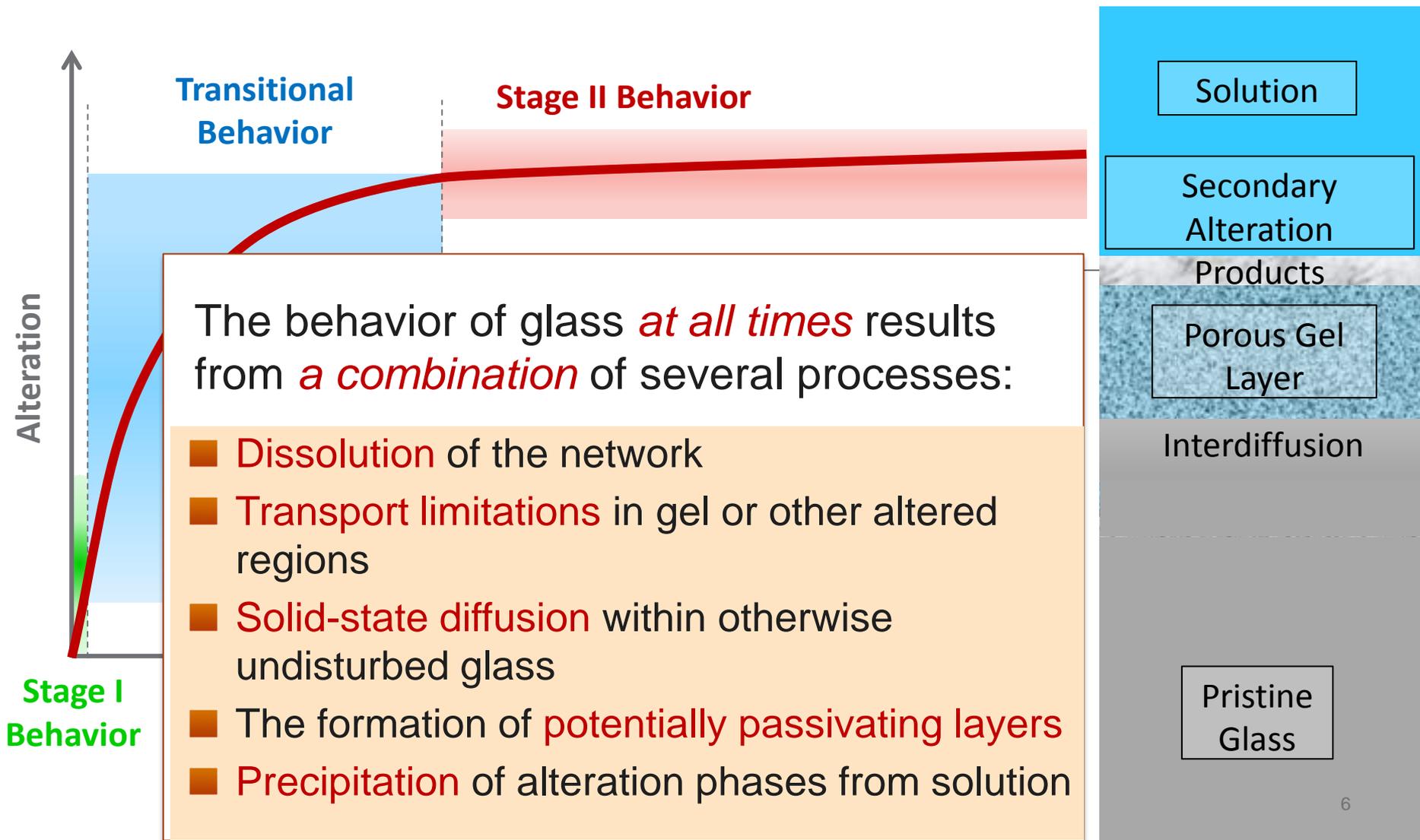
Solution

Interdiffusion

Pristine
Glass



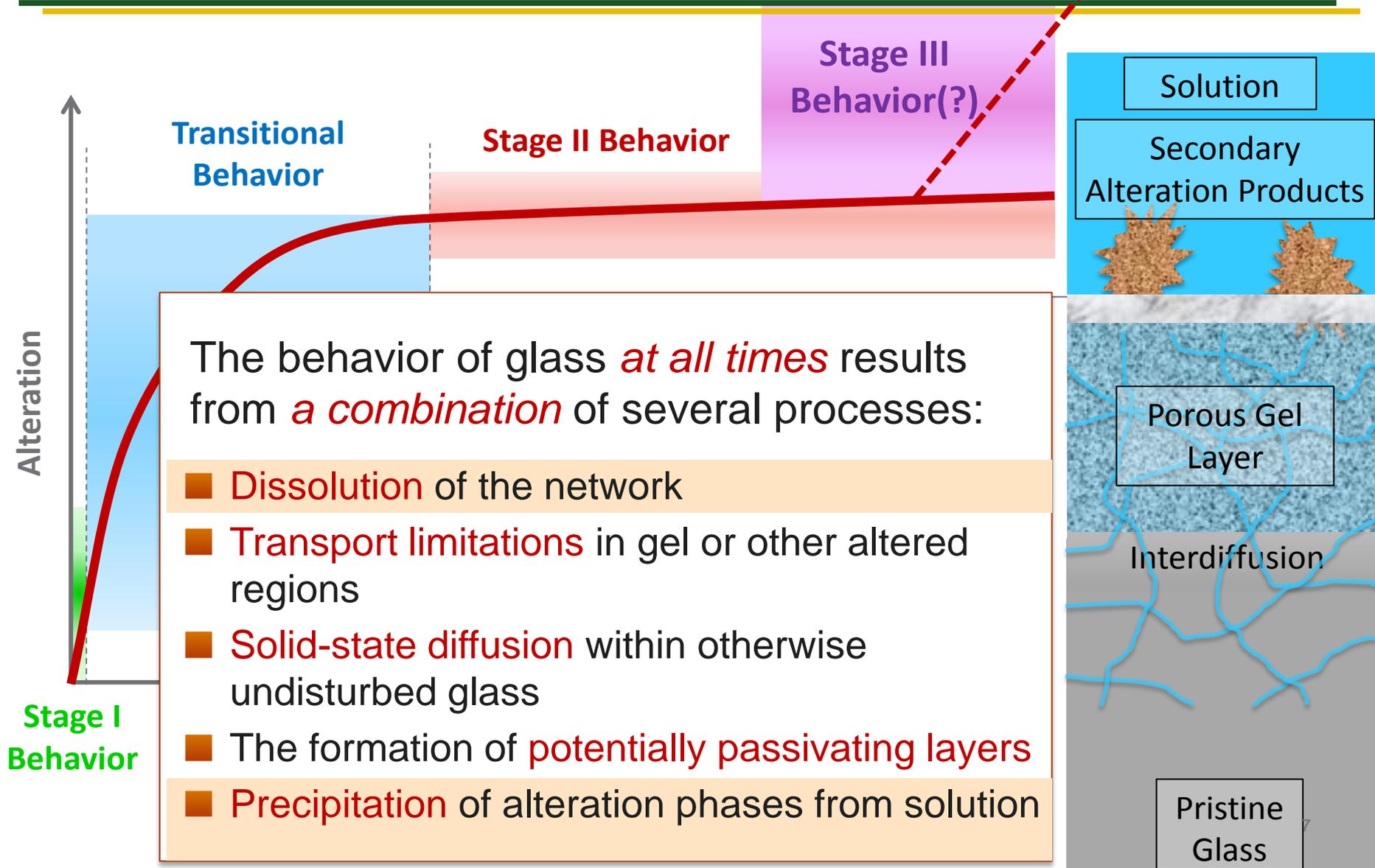
Current understanding of glass corrosion mechanisms





Current understanding of glass corrosion mechanisms

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The behavior of glass *at all times* results from *a combination* of several processes:

- **Dissolution** of the network
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- The formation of **potentially passivating layers**
- **Precipitation** of alteration phases from solution



Current understanding of glass corrosion mechanisms



- ▶ The behavior of glass *at all times* is generally believed to result from *a combination* of several processes at work:
 - **Dissolution** of the network
 - **Transport limitations** in gel or other altered regions
 - **Solid-state diffusion** within otherwise undisturbed glass
 - The formation of **a passivating layer** and gel from glass
 - **Precipitation** of alteration phases from solution

Different processes dominate at different conditions

This is being considered in model development



Mechanistic Approach – Mechanistic Experiments

- **Testing and modeling activities were planned based on the overall strategy outlined in ASTM C1174**
- **The goal is to provide a strong mechanistic foundation for model(s)**
- **The key objectives are to:**
 - (1) determine which mechanism(s) control the glass degradation rate during waste disposal, and
 - (2) provide the technical basis for a predictive model based on the appropriate process or processes
- **To ensure flexibility, the research considers a range of environmental variables**

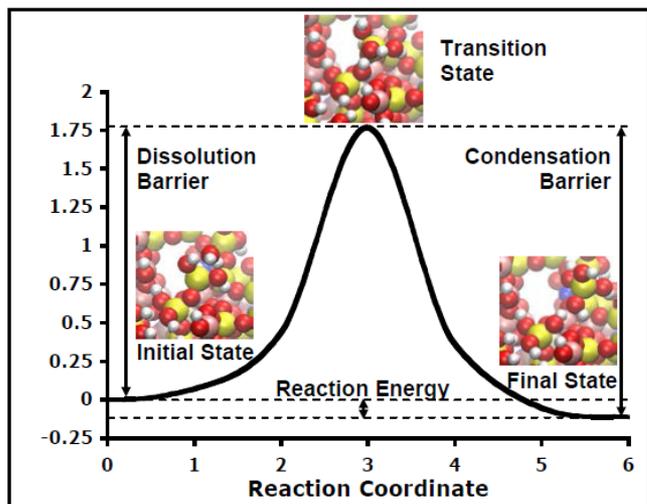
Experiments include both those targeted to explore a particular mechanism and more general examinations of behavior



Targeted Approach: *Dissolution of Network*

■ First-principles modeling of glass-water interactions

- Develop a set of energy barriers for modeling glass dissolution
- Use first principles calculations for dissolution reactions on protonated, neutral, and deprotonated sites
- Such calculations provide an otherwise unavailable method for discriminating between potential reaction mechanisms



Step 1	Initial State	Transition State	Final State
Q^1-Q^3	<p>1.75</p>	<p>2.42</p>	<p>4.30</p>
Q^2-Q^3	<p>1.68</p>	<p>2.19</p>	<p>3.15</p>
Q^3-Q^3	<p>1.73</p>	<p>2.29</p>	<p>3.53</p>



Recent Findings: *Dissolution of Network*

■ Temperature and pH effects on glass dissolution

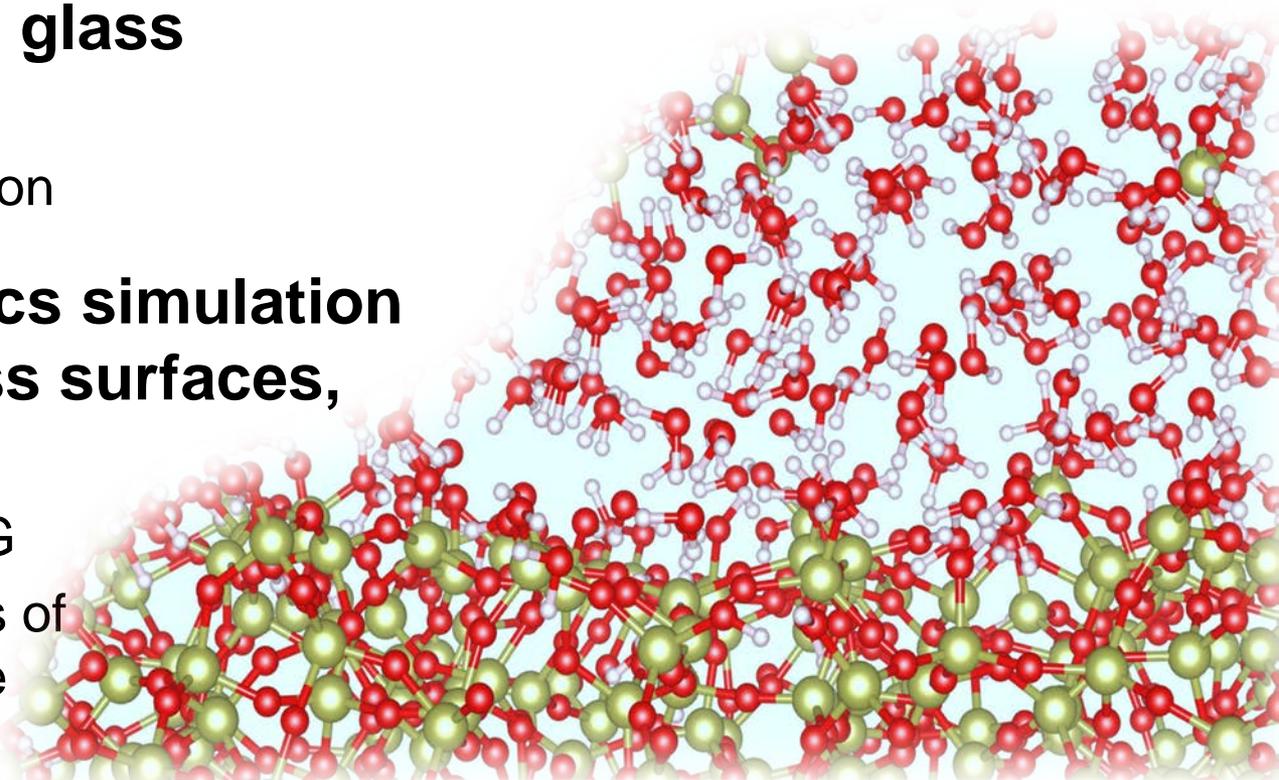
- Sensitivity analyses of rate-law parameters with glass composition
- Study into the pH dependence for dissolution rate equation

■ Examining the roughness at the barrier between the gel and the unreacted glass

- In situ techniques
- Impact of composition

■ Molecular dynamics simulation of bulk glass, glass surfaces, and surface gels

- MD modeling of ISG
- MD and MC models of porous gel structure





Targeted Approach:

The theory of a passivating layer

■ Questions:

- How does transport proceed to, from, and into the glass surface through a “mature” corrosion layer?
- Is diffusion or dissolution the controlling mechanism?

■ Hypothesis:

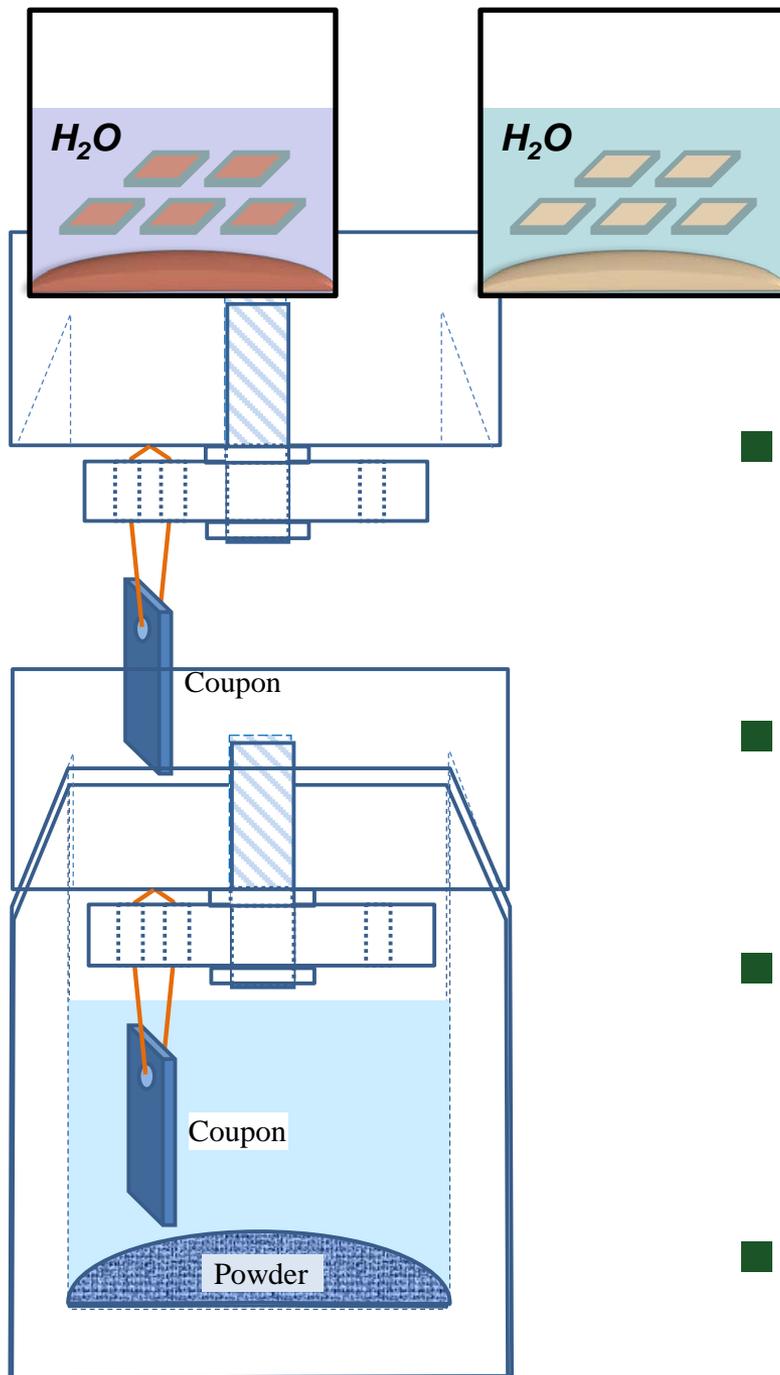
- To measure the diffusion of ions, we must **distinguish** ions in the glass and alteration phases from those in solution

■ Method

- Distinguish between glass and solution sources through **isotopic enrichment**

Experiment from slides 12-23 covered in (unless otherwise specified):

JV Ryan, WL Ebert, JJ Neeway, SN Kerisit, and PC Rieke. 2014. “A Mechanistic Approach to the Calculation of Glass Behavior over Geologic Time Scales” FCRD-SWF-2014-000029, PNNL-23691



Key	Isotopically Substituted	Natural Abundance
Glass		
Solution		

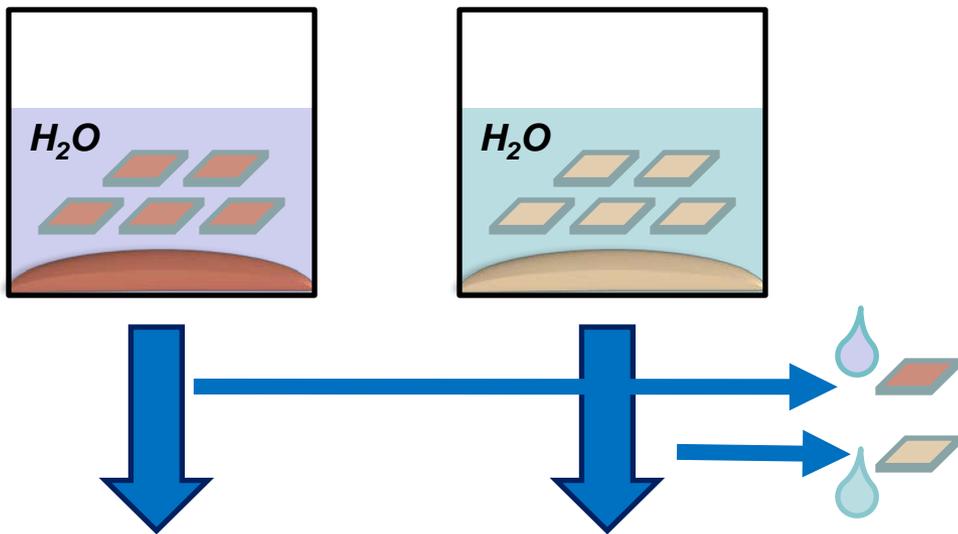
- **Synthesize glasses with operationally identical compositions using:**
 - Enriched isotope ratios
 - Natural (or depleted) isotope ratios
- **Process each glass into:**
 - Coupons (>10, ~10x5x1 mm)
 - Powder (32-75 μm)
- **Run parallel tests for the two glasses:**
 - Surface area to solution volume ratio: ~20,000 m^{-1}
 - PTFE reaction vessels
- **Place into ultrapure water and allow to corrode at 90 °C**

Isotope Substitution Studies

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Structural Role	Natural Dominant Isotope	Substituted Isotope	Natural Abundance	Enriched Abundance	Experiment Abundance	Enrichment (x natural)
Former	²⁸ Si	²⁹ Si	4.67%	80.0%	60.0%	12.9
Mobile Former	¹¹ B	¹⁰ B	19.97%	99.0%	99.0%	99.0*
Alkali Modifier	⁷ Li	⁶ Li	7.50%	95.0%	95.0%	12.7
AE Modifier	⁴⁰ Ca	⁴⁴ Ca	2.09%	96.5%	50.0%	24.0
Iron	⁵⁶ Fe	⁵⁷ Fe	2.20%	95.0%	95.0%	43.2
Other TM	⁶⁴ Zn	⁶⁸ Zn	18.80%	98.6%	98.6%	99.0*
Other TM	⁹⁸ Mo	⁹⁵ Mo	15.92%	94.3%	94.3%	94.0*

* Both glasses (“enriched” and “natural”) synthesized using enriched isotopes: one with the high atomic mass, one with the low



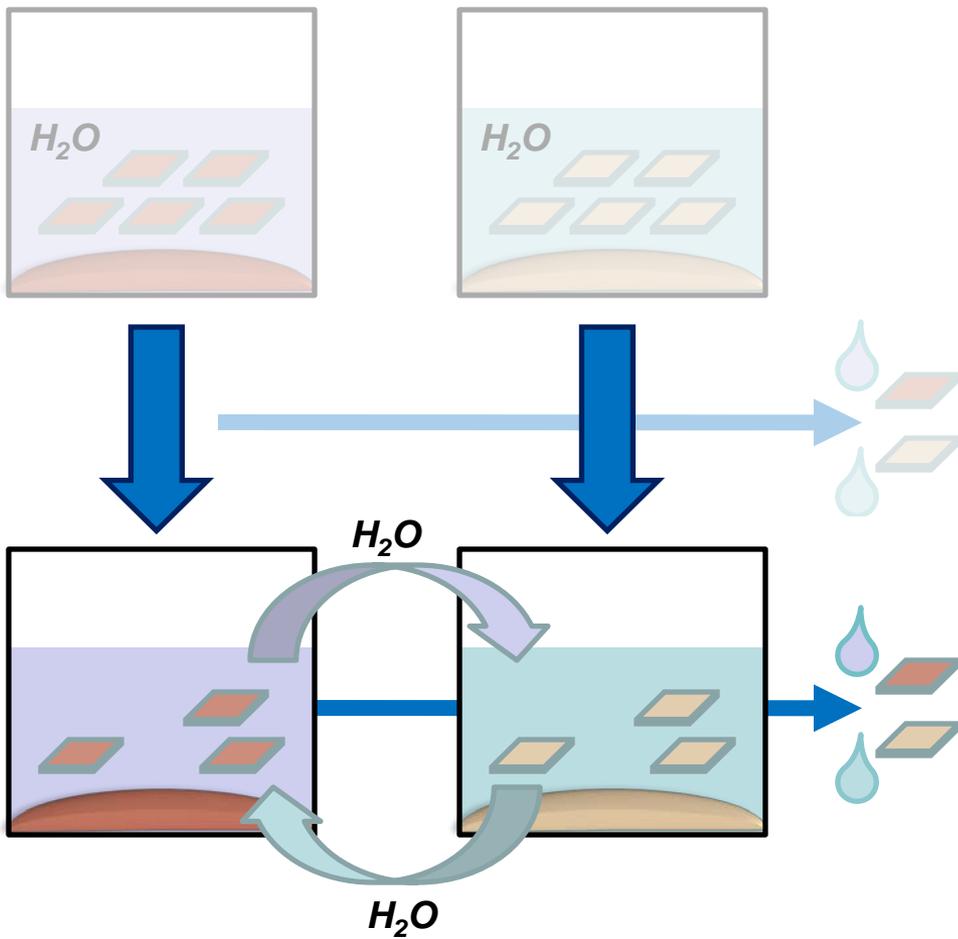
Key	Isotopically Substituted	Natural Abundance
Glass		
Solution		

Characterization Suite:

- Solution Analysis
- SIMS
- RBS
- FTIR
- SEM/EDS
- Scattering
- GIXRD
- XRD

■ **Monitor experiment:**

- Occasional solution samples (volume minimized, not replaced)
- 1-2 coupons



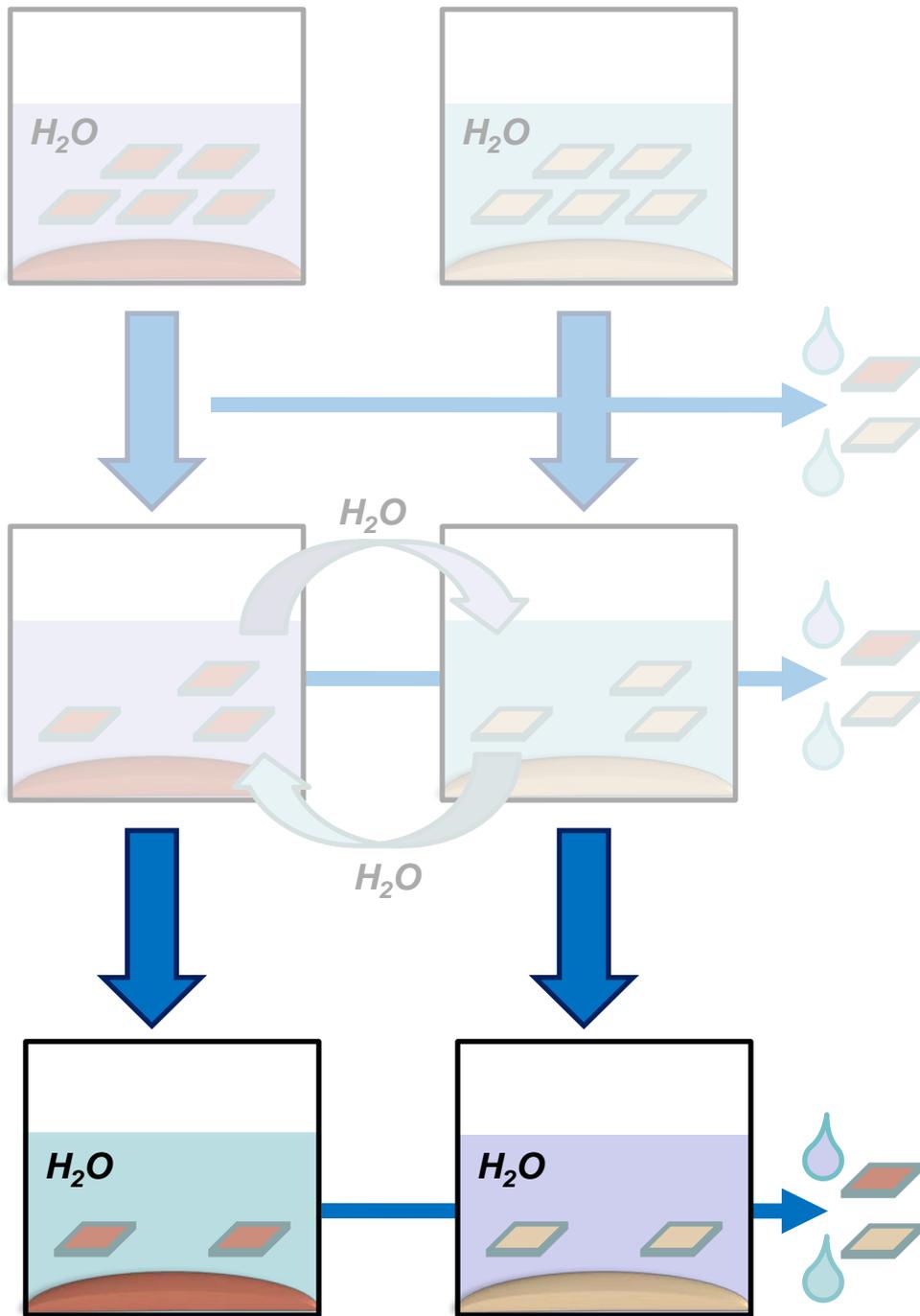
Key	Isotopically Substituted	Natural Abundance
Glass		
Solution		

■ **“Mature” gel layer formed:**

- ~200 days for SON68
- Rate reduction observed

■ **Decant liquids and switch**

- Enriched → Natural
- Natural → Enriched
- Minimize disturbance to powder
- Characterization suite



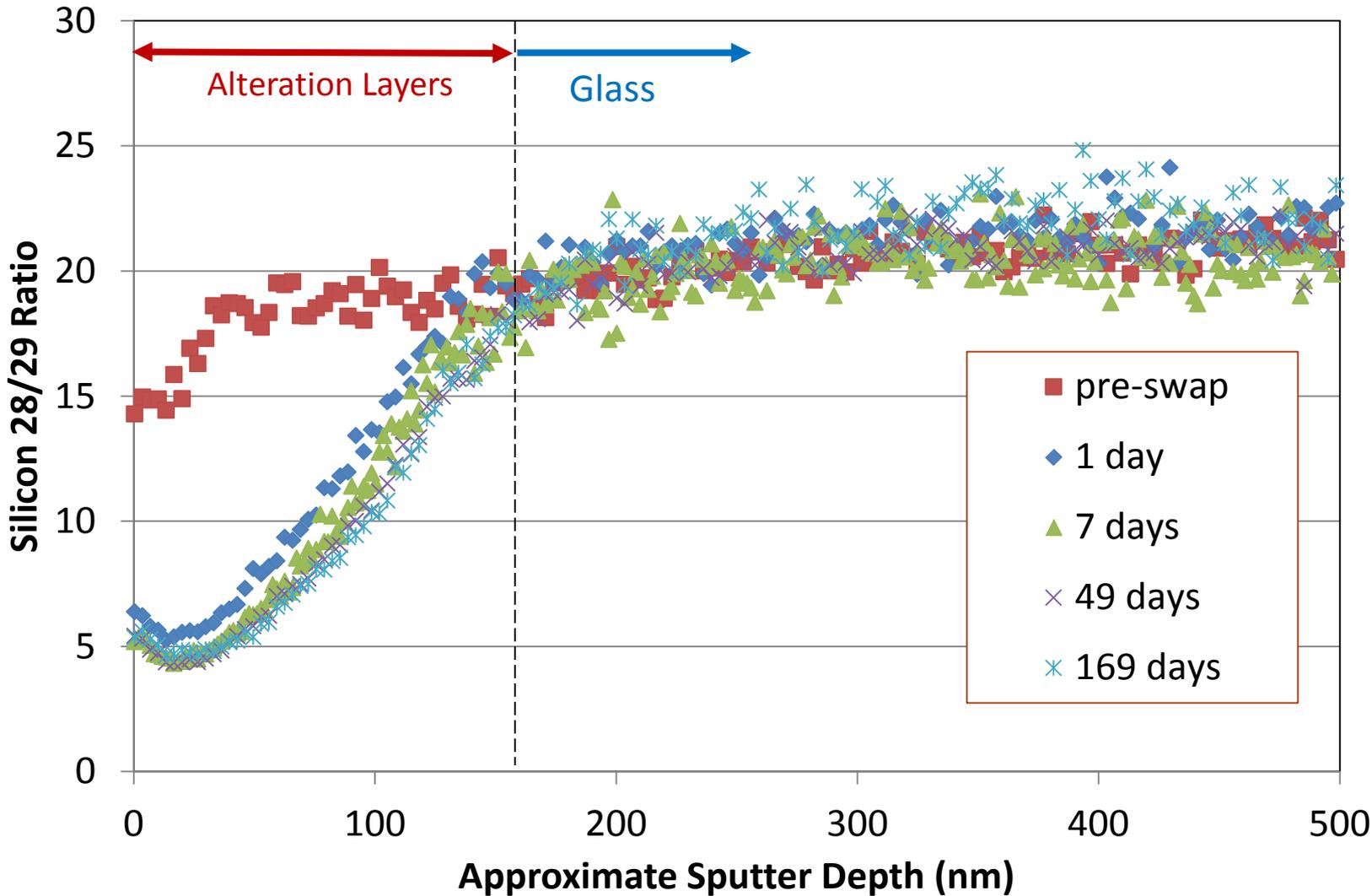
Key	Isotopically Substituted	Natural Abundance
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Solution		

■ Observe rate of return to isotopic equilibrium

- Monitor isotopic migration into and out of solid phase
- Monitor isotopic concentrations in solution
- Continue solid experiments at intervals until coupons depleted
- Some solid phase experiments may be applicable to powders... continue tests

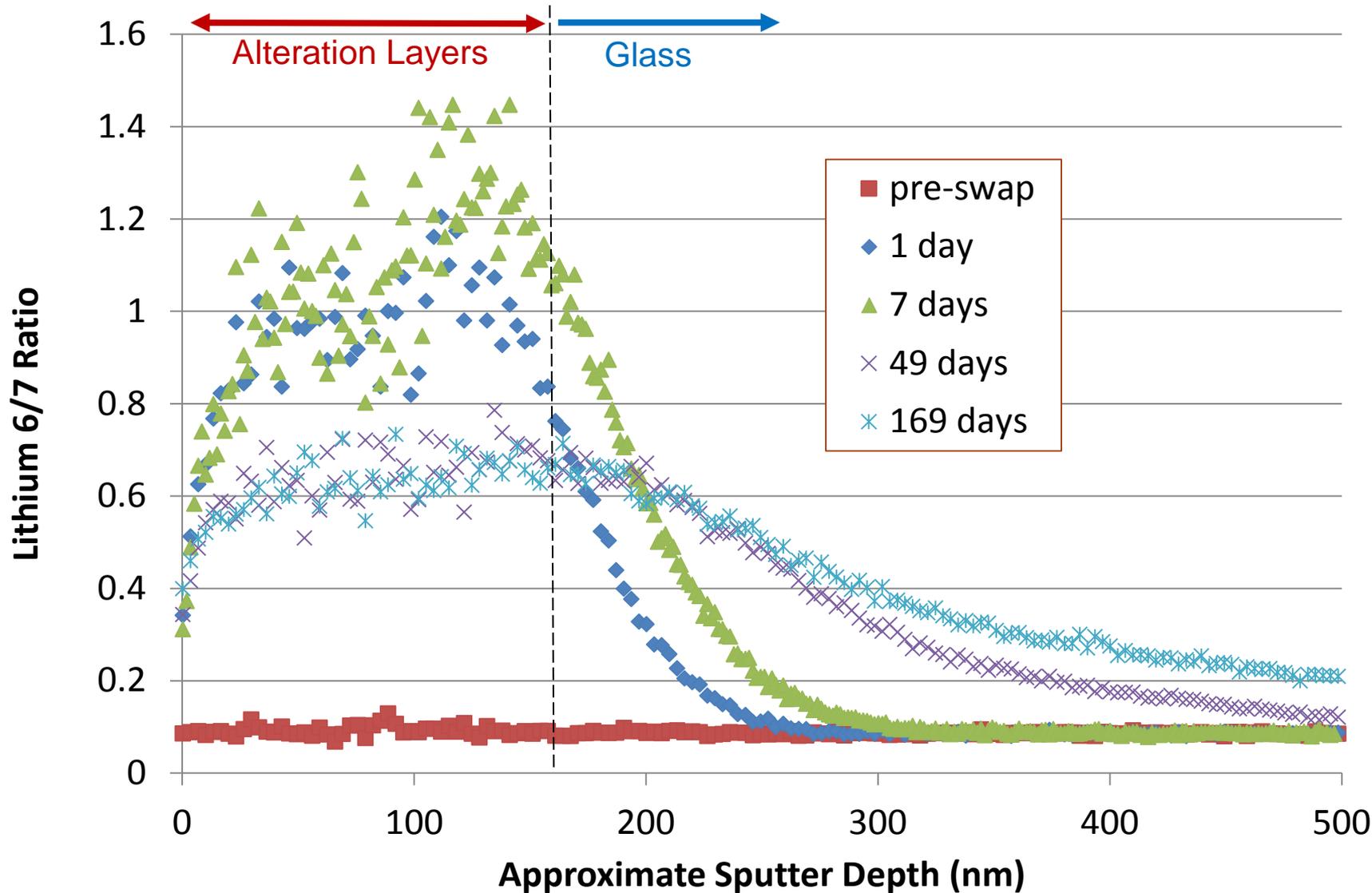


Isotopic evolution (TOF-SIMS): *Silicon*





Isotopic evolution (TOF-SIMS): *Lithium*





Summary of findings

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- **These experiments conclusively showed that the gel was not a transport barrier to the ions tracked**
- **The different tracer ions behaved quite differently:**
 - Silicon reacted only in the gel area
 - Lithium penetrated deep into the pristine glass
 - Boron was released at the gel-glass interface
 - Transition metals in solution did not appear to enter into the gel or glass
- **If there is a “passivating layer”, it is extremely thin**
- **ToF-SIMS did not have the resolution to answer many questions**
- **A new characterization technique was required**



Advanced characterization is needed to find passivating layer

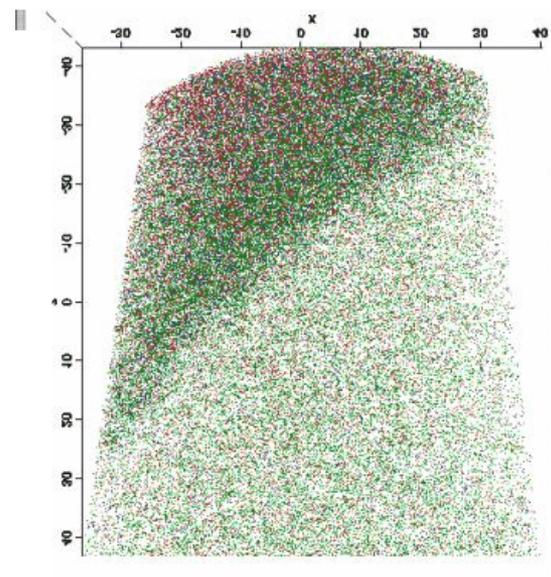
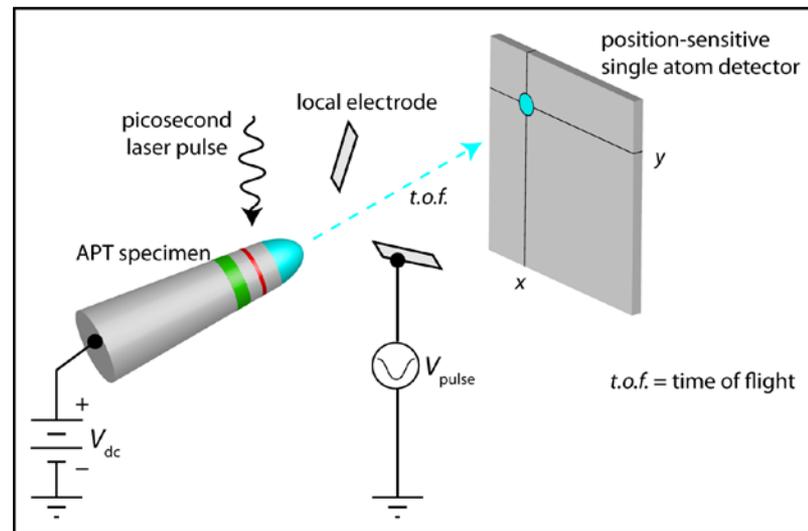
■ Theorized layer properties:

- Thin (1-10nm)
- Amorphous
- Composition of glass formers close to glass
- Dense relative to the porous gel
- Diffusion barrier to product/reactant?

■ Atom-probe Tomography (APT)

- Field-ion microscopy combined with time-of-flight mass spectrometry
- Result is a 3-D elemental map with single-atom sensitivity and sub-nm position accuracy (recently definitively demonstrated in oxides)

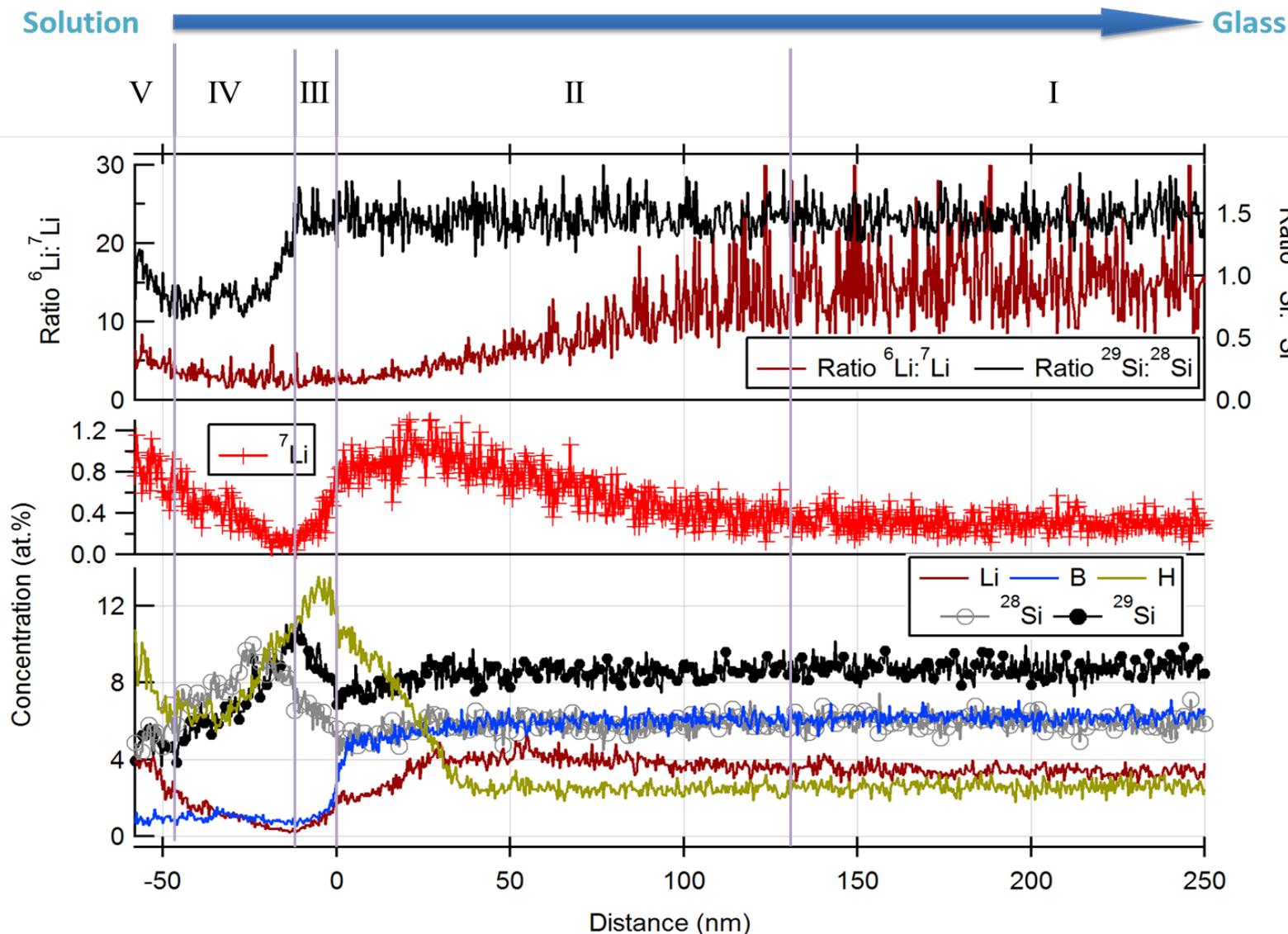
This effort produced the first APT results for multicomponent amorphous oxides





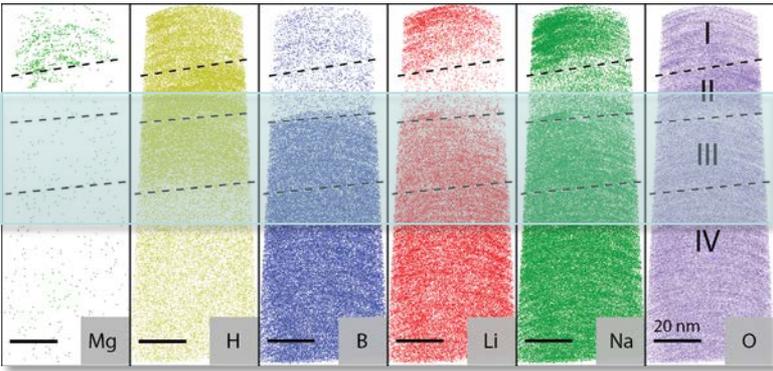
Isotopic Profiles using Atom Probe Tomography

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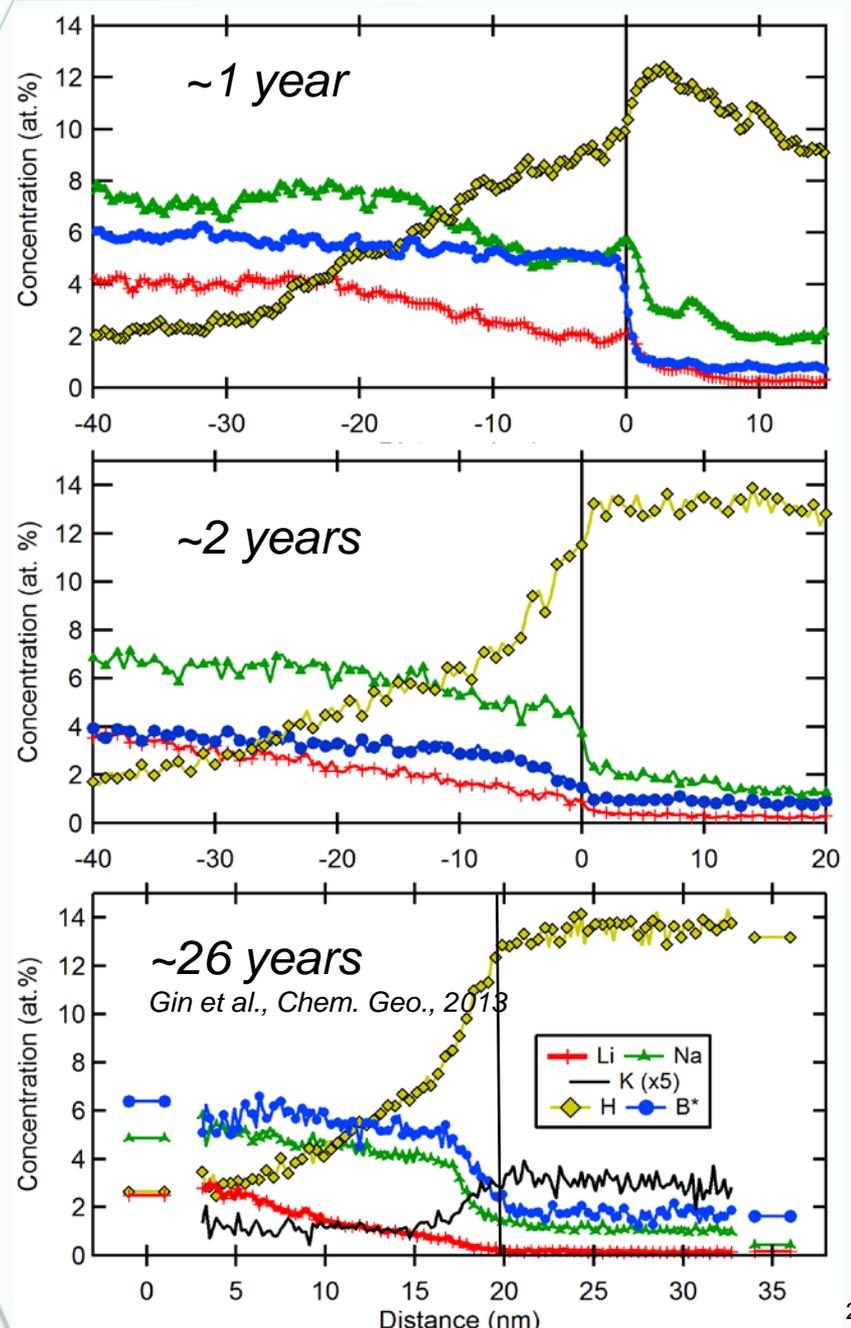




Elemental Profiles using Atom Probe Tomography



Pristine ← Solution





Enriched ^{29}Si Experiment

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- Now we would like to know more about the gel and the impact of any interfacial layer
- Create gels and then perturb system
- Monitor various ion and molecular transport using isotopic and dye tracking
 - International Simple Glass (ISG)
 - 16 glass coupons have been altered at 90°C in 380 mL of solution initially saturated / $(^{29}\text{SiO}_2)_{\text{am}}$ at $\text{pH}_{90^\circ\text{C}} 9$
 - $S/V = 0.6 \text{ cm}^{-1}$
 - Stage 1 : 209 d at $\text{pH}_{90^\circ\text{C}} 9$
 - Stage 2 : $\text{pH}_{90^\circ\text{C}} 11.5$
 - Isotope sensitive analytical techniques: MC-ICP-MS, ToF-SIMS, and APT



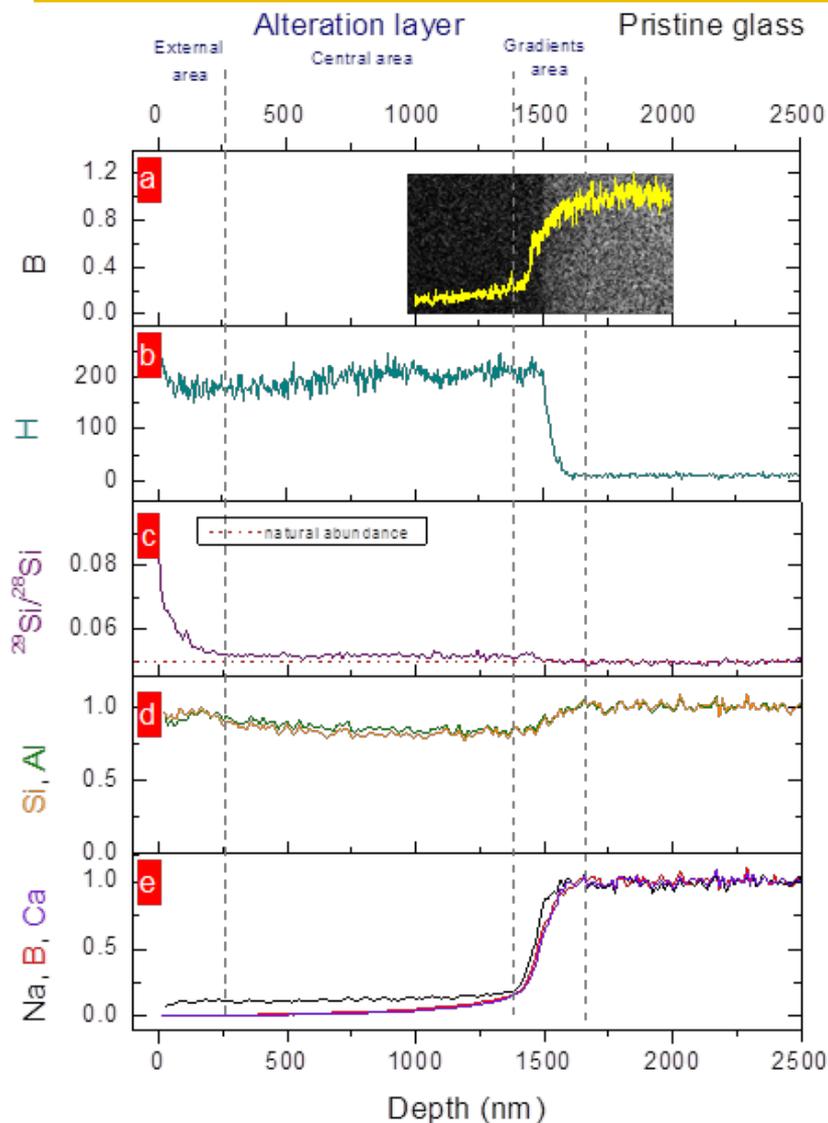
Experiment from slides 44-53 covered in (unless otherwise specified):

Gin S, P Jollivet, M Fournie, Z Wang, Z Zhu, AV Mitroshkov, and JV Ryan. 2015. "The Fate Of Silicon During Glass Corrosion Under Alkaline Conditions", *Geochimica et Cosmochimica Acta*, 151, p68–85.



Solid analysis of the 209d sample

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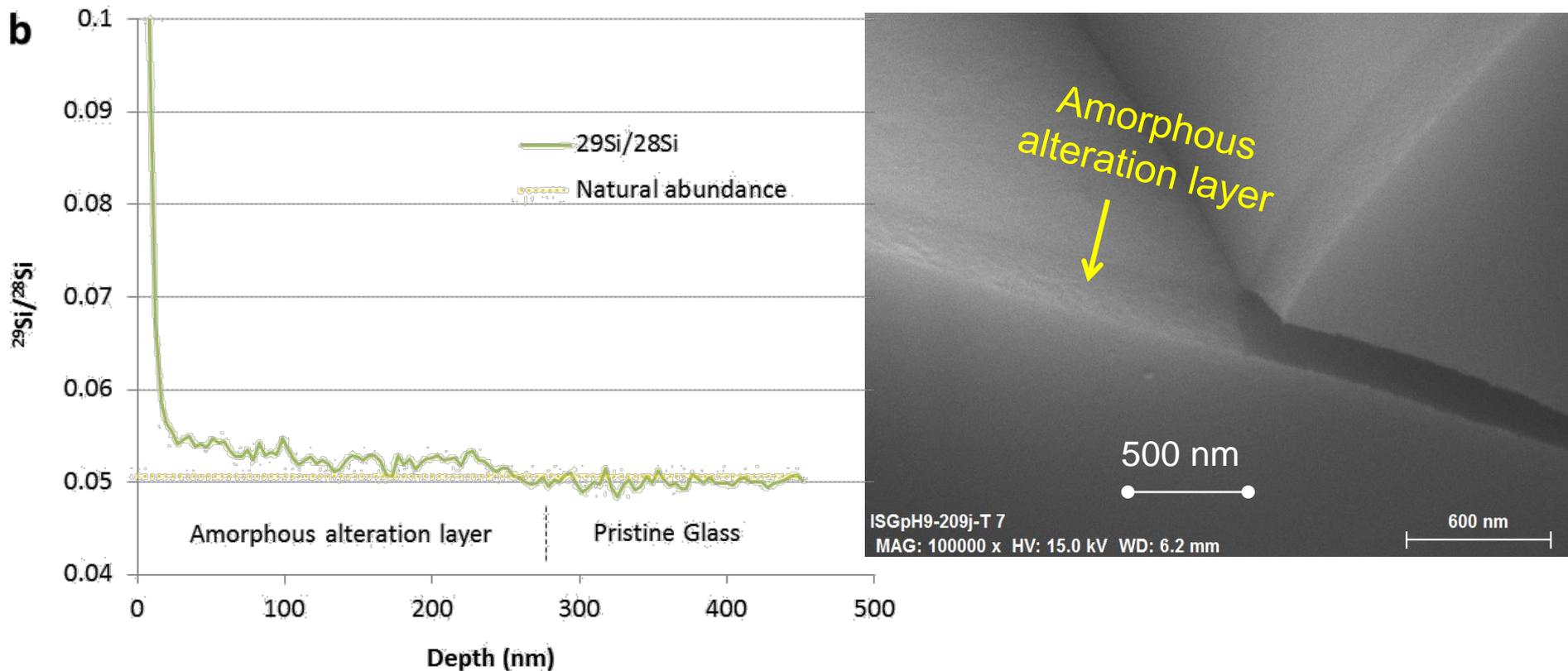


- B, Na, Ca are released congruently
- A tiny amount of ^{29}Si is found in the very surface of the gel
- No Si isotope equilibration
- ToF-SIMS profiles are confirmed by TEM, but later APT showed atomically sharp B front
- No simple diffusion model can account for such profiles

Gin, S., et al., 2015. "Origin and consequences of silicate glass passivation by surface layers".
Nature Comm. 6: p. 6360.



Solid analyses at pH 9 - 209 d (ToF-SIMS)



■ No Si isotope equilibration in gel region

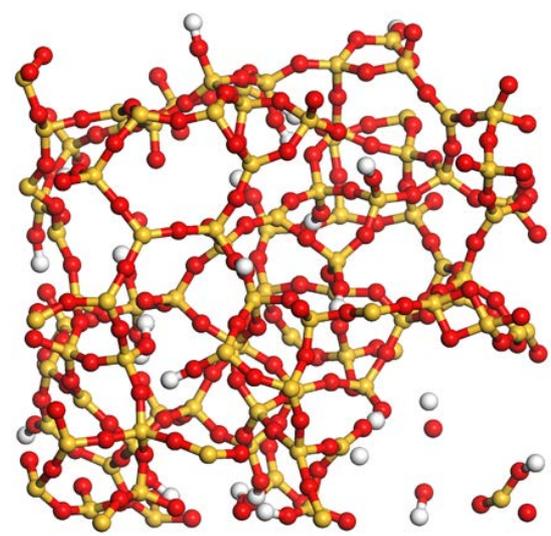
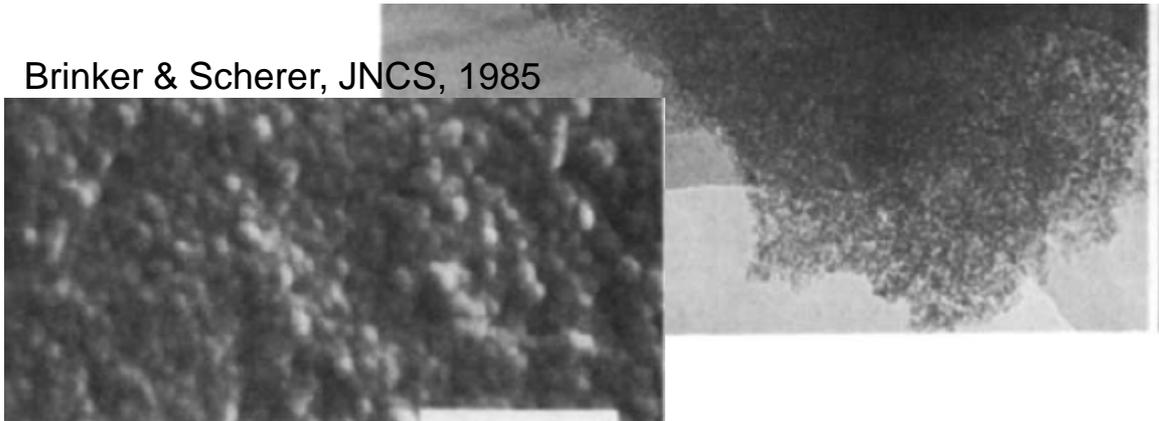
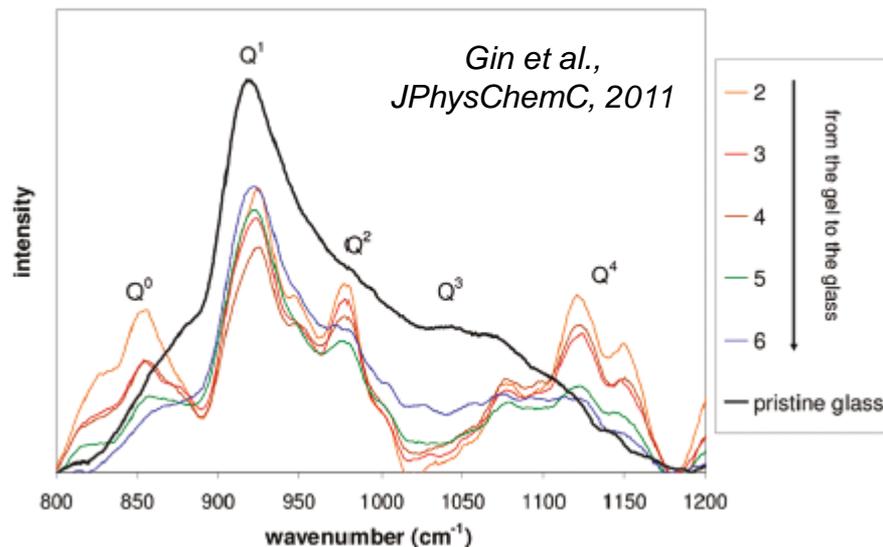
- Confirmation at pH 7
- Very few hydrolysis/condensation reactions



Gel structure is notably different from the glass

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- Gel composed of relatively insoluble species: Si, Al, Ca, Fe, Ln, some Na
- Highly porous, with SSA values ranging from 100-800 m²/g
- Different in structure from glass: *not simply a relic of glass*
- Structure and formation depends strongly on composition
- pH seems to also have an impact





Summary of observations

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- **Elemental profiles are much sharper than can be resolved with ToF-SIMS, nanoSIMS, or even traditional TEM**
- **Boron profile is less than 5nm in thickness** (and even this is generous)
- **Alkali ions appear to have both a steep “reaction front” interface and a diffusive profile within the glass**
- **The gel appears to form via the reorganization of the glass material, with a distinctly chemically and microstructurally different structure**
- **Some of the boron “gradients” observed in the past may have been due to an apparently intrinsic surface roughness produced by corrosion** [see S. Gin et al. (2017), *Geochimica et Cosmochimica Acta*, 202: p. 57-76]

This means that the breakdown of the glass wasteform occurs via dissolution.

If transport is impactful, it is likely via the concentration of ions in solution due to constrictions in an alteration layer



Recent Findings:

Transport Control in Alteration Layers

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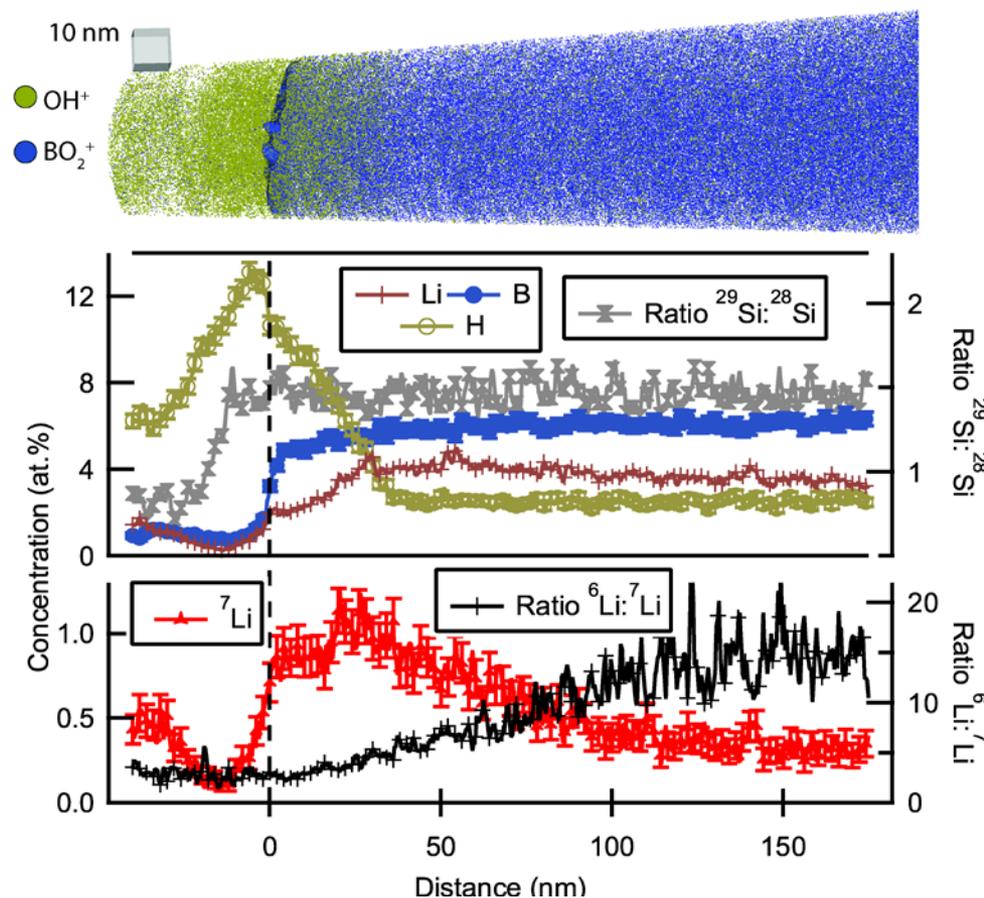
■ New experimental and characterization techniques have enabled new discoveries in this area

- Solution exchange experiments
- Isotopic tracing techniques
- Atom-scale characterization (APT, NanoSIMS, etc)

■ The elusive “Passivating Reactive Interphase”

■ The provenance of the amorphous gel

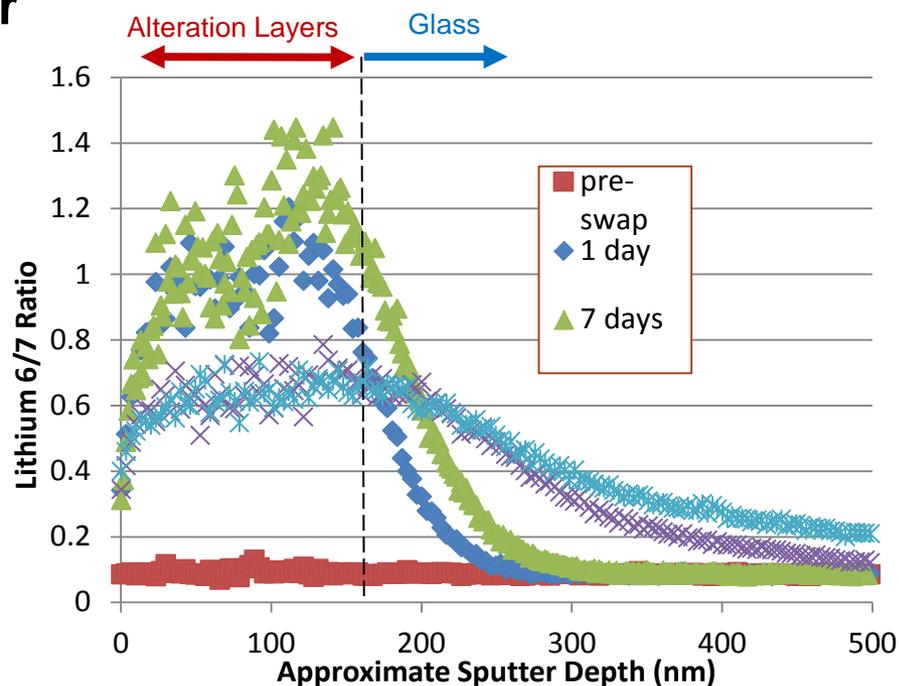
■ Latest theories are examining solution and interface behaviors in constricted pore spaces





Targeted Approach: *Ion-exchange model development*

- Ion exchange is a demonstrated phenomenon and the international community agrees that this mechanism plays a role in glass corrosion
- The previous experiment showed lithium quickly diffusing into the glass in a similar, if faster, manner to hydrogen
- Can **lithium be used as a proxy** for the hydrogen-containing species that is involved in ion-exchange?
- If so, can experiments isolating lithium diffusion be used to **model the ion-exchange mechanism for glass corrosion?**





Dimethyl sulphoxide (DMSO) *Li isotope tracing experiment*

Experiment

- Dimethyl sulphoxide (DMSO) used as non-aqueous solvent
- $^6\text{LiCl}$ used to track which ions came from solution
- SON68 and Li-ISG glass coupons

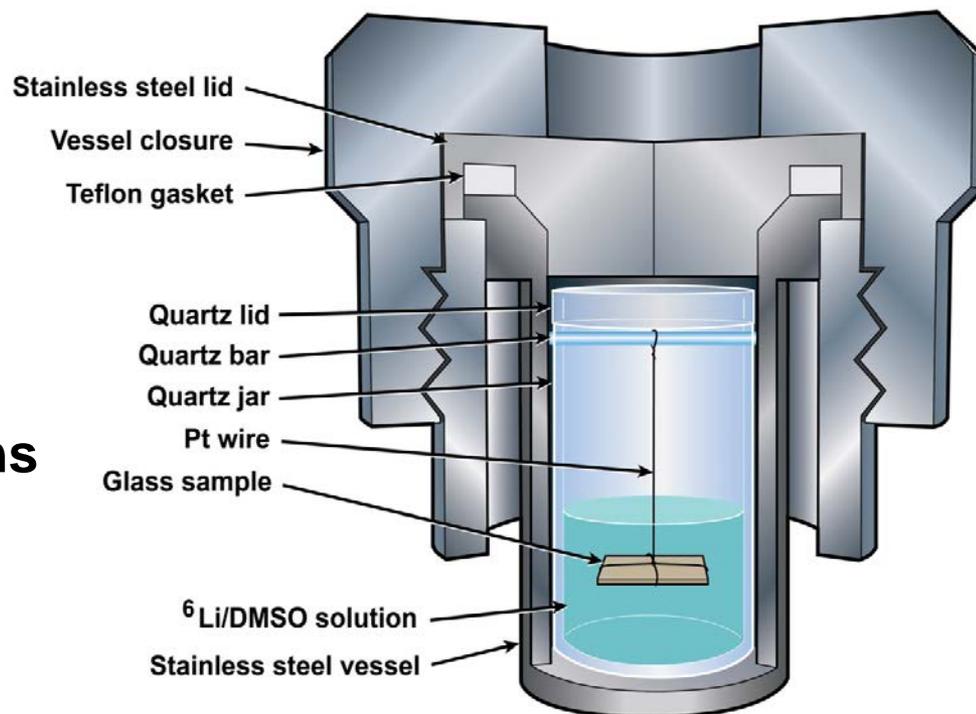
Characterization

- TOF-SIMS
- APT used to confirm profiles

Experiment from slides 57-65 covered in
(unless otherwise specified):

Neeway et al., JNCS 405, 2014 and

Neeway et al., J Phys Chem C, 120(17), 2016



Conditions:

Temperature: RT, 90, 150 °C (CJ6 and SON68)

60 and 120 °C (CJ6)

Time: 2 day to 9 months



Isolated Diffusion

- Fick's 2nd law

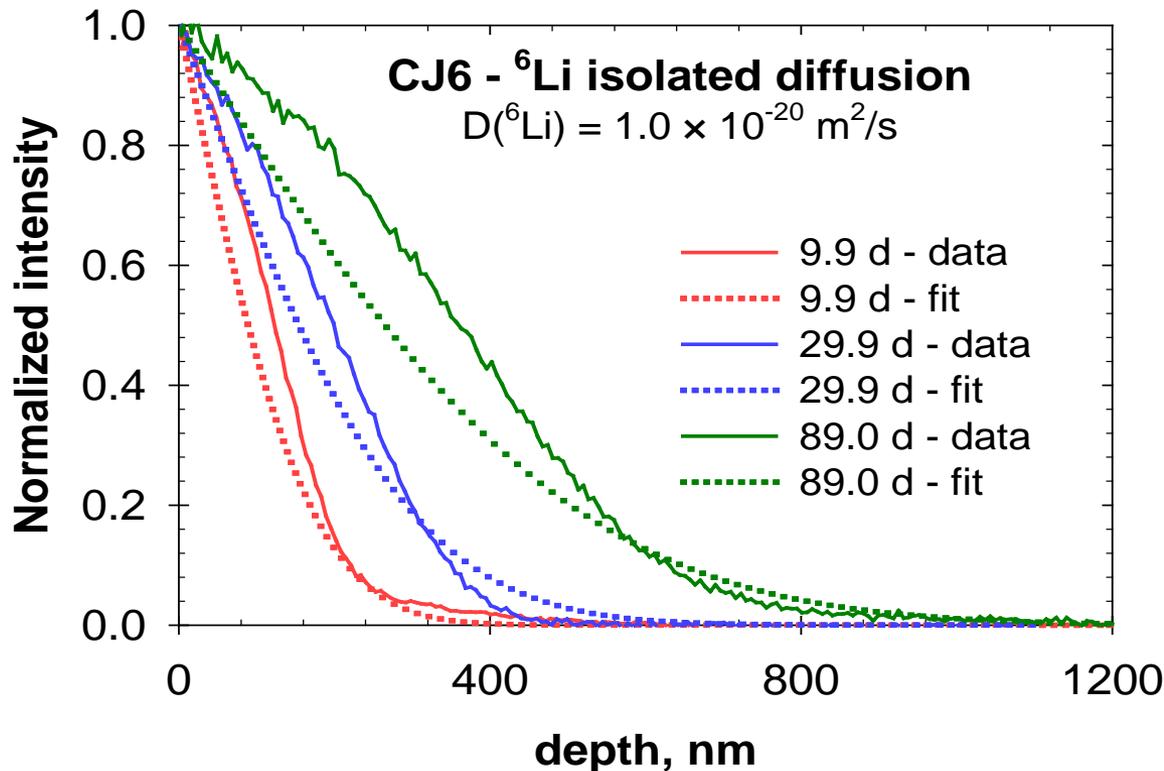
$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x'} \left(D \frac{\partial C}{\partial x'} \right)$$

- If D is constant, $C = C_0$ for $x' = 0$ and $t > 0$ and the initial condition $C = 0$ for $x' > 0$ and $t = 0$ (Crank, 1990)

$$C = C_0 \operatorname{erfc} \frac{x'}{2\sqrt{(Dt)}}$$

- If $D =$ coefficient of diffusion, $C =$ concentration of diffusing species, $x' =$ depth, and $t =$ time

(Hellmann, GCA, 1997)





Interdiffusion

- The inward diffusion of A and outward diffusion of B are not independent but are coupled through ion exchange

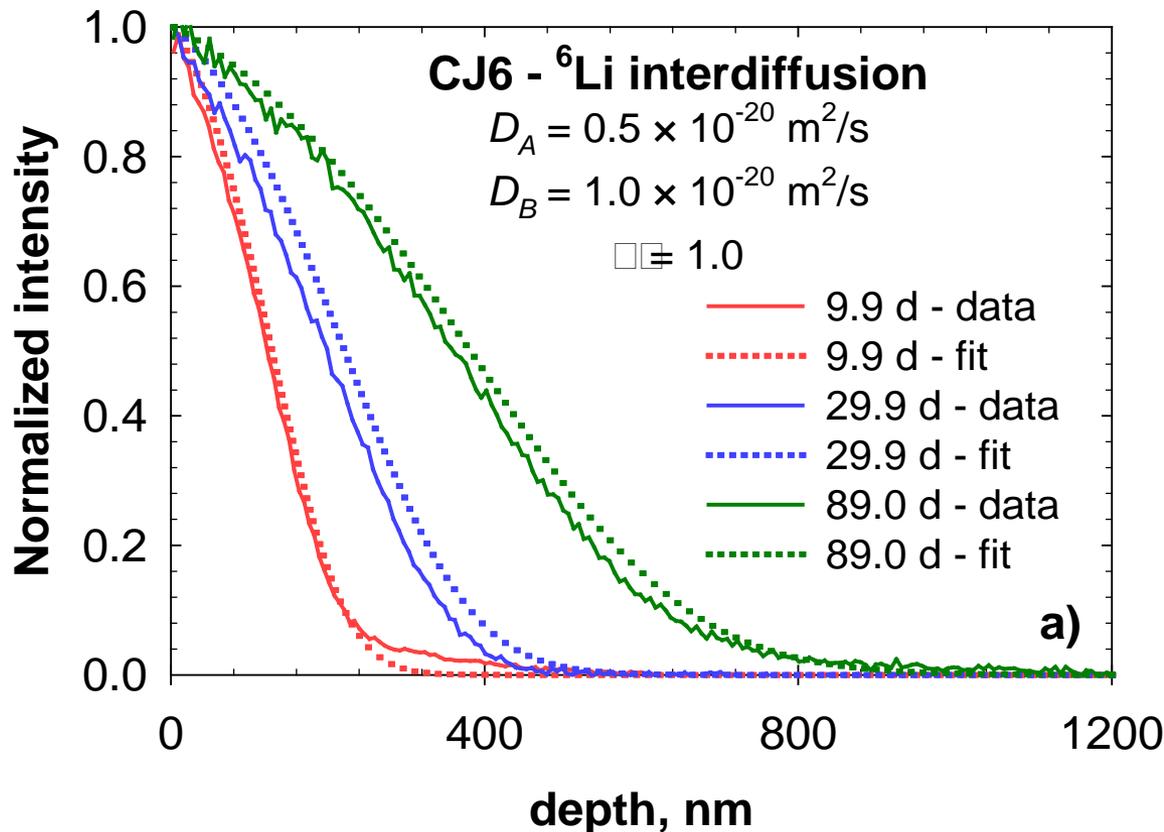
$$\tilde{D} = \frac{D_A D_B}{C_B D_B + (1 - C_B) D_A} = \frac{D_B}{1 + C_B b}$$

$$b = D_A / D_B - 1$$

- The diffusion of species can also be increased near the interface with a structural factor, α

$$\tilde{D}_\alpha = (1 + \alpha C_A) \tilde{D}$$

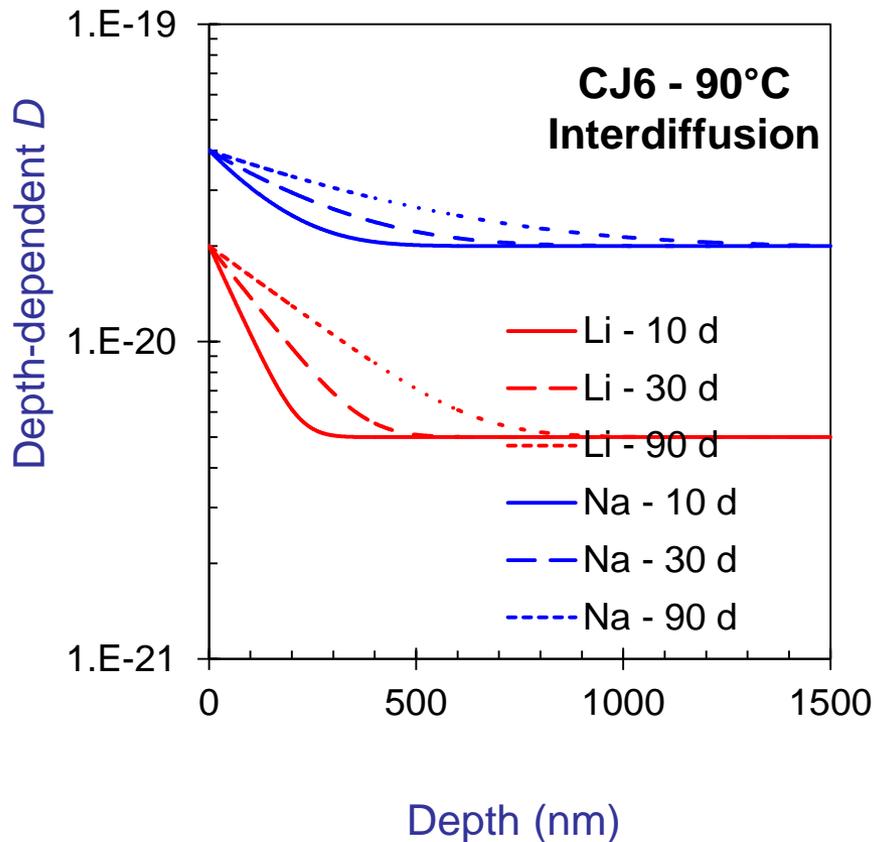
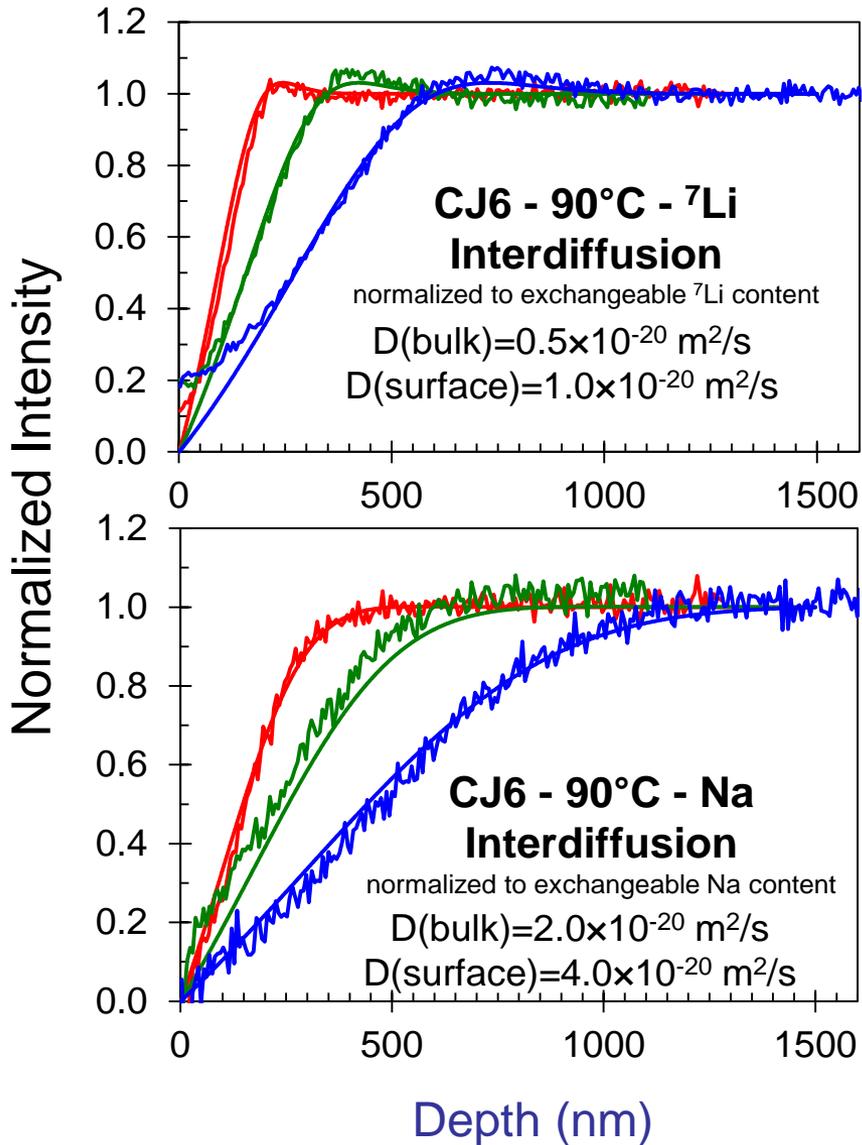
- The diffusion equation was solved on a 1D grid using finite difference method





Model fit – interdiffusion

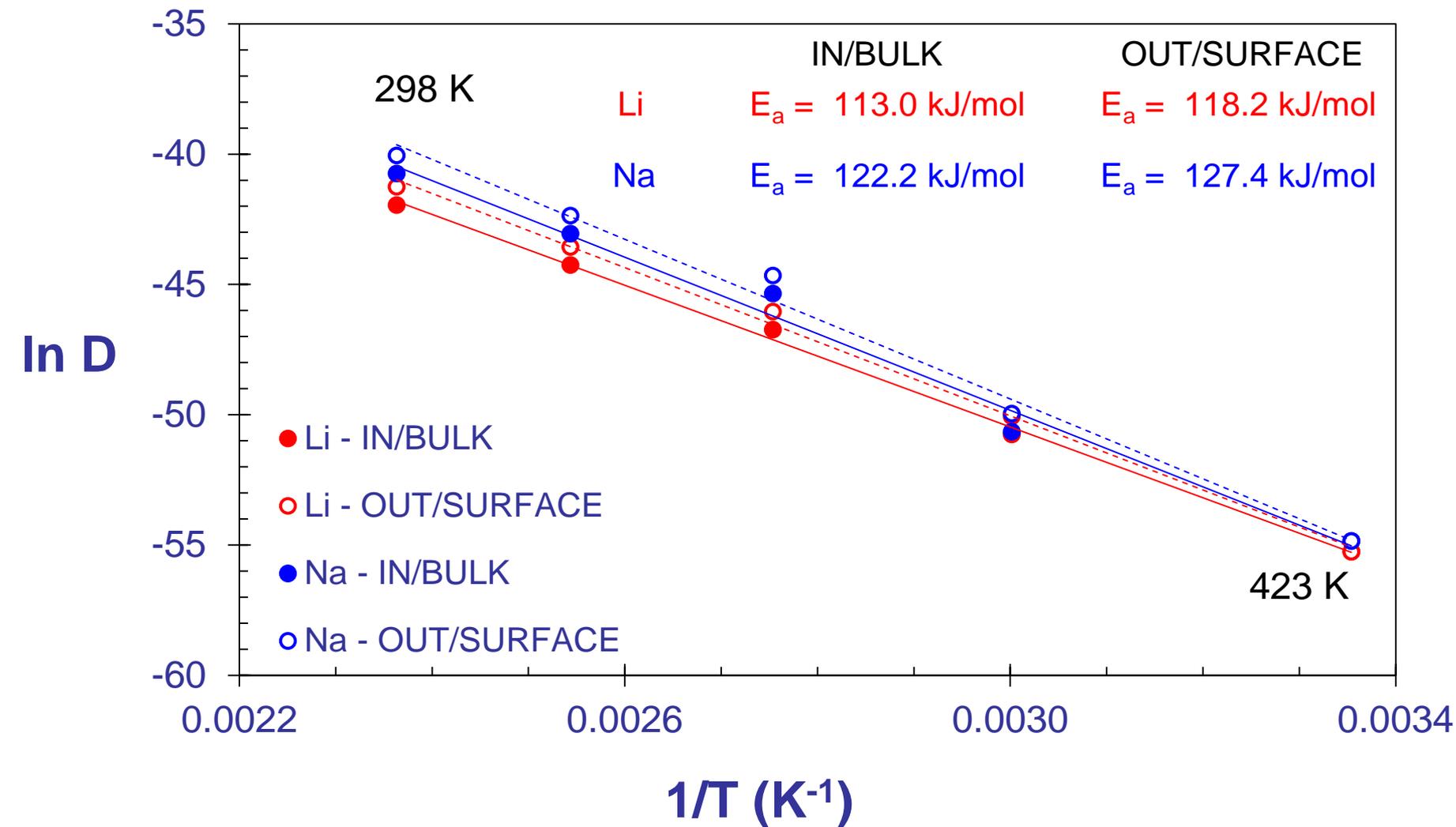
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Interdiffusion activation energy

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- Li, often used as a glass tracer in glass durability studies, exchanges with H, Na, and Li at different rates
- The outward diffusion of Na (bulk) is shown to be faster than the inward and outward diffusion of Li (surface)
 - Thought to be due to larger cation size and smaller field strength
 - Trend similar in water
 - **Only a portion of Na is available for interdiffusion**
- High activation energies for interdiffusion (113-127 kJ/mol)

These findings led to a model for solid-state alkali interdiffusion.

The applicability of the model for hydrogen still to be demonstrated and work remains to examine the reaction that introduces hydrogenated species into the solid glass

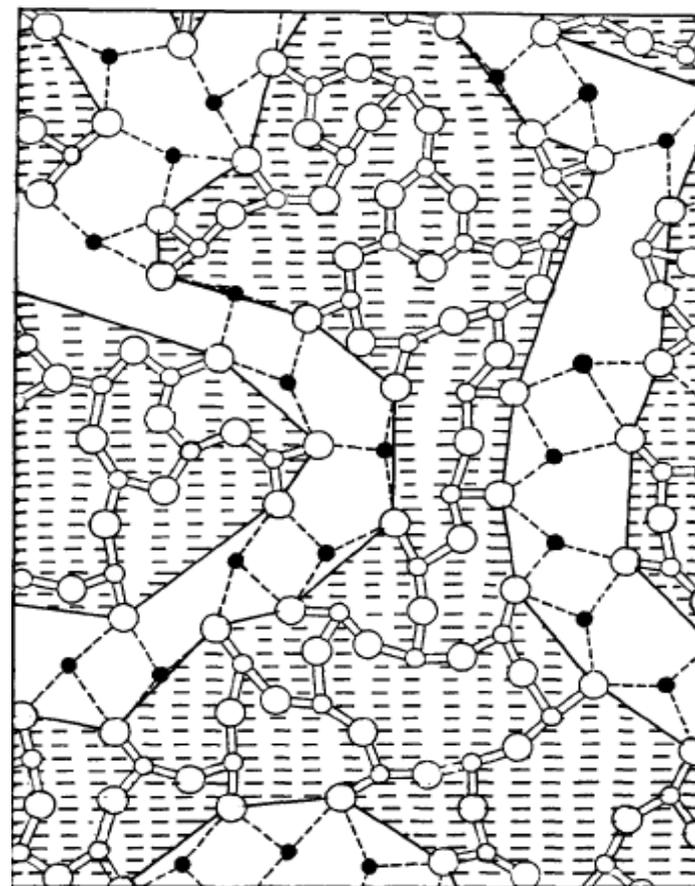
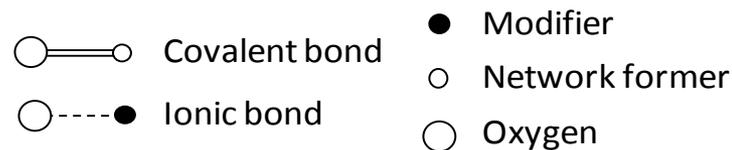


■ Ion exchange mechanisms

- Entire process takes two steps:
 - *One ion enters glass from solution while another exits*
 - *The ions within the glass then participate in solid-state interdiffusion*
- Various alkali behave differently in both steps

■ Medium-range order

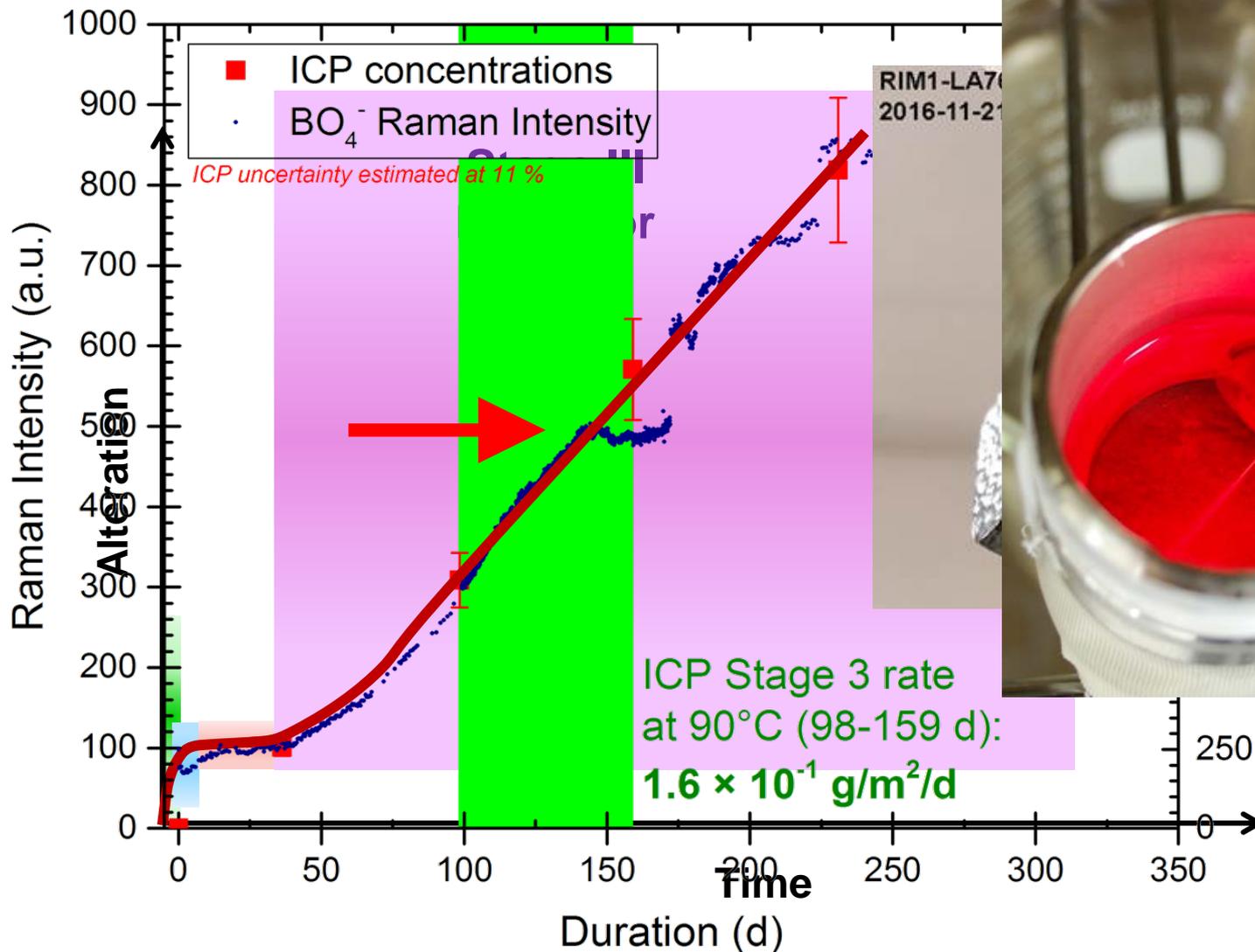
- Channeling and/or percolated soluble ions could lead to large increases in surface area
- Models predict channeling and some solution data suggest it, but only minor and tangential evidence in waste glass



Greaves, 1985, *J. Non-Cryst. Solids*, 71, 203–217



Targeted Approach: *In situ* monitoring of Stage III



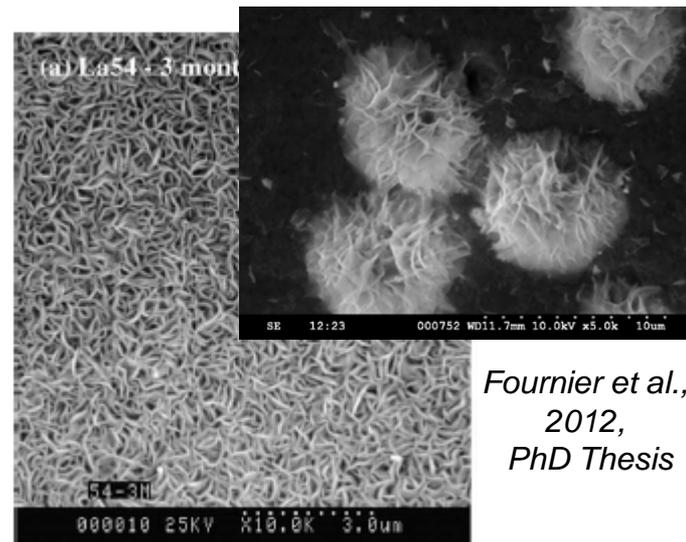


Recent Findings:

Crystalline alteration phase effects

- **Relationship between glass composition/structure and alteration phase formation**
- **Stage III**
 - Seeding and pH based triggering
 - Informatics-based approach
 - *In situ* examination
 - Coupled kinetics approach
 - International agreement

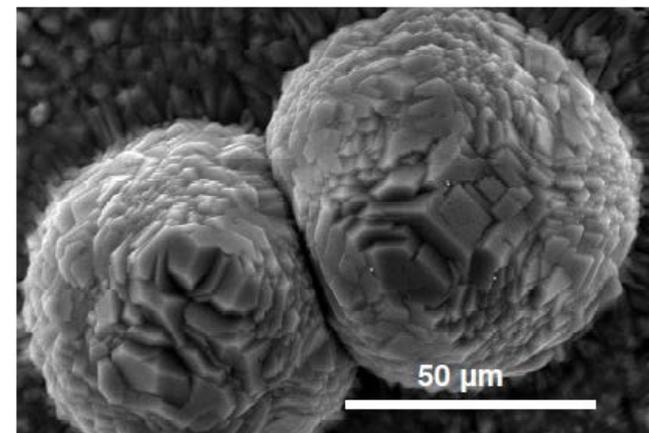
Whether or not Stage III behavior occurs contributes the highest uncertainty to the calculated rate.



*Fournier et al.,
2012,
PhD Thesis*

Valle et al. GCA, 2010, v 72, p3412

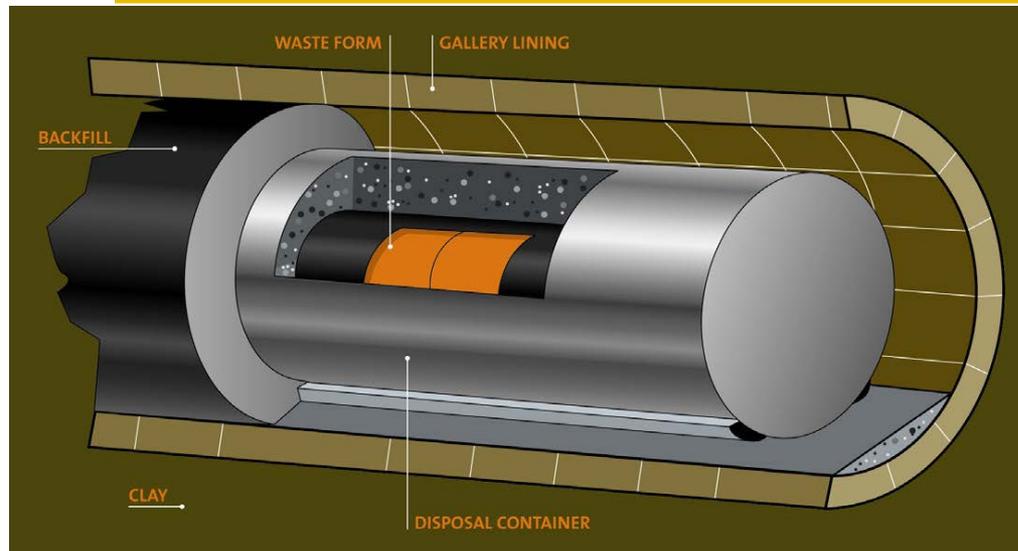
Ebert et al., 2011, FCRD-WAST-2011-000404





Targeted Approach: *Near-field impacts*

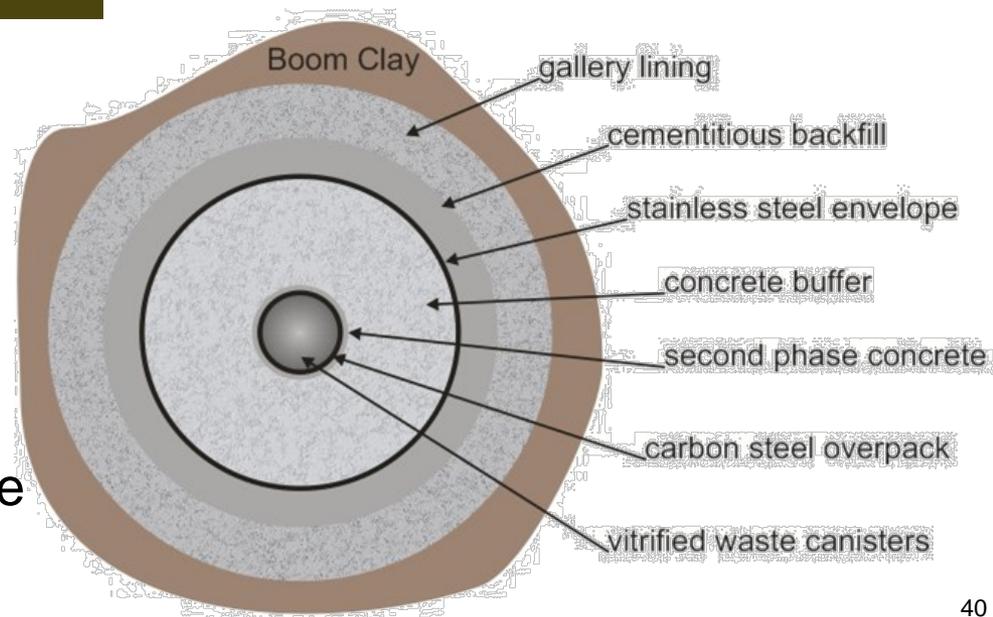
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- A multibarrier system to contain and isolate immobilized radioactive waste
- High pH a favorable environment for steel envelope and overpack



- Boundary conditions depend on expected evolution of water in contact with cement
- pH expected to decrease with time: 13.7 → 12.5 → 12 → 9
- Separate experiments target each condition to interrogate performance at various time periods

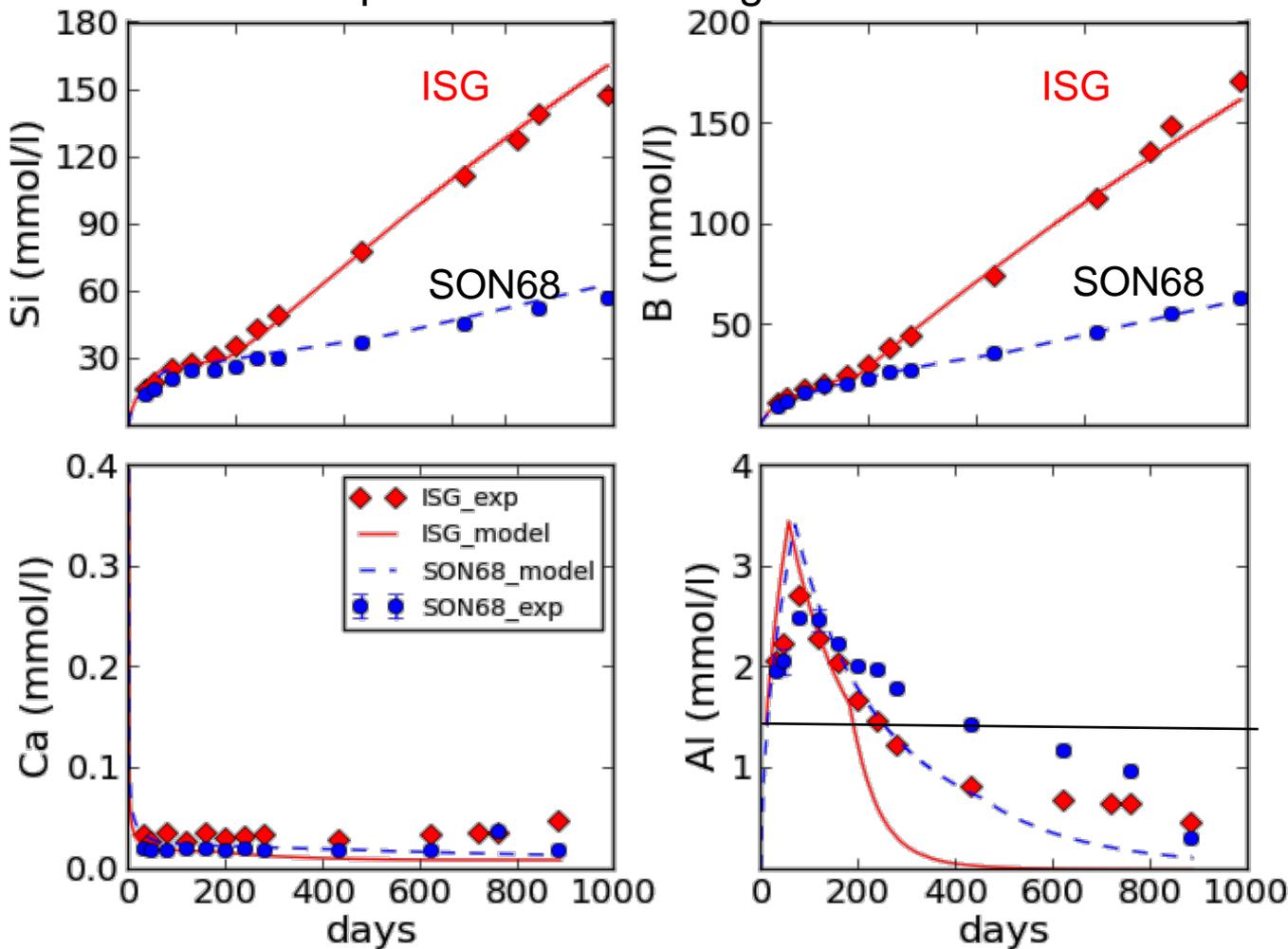




SON68 and ISG glass corrosion in young cement water @ 30 °C

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pH 13.4-13.6 during entire test



1.4
mMol



Recent Findings:

Near-field Environment Impacts

■ pH rise due to proximity to cements

- The impact of the Belgian supercontainer concept with waste form encased in concrete is relevant to cementitious WF co-disposal options

■ Impact of iron corrosion products

- Ancient studies of smelter (France) and buried sword (Japan) relate to canister corrosion impact studies (NEUP, PNNL, France)

■ The presence of magnesium (originating in glass or groundwater)

- Japan interested due to Mg in groundwater from nearby ocean
- UK interested due to elevated Mg in waste glass

■ Impact of corroding glass on near-field

- Cementing of sediments around *Iulia Felix* glass
- Geochemical modeling reproduced result

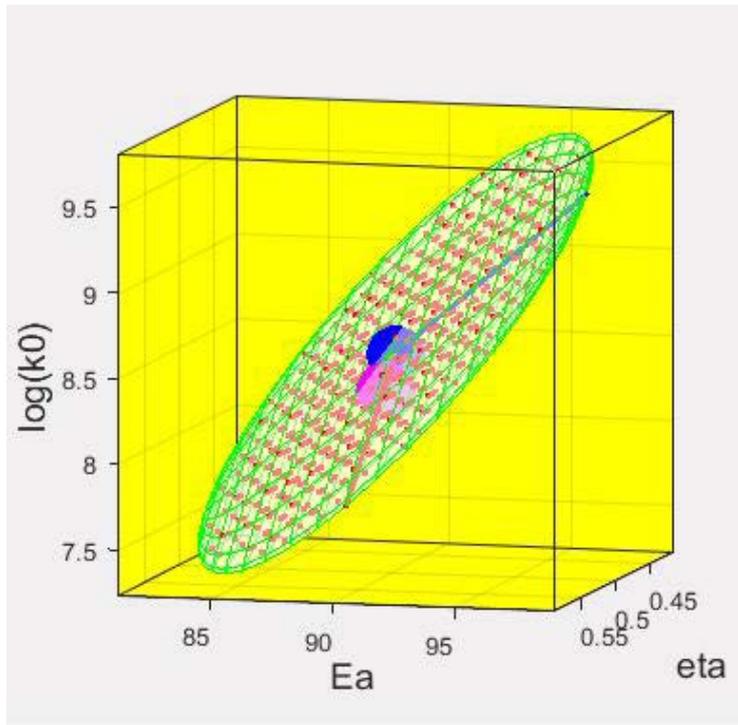
Strachan et al. App.Geochem.2013





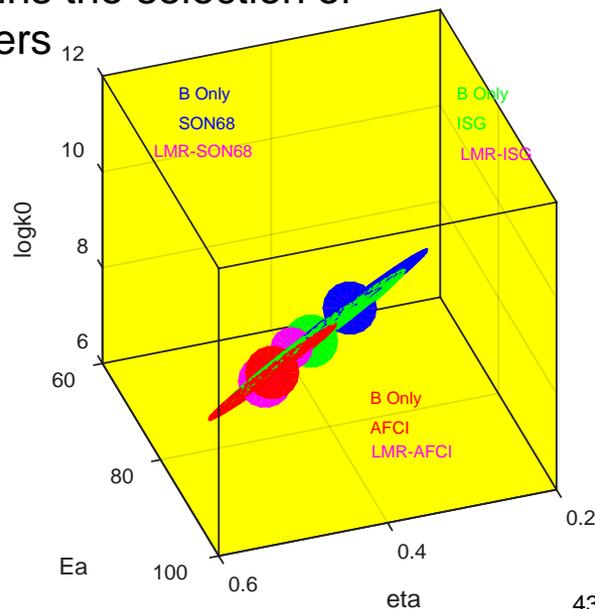
Targeted Approach: *Rate model parameterization*

Neeway et al. (2017) GCA (in submission)



Large Blue Dot - GCMT Mean
Large Magenta Dot - LMR Mean
Green Ellipse - 95% Confidence Interval Volume
Small Red Dots - Φ Values ~within Confidence Interval.

- Parameters are highly correlated and cannot be varied independently
- Ellipse is Nearly Flat – i.e. 2D
 - Original Data is 2D (pH & T)
- Parameter space can best be constrained by an ellipse
 - Significantly constrains the selection of acceptable parameters
 - Picking two parameters within ellipsoid essentially fixes the third





Recent Efforts:

Rate Model Development and Validation

Nuclear Energy
Environmental Management

- Various countries and programs use models that include different mechanisms, resulting in different rate equations
- Identifying controlling mechanisms at different stages and incorporating them into general rate models was a major subject of development
- The use of independent results to validate models is very important
 - Long-term static tests
 - Column, PUF, or lysimeter
 - Natural analogues
 - Ancient man-made analogues

A key question is the relative importance of dissolution and diffusion

Aagaard-Helgeson (AH)

$$r_{\text{net}} = k \prod_i a_i^{-\nu_{i,j}} \left[1 - \left(\frac{Q}{K} \right)^{1/\sigma} \right]$$

Silicate Minerals

Residual Rate (RR)

$$r_{\text{net}} = k \exp\left(-\frac{E_a}{RT}\right) a_{\text{H}^+}^{-\eta} \left[1 - \left(\frac{Q}{K} \right)^{1/\sigma} \right] + r_{\text{fin}}$$

Pristine Glass

Grambow-Müller (GM)

$$\frac{dC}{dt} = \frac{D_{\text{Hydr. Glass}}}{L^2} \left(\frac{d^2 C}{dx^2} \right) = U(t) \frac{dC}{dx}$$

Pristine Glass, Hydr. Glass, Gel Layer, Solution

GRAAL

$$\frac{de}{dt} = \frac{r_{\text{hydr}}}{e(t) D_{\text{PRI}}} \left(\frac{dE}{dt} \right) = r_{\text{diss}} \left(\frac{C_{\text{Si}}(t)}{C_{\text{sat}}} \right)$$

Pristine Glass, Eroded Glass, Solution



The critical question

Nuclear Energy
Environmental Management

What is the rate-limiting mechanism for **radionuclide release** from a glass waste form?

- **Complicated problem**
- **Coordinated approach leveraging particular national and international expertise**
- **Limit duplication, maintain confidence, collaborative ideas**



International Workshop on the Long-Term Corrosion of Glass - 2015

The answer depends on the conditions and time period in question



NWTRB questions addressed

Nuclear Energy
Environmental Management

- i. From DOE's perspective, what are the most important remaining technical uncertainties or gaps in data and understanding of the long-term performance of HLW glass? How is DOE addressing those uncertainties or gaps?**

- ii. What are the status and results of DOE R&D activities to understand and model the long-term performance of borosilicate HLW glass?**

- iii. Describe the results of recent DOE studies, if any, on natural and archeological analogs of nuclear waste glass. How are the results used to support assessments of the long-term performance of HLW glass?**

- iv. How is DOE integrating the results of international R&D activities and activities completed at different national laboratories in the U.S. on nuclear waste glass corrosion into its assessments of HLW glass long-term performance?**