U.S. DEPARTMENT OF ENERGY

Nuclear Energy

Environmental Management

NE Fuel Cycle Research & Development Program
EM Office of Technology Innovation & Development

Joint Glass Waste Form Performance Team

Joseph Ryan, PNNL

National Laboratories

Pacific Northwest NATIONAL LABORATORY

Argonne NATIONAL LABORATORY

SRNL

Sandia National Laboratories

BERKELEY LAB

International Partners

cea

JAEA

九州大学 KYUSHU UNIVERSITY

National Nuclear Laboratory

SCK•CEN

Subatech

University Support

PENNSTATE

RICE

MISSISSIPPI STATE UNIVERSITY

Study Objectives:

Respond to the pressing need to refine existing corrosion models:

- **Predict performance in wide range of environments**
- **Establish a strong scientific understanding to foster technical consensus**
- **Define mechanisms to facilitate accurate model development**
- **Ensure applicability to different waste forms**
- **Respond to opportunities for technical cooperation:**

There is an international need for consensus in this area, leading to our six-country collaboration:

USA, France, Japan, UK, Italy, Belgium

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Environmental Mgmt.

International *(Japan, Fr., US, UK, Bel.)* Long-Term Glass Corrosion Team

- *Series of workshops to share recent results and foster collaboration*
- *SharePoint web forum to enable direct data sharing for collaborative analysis*

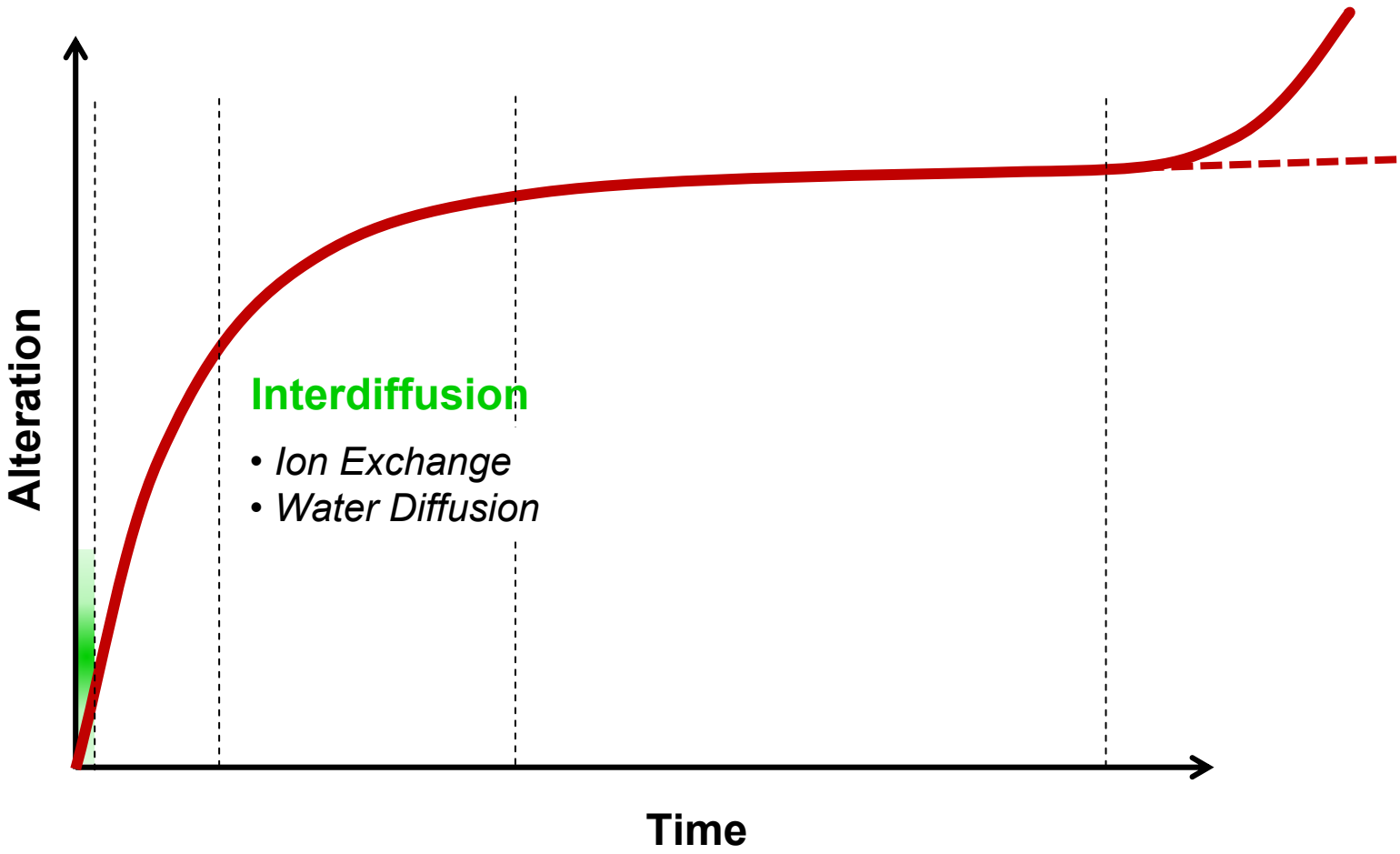
<u>Upcoming meetings:</u>

- *UK (in planning, January 2010)*
- *Savannah, GA as part of Glass Science meeting, May 2011*

Print Close

Glass Dissolution:

General scheme



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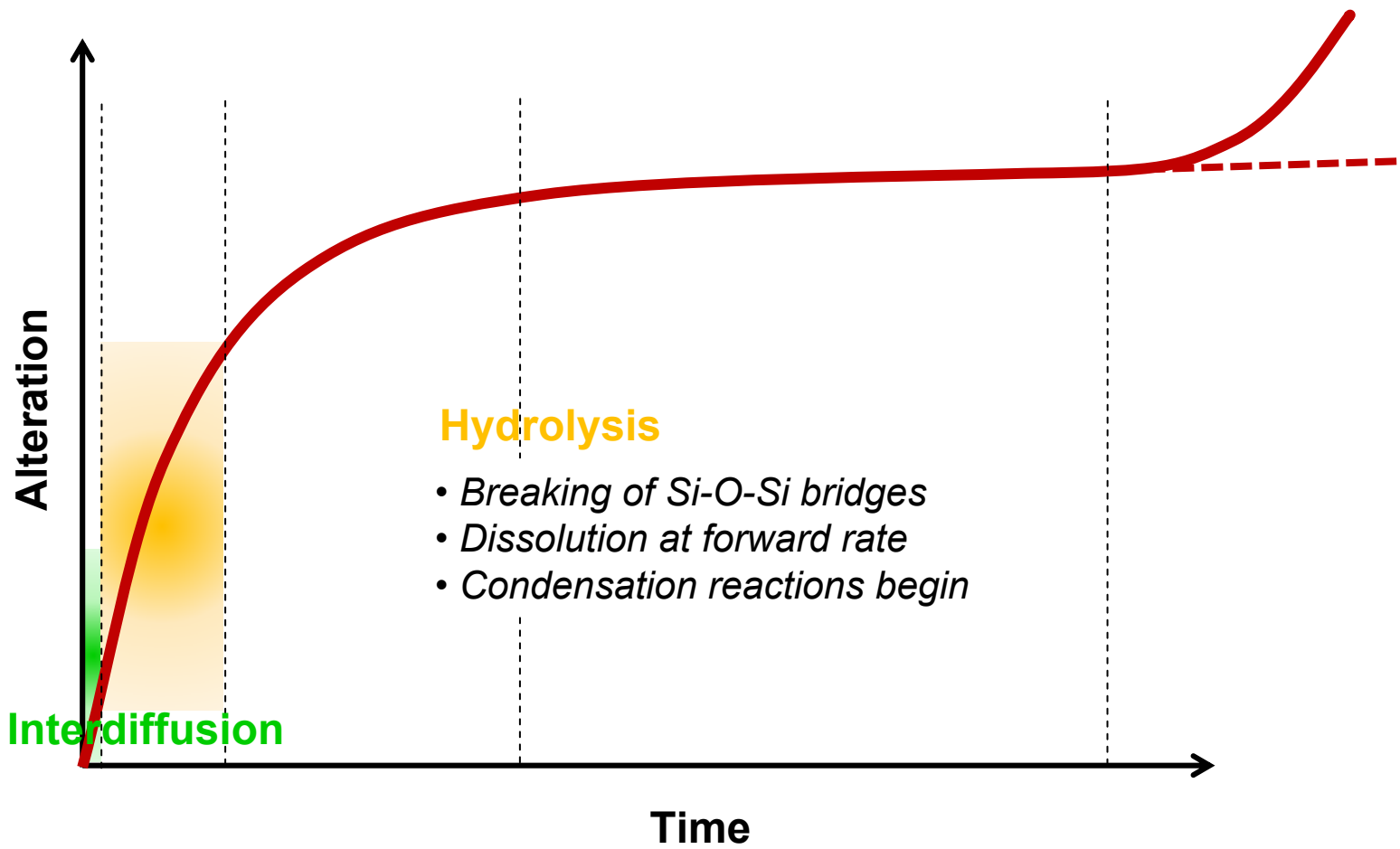

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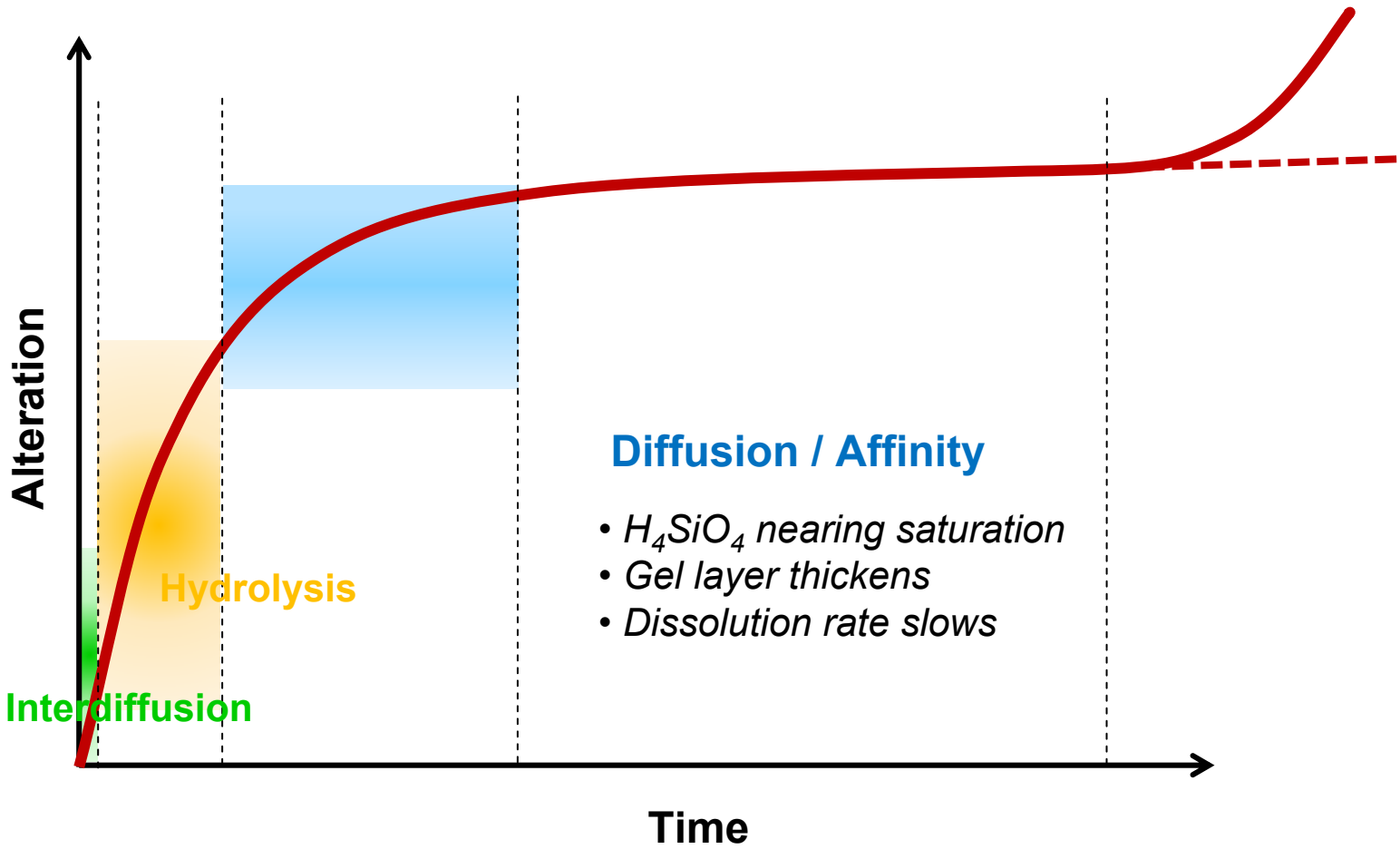

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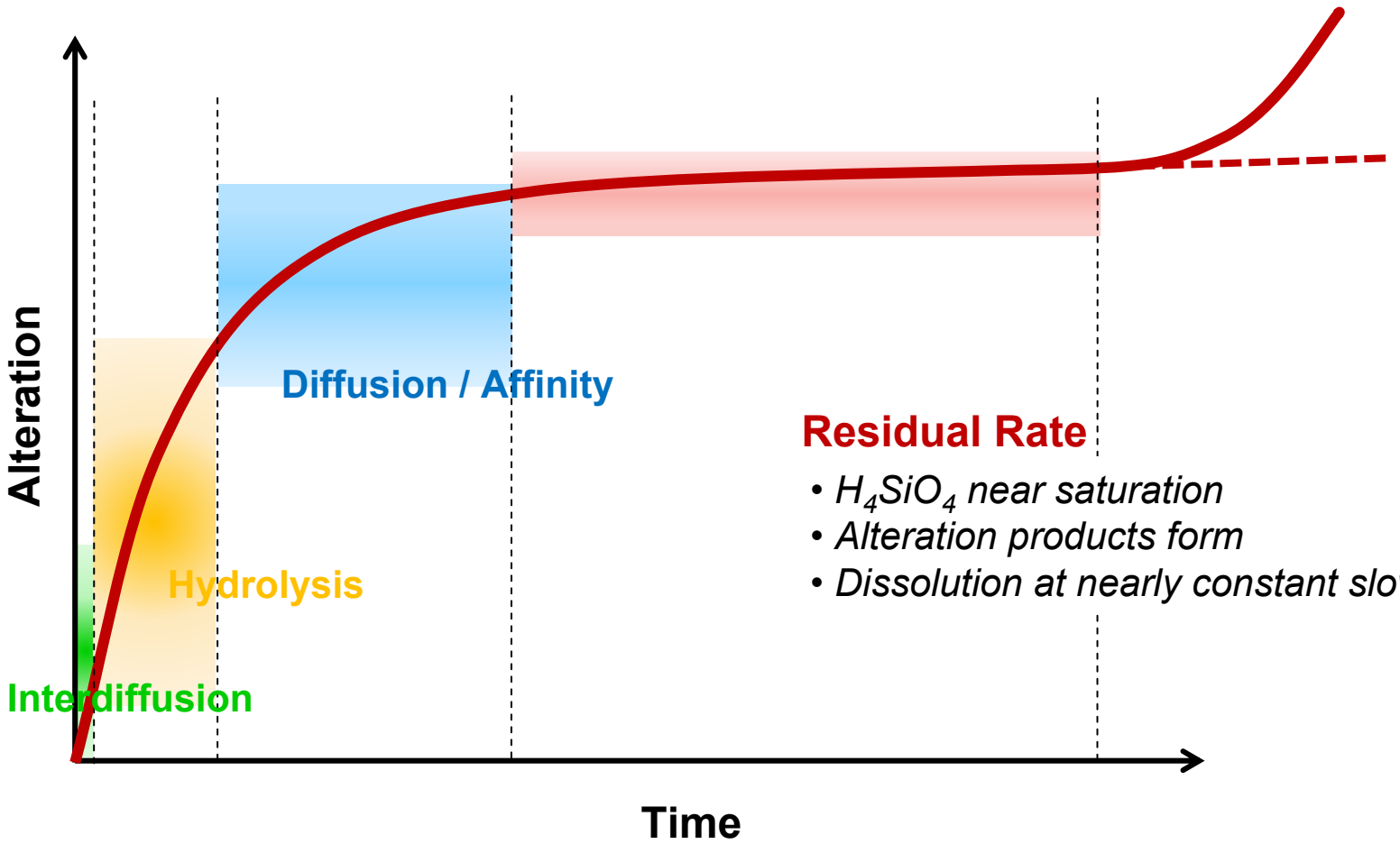

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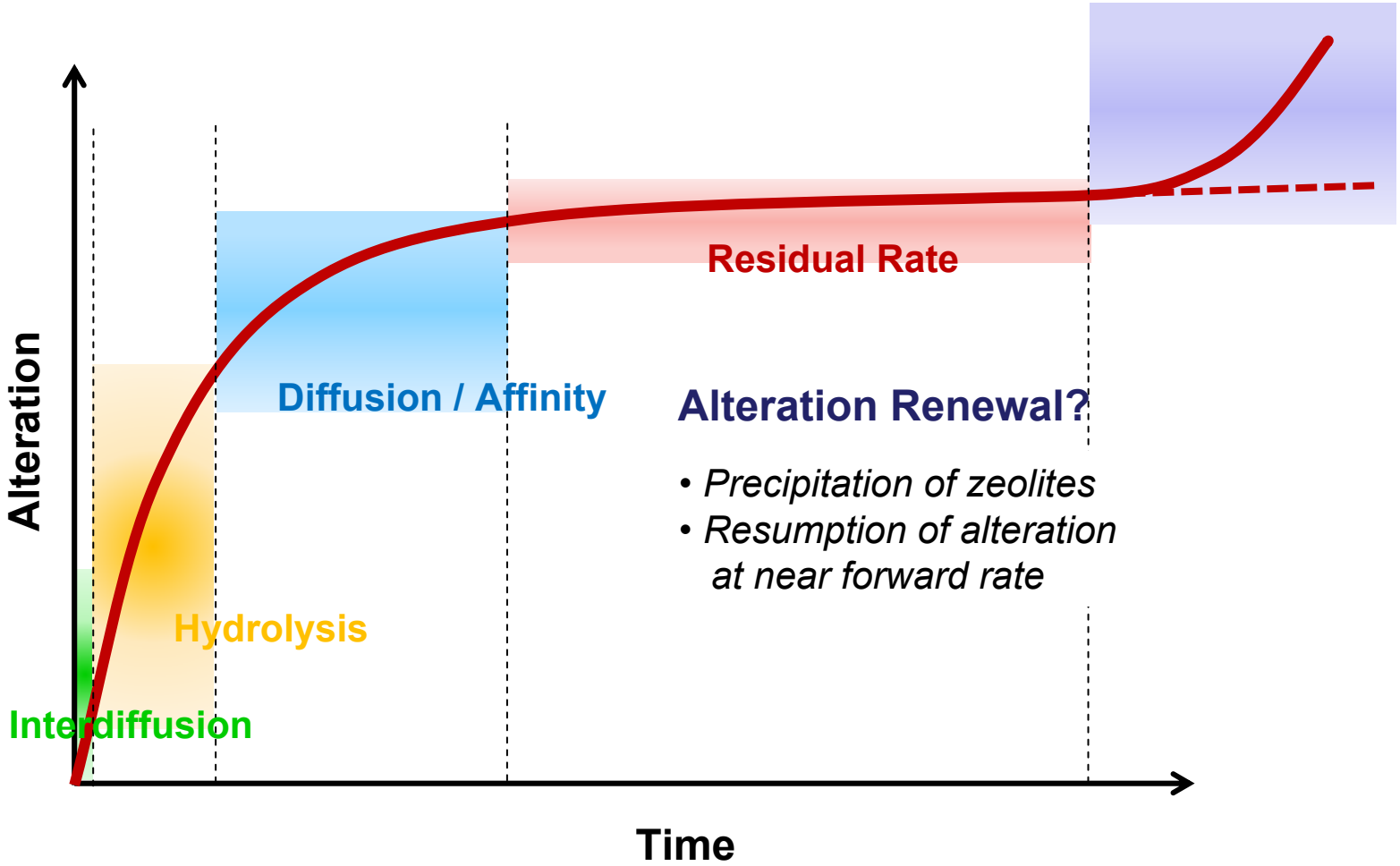
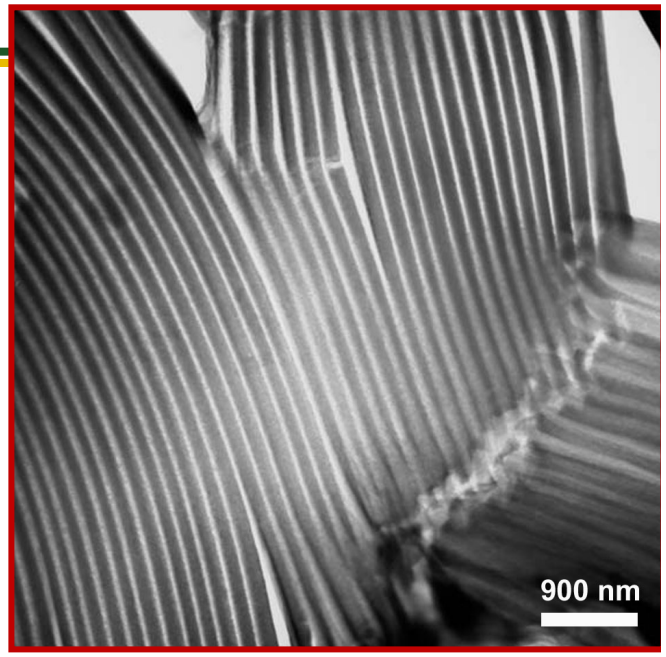


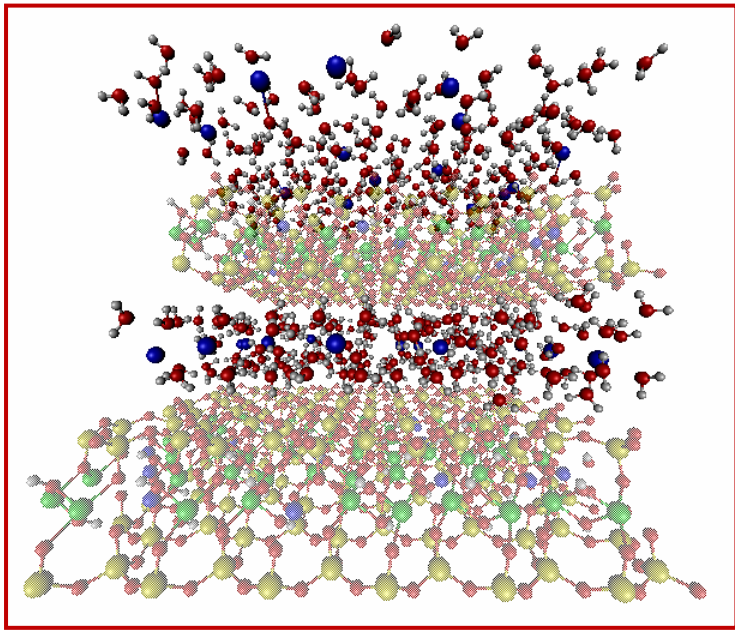
Glass Corrosion Research – *2010 Experimental Efforts*



- **Pacific Northwest National Lab:**
  - **NE -** Enriched isotopes to determine dissolution and diffusion characteristics
  - **EM -** Plan for estimating effective surface area
  - **NE -** Obtain ancient glasses with surrounding soil for analogue studies
  - **NE/EM -** Multi-condition SPFT experiments on SON68 and FCRD glass
  - **EM -** Neutron scattering study on the diffusion of water
- **Savannah River National Lab:**
  - **NE -** Extended PCT on SON68 and FCRD glass
  - **EM -** Evaluate composition effects on alteration products and pseudo-equilibrium constants by high S/V, long-time, PCT
- **Argonne National Lab:**
  - **NE -** SON68 and FCRD glass – improvement in parameter knowledge
  - **NE -** repository environment properties – library database

Glass Corrosion Research – *2010 Modeling Efforts*

- **Sandia National Laboratories:**
  - **NEAMS -** Establish plan for upscaling from atomistic to large scale models
  - **NE -** Coupled near-field and far-field performance modeling (*w/ ANL*)
  - **NEAMS -** IPSC code development



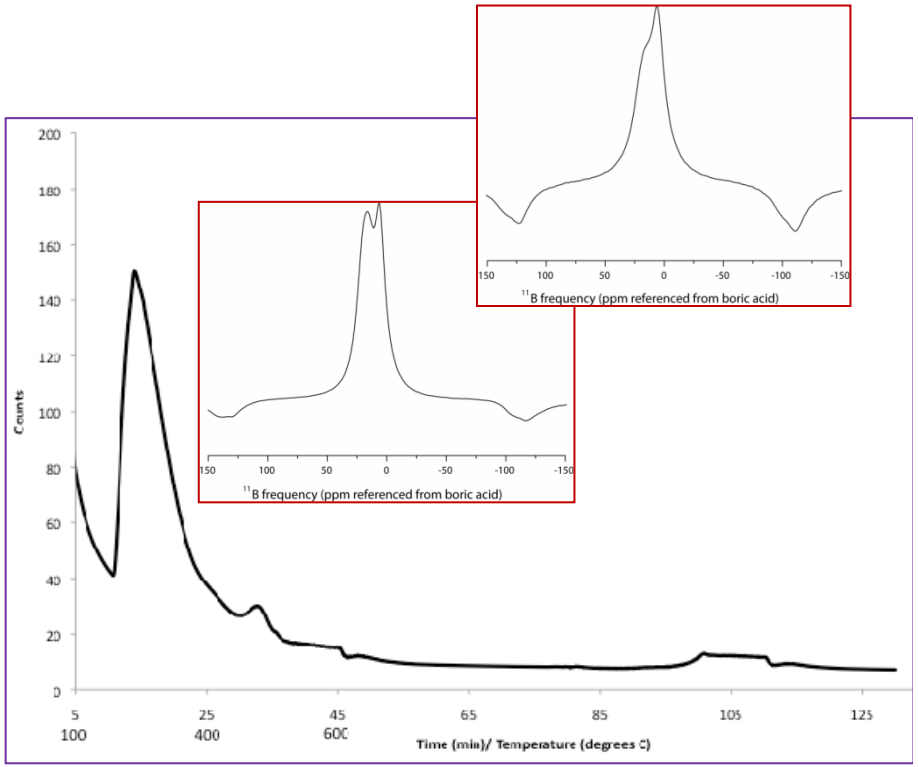
- **Lawrence Berkley National Lab:**
  - **NEAMS -** Extend reactive transport modeling to nano-scale, including diffusive motion through constricted pore space
  - **NEAMS -** MD/KMC models of transport properties
- **Pacific Northwest National Lab:**
  - **NE -** Identify secondary phase pathways
  - **NE -** Finite difference multi-scale modeling
- **Argonne National Lab:**
  - **NEAMS -** *Ab initio* on corrosion of feldspar to estimate pH effect on E
  - **NE -** Coupled near-field and far-field performance modeling *(w/ Sandia)*

Corrosion Work – *University Sub-contracts*

- **Rice University *(Andreas Luttge)***
  - "Evaluation of Alteration Phase Precipitation Kinetics"
  - Utilize Vertical Scanning Interferometry to study the growth of alteration phases
  - Direct quantification of intrinsic reaction rates *and* their spatial distribution

- **Penn State University *(Karl Mueller)***
  - "Investigation into the Surface Structure and Chemistry of Alteration Layers in Corroded Glasses"
  - Use surface-sensitive NMR and Inverse Gas Chromatography to investigate reactive surface sites
  - Distribution of site energetics as well as a correlation with surface structure

- **Mississippi State Univ., (*Ron Palmer*)**
  - *In situ* AFM of reacting glass

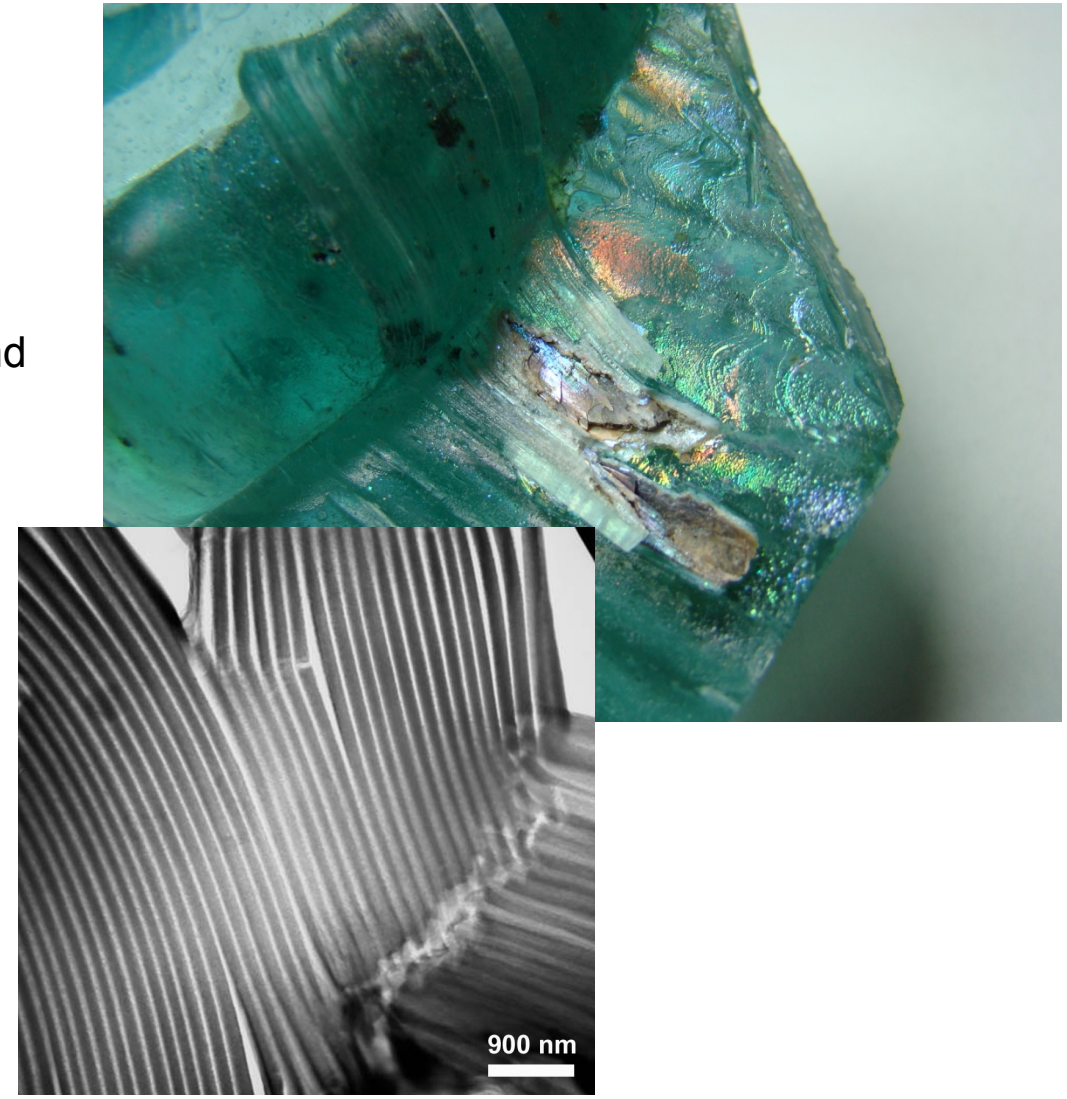


Italian Ancient Glasses

- **Iulia Felix**
  - Shipwreck from ~200AD
    - *Entering or exiting the port at Aquileia*
    - *Sunk in about 50 m of water*
  - Contents
    - *Mostly ceramic jars*
    - *One large wooden barrel with glass cullet – ca 400 kg*
      - **Colored**
      - **Colorless**
- **Aquileia**
  - Roman villa
    - *~ 1000 m^2 (11 000 ft^2)*
    - *First partially excavated -1930s*
    - *Currently being excavated and characterized*
  - An old Roman 'sea' port
  - Attacked by Attila, who diverted the river

Iulia Felix Glass

- **Silvestri et al. have performed extensive characterization**
- **Remaining unknowns:**
  - Cause of cemented sediment
  - Cause of lamellae
  - Difference between colorless and colored glasses
- **Use to waste management**
  - Insights into dominant glass dissolution mechanisms
  - Proof or not of current mechanism theories



Aquileia

- **Built in approximately 200 ce**
- **Approximately 1000 m^2 (11000 ft^2)**
- **Denis Strachan (PNNL) assisted in the archeological recovery**
- **Six glass artifacts found**
  - Three before we got there
    - *Soil and glass separated*
  - Three while we were there
    - ***Retrieved with glass and soil intact***
    - *Need a consolidation method*

Aquileia

- Bu
- Ap
- De
  th
- Si
  - Three while we were there
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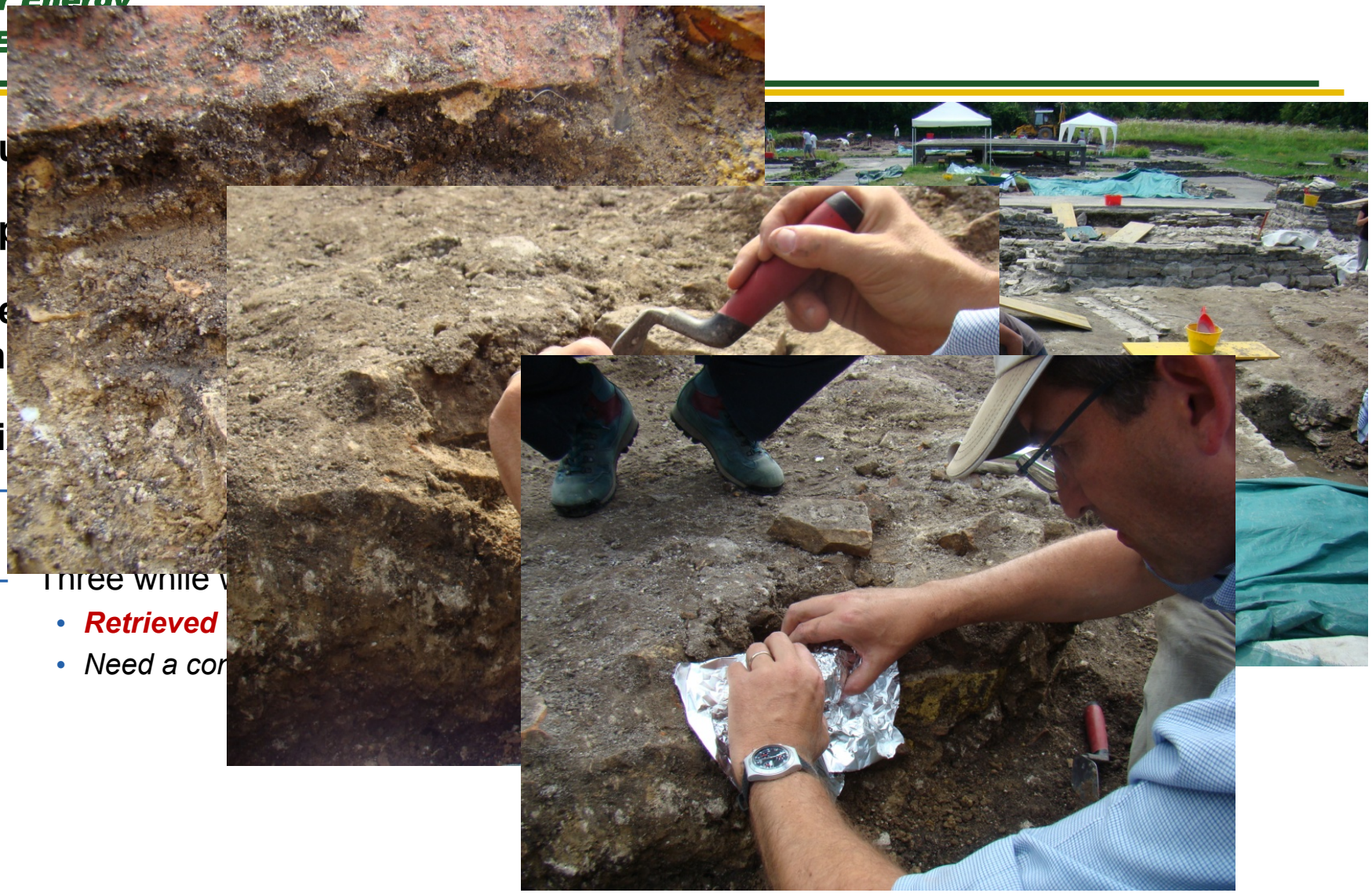
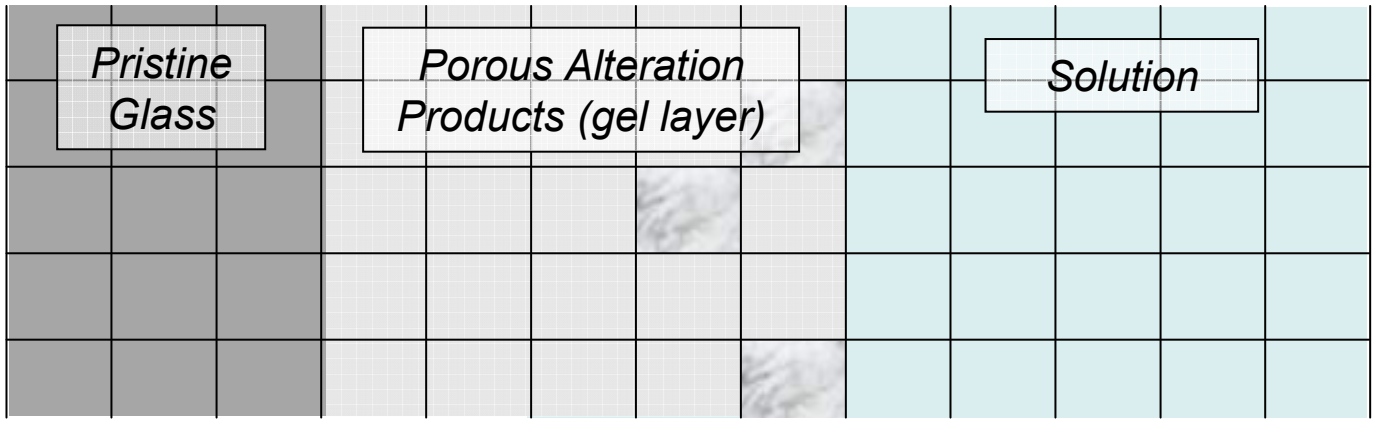


Finite Difference Modeling *Approach*

- **A classical method of numerical simulation**
  - Divide target region into a mesh
  - Solve diffusion-reaction equations at each mesh point

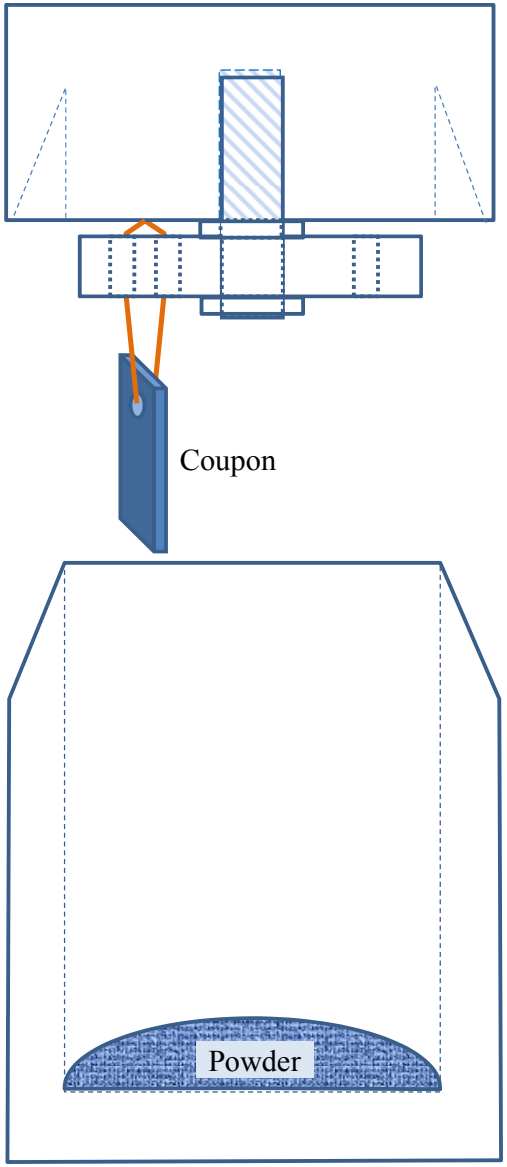


- **Inherently flexible**
- **Fast implementation**
- **Particularly suited for cases where materials and properties vary with spatial location in the mesh**

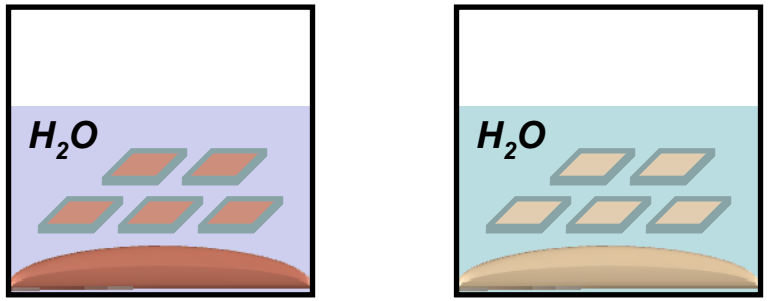
Finite Difference Modeling
Process

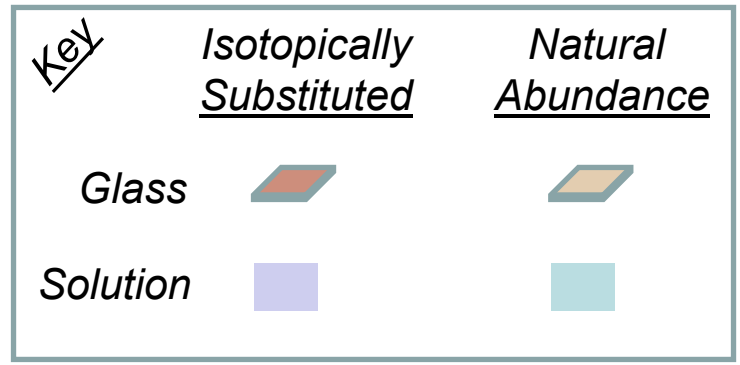
- **Start with model of reactive diffusion pathways with solution affinity boundary conditions**
- **Better estimates of diffusivity for a range of equilibrium and non-equilibrium boundary conditions**
- **Model evolution of**
  - 'Pore' sizes & 'pore' connectivities
  - Reactive diffusion pathways (local catalysis, etc)
- **Begin the D&A deconvolution by 'reverse engineering' transport pathways**
  - Similar to electrode designs for Li battery and fuel cells; diffusion barriers; mesoporous silica thin films
  - Use atomistic models for identified needs: activation energies, etc.
  - Verify by kMC and compare to high resolution experimental data

Diffusion Tracking via Isotopic Enrichment



- **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)
- **Surface area to volume ratio approximately 20,000 m^{-1}**





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  - Coupons (>10, ~10x5x1 mm)
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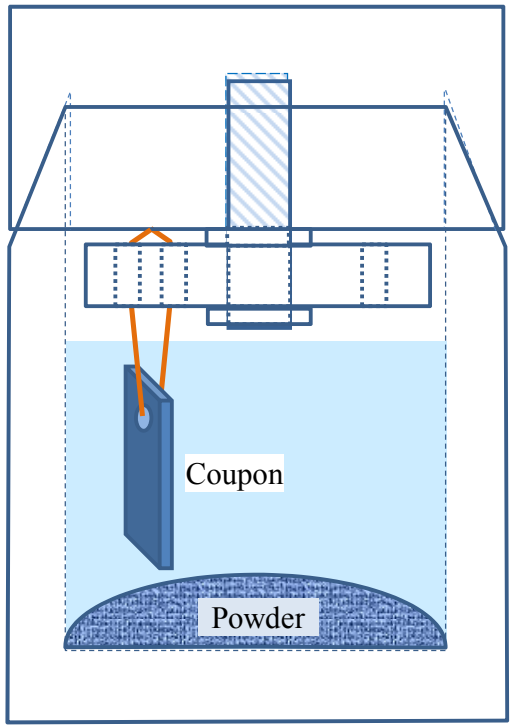
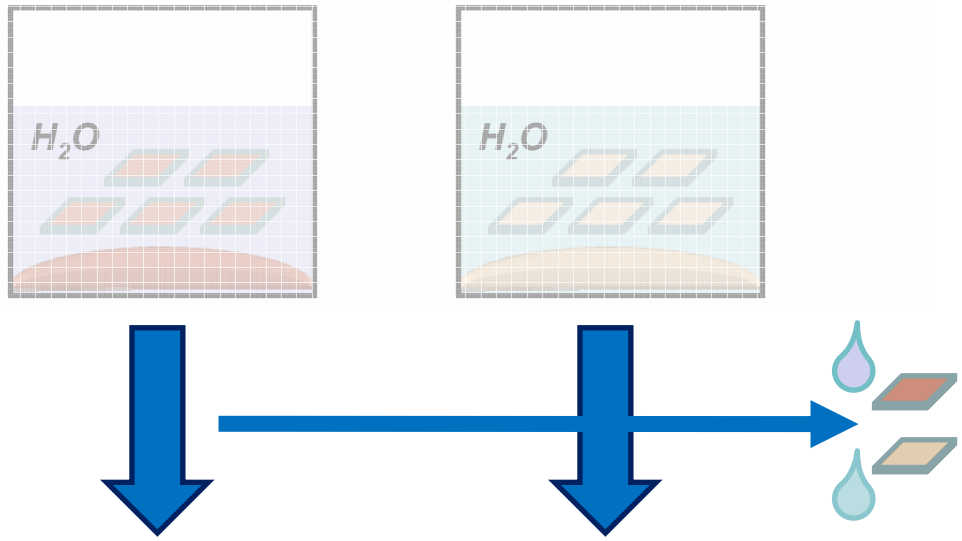
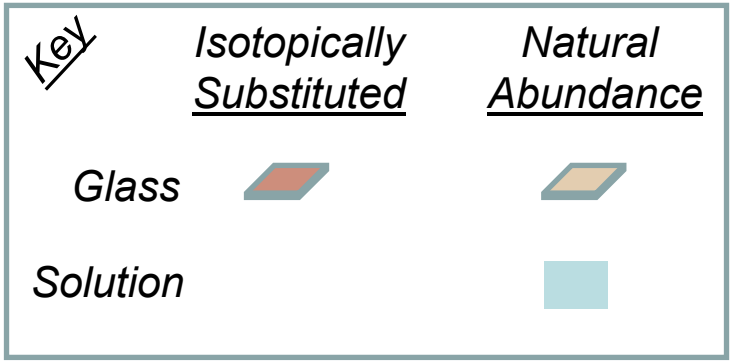
- **Surface area to volume ratio approximately 20,000 m^{-1}**
- **PTFE reaction vessel**
- **Place into ultrapure water and allow to corrode at 90 °C**



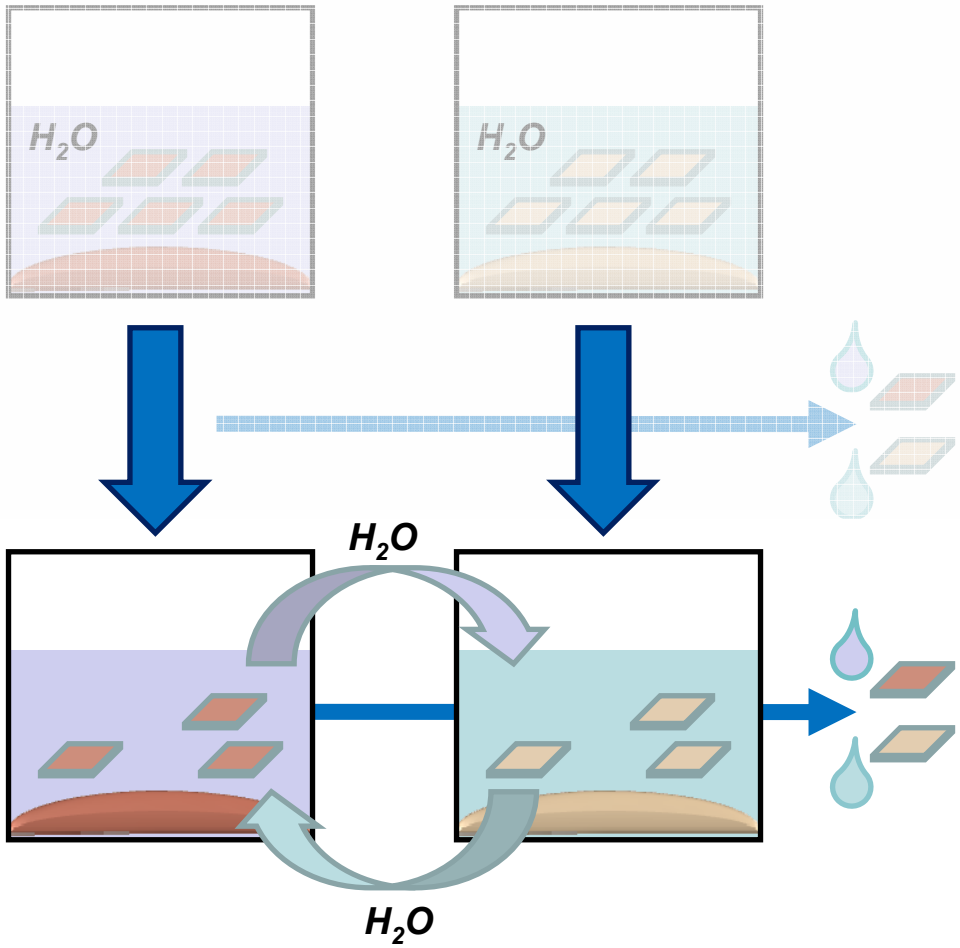


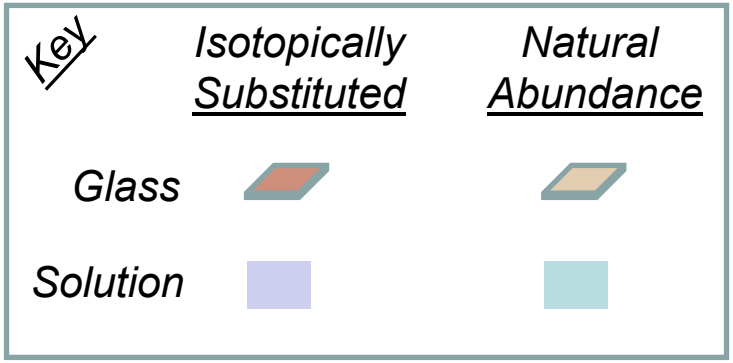


Characterization Suite:

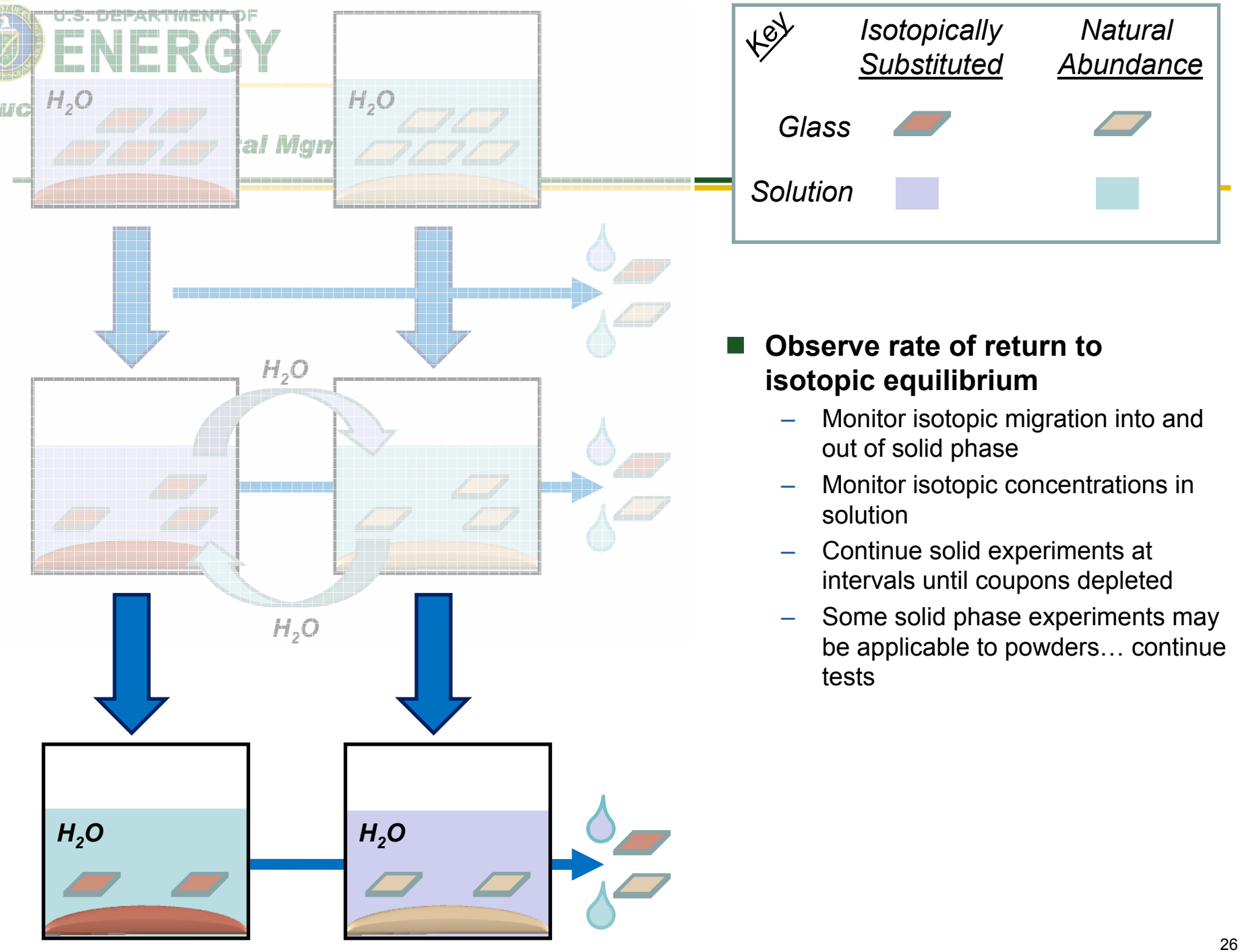
Solution Analysis
SIMS
RBS
FTIR
SEM/EDS
Scattering
GIXRD
XRD

- **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

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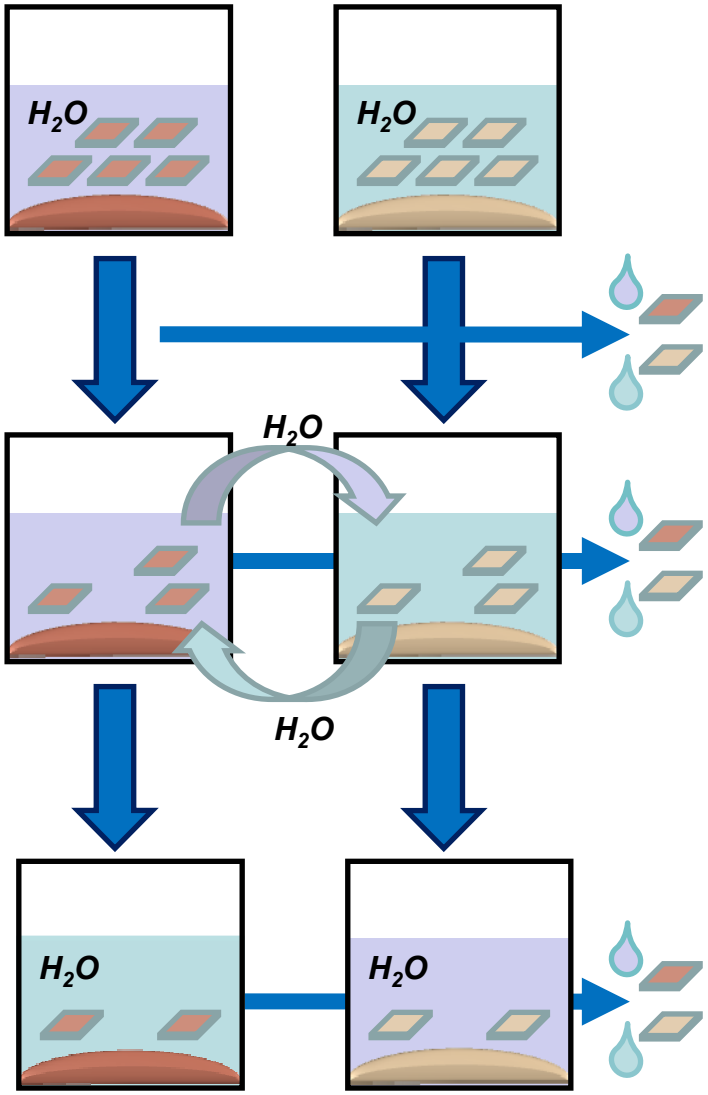
Diffusion Tracking via Isotopic Enrichment

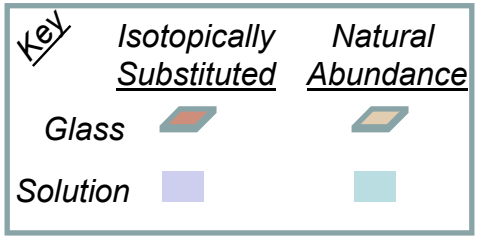


Goal:

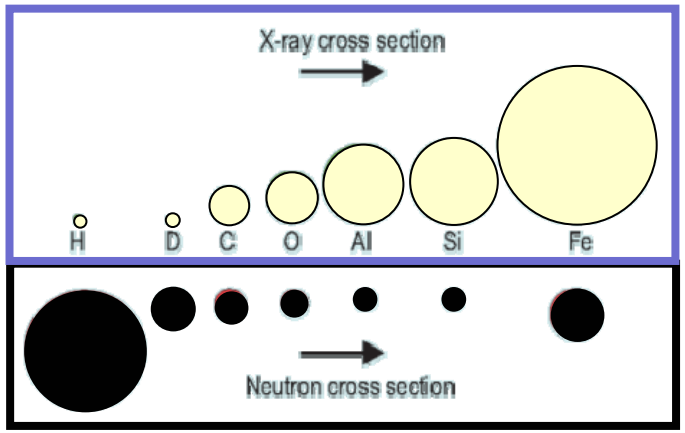
- **Investigate diffusion of multiple species through control of isotopics in solution and in the solid/gel**

Progress:

- **Prediction of results using geochemical modeling software**
- **Experiments have been initiated… solution exchange ~March 2011**
- **Established ICP-MS analysis protocol for isotope isolation**



Water Dynamics Study by Quasi-elastic Neutron Scattering



Goal:

- **Direct measurement of the diffusion constant of water in various structural configurations**

Experimental:

- **Sample characteristics:**
  - 10, 6, 2, and ~0 mol% water
  - Several corroded powders
- **NIST Center for Neutron Research: September 24th-October 8th, 2010.**
  - High Flux Back Scattering (HFBS)
  - Disk Chopper Spectrometer (DCS)
- **Hydrogen scatters neutrons strongly**
- **Glasses were made with low neutron cross-section isotopes**
- **Neutrons gain or lose energy from interaction with diffusing hydrogen in water (quasi-elastic)**
- **Plan to correlate with other techniques** *(e.g. SIMS, RBS/ERDA, NRA)*

Melting High Water-Content Glasses For QENS Diffusion Tests

Material: *Sodium boro-alumino-silicate glass contained in a welded platinum vessel*

Dopant: ***0, 2, 6, and 10 mol% H_2O***

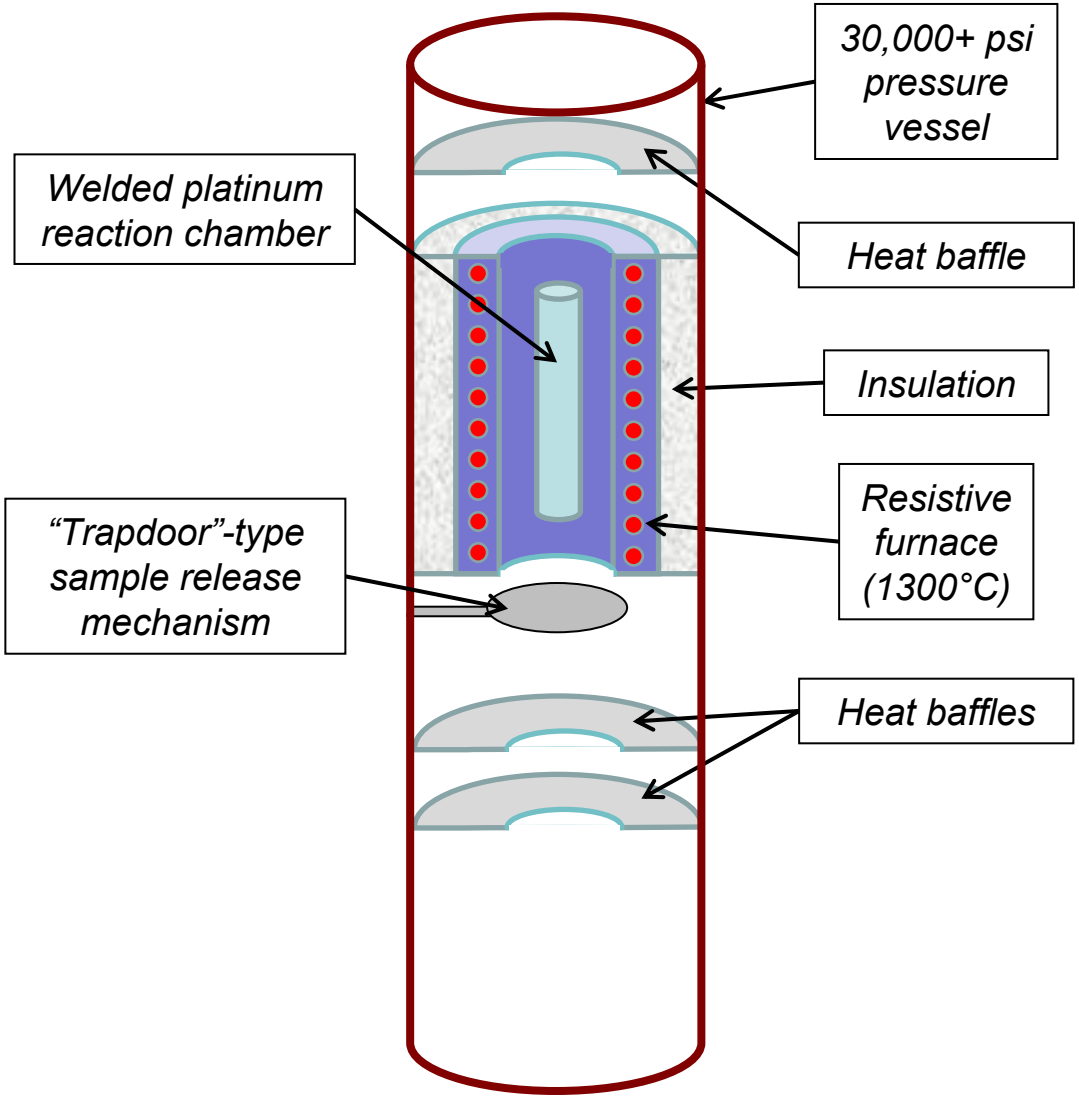
Mass of glass: *~5g*

Volume of glass: *~2 cm^3*

Temperature (hot zone): *1200°C*

Pressure: *~30,000 psi*

Dwell time @ max temp: *2 hours*



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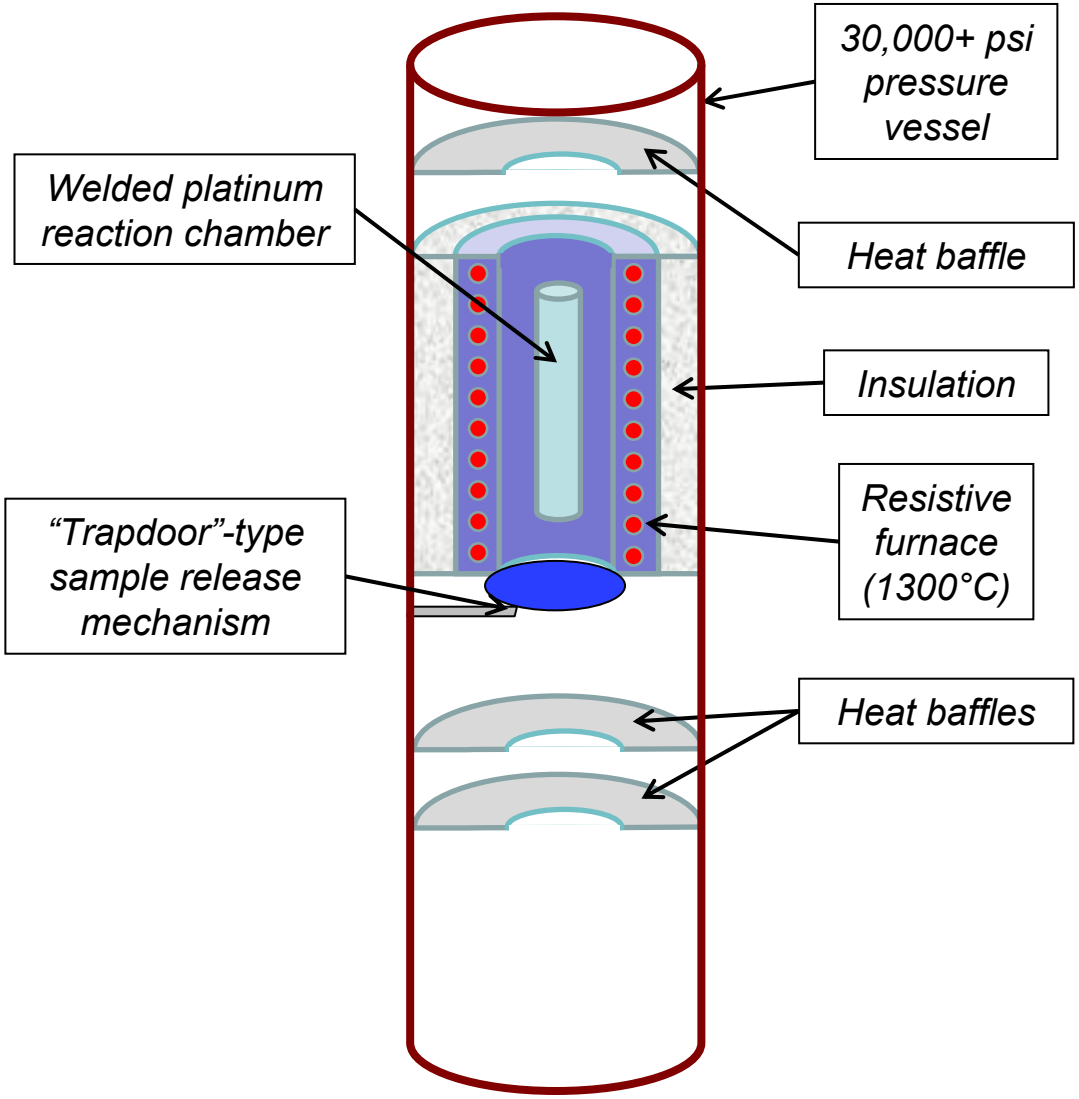

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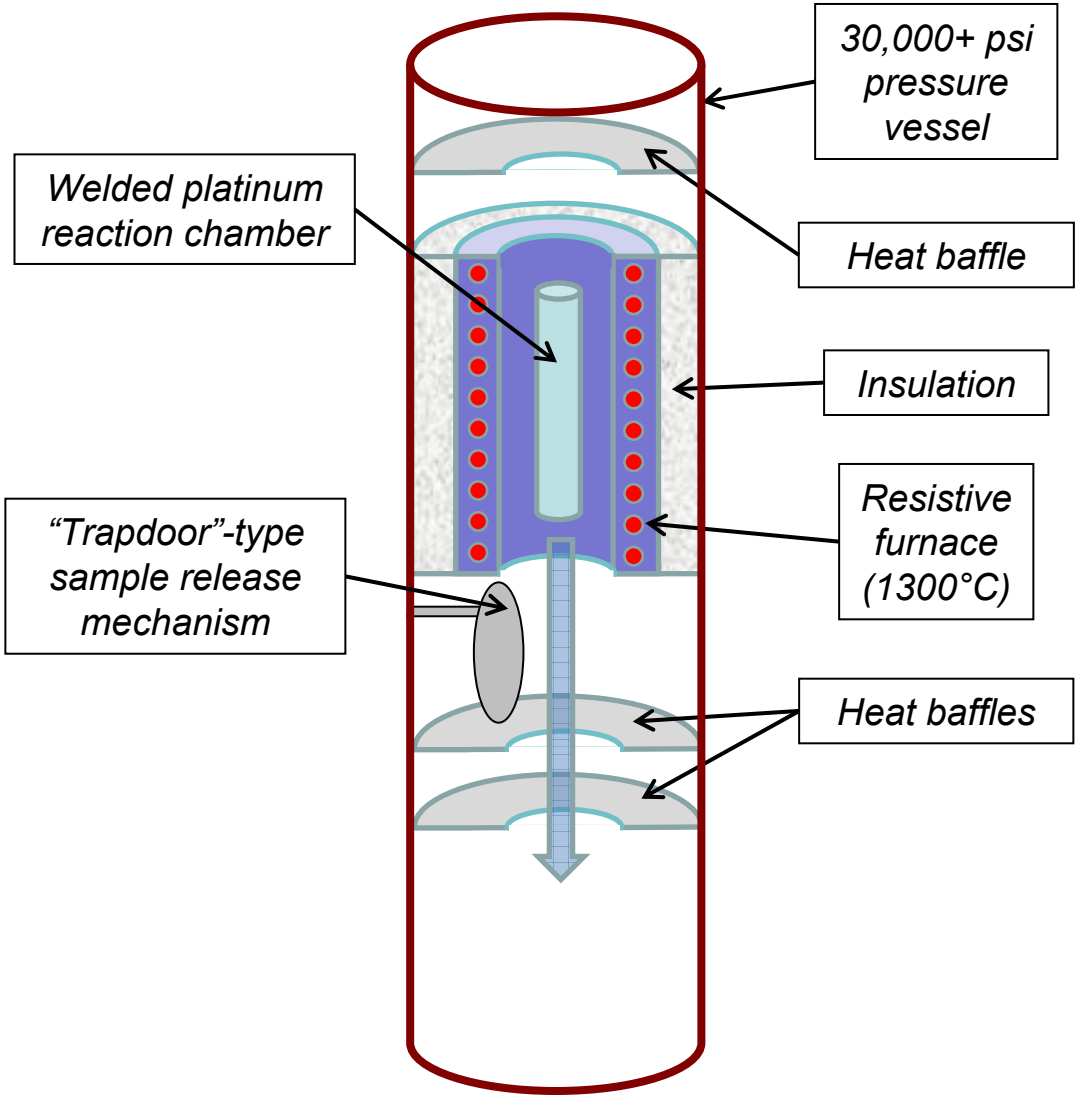

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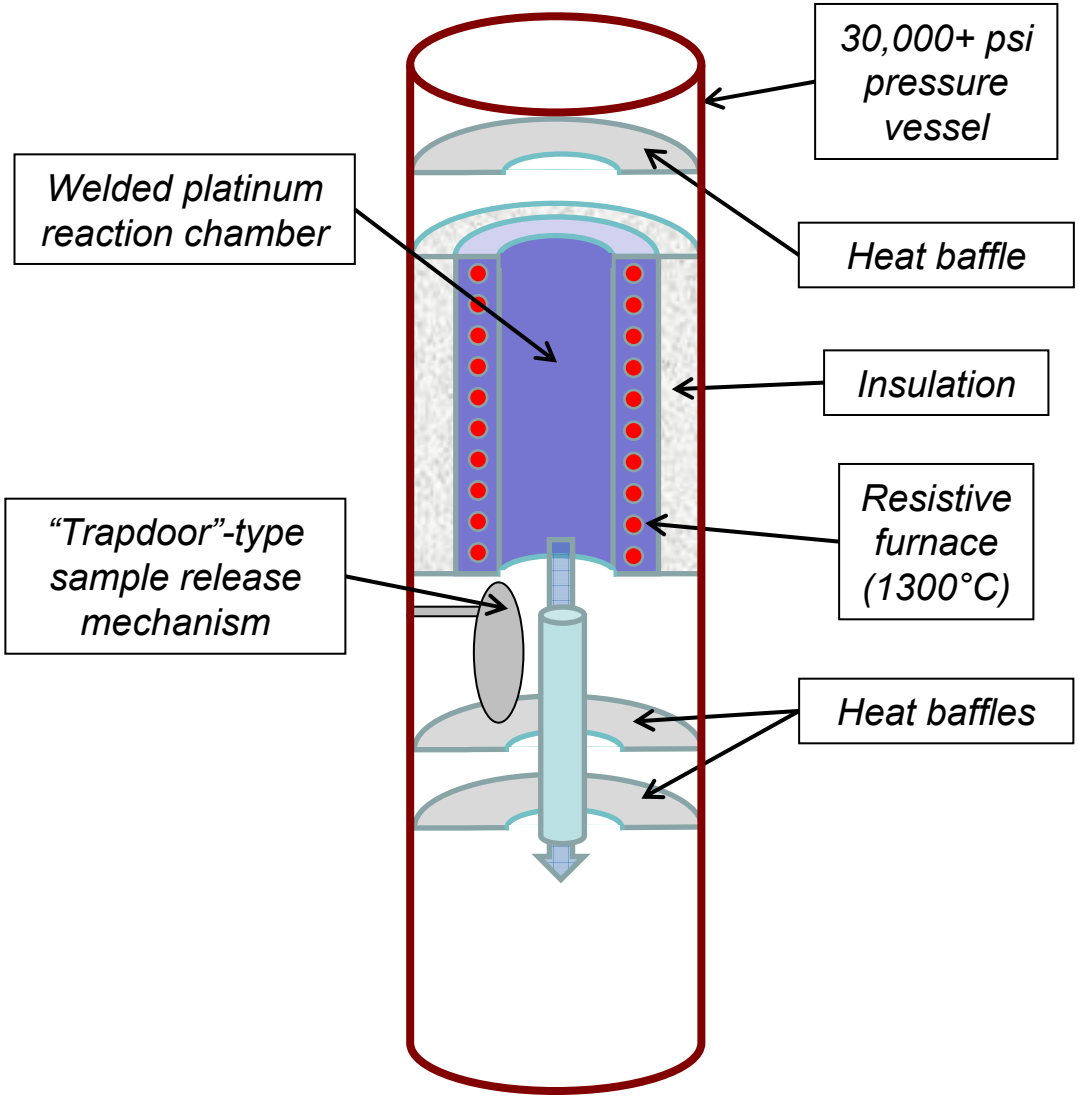

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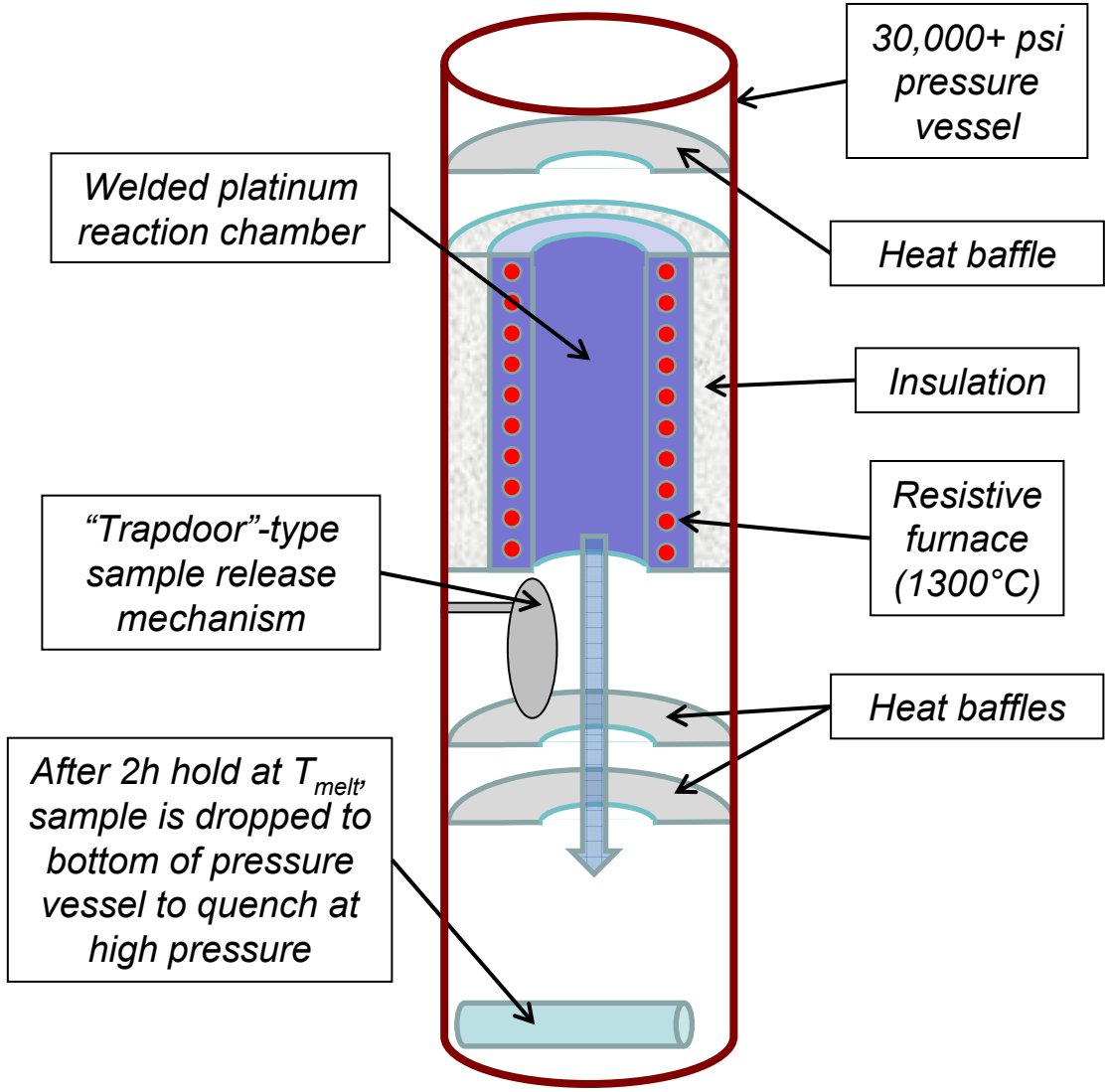

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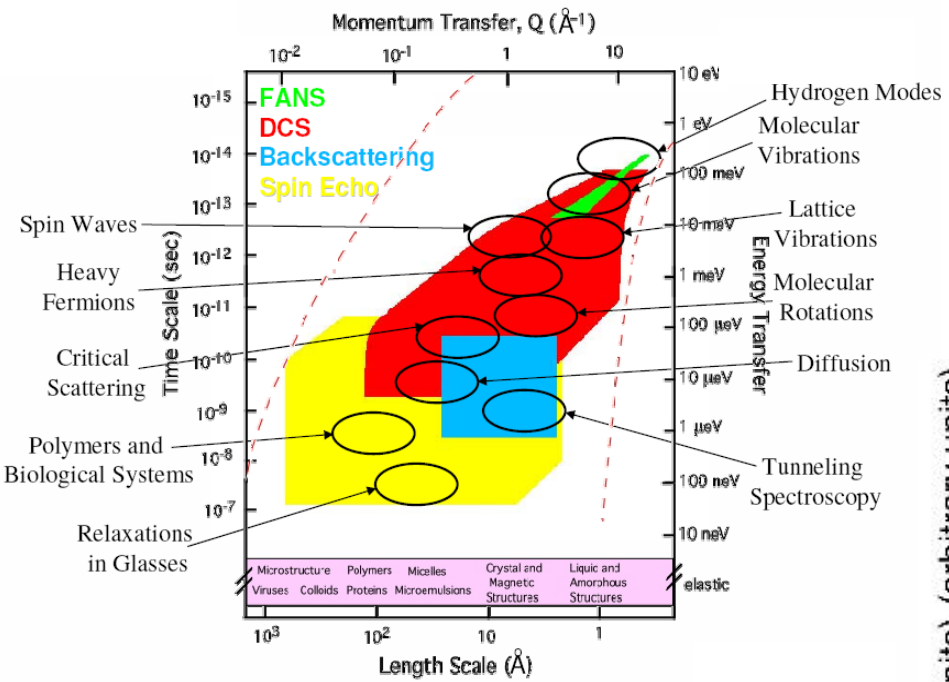
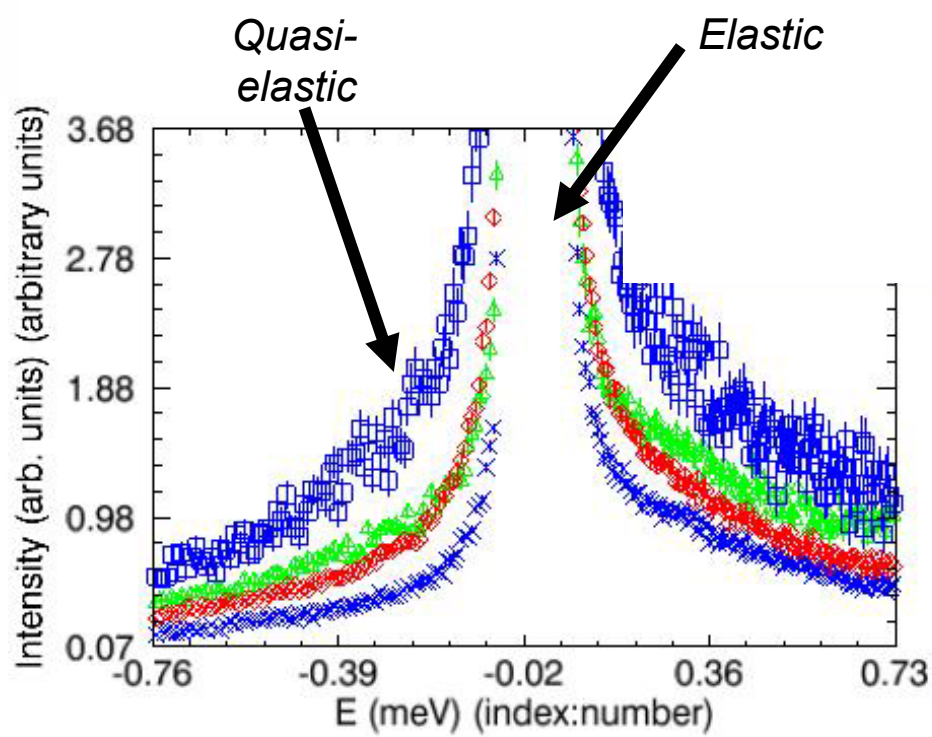


NIST NCNR summer school 2007 (John Copley)

- *High SA/V static test (333K)*
- *Vapor hydration test (293K)*
- *6 mol% water (293K)*
- *Vapor hydration test (40K)*

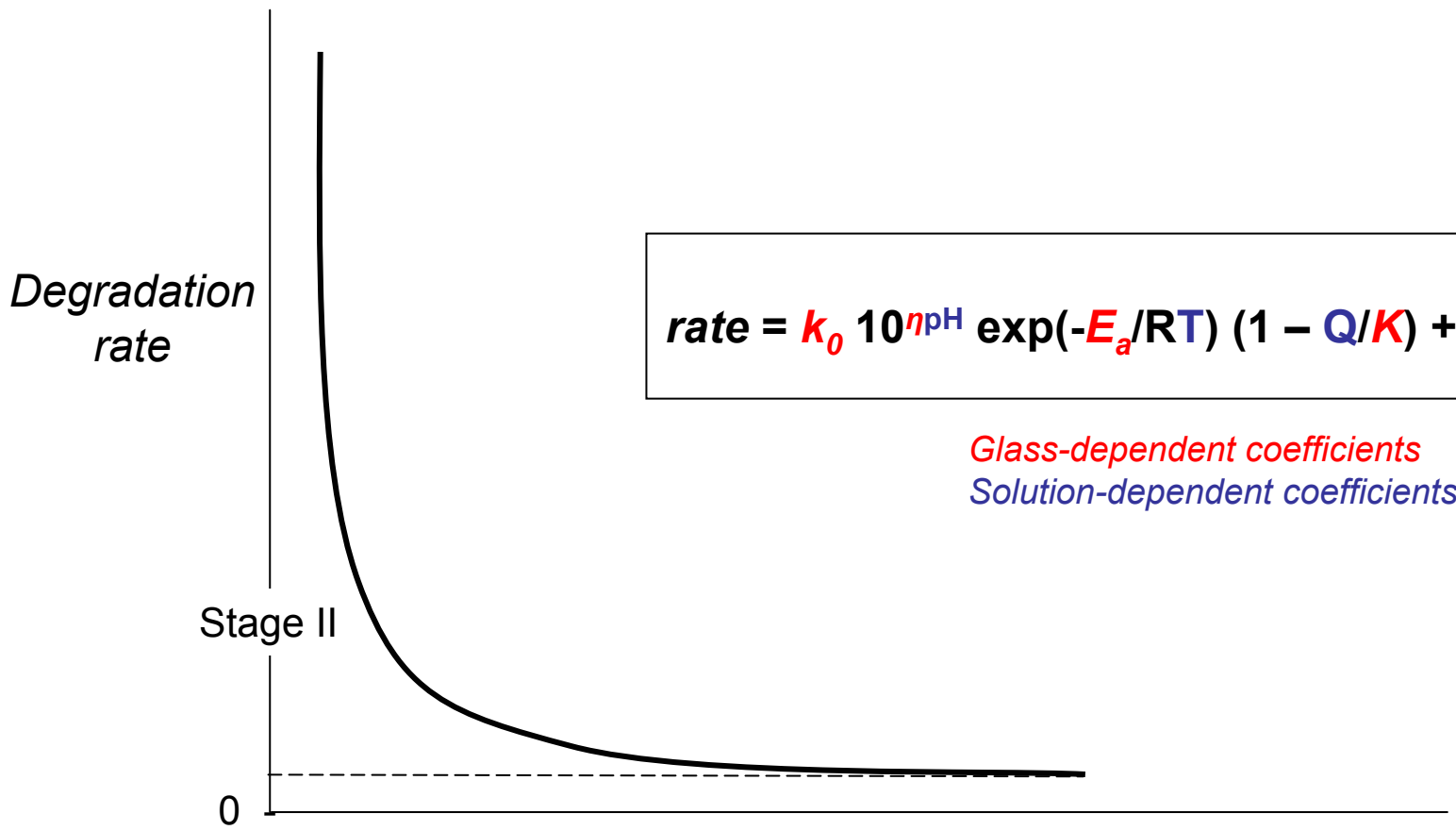


Joint Corrosion Tests: ANL, SRNL and PNNL

Joint Approach:

- **Combine the use of static (PCT), flow-through (SPFT), and MCC-1 approaches for key compositions**
- **Understand dominant processes at different stages of corrosion**
  - Initial reaction in dilute solutions,
  - approach to saturation,
  - effects of alteration phase formation
- **Develop degradation model to represent appropriate process**
- **Measure model parameter values**
- **Confirm degradation model under disposal site-relevant conditions**
- **Support atomistic and continuum models**

Schematic of Affinity Model Degradation Behavior (constant T, pH, S/V)

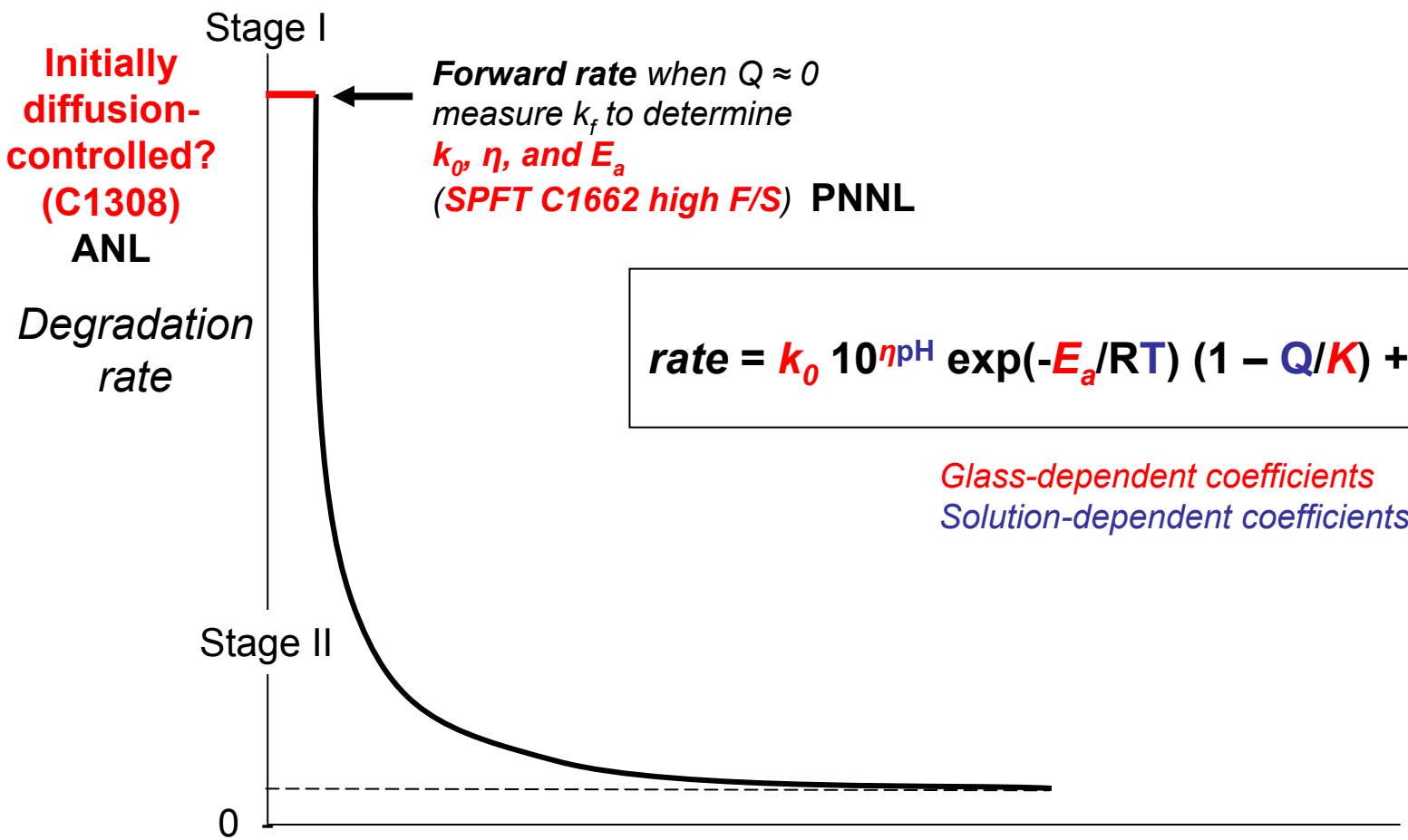


$$rate = k_0\, 10^{\eta pH} \exp(-E_a/RT)\,(1 - Q/K) + rate_{residual}$$

Glass-dependent coefficients
Solution-dependent coefficients

Reaction Progress (amount of glass dissolved- related to time)

Schematic of Affinity Model Degradation Behavior (constant T, pH, S/V)



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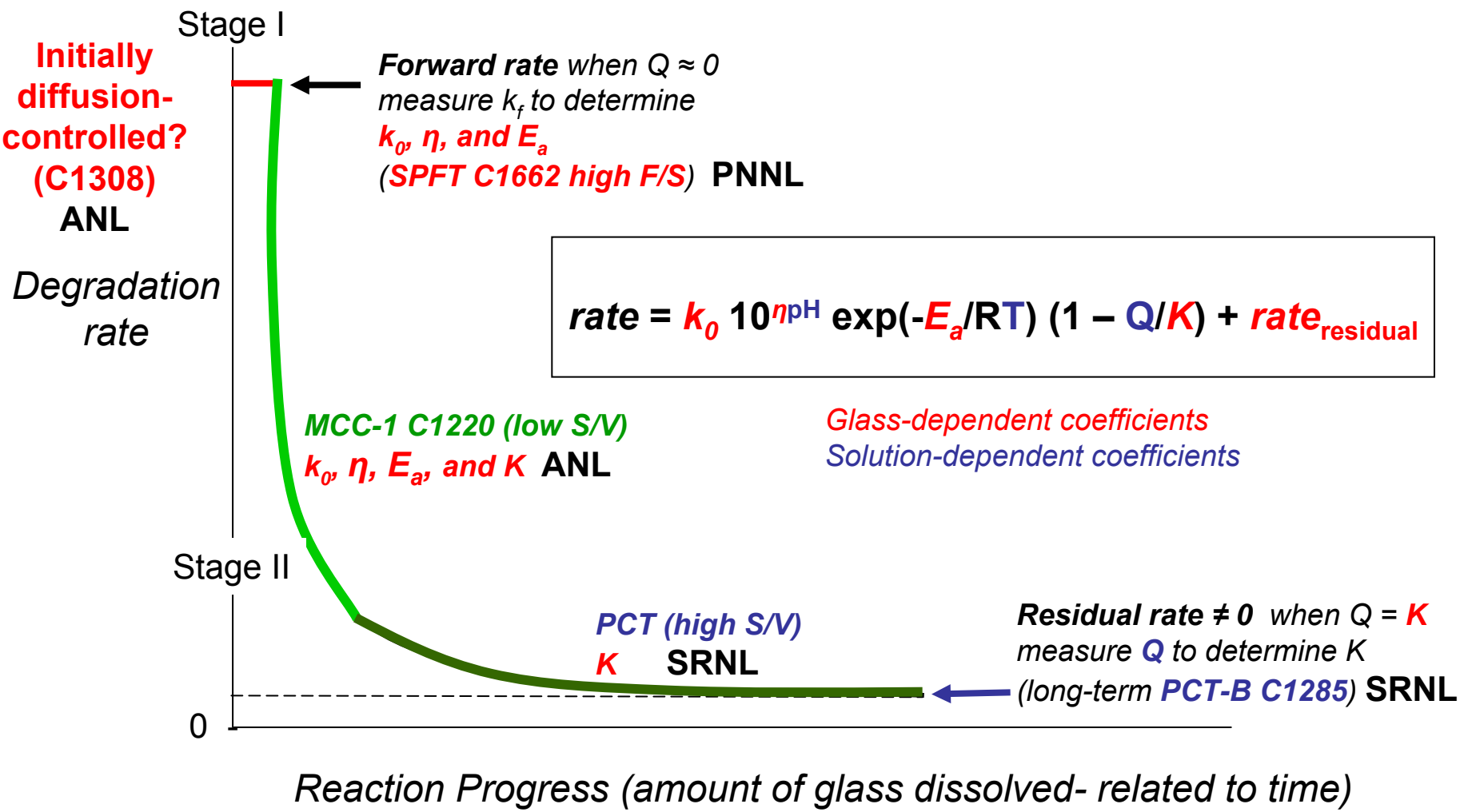
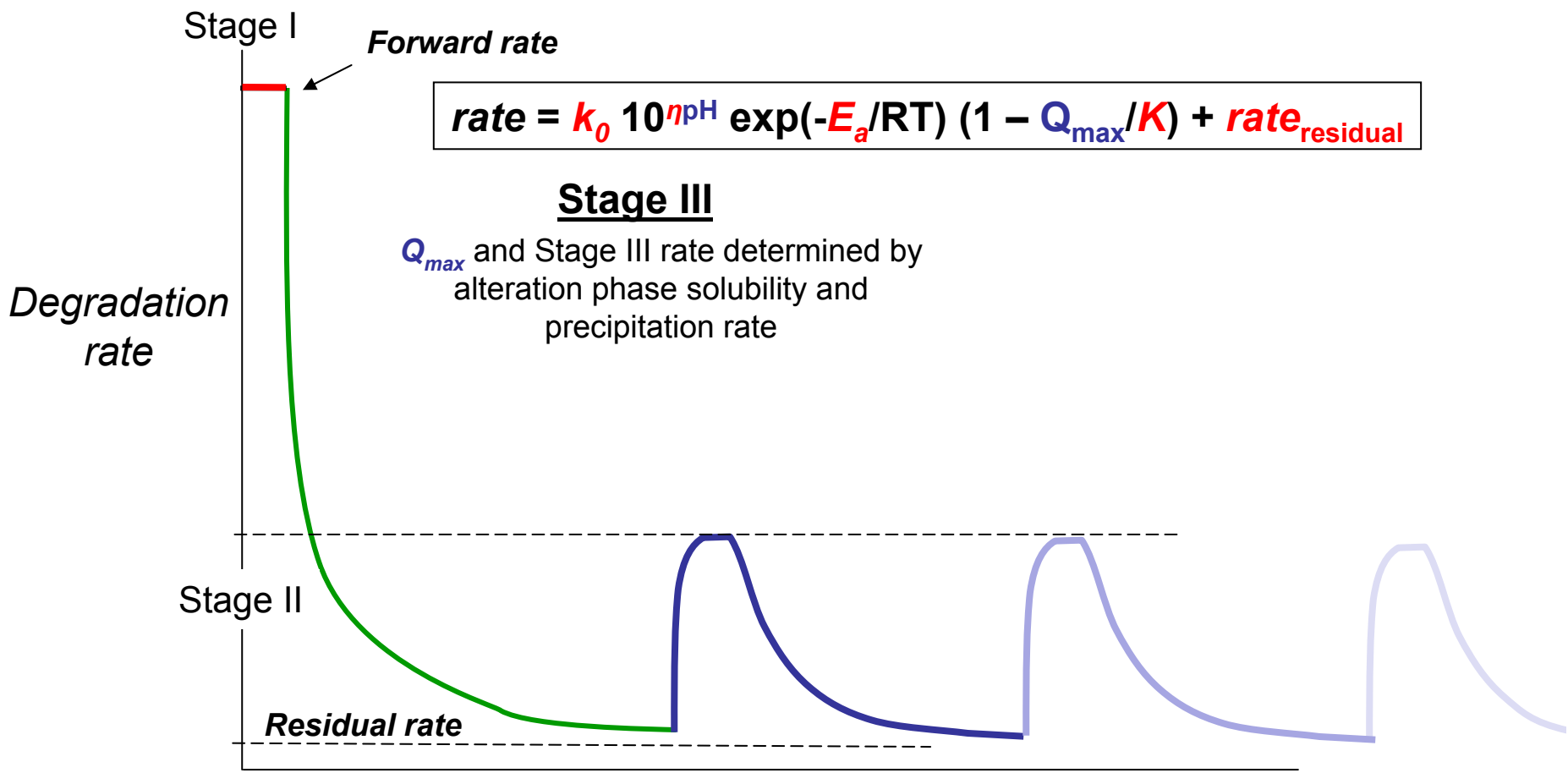


$$rate = k_0\, 10^{\eta pH} \exp(-E_a/RT)\,(1 - Q/K) + rate_{residual}$$

Glass-dependent coefficients
Solution-dependent coefficients

Schematic of Affinity Model Degradation Behavior with Stage III



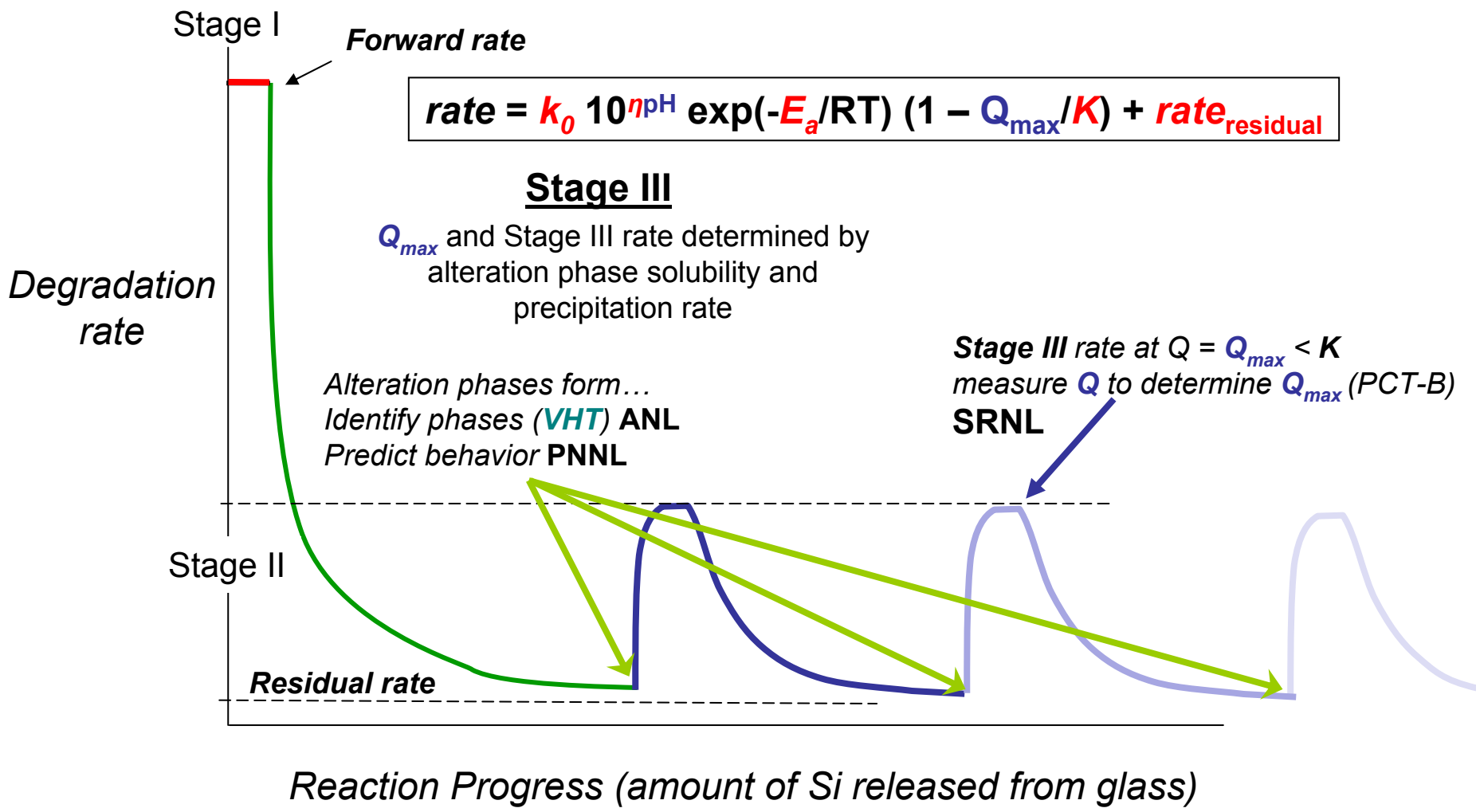
$$rate = k_0\, 10^{\eta pH} \exp(-E_a/RT)\,(1 - Q_{max}/K) + rate_{residual}$$

Stage III

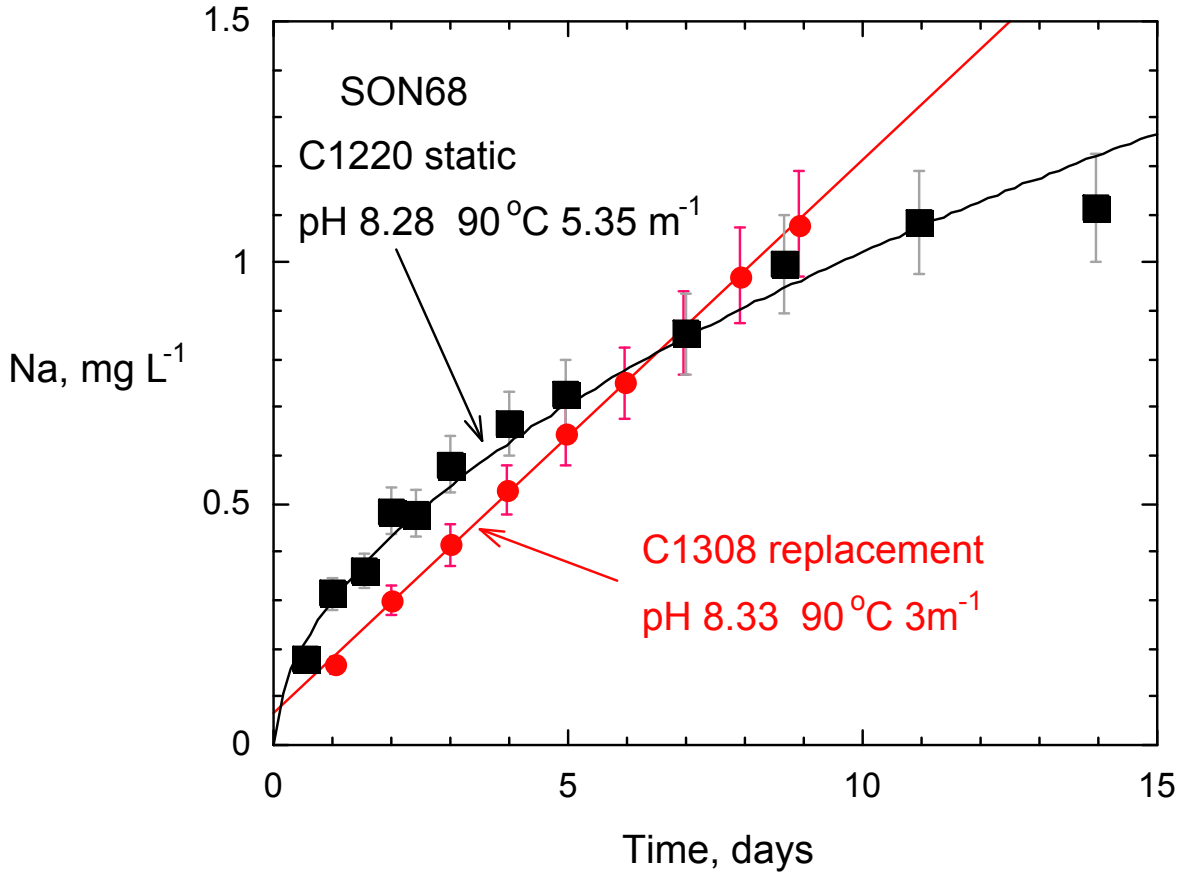
Q_{max} and Stage III rate determined by alteration phase solubility and precipitation rate

Reaction Progress (amount of Si released from glass)

Schematic of Affinity Model Degradation Behavior with Stage III

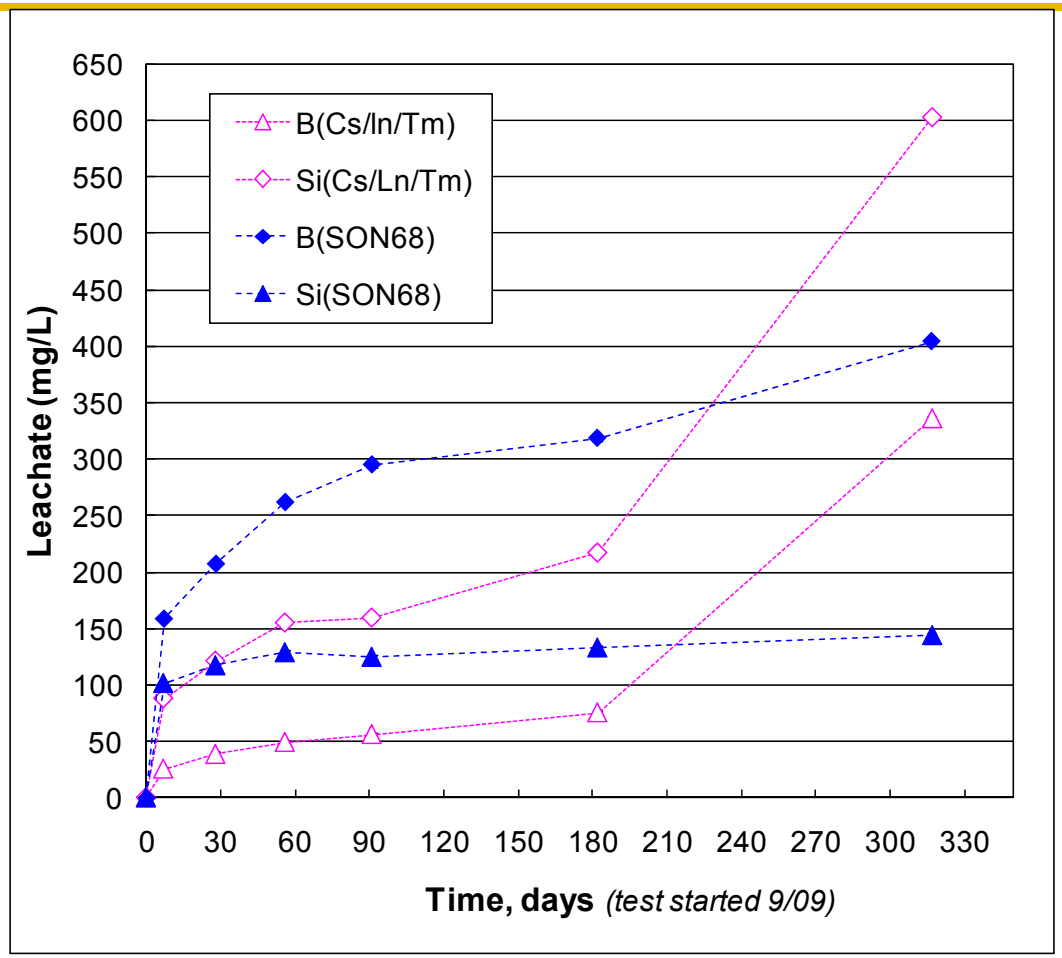


Static and Solution exchange tests at low S/V to study initial dissolution behavior



Initial releases of Na, Li, B, Si from SON68 glass are affected by solution composition.

Long-Term PCT at high S/V to study approach to saturation and alteration phase formation



$$Si = \kappa/(1/t + \kappa/K)$$

$k_f = 0.0065\ g\ m^{-2}\ d^{-1}$
$\kappa = 24.5\ mg\ L^{-1}\ d^{-1}$
$K = 168\ mg\ L^{-1}$

$\kappa = 64.6\ mg\ L^{-1}\ d^{-1}$
$K = 130\ mg\ L^{-1}$
$k_f = 0.017\ g\ m^{-2}\ d^{-1}$

- AFCI glass CSLNTM-1.5 shows Stage III behavior after ~165 days
- SON 68 glass does not show obvious Stage III behavior through 317 days

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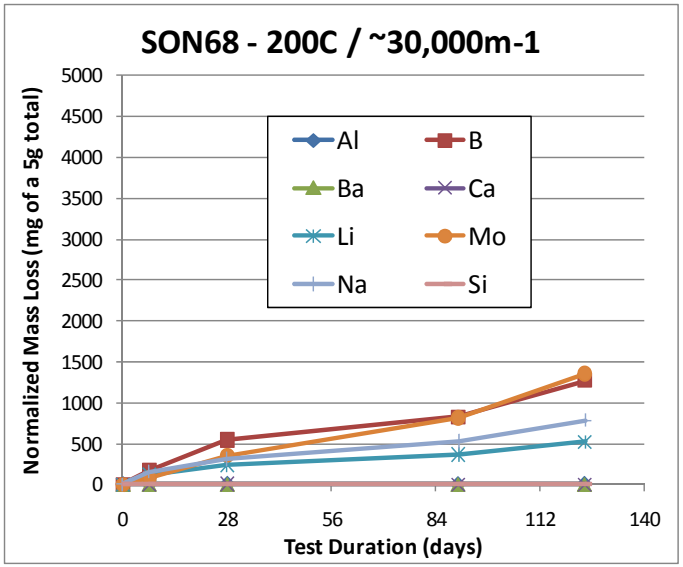
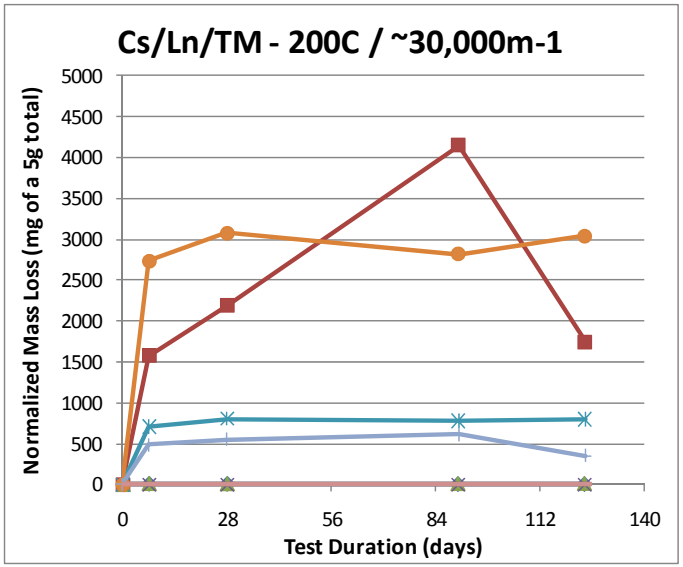
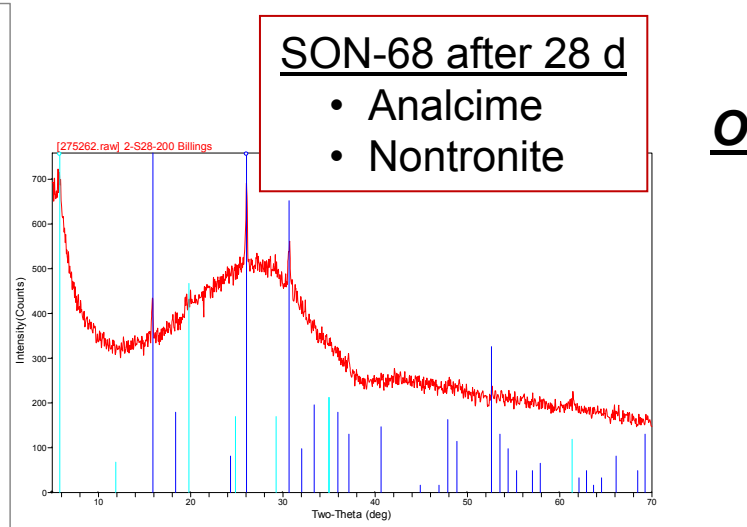
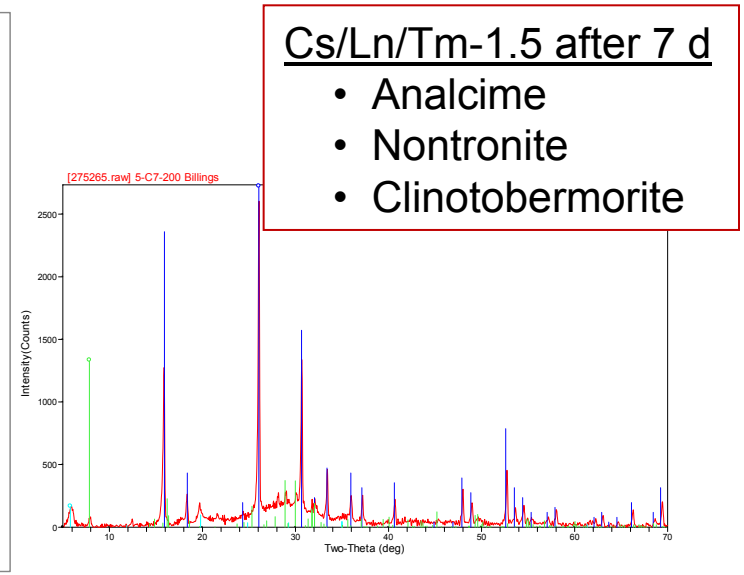
PCT-B at 200º C to Accelerate Reaction Progress and Alteration Phase Formation

Cs/Ln/Tm-1.5 and SON-68









Observations:

- SON-68 glass reacted significantly less
  - Solids appeared "normal" and could be routinely handled after testing
- Cs/Ln/Tm-1.5 glasses highly reacted after 7 and 28 d
  - Noticeable corrosion products on leach vessel
  - Leach solids "gelled" significantly and formed hardened mass after drying

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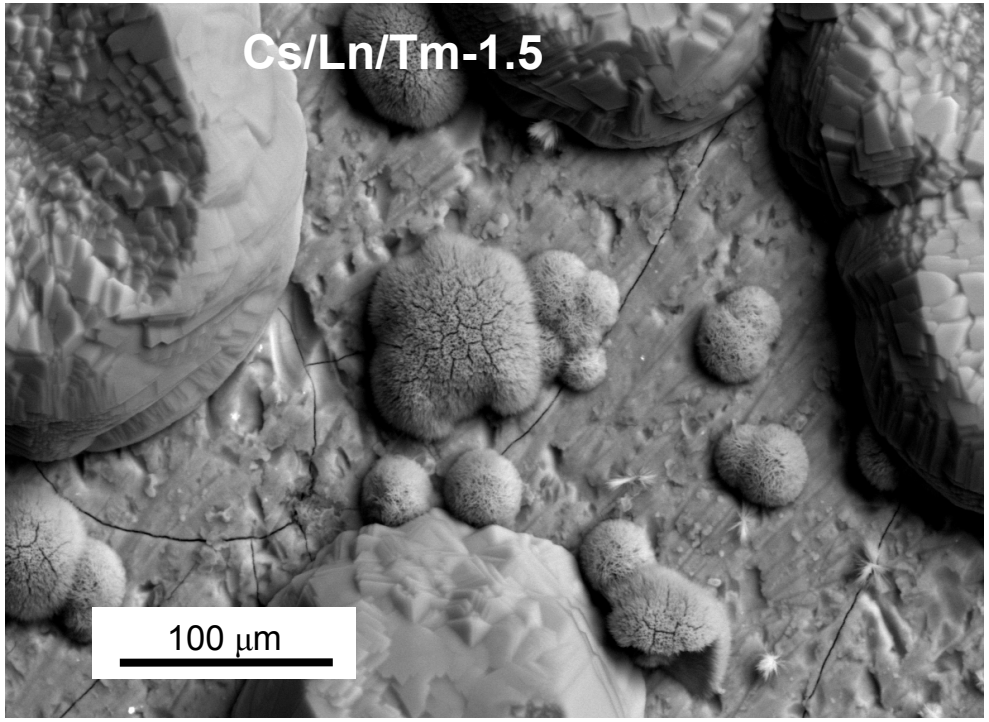
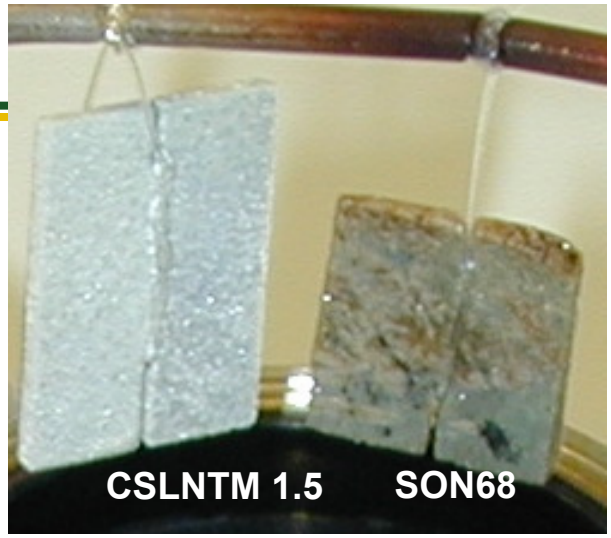
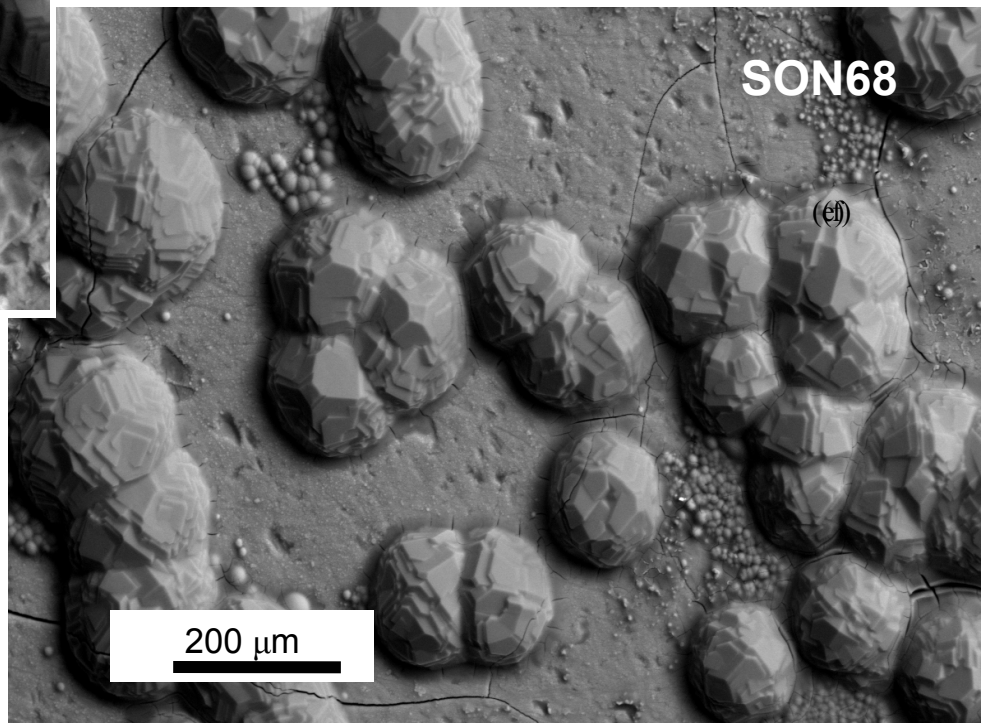
Alteration Phases in VHTs:

38-d at 200 °C







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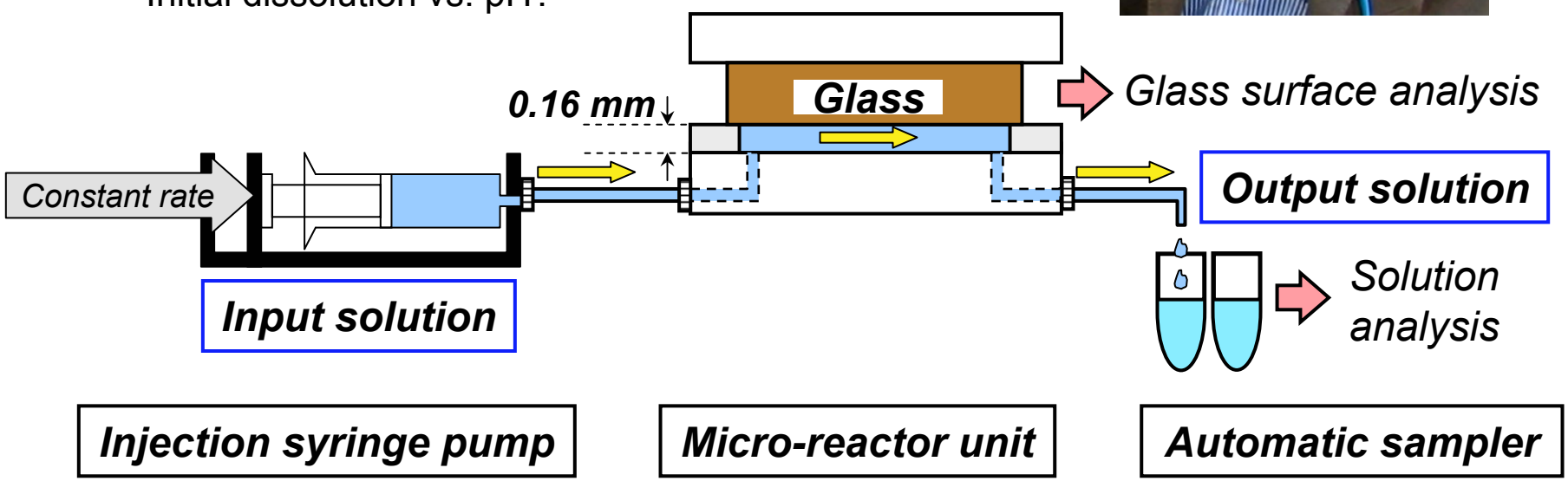
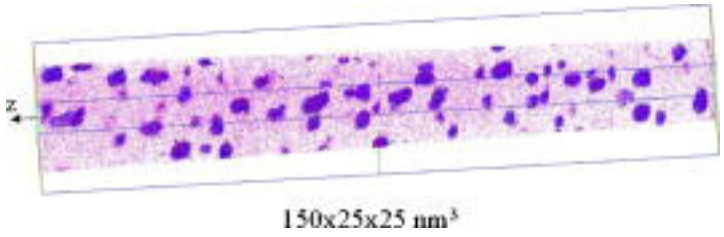
Current Collaboration – *Prof. Yaohiro Inagaki (Kyushu Univ.)*

- **Professor Inagaki recently spent ~3 weeks at PNNL (August 17 – September 11)**
- **Helping to install and expand innovative *microchannel flow-through method***
- **Chemical and structural characterization of various corrosion layers**
- **Exploration of altered surface layer in unsaturated conditions**
  - Protective characteristics?
  - Initial dissolution vs. pH?



Glass Corrosion Research – *2011 Experimental Efforts*



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- **Pacific Northwest National Lab:**
  - **NE -** Enriched isotope studies – DATA!!!
  - **NE -** Study effect of compositional differences on ancient glass corrosion
  - **EM -** pH dependence vs. surface experiment
  - **EM -** Neutron scattering study on the diffusion of water
  - **NE -** Characterize soil-glass system for ancient terrestrial glasses
  - **EM/NE -** Continue multi-condition SPFT experiments (acidic pH, multiple temps, etc.) but extend them into microchannel set-up
- **Savannah River and Argonne National Labs:**
  - **EM -** Continue extended PCT on SON68 and FCRD glass
  - **NE -** repository environment properties – library database
  - **NE/EM -** Conduct tests with synthetic saturated solutions and alteration phases formed in VHTs (Low-flow SPFT, Solution exchange tests, Modified PCT-B)
- **Penn State University (w/ PNNL):**
  - **NEUP -** Surface and interfacial structure effects on / resulting from corrosion

Glass Corrosion Research – *2011 Modeling Efforts*

- **Sandia National Laboratories:**
  - **NEAMS -** Upscaling from atomistic to large scale models
  - **NEAMS -** Cluster monte carlo models of moiety release
- **Lawrence Berkley National Lab:**
  - **NEAMS -** Extend reactive transport modeling to nano-scale, including diffusive motion through constricted pore space
  - **NEAMS -** Continuum modeling
- **Pacific Northwest National Lab:**
  - **EM -** Secondary phase formation
  - **NE -** Finite difference multi-scale modeling
- **Argonne National Lab:**
  - **NEAMS -** Apply *ab initio* models developed for corrosion of feldspar to glass systems
  - **NE -** Coupled near-field and far-field performance modeling *(w/ Sandia)*
- **Pennsylvania State University:**
  - **NEUP -** Cluster models to confirm NMR spectrum interpretation

Joint Glass Waste Form Performance Team:

Mark Aertsens (SCK-CEN), Amanda Billings (SRNL), Ian Bourg (LBNL), Charles Crawford (SRNL), Louise Criscenti (SNL), William Ebert (ANL), Pierre Frugier (CEA), Stéphane Gin (CEA), Bernd Grambow (Subatech), Mike Harrison (UK-NNL), Yaohiro Inagaki (Kyushu U.), Andreas Luttge (Rice U.), James Marra (SRNL), Seiichiro Mitsui (JAEA), Karl Mueller (PNNL), Jim Neeway (Subatech), Carlo Pantano (PSU), Eric Pierce (ORNL), Joe Ryan (PNNL), Alberta Silvestri (U. Padova), Carl Steefel (LBNL), Denis Strachan (PNNL), John Vienna (PNNL), Rick Williford (PNNL)

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