Sequestration of CO_2 in Basalt Formations

Project Number 58159 Task 1

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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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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

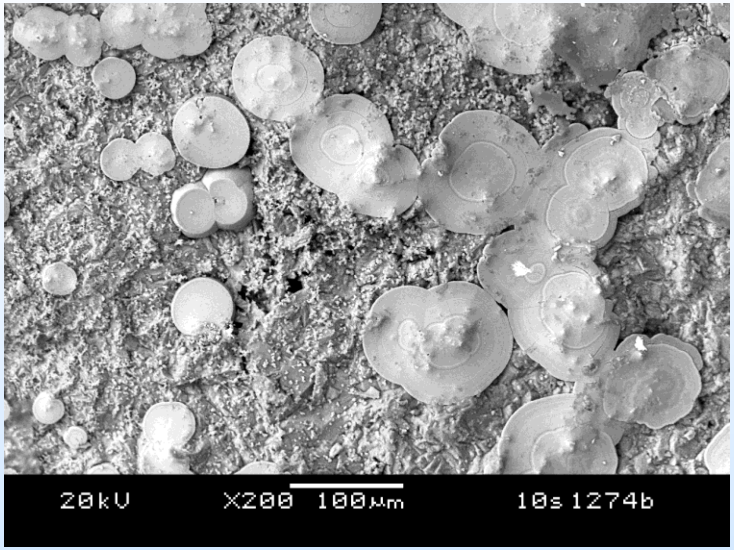
- Program goals addressed:
  - Technology development to predict CO_2 storage capacity
  - Demonstrate fate of injected CO_2 and most common contaminants
- Project benefits statement: This research project conducts modeling, laboratory studies, and pilot-scale research aimed at developing new technologies and new systems for utilization of basalt formations for long term subsurface storage of CO_2. Findings from this project will advance industries ability to predict CO_2 storage capacity in geologic formations.

Project Overview: Goals and Objectives

- Goal: Provide a path forward for commercial use of deep basalt formations for CO_2 sequestration
- Objective: Address key challenges associated with utilization of basalt formations as CO_2 storage units
  - Conduct laboratory research that addresses commercial-scale injection strategies
  - Provide laboratory measurements for predicting CO_2 fate and transport
  - Improved seismic imaging methods for basalt characterization

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 CO_2
  - High pressure $scCO_2$ batch experiments
    - Diverse set of basalt samples
    - Aqueous dominated reactions, long-term testing
  - Dominates the total carbonation rate in shallower reservoirs

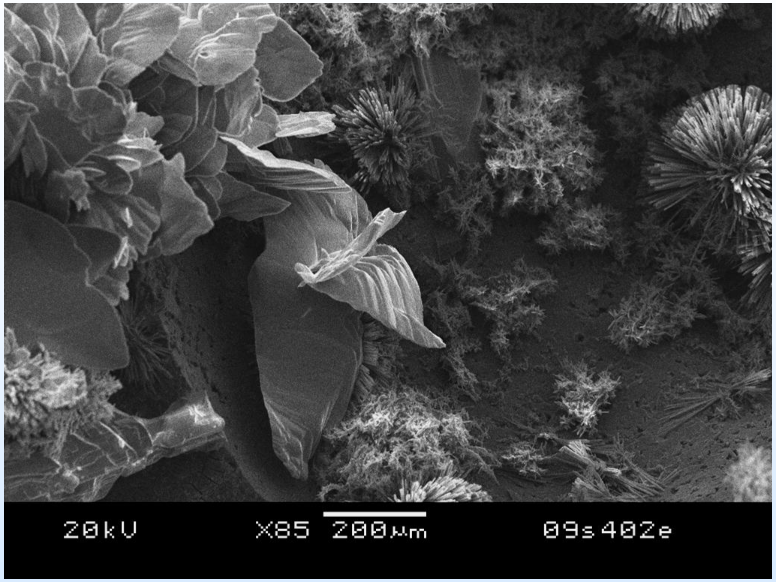


Columbia River Basalt with circular calcite coatings after exposure to wet $scCO_2$ for 100 days

- Basalt Reactions with Wet $scCO_2$
  - Dominant phase in contact with reservoir rock
  - Long-term experiments reveal rapid carbonation but system is treated as inert in all present reservoir simulators
  - Dominates the total carbonation rate in deeper reservoirs

Project Overview: Scope of work

- Multicomponent Gas Systems
  - Database to evaluate impact of injecting impure gas streams into basalts (such as in CarbFix project)
  - Testing shows carbonate accelerating with some basalts, interference in others
  - Current testing matrix includes SO_2-O_2-CO_2 mixtures



Hawaiian basalt after 84 days exposure to water and $scCO_2$ containing 1% SO_2

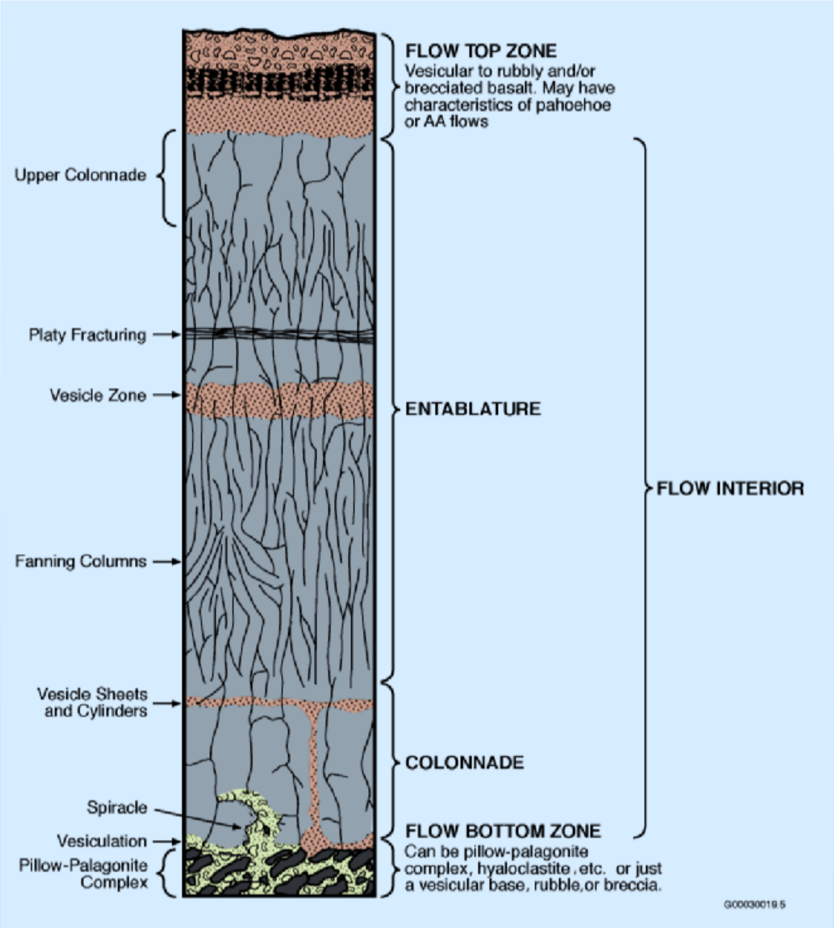
- Seismic Imaging
  - Assess potential for surface seismic monitoring of CO_2 plume
  - Utilize Wallula pilot borehole under BSCSP
  - Evaluate advanced signal processing algorithms for noise reduction and detection of CO_2 plume

Flood Basalt Features Relevant to CO_2 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

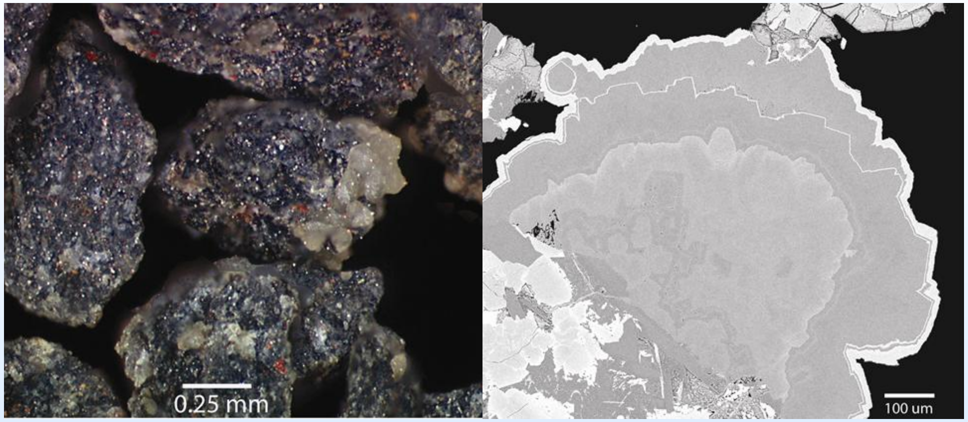
Layered Basalt Flow



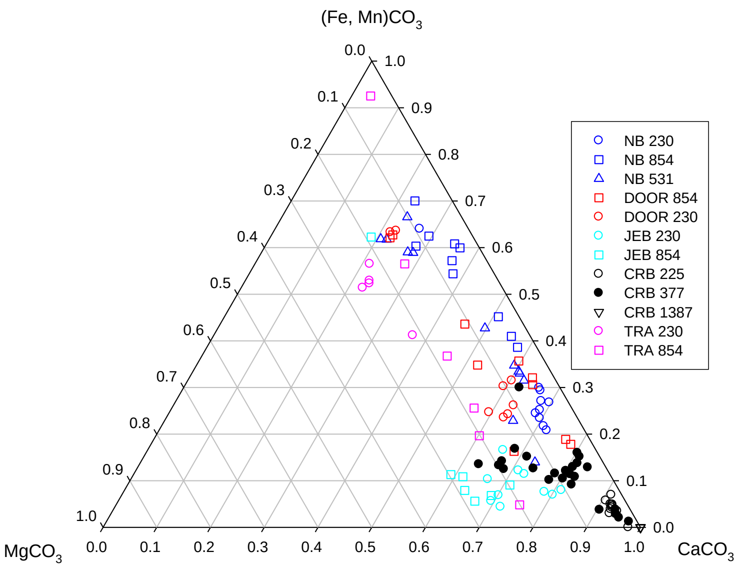
Carbonation of Basalts with Aqueous Dissolved $scCO_2$

- **Static Experiments**
  - Carbonate precipitates
    - Discrete particles
    - Chemical Variability
  - Calcite, cation substituted
- **Increased reservoir depths increase carbonation**
  - Transition from calcite to ankerite/kutnahorite
  - Cation substituted (Fe, Mn, & Mg

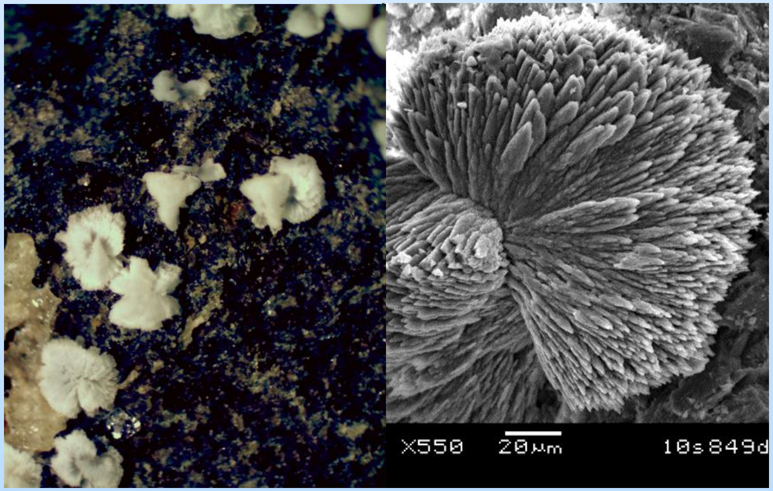
2.5 years, 100°C, 100 bar



Carbonate Chemistries



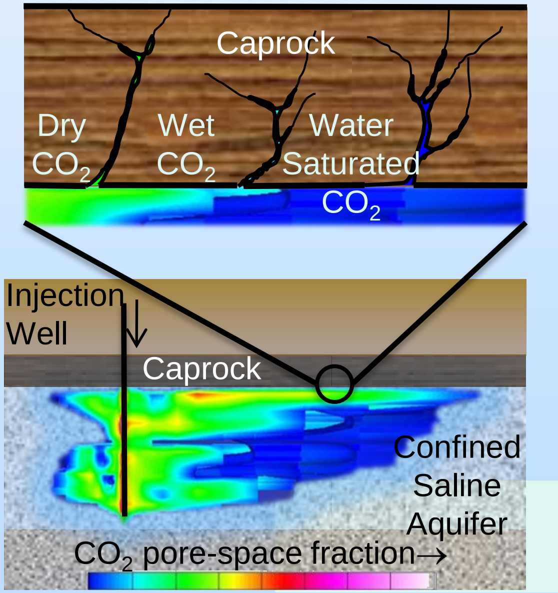
180 days, 137°C, 250 bar

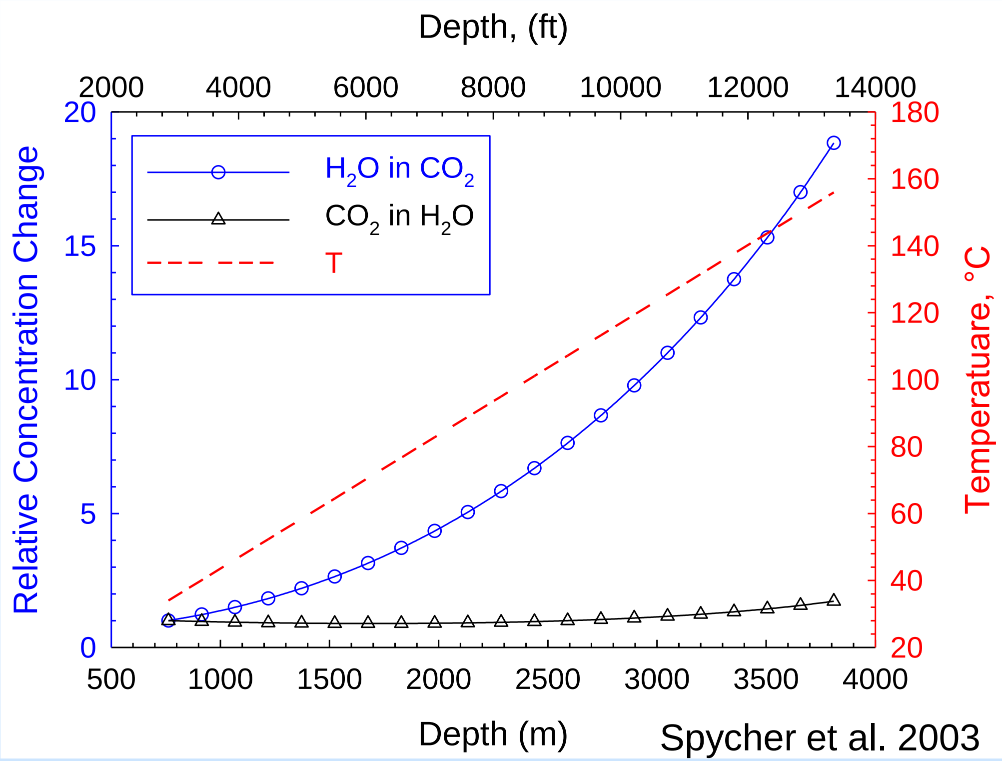


Phase Behavior of CO_2-H_2O Mixtures in Geological Sequestration

CO_2-H_2O Mixtures

- CO_2 solubility in water varies little with pressure and temperature
- H_2O solubility in $scCO_2$ is strongly dependent on depth
- An equivalent geochemical framework for chemical reactivity in wet $scCO_2$ does not yet exist



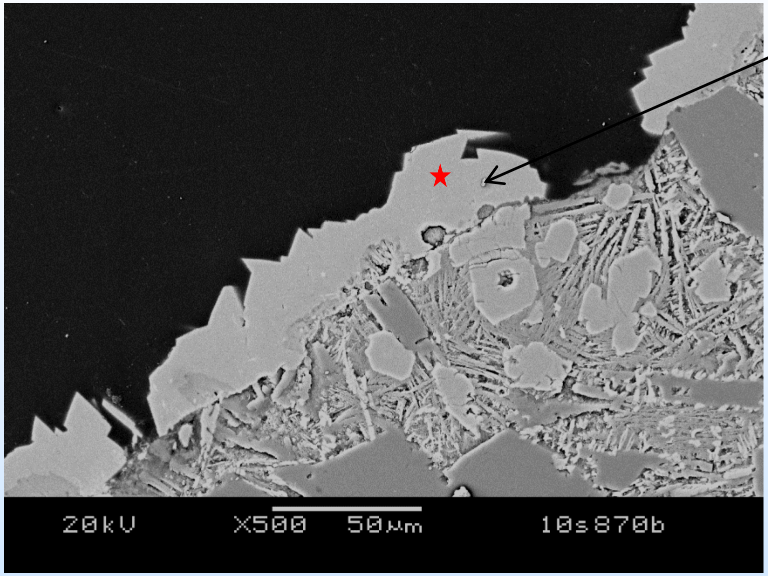


Spycher et al. 2003

Mineral transformation kinetics is potentially as great or greater in wet $scCO_2$

Reaction Products when Exposing Basalt to Wet $scCO_2$

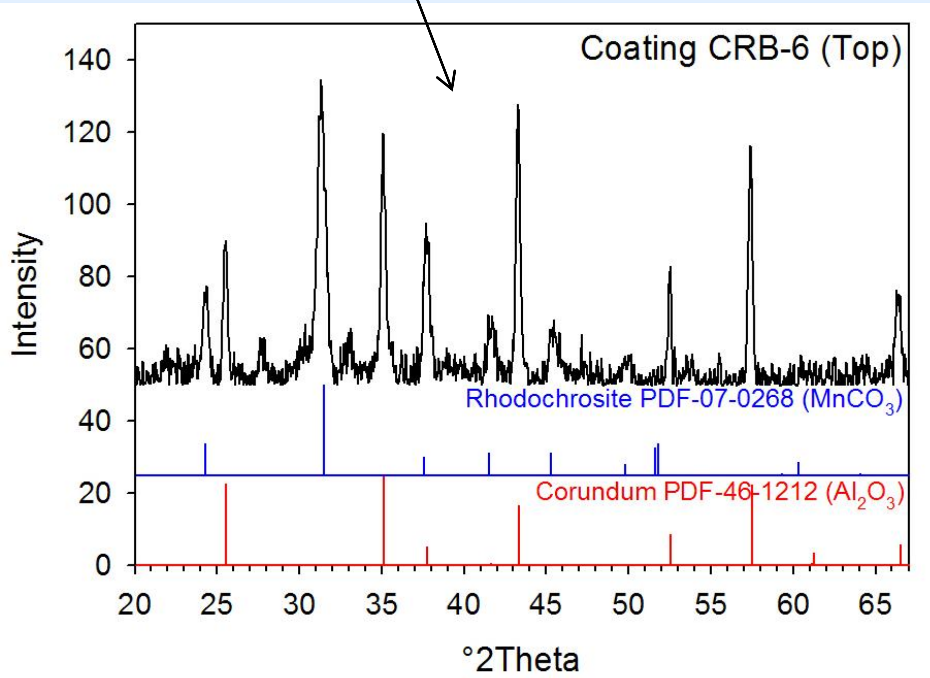
Polished Cross Section CRB

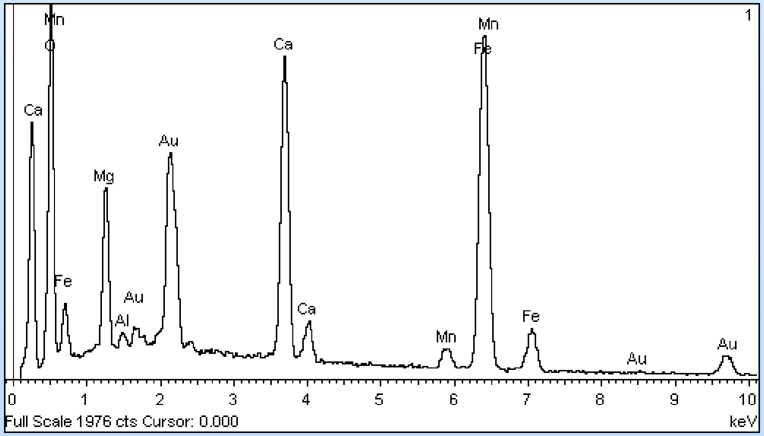


Thick red coating

31 MPa 137°C

7.5 MPa 34°C





Wet scCO$_2$ and Mineral Surface Interactions

What do we know?

- Thin water films develop on silicate minerals
- Water is key to carbonation of silicates

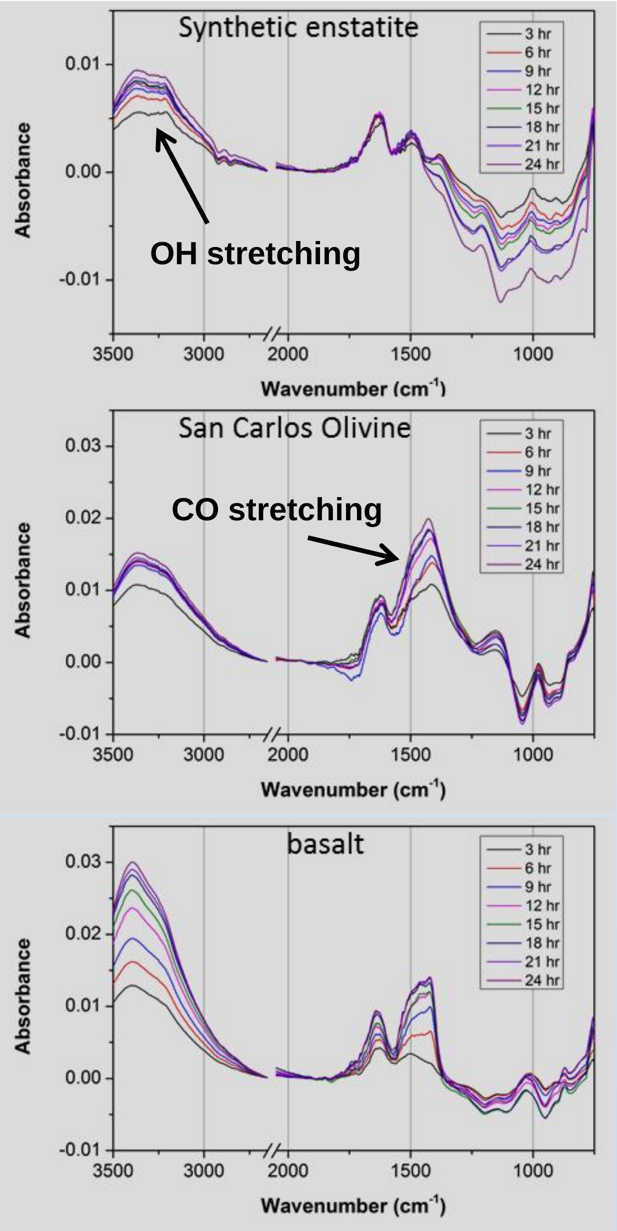
➢ Spectroscopy Studies

- In situ measurements at reservoir conditions
  - 50°C, 90 bar, water saturated scCO$_2$
- Observed water film growth, carbonate formation, and mineral dissolution

➢ Water film properties

- Enstatite least reactive
- Olivine most reactive
- Columbia River basalt develop thickest water films but intermediate reactivity

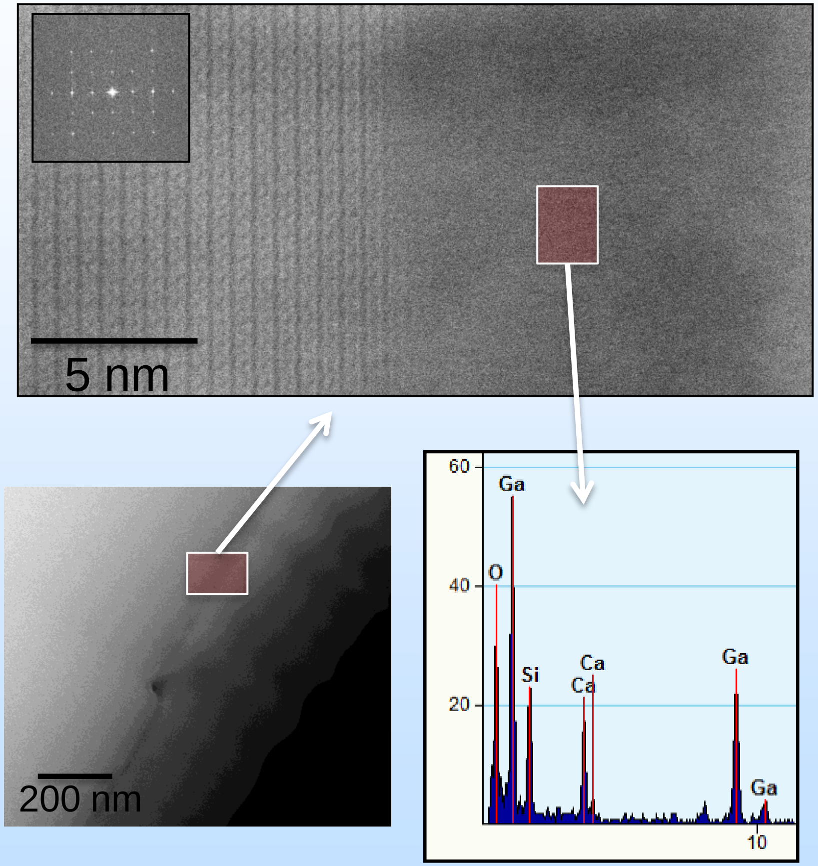
➢ New insights to water mediated reactions



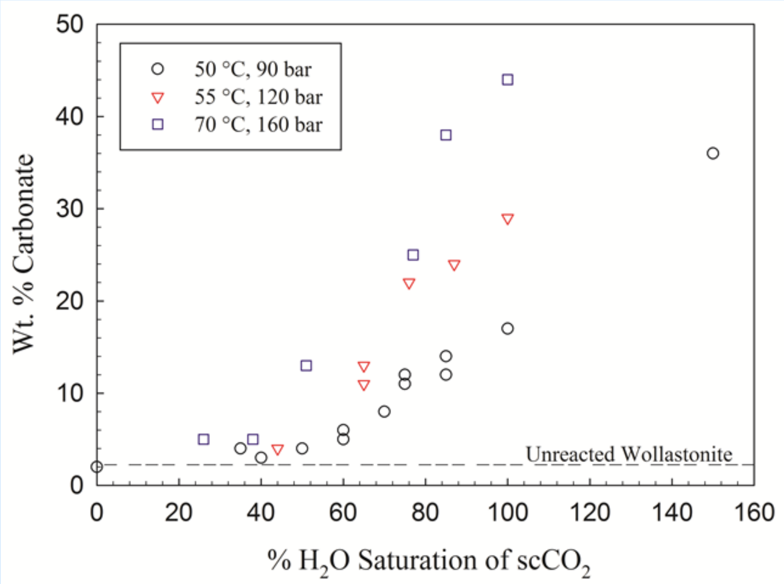
Initial Stages of Carbonation in wet $scCO_2$

- **Goal**: Determine role of water in wollastonite carbonation process.
- **Experimental Conditions**: Range of Temperatures (50 , 55 , 70 C) and pressure (90, 120, 180 bar), with dry to variable wet $scCO_2$.
- **Results**: Minimum amount of water required before carbonation proceeds.

50°C, 90 bar, 35% H_2O, 24 hours

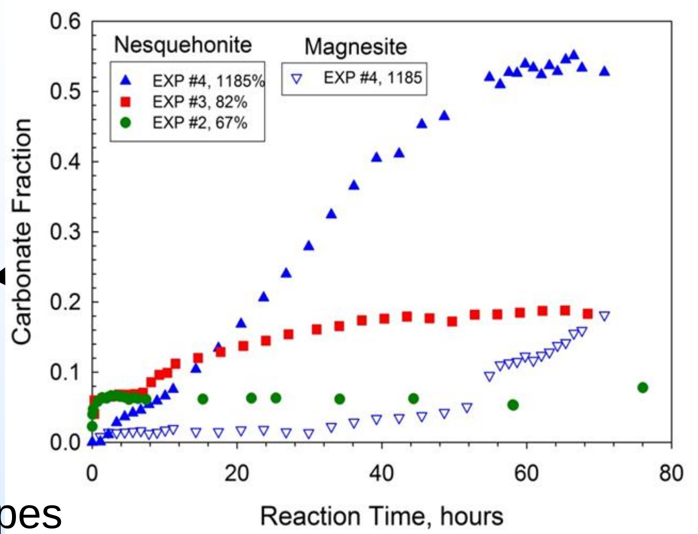


Quantitative in situ XRD Results



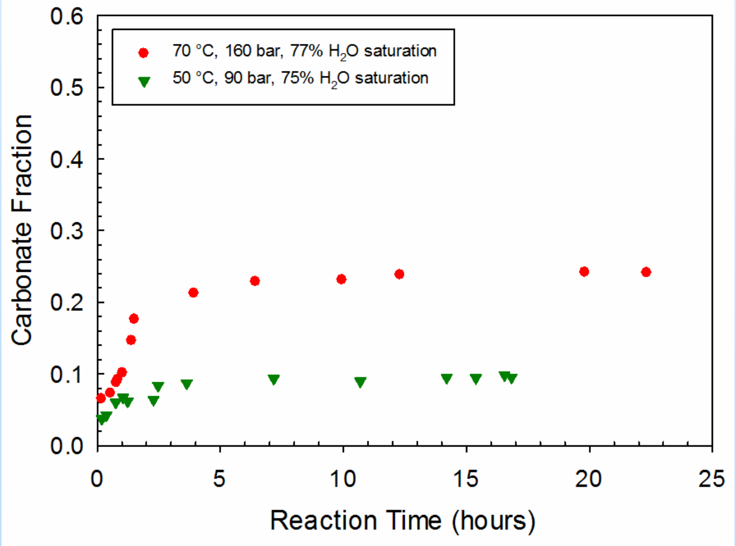
Silicate Carbonation in Wet $scCO_2$

Forsterite [Mg_2SiO_4] (isolated tetrahedra)



Different types of oxygen sharing

Wollastonite [$CaSiO_3$] (single chain)



- Reactions occurring between silicates and H_2O-$scCO_2$ fluids produce well crystallized carbonate minerals at laboratory time scales.
- Carbonation rates are initially fast, but attenuated in low water environments
- Water condensation on surface is key to carbonation of silicates
- Amorphous layers are the initial steps to carbonation
- Degrees of carbonation are dependent on reservoir depth

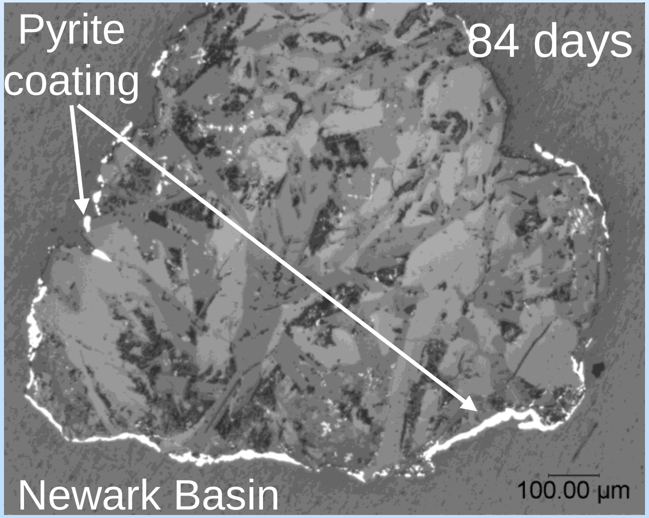
Schaef, H.T., McGrail, B.P., Loring, J.S., Bowden, M.E., Arey, B.W., and Rosso, K.M., 2012, "Forsterite [Mg_2SiO_4)] carbonation in wet supercritical CO_2: An *in situ* high pressure x-ray diffraction study, ES&T, DOI: 10.1021/es301126f.

Impacts of Contaminants on Mineral Carbonation

- **Pre- and Oxy-combustion gas streams**
  - SO_2, H_2S, O_2, NOx
  - Corrosive when mixed with H_2O and CO_2
- **Experimental Conditions**
  - Crushed basalt (0.42-2.0 mm)
  - Aqueous dominated, 90°C, 90 bar
  - CO_2 with ~ 1 wt% H_2S or SO_2
- **SO_2-CO_2 Testing**
  - Extensive dissolution
  - Secondary reaction products
    - Hexahydrite ($MgSO_4 \cdot 6H_2O$)
    - Fe sulfite ($FeSO_3 \cdot 2H_2O$)
    - Mg sulfite ($MgSO_3 \cdot 2H_2O$)
    - Mg thiosulfate hydrate ($MgS_2O_3 \cdot 6H_2O$)
- **H_2S-CO_2 system**
  - Pyrite and marcasite coatings (84 days)
  - Pyrite and carbonates (3.5 years)

SO_2-CO_2-H_2O

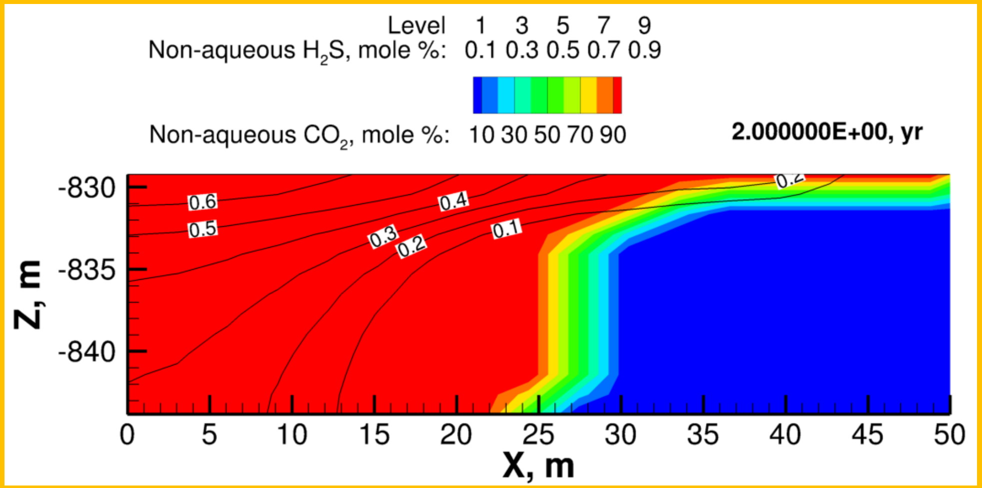
H_2S-CO_2-H_2O



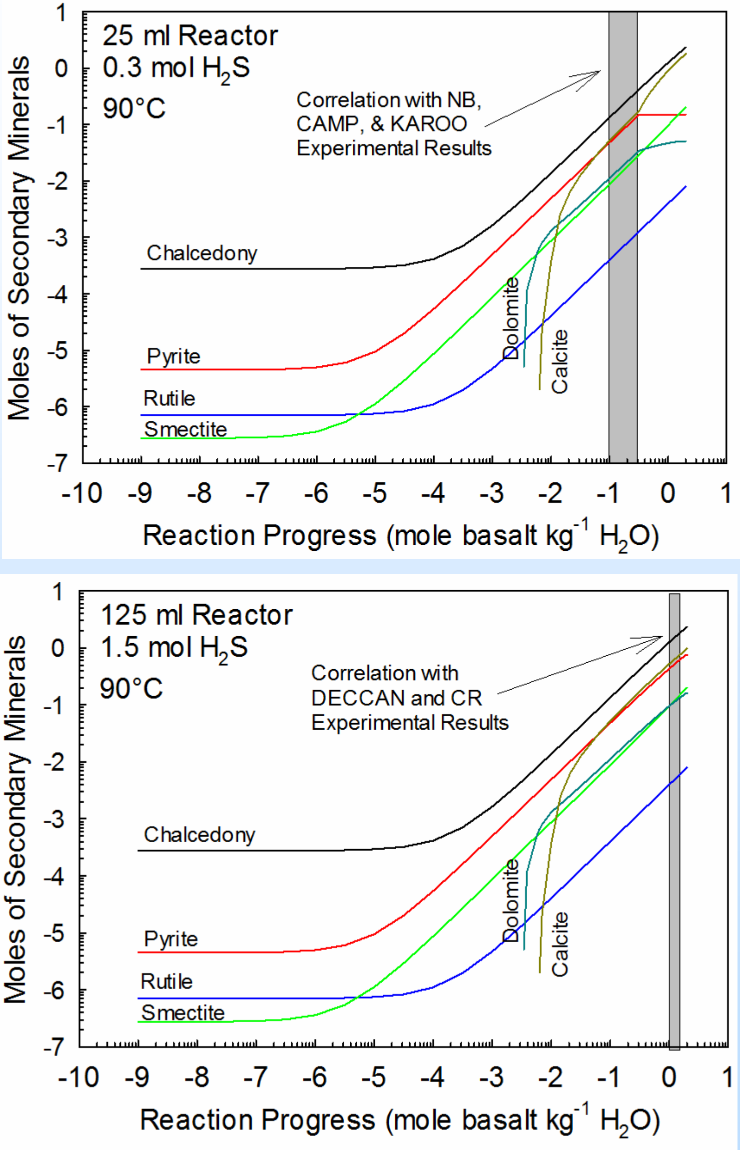
Connecting Laboratory Results and Batch Modeling to Reservoir Simulators

- Geochemical reaction path modeling with EQ3/6
  - Accurately predicts pyrite precipitation followed by carbonates
  - Rapid consumption of H_2S
  - Correlatable to basalt chemistry
- These results feed into reservoir simulations

CO_2 (flood) H_2S (contours) mole fraction



EQ3/6 Geochemical Modeling



Accomplishments

- Long term storage of CO_2 in basalt formations
  - Aqueous dominated reactions
    - Experiments show carbonate mineralization is relatively fast
    - Variable rates among basalts not correlated to bulk composition or mineralogical differences. New evidence pointing to key role of Fe(II)/Fe(III) redox chemistry
  - Water bearing supercritical CO_2 reactions
    - Carbonation significant and comparable to aqueous dominated system
    - Mineralization rates increase with reservoir depth
    - In situ techniques illustrate important role of water
  - Mixed gas systems (SO_2, H_2S)
    - Different reaction rates compared to pure CO_2
    - Precipitation of sulfur containing minerals
- Published laboratory results have significantly benefited and been directly used in pilot sequestration projects
  - Boise Wallula ICCS Project (Eastern Washington)
  - CarbFix Project (Hellisheidi, Iceland)
- Results also being applied for independent energy storage study in CRB

Summary

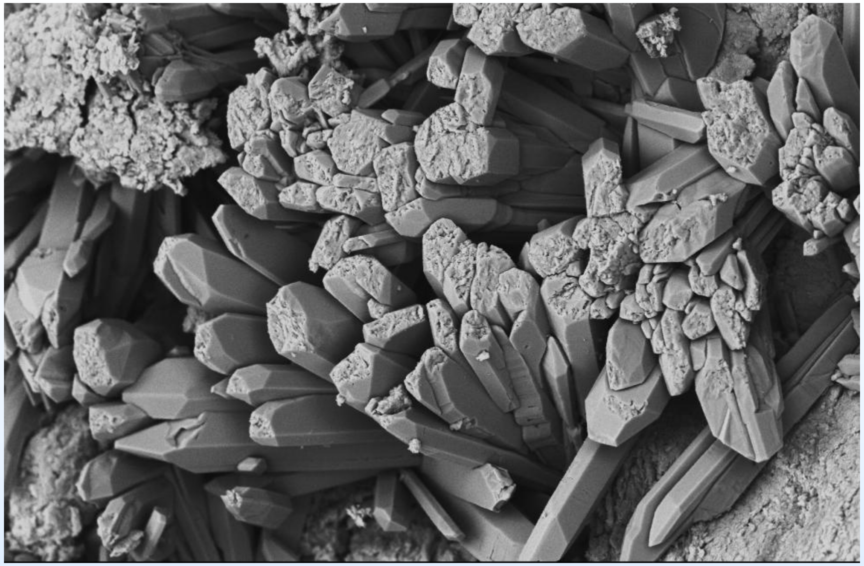
Key Findings

- Reactions occurring between basaltic rocks and H_2O-scCO_2 fluids produce well crystallized carbonate minerals at laboratory time scales.
- Reactions occurring in water bearing scCO_2 fluids are equally important.
- Sulfur species effectively and permanently removed from the scCO_2 phase.

Long Term Implications

- This research is providing a path forward for eventual commercial use of basalt formations for CO_2 sequestration.

> *"CO_2 storage in basalt formations is also a potentially important option for regions like the Indian subcontinent " IEG Technology Roadmap, 2009.*



Needles of aragonite growing on a basalt grain during exposure to wet scCO_2 for 377 days at 100°C and 90 bar.

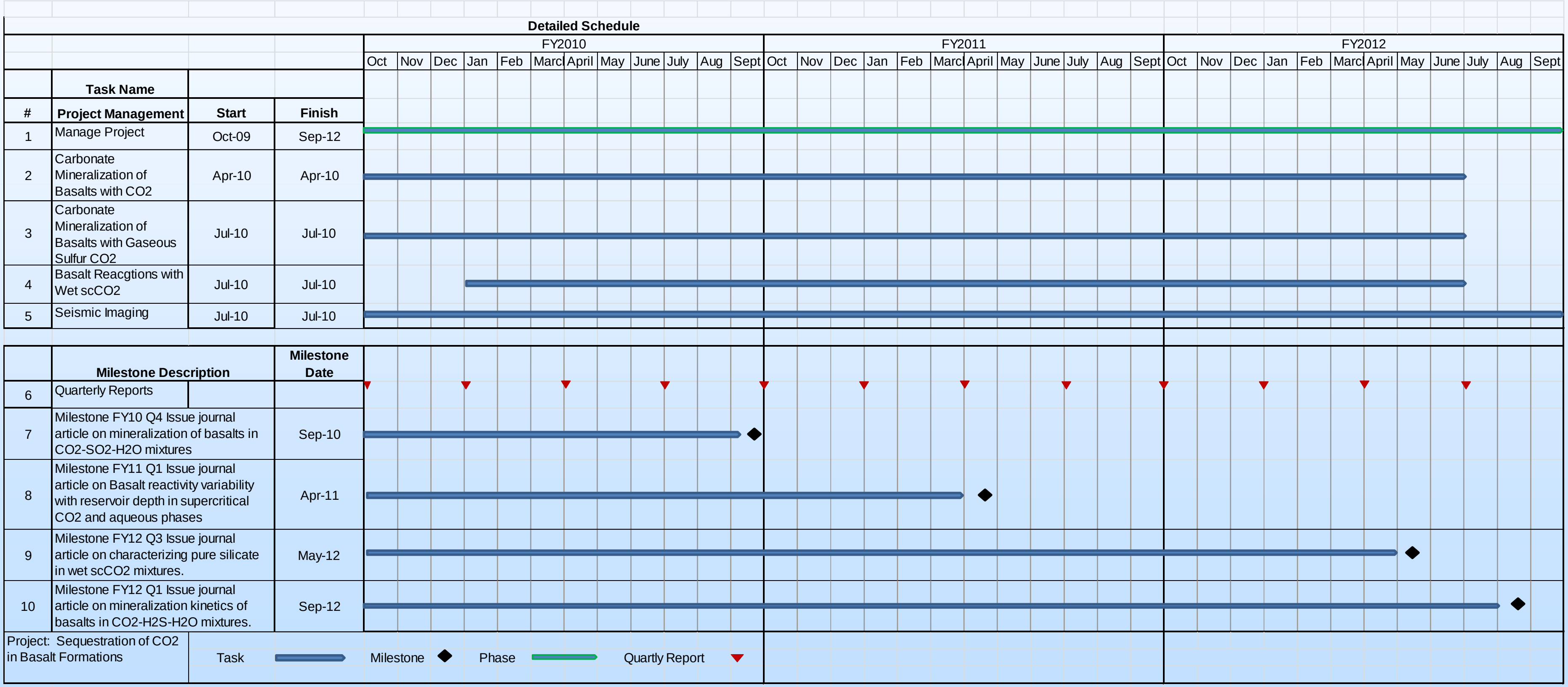
FY 13 Activity Summary

- Continue long term CO_2-H_2O basalt experiments
- Expand CO_2 based mixed gas studies to include variable mixtures of O_2, SO_2, & NO_x
- Initiate new laboratory measurements with *in situ* techniques

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



Detailed Schedule

FY2010: Oct Nov Dec Jan Feb Marc April May June July Aug Sept

FY2011: Oct Nov Dec Jan Feb Marc April May June July Aug Sept

FY2012: Oct Nov Dec Jan Feb Marc April May June July Aug Sept

#	Task Name **Project Management**	Start	Finish
1	Manage Project	Oct-09	Sep-12
2	Carbonate Mineralization of Basalts with CO2	Apr-10	Apr-10
3	Carbonate Mineralization of Basalts with Gaseous Sulfur CO2	Jul-10	Jul-10
4	Basalt Reacgtions with Wet scCO2	Jul-10	Jul-10
5	Seismic Imaging	Jul-10	Jul-10

	Milestone Description	**Milestone Date**
6	Quarterly Reports	
7	Milestone FY10 Q4 Issue journal article on mineralization of basalts in CO2-SO2-H2O mixtures	Sep-10
8	Milestone FY11 Q1 Issue journal article on Basalt reactivity variability with reservoir depth in supercritical CO2 and aqueous phases	Apr-11
9	Milestone FY12 Q3 Issue journal article on characterizing pure silicate in wet scCO2 mixtures.	May-12
10	Milestone FY12 Q1 Issue journal article on mineralization kinetics of basalts in CO2-H2S-H2O mixtures.	Sep-12

Project: Sequestration of CO2 in Basalt Formations

Task ▬ Milestone ◆ Phase ▬ Quartly Report ▼

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