SAND2015-6748C

Mixing-controlled reactive transport at the pore scale and its impact on flow field and upscaling of reactive transport

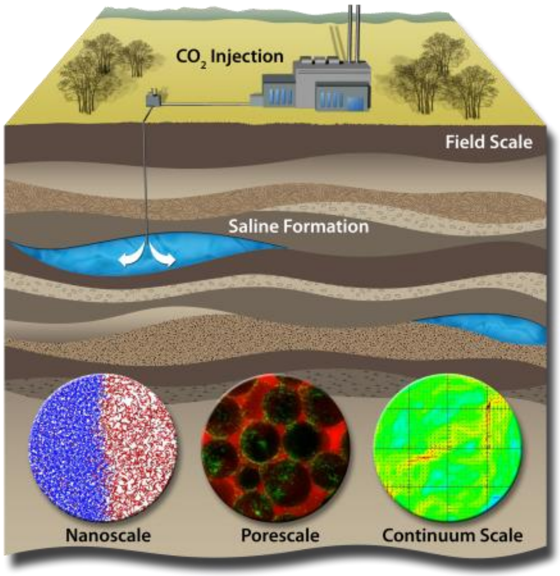
Hongkyu Yoon

August 20, 2015

Collaborators:

Thomas Dewers (SNL)

Jon Major, Peter Eichhubl (UT)



Sandia National Laboratories

Exceptional service in the national interest

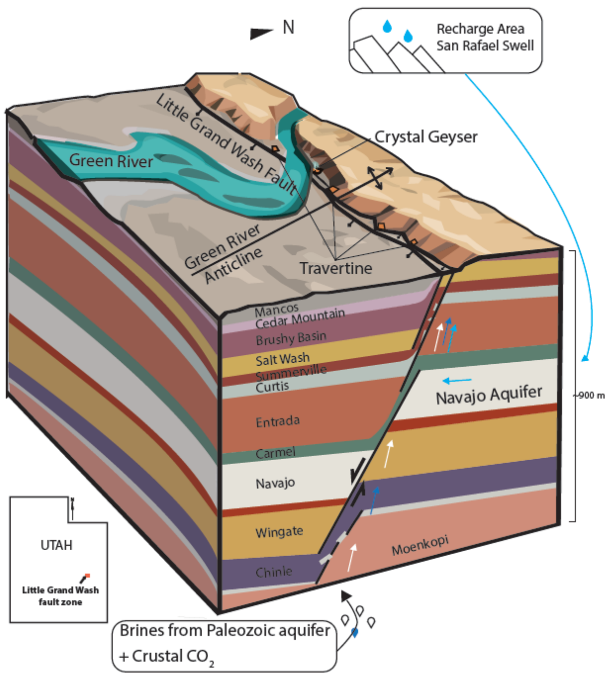
Acknowledgment: This work is supported as part of the Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001114.

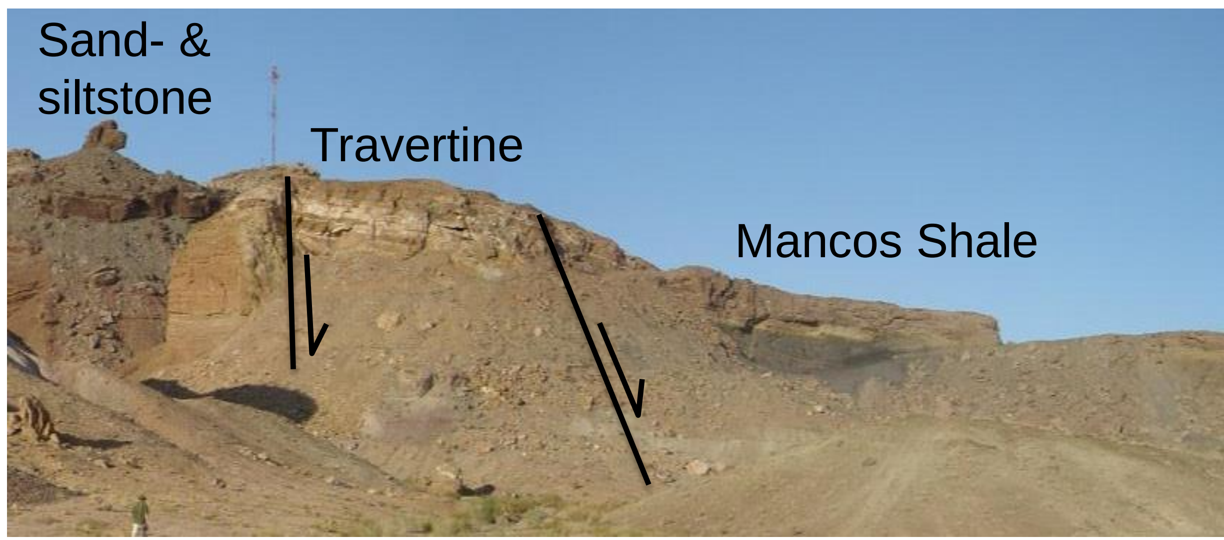
National Nuclear Security Administration

CFSES

Little Grand Wash Fault, Crystal Geyser, Utah

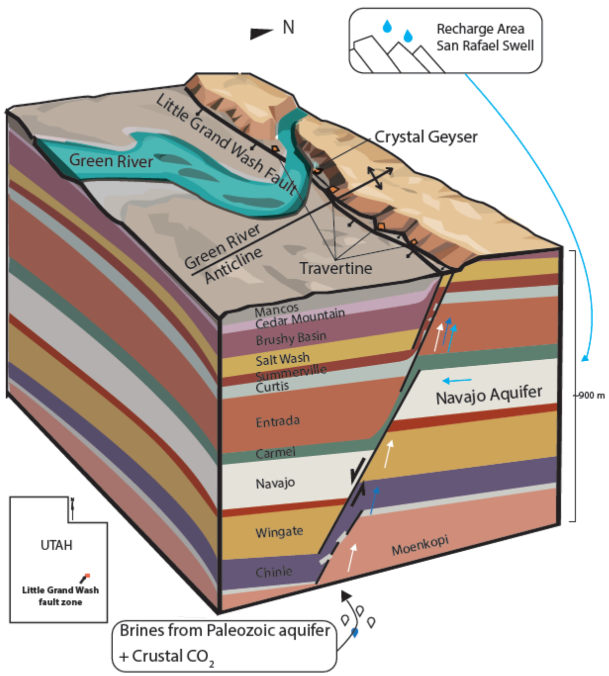
- Observations along the surface exposure of the Grand Wash fault indicate alteration zones of 10-50 m width with spacing on the order of 100 m
- Locations of conduits controlled by fault-segment intersections and topography
- Sandstone permeability reduced by 3 to 4 orders of magnitude in alteration zones by carbonate cementation





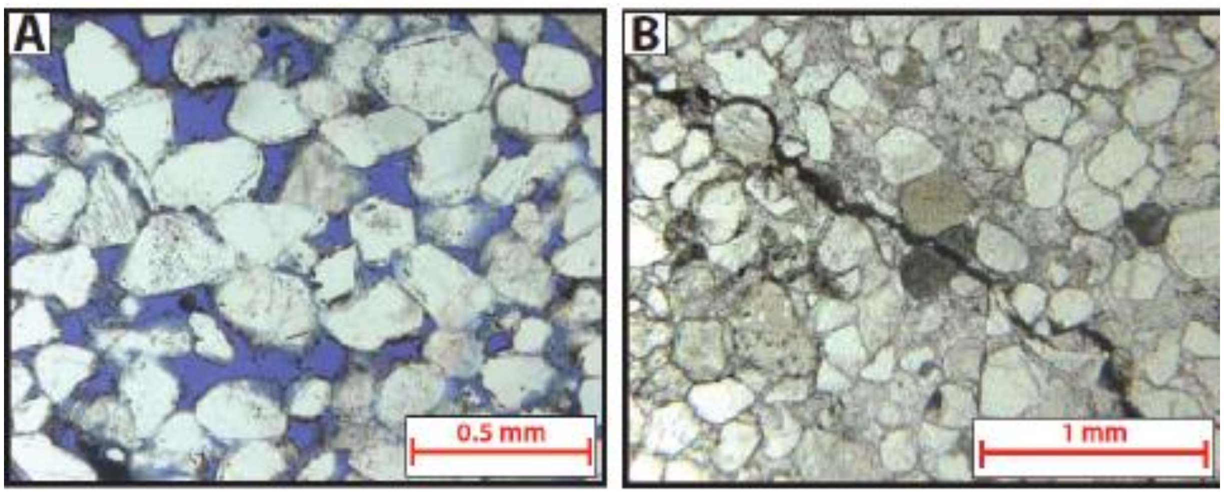
Little Grand Wash Fault, Crystal Geyser, Utah

- 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
- 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



Far from fault

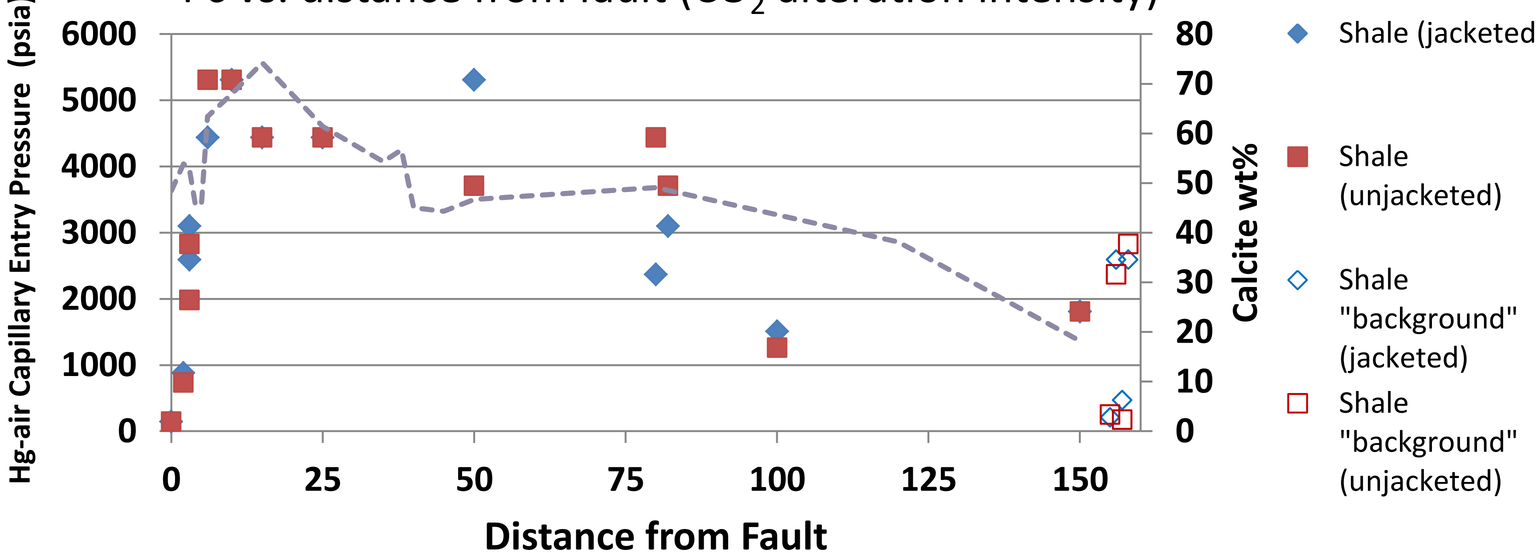
Near fault



Natural CO_2 alteration and shale seal capacity

Mancos Shale Transect

Pc vs. distance from fault (CO_2 alteration intensity)



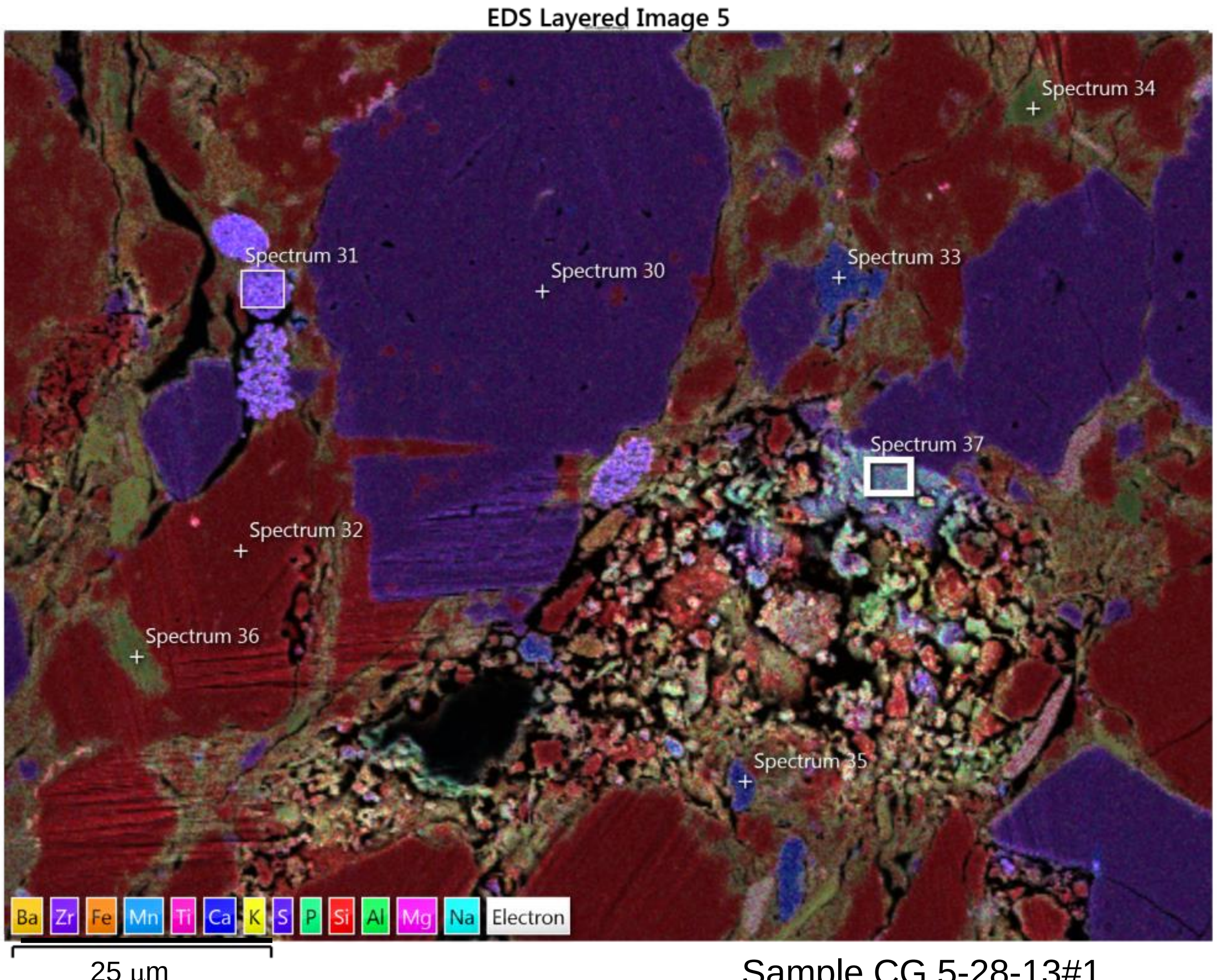
U.S. DEPARTMENT OF ENERGY | Office of Science

CFSES Center for Frontiers of Subsurface Energy Security

THE UNIVERSITY OF TEXAS AT AUSTIN

Sandia National Laboratories

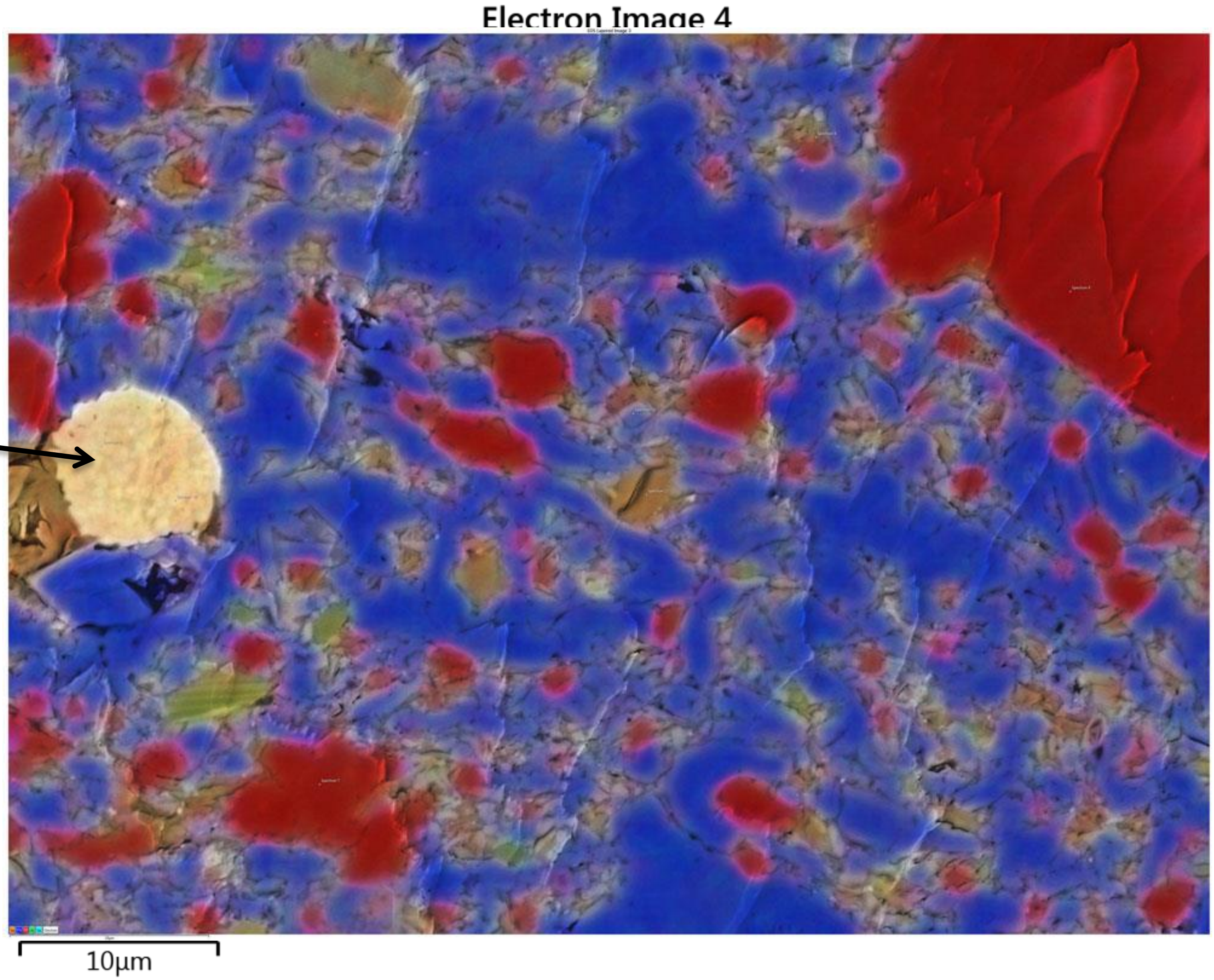
SEM images of unaltered shale (< 10 wt% carbonate)



Sample CG 5-28-13#1
Mancos Shale

SEM images of CO_2-altered shale (~60 wt% carbonate)

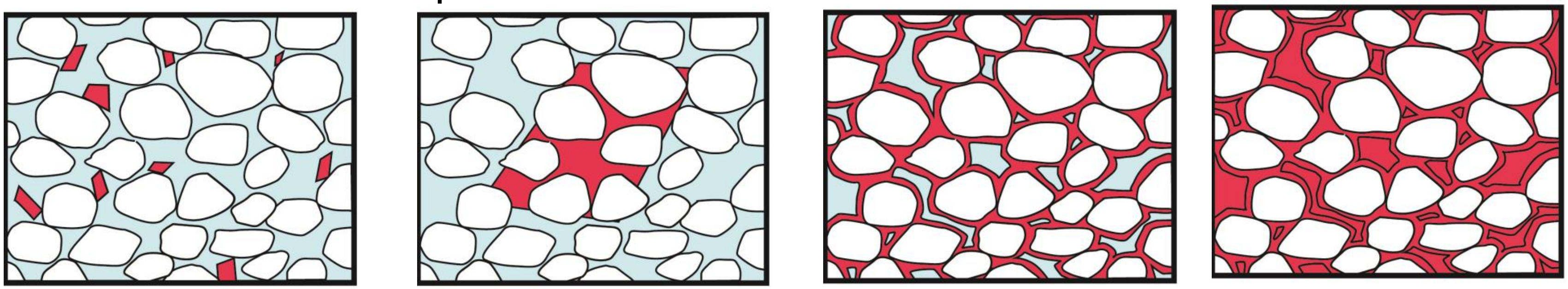
Pyrite framboid



Sample CG 5-23-12#6 (CO_2-altered Mancos Shale

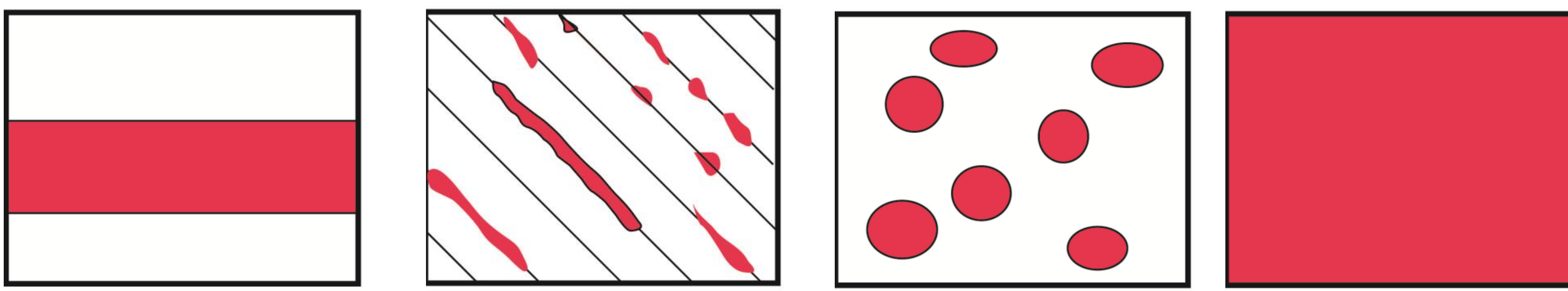
Conceptual Model of Cementation Patterns

Thin-Section Scale Spatial Distribution



Disseminated — Poikilotopic — Circumgranular — Pore filling

Lithofacies Scale Spatial Distribution



Cemented Layers — Textually Selective Concretions — Non-Textually Selective Concretions — Equal Distribution

Peter Mozley (NMT), Unpublished

U.S. DEPARTMENT OF ENERGY | Office of Science
CFSES Center for Frontiers of Subsurface Energy Security
THE UNIVERSITY OF TEXAS AT AUSTIN
Sandia National Laboratories

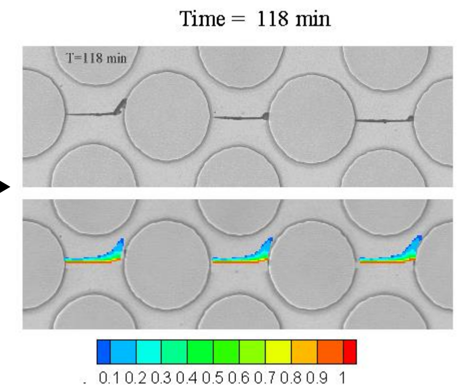
Reactive Transport Modeling Framework

- Pore scale reactive transport model can provide a tool to develop functional forms of reaction rates for $CaCO_3$ precipitation and dissolution as a function of system parameters based on fundamental principles without model assumptions
- Pore-scale modeling results will be able to develop the response functional forms of permeability, porosity, and surface area changes as a function of pore structures, volume, Pe, Da number, mineral types, and influent solution chemistry
- Response surface results can be used as input for continuum scale reactive transport modeling

System parameters

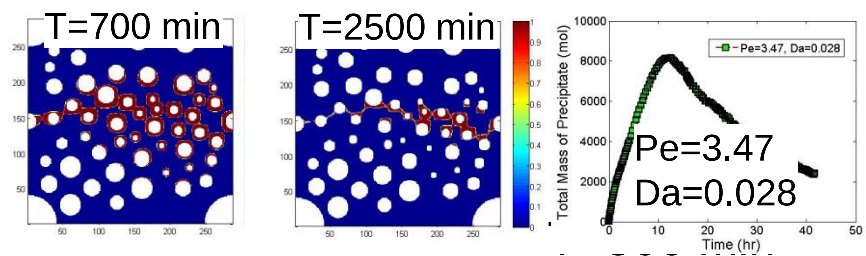
Flow rate, Mineral type

Chemistry (e.g., pH & CO3 conc)

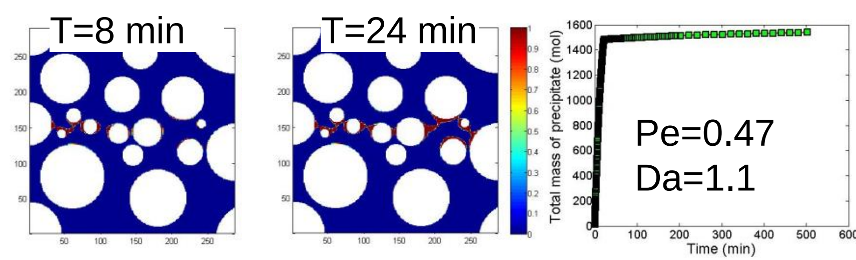


from Yoon et al. (2012)

Not far from equilibrium (log Q = ~0.7)

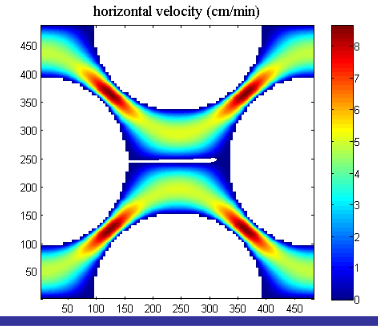


Far from equilibrium (log Q = ~3.7)



U.S. DEPARTMENT OF ENERGY | Office of Science | CFSES Center for Frontiers of Subsurface Energy Security | THE UNIVERSITY OF TEXAS AT AUSTIN | Sandia National Laboratories

Pore Scale Model Framework



Velocity at 1 micron resolution

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

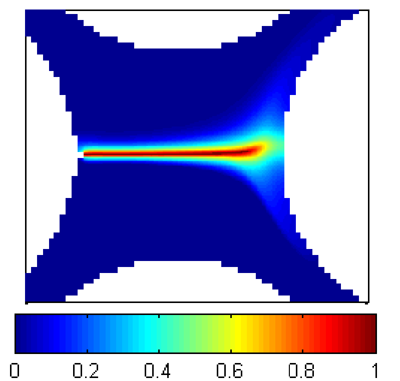
$$D \frac{\partial \Psi_j}{\partial \mathbf{n}} = -I_m$$

on reactive surface

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

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)

Functional Relationships based on Pore Scale Simulations

- Pe & Da numbers

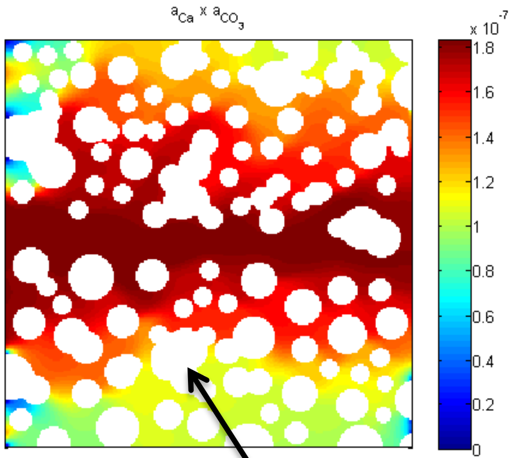
$Pe(uL/D) = 0.08, 0.8, 8$
$Da(kL/(K_{sp}^{0.5} \times D)) = 0.002, 0.02, 0.1$
$(K_{sp,\ calcite} = 3.3*10^{-9}\ M^2)$

- Chemical speciation

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

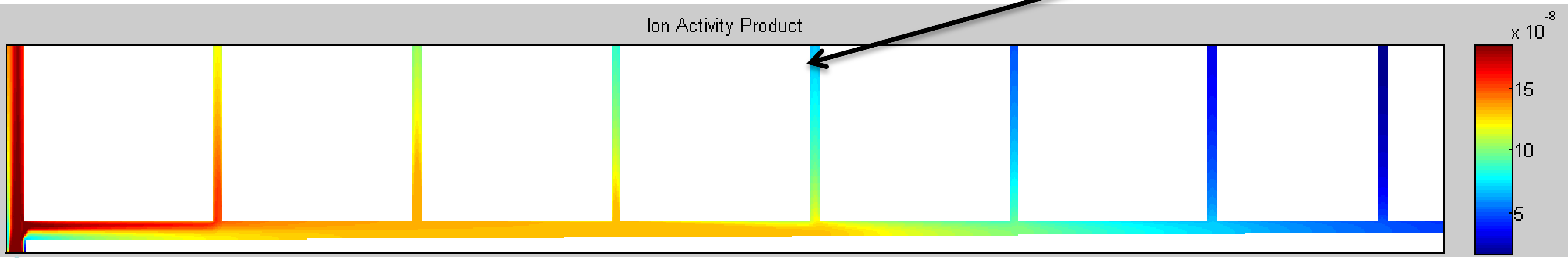
- Pore structures

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



Grain with reactive surface

fracture network with varying apertures and patterns



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

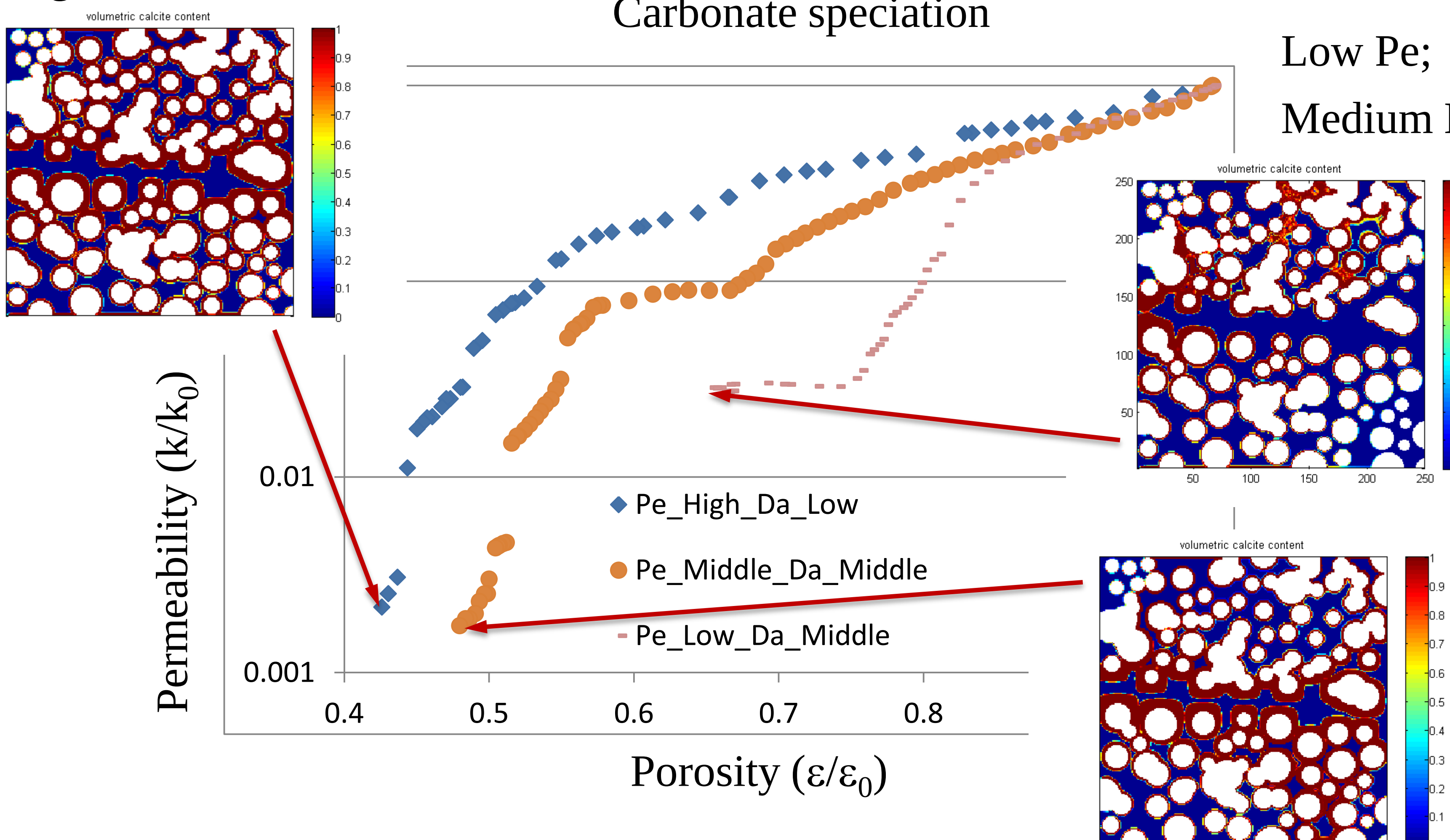
Length scale ~ 20cm

Yoon et al. (in prep)

Permeability-Porosity Relationships

High Pe; Low Da

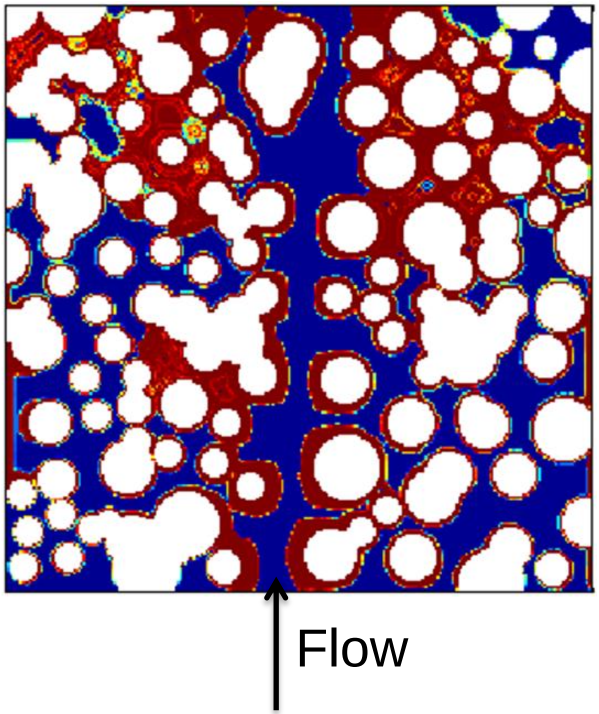
Low Pe; Medium Da



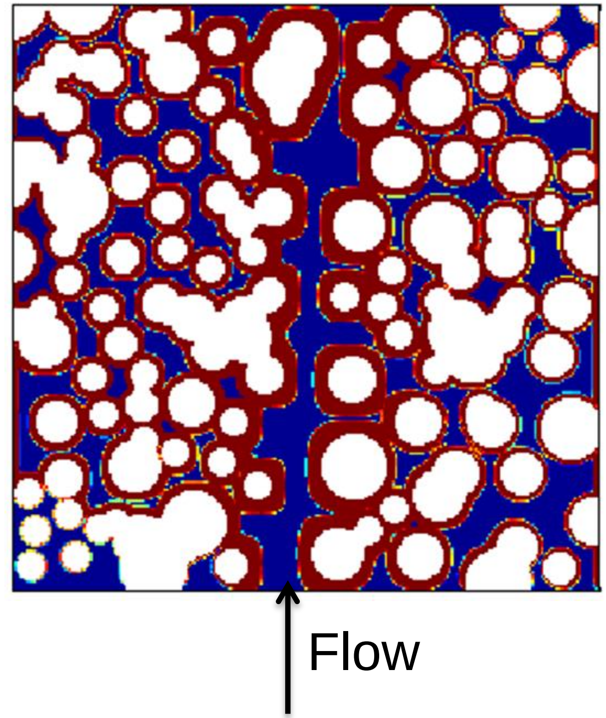
Medium Pe; Medium Da

Direction of precipitation and pore clogging

Medium Pe & High Da

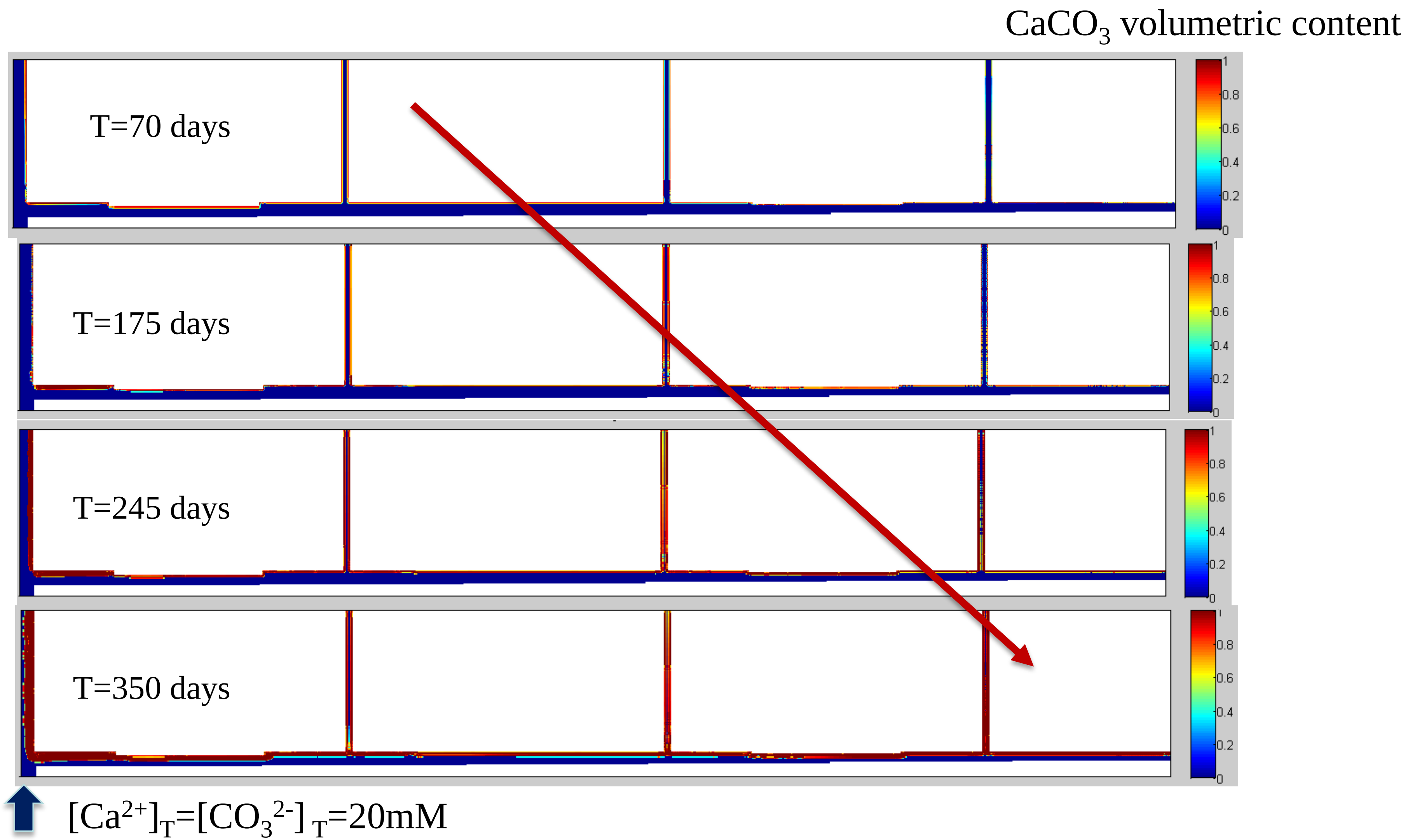


High Pe & Low Da



- Simulation results under two different Pe and Da regimes show fast precipitation from the top – this example show multiple possible pathways for field observations

High Pe & High Da



- Precipitation occurs near the main fault and clogging of fracture networks moves away from the main fault conduit as observed in the outcrop

Summary

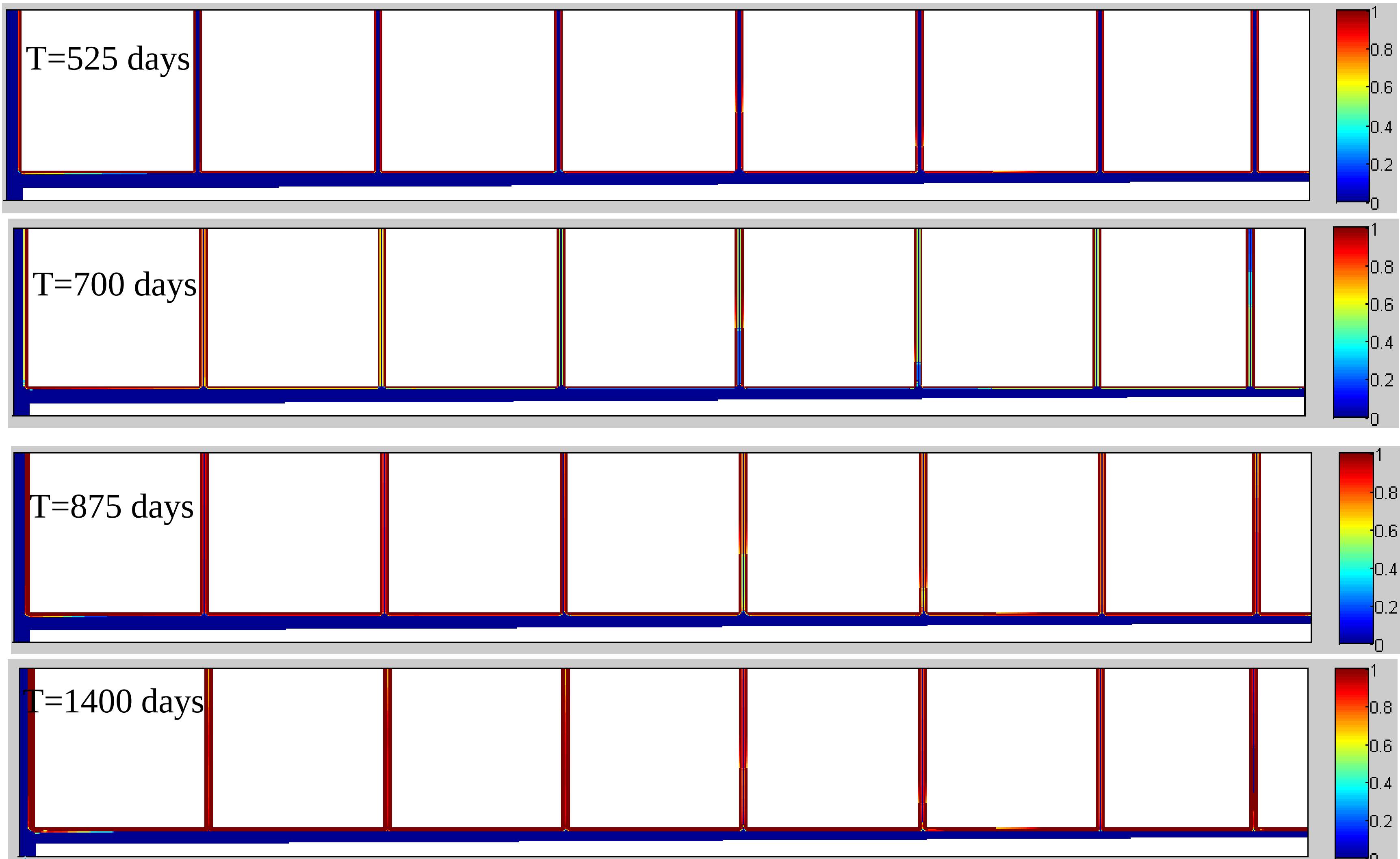
- Fault-controlled CO2 leakage conduits are sites of preferred carbonate pore and fracture cementation
- Carbonate cementations significantly increases caprock sealing capacity
- Vigorously tested pore-scale model was used to develop a permeability and porosity (k-ε) relationship for continuum-scale model
- Pore scale model was able to qualitatively capture pore clogging patterns in a simple fracture network model mimicking the Little Grand Wash fault
- An adaptive strategy to couple pore- and continuum scale will be tested against cement precipitation patterns observed in the Little Grand Wash fault
- Algorithms developed in this work will be implemented into a continuum scale reactive transport model

Questions?

Back-Up Slides

High Pe & Medium Da

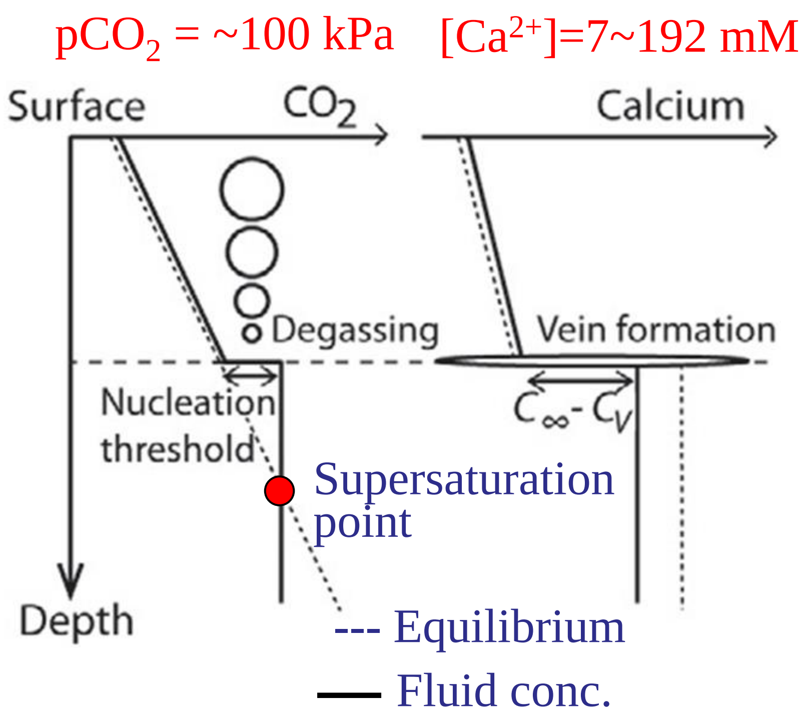
$CaCO_3$ volumetric content

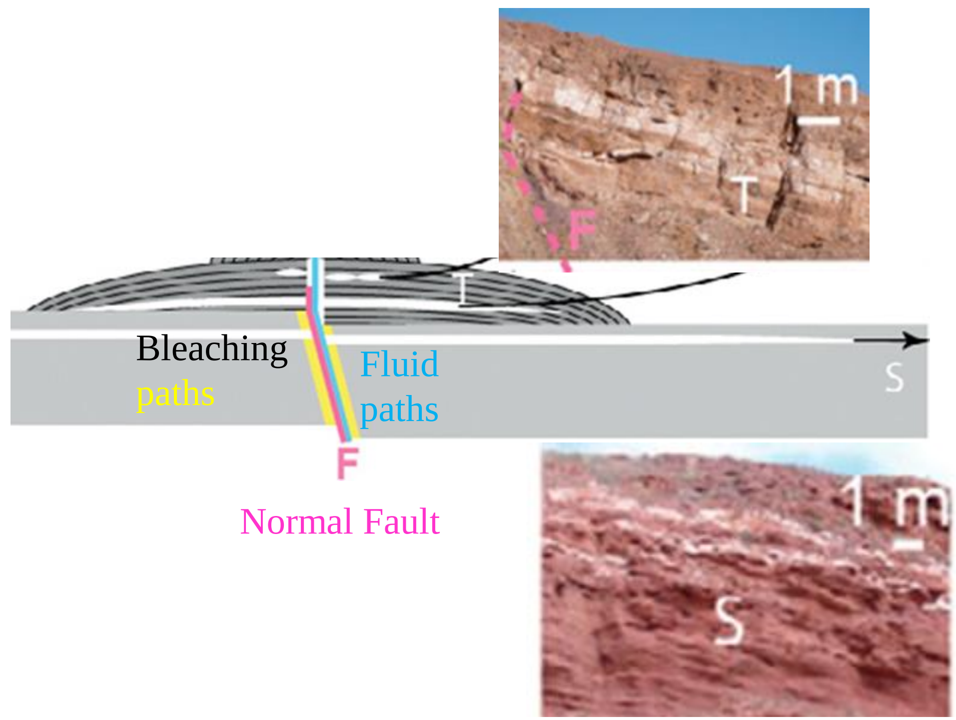


$[Ca^{2+}]_T=[CO_3^{2-}]_T$=20mM

Simple chemistry & mineralogy

- Spring water: Low temperature and Mg concentrations; high concentrations of dissolved CO_2 (pCO_2 = ~ 100 kPa)
- Aragonite precipitation indicates large, sudden increase of supersaturation with respect to $CaCO_3$ in solution -> high CO_2 degassing rate
- Both calcite and aragonite are present

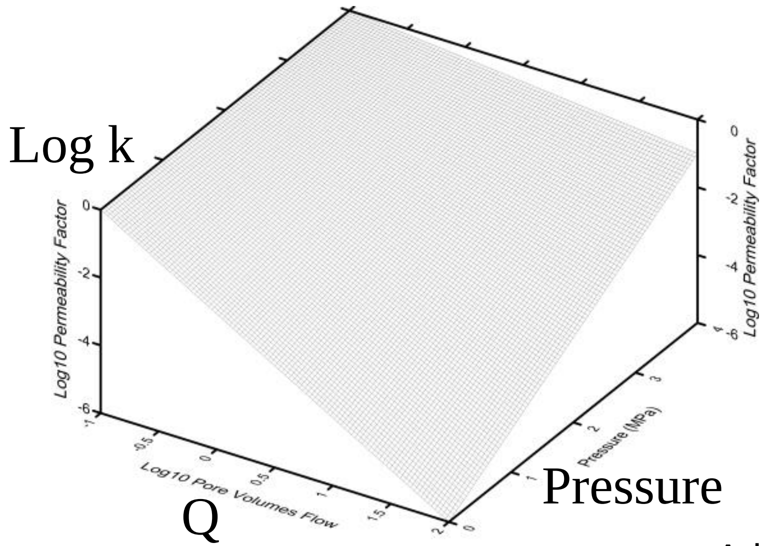




Gratier et al., Geology, 2012

Continuum Scale Reactive Transport Modeling

- Simplified, two-dimensional response surface
- Permeability reduction due to $CaCO_3$ 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 $CaCO_3$ solubility is associated with higher fluid pressure (greater depth)

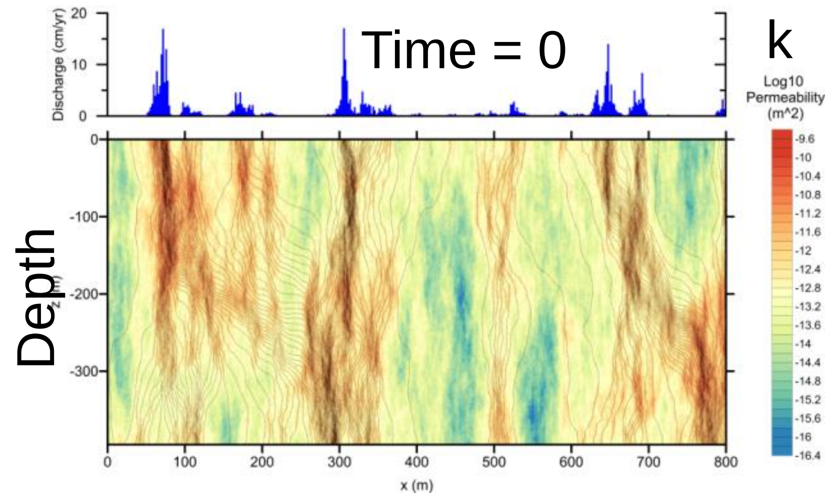


Adapted from Mehmani et al. (2012)

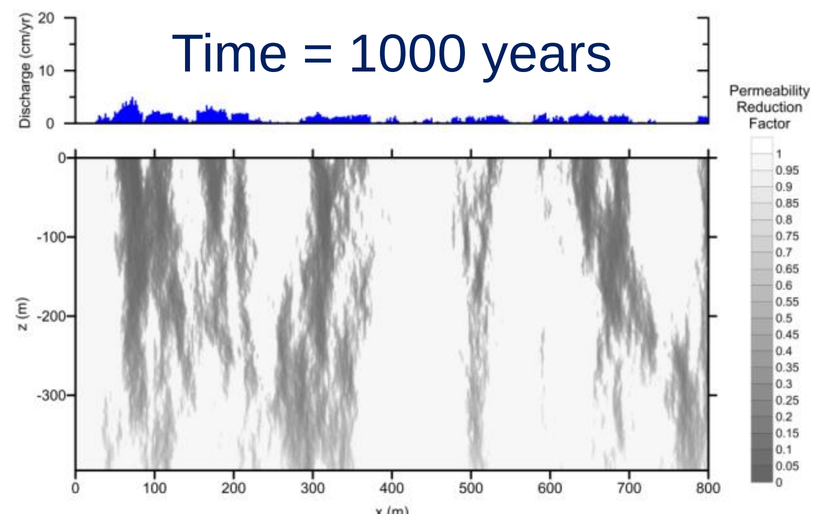
Crystal Geyser Site: Grand Wash Fault Modeling

- 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)

Discharge at the surface



- Transient flow simulation includes explicit updating of permeability (k) 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



Permeability reduction factor

U.S. DEPARTMENT OF ENERGY | Office of Science

CFSES Center for Frontiers of Subsurface Energy Security

THE UNIVERSITY OF TEXAS AT AUSTIN

Sandia National Laboratories

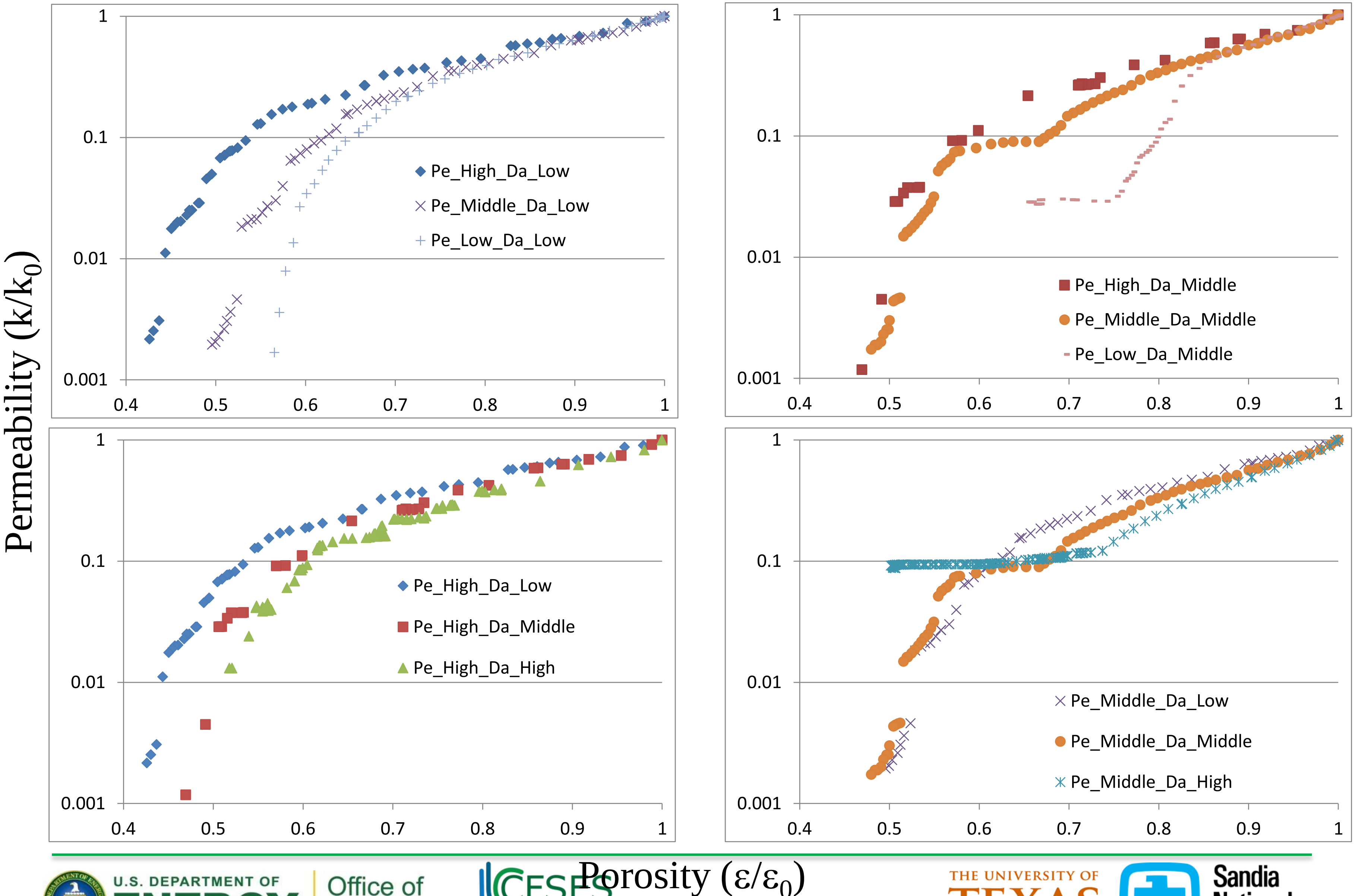
Functional relationships based on Pore Scale Simulations

- 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

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

Permeability-Porosity Relationships



U.S. DEPARTMENT OF ENERGY | Office of Science

CFSES Center for Frontiers of Subsurface Energy Security

THE UNIVERSITY OF TEXAS AT AUSTIN

Sandia National Laboratories

Field Observations