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Microscopic pore-scale analysis of calcium carbonate precipitation and dissolution kinetics in microfluidic experiments

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Sandia National Laboratories

Exceptional service in the national interest

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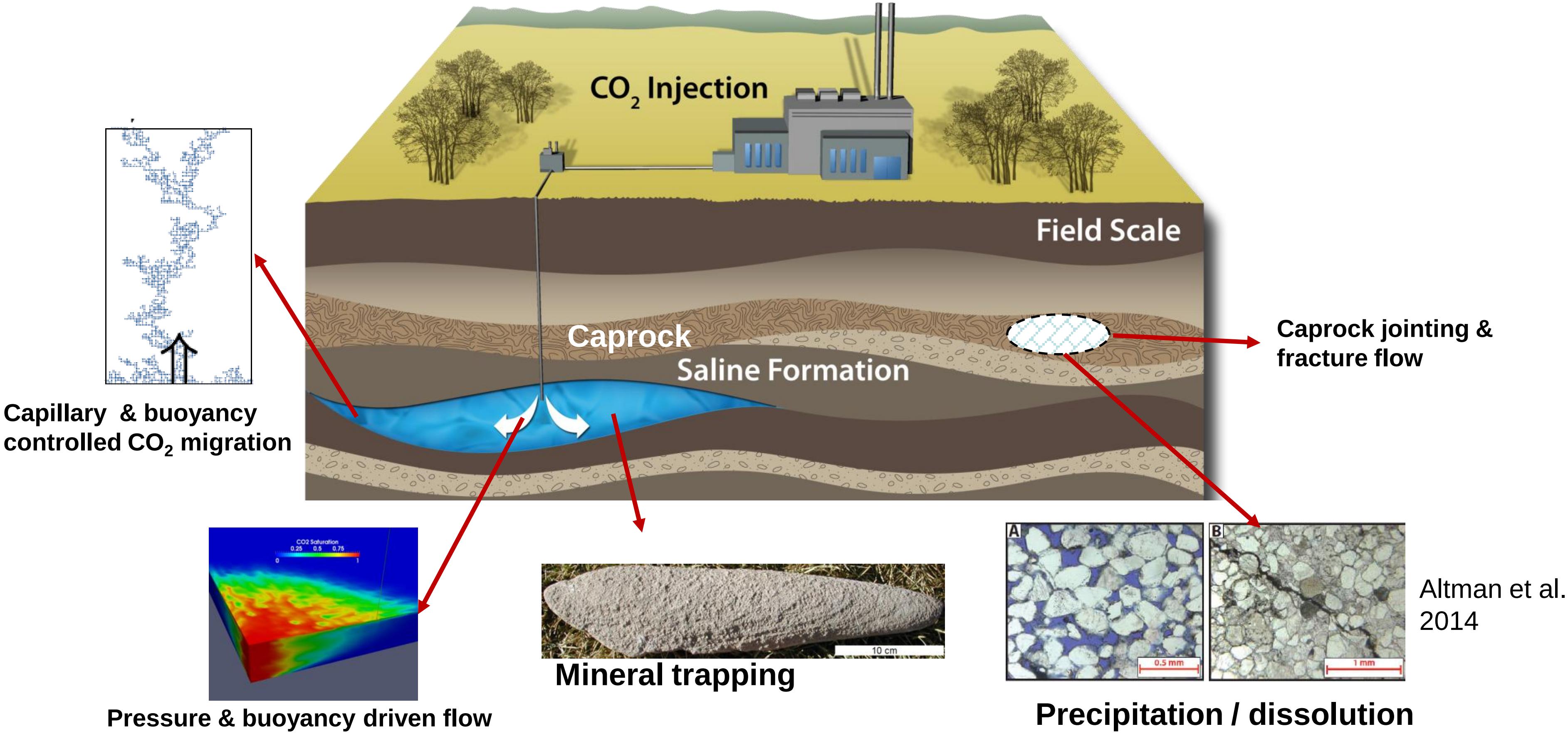
Outline

- Motivations
- Microfluidics & Pore scale reactive transport
- Precipitation & Dissolution
- Biomineralization
- Summary

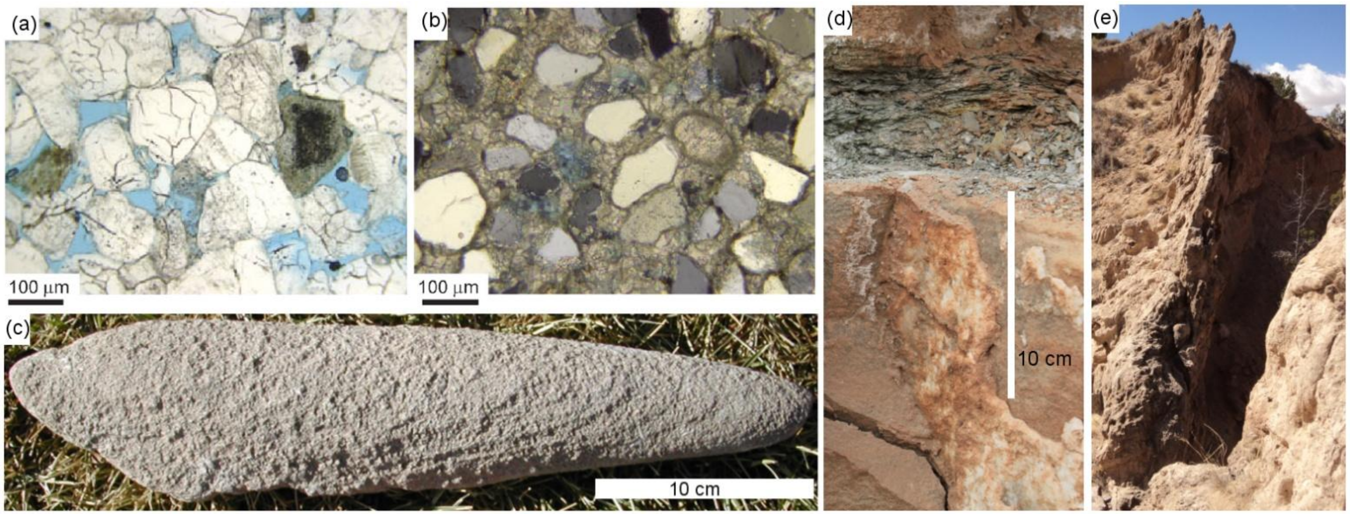
Reactive Transport Processes during Geological Carbon Storage



Earth and Energy Systems:

- ✓ Development of petroleum and geothermal reservoirs
- ✓ Geologic storage of CO2 and nuclear wastes
- ✓ Fate and transport of underground contaminants

Various Carbonate Precipitations

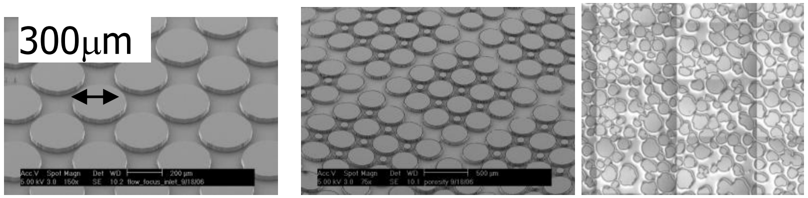


Yoon et al. RIMG, 2015

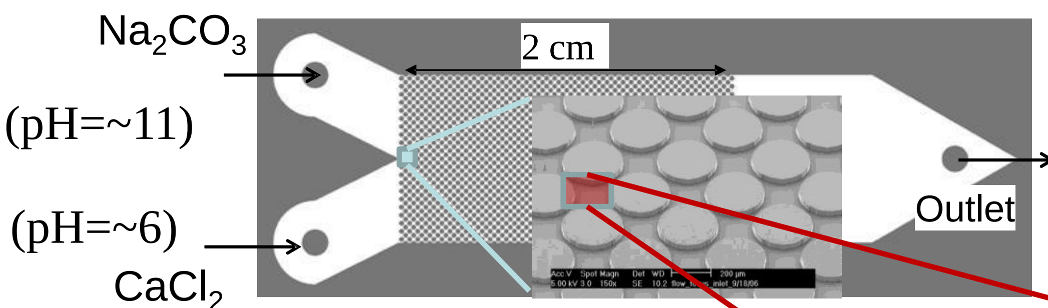
(a) Unaltered and (b) altered sandstone in the vicinity of a natural CO_2 seepage conduit (Little Grand Wash Fault, Utah, USA), (c) Uniform elongate concretion
(d) $CaCO_3$ precipitation along the vertical pathway sealed by a thin Mancos shale layer
(e) Calcite-cemented hanging-wall damage/mixed zone (Sand Hill Fault, New Mexico)

- **Pore-scale studies are necessary to better characterize changes in hydrologic properties**
  - Detailed information from pore-scale modeling can be used to derive hydrologic properties and constitutive relationships among them
  - Time-dependent information can be used to characterize changes of hydrological properties with time

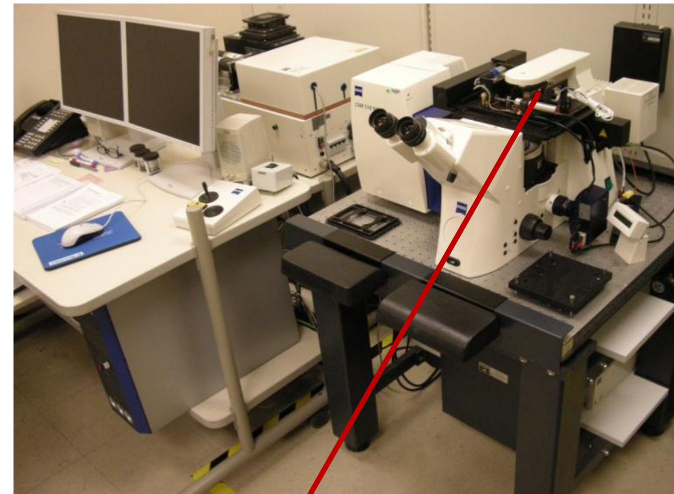
Microfludic Experiment

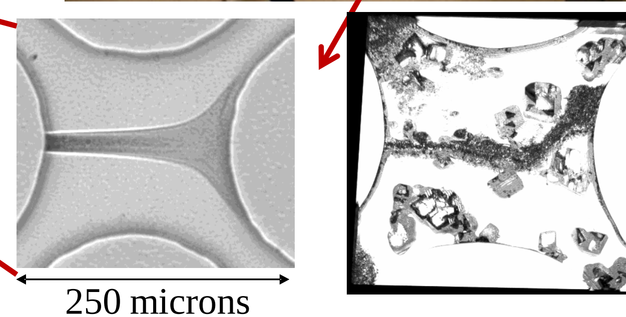


Regular cylinders Aggregates Irregular



Laser-Scanning Confocal Microscope
Optical Microscope





Microscopic image of calcium carbonate ($CaCO_3$) precipitates

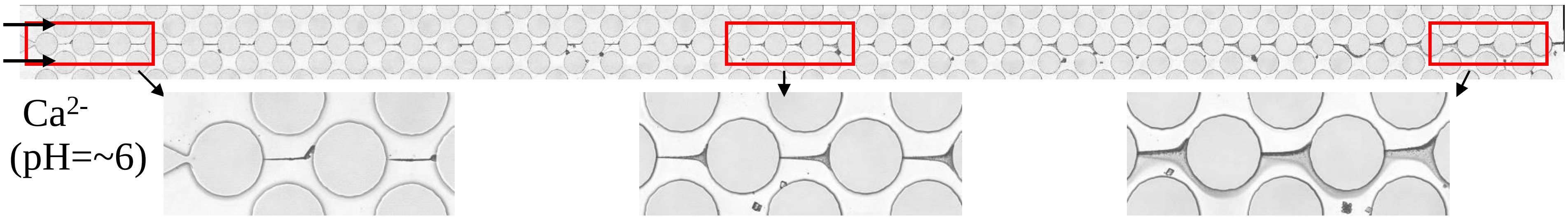
- Two solutions are mixing along the centerline and $CaCO_3$ precipitates
- Flowrate, concentrations, solution chemistry are controlling factors
- Microscopic images are taken over time
- Raman spectroscopy is used to identify thee structure of precipitates

Experimental Results

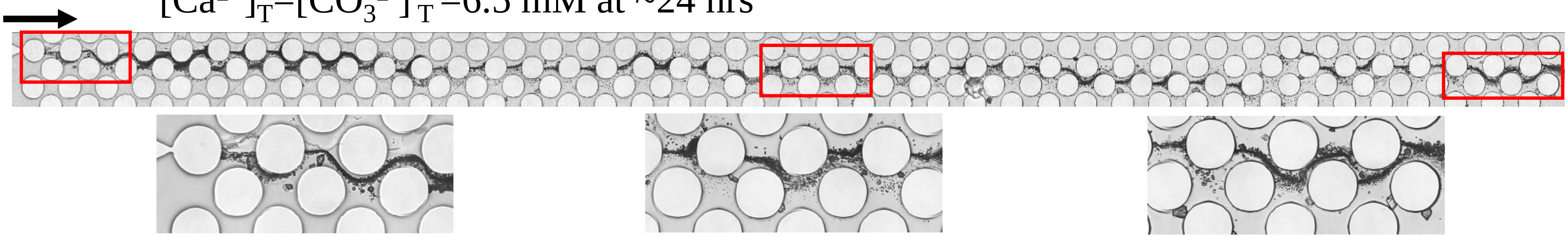
CO_3^{2-}(pH=~11) $[Ca^{2+}]_T = [CO_3^{2-}]_T$ =25 mM at ~2 hrs

Zhang et al., ES&T (2010)

Ca^{2-} (pH=~6)

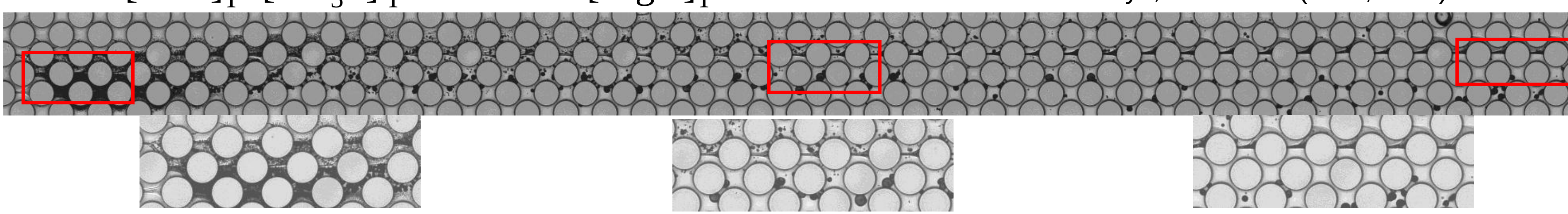


$[Ca^{2+}]_T = [CO_3^{2-}]_T$ =6.5 mM at ~24 hrs



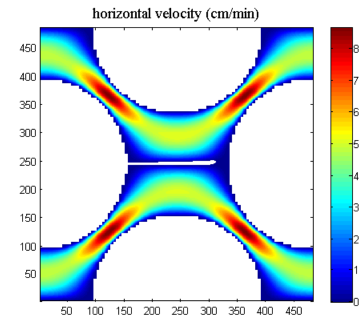
$[Ca^{2+}]_T = [CO_3^{2-}]_T$ =10mM & $[Mg^{2+}]_T$ =40 mM at ~16 hrs

Boyd, Yoon et al. (GCA, 2014)



- 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

Pore Scale Model Framework



Velocity

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

↓

Finite Volume Method: Reactive transport at pore scale

Δt

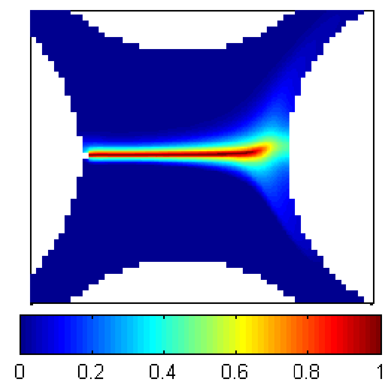
$$\Psi_j = C_j + \sum_{i=1}^{N_{eq}} \upsilon_{ji} C_i$$ Chemical equilibrium in bulk fluid (e.g., H^+, HCO_3^-, …)
Extended Debye-Hückel Equation for activity coefficients

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

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

Update of $CaCO_3$ volumetric content (V_m)

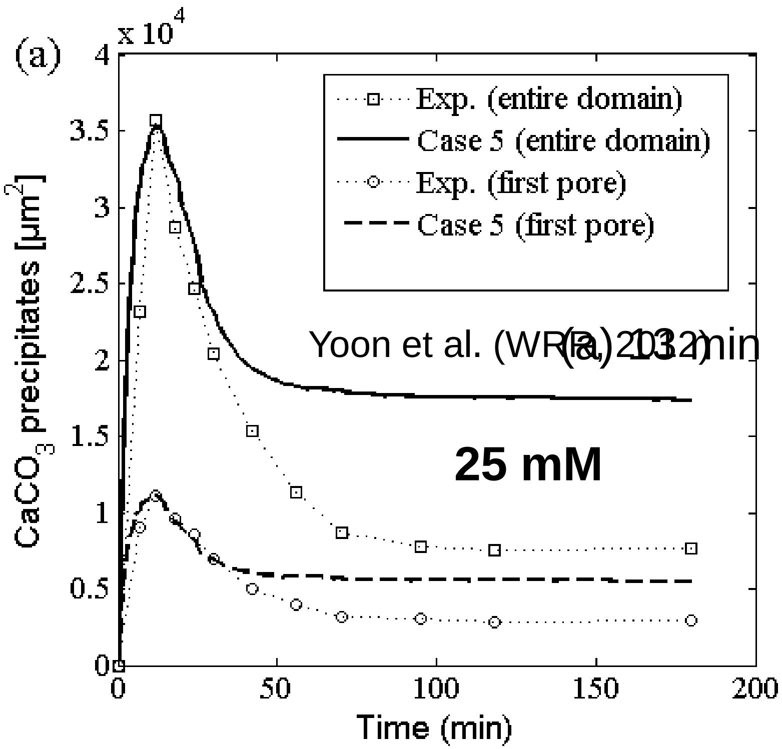
$$\frac{\partial V_m}{\partial t} = \overline{V_m} s_m k_{cc}\left(\left[\frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{sp}}\right]^n - 1\right)^m$$

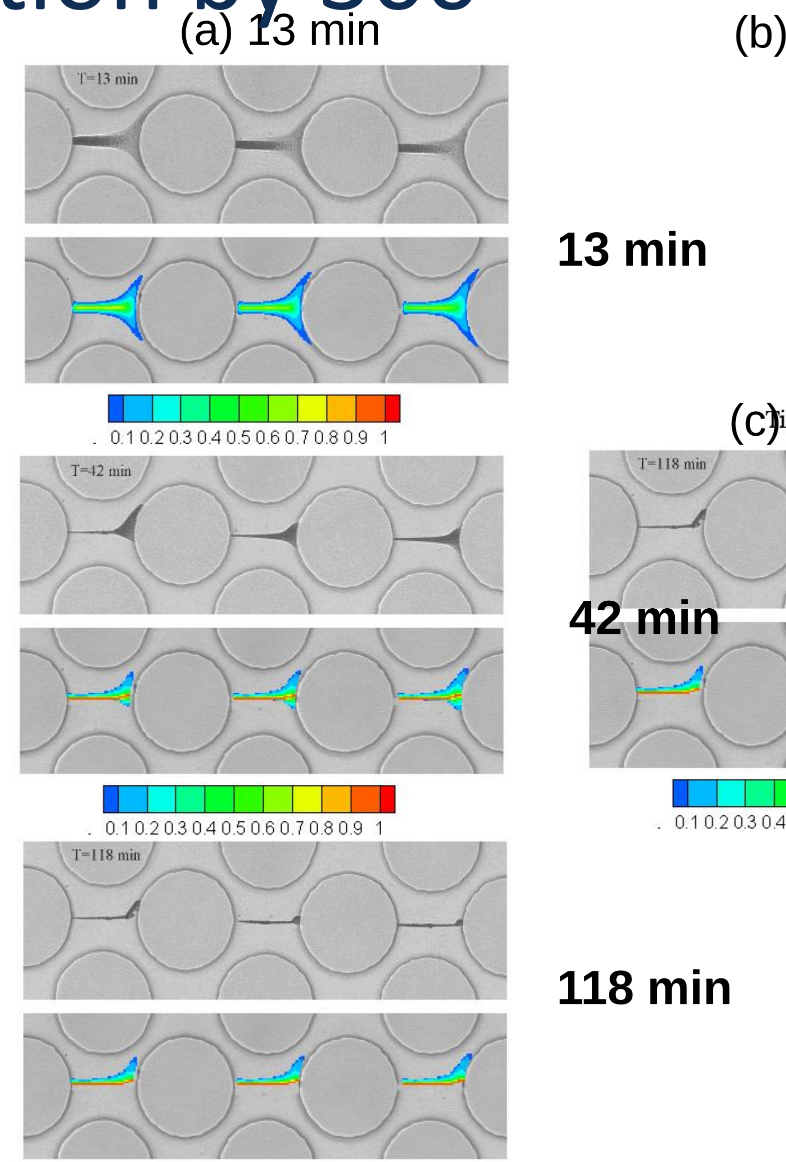


Mineral phase volumetric content

Yoon et al. (WRR, 2012)

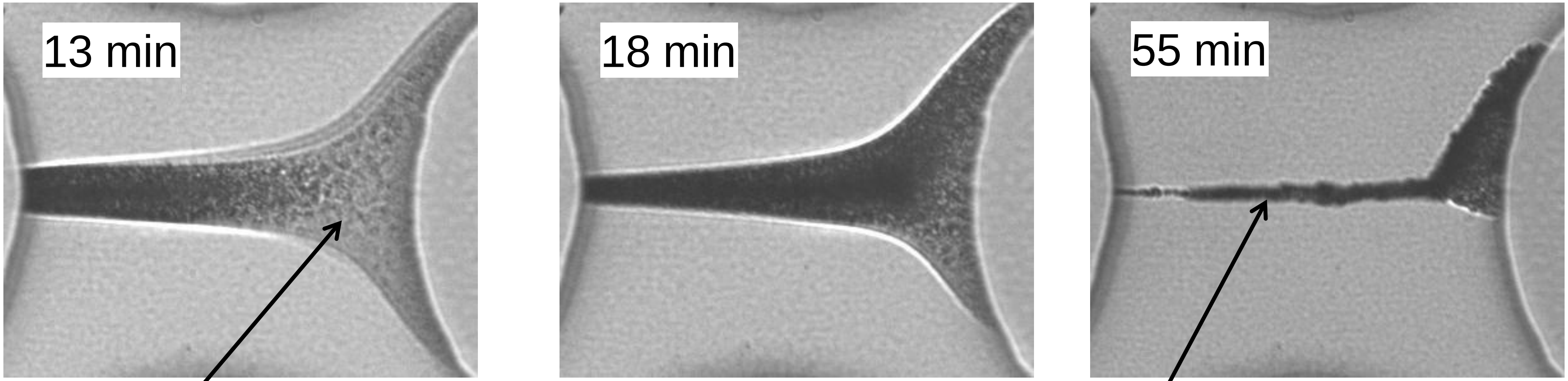
Simulation results: Increase surface area during dissolution by 300





- 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

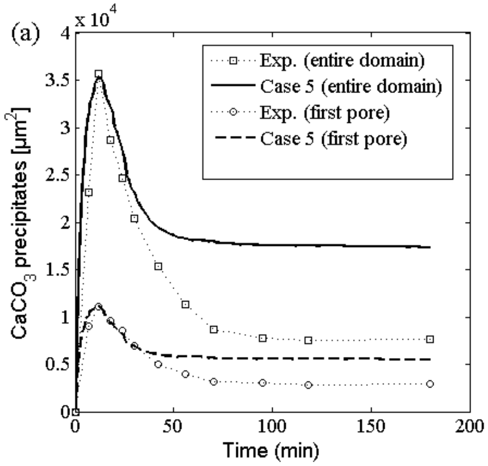


Amorphous Calcium Carbonate & Vaterite

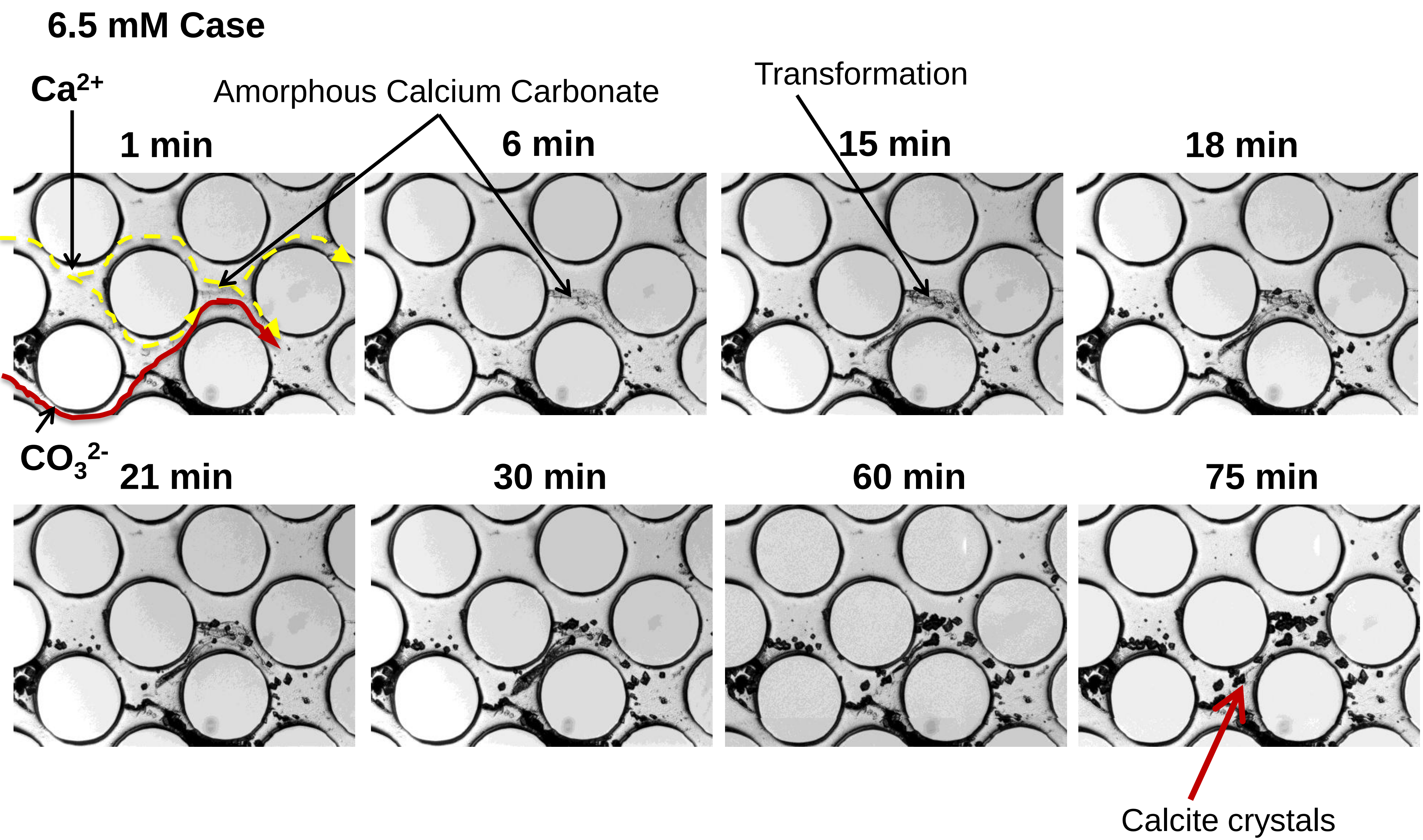
25 mM

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

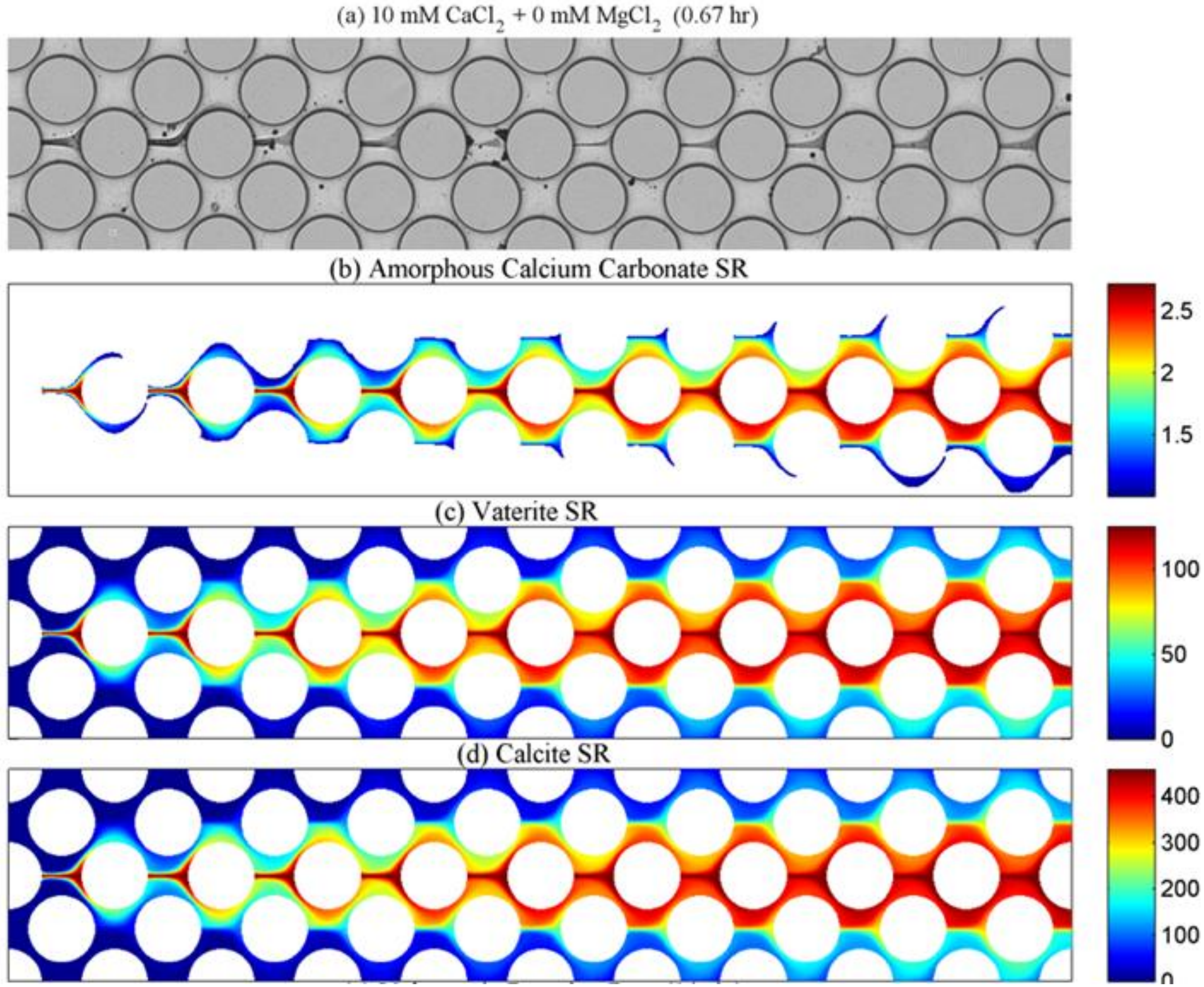


Calcium Carbonate: Polymorphs

Saturation Ratio (SR) = Ion Activity product / Ksp

SR>1: thermodynamically favorable to form

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



ACC $Ksp=10^{-6.25}$

Vaterite $Ksp=10^{-7.9}$

Calcite $Ksp=10^{-8.48}$

Boyd, Yoon et al. (GCA, 2014)

Experimental Result

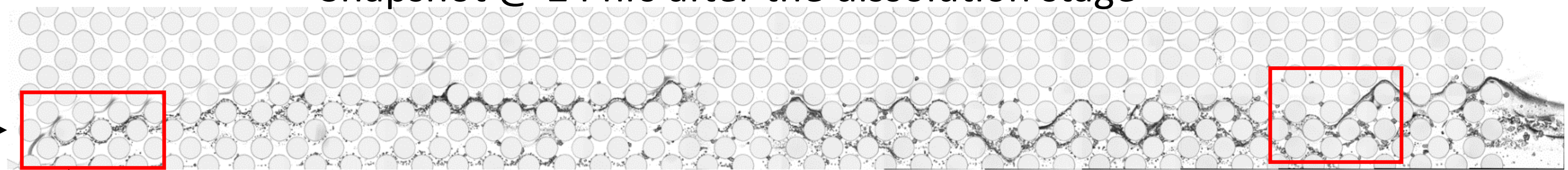
Precipitation stage: $[Ca^{2+}]_T = [CO_3^{2-}]_T = 10$ mM for 75 hrs

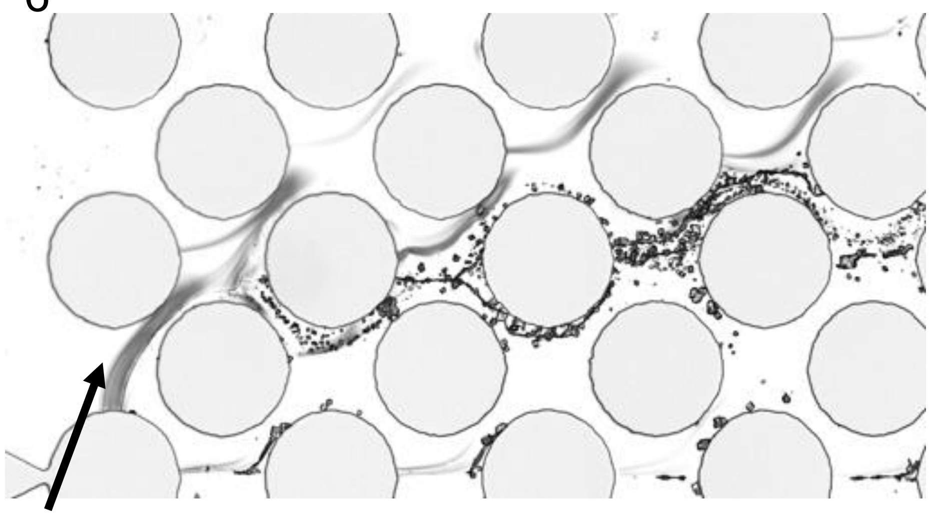
Dissolution stage: pH=4 solution into both sides

Snapshot @ 24 hrs after the dissolution stage

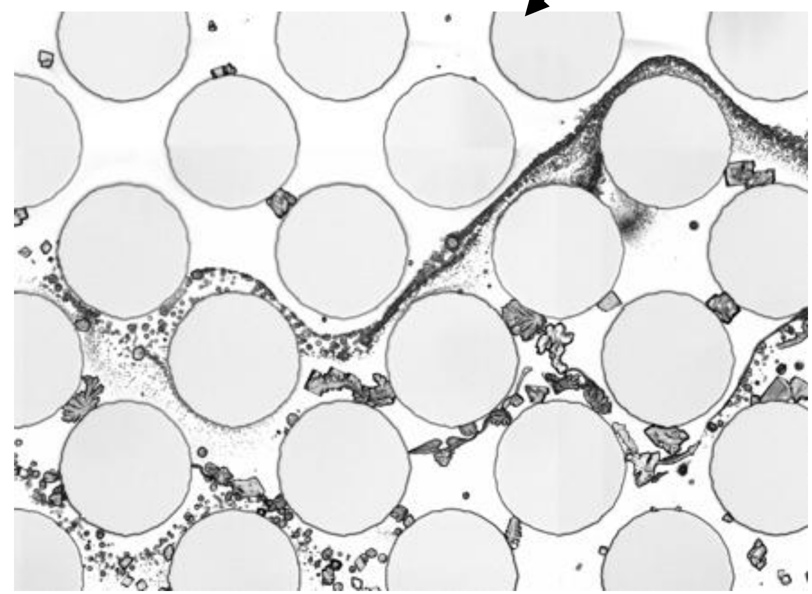
CO_3^{2-} @ pH=~11

Ca^{2-} @ pH=~6





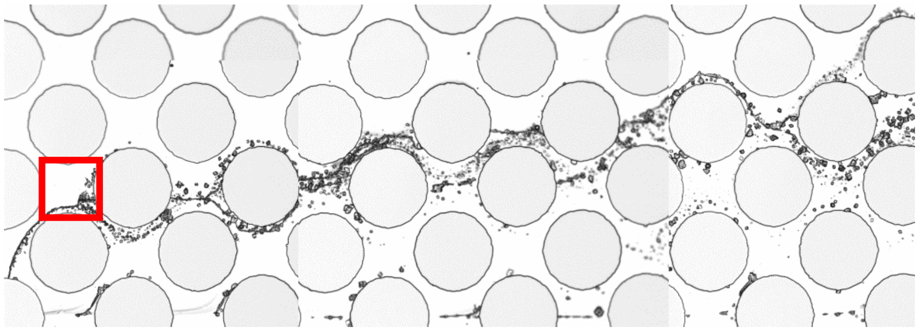
Dissolution step shows nano-particle movement similar to tracer transport

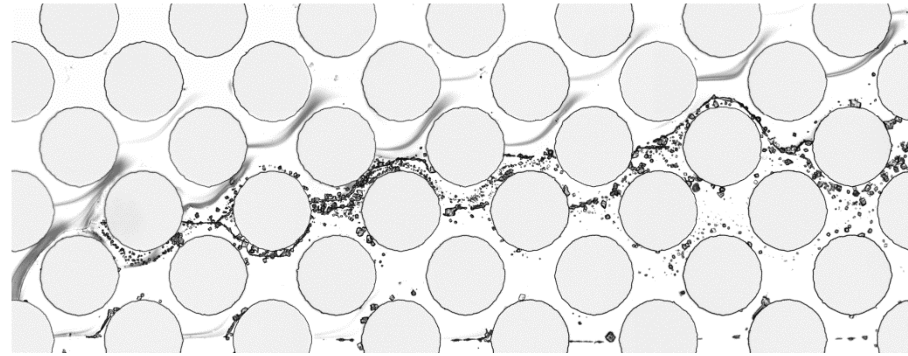


Precipitate morphology depends on concentration gradient, flow rate, and evolving pore structure

- Effective macroscale reaction rates have a component associated with flow dynamics
- Micromodel experiments reveal fundamental pore-scale reactive transport mechanisms

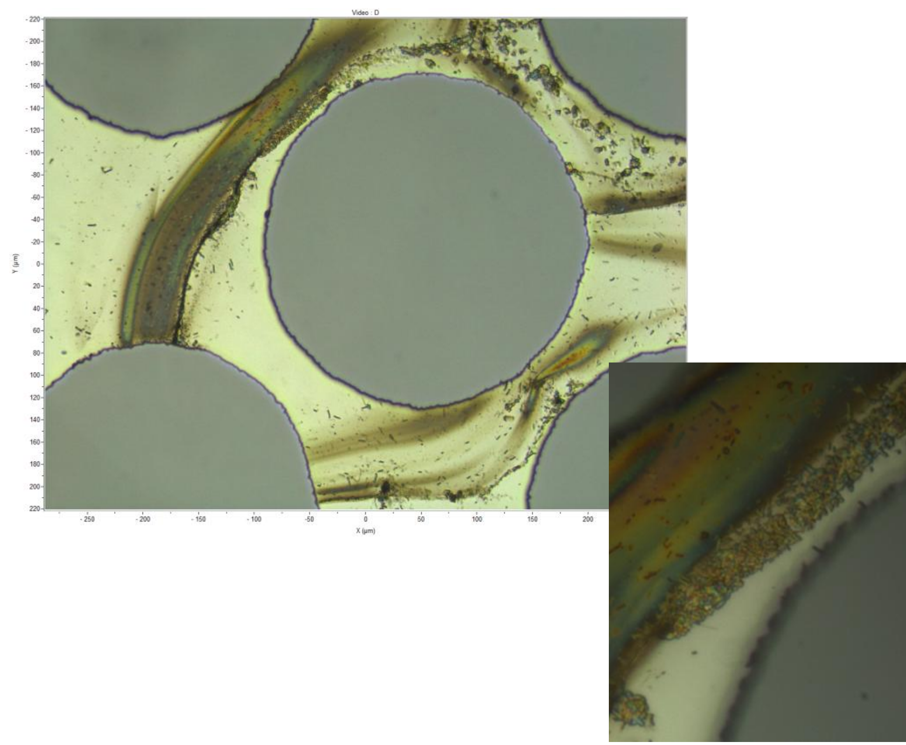
Experimental Result





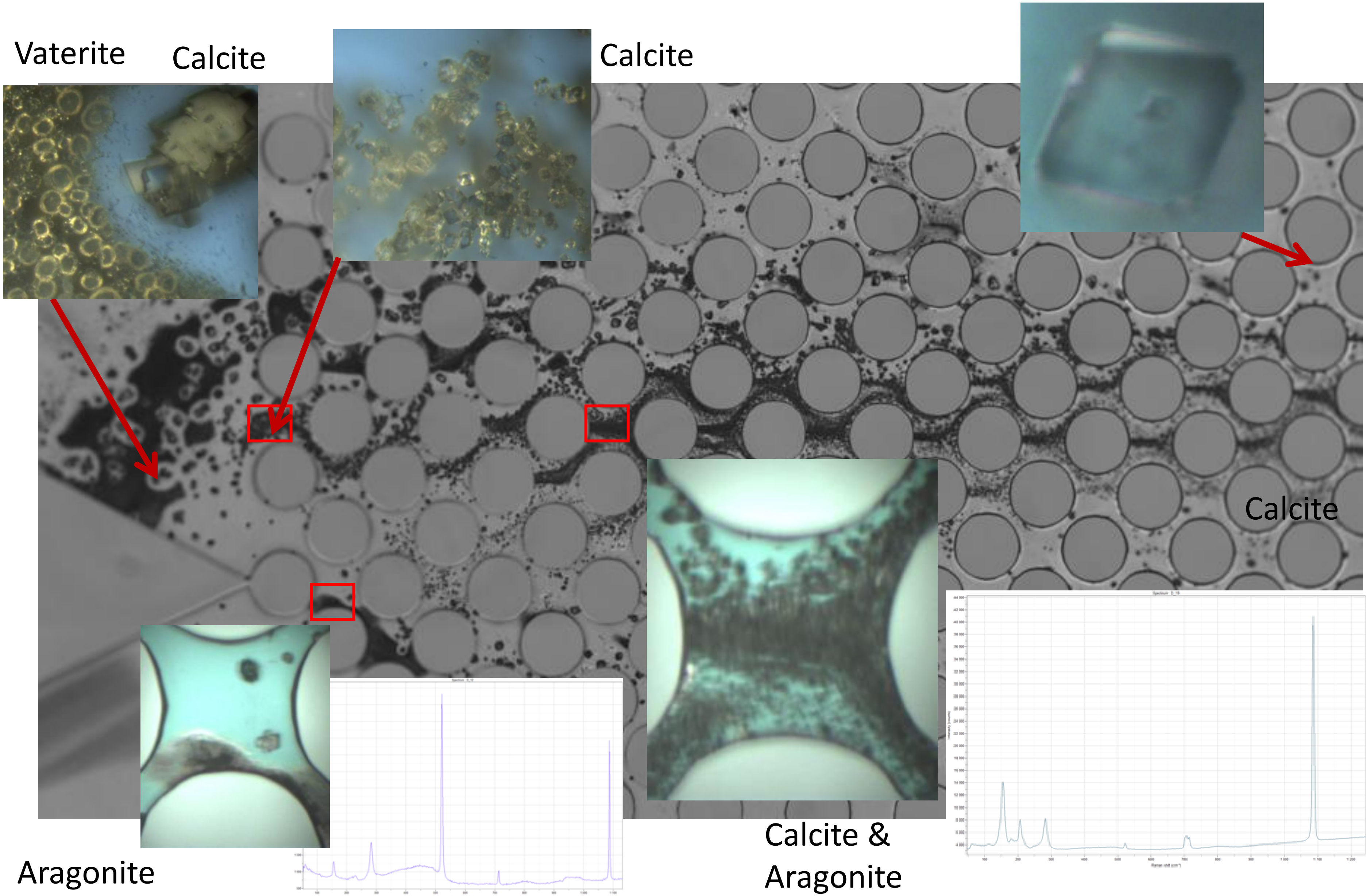
@ 24 hrs after the precipitation stage

@ 24 hrs after the dissolution stage



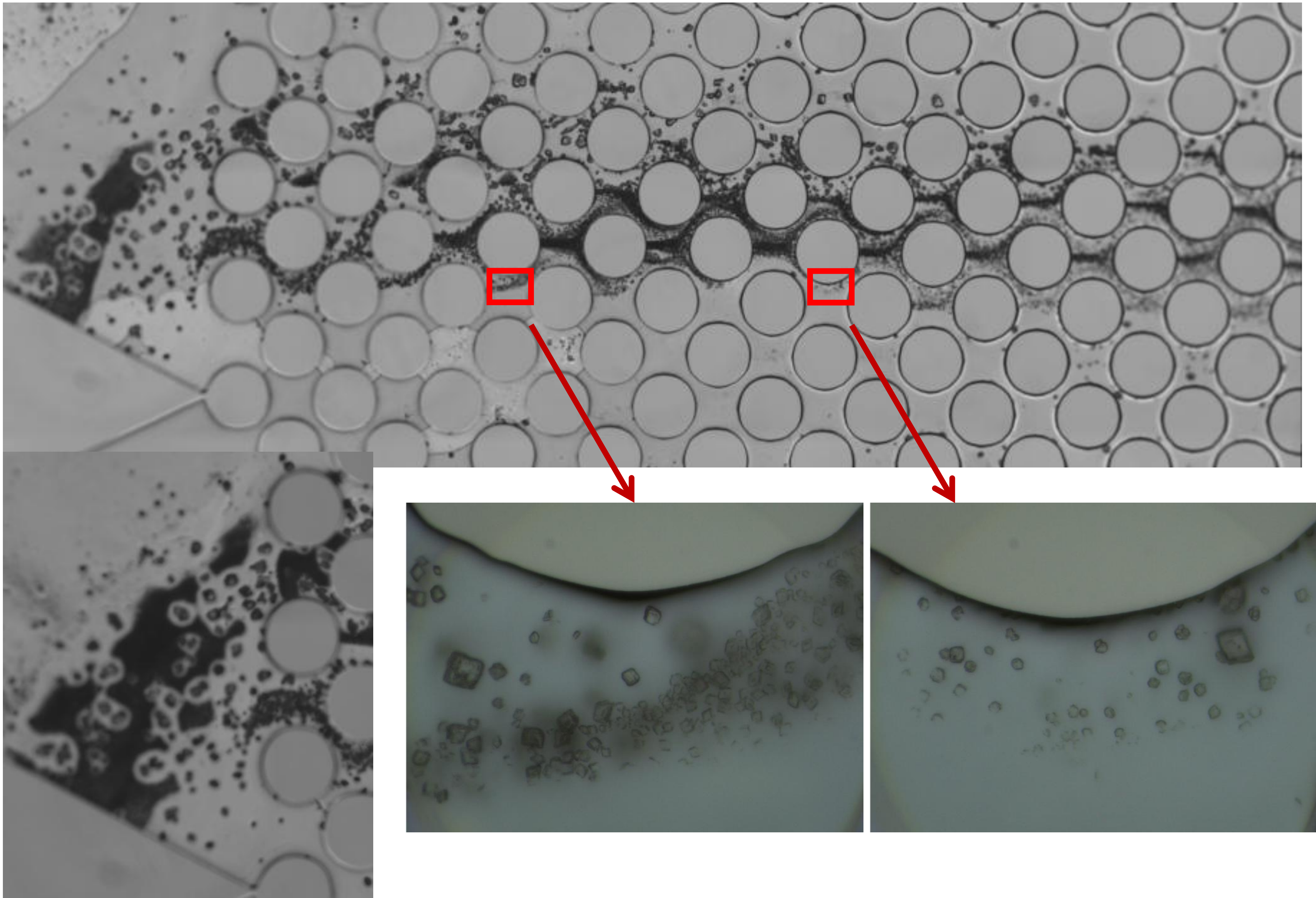
Calcium Carbonate Polymorphs

Raman Spectroscopy



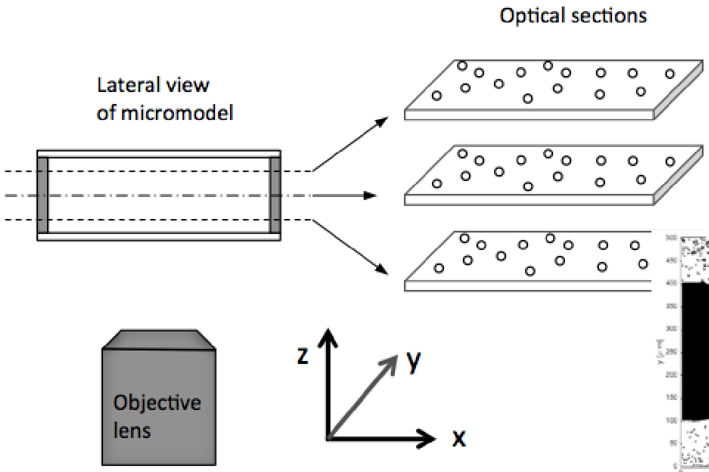
Calcium Carbonate Dissolution

14 hrs after the dissolution stage



3D flow and Precipitates

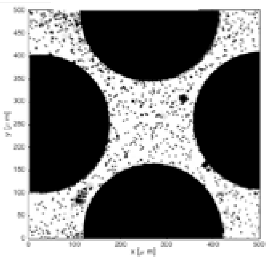
3D micro Particle Image Velocimetry (PIV) using Laser Scanning Confocal Microscopy



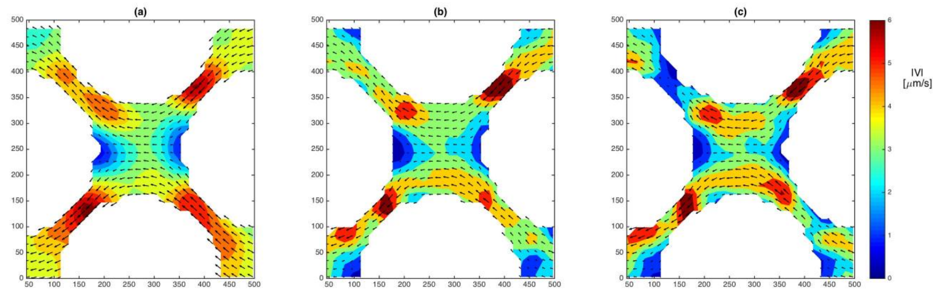
modified from Lima et al. (2006)

Steady, single-phase flow in Micromodel

Similar flow patterns at all depths
~ 3D effects are negligible



Particles

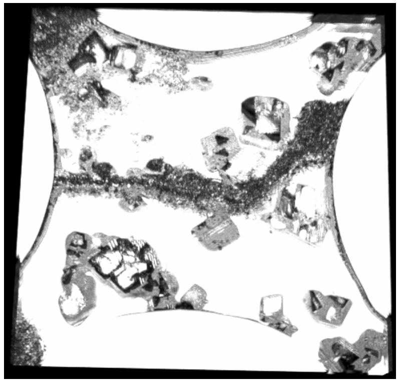


Bottom

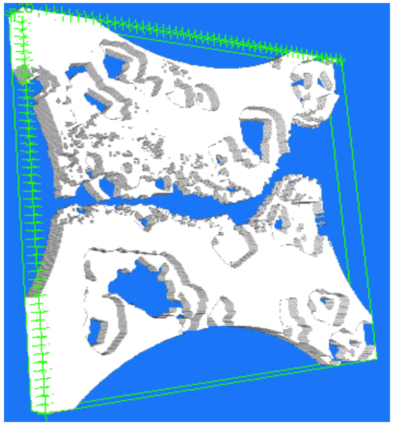
Middle

Top

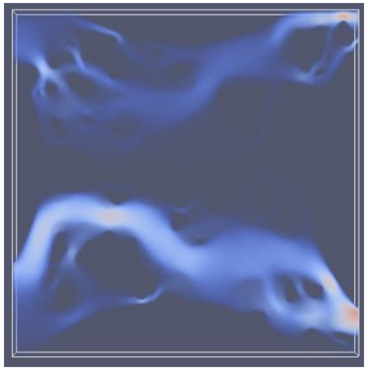
3D pore structure



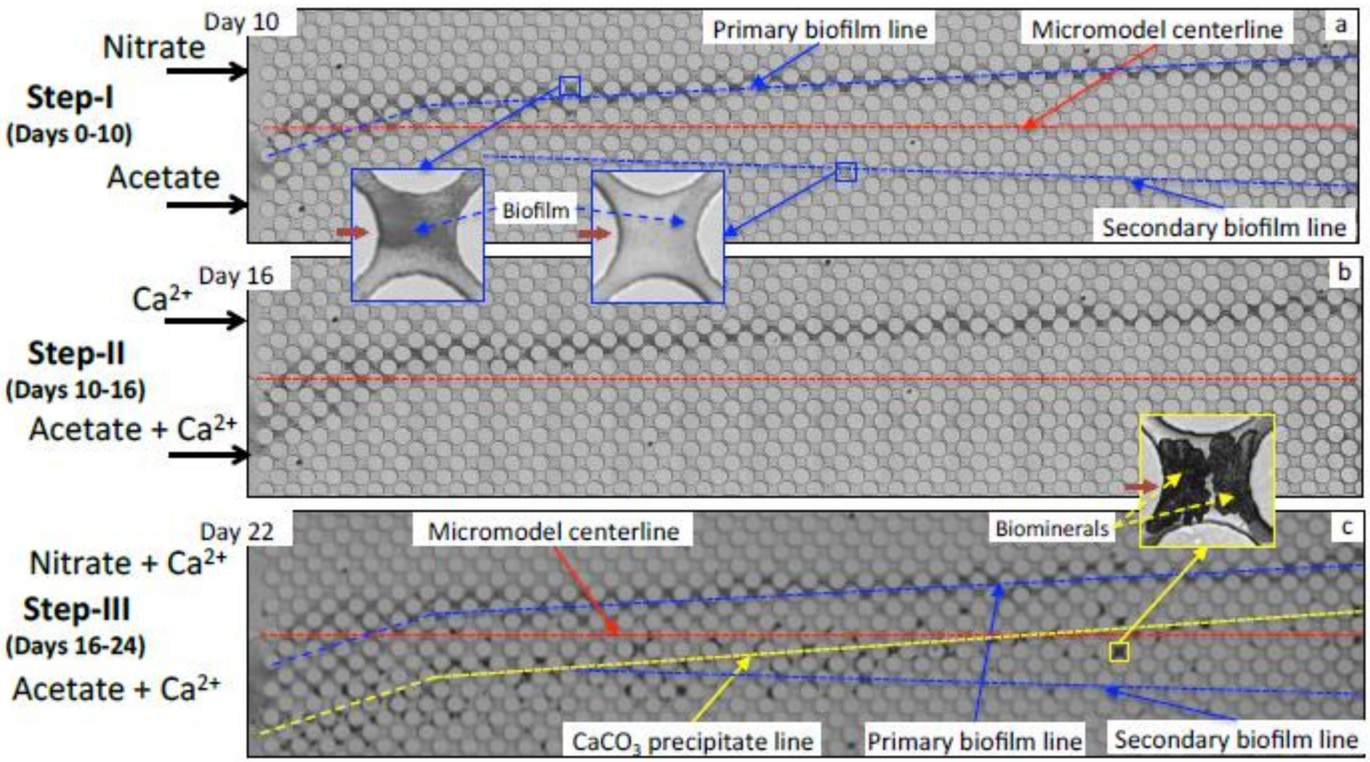
Pore structure

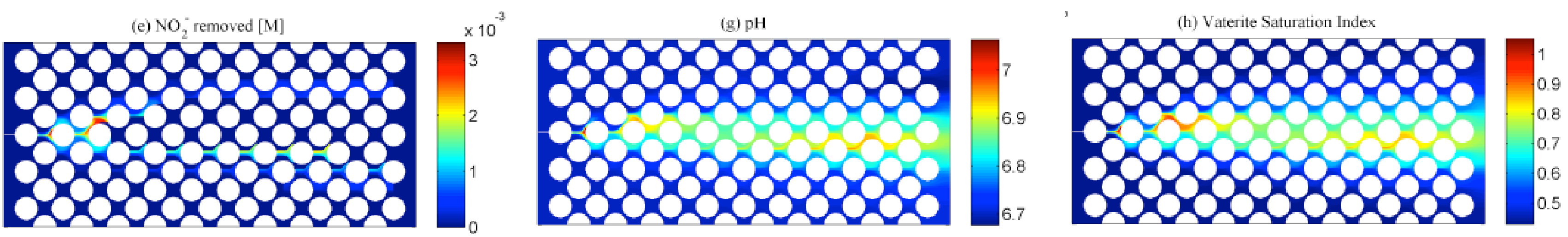


3D flow field



Biomineralization in a micromodel





Singh et al. (ES&T 2005)

Summary

- 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
- 3D effects may be important for precipitation and dissolution
- There are complex nonlinear feedbacks among flow, reactant transport and pore blocking due to precipitation and dissolution. Upscaling these reactions is a challenge.
- Pore-scale model can be used to test if pore-scale processes observed in micromodels is predicted, and to develop an upscaled reaction model