

CO₂ Utilization in Unconventional Reservoirs

Project Number 67897 Task 1

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U.S. Department of Energy
National Energy Technology Laboratory
Mastering the Subsurface through Technology Innovation
and Collaboration: Carbon Storage and Oil and Natural Gas Technologies Review Meeting
August 16-18, 2016

Presentation Outline

- Program Focus Area and DOE Connections
- Goals and Objectives
- Scope of Work
- Technical Discussion
- Accomplishments to Date
- Project Wrap-up
- Appendix (Organization Chart, Gantt Chart, and Bibliography)

Benefit to the Program

- Program goals addressed:
 - Technology development to predict CO₂ storage capacity
 - Demonstrate fate of injected CO₂
- Project benefits statement: This research project conducts modeling and laboratory studies to lower cost and to advance understanding of storing pure CO₂ and mixed gas emissions produced from post- and oxy-combustion flue gas in unconventional geologic reservoirs.

Project Overview:

Goals and Objectives

- Goal: Development of geologic storage technology with a near zero cost penalty goal – a grand challenge with enormous economic benefits.
- Objective: Employ a multidisciplinary approach for identifying key sequestration opportunities and for pursuing major research needs in:
 - Identifying R&D needs and pursuing R&D on promising low-cost technologies for utilizing CO₂ and CO₂ containing other constituents in depleted shale gas and shale oil reservoirs.
 - phase behavior and fate and transport of supercritical gas mixtures in fractured geologic formations.
 - casing material studies with water and mixed gas systems
 - development of acoustically responsive contrast agents for enhanced monitoring of injected CO₂.

Project Overview:

Scope of work

➤ Task 1 – Utilization in Unconventional Reservoirs

▪ 1.1 Storage in Depleted Shale Gas Reservoirs

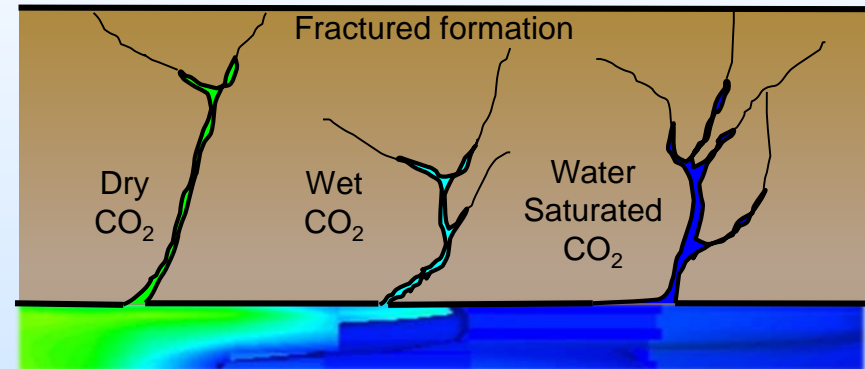
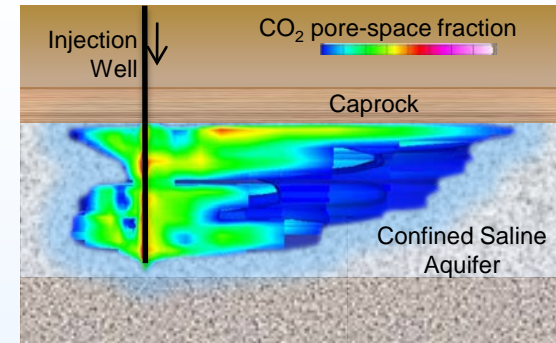
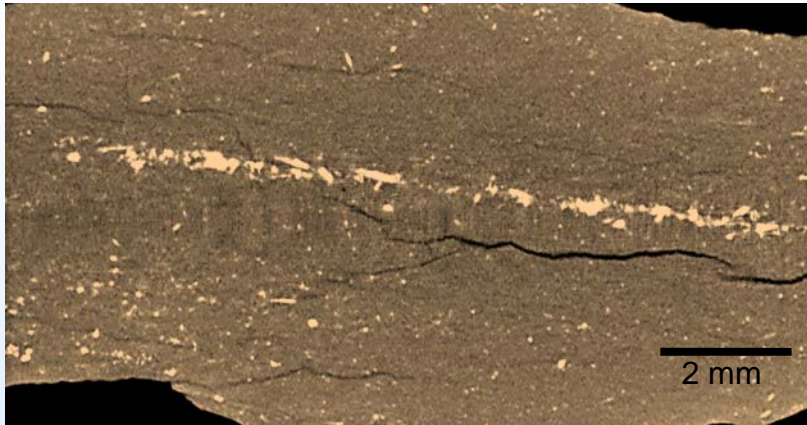
- Geochemical Aspects of Wet scCO₂ Fluids
- Supercritical CO₂ fluids and Clay Interactions
 - ❖ Structural changes to Na montmorillonites exposed to variable hydrated scCO₂ fluids
 - ❖ Cation/CO₂ interactions obtained from cation specific clays
 - ❖ MD simulations on CH₄/CO₂ sorption
- Competitive CH₄/CO₂ Sorption
 - ❖ Near infrared spectroscopy technique development
- Reservoir Modeling
 - ❖ Field scale simulation utilizing CO₂ in a depleted fractured shale reservoir utilizing CO₂
 - ❖ Incorporate laboratory findings to optimize methane production

▪ 1.2 Enhanced Monitoring Agents

- Impedance tube measurements with sand/nanoparticle composites performance testing in a laboratory setting
- Low-Frequency Seismic/Elastic Property Measurement System
 - Impose known stresses on a sample and measure the resulting strain
 - Results from Berea sandstone

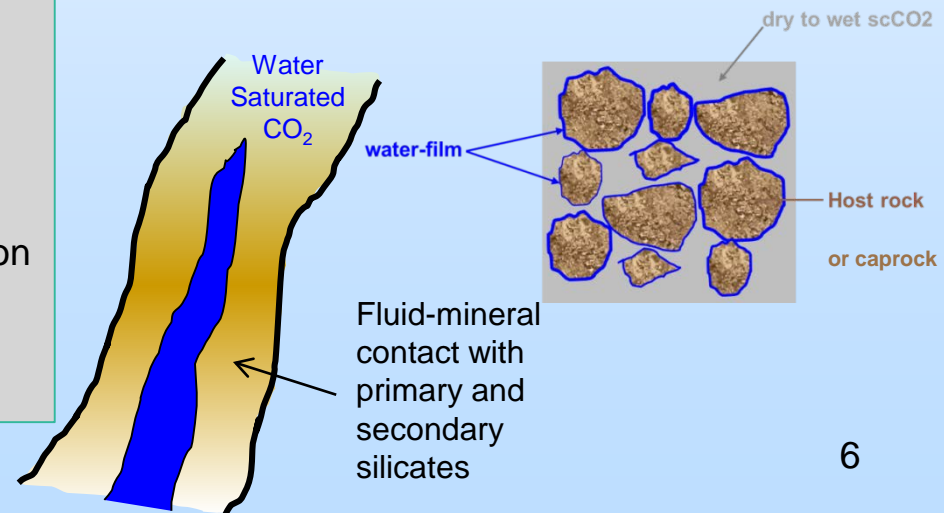
Geochemical Aspects of Wet scCO₂ Fluids

Woodford Shale



Early laboratory studies at PNNL demonstrate unusual behavior between water bearing scCO₂ fluids and clays. Key questions emerged:

- How significant are volume changes associated with swelling clays in the presences of CO₂?
- How do we predict conditions for fluid transmission through fractures (opening/self sealing)?
- What controls gas sorption processes and what role does water play in the presence of scCO₂.

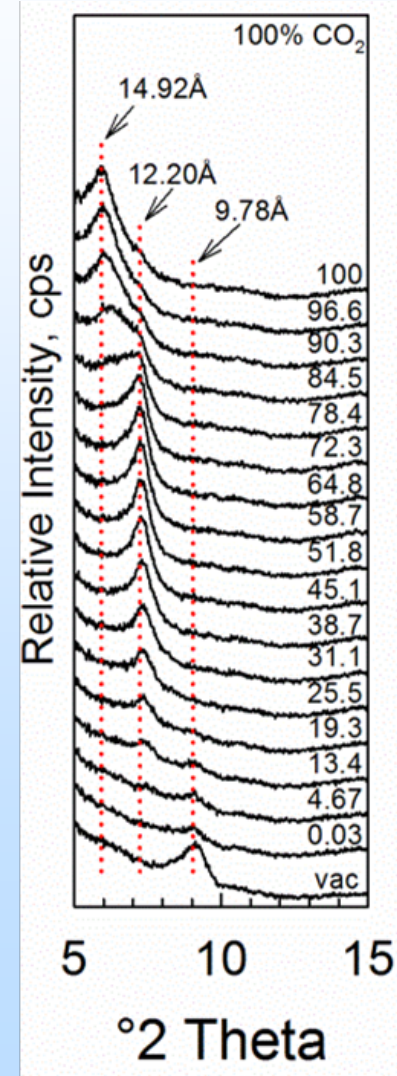
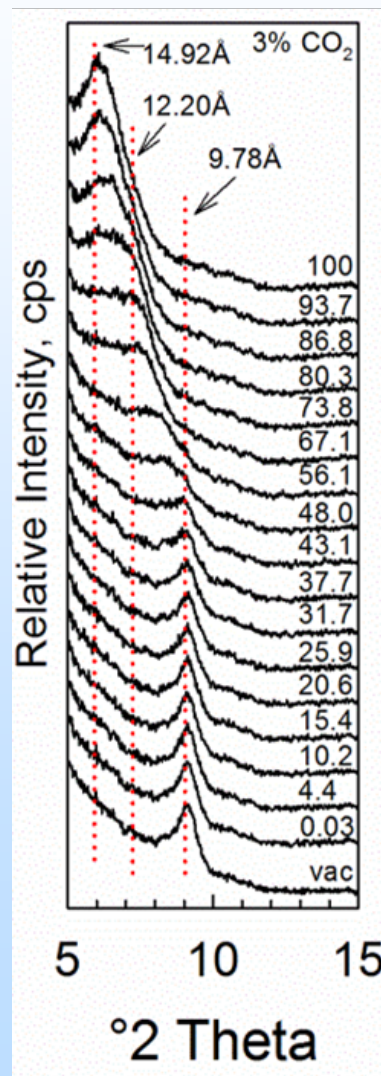
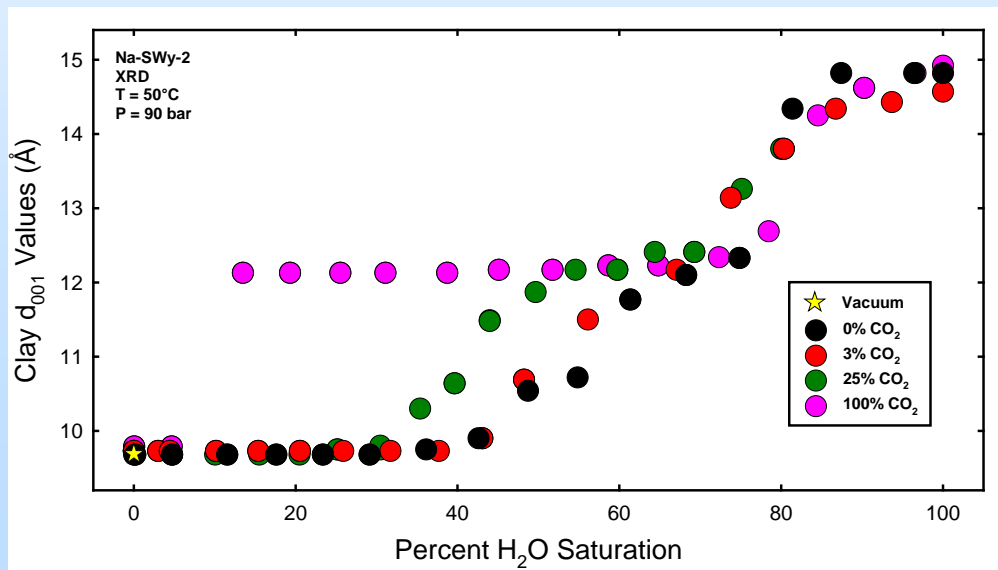


Interactions of Na Montmorillonites with Variable Hydrated scCO₂ Fluids

Pressurized *flow-through* XRD-FTIR capability collected from the Na-SWy-2 clay during exposure to variable amounts of dissolved water in CH₄ gas containing 3% CO₂ (left) and pure CO₂ (right).

- Transmission Pressurized IR and XRD Cell
- IR technique provides dissolved H₂O concentrations in supercritical fluids (HOH bending mode of dissolved water)
- XRD tracks structural changes of the clays (d001 basal reflection)
- Stacked XRD patterns illustrate structural changes occurring to the clays as a function of % water saturation

100 %, 25 %, 3 %, 0% CO₂ in CH₄

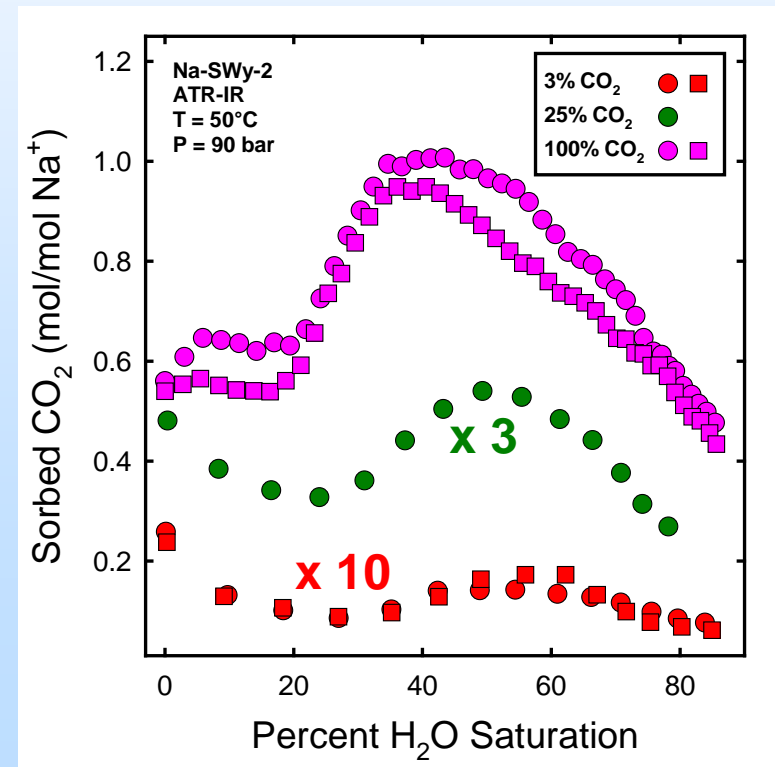
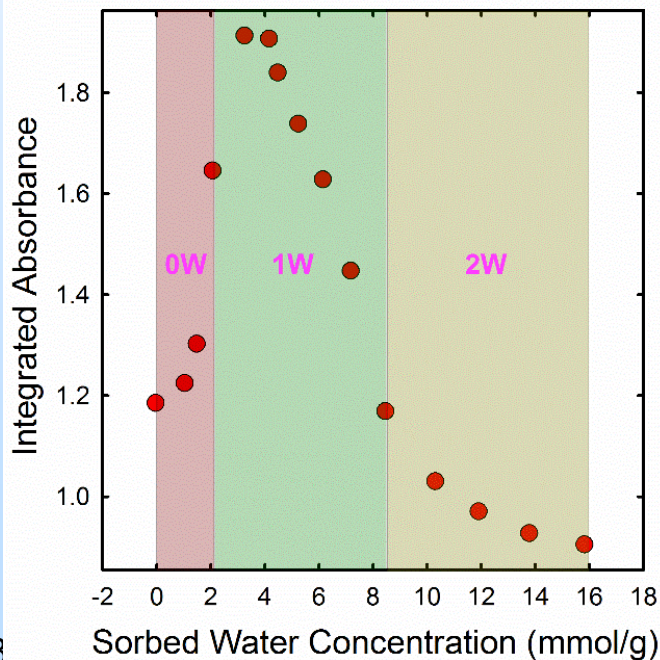


Interactions of Na Montmorillonites with Variable Hydrated scCO_2 Fluids

IR and XRD Experiments with Na-SWy-2 (90 bar and 50°C)

- ❑ During exposure to anhydrous CO_2 clay structure remains stable
- ❑ IR shows a dramatic increase in absorbance with expansion from 0W to 1W after the addition of a small amount of water
- ❑ Decreased CO_2 concentrations with increasing water
- ❑ Pressurized XRD coupled to IR provides a unique insight into structural changes in a mixed gas system (i.e. CO_2 , CH_4)

Na-SWy-2 Exposed to 100% CO_2



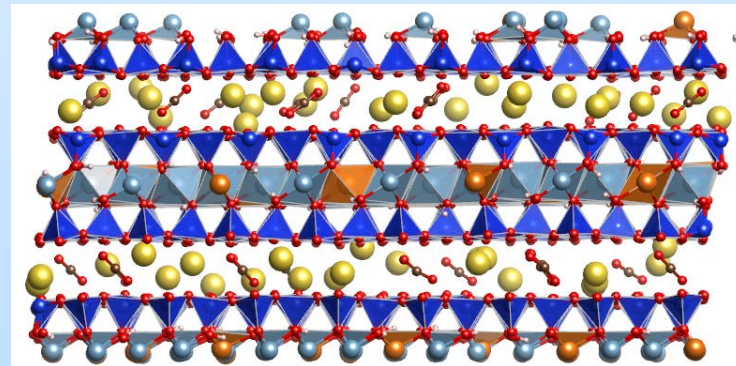
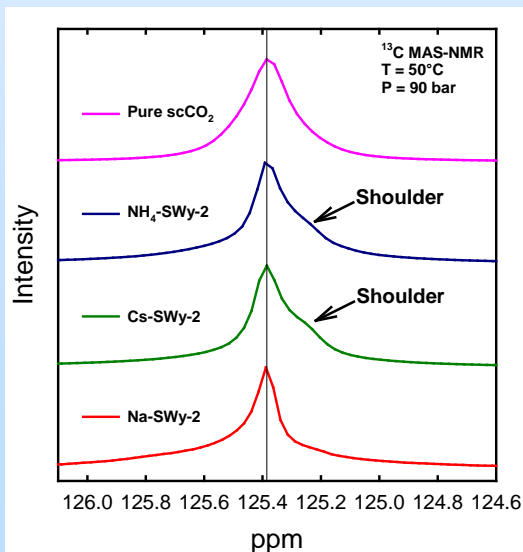
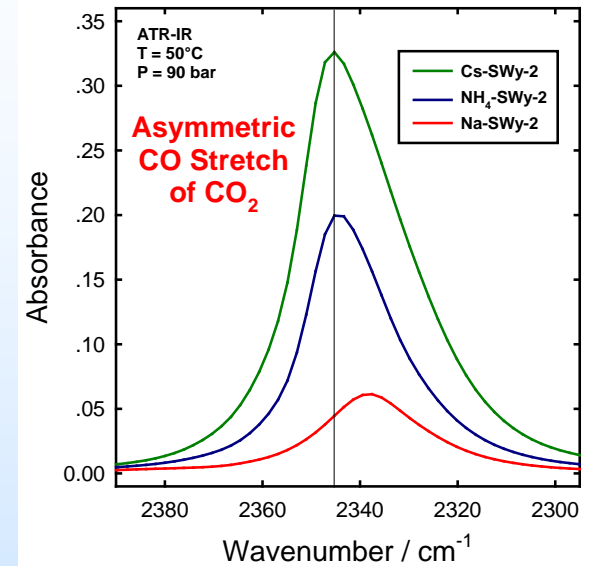
Cation and CO₂ interactions: What is happening in the clay interlayer?

ATR-IR spectra of CO₂ sorbed to Na-SWy-2, Cs-SWy-2 and NH₄-SWy-2 in the asymmetric CO stretching regions of CO₂.

- IR bands of CO₂ are at different positions for Cs⁺ and NH₄⁺
- Cs⁺ and NH₄⁺ cations are solvated by CO₂
- No shift in the Na-SWy-2

High Pressure ¹³C MAS-NMR of CO₂ sorbed to Na-SWy-2, Cs-SWy-2 and NH₄-SWy-2

- Shoulder absent in spectra for pure scCO₂ and scCO₂ exposed to Na-SWy-2
- Shoulder in spectra for Cs⁺ and NH₄⁺ indicate a different chemical environment

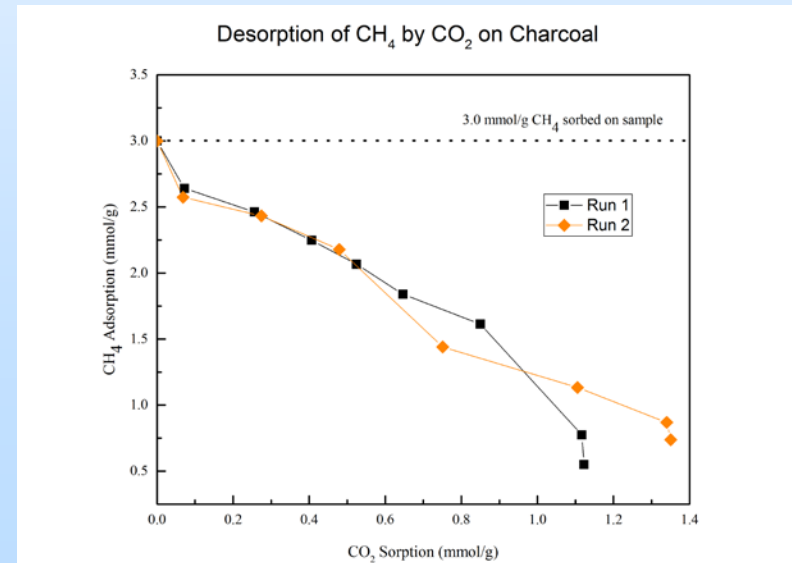
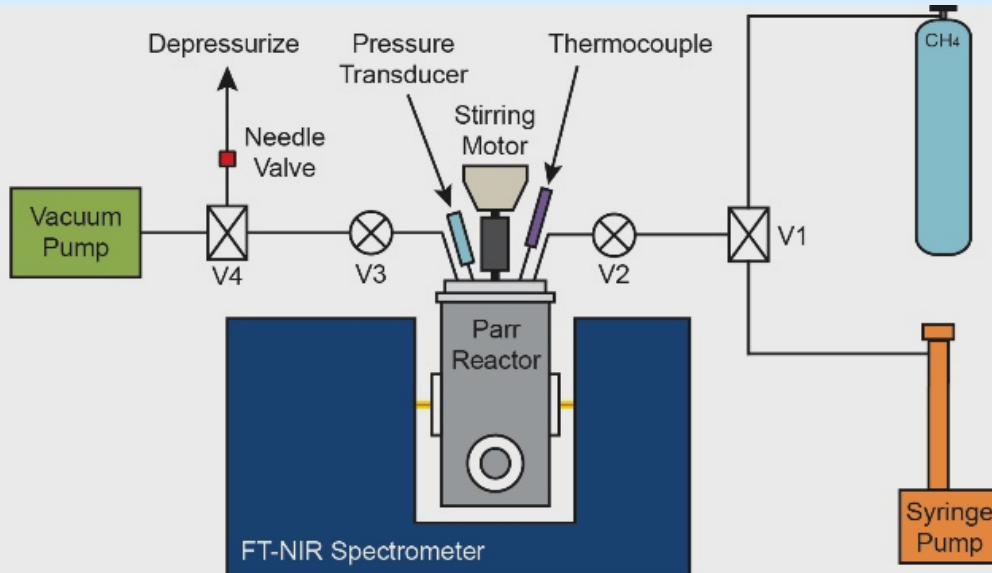
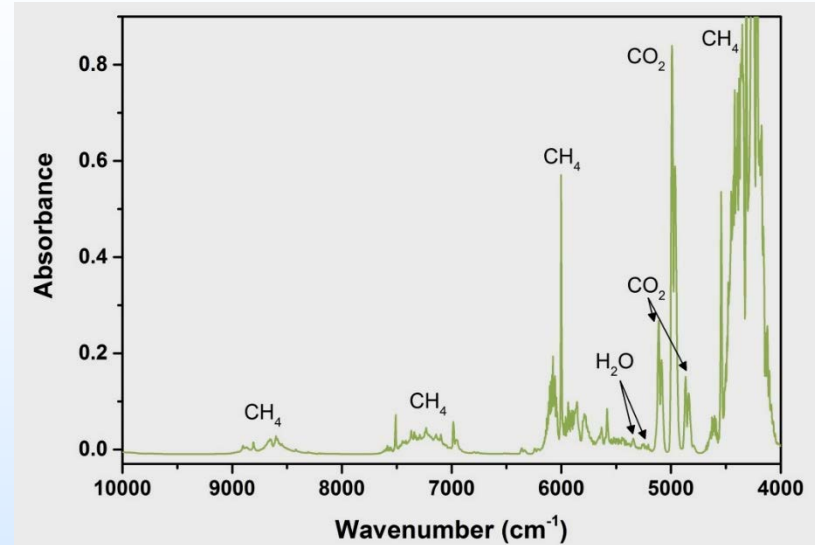


Through *in situ* measurements, atomistic models of scCO₂ and interlayer cation interactions are benchmarked and become key to developing molecular simulations of more complex systems.

In Situ NIRS Capability for Competitive CH₄/CO₂ Sorption Studies on Shales

Near-infrared spectroscopic (NIRS) capability for studying CH₄ and CO₂ sorption onto organic-rich shales.

- Each gas has unique spectral features, ideal for measuring competitive gas adsorption
- CH₄, integrated absorbance bands from 6721-7671 cm⁻¹ and 8244-9037 cm⁻¹
- CO₂, integrated absorbance bands from 4,800 to 5200 cm⁻¹



Modeling CO₂ Sorption on Clays for Reservoir Simulators

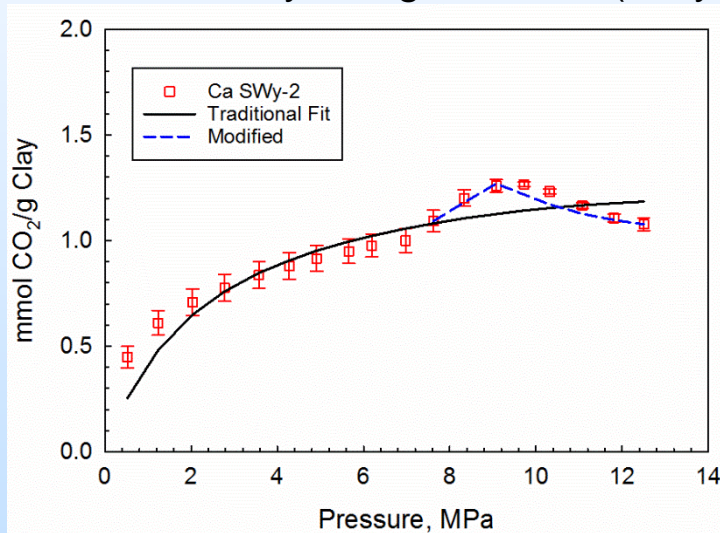
- STOMP-EOR simulates multiphase, multicomponent flow and transport of CO₂, methane and oil components coupled with geochemical reactions
- Simulations are used to investigate methane release via competitive CO₂ adsorption

Equilibrium constant, K_{eq} , as a function of the density of supercritical phase CO₂ (scCO₂):

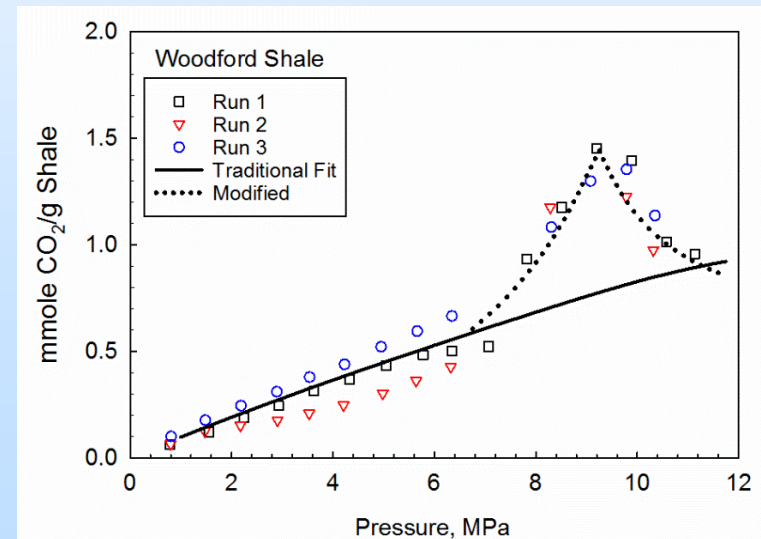
$$K_{eq} = \frac{C * \rho_{crit}}{|\rho_{crit} - \rho_{scCO_2}|}$$

Where a “critical” CO₂ density -the gaseous density beyond which CO₂ will begin desorbing- as well as an empirically fitted (clay-type specific) constant, C .

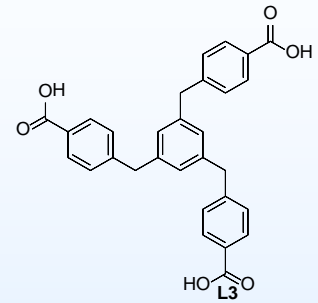
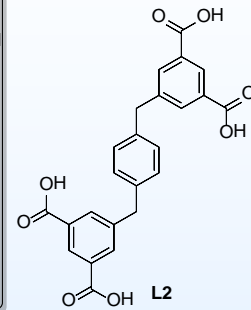
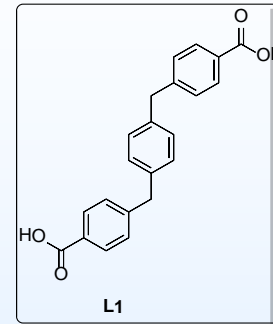
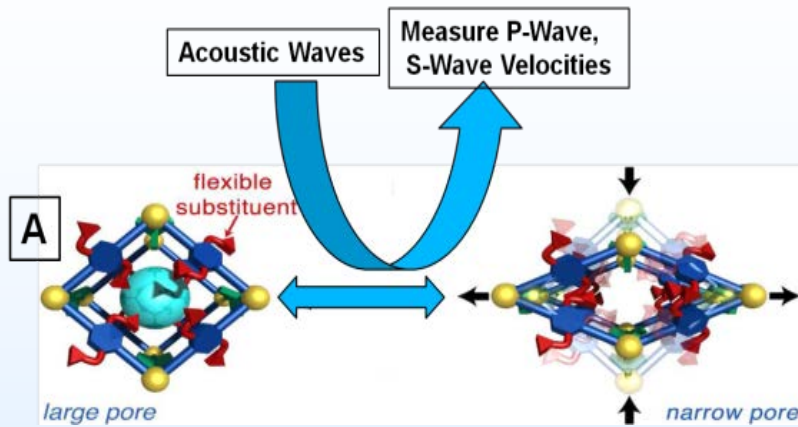
QCM Data for Wyoming Smectite (SWy-2)



MD simulations describe adsorption as initially driven by CO₂ film formation on the surface, but interactions in bulk CO₂ become more energetically favorable at higher pressures.

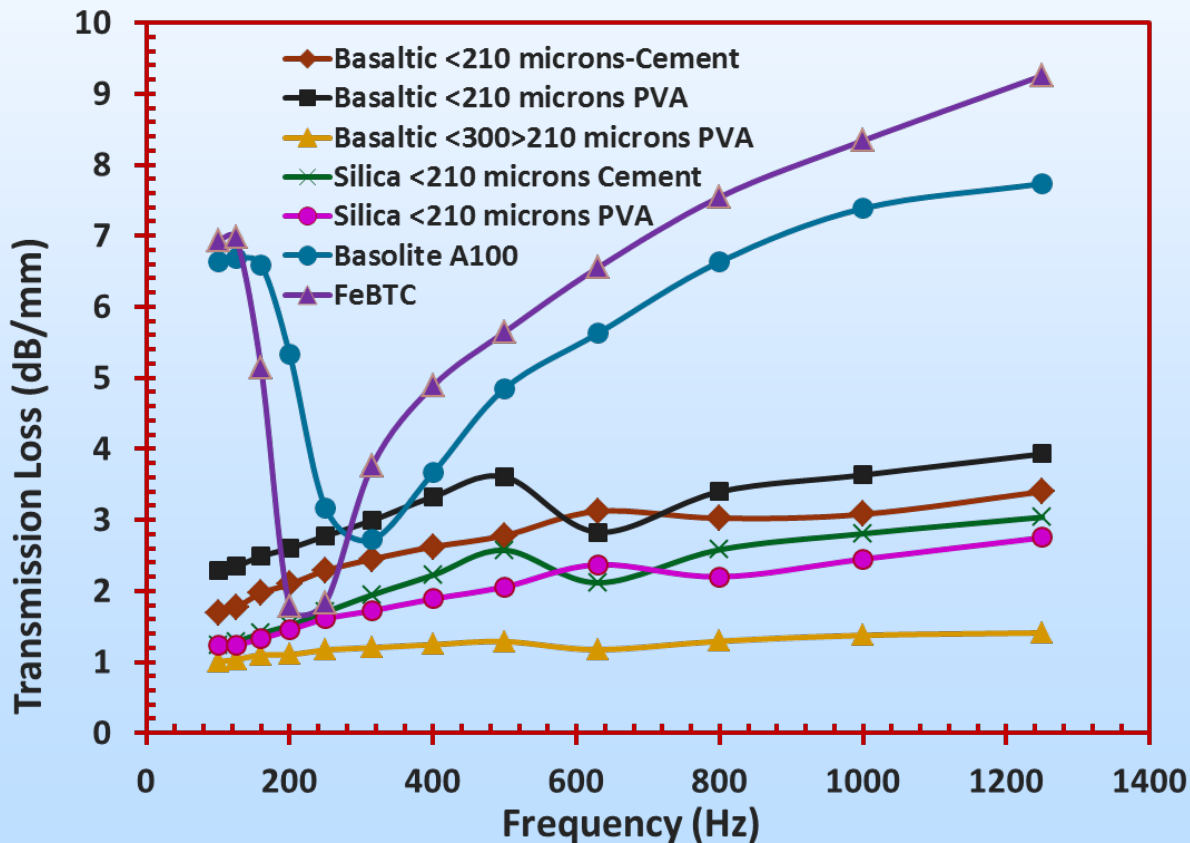


Acoustically Responsive Contrast Agents for Enhanced Monitoring of Injected CO₂



- MOF nanomaterials offer opportunity to expose a very large surface area in limited volume
- Introduction of flexible ligands in MOF structure allows for tuning of librational absorption modes that are detectible through conventional seismic imaging.
- Dispersion in scCO₂ to form a nanofluid provides for injectable acoustic contrast agent

Impedance Tube Measurements with Sand/Nanoparticle Composites

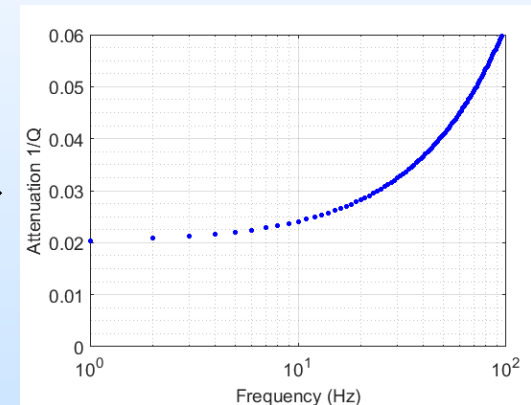
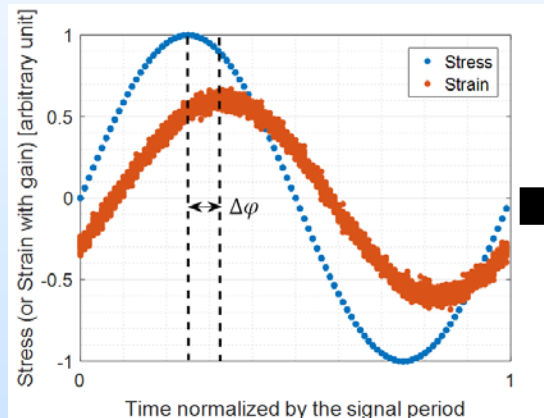
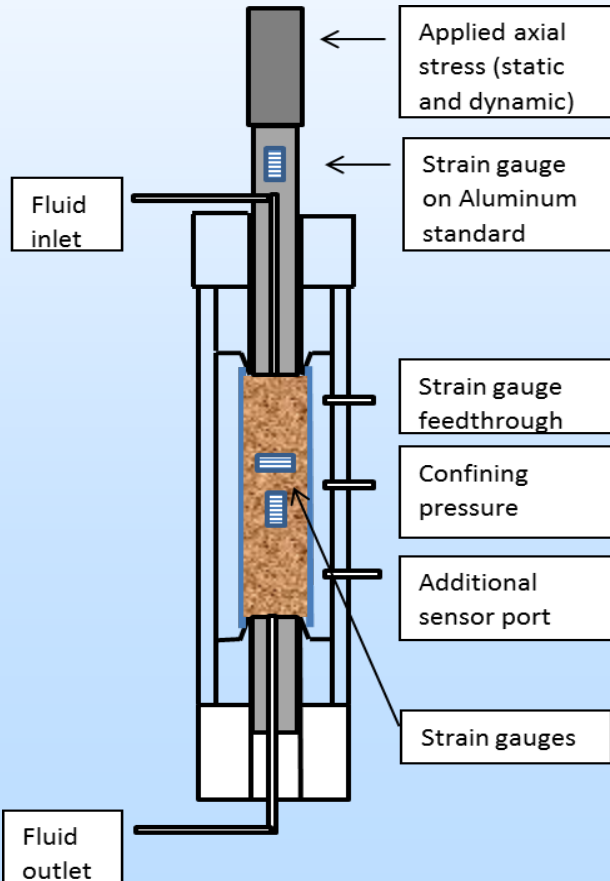


Sand-nanoparticle composites exhibit striking transmission loss shifts when compared to sand-water composites in the low frequency band (100 Hz to 500 Hz)

Low-Frequency Seismic/Elastic Property Measurement System

Laboratory technique developed to measure seismic attenuation and velocity on rock core at relevant frequencies (0-100 Hz) under high confining pressure.

- Impose known stress on sample and measure resulting strain (forced oscillation method)
- Both velocity and attenuation are key components in the wave propagation
- Phase shift between stress and strain provides information on attenuation
- Amplitude ratio provides velocity information (Young's Modulus)



Attenuation $1/Q$ is defined as: $\frac{1}{Q} = \tan(\Delta\varphi)$

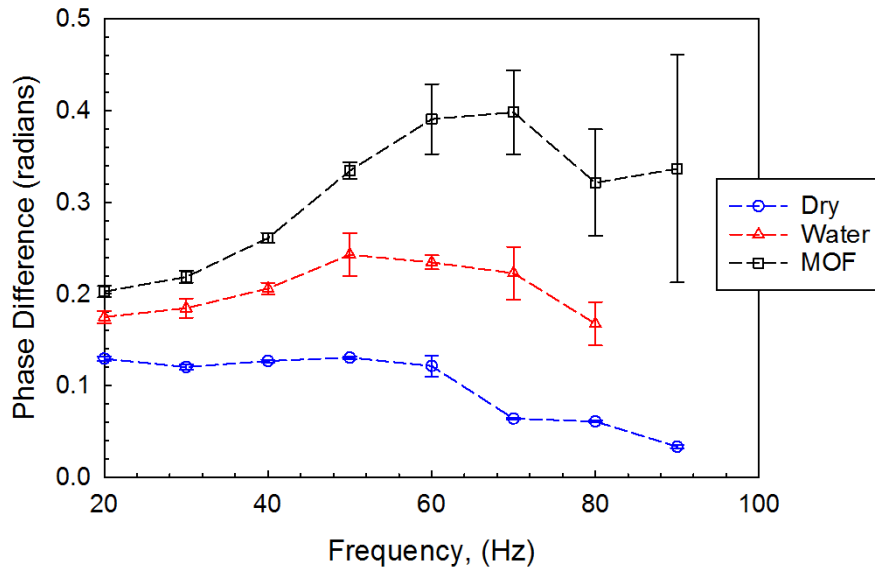
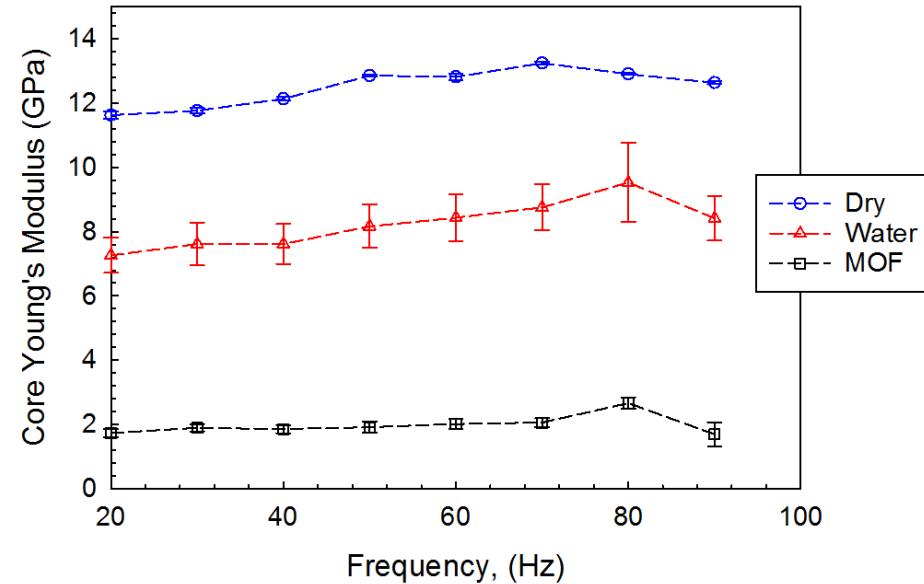
For small $\Delta\varphi$, $\frac{1}{Q} \approx \Delta\varphi$

Effect of injectates (nano MOFs) on wave propagation behaviors (e.g., refraction, reflection, and attenuation)

Evidence of Seismic Properties Being Altered in Berea Sand Stone Containing Injected MOFs

Mechanical property (Young's modulus) of Berea SS:

- Dry core: near constant value of ~12 GPa (similar to Tisato & Quintal 2013)
- Water saturated core: ~6-8 GPa with an observable increases at higher frequencies
- MOF fluid: large decrease compared to air and water (2 GPa)



Seismic attenuation in Berea SS:

- Dry core: near linear response up to 60 Hz (~0.13 radians)
- Water saturated core: slightly higher response (0.8-0.22 radians)
- MOF Fluid: increased attenuation above 50 Hz compared to air and water

Accomplishments to Date

- ▶ Completed a series of experiments relating volume changes to swelling clays in variable hydrated supercritical mixed gas fluids.
- ▶ Key *in situ* measurements identified CO₂-cation interactions in model clay minerals that can be used to bench mark molecular models
- ▶ Initiated a new NIR technique to characterize competitive CH₄/CO₂ processes occurring on model clay systems and natural shales
- ▶ Incorporating results from fundamental studies on CO₂ adsorption in shales into reservoir simulators to model at the field scale CH₄ production enhanced by injecting CO₂
- ▶ Developing advanced monitoring techniques that utilize an injectable nanomaterial to track CO₂ migration geologic reservoirs.

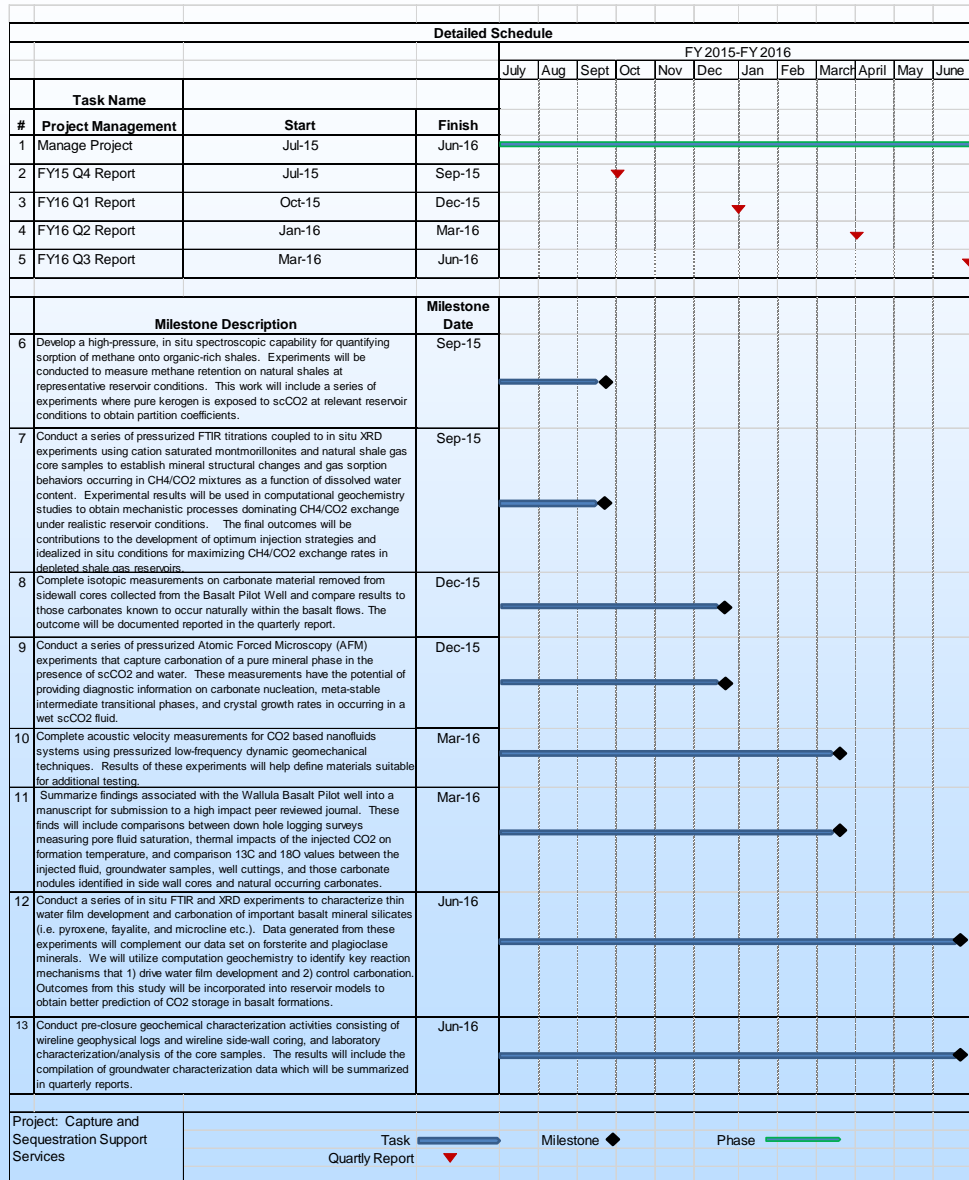
Appendix

- These slides will not be discussed during the presentation, **but are mandatory**

Organization Chart

- Project team has participants that cut across the Energy & Environment and Fundamental Sciences Directorates at PNNL
- Pacific Northwest National Laboratory is Operated by Battelle Memorial Institute for the Department of Energy

Gantt Chart



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Sequestration in Basalt Formations

Project Number 66799 Task 2

B. Peter McGrail

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Collaborating Institutions

University of Wyoming

U.S. Department of Energy
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Mastering the Subsurface through Technology Innovation
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Benefit to the Program

- Program goals addressed:
 - Technology development to predict CO₂ storage capacity
 - Demonstrate fate of injected CO₂ and most common contaminants
- Project benefits statement: This research project conducts modeling, laboratory studies, and pilot-scale research aimed at developing new technologies and new systems for utilization of CO₂ in unconventional geologic formations (basalts and shales) for long term subsurface storage and enhanced gas recovery. Findings from this project will advance industry's ability to predict CO₂ storage capacity in geologic formations.

Basalt Project Overview:

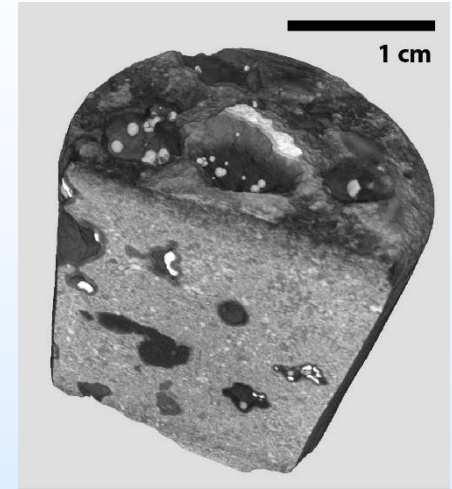
Goals and Objectives

- Goal: Provide a path forward for commercial use of deep basalt formations for CO₂ sequestration
- Objective: Address key challenges associated with utilization of basalt formations as CO₂ storage units
 - Conduct laboratory research that addresses commercial-scale injection strategies
 - Provide laboratory measurements for predicting CO₂ fate and transport
 - Support field activities associated with Wallula basalt pilot project

Basalt Project Overview:

Scope of work

- Carbonate Mineralization in Wet scCO_2 Fluids
 - Mineral reactivity and transformations in adsorbed H_2O films
 - Kinetics of forsterite carbonation in thin water films
 - MD Simulations
 - Visualizing mineral carbonation in wet scCO_2
 - Crystal growth
 - Mechanism of carbonation



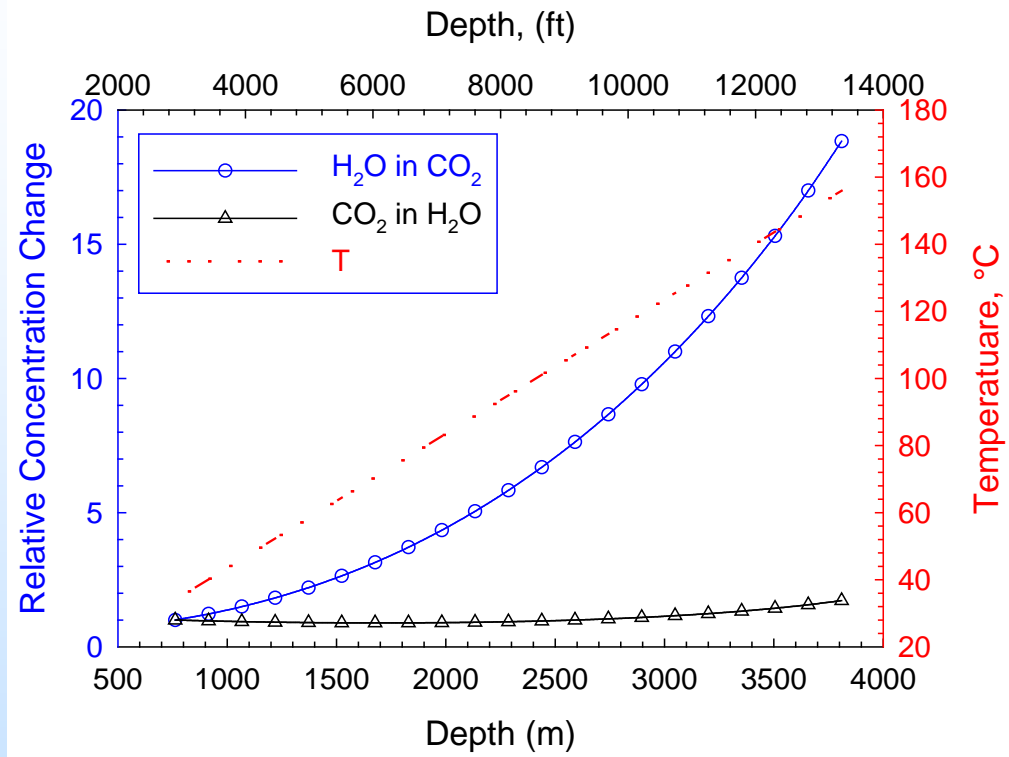
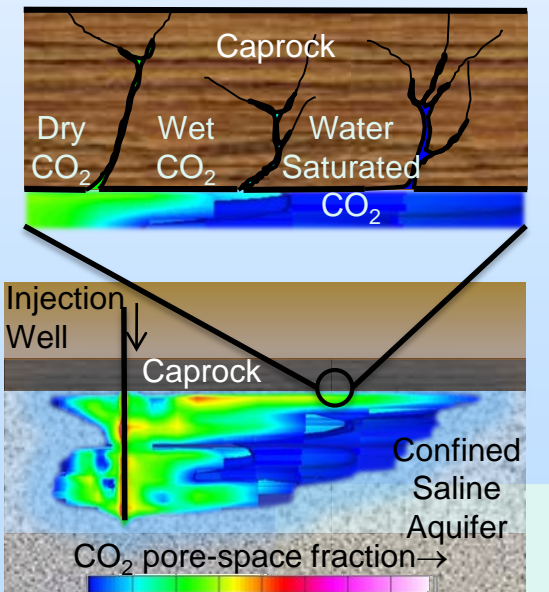
post-injection sidewall core recovered from 856.5 m.

- Wallula Basalt Pilot Study
 - Overview and update of pilot project
 - Final wireline and hydrologic characterization
 - Isotopic analysis on pre and post injection samples
 - nanoSIMS technique
 - Isotopic comparison of pre and post CO_2 injection

Phase Behavior of CO₂-H₂O Mixtures in Geological Sequestration

CO₂-H₂O Mixtures

- ☐ CO₂ solubility in water varies little with pressure and temperature
- ☐ H₂O solubility in scCO₂ is strongly dependent on depth
- ☐ An equivalent geochemical framework for chemical reactivity in wet scCO₂ does not yet exist



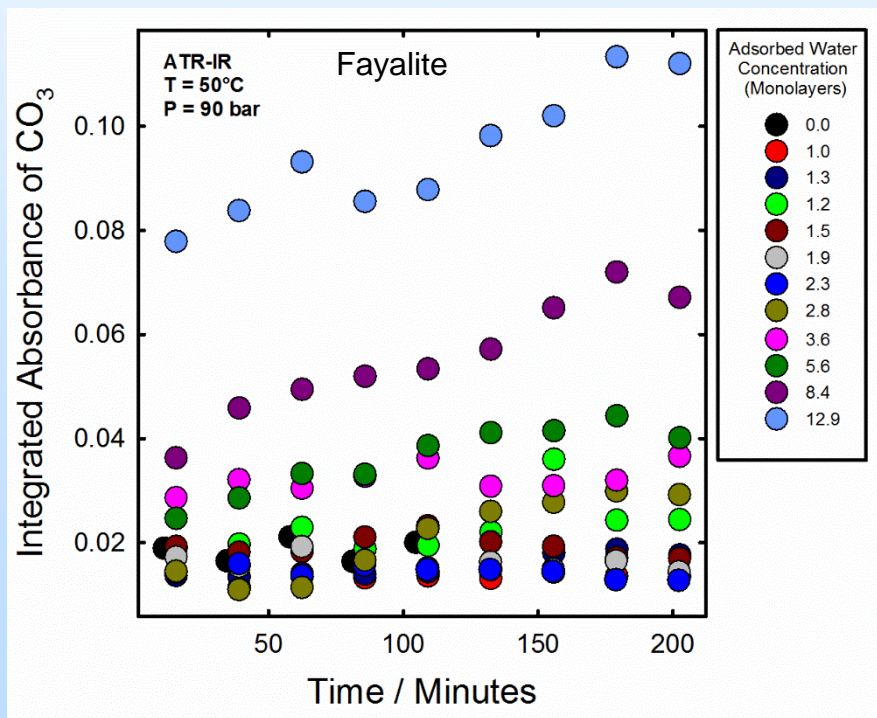
Mineral transformation kinetics is potentially as great or greater in wet scCO₂

Probing dynamic mineral reactivity and transformations in adsorbed H₂O films

Goal: Probing dynamic geochemistry occurring in adsorbed H₂O films.

Experimental Conditions: Constant temperature (50°C) and pressure (90 bar), with dry to variably wet scCO₂.

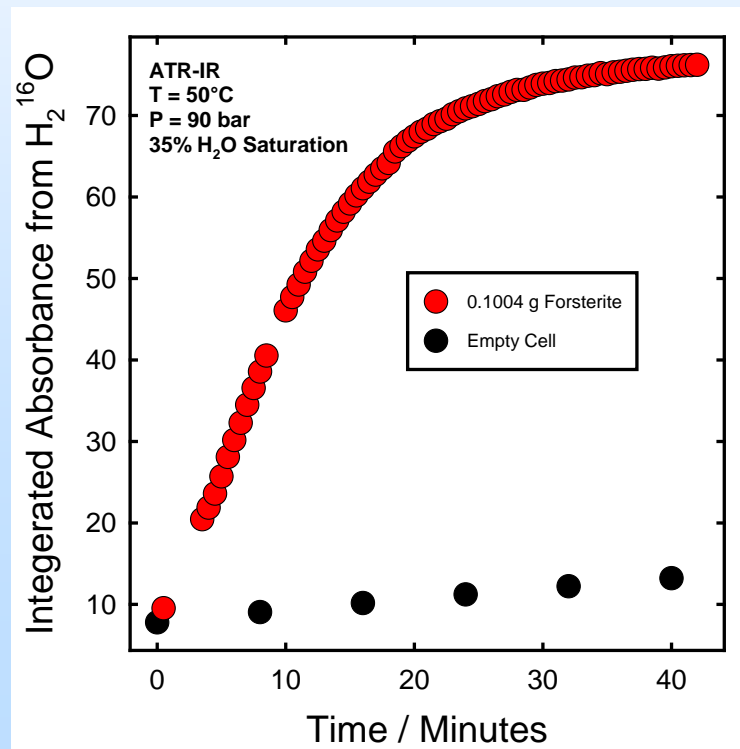
Results: Siderite precipitates, but only beyond a threshold adsorbed H₂O concentration of 5.6 monolayers.



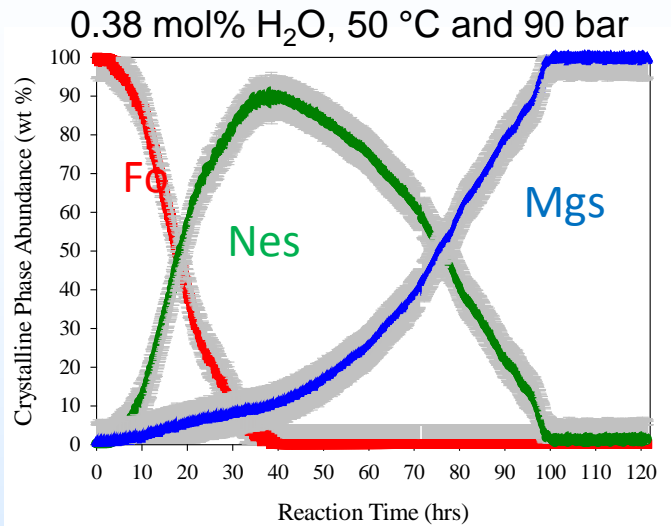
Goal: Role of adsorbed H₂O threshold concentration in carbonation reactivity.

Experimental Conditions: 50°C and 90 bar scCO₂, with 35% H₂O saturation, initially all dissolved water is enriched in ¹⁸O.

Results: Fast conversion of H₂¹⁸O to H₂¹⁶O with only ~2.5 monolayers adsorbed H₂O indicates carbonic acid formation

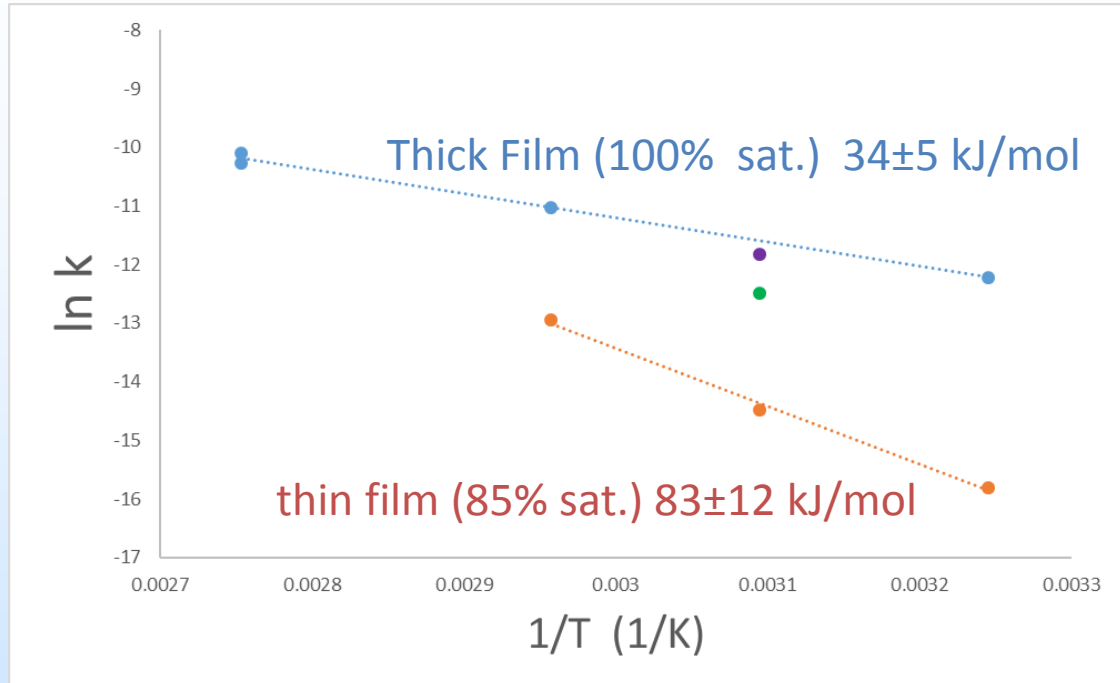


Kinetics of forsterite carbonation in thin water films quantified with in-situ HXRD



Fo-Forsterite
Nes-nesquehonite
Mgs-magnesite

Apparent activation energy for forsterite carbonation at 90 bar



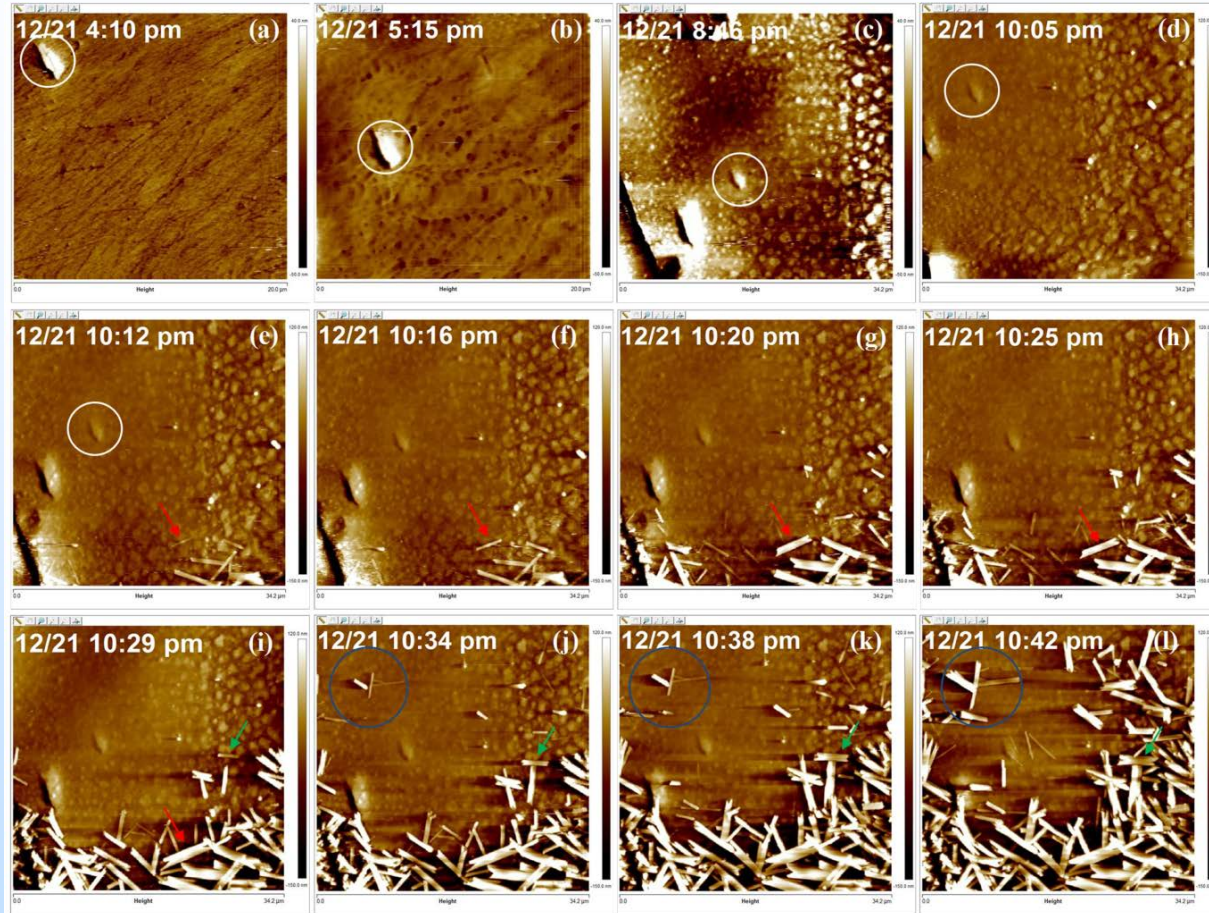
- Energy barrier for mineral transformation changes with water content
 - Apparent activation energy of coupled forsterite dissolution and Mg-carbonate precipitation doubles when water in the scCO₂ is 85%
 - Implications for mineralization in confined subsurface environments (pores, pore throats, and fractures)

Visualizing Mineral Carbonation in Wet scCO₂

Experimental Approach: Brucite, when exposed to a steady stream of humid scCO₂ at 50°C and 90 bar, forms rod-shaped nesquehonite clearly visible on the brucite surface.

Pressurized Atomic Forced Microscopy

- Carbonation in wet scCO₂
 - Controlling factors
 - Modeling parameters
- Carbonation Products
 - Nucleation sites
 - Growth habits and morphologies
- Intrinsic Rate Constants
 - Water concentrations in scCO₂
 - Variability in water film thickness

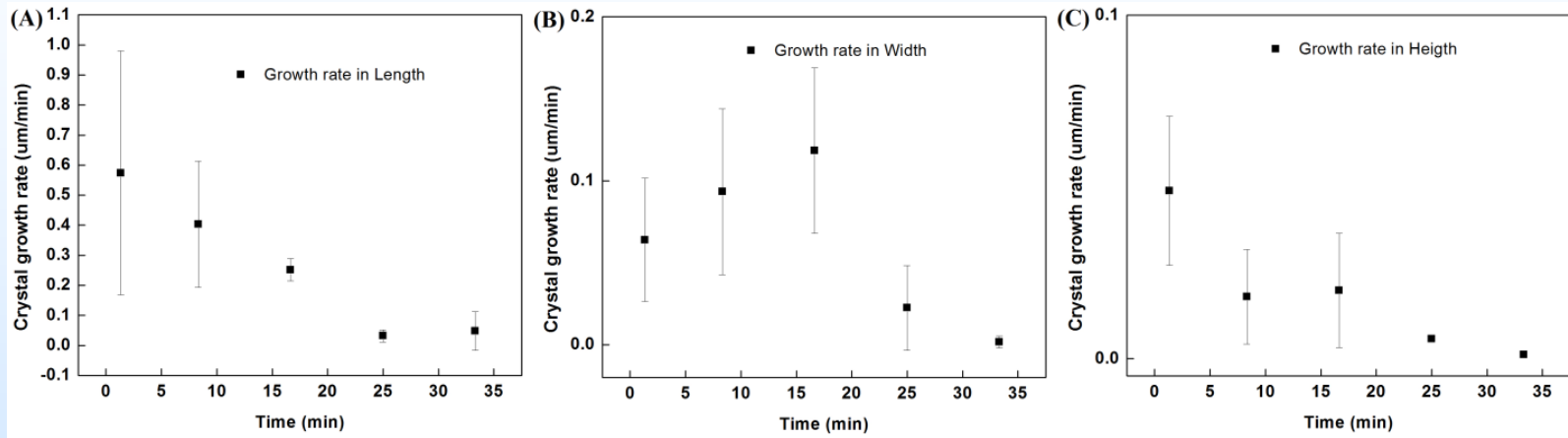


Mineral Carbonation: In-situ AFM images collected from a polished brucite surface during exposure to dry scCO₂ after (minutes): (a) 60, then after exposure to wet scCO₂ (water saturated) (b) 65, (c) 276, (d) 355, (e) 362, (f) 366, (g) 370, (h) 375, (i) 379, (j) 384, (k) 388, and (l) 392. Experimental conditions: 90 bar, 50°C, and a flow rate of 250 μ L/min.

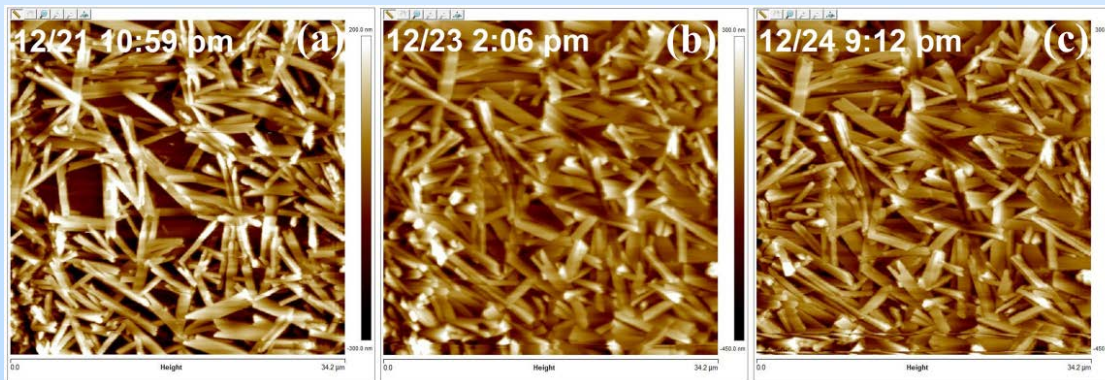
Visualizing Mineral Carbonation in Wet scCO₂

Crystal growth rate of the nesquehonite crystals

- Tracking nesquehonite growth rate in time lapsed images
- Rod-shaped crystal growth becomes attenuated with an increase in size whereas small rods experience accelerated growth during the initial formation period.



The crystal growth of rod-shaped crystals in length (A), width (B), and height (C) direction.



The brucite surface becomes almost completely covered by rod-shaped crystals after 7 h 15min and then was completely encased in rod-shaped crystals after 20 h 44 min.

Basalt Project Overview:

Scope of work

➤ Wallula Basalt Pilot Project Support

- Field Activities
 - Detailed wireline survey characterization
 - Groundwater sampling
 - Targeted side-wall coring
 - Extended hydrologic tests
 - Final well decommissioning/site demobilization.
- Laboratory Activities
 - Side wall core characterization.



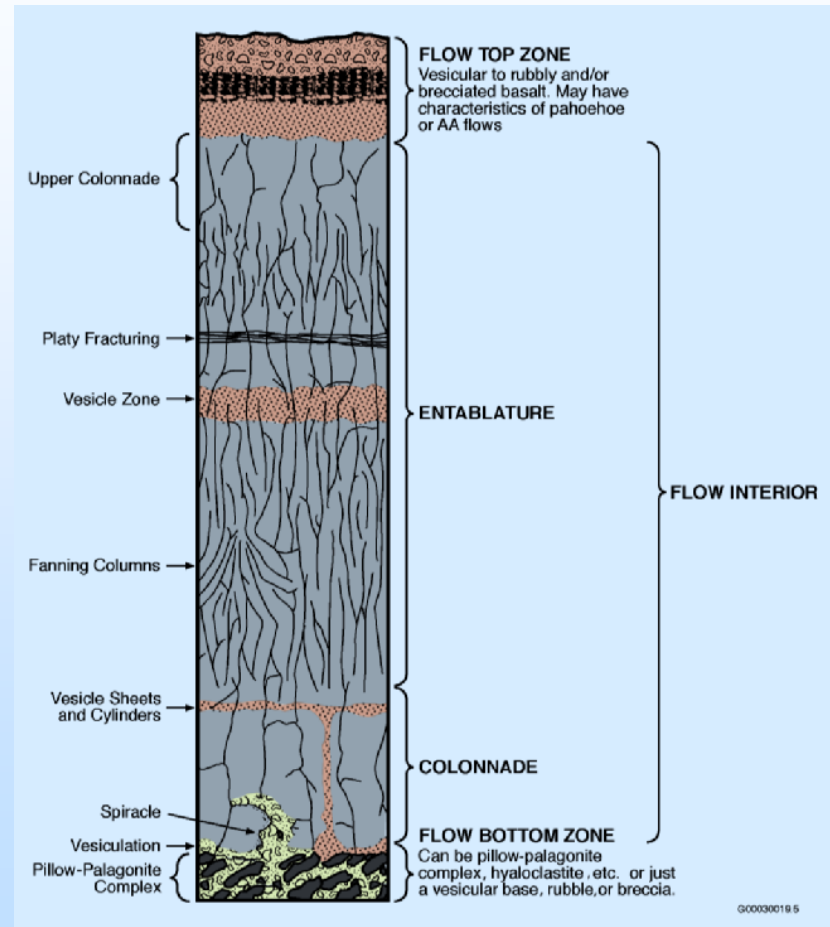
Flood Basalt Features Relevant to CO₂ Sequestration

- Formation process
 - Giant volcanic eruptions
 - Low viscosity lava
 - Large plateaus
 - Multiple layers
- Primary structures
 - Thick impermeable seals
 - Caprock (flow interior)
 - Regional extensive interbeds
 - Permeable vesicular and brecciated interflow zones
 - Injection targets
 - 15-20% of average flow

Deccan Trap Basalts



Layered Basalt Flow



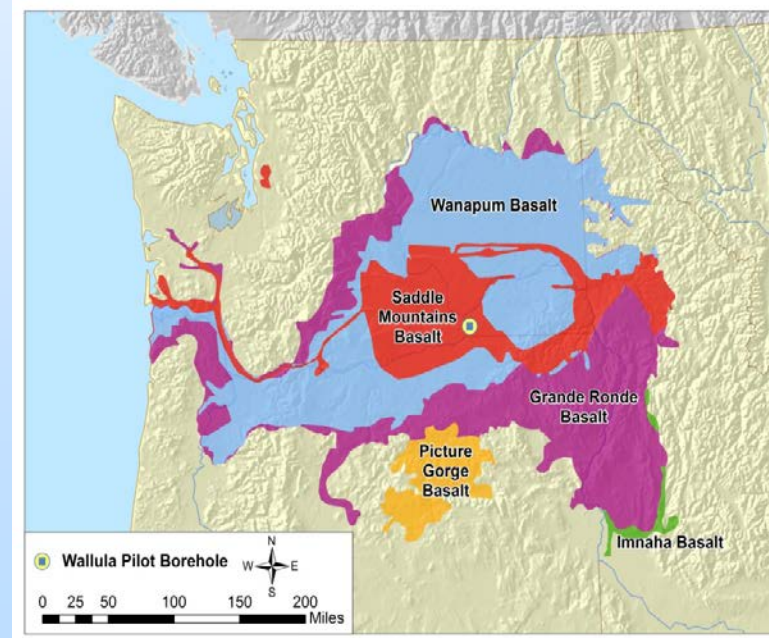
Wallula Basalt Carbon Sequestration Pilot Project

Project Background:

- Drilling initial test characterization and well completion: Jan. – May 2009
- Extended hydraulic test characterization: Feb. – March 2011 and Sept. – Nov. 2012
- ~1,000 MT CO₂ injection: July 17th – August 11th, 2013
- Post-injection air/soil monitoring and downhole fluid sampling performed for ~2 years following injection

Current Status:

- Final well characterization activities: June – July 2015
- Detailed wireline survey
- Targeted sidewall coring
- Extended hydrologic tests
- Final well decommissioning/site demobilization: August 2015

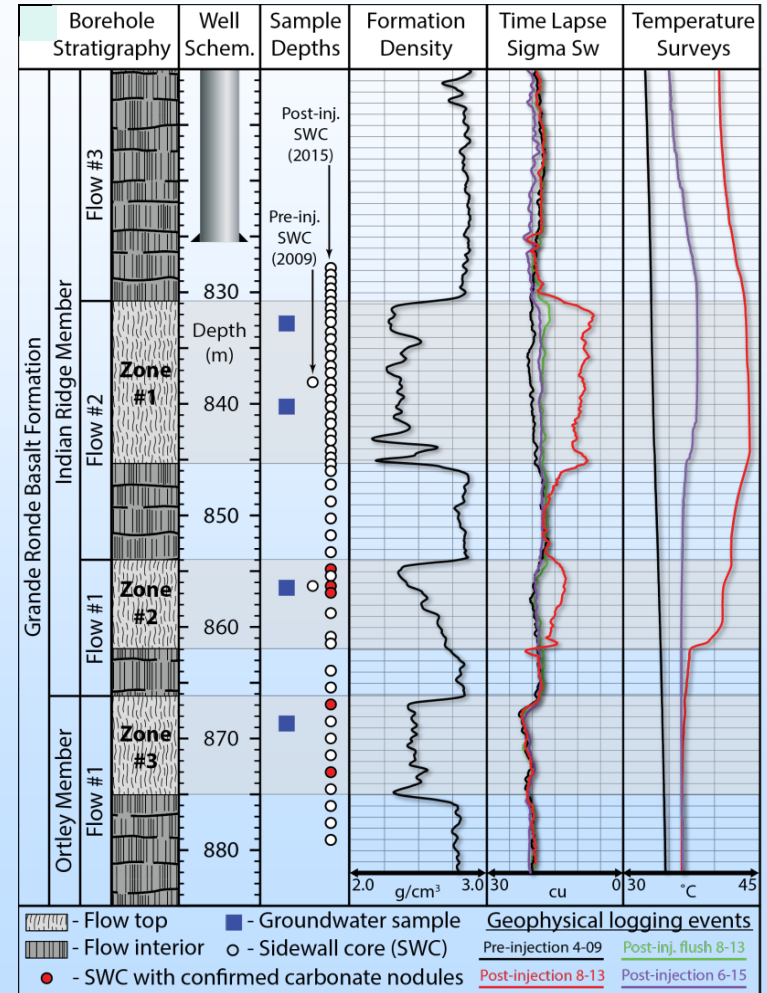


Wallula Basalt Pilot Well: Final Wireline and Hydrologic Characterization

- **Extended duration hydrologic injection test**
 - Assess large scale changes in aquifer reservoir hydraulics
 - 18,000 gallons of water was injected over 3.7 days (avg. rate of ~3.4 gpm).
 - Post injection recovery was monitored over a 5 day period
- **7 low-stress (i.e. $\Delta P \approx 13$ psi), near-field pressurized slug tests (i.e. pulse tests)**
 - Near-field reservoir hydraulic properties immediately surrounding the open borehole
- **Short-duration constant rate drawdown and recovery test**
 - Near-field reservoir hydraulic properties extending a few 10's of feet from the borehole

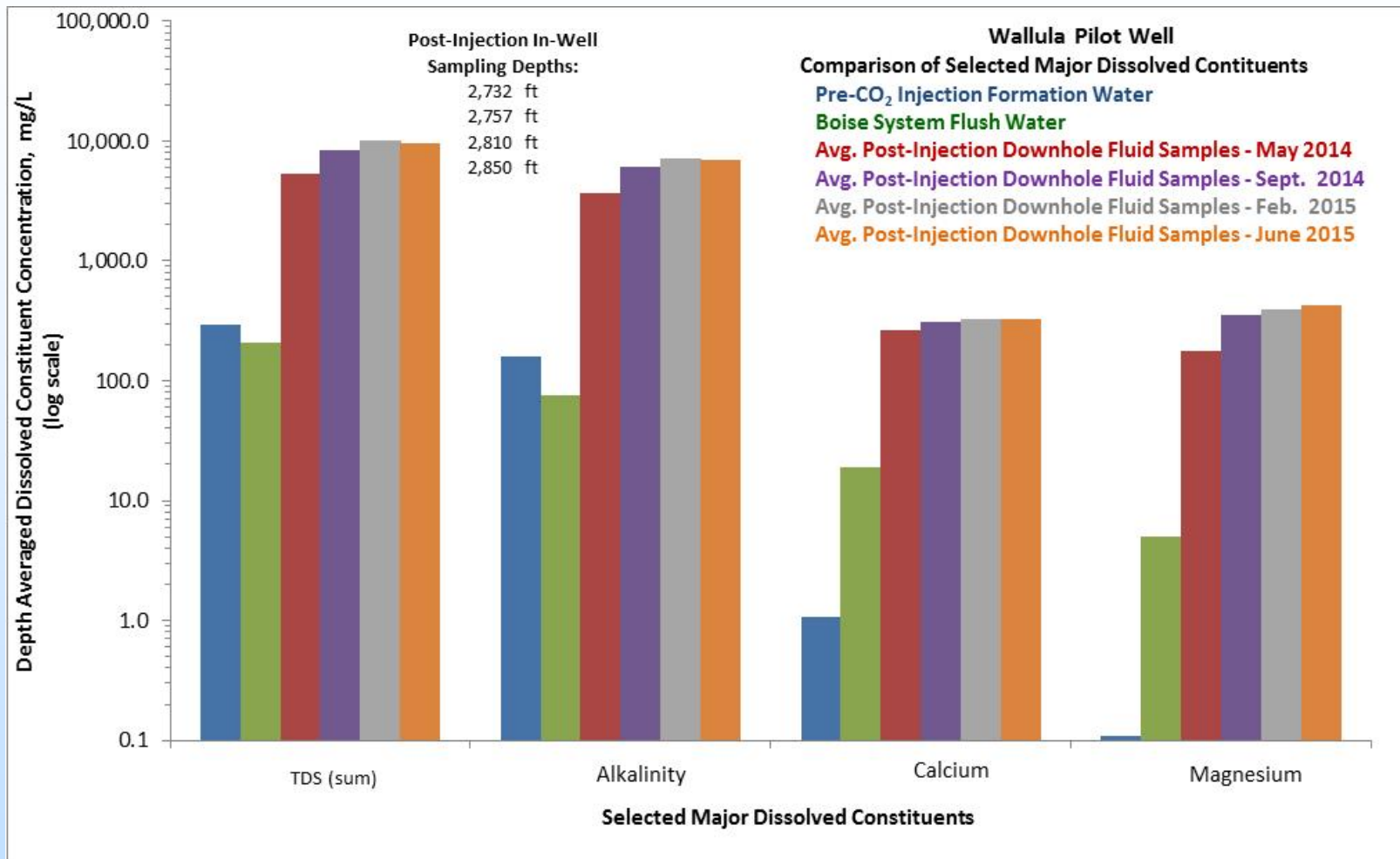


Detailed wireline survey for detecting CO₂ and geochemical and physical property changes (porosity) in injection zone basalt flow tops:



Injection zone still exhibits a well-defined temperature signature (+4 °F) 22-months after injection termination.

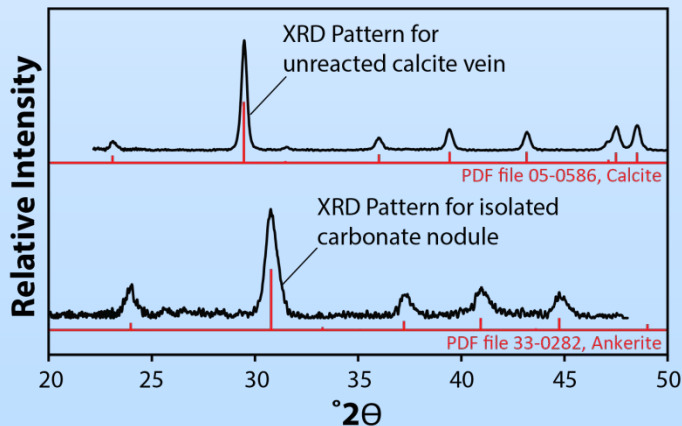
Wallula Basalt Pilot Well: Post Injection Downhole Fluid Sampling



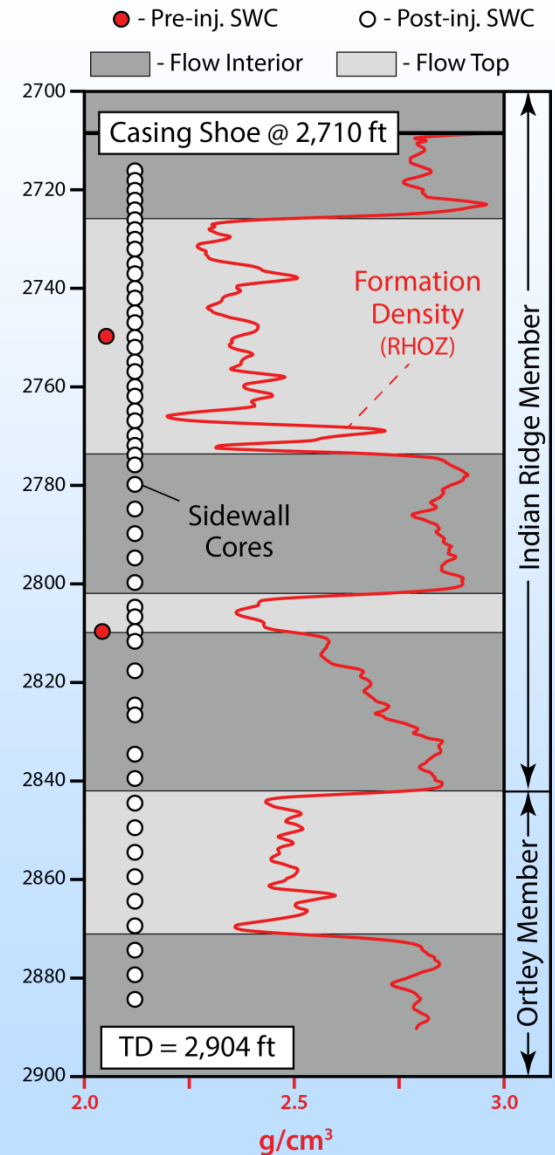
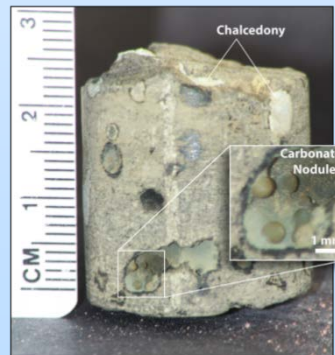
- Significant increases (factor of 10 to 100 higher) in post-injection fluid sample concentrations (e.g., TDS, alkalinity, Na, Ca, Mg, K)
- Concentrations continued to increase during post injection period (although at a declining rate)

Wallula Basalt Pilot Well: Initial Sidewall Core Characterization

- 50 sidewall cores were collected across the open borehole section between 2,716 – 2,900 ft bgs
- Carbonate reaction products observed on SWC samples occur both as large (up to ~1mm) nodules within open vesicles and as a coating on the borehole wall face of a few core samples
- XRD analysis of selected carbonate nodules identified ankerite as the only carbonate mineral present

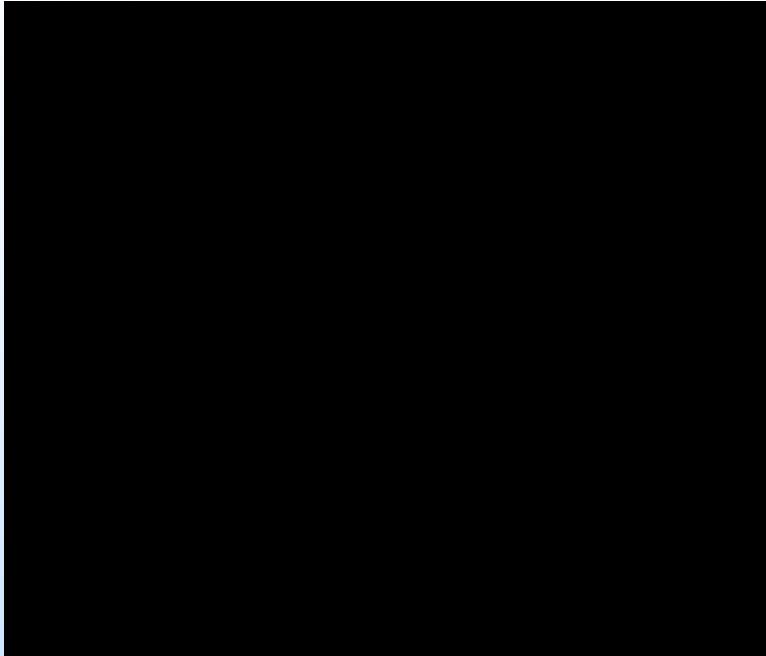


2,810 ft Core Sample (Post-injection)



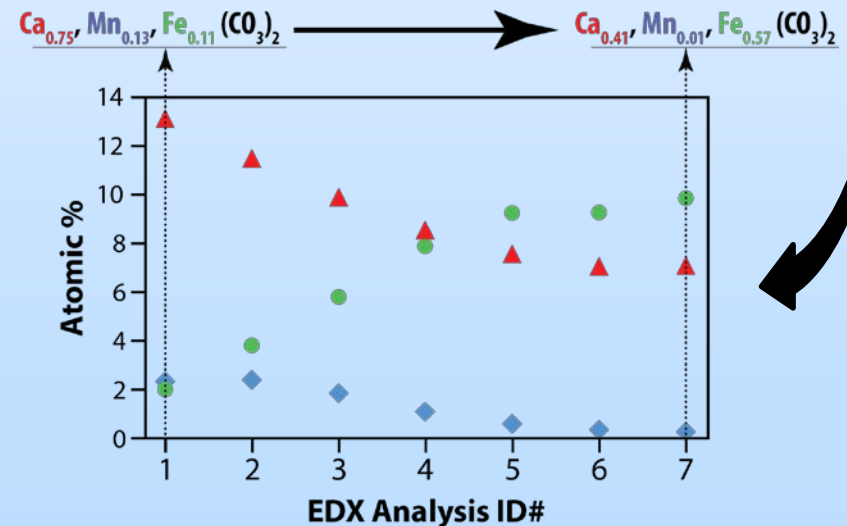
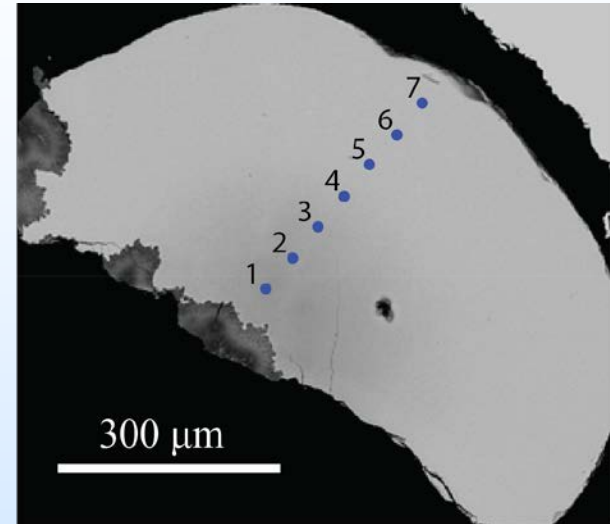
Wallula Basalt Pilot Well: Initial Sidewall Core Characterization

XMT imaging of post-injection sidewall core sample collected from 2,810 ft bgs



- XMT imaging shows likely ankerite nodules existing throughout core
- Chemically, these ankerite nodules are initially dominated by Ca, but become Fe rich as the precipitation progresses.

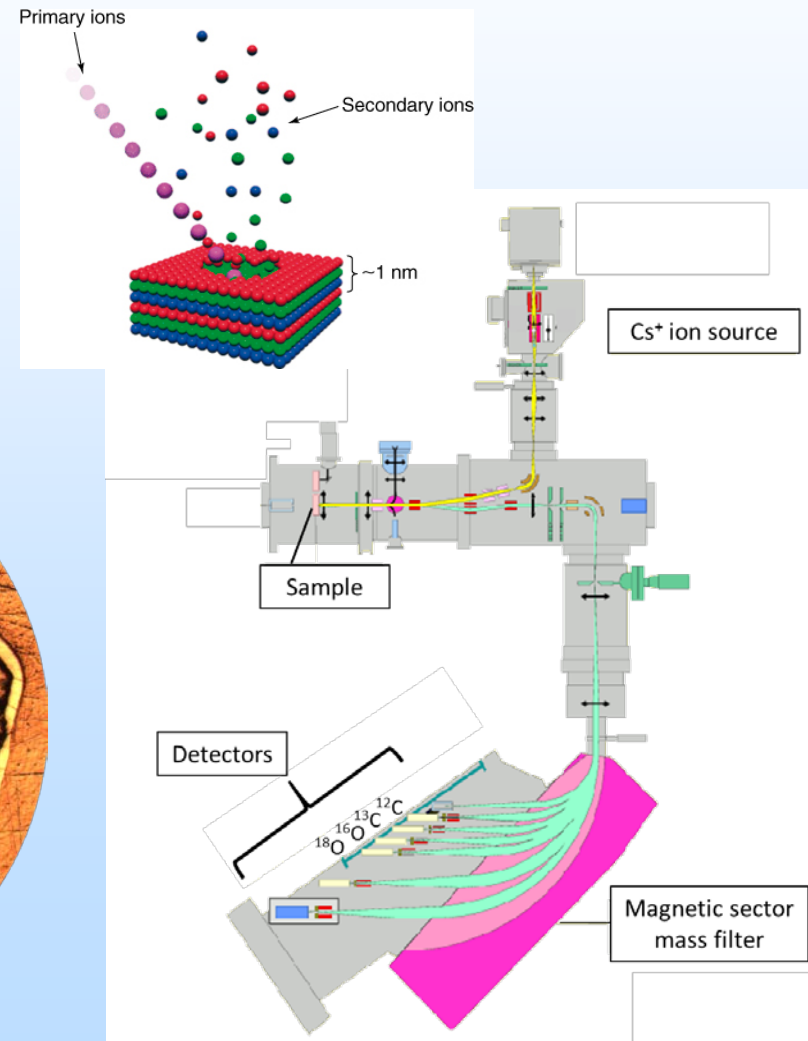
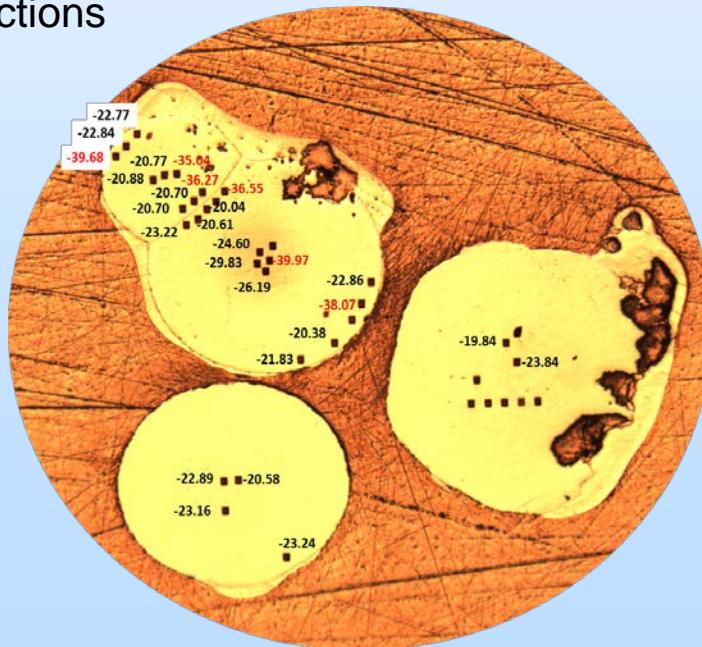
SEM micrograph of polished cross section of ankerite nodule (EDX analysis ID #)



Wallula Basalt Pilot Well: NanoSIMS Technique for Obtaining Delta $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ Ratios in Carbonates

Isotopic Characterization of Nodules

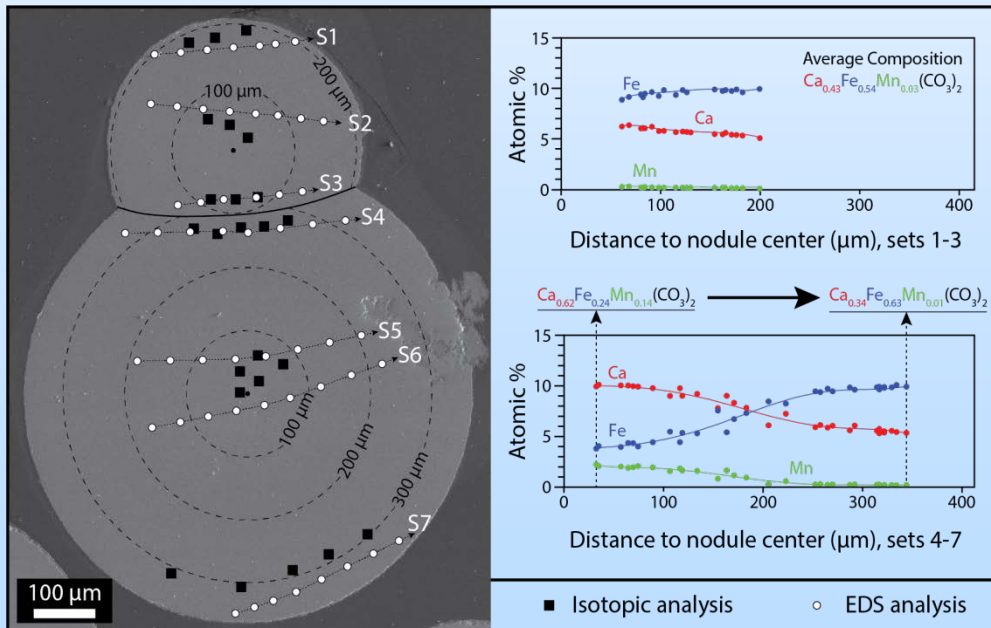
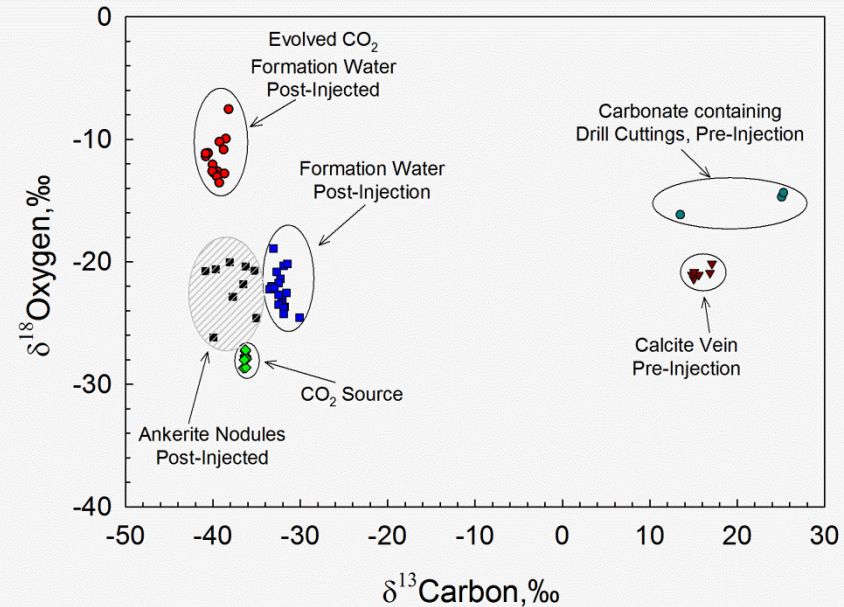
- Nano Secondary Ion Mass Spectrometry (NanoSIMS) was utilized to measure **delta oxygen-18 ($\delta^{18}\text{O}$)** and **delta carbon-13 ($\delta^{13}\text{C}$)** isotope ratios
- ~10 mg of ankerite nodules removed from SWC 857.1m
- Subsamples from natural calcite vein recovered in pre- CO_2 injection sidewall core
- Individual nodules mounted in epoxy and polished to obtain cross sections



Wallula Basalt Pilot Well: Isotopic Analysis on pre and post injection samples

Isotopic Data

- Ankerite nodules were depleted in $\delta^{13}\text{C}$ relative to natural occurring calcite
- Formation water, evolved CO_2 , & CO_2 source, were depleted in $\delta^{13}\text{C}$ (analyzed by outside laboratory)
- Natural calcite from wellbore and carbonates in drill cuttings (pre injection) enriched in $\delta^{13}\text{C}$



Key Findings

- Pre injection carbonate containing samples are enriched in $\delta^{13}\text{C}$ compared to post injected carbonates
- Metal cations such as Fe and Mn appearing in the ankerite nodules indicate a reaction between the basalt and CO_2
- Clear evidence of the injected CO_2 mineralizing into ankerite.

Summary

➤ Key Findings

- Carbonation process in adsorbed water films is complicated and is dependent on water film thickness.
- Precipitation of meta stable phases mark the initial steps of carbonation in wet scCO₂ fluids.
- Temperature logging shown to be a simple and cheap monitoring method for spatially tracking CO₂ injection
- Carbonates from post injection sidewall cores contain distinct isotopic signatures traceable to the injected CO₂.

“CO₂ storage in basalt formations is also a potentially important option for regions like the Indian subcontinent” IEG Technology Roadmap, 2009.



Cross sectioned nodules from core 2810 ft embedded in epoxy and polished for nanoSIMS analysis and then later for SEM-EDX.

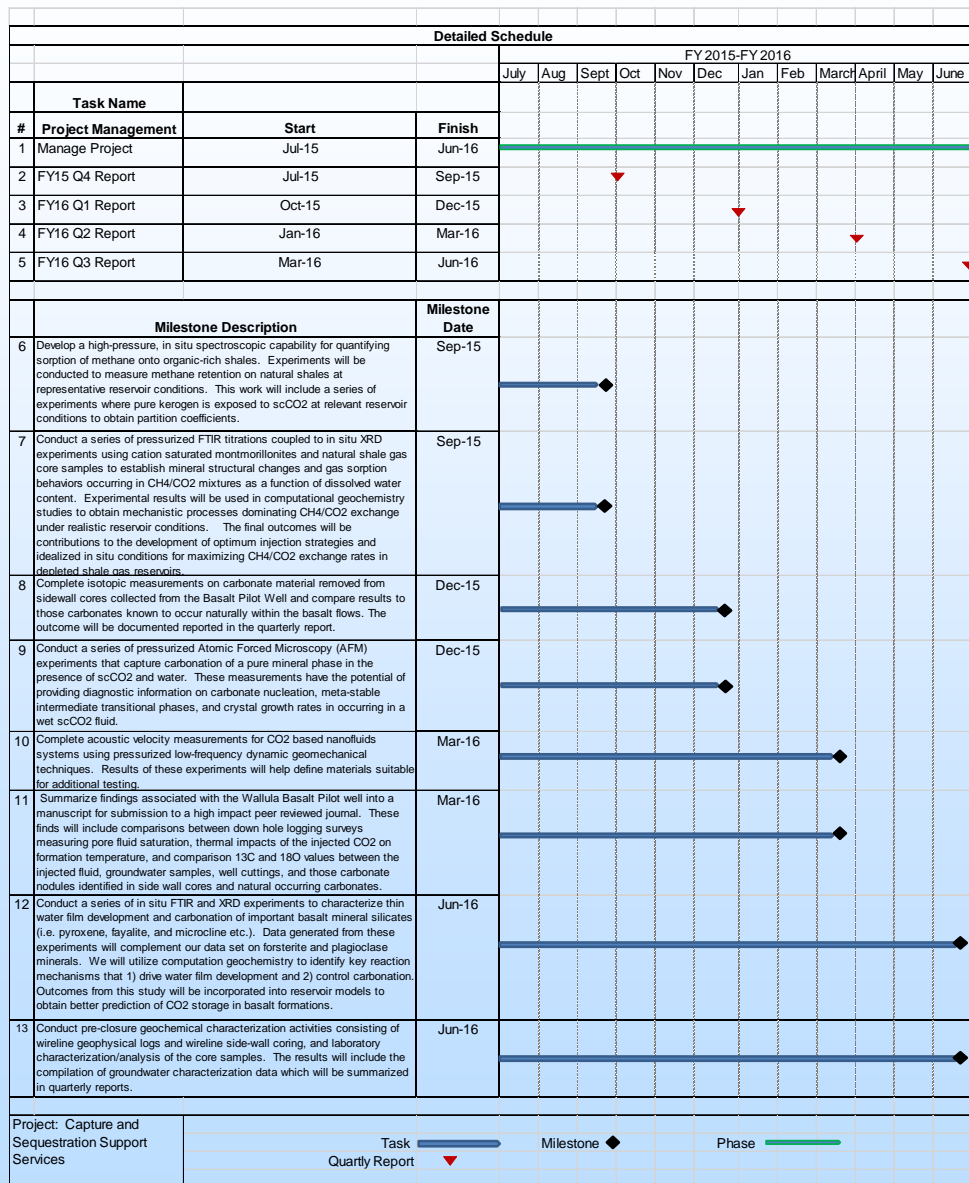
➤ FY 16 Planned Activity

- Continue investigating importance of importance of water bearing scCO₂ on carbonation reactions with relevant silicate minerals
- Summarize and publish results obtained from the Wallula Basalt Pilot Project

Organization Chart

- Project team has participants that cut across the Energy & Environment and Fundamental Sciences Directorates at PNNL
- Pacific Northwest National Laboratory is Operated by Battelle Memorial Institute for the Department of Energy

Gantt Chart



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