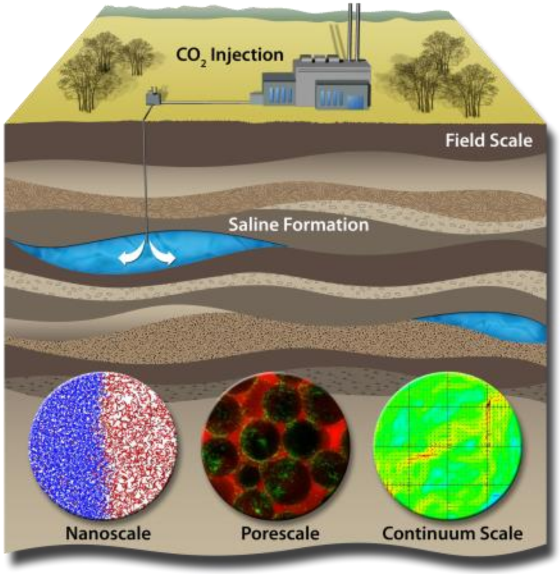
SAND2013-7394P

Mixing-controlled Reactive Transport at the Pore Scale and Upscaling of Reactive Transport

Hongkyu Yoon

September 5, 2013



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National Nuclear Security Administration

CFSES

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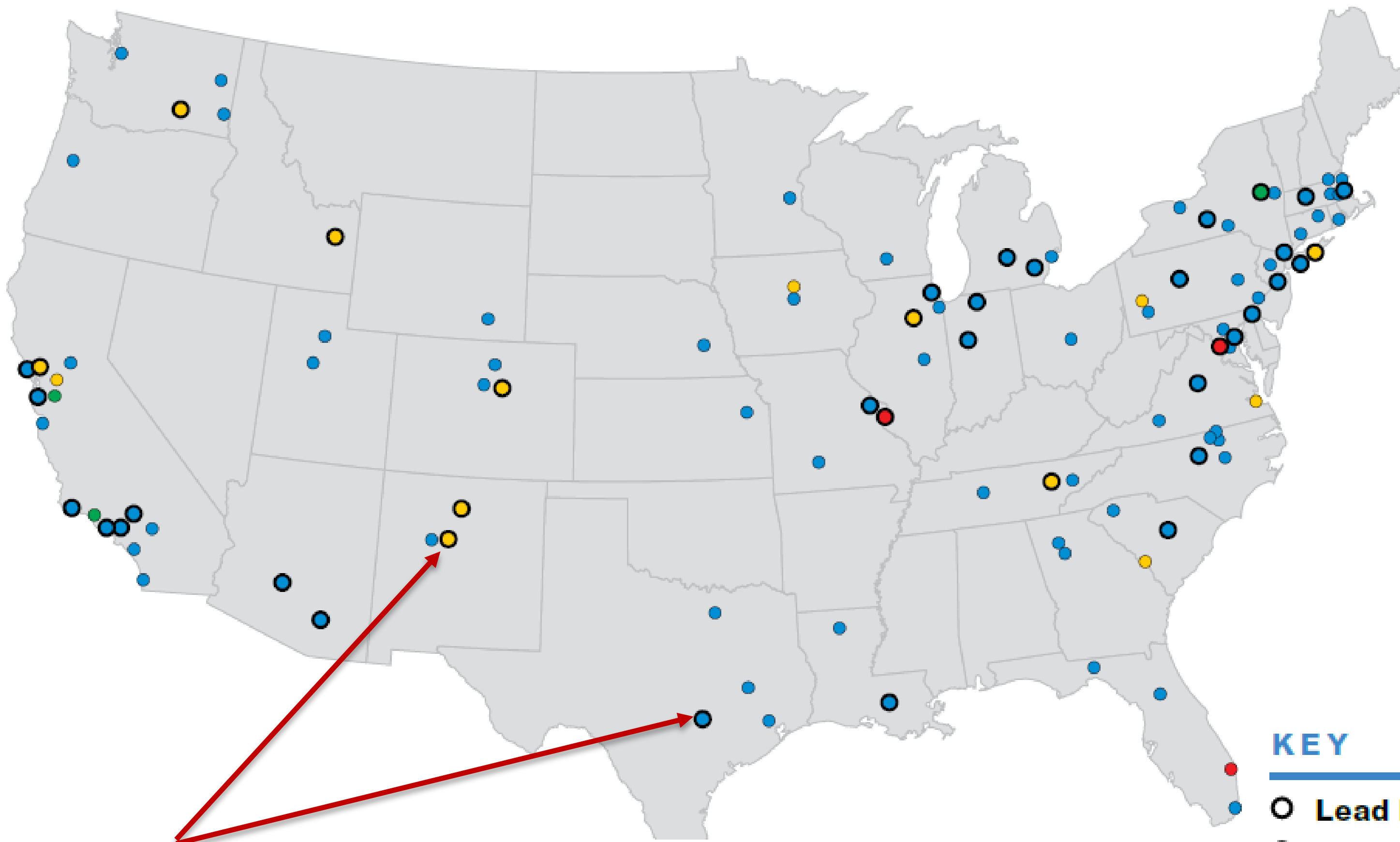
Outline

- Introduction
- Motivations
- Pore scale reactive transport
- Upscaling and ongoing effort

Energy Frontier Research Centers (EFRCs)



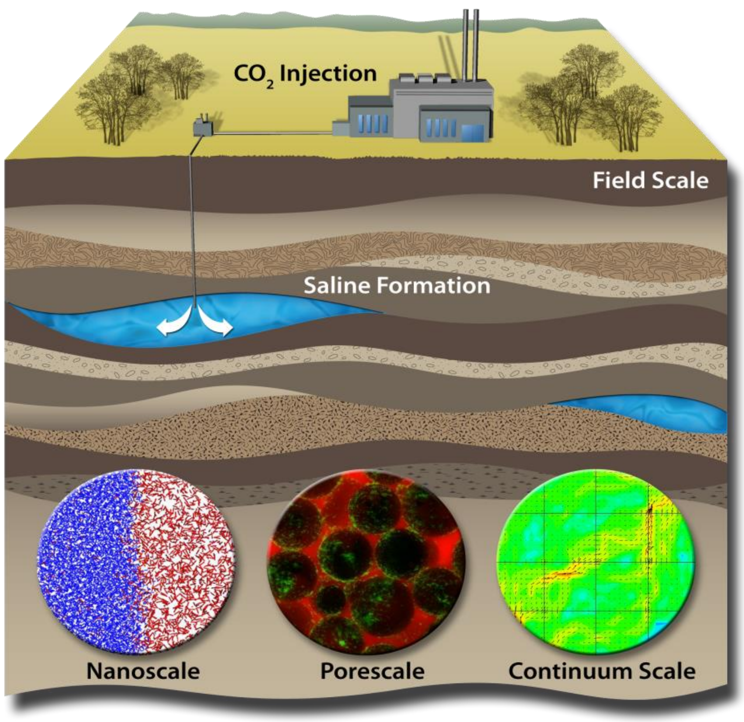
Center for Frontiers of Subsurface Energy Security (CFSES)

46 Lead Institutions
(31 universities,12 DOE national laboratories, 2 not-for-profit organizations, 1 corporate research laboratory.)

DOE EFRC (2011)
http://science.energy.gov/bes/efrc/

Center for Frontiers of Subsurface Energy Security (CFSES)

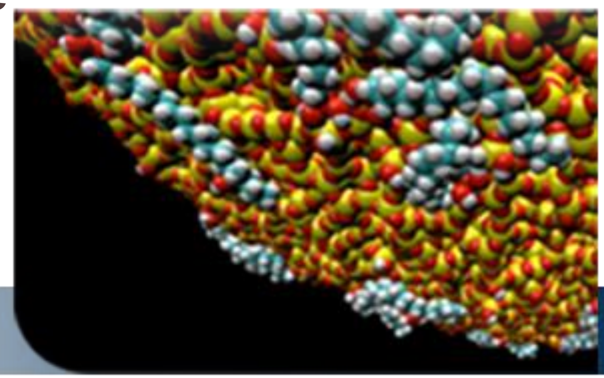
Our goal is a scientific understanding of the physical, chemical, and biological subsurface processes from the ***very small scale*** to the ***very large scale*** so that we can predict the behavior of CO_2 and other byproducts of the energy production that may need to be stored in the subsurface.



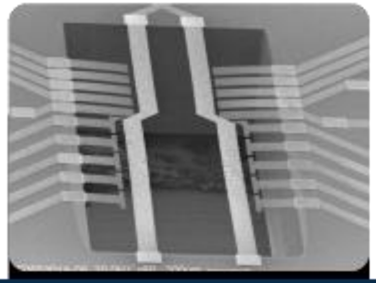
SNL Science and Engineering Foundations

Computing and information science

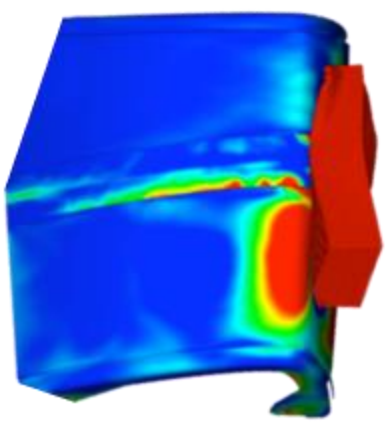
Materials science



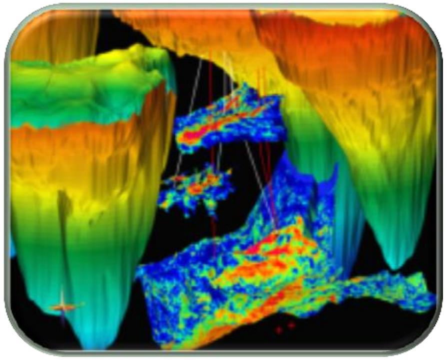
Nanodevices and microsystems



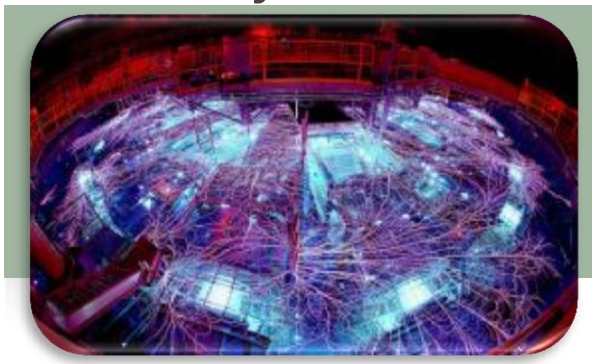
Engineering sciences



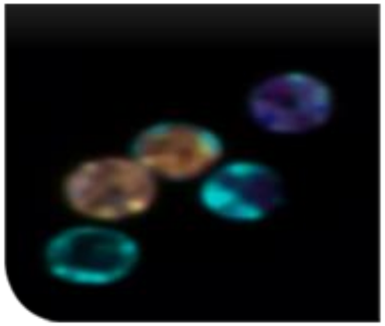
Geoscience



Radiation effects and high-energy density science



Bioscience



www.sandia.gov

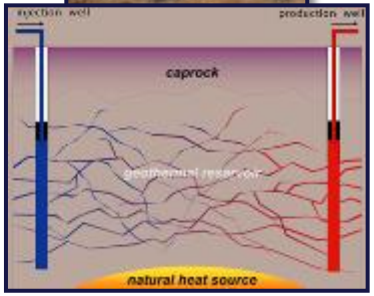
Geoscience Research & Applications Group

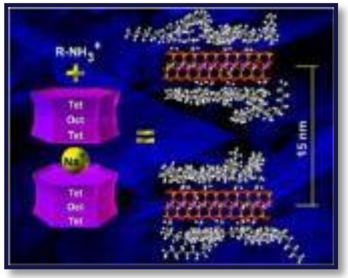
Overview

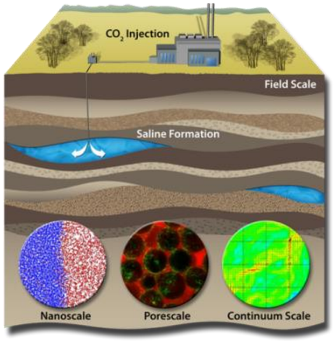
- Geotechnologies and Engineering
- Geophysics and Atmospheric Sciences
- Geomechanics
- Geochemistry
- Geothermal Research

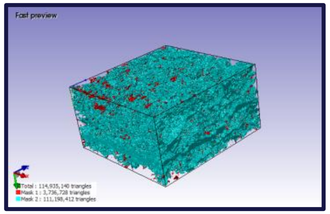
Technical foundation for Sandia missions connected with the Earth and atmosphere

- *Theory*
- *Model development*
- *Analysis*
- *Laboratory expertise*
- *Field activities*

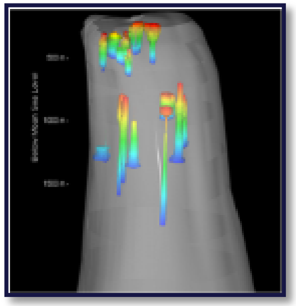








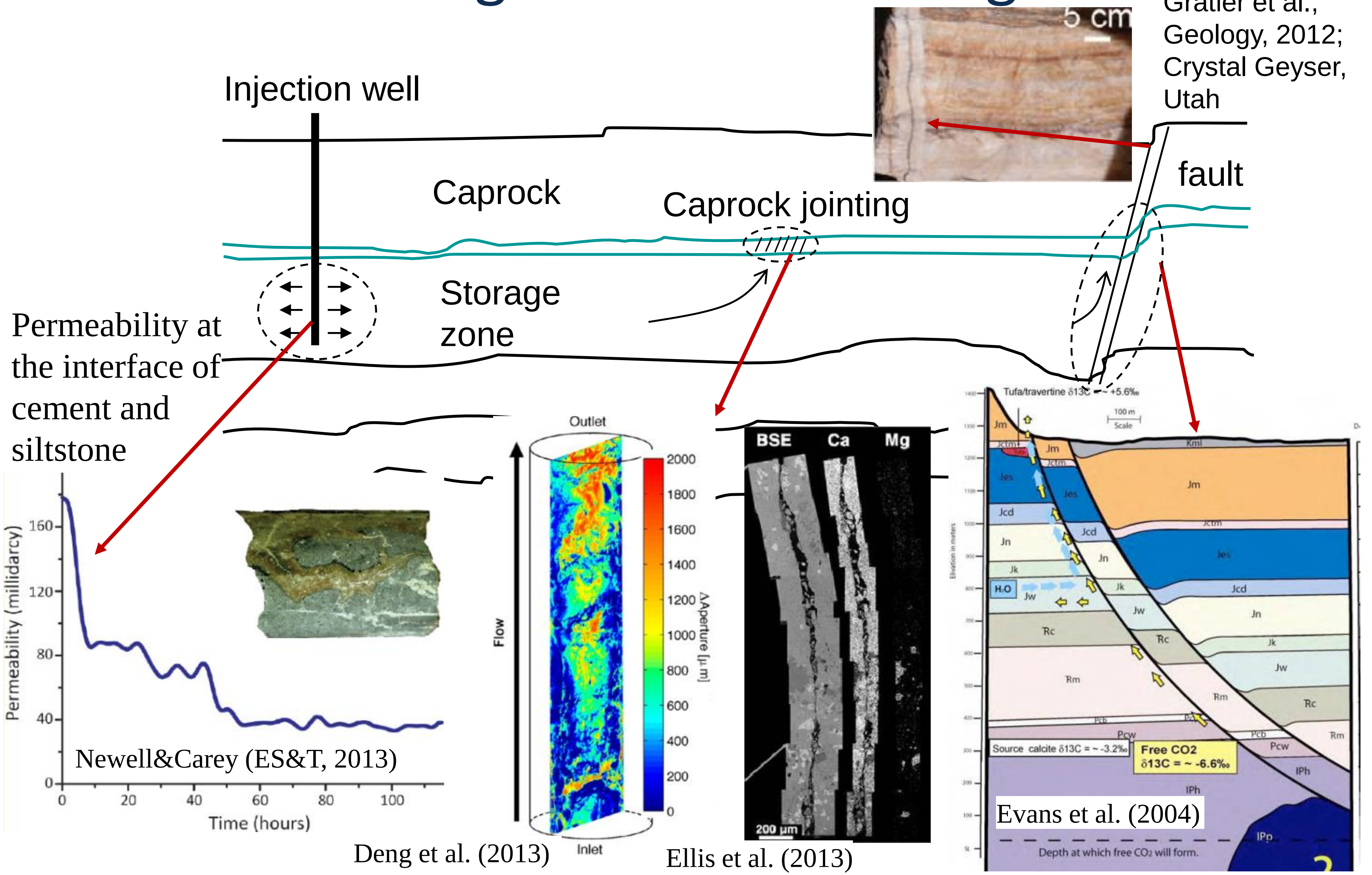
CANARY Event Detection Tool



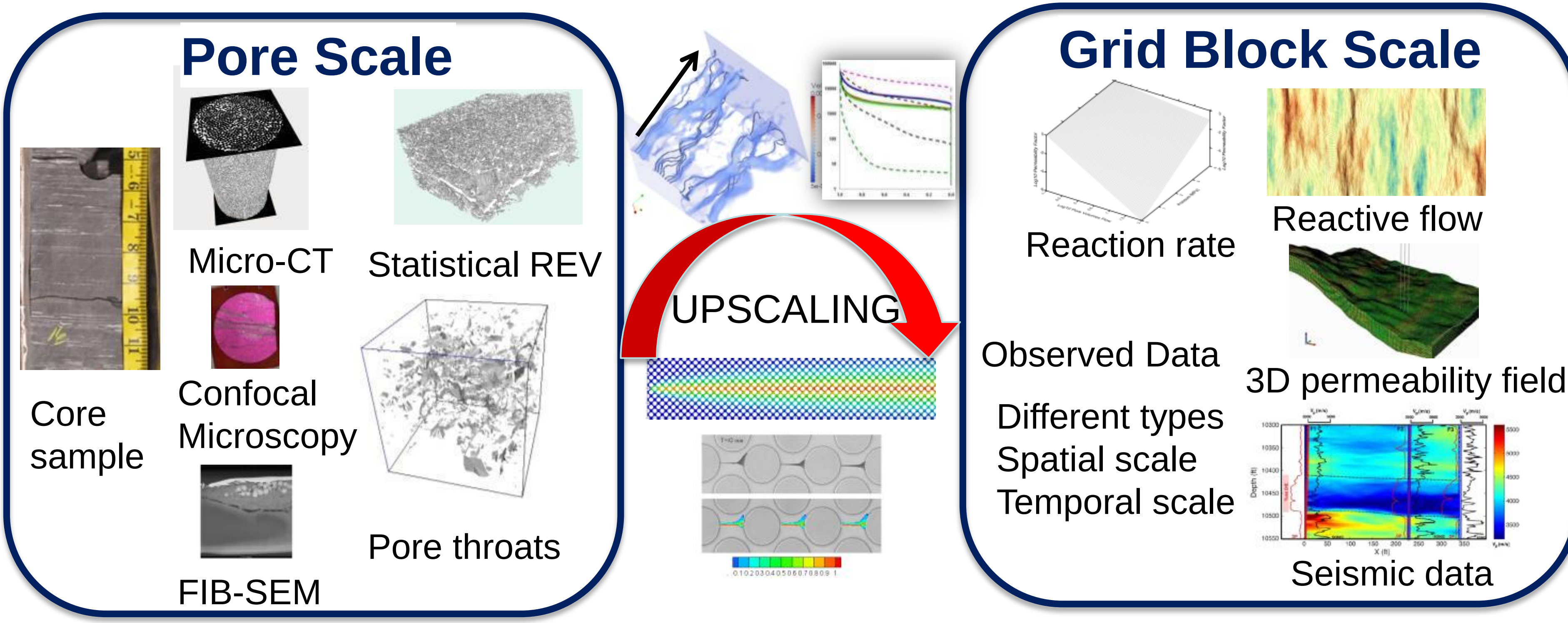
Caverns within Bayou Choctaw Salt Dome (Strategic Petroleum Reserve Program)

http://www.sandia.gov/research/research_foundations/geoscience/index.html

Reactive Transport Processes during Geological Carbon Storage



Multi-Scale Problems



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)

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)

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)

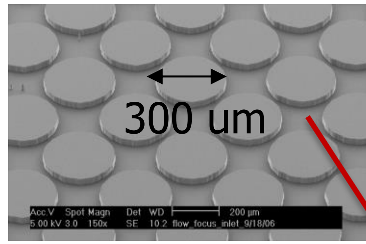
Micromodel Experiment

Micromodel Description

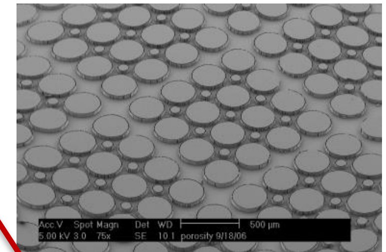
Depth: ~20 mm

Porosity: ~0.39

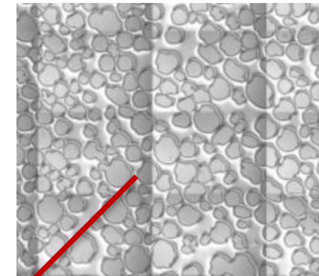
Flowrate: ~2 cm/min



Base Case
Small Cylinder



Aggregates



Irregular

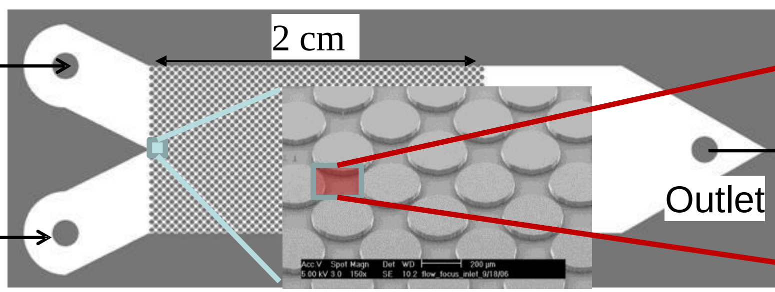
Thermal oxidation:
~ 100 micron thick oxide layer

Na_2CO_3

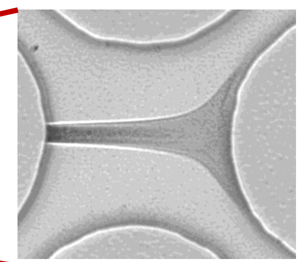
(pH=~11)

$CaCl_2$

(pH=~6)



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



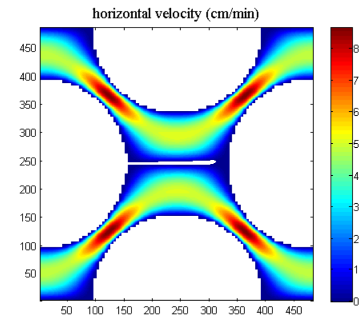
250 microns

Microscopic image of calcium carbonate ($CaCO_3$) precipitates

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

Pore Scale Model Framework

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



Velocity

Finite Volume Method: Reactive transport at pore scale

Δt

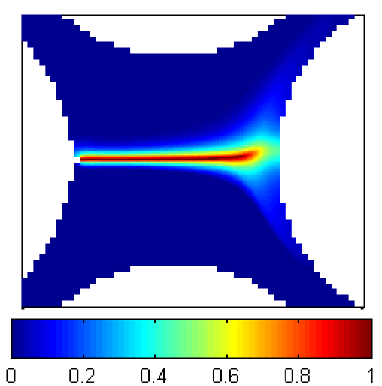
$$\Psi_j = C_j + \sum_{i=1}^{N_{eq}} \upsilon_{ji} C_i$$ Chemical equilibrium in bulk fluid (e.g., H^+, HCO_3^-, …)
Extended Debye-Hückel Equation for activity coefficients

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

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

Update of $CaCO_3$ volumetric content (V_m)

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



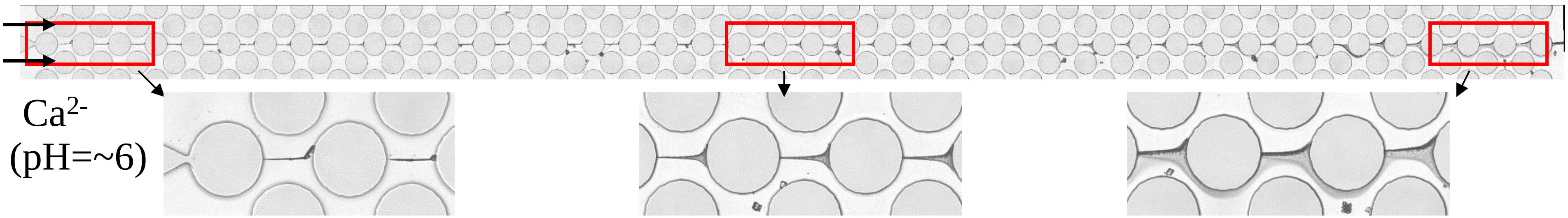
Mineral phase volumetric content

Yoon et al. (WRR, 2012)

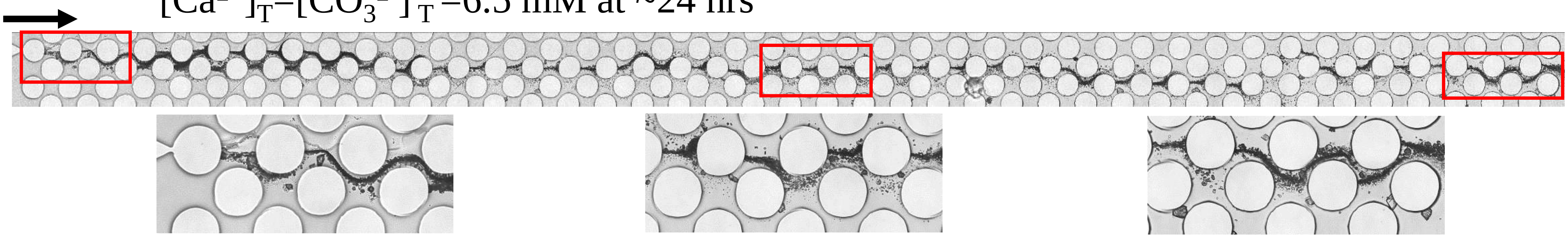
Experimental Results

CO_3^{2-}(pH=~11) $[Ca^{2+}]_T=[CO_3^{2-}]_T$ =25 mM at ~2 hrs

Zhang et al., ES&T (2010)

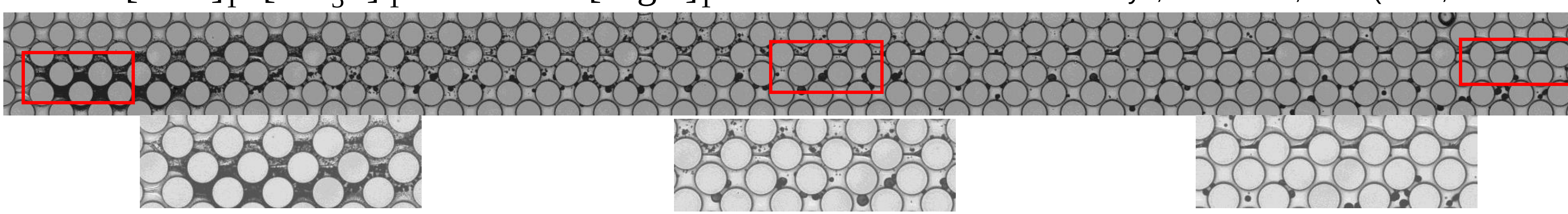


$[Ca^{2+}]_T=[CO_3^{2-}]_T$ =6.5 mM at ~24 hrs



$[Ca^{2+}]_T=[CO_3^{2-}]_T$ =10mM & $[Mg^{2+}]_T$ =40 mM at ~16 hrs

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

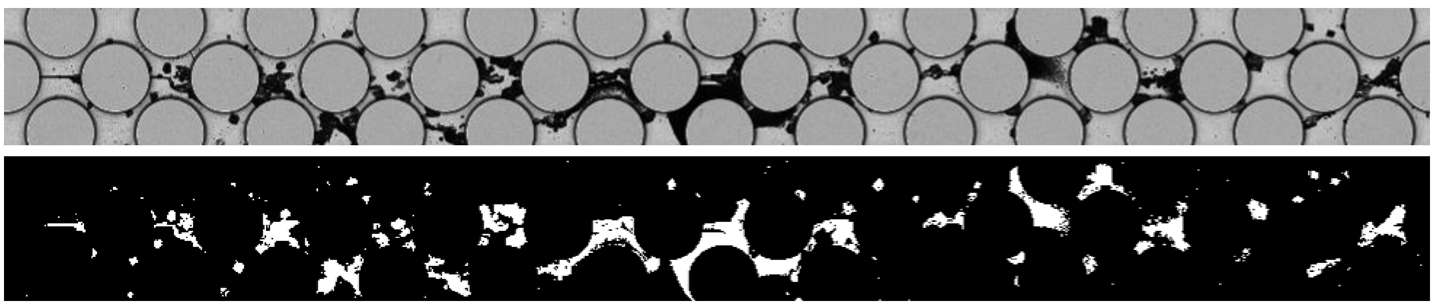


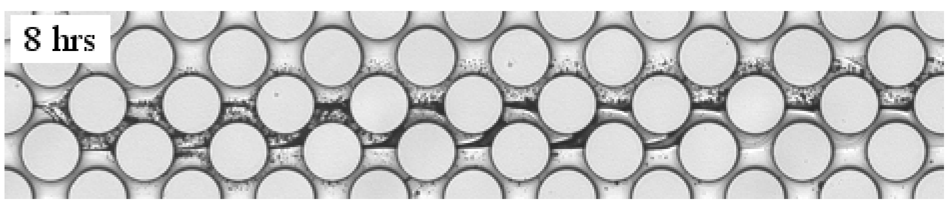
- Precipitation ~ along the centerline within 1-2 pore spaces in the transverse direction
- Width of the precipitate line ~ increase with distance from the inlet
- Rate of precipitation is concentration and species dependent

Image Analysis

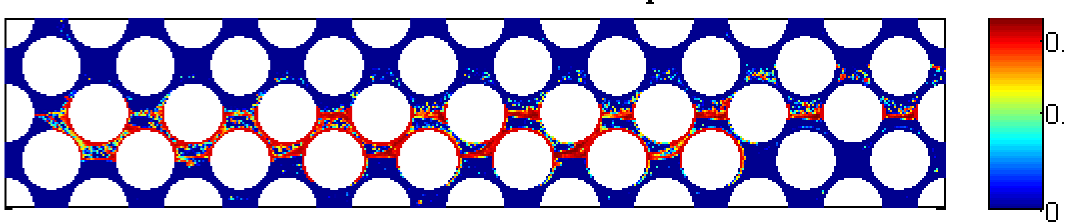
Otsu thresholding

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

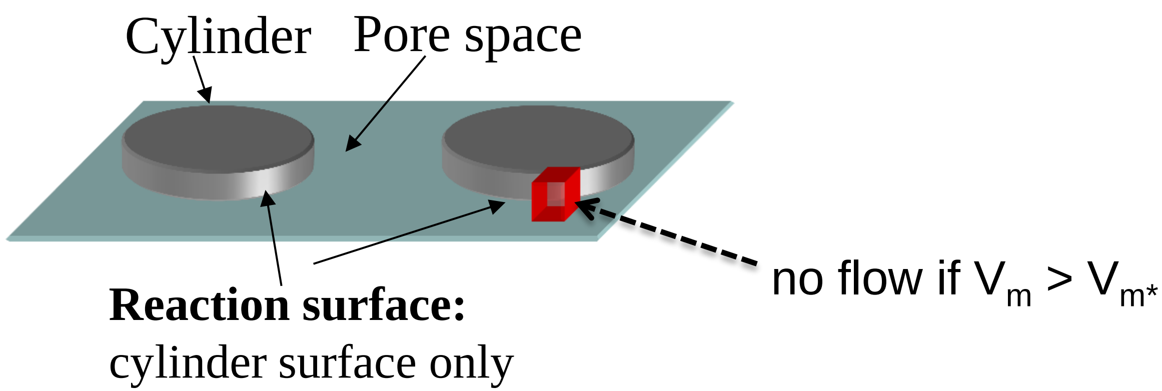




Volumetric Fraction of Precipitate



Results: Precipitation only at grain boundary



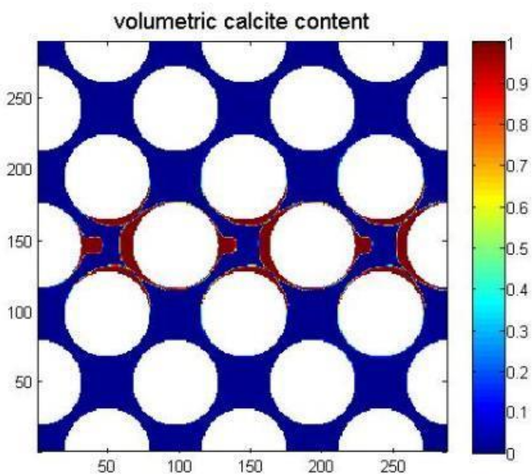
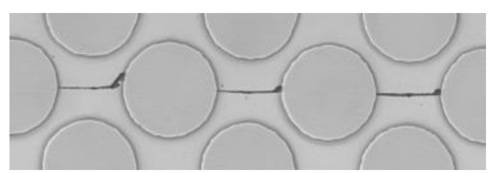
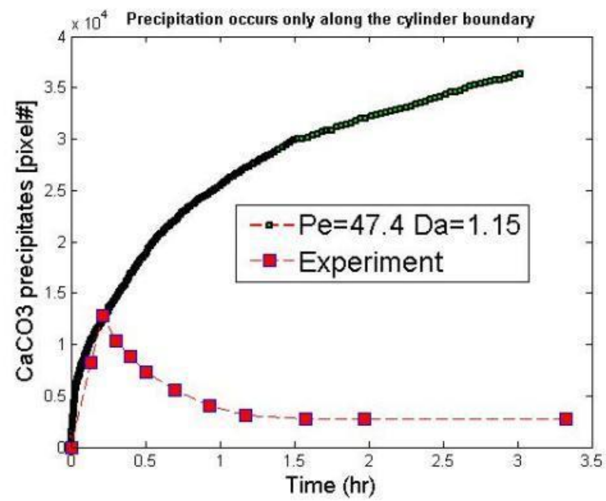


Image of precipitates at 180 min



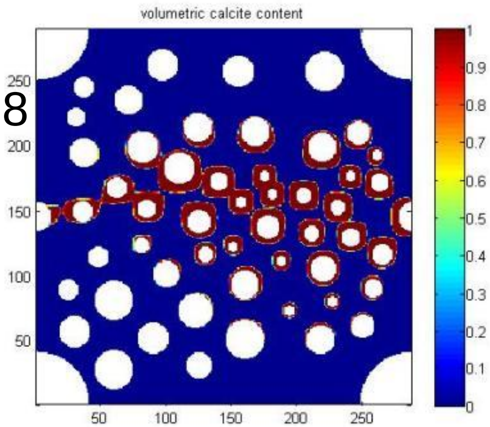
25 mM Experiment



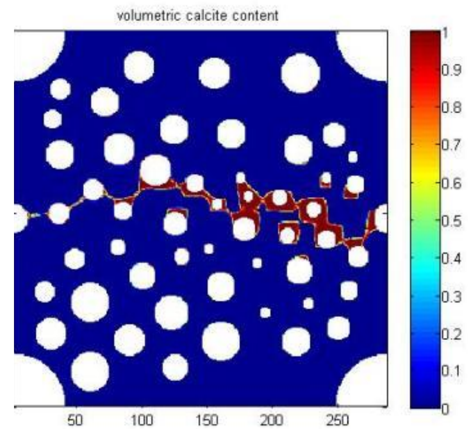
Precipitation patterns

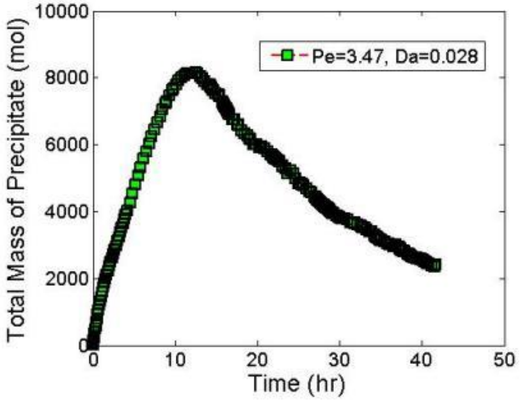
Pe=3.47
Da=0.028

T=700 min



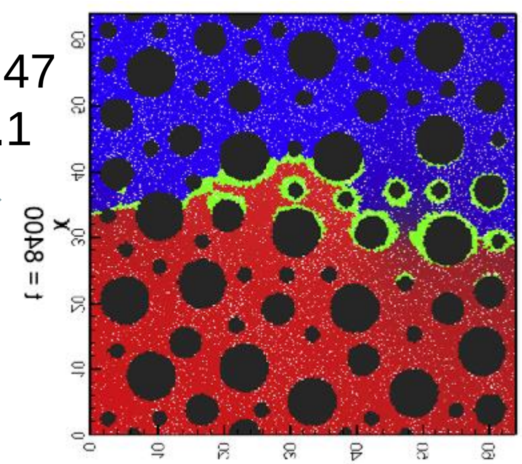
T=2500min



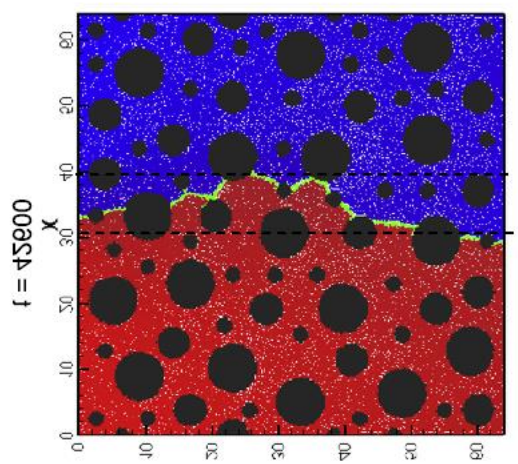


Pe=0.47
Da=1.1

T=8400



T=42600



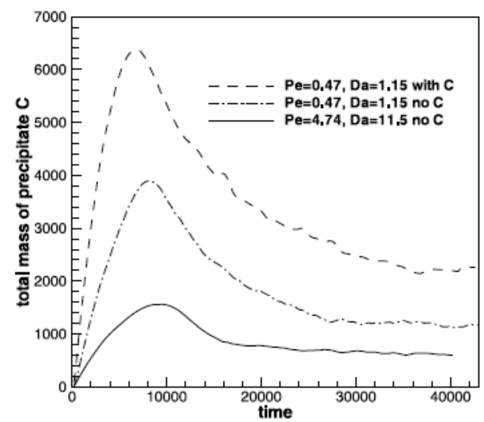
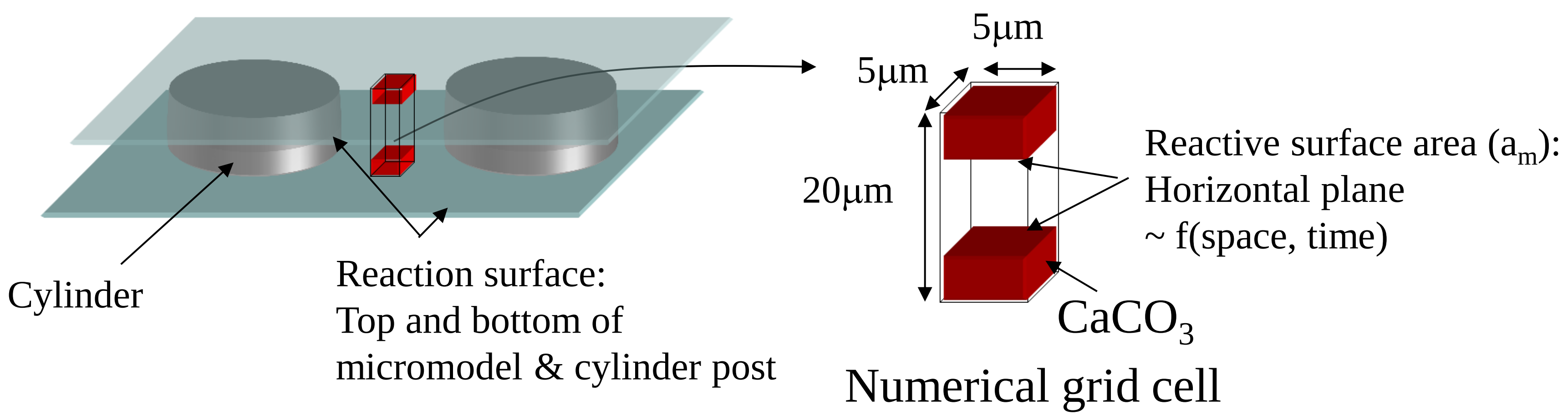


Figure 8. Time dependence of the total mass of precipitate *C* obtained from several simulations with and without the intermediate reaction produce, *C*, for different *Pe* and *Da*.

Tartakovsky et al. (WRR, 2008)

Reaction in a micromodel system

1. Quasi 3D grid cell for reactive surface

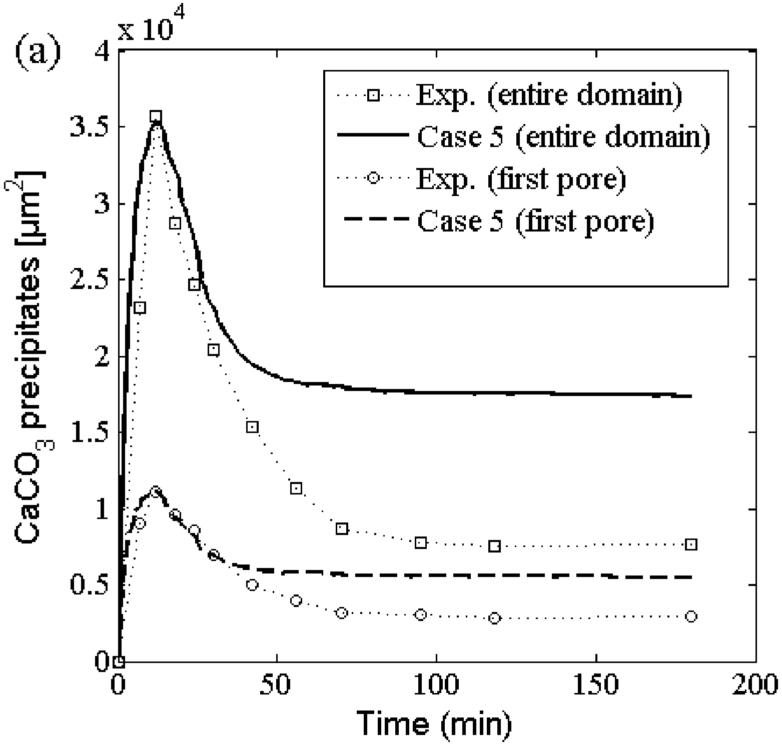


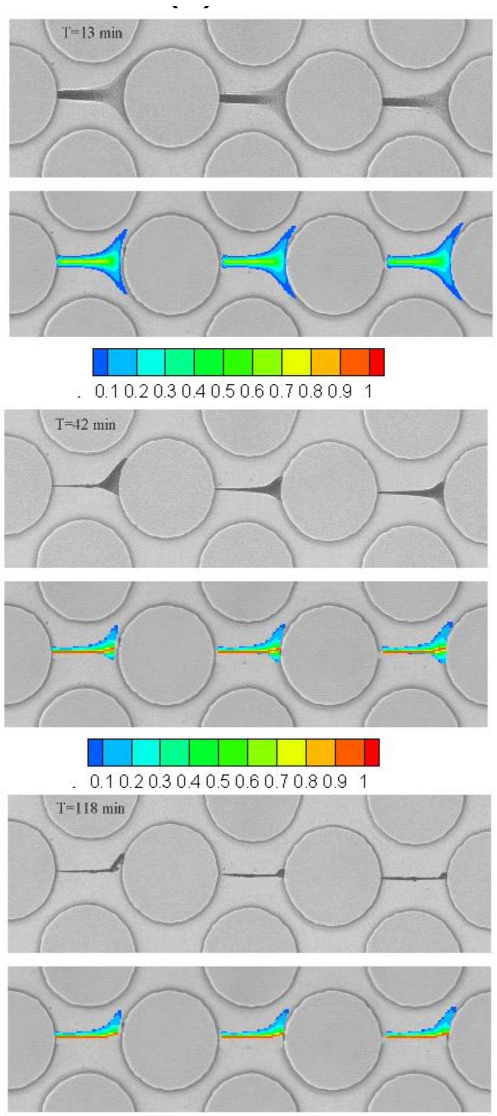
2. Effective diffusion coefficient = D_m * tortuosity (τ)

- $\tau(V_m) = (1 - V_m)^n$ 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





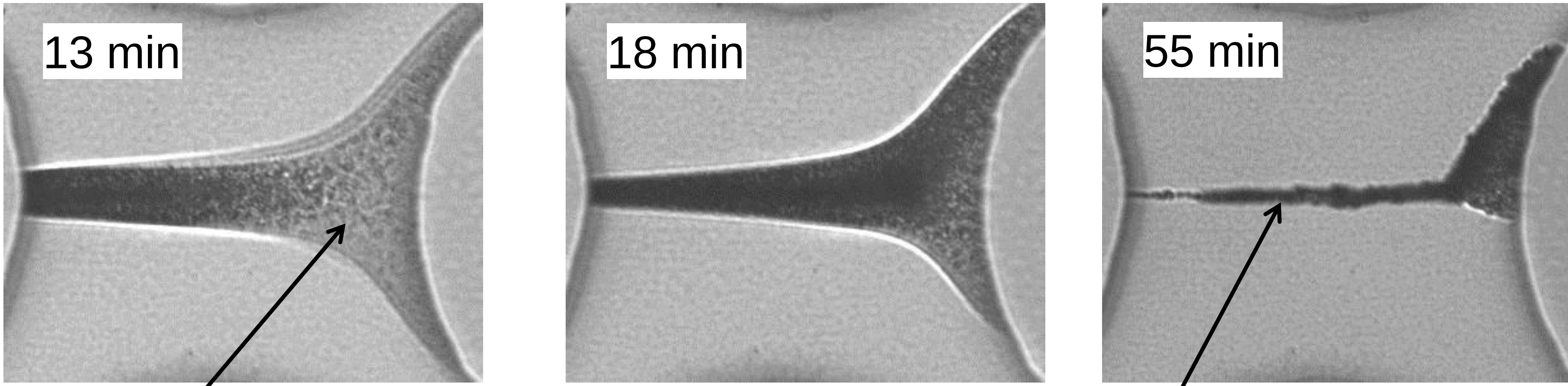
13 min

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

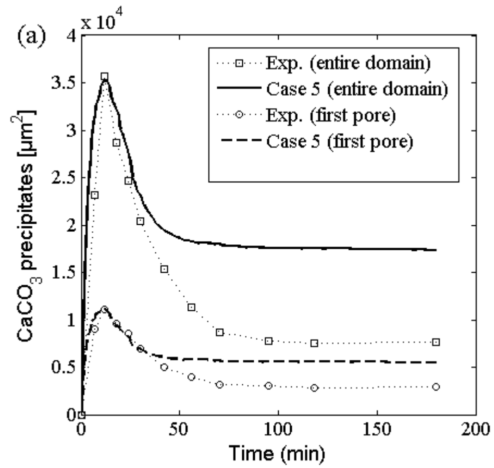
Matching simulation to late-time dissolution



Amorphous Calcium Carbonate
& Vaterite

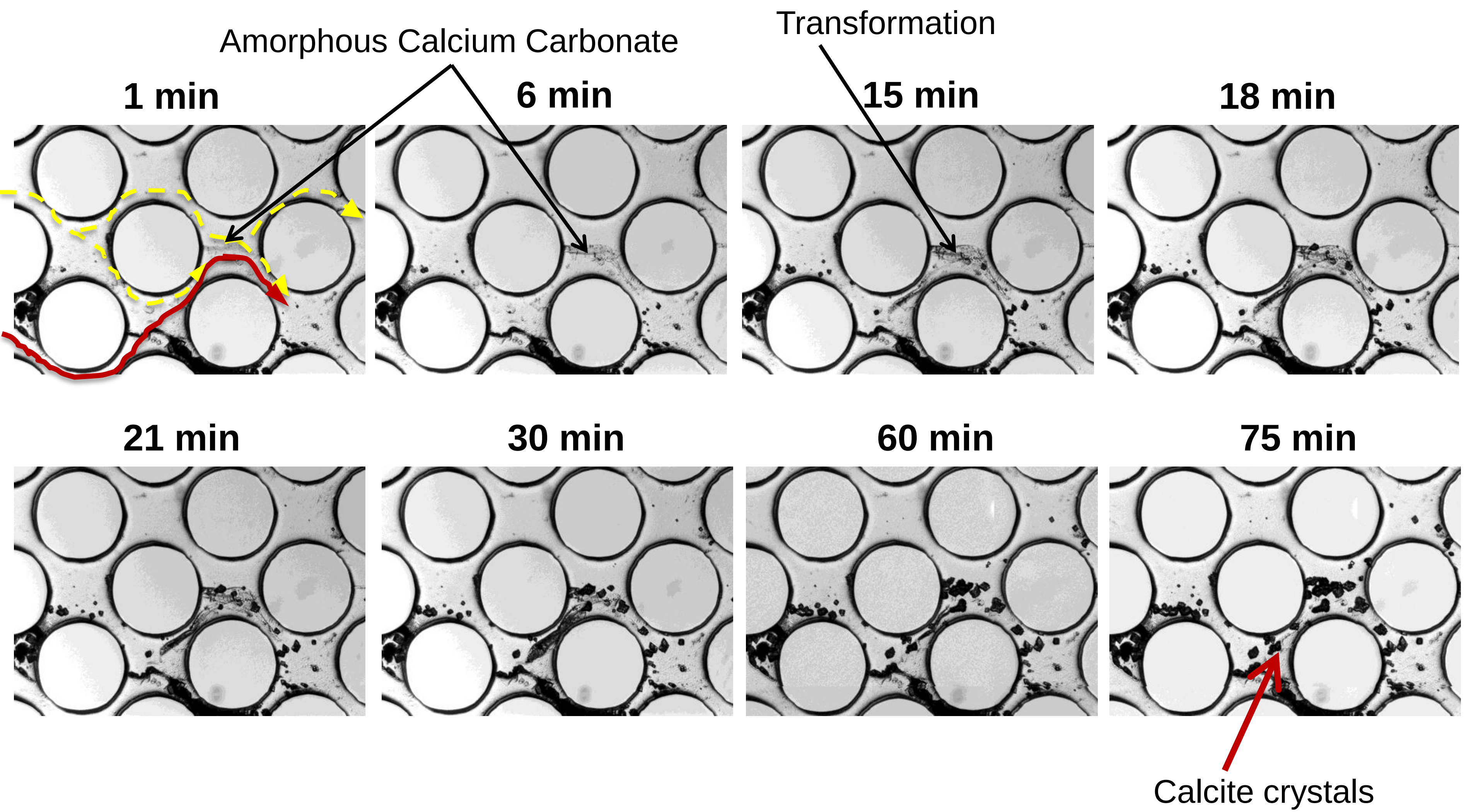
Predominantly Vaterite

- 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

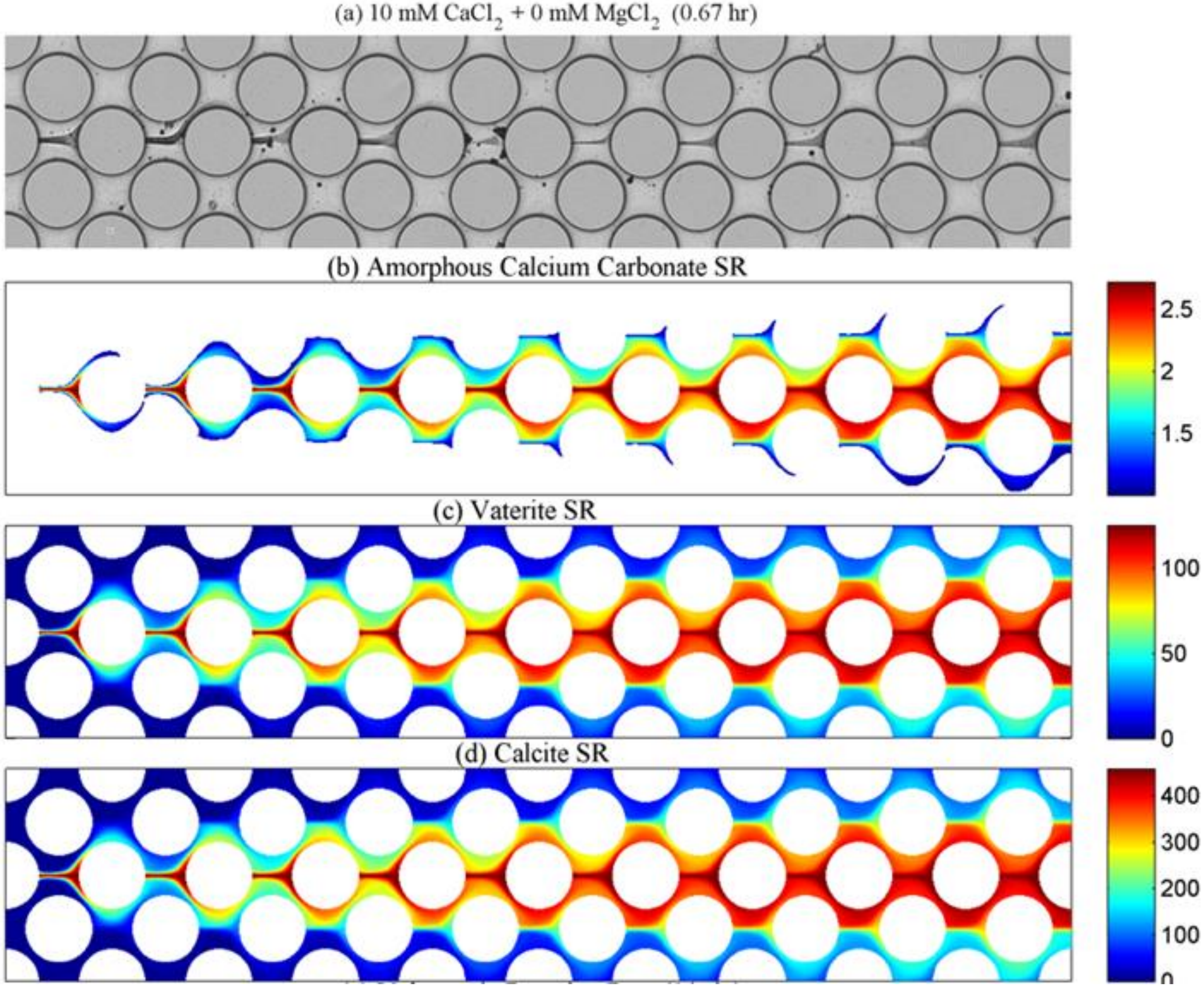
6.5 mM Case



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)

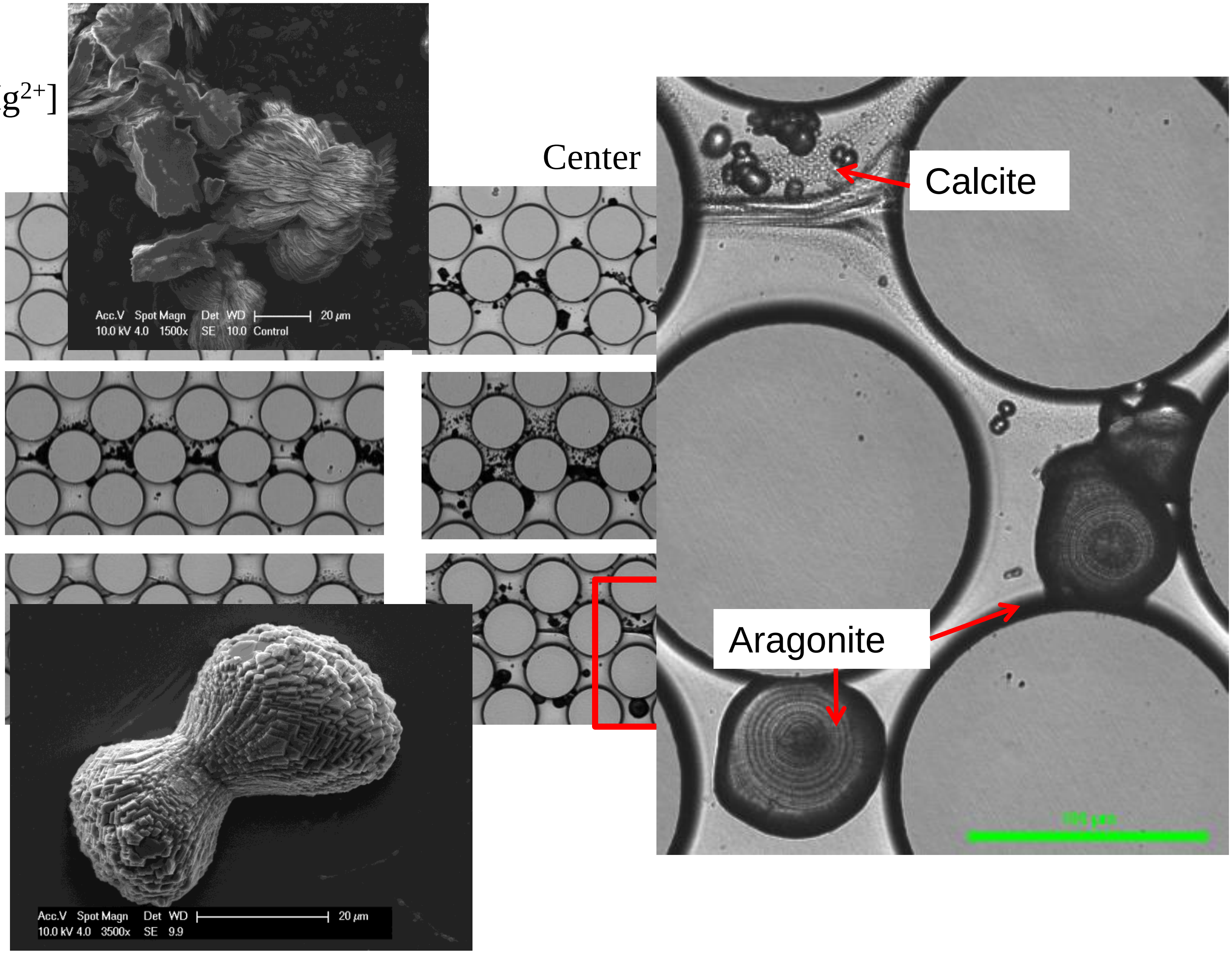
Adding Magnesium

Adding [Mg^{2+}]

[Mg^{2+}] =0mM

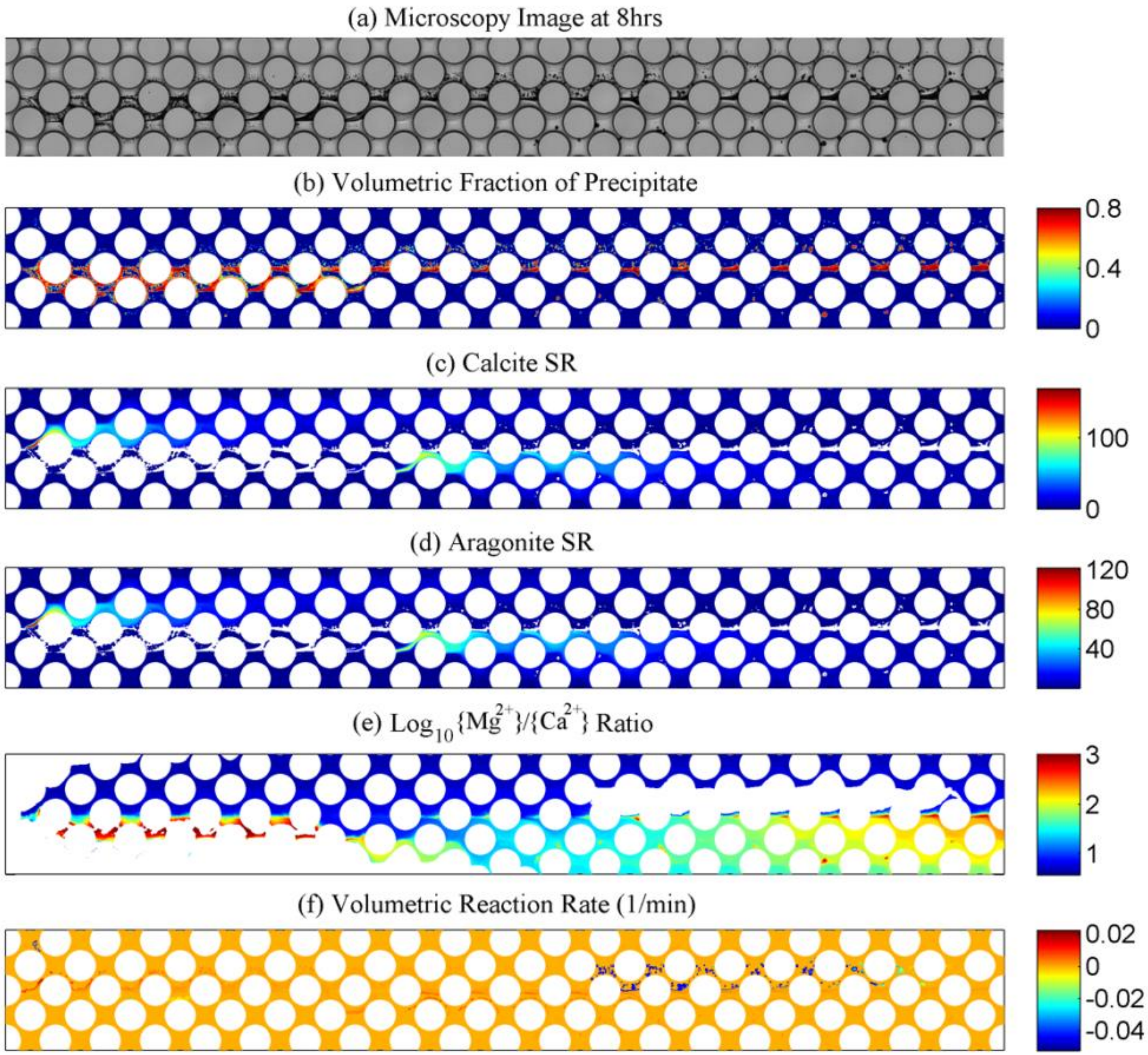
[Mg^{2+}] =10mM

[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)

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

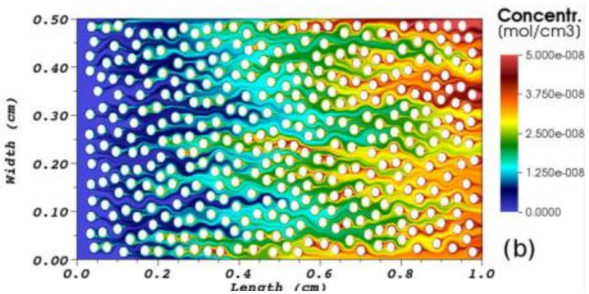
Upscaling/Hybrid modeling

No general method/ framework for upscaling:

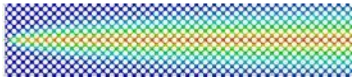
- Homogenization (multiple scale expansions)
- Volume averaging
- Pore network models (approx. physics) with mortar
- Mass balance principles based on pore scale models.
- Constitutive equation with closure based on detailed pore scale solutions (e.g., response function model)
- Hybrid pore-continuum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

Upscaled reaction rate

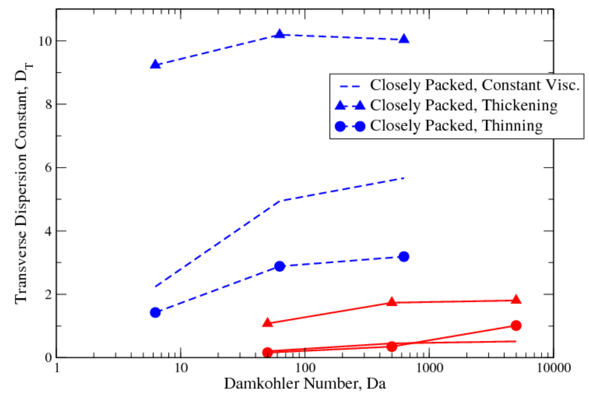
$$\dot{r}_{eff} = \frac{\left(\bar{C}_{in} - \bar{C}_{out}\right)Q}{\nu A} \qquad \bar{C}Q = \int_A \mathbf{u}c \bullet \mathbf{n}\, dS$$



Molins et al. WRR 2012

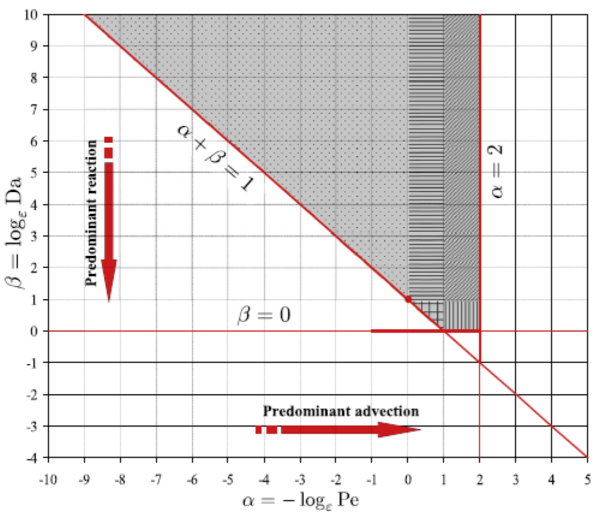


$$D_{T,R} = \frac{1}{X^3}\frac{9\pi v}{16 C_0^{\,2}\varphi^2}\left[\int_0^X m(x)\,dx\right]^2$$

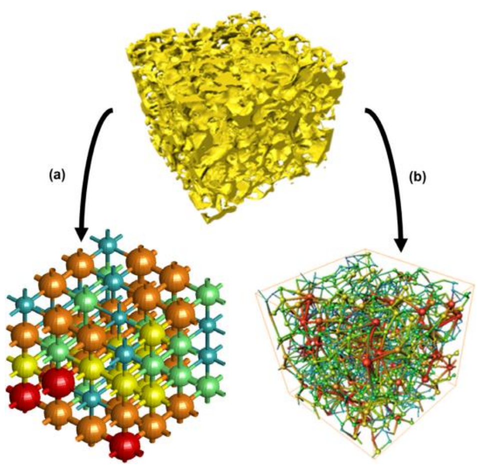


Upscaled dispersion

Davison, Yoon et al. (2012)



Battiato et al. (AWR, 2011)

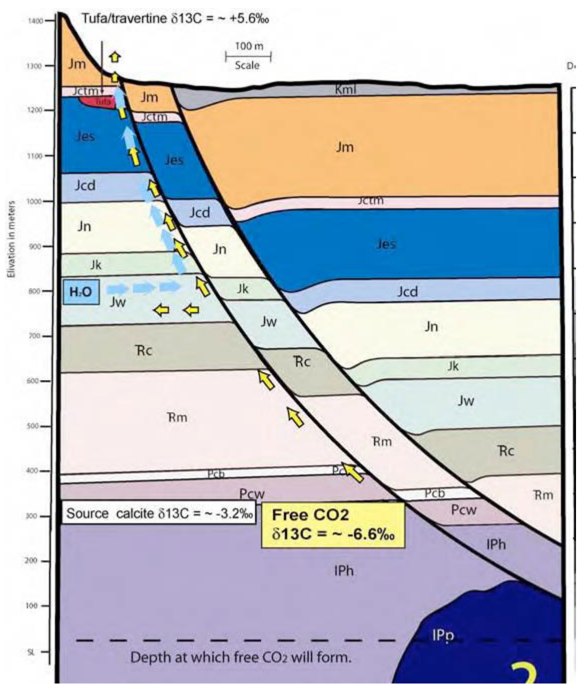


Pore network model

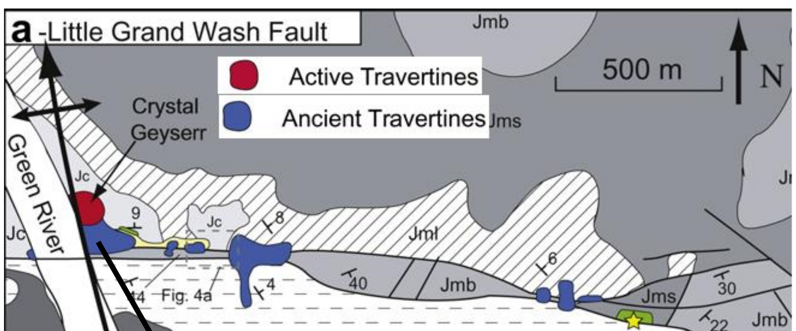
Varloteaux et al. (AWR, 2013)

Simulation of Little Grand Wash Fault

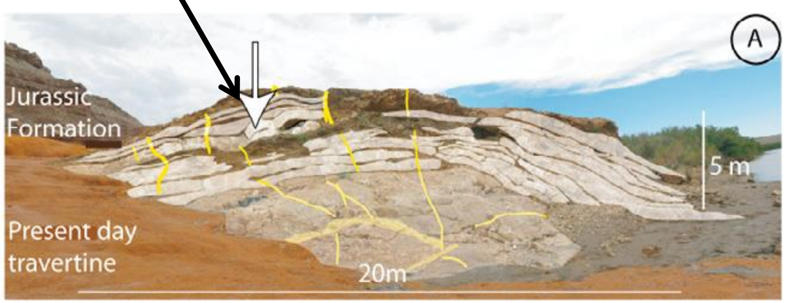
- Develop scheme for selecting appropriate model for CO_2 leakage based on surface observation of travertine mounds



Evans et al. (2004)



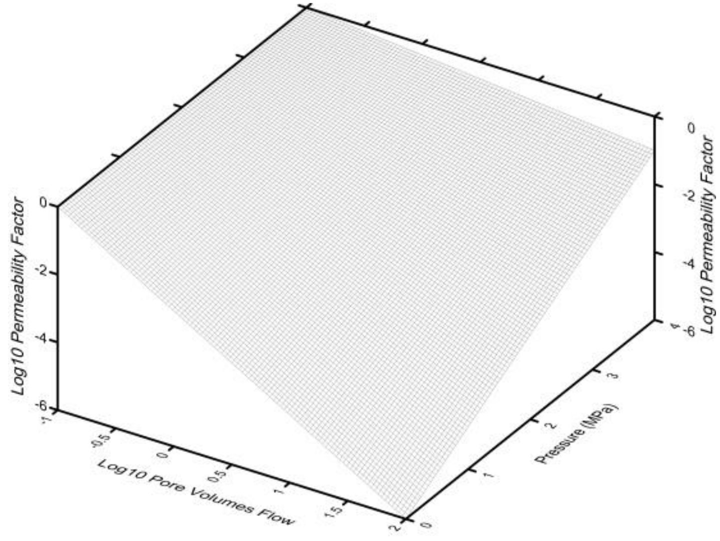
Dockrill and Shipton (2010)



Burnside (2010)

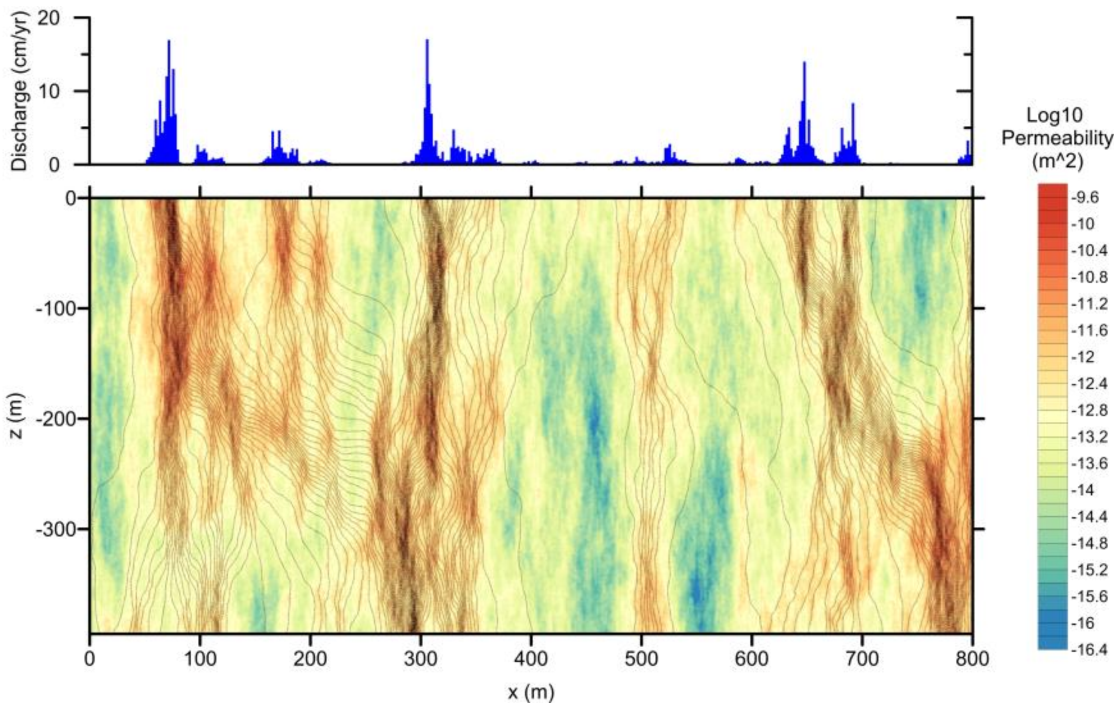
Crystal Geyser Site: Grand Wash Fault Modeling

- **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

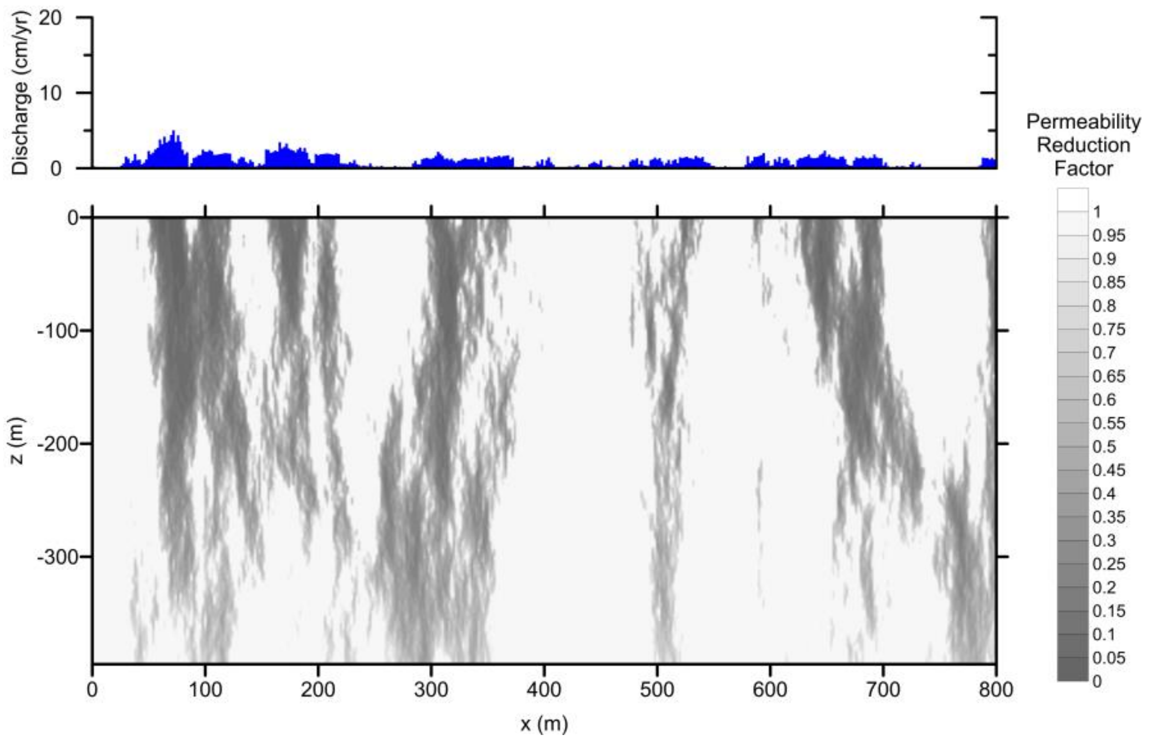
- **Unconditional geostatistical simulation of initial permeability is semi-quantitatively consistent with geologic mapping of fault segments and alteration**
- **Initial simulated steady-state flow pattern is qualitatively similar to the spacing of springs and seeps along the Grand Wash fault with spacings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

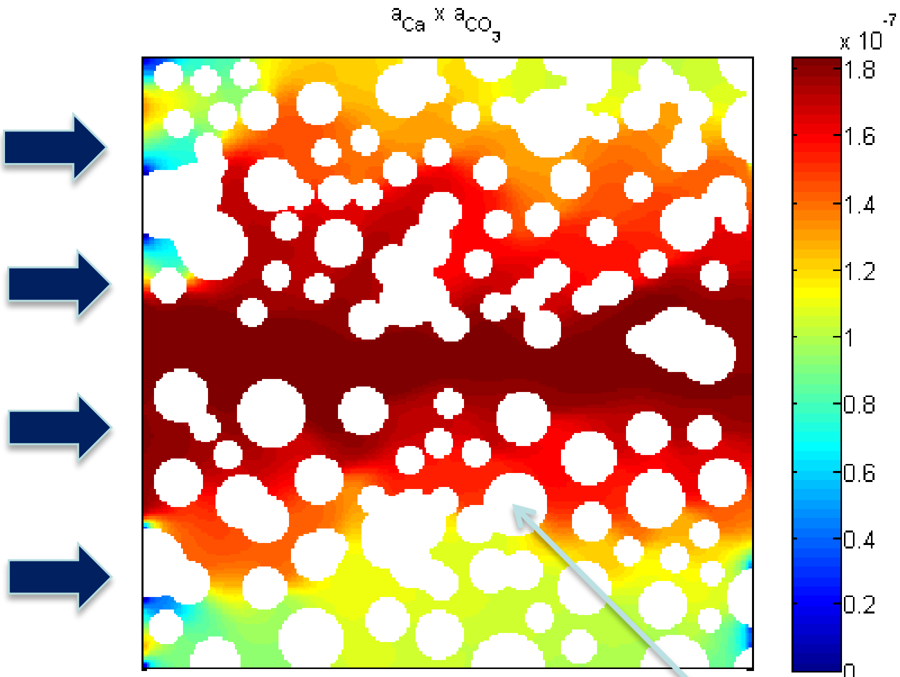
$[Ca^{2+}]_T = [CO_3^{2-}]_T = 20mM$

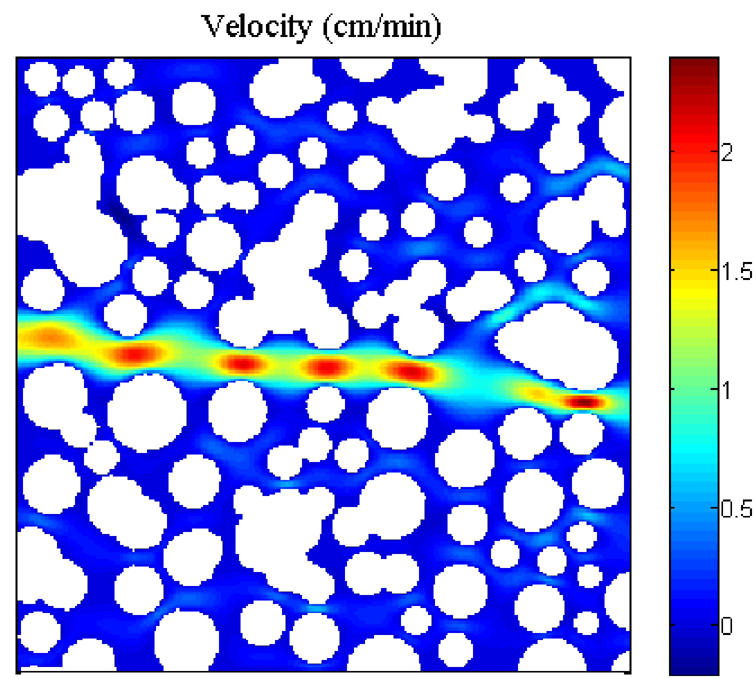
Pe (uL/D) = 0.08, 0.8, 8

Da $(kL/(K_{sp}^{0.5} \times D))$ = 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-}

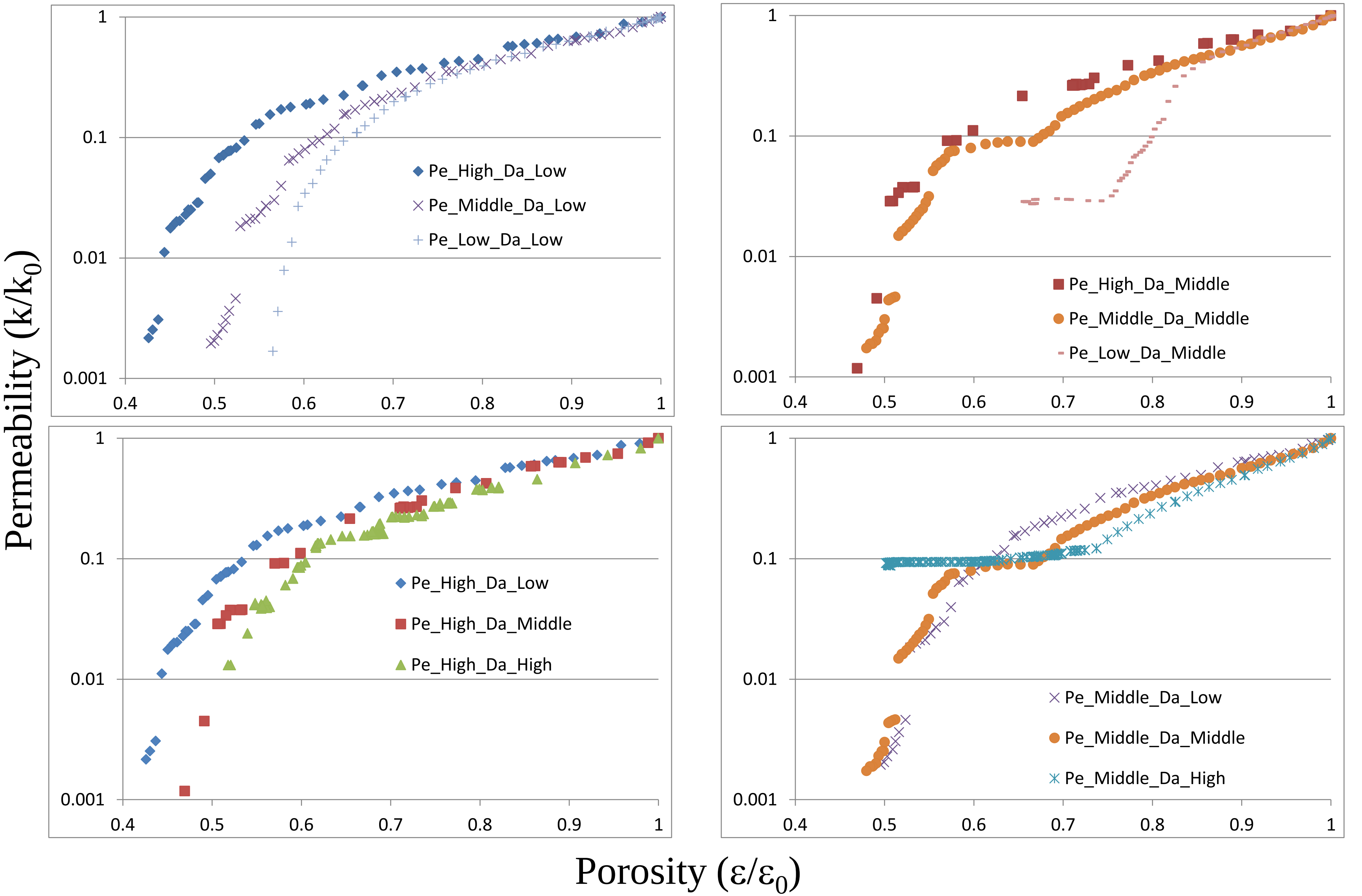




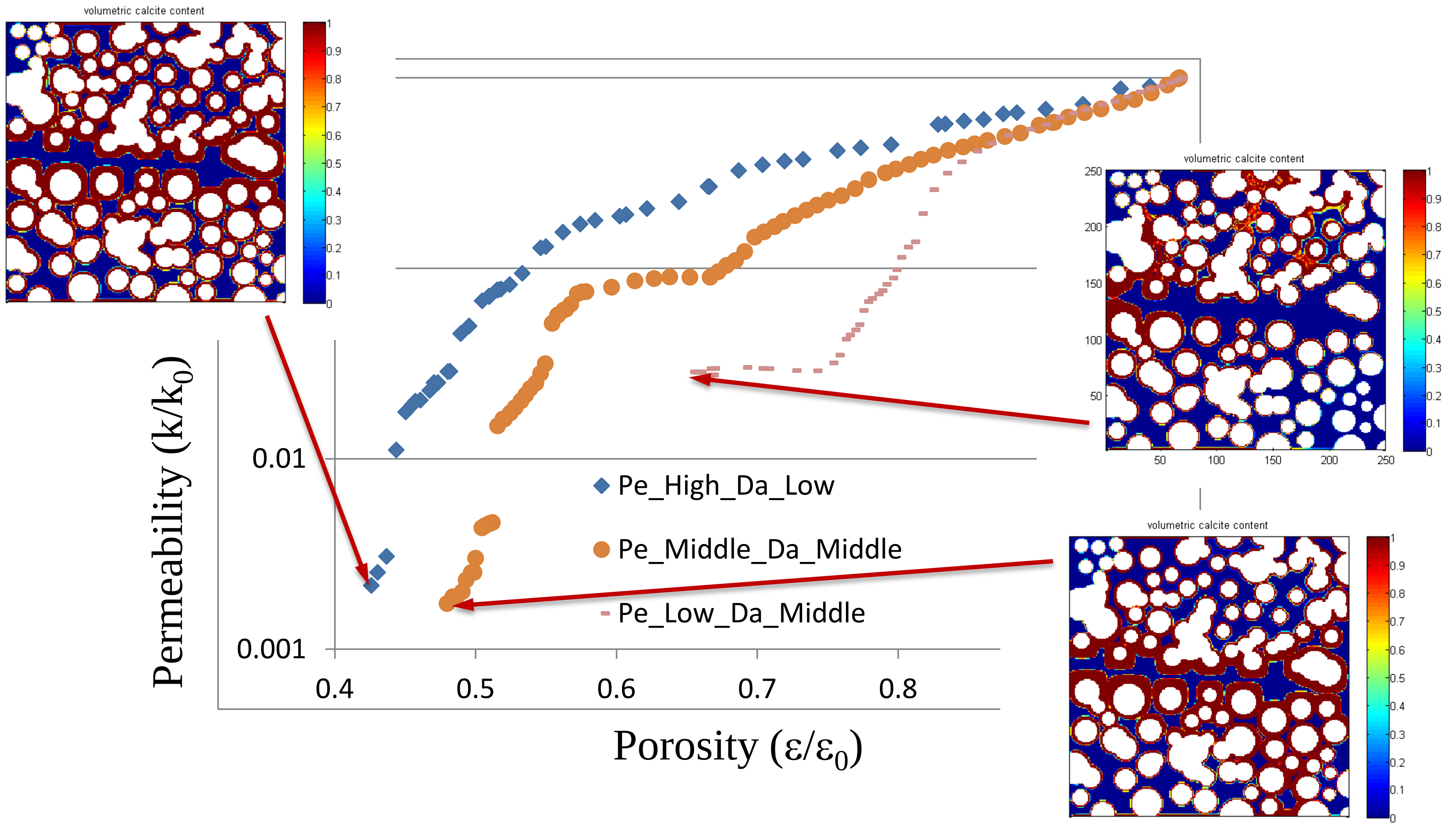
Ksp, calcite = 3.3×10^{-9} M^2

Solid with reactive surface

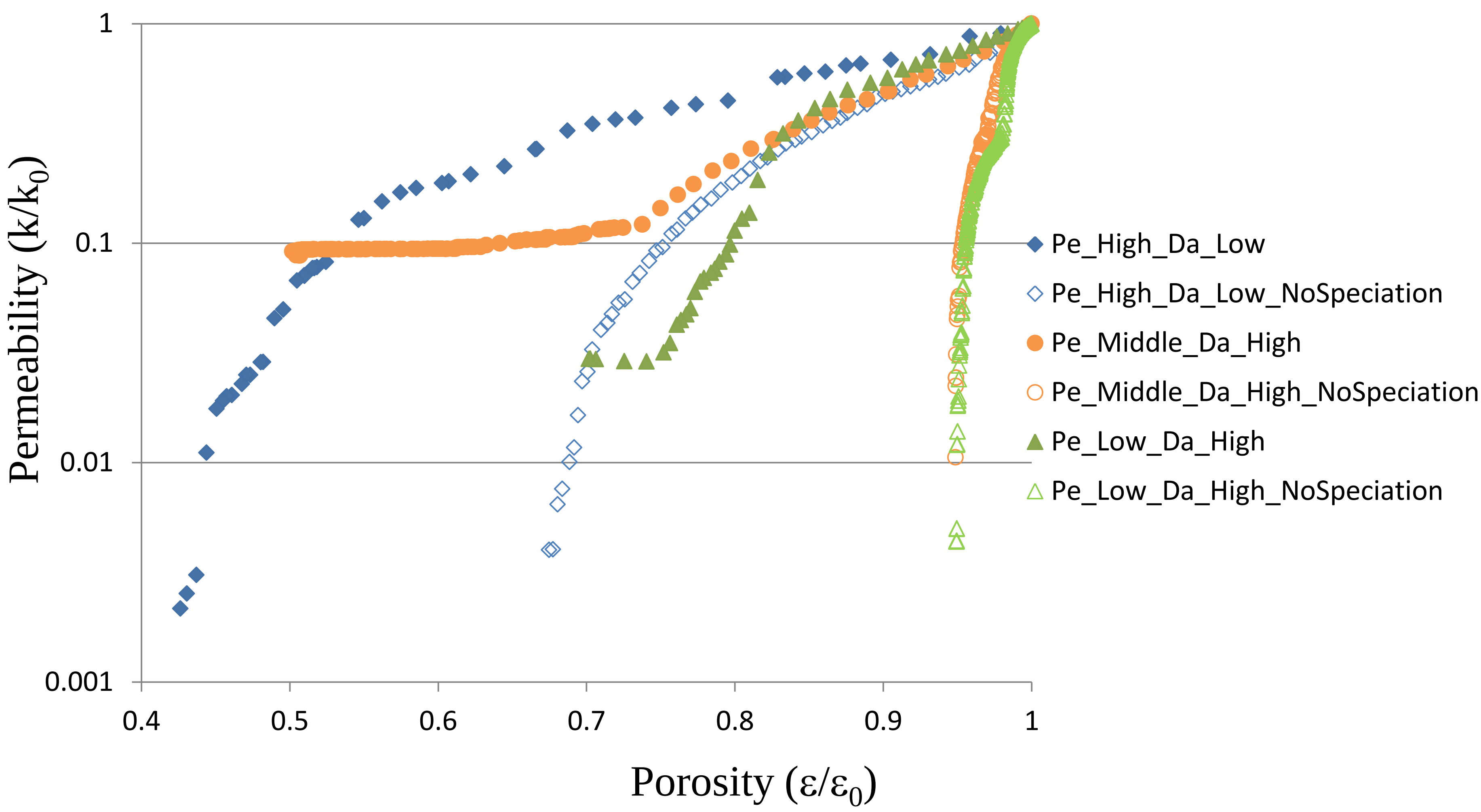
Response Function based on Pore Scale Simulations



Permeability-Porosity Relationships



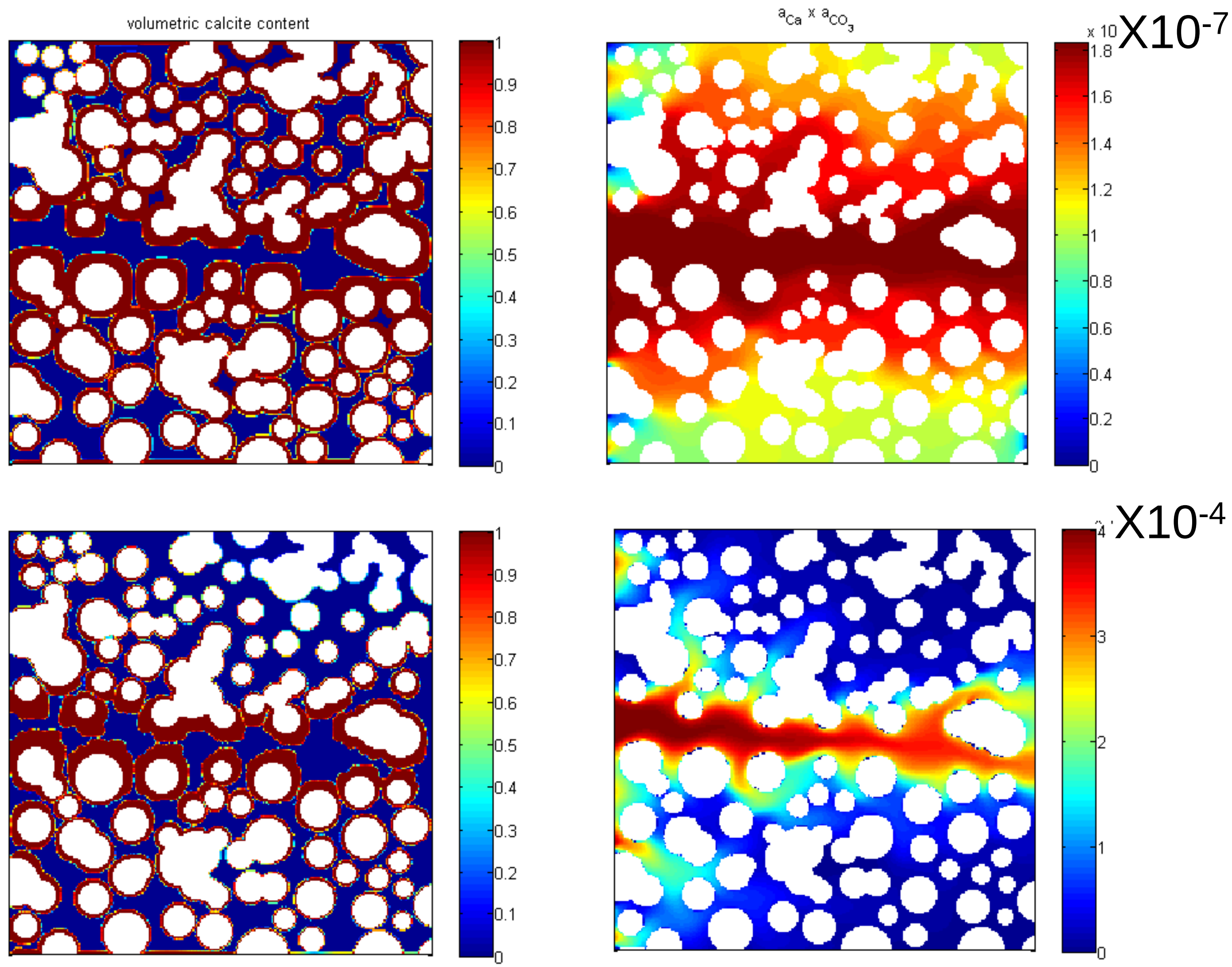
Chemical Speciation



High Pe & Low Da Case

Speciation

No speciation

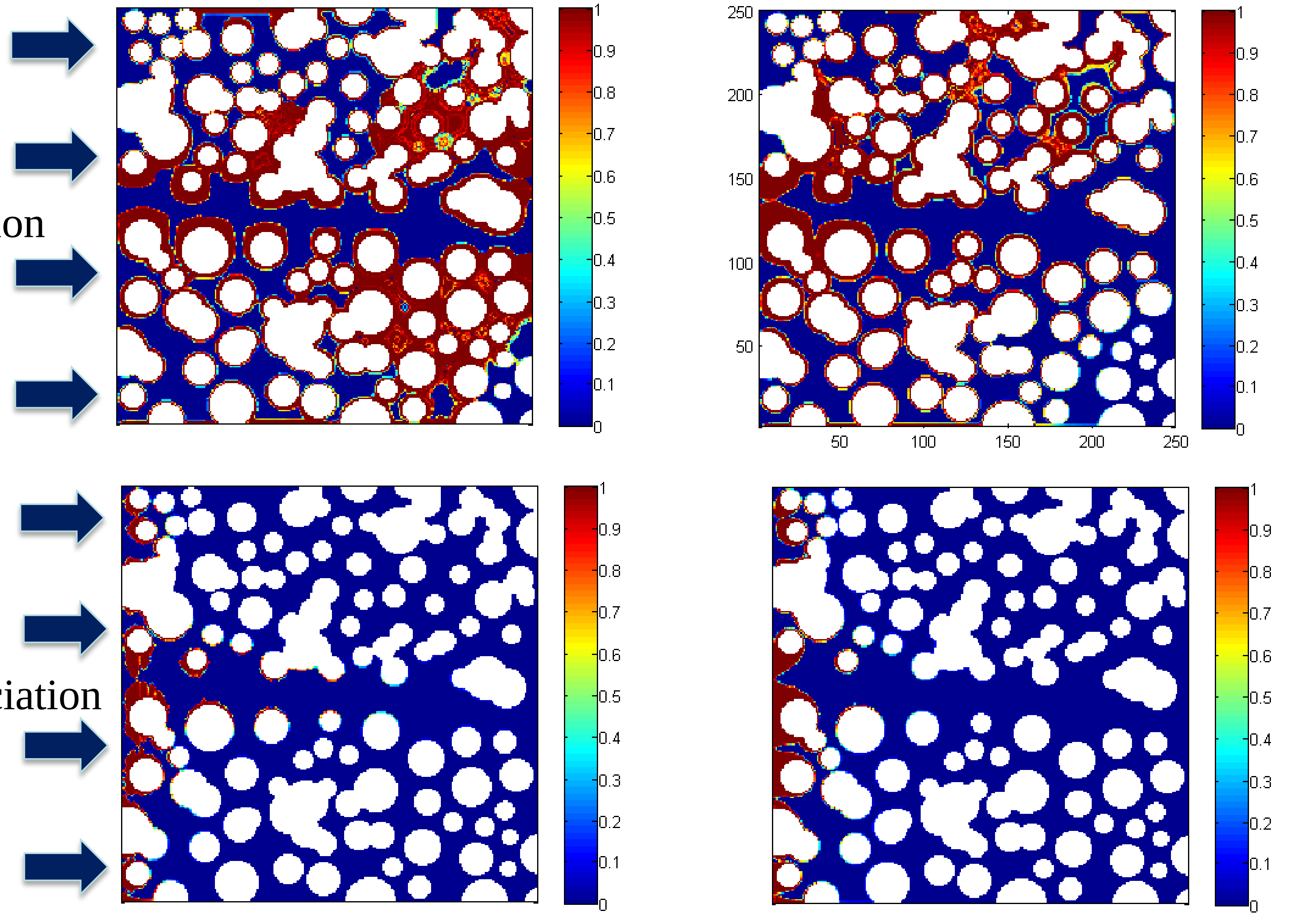


Pore clogging at the front

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 reduction model) for continuum-scale permeability and porosity (k-ε) relationships
- k-ε relationships will be affected by solution chemistry, chemical reaction, and pore structure configurations in addition to Pe and Da numbers
- An adaptive strategy to couple continuum and pore-scale using a response function approach will be tested

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