SAND2013-2989C

Pore-scale analysis of mixing-controlled calcium carbonate precipitation and dissolution kinetics in microfluidic experiments

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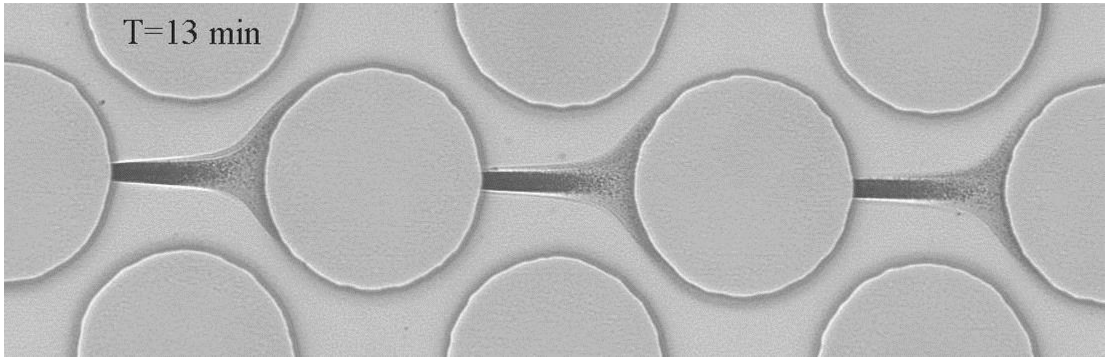
ACS 2013 Spring



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This material is based upon work supported as part of the **Center for Frontiers of Subsurface Energy Security**, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001114.
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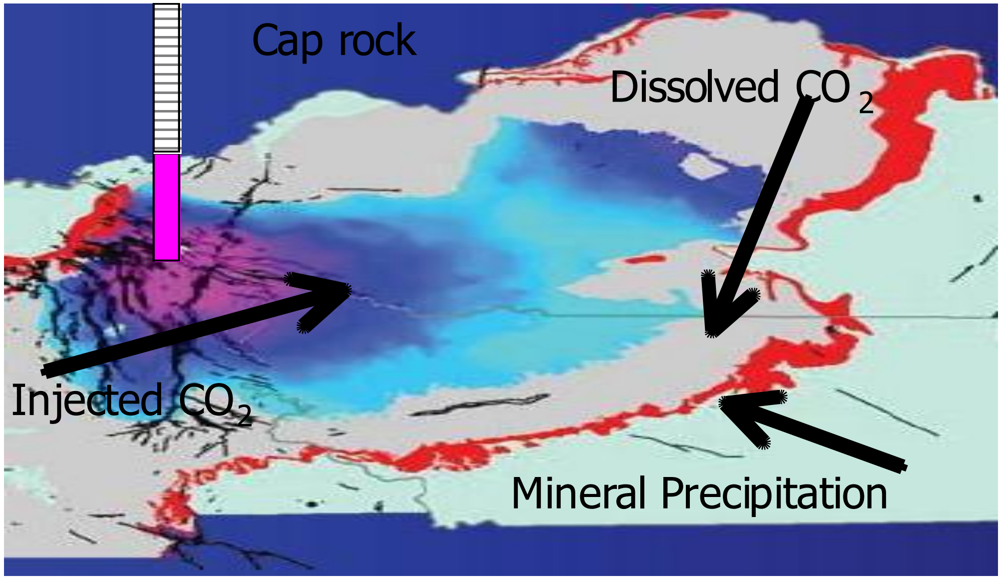
Pore scale mixing and reaction can affect CO_2 injection efficiency and storage capacity



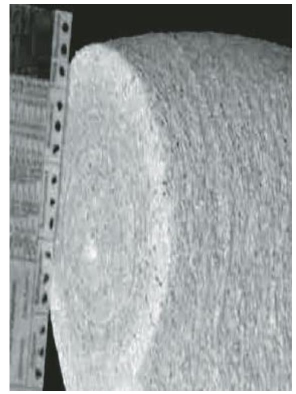
S.E. Greenberg (2007), Midwest Geological Sequestration Consortium

Natural Examples for mixing and reaction controlled $CaCO_3$ precipitations

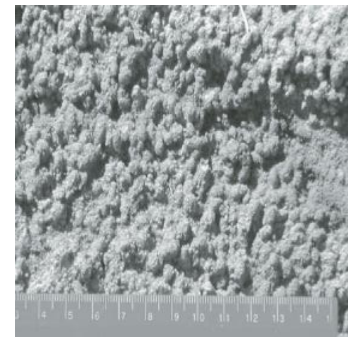
- Concretion Characteristics

Uniform elongate concretion

Zoned elongate concretion

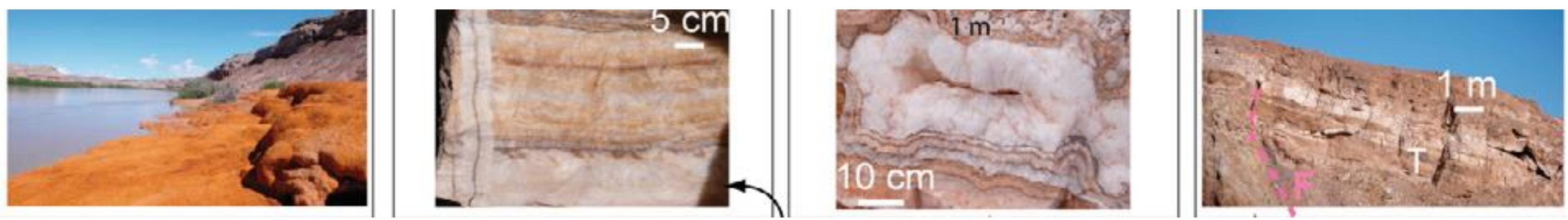


Composite concretion



Mozley and Davis, GSA Bulletin, 2005;
Rio Grande sediments

- Travertine with various deposits



Surface deposition

Vertical Fissure Travertine

Dissolution and redeposition

Horizontal white veins

Gratier et al., Geology, 2012; Crystal Geyser, Utah

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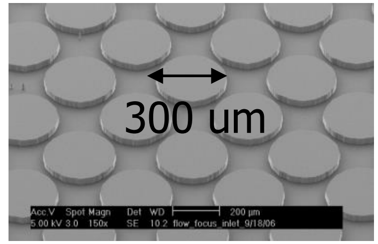
Experiment in a micromodel

Micromodel Description

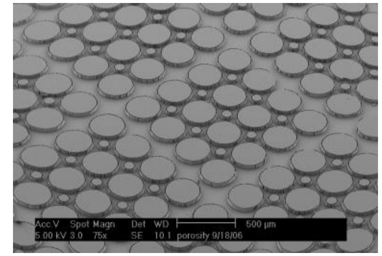
Depth: ~20 mm

Porosity: ~0.39

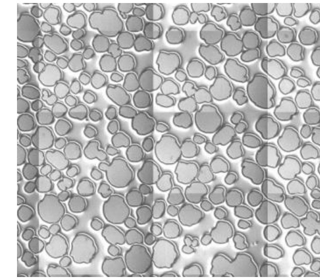
Flowrate: ~2 cm/min



Base Case
Small Cylinder



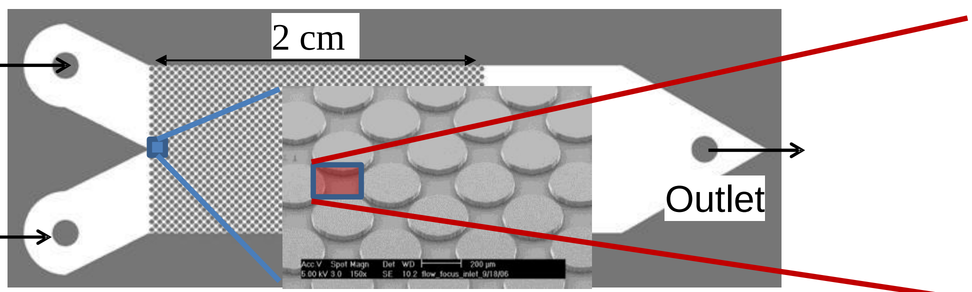
Aggregates



Irregular

Na_2CO_3

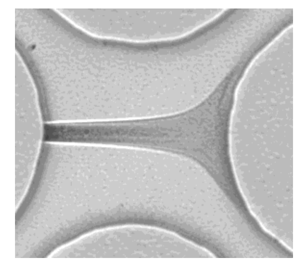
(pH=~11)



$CaCl_2$

(pH=~6)

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

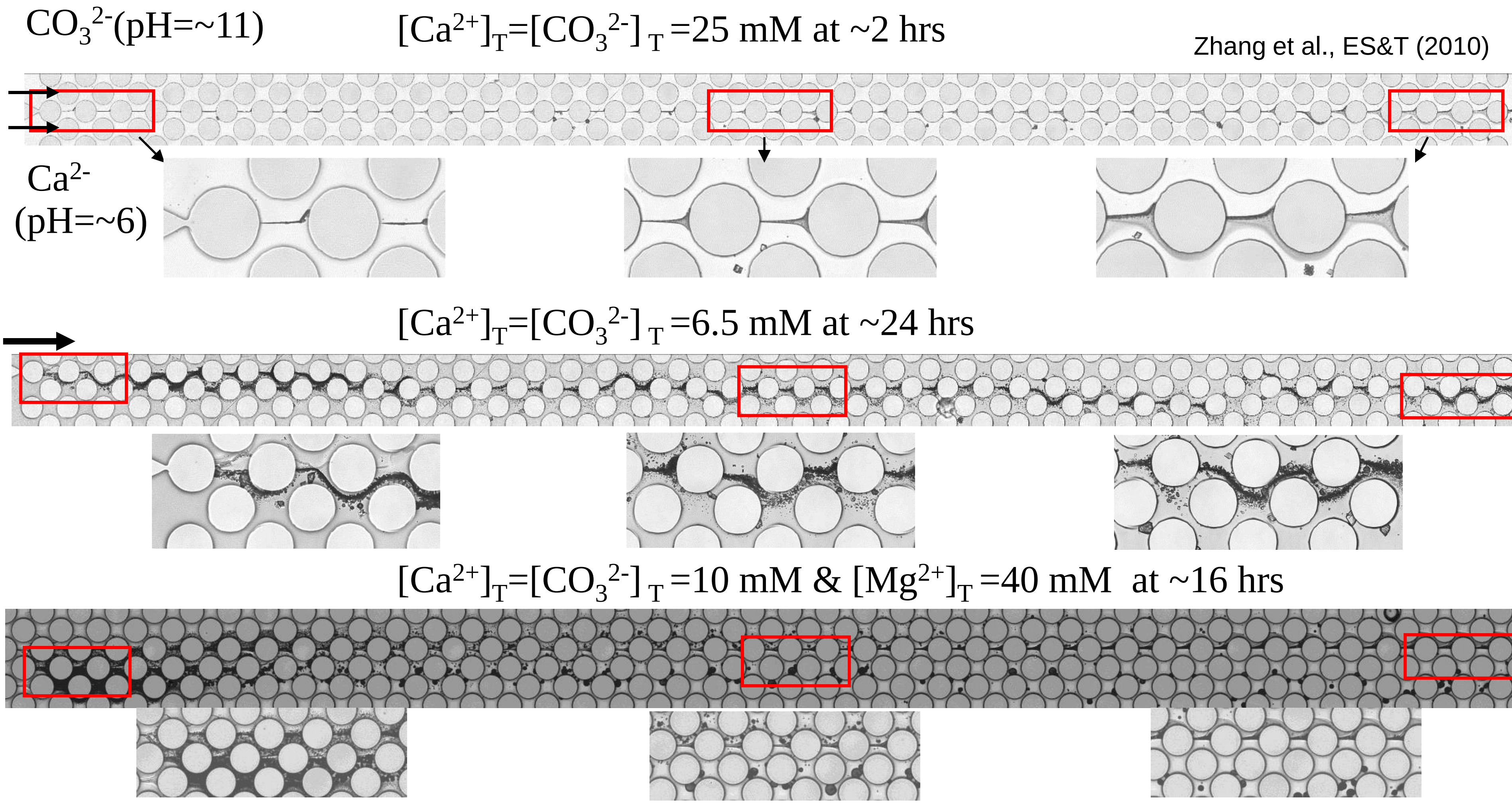


250 microns

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

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

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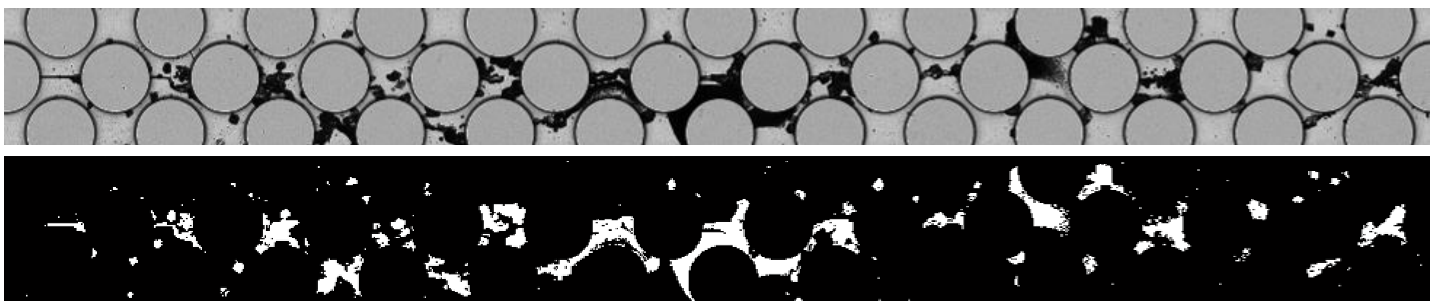
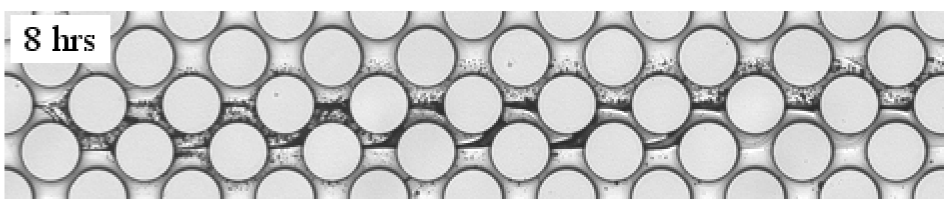
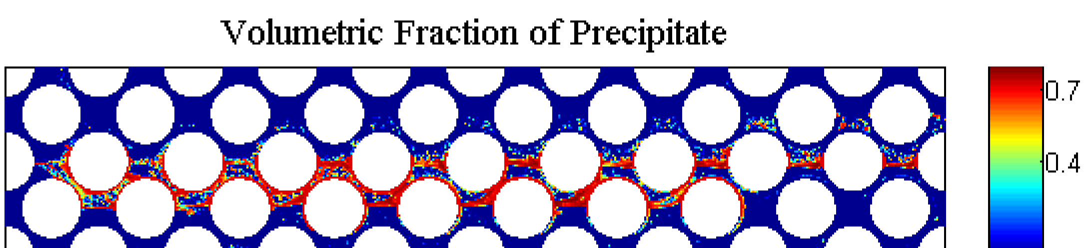
Image Analysis

Otsu thresholding

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







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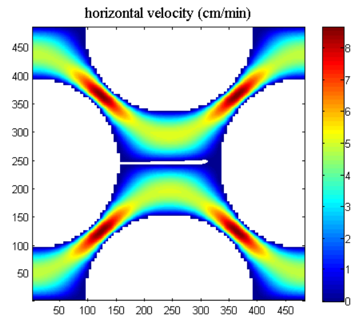
Pore Scale Model Framework



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

↓

Finite Volume Method: Reactive transport at pore scale

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

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

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

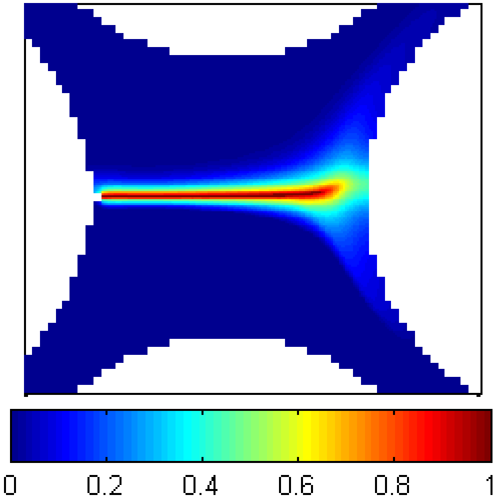
on reactive surface

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

Δt

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 PPT content

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Results –Precipitation only at grain boundary

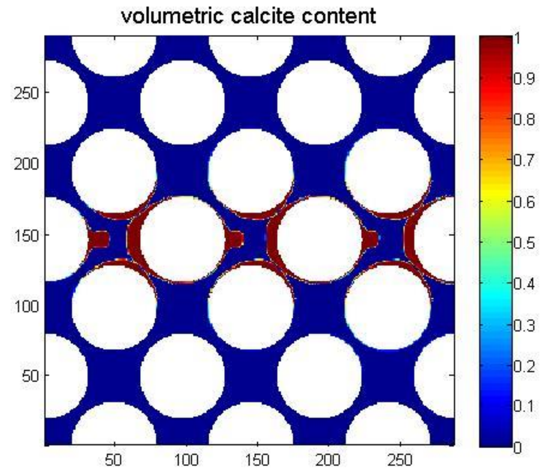
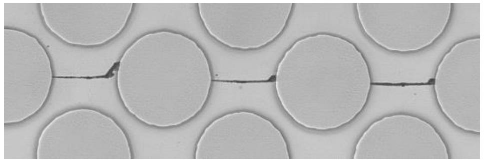
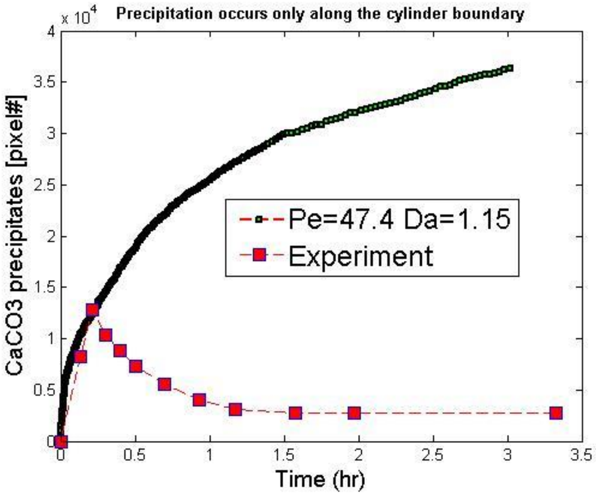
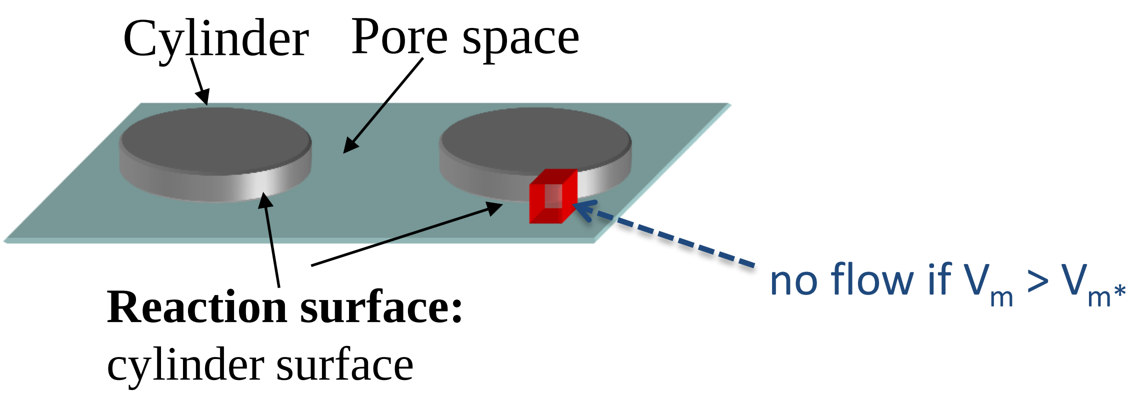


Image of precipitates at 180 min



25 mM Experiment

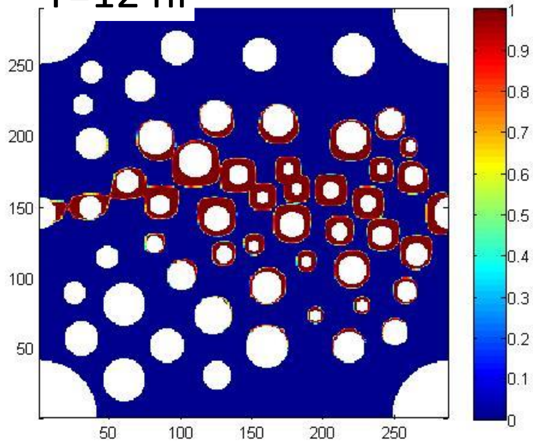




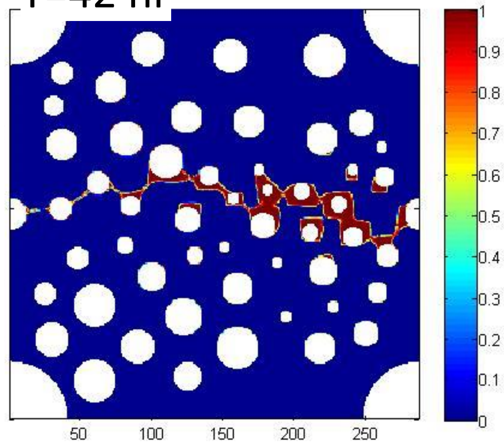
Results –Irregular pattern of grains & different values for SI

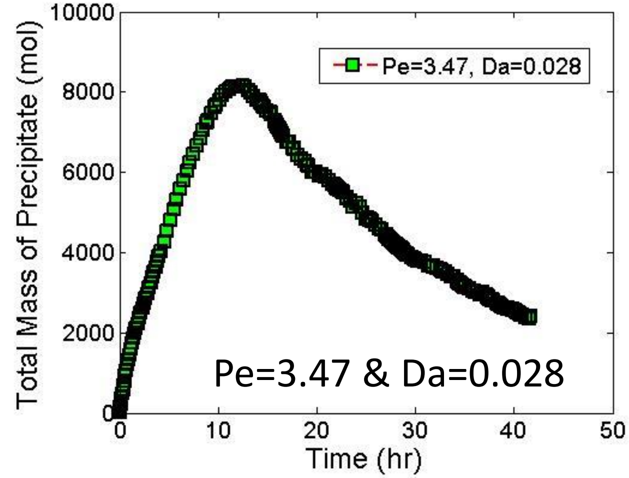
Near equilibrium (log SI = ~0.7)

T=12 hr



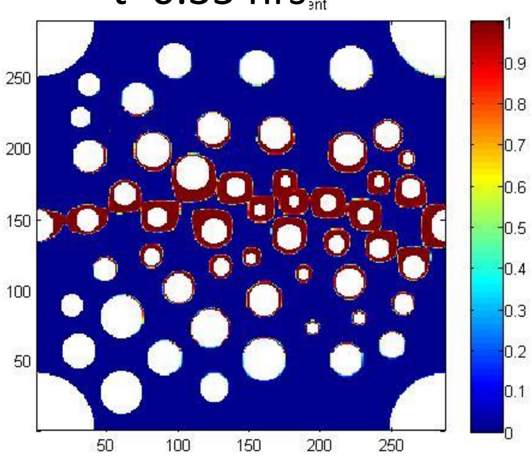
T=42 hr



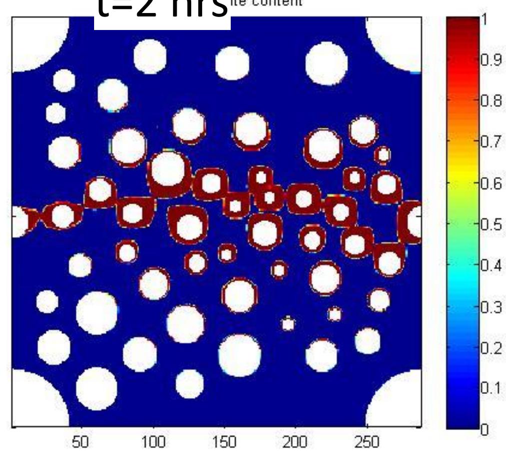


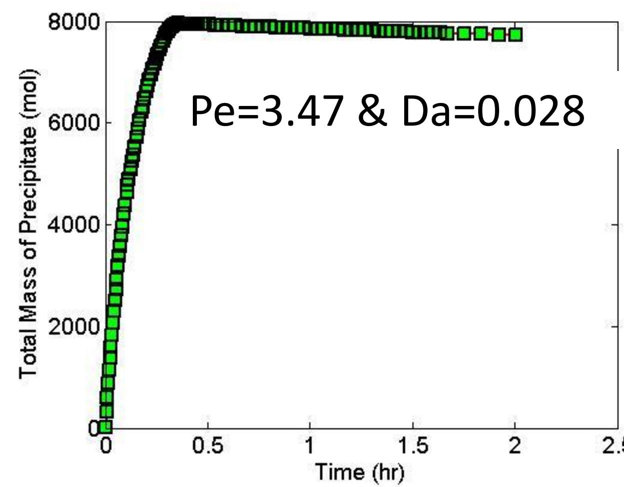
Far from equilibrium (log SI = ~2.7)

t=0.35 hrs



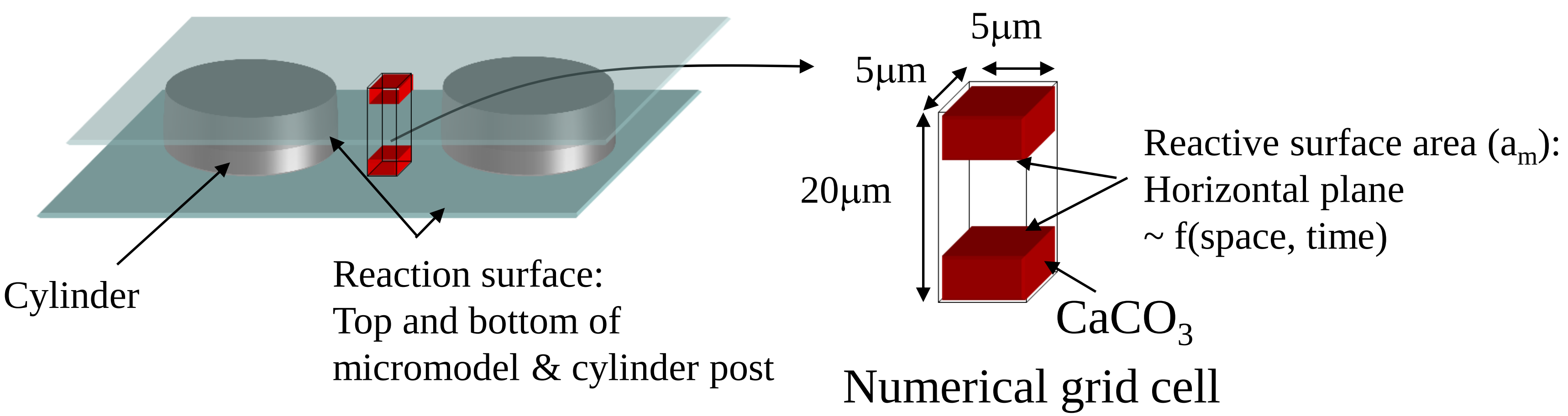
t=2 hrs





How can we model reactive transport in a micromodel system?

1. Quasi 3D grid cell for reactive surface

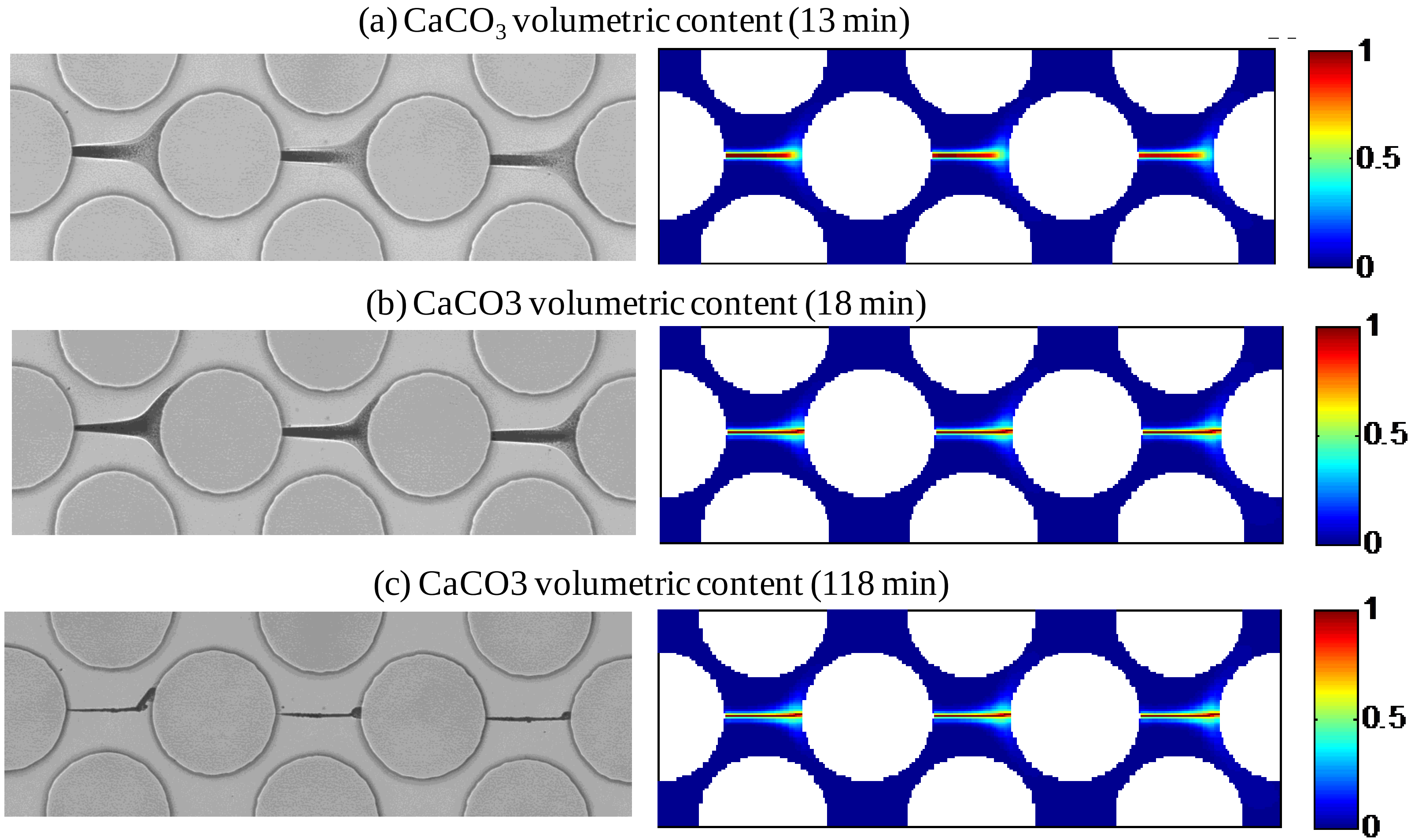


2. Effective diffusion coefficient = D_m * tortuosity (τ)

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

Yoon et al. (2012), WRR

Simulation results – hindered diffusion (n=2)



25 mM Experiment

Yoon et al. (2012), WRR

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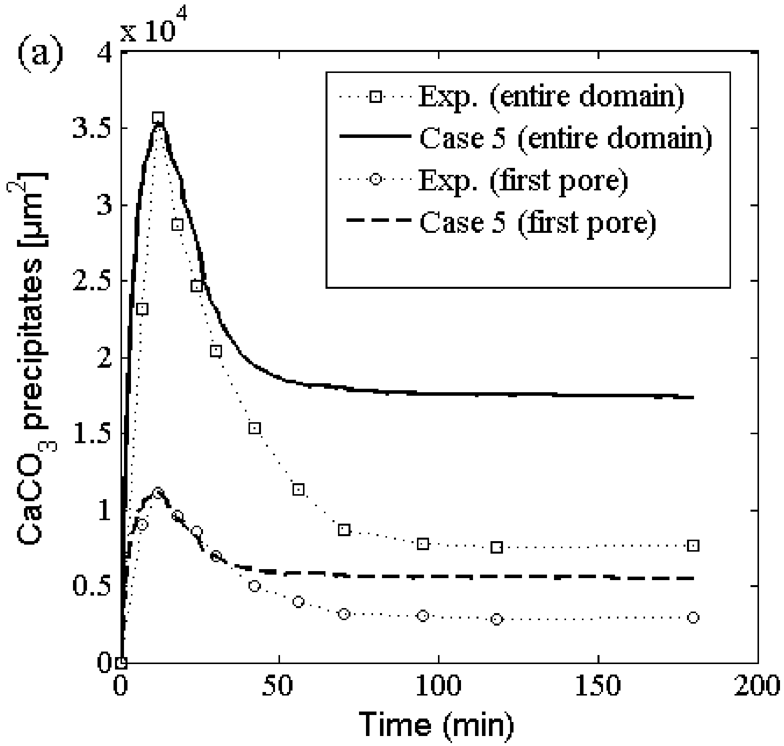
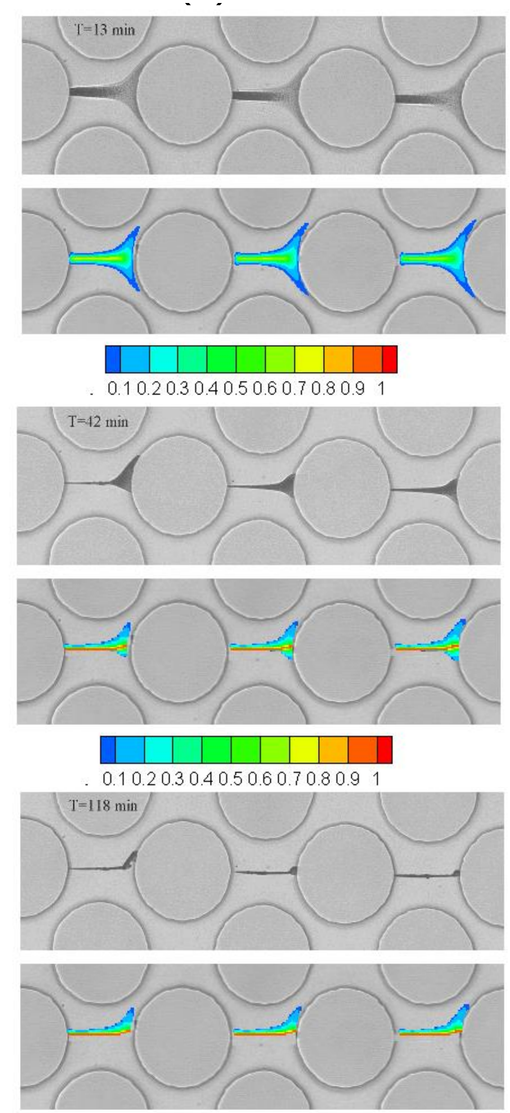
Simulation results – increase surface area during dissolution by 300





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

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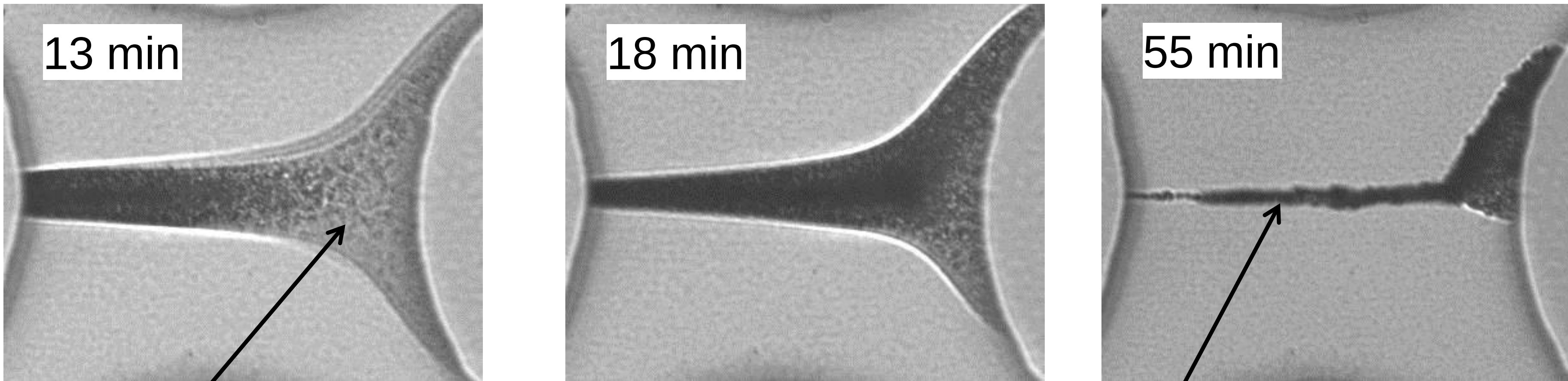
Matching simulation to late-time dissolution



Amorphous Calcium Carbonate & Vaterite

Predominantly Vaterite

- 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)

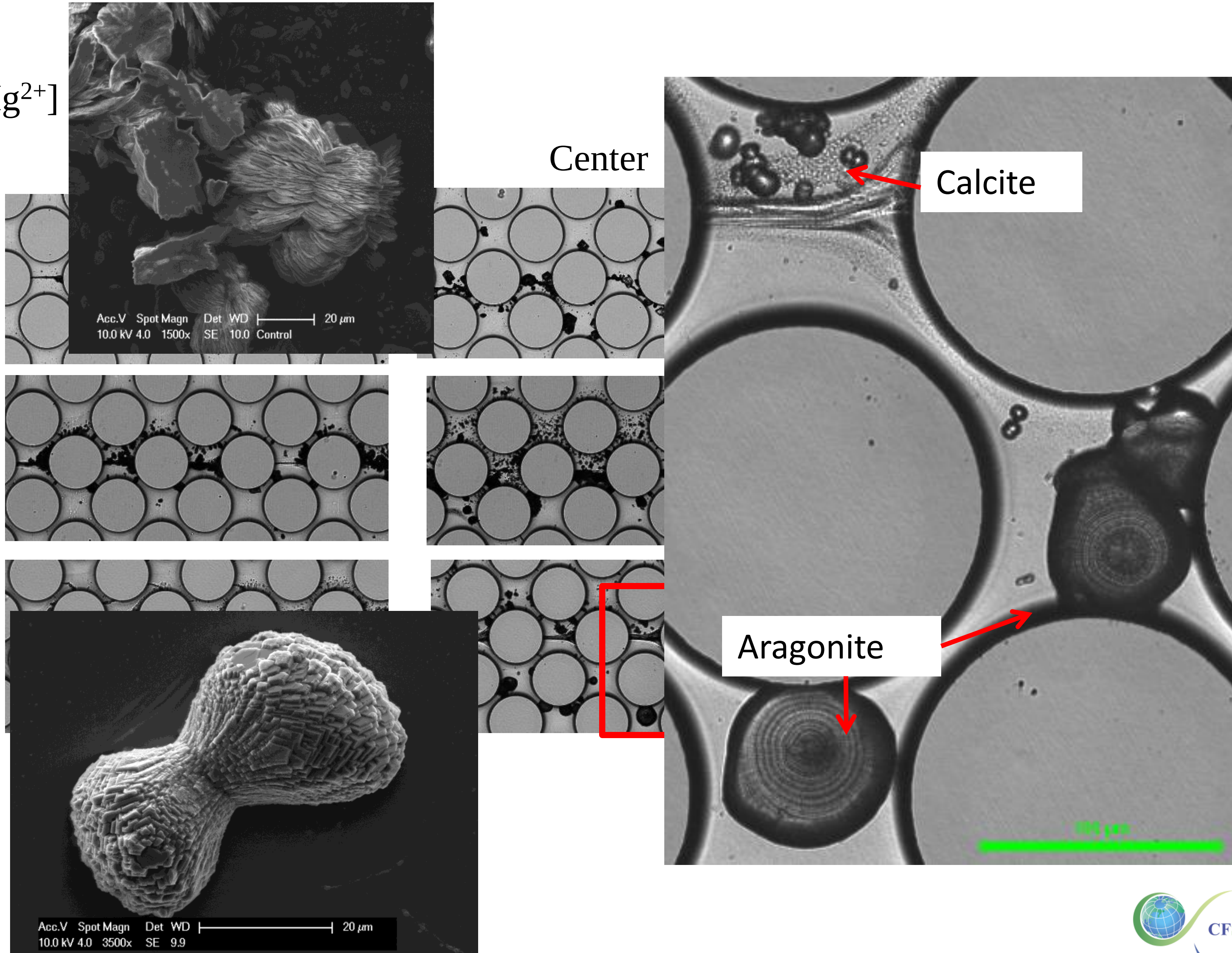
More chemistry, more complex?

Adding $[Mg^{2+}]$

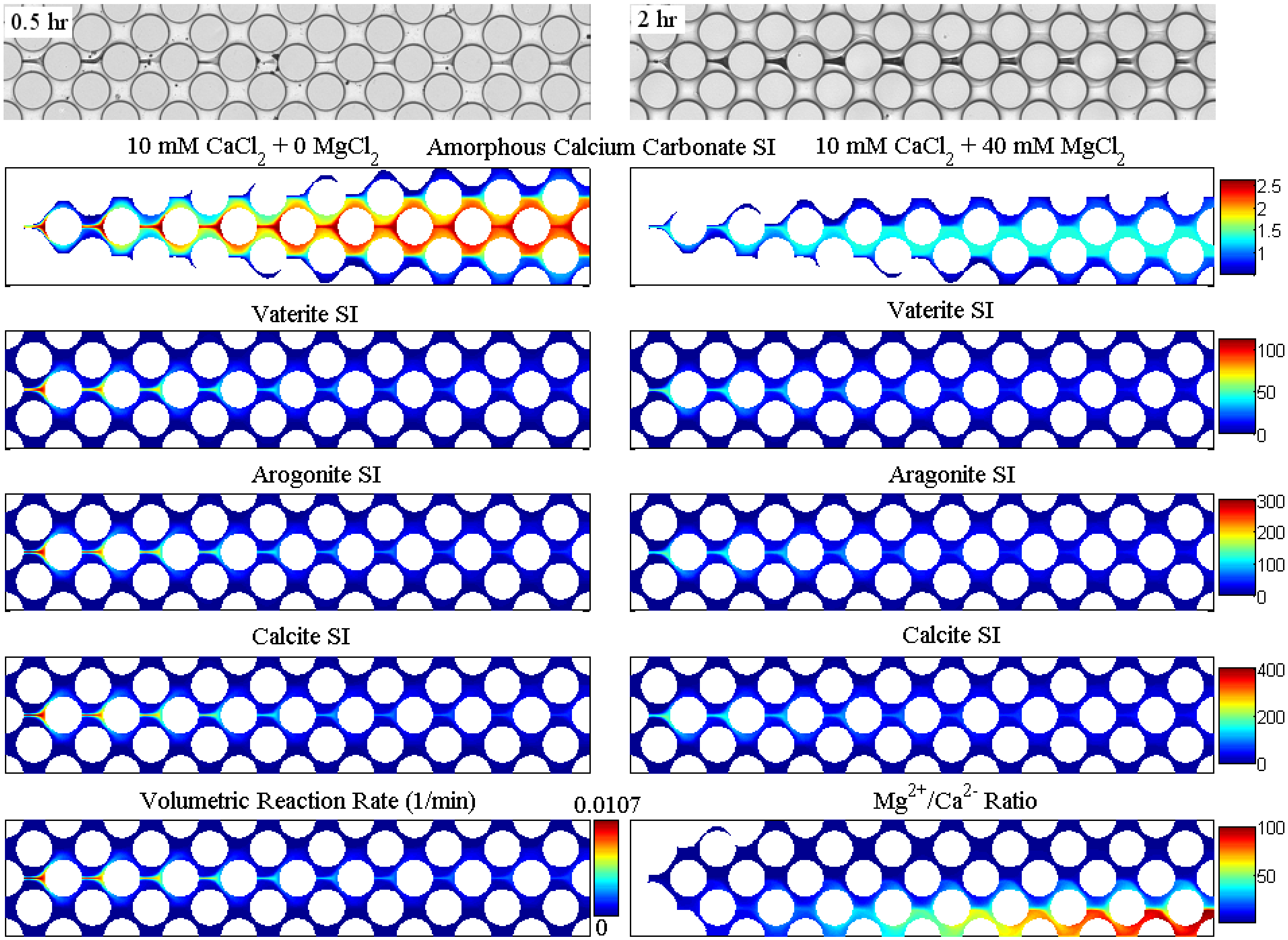
$[Mg^{2+}]$ =0mM

$[Mg^{2+}]$ =10mM

$[Mg^{2+}]$ =40mM



Impact of solution chemistry on calcium carbonate polymorphs



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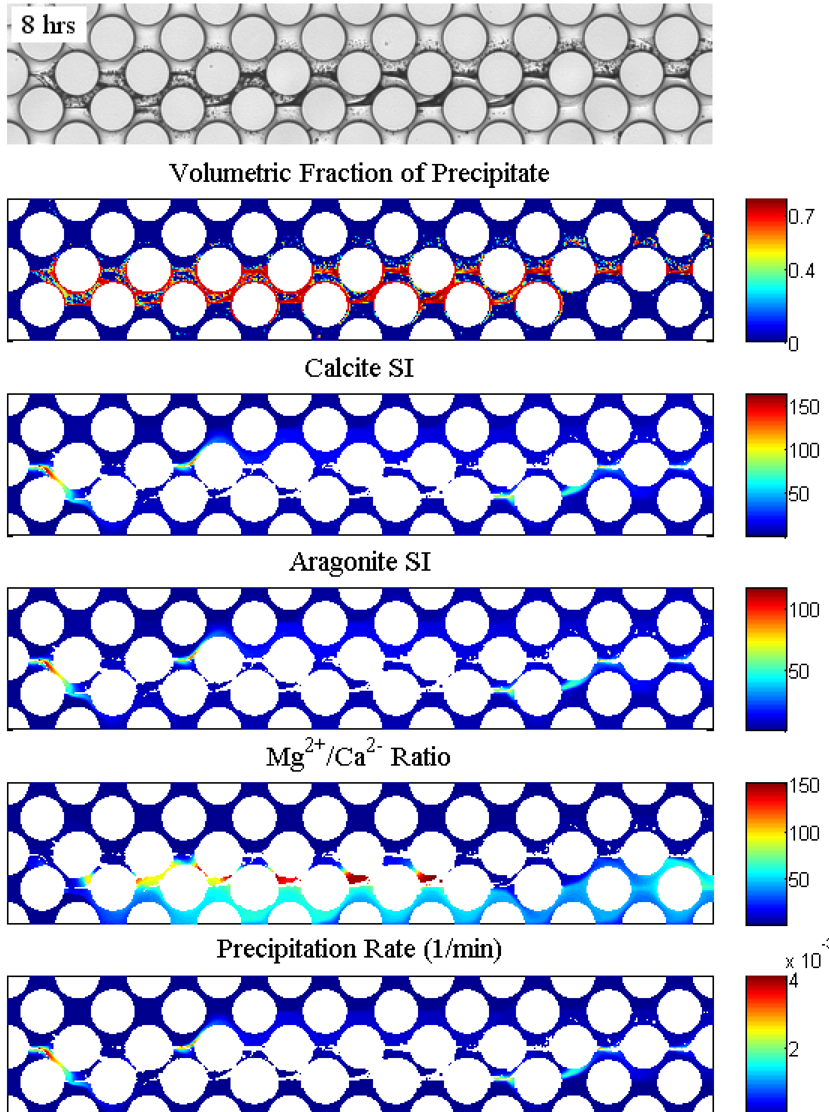
Impact of precipitation on flow pattern and reaction kinetics



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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

Questions?