Impact of Microstructure on the Containment and Migration of CO_2 in Fractured Basalts

Project Number DE-FE0023382

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National Energy Technology Laboratory

Carbon Storage R&D Project Review Meeting

Transforming Technology through Integration and Collaboration

August 18-20, 2015

Presentation Outline

- Project Overview
- Carbon Sequestration in Fractured Basalts
- Research Approach
- Technical Status
  - Basalt acquisition and characterization
  - Mineral carbonation
  - *In situ* solid-state ^{13}C NMR tool
  - Flow-through testing apparatus
- Summary and Opportunities

Benefit to the Program

- Program Goals Addressed
  - Improve reservoir storage efficiency while ensuring containment effectiveness.
  - Support ability to predict CO_2 storage capacity in geologic formations within ± 30 percent.
- Project Benefits
  - Generate datasets for evaluating the efficiency of carbon sequestration in fractured basalts.
  - Determine the extent to which mineral carbonation may either impede or enhance flow.
  - Develop the experimental infrastructure for evaluating CO_2 behavior in fractured materials.

Project Overview:
Goals and Objectives

- Overarching Project Objective: advance scientific and technical understanding of the impact of fracture microstructure on the flow and mineralization of CO_2 injected in fractured basalt.
- Budget Period I. Planning and Preliminary Experiments on Static Interactions with Basalts
  - Develop a library of natural and artificial basalts with a range of representative mineral contents and fracture microstructures.
  - Demonstrate the integration of bench-scale experiments with an array of characterization tools to identify the locations, amounts, and types of carbonate mineral trapping in fractured basalts.
  - Develop laboratory-scale system for evaluating CO_2-rich fluid interactions with fractured basalts.

Project Overview: Goals and Objectives

- Budget Period II. Evaluation of Static Conditions and Development of Flow-through Capabilities
  - Evaluate the effects of basalt composition and fracture properties on the extent and mechanisms of carbon sequestration in diffusion-limited zones.
  - Quantify the extent to which confining pressure controls the propagation of fractures in basalts upon reaction with CO_2.
  - Create data packages that can be used for model development.
  - Develop laboratory-scale equipment for NMR and CT of pressurized systems with advective flow.

Project Overview:
Goals and Objectives

- Budget Period III. Evaluation of Fractured Basalts with Flow of CO_2-Rich Fluids
  - Examine the impacts of precipitation and fracture development on the permeability of fractured basalt to CO_2-rich fluids.
  - Estimate the storage capacity of fractured basalts as a function of mineral content and fracture structure, and quantify storage by different mechanisms.
  - Demonstrate the application of advanced NMR and CT tools to fractured basalts with flow.
  - Develop data packages that can be used for reactive transport model development.

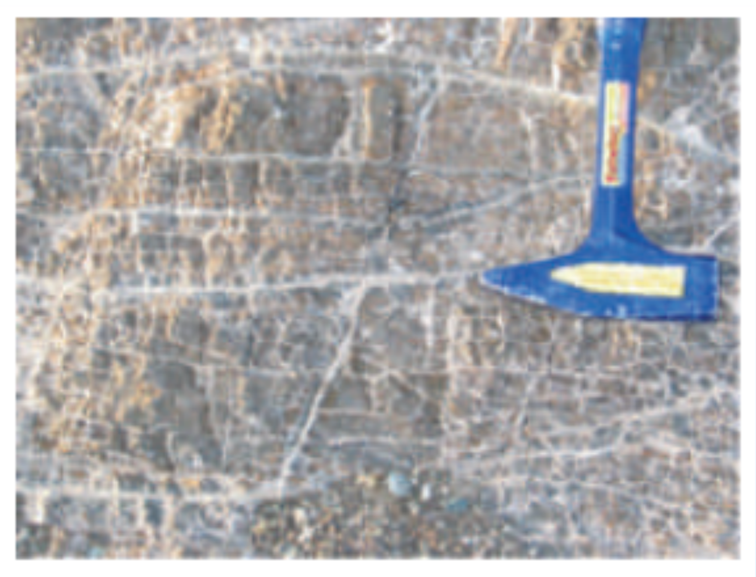
Project Overview:
Goals and Objectives

Go/No-Go Decision Point 1. To proceed to Budget Period II, the following criteria must be met.

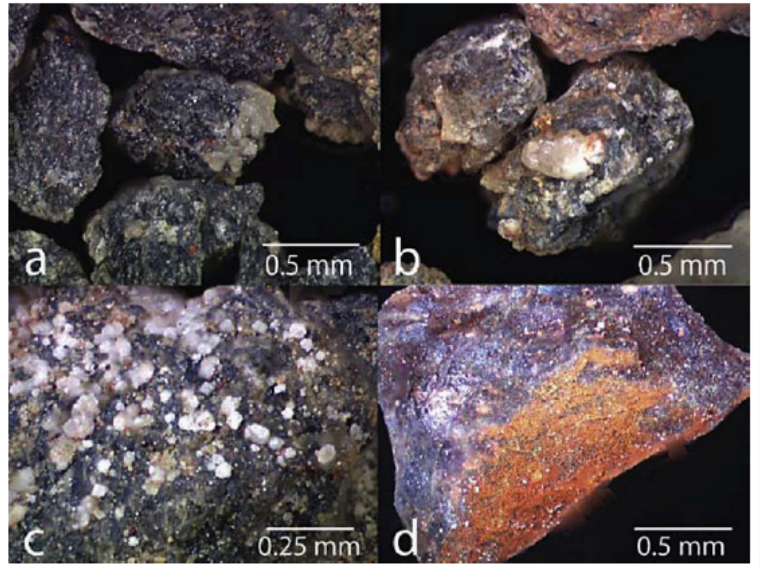
- A library of at least ten basalt samples with different compositions and fracture properties have been acquired and characterized.
- The reactor for performing static experiments with an applied confining pressure has been designed, fabricated, and tested with one sample.

Note: A "basalt sample" is a particular combination of composition and fracture property.

Sequestration in Magnesium-Rich Formations



Products of natural carbonation of peridotite (Oman).
Matter and Kelemen, *Nature Geoscience,* 2009

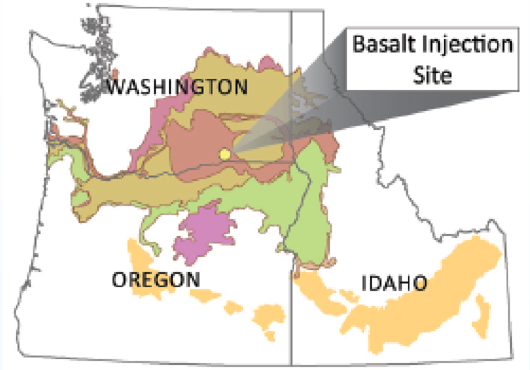


Carbonate precipitates on basalts after 854 days of reaction at 103 bar CO_2 and 100° C
Schaef et al., *Int. J. Greenhouse Gas Cont.,* 2010

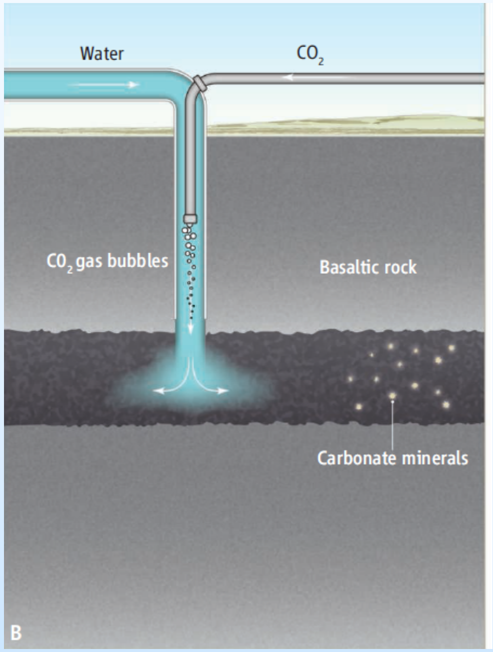
- Most target formations are sandstones, but mafic (Fe- and Mg-rich) rocks are alternative formations with high mineral trapping capacity.
- Continued fracturing of the rock may be promoted by temperature and volume changes from reactions.
- Also applicable to *ex situ* mineral carbonation in engineered reactors.

Pilot-Scale Injections into Basalts

Pilot-scale injections into basalts have been performed in Washington and in Iceland.



Location of 1000 ton pilot-scale test by the Big Sky Carbon Sequestration Partnership, 2013



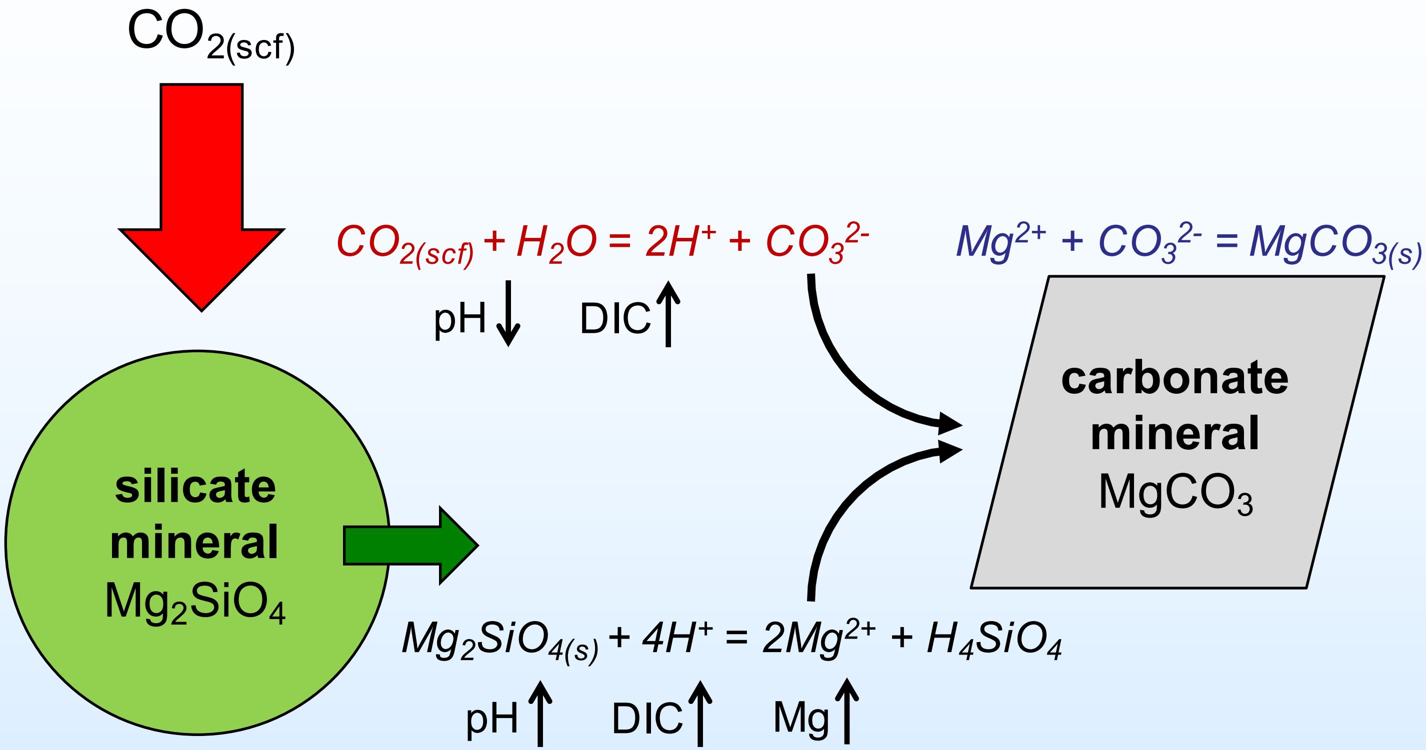
Gislason and Oelkers, *Science,* 2014

Calcite in a core retrieved from the site of the 2012 CarbFix injection of CO_2-rich water into basalt in Iceland.

80% of injected CO_2 mineralized within 1 year.

www.or.is/en/projects/carbfix/

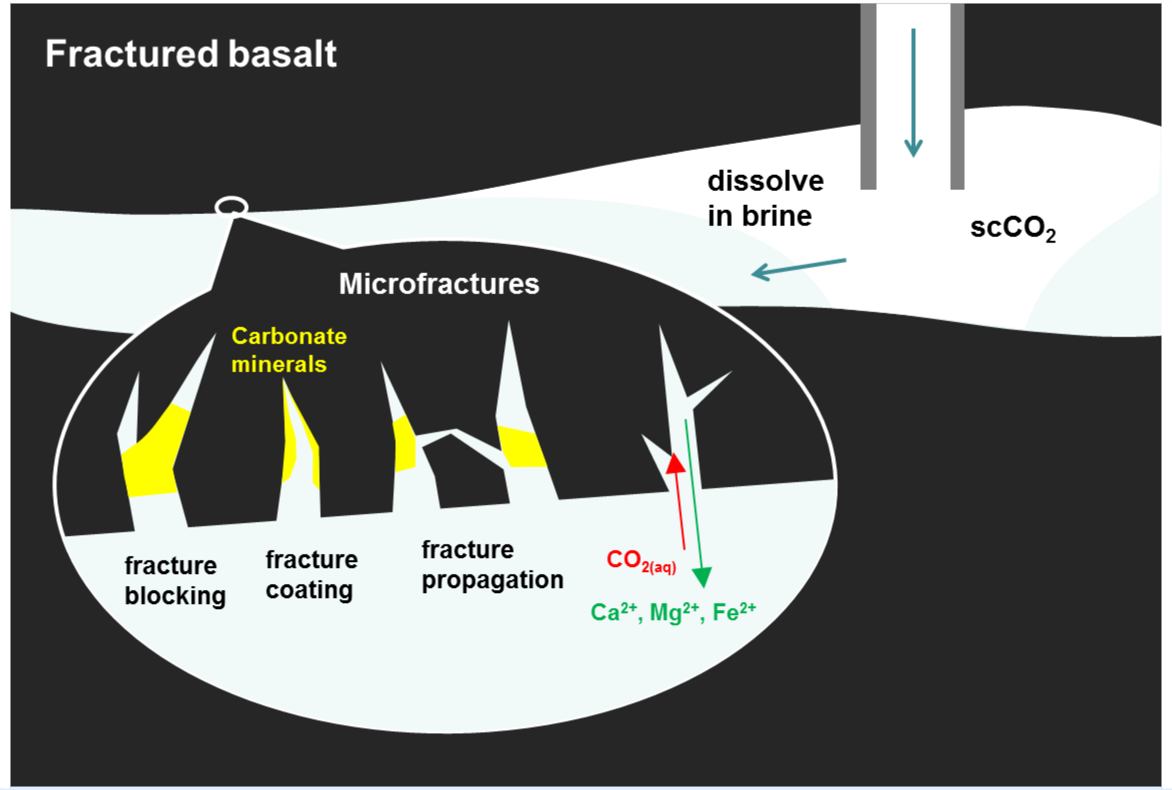
Methodology – Mineral Trapping



When and where do carbonate minerals precipitate in systems with high solid:water ratios and with mass transfer limitations?

How does precipitation affect transport properties?

Research Questions



- How do reactions proceed in fractured rocks?
- What volume of a mafic rock is available for sequestration?
- Will carbonate mineral precipitation impede or accelerate sequestration?

Research Approach

Fractured Basalts

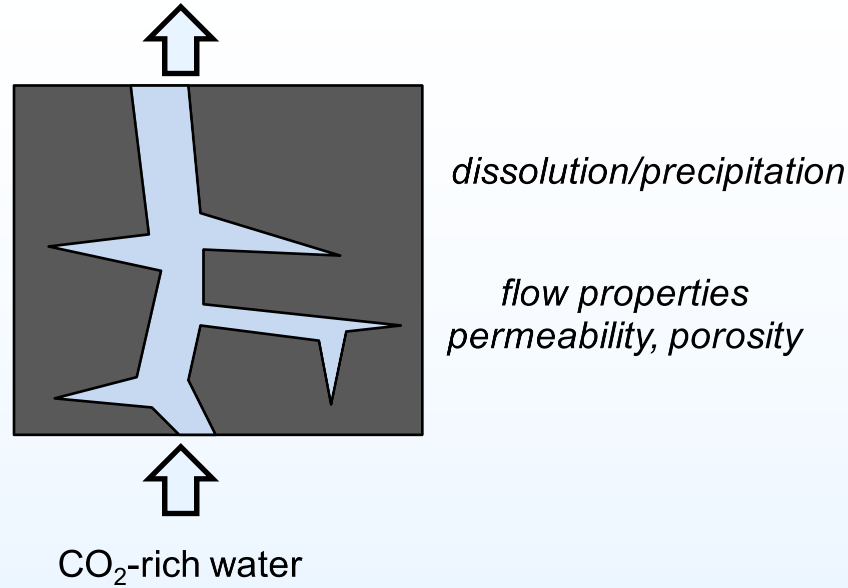
- Natural and artificial rocks
- Varying composition and fracture structure

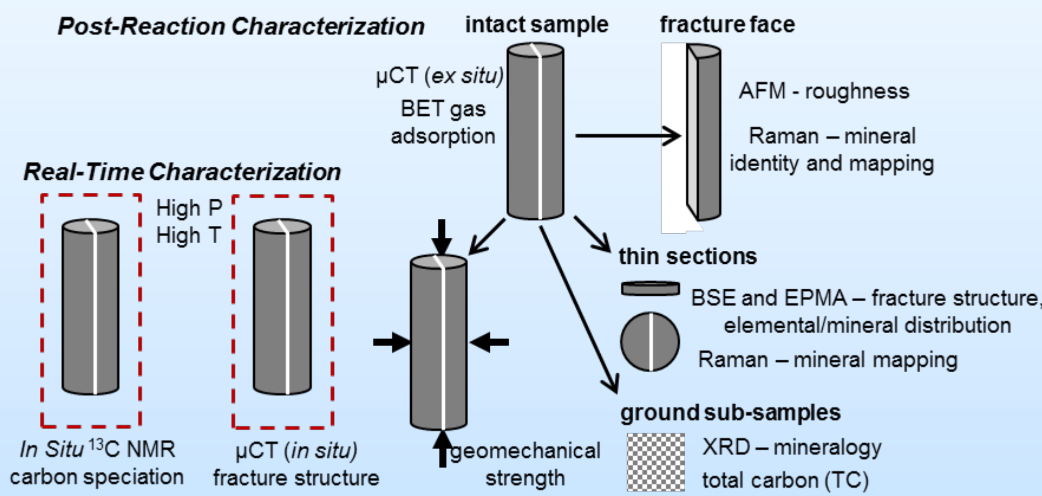
Bench-Scale Experiments

- Relevant pressure, temperature, and brine composition
- Static (dead-end fractures)
- Flow (monitor variation)
- With/without confining pressure

Characterization

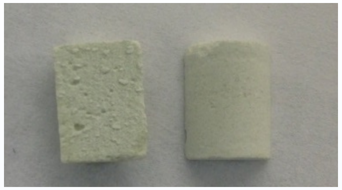
- Pre- and post-reaction
- *Ex situ* and *in situ* techniques.



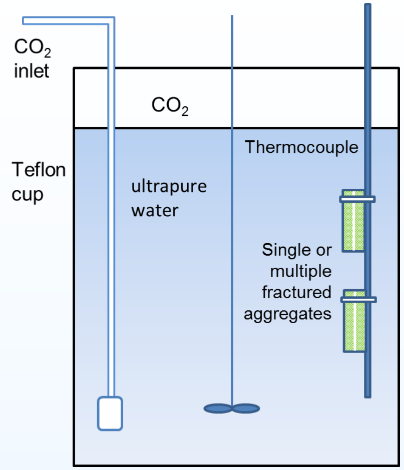


Forsterite Fractured Rock

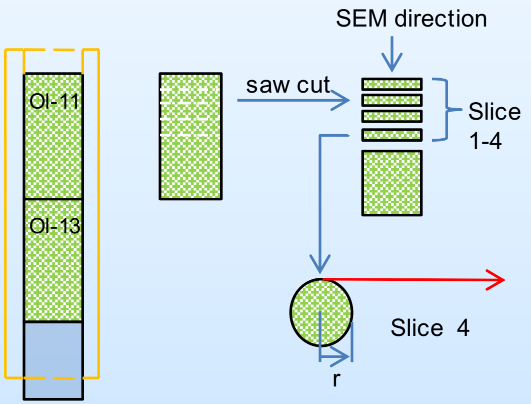
- Artificial aggregates of olivine (Fo_{90}) from vacuum sintering.
- Reacted for 15 days in water at 100 ºC 100 bar CO_2.
- Carbonate minerals form in narrow zones like fractures.

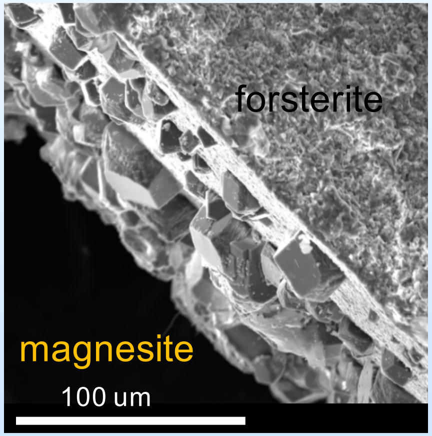


6 mm diameter
10 mm length
~25% porosity

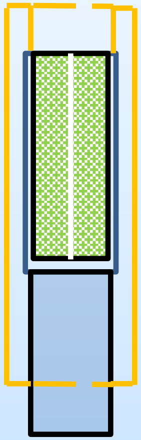


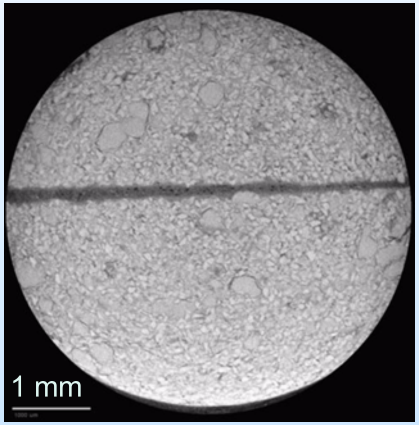
Mineralization in Tight Gap Between Rock and Tubing





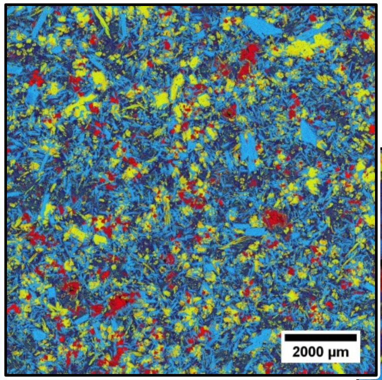
Post-Reaction Fracture Structure

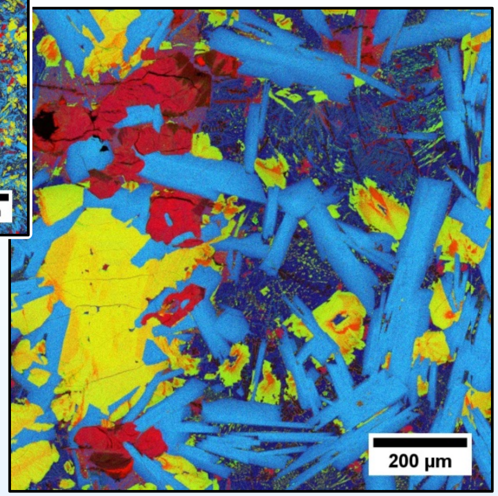


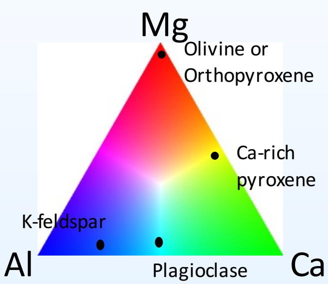


Starting Basalt: Composition

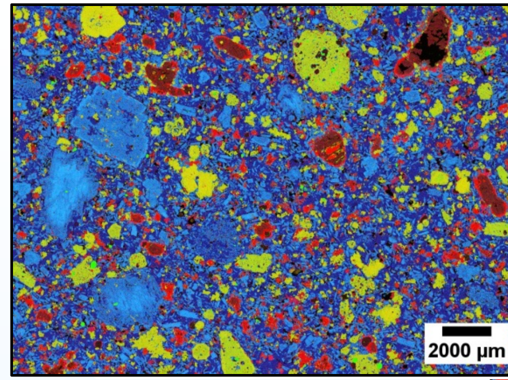
Columbia River Flood Basalt (WA)

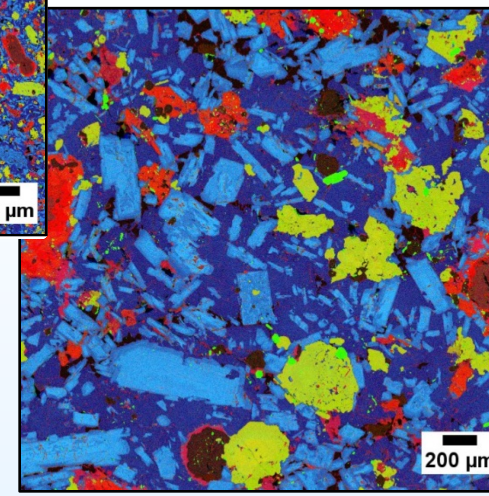


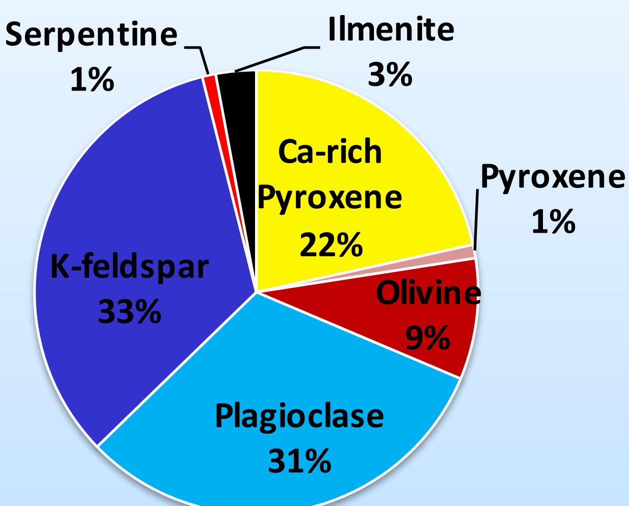


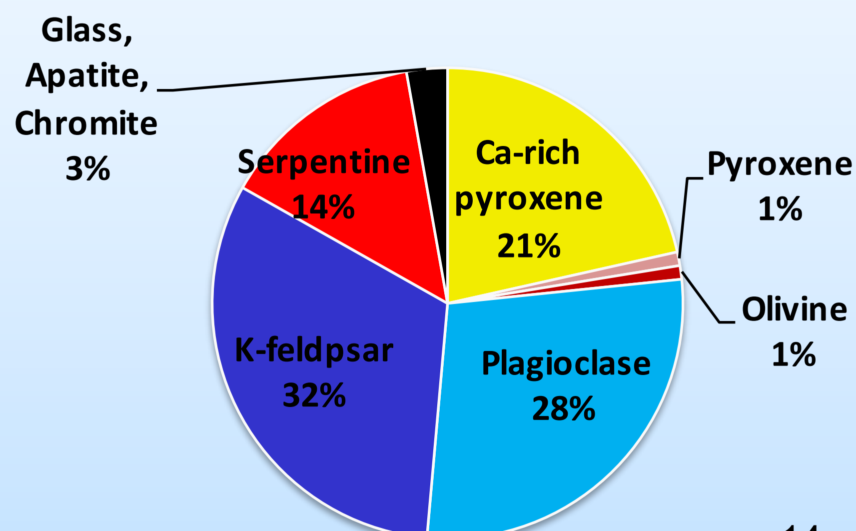


Serpentinized Basalt (CO)



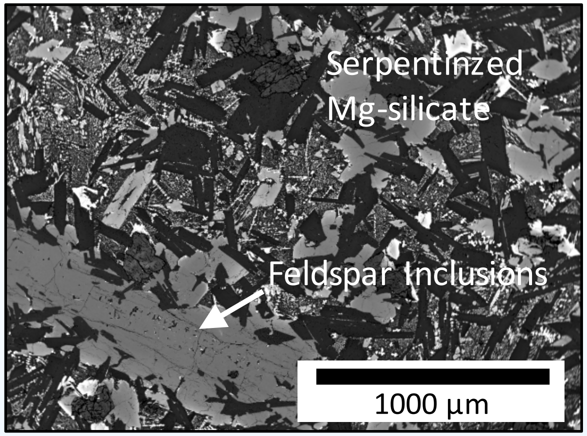




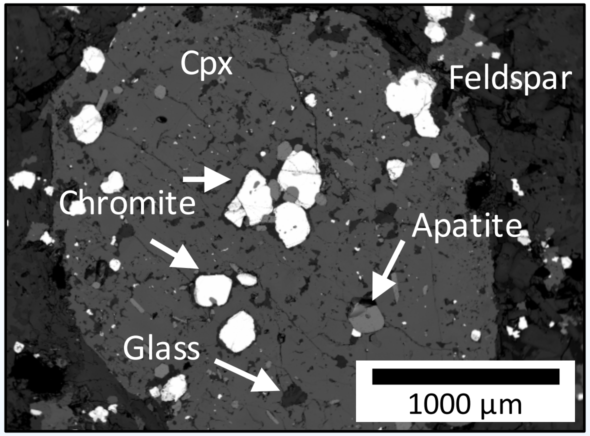


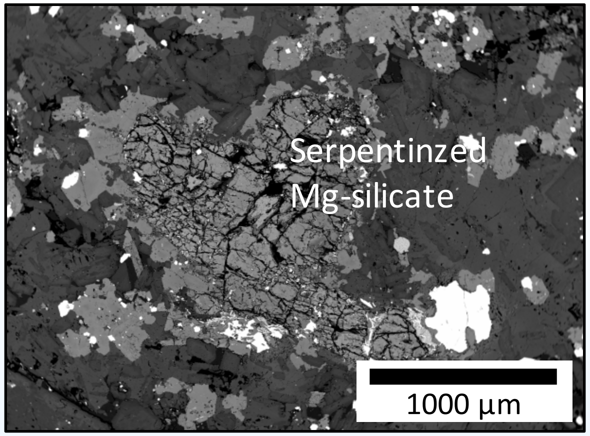
Starting Basalt: Microstructure

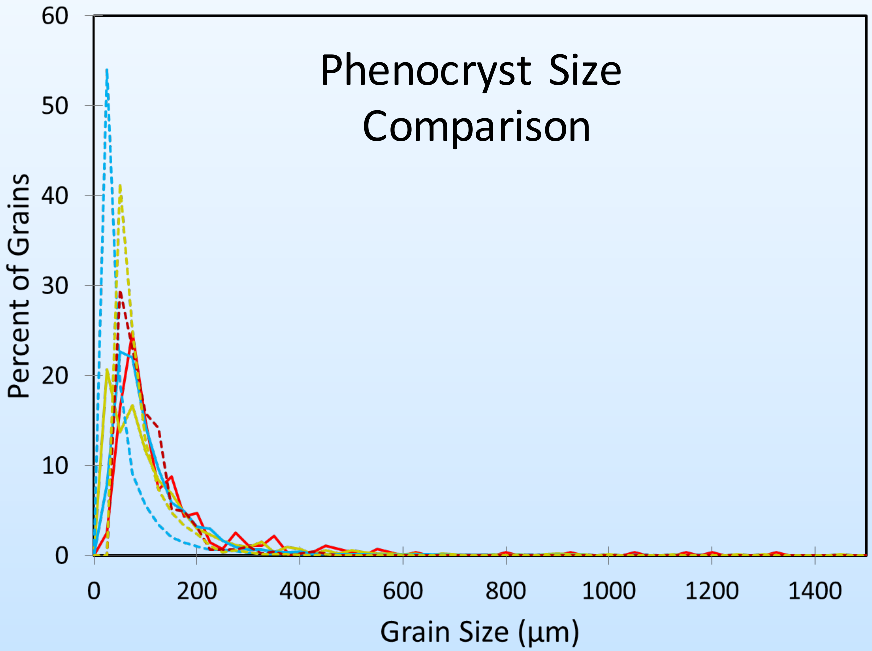
Columbia River flood basalt:



Olivine-rich basalt: Inclusions and serpentinized grains







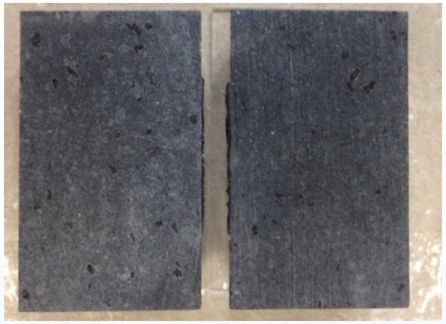
Average phenocryst size
Olivine-rich basalt:

- Ca-rich pyroxene: 123 µm
- Plagioclase: 99 µm
- Serpentine: 143 µm

Flood basalt:

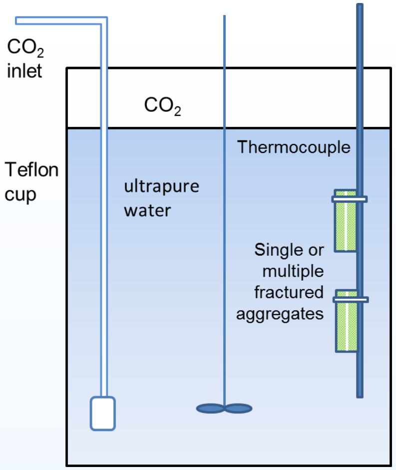
- Ca-rich pyroxene: 75 µm
- Plagioclase: 53 µm
- Olivine: 88 µm

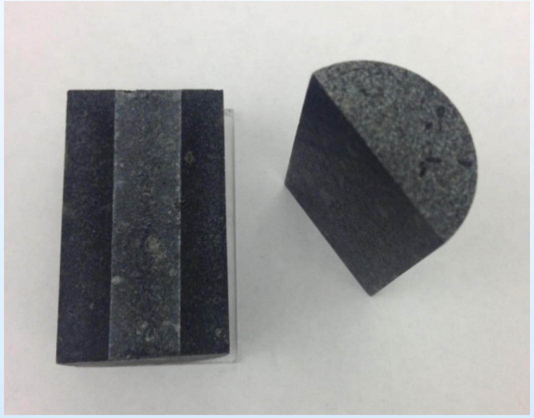
Basalt Fractured Core



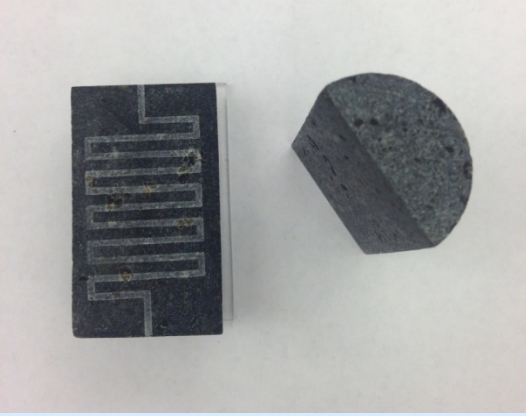
Saw-Cut Basalt
1-inch diameter, 1.6-inch length

Reassembled Core
Wrapped with Epoxy





Single Groove Pattern
10 mm wide
80-100 um depth



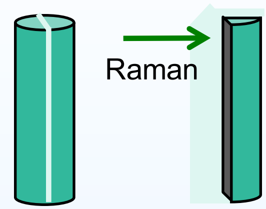
Meandering Pattern
1 mm wide
80-100 um depth

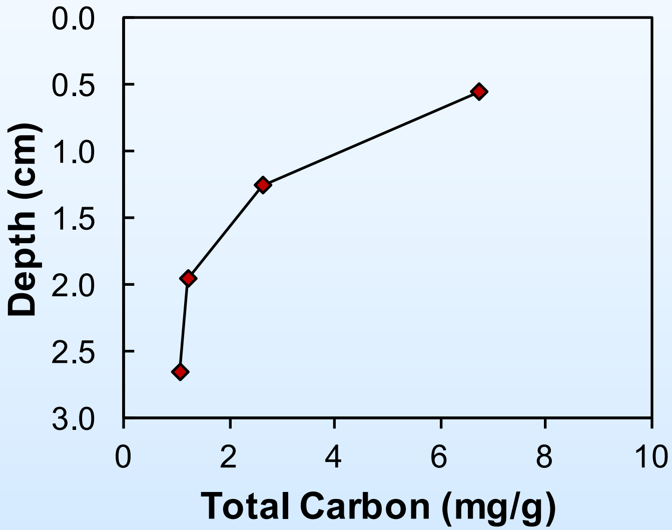
Static Experiments with Basalt

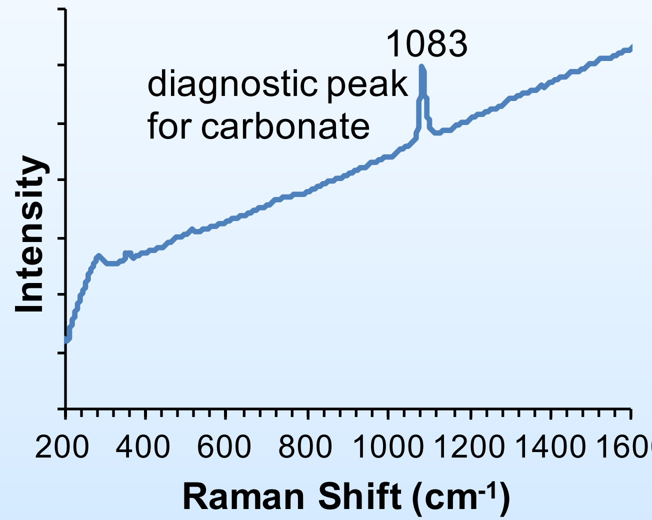
Serpentinized basalt (CO) reacted for 4 weeks at 150°C and 100 bar CO_2.

Packed bed loaded with powder

Half-inch fractured core coated with epoxy







- Spatially localized carbon accumulation.
- Direct evidence for carbonate mineral formation in fracture.

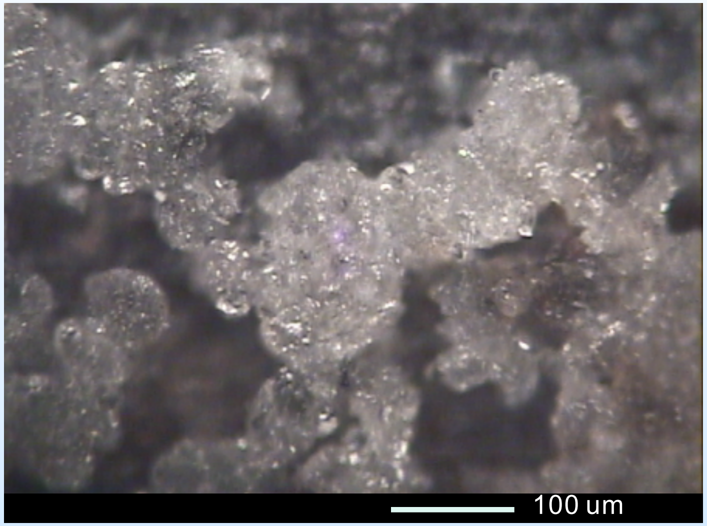
Static Experiments with Basalt

Pristine flood basalt (WA) reacted for 4 weeks at 150°C and 100 bar CO_2.



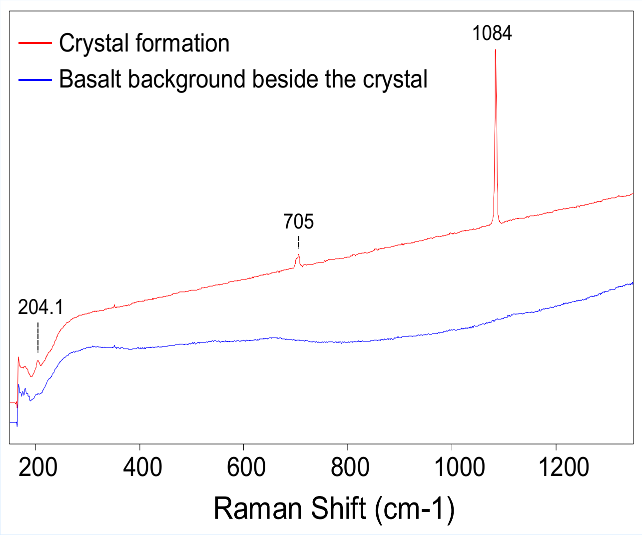
Sandpaper-roughened, saw-cut, 0.5-inch cores
~140 um fracture

Electron Microscopy



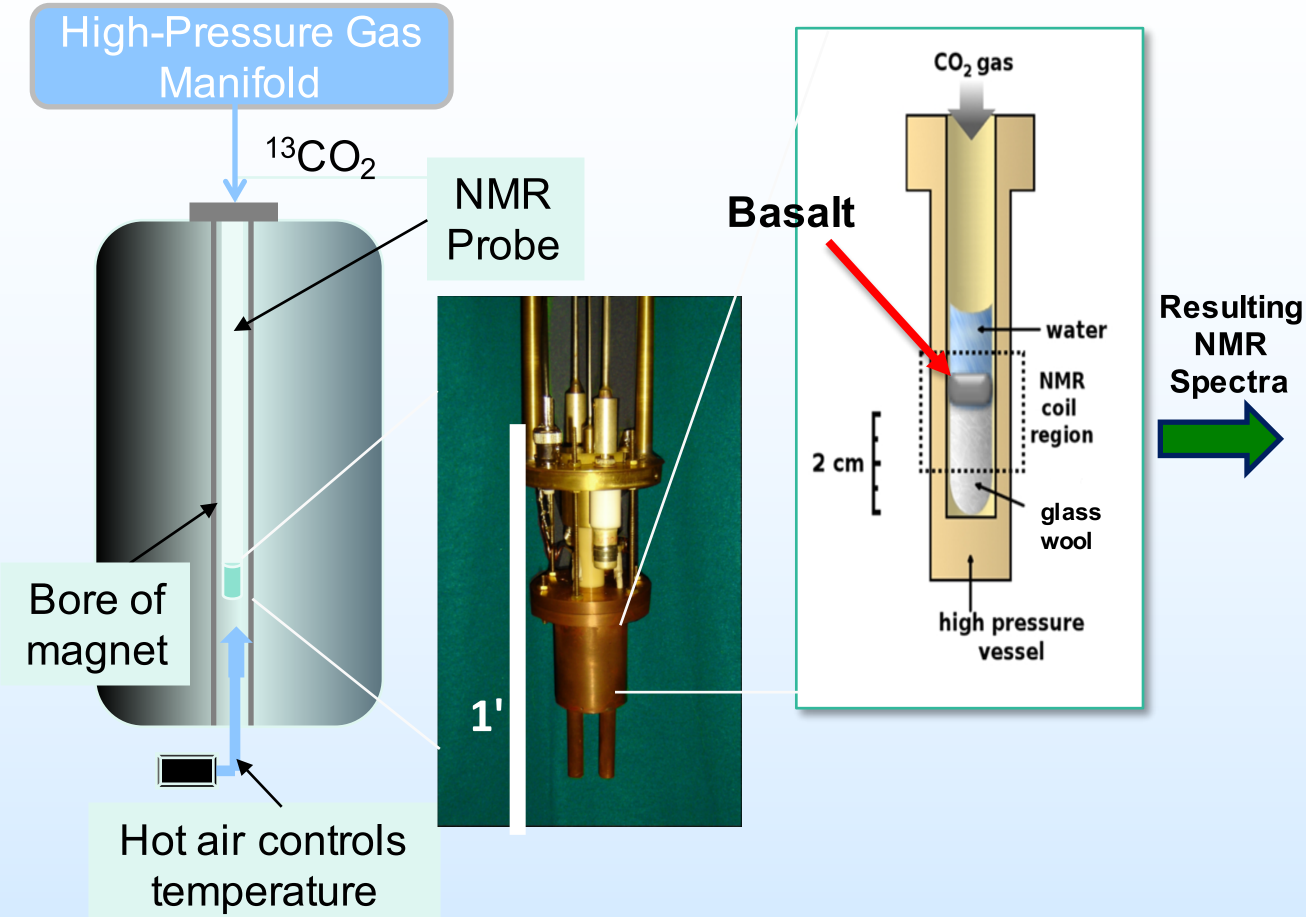
- Well-developed crystals have a location of maximum precipitation.

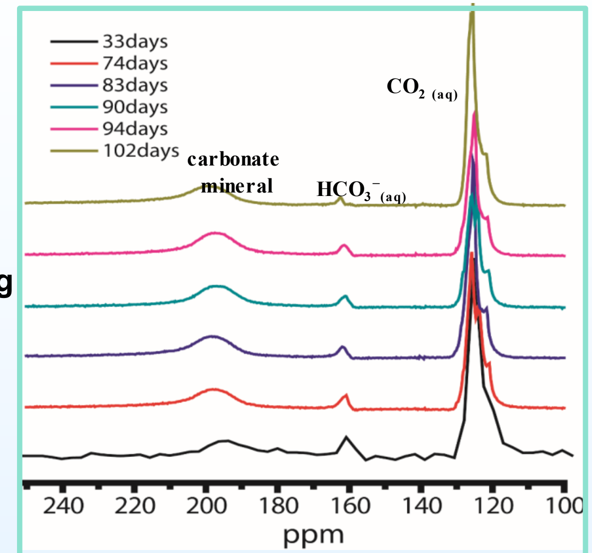
Raman Spectroscopy



- Aragonite ($CaCO_3$) identified.

High Pressure NMR Hardware





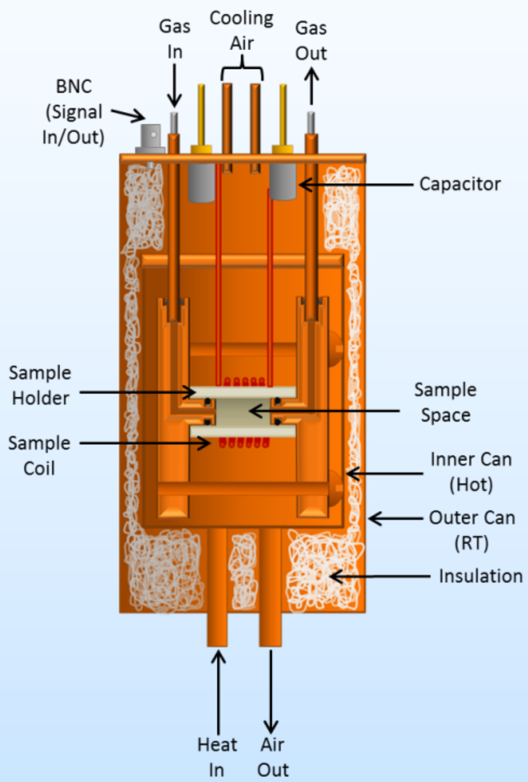
^{13}C NMR spectra taken at different reaction times. Temperature was 100°C and pressure decreased from 96.5 bar – 45 bar over the duration of the experiment.

- NMR is element-selective, quantitative, and non-destructive.
- ^{13}C NMR can track the growth of carbonate minerals.

High Pressure NMR Hardware

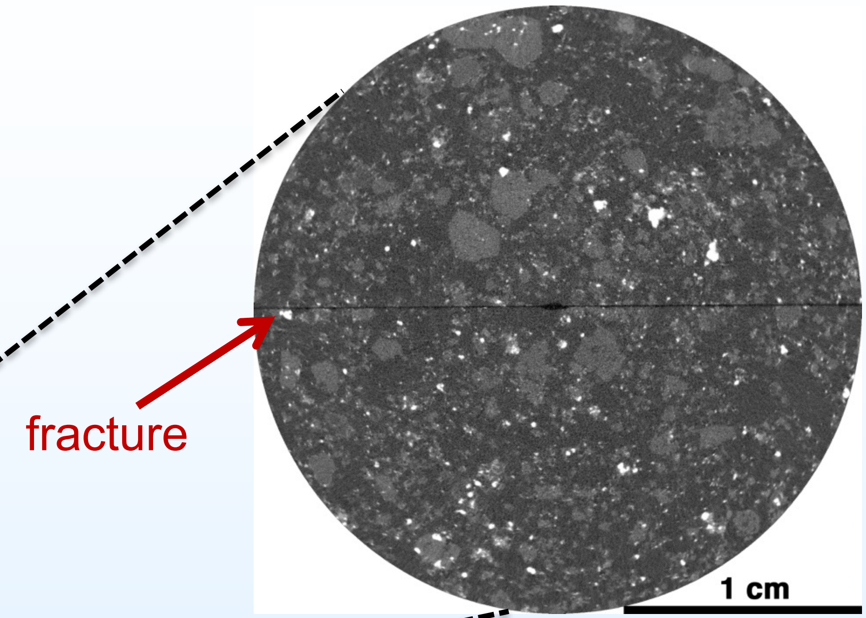
Flow-through Probe

- Fully constructed and able to get NMR
- Leak and pressure tested
- Heating and temperature control

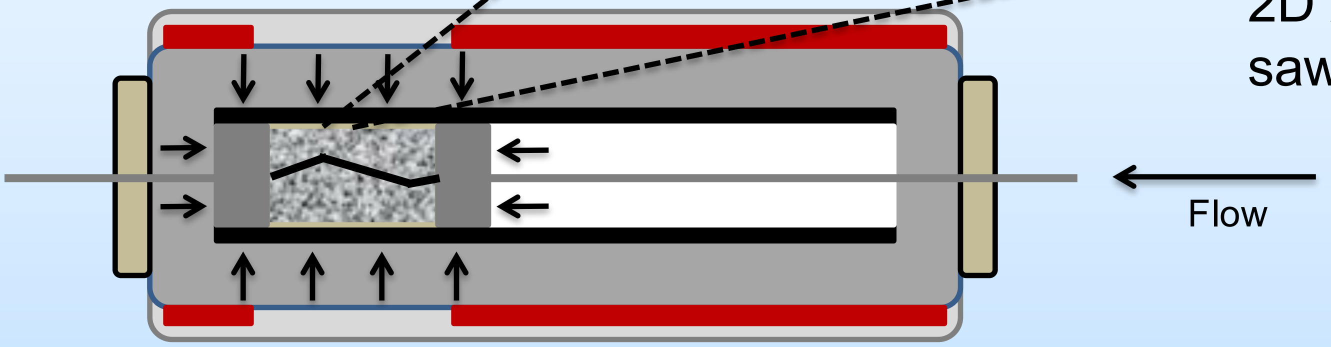


Flow-through Fractured Basalt

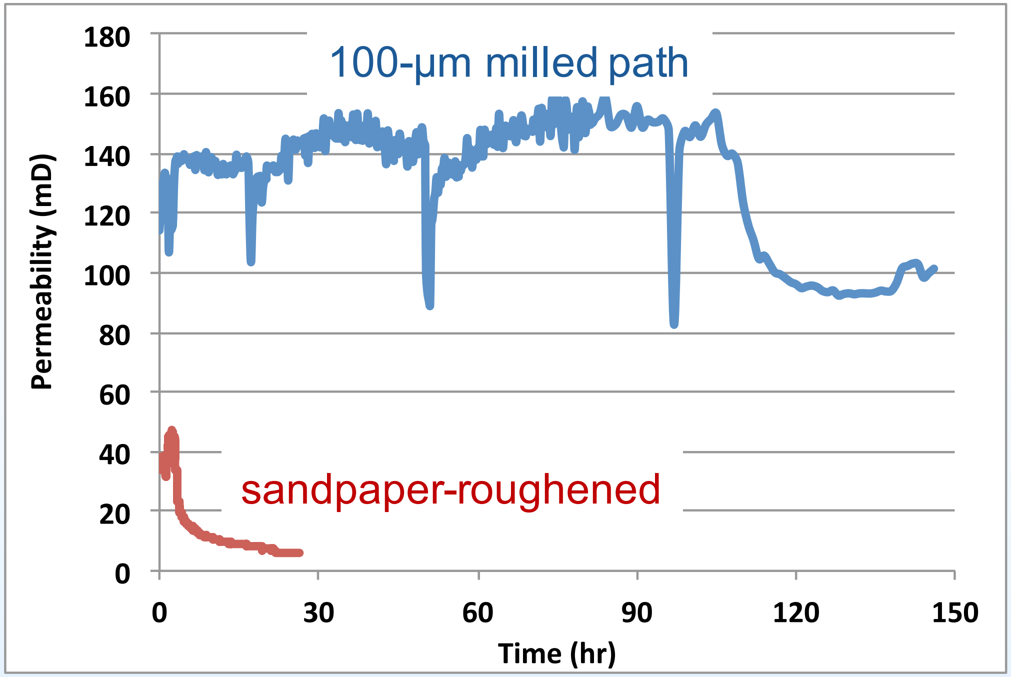
- Evaluate silicate dissolution and carbonate precipitation along fracture under confining stress.
- Examine effect of reactions on transport properties.



2D XCT section of saw-cut basalt core



Flow-through Fractured Basalt



<u>Preliminary experiments</u>

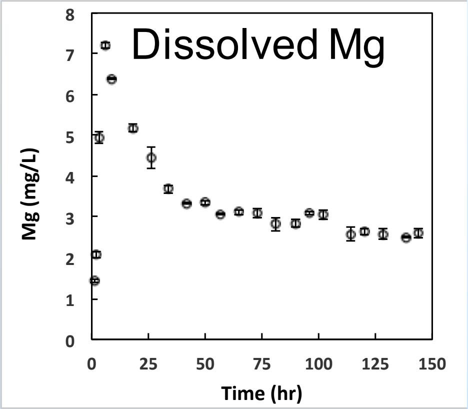
P_{CO2} = 100 bar

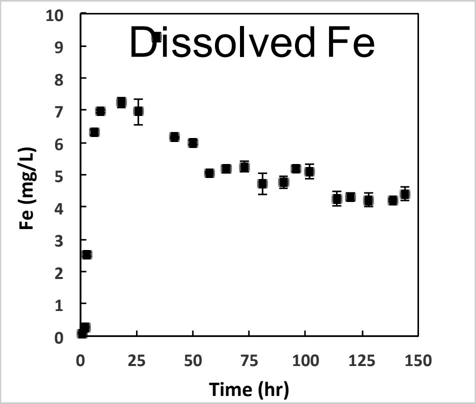
Confining pressure = 200-350 bar

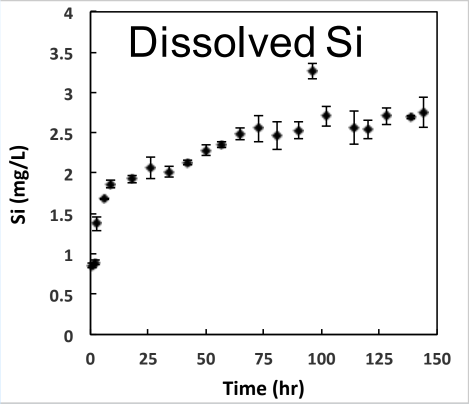
Temp = 50°C

Flow rate = 3-5 mL/h

CO_2-driven dissolution resulted in permeability decrease under confining stress







Washington University in St. Louis

Accomplishments to Date

- Acquisition, characterization, and fracture preparation of two natural basalts and one artificial basalt.
- Demonstration of carbonate mineral formation for all three materials upon reaction with CO_2-rich solutions.
- Integration of multiple techniques to characterize the location and identity of carbonate mineral formation.
- Development of a laboratory-scale system for evaluating CO_2-rich fluid interactions with fractured basalts held under confining pressure.

Decision Point Status

Go/No-Go Decision Point 1. To proceed to Budget Period II, the following criteria must be met.

- A library of at least ten basalt samples with different compositions and fracture properties have been acquired and characterized.
    - 8 samples acquired and characterized. At least 2 more by September 30

Natural Basalts	Status	Fracture Structure
olivine-rich, pristine (WA)	complete	roughened
		milled notch
		milled flowpath
olivine-rich, serpentinized (CO)	complete	roughened
		milled notch
		milled flowpath
Grand Ronde (WA)	coordinating acquisition with PNNL	
Synthetic Basalts (iron free)		
forsterite-rich	complete	roughened
		milled notch
pyroxene-rich	in progress	
quartz-containing	In progress	

Note: A "basalt sample" is a particular combination of composition and fracture property.

- The reactor for performing static experiments with an applied confining pressure has been designed, fabricated, and tested with one sample.
    - **fully complete**

Synergy Opportunities

- **Basalt Sequestration Projects:** we can share data and materials with others studying carbon sequestration in basalts (Pollyea and Benson project, Big Sky Carbon Sequestration Project) to generate complementary and not duplicative data.
- **Other Sequestration Projects:** our integrated approach can be used to examine impacts of fracture microstructure on CO_2 behavior in other reactive geologic materials (e.g., caprocks).
- **Modeling:** our project is generating a rich dataset that can be used to evaluate reactive transport models and models that link transport and goemechanical properties.
- **Technique Sharing:** we have unique abilities (e.g., solid state ^{13}C NMR) that can be brought to other groups and shared abilities (e.g., CT scans, triaxial tests) around which we can share best practices.

Summary

- Key Findings
  - Carbon mineralization in fractured basalts can result in mineral trapping on time-scales of years or less.
  - Carbonate precipitation can be visualized using both *ex situ* and *in situ* techniques.
  - Flow-through fractures in basalts can be achieved.
- Lessons Learned
  - Selection of materials is critical.
  - Our team has shared expertise in unexpected ways.
- Future Plans
  - Systematic set of experiments.
  - More experiments, including NMR and CT, with flow.

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http://pages.wustl.edu/fracturedbasalts

- Co-PI's: Mark Conradi, Brian Ellis (Michigan), Sophia Hayes, and Phil Skemer.
- Students and Postdocs: Yeunook Bae, Megan Bushlow, Jinlei Cui, Jeremy Moore, Erika Sesti, Minmeng Tang, Rachel Wells, Wei Xiong
- Other: Helene Couvy

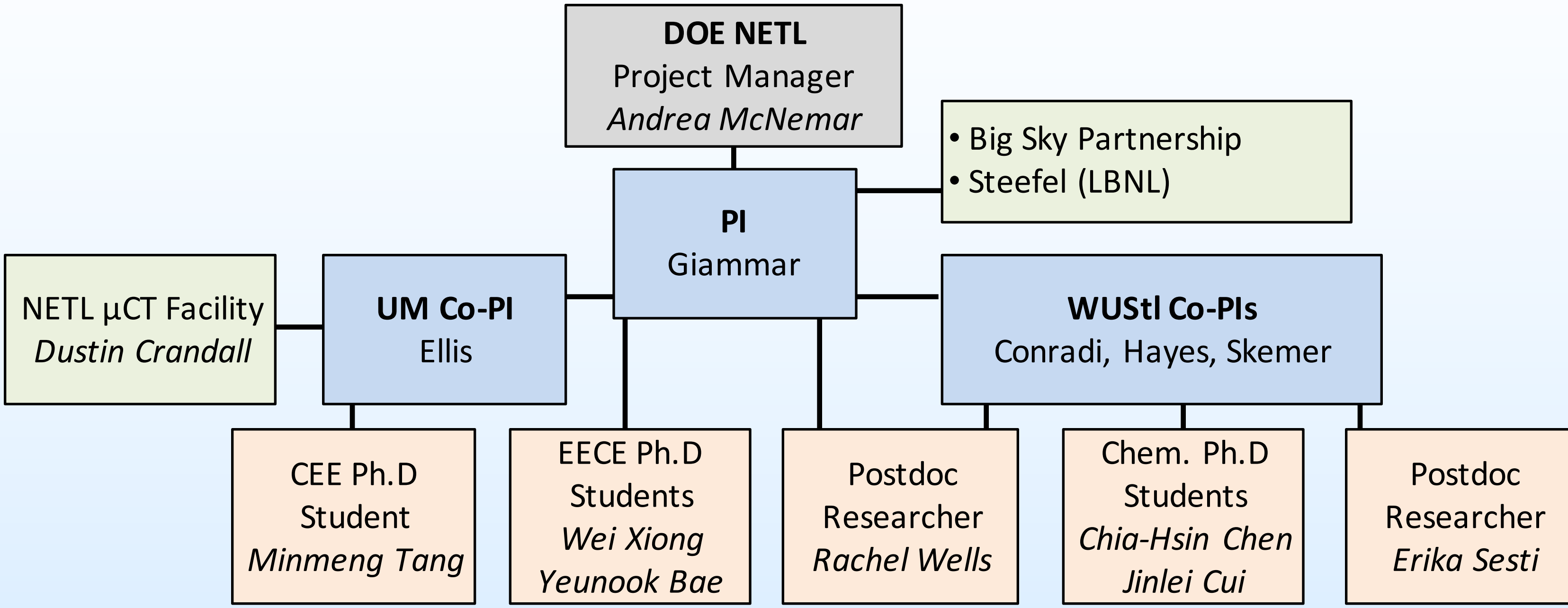
Appendix

– Organization Chart

– Gantt Chart

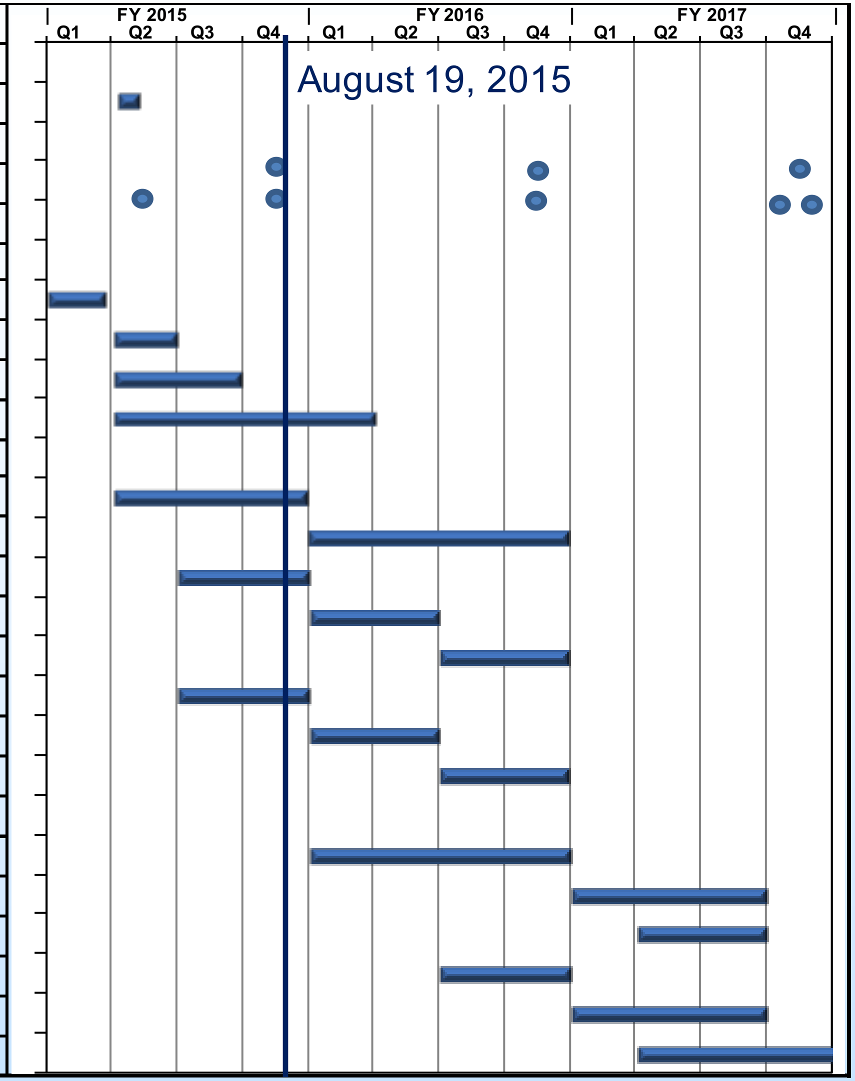
– Bibliography

Organization Chart



Gantt Chart

Task	Start Date	End Date
Task 1.0: Project Management & Planning		
Subtask 1.1: Update PMP	01/07/15	02/06/15
Subtask 1.2: Monthly & Quarterly Reporting	10/01/14	09/30/17
Subtask 1.3: Meetings		
Subtask 1.4: Reports and Deliverables		
Task 2.0: Prepare and Characterize Basalt Samples		
Subtask 2.1.1: Natural materials	10/01/14	12/23/14
Subtask 2.1.2: Synthetic materials	01/01/15	04/02/15
Subtask 2.1.3: Fracturing and characterization	01/01/15	06/30/15
Subtask 2.2: Sample Characterization	01/01/15	01/01/16
Task 3.0: Static Experiments		
Subtask 3.1.1: Screening in immersion	01/01/15	09/29/15
Subtask 3.1.2: Systematic immersion expts	09/29/15	09/28/16
Subtask 3.2.1: Confining pressure reactor test	04/01/15	10/01/15
Subtask 3.2.2: Confining pres. systematic expts.	10/01/15	04/01/16
Subtask 3.2.3: confining pressure uCT expt.	04/01/16	09/28/16
Subtask 3.3.1: *In situ* NMR prelim experiments	04/01/15	10/01/15
Subtask 3.3.2: *In situ* NMR syst. experiments	10/01/15	04/01/16
Subtask 3.4: Data integration and modeling	04/01/16	09/28/16
Task 4.0: Core Flooding Experiments		
Subtask 4.1.1: Reactor assembly and testing	10/01/15	09/30/16
Subtask 4.1.2: Experiments at UM	09/30/16	06/30/17
Subtask 4.1.3: Flow-through with uCT	01/01/17	06/30/17
Subtask 4.2.1: Flow-through NMR probe dev.	04/01/16	10/01/16
Subtask 4.2.2: Flow-through NMR expts.	10/01/16	
Subtask 4.3: Data integration and modeling	01/01/17	01/01/18



Washington University in St. Louis

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  - Giammar, D., Xiong, W., Hayes, S., Skemer, P., Conradi, M., Ellis, B., Moore, J., and D. Crandall, Characterization of mineral trapping within fractured basalts, *14th Annual Carbon Capture Utilization and Storage Conference,* April 28 – May 1, 2015, Pittsburgh, Pennsylvania.
  - Xiong, W. and D. Giammar, Carbon sequestration in fractured basalt, *Gordon Research Conference on Carbon Capture, Utilization and Storage*, May 31 – June 5, 2015, Easton, Massachusetts