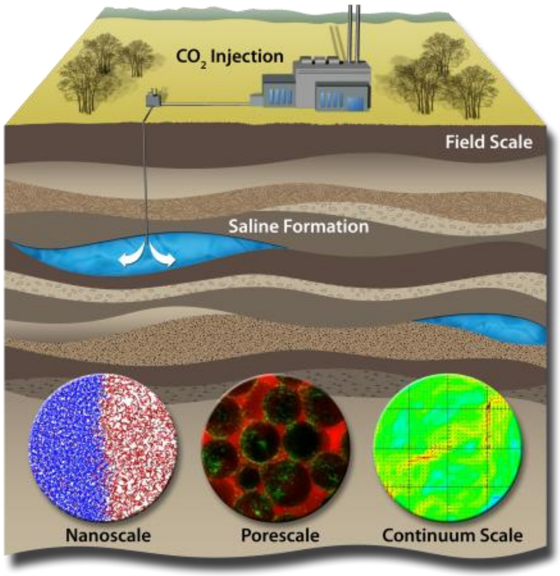
SAND2013-7370P

Mixing-controlled Reactive Transport at the Pore Scale and Its impact on Flow Field and Upscaling of Reactive Transport

Hongkyu Yoon

September 4, 2013



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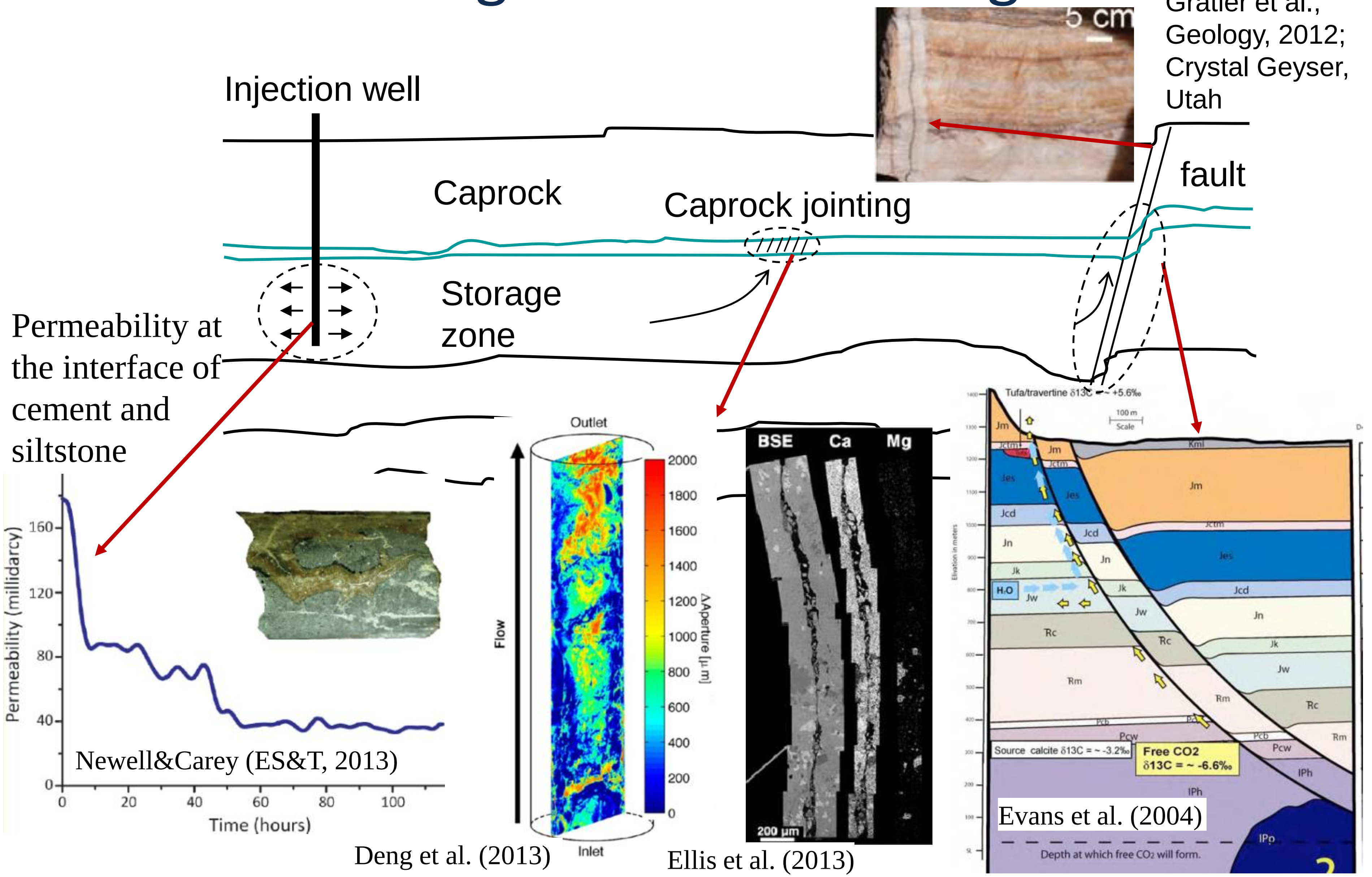
Outline

- **Motivations**
- Research Efforts
- Research Highlights
- Future Works

Reactive Transport Processes during Geological Carbon Storage

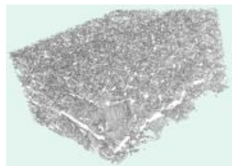


Multi-Scale Problems

Pore Scale

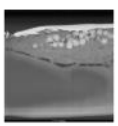
Core sample

Micro-CT

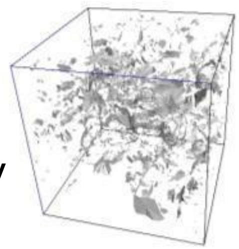


Statistical REV

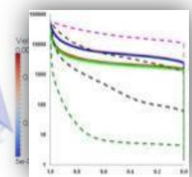
Confocal Microscopy



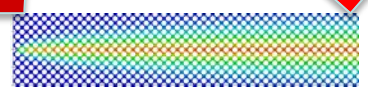
FIB-SEM

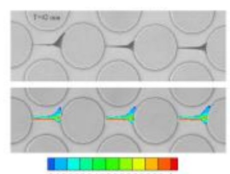


Pore throats

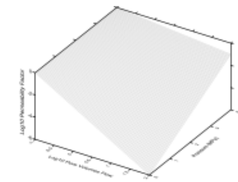


UPSCALING

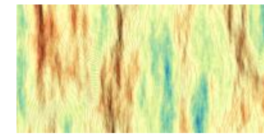




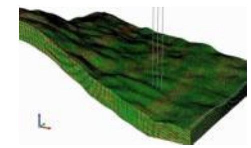
Grid Block Scale



Reaction rate



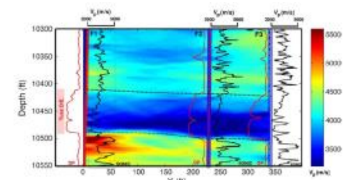
Reactive flow



3D permeability field

Observed Data

Different types
Spatial scale
Temporal scale



Seismic data

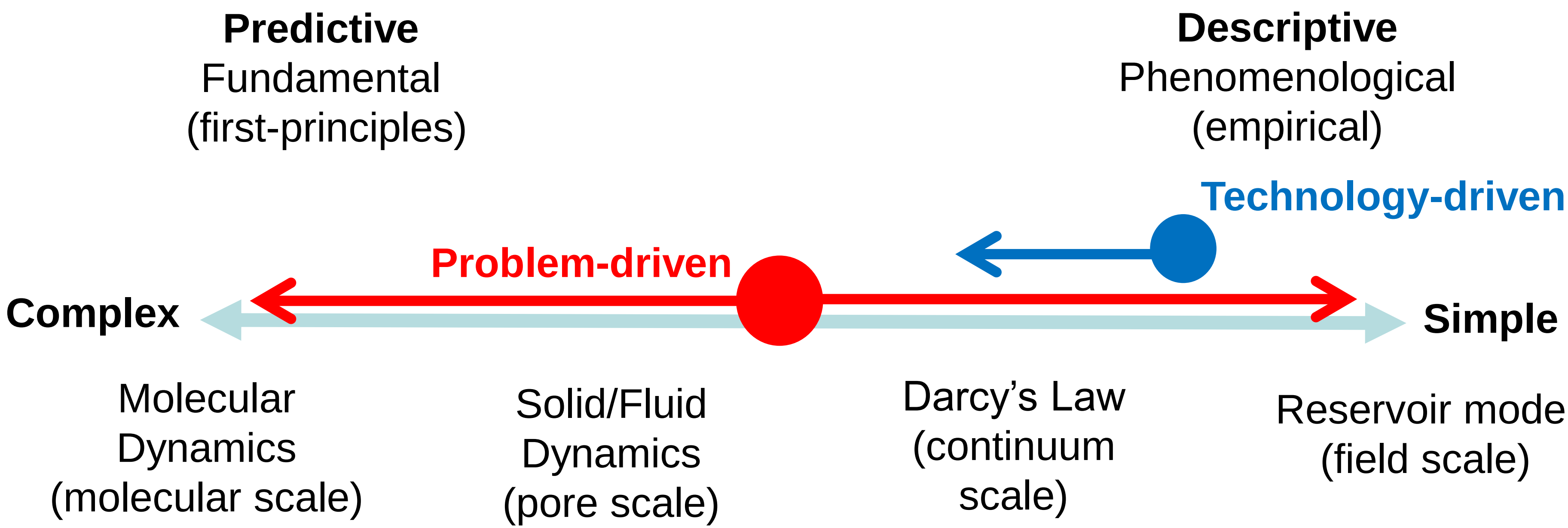
Predictive
Fundamental (first-principles)

Descriptive
Phenomenological (empirical)

Complex ⟷ **Simple**

Molecular Dynamics (molecular scale)	Solid/Fluid Dynamics (pore scale)	Darcy's Law (continuum scale)	Reservoir model (field scale)

What is the approximate level of complexity?



Where do we want (or need) to be?

Where can we be in practice?

Modified from Scheibe (2011)

Research Direction

- Develop experimental and numerical tools to study a comprehensive understanding of multi-physics processes over a range of scales (nano to field scales)
- Apply recent advances in tool development to bridge the gap between two questions

Example:
Pore Scale Reactive Transport

• Developed a novel pore scale reactive transport model of coupled fluid flow, reactive transport, and precipitation and dissolution using pore scale experiments in a microfluidic pore-network (i.e., micromodel)

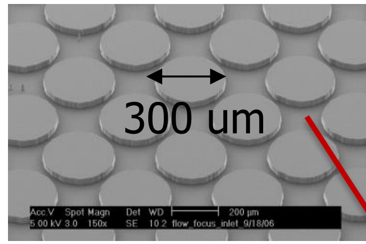
Micromodel Experiment

Micromodel Description

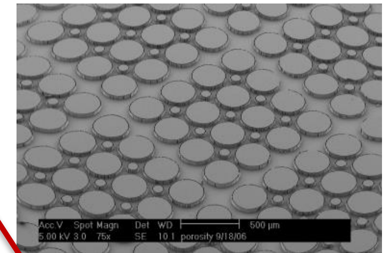
Depth: ~20 mm

Porosity: ~0.39

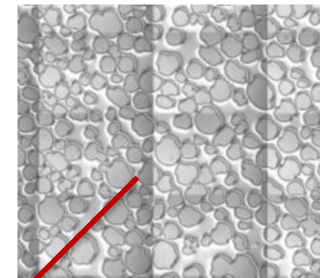
Flowrate: ~2 cm/min



Base Case
Small Cylinder



Aggregates

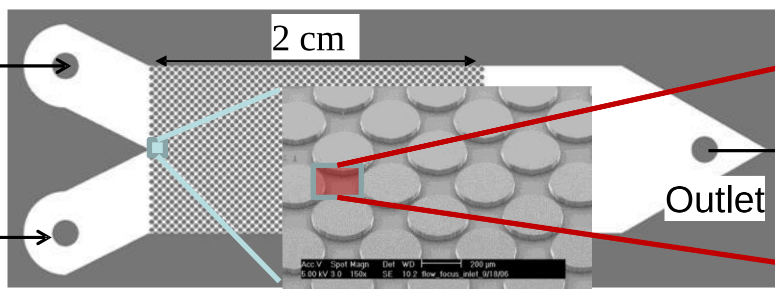


Irregular

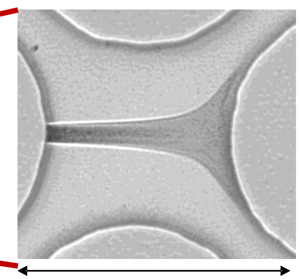
Thermal oxidation:
~ 100 micron thick oxide layer

Na_2CO_3
(pH=~11)

$CaCl_2$
(pH=~6)



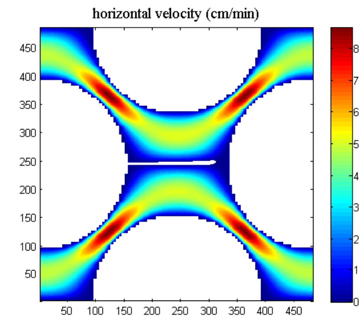
Zhang and Dehoff et al. ES&T (2010)



- Two solutions are mixing along the centerline and $CaCO_3$ precipitates
- Range of concentrations and solution chemistry vary
- Microscopic images are taken over time

Microscopic image of calcium carbonate ($CaCO_3$) precipitates

Pore Scale Model Framework



Velocity

Lattice Boltzmann Method:
Velocity field (u) at pore scale

↓

Finite Volume Method: Reactive transport at pore scale

Δt

$$\Psi_j = C_j + \sum_{i=1}^{N_{eq}} \upsilon_{ji} C_i$$

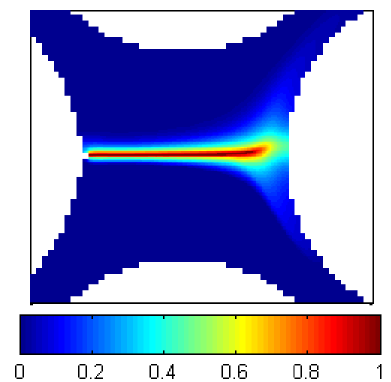
Chemical equilibrium in bulk fluid (e.g., H^+, HCO_3^-, …)
Extended Debye-Hückel Equation for activity coefficients

$$D\frac{\partial \Psi_j}{\partial \mathbf{n}} = -I_m \quad \text{on reactive surface}$$

$$I_m = k_{cc}\left(\left[\Omega\right]^n - 1\right)^m \qquad \Omega = \frac{Q_{CC}}{K_{sp}} \text{ or } \ln\left(\frac{Q_{CC}}{K_{sp}}\right)$$

Update of $CaCO_3$ volumetric content (V_m)

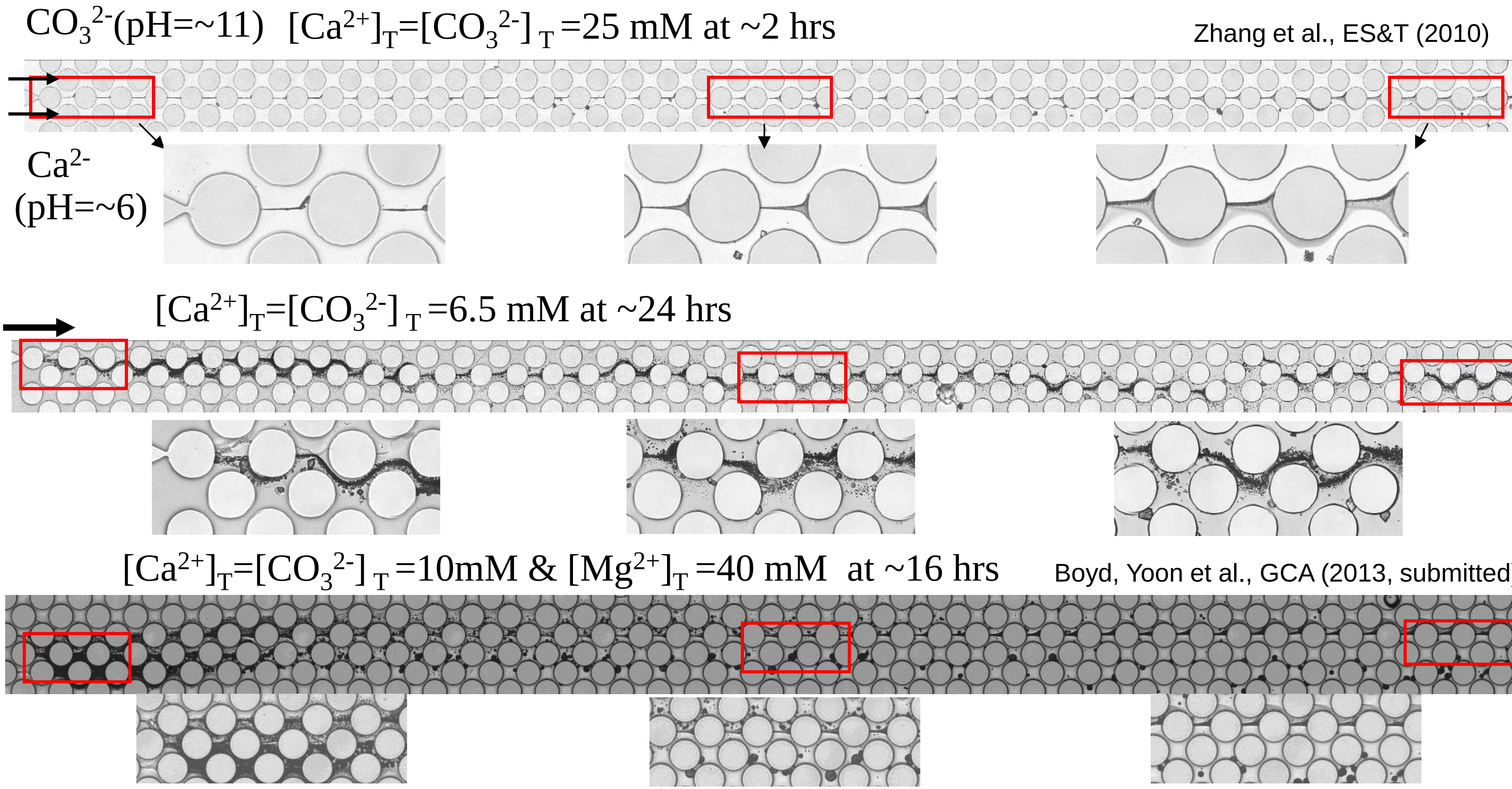
$$\frac{\partial V_m}{\partial t} = \overline{V_m} s_m k_{cc}\left(\left[\frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{sp}}\right]^n - 1\right)^m$$



Mineral phase volumetric content

Yoon et al. (WRR, 2012)

Experimental Results

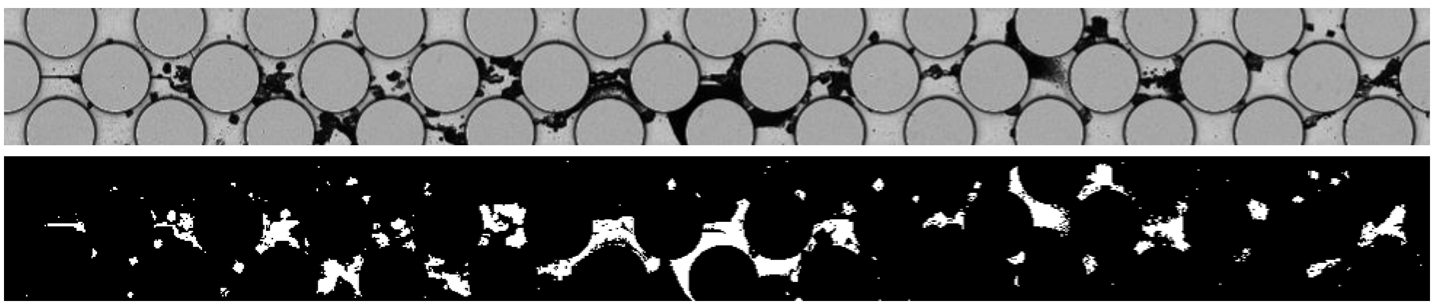


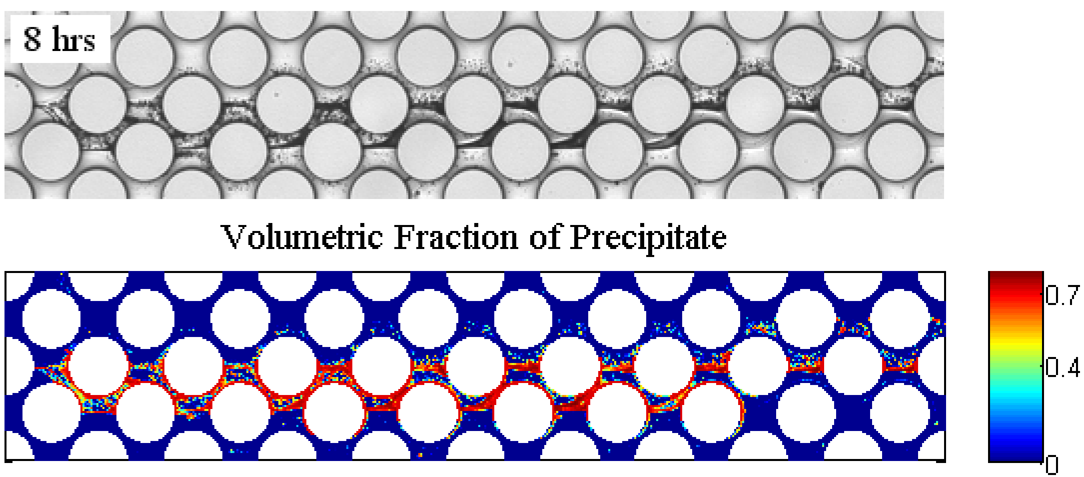
- Precipitation ~ along the centerline within 1-2 pore spaces in the transverse direction
- Width of the precipitate line ~ increase with distance from the inlet
- Rate of precipitation is concentration and species dependent

Image Analysis

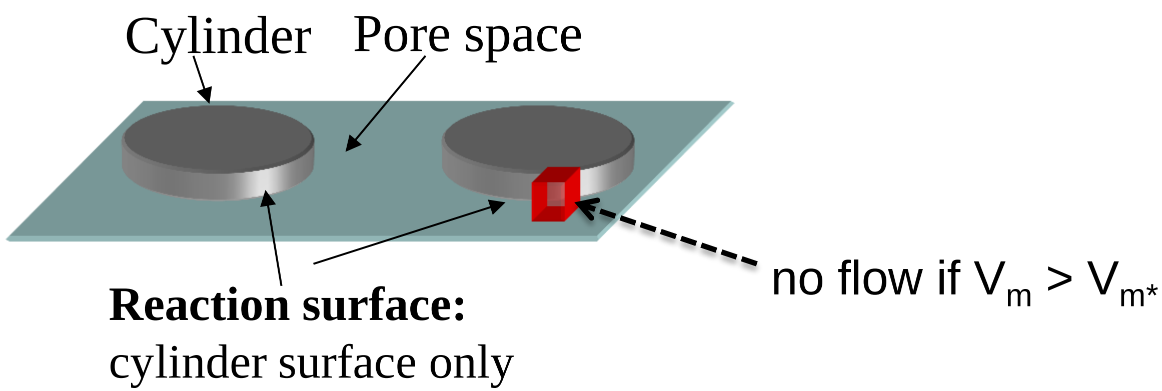
Otsu thresholding

- Pixels segmented into foreground and background
- Uses threshold values that result in minimum interclass variance between foreground and background





Results: Precipitation only at grain boundary



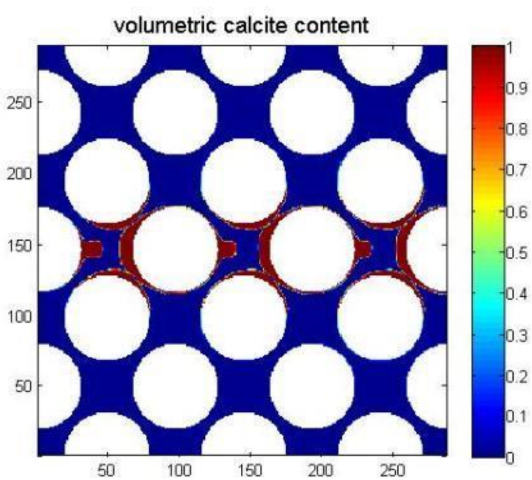
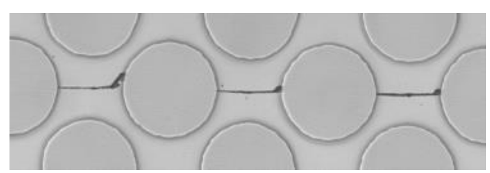
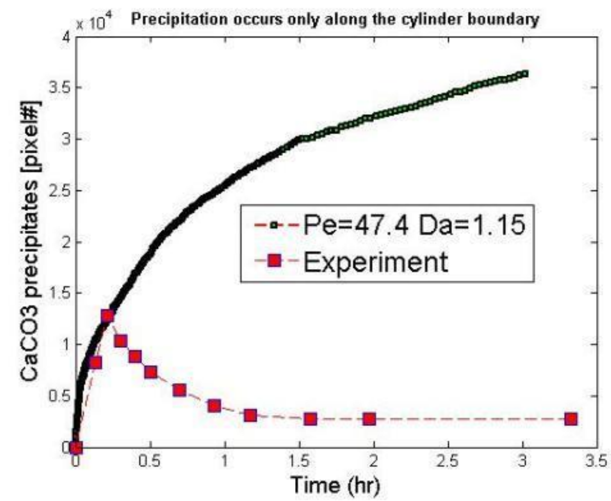


Image of precipitates at 180 min



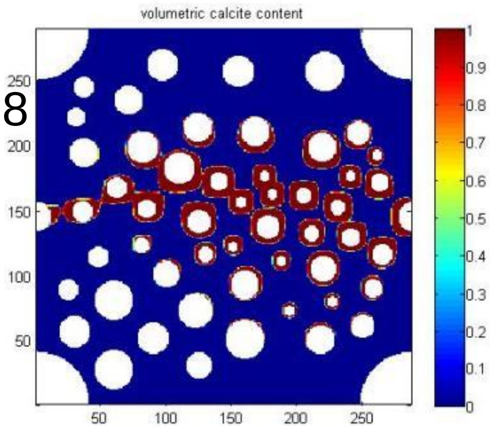
25 mM Experiment



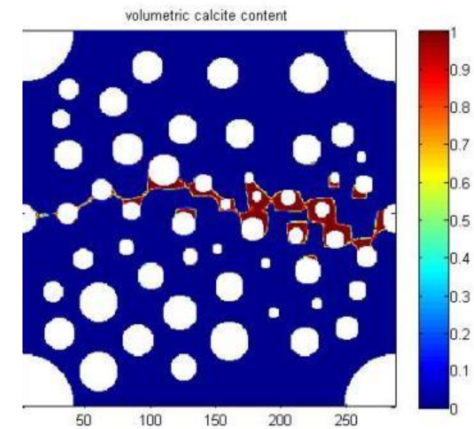
Precipitation patterns

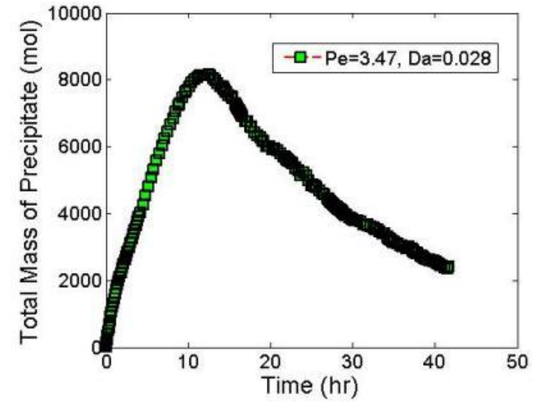
Pe=3.47
Da=0.028

T=700 min



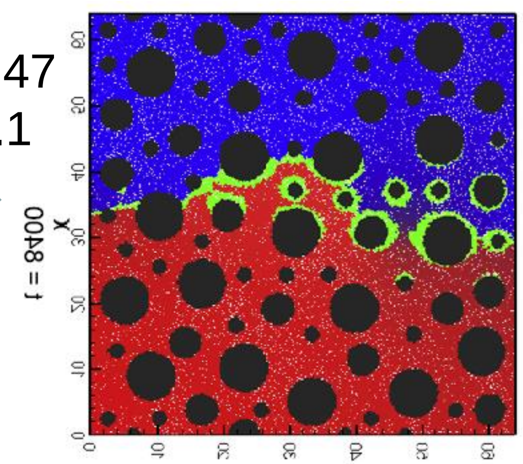
T=2500min



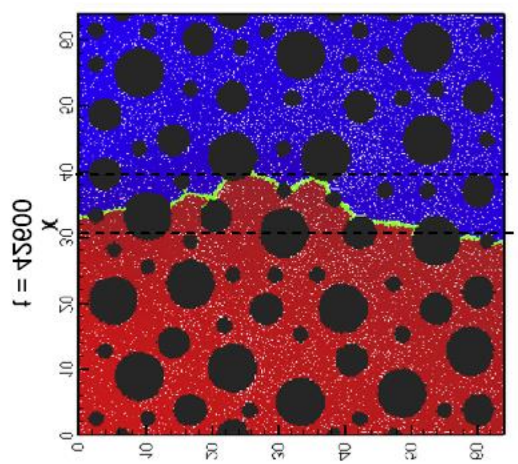


Pe=0.47
Da=1.1

T=8400



T=42600



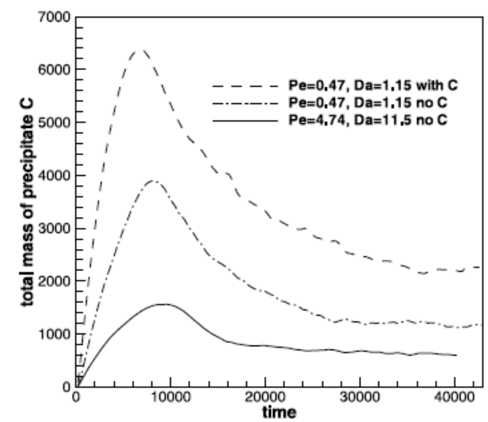
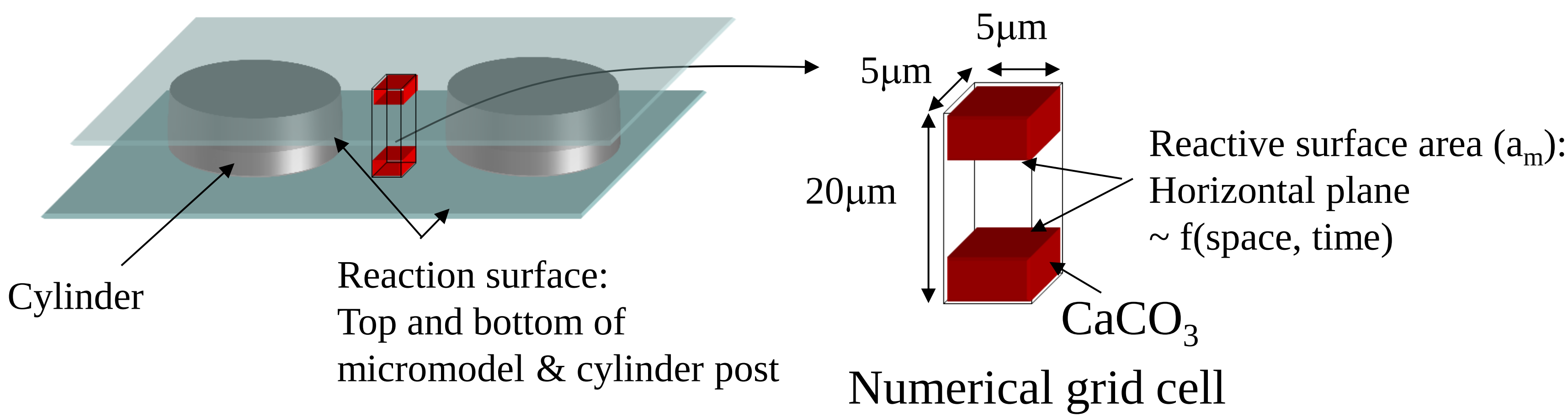


Figure 8. Time dependence of the total mass of precipitate *C* obtained from several simulations with and without the intermediate reaction produce, *C*, for different *Pe* and *Da*.

Tartakovsky et al. (WRR, 2008)

Reaction in a micromodel system

1. Quasi 3D grid cell for reactive surface

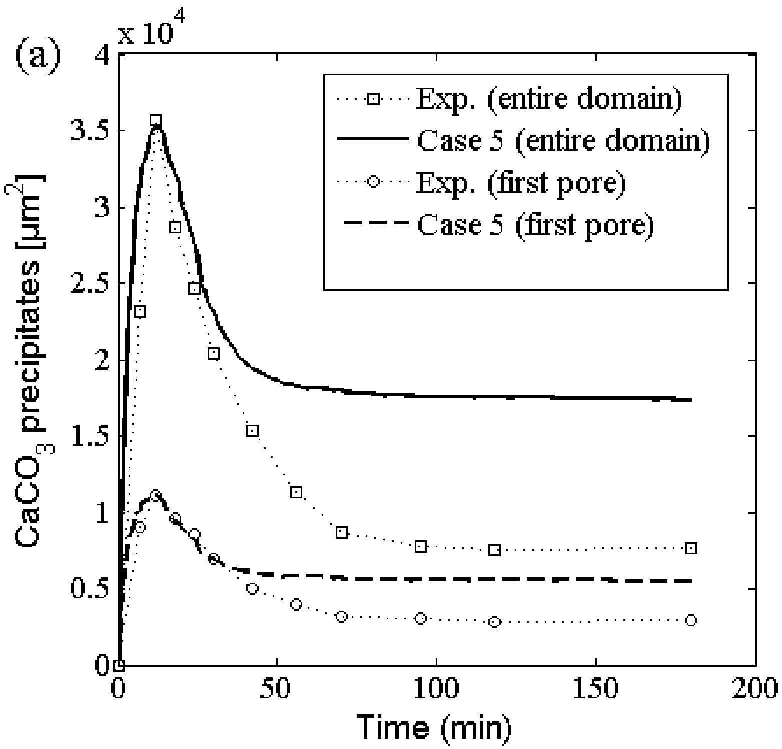


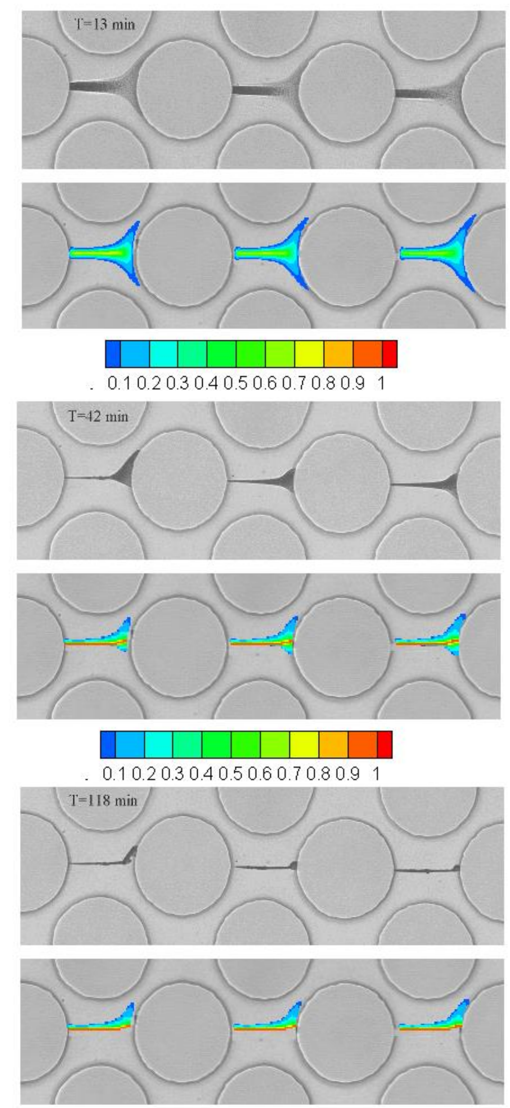
2. Effective diffusion coefficient = D_m * tortuosity (τ)

- $\tau(V_m) = (1- V_m)^n$ where n ~ 0 to 3
- Diffusion is allowed until the grid cell is fully occupied by $CaCO_3$

Yoon et al. (WRR, 2012)

Simulation results: Increase surface area during dissolution by 300





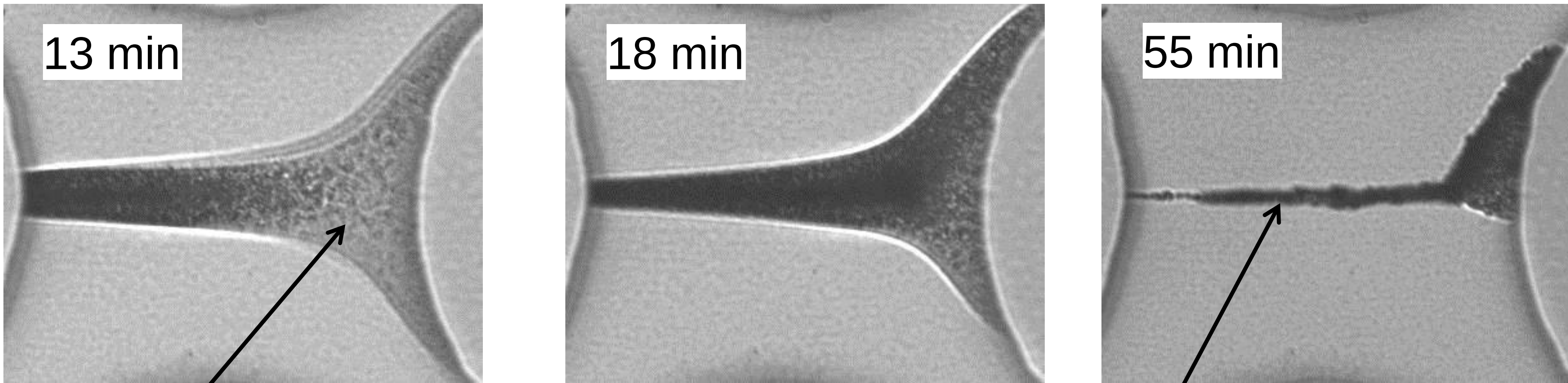
13 min

42 min

118 min

- Model results match thickness and area of precipitate until 30 min
- Model predicts dissolution below the centerline well, but not above the centerline

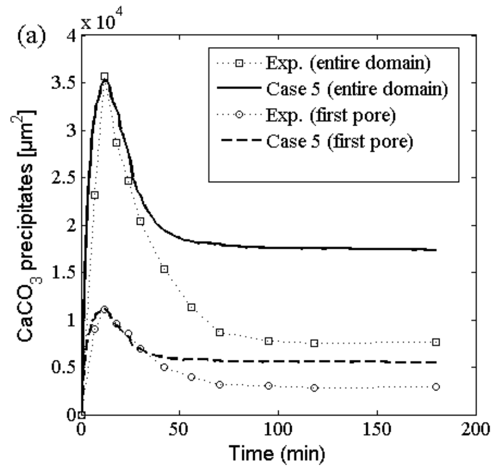
Matching simulation to late-time dissolution



Amorphous Calcium Carbonate & Vaterite

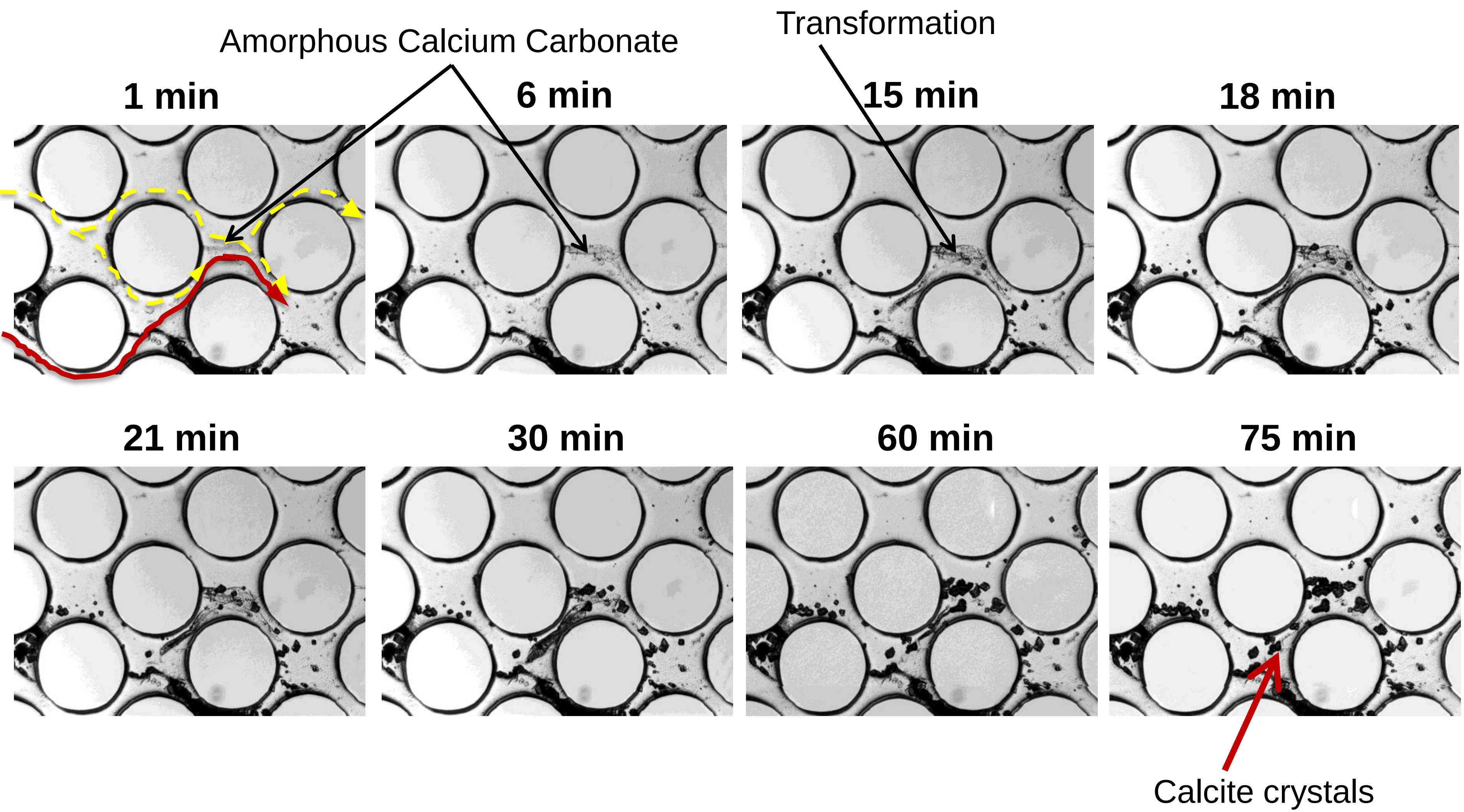
Predominantly Vaterite

- Increase in surface area over time
- Transformation to different forms of $CaCO_3$
- Stability of nano-particles after pore blocking (or reduced mixing along the centerline)
- Effect of nano-crystal size on solubility (Emmanuel and Ague, Chem. Geo. 2011)



Rapid precipitation and transformation

6.5 mM Case



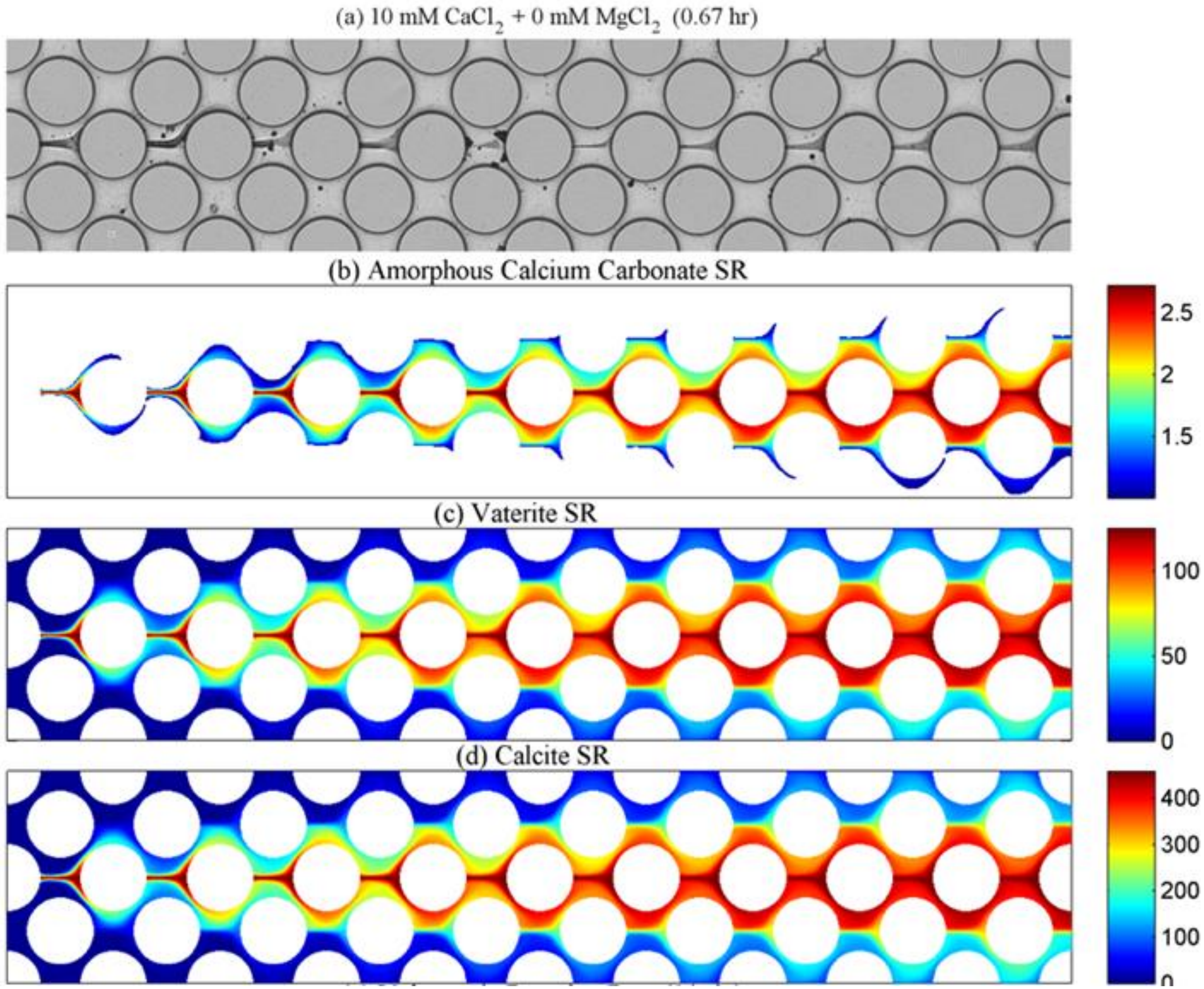
Calcium Carbonate: Polymorph

Saturation Ratio (SR) = Ion Activity product / Ksp
SR>1: thermodynamically favorable to form

$[Ca^{2+}]_T$=

$[CO_3^{2-}]_T$

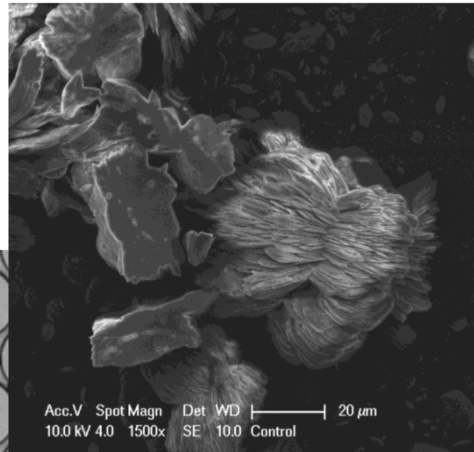
=10 mM



Boyd, Yoon et al. (2013, will be submitted, GCA)

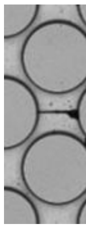
Adding Magnesium

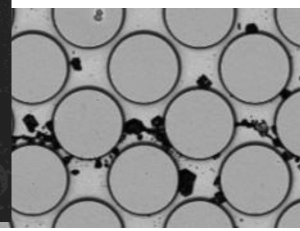
Adding [Mg^{2+}]



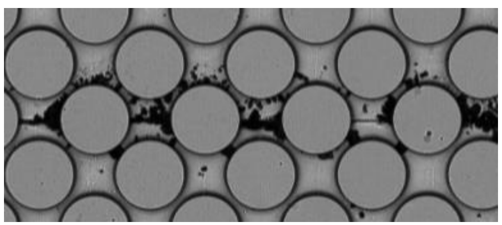
Center

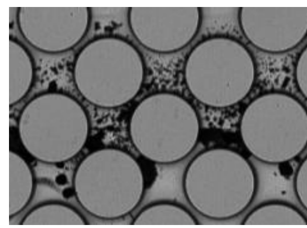
[Mg^{2+}]
=0mM



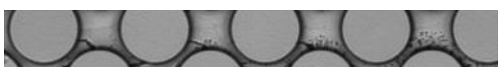


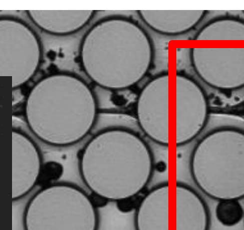
[Mg^{2+}]
=10mM

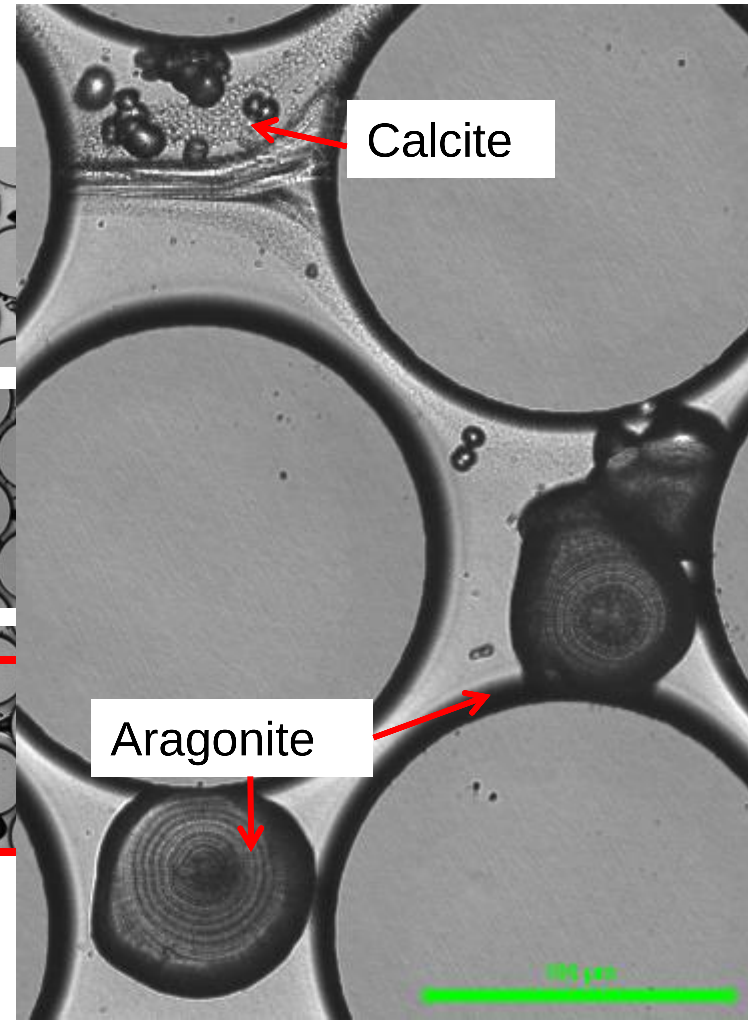


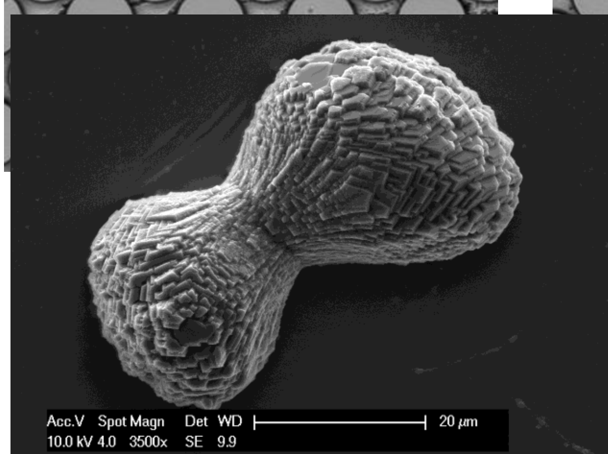


[Mg^{2+}]
=40mM



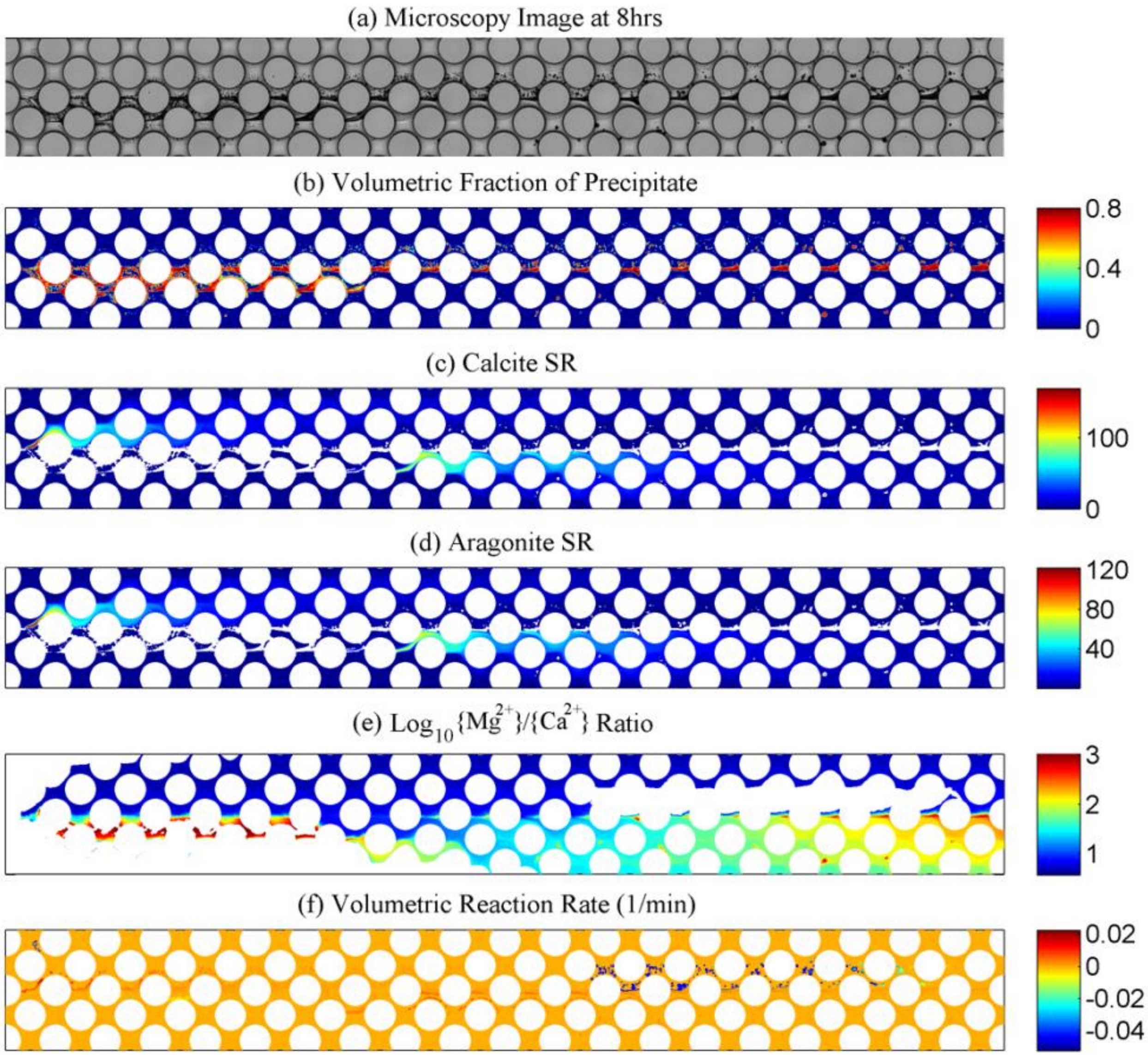






Impact of precipitation on flow pattern and reaction kinetics

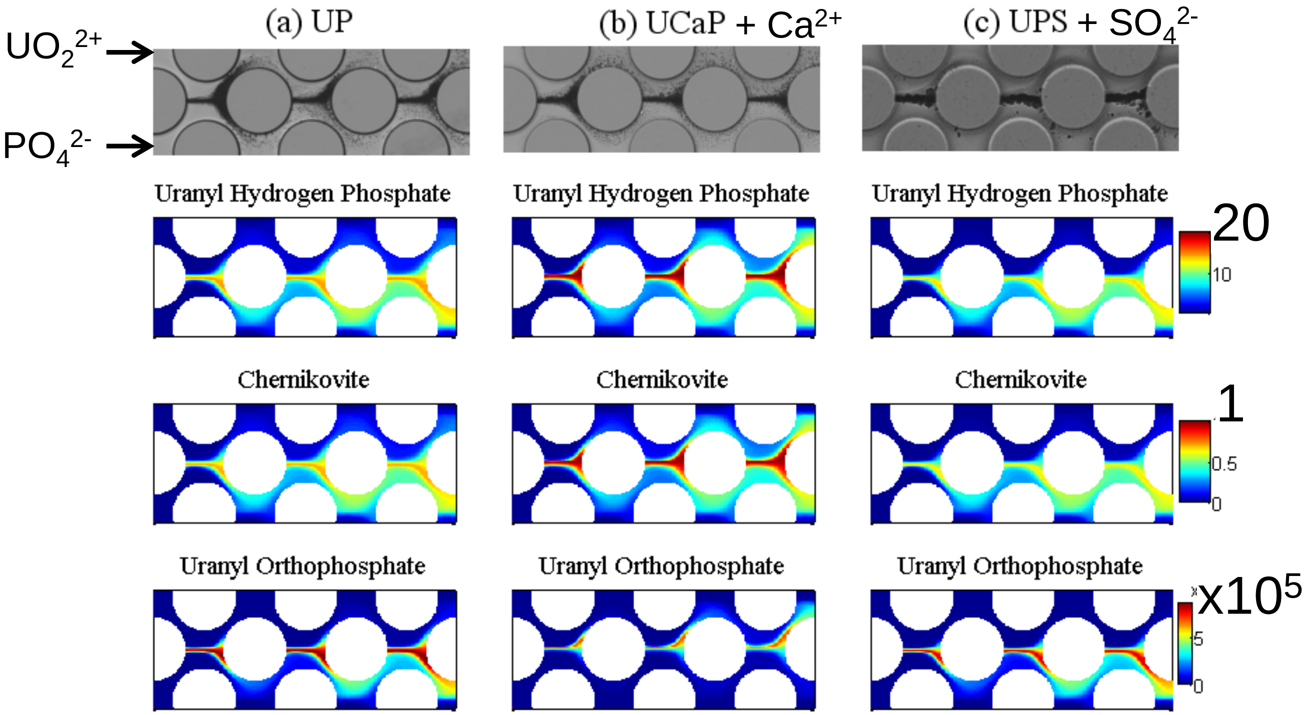
$[Ca^{2+}]_T=[CO_3^{2-}]_T=10mM$ & $[Mg^{2+}]_T=40$ mM



Boyd, Yoon et al. (2013, will be submitted, GCA)

Impact of Solution Chemistry

Saturation Ratio (SR) = Ion Activity product / Ksp
SR>1: thermodynamically favorable to form



Due to a kinetically controlled reaction,
only uranyl hydrogen phosphate (or chernikovite) is formed

Fanizza, Yoon et al. (2012)

Summary and Implications

- Mineral precipitation rate along flow direction is concentration dependent and limited by transverse mixing
- $CaCO_3$ mineral phases are concentration dependent
- Overall, reaction kinetics, crystal growth and morphology are spatially and temporally affected by solution chemistry and hydrodynamics at pore scale
- Pore-scale model can be used to test if pore-scale processes observed in micromodels is predicted, and to develop an upscaled reaction model

Upscaling and Ongoing effort

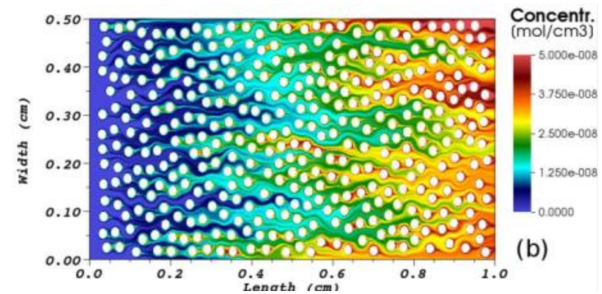
Upscaling/Hybrid modeling

No general method/ framework for upscaling:

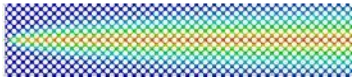
- Homogenization (multiple scale expansions)
- Volume averaging
- Pore network models (approx. physics)
- Mass balance principles based on pore scale models.
- Constitutive equation with closure based on detailed pore scale solutions (e.g., response function model)
- Hybrid pore-continuum approach

Upscaled reaction rate

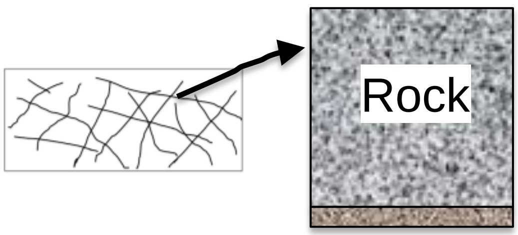
$$\dot{r}_{eff} = \frac{\left(\bar{C}_{in} - \bar{C}_{out}\right)Q}{\nu A} \qquad \bar{C}Q = \int_A \mathbf{u}c \bullet \mathbf{n}\, dS$$



Molins et al. WRR 2012

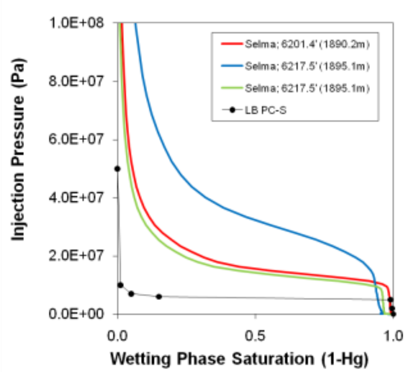


$$D_{T,R} = \frac{1}{X^3}\frac{9\pi v}{16C_0^{\,2}\varphi^2}\left[\int_0^X m(x)\,dx\right]^2$$

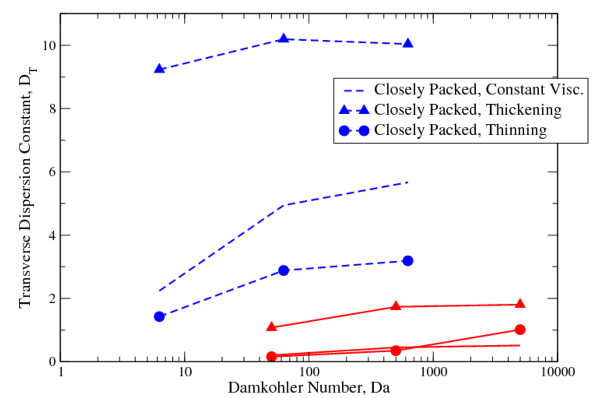


Joint

Geomodel (Kayanta):
Equivalent continuum joint model



Pc-Sw Curve

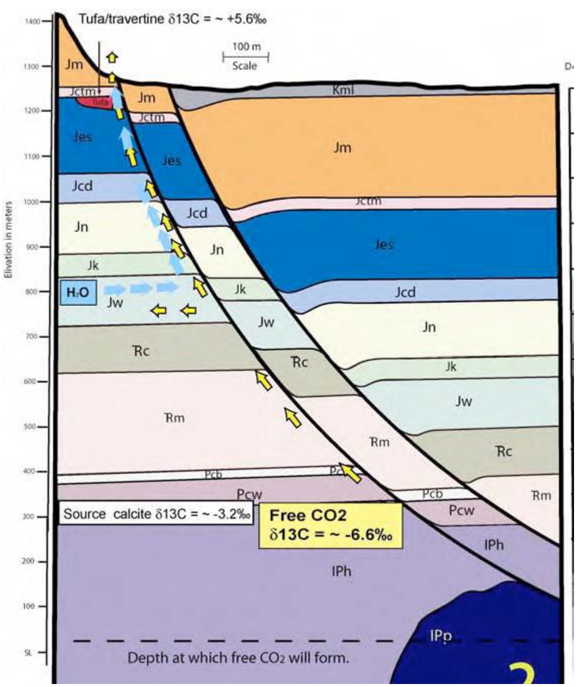


Upscaled dispersion

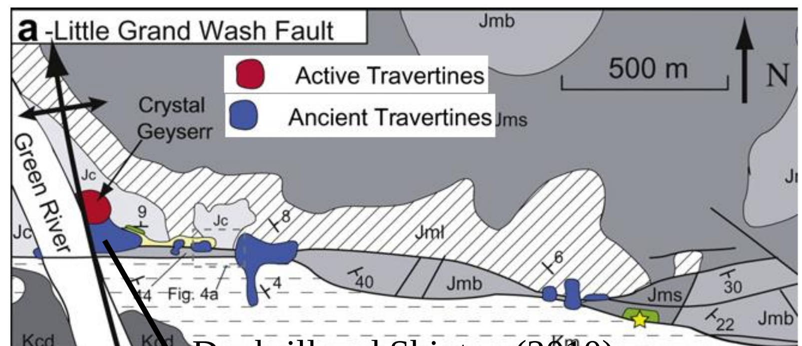
Davison, Yoon et al. (2012)

Simulation of Little Grand Wash Fault

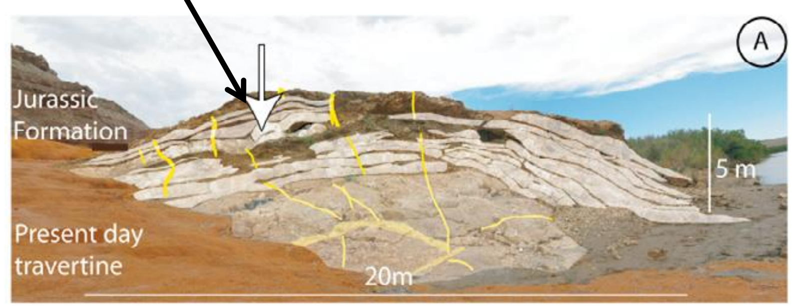
- Two hypotheses for CO_2 migration in the Crystal Geyser area:
  - <u>CO_2 gas release from mantle</u> along the fault
  - <u>CO_2 dissolved in groundwater</u> leaking up along the fault
- Develop scheme for selecting appropriate model for CO_2 leakage based on surface observation of travertine mounds



Evans et al. (2004)



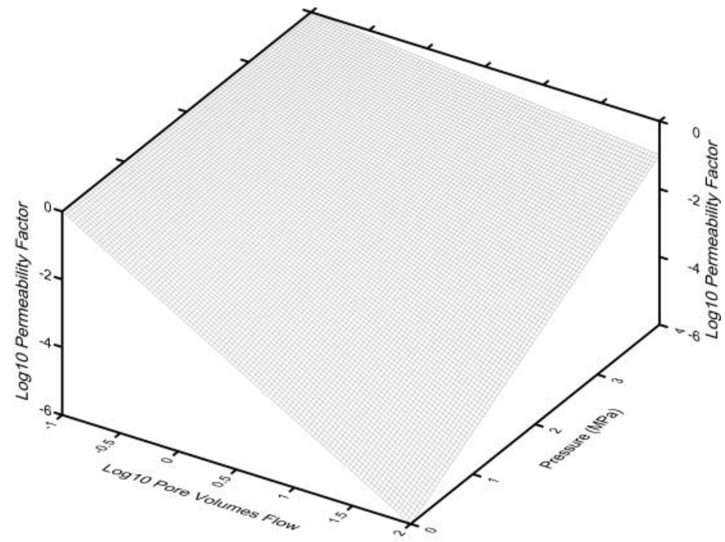
Dockrill and Shipton (2010)



Burnside (2010)

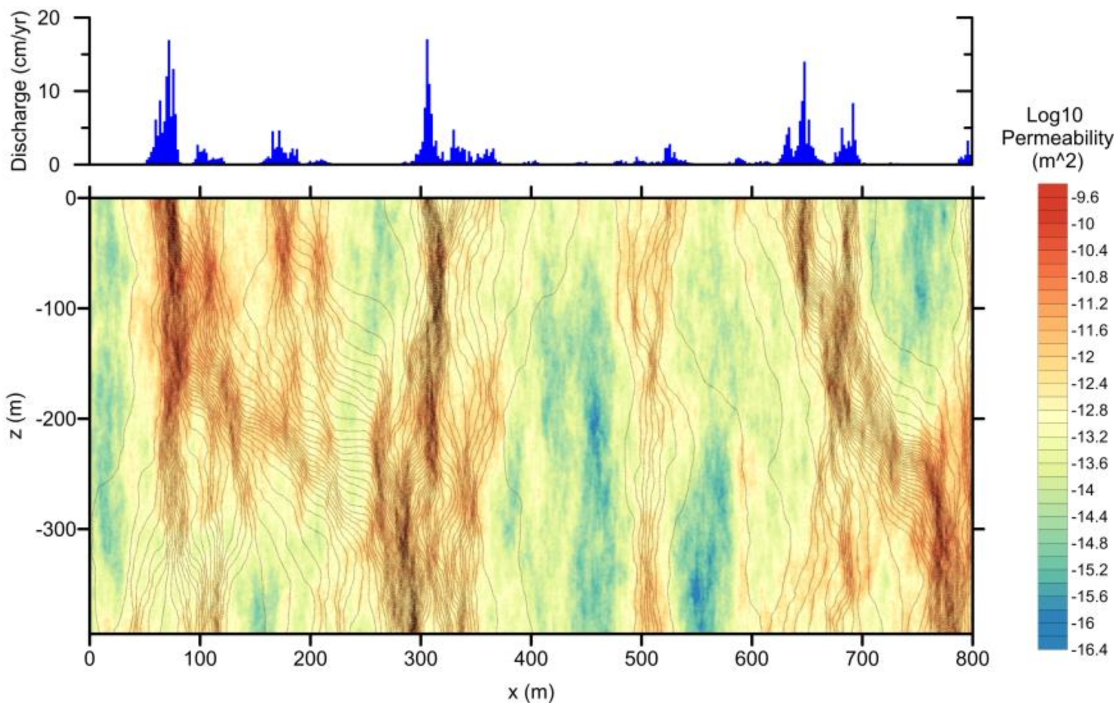
Crystal Geyser Site: Grand Wash Fault Modeling

- **Simplified, two-dimensional response surface defined for preliminary modeling example**
- **Permeability reduction due to calcite precipitation is a function of cumulative pore volume throughput of groundwater and as a function of fluid pressure**
- **Fluid pressure is taken as a gross proxy for chemical conditions in which higher calcite solubility is associated with higher fluid pressure (greater depth)**



Crystal Geyser Site: Grand Wash Fault Modeling

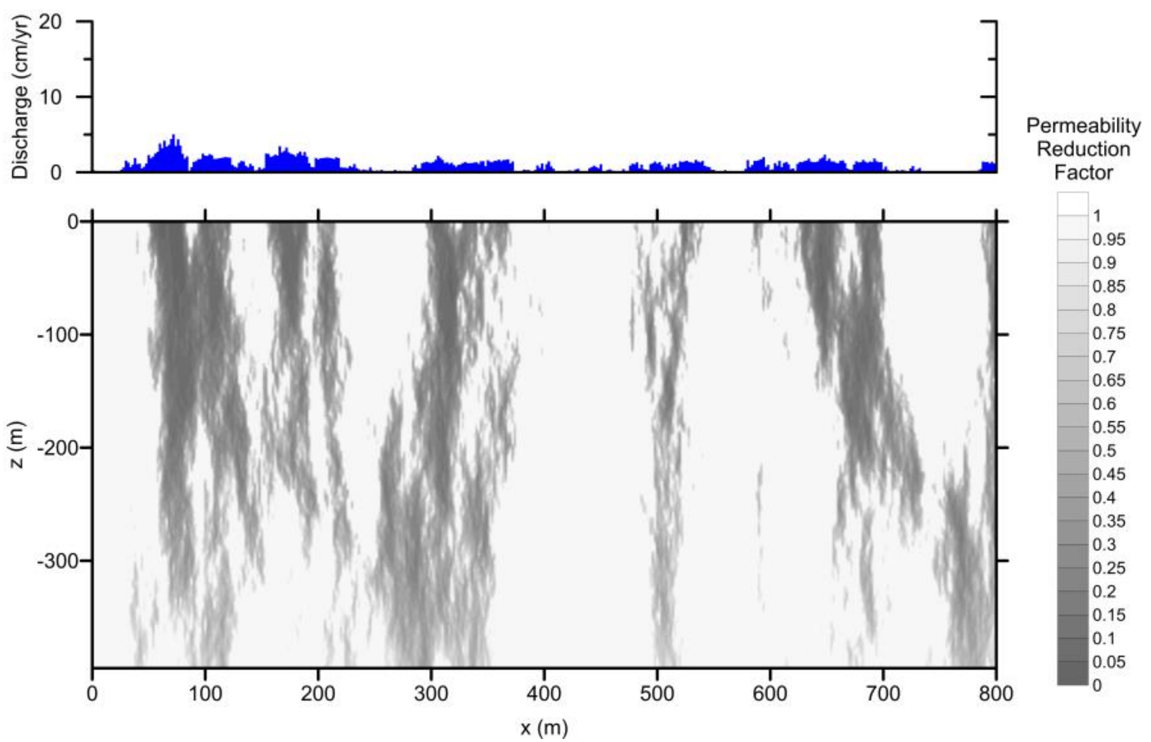
- **Unconditional geostatistical simulation of initial permeability is semi-quantitatively consistent with geologic mapping of fault segments and alteration**
- **Initial simulated steady-state flow pattern is qualitatively similar to the spacing of springs and seeps along the Grand Wash fault with spacings of 100's of m between locations of groundwater discharge**



Time = 0

Crystal Geyser Site: Grand Wash Fault Modeling

- **Transient flow simulation includes explicit updating of the permeability field at each time step using the response surface shown previously**
- **Permeability is reduced by several orders of magnitude by calcite precipitation, primarily in the shallower high-flow channels**
- **Evolution of the flow field results in more dispersed groundwater discharge at the surface**



Time = 1000 years

Response Function based on Pore Scale Simulations

Influx conditions

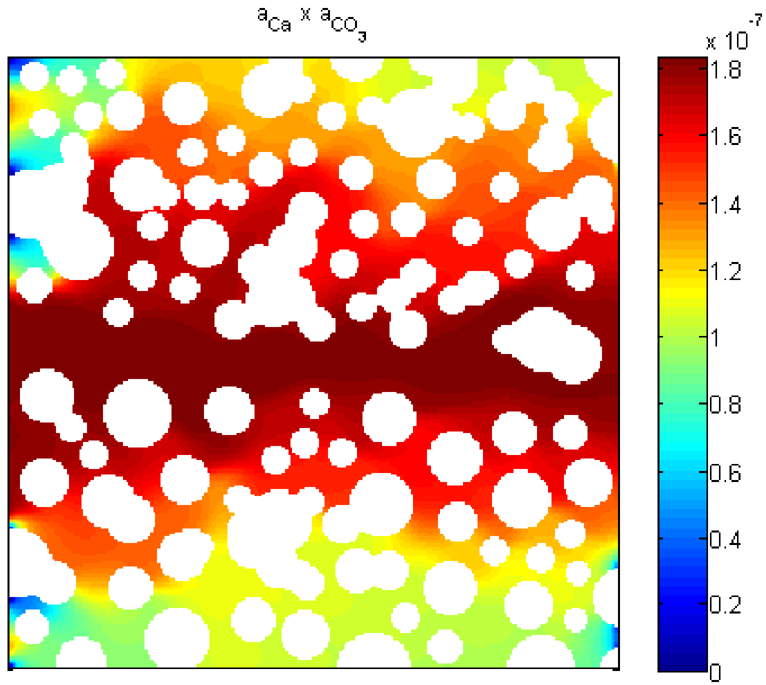
$[Ca^{2+}]_T=[CO_3^{2-}]_T=20mM$

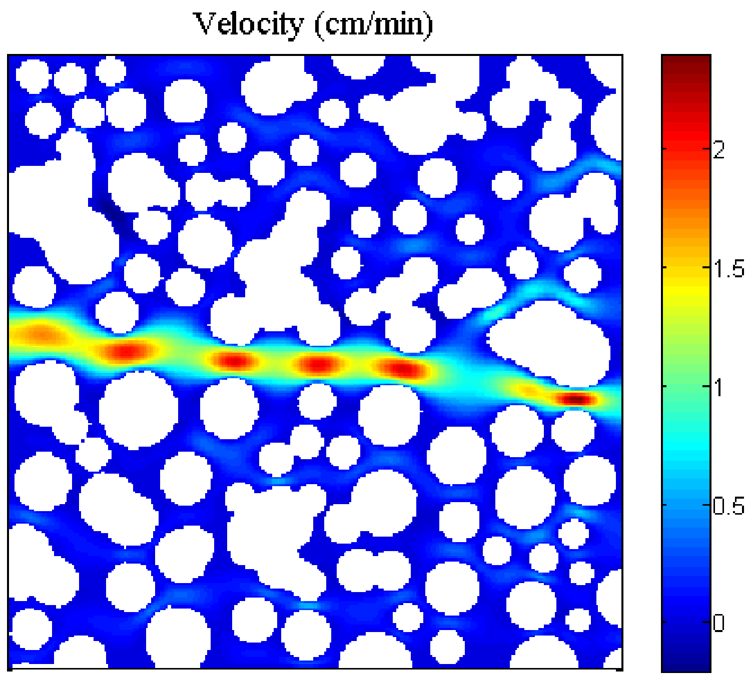
Pe = 0.08, 0.8, 8

Da = 0.002, 0.02, 0.1

Speciation: Ca^{2+}, H^+, CO_3^{2-} HCO_3^-, H_2CO_3

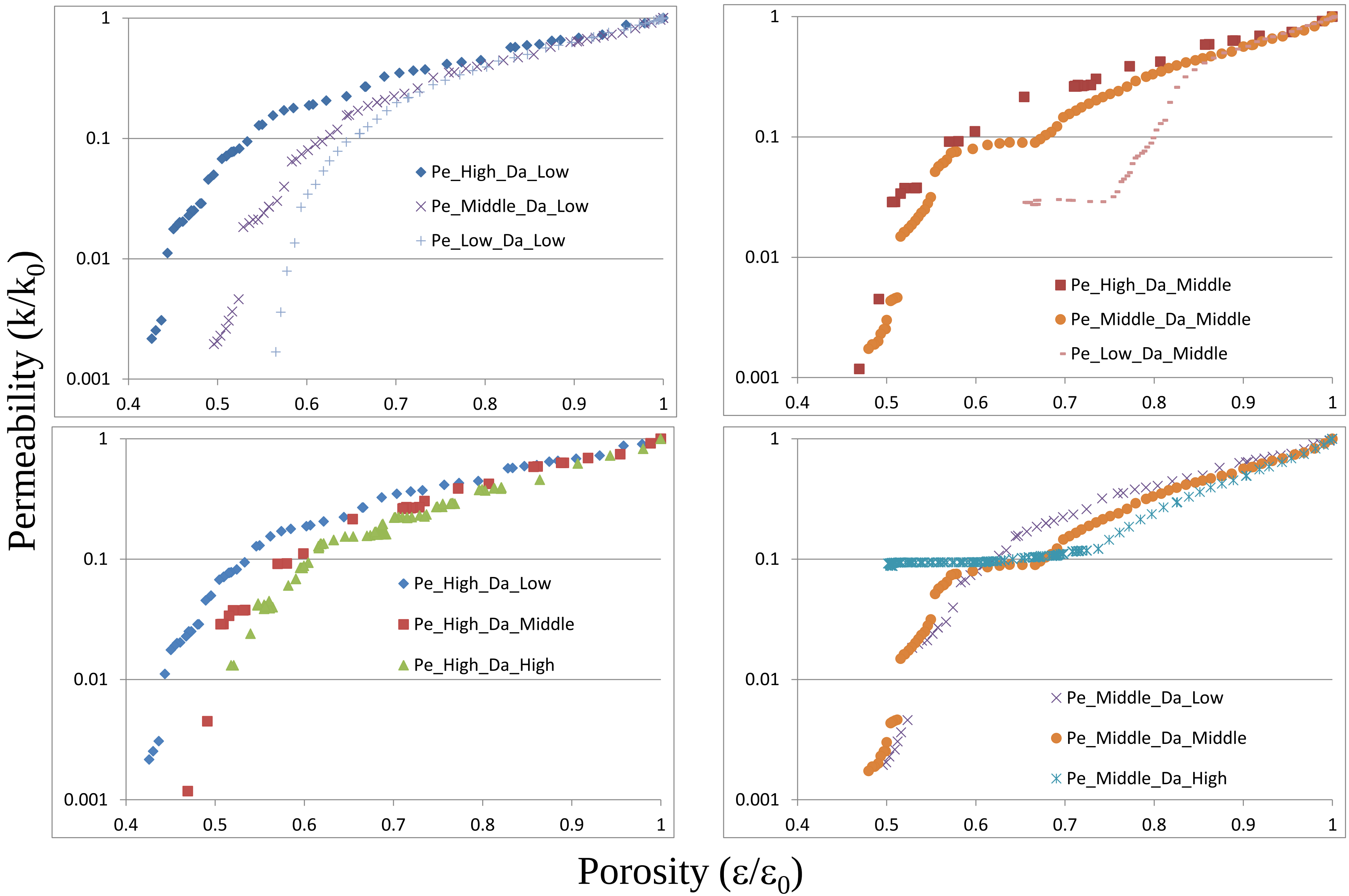
No speciation: Ca^{2+}, CO_3^{2-}



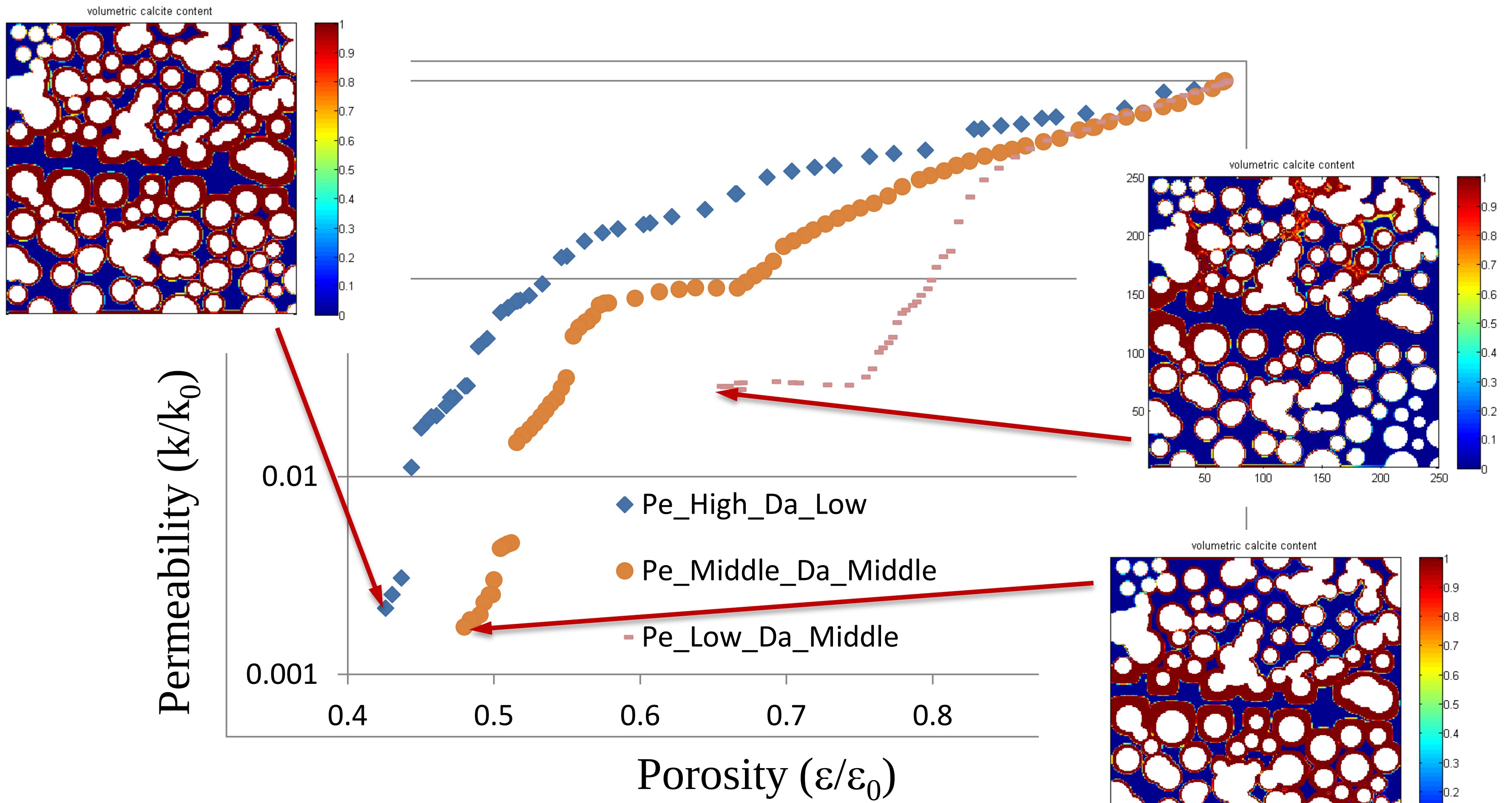


Ksp, calcite = $3.3*10^{-9}$ M^2

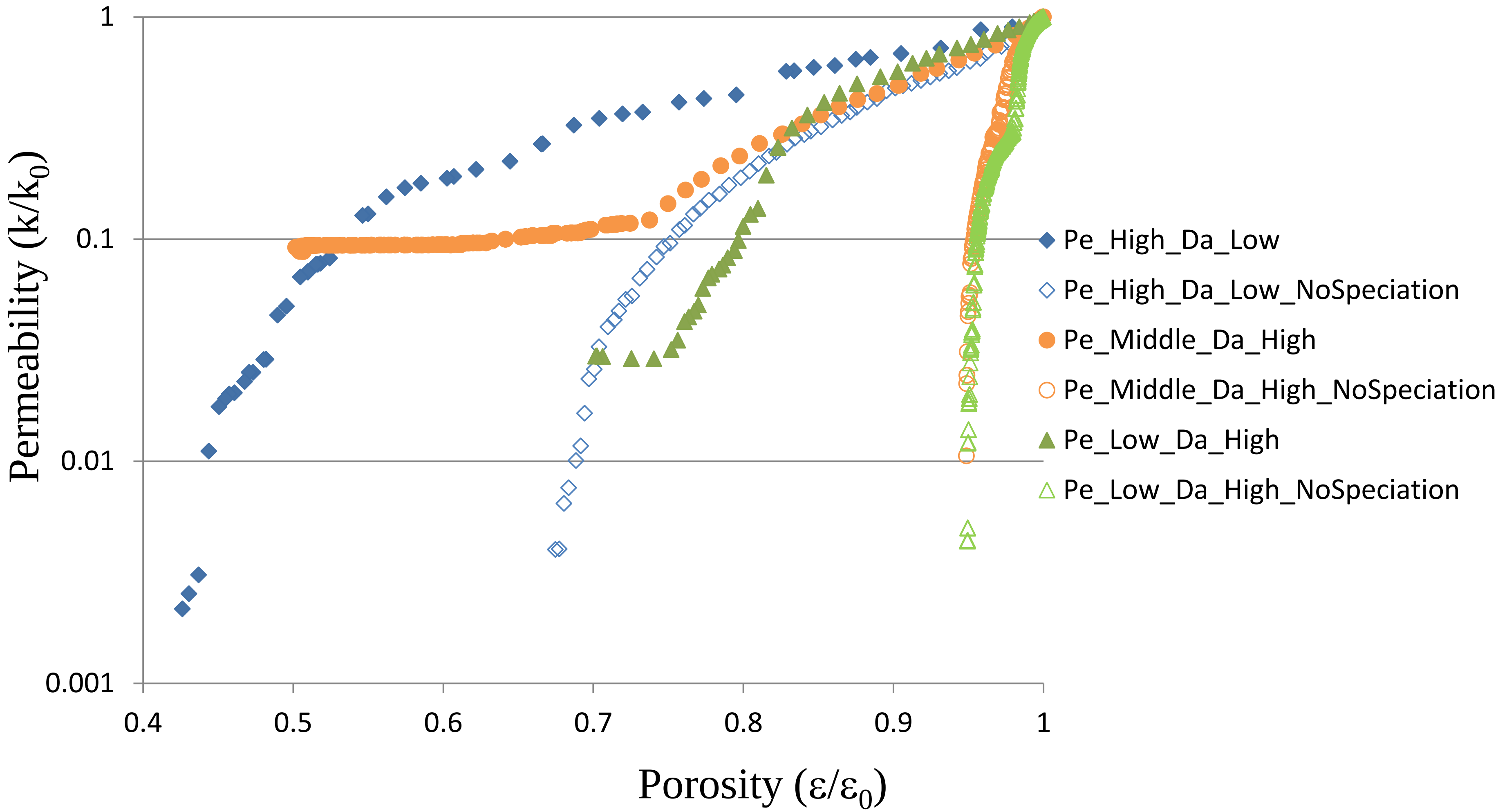
Response Function based on Pore Scale Simulations



Permeability-Porosity Relationships

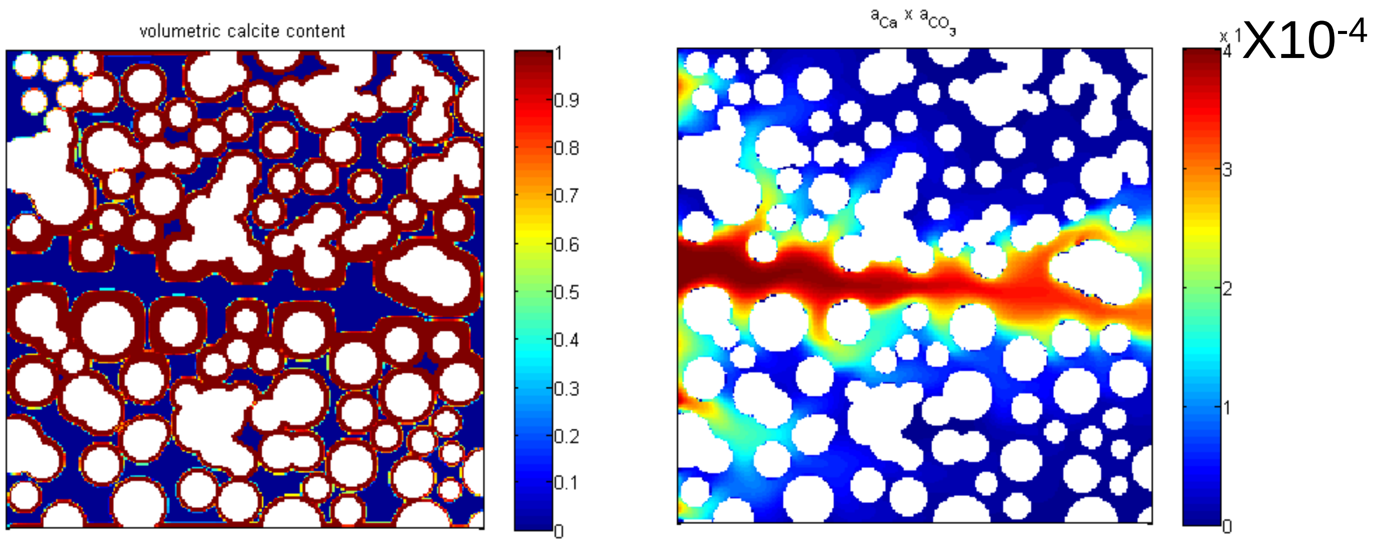


Chemical Speciation

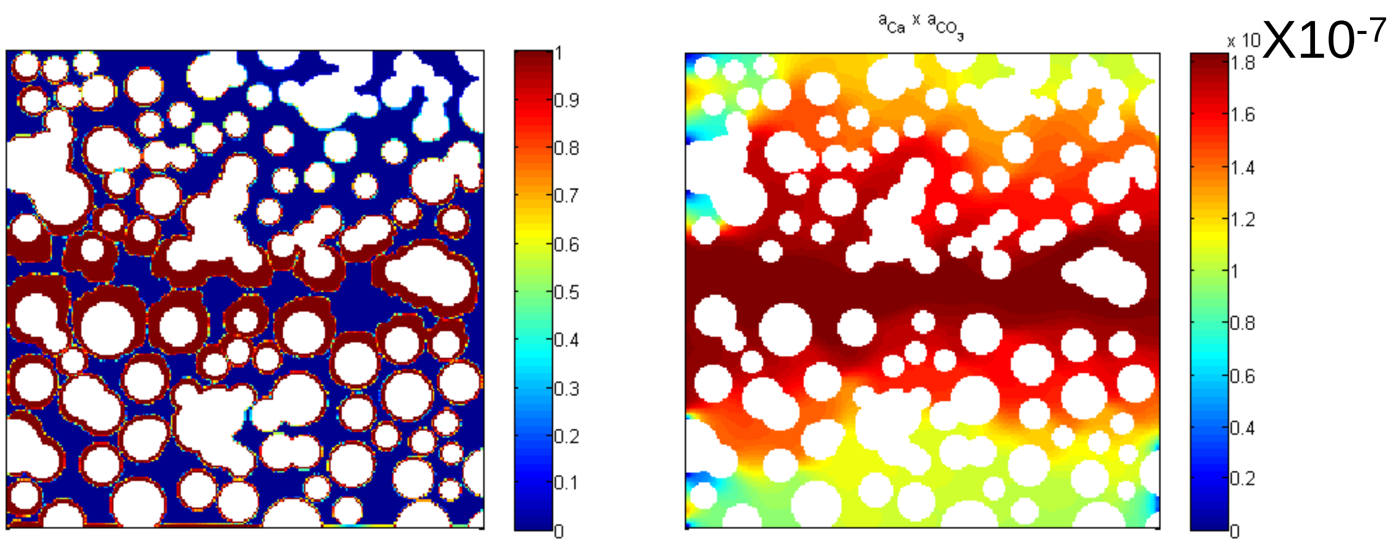


High Pe & Low Da

Speciation



No speciation

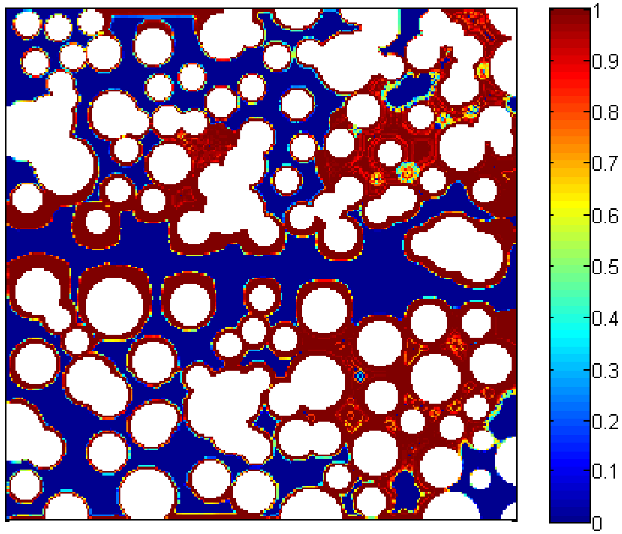


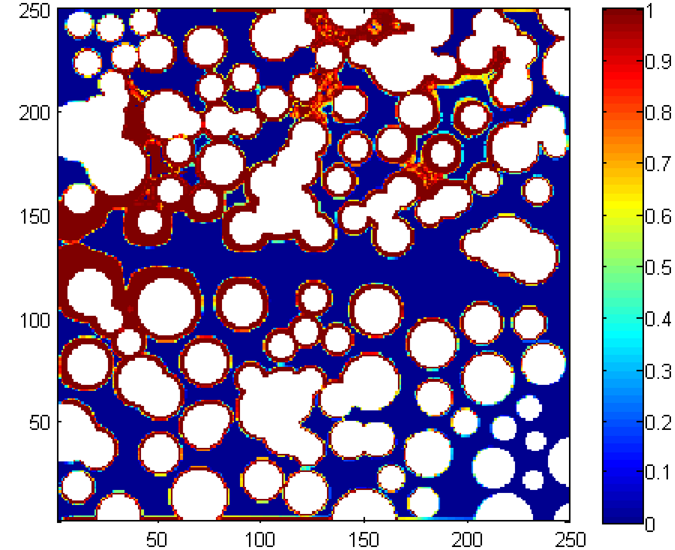
Comparison

Pe=0.8; Da=0.1

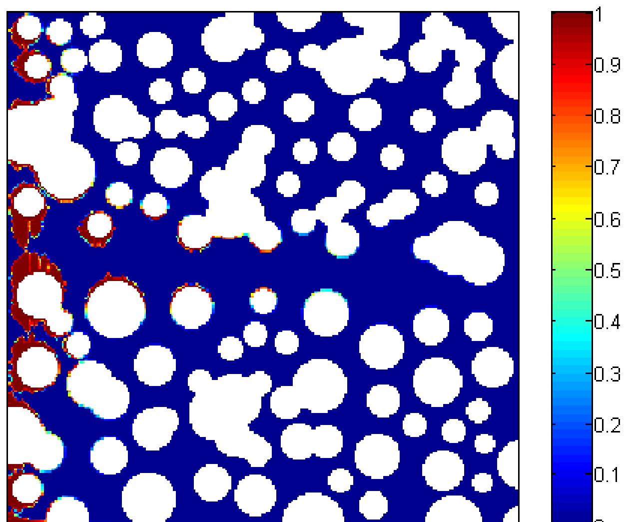
Pe=0.08; Da=0.02

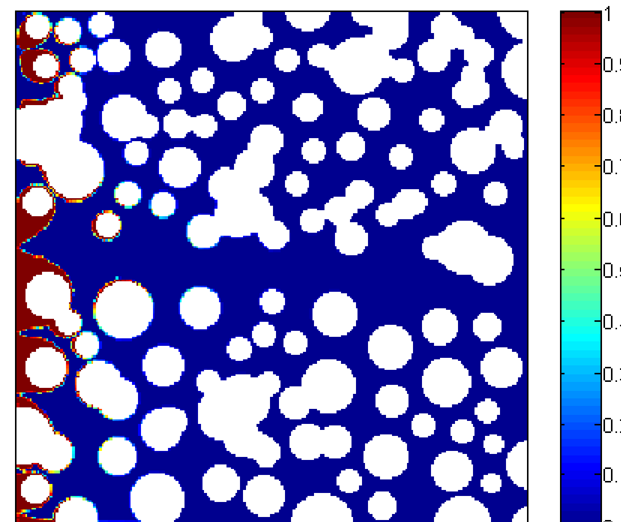
Speciation





No speciation





Summary and Implications

- Vigorously tested pore-scale model can be used to develop a response function (or dimension reduced model) for permeability and porosity (k-ε) relationships
- k-ε relationships will be affected by solution chemistry, chemical reaction, pore structure configurations in addition to Pe and Da numbers
- Adaptive strategy to couple continuum and pore-scale using a response function approach will be tested

Acknowledgments

- SNL

  Tom Dewers, Bill Arnold, Sean McKenna (former)

- Universities

  Peter Eichhubl, Jon Major, Sanjay Srinivasan (UT)

  Charlie Werth, Albert Valocchi (UIUC)

Supported by U.S. Department of Energy, the Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center