Impact of Microstructure on the Containment and Migration of CO$_2$ in Fractured Basalts
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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 CO₂.
  – 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 CO₂-Rich Fluids
  – Examine the impacts of precipitation and fracture development on the permeability of fractured basalt to CO₂-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

• 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.


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
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

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

\[ \text{silicate mineral } \text{Mg}_2\text{SiO}_4 \]

\[ \text{CO}_2^{(scf)} + H_2O = 2H^+ + CO_3^{2-} \]

\[ \text{pH}\downarrow \quad \text{DIC}\uparrow \]

\[ \text{carbonate mineral } \text{MgCO}_3 \]

\[ \text{Mg}^{2+} + CO_3^{2-} = \text{MgCO}_3^{(s)} \]

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 °C 100 bar CO$_2$.
- Carbonate minerals form in narrow zones like fractures.

Mineralization in Tight Gap Between Rock and Tubing

- 6 mm diameter
- 10 mm length
- ~25% porosity

Post-Reaction Fracture Structure
Starting Basalt: Composition

Columbia River Flood Basalt (WA)

- Ca-rich pyroxene: 22%
- Pyroxene: 1%
- Olivine: 9%
- Plagioclase: 31%
- K-feldspar: 33%
- Ca-rich pyroxene: 21%
- Pyroxene: 1%
- Olivine: 1%
- Serpentine: 14%
- Plagioclase: 28%
- Glass, Apatite, Chromite: 3%

Serpentinized Basalt (CO)

- Ilmenite: 3%
- Mg: Ca: Al
- Olivine or Orthopyroxene
- K-feldspar
- Plagioclase
- Ca-rich pyroxene
- Serpentine: 1%
Starting Basalt: Microstructure

Columbia River flood basalt:

- Serpentized Mg-silicate
- Feldspar inclusions

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$_2$.

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

Packed bed loaded with powder

Half-inch fractured core coated with epoxy

![Graph showing total carbon vs. depth](image)

![Raman shift spectra](image)

- Diagnostic peak for carbonate at 1083 cm$^{-1}$
Static Experiments with Basalt

Pristine flood basalt (WA) reacted for 4 weeks at 150°C and 100 bar CO₂.

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 (CaCO₃) identified.
High Pressure NMR Hardware

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

13C 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.
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.
Flow-through Fractured Basalt

Preliminary experiments
P_{CO_2} = 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

Dissolved Mg

Dissolved Fe

Dissolved Si
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.
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

<table>
<thead>
<tr>
<th>Type</th>
<th>Status</th>
<th>Fracture Structure</th>
</tr>
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<tbody>
<tr>
<td>olivine-rich, pristine (WA)</td>
<td>complete</td>
<td>roughened</td>
</tr>
<tr>
<td></td>
<td></td>
<td>milled notch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>milled flowpath</td>
</tr>
<tr>
<td>olivine-rich, serpentinized (CO)</td>
<td>complete</td>
<td>roughened</td>
</tr>
<tr>
<td></td>
<td></td>
<td>milled notch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>milled flowpath</td>
</tr>
<tr>
<td>Grand Ronde (WA)</td>
<td>coordinating acquisition with PNNL</td>
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</tbody>
</table>

### Synthetic Basalts (iron free)

<table>
<thead>
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<th>Type</th>
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<th>Fracture Structure</th>
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</thead>
<tbody>
<tr>
<td>forsterite-rich</td>
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<td>roughened</td>
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<tr>
<td></td>
<td></td>
<td>milled notch</td>
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<tr>
<td>pyroxene-rich</td>
<td>in progress</td>
<td></td>
</tr>
<tr>
<td>quartz-containing</td>
<td>In progress</td>
<td></td>
</tr>
</tbody>
</table>

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.
• 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
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Bibliography

• Conference Presentations: