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Microfluidics applications for calcium carbonate precipitation and dissolution and Sr isotopic fractionation

Hongkyu Yoon

Mario J. Martinez, Anastasia G. Ilgen,

Andrew Knight, & R. Charles Choens

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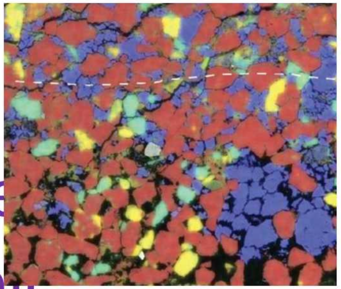
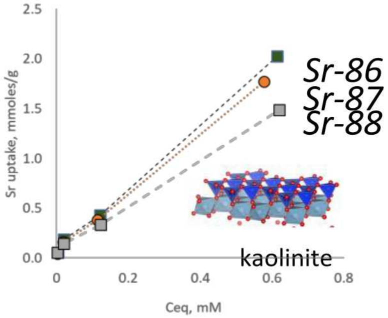
- Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center funded by the U.S. DOE BES (2009-2018)

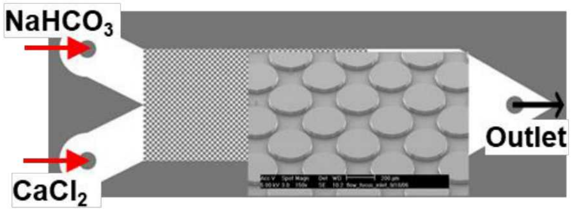
Research Efforts



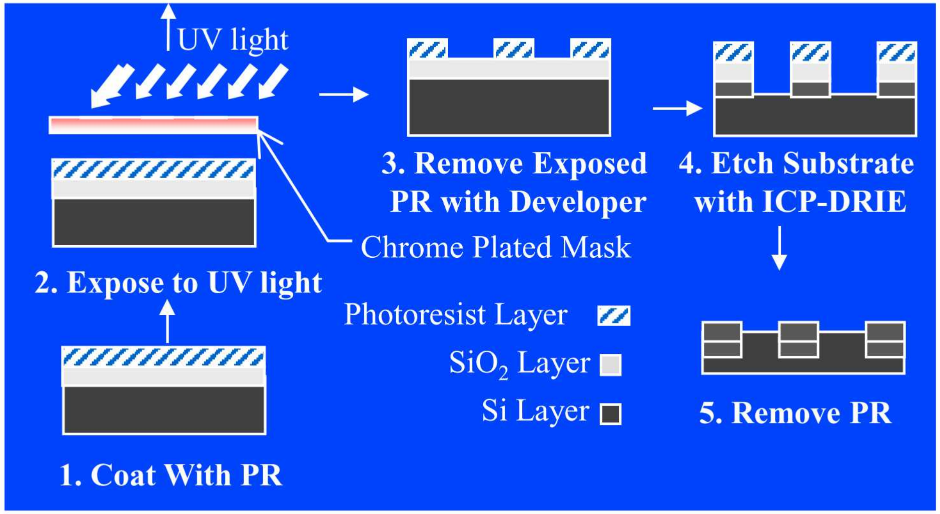
- Advance fundamental understanding of che
mechanical coupling associated with isotopic signatures in subsurface fluids to develop in situ sensors for rock deformation and failure

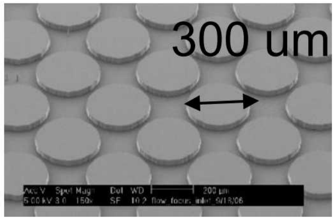
- Pore scale multiphase flow and reactive transport
- Isotopic fractionation of strontium during reactive transport
- Coupled chemical-mechanical response
- Upscaling from pore to continuum



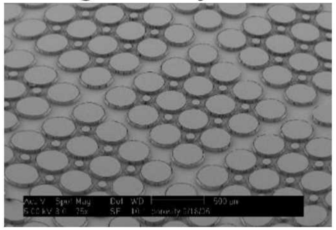


Microfluidic fabrication and patterns

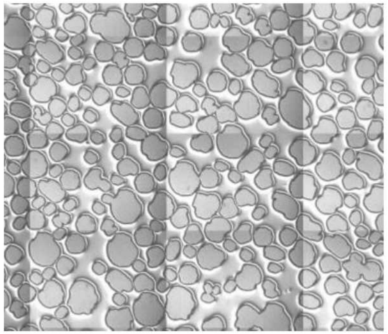




Regular Cylinder

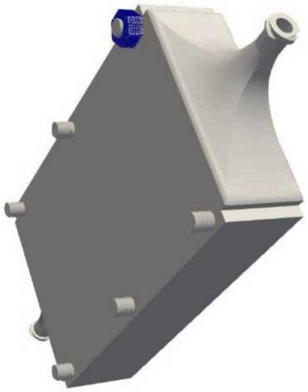


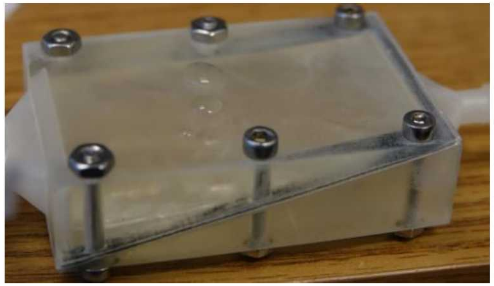
Aggregates

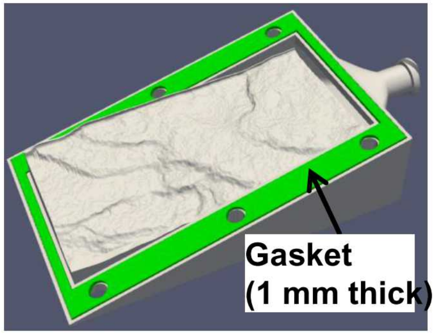


Real pattern

3D printing Applications





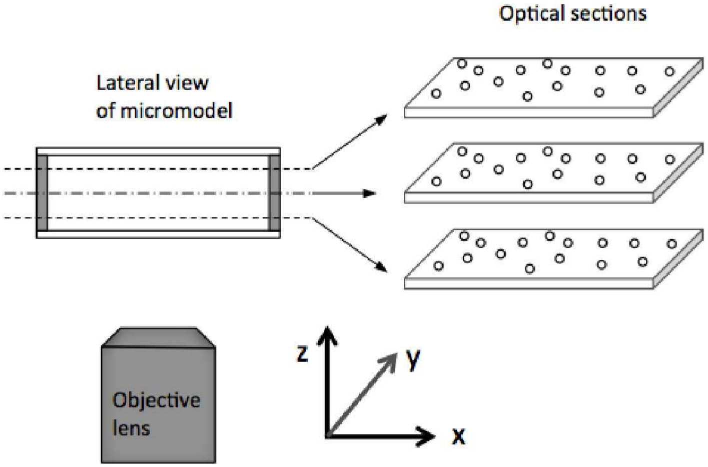


Laser Scanning Confocal Microscopy

Laser-scanning Confocal Microscope

Zeiss LSM510 Meta

3D flow fields



modified from Lima et al. (2006)

• Inverted optical & confocal microscope with epifluorescence and reflected differential interference contrast (DIC) microscopy
• Multiscale resolutions (5x – 50x) from 2μm to 0.2 μm resolution

Pore Scale Reactive Transport Experiments

• Pore scale experiments of (transversely mixing induced) reactive transport and precipitation & dissolution in a microfluidic pore-network

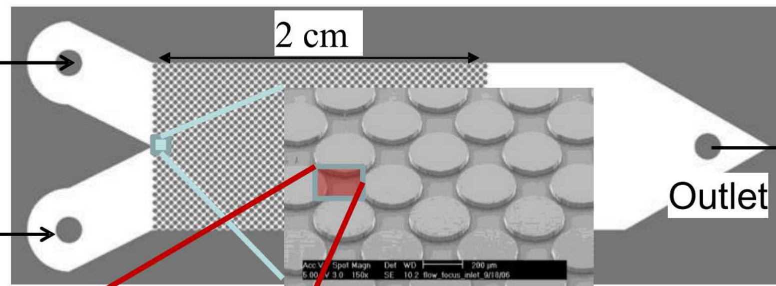
Syringe pump

harvardapparatus.com

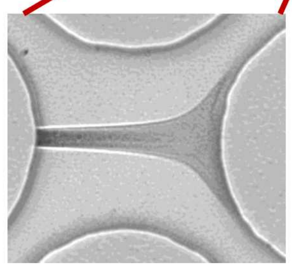
Experimental setup

Na_2CO_3, pH=11

$CaCl_2$, pH=6



Zhang et al. (2010)
Chojnicki et al. (under review, ES&T)



250 microns

Microscopic image of calcium carbonate ($CaCO_3$) precipitates

• Two solutions are mixing along the centerline and $CaCO_3$ precipitates
• Microscopic images are taken over time

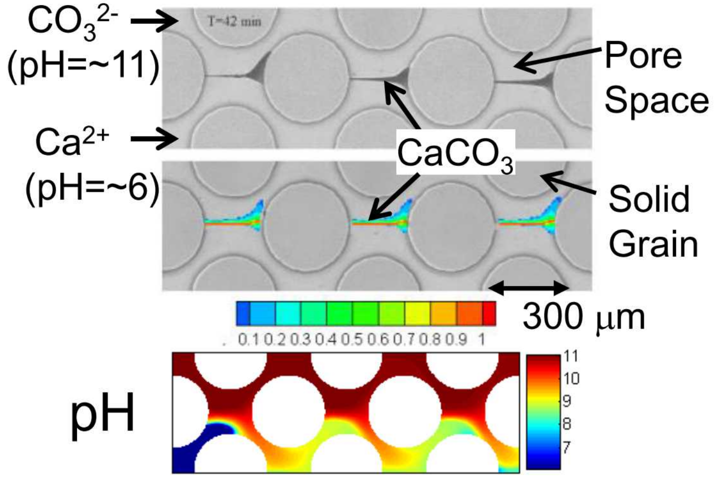
Pore Scale Modeling of Reactive Transport

Research Details

- Simulate experimental results of $CaCO_3$ precipitation and dissolution in a microfluidic pore network
- Improve understanding of the fundamental physico-chemical processes of $CaCO_3$ precipitation and dissolution at micro (pore) scale for coupled reactive transport systems

Applications

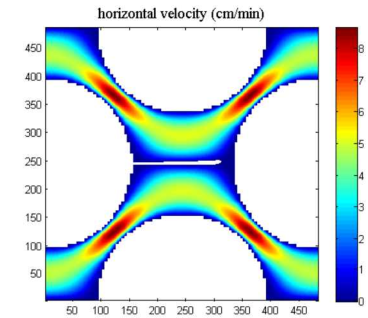
- Reaction rates ~ f(system parameters)



Experimental image (top)
Simulated $CaCO_3$ dist. (middle)
Simulated pH dist. (42min) (bottom)

Yoon et al. (2012)

Pore Scale Model Framework



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

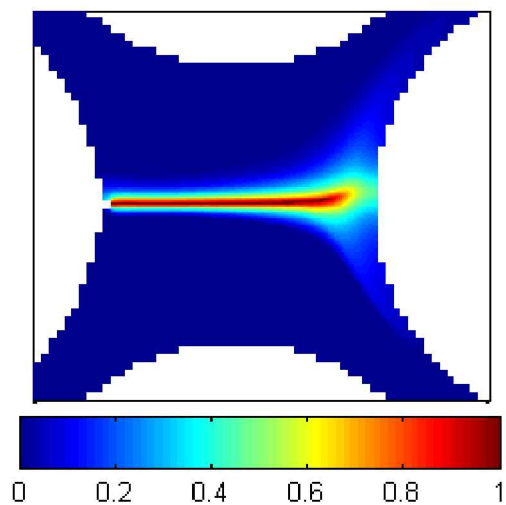
$$D\frac{\partial \Psi_j}{\partial \mathbf{n}} = -I_m$$

on reactive surface

$$I_m = -k_{cc}(1-\Omega) = -\left(k_1 a_{H^+} + k_2 a_{H_2CO_3} + k_3\right)\left(1 - \frac{Q_{cc}}{K_{sp}}\right)$$

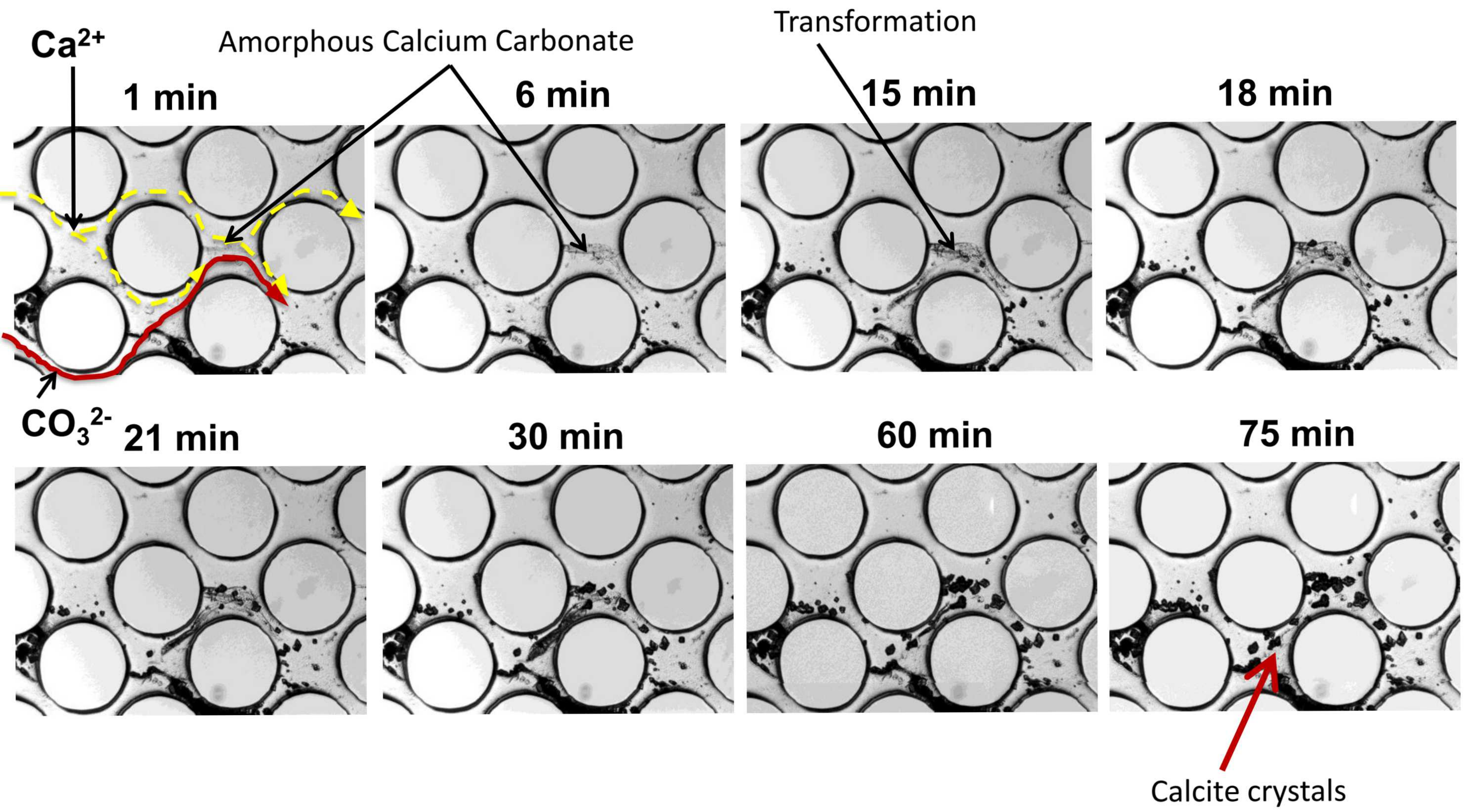
Update of $CaCO_3$ volumetric content (V_m)

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



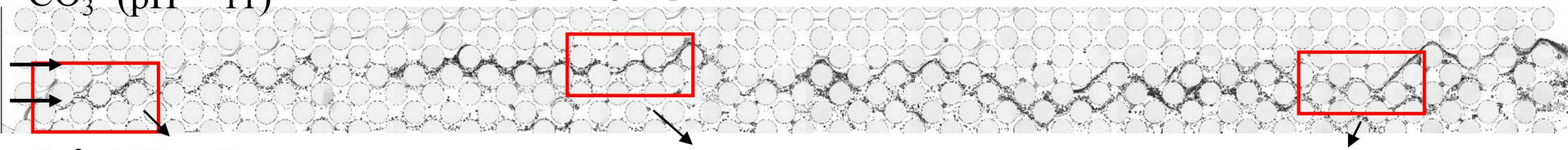
Volumetric calcite precipitate content

Reactive transport [& flow]

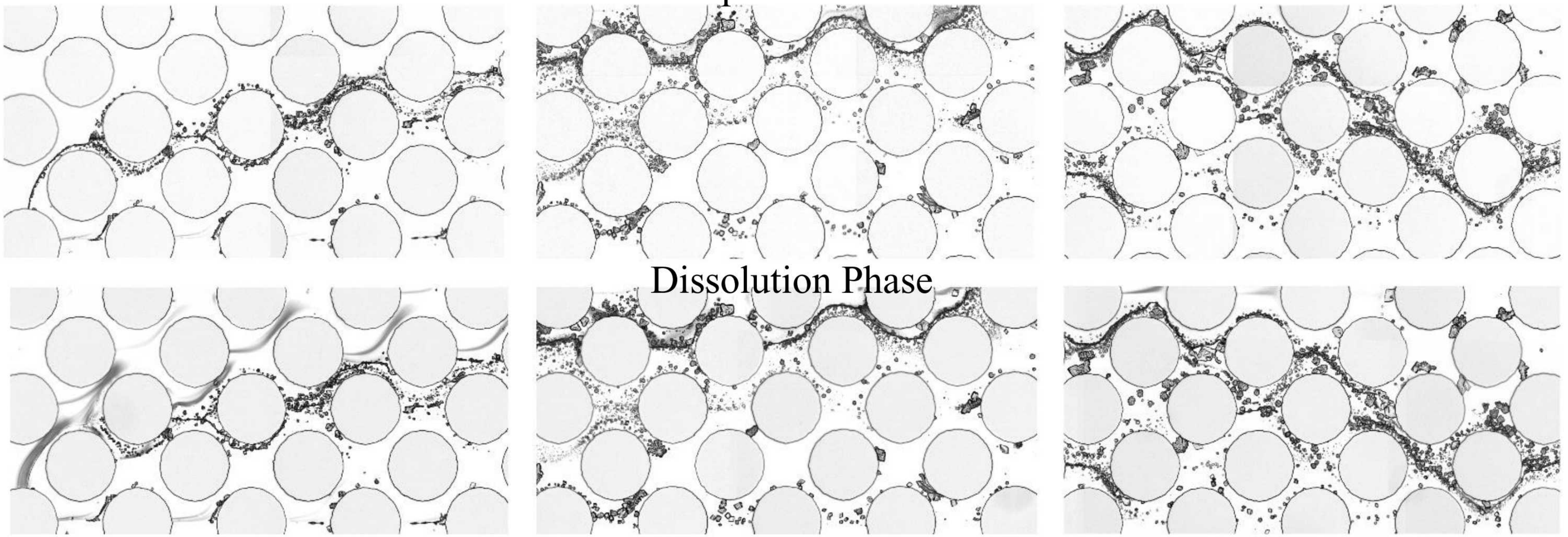


Experimental Results

$[Ca^{2+}]_T = [CO_3^{2-}]_T = 10$ mM at ~100 hrs



Precipitation Phase



- Precipitation ~ along the centerline within 1-3 pore spaces in the transverse direction
- Width of the precipitate line ~ increase with distance from the inlet
- Precipitation/dissolution rates are concentration and species dependent
- Dissolution creates nano-particle plume of reactive transport tracer

Image Analysis

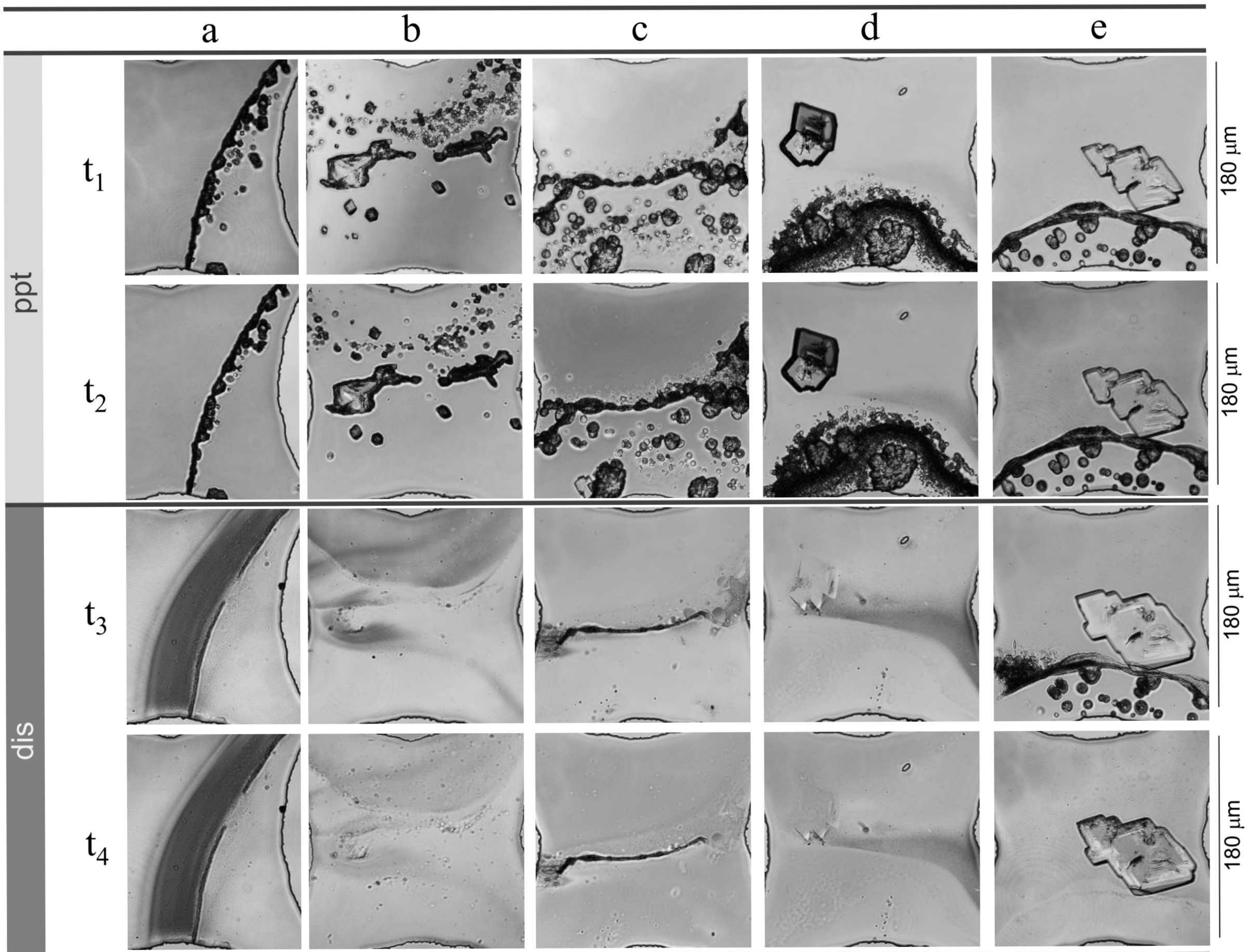
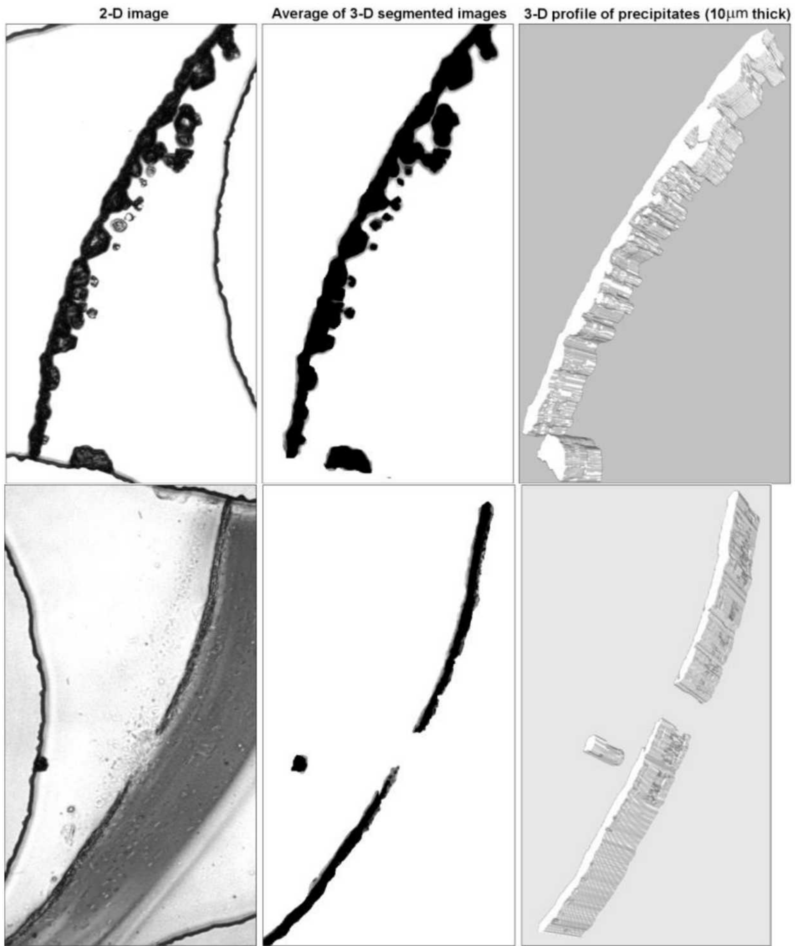
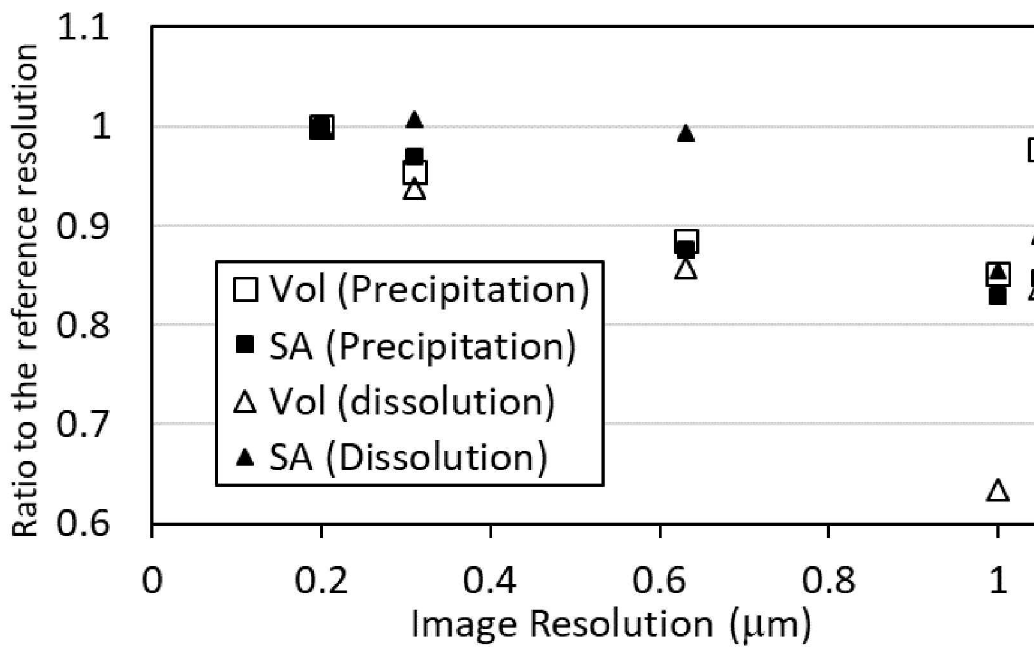


Image Analysis

- Segmentation is performed to estimate reaction rates and reactive surface areas
- Imaging resolution





Reactive Surface Areas

- What is a reactive surface area?
- Precipitation area, vertical surface area, effective surface area, …

Reactive surface area
(area/volume)

$$R = k\ A\left(\frac{IAP}{K_{eq}} - 1\right)$$

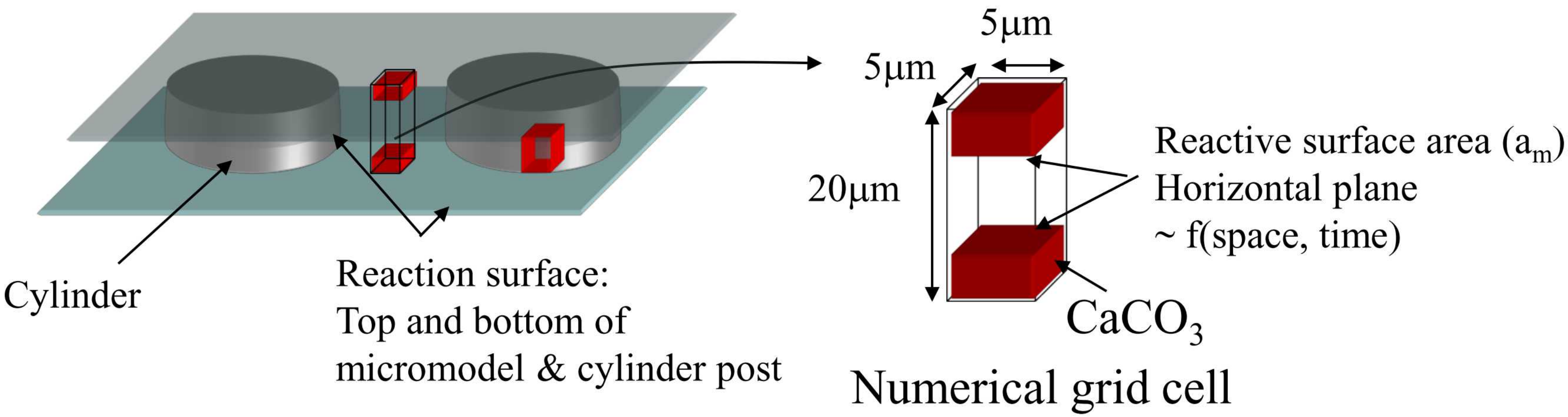
Extent of non-equilibrium

Reaction Rate
(mass/volume/time)

kinetic rate constant
(mass/area/time)

How can we model reactive transport in a microfluidic system?

1. Quasi 3D grid cell for reactive surface

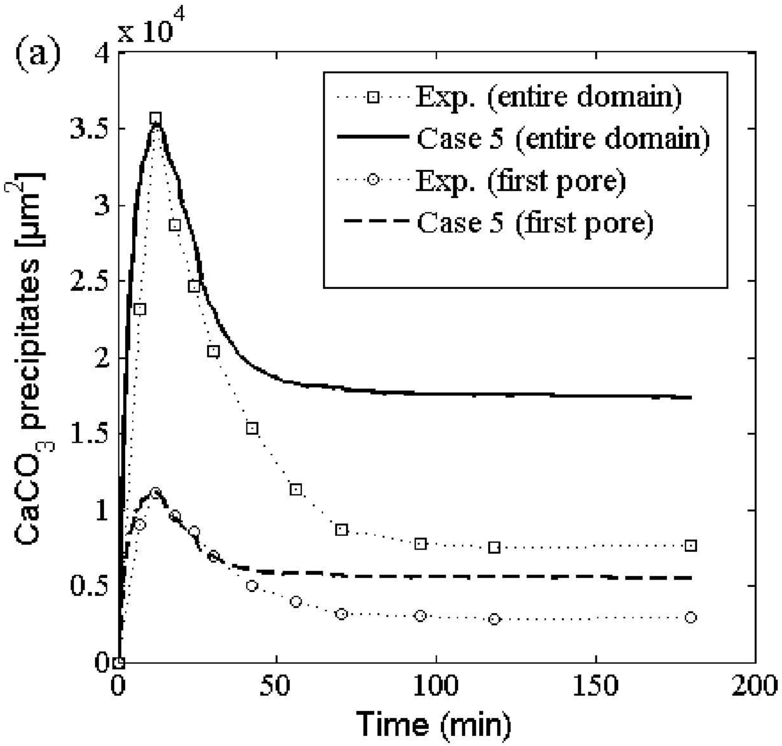


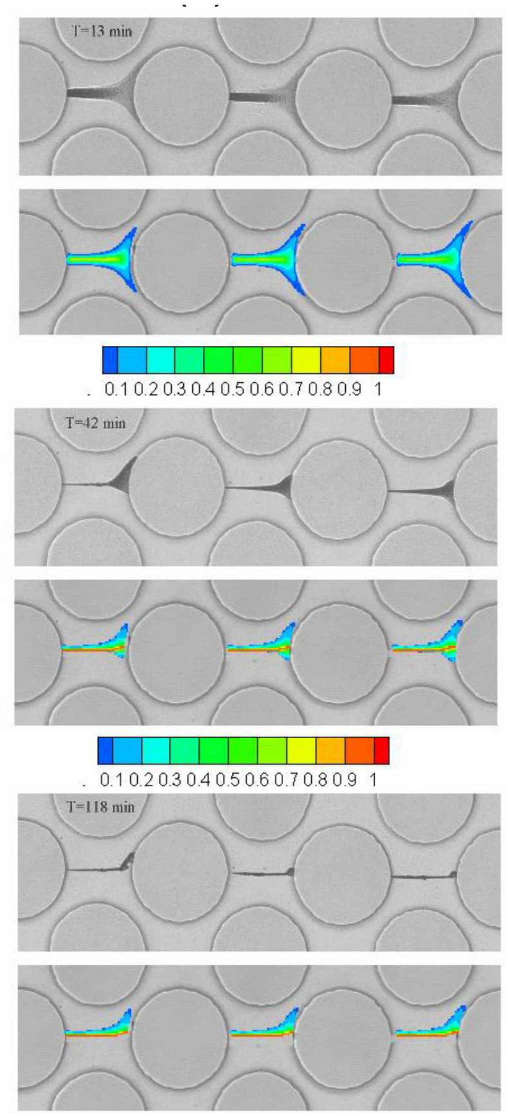
2. Effective diffusion coefficient = D_m * tortuosity (τ)

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

Yoon et al. (2012), WRR

Simulation results – increase surface area during dissolution by 300





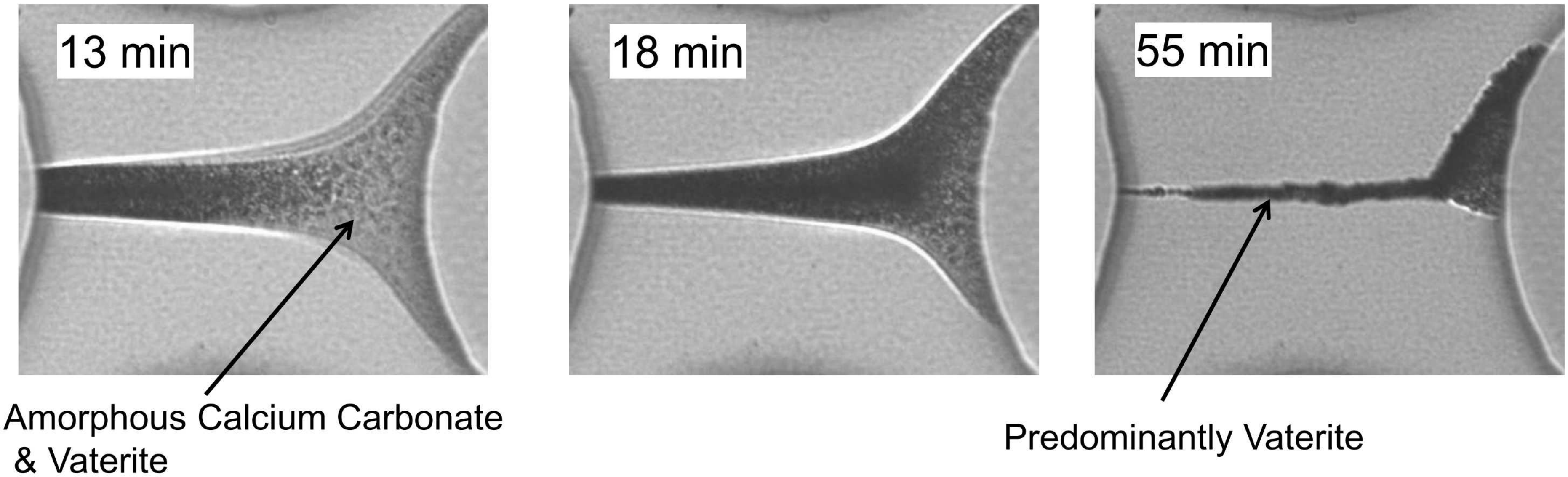
13 min

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

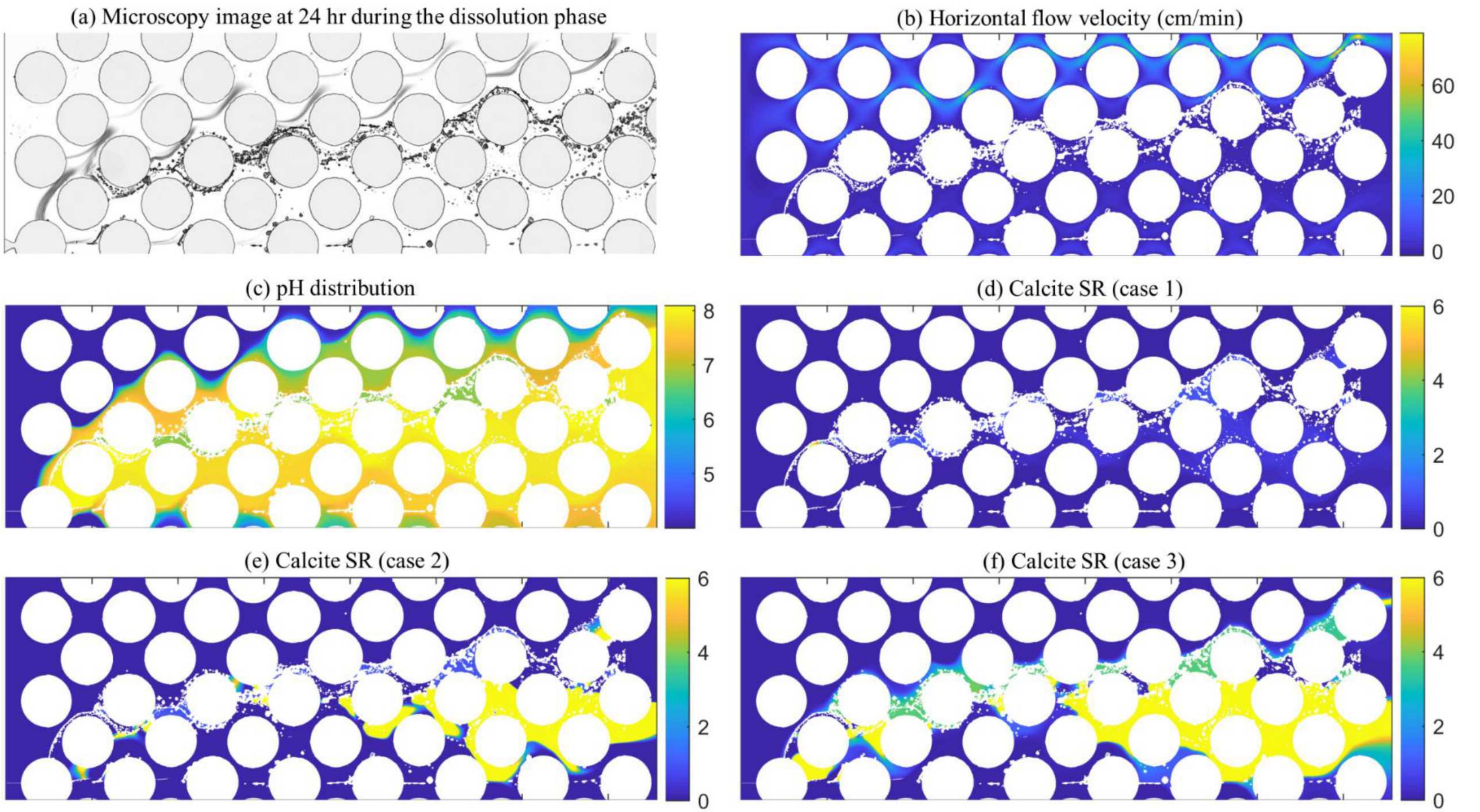
Matching simulation to late-time dissolution



- Increase in surface area over time
- Conversion to more dense form of $CaCO_3$
- Reaction rate derived from process-based growth model at nano-scale (Wolthers et al., GCA, 2012)
- Effect of nano-crystal size on solubility (Emmanuel and Ague, Chem. Geo. 2011)

$CaCO_3$ Dissolution Process

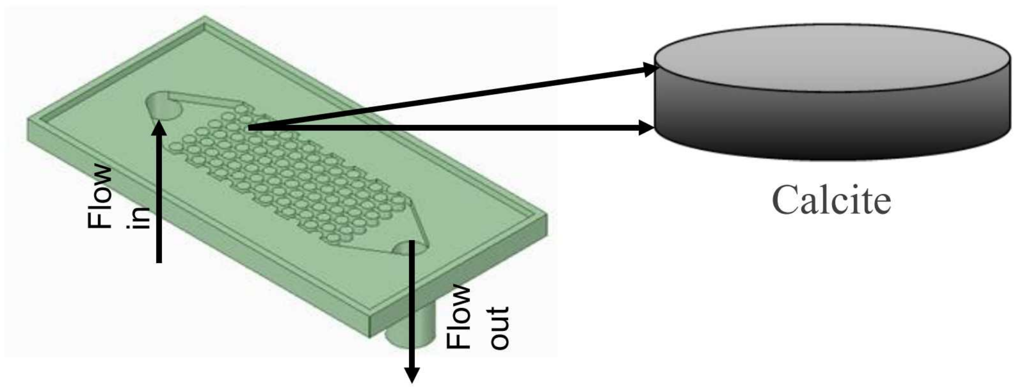
pH=4
DI water

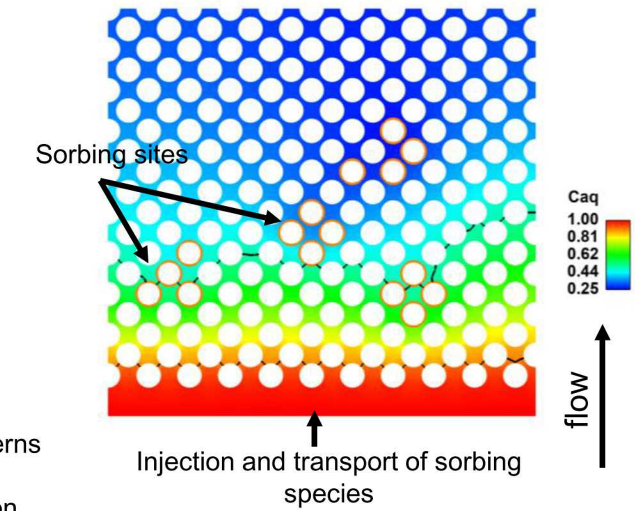


Chojnicki et al. ES&T, Under review

- Dissolution process is governed by flow patterns and dark plume of dissolved species is governed by local hydrodynamics and local chemistry (e.g., pH)

Ongoing Work

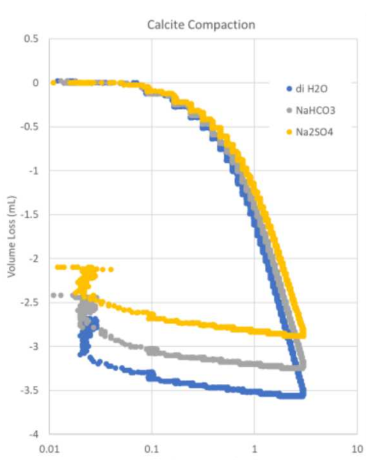




Testing bed of adsorption/desorption & precipitation/dissolution of calcium carbonate in real-rock mock-up

- Measurement of effluent concentrations of isotope in the presence of calcite obstacle patterns with known surface geometry and media structure
- Real-time imaging of change of calcium carbonate morphology with precipitation/dissolution
- Note: similar configuration will be employed into a nano-fluidic device

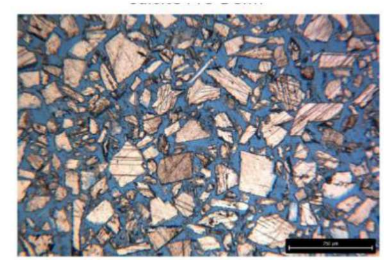
Hydrostatic compaction of granular calcite



Sr isotopes in calcite

86, ppb	87, ppb	88, ppb
30.504	22.413	279.844
%	%	%
9.17	6.74	84.10

Calcite pre-deformation



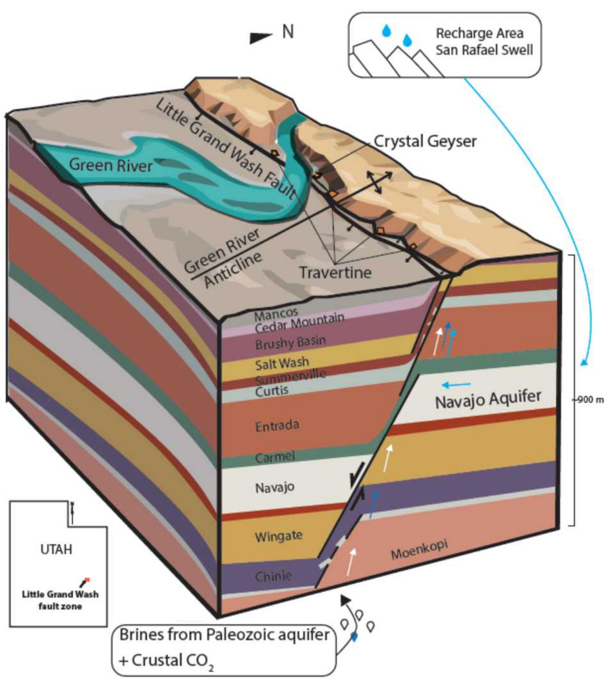
Calcite post-deformation

Summary and Implications

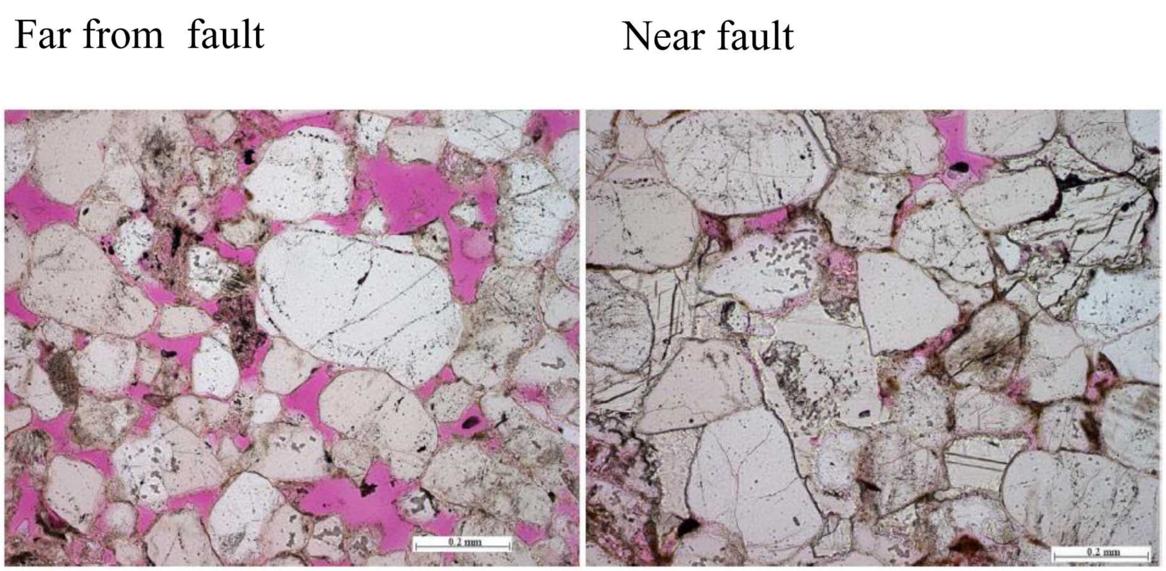
- Mineral precipitation rate along flow direction is concentration dependent and limited by transverse mixing
- $CaCO_3$ mineral phases are concentration dependent
- Overall, reaction kinetics, crystal growth and morphology are spatially and temporally affected by solution chemistry and hydrodynamics 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

Little Grand Wash Fault, Crystal Geyser, Utah

- Observations along the surface exposure of the Grand Wash fault indicate alteration zones of 10-50 m width with spacing on the order of 100 m
- Locations of conduits controlled by fault-segment intersections and/or topography
- Sandstone permeability reduced by 3 to 4 orders of magnitude in alteration zones by carbonate cementation

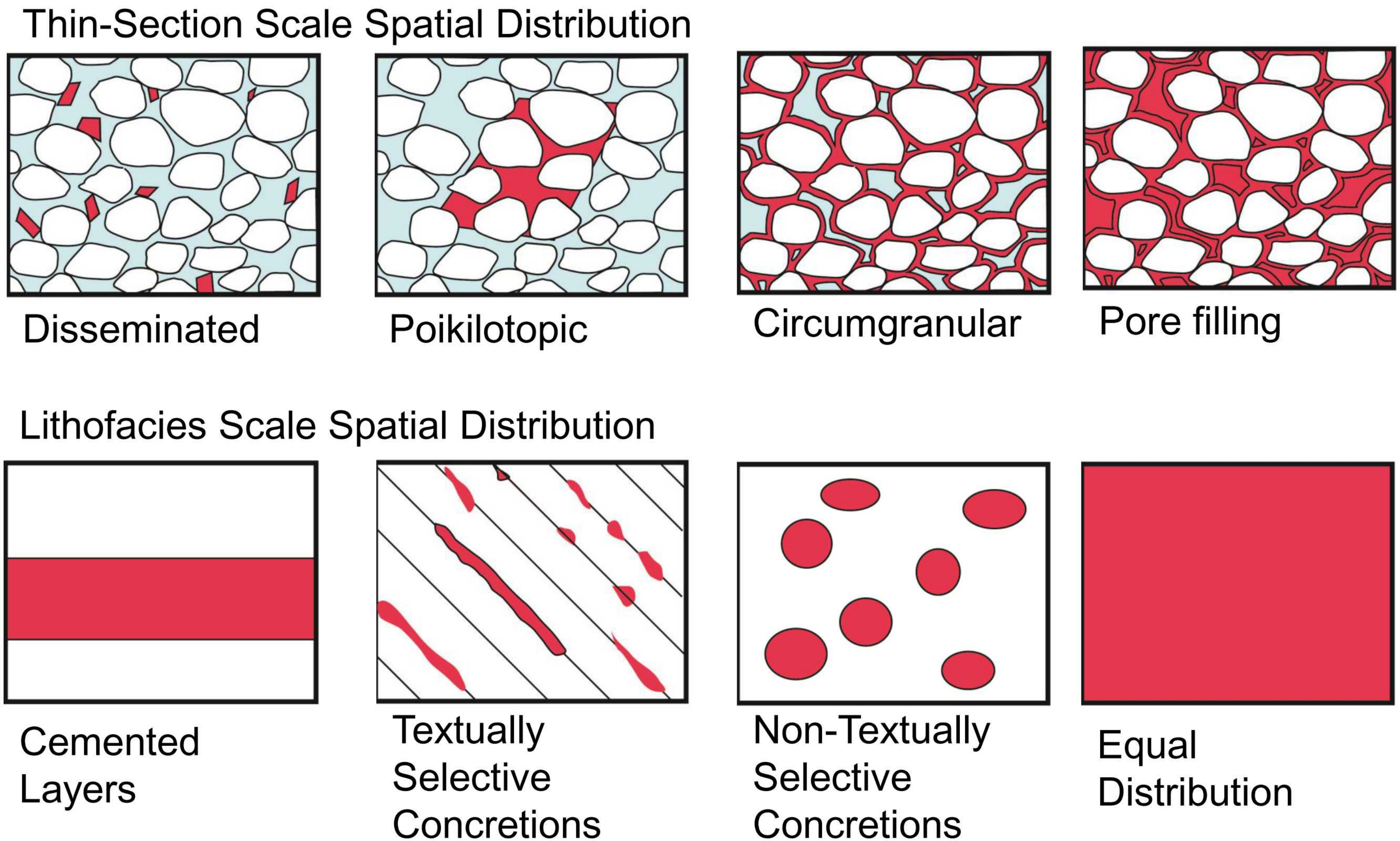


Altman et al. 2014



Yoon et al. JPSE 2017

Conceptual Model of Cementation Patterns



Peter Mozley (NMT), Unpublished

Pore scale modeling for response surface

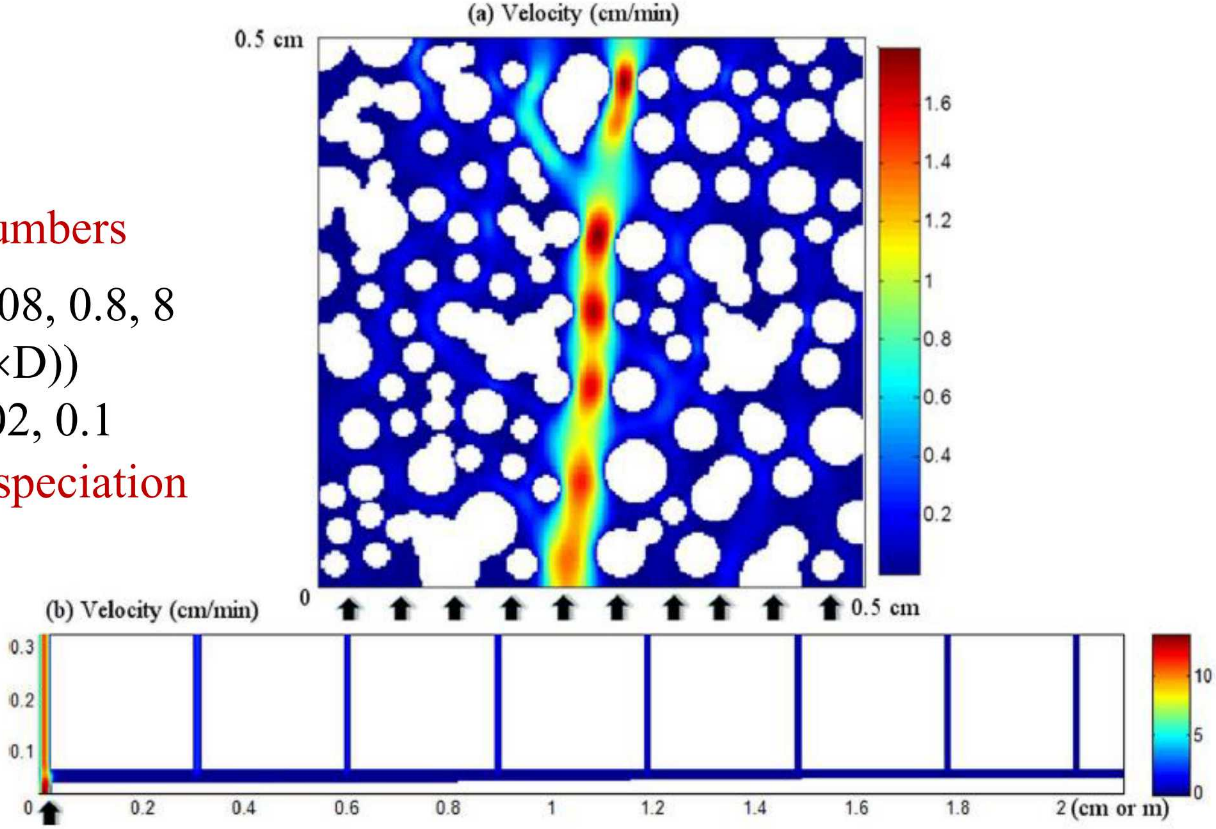
- Pore-scale modeling results will be able to develop the response functional forms of permeability, porosity, and surface area changes as a function of pore structures, volume, Pe, Da number, mineral types, and influent solution chemistry

- Pe & Da numbers

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

$Da(kL/(K_{sp}^{0.5} \times D))$
$= 0.002, 0.02, 0.1$

- Chemical speciation

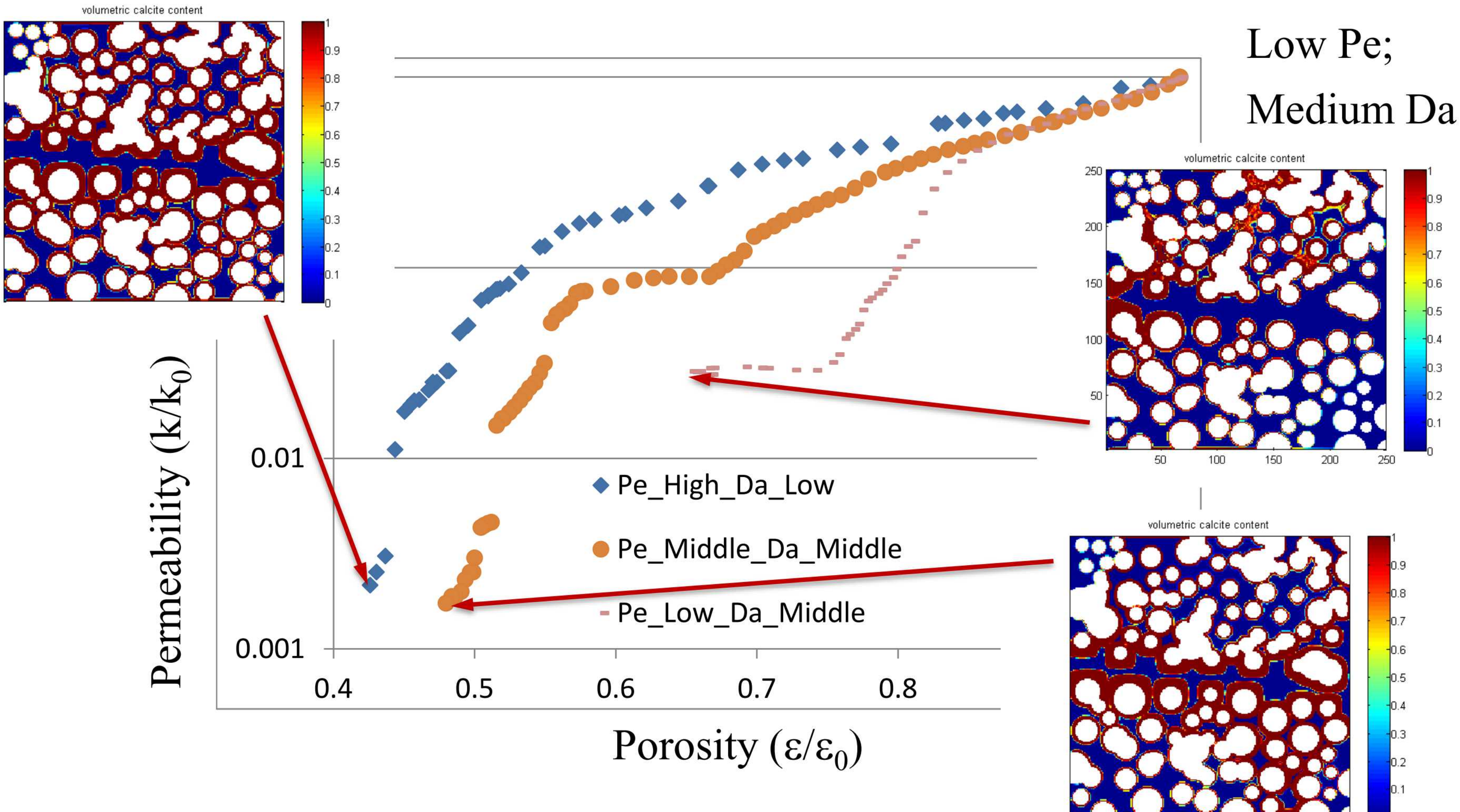


Yoon et al. JPSE 2017

Permeability-Porosity Relationships

High Pe; Low Da

Low Pe; Medium Da

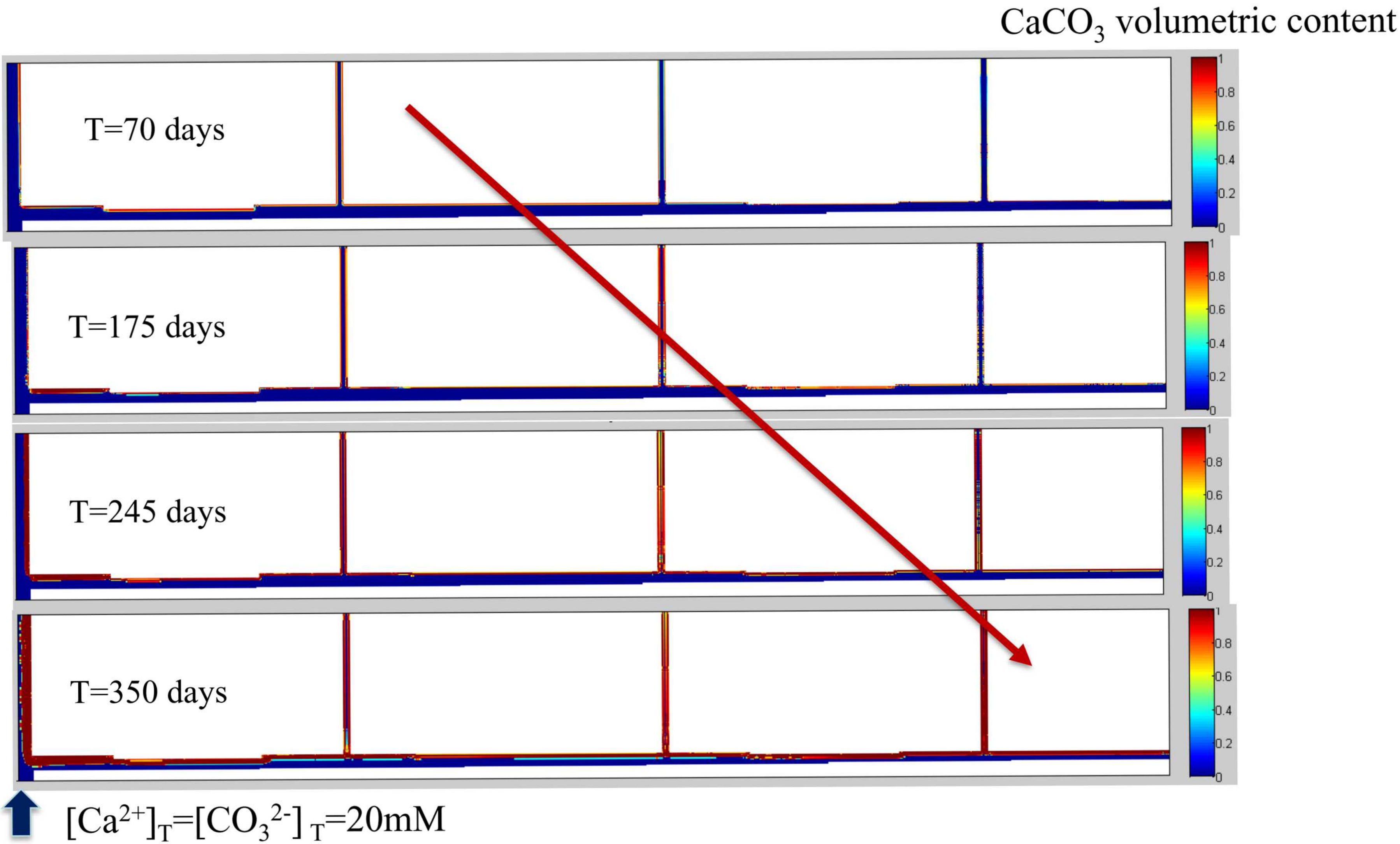


Medium Pe; Medium Da

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

Da $(kL/(K_{sp}^{0.5} \times D))$ = 0.002, 0.02, 0.1

High Pe & High Da



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

- Precipitation occurs near the main fault and clogging of fracture networks moves away from the main fault conduit as observed in the outcrop

Summary

- Detailed investigation of fault-controlled CO_2 leakage conduits in Little Grand Wash Fault, Crystal Geyser, Utah where carbonate cementations significantly decreases permeability
- Vigorously tested pore-scale model was used to develop a permeability and porosity (k-ε) relationship for continuum-scale model
- Pore scale model was able to qualitatively capture pore clogging patterns in a simple fracture network model mimicking the Little Grand Wash fault
- An adaptive strategy to couple pore- and continuum scale using machine/deep learning methods will be tested against cement precipitation patterns