SAND2022-3378C

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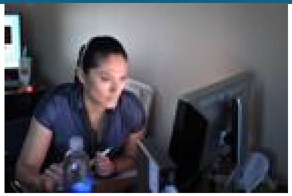
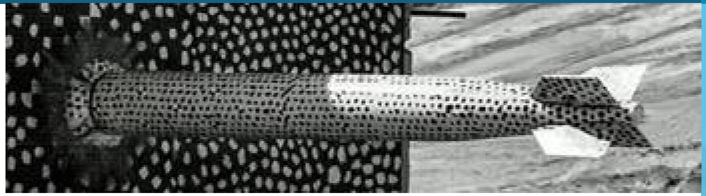
Microfluidics applications for reactive transport and flow behavior along mineral-fluid interfaces





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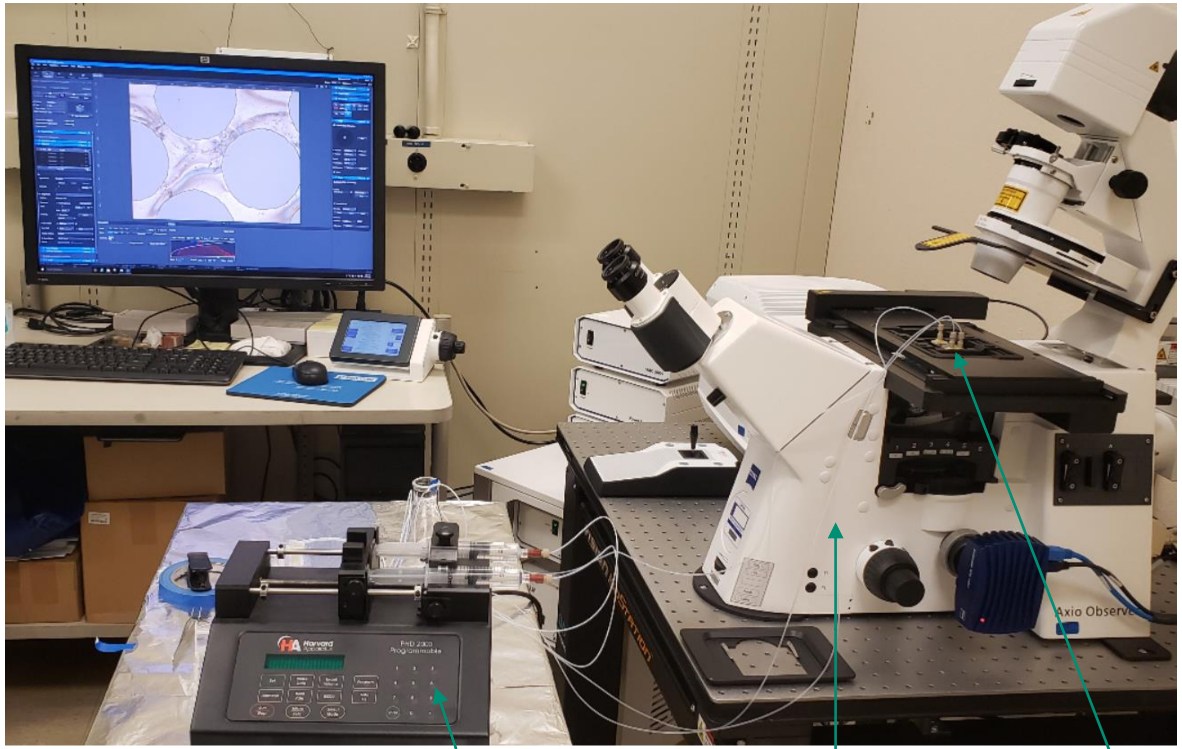
- **Motivations**
- **Reactive Transport in Microfluidic Porous Media - Methods**
- Precipitation and Dissolution Processes in Microfluidics
- Quantitative Analysis of Experimental Results
- Other Applications
- Summary

Motivations

- Fundamental understanding of pore scale reactive transport has been significantly improved over the past ~15+ years
- Various studies on hydrodynamics, reactive transport, and coupled processes (e.g., chemo-mechanical coupling) are motivated with many subsurface applications (geologic carbon storage, unconventional resources recovery, nuclear waste repository, geothermal energy, etc) and multiphysics in porous media (contaminant transport, fuel cells, flow& transport in varying saturated media, membrane filter systems, etc.)
- Both experimental and numerical capabilities have been improved with sensing and experimental apparatus and computational hardware & algorithms
- A few new emerging techniques can be utilized to improve these continuing efforts
- One overarching question is what fundamental knowledge needs to be improved and how micro- and macro-processes are meaningfully integrated depending on our scientific and practical interests

Optical & Laser Scanning Confocal Microscopy



Syringe pump Zeiss LSM900 Microfluidic device

- Inverted optical & confocal microscope with epifluorescence, transmitted, and reflected differential interference contrast (DIC) microscopy
- ZEISS Airyscan 2 detector
- Super resolution and fast scanning time with better SNR
- Multiscale resolutions (5x – 50x) from ~2.5μm to 0.1 μm resolution horizontally and up to 0.35 μm resolution over depth

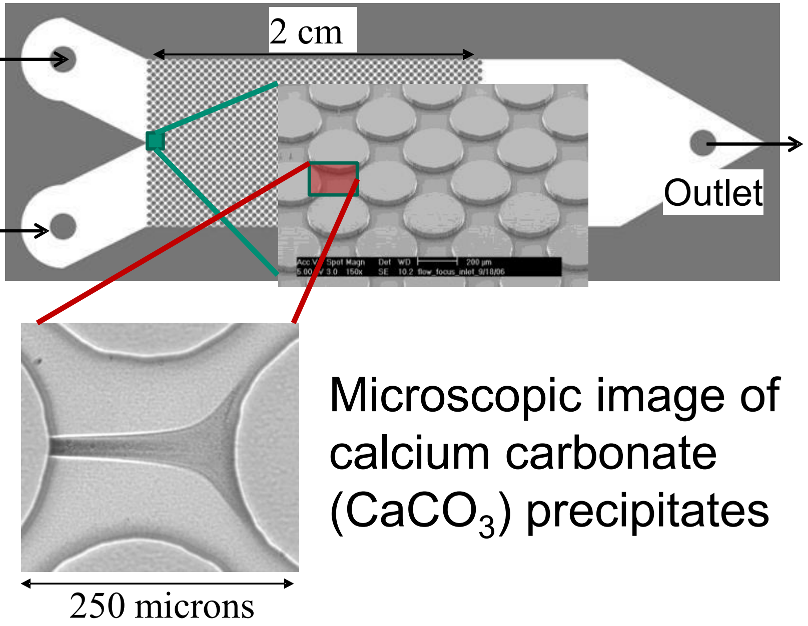
Zhang et al. (EST, 2010), Yoon et al. (WRR, 2012), Fanizza et al. (WRR, 2013), Boyd et al. (GCA, 2014), Singh et al. (EST, 2015), Yoon et al. (RiMG, 2016, EST 2019)

Experimental setup

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

Syringe pump/
ISCO pump

Experimental setup

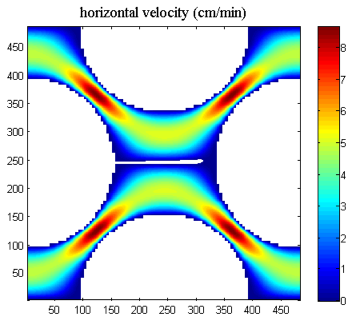


Microscopic image of calcium carbonate ($CaCO_3$) precipitates

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

Zhang et al. (ES&T, 2010)
Yoon et al. (ES&T, 2019)

Pore scale modeling with precipitation and dissolution



Navier-Stokes equation => Stokes equation with constant viscosity (independent of the species conc.) and at low Reynolds Re= ρ|**u**|*l* / μ«1

$$\nabla p = \mu \nabla^2 \mathbf{u} + \mathbf{F}.$$

Step 1: Velocity field (*u*) at pore scale (Lattice Boltzmann Method)

↓

Step 2: Reactive transport at pore scale (Finite Volume Method)

$$\frac{\partial \Psi_j}{\partial t} + (\mathbf{u} \cdot \nabla)\, \Psi_j - \nabla \cdot (D_j \nabla \Psi_j) = -\sum_{k=1}^{N_m} \upsilon_{jk} R_k + R_{\mathrm{bio}}$$

Yoon et al. (RiMG, 2015)

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

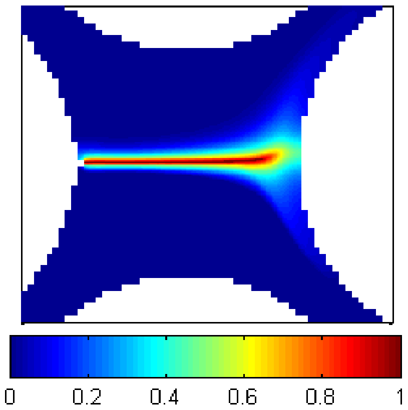
Charge balance equation is not considered.

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

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

Step 3: Update of $CaCO_3$ volumetric content (V_m)

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



Crystal growth: Cellular automata algorithm

Volumetric $CaCO_3$ content

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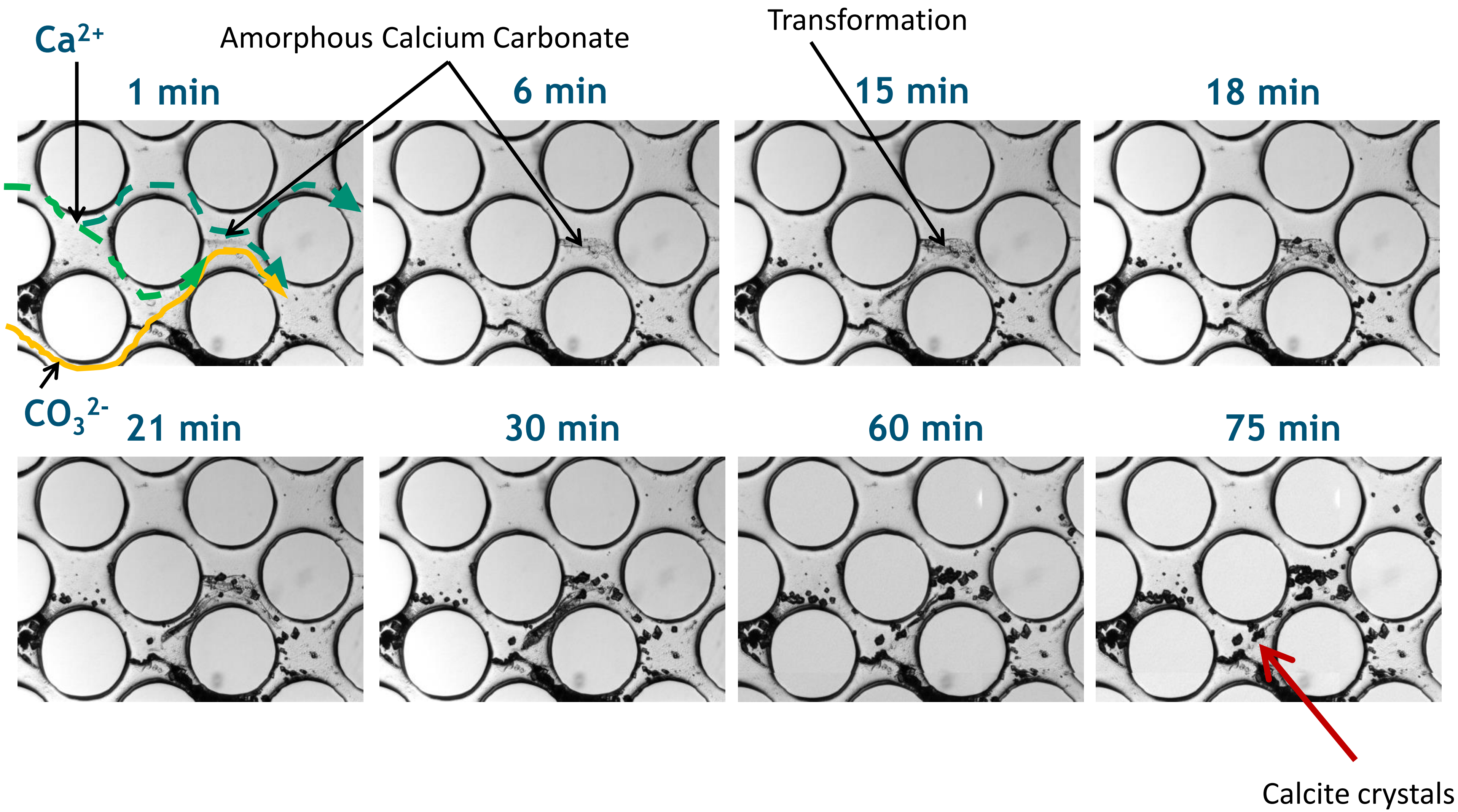
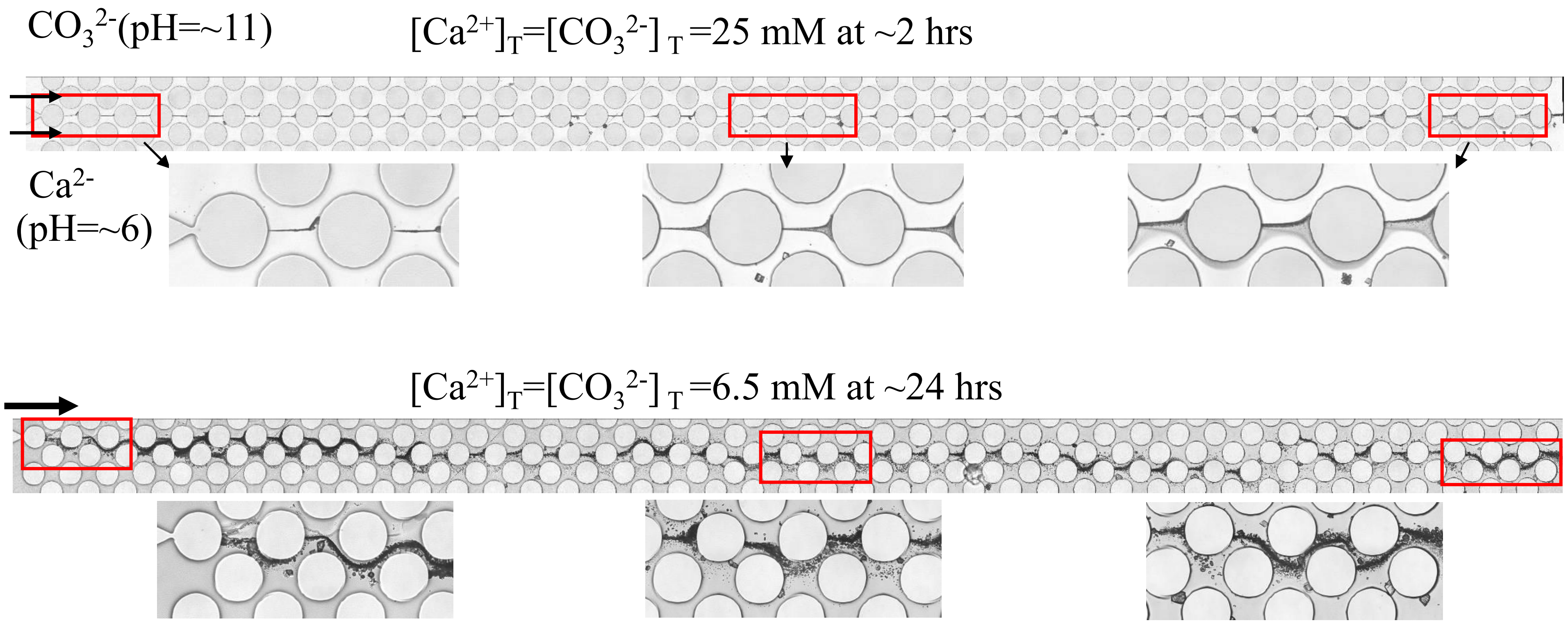
Reaction over time in a Microfluidic porous medium



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

Zhang et al., ES&T (2010)

Transversely mixing induced reaction in a microfluidic

- How is the reactive transport different from a batch system?
- Experimental observations:
  - ✓ $CaCO_3$ reaction products were only observed at a minimum concentration of ~6.5mM (a total concentration of Ca^{2+} and CO_3^{2-})
  - ✓ Nanoparticles were optically observed, indicating amorphous calcium carbonate (ACC) formation
  - ✓ Maintaining central precipitation lines was very difficult
- Simple calculation for saturation ratio (SR): $[Ca^{2+}]_{Total}=[CO_3^{2-}]_{Total}=6.5$ mM

Reaction gradient

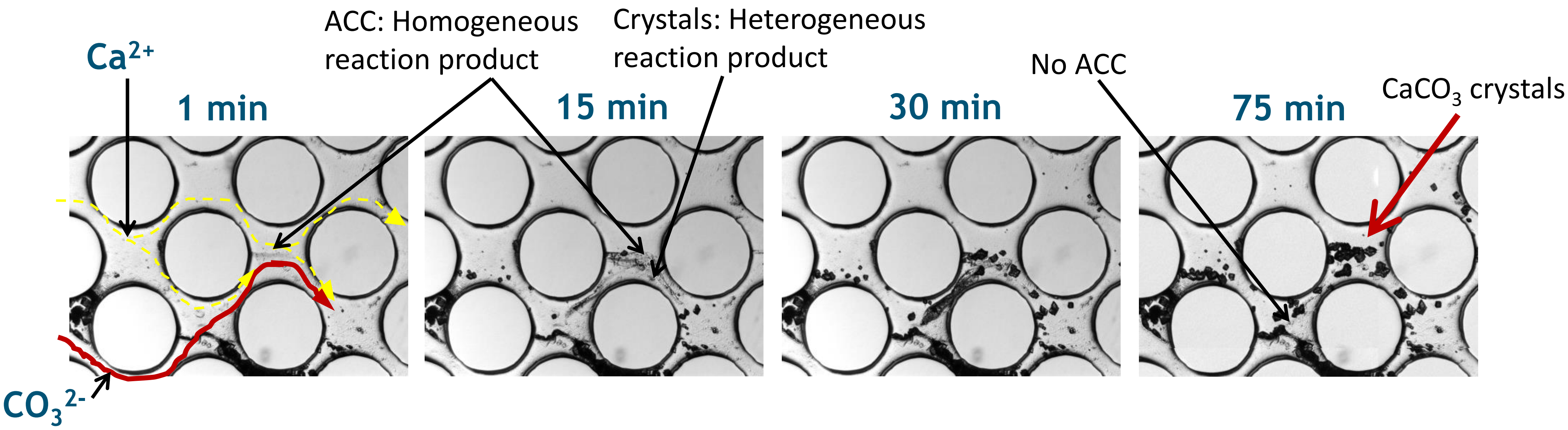
$$= \left(\frac{IAP}{K_{sp}} - 1\right)$$

$SR = IAP/\ K_{sp}$

$IAP = a_{Ca^{2+}} a_{CO_3^-}$

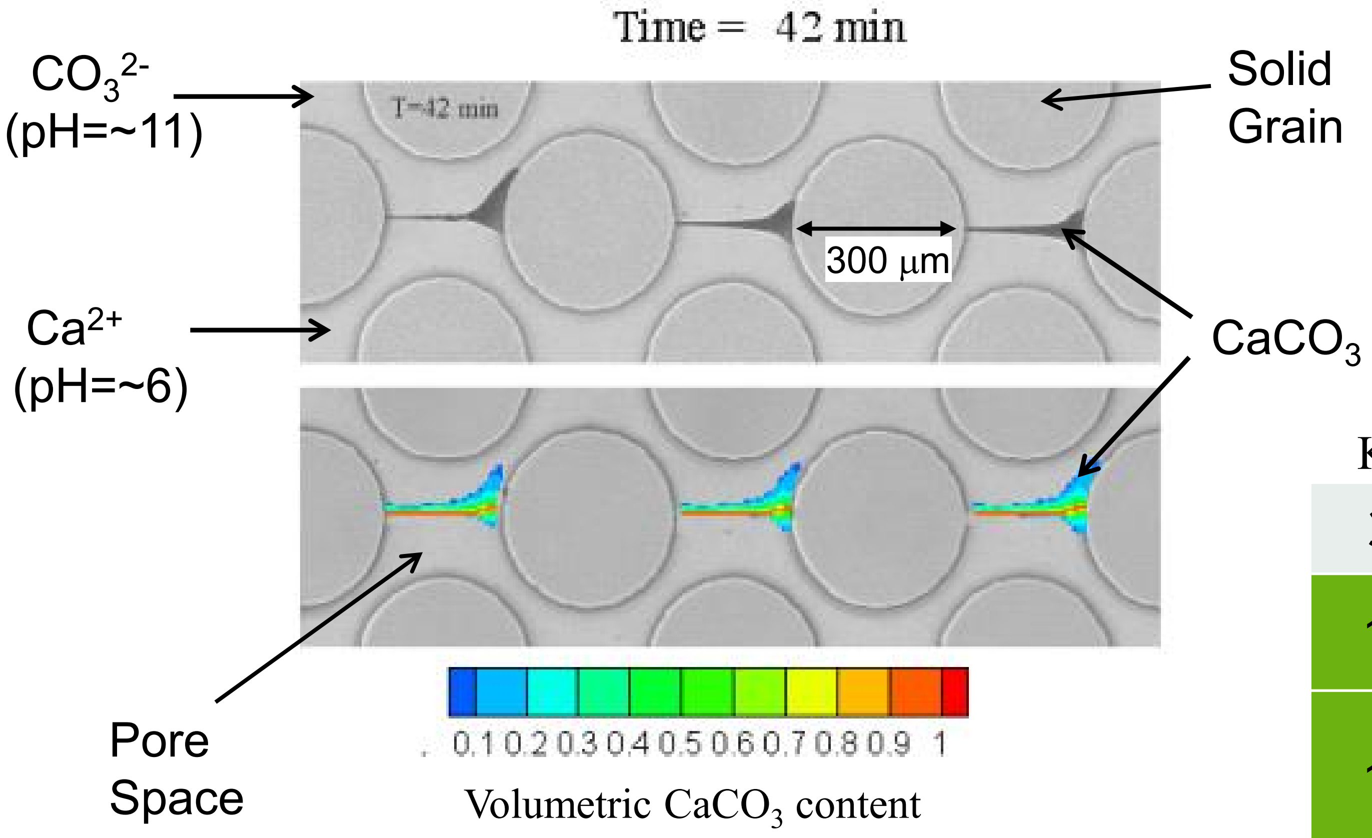
IAP (ion activity product)		Saturation Ratio K_{sp} (Calcite)	Saturation Ratio K_{sp} (ACC)	
mixing effect	activity	3.31E-09	5.58E-07	
1.06E-05	4.21E-06	1.27E+03	7.55E+00	$a_{CO_3^-}$ at pH of inlet solution (pH=11)
	3.83E-07	1.16E+02	6.86E-01	$a_{CO_3^-}$ at the mixing line (pH=9)

Transversely mixing induced reaction in a microfluidic

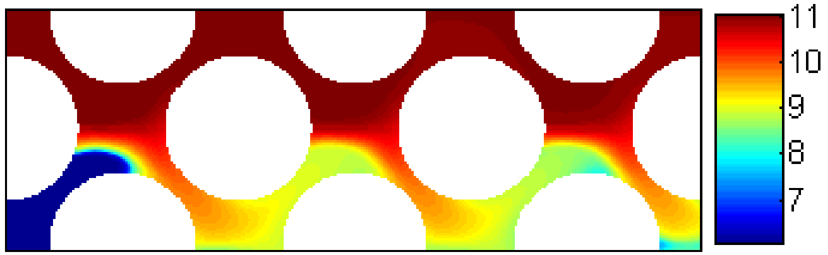


- Experimental observations:
  - ✓ Nanoparticles were optically observed, indicating amorphous calcium carbonate (ACC) formation. ➔ Initial ACC created $CaCO_3$ particles on microfluidic surfaces, creating favorable heterogeneous surface for $CaCO_3$ precipitation. Less structured particles become stable by transforming into more stable polymorphs

Simulated pH Distribution



Simulated pH distribution (42min)

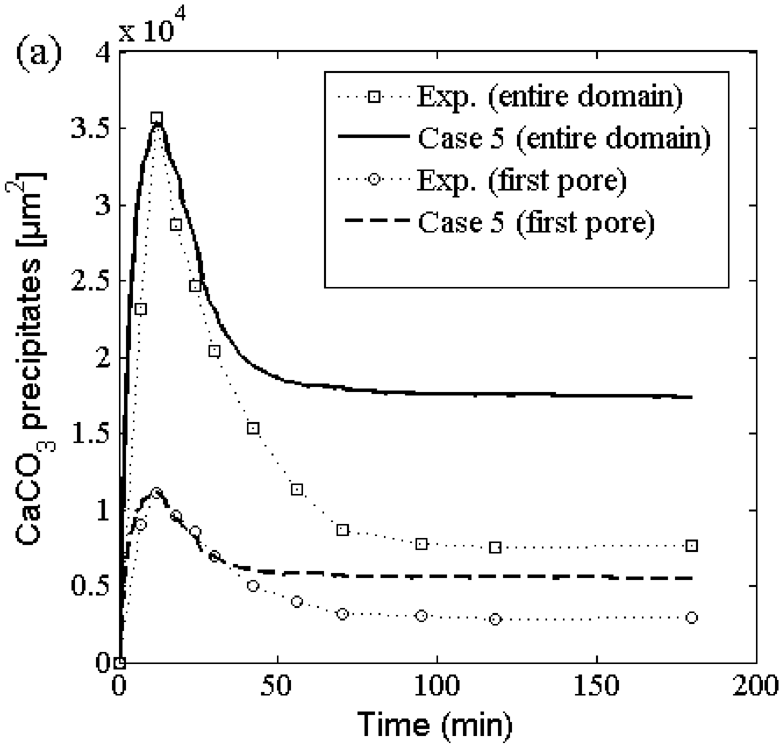


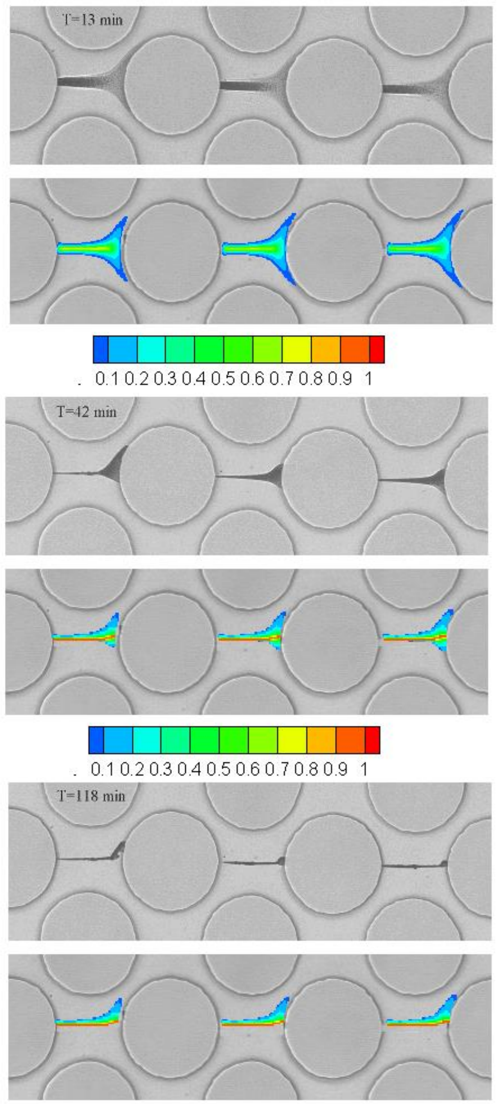
K_{sp} (Calcite)	K_{sp} (ACC)	
3.31E-09	5.58E-07	
1.27E+03	7.55E+00	$a_{CO_3^-}$ at pH of inlet solution (pH=11)
1.16E+02	6.86E-01	$a_{CO_3^-}$ at the mixing line (pH=9)

- Experimental observations:
  - ✓ $CaCO_3$ reaction products were only observed at a minimum concentration of ~6.5mM: IAP of Ca^{2+} and CO_3^{2-} needs to exceed K_{sp} of calcium carbonate (ACC) on non-favorable reaction surface (SiO_2) of the microfluidics

Yoon et al. (WRR, 2012)

Simulation results – Increasing reaction rate during dissolution by 300 (Case 5)





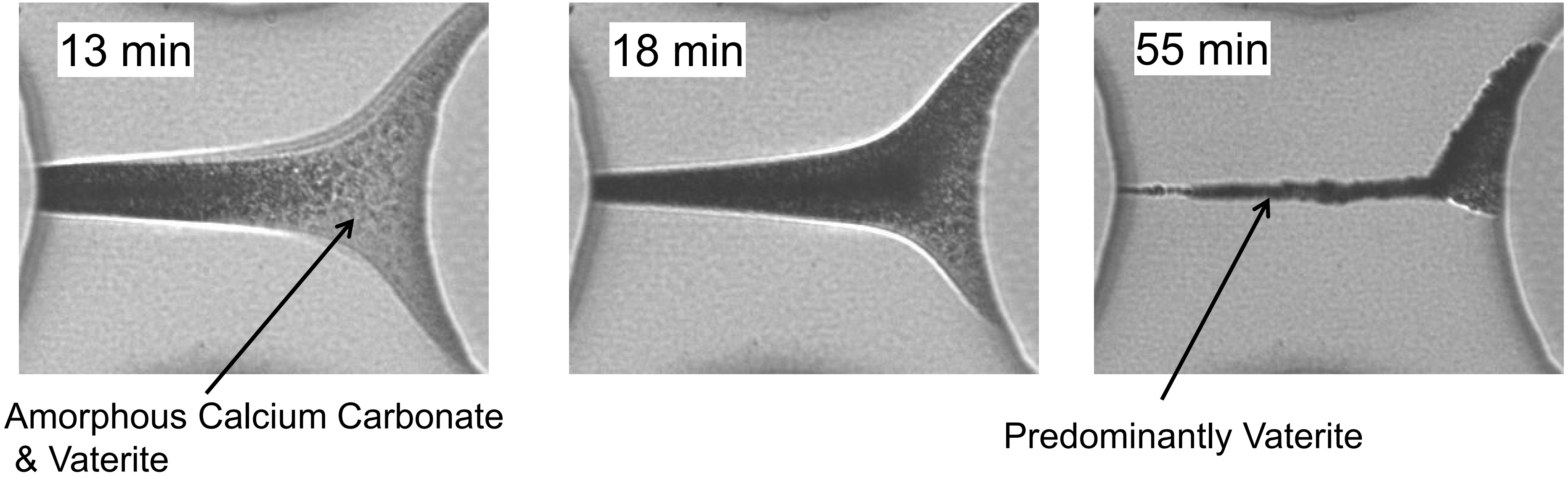
13 min

42 min

118 min

- Model results match thickness and area of precipitate until 30 min with a high dissolution rate (x300)
- Model predicts dissolution below the centerline well, but not above the centerline

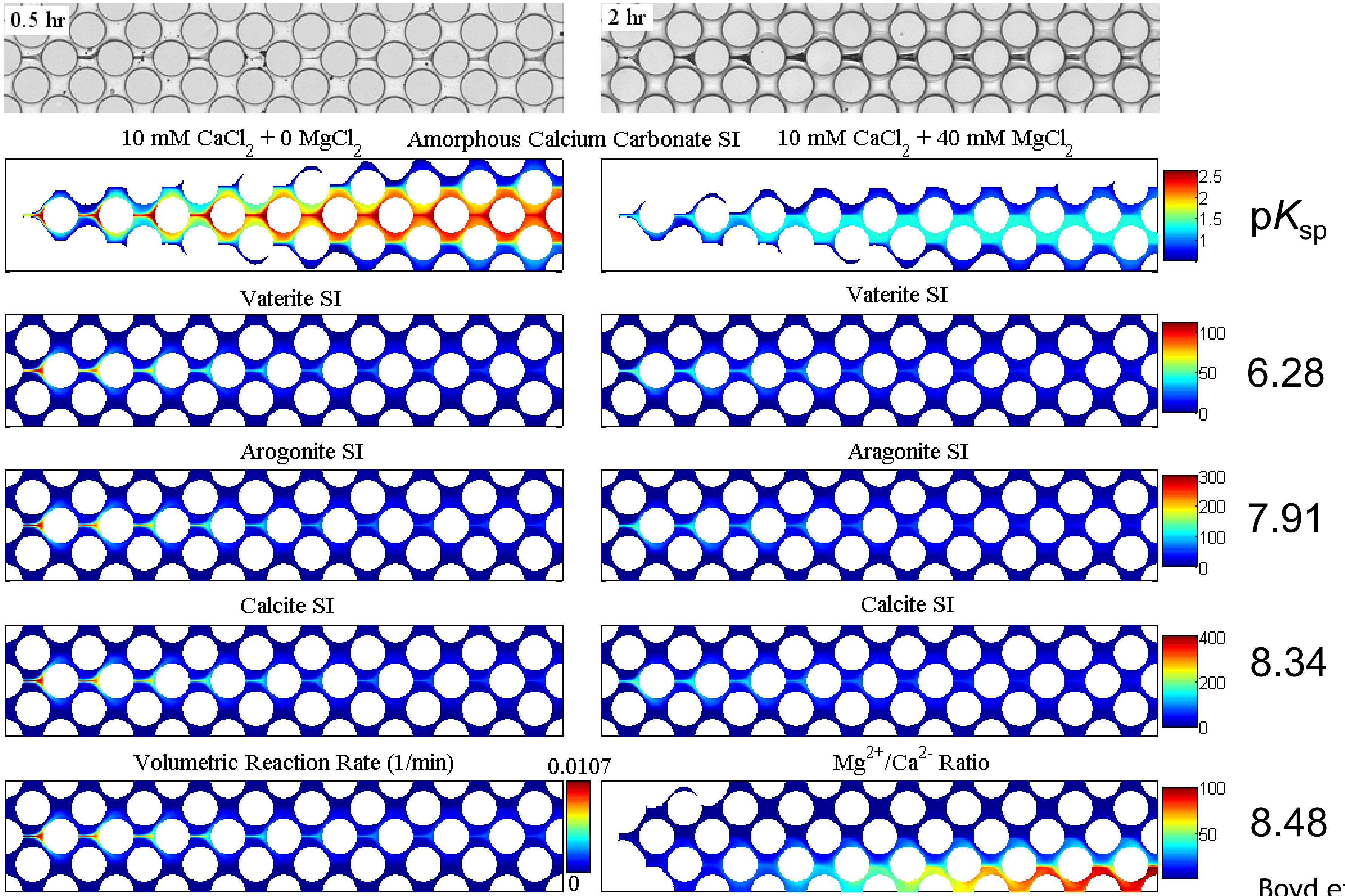
Instability of $CaCO_3$ precipitates



- The less stable precipitates became detached/dissolved, requiring high dissolution rate during dissolution phase (i.e., pore blocking phase)

- Experimental observations:
  - ✓Maintaining central precipitation lines was very difficult ➔ sometimes precipitates in one pore body lost the integrity of precipitates' block, resulting in rapid dissolution and diverting flow and transport pathways (wider precipitation)

Impact of solution chemistry (Ca only vs. Ca+Mg)



Boyd et al. (GCA, 2013)

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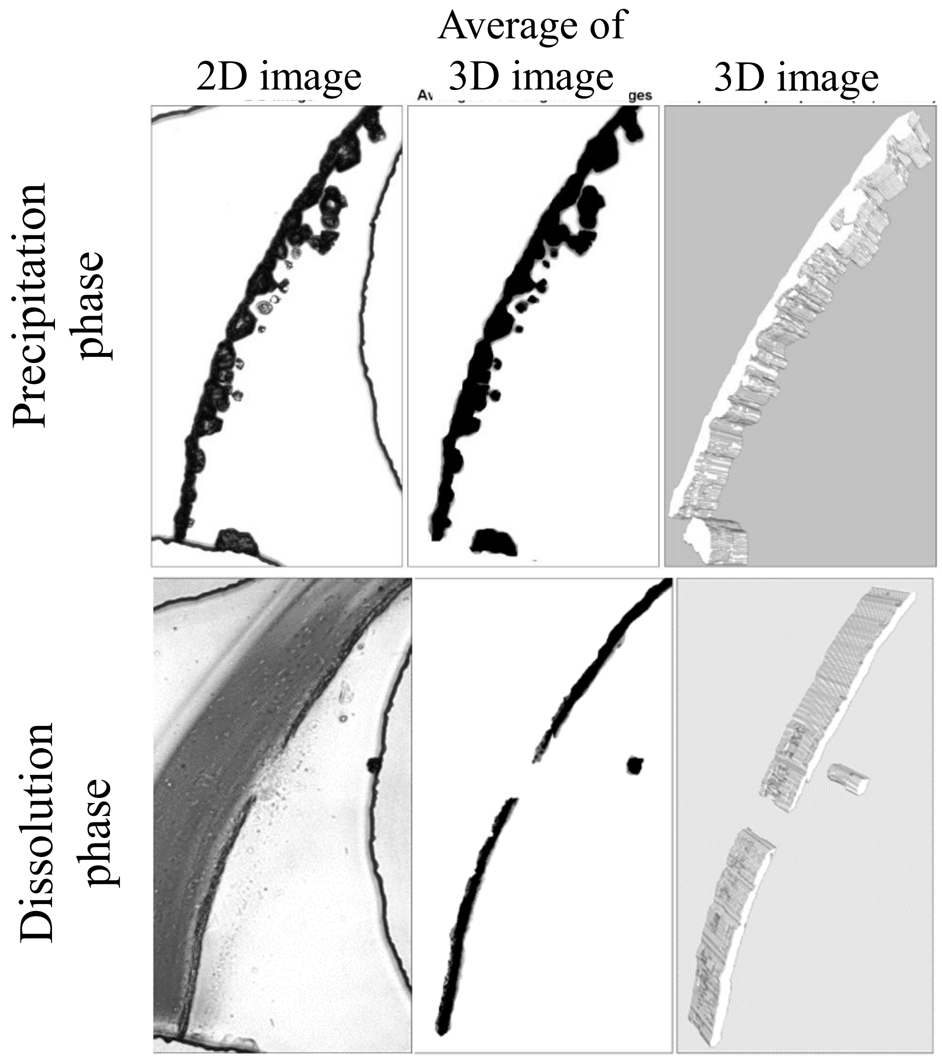
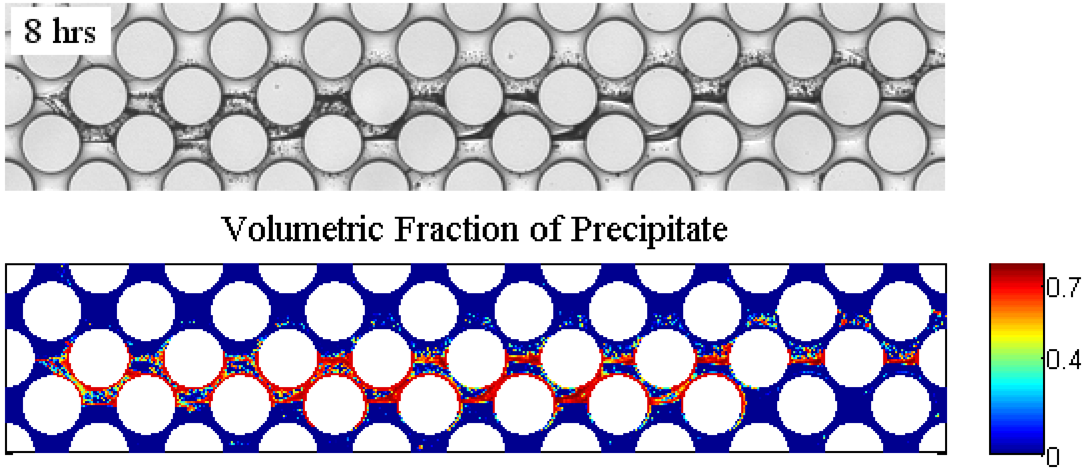
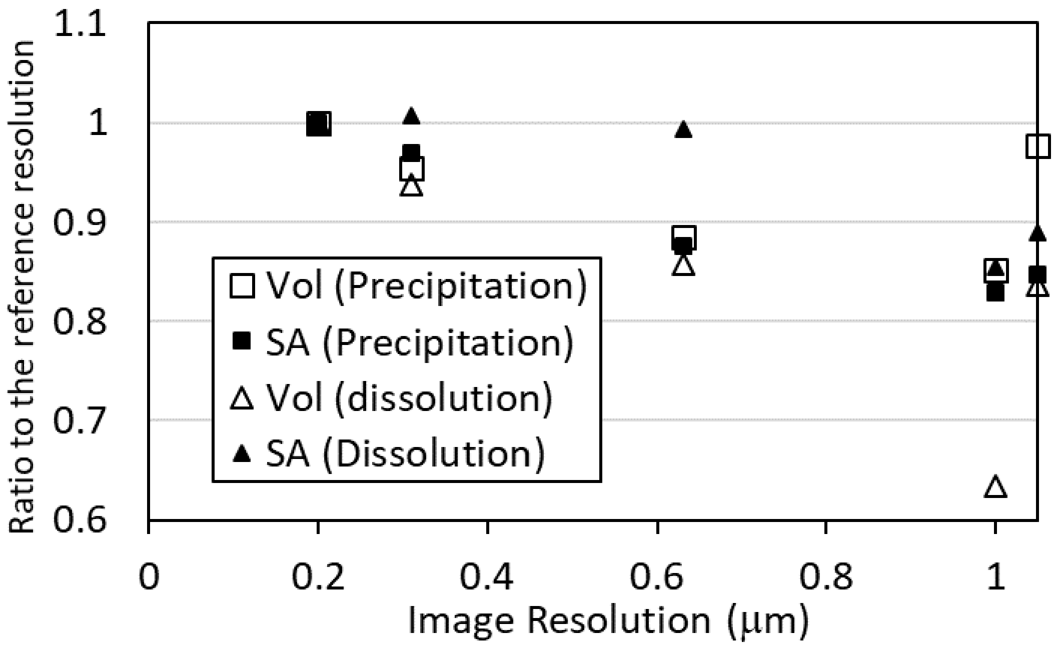
Image process for quantitative analysis

- Image segmentation for identifying pixels of precipitates, reactive surface area, and reaction rates

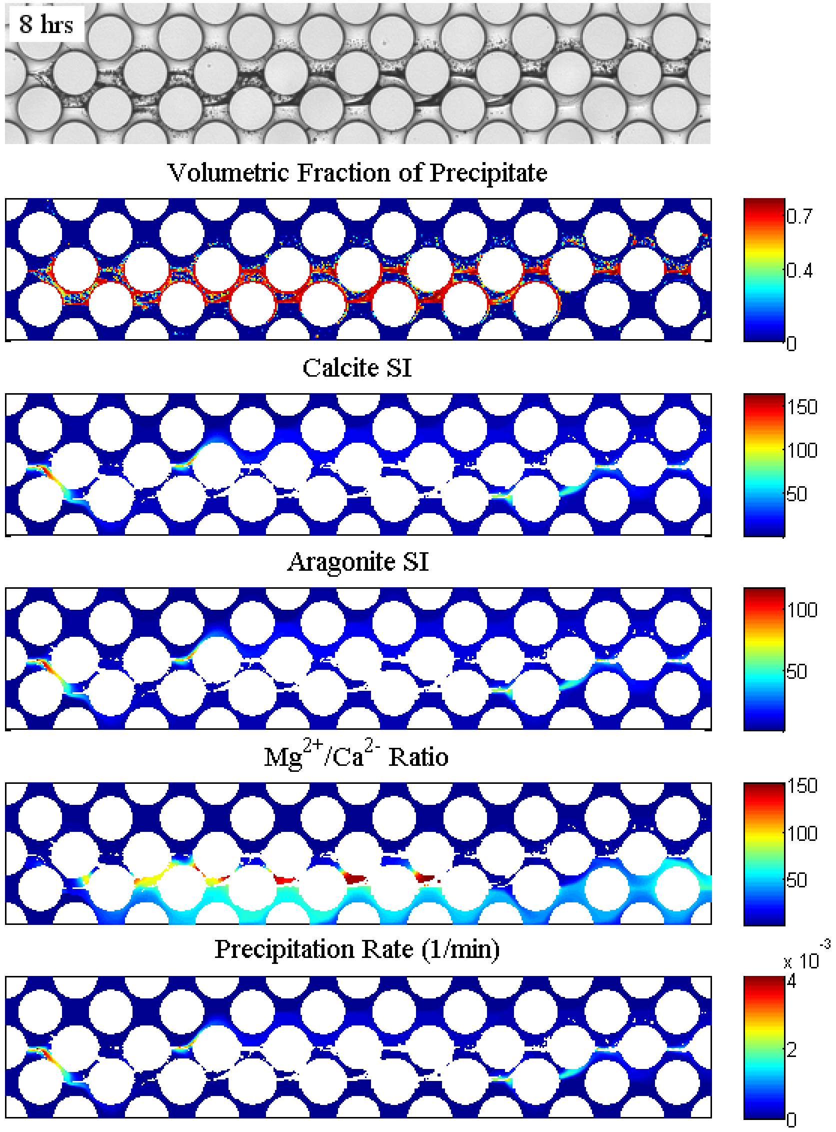






Yoon et al. (ES&T, 2019)

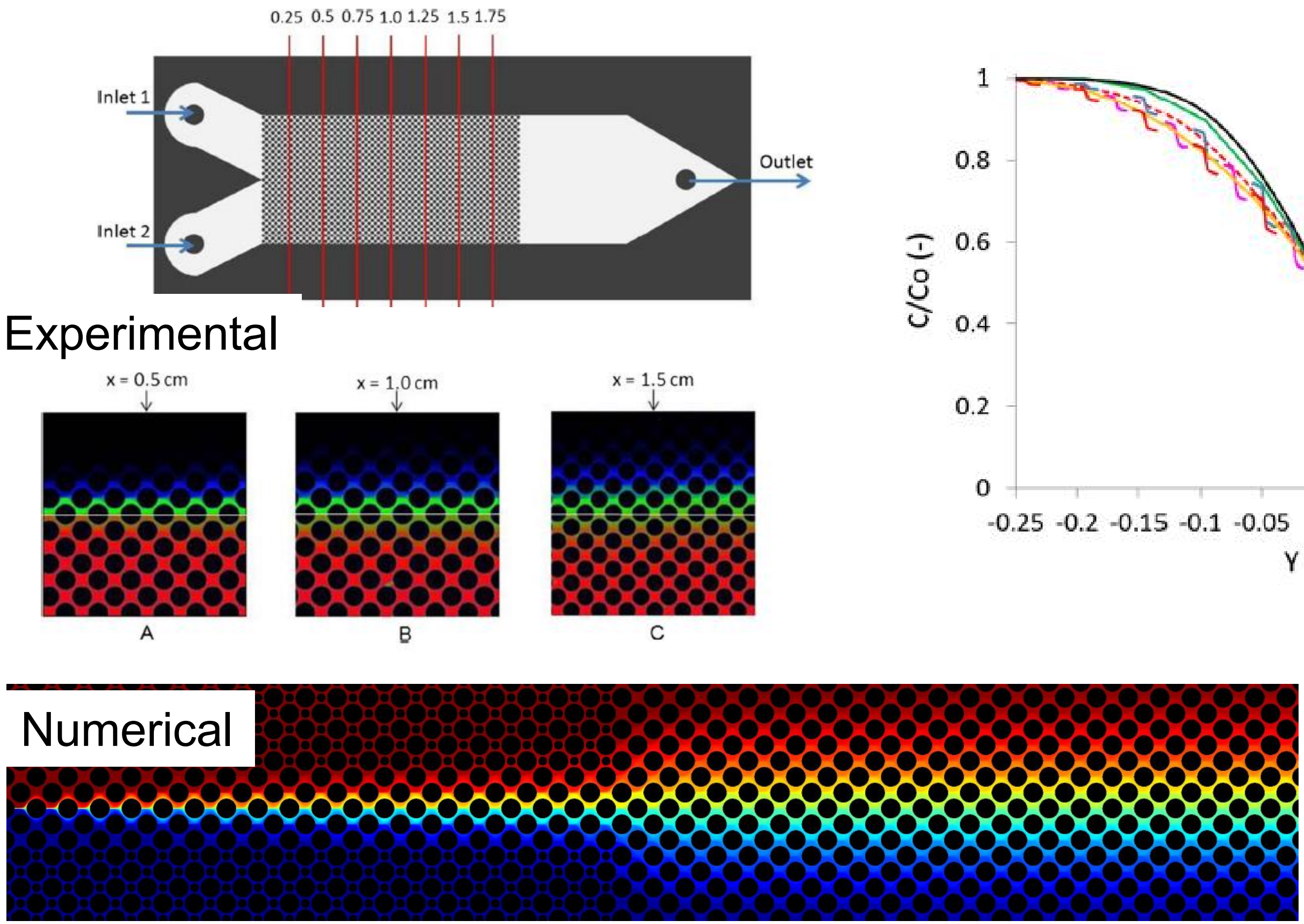
Impact of precipitation on flow patterns and reaction kinetics

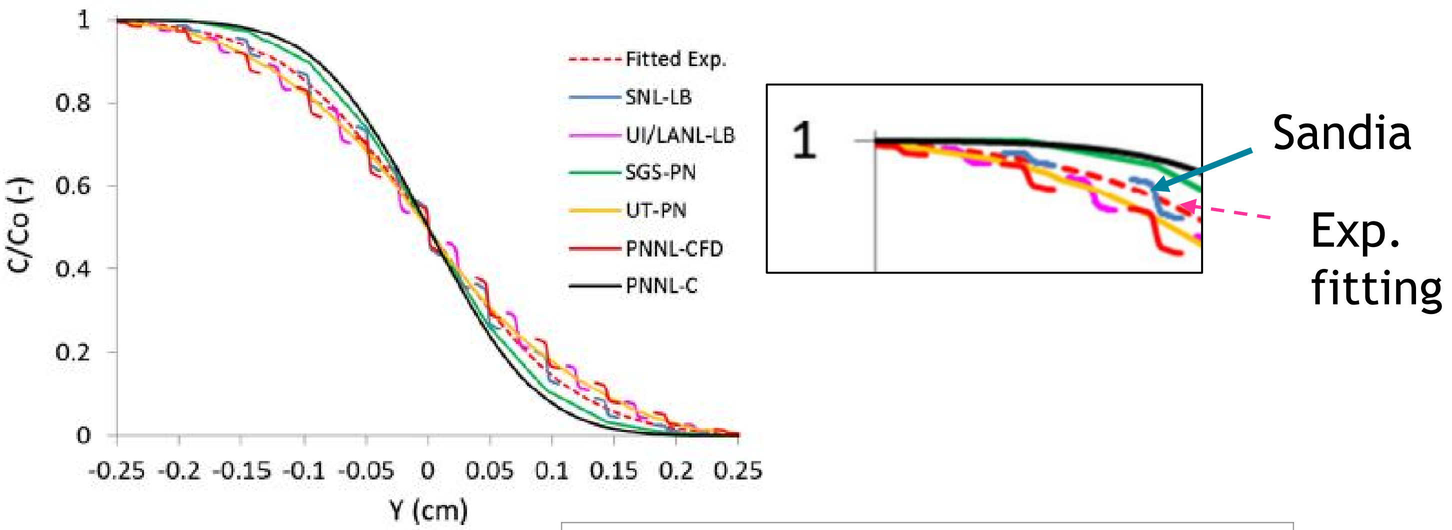


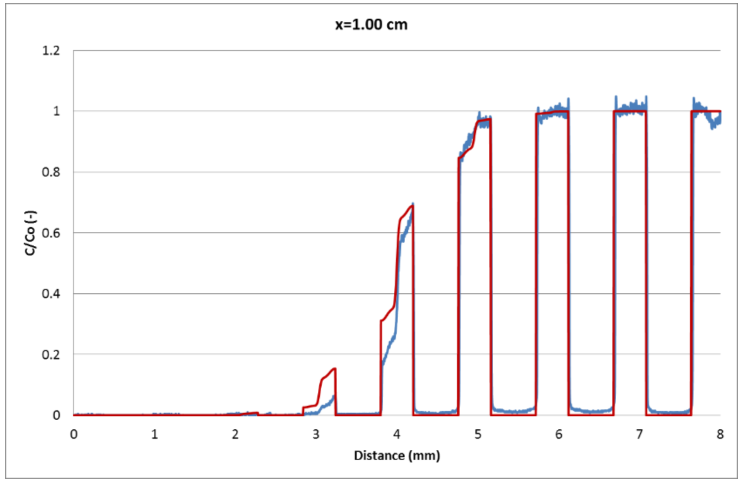
- Effective reactive surface area is lower than geometrical surface area

Boyd et al. (GCA, 2013)

Validation of pore scale modeling with tracer experiments







Four sets of nonreactive solute transport experiments in microfluidics

Quantitative comparison of experimental and numerical simulations

Oostrom et al. (Comput Geosci, 2016)

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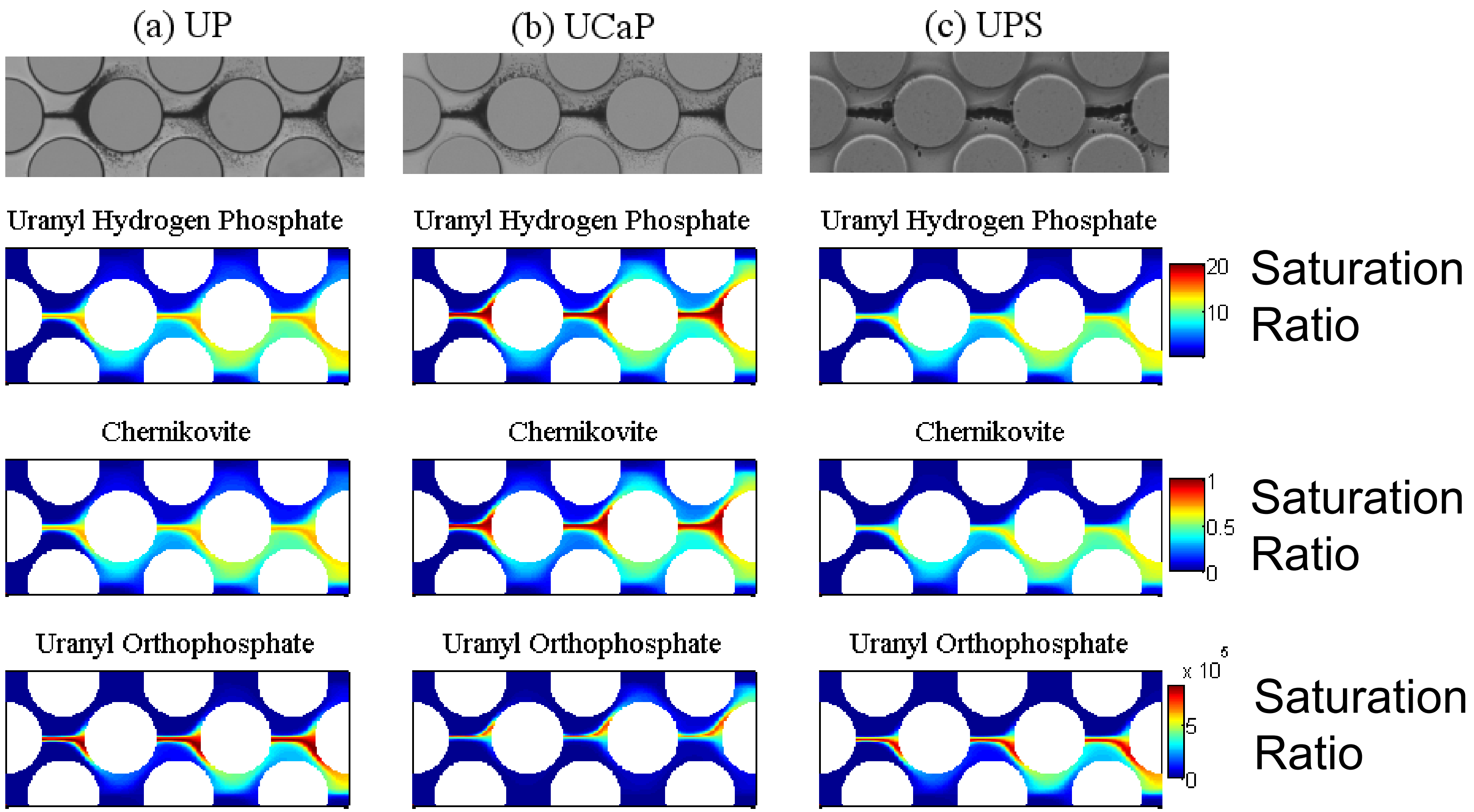
Impact of reaction kinetics (Uranyl phosphate ppt)

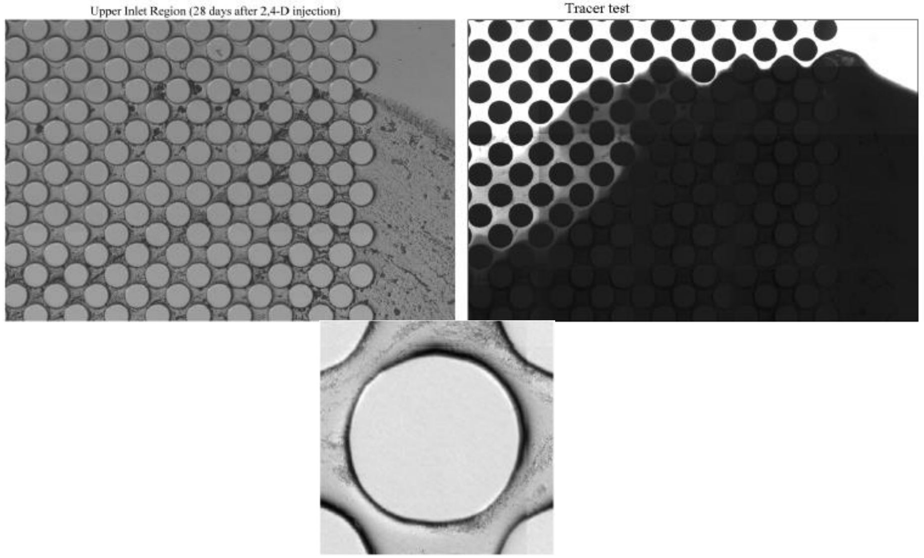


- Experimentally Chernikovite was observed first although other solid phases have much higher saturation ratio values
- Due to reaction kinetic effect, Uranyl hydrogen phosphate (i.e., chernikovite) is precipitated first

Fanizza, Yoon et al. (WRR, 2012)

Reactive Transport: Biochemical reactions

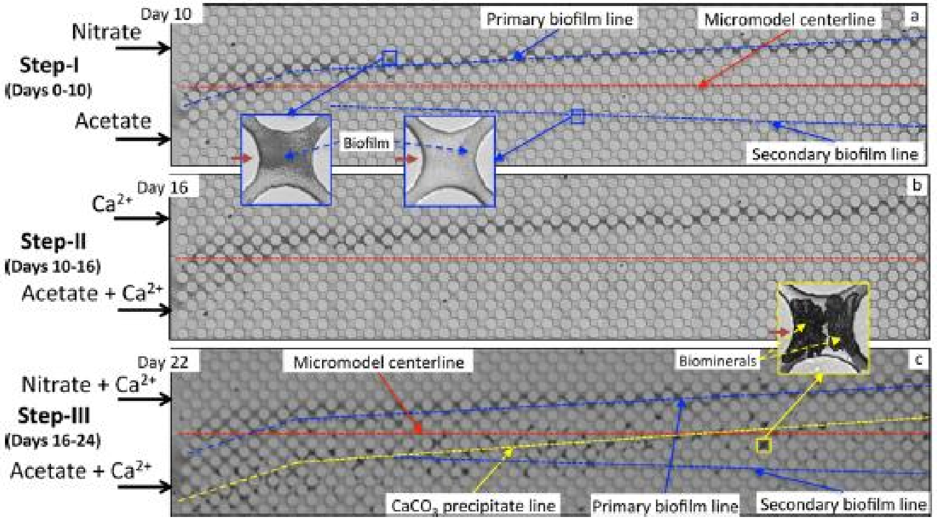
Adaptation of *Delftia acidovorans* for degradation of 2,4-dichlorophenoxy-acetate

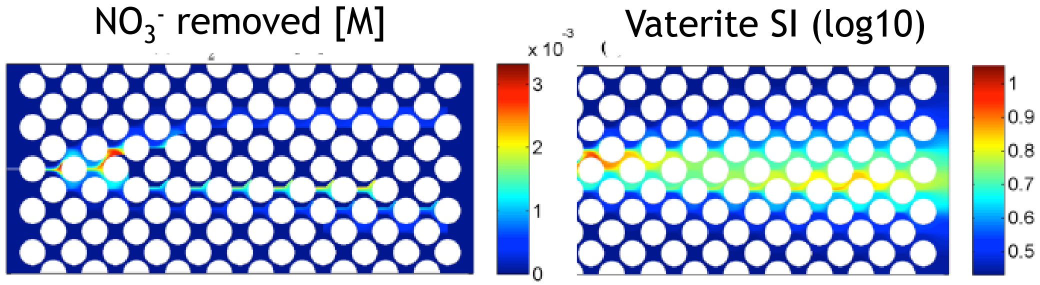


Bacteria adaptation experiments in flowing conditions (~ 1 year period)

Yoon et al. (Biodeg., 2014)

CaCO3 biomineralization with denitrification (*Pseudomonas stutzeri*)

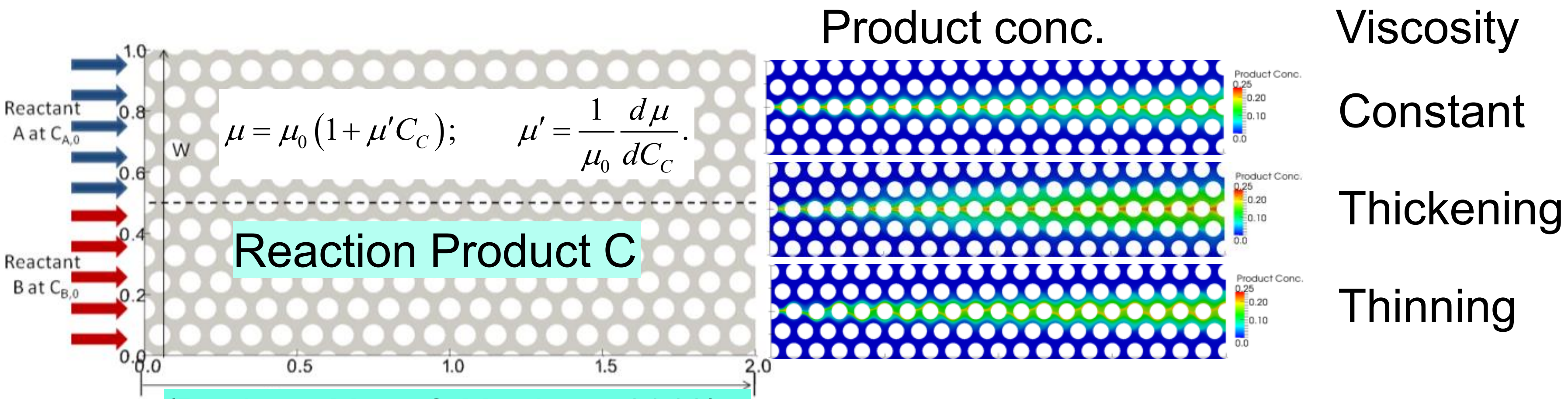




Singh, Yoon et al. (ES&T, 2015)

Pore-scale modeling for engineered systems

- Mixing-induced chemical reactions can alter fluid properties (e.g., viscosity and density), altering mixing efficiency and/or shear rate for engineered solutions



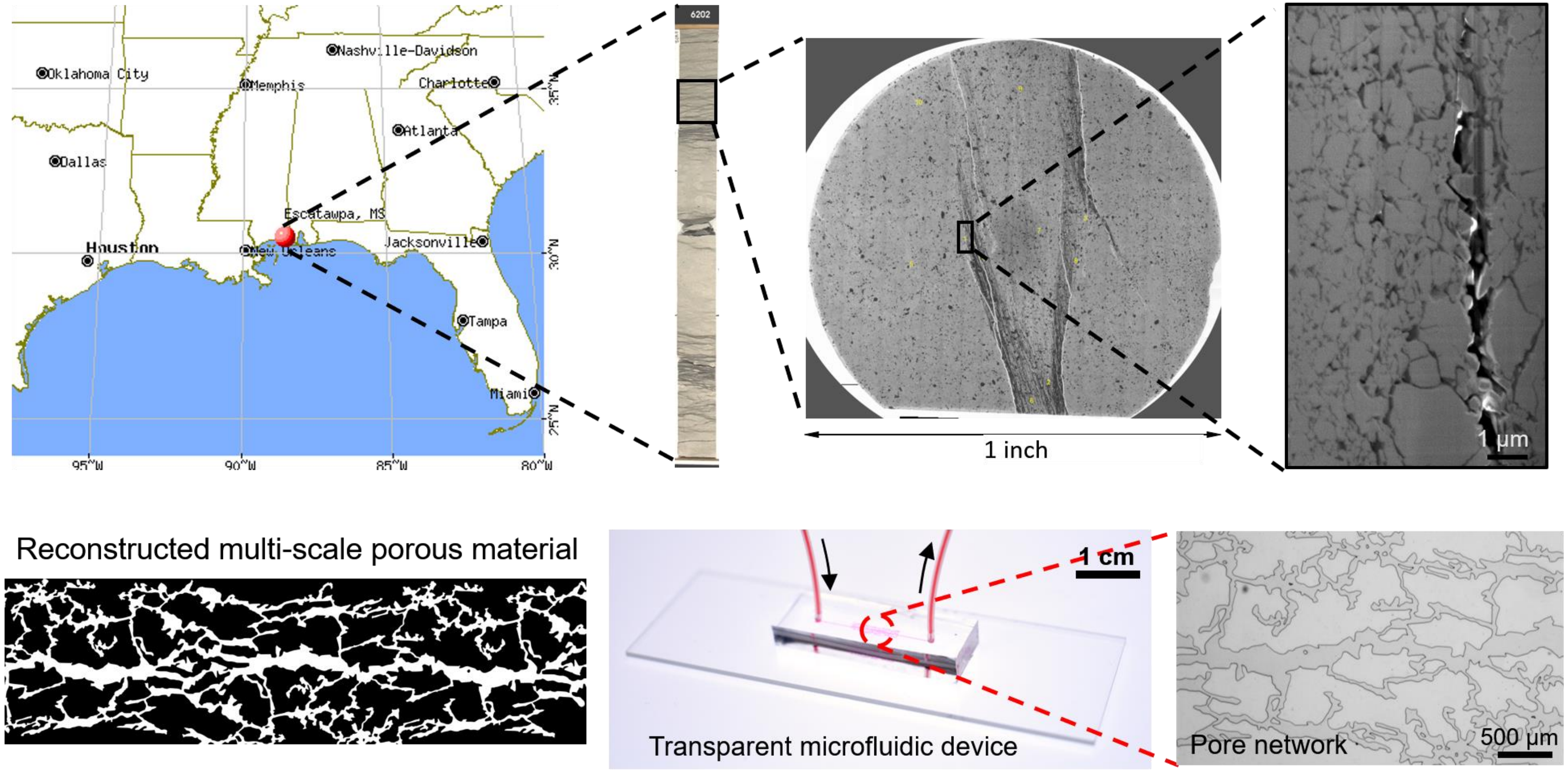
(Davison, Yoon & Martinez, 2012)

ARIA (Sandia CFD code) simulates the reactive Navier-Stokes equations, leading to estimates of mesoscale reaction-dependent dispersion coefficients

- Computationally powerful pore-scale model coupled with experimental results improves design and optimal delivery of engineered solutions (e.g., emulsion-stabilizing nanoparticles) under a variety of pore-geometry conditions

Davison et al. (AWR, 2012)

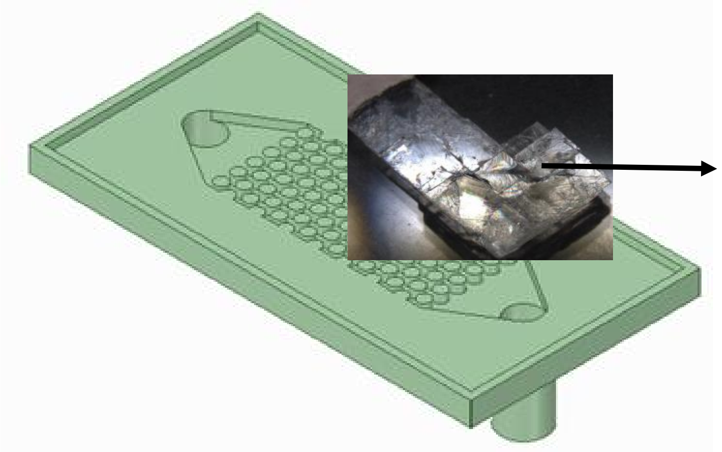
Microfluidic fabrication and Multiphase flow experiments



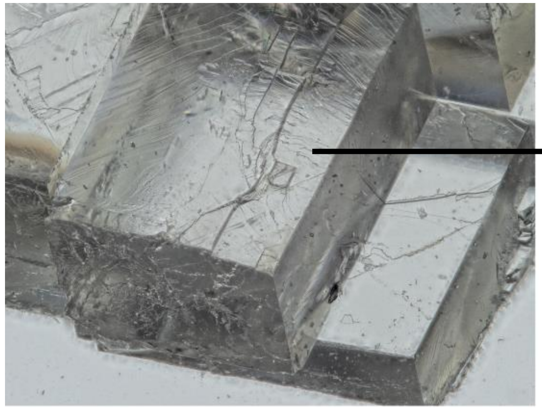
Park et al. (E&F, 2021)

3D printing-aided fluidic device

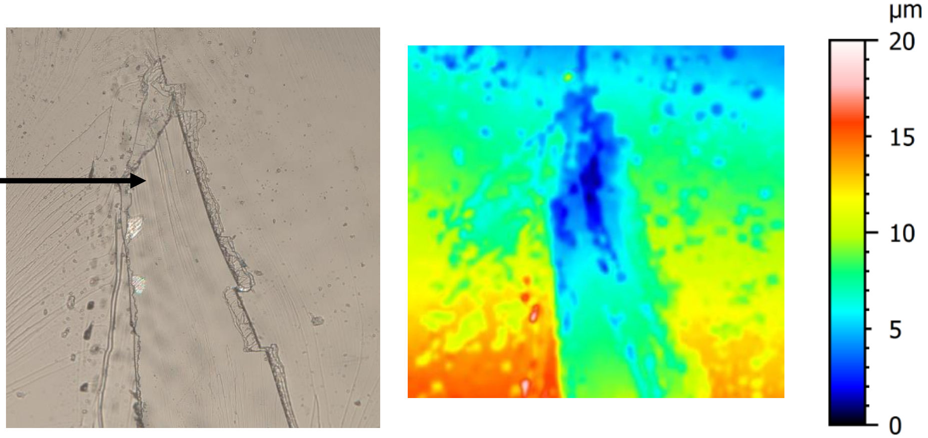
3D printed fluidic unit with real minerals



Calcite chip (clean vs. rough surfaces)



surface roughness



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

- Real-time imaging of change of $CaCO_3$ morphology with precipitation/dissolution
- Measurement of effluent concentrations with known surface geometry and media structure

Summary

- Microfluidic study enabled us to improve fundamental understanding of physico-chemical processes of $CaCO_3$ precipitation and dissolution
- Detailed investigation of reaction processes can be utilized to derive quantitative results of reactive transport processes
- Integration of experimental, numerical, and detailed data analysis will lead us to apply the reactive transport in microfluidic for many other problems
- An adaptive strategy to couple pore- and continuum scale using machine/deep learning methods will be tested against cement precipitation patterns