Lawrence Livermore National Laboratory

Enhanced porosity and permeability in carbonate CO_2 storage reservoirs: An experimental and modeling study

Project Number: FWP-FEW0174 – Task 5

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the
Infrastructure for CO_2 Storage
August 21-23, 2012

Presenter: Susan Carroll
Yue Hao
Megan Smith

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Presentation Outline

- Benefit to Program
- Project Overview
- Technical Status
- Accomplishments
- Summary
- Appendix

Benefit to the Program

- This research project quantifies relationships between fluid flow, heterogeneity, and reaction rates specific to carbon storage in carbonate reservoirs by integrating characterization, solution chemistry, and simulated data.

- This project meets the Carbon Storage Program goals to develop technologies that will support industries' ability to predict CO_2 storage capacity in geologic formations to within ±30 percent.

Project Overview

Goals and Objectives

- The goal of this project is to calibrate key parameters in reactive transport models that will be used to predict final storage of CO_2 in carbonate EOR fields.

- This project will advance science-based forecasting for the transition of CO_2 – EOR operations to storage sites.

- Success is tied to the ability to scale reactive-flow and transport parameters from the pore scale to larger scales where characterization data are limited.

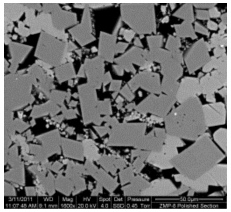
Technical Status

- The research scope consists of three major tasks:
  - Model calibration against existing experimental data base on carbonate rocks from the Midale-Weyburn Carbon Storage Project (focus of today’s presentation)
  - Experimental and characterization data at larger scales (less detail)
  - Refined model and parameter scaling towards predicting changes in reservoir porosity and permeability

Motivation & Objectives

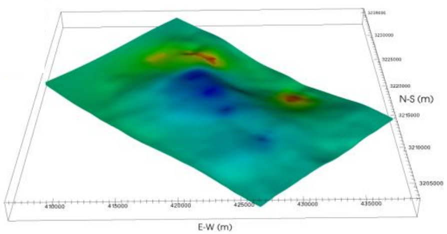
- The chemical mineral-fluid interactions induced by CO_2 injection have a major effect on rock porosity and permeability evolution, which may potentially alter the behavior or performance of CO_2 geological storage and EOR operations;

- The mineral dissolution/precipitation and associated flow and reactive transport processes in porous media are described at different scales;



Pore (microscopic) scale ~ µm

Core (laboratory) scale ~ cm

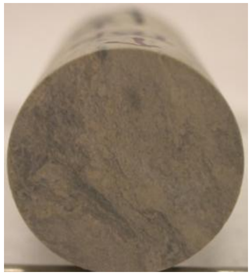


Large (reservoir/field) scale ~ km

- Reactive transport modeling represents a critical component in assessment of geochemical impact of CO_2 water-rock interactions;

- **However, a lack of proper calibration or upscaling of the effective macroscopic parameters over large field-scales hinders accurate reactive-transport modeling of CO_2 fate and transport.**

Reservoir Units and Core Sample Collection

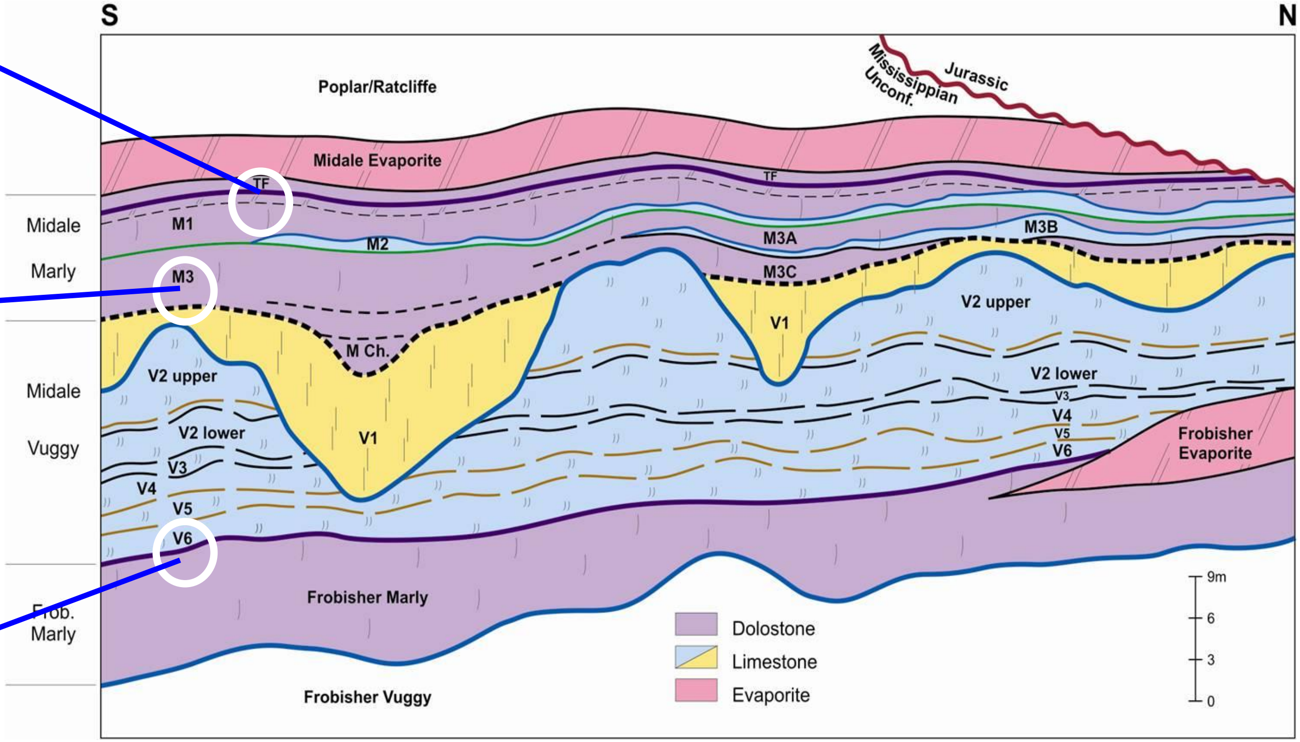


Three Fingers Evaporite

Midale Marly Dolostone

Midale Vuggy Limestone

Weyburn Flow Unit Model

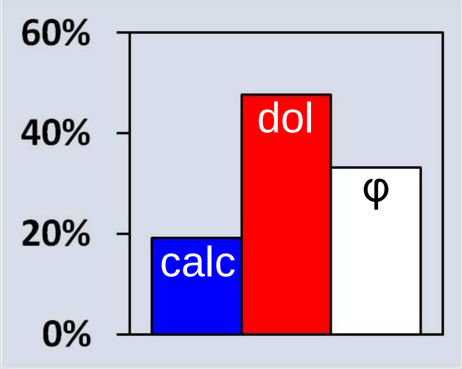


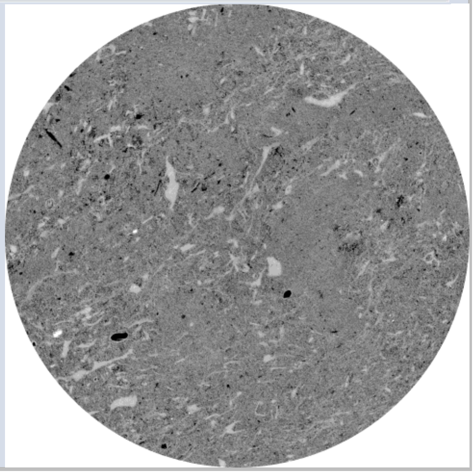
from Whittaker, PTRC

Reservoir flow units have different properties

Marly Dolostone

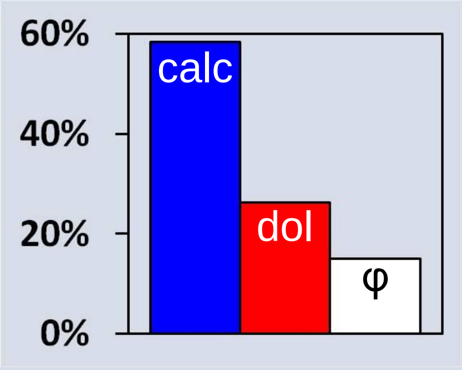
k_{init} 1-2 mD

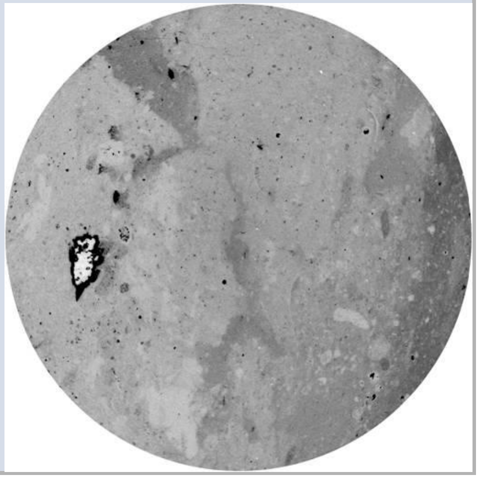




Vuggy Limestone

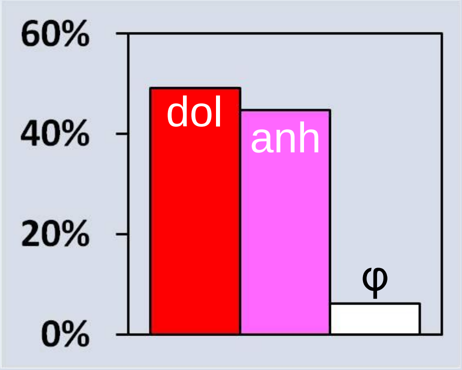
k_{init} 0.01-0.03 mD





Three Fingers Evaporite

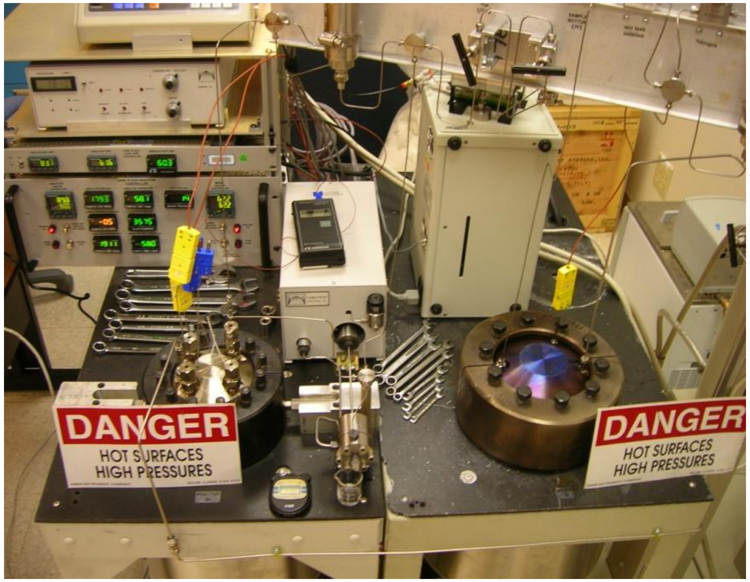
k_{init} = 0.5 μD

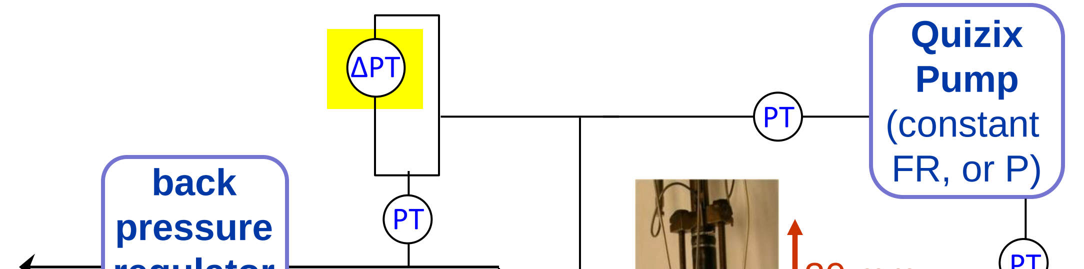


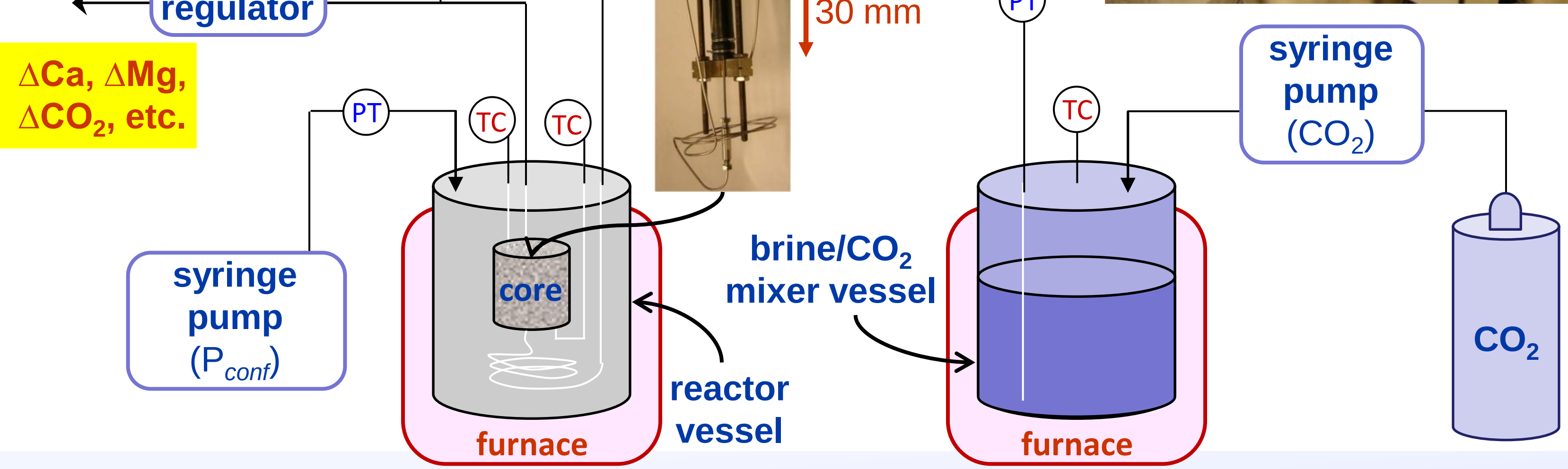
- XCMT images provided by Yelena Sholokhova

Core-Flood Experimental Conditions

- T = 60°C
- FR = 0.05 $^{mL}/_{min}$*
- P_{conf} = 24.8MPa
- P_{out} = 12.4 MPa
- 1.1m NaCl brine, equilibrium with calcite
- fluid pCO_2 = 3; 2; 1; and 0.5 MPa







Reactive Transport Modeling of CO_2 Core Flooding Experiments

- ☐ 3-D continuum-scale reactive transport models
- ☐ Boundary conditions mimic those observed under experiments
- ☐ Dolomite and calcite reaction kinetics

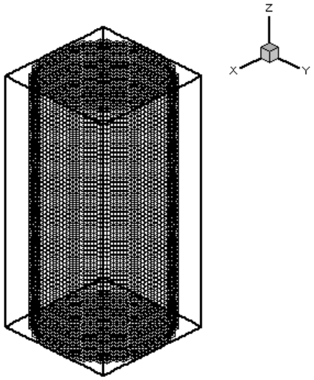
$$\frac{dn}{dt} = -Sk_{298.15}\, e^{-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)}\left(1-\frac{Q}{K_{eq}}\right)$$

- ☐ Porosity – Permeability – Surface Area

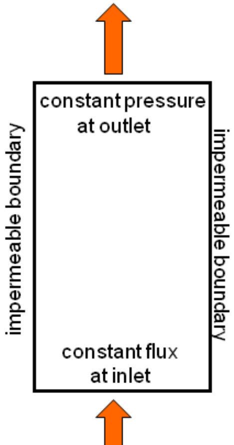
$$K = K_0\left(\frac{\phi}{\phi_0}\right)^n$$

$$S = S_0\left(\frac{C}{C_0}\right)^{2/3}\left(\frac{\phi}{\phi_0}\right)^{2/3}$$

Core Sample



Grid = 250 microns



Model Domain

Reactions
calcite + H^+ = Ca^{++} + HCO_3^-
dolomite + $2H^+$ = Ca^{++} + Mg^{++} + $2HCO_3^-$
$CO_{2(aq)}$ + H_2O = H^+ + HCO_3^-
$MgHCO_3^+$ = Mg^{++} + HCO_3^-
$CaCO_{3(aq)}$ + H^+ = Ca^{++} + HCO_3^-
$CaHCO_3^+$ = Ca^{++} + HCO_3^-

Summary of parameter results for 3D continuum model

- Chemical Model - Use laboratory derived parameters
  - Rate equations tied to equilibrium
  - Rate constants
  - Activation energies – temperature dependence
  - Equilibrium constants (slight adjustment for dolomite)

$$\frac{dn}{dt} = -Sk_{298.15}\, e^{-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)}\left(1-\frac{Q}{K_{eq}}\right)$$

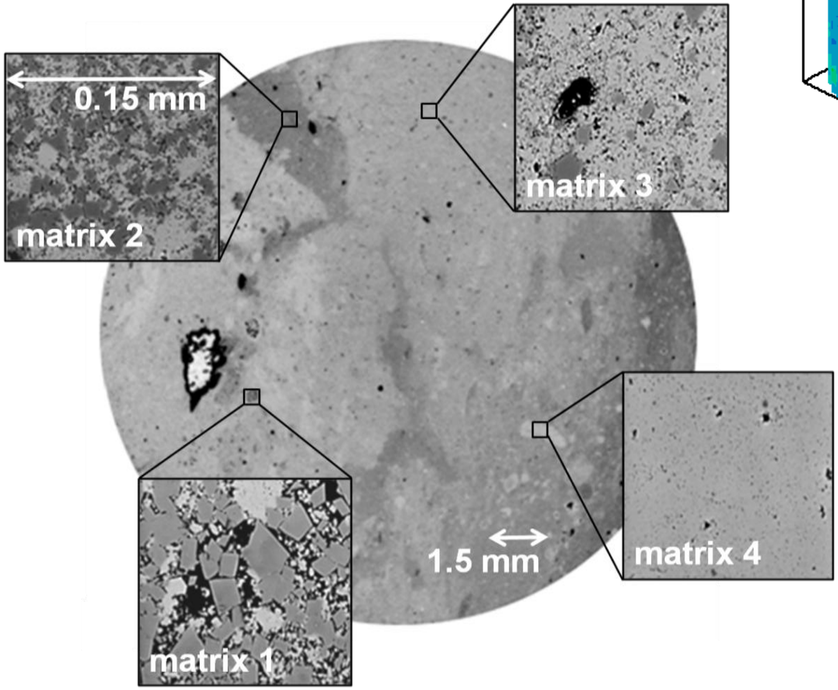
- Porosity – Permeability – Surface Area
  - Change surface area in proportion to decreasing spherical grains
  - “n” is dependent on sample heterogeneity
  - Porous and homogeneous Marly, n = 3
  - Impermeable and heterogeneous Vuggy, n = 8

$$S = S_0 \left(\frac{C}{C_0}\right)^{2/3} \left(\frac{\phi}{\phi_0}\right)^{2/3}$$

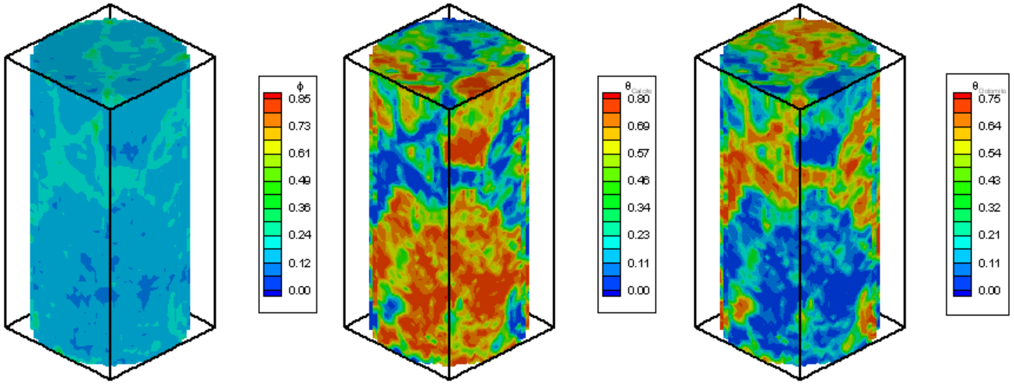
$$K = K_0 \left(\frac{\phi}{\phi_0}\right)^{n}$$

Apply arithmetic averaging to scale characterization data to simulation grid

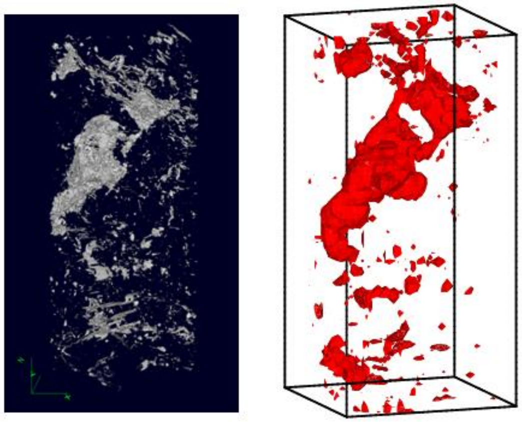
$$\phi_i = \frac{\sum_{\alpha}^{N_p} N_\alpha \phi_\alpha}{\sum_{\alpha}^{N_p} N_\alpha}$$



Simulation Model for Vuggy Limestone (3 Mpa)



Porosity Calcite Dolomite

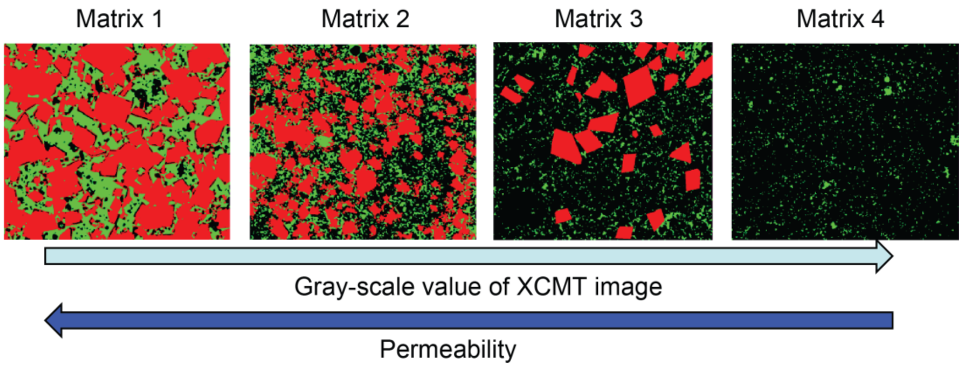


Measured and Modeled Porosity

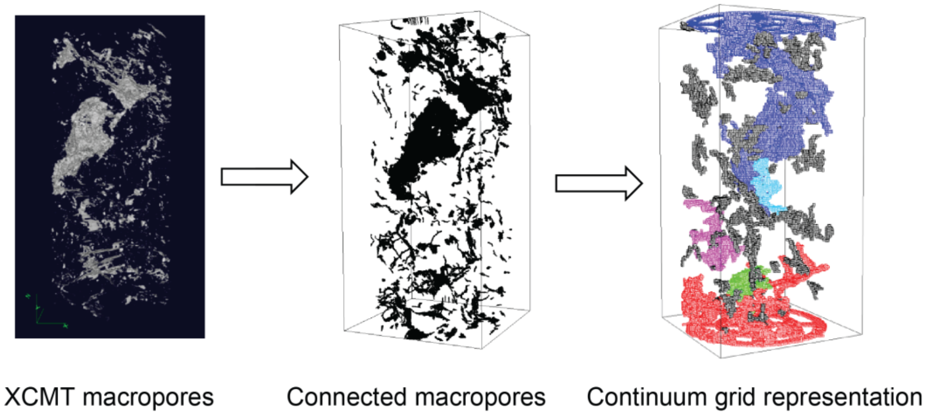
Estimate grid by grid effective permeability

- The gray-scale specific permeability is assigned based on qualitative assessment of micro-pore connection from segmented 2D BSE images;
- The numerical grid-block based permeability is evaluated by assessing the pore connectivity between the modeling grids , and then mapping the clusters of macro-pores, fractures, and highly permeable zones observed onto a three-dimensional regularly spaced finite difference grid (Botros et al., 2008);
- The permeability is further calibrated by matching model results with experimental measurement and tomography data.

A. Estimate permeability due to microporosity for each XCMT gray scale from 2D BSE images (to 10s μ)



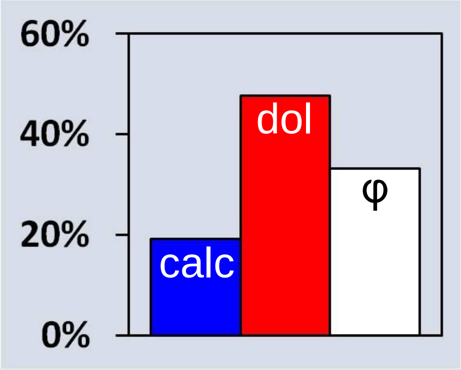
B. Continuum grid permeability is estimated from connection of macro and micropores

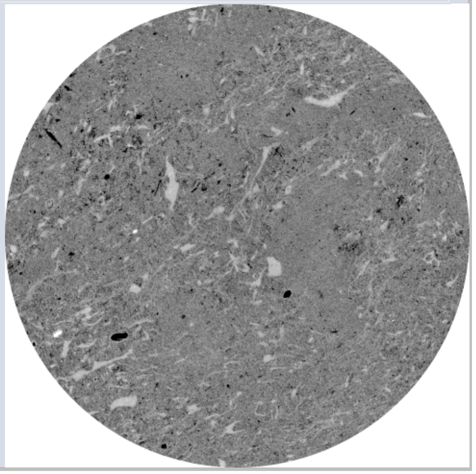


Reservoir flow units have different properties

Marly Dolostone

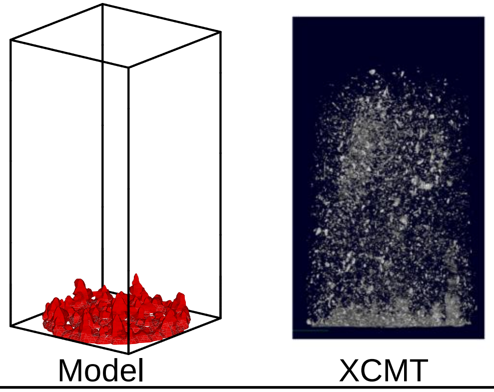
k_{init} 1-2 mD



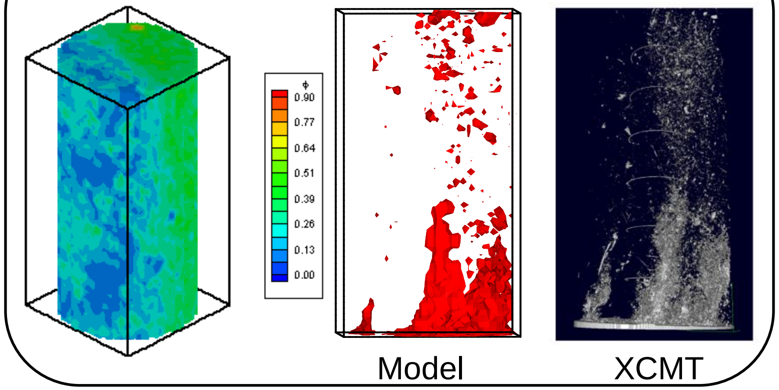


Marly dolostone yields stable dissolution fronts that can be described by 3D and 1D reactive transport models

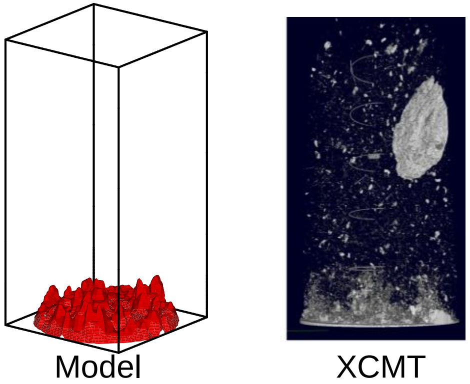
pCO_2 = 3 MPa



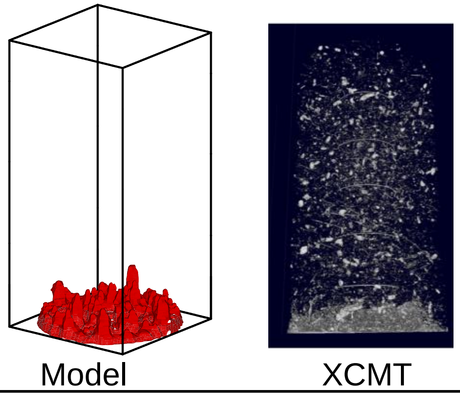
pCO_2 = 1 MPa



pCO_2 = 2 MPa

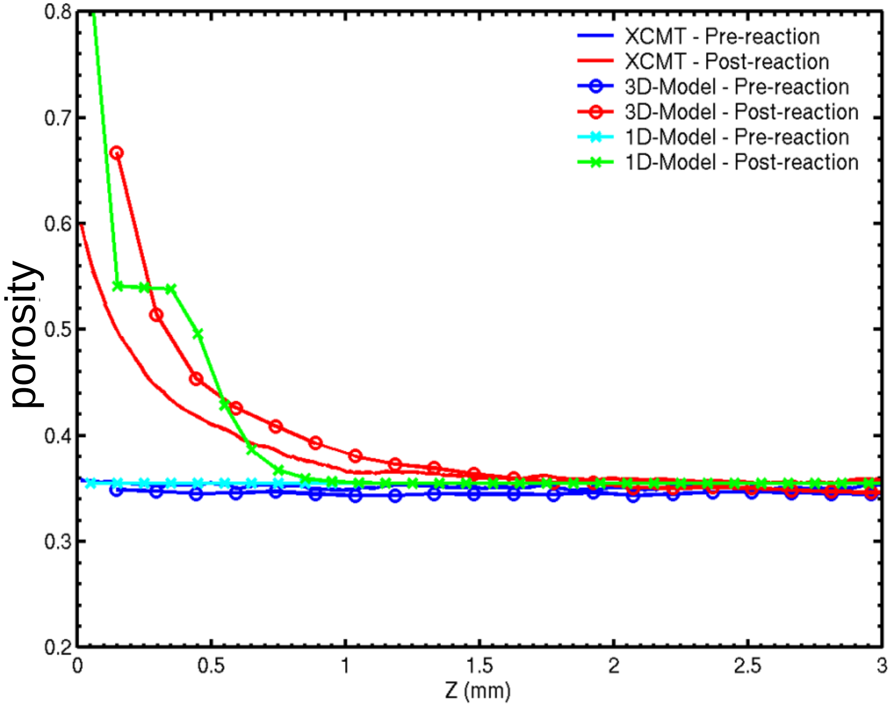


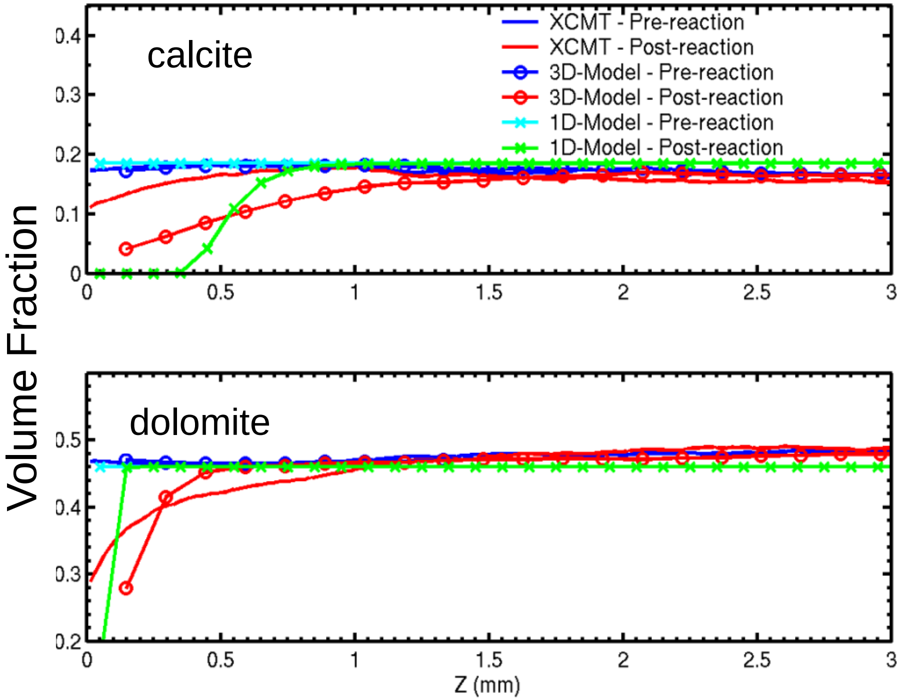
pCO_2 = 0.5 MPa



3D and 1D reactive transport data are in good agreement with measured data

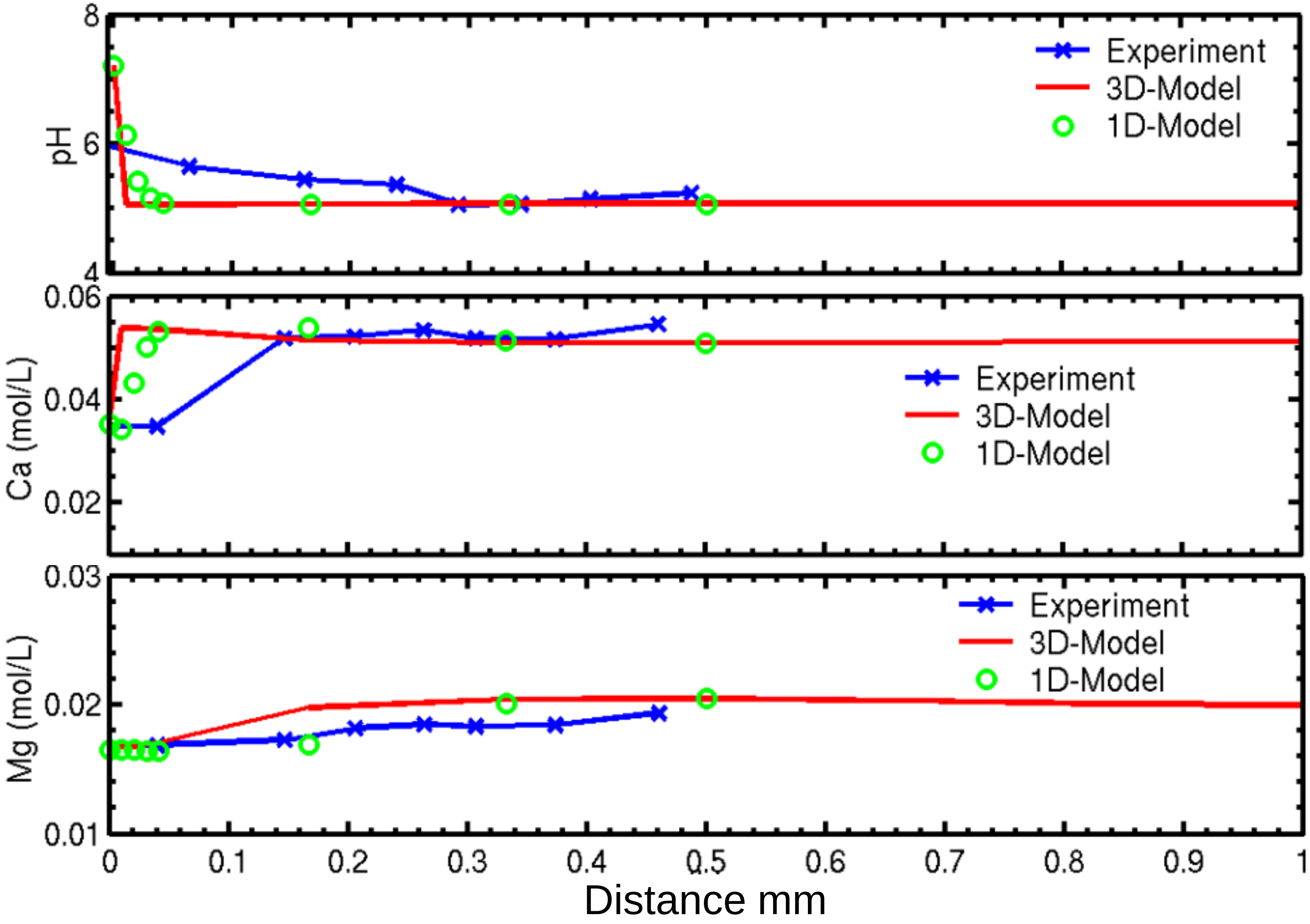
Marly Dolostone pCO_2 = 3 MPa
Measured Porosity and mineral volume





3D and 1D reactive transport data are in good agreement with measured data

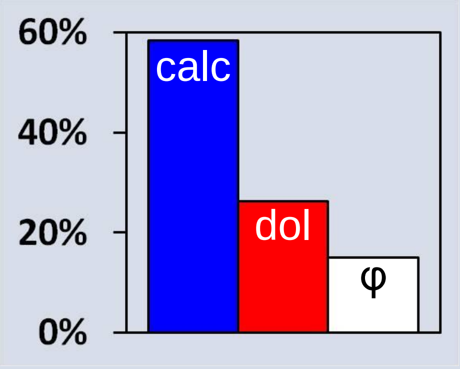
Solution Chemistry; Marly Dolostone reacted at pCO_2 = 3 MPa

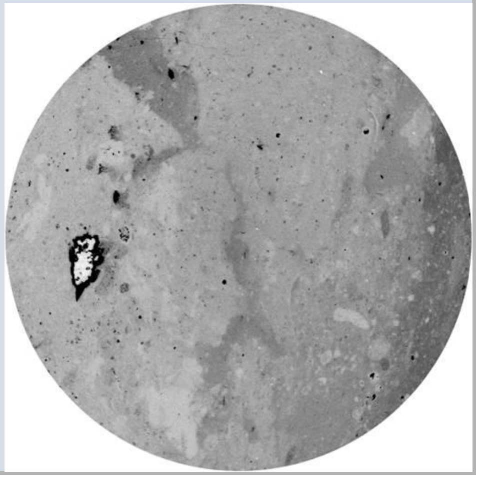


Reservoir flow units have different properties

Vuggy Limestone

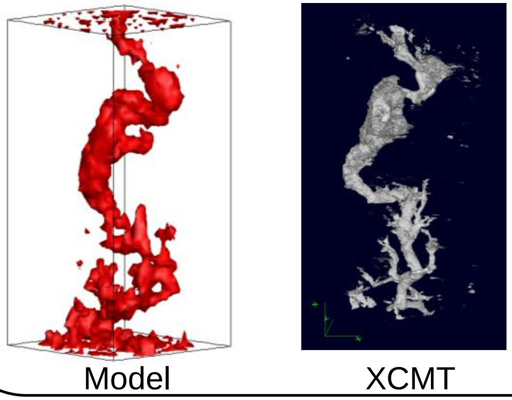
k_{init} 0.01-0.03 mD



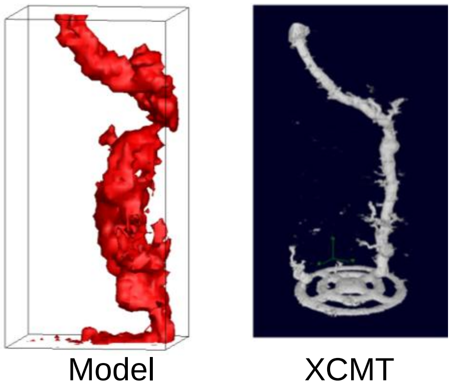


Vuggy limestone yields unstable dissolution fronts that can be described by 3D transport models

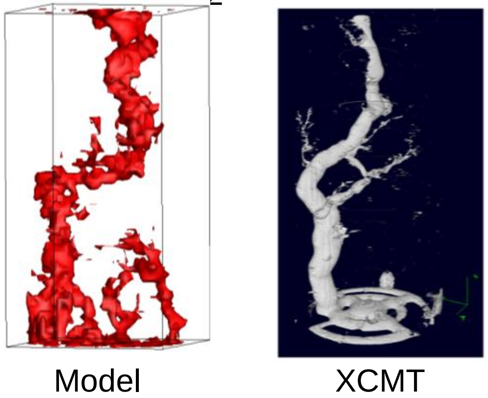
pCO_2 = 3 MPa



pCO_2 = 1 MPa



pCO_2 = 2 MPa



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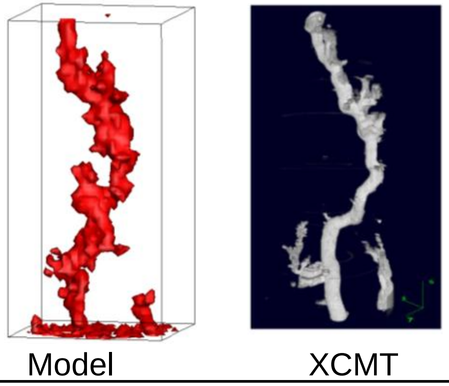

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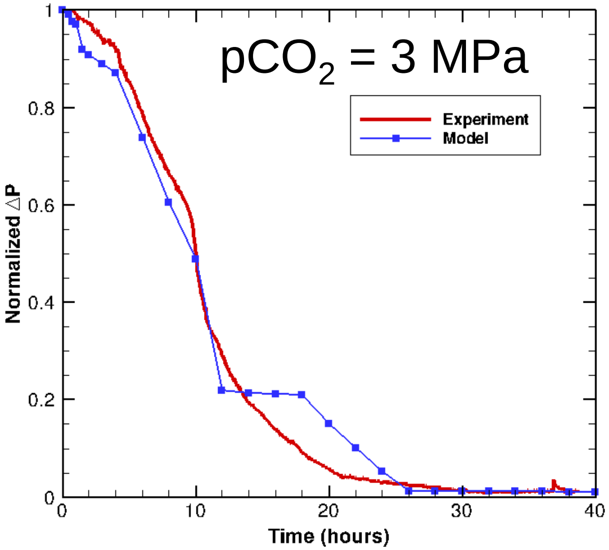
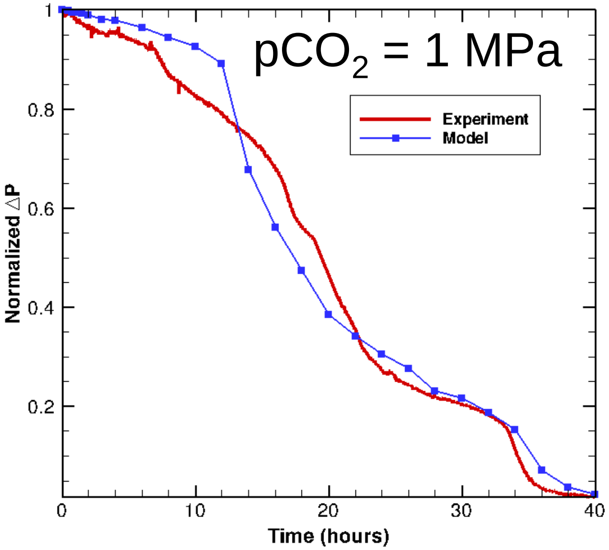
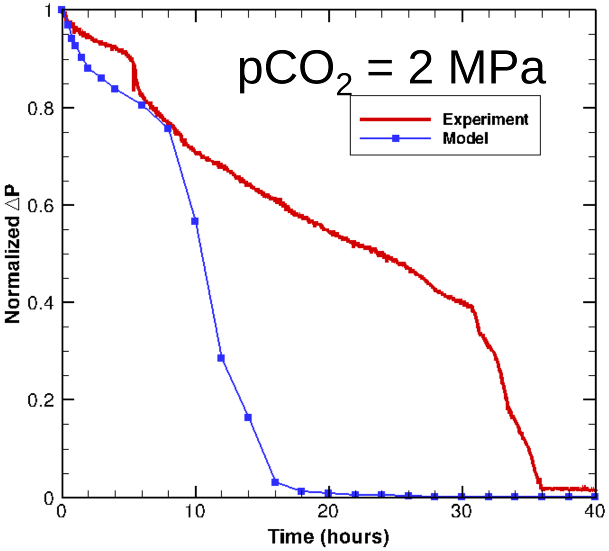
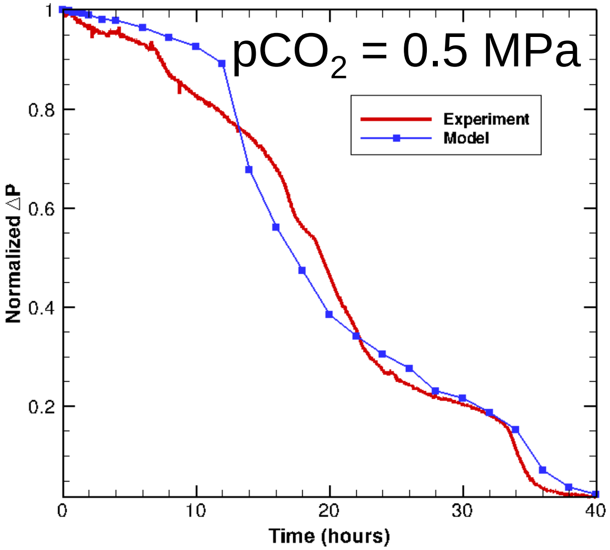


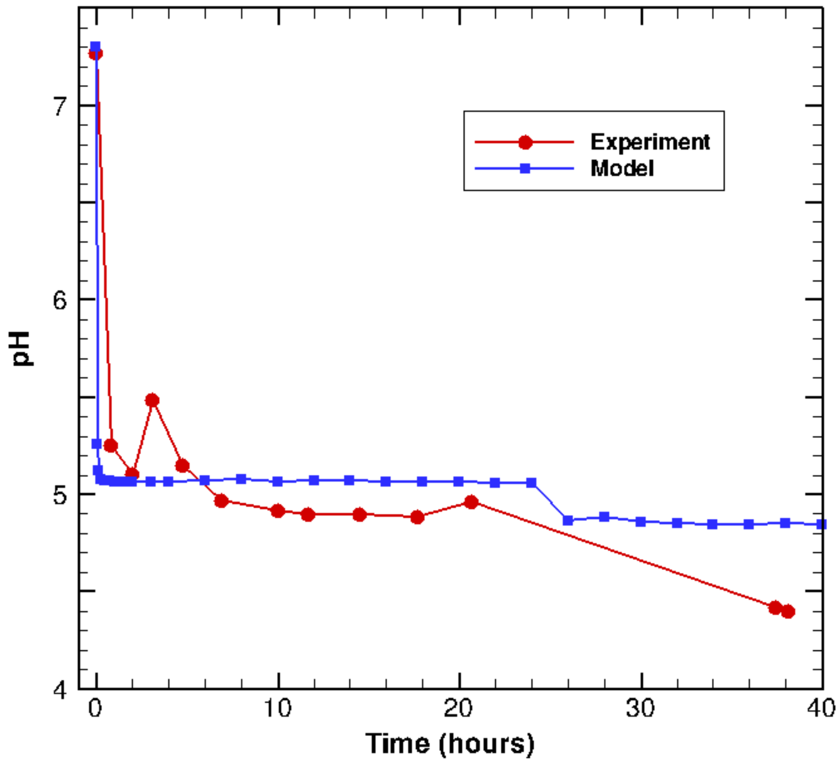




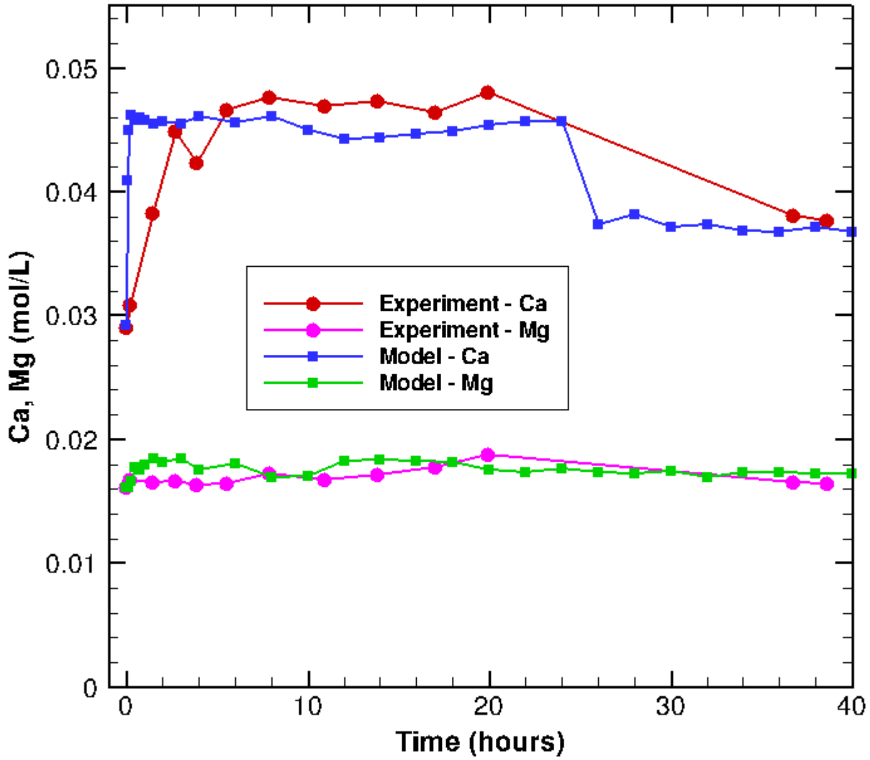


3D reactive transport solution chemistry are in good agreement with measured data

$pCO_2 = 3$ MPa



Model-experiment Comparison of pH



Model-experiment comparison of solution chemistry

Accomplishments: Parameter results for 3D continuum model

- Chemical Model - Use laboratory derived parameters
  - Rate equations tied to equilibrium
  - Rate constants
  - Activation energies – temperature dependence
  - Equilibrium constants (slight adjustment for dolomite)

$$\frac{dn}{dt} = -Sk_{298.15}\, e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)}\left(1 - \frac{Q}{K_{eq}}\right)$$

- Porosity – Permeability – Surface Area
  - Change surface area in proportion to decreasing spherical grains
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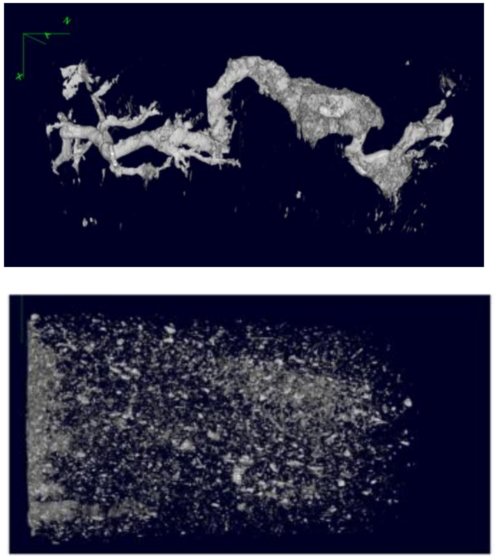
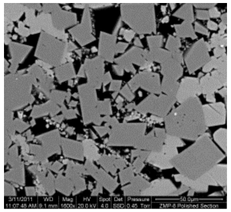
$$S = S_0 \left(\frac{C}{C_0}\right)^{2/3} \left(\frac{\phi}{\phi_0}\right)^{2/3}$$

$$K = K_0 \left(\frac{\phi}{\phi_0}\right)^{n}$$

Implications for reservoir scale simulations for CCUS

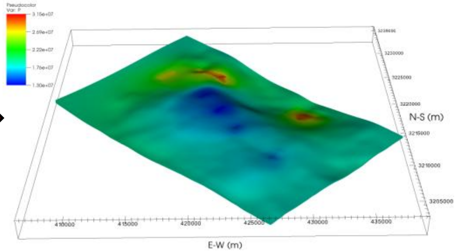


- ☐ Key Findings
  - ➢ Anisotropic permeability and mineral dissolution play dominant roles on porosity and permeability changes that will occur during CCUS operations
  - ➢ Calibrated several reactive transport parameters that scale from microns to centimeters
  - ➢ Geochemical parameters for carbonate minerals appear to be independent of scale
  - ➢ Porosity – Permeability relationships are dependent on sample heterogeneity
- ☐ Future plans are to conduct experiments and modeling at larger scales



Pore (microscopic) scale ~ µm

Core (laboratory) scale ~ cm

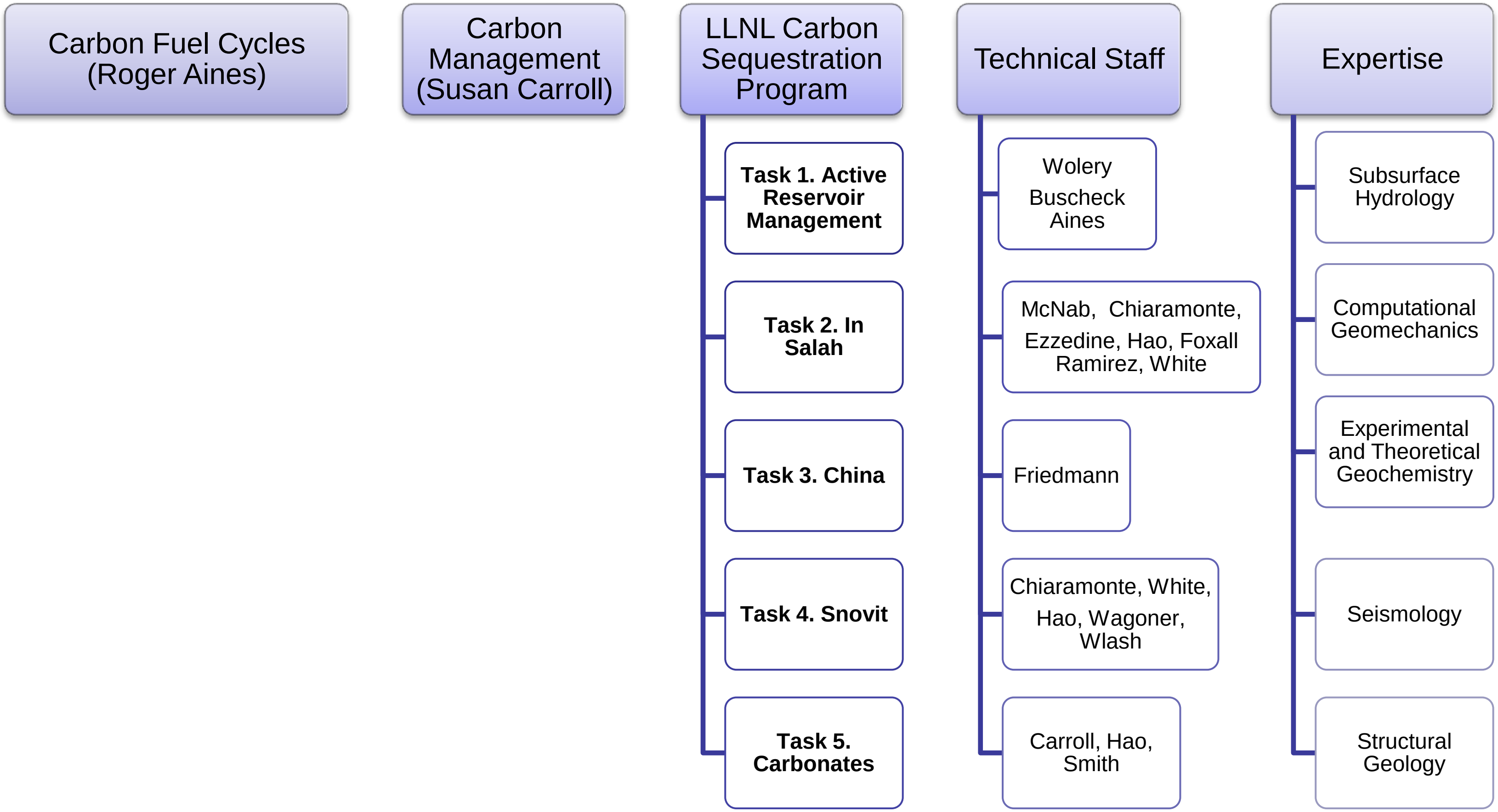


Large (reservoir/field) scale ~ km

Appendix

- Organizational Chart
- Ghant Chart
- Bibliography

Organization Chart



Carbon Fuel Cycles (Roger Aines)

Carbon Management (Susan Carroll)

LLNL Carbon Sequestration Program

- **Task 1. Active Reservoir Management**
- **Task 2. In Salah**
- **Task 3. China**
- **Task 4. Snovit**
- **Task 5. Carbonates**

Technical Staff

- Wolery Buscheck Aines
- McNab, Chiaramonte, Ezzedine, Hao, Foxall Ramirez, White
- Friedmann
- Chiaramonte, White, Hao, Wagoner, Wlash
- Carroll, Hao, Smith

Expertise

- Subsurface Hydrology
- Computational Geomechanics
- Experimental and Theoretical Geochemistry
- Seismology
- Structural Geology

Gantt Chart: Task 5 Carbonates

		Fiscal Year 2012				Fiscal Year 2013				Fiscal Year 2013			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
5.1.1	Finish model calibration with Weyburn data	🟨	🟨	🟨	🟨	🟨							
5.1.2	Finish premodel simulations for new experiments		🟨				🟨						
5.1.3	Refine model using new data						🟨	🟨	🟨	🟨	🟨	🟨	🟨
5.1.1	Experimental Design	🟨	🟨										
5.2.2	Conduct experiments			🟨	🟨	🟨	🟨	🟨	🟨				
5.2.3	Interpret experimental results						🟨	🟨	🟨	🟨	🟨		

Bibliography

- Smith, M., Sholokhova, Y., Hao Y., and Carroll, S., 2012, Evaporite caprock integrity: An experimental study of reactive mineralogy and pore – scale heterogeneity during brine – CO_2 exposure. Environmental Science and Technology, (in press); dx.doi.org/es3012723.

- Smith, M., Sholokhova, Y., Hao Y., and Carroll, S., 2012 (in revision), Evolution of Carbonate Dissolution Features Produced under Variable pCO_2 Conditions Relevant to CO_2-EOR and Geologic CO_2 Storage, Geochimica et Cosmochimica Acta

- Carroll, S. Hao, Y., Smith, M., Sholokhova, Y. (2012 in review), Development of scaling parameters to describe CO2-carbonate-rock interactions for the Marly Dolostone and Vuggy Limestone, I J Greenhouse Gas Control