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Experimental & analytical techniques to investigate glass corrosion

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U.S. DEPARTMENT OF ENERGY BATTELLE
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Joint ICTP-IAEA International School on Nuclear Waste Vitrification
Trieste, Italy

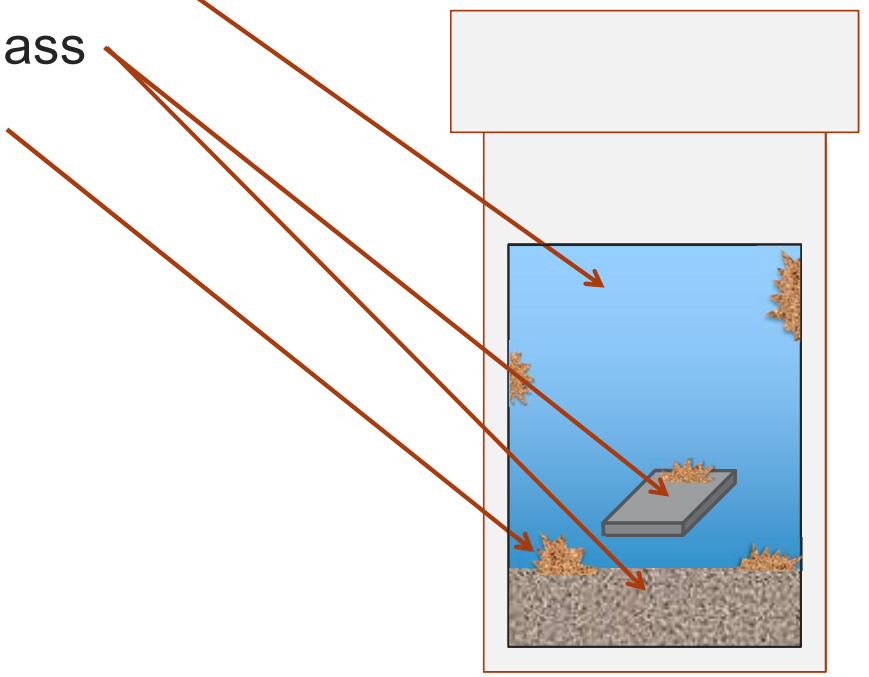
September 25th, 2019

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

- Dissolution
- Molecular diffusion
- Ion exchange reaction
- Interdiffusion
- Formation of altered material
- Reactive transport
- Diffusive transport through altered layers
- Secondary phase formation
- Environmental interaction

What can we monitor?

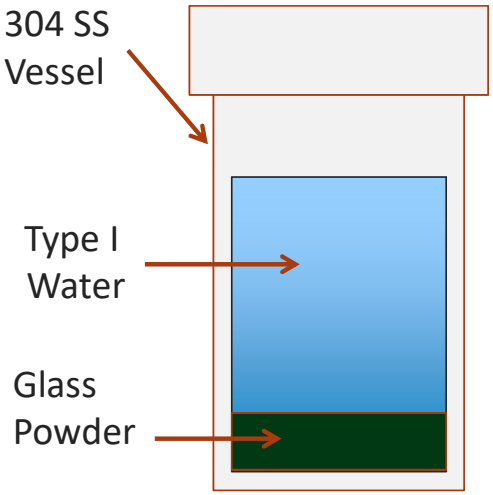
- What happens to the solution
- What happens to the glass
- What happens nearby

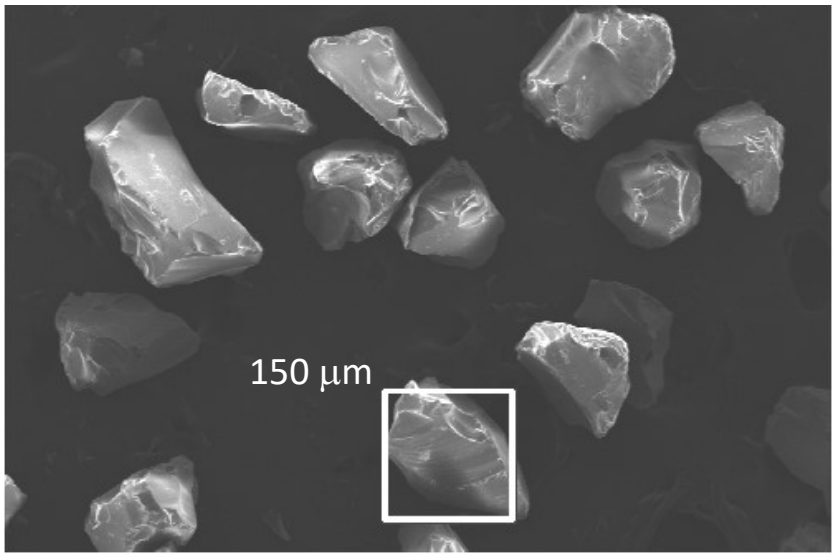


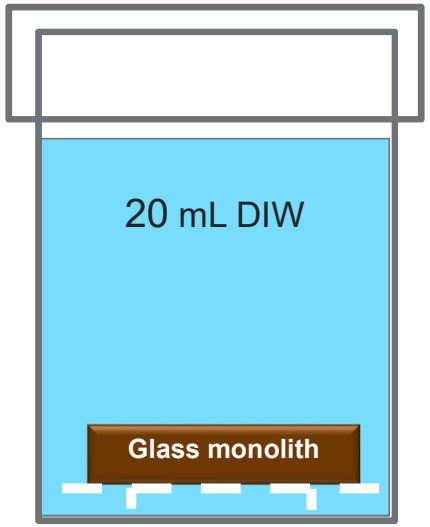
Standardized Static Tests

- **Product Consistency Test (PCT)** (ASTM C1285)
  - Ground glass soaked in DIW at temperature
  - Glass component concentrations measured in solution after test
  - Typical (Method A): 7-d, 90°C, 1:10 g_{glass}:mL, DIW, 2000 m^{-1}, 100 to 200 mesh sieves (49 to 150 µm)

- **Materials Characterization Center Test 1 (MCC1)** (ASTM C1220)
  - Static conditions
  - 28-d, 90°C, DIW, 10 m^{-1}

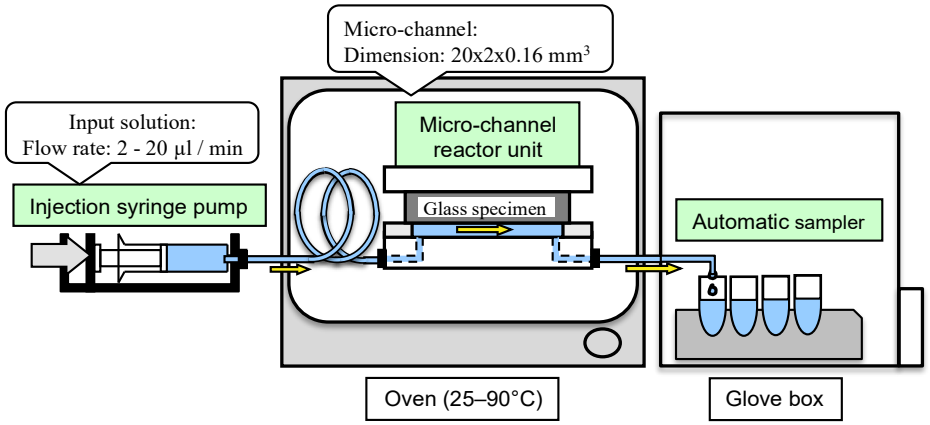






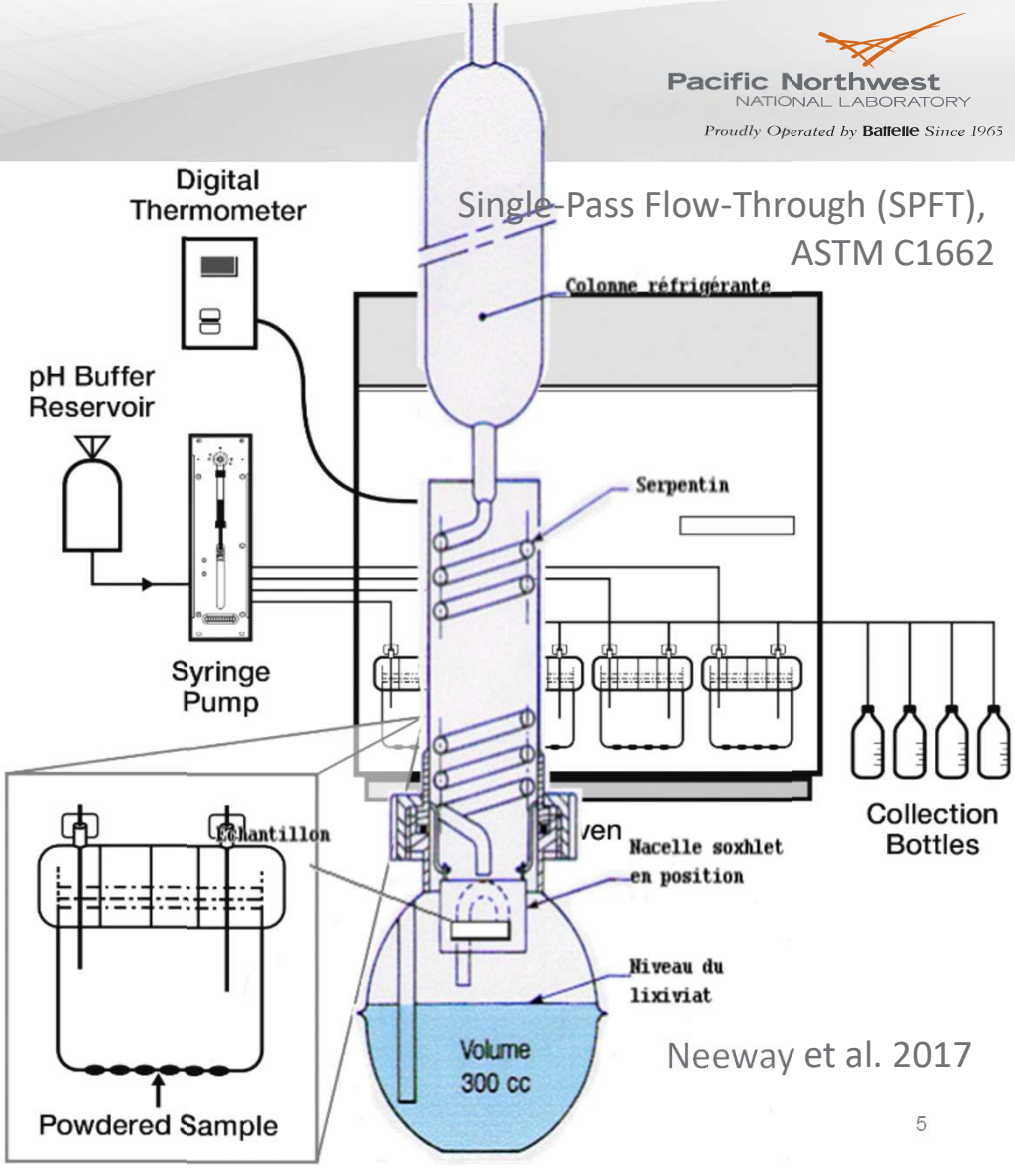
Flow-through tests

- Dilute and/or flow-through test 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)



Microchannel Flow-through (MCFT)
Y. Inagaki (2014) Procedia Materials Science, 7, pp 172-178

Single-Pass Flow-Through (SPFT), ASTM C1662

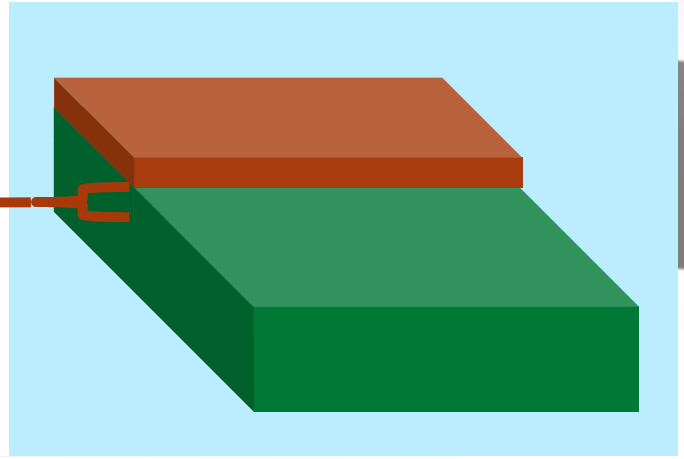


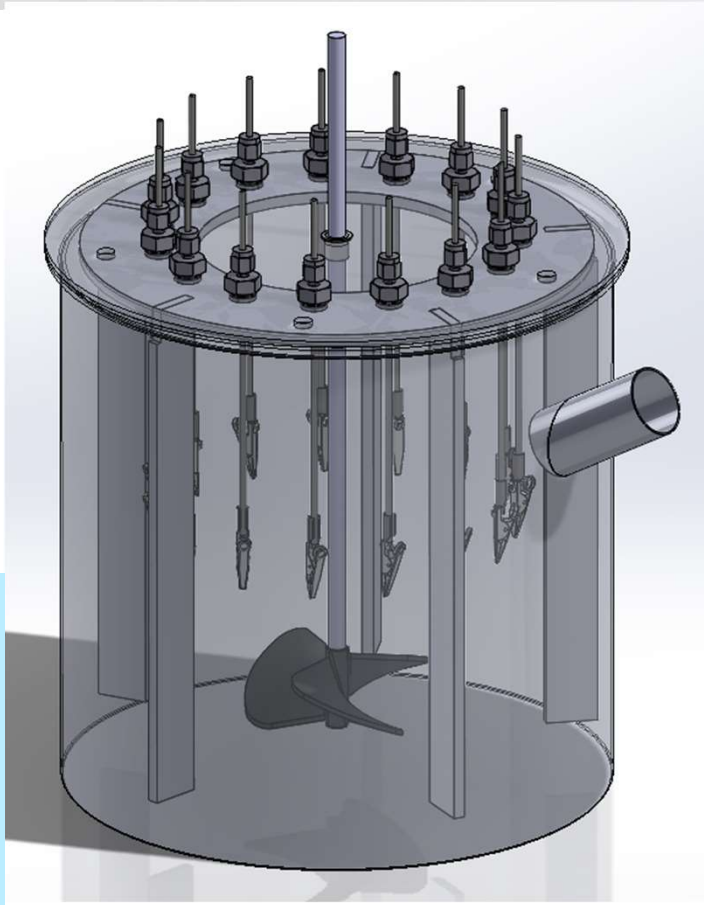
Neeway et al. 2017

Stirred Reactor Coupon Analysis (SRCA)

- Dissolution rate measured as a difference between masked and unmasked areas of a glass coupon
- Coupons of multiple glasses in a single reactor and a measured step height to determine rates
- Solution agitation ensures turbulent flow
- Minimizes testing program (more data, quicker)
- Allows composition–parameter correlation modeling

$$\text{rate} = \frac{\Delta \text{ height} \times \text{density}}{\Delta \text{ time}}$$





Column and real-scale tests

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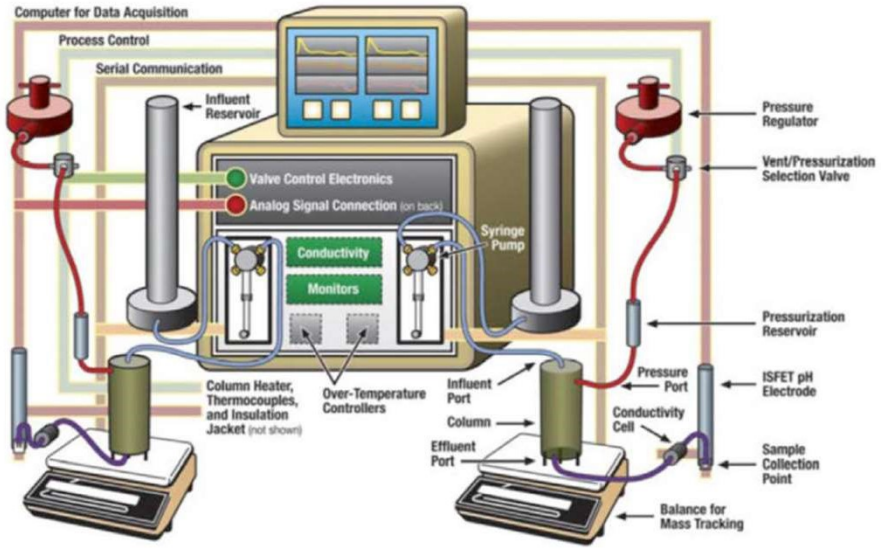
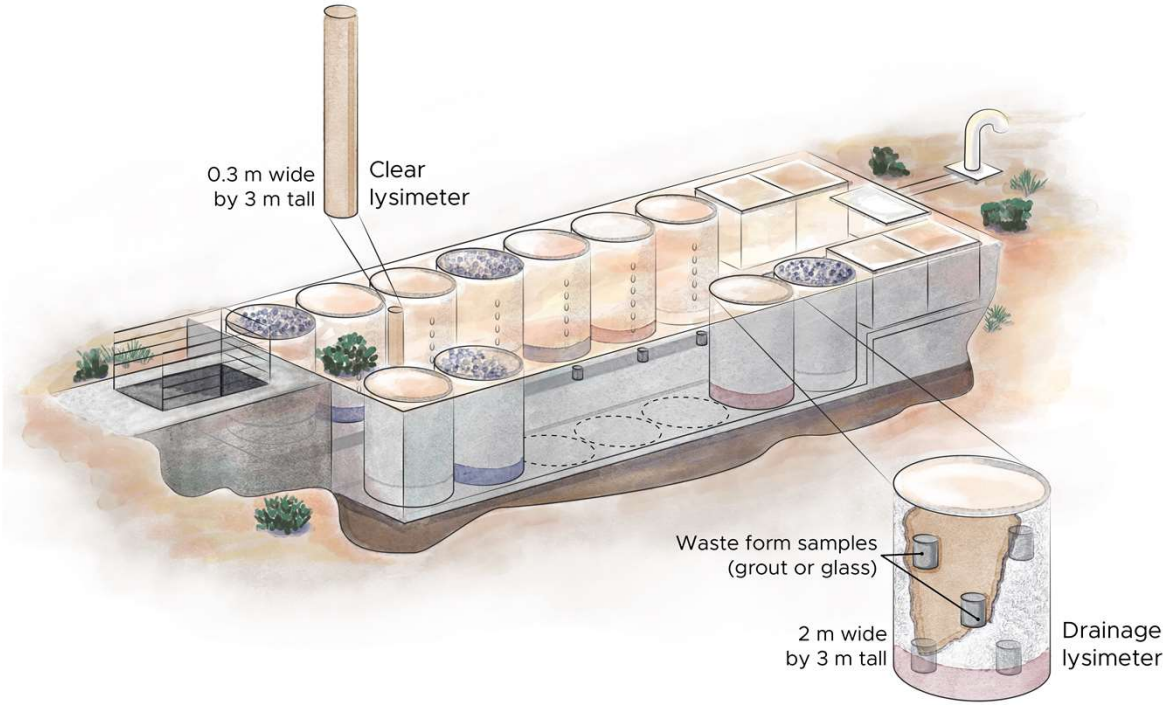
Pressurized Unsaturated Flow

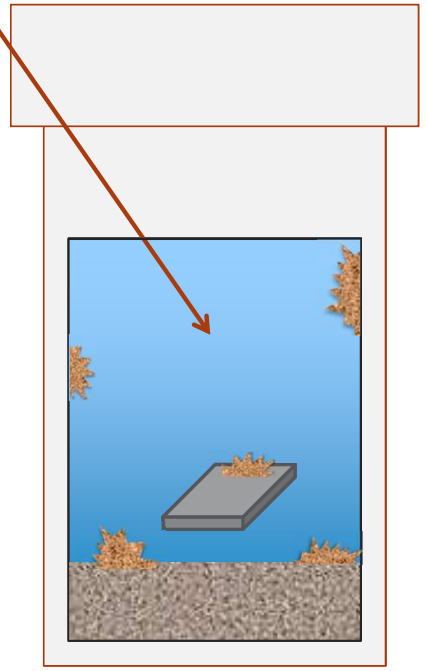


Field Lysimeter



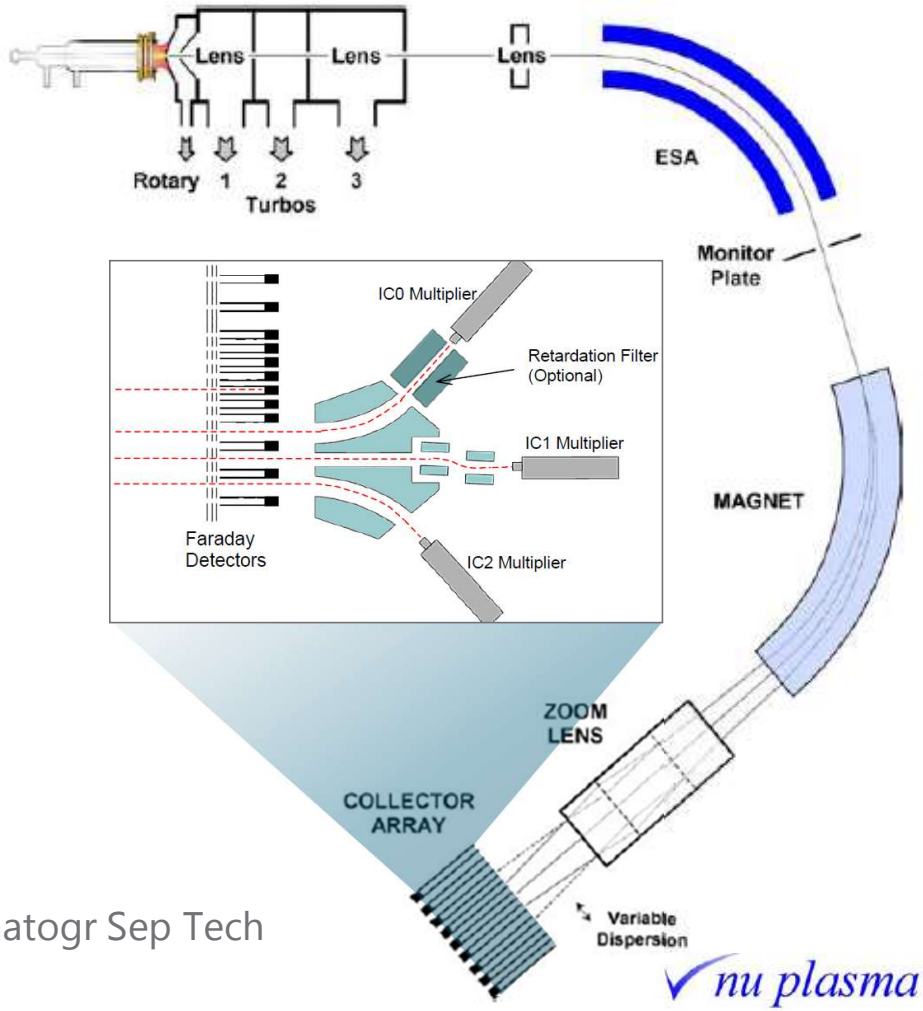
What can we monitor?
Solution analyses

- **Solution Composition**
  - ICP – OES/AES
  - ICP – MS
  - Multi-collector – MS
- **Solution Reactivity**
  - pH
  - Redox (Eh)
- **NMR**
- **Optical Spectroscopy**
  - **Raman**
  - UV-Vis



ICP-Mass Spectroscopy

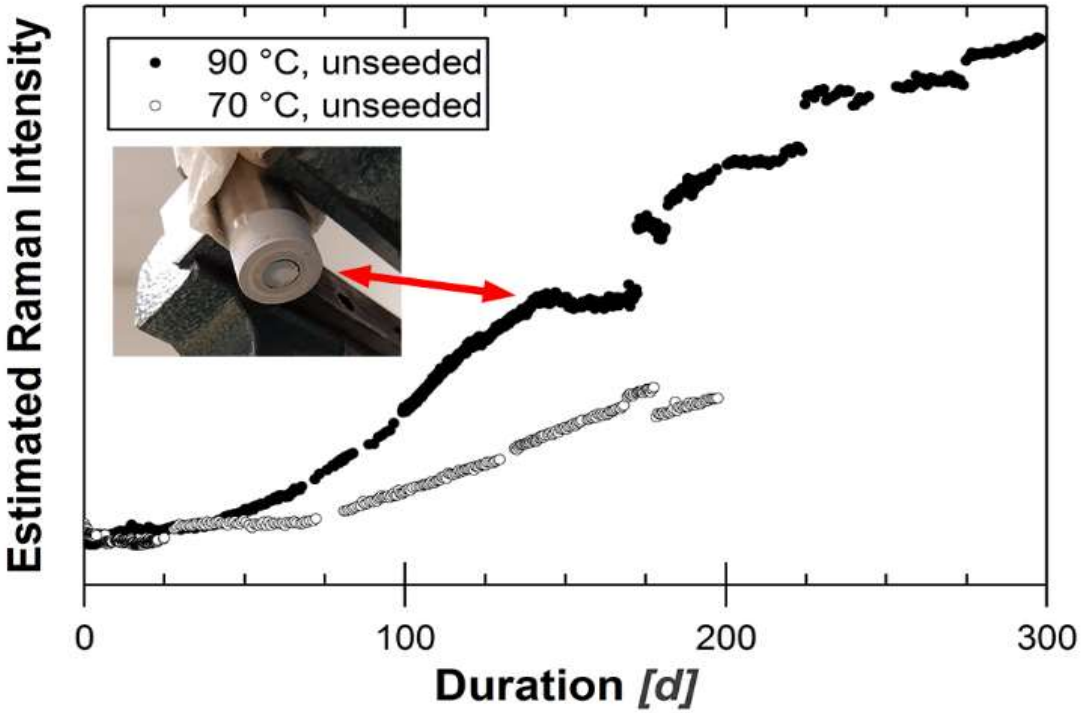
- The Challenge:
  - Multi-component glass
  - Mass range from ^{6}Li to ^{160}Gd
  - Isotopic resolution required
  - Concentrations run from mg/L (Si) to ng/L (traces)
  - Problematic interferences, for example:
    - ^{28}Si-H vs. ^{29}Si
    - ^{40}Ca vs. ^{40}Ar

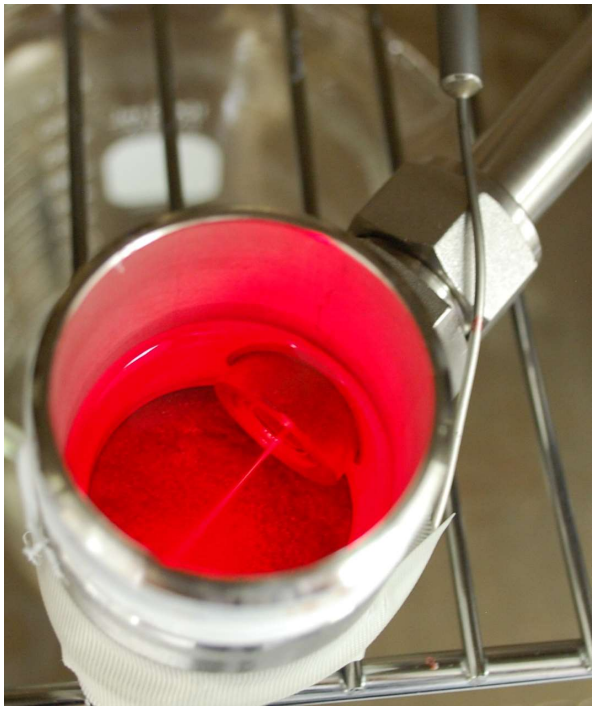


Mitroshkov et al., J Chromatogr Sep Tech 2016, 7:2

In-situ solution monitoring

- Raman spectroscopy can be used to take real-time measurements of pH and B concentration
- Monitoring can be used to evaluate sudden changes in corrosion behavior such as Stage III without perturbing experiment





Parruzot et al, (2018) Analytical Chem, **90**(20):11812-11819
George, J.L. and R.K. Brow (2015) JNCS, **426**: p. 116-124.

What can we monitor?
Glass analyses

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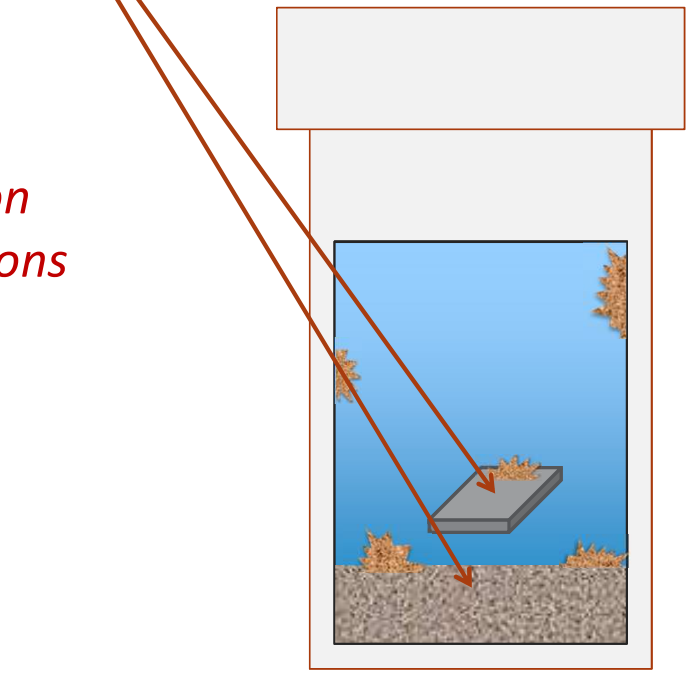
- **Microscopy**
  - Optical, SEM, TEM

Uses:
Multiscale analyses
Combination with other techniques
Highly available

Limitations:
Sample preparation
Geometric limitations
Vacuum



- **Profilometry**
  - Optical, stylus, AFM, cross-section
  - Ellipsometry

What can we monitor?
Glass analyses

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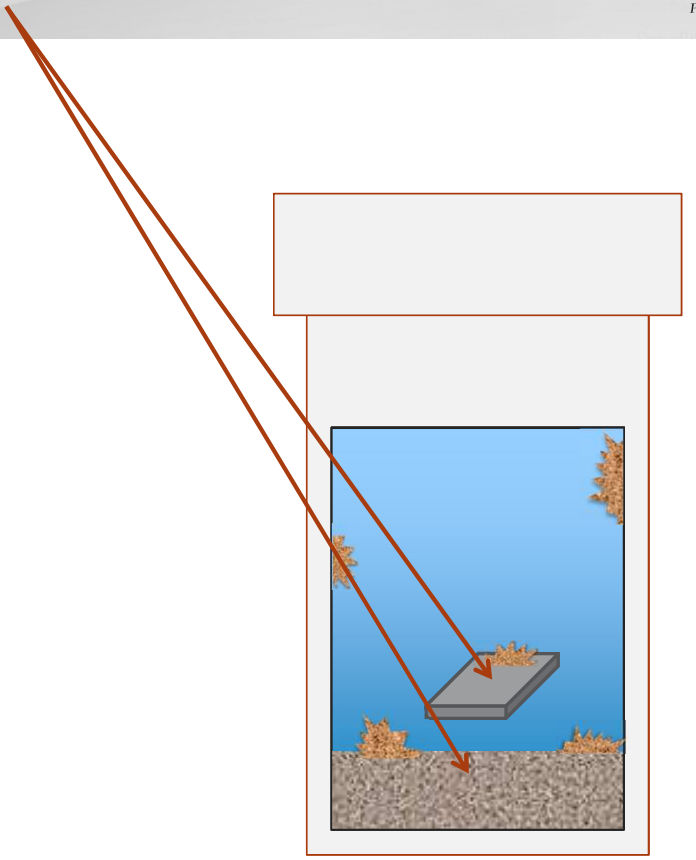
- **Composition**
  - Digestion
  - XRF
  - **SIMS**
  - **APT**
- **Chemical Structure**
  - **NMR**
  - EELS
  - **Raman**
  - XAS



Cutting edge:
Raman analysis of solution AND solids

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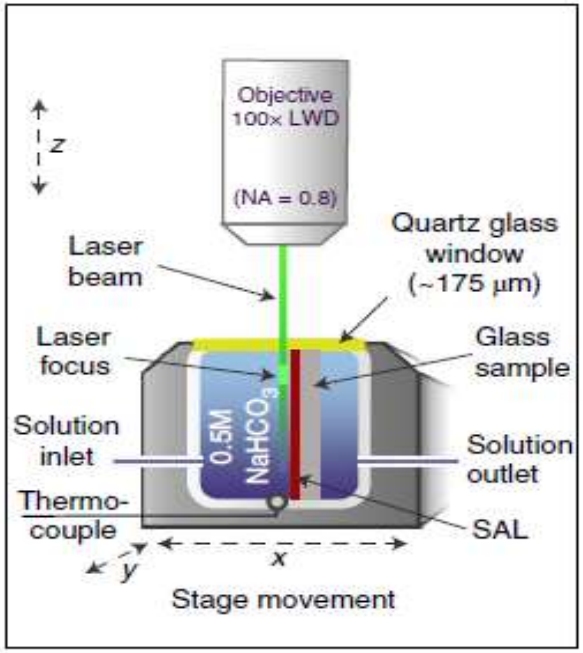
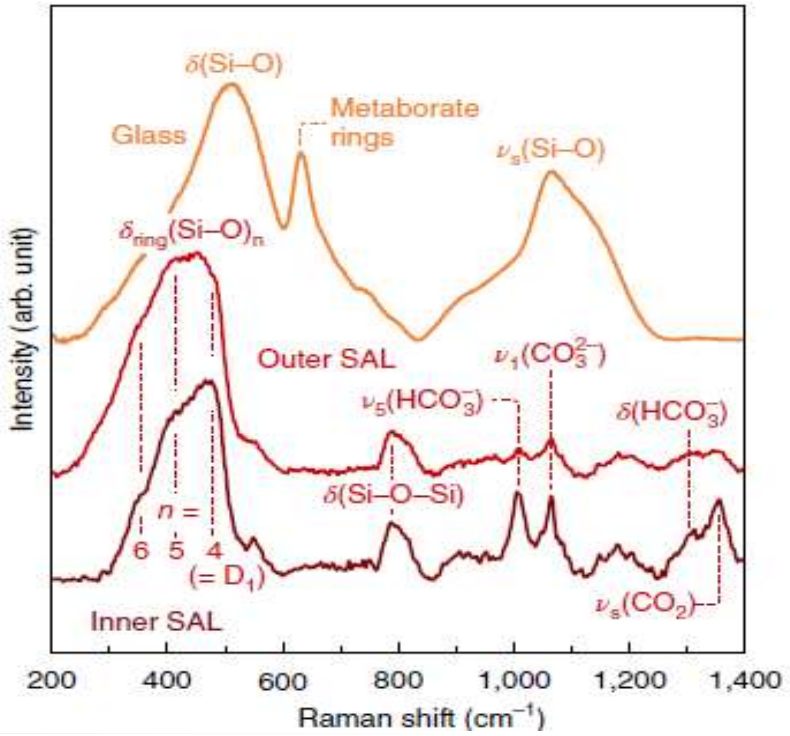
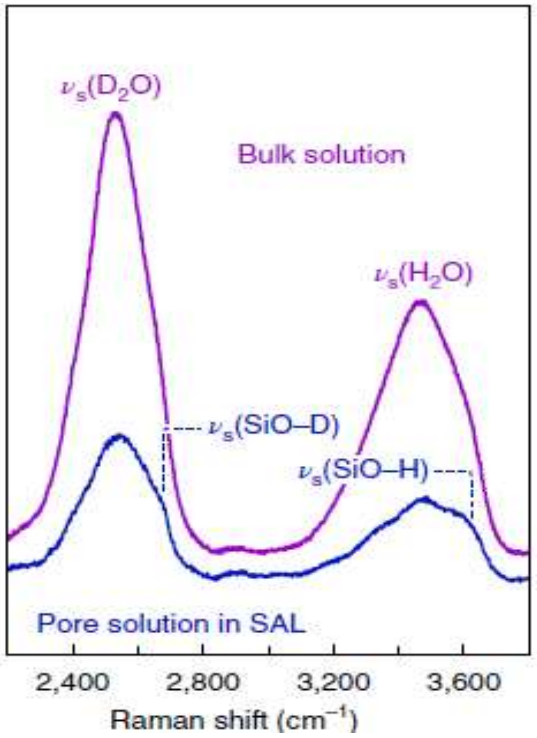
- A special cell has been developed by a group in Germany where confocal Raman can be scanned across both the solid and liquid
- Shows changes in speciation & pH within porous area – the chemistry is **different**







Geisler et al. (2019) NatMat, **18**, 342–348

Nuclear Magnetic Resonance (NMR) can be used with position-sensitive techniques

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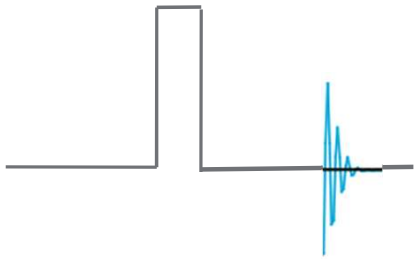
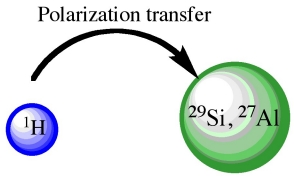
Bulk Environments:

Bloch Decay Magic Angle Spinning (MAS)



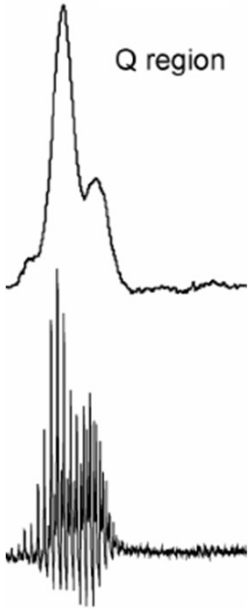
Surface-sensitive:

Cross-polarization (CP) MAS



Surface-sensitive with Increased Signal:

CP-Carr-Purcell-Meiboom-Gill (CPMG) MAS



Hartmann, S. R.; Hahn, E. L., *Phys. Rev.* **1962,** *128* (5), 2042.

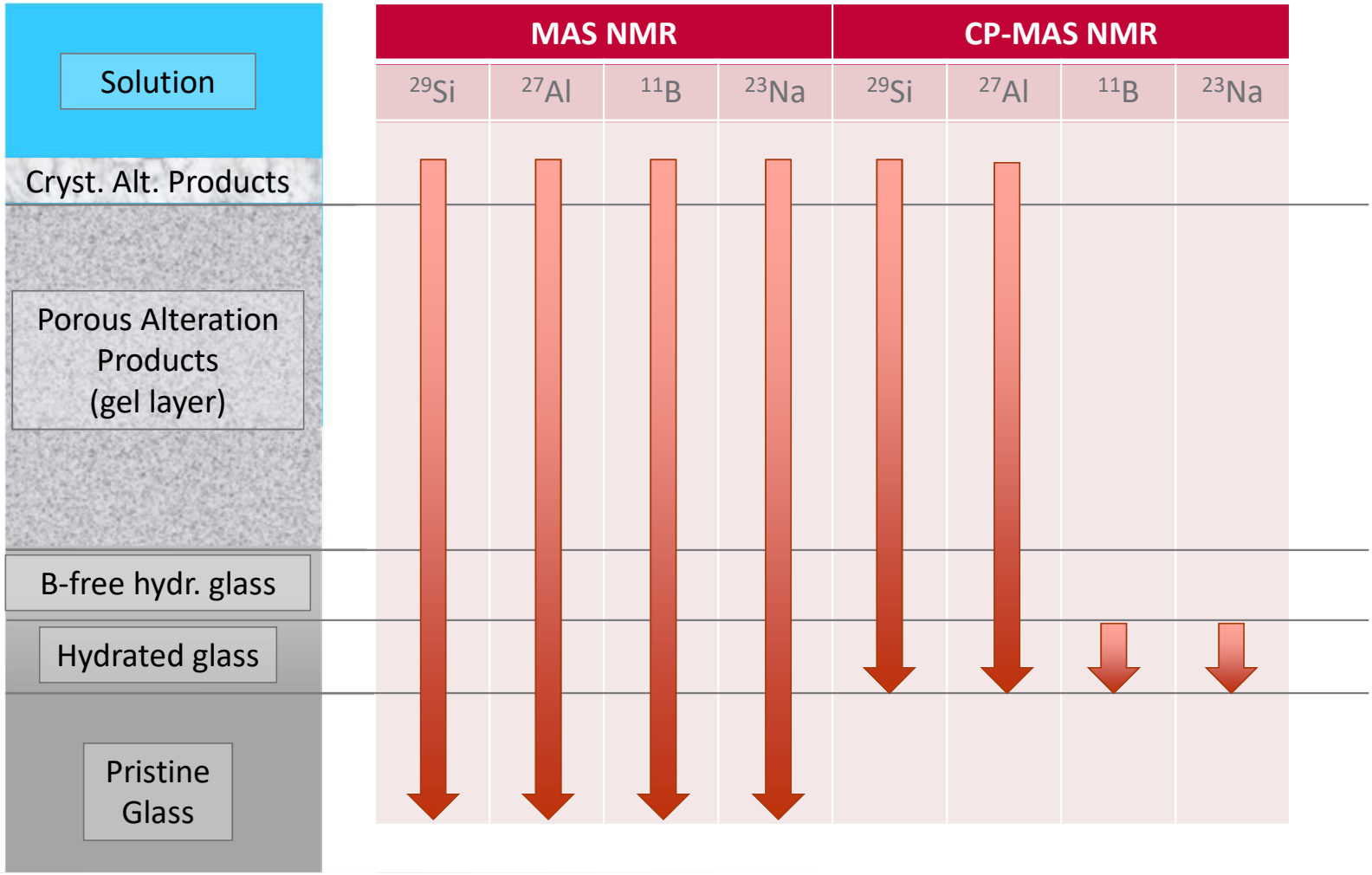
Pines, A., *J. Chem. Phys.* **1973,** *59* (2), 569-590.

Carr, H.Y.; Purcell, E.M., *Phys. Rev.* **1954**, *94*, 630-638.

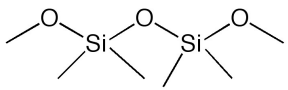
Meiboom, S.; Gill, D., *Rev. Sci. Instrum*. **1958**, *29*, 688-691.

Levitt, M. H., *Spin Dynamics: Basics of Nuclear Magnetic Resonance*. **2001.** John Wiley & Sons.

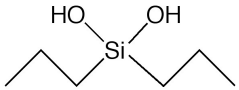
Position-sensitive NMR Techniques



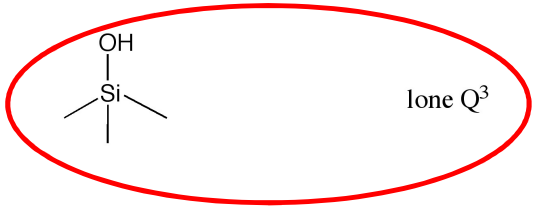
NMR can also be used to evaluate reactive surface area



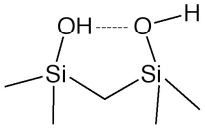
siloxane Q^4



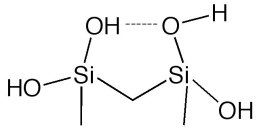
geminal Q^2



lone Q^3

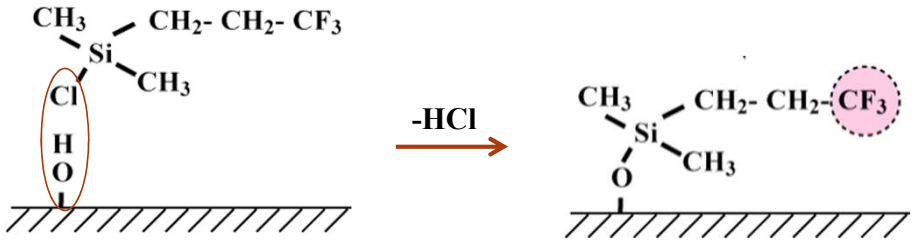


Vicinal Q^3



H-bonded geminal Q^2

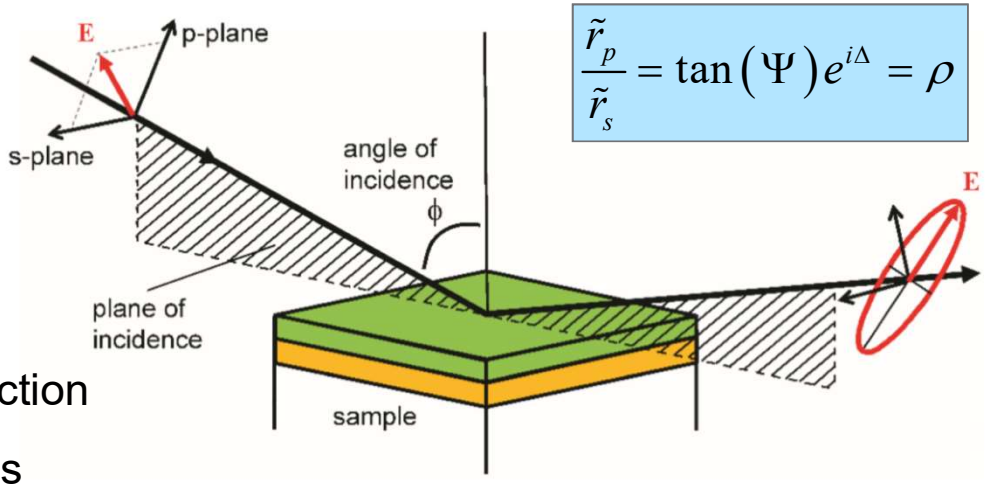
R. Fry, N. Tsomaia, C. Pantano, and K. T. Mueller, *J. Am. Chem. Soc.* **125**, 2378 (2003).



Sample	SON68 PSU (OH/nm^2)
Non-leached	0.16 ± 0.05
2 week	0.24 ± 0.05
1 month	0.3 ± 0.2*
2 months	0.45 ± 0.08
3 months	0.41 ± 0.04
4 months	0.4 ± 0.1*
5 months	0.38 ± 0.05

Spectroscopic Ellipsometry

- **Spectroscopic ellipsometry measures the polarization change as light interacts with a sample**



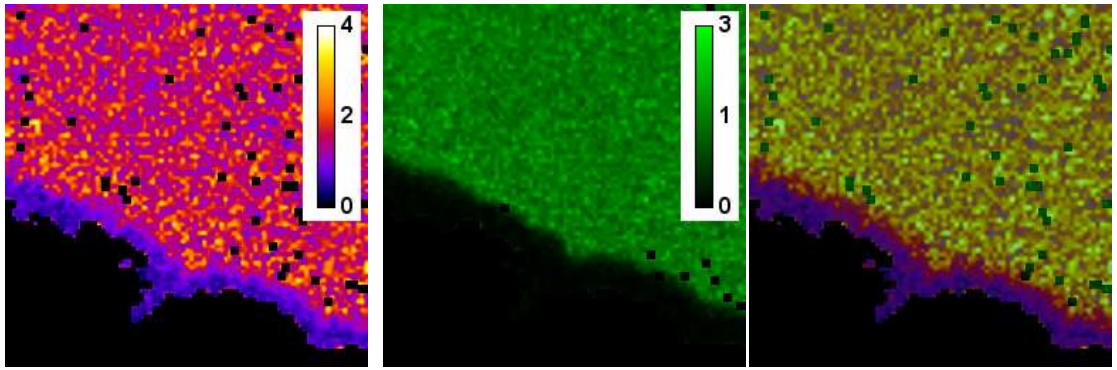
$$\frac{\tilde{r}_p}{\tilde{r}_s} = \tan(\Psi)e^{i\Delta} = \rho$$

- Measure r_p/r_s : ratio of change in polarization of reflected light
- **Del (Δ)** is the phase difference induced by the reflection
- **tan(Psi (Ψ))** is the ratio of the amplitude diminutions

- **For a thin film on a smooth substrate, ellipsometry can provide:**
  - Film/layer thickness
  - Index of refraction (*n*)
  - Extinction coefficient (*k*)
  - **Relative porosity** (given relatively well known parameters)
- **Caveats:**
  - Thickness, *n*, and *k* are **3 variables**, …but ellipsometry only **measures 2 quantities** (Ψ and Δ)
  - **Modeling** is required to determine properties from ellipsometric Ψ and Δ data

Secondary Ion Mass Spectroscopy (SIMS)

- Effectively ion-induced “sandblasting” of the surface
- Destructive technique, measuring what ions were just removed from the sample surface



$^{29}Si/^{28}Si$ Normalized $^{10}B^{16}O_2$ Overlay

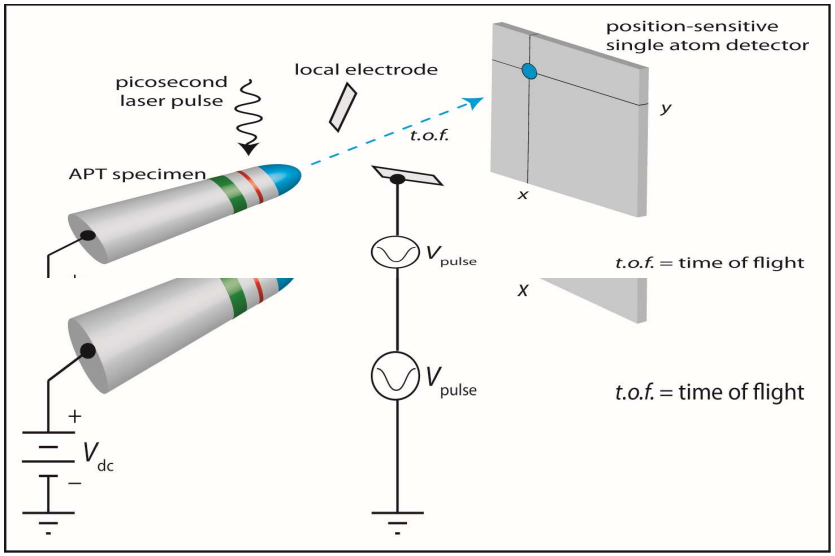
Strengths of SIMS:

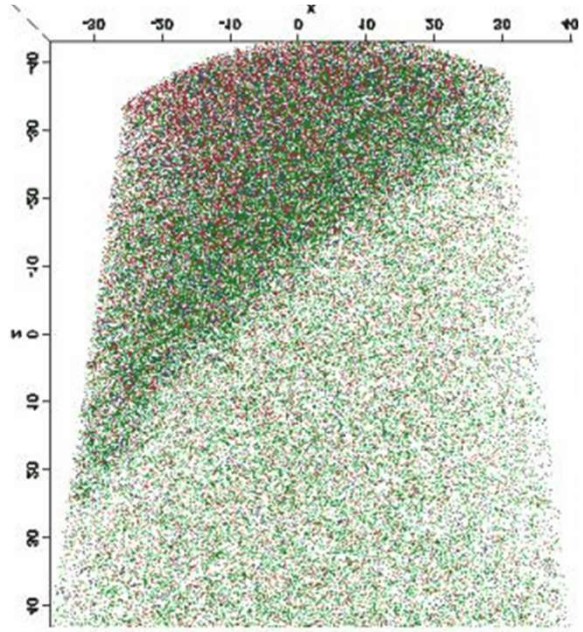
- Good Z-resolution
- 2D mapping capability
- Simple sample preparation
- Isotopic sensitivity
- Relatively quick measurement

Weaknesses of SIMS:

- Problems with depth calibration
- Resolution not high enough to see some features
- Large-area measurement, resulting in profile broadening
- High-vacuum technique
- Complex mass spectra

Atom Probe Tomography (APT)





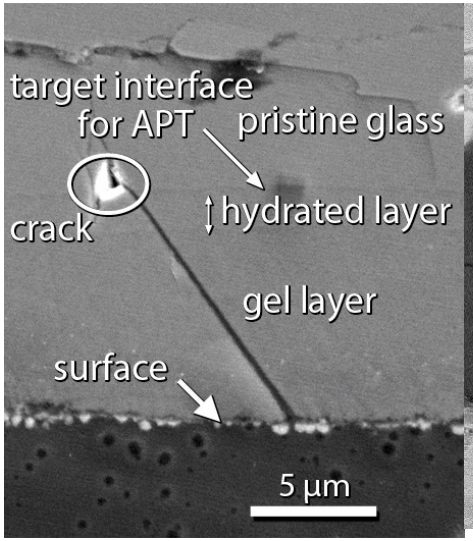
- Field-ion microscopy combined with time-of-flight mass spectrometry
- Result is a 3-D elemental map with single-atom sensitivity and sub-nm position accuracy (only recently routine for oxides!)
- Requires needle-shaped specimen with 50–150 nm tip diameter

Schreiber and Ryan (2015) "Atom Probe Tomography of Glasses" in *Modern Glass Characterization*, Ed. Mario Affatigato.

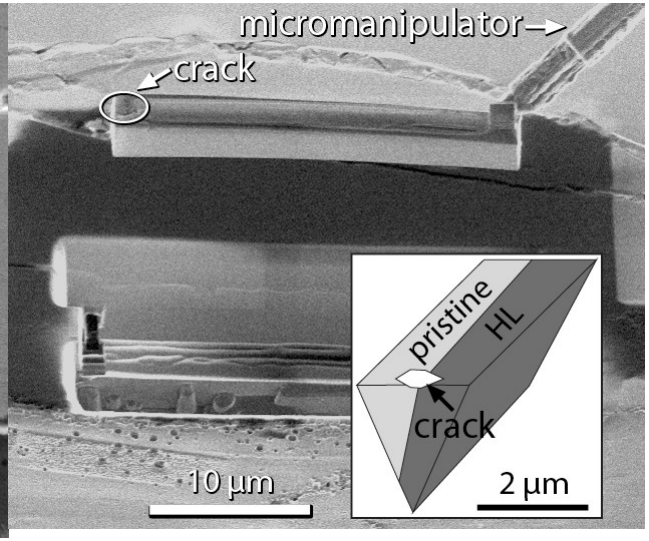
FIB Processing of APT Specimens

1) Identify area of interest with SEM (interface of HL and pristine glass)
2) Extract wedge-shaped bar containing interface
3) Mount 2×2 μm^2 pieces onto several Si microposts (~7/lift-out bar)
4) Annular mill using FIB (focused beam of Ga^+ ions) to shape tip
5) Final conical specimen with end diameter <100 nm

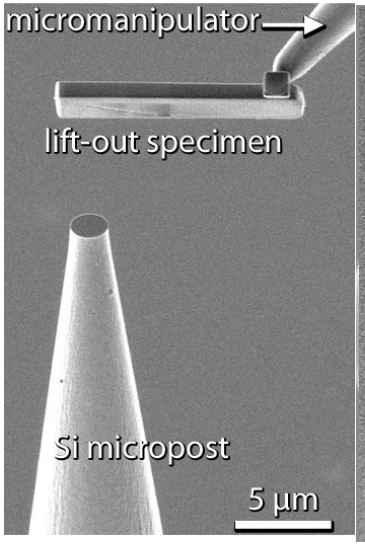
1: Identify



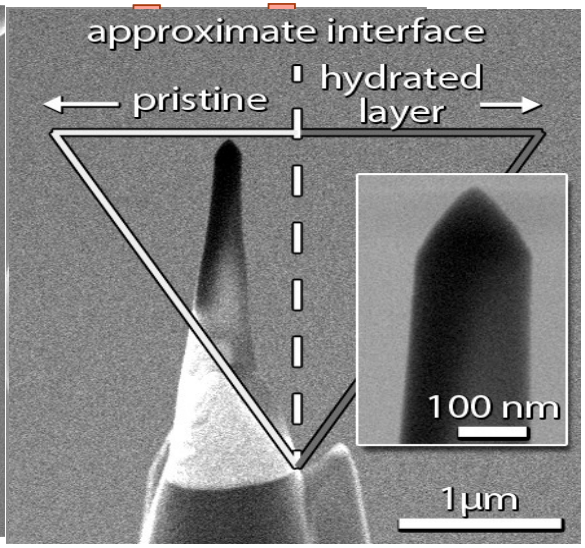
2: Extract



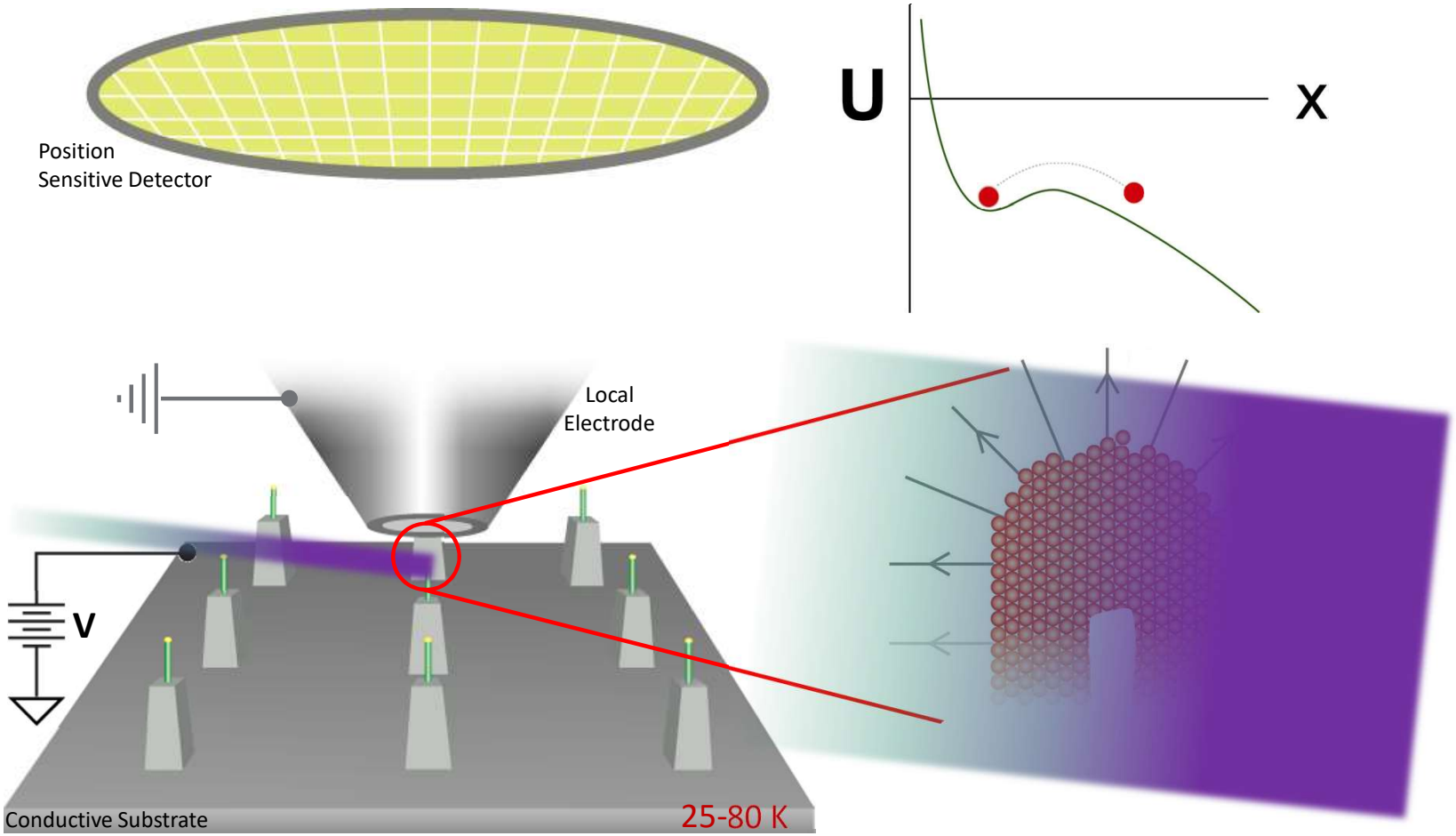
3: Mount



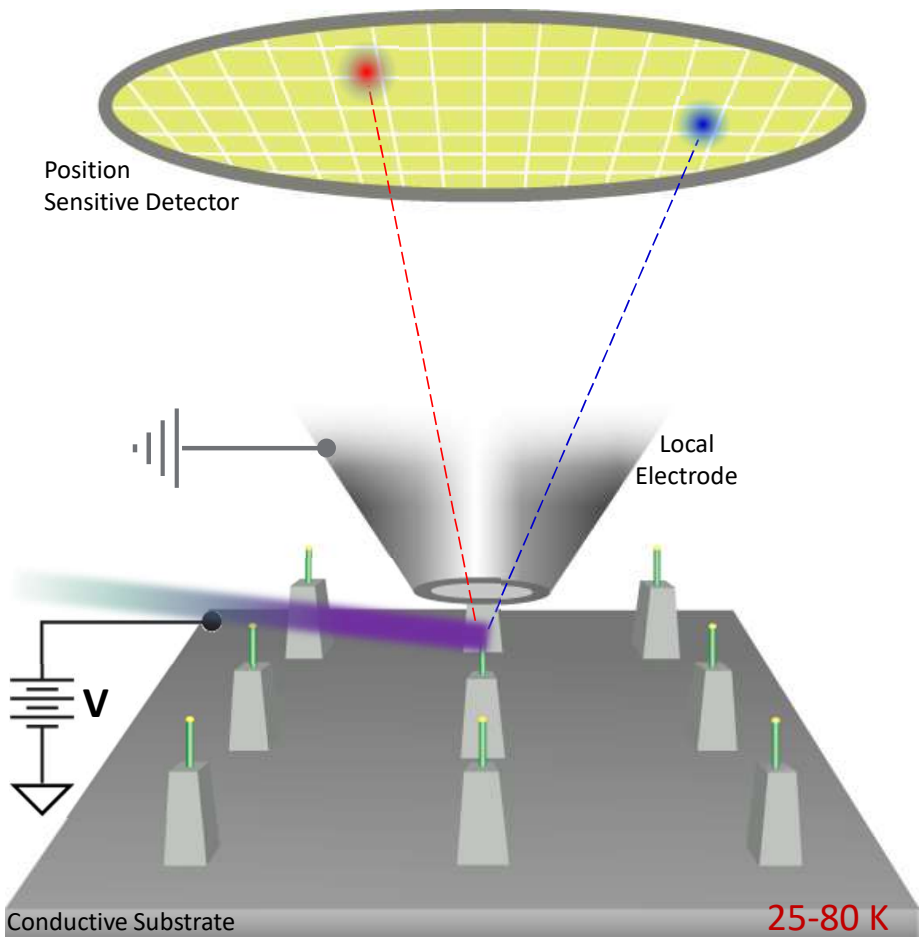
5: Final Sample

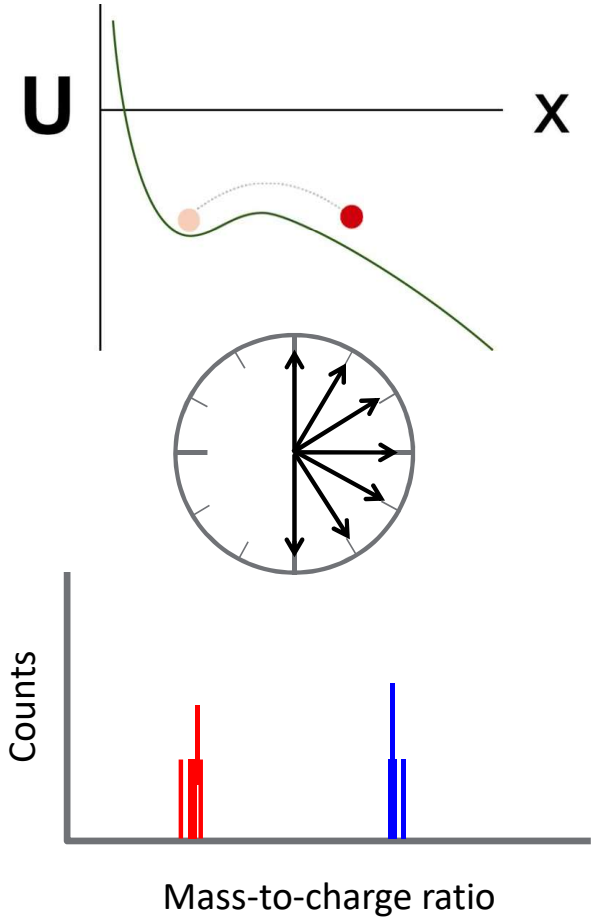


Local Electrode Atom Probe (LEAP) Tomography

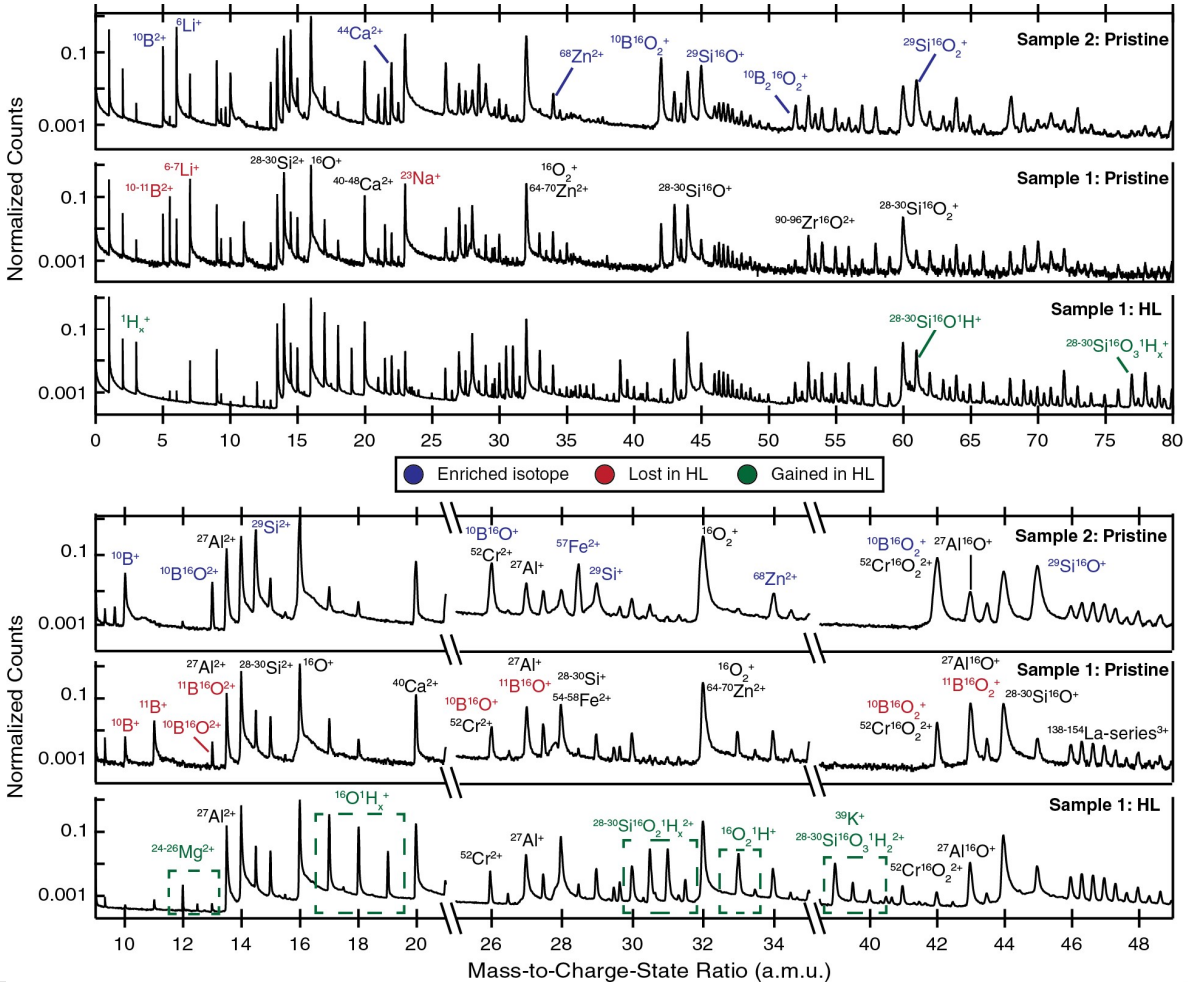


Local Electrode Atom Probe (LEAP) Tomography





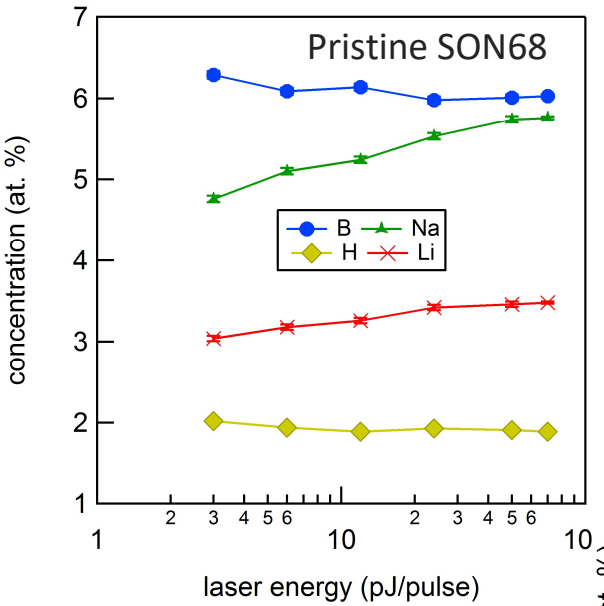
Challenges for Compositional Accuracy: Mass Spectra and Peak Identification

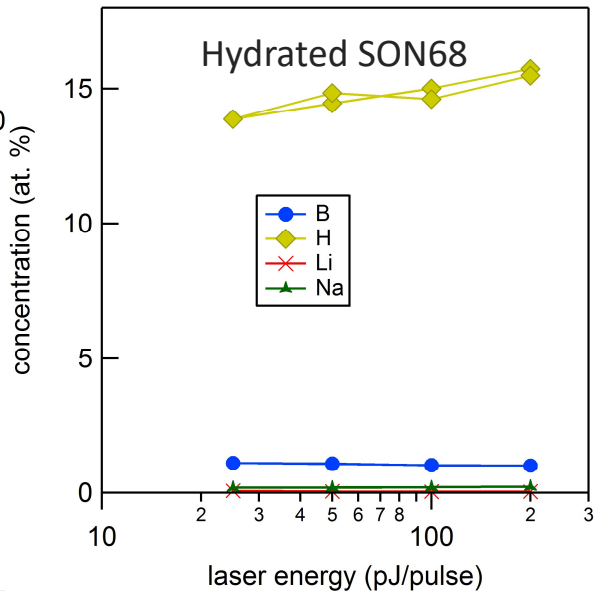


- ~31 elements
- >160 peaks
- Peak ID can be terrible and confusing
- Compare samples with natural isotopes with unnatural ratios to help

Schreiber and Ryan (2015) "Atom Probe Tomography of Glasses" in *Modern Glass Characterization*, Ed. Mario Affatigato.

Complications:
Alkali composition





- Alkali concentration determined for a *single tip* as a function of laser energy
- Decreasing laser energy → higher selective loss of all alkalis
  - DC evap. loss?
  - Cation migration?
- Na seems most sensitive
- H content in hydrated glass less affected than Na

APT is a powerful technique for corroded glass, but large weaknesses remain

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Strengths of APT:

- Superior spatial resolution to TEM- or SIMS-based methods
- Isotopic tracking in 3D
- Reasonable composition accuracy
- Composition gradients viewable for complex shapes

Weaknesses of APT:

- Yield can be low (material dependent in surprising ways)
- Mass spectra are very challenging (~31 component material)
- FIB targeting can be unreliable
  - Little to no contrast by SEM
  - Beam sensitivity of the glass (especially hydrated glass)
  - FIB can dramatically alter your measured composition (Na in particular)
- Alkali concentration most questionable, but seems OK spatially (no evidence for migration in our studies)
- SLOW

Cutting edge:
Cryogenic preparation for SIMS

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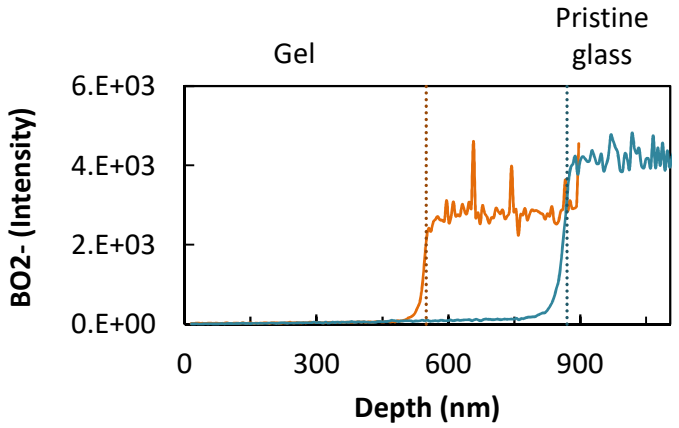
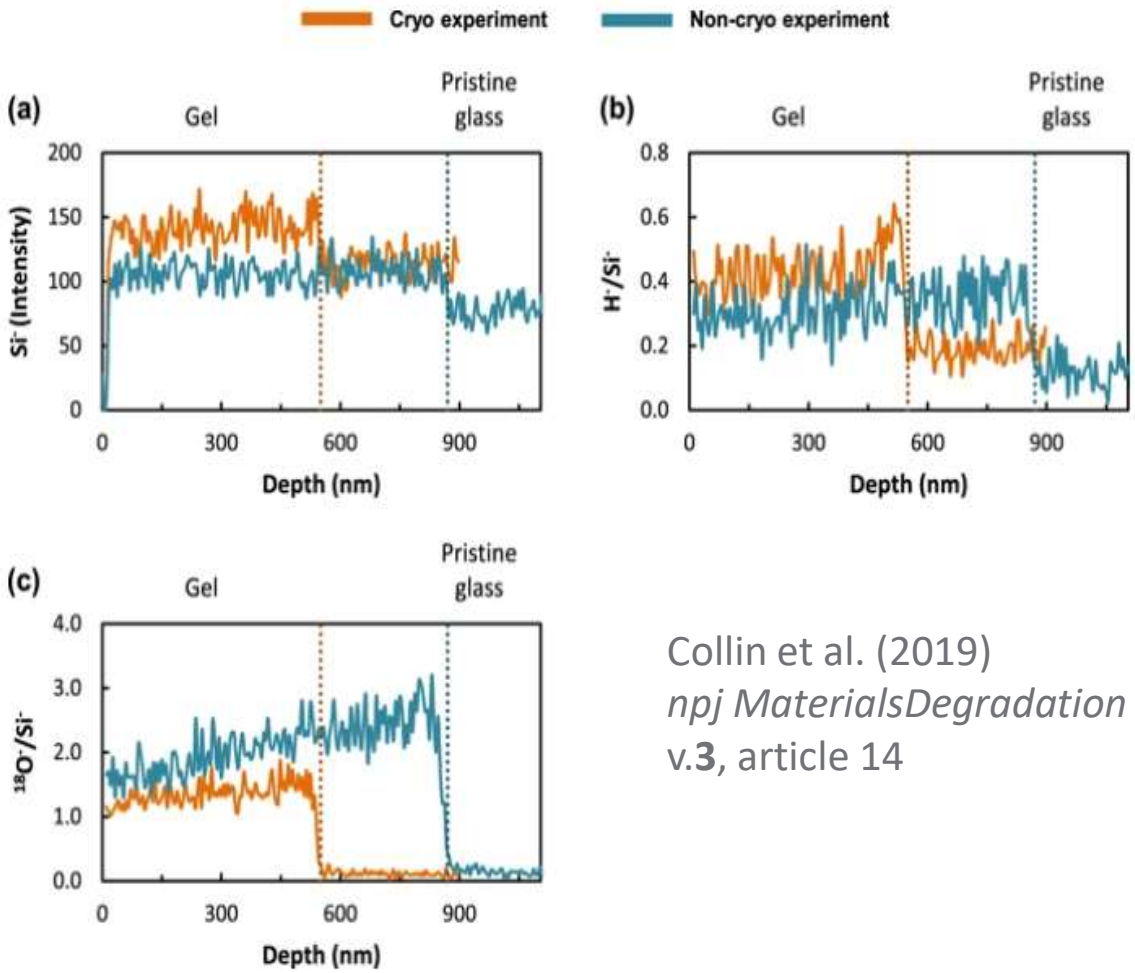
- Mobile elements and vacuum sensitive molecules (like water) can be kept in place by cryogenic techniques
- Through careful manipulation and with a cryogenic stage, hydrated, but frozen, samples can be analyzed





Collin et al. (2019)
npj MaterialsDegradation
v.**3**, article 14

Cutting edge:
Cryogenic preparation for APT

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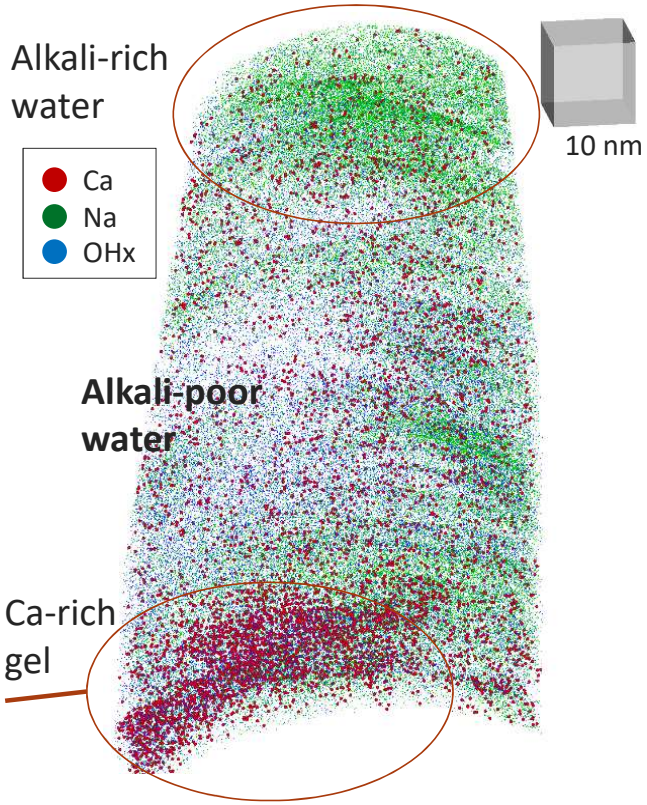
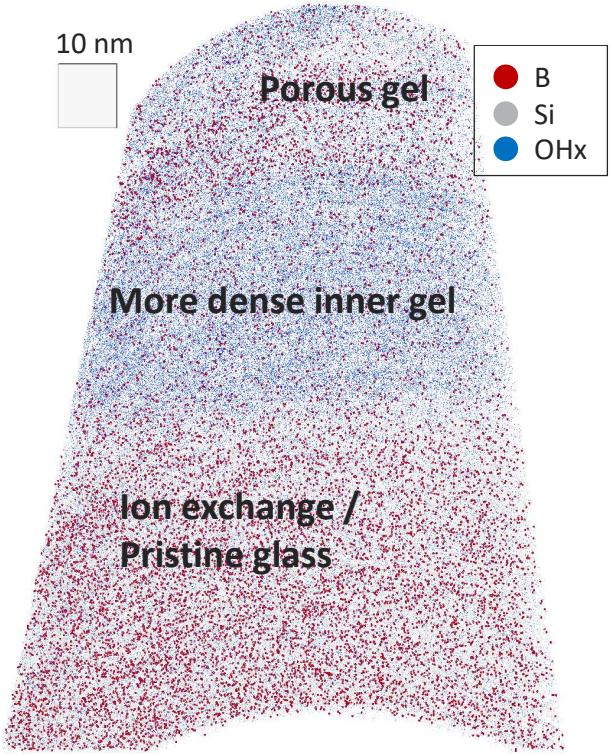


Mechanical Stability

- Gels are inherently weak
- Upon drying, gels can crack and spall
- Interface often does not withstand the forces generated during APT
- Gel structure collapses; not "true"
- APT does not "see" empty space; voids are difficult to image

Solution Composition

- Opens the possibility of measuring differences in solutions within gel
- Developed method to **flash-freeze, cryogenically prepare,** and **analyze** surface layers using APT



First-ever APT characterization of a cryogenically prepared, site-specific liftout specimen

Schreiber et al. (2018) Ultramicroscopy, **194**, p 89-99

Cutting edge:
Cryogenic preparation

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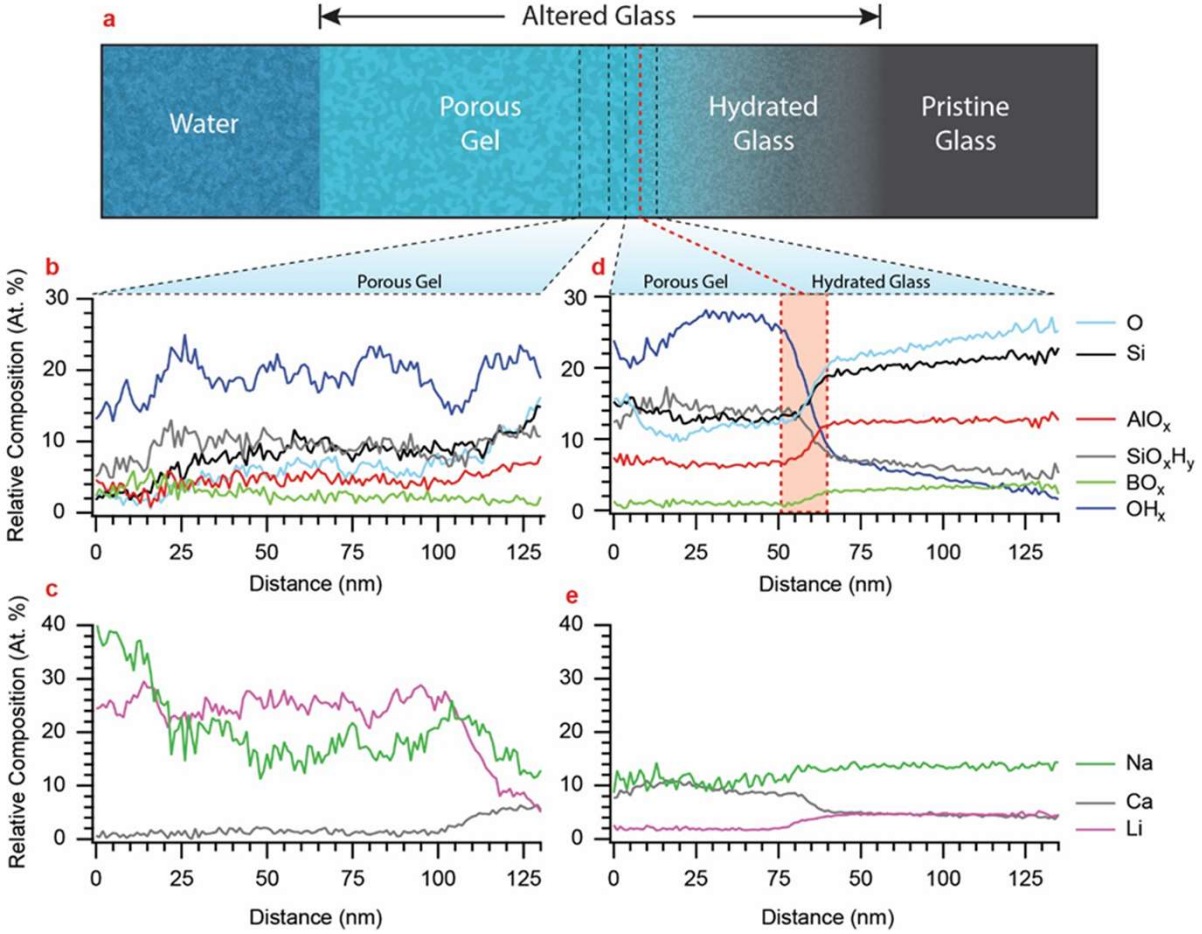
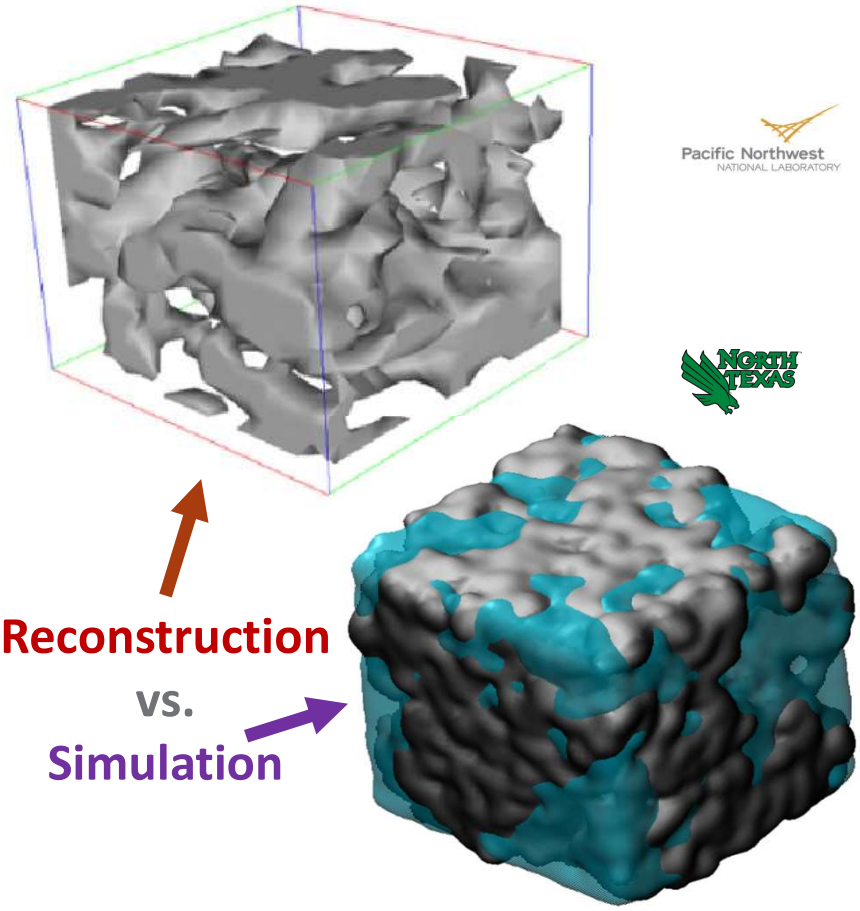
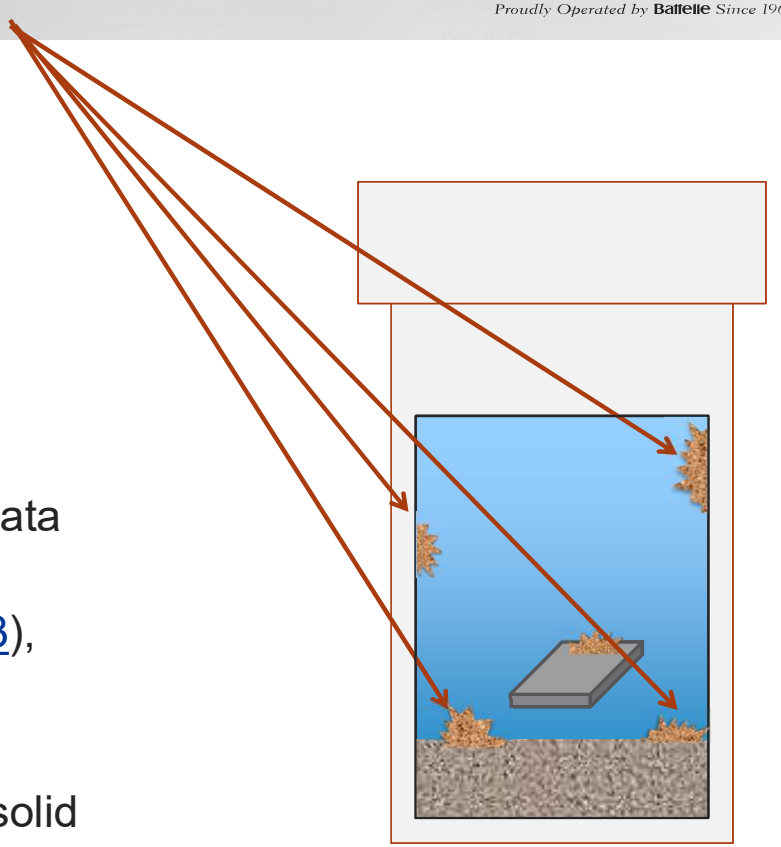




Perea et al., in preparation

What can we monitor?
New Phase Analyses

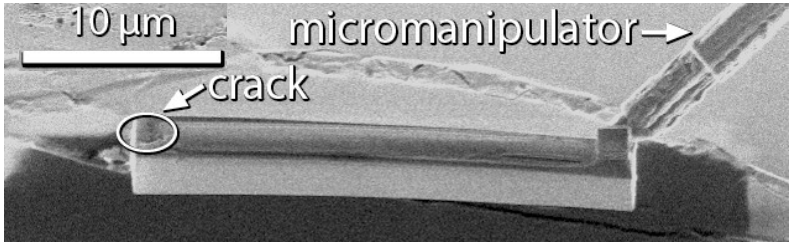
- **Crystallographic**
  - ED, XRD
  - Optical
- **Geochemical modeling**
  - Calculation of dissolution and precipitation based on databases of thermodynamic (and sometimes kinetic) data
  - Geochemist's Workbench (www.gwb.com), EQ-3/6, PHREEQ-C (www.usgs.gov/software/phreeqc-version-3), CHESS/HYTEC, GEMS-PSI, WATEQ4F
  - Problem: Most glass alteration phases are amorphous solid solutions and are **not included** in most databases
  - Problem: There is strong evidence that the most abundant alteration phase (gel) is **not (always?) formed by precipitation**



Combining Characterization Techniques

Given the multitude of mechanisms working in concert during glass corrosion, the characterization often must be similarly complex

- One technique is often not enough to obtain a full picture of what is going on
- One technique "calibrates" the result of another
- A need to monitor both the solution and solid
- **Different structures require different techniques**
- **Obtain information to feed modeling efforts**



In order to gain new understanding, well-designed experiments are critical

- Targeted to mechanisms
  - Which mechanism does the experiment target?
  - Are other experiments required to isolate a mechanism?

This is easier said than done for glass corrosion, where mechanisms co-operate and influence each other

- Dissolution
- Molecular diffusion
- Ion exchange reaction
- Interdiffusion
- Formation of altered material
- Reactive transport
- Diffusive transport through altered layers
- Secondary phase formation
- Environmental interaction

A cautionary tale

Vapor Hydration Test (VHT) – ASTM C1663-17

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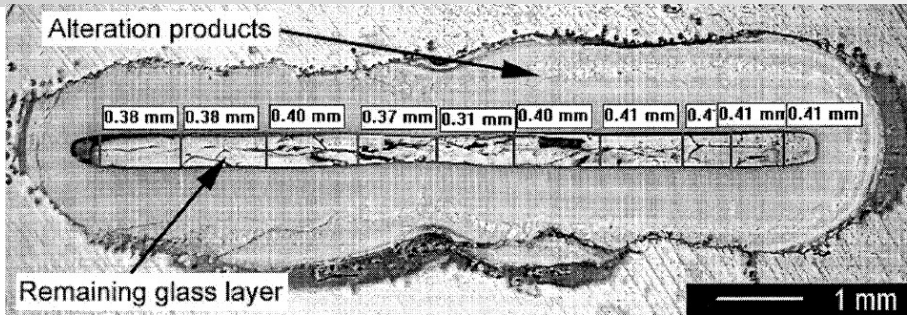
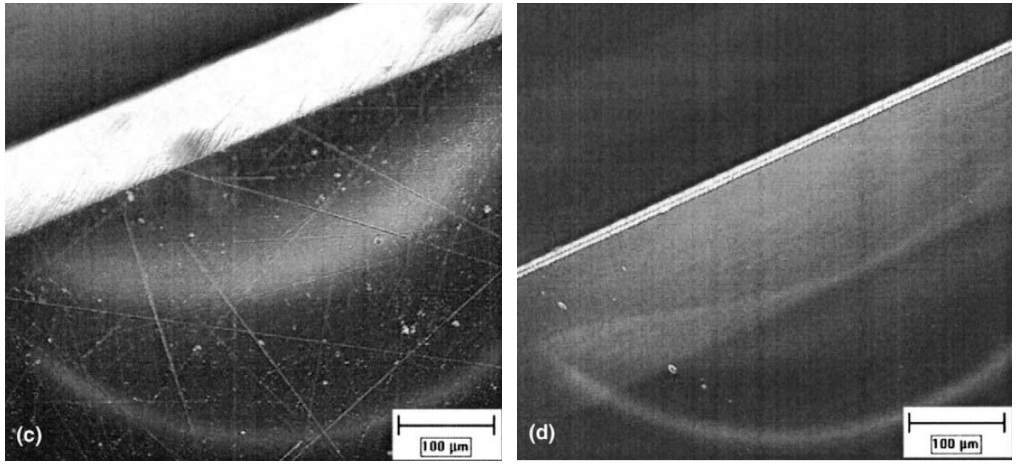
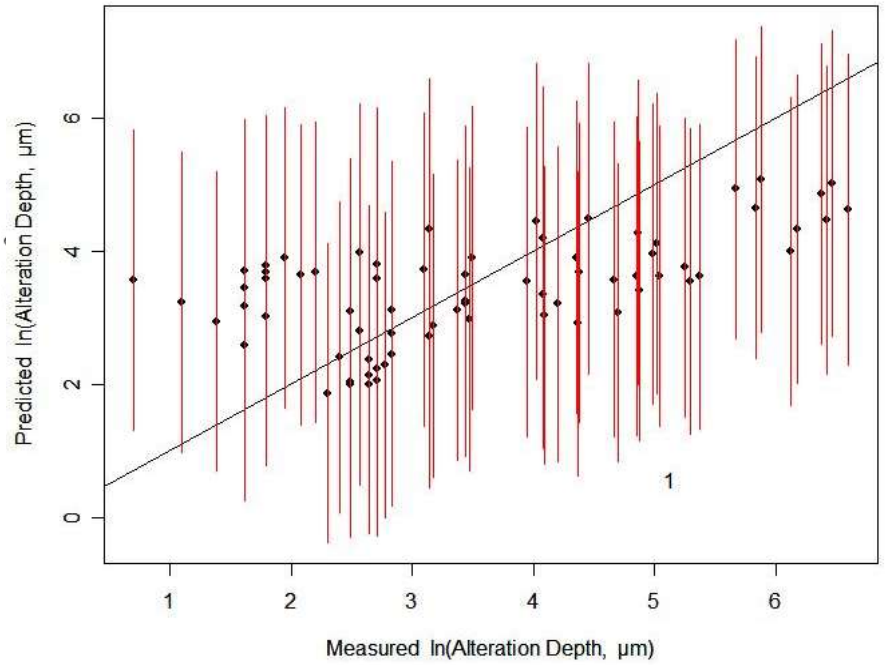
- Targeted to mechanism → ***Stage III***
- Well-controlled
  - Is a control used?
  - Are experiments run in duplicates (or higher)?
  - Do other variables impact the result more than the tested ones?







In order to gain new understanding, well-designed experiments are critical

- Targeted to mechanisms
- Well-controlled
- Understanding of the “question”

"The Answer to the Great Question... Of Life, the Universe and Everything... Is..." said Deep Thought, and paused.
"Yes...!!!...?"
"Forty-two," said Deep Thought, with infinite majesty and calm.”

“Forty-two!" yelled Loonquawl. "Is that all you've got to show for seven and a half million years' work?"

"I checked it very thoroughly," said the computer, "and that quite definitely is the answer. **I think the problem, to be quite honest with you, is that you've never actually known what the question is.**”

D. Adams, Hitchhikers Guide to the Galaxy, 1979

In order to gain new understanding, well-designed experiments are critical

- Targeted to mechanisms
- Well-controlled
- Understanding of the "question"
  - Is your modification of the experiment doing more than you thought?

The experiment will always do precisely what physics and chemistry demand of it.

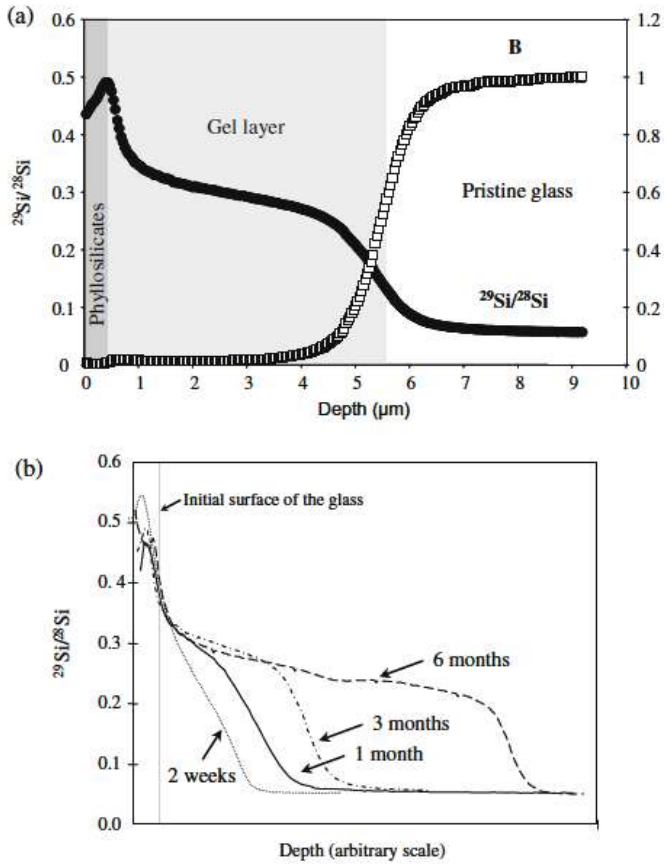
Whether those demands are sufficiently controlled is up to the researcher.

Common Problems for Glass Corrosion Experiments

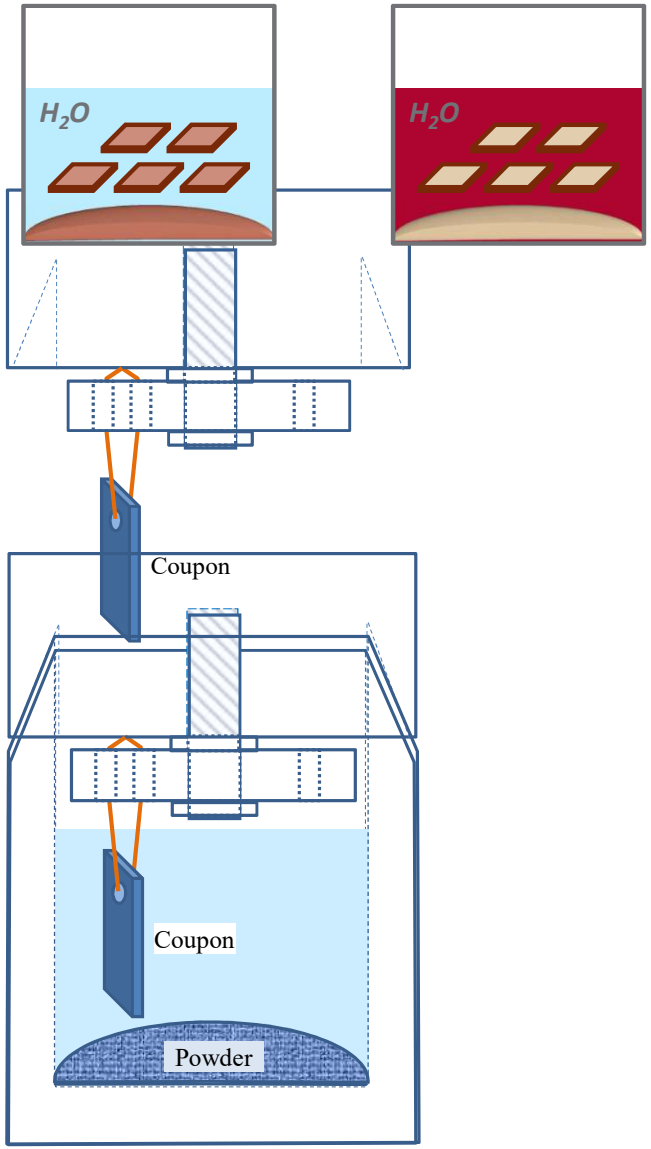
- Poor mass-balance
- Limits of resolution
- Unknown conditions
- Unknown sources of error
- Convolution of mechanisms

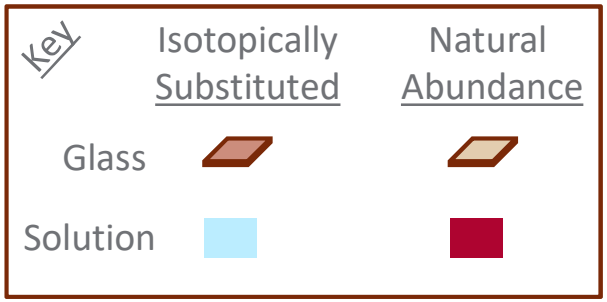
Isotope substitution – Transport tracking

- Question:
  - How does transport proceed to, from, and into the glass surface through a “mature” corrosion layer?
- Hypothesis:
  - For the diffusion of ions to be measurable, we must **distinguish** between pristine glass ions and those in solution
- Method
  - Identify materials through **isotopic enrichment**



*Valle et al, GCA, **74** (2010) 3412-31*





- 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

Selections for stable isotope substitution Studies

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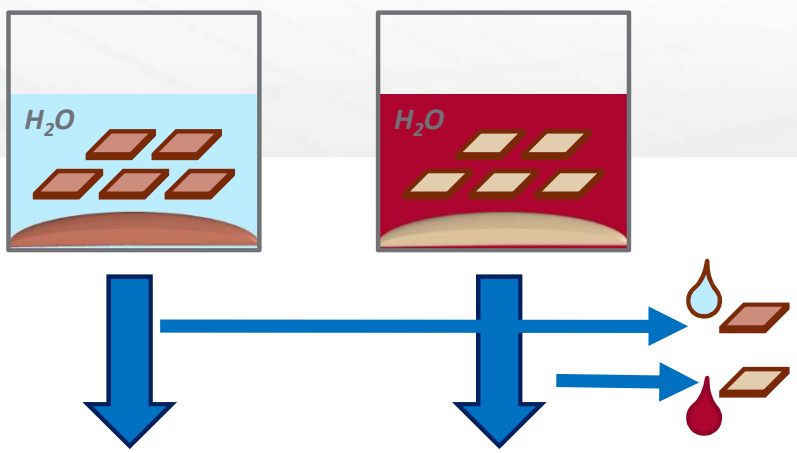
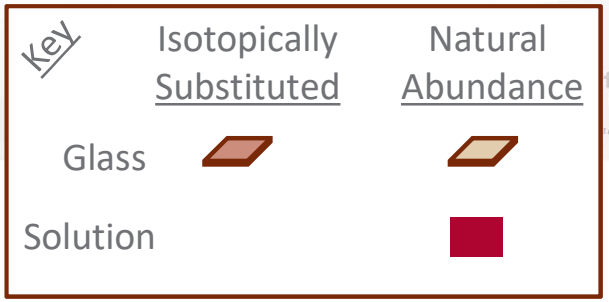
Glass Category	Natural Dominant Isotope	Substituted Isotope	Natural Abundance	Enriched Abundance	Experiment Abundance	Enrichment (*x* natural)	
Former	^{28}Si	**^{29}Si**	4.67%	80.0%	60.0%	12.9	Y
Mobile Former	^{11}B	**^{10}B**	19.97%	99.0%	99.0%	99.0*	Y
Alkali Modifier	^{7}Li	**^{6}Li**	7.50%	95.0%	95.0%	12.7	Y
AE Modifier	^{40}Ca	**^{44}Ca**	2.09%	96.5%	50.0%	24.0	N
Iron	^{56}Fe	**^{57}Fe**	2.20%	95.0%	95.0%	43.2	N
Other TM	^{64}Zn	**^{68}Zn**	18.80%	98.6%	98.6%	5.2	Y
Other TM	^{98}Mo	**^{95}Mo**	15.92%	99.0%	99.0%	99.0*	N

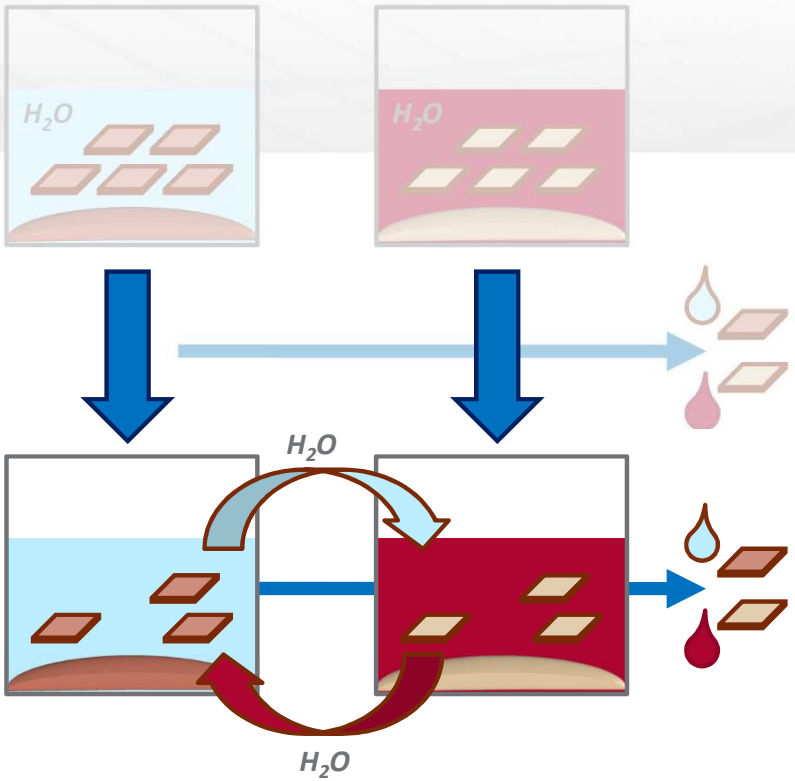


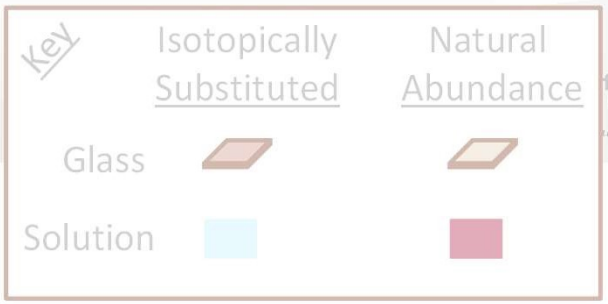


Characterization Suite:

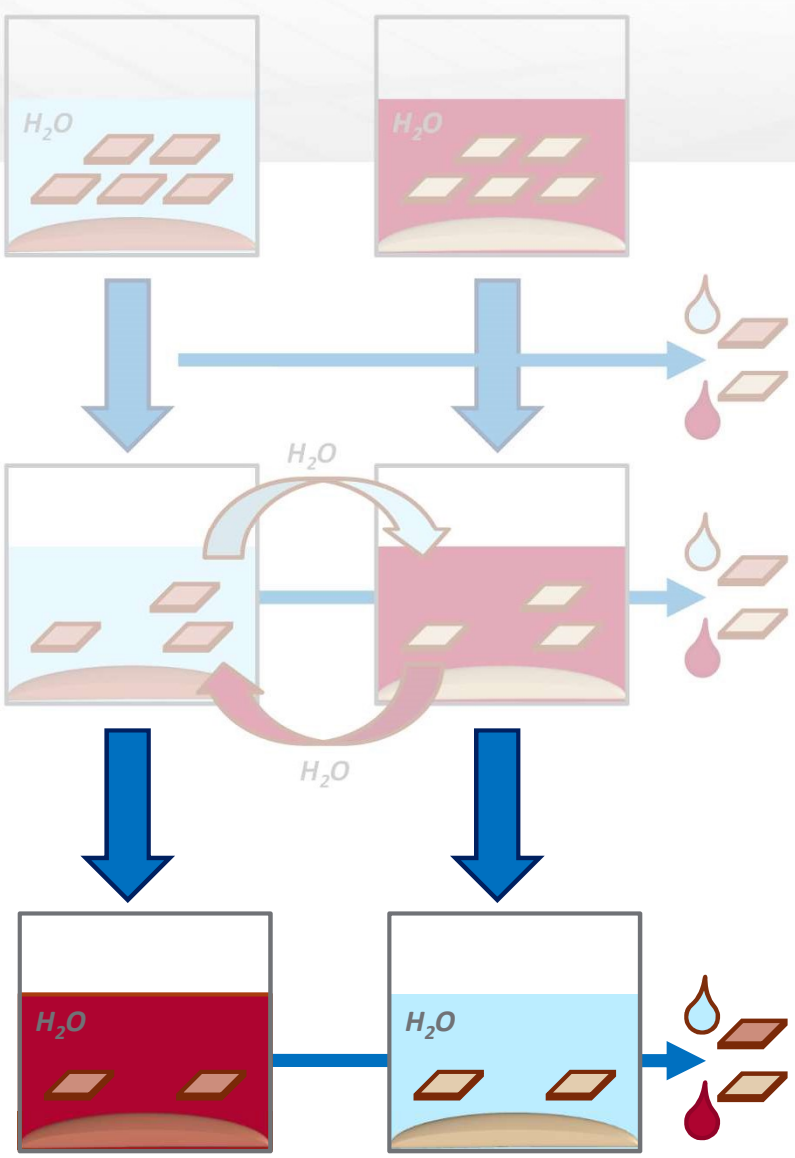
Solution Analysis
SIMS
RBS
FTIR
SEM/EDS
Scattering
GIXRD
XRD

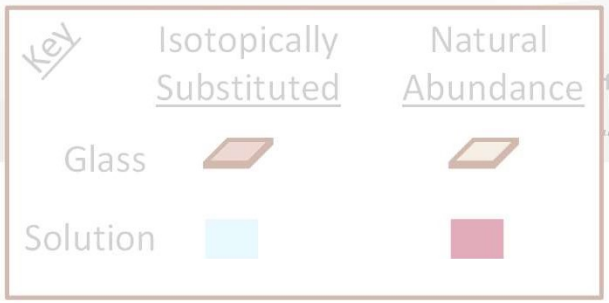
- Monitor experiment:
  - Occasional solution samples (volume minimized, not replaced)
  - 1-2 coupons





- "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





- 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

…and then results lead to more questions

Gel formation? Impact of interfacial layer?

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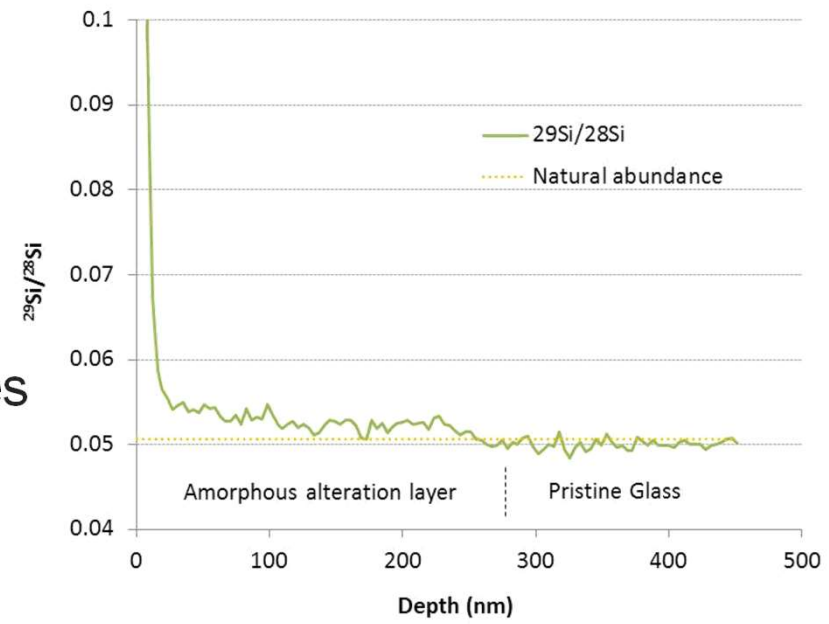
- Led to studies where gels are created and then perturbed
- Monitor various ion and molecular transport using isotopic and dye tracking
- No Si isotope equilibration
- APT showed atomically sharp B front
- No simple diffusion model can account for such profiles



Experiment covered in:

Gin et al.. 2015.*Geochimica et Cosmochimica Acta*, 151, p68–85.

Gin, S., et al., 2015. Nature Comm. 6: p. 6360.

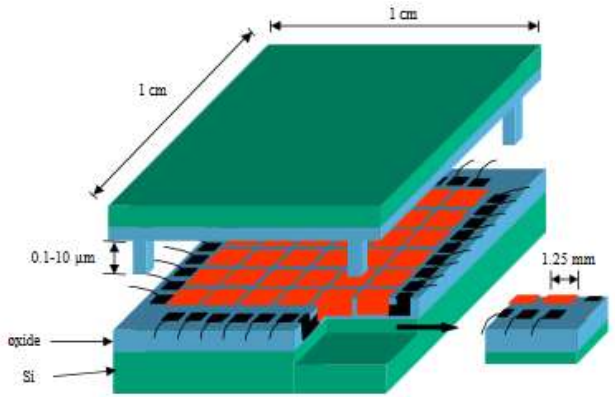
Summary of observations

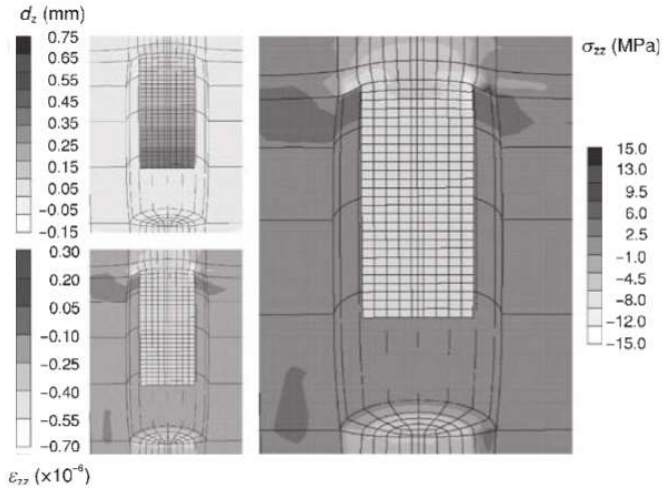
- Elemental profiles are much sharper than can be resolved with ToF-SIMS, nanoSIMS, or even traditional TEM
- Boron profile is less than 5nm in thickness (and even this is generous)
- Alkali ions appear to have both a steep "reaction front" interface and a diffusive profile within the glass
- The gel 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 Gin, S., et al. 2017. GCA, 202: p. 57-76.]

This means that the breakdown of the glass network occurs via dissolution. If transport is impactful, it is likely via the concentration of ions in solution due to constrictions in an alteration layer

Look to other systems

- Scientists studying **other materials systems** have developed experiments targeting mechanisms just beginning to be looked at for glasses
- Metallic Corrosion
  - Redox potential
  - Crevice chemistry
  - Designed-flaw tests
- Ceramic Evolution (particularly cements)
  - Changes in geochemistry with water content
  - Structure, chemistry, and **creep evolution** over long time scales





Finis

- In order to gain **new insights into the mechanisms** of glass corrosion, it is necessary to design tests that go **far beyond the standard tests**
- However, following the standards is a good way to relate results
  - Static tests – PCT
  - Flow-through tests – SPFT, Soxhlet, Micro-Channel-Flow-Through (MCFT)
  - Column tests – Pressurized Unsaturated Flow, Lysimeter
- Tests should be designed carefully to isolate mechanisms as much as possible
- Use targeted, complementary characterization techniques to get most out of tests
- Look to other materials systems for innovative testing ideas