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NEAMS Waste IPSC

Subcontinuum modeling for waste forms

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NEAMS Fall 2010 PI Meeting
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NNSA National Nuclear Security Administration

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Waste-IPSC system model

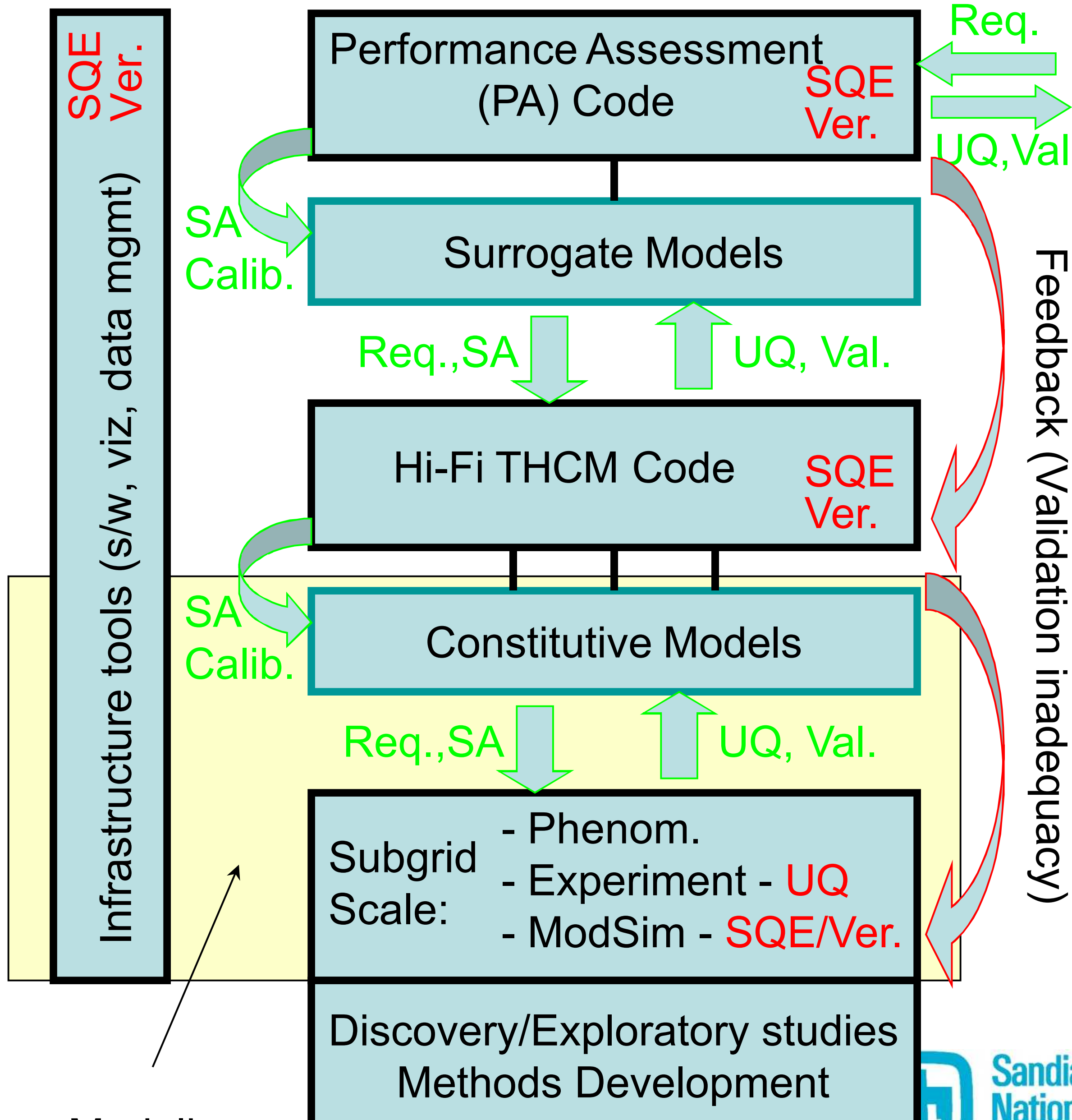
A System with well-defined processes

Requirements-driven (PIRT)

Qualified applications (SQE/Ver.)

VV/UQ'd data flow

Traceability



Subcontinuum Modeling

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Waste subcontinuum overview

- Goal:

Constitutive models for waste form degradation and near-field phenomena that replace phenomenological models (empirical fits) with science(subscale)-based models, improving predictive quality of models, with quantitative confidence. Ultimately: predictive models for radiological source term from degrading waste.

- Partners/collaborators/coordination …
  - FMM: fundamental methods capabilities, V&V guidelines
  - VU: development of VV-UQ for upscaling, V&V guidelines
  - FCRD Waste Campaign and UFD: validation data, experimental knowledge
  - Leveraged efforts: e.g. BES, NEUP, …

- Overall scope:
  - Waste forms: Glass, ceramics, metals, UNF, …
  - Barriers: oxidizing/reducing, clay/salt/granite/tuff, …

- Challenge problem downselect: glass
  - Other waste forms to be brought on in stages

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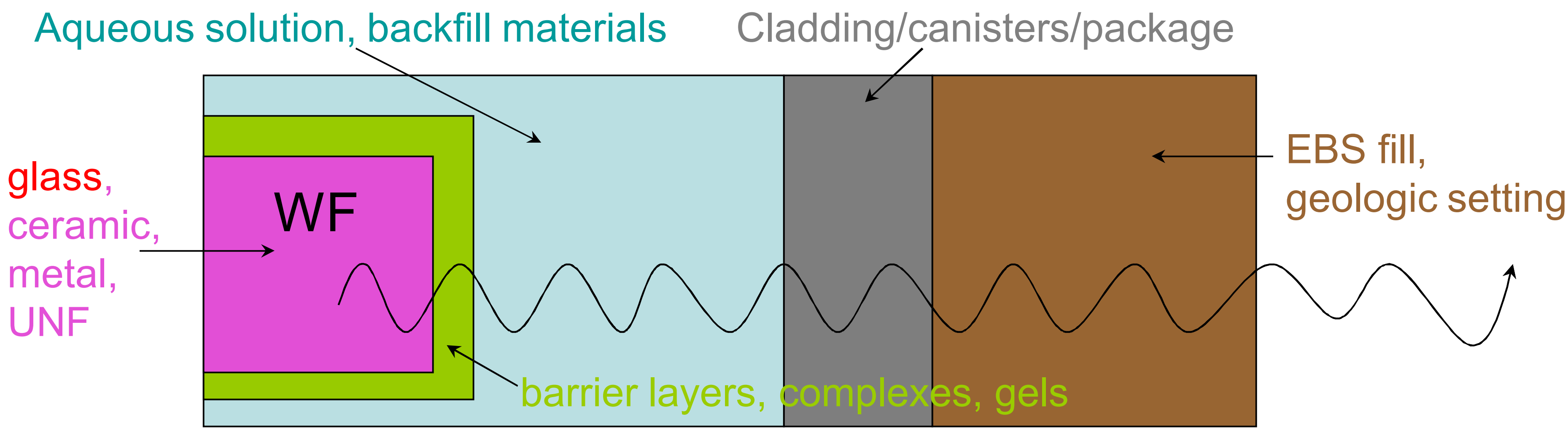
Challenge Milestone 2
Waste form and waste package



- Convergence of divergent continuum PIRTs:
  - From subcontinuum perspective, waste+environments are similar
  - Glass to start (and to prove approaches)
  - Later: ceramics and metals (contingent on support and success)
- Challenges
  - Science within scale - local chemistry right (e.g., solvation, f-electron?)
  - Upscaling - propagating mechanistic processes into collective behavior
  - Time scale - extending defensible predictions to geological time scales

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Glass waste role in waste disposal performance

- Historical (e.g. Yucca Mountain) radiological release rates “pessimistic”
  - Very conservative to enable defensible estimates
  - Place heavy dependence upon engineered barriers to meet margins
- Glass durability may extend isolation of radionuclides, performance of disposal
  - Glass - archeological and geological - has slower long-term degradation
  - Coupled chemical processes decrease short-time degradation rates
  - Durability of glass is important component to disposal performance
- Steps in degradation process
  - Initial attack - direct glass-aqueous contact, with fast dissolution
  - Evolution - formation of alteration layers (gels, secondary phases)
  - Maturation - steady state, slow long-term degradation
  - Reinitiate attack - exposing new pristine glass surfaces

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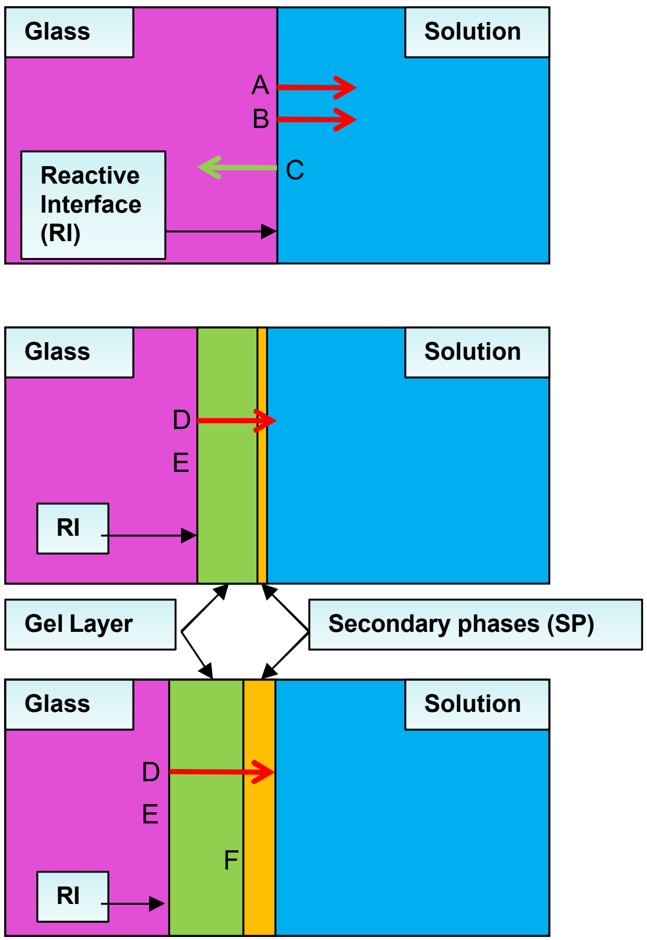
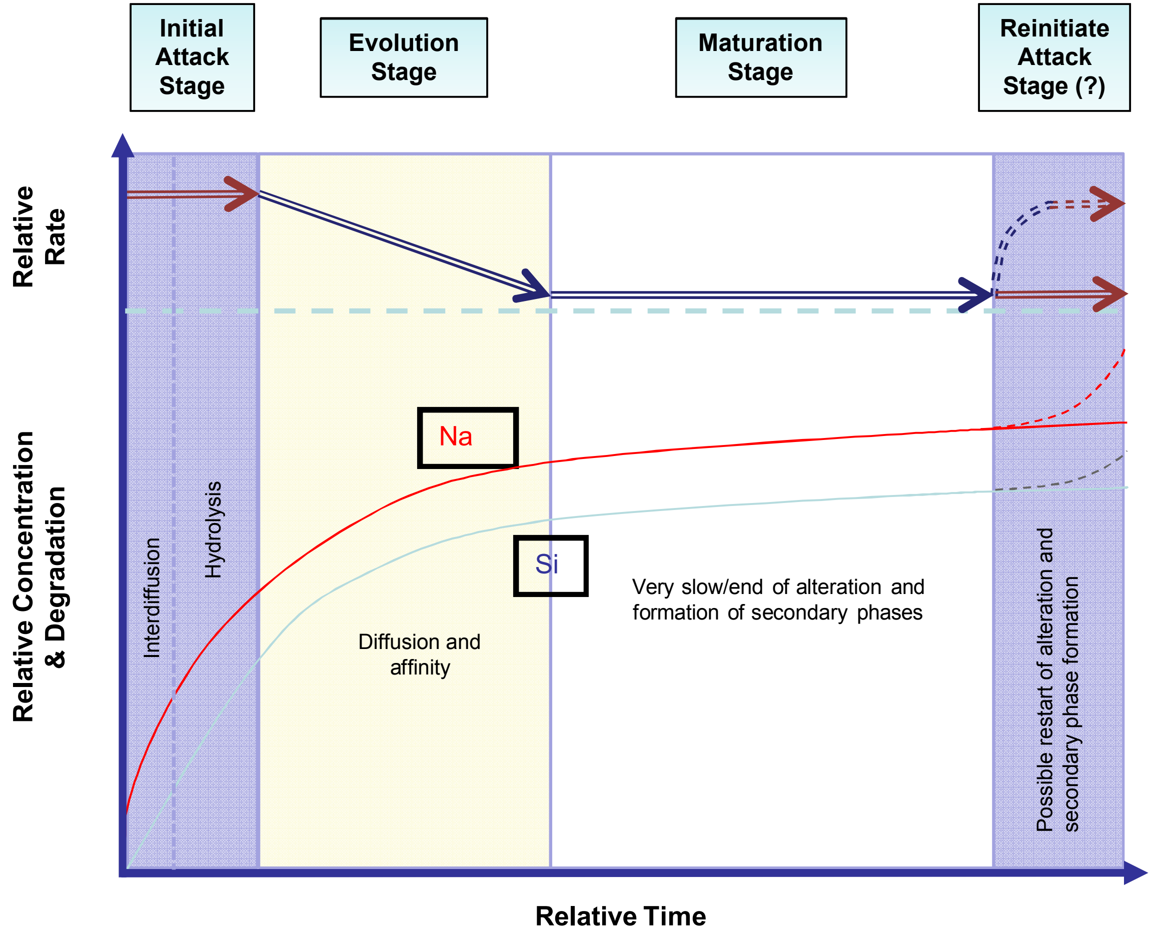
Anatomy of glass dissolution

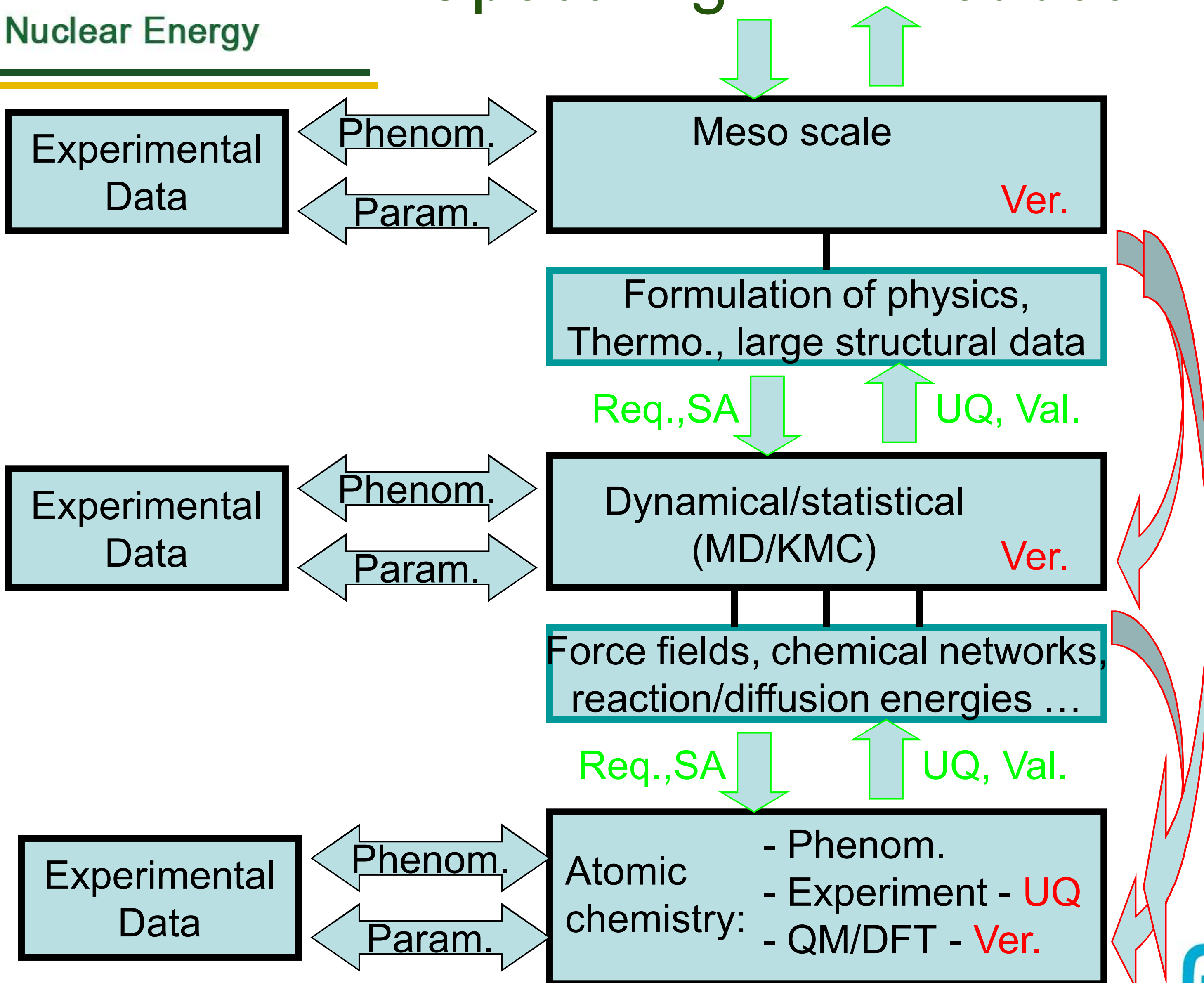




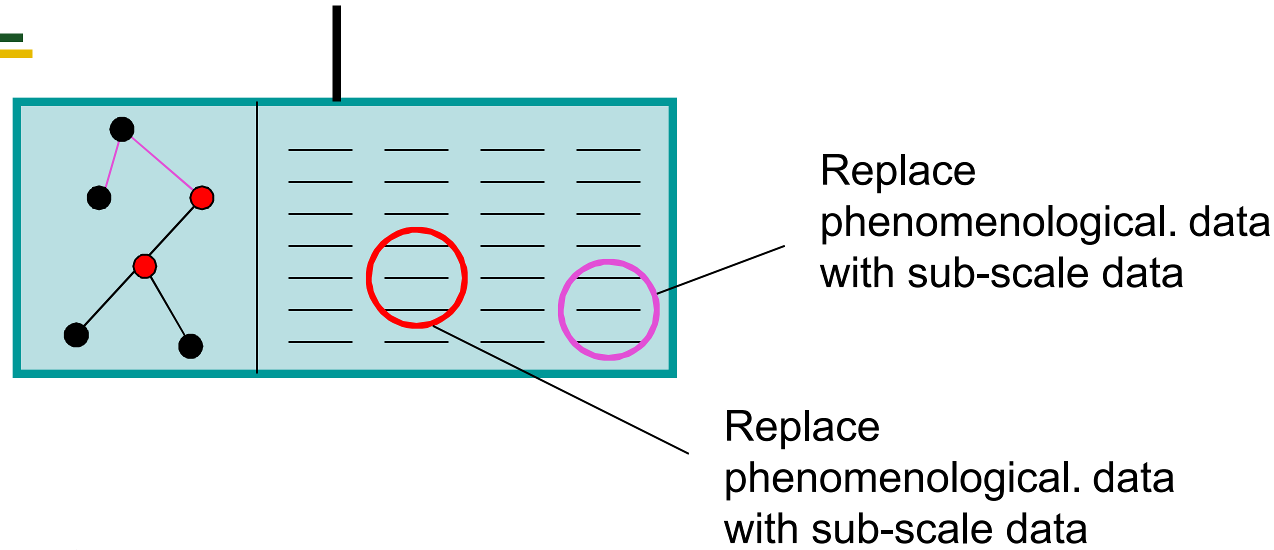
A – rate of alkali surface release
B – rate of Si, Al surface detachment (tends to be limiting)
C – rate of H_2O diffusion into glass

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

Upscaling within subcontinuum



Upscaling - “A miracle happens”



Two challenges:

1) accuracy of parameters
2) adequacy of physics abstractions

Model parameters always refit (calibrated) for validation of application

Internal consistency (e.g. thermodynamic)
Model incompleteness

Physics abstraction mixes parameters (dependencies)

and may not be (quantitatively) reducible to sub-scale processes

Bridging this divide is unsolved challenge: more failures than successes

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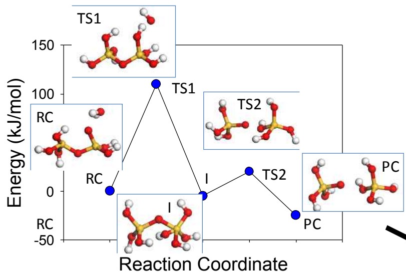
Aluminosilicate dissolution - upscaling gaps

Gap 2

❖Mesoscale models are used to test dissolution scenarios – not completely predictive.

❖Not clear how to link mesoscale models directly to continuum models or develop new constitutive equations from them.

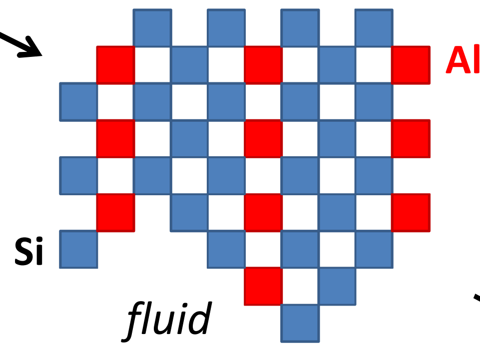
Atomic/Quantum



Ab initio cluster calculations to determine bond-breaking energies

Gap 1

"Mesoscale"



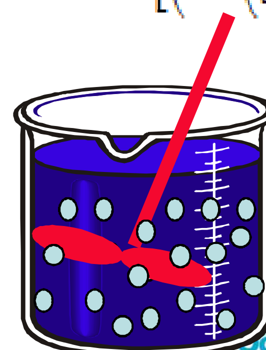
Stochastic Monte Carlo Modeling of the dissolution and re-precipitation of crystal units SiO_4 and AlO_4

Constitutive equations developed to fit leach data from bulk experiments.

Continuum

Gap 2

$$r = k \prod_{i=1, i\neq k}^{i} \left[\frac{K_i \left(\frac{a_{H^+}^{v_i}}{a_{M_i}^{v_i}} \right)^s}{\left(1 + K_i \left(\frac{a_{H^+}^{v_i}}{a_{M_i}^{v_i}}\right)\right)^s} \right]$$



Gap 1

❖No consensus on how activation energies for bond-breaking should be modeled in cluster calculations

❖Not clear how to go from the energy of breaking one bond to dissolving "crystal units"

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Upscaling strategy - incremental complexity

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

Upscaling strategy - downscaling, too

- Start with corroded archeological/geological glass …
  - Natural or archeological analogs of long-term corrosion of glass
- … formulate reactive transport model to reproduce observed behavior
  - Reactive transport models for millimeter-scale simulations
  - Discover and test formulations that describe long-term evolution
  - Interim stage: phenomenological constitutive models
- … associated elements of model with underlying chemical process
  - TST interpretation in terms of activations barriers: reaction/diffusion
  - Postulate a chemical interpretation to reactive transport model
- … use lower scale methods (e.g., MD) to test formulation and parameters
  - Bulk/surface/gel … cracking, porosity contributions to surface area,
  - Test-verify/validate downscaled model
  - Mat: phenomenological models
- … connect to upscaling subcontinuum models
  - Mature stage: refined subcontinuum-based constitutive models
- … develop/refine constitutive models for continuum scale dissolution

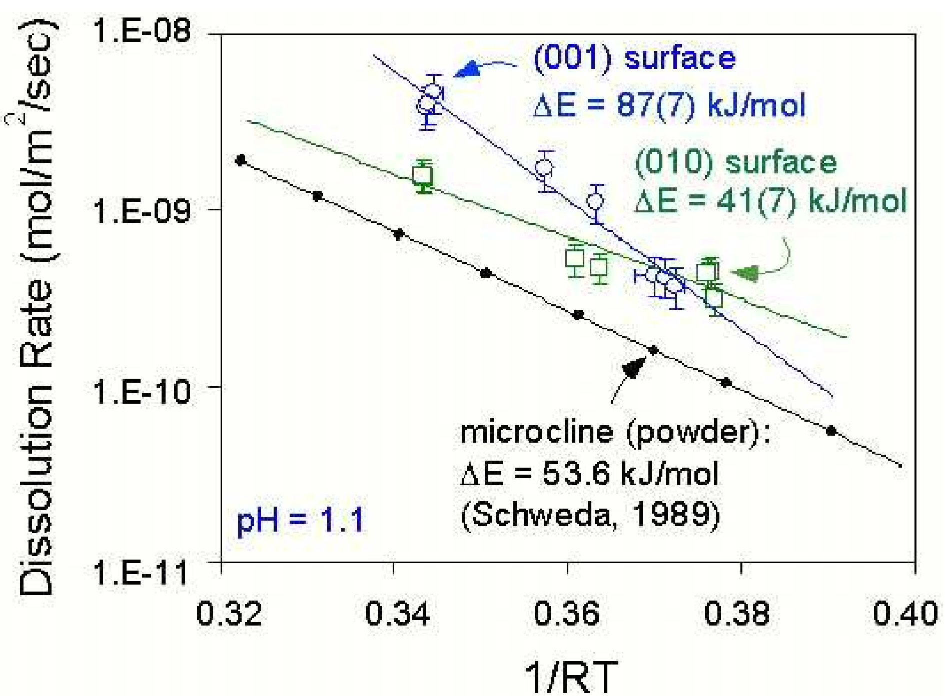
Upscaling: Dissolution of orthoclase

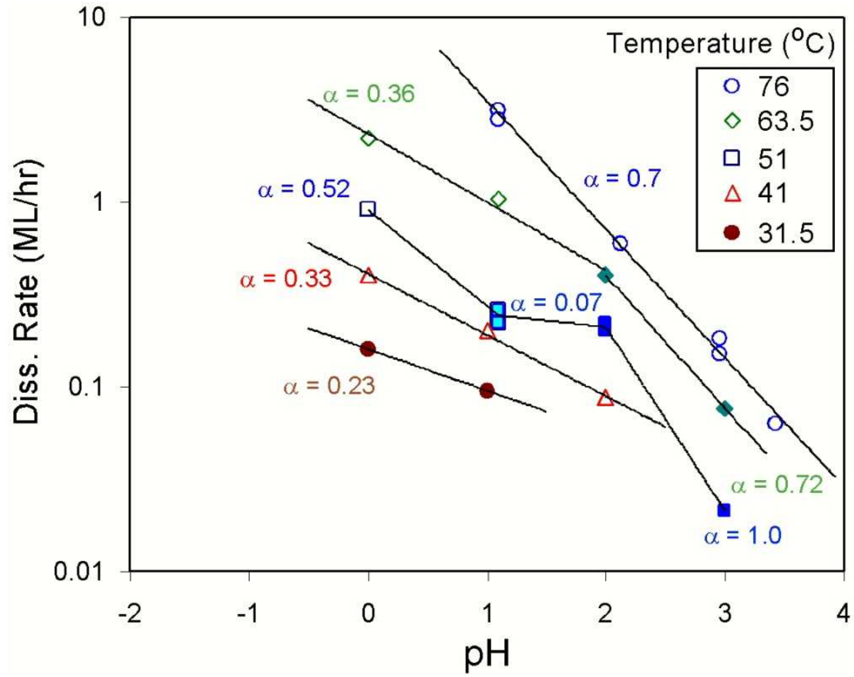
Zapol, Cunnane, et al. (ANL)

"Simple" case: orthoclase $KAlSi_3O_8$ surface dissolution

- Different surface orientations have different rates*
- The rates have pronounced temperature and pH dependence
- Forms secondary phases , PRI
- Experimental data and support are available

$$\text{Rate} = A \exp(-\Delta E/RT)\,[H^+]^{\alpha}$$





- Model development on well-characterized systems will lead to quantitative approaches to glass dissolution

*P. Fenter et al., *GCA*, **67**, 197-211 (2003)

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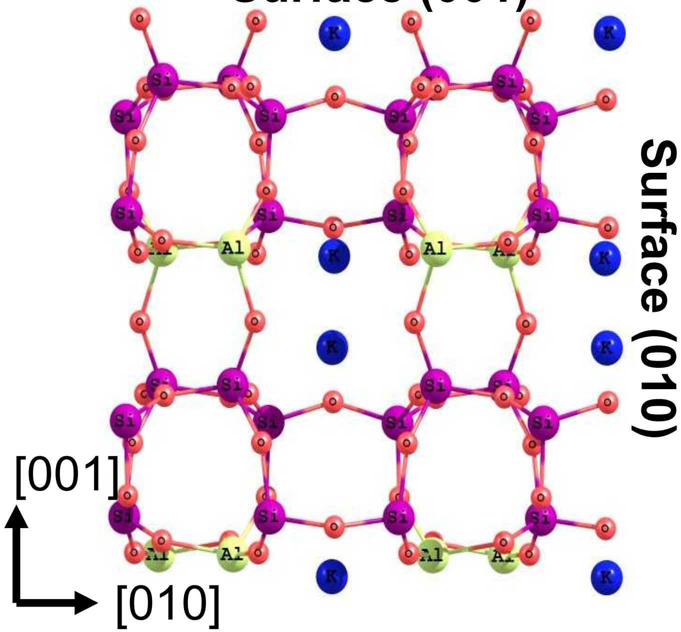
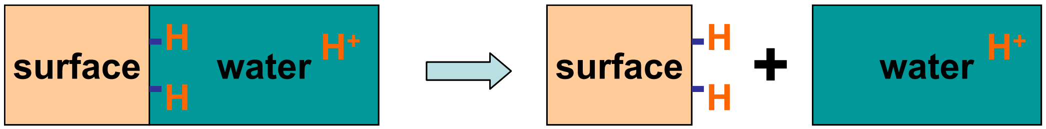
Upscaling:
Orthoclase - DFT models of surface sites

Surface (001)



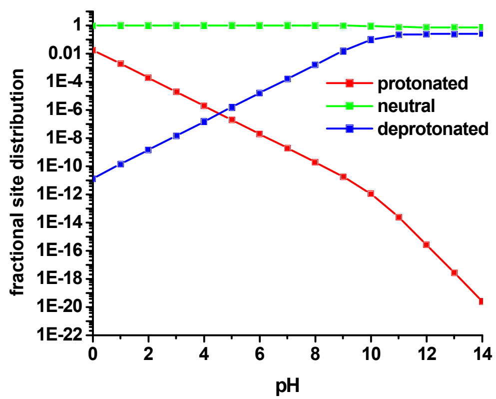
Model

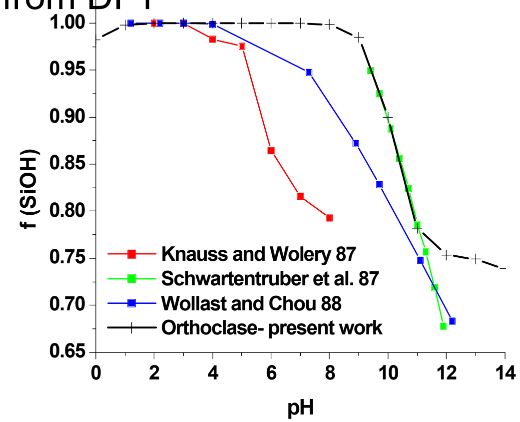


Calculation of free energy change ΔG_j for each state j

$$\Delta G_j = E_j\left(\text{surf} + n_j \text{H}^+\right) - E(\text{surf}) - n_j \mu(\text{H}^+, \text{aq}, \text{pH})$$

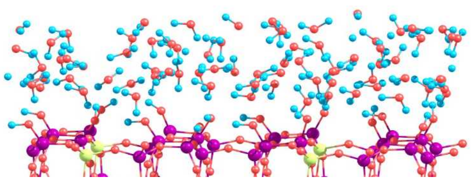
where surface energies are from DFT





F(SiOH) vs Quartz expt. data

Water structure from MD



- Site distribution of Orthoclase Si-rich surface is in agreement with experimental data for quartz

Calculated point of zero net proton charge ~ 4.5
Comparable to expt. value of 3.0 - 6.1 (feldspar)*

*L. L. Stillings, et al. GCA 59, 1473 (1995).

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Upscaling: Glass dissolution gaps

Gap 2

❖Mesoscale models are used to test dissolution scenarios – not completely predictive.

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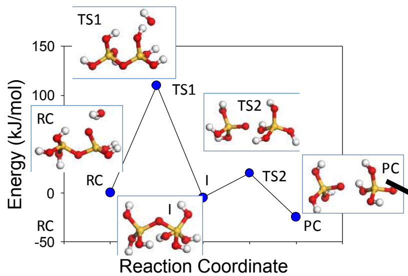

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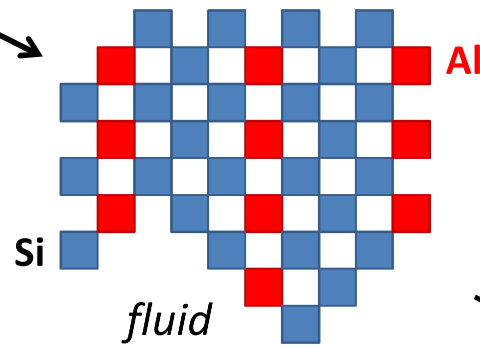

Stochastic Monte Carlo Modeling of the dissolution and re-precipitation of crystal units SiO_4 and AlO_4

Gap 2

Constituitive equations developed to fit leach data from bulk experiments.

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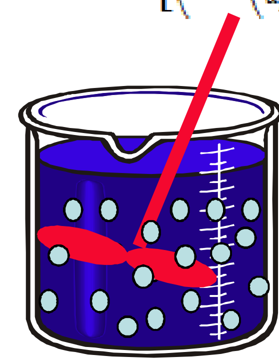

Gap 3

❖Aluminosilicate crystal dissolution → Nuclear Waste Glass Dissolution

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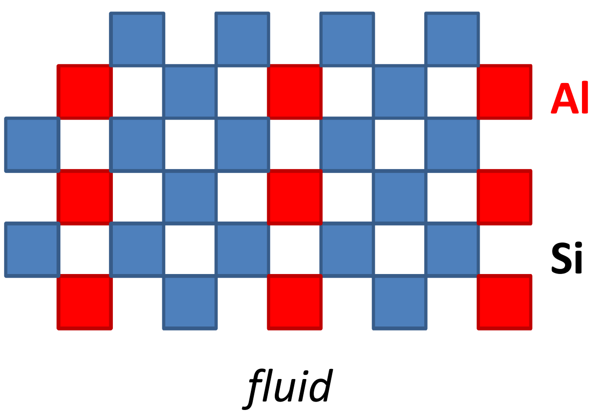
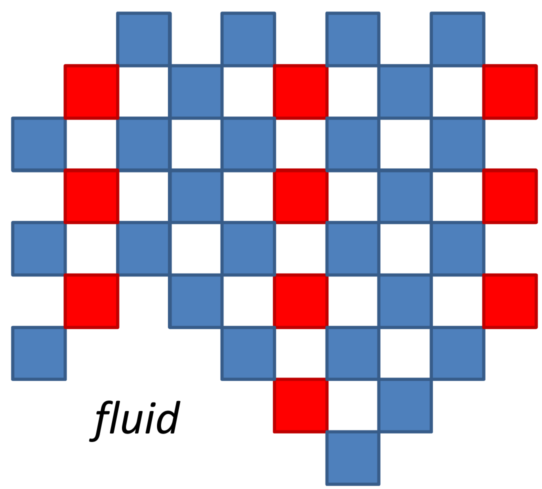
Upscaling: Larger scale feldspar dissolution

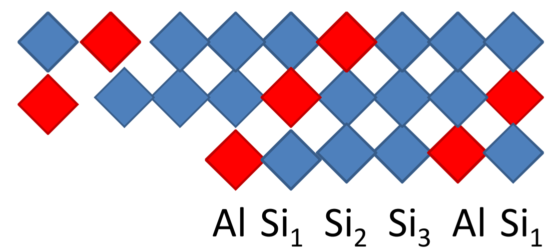
(A) The four coordinated framework is displayed in two dimensions. The $AlSi_3$ stoichiometry is representative of the feldspar series. The reactive surface shown consists of all Q_2 sites requiring two new bonds to attach a new unit.



(B) Surface in (A) after reaction with a fluid. The reactive sites grow (or dissolve) quickly to produce new surfaces.



(C) A diagonal face of the model crystal which grows or dissolves in an orderly step-controlled fashion. An Al kink site is shown. Note the different kink sites produced by the removal of the Al kink atom and subsequent Si atoms along the step. These kink sites are labeled Al, Si_1, Si_2, and Si_3



(***after Lasaga and Luttge, 2005***)

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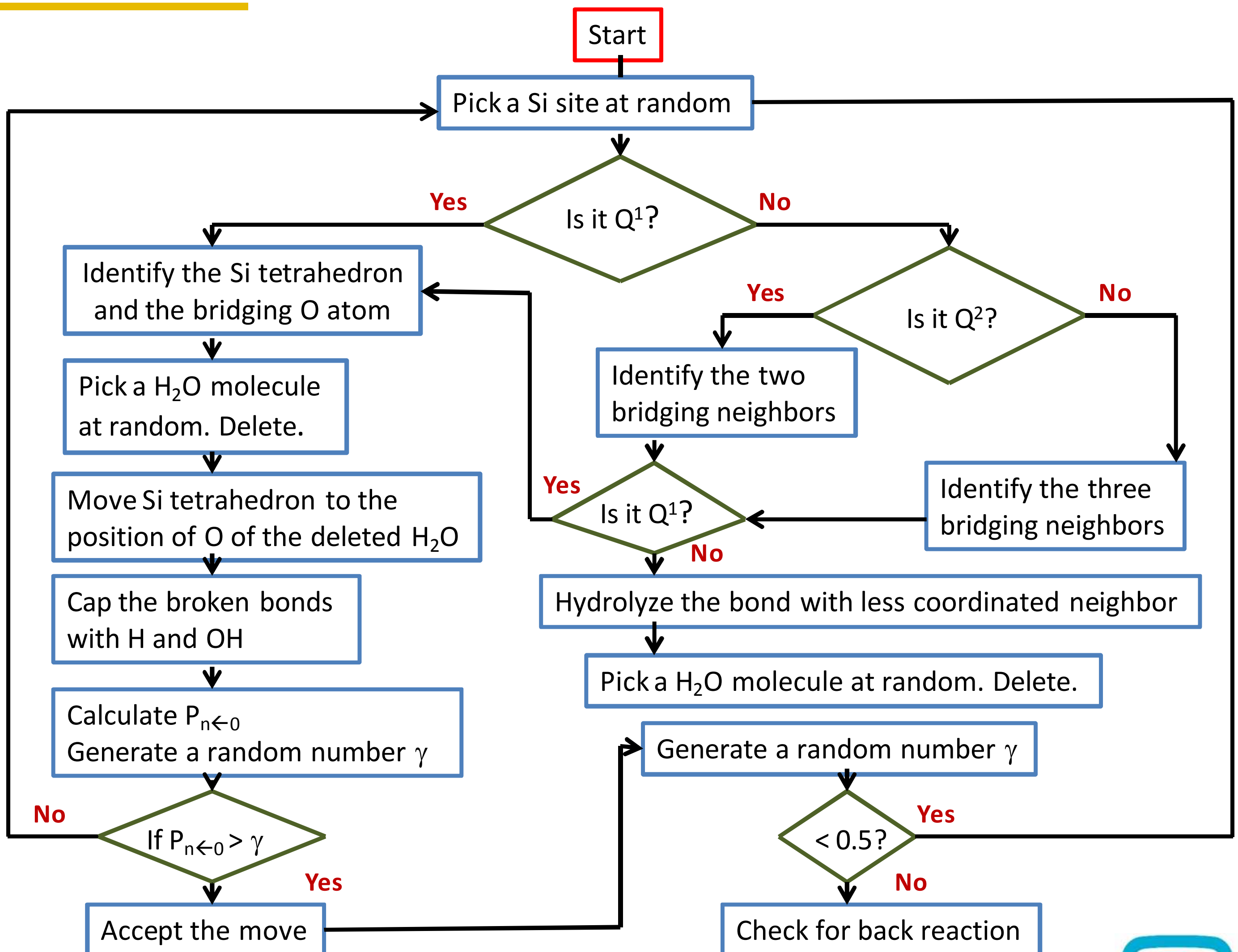
Monte Carlo model for stepwise dissolution (of feldspar)



(Nangia and Garrison, 2010)

Long-time scale validation: Archeological glass

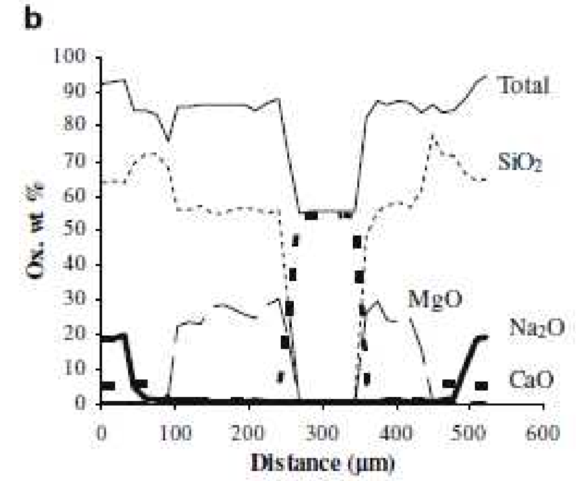
Carl Steefel, Ian Bourg, Benjamin Andre (LBNL)

Continuum modeling for Roman Glass - at 1800 years.

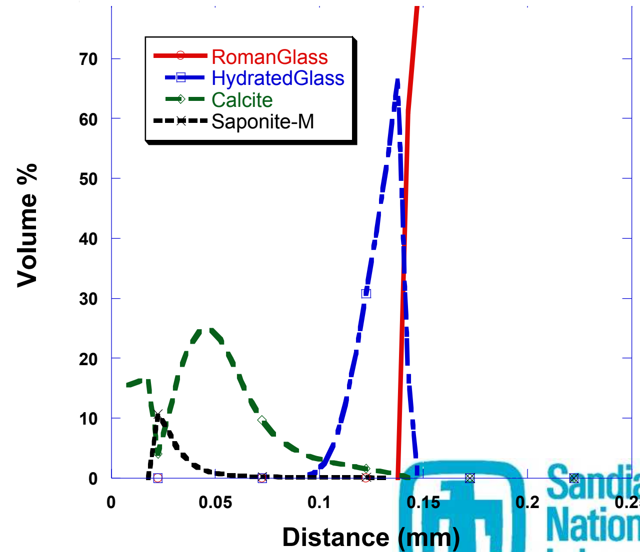
- **Pristine glass is hydrolyzed, with loss of Na_2O by H_2O**
- **Hydrated glass dissolves**
- **pH rises due to exchange and dissolution**
- **Smectite and calcite form**
- **Very low diffusivities required**

- **Goal: replace/augment empirical rate laws with sub-grid-informed chemistry, extend to WF glasses**

Roman glass



Continuum simulation



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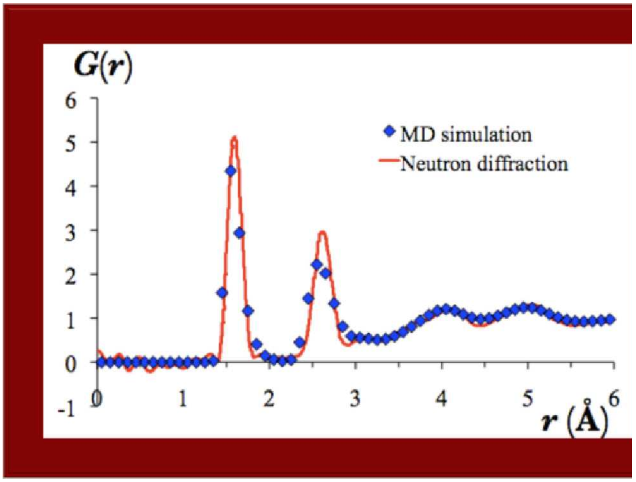
Downscaling: Conceptual Model for Glass Corrosion

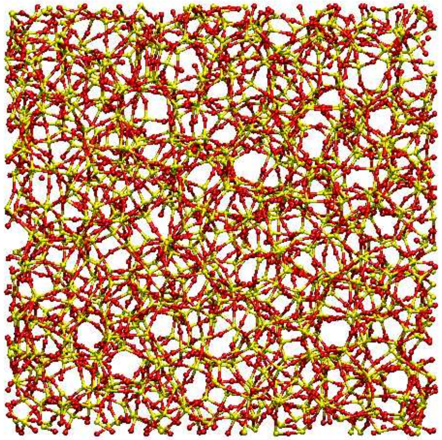
- Hydration of glass, replacement of Na_2O by H_2O, leaching of Na^+
- Dissolution of hydrated glass, with rate controlled by pH and reaction affinity (ΔG)
- Gradual formation of more stable silicate and carbonate phases (smectite, calcite)
- Interaction with near-field materials via diffusion and sorption

Downscaling: Molecular models

Carl Steefel, Ian Bourg, Benjamin Andre, LBNL

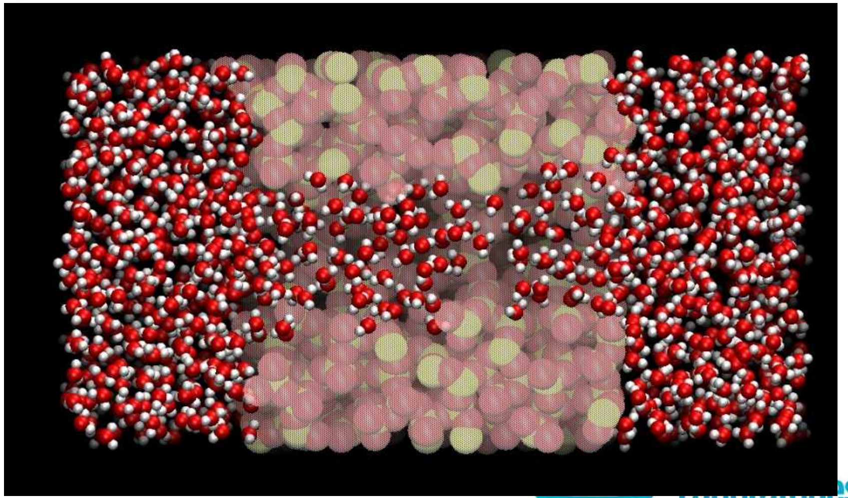
Use sub-scale molecular models to test and inform conceptual continuum models





Test of inter-atomic potentials against neutron-diffraction determined structure for glass

Simulations will determine water structure and diffusion coefficients in model SiO_2 nanopores as a function of pore radius and silanol site density



Subcontinuum modeling requirements

- Verified sub-continuum methods to fill gaps in WF requirements
- Multiscale methods to bridge the atomistic-to-continuum gap
  - Upscaling techniques to create accurate constitutive models for continuum codes
  - Constitutive models for key state and transport properties as functions of species mass fractions
  - Constitutive models for fundamental physical processes that account for microstructure evolution, chemistry, radiation damage, and time
  - Constitutive models whose range, errors and uncertainties are well-understood and quantified
- VV-UQ through-out chain
- Traceability, reproducibility, documentation

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Plan for FY11 and forward

- Incremental upscaling to glass corrosion
  - Milestone: feldspar dissolution (ANL)
  - Progress: work on amorphous glass, multicomponent, upscaling
  - Milestone: Upscaling progress report (SNL,ANL,LBNL)
- Long-time validation
  - Milestone: archeological glass corrosion (LBNL)
  - Progess: delivery of interim constitutive descriptions
- Downscaling glass dissolution
  - Milestone: LBNL molecule modeling
- VV-UQ integration into subcontinuum activities
  - Milestone: July 2011, VV-UQ protocols for subcontinuum codes
  - Progress: Upscaling techniques and UQ (with VU)
  - Progress: insinuation of protocols into ongoing work
- Filling scope
  - Expanding to ceramics and metals - scoping and gap studies
  - Continuing to coordinate efforts outside (FCRD WFC/UFD, ...)

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*** Multiscale Modeling of Glass Corrosion

Carl I. Steefel
Ian Bourg

Lawrence Berkeley National Laboratory

(from Glass Corrosion Workshop
September 30, 2009)

--- extra slides ---

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Big challenges:
Phenomena

- Actinides - experiments will be limited
  - Inadequate quantum methods (and FF) - solid state and chemistry
  - Validation? - little experiment
- Electrochemistry - corrosion, temperature, pH, gradients, ….
- Nucleation-driven processes - gas bubbles, secondary phases, cracks
- Long-time evolution/rare events - geologic time scales
  - Very slow evolution rates - phase alteration/corrosion
  - Very slow diffusion constants - transport
  - Validation? - short time-scale methods
- Disorder - length scales
  - amorphous glasses, solid phases, grain boundaries
- Upscaling - bridging between levels of fidelity
  - Between sub-grid methods (e.g. FF from QM?)
  - From discrete atomistics to state variables
  - Abstracted model and realization
  - VV-UQ?

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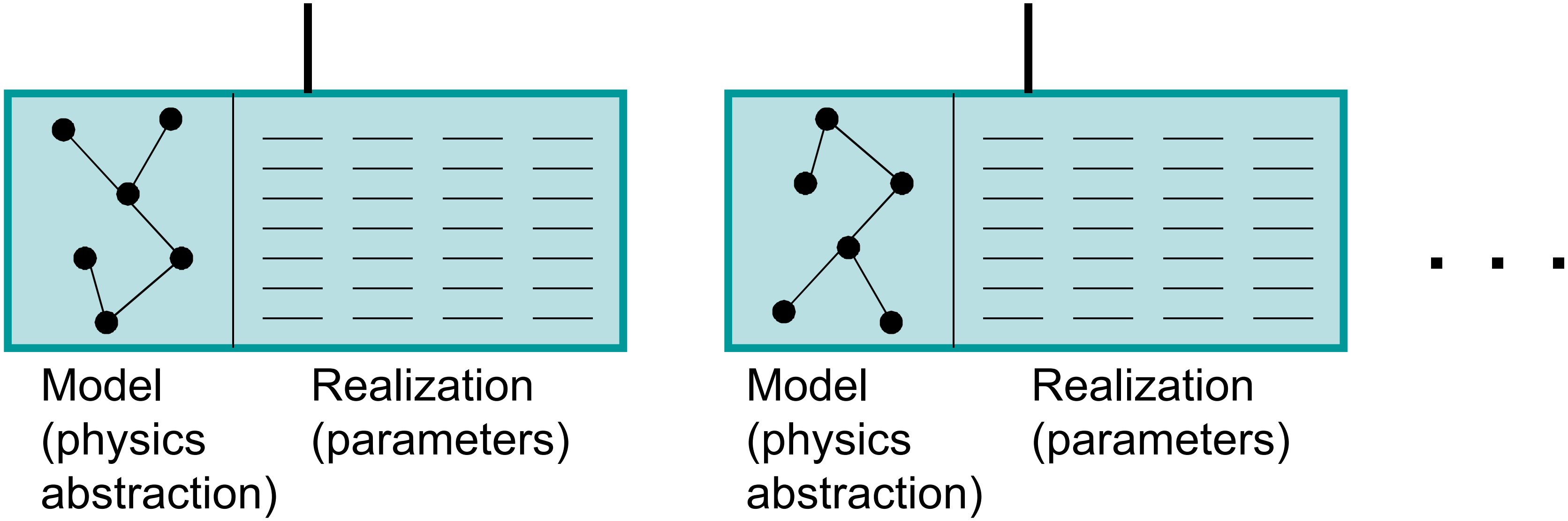
Anatomy of a model - two parts

(1) a physics abstraction, coarse-grained model
(2) parameter values that populate the model



- Phenomenological models - heuristic, irreducible
  - fit and calibrated to specific range
  - interpolative, not extrapolative

- Subgrid-physics-aware models - hand-off multiscale
  - potentially extrapolative (predictive)
  - experimental or modsim data
  - there is still fitting (calibration)

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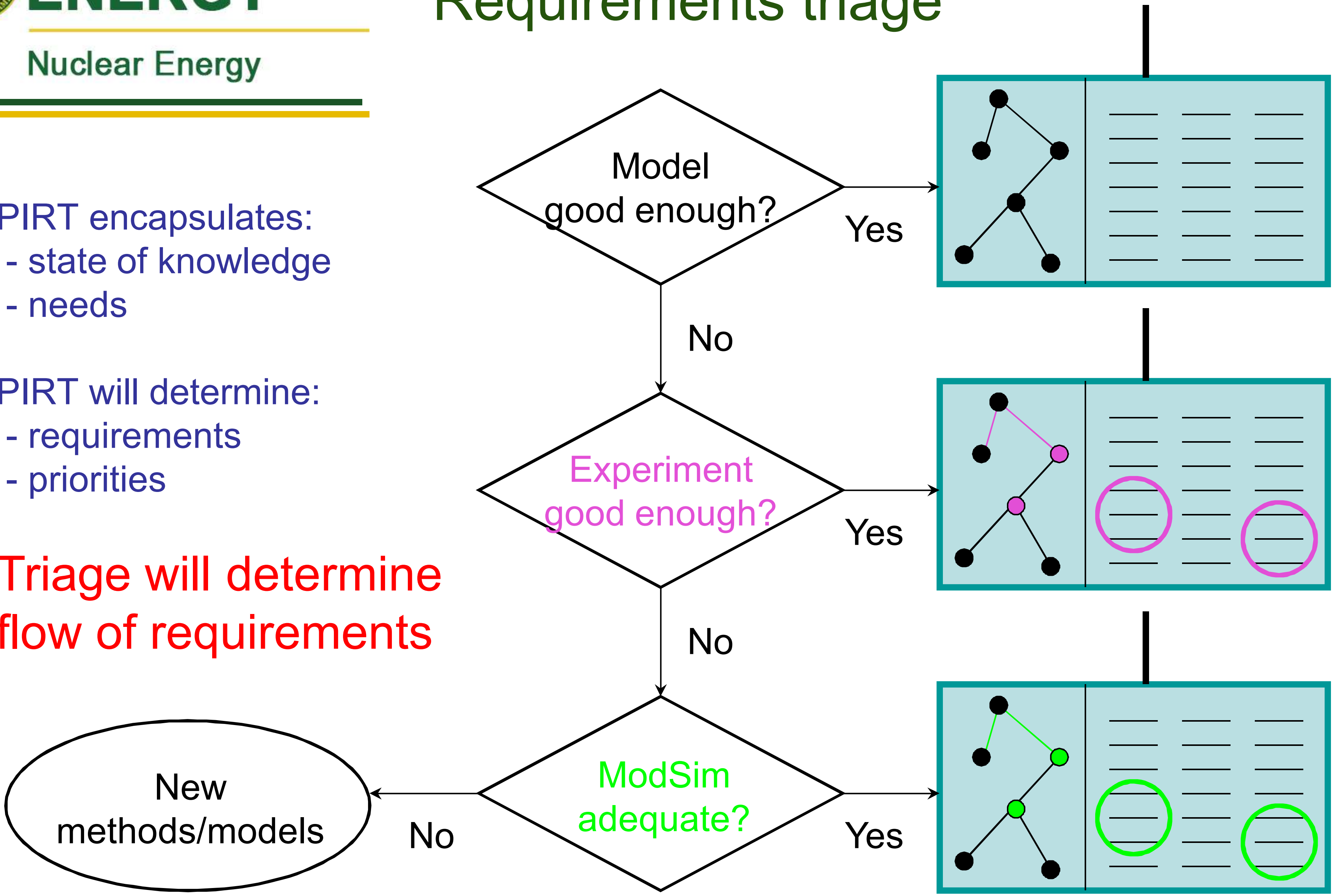
Requirements triage

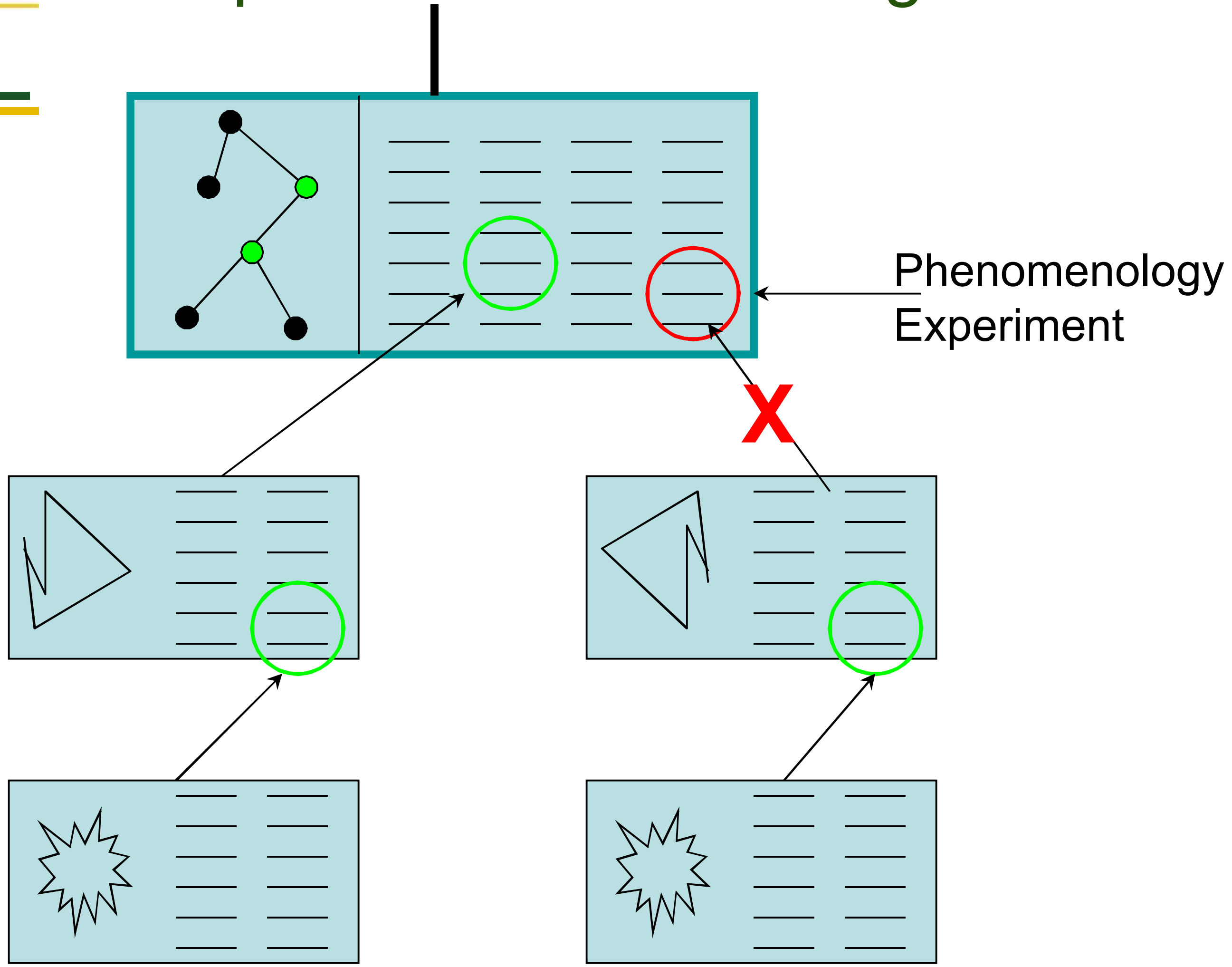
PIRT encapsulates:
- state of knowledge
- needs

PIRT will determine:
- requirements
- priorities

Triage will determine flow of requirements



Requirements: Line of sight



PIRTs will determine relevance of candidate simulations - requirements

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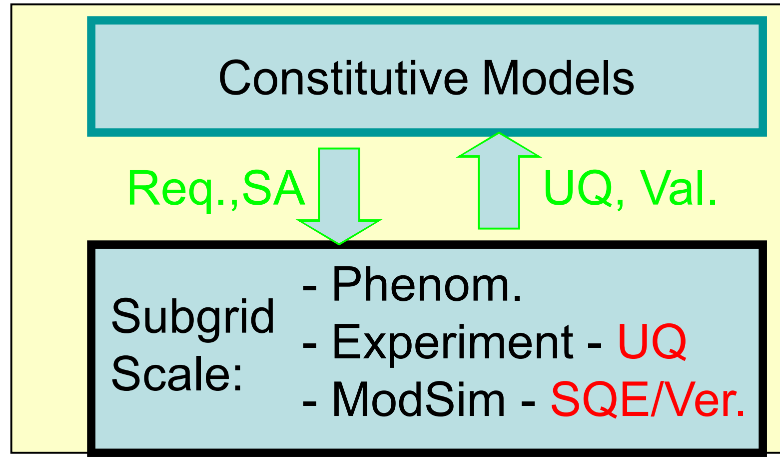
VV/UQ required throughout system

Into high-consequence decisions:
All data/process flows must be …

Traceable - provenance recorded
Reproducible - by others
With quantified confidence - VV/UQ



Required elements from all simulations feeding the system:

1) Necessary - Line-of-sight into system requirements

2) Qualified - Verified codes/applications - (confidence in methods)
Known codes (versions) with confirmed capabilities

3) Validated - quantified errors and uncertainties

4) Documented - sufficient to be reproducible (by others, 10 year later)
inputs and outputs, “rogue” results will not pass

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