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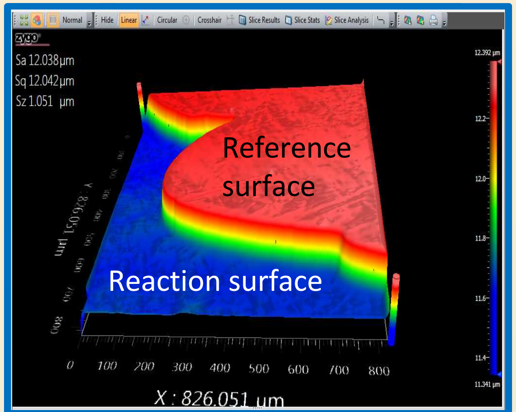

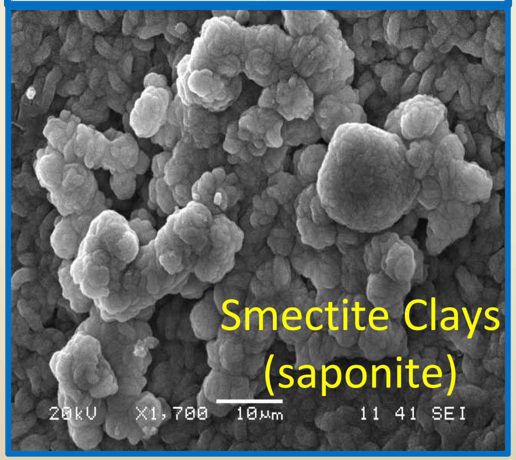

Dissolution of Borosilicate Glass in NaCl and $MgCl_2$ Solutions: Implications for Disposal in Rock Salt

ANS Carlsbad: February 22, 2018

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Outline

- Where does nuclear waste come from?
- The “Waste Storage Dilemma”.
- Glass as an immobilization matrix.
- Experimental Strategy.
- Dissolution behaviour of nuclear waste glass.
- Solution modeling.
- (Rather surprising) Results.
- Conclusions.

Objectives

- Quantify the dissolution rate of the International Simple Glass (ISG) over a range of NaCl and $MgCl_2$ concentrations at 90^{o}C and pH(25^{o}C) = 9 using:
  - Chemical assay on powders
  - Chemical assay on monoliths
- Evaluate if dissolved NaCl enhances or suppresses rates.
- What mechanism controls the rate of glass dissolution in brine solutions?
- Determine if $MgCl_2$enhances or suppresses rates.
- What secondary phases precipitate, and what are their effects?

Motivations—Both Practical and Theoretical

Practical Considerations

- No decision yet on the geologic setting of the repository for high level waste.
  - Granite
  - Shales/mudrocks
  - Tuff
  - Salt (brine solutions)
- Repeated cycles of evaporation/condensation result in high ionic strength brines.
- Even in granite, solutions are not necessarily dilute.

Theoretical Considerations

- How does ionic strength and the activity of water factor into the rate equation?

$$Rate = k_0 \cdot (a_{SiO_2}) \cdot (a_{H_2O})^2 \cdot \left(1 - \frac{Q}{K}\right)$$

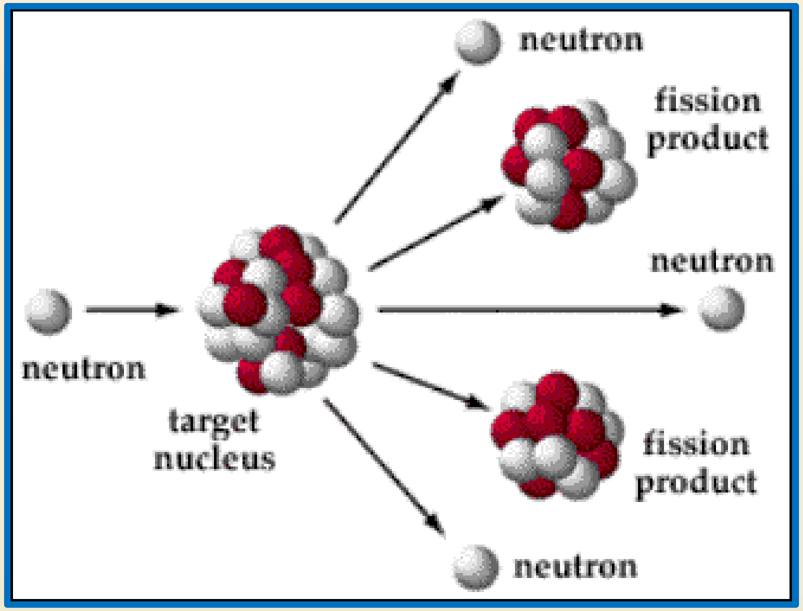
  - Dove & Crerar (1990) GCA 54, 955-969

- Previous work indicates that the dissolution rates of silica polymorphs are enhanced by the presence of NaCl:
  - Dove & Nix (1997) GCA 61, 3329-3340—Quartz
  - Icenhower & Dove (2000) GCA 64, 4193-4203—Amorphous SiO_2
- Will multicomponent borosilicate glass behave the same way?

Where Does High-Level Nuclear Waste Come From?

- Uranium ore, consisting of:
  - 99.27% ^{238}U
  - 0.72% ^{235}U
  - 0.006% ^{234}U
- Only ^{235}U is fissile
- Uranium fuel must therefore be enriched (increase amount of ^{235}U to 3%)
  - Gaseous diffusion of uranium hexafluoride
  - Requires a set of centrifuges working in a linear array (hard part)

Fission Reactions and Production of Radionuclide Elements

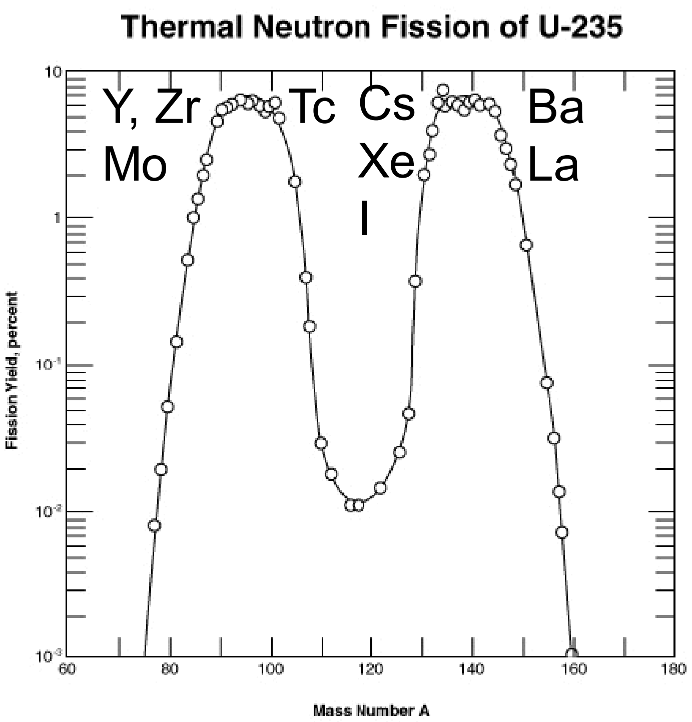


- Atom of ^{235}U splits into two fragments (Fission Products)
- Absorption of neutron in ^{238}U to produce Transuranic Elements

Bimodal Distribution of Fission Products

Fission Products

Fission yield is the relative amounts of nuclides formed in fission reactions. The fission yield curve shown here shows most fission reactions split fission atoms into two unequal fragments.



Nuclear Fission

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What are the Principal Radionuclides?

Nuclide: Fission Product and Half-Life		Nuclide: Transuranic Isotope and Half-Life	
I-129	15,700,000 years	Np-237	2,100,000 years
Tc-99	215,000 years	Pu-239	24,000 years
Cs-137	30 years	Pu-240	6,500 years
Sr-90	28 years	Am-241	460 years

Can these elements be safely immobilized for the duration of their existence?

Example of the Nuclear Waste Legacy: Hanford (Washington State)

- Hanford is situated in Washington State, east of the Cascade range.
- At the confluence of the Snake, Yakima, and Columbia Rivers.
- Located in the “Columbia Basin”, in semi-arid sage brush steepe.

Construction of Hanford: 1940's

Waste Disposal at Hanford

- Waste dissolved into aqueous solutions; 550 *million* gallons of waste.
- Solution treated with NaOH to increase lifespan of tanks.
- Stored in 177 single- or double-shell underground tanks.
- Other waste, including low activity radioactive materials, disposed in shallow trenches.

What Could Possibly Go Wrong?

- Nearly one-third of the tanks are known or suspected to have developed leaks.
- About 190 kg of plutonium leaked/lost or disposed to soil.
- Numerous waste dumps, many of which have not been located, are contaminating the site.
- Groundwater movement is toward the Columbia river.

Example: Leak from Tank in 241-BX "Tank Farm"

- Accidental overfill in 1951.
- Nearly 265,000 liters of solution released.
- Some 10,000 kg of U plus many other dissolved radionuclide elements released to sediments.
- Depth of penetration into sediments unknown; at least 140 feet.
- Difficult to predict mobility of U or Tc and to immobilize or remediate.

Why Above Surface Disposal is Unacceptable

Disposal must be for >20,000 years, so waste must not be vulnerable to:

- **Floods**
- **Tornadoes**
- **Theft**
- **Political instability**
- **Accidental exposure**
- **Fire**

2000 Was a Bad Year!

Range fires at the following Government sites:

- Los Alamos, New Mexico
- INEEL, Idaho
- Hanford, Washington

The fire at Hanford threatened:

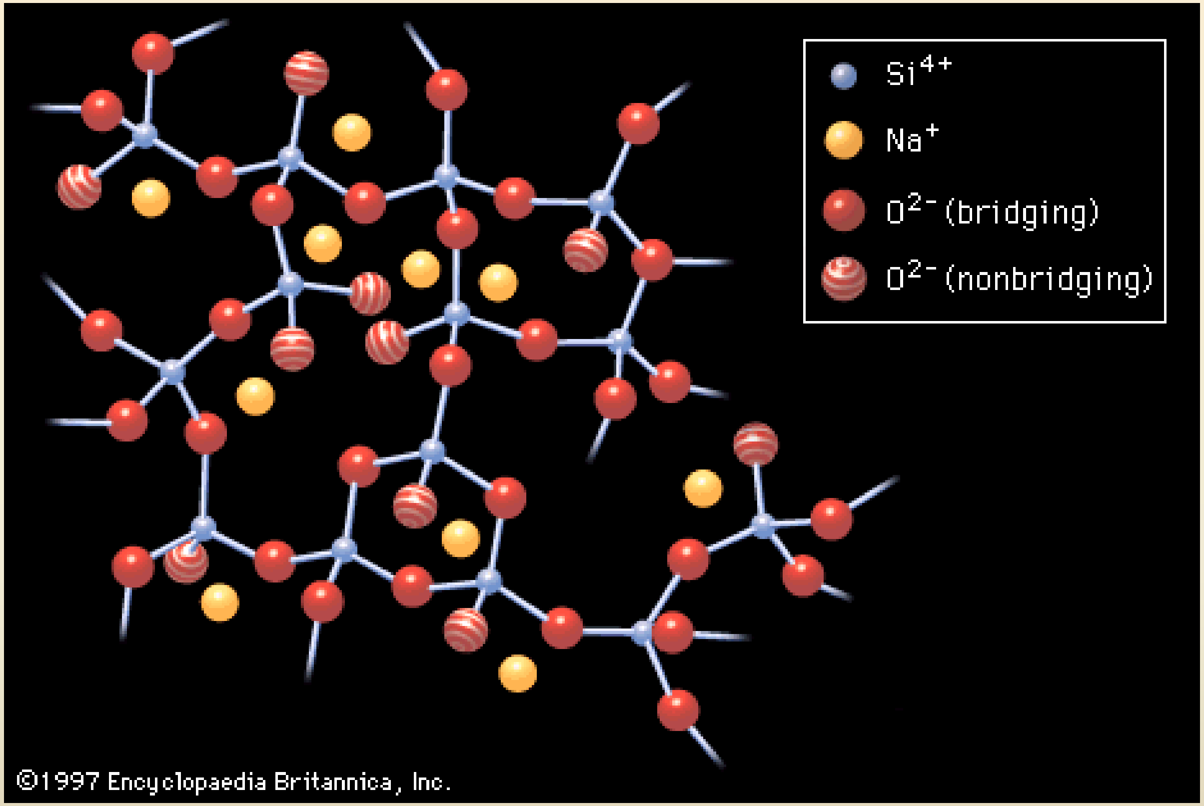
- Plutonium products
- U^0 dump

Why Glass as an Immobilization Matrix?

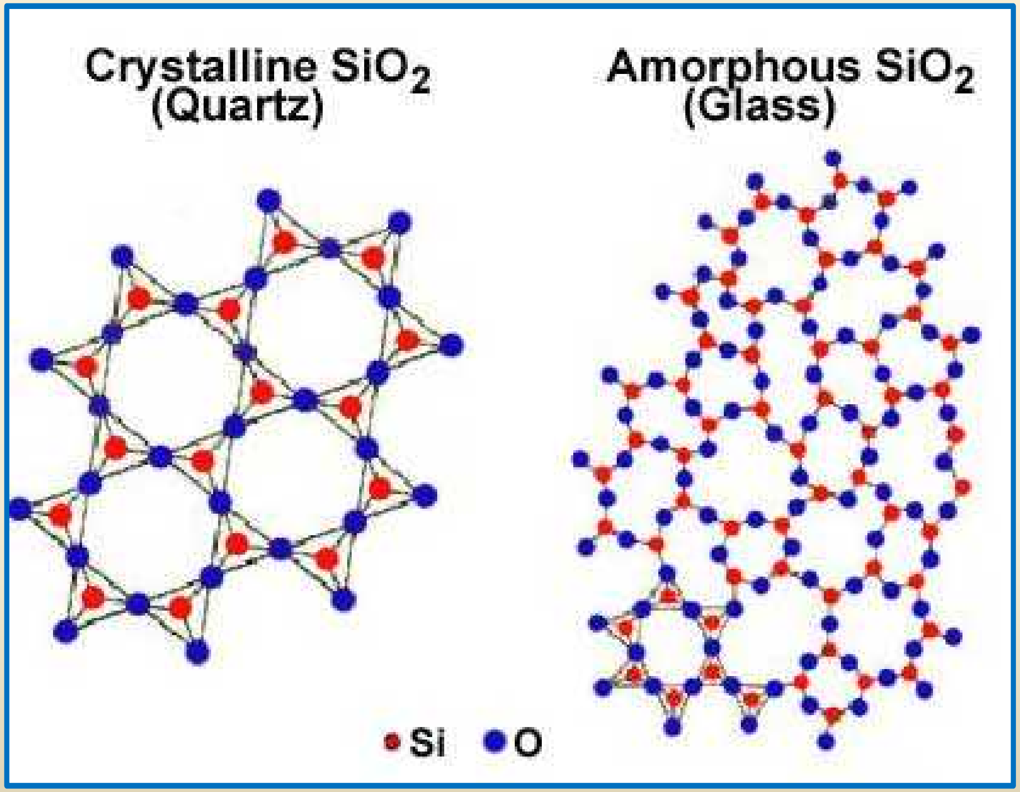
- The immobilization strategy depends on:
  - Bonding radionuclide elements into a solid framework
  - This framework must accommodate different cations/anions, must be resistant to both aqueous solution and radiation damage.
- These criteria are met with borosilicate glass.
  - Also, ease of work (low viscosity due to boron), many decades of accumulated knowledge.

Melt Waste Along with Glass Forming Components (Frit)

Molecular Structure of Glass

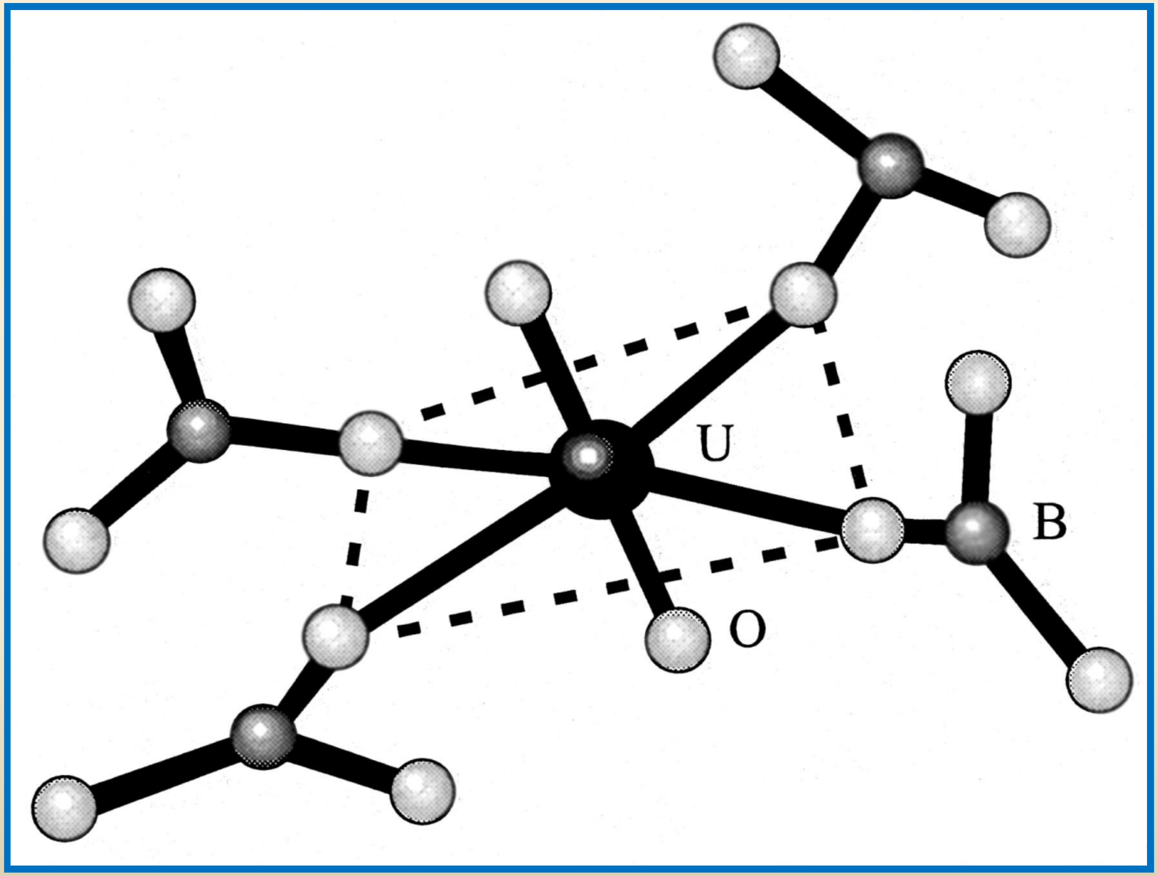


The Difference Between Crystalline and Amorphous Material



What is the Cause of Colour in This Glass?

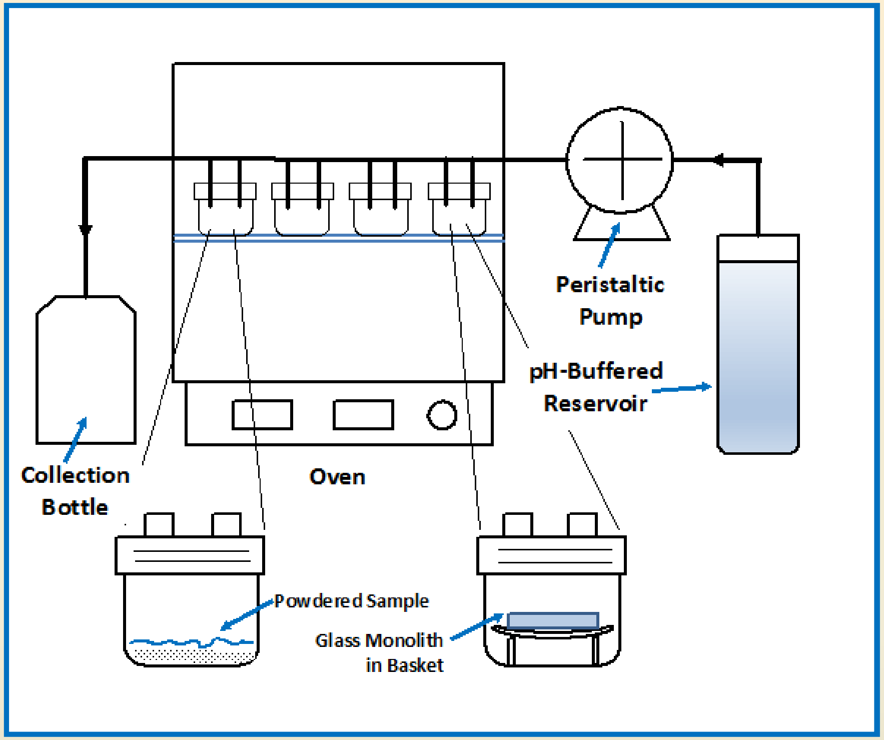
Bonding of Uranium in Waste Glass



Dissolution Experiments

- Single-Pass Flow-Through (SPFT)
- Static
- Answer distinctly different questions

Experimental Setup-Flow Through



- Glass powder or monolith of known surface area.
- Solution flow rate constant.
- Reactors behave like a CSTR.
- Powder and monoliths in separate reactors, but at same *q*/S ratio.
- Effluent collected and analyzed for release of elements.

$$rate_i = \frac{(C_i^{out} - C_i^{b})q}{f_i S}$$

Experimental Rate Theory

- Glass and water reach steady-state, ***NOT*** equilibrium
- Experiments ***NOT*** carried out under natural conditions
  - Flow rate
  - Temperature
  - pH
- Goal is to parameterize the rate equation

Kinetic Treatment of Dissolution Rates

$$\text{rate} = k_o S \exp\left(\frac{-E_a}{RT}\right)^{\sigma} a_{H^+}^{\eta_{H^+}} g(I) f(\Delta G_r) \prod_i a_i^{\eta_i}$$

Surface area

Tempkin coefficient

Ionic strength dependence

Catalysis / inhibition

Rate constant

pH dependence

Activation Energy

Free energy dependence

Solution Preparation-Flow Through

- Solutions buffered with 0.015 M TRIS solution.
- A range of NaCl concentrations (no NaCl to 4.0 m NaCl).
- A range of $MgCl_2$ concentrations (no $MgCl_2$ to 2.5 m $MgCl_2$).
- Experiments with combined NaCl and $MgCl_2$ (simplified GWB).
- Initial solutions at pH(25^{o}C) = 9.0

Experimental Setup-Static Experiments

- Reactors situated in constant temperature oven.
  - Sampled every few days initially, then once a month.
  - Track pH and release of elements from glass to solution.
- Goal: To determine which secondary phases are stable.
- Do these secondary phases affect the rates?

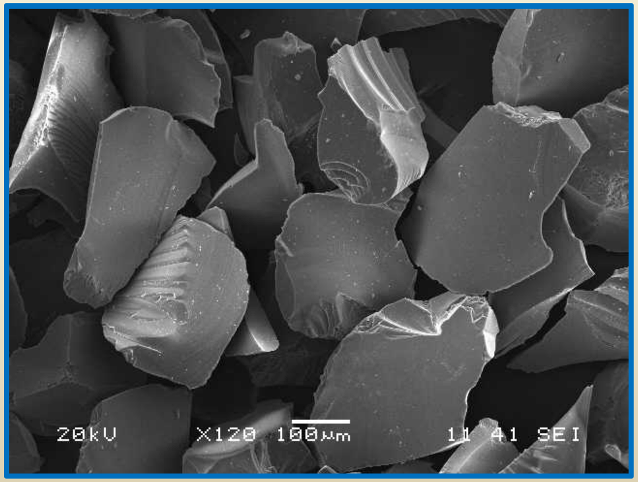
Solution Preparation-Static Experiments

- Solutions unbuffered.
  - pH tracked to determine what reactions control hydronium ion concentration.
- A range of NaCl concentrations (no NaCl to 4.0 m NaCl).
- A range of $MgCl_2$ concentrations (no $MgCl_2$ to 2.5 m $MgCl_2$).
- Experiments with combined NaCl and $MgCl_2$ (simplified GWB).
- Initial solutions at pH(25^oC) = 9.0
  - Correction factor required; determined analytically.
  - $pC_H+ = pH_{obs} + A$

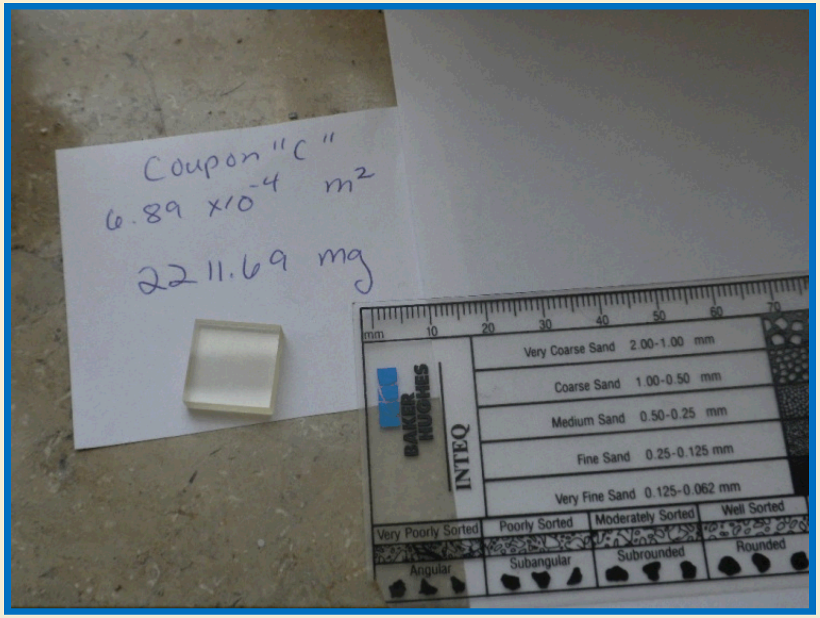
Glass Preparation & Surface Area (SA)

Powders

- 20 -30 mesh-size (850 – 600 micrometer diameter)
- BET SA: 5.7 x 10^{-3} m^2/g
- Geo SA: 3.3 x 10^{-3} m^2/g
- 0.20 g powder

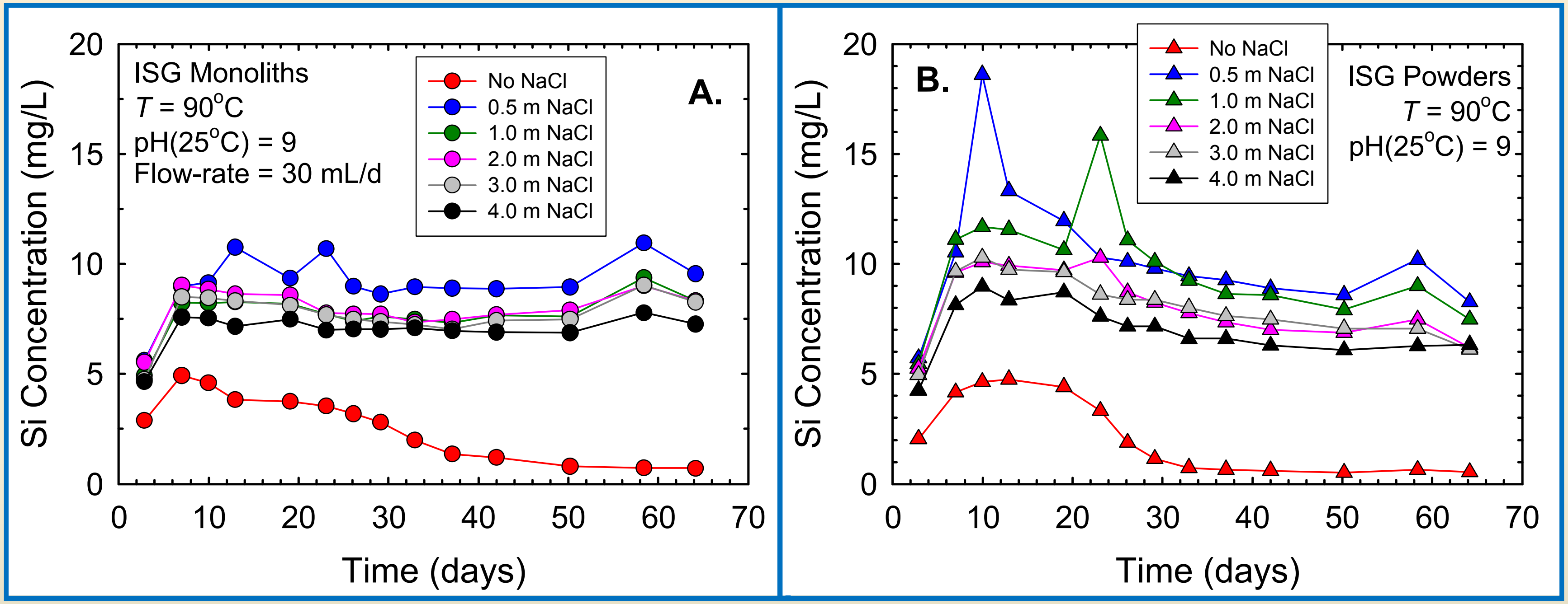


Monoliths



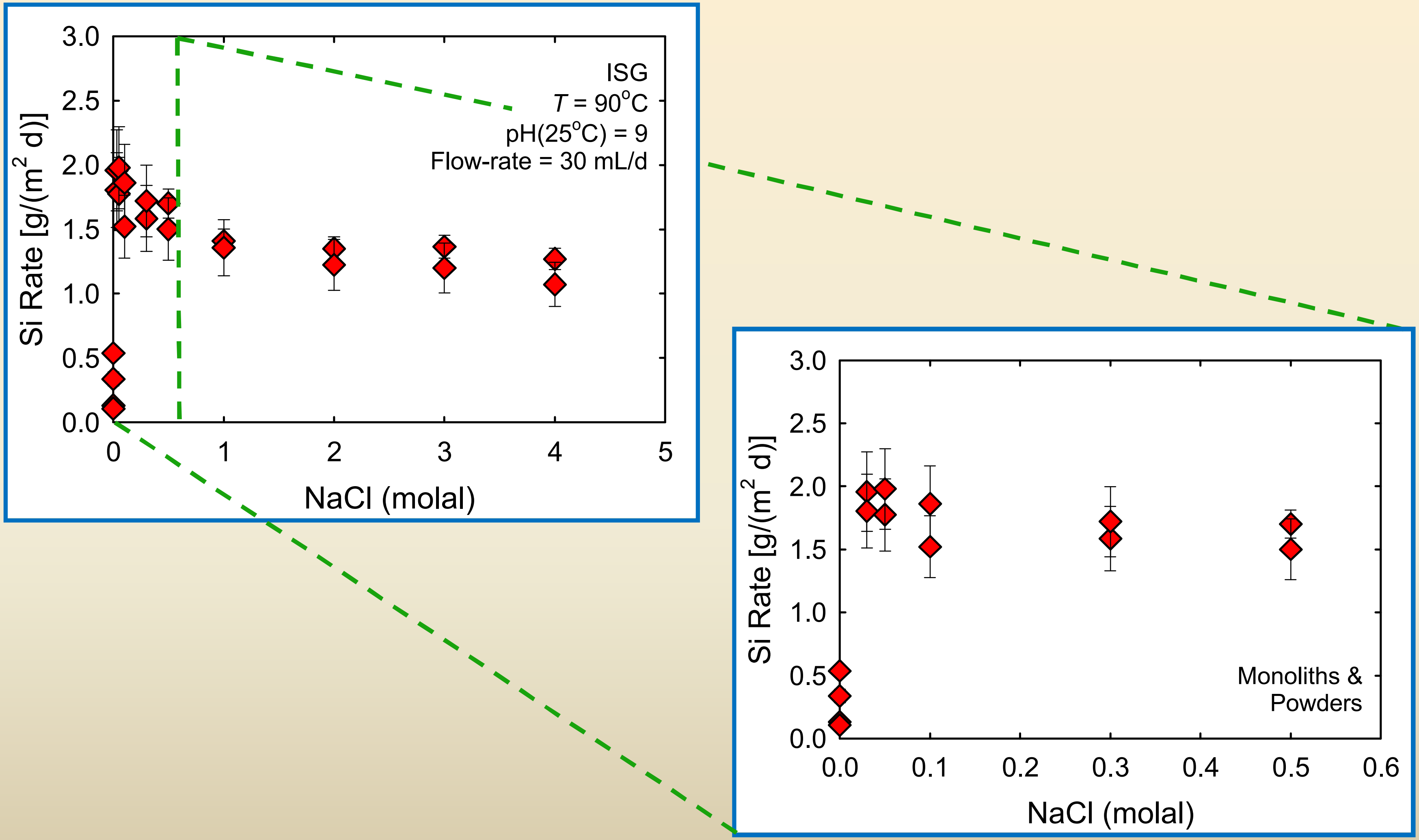
- Cut and polish glass monoliths.
- Measure monolith dimensions using calibrated electronic calipers.
- Better control over SA

Flow-Through Experiments:
Approach to Steady-State



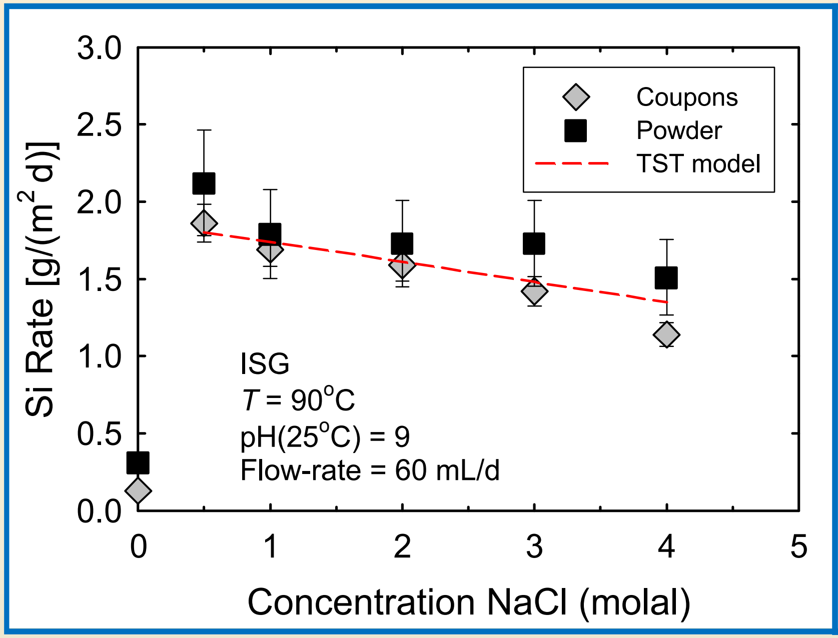
Flow-Through Experiments:

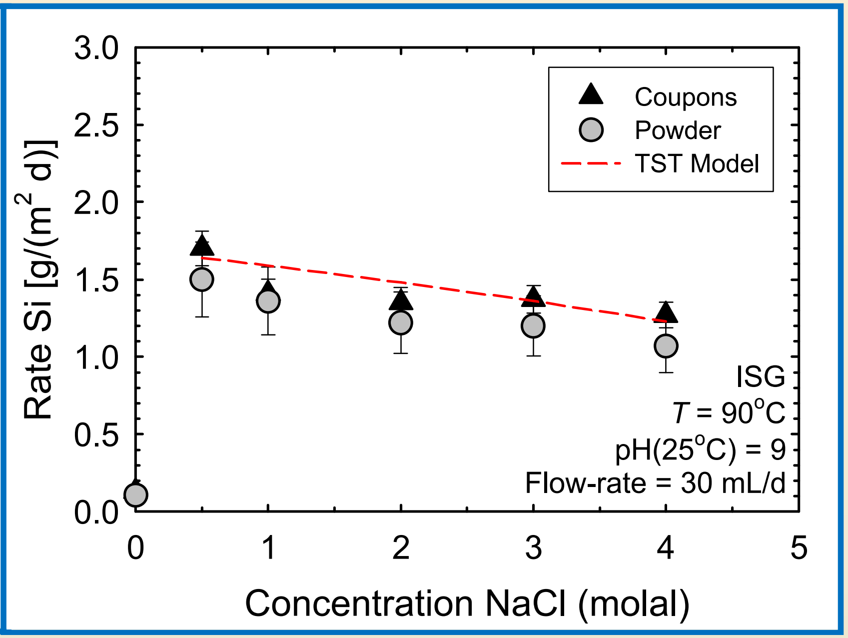
Rate Catalysis by NaCl



Flow-Through Experiments:

Dissolution Rate vs. NaCl Concentration



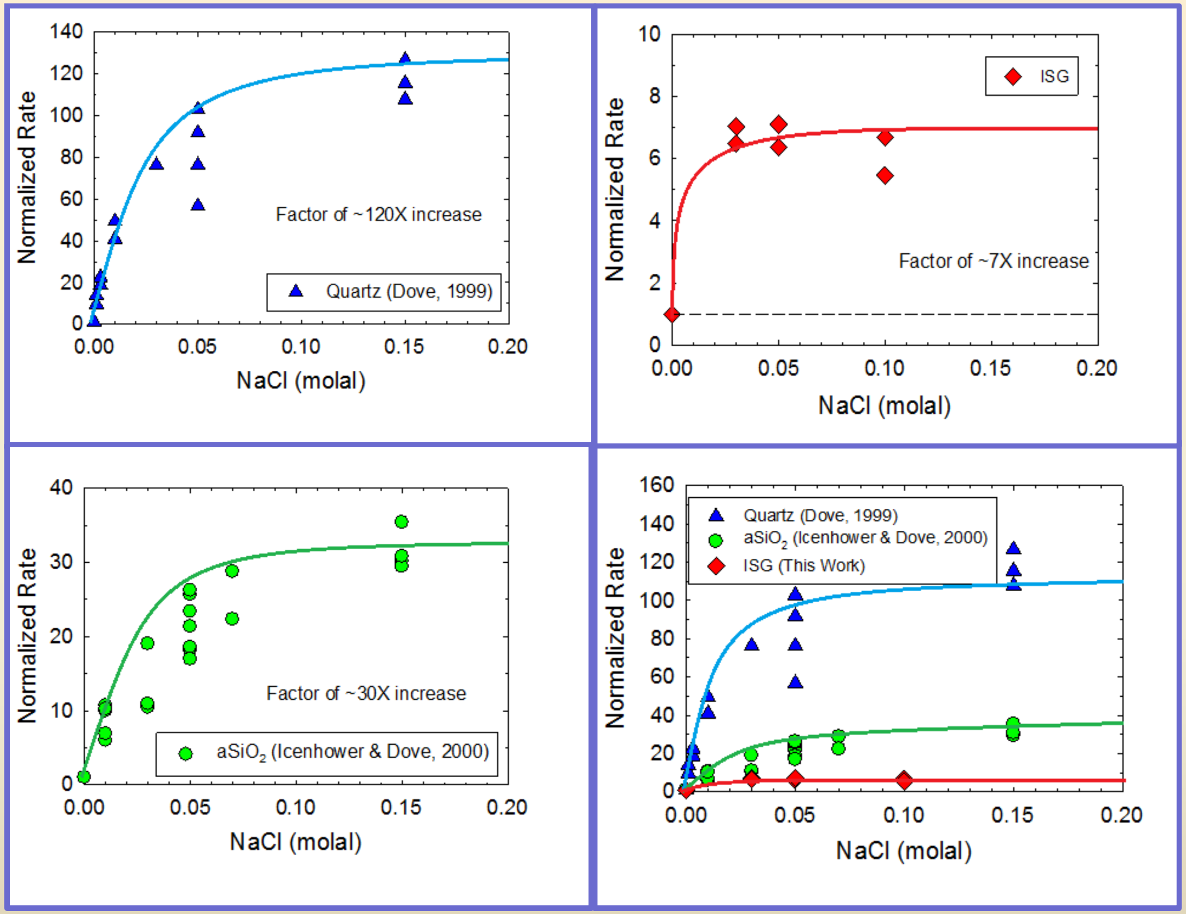


$$Rate = k_0 \cdot (a_{SiO_2}) \cdot (a_{H_2O})^2 \cdot \left(1 - \frac{Q}{K}\right)$$

Note: TST = Transition State Theory

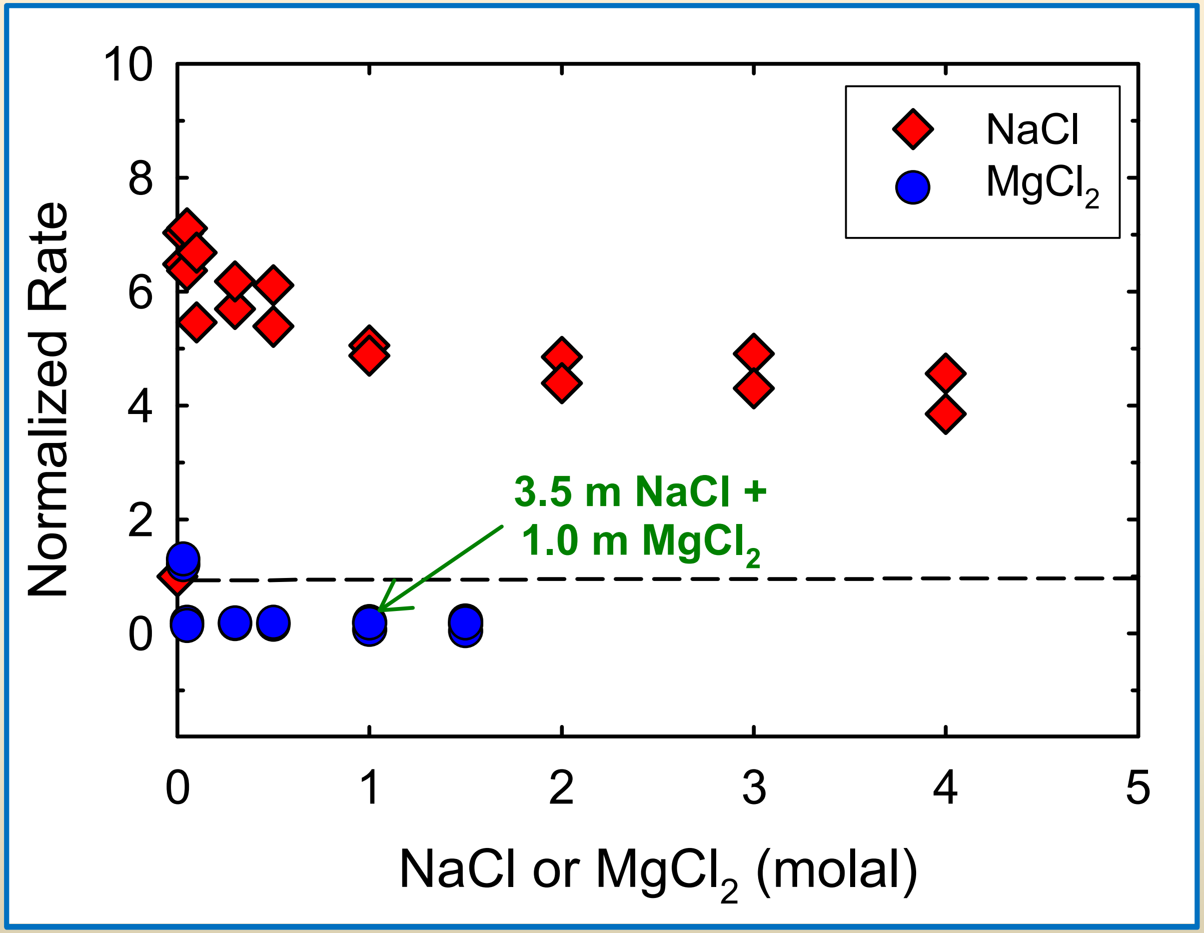
Flow-Through Experiments:

Enhancement of Rates by NaCl



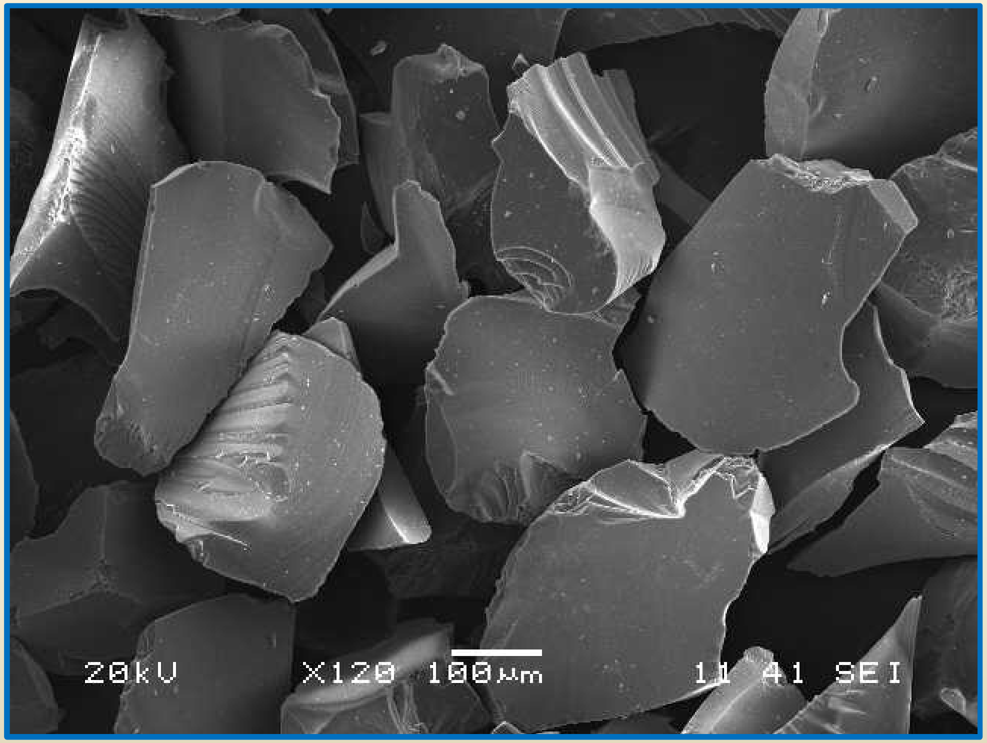
Flow-Through Experiments:

Effects of $MgCl_2$ on Glass Rates



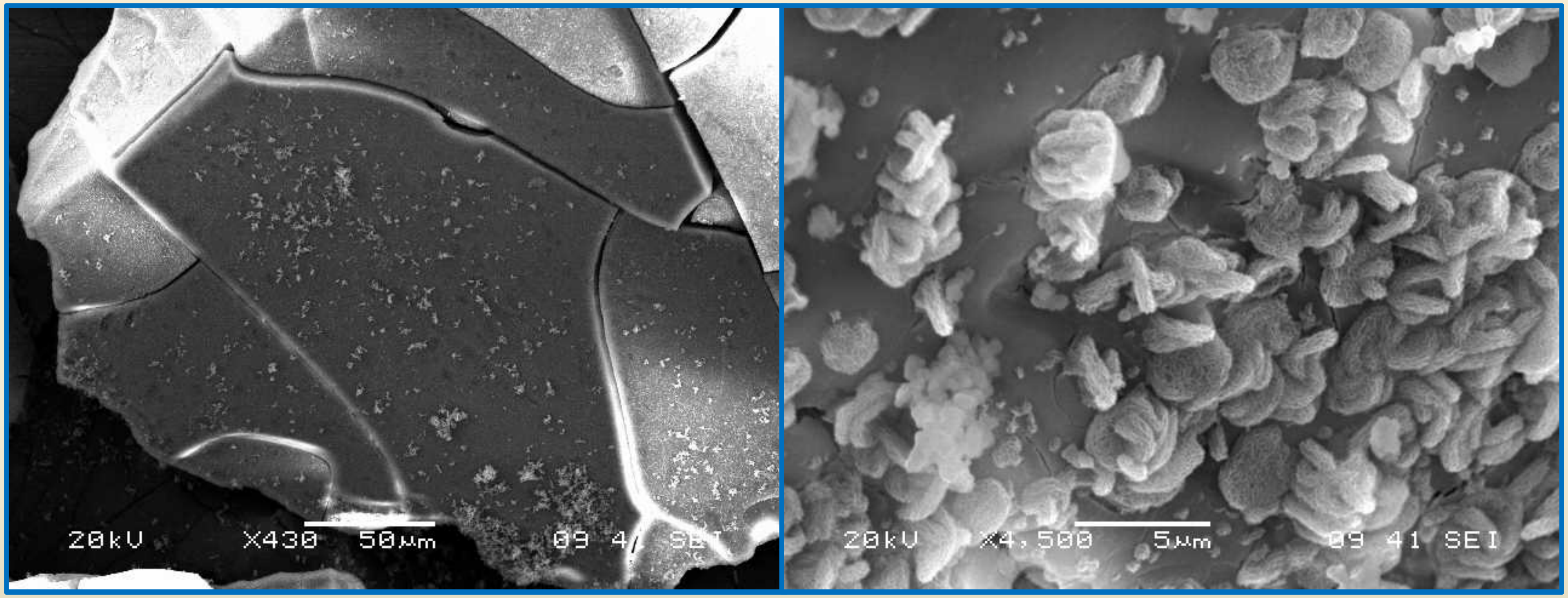
Static Experiments-SEM

Unreacted Powders



Static Experiments-SEM

Powders reacted in Deionized Water



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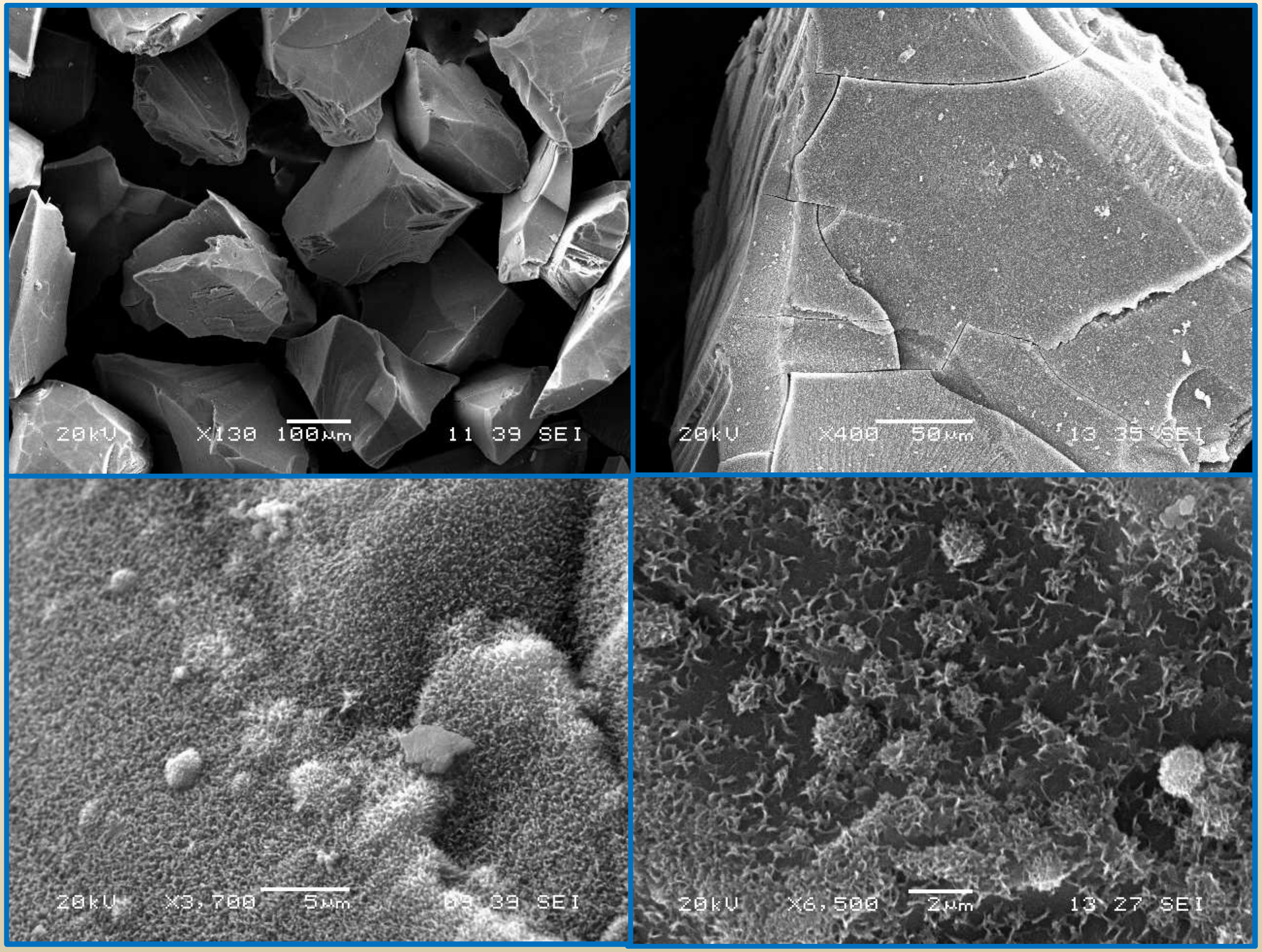
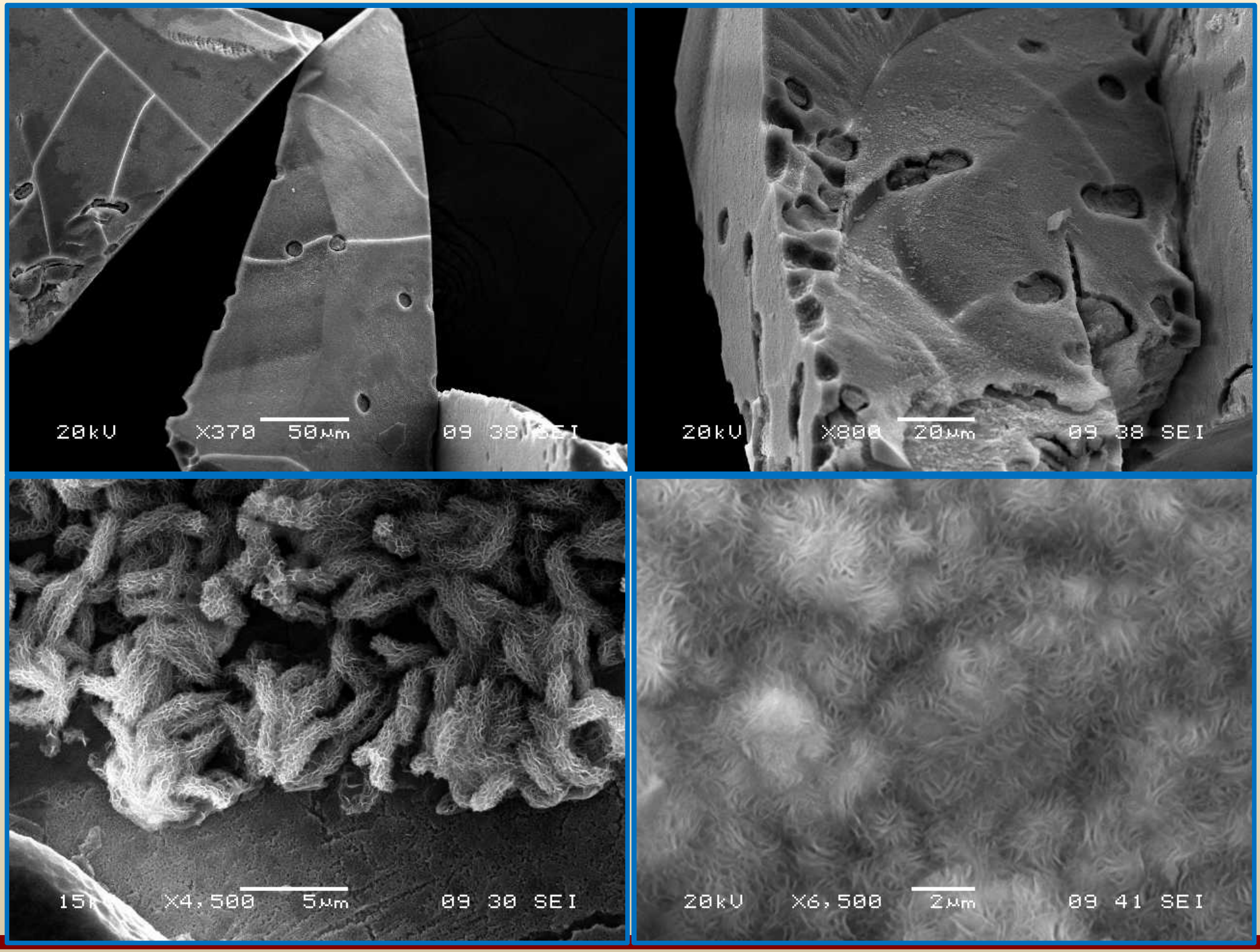
Static Experiments-SEM

Powders reacted in NaCl solutions



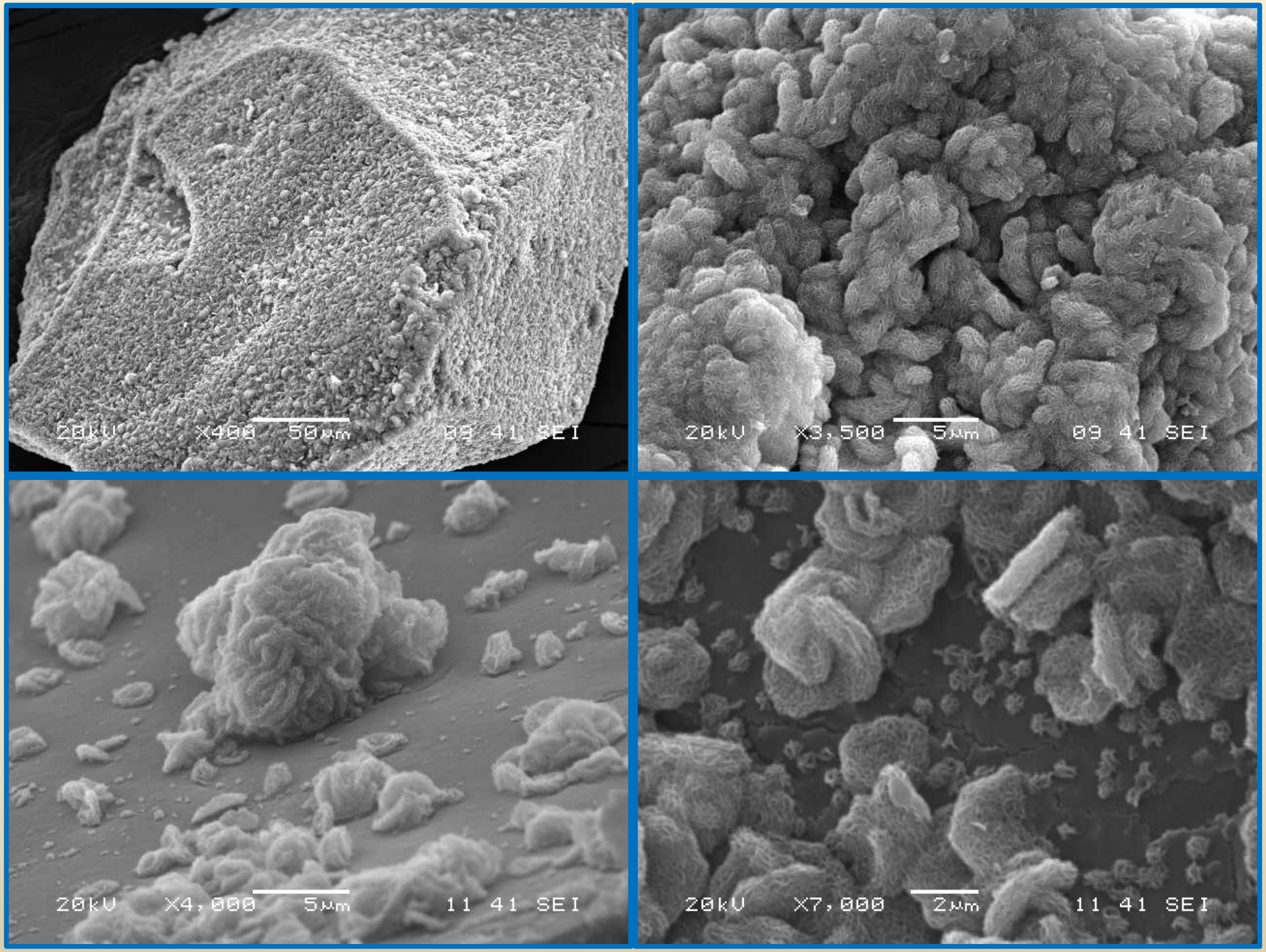
Static Experiments-SEM

Powders reacted in $MgCl_2$ solutions



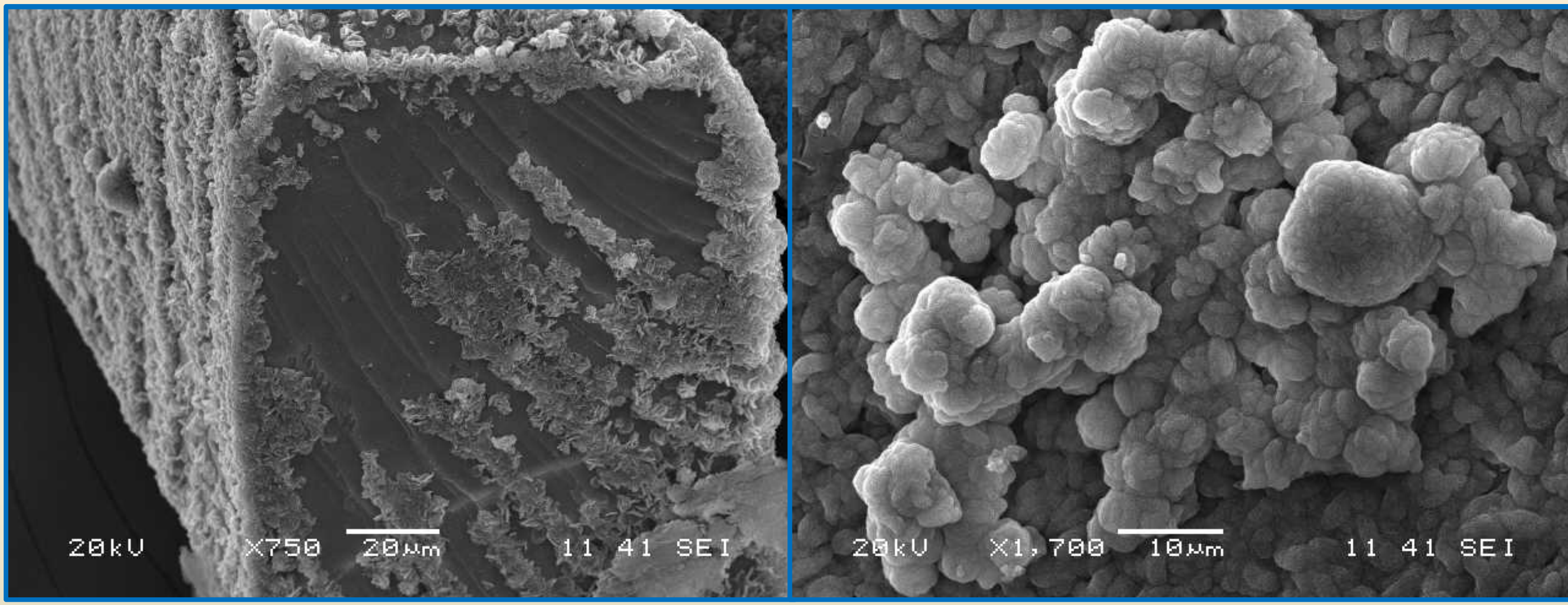
Static Experiments-SEM

Powders reacted in $MgCl_2$ solutions



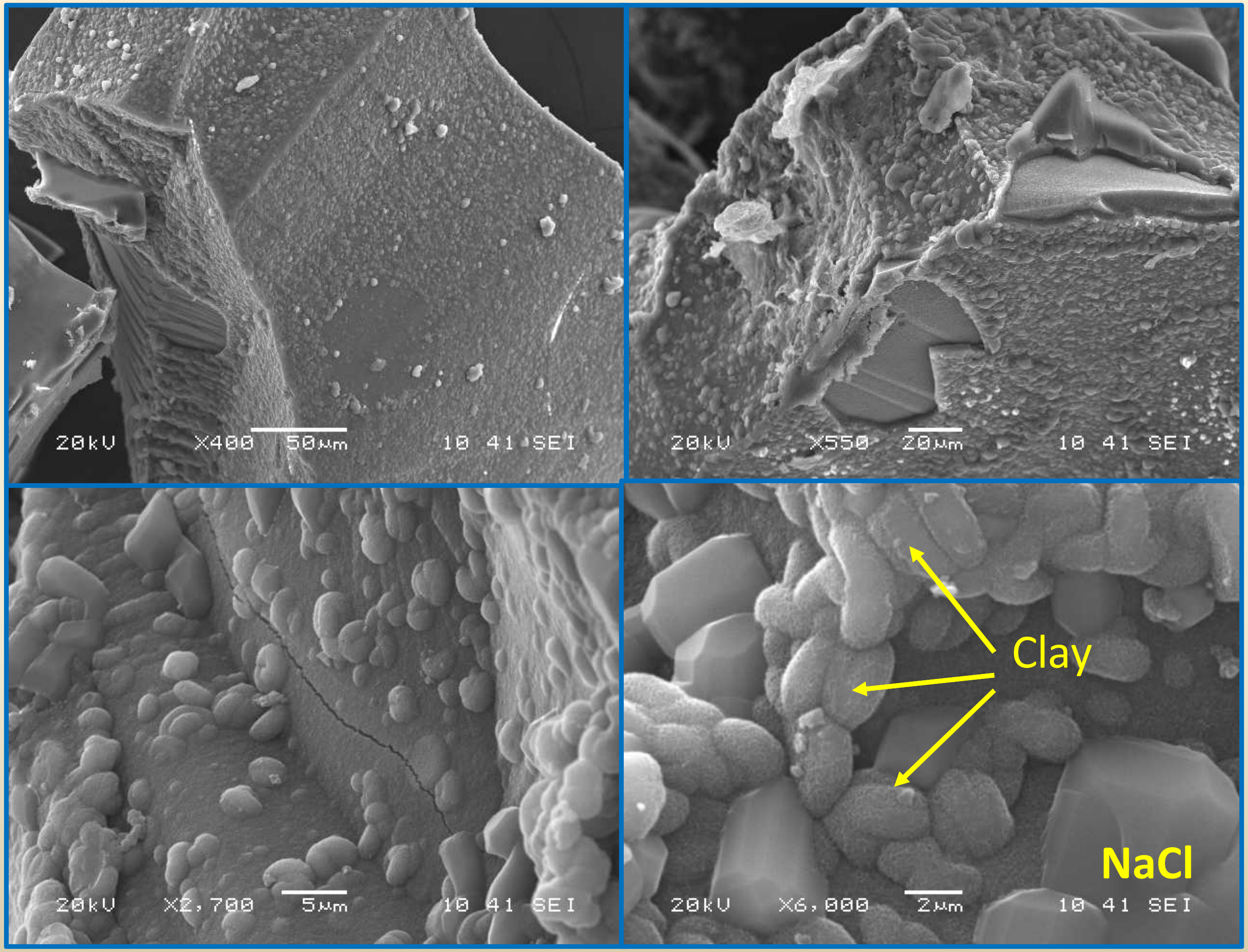
Static Experiments-SEM

Powders reacted in $MgCl_2$ solutions



Static Experiments-SEM

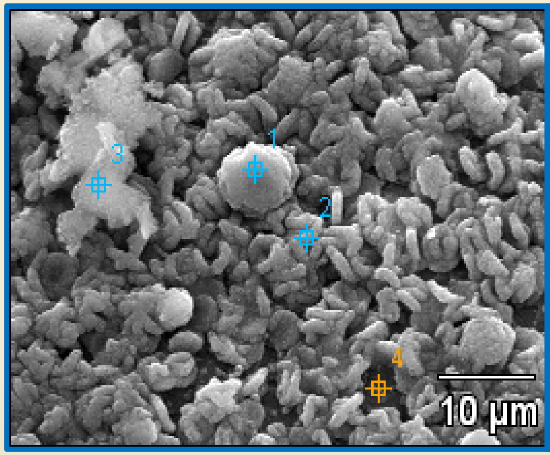
Powders reacted in NaCl + $MgCl_2$ solutions



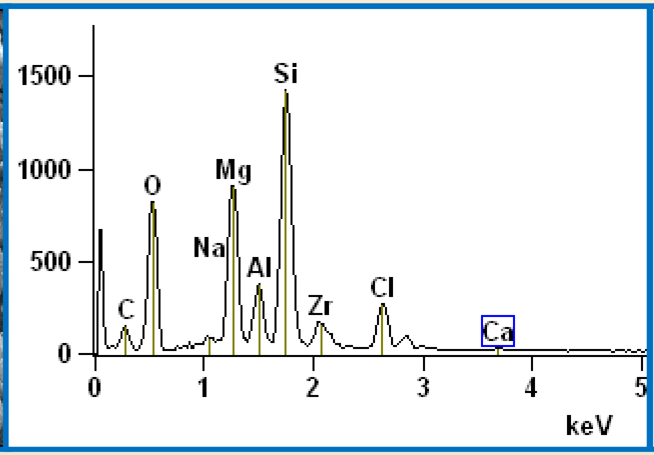
Static Experiments-SEM

Clays identified as saponite (smectite)

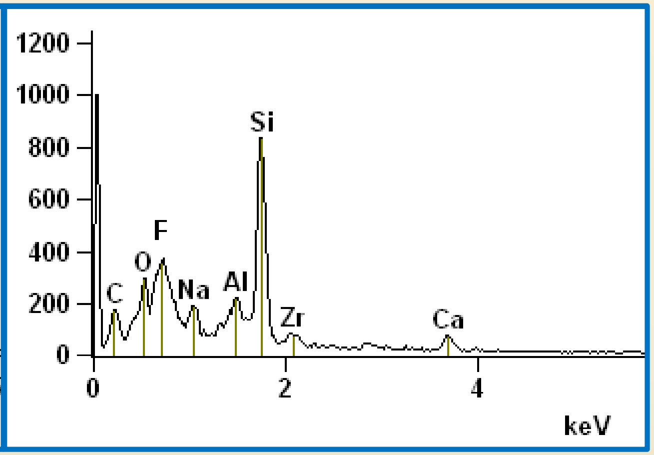
SEM image; clays



EDS of clays

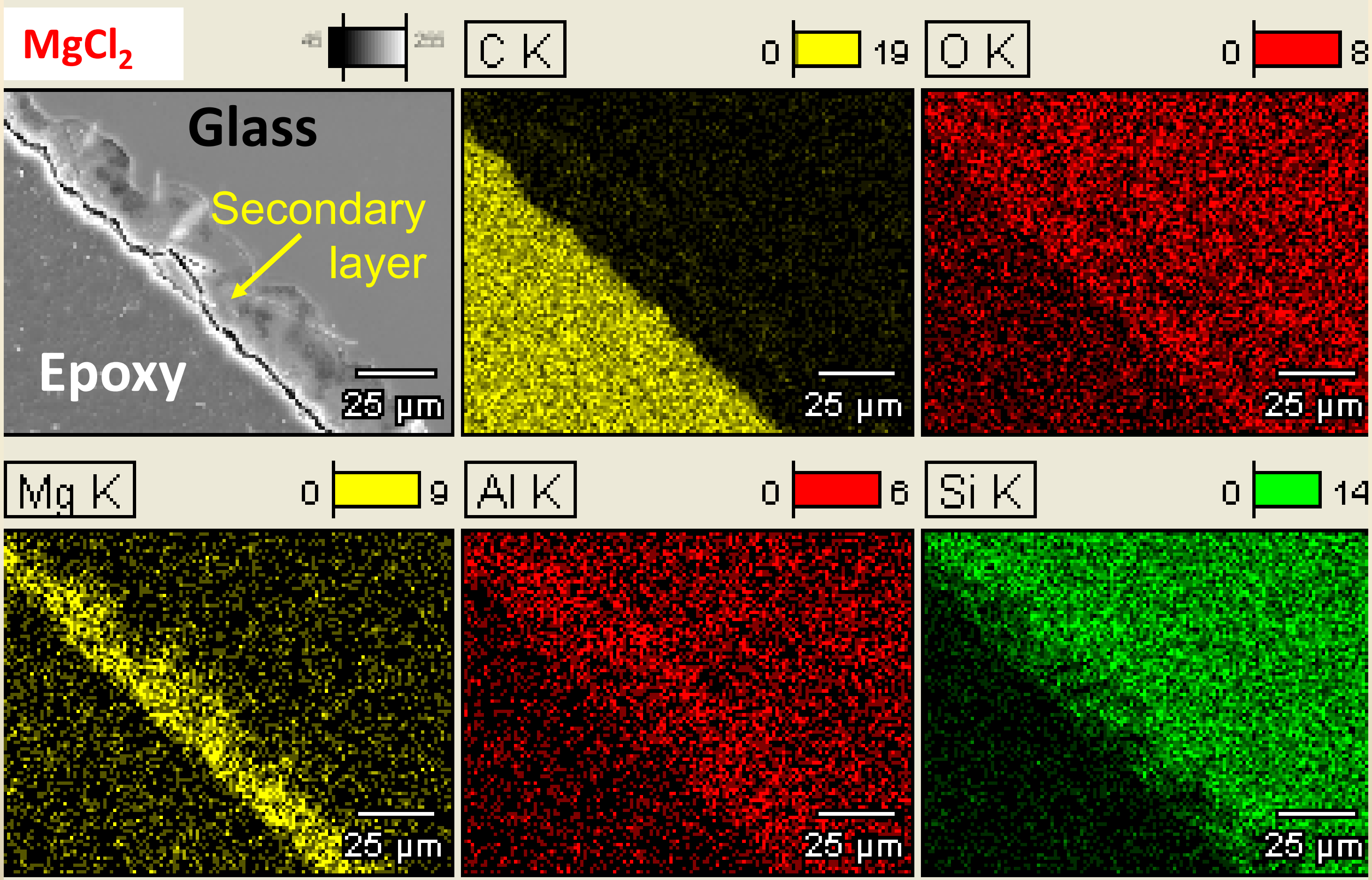


EDS of unreacted glass

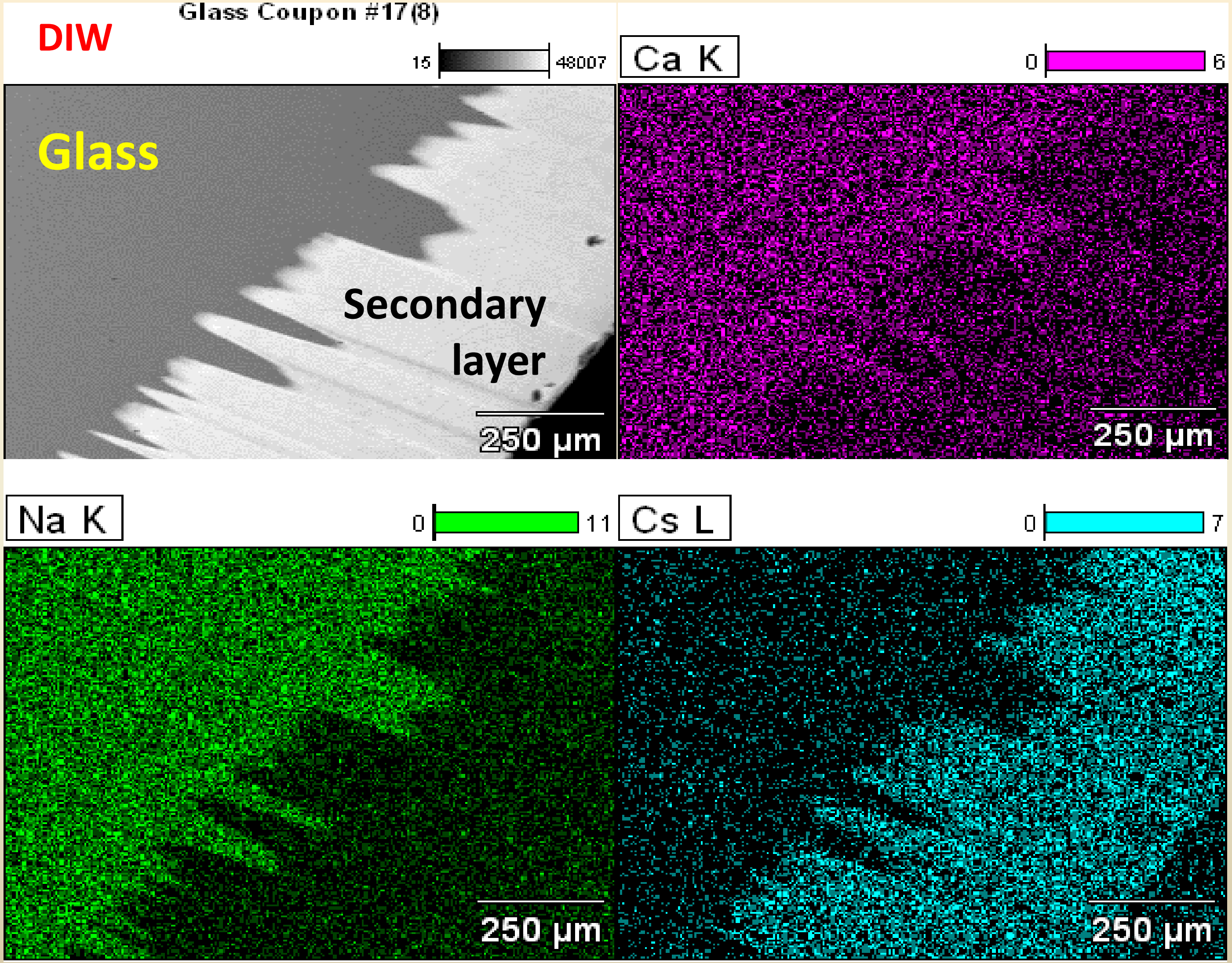


Static Experiments-SEM

X-ray mapping showing element distribution

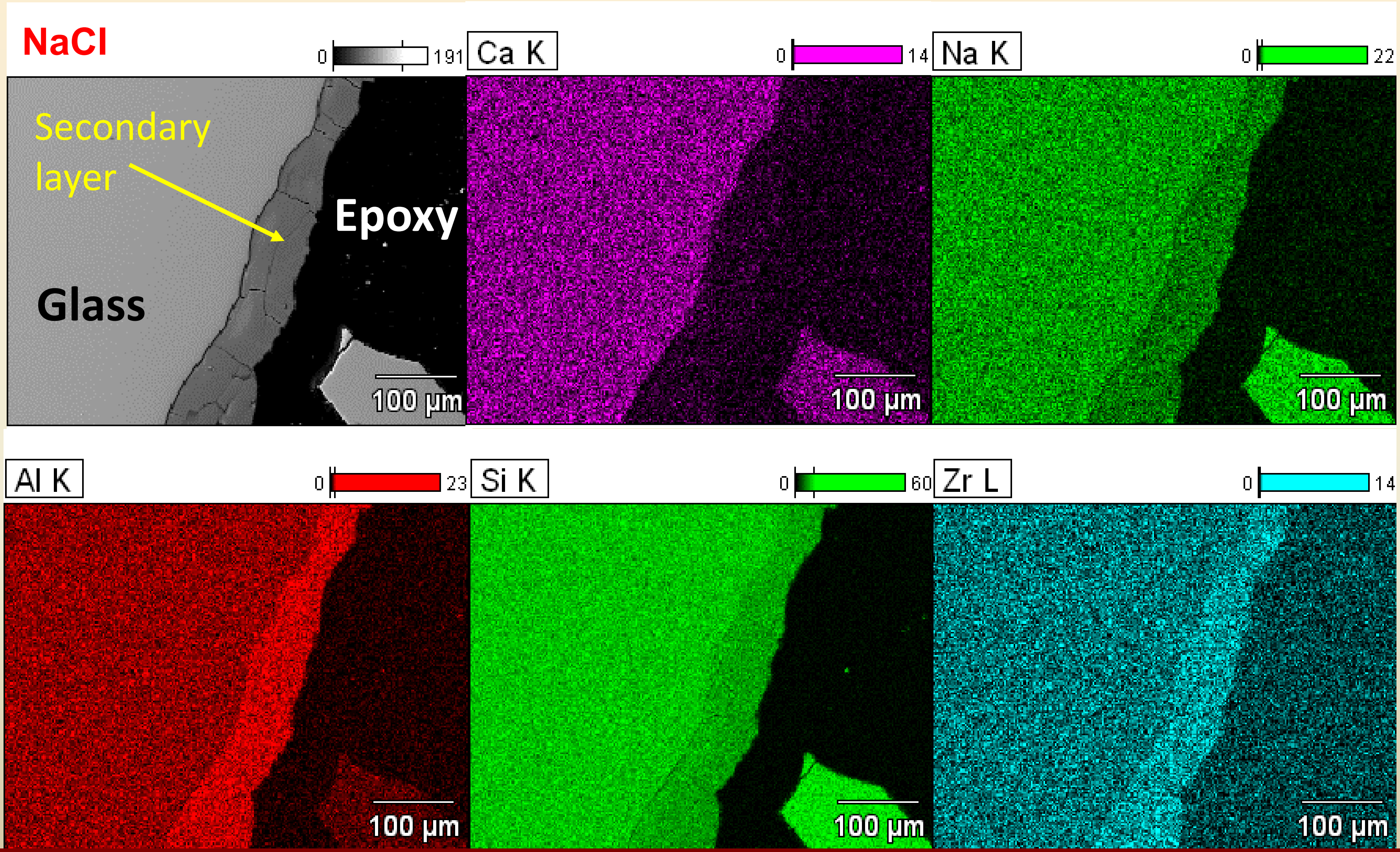


Flow-Through Experiments on "Monoliths" (Coupons)-SEM
X-ray mapping showing element Distributions



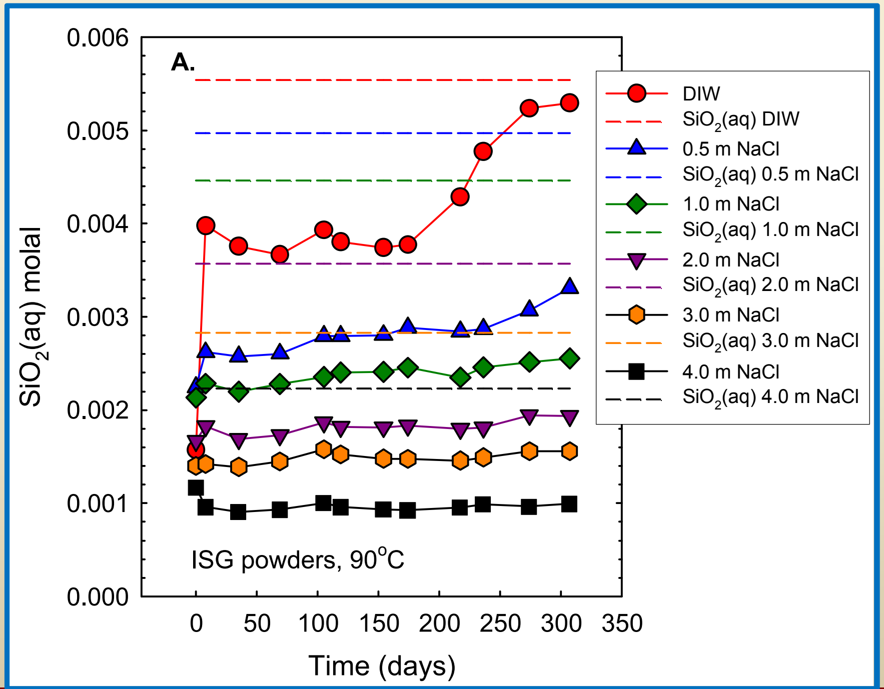
Flow-Through Experiments on “Monoliths” (Coupons)-SEM

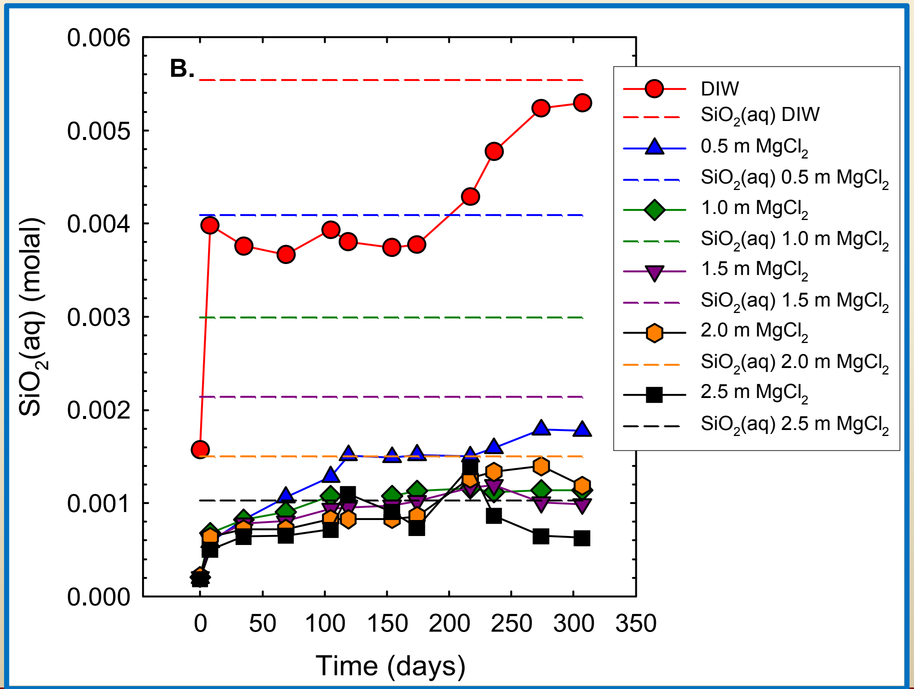
X-ray mapping showing element Distributions



Modeling Silica Saturation in Static Experiments

- Saturation of SiO_2(am) in NaCl and $MgCl_2$ solutions not yet worked out.
- Accordingly, we constructed a model for silica saturation based on Pitzer parameters. See: Icenhower et al. (2018) *GCA*





Equilibrium with Saponite

(Mg-rich trioctahedral smectite or clay)

Saponite

Results of saponite synthesis experiments can be found in Xiong et al. (2018) *npj Materials Degradation*

$$Na_{0.95}Mg_{5.90}[(Si_{7.07}Al_{0.99})O_{20}](OH)_4 + 2.38OH^- + 5.86H_2O(l) \rightleftharpoons 0.95Na^+ + 5.90Mg^{2+}$$

$$+ 0.99Al(OH)_4^- + 7.07H_2SiO_4^{2-}$$

Log *K* expression for the dissolution of saponite:

$$K^0 = \frac{(a_{Na^+})^{0.95} \times (a_{Mg^{2+}})^{5.90} \times (a_{Al(OH)_4^-})^{0.99} \times (a_{H_2SiOH_4^{2-}})^{7.07}}{(a_{OH^-})^{2.38} \times (a_{H_2O})^{5.86}}$$

$$SI = \frac{Q}{K^\circ}$$

Experiments	Saturation Index,
S-15 at $m_{\Sigma Mg}$ = 1.26	7.80
S-15 at $m_{\Sigma Mg}$ = 1.39	8.93
S-17 at $m_{\Sigma Mg}$ = 1.45	4.47
S-17 at $m_{\Sigma Mg}$ = 1.60	6.90
S-17 at $m_{\Sigma Mg}$ = 1.96	11.83
S-19 at $m_{\Sigma Mg}$ = 1.90	-0.39

Conclusions

- With the addition of NaCl rates increase sharply.
- At higher concentrations of NaCl, the rates drop as the activity of water decreases, as predicted by models.
- The rate catalysis behavior of ISG is similar, but smaller in scale, than that displayed by quartz and amorphous silica.
- Higher concentrations of $MgCl_2$ suppress rates.
- Rates in NaCl and $MgCl_2$ drop because:
  - Formation of secondary phases on glass surface prevent water from reaching surface
  - Setting silicic acid activities through saturation.
- Disposing of HLW glass could be accomplished in rock salt.

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- Thanks to Kris Kuhlman for continued support as Salt R&D changed directions.
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  - Yongliang Xiong—Saponite saturation modeling.
  - Heather Burton and Cassie Marrs—Solution analyses.
  - Leslie Kirkes—pcH correction, SEM.
  - Jandi Knox—BET and SEM.

Static Experiments-SEM

X-ray mapping shows phase distribution