Upscaling of Mixing-controlled Reactive Transport

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We combine laboratory micro-scale experimental and modeling efforts to examine:

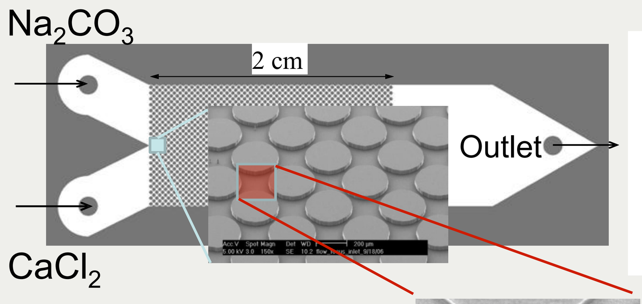
- How does $scCO_2$ interact with brines and mineral surfaces? [**multiphase flow**]
- What are the relevant physics of dissolved CO_2 transport? [**reactive transport and rock-fluid interactions**]
- How can pore scale processes be synthesized and upscaled into more powerful continuum models? [**upscaling**]

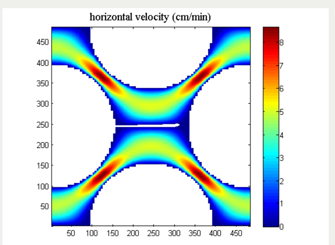
Pore Scale Modeling for Reactive Transport

- Transverse mixing-induced calcium carbonate ($CaCO_3$) precipitation

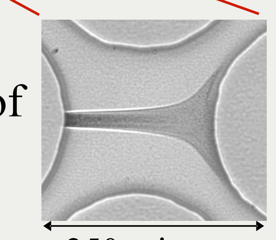
Experimental setup

Pore scale modeling



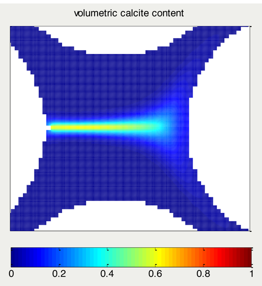


Lattice Boltzmann method for water flow velocity at 1μm resolution



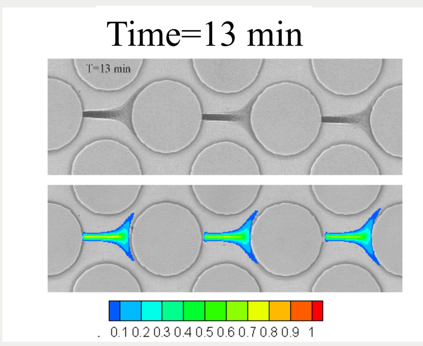
Microscopic image of $CaCO_3$ precipitates at 0.6μm resolution

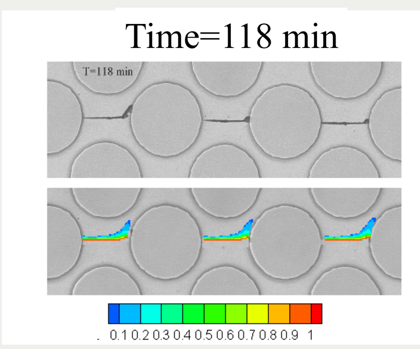
250 microns

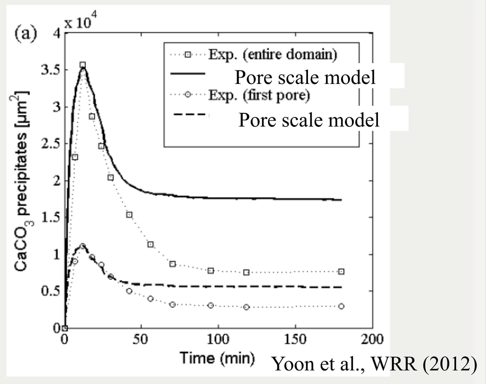


Numerical simulation result of $CaCO_3$ precipitation

Reactive Transport Results





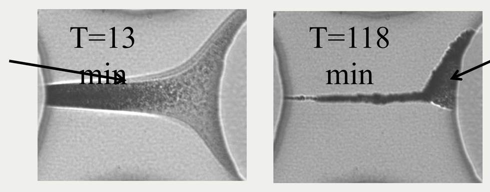


Yoon et al., WRR (2012)

Colorbar: $CaCO_3$ volumetric content (V_m)

- Simulations capture precipitation & dissolution patterns observed in the micromodel
- A decrease of precipitate area (dissolution) was captured by using a dissolution factor which accounts for high surface area of nano-particles, transformation to different forms of $CaCO_3$, and stability of nano-particles after pore blocking as shown below

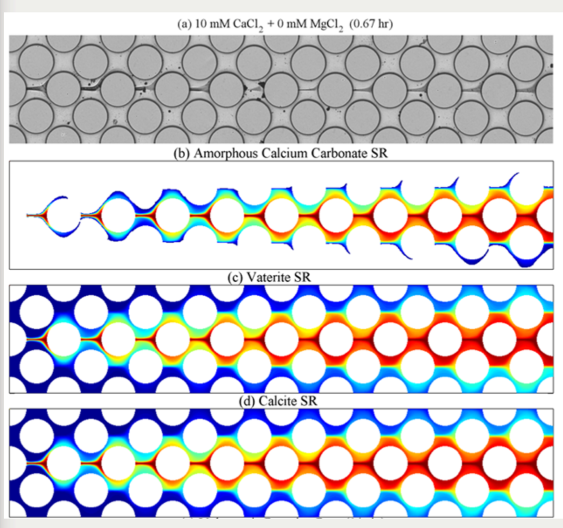
Amorphous $CaCO_3$ & Vaterite



Predominantly vaterite

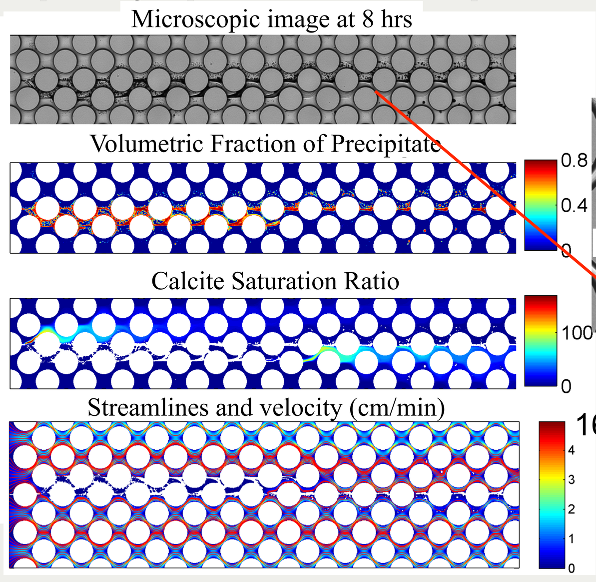
Calcium Carbonate: Polymorphs

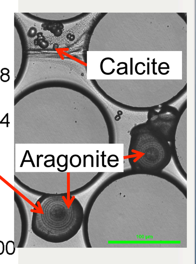
$[Ca^{2+}]_T=[CO_3^{2-}]_T=6.5$ mM



Boyd, Yoon et al. (GCA, 2014)

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



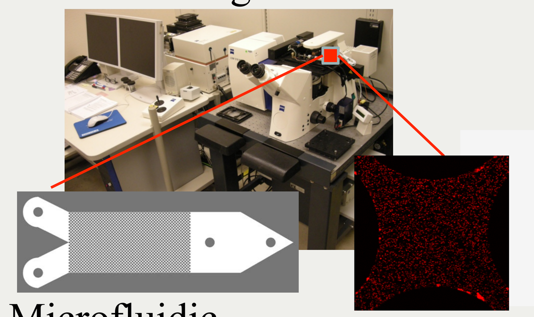


- Mineral precipitation rate along flow direction is concentration dependent and limited by transverse mixing
- $CaCO_3$ mineral phases (i.e., polymorphs) are chemistry dependent and affected by flow and kinetics
- Overall, reaction kinetics, crystal growth and morphology are spatially and temporally affected by solution chemistry and hydrodynamics at pore scale
- Pore-scale model will be used to test if pore-scale processes observed in micromodels is predicted, and to develop an upscaled reaction model

3D Flow Field in a micromodel

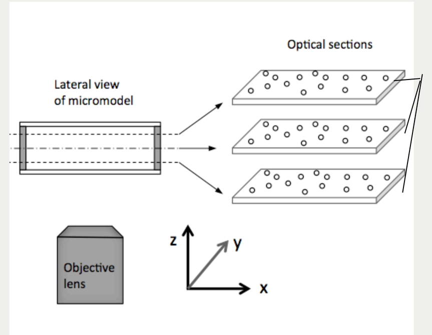
Experimental setup

3D Laser scanning confocal microscope



Microfluidic pore network

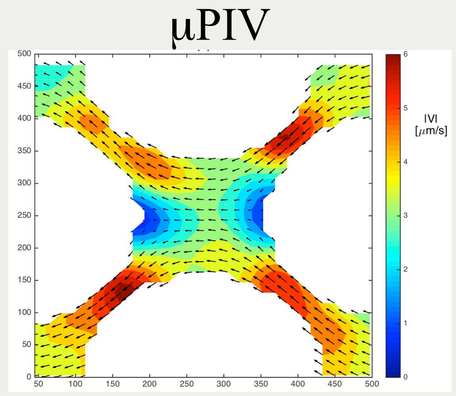
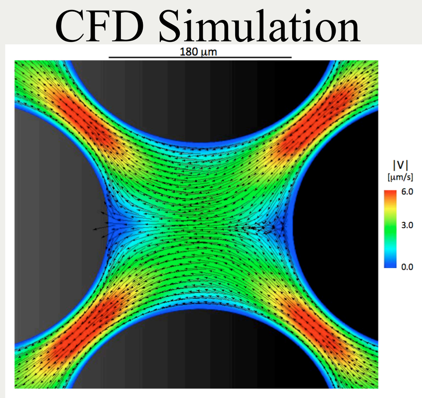
Particle image in pore body

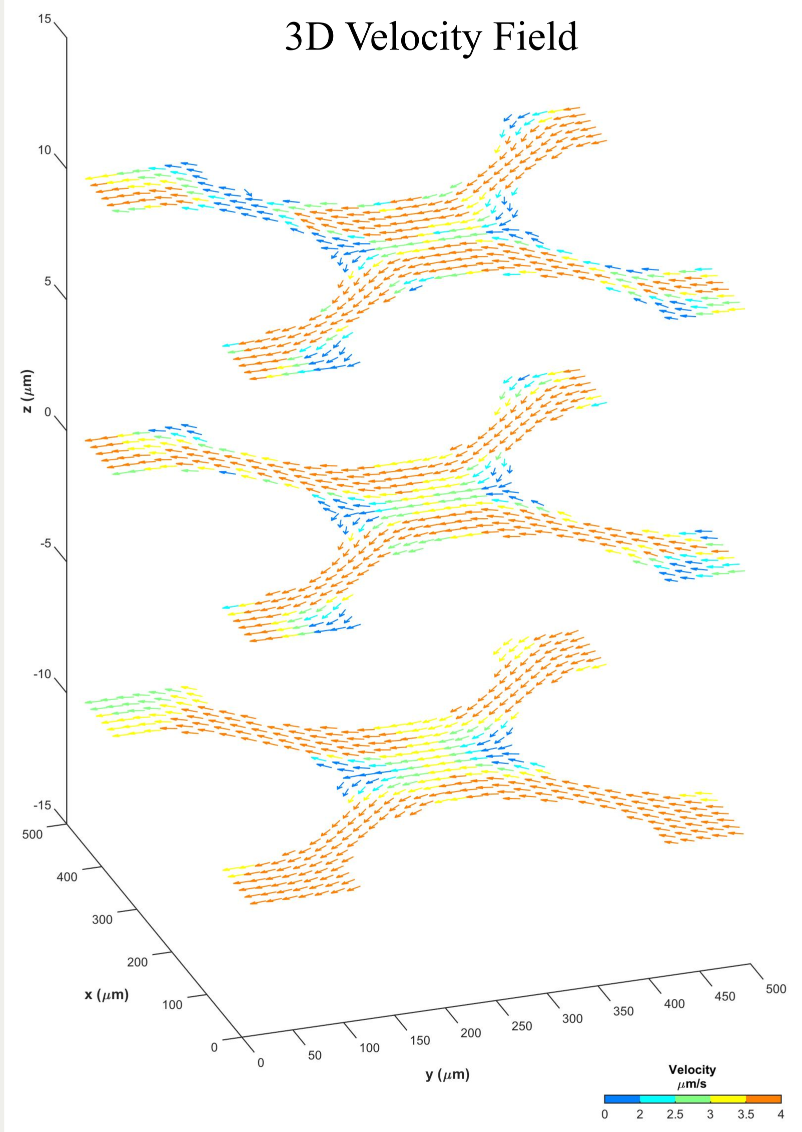


2D slices of 3D field

Results

2D Velocity Field

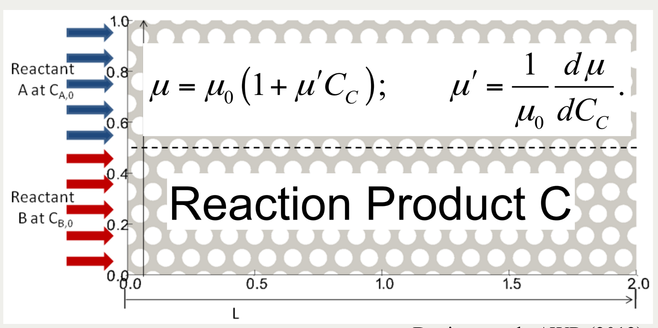
Condition	μPIV	CFD Simulation
Steady, single-phase flow with a constant pore geometry		



- Each field is time-averaged over 200 instants
- Each 2D velocity field shows fast flow in narrow pore throats and slow flow in wide pore bodies
- Good agreement between observed and simulated 2D fields
- Flow is uniform with depth, shown by similar patterns at all heights
- 3D effects minimal in the steady flow and uniform geometry condition

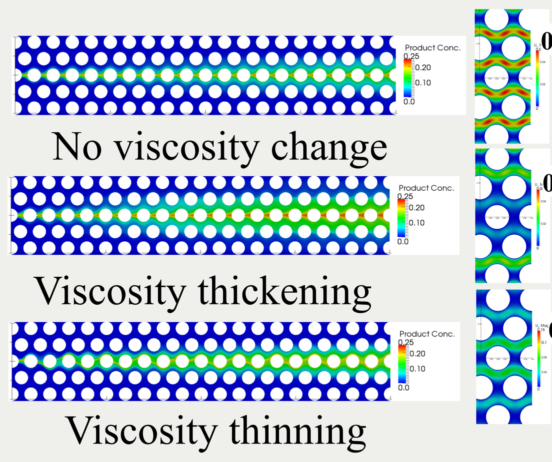
Simulated flow in a micromodel

- Mixing-induced chemical reactions can alter fluid properties (viscosity and density), mixing efficiency, and shear rate for engineered solutions



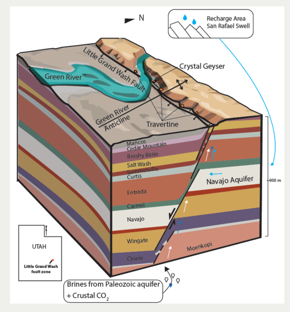
Davison et al., AWR (2012)

ARIA (Sandia CFD Simulator)

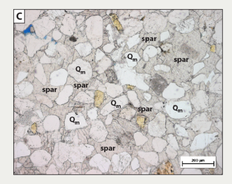


- Pore scale model with high performance computing capability was used to test reactive transport experimental results under a variety of pore-geometry conditions
- Same model will be used to test flow experimental results under a variety of pore-geometry conditions
- Simulator reproduces flow experimental results under steady and constant geometry condition

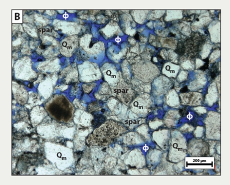
Natural Analogue for Carbonate Sealing of CO_2 Leakage Pathways



Little Grand Wash Fault, Crystal Geyser, Utah



Inside fault zone: Porosity completely filled with calcite spar

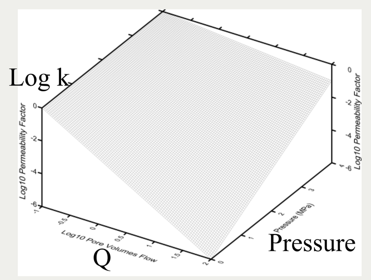


Outside fault zone: High porosity and absence of calcite cement

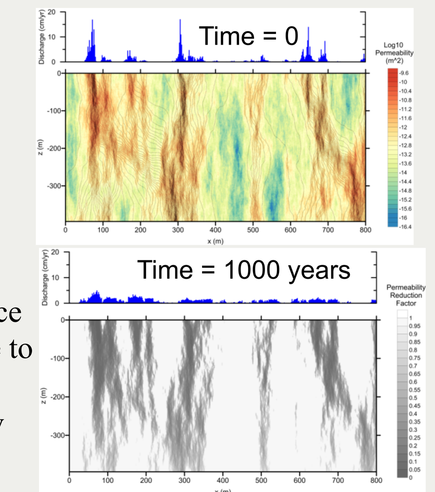
Courtesy of P. Eichhubl

- 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 topography
- Sandstone permeability reduced by 3 to 4 orders of magnitude in alteration zones by carbonate cementation

Continuum Scale Modeling



- Simplified 2-D response surface
- Permeability (k) reduction due to calcite precipitation is a function of groundwater flow (Q) and fluid pressure (P)



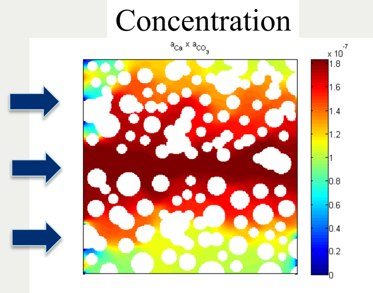
- Unconditional geostatistical simulation
- Initial flow pattern is qualitatively similar to the spacing of seeps along the Grand Wash fault (~100's m)
- k is reduced by several orders of magnitude by calcite precipitation, primarily in the shallower high-flow channels
- Evolution of the flow field results in more dispersed groundwater discharge at the surface than observed

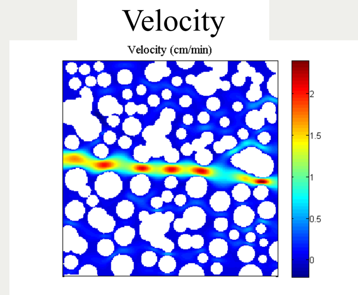
Response Function based on Pore Scale Simulations

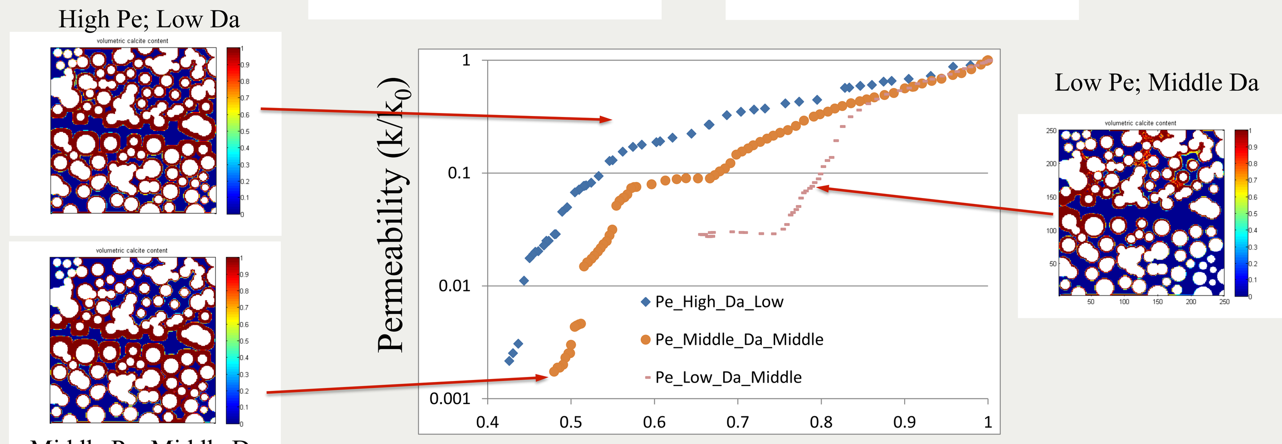
- Phenomenological power law relations for continuum scale model can be derived from pore scale simulations (permeability-porosity, tortuosity-porosity, surface area-porosity)

Influx conditions

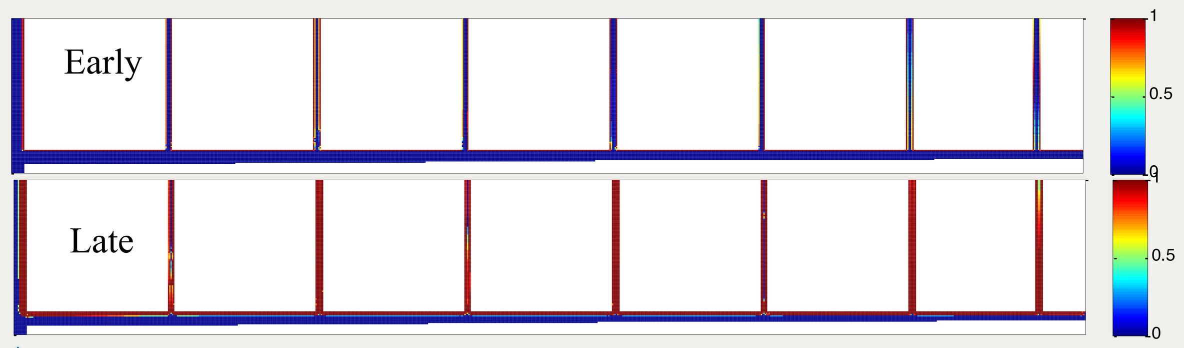
$[Ca^{2+}]_T=[CO_3^{2-}]_T$ =20mM







Volumetric Calcite Content



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

Summary and Implications

- Vigorously tested pore-scale model can be used to develop a response function (or dimension reduction model) for continuum-scale relationships
- k-ε and surface area-ε relationships will be developed over a range of solution chemistry, chemical reaction, and pore structure configurations
- An adaptive strategy to couple continuum and pore-scale using a response function approach as well as hybrid pore-continuum model using p-Flotran) will be tested

Selected Publications

- Davison, S. M., H. Yoon, M. J. Martinez (2012), Pore scale analysis of the impact of mixing-induced reaction dependent viscosity variations, Advances in Water Resources, 38, 70-80.
- Yoon, H., A. J.Valocchi, C. J.Werth, and T.Dewers (2012), Pore-scale simulation of mixing-induced calcium carbonate precipitation and dissolution in a microfluidic pore network, Water Resour. Res., 48, W02524, doi: 10.1029/2011WR011192.
- Boyd T, Yoon H, Zhang C, Dehoff K, Fouke B, Valocchi AJ, Werth CJ (2014) Infl uence of Mg2+ on CaCO3 precipitation during subsurface reactive transport in a homogeneous silicon-etched pore network. Geochim Cosmochim Acta 135:321–335
- Martinez MJ, Stone CM, Notz PK, Turner DZ, Hopkins PL, Subia S, et al. Computational thermal, chemical, fluid, and solid mechanics for geosystems management. Technical Report, SAND2011-6643, Sandia National Laboratories, Albuquerque, NM 2011.

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