# Sequestration of $CO_2$ in Basalt Formations

## Project Number 58159 Task 1

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Collaborators

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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 20-22, 2013

# 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

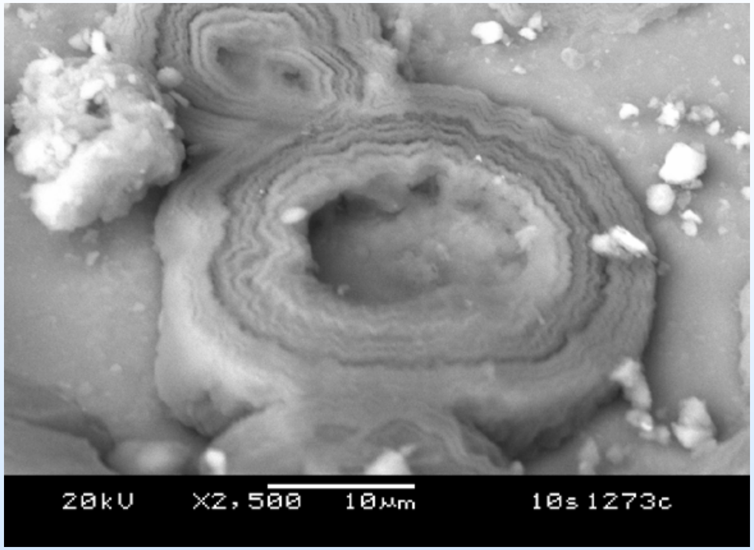
- Program goals addressed:
  - Technology development to predict $CO_2$ storage capacity
  - Demonstrate fate of injected $CO_2$ and most common contaminants
- Project benefits statement: This research project conducts modeling, laboratory studies, and pilot-scale research aimed at developing new technologies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

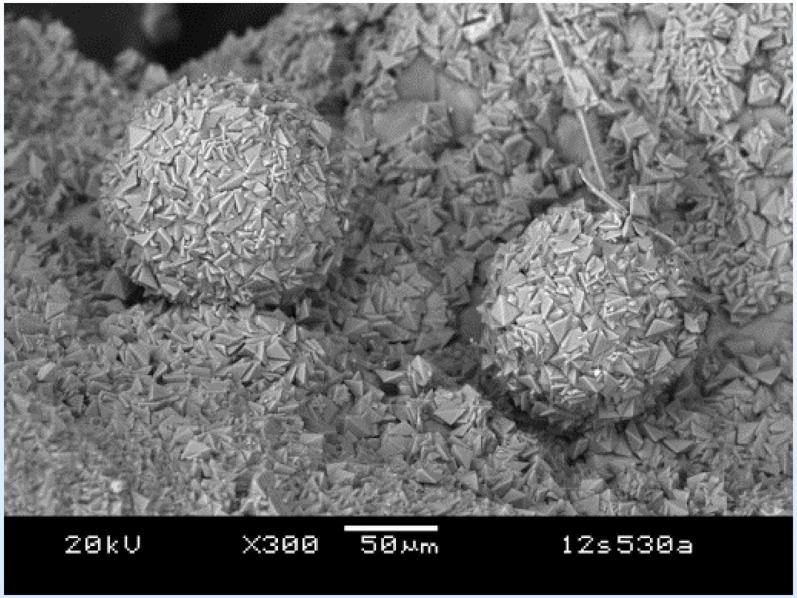


Basalt with circular calcite coatings after exposure to wet $scCO_2$ for 100 days.

- 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
  - Carbonation rate in deeper reservoirs significant

# **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 $CO_2$ mixtures containing $SO_2$, $O_2$, and $H_2S$



KAROO basalt after 84 days exposure to water and $scCO_2$ containing 1% $O_2$ and $SO_2$

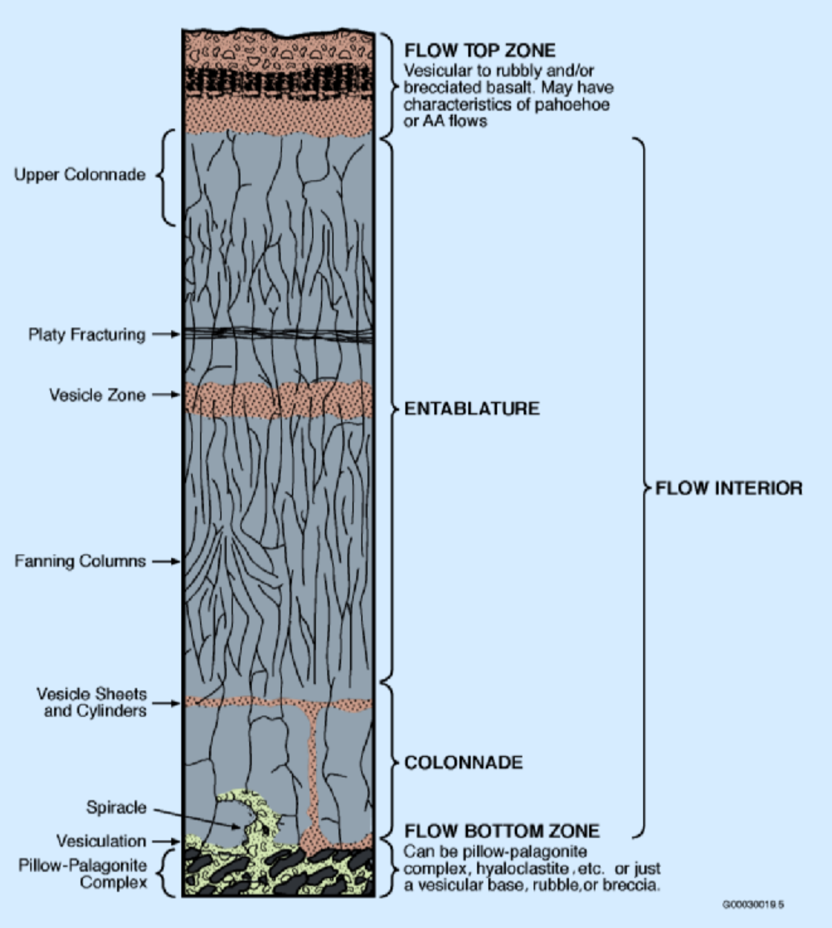
- Seismic Imaging
  - Assess potential for surface seismic monitoring of $CO_2$ plume
  - Utilize Wallula pilot borehole
  - Evaluate advanced signal processing algorithms for noise reduction and detection of $CO_2$ plume

# 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

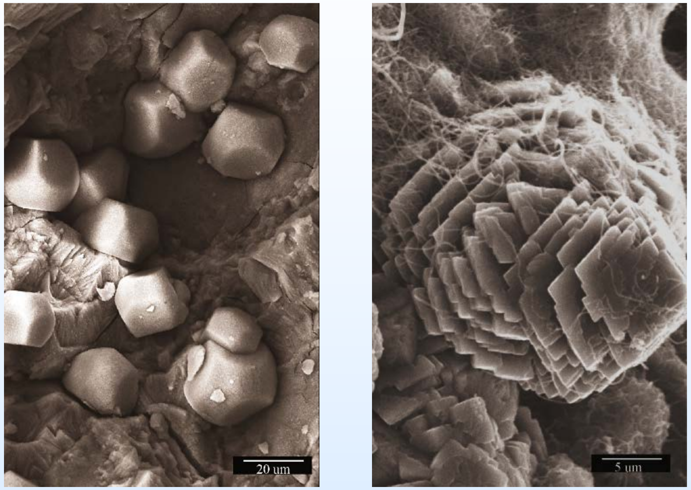
Deccan Trap Basalts

Layered Basalt Flow



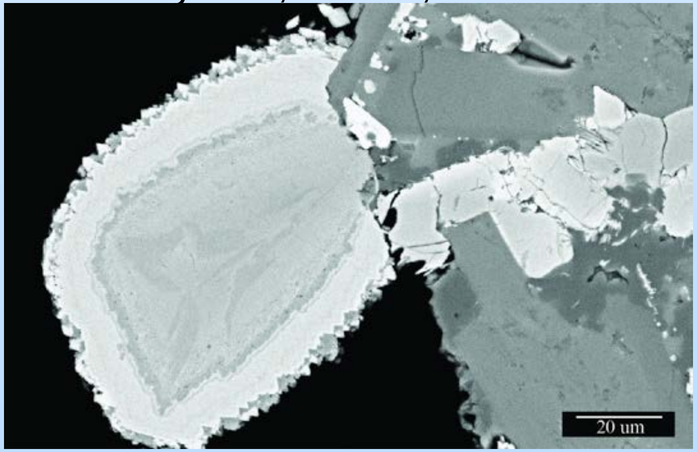
# Carbonation of Basalts with Aqueous Dissolved $scCO_2$

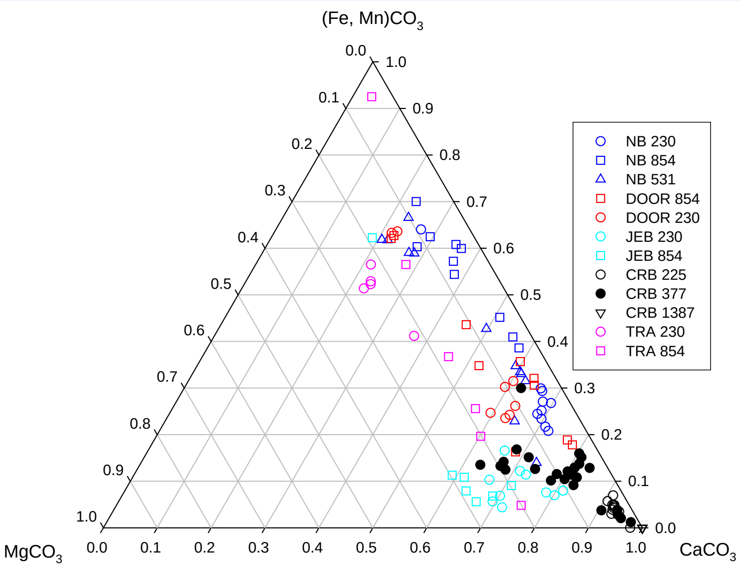
- **Static Experiments**
  - Carbonate precipitates
    - Discrete particles
    - Chemical variability
  - Calcite, cation substituted
- **Multi Year Testing**
  - Cation substitution (Fe, Mn, & Mg) increases with duration
  - Surface coating expand into available pore spaces



Carbonate Chemistries

2.5 years, 100°C, 100 bar

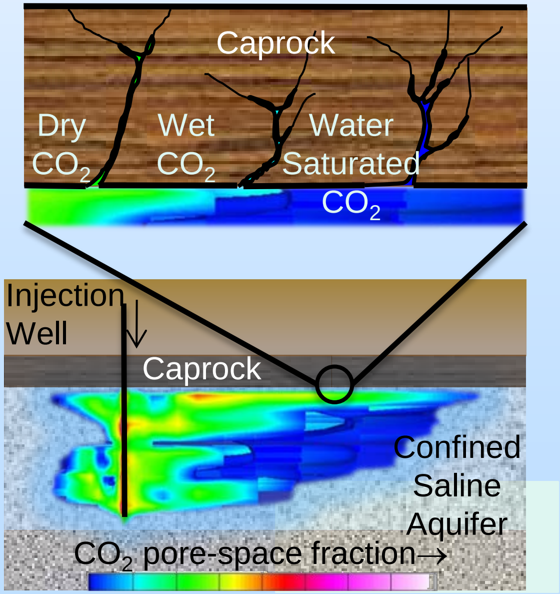


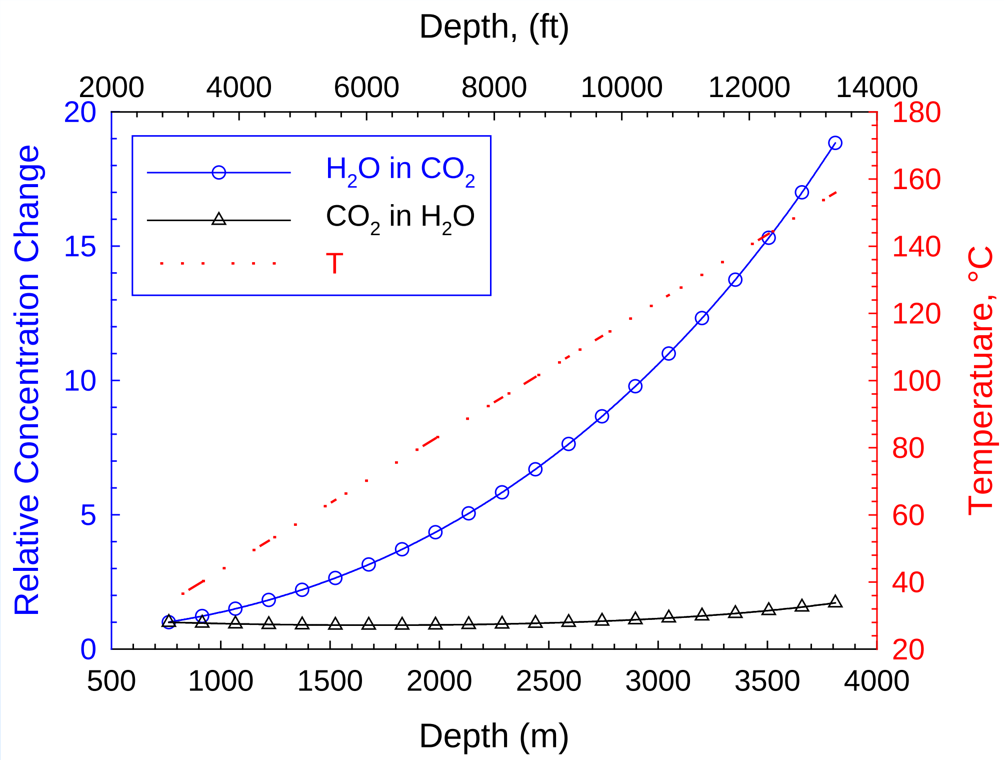


# Phase Behavior of $CO_2$-$H_2O$ Mixtures in Geological Sequestration

## $CO_2$-$H_2O$ 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

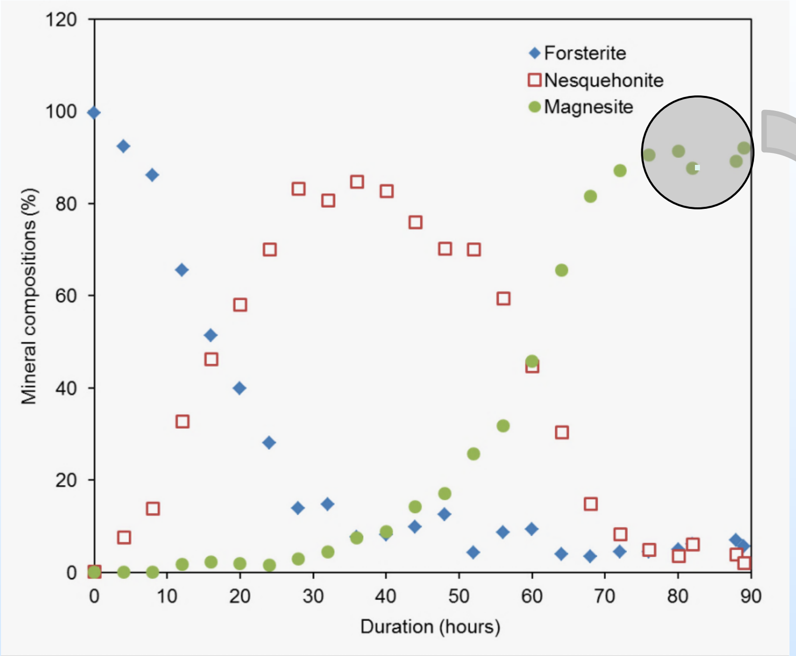


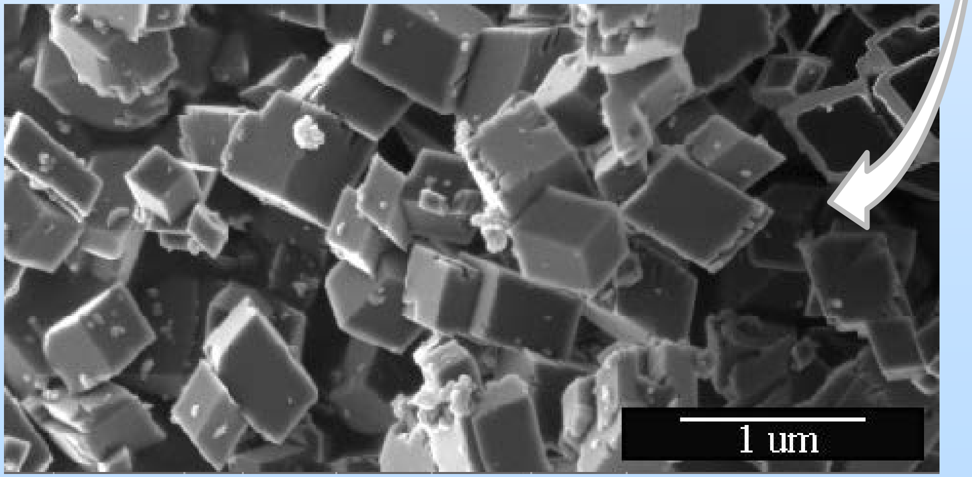


*Mineral transformation kinetics is potentially as great or greater in wet $scCO_2$*

# Intermediate Crystalline Phases During Silicate Carbonation in Wet $scCO_2$

Forsterite [$Mg_2SiO_4$] (isolated tetrahedra)





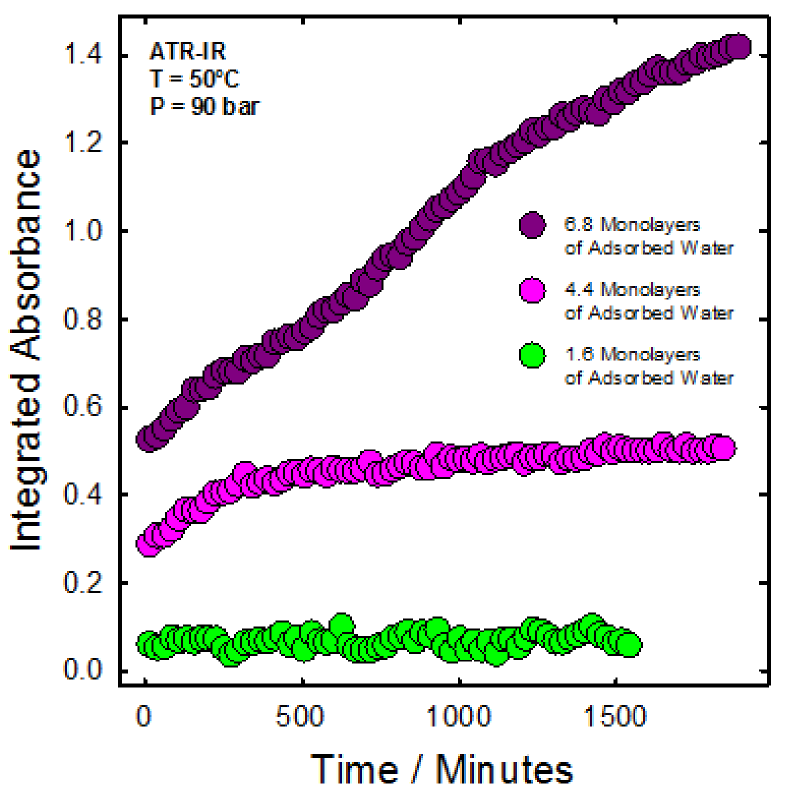
- Reactions occurring between silicates and $H_2O$-$scCO_2$ fluids produce well crystallized carbonate minerals at laboratory time scales.
- Water condensation on surface is key to carbonation of silicates
- Amorphous layers are the initial steps to carbonation
- Carbonation rates are initially fast, resulting in metastable phases
- Final product is a stable anhydrous carbonates

*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.” in ES&T, vol 47, 174-181.

# Silicate Carbonation in wet $scCO_2$

- **Goal**: Determine dependence of metal carbonate formation on the properties of adsorbed water films.
- **Experimental Conditions**: Constant temperature (50°C) and pressure (90 bar), with dry to variable wet $scCO_2$.
- **Results**: Reactivity of forsterite with wet-$scCO_2$ occurs in distinct adsorbed water concentration threshold regimes:
  - $\leq$ 2 monolayers: highly-structured chemisorbed waters and bicarbonates.
  - ~2 to ~5 monolayers: Limited carbonation (hydrated)
  - >5 monolayers: Continuous carbonation

ATR-IR Titration Results
(CO stretching bands of carbonate)



Thompson, C. J., Martin, P. F., Chen, J., Schaef, H. T.; Rosso, K. M., Felmy, A. R., Loring, J. S. (2013) "Automated High-Pressure Titration System with In Situ Infrared Spectroscopic Detection", Reviews of Scientific Instruments, submitted.

# 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

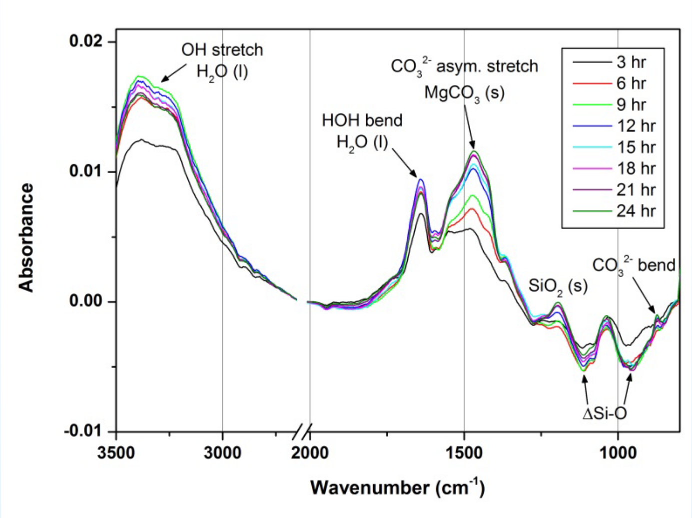
## ➢ *In Situ* Infrared Spectroscopy Studies

- Experiments conducted at reservoir conditions
  - 50°C, 90 bar, water saturated $scCO_2$
- Observed water film growth, mineral dissolution , carbonate formation, and precipitation of amorphous silica (enstatite)

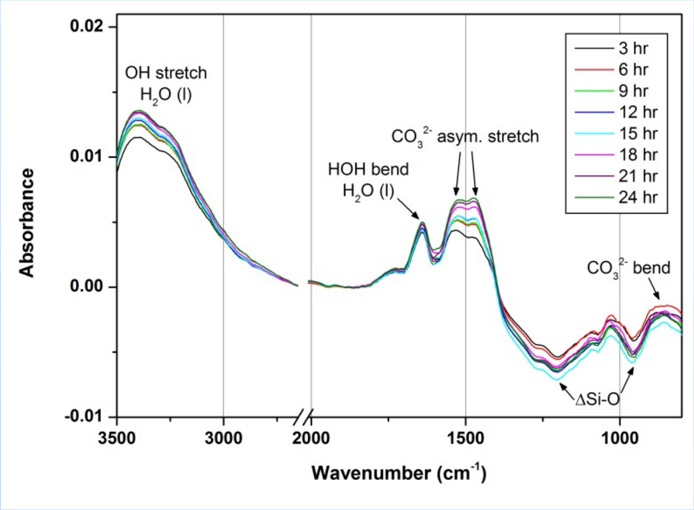
## ➢ Reactive Behavior

- Enstatite: 1.1 % conversion to $MgCO_3$
- Plagioclase: 0.3% conversion to $CaCO_3/Na_2CO_3$

**Natural Enstatite ($MgSiO_3$)**

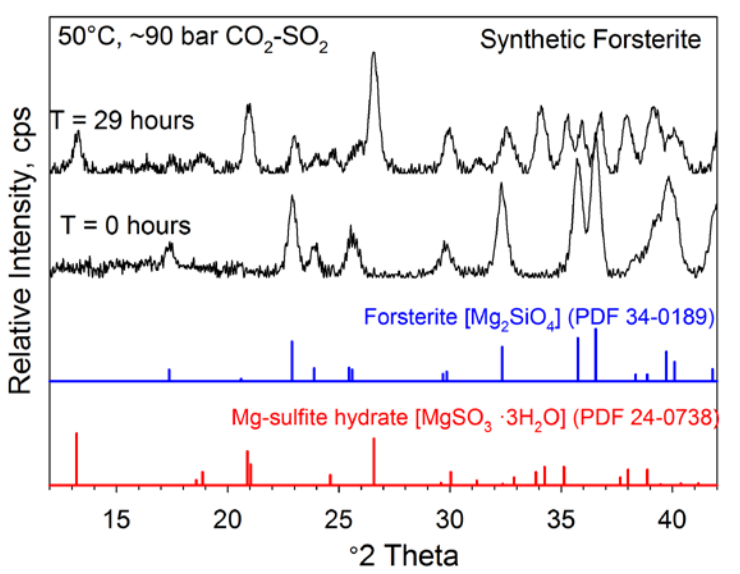


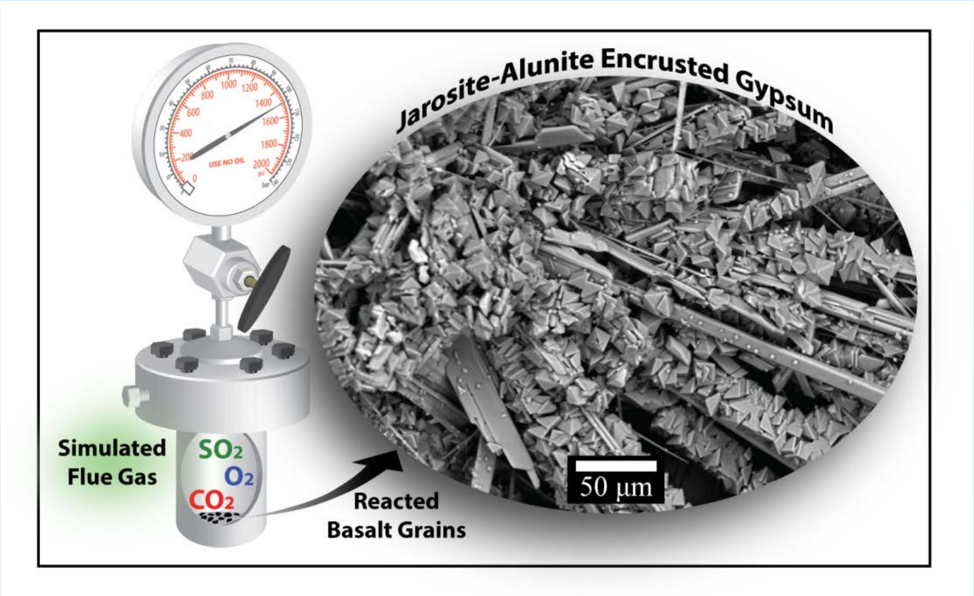
**Plagioclase [$(Ca,Na)(Al,Si)_4O_8$]**



# 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 $CO_2$
- **$SO_2$-$CO_2$ Testing**
  - Extensive dissolution
  - *In situ* XRD identified sulfite minerals
    - Mg sulfite ($MgSO_3 \cdot 3H_2O$)
- **$SO_2$-$CO_2$-$O_2$ system**
  - Gypsum, jarosite-alunite phases
  - Extreme pH conditions
  - Carbonation onset after ~100 days testing





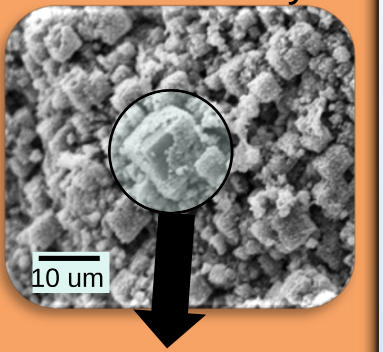
# Reactions Between Basalt and $scCO_2$ containing 1% $H_2S$ (538 days)

## Dynamic System

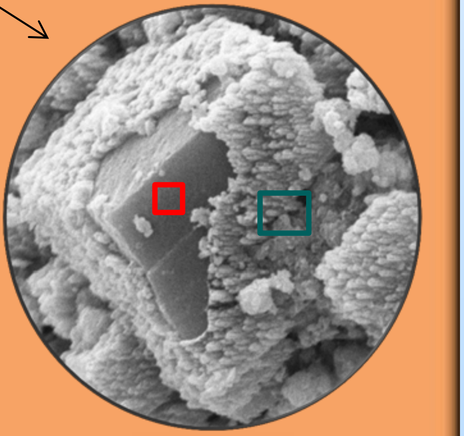
- Well crystallized surface coatings
- Various degrees of carbonation preceding pyrite formation

reacted CR grains

Dolomite and Pyrite



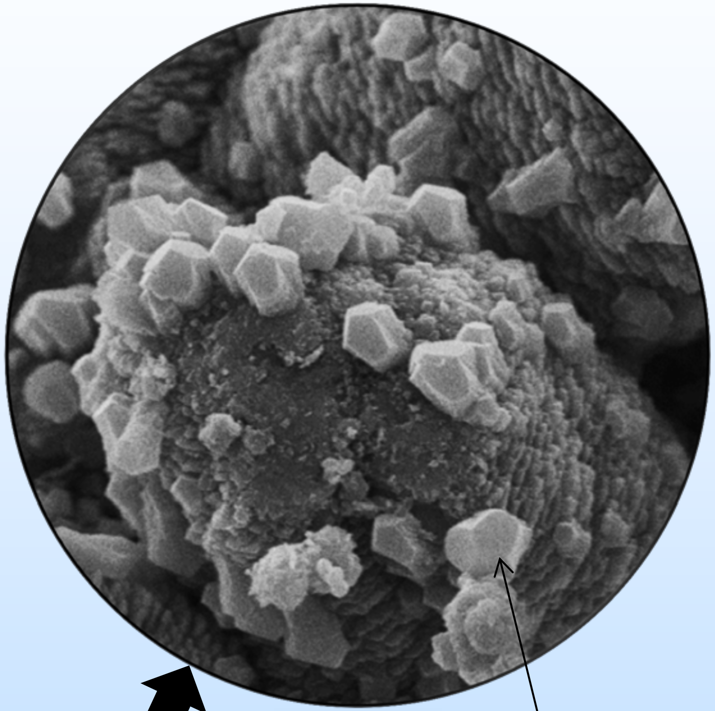
Pyrite observed coating a large dolomite grain on CR basalt

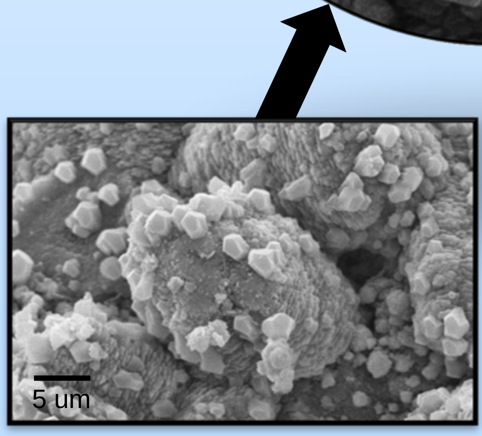


EDX Analysis

| Element | Wt% | |
|---|---|---|
| Carbon | 27 | 20 |
| Oxygen | 45 | 47 |
| Magnesium | 9 | 5 |
| Calcium | 18 | 19 |
| Iron | 1 | 4 |
| Sulfur | nd | 4 |

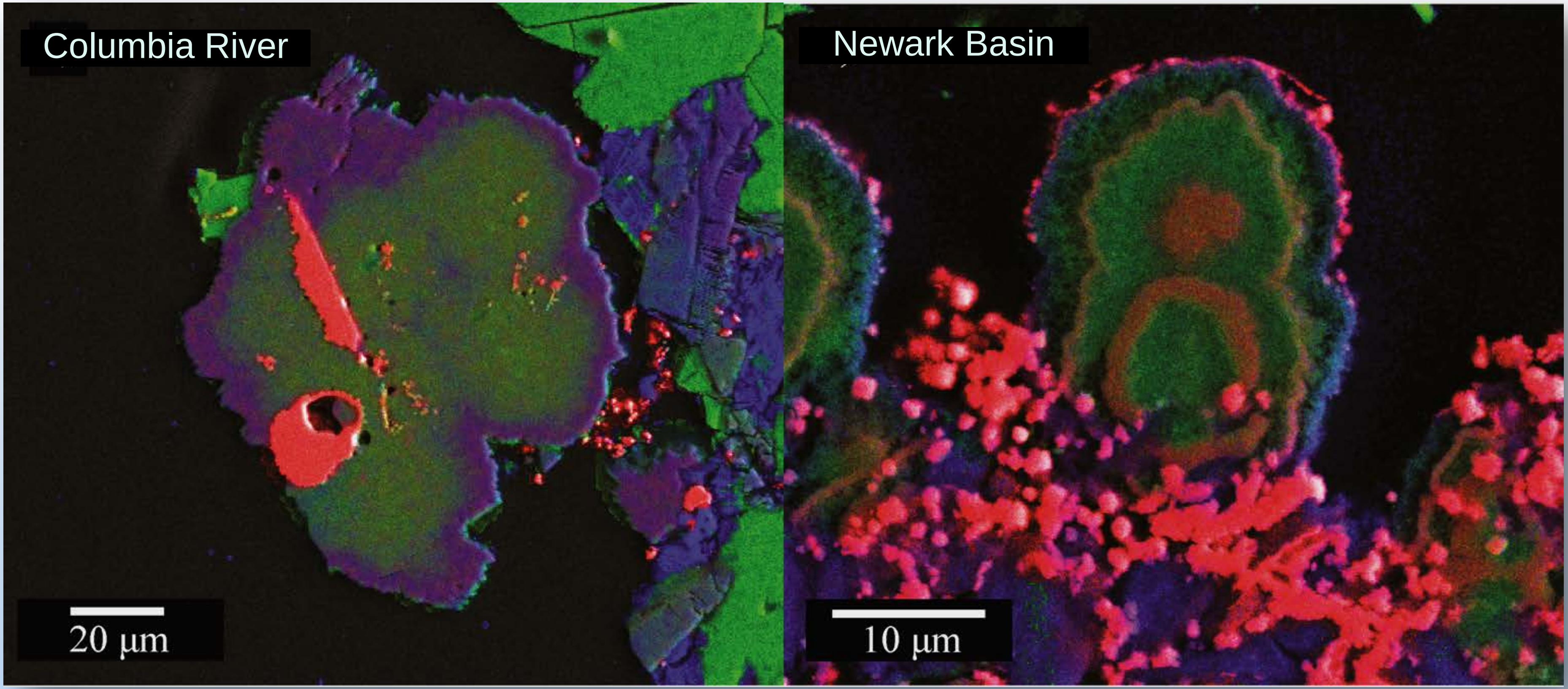
Large dolomite grain on CAMP basalt





Well developed calcite crystals

# Chemical Variations Occurring within Precipitates exposed to $scCO_2$ containing 1% $H_2S$ (1250 days)



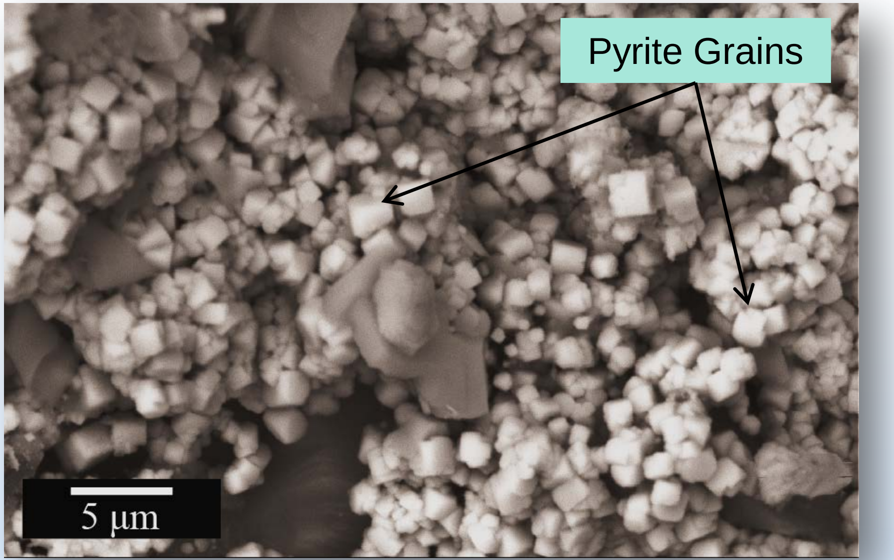
Color Key

🟥 = Iron and Sulfur

🟩 = Calcium

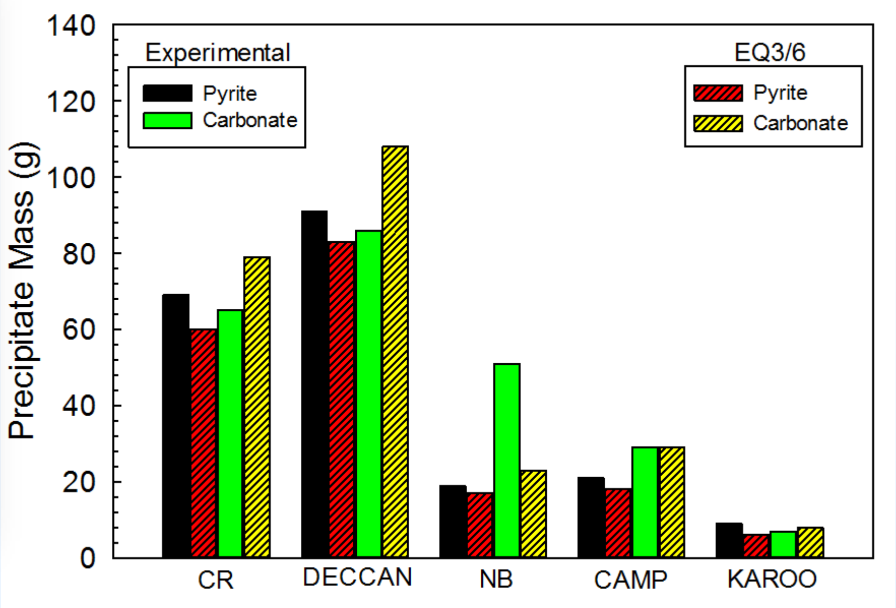
🟦 = Magnesium

# Characterizing Surface Corrosion



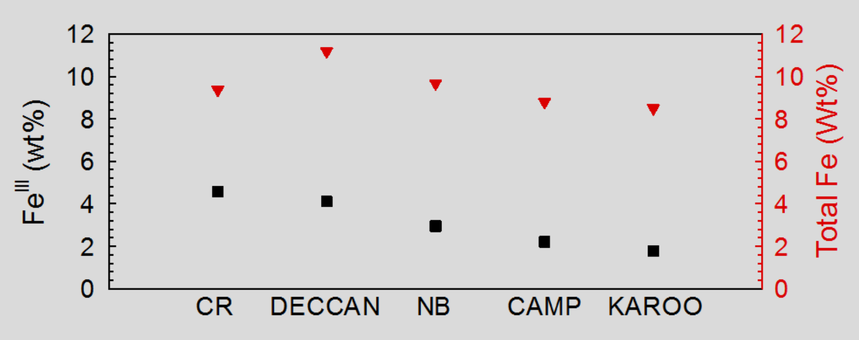
## Acid Digestion Results

(Scaled to 1 kg $H_2O$)



- **Reaction Products**
  - Corrosion correlatable to amount of $H_2S$ in reactor
  - Carbonates formed regardless of $H_2S$ content
- **Variable Reaction Rates**
  - Most reactive basalts contain highest amount of $Fe^{(III)}$
  - KAROO-low $Fe^{(III)}$ content

## Fe Content

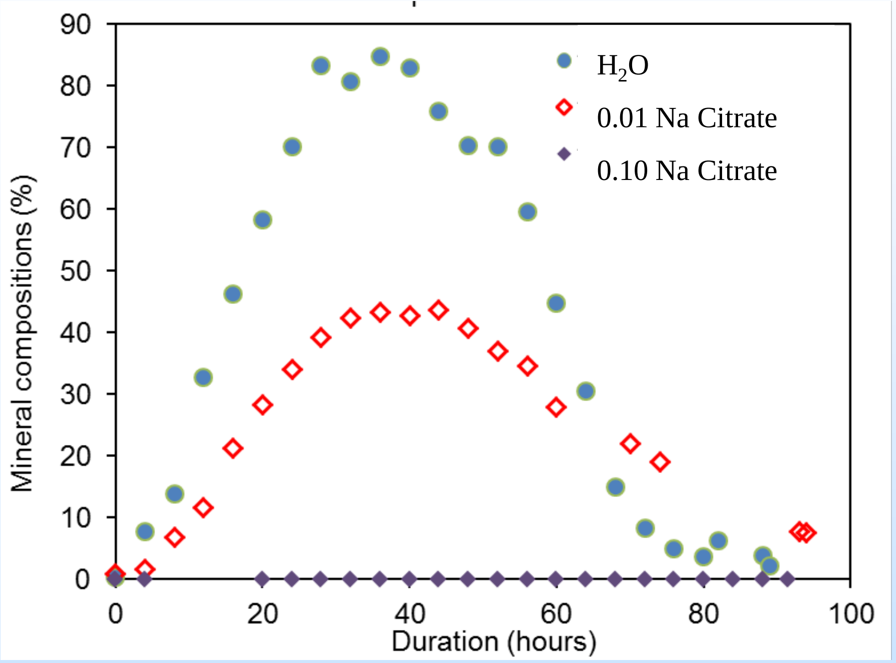


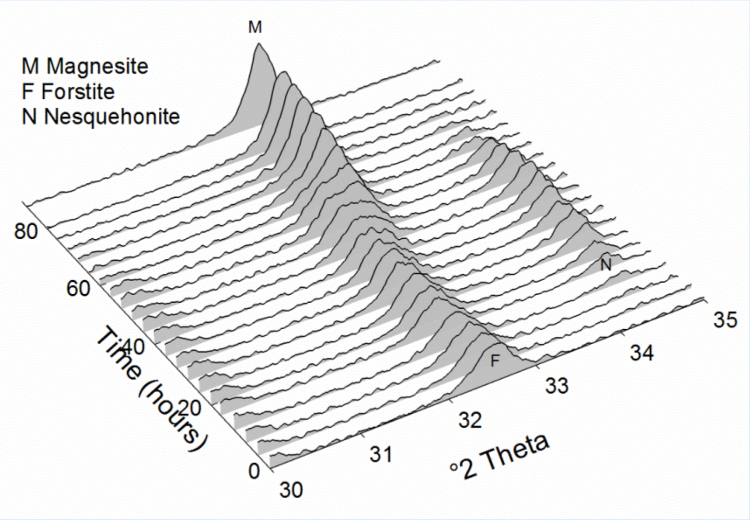
Schaef, H. T., B. P. McGrail, et al. (2013). "Mineralization of basalts in the $CO_2$-$H_2O$-$H_2S$ system ." International Journal of Greenhouse Gas Control, vol 16, 187-196

# Forsterite Carbonation in the Presence of Wet sc$CO_2$ and Na Citrate

- Impacts of organics
  - Presence of Na-citrate inhibits metastable phases
  - Overall carbonation attenuated
  - Evidence of hydrated amorphous phases in TGA-MS
- Organic compounds mobilize in sc$CO_2$ and impact silicate carbonation.

Nesquehonite Formation





*This work is a part of a collaborative effort between Yale University and PNNL.*

# Pilot Studies and Commercial Partnerships

- Demonstration project
  - Injection of ~1000 metric tons $CO_2$ in to CR basalts
  - Side wall core retrieval during FY14
- Underground thermal energy storage concept
  - Utilize similar basalt reservoirs as CCUS
  - Subsurface energy storage solution

**Wallula Basalt Pilot Project**

**Underground Thermal Energy Storage**

BONNEVILLE
POWER ADMINISTRATION

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SEQUESTRATION PARTNERSHIP

# Accomplishments

- Basalt formations are a viable option for long term storage of $CO_2$
  - Water bearing supercritical $CO_2$ reactions
    - Carbonation significant and comparable to aqueous dominated system
    - Intermediate carbonate phases precursor to stable carbonates
    - In situ techniques illustrate important role of water in carbonation processes
  - Mixed gas systems ($SO_2$, $H_2S$, $O_2$)
    - Precipitation of sulfur containing minerals
    - Variable reactivities associated with different basalts
    - New evidence pointing to key role of Fe(II)/Fe(III) redox chemistry
    - Subsurface chemistry is key to co-sequestration
  - Implications of organics on silicate carbonation in wet $scCO_2$
- Collaboration with University of Hawaii and Yale Univeristy
- Published laboratory results have significantly benefited and been directly used in pilot sequestration projects
  - CarbFix Project (Hellisheidi, Iceland)
  - Boise Wallula ICCS Project (Eastern Washington)
- Results also being applied for independent energy storage study in CRB

# Summary

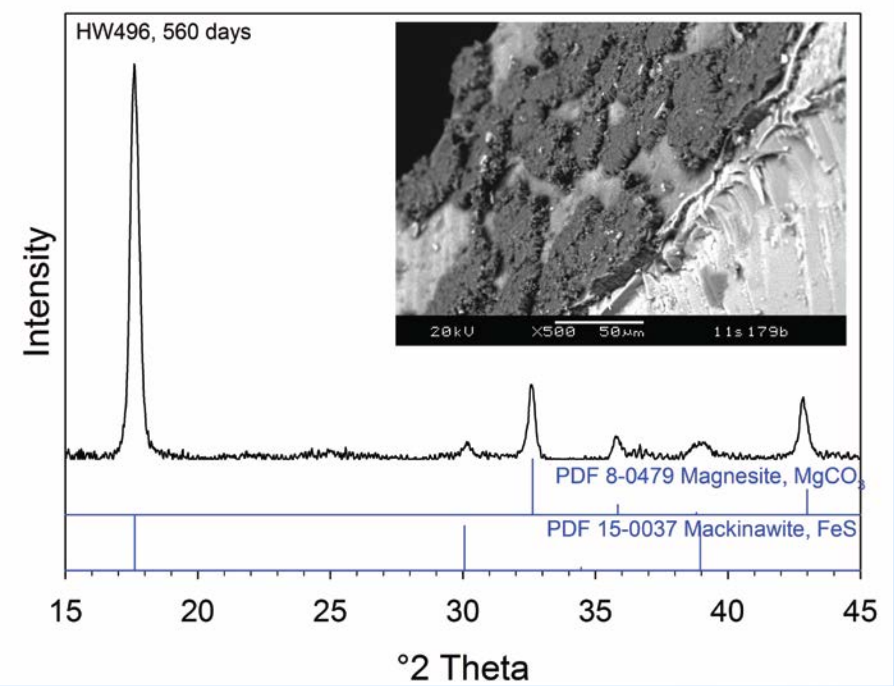
## Key Findings

- Reactions occurring between basaltic rocks and $H_2O$-$scCO_2$ fluids produce carbonate minerals.
- Reactions occurring in water bearing $scCO_2$ fluids are equally important.
- Sulfur species effectively and permanently removed from $scCO_2$.
- Organic compounds mobilize in wet $scCO_2$ and impact carbonation.

## 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.*



*Reaction products on olivine grain*

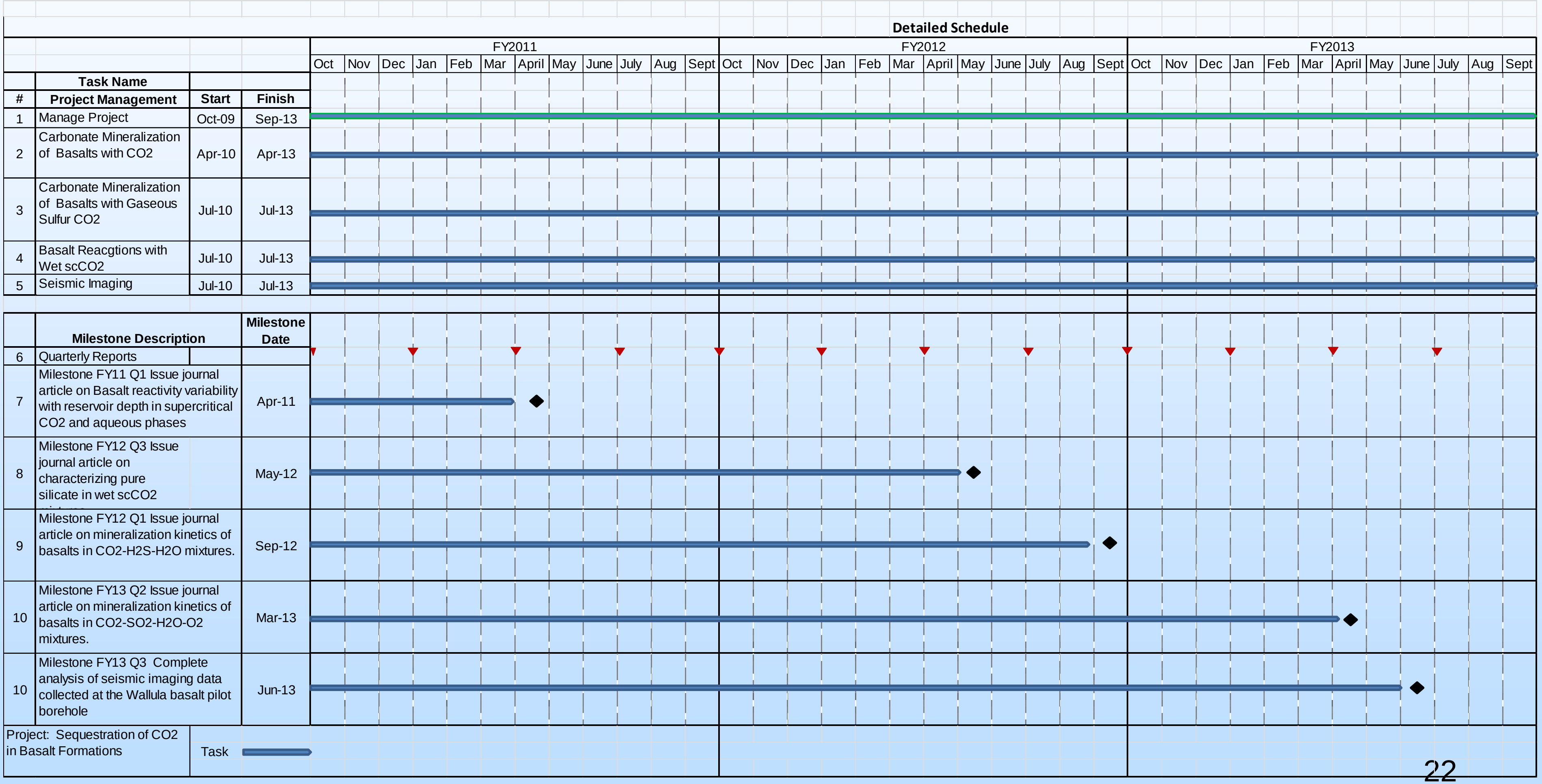
## FY 14 Activity Summary

- Continue long term basalt experiments with supercritical acid gases.
- Expanded scope to examine importance of water bearing $scCO_2$
- Continued support for 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



| # | Task Name<br>Project Management | Start | Finish |
|---|---|---|---|
| 1 | Manage Project | Oct-09 | Sep-13 |
| 2 | Carbonate Mineralization of Basalts with CO2 | Apr-10 | Apr-13 |
| 3 | Carbonate Mineralization of Basalts with Gaseous Sulfur CO2 | Jul-10 | Jul-13 |
| 4 | Basalt Reacgtions with Wet scCO2 | Jul-10 | Jul-13 |
| 5 | Seismic Imaging | Jul-10 | Jul-13 |

| # | Milestone Description | Milestone Date |
|---|---|---|
| 6 | Quarterly Reports | |
| 7 | Milestone FY11 Q1 Issue journal article on Basalt reactivity variability with reservoir depth in supercritical CO2 and aqueous phases | Apr-11 |
| 8 | Milestone FY12 Q3 Issue journal article on characterizing pure silicate in wet scCO2 | May-12 |
| 9 | Milestone FY12 Q1 Issue journal article on mineralization kinetics of basalts in CO2-H2S-H2O mixtures. | Sep-12 |
| 10 | Milestone FY13 Q2 Issue journal article on mineralization kinetics of basalts in CO2-SO2-H2O-O2 mixtures. | Mar-13 |
| 10 | Milestone FY13 Q3 Complete analysis of seismic imaging data collected at the Wallula basalt pilot borehole | Jun-13 |

Project: Sequestration of CO2 in Basalt Formations

Task

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