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

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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 over a range of carbonate rock types and permeability.

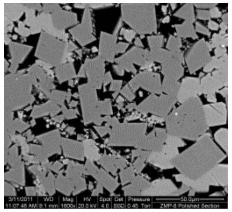
Benefit to the Program

- 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 simulation 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.

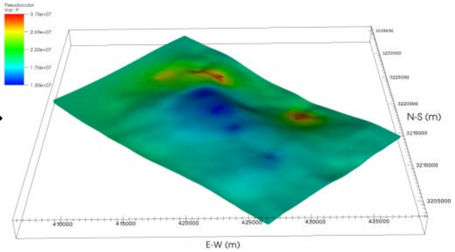
Technical Status

Task 5.1 – Predict porosity and permeability evolution in carbonate storage reservoirs

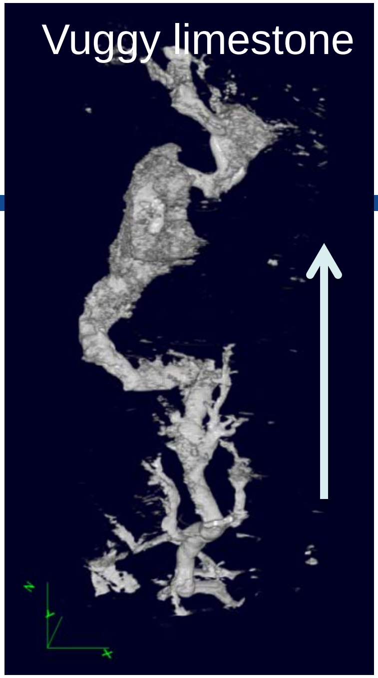


Pore (microscopic) scale ~ µm

Core (laboratory) scale ~ cm



Large (reservoir/field) scale ~ km



Important findings from Weyburn study

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^-

Mineral Reaction Rates

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

Permeability-Porosity n ~3 to 8

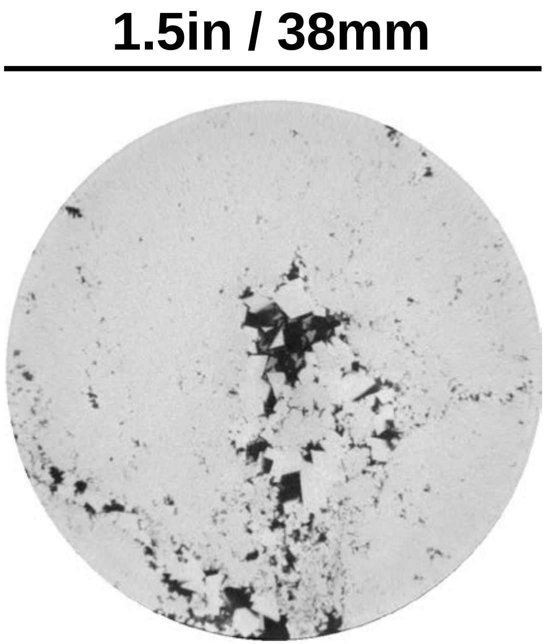
$$K_t = K_0\left(\frac{\phi_t}{\phi_0}\right)^n$$

Surface Area-Porosity m = 2/3

$$S_t = S_0\left(\frac{\theta_t}{\theta_0}\frac{\phi_t}{\phi_0}\right)^m$$

Key Characteristics Arbuckle Carbonates Cores

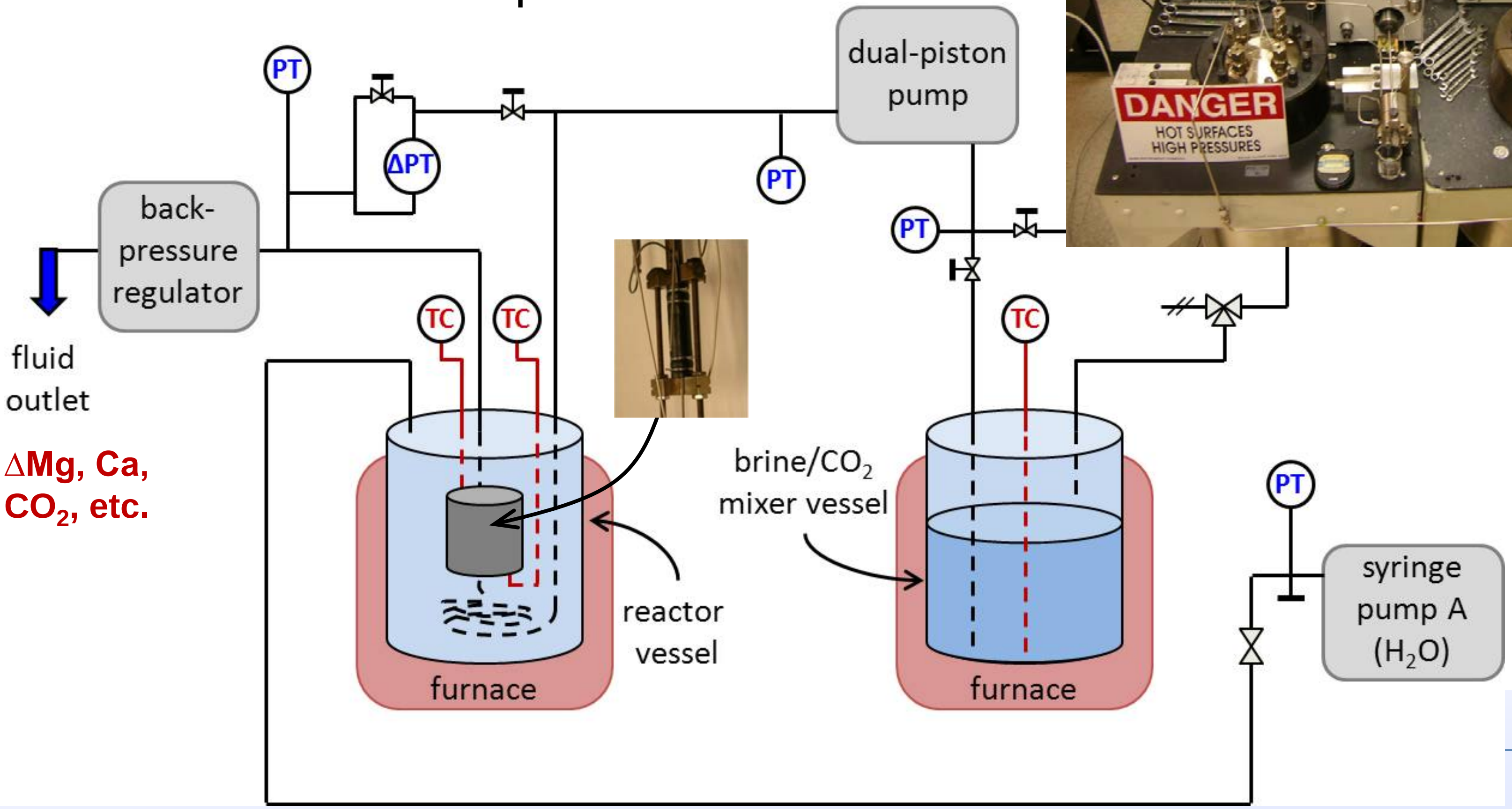
- Highly impermeable compared to downhole estimates
- Dominated by less reactive dolomite
- Dominated by fracture flow



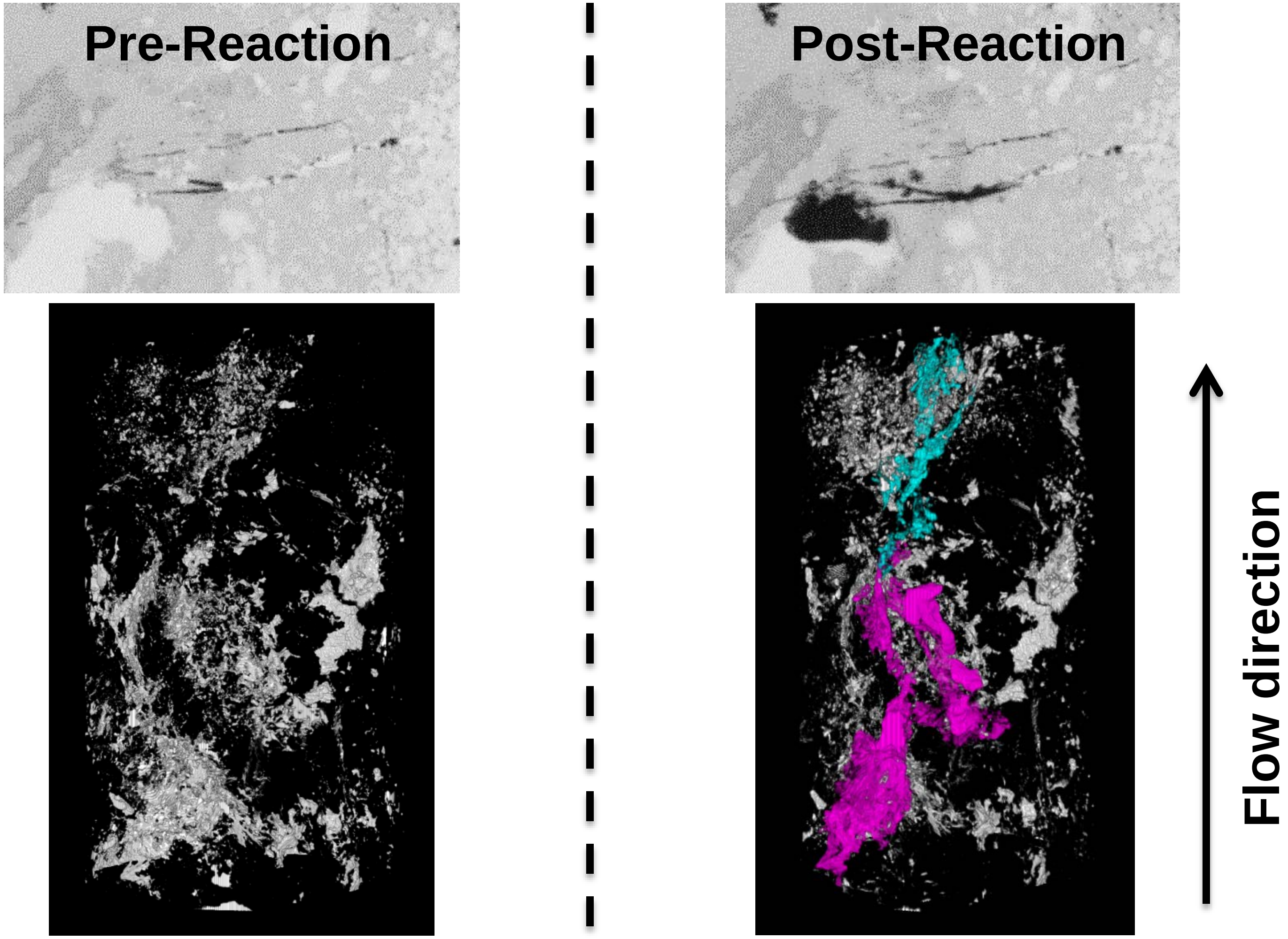
2.5x increase in diameter for "second-generation" Injection zone samples

Conducted core flood experiments on 2 samples from baffle zones and one from injection zone

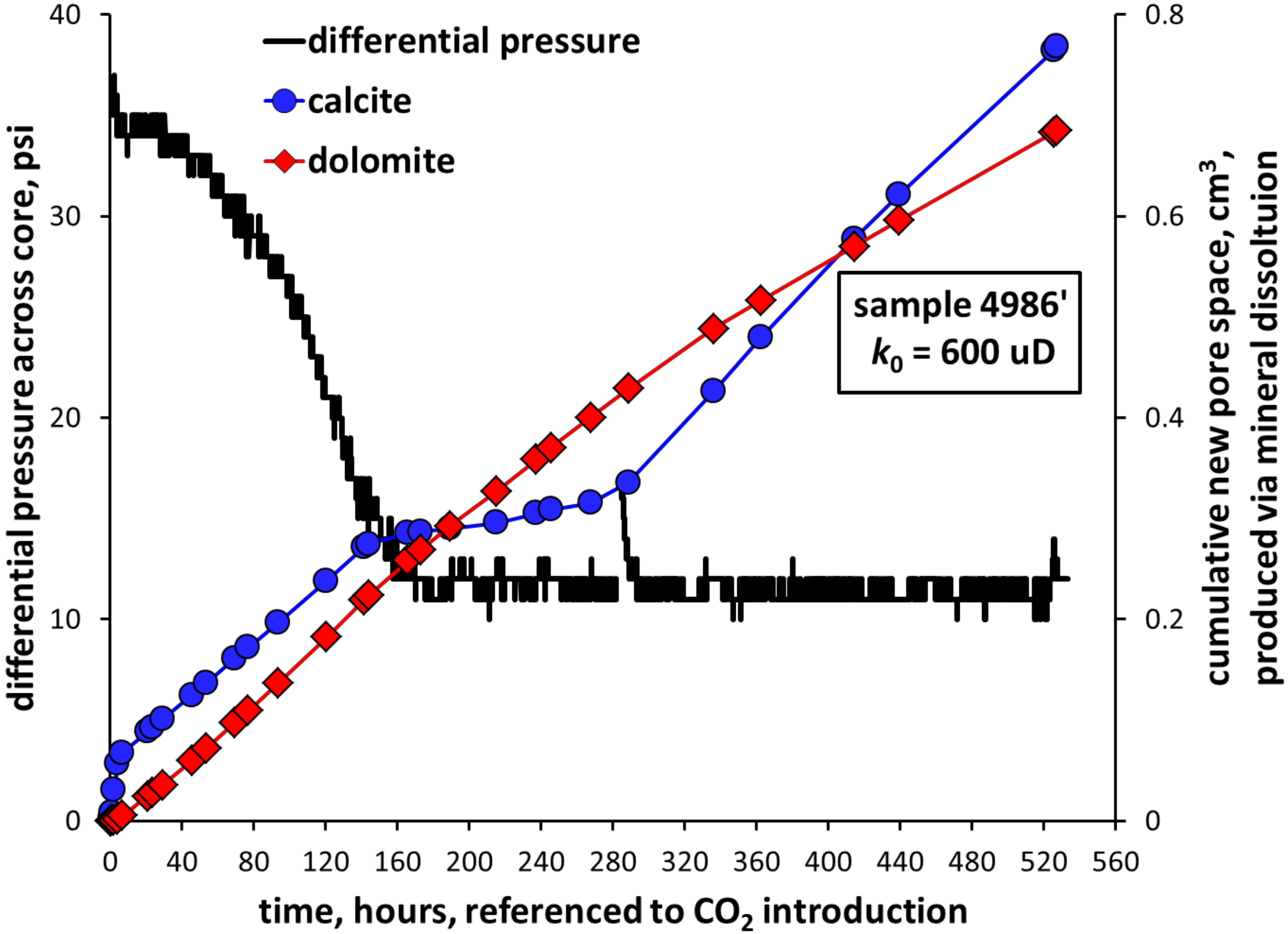
- 60°C temp, 25 MPa confining pressure
- constant flowrate 0.034 mL/min
- 1.1m NaCl brine with $p\mathrm{CO_2}$ = 3 MPa, at carbonate equilibrium



Enhanced fracture permeability in the injection zone



Observe similar volumes of calcite and dolomite dissolution based on solution chemistry



Reactive Transport Model

Reactions
calcite + H^+ = Ca^{++} + HCO_3^-
dolomite + $2H^+$ = Ca^{++} + Mg^{++} + $2HCO_3^-$
$CO_{2(aq)}$ + H_2O = H^+ + HCO_3^-
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Mineral Reaction Rates

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

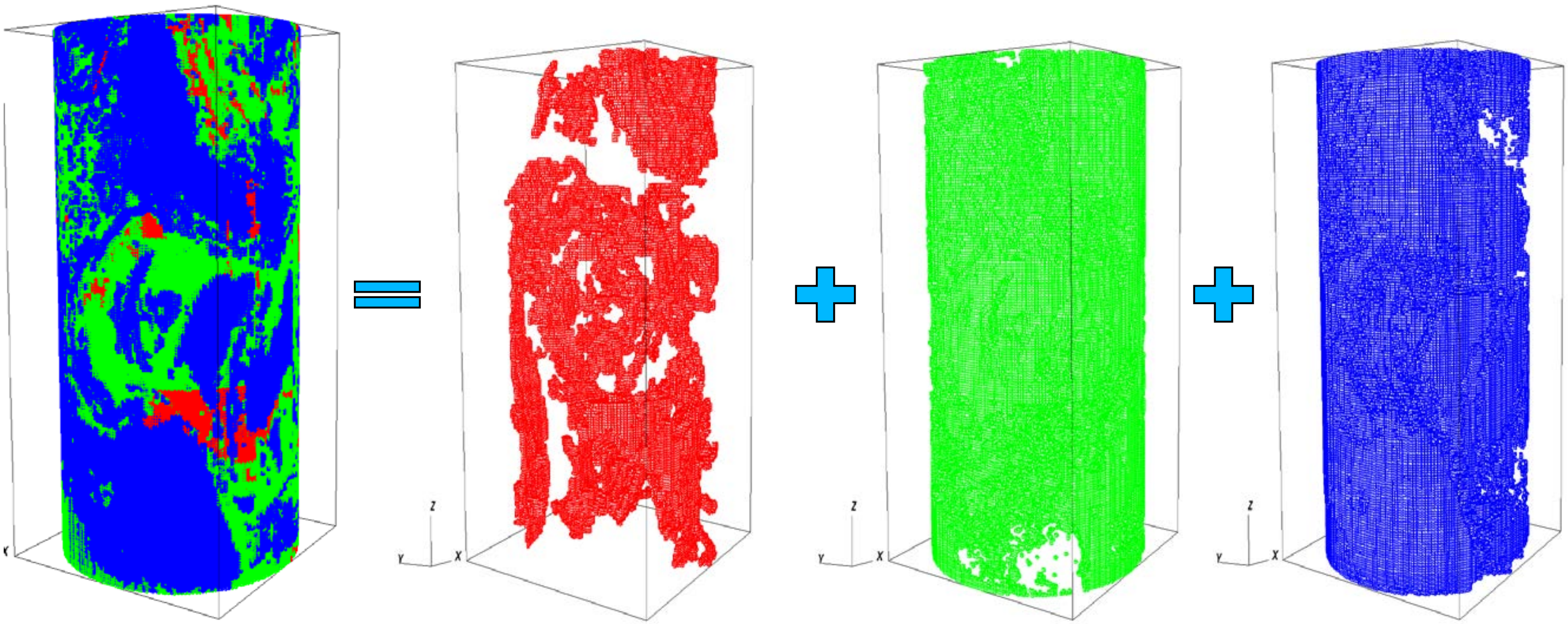
Permeability-Porosity n – best fit

$$K_t = K_0 \left(\frac{\phi_t}{\phi_0}\right)^n$$

Surface Area-Porosity m – best fit

$$S_t = S_0 \left(\frac{\theta_t}{\theta_0}\frac{\phi_t}{\phi_0}\right)^m$$

Nested Grid
300^3 μm^3 grid – three distinct regions



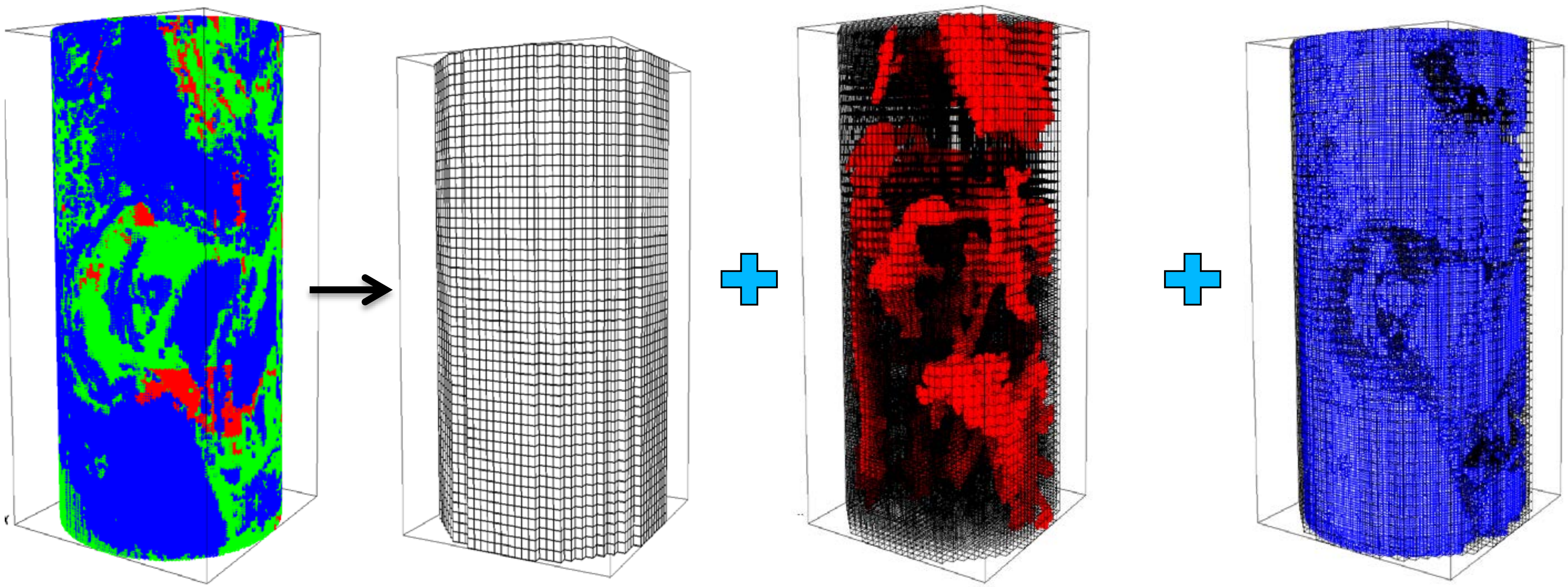
full domain

high permeable zones
(e.g. fractures)

medium permeable zones
(e.g. dolomite)

low permeable zones
(e.g. calcite clusters)

Map connected fractures and macro pores to coarser grid



fracture and macro-pore representation with the grid scale of 300 µm

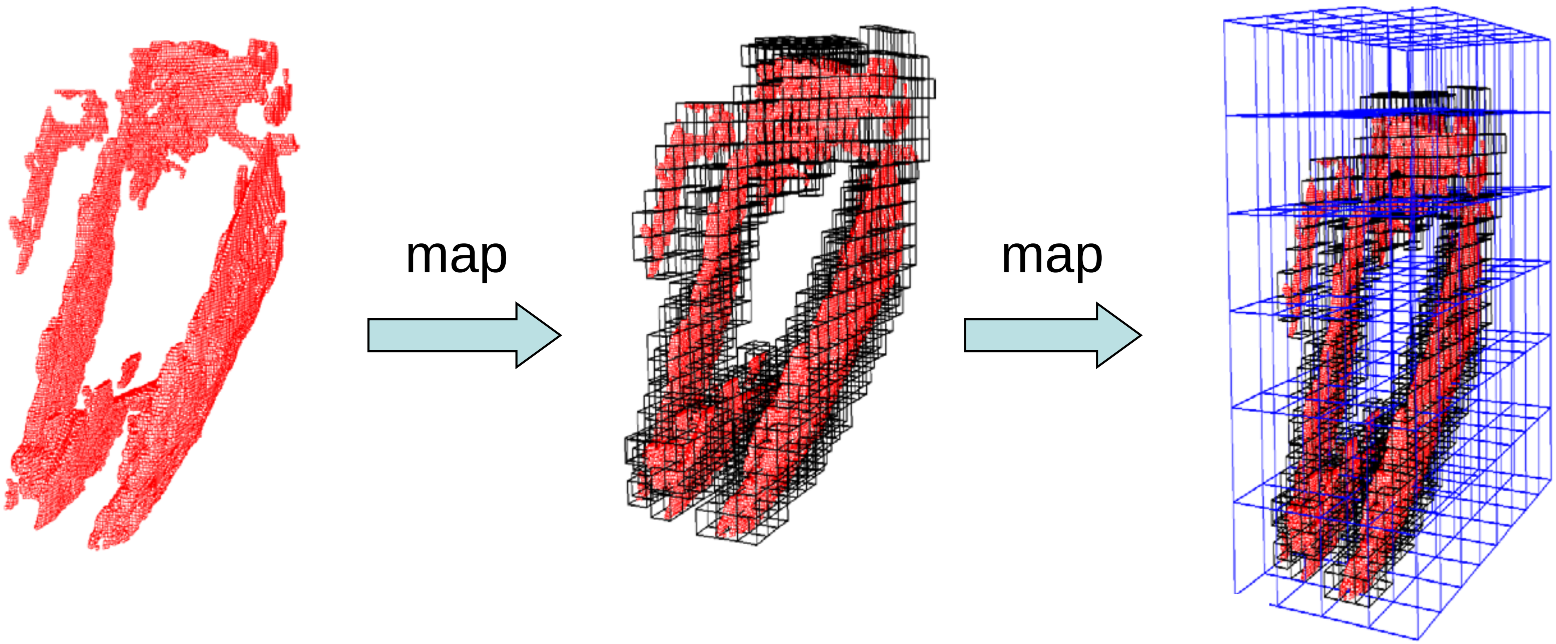
coarser regular grid system with the grid scale as 1 mm

mapped high permeable zones

mapped low permeable zones

Note that the mapped medium permeable zones are not shown here.

Example of nested gridding of individual fractures onto coarser grid

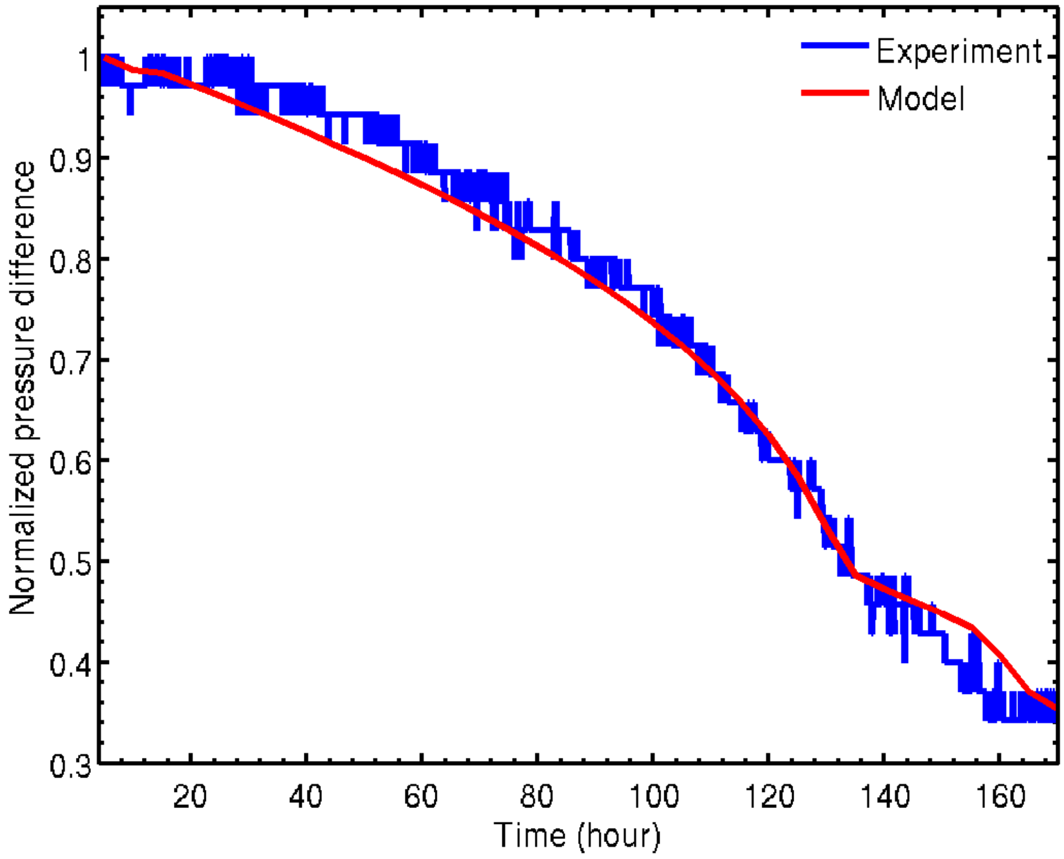


individual fractures extracted from XCMT data (image resolution 42.6 μm)

individual fractures represented by 300 μm grids

individual fractures represented by 1 mm grids

Excellent match to pressure curve



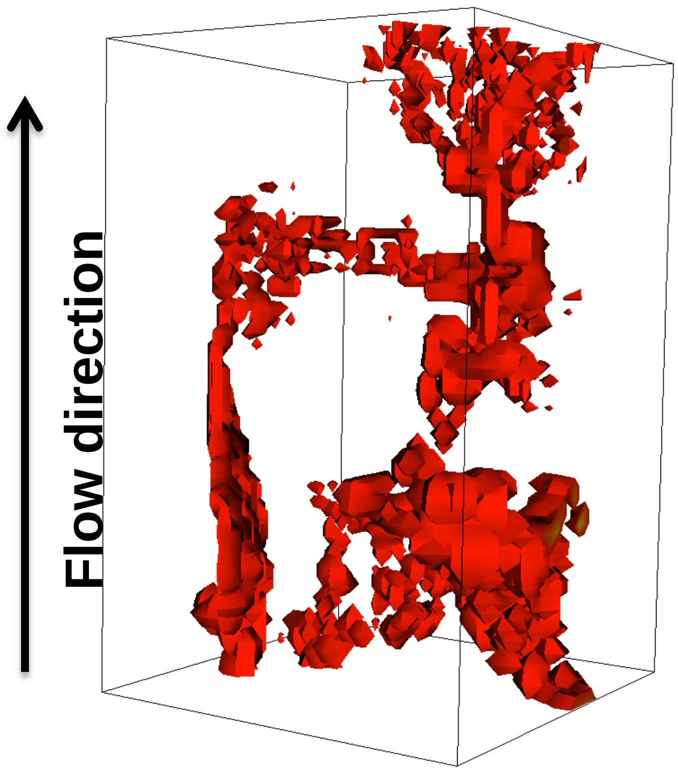
Permeability-Porosity n ~1.8

$$K_t = K_0 \left(\frac{\phi_t}{\phi_0} \right)^n$$

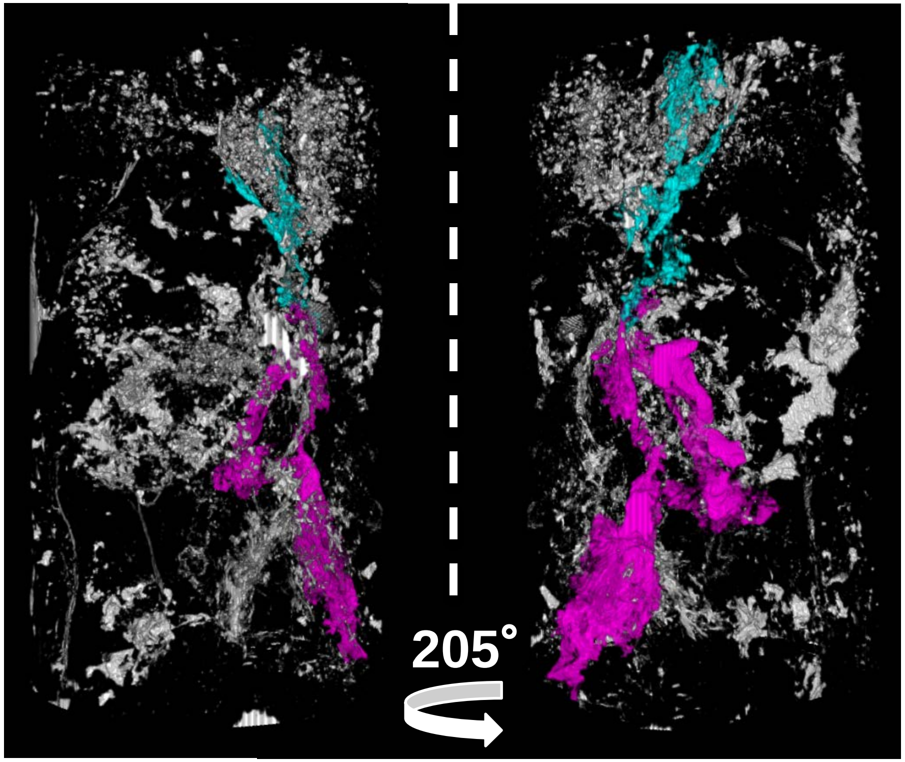
Surface Area-Porosity m = 9

$$S_t = S_0 \left(\frac{\theta_t}{\theta_0} \frac{\phi_t}{\phi_0} \right)^m$$

Larger model grid size over estimates porosity increase

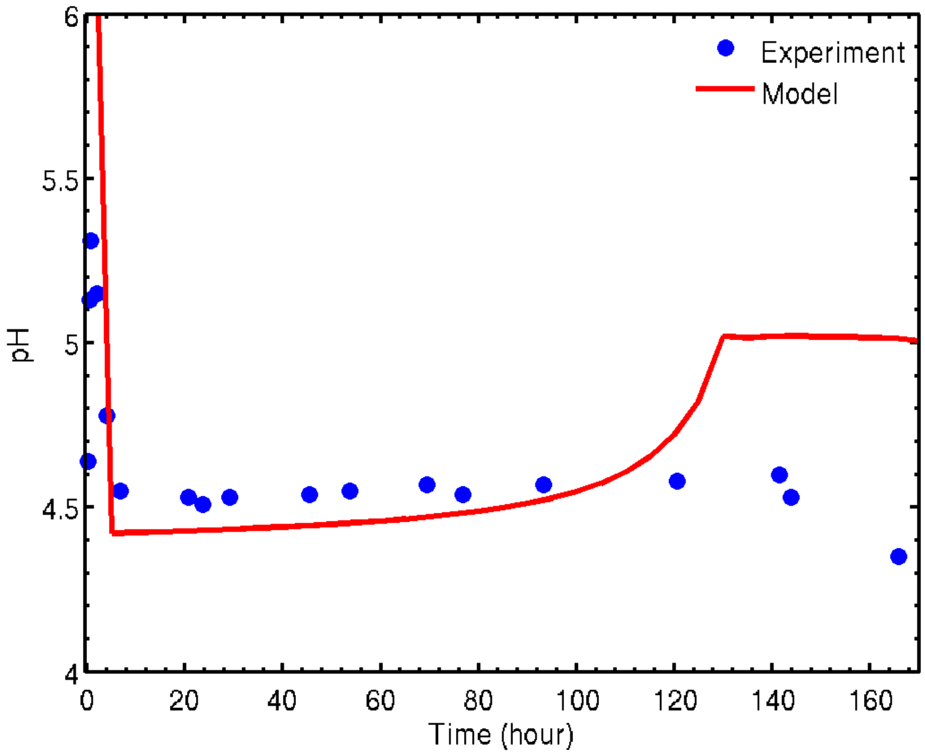


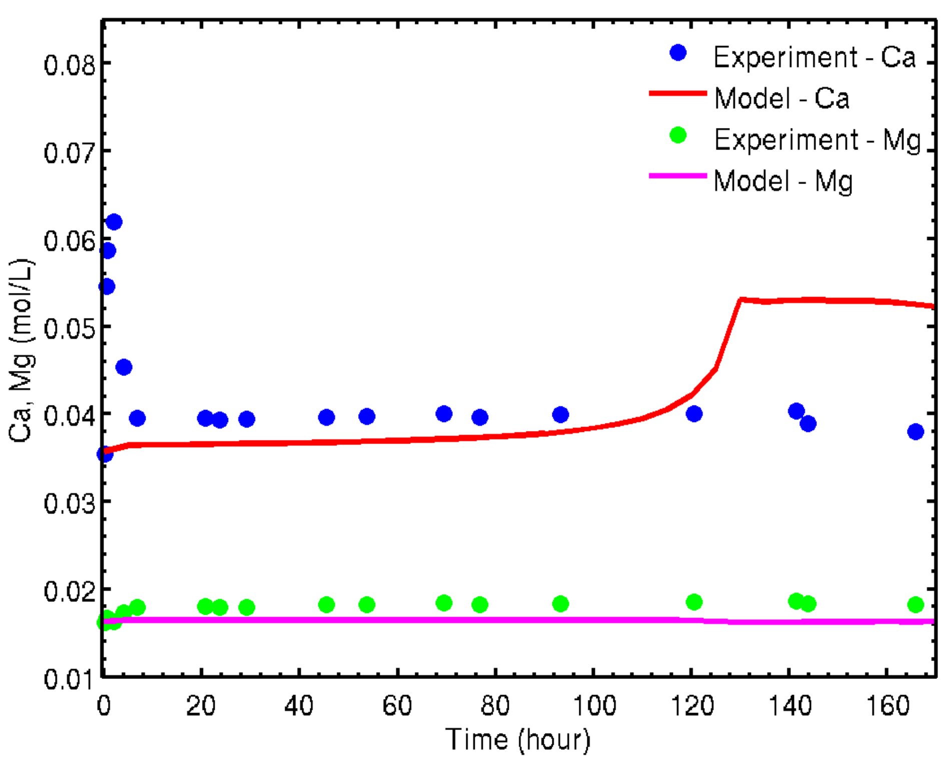
Model
300^3 µm^3 – 1 mm^3



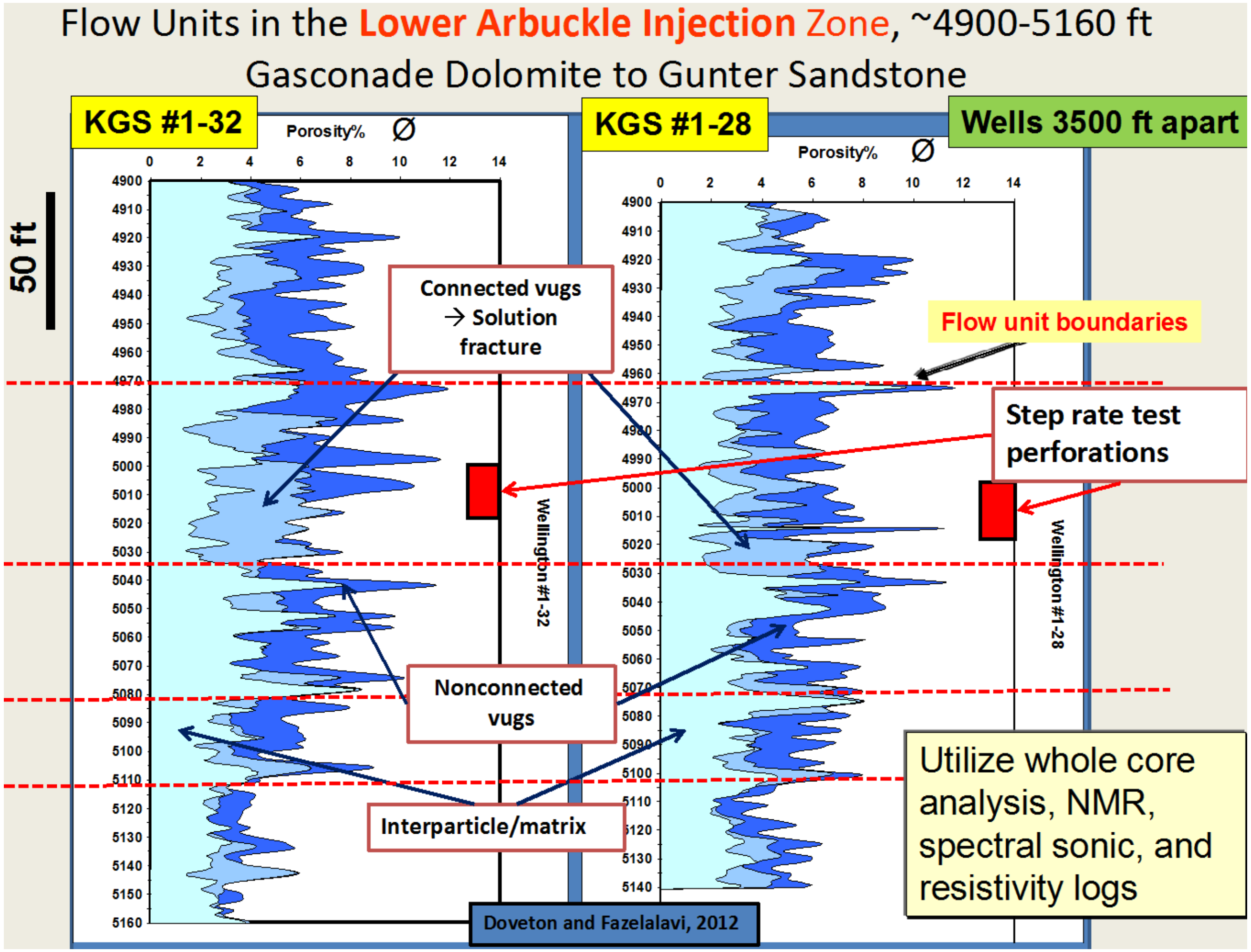
Tomography
~40^3 µm^3

Model predicts more calcite dissolution at later times resulting in higher pH





Task 5.2 – Experimental calibration of NMR well logs to estimate permeability in carbonate reservoirs

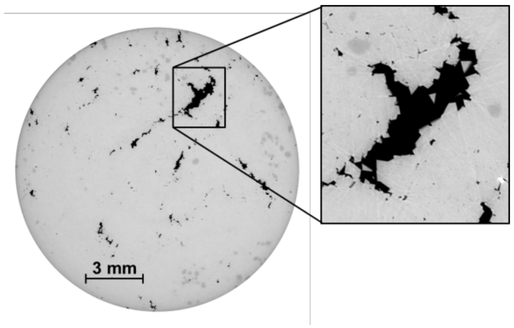


Methodology needed to refine permeability determination

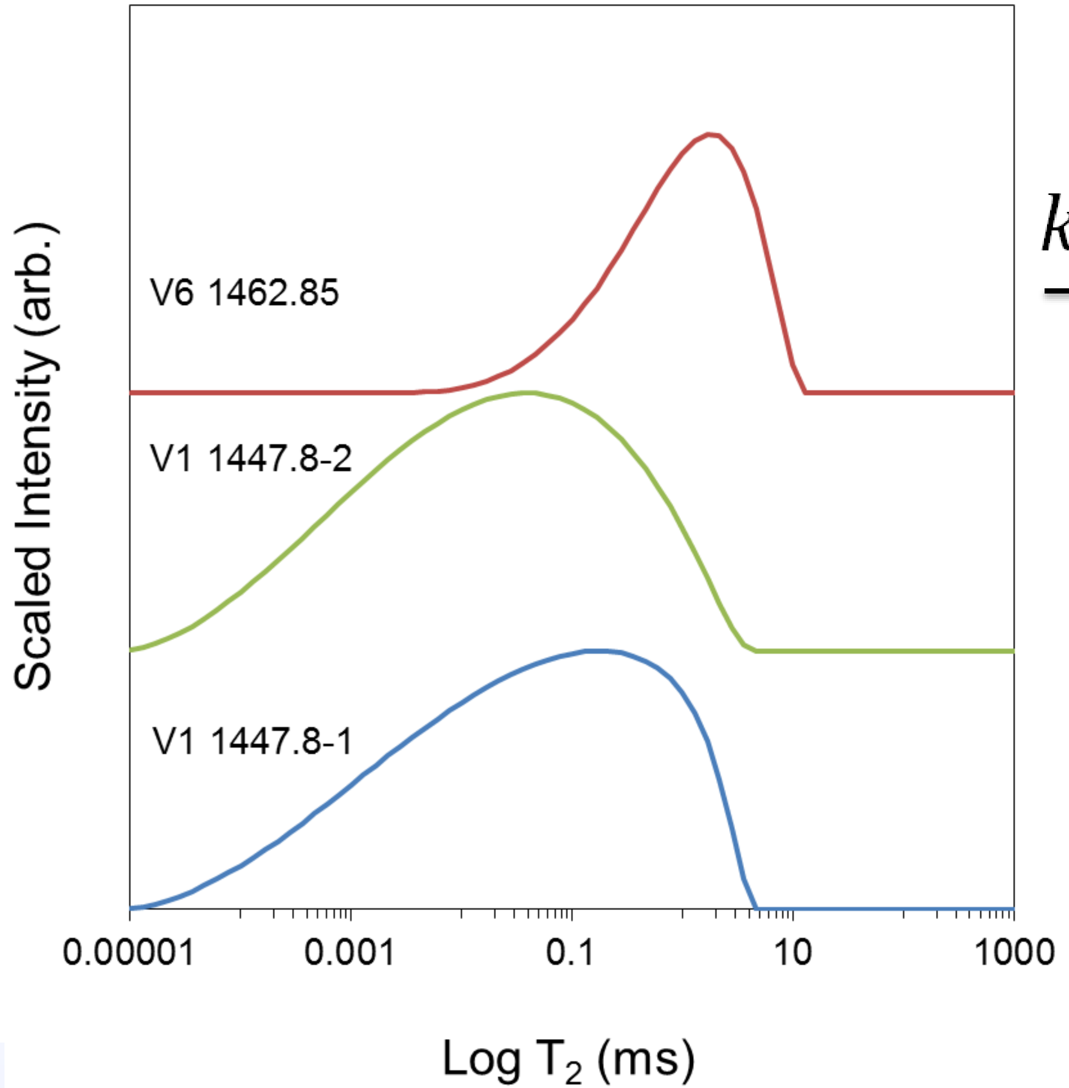
- NMR – extract V/S for complex pore geometry
  - Measure φ , T_2, ρ
- X-ray tomography
  - Measure V/S (resolution dependent)
- Independent measure permeability
- Two distinct carbonate lithologies
  - Arbuckle Dolostone, Wellington Kansas
  - Weyburn Limestone and Marly Dolostone, Canada

$$k = A \cdot T_{LM}^2 \cdot \varphi^4$$

$$T_2 = \frac{1}{\rho}\left(\frac{V}{S}\right) + T_{2B}$$



Weyburn cores provide independent calibration data set: k_{meas} ~0.05 mD



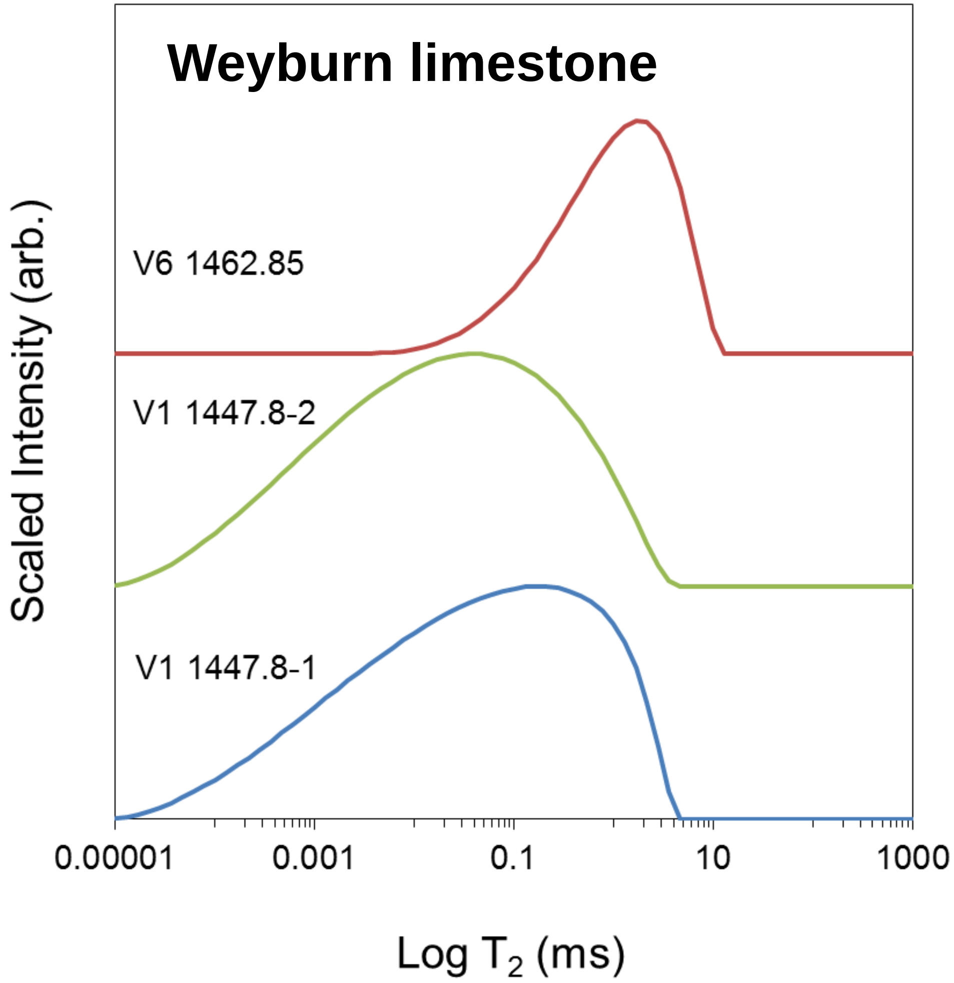
$$k = A \cdot T_{LM}^2 \cdot \varphi^4$$

0.005 mD

0.0000003 mD

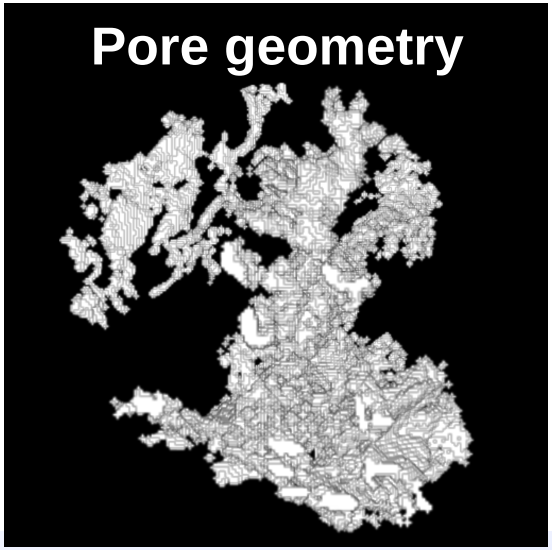
0.000004 mD

Estimates of permeability from NMR measurements depend on pore geometry



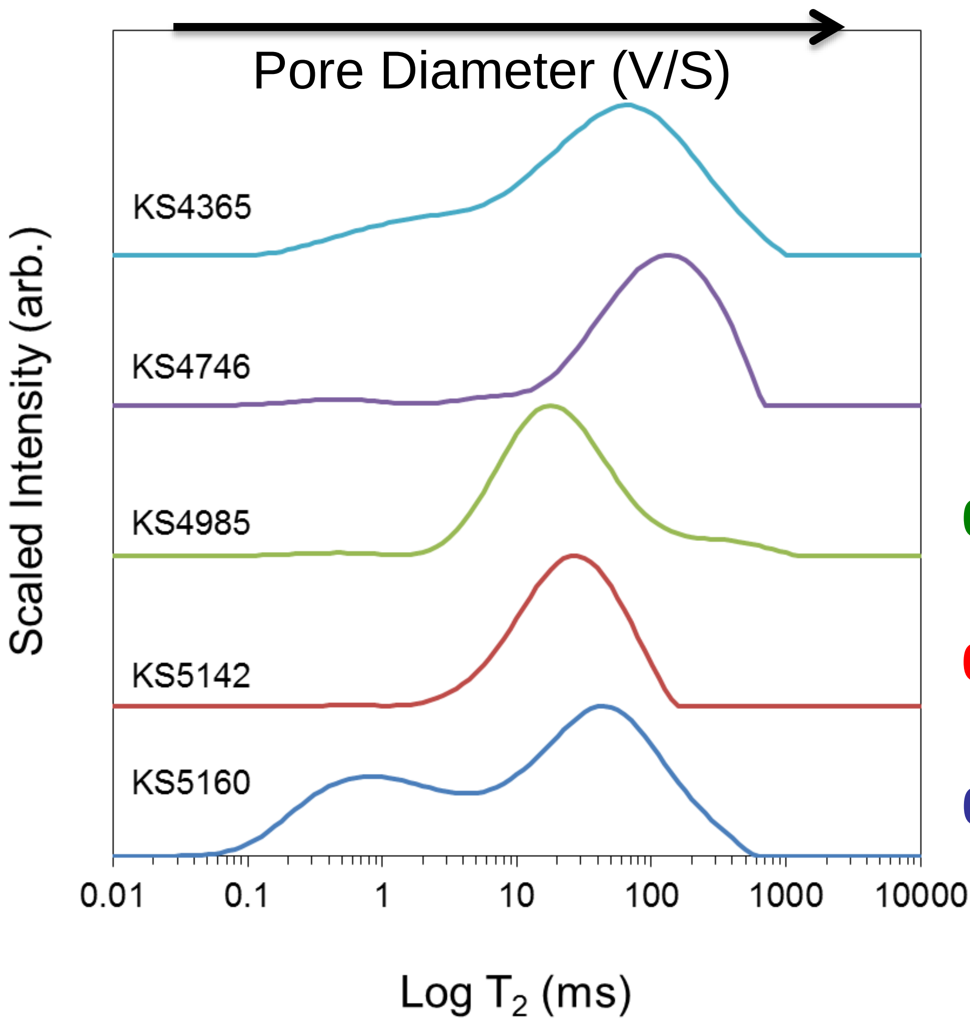
$$k = A \cdot T_{LM}^{2} \cdot \varphi^{4}$$

$$T_2 = \frac{1}{\rho}\left(\frac{V}{S}\right) + T_{2B}$$



Preliminary results from Wellington core: Injection zone permeability varies by 3 orders of magnitude

$$k = A \cdot T_{LM}^2 \cdot \varphi^4$$



0.005 mD — **Baffle zone**

3 mD

0.06 mD

0.3 mD

0.002 mD

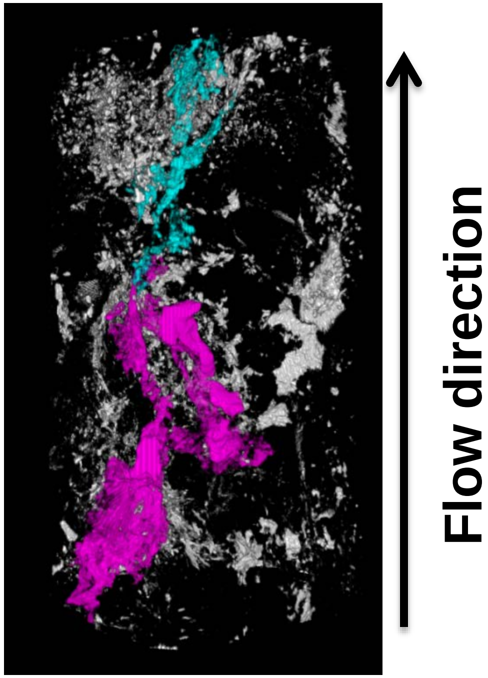
Injection Zone

Accomplishments FY14

- Task 5.1 – Predict porosity and permeability evolution in carbonate storage reservoirs
  - Conducted reactive transport experiments with core from the Arbuckle Dolostone, Wellington Kansas
  - Developed a reactive-transport model that captures dissolution induced increases in fracture permeability
- Task 5.2 – Experimental calibration of NMR well logs to estimate permeability in carbonate reservoirs
  - Developed a methodology to refine permeability estimates from NMR well logs in carbonate storage reservoirs
  - Started NMR and tomography analysis of Arbuckle Dolostone, Vuggy Limestone, and Marly Dolostone

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
  - Preliminary – Porosity/Permeability/Surface Area
    - Fracture flow requires different power functions
  - NMR should prove to be a useful tool to estimate reservoir permeability once calibrated
- Future plans are to
  - Conduct several more experiments to capture a range sample heterogeneity for the Arbuckle
  - Develop more robust calibration of primary reactive-transport equation
  - Finish and apply NMR permeability calibration to well log data and perhaps another site.

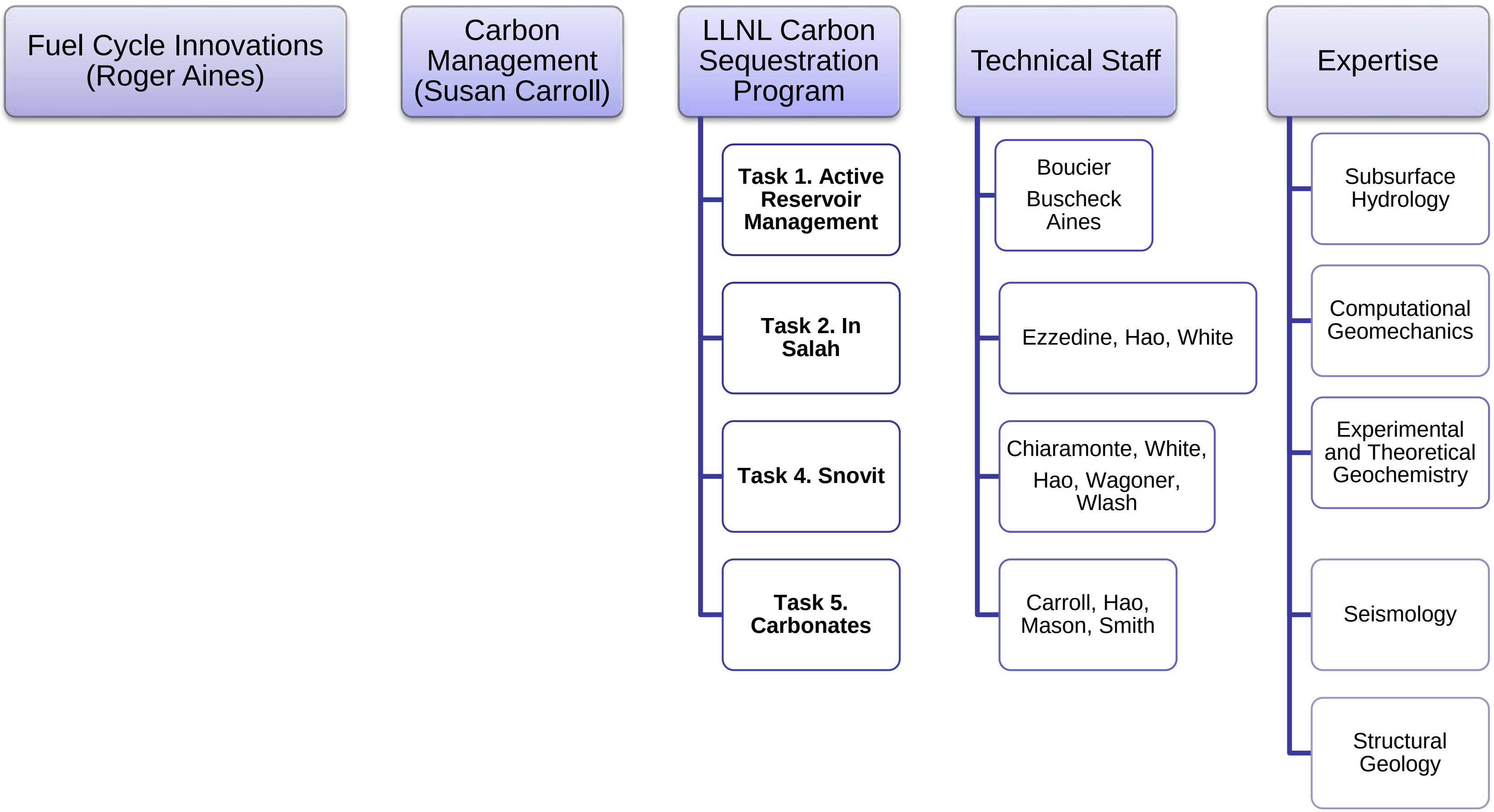


Arbuckle Injection Zone
10 fold increase in permeability

Appendix

- Organizational Chart
- Gantt Chart
- Bibliography

Organization Chart



Gantt Chart: Task 5 Carbonates

Task	Milestone Description*	Fiscal Year 2014				Planned Start Date	Planned End Date	Actual Start Date	Actual End Date	Comment
		Q1	Q2	Q3	Q4					
5.1.1.1	Commence Reactive Transport Model					10/1/11				complete
5.1.1.2	Finish Model Calibration for Weyburn data set					10/1/11	11/1/12	10/1/11	1/15/13	complete
5.1.1.3	Finish Pre model of experiments					11/1/12	2/1/13	11/1/12	6/15/13	complete
5.1.2.1	Finish plan for core flood experiments					10/1/11	12/1/12			complete
5.1.2.2	Commence experiments					12/1/12				complete
5.1.2.3	Conduct experiments						9/30/14			
5.1.3.1	Refine model to data from carbonate experiments					1/30/14	9/30/14			
5.2.1.1	Finish protocol for NMR calibration study					10/1/13	11/30/13			
5.2.1.2	Secure core samples from KGS and submit for tomography imaging analysis					10/1/13	1/15/14			
5.2.1.3	Evaluate heterogeneity from tomography anlaysis					1/30/14	3/15/14			
5.2.1.4	Conduct NMR/MRI analysis					6/30/14	1/30/15			
5.2.2	Develop permeability model using NMR, tomography, and permeability data					1/30/15	6/30/15			
5.2.3	Apply new model to Kansas well log data					6/30/15	9/30/15			

Bibliography

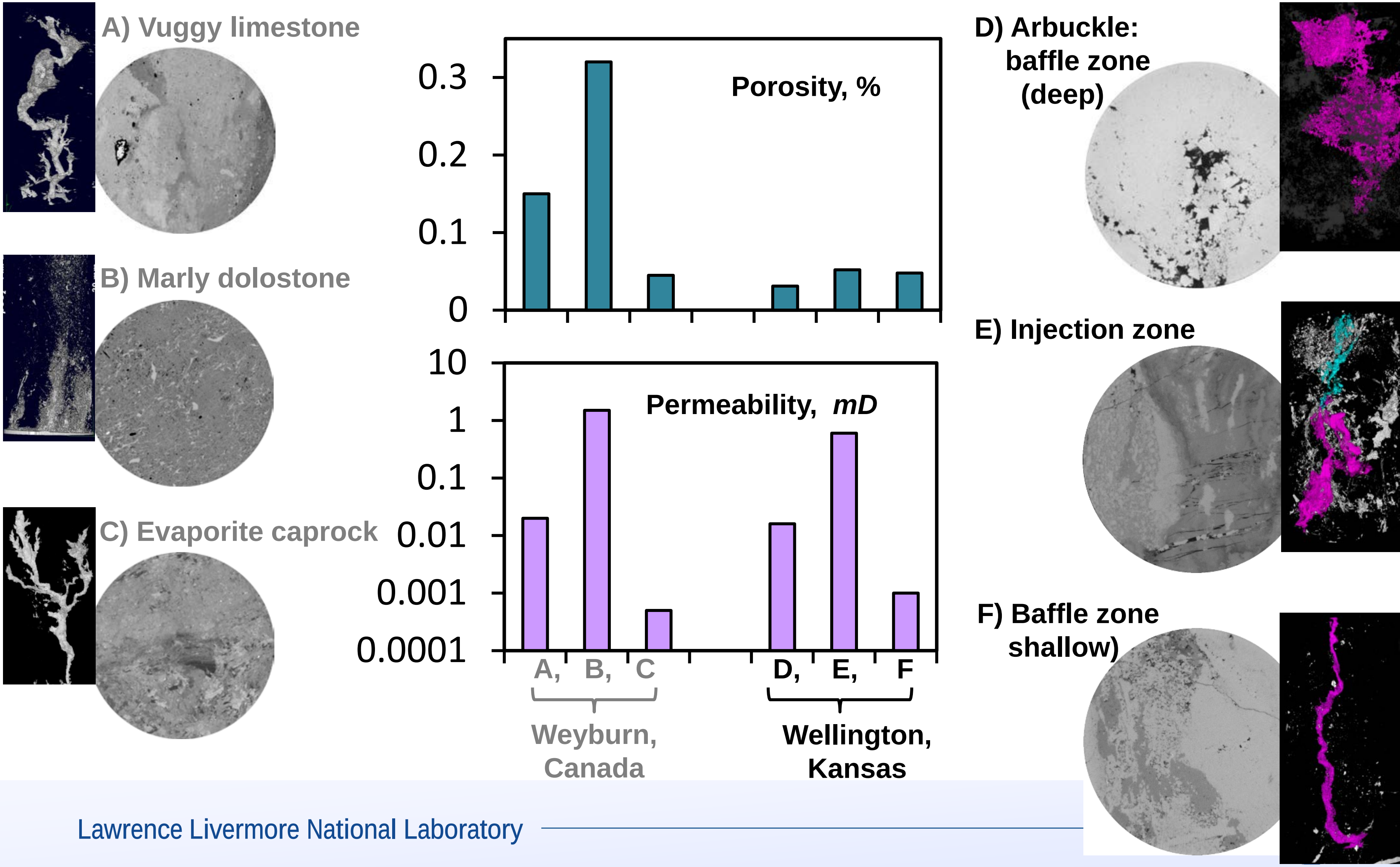
- Smith, M., Sholokhova, Y., Hao Y., and Carroll, S., 2013, Evaporite caprock integrity: An experimental study of reactive mineralogy and pore – scale heterogeneity during brine – CO_2 exposure. Environmental Science and Technology, http://dx.doi.org/es3012723.

- Carroll, S. Hao, Y., Smith, M., Sholokhova, Y. (2013), Development of scaling parameters to describe CO_2-carbonate-rock interactions for the Marly Dolostone and Vuggy Limestone, *I J Greenhouse Gas Control*, http://dx.doi.org/10.1016/j.ijggc.2012.12.026

- Hao, Y., Smith, M., Sholokhova, Y., and Carroll, S. (2013) CO_2-induced dissolution of low permeability carbonates. Part 1: Numerical modeling of experiments, *Advances in Water Resources* http://dx.doi.org/10.1016/j.advwatres.2013.09.009

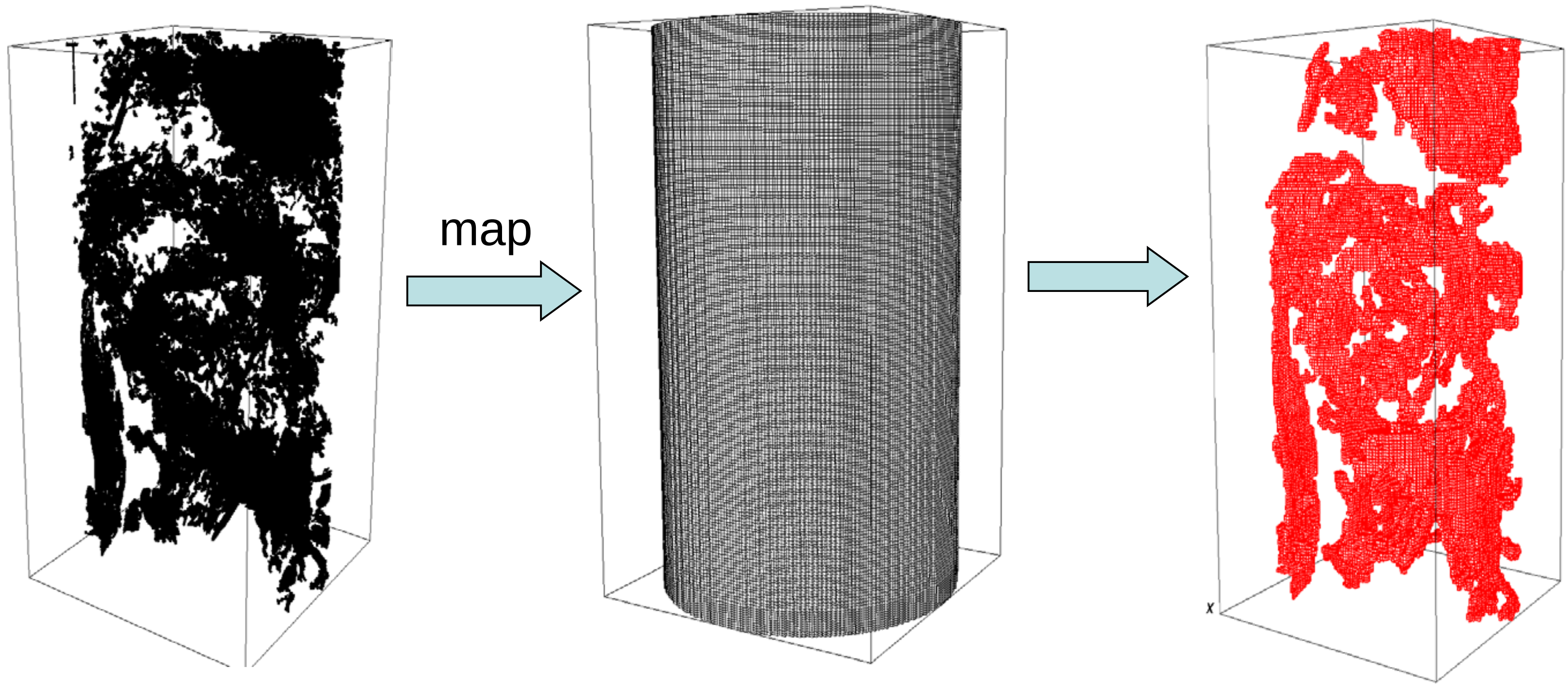
- Smith, M. Sholokhova, Y., Hao, Y., and Carroll, S. (2013) CO_2-induced dissolution of low permeability carbonates. Part 2: Characterization and experiments, *Advances in Water Resources* http://dx.doi.org/10.1016/j.advwatres.2013.09.008

Task 5.1 – Predict porosity and permeability evolution in carbonate storage reservoirs



Nested grid model to scale mineral and pore distribution from tomography resolution (~40^3 u^3) to model grid (1 mm^3)

- The connected fractures and macro pore clusters were then mapped onto a regular grid system with the grid block size as ~300^3 µm^3



connected fractures/macro-pores in XCMT images (image resolution: 42.6 µm)

regular grid system with the grid size as ~ 300 µm

connected fractures at a grid scale of ~ 300 µm