



Chemical Durability of Nuclear Waste Glasses

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Presented for

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Trieste, Italy*

September 25th, 2019

The most important criterion

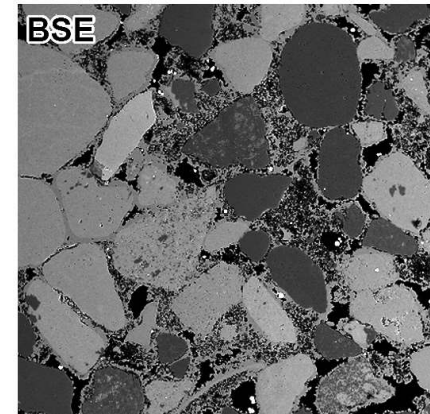
- ▶ Nuclear waste disposal requires:
 - Controlled release of disposed radionuclides
 - Long-term control: 10^5 to 10^6 years

To demonstrate long-term durability of glass, we must ***understand the mechanisms*** that govern **radionuclide release** over all time scales

- ▶ Enable the reliance on the native durability of the waste form
- ▶ Decrease necessity for engineered barrier systems
- ▶ Universality to various repository environments
- ▶ Increased public confidence and better data for regulatory approval



Glass artifact images
used courtesy of the
Corning Museum of Glass



What do we get?

Durability testing for nuclear waste glasses

- ▶ What do we want to know?
 - How quickly do species leach out of the glass?
 - What happens physically to the glass during corrosion?
- ▶ How can we assess this?
 - Um... stick it in water?
 - Yes, but for how long? And...
- ▶ What factors do we need to consider?

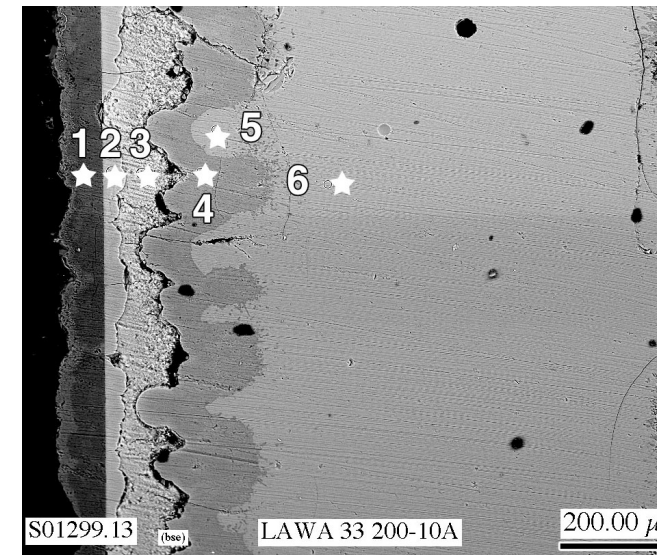
Intrinsic:

- Glass composition
- Glass structure / homogeneity
- Processing considerations (T_f , stress, shape, etc.)
- Internal radiation

Extrinsic:

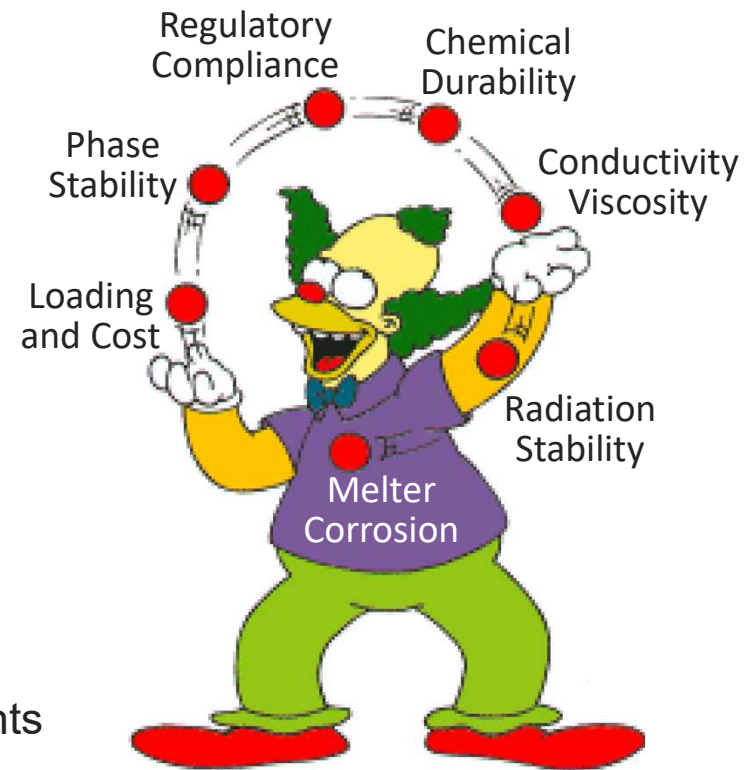
- pH and chemistry of the attacking solution
- Temperature
- Time
- Experimental conditions (SA/V, mixing, etc.)

Vienna et al. 2001



Glass is not glass is not glass...

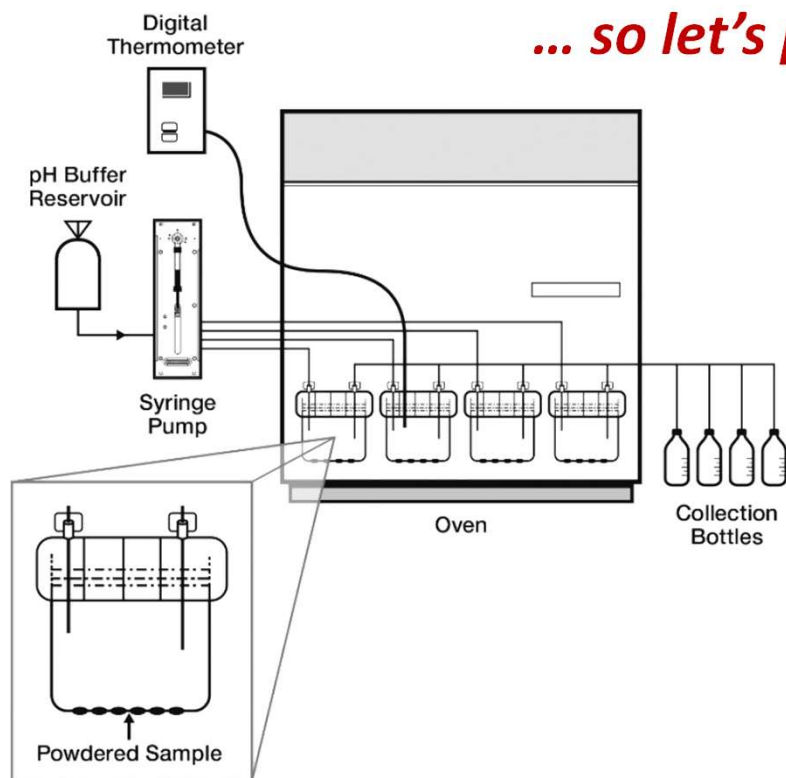
- ▶ Waste glasses are designed to meet specific physical, chemical, and regulatory compliance constraints
- ▶ Glasses are designed **specifically for waste compositions to be immobilized**, examples:
 - US tank waste primarily composed of cold chemicals with high composition variability and low radioactivity
 - French UOx HLW is primarily fission products with consistent composition and high radioactivity
 - US ILAW (Immobilized Low-Activity Waste) is designed for high alkali content and high throughput
 - Some UK glasses need to accommodate high Mg contents
 - Russian (and others) alumino-phosphate systems



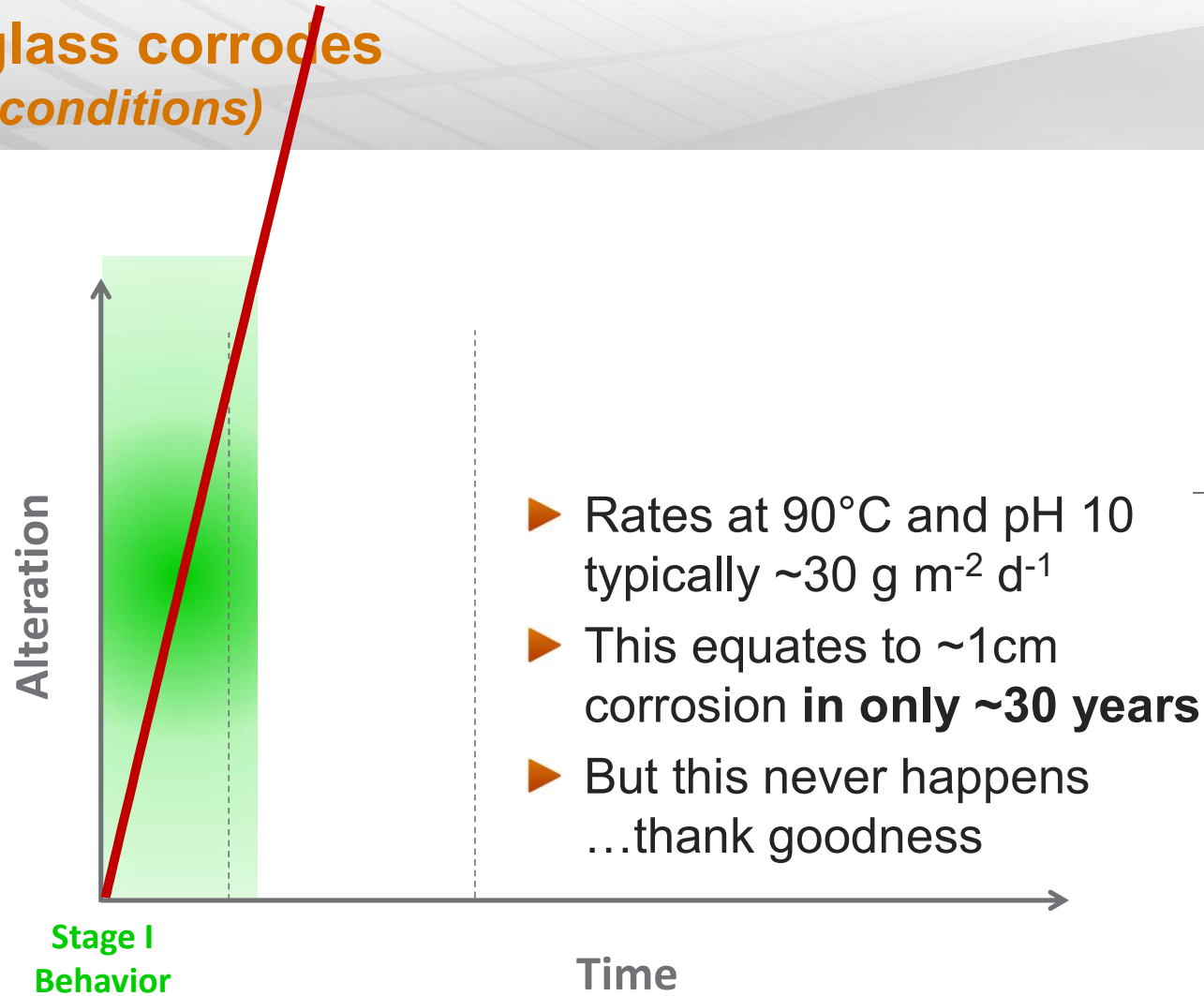
Yes, but...

Boro-alumino-silicate glasses do behave similarly in similar conditions

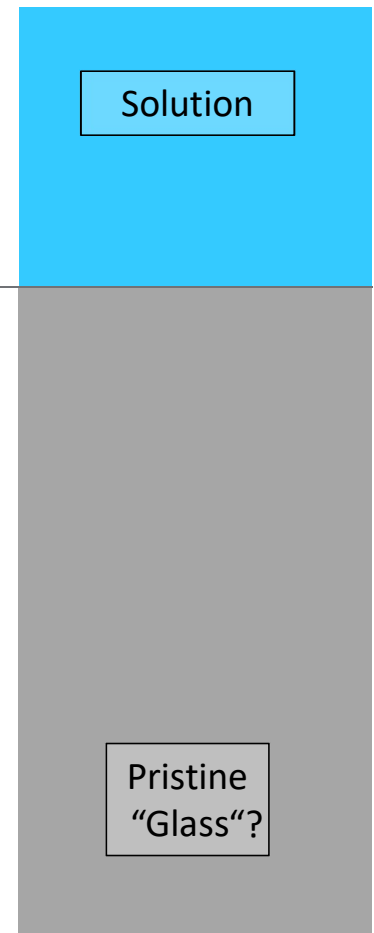
... so let's put them in some water!



How glass corrodes (dilute conditions)



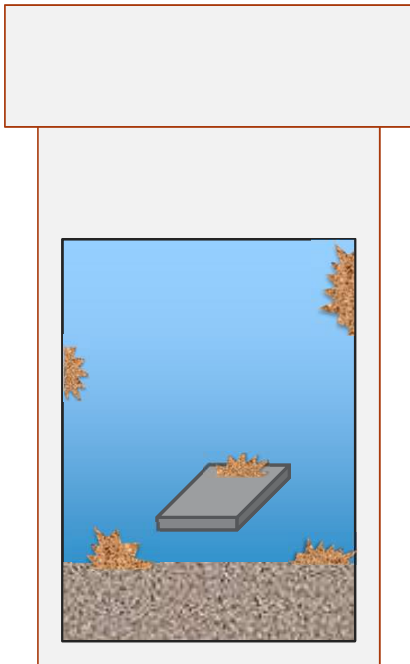
Surface Evolution



Ok, maybe not THAT much water...

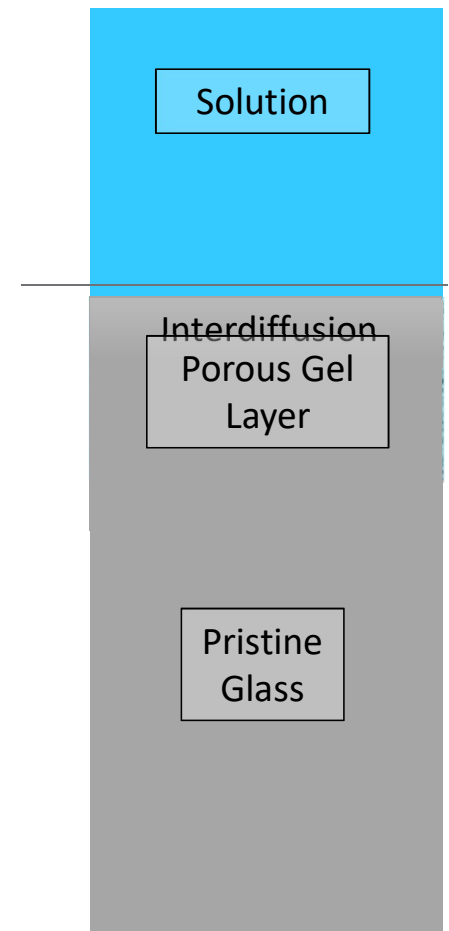
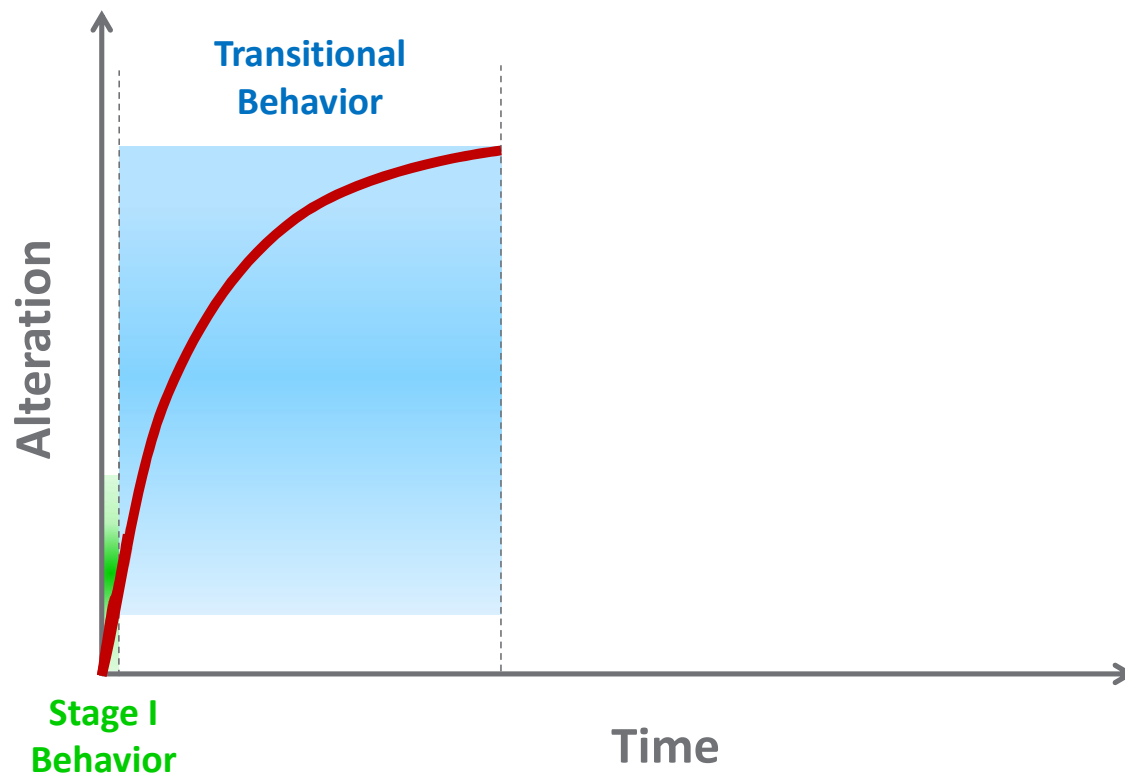
When glass ions accumulate in solution, various “interesting things” begin to occur

... so let's put them in STILL water!

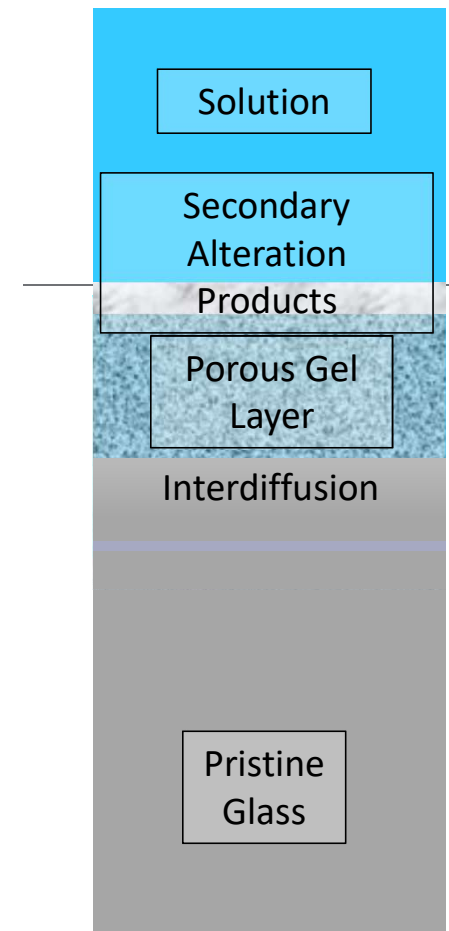
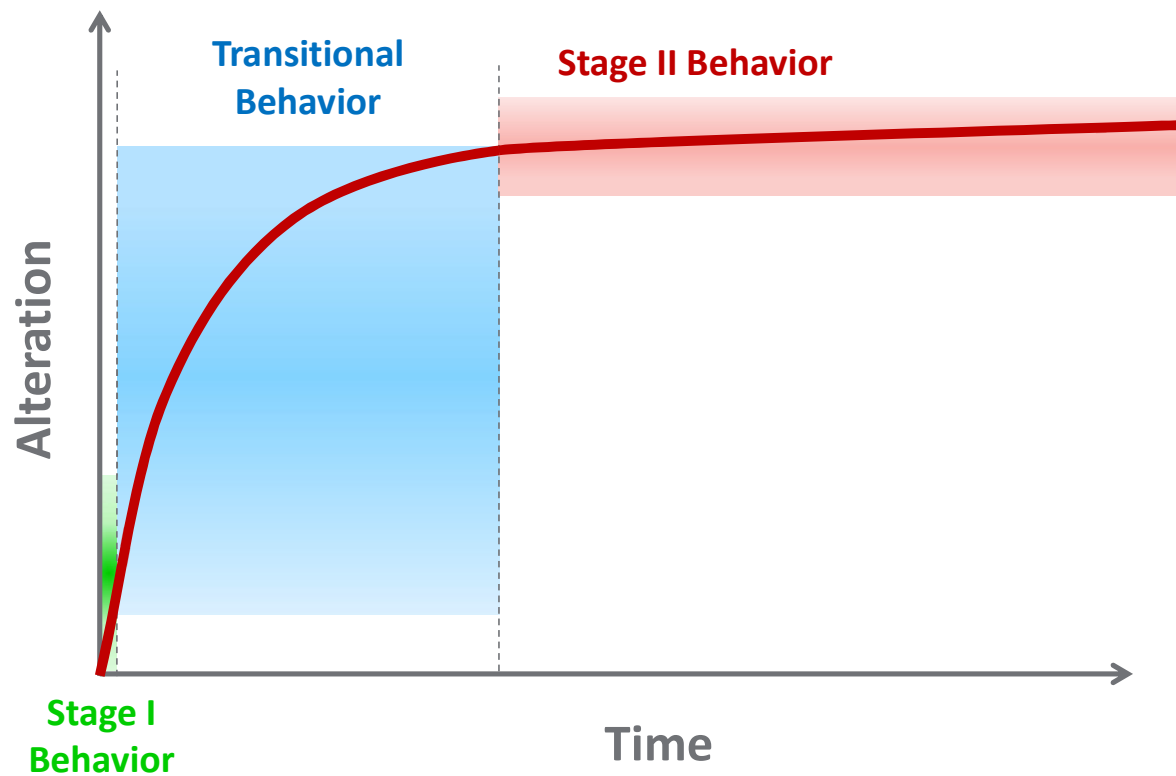


- ▶ Can be REALLY slow...
- ▶ Accelerate the test by
 - Increased surface area (powders)
 - Increased temperature
 - Getters / Complexants
 - Seeds

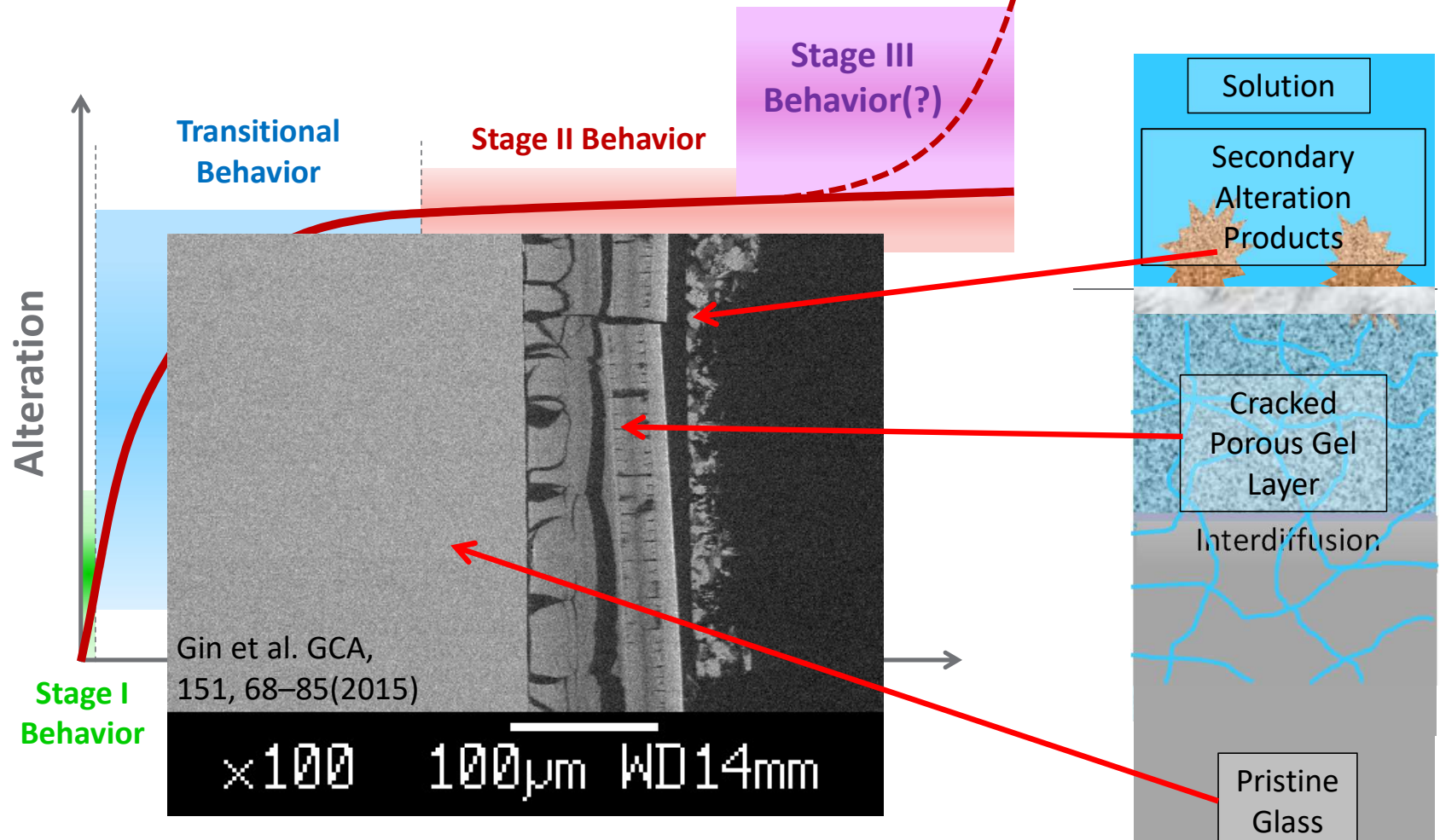
How glass corrodes (static conditions)



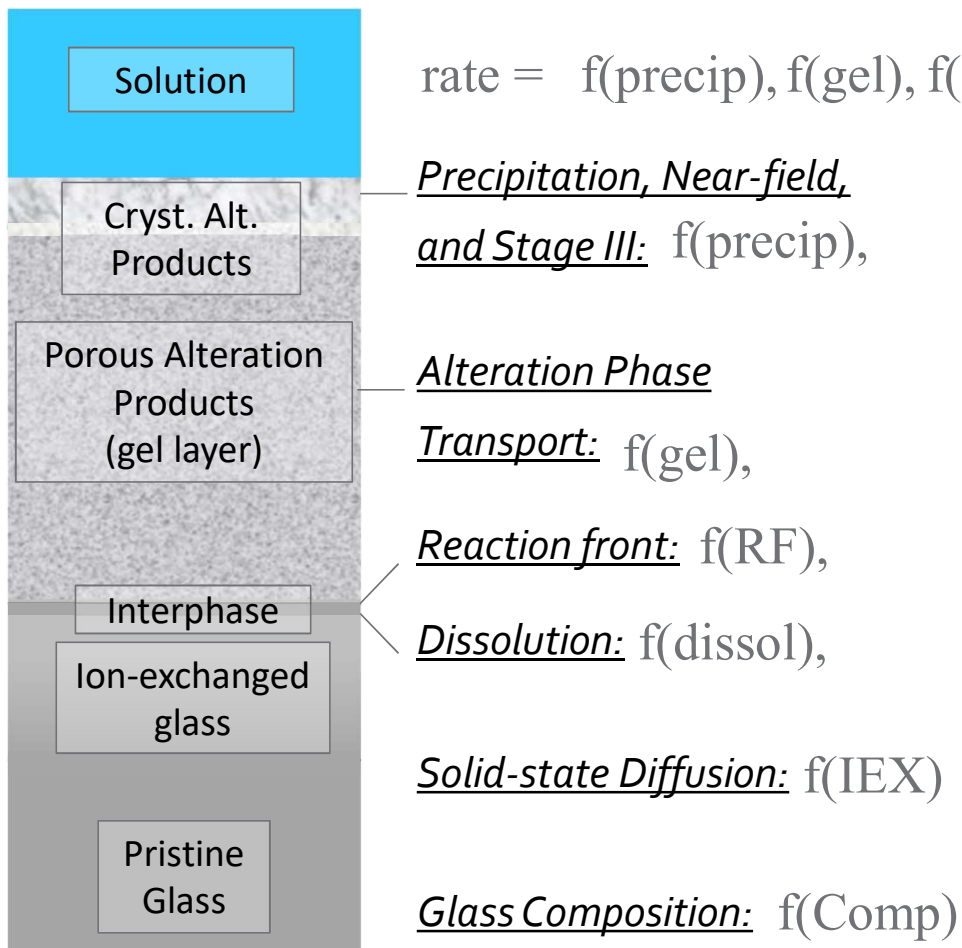
How glass corrodes (static conditions)



How glass corrodes (static conditions)



So what's going on?



The behavior of glass *at all times* is generally believed to result from *a combination* of many mechanistic processes at work:

- **Dissolution** of the network
- **Solid-state diffusion** within otherwise undisturbed glass
- **Transformation** of glass into gel at the active reaction front
- **Transport limitations** in gel/altered regions
- **Condensation/Precipitation reactions** to form alteration phases from solution

*Explaining long-term behavior
requires a combination of mechanisms!*



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Dissolution Mechanisms

Example Reaction Rate Model (without transport)

- ▶ Forward dissolution rate, r_f = the rate at which glass dissolves into solution at specific values of the T and pH in the absence of back reactions
- ▶ Dissolution rate most likely to be directly impacted by structure and composition of glass

$$r_i = v_i k_0 a_{H^+}^{\pm\eta} \exp\left(\frac{-E_a}{RT}\right) \left[1 - \left(\frac{Q}{K_g} \right)^\sigma \right] + \text{potential other terms}$$

r_i = normalized glass dissolution rate
(based on element i), g m⁻² d⁻¹

r_f = forward glass dissolution rate, g m⁻² d⁻¹

v_i = stoichiometric coefficient for element i in glass

k_0 = intrinsic rate constant, g m⁻² d⁻¹

a_{H^+} = hydrogen ion activity

η = pH power law coefficient (dependent on pH regime)

E_a = apparent activation energy, J mol⁻¹

R = gas constant, J mol⁻¹ K⁻¹

T = absolute temperature, K

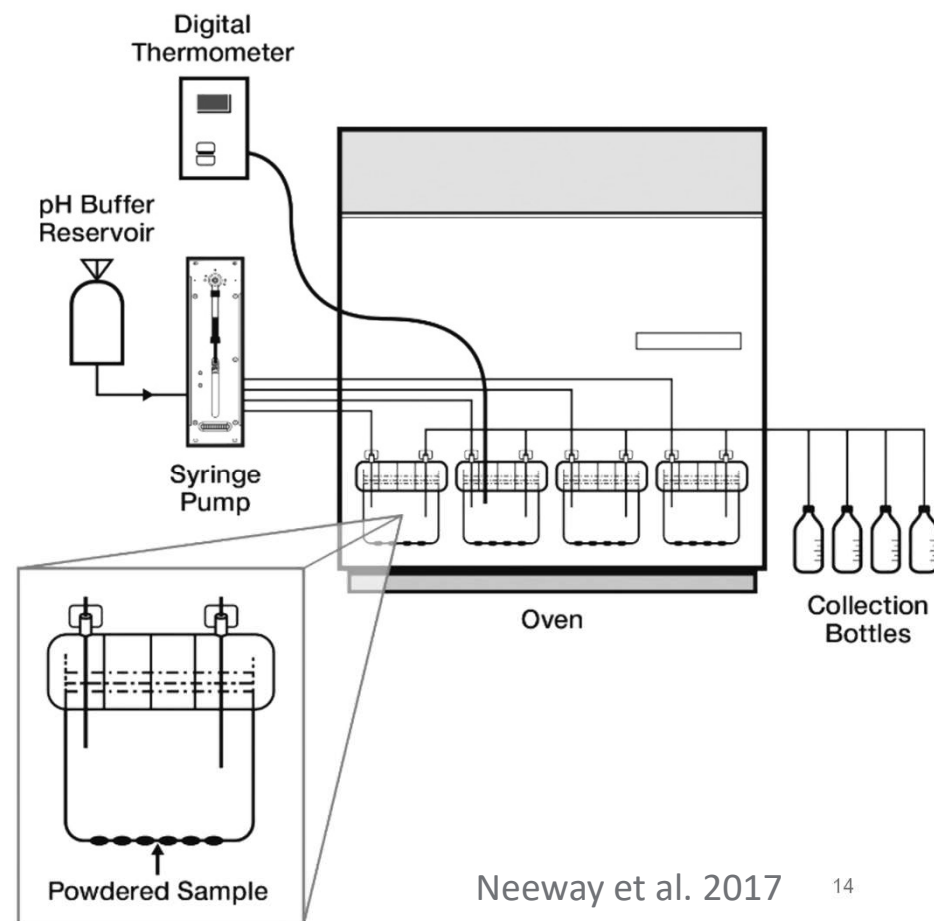
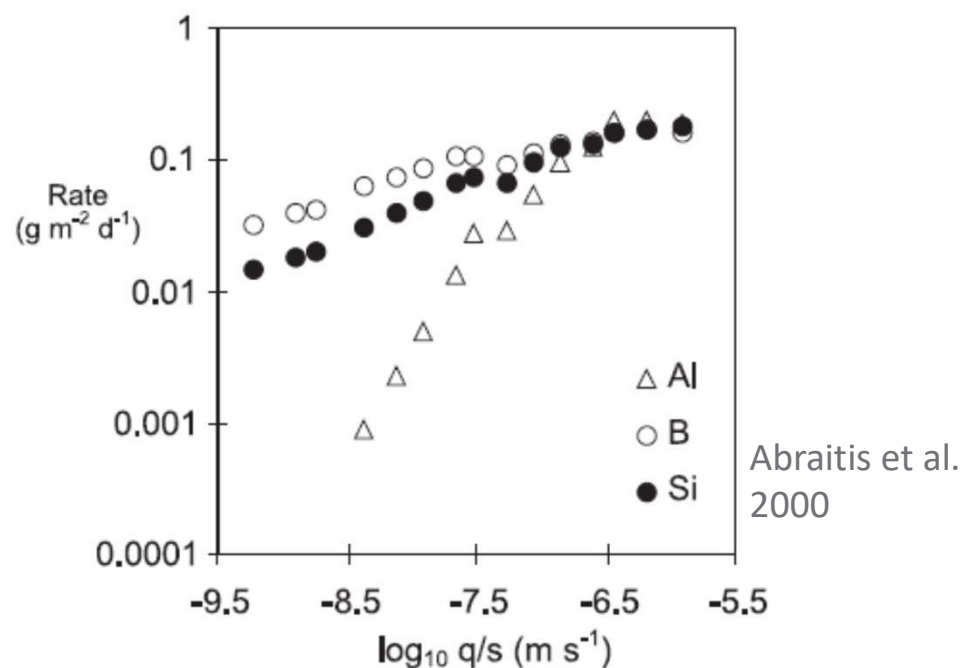
Q = ion-activity product of rate controlling species

K_g = pseudo-equilibrium constant for glass

σ = reaction order (Temkin coefficient)

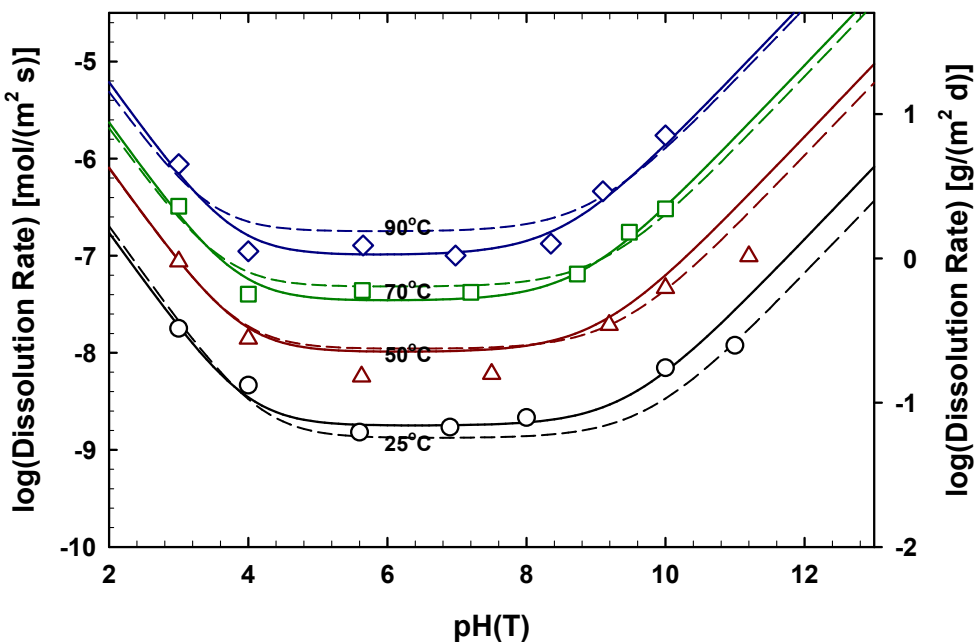
Isolation of Individual Effects

- ▶ Single-pass flow-through test (SPFT, ASTM C1662) can be used to measure effects of individual parameters
- ▶ Measure impacts of pH, T, $[H_4SiO_4]$ and $[Al(OH)_4^-]$
- ▶ Avoid feed-back effects by high flow rate/surface area (q/s)



Neeway et al. 2017

pH and Temperature Impacts



- ▶ Hydrolysis rate depends on:
 - Bond length and bond angle (stretched O-Si-O bonds favor hydrolysis)
 - Site protonation (high or low pH)
 - Energetics (temperature)
- ▶ Arrhenius fit seems best for temperature profile
- ▶ Some debate on how best to associate full pH dependence curve

$$R = k_i \left[\exp\left(\frac{-E_{aH^+}}{RT}\right) a_H^{\eta_a} + \exp\left(\frac{-E_{aH_2O}}{RT}\right) + \exp\left(\frac{-E_{aOH^-}}{RT}\right) a_{OH}^{\eta_b} \right]$$

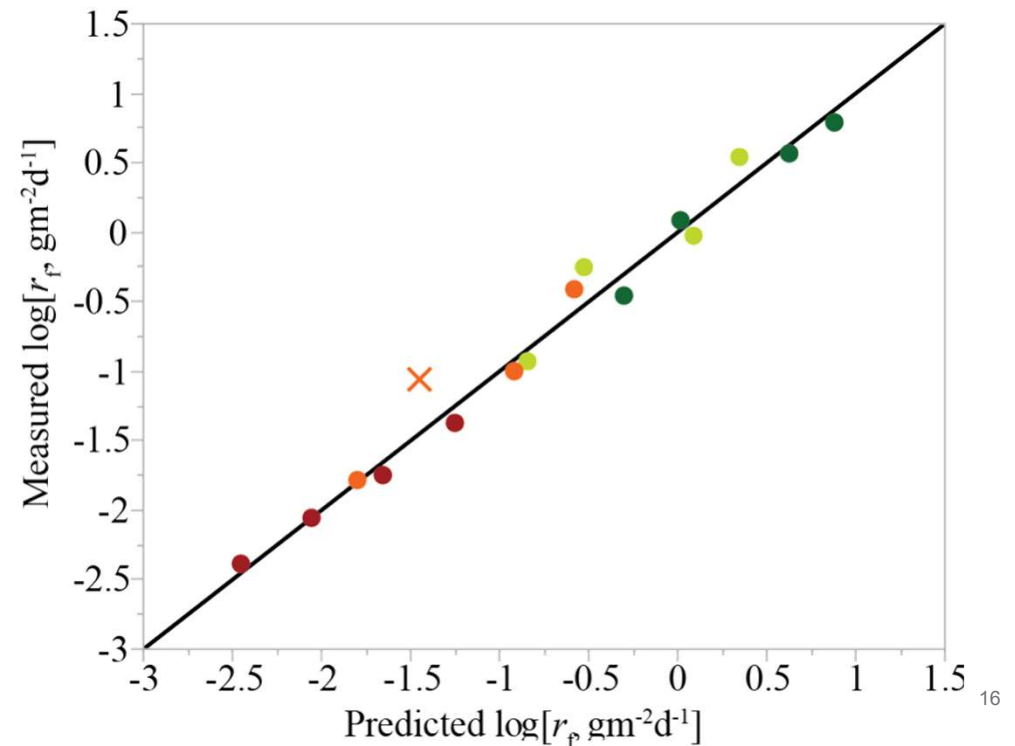
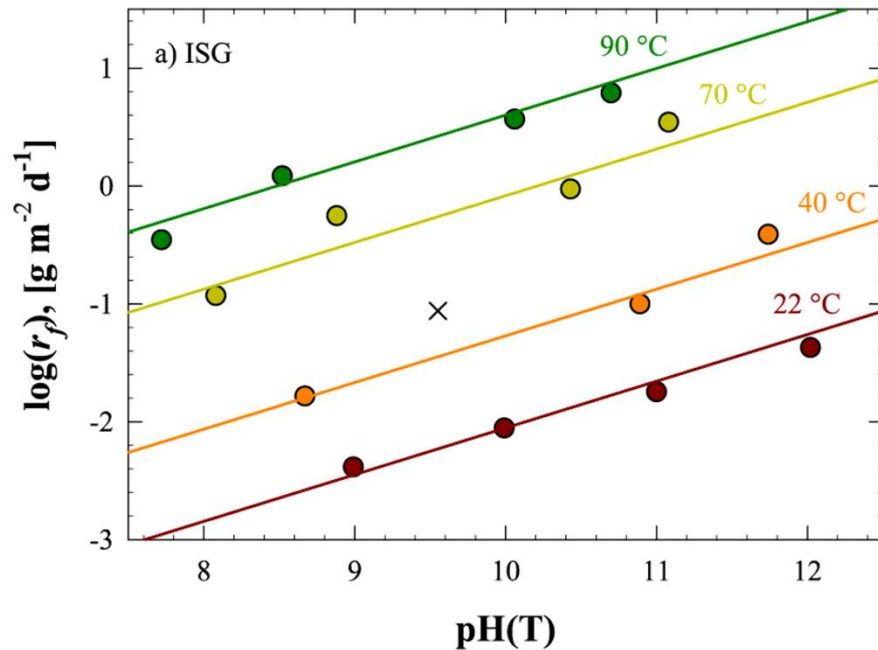
DM Strachan, (2017) *Geochimica et Cosmochimica Acta*, 219, 111-123

Modeling the Data for Individual Glass

- ▶ Measure r_f of glass with systematic variation in pH and T
- ▶ Fit data to linear equation:

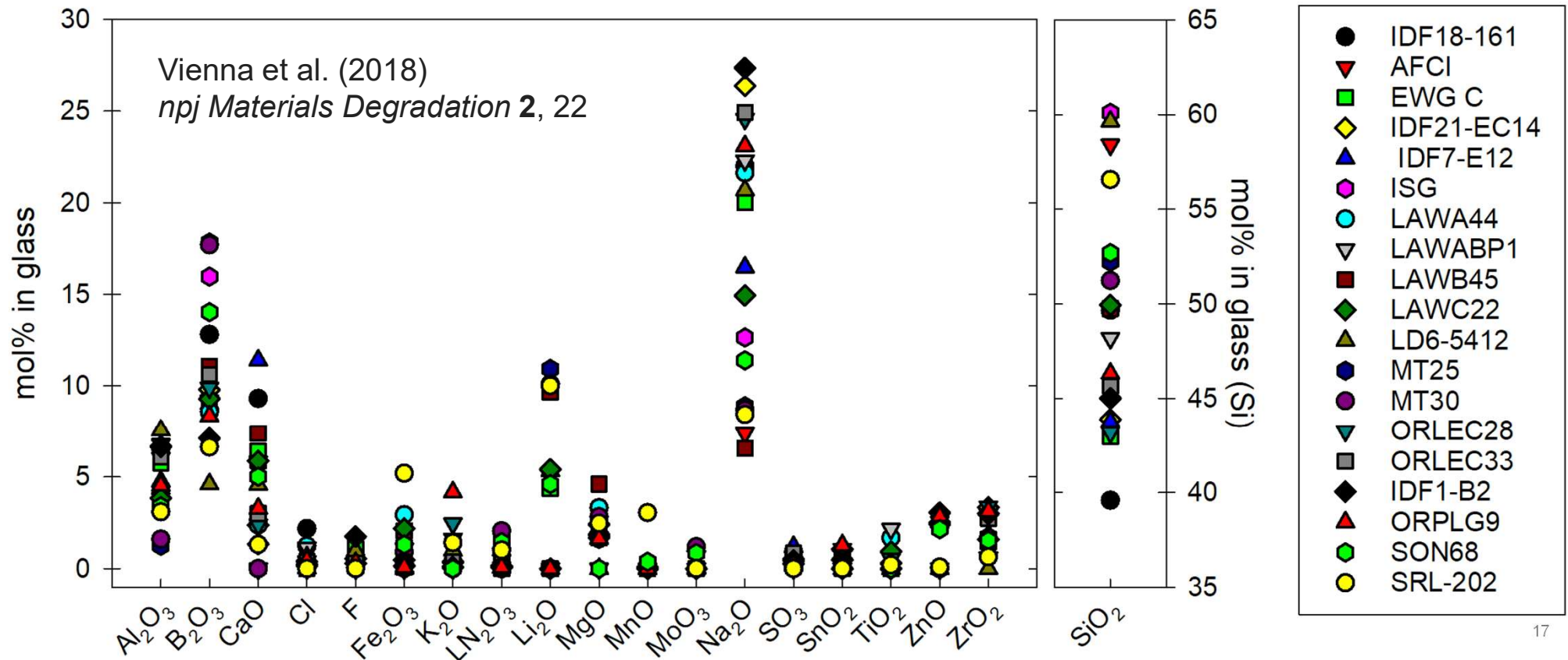
$$\log[r_f] = \log[k_0] + \eta \cdot pH - E_a \cdot \frac{\log[e]}{RT}$$

$$\begin{aligned} \log[k_0] &= 8.37 \pm 0.92 \text{ gm}^{-2}\text{d}^{-1} \\ \eta &= 0.396 \pm 0.060 \\ E_a &= 81.6 \pm 6.1 \text{ kJmol}^{-1} \\ R^2 &= 0.983 \\ \text{RMSE} &= 0.141 \end{aligned}$$



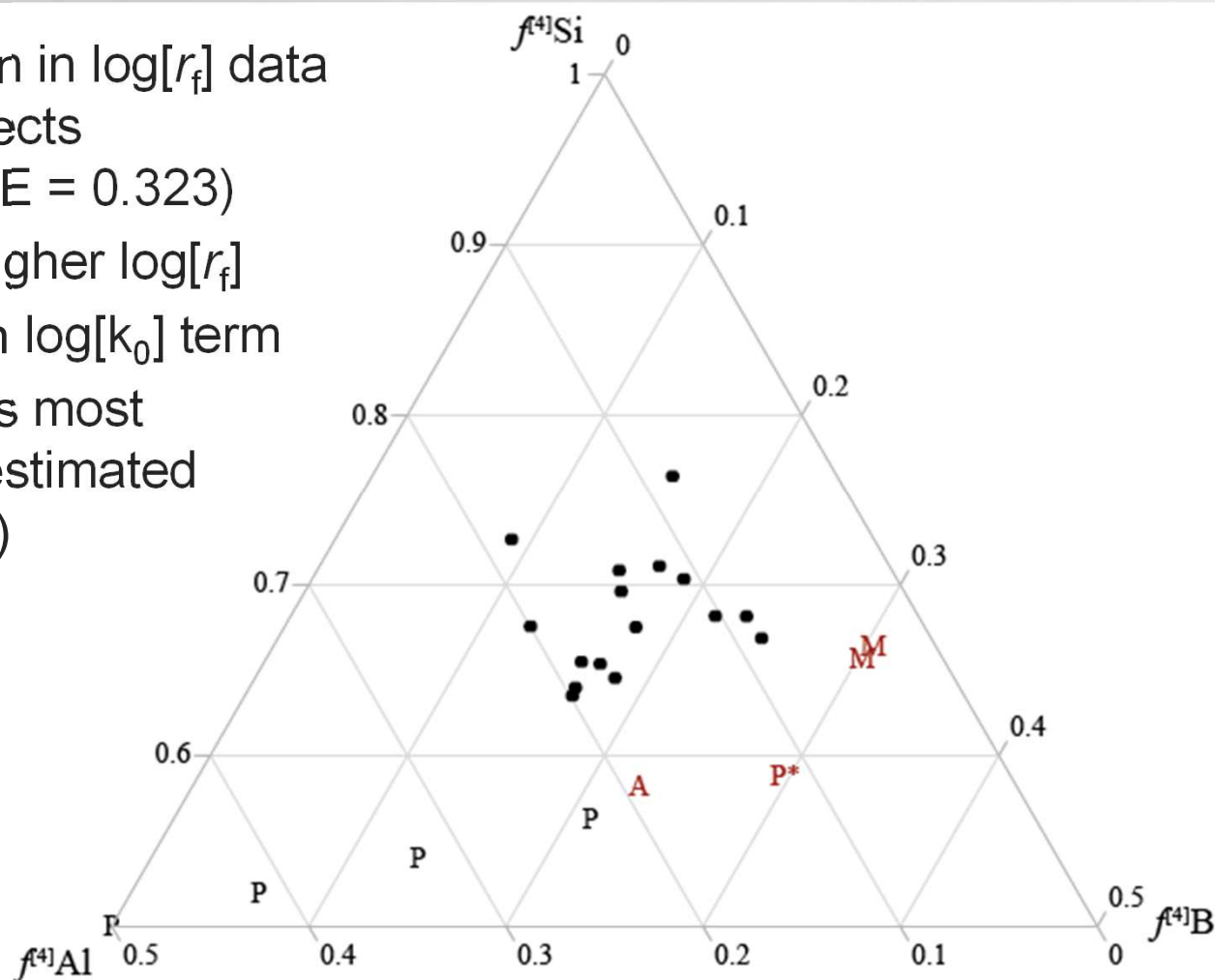
Glass Composition Effects on Forward Rate

- ▶ 19 glasses all measured by SPFT with systematic variation in pH (7 to 13) and T (23° to 90°C)
- ▶ Include broad range of compositions (US HLW glasses, US LAW glasses, International glasses)



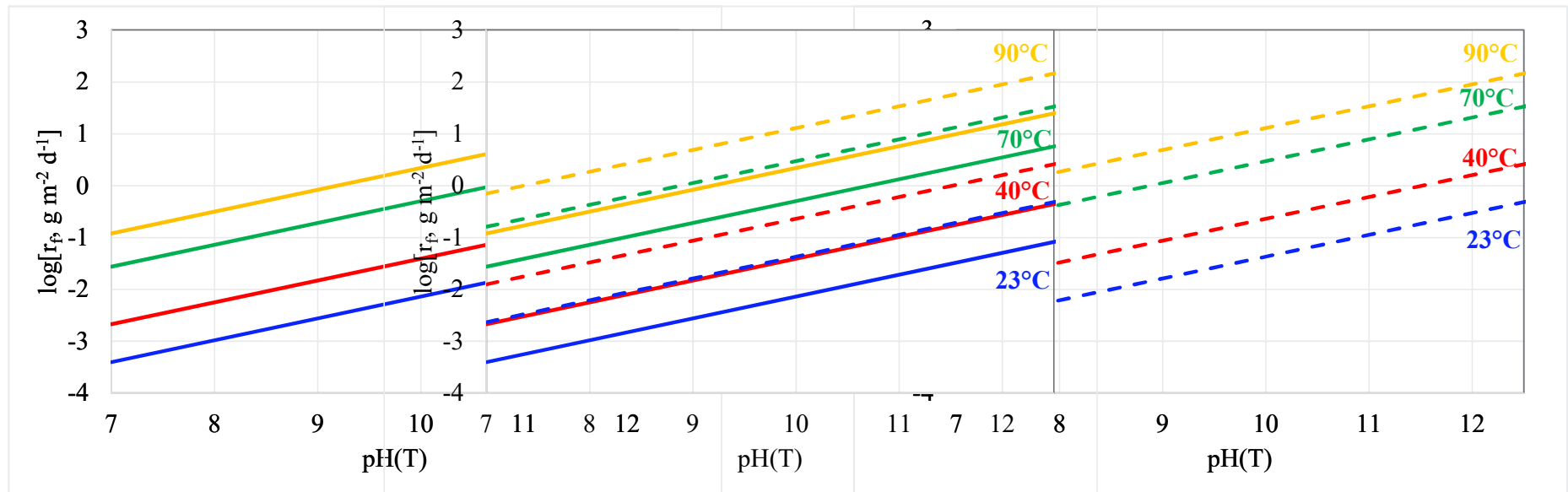
Simultaneously Fit r_f to pH, T, and Composition

- ▶ Model explaining 90% of variation in $\log[r_f]$ data obtained with no composition effects ($R^2_{\text{fit}} = 0.896$, $R^2_{\text{val}} = 0.894$, RMSE = 0.323)
- ▶ Three glasses have noticeably higher $\log[r_f]$
- ▶ Composition effects only found in $\log[k_0]$ term
- ▶ Composition effects model shows most significant composition effect is estimated fraction tetrahedra from $^{[4]}\text{B}$ ($f^{[4]}\text{B}$)
 - Effect non-linear, best modeled by step-function change



End Result

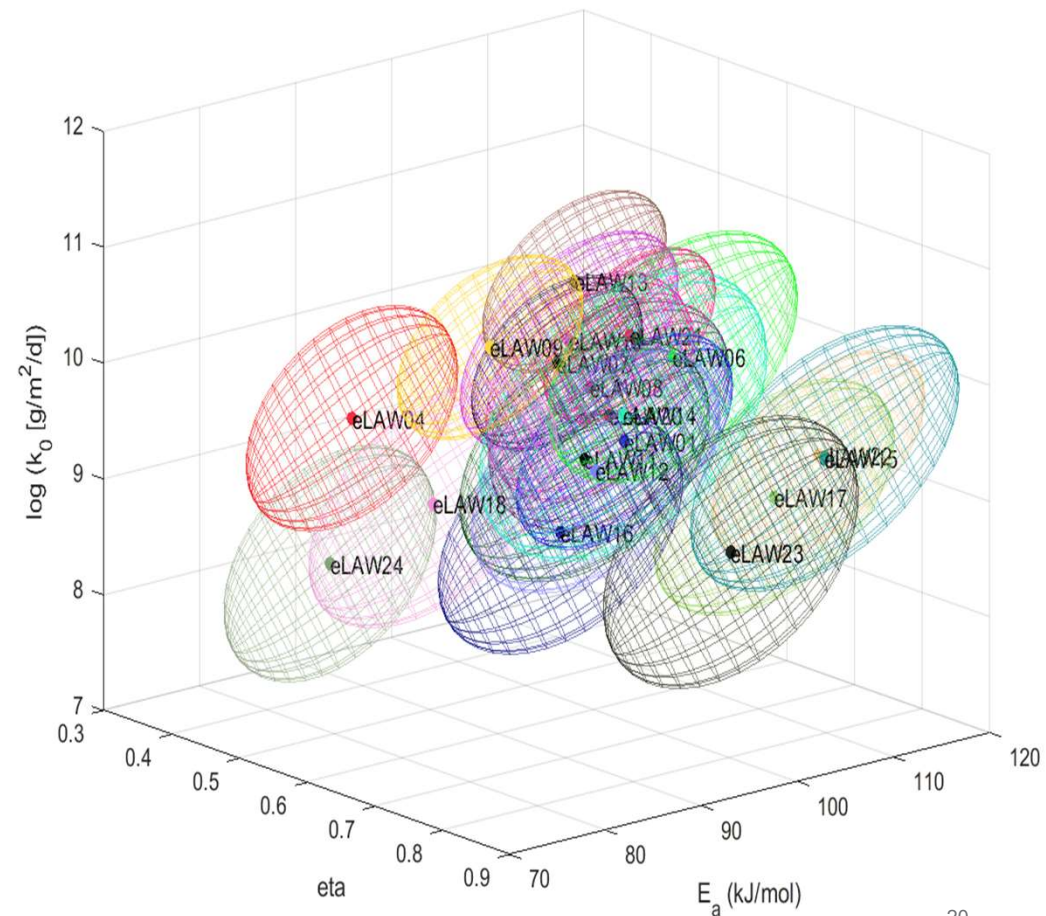
$$\log[r_f (g \cdot m^{-2} \cdot d^{-1})] = \begin{cases} \text{below threshold} \Rightarrow 7.09 + 0.421 pH_{(T)} - 76,200 \frac{\log(e)}{RT} \\ \text{above threshold} \Rightarrow 7.86 + 0.421 pH_{(T)} - 76,200 \frac{\log(e)}{RT} \end{cases}$$



Forward Rate Parameter Correlation

$$r_i = v_i k_0 a_H^{-\eta} \exp\left(\frac{-E_a}{RT}\right) \left[1 - \frac{Q}{K_g}\right]^\sigma$$

- ▶ Because there are three parameters with only two variables (T and pH), parameters are correlated:
 - $[\log k_0, \eta] = 30\%$
 - $[\log k_0, E_a] = 81\%$
 - $[E_a, \eta] = 30\%$
- ▶ Although there are some differences in forward rate, the general behaviors are the same for all compositions

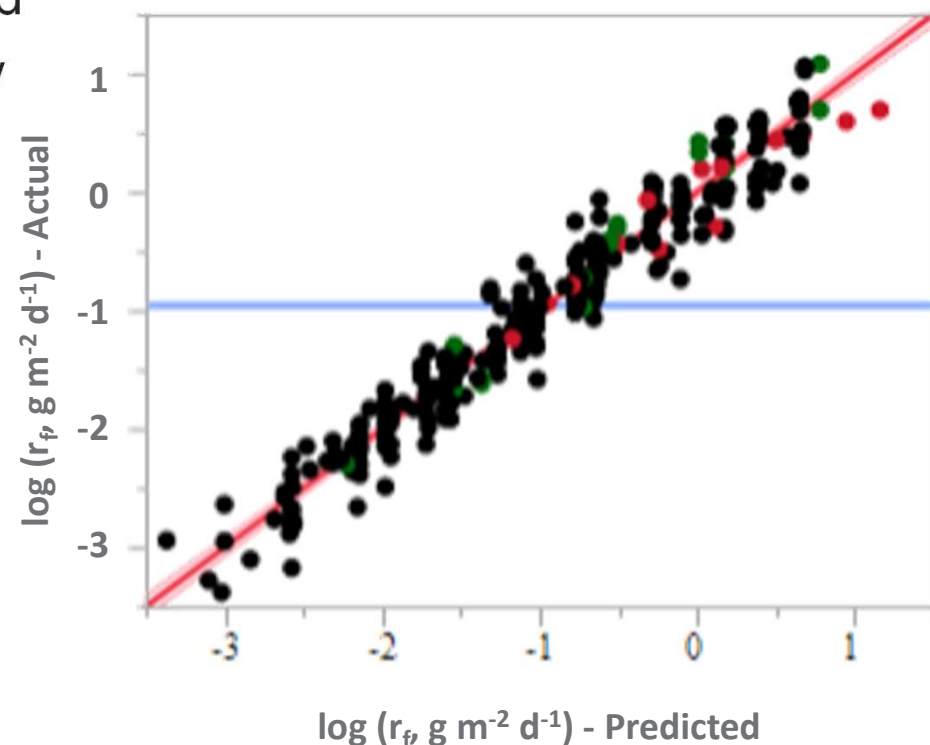


Summary of Modeling Results

- ▶ Composition effects on r_f in caustic solution are relatively small over a broad composition space
- ▶ They are best modeled using a $f^{[4]}B = 0.22$ threshold with rate being composition independent above and below the threshold
- ▶ The exact location of the threshold and any composition effects outside of the regions tested here are uncertain

Most alumino-borosilicate glasses behave similarly in terms of initial forward rate

Vienna et al. (2018)
npj Materials Degradation **2**, 22





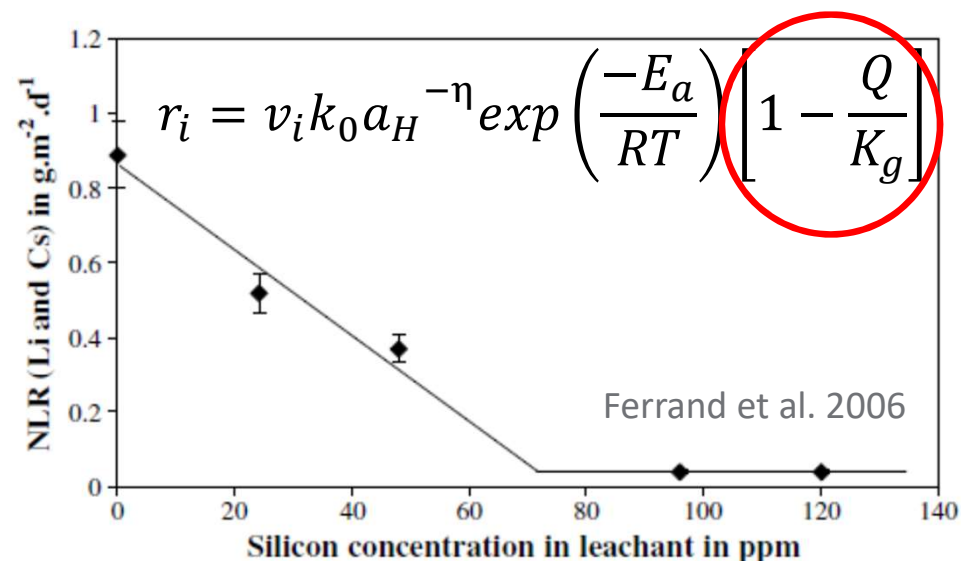
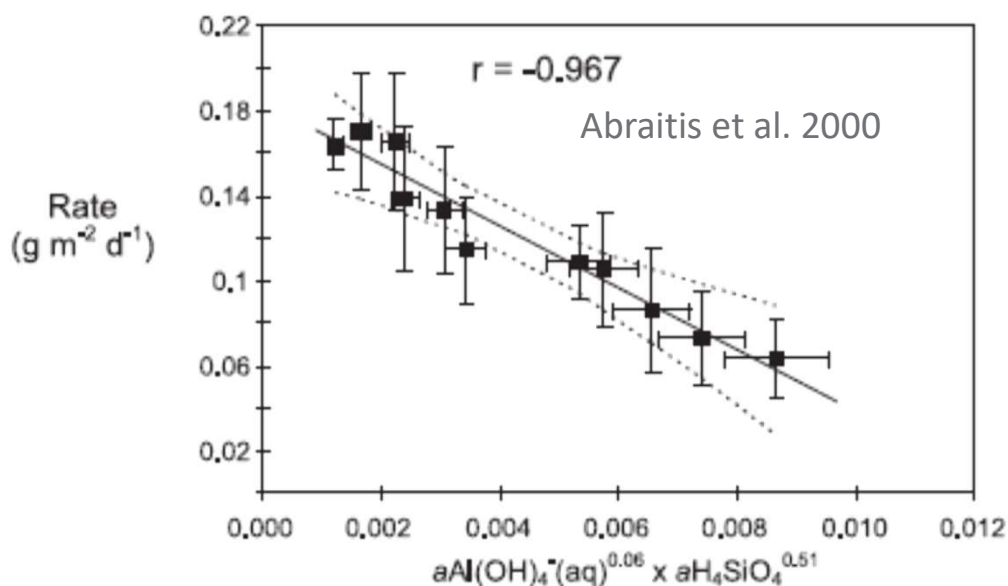
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Condensation Mechanisms

Impact of species in solution on dissolution

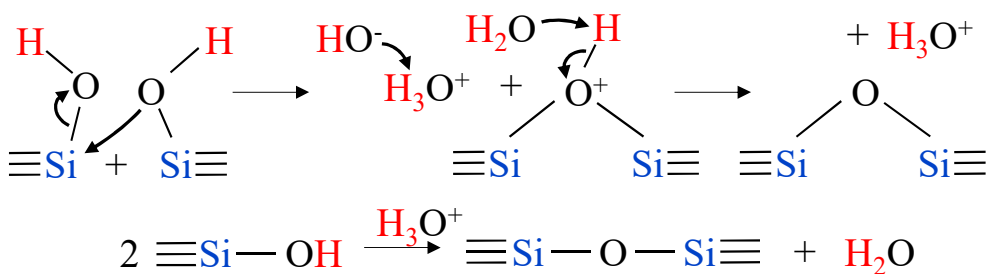
- ▶ Not really “condensation”, rather “slowing dissolution”
- ▶ When network ions in solution build up, the dissolution rates decrease
- ▶ Most dramatic and obvious from silicon, but aluminum also is impactful



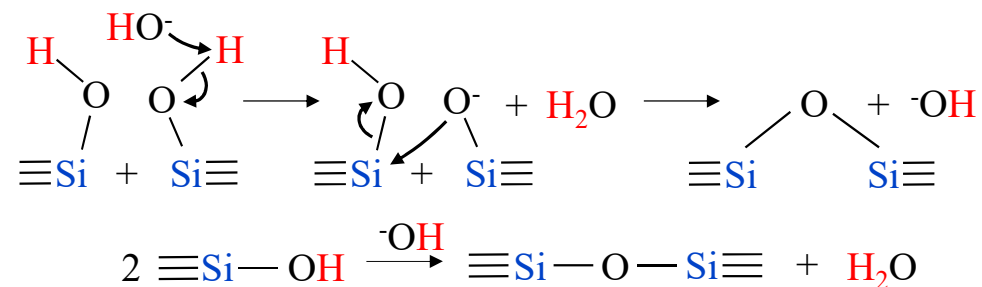
- ▶ Observed silicon response seems VERY technique dependent
- ▶ May be the fact that the reactions do not work in isolation, but rather involve many ions in concert

Condensation Mechanisms

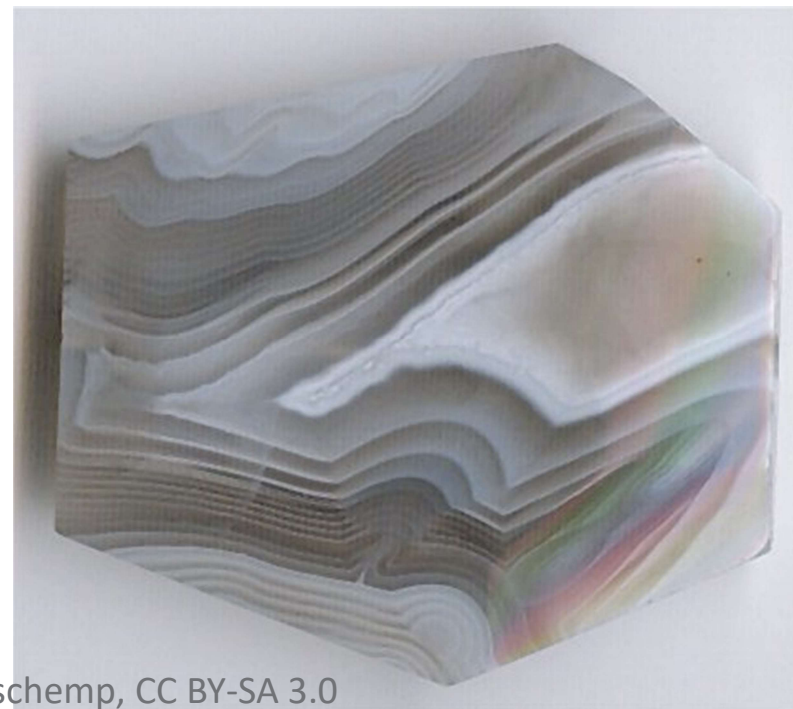
Low-pH case



High-pH case

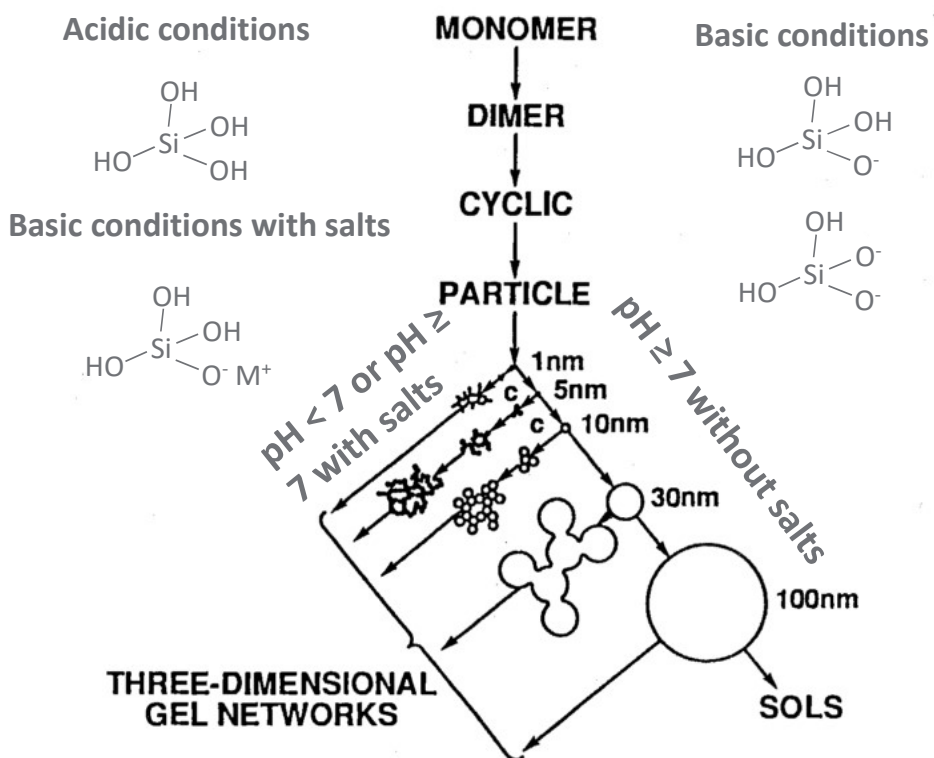


- ▶ Reformation of amorphous structure is ongoing during corrosion
- ▶ Thermodynamic pathways include amorphous alteration layers as well as crystalline phases



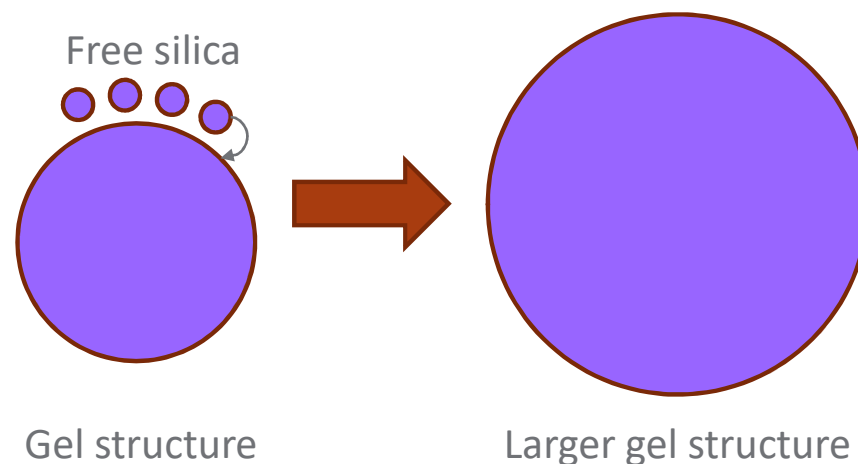
By Pschemp, CC BY-SA 3.0

Condensation Mechanisms



Explains smaller structures for SG-3

Ostwald Ripening



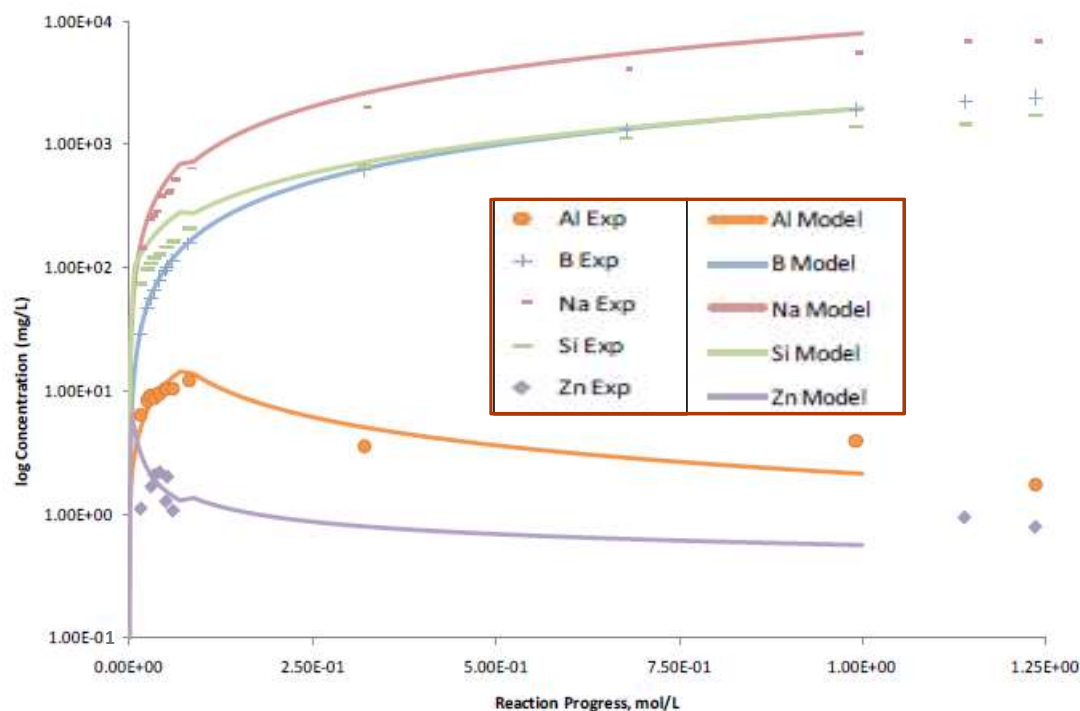
More small species available → More Ostwald Ripening → Larger structures

Reiser et al. (2019)
ACS Omega <https://doi.org/10.1021/acsomega.9b00491>
and npj-Materials Degradation (in proof)

Iler, R. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; John Wiley & Sons, Inc.: United States, 1979.

Problems with affinity-based models

- ▶ Amorphous materials CAN be in equilibrium with solution
- ▶ When taken to logical conclusion, a purely affinity-based model requires the precipitation of secondary phases for corrosion to continue
- ▶ Which can be done (and is included in most models), but brings up some major questions:
 - Why does dissolution still occur at silica “saturation”?
 - Why does the silica concentration continue to increase?



Pierce et al. (2011), Integrated Disposal Facility
FY 2011 Glass Testing Summary Report, PNNL-20781

GEL

PRI

IEX



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Solid-state Diffusion Mechanisms

Solid-state Diffusion Types

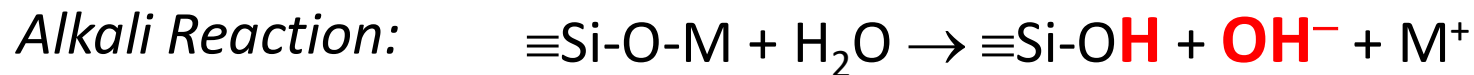


Molecular Diffusion:

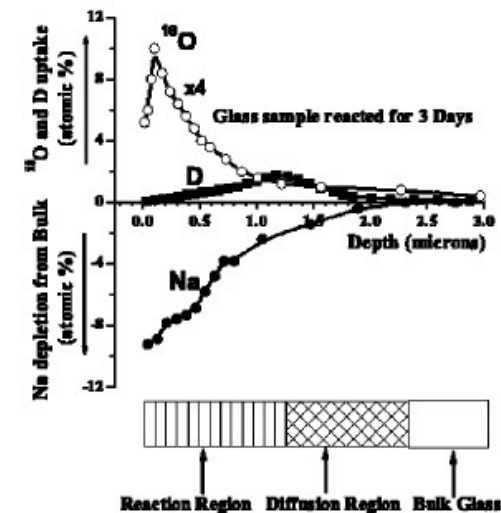
$$\frac{\delta[H_2O_{tot}]}{\delta t} = \frac{\delta}{\delta x} \left\{ D_{H_2O} \frac{\delta[H_2O_m]}{\delta x} + D_{OH} \frac{\delta[OH]/2}{\delta x} \right\}$$

Interdiffusion:

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



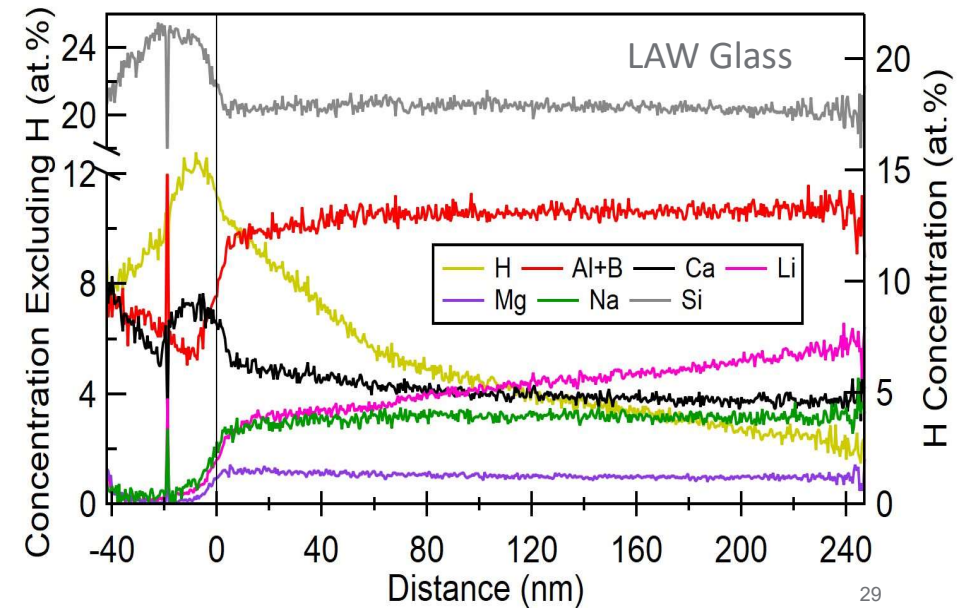
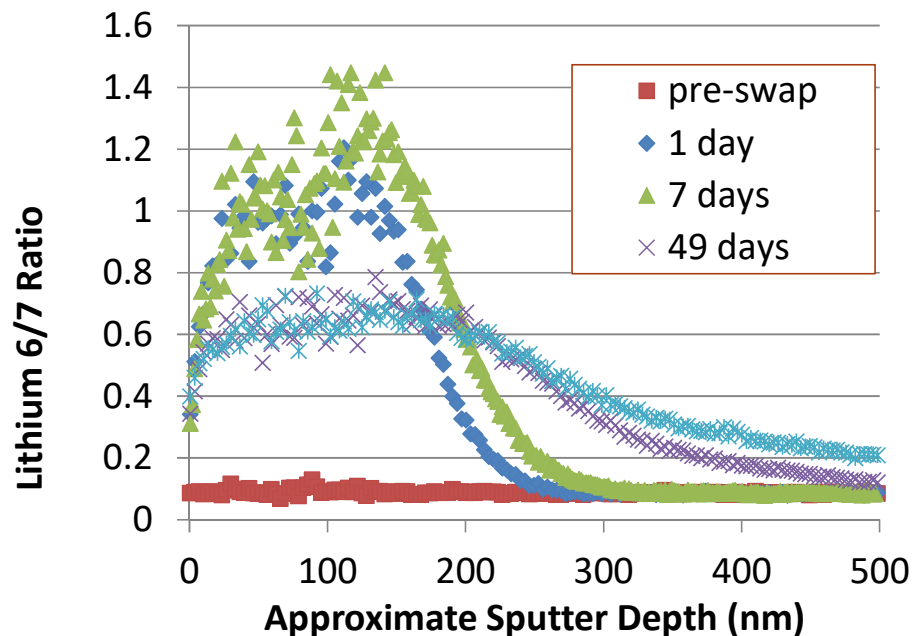
- ▶ While interdiffusion is traceable, there is a question of whether it impacts durability
- ▶ The reaction that dissociates water is much more impactful... increasing pH
- ▶ Also can potentially release some radionuclides directly, but not a major source



Interdiffusion



- ▶ Different species exhibit different profiles
- ▶ Profiles also vary significantly with glass composition
- ▶ Depths are not consistent
- ▶ Not a simple or isolated process



Alkali mobility is a function of alkali type and local structure

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

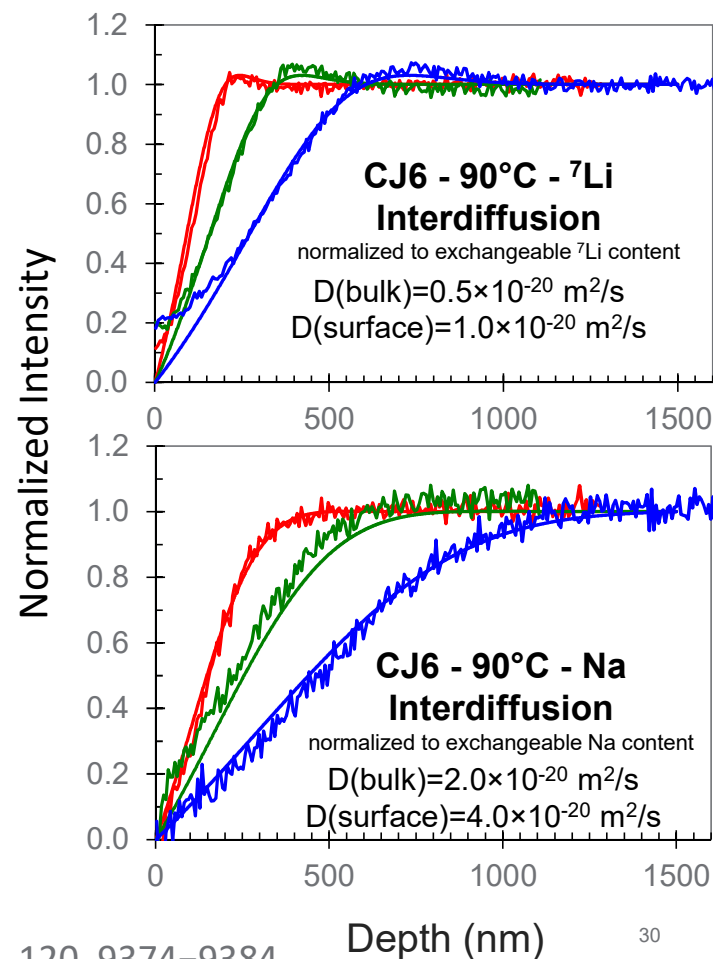
$$\tilde{D} = \frac{D_A D_B}{C_B D_B + (1 - C_B) D_A} = \frac{D_B}{1 + C_B b}$$

$$b = D_A / D_B - 1$$

- ▶ 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

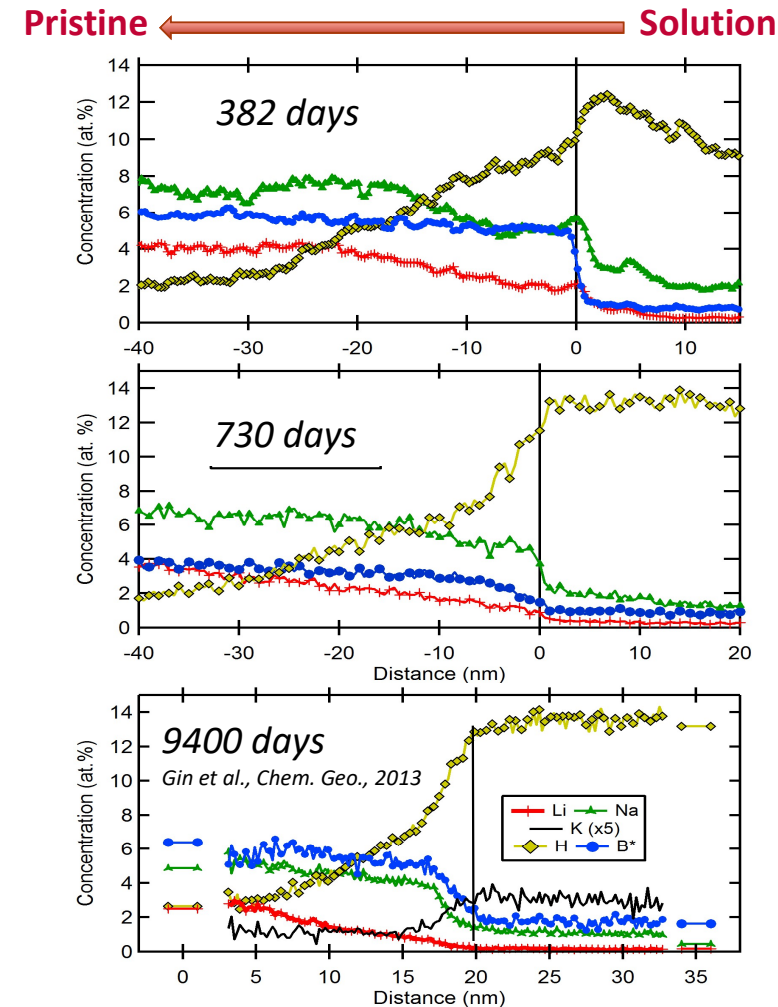


Solid-state Diffusion Mechanism Impacts

- ▶ All agree that ion exchange and molecular water infusion are diffusive processes

$$r_{IEX} = A_0 \exp\left(-\frac{E_a}{RT}\right) t^{-p}$$

- ▶ Over the long term, these processes are expected to result in a steady-state impact
- ▶ This impact is very likely to be low:
 - Small pH increases
 - Potential increase in buried interface reactivity





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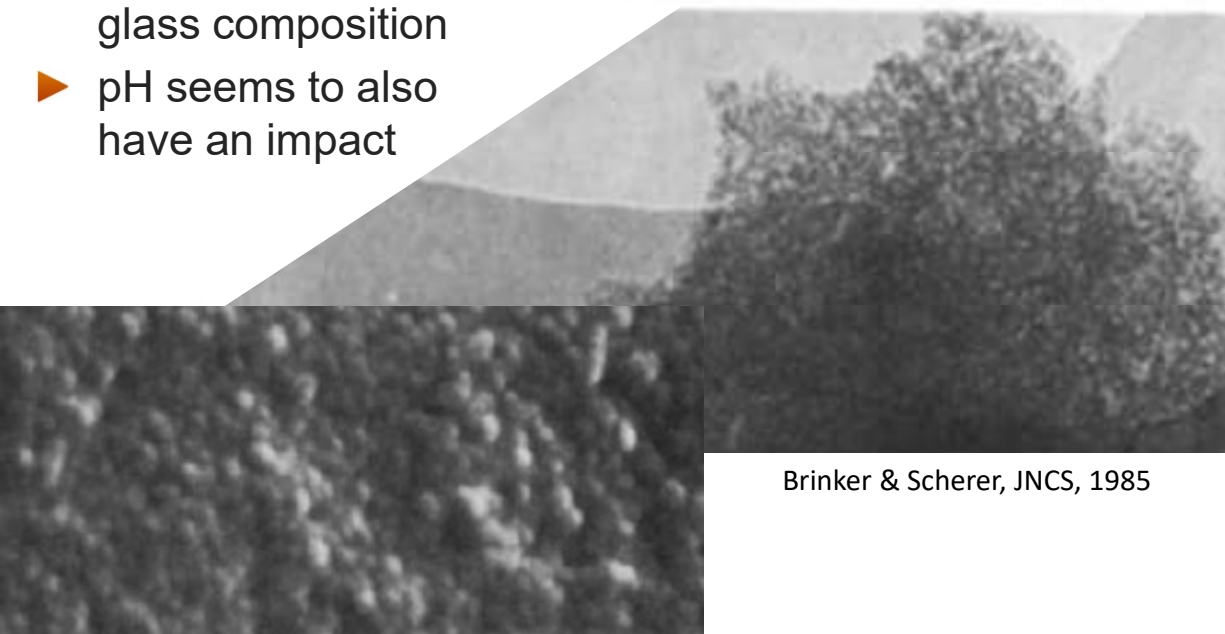
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Constricted Aqueous Transport Mechanisms

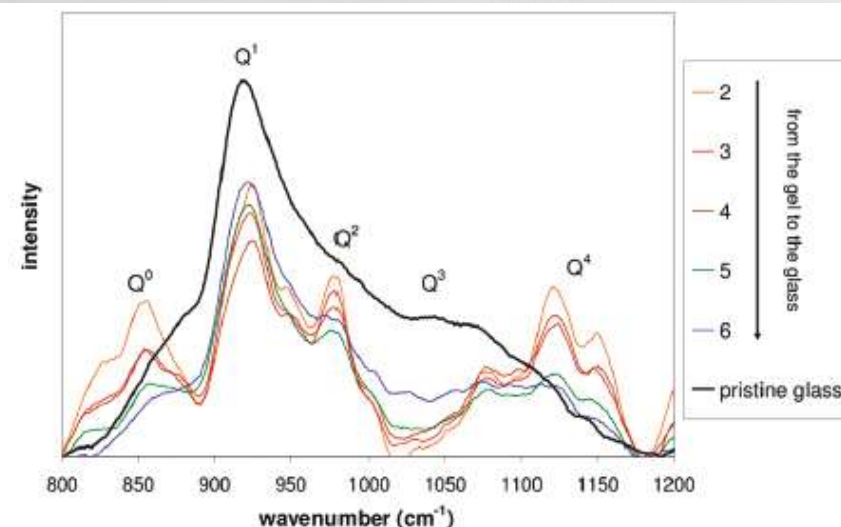
Porous Gel Provenance



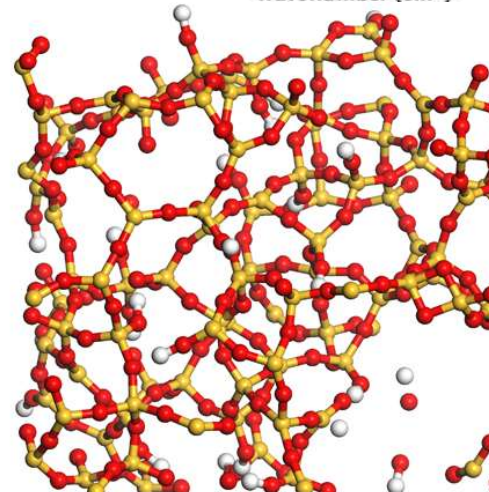
- ▶ Gel composed of relatively insoluble species: Si, Al, Ca, Fe, Ln, some Na
- ▶ Highly porous, with SSA values from 100-800 m²/g
- ▶ Different in structure from glass, even when not formed by precipitation: **NOT a relic**
- ▶ Structure and formation depends strongly on glass composition
- ▶ pH seems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



Brinker & Scherer, JNCS, 1985



Gin et al., JPhysChemC, 2011

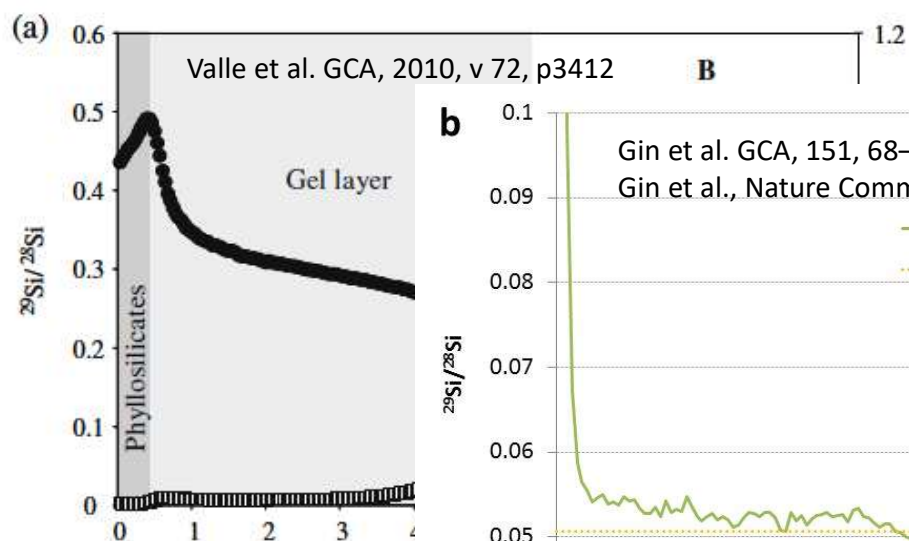


Mellott, PhD Thesis,
Penn State University, 2003

Porous Gel Provenance, cont'd.

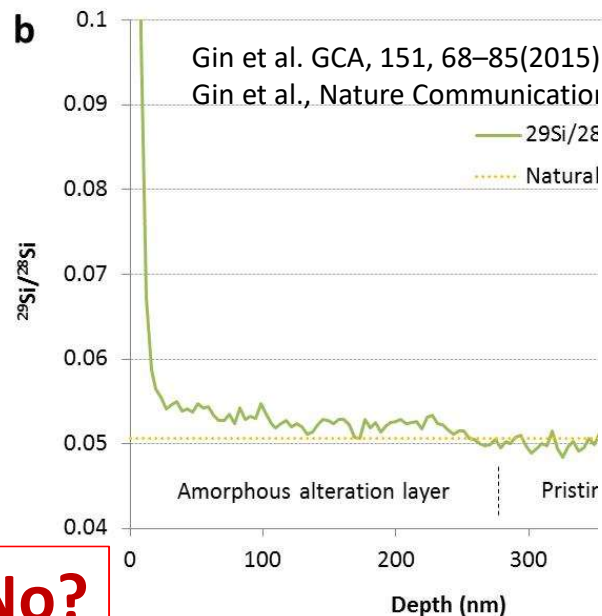


- Question of whether or not silica from solution is incorporated into gel

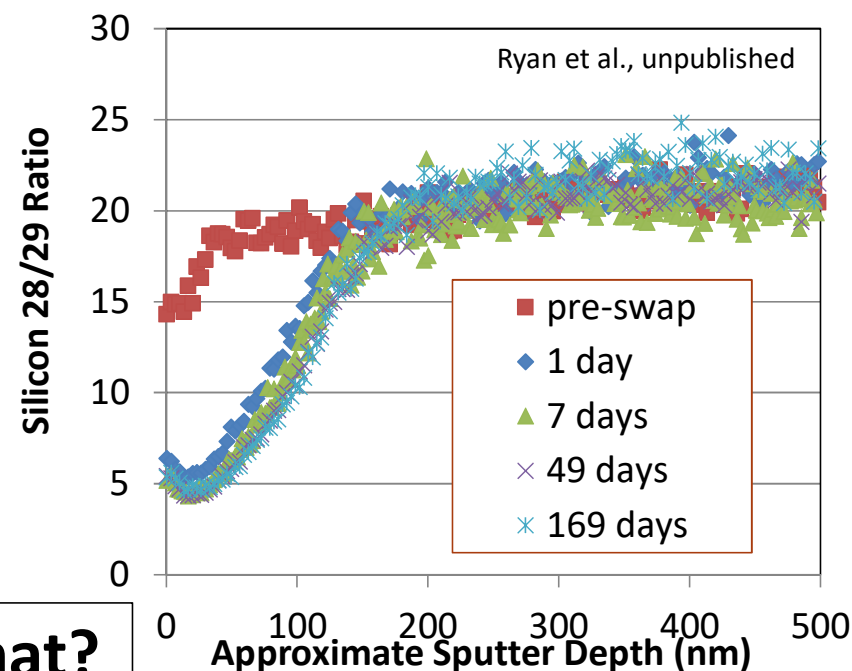


Yes?

No?



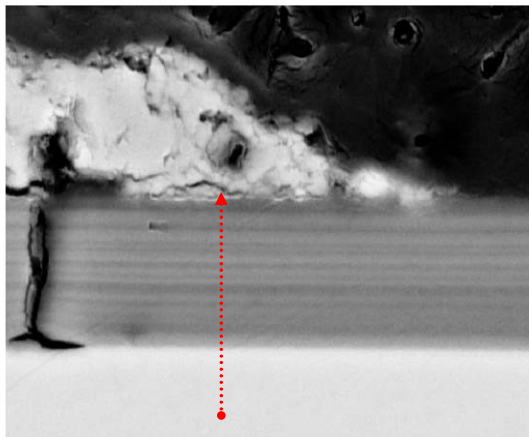
Somewhat?



Oscillatory behaviour

- Oscillatory layers have been observed in a number of systems by a range of authors

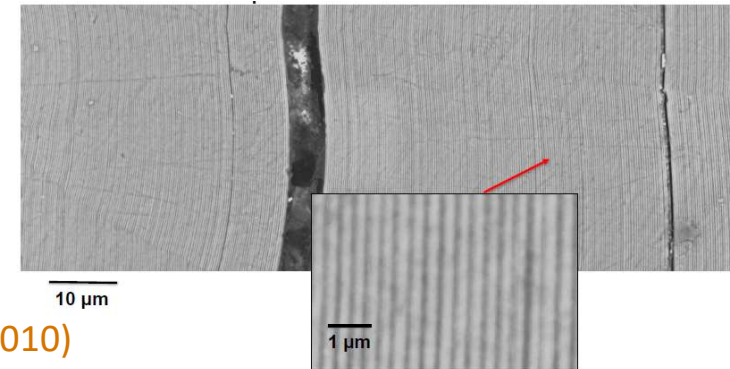
Glass buried for 288 years;
Hangleton – house destroyed
by fire 5/31/1666;
Glass fragment unearthed
1954; Buried in calcerous soil



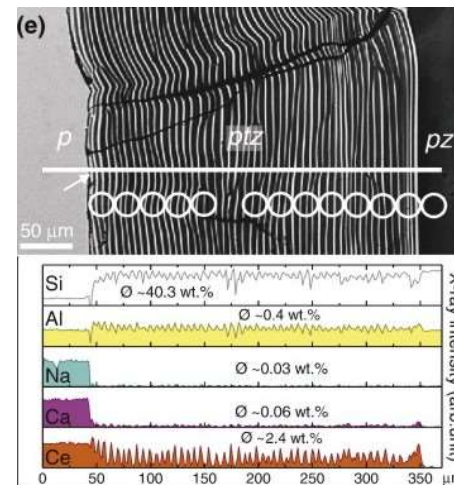
Model medieval glass after
9 years burial at Ballidon
(R. Hand, U. Sheffield)



Newton (1966) *Glass Technol.* 7, 22-25



Geisler et al. (2010)
JNCS 356, 1458–1465



Iulia Felix shipwreck about
30km west of where you're
sitting, about 1800 years
underwater with about 1800
observed layers...
(Buck, Ryan, et al. in revision)

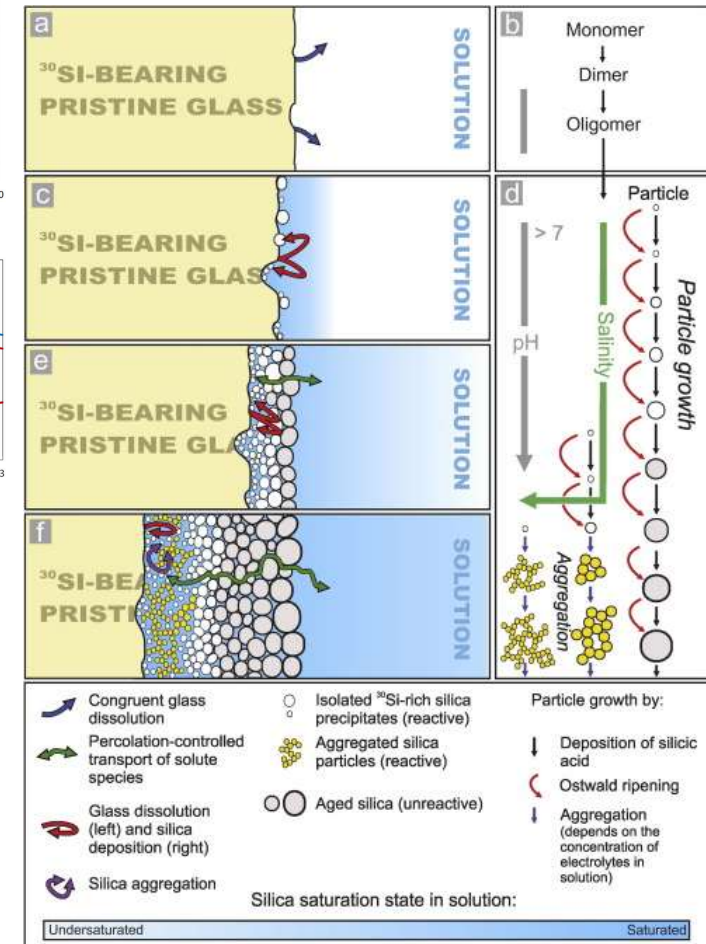
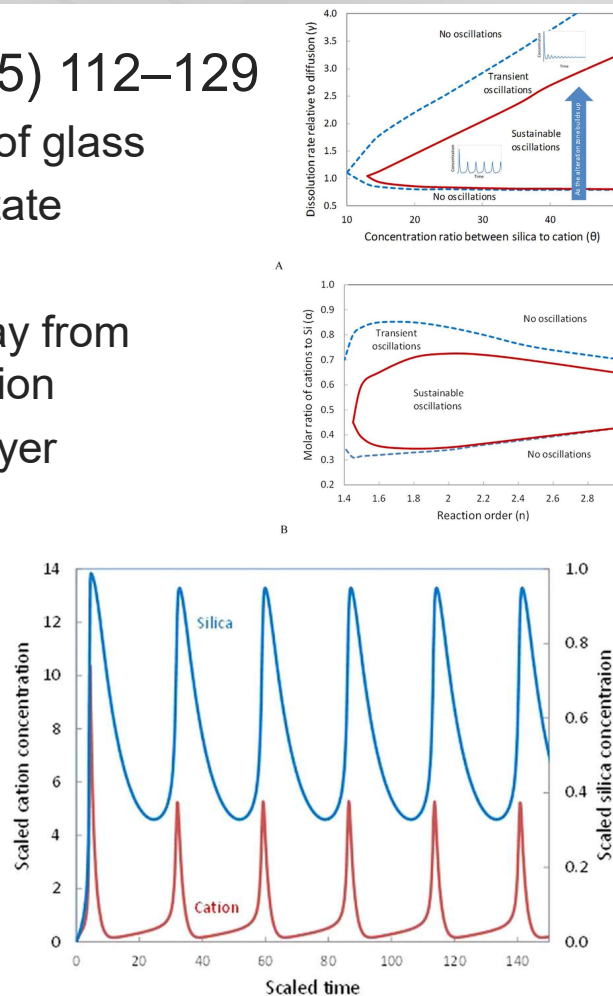
Oscillatory behaviour

► Geisler *et al.* GCA **158** (2015) 112–129

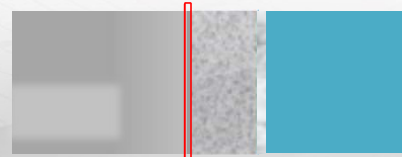
- Initially congruent dissolution of glass
- Silica particles start to precipitate
- Grow by Ostwald ripening
- Interfacial solution moves away from equilibrium with external solution
- Transport through the silica layer becomes important

► Wang *et al.* (2016) Sci. Rep. **6**, 30256

- Non-linear dynamics model

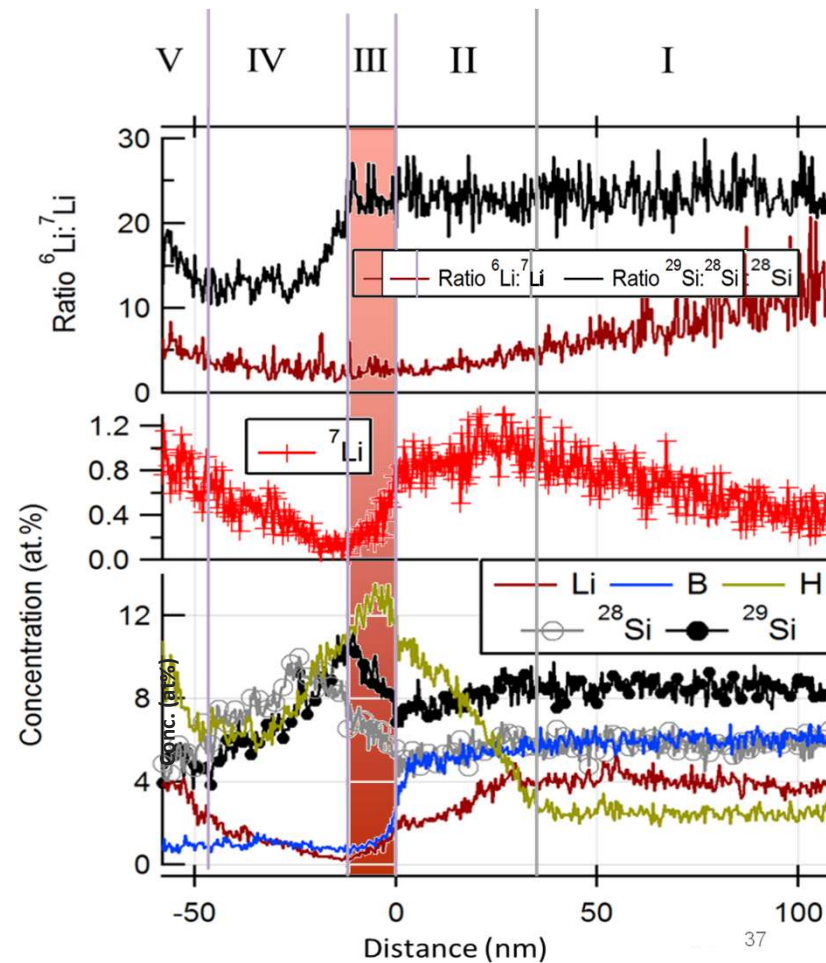
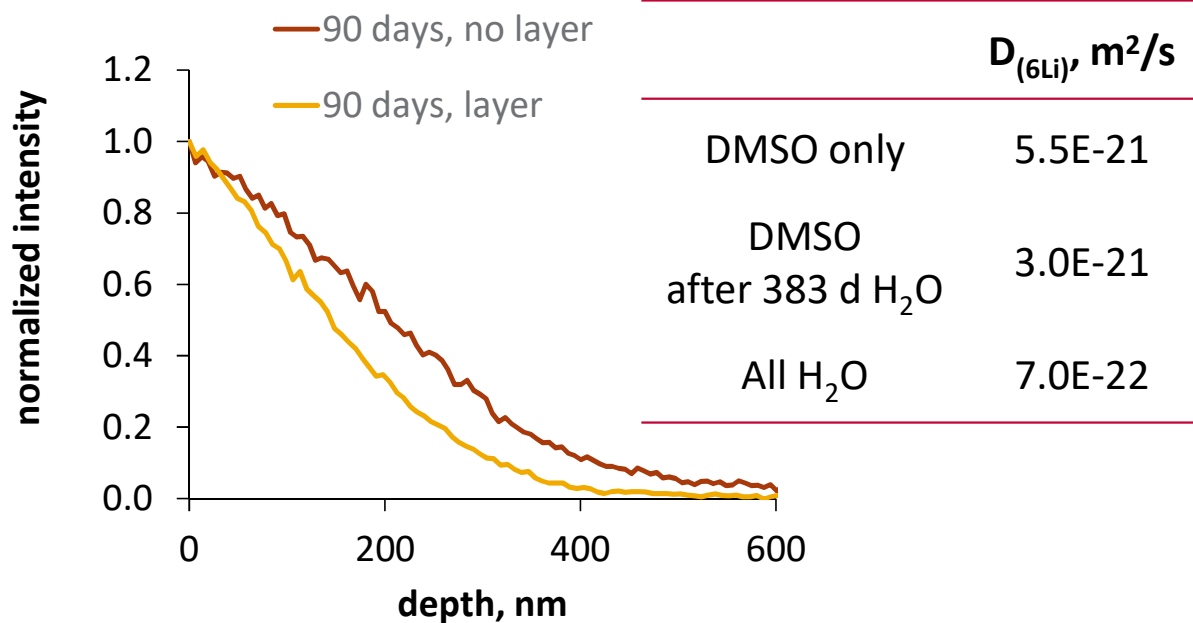


“Passivating Reactive Interphase”



Yes, but how do we know it's there?

- ▶ Only now getting small pieces of direct evidence
- ▶ More data, please!!



Problems with transport-based model

- ▶ Empirical rate equation
- ▶ What if the Stage II rate is constant?
- ▶ What is the medium limiting diffusion?
Why can't we "find" it?
- ▶ Why is there no correlation b/w rate and gel thickness?
- ▶ What is diffusing?

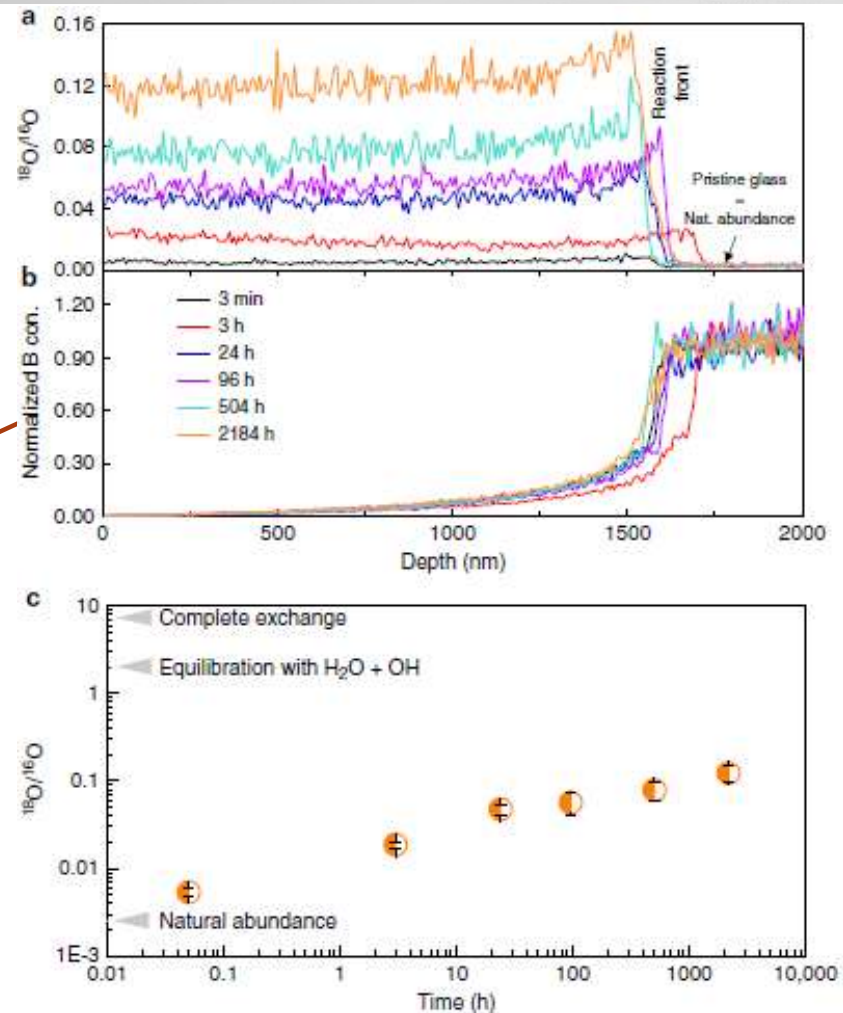
■ Boron?

■ H_2O ?

Gin et al. *Nature Comm.* (2018)
DOI: 10.1038/s41467-018-04511-2

The diffusion of water IN through the gel will not be slower than the diffusion of dissolved species OUT of the gel

Extrapolated to 100°C
 $D_B \approx 10^{-9} \text{ m}^2/\text{s}$



GEL

PRI

IEX

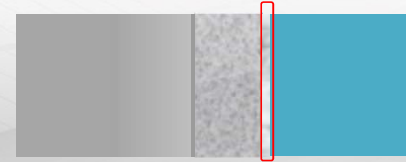


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Secondary Phase Precipitation Mechanisms

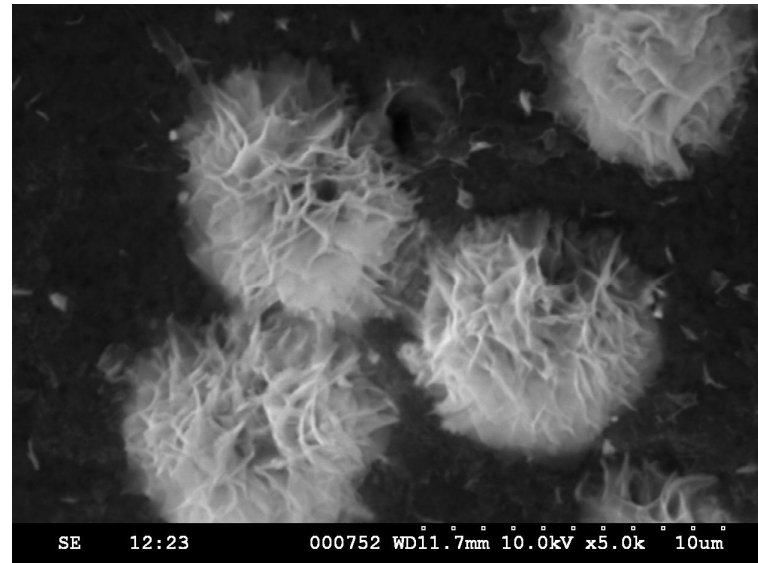
Impact of Secondary Phases



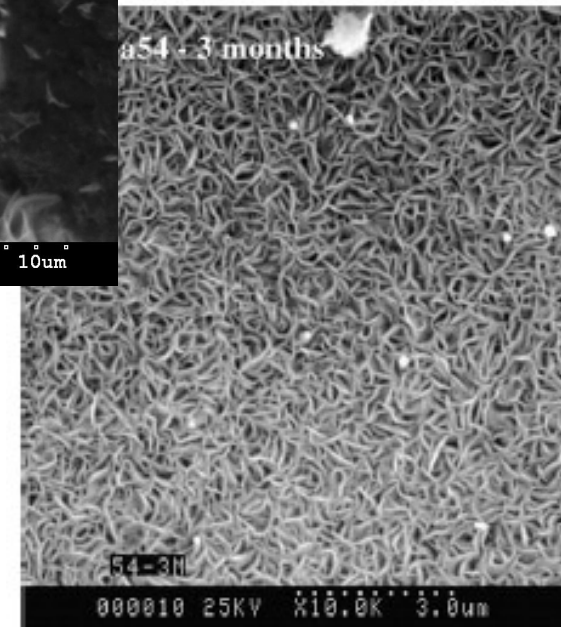
Phyllosilicate-like

- ▶ Most common precipitates observed in glass corrosion
- ▶ Mainly amorphous; more crystalline at long times
- ▶ Uniform surface coverage
- ▶ Usually surface, few inside gel
- ▶ Observed at long Stage II AND during Stage III
- ▶ Mostly precipitates – less evidence for gel transition

Fortner et al., 2012, FCRD-SWF-2012-000266



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

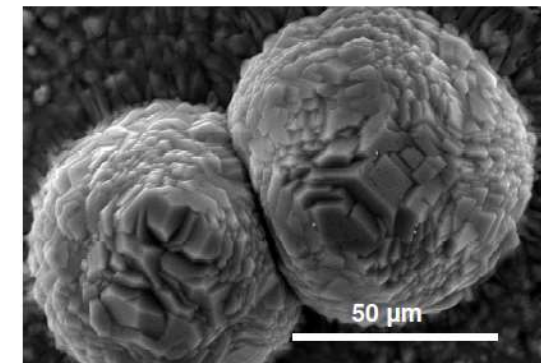
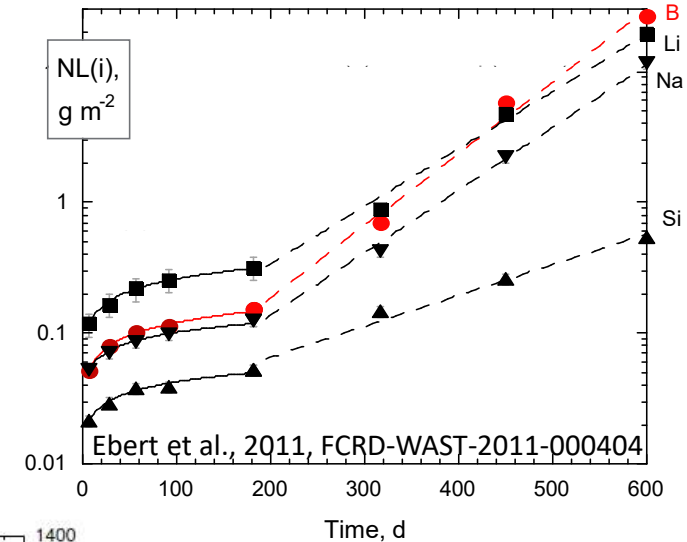
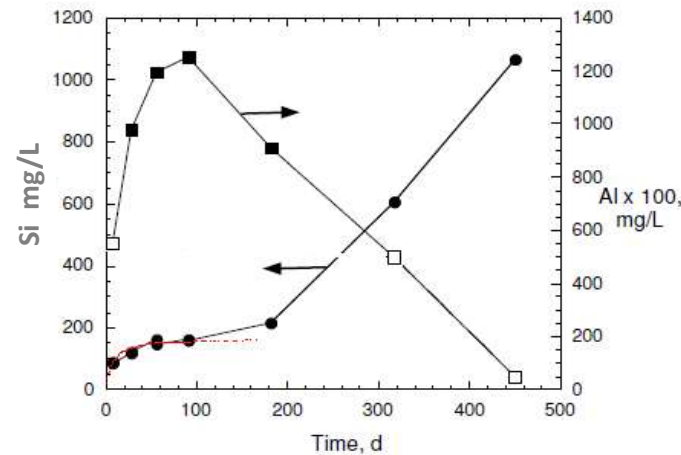
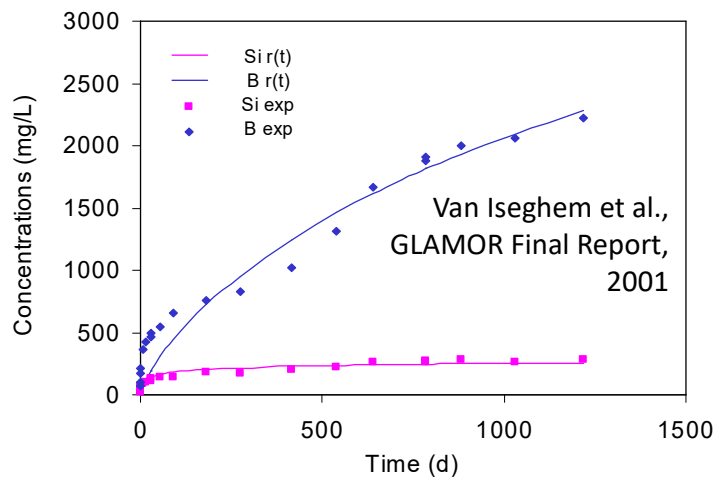


While this type of precipitation may influence residual rate, has low impact on performance

Stage III Secondary Phases

Zeolite-like

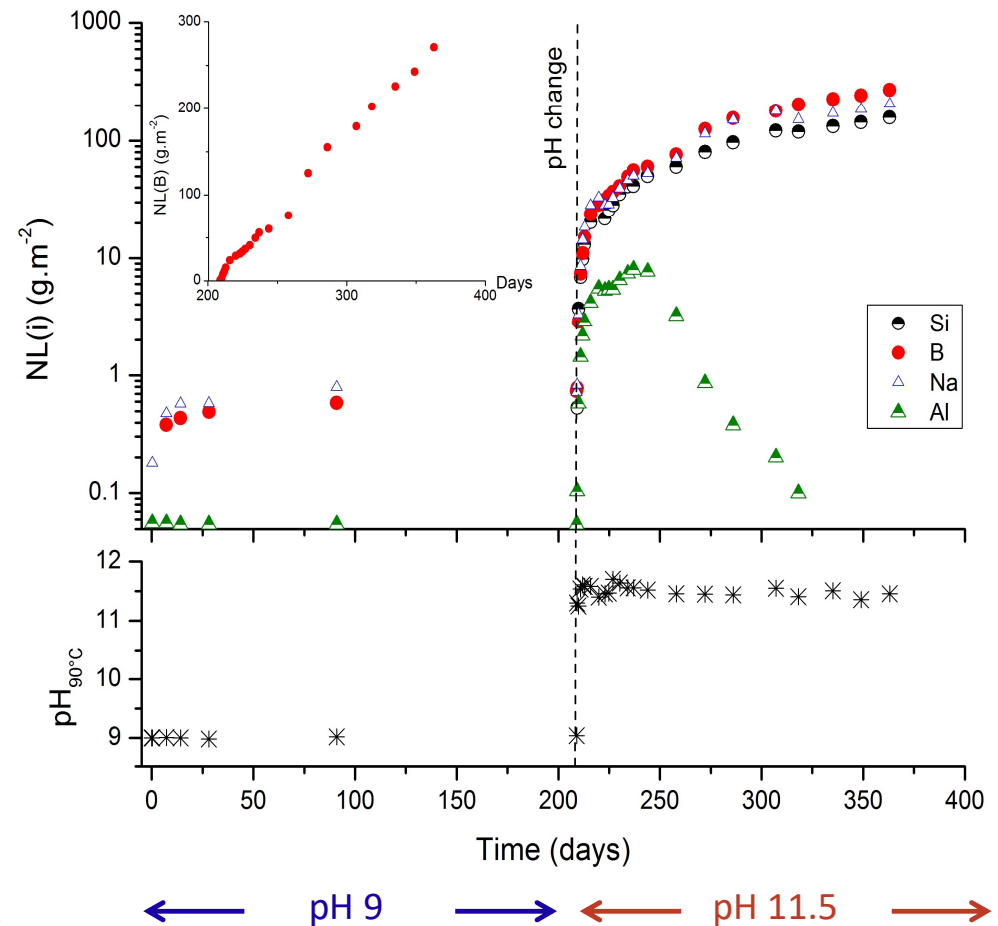
- ▶ Also can happen with Fe- or Mg-silicate formation
- ▶ Often correlated with the consumption of solution alumina, but an increase in silica in solution
- ▶ Acceleration of alteration can be permanent (until complete dissolution) or the system can return to a residual rate
- ▶ This “pulsing” can happen many times



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

Stage III Observations

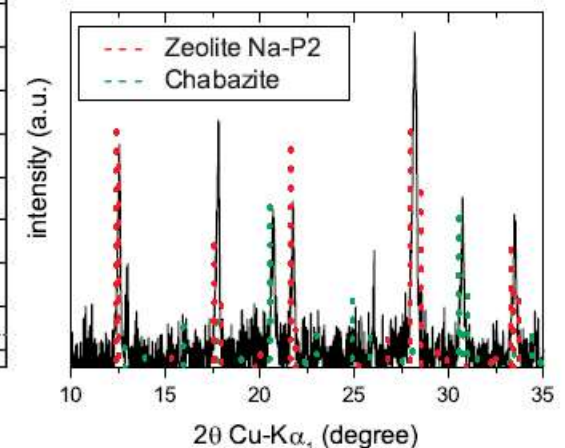
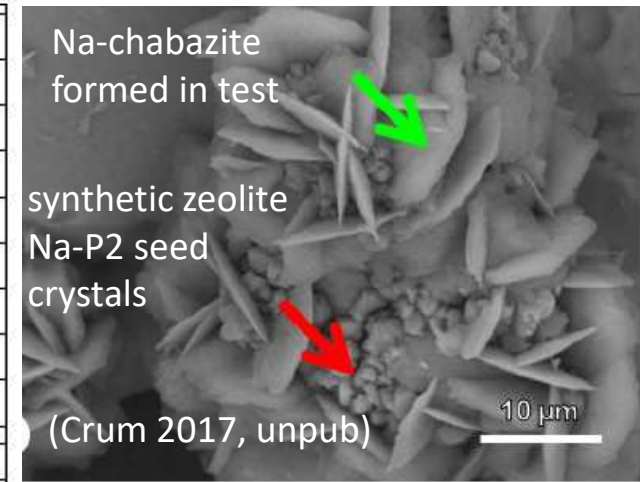
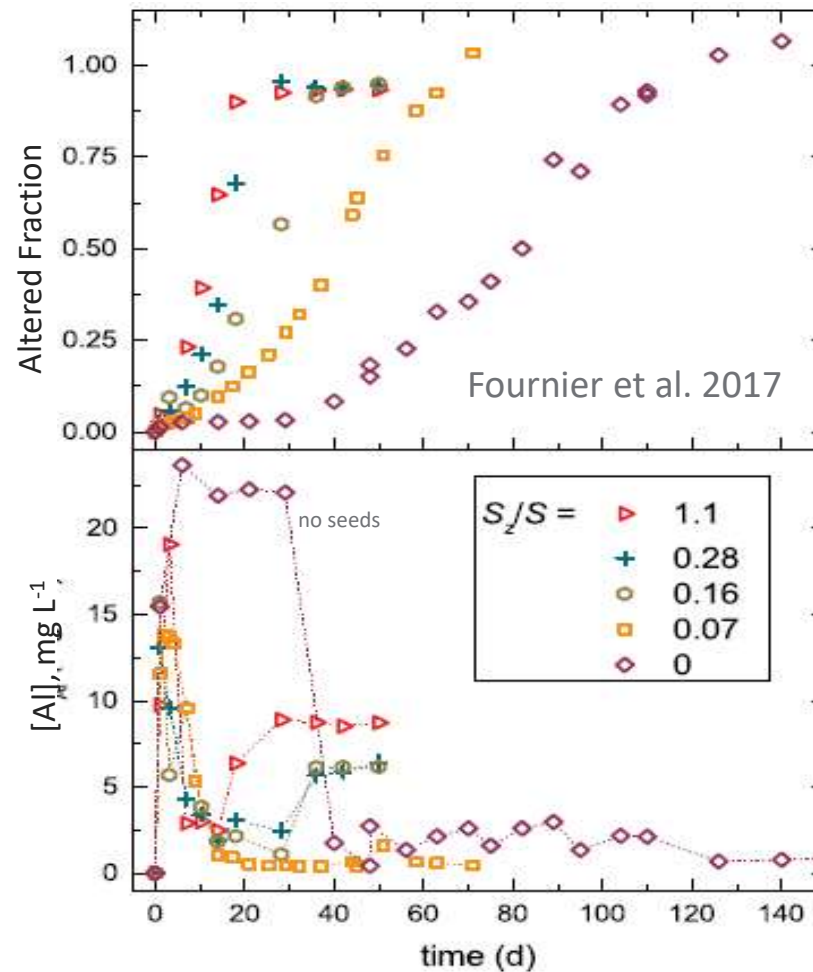
- ▶ Increasing pH of ISG glass corroding in static conditions initiates Stage III
- ▶ Stage III is often associated with higher pH conditions, but not always
- ▶ Si, B, Na concentrations increase while Al concentration decreases
 - In unperturbed static tests, $[Al] \downarrow$ usually precedes rate acceleration
- ▶ Generally, linear rate



Gin et al. 2015

Stage III – Artificial initiation

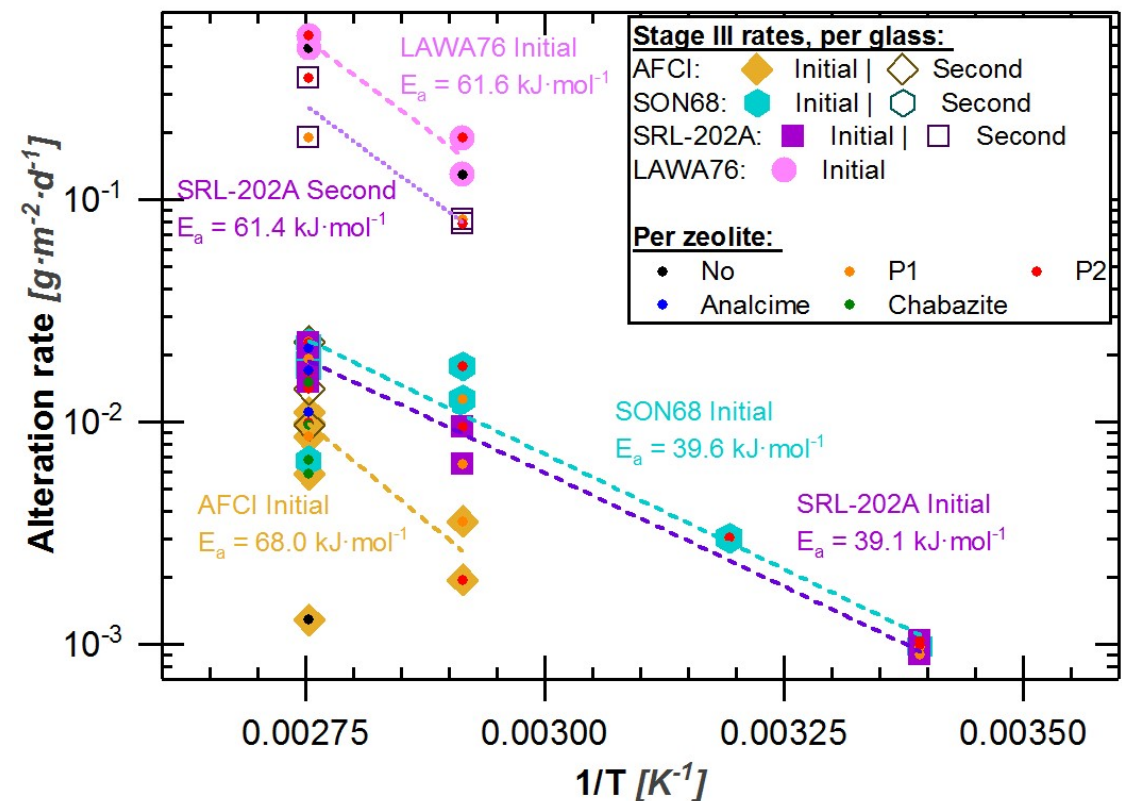
- ▶ Stage III can be induced (or initiated earlier) by seeding with certain zeolites
- ▶ Na-P1 and Na-P2, but not Analcime and Clinoptilolite



Temperature effect on Stage III alteration

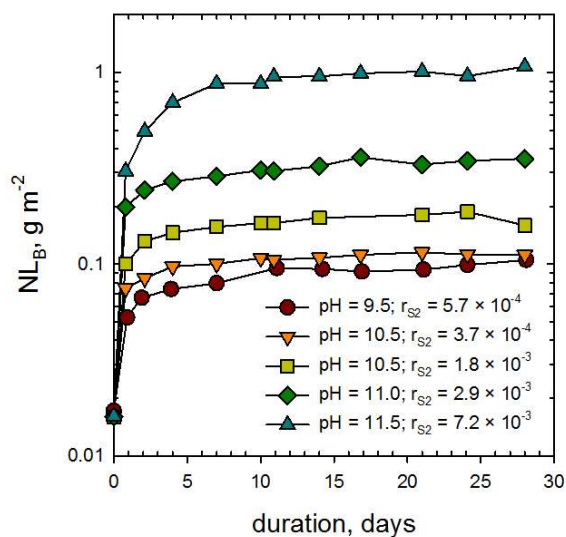
- ▶ All glasses show an alteration rate acceleration upon zeolite addition at tested conditions (21°C to 90°C)
- ▶ Two different activation energies:
 - When rate is sustained, $E_a > 60$ kJ/mol
 - When the rate slows down, $E_a \approx 40$ kJ/mol
- ▶ Two different processes?

Parruzot et al. (2019) Journal of Nuclear Materials 523, 490-512



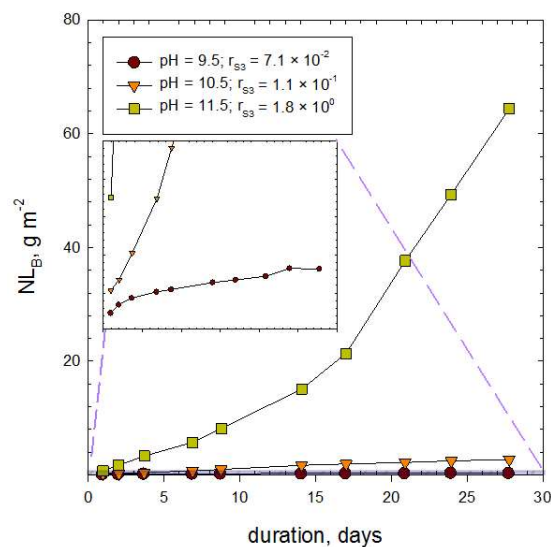
Results from solution data

No zeolite addition



No Stage III behavior

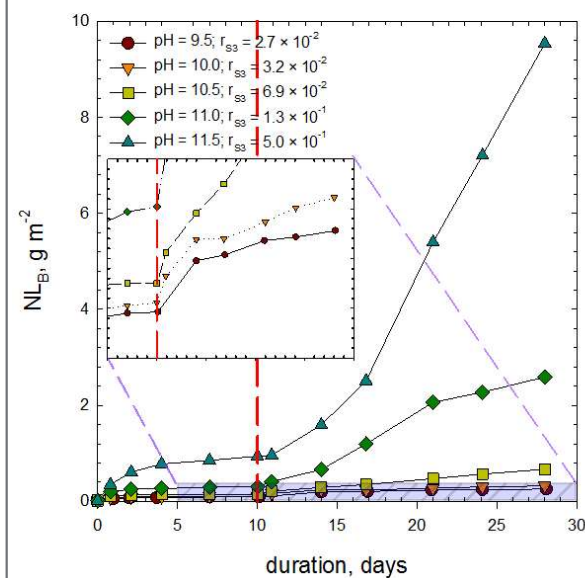
Zeolite added at $t = 0$ days



Sustained Stage III (pH ≥ 10.5)

Alteration rate is slowing down (pH 9.5)

Zeolite added at $t = 10$ days



Sustained Stage III (pH ≥ 10.5)

Acceleration/slow down (pH ≤ 10.0)

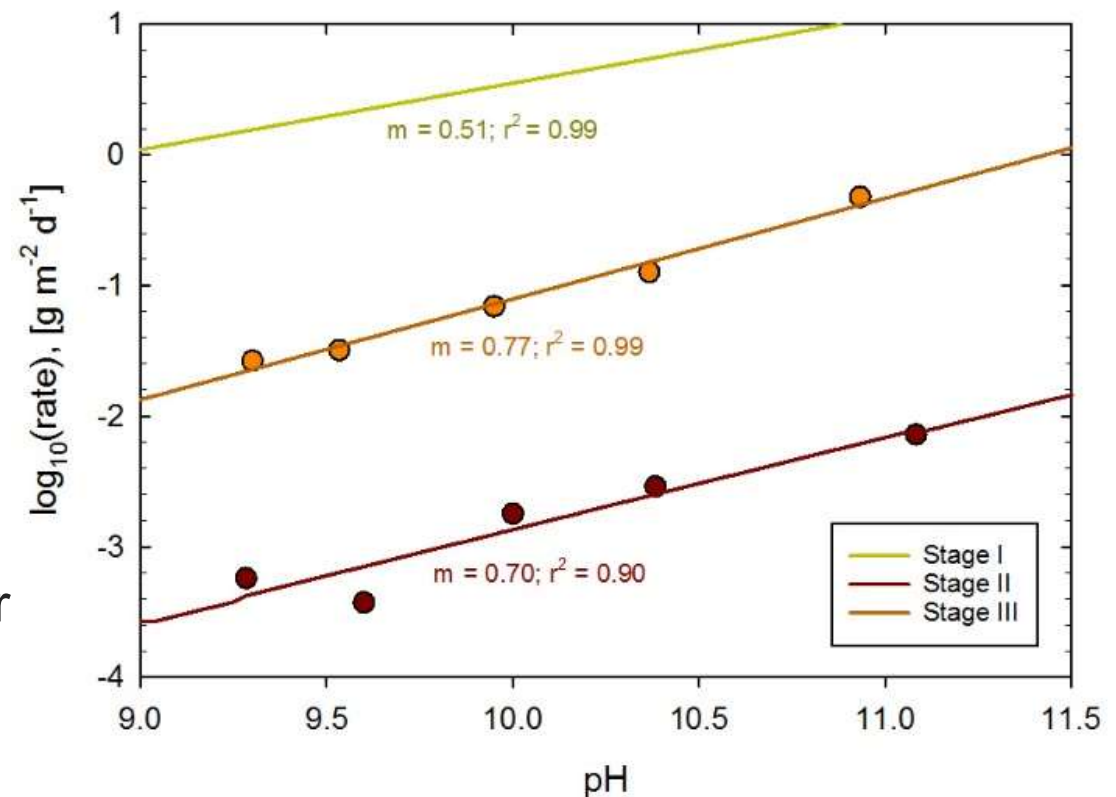
pH effect on Stage III Alteration

Stage I rates: Neeway et al. (2018) Geochim. Cosmochim. Acta 226 132-148
Others: Parruzot et al. (2019) Journal of Nuclear Materials 523, 490-512

- ▶ Stage I (forward) rates from Neeway et al.
- ▶ Stage II and Stage III from Parruzot et al.

$$r_{\text{Stage I}} > r_{\text{Stage III}} > r_{\text{Stage II}}$$

- ▶ Composition of the alteration layer and solution impact Stage III behavior





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Mathematical Corrosion Models

General Modeling Approach

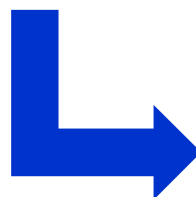
- Contaminant transport is modeled using the reaction-advection-dispersion equation:

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} - v_x \frac{dC}{dx} - \frac{\rho_b}{\theta} \left(\frac{dC_s}{dt} \right)_{\text{sorption}} + \sum_{k=1}^{N_s} \left(\frac{dC}{dt} \right)_{\text{reaction } k}$$

- Solution mass balance equation (SMBE) of species i

$$\frac{dC_i^{\text{sol}}}{dt} = \underbrace{\frac{S}{V} J_i^{\text{gls}} \Big|_{x=0}}_{\text{FLUX OUT OF GLASS}} - \underbrace{\frac{F_v}{V} (C_i^{\text{sol}} - C_i^{\text{eff}})}_{\text{FLOW IN/OUT OF SOLUTION}} - \underbrace{\frac{dC_i^{\text{min}}}{dt}}_{\text{MINERAL FORMATION}}$$

Mechanistic
Models

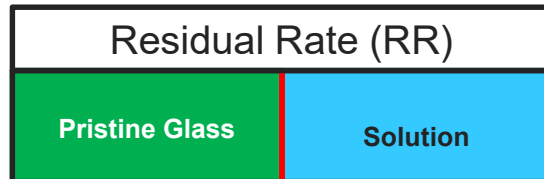


- ☐ Aagaard-Helgeson
- ☐ Residual rate
- ☐ Grambow-Müller
- ☐ GRAAL
- ☐ ILAW PA

↓
SiO₂(am)
Al(OH)₃
Etc.

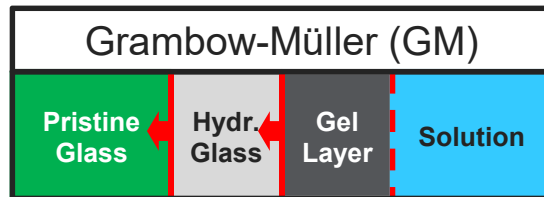
C	concentration
D	dispersion coef
v	advective flow
C _s	sorbed concentration
N _s	number of sinks/sources
ρ	density of EBS
θ	porosity of EBS
t	time
S	surface area
V	volume
x	depth in glass
F _v	flow
sol	solution
gls	glass
eff	effluent
min	mineral

Predictive Models



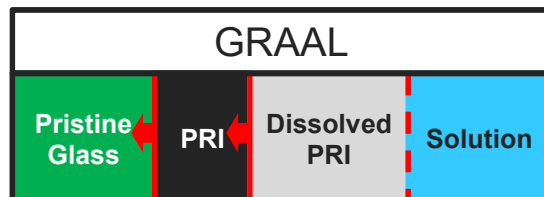
$$r_{\text{net}} = k \exp\left(-\frac{E_a}{RT}\right) a_{\text{H}^+}^{-\eta} \left[1 - \left(\frac{Q}{K}\right)^{1/\sigma}\right] + r_{\text{res}}$$

Pierce et al. 2004



$$\frac{dC}{dt} = D_{\text{H}_2\text{O}} \frac{d^2C}{dx^2} - r_{\text{matrix}}(t) \frac{dC}{dx}$$

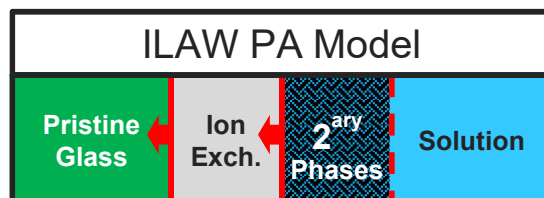
Grambow and Muller 2001



$$\frac{dE}{dt} = r_{\text{diss}} \left(1 - \frac{C_{\text{Si}}(t)}{C_{\text{sat}}}\right) \quad \frac{de}{dt} = \frac{r_{\text{hydr}}}{1 + \frac{e(t)r_{\text{hydr}}}{D_{\text{PRI}}}} - \frac{dE}{dt}$$

Frugier et al. 2008, 2016

+ Secondary Phases



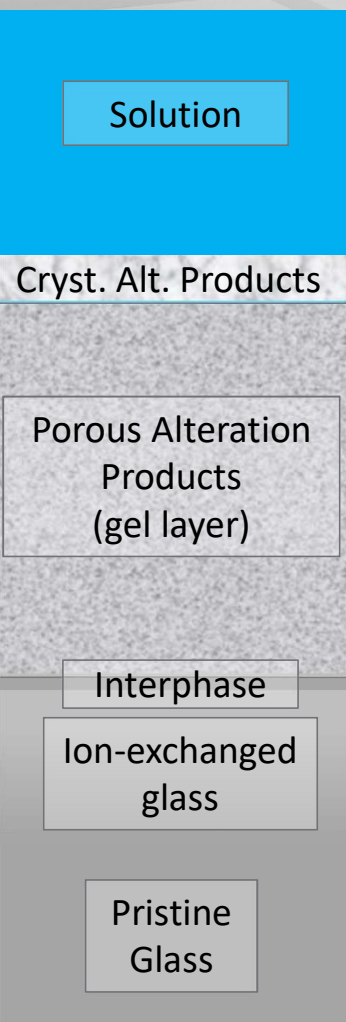
$$r_i = k_0 a_{\text{H}}^{-\eta} \exp\left(\frac{-E_a}{RT}\right) \left[1 - \frac{q}{K_g}\right]$$

Ryan & Freedman 2015
PNNL-23503, Rev. 1

$$r_{\text{Na}} = A_o \frac{\exp\left(-\frac{E_a}{RT}\right)}{t^p} \quad \text{+ Secondary Phases}$$

Rieke and Kerisit 2015

Model discrepancies have led to targeted research



Reaction affinity models:

- ▶ Corrosion proceeds even with high solution silica
- ▶ Corrosion slows at high pH, when silica is extremely soluble
- ▶ A thermodynamically metastable amorphous silicate is being created RIGHT ON TOP of the glass
- ▶ Simple geochemical sinks do not fully account for a constant "residual rate"

Transport limiting models

- ▶ The diffusing species is not defined (H⁺ and water both extremely unlikely)
- ▶ The medium limiting diffusion is poorly known (no correlation with gel thickness)
- ▶ Gel formation is tricky to account for (either mathematical or geochemical)

Dissolution / Reprecipitation models

- ▶ Predicted "gap" at interface does not agree with mechanically stable gel in most conditions
- ▶ Gel formation not solely from reprecipitation
- ▶ Most of the above models do it this way anyway out of necessity

Models are needed that recreate ALL the observed structures and behaviors

How to link mechanistic models to PA models

- ▶ Existing models are necessarily simple
- ▶ Any new corrosion model will also have to be sufficiently simple to enable large-scale simulations using a more complex performance assessment model
- ▶ However, its formulation has to be grounded in detailed, validated mechanistic models.

This is the state of the art.

**Better mechanistic understanding informing
intelligently-simplified models are needed**

