

Utilization of CO₂ in Unconventional Reservoirs

Project Number 58159

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Collaborating Institutions

University of Wyoming

University of Hawaii

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the
Infrastructure for CO₂ Storage
August 18-21, 2015

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 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

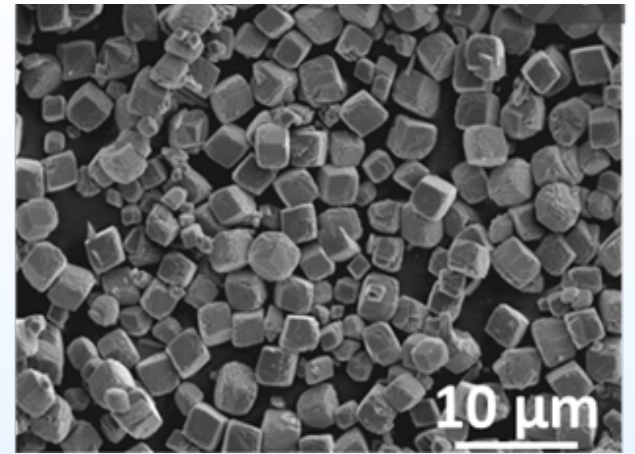
- Goal: Provide a path forward for commercial use of deep basalt formations for CO₂ sequestration
- Objective: Address key challenges associated with utilization of basalt formations as CO₂ storage units
 - Conduct laboratory research that addresses commercial-scale injection strategies
 - Provide laboratory measurements for predicting CO₂ fate and transport
 - Improved seismic imaging methods for basalt characterization

Basalt Project Overview:

Scope of work

➤ Carbonate Mineralization of Basalts in Aqueous-Dominated Fluids

- Carbonation rates and key variables important to evaluating long term storage of CO₂
- High pressure scCO₂ batch experiments
 - Low temperature magnesite
 - Aqueous dominated reactions, long-term testing



Magnesite particles forming after 56 days at 50°C and 90 bar.

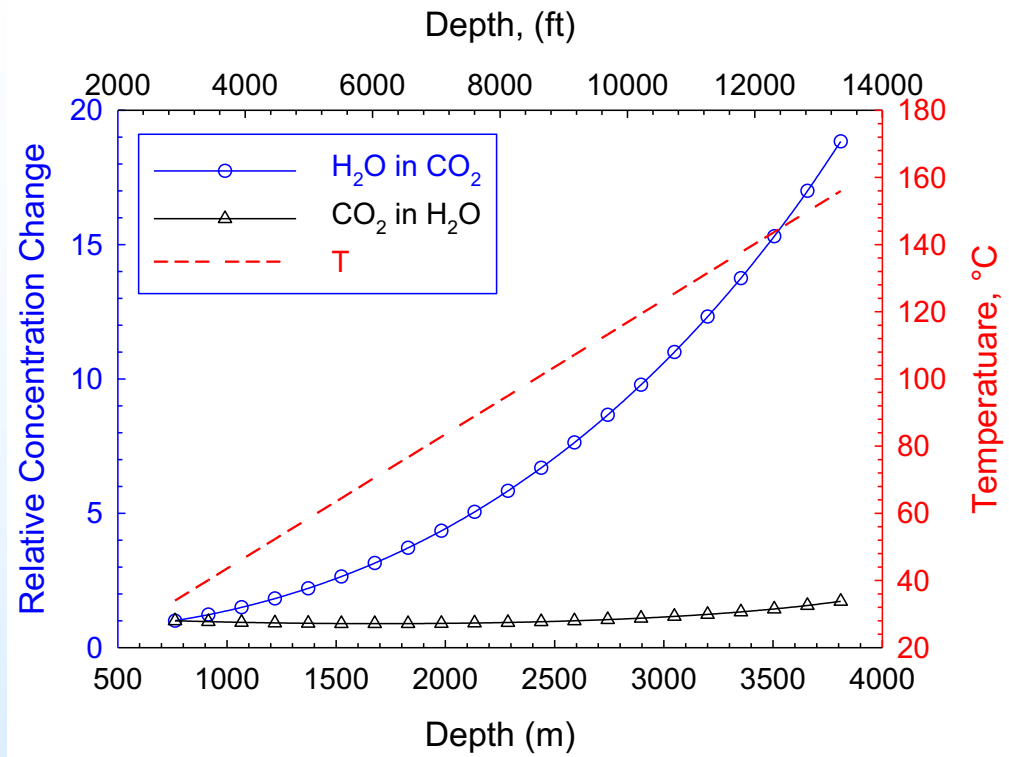
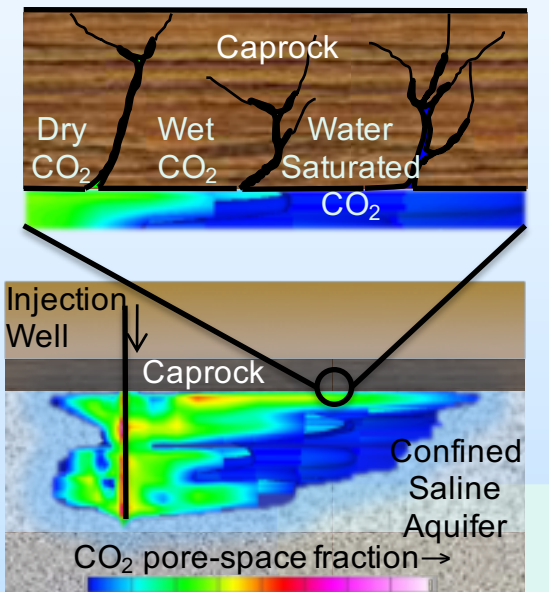
➤ Basalt Reactions with Wet scCO₂

- Dynamic geochemistry occurring in adsorbed H₂O films.
- Visualization of Mineral Carbonation in Wet scCO₂
- Impacts of Organic Ligands on Carbonation
- Modeling Silicate Surfaces in Contact with scCO₂ using AIMD Simulations

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

Dynamic mineral reactivity and crystalline product formation in H₂O films

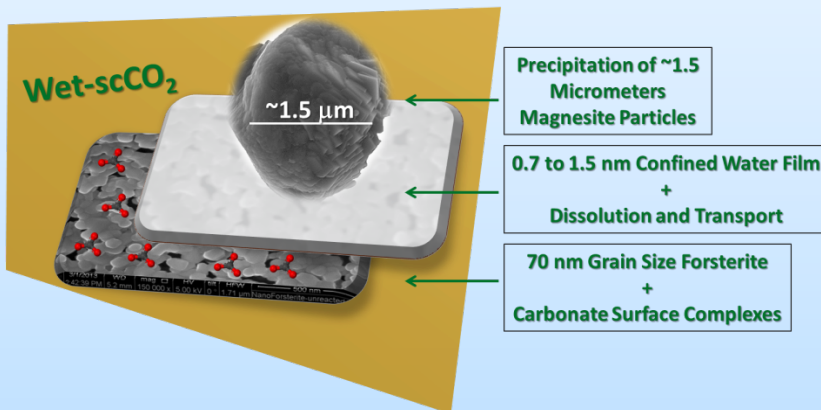
Water film Growth

Goal: Characterize the dynamic geochemistry occurring in adsorbed H₂O films.

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

Results: Mg-carbonate surface complexes predominate before a threshold adsorbed H₂O concentration. Beyond the threshold adsorbed H₂O concentration, magnesite precipitates.

Carbonate Precipitation



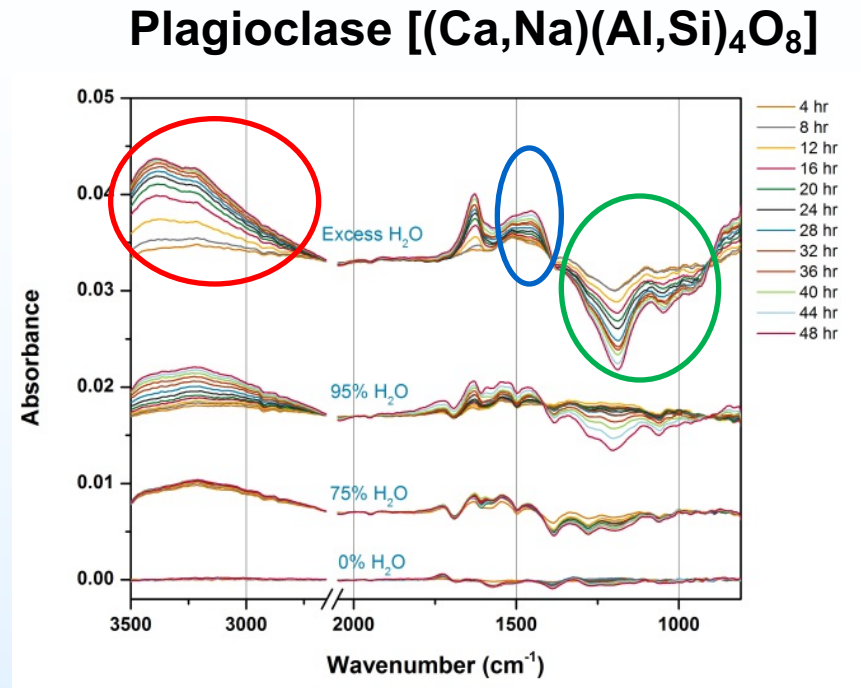
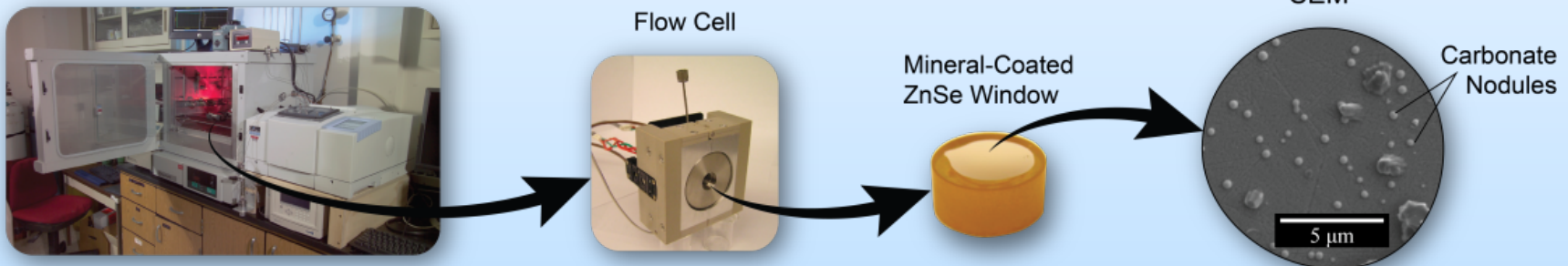
Wet scCO₂ and Mineral Surface Interactions

Goal: Characterize the dynamic geochemistry occurring in adsorbed H₂O films

- Water film growth (OH stretch)
- Carbonate precipitation (Asymmetric CO stretching bands)
- Mineral dissolution and precipitation of amorphous silica (SiO stretching bands)

Implications: Significant reactivity highlights need for reservoir simulators to account for reaction kinetics in wet scCO₂ fluids.

In Situ, High-Pressure IR Spectroscopy



Other minerals studied: forsterite, albite, brucite, antigorite, and enstatite, and microcline

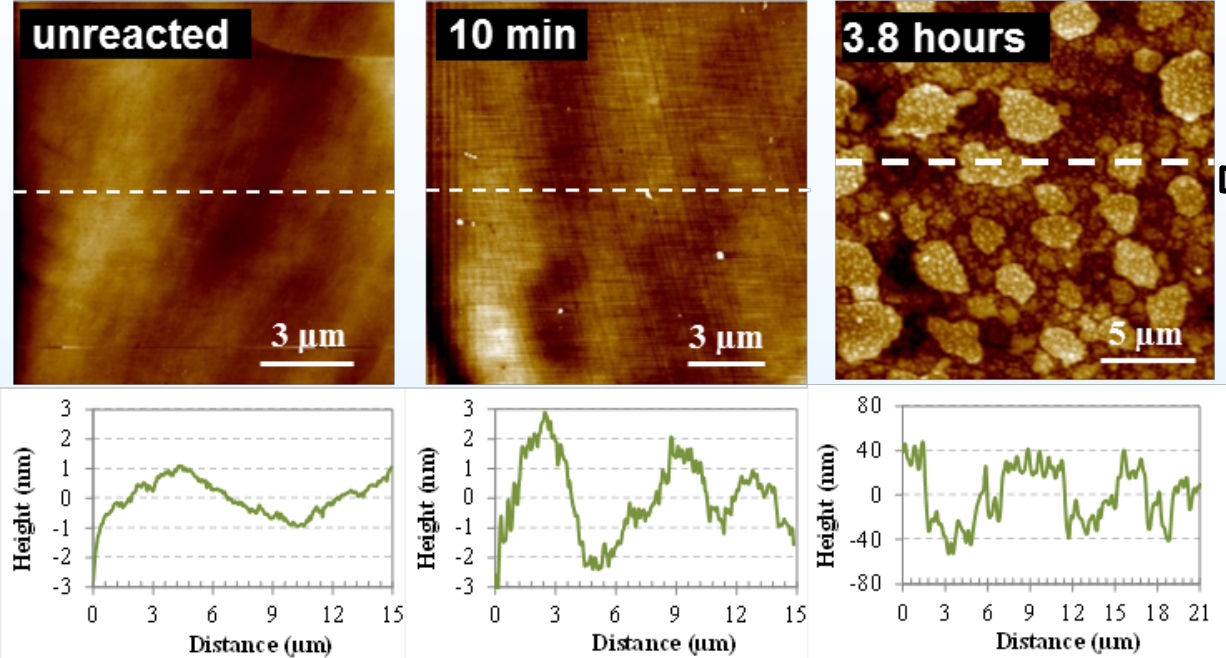
Visualizing Mineral Carbonation in Wet scCO₂

Pressurized Atomic Forced Microscopy

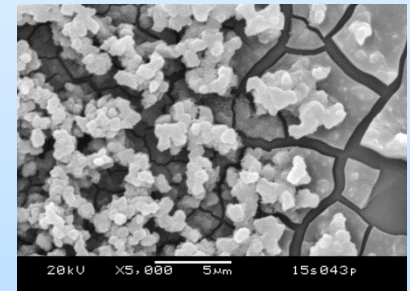
- Carbonation in wet scCO₂
 - Controlling factors
 - Modeling parameters
- Carbonation Products
 - Nucleation sites
 - Growth habits and morphologies
- Intrinsic Rate Constants
 - Water concentrations in scCO₂
 - Variability in water film thickness



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



Mineral Carbonation: *in-situ* AFM images of brucite surface, 1) unreacted, and after contact with wet scCO₂ for 2) 10 minutes and 3) 3.8 hours (50 °C, 90 bar).

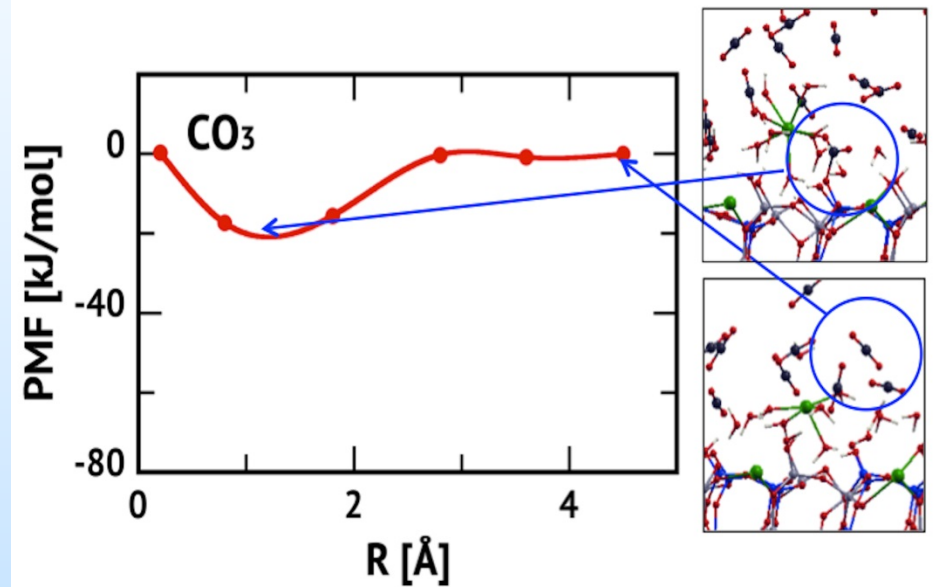
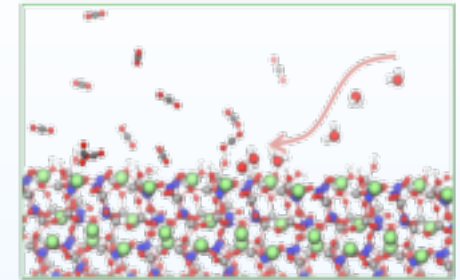
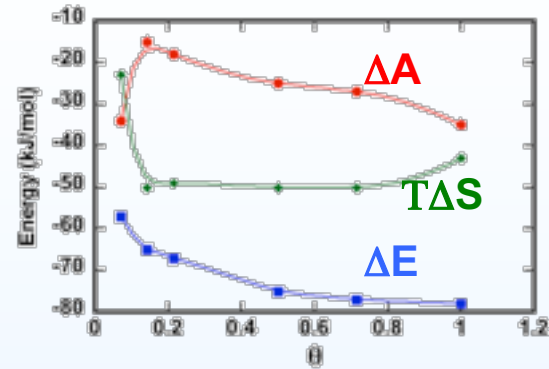


AIMD Simulations Designed to Model Water film Growth on Silicate Surface in Contact with Wet scCO₂

- ▶ AIMD simulations of free energy of adsorption and reactivity at a Mineral/H₂O/scCO₂ interface

- Mechanism of water layer nucleation and growth at solid/liquid interfaces occurs even at the low (10⁻⁴) water solubility in scCO₂.
- Water facilitates reactivity to form cation vacancies on the surface, leading to carbonate formation, in agreement with exp. observations.

- ▶ Wet scCO₂ can lead to unique speciation, structural transformations, and unexpected reactivity at solid/liquid interfaces.



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.



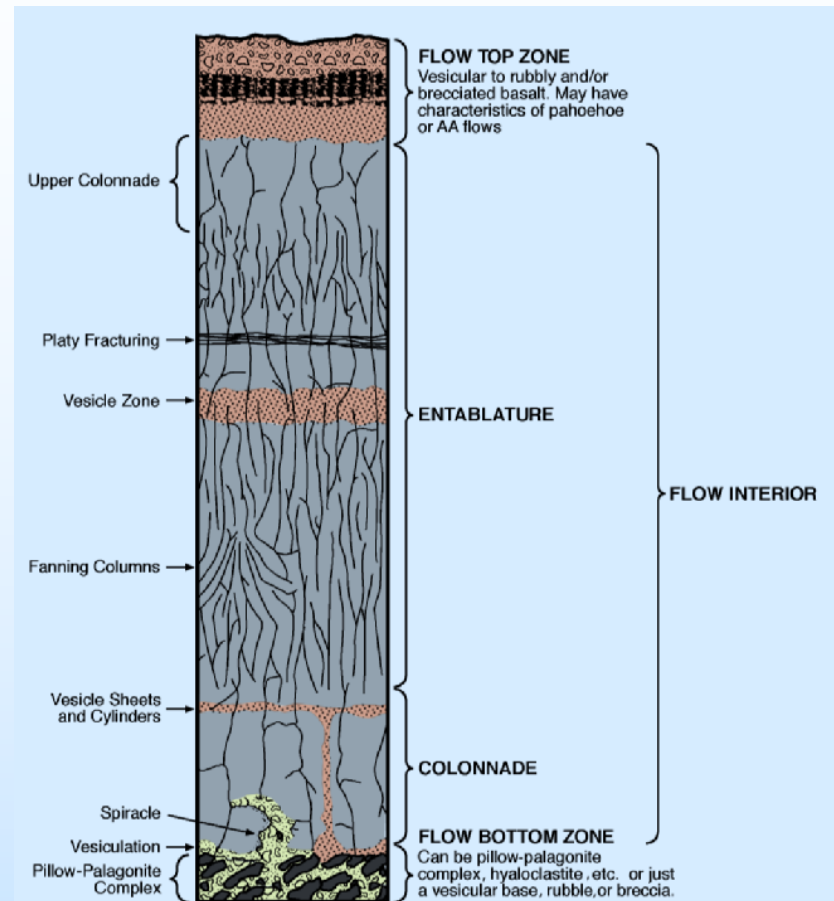
Flood Basalt Features Relevant to CO₂ Sequestration

- 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



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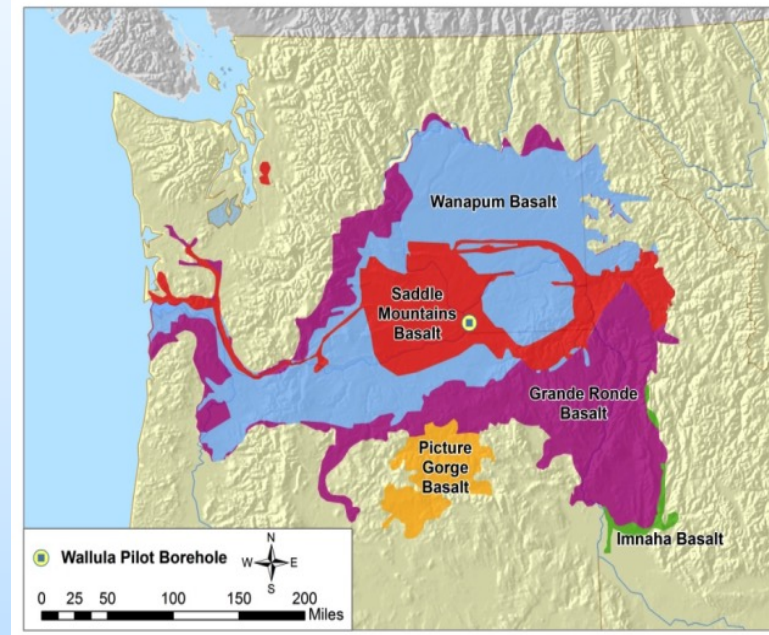
Wallula Basalt Carbon Sequestration Pilot Project

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

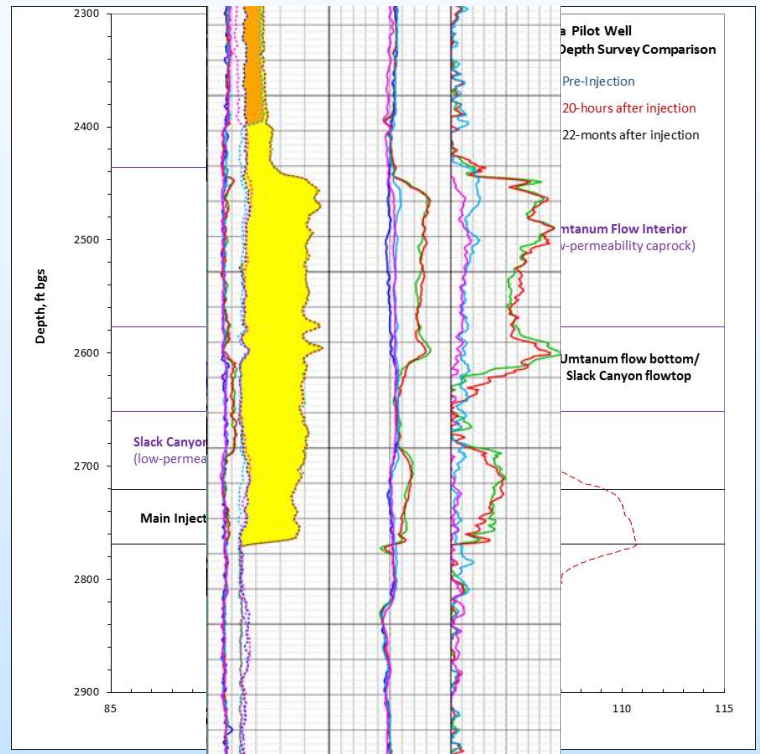
- **Extended duration hydrologic injection test**
 - Assess large scale changes in aquifer reservoir hydraulics
 - 18,000 gallons of water was injected over 3.7 days (avg. rate of ~3.4 gpm).
 - Post injection recovery was monitored over a 5 day period
- **7 low-stress (i.e. $\Delta P \approx 13$ psi), 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:

- Fluid temperature/pressure/gamma (4-2,901 ft)
- Platform Express logging suite (2,400 – 2,904 ft)
- Formation Micro Imager (2,720 – 2,904)
- Residual Saturation Tool – Sigma (100 – 2,904 ft)
- Residual Saturation – Carbon/Oxygen (2,710 – 2,904)

Fluid Temperature Logging Results



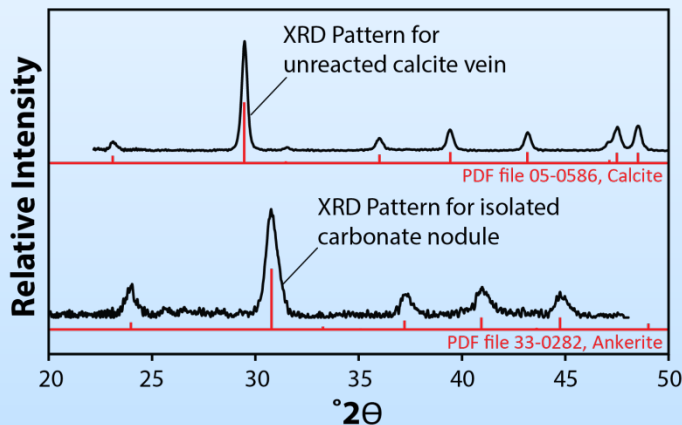
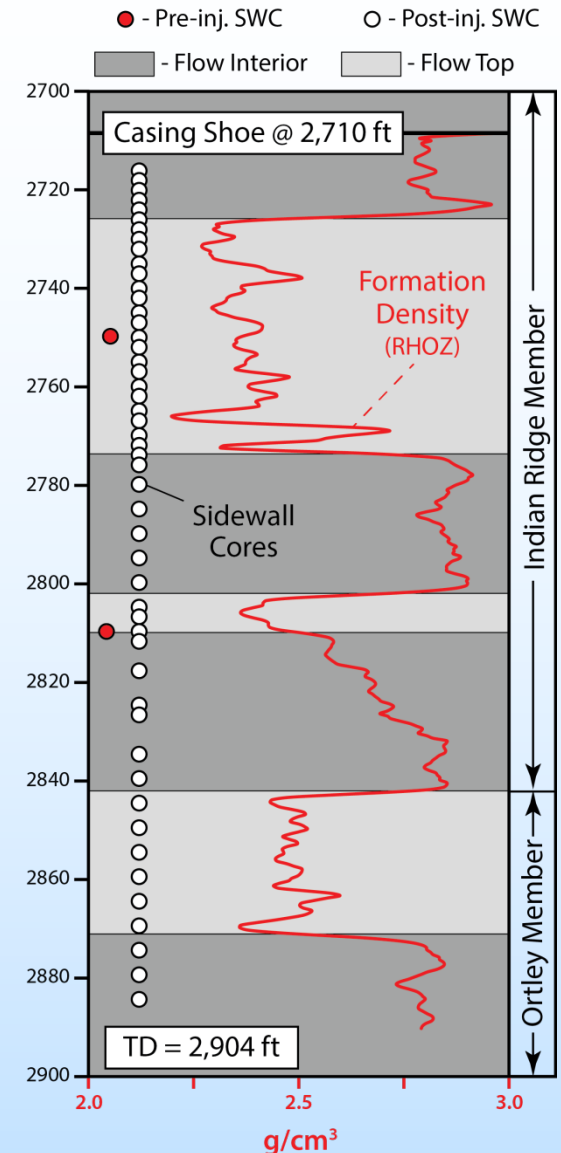
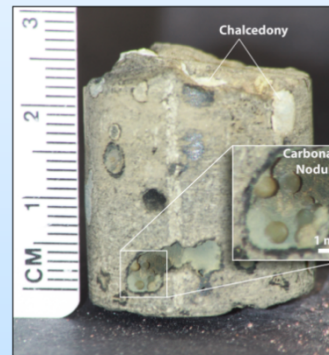
Injection zone still exhibits a well-defined temperature signature (+4 °F) 22-months after injection termination.

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
- Potential 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

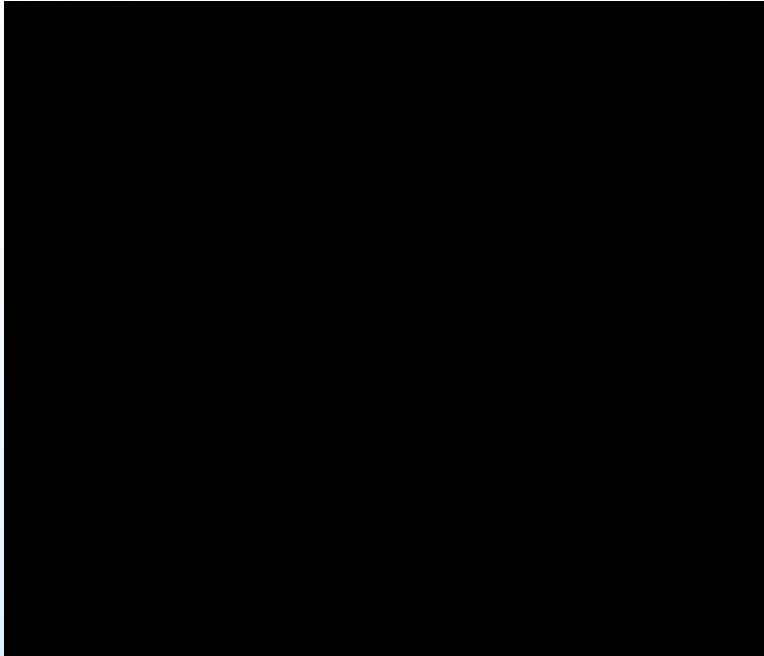


2,810 ft Core Sample (Post-injection)

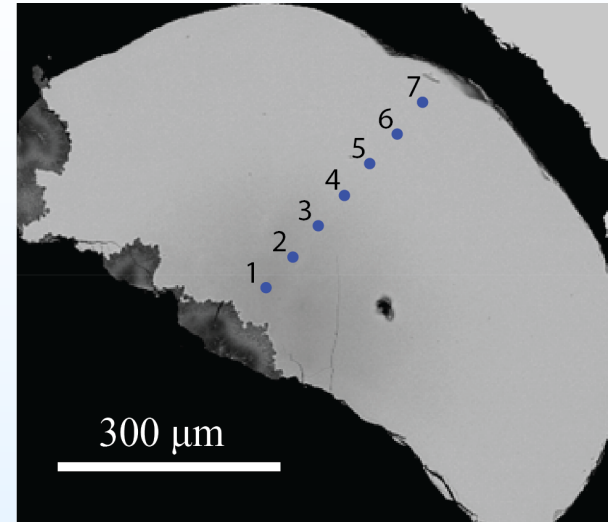


Wallula Basalt Pilot Well: Initial Sidewall Core Characterization

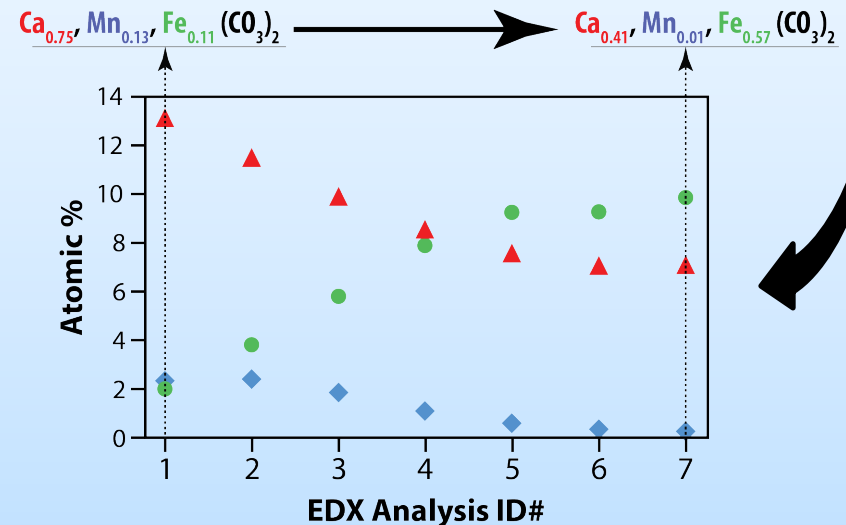
XMT imaging of post-injection sidewall core sample collected from 2,810 ft bgs



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



- 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.

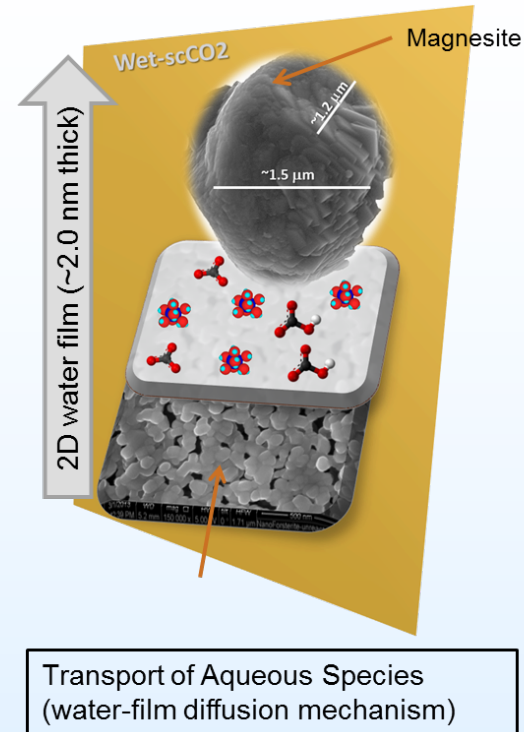


Summary

➤ Key Findings

- Reactions occurring between silicate minerals and H_2O - scCO_2 fluids produce well crystallized carbonate minerals at laboratory time scales.
- Carbonation occurs after adsorbed water films become thick enough to solvate and transport cations and bicarbonate ions.
- Atomistic modeling provides insights into dynamic chemical environment occurring in thin water films.
- Basalt Pilot Project providing first time evidence of *in situ* carbonation analogous to laboratory results

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



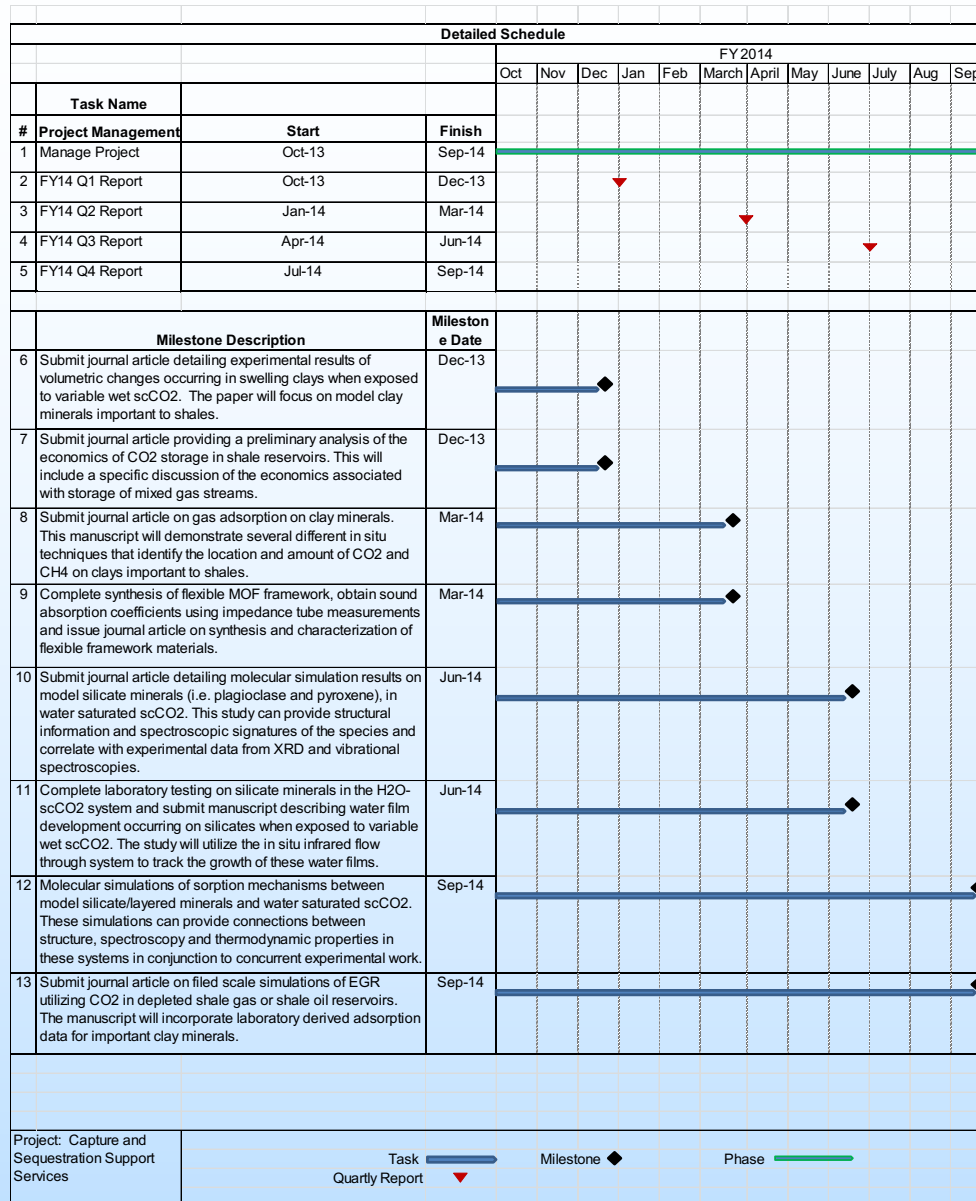
➤ FY 16 Planned Activity

- Expanded scope to examine importance of water bearing scCO_2 on relevant silicate minerals
- Continued laboratory support for basalt pilot project including isotopic characterization of carbonate precipitates

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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Utilization and Storage of CO₂ in Unconventional Reservoirs

Project Number 58159 Task 2

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Pacific Northwest National Laboratory

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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 2 – Utilization in Unconventional Reservoirs

■ 2.1 Storage in Depleted Shale Gas Reservoirs

- Economics of Utilizing CO₂ in Depleted Shale Gas Reservoirs
- Laboratory Studies
 - ❖ Probing structural changes on natural shale samples during scCO₂ exposure
 - ❖ Characterizing Water Film Development and Mineral Stability during exposure to wet acid gases
 - ❖ Quantify water solubility in CH₄/CO₂ gas mixtures at reservoir conditions
 - ❖ Distinguish interactions between metal cations and scCO₂: chemical reactivity versus physisorption processes
- Molecular Dynamics Modeling
 - ❖ Independent check on the sorption behavior of CO₂ on the external surfaces of minerals
 - ❖ Provide mechanistic insight into CO₂ intercalation
- Reservoir Modeling
 - ❖ Field scale simulation utilizing CO₂ in a depleted fractured shale reservoir utilizing CO₂
 - ❖ Incorporate laboratory findings to optimize methane production

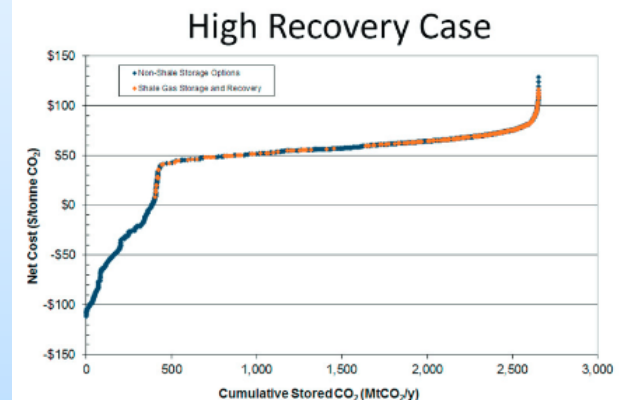
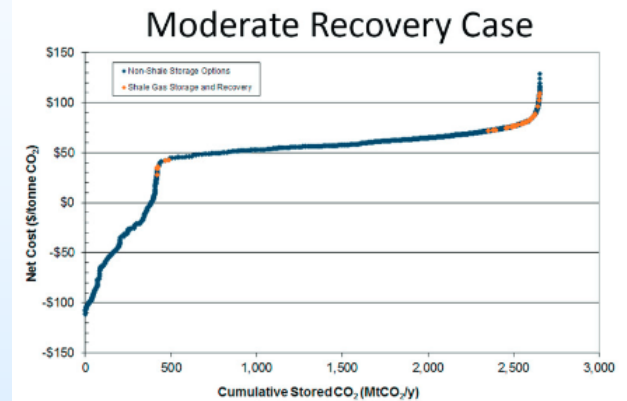
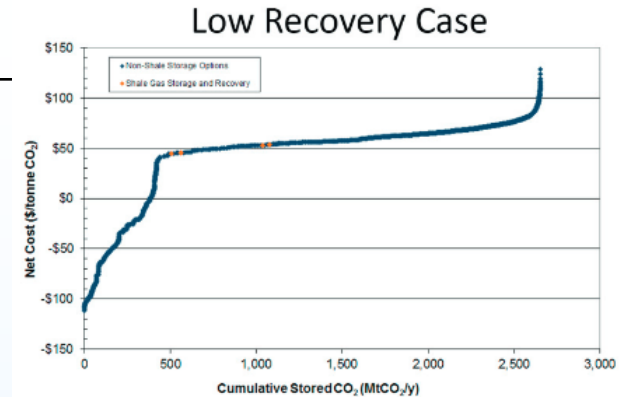
■ 2.2 Enhanced Monitoring Agents

- Synthesis methods and performance testing in a laboratory setting
- Newly developed laboratory technique for low frequency measurements

Costs, Offsetting Revenues, and Deployment Potential of EGR in Gas Shales

- Using three CO₂:CH₄ recovery relationships taken from the literature, Davidson & McGrail (2015) developed revenue estimates associated with the CO₂ injection phase of a shale-based CCS project
- These three revenue cases were used to parameterize scenarios evaluated via least-cost optimized source-sink pairing to generate cost curves for CCS in the U.S. to illustrate the impact of CO₂:CH₄ response on the potential for shale-based CCUS deployment
- Variation in the final cost curves suggests that resolving uncertainty around reservoir response is necessary to understanding the commercial potential of shale-based storage, and to help identify lower cost targets for deployment
- This work has been used to help focus current and future experimental efforts to allow for refinement of resource estimates and operational costs. Specific areas of interest include:
 - Bulk incremental recovery response
 - Relative sorption of CO₂ and CH₄ on mineral and organic shale components
 - Compositional effects on swelling and permeability changes
 - Efficacy of fractures and diffusion processes for CO₂ and CH₄ transport
 - Storage mechanisms (sorption vs free-phase)

Case	Revenue (\$/tCO ₂)	Shale-based Projects (#)	Storage (MtCO ₂ /y)
Low Gas Recovery	\$0.52	5	1
Moderate Gas Recovery	\$11.44	44	20
High Gas Recovery	\$18.46	303	600

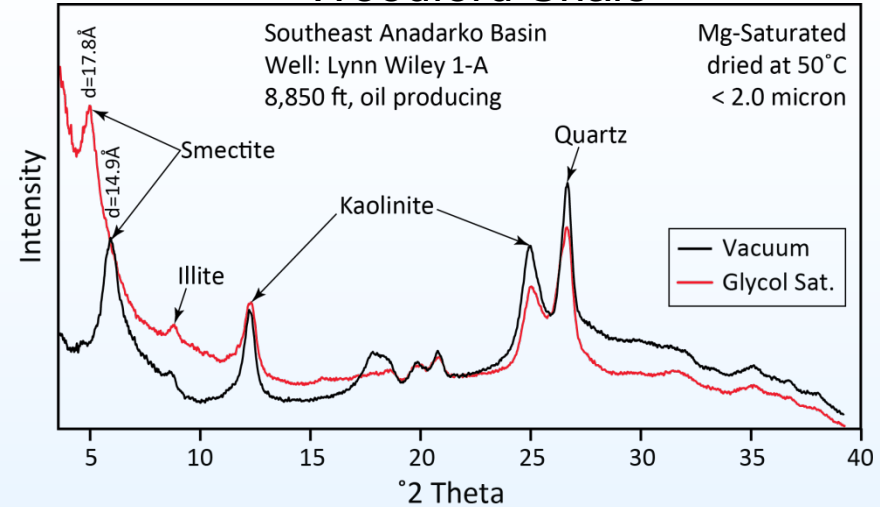


Laboratory Studies: Probing Structural Changes with HXRD

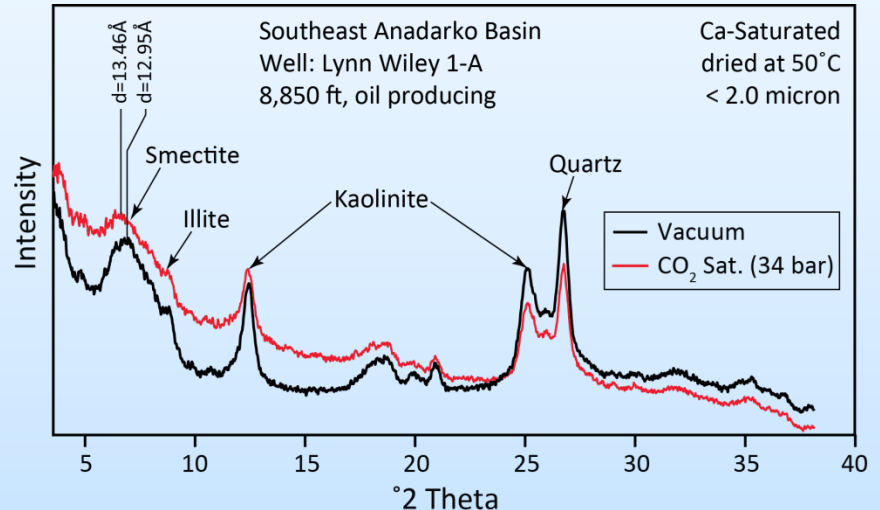
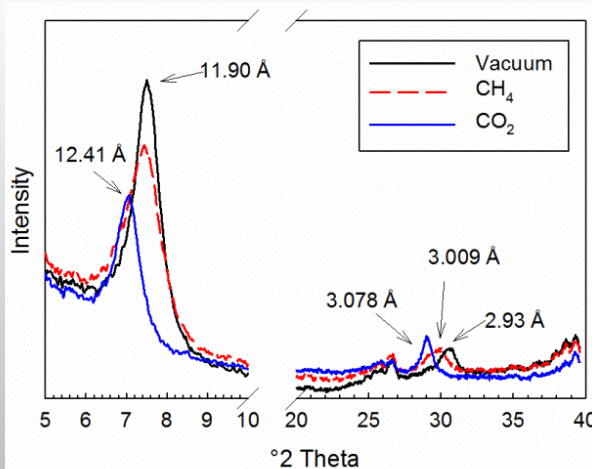
Goal: Characterize shale stability (i.e., swelling, shrinking) in the presence of scCO₂ and water

- Woodford shale contains quartz, illite, kaolinite, and smectite
- No observable instability when in contact with anhydrous scCO₂
- Minor amount of swelling during exposure to scCO₂

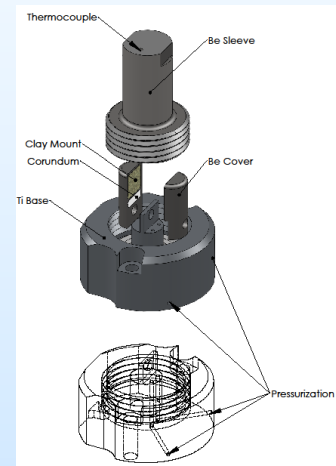
Woodford Shale



Montmorillonite (SWy-2) swells with scCO₂, but not with CH₄.



Technique Reference : Schaefer, H. T., E. S. Ilton, O. Qafoku, P. F. Martin, A. R. Felmy and K. M. Rosso (2012). "In situ XRD Study of Ca²⁺ Saturated Montmorillonite (STX-1) Exposed to Anhydrous and Wet scCO₂." IJGGC, 220-229.

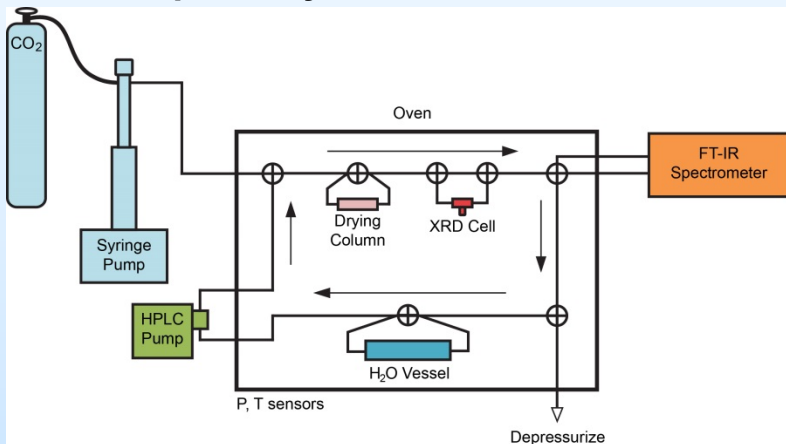
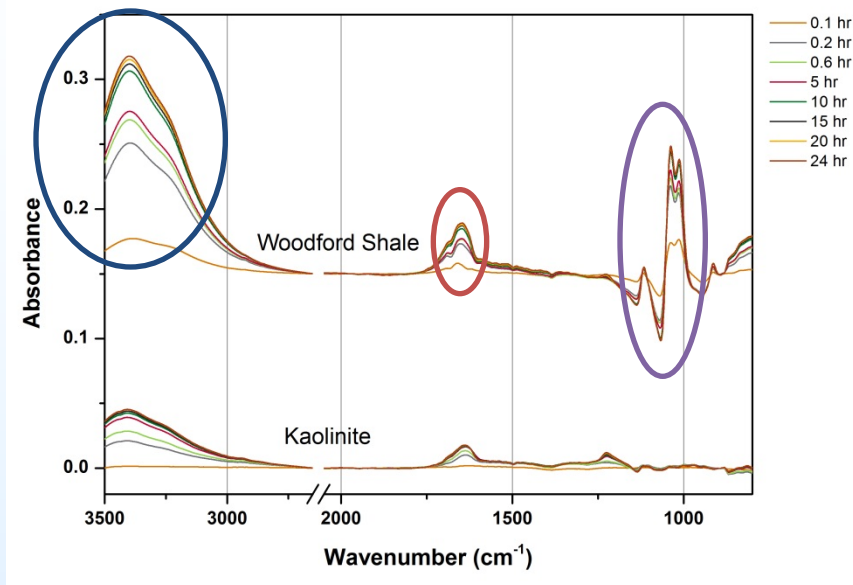


Tracking Water Film Development and Mineral Stability with *In Situ* IR Spectroscopy

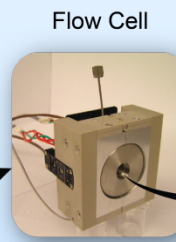
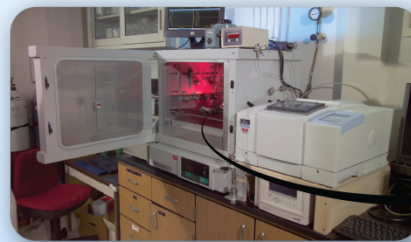
High-pressure *in situ* IR spectroscopy study of Woodford Shale and Kaolinite exposed to water-saturated scCO₂ (50 °C, 90 bar) for 24 hr

- Water film growth (OH stretch)
- Water film growth (HOH bend)
- Structural changes (expansion) with varying hydration (SiO and AlO stretching bands)

Water partitions between wet scCO₂ and shale, resulting in water films, structural changes, and possible changes in strength and porosity.



In Situ, High-Pressure IR Spectroscopy



Mineral-Coated ZnSe Window

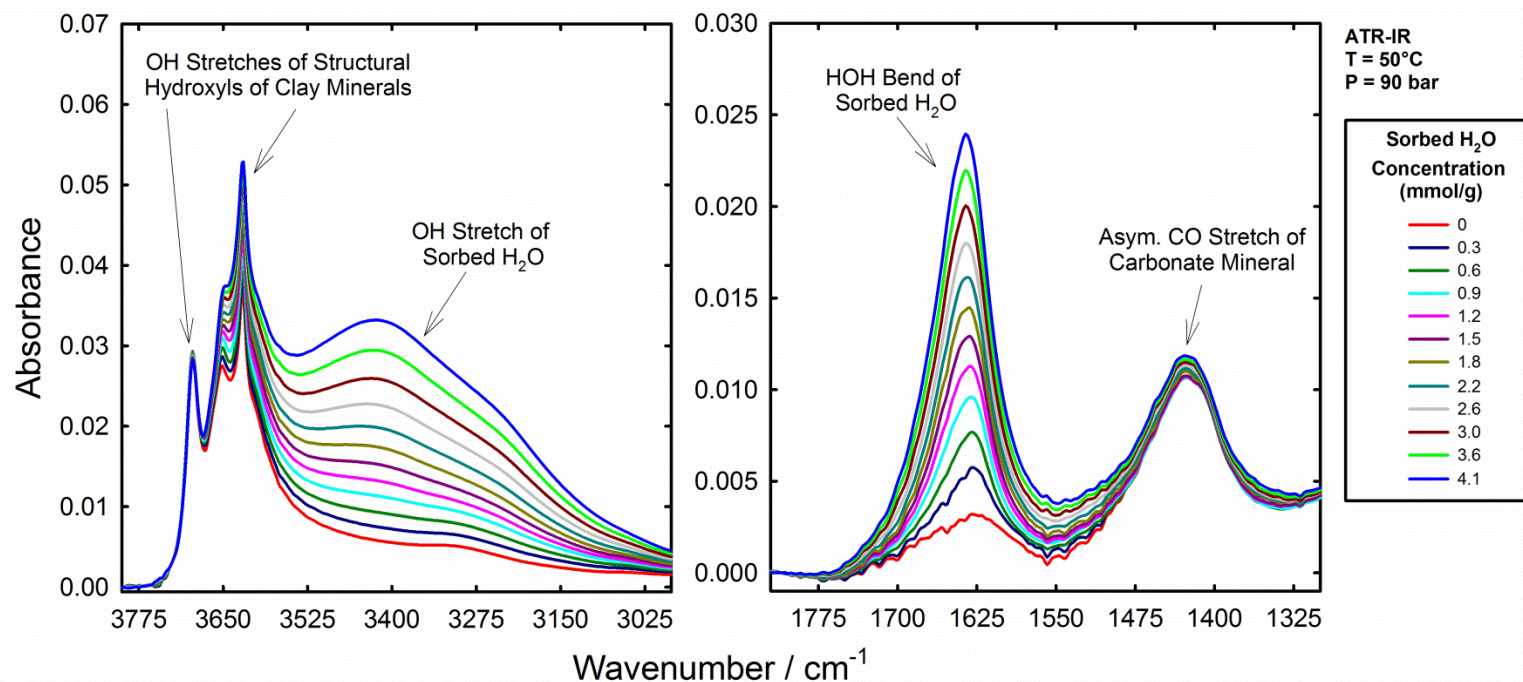
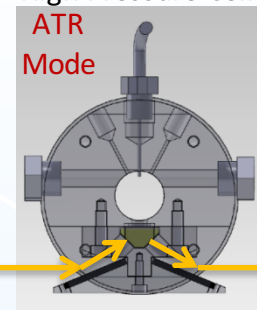


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IR Spectroscopic Titrations of a Woodford Shale Sample: ATR-IR Data

- ▶ ATR-IR data provides molecular-level information about the water and CO₂ interactions with clays.
 - Chemometric analysis indicates H₂O molecules exist in multiple chemical environments as a function of total water concentration.
- ▶ Mineral stability as a function of dissolved H₂O
 - Precipitation and dissolution
 - Intermediate metastable phases

Cross Section of High Pressure Cell



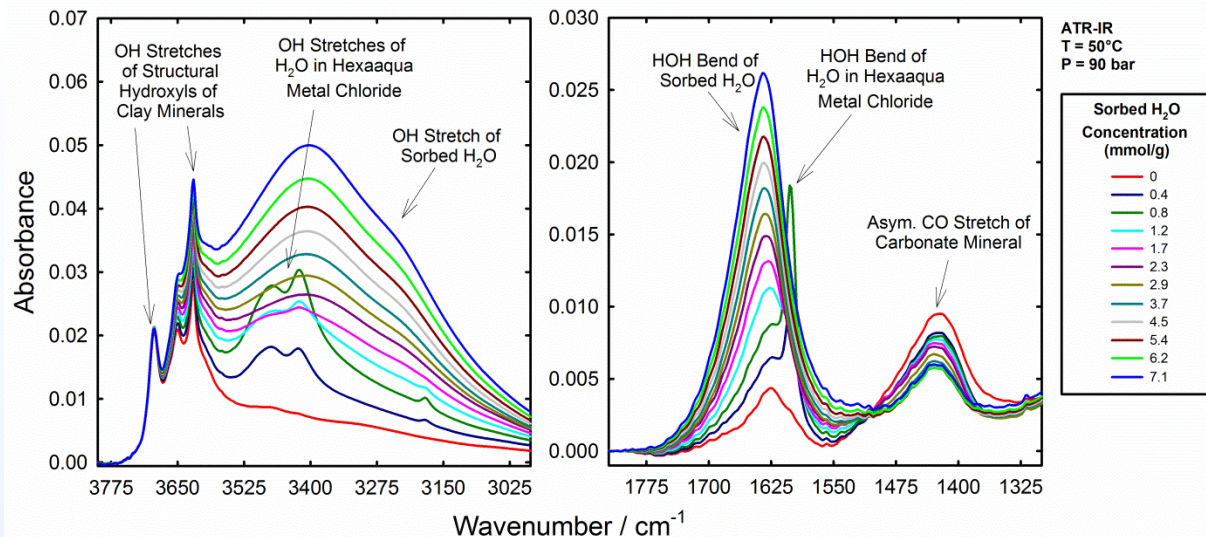
IR Spectroscopic Titrations of a Woodford Shale Sample in a CO₂-HCl Mixture

► **Objective:** Investigate Woodford shale reactivity in a CO₂-HCl-H₂O mixed gas system

► **Observations:**

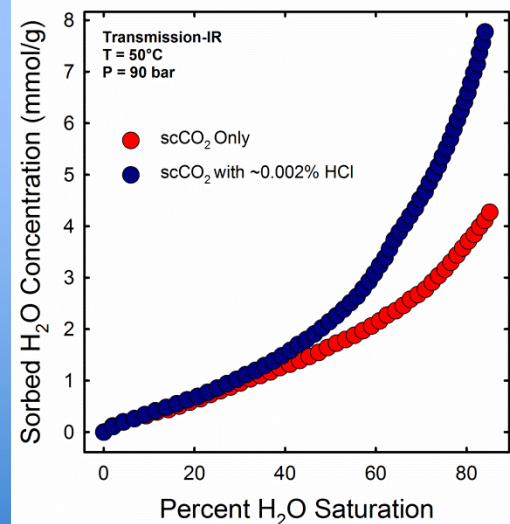
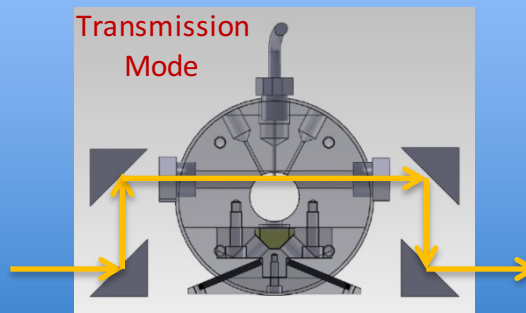
- Before H₂O addition, no observable differences compared to the pure CO₂ system
- Initial H₂O uptake indicates a secondary phase (hydrated metal chloride)
- Carbonate mineral begins dissolving
- Higher water content dissolves metal chloride

► **Implication:** Tracking mineral-fluid interactions at reservoir conditions provides insight into geochemical processes.



Transmission IR: Quantitative information on H₂O partitioning onto mineral surface.

Cross Section of High Pressure Cell

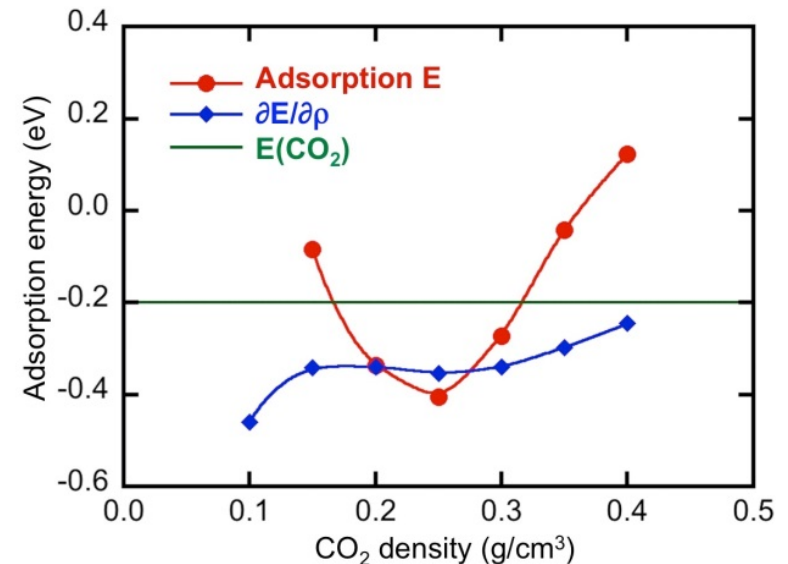
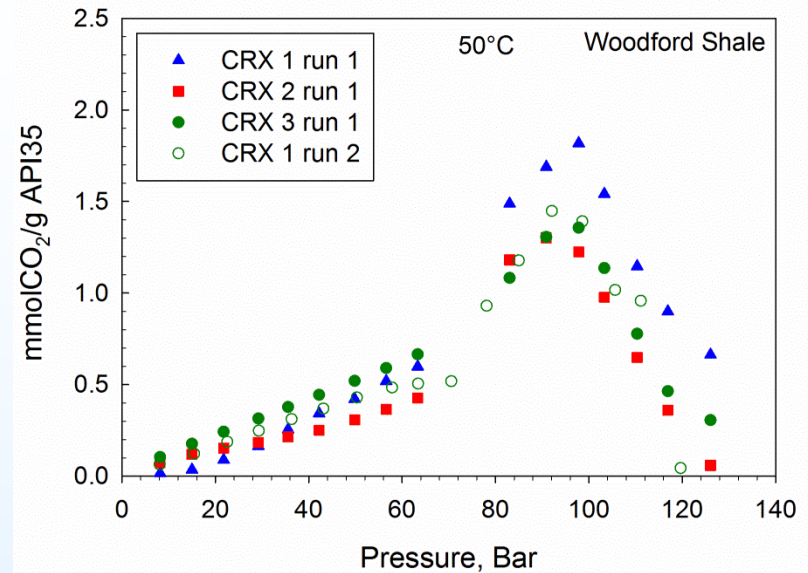


Surface Condensation of CO₂ on Minerals

Goal: Quantify unusual behavior of CO₂ sorption on important shale minerals

In situ quartz crystal microbalance technique used to determine CO₂ sorption on clay fraction of Woodford shale sample

- Absolute mass change
- High mass sensitivity for micro weighing in pressurized environments
- Use N₂ to establish surface roughness correction factors (i.e. N₂ ~0.2 mmol/g clay)
- Sorption was nearly linear on shale through the gaseous phase, but increased dramatically in the supercritical phase and peaked at ~90 Bar before desorbing.
- Molecular simulations describe adsorption as initially driven by CO₂ film formation on the surface, resulting in adsorption energies more favorable than the average CO₂-CO₂ interaction in bulk scCO₂.
- At higher pressures, the interactions in bulk CO₂ become more energetically favorable.

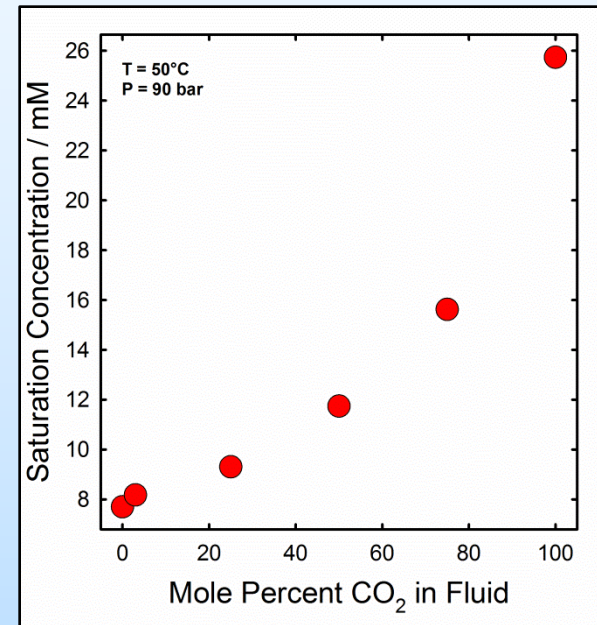
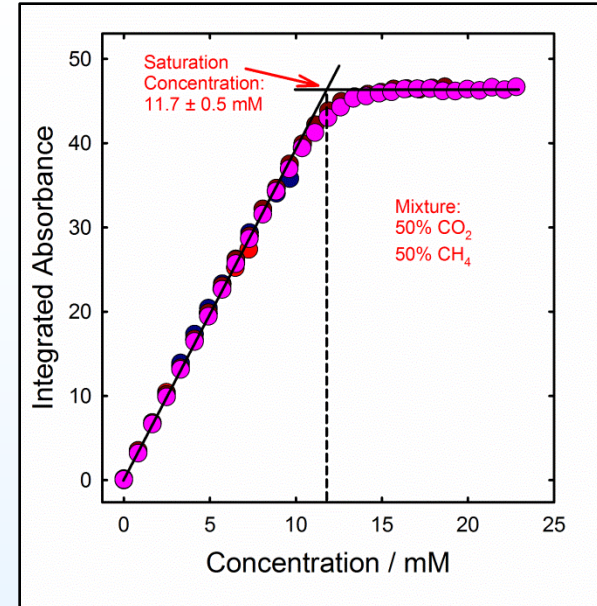


Characterizing Mixed Gas Systems ($\text{H}_2\text{O}/\text{CO}_2/\text{CH}_4$)

Experimental water solubility data for mixed gas systems are scarce.

- Gas mixtures with compositions between pure methane and pure carbon dioxide were titrated with water at 50°C and 90 bar using an in situ IR spectroscopic titration capability.
- Each gas mixture shows a linear increase of dissolved water until saturation is reached, indicated by a plateau in the data (top graph).
- Overall, these titration results show an increase in water solubility that correlates with CO_2 concentrations (bottom graph).

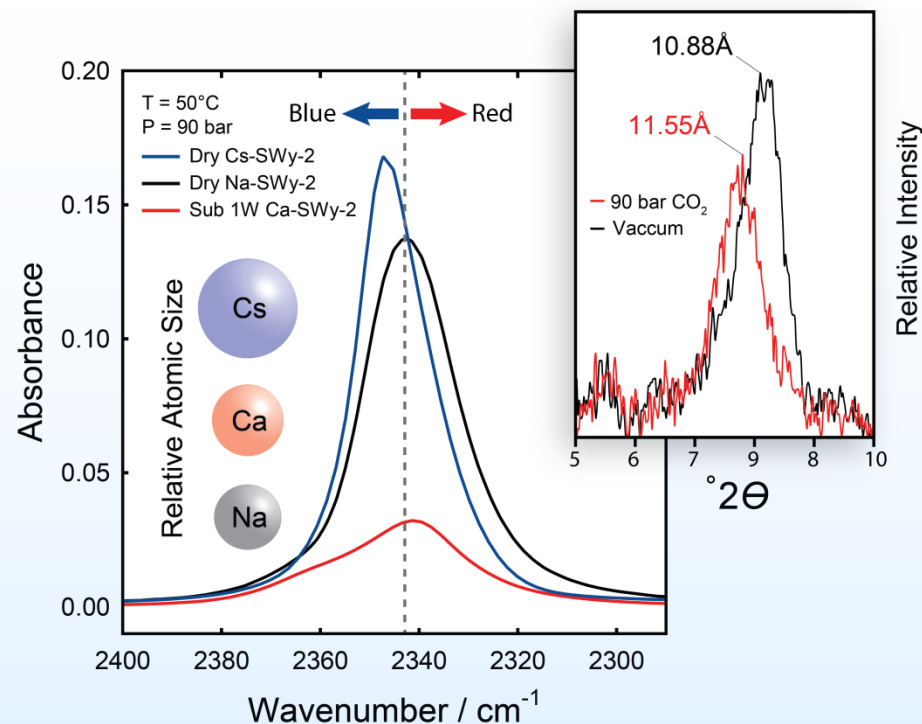
Application: These data are necessary to understand competitive gas sorption processes and clay hydration and expansion mechanisms occurring in shales.



Distinguishing CO₂ Interactions in Model Clay Systems During Exposure to CO₂ and H₂O

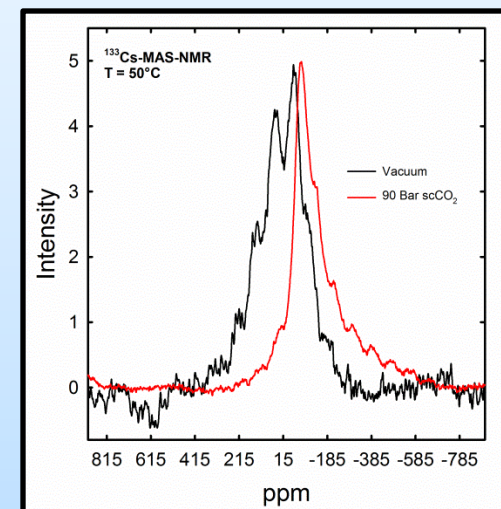
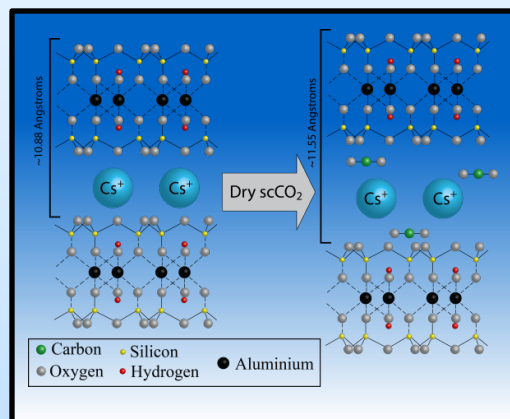
Interaction between CO₂ and interlayer Cs⁺ cations

- HXRD shows a large basal spacing shift from 10.88Å (anhydrous) to 11.55Å in the presence of dry scCO₂
- No expansion with dry N₂
- IR spectroscopy reveals a blue shift of the asymmetrical CO shift of the CO₂ molecule
- No measurable IR shifts with hydrated metal cations (i.e. Ca, Na, and Mg)
- MAS-NMR indicates a large shift for the ¹³³Cs in the presence of scCO₂



Theory predicts measurable CO₂ and cation interactions

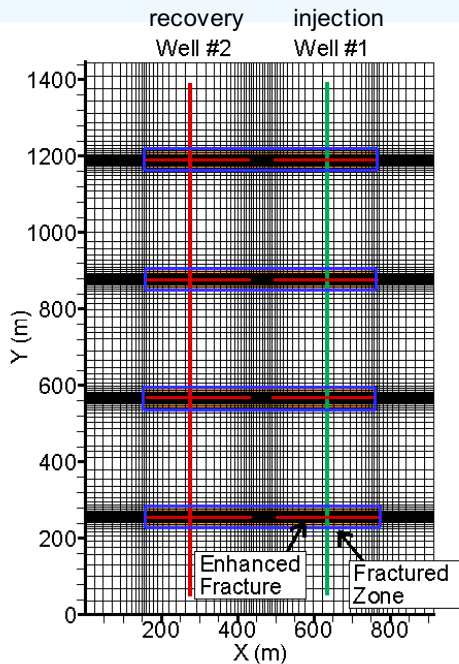
- Cryscenti and Cygan, 2013
- Myshakin et al., 2013
- Glezakou et al., 2014



Modeling Enhanced Recovery of Methane with CO₂

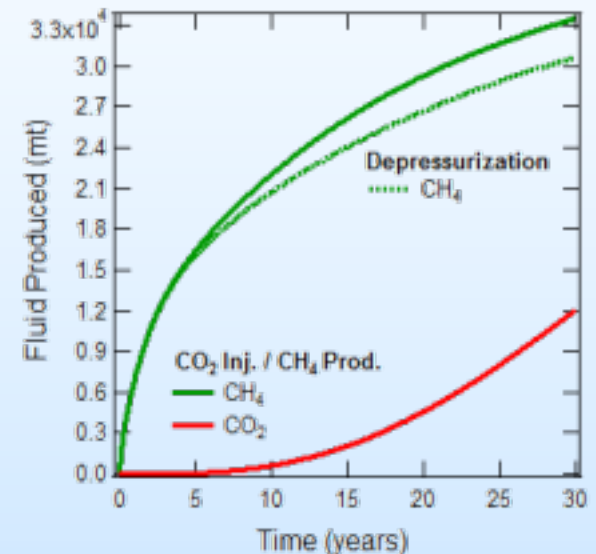
- STOMP-EOR simulates multiphase, multicomponent flow and transport of CO₂, methane and oil components coupled with geochemical reactions
- Simulations are used to investigate methane release via competitive CO₂ adsorption at the field scale by injecting CO₂ while producing CH₄.

Scenario: Hydraulic fracture stages in CO₂ injection and CH₄ production wells



- Advection through hydraulic and natural fractures
- Diffusion and desorption from the shale matrix

Results: Methane recovery with and without simultaneous CO₂ injection



- With CO₂ injection, CH₄ production increased after 3 years
- Desorbed CH₄ increased from 5 to 31%
- Clay minerals and organics adsorbed similar amounts of CO₂
- Stored 80 metric kilotons of CO₂

Accomplishments to Date

- ▶ Key *in situ* measurements conducted with field samples provide insights into gas sorption processes
- ▶ Laboratory studies coupled with atomistic simulations are essential to deriving fundamental geochemical information at reservoir conditions.
- ▶ Building a data base for reaction mechanisms and dominant geochemical processes for formulation and incorporation into reservoir simulators.
- ▶ Incorporating results from fundamental studies on competitive CH₄/CO₂ adsorption in shales into reservoir simulators to model at the field scale CH₄ production enhanced by injecting CO₂

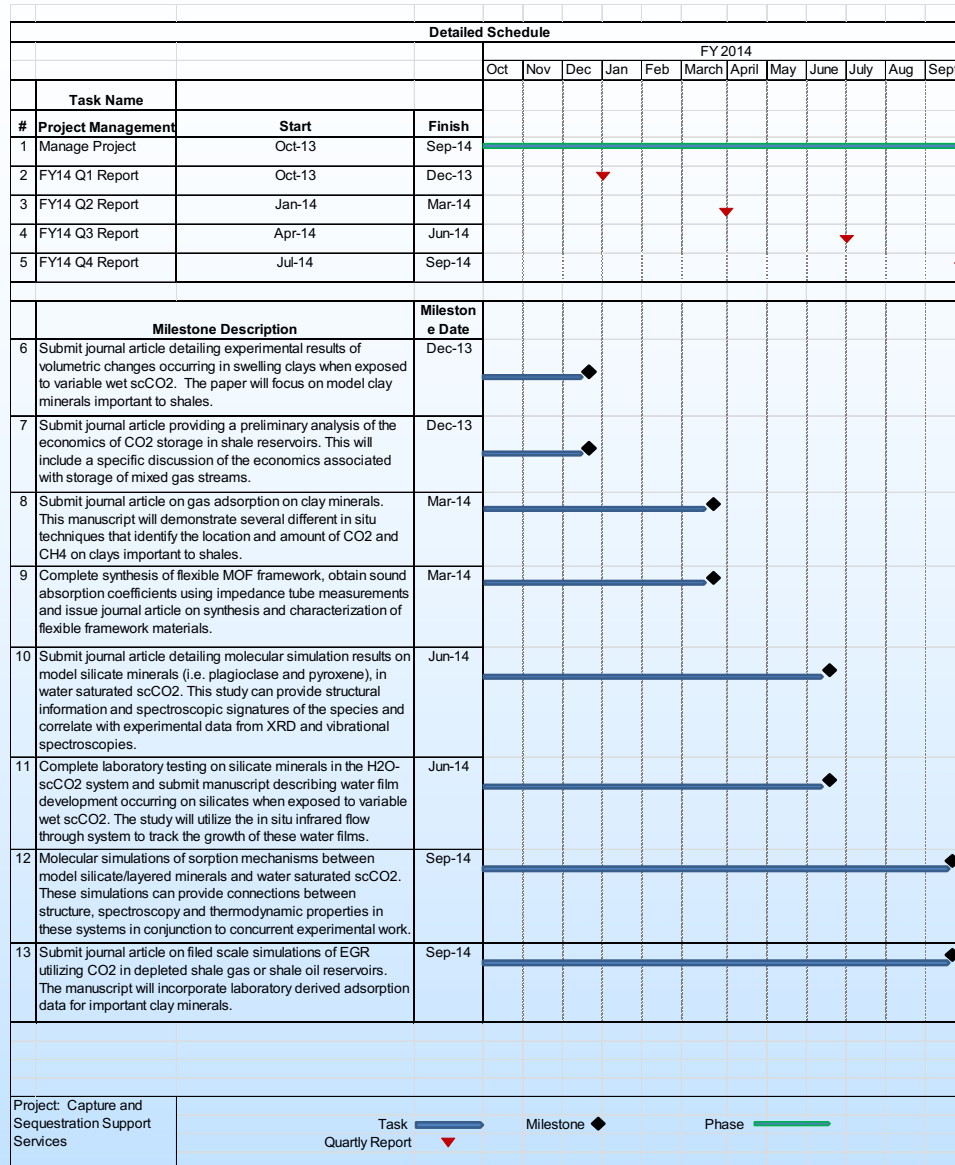
Appendix

- 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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