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Upscaling of reaction rates in reactive transport using pore-scale reactive transport model

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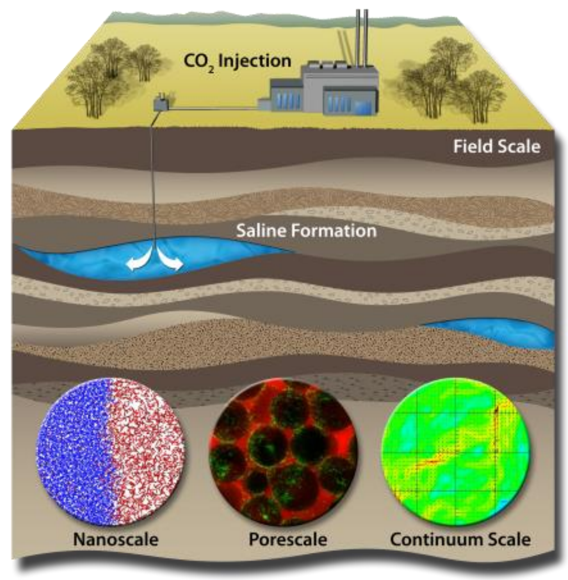

Sandia National Laboratories

Exceptional service in the national interest

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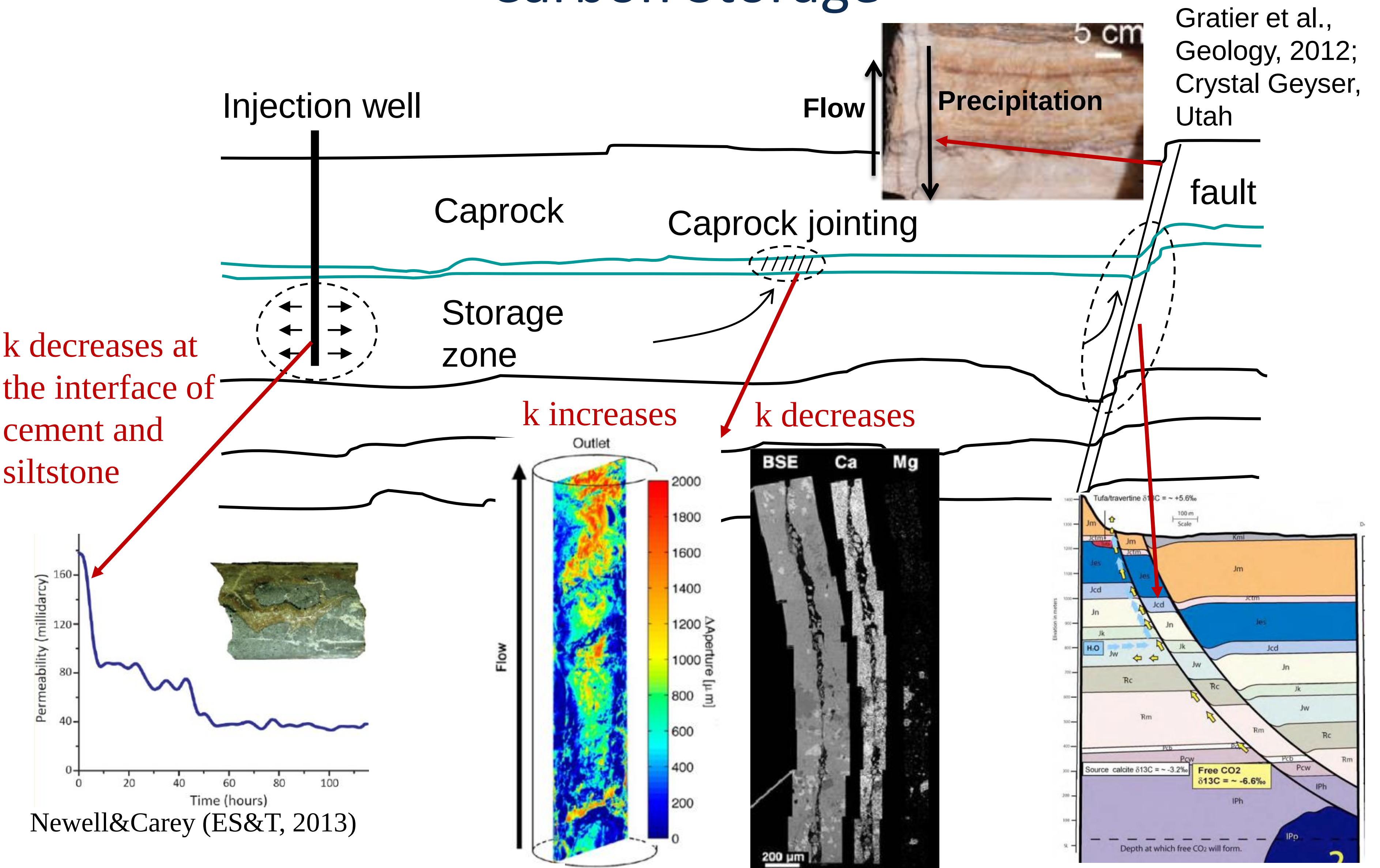
National Nuclear Security Administration

CFSES

Reactive Transport Processes during Geological Carbon Storage



Newell&Carey (ES&T, 2013)

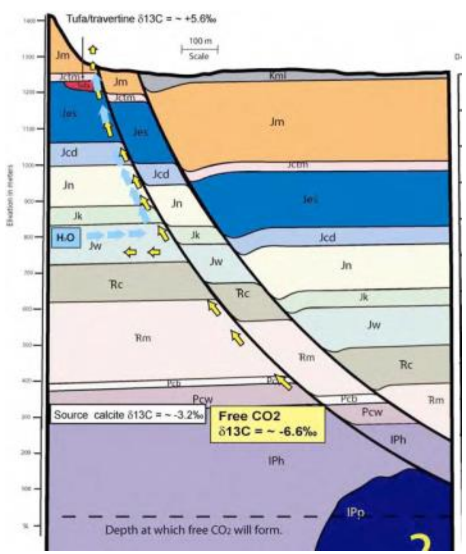
Deng et al. (2013)

Ellis et al. (2013)

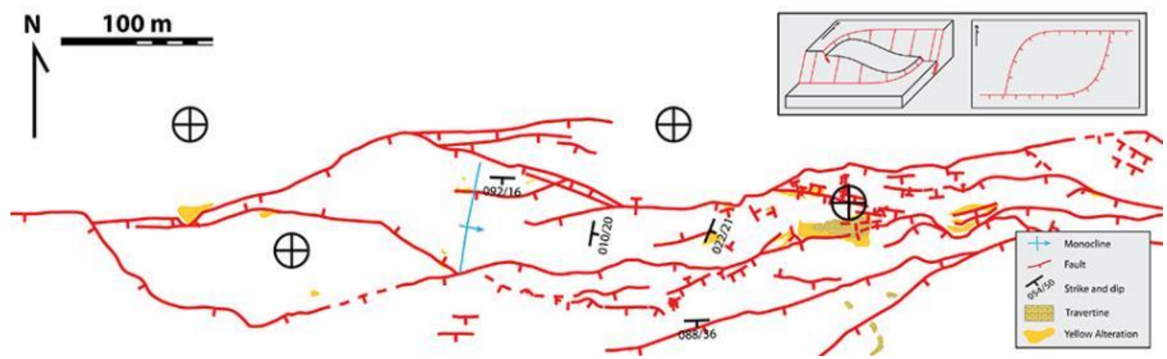
Evans et al. (2004)

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
- Different flow conduits active at different times
- 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



Evans et al. (2004)

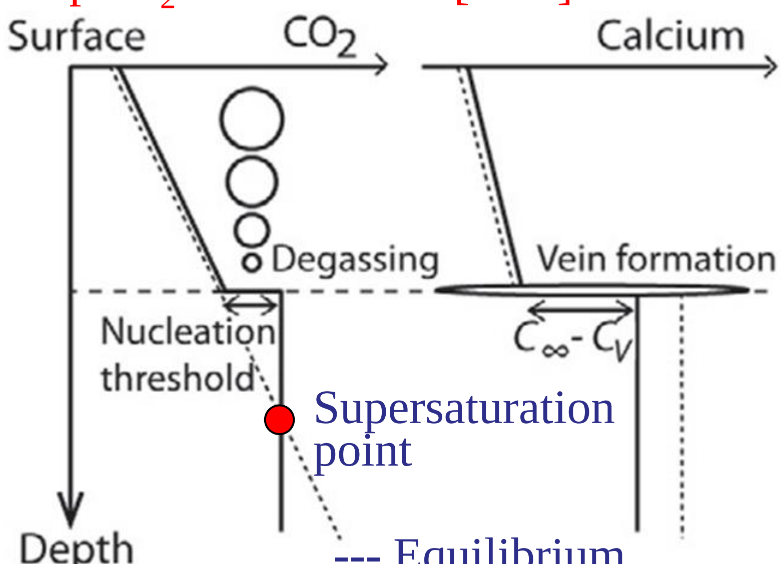


From Peter Eichhubl

Succinct chemistry & mineralogy

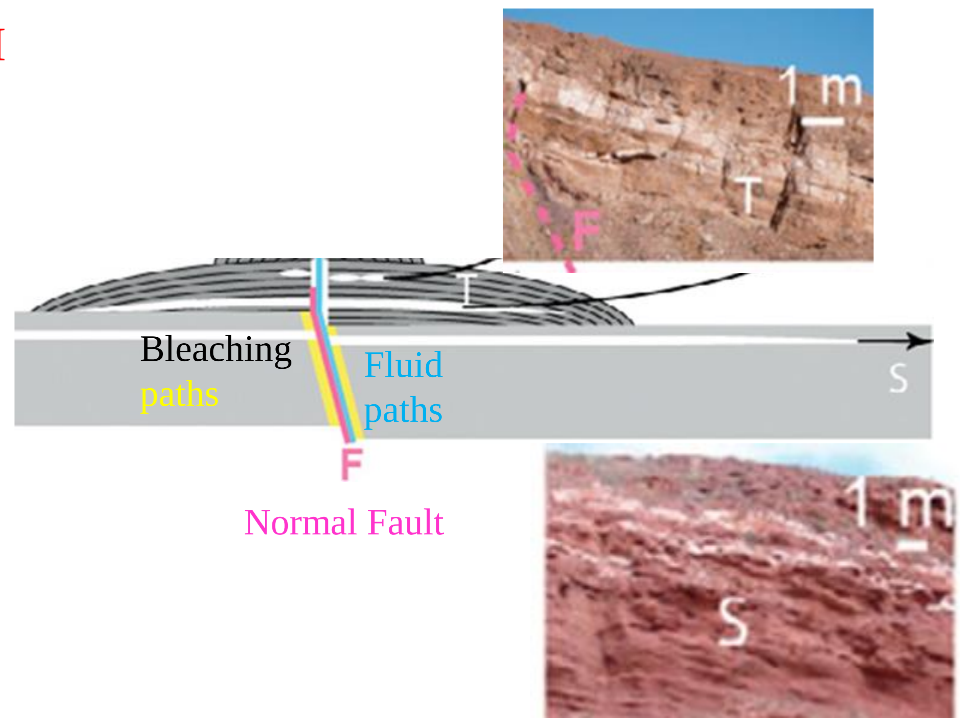
- Spring water: Low temperature and Mg concentrations
- Aragonite (metastable $CaCO_3$ phase) precipitation indicates large, sudden increase of supersaturation with respect to $CaCO_3$ in solution -> high CO_2 degassing rate
- Springs: high concentrations of dissolved CO_2 (pCO_2 = ~ 100 kPa)
- Both calcite and aragonite are present
- For some horizontal travertine veins, veins grow top to bottom (U-Th dating)

pCO_2 = ~100 kPa $[Ca^{2+}]$=7~192 mM



--- Equilibrium

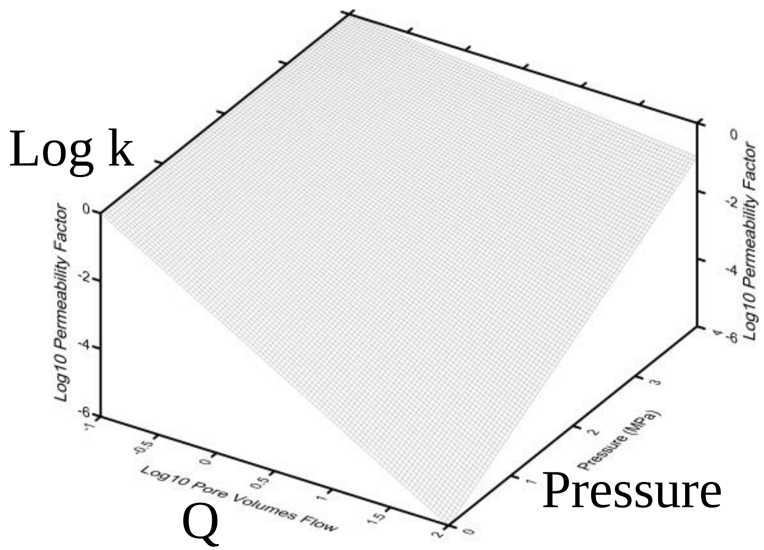
— Fluid conc.



Gratier et al., Geology, 2012

Crystal Geyser Site: Grand Wash Fault Modeling

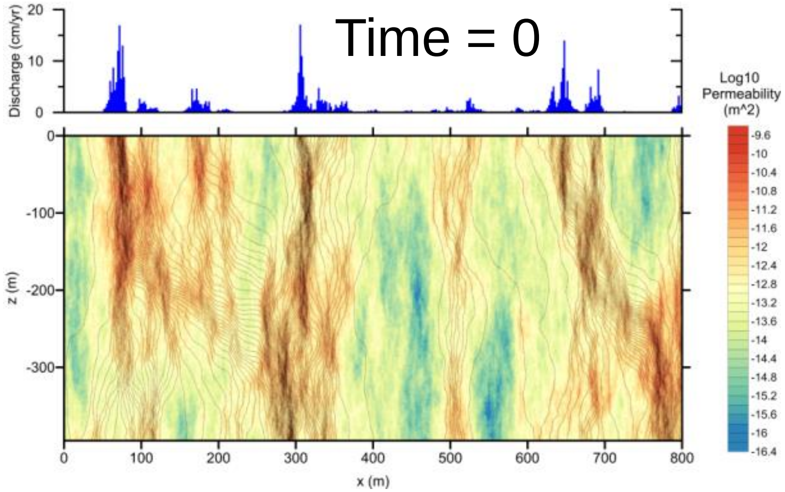
- Simplified, two-dimensional response surface
- Permeability reduction due to calcite precipitation is a function of cumulative pore volume (Q) of groundwater and fluid pressure (P)
- Fluid pressure is taken as a gross proxy for chemical conditions in which higher calcite solubility is associated with higher fluid pressure (greater depth)



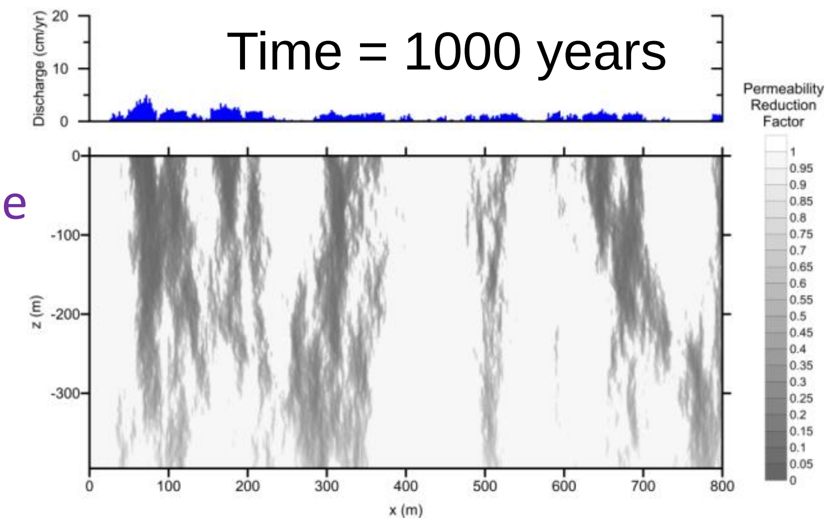
Adapted from Mehmani et al. (2012)

Crystal Geyser Site: Grand Wash Fault Modeling

- Unconditional geostatistical simulation
- Initial simulated steady-state flow pattern is qualitatively similar to the spacing of seeps along the Grand Wash fault (~100's of m between locations of groundwater discharge)



- Transient flow simulation includes explicit updating of k field at each time step using the response surface (FEHM)
- 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



Response Function based on Pore Scale Simulations

- Vigorously tested pore-scale model can be used to develop a response function (or dimension reduction model) for continuum-scale permeability and porosity (k-ε) relationships
- k-ε and surface area-ε relationships will be developed over a range of solution chemistry, chemical reaction, and pore structure configurations in addition to Pe and Da numbers

Changes in porosity due to precipitation ~tortuosity and permeability by phenomenological power law relations

$$\tau(\varphi) = \tau_0 \left(\frac{\varphi}{\varphi_0}\right)^n \qquad k(\varphi) = k_0 \left(\frac{\varphi}{\varphi_0}\right)^n \qquad a_{\mathrm{cc}} = a_{\mathrm{cc}}^0 \left(\frac{\varphi}{\varphi_0}\right)^{2/3}$$

Response Function based on Pore Scale Simulations

- Pe & Da numbers

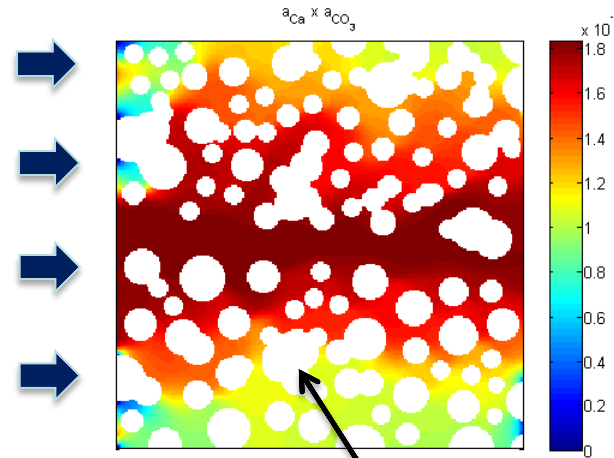
$Pe(uL/D) = 0.08, 0.8, 8$
$Da(kL/(K_{sp}^{0.5} \times D)) = 0.002, 0.02, 0.1$
$(K_{sp, calcite} = 3.3*10^{-9}\ M^2)$

- Chemical speciation

Speciation: Ca^{2+}, H^+, CO_3^{2-} HCO_3^- , H_2CO_3
No speciation: Ca^{2+}, CO_3^{2-}

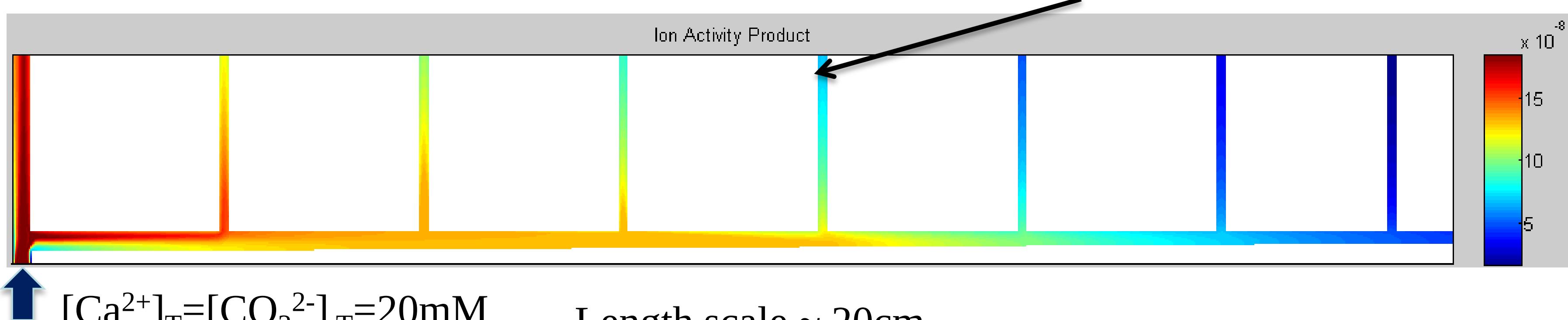
- Pore structures

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



Grain with reactive surface

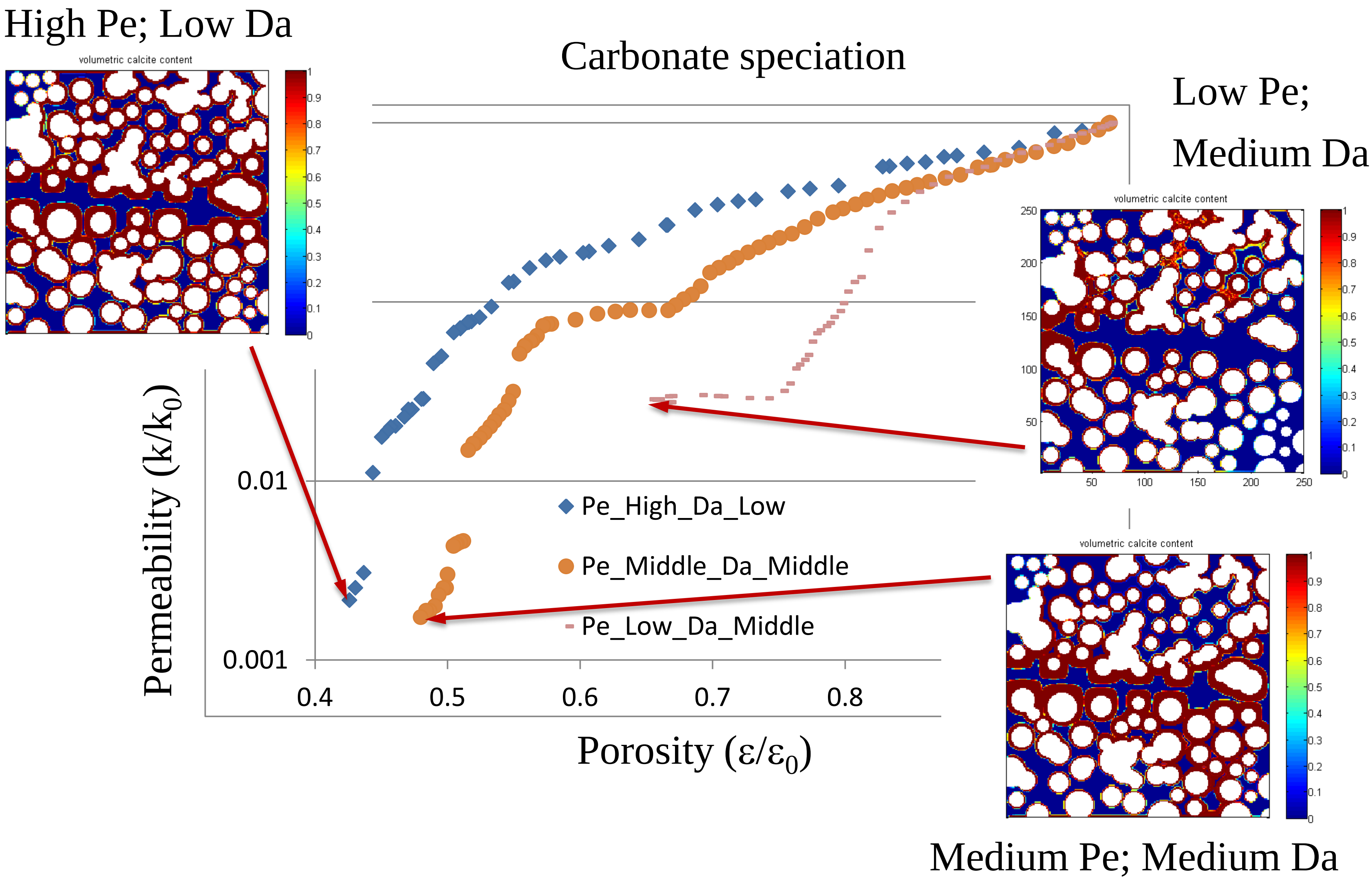
fracture network with varying apertures and patterns



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

Length scale ~ 20cm

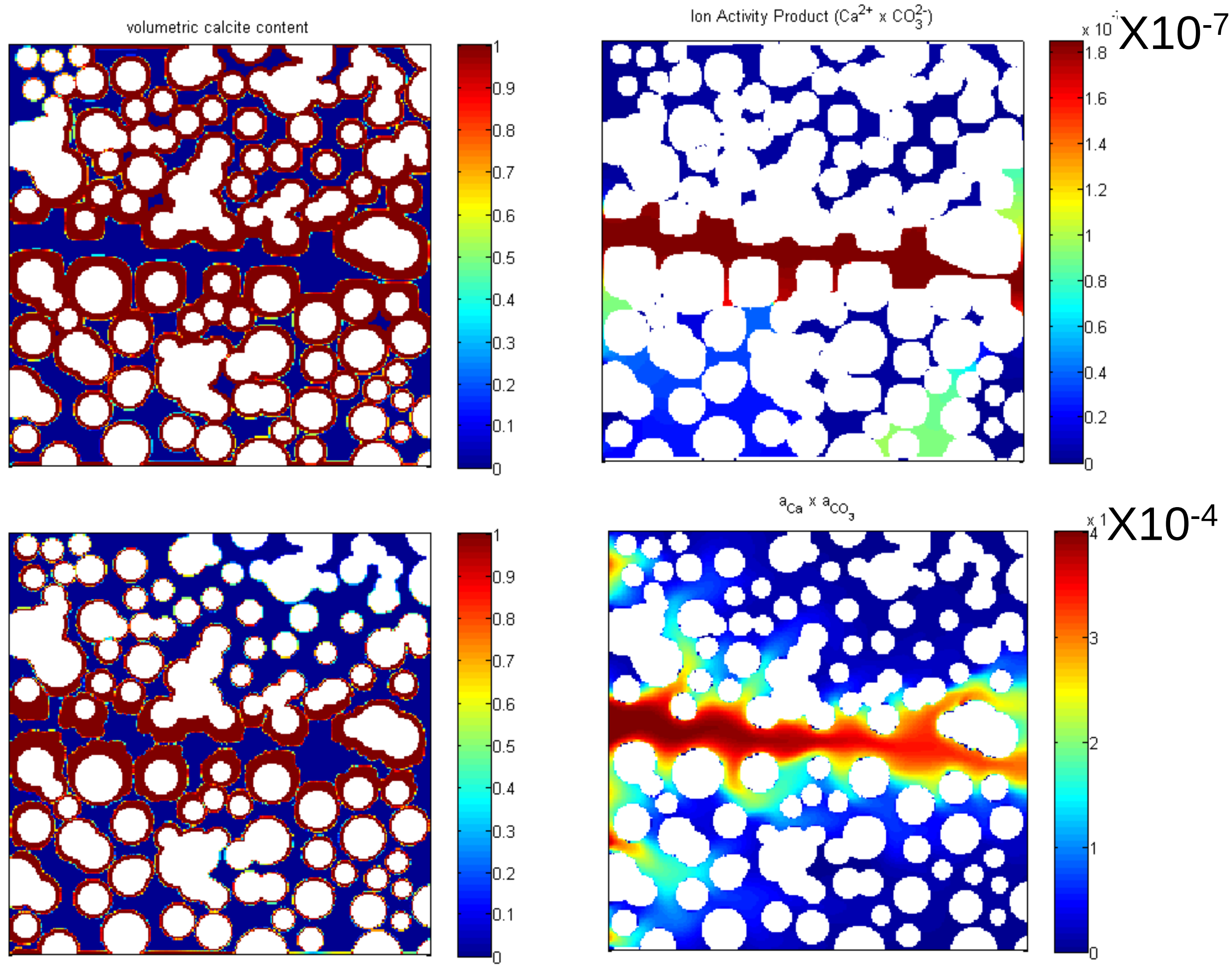
Permeability-Porosity Relationships



High Pe & Low Da

Speciation

No speciation

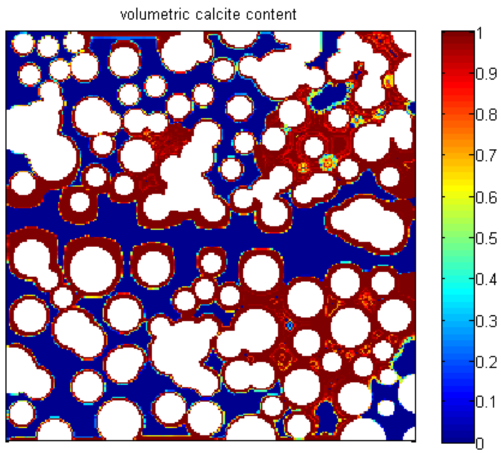


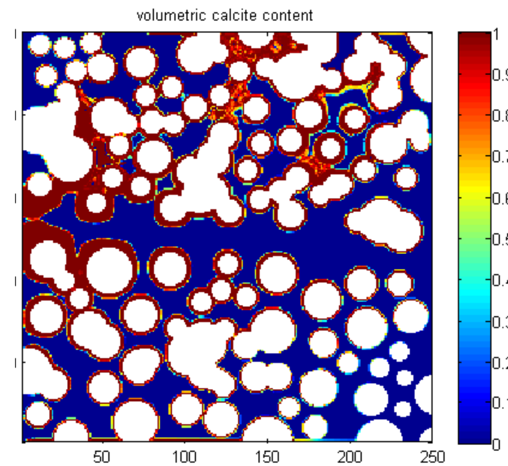
Pore clogging at the front

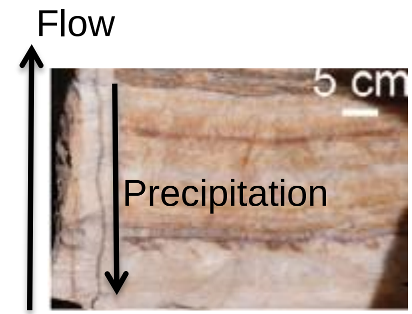
Medium Pe; High Da

Low Pe; Medium Da

Speciation

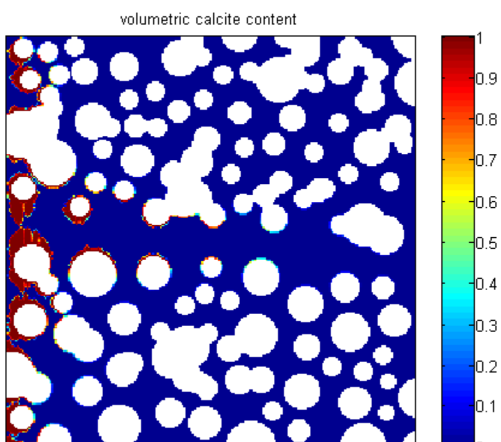


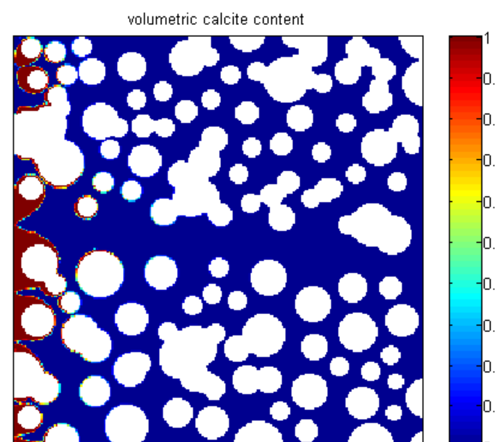




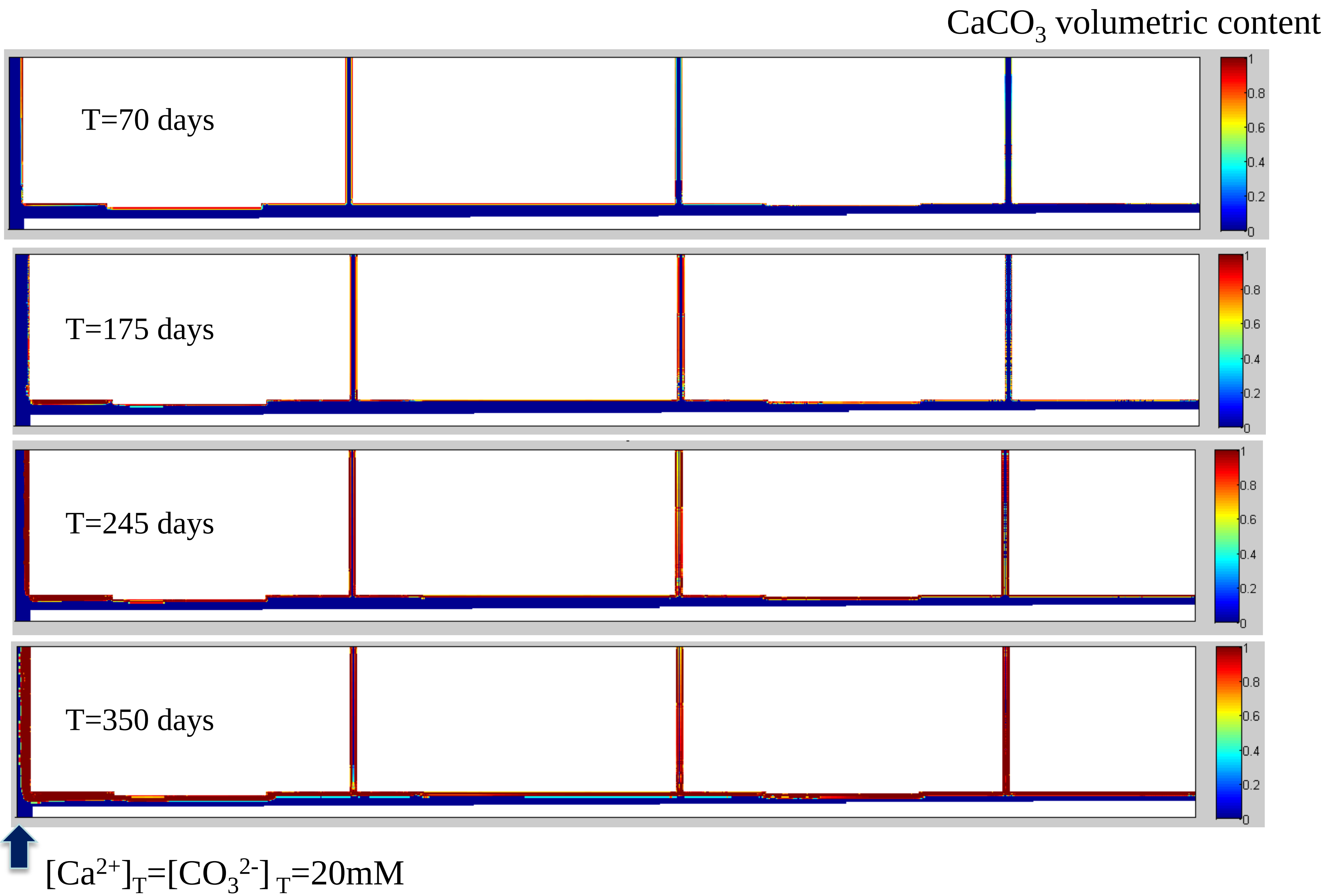
Gratier et al. (2012);
Crystal Geyser, Utah

No speciation



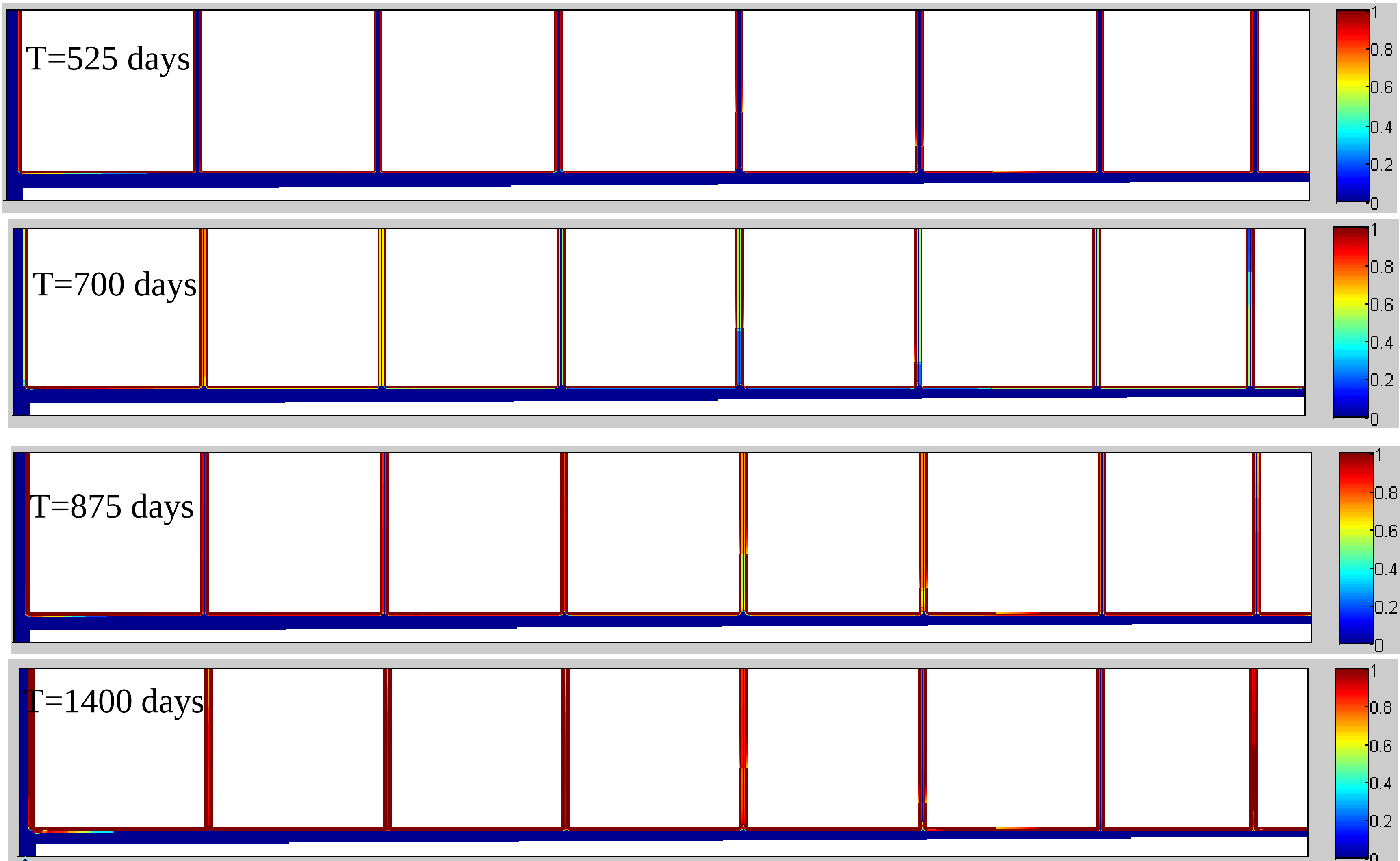


High Pe & High Da



High Pe & Medium Da

$CaCO_3$ volumetric content



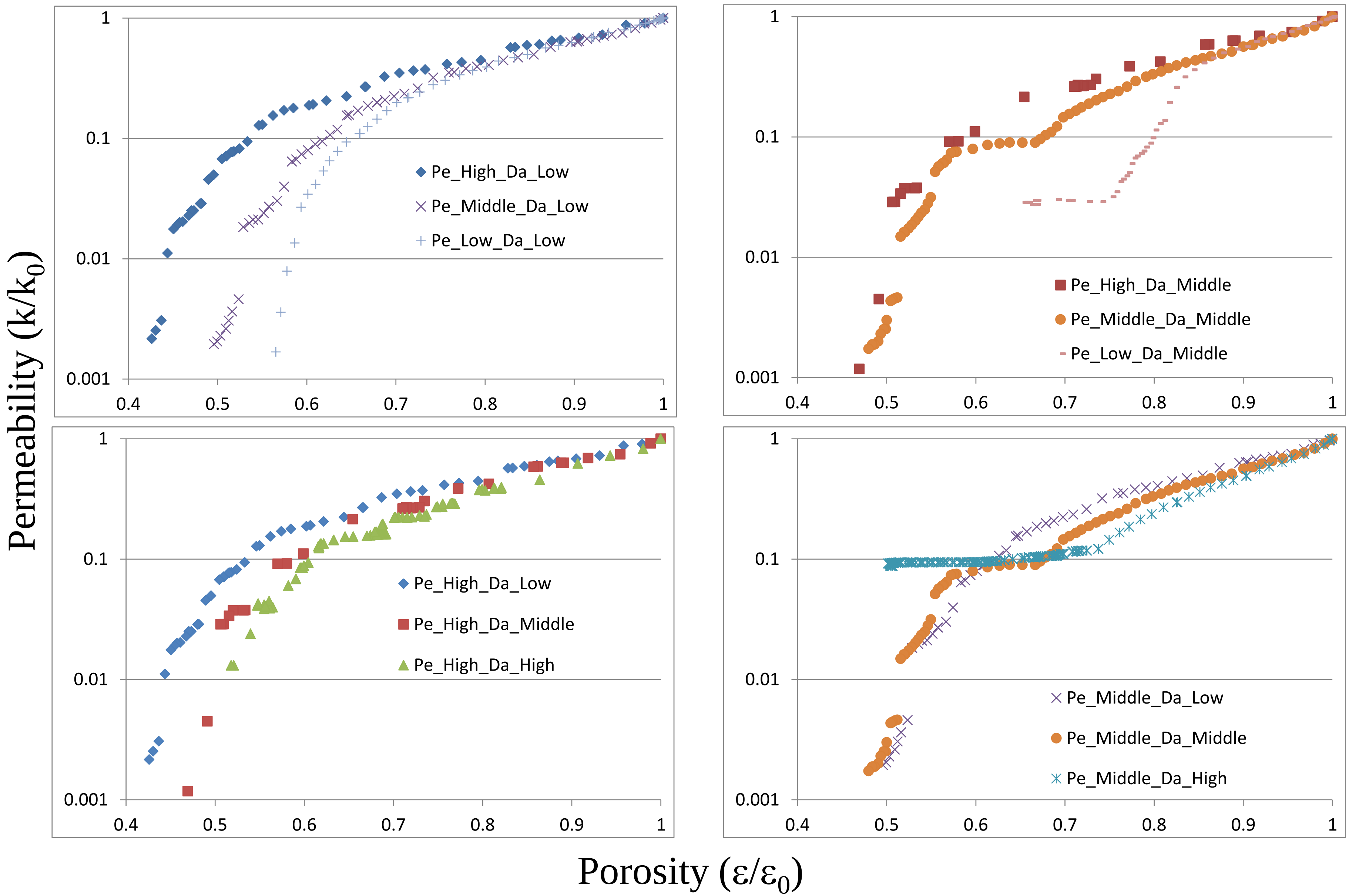
$[Ca^{2+}]_T=[CO_3^{2-}]_T=20mM$

Summary

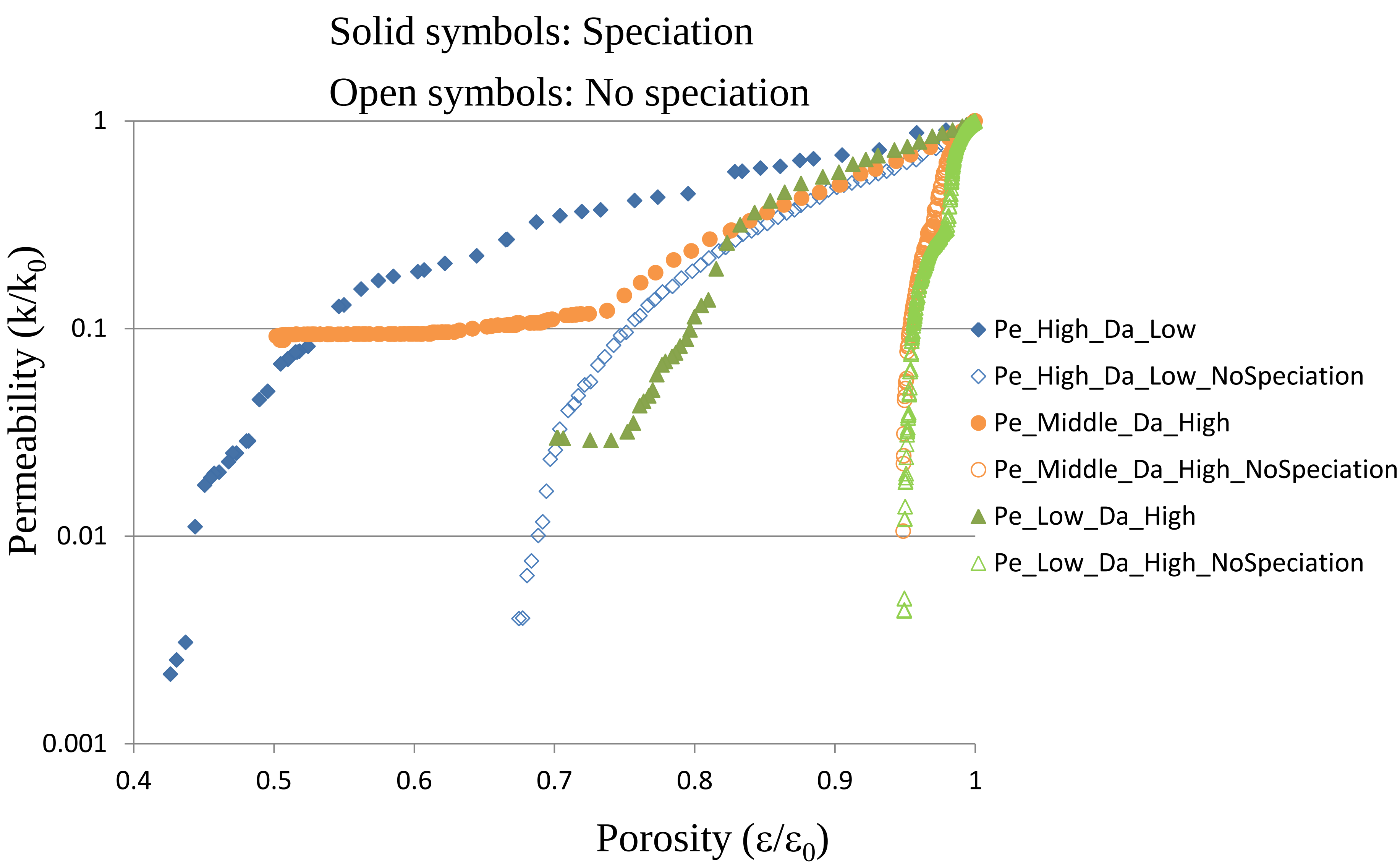
- Vigorously tested pore-scale model was used to develop a response function (or dimension reduction model) for continuum-scale permeability and porosity (k-ε) relationships
- Pore scale model was able to qualitatively capture pore clogging patterns observed at the Little Grand Wash Fault
- An adaptive strategy to couple pore- and continuum scale using a response function approach will be tested against travertine patterns observed in the Little Grand Wash Fault
- Algorithms developed in this work will be implemented into a continuum scale reactive transport model (p-FLOTRAN)

Questions?

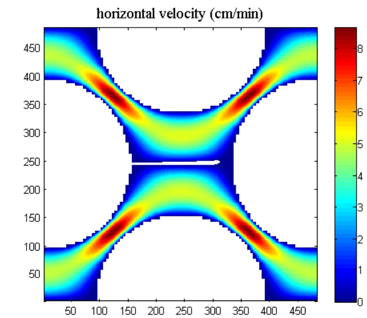
Permeability-Porosity Relationships



Chemical Speciation



Pore Scale Model Framework



Velocity at 1 micron resolution

Δt

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

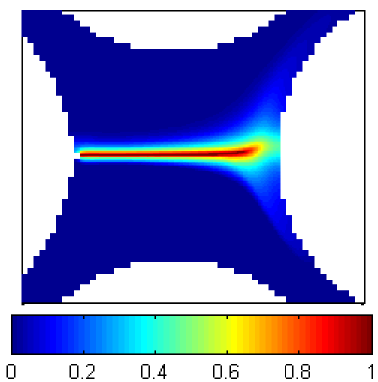
$$D \frac{\partial \Psi_j}{\partial \mathbf{n}} = -I_m$$

on reactive surface

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

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)

Fracture network